Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Rhodium(III)-catalyzed *ortho*-alkenylation using a cyclic *N*-phosphoryl ketimine as the directing group

Yu-Qin Zhu, Liu Qin, Qiang Song, Fu Su, Yan-Jun Xu* and Lin Dong*

Key laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry, West China School of Pharmacy,

Sichuan University, Chengdu, 610041 (China)

E-mail: dongl@scu.edu.cn

Supporting Information

Table of Contents

1. General Methods

NMR data were obtained for ^{1}H at 400 MHz or 600 MHz, and for ^{13}C at 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether. Cyclic *N*-phosphoryl ketimines were prepared according to the reported procedure.[1] Acrylates were commercially available.

2. General Procedure for the Synthesis of *ortho*-olefinated cyclic *N*-phosphoryl ketimines derivatives (3aa)

1a (28.7 mg, 0.1 mmol), methyl acrylate **2a** (45.3 μL, 0.5 mmol), $[Cp^*RhCl_2]_2$ (1.6 mmol, 2.5 mol %), AgOAc (1.7 mg, 0.1 equiv), $Cu(OAc)_2{\cdot}H_2O$ (22.0 mg, 1.1 equiv) was stirred in DCE (1.0 mL) under Ar atmosphere at 120 ^{o}C. After methyl acrylate was completely consumed (monitored by TLC), the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:2.5) to give the product **3aa** as a brown oil (34.9 mg, 94%).

3. Synthetic Transformations of 3aa.

General Procedure for Synthesis of phosphonamide 5

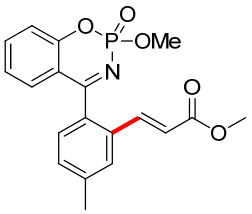
Ortho-olefinated cyclic *N*-phosphoryl ketimine (**3aa**) (18.6 mg, 0.05 mmol) was dissolved in MeOH (1.5 mL) and then was cooled to 0 ^{o}C. $NaBH_4$ (3.9 mg, 2.0 equiv) was added slowly to the solution. After the formation of organophosphorus intermediate **4** was complete by TLC, the reaction was allowed to warm to room temperature and stirred 3 h. The resulting solvent was extracted with DCM (3 x 3 mL), and the organics was concentrated under vacuum. The residue was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:1) to give the corresponding phosphonamide **5** as a colourless oil (9.3 mg, 46%).

General Procedure for Synthesis of phosphonamide 6

Ortho-olefinated cyclic *N*-phosphoryl ketimine (**3aa**) (18.6 mg, 0.05 mmol) was dissolved in MeOH (1.5 mL) and then was cooled to 0 ^{o}C. $NaBH_4$ (3.9 mg, 2.0 equiv) was added slowly to the solution. After the formation of organophosphorus intermediate **4** was complete, K_2CO_3 (8.3 mg, 1.2 equiv) was added slowly to the reaction mixture, the reaction was allowed to warm to room temperature and stirred 17 h. The resulting suspension was extracted with DCM (3 x 5 mL), and the organics was concentrated under vacuum. The residue was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:1) to give the corresponding phosphonamide **6** as a colourless solid (18.9 mg, 94%).

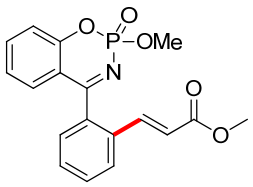
4. Characterization Data

(E)-methyl-3-(2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methylphenyl)acrylate (**3aa**). 12 h, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.56 (m, 3H), 7.33-7.21 (m, 4H), 7.10 (t, J = 8.0 Hz, 1H), 6.37 (d, J = 15.6 Hz, 1H), 3.98 (d, J = 11.6 Hz, 3H), 3.70 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8 (d, J = 5.9 Hz), 166.7, 154.3 (d, J = 5.7

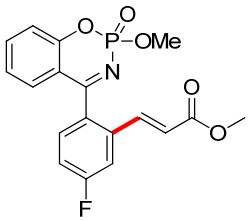


Hz), 141.1, 140.9, 136.1, 134.8 (d, J = 24.2 Hz), 133.0, 131.2, 130.6, 129.3, 127.7, 123.9, 120.5, 119.8 (d, J = 7.3 Hz), 119.3 (d, J = 25.9 Hz), 55.0 (d, J = 6.5 Hz), 51.8, 21.5 ppm. ESI HRMS: calcd. for $C_{19}H_{18}NO_5P$ [M + H^+] 372.1002, found 372.1002.

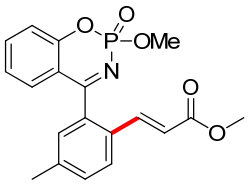
(E)-methyl-3-(2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)phenyl)acrylate (**3ba**). 12 h, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 7.2 Hz, 1H), 7.63-7.51 (m, 4H), 7.44 (d, J = 6.0 Hz, 1H), 7.29 (d, J = 8.8 Hz, 1H), 7.21-7.19 (m, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 4.00 (d, J = 11.6 Hz, 3H), 3.71 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.7 (d, J = 6.0 Hz), 165.6, 153.2 (d, J = 5.7 Hz), 140.1, 136.4 (d, J = 24.1 Hz), 135.2, 131.9, 130.1, 129.5, 128.8, 128.1, 126.1, 123.0, 119.8, 118.8 (d, J = 7.4 Hz), 118.1 (d, J = 26.0 Hz), 54.0 (d, J = 6.5 Hz), 50.8 ppm. ESI HRMS: calcd. for $C_{18}H_{16}NO_5P$ [M + H^+] 358.0844, found 358.0844.



(E)-methyl-3-(5-methoxy-2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)phenyl)acrylate (**3ca**). 12 h, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.58 (m, 2H), 7.41 (d, J = 8.8 Hz, 1H), 7.29-7.27 (m, 2H), 7.23 (d, J = 2.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.04 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 6.37(d, J = 16.0 Hz, 1H), 3.99 (d, J = 11.6 Hz, 3H), 3.92 (s, 3H), 3.72 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3 (d, J = 5.7 Hz), 166.6, 161.2, 154.3 (d, J = 5.6 Hz), 141.6, 136.0, 135.2, 131.3 (d, J = 5.9 Hz), 130.0 (d, J = 24.5 Hz), 123.9, 120.8, 119.8 (d, J = 7.4 Hz), 119.5 (d, J = 25.7 Hz), 115.3, 112.3, 55.6, 55.0 (d, J = 6.5 Hz), 51.8 ppm. ESI HRMS: calcd. for $C_{19}H_{18}NO_6P$ [M + H^+] 388.0950, found 388.0949.



(E)-methyl-3-(5-fluoro-2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)phenyl)acrylate (**3da**). 12 h, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.49 (m, 2H), 7.40-7.36 (m, 2H), 7.23-7.04 (m, 4H), 6.31 (d, J = 15.6 Hz, 1H), 3.93 (d, J = 12.0 Hz, 3H), 3.65 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5 (d, J = 5.6 Hz), 165.2, 163.8, 161.3, 153.3 (d, J = 5.7 Hz), 139.0 (d, J = 2.1 Hz), 135.3, 134.8 (d, J = 8.0 Hz), 132.5 (dd, J_1 = 3.3 Hz, J_2 = 24.6 Hz), 130.5 (d, J = 8.7 Hz), 129.9, 123.0, 120.9, 118.9 (d, J = 7.4 Hz), 118.1 (d, J = 25.8 Hz), 116.0 (d, J = 22.0 Hz), 112.9 (d, J = 22.7 Hz), 54.1 (d, J = 6.5 Hz), 50.9 ppm. ESI HRMS: calcd. for $C_{18}H_{15}FNO_5P$ [M + H^+] 376.0750, found 376.0751.



(E)-methyl-3-(2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-4-methylphenyl)acrylate (**3ea**). 12 h, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.52 (m, 3H), 7.38-7.26 (m, 3H), 7.20-7.09 (m, 2H), 6.35 (d, J = 15.6 Hz, 1H), 4.00 (d, J = 11.6 Hz, 3H), 3.69 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.0 (d, J = 6.0 Hz), 166.7, 154.2 (d, J = 5.7 Hz), 141.0, 140.6, 137.5 (d, J = 24.0 Hz), 136.2, 131.4, 131.2, 130.0, 129.5, 127.0, 124.0, 119.7 (d, J = 7.3 Hz), 119.2 (d, J = 26.1 Hz), 55.0 (d, J = 6.6 Hz), 51.7, 21.3 ppm. ESI HRMS: calcd. for $C_{19}H_{18}NO_5P$ [M + H^+] 372.1001, found 372.0997.

(E)-methyl-3-(2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)thiophen-3-yl) acrylate (**3fa**)**.** 12 h, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.54 (m, 4H), 7.41 (d, *J* = 5.2 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.32 (d, *J* = 15.6 Hz, 1H), 3.98 (d, *J* = 11.6 Hz, 3H), 3.70 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3 (d, *J* = 5.7 Hz), 166.6, 161.2, 154.3 (d, *J* = 5.6 Hz), 141.6, 136.0, 135.2, 131.3 (d, *J* = 5.9 Hz), 130.0 (d, *J* = 24.5 Hz), 123.9, 120.8, 119.8 (d, *J* = 7.4 Hz), 119.5 (d, *J* = 25.7 Hz), 115.3, 112.3, 55.6, 55.0 (d, *J* = 6.5 Hz), 51.8 ppm. ESI HRMS: $C_{16}H_{14}NO_5PS$ [M + H^+] 364.0409, found 364.0402.

(E)-methyl-3-(2-(2,8-dimethoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methylphen yl)acrylate (**3ga**)**.** 12 h, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 15.6 Hz 1H), 7.55 (s, 1H), 7.35-7.30 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.77 (dd, J_1 = 1.2 Hz, J_2 = 8Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.99 (d, *J* = 12.0 Hz, 3H), 3.96 (s, 3H), 3.71 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.9 (d, *J* = 6.0 Hz), 166.7, 149.3 (d, *J* = 6.1 Hz), 144.0 (d, *J* = 5.4 Hz), 141.4, 140.7 135.2, 135.0, 132.9, 130.5,129.3, 127.6, 123.3, 122.3, 120.4, 120.1, 119.8, 118.0, 56.6, 55.1 (d, *J* = 5.6 Hz), 51.7, 21.4 ppm. ESI HRMS: calcd. for $C_{20}H_{20}NO_6P$ [M + H^+] 402.1106, found 402.1102.

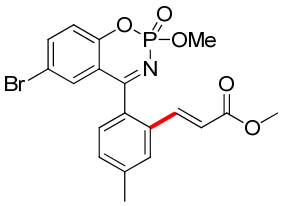
(E)-methyl-3-(2-(2-methoxy-7-methyl-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methy lphenyl)acrylate (**3ha**). 12 h, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 16.0 Hz, 1H), 7.56 (s, 1H), 7.32 (s, 2H), 7.09-7.07 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 3.97 (d, *J* = 12.0 Hz, 3H), 3.71 (s, 3H), 2.46 (s, 3H), 2.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.7 (d, *J* = 5.8 Hz), 166.7, 154.3 (d, *J* = 5.7 Hz), 148.2, 141.5, 140.7, 135.0 (d, *J* = 24.4 Hz), 132.9, 131.0, 130.5, 129.2, 127.6, 124.9, 120.3, 119.9 (d, *J* = 7.3 Hz), 117.1 (d, *J* = 26.0 Hz), 54.9 (d, *J* = 6.6 Hz), 51.7, 21.9, 21.4 ppm. ESI HRMS: calcd. for $C_{20}H_{20}NO_5P$ [M + H^+] 386.1157, found 386.1154.

(E)-methyl-3-(2-(7-chloro-2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methy lphenyl)acrylate (**3ia**). 12 h, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.57 (m, 2H), 7.32-7.28 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.08 (dd, J_1 = 1.6 Hz, J_2 = 8.4Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 4.00 (d, *J* = 11.6 Hz, 3H), 3.72 (s, 3H), 2.47 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.9 (d, *J* = 6.0 Hz), 166.6, 154.7 (d, *J* = 5.4 Hz), 141.9 (d, *J* = 1.5 Hz), 141.2(d, *J* = 1.5 Hz), 134.3 (d, *J* = 24.1 Hz), 133.0, 132.1, 130.7, 129.2, 127.8, 124.5, 120.7, 120.1 (d, *J* = 7.6 Hz), 117.8 (d, *J* = 26.5 Hz), 55.1 (d, *J* = 6.6 Hz), 51.8, 21.5 ppm. ESI HRMS: calcd. for $C_{19}H_{17}ClNO_5P$ [M + H^+] 406.0611, found 406.0609.

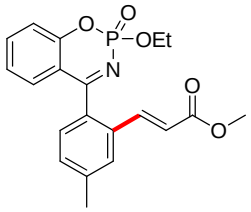
(E)-methyl-3-(2-(2-methoxy-6-methyl-2-oxido-2H-benzo[e][1,3,2]oxaza phosphinin-4-yl)-5-methylphenyl)acrylate (**3ja**). 12 h, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.57 (m, 2H), 7.41-7.27 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.98 (s, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.97 (d, *J* =

11.6 Hz, 3H), 3.71 (s, 3H), 2.48 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.9 (d, *J* = 5.9 Hz), 166.7, 152.3 (d, *J* = 5.6 Hz), 141.5, 140.7, 136.9, 134.9 (d, *J* = 24.1 Hz), 133.7, 133.0, 131.0, 130.5, 129.2, 127.7, 120.3, 119.4 (d, *J* = 7.4 Hz), 119.0 (d, *J* = 25.7 Hz), 54.9 (d, *J* = 6.6 Hz), 51.8, 21.5, 20.7 ppm. ESI HRMS: calcd. for $C_{20}H_{20}NO_5P$ [M + H^+] 386.1157, found 386.1153.

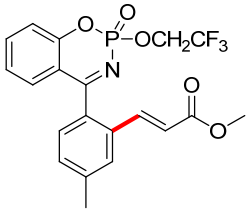
(E)-methyl-3-(2-(6-bromo-2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methylphenyl)acrylate (**3ka**). 12 h, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.63 (m, 2H), 7.58 (s, 1H), 7.36-7.27 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.00 (d, *J* = 11.6 Hz, 3H), 3.73 (s, 3H), 2.49 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3 (d, *J* = 6.2 Hz), 166.6, 153.3 (d, *J* = 5.5 Hz), 141.4, 141.2, 138.7, 133.9 (d, *J* = 23.8 Hz), 133.4, 133.2, 130.7, 129.3, 128.0, 121.6 (d, *J* = 7.3 Hz), 120.8, 120.5 (d, *J* = 26.3 Hz), 116.3, 55.2 (d, *J* = 6.5 Hz), 51.8, 21.5 ppm. ESI HRMS: calcd. for $C_{19}H_{17}BrNO_5P$ [M + H^+] 450.0106, found 450.0103.



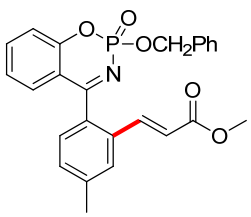
(E)-methyl-3-(2-(2-ethoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methylphenyl)acrylate (**3la**). 12 h, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.56 (m, 3H), 7.33-7.20 (m, 4H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 4.40-4.36 (m, 2H), 3.71 (s, 3H), 2.47 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3 (d, *J* = 5.9 Hz), 165.6, 153.2 (d, *J* = 5.7 Hz), 140.4, 139.7, 134.9, 133.8 (d, *J* = 24.3 Hz), 132.0, 130.1, 129.5, 128.2, 126.7, 122.8, 119.5, 118.7 (d, *J* = 7.3 Hz), 118.2 (d, *J* = 26.0 Hz), 64.1 (d, *J* = 6.5 Hz), 50.7, 20.4, 15.4 (d, *J* = 6.3 Hz) ppm. ESI HRMS: calcd. for $C_{20}H_{20}NO_5P$ [M + H^+] 386.1157, found 386.1161.



(E)-methyl-3-(5-methyl-2-(2-oxido-2-(2,2,2-trifluoroethoxy)-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)phenyl)acrylate (**3ma**). 12 h, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.57 (m, 3H), 7.33-7.27 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 4.75-4.56 (m, 2H), 3.71 (s, 3H), 2.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.3 (d, *J* = 5.9 Hz), 166.6, 154.0 (d, *J* = 5.7 Hz), 141.2 (d, *J* = 5.2 Hz), 136.5, 134.3 (d, *J* = 24.9 Hz), 133.3, 131.5, 130.5, 129.4, 127.9, 124.3, 122.5 (dd, J_1 = 8.9 Hz, J_2 = 276.1 Hz), 120.8, 119.8 (d, *J* = 7.7 Hz), 119.0 (d, *J* = 26.7 Hz), 63.9 (dq, J_1 = 5.1 Hz, J_2 = 37.9 Hz), 51.7, 21.5 ppm. ESI HRMS: calcd. for $C_{20}H_{17}F_3NO_5P$ [M + H^+] 440.0875, found 440.0872.



(E)-methyl-3-(2-(2-(benzyloxy)-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methylphenyl)acrylate (**3na**). 12 h, 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.56 (m, 3H), 7.45-7.31 (m, 7H), 7.21-7.19 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 5.41-5.27 (m, 2H), 3.65 (s, 3H), 2.47 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8 (d, *J* = 6.0 Hz), 166.6, 154.2 (d, *J* = 5.6 Hz), 141.4, 140.8, 136.0, 135.7 (d, *J* = 6.7 Hz), 134.8 (d, *J* = 24.3 Hz), 133.1, 131.2, 130.5, 129.3, 128.6, 128.1, 127.7, 123.8, 120.6, 119.8 (d, *J* = 7.4 Hz), 119.3 (d, *J* = 26.3 Hz), 70.0 (d, *J* = 6.2 Hz), 51.7, 21.4 ppm. ESI HRMS:



calcd. for $C_{25}H_{22}NO_5P$ [M + H^+] 448.1314, found 448.1310.

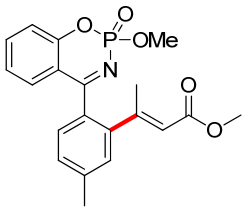
(E)-ethyl-3-(2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methylphenyl) acrylate (**3ab**). 12 h, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.57 (m, 3H), 7.36-7.22 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 4.16 (q, J_1 = 7.2 Hz, J_2 = 14.0 Hz, 2H), 3.98 (d, *J* = 11.6 Hz, 3H), 2.46 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.9 (d, *J* = 5.9 Hz), 166.2, 154.2 (d, *J* = 5.6 Hz), 141.1, 140.9, 136.1, 134.7 (d, *J* = 24.2 Hz), 133.1, 131.3, 130.5, 129.3, 127.6, 123.9, 120.9, 119.7 (d, *J* = 7.4 Hz), 119.3 (d, *J* = 25.9 Hz), 60.6, 55.0 (d, *J* = 6.6 Hz), 21.4, 14.2 ppm. ESI HRMS: calcd. for $C_{20}H_{20}NO_5P$ [M + H^+] 386.1157, found 386.1152.

(E)-tert-butyl-3-(2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methylphenyl)acrylate (**3ac**). 12 h, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.56 (m, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.36-7.22 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 3.98 (d, *J* = 11.6 Hz, 3H), 2.46 (s, 3H), 1.42 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.0 (d, *J* = 5.9 Hz), 165.4, 154.2 (d, *J* = 5.7 Hz), 140.8, 140.1, 136.0, 134.7 (d, *J* = 24.2 Hz), 133.2, 131.3, 130.3, 129.2, 127.5, 123.9, 122.8, 119.7 (d, *J* = 7.4 Hz), 119.4 (d, *J* = 26.0 Hz), 80.6, 55.0 (d, *J* = 6.6 Hz), 28.0, 21.4 ppm. ESI HRMS: calcd. for $C_{22}H_{24}NO_5P$ [M + H^+] 414.1470, found 414.1463.

(E)-phenyl-3-(2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methylphenyl)- acrylate (**3ad**). 12 h, 53 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 12.0 Hz, 1H), 7.66 (s, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.37-7.07 (m, 10H), 6.58 (d, *J* = 15.6 Hz, 1H), 3.95(d, *J* = 11.6 Hz, 3H), 2.50 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.6 (d, *J* = 5.9 Hz), 164.7, 154.3 (d, *J* = 5.7 Hz), 150.6, 143.1, 141.0, 136.1, 134.9 (d, *J* = 24.2 Hz), 132.9, 131.2, 130.9, 129.5, 129.4, 127.8, 125.8, 123.9, 121.5, 119.9, 119.8 (d, *J* = 7.5 Hz), 119.3 (d, *J* = 25.9 Hz), 55.0 (d, *J* = 6.7 Hz), 21.5 ppm. ESI HRMS: calcd. for $C_{24}H_{20}NO_5P$ [M + H^+] 434.1457, found 434.1458.

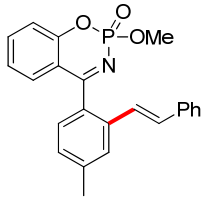
(E)-benzyl-3-(2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methylphenyl)- acrylate (**3ae**). 12 h, 81 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.58 (m, 3H), 7.38-7.22 (m, 9H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 5.15 (s, 2H), 3.91 (d, *J* = 12.0 Hz, 3H), 2.47 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.8 (d, *J* = 5.9 Hz), 166.9, 154.2 (d, *J* = 5.7 Hz), 141.7, 140.9, 136.0, 135.9, 134.9 (d, *J* = 24.2 Hz), 133.0, 131.2, 130.7, 129.3, 128.6, 128.2, 128.1, 127.6, 123.9, 120.5, 119.7 (d, *J* = 7.4 Hz), 119.4 (d, *J* = 26.0 Hz), 66.3, 54.9 (d, *J* = 6.6 Hz), 21.4 ppm. ESI HRMS: calcd. for $C_{25}H_{22}NO_5P$ [M + H^+] 448.1314, found 448.1308.

(E)-methyl-3-(2-(2-methoxy-2-oxido-2H-benzo[e][1,3,2]oxazaphosphinin-4-yl)-5-methylphenyl)but-2-enoate (**3af**). 12 h, 50 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.47 (m, 1H), 7.32 (d, *J* =



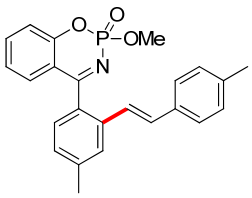
7.6 Hz, 1H), 7.22-7.12 (m, 4H), 7.03 (t, *J* = 7.6 Hz, 1H), 5.68 (s, 1H), 3.85 (d, *J* = 11.6 Hz, 3H), 3.55 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.7 (d, *J* = 4.5 Hz), 165.2, 155.0, 153.1 (d, *J* = 5.3 Hz), 142.1, 134.7, 129.6, 128.6, 127.9, 127.8, 122.6, 119.3, 118.7 (d, *J* = 7.2 Hz), 53.9 (d, *J* = 6.7 Hz), 50.0, 20.4, 19.6 ppm. ESI HRMS: calcd. for $C_{20}H_{20}NO_5P$ [M + Na^+] 408.0977, found 408.0972.

(E)-2-methoxy-4-(4-methyl-2-styrylphenyl)-2H-benzo[e][1,3,2]oxazaphosphinine-2-oxide (**3ag**).

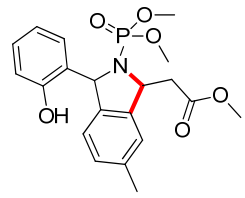


24 h, 90 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H),7.55 (t, *J* = 8.0 Hz, 1H), 7.31-7.20 (m, 9H), 7.09-7.02 (m, 3H), 3.98 (d, *J* = 11.2 Hz, 3H), 2.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.2 (d, *J* = 5.8 Hz), 154.1 (d, *J* = 5.6 Hz), 140.6, 136.9, 135.9, 135.8, 133.3 (d, *J* = 24.0 Hz), 131.6, 131.4, 129.0, 128.7, 128.2, 128.0, 126.6 (d, *J* = 7.4 Hz), 125.5, 123.8, 119.6 (d, *J* = 7.4 Hz), 119.5 (d, *J* = 26.2 Hz), 54.9 (d, *J* = 6.4 Hz), 21.6 ppm. ESI HRMS: calcd. for $C_{23}H_{20}NO_3P$ [M + H^+] 390.1259, found 390.1257.

(E)-2-methoxy-4-(4-methyl-2-(4-methylstyryl)phenyl)-2H-benzo[e][1,3,2]oxazaphosphinine-2-oxide (**3ah**). 24 h, 89 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.31-7.17 (m, 6H), 7.09-6.99 (m, 5H), 3.98 (d, *J* = 11.6 Hz, 3H), 2.47 (s, 3H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.1 (d, *J* = 6.6 Hz), 154.1 (d, *J* = 5.2 Hz), 140.5, 138.0, 136.1, 135.7, 134.2, 133.2, 131.6, 131.3, 129.4, 129.0, 128.0, 126.5 (d, *J* = 10.4 Hz), 124.5, 123.8, 119.6 (d, *J* = 7.4 Hz), 119.5 (d, *J* = 26.1 Hz), 54.9 (d, *J* = 6.4 Hz), 21.6, 21.2 ppm. ESI HRMS: calcd. for $C_{24}H_{22}NO_3P$ [M + H^+] 404.1416, found 404.1414.



(E)-methyl-3-(2-(((dimethoxyphosphoryl)amino)(2-hydroxyphenyl)methyl)-5-methylphenyl)acrylate (**5**). 3 h, 46 % yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.06 (d, *J* = 15.6 Hz, 1H),7.52 (d, *J* = 8.4 Hz, 1H), 7.30 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.97-6.91 (m, 2H), 6.76 (t, *J* = 7.8 Hz, 1H), 6.22 (d, *J* = 15.6 Hz, 1H), 5.84 (t, *J* = 10.2 Hz, 1H), 4.25 (t, *J* = 12.0 Hz, 1H), 3.75 (s, 3H), 3.61 (d, *J* = 10.8 Hz, 3H), 3.56 (d, *J* = 10.8 Hz, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 154.3, 142.4, 138.5 (d, *J* = 5.0 Hz), 137.2, 132.5, 130.7, 128.9, 128.4 (d, *J* = 4.7 Hz), 128.3, 119.9 (d, *J* = 18.5 Hz), 117.0, 53.4 (d, *J* = 5.2 Hz), 52.6, 51.7, 21.0 ppm. ESI HRMS: calcd. for $C_{20}H_{24}NO_6P$ [M + Na^+] 428.1239, found 428.1238.



methyl-2-(2-(dimethoxyphosphoryl)-3-(2-hydroxyphenyl)-6-methylisoindolin-1-yl)acetate (**6**). 17 h, 94 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.47 (s, 1H), 7.18-7.12 (m, 3H), 7.02-6.94 (m, 2H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 6.8 Hz, 1H), 5.21-5.18 (m, 1H), 3.73-3.67 (m, 6H), 3.45 (d, *J* = 11.6 Hz, 3H), 2.84-2.64 (m, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 155.7, 141.6 (d, *J* = 8.1 Hz), 138.1, 137.4 (d, *J* = 8.7 Hz), 130.9, 129.5, 129.5, 128.7, 123.9, 123.0, 120.5, 119.3, 62.6 (d, *J* = 6.8 Hz), 60.1 (d, *J* = 4.2 Hz),

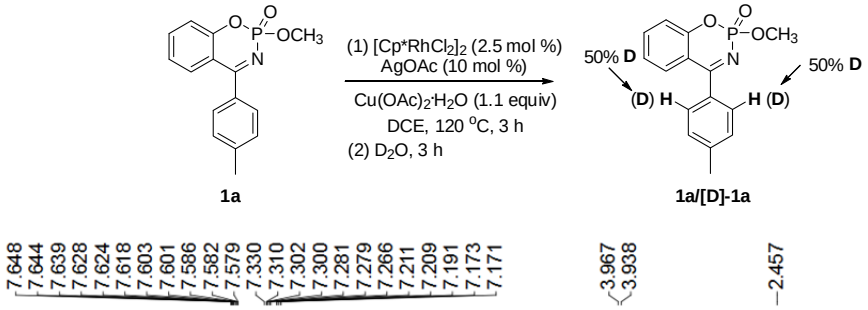
53.1 (d, J = 5.8 Hz), 53.0 (d, J = 5.3 Hz), 51.7, 43.2, 21.4 ppm. ESI HRMS: calcd. for $C_{20}H_{22}NO_6P$ [M + H^+] 406.1419, found 406.1422.

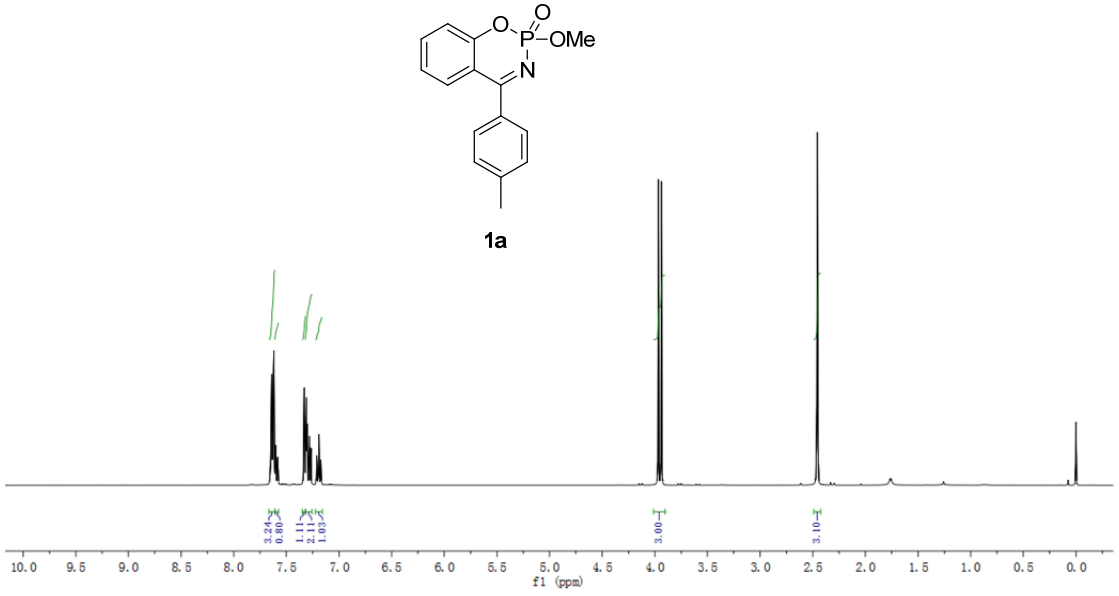
Reference

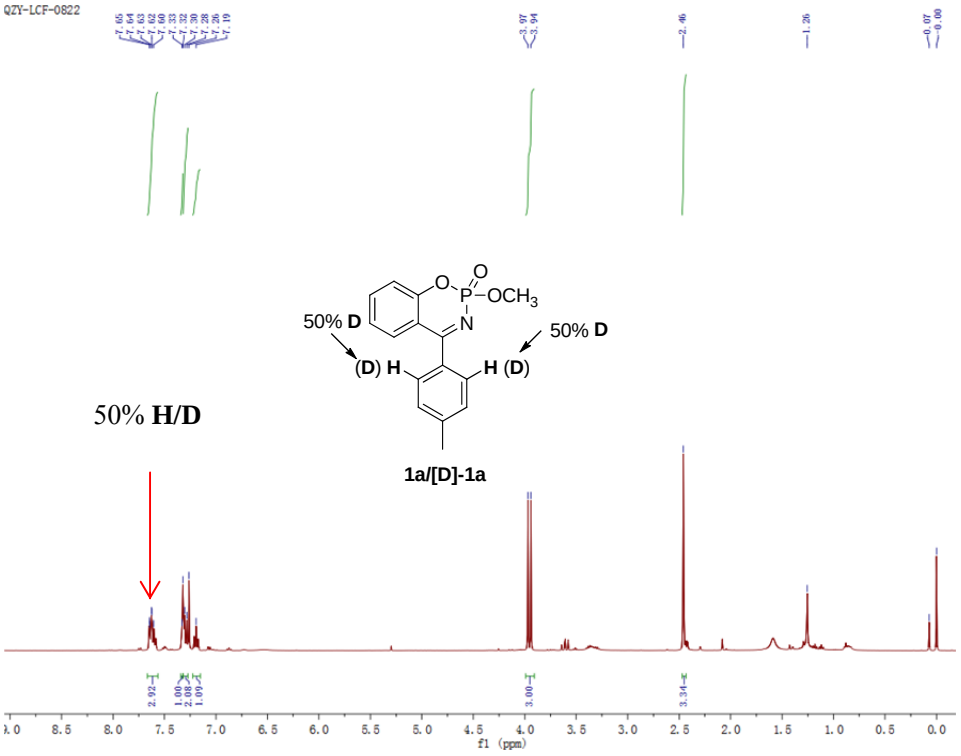
1 S.-S. Li, L. Wu, L. Qin, Y.-Q. Zhu, F. Su, Y.-J. Xu, L. Dong, *Org. Lett.*, DOI: 10.1021/acs.orglett. 6b01895.

5. **Mechanism Study.**

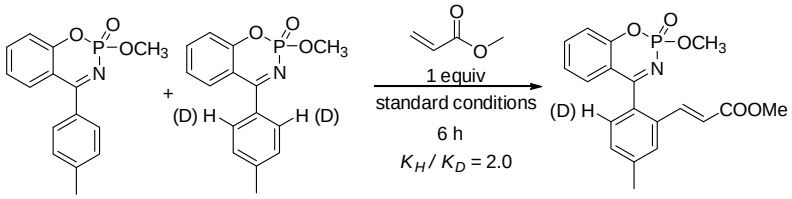
Deuterium-labeling experiments were carried out to study the mechanism of this coupling reaction. **1a** (0.1 mmol) was stirred in the absence of alkene for 3 h under standard condition, then D_2O (100 μL) was added and stirred for 3 h. The deuterium rate was obtained from ^{1}H NMR.







To investigate the mechanism of this reaction, deuterium experiments and a kinetic isotope effect (KIE) study were conducted. DKIE of 2 was observed, thus indicating that C-H bond cleavage might be involved in the rate-determining step.

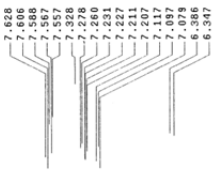


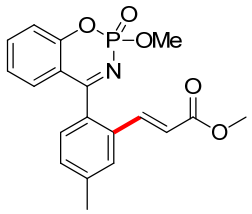
1a **1a/[D]-1a**, 50% D

1a/[D]-**1a** = 1:1

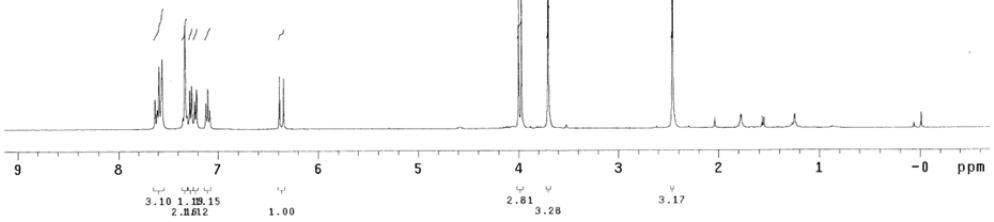
3aa-D/H

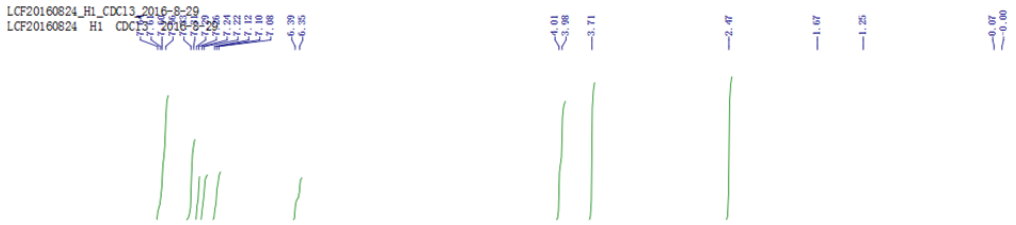
70%

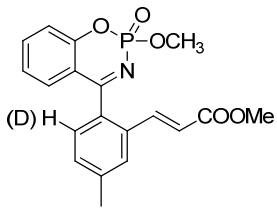




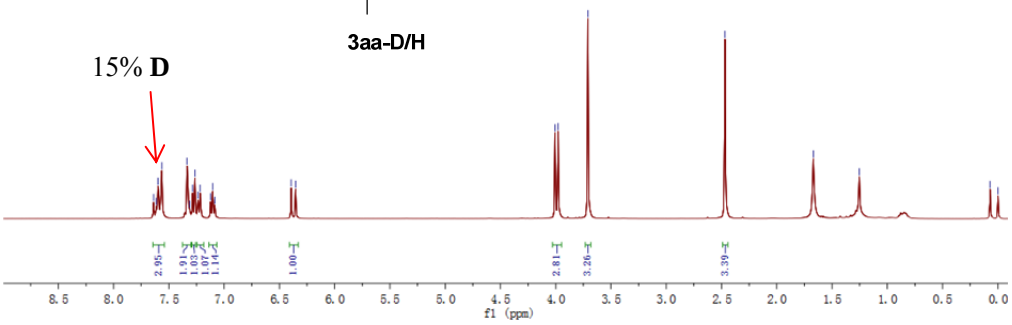
3aa



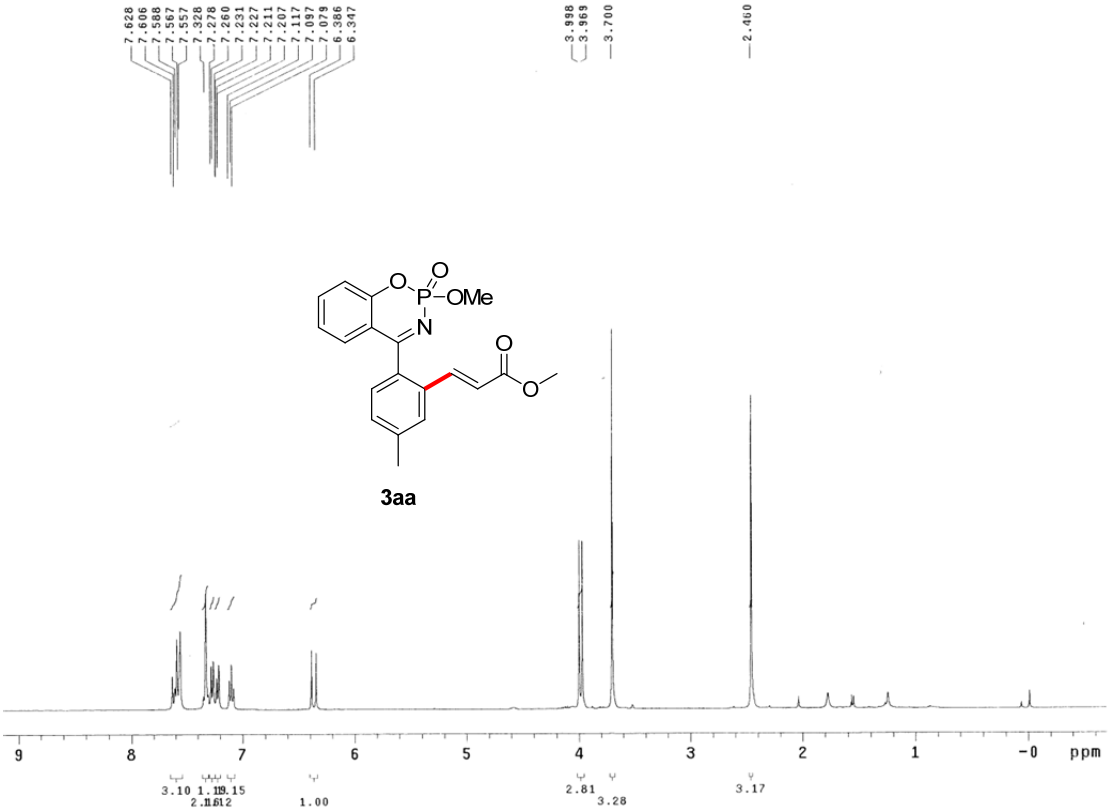


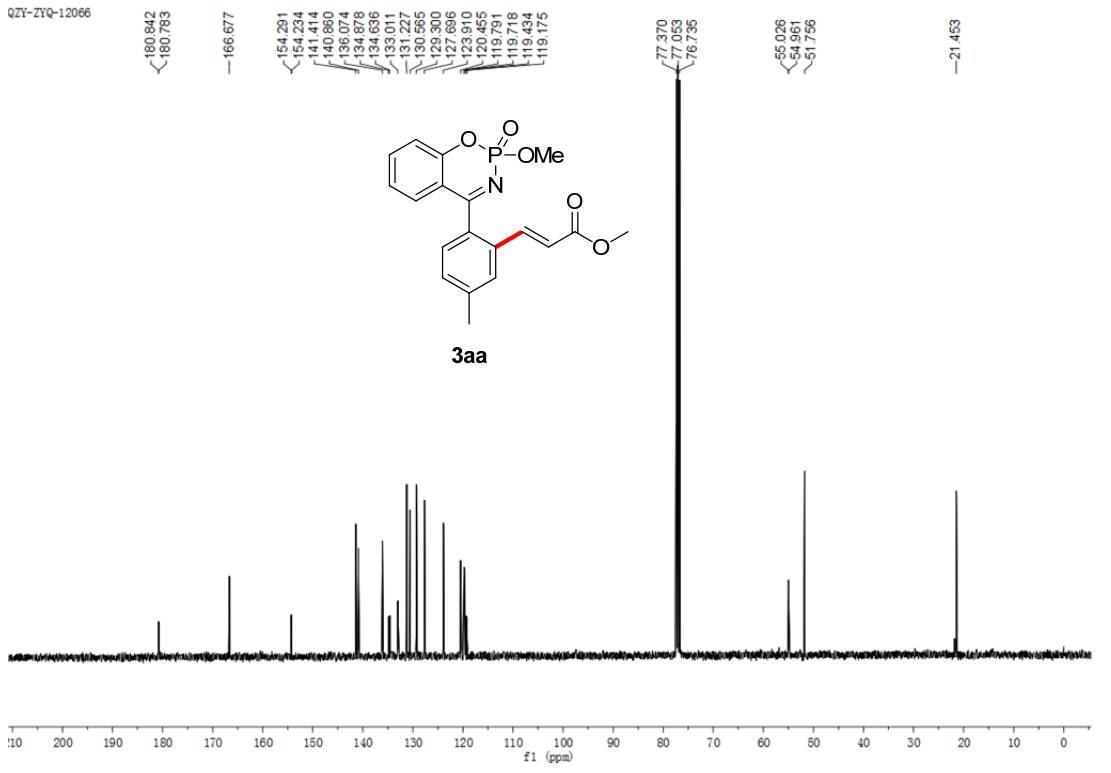


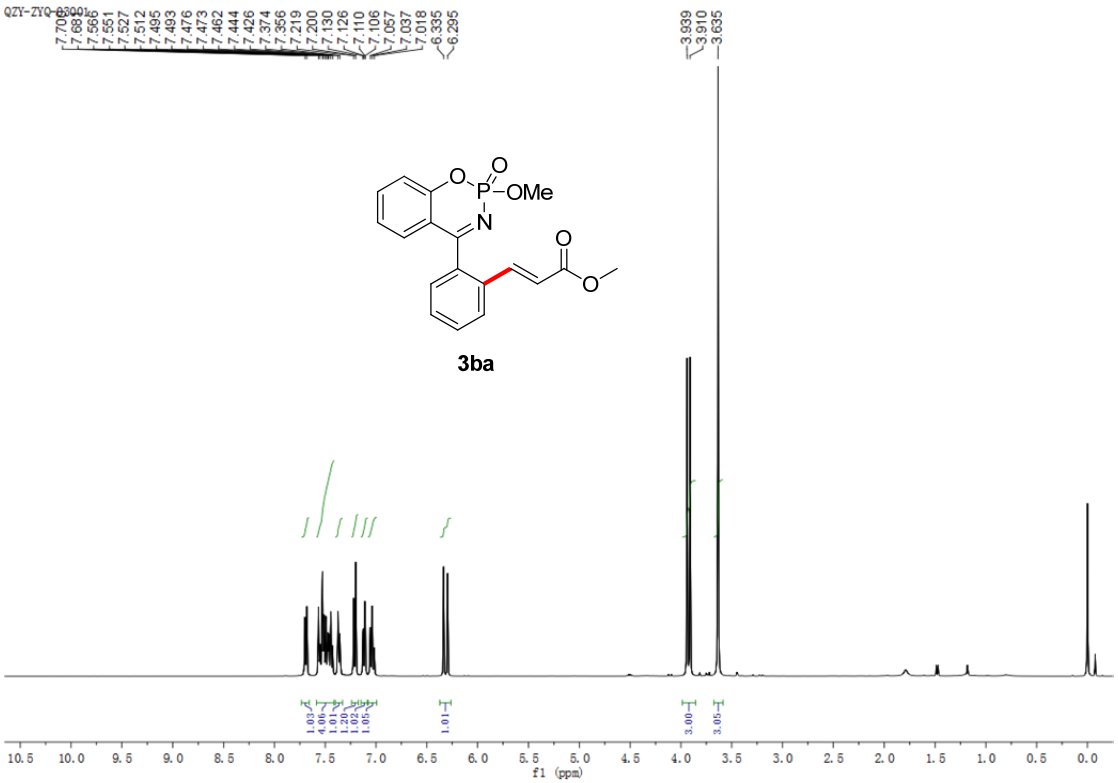
3aa-D/H

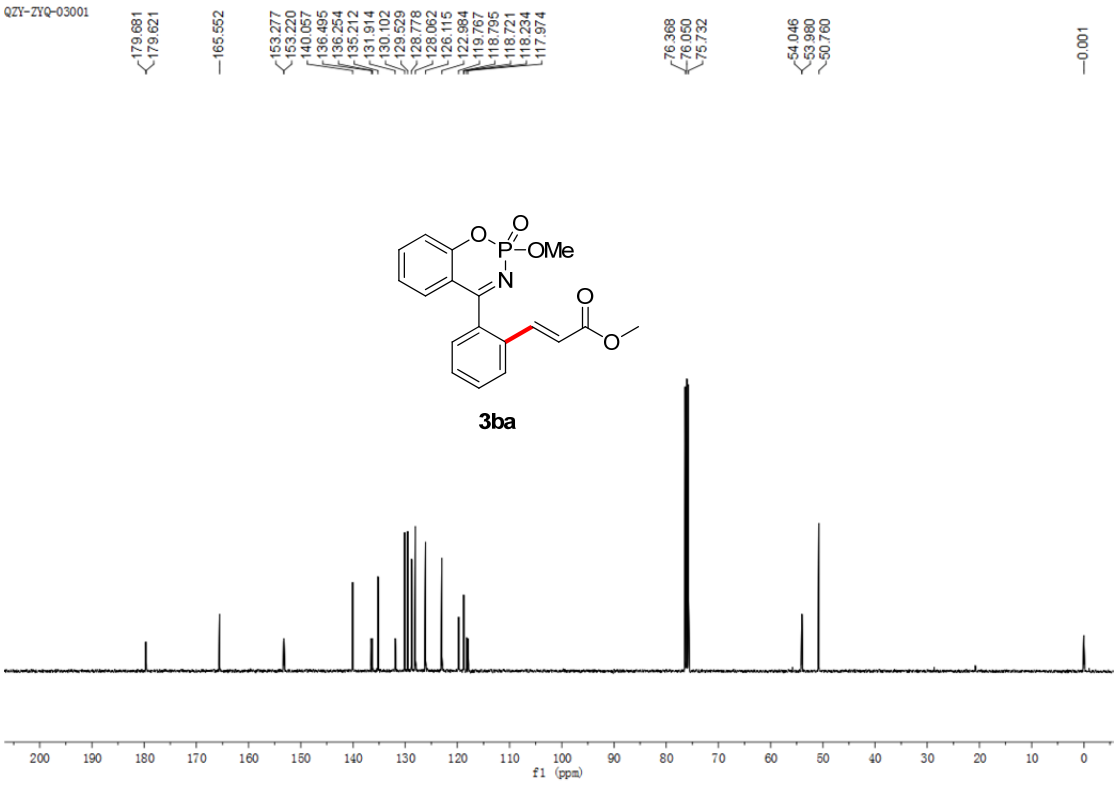


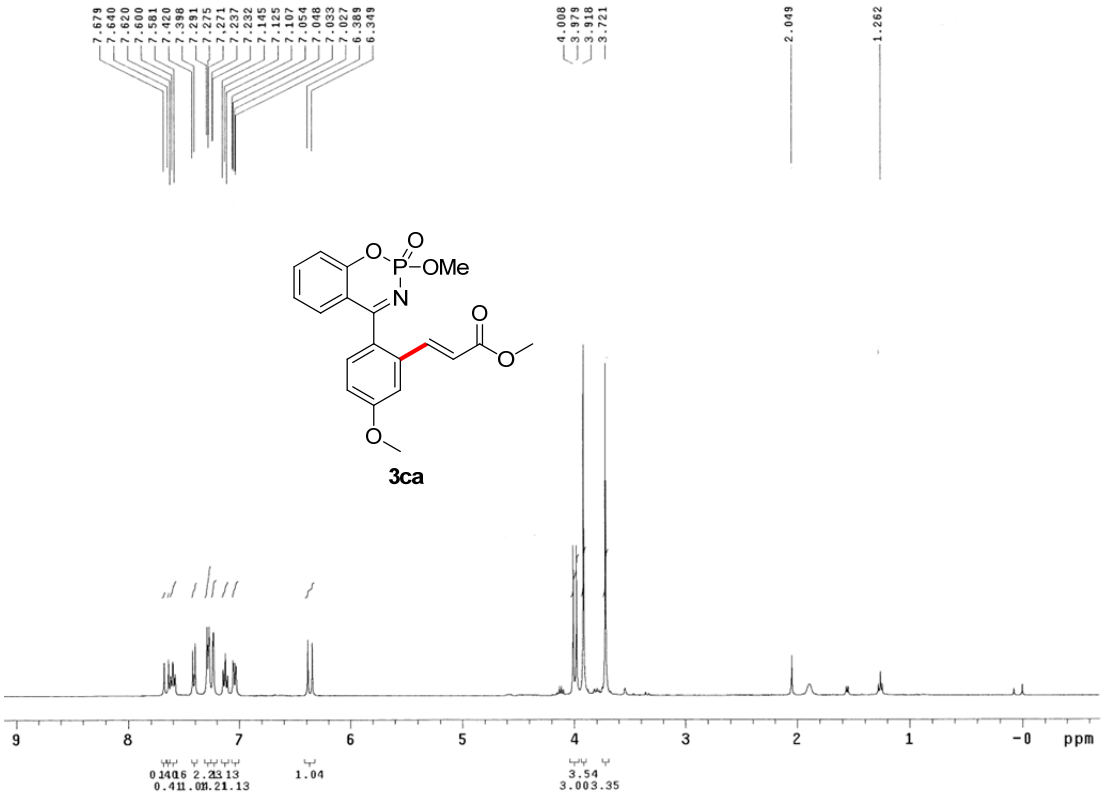
6. **NMR Spectra.**

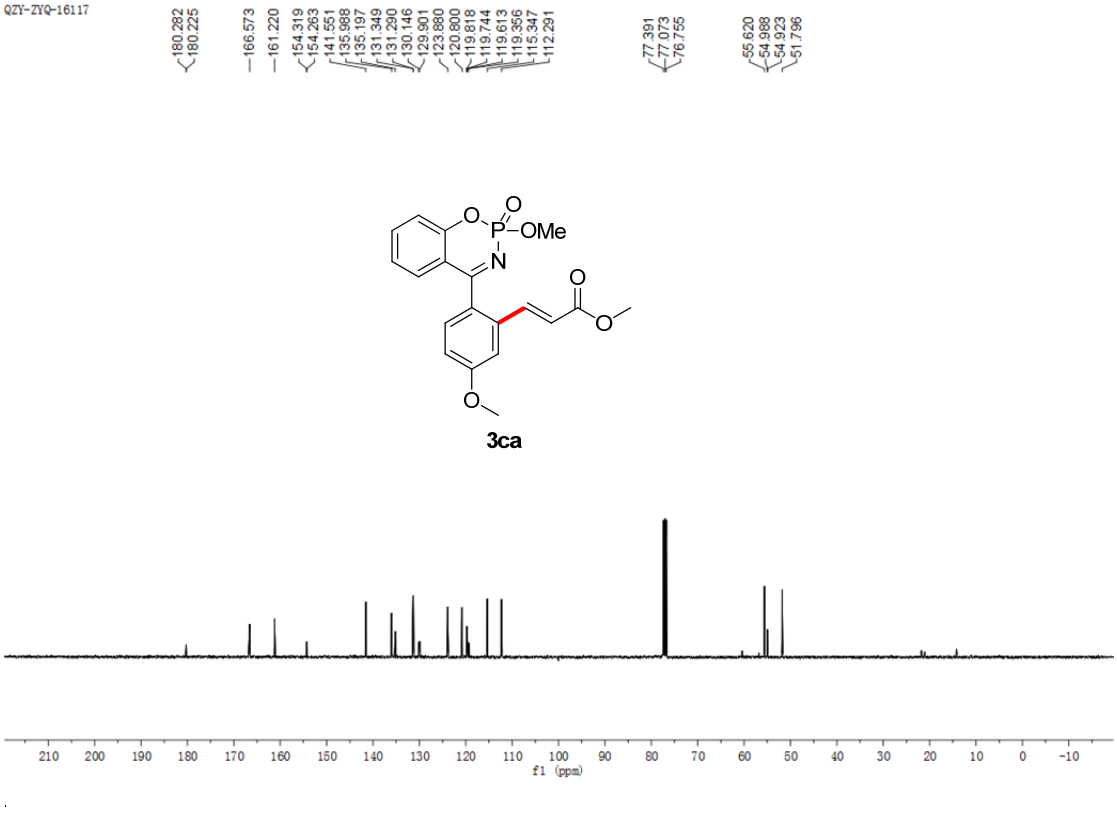


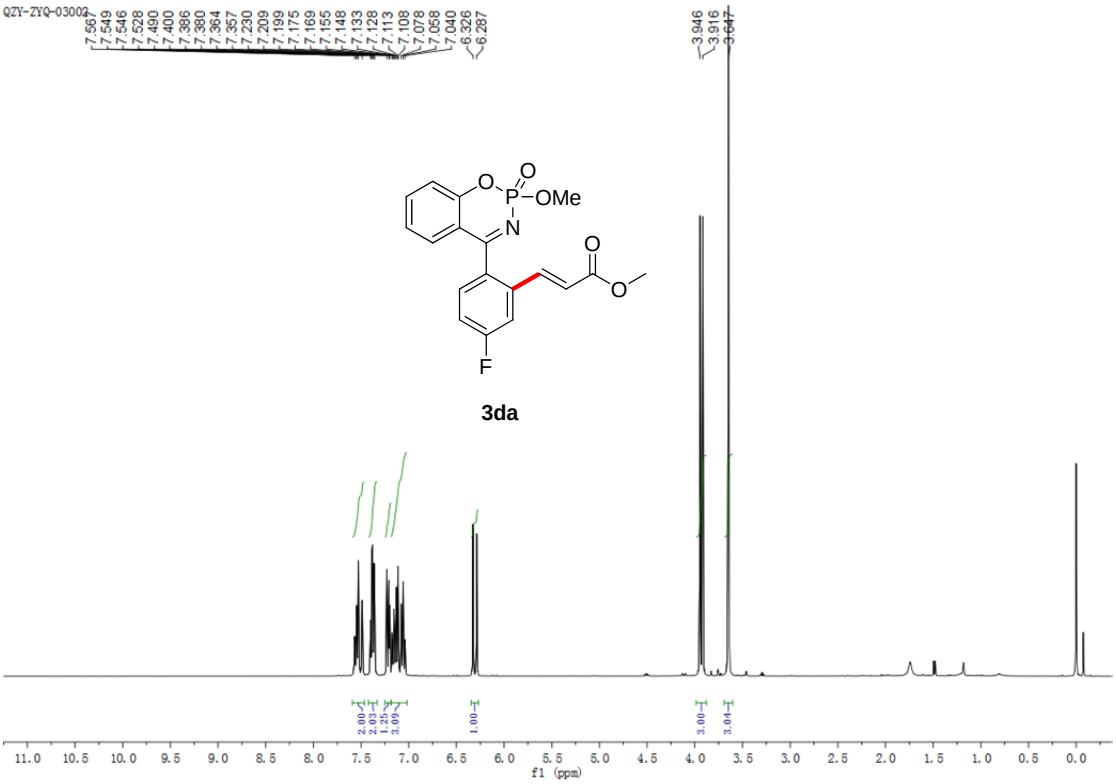



QZY-ZYQ-03001
7.708
7.683
7.566
7.551
7.527
7.512
7.495
7.493
7.476
7.473
7.462
7.444
7.426
7.374
7.356
7.219
7.200
7.130
7.126
7.110
7.106
7.057
7.037
7.018
6.335
6.295
3.939
3.910
3.635
O
O
P
OMe
N
O
O
3ba
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

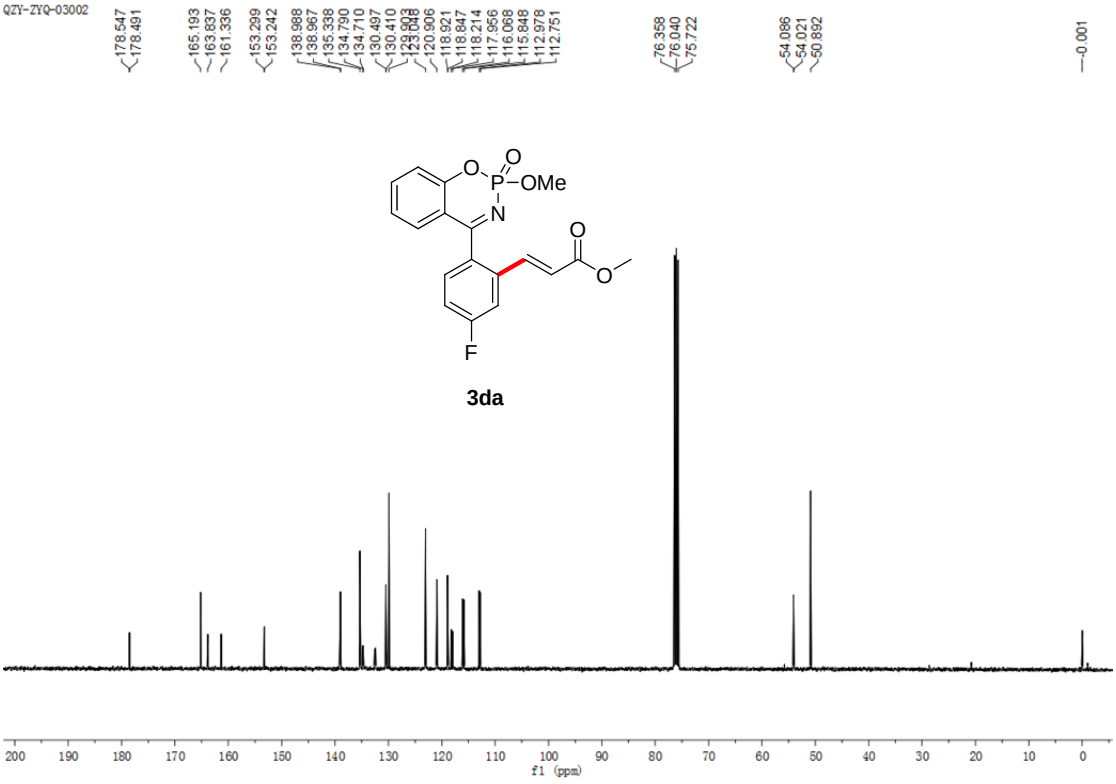

QZY-ZYQ-03001
179.681
179.621
165.552
153.277
153.220
140.057
136.495
136.254
135.212
131.914
130.102
129.529
128.778
128.062
126.115
122.984
119.767
118.795
118.721
118.234
117.974
76.368
76.050
75.732
54.046
53.980
50.760
0.001
O
O
P
OMe
N
O
O
3ba
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.679
7.640
7.620
7.600
7.581
7.420
7.398
7.291
7.275
7.271
7.237
7.232
7.145
7.125
7.107
7.054
7.048
7.033
7.027
6.389
6.349
4.008
3.979
3.918
3.721
2.049
1.262
O
O
P
OMe
N
O
O
O
3ca
9
8
7
6
5
4
3
2
1
-0
ppm
0.41
1.06
2.23
3.13
1.04
3.54
3.00
3.35

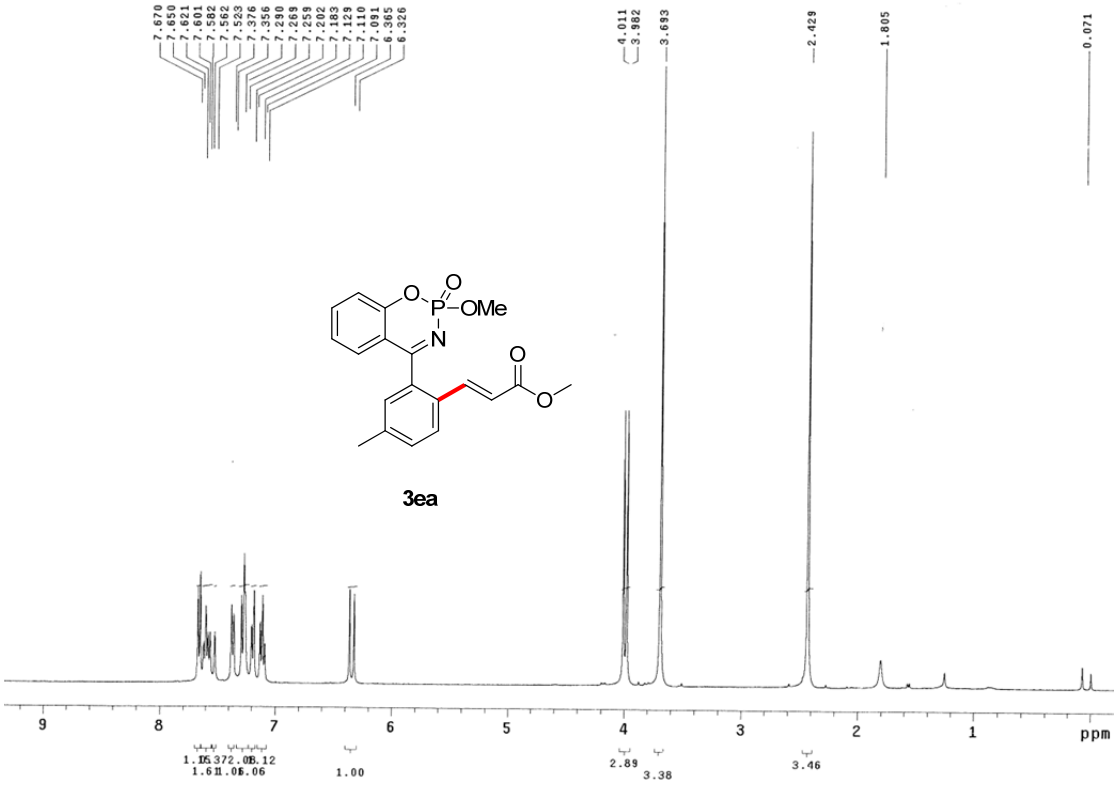

QZY-ZYQ-16117
180.282
180.225
166.573
161.220
154.319
154.263
141.551
135.988
135.197
131.349
131.290
130.146
129.901
123.880
120.800
119.818
119.744
119.613
119.356
115.347
112.291
77.391
77.073
76.755
55.620
54.988
54.923
51.796
O
O
P
OMe
N
O
O
O
3ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


QZY-ZYQ-03002
7.567
7.549
7.546
7.528
7.490
7.400
7.386
7.380
7.364
7.357
7.230
7.209
7.199
7.175
7.169
7.155
7.148
7.133
7.128
7.113
7.108
7.078
7.058
7.040
6.326
6.287
3.946
3.916
3.647
O
P
OMe
N
O
O
F
2.00
2.03
1.25
3.09
1.00
3.00
3.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

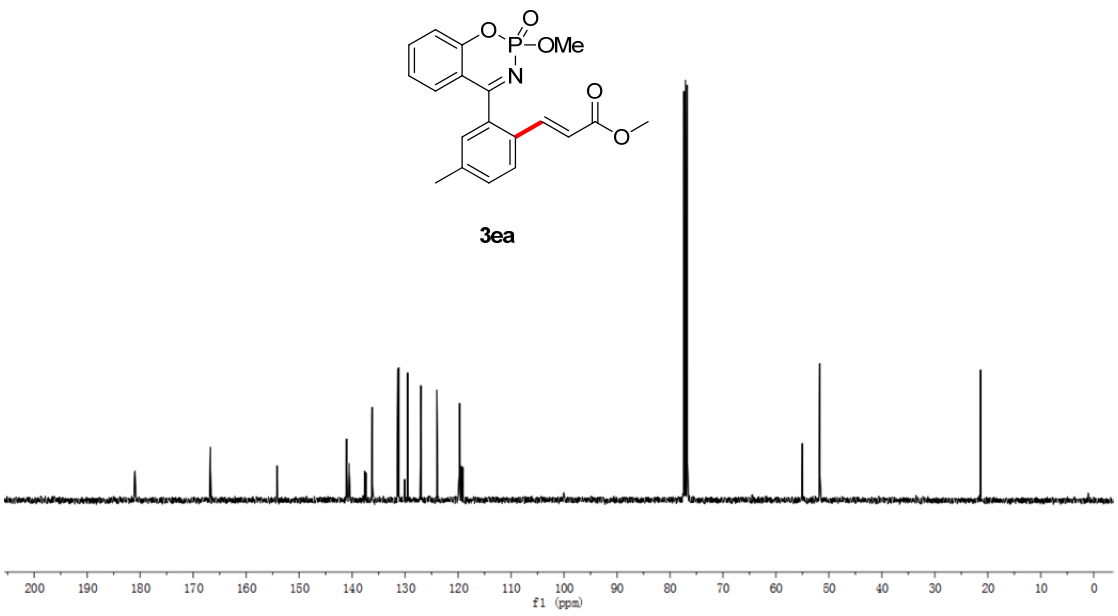
3da


QZY-ZYQ-03002
178.547
178.491
165.193
163.837
161.336
153.299
153.242
138.988
138.967
135.338
134.790
134.710
130.497
130.410
129.903
123.048
120.906
118.921
118.847
118.214
117.956
116.068
115.848
112.978
112.751
76.358
76.040
75.722
54.086
54.021
50.892
0.001
O
P
OMe
N
O
O
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

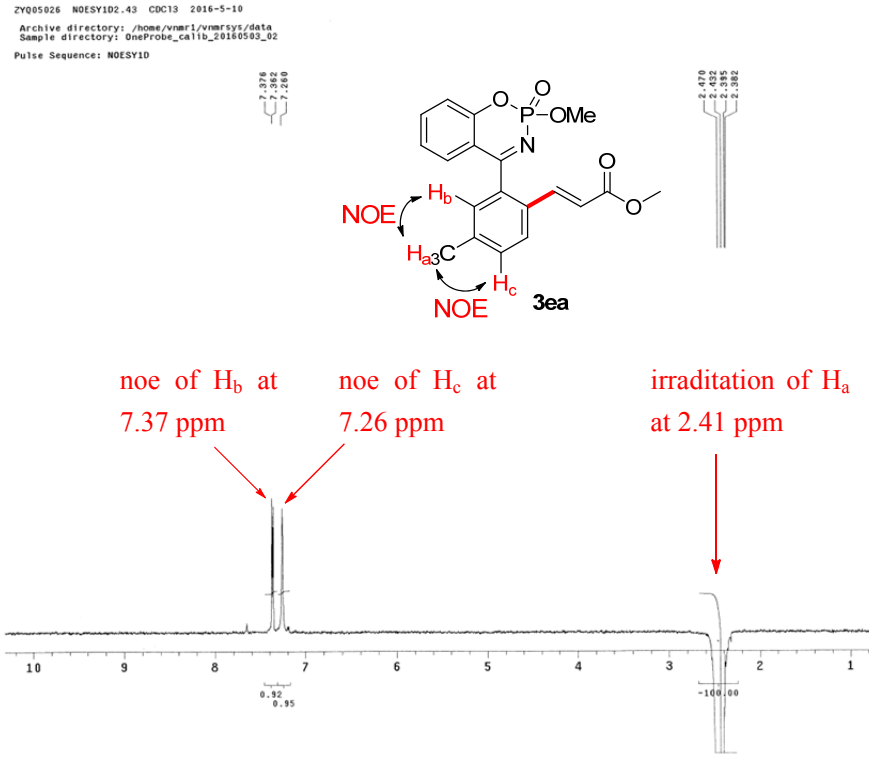
3da

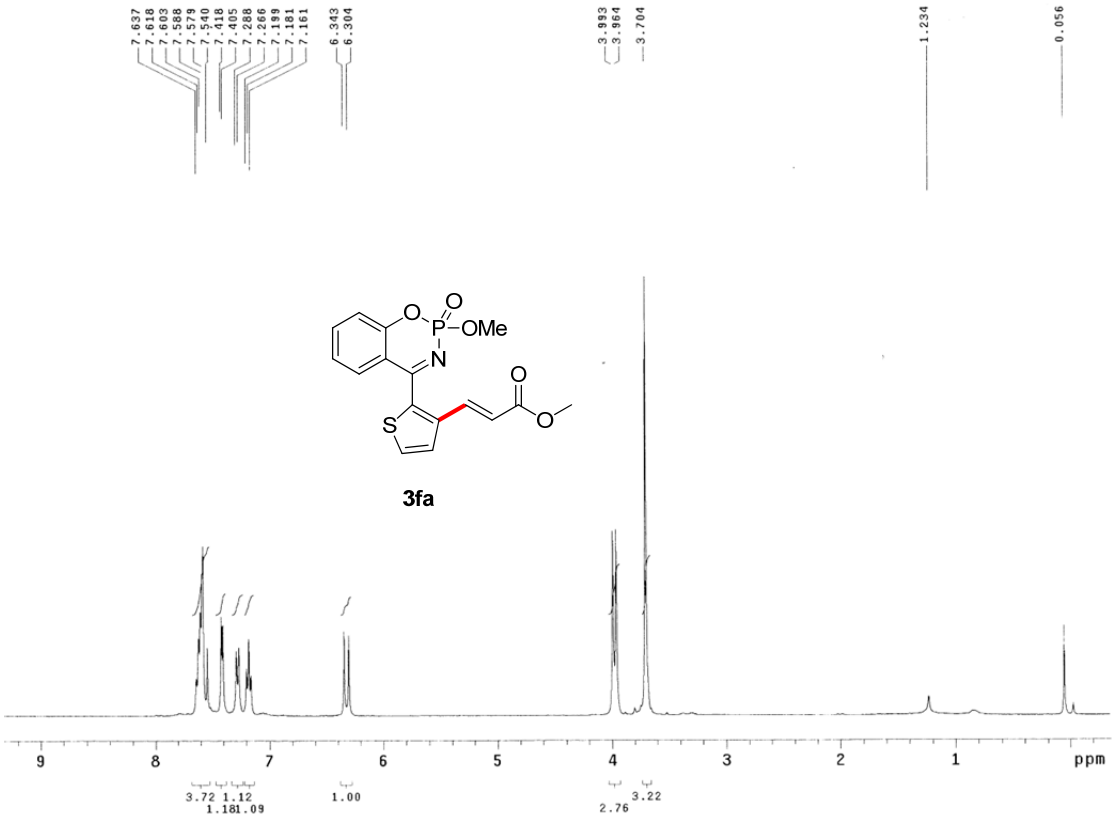

7.670
7.650
7.621
7.601
7.582
7.562
7.523
7.376
7.356
7.290
7.269
7.259
7.202
7.183
7.129
7.110
7.091
6.365
6.326
4.011
3.982
3.693
2.429
1.805
0.071
O
P
OMe
N
O
O
9
8
7
6
5
4
3
2
1
ppm
1.00
2.89
3.38
3.46

3ea


QZY-ZYQ-05026
181.000
180.940
166.739
154.219
154.162
141.004
140.567
137.612
137.372
136.170
131.350
131.178
130.045
129.508
127.018
123.985
119.783
119.710
119.309
119.048
77.365
77.047
76.729
55.059
54.993
51.700
21.345
O
P
OMe
N
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

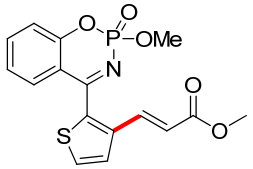
3ea


ZYQ05026 NOESY1D2.43 CDCl3 2016-5-10
Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: OneProbe_calib_20160503_02
Pulse Sequence: NOESY1D
NOE
NOE
3ea
noe of Hb at 7.37 ppm
noe of Hc at 7.26 ppm
irraditation of Ha at 2.41 ppm
ppm

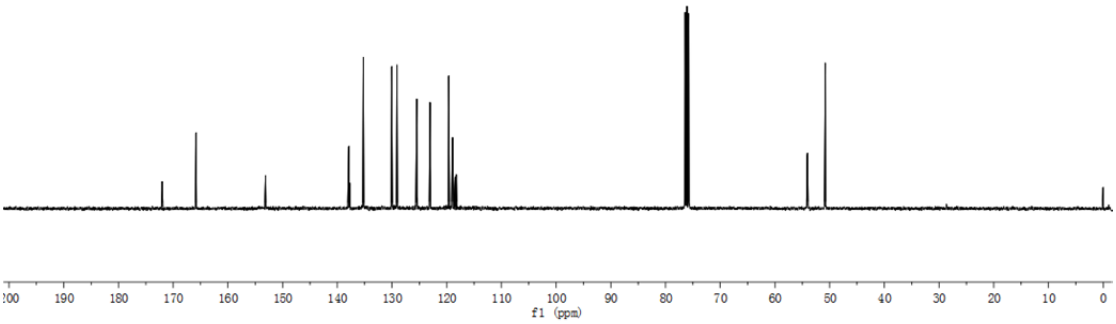

3fa
ppm

QZY-ZYQ-03006

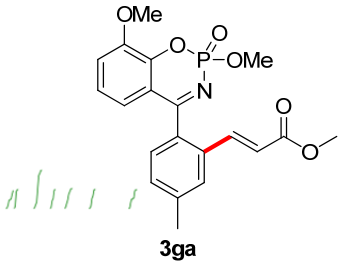
171.993
171.956
165.818
153.170
153.116
138.032
137.880
137.751
135.260
135.244
130.050
129.085
125.487
123.047
119.629
118.976
118.902
118.488
118.239
76.402
76.084
75.766
54.095
54.031
50.798
0.000



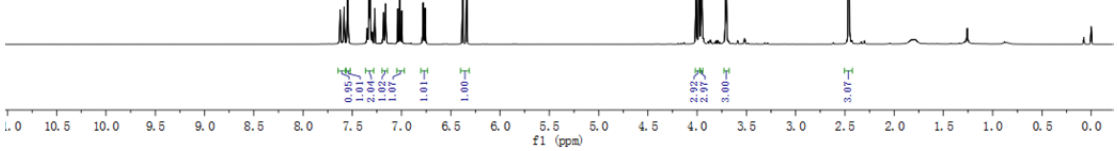
3fa

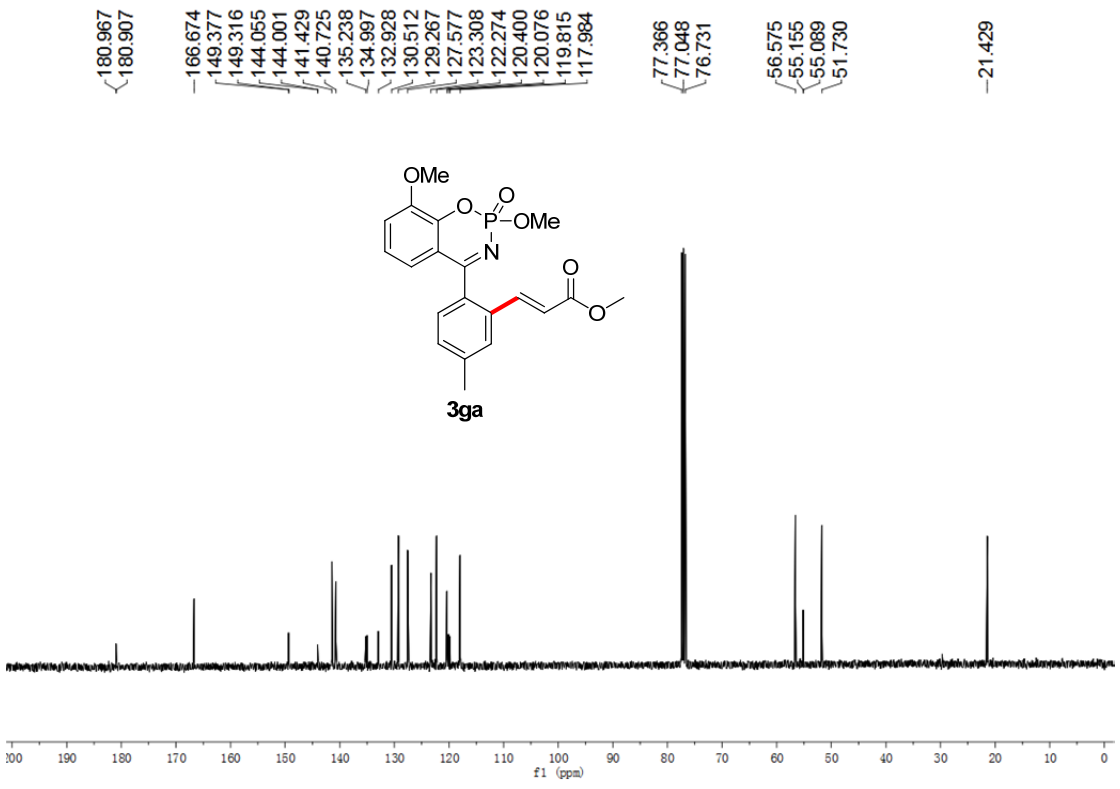


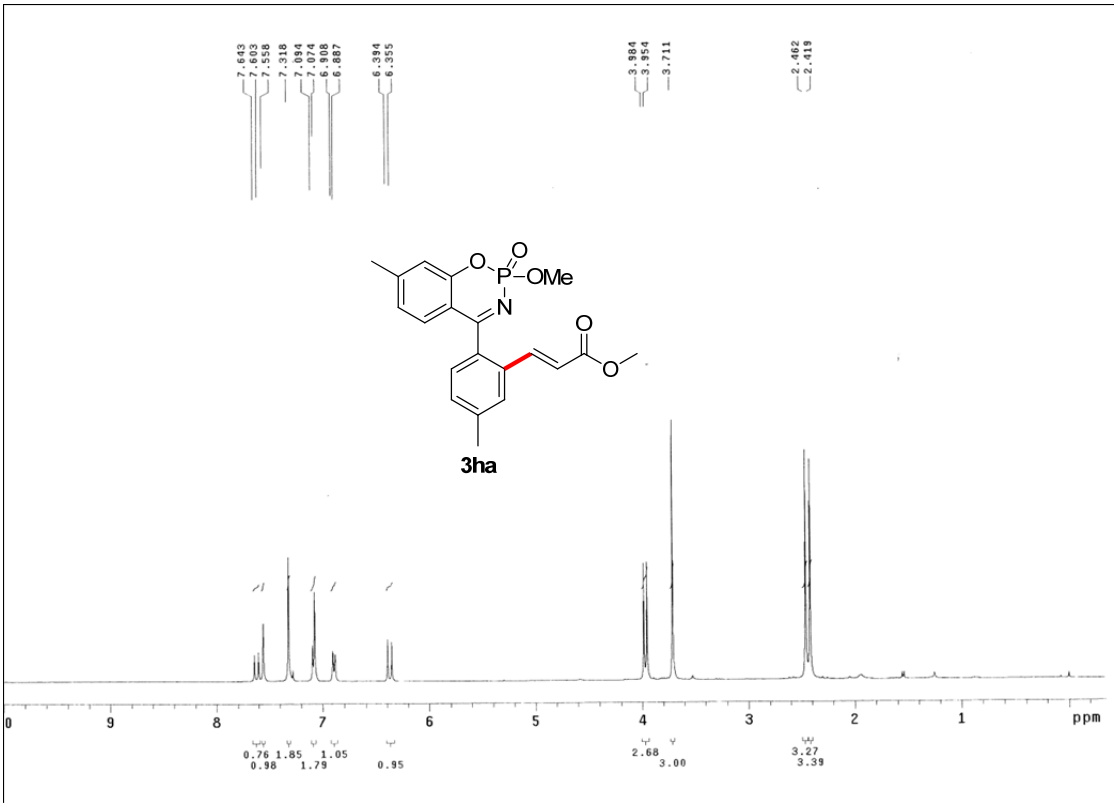
7.623
7.584
7.546
7.348
7.329
7.319
7.299
7.272
7.182
7.162
7.037
7.017
6.997
6.781
6.778
6.761
6.758
6.380
6.340
4.009
3.979
3.955
3.706
2.460



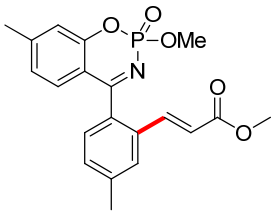
3ga



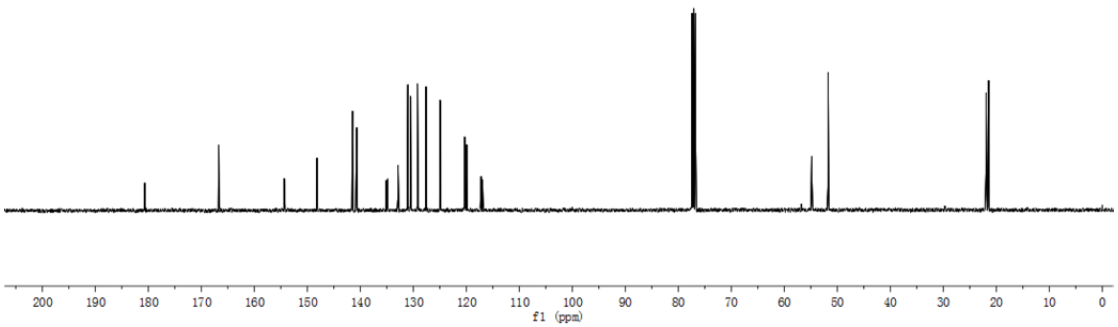

180.967
180.907
166.674
149.377
149.316
144.055
144.001
141.429
140.725
135.238
134.997
132.928
130.512
129.267
127.577
123.308
122.274
120.400
120.076
119.815
117.984
77.366
77.048
76.731
56.575
55.155
55.089
51.730
21.429
OMe
O
P
OMe
N
O
O
3ga
f1 (ppm)

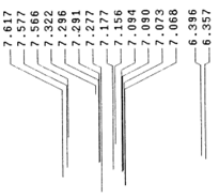

7.643
7.603
7.558
7.318
7.094
7.074
6.908
6.887
6.394
6.355
3.984
3.954
3.711
2.462
2.419
O
P
OMe
N
O
O
3ha
ppm
0.76
0.98
1.85
1.79
1.05
0.95
2.68
3.00
3.27
3.39


QZY-ZYQ-03020
180.732
180.674
166.714
154.370
154.313
148.166
141.483
140.677
135.095
134.851
132.889
131.015
130.547
129.206
127.611
124.942
120.316
119.937
119.864
117.206
116.946
77.399
77.081
76.763
54.889
54.823
51.728
21.923
21.432

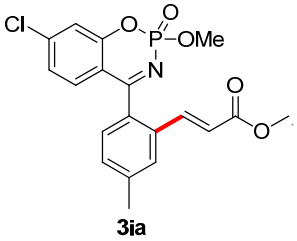

O
O
P
OMe
N
O
O

3ha

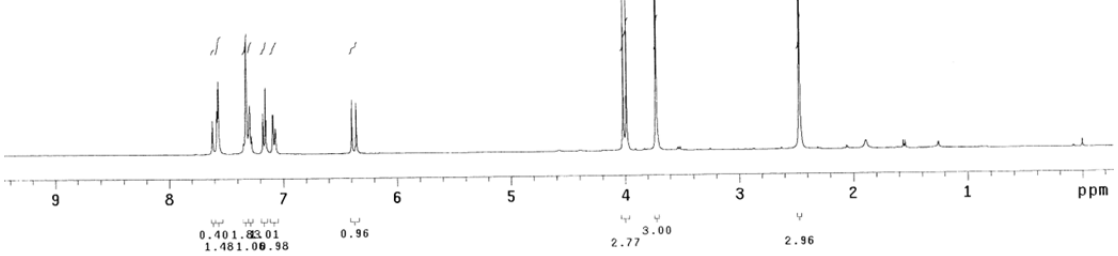

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

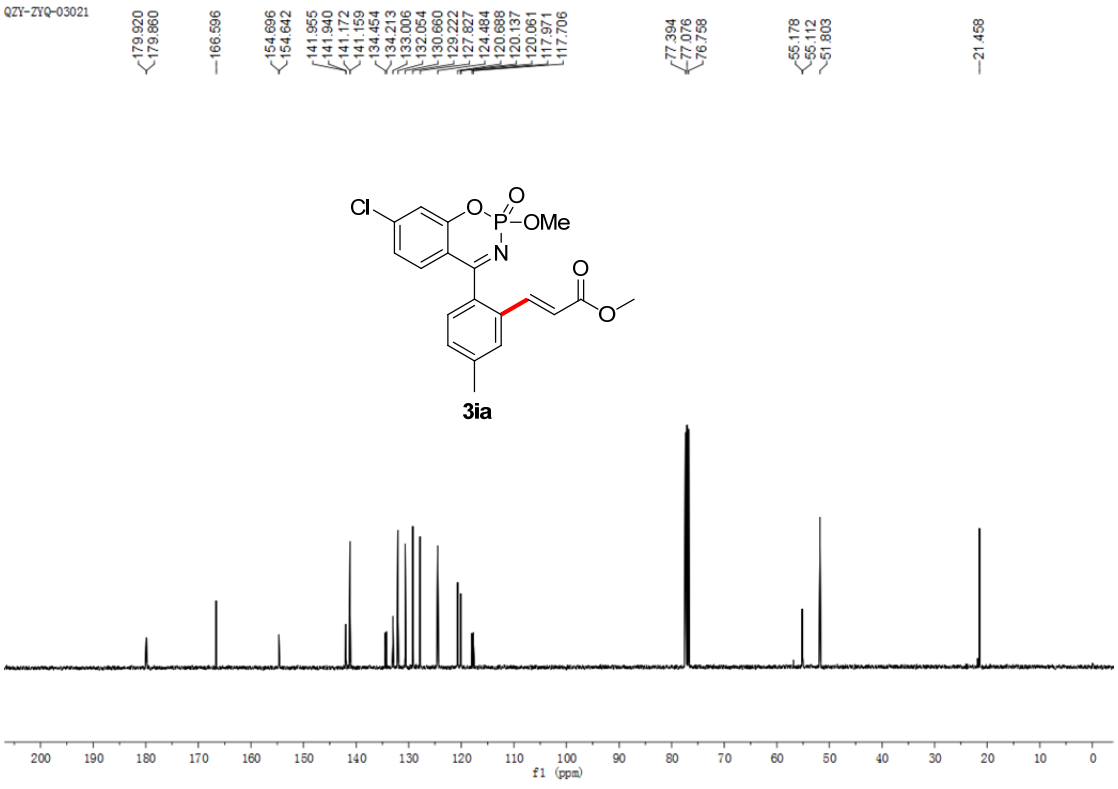

7.617
7.577
7.566
7.322
7.296
7.291
7.277
7.177
7.156
7.094
7.090
7.073
7.068
6.396
6.357


4.015
3.986
3.724
2.469

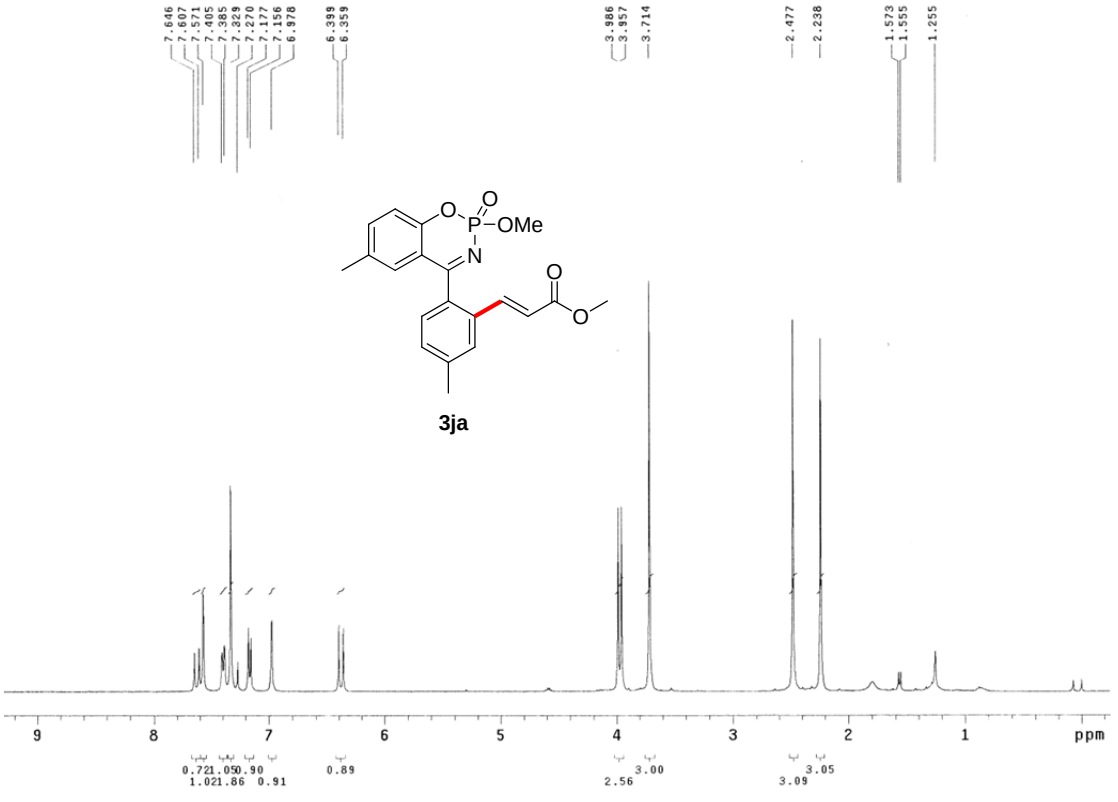

Cl
O
O
P
OMe
N
O
O

3ia


9
8
7
6
5
4
3
2
1
ppm
0.40
1.48
1.83
1.00
3.01
0.98
0.96
2.77
3.00
2.96


QZY-ZYQ-03021
179.920
179.860
166.596
154.696
154.642
141.955
141.940
141.172
141.159
134.454
134.213
133.006
132.054
130.660
129.222
127.827
124.484
120.688
120.137
120.061
117.971
117.706
77.394
77.076
76.758
55.178
55.112
51.803
21.458
Cl
O
P
OMe
N
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

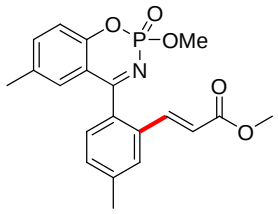
3ia


7.646
7.607
7.571
7.405
7.385
7.329
7.270
7.177
7.156
6.978
6.399
6.359
3.986
3.957
3.714
2.477
2.238
1.573
1.555
1.255
O
P
OMe
N
O
O
9
8
7
6
5
4
3
2
1
ppm
0.72
1.05
0.90
1.02
1.86
0.91
0.89
2.56
3.00
3.09
3.05

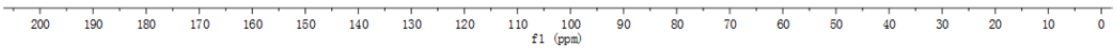
3ja

QZY-ZYQ-03018

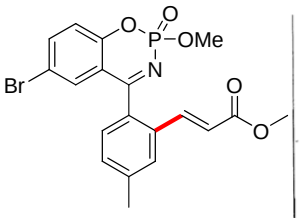
180.926
180.867
166.721
152.333
152.277
141.537
140.737
136.913
133.668
131.020
130.531
129.237
120.343
119.485
119.411
119.125
118.868
77.370
77.052
76.734
54.944
54.878
51.750
21.470
20.670



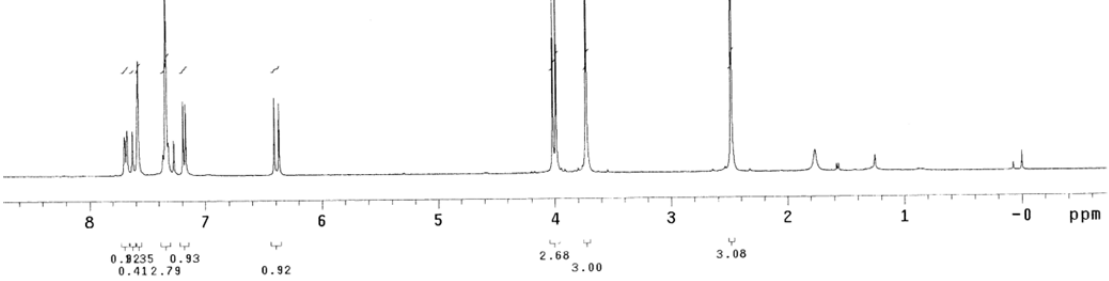
3ja

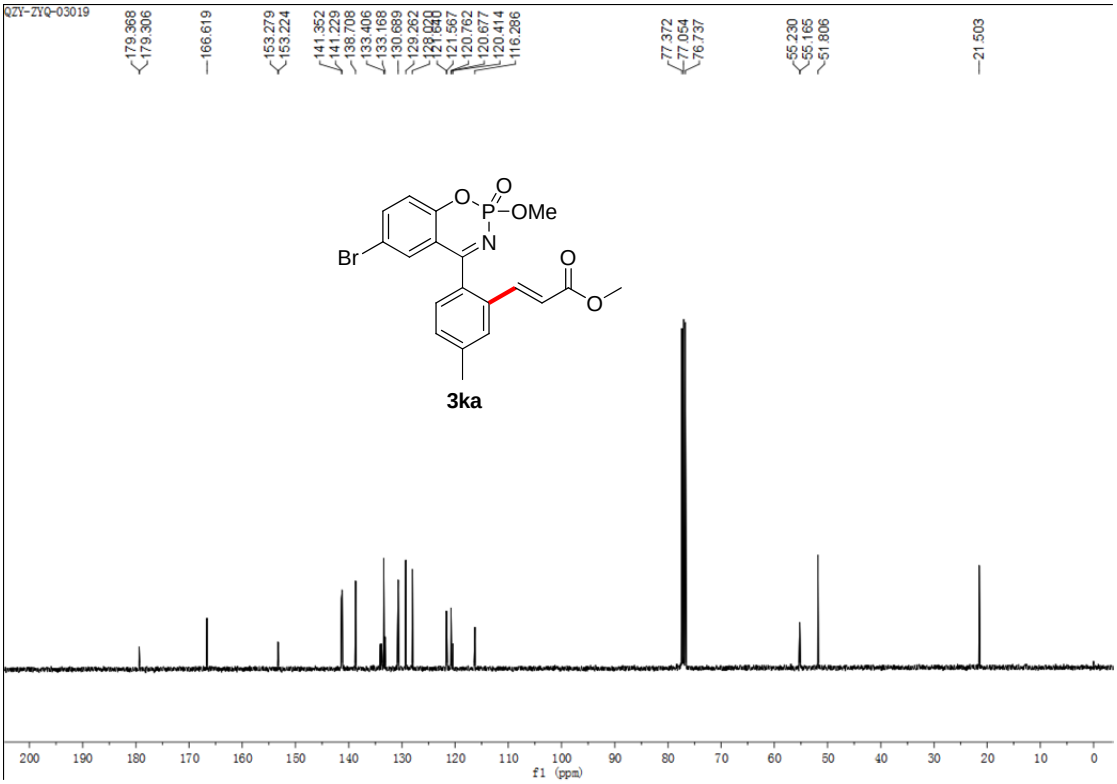


7.699
7.677
7.629
7.581
7.363
7.337
7.317
7.270
7.191
7.170
6.411
6.371
4.018
3.989
3.731
2.486
1.764
0.000



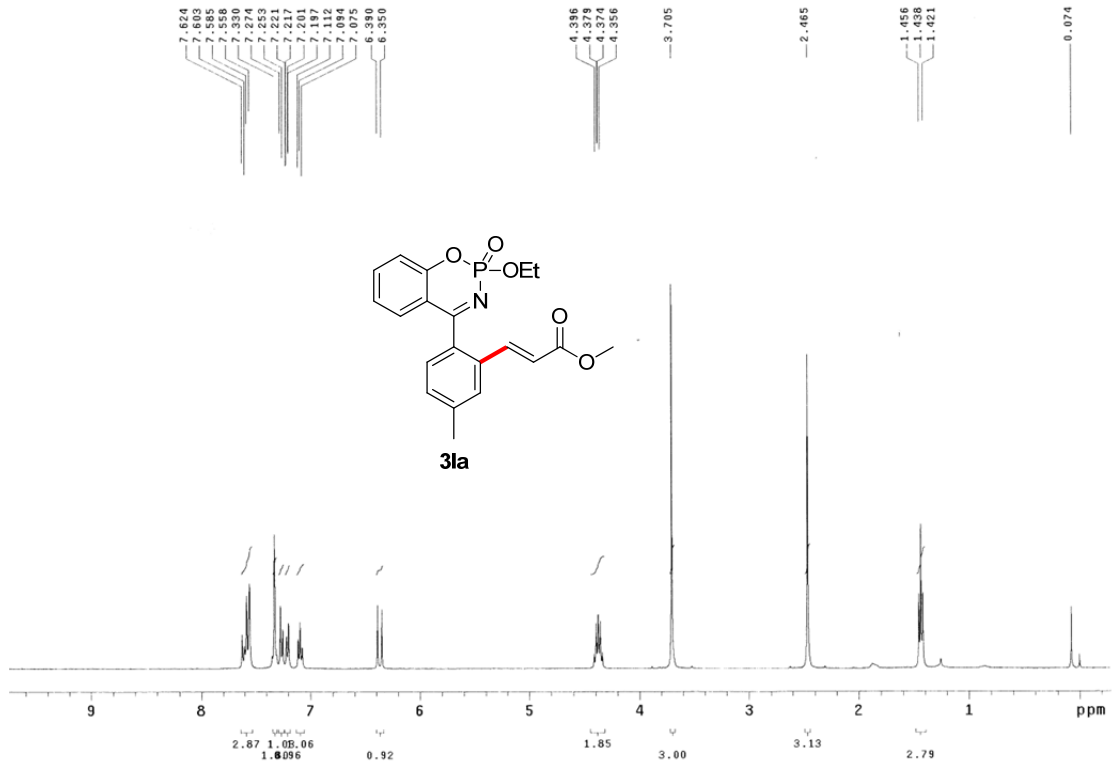
3ka



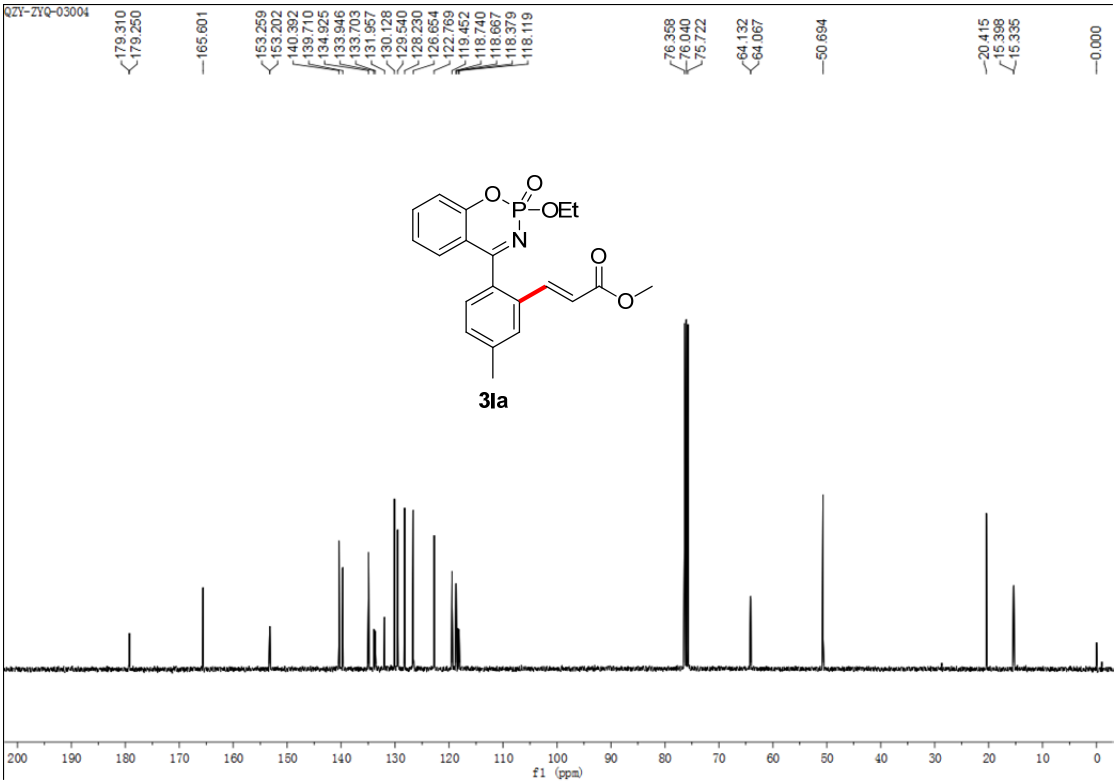

QZY-ZYQ-03019
179.368
179.306
166.619
153.279
153.224
141.352
141.229
138.708
133.406
133.168
130.689
129.262
121.567
120.762
120.677
120.414
116.286
77.372
77.054
76.737
55.230
55.165
51.806
21.503
O
P
OMe
N
Br
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

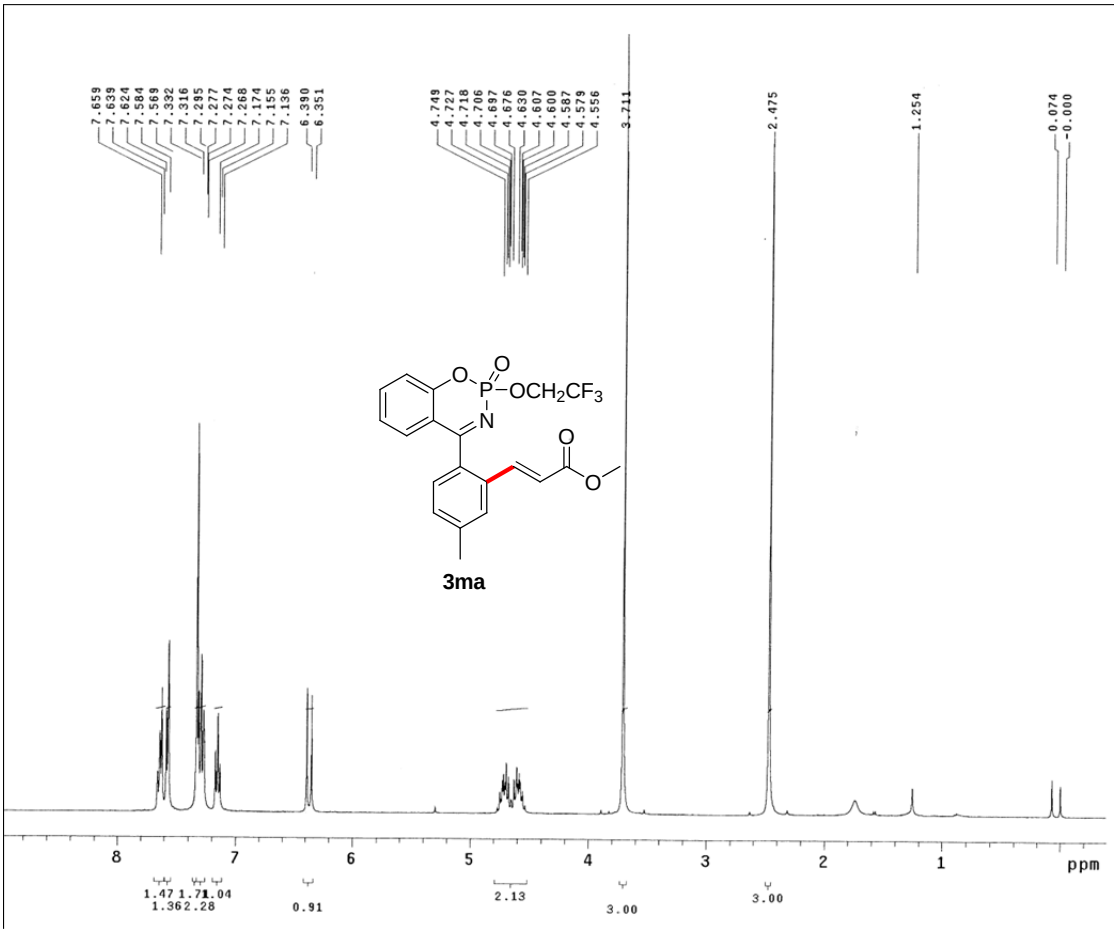
3ka

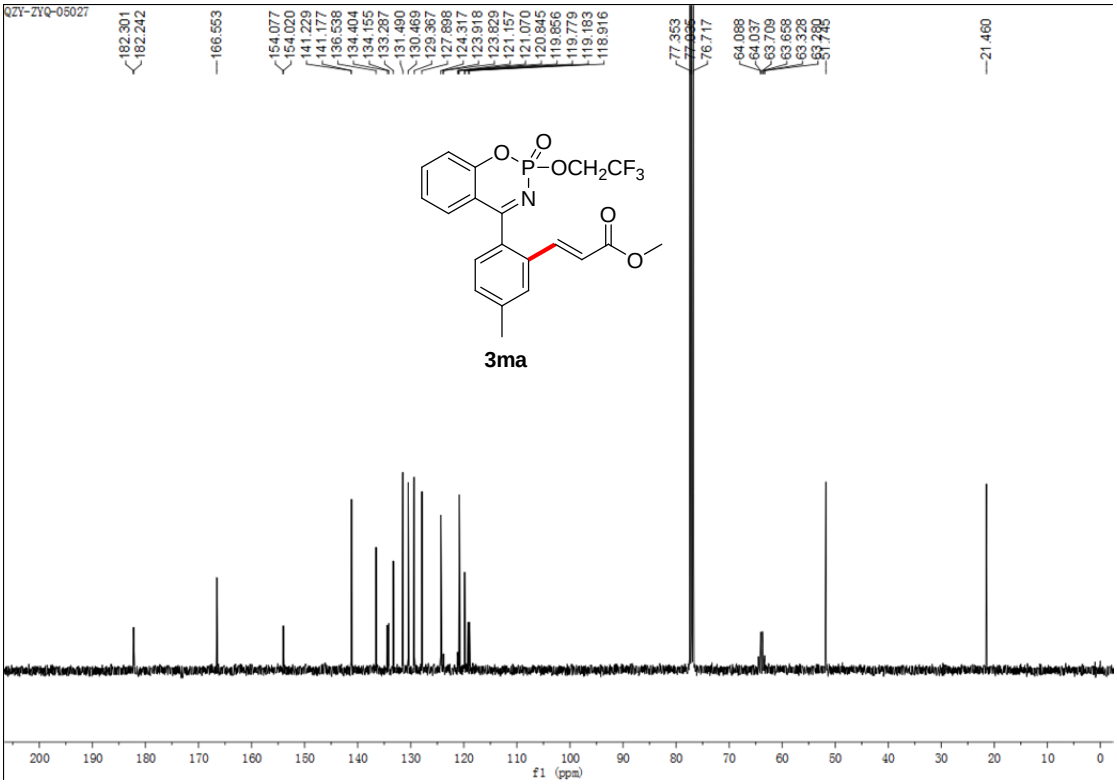
.


7.624
7.603
7.585
7.558
7.330
7.274
7.253
7.221
7.217
7.201
7.197
7.112
7.094
7.075
6.390
6.350
4.396
4.379
4.374
4.356
3.705
2.465
1.456
1.438
1.421
0.074
O
P
OEt
N
O
O
9 8 7 6 5 4 3 2 1 ppm
2.87
1.00
1.06
1.8096
0.92
1.85
3.00
3.13
2.79

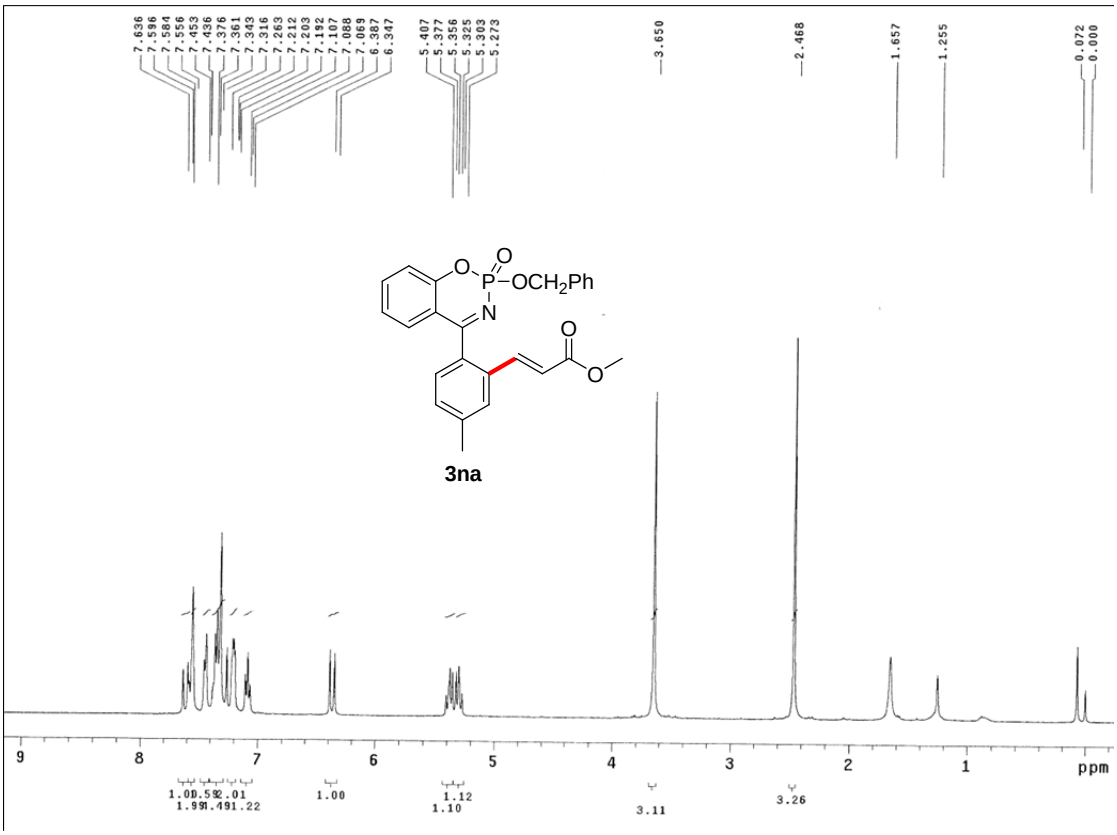
3la


QZY-ZYQ-03004
179.310
179.250
165.601
153.259
153.202
140.392
139.710
134.925
133.946
133.703
131.957
130.128
129.540
128.230
126.654
122.769
119.452
118.740
118.667
118.379
118.119
76.358
76.040
75.722
64.132
64.067
50.694
20.415
15.398
15.335
0.000
O
P
OEt
N
O
O
3la
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

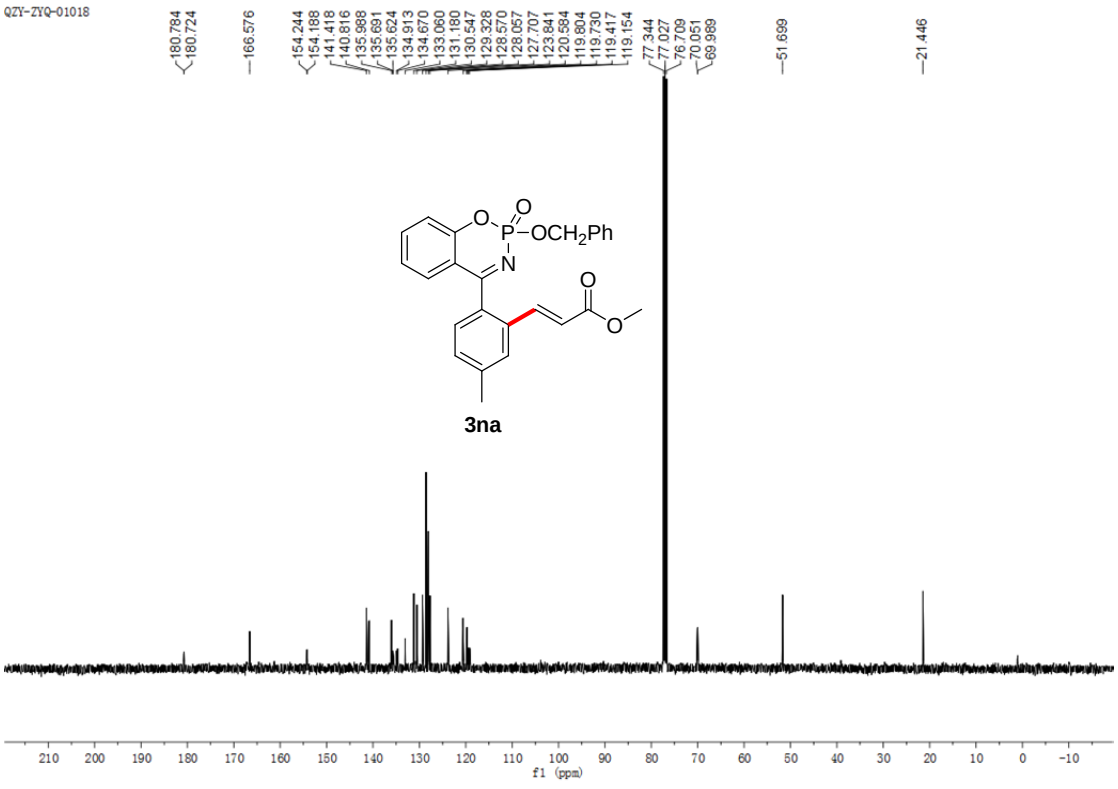

7.659
7.639
7.624
7.584
7.569
7.392
7.316
7.295
7.277
7.274
7.268
7.174
7.155
7.136
6.390
6.351
4.749
4.727
4.718
4.706
4.697
4.676
4.630
4.607
4.600
4.587
4.579
4.556
3.711
2.475
1.254
0.074
0.000
O
P
OCH2CF3
N
O
O
3ma
8
7
6
5
4
3
2
1
ppm
1.47
1.71
1.04
1.36
2.28
0.91
2.13
3.00
3.00


QZY-ZYQ-05027
182.301
182.242
166.553
154.077
154.020
141.229
141.177
136.538
134.404
134.155
133.287
131.490
130.469
129.367
127.898
124.317
123.918
123.829
121.157
121.070
120.845
119.856
119.779
119.183
118.916
77.353
77.036
76.717
64.088
64.037
63.709
63.658
63.328
51.780
21.460
O
P
OCH2CF3
N
O
O
f1 (ppm)

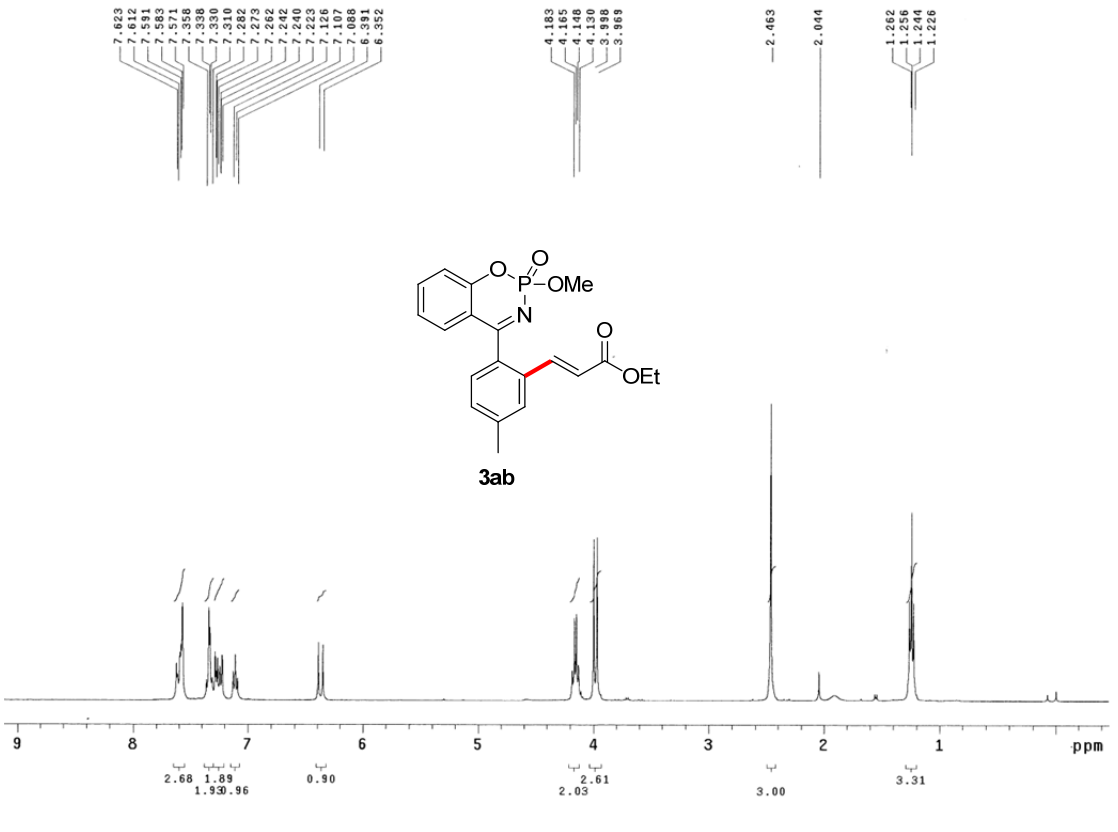
3ma


7.636
7.596
7.584
7.556
7.453
7.436
7.376
7.361
7.343
7.316
7.263
7.212
7.203
7.192
7.107
7.088
7.069
6.387
6.347
5.407
5.377
5.356
5.325
5.303
5.273
3.650
2.468
1.657
1.255
0.072
0.000
O
P
OCH2Ph
N
O
O
ppm
1.00
1.12
1.10
3.11
3.26

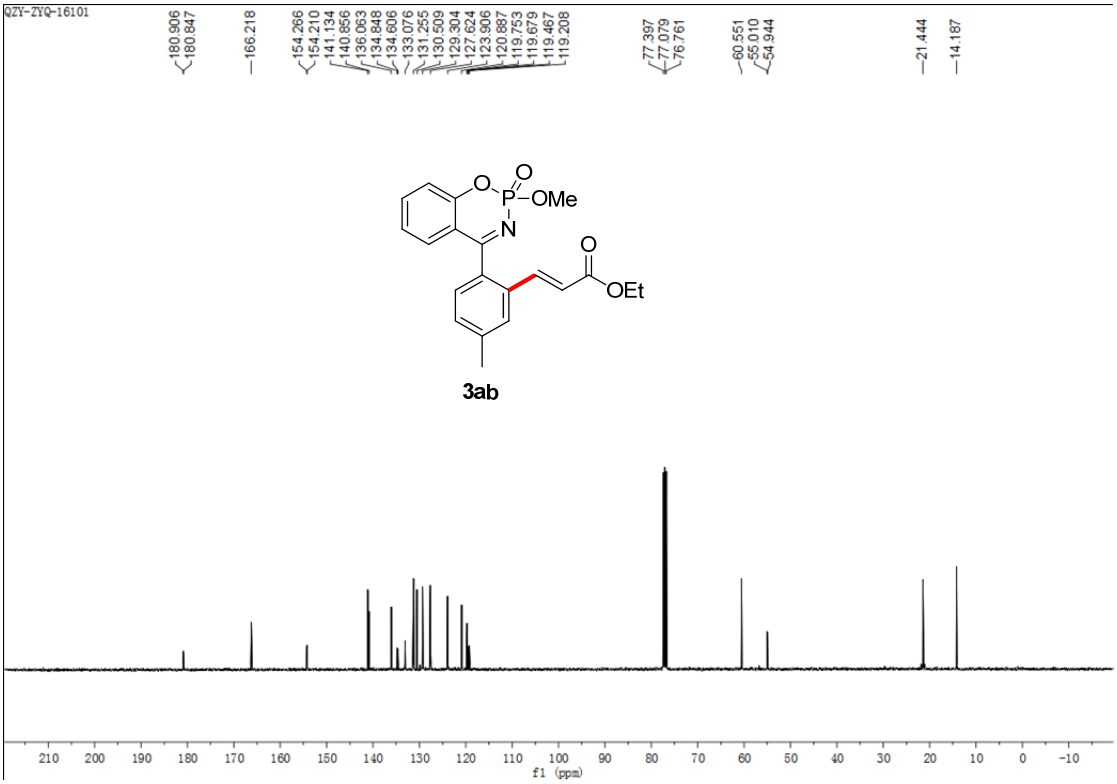
3na


QZY-ZYQ-01018
180.784
180.724
166.576
154.244
154.188
141.418
140.816
135.988
135.691
135.624
134.913
134.670
133.060
131.180
130.547
129.328
128.570
128.057
127.707
123.841
120.584
119.804
119.730
119.417
119.154
77.344
77.027
76.709
70.051
69.989
51.699
21.446
O
O
P
OCH2Ph
N
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

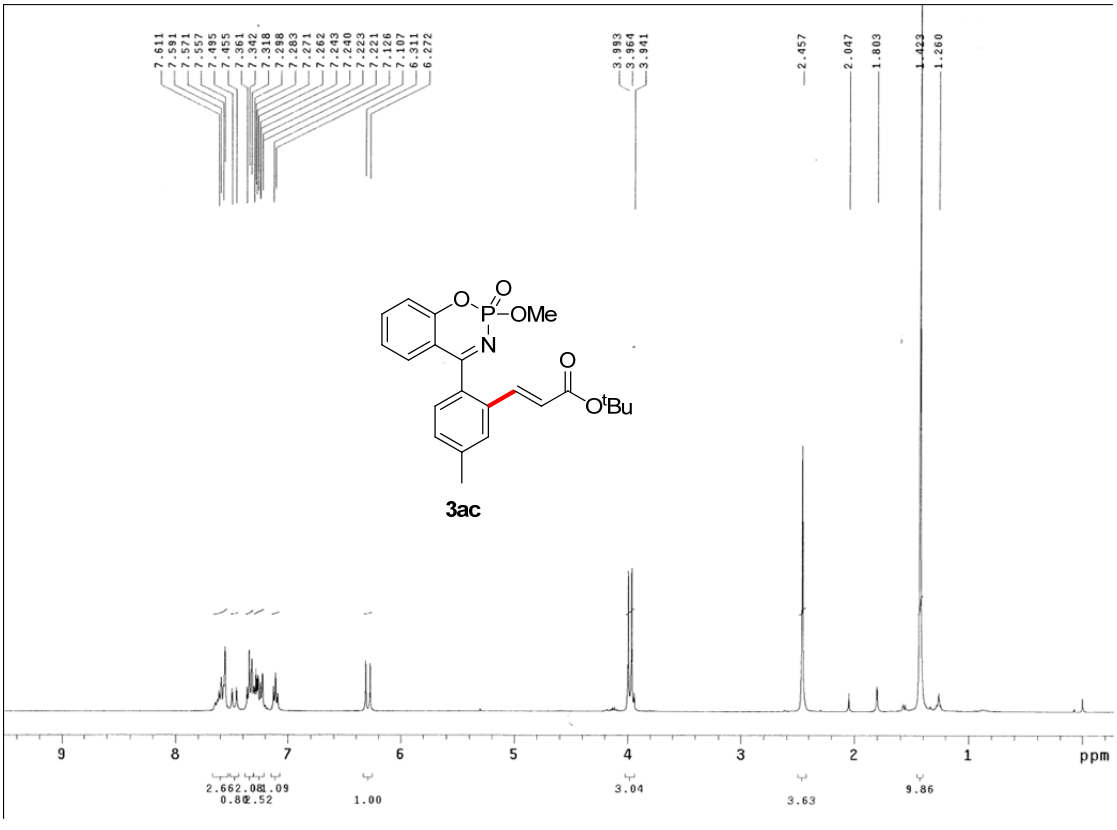
3na


7.623
7.612
7.591
7.583
7.571
7.356
7.338
7.330
7.310
7.282
7.273
7.262
7.242
7.240
7.223
7.126
7.107
7.088
6.391
6.352
4.183
4.165
4.148
4.130
3.198
3.969
2.463
2.044
1.262
1.256
1.244
1.226
O
O
P
OMe
N
O
OEt
9 8 7 6 5 4 3 2 1 ppm
2.68
1.89
1.93
0.96
0.90
2.61
2.03
3.00
3.31

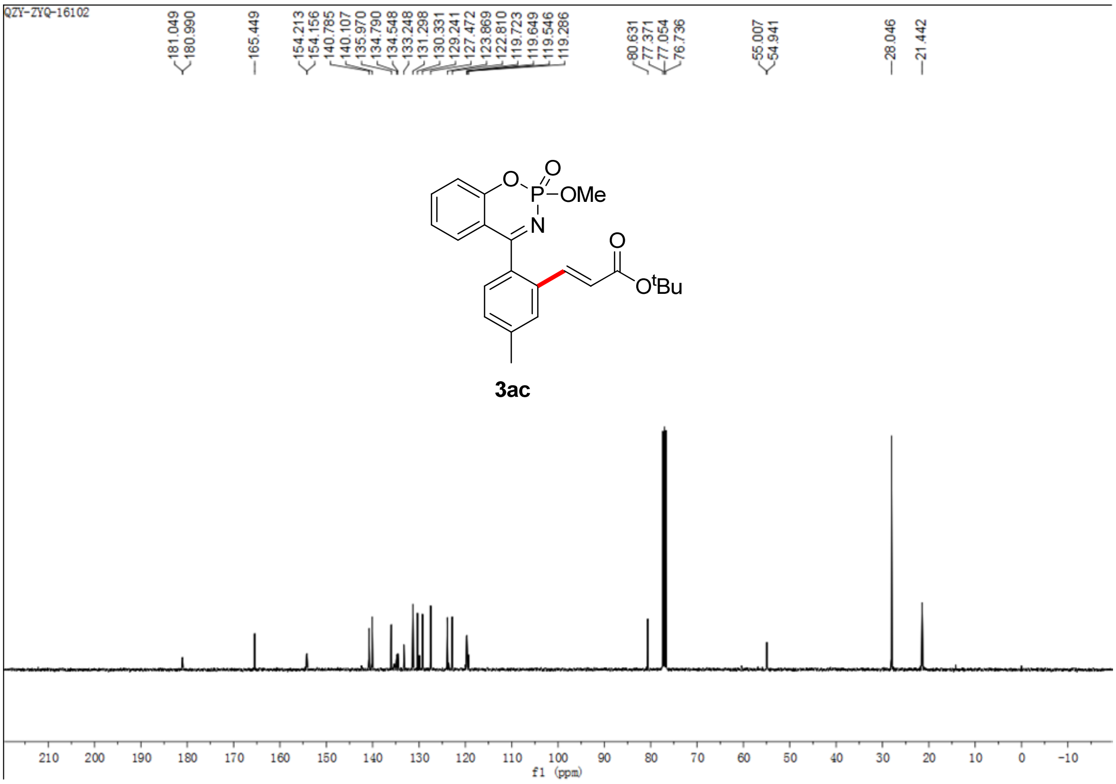
3ab

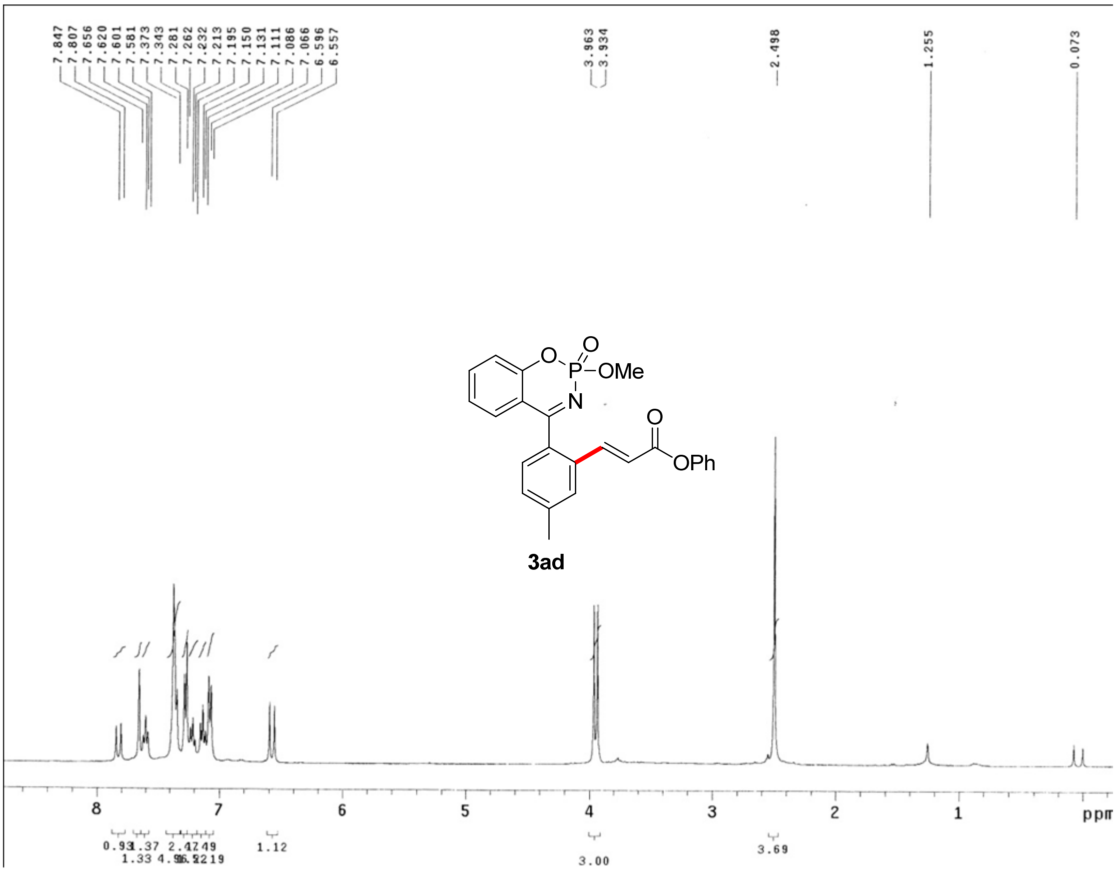

QZY-ZYQ-16101
180.906
180.847
166.218
154.266
154.210
141.134
140.856
136.063
134.848
134.606
133.076
131.255
130.509
129.304
127.624
123.906
120.887
119.753
119.679
119.467
119.208
77.397
77.079
76.761
60.551
55.010
54.944
21.444
14.187
O
O
P
OMe
N
O
OEt
f1 (ppm)

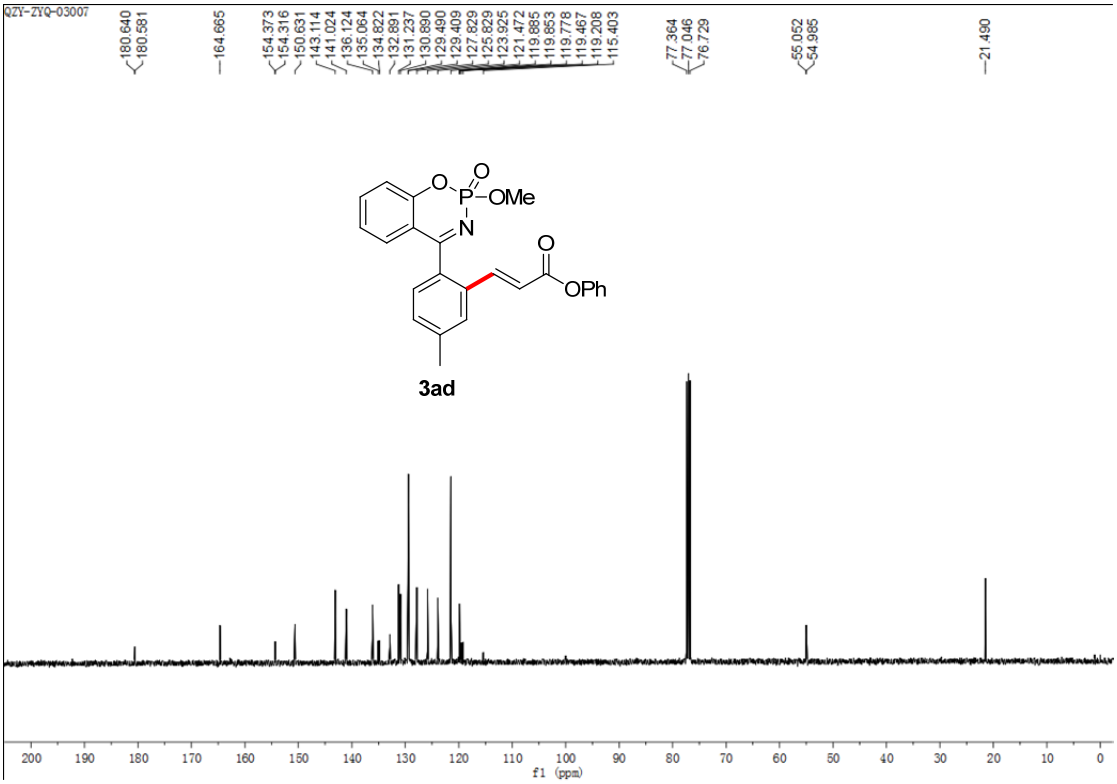
3ab


7.611
7.591
7.571
7.557
7.495
7.455
7.361
7.342
7.318
7.288
7.283
7.271
7.262
7.243
7.240
7.223
7.221
7.126
7.107
6.311
6.272
3.993
3.964
3.941
2.457
2.047
1.803
1.423
1.260
O
O
P
OMe
N
O
O^{t}Bu
ppm
2.66
2.08
1.09
0.80
2.52
1.00
3.04
3.63
9.86

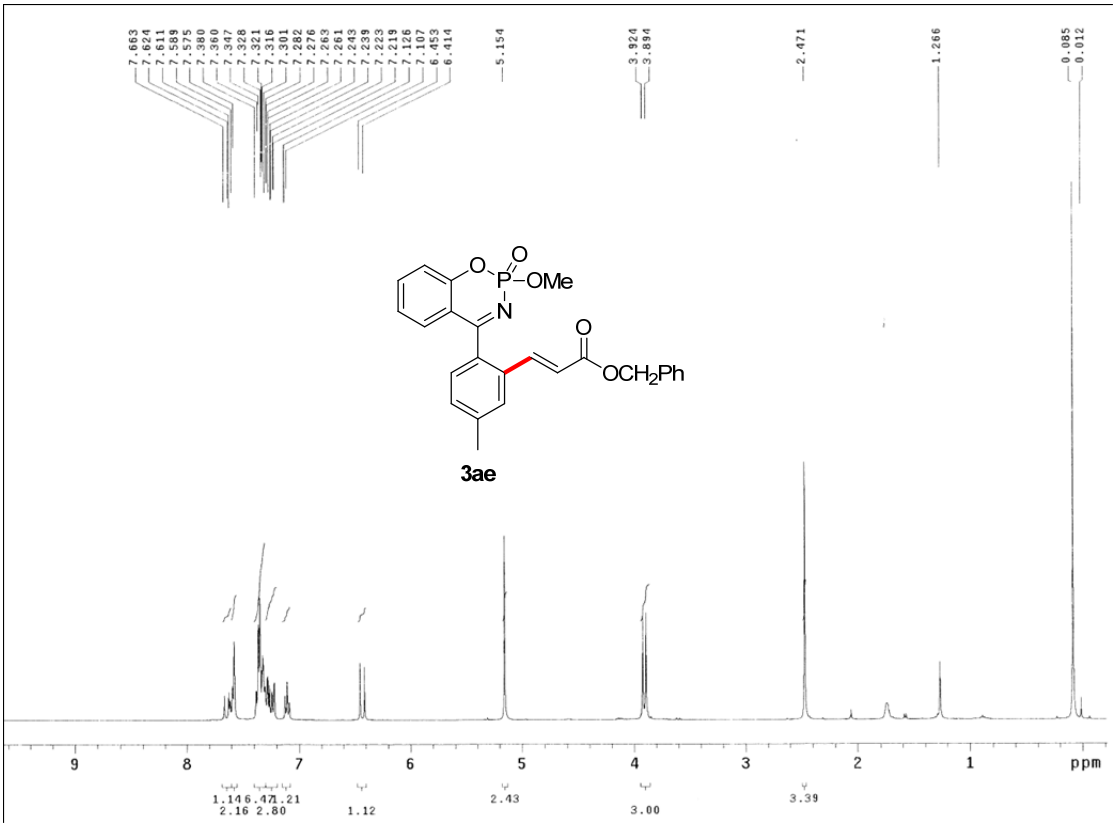
3ac


QZY-ZYQ-16102
181.049
180.990
165.449
154.213
154.156
140.785
140.107
135.970
134.790
134.548
133.248
131.298
130.331
129.241
127.472
123.869
122.810
119.723
119.649
119.546
119.286
80.631
77.371
77.054
76.736
55.007
54.941
28.046
21.442
O
P
O
OMe
N
O
O^tBu
3ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

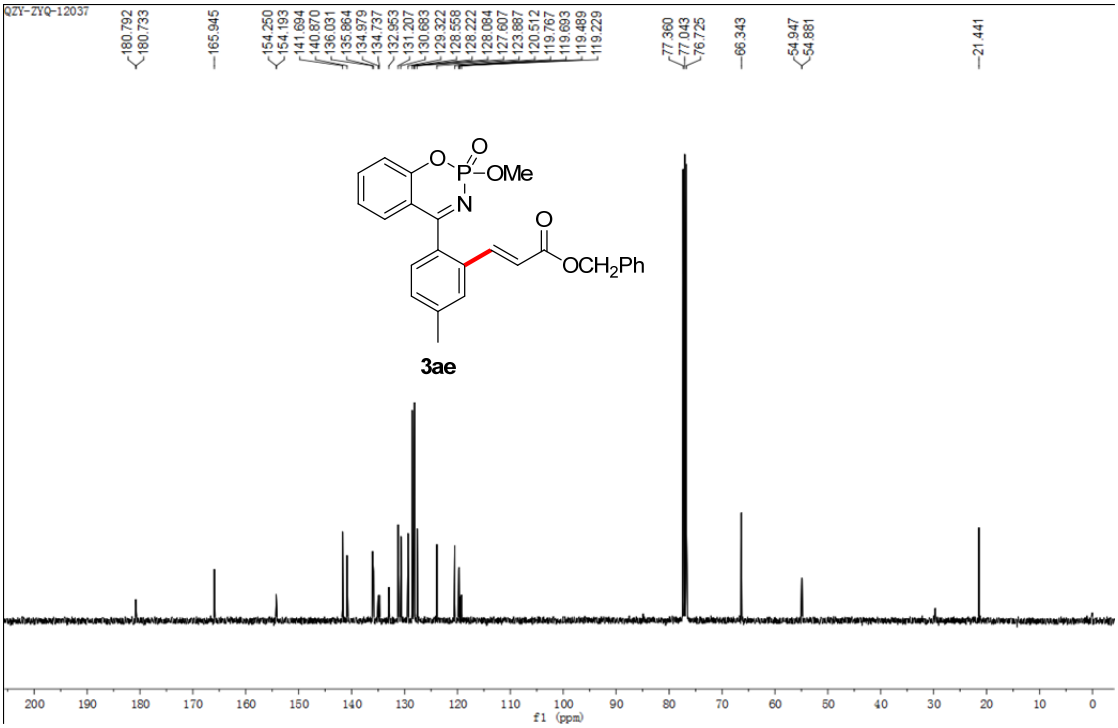

7.847
7.807
7.656
7.620
7.601
7.581
7.373
7.343
7.281
7.262
7.232
7.213
7.195
7.150
7.131
7.111
7.086
7.066
6.596
6.557
3.963
3.934
2.498
1.255
0.073
O
P
O
OMe
N
O
OPh
3ad
8 7 6 5 4 3 2 1 ppm
0.93 1.37 2.41 7.49 1.12
1.33 4.96 6.52 19
3.00
3.69

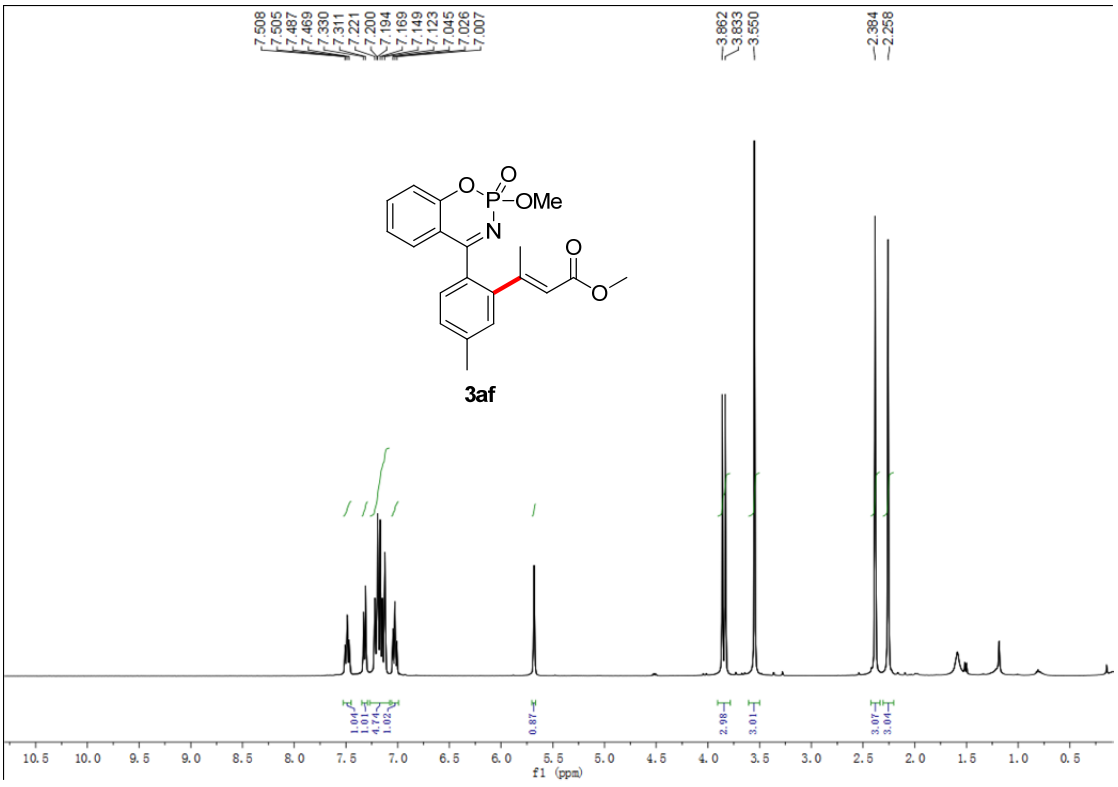

QZY-ZYQ-03007
180.640
180.581
164.665
154.373
154.316
150.631
143.114
141.024
136.124
135.064
134.822
132.891
131.237
130.890
129.490
129.409
127.829
125.829
123.925
121.472
119.885
119.853
119.778
119.467
119.208
115.403
77.364
77.046
76.729
55.052
54.985
21.490
O
P
OMe
N
O
OPh
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

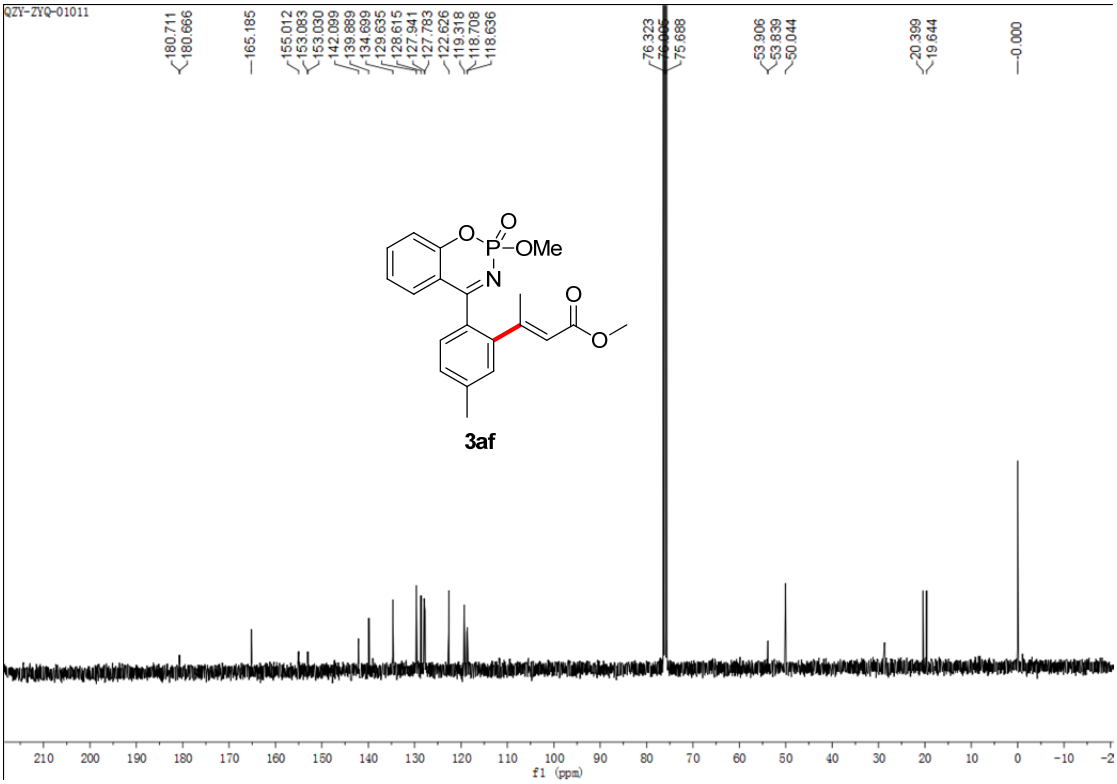
3ad


7.663
7.624
7.611
7.589
7.575
7.380
7.360
7.347
7.328
7.321
7.316
7.301
7.282
7.276
7.263
7.261
7.243
7.239
7.223
7.219
7.126
7.107
6.453
6.414
5.154
3.924
3.894
2.471
1.266
0.085
0.012
O
P
OMe
N
O
OCH2Ph
9
8
7
6
5
4
3
2
1
ppm
1.14
6.47
1.21
2.16
2.80
1.12
2.43
3.00
3.39

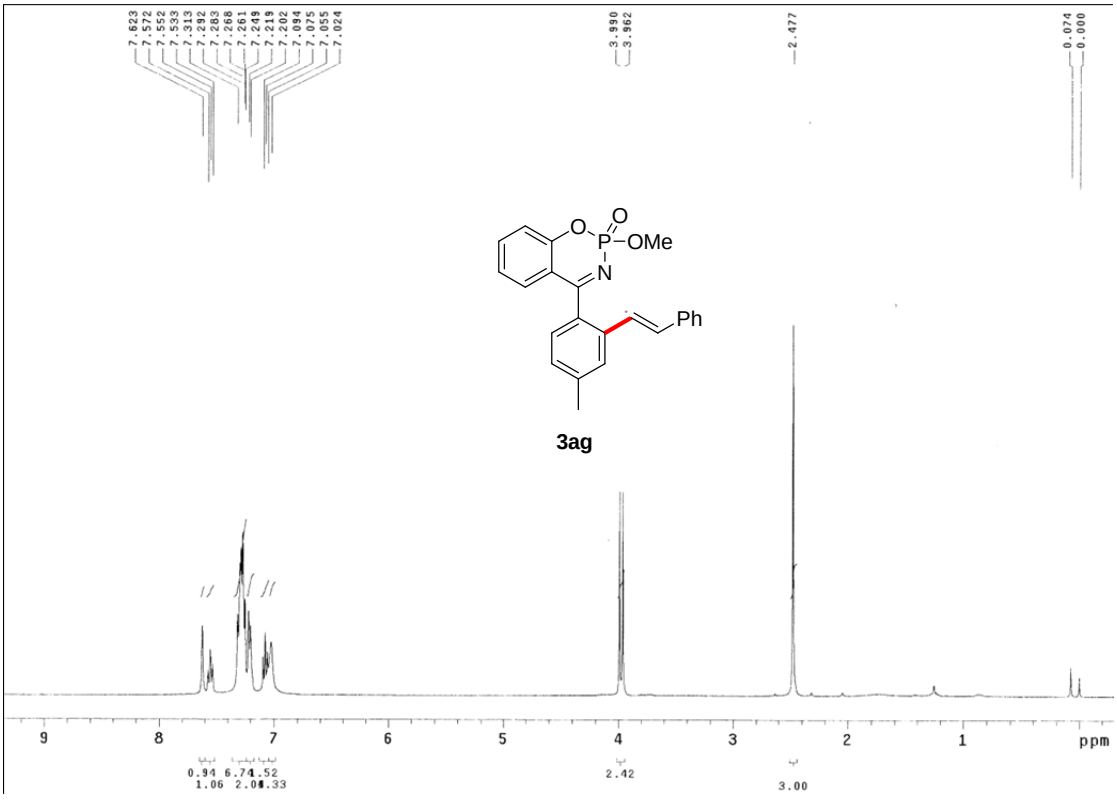
3ae


QZY-ZYQ-12037
180.792
180.733
165.945
154.250
154.193
141.694
140.870
136.031
135.864
134.979
134.737
132.953
131.207
130.683
129.322
128.558
128.222
128.084
127.607
123.887
120.512
119.767
119.693
119.489
119.229
77.360
77.043
76.725
66.343
54.947
54.881
21.441
O
P
OMe
N
O
OCH2Ph
3ae
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

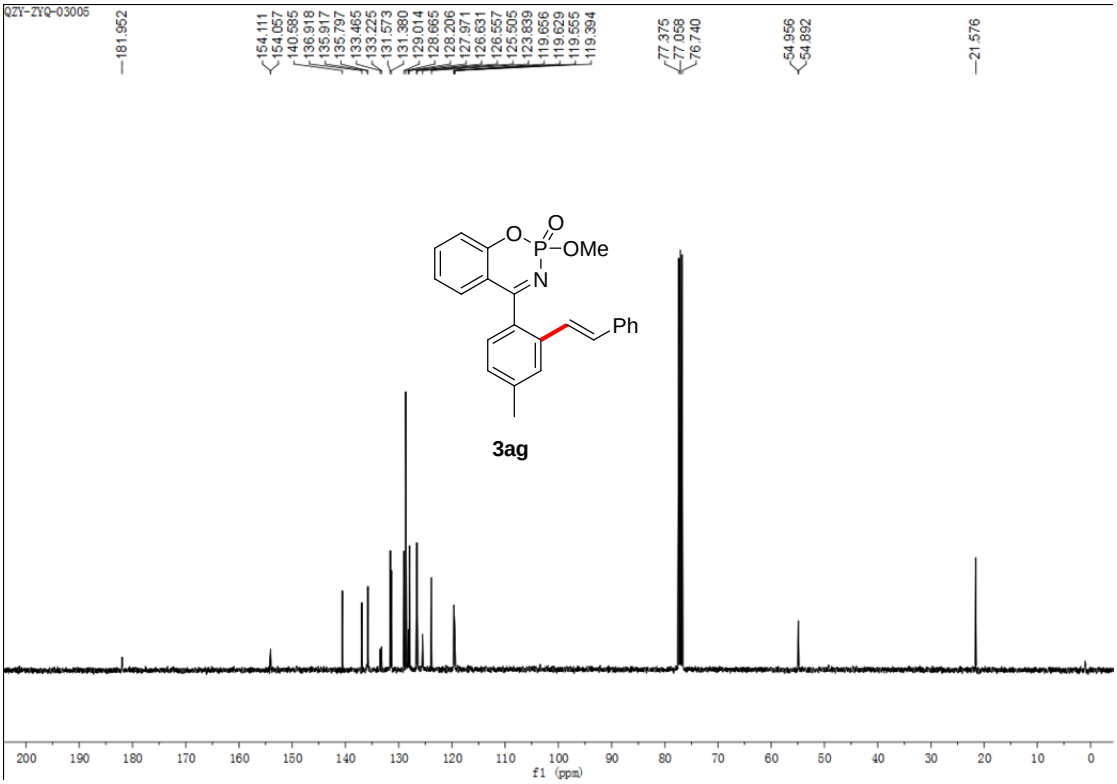

7.508
7.505
7.487
7.469
7.330
7.311
7.221
7.200
7.194
7.169
7.149
7.123
7.045
7.026
7.007
3.862
3.833
3.550
2.384
2.258
O
P
OMe
N
O
O
3af
1.04
1.01
4.74
1.02
0.87
2.98
3.01
3.07
3.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


QZY-ZYQ-01011
180.711
180.666
165.185
155.012
153.083
153.030
142.099
139.889
134.699
129.635
128.615
127.941
127.783
122.626
119.318
118.708
118.636
76.323
75.688
53.906
53.839
50.044
20.399
19.644
0.000
O
P
OMe
N
O
O
f1 (ppm)

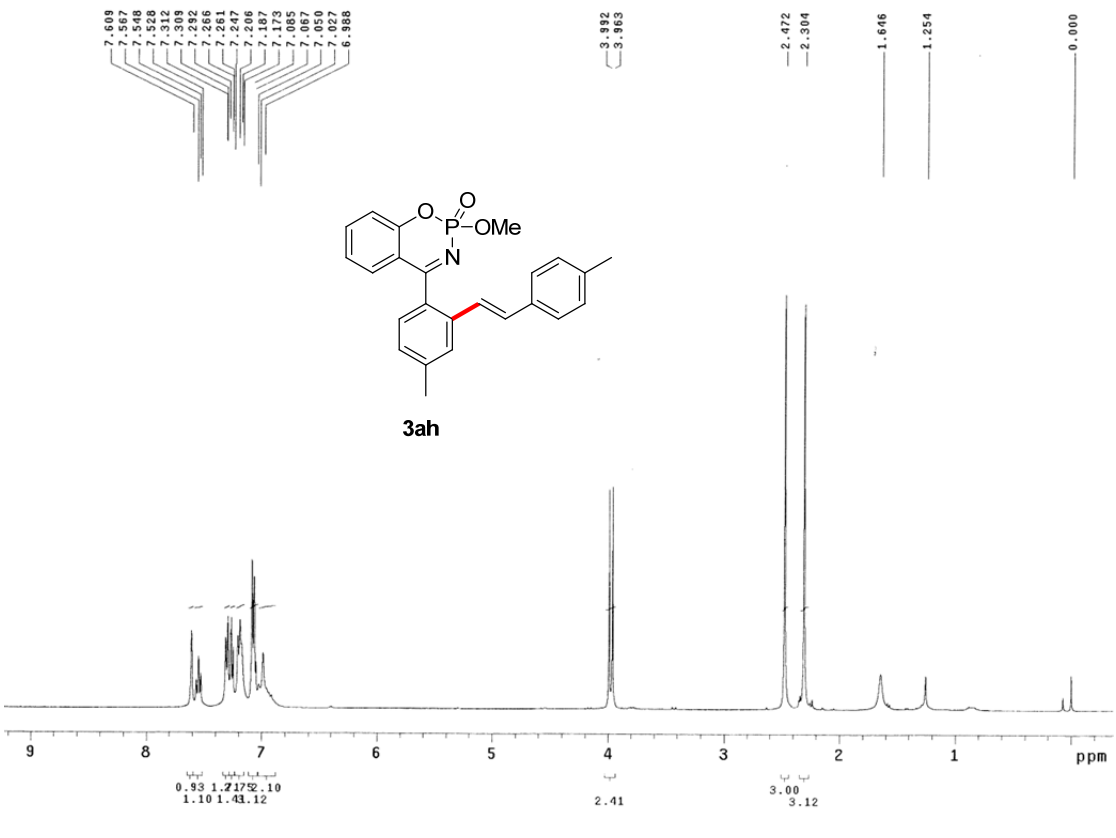
3af


7.623
7.572
7.552
7.533
7.313
7.292
7.283
7.266
7.261
7.249
7.219
7.202
7.094
7.075
7.055
7.024
3.990
3.962
2.477
0.074
0.000
O
P
OMe
N
Ph
ppm
0.94
6.74
4.52
1.06
2.08
1.33
2.42
3.00

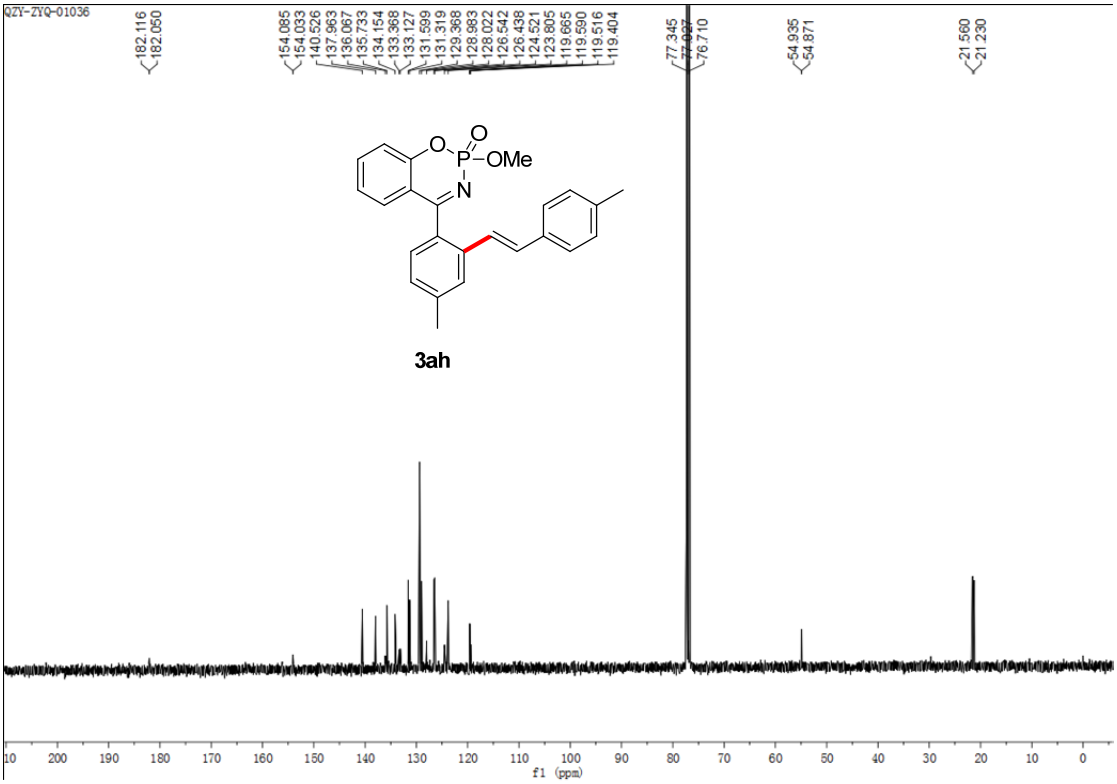
3ag


QZY-ZYQ-03005
181.952
154.111
154.057
140.585
136.918
135.917
135.797
133.465
133.225
131.573
131.380
129.014
128.665
128.206
127.971
126.631
126.557
125.505
123.839
119.656
119.629
119.555
119.394
77.375
77.058
76.740
54.956
54.892
21.576
O
P
OMe
N
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

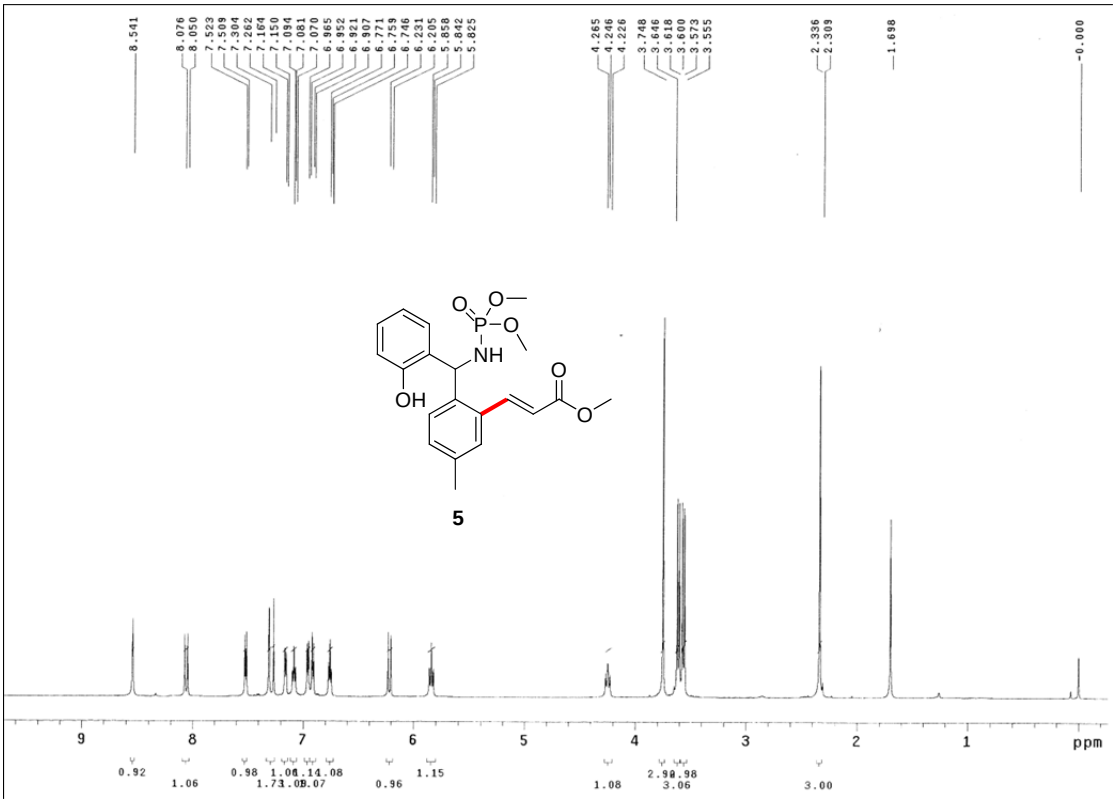
3ag


7.609
7.567
7.548
7.528
7.312
7.309
7.292
7.266
7.261
7.247
7.206
7.187
7.173
7.085
7.067
7.050
7.027
6.988
3.992
3.963
2.472
2.304
1.646
1.254
0.000
O
P
OMe
N
9
8
7
6
5
4
3
2
1
ppm
0.93
1.10
1.71
1.43
2.10
1.12
2.41
3.00
3.12

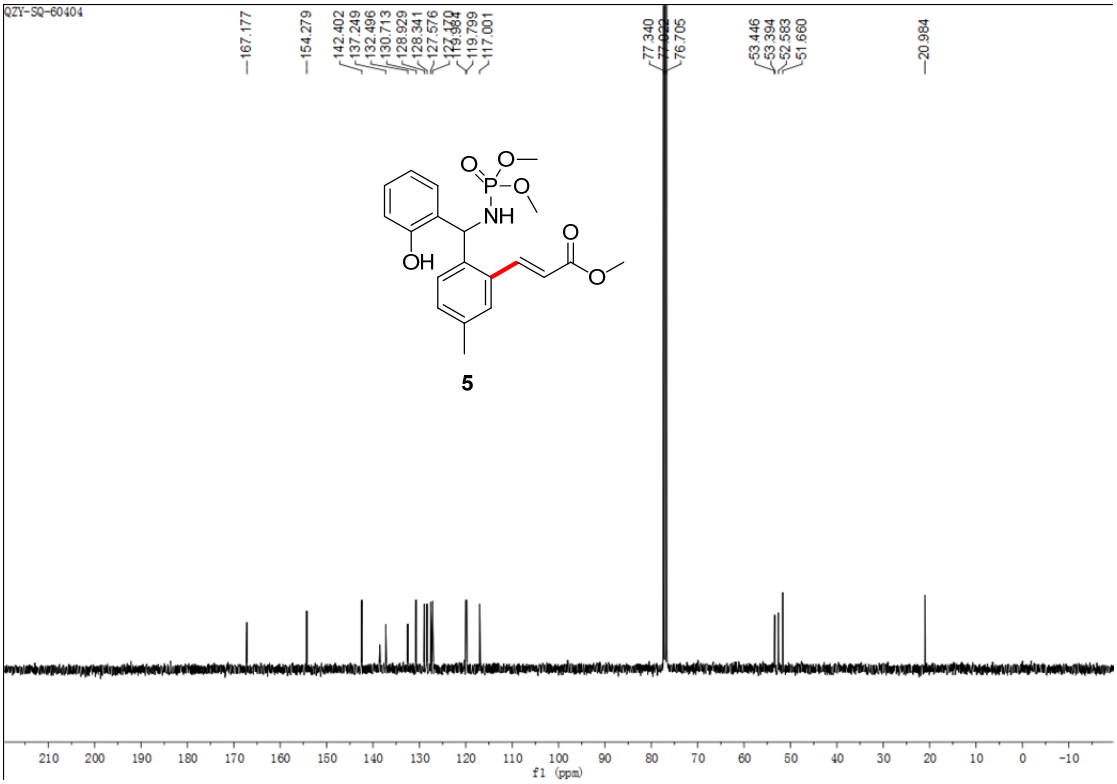
3ah


QZY-ZYQ-01036
182.116
182.050
154.085
154.033
140.526
137.963
136.067
135.733
134.154
133.368
133.127
131.599
131.319
129.368
128.983
128.022
126.542
126.438
124.521
123.805
119.665
119.590
119.516
119.404
77.345
77.027
76.710
54.935
54.871
21.560
21.230
O
O
P
OMe
N
f1 (ppm)

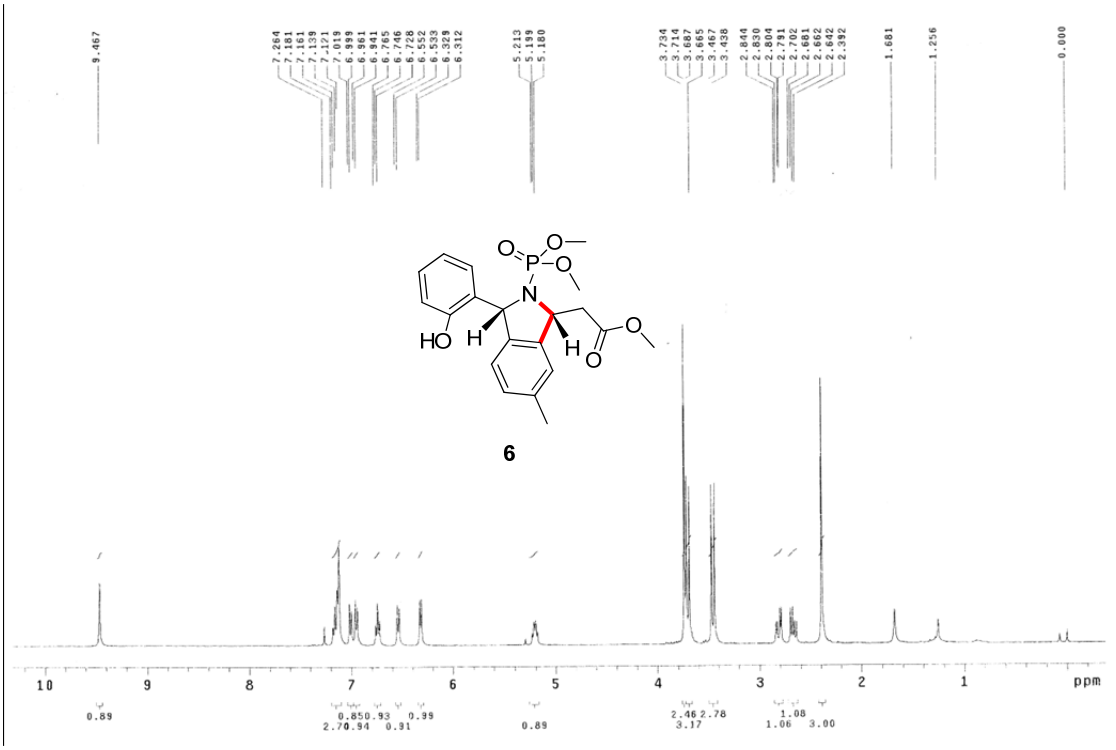
3ah


8.541
8.076
8.050
7.523
7.509
7.304
7.262
7.164
7.150
7.094
7.081
7.070
6.965
6.952
6.921
6.907
6.771
6.759
6.746
6.231
6.205
5.858
5.842
5.825
4.265
4.246
4.226
3.748
3.646
3.618
3.600
3.573
3.555
2.336
2.309
1.698
0.000
O
O
P
O
NH
OH
O
O
ppm
0.92
1.06
0.98
1.73
1.06
1.08
1.14
1.07
0.96
1.15
1.08
2.99
2.98
3.06
3.00

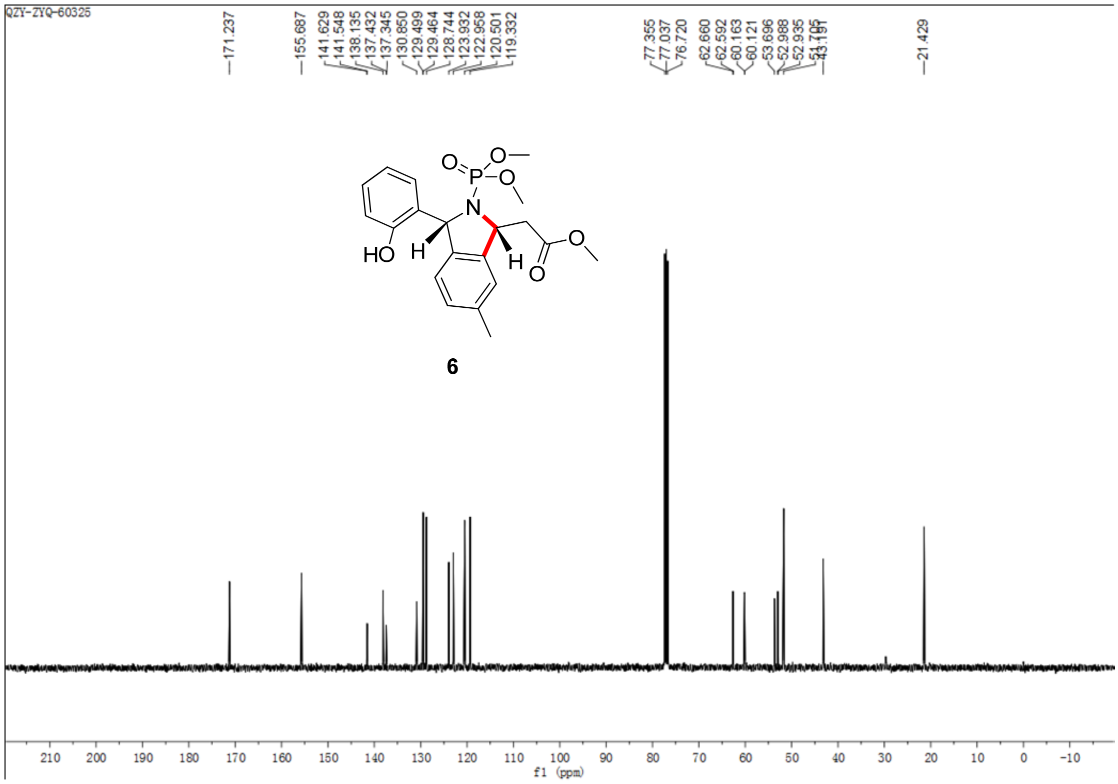
5

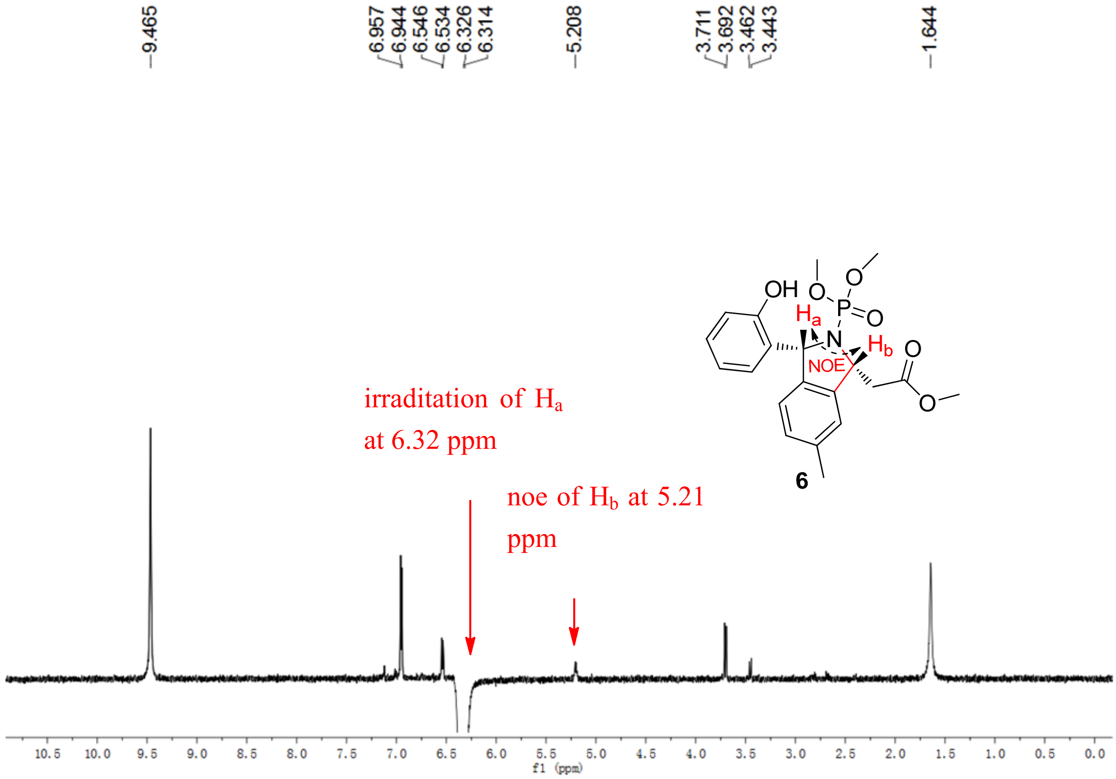

QZY-SQ-60404
167.177
154.279
142.402
137.249
132.496
130.713
128.929
128.341
127.576
127.170
119.984
119.799
117.001
77.340
77.023
76.705
53.446
53.394
52.583
51.660
20.984
f1 (ppm)

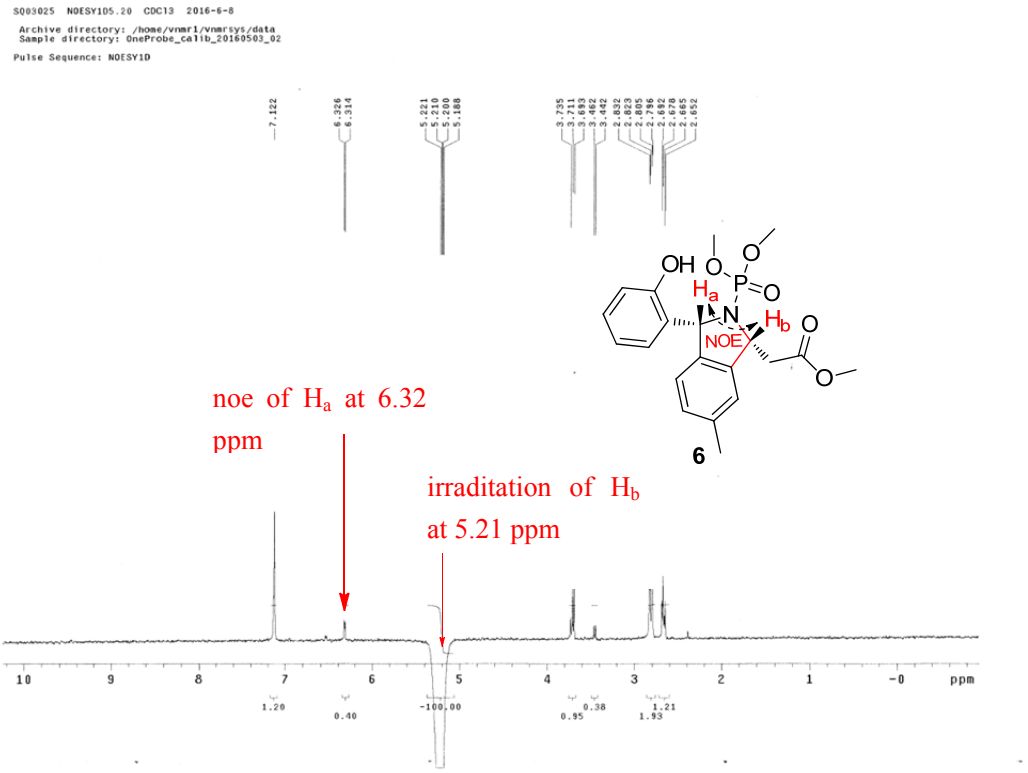
5


9.467
7.264
7.181
7.161
7.139
7.121
7.018
6.999
6.961
6.941
6.765
6.746
6.728
6.552
6.533
6.329
6.312
5.213
5.199
5.180
3.734
3.714
3.687
3.665
3.467
3.438
2.844
2.830
2.804
2.791
2.702
2.681
2.662
2.642
2.392
1.681
1.256
0.000
ppm
0.89
0.85
0.93
0.99
2.70
0.94
0.91
0.89
2.46
2.78
3.17
1.08
1.06
3.00

6


QZY-ZYQ-60325
171.237
155.687
141.629
141.548
138.135
137.432
137.345
130.850
129.499
129.464
128.744
123.932
122.958
120.501
119.332
77.355
77.037
76.720
62.660
62.592
60.163
60.121
53.696
52.988
52.935
51.705
43.191
21.429
HO
H
N
P
O
H
6
f1 (ppm)


9.465
6.957
6.944
6.546
6.534
6.326
6.314
5.208
3.711
3.692
3.462
3.443
1.644
irraditation of H$_a$ at 6.32 ppm
noe of H$_b$ at 5.21 ppm
OH
H$_a$
H$_b$
NOE
6
f1 (ppm)


S003025 NOESY1D5.20 CDCl3 2016-6-8
Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: OneProbe_calib_20160503_02
Pulse Sequence: NOESY1D
7.122
6.326
6.314
5.221
5.210
5.200
5.188
3.735
3.711
3.693
3.682
3.442
2.832
2.823
2.805
2.795
2.692
2.678
2.665
2.652
OH
O
O
P
O
Ha
N
Hb
O
O
NOE
6
noe of Ha at 6.32 ppm
irraditation of Hb at 5.21 ppm
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.20
0.40
-100.00
0.95
0.38
1.93
1.21