Supporting Information (SI)

Organocatalytic Asymmetric Decarboxylative Mannich Reaction of *β*-Keto Acids with Cyclic *α*-Ketiminophosphonates: Access to Quaternary *α*-Aminophosphonates

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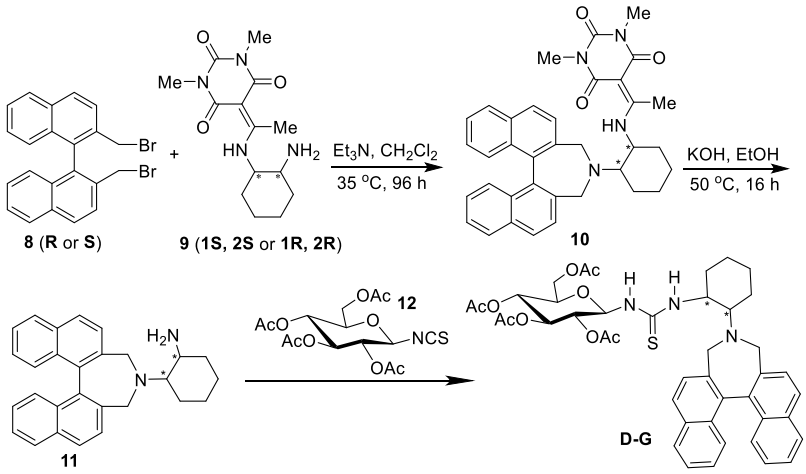
General information

^{1}H, ^{13}C, ^{31}P and ^{19}F were recorded on Bruker AV 400 MHz instrument at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), 162MHz (^{35}P NMR) as well as 376 MHz (^{19}F NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external CCl_3F, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br(broad). Coupling constants were reported in Hertz (Hz). MS were recorded on a VG ZABHS spectrometer with the ESI resource. High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker miorOTOF-QII instrument. Optical rotations were determined using an Autopol IV-T. IR spectra were recordedon an AVATAR 360 FT-IR spectromer. HPLC analyses were carried out on a SHIMADZU Model LC-2030C 3D instrument. X-ray structural analysis was conducted on the XtaLAB mini instrument.

Materials: Diethyl ether, THF and toluene were distilled from sodium/benzophenone prior to use; CCl_4 and CH_2Cl_2 was distilled from CaH_2, 5 Å MS is removed water by high temperature vacuum. All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography. All of the *β*-keto acids,[1] cyclic *α*-ketiminophosphonates,[2] and saccharide-based bifunctional thiourea catalysts **4a-g**[3-4] were prepared according to the reported procedures.

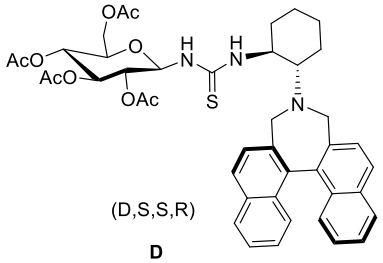
General procedure for the preparation of saccharide-based bifunctional thiourea catalysts



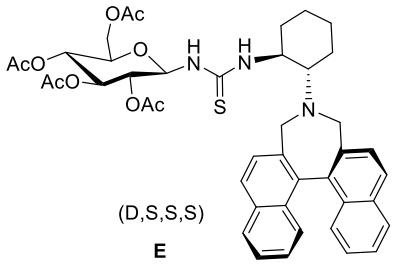
The preparation of 10:[4] A solution of (***R*** or ***S***)-2,2'-dibromomethyl-1,1'-binaphthalene **8** (726 mg, 1.65 mmol), Et_3N (277 μL, 3.3 mmol), and DAB-mono-protected (**1*S*, 2*S***) or (**1*R*, 2*R***)-cyclohexyldiamine **9** (441 mg, 1.5 mmol) in dry CH_2Cl_2 (15 mL) was stirred at 35 ℃ under a nitrogen atmosphere. After stirring for 96 h, the reaction mixture was quenched by the addition of water, extracted with EtOAc and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography to afford the product **10** (582 mg, 68% yield).

The preparation of 11:[4] A solution of **10** (572 mg, 1 mmol) and KOH (280 mg, 5 mmol) in 96% ethanol solution (15 mL) was stirred at 50 ℃ for 16 h under nitrogen atmosphere. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography to provide the product **11** (322 mg, 82% yield).

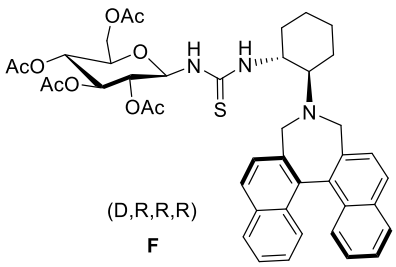
The preparation of saccharide-based bifunctional thiourea catalysts D-G:[3] To a stirred solution of **11** (392 mg, 1.0 mmol) in dry dichloromethane (5 mL) was added a solution of saccharide-derived isothiocyanates **12** (389 mg 1.0 mmol) in dry dichloromethane (5 mL) at 0 ℃. The mixture was stirred at room temperature for 24 h (TLC) and concentrated. The resulting residue was chromatographed with the eluent (PE/EA = 3/1, includig 5% MeOH) to give the light yellow solid **D-G**.



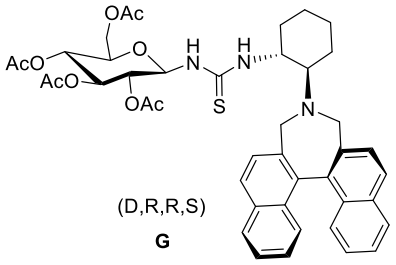
(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(3-((1*S*,2*S*)-2-(3*H*-dinaphtho[2,1-c:1',2'-e]azepin-4(5*H*)-yl)cyclohexyl)thioureido)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (D): light yellow solid; 547 mg, 70% yield; m.p.: 120-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 22.7, 8.2 Hz, 4H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 6.77 (s, 1H), 5.51 (s, 1H), 5.23 (t, *J* = 9.4 Hz, 1H), 5.00 (t, *J* = 9.7 Hz, 1H), 4.75 (s, 1H), 3.97 (d, *J* = 119.2 Hz, 3H), 3.65 (d, *J* = 11.4 Hz, 3H), 3.46 (d, *J* = 11.9 Hz, 2H), 2.62 (t, *J* = 9.4 Hz, 2H), 2.13 – 1.85 (m, 9H), 1.81 – 0.78 (m, 11H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.7, 170.8, 170.5, 169.8, 169.5, 134.8, 133.8, 132.9, 131.2, 128.7, 128.2, 128.0, 127.4, 125.8, 125.5, 82.5, 77.4, 73.2, 72.8, 70.6, 68.1, 67.9, 61.5, 56.9, 51.3, 32.5, 27.2, 25.5, 24.3, 20.7, 20.6, 20.5, 20.0; **HRMS (ESI)** found m/z 782.3110 $[M + H]^+$, calcd for $C_{43}H_{48}N_3O_9S$ 782.3111.



(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(3-((1*S*,2*S*)-2-((*S*)-3*H*-dinaphtho[2,1-c:1',2'-e]azepin-4(5*H*)-yl)cyclohexyl)thioureido)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (E): light yellow solid; 406 mg, 52% yield; m.p.: 119-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 14.6, 8.2 Hz, 4H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.57 – 7.36 (m, 4H), 7.33 – 7.16 (m, 2H), 6.32 (s, 1H), 5.43 (s, 1H), 5.22 (dt, *J* = 38.2, 8.7 Hz, 2H), 4.68 (s, 1H), 3.80 (d, *J* = 11.4 Hz, 2H), 3.69 – 3.13 (m, 5H), 2.83 (s, 1H), 2.27 – 1.93 (m, 10H), 1.75 (t, *J* = 21.4 Hz, 6H), 1.28 (ddd, *J* = 28.3, 22.8, 10.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.3, 171.2, 170.3, 170.2, 169.7, 135.3, 133.6, 133.2, 131.4, 129.1, 128.5, 127.8, 127.5, 126.2, 125.8, 83.0, 77.4, 73.3, 73.2, 70.6, 69.3, 68.4, 62.1, 53.6, 53.1, 33.2, 28.1, 25.5, 24.8, 21.04, 20.9, 20.8, 20.7; **HRMS (ESI)** found m/z 782.3111 $[M + H]^+$, calcd for $C_{43}H_{48}N_3O_9S$ 782.3111.

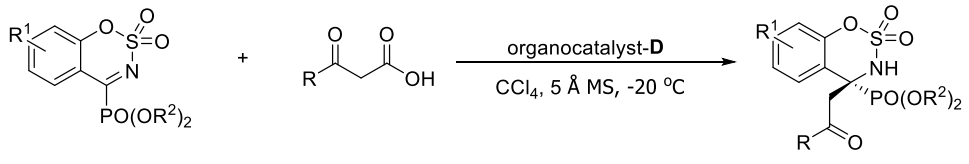


(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(3-((1*R*,2*R*)-2-(3*H*-dinaphtho[2,1-c:1',2'-e]azepin-4(5*H*)-yl)cyclohexyl)thioureido)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4,5-triyltriacetate (F): light yellow solid; 351 mg, 45% yield; m.p.: 170-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 13.6, 8.2 Hz, 4H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.36 (m, 4H), 7.30 – 7.21 (m, 2H), 6.67 (s, 1H), 5.77 (s, 1H), 5.35 (t, *J* = 9.3 Hz, 1H), 5.25 – 5.13 (m, 1H), 4.87 (s, 1H), 4.43 (dd, *J* = 12.3, 3.7 Hz, 1H), 4.21 (d, *J* = 11.2 Hz, 1H), 4.00 – 3.74 (m, 2H), 3.55 (s, 3H), 2.93 – 2.75 (m, 1H), 2.57 (s, 1H), 2.16 (s, 3H), 2.12 – 1.95 (m, 11H), 1.72 (dd, *J* = 19.2, 11.8 Hz, 3H), 1.37 – 1.19 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.0, 171.3, 170.8, 170.0, 169.8, 134.9, 134.4, 133.2, 131.4, 129.0, 128.4, 127.8, 127.5, 125.9, 125.6, 83.1, 77.4, 73.3, 73.0, 71.0, 69.5, 68.4, 62.1, 56.8, 52.2, 33.0, 27.7, 25.7, 24.6, 21.0, 21.0, 20.7, 20.71; **HRMS (ESI)** found m/z 782.3096 $[M + H]^+$, calcd for $C_{43}H_{48}N_3O_9S$ 782.3111.



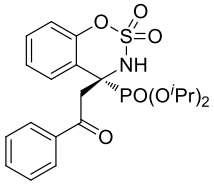
(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(3-((1*R*,2*R*)-2-((*S*)-3*H*-dinaphtho[2,1-c:1',2'-e]azepin-4(5*H*)-yl)cyclohexyl)thioureido)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (G): light yellow solid; 508 mg, 65% yield; m.p.: 132-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 13.4, 8.2 Hz, 4H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.19 (m, 2H), 6.69 (s, 1H), 5.63 (s, 1H), 5.31 (t, *J* = 9.4 Hz, 1H), 4.96 (dt, *J* = 19.6, 9.7 Hz, 2H), 4.26 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.02 (d, *J* = 11.2 Hz, 1H), 3.84 (t, *J* = 19.3 Hz, 2H), 3.55 (q, *J* = 12.5 Hz, 4H), 2.68 (dd, *J* = 32.1, 21.6 Hz, 2H), 2.00 (dd, *J* = 18.4, 2.0 Hz, 12H), 1.73 (t, *J* = 15.3 Hz, 3H), 1.46 (dd, *J* = 26.4, 13.1 Hz, 1H), 1.36 – 1.19 (m, 2H), 1.12 (dd, *J* = 22.8, 12.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.8, 171.8, 170.7, 169.9, 169.7, 134.9, 134.0, 133.1, 131.4, 128.9, 128.4, 128.2, 127.6, 125.9, 125.6, 83.0, 77.4, 73.4, 72.8, 71.2, 68.4, 67.6, 61.8, 56.4, 51.2, 32.9, 27.3, 25.9, 24.7, 20.9, 20.9, 20.7; **HRMS (ESI)** found m/z 782.3099 $[M + H]^+$, calcd for $C_{43}H_{48}N_3O_9S$ 782.3111.

General procedure for the Mannich reaction of *α*-ketiminophosphonates 1 with *β*-keto acids 2



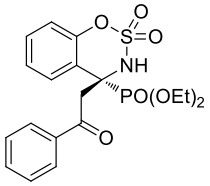
To a 10 mL Schlenk flask equipped with a stirring bar was added *α*-ketiminophosphonates **1**

(0.2 mmol), chiral novel bifunctional amine-thiourea (0.002 mmol, 1 mol %), 5 Å MS (400 mg) and *β*-keto acids **2** (0.3 mmol, 1.5 equiv). CCl_4 (2.0 mL) was added to the mixture. Then the resulting mixture was stirred at –20 °C until the completion of the reaction (monitored by TLC), concentrated under vacuum, and the residue was purified by flash chromatography on silica gel (eluting with dichloromethane/methanol = 160/1) to give the desired product **3**.



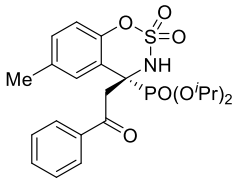
3a

(*R*)-diisopropyl(2,2-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3a): white solid; 78.5 mg; 84% yield; 99% ee; [determined by **HPLC** analysis Daicel Chirapak AS-H, *n*-Hex/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm UV detector, t_R = 12.0 min (minor) and t_R = 15.0 min (major)]; m.p.: 184-186 °C; $[\alpha]_D^{20}$ 7.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 4.0 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 4.66 (dq, *J* = 12.4, 6.2 Hz, 1H), 4.35 (dq, *J* = 12.5, 6.2 Hz, 1H), 4.09 (dd, *J* = 16.6, 6.1 Hz, 1H), 3.81 (dd, *J* = 26.4, 16.6 Hz, 1H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.18 (dd, *J* = 21.3, 6.2 Hz, 6H), 0.77 (d, *J* = 6.2 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.78 (d, *J* = 26.4 Hz, 1P) ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3 (d, *J* = 3.5 Hz), 150.2 (d, *J* = 7.3 Hz), 136.9, 134.0, 130.4 (d, *J* = 2.3 Hz), 128.8, 128.6, 128.0 (d, *J* = 3.3 Hz), 125.8 (d, *J* = 2.4 Hz), 121.0 (d, *J* = 4.5 Hz), 119.7 (d, *J* = 1.2 Hz), 73.8 (dd, *J* = 57.9, 8.0 Hz), 63.9, 62.3, 42.1 (d, *J* = 2.9 Hz), 24.2 (d, *J* = 2.6 Hz), 23.9 (d, *J* = 3.6 Hz), 23.5 (d, *J* = 5.5 Hz), 22.8 (d, *J* = 6.1 Hz); **HRMS (ESI)** found m/z 490.1067 $[M + Na]^+$, calcd for $C_{21}H_{26}NO_7NaPS$ 490.1065.



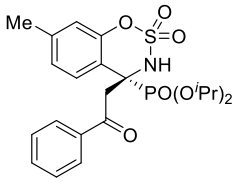
3b

(*R*)-diethyl(2,2-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3b): white solid; 80.8 mg; 92% yield; 99.5% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 80/20, 0.8 mL/min, 254 nm UV detector, t_R = 17.9 min (minor) and t_R = 20.1 min (major)]; m.p.: 197-199 °C; $[\alpha]_D^{20}$ 12.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 6.8 Hz, 1H), 7.58 (t, *J* = 6.6 Hz, 1H), 7.45 (t, *J* = 7.0 Hz, 2H), 7.41 – 7.32 (m, 1H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 4.25 – 3.82 (m, 5H), 3.72 (dd, *J* = 15.2, 7.6 Hz, 1H), 1.23 (t, *J* = 6.5 Hz, 3H), 1.03 (t, *J* = 6.7 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.50 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3 (d, *J* = 3.5 Hz), 150.1 (d, *J* = 7.1 Hz), 136.6, 134.1, 130.4 (d, *J* = 1.3 Hz), 128.8, 128.5, 127.9 (d, *J* = 3.0 Hz), 125.8, 120.87 (d, *J* = 3.6 Hz), 119.7, 64.6 (dd, *J* = 22.9, 7.8 Hz), 63.9, 62.2, 43.0, 16.2 (d, *J* = 5.6 Hz), 16.1 (d, *J* = 5.6 Hz); **HRMS** (ESI) found m/z 462.0753 $[M + Na]^+$, calcd for $C_{19}H_{22}NO_7NaPS$ 462.0752.



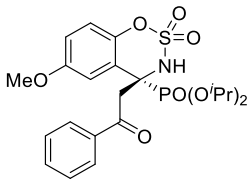
3c

(*R*)-diisopropyl(6-methyl-2,2-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3c): white solid; 83.0 mg; 86% yield; 97% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 80/20, 1 mL/min, 254 nm UV detector, t_R = 9.1 min (minor) and t_R = 12.0 min (major)]; m.p.: 172-175 °C; $[\alpha]_D^{20}$ 34 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 1H), 4.64 (dq, *J* = 12.3, 6.1 Hz, 1H), 4.35 (dq, *J* = 12.4, 6.1 Hz, 1H), 4.09 (dd, *J* = 16.6, 5.9 Hz, 1H), 3.76 (dd, *J* = 27.0, 16.6 Hz, 1H), 2.38 (s, 3H), 1.29 (d, *J* = 6.1 Hz, 3H), 1.17 (dd, *J* = 20.0, 6.1 Hz, 6H), 0.78 (d, *J* = 6.1 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.80 (d, *J* = 26.8 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4 (d, *J* = 3.1 Hz), 148.0 (d, *J* = 7.3 Hz), 136.9, 135.7 (d, *J* = 2.5 Hz), 133.9, 131.0 (d, *J* = 2.2 Hz), 128.7, 128.6, 128.1 (d, *J* = 3.3 Hz), 120.5 (d, *J* = 4.5 Hz), 119.4 (d, *J* = 0.8 Hz), 73.8 (dd, *J* = 87.3, 8.0 Hz), 63.6, 62.5, 42.0 (d, *J* = 2.9 Hz), 24.2 (d, *J* = 2.6 Hz), 24.0 (d, *J* = 3.6 Hz), 23.5 (d, *J* = 5.5 Hz), 22.8 (d, *J* = 6.0 Hz); **HRMS** (ESI) found m/z 482.1390 $[M + H]^+$, calcd for $C_{22}H_{29}NO_7PS$ 482.1402.



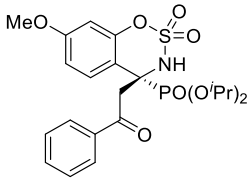
3d

(*R*)-diisopropyl(7-methyl-2,2-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3d): white solid; 85.0 mg; 88% yield; 90% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 80/20, 1 mL/min, 254 nm UV detector, t_R = 15.3 min (minor) and t_R = 18.8 min (major)]; m.p.: 192-195 °C; $[\alpha]_D^{20}$ 27.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.3 Hz, 2H), 7.69 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 3.9 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.89 (s, 1H), 4.73 – 4.54 (m, 1H), 4.44 – 4.24 (m, 1H), 4.07 (dd, *J* = 16.5, 6.0 Hz, 1H), 3.73 (dd, *J* = 26.6, 16.5 Hz, 1H), 2.36 (s, 3H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.20 (d, *J* = 6.1 Hz, 3H), 1.12 (d, *J* = 6.2 Hz, 3H), 0.78 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.90 (d, *J* = 26.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4 (d, *J* = 3.3 Hz), 150.0 (d, *J* = 7.3 Hz), 141.2 (d, *J* = 2.5 Hz), 137.0, 133.9, 128.7 (d, *J* = 14.0 Hz), 127.7 (d, *J* = 3.3 Hz), 126.7 (d, *J* = 2.5 Hz), 119.9 (d, *J* = 1.2 Hz), 117.8 (d, *J* = 4.6 Hz), 74.0 (d, *J* = 7.8 Hz), 73.4 (d, *J* = 8.2 Hz), 63.7, 62.1, 42.0 (d, *J* = 3.3 Hz), 24.2 (d, *J* = 2.5 Hz), 23.9 (d, *J* = 3.6 Hz), 23.5 (d, *J* = 5.5 Hz), 22.8 (d, *J* = 6.1 Hz), 21.0; **HRMS** (ESI) found m/z 504.1223 $[M + Na]^+$, calcd for $C_{22}H_{28}NO_7NaPS$ 504.1222.



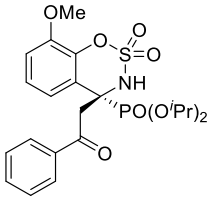
3e

(*R*)-diisopropyl(6-methoxy-2,2-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3e): white solid; 84.0 mg; 84% yield; 96.7% ee; [determined by **HPLC** analysis Daicel Chirapak, AS-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 15.2 min (minor) and t_R = 22.9 min (major)]; m.p.: 174-177 °C; $[\alpha]_D^{20}$ -2 (*c* 0.1, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.34 (s, 1H), 7.18 (s, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 6.93 – 6.84 (m, 1H), 4.64 (dq, *J* = 12.4, 6.2 Hz, 1H), 4.41 (dq, *J* = 12.5, 6.2 Hz, 1H), 4.05 (dd, *J* = 16.6, 6.2 Hz, 1H), 3.93 – 3.62 (m, 4H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 6.1 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.83 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.79 (dd, *J* = 26.0, 3.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2 (d, *J* = 3.2 Hz), 157.0 (d, *J* = 2.6 Hz), 143.8 (d, *J* = 7.3 Hz), 136.9, 134.0, 128.8, 128.7, 121.7 (d, *J* = 4.6 Hz), 120.4, 115.8 (d, *J* = 2.3 Hz), 112.8 (d, *J* = 3.2 Hz), 73.8 (dd, *J* = 55.2, 8.0 Hz), 63.9, 62.3, 55.9, 42.1 (d, *J* = 2.7 Hz), 24.2 (d, *J* = 2.7 Hz), 24.0 (d, *J* = 3.6 Hz), 23.5 (d, *J* = 5.5 Hz), 22.9 (d, *J* = 6.0 Hz); **HRMS** (ESI) found m/z 520.1171 $[M + Na]^+$, calcd for $C_{22}H_{28}NO_8NaPS$ 520.1171.



3f

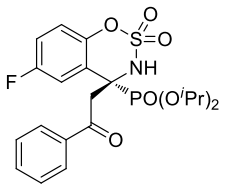
(*R*)-diisopropyl(7-methoxy-2,2-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3f): white solid; 71.6 mg; 72% yield; 96% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 80/20, 1 mL/min, 254 nm UV detector, t_R = 16.9 min (minor) and t_R = 20.8 min (major)]; m.p.: 179-183 °C; $[\alpha]_D^{20}$ -2.4 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.59 (t, *J* = 7.1 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 2.8 Hz, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 6.59 (s, 1H), 4.63 (dq, *J* = 12.1, 5.9 Hz, 1H), 4.34 (dq, *J* = 12.0, 5.9 Hz, 1H), 4.04 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.81 (s, 3H), 3.71 (dd, *J* = 26.1, 16.5 Hz, 1H), 1.28 (d, *J* = 6.0 Hz, 3H), 1.21 (d, *J* = 6.0 Hz, 3H), 1.12 (d, *J* = 6.0 Hz, 3H), 0.82 (d, *J* = 6.0 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.97 (d, *J* = 26.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5 (d, *J* = 3.5 Hz), 160.9 (d, *J* = 1.9 Hz), 151.0 (d, *J* = 7.3 Hz), 137.0, 133.9, 128.7, 128.6, 112.6 (d, *J* = 2.0 Hz), 112.4 (d, *J* = 4.5 Hz), 104.3, 74.0 (d, *J* = 7.8 Hz), 73.4 (d, *J* = 8.2 Hz), 63.4, 61.8, 55.7, 42.0 (d, *J* = 3.5 Hz), 24.3 (d, *J* = 2.2 Hz), 23.9 (d, *J* = 3.6 Hz), 23.5 (d, *J* = 5.4 Hz), 22.9 (d, *J* = 6.1 Hz); **HRMS** (ESI) found m/z 520.1175 $[M + Na]^+$, calcd for $C_{22}H_{28}NO_8NaPS$ 520.1171.



3g

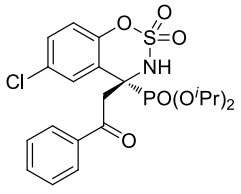
(*R*)-diisopropyl(8-methoxy-2,2-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3g): white solid; 84.0 mg; 84% yield; 98.5% ee; [determined by

HPLC analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 80/20, 1 mL/min, 254 nm UV detector, t_R = 18.6 min (major) and t_R = 41.7 min (minor)]; m.p.: 184-187 °C; $[\alpha]_D^{20}$ 2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.20 (dd, *J* = 10.4, 5.4 Hz, 2H), 6.95 (d, *J* = 8.2 Hz, 1H), 4.64 (dq, *J* = 12.3, 6.1 Hz, 1H), 4.36 (dq, *J* = 12.4, 6.2 Hz, 1H), 4.07 (dd, *J* = 16.7, 6.0 Hz, 1H), 3.95 – 3.70 (m, 4H), 1.29 (d, *J* = 6.1 Hz, 3H), 1.20 (d, *J* = 6.1 Hz, 3H), 1.14 (d, *J* = 6.1 Hz, 3H), 0.79 (d, *J* = 6.1 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.71 (d, *J* = 26.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4 (d, *J* = 3.4 Hz), 149.4 (d, *J* = 0.9 Hz), 140.0 (d, *J* = 7.4 Hz), 137.0, 133.9, 128.7, 128.6, 125.5 (d, *J* = 2.5 Hz), 122.0 (d, *J* = 4.2 Hz), 118.9 (d, *J* = 3.3 Hz), 112.8 (d, *J* = 2.1 Hz), 73.8 (dd, *J* = 52.9, 8.0 Hz), 64.1, 62.5, 56.4, 42.1 (d, *J* = 2.9 Hz), 24.2 (d, *J* = 2.6 Hz), 24.0 (d, *J* = 3.6 Hz), 23.6 (d, *J* = 5.5 Hz), 22.8 (d, *J* = 6.2 Hz); **HRMS** (ESI) found m/z 520.1165 $[M + Na]^+$, calcd for $C_{22}H_{28}NO_8NaPS$ 520.1171.



3h

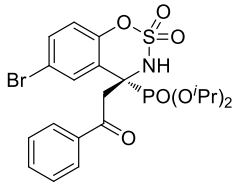
(*R*)-diisopropyl(6-fluoro-2,2-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3h): white solid; 80.0 mg; 82% yield; 95% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 26.0 min (minor) and t_R = 38.8 min (major)]; m.p.: 195-197 °C; $[\alpha]_D^{20}$ 20.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.61 (dt, *J* = 17.8, 12.2 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.27 (s, 1H), 7.14 – 7.01 (m, 2H), 4.67 (dq, *J* = 12.4, 6.2 Hz, 1H), 4.47 (dd, *J* = 12.5, 6.3 Hz, 1H), 4.04 (dd, *J* = 16.7, 6.1 Hz, 1H), 3.80 (dd, *J* = 25.3, 16.7 Hz, 1H), 1.29 (d, *J* = 6.1 Hz, 3H), 1.24 (d, *J* = 6.1 Hz, 3H), 1.16 (d, *J* = 6.1 Hz, 3H), 0.89 (d, *J* = 6.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.17 – -114.38 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.27 (d, *J* = 25.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7 (d, *J* = 3.8 Hz), 159.4 (dd, *J* = 246.0, 3.0 Hz), 146.1 (dd, *J* = 7.2, 2.7 Hz), 136.7, 134.1, 128.8, 128.6, 122.8 (dd, *J* = 7.9, 4.5 Hz), 121.1 (dd, *J* = 8.5, 1.1 Hz), 117.3 (dd, *J* = 23.7, 2.3 Hz), 114.8 (dd, *J* = 26.5, 3.2 Hz), 74.1 (dd, *J* = 26.8, 8.0 Hz), 63.8 (d, *J* = 1.7 Hz), 62.2 (d, *J* = 1.7 Hz), 42.0 (d, *J* = 2.3 Hz), 24.1 (dd, *J* = 15.7, 3.2 Hz), 23.5 (d, *J* = 5.6 Hz), 23.0 (d, *J* = 5.9 Hz); **HRMS** (ESI) found m/z 508.0972 $[M + Na]^+$, calcd for $C_{21}H_{25}NO_7NaPSF$ 508.0971.



3i

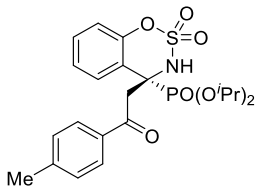
(*R*)-diisopropyl(6-chloro-2,2-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3i): white solid; 85.0 mg; 85% yield; 97% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 80/20, 1 mL/min, 254 nm UV detector, t_R = 9.4 min (minor) and t_R = 20.3 min (major)]; m.p.: 191-193 °C; $[\alpha]_D^{20}$ 35.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR

(400 MHz, $CDCl_3$) δ 8.06 – 7.91 (m, 2H), 7.79 (t, J = 2.2 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.39 – 7.29 (m, 1H), 7.25 (s, 1H), 7.03 (d, J = 8.8 Hz, 1H), 4.67 (dh, J = 12.3, 6.2 Hz, 1H), 4.55 – 4.38 (m, 1H), 4.03 (dd, J = 16.7, 6.1 Hz, 1H), 3.80 (dd, J = 25.6, 16.7 Hz, 1H), 1.29 (d, J = 6.2 Hz, 3H), 1.24 (d, J = 6.2 Hz, 3H), 1.18 (d, J = 6.2 Hz, 3H), 0.89 (d, J = 6.2 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.20 (d, J = 25.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (dd, J = 3.6, 1.2 Hz), 148.6 (d, J = 7.1 Hz), 136.7, 134.1, 131.2 (d, J = 3.0 Hz), 130.3 (d, J = 2.3 Hz), 128.8, 128.6, 127.8 (d, J = 3.3 Hz), 122.8 (d, J = 4.5 Hz), 121.0 (d, J = 1.2 Hz), 74.1 (dd, J = 19.9, 7.9 Hz), 63.8, 62.1, 42.0 (d, J = 2.0 Hz), 24.2 (d, J = 3.1 Hz), 24.0 (d, J = 3.4 Hz), 23.5 (d, J = 5.7 Hz), 23.0 (d, J = 5.8 Hz); **HRMS** (ESI) found m/z 524.0679 $[M + Na]^+$, calcd for $C_{21}H_{25}NO_7NaPSCl$ 524.0676.



3j

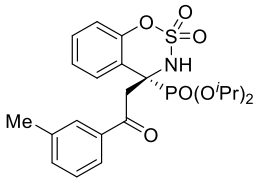
(*R*)-diisopropyl(6-bromo-2,2-dioxido-4-(2-oxo-2-phenylethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3j): white solid; 94.0 mg; 86% yield; 96% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 80/20, 1 mL/min, 254 nm UV detector, t_R = 9.5 min (minor) and t_R = 23.0 min (major)]; m.p.: 152-154 °C; $[\alpha]_D^{20}$ 38.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.93 (t, J = 2.1 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.54 – 7.42 (m, 3H), 7.24 (d, J = 2.9 Hz, 1H), 6.97 (d, J = 8.7 Hz, 1H), 4.68 (dq, J = 12.4, 6.2 Hz, 1H), 4.48 (dq, J = 12.5, 6.2 Hz, 1H), 4.02 (dd, J = 16.7, 6.1 Hz, 1H), 3.80 (dd, J = 25.6, 16.7 Hz, 1H), 1.30 (d, J = 6.2 Hz, 3H), 1.24 (d, J = 6.1 Hz, 3H), 1.19 (d, J = 6.2 Hz, 3H), 0.89 (d, J = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.21 (d, J = 25.5 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9 (d, J = 3.5 Hz), 149.2 (d, J = 7.0 Hz), 136.7, 134.1, 133.3 (d, J = 2.1 Hz), 130.7 (d, J = 3.2 Hz), 128.8, 128.6, 123.2 (d, J = 4.5 Hz), 121.3, 118.6 (d, J = 3.0 Hz), 74.1 (dd, J = 26.2, 7.9 Hz), 63.4, 62.3, 42.0 (d, J = 2.2 Hz), 24.2 (d, J = 3.0 Hz), 24.0 (d, J = 3.3 Hz), 23.5 (d, J = 5.7 Hz), 23.0 (d, J = 5.7 Hz); **HRMS** (ESI) found m/z 568.0165 $[M + Na]^+$, calcd for $C_{21}H_{25}NO_7NaPSBr$ 568.0170.



3k

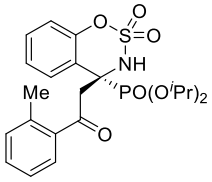
(*R*)-diisopropyl(2,2-dioxido-4-(2-oxo-2-(p-tolyl)ethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3k): white solid; 89.0 mg; 92% yield; 98% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm UV detector, t_R = 32.6 min (minor) and t_R = 37.5 min (major)]; m.p.: 189-190 °C; $[\alpha]_D^{20}$ 8 (*c* 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.3 Hz, 2H), 7.84 (dt, J = 8.0, 1.8 Hz, 1H), 7.38 (ddd, J = 8.3, 5.3, 3.7 Hz, 1H), 7.34 (d, J = 4.4 Hz, 1H), 7.29 (dd, J = 8.6, 1.8 Hz, 2H), 7.26 (s, 1H), 7.08 (d, J = 8.2 Hz, 1H), 4.65 (dq, J = 12.5, 6.2 Hz, 1H), 4.35 (dq, J = 12.5, 6.2 Hz, 1H), 4.06 (dd, J = 16.6, 6.1 Hz, 1H), 3.77 (dd, J = 26.1, 16.6 Hz, 1H), 2.42 (s, 3H), 1.30 (d, J = 6.2 Hz, 3H), 1.20 (d, J = 6.2 Hz, 3H), 1.15 (d, J = 6.2 Hz, 3H), 0.77 (d, J = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.80 (d, J

= 26.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0 (d, J = 3.7 Hz), 150.3 (d, J = 7.2 Hz), 145.1, 134.5, 130.4 (d, J = 2.3 Hz), 129.5, 128.8, 128.1 (d, J = 3.3 Hz), 125.9 (d, J = 2.4 Hz), 121.1 (d, J = 4.3 Hz), 119.7 (d, J = 1.2 Hz), 73.9 (dd, J = 58.9, 8.0 Hz), 64.1, 62.4, 41.8 (d, J = 2.8 Hz), 24.3 (d, J = 2.6 Hz), 24.0 (d, J = 3.6 Hz), 23.7 (d, J = 5.5 Hz), 22.8 (d, J = 6.2 Hz), 21.8; **HRMS** (ESI) found m/z 482.1394 $[M + H]^+$, calcd for $C_{22}H_{29}NO_7PS$ 482.1402.



3l

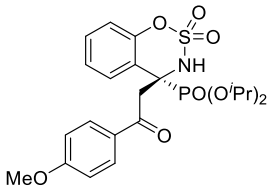
(*R*)-diisopropyl(2,2-dioxido-4-(2-oxo-2-(m-tolyl)ethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3l): white solid; 80.0 mg; 83% yield; 95% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 23.3 min (minor) and t_R = 25.7 min (major)]; m.p.: 163-166^{o}C; $[\alpha]_D^{20}$ 6 (*c* 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 14.6, 8.2 Hz, 3H), 7.44 – 7.23 (m, 5H), 7.08 (d, J = 8.1 Hz, 1H), 4.67 (dq, J = 12.4, 6.2 Hz, 1H), 4.36 (dq, J = 12.4, 6.2 Hz, 1H), 4.05 (dd, J = 16.8, 6.2 Hz, 1H), 3.82 (dd, J = 25.7, 16.8 Hz, 1H), 2.40 (s, 3H), 1.30 (d, J = 6.1 Hz, 3H), 1.19 (dd, J = 14.0, 6.1 Hz, 6H), 0.77 (d, J = 6.1 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.80 (d, J = 25.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6 (d, J = 3.8 Hz), 150.2 (d, J = 7.2 Hz), 138.6, 136.9, 134.8, 130.4 (d, J = 2.3 Hz), 129.0, 128.7, 128.1 (d, J = 3.3 Hz), 125.9 (d, J = 3.1 Hz), 121.1 (d, J = 4.3 Hz), 119.7 (d, J = 1.1 Hz), 73.9 (dd, J = 53.6, 8.0 Hz), 64.0, 62.3, 42.2 (d, J = 2.4 Hz), 24.3 (d, J = 2.6 Hz), 24.0 (d, J = 3.6 Hz), 23.6 (d, J = 5.5 Hz), 22.8 (d, J = 6.1 Hz), 21.4; **HRMS** (ESI) found m/z 504.1221 $[M + Na]^+$, calcd for $C_{22}H_{28}NO_7NaPS$ 504.1222.



3m

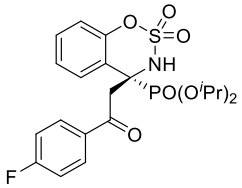
(*R*)-diisopropyl(2,2-dioxido-4-(2-oxo-2-(o-tolyl)ethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3m): white solid; 83.8 mg; 87% yield; 94% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 15.2 min (minor) and t_R = 24.8 min (major)]; m.p.: 124-126 ^{o}C; $[\alpha]_D^{20}$ 17.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, J = 23.6, 7.8 Hz, 2H), 7.38 (dd, J = 14.4, 6.3 Hz, 3H), 7.26 (dd, J = 19.2, 7.6 Hz, 3H), 7.08 (d, J = 8.2 Hz, 1H), 4.74 (dq, J = 12.4, 6.2 Hz, 1H), 4.36 (dq, J = 12.5, 6.2 Hz, 1H), 3.96 (dd, J = 17.0, 6.2 Hz, 1H), 3.79 (dd, J = 26.3, 17.0 Hz, 1H), 2.46 (s, 3H), 1.33 (d, J = 6.1 Hz, 3H), 1.27 – 1.14 (m, 6H), 0.76 (d, J = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.96 (d, J = 26.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3 (d, J = 3.5 Hz), 150.1 (d, J = 7.2 Hz), 138.7, 137.6, 132.1 (d, J = 5.3 Hz), 130.3 (d, J = 2.3 Hz), 129.1, 127.9 (d, J = 3.4 Hz), 125.8 (d, J = 3.6 Hz), 121.0 (d, J = 4.5 Hz), 119.6 (d, J = 1.2 Hz), 73.8 (dd, J = 41.5, 8.0 Hz), 64.1, 62.5, 44.9 (d, J = 3.0 Hz), 24.2 (d, J = 2.6 Hz), 24.1 (d, J = 3.6 Hz), 23.7 (d, J = 5.5 Hz), 22.8 (d, J = 6.2 Hz), 21.2;

HRMS (ESI) found m/z 504.1209 $[M + Na]^+$, calcd for $C_{22}H_{28}NO_7NaPS$ 504.1222.



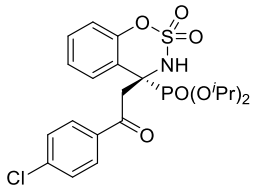
3n

(*R*)-diisopropyl(4-(2-(4-methoxyphenyl)-2-oxoethyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3n): white solid; 84.0 mg; 84% yield; 98.8% ee; [determined by **HPLC** analysis Daicel Chirapak, AS-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 15.7 min (minor) and t_R = 19.7 min (major)]; m.p.: 194-196 °C; $[\alpha]_D^{20}$ 39.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.38 (dd, *J* = 15.0, 6.0 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.63 (dq, *J* = 12.4, 6.2 Hz, 1H), 4.33 (dq, *J* = 12.5, 6.2 Hz, 1H), 4.01 (dd, *J* = 16.3, 6.0 Hz, 1H), 3.87 (s, 3H), 3.72 (dd, *J* = 26.1, 16.3 Hz, 1H), 1.29 (d, *J* = 6.1 Hz, 3H), 1.19 (d, *J* = 6.1 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H), 0.75 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.78 (d, *J* = 25.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8 (d, *J* = 3.7 Hz), 164.3, 150.2 (d, *J* = 7.2 Hz), 131.1, 130.3 (d, *J* = 2.4 Hz), 129.9, 128.0 (d, *J* = 3.3 Hz), 125.8 (d, *J* = 2.4 Hz), 121.0 (d, *J* = 4.0 Hz), 119.6 (d, *J* = 1.1 Hz), 113.9, 73.8 (dd, *J* = 63.0, 8.0 Hz), 64.0, 62.4, 55.6, 41.3 (d, *J* = 2.7 Hz), 24.3 (d, *J* = 2.5 Hz), 23.9 (d, *J* = 3.7 Hz), 23.6 (d, *J* = 5.5 Hz), 22.7 (d, *J* = 6.2 Hz); **HRMS** (ESI) found m/z 520.1174 $[M + Na]^+$, calcd for $C_{22}H_{28}NO_8NaPS$ 520.1171.



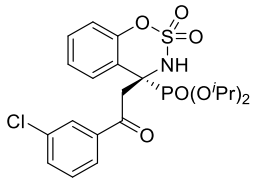
3o

(*R*)-diisopropyl(4-(2-(4-fluorophenyl)-2-oxoethyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3o): white solid; 90.0 mg; 93% yield; 96% ee; [determined by **HPLC** analysis Daicel Chirapak, AS-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 10.6 min (minor) and t_R = 15.4 min (major)]; m.p.: 178-180 °C; $[\alpha]_D^{20}$ 4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.19 – 7.00 (m, 4H), 4.65 (dq, *J* = 12.4, 6.2 Hz, 1H), 4.34 (dq, *J* = 12.5, 6.2 Hz, 1H), 4.06 (dd, *J* = 16.5, 6.0 Hz, 1H), 3.77 (dd, *J* = 26.7, 16.4 Hz, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.20 (d, *J* = 6.1 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H), 0.75 (d, *J* = 6.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.41 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.72 (d, *J* = 25.6 Hz) ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6 (d, J = 3.2 Hz), 166.3 (d, *J* = 256.5 Hz), 150.1 (d, *J* = 7.3 Hz), 133.4 (d, *J* = 2.9 Hz), 131.5, 131.4, 130.5 (d, *J* = 2.2 Hz), 128.0 (d, *J* = 3.3 Hz), 125.9 (d, *J* = 2.3 Hz), 120.9 (d, *J* = 4.6 Hz), 119.7, 116.1, 115.8, 73.9 (dd, J = 65.5, 8.0 Hz), 63.8, 62.2, 42.0 (d, *J* = 2.8 Hz), 24.2 (d, *J* = 2.4 Hz), 23.9 (d, *J* = 3.6 Hz), 23.6 (d, *J* = 5.5 Hz), 22.7 (d, *J* = 6.1 Hz); **HRMS** (ESI) found m/z 508.0973 $[M + Na]^+$, calcd for $C_{21}H_{25}NO_7NaPSF$ 508.0971.



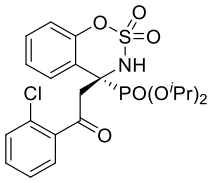
3p

(*R*)-diisopropyl(4-(2-(4-chlorophenyl)-2-oxoethyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3p): white solid; 91.0 mg; 90% yield; 98% ee; [determined by **HPLC** analysis Daicel Chirapak, AS-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 11.1 min (minor) and t_R = 16.1 min (major)]; m.p.: 188-191 ^oC; $[\alpha]_D^{20}$ 28.8 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.83 (dt, *J* = 7.9, 1.6 Hz, 1H), 7.50 – 7.36 (m, 3H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 2H), 4.74 – 4.57 (m, 1H), 4.43 – 4.26 (m, 1H), 4.06 (dd, *J* = 16.5, 6.1 Hz, 1H), 3.78 (dd, *J* = 26.6, 16.5 Hz, 1H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 6.1 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H), 0.76 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.65 (d, *J* = 26.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0 (d, *J* = 3.3 Hz), 150.1 (d, *J* = 7.3 Hz), 140.5, 135.3, 130.5 (d, *J* = 2.4 Hz), 130.0, 129.1, 128.0 (d, *J* = 3.4 Hz), 125.9 (d, *J* = 2.5 Hz), 120.8 (d, *J* = 4.7 Hz), 119.7 (d, *J* = 1.2 Hz), 74.0 (dd, *J* = 62.7, 8.0 Hz), 63.78, 62.2, 42.2 (d, *J* = 2.9 Hz), 24.2 (d, *J* = 2.5 Hz), 23.9 (d, *J* = 3.6 Hz), 23.6 (d, *J* = 5.5 Hz), 22.8 (d, *J* = 6.2 Hz); **HRMS** (ESI) found m/z 524.0665 $[M + Na]^+$, calcd for $C_{21}H_{25}NO_7NaPSCl$ 524.0676.



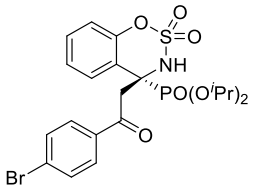
3q

(*R*)-diisopropyl(4-(2-(3-chlorophenyl)-2-oxoethyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3q): white solid; 81.0 mg; 80% yield; 95% ee; [determined by **HPLC** analysis Daicel Chirapak, AS-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 18.8 min (minor) and t_R = 22.4 min (major)]; m.p.: 171-173 ^oC; $[\alpha]_D^{20}$ 22 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (t, *J* = 1.8 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.82 (dt, *J* = 8.0, 1.7 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.47 – 7.35 (m, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 6.98 (s, 1H), 4.75 – 4.59 (m, 1H), 4.44 – 4.26 (m, 1H), 4.04 (dd, *J* = 16.7, 6.2 Hz, 1H), 3.79 (dd, *J* = 26.6, 16.7 Hz, 1H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.18 (dd, *J* = 12.4, 6.2 Hz, 6H), 0.76 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.66 (dd, *J* = 26.5, 5.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9 (d, *J* = 3.1 Hz), 150.1 (d, *J* = 7.2 Hz), 138.4, 135.1, 133.8, 130.5 (d, *J* = 2.3 Hz), 130.1, 128.5, 128.0 (d, *J* = 3.4 Hz), 126.7, 125.9 (d, *J* = 2.4 Hz), 120.8 (d, *J* = 4.9 Hz), 119.7 (d, *J* = 1.1 Hz), 74.0 (dd, *J* = 54.5, 8.0 Hz), 63.7, 62.1, 42.5 (d, *J* = 2.9 Hz), 24.2 (d, *J* = 2.6 Hz), 24.0 (d, *J* = 3.6 Hz), 23.6 (d, *J* = 5.5 Hz), 22.8 (d, *J* = 6.1 Hz); **HRMS** (ESI) found m/z 524.0676 $[M + Na]^+$, calcd for $C_{21}H_{25}NO_7NaPSCl$ 524.0676.



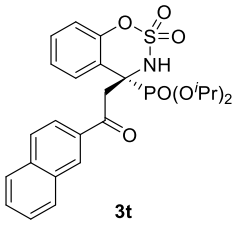
3r

(*R*)-diisopropyl(4-(2-(2-chlorophenyl)-2-oxoethyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3r): white solid; 83.0 mg; 83% yield; 95% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 36.9 min (minor) and t_R = 52.0 min (major)]; m.p.: 188-190 ^oC; $[\alpha]_D^{20}$ -12.4 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.28 (m, 4H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 3.2 Hz, 1H), 4.78 (dh, *J* = 12.4, 6.1 Hz, 1H), 4.43 – 4.29 (m, 1H), 4.04 – 3.86 (m, 2H), 1.34 (d, *J* = 6.2 Hz, 3H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 6.1 Hz, 3H), 0.77 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.64 (d, *J* = 23.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8 (d, *J* = 4.0 Hz), 150.1 (d, *J* = 7.2 Hz), 138.9, 132.6, 131.2, 130.8 – 130.3 (m), 129.9, 128.0 (d, *J* = 3.4 Hz), 127.2, 125.9 (d, *J* = 2.4 Hz), 120.9 (d, *J* = 4.9 Hz), 119.8 (d, *J* = 1.2 Hz), 77.5, 77.2, 76.8, 74.0 (dd, *J* = 15.0, 7.9 Hz), 64.0, 62.4, 46.9 (d, *J* = 2.9 Hz), 24.3 (d, *J* = 2.6 Hz), 24.2 (d, *J* = 3.5 Hz), 23.8 (d, *J* = 5.6 Hz), 22.9 (d, *J* = 6.2 Hz); **HRMS** (ESI) found m/z 524.0685 $[M + Na]^+$, calcd for $C_{21}H_{25}NO_7NaPSCl$ 524.0676.



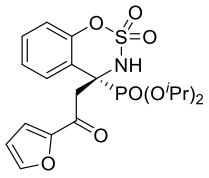
3s

(*R*)-diisopropyl(4-(2-(4-bromophenyl)-2-oxoethyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3s): white solid; 88.6 mg; 81% yield; 98% ee; [determined by **HPLC** analysis Daicel Chirapak, AS-H, *n*-Hex/*i*-PrOH = 95/15, 1 mL/min, 254 nm UV detector, t_R = 22.8 min (minor) and t_R = 33.0 min (major)]; m.p.: 187-190 ^oC; $[\alpha]_D^{20}$ 30.4 (*c* 0.5, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 12.6, 6.0 Hz, 2H), 4.65 (dq, *J* = 12.4, 6.2 Hz, 1H), 4.34 (dq, *J* = 12.5, 6.2 Hz, 1H), 4.04 (dd, *J* = 16.5, 6.1 Hz, 1H), 3.77 (dd, *J* = 26.7, 16.5 Hz, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.20 (d, *J* = 6.1 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.75 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.65 (d, *J* = 27.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3 (d, *J* = 3.2 Hz), 150.2 (d, *J* = 7.3 Hz), 135.8, 132.2, 131.9, 130.6 (d, *J* = 2.3 Hz), 130.2, 128.1 (d, *J* = 3.4 Hz), 126.0 (d, *J* = 2.4 Hz), 120.9 (d, *J* = 4.8 Hz), 119.9 (d, *J* = 1.1 Hz), 74.1 (dd, *J* = 62.4, 8.0 Hz), 63.9, 62.3, 42.3 (d, *J* = 3.0 Hz), 24.4 (d, *J* = 2.5 Hz), 24.1 (d, *J* = 3.6 Hz), 23.7 (d, *J* = 5.5 Hz), 22.9 (d, *J* = 6.2 Hz); **HRMS** (ESI) found m/z 546.0343 $[M + H]^+$, calcd for $C_{21}H_{26}NO_7PSBr$ 546.0351.



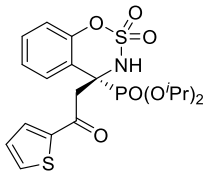
3t

(*R*)-diisopropyl(4-(2-(naphthalen-2-yl)-2-oxoethyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3t): white solid; 92.0 mg; 89% yield; >99% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 80/20, 1 mL/min, 254 nm UV detector, t_R = 11.8 min (minor) and t_R = 18.0 min (major)]; m.p.: 191-194 °C; $[\alpha]_D^{20}$ 54 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.02 (dd, *J* = 15.3, 8.3 Hz, 2H), 7.90 (dd, *J* = 15.8, 7.6 Hz, 3H), 7.60 (dt, *J* = 14.6, 7.0 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 4.66 (dq, *J* = 12.1, 6.1 Hz, 1H), 4.36 (dq, *J* = 12.2, 6.1 Hz, 1H), 4.22 (dd, *J* = 16.5, 5.9 Hz, 1H), 3.94 (dd, *J* = 26.0, 16.5 Hz, 1H), 1.30 (d, *J* = 6.0 Hz, 3H), 1.21 (d, *J* = 6.0 Hz, 3H), 1.13 (d, *J* = 6.0 Hz, 3H), 0.76 (d, *J* = 6.0 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.81 (d, *J* = 25.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3 (d, *J* = 3.6 Hz), 150.4 (d, *J* = 7.1 Hz), 136.0, 134.3, 132.5, 131.0, 130.5 (d, *J* = 2.3 Hz), 130.0, 129.2, 128.8, 128.2 (d, *J* = 3.3 Hz), 127.9, 127.1, 126.0 (d, *J* = 2.3 Hz), 123.8, 121.1 (d, *J* = 4.2 Hz), 119.8 (d, *J* = 0.9 Hz), 74.0 (dd, *J* = 58.6, 8.0 Hz), 64.1, 62.5, 42.2 (d, *J* = 2.7 Hz), 24.4 (d, *J* = 2.5 Hz), 24.1 (d, *J* = 3.7 Hz), 23.7 (d, *J* = 5.4 Hz), 22.9 (d, *J* = 6.1 Hz); **HRMS** (ESI) found m/z 540.1227 $[M + Na]^+$, calcd for $C_{25}H_{28}NO_7NaPS$ 540.1222.



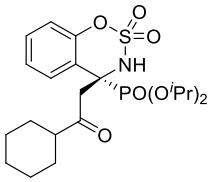
3u

(*R*)-diisopropyl(4-(2-(furan-2-yl)-2-oxoethyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3u): white solid; 74.1 mg; 81% yield; 98% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 80/20, 1 mL/min, 254 nm UV detector, t_R = 14.8 min (minor) and t_R = 22.8 min (major)]; m.p.: 168-171 °C; $[\alpha]_D^{20}$ 36.8 (*c* 1.9, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dt, *J* = 8.0, 1.8 Hz, 1H), 7.63 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.27 (td, *J* = 7.7, 1.1 Hz, 1H), 7.08 (s, 1H), 7.01 (d, *J* = 4.5 Hz, 1H), 6.56 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.74 – 4.55 (m, *J* = 6.2 Hz, 1H), 4.39 – 4.22 (m, 1H), 3.89 (dd, *J* = 16.0, 6.1 Hz, 1H), 3.69 (dd, *J* = 26.0, 16.0 Hz, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.18 (dd, *J* = 12.2, 6.2 Hz, 6H), 0.76 (d, *J* = 6.2 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.44 (d, *J* = 25.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.99 (d, *J* = 3.9 Hz), 152.42, 150.31 (d, *J* = 7.1 Hz), 147.67, 130.55 (d, *J* = 2.4 Hz), 128.25 (d, *J* = 3.4 Hz), 125.91 (d, *J* = 2.5 Hz), 120.72 (d, *J* = 4.4 Hz), 119.75 (d, *J* = 1.3 Hz), 119.63, 112.97, 73.91 (dd, *J* = 64.9, 8.0 Hz), 63.90, 62.28, 41.99 (d, *J* = 2.6 Hz), 24.35 (d, *J* = 2.5 Hz), 24.01 (d, *J* = 3.7 Hz), 23.63 (d, *J* = 5.4 Hz), 22.82 (d, *J* = 6.3 Hz); **HRMS** (ESI) found m/z 480.0842 $[M + Na]^+$, calcd for $C_{19}H_{24}NO_8NaPS$ 480.0858.



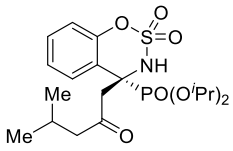
3v

(*R*)-diisopropyl(2,2-dioxido-4-(2-oxo-2-(thiophen-2-yl)ethyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3v): white solid; 77.9 mg; 82% yield; 96% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 80/20, 1 mL/min, 254 nm UV detector, t_R = 14.4 min (minor) and t_R = 22.2 min (major)]; m.p.: 172-174 °C; $[\alpha]_D^{20}$ 29.2 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.82 (m, 2H), 7.72 (dd, *J* = 4.9, 0.7 Hz, 1H), 7.47 – 7.35 (m, 1H), 7.34 – 7.24 (m, 1H), 7.16 (dd, *J* = 4.7, 4.1 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.73 – 4.55 (m, 1H), 4.41 – 4.24 (m, 1H), 3.96 (dd, *J* = 15.8, 6.0 Hz, 1H), 3.75 (dd, *J* = 26.3, 15.8 Hz, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 6.1 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.75 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.43 (d, *J* = 25.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5 (d, *J* = 3.7 Hz), 150.3 (d, *J* = 7.3 Hz), 144.3, 135.8, 134.1, 130.6 (d, *J* = 2.3 Hz), 128.6, 128.2 (d, *J* = 3.3 Hz), 125.9 (d, *J* = 2.5 Hz), 120.7 (d, *J* = 4.3 Hz), 119.8 (d, *J* = 1.2 Hz), 73.9 (dd, *J* = 72.6, 8.0 Hz), 63.9, 62.3, 42.7 (d, *J* = 2.6 Hz), 24.3 (d, *J* = 2.4 Hz), 24.0 (d, *J* = 3.8 Hz), 23.6 (d, *J* = 5.4 Hz), 22.8 (d, *J* = 6.3 Hz); **HRMS** (ESI) found m/z 496.0626 $[M + Na]^+$, calcd for $C_{19}H_{24}NO_7NaPS_2$ 496.0629.



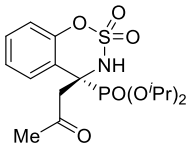
3w

(*R*)-diisopropyl(4-(2-cyclohexyl-2-oxoethyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3w): white solid; 72.0 mg; 76% yield; 93% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 190 nm UV detector, t_R = 17.7 min (major) and t_R = 22.6 min (minor)]; m.p.: 104-107 °C; $[\alpha]_D^{20}$ 1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dt, *J* = 8.0, 1.7 Hz, 1H), 7.42 – 7.32 (m, 1H), 7.25 (dd, *J* = 10.3, 3.7 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 1H), 4.80 – 4.65 (m, 1H), 4.40 – 4.26 (m, 1H), 3.54 – 3.32 (m, 2H), 2.38 (ddd, *J* = 11.1, 7.3, 3.3 Hz, 1H), 1.97 – 1.61 (m, 5H), 1.41 – 1.17 (m, 14H), 0.77 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.90 (d, *J* = 24.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.4 (d, *J* = 3.1 Hz), 150.1 (d, *J* = 7.2 Hz), 130.4 (d, *J* = 2.4 Hz), 127.9 (d, *J* = 3.4 Hz), 125.9 (d, *J* = 2.5 Hz), 121.2 (d, *J* = 4.5 Hz), 119.7 (d, *J* = 1.2 Hz), 73.9 (dd, *J* = 41.1, 8.1 Hz), 63.7, 62.1, 52.2, 44.4 (d, *J* = 3.1 Hz), 28.2, 28.0, 25.8, 25.6, 25.5, 24.3 (d, *J* = 2.6 Hz), 24.1 (d, *J* = 3.8 Hz), 23.9 (d, *J* = 5.3 Hz), 22.9 (d, *J* = 6.2 Hz); **HRMS** (ESI) found m/z 496.1534 $[M + Na]^+$, calcd for $C_{21}H_{32}NO_7NaPS$ 496.1535.



3x

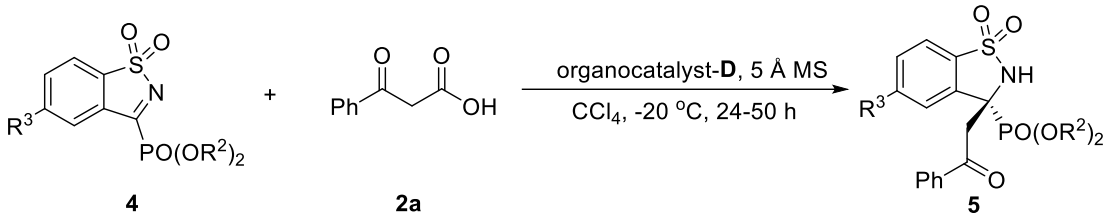
(*R*)-diisopropyl(4-(4-methyl-2-oxopentyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3x): white solid; 69.8 mg; 78% yield; 92.5% ee; [determined by **HPLC** analysis Daicel Chirapak, AS-H, *n*-Hex/*i*-PrOH = 90/10, 0.6 mL/min, 190 nm UV detector, t_R = 24.7 min (minor) and t_R = 27.1 min (major)]; m.p.: 65-67 °C; $[\alpha]_D^{20}$ -5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dt, *J* = 8.0, 1.8 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.30 – 7.22 (m, 1H), 7.12 (s, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 4.82 – 4.67 (m, *J* = 6.2 Hz, 1H), 4.42 – 4.28 (m, 1H), 3.49 – 3.23 (m, 2H), 2.37 (qd, *J* = 16.5, 6.9 Hz, 2H), 2.19 – 2.05 (m, 1H), 1.34 (dd, *J* = 13.0, 6.2 Hz, 6H), 1.21 (d, *J* = 6.2 Hz, 3H), 0.90 (dd, *J* = 9.1, 6.7 Hz, 6H), 0.78 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.11 – 15.41 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.0 (d, *J* = 3.6 Hz), 150.1 (d, *J* = 7.2 Hz), 130.4 (d, *J* = 2.4 Hz), 127.9 (d, *J* = 3.4 Hz), 125.9 (d, *J* = 2.5 Hz), 120.9 (d, *J* = 4.5 Hz), 119.7 (d, *J* = 1.2 Hz), 74.9 (d, *J* = 7.8 Hz), 73.6 (d, *J* = 8.2 Hz), 63.5, 61.9, 53.7, 46.5 (d, *J* = 2.7 Hz), 24.3 (d, *J* = 3.6 Hz), 24.0 (d, *J* = 3.9 Hz), 23.8 (d, *J* = 5.3 Hz), 22.8 (d, *J* = 6.2 Hz), 22.5; **HRMS** (ESI) found m/z 470.1378 $[M + Na]^+$, calcd for $C_{19}H_{30}NO_7NaPS$ 470.1378.



3y

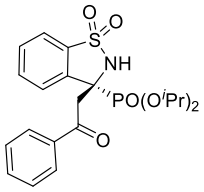
(*R*)-diisopropyl(2,2-dioxido-4-(2-oxopropyl)-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (3y): white solid; 65.0 mg; 80% yield; 90% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 190 nm UV detector, t_R = 14.2 min (minor) and t_R = 20.2 min (major)]; m.p.: 144-146 °C; $[\alpha]_D^{20}$ -6.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dt, *J* = 8.0, 1.8 Hz, 1H), 7.43 – 7.33 (m, 1H), 7.31 – 7.22 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.91 (s, 1H), 4.83 – 4.66 (m, 1H), 4.41 – 4.27 (m, 1H), 3.40 (dd, *J* = 21.4, 14.8 Hz, 2H), 2.25 (s, 3H), 1.34 (dd, *J* = 11.1, 6.2 Hz, 6H), 1.21 (d, *J* = 6.2 Hz, 3H), 0.79 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.00 – 15.42 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.7 (d, *J* = 3.7 Hz), 150.1 (d, *J* = 7.2 Hz), 130.5 (d, *J* = 2.4 Hz), 128.0 (d, *J* = 3.4 Hz), 125.9 (d, *J* = 2.5 Hz), 120.8 (d, *J* = 4.8 Hz), 119.7 (d, *J* = 1.4 Hz), 74.0 (dd, *J* = 51.1, 8.0 Hz), 63.4, 61.8, 47.1 (d, *J* = 2.8 Hz), 32.2, 24.3 (d, *J* = 2.6 Hz), 24.0 (d, *J* = 3.7 Hz), 23.8 (d, *J* = 5.4 Hz), 22.9 (d, *J* = 6.1 Hz); **HRMS** (ESI) found m/z 428.0910 $[M + Na]^+$, calcd for $C_{16}H_{24}NO_7NaPS$ 428.0909.

General procedure for the Mannich reaction of five-membered cyclic *α*-ketiminophosphonates 4 with *β*-keto acid 2a:



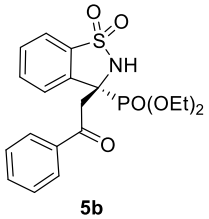
4 2a 5

To a 10 mL Schlenk flask equipped with a stirring bar was added α-ketiminophosphonates **4** (0.2 mmol), catalyst-**D** (0.01 mmol, **5** mol%), 5 Å MS (400 mg) and β-keto acid **2a** (0.3 mmol, 1.5 equiv). CCl_4 (2.0 mL) was added to the mixture. Then the resulting mixture was stirred at -20 °C until the completion of the reaction (monitored by TLC), concentrated under vacuum, and the residue was purified by flash chromatography on silica gel (eluting with dichloromethane/methanol = 160/1) to give the desired product **5**.



5a

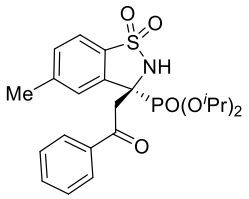
(*R*)-diisopropyl(1,1-dioxido-3-(2-oxo-2-phenylethyl)-2,3-dihydrobenzo[*d*]isothiazol-3-yl)phosphonate (5a): white solid; 70.0 mg; 77% yield; 91% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 69.7 min (major) and t_R = 82.0 min (minor)]; m.p.: 169-171 °C; $[\alpha]_D^{20}$ 32.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.84 (dd, *J* = 16.8, 7.6 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.58 (dd, *J* = 13.3, 7.0 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.90 (s, 1H), 4.66 (dq, *J* = 12.0, 6.0 Hz, 1H), 4.32 (dq, *J* = 12.2, 6.0 Hz, 1H), 4.21 (dd, *J* = 16.1, 5.4 Hz, 1H), 3.22 (dd, *J* = 21.2, 16.1 Hz, 1H), 1.21 (dd, *J* = 19.4, 6.0 Hz, 6H), 1.09 (d, *J* = 6.0 Hz, 3H), 0.73 (d, *J* = 6.1 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.07 (d, *J* = 20.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0 (d, *J* = 6.2 Hz), 136.8, 136.5 (d, *J* = 2.9 Hz), 135.2 (d, *J* = 5.0 Hz), 134.0, 133.2 (d, *J* = 2.2 Hz), 130.3 (d, *J* = 2.3 Hz), 128.8, 128.7, 125.3 (d, *J* = 2.5 Hz), 121.8 (d, *J* = 1.3 Hz), 73.8 (dd, *J* = 16.0, 7.9 Hz), 63.5, 61.8, 41.4 (d, *J* = 4.8 Hz), 24.2 (d, *J* = 2.8 Hz), 23.9 (d, *J* = 3.9 Hz), 23.7 (d, *J* = 5.2 Hz), 22.8 (d, *J* = 5.7 Hz); **HRMS** (ESI) found m/z 474.1116 $[M + Na]^+$, calcd for $C_{21}H_{26}NO_6NaPS$ 474.1116.



5b

(*R*)-diethyl(1,1-dioxido-3-(2-oxo-2-phenylethyl)-2,3-dihydrobenzo[*d*]isothiazol-3-yl)phosphonate (5b): white solid; 69.4 mg; 82% yield; 91% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 70/30, 1 mL/min, 254 nm UV detector, t_R = 14.2 min (minor) and t_R = 17.8 min (major)]; m.p.: 145-148 °C; $[\alpha]_D^{20}$ 39.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz,

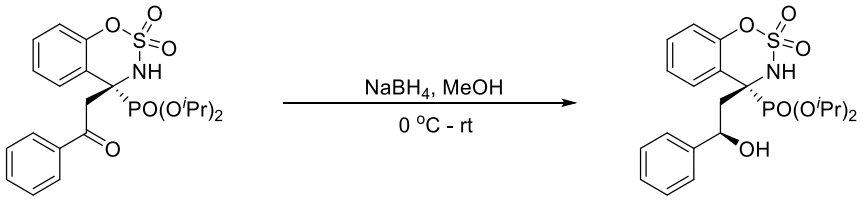
$CDCl_3$) δ 7.97 (d, J = 7.5 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.72 – 7.52 (m, 3H), 7.45 (t, J = 7.6 Hz, 2H), 6.93 (s, 1H), 4.22 (dd, J = 16.4, 5.8 Hz, 1H), 4.17 – 4.01 (m, 2H), 3.90 (qt, J = 14.2, 7.1 Hz, 1H), 3.78 – 3.64 (m, 1H), 3.32 (dd, J = 20.3, 16.5 Hz, 1H), 1.15 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.0 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.69 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7 (d, J = 7.3 Hz), 136.6, 136.4 (d, J = 2.9 Hz), 135.1 (d, J = 4.9 Hz), 134.1, 133.3 (d, J = 2.4 Hz), 130.3 (d, J = 2.2 Hz), 128.8, 128.6, 125.2 (d, J = 2.5 Hz), 121.8 (d, J = 1.7 Hz), 64.7 (dd, J = 19.8, 7.7 Hz), 63.4, 61.8, 41.3 (d, J = 4.7 Hz), 16.3 (d, J = 5.6 Hz), 16.1 (d, J = 5.5 Hz); **HRMS** (ESI) found m/z 446.0806 $[M + Na]^+$, calcd for $C_{19}H_{22}NO_6NaPS$ 446.0803.



5c

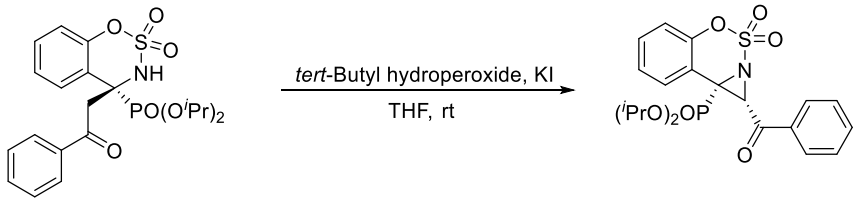
(*R*)-diisopropyl(5-methyl-1,1-dioxido-3-(2-oxo-2-phenylethyl)-2,3-dihydrobenzo[*d*]isothiazol-3-yl)phosphonate (5c): white solid; 75.4 mg; 81% yield; 90% ee; [determined by **HPLC** analysis Daicel Chirapak, AD-H, *n*-Hex/*i*-PrOH = 90/10, 1 mL/min, 254 nm UV detector, t_R = 49.9 min (major) and t_R = 60.1 min (minor)]; m.p.: 137-140 ^{o}C; $[\alpha]_D^{20}$ -5.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.94 (m, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.66 (s, 1H), 7.63 – 7.55 (m, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 6.79 (s, 1H), 4.74 – 4.58 (m, 1H), 4.42 – 4.27 (m, 1H), 4.21 (dd, J = 16.0, 5.5 Hz, 1H), 3.16 (dd, J = 22.4, 16.0 Hz, 1H), 2.48 (s, 3H), 1.25 (d, J = 6.2 Hz, 3H), 1.20 (d, J = 6.2 Hz, 3H), 1.11 (d, J = 6.2 Hz, 3H), 0.75 (d, J = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.41 – 15.69 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4 (d, J = 5.4 Hz), 144.4 (d, J = 2.3 Hz), 137.0, 136.9 (d, J = 2.9 Hz), 134.1, 132.6 (d, J = 5.0 Hz), 131.3 (d, J = 2.2 Hz), 128.9, 128.8, 125.4 (d, J = 2.5 Hz), 121.7 (d, J = 1.7 Hz), 73.9 (dd, J = 28.6, 8.0 Hz), 63.4, 61.7, 41.7 (d, J = 4.9 Hz), 24.3 (d, J = 2.8 Hz), 24.0 (d, J = 4.1 Hz), 23.8 (d, J = 5.1 Hz), 22.9 (d, J = 5.7 Hz), 22.0; **HRMS** (ESI) found m/z 488.1269 $[M + Na]^+$, calcd for $C_{22}H_{28}NO_6NaPS$ 488.1273.

The procedure for further synthetic transformation:



3a: 99% ee

6, 90%, 17:1 dr, 96% ee

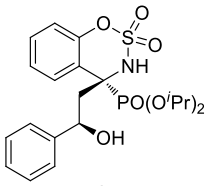


3a: 99% ee

7, 61%, 93% ee

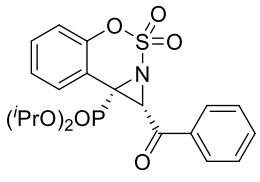
To a vigorously stirred solution of **3a** (93.5 mg, 0.2 mmol) in MeOH (3.0 mL) at 0 °C was added $NaBH_4$ (38.0 mg, 1 mmol) over 3 minutes. The resulting mixture was stirred for 2 h at room temperature. The reaction mixture was treated with 3 mL aqueous HCl (1 M). The solvent was removed under reduced pressure and the residue was extract with ethyl acetate (10 mL×3). The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4 and concentrated under reduced pressure, the diastereoselectivity of **6** was determined by ^{1}HNMR of the crude reaction mixture. The recovered crude product was purified by flash chromatography on silica gel (PE/EA = 2/1) to afford compound **6** (84.5 mg) as a white solid in 90% yield and 96% ee.

The mixture of **3a** (0.2 mmol), KI (0.4 mmol), TBHP (0.4 mmol) in THF (2.0 mL) were added into a 10 mL Schlenk flask equipped with a stirring bar under air atmosphere. The reaction was stirred at 0 °C for 3 h, and allowed to warm to room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was washed with saturated aqueous $Na_2S_2O_3$ and extracted with ethyl acetate for three times. The combined organic layers were dried over anhydrous $MgSO_4$ and the solvents were removed in vacuo. The residue was purified by flash column chromatography on silica gel (PE/EA = 5/1) to give the product **7**.



6

diisopropyl((4*R*)-4-(2-hydroxy-2-phenylethyl)-2,2-dioxido-3,4-dihydrobenzo[*e*][1,2,3]oxathiazin-4-yl)phosphonate (6): white solid; 84.5 mg; 90% yield; 17:1 dr (^{1}H NMR analysis); 96% ee; [determined by **HPLC** analysis Daicel Chirapak, IA, *n*-Hex/*i*-PrOH = 75/25, 1 mL/min, 190 nm UV detector, t_R = 9.0 min (minor) and t_R = 14.3 min (major)]; m.p.: 134-137 °C; $[\alpha]_D^{20}$ 39.6 (*c* 1.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dt, *J* = 8.0, 1.7 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.22 (m, 4H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 5.52 (dd, *J* = 11.2, 1.5 Hz, 1H), 4.95 – 4.81 (m, 1H), 4.42 (dh, *J* = 12.4, 6.2 Hz, 1H), 2.81 (ddd, *J* = 29.4, 15.0, 11.4 Hz, 1H), 2.34 (ddd, *J* = 15.0, 4.3, 2.0 Hz, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.24 (dd, *J* = 8.1, 6.3 Hz, 6H), 1.08 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.98 (d, *J* = 29.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.10 (d, *J* = 7.0 Hz), 144.57 – 144.34 (m), 130.07 (d, *J* = 2.4 Hz), 128.66, 128.47 (d, *J* = 3.1 Hz), 127.88 – 127.78 (m), 125.68, 125.64, 122.25 – 121.93 (m), 119.56, 74.70 – 72.94 (m), 72.25 (d, *J* = 3.4 Hz), 66.02, 64.41, 45.14, 24.36 (d, *J* = 2.9 Hz), 24.05, 23.63 (d, *J* = 6.8 Hz), 23.52; **HRMS** (ESI) found m/z 492.1218 $[M + Na]^+$, calcd for $C_{21}H_{28}NO_7NaPS$ 492.1222.



7

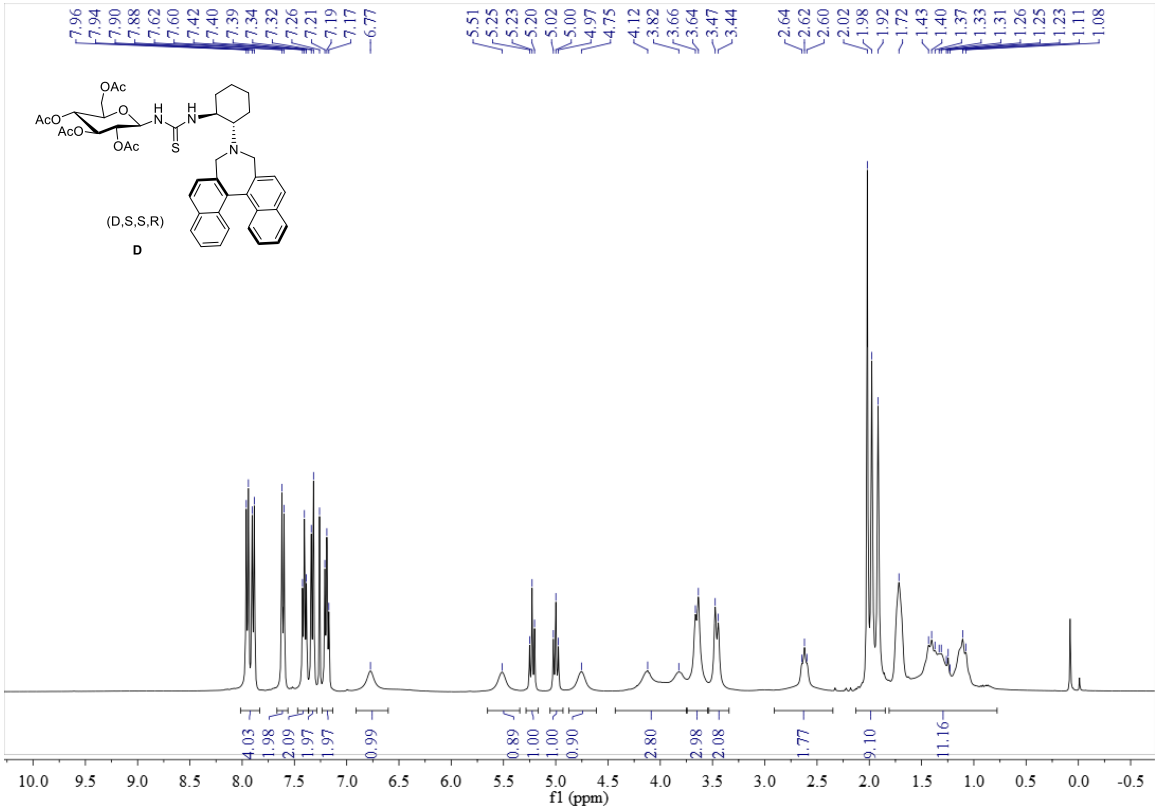
diisopropyl((1*R*,8b*S*)-1-(cyclohexanecarbonyl)-3,3-dioxido-1,8b-dihydroazirino[1,2-c]benzo[

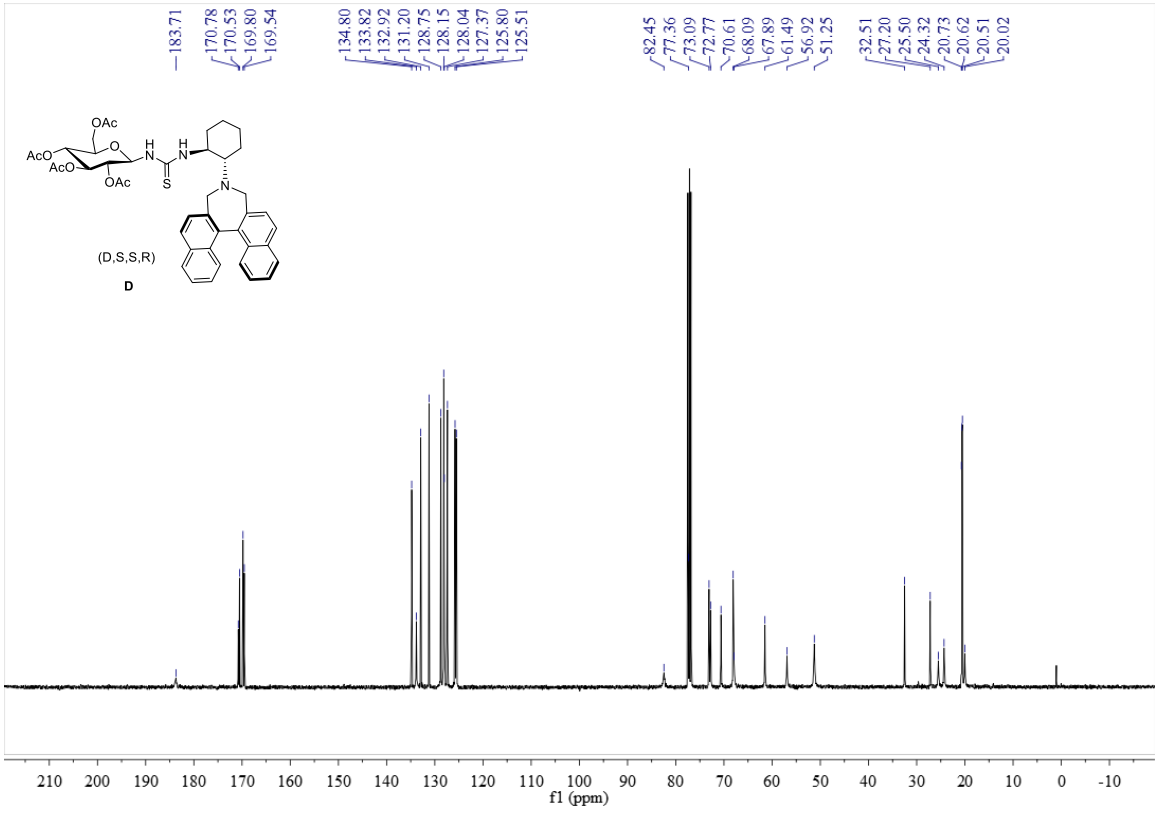
***e*][1,2,3]oxathiazin-8b-yl)phosphonate (7):** white solid; 56.8 mg; 61% yield; 93% ee; [determined by **HPLC** analysis Daicel Chirapak, IC, *n*-Hex/*i*-PrOH = 70/30, 1 mL/min, 254 nm UV detector, t_R = 11.0 min (minor) and t_R = 12.6 min (major)]; m.p.: 126-128 °C; $[\alpha]_D^{20}$ -28 (*c* 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.16 – 8.08 (m, 2H), 7.62 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.46 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 (td, *J* = 7.7, 1.3 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 4.80 – 4.65 (m, 2H), 4.39 (d, *J* = 6.8 Hz, 1H), 1.32 (d, *J* = 6.2 Hz, 3H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.2 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.09 (q, *J* = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 149.7 (d, *J* = 8.2 Hz), 135.0, 134.2, 130.9, 130.2 (d, *J* = 0.9 Hz), 129.2, 128.8, 126.9, 119.9 (d, *J* = 0.9 Hz), 118.0 (d, *J* = 9.2 Hz), 74.1 (dd, *J* = 51.0, 6.7 Hz), 53.2, 52.1, 50.1, 24.3 (d, *J* = 2.8 Hz), 23.8 (d, *J* = 3.3 Hz), 23.5 (d, *J* = 5.6 Hz), 23.3 (d, *J* = 6.2 Hz); **HRMS** (ESI) found m/z 488.0914 $[M + Na]^+$, calcd for $C_{21}H_{24}NO_7NaPS$ 488.0909.

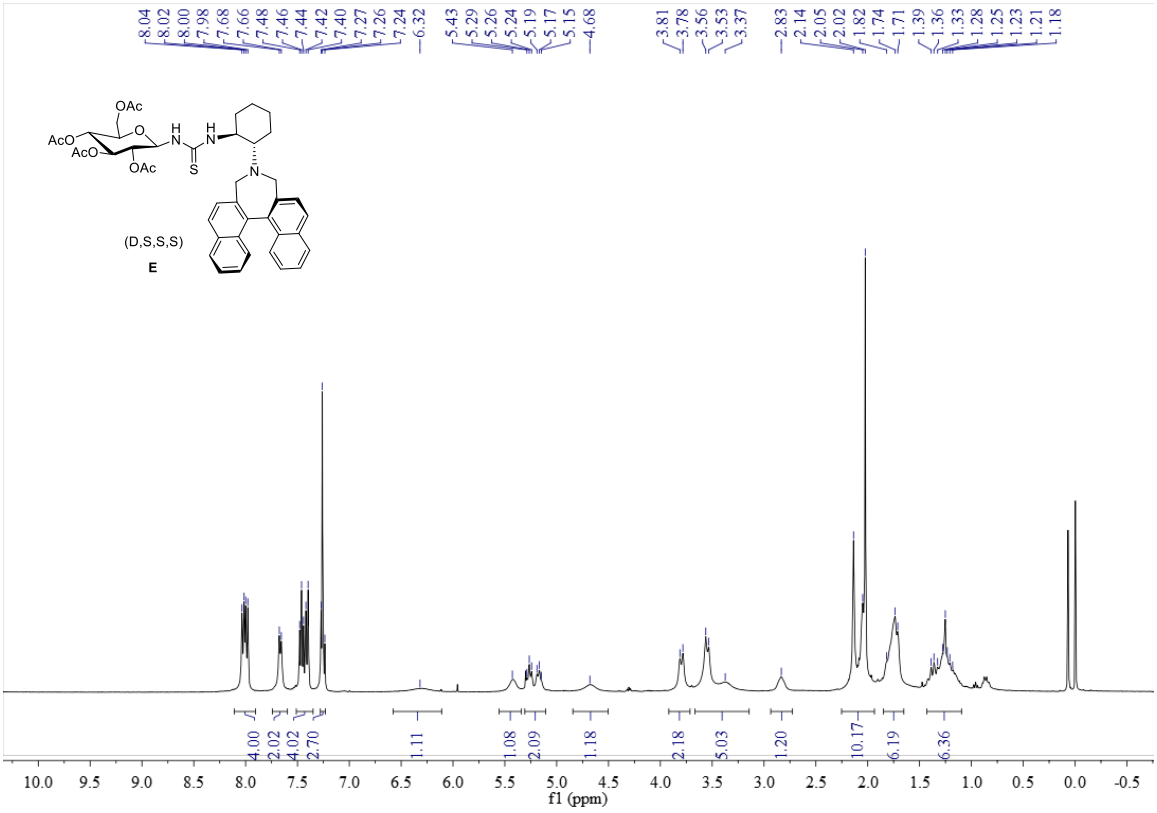
Reference

1. Evans, D. A.; Mito, S.; Seidel, D. *J. Am. Chem. Soc*. **2007**, *129*, 11583.
2. Zhong, Y.-B.; Wu, X.-G.; Chen, M.-W.; Zhou, Y.-G.; *Org. Lett*. **2016**, *18*, 692.
3. (a) Mitchell, J. M.; Finney, N. S. *Tetrahedron Lett*. **2000**, *41*, 8431. (b) Liu, K.; Cui, H.-F.; Nie, J.; Dong, K.-Y.; Li, X.-J.; Ma, J.-A. *Org. Lett*. **2007**, *9*, 923. (c) Li, X.-J.; Liu, K.; Ma, H.; Nie, J.; Ma, J.-A. *Synlett*, **2008**, 3242. (d) Ma, H.; Liu, K.; Zhang, F.-G.; Zhu, C.-L.; Nie, J.; Ma, J.-A. *J. Org. Chem*. **2010**, *75*, 1402. (e) Li, F.;. Sun, L.; Teng, Y.; Yu, P.; Zhao, C.-G.; Ma, J.-A. *Chem. Eur. J*. **2012**, *18*, 14255.
4. Peng, F.-Z.; Shao, Z.-H.; Fan, B.-M.; Song, H.; Li, G.-P.; Zhang, H.-B. *J. Org. Chem*. **2008**, *73*, 5202.
5. Kobayashi, S.; Tanaka, H.; Amii, H.; Uneyama, K. *Tatrahedron*, **2003**, *59*, 1547.

NMR spectra of the related compounds



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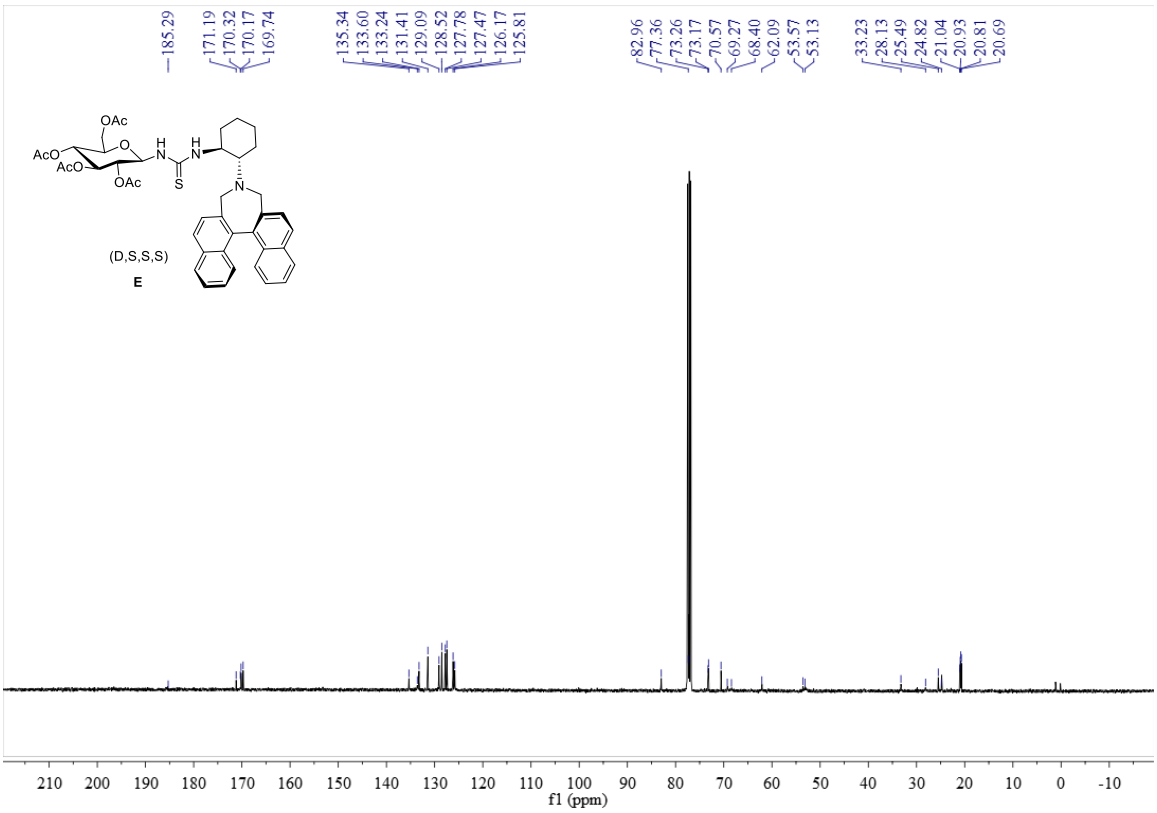
7.24
6.32
5.43
5.29
5.26
5.24
5.19
5.17
5.15
4.68
3.81
3.78
3.56
3.53
3.37
2.83
2.14
2.05
2.02
1.82
1.74
1.71
1.39
1.36
1.33
1.28
1.25
1.23
1.21
1.18
OAc
AcO
AcO
OAc
O
H
N
H
N
S
N
(D,S,S,S)
E
4.00
2.02
4.02
2.70
1.11
1.08
2.09
1.18
2.18
5.03
1.20
10.17
6.19
6.36
f1 (ppm)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77.36
73.26
73.17
70.57
69.27
68.40
62.09
53.57
53.13
33.23
28.13
25.49
24.82
21.04
20.93
20.81
20.69
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AcO
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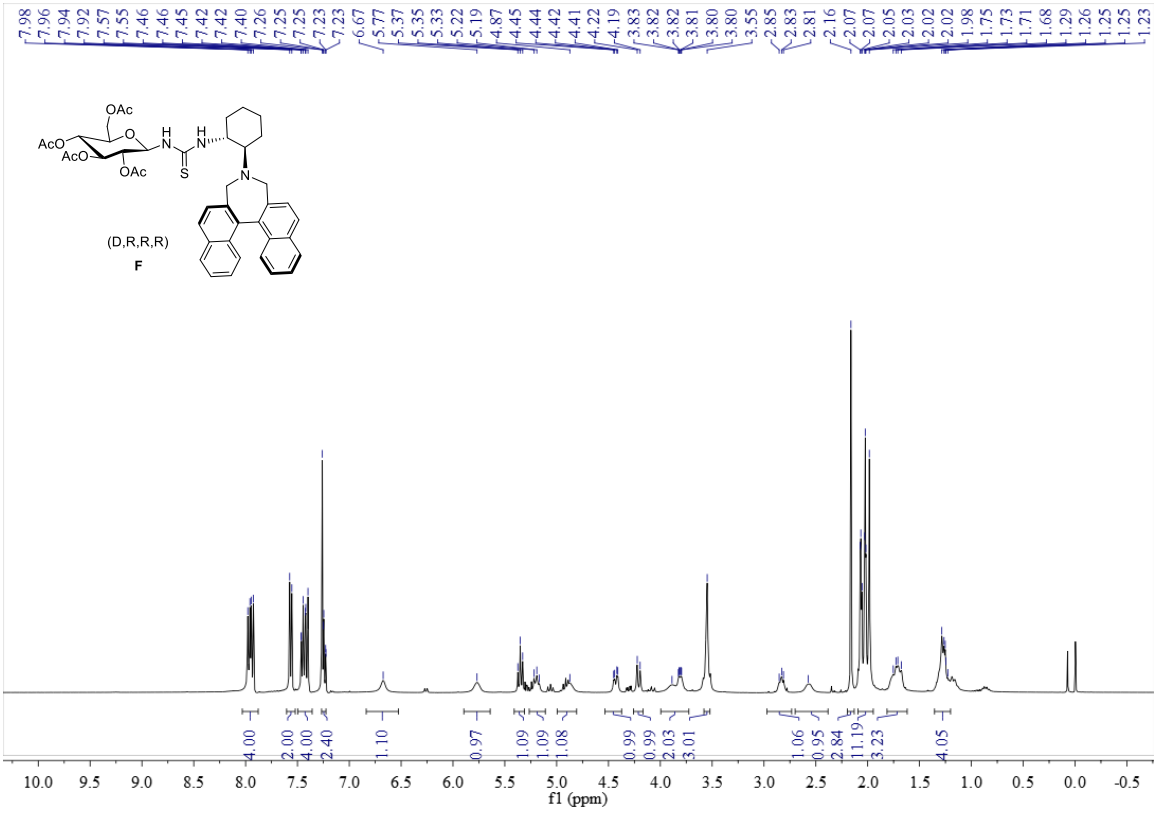
H
N
H
N
S
N
(D,S,S,S)
E
f1 (ppm)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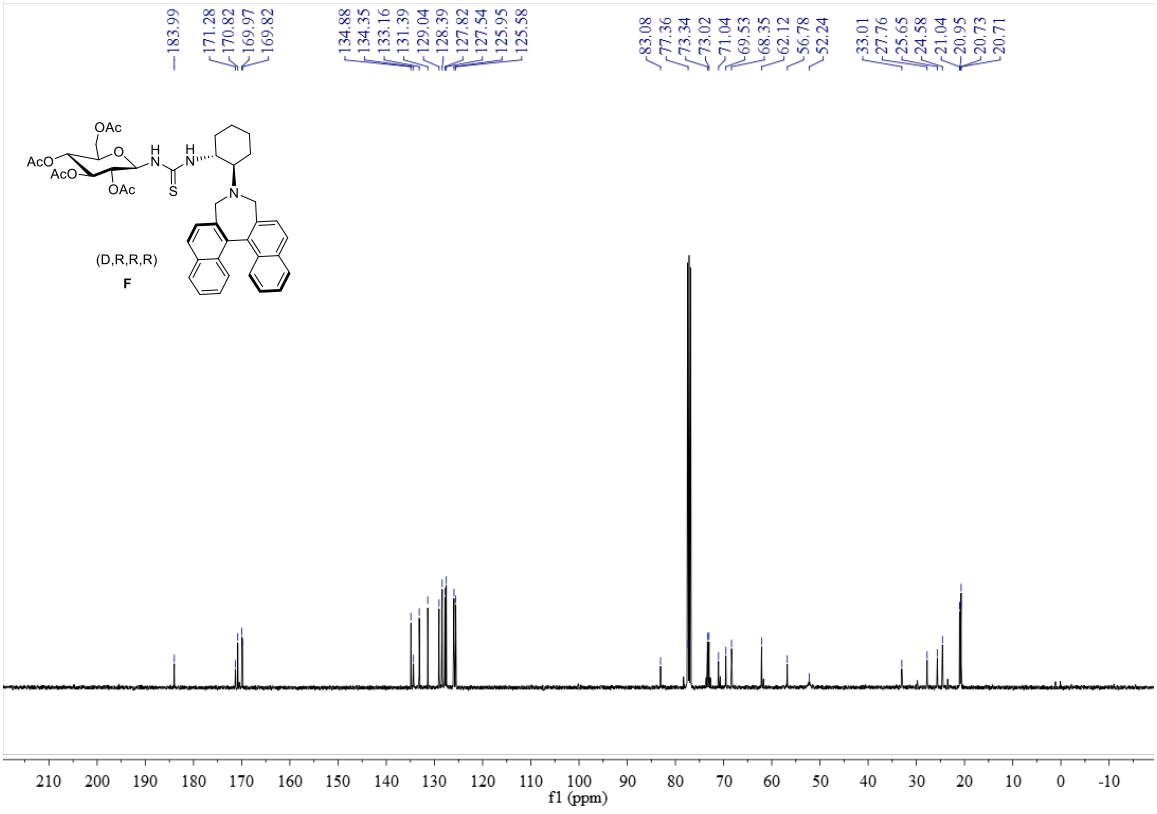
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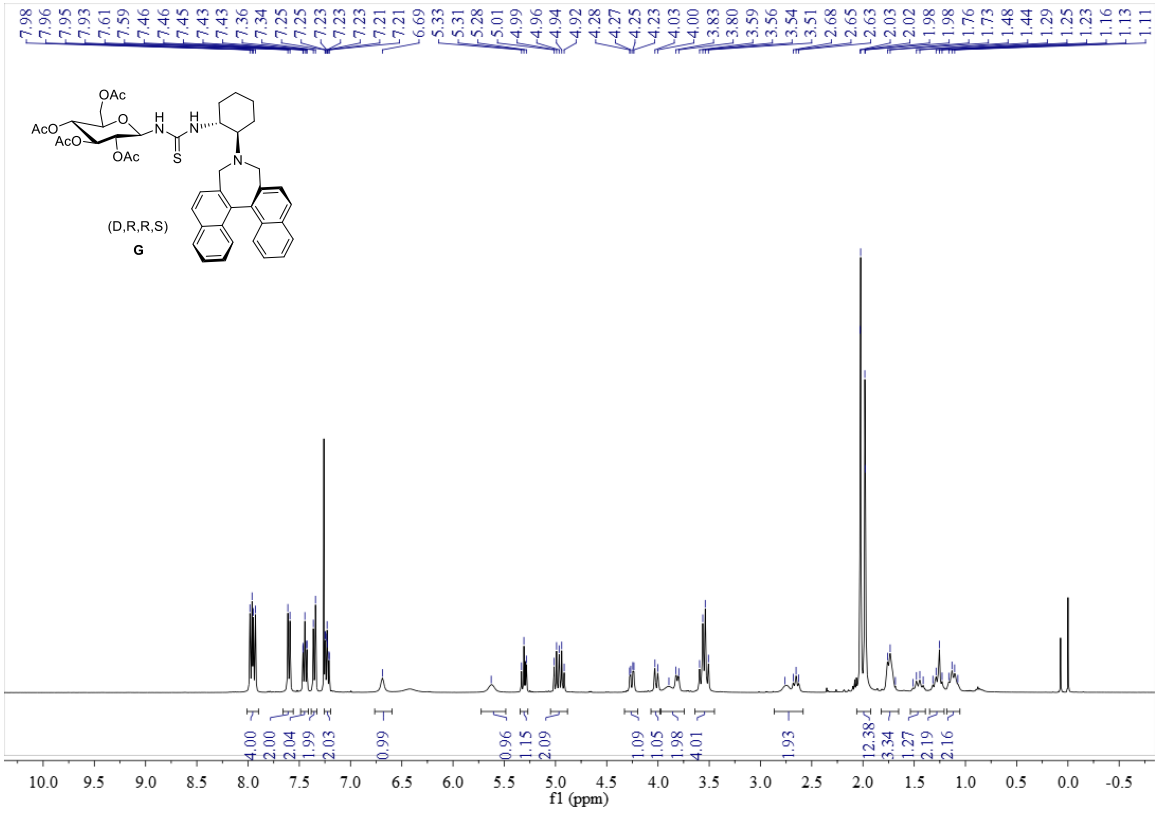
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G
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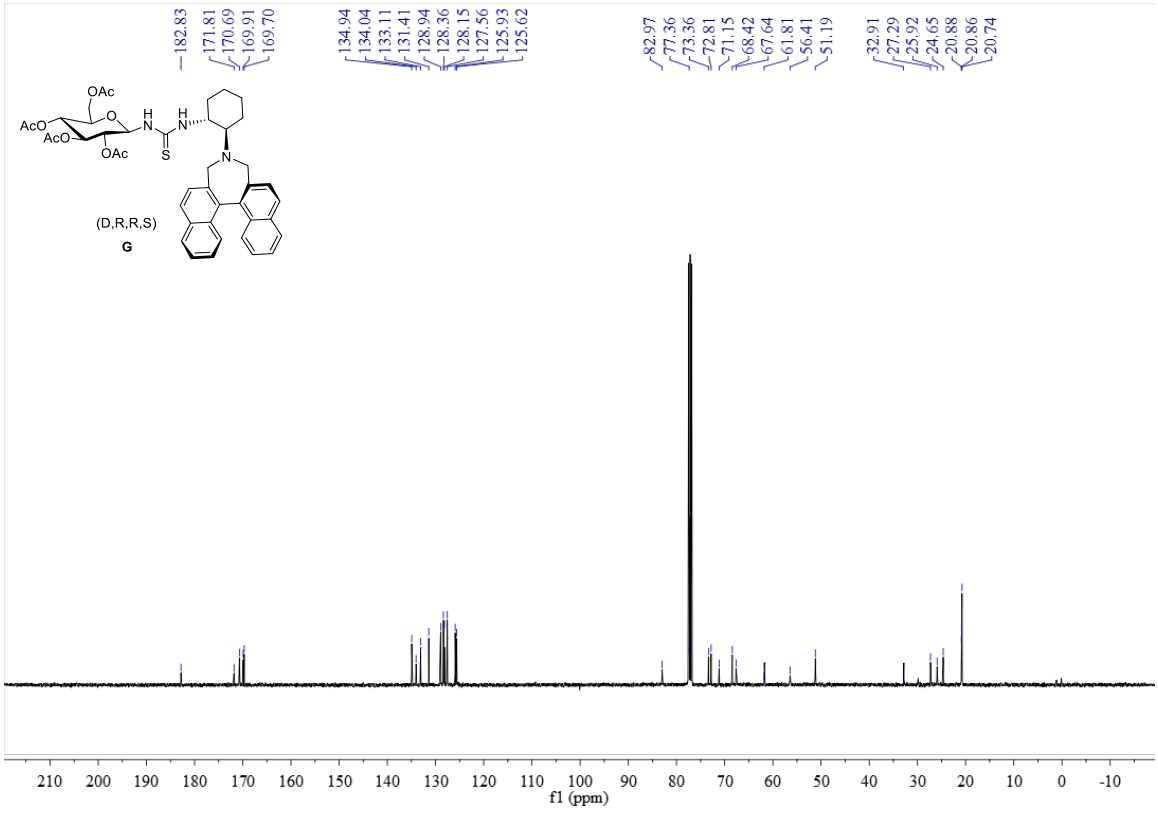
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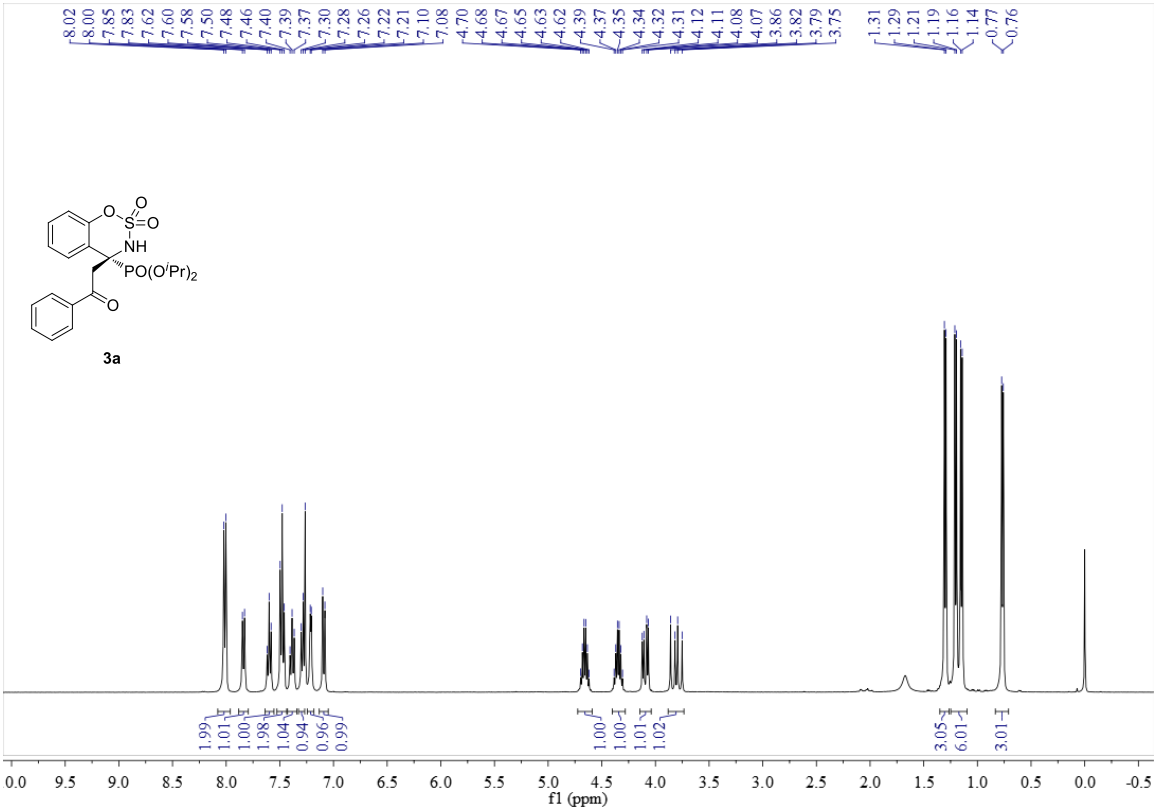
G
f1 (ppm)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7.22
7.21
7.10
7.08
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4.63
4.62
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4.34
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4.08
4.07
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0.76
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NH
PO(OiPr)2
O
3a
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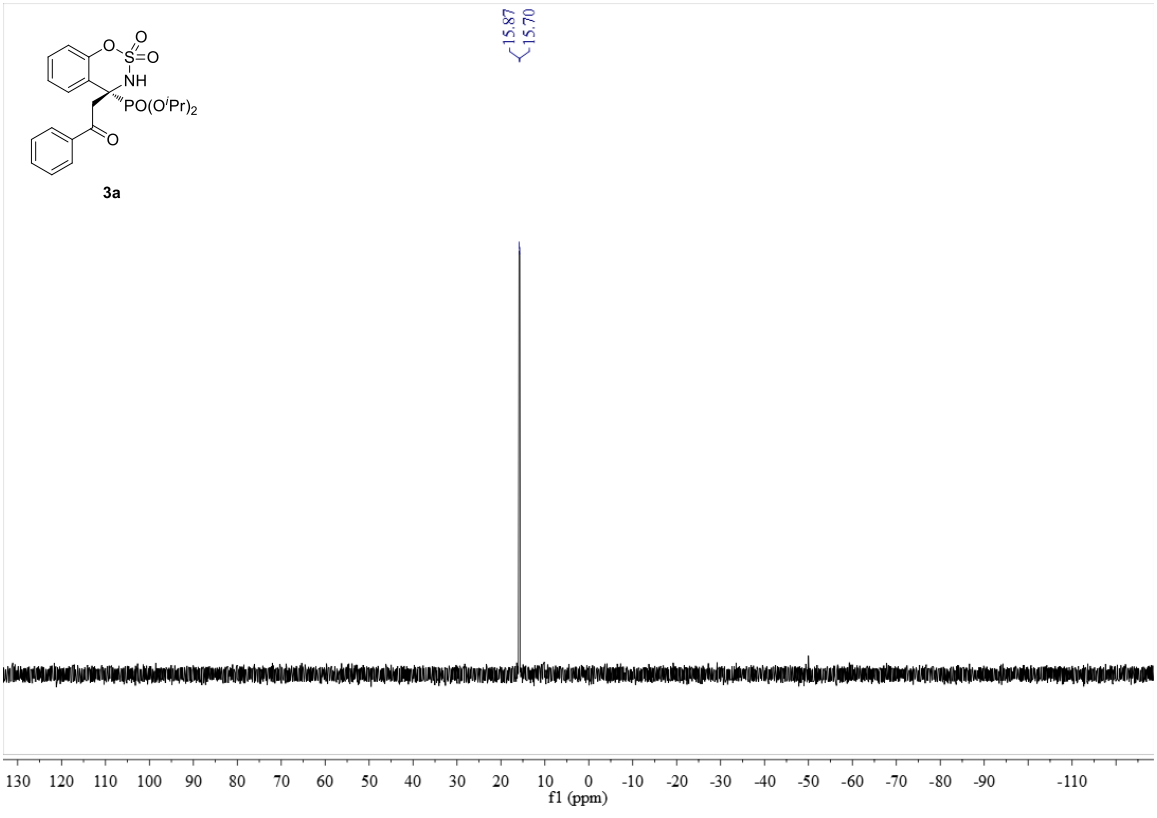
1.01
1.00
1.98
1.04
0.94
0.96
0.99
1.00
1.00
1.01
1.02
3.05
6.01
3.01
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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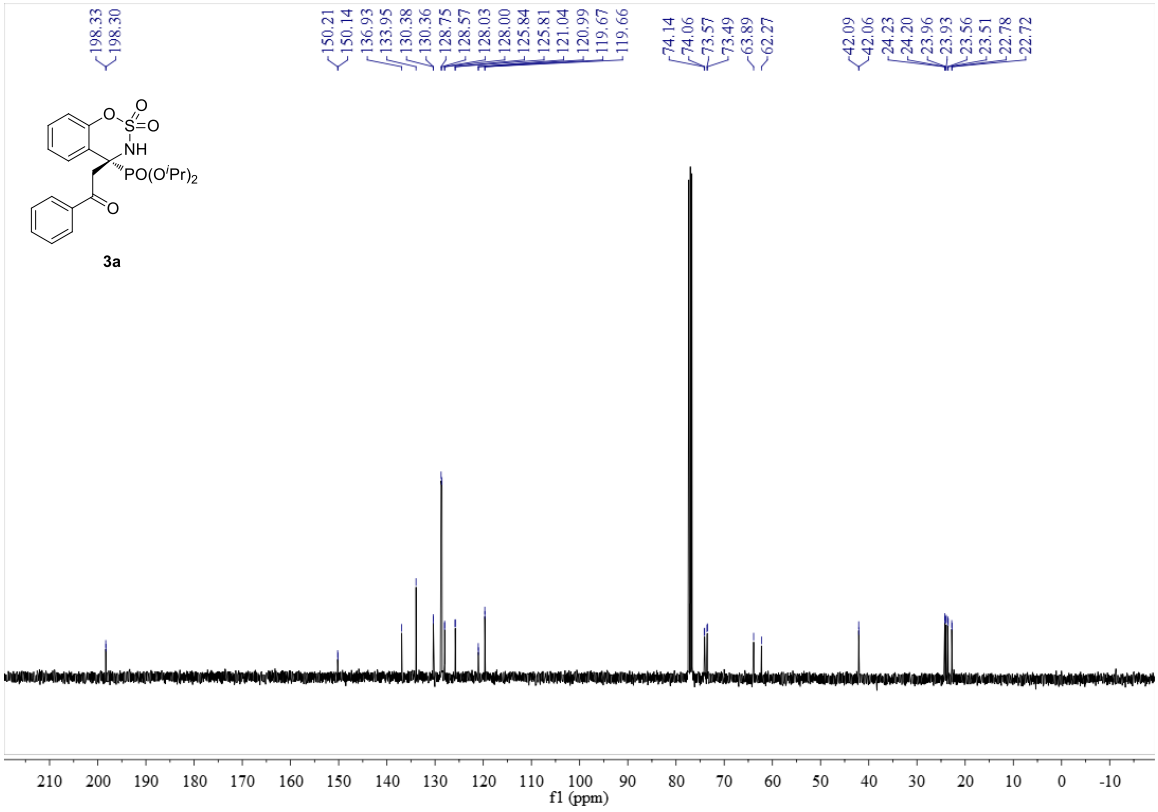
f1 (ppm)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74.06
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42.06
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24.20
23.96
23.93
23.56
23.51
22.78
22.72
O
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NH
PO(O^{i}Pr)$_2$
O
3a
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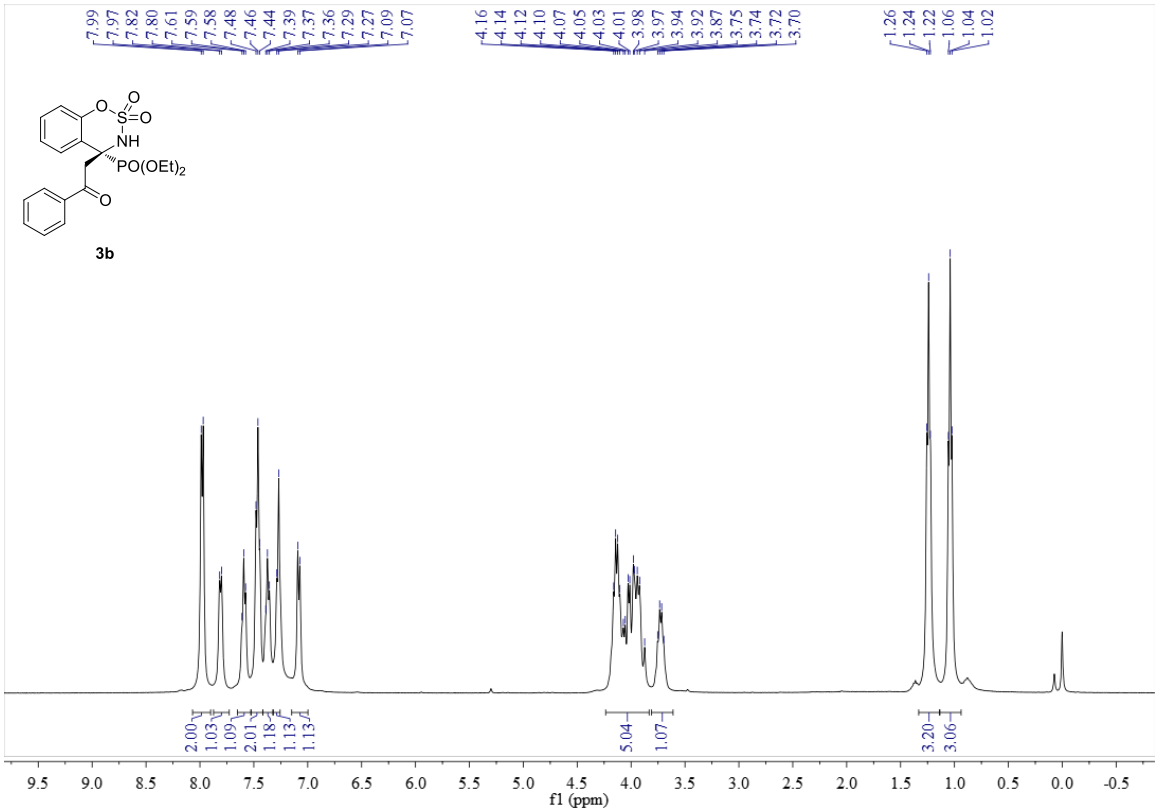
f1 (ppm)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7.37
7.36
7.29
7.27
7.09
7.07
4.16
4.14
4.12
4.10
4.07
4.05
4.03
4.01
3.98
3.97
3.94
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3.87
3.75
3.74
3.72
3.70
1.26
1.24
1.22
1.06
1.04
1.02
O
S=O
NH
PO(OEt)$_2$
O
3b
2.00
1.03
1.09
2.01
1.18
1.13
1.13
5.04
1.07
3.20
3.06
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 -0.5
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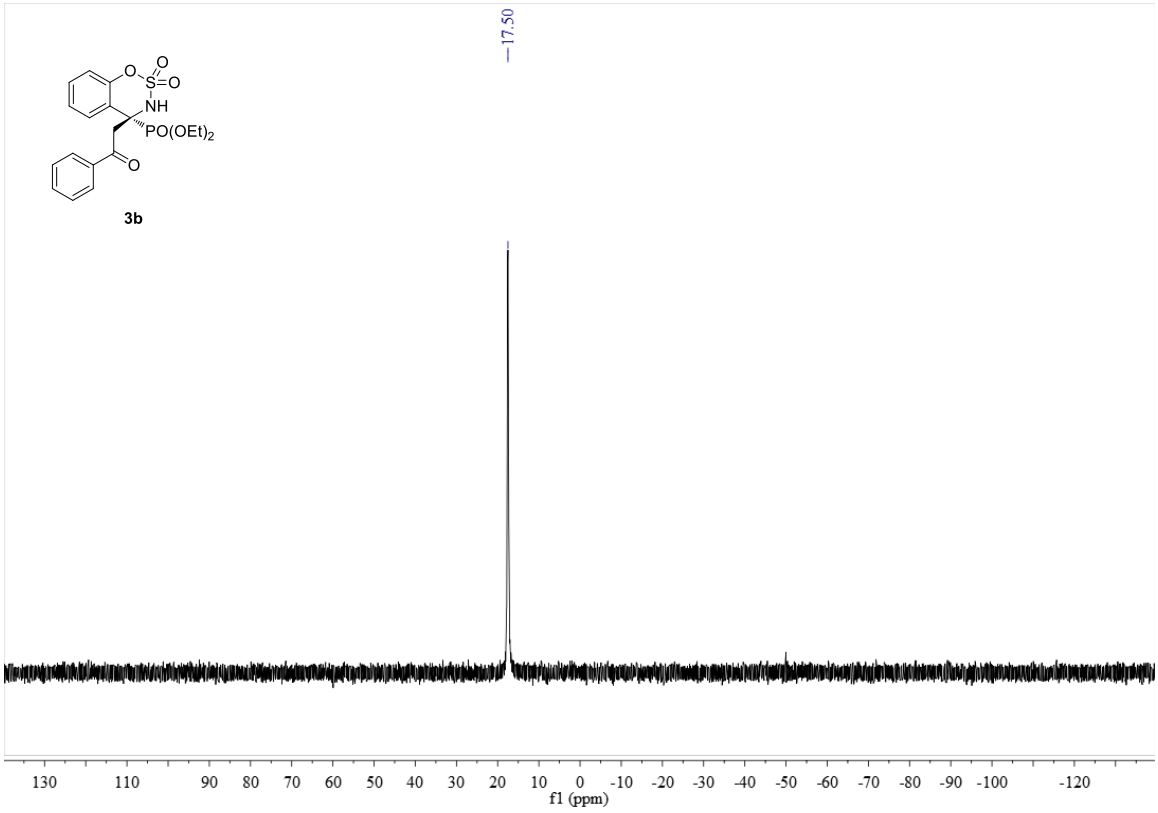
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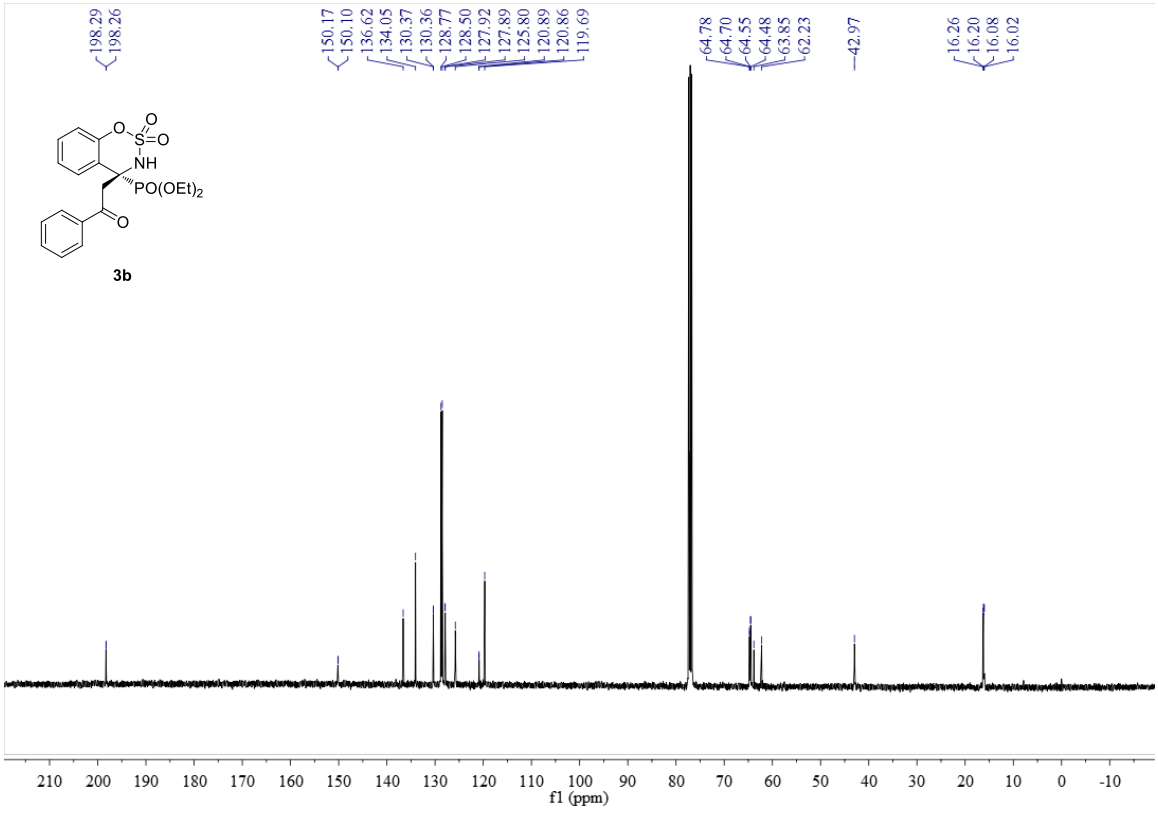
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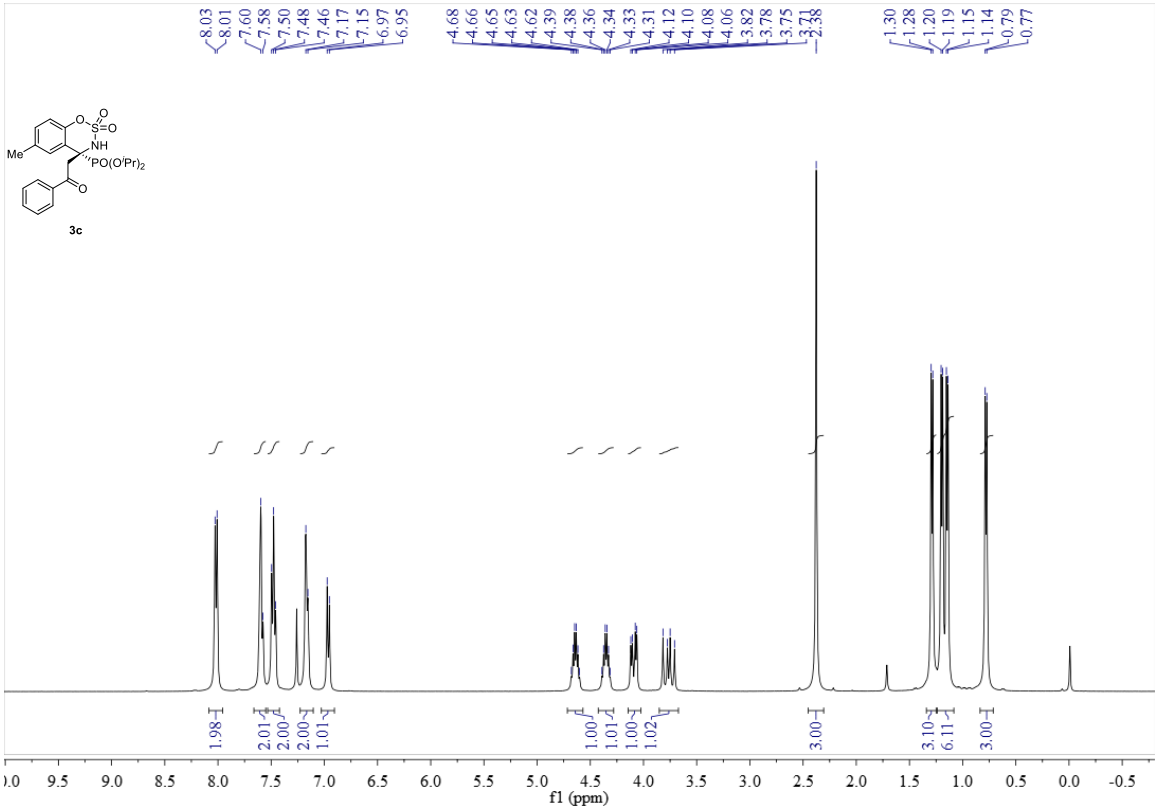
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3c
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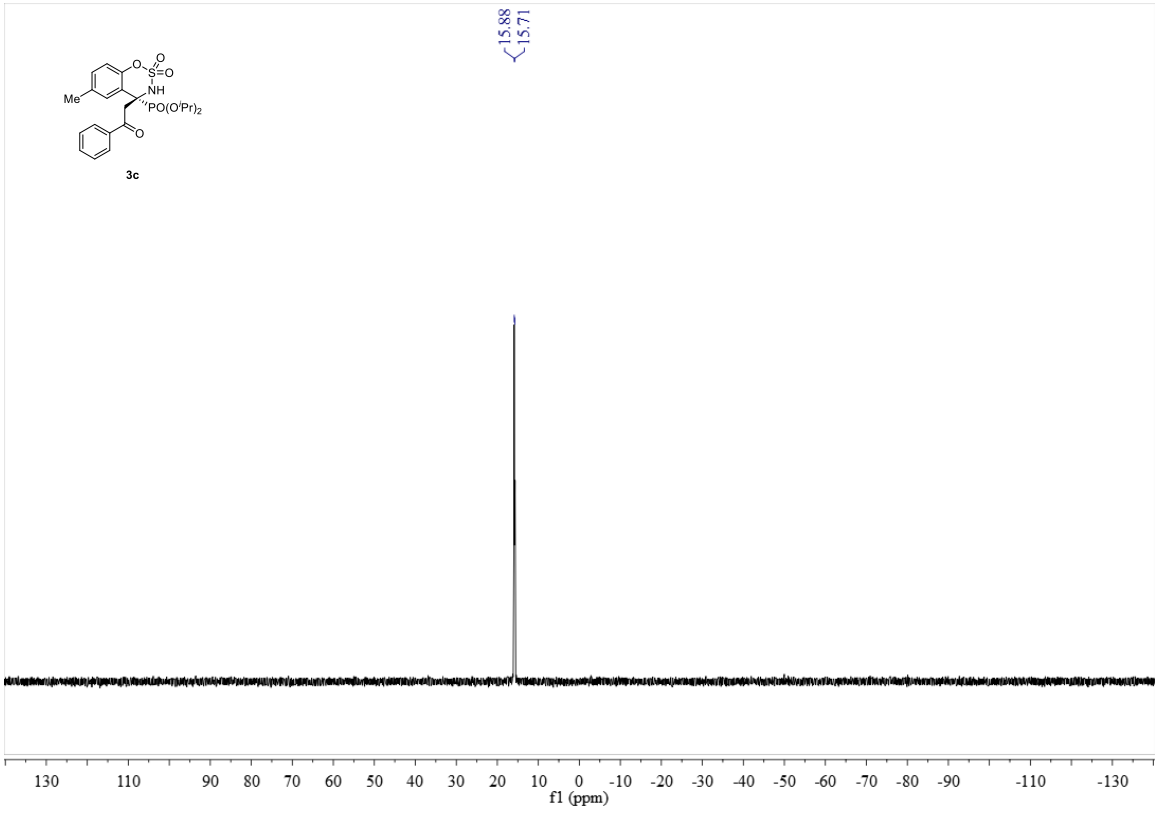
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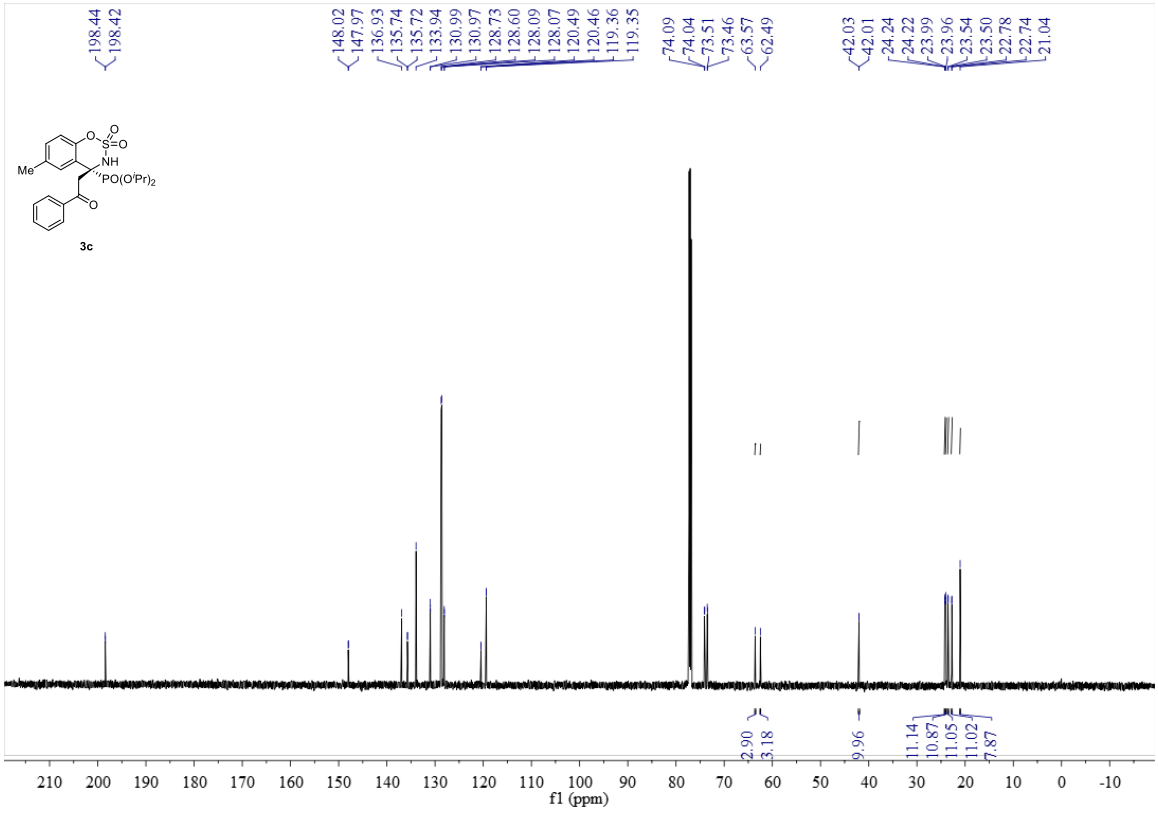
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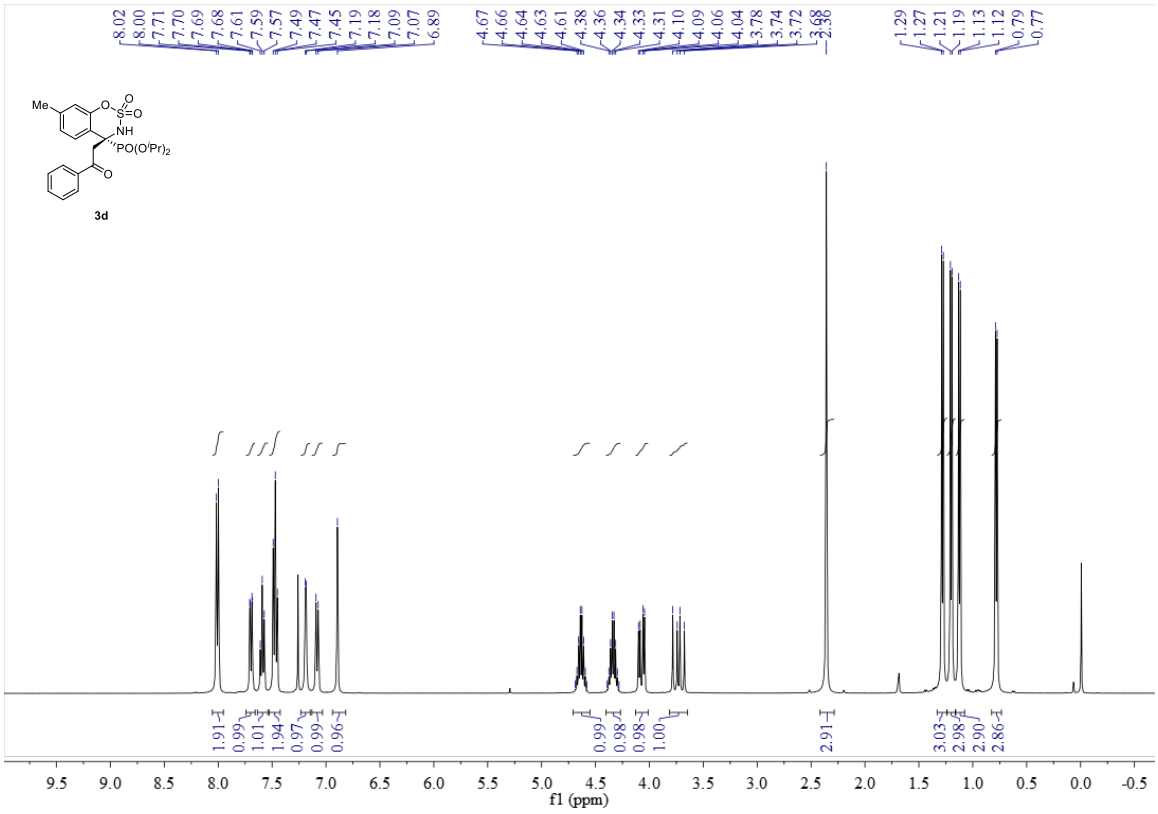
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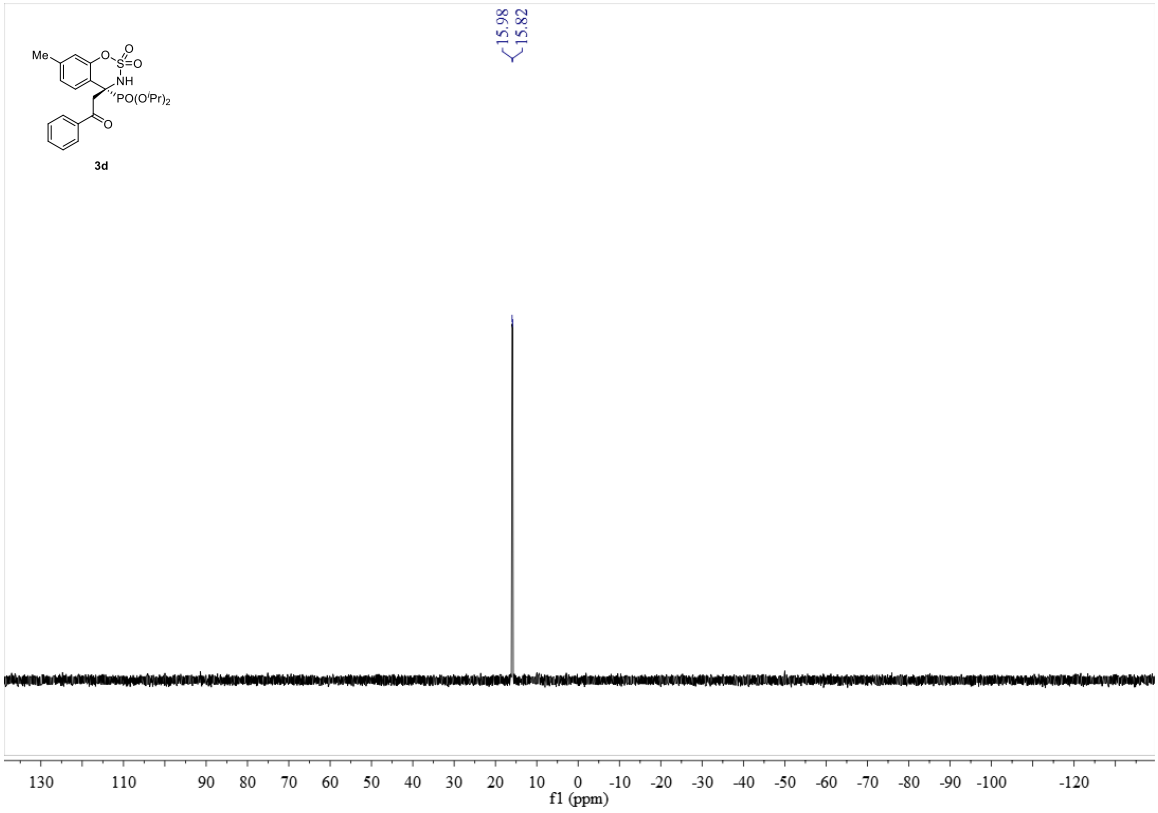
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S
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NH
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O
3d
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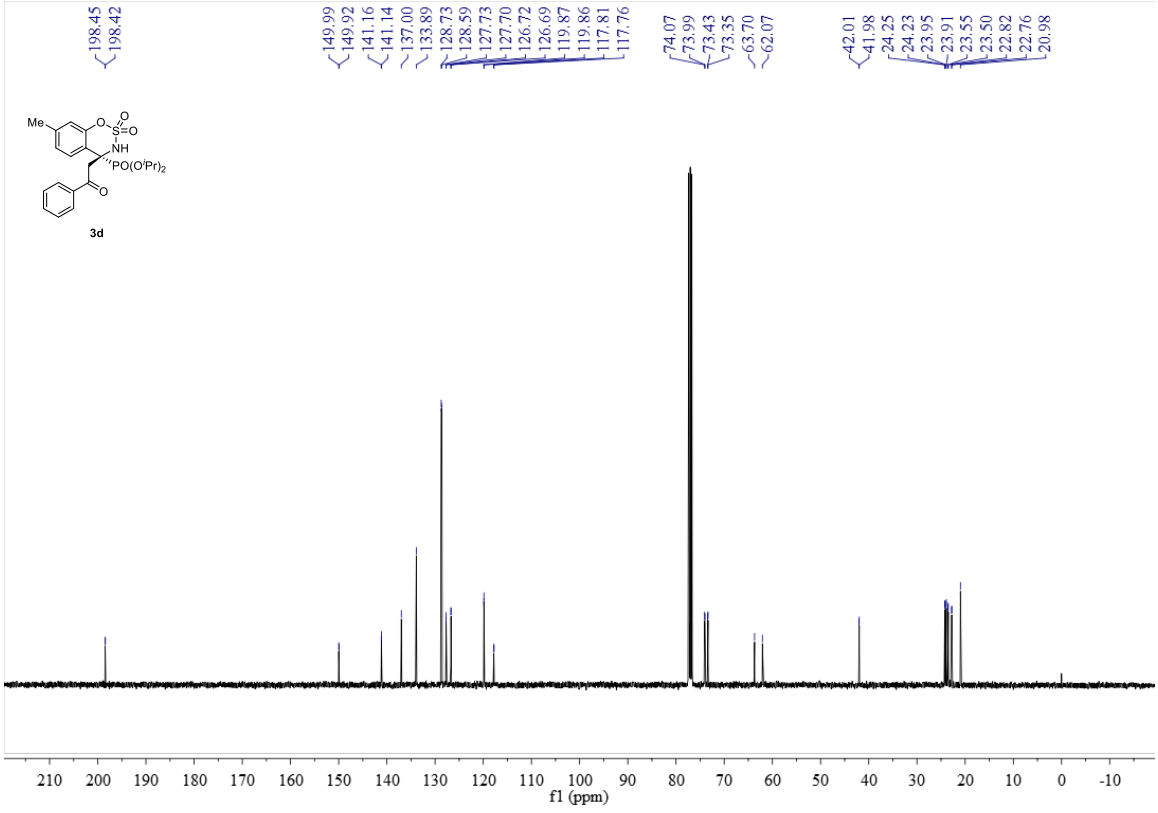
f1 (ppm)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42.01
41.98
24.25
24.23
23.95
23.91
23.55
23.50
22.82
22.76
20.98
Me
O
S
O
NH
PO(O^{i}Pr)$_2$
O
3d
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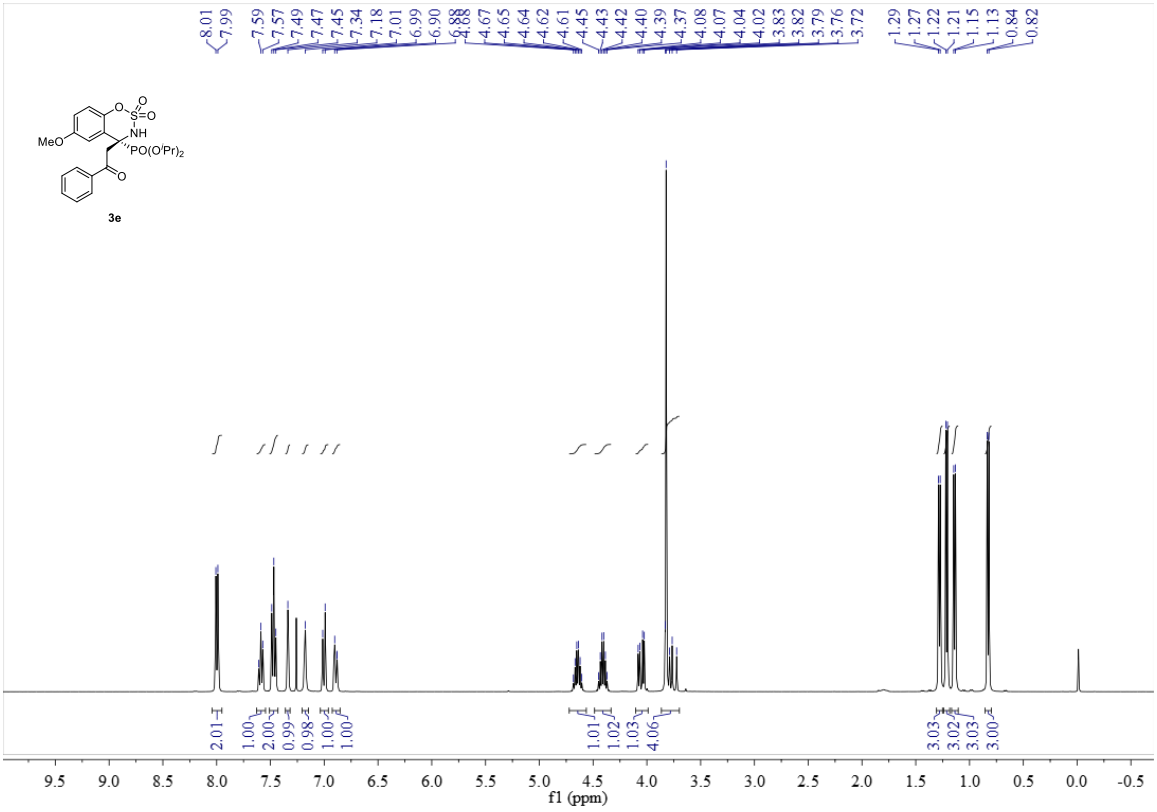
f1 (ppm)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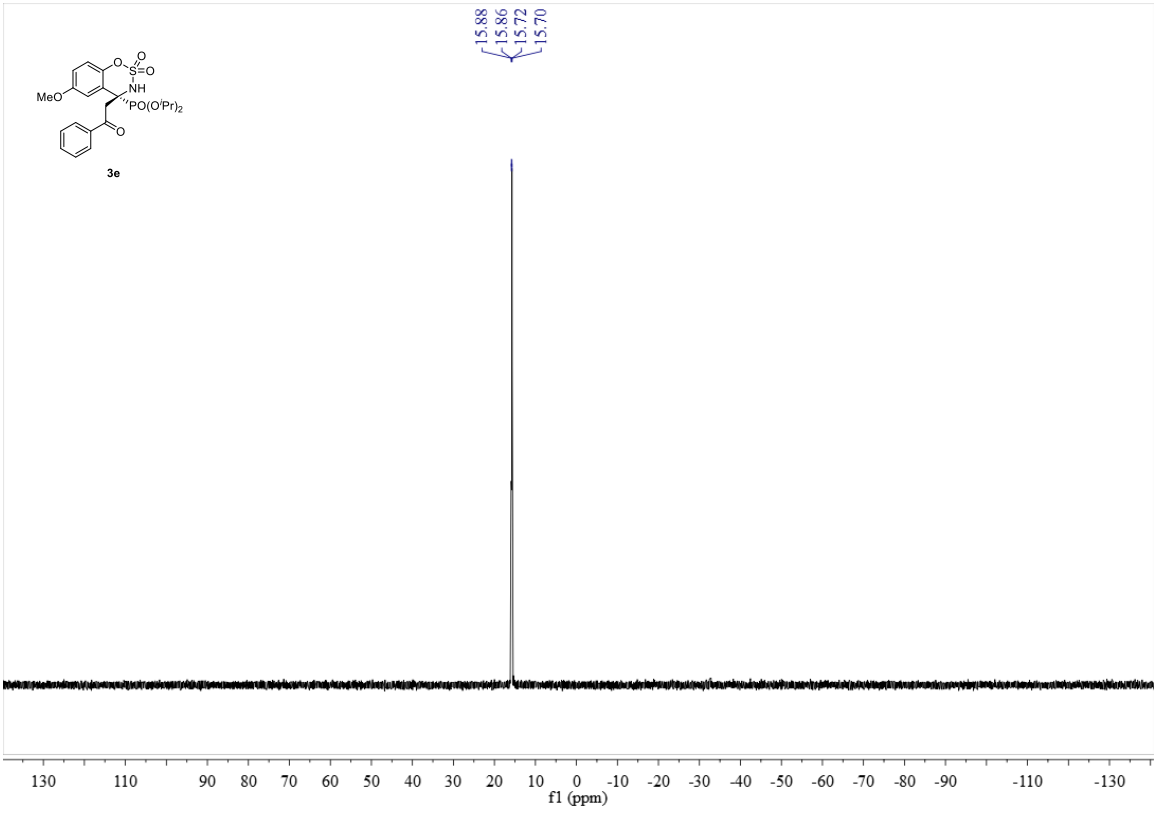
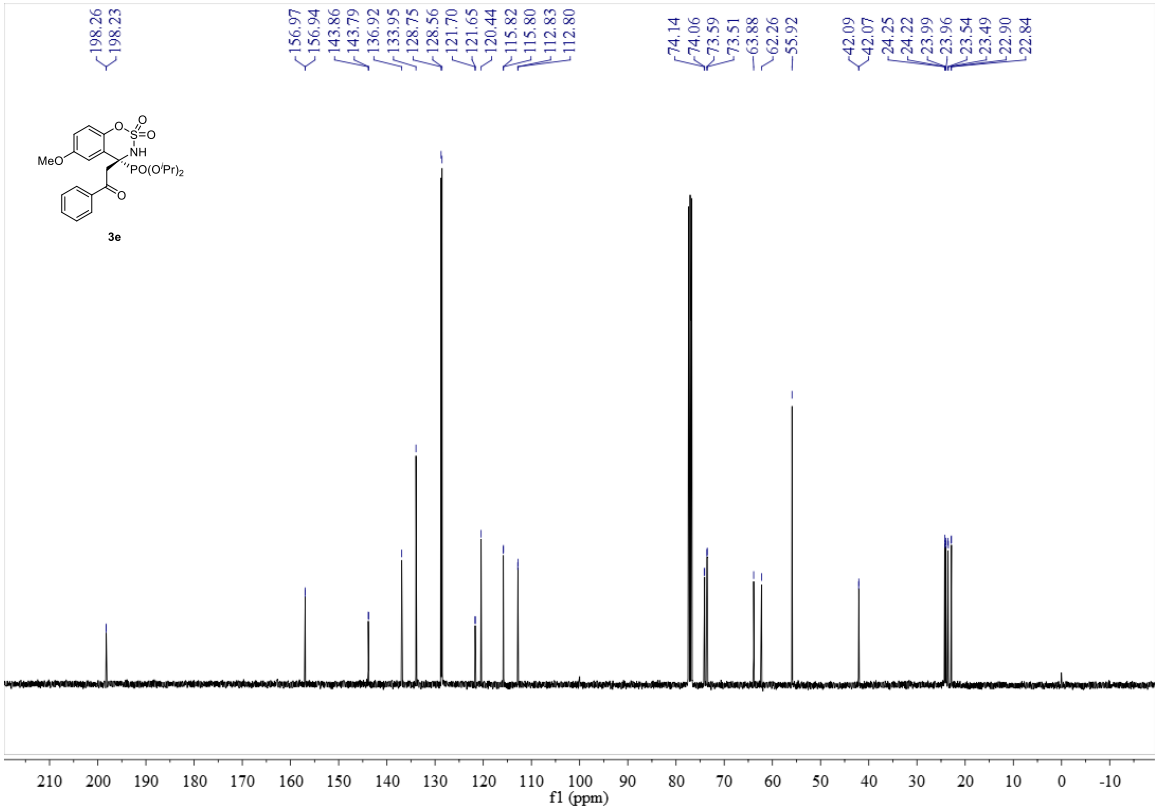
6.88
4.67
4.65
4.64
4.62
4.61
4.45
4.43
4.42
4.40
4.39
4.37
4.08
4.07
4.04
4.02
3.83
3.82
3.79
3.76
3.72
1.29
1.27
1.22
1.21
1.15
1.13
0.84
0.82
MeO
NH
PO(OiPr)2
3e
2.01
1.00
2.00
0.99
0.98
1.00
1.00
1.01
1.02
1.03
4.06
3.03
3.02
3.03
3.00
f1 (ppm)


15.88
15.86
15.72
15.70
MeO
NH
PO(OiPr)2
3e
f1 (ppm)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198.23
156.97
156.94
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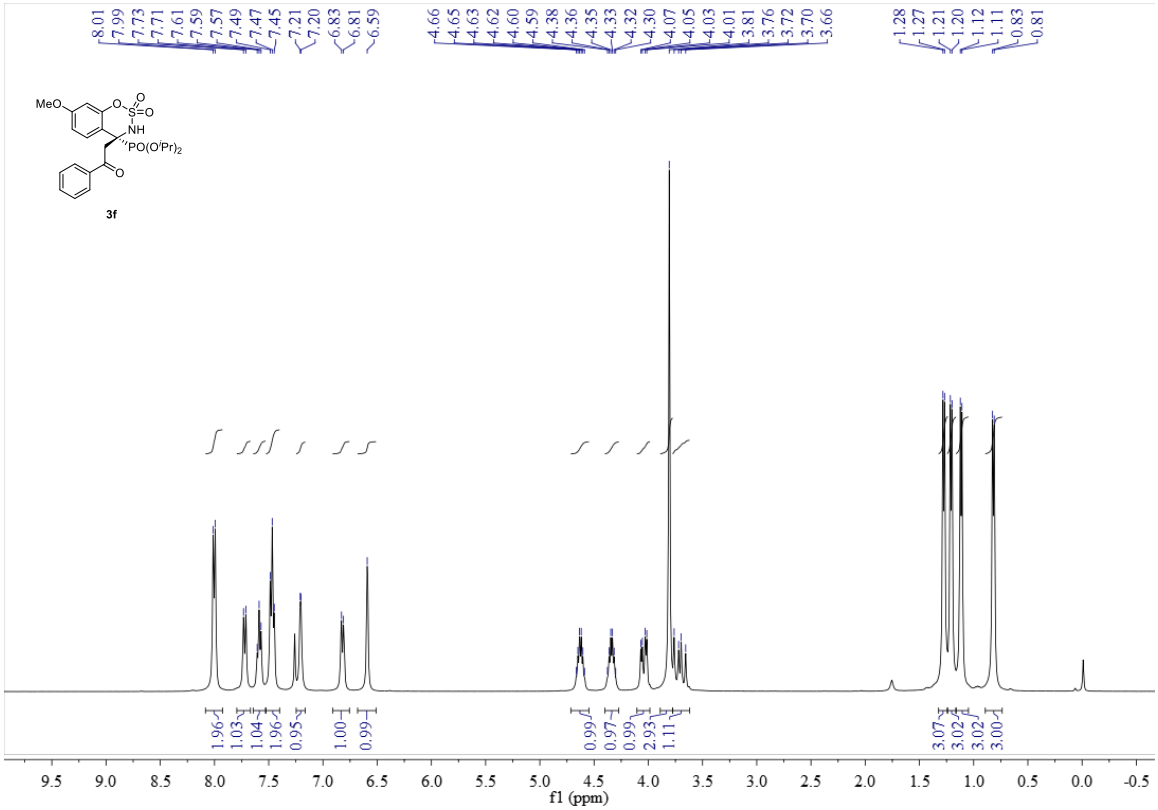
143.79
136.92
133.95
128.75
128.56
121.70
121.65
120.44
115.82
115.80
112.83
112.80
74.14
74.06
73.59
73.51
63.88
62.26
55.92
42.09
42.07
24.25
24.22
23.99
23.96
23.54
23.49
22.90
22.84
MeO
NH
PO(O^{i}Pr)$_2$
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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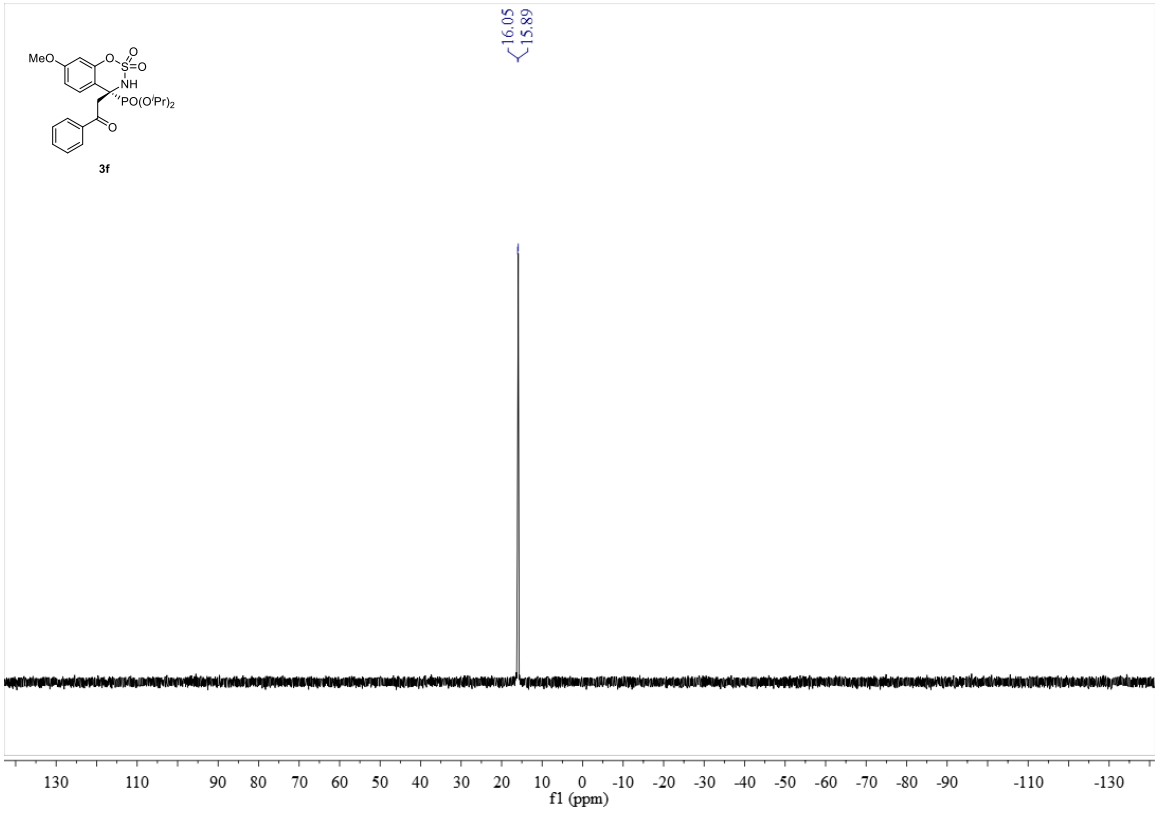
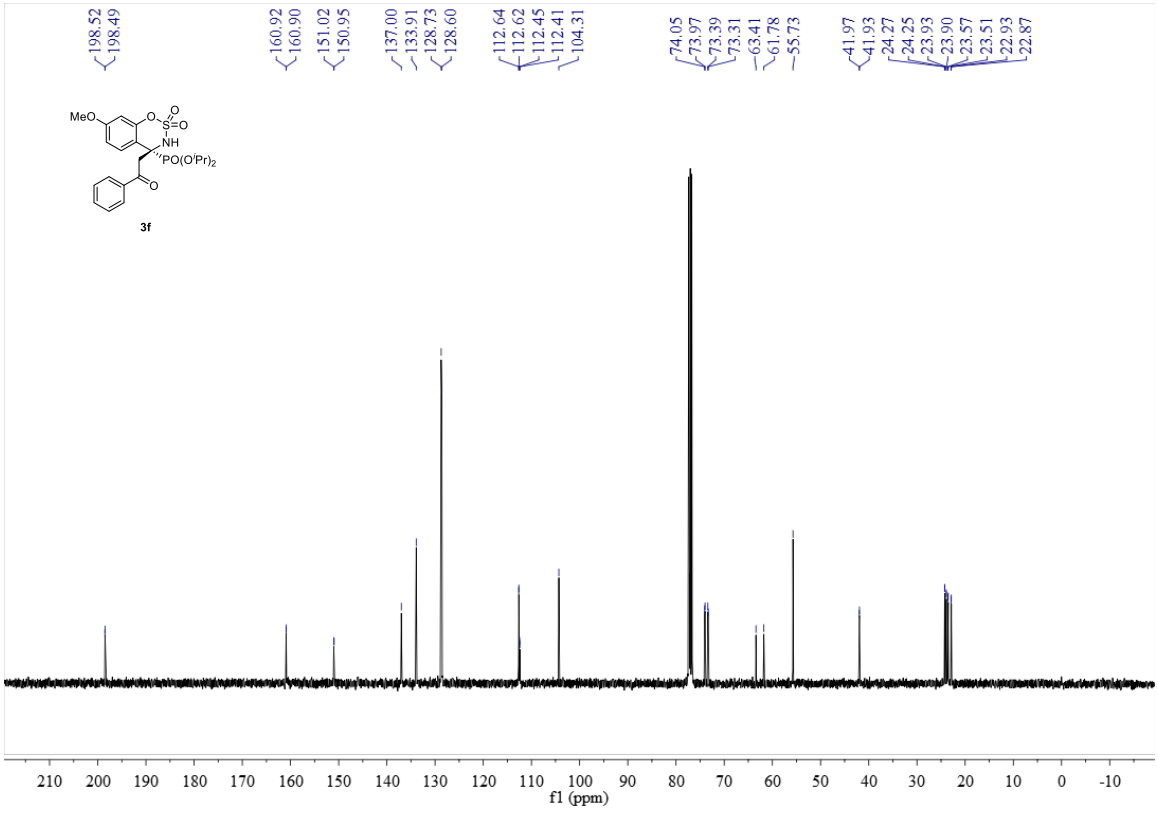
7.99
7.73
7.71
7.61
7.59
7.57
7.49
7.47
7.45
7.21
7.20
6.83
6.81
6.59
4.66
4.65
4.63
4.62
4.60
4.59
4.38
4.36
4.35
4.33
4.32
4.30
4.07
4.05
4.03
4.01
3.81
3.76
3.72
3.70
3.66
1.28
1.27
1.21
1.20
1.12
1.11
0.83
0.81
MeO
NH
PO(O^{i}Pr)$_2$
3f
1.96
1.03
1.04
1.96
0.95
1.00
0.99
0.99
0.97
0.99
2.93
1.11
3.07
3.02
3.02
3.00
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 -0.5
f1 (ppm)


16.05
15.89
MeO
NH
PO(OiPr)2
3f
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)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198.49
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151.02
150.95
137.00
133.91
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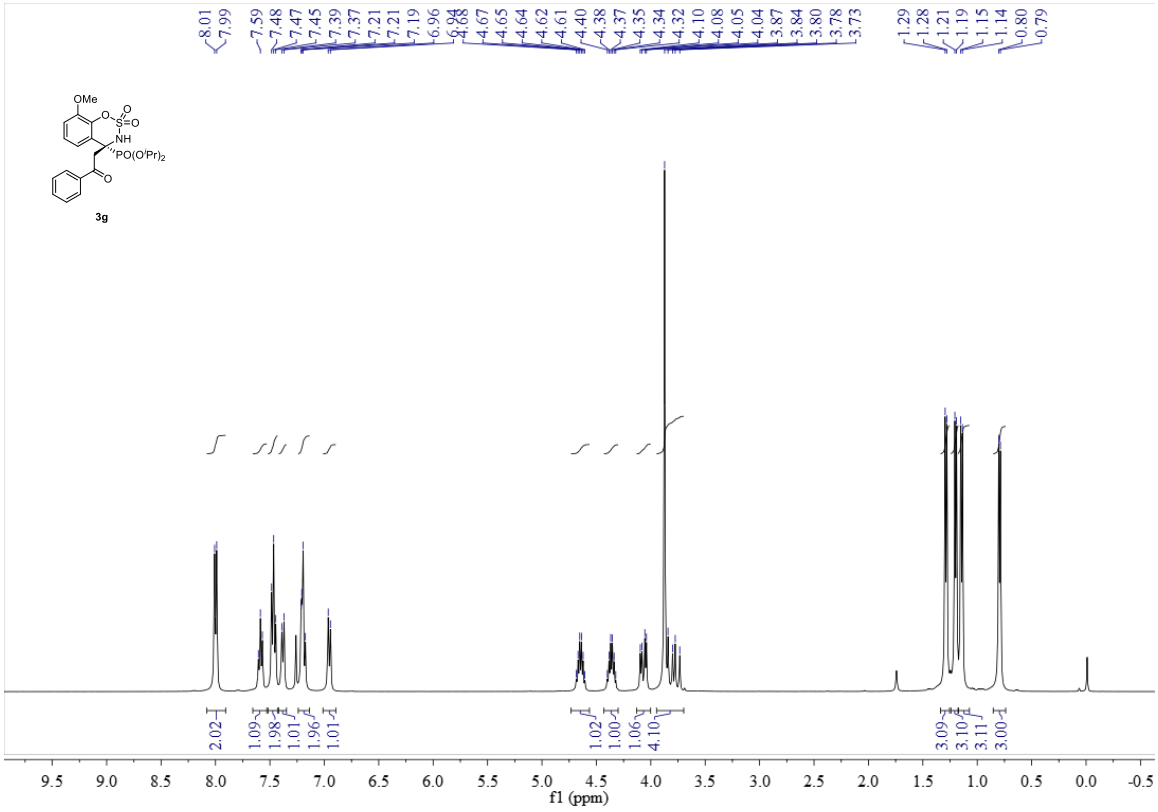
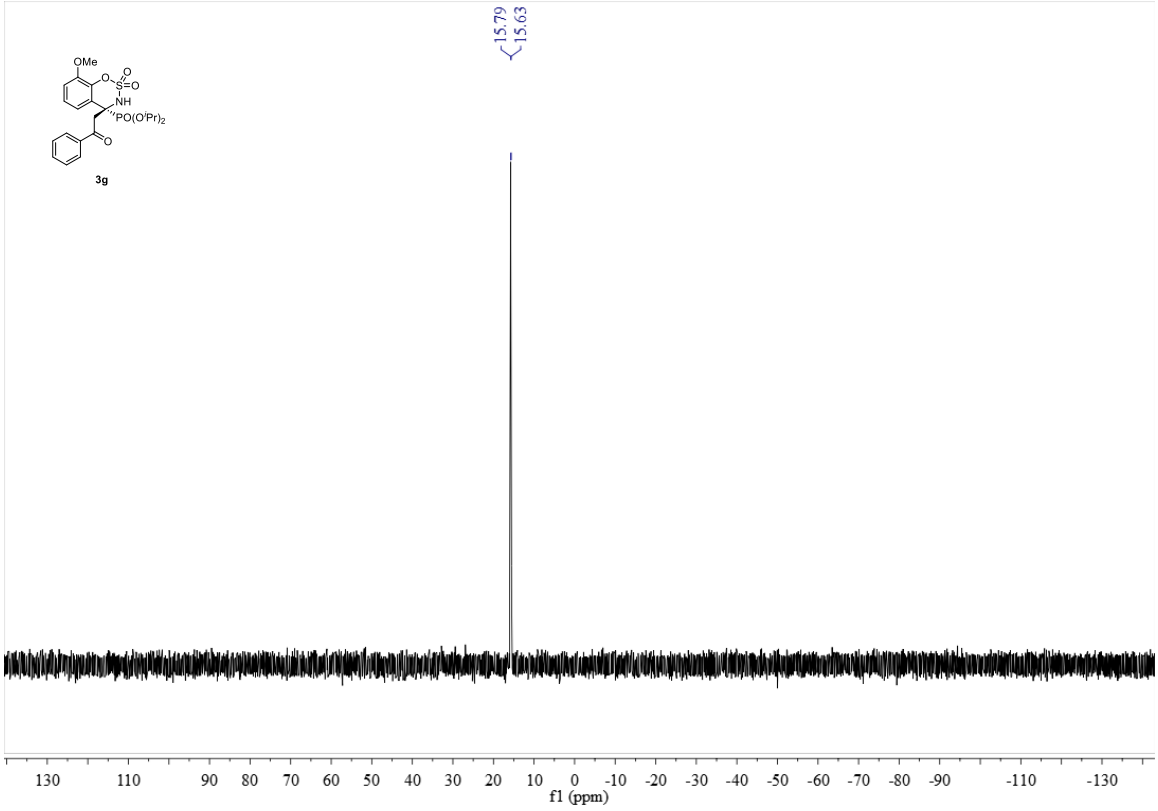
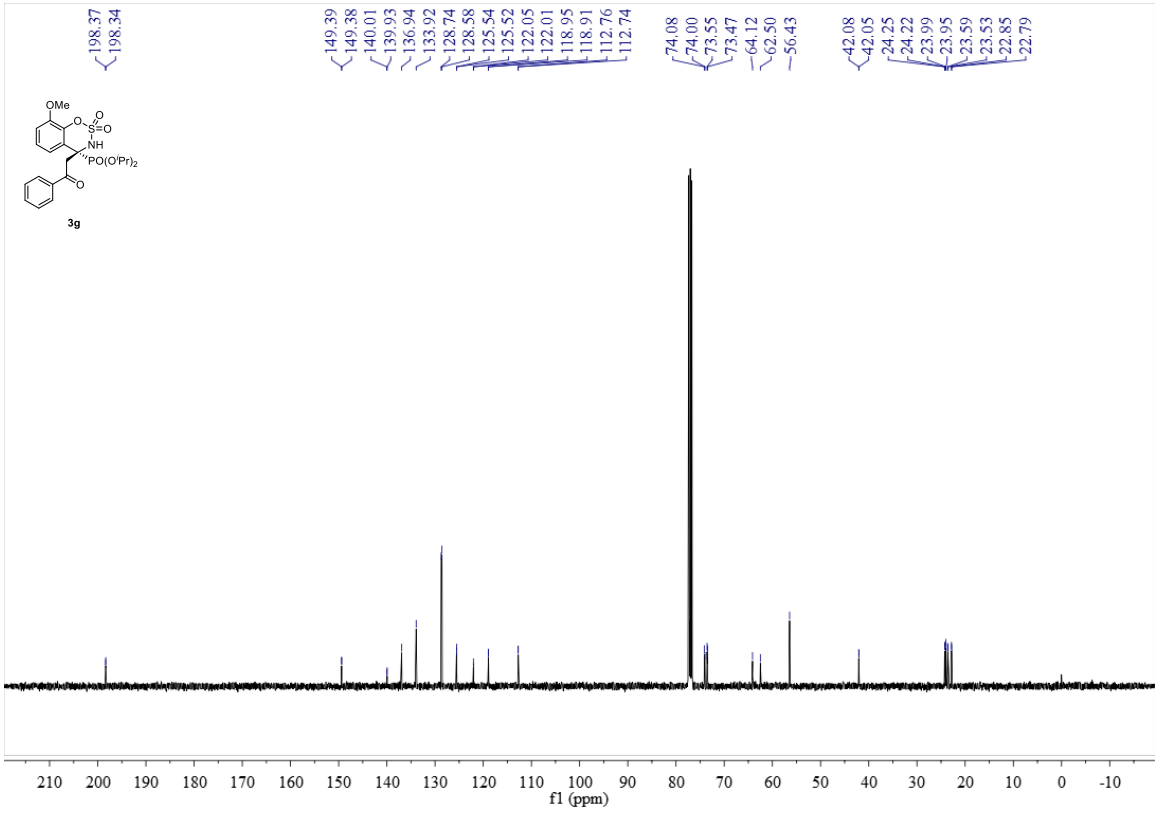
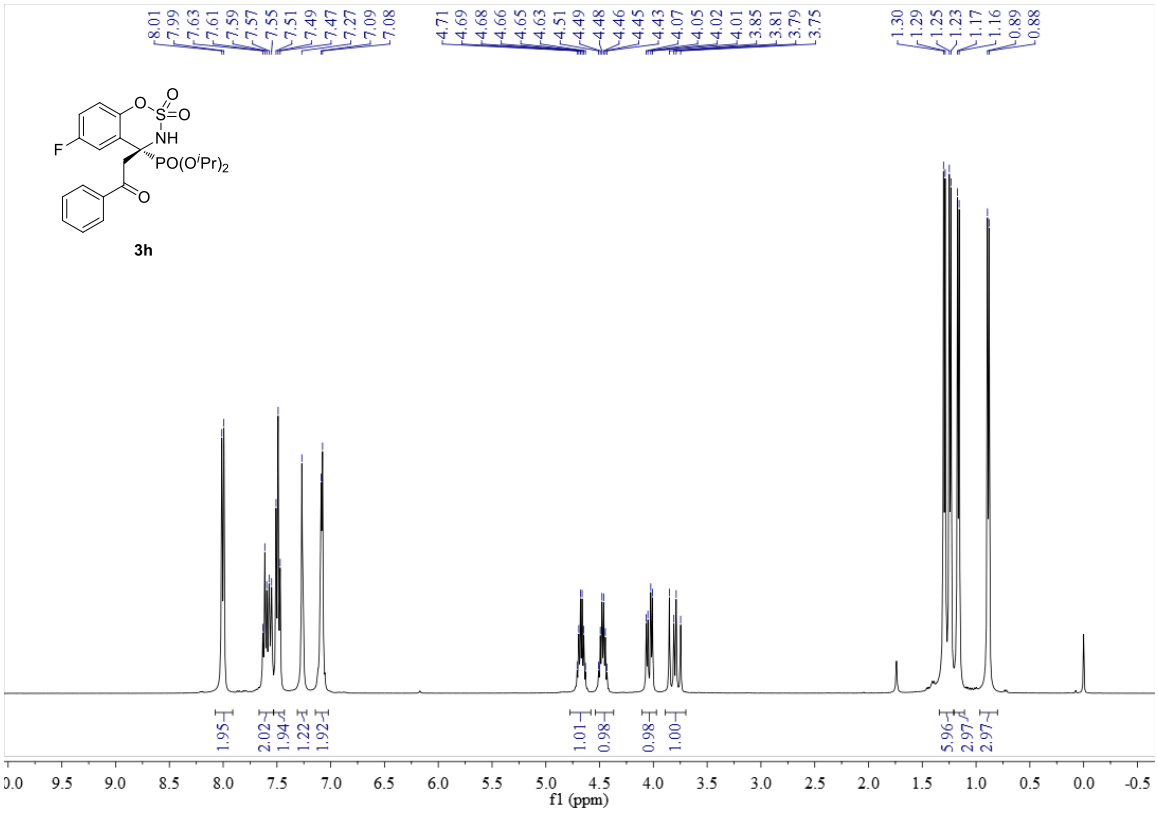
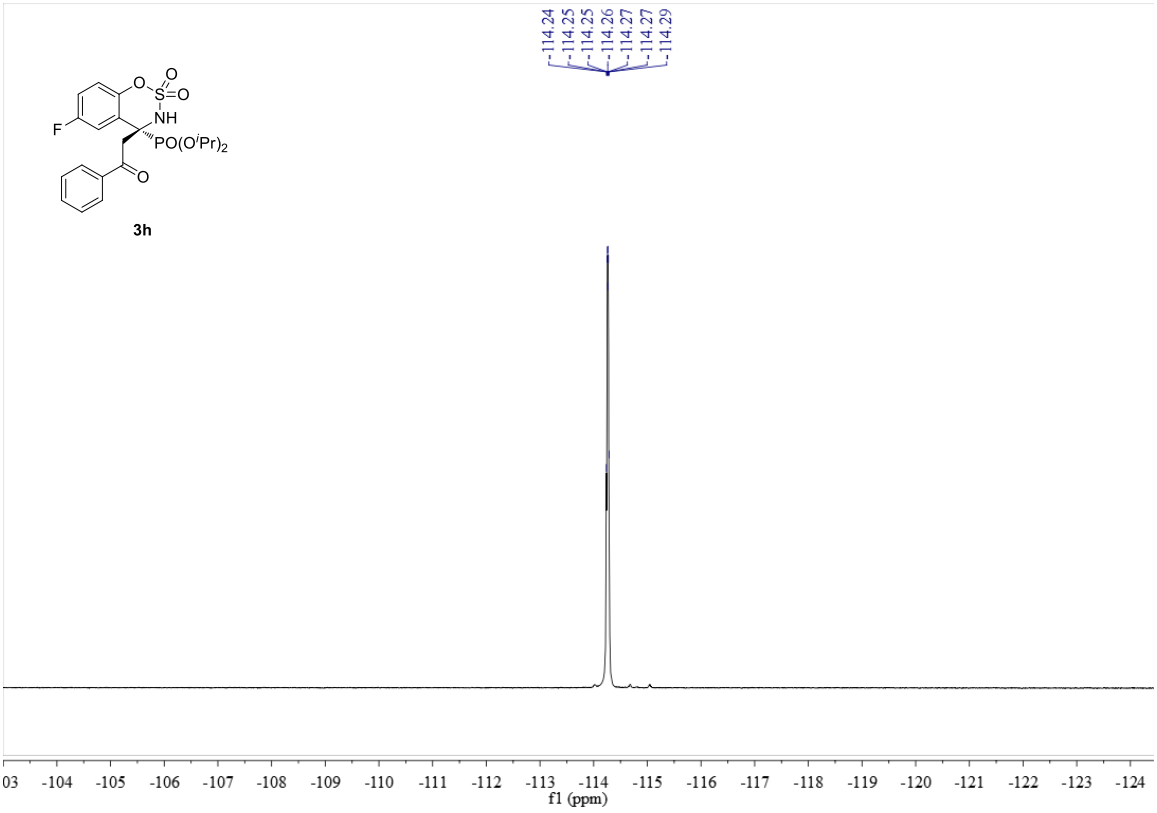
128.60
112.64
112.62
112.45
112.41
104.31
74.05
73.97
73.39
73.31
63.41
61.78
55.73
41.97
41.93
24.27
24.25
23.93
23.90
23.57
23.51
22.93
22.87
MeO
NH
PO(OiPr)2
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

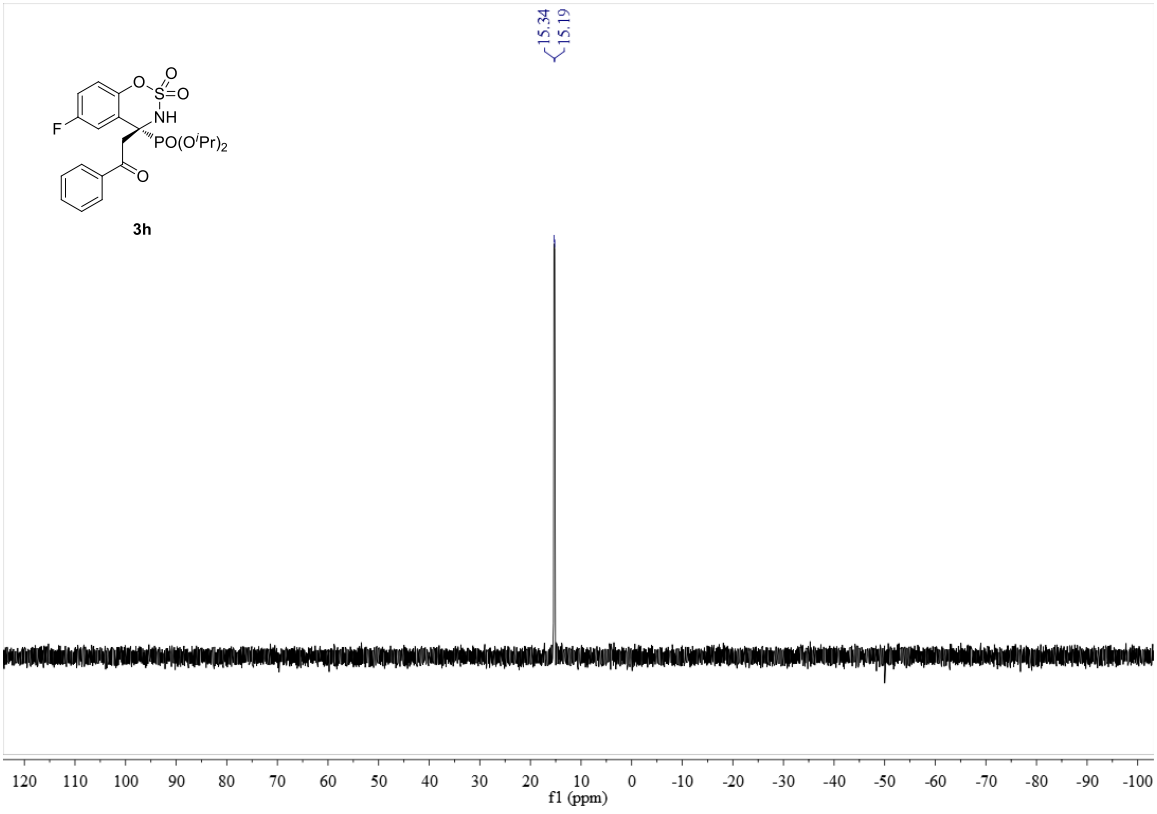

8.01
7.99
7.59
7.48
7.47
7.45
7.39
7.37
7.21
7.21
7.19
6.96
6.94
4.67
4.65
4.64
4.62
4.61
4.40
4.38
4.37
4.35
4.34
4.32
4.10
4.08
4.05
4.04
3.87
3.84
3.80
3.78
3.73
1.29
1.28
1.21
1.19
1.15
1.14
0.80
0.79
OMe
O
S
O
NH
PO(OiPr)2
O
3g
2.02
1.09
1.98
1.01
1.96
1.01
1.02
1.00
1.06
4.10
3.09
3.10
3.11
3.00
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 -0.5
f1 (ppm)

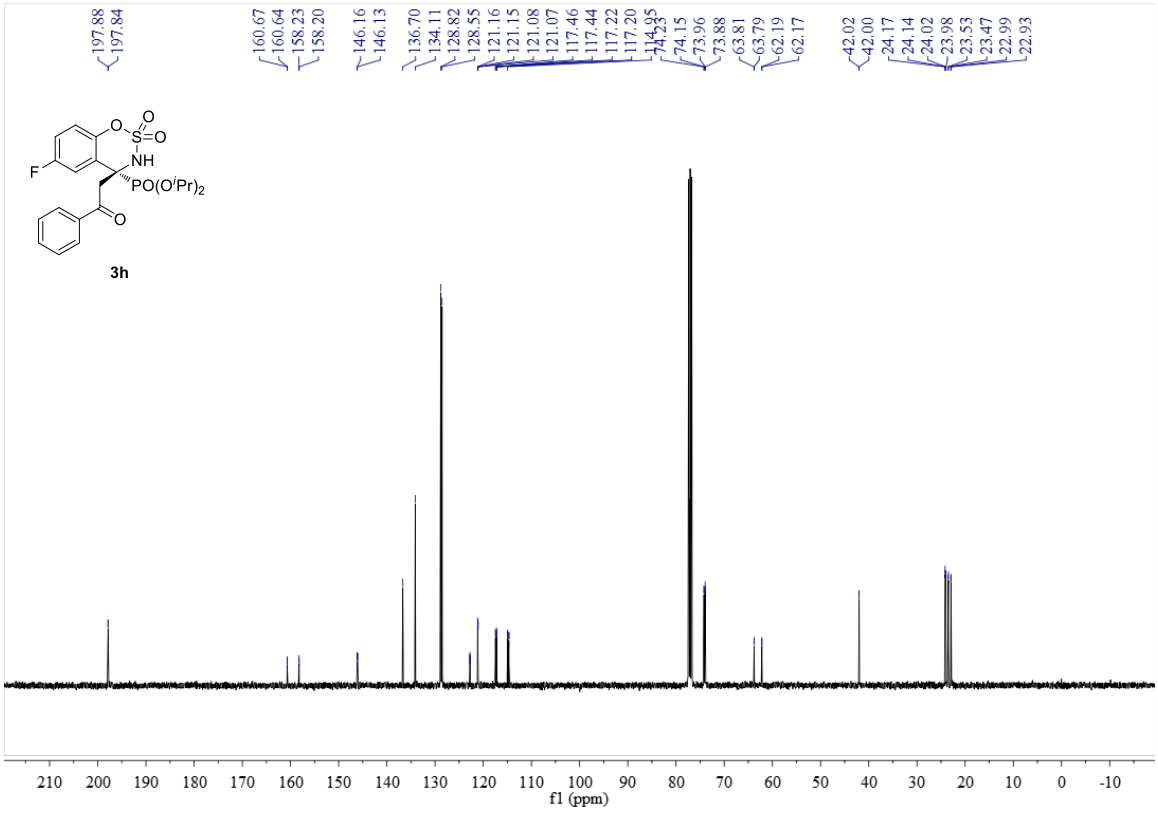

15.79
15.63
OMe
O
S
O
NH
PO(OiPr)2
O
3g
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)


198.37
198.34
149.39
149.38
140.01
139.93
136.94
133.92
128.74
128.58
125.54
125.52
122.05
122.01
118.95
118.91
112.76
112.74
74.08
74.00
73.55
73.47
64.12
62.50
56.43
42.08
42.05
24.25
24.22
23.99
23.95
23.59
23.53
22.85
22.79
OMe
NH
PO(O^{i}Pr)$_2$
3g
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)


8.01
7.99
7.63
7.61
7.59
7.57
7.55
7.51
7.49
7.47
7.27
7.09
7.08
4.71
4.69
4.68
4.66
4.65
4.63
4.51
4.49
4.48
4.46
4.45
4.43
4.07
4.05
4.02
4.01
3.85
3.81
3.79
3.75
1.30
1.29
1.25
1.23
1.17
1.16
0.89
0.88
F
NH
PO(O^{i}Pr)$_2$
3h
1.95
2.02
1.94
1.22
1.92
1.01
0.98
0.98
1.00
5.96
2.97
2.97
f1 (ppm)


-114.24
-114.25
-114.25
-114.26
-114.27
-114.27
-114.29
F
O
S
O
NH
PO(O^{i}Pr)$_2$
O
3h
03 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 -122 -123 -124
f1 (ppm)


15.34
15.19
F
O
S
O
NH
PO(O^{i}Pr)$_2$
O
3h
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)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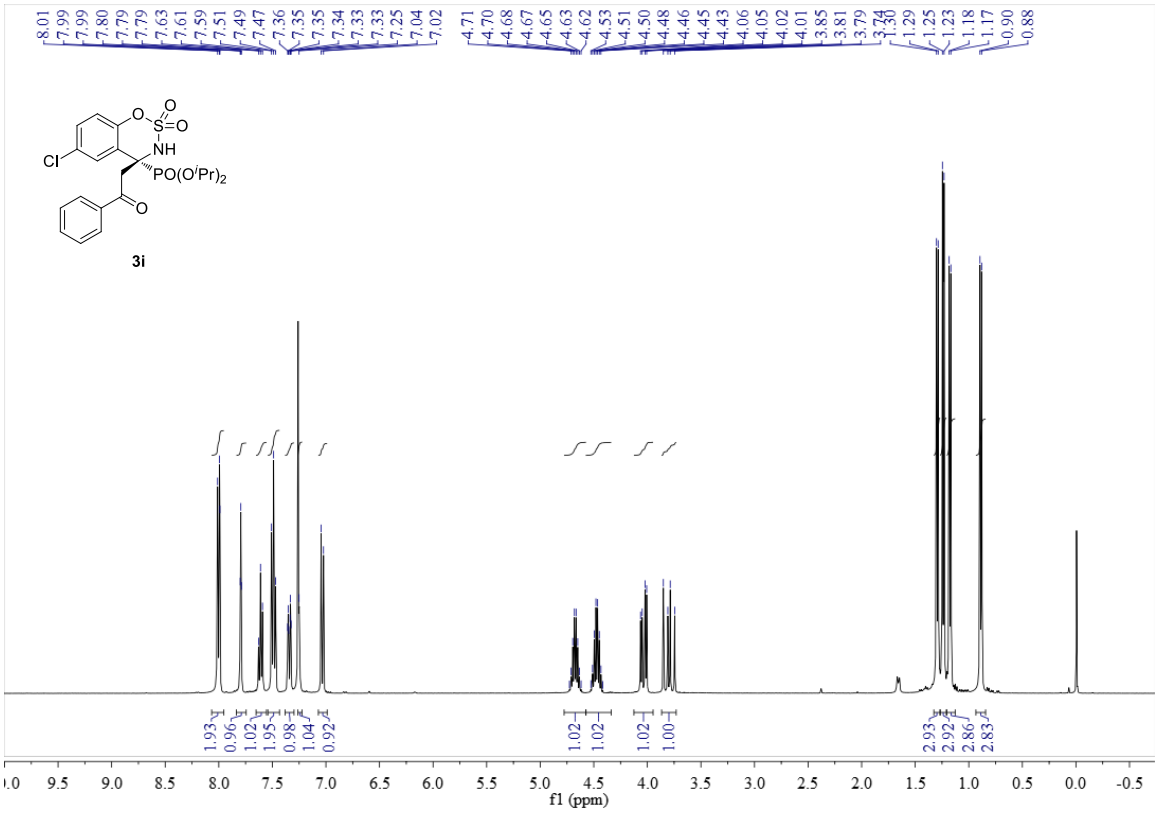
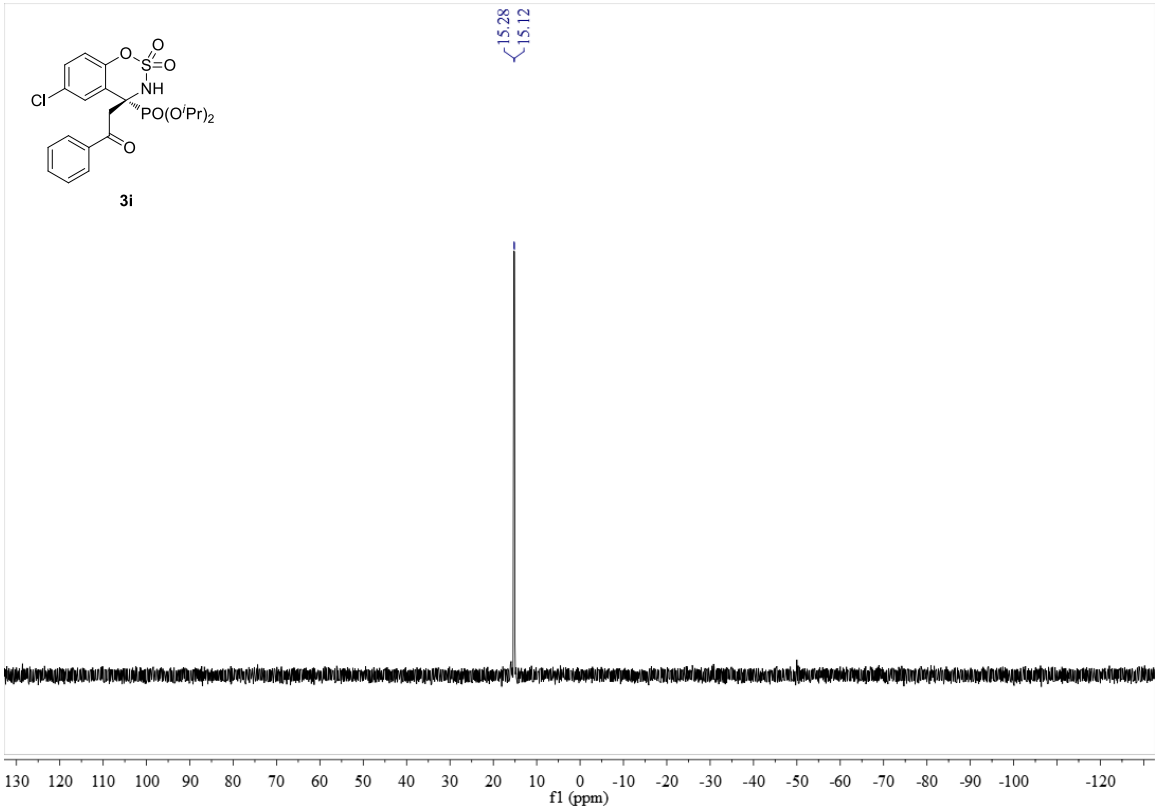
197.84
160.67
160.64
158.23
158.20
146.16
146.13
136.70
134.11
128.82
128.55
121.16
121.15
121.08
121.07
117.46
117.44
117.22
117.20
74.15
73.96
73.88
63.81
63.79
62.19
62.17
42.02
42.00
24.17
24.14
24.02
23.98
23.53
23.47
22.99
22.93
F
O
S
NH
PO(O^{i}Pr)$_2$
3h
f1 (ppm)


8.01
7.99
7.99
7.80
7.79
7.79
7.63
7.61
7.59
7.51
7.49
7.47
7.36
7.35
7.35
7.34
7.33
7.33
7.25
7.04
7.02
4.71
4.70
4.68
4.67
4.65
4.63
4.62
4.53
4.51
4.50
4.48
4.46
4.45
4.43
4.06
4.05
4.02
4.01
3.85
3.81
3.79
3.74
1.30
1.29
1.25
1.23
1.18
1.17
0.90
0.88
Cl
O
S
NH
PO(O^{i}Pr)$_2$
3i
1.93
0.96
1.02
1.95
0.98
1.04
0.92
1.02
1.02
1.02
1.00
2.93
2.92
2.86
2.83
f1 (ppm)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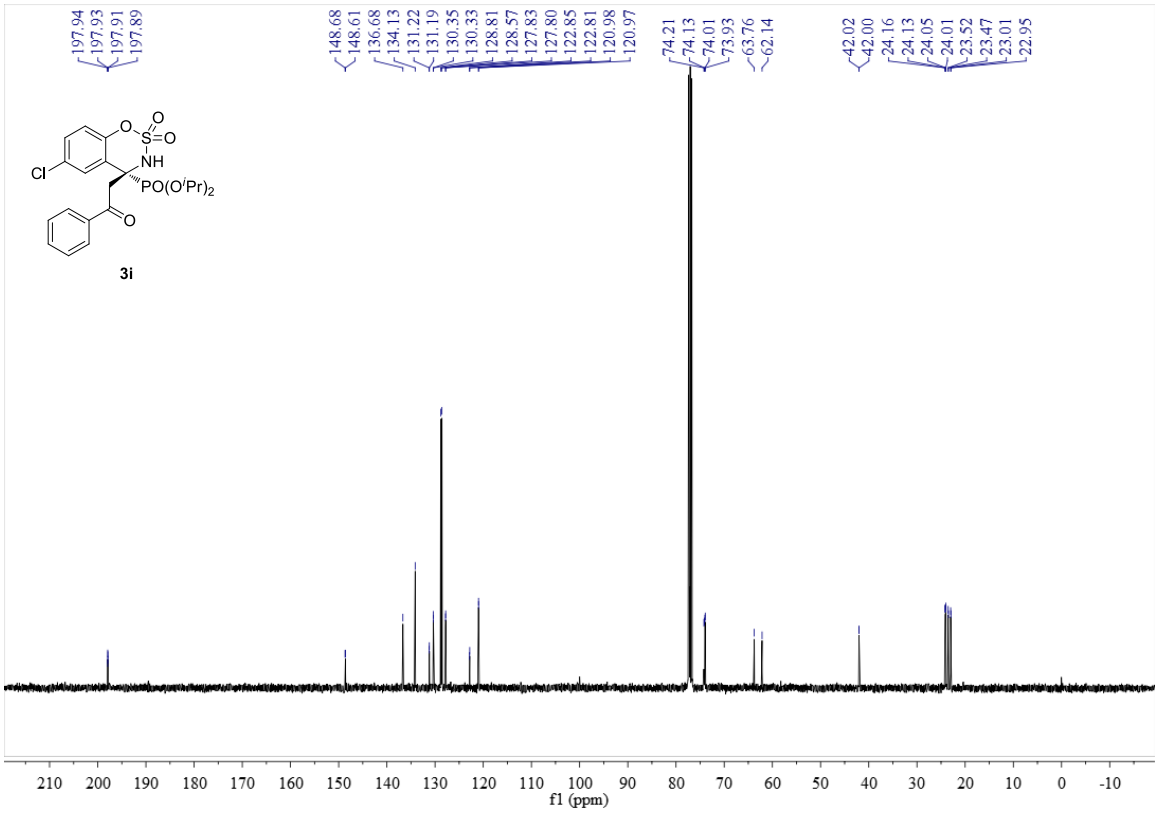
15.12
Cl
NH
PO(O^{i}Pr)$_2$
3i
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120
f1 (ppm)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197.93
197.91
197.89
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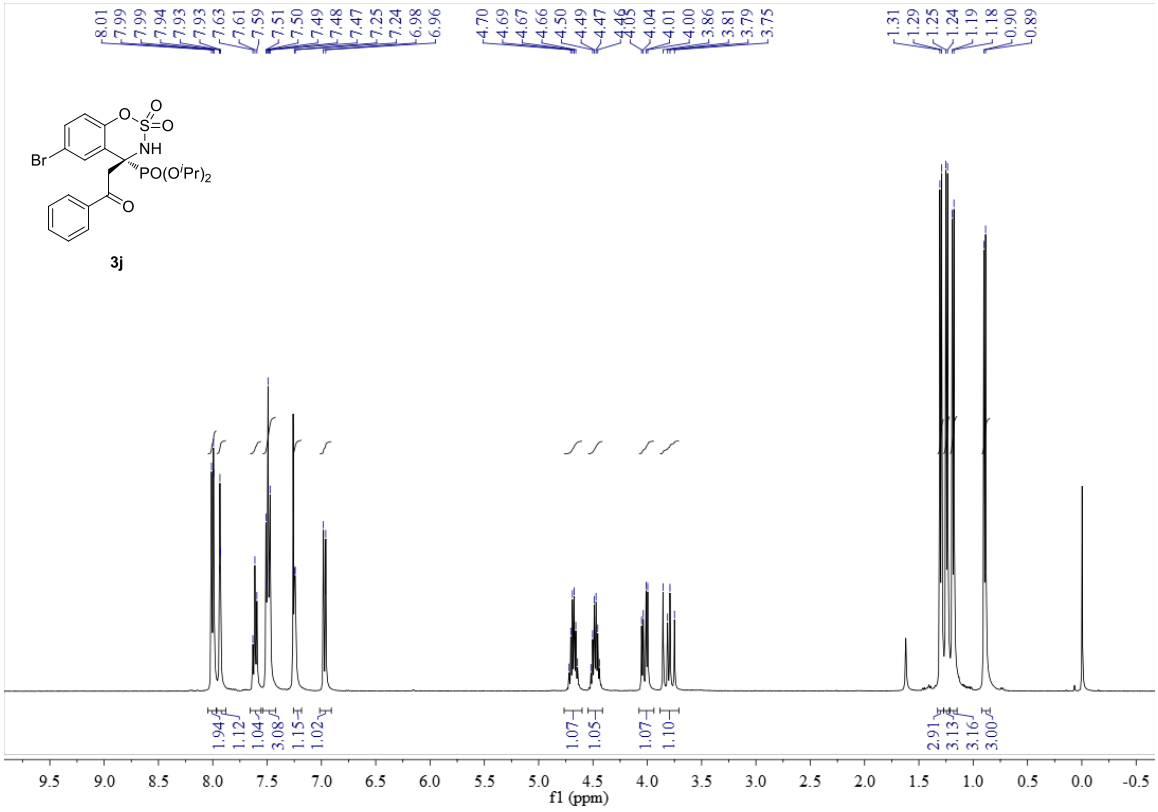
148.61
136.68
134.13
131.22
131.19
130.35
130.33
128.81
128.57
127.83
127.80
122.85
122.81
120.98
120.97
74.21
74.13
74.01
73.93
63.76
62.14
42.02
42.00
24.16
24.13
24.05
24.01
23.52
23.47
23.01
22.95
Cl
NH
PO(O^{i}Pr)$_2$
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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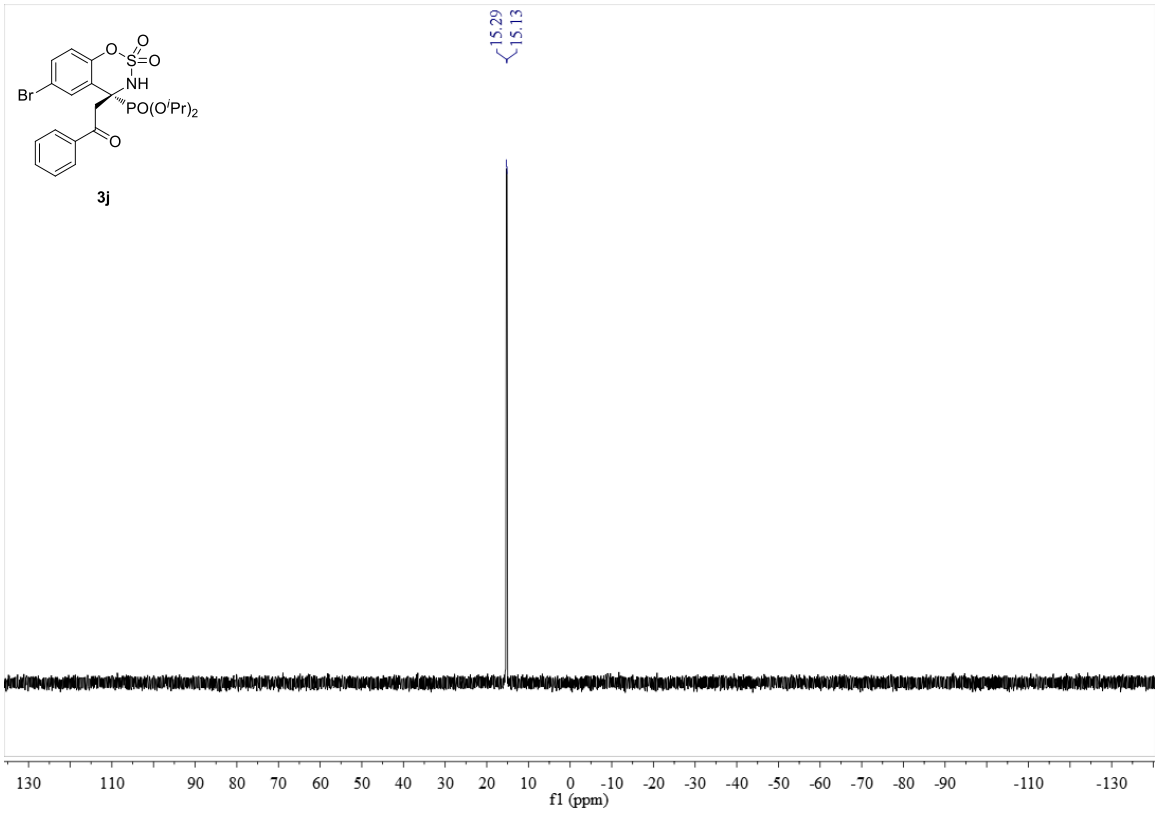
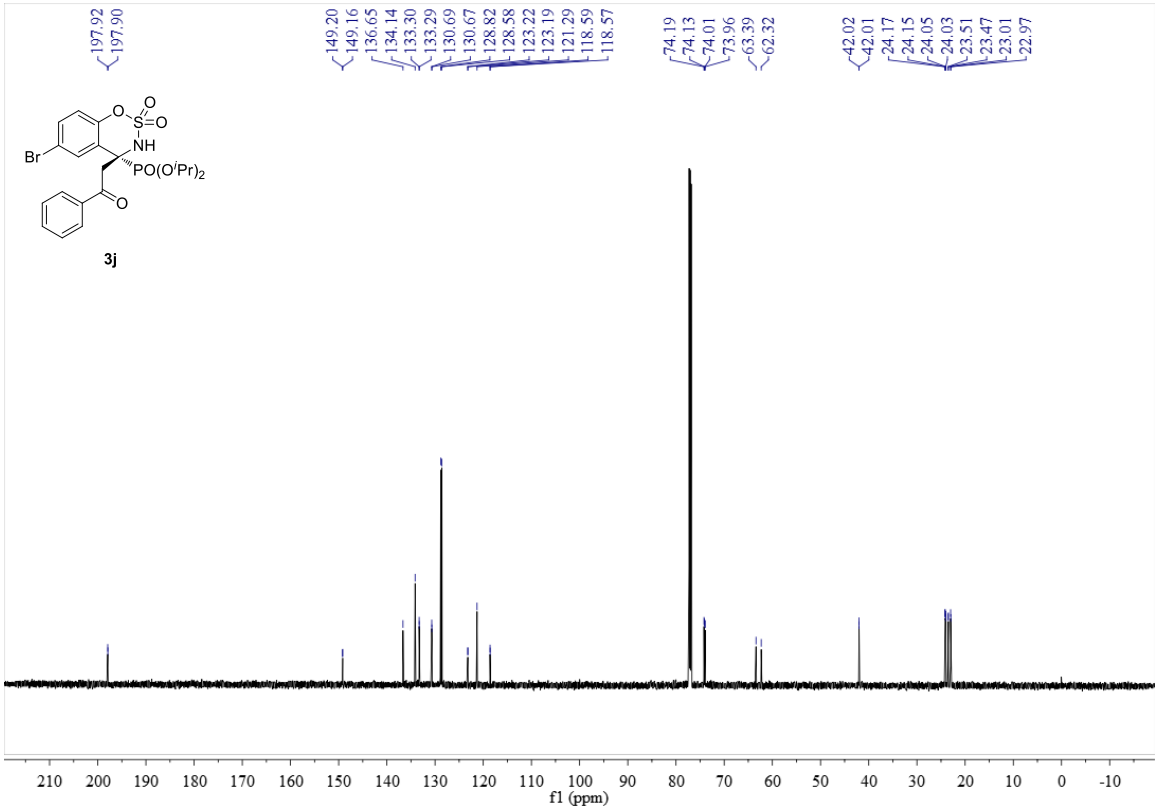
7.99
7.99
7.94
7.93
7.93
7.63
7.61
7.59
7.51
7.50
7.49
7.48
7.47
7.25
7.24
6.98
6.96
4.70
4.69
4.67
4.66
4.50
4.49
4.47
4.46
4.05
4.04
4.01
4.00
3.86
3.81
3.79
3.75
1.31
1.29
1.25
1.24
1.19
1.18
0.90
0.89
Br
NH
PO(O^{i}Pr)$_2$
3j
1.94
1.12
1.04
3.08
1.15
1.02
1.07
1.05
1.07
1.10
2.91
3.13
3.16
3.00
f1 (ppm)


15.29
15.13
Br
NH
PO(O^{i}Pr)$_2$
3j
f1 (ppm)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197.90
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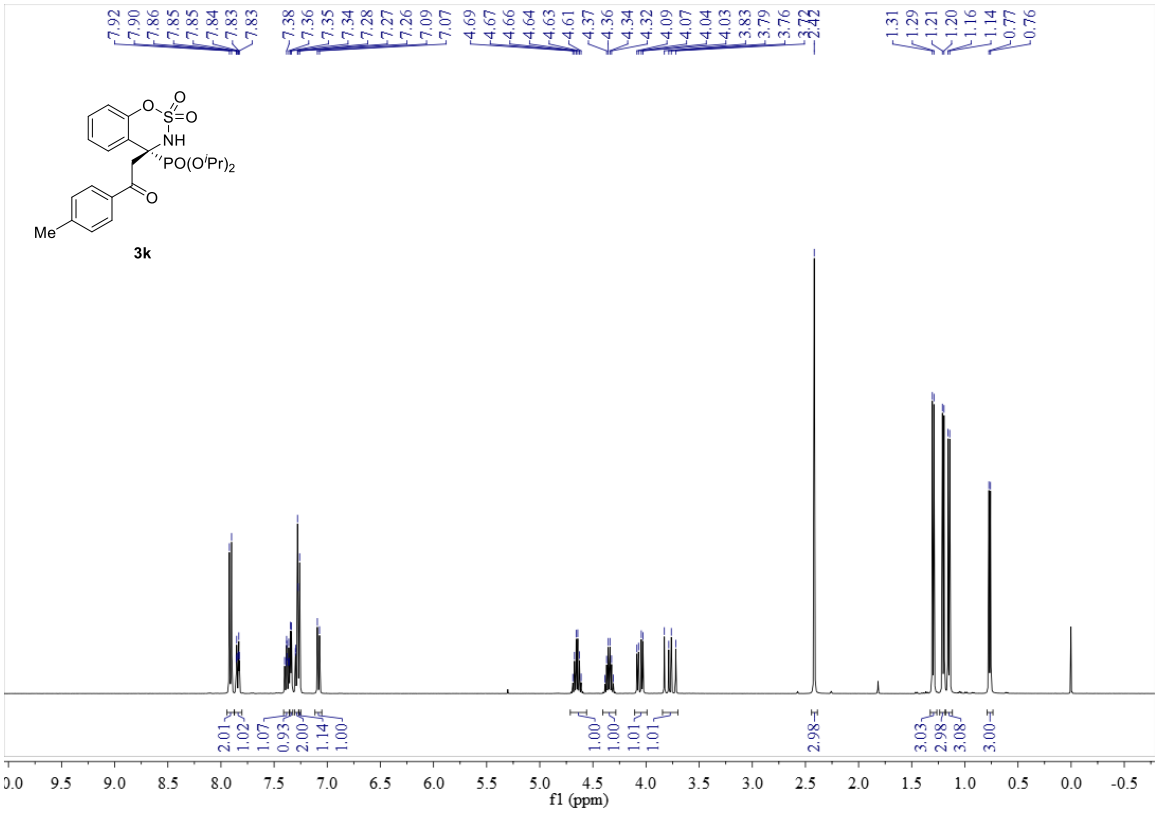
134.14
133.30
133.29
130.69
130.67
128.82
128.58
123.22
123.19
121.29
118.59
118.57
74.19
74.13
74.01
73.96
63.39
62.32
42.02
42.01
24.17
24.15
24.05
24.03
23.51
23.47
23.01
22.97
Br
NH
PO(O^{i}Pr)$_2$
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.90
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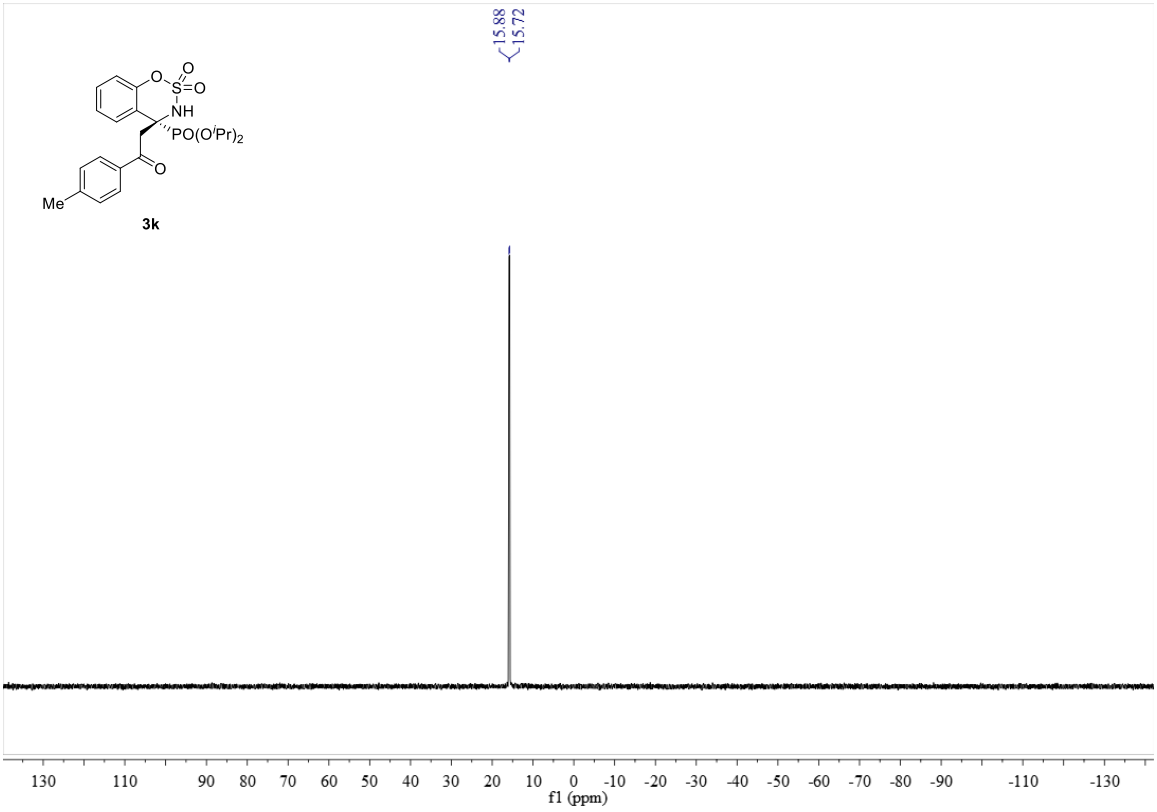
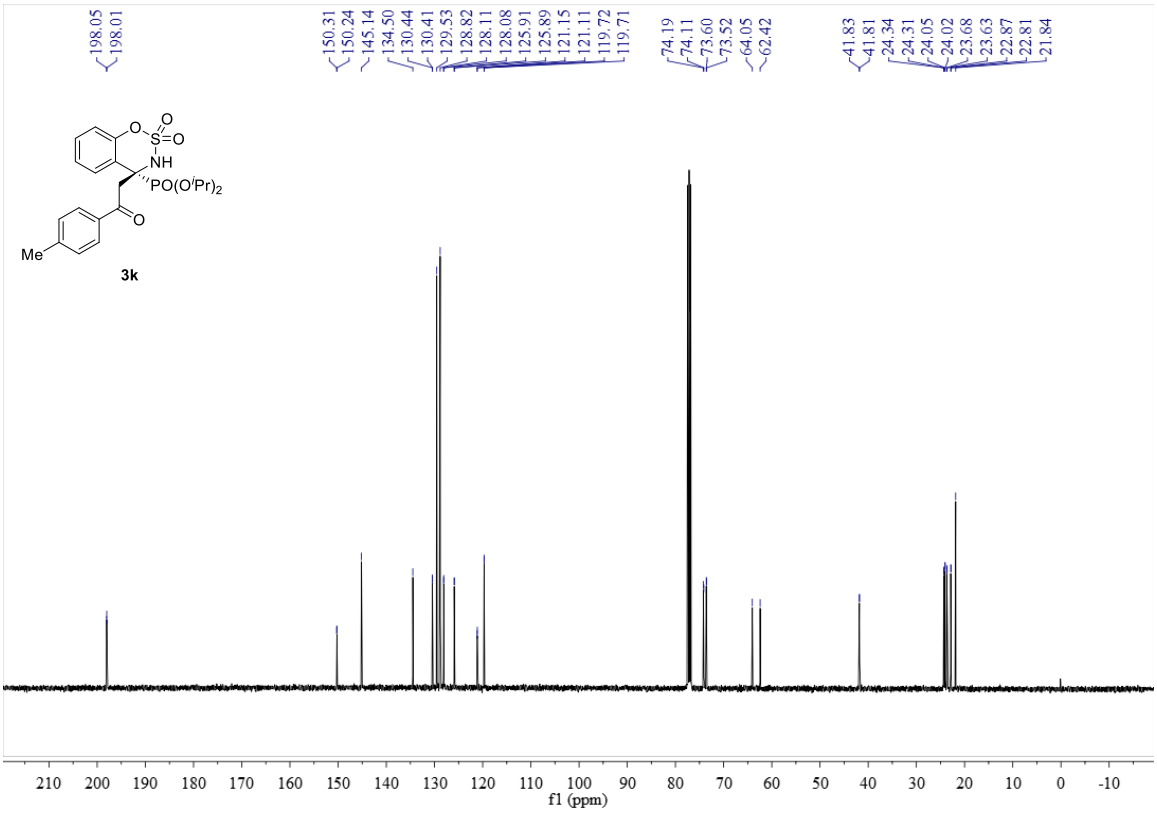
7.85
7.84
7.83
7.83
7.38
7.36
7.35
7.34
7.28
7.27
7.26
7.09
7.07
4.69
4.67
4.66
4.64
4.63
4.61
4.37
4.36
4.34
4.32
4.09
4.07
4.04
4.03
3.83
3.79
3.76
1.31
1.29
1.21
1.20
1.16
1.14
0.77
0.76
NH
PO(O^{i}Pr)$_2$
Me
3k
2.01
1.02
1.07
0.93
2.00
1.14
1.00
1.00
1.00
1.01
1.01
2.98
3.03
2.98
3.08
3.00
f1 (ppm)


15.88
15.72
NH
PO(O^{i}Pr)$_2$
Me
3k
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)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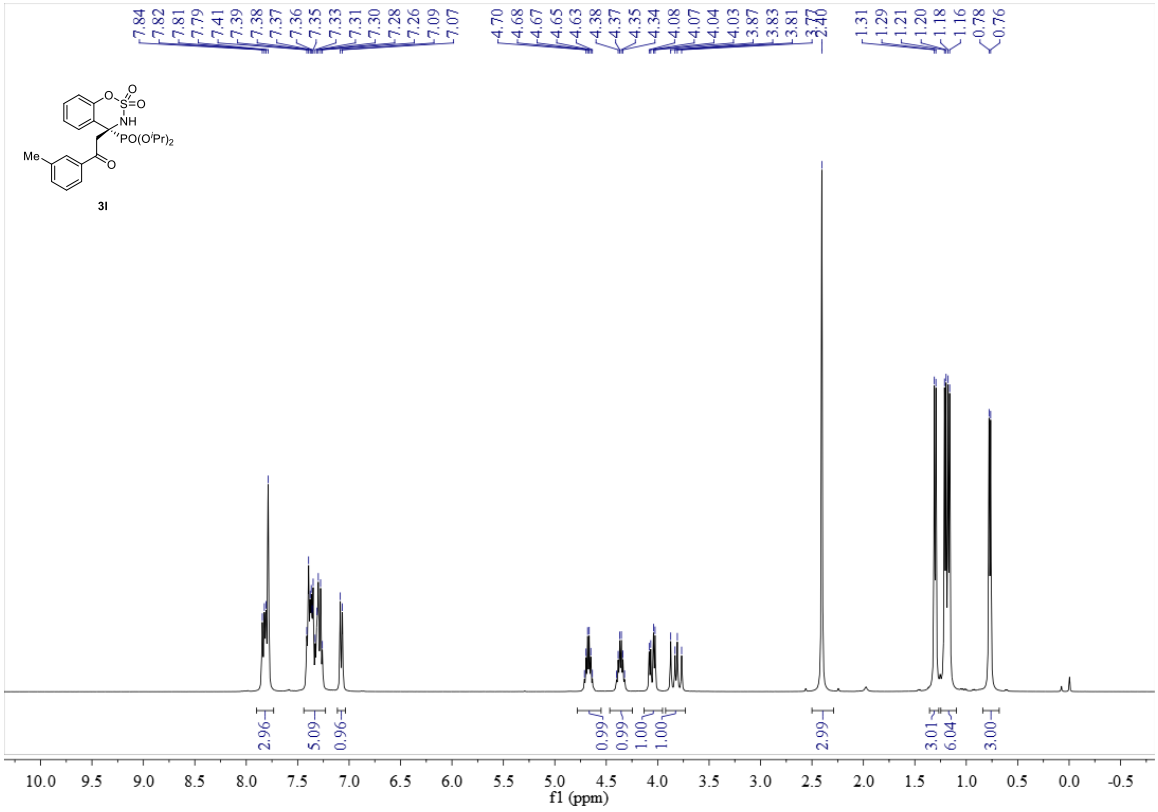
198.01
150.31
150.24
145.14
134.50
130.44
130.41
129.53
128.82
128.11
128.08
125.91
125.89
121.15
121.11
119.72
119.71
74.19
74.11
73.60
73.52
64.05
62.42
41.83
41.81
24.34
24.31
24.05
24.02
23.68
23.63
22.87
22.81
21.84
NH
PO(O^{i}Pr)$_2$
Me
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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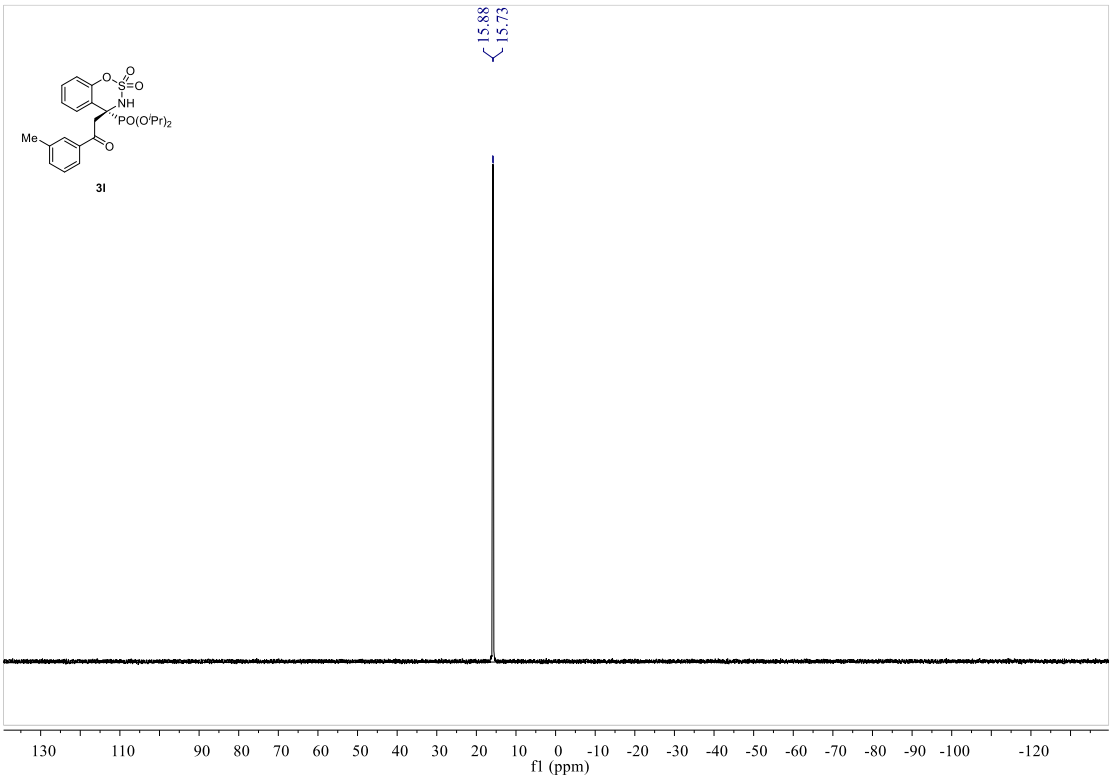
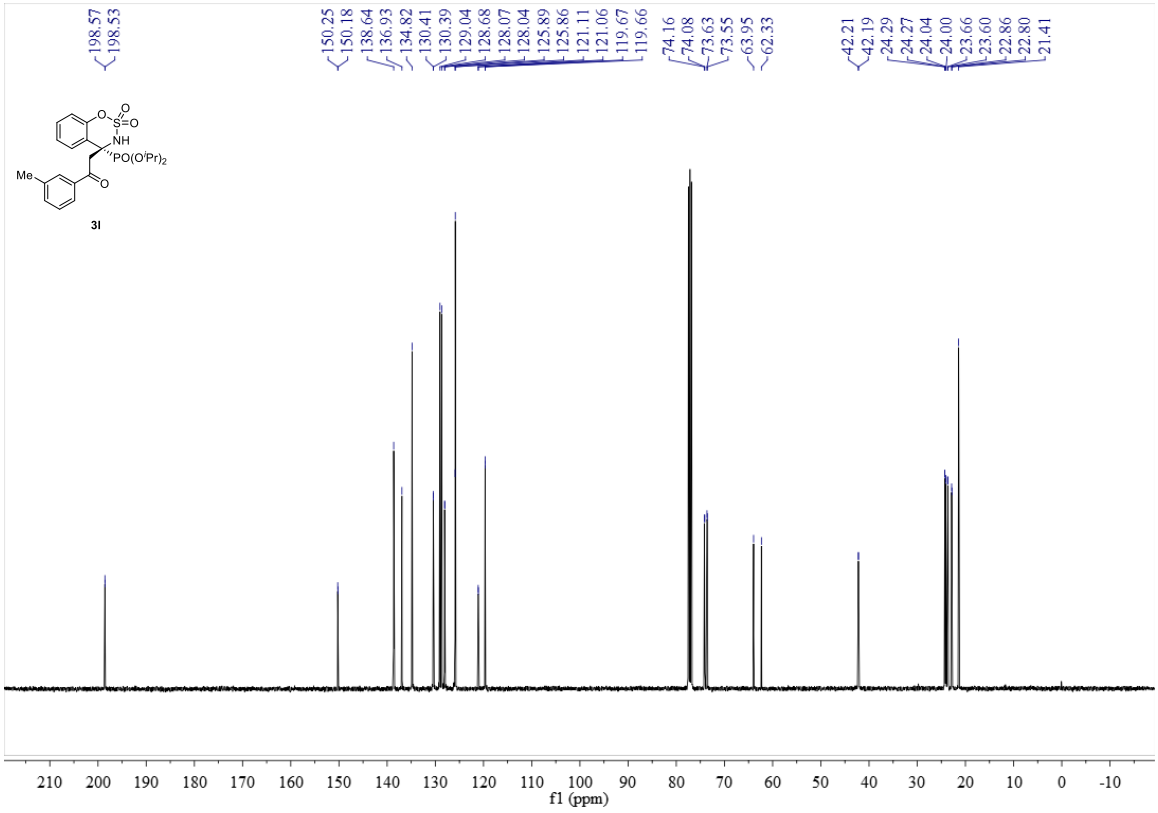
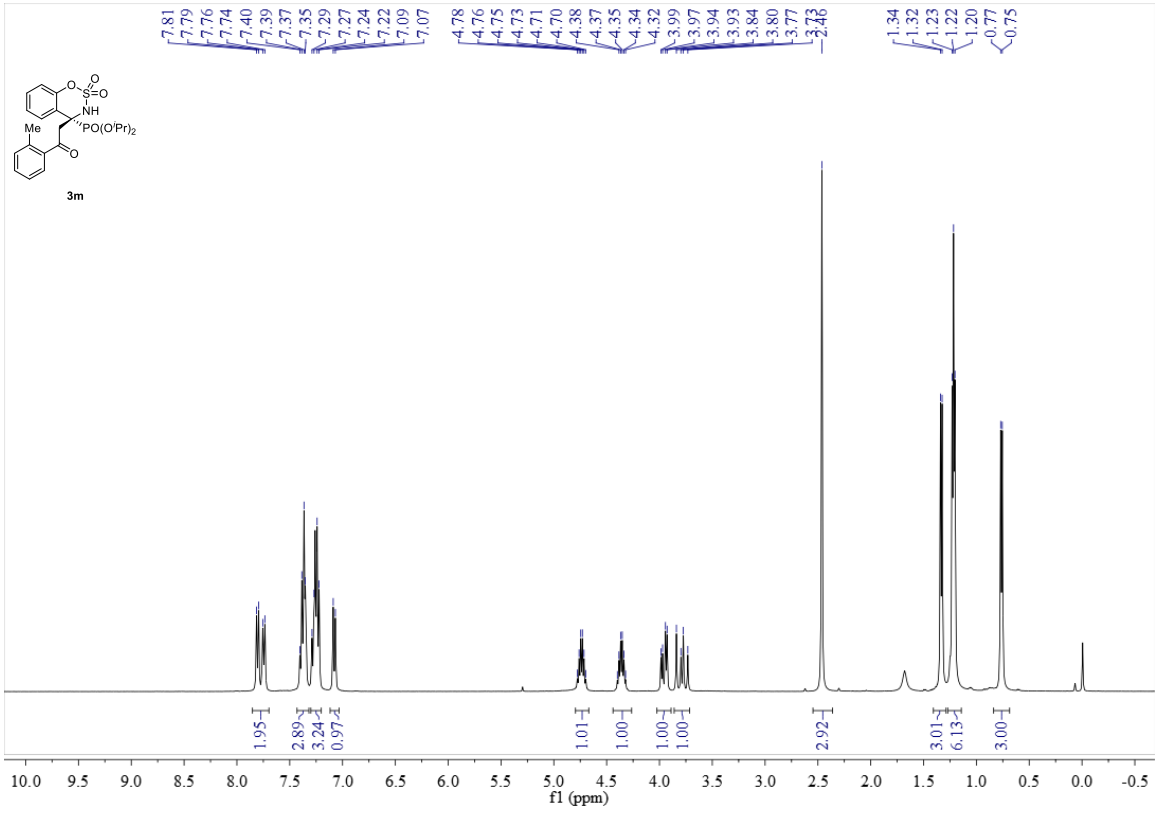
7.82
7.81
7.79
7.41
7.39
7.38
7.37
7.36
7.35
7.33
7.31
7.30
7.28
7.26
7.09
7.07
4.70
4.68
4.67
4.65
4.63
4.38
4.37
4.35
4.34
4.08
4.07
4.04
4.03
3.87
3.83
3.81
3.77
2.40
1.31
1.29
1.21
1.20
1.18
1.16
0.78
0.76
NH
PO(OiPr)2
Me
O
3l
2.96
5.09
0.96
0.99
0.99
1.00
1.00
2.99
3.01
6.04
3.00
10.0 9.5 9.0 8.5 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 -0.5
f1 (ppm)


15.88
15.73
NH
PO(OiPr)2
Me
O
3l
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120
f1 (ppm)


198.57
198.53
150.25
150.18
138.64
136.93
134.82
130.41
130.39
129.04
128.68
128.07
128.04
125.89
125.86
121.11
121.06
119.67
119.66
74.16
74.08
73.63
73.55
63.95
62.33
42.21
42.19
24.29
24.27
24.04
24.00
23.66
23.60
22.86
22.80
21.41
Me
PO(OiPr)2
3l
f1 (ppm)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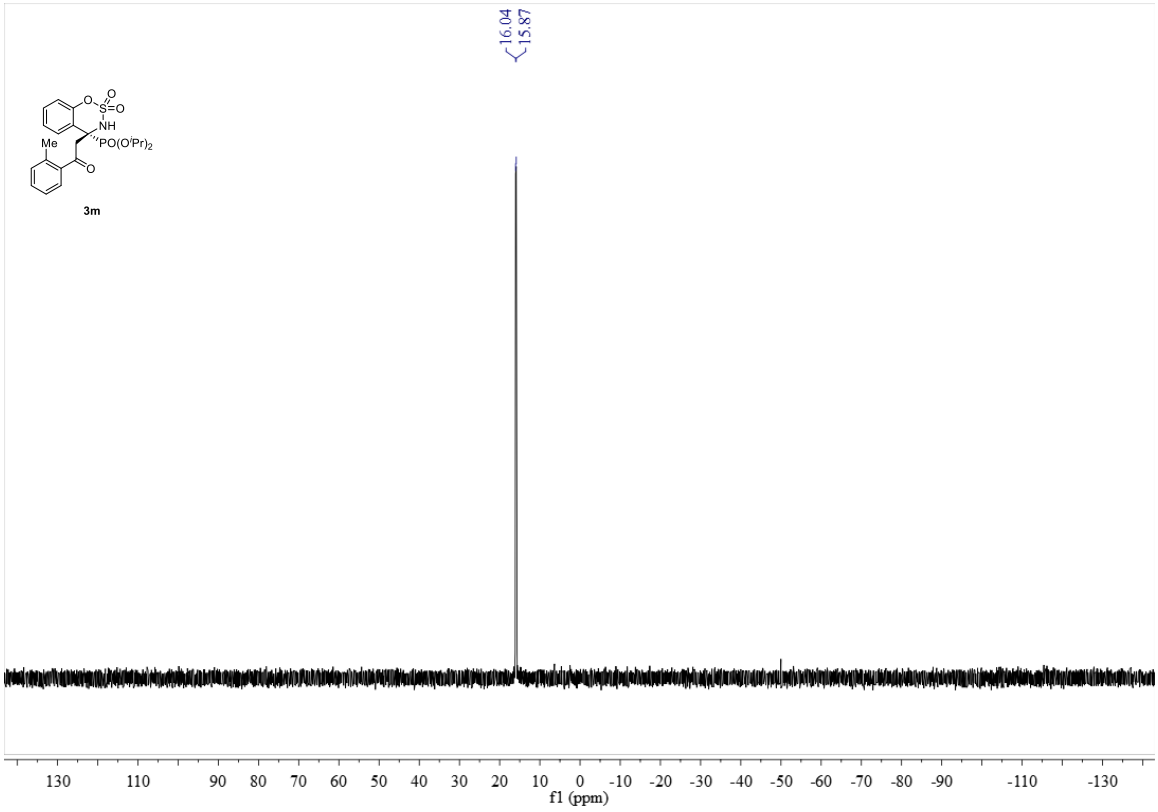
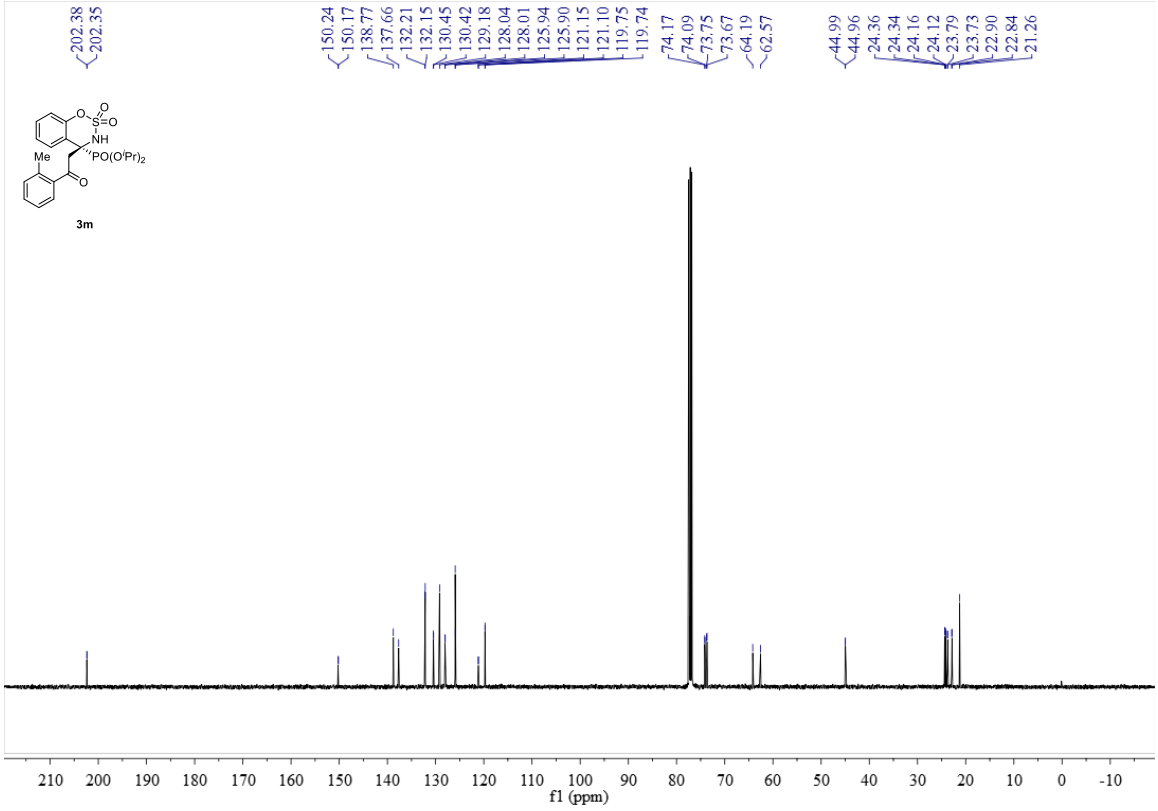
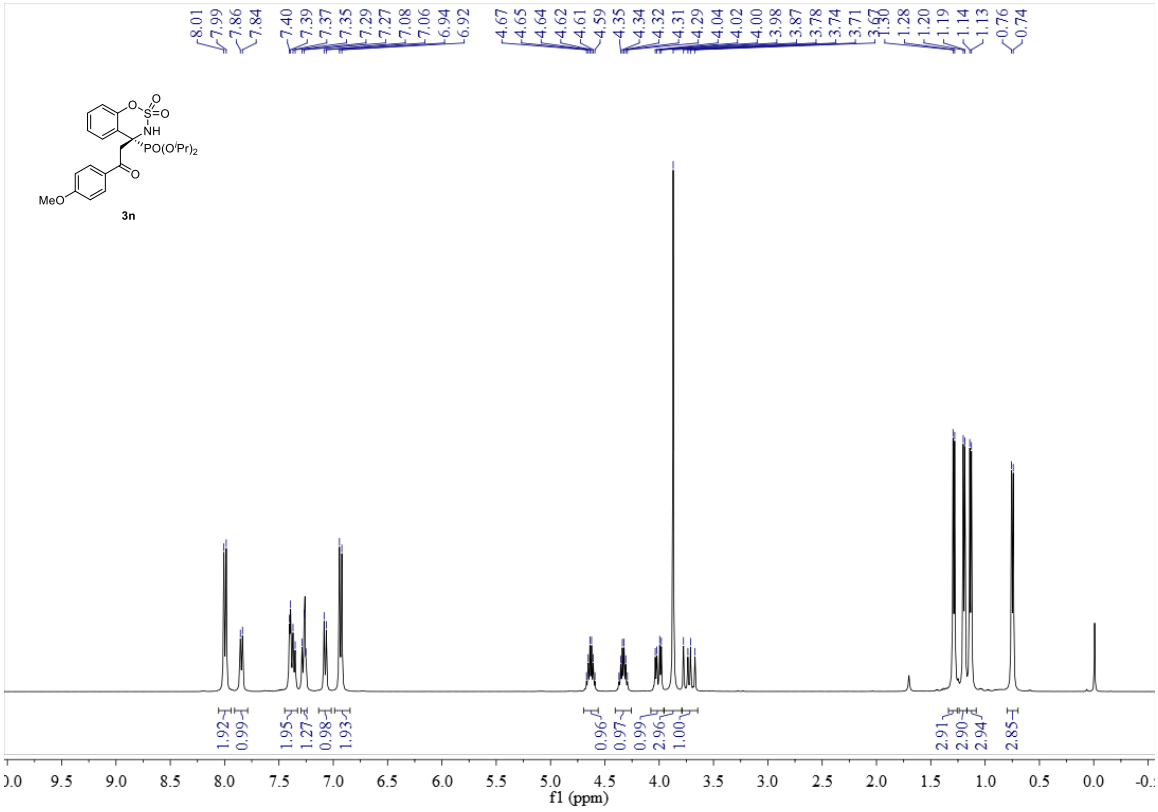
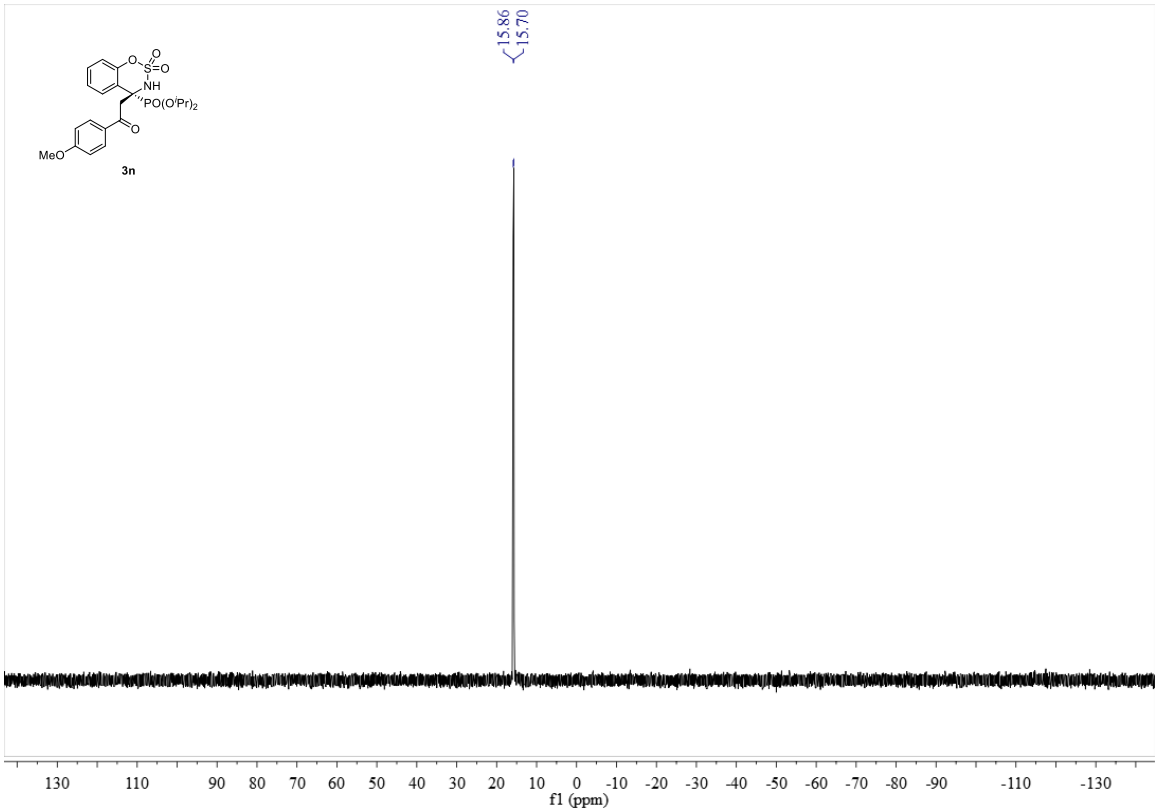
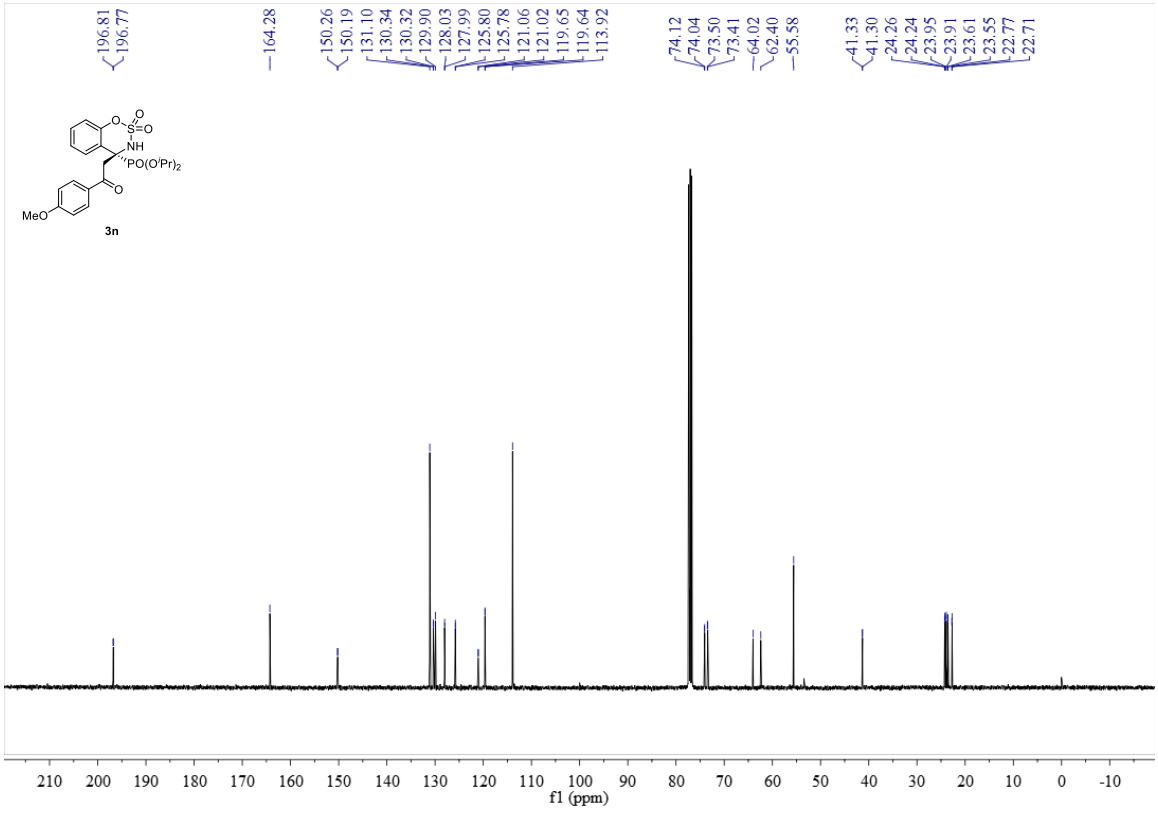
7.79
7.76
7.74
7.40
7.39
7.37
7.35
7.29
7.27
7.24
7.22
7.09
7.07
4.78
4.76
4.75
4.73
4.71
4.70
4.38
4.37
4.35
4.34
4.32
3.99
3.97
3.94
3.93
3.84
3.80
3.77
3.73
2.46
1.34
1.32
1.23
1.22
1.20
0.77
0.75
Me
PO(OiPr)2
3m
1.95
2.89
3.24
0.97
1.01
1.00
1.00
1.00
2.92
3.01
6.13
3.00
f1 (ppm)

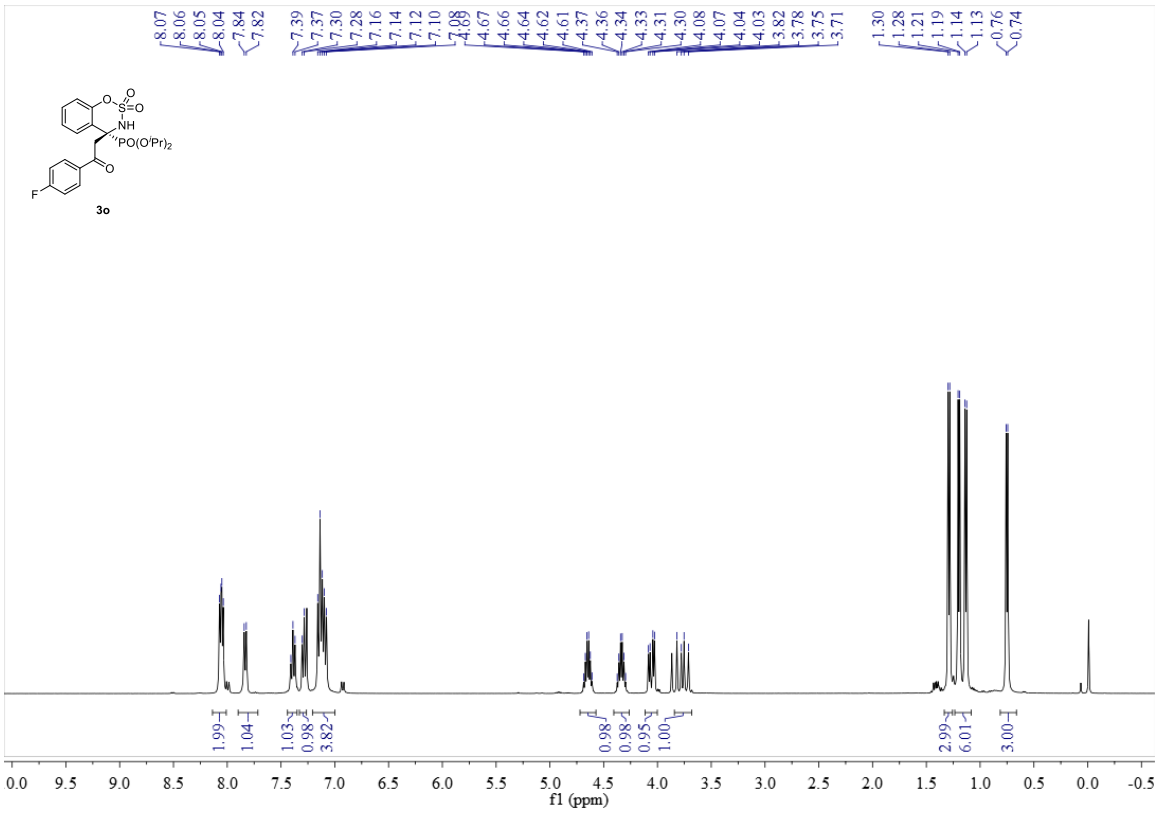

16.04
15.87
3m
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
f1 (ppm)


202.38
202.35
150.24
150.17
138.77
137.66
132.21
132.15
130.45
130.42
129.18
128.04
128.01
125.94
125.90
121.15
121.10
119.75
119.74
74.17
74.09
73.75
73.67
64.19
62.57
44.99
44.96
24.36
24.34
24.16
24.12
23.79
23.73
22.90
22.84
21.26
3m
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)


8.01
7.99
7.86
7.84
7.40
7.39
7.37
7.35
7.29
7.27
7.08
7.06
6.94
6.92
4.67
4.65
4.64
4.62
4.61
4.59
4.35
4.34
4.32
4.31
4.29
4.04
4.02
4.00
3.98
3.87
3.78
3.74
3.71
1.28
1.20
1.19
1.14
1.13
0.76
0.74
1.92
0.99
1.95
1.27
0.98
1.93
0.96
0.97
0.99
2.96
1.00
2.91
2.90
2.94
2.85
f1 (ppm)
MeO
PO(OiPr)2
3n


15.86
15.70
f1 (ppm)
MeO
PO(OiPr)2
3n


196.81
196.77
164.28
150.26
150.19
131.10
130.34
130.32
129.90
128.03
127.99
125.80
125.78
121.06
121.02
119.65
119.64
113.92
74.12
74.04
73.50
73.41
64.02
62.40
55.58
41.33
41.30
24.26
24.24
23.95
23.91
23.61
23.55
22.77
22.71
MeO
3n
f1 (ppm)


8.07
8.06
8.05
8.04
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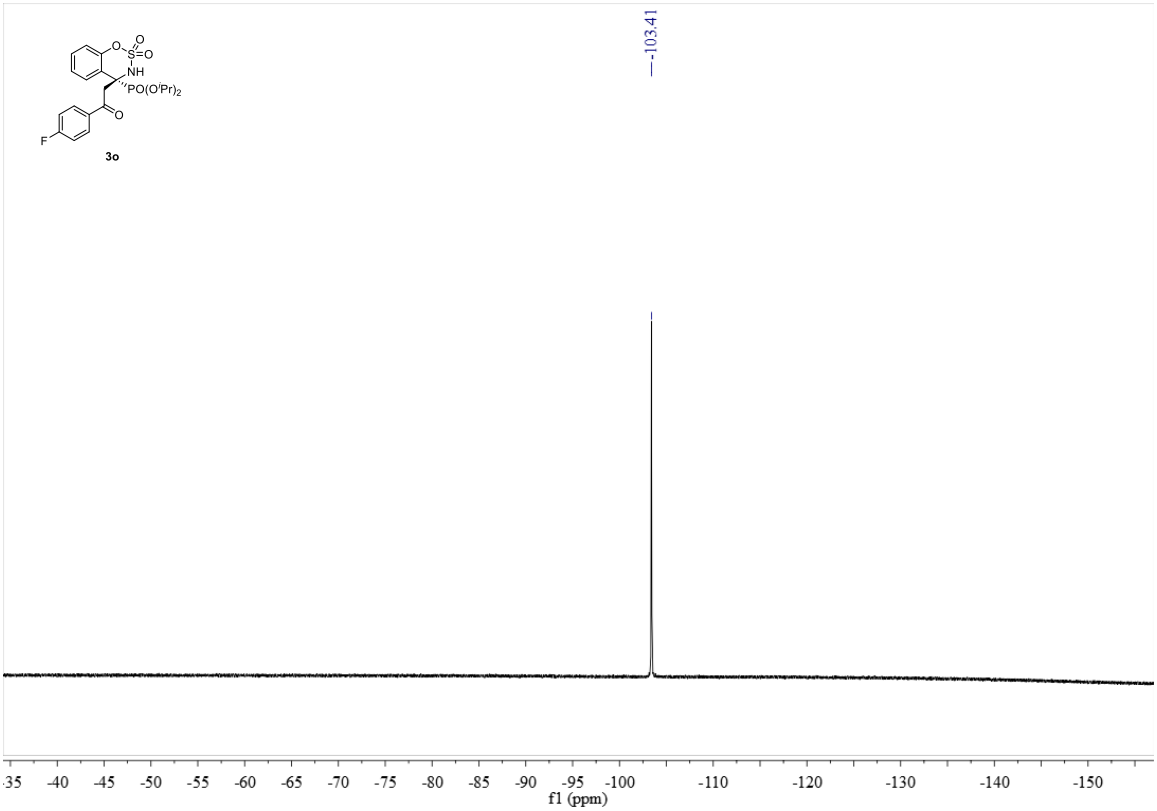
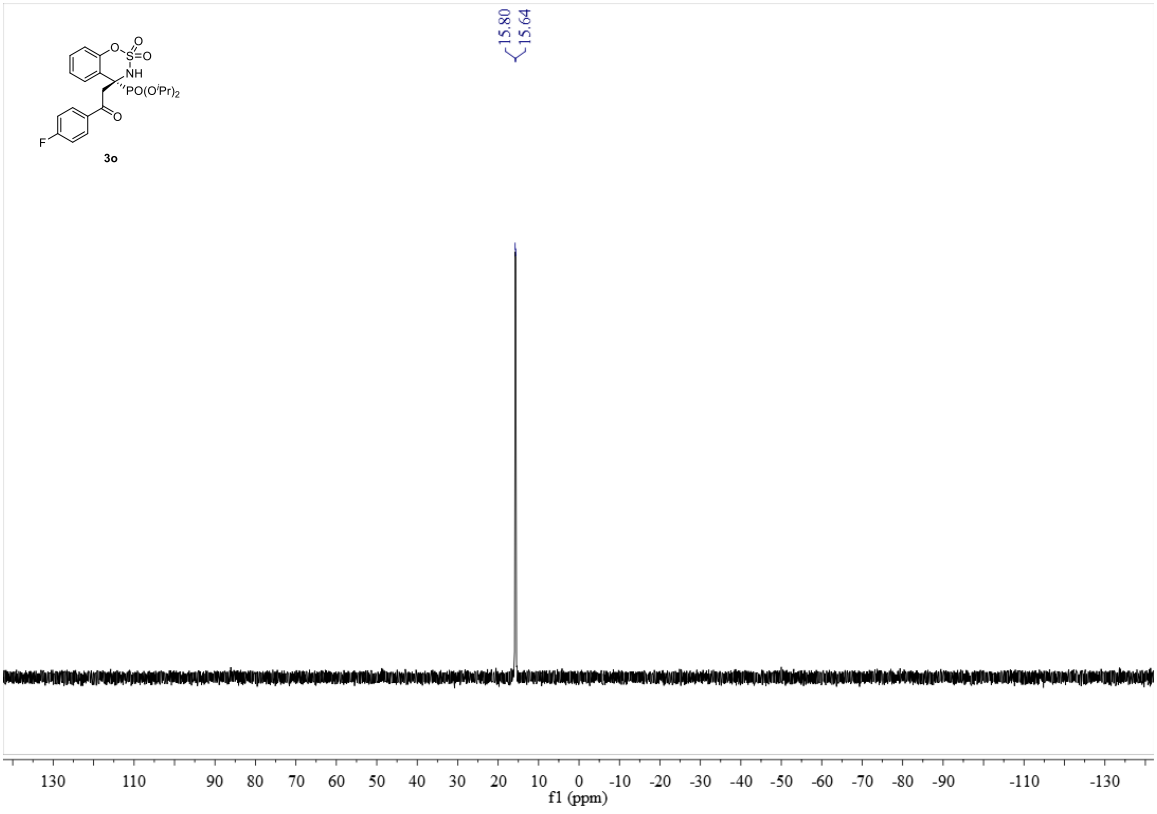
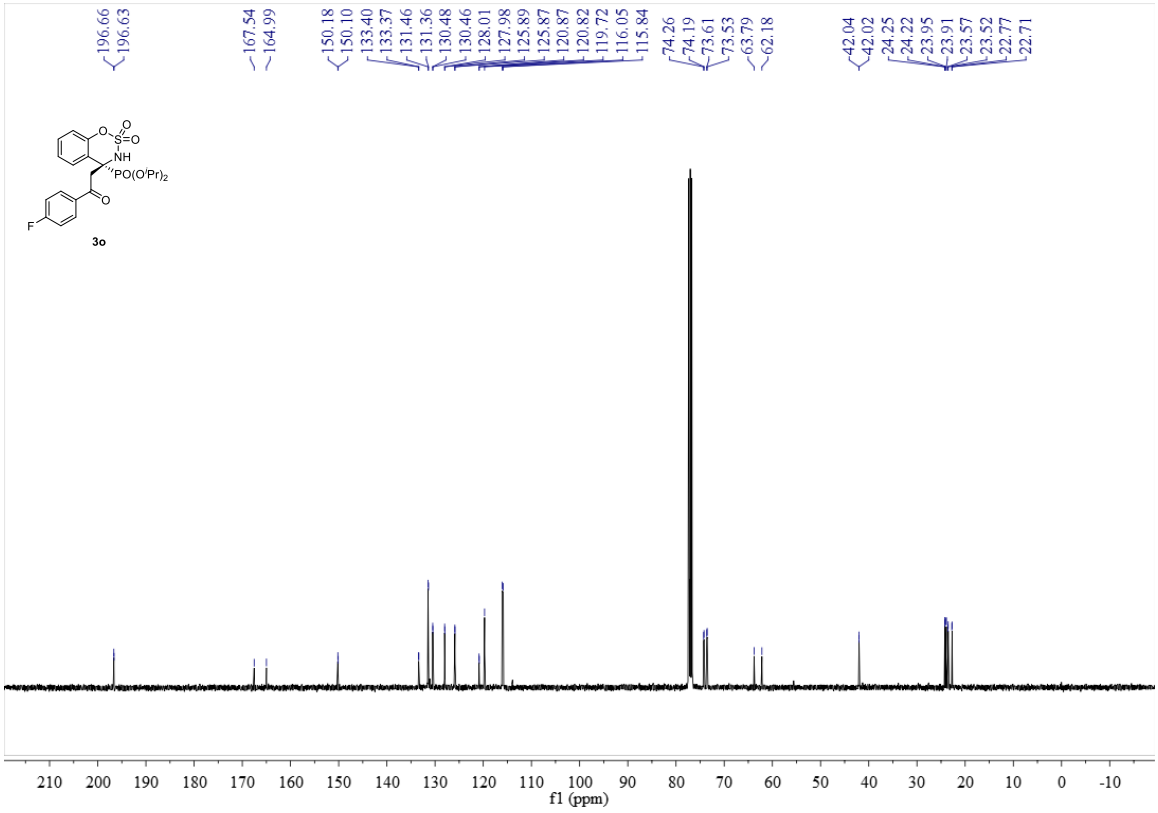
7.82
7.39
7.37
7.30
7.28
7.16
7.14
7.12
7.10
4.67
4.66
4.64
4.62
4.61
4.37
4.36
4.34
4.33
4.31
4.30
4.08
4.07
4.04
4.03
3.82
3.78
3.75
3.71
1.30
1.28
1.21
1.19
1.14
1.13
0.76
0.74
F
3o
1.99
1.04
1.03
0.98
3.82
0.98
0.98
0.95
1.00
2.99
6.01
3.00
f1 (ppm)


-103.41
3o
35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150
f1 (ppm)


15.80
15.64
3o
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)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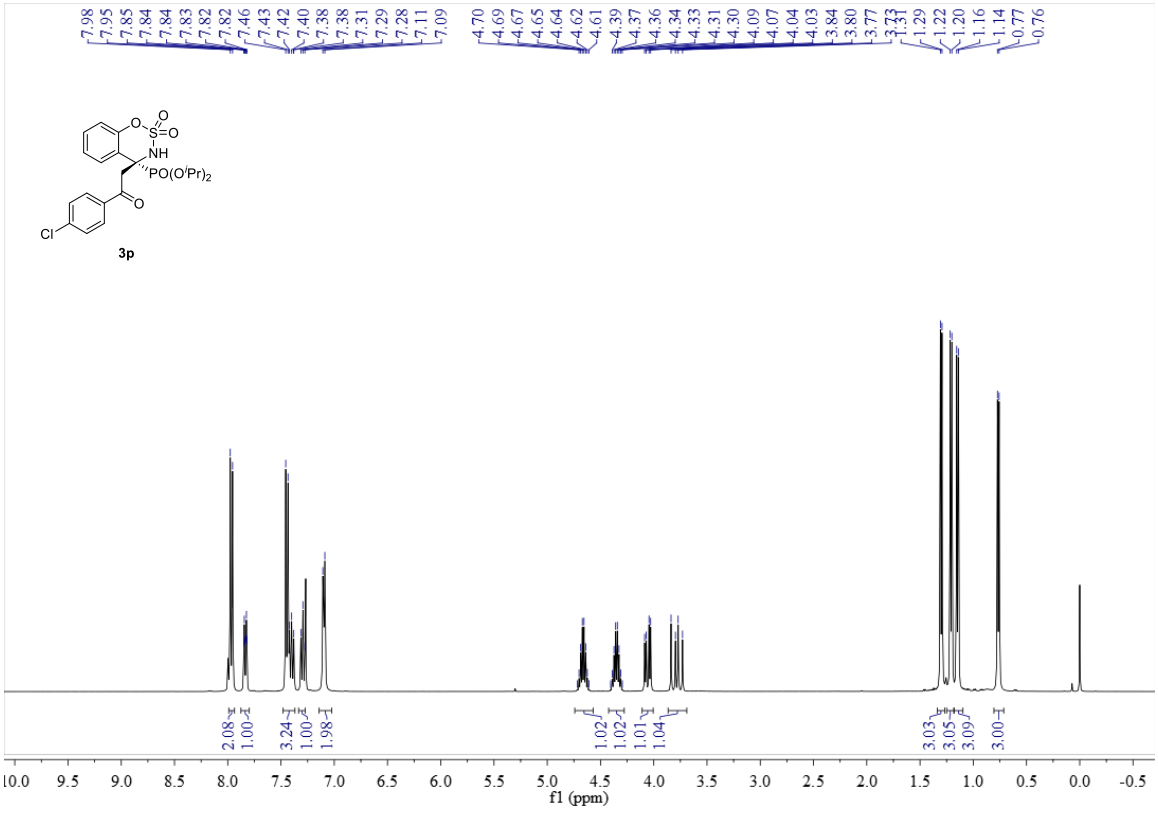
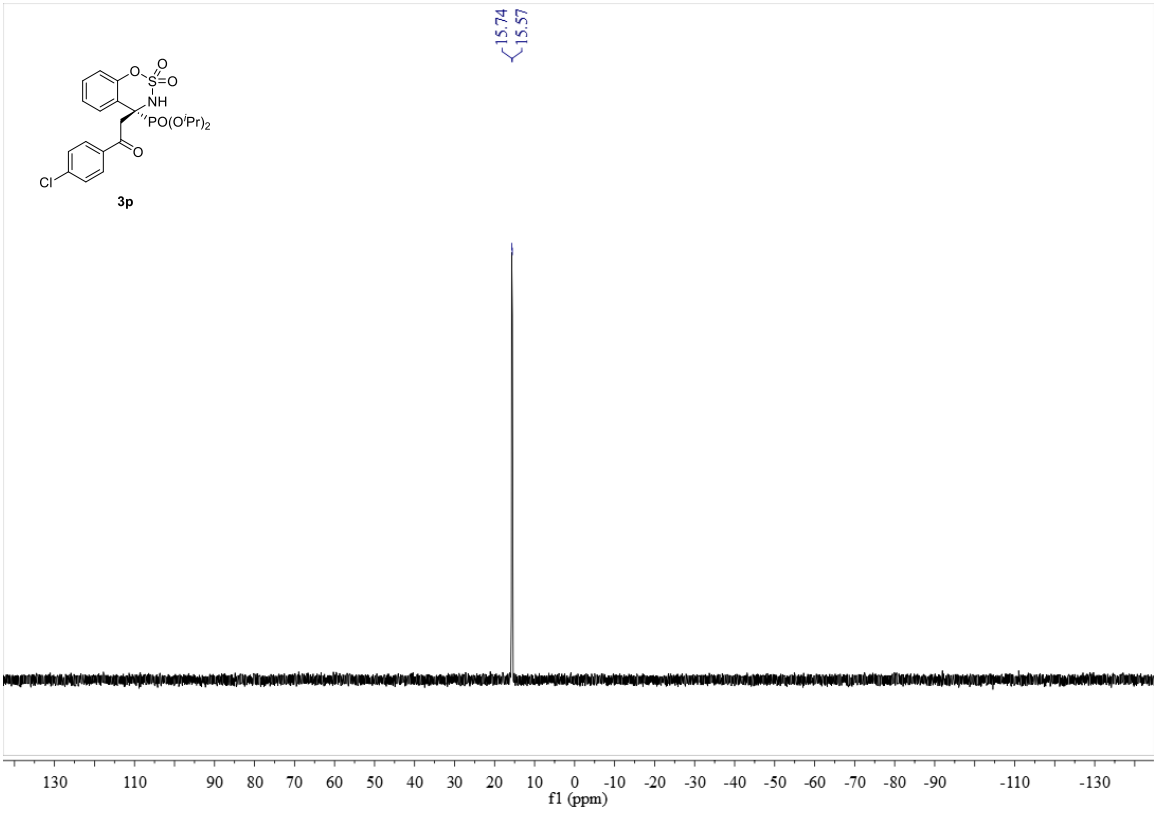
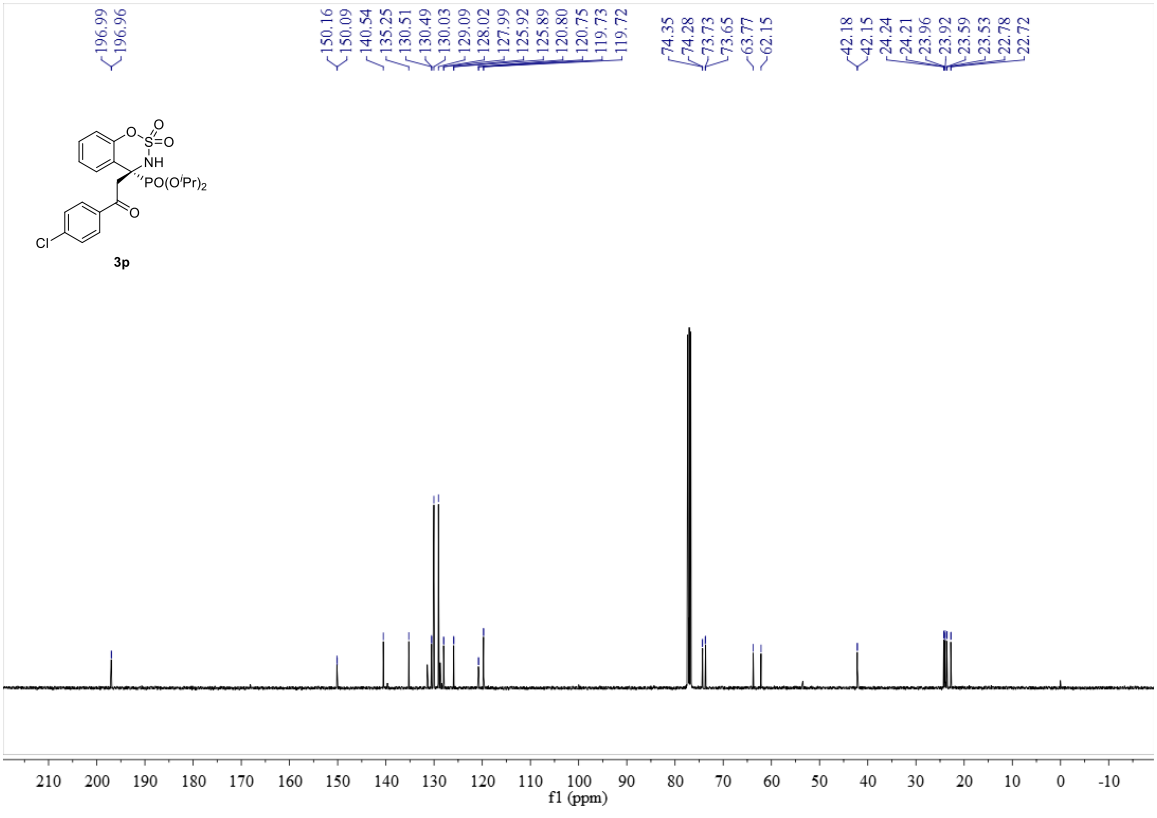
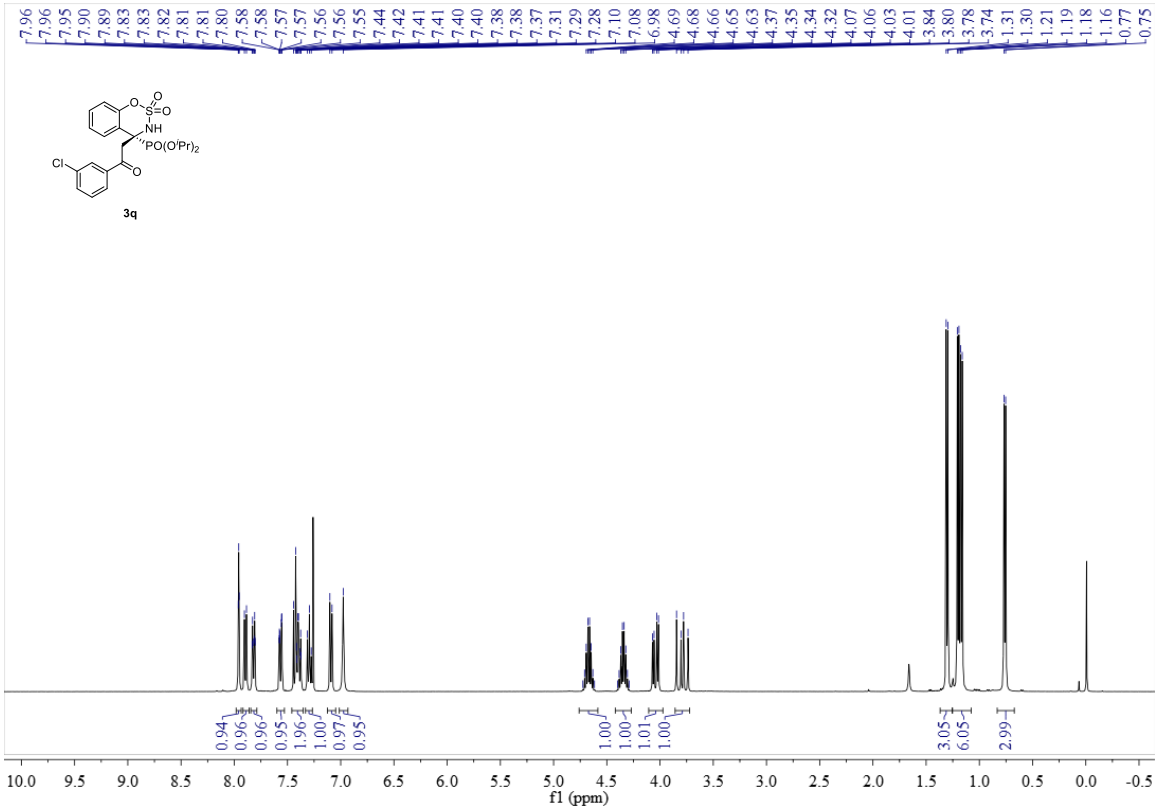
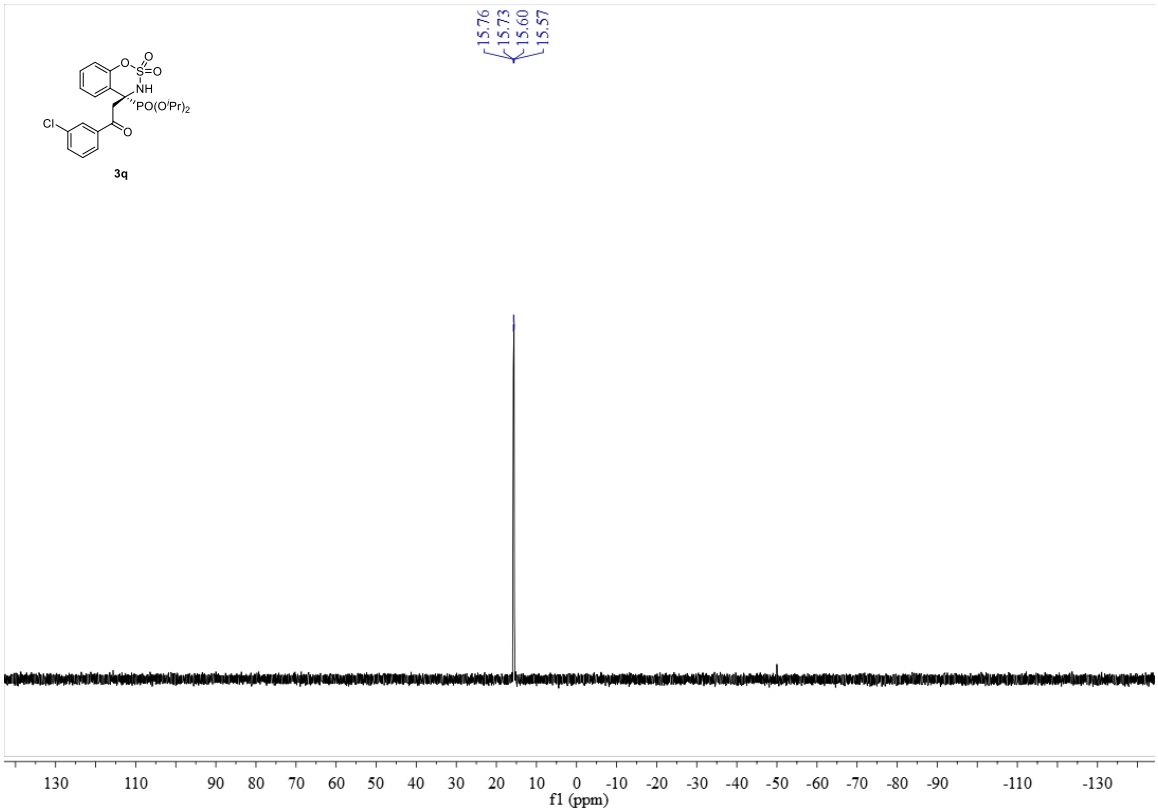
196.63
167.54
164.99
150.18
150.10
133.40
133.37
131.46
131.36
130.48
130.46
128.01
127.98
125.89
125.87
120.87
120.82
119.72
116.05
115.84
74.26
74.19
73.61
73.53
63.79
62.18
42.04
42.02
24.25
24.22
23.95
23.91
23.57
23.52
22.77
22.71
NH
PO(OiPr)2
F
3o
f1 (ppm)

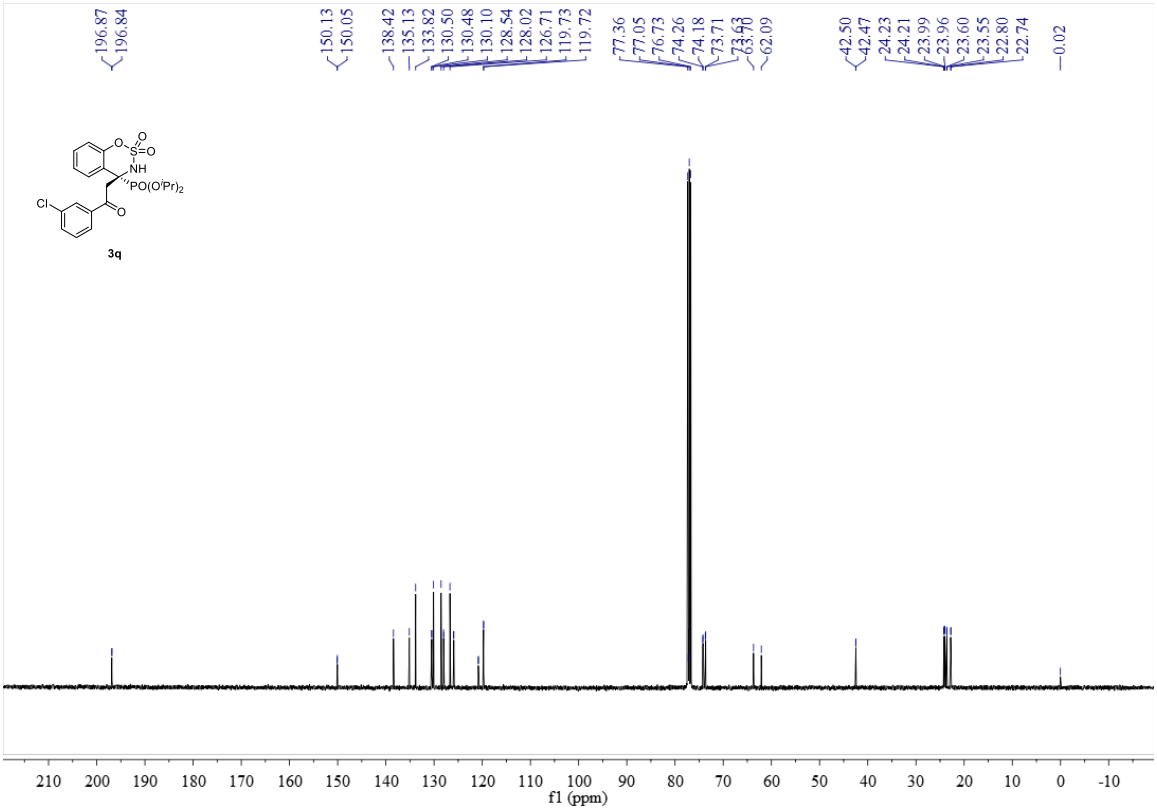

7.98
7.95
7.85
7.84
7.84
7.83
7.82
7.82
7.46
7.43
7.42
7.40
7.38
7.38
7.31
7.29
7.28
7.11
7.09
4.70
4.69
4.67
4.65
4.64
4.62
4.61
4.39
4.37
4.36
4.34
4.33
4.31
4.30
4.09
4.07
4.04
4.03
3.84
3.80
3.77
1.31
1.29
1.22
1.20
1.16
1.14
0.77
0.76
NH
PO(OiPr)2
Cl
3p
2.08
1.00
3.24
1.00
1.98
1.02
1.02
1.01
1.04
3.03
3.05
3.09
3.00
f1 (ppm)


15.74
15.57
3p
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
f1 (ppm)


196.99
196.96
150.16
150.09
140.54
135.25
130.51
130.49
130.03
129.09
128.02
127.99
125.92
125.89
120.80
120.75
119.73
119.72
74.35
74.28
73.73
73.65
63.77
62.15
42.18
42.15
24.24
24.21
23.96
23.92
23.59
23.53
22.78
22.72
3p
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)


7.96 7.96 7.95 7.90 7.89 7.83 7.83 7.82 7.81 7.81 7.80 7.58 7.58 7.57 7.57 7.56 7.56 7.55 7.44 7.42 7.41 7.41 7.40 7.40 7.38 7.38 7.37 7.31 7.29 7.28 7.10 7.08 6.98 4.69 4.68 4.66 4.65 4.63 4.37 4.35 4.34 4.32 4.07 4.06 4.03 4.01 3.84 3.80 3.78 3.74 1.31 1.30 1.21 1.19 1.18 1.16 0.77 0.75
NH
PO(OiPr)2
Cl
O
3q
0.94 0.96 0.96 0.95 1.96 1.00 0.97 0.95
1.00 1.00 1.01 1.00
3.05 6.05 2.99
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 -0.5
f1 (ppm)


15.76
15.73
15.60
15.57
NH
PO(OiPr)2
Cl
O
3q
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)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196.84
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150.05
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135.13
133.82
130.50
130.48
130.10
128.54
128.02
126.71
119.73
119.72
77.36
77.05
76.73
74.26
74.18
73.71
63.70
62.09
42.50
42.47
24.23
24.21
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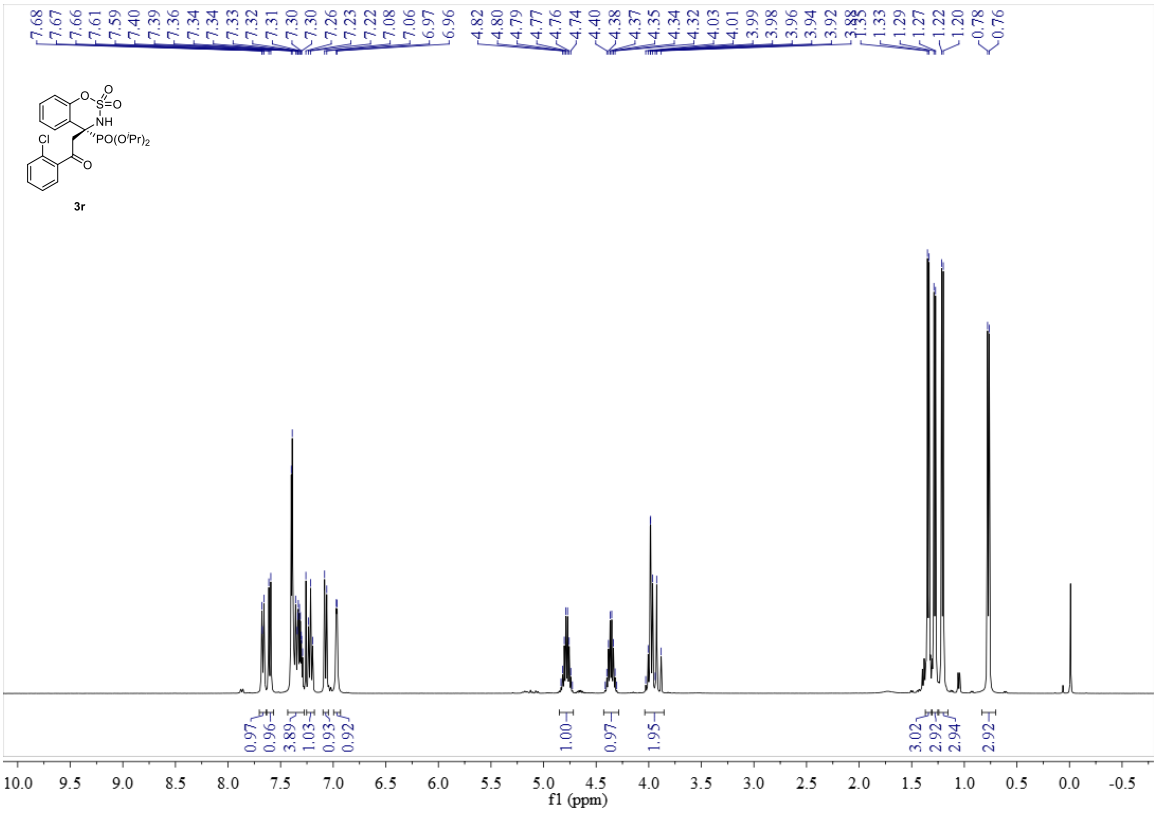
23.55
22.80
22.74
0.02
NH
PO(O'Pr)2
Cl
3q
f1 (ppm)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7.36
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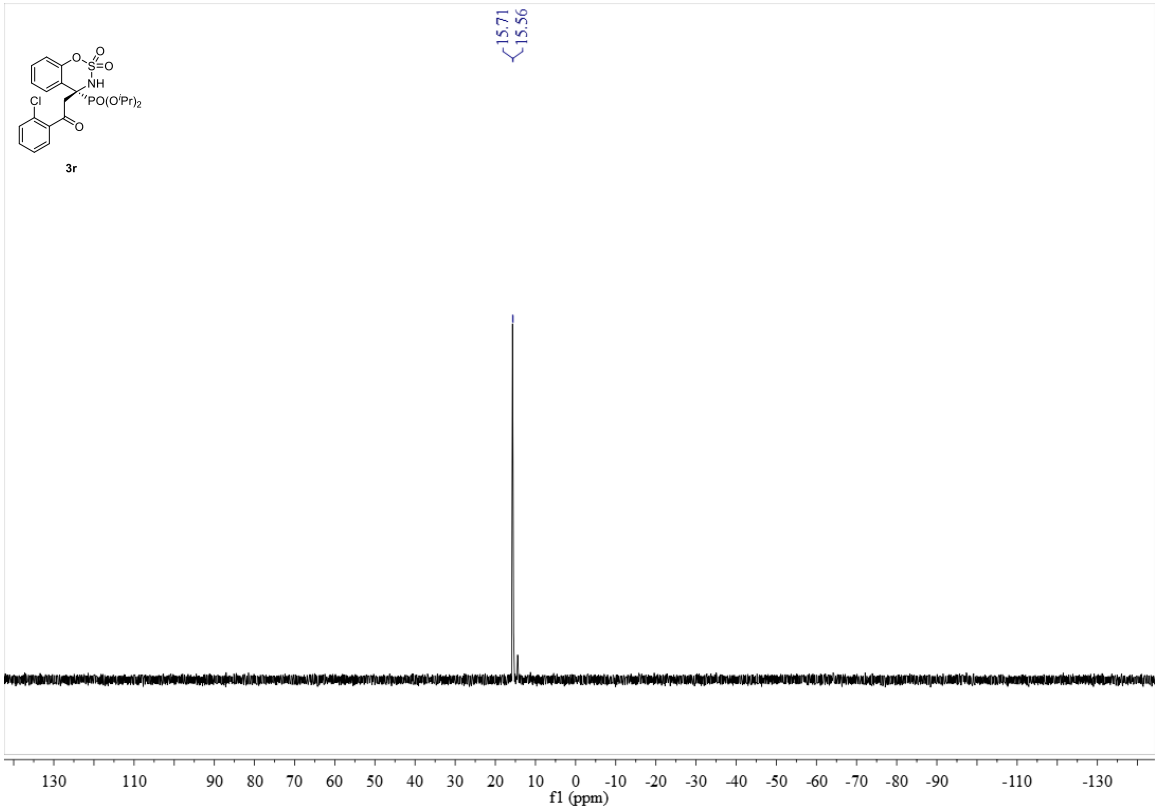
7.34
7.33
7.32
7.31
7.30
7.30
7.26
7.23
7.22
7.08
7.06
6.97
6.96
4.82
4.80
4.79
4.77
4.76
4.74
4.40
4.38
4.37
4.35
4.34
4.32
4.03
4.01
3.99
3.98
3.96
3.94
3.92
1.33
1.29
1.27
1.22
1.20
0.78
0.76
NH
PO(O'Pr)2
Cl
3r
0.97
0.96
3.89
1.03
0.93
0.92
1.00
0.97
1.95
3.02
2.92
2.94
2.92
f1 (ppm)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15.56
3r
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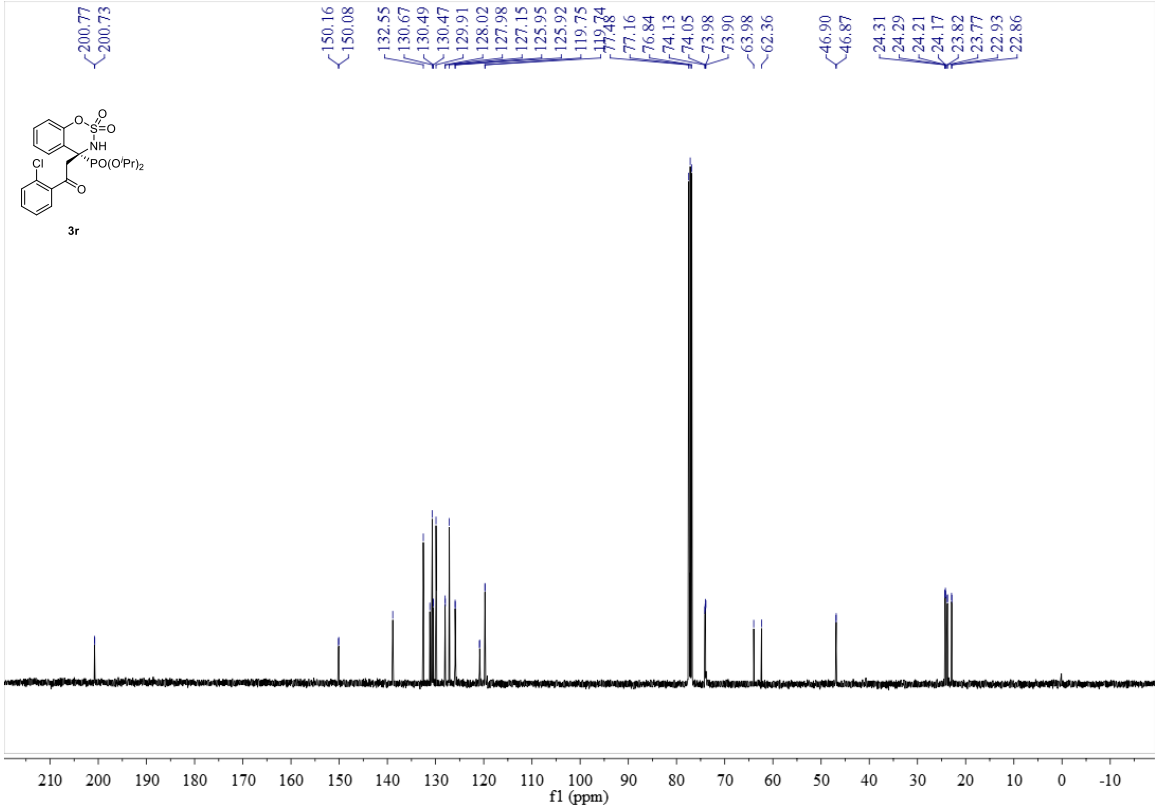
f1 (ppm)


200.77
200.73
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150.08
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130.67
130.49
130.47
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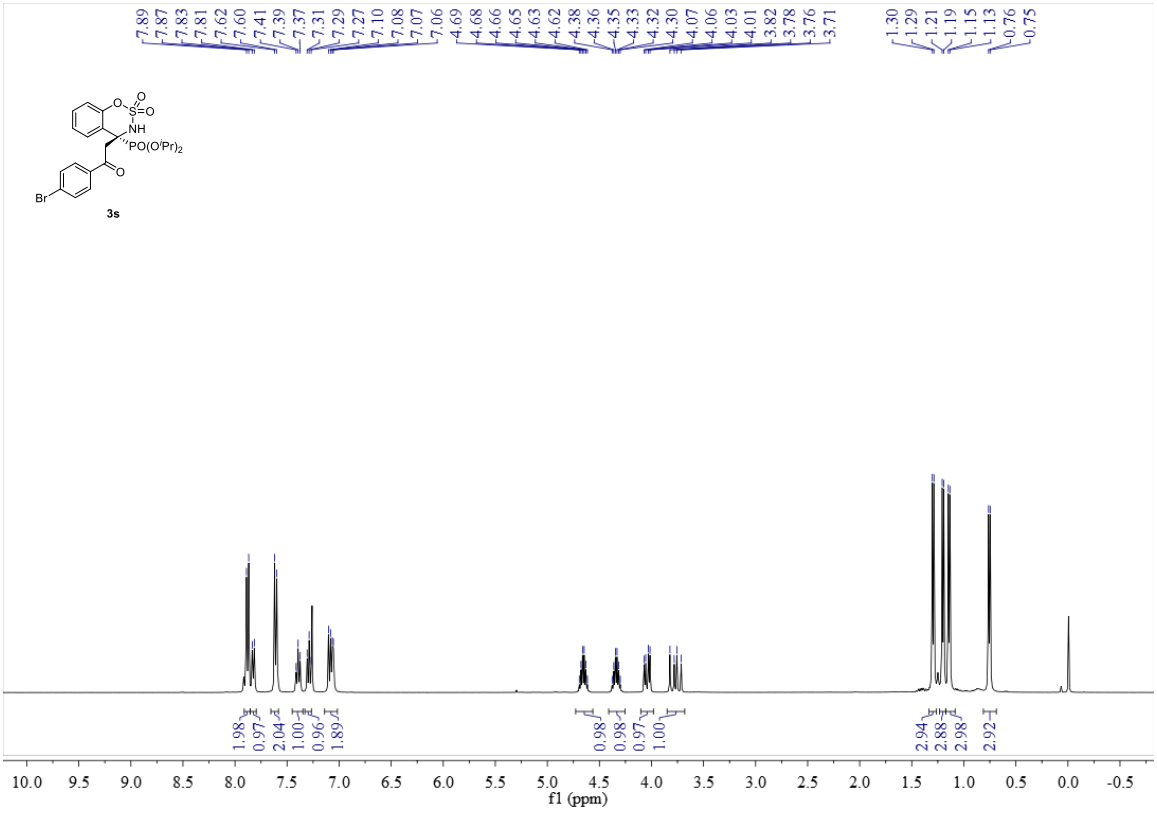
128.02
127.98
127.15
125.95
125.92
119.75
119.74
77.48
77.16
76.84
74.13
74.05
73.98
73.90
63.98
62.36
46.90
46.87
24.31
24.29
24.21
24.17
23.82
23.77
22.93
22.86
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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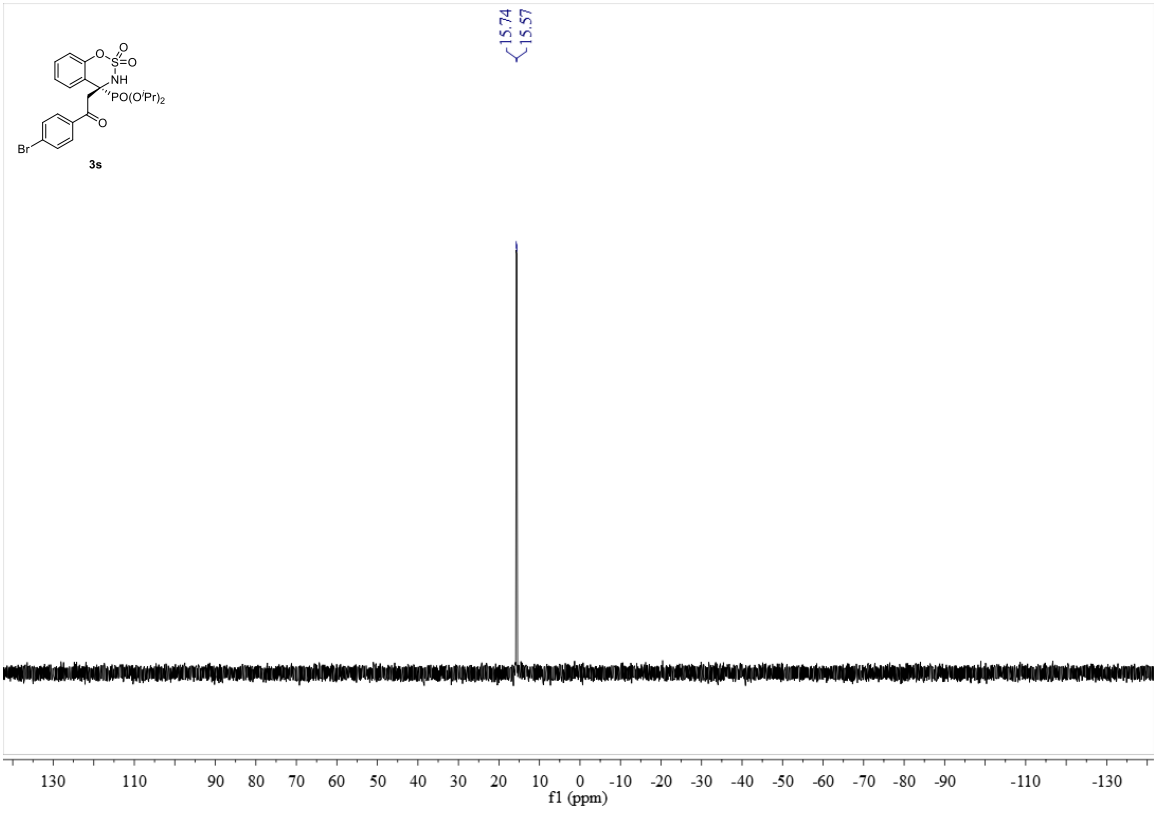
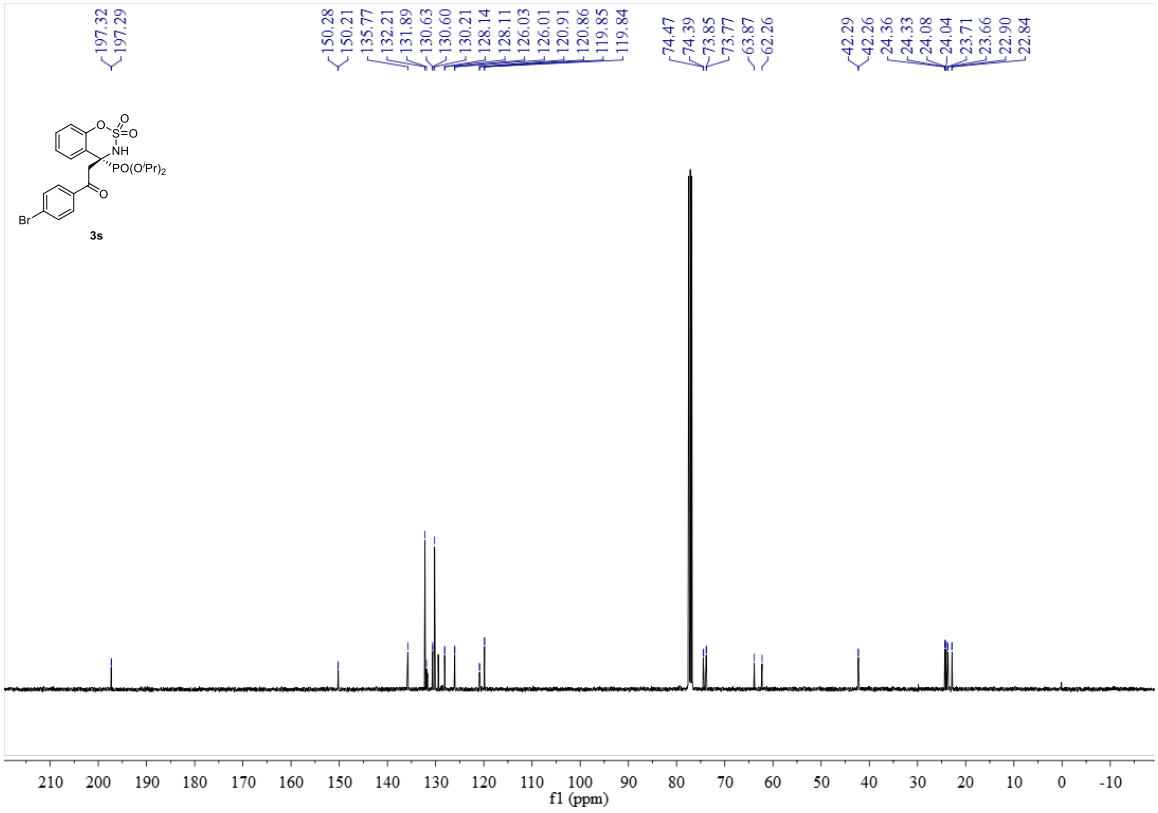
7.60
7.41
7.39
7.37
7.31
7.29
7.27
7.10
7.08
7.07
7.06
4.69
4.68
4.66
4.65
4.63
4.62
4.38
4.36
4.35
4.33
4.32
4.30
4.07
4.06
4.03
4.01
3.82
3.78
3.76
3.71
1.30
1.29
1.21
1.19
1.15
1.13
0.76
0.75
NH
PO(O^{i}Pr)$_2$
Br
3s
1.98
0.97
2.04
1.00
0.96
1.89
0.98
0.98
0.97
1.00
2.94
2.88
2.98
2.92
f1 (ppm)


15.74
15.57
NH
PO(O^{i}Pr)$_2$
Br
3s
f1 (ppm)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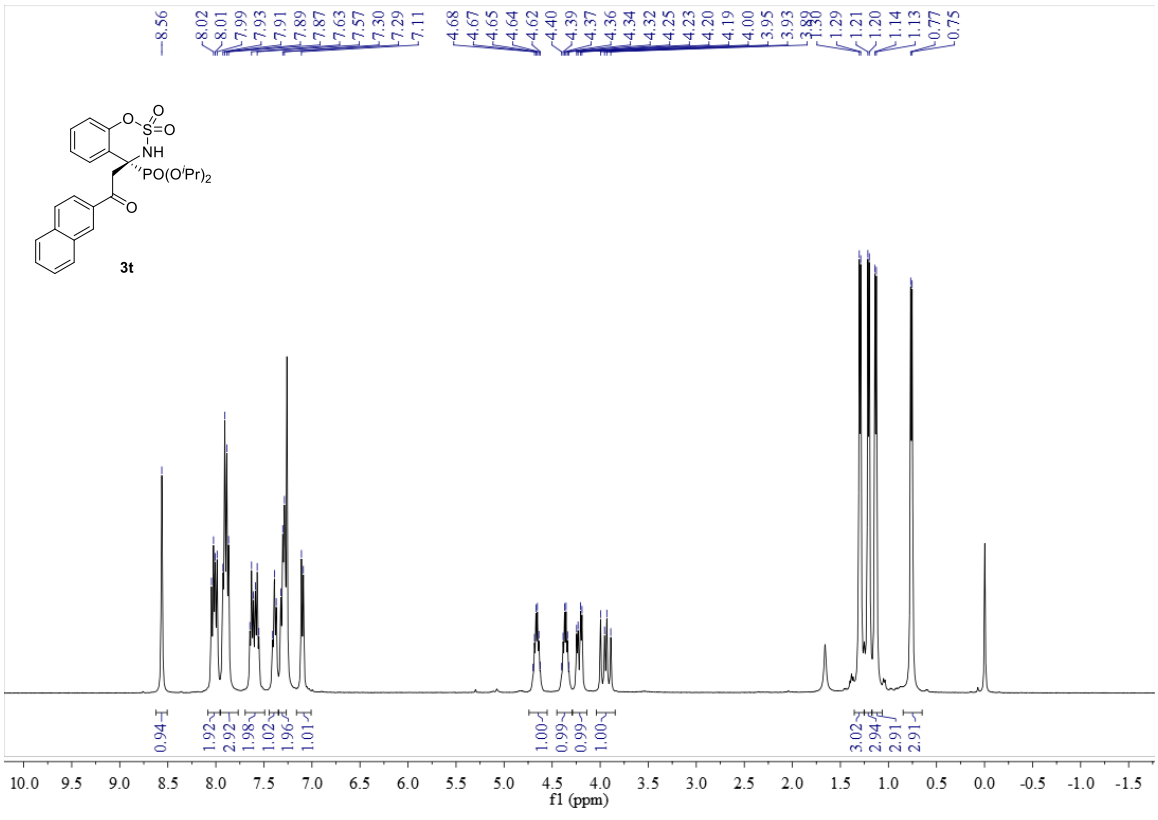
135.77
132.21
131.89
130.63
130.60
130.21
128.14
128.11
126.03
126.01
120.91
120.86
119.85
119.84
74.47
74.39
73.85
73.77
63.87
62.26
42.29
42.26
24.36
24.33
24.08
24.04
23.71
23.66
22.90
22.84
NH
PO(OiPr)2
Br
3s
f1 (ppm)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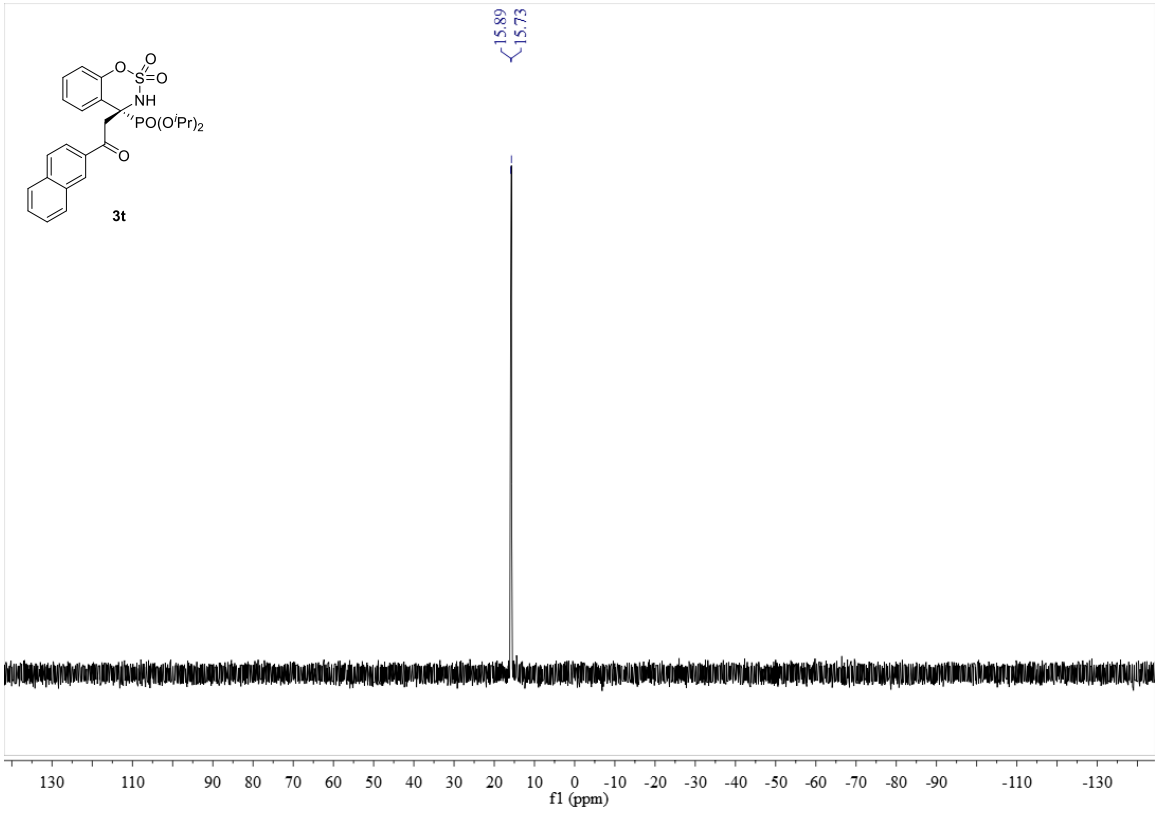
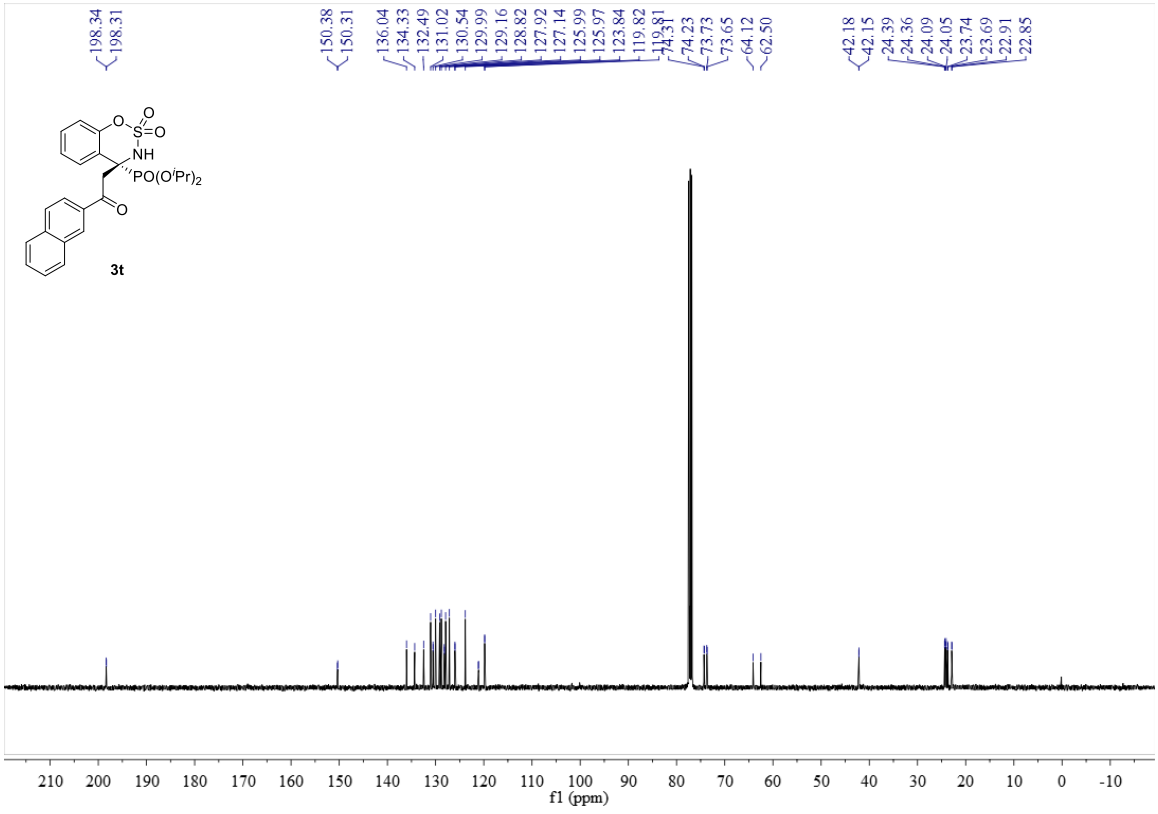
7.91
7.89
7.87
7.63
7.57
7.30
7.29
7.11
4.68
4.67
4.65
4.64
4.62
4.40
4.39
4.37
4.36
4.34
4.32
4.25
4.23
4.20
4.19
4.00
3.95
3.93
1.30
1.29
1.21
1.20
1.14
1.13
0.77
0.75
NH
PO(OiPr)2
3t
0.94
1.92
2.92
1.98
1.02
1.96
1.01
1.00
0.99
0.99
1.00
3.02
2.94
2.91
2.91
f1 (ppm)


15.89
15.73
3t
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)


198.34
198.31
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150.31
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134.33
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131.02
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129.16
128.82
127.92
127.14
125.99
125.97
123.84
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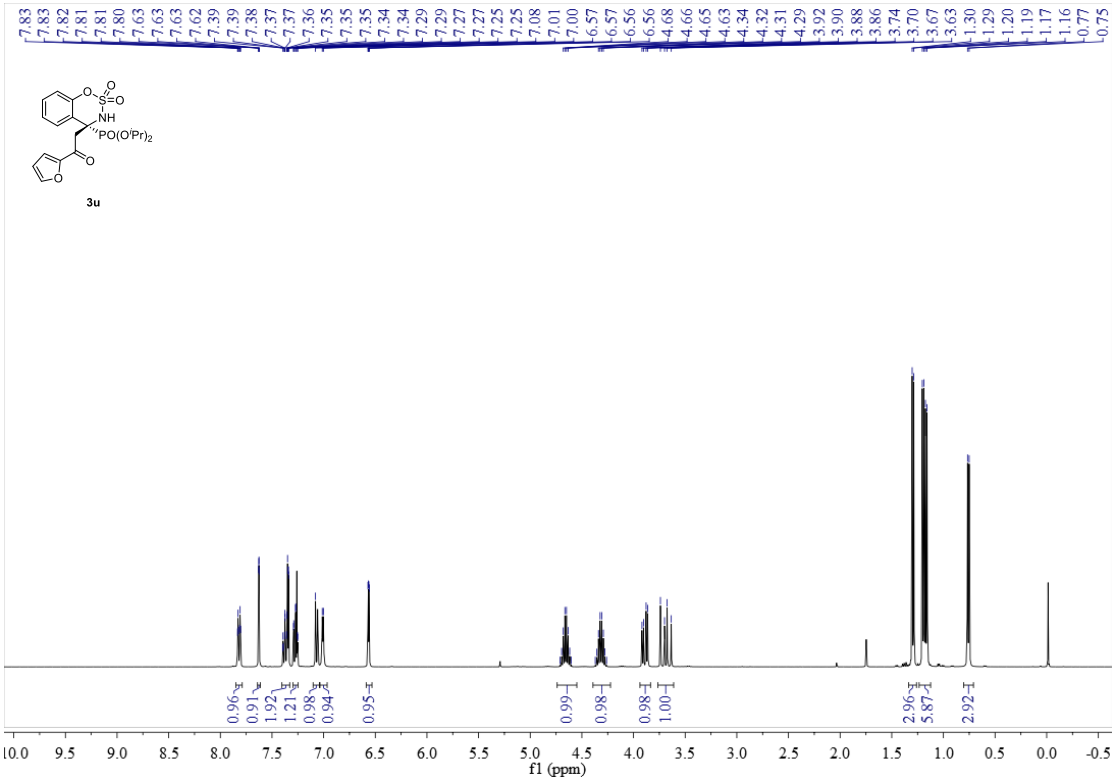
119.81
74.31
74.23
73.73
73.65
64.12
62.50
42.18
42.15
24.39
24.36
24.09
24.05
23.74
23.69
22.91
22.85
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.83
7.82
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7.62
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7.39
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7.37
7.37
7.36
7.35
7.35
7.35
7.34
7.34
7.29
7.29
7.27
7.27
7.25
7.25
7.08
7.01
7.00
6.57
6.56
6.56
6.56
4.68
4.66
4.65
4.63
4.34
4.32
4.31
4.29
3.92
3.90
3.88
3.86
3.74
3.70
3.67
3.63
1.30
1.29
1.20
1.19
1.17
1.16
0.77
0.75
NH
PO(O'Pr)2
3u
0.96
0.91
1.92
1.21
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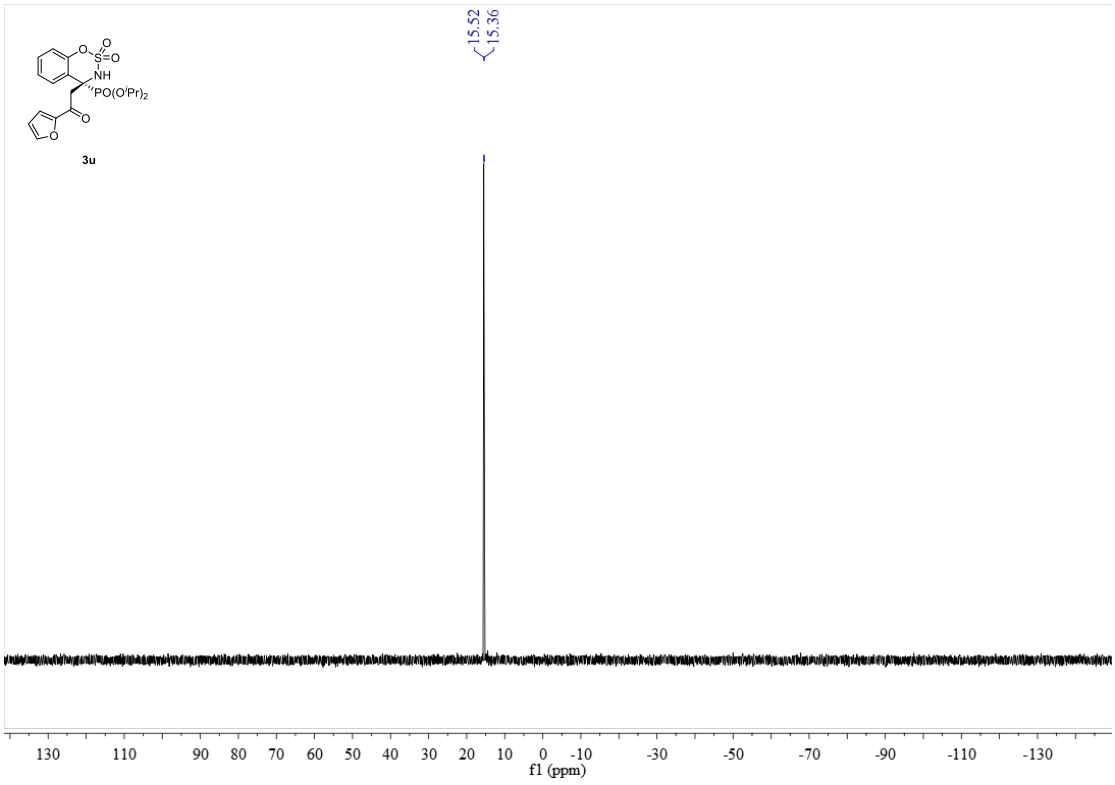
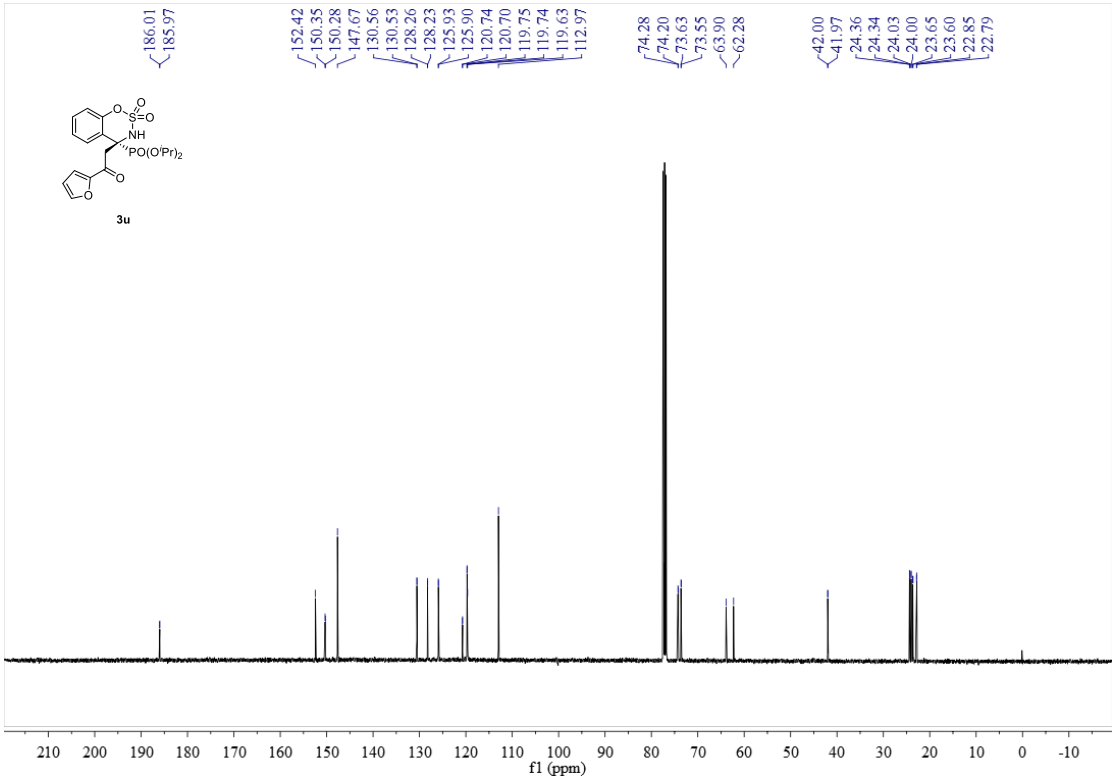
0.95
0.99
0.98
0.98
1.00
2.96
5.87
2.92
f1 (ppm)


15.52
15.36
NH
PO(O'Pr)2
3u
f1 (ppm)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130.53
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128.23
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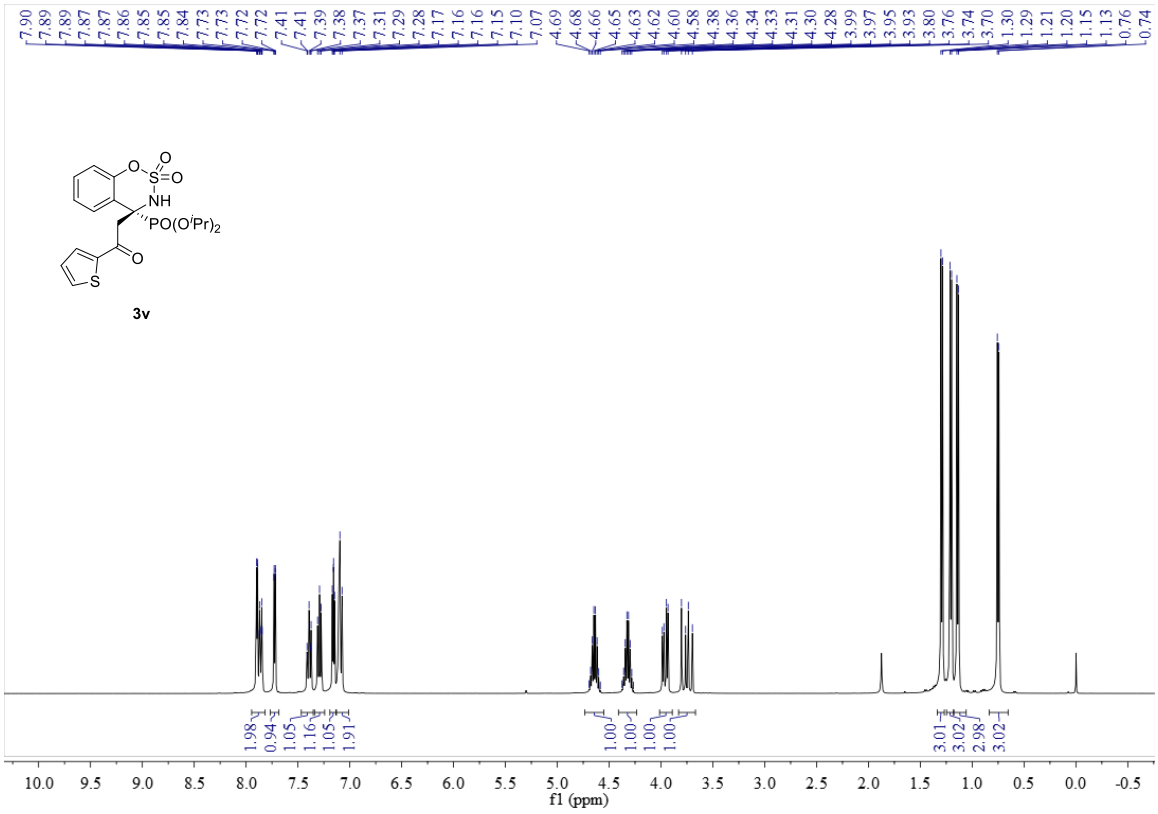
125.90
120.74
120.70
119.75
119.74
119.63
112.97
74.28
74.20
73.63
73.55
63.90
62.28
42.00
41.97
24.36
24.34
24.03
24.00
23.65
23.60
22.85
22.79
3u
f1 (ppm)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7.85
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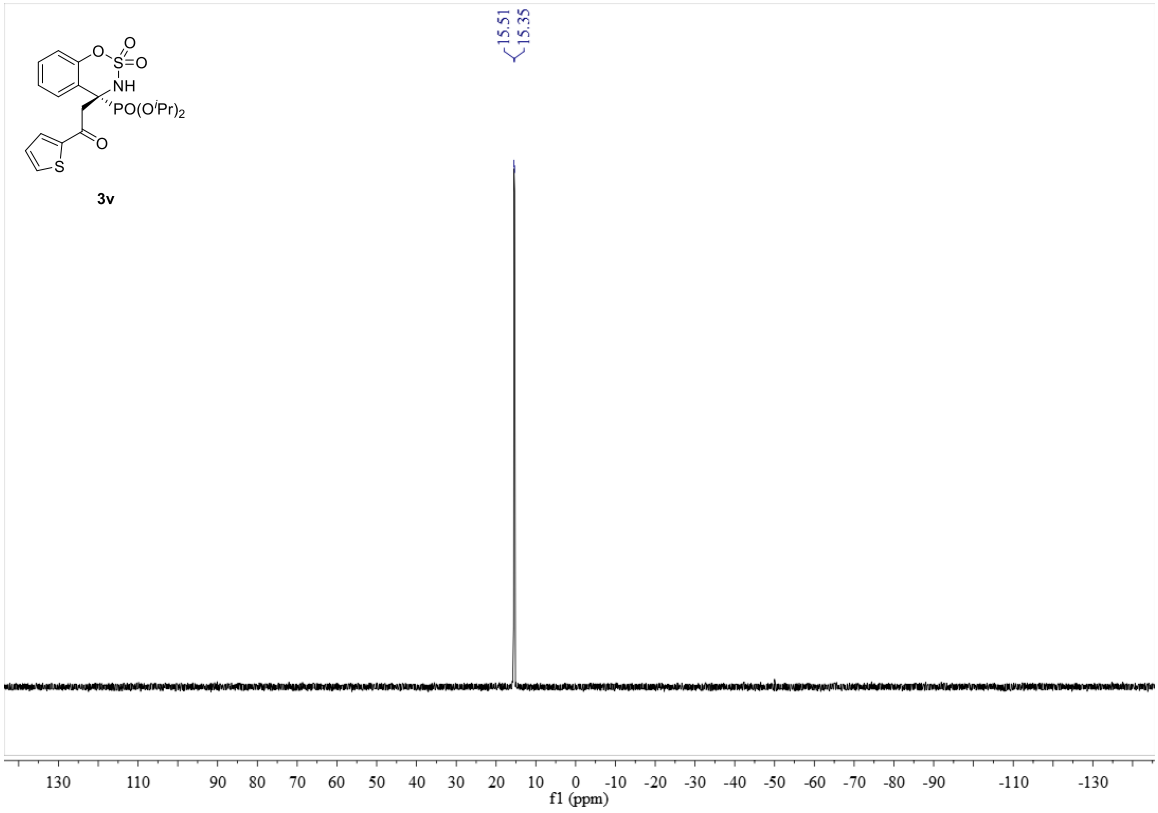
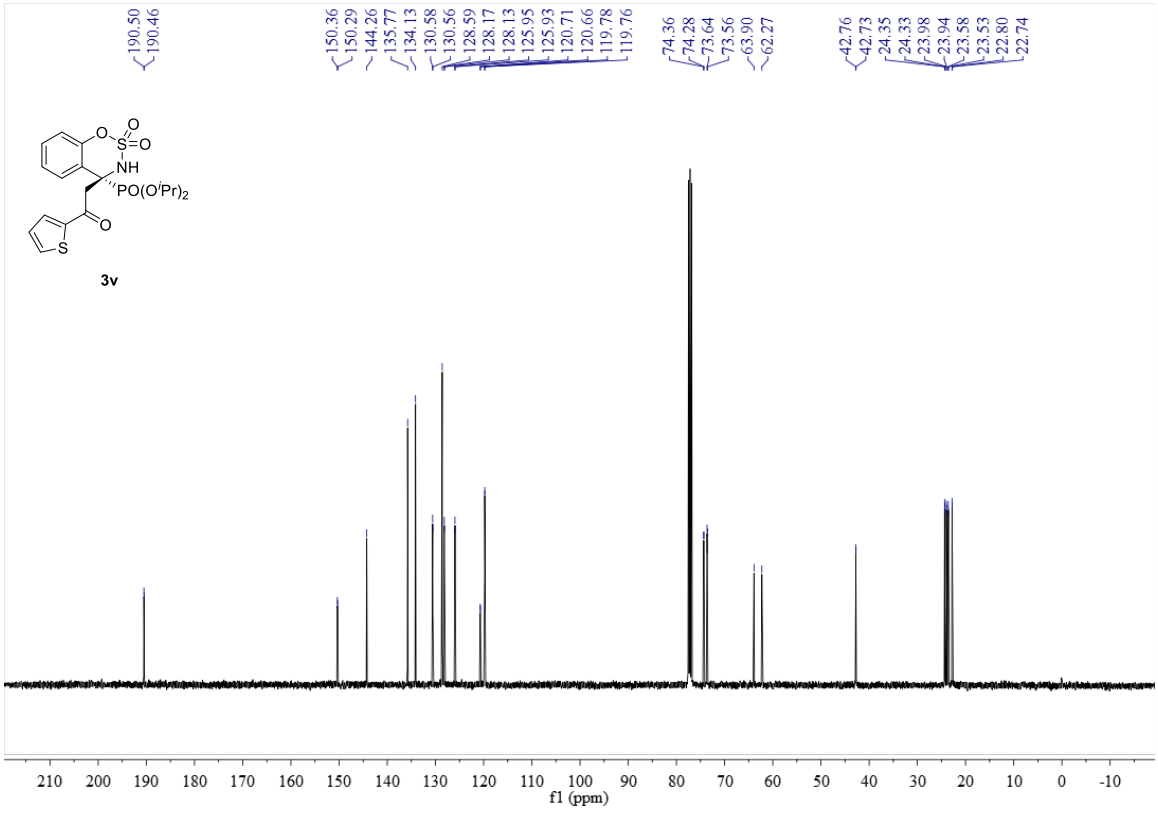
7.72
7.41
7.41
7.39
7.38
7.37
7.31
7.29
7.28
7.17
7.16
7.16
7.15
7.10
7.07
4.69
4.68
4.66
4.65
4.63
4.62
4.60
4.58
4.38
4.36
4.34
4.33
4.31
4.30
4.28
3.99
3.97
3.95
3.93
3.80
3.76
3.74
3.70
1.30
1.29
1.21
1.20
1.15
1.13
0.76
0.74
1.98
0.94
1.05
1.16
1.05
1.91
1.00
1.00
1.00
1.00
3.01
3.02
2.98
3.02
3v
f1 (ppm)


15.51
15.35
3v
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
f1 (ppm)


190.50
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144.26
135.77
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130.58
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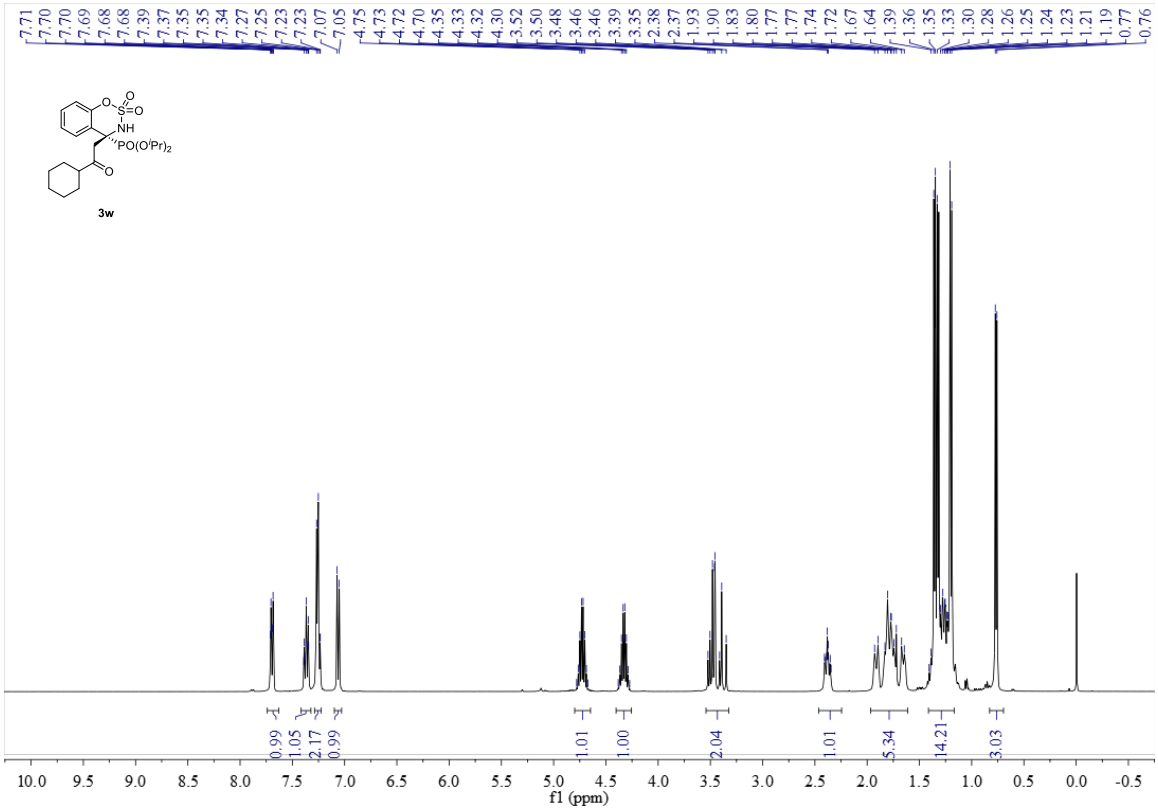
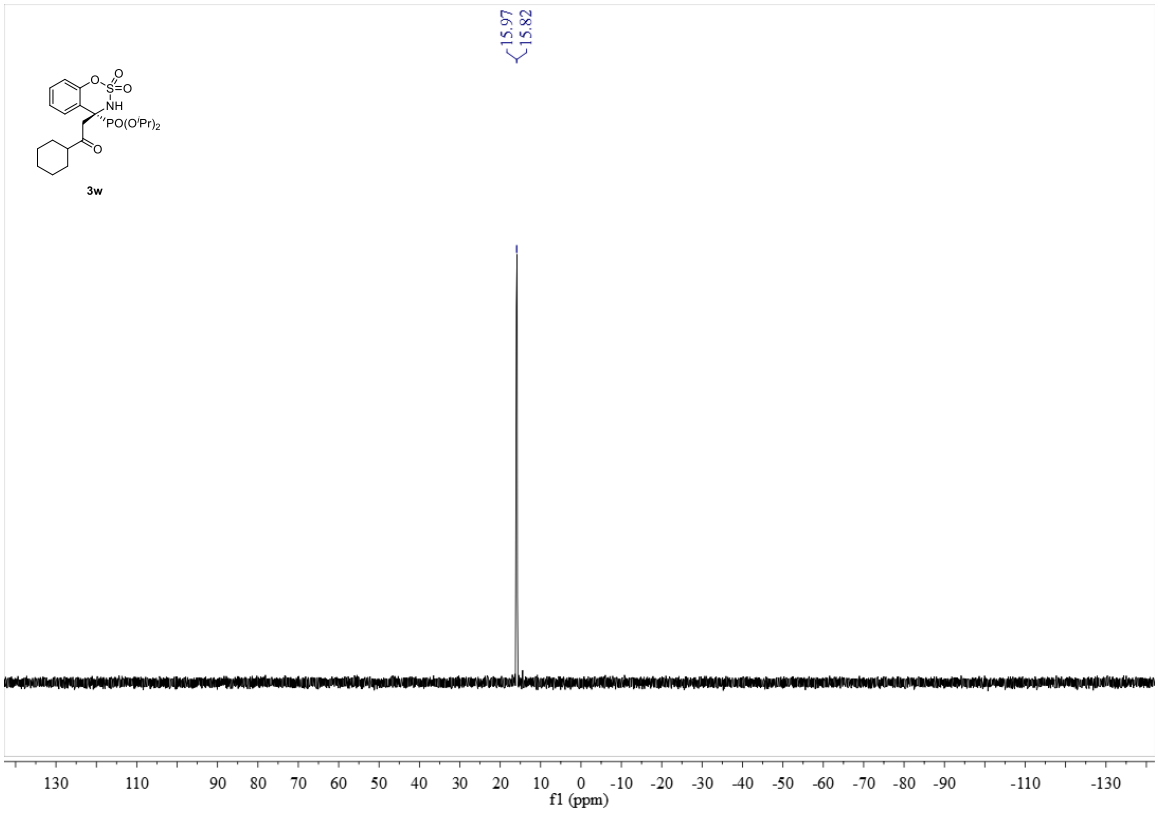
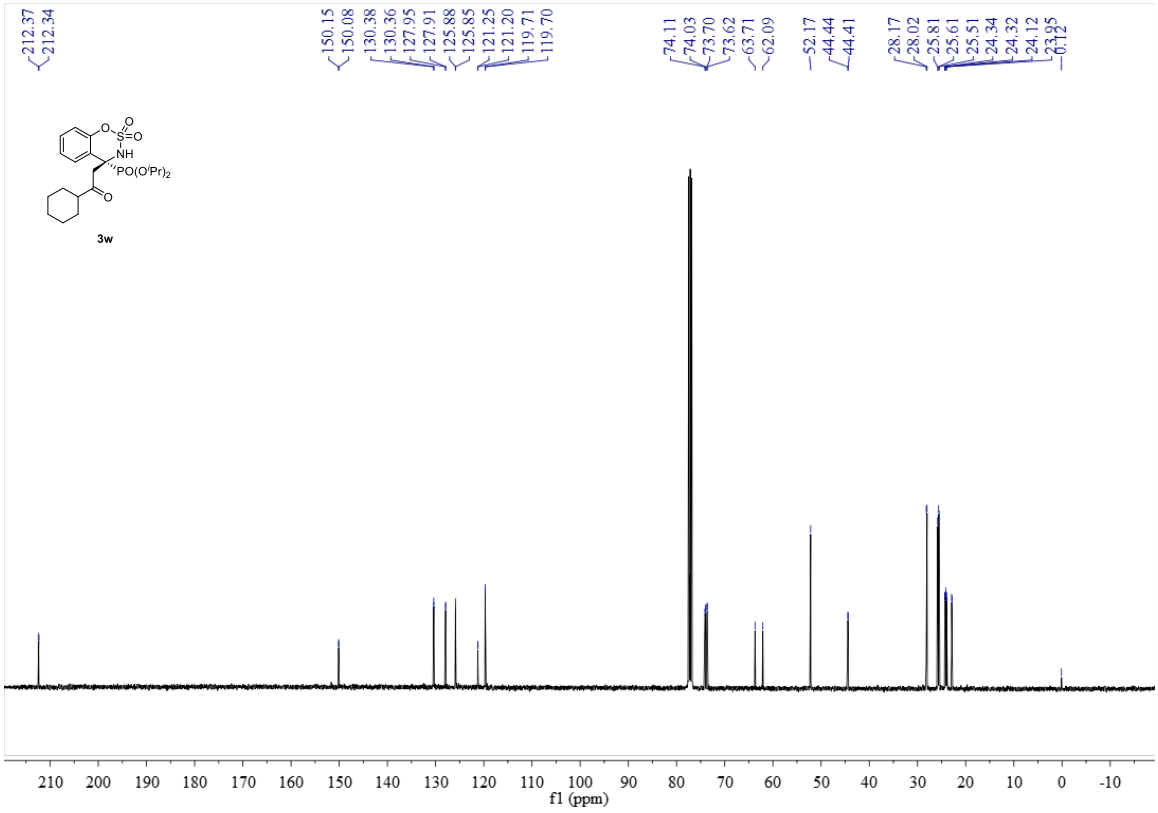
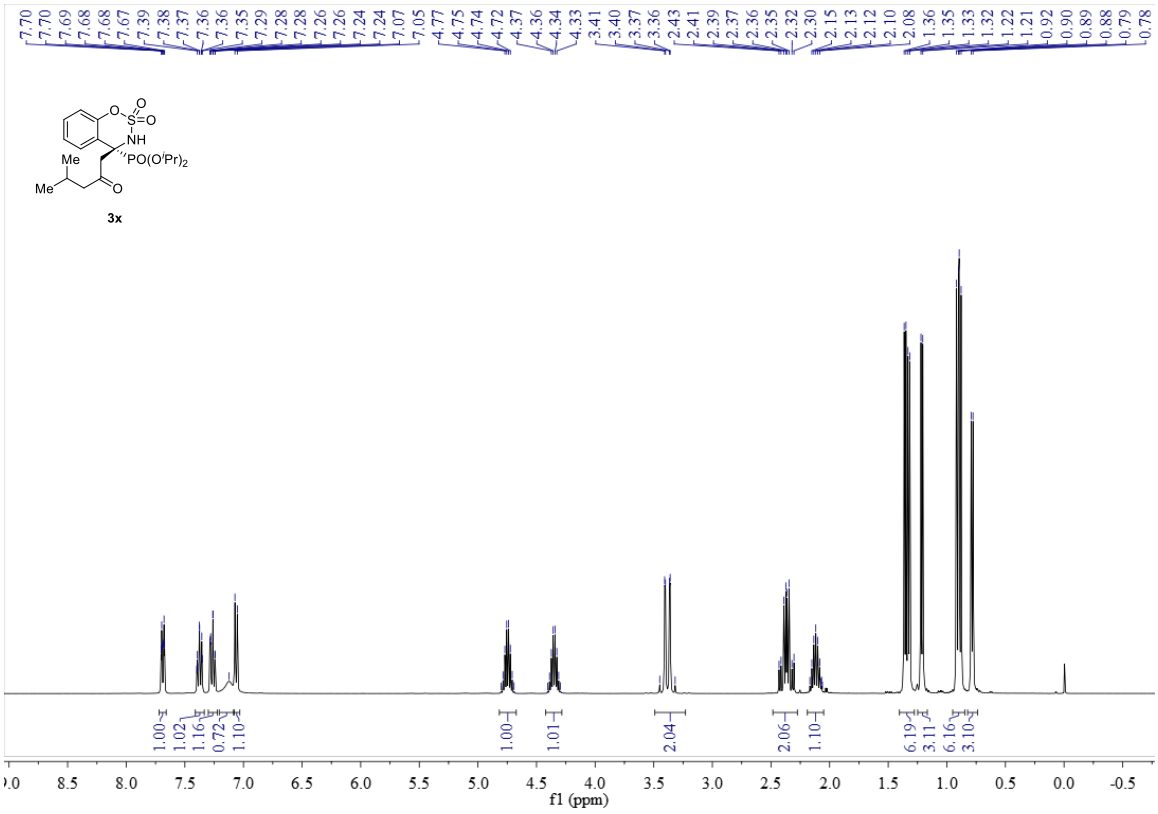
128.59
128.17
128.13
125.95
125.93
120.71
120.66
119.78
119.76
74.36
74.28
73.64
73.56
63.90
62.27
42.76
42.73
24.35
24.33
23.98
23.94
23.58
23.53
22.80
22.74
3v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.71 7.70 7.70 7.69 7.68 7.68 7.39 7.37 7.35 7.35 7.34 7.27 7.25 7.23 7.23 7.07 7.05
4.75 4.73 4.72 4.70 4.35 4.33 4.32 4.30 3.52 3.50 3.48 3.46 3.46 3.39 3.35 2.38 2.37 1.93 1.90 1.83 1.80 1.77 1.77 1.74 1.72 1.67 1.64 1.39 1.36 1.35 1.33 1.30 1.28 1.26 1.25 1.24 1.23 1.21 1.19 0.77 0.76
O
O
S
O
NH
PO(OiPr)2
O
3w
0.99 1.05 2.17 0.99 1.01 1.00 2.04 1.01 5.34 14.21 3.03
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 -0.5
f1 (ppm)


15.97
15.82
O
O
S
O
NH
PO(OiPr)2
O
3w
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)


212.37
212.34
150.15
150.08
130.38
130.36
127.95
127.91
125.88
125.85
121.25
121.20
119.71
119.70
74.11
74.03
73.70
73.62
63.71
62.09
52.17
44.44
44.41
28.17
28.02
25.81
25.61
25.51
24.34
24.32
24.12
23.95
6.12
NH
PO(O'Pr)2
3w
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)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7.68
7.67
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7.38
7.37
7.36
7.36
7.35
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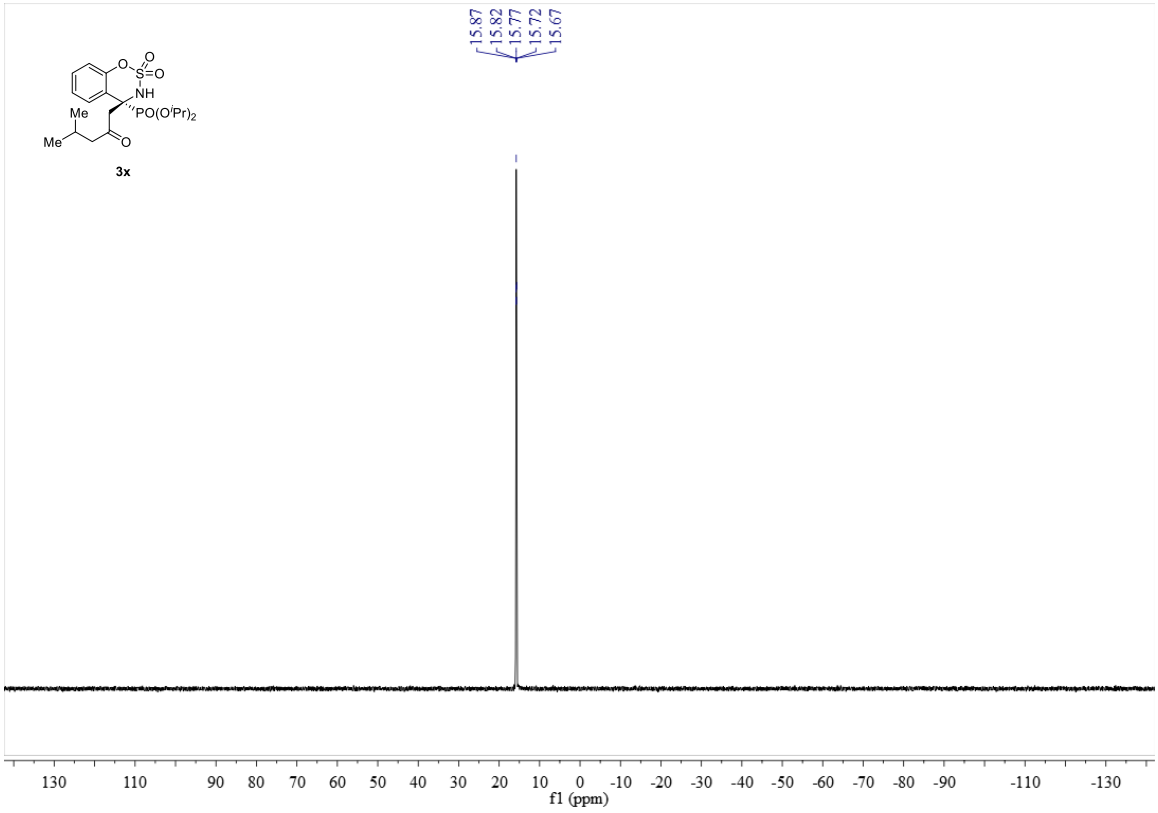
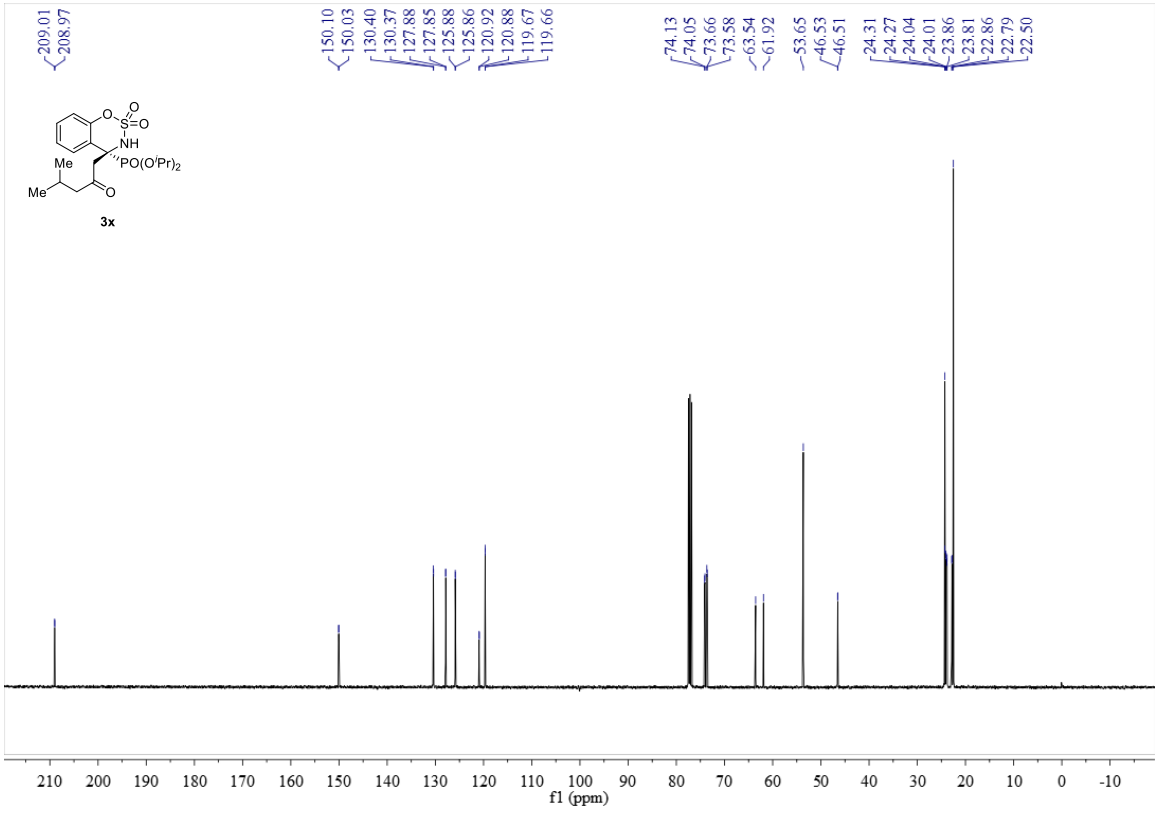
7.28
7.28
7.26
7.26
7.24
7.24
7.07
7.05
4.77
4.75
4.74
4.72
4.37
4.36
4.34
4.33
3.41
3.40
3.37
3.36
2.43
2.41
2.39
2.37
2.36
2.35
2.32
2.30
2.15
2.13
2.12
2.10
2.08
1.36
1.35
1.33
1.32
1.22
1.21
0.92
0.90
0.89
0.88
0.79
0.78
NH
PO(O'Pr)2
Me
Me
3x
1.00
1.02
1.16
0.72
1.10
1.00
1.01
2.04
2.06
1.10
6.19
3.11
6.16
3.10
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 -0.5
f1 (ppm)


15.87
15.82
15.77
15.72
15.67
3x
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)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208.97
150.10
150.03
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130.37
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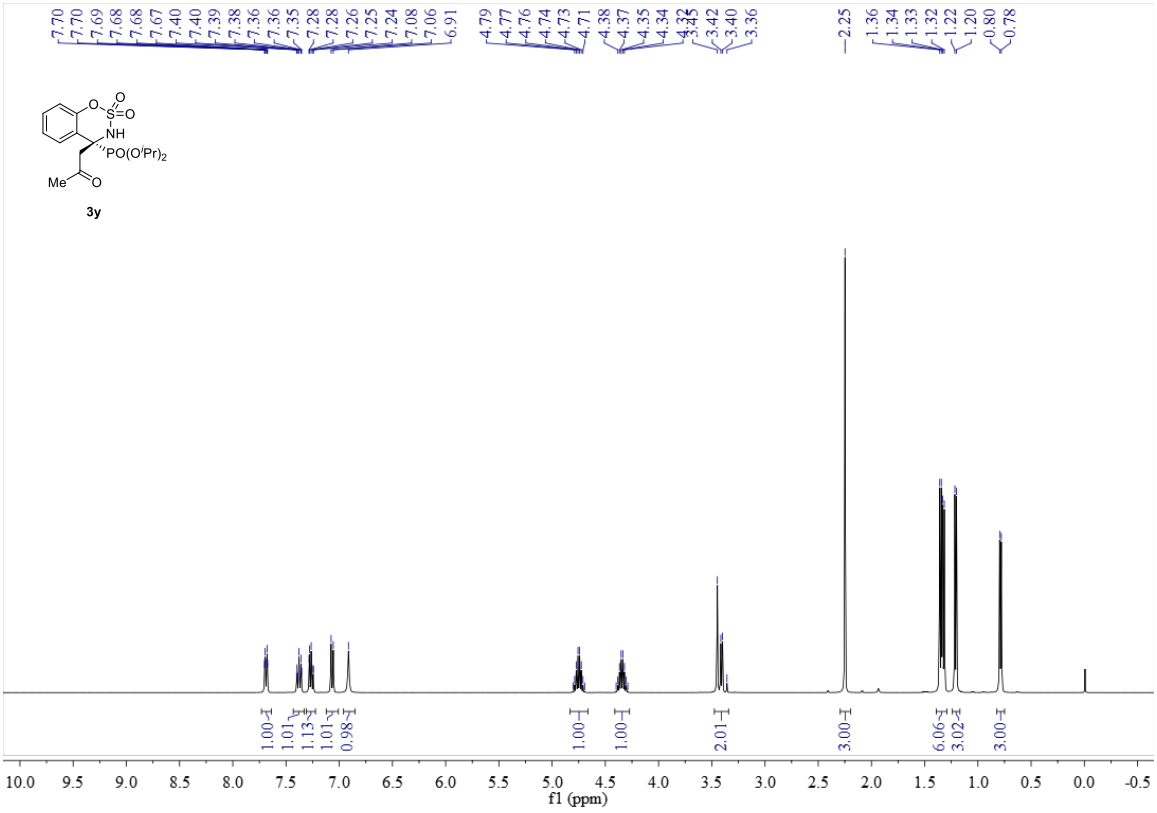
127.85
125.88
125.86
120.92
120.88
119.67
119.66
74.13
74.05
73.66
73.58
63.54
61.92
53.65
46.53
46.51
24.31
24.27
24.04
24.01
23.86
23.81
22.86
22.79
22.50
3x
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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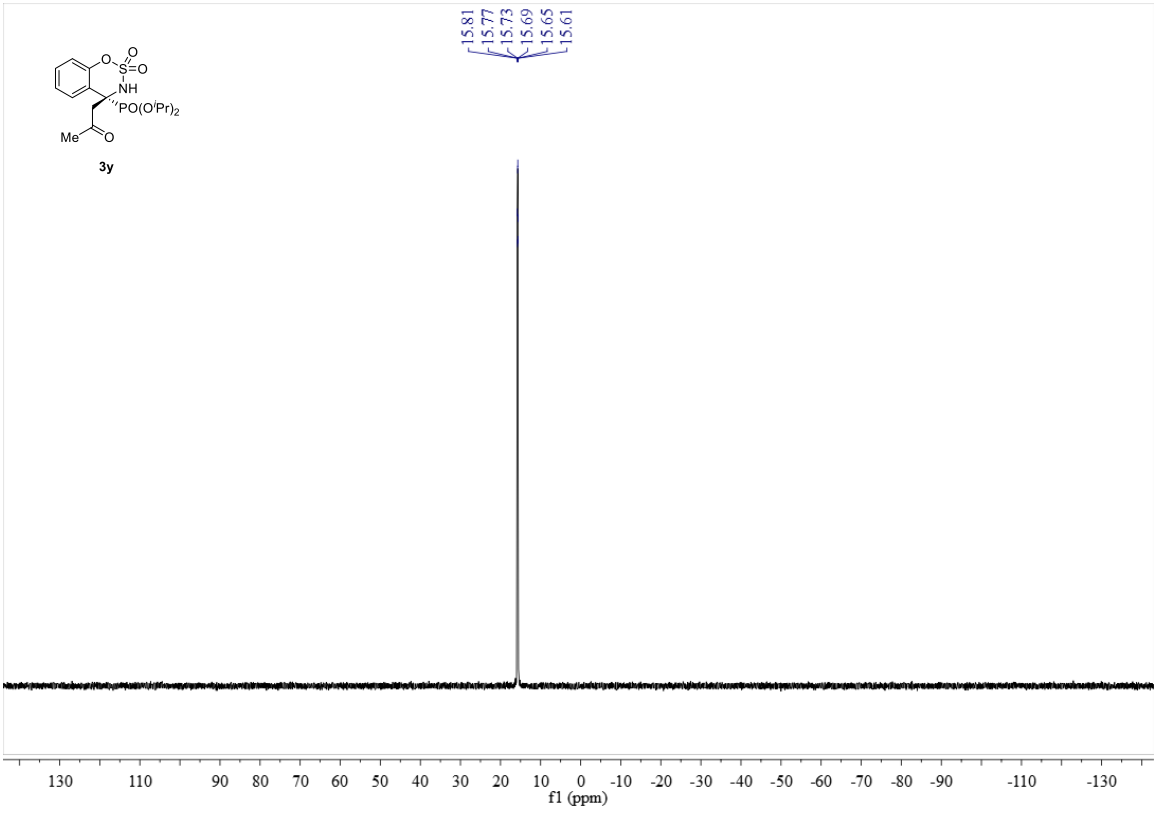
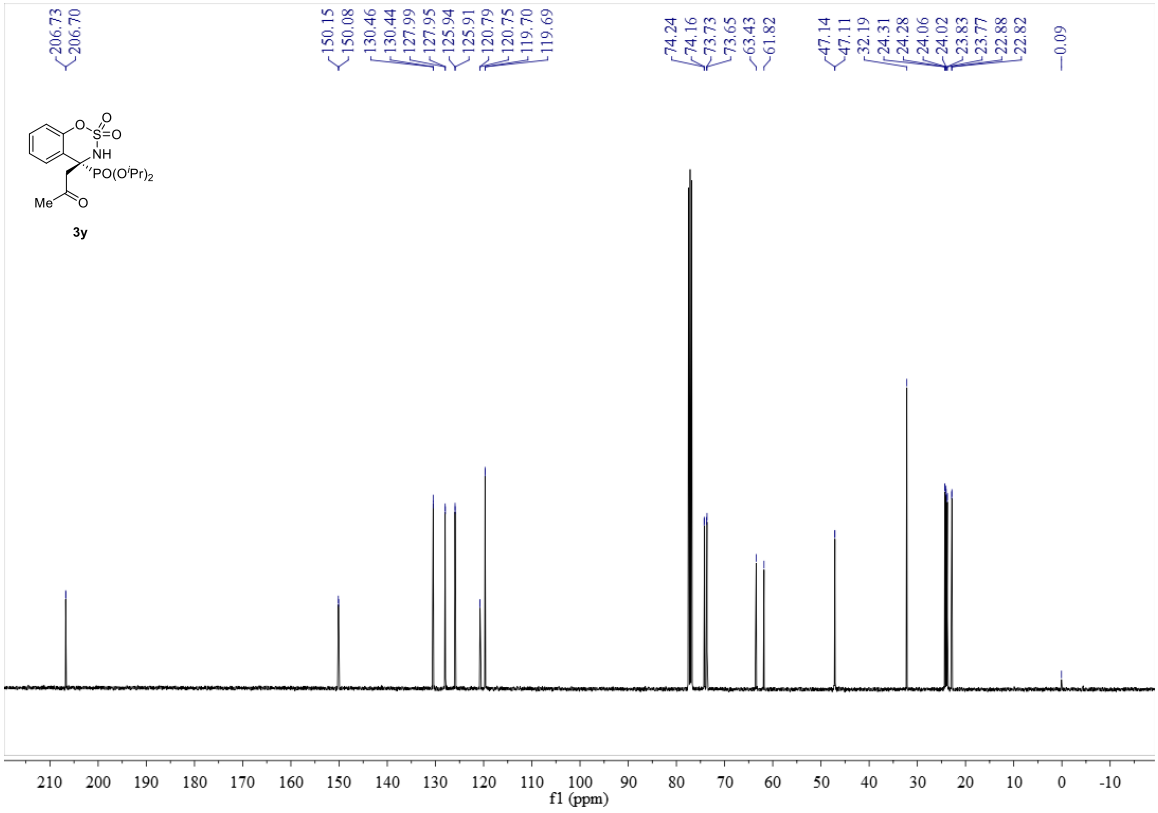
7.70
7.69
7.68
7.68
7.67
7.40
7.40
7.39
7.38
7.36
7.36
7.35
7.28
7.28
7.26
7.25
7.24
7.08
7.06
6.91
4.79
4.77
4.76
4.74
4.73
4.71
4.38
4.37
4.35
4.34
4.32
3.45
3.42
3.40
3.36
2.25
1.36
1.34
1.33
1.32
1.22
1.20
0.80
0.78
O
S
O
NH
PO(OiPr)2
Me
O
3y
1.00
1.01
1.13
1.01
0.98
1.00
1.00
2.01
3.00
6.06
3.02
3.00
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 -0.5
f1 (ppm)


15.81
15.77
15.73
15.69
15.65
15.61
O
S
O
NH
PO(OiPr)2
Me
O
3y
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)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130.44
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127.95
125.94
125.91
120.79
120.75
119.70
119.69
74.24
74.16
73.73
73.65
63.43
61.82
47.14
47.11
32.19
24.31
24.28
24.06
24.02
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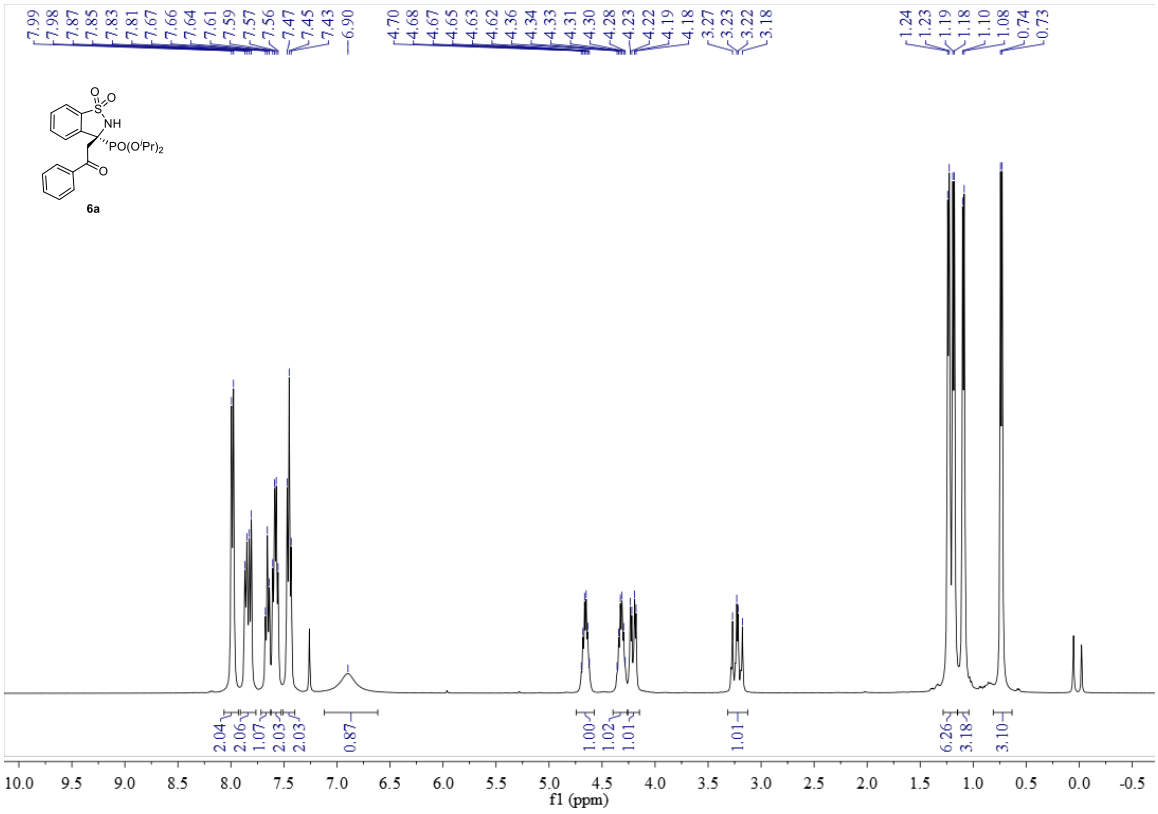
23.77
22.88
22.82
0.09
NH
PO(OiPr)2
Me
O
3y
f1 (ppm)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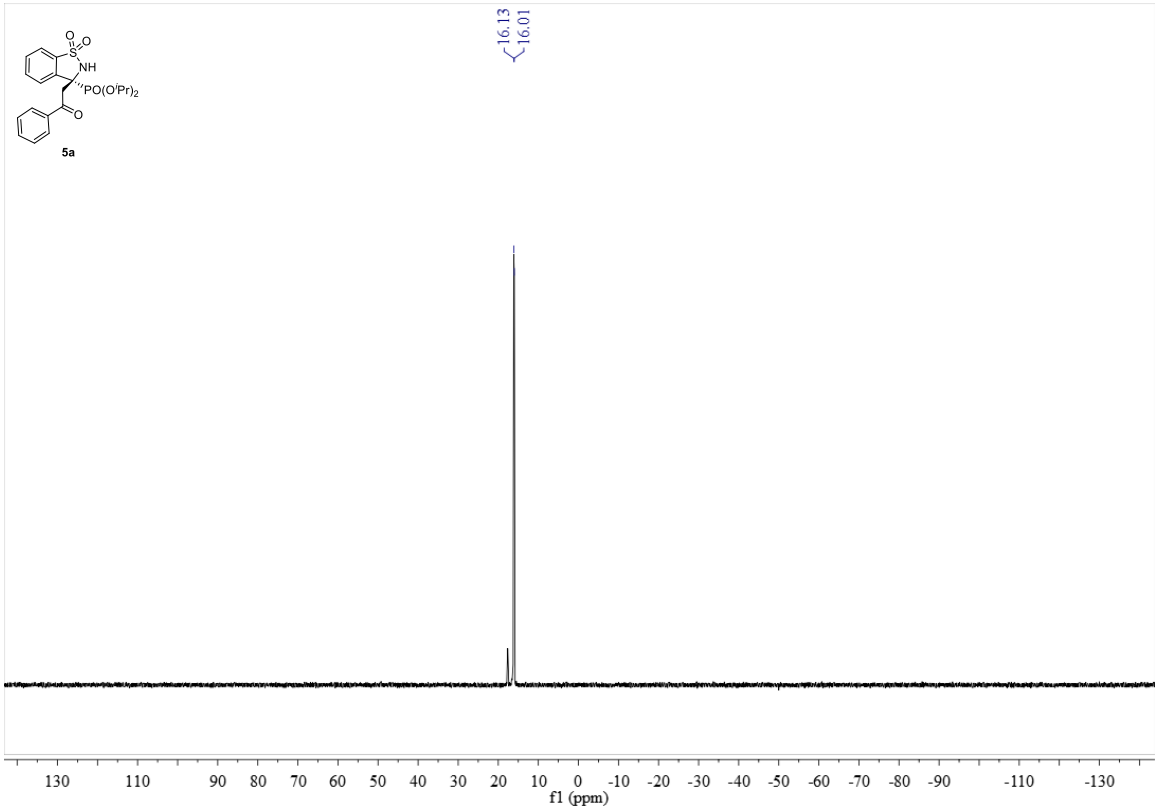
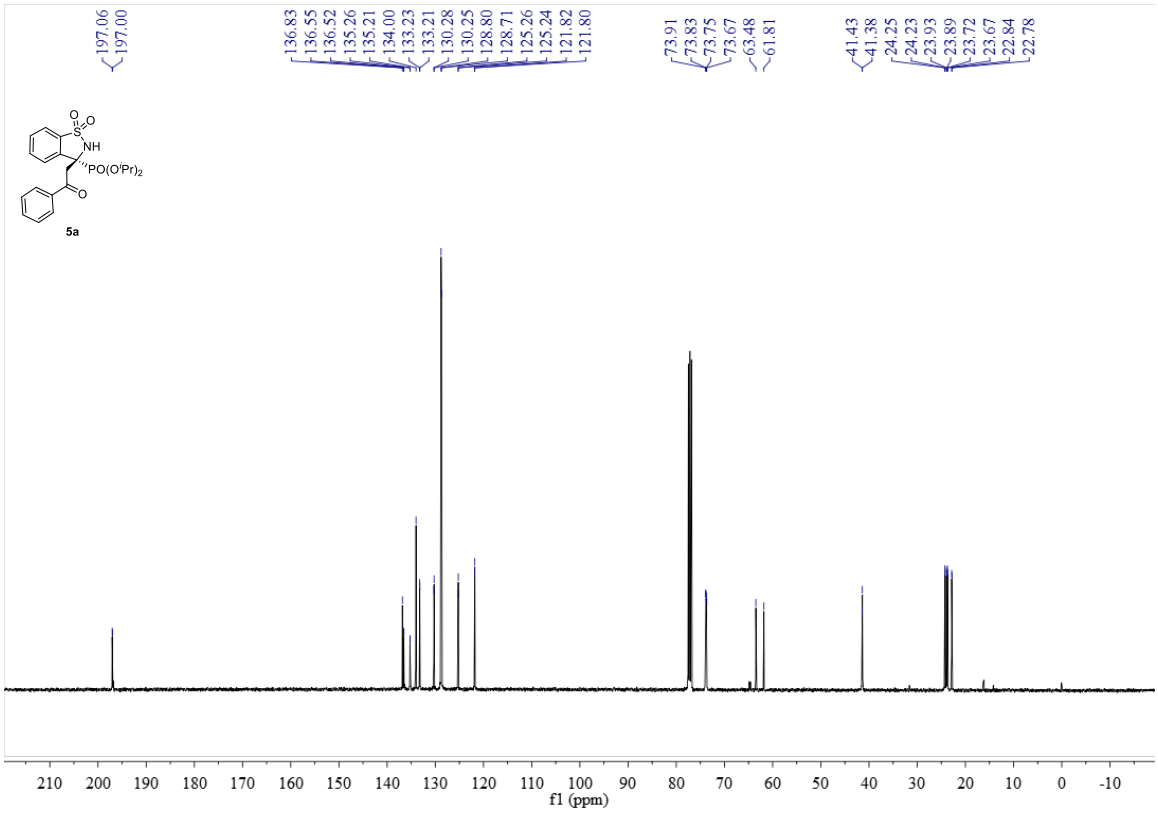
7.66
7.64
7.61
7.59
7.57
7.56
7.47
7.45
7.43
6.90
4.70
4.68
4.67
4.65
4.63
4.62
4.36
4.34
4.33
4.31
4.30
4.28
4.23
4.22
4.19
4.18
3.27
3.23
3.22
3.18
1.24
1.23
1.19
1.18
1.10
1.08
0.74
0.73
NH
PO(OiPr)2
O
6a
2.04
2.06
1.07
2.03
2.03
0.87
1.00
1.02
1.01
1.01
6.26
3.18
3.10
f1 (ppm)


16.13
16.01
5a
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)


197.06
197.00
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133.21
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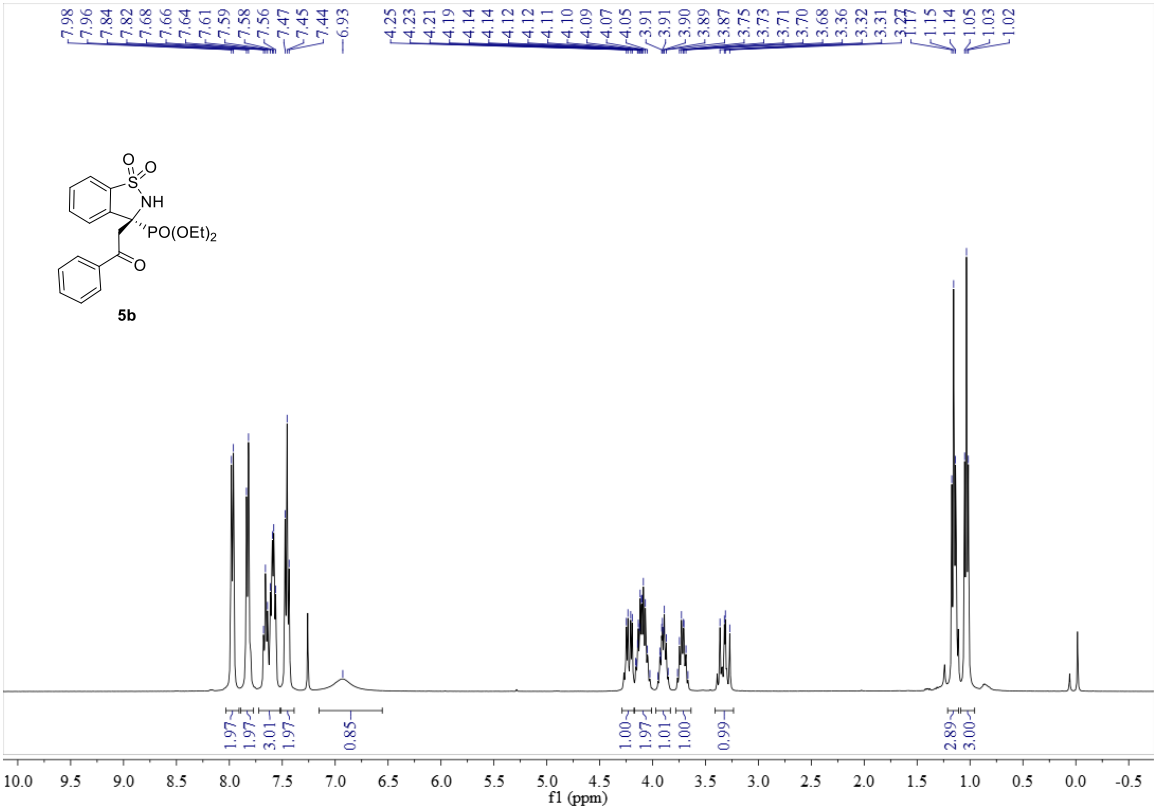
128.80
128.71
125.26
125.24
121.82
121.80
73.91
73.83
73.75
73.67
63.48
61.81
41.43
41.38
24.25
24.23
23.93
23.89
23.72
23.67
22.84
22.78
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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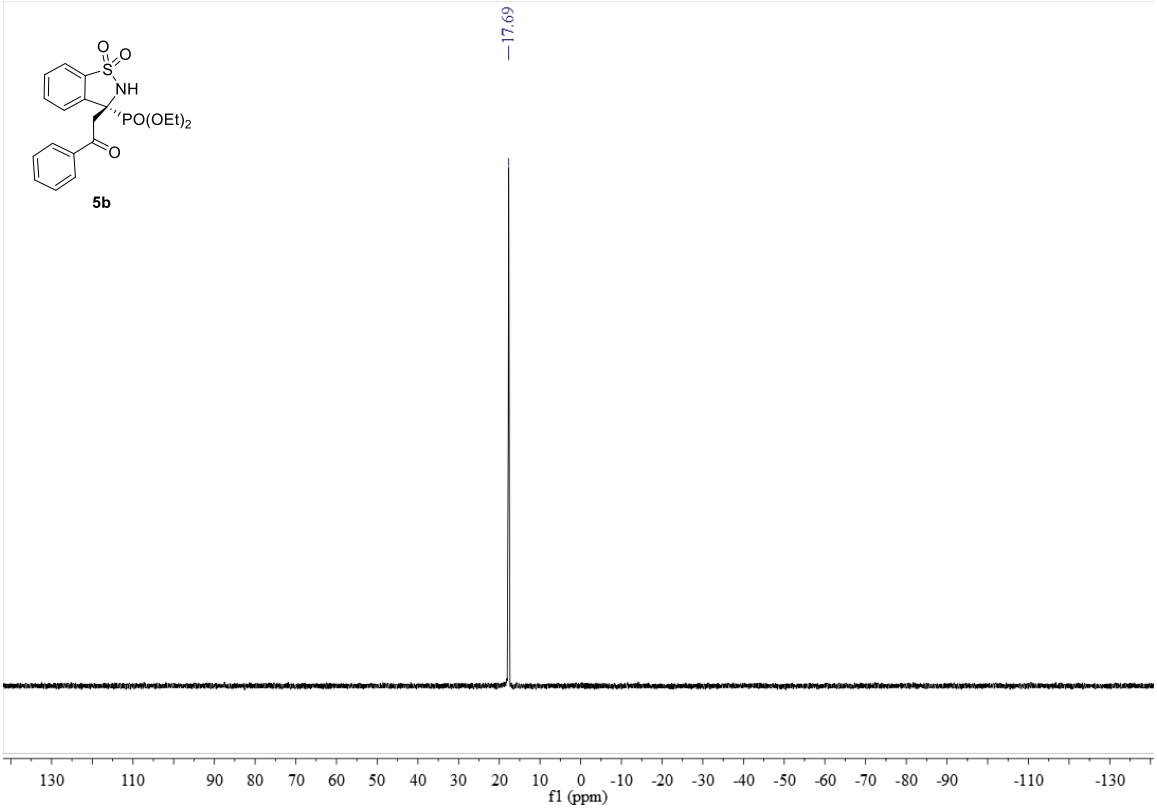
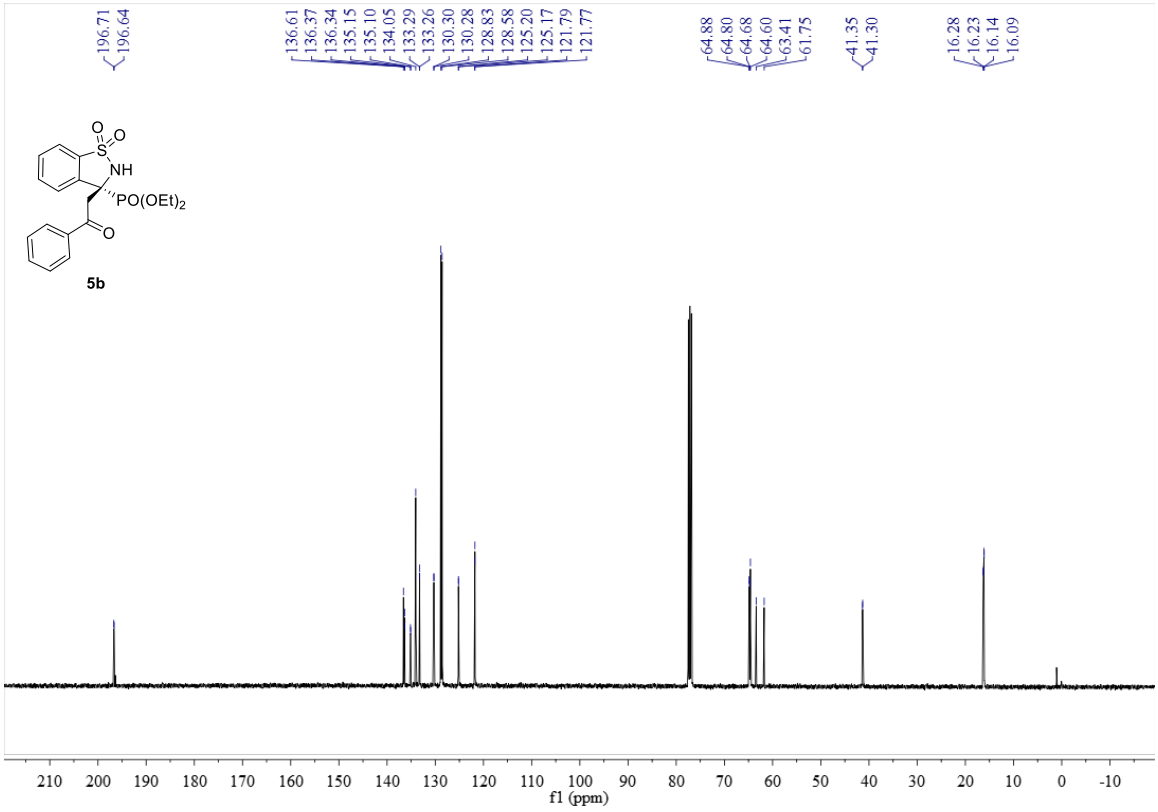
7.66
7.64
7.61
7.59
7.58
7.56
7.47
7.45
7.44
6.93
4.25
4.23
4.21
4.19
4.14
4.14
4.12
4.12
4.11
4.10
4.09
4.07
4.05
3.91
3.91
3.90
3.89
3.87
3.75
3.73
3.71
3.70
3.68
3.36
3.32
3.31
1.17
1.15
1.14
1.05
1.03
1.02
O
O
S
NH
PO(OEt)2
O
5b
1.97
1.97
3.01
1.97
0.85
1.00
1.97
1.01
1.00
0.99
2.89
3.00
10.0 9.5 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 -0.5
f1 (ppm)


17.69
O
O
S
NH
PO(OEt)2
O
5b
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)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196.64
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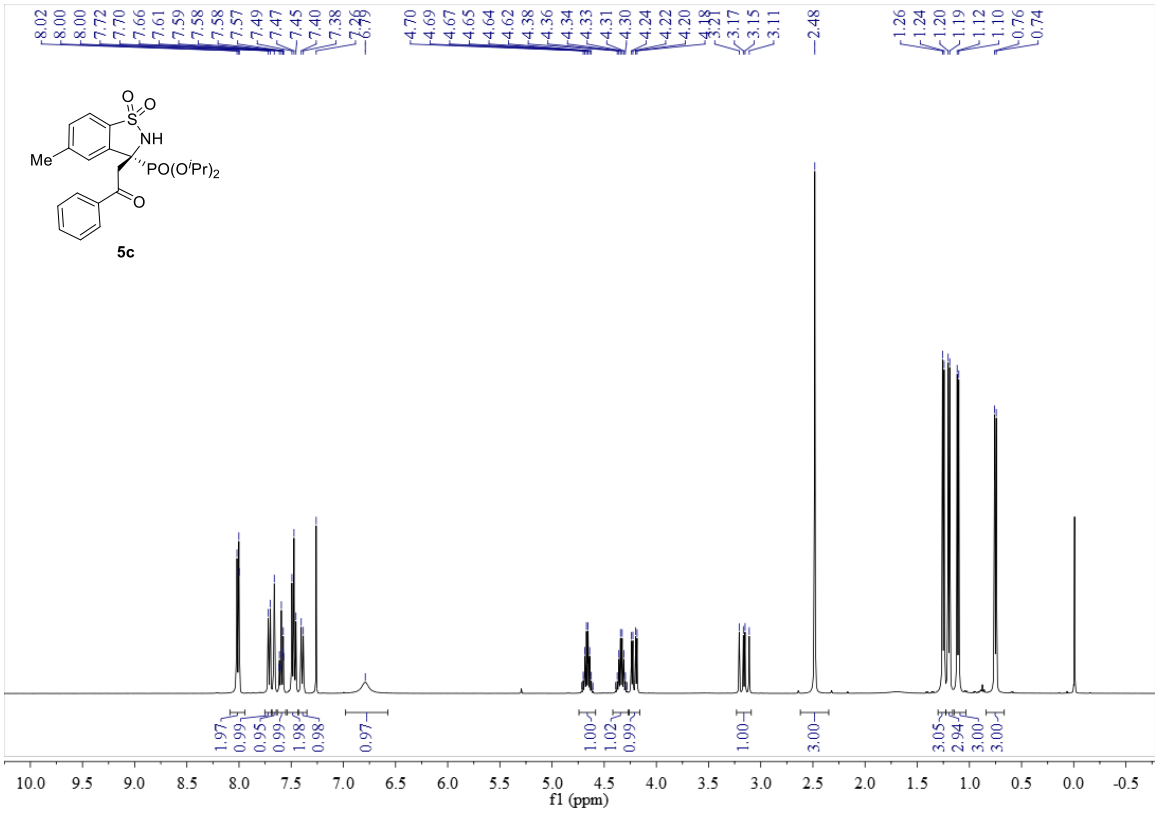
136.37
136.34
135.15
135.10
134.05
133.29
133.26
130.30
130.28
128.83
128.58
125.20
125.17
121.79
121.77
64.88
64.80
64.68
64.60
63.41
61.75
41.35
41.30
16.28
16.23
16.14
16.09
O
O
S
NH
PO(OEt)2
O
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.00
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7.66
7.61
7.59
7.58
7.58
7.57
7.49
7.47
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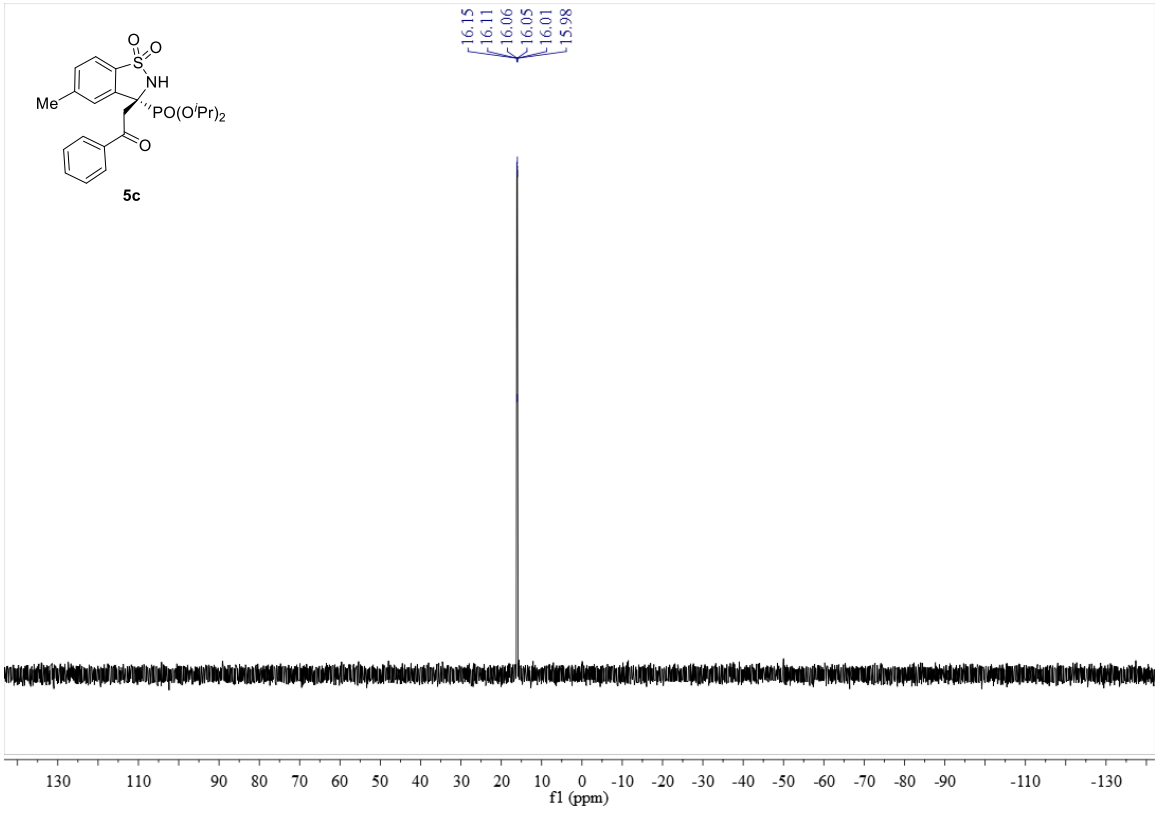
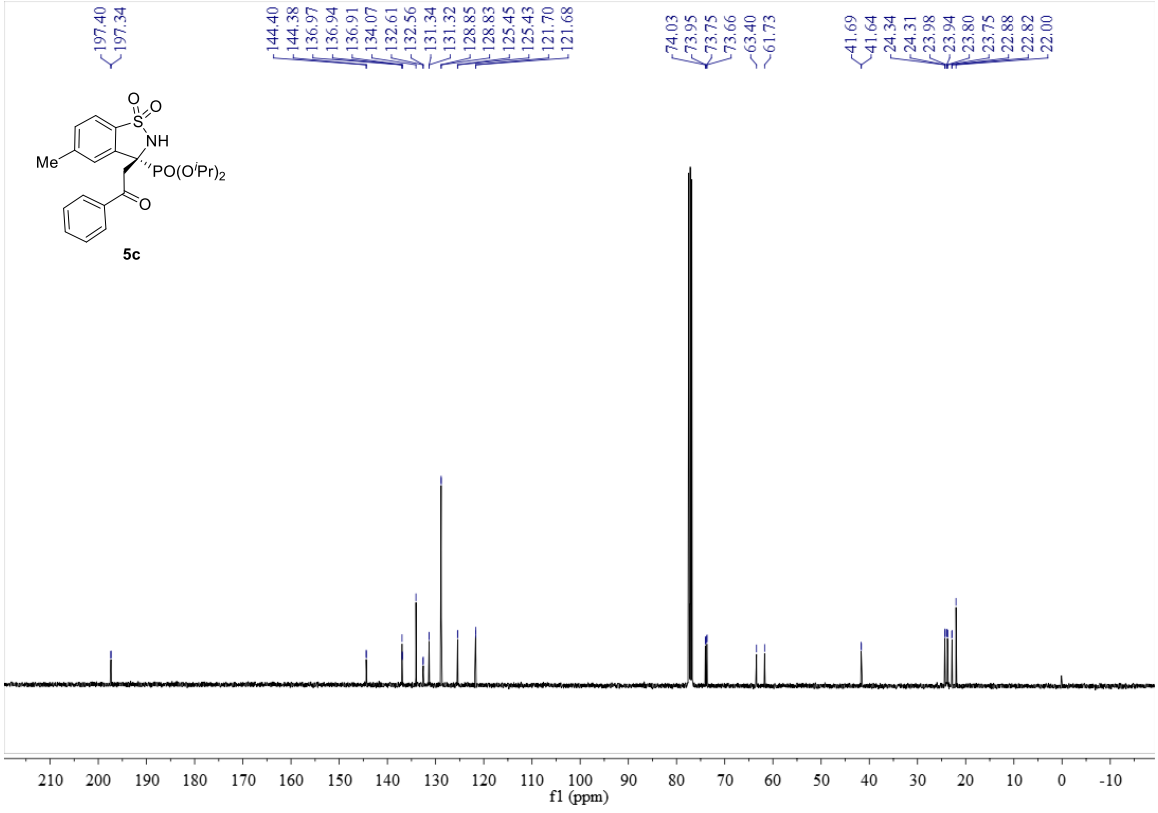
7.40
7.38
7.28
6.79
4.70
4.69
4.67
4.65
4.64
4.62
4.38
4.36
4.34
4.33
4.31
4.30
4.24
4.22
4.20
4.18
3.21
3.17
3.15
3.11
2.48
1.26
1.24
1.20
1.19
1.12
1.10
0.76
0.74
O
O
S
NH
Me
PO(OiPr)2
O
5c
1.97
0.99
0.95
0.99
1.98
0.98
0.97
1.00
1.02
0.99
1.00
3.00
3.05
2.94
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 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 -0.5
f1 (ppm)


16.15
16.11
16.06
16.05
16.01
15.98
Me
NH
PO(O^{i}Pr)$_2$
5c
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)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144.40
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136.94
136.91
134.07
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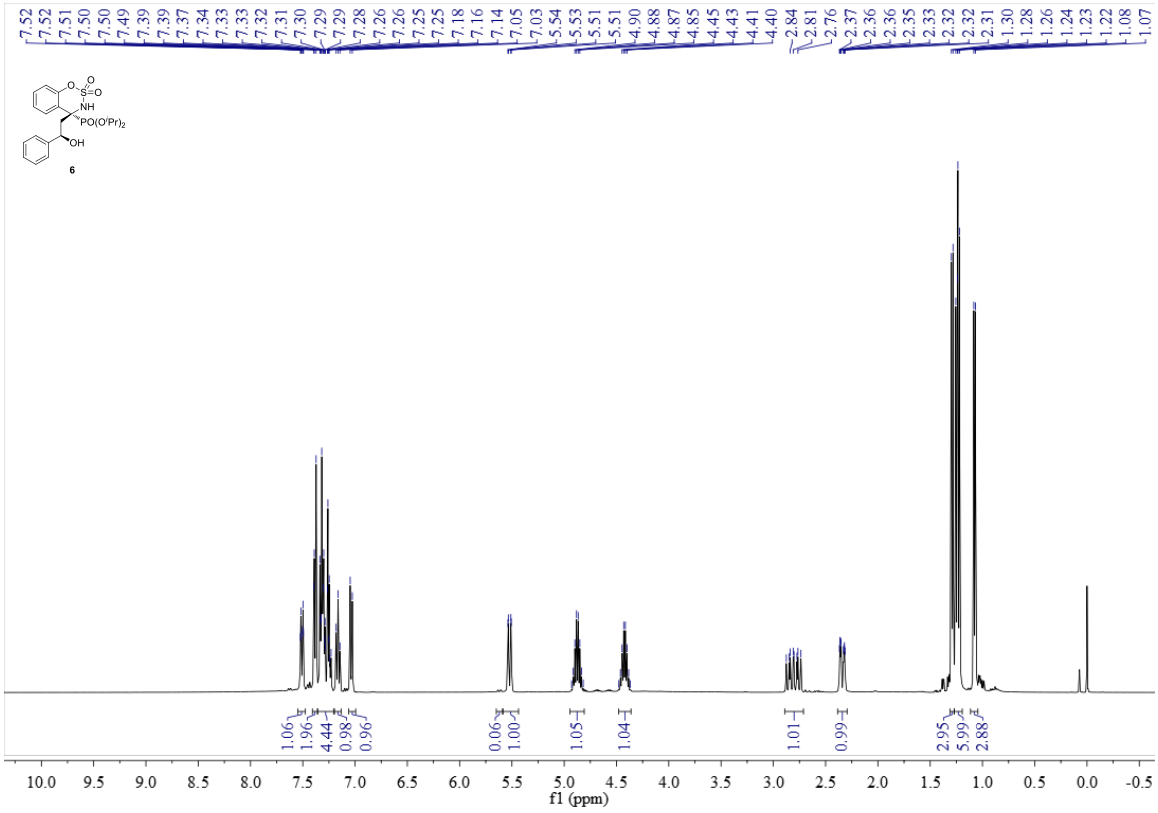
132.56
131.34
131.32
128.85
128.83
125.45
125.43
121.70
121.68
74.03
73.95
73.75
73.66
63.40
61.73
41.69
41.64
24.34
24.31
23.98
23.94
23.80
23.75
22.88
22.82
22.00
Me
NH
PO(O^{i}Pr)$_2$
5c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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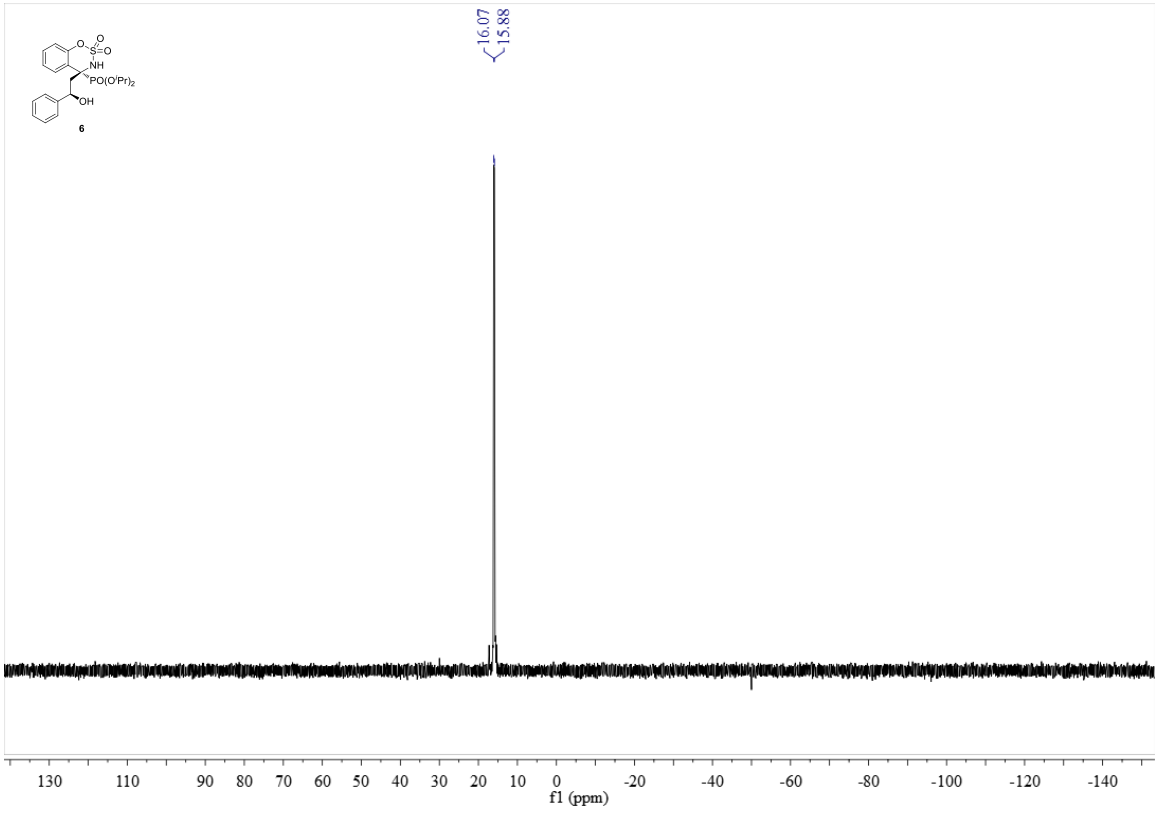
NH
PO(O'Pr)2
OH
6
1.06 1.96 4.44 0.98 0.96 0.06 1.00 1.05 1.04 1.01 0.99 2.95 5.99 2.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


16.07
15.88
NH
PO(O'Pr)2
OH
6
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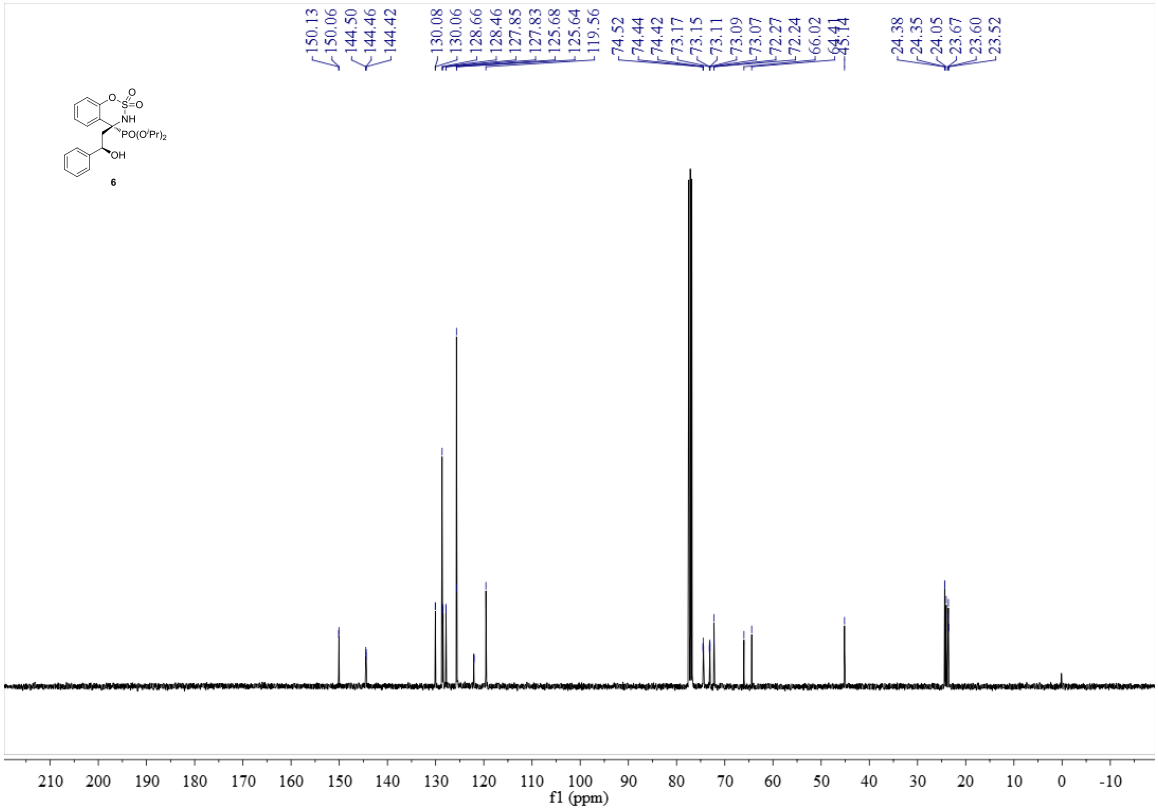
f1 (ppm)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125.64
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74.52
74.44
74.42
73.17
73.15
73.11
73.09
73.07
72.27
72.24
66.02
64.41
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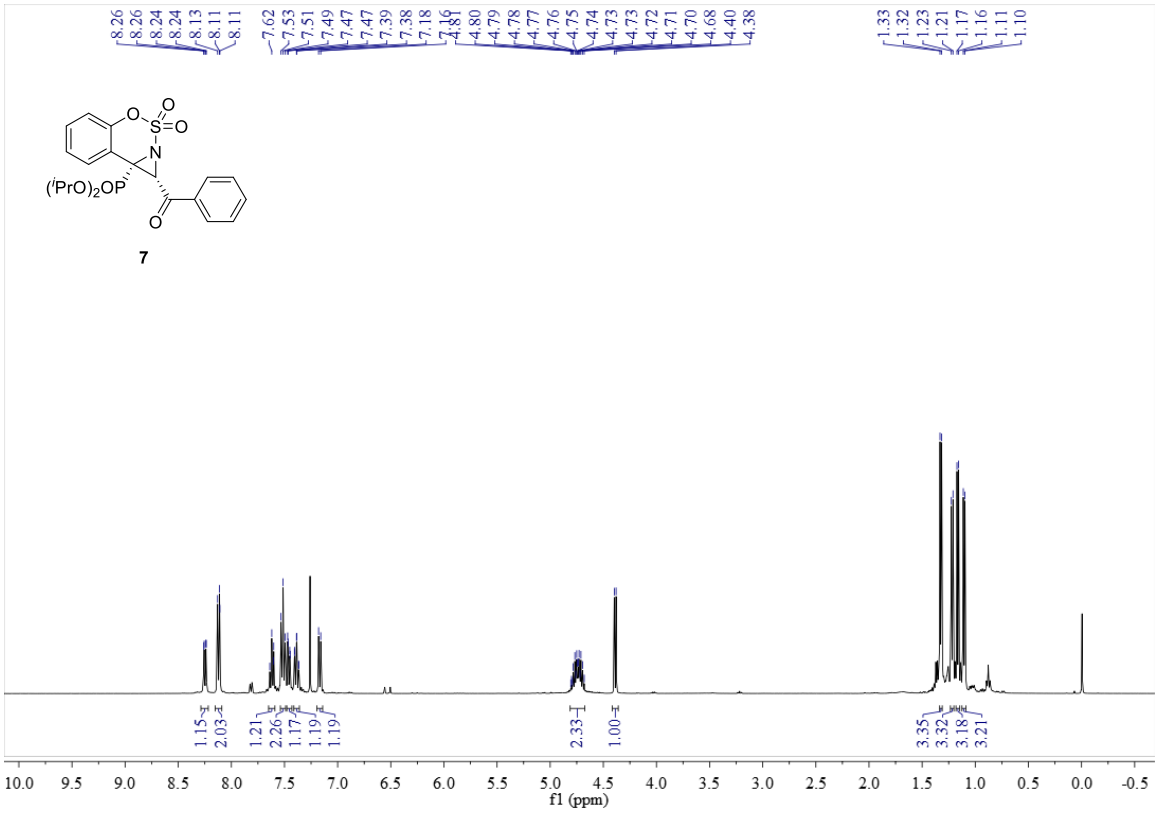
23.52
NH
PO(OiPr)2
OH
6
f1 (ppm)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7.51
7.49
7.47
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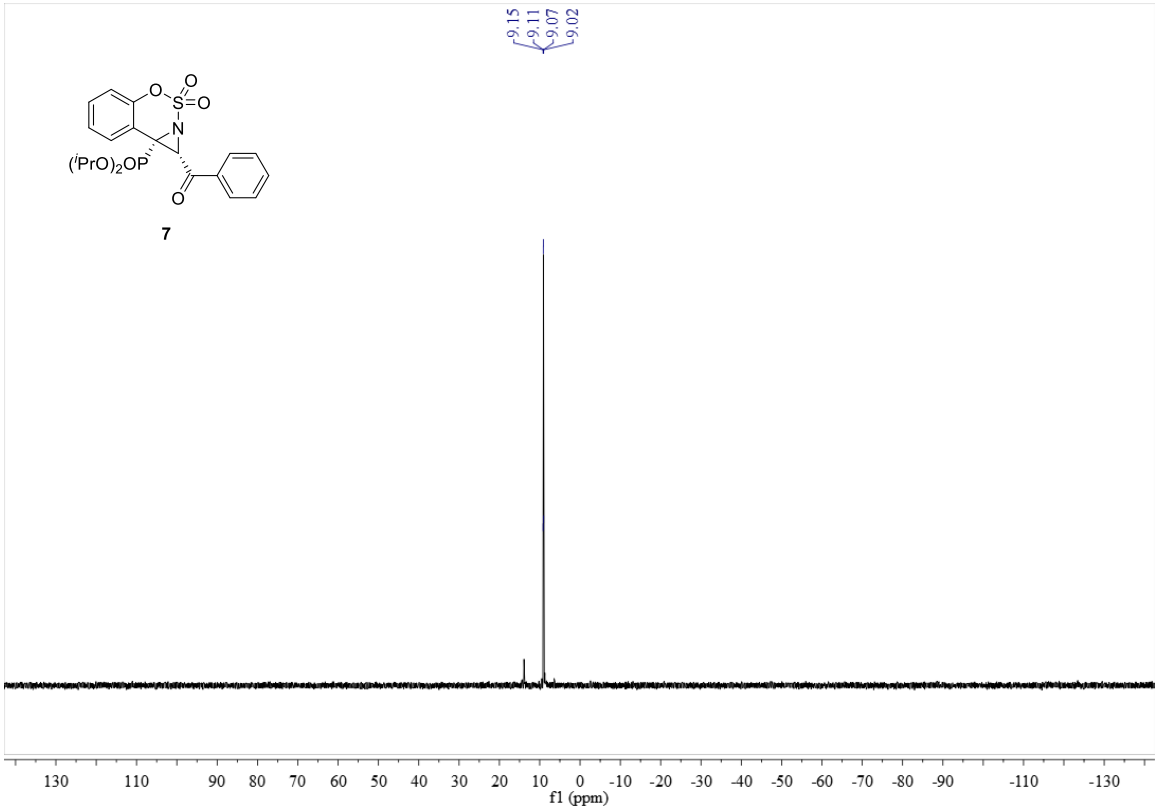
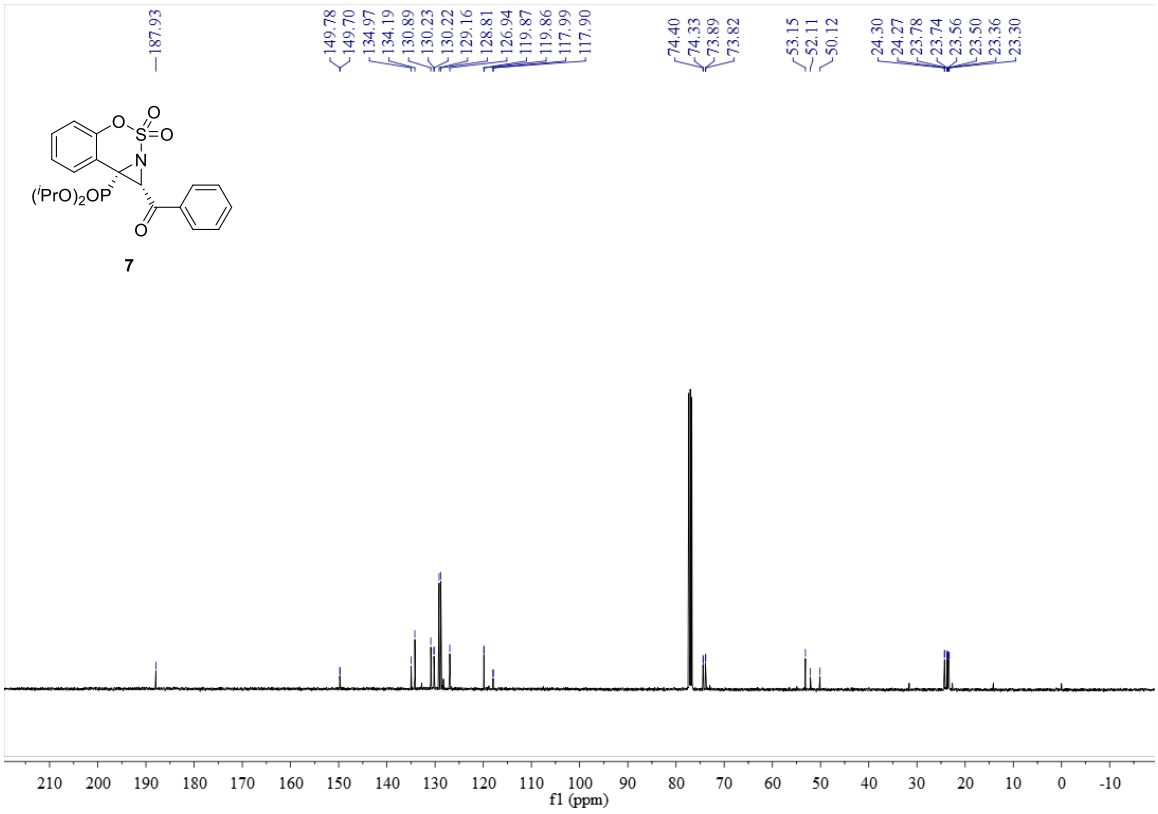
7.39
7.38
7.18
7.16
4.81
4.80
4.79
4.78
4.77
4.76
4.75
4.74
4.73
4.73
4.72
4.71
4.70
4.68
4.40
4.38
1.33
1.32
1.23
1.21
1.17
1.16
1.11
1.10
(iPrO)2OP
7
1.15
2.03
1.21
2.26
1.17
1.19
1.19
2.33
1.00
3.35
3.32
3.18
3.21
f1 (ppm)


9.15
9.11
9.07
9.02
O
O
S
O
N
(iPrO)2OP
O
7
130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)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130.23
130.22
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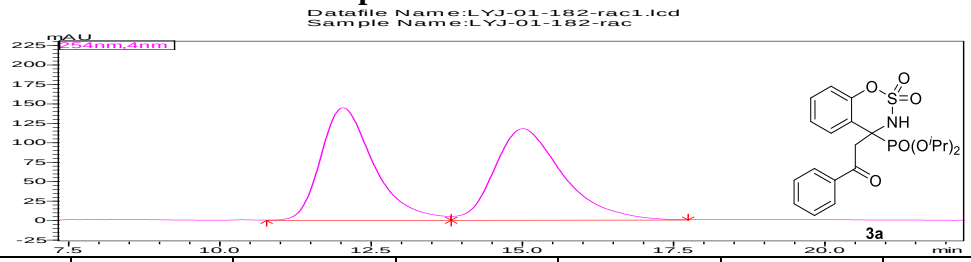
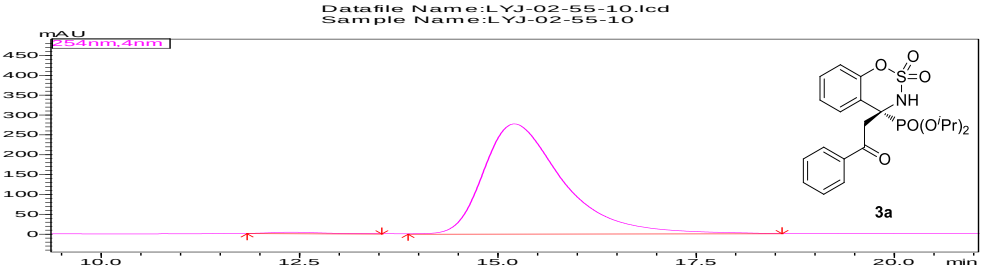
128.81
126.94
119.87
119.86
117.99
117.90
74.40
74.33
73.89
73.82
53.15
52.11
50.12
24.30
24.27
23.78
23.74
23.56
23.50
23.36
23.30
O
O
S
O
N
(iPrO)2OP
O
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

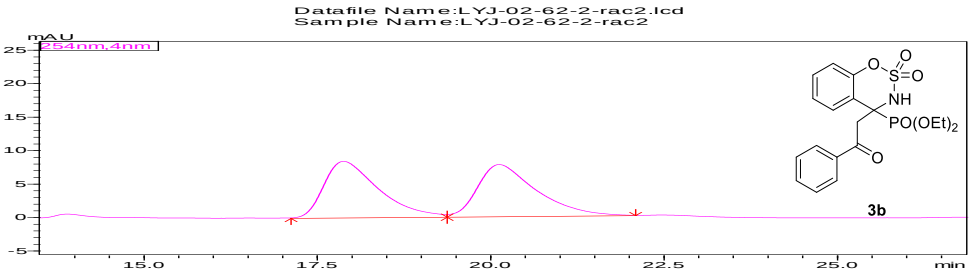
HPLC charts of the related compounds



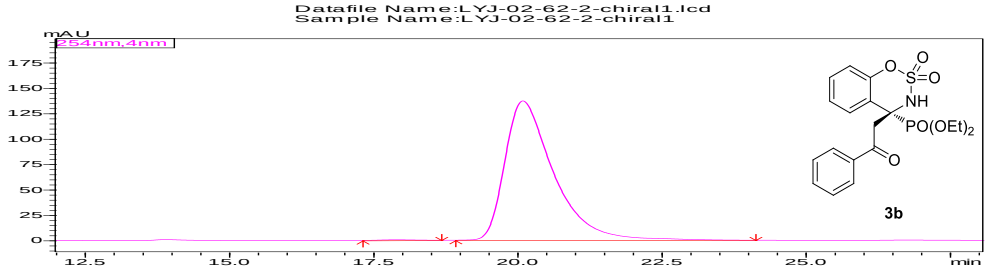
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	12.049	49.038	8774930	144241		0.000
2	15.029	50.962	9119282	117190	V	0.000
Total		100.000	17894212	261432		0.000



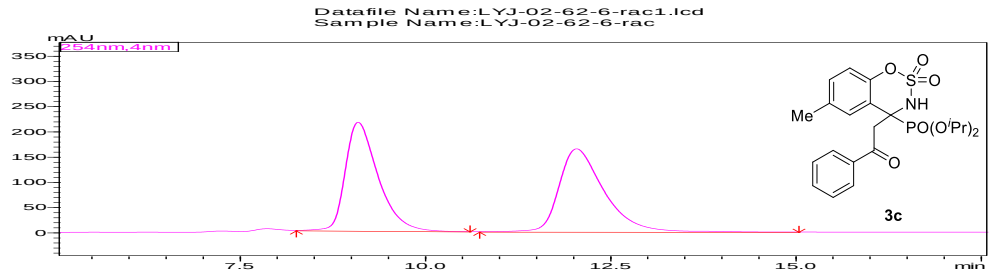
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	12.403	0.655	126108	3019		0.000
2	15.220	99.345	19118068	276256		0.000
Total		100.000	19244175	279275		0.000



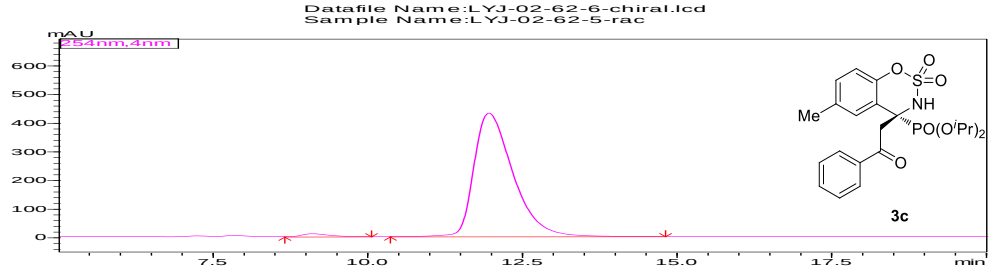
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	17.892	50.187	456149	8397		0.000
2	20.136	49.813	452741	7748	V	0.000
Total		100.000	908891	16145		0.000



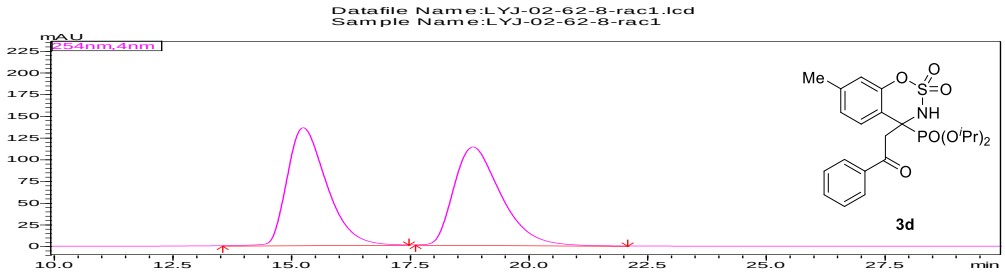
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	17.913	0.274	22102	520		0.000
2	20.102	99.726	8047888	136944		0.000
Total		100.000	8069990	137464		0.000



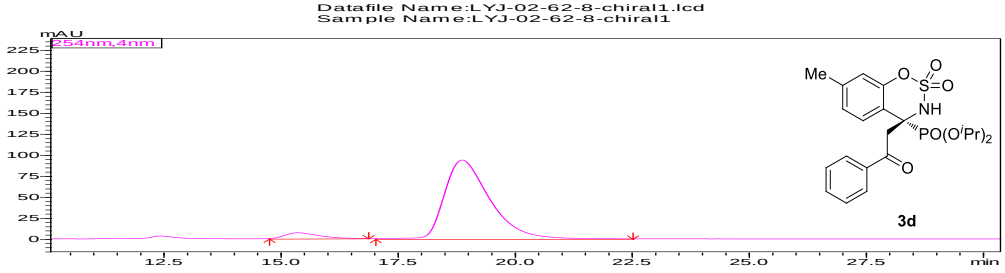
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	9.105	48.834	6589006	215021		0.000
2	12.053	51.166	6903586	164406	S	0.000
Total		100.000	13492592	379427		0.000



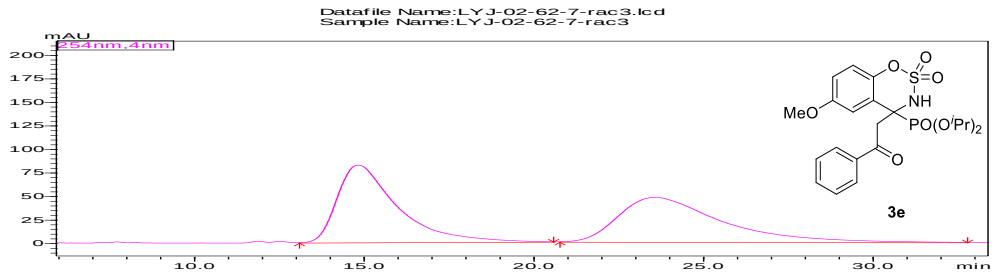
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	9.117	1.537	295054	10216		0.000
2	11.975	98.463	18900334	430812		0.000
Total		100.000	19195388	441027		0.000



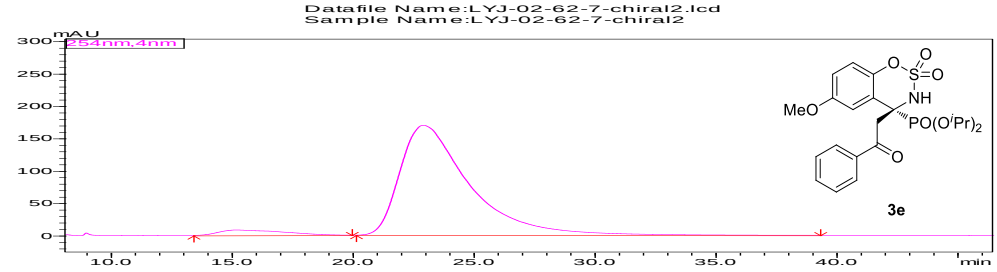
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	15.261	50.115	7808055	135422		0.000
2	18.840	49.885	7772210	113021		0.000
Total		100.000	15580265	248443		0.000



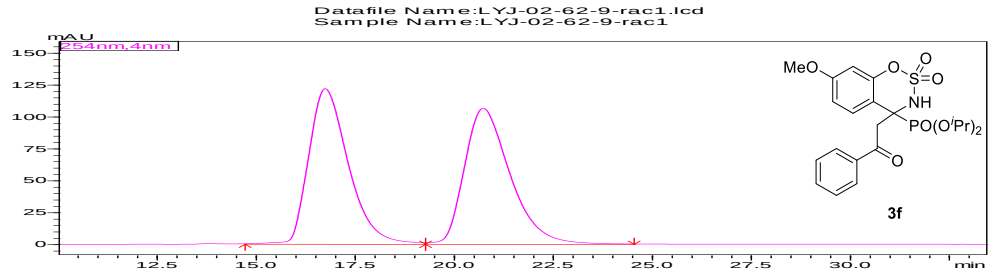
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	15.379	5.085	336842	6918	M	0.000
2	18.888	94.915	6286990	93768	M	0.000
Total		100.000	6623832	100685		0.000



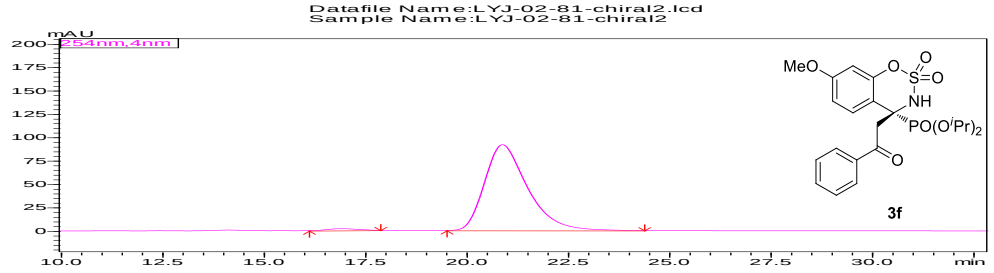
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	14.846	50.568	10073398	81931		0.000
2	23.559	49.432	9846940	47148		0.000
Total		100.000	19920338	129079		0.000



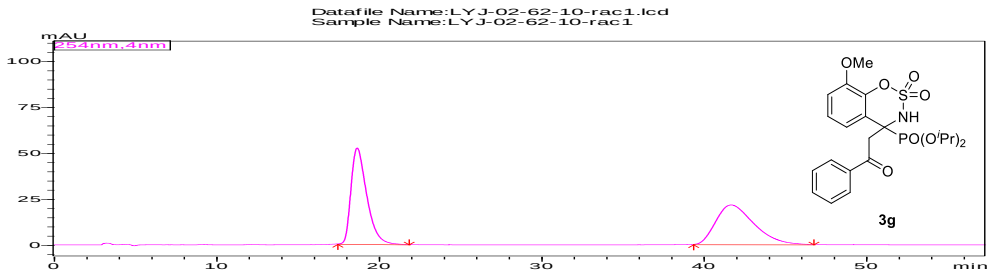
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	15.208	4.308	1523399	8256		0.000
2	22.930	95.692	33840388	169562	M	0.000
Total		100.000	35363787	177818		0.000



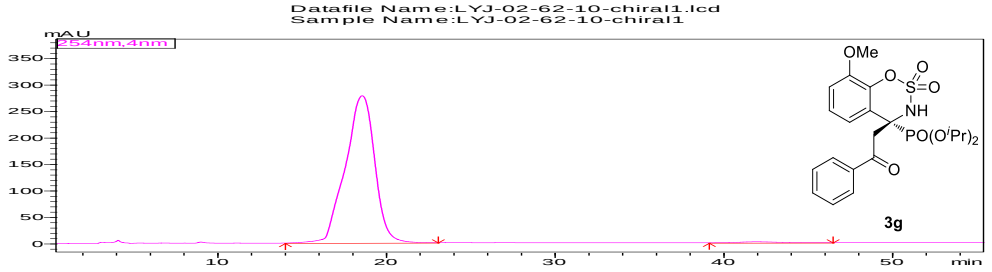
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	16.765	49.882	8419864	121490		0.000
2	20.754	50.118	8459729	106218	V	0.000
Total		100.000	16879593	227708		0.000



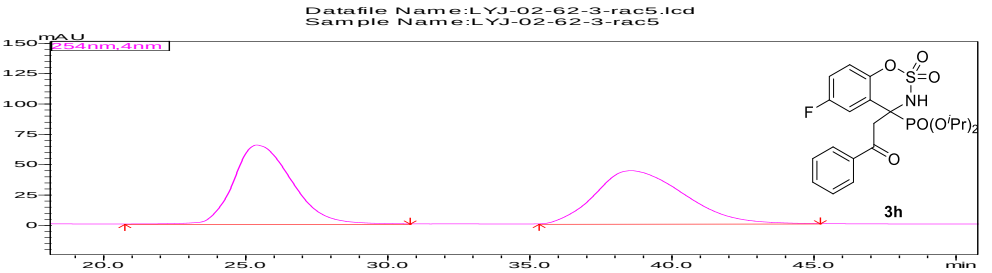
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	16.932	1.403	95686	1905		0.000
2	20.897	98.597	6722238	91739		0.000
Total		100.000	6817923	93644		0.000



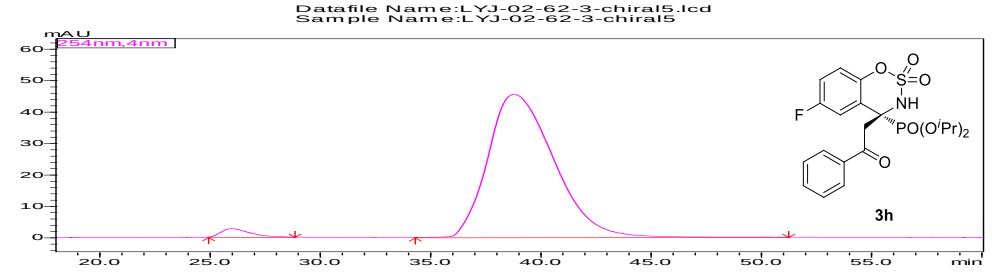
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	18.695	50.258	3522027	52345		0.000
2	41.720	49.742	3485907	21494		0.000
Total		100.000	7007935	73839		0.000



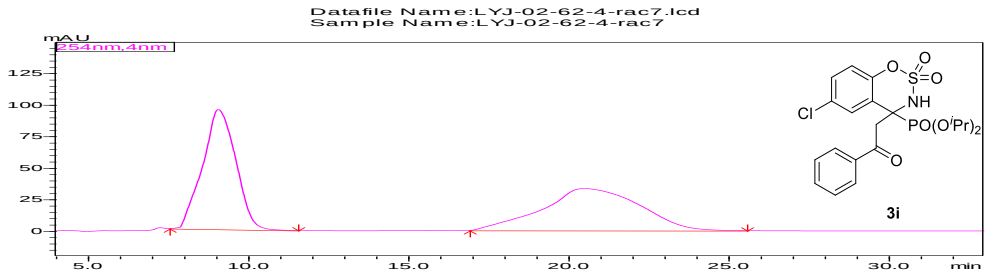
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	18.617	99.204	33664088	278014		0.000
2	41.927	0.796	270230	1779	M	0.000
Total		100.000	33934318	279793		0.000



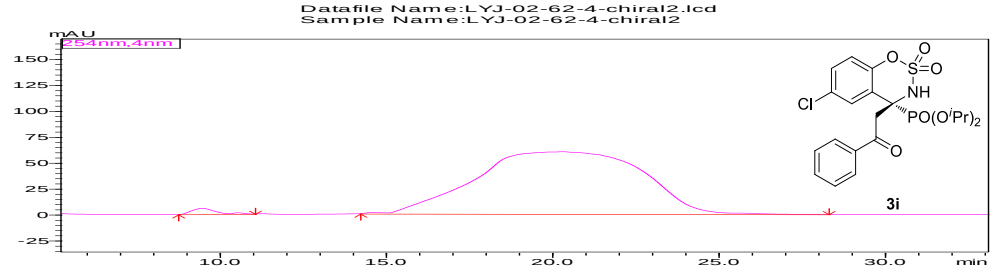
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	25.424	49.217	9192207	64949	M	0.000
2	38.600	50.783	9484769	43742		0.000
Total		100.000	18676976	108691		0.000



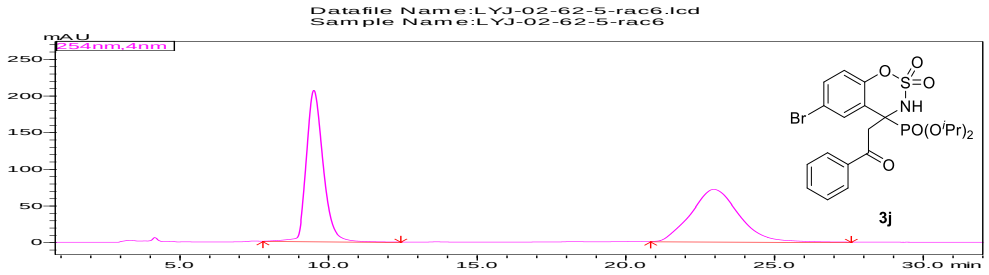
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	26.009	2.479	239796	2680	M	0.000
2	38.832	97.521	9433962	45510	M	0.000
Total		100.000	9673758	48190		0.000



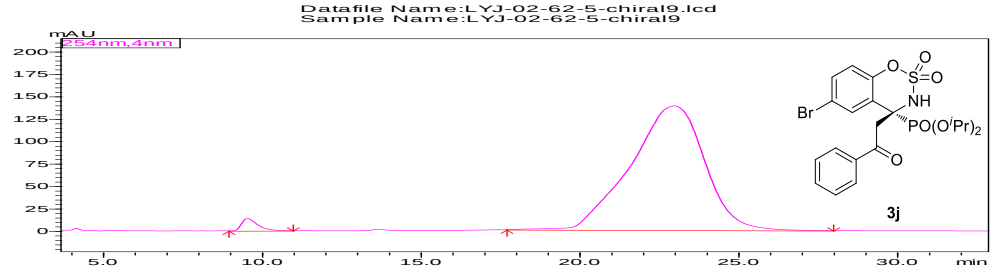
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	9.078	49.347	6849872	95000		0.000
2	20.524	50.653	7031074	33240		0.000
Total		100.000	13880946	128240		0.000



Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	9.488	1.358	289403	5764	M	0.000
2	20.336	98.642	21025856	60003	M	0.000
Total		100.000	21315259	65767		0.000

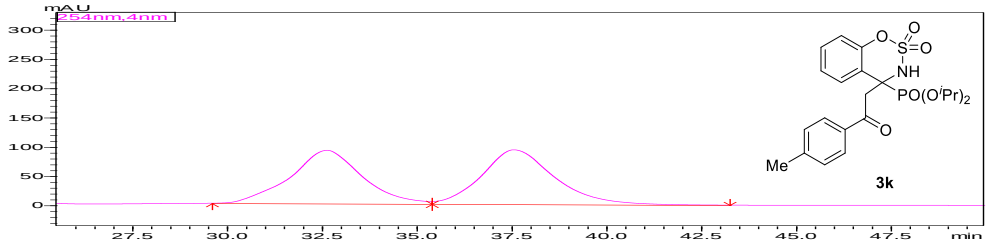


Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	9.539	50.266	8009733	206131		0.000
2	22.991	49.734	7924824	71244		0.000
Total		100.000	15934557	277376		0.000



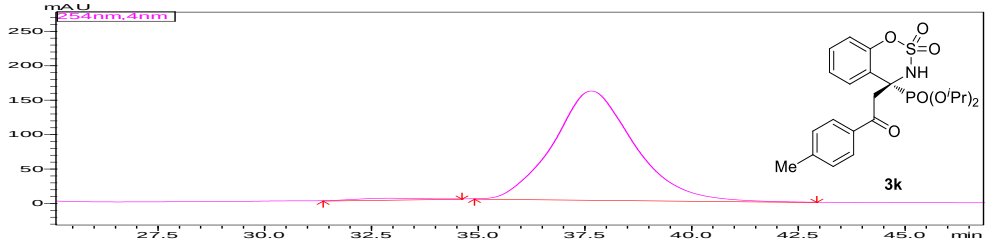
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	9.563	2.081	477180	13626		0.000
2	22.995	97.919	22451188	138670		0.000
Total		100.000	22928368	152296		0.000

Datafile Name:LYJ-02-61-1-rac28.lcd
Sample Name:LYJ-02-61-1-rac28



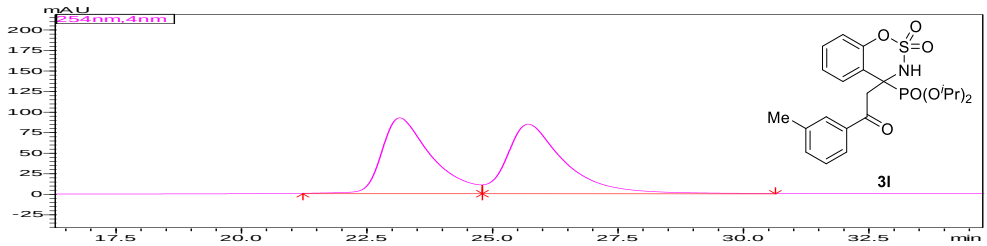
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	32.647	49.078	11939199	91109		0.000
2	37.572	50.922	12387928	93085	V	0.000
Total		100.000	24327127	184194		0.000

Datafile Name:LYJ-02-61-1-chiral4.lcd
Sample Name:LYJ-02-61-1-chiral4



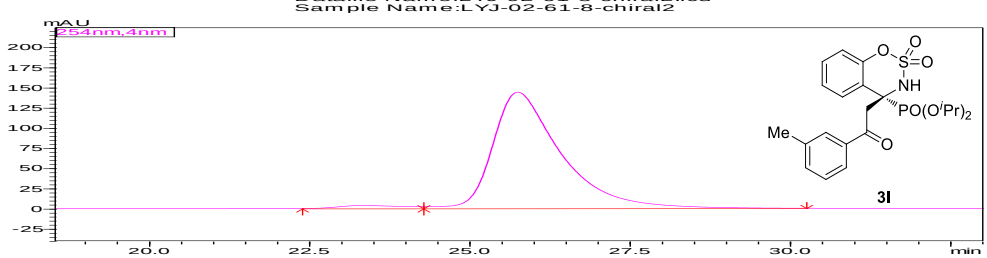
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	32.969	1.068	224266	2249	M	0.000
2	37.672	98.932	20780162	158050		0.000
Total		100.000	21004428	160299		0.000

Datafile Name:LYJ-02-61-8-rac10.lcd
Sample Name:LYJ-02-61-8-rac10

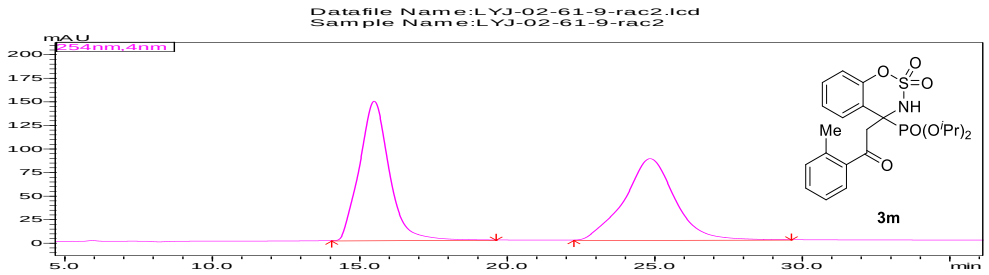


Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	23.173	48.681	6264688	91875		0.000
2	25.731	51.319	6604251	84175	V	0.000
Total		100.000	12868938	176050		0.000

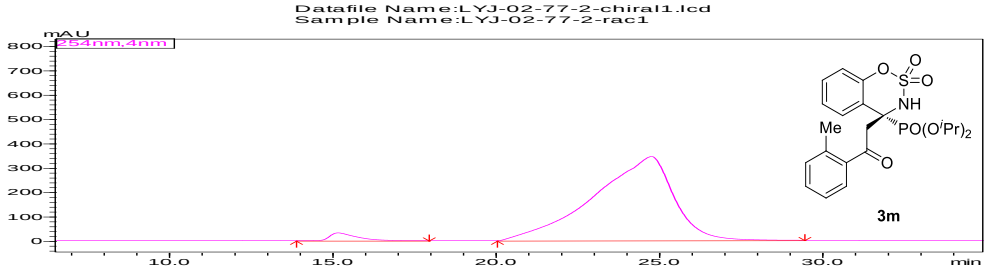
Datafile Name:LYJ-02-61-8-chiral2.lcd
Sample Name:LYJ-02-61-8-chiral2



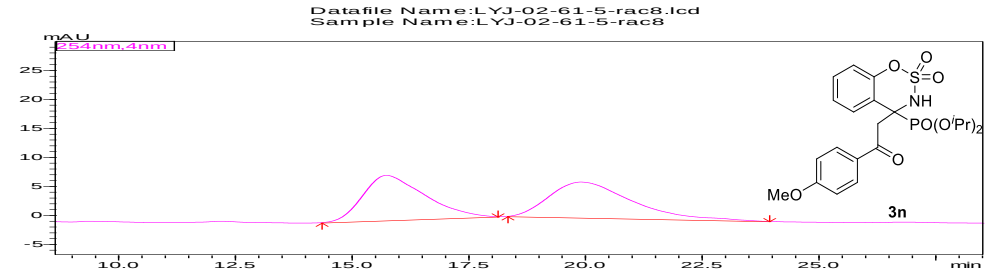
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	23.359	2.368	257893	3700		0.000
2	25.762	97.632	10633317	144054	V	0.000
Total		100.000	10891210	147753		0.000



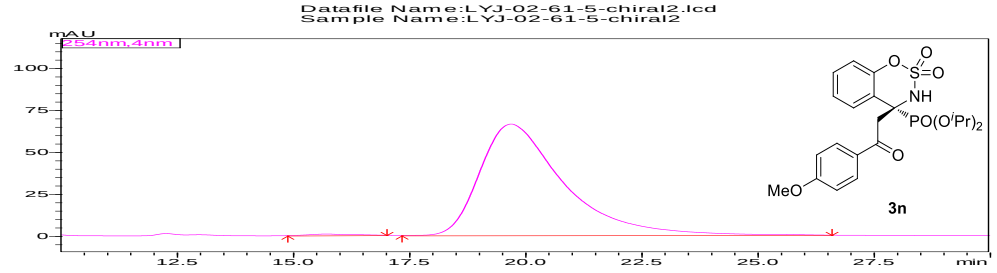
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	15.518	50.364	10342159	147745		0.000
2	24.876	49.636	10192562	86201		0.000
Total		100.000	20534721	233946		0.000



Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	15.188	2.987	1795918	31870		0.000
2	24.782	97.013	58327651	344471		0.000
Total		100.000	60123569	376341		0.000

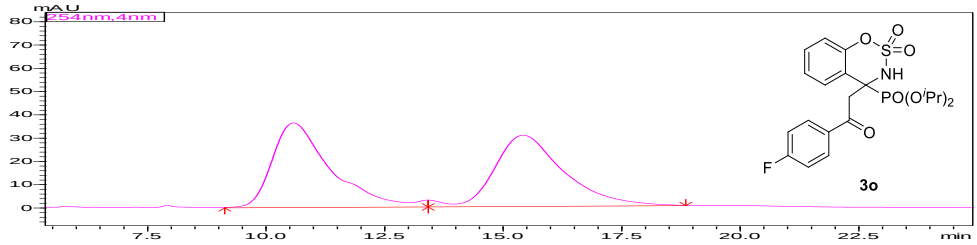


Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	15.754	48.666	713085	7778		0.000
2	19.922	51.334	752180	6159		0.000
Total		100.000	1465265	13937		0.000



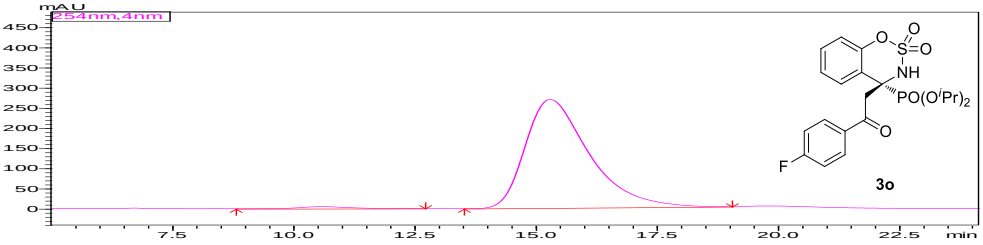
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	15.732	0.610	50973	862	M	0.000
2	19.707	99.390	8309666	66318	M	0.000
Total		100.000	8360639	67180		0.000

Datafile Name:LYJ-02-61-2-rac5.lcd
Sample Name:LYJ-02-61-2-rac5



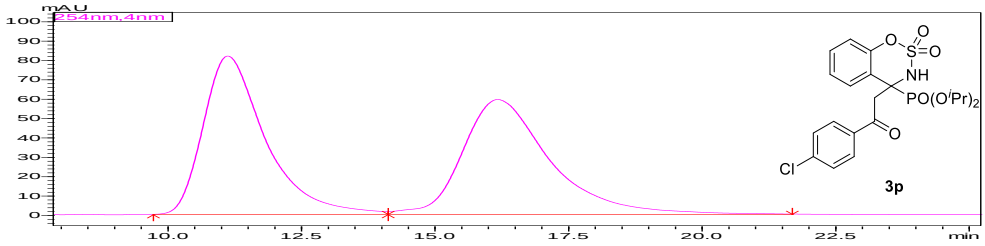
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	10.604	50.111	3087040	36171	M	0.000
2	15.439	49.889	3073351	30424	V M	0.000
Total		100.000	6160391	66595		0.000

Datafile Name:LYJ-02-61-2-chiral3.lcd
Sample Name:LYJ-02-61-2-chiral3



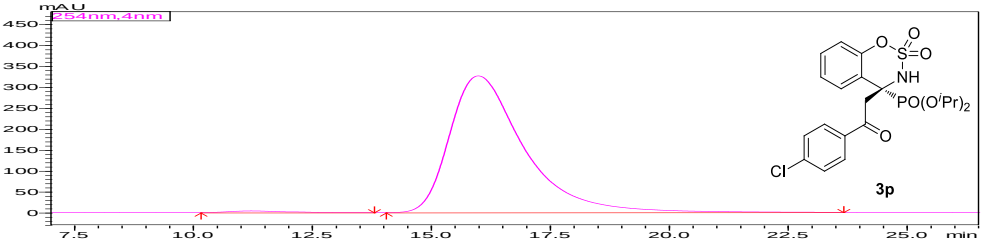
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	10.589	1.376	342878	4854	M	0.000
2	15.305	98.624	24578876	269291	M	0.000
Total		100.000	24921754	274146		0.000

Datafile Name:LYJ-02-61-3-rac3.lcd
Sample Name:LYJ-02-61-3-rac3

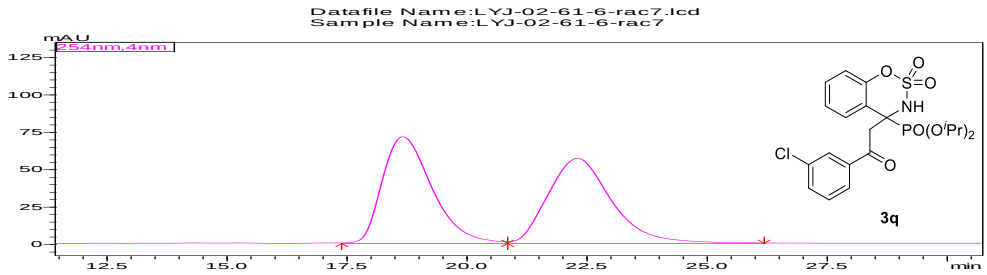


Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	11.137	49.690	6605067	81669		0.000
2	16.189	50.310	6687520	59200	V	0.000
Total		100.000	13292587	140869		0.000

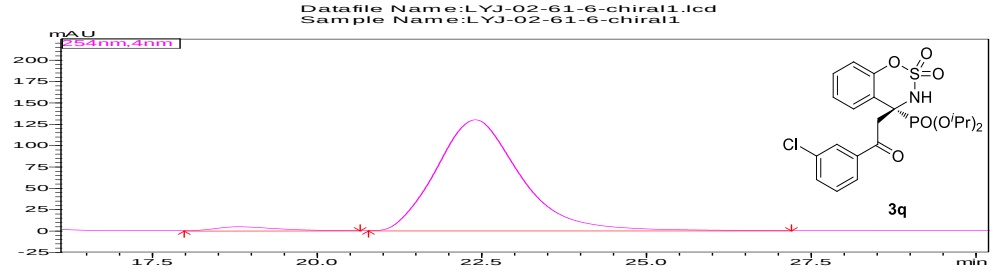
Datafile Name:LYJ-02-61-3-chiral3.lcd
Sample Name:LYJ-02-61-3-chiral



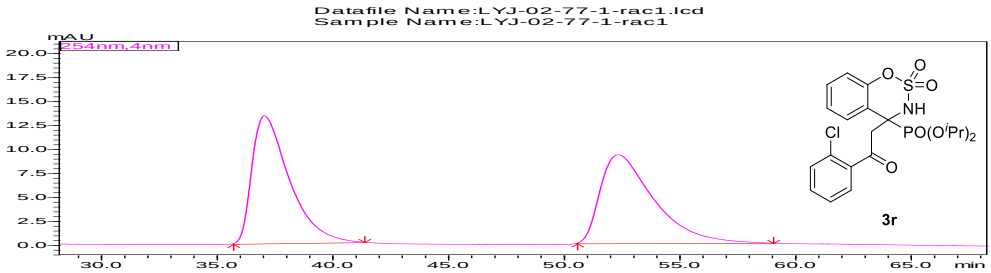
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	11.234	0.878	313800	3959		0.000
2	16.007	99.122	35406427	326259		0.000
Total		100.000	35720227	330219		0.000



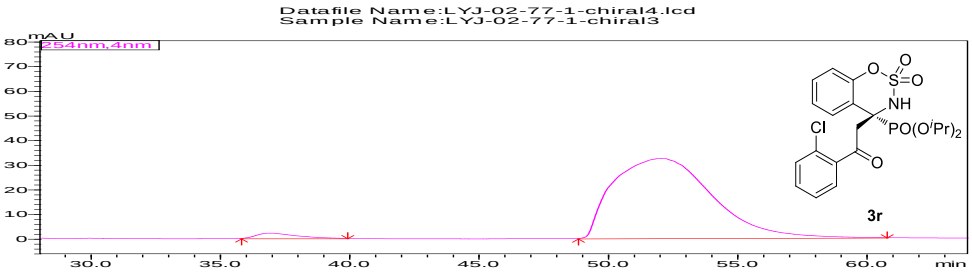
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	18.676	49.701	5074036	70941		0.000
2	22.322	50.299	5135178	56637	V	0.000
Total		100.000	10209213	127578		0.000



Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	18.821	2.348	274722	4481		0.000
2	22.419	97.652	11426940	129634		0.000
Total		100.000	11701662	134115		0.000

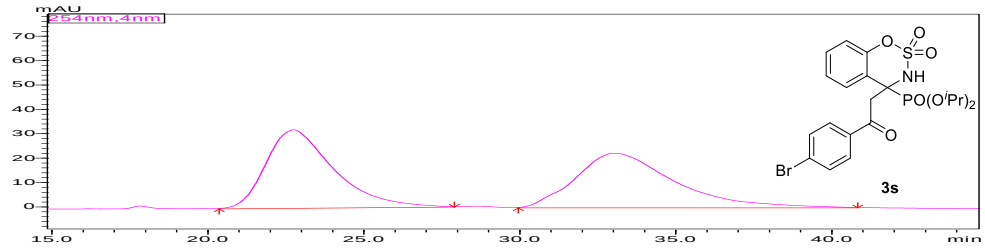


Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	37.075	50.190	1496490	13325		0.000
2	52.351	49.810	1485161	9224	M	0.000
Total		100.000	2981651	22549		0.000



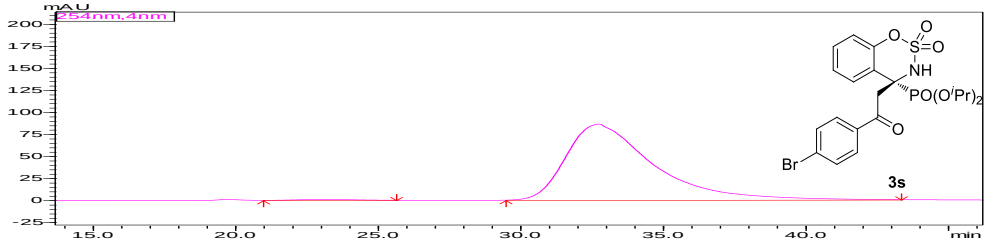
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	36.980	2.544	224278	2147		0.000
2	52.002	97.456	8591013	32385	M	0.000
Total		100.000	8815291	34531		0.000

Datafile Name:LYJ-02-61-4-rac3.lcd
Sample Name:LYJ-02-61-4-rac3



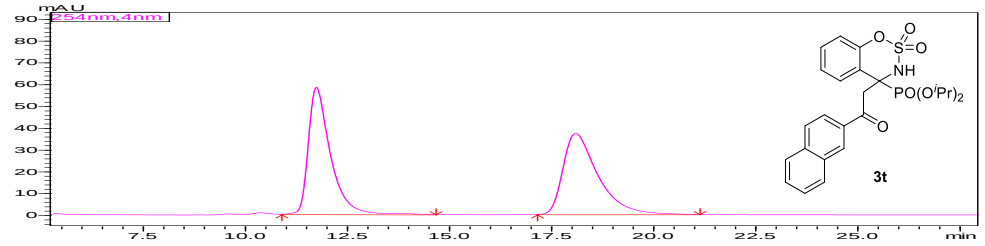
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	22.784	49.867	4804725	32035		0.000
2	33.064	50.133	4830330	22185		0.000
Total		100.000	9635055	54220		0.000

Datafile Name:LYJ-02-61-4-chiral3.lcd
Sample Name:LYJ-02-61-4-chiral3



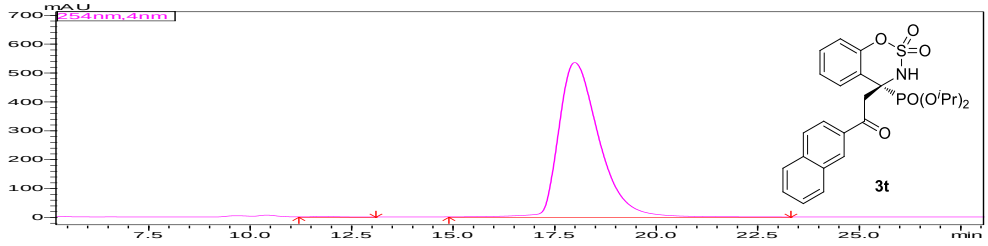
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	23.108	0.680	124466	937	M	0.680
2	32.758	99.320	18190121	86137	M	99.320
Total		100.000	18314587	87074		100.000

Datafile Name:LYJ-02-61-11-rac6.lcd
Sample Name:LYJ-02-61-11-rac6



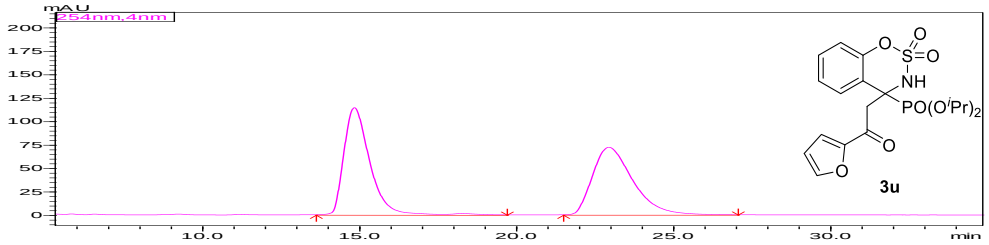
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	11.763	49.856	2187150	58213	S	0.000
2	18.110	50.144	2199818	37214		0.000
Total		100.000	4386968	95427		0.000

Datafile Name:LYJ-02-61-11-chiral2.lcd
Sample Name:LYJ-02-61-11-chiral2



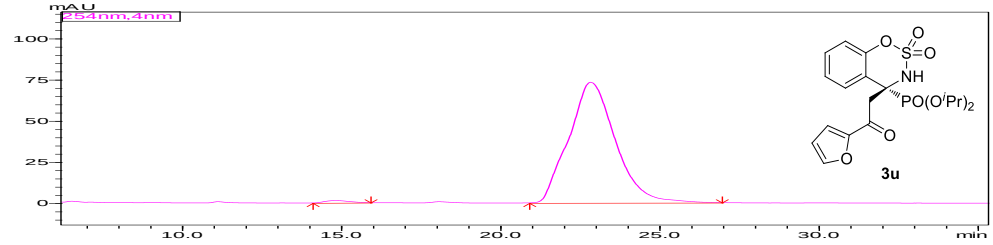
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	11.792	0.145	53048	1610	M	0.000
2	18.018	99.855	36577973	534344		0.000
Total		100.000	36631021	535954		0.000

Datafile Name:LYJ-02-61-13-rac2.lcd
Sample Name:LYJ-02-61-13-rac2



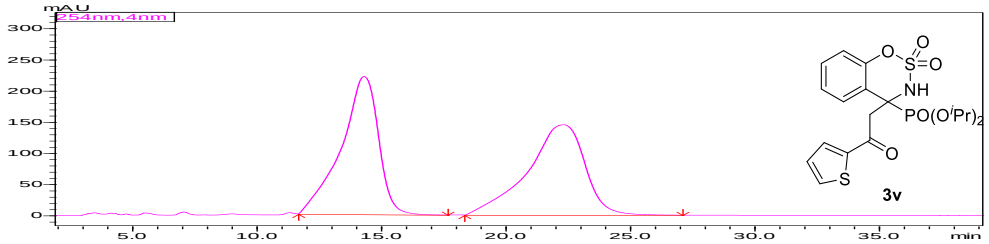
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	14.862	50.570	6541264	114204	S	0.000
2	22.967	49.430	6393911	72002		0.000
Total		100.000	12935174	186206		0.000

Datafile Name:LYJ-02-61-13-chiral1.lcd
Sample Name:LYJ-02-61-13-chiral1



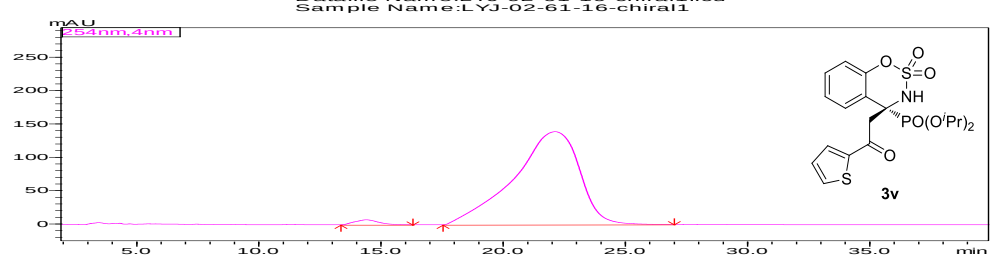
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	14.832	0.966	72633	1384		0.000
2	22.849	99.034	7444084	73203		0.000
Total		100.000	7516717	74587		0.000

Datafile Name:LYJ-02-61-16-rac2.lcd
Sample Name:LYJ-02-61-16-rac2



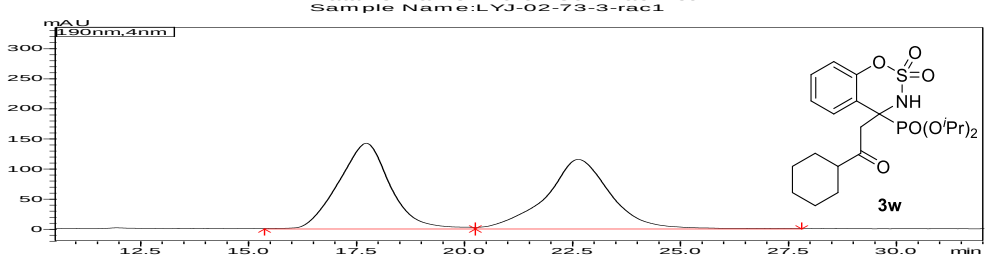
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	14.334	49.919	23041781	220905		0.000
2	22.359	50.081	23116857	144810		0.000
Total		100.000	46158638	365715		0.000

Datafile Name:LYJ-02-61-16-chiral1.lcd
Sample Name:LYJ-02-61-16-chiral1



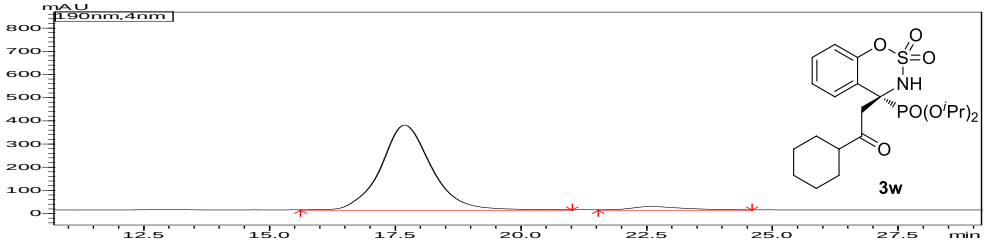
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	14.432	1.853	492158	7387		0.000
2	22.164	98.147	26062355	139453		0.000
Total		100.000	26554513	146841		0.000

Datafile Name:LYJ-02-80-4-rac1.lcd
Sample Name:LYJ-02-73-3-rac1



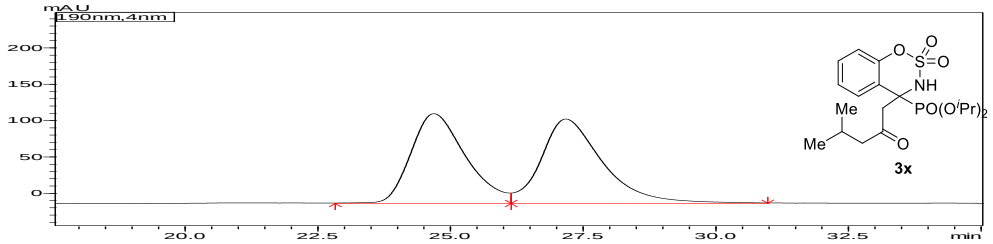
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	17.750	50.063	577231	7202	M	0.000
2	22.659	49.937	575783	5763	M	0.000
Total		100.000	1153014	12965		0.000

Datafile Name:LYJ-02-80-4-chiral2.lcd
Sample Name:LYJ-02-80-4-chiral2



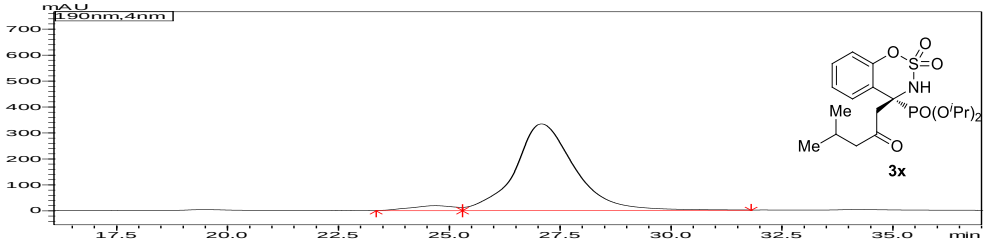
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	17.707	96.850	1308783	19989		0.000
2	22.589	3.150	42572	672	M	0.000
Total		100.000	1351356	20661		0.000

Datafile Name:LYJ-02-80-2-rac3 0.6ml.lcd
Sample Name:LYJ-02-80-2-rac3

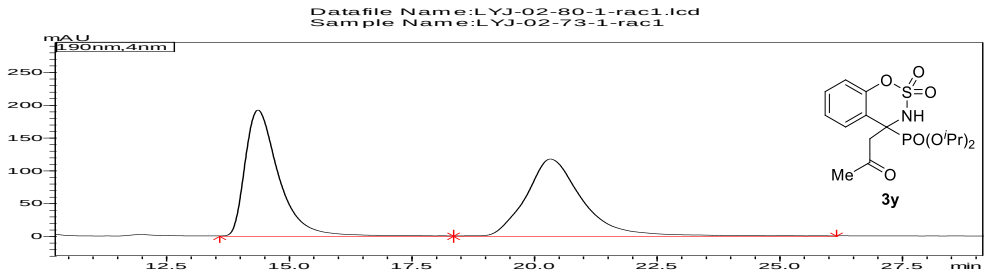


Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	24.704	49.745	421707	6257		0.000
2	27.193	50.255	426027	5757	V	0.000
Total		100.000	847734	12013		0.000

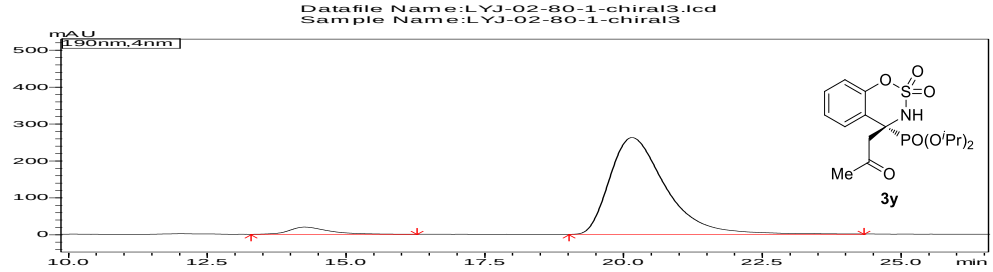
Datafile Name:LYJ-02-80-2-chiral3.lcd
Sample Name:LYJ-02-80-2-chiral1



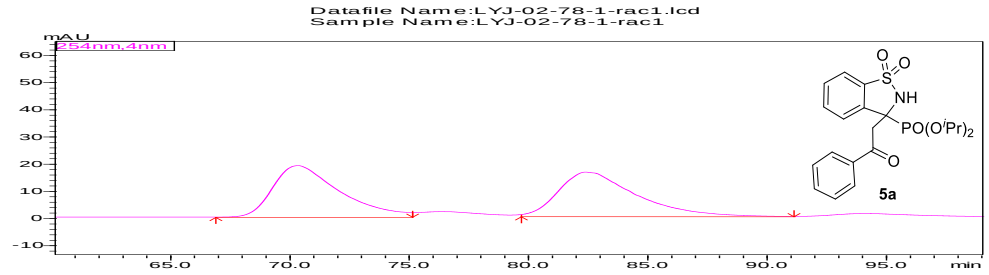
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	24.706	3.803	65906	951	M	0.000
2	27.104	96.197	1666921	18505	M	0.000
Total		100.000	1732827	19457		0.000



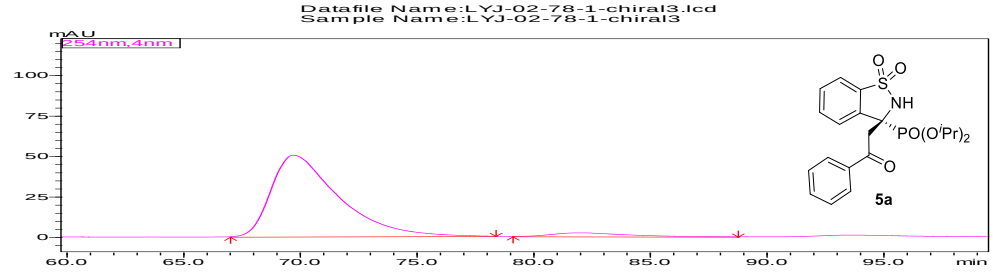
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	14.383	50.775	478267	10385		0.000
2	20.354	49.225	463660	6139		0.000
Total		100.000	941927	16524		0.000



Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	14.247	6.425	65806	1220		0.000
2	20.172	93.575	958411	14243		0.000
Total		100.000	1024217	15463		0.000

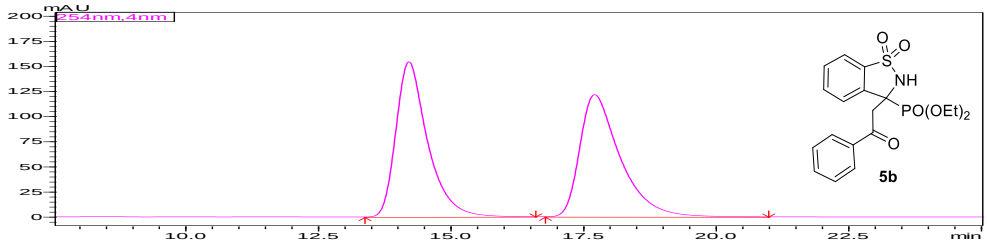


Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	70.373	49.968	3654100	18875	M	0.000
2	82.432	50.032	3658723	16293	M	0.000
Total		100.000	7312823	35168		0.000



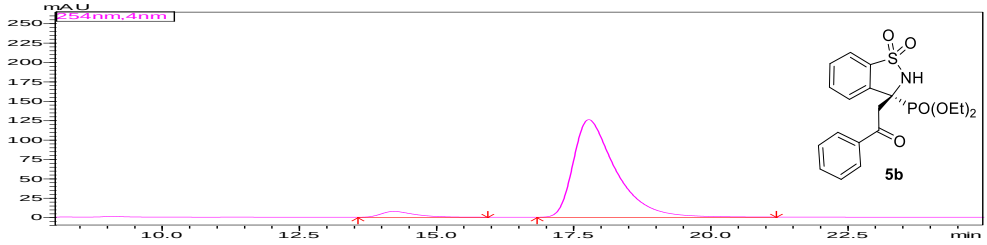
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	69.733	95.497	10072117	50306		0.000
2	82.048	4.503	474937	2252	M	0.000
Total		100.000	10547054	52559		0.000

Datafile Name:LYJ-02-78-2-rac1.lcd
Sample Name:LYJ-02-78-2-rac1



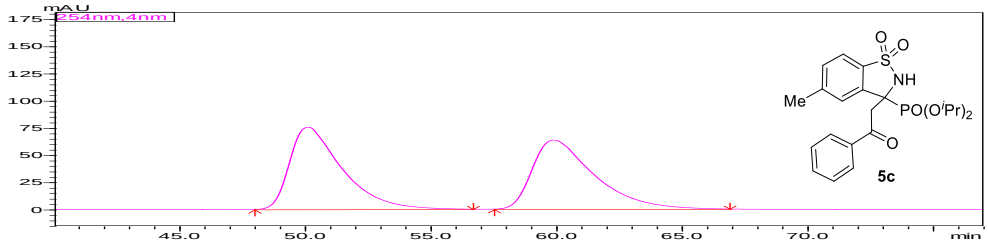
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	14.223	49.958	6414928	154391		0.000
2	17.726	50.042	6425836	121558		0.000
Total		100.000	12840763	275949		0.000

Datafile Name:LYJ-02-78-2-chiral2.lcd
Sample Name:LYJ-02-78-2-chiral2



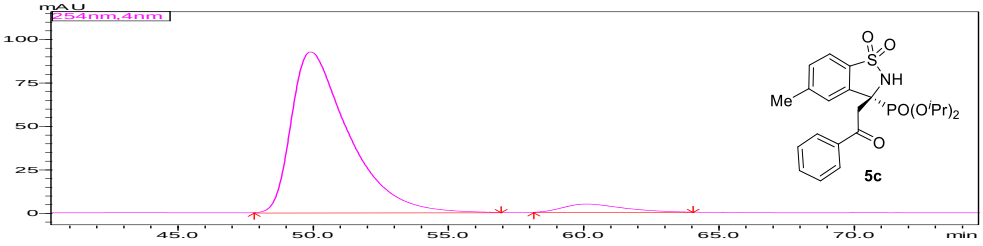
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	14.242	4.465	315502	7470		0.000
2	17.793	95.535	6750679	125668		0.000
Total		100.000	7066181	133138		0.000

Datafile Name:LYJ-02-78-3-rac1.lcd
Sample Name:LYJ-02-78-3-rac1

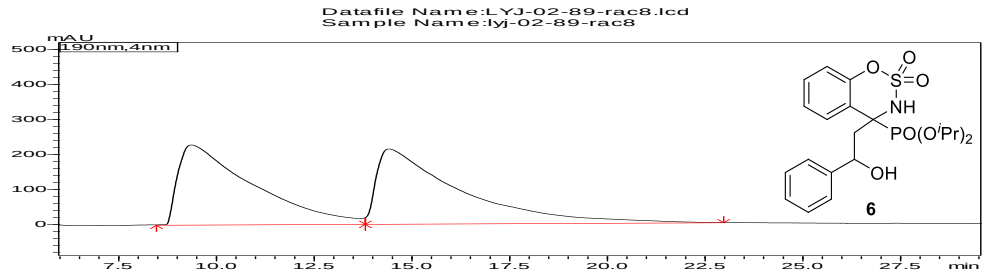


Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	50.147	50.234	10943937	75524		0.000
2	59.906	49.766	10841922	63438		0.000
Total		100.000	21785860	138962		0.000

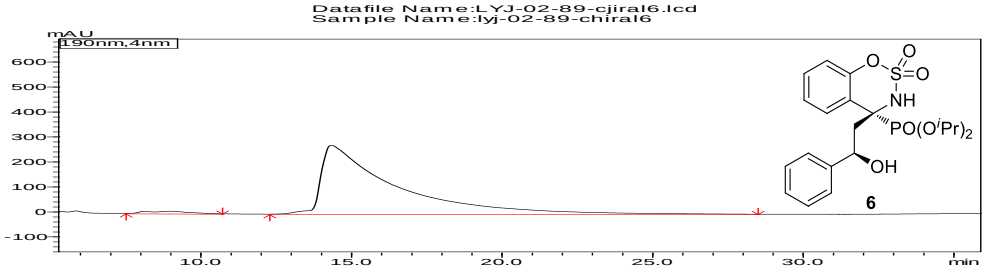
Datafile Name:LYJ-02-78-3-chiral1.lcd
Sample Name:LYJ-02-78-3-chiral1



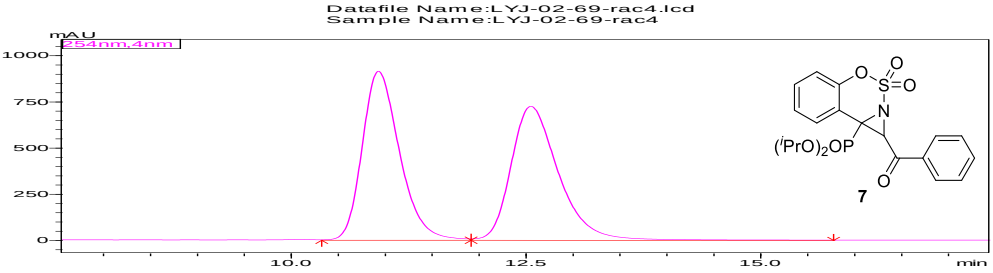
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	49.934	94.979	13532861	92379		0.000
2	60.174	5.021	715475	4705		0.000
Total		100.000	14248336	97084		0.000



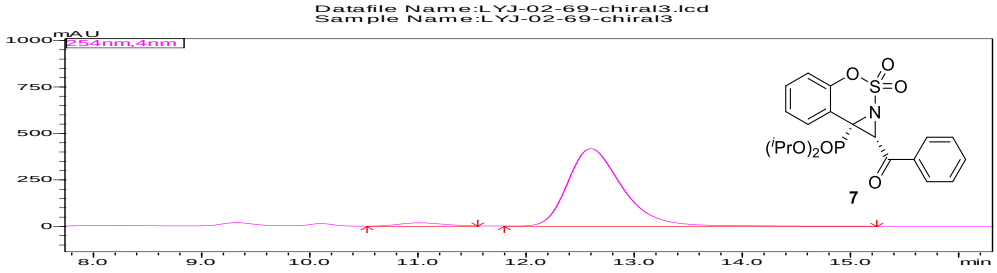
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	9.384	49.125	30207696	228111	M	49.125
2	14.438	50.875	31283839	214281	SV M	50.875
Total		100.000	61491535	442393		100.000



Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	8.996	1.883	887486	9484	M	1.883
2	14.359	98.117	46244635	275515	S	98.117
Total		100.000	47132121	284999		100.000



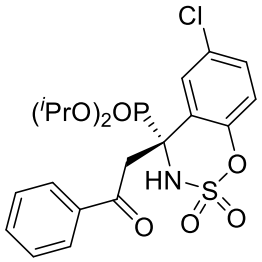
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	10.939	49.886	25124833	912871		0.000
2	12.562	50.114	25239169	723800	V	0.000
Total		100.000	50364001	1636671		0.000



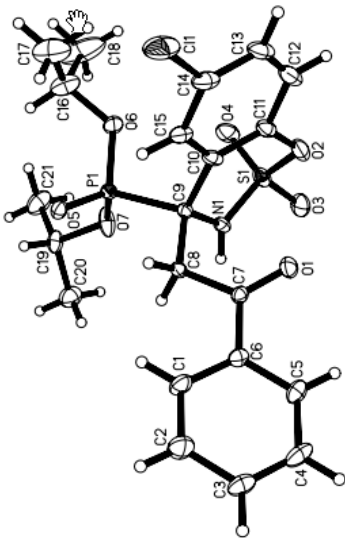
Peak#	Ret. Time	Area%	Area	Height	Mark	Conc.
1	11.024	3.162	474209	17195	M	0.000
2	12.606	96.838	14524785	416702		0.000
Total		100.000	14998994	433897		0.000

X-Ray crystallographic data

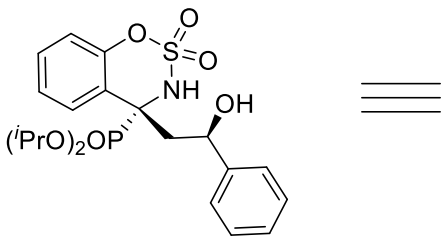
The X-ray crystallographic structures for **3i**, **6** and **7**. ORTEP representation with 50% probability thermal ellipsoids. Solvent is omitted for clarity. Crystal data have been deposited to CCDC, numbers 1836536, 1840570 and 1836549.



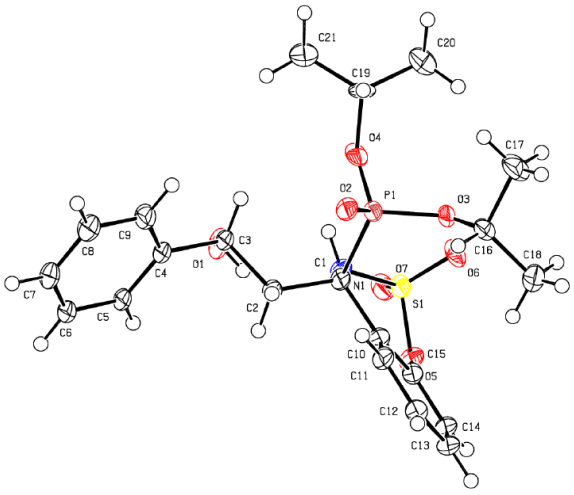
3i



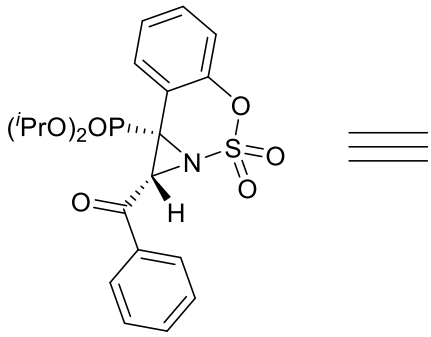
Empirical formula	$C_{21}H_{25}ClNO_7PS$
Identification code	*T*
Formula weight	501.90
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 20.177(2) Å alpha = 90 deg. b = 12.4566(14) Å beta = 90 deg. c = 9.3204(10) Å gamma = 90 deg.
Volume	2342.6 (4) $Å^3$
Z, Calculated density	4, 1.423 Mg/m^3
Absorption coefficient	0.363 mm^{-1}
F (000)	1048
Crystal size	0.55 x 0.2 x 0.2 mm
Theta range for data collection	2.60 to 27.36 deg.
Limiting indices	-23<=h<=23, -14<=k<=14, -10<=l<=11
Reflections collected / unique	64591 / 4126 [R(int) = 0.0826]
Completeness to theta = 25.000	99.9 %
Data / restraints / parameters	4126 / 0 / 289
Goodness-of-fit on F^2	1.141
Final R indices [I>2sigma(I)]	R_1 = 0.0563, wR_2 = 0.1579
R indices (all data)	R_1 = 0.0597, wR_2 = 0.1597
Absolute structure parameter	0.05(14)
Largest diff. peak and hole	0.570 and -0.387 e.$Å^{-3}$



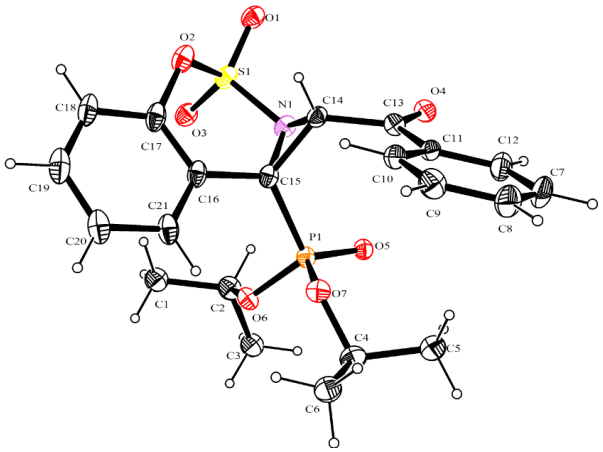
6



Empirical formula	$C_{21}H_{28}NO_7PS$
Identification code	*20180427-LYJ*
Formula weight	469.47
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 10.5690(4) Å alpha = 90 deg. b = 14.2467(2) Å beta = 90 deg. c = 15.3690(2) Å gamma = 90 deg.
Volume	2314.16(10) $Å^3$
Z, Calculated density	4, 1.347 Mg/m^3
Absorption coefficient	2.257 mm^{-1}
F (000)	992.0
Crystal size	0.15 x 0.1 x 0.05 mm
Theta range for data collection	8.462 to 133.136 deg.
Limiting indices	-6<=h<=12, -16<=k<=15, -18<=l<=18
Reflections collected	7194
Independent reflections	3828 [Rint = 0.1272, Rsigma = 0.1197]
Completeness to theta = 66.97	99.71%
Data / restraints / parameters	3828 / 361 / 285
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R_1 = 0.1047, wR_2 = 0.2551
R indices (all data)	R_1 = 0.1158, wR_2 = 0.2663
Absolute structure parameter	0.03(6)
Largest diff. peak and hole	0.73 and -0.81 e.$Å^{-3}$



7



Empirical formula	$C_{21}H_{24}NO_7PS$
Identification code	*t*
Formula weight	465.44
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system, space group	Orthorhombic, P 1 21 1
Unit cell dimensions	a = 9.6268(3) Å alpha = 90 deg. b = 10.3922(4) Å beta = 93.6320 deg. c = 19.123(4) Å gamma = 90 deg.
Volume	1151.37 (7) $Å^3$
Z, Calculated density	2, 1.343 Mg/m^3
Absorption coefficient	2.268 mm^{-1}
F (000)	488
Crystal size	0.03 x 0.04 x 0.05 mm
Theta range for data collection	4.25 to 74.42 deg.
Limiting indices	-11<=h<=12, -12<=k<=12, -14<=l<=14
Reflections collected / unique	15006 / 4249 [R(int) = 0.0705]
Completeness to theta = 74.416	99.6 %
Data / restraints / parameters	4552 / 801 / 374
Goodness-of-fit on F^2	1.103
Final R indices [I>2sigma(I)]	R_1 = 0.0705, wR_2 = 0.1916
R indices (all data)	R_1 = 0.0745, wR_2 = 0.1864
Absolute structure parameter	0.06(5)
Largest diff. peak and hole	0.450 and -0.691 e.$Å^{-3}$