Supporting Information

Palladium-Catalyzed Direct C-3 Oxidative Alkenylation of Phosphachromones

Dongjin Kang, Jaeyoung Cho, and Phil Ho Lee*

Department of Chemistry, Kangwon National University, Chuncheon 200-701, Republic of Korea

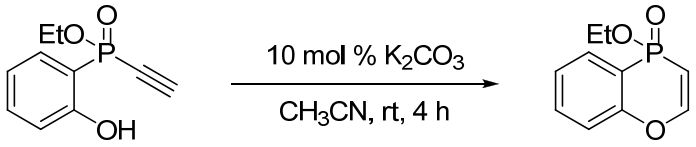
phlee@kangwon.ac.kr

Table of Contents

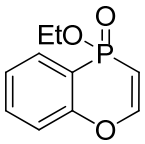
Experimental Section

General: Reactions were carried out in oven-dried glassware under air. Commercial reagents were purchased from Aldrich Inc., Alfa Aesar Co., and other commercial suppliers and were used without purification, and all solvents were reaction grade. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel pre-coated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using silica gel (230-400 mesh). ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{31}P NMR (121 MHz or 141 MHz) spectra were recorded on NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.26 for ^{1}H and δ 77.0 for ^{13}C). Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. Mass spectra were obtained from the KBSI on high resolution mass spectrometer. Melting points were determined in open capillary tube.

Typical experimental procedures for synthesis of phosphachromone:

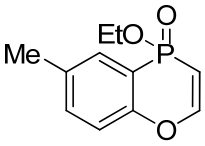


To a solution of K_2CO_3 (92.0 mg, 0.663 mmol) in acetonitrile (20.0 mL) were added ethyl 2-hydroxyphenyl(ethynyl)phosphinate[1a] (1.39 g, 6.63 mmol) in acetonitrile (5.0 mL). The reaction mixture was stirred at room temperature for 4 h and filtered over silica gel. Silica gel column chromatography (ethyl acetate:hexane = 2:1) gave 4-ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide **1a** (1.2 g, 5.7 mmol, 86%) as pale yellow solid.[1b]



1a

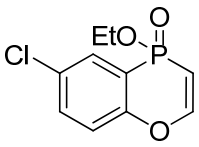
4-Ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide (1a): Pale yellow solid. Melting point: 35-40 ^oC; ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS) δ 7.87 (ddd, J = 13.5, 7.8, 1.7 Hz, 1H), 7.60-7.55 (m, 1H), 7.43 (dd, J = 29.2, 8.7 Hz, 1H), 7.36-7.32 (m, 1H), 7.25-7.21 (m, 1H), 5.59 (dd, J = 8.7, 0.9 Hz, 1H), 4.07-3.93 (m, 2H), 1.30 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^oC, TMS) δ 157.0 (d, J_{cp} = 4.0 Hz), 155.1 (d, J_{cp} = 1.9 Hz), 133.2, 128.9, 124.8 (d, J_{cp} = 10.9 Hz), 118.5, (d, J_{cp} = 6.3 Hz), 116.6 (d, J_{cp} = 130.4 Hz), 96.6 (d, J_{cp} = 131.5 Hz), 61.85 (d, J_{cp} = 6.2 Hz), 16.47 (d, J_{cp} = 6.7 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^oC) δ 7.9; IR (film) 3055, 2982, 2937, 2900, 1606, 1440, 1285, 1219, 1041, 955, 768 cm^{-1}; HRMS (EI): *m/z* calcd For $C_{10}H_{11}O_3P$: 210.0446; found: 210.0443.



1b

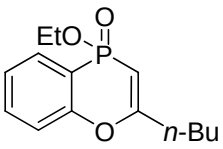
4-Ethoxy-6-methyl-4*H*-1,4-benzoxaphosphorin-4-oxide (1b): White solid. Melting point: 60-65 ^oC; ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS) δ 7.64 (d, J = 13.6 Hz, 1H), 7.46-7.35 (m, 2H), 7.12 (t, J = 8.0 Hz, 1H), 5.55 (d, J = 8.6 Hz, 1H), 4.03-3.93 (m, 2H), 2.39 (s, 3H), 1.30 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^oC, TMS) δ 155.2 (d, J_{cp} = 2.1 Hz), 155.1 (d, J_{cp} = 4.1 Hz), 134.6 (d, J_{cp} = 10.8 Hz), 134.3 (d, J_{cp} = 1.4 Hz), 128.2 (d, J_{cp} = 2.5 Hz), 118.3 (d, J_{cp} = 6.8 Hz), 116.0 (d, J_{cp} = 130.8 Hz), 96.1 (d, J_{cp} = 131.9 Hz), 61.8 (d, J_{cp} = 6.1 Hz), 20.7, 16.4 (d, J_{cp} = 6.8 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^oC) δ

8.5; IR (film) 3048, 2981, 2927, 2900, 1605, 1480, 1285, 1211, 1032, 954, 760 cm^{-1}; HRMS (EI): *m/z* calcd For $C_{11}H_{13}O_3P$: 224.0602; found: 224.0599.



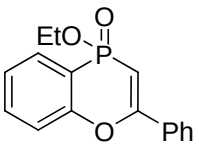
1c

6-Chloro-4-ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide (1c): White solid. Melting point:128-130 ^oC; ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS) δ 7.82 (dd, *J* = 13.5, 2.6 Hz, 1H), 7.51 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.41 (dd, *J* = 29.5, 8.7 Hz, 1H), 7.19 (dd, *J* = 8.9, 7.5 Hz, 1H), 5.60 (dd, *J* = 8.6, 0.8 Hz, 1H), 4.09-4.02 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^oC, TMS) δ 155.3 (d, J_{cp} = 3.6 Hz), 155.0 (d, J_{cp} = 2.3 Hz), 133.5 (d, J_{cp} = 1.4 Hz), 130.3 (d, J_{cp} = 13.6 Hz), 128.2 (d, J_{cp} = 2.9 Hz), 120.4 (d, J_{cp} = 6.7 Hz), 118.2 (d, J_{cp} = 128.9 Hz), 96.6 (d, J_{cp} = 134.2 Hz), 62.1 (d, J_{cp} = 6.3 Hz), 16.5 (d, J_{cp} = 6.7 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^oC) δ 6.3; IR (film) 3059, 3025, 2981, 2897, 1607, 1467, 1392, 1279, 1211, 1028, 958, 818 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{10}H_{10}ClO_3P$: 244.0056; found: 244.0057.



1d

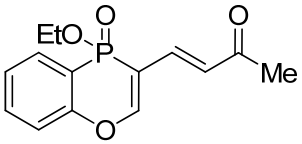
2-Butyl-4-ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide (1d)[2]: Brown oil; ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS) δ 7.85 (ddd, *J* = 13.1, 7.7, 1.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.01-3.91 (m, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 1.66 (quintet, *J* = 7.4 Hz, 2H), 1.41 (quintet, *J* = 7.4 Hz, 2H), 1.28 (t, *J* = 7.0 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^oC, TMS) δ 169.1, 157.0 (d, J_{cp} = 5.1 Hz), 133.1 (d, J_{cp} = 1.3 Hz), 128.7 (d, J_{cp} = 2.8 Hz), 124.5 (d, J_{cp} = 10.6 Hz), 118.4 (d, J_{cp} = 6.6 Hz), 115.5 (d, J_{cp} = 130.5 Hz), 91.5 (d, J_{cp} = 135.4 Hz), 61.6 (d, J_{cp} = 6.2 Hz), 36.5 (d, J_{cp} = 10.7 Hz), 28.8, 22.1, 16.5 (d, J_{cp} = 6.8 Hz), 13.8; ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^oC) δ 11.9; IR (film) 3026, 2958, 2931, 2871, 1625, 1440, 1224, 1034, 849, 766 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{14}H_{19}O_3P$: 266.1072; found: 266.1069.



1e

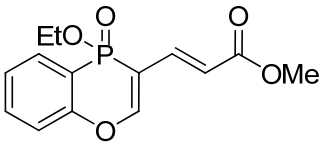
4-Ethoxy-2-phenyl-4*H*-1,4-benzoxaphosphorin-4-oxide (1e)[2]: Pale yellow solid. Melting point: 75-80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.92 (ddd, *J* = 13.3, 7.7, 1.6 Hz, 1H), 7.84-7.81 (m, 2H), 7.64-7.60 (m, 1H), 7.52-7.46 (m, 3H), 7.41-7.35 (m, 2H), 6.00 (d, *J* = 2.8 Hz, 1H), 4.10-3.96 (m, 2H), 1.31 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 163.4, 156.8 (d, J_{cp} = 5.1 Hz), 133.6 (d, J_{cp} = 11.7 Hz), 133.388 (d, J_{cp} = 1.3 Hz), 131.0, 128.8, 128.7 (d, J_{cp} = 2.8 Hz), 126.2, 124.9 (d, J_{cp} = 10.6 Hz), 118.67 (d, J_{cp} = 6.6 Hz), 115.5 (d, J_{cp} = 131.1 Hz), 90.5 (d, J_{cp} = 135.4 Hz), 61.8 (d, J_{cp} = 6.1 Hz), 16.5 (d, J_{cp} = 6.9 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 12.0; IR (film) 3058, 2982, 2936, 2900, 1612, 1440, 1236, 1025, 953, 762 cm^{-1}; HRMS (EI): *m/z* calcd For $C_{16}H_{15}O_3P$: 286.0759; found: 286.0756.

Typical experimental procedures for Pd-catalyzed oxidative cross-coupling reaction: To a 1 mL screw-capped V-vial of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), $Cu(OAc)_2$ (109.0 mg, 0.6 mmol), Ag_2CO_3 (166.0 mg, 0.6 mmol) and 4-ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide **1a** (42.0 mg, 0.2 mmol) was added methyl vinyl ketone **2a** (32.0 μL, 0.4 mmol) and pivalic acid (1.0 mL) in air condition. After being stirred at 80 ^{o}C for 6 h, the reaction mixture was quenched with sat-$NaHCO_3$ (10 mL). The aqueous layer was extracted with ethyl acetate (10 mL x 3), and the combined organic layers were washed with sat-NH_4Cl (10 mL), brine (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using acetone:dichloromethane = 1:3 to give (*E*)-4-ethoxy-3-(3-oxobut-1-enyl)-4*H*-1,4-benzoxaphosphorin-4-oxide **3a** (49.0 mg, 0.176 mmol, 88%).



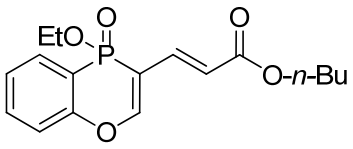
3a

(*E*)-4-Ethoxy-3-(3-oxobut-1-enyl)-4*H*-1,4-benzoxaphosphorin-4-oxide (3a): Pale yellow solid. Melting point: 65-70 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.93 (ddd, *J* = 13.5, 7.8, 1.6 Hz, 1H), 7.69 (d, *J* = 25.1 Hz, 1H), 7.64-7.60 (m, 1H), 7.42-7.38 (m, 1H), 7.30-7.26 (m, 1H), 7.18 (dd, *J* = 21.6, 16.0 Hz, 1H), 7.04 (d, *J* = 16.0 Hz, 1H), 4.04-3.87 (m, 2H), 2.33 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 197.4, 158.0 (d, J_{cp} = 3.7 Hz), 156.3 (d, J_{cp} = 3.8 Hz), 136.0 (d, J_{cp} = 2.1 Hz), 133.8 (d, J_{cp} = 1.2 Hz), 129.063, 129.057 (d, J_{cp} = 7.3 Hz), 125.5 (d, J_{cp} = 11.0 Hz), 118.5 (d, J_{cp} = 6.3 Hz), 115.7 (d, J_{cp} = 130.6 Hz), 109.1 (d, J_{cp} = 127.5 Hz), 62.7 (d, J_{cp} = 6.5 Hz), 29.1, 16.2 (d, J_{cp} = 7.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 7.6; IR (film) 3049, 2983, 2938, 2902, 1665, 1614, 1596, 1439, 1287, 1253, 1032, 957, 764 cm^{-1}; HRMS (EI): *m/z* calcd For $C_{14}H_{15}O_4P$: 278.0708; found: 278.0709.



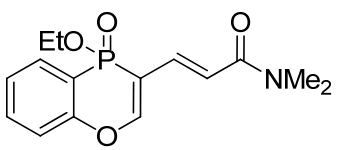
3b

(*E*)-Methyl 3-(4-ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)acrylate (3b): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.91 (ddd, *J* = 13.5, 7.7, 1.6 Hz, 1H), 7.66 (d, *J* = 12.8 Hz, 1H), 7.63-7.59 (m, 1H), 7.41-7.36 (m, 1H), 7.31 (dd, *J* = 22.1, 16.0 Hz, 1H), 7.29-7.25 (m, 1H), 6.72 (dd, *J* = 15.9, 0.6 Hz, 1H), 4.06-3.89 (m, 2H), 3.78 (m, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 167.1, 157.5 (d, J_{cp} = 3.4 Hz), 156.2 (d, J_{cp} = 3.8 Hz), 138.1 (d, J_{cp} = 1.9 Hz), 133.7 (d, J_{cp} = 1.3 Hz), 129.0 (d, J_{cp} = 2.7 Hz), 125.5 (d, J_{cp} = 11.0 Hz), 121.1 (d, J_{cp} = 4.3 Hz), 118.5 (d, J_{cp} = 6.3 Hz), 115.8 (d, J_{cp} = 130.9 Hz), 109.1 (d, J_{cp} = 127.2 Hz), 62.7 (d, J_{cp} = 6.5 Hz), 51.7, 16.3 (d, J_{cp} = 7.1 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 7.5; IR (film) 3041, 2984, 2950, 2901, 2844, 1715, 1624, 1597, 1438, 1291, 1170, 1033, 764 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{14}H_{15}O_5P$: 294.0657; found: 294.0650.



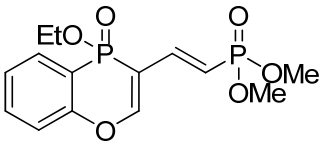
3c

(*E*)-Butyl 3-(4-ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)acrylate (3c): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.91 (ddd, *J* = 13.5, 7.8, 1.6 Hz, 1H), 7.65 (d, *J* = 25.2 Hz, 1H), 7.63-7.59 (m, 1H), 7.41-7.36 (m, 1H), 7.29 (dd, *J* = 22.4, 16.0 Hz, 1H), 7.29-7.25 (m, 1H), 6.71 (dd, *J* = 16.0, 0.6 Hz, 1H), 4.24-4.12 (m, 2H), 4.06-3.88 (m, 2H), 1.67 (quintet, *J* = 7.0 Hz, 2H), 1.42 (quintet, *J* = 7.4 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 166.8, 157.3 (d, J_{cp} = 3.5 Hz), 156.3 (d, J_{cp} = 3.7 Hz), 137.7 (d, J_{cp} = 1.9 Hz), 133.7 (d, J_{cp} = 1.1 Hz), 129.0 (d, J_{cp} = 2.8 Hz), 125.4 (d, J_{cp} = 11.0 Hz), 121.7 (d, J_{cp} = 4.2 Hz), 118.5 (d, J_{cp} = 6.5 Hz), 115.8 (d, J_{cp} = 130.8 Hz), 109.1 (d, J_{cp} = 127.3 Hz), 64.5 (d, J_{cp} = 6.5 Hz), 30.7, 19.1, 16.2 (d, J_{cp} = 7.1 Hz), 13.7; ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 7.6; IR (film) 3043, 2959, 2934, 2873, 1710, 1626, 1597, 1439, 1289, 1171, 1032, 955, 764 cm^{-1}; HRMS (EI): *m/z* calcd For $C_{17}H_{21}O_5P$: 336.1127; found: 336.1124.



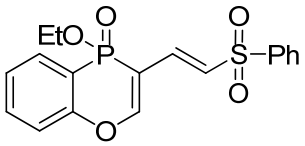
3d

(*E*)-*N*,*N*-Dimethyl 3-(4-ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)acrylamide (3d): White solid. Melting point: 140-145 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.90 (ddd, *J* = 13.4, 7.8, 1.6 Hz, 1H), 7.65 (d, *J* = 25.5 Hz, 1H), 7.63-7.59 (m, 1H), 7.40-7.36 (m, 1H), 7.30-7.24 (m, 3H), 3.96-3.76 (m, 2H), 3.16 (s, 3H), 3.05 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 166.3, 156.8 (d, J_{cp} = 3.5 Hz), 156.5 (d, J_{cp} = 4.0 Hz), 135.2 (d, J_{cp} = 1.3 Hz), 133.7 (d, J_{cp} = 1.3 Hz), 129.0 (d, J_{cp} = 2.8 Hz), 125.3 (d, J_{cp} = 11.0 Hz), 121.1 (d, J_{cp} = 3.8 Hz), 118.5 (d, J_{cp} = 6.5 Hz), 115.4 (d, J_{cp} = 129.9 Hz), 109.2 (d, J_{cp} = 125.9 Hz), 62.6 (d, J_{cp} = 6.3 Hz), 37.4, 35.8, 16.2 (d, J_{cp} = 7.3 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 8.4; IR (film) 3043, 2981, 2936, 2905, 1645, 1599, 1439, 1284, 1224, 1032, 955, 765 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{15}H_{18}NO_4P$: 307.0973; found: 307.0971.



3e

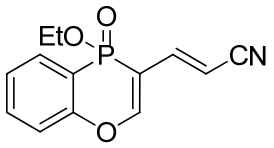
(*E*)-Dimethyl 3-(4-ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)vinylphosphonate (3e): White solid. Melting point: 105-107 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.90 (ddd, *J* = 13.5, 7.8, 1.6 Hz, 1H), 7.64 (d, *J* = 25.1 Hz, 1H), 7.64-7.60 (m, 1H), 7.41-7.37 (m, 1H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.23-7.07 (m, 1H), 6.55 (t, *J* = 17.5 Hz, 1H), 4.03-3.87 (m, 2H), 3.77 (d, *J* = 1.2 Hz, 3H), 3.74 (d, *J* = 1.3 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 157.5 (d, J_{cp} = 3.4 Hz), 156.2 (d, J_{cp} = 3.7 Hz), 142.9 (dd, J_{cp} = 7.3, 1.9 Hz), 133.7, 128.9 (d, J_{cp} = 2.8 Hz), 125.5 (d, J_{cp} = 11.1 Hz), 118.5 (d, J_{cp} = 6.5 Hz), 116.5 (dd, J_{cp} = 189.6, 4.2 Hz), 115.8 (d, J_{cp} = 131.1 Hz), 109.6 (dd, J_{cp} = 126.9, 25.9 Hz), 62.7 (d, J_{cp} = 6.6 Hz), 52.4 (dd, J_{cp} = 24.9, 5.3 Hz), 16.2 (d, J_{cp} = 6.6 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 21.17 (d, *J* = 3.1 Hz), 7.57 (d, *J* = 3.2 Hz); IR (film) 3040, 2985, 2952, 2902, 2850, 1606, 1439, 1283, 1230, 1030, 828, 767 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{14}H_{18}O_6P_2$: 344.0579; found: 344.0577.



3f

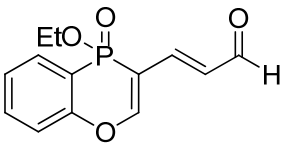
(*E*)-Phenyl [2-(4-ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)ethen-1-yl]sulfone (3f): White solid. Melting point: 48-50 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.90-7.84 (m, 1H), 7.73 (d, *J* = 24.5 Hz, 1H), 7.64-7.51 (m, 4H), 7.41-7.22 (m, 4H), 3.98-3.83 (m, 2H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 158.7 (d, J_{cp} = 3.3 Hz), 156.2 (d, J_{cp} = 3.7 Hz), 140.4, 135.9 (d, J_{cp} = 1.7 Hz), 133.9 (d, J_{cp} = 1.2 Hz), 133.4, 130.0 (d, J_{cp} = 3.9 Hz), 129.3, 128.9 (d, J_{cp} = 2.8 Hz), 127.7, 125.8 (d, J_{cp} = 11.1 Hz), 118.7 (d, J_{cp} = 6.5 Hz), 115.6 (d, J_{cp} = 132.4 Hz), 107.5 (d, J_{cp} =

127.5 Hz), 62.9 (d, J_{cp} = 6.6 Hz), 16.1 (d, J_{cp} = 7.0 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 6.9; IR (film) 3054, 2984, 2938, 2901, 1605, 1558, 1440, 1321, 1282, 1146, 1086, 1030, 958, 762 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{18}H_{17}O_5PS$: 376.0534; found: 376.0534.



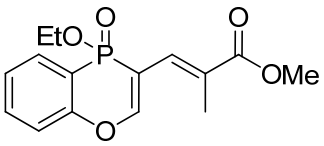
3g

(*E*)-3-(4-Ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)acrylonitrile (3g): White solid. Melting point: 131-133 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.91 (ddd, *J* = 13.6, 7.8, 1.6 Hz, 1H), 7.66-7.62 (m, 1H), 7.63 (d, *J* = 24.5 Hz, 1H), 7.44-7.40 (m, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 6.98 (dd, *J* = 21.3, 16.4 Hz, 1H), 6.28 (d, *J* = 16.6 Hz, 1H), 4.04-3.90 (m, 2H), 1.28 (t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 157.6 (d, J_{cp} = 2.8 Hz), 156.1 (d, J_{cp} = 3.7 Hz), 143.9 (d, J_{cp} = 1.9 Hz), 134.0 (d, J_{cp} = 1.3 Hz),128.9 (d, J_{cp} = 3.0 Hz), 125.8 (d, J_{cp} = 11.2 Hz), 118.7 (d, J_{cp} = 6.5 Hz), 117.8, 115.5 (d, J_{cp} = 132.2 Hz), 108.9 (d, J_{cp} = 126.7 Hz), 99.9 (d, J_{cp} = 5.1 Hz), 62.9 (d, J_{cp} = 6.5 Hz), 16.3 (d, J_{cp} = 7.1 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 7.1; IR (film) 3054, 2984, 2938, 2901, 2217, 1611, 1560, 1439, 1289, 1224, 1031, 961, 762 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{13}H_{12}NO_3P$: 261.0555; found: 261.0552.



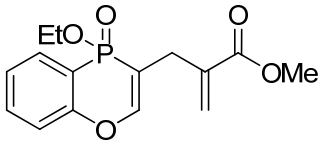
3h

(*E*)-3-(4-Ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)acrolein (3h): White solid. Melting point: 78-80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 9.58 (d, *J* = 7.3 Hz, 1H), 7.92 (ddd, *J* = 13.6, 7.8, 1.6 Hz, 1H), 7.76 (d, *J* = 24.8 Hz, 1H), 7.66-7.62 (m, 1H), 7.44-7.39 (m, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.12 (dd, *J* = 21.0, 16.0 Hz, 1H), 6.95 (dd, *J* = 16.0, 7.3 Hz, 1H), 4.10-3.94 (m, 2H), 1.28 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 192.8, 157.8 (d, J_{cp} = 3.5 Hz), 156.1 (d, J_{cp} = 3.7 Hz), 145.4 (d, J_{cp} = 2.6 Hz), 133.9 (d, J_{cp} = 1.3 Hz), 131.4 (d, J_{cp} = 3.9 Hz), 129.1 (d, J_{cp} = 11.1 Hz), 118.6 (d, J_{cp} = 6.5 Hz), 116.0 (d, J_{cp} = 131.7 Hz), 109.6 (d, J_{cp} = 127.9 Hz), 62.9 (d, J_{cp} = 6.5 Hz), 16.3 (d, J_{cp} = 6.9 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 6.7; IR (film) 3049, 2984, 2937, 2901, 2821, 2730, 1680, 1614, 1557, 1439, 1284, 1225, 1031, 957, 764 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{13}H_{13}O_4P$: 264.0551; found: 264.0549.



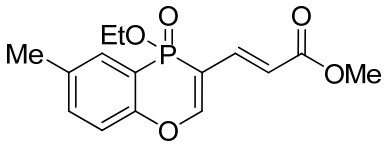
3i

(*E*)-Methyl 3-(4-ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)methacrylate (3i): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.90 (ddd, *J* = 13.4, 7.8, 1.4 Hz, 1H), 7.62-7.58 (m, 1H), 7.45-7.34 (m, 3H), 7.28-7.24 (m, 1H), 4.08-3.93 (m, 2H), 3.80 (s, 3H), 2.13 (t, *J* = 1.6 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 168.0, 156.6 (d, J_{cp} = 4.2 Hz), 153.9 (d, J_{cp} = 2.1 Hz), 133.5 (d, J_{cp} = 1.2 Hz), 131.4 (d, J_{cp} = 8.2 Hz), 129.3 (d, J_{cp} = 1.0 Hz), 129.1 (d, J_{cp} = 2.7 Hz), 125.1 (d, J_{cp} = 11.0 Hz), 118.5 (d, J_{cp} = 6.5 Hz), 115.7 (d, J_{cp} = 131.1 Hz), 108.5 (d, J_{cp} = 127.5 Hz), 62.4 (d, J_{cp} = 6.4 Hz), 52.2, 16.4 (d, J_{cp} = 6.7 Hz), 14.4; ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 8.2; IR (film) 3063, 2982, 2949, 2989, 1713, 1603, 1438, 1267, 1224, 1030, 952 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{15}H_{17}O_5P$: 308.0814; found: 308.0812.



3i'

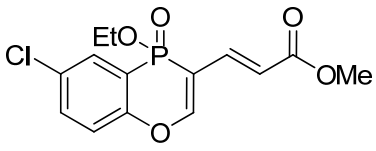
Methyl [2-(4-ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)methyl]acrylate (3i'): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.84 (ddd, *J* = 13.2, 7.8, 1.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.36-7.28 (m, 2H), 7.21-7.17 (m, 1H), 6.35 (s, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 3.97-3.79 (m, 2H), 3.77 (s, 3H), 3.52-3.32 (m, 2H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 166.9, 157.0 (d, J_{cp} = 3.9 Hz), 153.0 (d, J_{cp} = 3.7 Hz), 137.0 (d, J_{cp} = 3.5 Hz), 133.1 (d, J_{cp} = 1.2 Hz), 128.7 (d, J_{cp} = 2.7 Hz), 128.3, 124.5 (d, J_{cp} = 10.7 Hz), 118.3 (d, J_{cp} = 6.2 Hz), 115.6 (d, J_{cp} = 127.9 Hz), 106.9 (d, J_{cp} = 129.5 Hz), 61.9 (d, J_{cp} = 6.2 Hz), 52.0, 29.0 (d, J_{cp} = 3.4 Hz), 16.3 (d, J_{cp} = 7.1 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 11.5; IR (film) 3058, 2984, 2952, 2926, 2849, 1719, 1619, 1440, 1279, 1222, 1033, 952, 765 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{15}H_{17}O_5P$: 308.0814; found: 308.0814.



3j

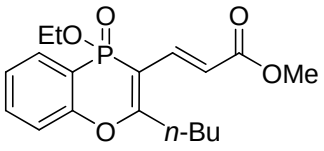
(*E*)-Methyl 3-(4-ethoxy-6-methyl-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)acrylate (3j): White solid. Melting point: 125-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.68 (dd, *J* = 13.7, 1.4 Hz, 1H), 7.64 (d, *J* = 25.0 Hz, 1H), 7.40 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.31 (dd, *J* = 22.0, 16.0 Hz, 1H), 7.16 (dd, *J* =

8.4, 7.4 Hz, 1H), 6.71 (dd, *J* = 16.0, 0.6 Hz, 1H), 4.04-3.88 (m, 2H), 3.78 (s, 3H), 2.42 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 167.1, 157.6 (d, J_{cp} = 3.6 Hz), 154.4 (d, J_{cp} = 3.9 Hz), 138.2 (d, J_{cp} = 1.8 Hz), 135.5 (d, J_{cp} = 11.0 Hz), 134.7 (d, J_{cp} = 1.7 Hz), 128.4 (d, J_{cp} = 2.7 Hz), 120.8 (d, J_{cp} = 4.3 Hz), 118.3 (d, J_{cp} = 7.0 Hz), 115.4 (d, J_{cp} = 130.7 Hz), 108.7 (d, J_{cp} = 127.0 Hz), 62.7 (d, J_{cp} = 6.4 Hz), 51.6, 20.8, 16.2 (d, J_{cp} = 7.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 8.0; IR (film) 3046, 3023, 2983, 2949, 1711, 1624, 1598, 1480, 1292, 1169, 1033, 955 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{15}H_{17}O_5P$: 308.0814; found: 308.0817.



3k

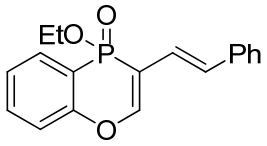
(*E*)-Methyl 3-(6-chloro-4-ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)acrylate (3k): Pale yellow solid. Melting point: 185-187 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.85 (dd, *J* = 13.6, 2.5 Hz, 1H), 7.63 (d, *J* = 25.4 Hz, 1H), 7.55 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.35-7.21 (m, 2H), 6.70 (dd, *J* = 16.0, 0.6 Hz, 1H), 4.10-3.98 (m, 2H), 3.78 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 166.9, 157.2 (d, J_{cp} = 3.5 Hz), 154.5 (d, J_{cp} = 3.5 Hz), 137.6 (d, J_{cp} = 2.0 Hz), 133.9 (d, J_{cp} = 1.7 Hz), 131.0 (d, J_{cp} = 13.9 Hz), 128.3 (d, J_{cp} = 3.4 Hz), 121.6 (d, J_{cp} = 4.3 Hz), 120.3 (d, J_{cp} = 7.2 Hz), 117.5 (d, J_{cp} = 128.6 Hz), 109.2 (d, J_{cp} = 129.3 Hz), 63.1 (d, J_{cp} = 6.6 Hz), 51.7, 16.3 (d, J_{cp} = 7.1 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 6.2; IR (film) 3043, 2984, 2949, 2847, 1712, 1624, 1592, 1463, 1273, 1169, 1027, 958, 765 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{14}H_{14}ClO_5P$: 328.0267; found: 328.0270.



3l

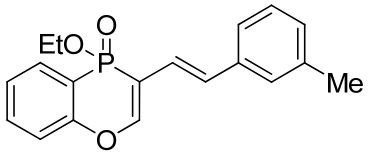
(*E*)-Methyl 3-(2-butyl-4-ethoxy-4-oxo-4*H*-1,4-benzoxaphosphorin-3-yl)acrylate (3l): Colorless oil ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.87 (ddd, *J* = 13.1, 7.7, 1.6 Hz, 1H), 7.61 (dd, *J* = 21.3, 16.0 Hz, 1H), 7.37-7.32 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.84 (dd, *J* = 16.0, 1.2 Hz, 1H), 4.00-3.84 (m, 2H), 3.78 (s, 3H), 2.81-2.66 (m, 2H), 1.70 (quintet, *J* = 7.5 Hz, 2H), 1.43 (sextet, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 170.27 (d, J_{cp} = 2.8 Hz), 167.5, 156.1 (d, J_{cp} = 4.5 Hz), 136.8 (d, J_{cp} = 2.1 Hz), 133.5 (d, J_{cp} = 1.1 Hz), 128.8 (d, J_{cp} = 3.0 Hz), 125.0 (d, J_{cp} = 11.0 Hz), 121.0 (d, J_{cp} = 4.5 Hz), 118.2 (d, J_{cp} = 6.5 Hz), 115.2 (d, J_{cp} = 130.9 Hz), 103.5 (d, J_{cp} = 127.6 Hz), 62.4 (d, J_{cp} = 6.3 Hz), 51.6, 32.6 (d, J_{cp} = 7.3 Hz), 29.9, 22.2, 16.2 (d, J_{cp} = 7.0 Hz),

13.7; ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 10.2; IR (film) 3019, 2957, 2933, 2872, 1716, 1617, 1439, 1298, 1230, 1033, 952, 764 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{18}H_{23}O_5P$: 350.1283; found: 350.1284.



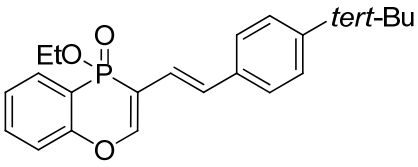
4a

(*E*)-4-Ethoxy-3-(2-phenylethenyl)-4*H*-1,4-benzoxaphosphorin-4-oxide (4a): Pale yellow solid. Melting point: 90-95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.93 (ddd, *J* = 13.3, 7.8, 1.5 Hz, 1H), 7.60-7.55 (m, 1H), 7.54 (d, *J* = 26.2 Hz, 1H), 7.48-7.46 (m, 2H), 7.37-7.32 (m, 4H), 7.27-7.21 (m, 2H), 6.68 (ddd, *J* = 20.6, 16.4, 0.5 Hz, 1H), 4.06-3.87 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 156.6 (d, J_{cp} = 3.9 Hz), 152.9 (d, J_{cp} = 3.3 Hz), 137.1, 133.3 (d, J_{cp} = 1.2 Hz), 132.4 (d, J_{cp} = 5.2 Hz), 129.1 (d, J_{cp} = 2.8 Hz), 128.6, 127.8, 126.4, 124.8 (d, J_{cp} = 11.0 Hz), 121.0 (d, J_{cp} = 1.7 Hz), 118.3 (d, J_{cp} = 6.5 Hz), 115.5 (d, J_{cp} = 129.9 Hz), 110.7 (d, J_{cp} = 125.7 Hz), 62.6 (d, J_{cp} = 6.4 Hz), 16.3 (d, J_{cp} = 7.1 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 9.6; IR (film) 3076, 3056, 3029, 2981, 2937, 2899, 1592, 1559, 1439, 1283, 1214, 1035, 961, 760 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{18}H_{17}O_3P$: 312.0915; found: 312.0918.



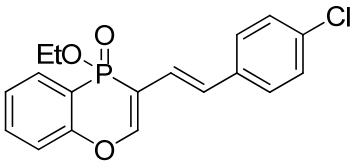
4b

(*E*)-4-Ethoxy-3-[2-(3-methylphenyl)ethenyl]-4*H*-1,4-benzoxaphosphorin-4-oxide (4b): White solid. Melting point: 118-120 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.91 (ddd, *J* = 13.3, 7.8, 1.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.52 (d, *J* = 26.2 Hz, 1H), 7.34-7.19 (m, 6H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.67 (dd, *J* = 20.6, 16.4 Hz, 1H), 4.05-3.85 (m, 2H), 2.35 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 156.6 (d, J_{cp} = 3.8 Hz), 152.7 (d, J_{cp} = 3.5 Hz), 138.2, 137.0, 133.3, 132.5 (d, J_{cp} = 5.2 Hz), 129.1 (d, J_{cp} = 2.8 Hz), 128.6 (d, J_{cp} = 11.0 Hz), 127.1, 124.8 (d, J_{cp} = 11.0 Hz), 123.5, 120.8 (d, J_{cp} = 1.9 Hz), 118.3 (d, J_{cp} = 6.3 Hz), 115.6 (d, J_{cp} = 129.8 Hz), 110.8 (d, J_{cp} = 125.6 Hz), 62.6 (d, J_{cp} = 6.4 Hz), 21.4, 16.3 (d, J_{cp} = 7.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 9.4; IR (film) 3041, 2981, 2935, 2899, 1593, 1439, 1282, 1228, 1035, 960, 762 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{19}H_{19}O_3P$: 326.1072; found: 326.1072.



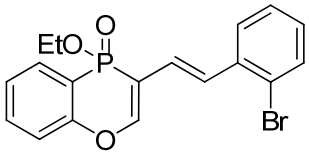
4c

(*E*)-3-[2-(4-*tert*-Butylphenyl)ethenyl]-4-ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide (4c): White solid. Melting point: 130-132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.92 (ddd, *J* = 13.3, 7.7, 1.6 Hz, 1H), 7.59-7.55 (m, 1H), 7.52 (d, *J* = 26.3 Hz, 1H), 7.43-7.32 (m, 6H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.65 (ddd, *J* = 20.5, 16.4, 0.4 Hz, 1H), 4.06-3.86 (m, 2H), 1.32 (s, 9H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 156.6 (d, J_{cp} = 3.8 Hz), 152.7 (d, J_{cp} = 3.4 Hz), 151.0, 134.4, 133.3, 132.2 (d, J_{cp} = 5.2 Hz), 129.1 (d, J_{cp} = 2.7 Hz), 126.1, 125.6, 124.8 (d, J_{cp} = 11.0 Hz), 120.2 (d, J_{cp} = 1.9 Hz), 118.3 (d, J_{cp} = 6.5 Hz), 115.5 (d, J_{cp} = 130.0 Hz), 110.8 (d, J_{cp} = 125.6 Hz), 62.6 (d, J_{cp} = 6.3 Hz), 34.6, 31.3, 16.3 (d, J_{cp} = 7.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 9.6; IR (film) 3046, 2962, 2902, 2868, 1724, 1594, 1439, 1283, 1220, 1036, 961, 761 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{22}H_{25}O_3P$: 368.1541; found: 368.1542.



4d

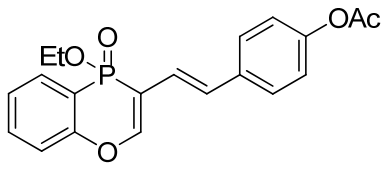
(*E*)-3-[2-(4-Chlorophenyl)ethenyl]-4-ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide (4d): White solid. Melting point: 121-125 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.92 (ddd, *J* = 13.3, 7.8, 1.6 Hz, 1H), 7.60-7.55 (m, 1H), 7.54 (d, *J* = 26.1 Hz, 1H), 7.39-7.27 (m, 6H), 7.24-7.20 (m, 1H), 6.64 (ddd, *J* = 20.7, 16.4, 0.4 Hz, 1H), 4.04-3.85 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 156.6 (d, J_{cp} = 4.1 Hz), 153.3 (d, J_{cp} = 3.2 Hz), 135.6, 133.4 (d, J_{cp} = 1.0 Hz), 133.4, 130.9 (d, J_{cp} = 5.1 Hz), 129.0 (d, J_{cp} = 2.7 Hz), 128.8, 127.5, 124.9 (d, J_{cp} = 10.9 Hz), 121.8 (d, J_{cp} = 1.9 Hz), 118.3 (d, J_{cp} = 6.5 Hz), 115.4 (d, J_{cp} = 129.9 Hz), 110.4 (d, J_{cp} = 125.8 Hz), 62.6 (d, J_{cp} = 6.3 Hz), 16.3 (d, J_{cp} = 7.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 9.3; IR (film) 3046, 2981, 2937, 2899, 1599, 1439, 1278, 1224, 1035, 959, 759 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{18}H_{16}ClO_3P$: 346.0526; found: 346.0527.



4e

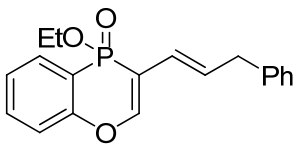
(*E*)-3-[2-(2-Bromophenyl)ethenyl]-4-ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide (4e): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.93 (ddd, *J* = 13.4, 7.7, 1.6 Hz, 1H), 7.66 (d, *J* = 16.2 Hz,

1H), 7.59-7.53 (m, 4H), 7.36-7.32 (m, 1H), 7.29-7.25 (m, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.10 (td, J = 7.9, 1.5 Hz, 1H), 6.61 (dd, J = 20.0, 16.3 Hz, 1H), 4.18-3.99 (m, 2H), 1.32 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 156.5 (d, J_{cp} = 3.8 Hz), 153.4 (d, J_{cp} = 3.4 Hz), 137.1, 133.4 (d, J_{cp} = 1.2 Hz), 133.0, 131.1 (d, J_{cp} = 5.3 Hz), 129.0 (d, J_{cp} = 2.8 Hz), 128.9, 127.5, 126.5, 124.9 (d, J_{cp} = 11.0 Hz), 124.0, 123.9 (d, J_{cp} = 1.7 Hz), 118.3 (d, J_{cp} = 6.5 Hz), 115.7 (d, J_{cp} = 130.7 Hz), 110.8 (d, J_{cp} = 126.4 Hz), 62.8 (d, J_{cp} = 6.5 Hz), 16.5 (d, J_{cp} = 7.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 9.0; IR (film) 3056, 2980, 2935, 2898, 1597, 1559, 1438, 1279, 1221, 1032, 959, 759 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{18}H_{16}BrO_3P$: 390.0020; found: 390.0021.



4f

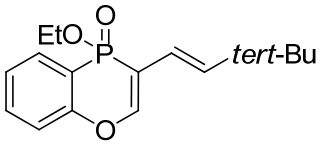
(*E*)-3-[2-(4-Acetoxyphenyl)ethenyl]-4-ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide (4f): Pale yellow solid. Melting point: 158-160 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.92 (ddd, J = 13.3, 7.8, 1.5 Hz, 1H), 7.60-7.55 (m, 1H), 7.53 (d, J = 26.2 Hz, 1H), 7.49-7.45 (m, 2H), 7.37-7.32 (m, 2H), 7.24-7.21 (m, 1H), 7.08-7.05 (m, 2H), 6.63 (ddd, J = 20.6, 16.4, 0.5 Hz, 1H), 4.04-3.85 (m, 2H), 2.30 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 169.4, 156.6 (d, J_{cp} = 3.8 Hz), 153.1 (d, J_{cp} = 3.2 Hz), 150.2, 134.9, 133.4 (d, J_{cp} = 1.1 Hz), 131.3 (d, J_{cp} = 5.1 Hz), 129.0 (d, J_{cp} = 2.6 Hz), 127.3, 124.8 (d, J_{cp} = 11.0 Hz), 121.8, 121.3 (d, J_{cp} = 1.9 Hz), 118.3 (d, J_{cp} = 6.3 Hz), 115.5 (d, J_{cp} = 130.0 Hz), 110.6 (d, J_{cp} = 125.6 Hz), 62.6 (d, J_{cp} = 6.5 Hz), 21.1, 16.3 (d, J_{cp} = 7.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 9.4; IR (film) 3046, 2983, 2937, 2900, 2358, 1754, 1602, 1439, 1283, 1217, 1197, 1035, 958, 763 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{20}H_{19}O_5P$: 370.0970; found: 370.0969.



4g

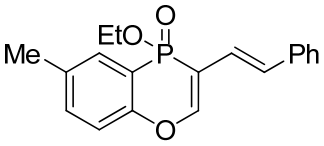
(*E*)-4-Ethoxy-3-[3-phenyl-1-propen-1-yl]-4*H*-1,4-benzoxaphosphorin-4-oxide (4g): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.86 (ddd, J = 13.2, 7.8, 1.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.39-7.37 (m, 2H), 7.32-7.29 (m, 3H), 7.26 (d, J = 26.3 Hz, 1H), 7.24-7.17 (m, 2H), 6.57 (d, J = 15.8 Hz, 1H), 6.31 (dt, J = 15.7, 6.8 Hz, 1H), 4.03-3.86 (m, 2H), 3.43-3.25 (m, 2H), 1.23 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 157.2 (d, J_{cp} = 4.2 Hz), 151.8 (d, J_{cp} = 3.9 Hz), 137.0, 133.2 (d, J_{cp} = 1.1 Hz), 132.7, 128.8 (d, J_{cp} = 2.6 Hz), 128.6, 127.5, 126.27 (d, J_{cp} = 5.1 Hz), 126.22, 124.5 (d, J_{cp} = 10.7

Hz), 118.3 (d, J_{cp} = 6.4 Hz), 115.5 (d, J_{cp} = 127.5 Hz), 108.7 (d, J_{cp} = 128.1 Hz), 62.0 (d, J_{cp} = 6.2 Hz), 29.6 (d, J_{cp} = 3.4 Hz), 16.4 (d, J_{cp} = 6.9 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 11.7; IR (film) 3057, 3025, 2981, 2934, 2899, 1619, 1440, 1280, 1223, 1034, 954, 761 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{19}H_{19}O_3P$: 326.1072; found: 326.1075.



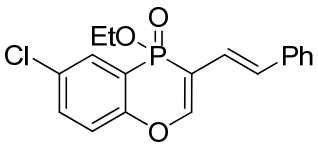
4h

(*E*)-3-[3,3-Dimethyl-1-buten-1-yl]-4-ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide (4h): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.88 (ddd, *J* = 13.2, 7.8, 1.6 Hz, 1H), 7.57-7.52 (m, 1H), 7.36 (d, *J* = 26.8 Hz, 1H), 7.33-7.29 (m, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.46 (dd, *J* = 16.2, 1.4 Hz, 1H), 5.89 (dd, *J* = 19.2, 16.3 Hz, 1H), 4.02-3.85 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 156.7 (d, J_{cp} = 4.0 Hz), 151.5 (d, J_{cp} = 3.5 Hz), 145.7 (d, J_{cp} = 5.2 Hz), 133.1 (d, J_{cp} = 1.1 Hz), 129.0 (d, J_{cp} = 2.8 Hz), 124.5 (d, J_{cp} = 10.9 Hz), 118.2 (d, J_{cp} = 6.4 Hz), 116.7 (d, J_{cp} = 1.7 Hz), 115.6 (d, J_{cp} = 129.6 Hz), 110.6 (d, J_{cp} = 126.5 Hz), 62.4 (d, J_{cp} = 6.3 Hz), 33.9, 29.3, 16.3 (d, J_{cp} = 6.9 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 10.0; IR (film) 3045, 2959, 2902, 2865, 1738, 1598, 1440, 1275, 1229, 1037, 952, 762 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{16}H_{21}O_3P$: 292.1228; found: 292.1226.



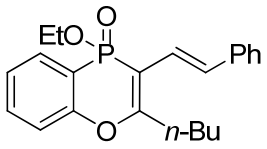
4i

(*E*)-4-Ethoxy-6-methyl-3-(2-phenylethenyl)-4*H*-1,4-benzoxaphosphorin-4-oxide (4i): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.69 (dd, *J* = 13.5, 1.7 Hz, 1H), 7.52 (d, *J* = 26.2 Hz, 1H), 7.48-7.46 (m, 2H), 7.38-7.31 (m, 4H), 7.26-7.22 (m, 1H), 7.12 (dd, *J* = 8.4, 7.4 Hz, 1H), 4.04-3.85 (m, 2H), 2.41 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 154.8 (d, J_{cp} = 3.8 Hz), 153.1 (d, J_{cp} = 3.4 Hz), 137.2, 134.7 (d, J_{cp} = 10.9 Hz), 134.4 (d, J_{cp} = 1.4 Hz), 132.1 (d, J_{cp} = 5.2 Hz), 128.6, 128.4 (d, J_{cp} = 2.8 Hz), 127.7, 126.3, 121.2 (d, J_{cp} = 1.7 Hz), 118.1 (d, J_{cp} = 7.0 Hz), 115.1 (d, J_{cp} = 129.6 Hz), 110.3 (d, J_{cp} = 125.4 Hz), 62.6 (d, J_{cp} = 6.4 Hz), 20.8, 16.3 (d, J_{cp} = 7.3 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 9.9; IR (film) 3044, 2982, 2925, 2899, 1711, 1597, 1480, 1392, 1284, 1035, 960, 735 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{19}H_{19}O_3P$: 326.1072; found: 326.1073.



4j

(*E*)-6-Chloro-4-ethoxy-3-(2-phenylethenyl)-4*H*-1,4-benzoxaphosphorin-4-oxide (4j): Pale yellow solid. Melting point: 90-95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.80 (dd, *J* = 13.4, 2.6 Hz, 1H), 7.47-7.38 (m, 4H), 7.28-7.24 (m, 3H), 7.20-7.16 (, 1H), 7.10 (dd, *J* = 8.9, 7.4 Hz, 1H), 6.59 (dd, *J* = 20.8, 16.4 Hz, 1H), 4.04-3.86 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 153.9 (d, J_{cp} = 3.6 Hz), 151.7 (d, J_{cp} = 3.2 Hz), 135.9, 132.6 (d, J_{cp} = 1.3 Hz), 131.8 (d, J_{cp} = 5.2 Hz), 129.3 (d, J_{cp} = 13.8 Hz), 127.6, 127.3 (d, J_{cp} = 3.1 Hz), 126.9, 125.4, 119.5 (d, J_{cp} = 2.0 Hz), 119.1 (d, J_{cp} = 7.2 Hz), 116.1 (d, J_{cp} = 127.6 Hz), 109.6 (d, J_{cp} = 127.7 Hz), 61.9 (d, J_{cp} = 6.5 Hz), 15.3 (d, J_{cp} = 7.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 8.3; IR (film) 3056, 2964, 2903, 2870, 1712, 1590, 1464, 1389, 1261, 1030, 961 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{18}H_{16}ClO_3P$: 346.0526; found: 346.0527.

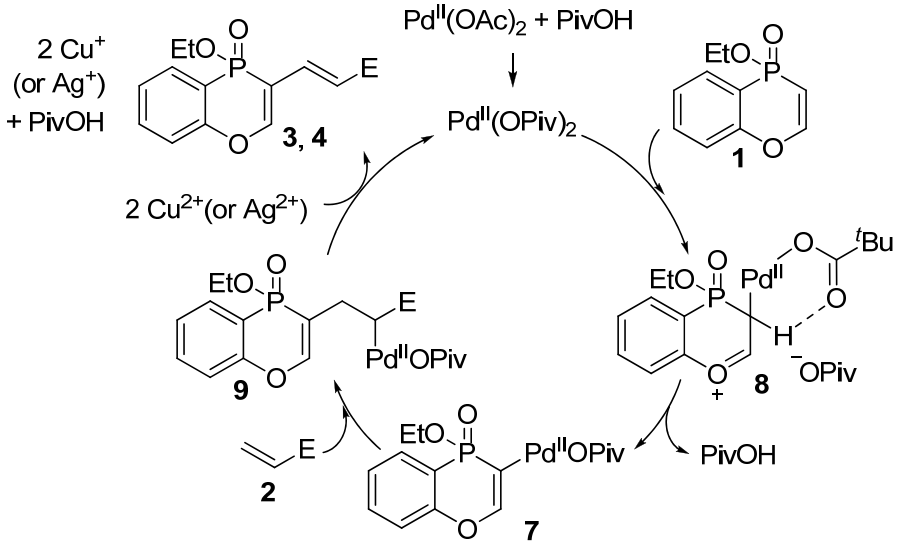


4k

(*E*)-2-Butyl-4-ethoxy-3-(2-phenylethenyl)-4*H*-1,4-benzoxaphosphorin-4-oxide (4k): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 7.87 (ddd, *J* = 12.9, 7.8, 1.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.49-7.44 (m, 3H), 7.37-7.31 (m, 3H), 7.29-7.23 (m, 1H), 7.22-7.18 (m, 1H), 6.86 (dd, *J* = 19.2, 16.4 Hz, 1H), 4.03-3.84 (m, 2H), 2.78-2.64 (m, 2H), 1.72 (quintet, *J* = 7.5 Hz, 2H), 1.49-1.40 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS) δ 165.5 (d, J_{cp} = 2.9 Hz), 156.5 (d, J_{cp} = 4.5 Hz), 137.7, 133.1, 133.0 (d, J_{cp} = 5.2 Hz), 128.8 (d, J_{cp} = 2.9 Hz), 128.6, 127.7, 126.4, 124.4 (d, J_{cp} = 10.9 Hz), 120.1 (d, J_{cp} = 1.5 Hz), 118.1 (d, J_{cp} = 6.5 Hz), 115.1 (d, J_{cp} = 129.7 Hz), 104.9 (d, J_{cp} = 126.4 Hz), 62.3 (d, J_{cp} = 6.5 Hz), 32.5 (d, J_{cp} = 7.9 Hz), 29.7, 22.4, 16.3 (d, J_{cp} = 7.2 Hz), 13.8; ^{31}P NMR (161 MHz, $CDCl_3$, 25 ^{o}C) δ 11.6; IR (film) 3056, 3023, 2957, 2930, 2870, 1603, 1590, 1561, 1440, 1270, 1226, 1036, 954, 755 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{22}H_{25}O_3P$: 368.1541; found: 368.1544.

Deuterium experimental procedures: To a suspension of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), $Cu(OAc)_2$ (109.0 mg, 0.6 mmol), Ag_2CO_3 (166.0 mg, 0.6 mmol) and 4-ethoxy-4*H*-1,4-benzoxaphosphorin-4-oxide **1a** (42.0 mg, 0.2 mmol) in screw-capped V-vial (1 mL) was added D_2O (2 mmol) and DMF (1.0 mL) in air condition. After being stirred at 80 ^{o}C for 2 h, the reaction mixture was quenched with H_2O (10 mL). The aqueous layer was extracted with ethyl acetate (10 mL x 3), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The ratio of H/D exchange was determined by ^{1}H NMR.

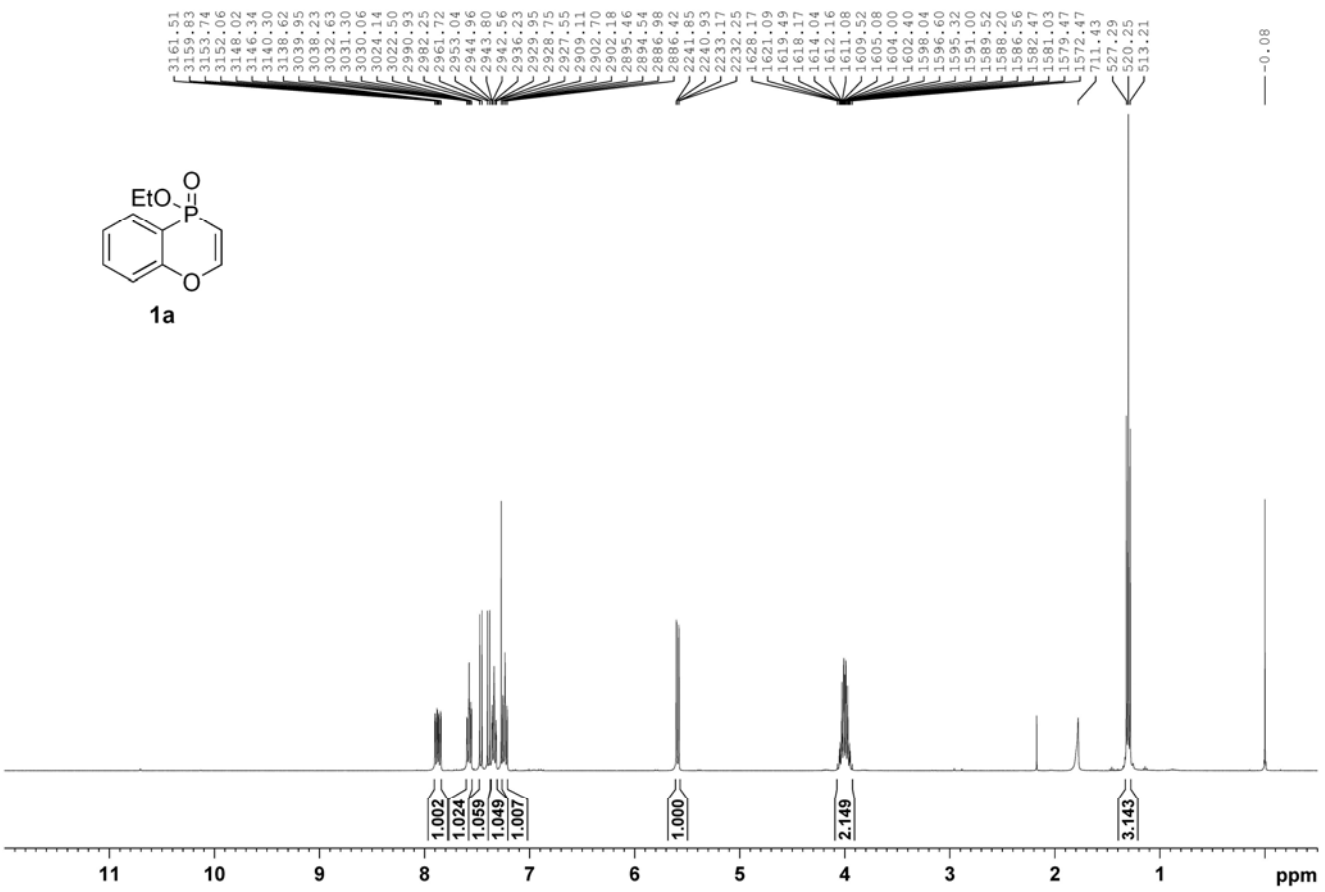
A plausible mechanism for the reaction of phosphachromone with alkene is described in Scheme 1. Electrophilic palladation of phosphachromone at the C-3 position with the Pd(II) species was favorable owing to the more nucleophilic C-3 position, thereby providing the intermediate **7** and then, the C3-palladated species **7** inserted into the alkene **2**. After that, the subsequent reductive elimination of a Pd/alkyl intermediate **9** furnished the desired C-3 alkenylated coupling product **3** and **4**. Finally, the re-oxidation by $Cu(OAc)_2$ regenerated the Pd(II) catalyst to back into the catalytic cycle.

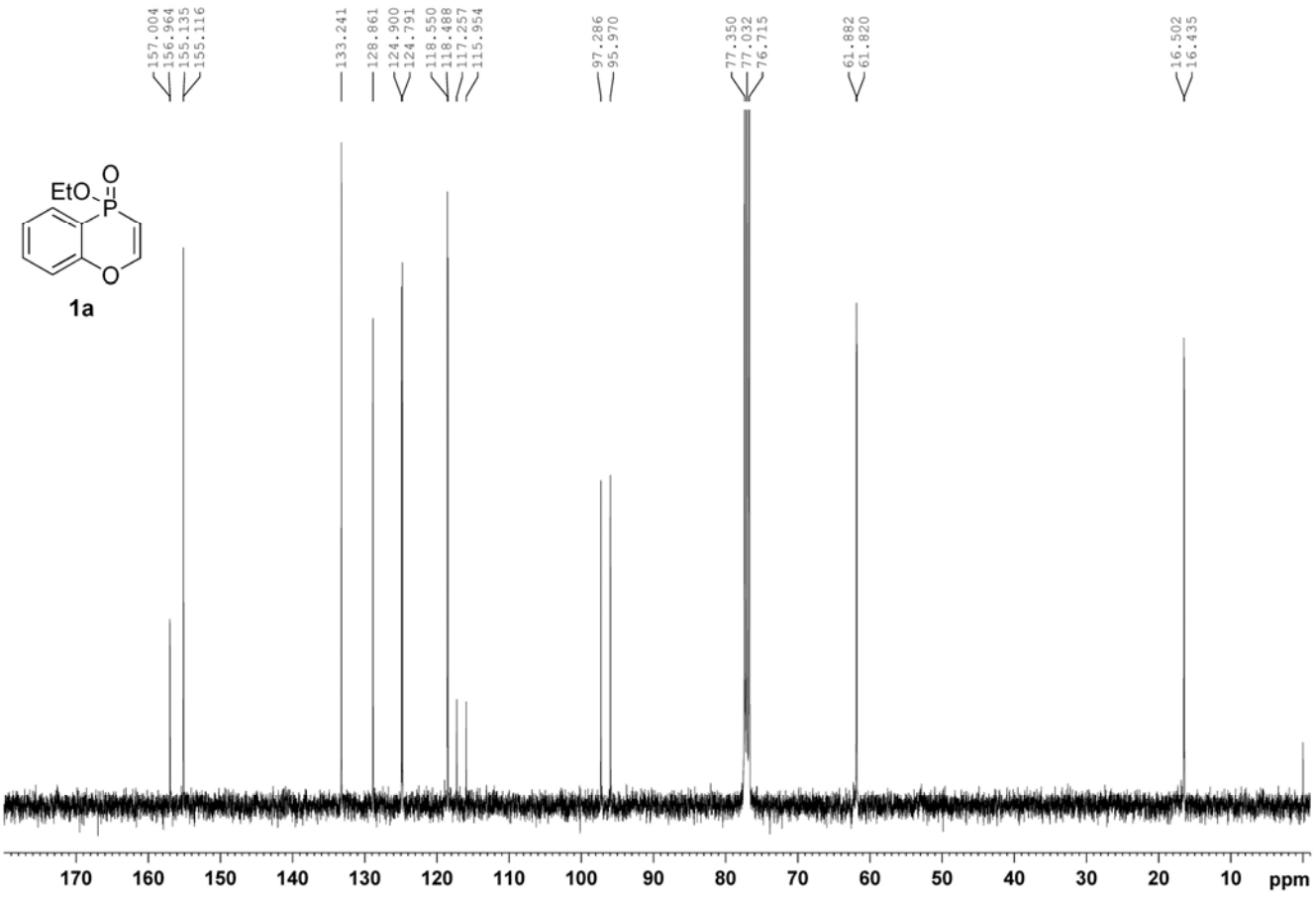


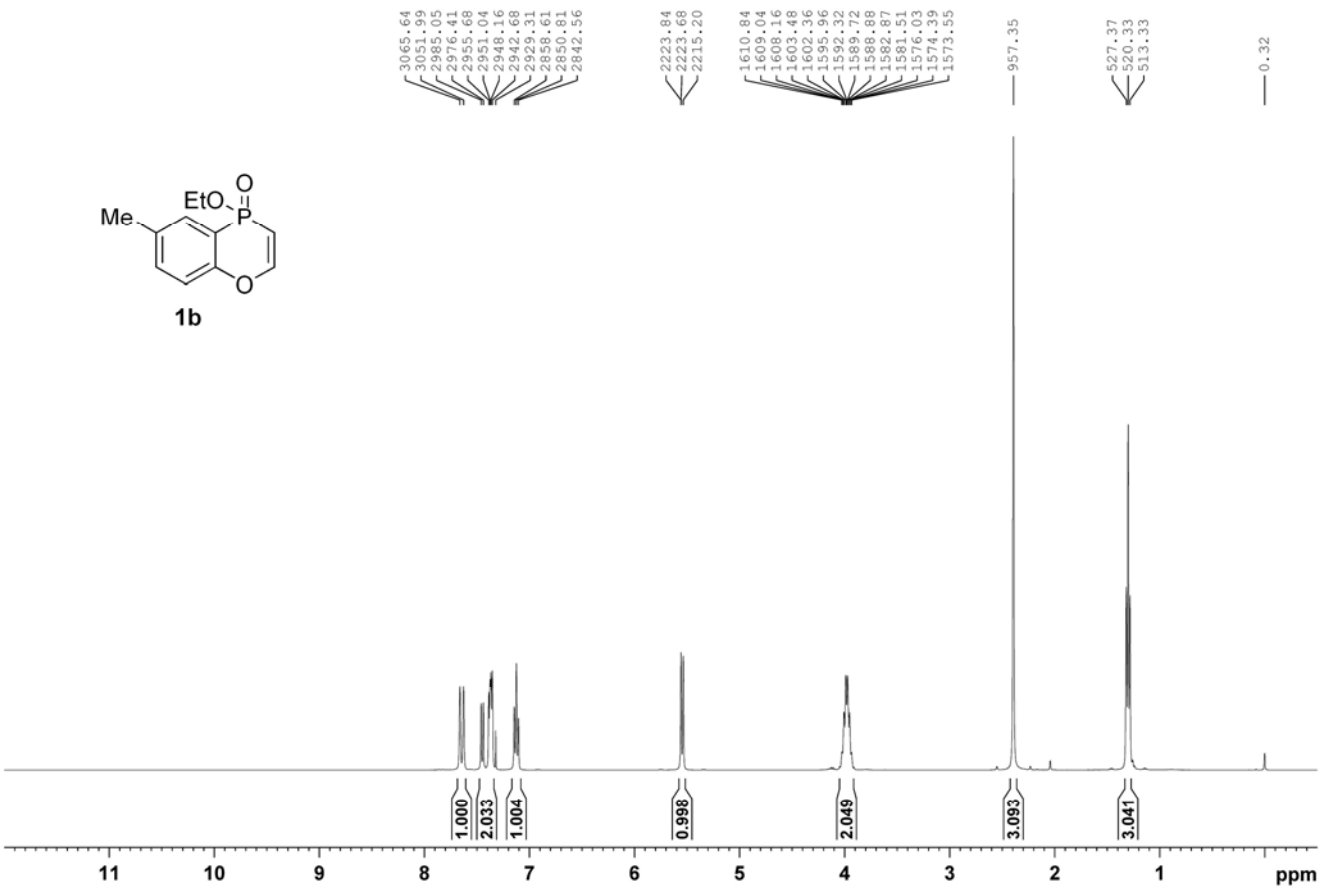
Scheme 1 A plausible mechanism.

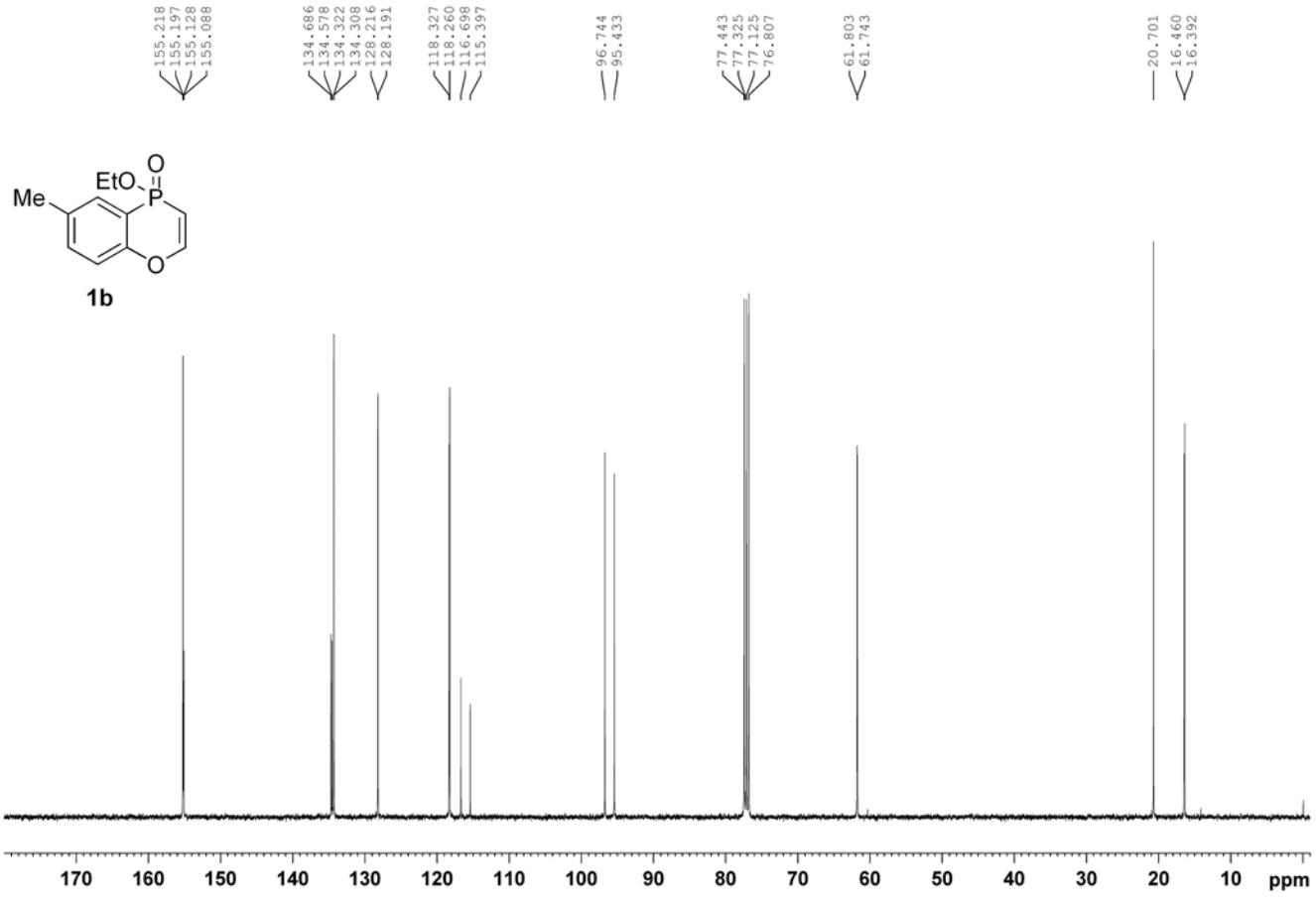
References

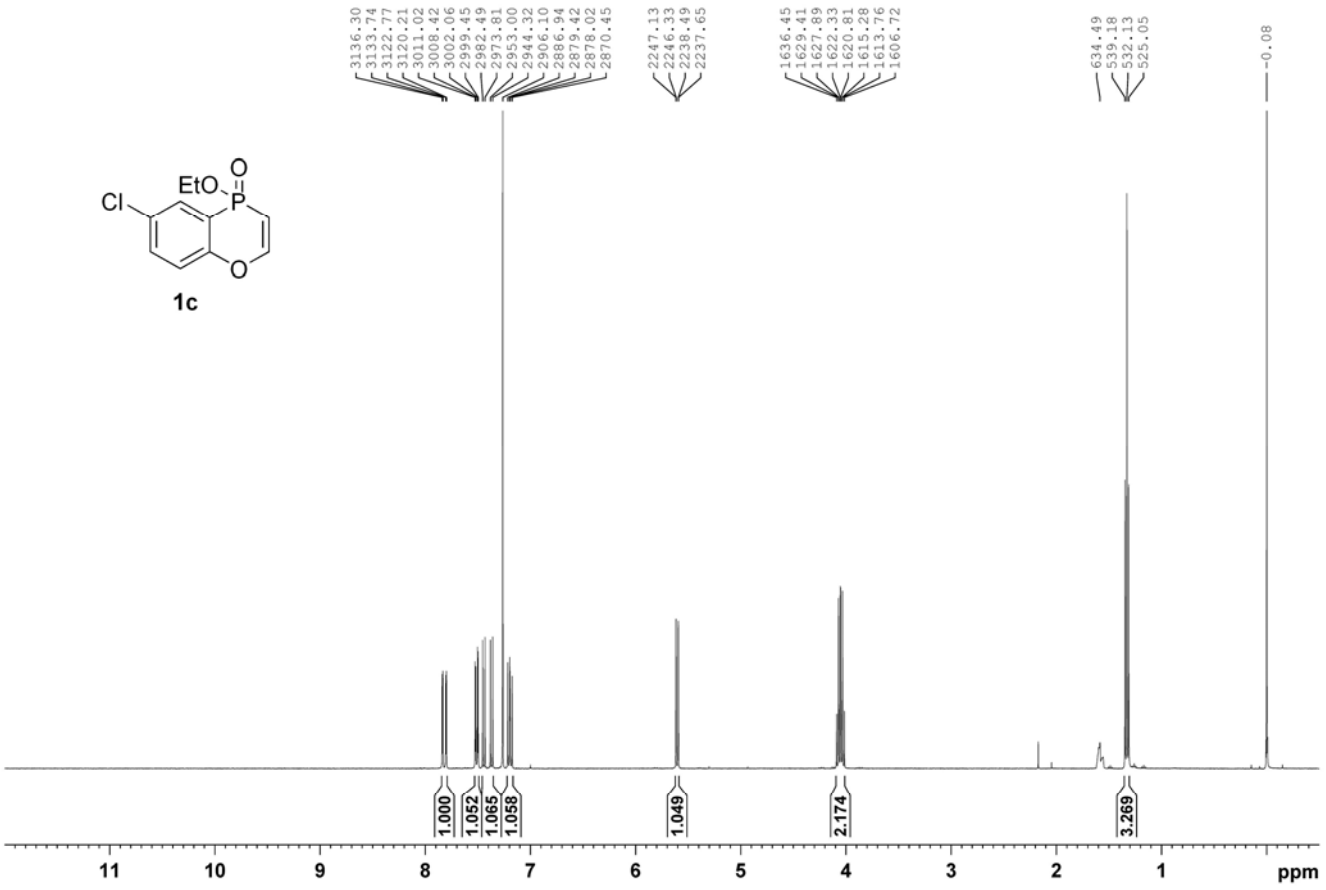
1. (*a*) L. Xie, Y. Ding, Y. Wang and Y.-X. Ding, *Chin. J. Chem.*, 2009, **27**, 1387; (*b*) A.-Y. Peng, Y. Du, Y. Wei, L. Xie and Y.-X. Ding, *Heteroatom. Chem.*, 2011, **22**, 649.
2. L. Xie, J. Ma and Y.-X. Ding, *Tetrahedron Lett.*, 2008, **49**, 847.

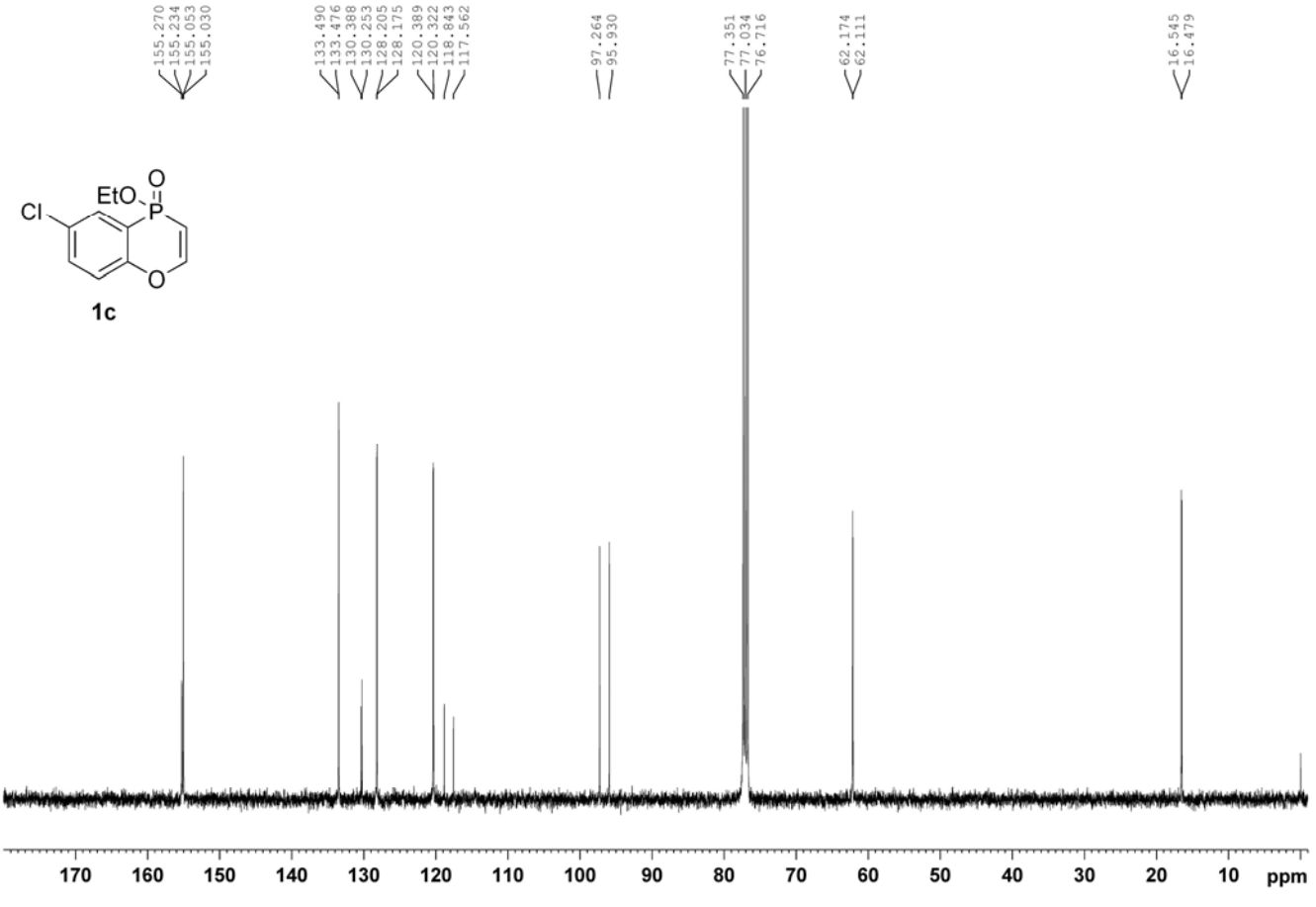

EtO
O
P
O
1a
1.002
1.024
1.059
1.049
1.007
1.000
2.149
3.143
ppm

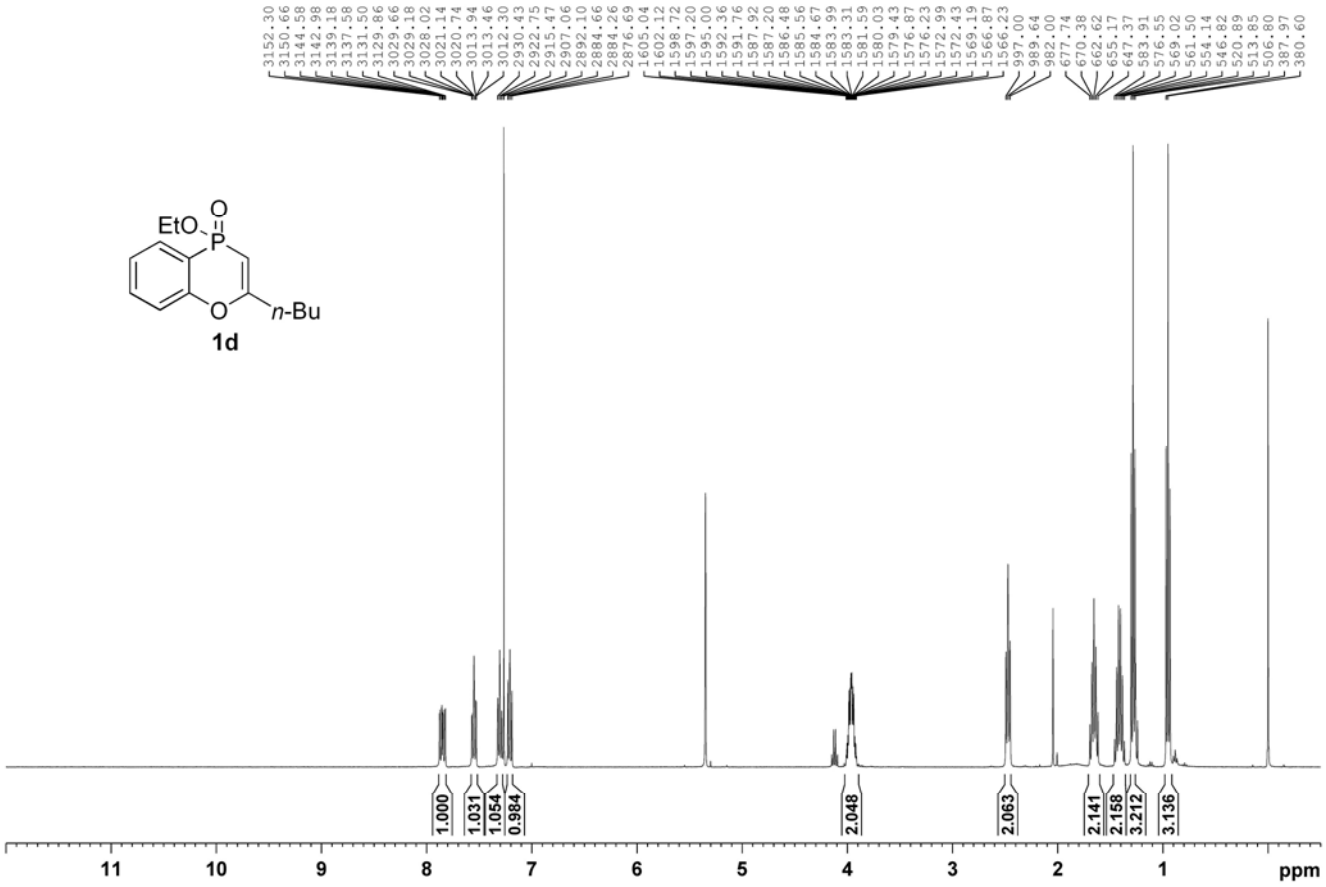

EtO
O
P
O
1a
ppm

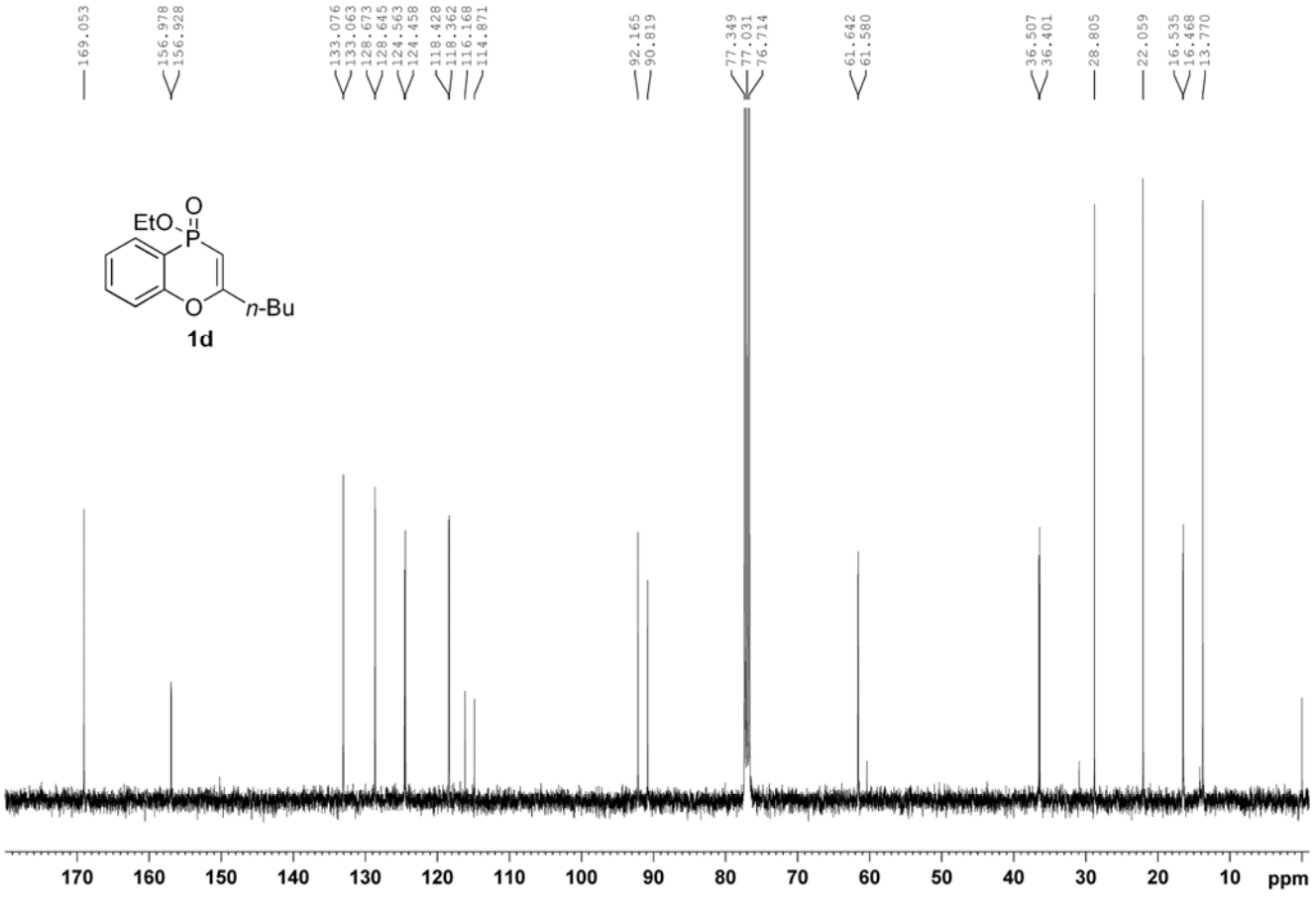

3065.64
3051.99
2985.05
2976.41
2955.68
2951.04
2948.16
2942.68
2929.31
2858.61
2850.81
2842.56
2223.84
2223.68
2215.20
1610.84
1609.04
1608.16
1603.48
1602.36
1595.96
1592.32
1589.72
1588.88
1582.87
1581.51
1576.03
1574.39
1573.55
957.35
527.37
520.33
513.33
0.32
EtO
O
P
Me
O
1b
1.000
2.033
1.004
0.998
2.049
3.093
3.041
11
10
9
8
7
6
5
4
3
2
1
ppm

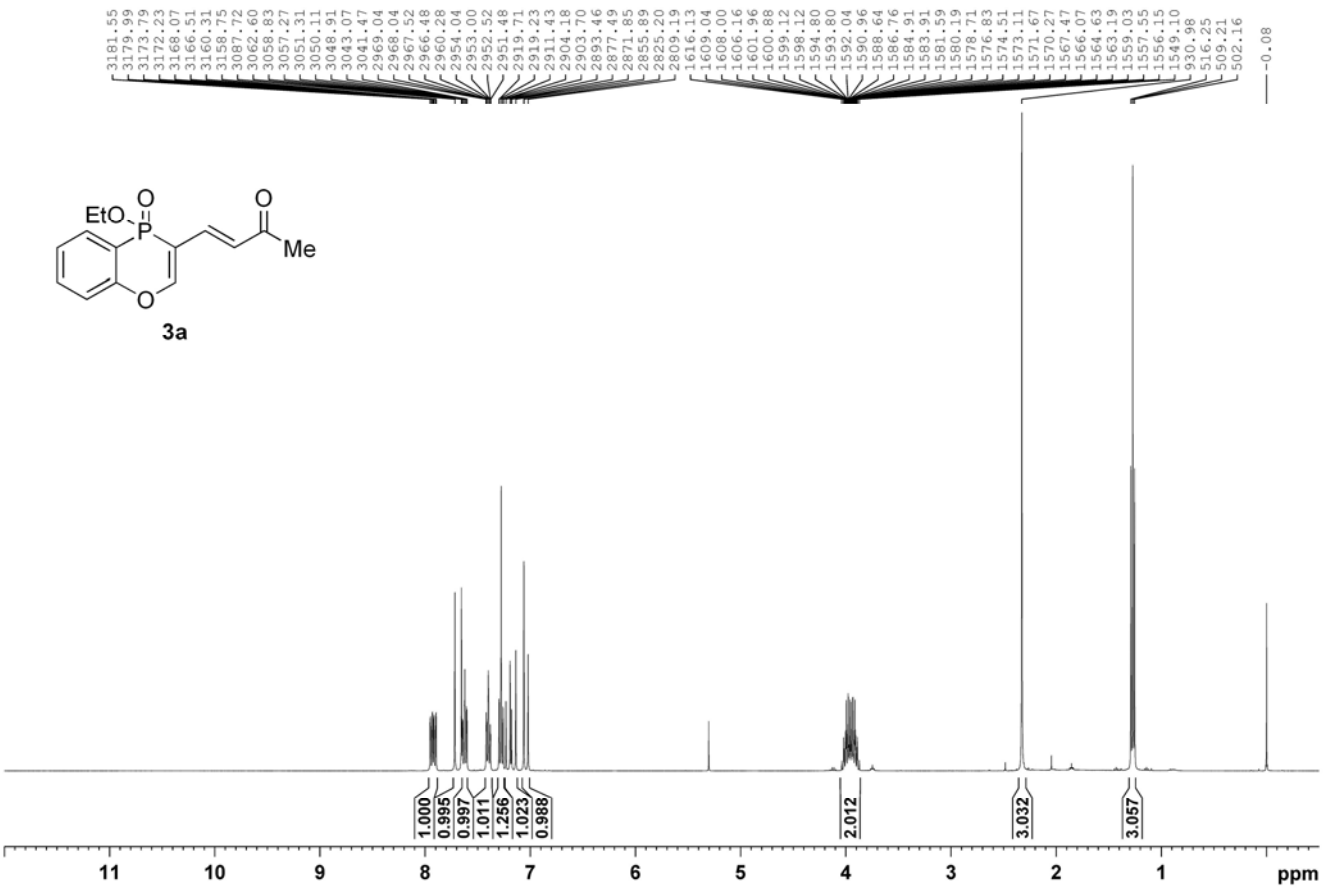

155.218
155.197
155.128
155.088
134.686
134.578
134.322
134.308
128.216
128.191
118.327
118.260
116.698
115.397
96.744
95.433
77.443
77.325
77.125
76.807
61.803
61.743
20.701
16.460
16.392
EtO
O
P
Me
O
1b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

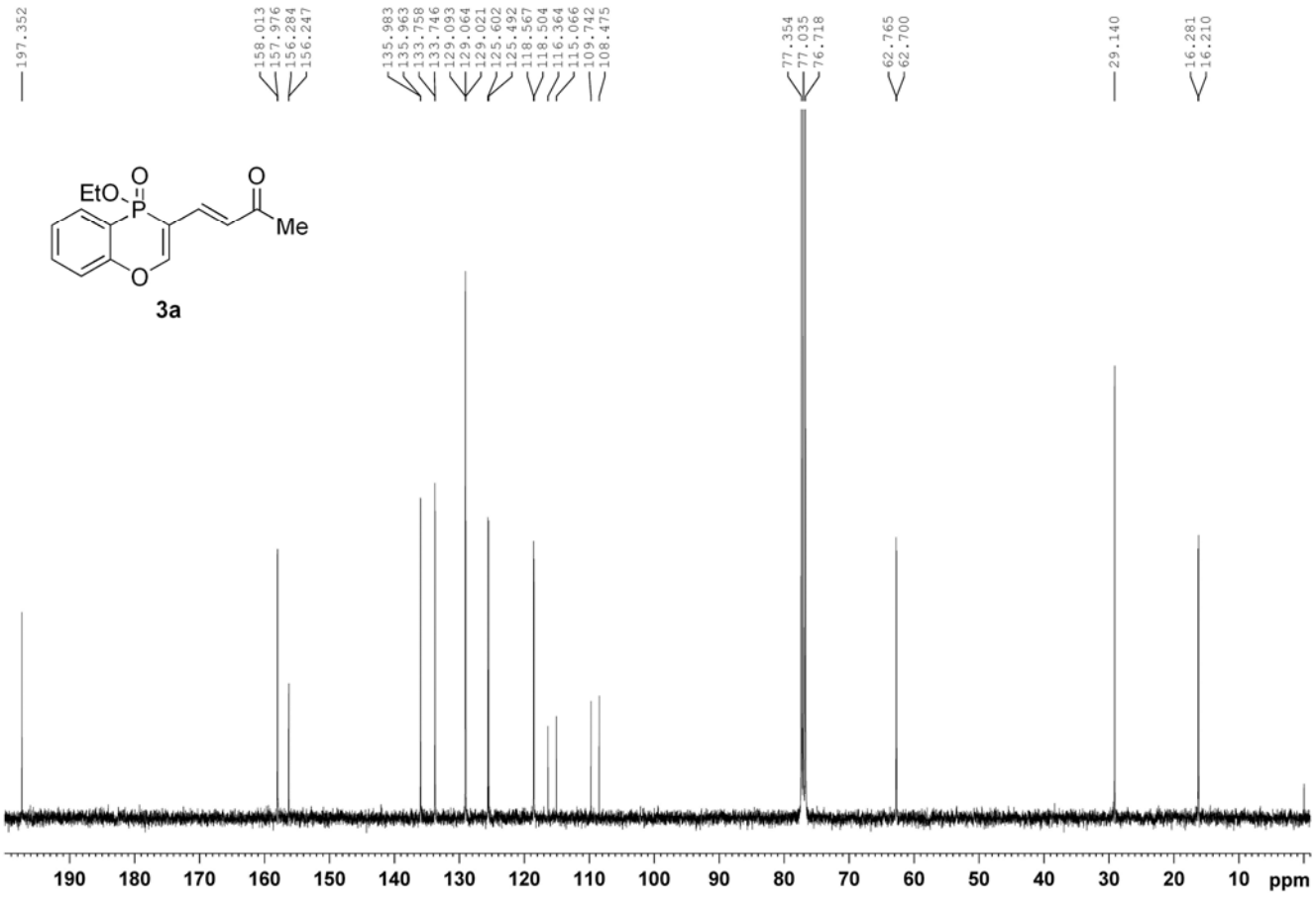

3136.30
3133.74
3122.77
3120.21
3011.02
3008.42
3002.06
2999.45
2982.49
2973.81
2953.00
2944.32
2906.10
2886.94
2879.42
2878.02
2870.45
2247.13
2246.33
2238.49
2237.65
1636.45
1629.41
1627.89
1622.33
1620.81
1615.28
1613.76
1606.72
634.49
539.18
532.13
525.05
-0.08
EtO
O
P
Cl
O
1c
1.000
1.052
1.065
1.058
1.049
2.174
3.269
11
10
9
8
7
6
5
4
3
2
1
ppm

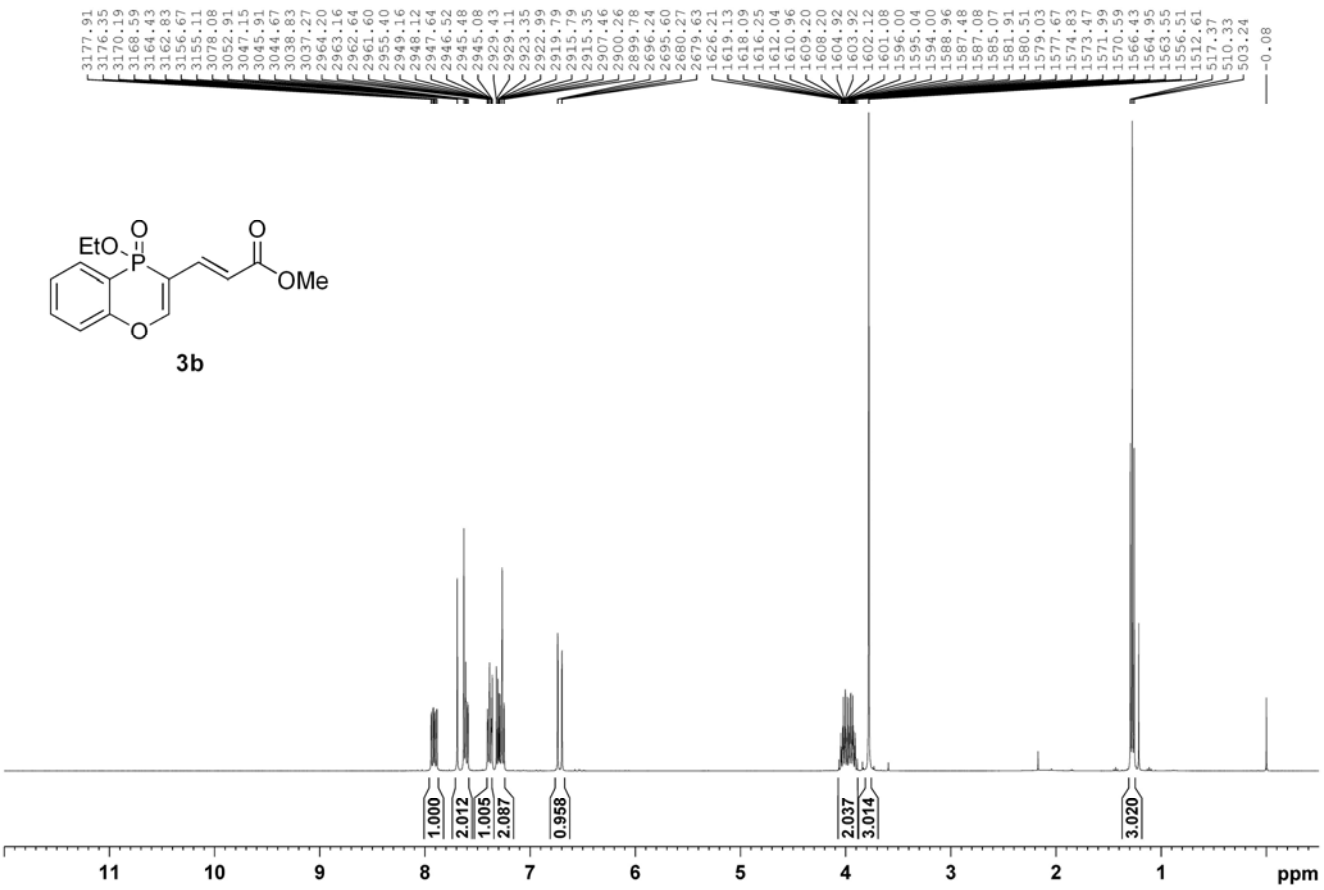

155.270
155.234
155.053
155.030
133.490
133.476
130.388
130.253
128.205
128.175
120.389
120.322
118.843
117.562
97.264
95.930
77.351
77.034
76.716
62.174
62.111
16.545
16.479
EtO
O
P
Cl
O
1c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

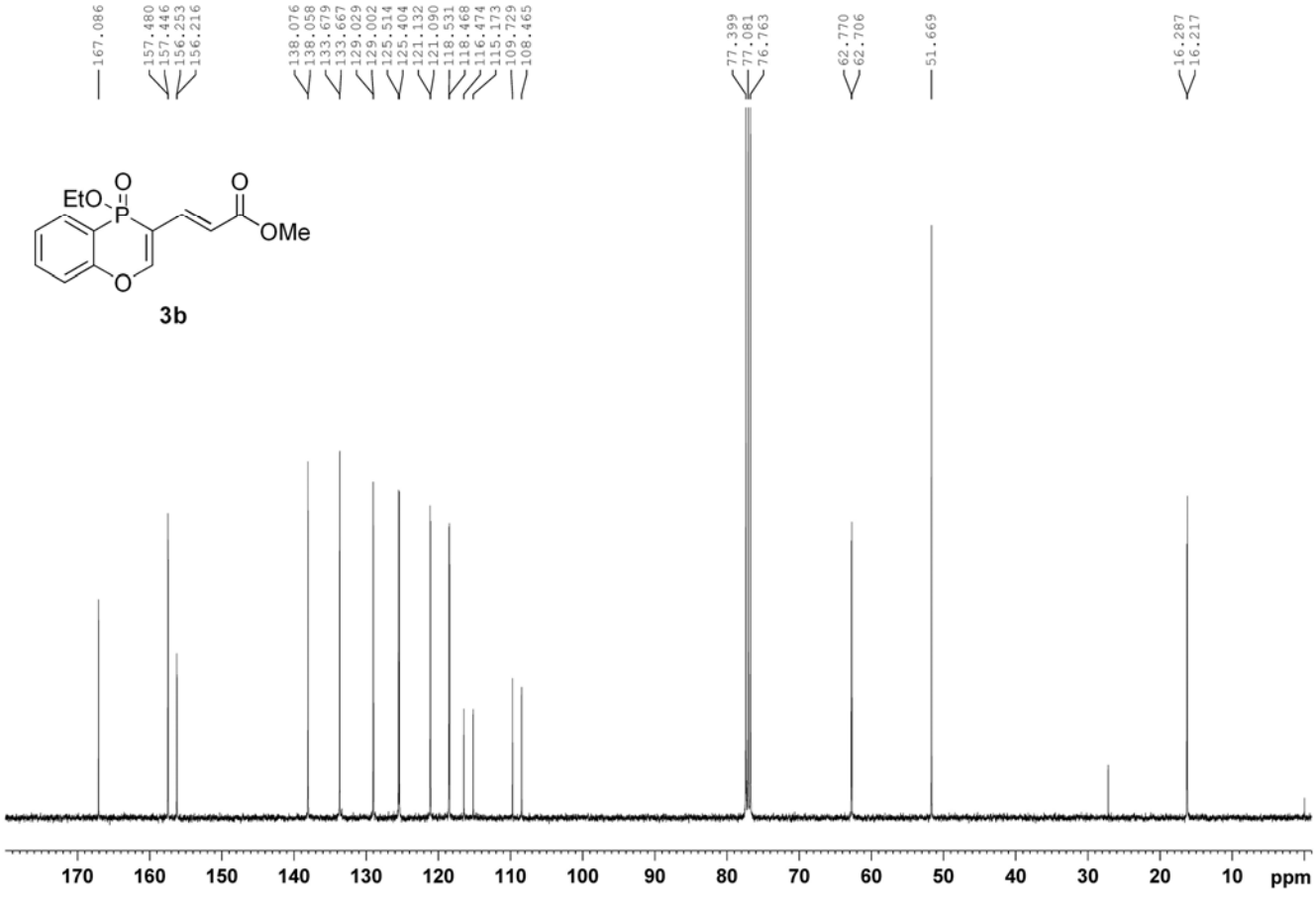

3152.30
3150.66
3144.58
3142.98
3139.18
3137.58
3131.50
3129.86
3029.66
3029.18
3028.02
3021.14
3020.74
3013.94
3013.46
3012.30
2930.43
2922.75
2915.47
2907.06
2892.10
2884.66
2884.26
2876.69
1605.04
1602.12
1598.72
1597.20
1595.00
1592.36
1591.76
1587.92
1587.20
1586.48
1585.56
1584.67
1583.99
1583.31
1581.59
1580.03
1579.43
1576.87
1576.23
1572.99
1572.43
1569.19
1566.87
1566.23
997.00
989.64
982.00
677.74
670.38
662.62
655.17
647.37
583.91
576.55
569.02
561.50
554.14
546.82
520.89
513.85
506.80
387.97
380.60
EtO
O
P
O
n-Bu
1d
1.000
1.031
1.054
0.984
2.048
2.063
2.141
2.158
3.212
3.136
11
10
9
8
7
6
5
4
3
2
1
ppm

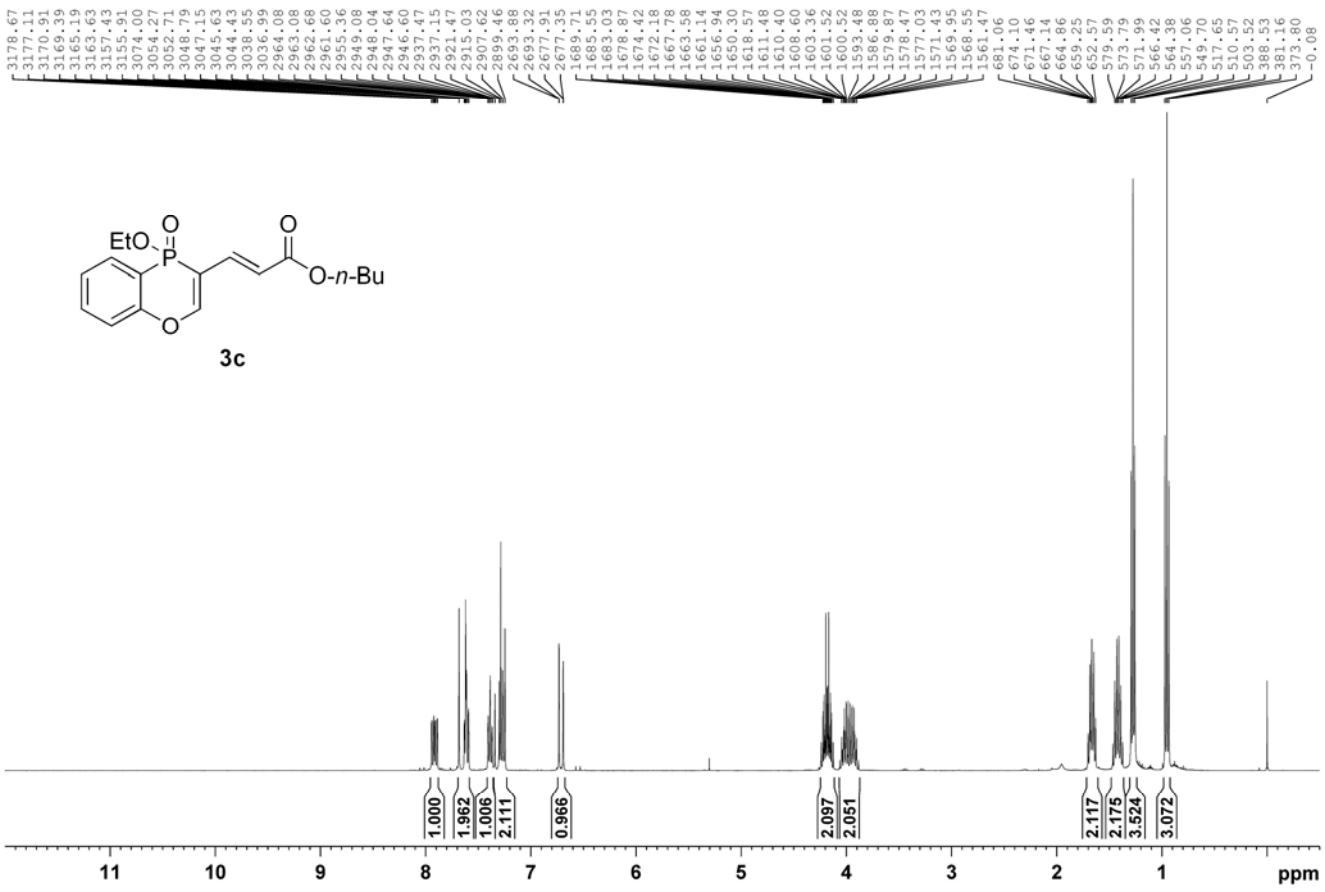

169.053
156.978
156.928
133.076
133.063
128.673
128.645
124.563
124.458
118.428
118.362
116.168
114.871
92.165
90.819
77.349
77.031
76.714
61.642
61.580
36.507
36.401
28.805
22.059
16.535
16.468
13.770
EtO
O
P
O
n-Bu
1d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

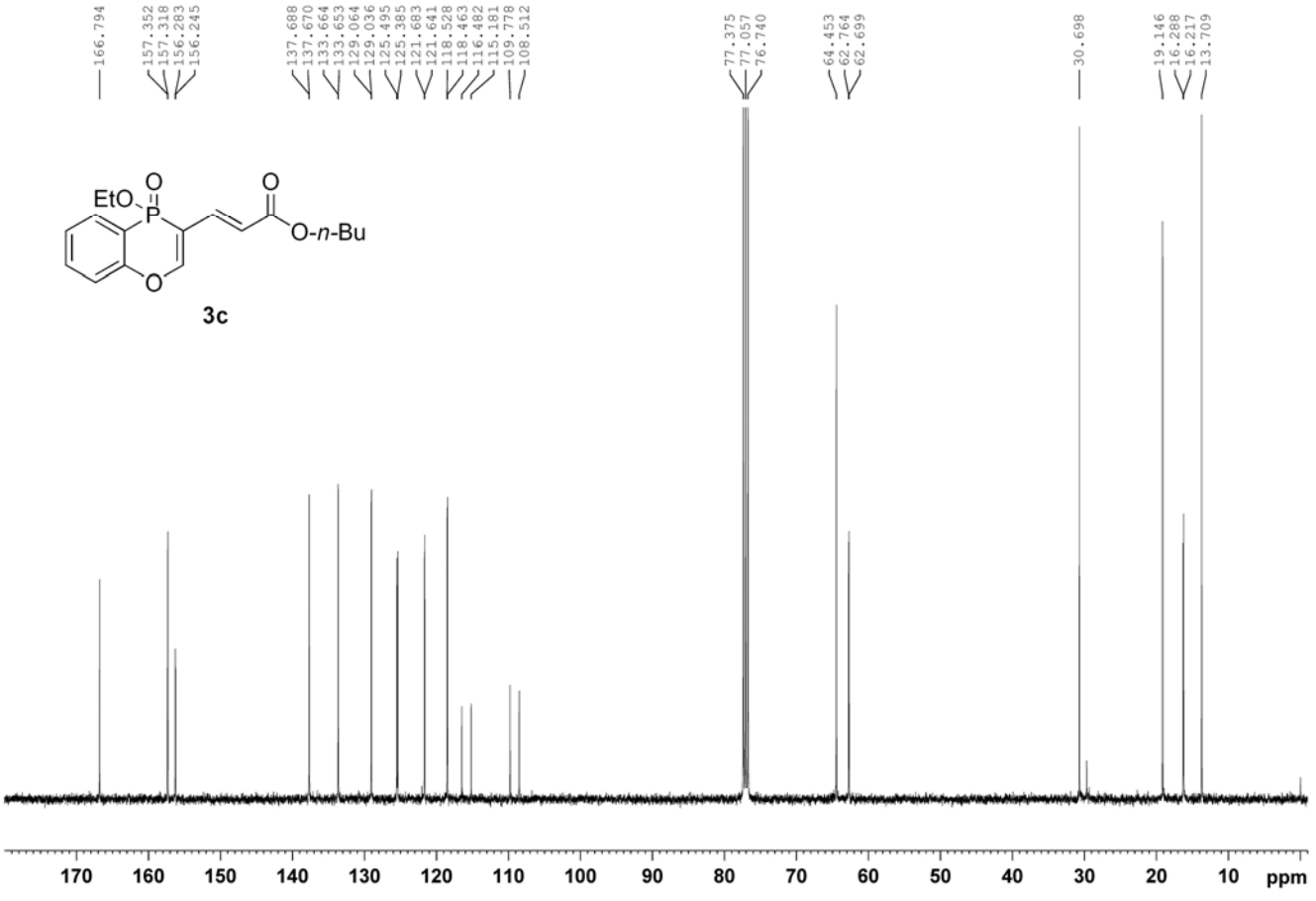

3a
1.000
0.995
0.997
1.011
1.256
1.023
0.988
2.012
3.032
3.057
ppm

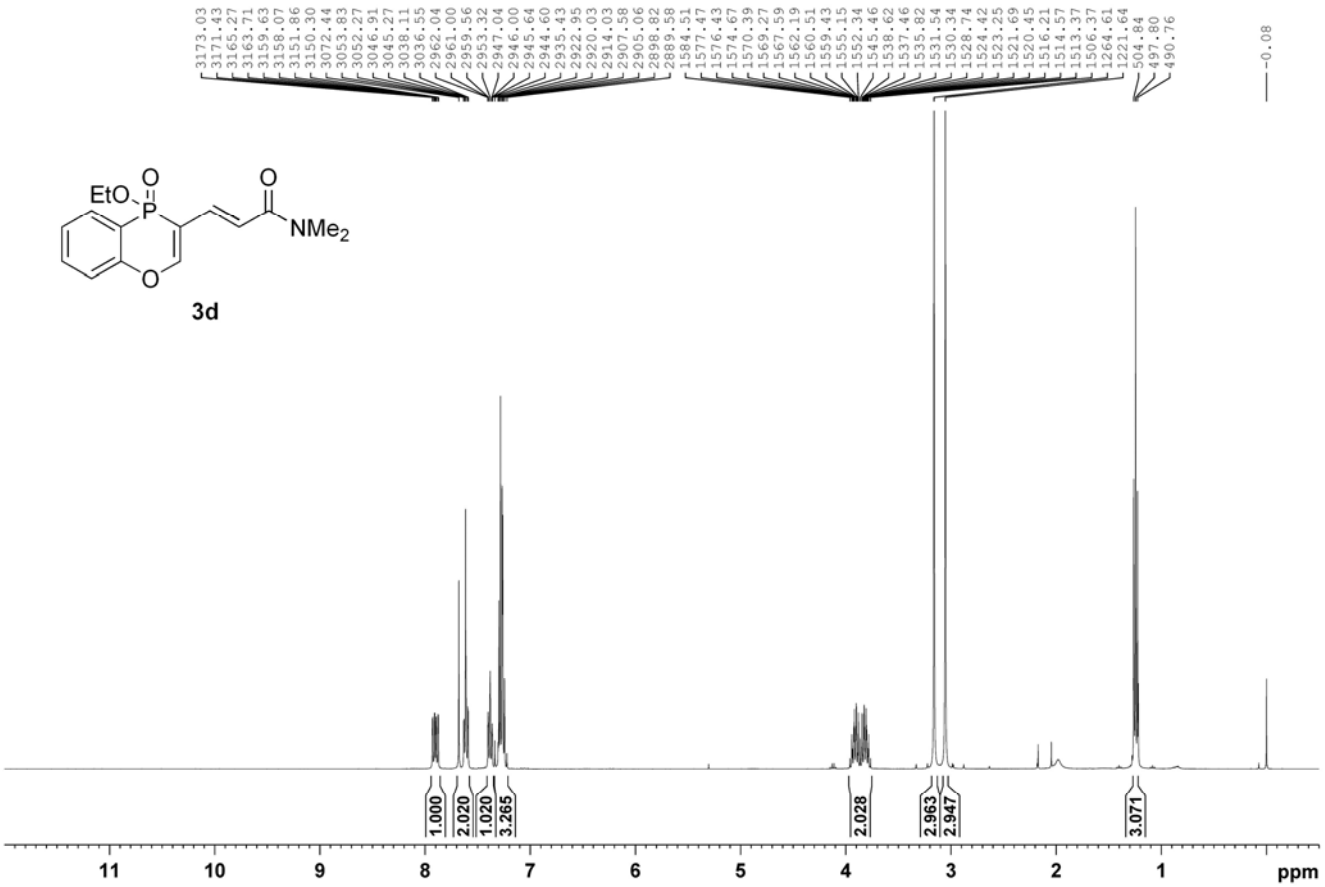

3a
ppm

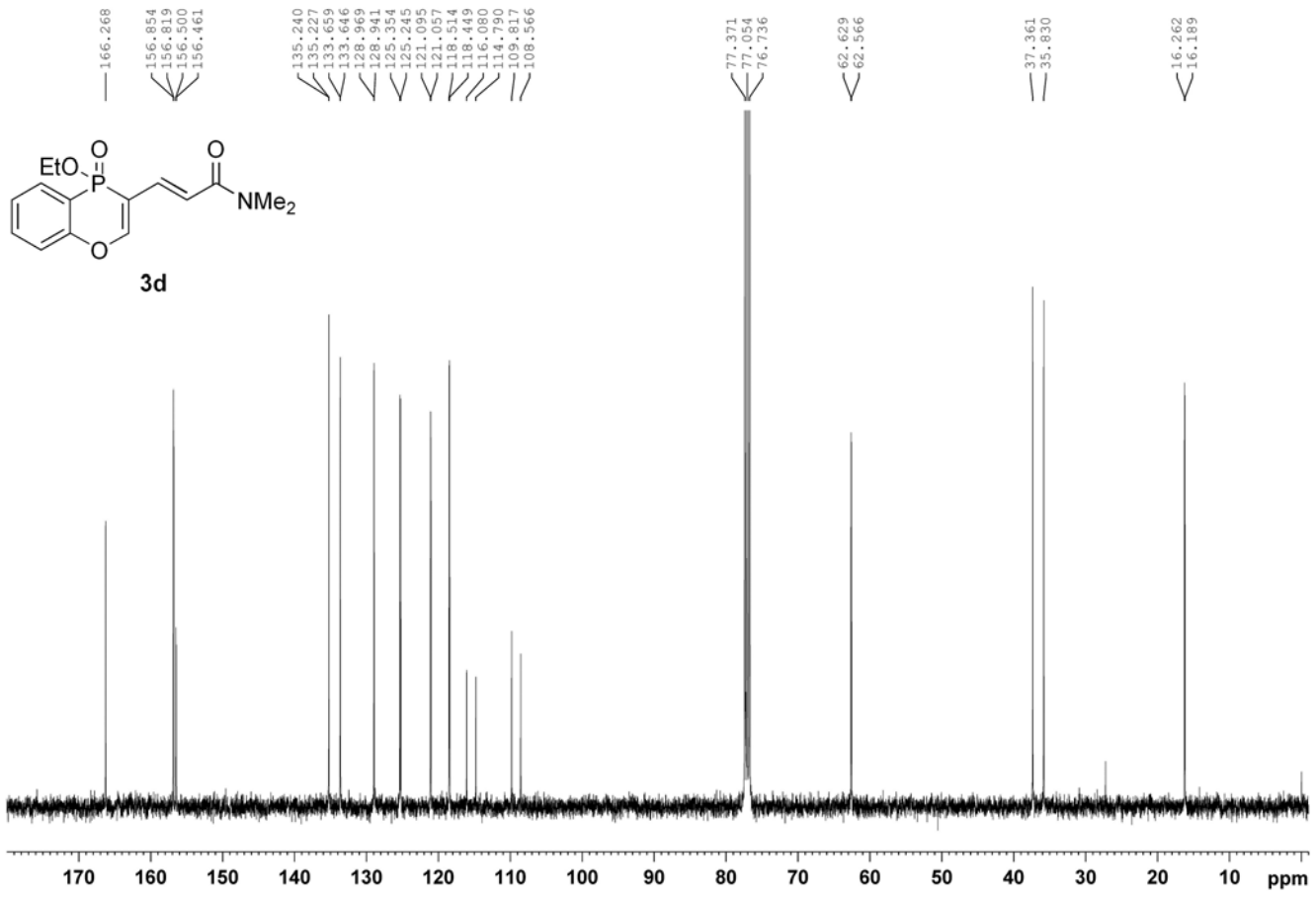

EtO
P
O
O
OMe
O
3b
1.000
2.012
1.005
2.087
0.958
2.037
3.014
3.020
ppm

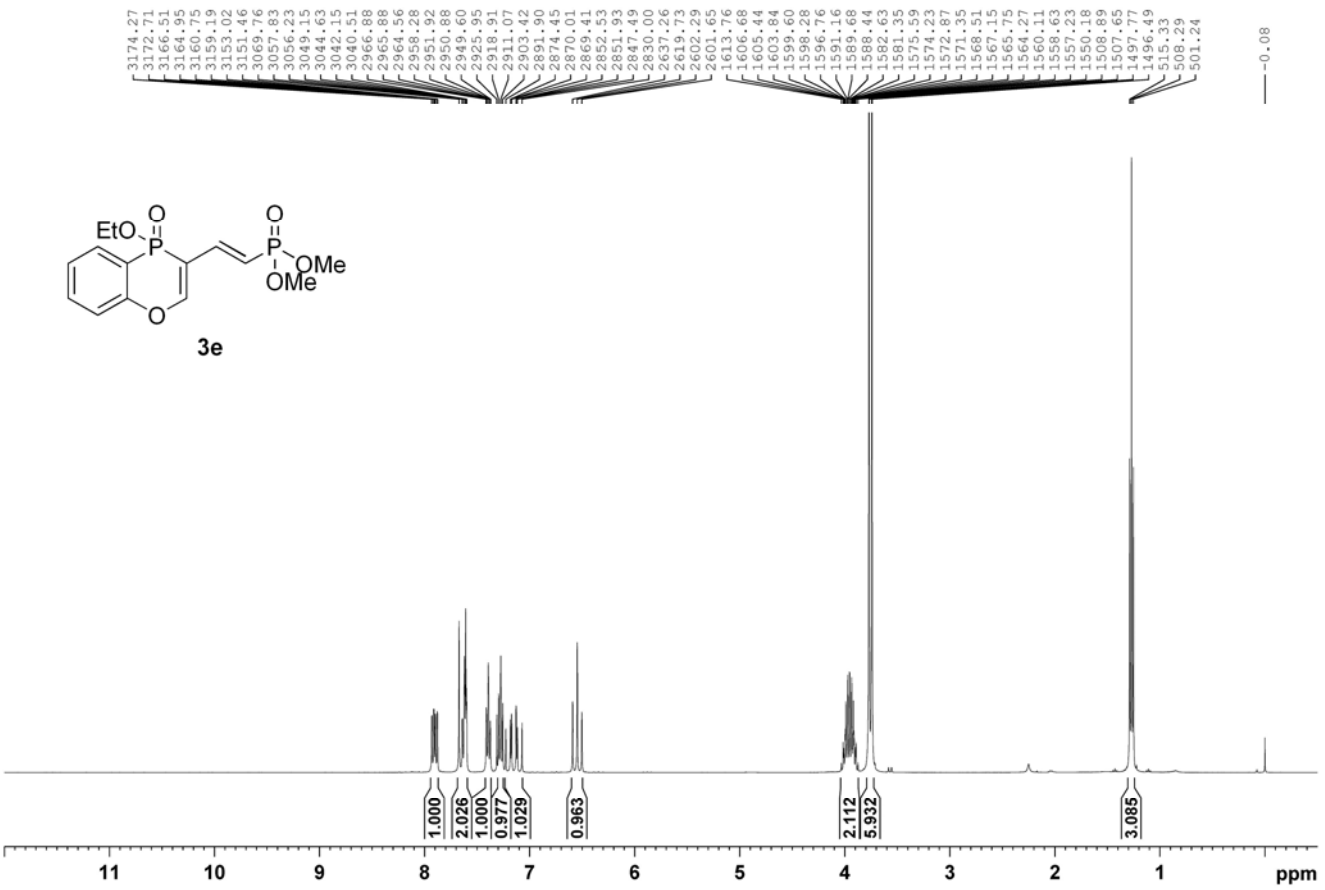

EtO
P
O
O
OMe
O
3b
ppm

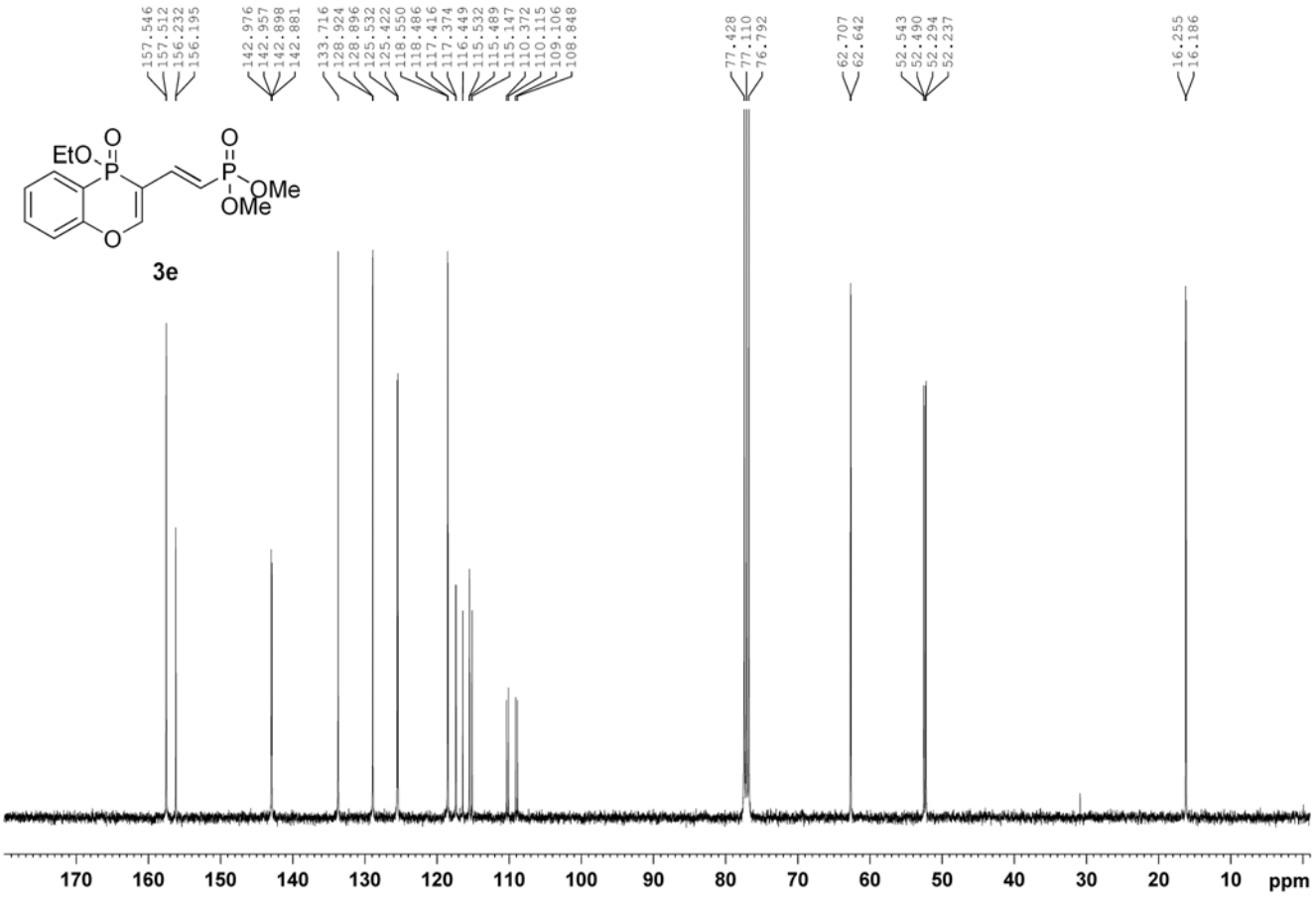

EtO
O
P
O
O
O-n-Bu
O
3c
1.000
1.962
1.006
2.111
0.966
2.097
2.051
2.117
2.175
3.524
3.072
ppm

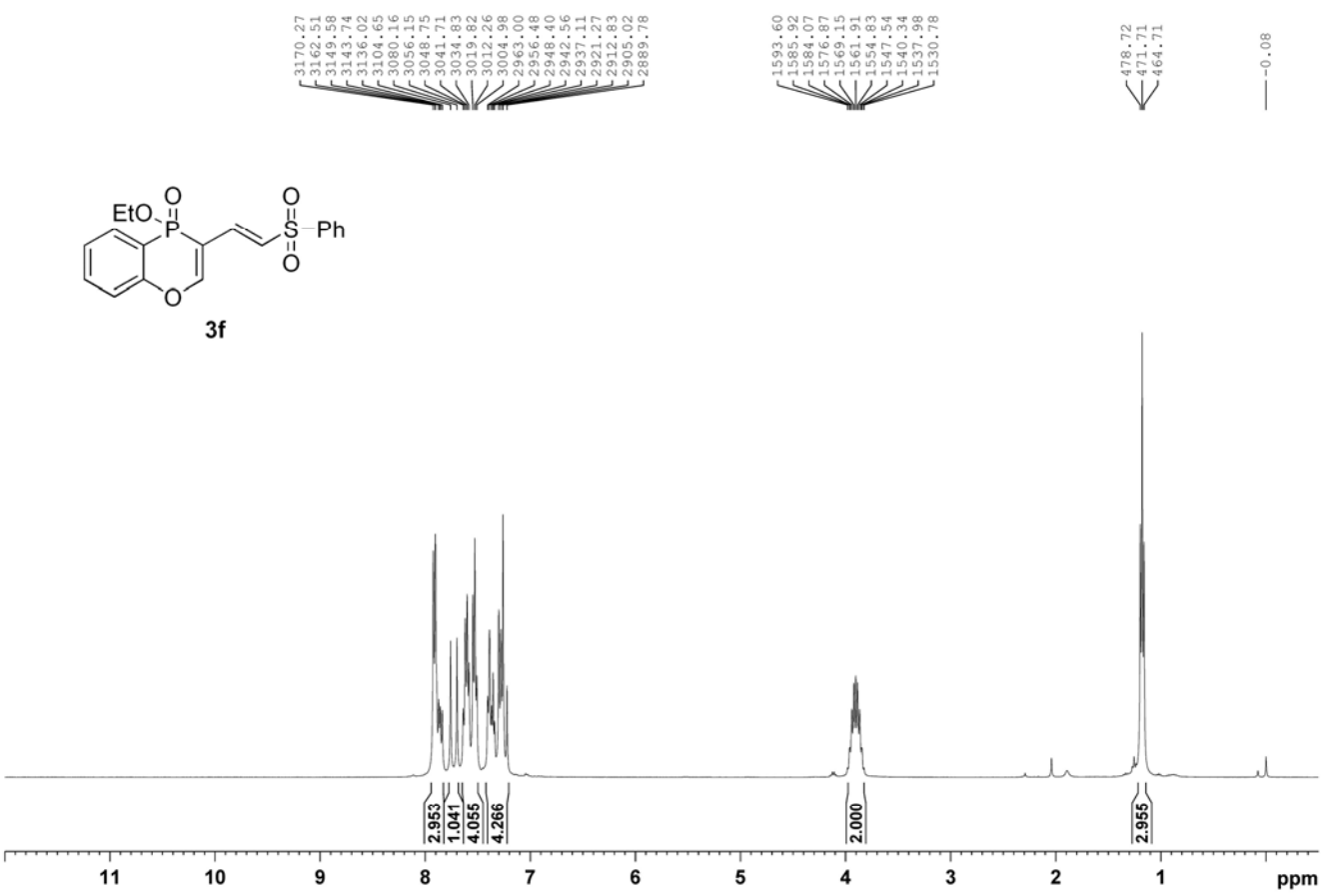

EtO
O
P
O
O
O-n-Bu
O
3c
ppm

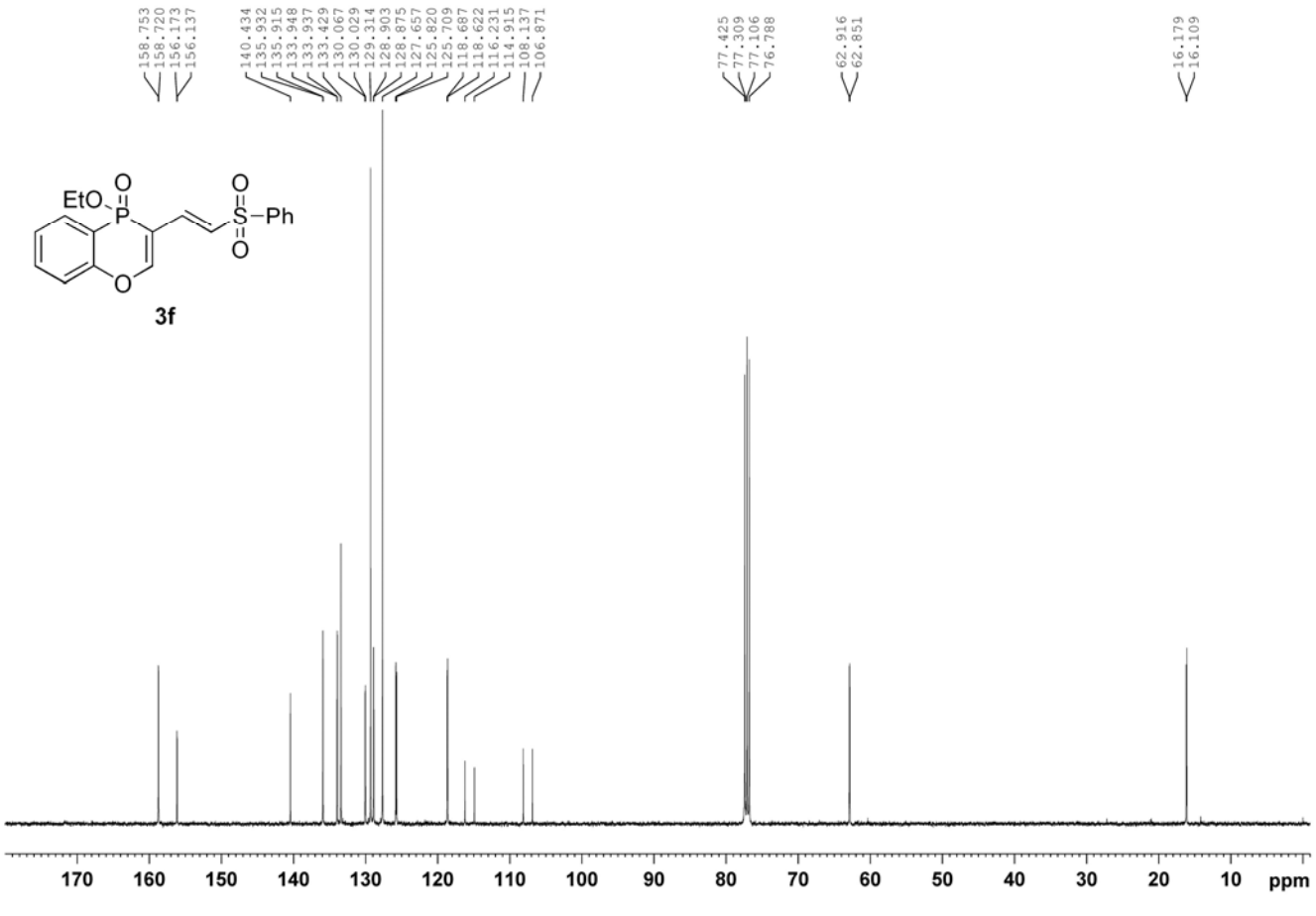

3d
1.000
2.020
1.020
3.265
2.028
2.963
2.947
3.071
ppm

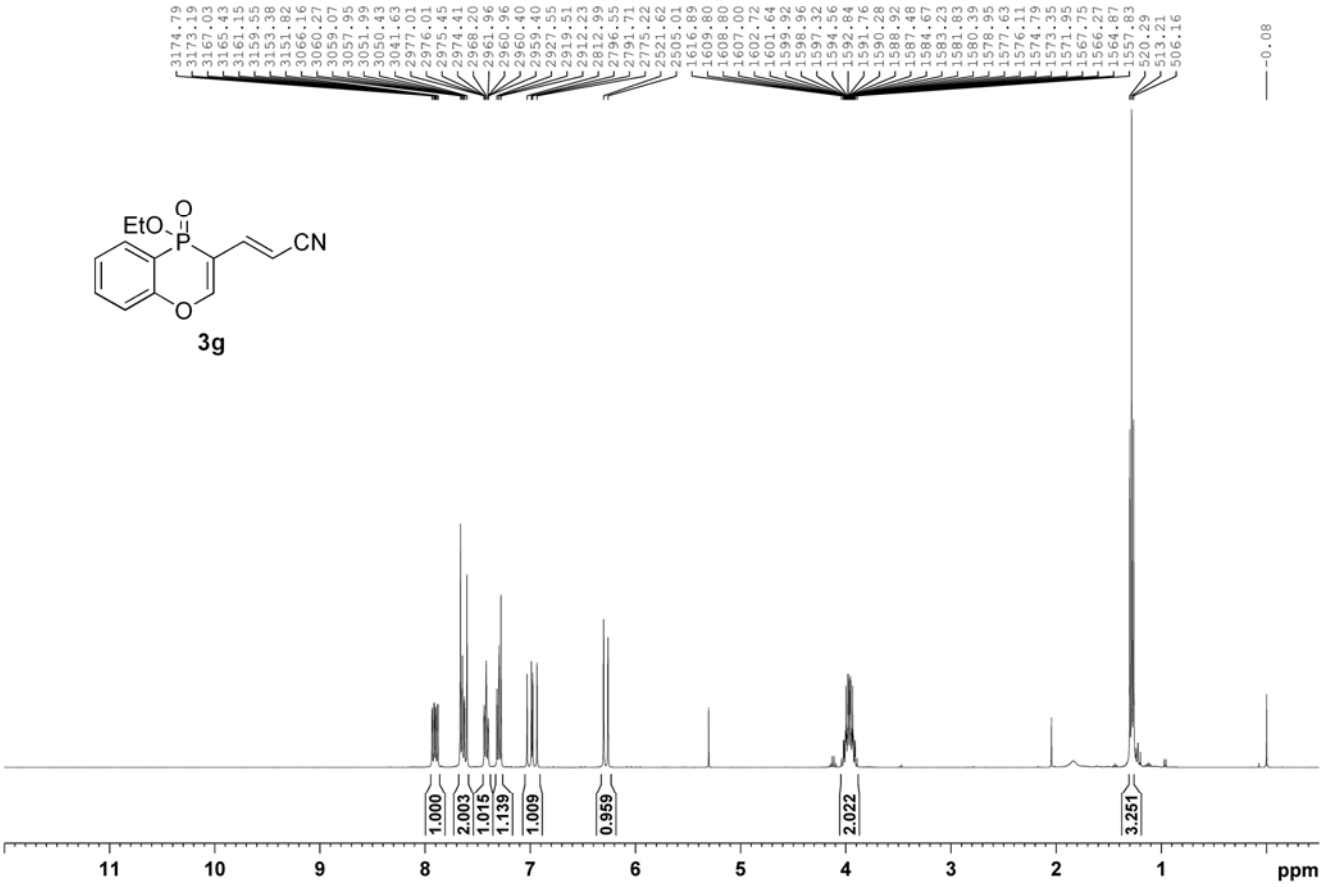

3d
ppm

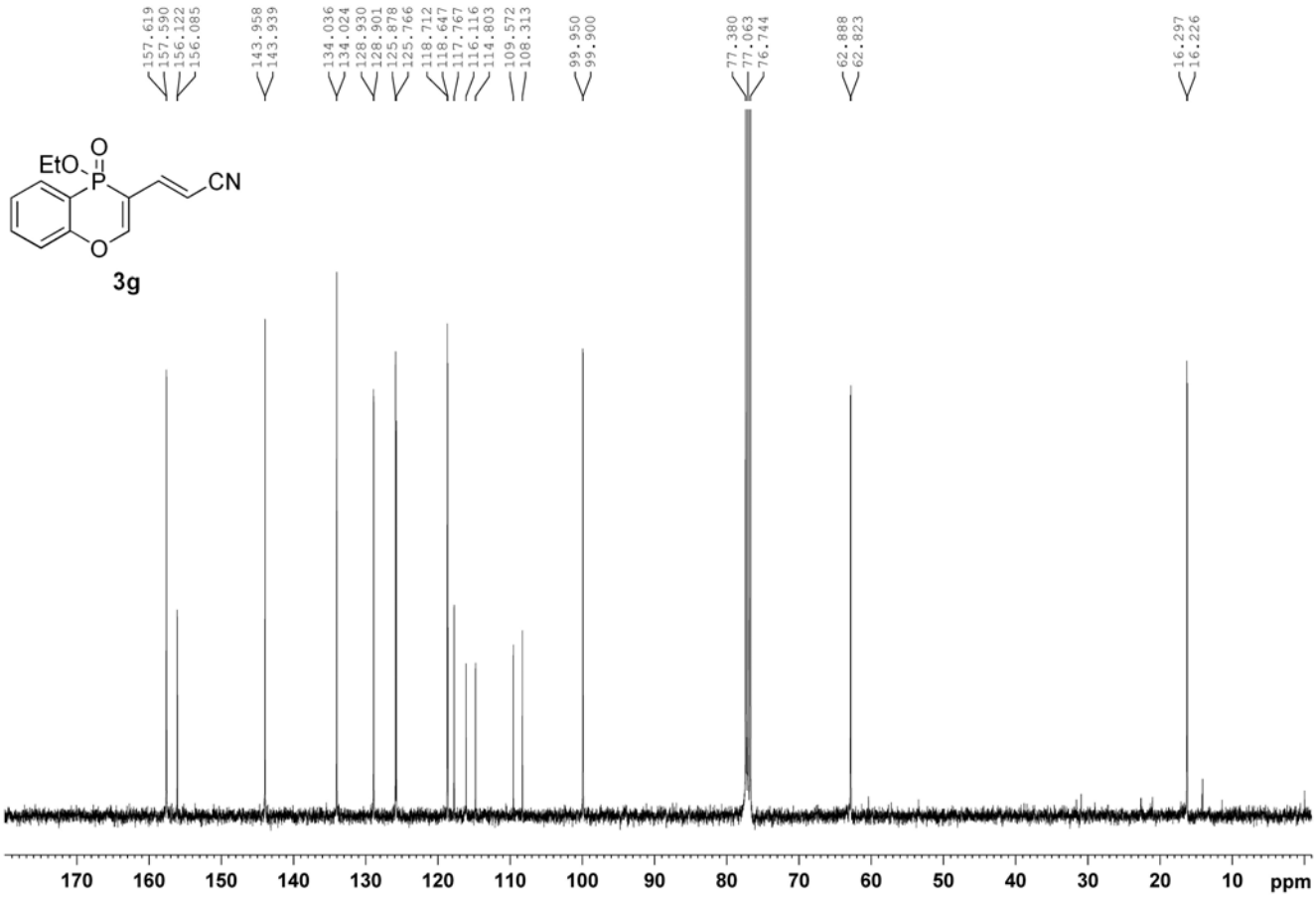

3174.27
3172.71
3166.51
3164.95
3160.75
3159.19
3153.02
3151.46
3069.76
3057.83
3056.23
3049.15
3044.63
3042.15
3040.51
2966.88
2965.88
2964.56
2958.28
2951.92
2950.88
2949.60
2925.95
2918.91
2911.07
2903.42
2891.90
2874.45
2870.01
2869.41
2852.53
2851.93
2847.49
2830.00
2637.26
2619.73
2602.29
2601.65
1613.76
1606.68
1605.44
1603.84
1599.60
1598.28
1596.76
1591.16
1589.68
1588.44
1582.63
1581.35
1575.59
1574.23
1572.87
1571.35
1568.51
1567.15
1565.75
1564.27
1560.11
1558.63
1557.23
1550.18
1508.89
1507.65
1497.77
1496.49
515.33
508.29
501.24
-0.08
EtO
O
P
O
P
OMe
OMe
O
3e
1.000
2.026
1.000
0.977
1.029
0.963
2.112
5.932
3.085
11
10
9
8
7
6
5
4
3
2
1
ppm

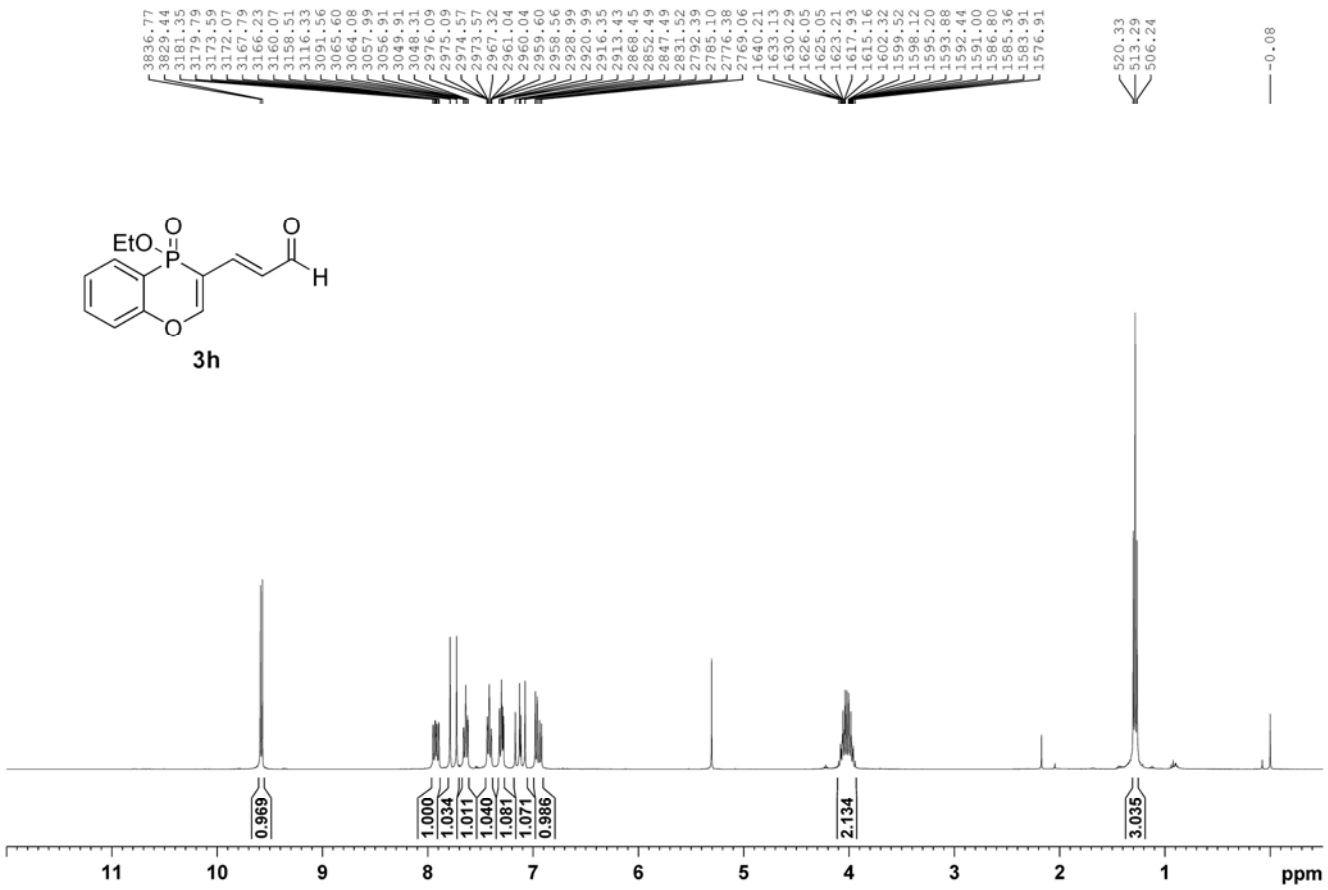

157.546
157.512
156.232
156.195
142.976
142.957
142.898
142.881
133.716
128.924
128.896
125.532
125.422
118.550
118.486
117.416
117.374
116.449
115.532
115.489
115.147
110.372
110.115
109.106
108.848
77.428
77.110
76.792
62.707
62.642
52.543
52.490
52.294
52.237
16.255
16.186
EtO
O
P
O
P
OMe
OMe
O
3e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

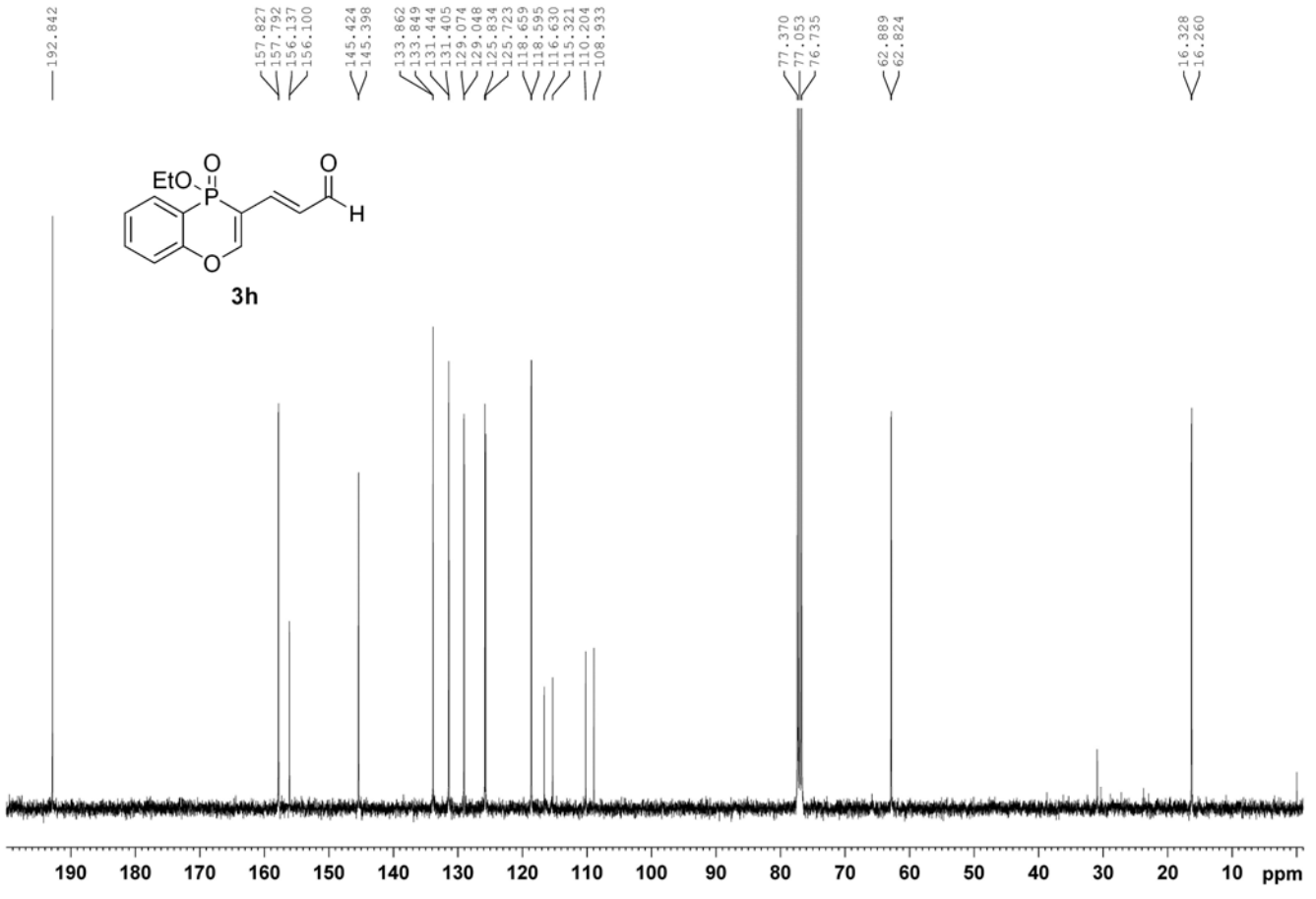

3170.27
3162.51
3149.58
3143.74
3136.02
3104.65
3080.16
3056.15
3048.75
3041.71
3034.83
3019.82
3012.26
3004.98
2963.00
2956.48
2948.40
2942.56
2937.11
2921.27
2912.83
2905.02
2889.78
1593.60
1585.92
1584.07
1576.87
1569.15
1561.91
1554.83
1547.54
1540.34
1537.98
1530.78
478.72
471.71
464.71
-0.08
EtO
O
P
O
O
S
Ph
O
O
3f
2.953
1.041
4.055
4.266
2.000
2.955
11
10
9
8
7
6
5
4
3
2
1
ppm

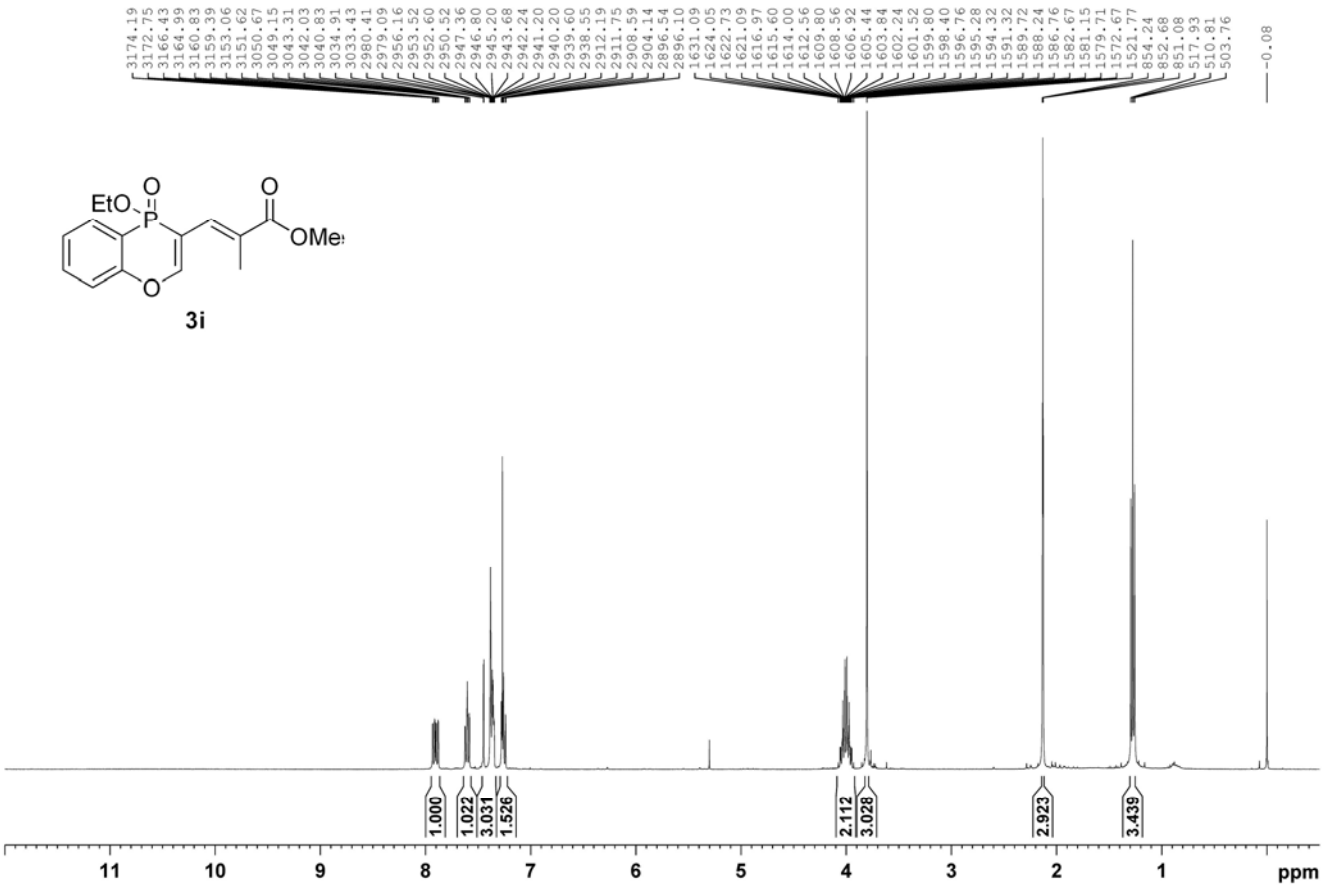

158.753
158.720
156.173
156.137
140.434
135.932
135.915
133.948
133.937
133.429
130.067
130.029
129.314
128.903
128.875
127.657
125.820
125.709
118.687
118.622
116.231
114.915
108.137
106.871
77.425
77.309
77.106
76.788
62.916
62.851
16.179
16.109
EtO
O
P
O
O
S
Ph
O
O
3f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

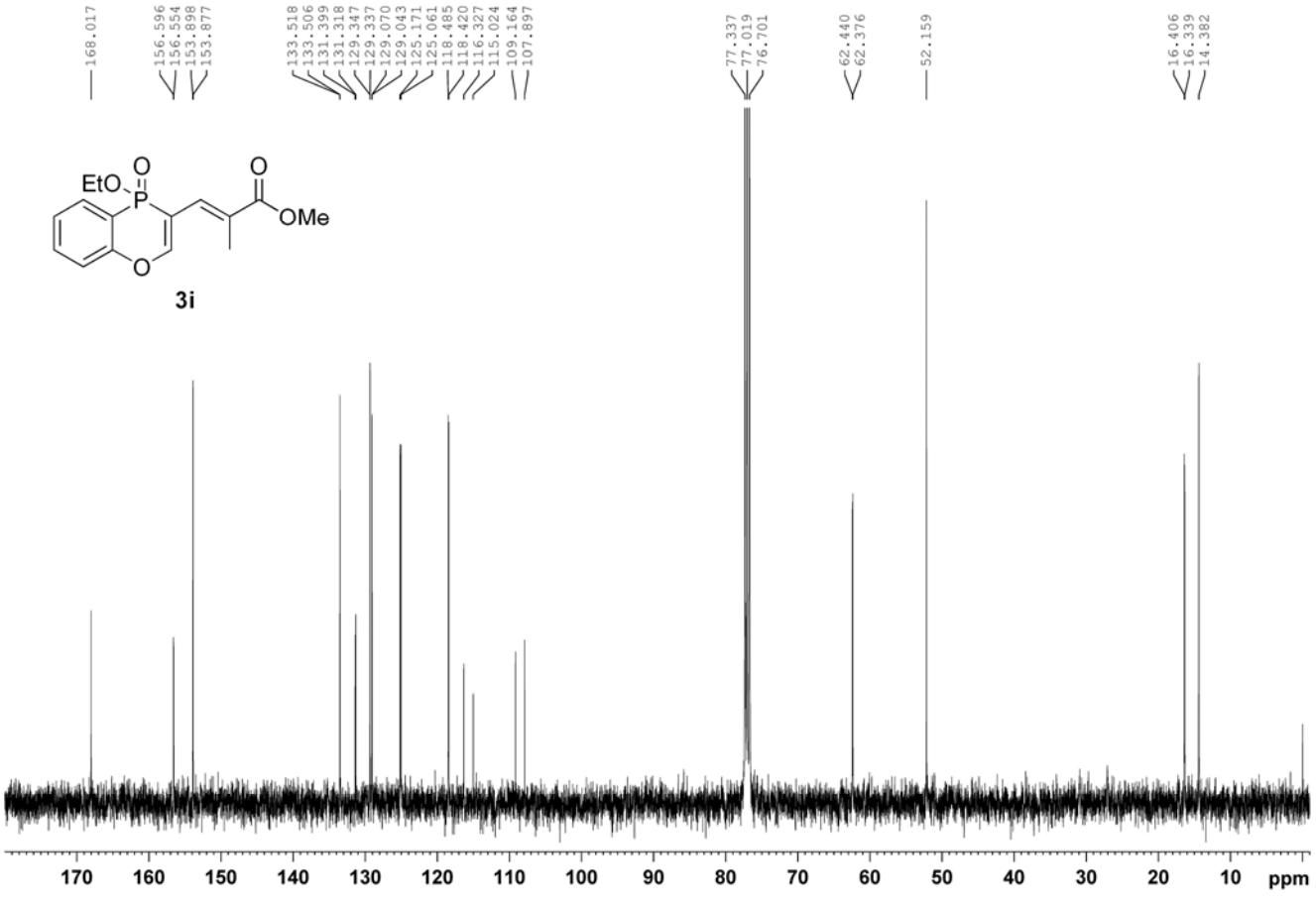

3174.79
3173.19
3167.03
3165.43
3161.15
3159.55
3153.38
3151.82
3066.16
3060.27
3059.07
3057.95
3051.99
3050.43
3041.63
2977.01
2976.01
2975.45
2974.41
2968.20
2961.96
2960.96
2960.40
2959.40
2927.55
2919.51
2912.23
2812.99
2796.55
2791.71
2775.22
2521.62
2505.01
1616.89
1609.80
1608.80
1607.00
1602.72
1601.64
1599.92
1598.96
1597.32
1594.56
1592.84
1591.76
1590.28
1588.92
1587.48
1584.67
1583.23
1581.83
1580.39
1578.95
1577.63
1576.11
1574.79
1573.35
1571.95
1567.75
1566.27
1564.87
1557.83
520.29
513.21
506.16
-0.08
EtO
O
P
CN
O
3g
1.000
2.003
1.015
1.139
1.009
0.959
2.022
3.251
11
10
9
8
7
6
5
4
3
2
1
ppm

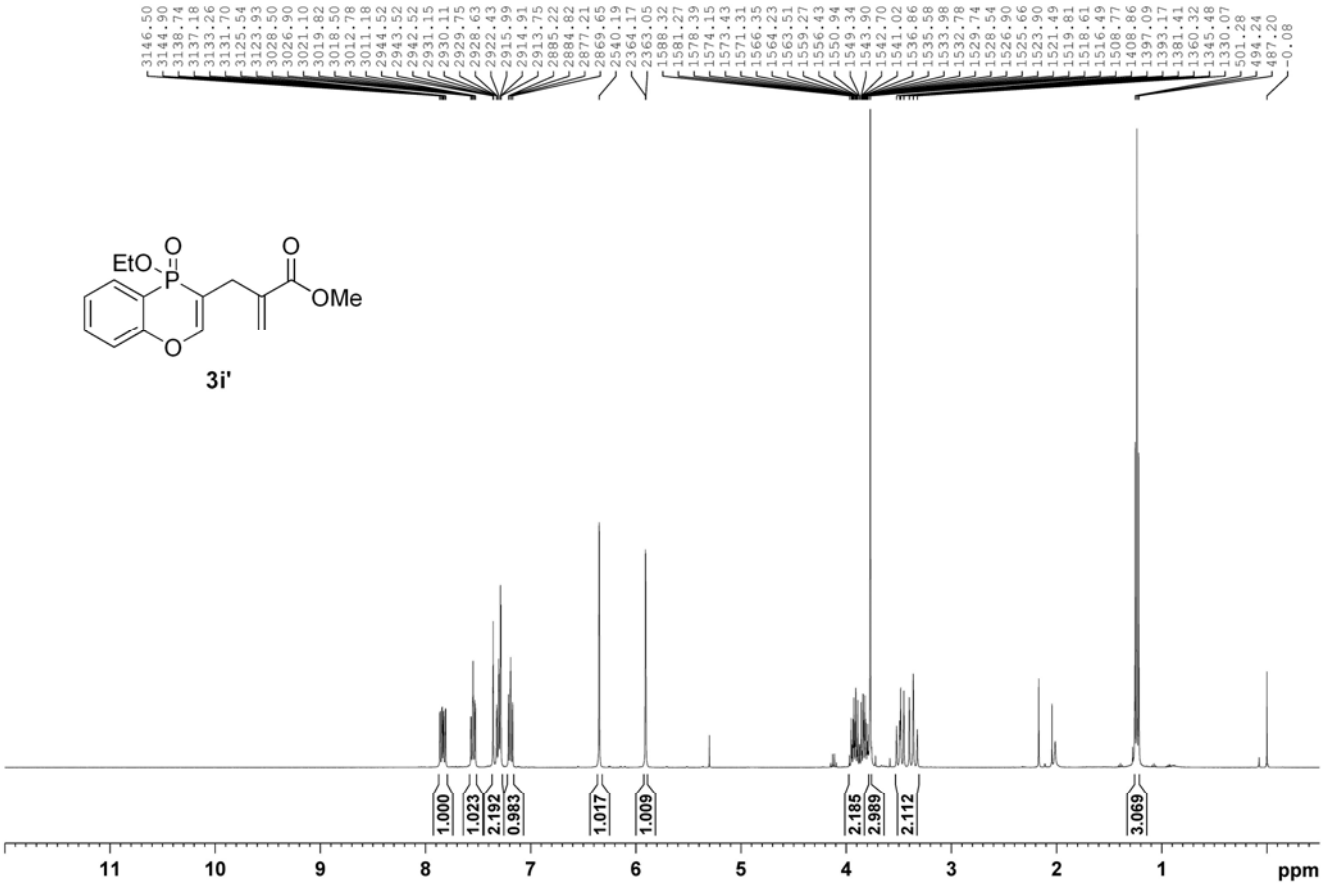

157.619
157.590
156.122
156.085
143.958
143.939
134.036
134.024
128.930
128.901
125.878
125.766
118.712
118.647
117.767
116.116
114.803
109.572
108.313
99.950
99.900
77.380
77.063
76.744
62.888
62.823
16.297
16.226
EtO
O
P
CN
O
3g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

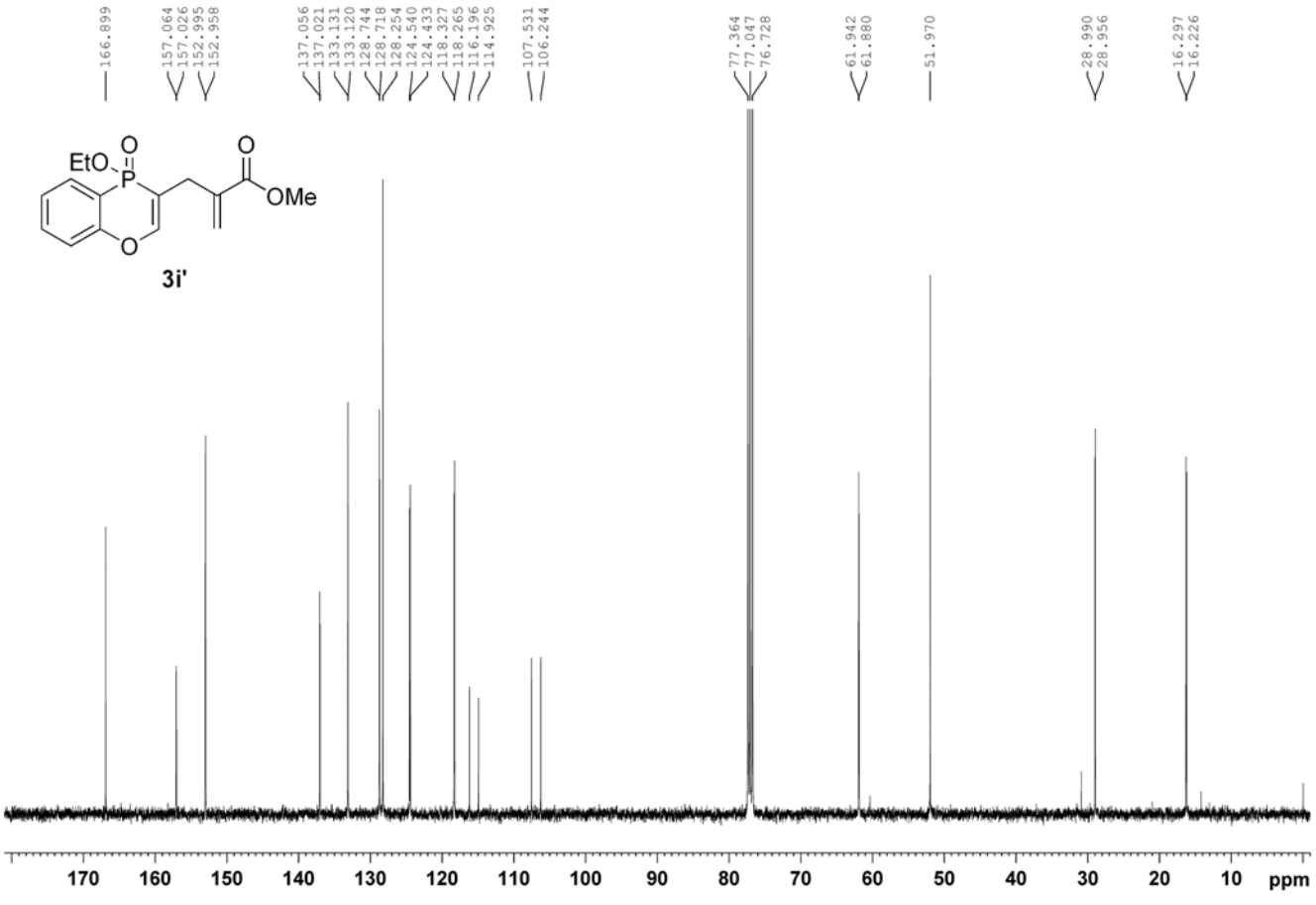

3836.77
3829.44
3181.35
3179.79
3173.59
3172.07
3167.79
3166.23
3160.07
3158.51
3116.33
3091.56
3065.60
3064.08
3057.99
3056.91
3049.91
3048.31
2976.09
2975.09
2974.57
2973.57
2967.32
2961.04
2960.04
2959.60
2958.56
2928.99
2920.99
2916.35
2913.43
2868.45
2852.49
2847.49
2831.52
2792.39
2785.10
2776.38
2769.06
1640.21
1633.13
1630.29
1626.05
1625.05
1623.21
1617.93
1615.16
1602.32
1599.52
1598.12
1595.20
1593.88
1592.44
1591.00
1586.80
1585.36
1583.91
1576.91
520.33
513.29
506.24
-0.08
EtO
O
P
O
O
H
O
3h
0.969
1.000
1.034
1.011
1.040
1.081
1.071
0.986
2.134
3.035
11
10
9
8
7
6
5
4
3
2
1
ppm

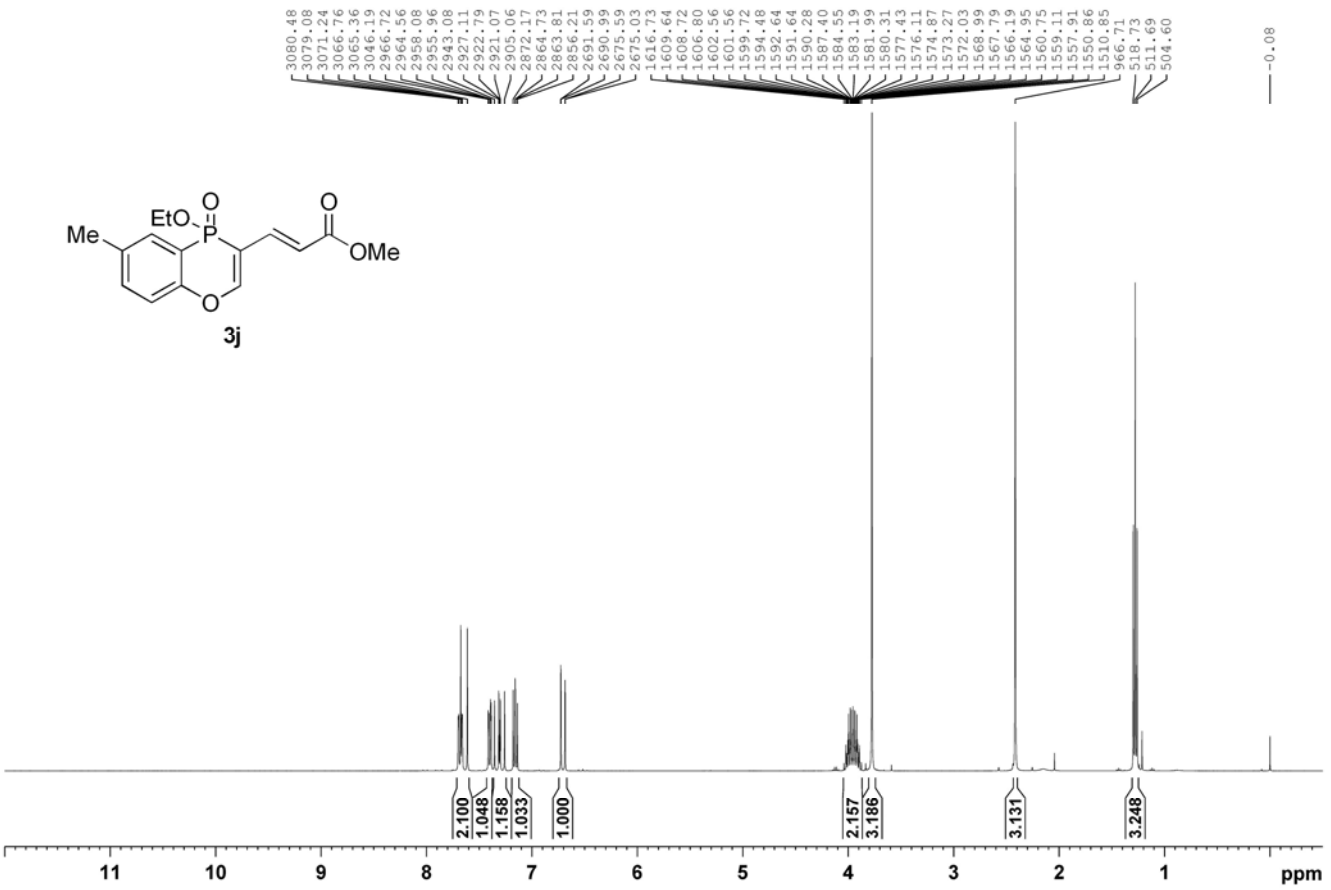

192.842
157.827
157.792
156.137
156.100
145.424
145.398
133.862
133.849
131.444
131.405
129.074
129.048
125.834
125.723
118.659
118.595
116.630
115.321
110.204
108.933
77.370
77.053
76.735
62.889
62.824
16.328
16.260
EtO
O
P
O
O
H
O
3h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

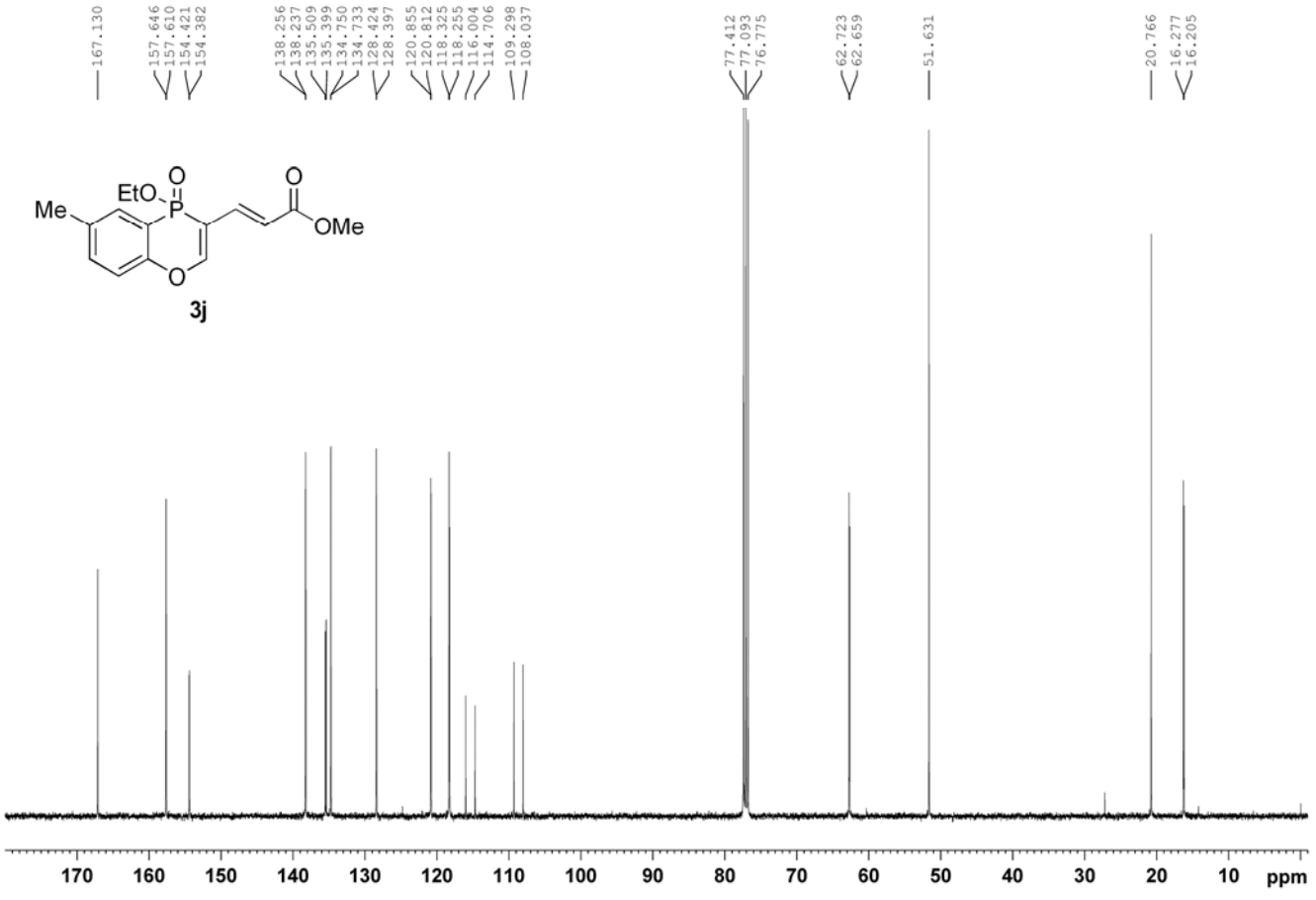

3174.19
3172.75
3166.43
3164.99
3160.83
3159.39
3153.06
3151.62
3050.67
3049.15
3043.31
3042.03
3040.83
3034.91
3033.43
2980.41
2979.09
2956.16
2953.52
2952.60
2950.52
2947.36
2946.80
2945.20
2943.68
2942.24
2941.20
2940.20
2939.60
2938.55
2912.19
2911.75
2908.59
2904.14
2896.54
2896.10
1631.09
1624.05
1622.73
1621.09
1616.97
1615.60
1614.00
1612.56
1609.80
1608.56
1606.92
1605.44
1603.84
1602.24
1601.52
1599.80
1598.40
1596.76
1595.28
1594.32
1591.32
1589.72
1588.24
1586.76
1582.67
1581.15
1579.71
1572.67
1521.77
854.24
852.68
851.08
517.93
510.81
503.76
-0.08
EtO
O
P
O
O
OMe
O
3i
1.000
1.022
3.031
1.526
2.112
3.028
2.923
3.439
11
10
9
8
7
6
5
4
3
2
1
ppm

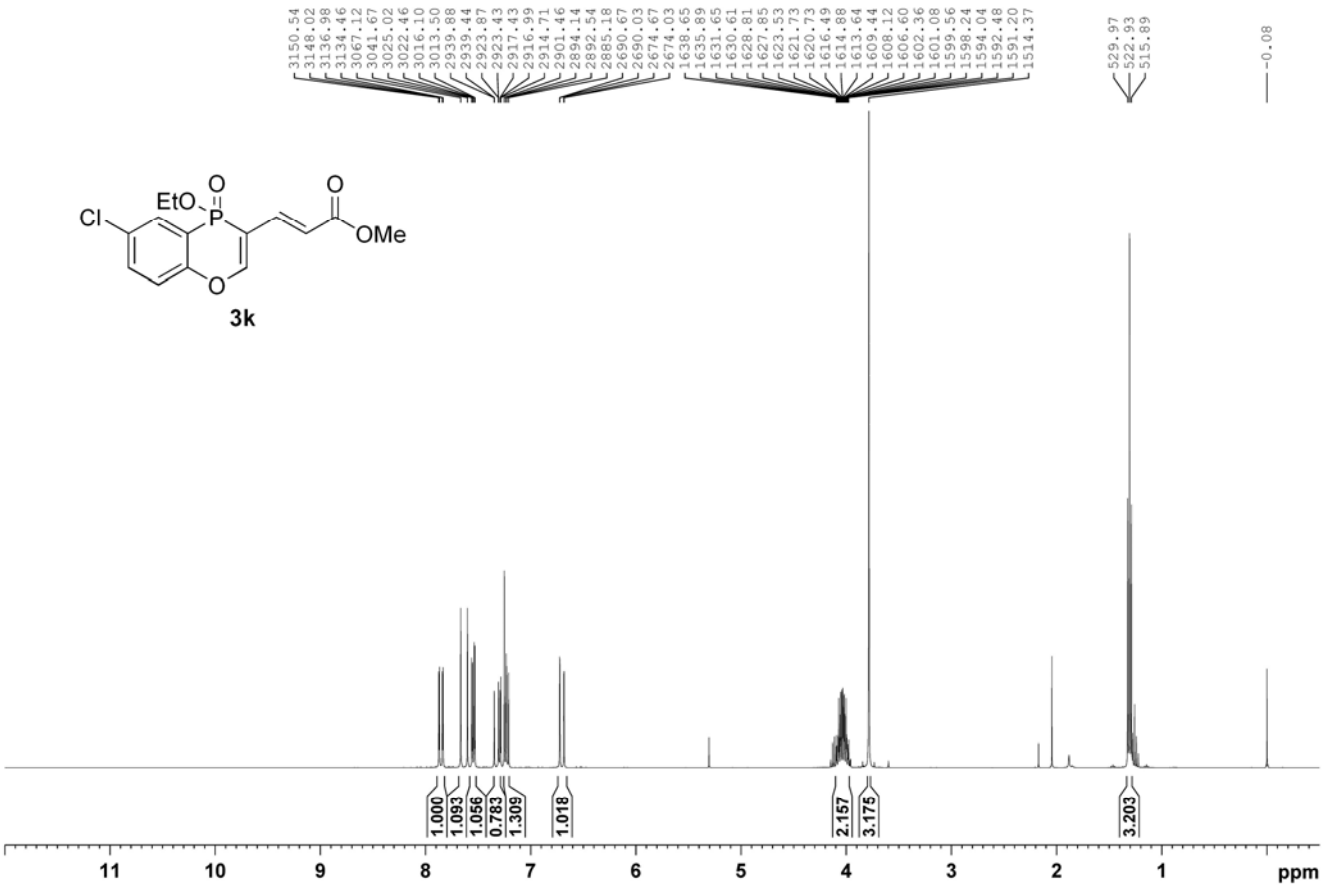

168.017
156.596
156.554
153.898
153.877
133.518
133.506
131.399
131.318
129.347
129.337
129.070
129.043
125.171
125.061
118.485
118.420
116.327
115.024
109.164
107.897
77.337
77.019
76.701
62.440
62.376
52.159
16.406
16.339
14.382
EtO
O
P
O
O
OMe
O
3i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

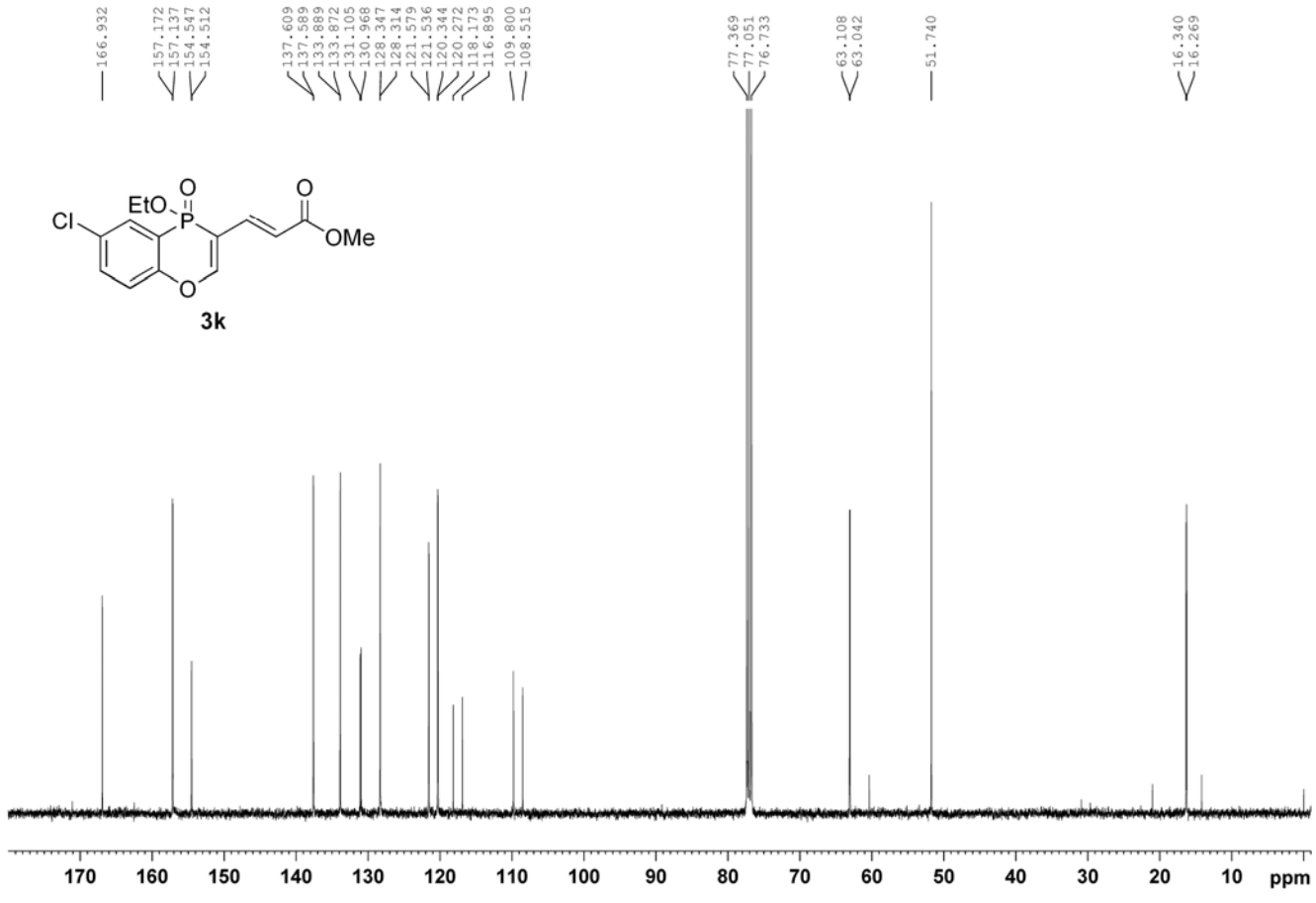


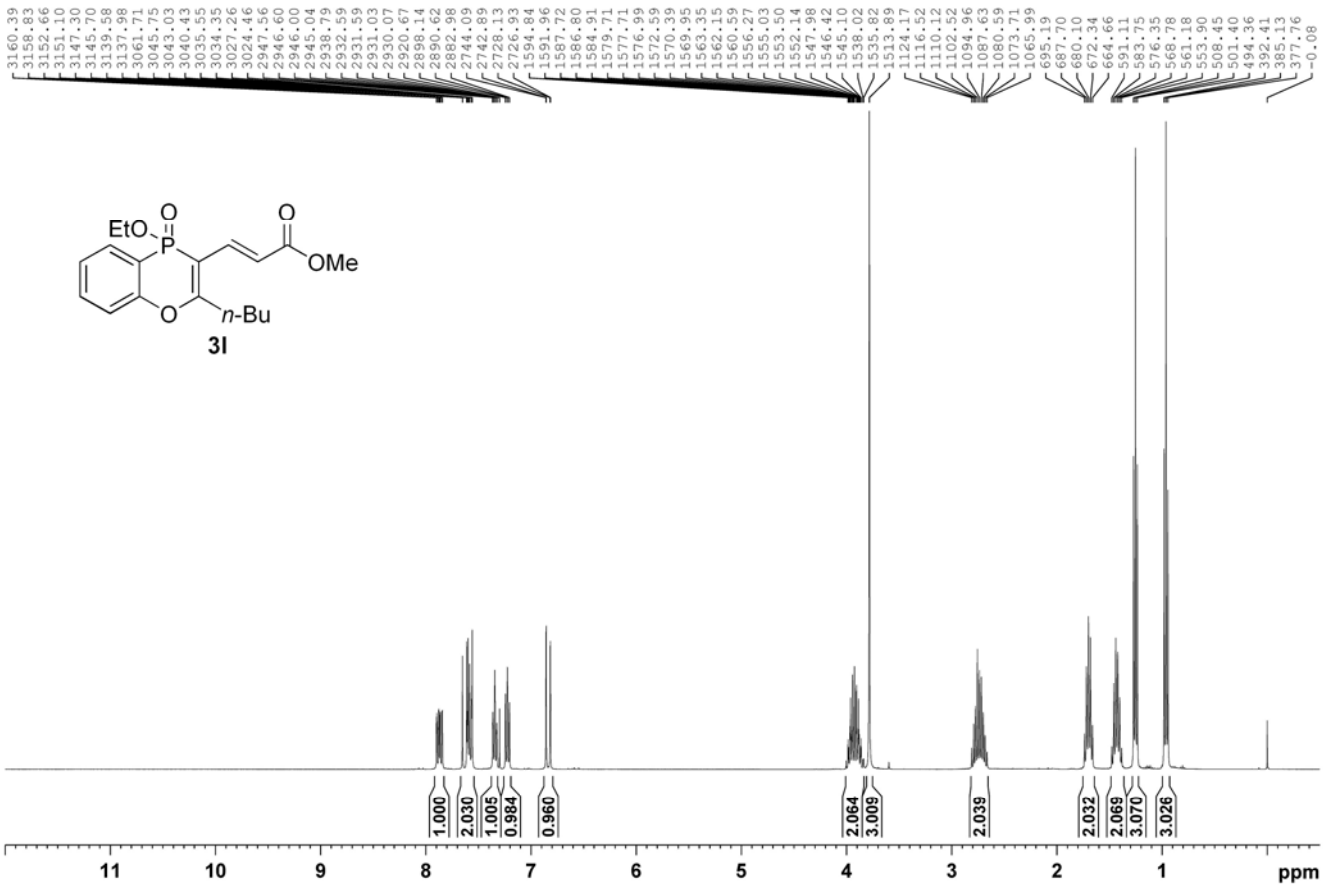


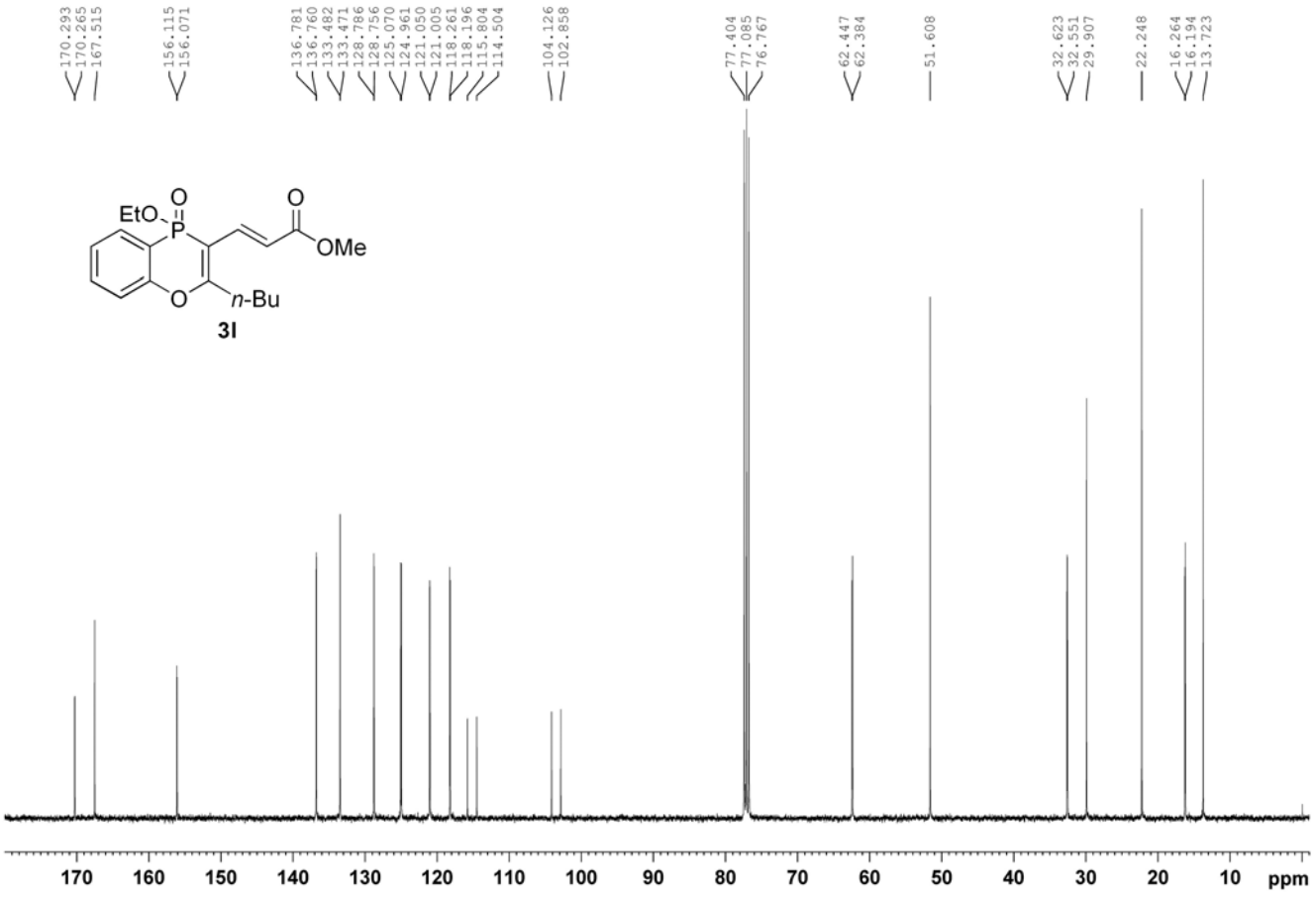

3j
ppm

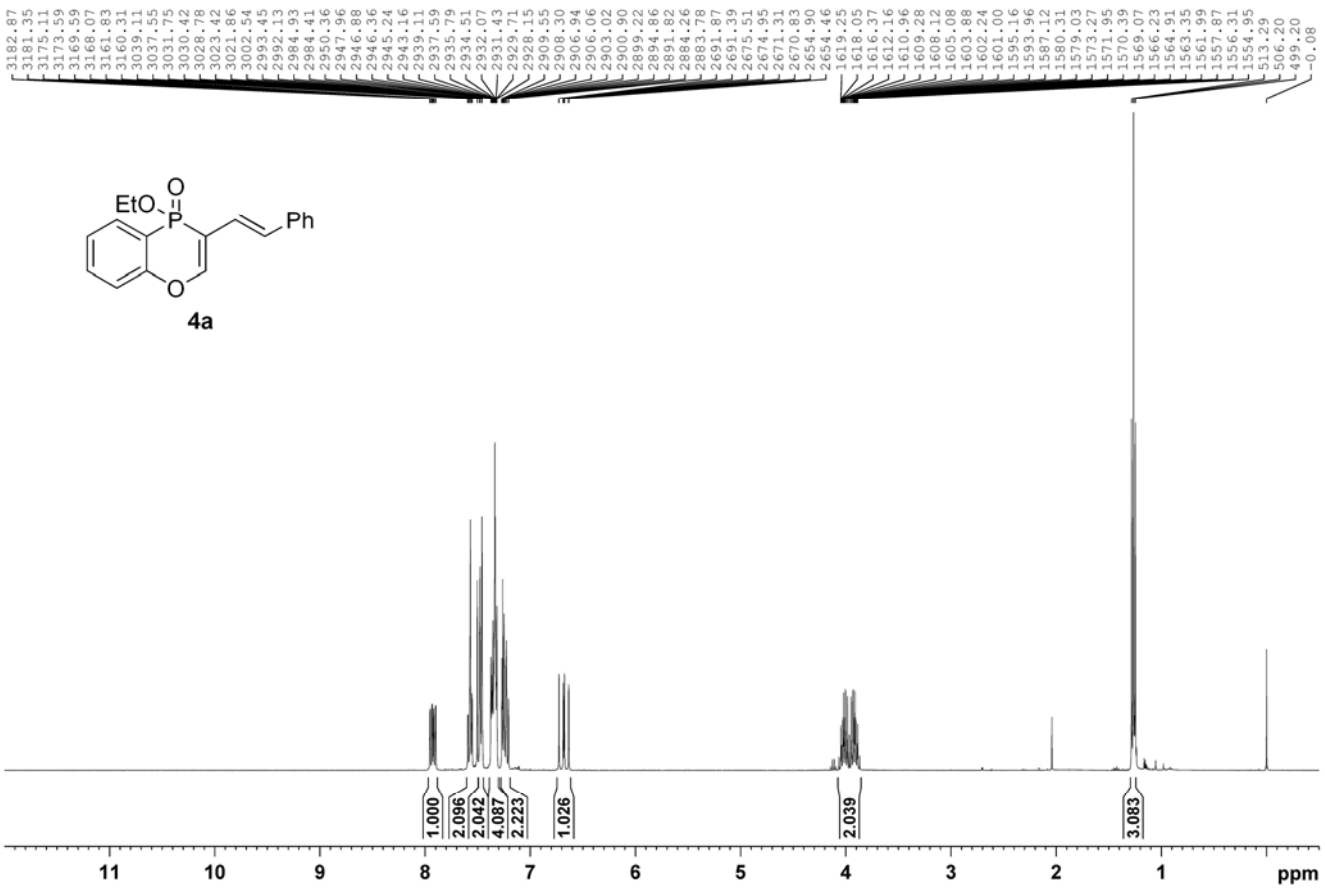

3j
ppm

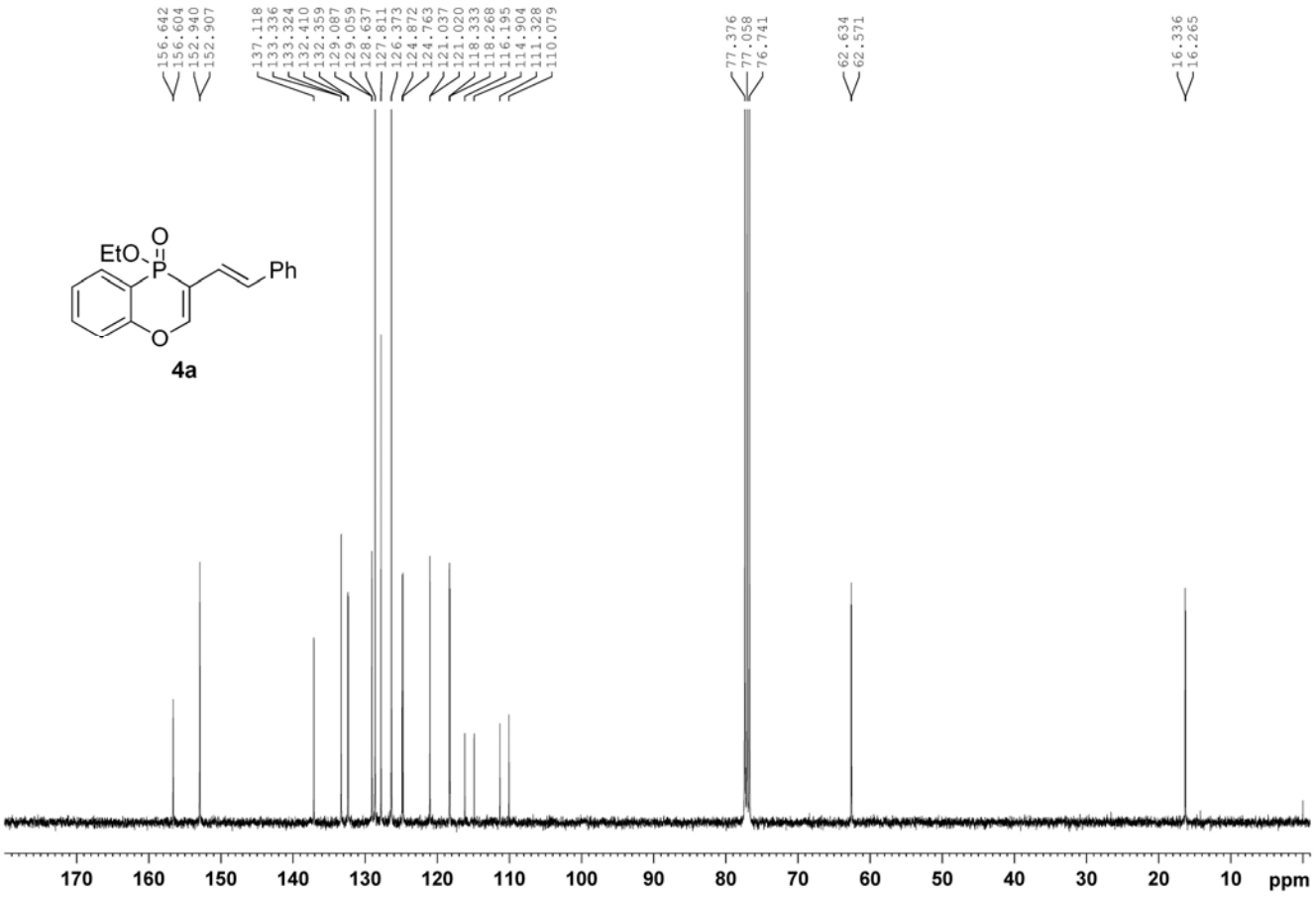

3150.54
3148.02
3136.98
3134.46
3067.12
3041.67
3025.02
3022.46
3016.10
3013.50
2939.88
2939.44
2923.87
2923.43
2917.43
2916.99
2914.71
2901.46
2894.14
2892.54
2885.18
2690.67
2690.03
2674.67
2674.03
1638.65
1635.89
1631.65
1630.61
1628.81
1627.85
1623.53
1621.73
1620.73
1616.49
1614.88
1613.64
1609.44
1608.12
1606.60
1602.36
1601.08
1599.56
1598.24
1594.04
1592.48
1591.20
1514.37
529.97
522.93
515.89
-0.08
EtO
O
P
O
Cl
O
OMe
O
3k
1.000
1.093
1.056
0.783
1.309
1.018
2.157
3.175
3.203
11
10
9
8
7
6
5
4
3
2
1
ppm

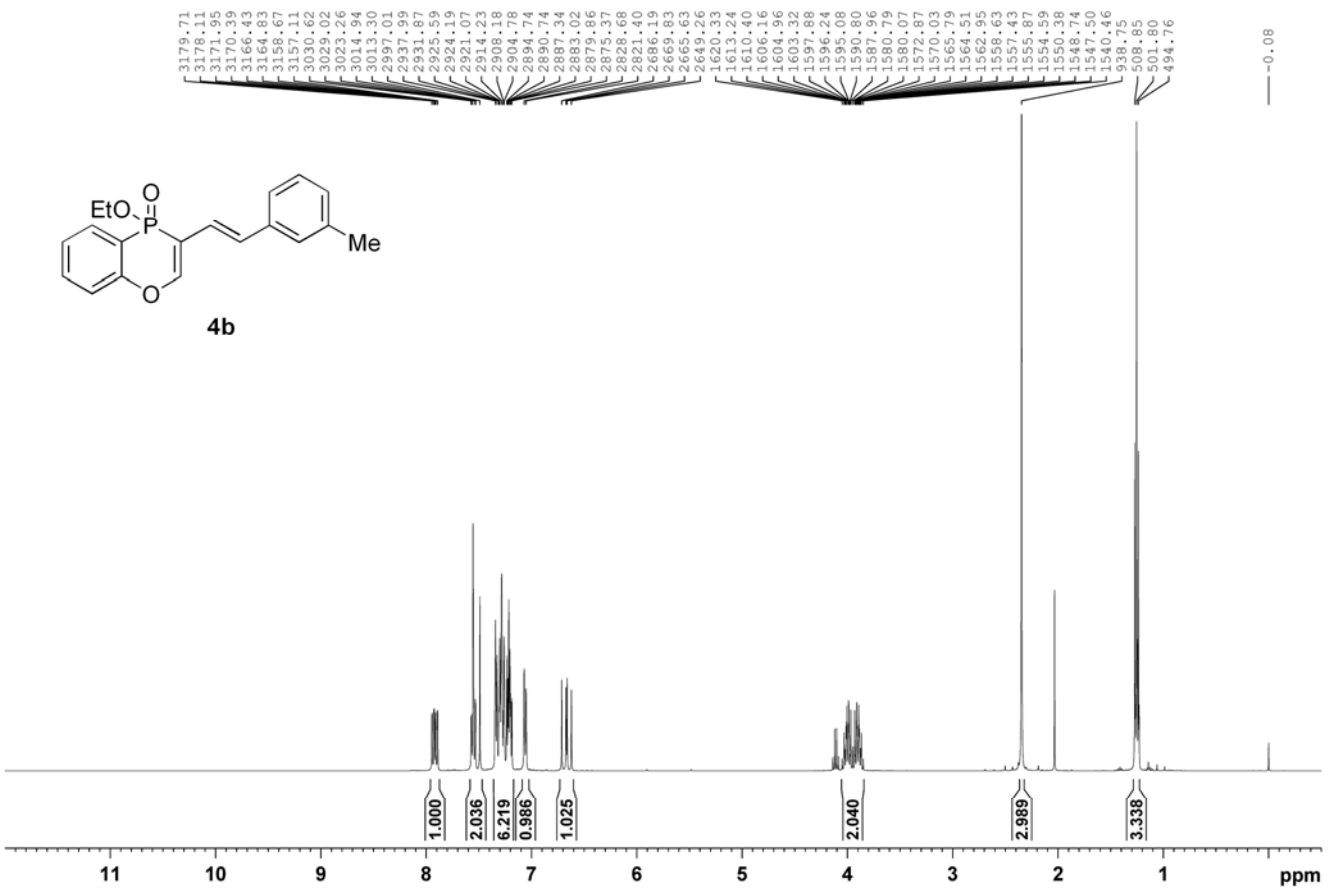

166.932
157.172
157.137
154.547
154.512
137.609
137.589
133.889
133.872
131.105
130.968
128.347
128.314
121.579
121.536
120.344
120.272
118.173
116.895
109.800
108.515
77.369
77.051
76.733
63.108
63.042
51.740
16.340
16.269
EtO
O
P
O
Cl
O
OMe
O
3k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

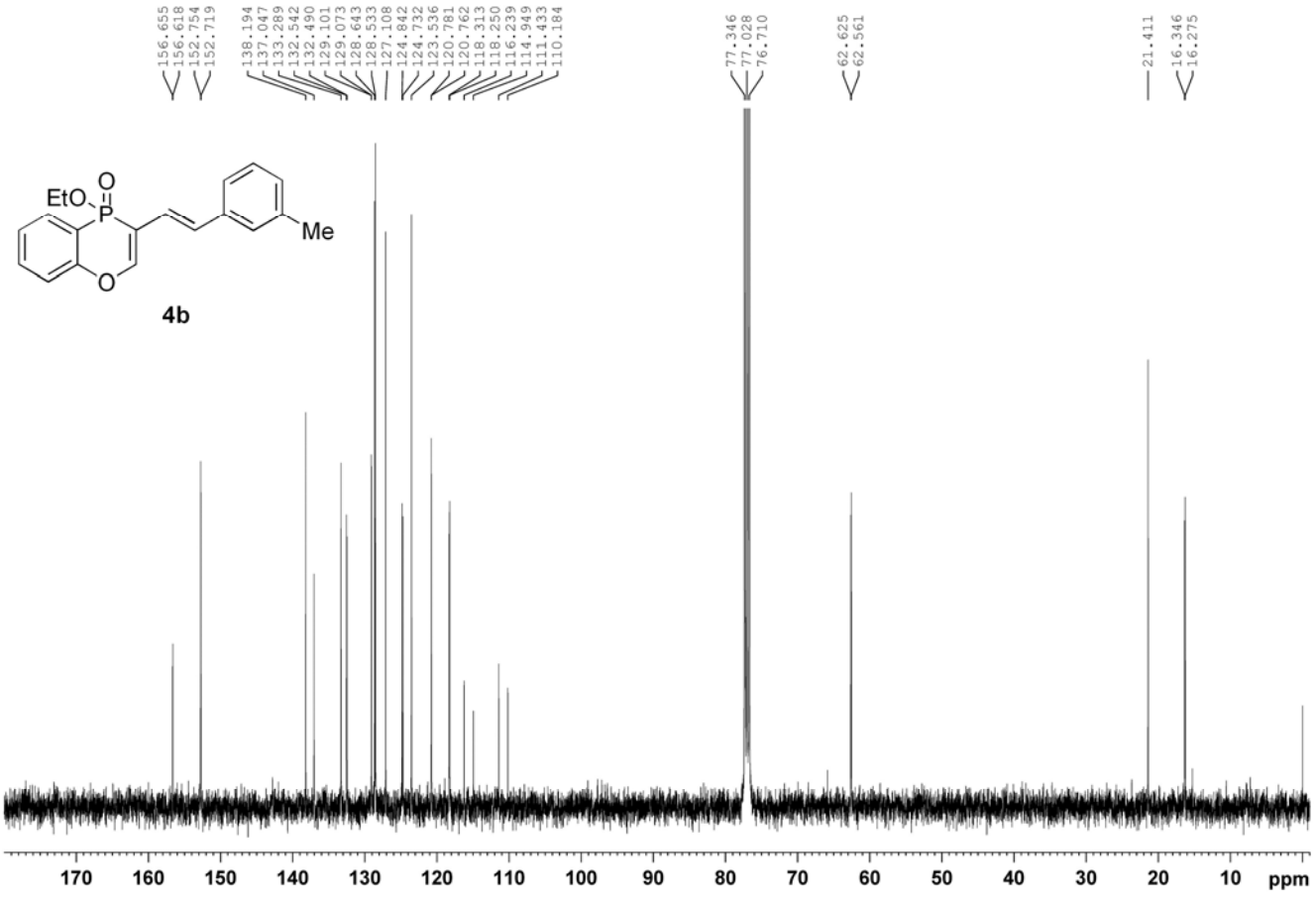

EtO
O
P
O
O
OMe
O
n-Bu
3l
1.000
2.030
1.005
0.984
0.960
2.064
3.009
2.039
2.032
2.069
3.070
3.026
11
10
9
8
7
6
5
4
3
2
1
ppm

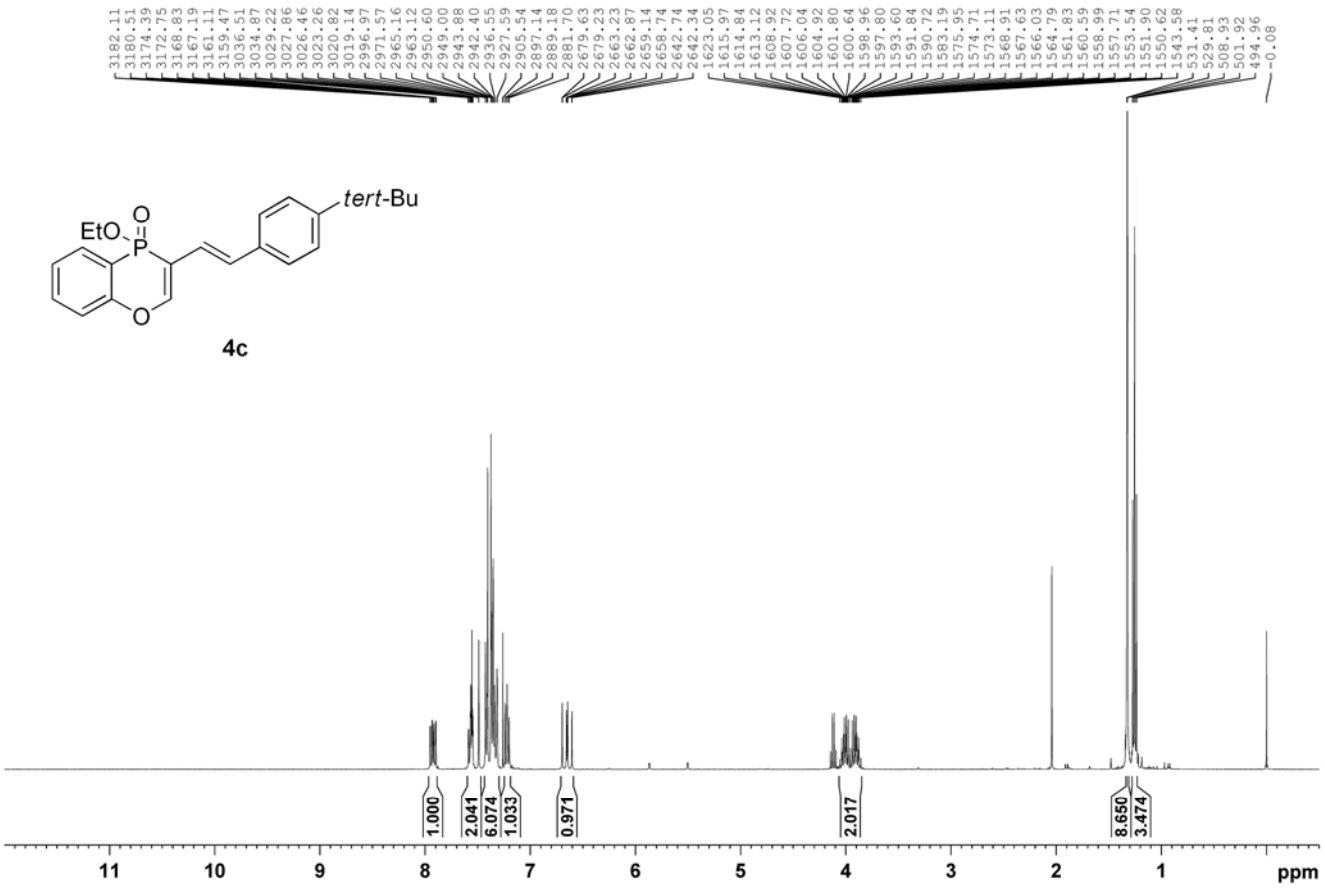

EtO
O
P
O
O
OMe
O
n-Bu
3l
170.293
170.265
167.515
156.115
156.071
136.781
136.760
133.482
133.471
128.786
128.756
125.070
124.961
121.050
121.005
118.261
118.196
115.804
114.504
104.126
102.858
77.404
77.085
76.767
62.447
62.384
51.608
32.623
32.551
29.907
22.248
16.264
16.194
13.723
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

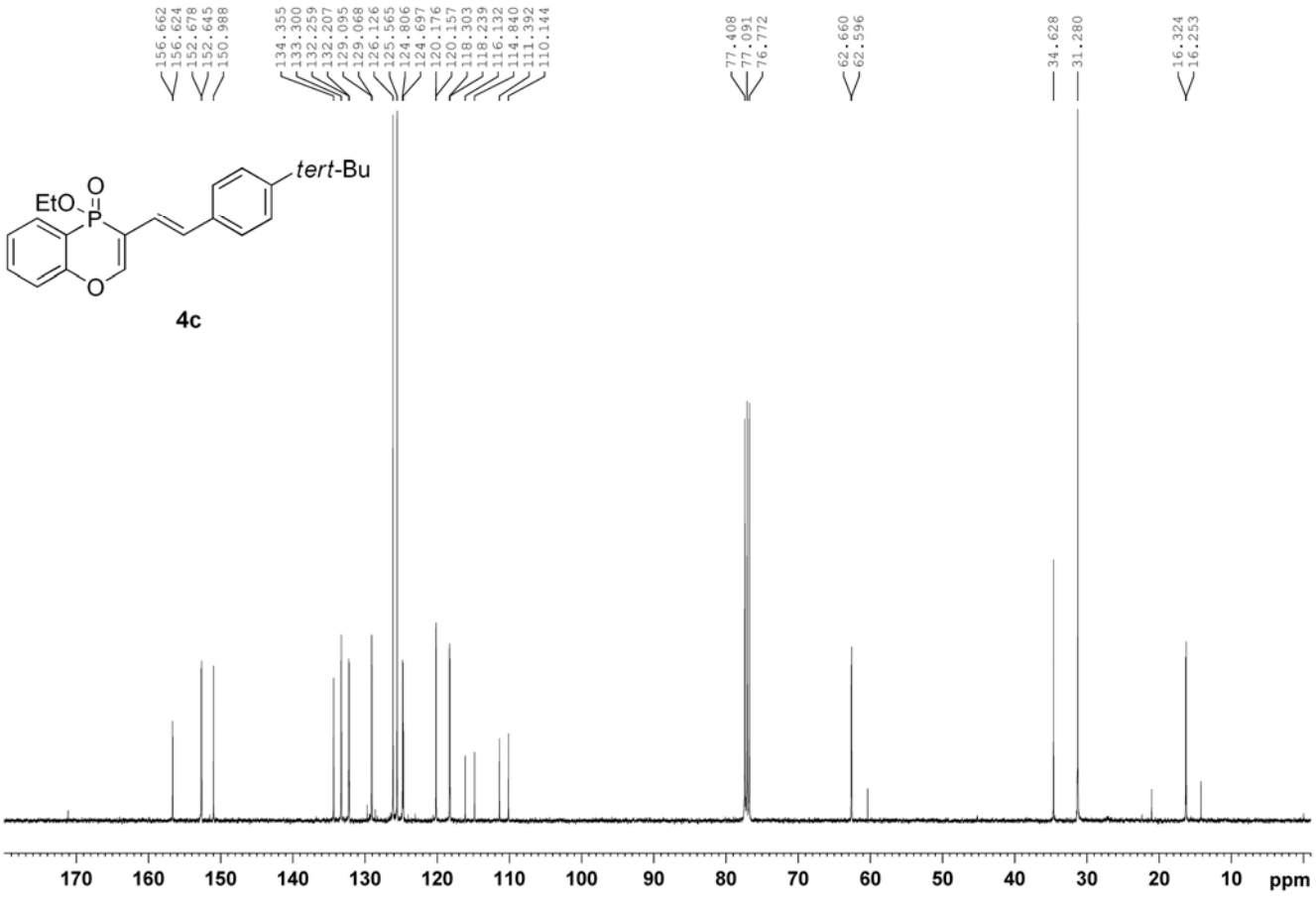

EtO
O
P
Ph
O
4a
1.000
2.096
2.042
4.087
2.223
1.026
2.039
3.083
ppm

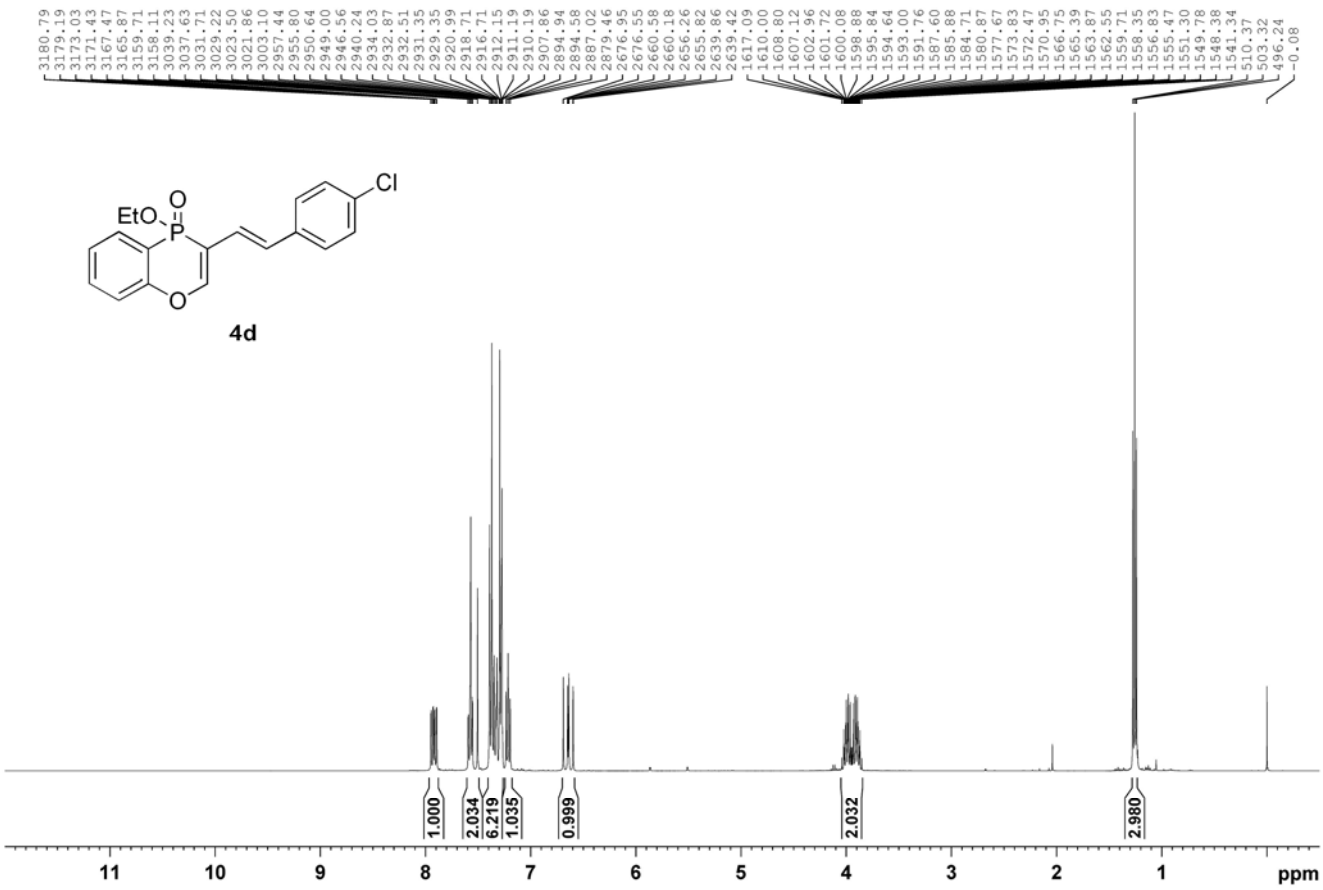

EtO
O
P
Ph
O
4a
ppm

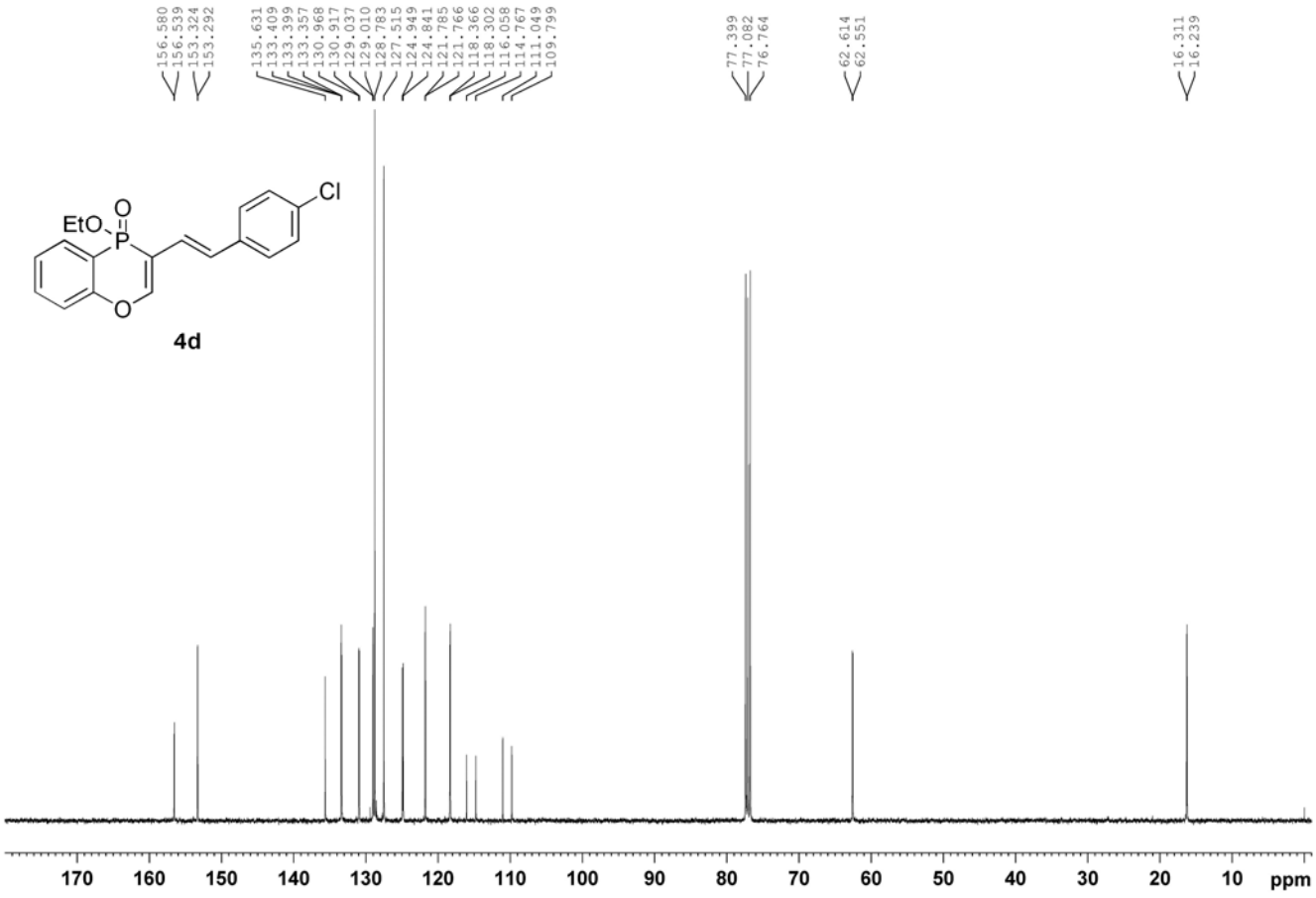

EtO
O
P
O
Me
4b
1.000
2.036
6.219
0.986
1.025
2.040
2.989
3.338
ppm

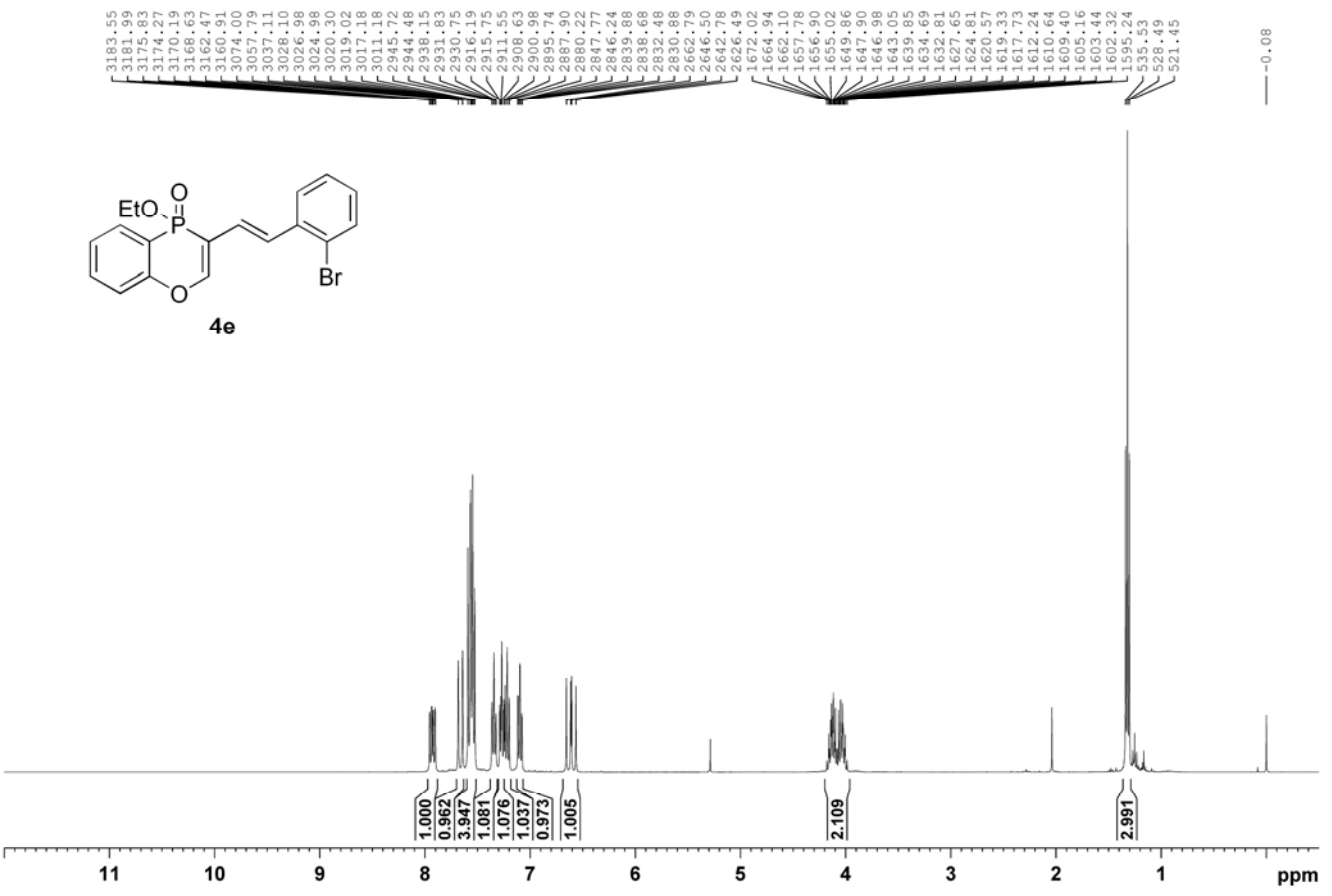

EtO
O
P
O
Me
4b
77.346
77.028
76.710
62.625
62.561
21.411
16.346
16.275
ppm

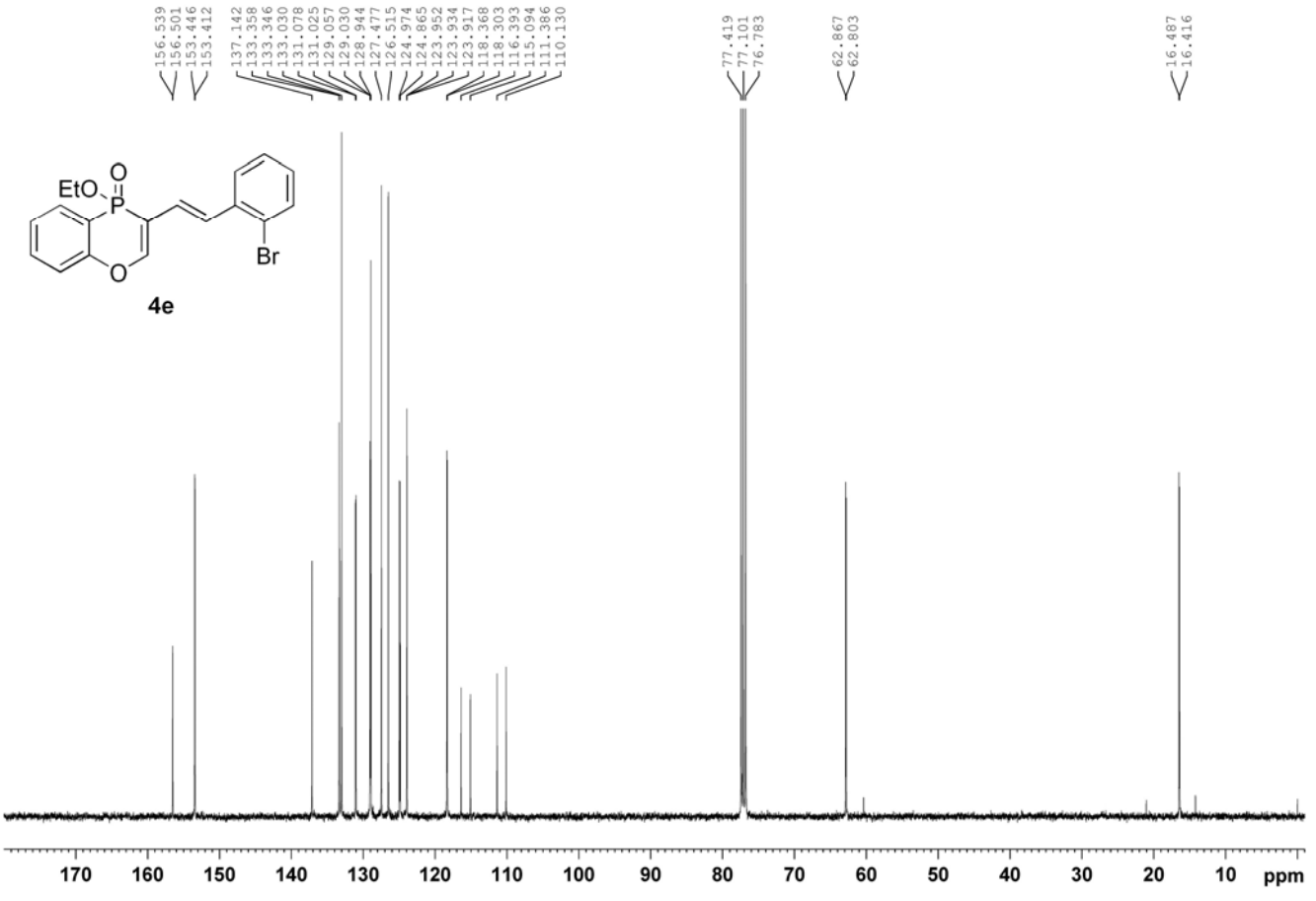

tert-Bu
EtO
O
P
O
4c
1.000
2.041
6.074
1.033
0.971
2.017
8.650
3.474
ppm

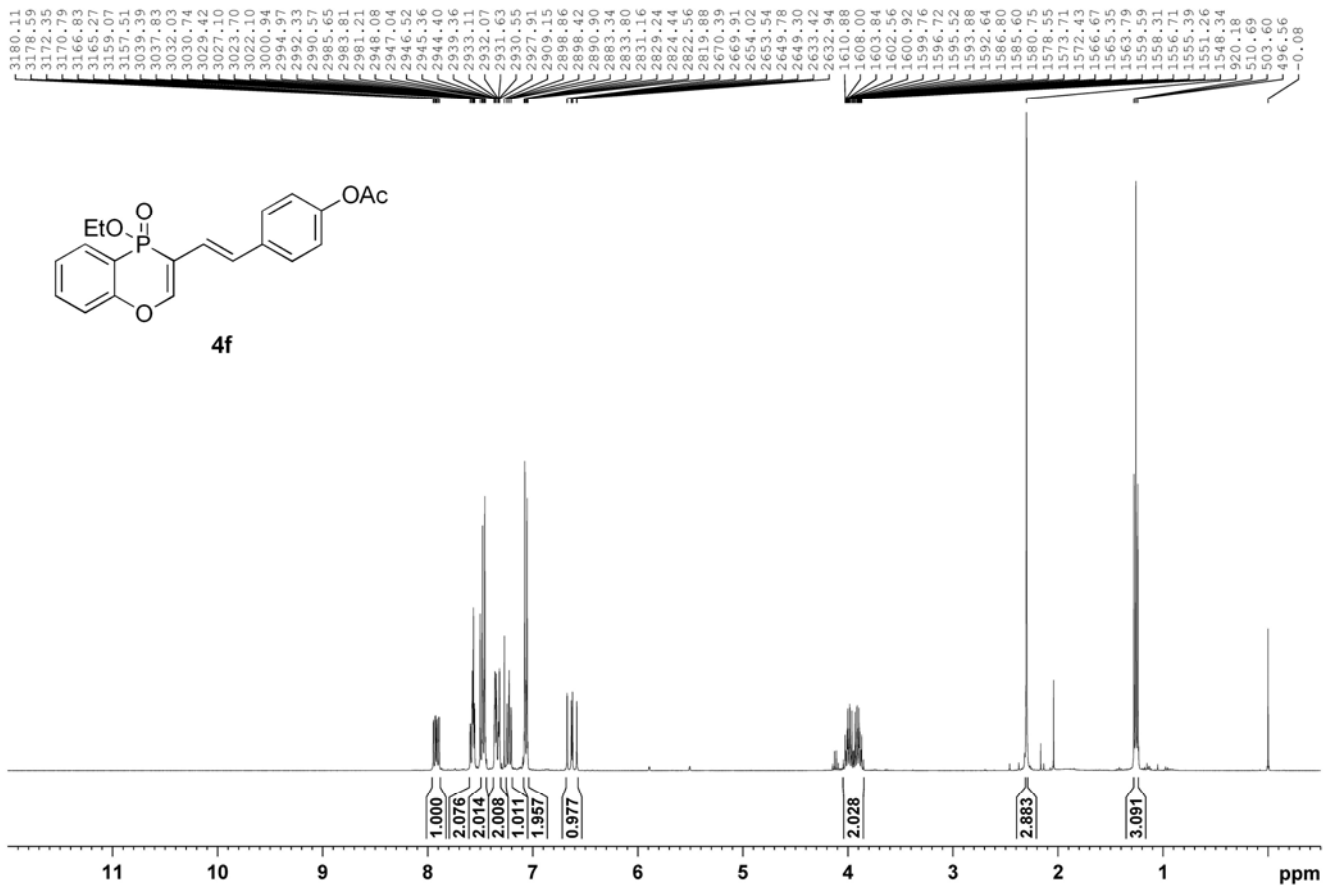

tert-Bu
EtO
O
P
O
4c
ppm

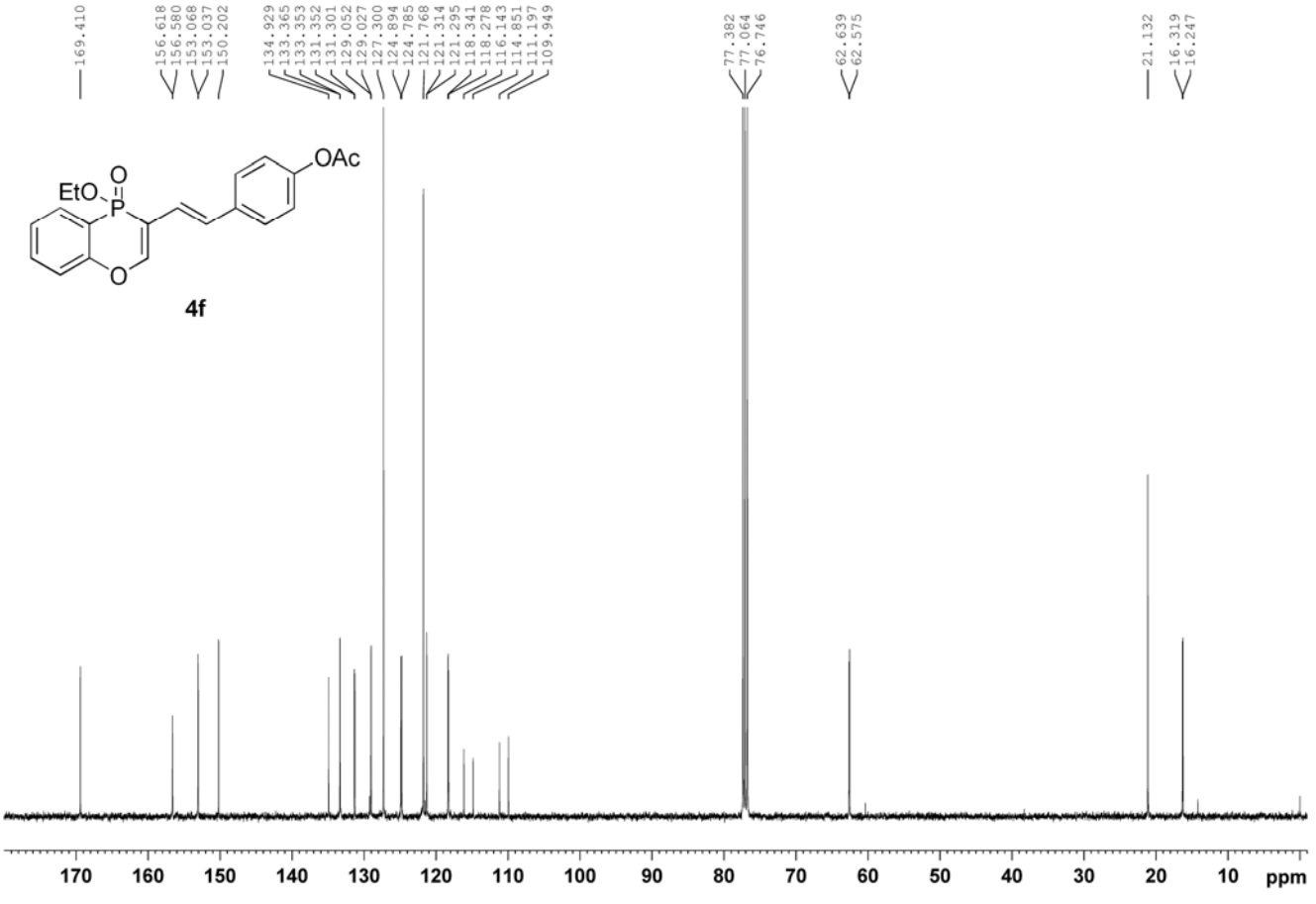

4d
1.000
2.034
6.219
1.035
0.999
2.032
2.980
ppm

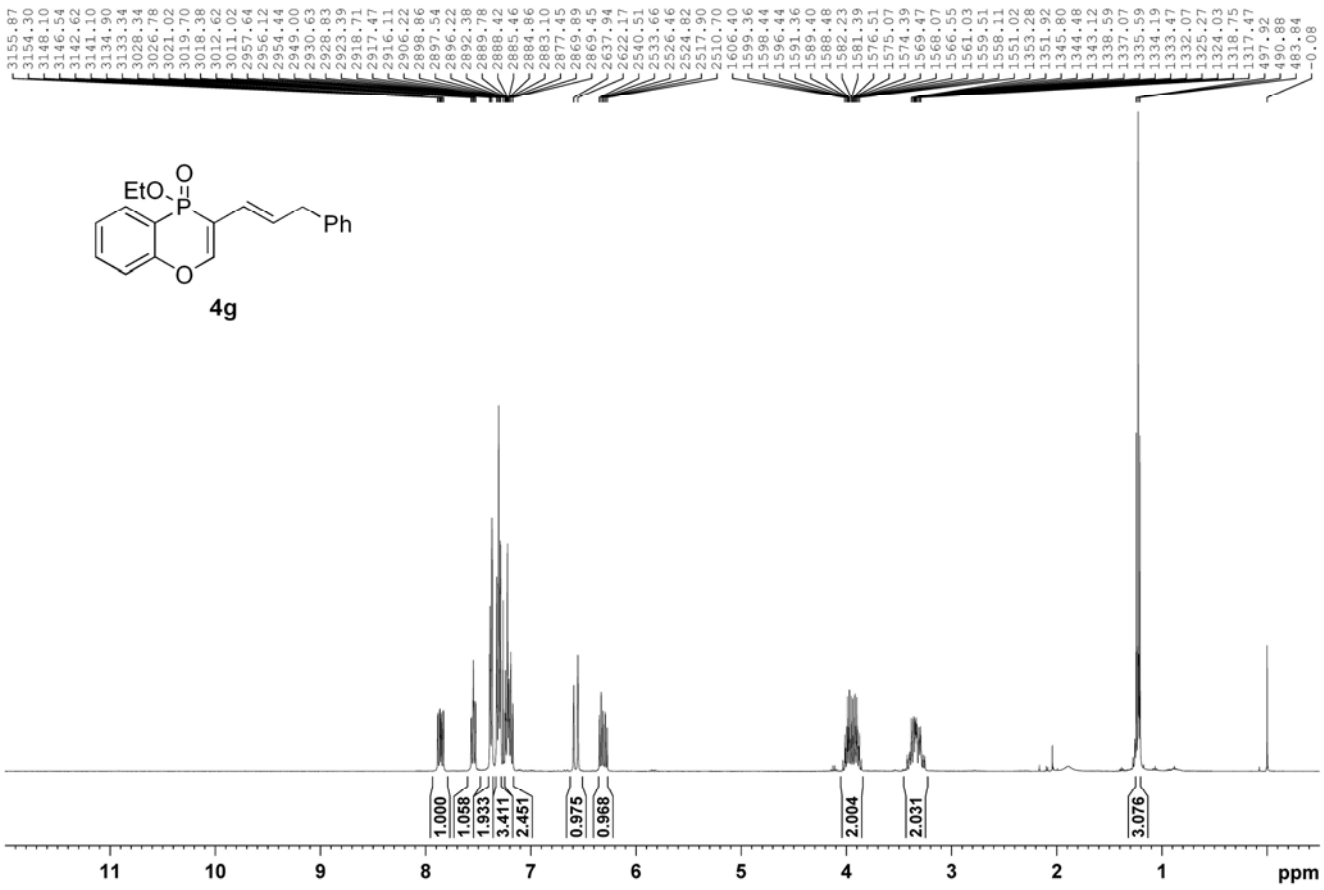

4d
ppm

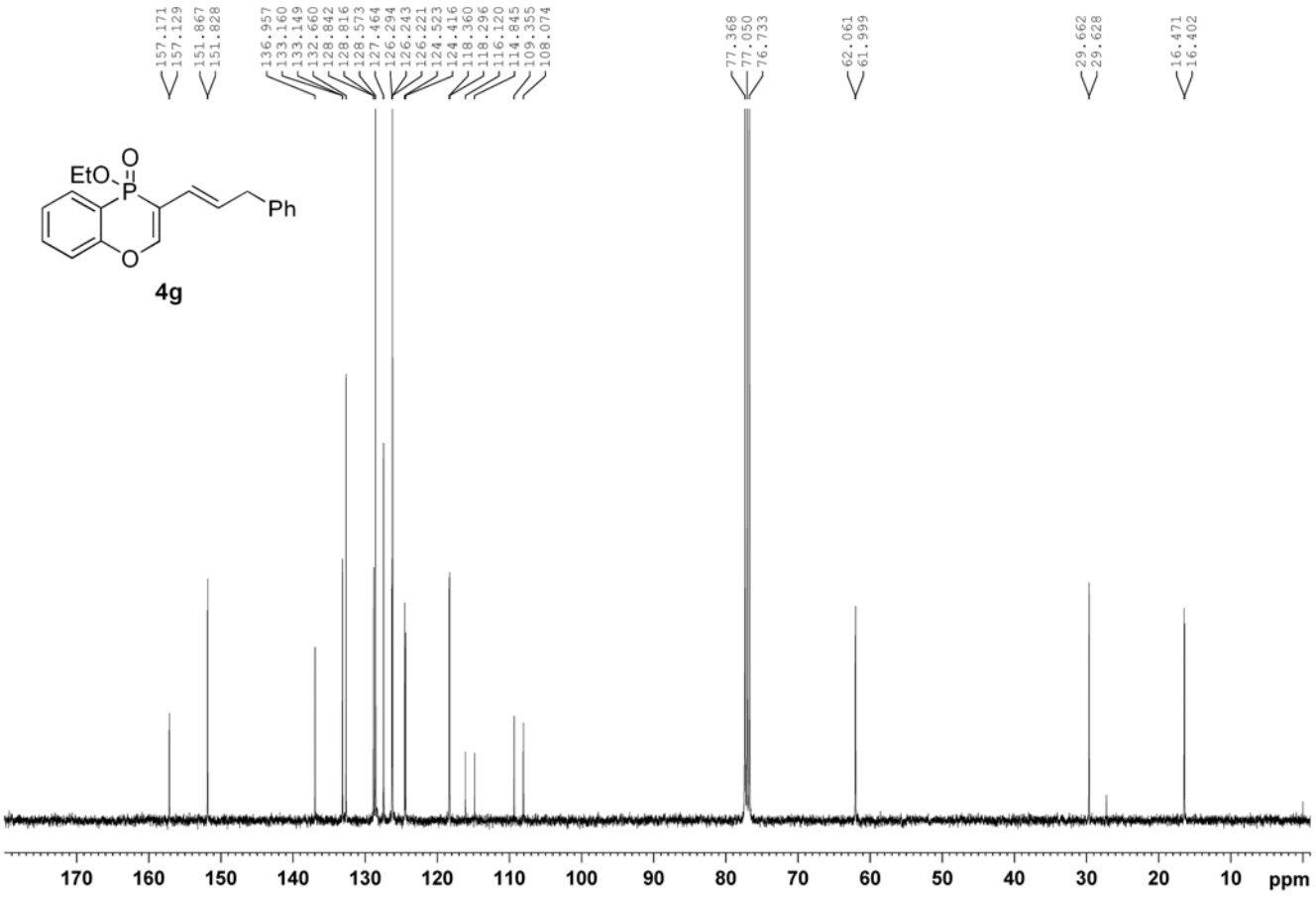

EtO
O
P
O
Br
4e
1.000
0.962
3.947
1.081
1.076
1.037
0.973
1.005
2.109
2.991
ppm

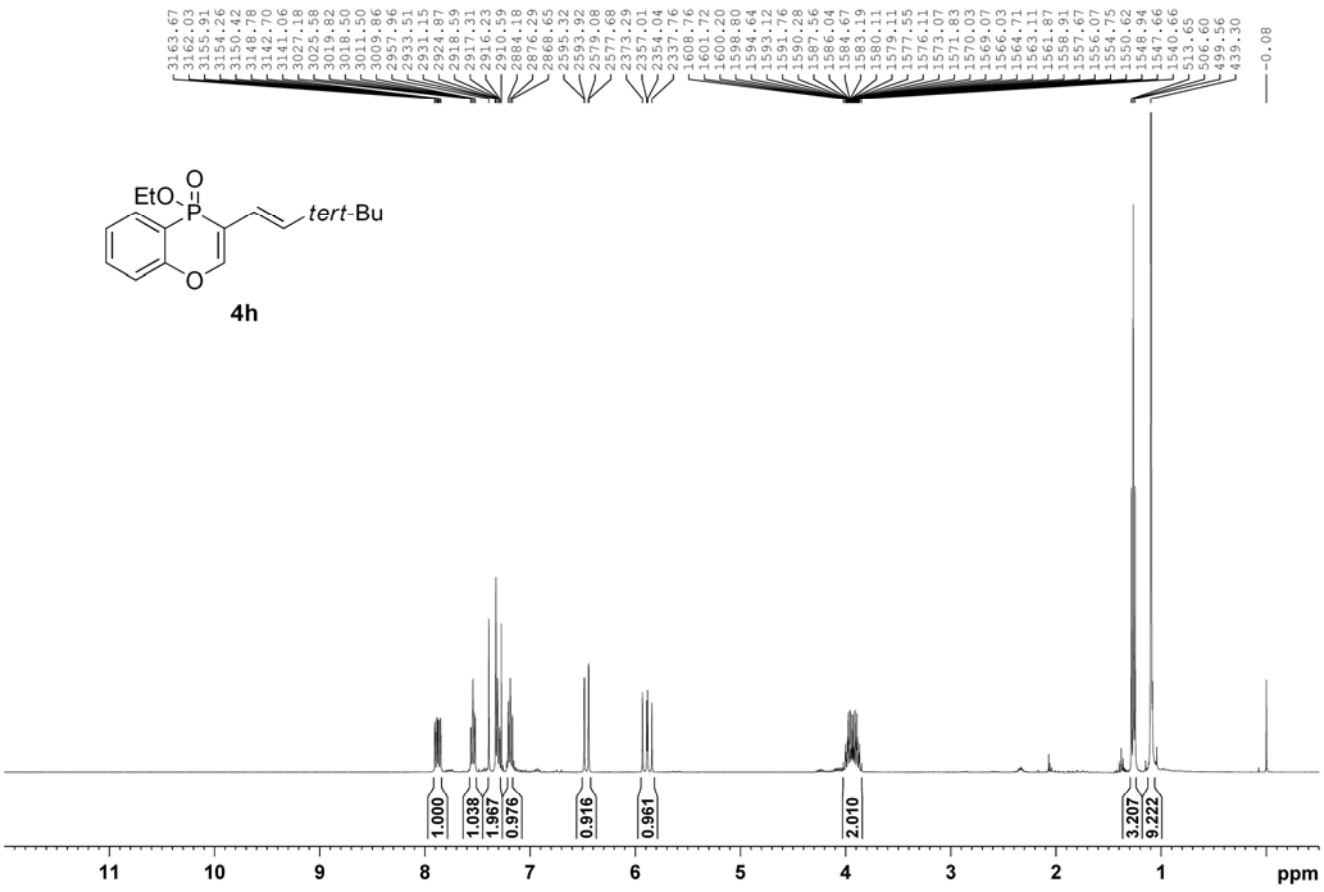

EtO
O
P
O
Br
4e
ppm

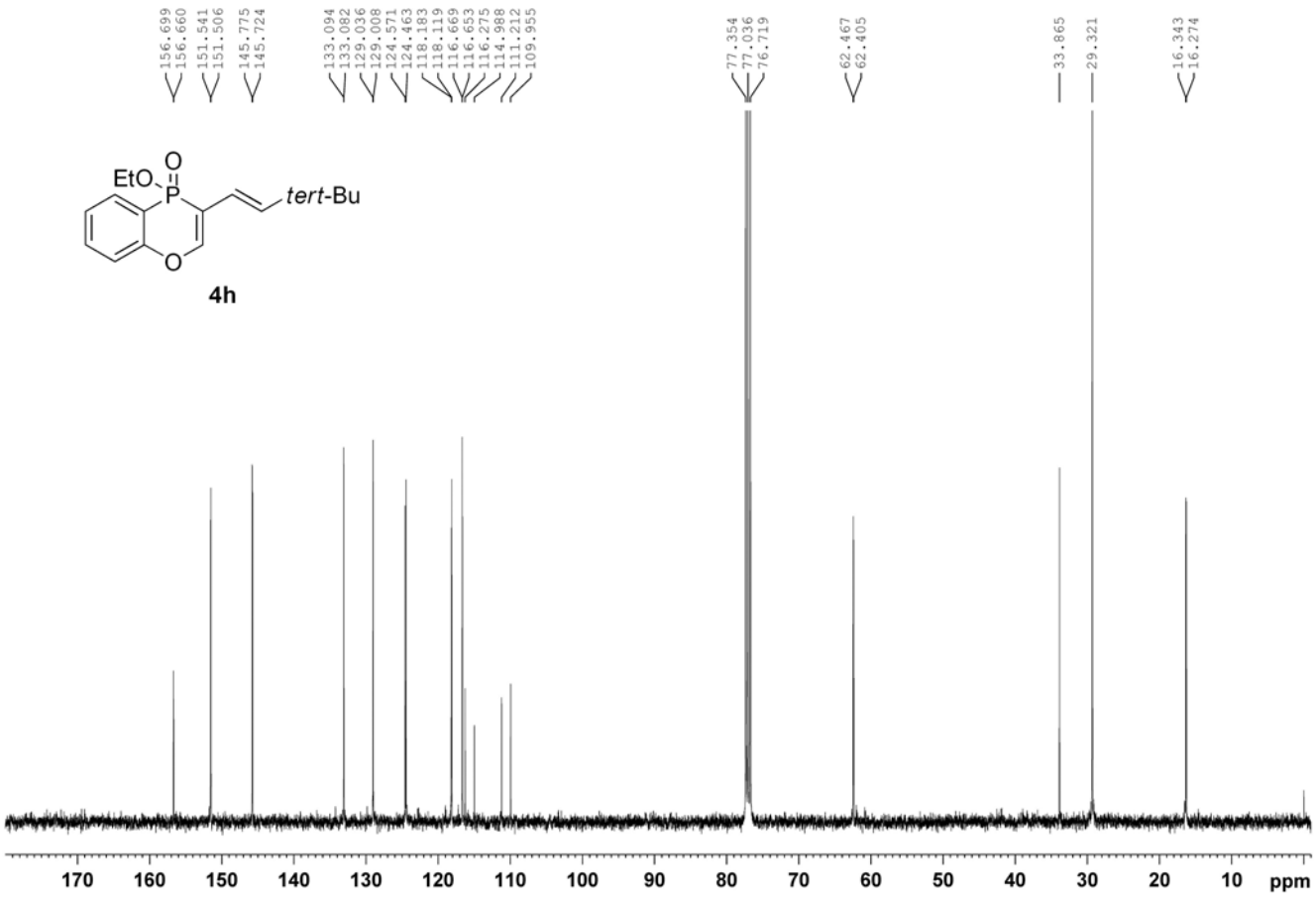

3180.11
3178.59
3172.35
3170.79
3166.83
3165.27
3159.07
3157.51
3039.39
3037.83
3032.03
3030.74
3029.42
3027.10
3023.70
3022.10
3000.94
2994.97
2992.33
2990.57
2985.65
2983.81
2981.21
2948.08
2947.04
2946.52
2945.36
2944.40
2939.36
2933.11
2932.07
2931.63
2930.55
2927.91
2909.15
2898.86
2898.42
2890.90
2883.34
2833.80
2831.16
2829.24
2824.44
2822.56
2819.88
2670.39
2669.91
2654.02
2653.54
2649.78
2649.30
2632.94
1610.88
1608.00
1603.84
1602.56
1600.92
1599.76
1596.72
1595.52
1593.88
1592.64
1586.80
1585.60
1580.75
1578.55
1573.71
1572.43
1566.67
1565.35
1563.79
1559.59
1558.31
1556.71
1555.39
1551.26
1548.34
920.18
510.69
503.60
496.56
-0.08
EtO
O
P
O
OAc
4f
1.000
2.076
2.014
2.008
1.011
1.957
0.977
2.028
2.883
3.091
11
10
9
8
7
6
5
4
3
2
1
ppm

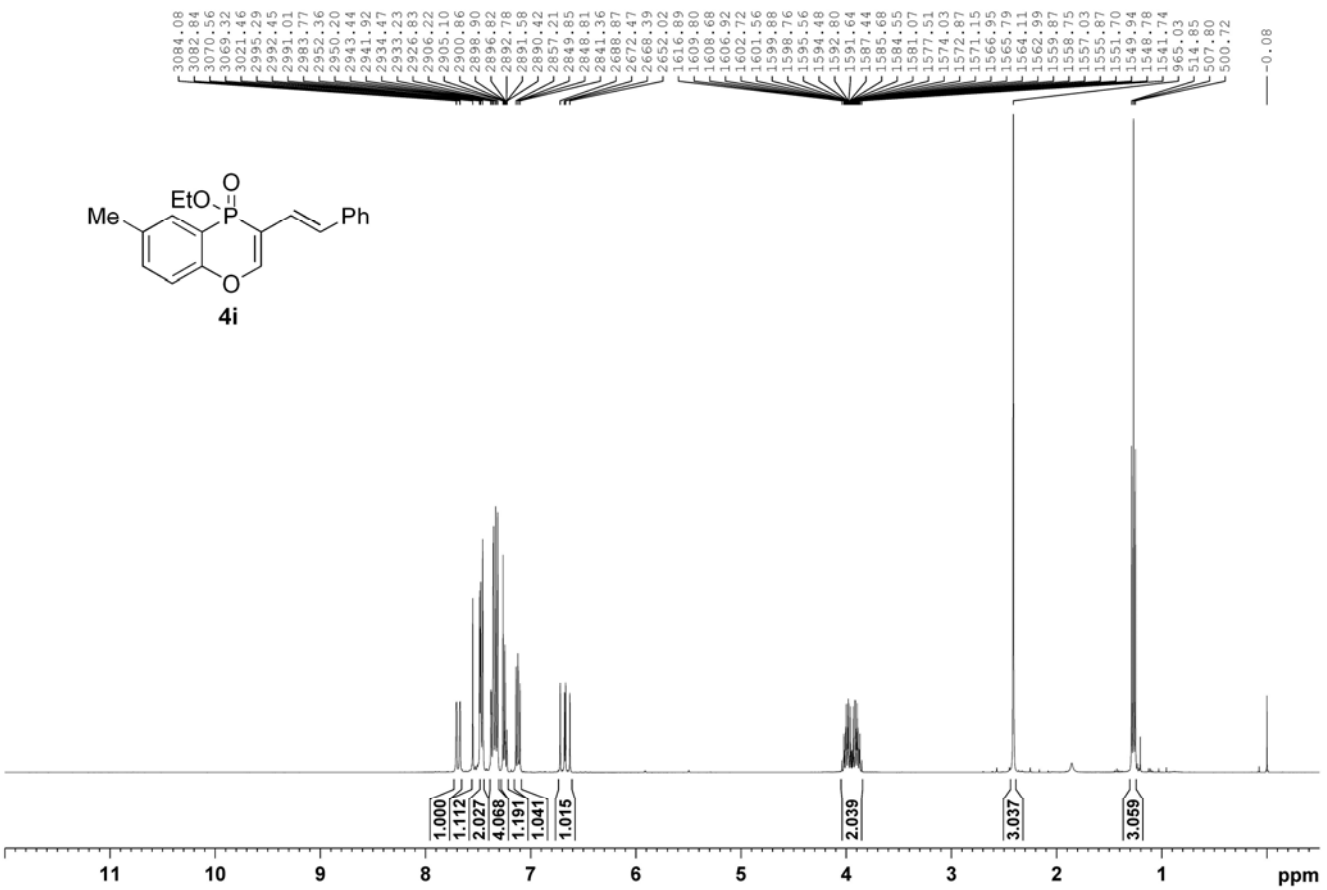

169.410
156.618
156.580
153.068
153.037
150.202
134.929
133.365
133.353
131.352
131.301
129.052
129.027
127.300
124.894
124.785
121.768
121.314
121.295
118.341
118.278
116.143
114.851
111.197
109.949
77.382
77.064
76.746
62.639
62.575
21.132
16.319
16.247
EtO
O
P
O
OAc
4f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

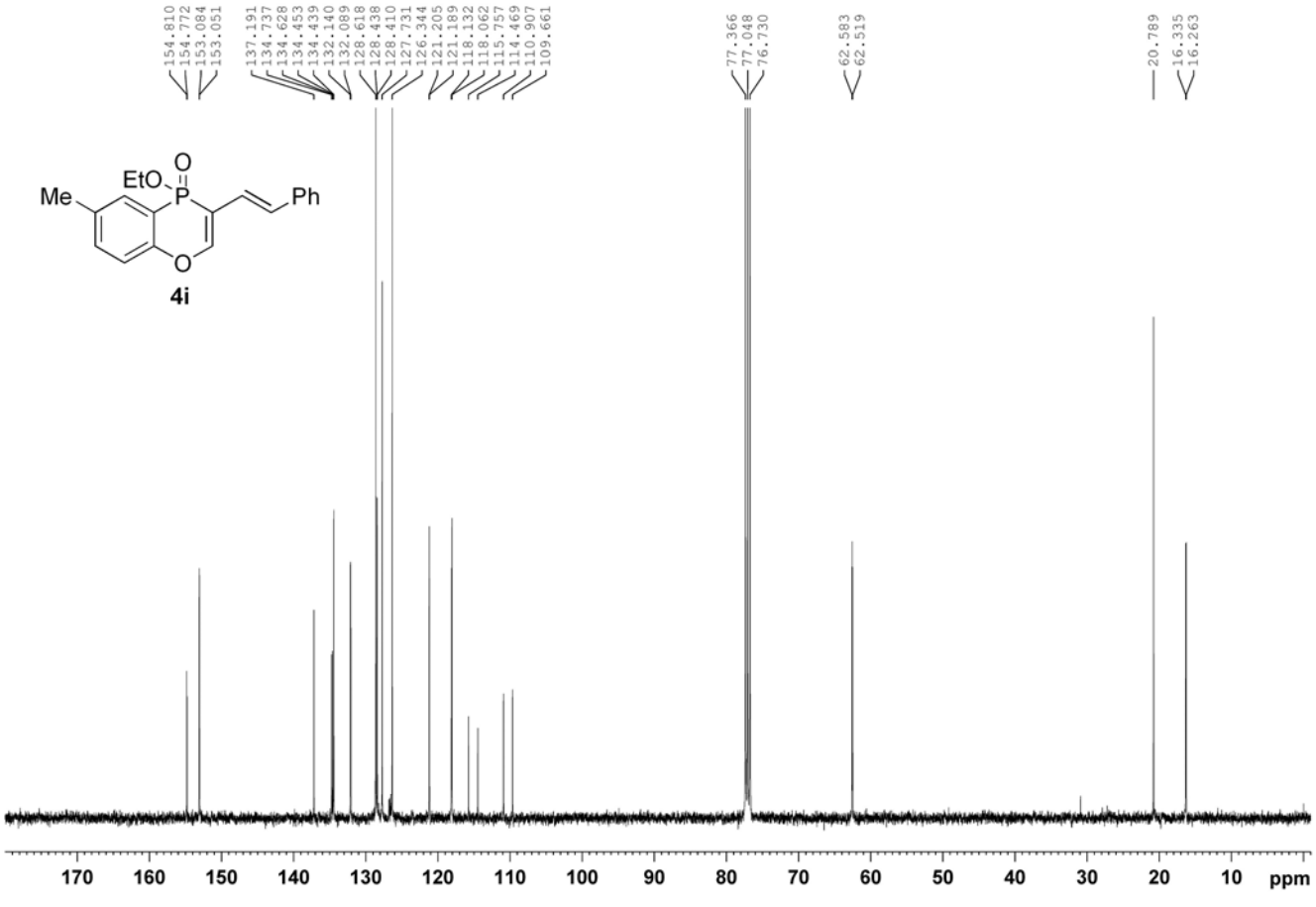

EtO
O
P
Ph
O
4g
1.000
1.058
1.933
3.411
2.451
0.975
0.968
2.004
2.031
3.076
ppm

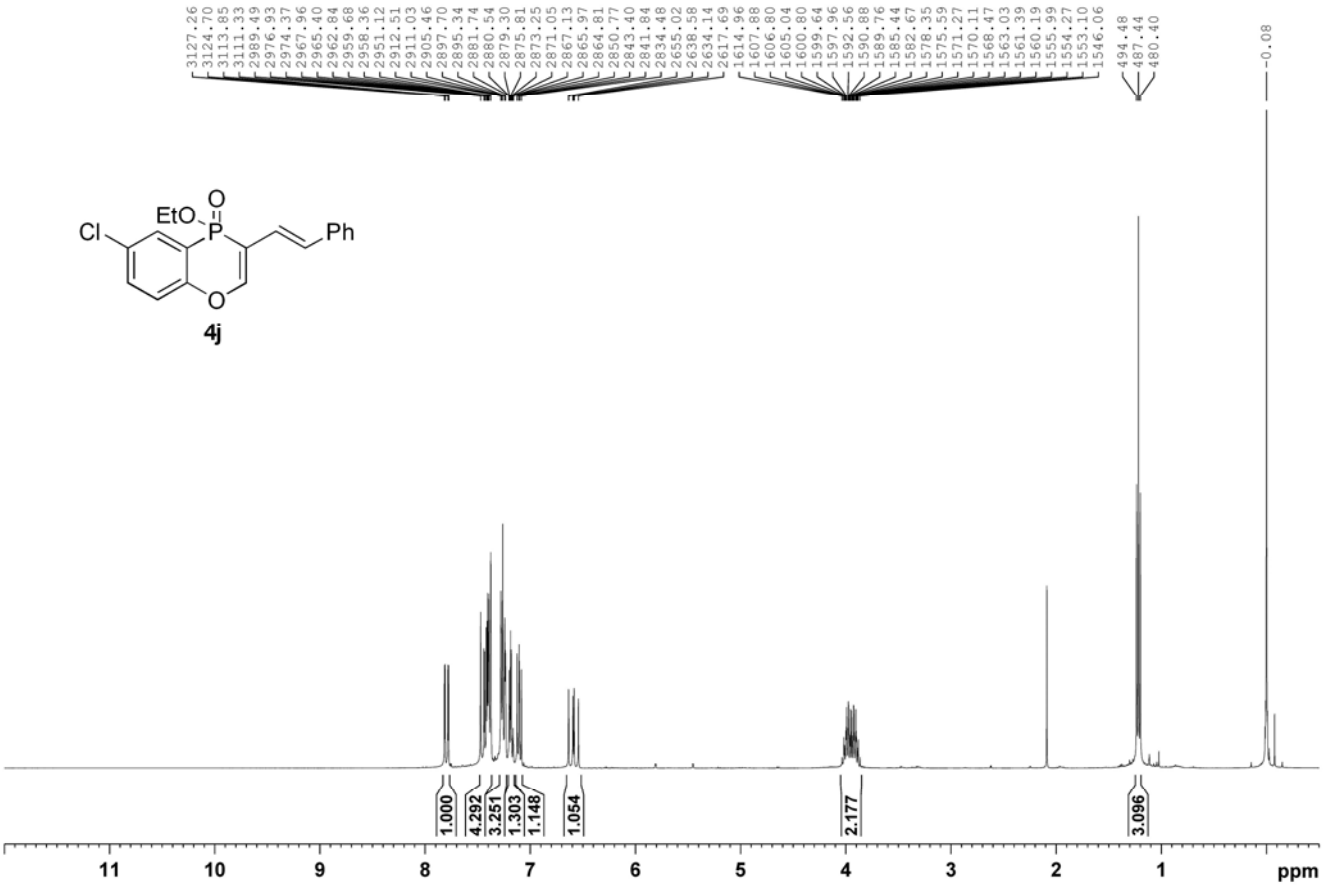

EtO
O
P
Ph
O
4g
ppm

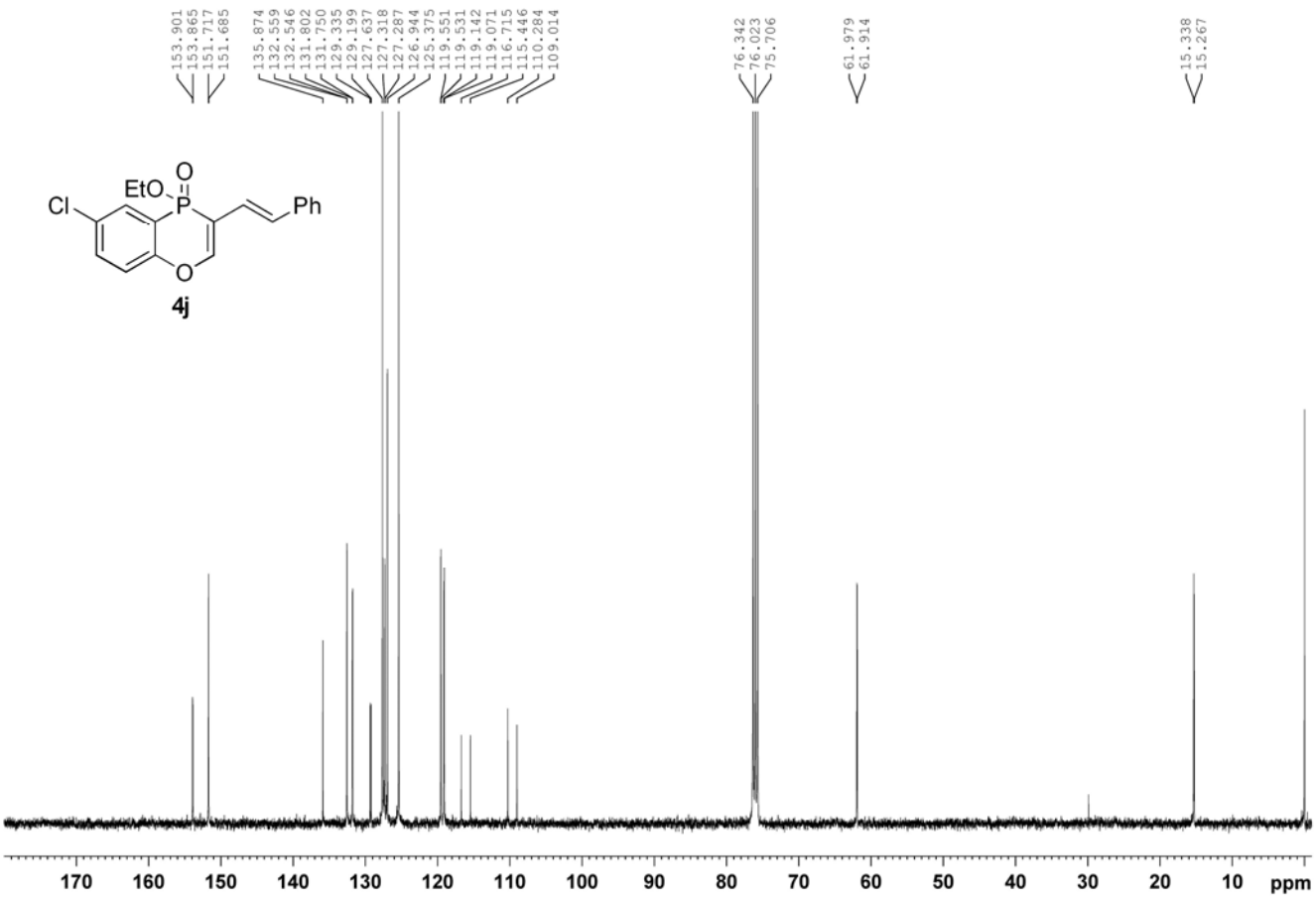

EtO
O
P
O
tert-Bu
4h
1.000
1.038
1.967
0.976
0.916
0.961
2.010
3.207
9.222
ppm

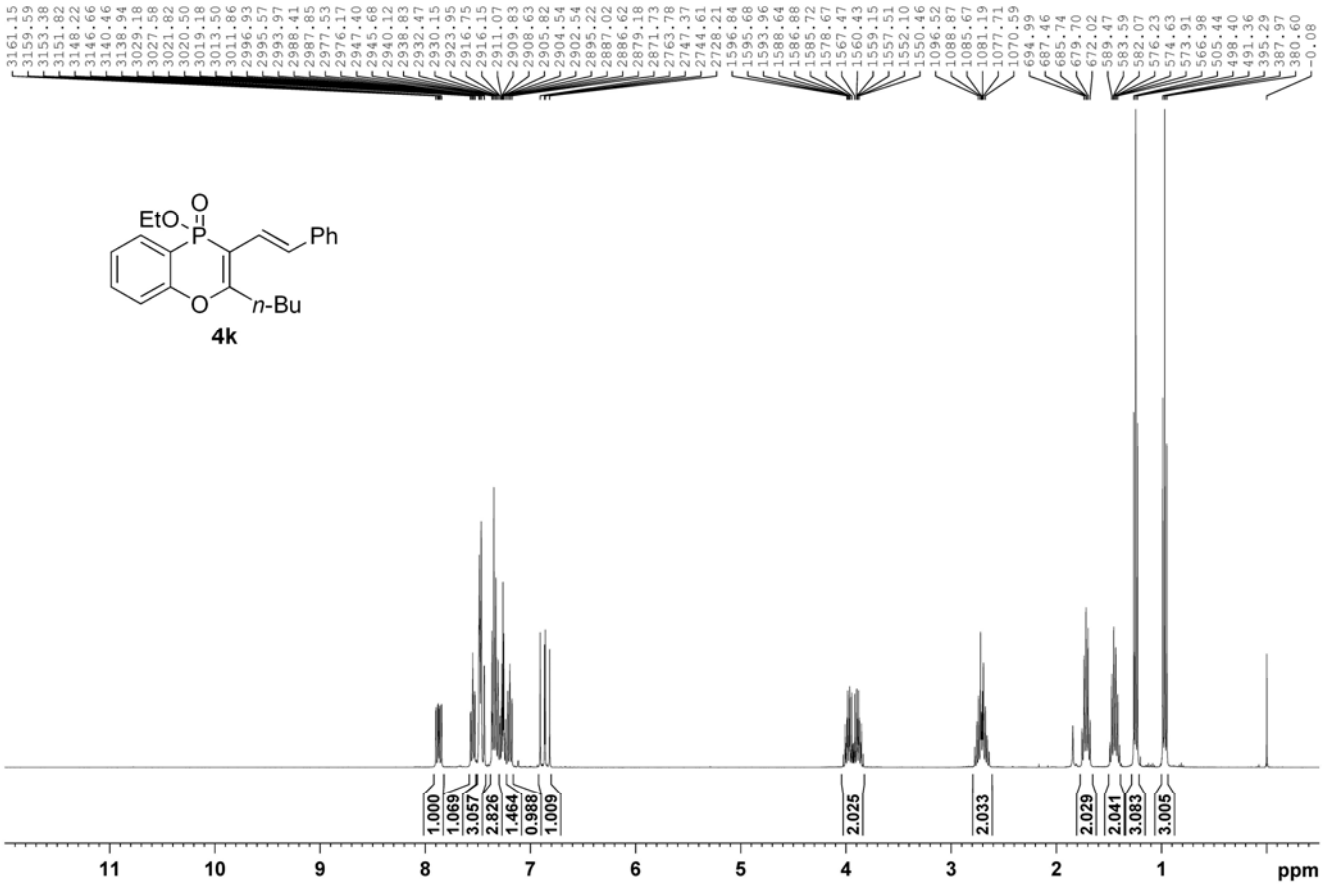

EtO
O
P
O
tert-Bu
4h
ppm

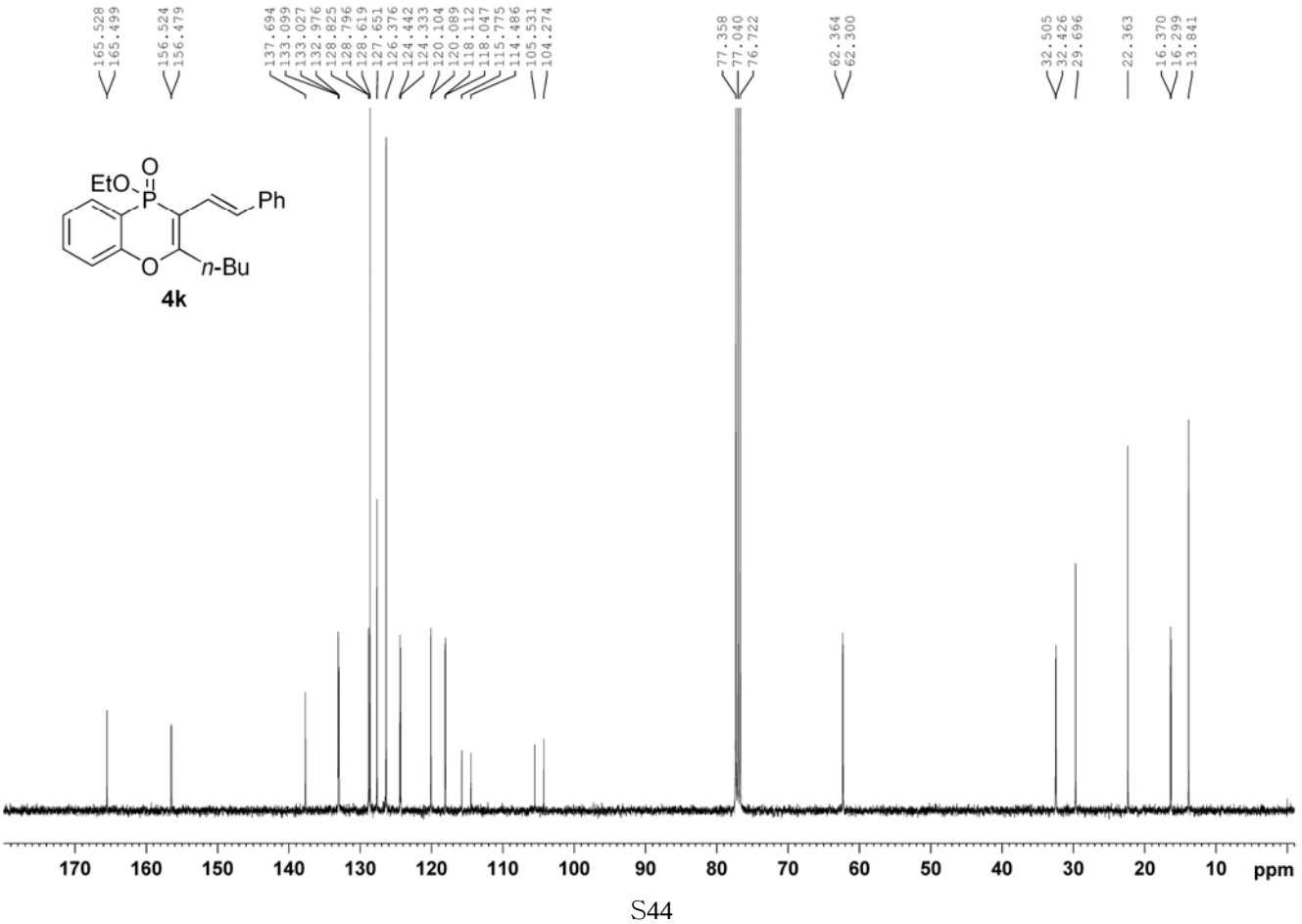

3084.08
3082.84
3070.56
3069.32
3021.46
2995.29
2992.45
2991.01
2983.77
2952.36
2950.20
2943.44
2941.92
2934.47
2933.23
2926.83
2906.22
2905.10
2900.86
2898.90
2896.82
2892.78
2891.58
2890.42
2857.21
2849.85
2848.81
2841.36
2680.87
2672.47
2668.39
2652.02
1616.89
1609.80
1608.68
1606.92
1602.72
1601.56
1599.88
1598.76
1595.56
1594.48
1592.80
1591.64
1587.44
1585.68
1584.55
1581.07
1577.51
1574.03
1572.87
1571.15
1566.95
1565.79
1564.11
1562.99
1559.87
1558.75
1557.03
1555.87
1551.70
1549.94
1548.78
1541.74
965.03
514.85
507.80
500.72
-0.08
EtO
O
P
Me
Ph
O
4i
1.000
1.112
2.027
4.068
1.191
1.041
1.015
2.039
3.037
3.059
11
10
9
8
7
6
5
4
3
2
1
ppm

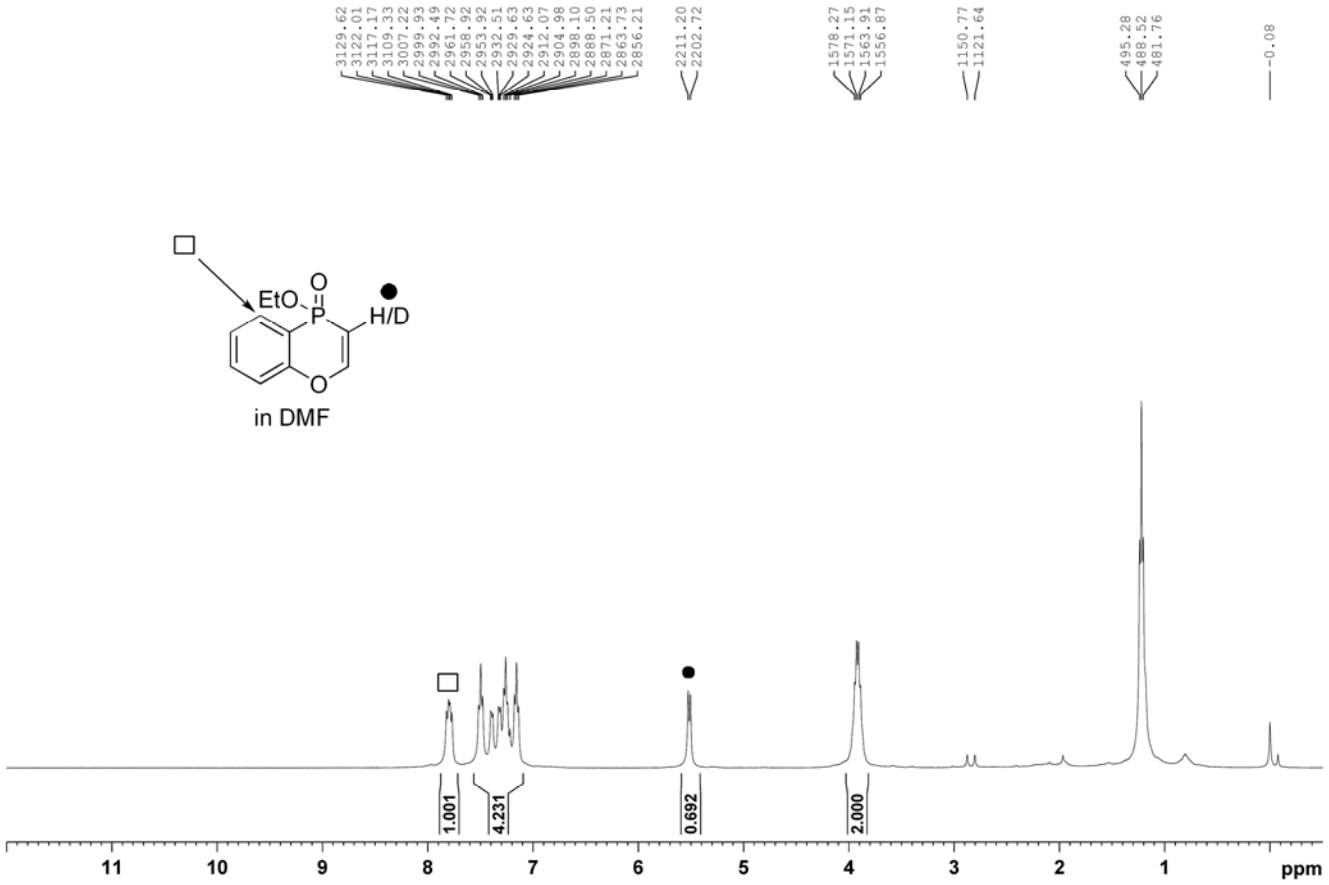

154.810
154.772
153.084
153.051
137.191
134.737
134.628
134.453
134.439
132.140
132.089
128.618
128.438
128.410
127.731
126.344
121.205
121.189
118.132
118.062
115.757
114.469
110.907
109.661
77.366
77.048
76.730
62.583
62.519
20.789
16.335
16.263
EtO
O
P
Me
Ph
O
4i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

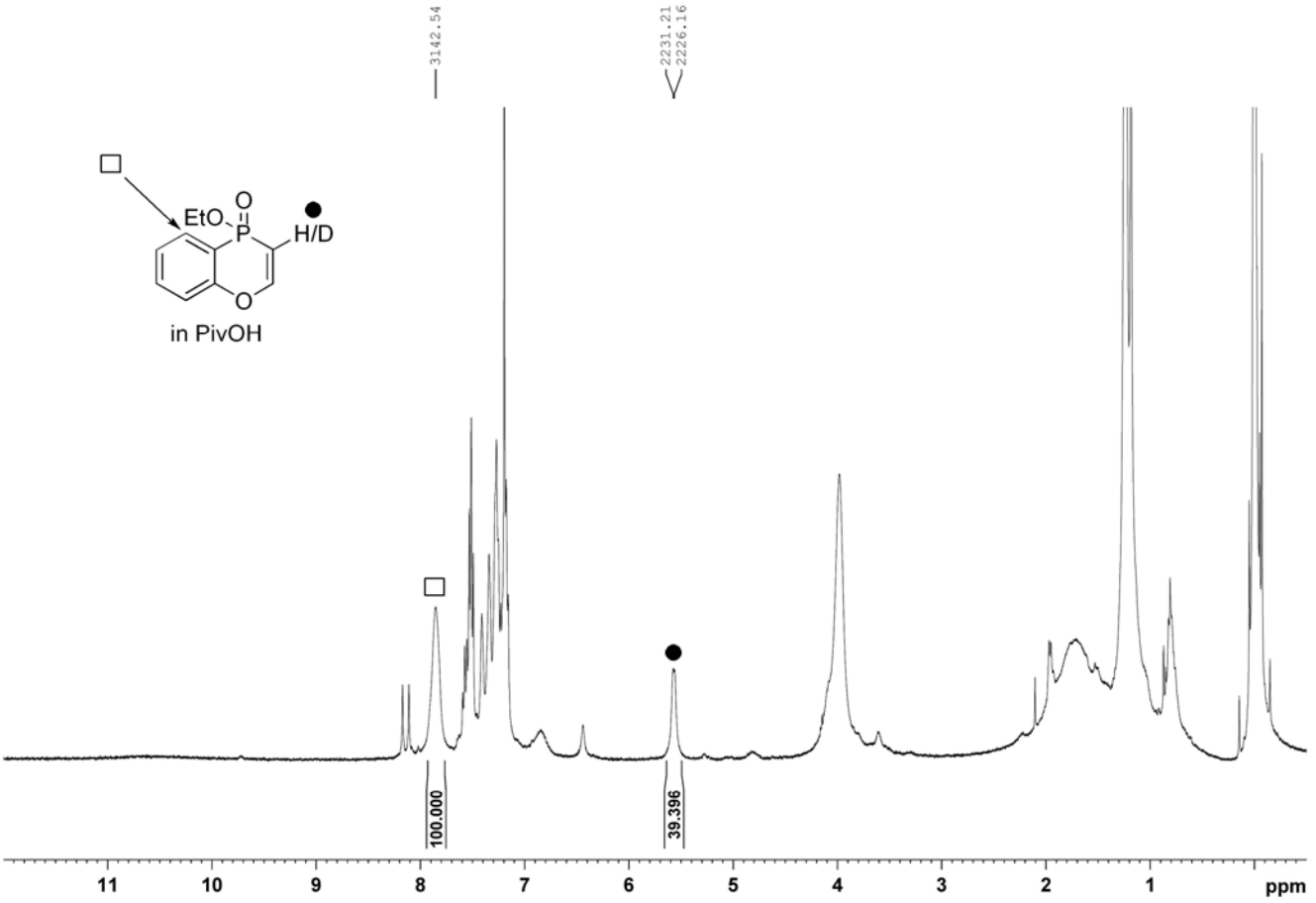

3127.26
3124.70
3113.85
3111.33
2989.49
2976.93
2974.37
2967.96
2965.40
2962.84
2959.68
2958.36
2951.12
2912.51
2911.03
2905.46
2897.70
2895.34
2881.74
2880.54
2879.30
2875.81
2873.25
2871.05
2867.13
2865.97
2864.81
2850.77
2843.40
2841.84
2834.48
2655.02
2638.58
2634.14
2617.69
1614.96
1607.88
1606.80
1605.04
1600.80
1599.64
1597.96
1592.56
1590.88
1589.76
1585.44
1582.67
1578.35
1575.59
1571.27
1570.11
1568.47
1563.03
1561.39
1560.19
1555.99
1554.27
1553.10
1546.06
494.48
487.44
480.40
-0.08
Cl
EtO
O
P
Ph
O
4j
1.000
4.292
3.251
1.303
1.148
1.054
2.177
3.096
11
10
9
8
7
6
5
4
3
2
1
ppm


153.901
153.865
151.717
151.685
135.874
132.559
132.546
131.802
131.750
129.335
129.199
127.637
127.318
127.287
126.944
125.375
119.551
119.531
119.142
119.071
116.715
115.446
110.284
109.014
76.342
76.023
75.706
61.979
61.914
15.338
15.267
Cl
EtO
O
P
Ph
O
4j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


EtO
O
P
Ph
n-Bu
O
4k
1.000
1.069
3.057
2.826
1.464
0.988
1.009
2.025
2.033
2.029
2.041
3.083
3.005
ppm


EtO
O
P
Ph
n-Bu
O
4k
ppm


3129.62
3122.01
3117.17
3109.33
3007.22
2999.93
2992.49
2961.72
2958.92
2953.92
2932.51
2929.63
2924.63
2912.07
2904.98
2898.10
2888.50
2871.21
2863.73
2856.21
2211.20
2202.72
1578.27
1571.15
1563.91
1556.87
1150.77
1121.64
495.28
488.52
481.76
-0.08
EtO
O
P
H/D
O
in DMF
1.001
4.231
0.692
2.000
11
10
9
8
7
6
5
4
3
2
1
ppm


3142.54
2231.21
2226.16
EtO
O
P
H/D
O
in PivOH
100.000
39.396
11
10
9
8
7
6
5
4
3
2
1
ppm