Supplementary Material (ESI) for RSC Advances
This journal is (c) The Royal Society of Chemistry 2013

Supporting Information

Regioselective asymmetric stereoablative O-alkylation of *α*-nitrophosphonates *via o*-azaxylylene intermediates generated *in situ* from 3-bromooxindoles

Xiaohua Xie, Linhai Jing,* Dabin Qin, Wujun He, Song Wu, Lunqiang Jin and Gan Luo

Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, China West Normal University, Nan Chong 637002, PR China.

E-mail: jlhhxg@cwnu.edu.cn

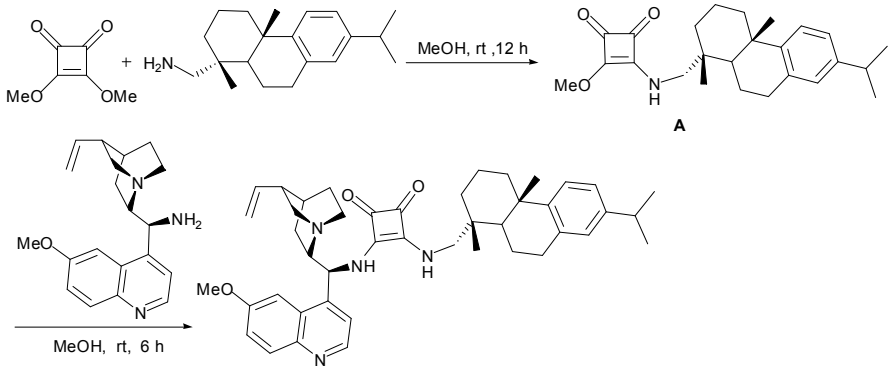
Contents

1. General experimental details

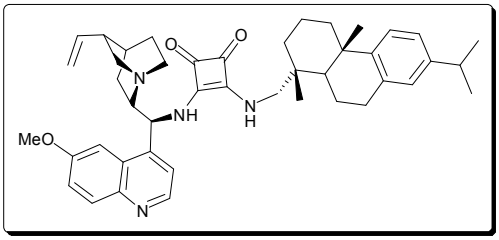
All solvents were purified by using standard methods prior to use. Nitrophosphonates **1a-1f** were prepared according to the method reported in the literature.[1] 3-Bromooxindoles **2a-2r** were prepared according to the literature procedure.[2] Catalysts **3a-3c** were prepared according to the reported procedure.[3] Catalysts **3d-3j** were prepared according to the method previously described.[4]

All reactions were carried out in reaction tubes with magnetic stirring and no special precautions were taken to exclude air from the reaction vessel. Column chromatography was performed on silica gel (200−300 mesh) eluting with ethyl acetate and petroleum ether. TLC was performed on pre-coated silica gel plates. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz and ^{31}P NMR spectra were recorded at 162 MHz (Bruker Avance II 400) with $CDCl_3$ as solvent, Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. HRMS was recorded on a Bruker micrOTOF-Q II mass spectrometer. Enantiomeric excess (ee) were determined by HPLC analysis on a Shimadzu LC-20A. Optical rotation data were examined in $CHCl_3$ solution at 25 °C.

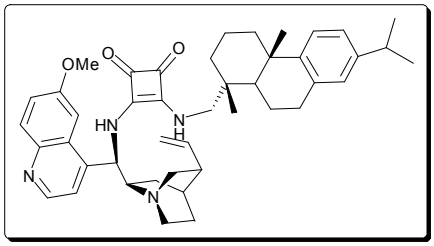
2. General procedure for the synthesis of new squaramide catalysts



To a solution of dimethyl squarate (213.2 mg, 1.5 mmol) in MeOH (5 mL) was added (+)-dehydroabietylamine (427.9 mg, 1.5 mmol) in MeOH (2 mL). The reaction mixture was stirred at room temperature for 12 h and then concentrated in vacuo to afford the intermediate **A** as a white solid without further purification. To a solution of **A** (118.6 mg, 0.3 mmol) in MeOH (4 mL) was added a solution of quinine amine (106.7 mg, 0.33 mmol) in MeOH (1 mL). After 6 h, the reaction mixture was filtered, and the residue was subjected to flash chromatograph (DCM/MeOH 20:1) on silica gel to afford squaramide catalyst (148.3 mg, 72 %) as a white solid. Other three squaramide catalysts were synthesized according to the similar procedure.

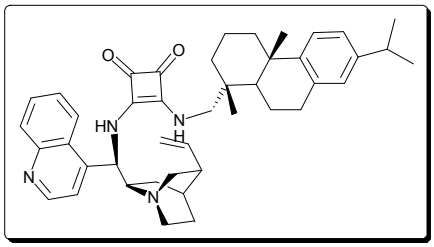


White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.75 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.79 (s, 2H), 7.54 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.27 (s, 1H), 7.09 (d, *J* = 7.3 Hz, 1H)，6.91 (d, *J* = 6.8 Hz, 1H), 6.81 (s, 1H), 5.90 (s, 2H), 4.94 (t, *J* = 13.2 Hz, 2H), 3.88 (s, 3H), 3.52 (s, 2H), 3.24 (s, 3H), 2.92 (s, 1H), 2.74 (s, 2H), 2.65 (s, 1H), 2.19 (t, *J* = 13.6 Hz, 2H), 1.75 (s, 1H), 1.64 (s, 1H), 1.51 (s, 3H), 1.44 (s, 3H), 1.29 (t, *J* = 13.1 Hz, 3H), 1.11 (t, *J* = 10.2 Hz, 1H), 0.87 (s, 1H), 0.79 (s, 3H), 0.71 (s, 1H), 0.56 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 182.90, 182.37, 168.71, 167.42, 158.31, 148.16, 147.19, 145.34, 144.76, 143.94, 142.56, 134,71, 131.88, 128.03, 126.86, 124.51, 124.03, 122.33, 119.99, 114.65, 102.08, 60.21, 59.30, 56.12, 54.26, 44.80, 38.31, 37.69, 37.44, 35.43, 33.30, 32,49, 30.11, 27.76, 26.68, 25.56, 24.35, 21.17, 20.24, 19.75, 18.51; **HRMS *m/z* (ESI):** Calcd for $C_{44}H_{54}N_4O_3$ $[M+Na]^+$: 709.4094; Found: 709.4085.

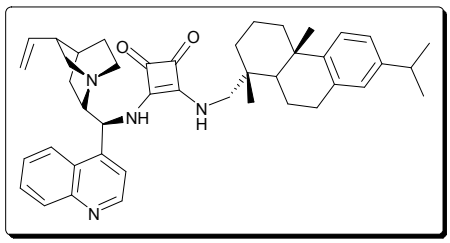


White solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72 (d, *J* = 3.6 Hz, 1H), 7.92 (d, *J* = 9.1 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.72 (s, 1H), 7.55 (s, 1H), 7.37 (t, J = 11.4 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.66 (s, 1H), 6.00 (s, 1H), 5.84-5.79 (m, 1H), 5.18 (d, *J* = 17.3 Hz, 1H), 5.03 (d, *J* = 10.4 Hz, 1H), 3.89 (s, 3H), 3.54 (s, 2H), 3.23 (d, *J* = 8.8 Hz, 3H), 2.90 (t, *J* = 12.3 Hz, 2H), 2.78 (d, 10.9 Hz, 1H), 2.69 (t, *J* = 7.1 Hz, 2H), 2.19 (d, *J* = 13.0 Hz, 2H), 1.73 (s, 1H), 1.65 (s,

1H), 1.55 (s, 5H), 1.24 (d, *J* = 12.5 Hz, 4H), 1.10 (d, *J* = 7.0 Hz, 9H), 0.87 (s, 1H), 0.82 (s, 3H), 0.74 (s, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 182.88, 182.24, 168.40, 167.43, 158.31, 148.16, 147.19, 145.41, 144.71, 143.81, 141.14, 134.58, 131.86, 128.12, 126.78, 124.60, 124.00, 122.54, 119.76, 114.94, 101.89, 59.05, 56.10, 54.27, 49.48, 46.05, 44.94, 38.32, 37.60, 37.43, 35.50, 33.30, 30.18, 27.70, 26.52, 25.97, 25.54, 24.36, 24.33, 18.56, 18.47, 18.41; **HRMS *m/z* (ESI):** Calcd for $C_{44}H_{54}N_4O_3$ $[M+Na]^+$: 709.4094; Found: 709.4077.

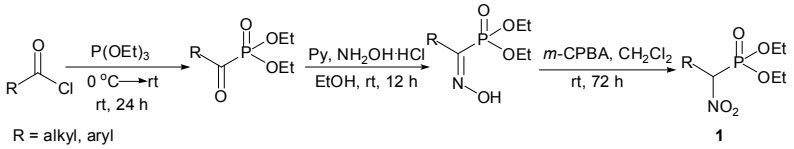


White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.88 (d, *J* = 3.9 Hz, 1H), 8.39 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.81-7.73 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.58 (s, 1H), 7.31 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.70 (s, 1H), 5.85-5.76 (m,1H), 5.15 (d, *J* = 17.2 Hz, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 3.51 (s, 2H), 3.29 (s, 1H), 2.71 (t, *J* = 7.1 Hz, 3H), 2.21 (s, 2H), 1.73 (s, 1H), 1.65 (s, 1H), 1.53 (s, 5H), 1.23 (t, *J* = 12.0 Hz, 4H), 1.09 (t, *J* = 5.4 Hz, 9H), 0.88 (s, 1H), 0.82 (s, 3H), 0.75 (s, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 182.76, 182.49, 168.50, 167.46, 150.79, 148.56, 147.19, 145.73, 145.39, 141.05, 134.61, 130.37, 129.87, 127.48, 126.89, 126.83, 124.52, 124.00, 123.73, 119.68, 115.02, 60.21, 59.65, 54.32, 53.15, 49.42, 46.39, 45.02, 38.33, 37.63, 37.42, 35.51, 33.30, 30.09, 29.43, 27.74, 26.50, 25.68, 25.54, 24.34, 18.48; **HRMS *m/z* (ESI):** Calcd for $C_{43}H_{52}N_4O_2$ $[M+Na]^+$: 679.3988; Found: 679.3985.



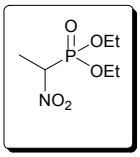
White solid; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.92 (d, *J* = 3.9 Hz, 1H), 8.47 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 7.0 Hz, 1H),7.58 (s, 1H), 7.30 (s, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 5.91-5.83 (m, 2H), 4.93 (t, *J* = 15.1 Hz, 2H), 3.52 (d, *J* = 6.3 Hz, 2H), 3.26 (d, *J* = 6.5 Hz, 3H), 2.95 (t, *J* = 11.4 Hz, 1H), 2.75 (s, 2H), 2.66 (s, 1H), 2.24 (d, *J* = 11.7 Hz, 1H), 2.16 (s, 1H), 1.76 (s, 1H), 1.68 (d, *J* = 11.9 Hz, 1H), 1.51-1.57 (m, 5H), 1.31 (t, *J* = 11.1 Hz, 4H), 1.13 (t, *J* = 9.0 Hz, 9 H), 0.90 (s, 1 H), 0.81 (s, 3H), 0.61 (s, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 182.74, 182.56, 168.75, 167.47, 150.86, 148.58, 147.24, 145.89, 145.39, 142.58, 134.75, 130.37, 129.88, 127.55, 126.89, 124.56, 124.07, 123.98, 119.94, 114.70, 59.86, 55.97, 54.26, 44.85, 38.34, 37.74, 37.48, 35.47, 33.32, 30.14, 27.69, 26.41, 25.62, 24.39, 20.30, 19.79, 18.54, 18.47; **HRMS *m/z* (ESI):** Calcd for $C_{43}H_{52}N_4O_2$ $[M+Na]^+$: 679.3988; Found: 679.3990.

3. General procedure for the synthesis of diethyl *α*-nitrophosphonate 1[1]

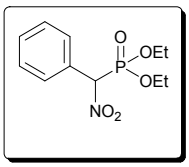


Triethyl phosphite (20 mmol) was slowly added to acyl chloride (25 mmol) at 0 °C. After being stirred at rt for 24 h, the reaction mixture was concentrated under vacuo and crude product was used for the next step without purification. To the solution of crude diethyl *α*-keto phosphonate (19.5 mmol) in ethanol (6 mL), hydroxylamine hydrochloride (25 mmol) was added followed by pyridine (35 mmol). After being stirred at rt for 12 h, the mixture was concentrated under vacuo, and the resulting residue was dissolved in CH_2Cl_2 (100 mL) and washed with 3N HCl (2 × 20 mL), water (1 × 20 mL) and brine (1 × 20 mL). Organic phase was dried over anhydrous Na_2SO_4, concentrated in vacuo to afford light yellow oil, which was used for the next step without purification.

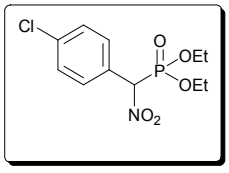
To the solution of crude 1-hydroxyiminophosphonate (19 mmol) in CH_2Cl_2 (40 mL), *m*-CPBA (30 mol) was added. The resulting reaction mixture was stirred at rt for 72 h, and the organic layer was washed with the mixture of sat. aqueous $NaHCO_3$ and 10% aqueous $Na_2S_2O_3$ (2 × 50 mL), brine (1 × 100 mL) and dried over anhydrous Na_2SO_4. After the solvent being removed under reduced pressure, the residue was purified by column chromatography over silica gel (200-300 mesh) with PE/EtOAc (5:1) as eluting solvent to afford the corresponding product **1** as yellow oil.



Diethyl (1-nitroethyl)phosphonate (1a)[1]: Yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.03-4.94 (m, 1H), 4.26-4.18 (m, 3H), 4.13-4.06 (m, 1H), 1.82-1.76 (m, 3H), 1.38-1.32 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 79.43 (d, *J* = 143.6 Hz), 64.35 (d, *J* = 6.8 Hz), 64.19 (d, *J* = 6.5 Hz), 16.26 (t, *J* = 5.3 Hz), 16.10 (d, *J* = 6.7 Hz), 14.43 (d, J = 3.8 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 13.49; **HRMS *m/z* (ESI):** Calcd for $C_6H_{14}NO_5P$ $[M+Na]^+$: 234.0508, Found: 234.0512.

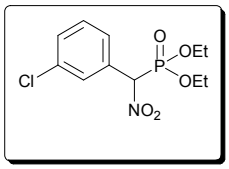


Diethyl [nitro(phenyl)methyl]phosphonate (1b)[5]: Yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 (t, *J* = 3.7 Hz, 2H), 7.43 (d, *J* = 6.8 Hz, 3H), 5.93 (d, *J* = 16.8 Hz, 1H), 4.23-4.07 (m, 3H), 4.02-3.96 (m, 1H), 1.32 (t, *J* = 6.8 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, CDCl3):** δ 130.35 (d, *J* = 2.0 Hz), 129.67, 129.60, 128.96 (d, *J* = 6.5Hz), 88.07 (d, *J* = 148.0 Hz), 64.64 (d, *J* = 8.2 Hz), 64.52, 16.23 (d, *J* = 5.8 Hz), 16.12 (d, *J* = 5.8 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 10.26; **HRMS *m/z* (ESI):** Calcd for $C_{11}H_{16}NO_5P$ $[M+Na]^+$: 296.0664, Found: 296.0666.

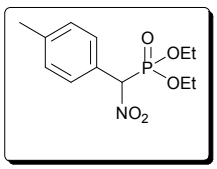


Diethyl [(4-chlorophenyl)(nitro)methyl]phosphonate (1c): Yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.61 (t, *J* = 4.1 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 5.90 (d, *J* = 17.0 Hz, 1H), 4.24-4.10 (m, 3H), 4.08-4.00 (m, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz,

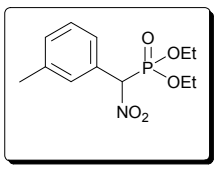
3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.69, 131.10 (d, *J* = 6.5 Hz), 129.21, 126.74 (d, *J* = 4.5 Hz), 87.23 (d, *J* = 147.7 Hz), 64.85 (d, *J* = 7.0 Hz), 64.65 (d, *J* = 6.7 Hz), 16.23 (d, *J* = 6.3 Hz), 16.09 (d, *J* = 8.0 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 9.91; **HRMS *m/z* (ESI):** Calcd for $C_{11}H_{15}ClNO_5P$ $[M+Na]^+$: 330.0274, Found: 330.0278.



Diethyl [(3-chlorophenyl)(nitro)methyl]phosphonate (1d): Yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 1.4 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 5.89 (d, *J* = 16.9 Hz, 1H), 4.06-4.24 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 134.91, 130.57 (d, *J* = 2.1 Hz), 130.18, 129.95 (d, *J* = 4.8 Hz), 129.72 (d, *J* = 6.5 Hz), 127.85 (d, *J* = 6.4 Hz), 88.40 (d, *J* = 147.1 Hz), 64.93 (d, *J* = 7.1 Hz), 64.71 (d, *J* = 6.7 Hz), 16.25 (d, *J* = 5.7 Hz), 16.18 (d, *J* = 5.9 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 9.63; **HRMS *m/z* (ESI):** Calcd for $C_{11}H_{15}ClNO_5P$ $[M+Na]^+$: 330.0274, Found: 330.0259.

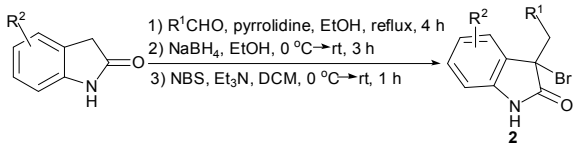


Diethyl [(4-methylphenyl)(nitro)methyl]phosphonate (1e): Yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51 (d, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 5.88 (d, *J* = 16.7 Hz, 1H), 4.21-4.07 (m, 3H), 3.93-4.00 (m, 1H), 2.34 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 140.58, 129.62, 129.61 (d, *J* = 7.5 Hz), 129.53, 125.28 (d, *J* = 4.7 Hz), 88.84 (d, *J* = 148.7 Hz), 64.56 (d, *J* = 5.0 Hz), 64.50 (d, *J* = 4.5 Hz), 21.20, 16.21 (d, *J* = 5.9 Hz), 16.12 (d, *J* = 5.7 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 10.51; **HRMS *m/z* (ESI):** Calcd for $C_{12}H_{18}NO_5P$ $[M+Na]^+$: 310.0821, Found: 310.0820.

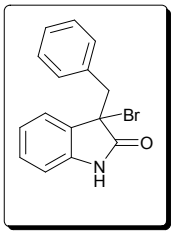


Diethyl [(3-methylphenyl)(nitro)methyl]phosphonate (1f): Yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.44 (d, *J* = 6.1 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 1H), 5.90 (d, *J* = 16.6 Hz, 1H), 4.19-4.09 (m, 3H), 4.04-3.98 (m, 1H), 2.38 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.84, 131.12 (d, *J* = 2.0 Hz), 130.13 (d, *J* = 6.5 Hz), 128.82, 128.08 (d, *J* = 4.5 Hz), 126.65 (d, *J* = 6.3 Hz), 88.11 (d, *J* = 148.3 Hz), 64.66 (d, *J* = 7.1 Hz), 64.53 (d, *J* = 6.7 Hz), 21.32, 16.23 (d, *J* = 5.8 Hz), 16.13 (d, *J* = 5.7 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 10.40; **HRMS *m/z* (ESI):** Calcd for $C_{12}H_{18}NO_5P$ $[M+Na]^+$: 310.0821, Found: 310.0821.

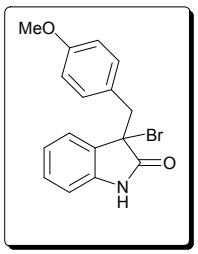
4. General procedure for the synthesis of 3-bromooxindoles 2[2]



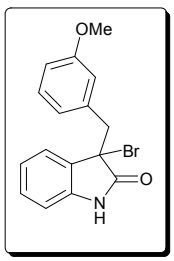
A mixture of indolin-2-one (5 mmol), aldehyde (5 mmol) and pyrrolidine (0.05 mL) in ethanol (25 mL) was heated to reflux for 4 h. After the mixture was cooled to 0 °C, sodium hydroborate (15 mmol) was added in batches. The resulting mixture was stirred at rt for 3 h, quenched by water and extracted by dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was dissolved in dichloromethane (20 mL) and triethylamine (0.1 mL) was added. The resulting mixture was cooled to 0 °C and then *N*-bromosuccinimide (5.1 mmol) was added over 30 minutes by portion. The reaction was then warmed to room temperature and stirred for 1 h. After being concentrated in vacuo, the residue was subjected to flash chromatograph (PE/EtOAc 13:1) on silica gel to afford 3-bromooxindole **2** as a light yellow solid.



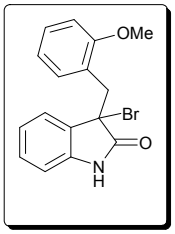
3-Benzyl-3-bromo-2,3-dihydro-1H-indol-2-one (2a)[2a]: Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.29 (s, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.15-7.07 (m, 4H), 7.01 (d, *J* = 6.8 Hz, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 3.76-3.67 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.22, 139.67, 134.13, 130.43, 130.13, 129.59, 128.13, 127.33, 125.52, 123.07 , 110.67, 56.56, 45.06; **HRMS *m/z* (ESI):** Calcd for $C_{15}H_{12}BrNO$ $[M+Na]^+$: 324.0000; Found: 324.0006.



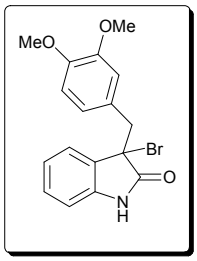
3-Bromo-3-[(4-methoxyphenyl)methyl]-2,3-dihydro-1H-indol-2-one (2b): Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 (s, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 2H), 3.70-3.64 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.33, 158.68, 139.57, 131.52, 130.08, 129.73, 126.17, 125.46, 123.05, 113.50, 110.71, 56.72, 55.05, 44.21; **HRMS *m/z* (ESI):** Calcd for $C_{16}H_{14}BrNO_2$ $[M+Na]^+$: 354.0106; Found: 354.0099.



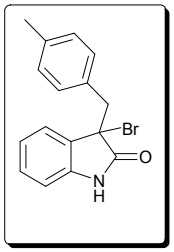
3-Bromo-3-[(3-methoxyphenyl)methyl]-2,3-dihydro-1H-indol-2-one (2c): Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.22 (s, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.68-6.66 (m, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 6.52 (s, 1H), 3.75-3.65 (m, 2H), 3.59 (d, *J* = 5.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.04, 159.14, 139.67, 135.55, 130.13, 129.66, 129.08, 125.48, 123.05, 122.80, 115.44, 113.42, 110.64, 56.38, 55.00, 45.09; **HRMS *m/z* (ESI):** Calcd for $C_{16}H_{14}BrNO_2$ $[M+Na]^+$: 354.0106; Found: 354.0099.



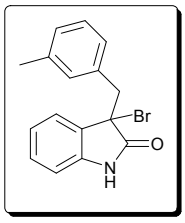
3-Bromo-3-[(2-methoxyphenyl)methyl]-2,3-dihydro-1H-indol-2-one (2d): Llight yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 (s, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.20-7.09 (m, 3H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.77-6.70 (m, 2H), 6.62 (d, *J* = 8.2 Hz, 1H), 4.01 (d, *J* = 13.6 Hz, 1H), 3.65 (d, *J* = 13.6 Hz, 1H), 3.57 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.60, 157.14, 139.42, 131.48, 129.81, 129.75, 128.75, 126.29, 123.19, 122.29, 120.26, 110.12, 110.05, 57.18, 54.63, 37.66; **HRMS *m/z* (ESI):** Calcd for $C_{16}H_{14}BrNO_2$ $[M+Na]^+$: 354.0106; Found: 354.0094.



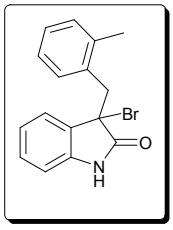
3-Bromo-3-[(3,4-dimethoxyphenyl)methyl]-2,3-dihydro-1H-indol-2-one (2e): Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (s, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.59 (t, *J* = 9.8 Hz, 2H), 6.41 (s, 1H), 3.77 (s, 3H), 3.71-3.65 (m, 2H), 3.60 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.61, 148.16, 148.09, 139.72, 130.09, 129.87, 126.50, 125.45, 122.96, 122.88, 113.28, 110.66, 110.52, 56.33, 55.65, 55.57, 44.84; **HRMS *m/z* (ESI):** Calcd for $C_{17}H_{16}BrNO_3$ $[M+Na]^+$:384.0212; Found: 384.0202.



3-Bromo-3-[(4-methylphenyl)methyl]-2,3-dihydro-1H-indol-2-one (2f)[2a]**:** Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (s, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 8.9 Hz, 4H), 6.74 (d, *J* = 7.8 Hz, 1H), 3.72-3.63 (m, 2H), 2.21 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.12, 139.65, 136.91, 131.05, 130.31, 130.04, 129.73, 128.84, 125.52, 123.02, 110.61, 56.65, 44.64, 21.04; **HRMS *m/z* (ESI):** Calcd for $C_{16}H_{14}BrNO$ $[M+Na]^+$: 338.0157; Found: 338.0160.

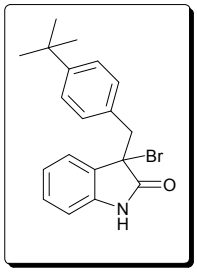


3-Bromo-3-[(3-methylphenyl)methyl]-2,3-dihydro-1H-indol-2-one (2g)[2a]**:** Light yellow solid **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.02-6.90 (m, 2H), 6.82 (s, 1H), 6.78 (d, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 3.72-3.63 (m, 2H), 2.16 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.97, 139.59, 137.69, 134.03, 131.24, 130.05, 129.69, 128.03, 127.93, 127.42, 125.58, 122.99, 110.52, 56.54, 44.98, 21.21; **HRMS *m/z* (ESI):** Calcd for $C_{16}H_{14}BrNO$ $[M+Na]^+$: 338.0157; Found: 338.0169.

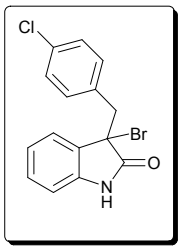


3-Bromo-3-[(2-methylphenyl)methyl]-2,3-dihydro-1H-indol-2-one (2h)[2a]**:** Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (s, 1H), 7.24-7.19 (m, 2H), 7.11-6.98 (m, 5H), 6.80 (d, *J* = 7.7 Hz, 1H), 3.76-3.68 (m, 2H), 2.18 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.24, 139.45,

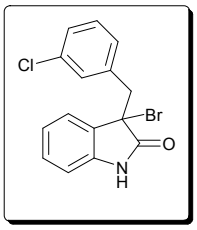
137.36, 132.85, 130.55, 130.51, 130.12, 129.97, 127.46, 125.95, 125.58, 122.99, 110.45, 57.16, 40.94, 20.10; **HRMS** *m/z* **(ESI):** Calcd for $C_{16}H_{14}BrNO$ $[M+Na]^+$: 338.0157; Found: 338.0163.



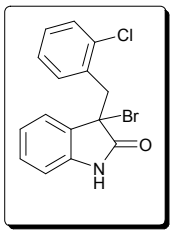
3-Bromo-3-[(4-tert-butylphenyl)methyl]-2,3-dihydro-1H-indol-2-one (2i): Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (s, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 15.3 Hz, 1H), 7.14-7.07 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.78-6.75 (m, 1H), 3.68 (s, 2H), 1.21 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.66, 150.15, 139.83, 131.10, 130.15, 130.10, 129.81, 125.50, 125.08, 123.04, 110.90, 56.94, 44.41, 34.40, 31.26; **HRMS** *m/z* **(ESI):** Calcd for $C_{19}H_{20}BrNO$ $[M+Na]^+$: 380.0626; Found: 380.0639.



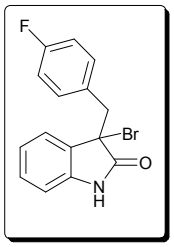
3-Bromo-3-[(4-chlorophenyl)methyl]-2,3-dihydro-1H-indol-2-one (2j)[2a]**:** Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (s, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.12-7.06 (m, 3H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.72 (t, *J* = 7.6 Hz, 1H), 3.71 (d, *J* = 13.4 Hz, 1H), 3.65 (d, *J* = 13.4 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.42, 139.47, 133.38, 132.60, 131.76, 130.29, 129.28, 128.33, 125.43, 123.21, 110.61, 55.85, 44.38; **HRMS** *m/z* **(ESI):** Calcd for $C_{15}H_{11}BrClNO$ $[M+Na]^+$: 357.9611; Found:357.9598.



3-Bromo-3-[(3-chlorophenyl)methyl]-2,3-dihydro-1H-indol-2-one (2k)[2a]**:** Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.22 (s, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.05-6.89 (m, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 3.70 (d, *J* = 13.5 Hz, 1H), 3.64 (d, *J* = 13.5 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.61, 139.49, 136.08, 133.86, 130.48, 130.35, 129.36, 129.19, 128.60, 127.61, 125.45, 123.25, 110.70, 55.84, 44.57; **HRMS** *m/z* **(ESI):** Calcd for $C_{15}H_{11}BrClNO$ $[M+Na]^+$: 357.9611; Found: 357.9597.

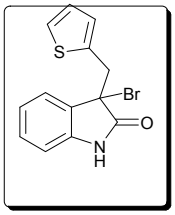


3-Bromo-3-[(2-chlorophenyl)methyl]-2,3-dihydro-1H-indol-2-one (2l)[2a]**:** Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (s, 1H), 7.37-7.33 (m, 2H), 7.23-7.17 (m, 2H), 7.13-7.08 (m, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 4.05 (d, *J* = 14.2 Hz, 1H), 3.84 (d, *J* = 14.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.09, 139.17, 134.77, 132.67, 131.51, 130.19, 129.65, 129.16, 128.84, 126.72, 126.31, 123.03, 110.26, 56.45, 40.57; **HRMS** *m/z* **(ESI):** Calcd for $C_{15}H_{11}BrClNO$ $[M+Na]^+$: 357.9611; Found: 357.9607.

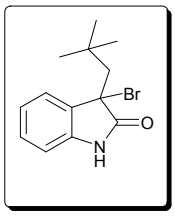


3-Bromo-3-[(4-fluorophenyl)methyl]-2,3-dihydro-1H-indol-2-one (2m): Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.98-6.94 (m, 2H), 6.80-6.72 (m, 3H), 3.74-3.63 (m, 2H); **^{13}C NMR**

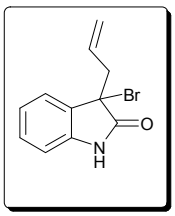
(100 MHz, $CDCl_3$) δ 175.57, 163.23 (d, *J* = 244.9 Hz), 139.49, 132.07 (d, *J* = 8.1 Hz), 130.24, 129.89 (d, *J* = 3.3 Hz), 129.37, 125.44, 123.20, 115.15 (d, *J* = 21.2 Hz), 110.54, 56.07, 44.26; **HRMS** *m/z* **(ESI):** Calcd for $C_{15}H_{11}BrFNO$ [M+Na]+: 341.9906; Found: 341.9904.



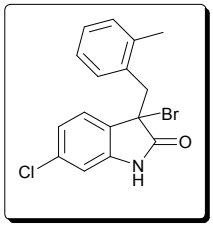
3-Bromo-3-(thiophen-2-ylmethyl)-2,3-dihydro-1H-indol-2-one (2n)[2a]**:** Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.41 (s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 5.0 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 3H), 6.76 (t, *J* = 4.3 Hz, 1H), 6.72 (d, *J* = 3.1 Hz, 1H), 4.00 (d, *J* = 14.5 Hz, 1H), 3.89 (d, *J* = 14.5 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.17, 140.13, 135.64, 130.45, 129.48, 128.16, 126.60, 125.47, 125.24, 123.30, 110.89, 55.44, 39.26; **HRMS** *m/z* **(ESI):** Calcd for $C_{13}H_{10}BrNOS$ $[M+Na]^+$: 329.9564; Found: 329.9567.



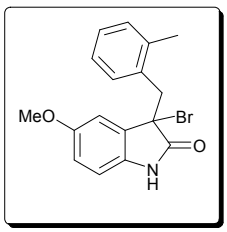
3-Bromo-3-(2,2-dimethylpropyl)-2,3-dihydro-1H-indol-2-one (2o): Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.53 (s, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.28(t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz,1H), 6.94 (d, *J* = 7.7 Hz, 1H), 2.78 (d, *J* = 14.2 Hz, 1H), 2.62 (d, *J* = 14.2 Hz, 1H), 0.74 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.24, 139.27, 130.49, 130.17, 126.29, 122.91, 110.88, 58.07, 51.25, 33.30, 30.67; **HRMS** *m/z* **(ESI):** Calcd for $C_{13}H_{16}BrNO$ $[M+Na]^+$: 304.0313; Found: 304.0310.



3-Bromo-3-allyl-2,3-dihydro-1H-indol-2-one (2p) [2a]**:** Light yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.05 (s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.62-5.52 (m, 1H), 5.12 (t, *J* = 15.7 Hz, 1H), 3.15 (dd, *J* = 6.3 Hz, 6.2 Hz, 1H), 3.05 (dd, *J* = 7.8 Hz, 7.9 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.63, 139.70, 130.76, 130.16, 130.01, 125.06, 123.31, 120.91, 110.89, 55.51, 43.28; **HRMS** *m/z* **(ESI):** Calcd for $C_{11}H_{10}BrNO$ $[M+Na]^+$: 273.9844; Found: 273.9839.



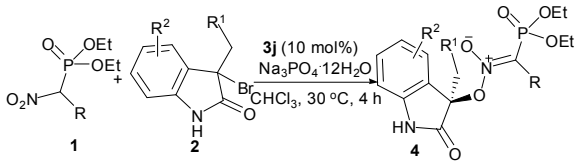
3-Bromo-6-chloro-3-[(2-methylphenyl)methyl]-2,3-dihydro-1H-indol-2-one (2q): Llight yellow solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (s, 1H), 7.11-7.05 (m, 4H), 7.01 (t, *J* = 7.4 Hz, 2H), 6.84 (s, 1H), 3.74-3.65 (m, 2H), 2.19 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.20, 140.44, 137.26, 135.87, 132.53, 130.70, 130.45, 128.36, 127.66, 126.90, 125.75, 123.13, 111.13, 56.18, 40.76, 20.14; **HRMS** *m/z* **(ESI):** Calcd for $C_{16}H_{13}BrClNO$ $[M+Na]^+$: 371.9767; Found: 371.9767.



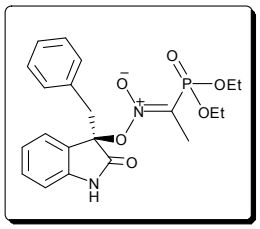
3-Bromo-5-methoxy-3-[(2-methylphenyl)methyl]-2,3-dihydro-1H-indol-2-one (2r): Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.13-7.00 (m, 4H), 6.78-

6.76 (m, 1H), 6.71 (d, *J* = 8.7 Hz, 2H), 3.71 (s, 3H), 3.69 (d, *J* = 7.7 Hz, 2H), 2.18 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.18, 155.94, 137.43, 132.84, 132.67, 130.94, 130.53, 127.52, 125.65, 115.76, 112.04, 110.99, 57.44, 55.76, 40.86, 20.15; **HRMS *m/z* (ESI):** Calcd for $C_{17}H_{16}BrNO_2$ $[M+Na]^+$: 368.0262; Found: 368.0262.

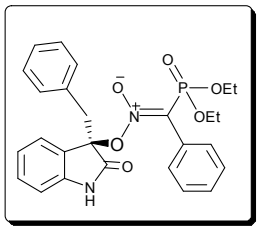
5. General procedure for the addition of diethyl *α*-nitrophosphonates to 3-bromooxindoles



Diethyl *α*-nitrophosphonate **1** (0.11mmol), catalyst **3j** (0.01 mmol) and chloroform (1 mL) were added to an oven dried tube, and the mixture was stirred at rt for 5 minutes. Then, 3-bromooxindole **2** (0.1 mmol) and $Na_3PO_4 \cdot 12H_2O$ (0.11 mmol) was added. After being stirred at 30 ºC for 4 h, the reaction mixture was purified by flash chromatography on silica gel (PE/EtOAc 3:1-1:1) to afford the corresponding products **4**. The enantiomeric excess was determined by chiral-phase HPLC analysis.

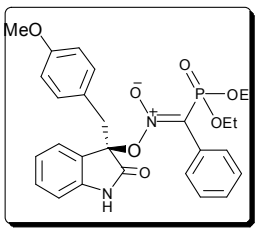


N-{[(3R)-3-benzyl-2-oxo-2,3-dihydro-1H-indol-3-yl]oxy}-1-(diethoxyphosphoryl)ethanimine oxide (4a): The reaction was carried out following the general procedure using **1a** (23.2 mg, 0.11mmol), **2a** (30.1 mg, 0.1mmol) to afford **4a:** Yellow oil; 27.7 mg, 64% yield; 81:19 *Z*/*E*; $[\alpha]_D^{25}$ -51.1 (*c* 0.59, $CHCl_3$); **HPLC:** Chiralpak AD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 10.64 min (major), 15.69 min (minor), 84% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89 (s, 1H), 7.23 (t, *J* = 10.2 Hz, 4H), 7.03 (d, *J* = 6.8 Hz, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.78 (t, *J* = 7.1 Hz, 1H), 6.62 (d, *J* = 6.9 Hz, 1H), 4.03 (s, 2H), 3.83-3.77 (m, 1H), 3.64-3.58 (m, 1H), 3.45 (d, *J* = 13.6 Hz, 1H), 2.99 (d, *J* = 13.5 Hz, 1H), 2.22 (d, *J* = 11.4 Hz, 3H), 1.22-1.19 (m, 3H), 0.97 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.82, 141.51, 132.53, 131.17, 130.06, 130.03, 127.89, 127.51, 124.13, 121.71, 110.64, 110.56, 82.34, 63.82 (d, *J* = 6.1 Hz), 63.33 (d, *J* = 5.7 Hz), 41.00, 16.06 (d, *J* = 6.5 Hz), 15.54 (d, *J* = 6.8 Hz), 15.43 (d, *J* = 9.2 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 6.01; **HRMS *m/z* (ESI):** Calcd for $C_{21}H_{25}N_2O_6P$ $[M+Na]^+$: 455.1348, Found: 455.1348.

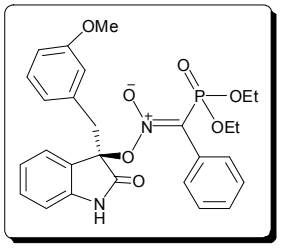


N-{[(3R)-3-benzyl-2-oxo-2,3-dihydro-1H-indol-3-yl]oxy}-1-(diethoxyphosphoryl)-1-phenylmethanimine oxide (4b): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2a** (30.1 mg, 0.1mmol) to afford **4b**: Yellow solid; 37.1 mg, 75% yield; m.p. 25-26 ºC; 92:8 *Z*/*E*; $[\alpha]_D^{25}$ -51.5 (*c* 0.37, $CHCl_3$); **HPLC:** Chiralpak AD-H (85:15 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 22.94 min (major), 26.17 min (minor), 75% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92 (s, 1H), 7.51-7.45 (m, 5H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 2H), 6.86-6.79 (m, 2H), 6.52 (d, *J* = 7.4 Hz, 2H), 6.31 (t, *J* = 7.1 Hz, 1H), 4.00-3.92 (m, 3H), 3.75-3.69 (m, 1H), 3.21 (d, *J* = 13.9 Hz, 1H), 2.71 (t, *J* = 14.4 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.77, 141.29, 132.52, 130.78, 130.12 (d, *J* = 3.9 Hz), 130.00, 129.80, 129.72, 129.32, 128.51, 127.66, 126.86, 125.16, 124,38, 121.62, 110.52, 82.68, 63.90 (d, *J*= 6.0 Hz), 63.64 (d, *J* = 5.8 Hz), 40.79, 16.03 (d, *J* = 6.7 Hz), 15.93 (d, *J* = 6.9 Hz); **^{31}P NMR**

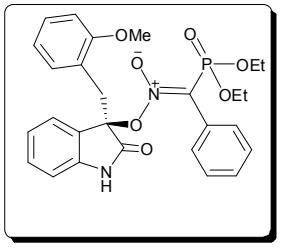
(162 MHz, $CDCl_3$): δ = 5.09; **HRMS** *m/z* **(ESI):** Calcd for $C_{26}H_{27}N_2O_6P$ [M+Na]$^+$: 517.1505, Found: 517.1495.



2-({Ethoxy[({[(3R)-3-[(4-methoxyphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl]phosphoryl}oxy)ethylidyne (4c): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2b** (33.1 mg, 0.1mmol) to afford **4c**: Yellow solid; 35.6 mg, 68% yield; m.p. 47-48 °C; 90:10 *Z*/*E*; $[\alpha]_D^{25}$ -56.0 (*c* 0.36, $CHCl_3$); **HPLC:** Chiralpak AD-H (70:30 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 11.96 min (minor), 12.82 min (major), 81% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (s, 1H), 7.49 (t, *J* = 6.4 Hz, 3H), 7.47 (d, *J* = 4.2 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.49-6.42 (m, 4H), 6.37 (d, *J* = 7.2 Hz, 1H), 4.03-3.91 (m, 3H), 3.76-3.69 (m, 4H), 3.15 (d, *J* = 14.0 Hz, 1H), 2.68 (d, *J* = 14.0 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.33, 158.43, 141.06, 131.78, 130.15 (d, *J* = 4.1 Hz), 129.91, 129.81, 129.25, 128.48, 125.38, 124.46, 124.42, 121.73, 113.06, 110.24, 82.59, 63.82 (d, *J* = 5.9 Hz), 63.59 (d, *J* = 5.8 Hz), 55.09, 39.99, 16.03 (d, *J* = 6.6 Hz), 15.93 (d, *J* = 6.9 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.09; **HRMS** *m/z* **(ESI):** Calcd for $C_{27}H_{29}N_2O_7P$ [M+Na]$^+$: 547.1610, Found: 547.1603.

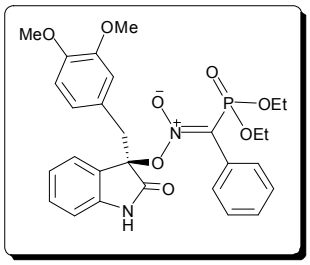


2-({Ethoxy[({[(3R)-3-[(3-methoxyphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl]phosphoryl}oxy)ethylidyne (4d): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2c** (33.1 mg, 0.1mmol) to afford **4d**: Yellow solid; 38.3 mg, 73% yield; m.p. 39-40 °C; 92:8 *Z*/*E*; $[\alpha]_D^{25}$ -65.1 (*c* 0.76, $CHCl_3$); **HPLC:** Chiralpak OD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 11.49 min (minor), 19.23 min (major), 82% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 (s, 1H), 7.47 (s, 5H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.92-6.83 (m, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 7.3 Hz, 1H), 6.15 (t, *J* = 9.1 Hz, 2H), 4.00-3.92 (m, 3H), 3.80-3.72 (m, 1H), 3.55 (s, 3H), 3.15 (d, *J* = 13.6 Hz, 1H), 2.76 (d, *J* = 13.6 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.68, 158.69, 141.50, 133.81, 130.10 (d, *J* = 4.3 Hz), 129.71, 129.63, 129.29, 128.71, 128.39, 125.31, 124.30, 123.16, 121.57, 116.17, 112.87, 110.68, 82.84, 63.92 (d, *J* = 5.9 Hz), 63.71 (d, *J* = 5.8 Hz), 54.98, 40.88, 16.03 (d, *J* = 6.9 Hz), 15.95 (d, *J* = 6.9 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.20; **HRMS** *m/z* **(ESI):** Calcd for $C_{27}H_{29}N_2O_7P$ [M+Na]$^+$: 547.1610, Found: 547.1595.

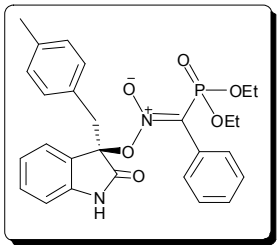


2-({Ethoxy[({[(3R)-3-[(2-methoxyphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl]phosphoryl}oxy)ethylidyne (4e): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2d** (33.1 mg, 0.1mmol) to afford **4e**: Yellow solid; 38.3 mg, 73% yield; m.p. 75-76 °C; 91:9 *Z*/*E*; $[\alpha]_D^{25}$ -88.6 (*c* 0.55, $CHCl_3$); **HPLC:** Chiralpak AD-H (80:20 *n*-hexane/*i*-PrOH, 1.0

mL/min, 254 nm, t_R = 11.80 min (major), 21.88 min (minor), 91% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.36 (s, 1H), 7.50-7.44 (m, 5H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.1 Hz, 1H), 6.82-6.75 (m, 2H), 6.55 (d, *J* = 17.3 Hz, 1H), 6.49-6.42 (m, 2H), 6.18 (d, *J* = 7.4 Hz, 1H), 4.03-3.90 (m, 3H), 3.74-3.64 (m, 1H), 3.22 (s, 3H), 3.14 (d, *J* = 14.1 Hz, 1H), 3.01 (d, *J* = 14.1 Hz, 1H), 1.10 (t, *J* = 6.9 Hz, 3H), 0.99 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 177.38, 157.62, 141.20, 131.99, 130.18 (d, *J* = 4.1 Hz), 129.84, 129.76, 129.56, 129.23, 128.45, 128.21, 125.71, 123.71, 121.48, 121.21, 120.05, 110.28, 109.82, 82.81, 63.96 (d, *J* = 5.97 Hz), 63.64 (d, *J* = 5.7 Hz), 54.68, 33.17, 16.07 (d, *J* = 6.6 Hz), 15.95 (d, *J* = 7.0 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.18; **HRMS *m/z* (ESI):** Calcd for $C_{27}H_{29}N_2O_7P$ $[M+Na]^+$: 547.1610, Found: 547.1602.

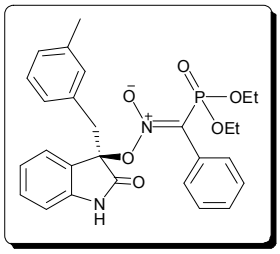


2-({[({[(3R)-3-[(Dimethoxyphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl](ethoxy)phosphoryl}oxy)ethylidyne (4f): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2e** (36.1 mg, 0.1mmol) to afford **4f**: Yellow solid; 33.8 mg, 61% yield; m.p. 49-50 °C; 91:9 *Z*/*E*; $[\alpha]_D^{25}$ -73.4 (*c* 0.38, $CHCl_3$); **HPLC:** Chiralpak AD-H (75:25 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 14.23 min (minor), 17.24 min (major), 81% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 (s, 1H), 7.47 (s, 5H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 6.20 (d, *J* = 8.1 Hz, 1H), 6.05 (s, 1H), 4.00-3.93 (m, 3H), 3.80 (s, 3H), 3.77-3.71 (m, 1H), 3.50 (s, 3H), 3.09 (d, *J* = 8.1 Hz, 1H), 2.78 (d, *J* = 13.6 Hz, 1H), 1.11 (t, *J* = 6.9 Hz, 3H), 1.03 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.41, 147.86, 147.69, 141.46, 130.15 (d, *J* = 3.9 Hz), 130.02, 129.82, 129.74, 129.22, 128.32, 125.61, 124.48, 124.31, 123.11, 121.57, 113.90, 110.60, 110.50, 82.95, 63.89 (d, *J* = 5.9 Hz), 63.71 (d, *J* = 5.7 Hz), 55.68, 55.58, 40.44, 16.06, 15.99 (d, *J* = 7.4 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.17; **HRMS *m/z* (ESI):** Calcd for $C_{28}H_{31}N_2O_8P$ $[M+Na]^+$: 577.1716, Found: 577.1696.

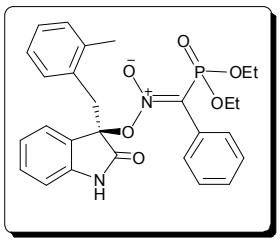


2-({Ethoxy[({[(3R)-3-[(4-methylphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl]phosphoryl}oxy)ethylidyne (4g): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2f** (31.5 mg, 0.1mmol) to afford **4g**: Yellow solid; 40.6 mg, 80% yield; m.p. 45-46 °C; 92:8 *Z*/*E*; $[\alpha]_D^{25}$ -58.3 (*c* 0.41, $CHCl_3$); **HPLC:** Chiralpak OD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 10.70 min (minor), 16.54 min (major), 83% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 (s, 1H), 7.51-7.45 (m, 5H), 7.21 (t, *J* = 7.32, Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.79-6.74 (m, 3H), 6.40 (t, *J* = 6.8 Hz, 3H), 4.03-3.91 (m, 3H), 3.78-3.68 (m, 1H), 3.16 (d, *J* = 13.9 Hz, 1H), 2.70 (d, *J* = 13.9 Hz, 1H), 2.24 (s, 3H), 1.11 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.80, 141.34, 136.40, 130.62, 130.14 (d, *J* = 3.9 Hz), 129.93, 129.83, 129.75, 129.32, 129.26, 128.46, 128.38, 125.31, 124.37, 121.57,

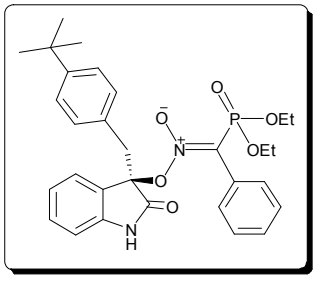
110.52, 82.76, 63.90 (d, J = 6.0 Hz), 63.65 (d, J = 5.8 Hz), 40.42, 21.08, 16.03 (d, J = 6.7 Hz), 15.93 (d, J = 6.9 Hz); **^{31}P NMR (168 MHz, $CDCl_3$):** δ = 5.15; **HRMS** *m/z* **(ESI):** Calcd for $C_{27}H_{29}N_2O_6P$ $[M+Na]^+$: 531.1661, Found: 531.1654.



2-({Ethoxy[({[(3R)-3-[(3-methylphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl]phosphoryl}oxy)ethylidyne (4h): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2g** (31.5 mg, 0.1mmol) to afford **4h**: Yellow solid; 33.0 mg, 65% yield; m.p. 40-41 ^{o}C; 91:9 *Z*/*E*; $[\alpha]_D^{25}$ -70.2 (*c* 0.42, $CHCl_3$); **HPLC:** Chiralpak AD-H (90:10 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 40.88 min (major), 45.90 min (minor), 88% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (s, 1H), 7.49 (m, 5H), 7.21 (t, J = 7.6 Hz, 1H), 6.93-6.76 (m, 4H), 6.45 (d, J = 7.3 Hz, 1H), 6.39 (s, 1H), 6.32 (d, J = 7.5 Hz, 1H), 4.03-3.92 (m, 3H), 3.78-3.72 (m, 1H), 3.15 (d, J = 13.7 Hz, 1H), 2.73 (d, J = 13.7 Hz,1 H), 2.10 (s, 3H), 1.11 (t, J = 7.0 Hz, 3H), 1.03 (t, J = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.72, 141.29, 137.04, 132.32, 131.63, 130.14 (d, J = 4.1 Hz), 129.92, 129.81, 129.72, 129.32, 128.41, 127.78, 127.68, 127.60, 125.47, 124.36, 121.54, 110.52, 82.73, 63.90 (d, J = 5.9 Hz), 63.70 (d, J = 5.7 Hz), 40.81, 21.26, 16.03 (d, J = 6.7 Hz), 15.95 (d, J = 7.2 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.21; **HRMS** *m/z* **(ESI):** Calcd for $C_{27}H_{29}N_2O_6P$ $[M+Na]^+$: 531.1661, Found: 531.1646.

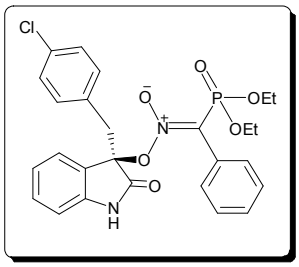


2-({Ethoxy[({[(3R)-3-[(2-methylphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl]phosphoryl}oxy)ethylidyne (4i): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2h** (31.5 mg, 0.1mmol) to afford **4i**: Yellow solid; 40.6 mg, 80% yield; m.p. 44-45 ^{o}C; 94:6 *Z*/*E*; $[\alpha]_D^{25}$ -66.7 (*c* 0.57, $CHCl_3$); **HPLC:** Chiralpak OD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 10.04 min (minor), 12.75 min (major), 92% ee; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.30 (s, 1H), 7.51 (d, J = 7.0 Hz, 3H), 7.42 (d, J = 6.6 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 7.03 (t, J = 7.3 Hz, 1H), 6.88 (t, J = 7.2 Hz, 2H), 6.79 (t, J = 7.4 Hz, 1H), 6.70 (t, J = 7.4 Hz, 1H), 6.37 (d, J = 7.4 Hz, 1H), 6.12 (d, J = 7.2 Hz, 1H), 4.03-3.93 (m, 3H), 3.76-3.71 (m, 1H), 3.19 (d, J = 14.7 Hz, 1H), 2.85 (d, J = 14.5 Hz, 1H), 1.53 (s, 3H), 1.11 (t, J = 6.3 Hz, 3H), 1.01 (t, J = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 177.53, 141.26, 137.74, 131.53, 131.38, 130.07 (d, J = 3.9 Hz), 129.96, 129.78, 129.65, 129.30, 128.30, 126.93, 125.42, 125.10, 124.13, 121.60, 110.60, 82.69, 63.96 (d, J = 6.0 Hz), 63.66 (d, J = 5.8 Hz), 36.71, 19.18, 15.04 (d, J = 6.6 Hz), 15.94 (d, J = 6.9 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.09; **HRMS** *m/z* **(ESI):** Calcd for $C_{27}H_{29}N_2O_6P$ $[M+Na]^+$: 531.1661, Found: 531.1644.

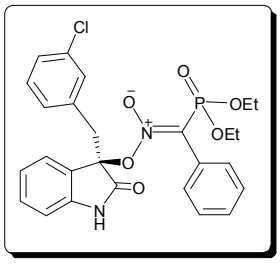


2-(4-{[(3R)-3-({[(Diethoxyphosphoryl)(phenyl)methylidene]-oxo-λ^5-azanylidene}oxy)-2-oxo-1λ^2-indol-3- yl]methyl}phenyl)-2-methylpropylidyne (4j):

The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2i** (35.7 mg, 0.1mmol) to afford **4j**: White solid; 46.2 mg, 84% yield; m.p. 101-102 °C; 93:7 *Z*/*E*; $[\alpha]_D^{25}$ -44.5 (*c* 0.50, $CHCl_3$); **HPLC:** Chiralpak OD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 8.52 min (minor), 13.95 min (major), 80% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99 (s, 1H), 7.52-7.42 (m, 5H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.87-6.81 (m, 2H), 6.46 (d, *J* = 8.2 Hz, 2H), 6.28 (d, *J* = 7.4 Hz, 1H), 4.03-3.89 (m, 3H), 3.75-3.67 (m, 1H), 3.20 (d, *J* = 14.0 Hz, 1H), 2.66 (d, *J* = 14.0 Hz, 1H), 1.26 (s, 9H), 1.10 (t, *J* = 7.0 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 177.13, 149.59, 141.46, 130.48, 130.13 (d, *J* = 4.0 Hz), 129.96, 129.78, 129.69, 129.44, 129.28, 128.45, 125.13, 124.55, 124.48, 121.47, 110.62, 82.83, 63.94 (d, *J* = 6.0 Hz), 63.62 (d, *J* = 5.7 Hz), 40.33, 34.33, 31.31, 16.04 (d, *J* = 6.6 Hz), 15.92 (d, *J* = 6.9 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.10; **HRMS** *m/z* **(ESI):** Calcd for $C_{30}H_{35}N_2O_6P$ $[M+Na]^+$: 573.2131, Found: 573.2107.

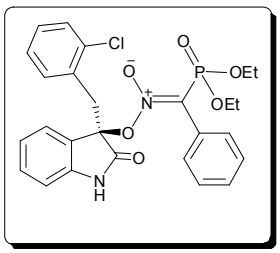


2-({[({[(3R)-3-[(4-Chlorophenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl](ethoxy)phosphoryl}oxy)ethylidyne (4k): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2j** (33.5 mg, 0.1mmol) to afford **4k**: Yellow solid; 37.5 mg, 71% yield; m.p. 83-84 °C; 91:9 *Z*/*E*; $[\alpha]_D^{25}$ -45.5 (*c* 0.35, $CHCl_3$); **HPLC:** Chiralpak AD-H (85:15 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 25.75 min (major), 31.04 min (minor), 73% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06 (s, 1H), 7.50 (t, *J* = 6.5 Hz, 3H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.92-6.81 (m, 4H), 6.45 (d, *J* = 8.3 Hz, 2H), 6.34 (d, *J* = 7.5 Hz, 1H), 4.02-3.90 (m, 3H), 3.77-3.70 (m, 1H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.67 (d, *J* = 14.0 Hz, 1H), 1.09 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR(100 MHz, $CDCl_3$):** δ 176.61, 141.39, 132.87, 132.06, 131.10, 130.18, 130.05 (d, *J* = 4.0 Hz), 129.78, 129.70, 129.39, 128.57, 127.83, 124.87, 124.22, 121.66, 110.77, 82.32, 63.96 (d, *J* = 6.0 Hz), 63.74, 40.18, 16.01 (d, *J* = 6.9 Hz), 15.93 (d, *J* = 7.3 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 4.94; **HRMS** *m/z* **(ESI):** Calcd for $C_{26}H_{26}ClN_2O_6P$ $[M+Na]^+$: 551.1115, Found: 551.1121.

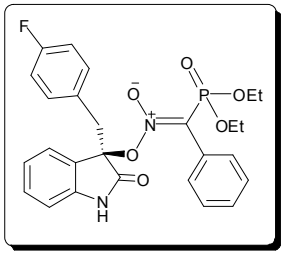


2-({[({[(3R)-3-[(3-Chlorophenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl](ethoxy)phosphoryl}oxy)ethylidyne (4l): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2k** (33.5 mg, 0.1mmol) to afford **4l**: Yellow solid; 35.9 mg, 68% yield; m.p. 42-43 °C; 91:9 *Z*/*E*; $[\alpha]_D^{25}$ -108.2 (*c* 0.26, $CHCl_3$); **HPLC:** Chiralpak AD-H (70:30 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 8.45 min (minor), 8.98 min (major), 73% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.21 (s, 1H), 7.51-7.45 (m, 5H), 7.27-7.21 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.92-6.80 (m, 3H), 6.58 (s, 1H), 6.42 (t, *J* = 6.1 Hz, 2H), 3.96-3.92 (m, 3H), 3.80-3.73 (m, 1H), 3.15 (d, *J* = 13.9 Hz, 1H), 2.71 (d, *J* = 13.9 Hz, 1H), 1.10 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz), $CDCl_3$):** δ 176.46,

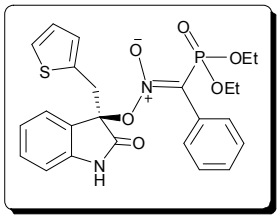
141.37, 134.59, 133.28, 130.79, 130.23, 129.98 (d, J = 3.9 Hz), 129.62, 129.52, 128.97, 128.51, 127.24, 124.99, 124.15, 121.69, 119.21, 117.22, 110.82, 82.33, 63.95 (d, J = 5.9 Hz), 63.75 (d, J = 5.8 Hz), 40.51, 16.06, 15.94 (d, J = 7.3 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.01; **HRMS *m/z* (ESI):** Calcd for $C_{26}H_{26}ClN_2O_6P$ $[M+Na]^+$: 551.1115, Found: 551.1137.



2-({[({[(3R)-3-[(2-Chlorophenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl](ethoxy)phosphoryl}oxy)ethylidyne (4m): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2l** (33.5 mg, 0.1mmol) to afford **4m**: Yellow solid, 39.6 mg, 75% yield; m.p. 62-63 °C; 92:8 *Z*/*E*; $[\alpha]_D^{25}$ -77.4 (*c* 0.49, $CHCl_3$); **HPLC:** Chiralpak AD-H (80:20 *n*-hexane/*i*-PrOH, 1.0mL/min, 254nm, t_R = 11.05 min (major), 19.65 min (minor), 84% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.28 (s, 1H), 7.52-7.43 (m, 5H), 7.24-7.20 (m, 1H), 7.11-7.03 (m, 2H), 6.85 (d, J = 7.8 Hz, 1H), 6.81-6.72 (m, 2H), 6.48-6.46 (m, 1H), 6.10 (d, J = 7.3 Hz, 1H), 4.03-3.91 (m, 3H), 3.75-3.65 (m, 1H), 3.20 (s, 2H), 1.10 t, J = 7.0 Hz, 3H), 1.00 (t, J = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.97, 141.36, 135.52, 132.40, 131.23, 130.16 (d, J = 3.9 Hz), 130.06, 129.84, 129.76, 129.33, 128.88, 128.57, 128.28, 126.29, 124.68, 123.74, 121.77, 110.63, 82.33, 64.00 (d, J = 6.0 Hz), 63.68 (d, J = 5.8 Hz), 36.71, 16.03 (d, J = 6.6 Hz), 15.92 (d, J = 7.0 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 4.93; **HRMS (ESI+):** Calcd for $C_{26}H_{26}ClN_2O_6P$ $[M+Na]^+$: 551.1115, Found: 551.1103.

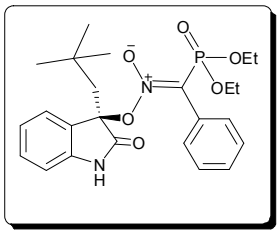


2-({Ethoxy[({[(3R)-3-[(4-fluorophenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl]phosphoryl}oxy)ethylidyne (4n): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2m** (31.9 mg, 0.1mmol) to afford **4n**: Yellow solid; 34.8 mg, 68% yield; m.p. 87-88 °C; 92:8 *Z*/*E*; $[\alpha]_D^{25}$ -44.8 (*c* 0.26, $CHCl_3$); **HPLC:** Chiralpak AD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 17.03 min (major), 18.64 min (minor), 71% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.05 (s, 1H), 7.50 (t, J = 6.9 Hz, 3H), 7.45 (d, J = 5.4 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 6.88-6.81 (m, 2H), 6.63 (t, J = 8.6 Hz, 2H), 6.49-6.45 (m, 2H), 6.30 (t, J = 7.1 Hz, 1H), 4.00-3.91 (m, 3H), 3.76-3.68 (m, 1H), 3.19 (d, J = 14.1 Hz, 1H), 2.68 (d, J = 14.1 Hz, 1H), 1.09 (t, J = 7.0 Hz, 3H), 1.01 (t, J = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.78, 163.80 (d, J = 244.0 Hz), 141.42, 132.29 (d, J = 8.0 Hz), 130.13, 130.09 (d, J = 4.1Hz), 129.81, 129.72, 129.36, 128.56, 128.33 (d, J = 3.1 Hz), 124.92, 124.23, 121.62, 114.52 (d, J = 21.1 Hz), 110.74, 82.55, 63.96 (d, J = 6.0 Hz), 63.69 (d, J = 5.8 Hz), 39.99, 16.01 (d, J = 6.7 Hz), 15.91 (d, J = 7.0 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 4.97; **HRMS *m/z* (ESI):** Calcd for $C_{26}H_{26}FN_2O_6P$ $[M+Na]^+$: 535.1411, Found: 535.1396.

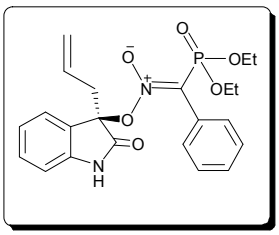


2-({Ethoxy[({[(3R)-2-oxo-3-(thiophen-2-ylmethyl)-1λ^2-indol-3-yl]oxy}-oxo-λ^5-

azanylidene)(phenyl)methyl]phosphoryl}oxy)ethylidyne (4o): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2n** (30.7 mg, 0.1mmol) to afford **4o**: Yellow solid; 36.0 mg, 72% yield; m.p. 38-39 °C; 93:7 *Z*/*E*; $[\alpha]_D^{25}$ -44.9 (*c* 0.23, $CHCl_3$); **HPLC**: Chiralpak AD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 21.49 min (minor), 23.93 min (major), 84% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.03 (s, 1H), 7.49 (s, 5H), 7.24 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 5.2 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.69-6.67 (m, 1H), 6.55 (d, *J* = 7.3 Hz, 1H), 6.23 (d, *J* = 3.0 Hz, 1H), 4.04-3.93 (m, 3H), 3.80-3.72 (m, 1H), 3.35 (d, *J* = 14.8 Hz, 1H), 3.04 (d, *J* = 14.8 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.31, 141.70, 133.62, 130.32, 130.19 (d, *J* = 3.9 Hz), 129.78, 129.70, 129.35, 128.56, 126.51, 125.04, 124.95, 124.09, 121.85, 110.72, 82.35, 63.99 (d, *J* = 6.0 Hz), 63.74 (d, *J* = 5.8 Hz), 34.87, 16.03 (d, *J* = 6.7 Hz), 15.94 (d, *J* = 6.9 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.09; **HRMS** *m/z* **(ESI):** Calcd for $C_{24}H_{31}N_2O_6P$ $[M+Na]^+$: 523.1069, Found: 523.1049.

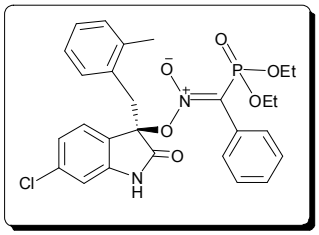


3-[(3R)-3-({[(Diethoxyphosphoryl)(phenyl)methylidene]-oxo-λ^5-azanylidene}oxy)-2-oxo-1λ^2-indol-3-yl]- 2,2-dimethylpropylidyne (4p): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2o** (28.1 mg, 0.1mmol) to afford **4p**: Yellow solid; 33.7 mg, 71% yield; m.p. 39-40 °C; 92:8 *Z*/*E*; $[\alpha]_D^{25}$ -58.4 (*c* 0.32, $CHCl_3$); **HPLC:** Chiralpak OD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 6.06 min (minor), 12.49 min (major), 90% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16 (s, 1H), 7.45 (t, *J* = 6.5 Hz, 5H), 7.26 (d, *J* = 10.1 Hz, 1H), 7.00 (s, 2H), 6.86 (d, *J* = 7.7 Hz, 1H), 4.02-3.89 (m, 3H), 3.72-3.66 (m, 1H), 1.90 (d, *J* = 14.0 Hz, 1H), 1.65 (d, *J* = 14.0 Hz, 1H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H), 0.63 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 177.24, 142.13, 130.31, 130.25 (d, *J* = 4.1 Hz), 130.02, 129.93, 129.19, 128.15, 126.34, 124.69, 121.77, 110.66, 83.67, 63.83 (d, *J* = 5.9 Hz), 63.51 (d, *J* = 5.8 Hz), 46.76, 30.66, 16.07 (d, *J* = 6.6 Hz), 15.97 (d, *J* = 7.2 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.39; **HRMS** *m/z* **(ESI):** Calcd for $C_{21}H_{25}N_2O_6P$ $[M+Na]^+$: 497.1920, Found: 497.1799.

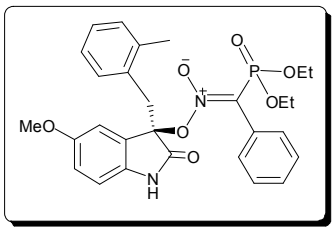


1-(diethoxyphosphoryl)-N-{[(3R)-2-oxo-3-(prop-2-en-1-yl)-2,3-dihydro-1H-indol-3-yl]oxy}-1-phenylmethanimine oxide (4q): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2p** (25.1 mg, 0.1mmol) to afford **4q**: Colourless oil; 34.4 mg, 80% yield; 81:19 *Z*/*E*; $[\alpha]_D^{25}$ -69.1 (*c* 0.29, $CHCl_3$); **HPLC:** Chiralpak OD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 12.81 min (minor), 18.45 min (major), 70% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.69 (s, 1H), 7.51-7.44 (m, 5H), 7.25 (t, *J* = 6.0 Hz, 1H), 6.98 (d, *J* = 6.3 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 5.27-5.17 (m, 1H), 4.90-4.80 (m, 2H), 4.03-3.92 (m, 3H), 3.77-3.67 (m, 1H), 2.57 (dd, *J* = 6.5 Hz, 6.0 Hz, 1H), 2.30 (dd, *J* = 8.3 Hz, 8.3 Hz, 1H), 1.11 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.52, 141.61, 130.21(d, *J* = 4.5 Hz), 129.77, 129.68, 129.25, 128.67, 128.11, 125.44, 123.88, 121.89, 120.87, 110.77, 82.20, 63.92 (d, *J* = 5.9 Hz), 63.63 (d, *J* = 5.7

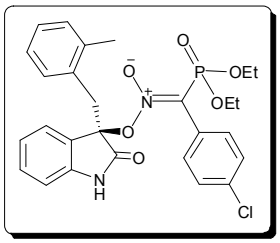
Hz), 39.10, 16.05 (d, *J* = 6.7 Hz), 15.95 (d, *J* = 7.1 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.15; **HRMS** *m/z* **(ESI):** Calcd for $C_{22}H_{25}N_2O_6P$ [M+Na]$^+$: 467.1348, Found: 467.1360.



2-({[({[(3R)-6-Chloro-3-[(2-methylphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl](ethoxy)phosphoryl}oxy)ethylidyne (4r): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2q** (34.9 mg, 0.1mmol) to afford **4r**: Yellow solid; 37.9 mg, 70% yield; m.p. 75-76 °C; 92:8 *Z*/*E*; $[\alpha]_D^{25}$ -102.9 (*c* 0.30, $CHCl_3$); **HPLC**: Chiralpak OD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 7.88 min (minor), 9.95 min (major), 75% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.75 (s, 1H), 7.53-7.40 (m, 5H), 7.02 (t, *J* = 7.4Hz, 1H), 6.94-6.86 (m, 2H), 6.77-6.68 (m, 2H), 6.33 (d, *J* = 7.3 Hz, 1H), 5.99-5.94 (m, 1H), 4.05-3.93 (m, 3H), 3.88-3.75 (m, 1H), 3.16 (d, *J* = 14.7 Hz, 1H), 2.81 (d, *J* = 14.7 Hz, 1H), 1.55 (s, 3H), 1.13-1.03 (m, 6H) ; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 177.07, 142.52, 137.65, 135.73, 131.37, 131.28, 130.00 (d, *J* = 4.0 Hz), 129.91, 129.57, 129.48, 129.43, 128.64, 127.11, 125.48, 124.89, 123.72, 121.55, 111.23, 82.05, 64.00 (d, *J* = 6.1 Hz), 63.90 (d, *J* = 5.9 Hz), 36.62, 19.32, 15.98 (d, *J* = 5.2 Hz), 15.93 (d, *J* = 5.5 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.12; **HRMS** *m/z* **(ESI):** Calcd for $C_{27}H_{28}ClN_2O_6P$ [M+Na]$^+$: 565.1272, Found: 565.1253.

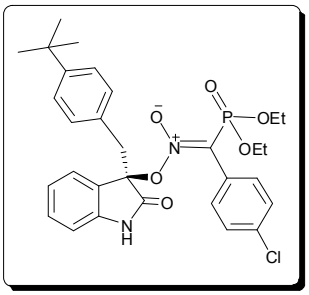


2-({Ethoxy[({[(3R)-5-methoxy-3-[(2-methylphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)(phenyl)methyl]phosphoryl}oxy)ethylidyne (4s): The reaction was carried out following the general procedure using **1b** (30.0 mg, 0.11mmol), **2r** (34.5 mg, 0.1mmol) to afford **4s**: Yellow solid; 34.4 mg, 64% yield; m.p. 85-86 °C; 91:9 *Z*/*E*; $[\alpha]_D^{25}$ -67.9 (*c* 0.26, $CHCl_3$); **HPLC**: Chiralpak OD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254nm, t_R = 13.19 min (minor), 18.51 min (major), 83% ee; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 7.52-7.47 (m, 3H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.81-6.74 (m, 2H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.35 (d, *J* = 7.5 Hz, 1H), 5.61 (d, *J* = 10.9 Hz, 1H), 4.03-3.93 (m, 3H), 3.81-3.71 (m, 1H), 3.50 (s, 3H), 3.18 (d, *J* = 14.7 Hz, 1H), 2.84 (d, *J* = 14.7 Hz, 1H), 1.53 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 177.45, 154.95, 137.84, 134.44, 131.56, 131.34, 130.08 (d, *J* = 4.1 Hz), 129.80, 129.74, 129.35, 128.57, 126.99, 126.13, 125.47, 115.49, 111.08, 110.45, 82.87, 63.92 (d, *J* = 5.9 Hz), 63.71 (d, *J* = 5.8 Hz), 55.55, 36.73, 19.21, 16.00 (d, *J* = 6.3 Hz), 15.89 (d, *J* = 7.0 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.09; **HRMS** *m/z* **(ESI):** Calcd for $C_{28}H_{31}N_2O_7P$ [M+Na]$^+$: 561.1767, Found: 561.1748.

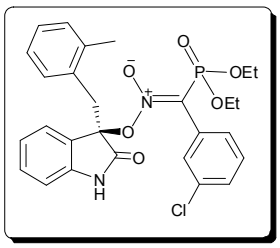


2-({[(4-Chlorophenyl)({[(3R)-3-[(2-methylphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}- oxo-λ^5-azanylidene)methyl](ethoxy)phosphoryl}oxy)ethylidyne (4t): The reaction was carried out following the general procedure using **1c** (33.8 mg, 0.11mmol), **2h** (31.5 mg, 0.1mmol) to afford **4t**: Yellow solid; 43.4 mg, 80% yield; m.p. 57-58 °C;

93:7 *Z*/*E*; $[\alpha]_D^{25}$ -89.6 (*c* 0.13, $CHCl_3$); **HPLC**: Chiralpak OD-H (70:30 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 8.25 min (minor), 9.68 min (major), 81% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.07 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.93-6.68 (m, 2H), 6.82-6.77 (m, 2H), 6.42 (d, *J* = 7.5 Hz, 1H), 6.11 (d, *J* = 7.4 Hz, 1H), 4.04-3.88 (m, 3H), 3.74-3.68 (m, 1H), 3.19 (d, *J* = 14.7 Hz, 1H), 2.84 (d, *J* = 14.7 Hz, 1H), 1.55 (s, 3H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 177.28, 141.17, 137.78, 135.58, 131.45 (d, *J* = 4.1 Hz), 131.37, 131.29, 130.11, 129.95, 128.89, 128.21, 128.13, 127.20, 125.37, 124.92, 124.20, 121.73, 110.58, 82.76, 64.06 (d, *J* = 5.9 Hz), 63.74 (d, *J* = 5.9 Hz), 36.82, 19.24, 16.05 (d, *J* = 6.6 Hz), 15.93 (d, *J* = 6.9 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 4.57; **HRMS** *m/z* **(ESI):** Calcd for $C_{27}H_{28}ClN_2O_6P$ $[M+Na]^+$: 565.1272, Found: 565.1262.

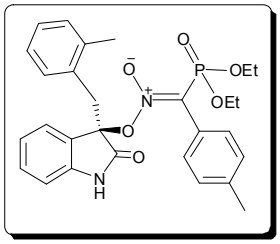


2-(4-{[(3R)-3-({[(4-Chlorophenyl)(diethoxyphosphoryl)methylidene]-oxo-λ^5-azanylidene}oxy)-2-oxo-1λ^2-indol-3-yl]methyl}phenyl)-2-methylpropylidyne (4u): The reaction was carried out following the general procedure using **1c** (33.8 mg, 0.11mmol), **2i** (35.7 mg, 0.1mmol) to afford **4u**: Yellow solid; 43.8 mg, 75% yield; m.p. 85-86 °C; 92:8 *Z*/*E*; $[\alpha]_D^{25}$ -63.3 (*c* 0.48, $CHCl_3$); **HPLC**: Chiralpak AD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 10.30 min (major), 17.97 min (minor), 70% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.35 (s, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.0 Hz, 2H), 6.46 (d, *J* = 7.8 Hz, 2H), 6.21 (d, *J* = 7.5 Hz, 1H), 4.03-3.86 (m, 3H), 3.72-3.66 (m, 1H), 3.23 (d, *J* = 14.1 Hz, 1H), 2.64 (d, *J* = 14.1 Hz, 1H), 1.28 (s, 9H), 1.12(t, *J* = 6.9 Hz, 3H), 1.00 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 177.00, 150.01, 141.47, 135.46, 131.58 (d, *J* = 4.0 Hz), 130.49, 130.05, 129.30, 128.79, 128.32, 128.24, 124.90, 124.55, 124.49, 121.50, 110.60, 82.90, 64.03 (d, *J* = 6.0 Hz), 63.68 (d, *J* = 5.8 Hz), 40.31, 34.37, 31.30, 16.07 (d, *J* = 6.4 Hz), 15.93 (d, *J* = 7.0 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 4.59; **HRMS** *m/z* **(ESI):** Calcd for $C_{30}H_{34}ClN_2O_6P$ $[M+Na]^+$: 607.1741, Found: 607.1728.

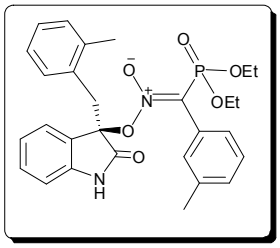


2-({[(3-Chlorophenyl)({[(3R)-3-[(2-methylphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}- oxo-λ^5-azanylidene)methyl](ethoxy)phosphoryl}oxy)ethylidyne (4v): The reaction was carried out following the general procedure using **1d** (33.8 mg, 0.11mmol), **2h** (31.5 mg, 0.1mmol) to afford **4v**: Yellow solid; 36.9 mg, 68% yield; m.p. 55-56 °C; 93:7 *Z*/*E*; $[\alpha]_D^{25}$ -66.6 (*c* 0.23, $CHCl_3$); **HPLC**: Chiralpak AD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 8.21 min (major), 13.85 min (minor), 71% ee; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (s, 1H), 7.64 (d, *J* = 6.9 Hz, 1H), 7.57-7.45 (m, 3H), 7.29-7.24 (m, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.88-6.85 (m, 1H), 6.80-6.75 (m, 2H), 6.36 (d, *J* = 7.4 Hz, 1H), 6.23 (d, *J* = 7.5 Hz, 1H), 4.13 – 4.01 (m, 3H), 3.98-3.86 (m, 1H), 3.11 (d, *J* = 14.6 Hz, 1H), 2.82 (d, *J* = 14.6 Hz, 1H), 1.50 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 176.66, 140.52, 137.74, 134.42, 132.21

(d, *J* = 3.7 Hz), 131.53, 131.19, 130.90, 130.81, 129.83, 129.79, 129.66, 128.84, 127.18, 127.15, 125.39, 124.88, 124.27, 121.84, 110.12, 81.89, 64.00, 63.92 (d, *J* = 5.6 Hz), 37.05, 19.16, 15.98 (d, *J* = 6.3 Hz), 15.89; **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 4.10; **HRMS** *m/z* **(ESI):** Calcd for $C_{27}H_{28}ClN_2O_6P$ [M+Na]$^+$: 565.1272, Found: 565.1259.



2-({Ethoxy[(4-methylphenyl)({[(3R)-3-[(2-methylphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)methyl]phosphoryl}oxy)ethylidyne (4w): The reaction was carried out following the general procedure using **1e** (31.6 mg, 0.11mmol), **2h** (31.5 mg, 0.1mmol) to afford **4w**: Yellow solid; 35.5 mg, 68% yield; m.p. 78-79 °C; 92:8 *Z*/*E*; $[\alpha]_D^{25}$ -85.6 (*c* 0.21, $CHCl_3$); **HPLC**: Chiralpak AD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 8.54 min (major), 20.81 min (minor), 82% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.26 (s, 1H), 7.28 (s, 4H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.87 (t, *J* = 7.1 Hz, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 1H), 6.10 (d, *J* = 7.4 Hz, 1H), 4.02-3.87 (m, 3H), 3.73-3.63 (m, 1H), 3.18 (d, *J* = 14.7 Hz, 1H), 2.84 (d, *J* = 14.6 Hz, 1H), 2.50 (s, 3H), 1.53 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H), 0.99 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 177.58, 141.29, 139.26, 139.25, 37.78, 131.58, 131.53, 129.94 (d, *J* = 3.8 Hz), 129.75, 129.23, 126.89, 126.75, 126.67, 125.23, 125.06, 124.22, 121.57, 110.57, 82.64, 63.90 (d, *J* = 5.9 Hz), 63.57 (d, *J* = 5.7 Hz), 36.71, 21.52, 19.24, 16.04 (d, *J* = 6.6 Hz), 15.93 (d, *J* = 6.8 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.31; **HRMS** *m/z* **(ESI):** Calcd for $C_{28}H_{31}N_2O_6P$ [M+Na]$^+$: 545.1818, Found: 545.1817.

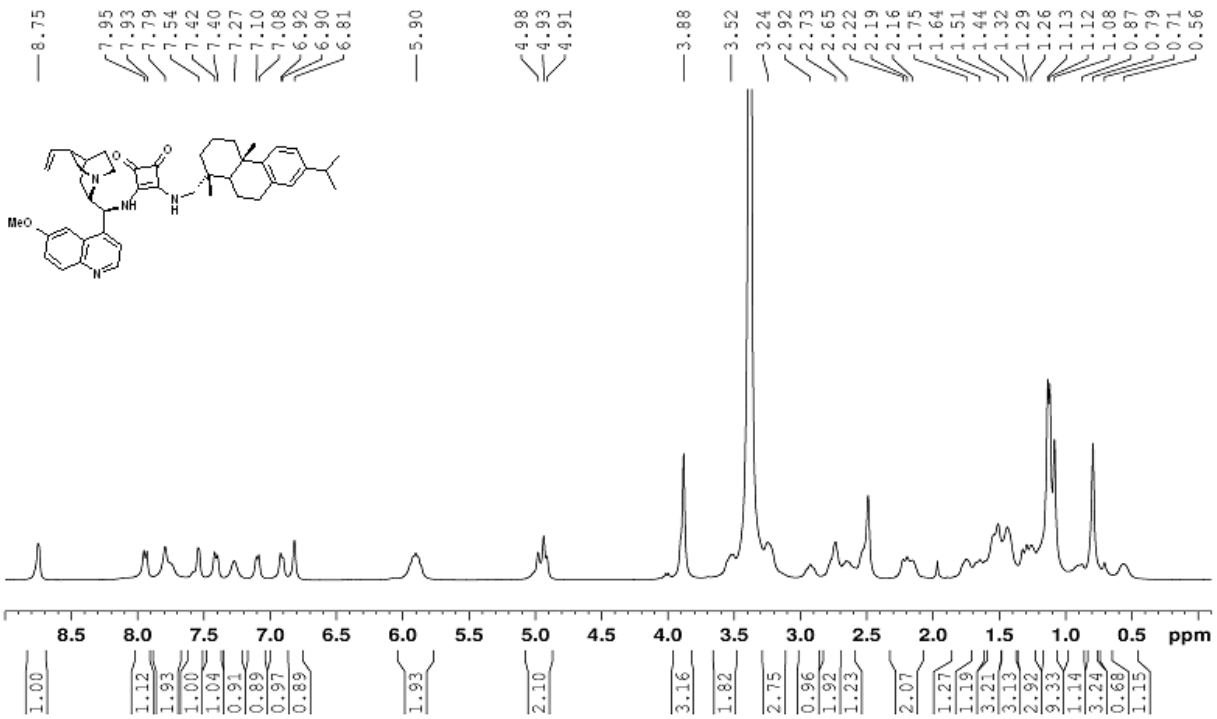


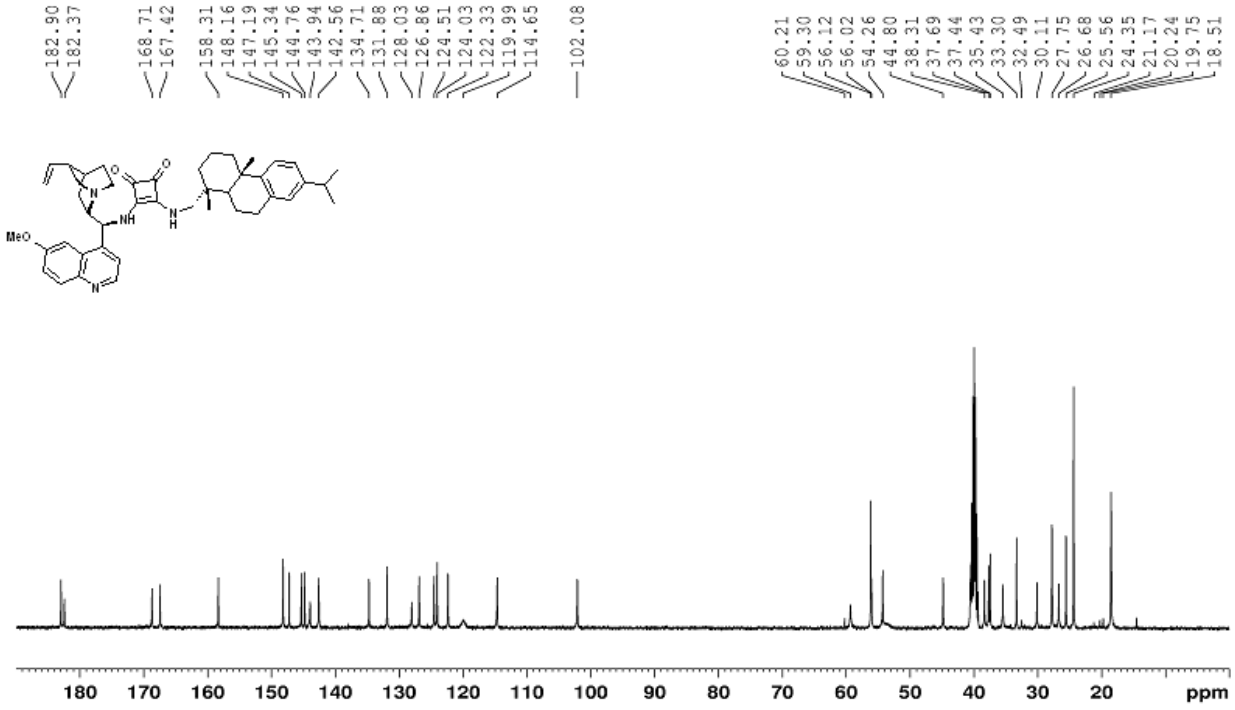
2-({Ethoxy[(3-methylphenyl)({[(3R)-3-[(2-methylphenyl)methyl]-2-oxo-1λ^2-indol-3-yl]oxy}-oxo-λ^5-azanylidene)methyl]phosphoryl}oxy)ethylidyne (4x): The reaction was carried out following the general procedure using **1f** (31.6 mg, 0.11mmol), **2h** (31.5 mg, 0.1mmol) to afford **4x**: Yellow solid; 37.8 mg, 72% yield; m.p. 42-43 °C; 92:8 *Z*/*E*; $[\alpha]_D^{25}$ -74.7 (*c* 0.46, $CHCl_3$); **HPLC**: Chiralpak OD-H (80:20 *n*-hexane/*i*-PrOH, 1.0 mL/min, 254 nm, t_R = 9.55 min (minor), 11.16 min (major), 90% ee; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.22 (s, 1H), 7.38-7.31 (m, 2H), 7.24-7.17 (m, 3H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.35 (d, *J* = 9.3 Hz, 1H), 6.10 (d, *J* = 7.4 Hz, 1H), 4.02-3.89 (m, 3H), 3.76-3.67 (m, 1H), 3.18 (d, *J* = 14.7 Hz, 1H), 2.83 (d, *J* = 14.6 Hz, 1H), 2.44 (s, 3H), 1.52 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz), $CDCl_3$):** δ 177.52, 141.24, 138.19, 137.75, 131.56, 131.37, 130.47 (d, *J* = 4.0 Hz), 130.13, 129.93, 129.74, 129.59, 129.51, 128.50, 127.04 (d, *J* = 3.9 Hz), 126.90, 125.29, 125.14, 124.17, 121.60, 110.55, 82.59, 63.92 (d, *J* = 6.0 Hz), 63.65 (d, *J* = 5.8 Hz), 36.72, 21.43, 19.16, 16.00 (d, *J* = 6.7 Hz), 15.89 (d, *J* = 7.0 Hz); **^{31}P NMR (162 MHz, $CDCl_3$):** δ = 5.13; **HRMS** *m/z* **(ESI):** Calcd for $C_{28}H_{31}N_2O_6P$ [M+Na]$^+$: 545.1818, Found: 545.1812.

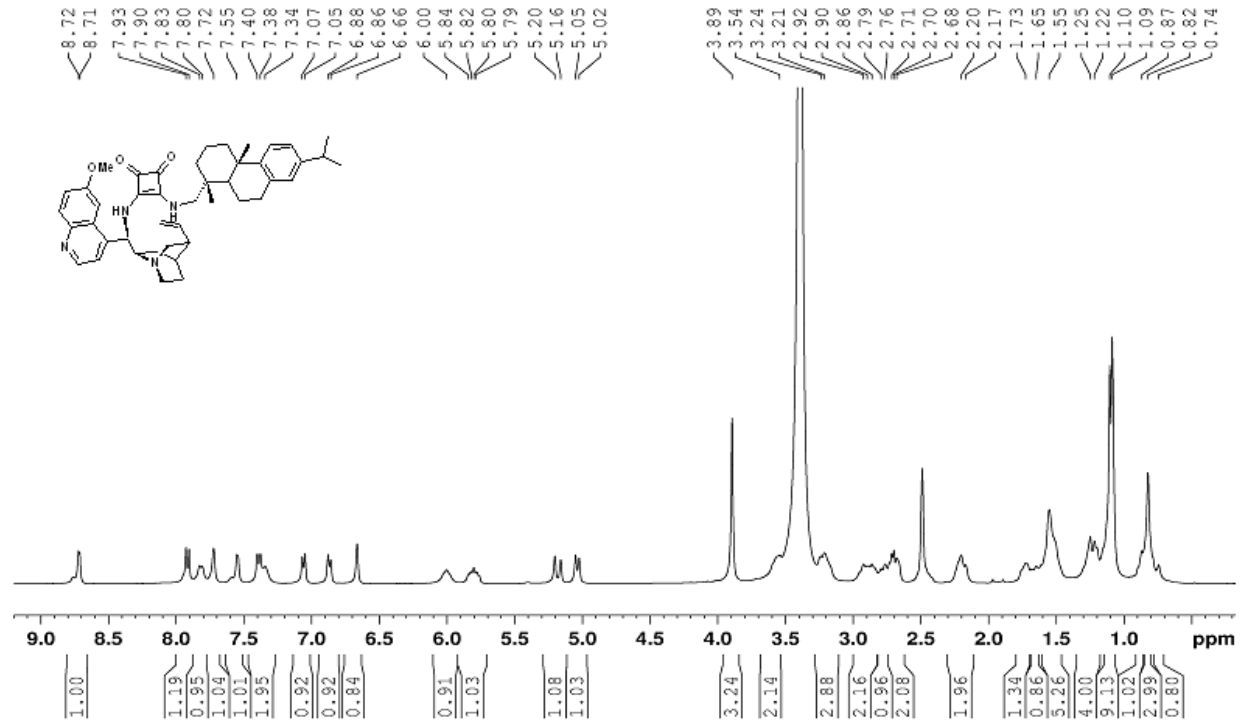
6. References

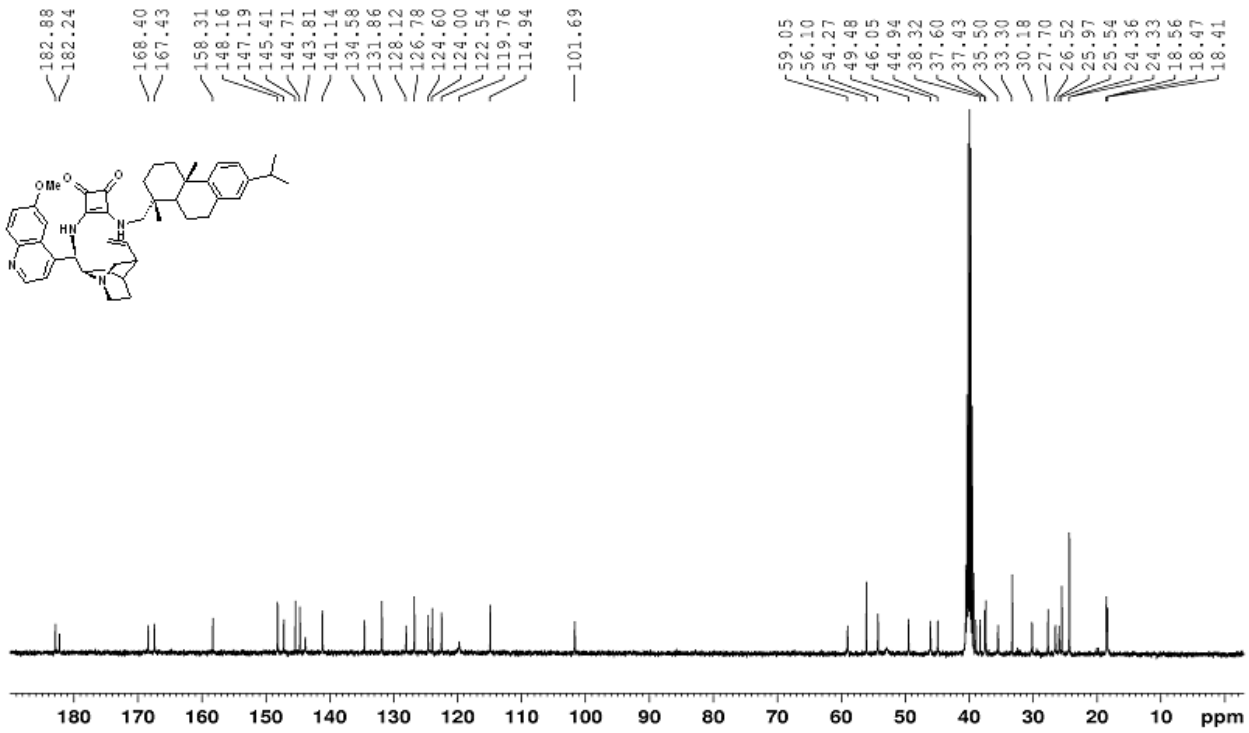
1. C. B. Tripathi, S. Kayal and S. Mukherjee, *Org. Lett.*, 2012**, 14**, 3296.
2. (*a*) Y.-H. Liao, Z.-J. Wu, W.-Y. Han, X.-M. Zhang and W.-C. Yuan, *Chem. Eur. J.* 2012**, 18**, 8916; (*b*) J. Zuo, Y.-H. Liao, X.-M. Zhang and W.-C. Yuan, *J. Org. Chem.* 2012**, 77**, 11325.
3. (*a*) B.-J. Li, L. Jiang, M. Liu, Y.-C. Chen, L.-S. Ding and Y. Wu, *Synlett,* 2005, 603; (*b*) B. Vakulya, S. Varga, A. Csámpai and T. Soós, *Org. Lett.*, 2005, **7**, 1967; (*c*) T.-Y. Liu, J. Long, B.-J. Li, L. Jiang, R. Li, Y. Wu, L.-S. Ding and Y.-C. Chen, *Org. Biomol. Chem.*, 2006, **4**, 2097; (*d*) T. Okino, Y. Hoashi and Y. Takemoto, *J. Am. Chem. Soc.*, 2003**, 125**, 12672.
4. (*a*) J. P. Malerich, K. Hagihara and V. H. Rawal, ***J.** Am. Chem. Soc.*, 2008, **130**, 14416; (*b*) Y. Qian, G. Ma, A. Lv, H.-L. Zhu, J. Zhao and V. H. Rawal, *Chem. Commun.*, 2010, **46**, 3004; (*c*) L. Dai, S.-X. Wang and F.-E. Chen, *Adv. Synth. Catal.* 2010, **352**, 2137; (*d*) Z. Dong, G. Qiu, H.-B. Zhou and C. Dong, *Tetrahedron: Asymmetry*, 2012, **23**, 1550.
5. D. Green, S. Elgendy, G. Patel, J. A. Baban, E. Skordalakes, W. Husman, V. V. Kakkar and J. Deadman, *Phosphorus Sulfur*, 1996, **113**, 303.

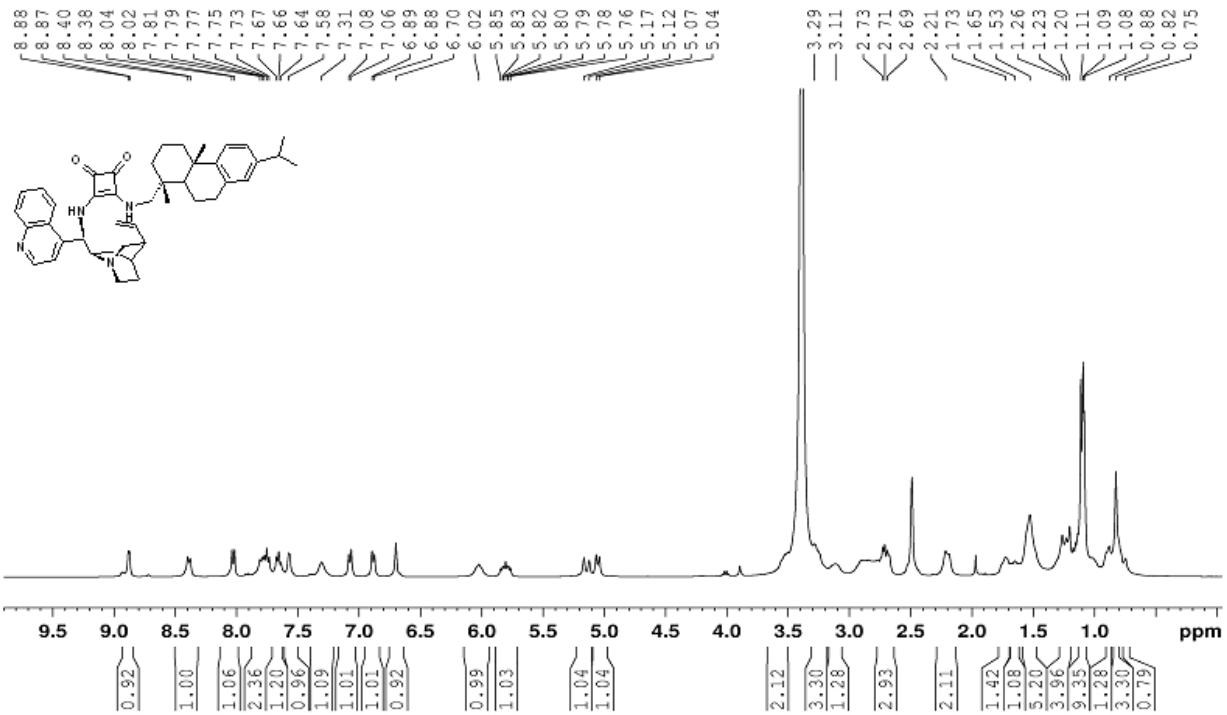
7. **NMR Spectra**

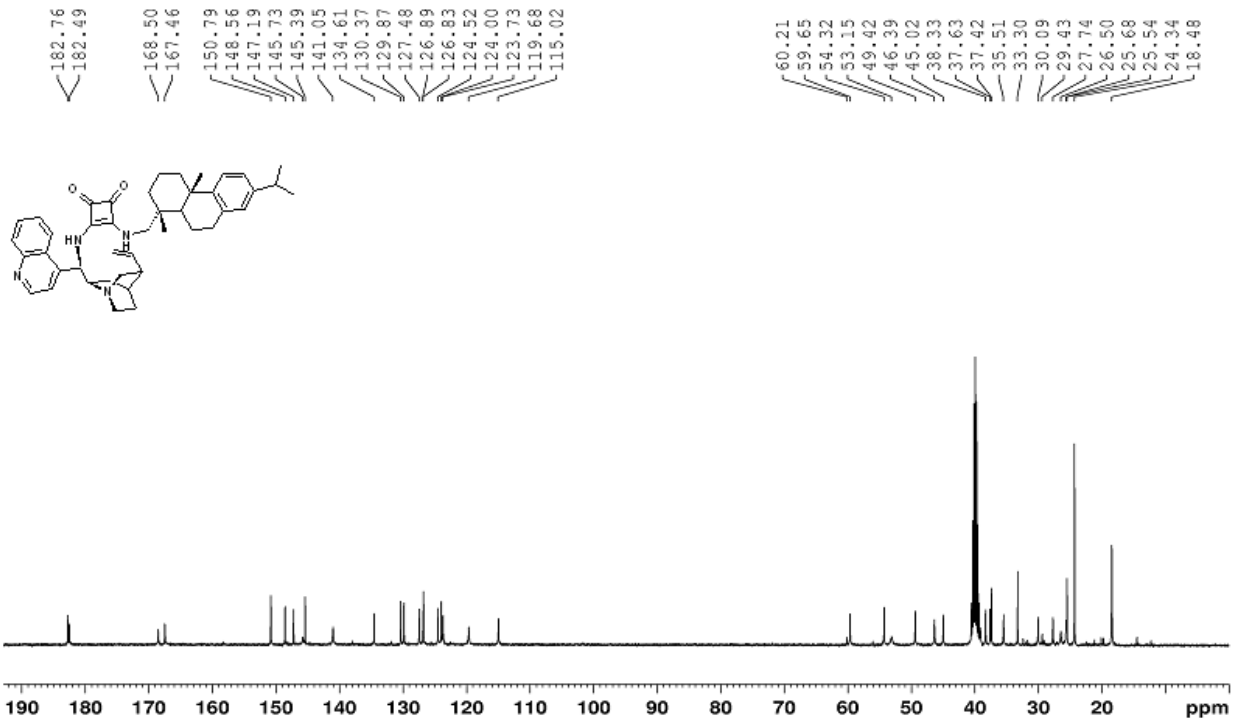


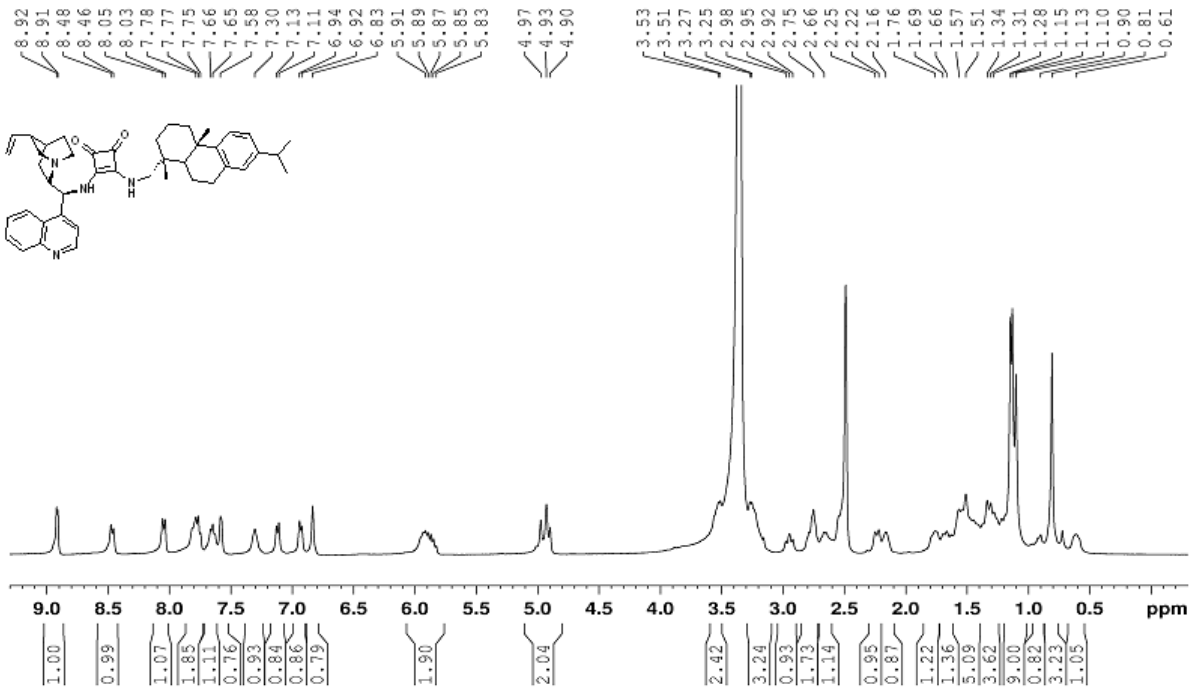


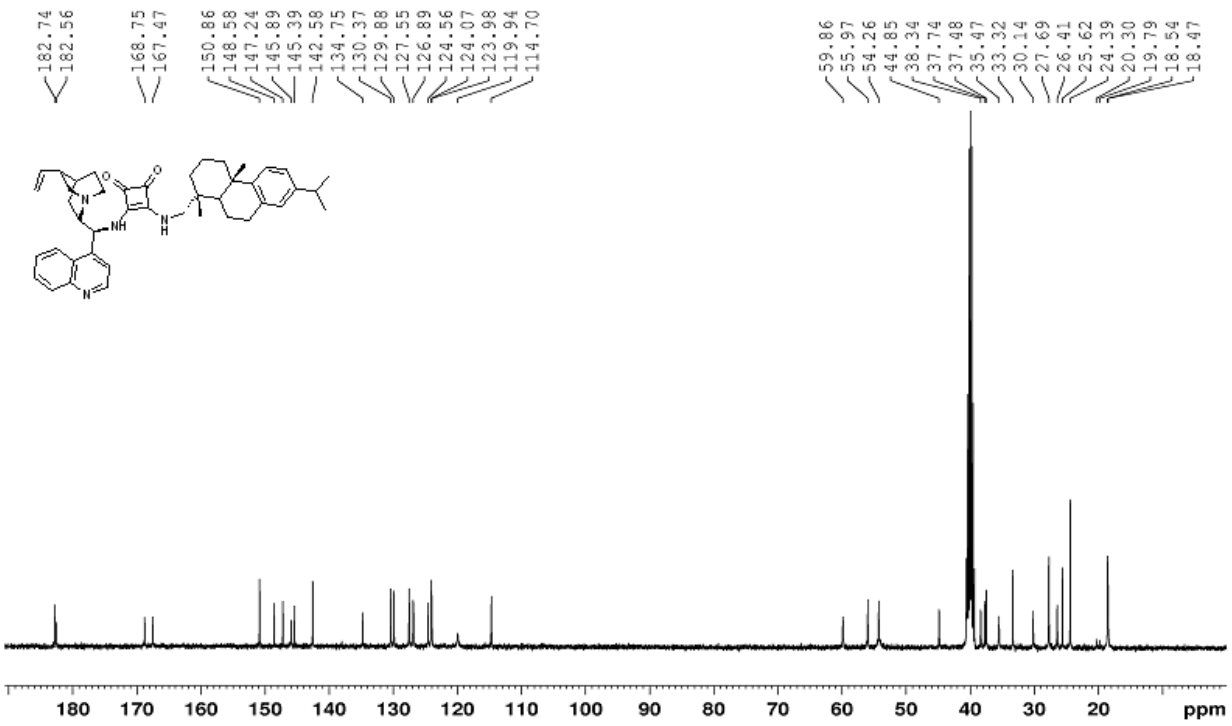

8.72
8.71
7.93
7.90
7.83
7.80
7.72
7.55
7.40
7.38
7.34
7.07
7.05
6.88
6.86
6.66
6.00
5.84
5.82
5.80
5.79
5.20
5.16
5.05
5.02
3.89
3.54
3.24
3.21
2.92
2.90
2.86
2.79
2.76
2.71
2.70
2.68
2.20
2.17
1.73
1.65
1.55
1.25
1.22
1.10
1.09
0.87
0.82
0.74
OMe
HN
N
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.19
0.95
1.04
1.01
1.95
0.92
0.92
0.84
0.91
1.03
1.08
1.03
3.24
2.14
2.88
2.16
0.96
2.08
1.96
1.34
0.86
5.26
4.00
9.13
1.02
2.99
0.80


182.88
182.24
168.40
167.43
158.31
148.16
147.19
145.41
144.71
143.81
141.14
134.58
131.86
128.12
126.78
124.60
124.00
122.54
119.76
114.94
101.69
59.05
56.10
54.27
49.48
46.05
44.94
38.32
37.60
37.43
35.50
33.30
30.18
27.70
26.52
25.97
25.54
24.36
24.33
18.56
18.47
18.41
OMe
HN
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

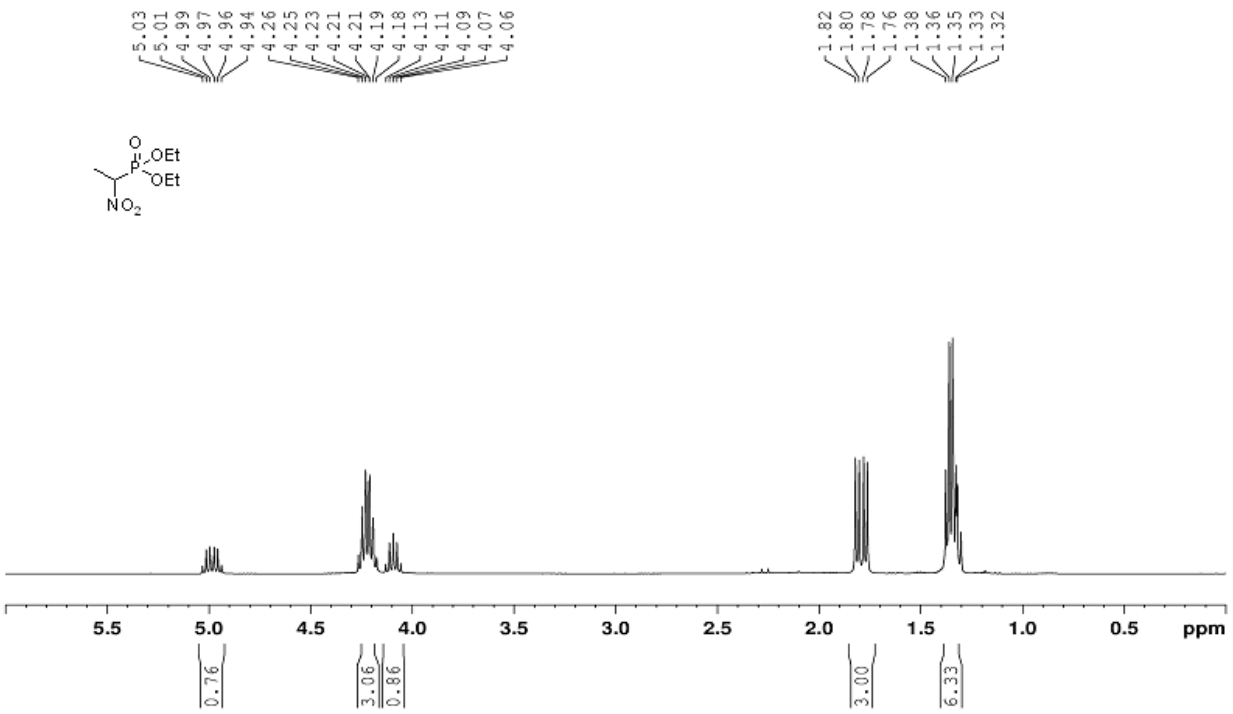

8.88
8.87
8.40
8.38
8.04
8.02
7.81
7.79
7.77
7.75
7.73
7.67
7.66
7.64
7.58
7.31
7.08
7.06
6.89
6.88
6.70
6.02
5.85
5.83
5.82
5.80
5.79
5.78
5.76
5.17
5.12
5.07
5.04
3.29
3.11
2.73
2.71
2.69
2.21
1.73
1.65
1.53
1.26
1.23
1.20
1.11
1.09
1.08
0.88
0.82
0.75
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.92
1.00
1.06
2.36
1.20
0.96
1.09
1.01
1.01
0.92
0.99
1.03
1.04
1.04
2.12
3.30
1.28
2.93
2.11
1.42
1.08
5.20
3.96
9.35
1.28
3.30
0.79

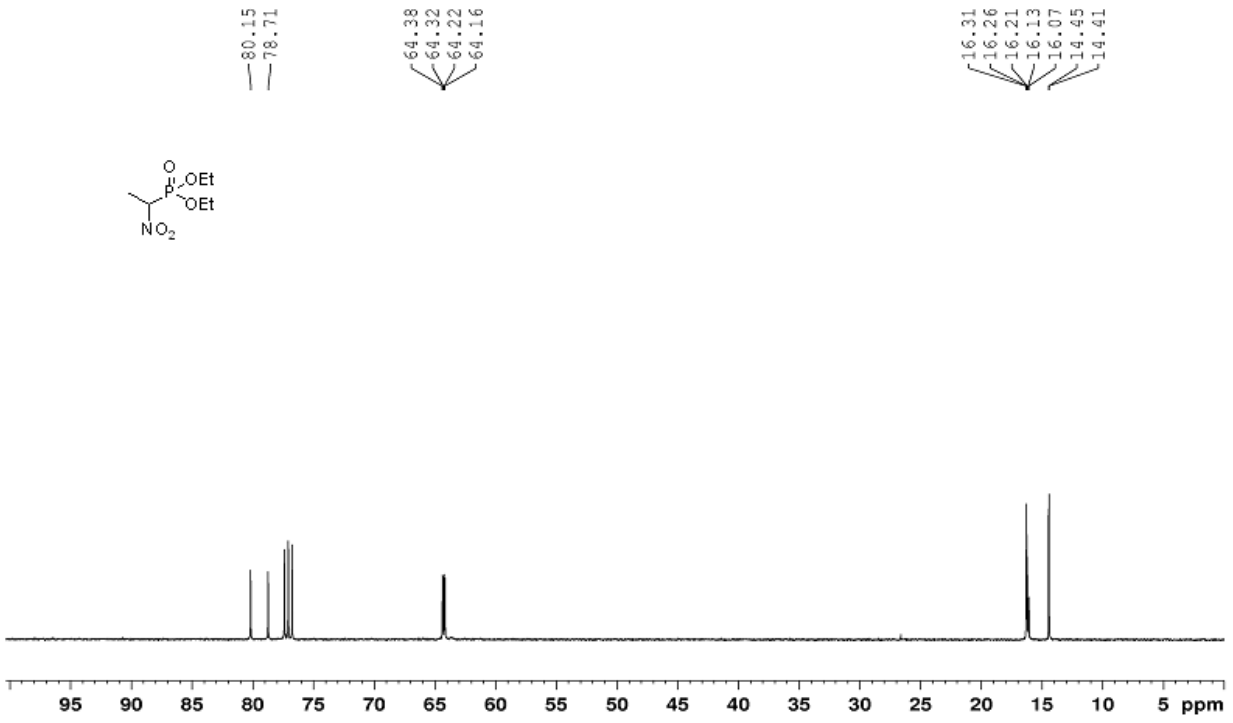

182.76
182.49
168.50
167.46
150.79
148.56
147.19
145.73
145.39
141.05
134.61
130.37
129.87
127.48
126.89
126.83
124.52
124.00
123.73
119.68
115.02
60.21
59.65
54.32
53.15
49.42
46.39
45.02
38.33
37.63
37.42
35.51
33.30
30.09
29.43
27.74
26.50
25.68
25.54
24.34
18.48
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

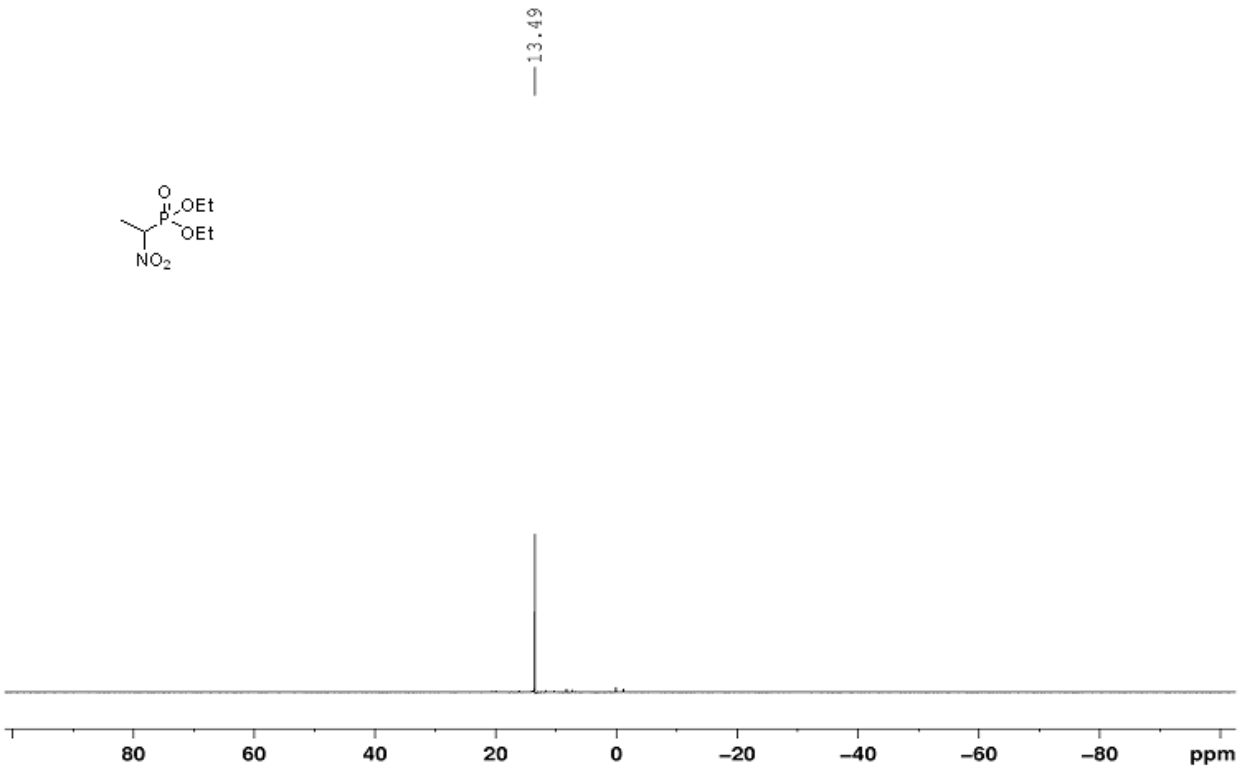

8.92
8.91
8.48
8.46
8.05
8.03
7.78
7.77
7.75
7.66
7.65
7.58
7.30
7.13
7.11
6.94
6.92
6.83
5.91
5.89
5.87
5.85
5.83
4.97
4.93
4.90
3.53
3.51
3.27
3.25
2.98
2.95
2.92
2.75
2.66
2.25
2.22
2.16
1.76
1.69
1.66
1.57
1.51
1.34
1.31
1.28
1.15
1.13
1.10
0.90
0.81
0.61
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.99
1.07
1.85
1.11
0.76
0.93
0.84
0.86
0.79
1.90
2.04
2.42
3.24
0.93
1.73
1.14
0.95
0.87
1.22
1.36
5.09
3.62
9.00
0.82
3.23
1.05


182.74
182.56
168.75
167.47
150.86
148.58
147.24
145.89
145.39
142.58
134.75
130.37
129.88
127.55
126.89
124.56
124.07
123.98
119.94
114.70
59.86
55.97
54.26
44.85
38.34
37.74
37.48
35.47
33.32
30.14
27.69
26.41
25.62
24.39
20.30
19.79
18.54
18.47
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

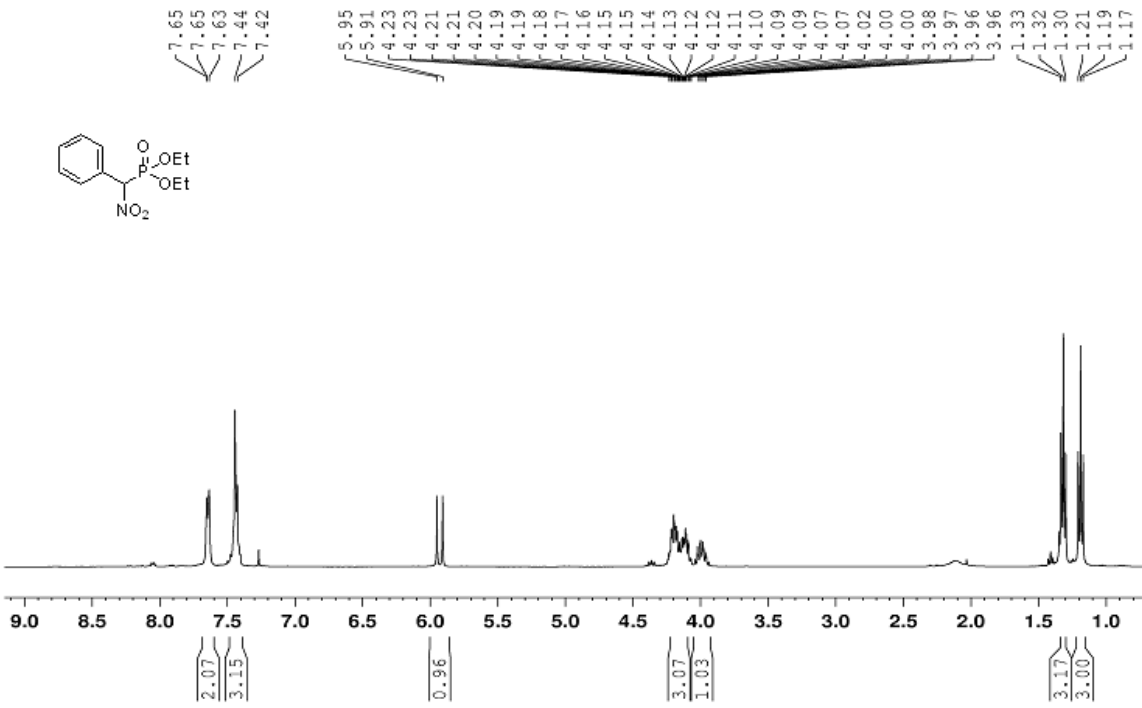
1a

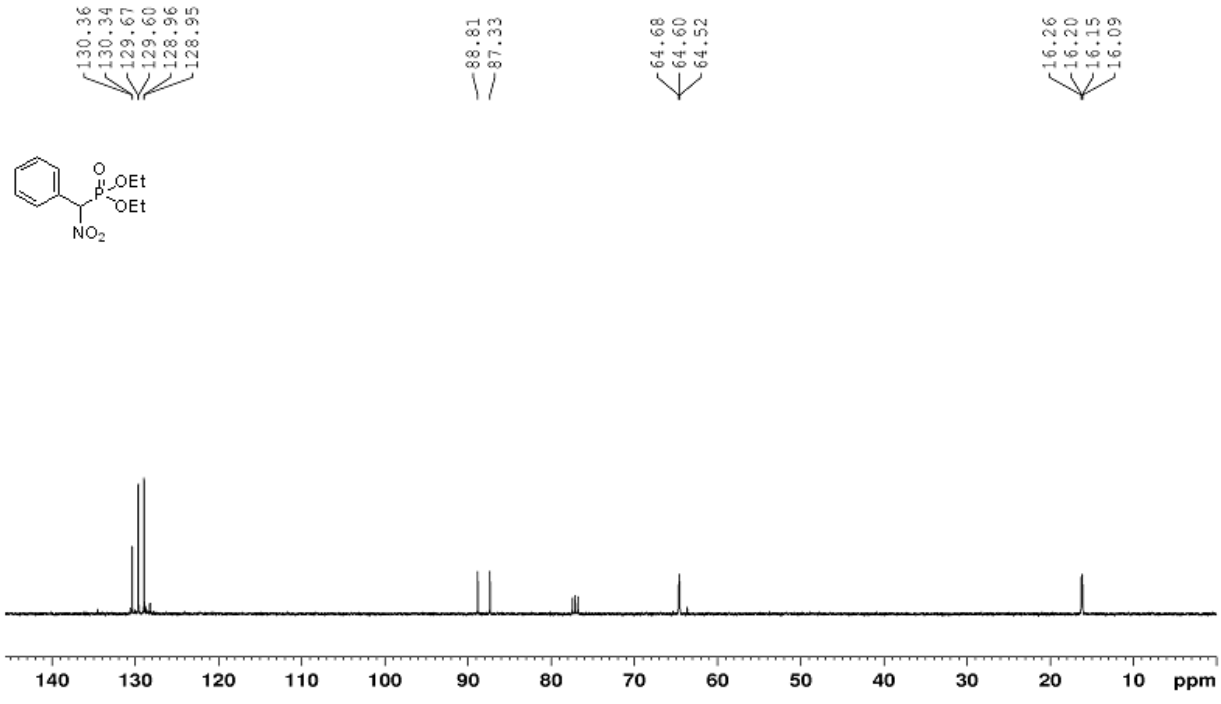

5.03
5.01
4.99
4.97
4.96
4.94
4.26
4.25
4.23
4.21
4.21
4.19
4.18
4.13
4.11
4.09
4.07
4.06
1.82
1.80
1.78
1.76
1.38
1.36
1.35
1.33
1.32
O
OEt
P
OEt
NO2
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.76
3.06
0.86
3.00
6.33

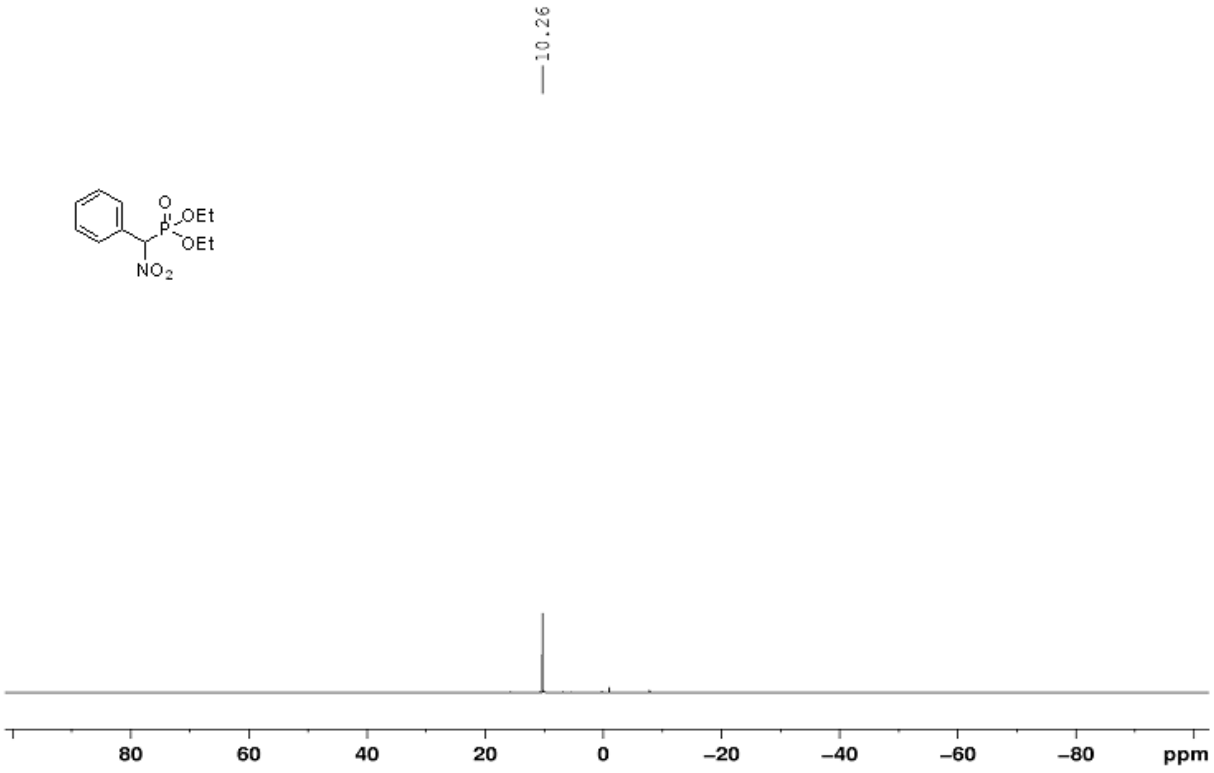

80.15
78.71
64.38
64.32
64.22
64.16
16.31
16.26
16.21
16.13
16.07
14.45
14.41
O
OEt
P
OEt
NO2
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
ppm


13.49
O
OEt
P
OEt
NO2
80
60
40
20
0
−20
−40
−60
−80
ppm

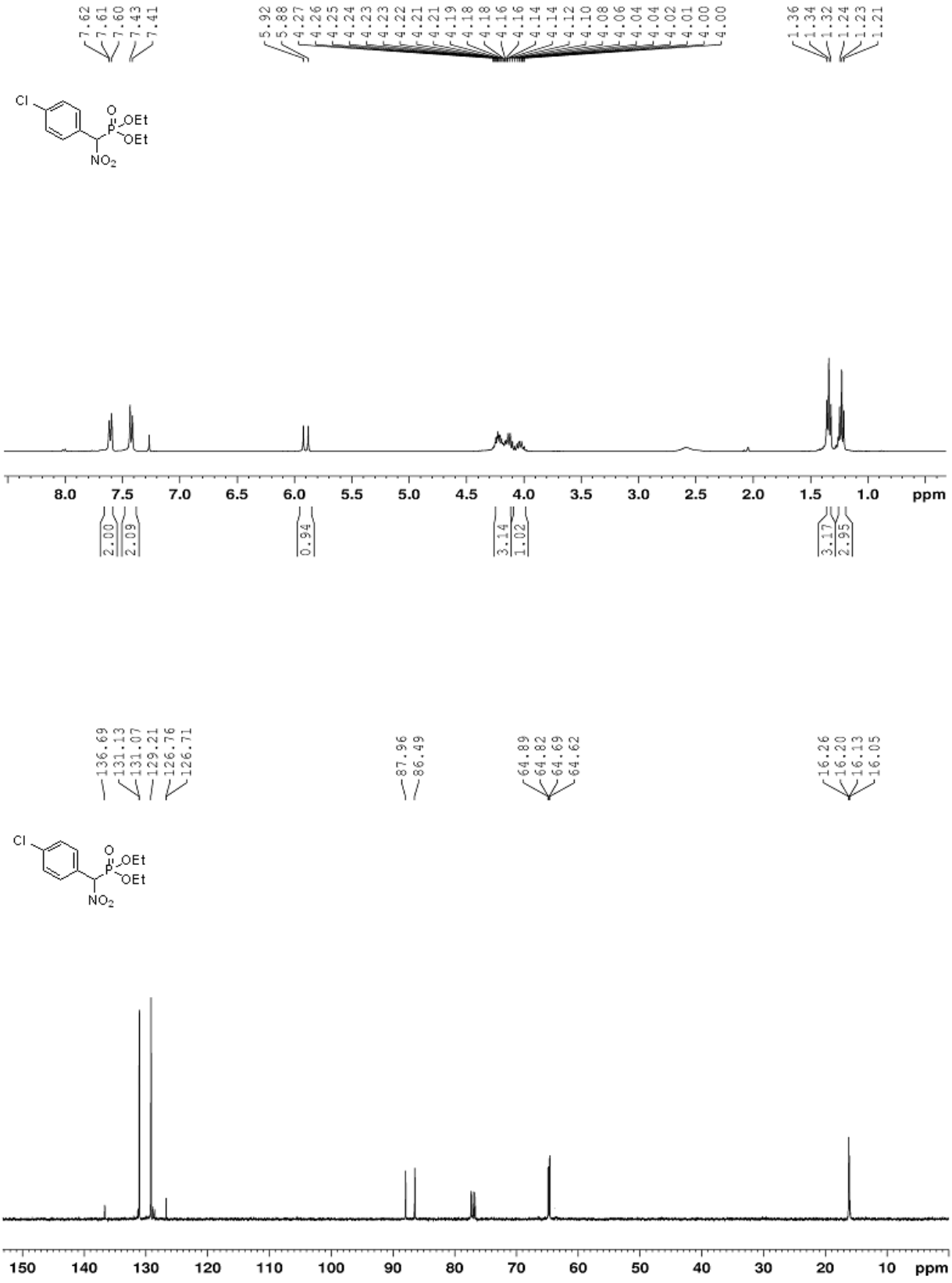
1b

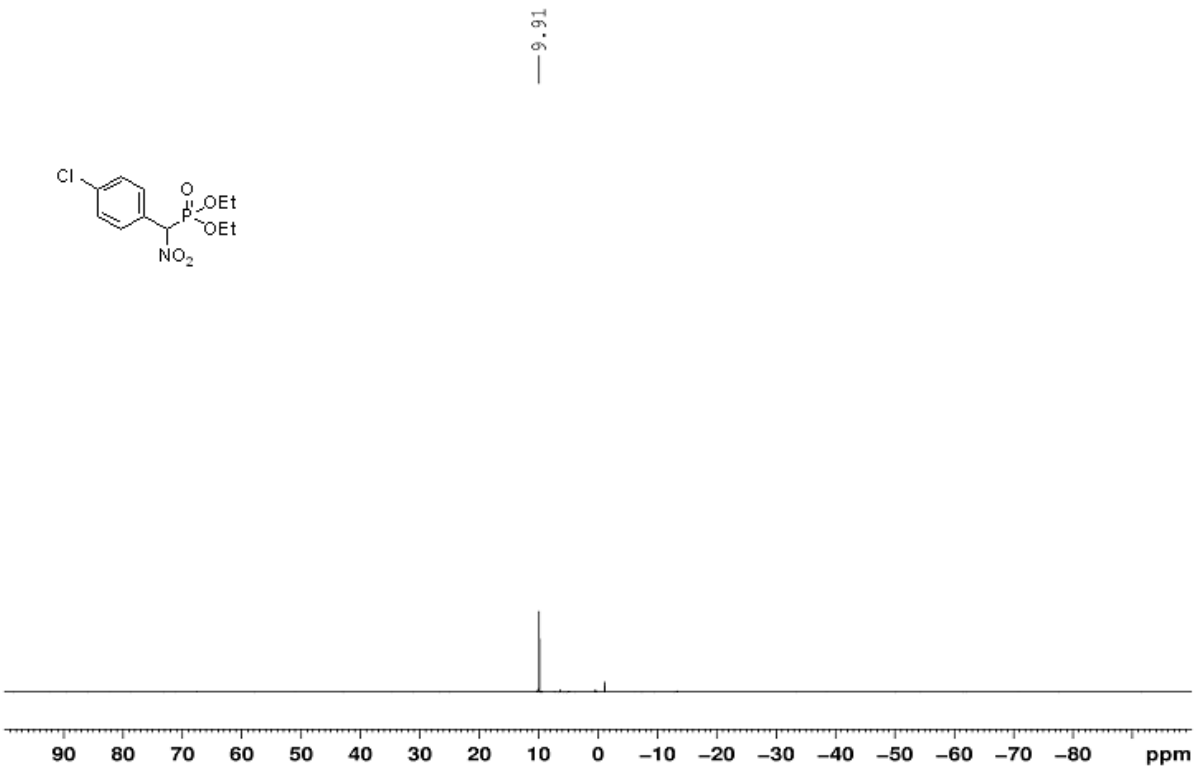

7.65
7.65
7.63
7.44
7.42
5.95
5.91
4.23
4.23
4.21
4.21
4.20
4.19
4.19
4.18
4.17
4.16
4.15
4.15
4.14
4.13
4.12
4.12
4.11
4.10
4.09
4.09
4.07
4.07
4.02
4.00
4.00
3.98
3.97
3.96
3.96
1.33
1.32
1.30
1.21
1.19
1.17
OEt
OEt
NO2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.07
3.15
0.96
3.07
1.03
3.17
3.00


130.36
130.34
129.67
129.60
128.96
128.95
88.81
87.33
64.68
64.60
64.52
16.26
16.20
16.15
16.09
OEt
OEt
NO2
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

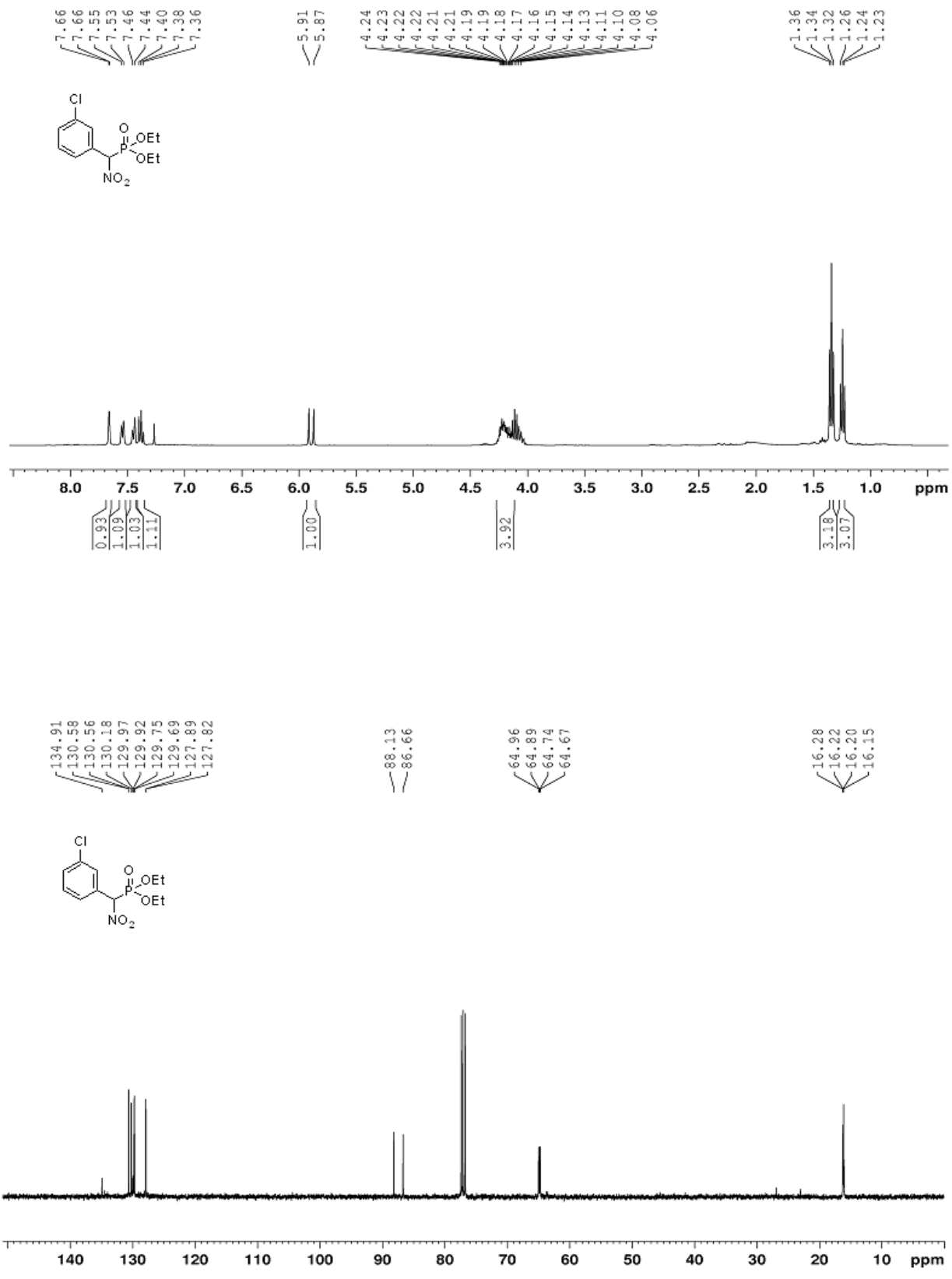

10.26
O
OEt
P
OEt
NO2
80
60
40
20
0
−20
−40
−60
−80
ppm

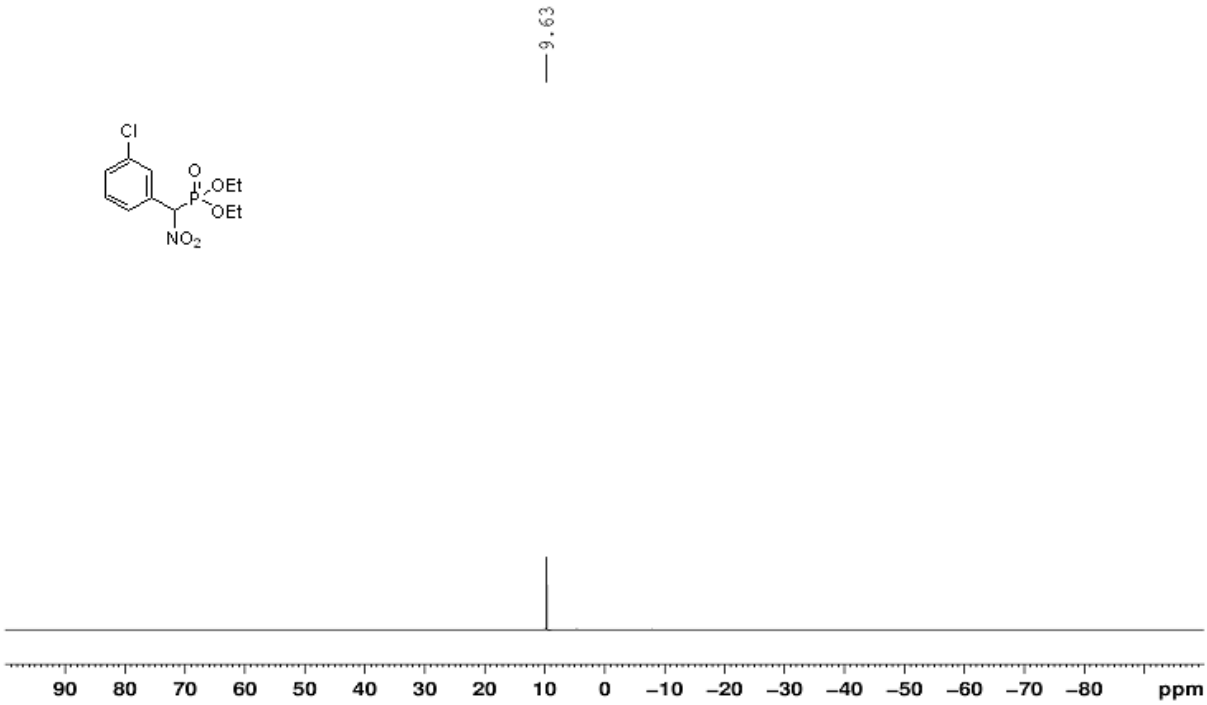
1c


7.62
7.61
7.60
7.43
7.41
5.92
5.88
4.27
4.26
4.25
4.24
4.23
4.23
4.22
4.21
4.21
4.19
4.18
4.18
4.16
4.16
4.14
4.14
4.12
4.10
4.08
4.06
4.04
4.04
4.02
4.01
4.00
4.00
1.36
1.34
1.32
1.24
1.23
1.21
Cl
O
OEt
P
OEt
NO2
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
ppm
2.00
2.09
0.94
3.14
1.02
3.17
2.95
136.69
131.13
131.07
129.21
126.76
126.71
87.96
86.49
64.89
64.82
64.69
64.62
16.26
16.20
16.13
16.05
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

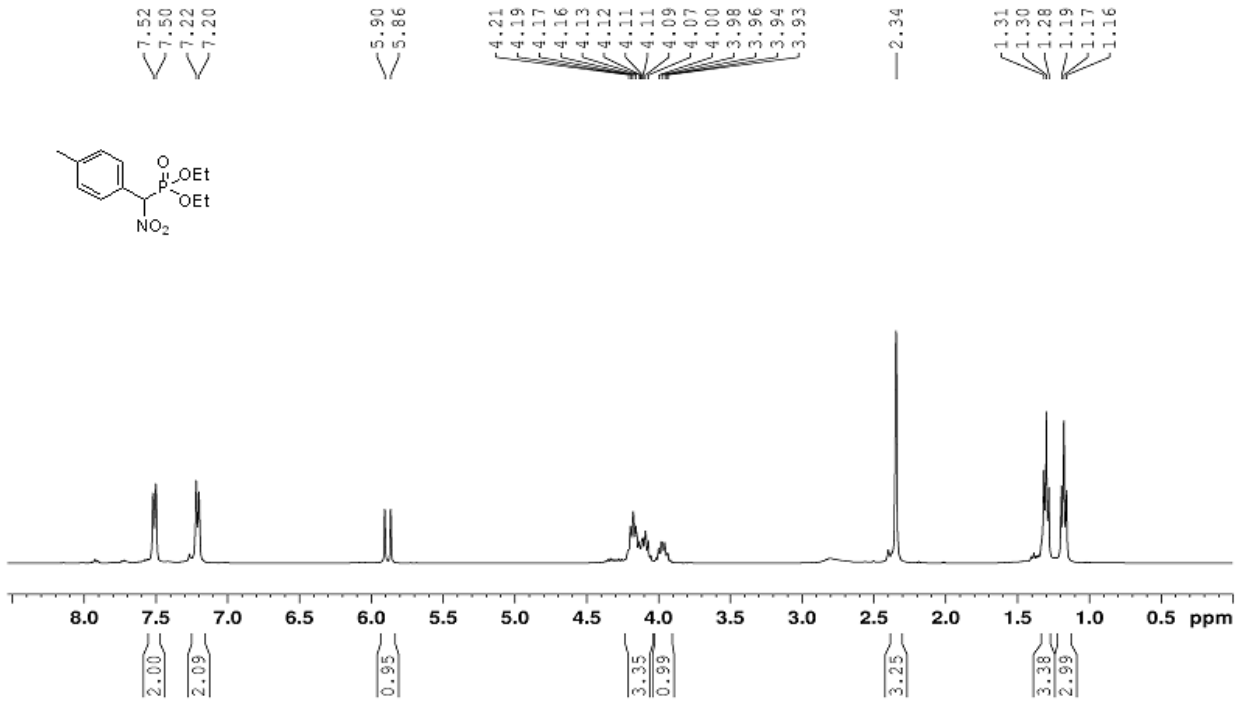

9.91
Cl
O
OEt
P
OEt
NO2
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

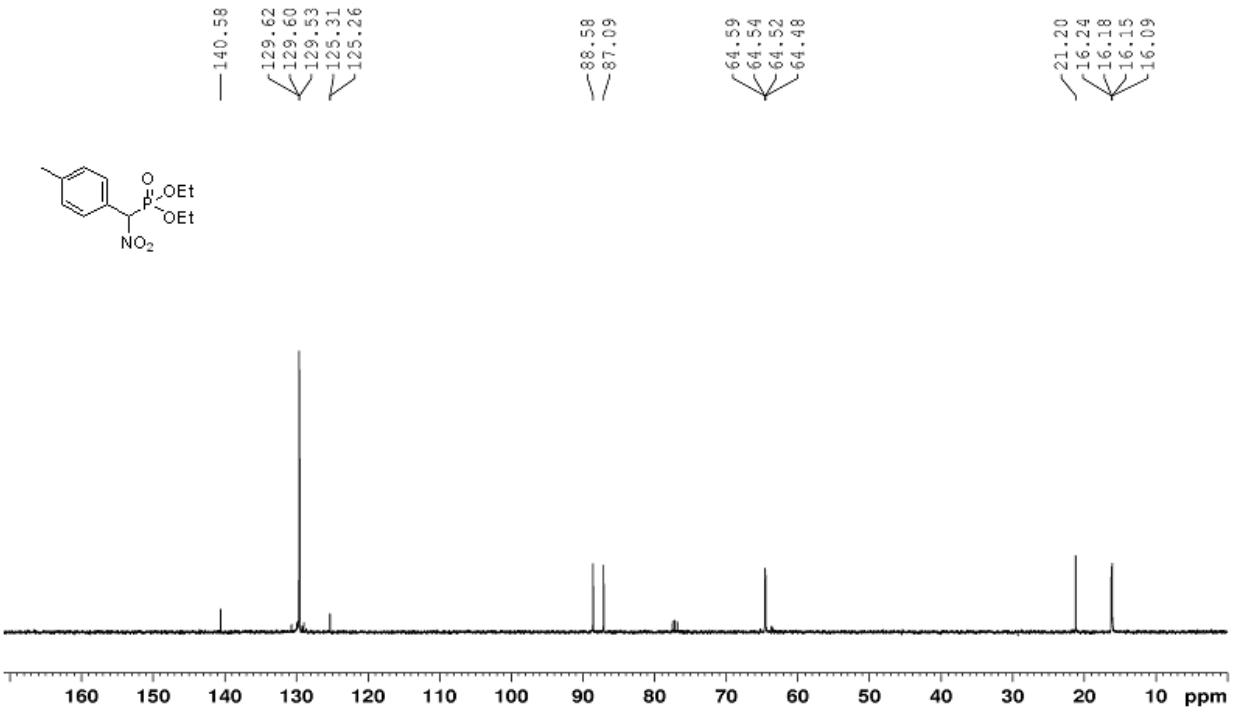
1d

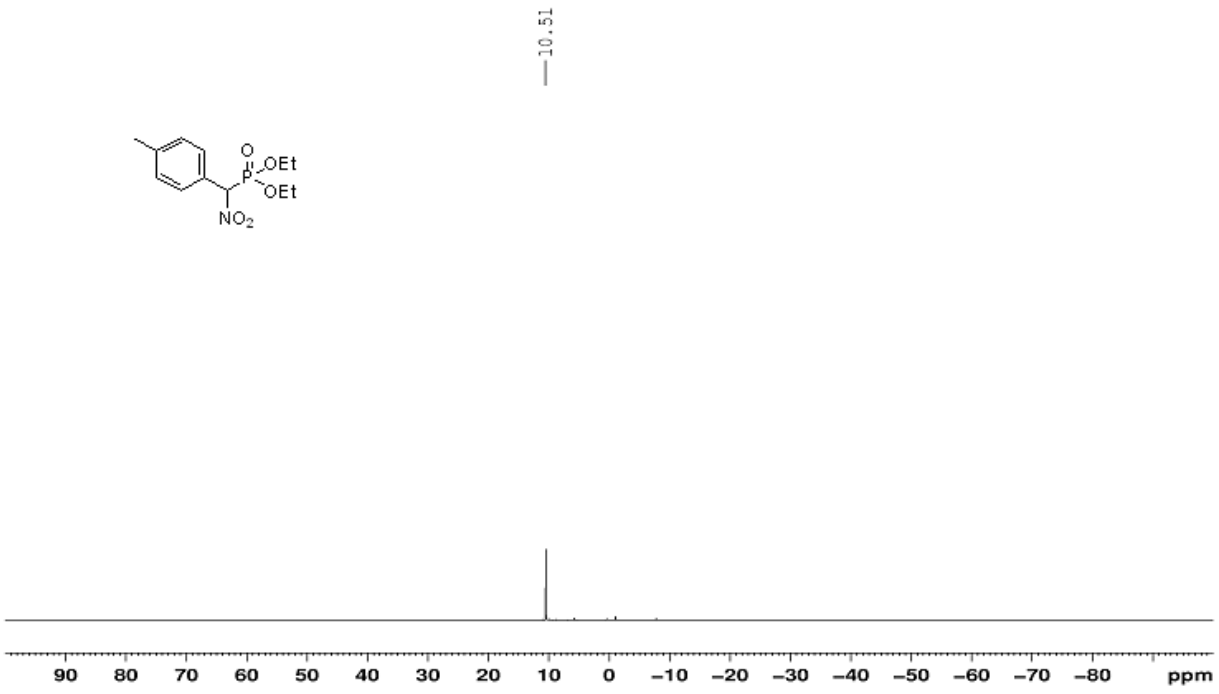

7.66
7.66
7.55
7.53
7.46
7.44
7.40
7.38
7.36
5.91
5.87
4.24
4.23
4.22
4.22
4.21
4.21
4.19
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.11
4.10
4.08
4.06
1.36
1.34
1.32
1.26
1.24
1.23
Cl
O
OEt
P
OEt
NO2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.93
1.09
1.03
1.11
1.00
3.92
3.18
3.07
134.91
130.58
130.56
130.18
129.97
129.92
129.75
129.69
127.89
127.82
88.13
86.66
64.96
64.89
64.74
64.67
16.28
16.22
16.20
16.15
Cl
O
OEt
P
OEt
NO2
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.63
Cl
O
OEt
P
OEt
NO2
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

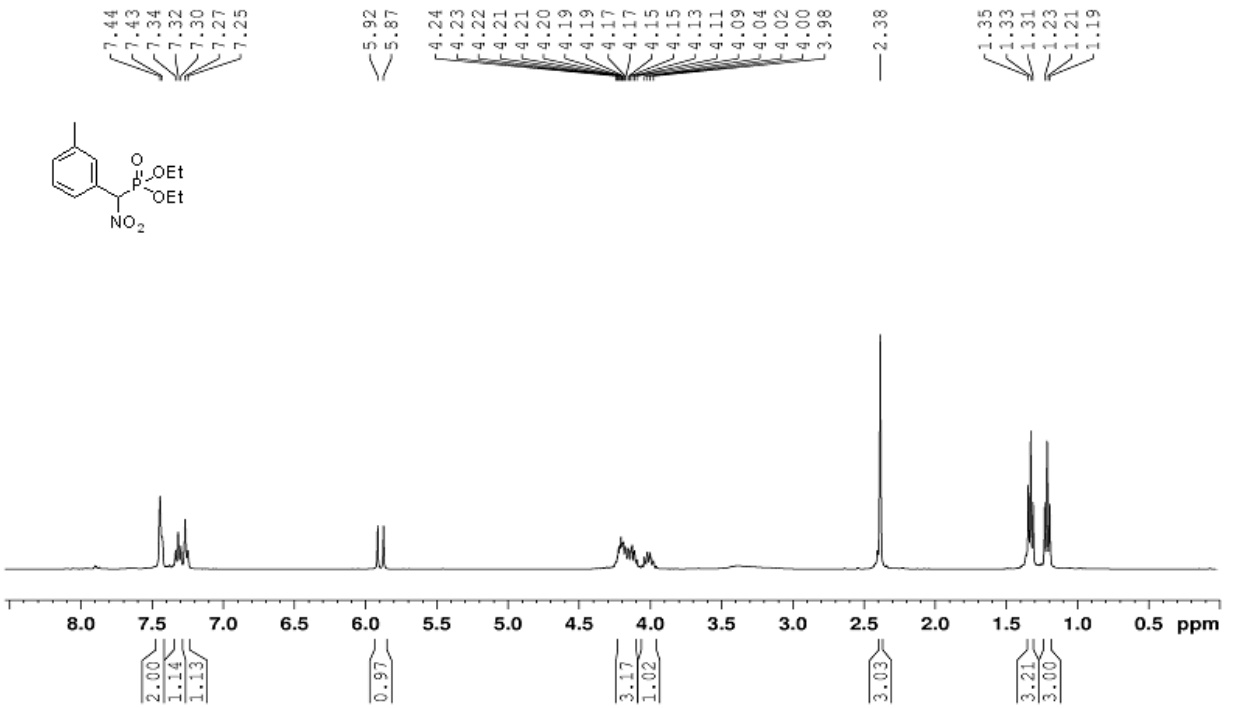
1e

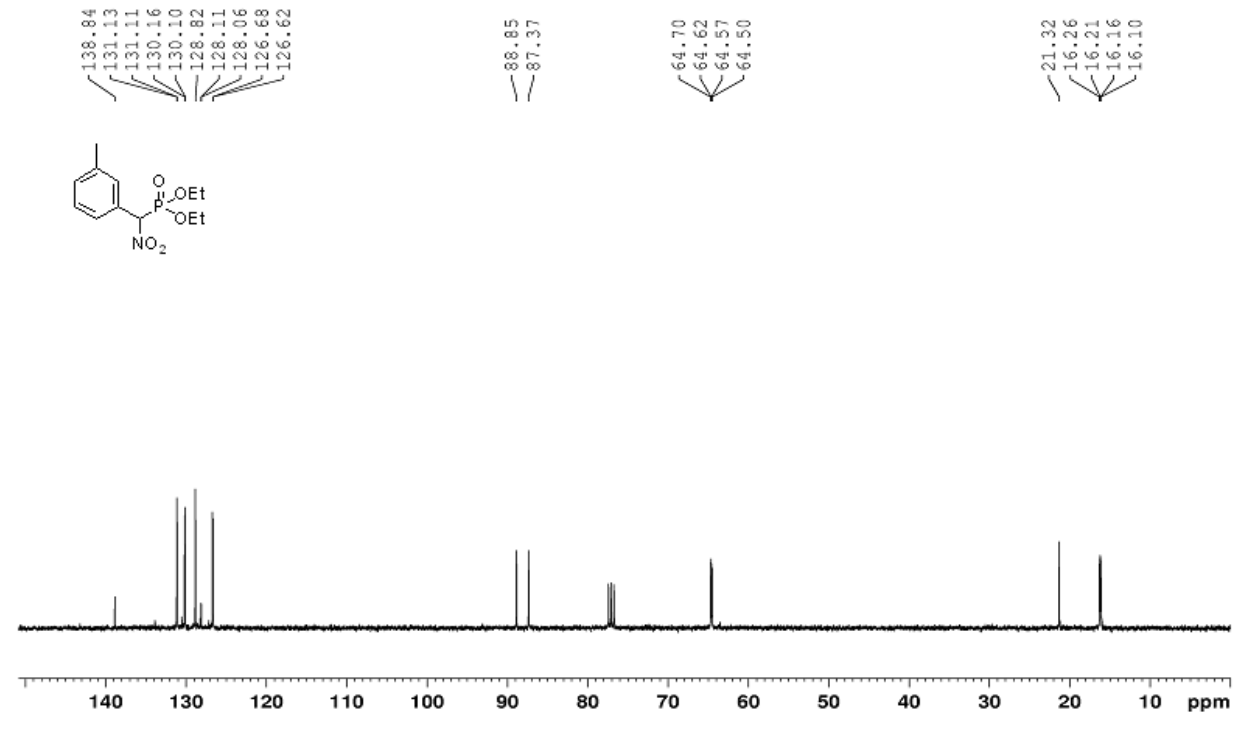

7.52
7.50
7.22
7.20
5.90
5.86
4.21
4.19
4.17
4.16
4.13
4.12
4.11
4.11
4.09
4.07
4.00
3.98
3.96
3.94
3.93
2.34
1.31
1.30
1.28
1.19
1.17
1.16
OEt
OEt
NO2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.09
0.95
3.35
0.99
3.25
3.38
2.99

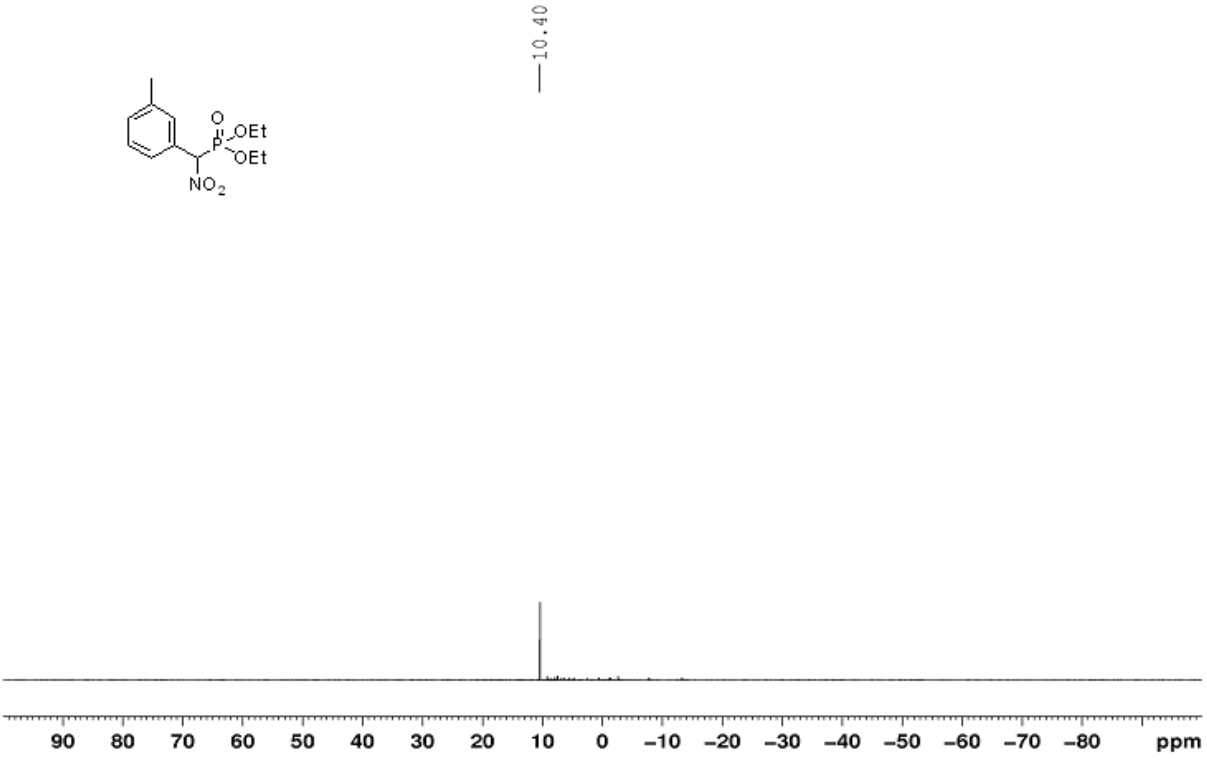

140.58
129.62
129.60
129.53
125.31
125.26
88.58
87.09
64.59
64.54
64.52
64.48
21.20
16.24
16.18
16.15
16.09
OEt
OEt
NO2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


10.51
O
OEt
P
OEt
NO2
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

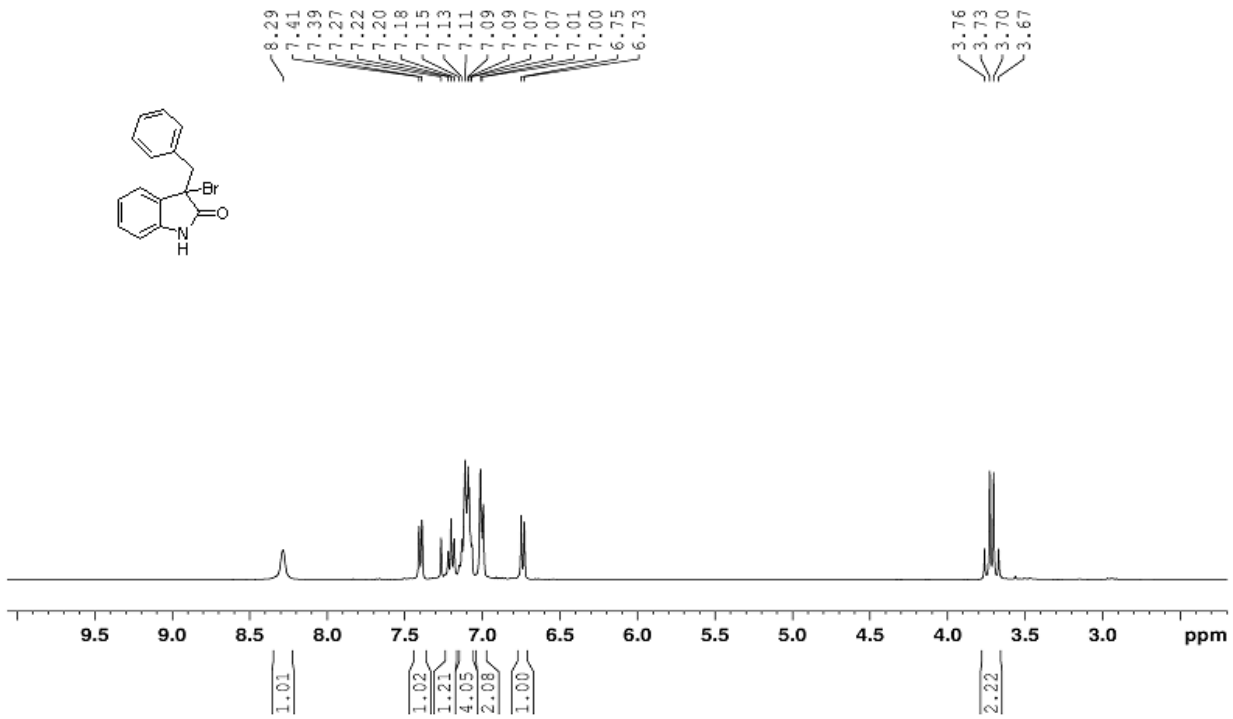
1f

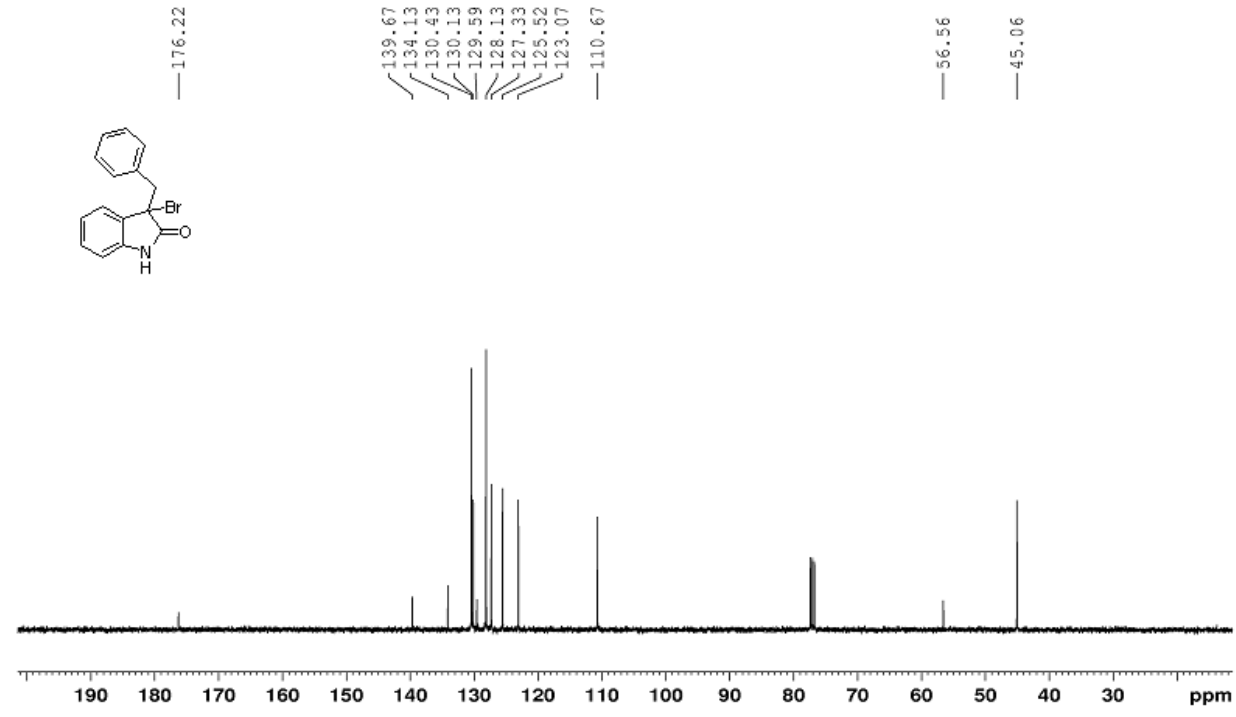

7.44
7.43
7.34
7.32
7.30
7.27
7.25
5.92
5.87
4.24
4.23
4.22
4.21
4.21
4.20
4.19
4.19
4.17
4.17
4.15
4.15
4.13
4.11
4.09
4.04
4.02
4.00
3.98
2.38
1.35
1.33
1.31
1.23
1.21
1.19
OEt
OEt
NO2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.14
1.13
0.97
3.17
1.02
3.03
3.21
3.00


138.84
131.13
131.11
130.16
130.10
128.82
128.11
128.06
126.68
126.62
88.85
87.37
64.70
64.62
64.57
64.50
21.32
16.26
16.21
16.16
16.10
OEt
OEt
NO2
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

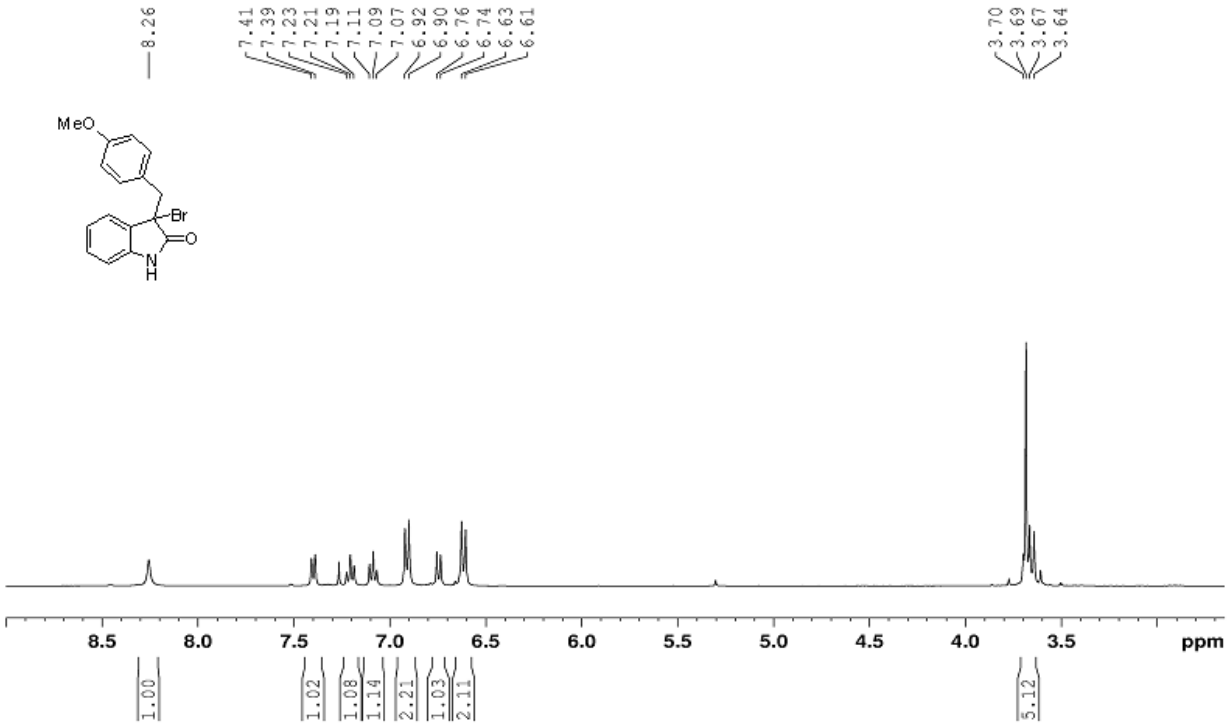

10.40
O
OEt
P
OEt
NO2
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 ppm

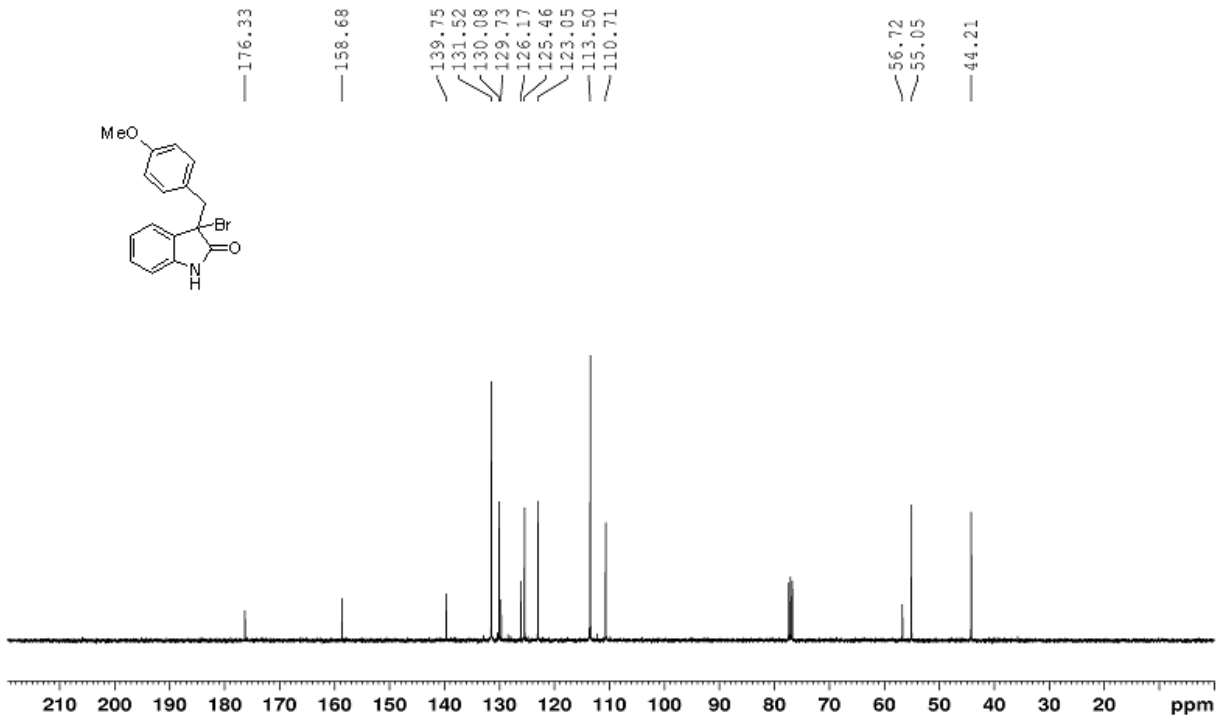
2a


8.29
7.41
7.39
7.27
7.22
7.20
7.18
7.15
7.13
7.11
7.09
7.09
7.07
7.07
7.01
7.00
6.75
6.73
3.76
3.73
3.70
3.67
Br
O
N
H
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
ppm
1.01
1.02
1.21
4.05
2.08
1.00
2.22

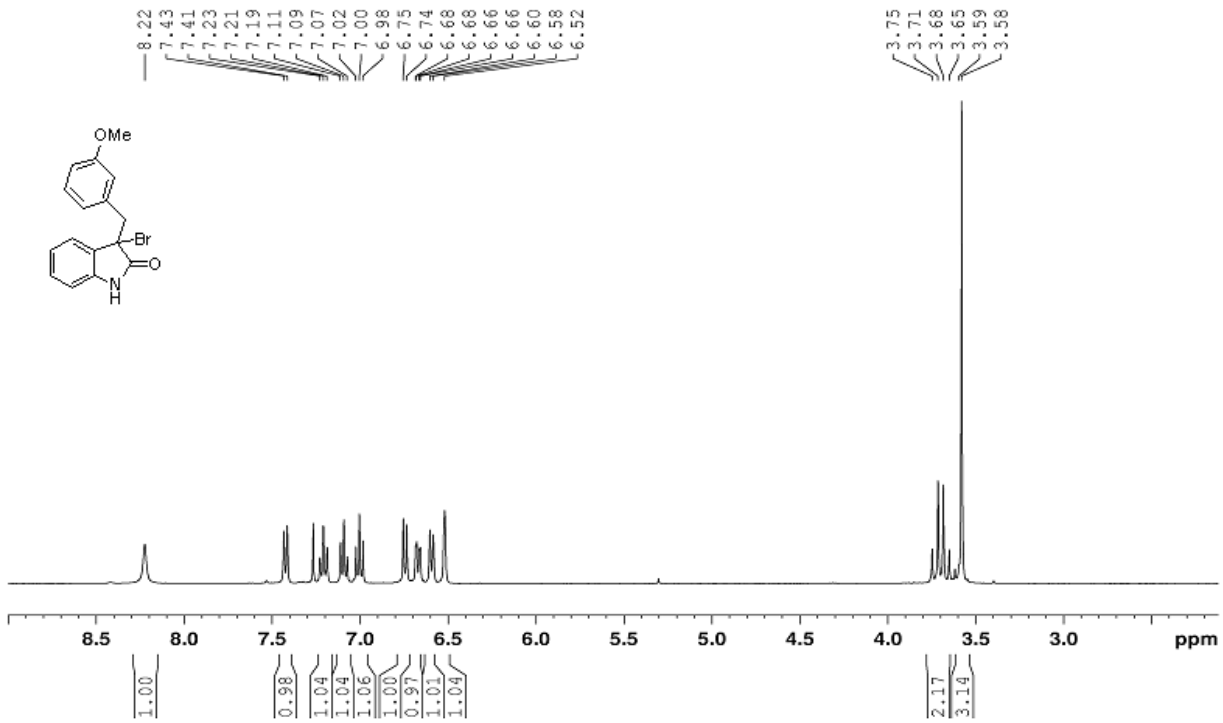

176.22
139.67
134.13
130.43
130.13
129.59
128.13
127.33
125.52
123.07
110.67
56.56
45.06
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

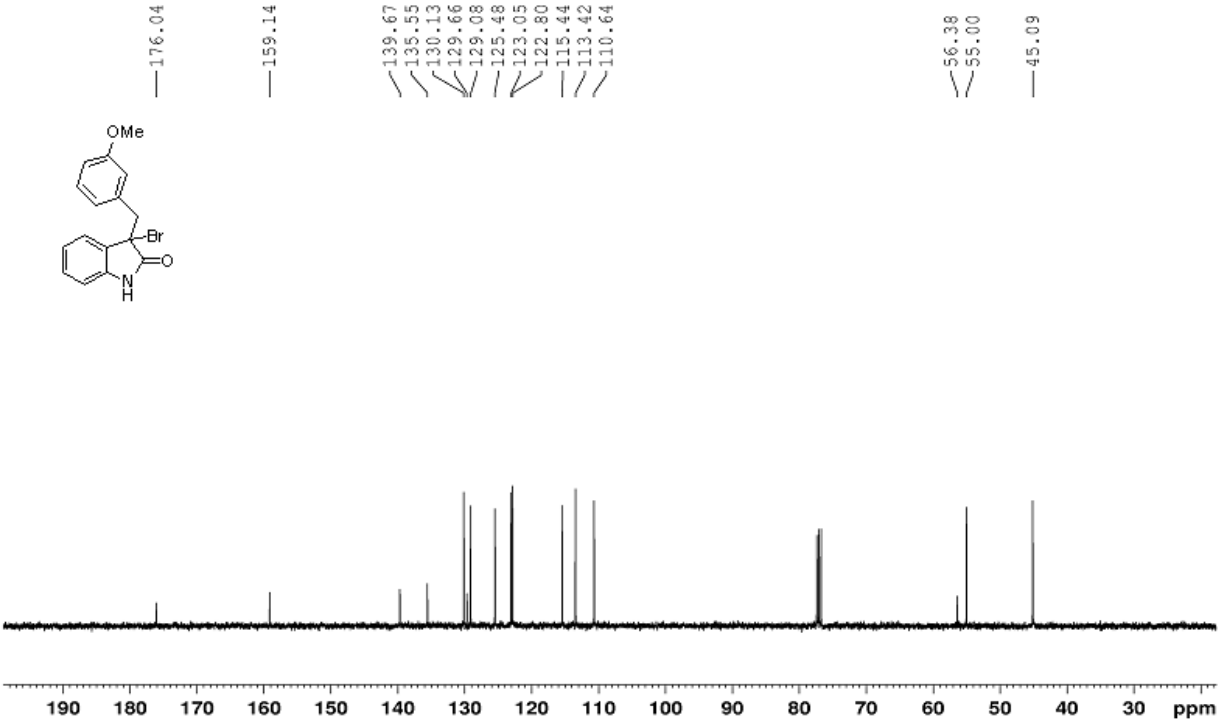
2b


8.26
7.41
7.39
7.23
7.21
7.19
7.11
7.09
7.07
6.92
6.90
6.76
6.74
6.63
6.61
3.70
3.69
3.67
3.64
MeO
Br
O
N
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
1.00
1.02
1.08
1.14
2.21
1.03
2.11
5.12

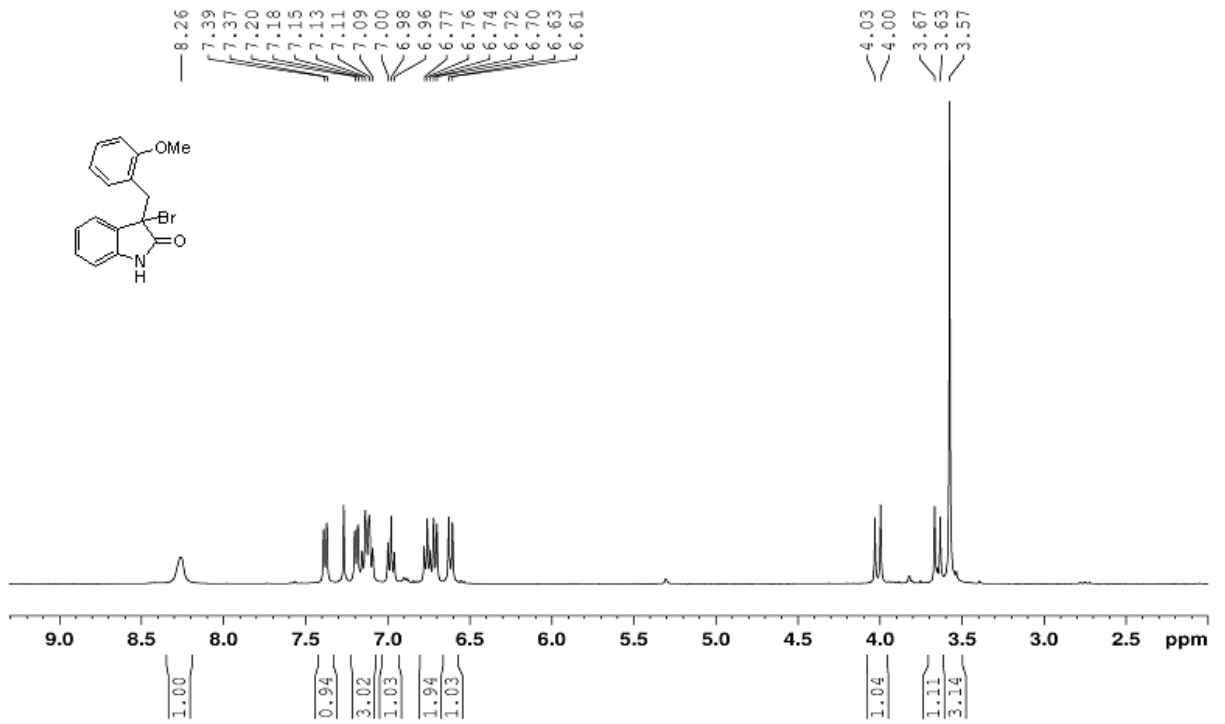

176.33
158.68
139.75
131.52
130.08
129.73
126.17
125.46
123.05
113.50
110.71
56.72
55.05
44.21
MeO
Br
O
N
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

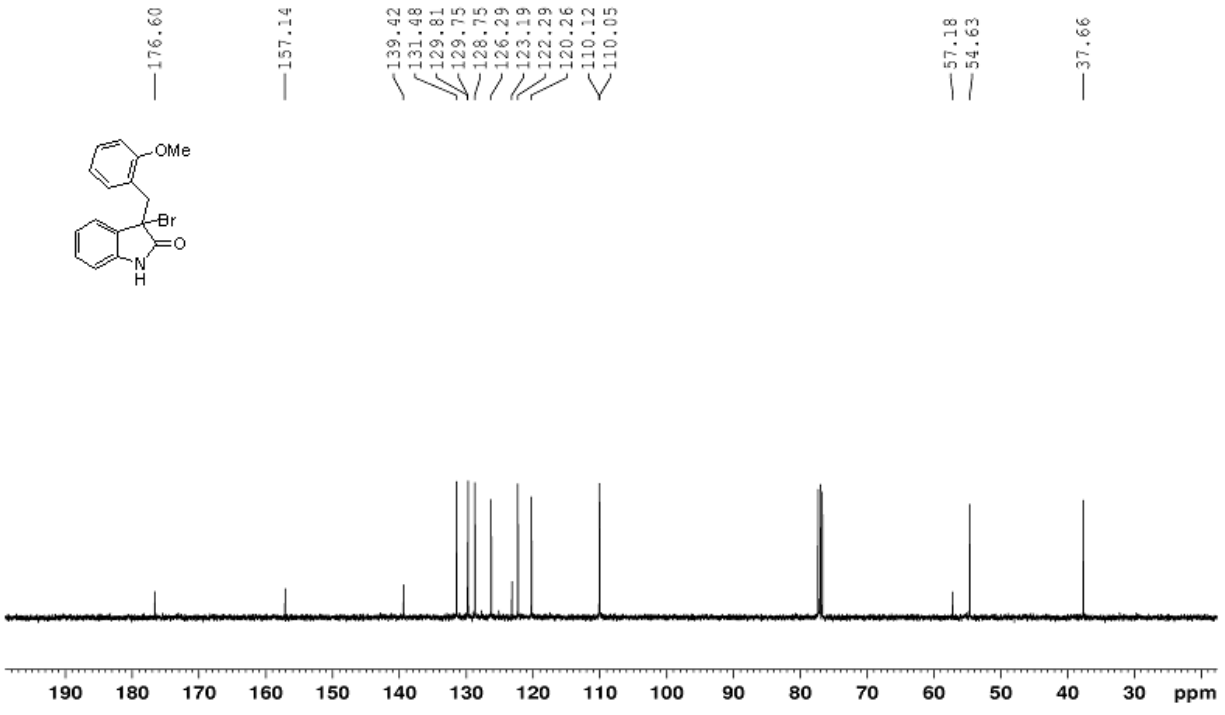
2c


8.22
7.43
7.41
7.23
7.21
7.19
7.11
7.09
7.07
7.02
7.00
6.98
6.75
6.74
6.68
6.68
6.66
6.66
6.60
6.58
6.52
3.75
3.71
3.68
3.65
3.59
3.58
OMe
Br
O
N
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.00
0.98
1.04
1.04
1.06
1.00
0.97
1.01
1.04
2.17
3.14

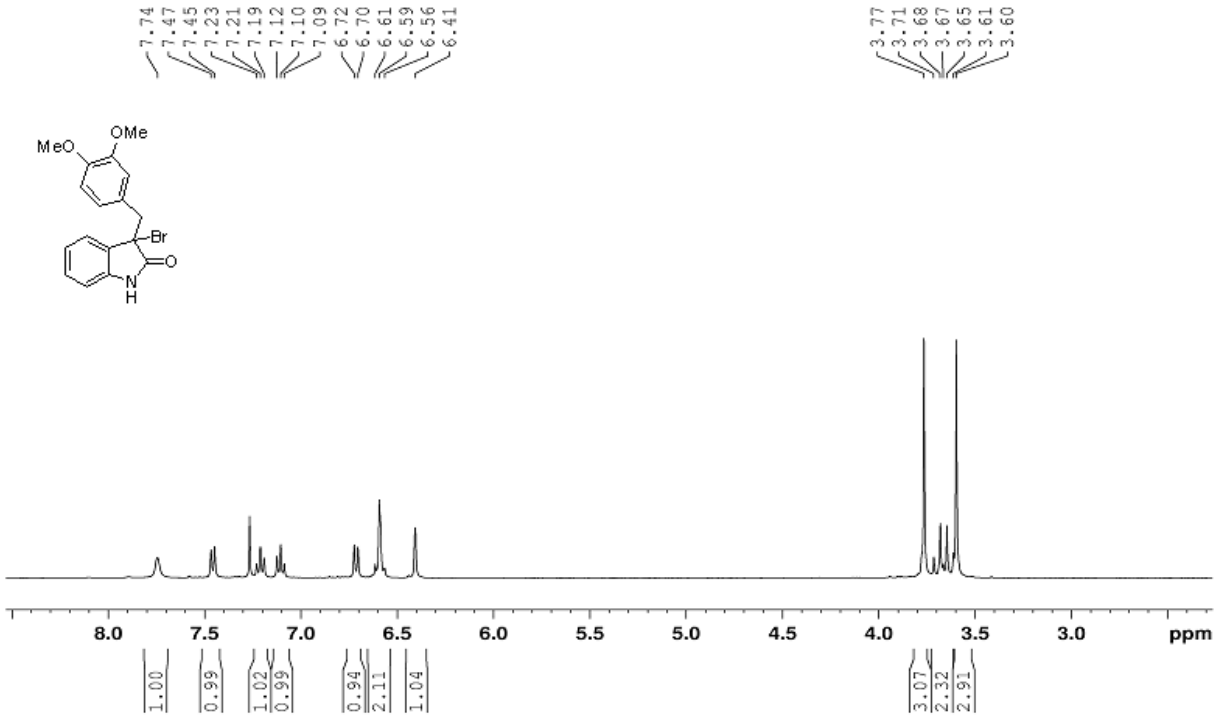

176.04
159.14
139.67
135.55
130.13
129.66
129.08
125.48
123.05
122.80
115.44
113.42
110.64
56.38
55.00
45.09
OMe
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

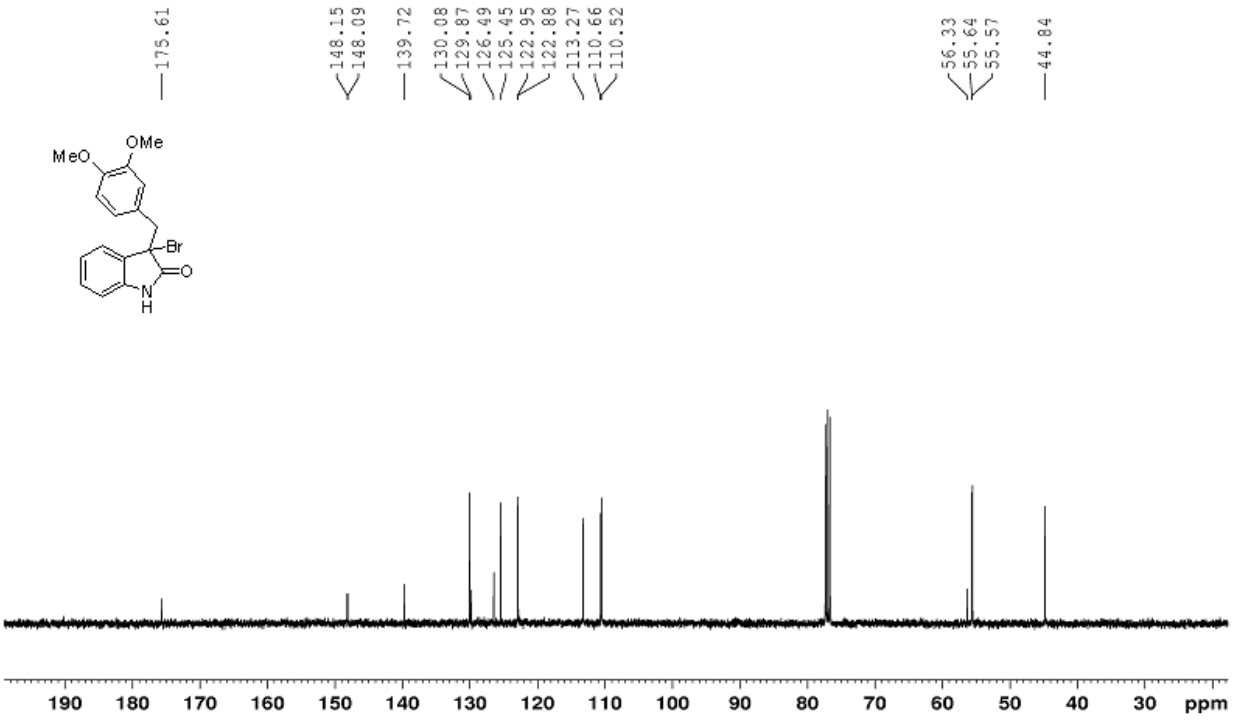
2d


8.26
7.39
7.37
7.20
7.18
7.15
7.13
7.11
7.09
7.00
6.98
6.96
6.77
6.76
6.74
6.72
6.70
6.63
6.61
4.03
4.00
3.67
3.63
3.57
OMe
Br
O
N
H
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
ppm
1.00
0.94
3.02
1.03
1.94
1.03
1.04
1.11
3.14

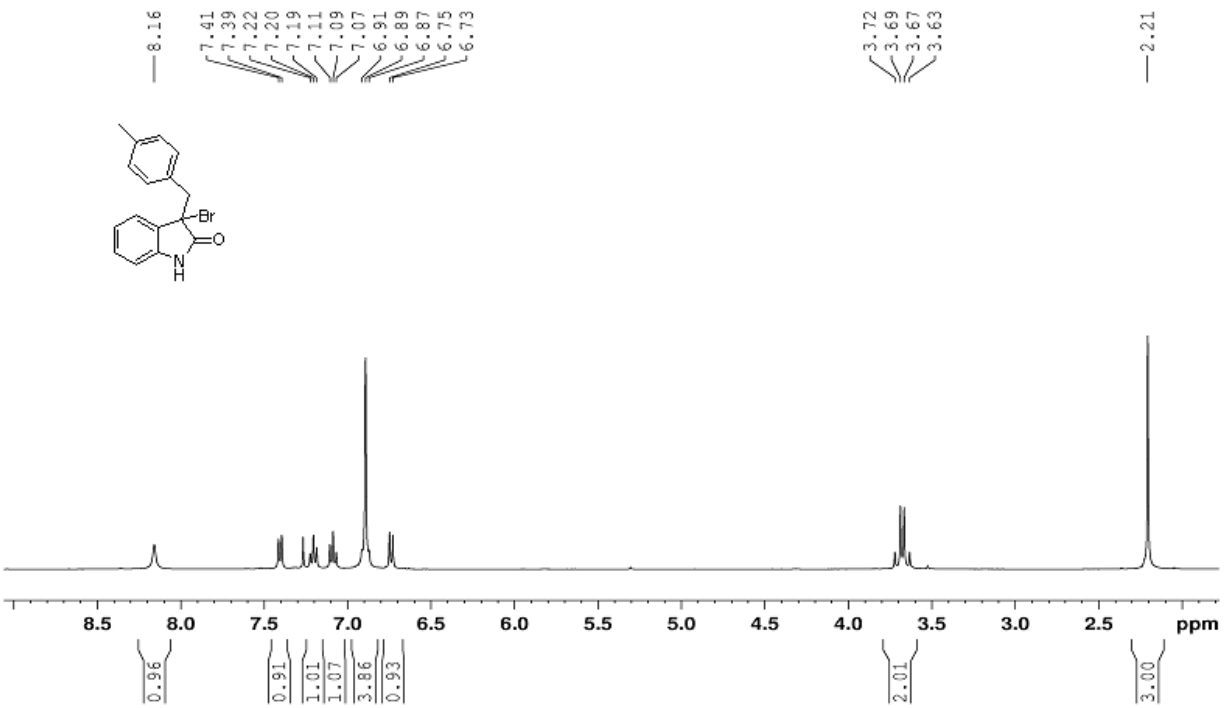

176.60
157.14
139.42
131.48
129.81
129.75
128.75
126.29
123.19
122.29
120.26
110.12
110.05
57.18
54.63
37.66
OMe
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

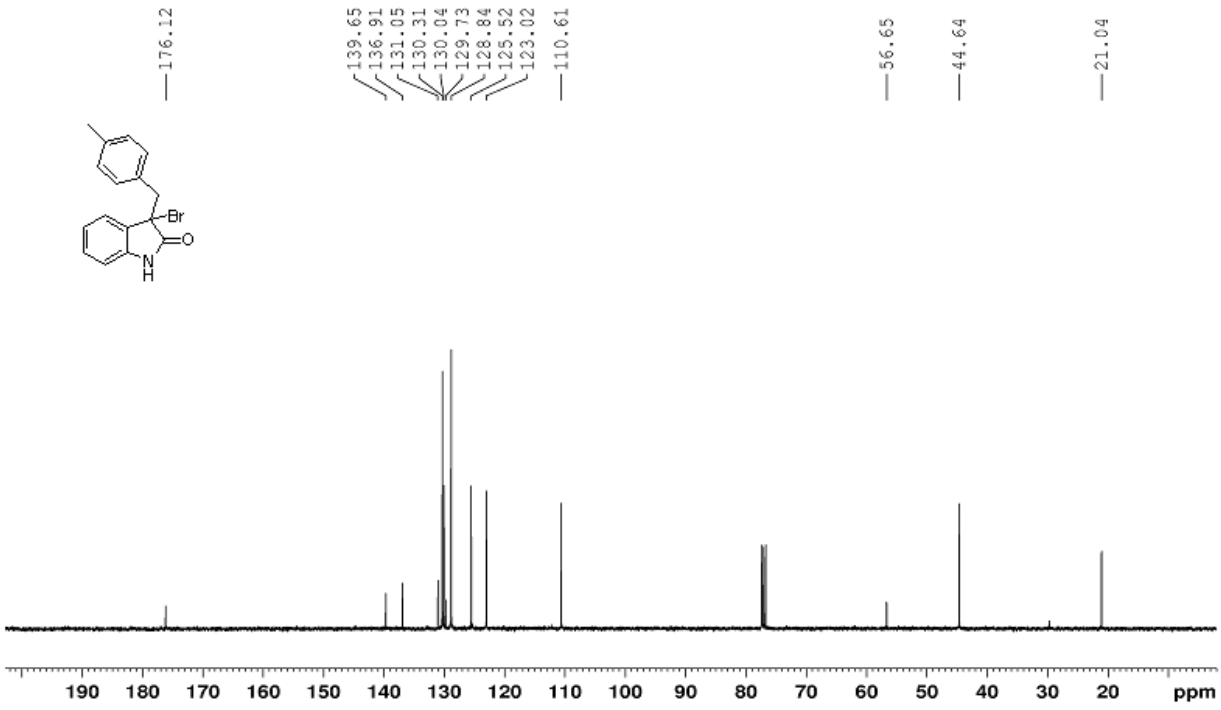
2e


7.74
7.47
7.45
7.23
7.21
7.19
7.12
7.10
7.09
6.72
6.70
6.61
6.59
6.56
6.41
3.77
3.71
3.68
3.67
3.65
3.61
3.60
MeO
OMe
Br
O
N
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.00
0.99
1.02
0.99
0.94
2.11
1.04
3.07
2.32
2.91

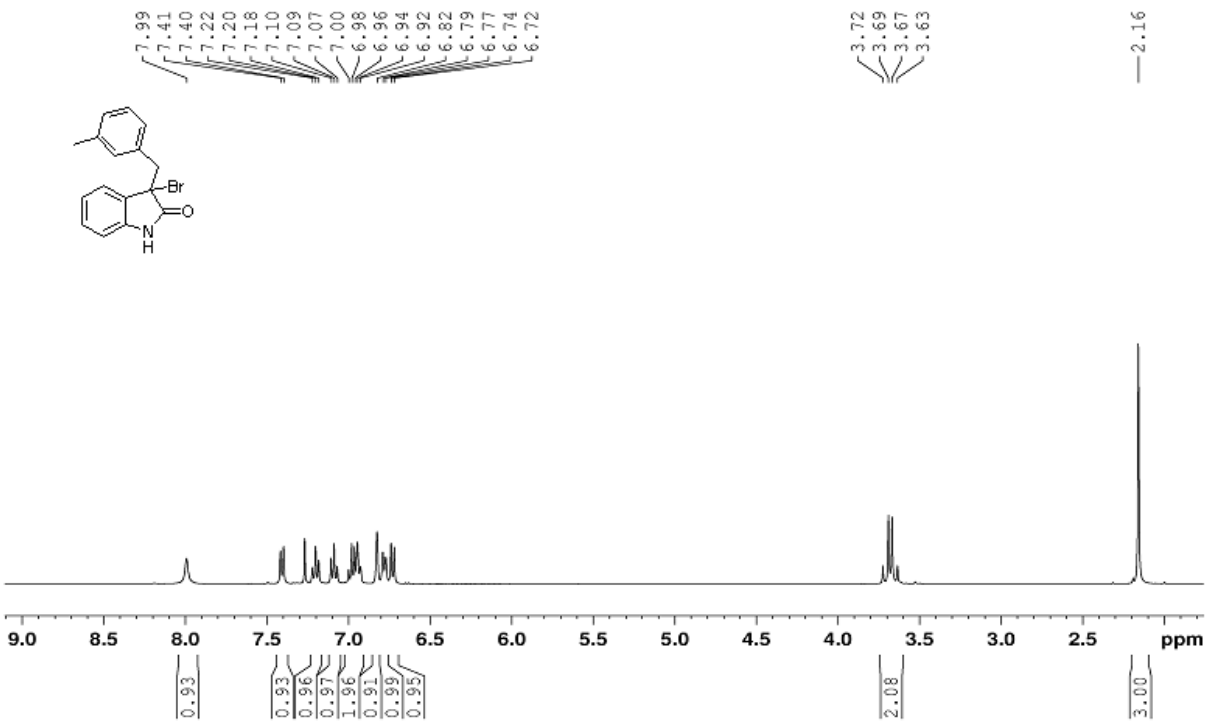

175.61
148.15
148.09
139.72
130.08
129.87
126.49
125.45
122.95
122.88
113.27
110.66
110.52
56.33
55.64
55.57
44.84
MeO
OMe
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

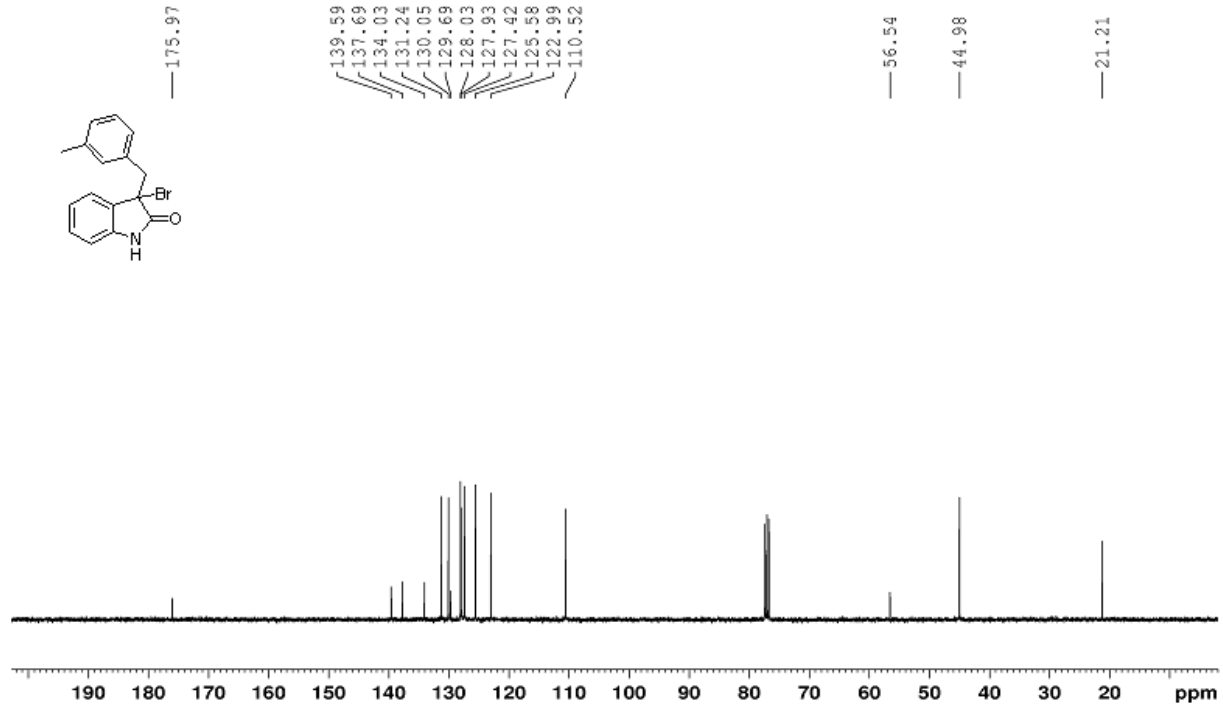
2f


8.16
7.41
7.39
7.22
7.20
7.19
7.11
7.09
7.07
6.91
6.89
6.87
6.75
6.73
3.72
3.69
3.67
3.63
2.21
Br
O
N
H
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
ppm
0.96
0.91
1.01
1.07
3.86
0.93
2.01
3.00

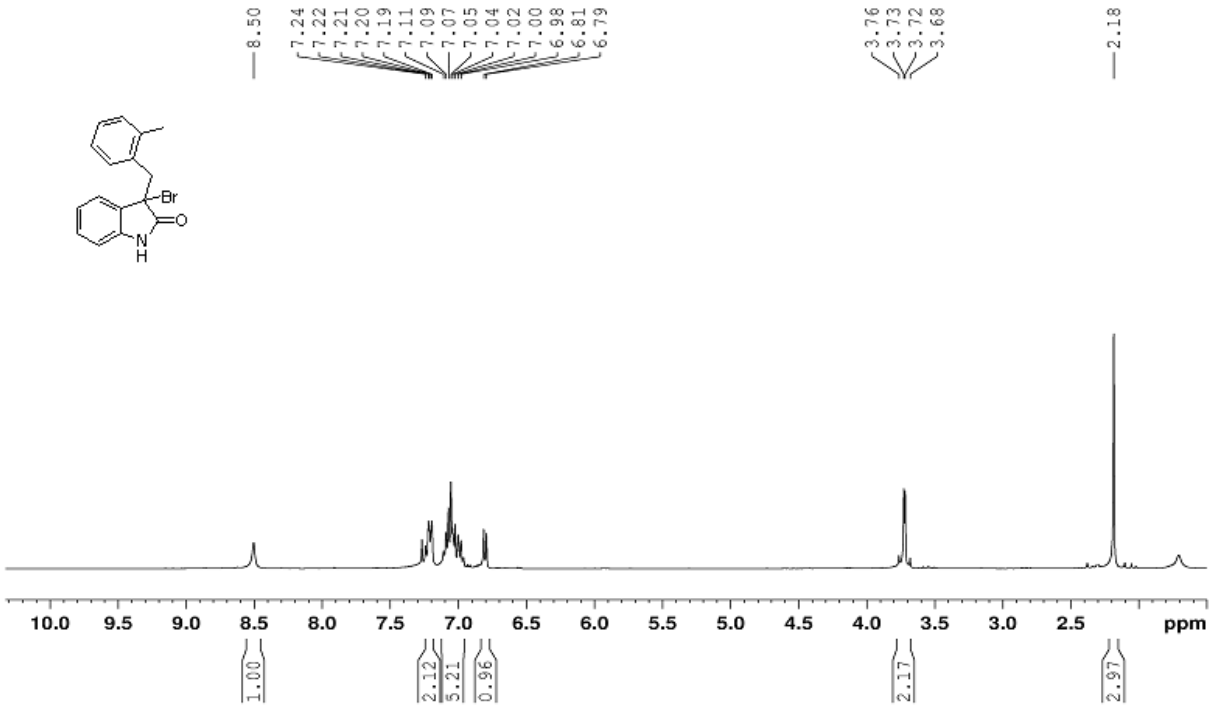

176.12
139.65
136.91
131.05
130.31
130.04
129.73
128.84
125.52
123.02
110.61
56.65
44.64
21.04
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

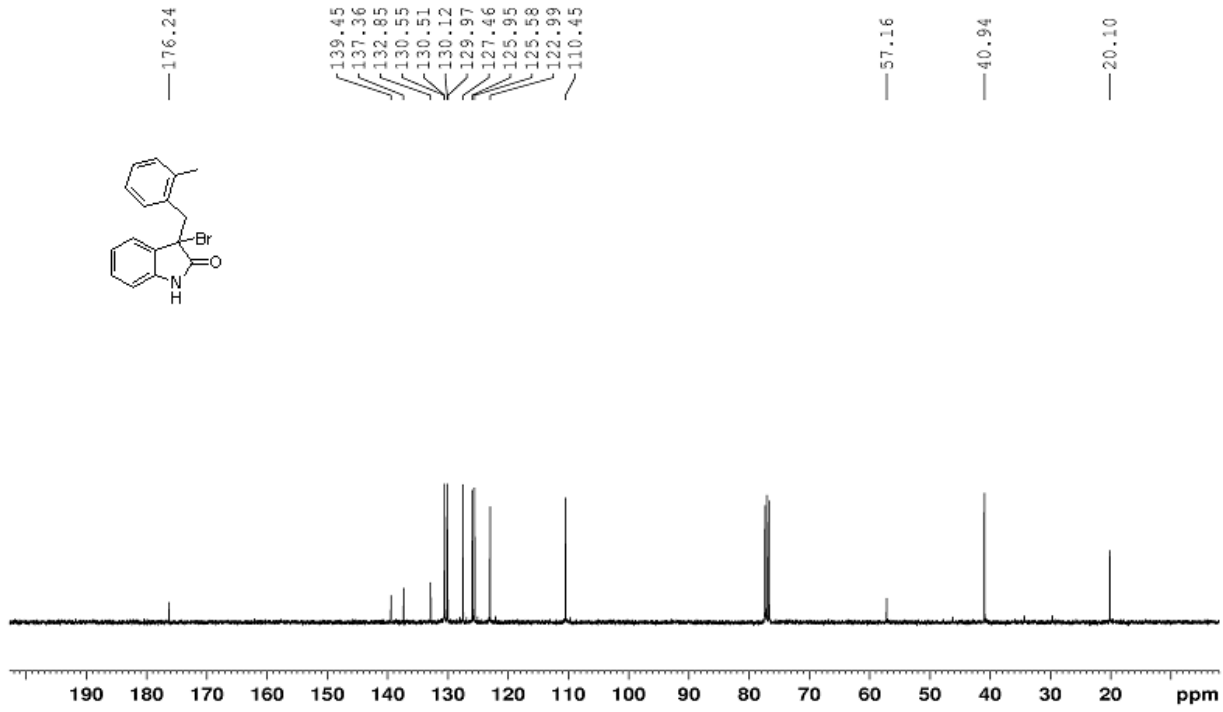
2g


7.99
7.41
7.40
7.22
7.20
7.18
7.10
7.09
7.07
7.00
6.98
6.96
6.94
6.92
6.82
6.79
6.77
6.74
6.72
3.72
3.69
3.67
3.63
2.16
Br
O
N
H
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
ppm
0.93
0.93
0.96
0.97
1.96
0.91
0.99
0.95
2.08
3.00

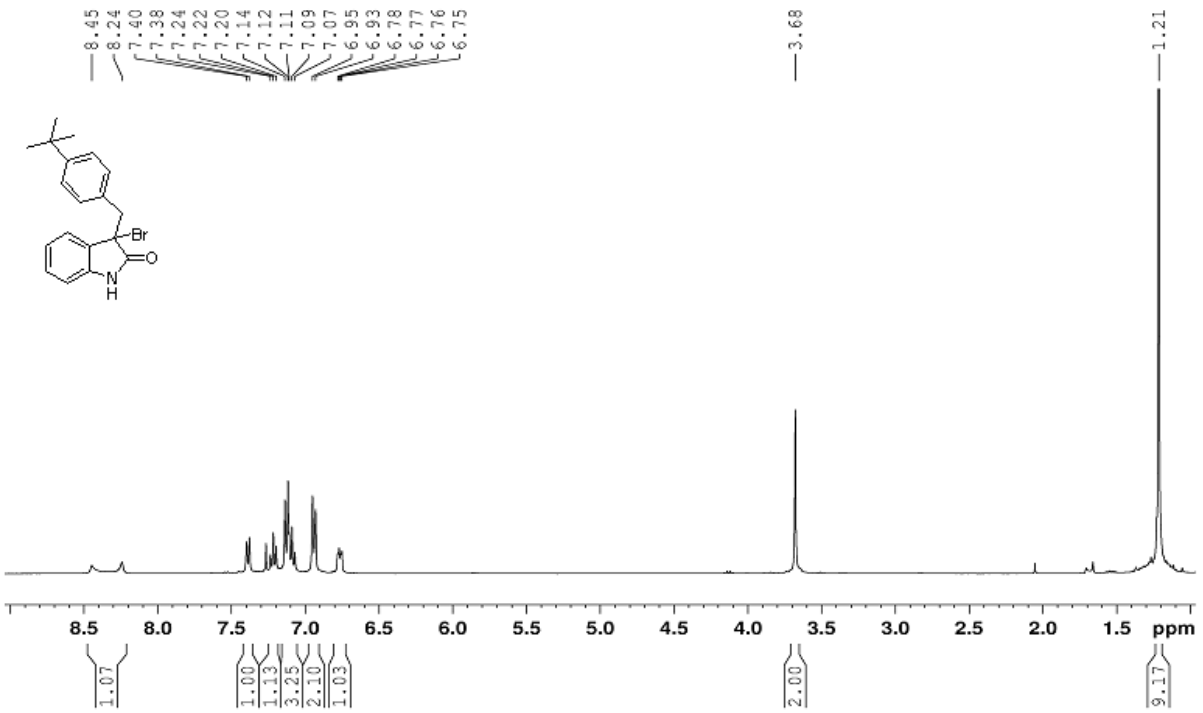

175.97
139.59
137.69
134.03
131.24
130.05
129.69
128.03
127.93
127.42
125.58
122.99
110.52
56.54
44.98
21.21
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

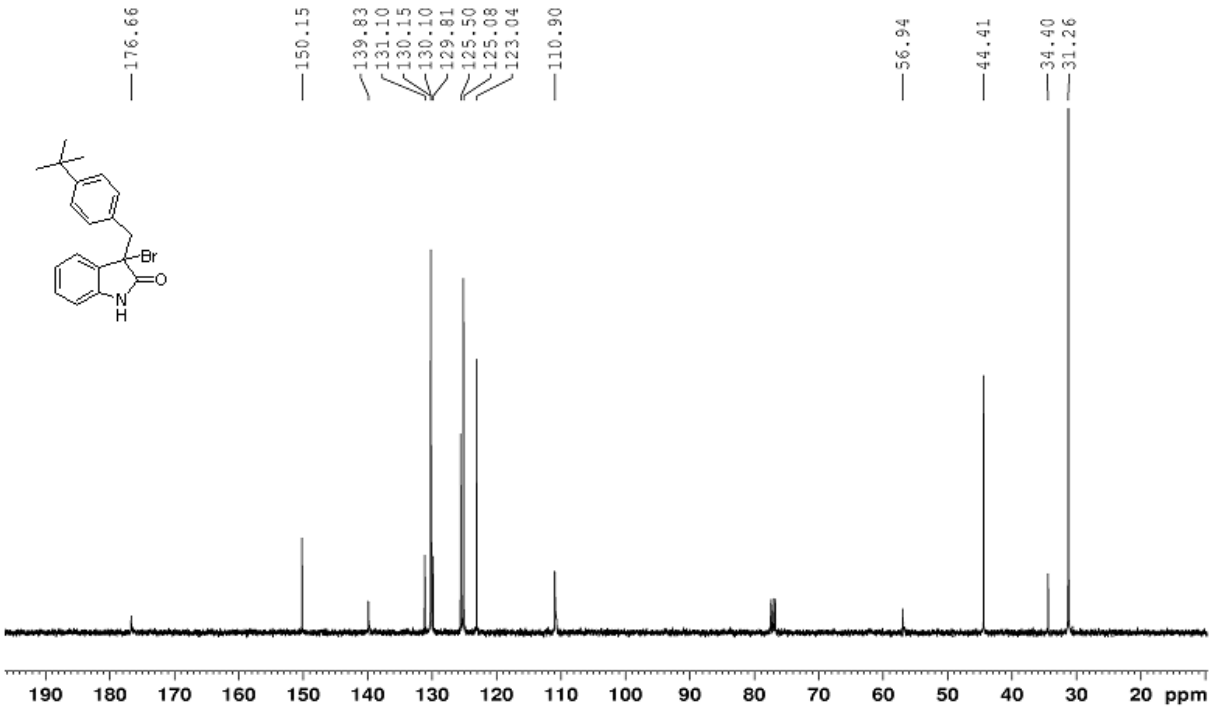
2h


8.50
7.24
7.22
7.21
7.20
7.19
7.11
7.09
7.07
7.05
7.04
7.02
7.00
6.98
6.81
6.79
3.76
3.73
3.72
3.68
2.18
Br
O
N
H
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
ppm
1.00
2.12
3.21
0.96
2.17
2.97

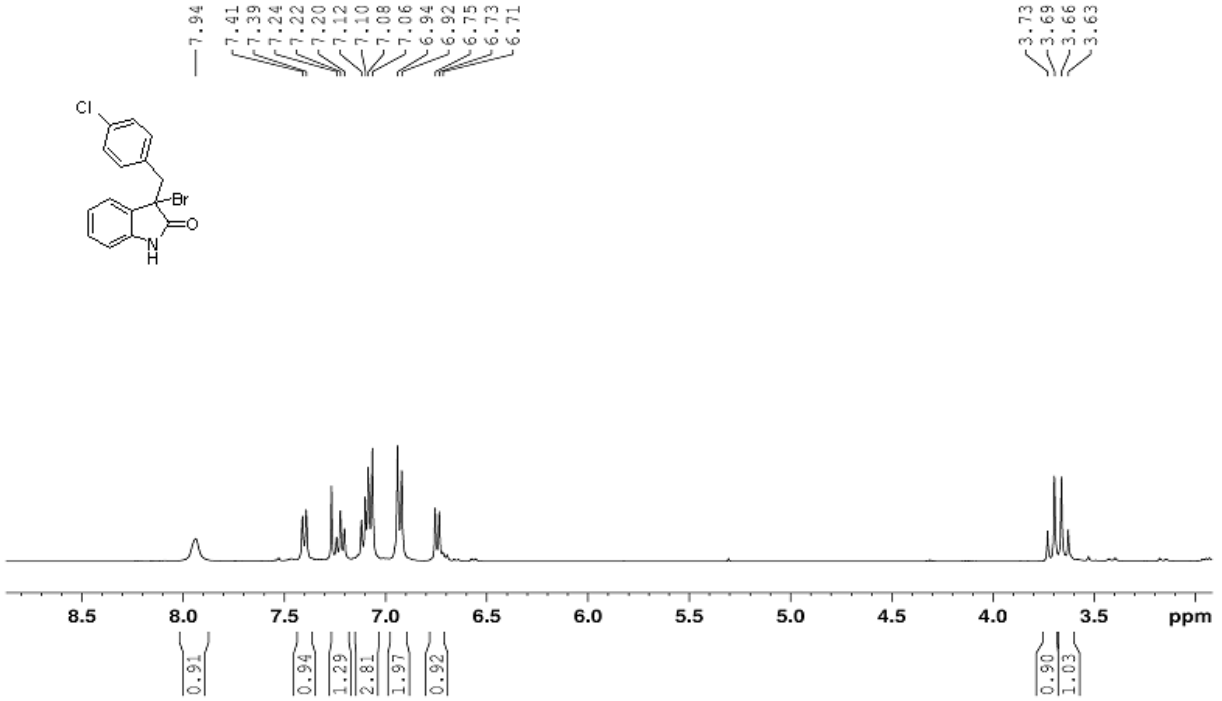

176.24
139.45
137.36
132.85
130.55
130.51
130.12
129.97
127.46
125.95
125.58
122.99
110.45
57.16
40.94
20.10
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

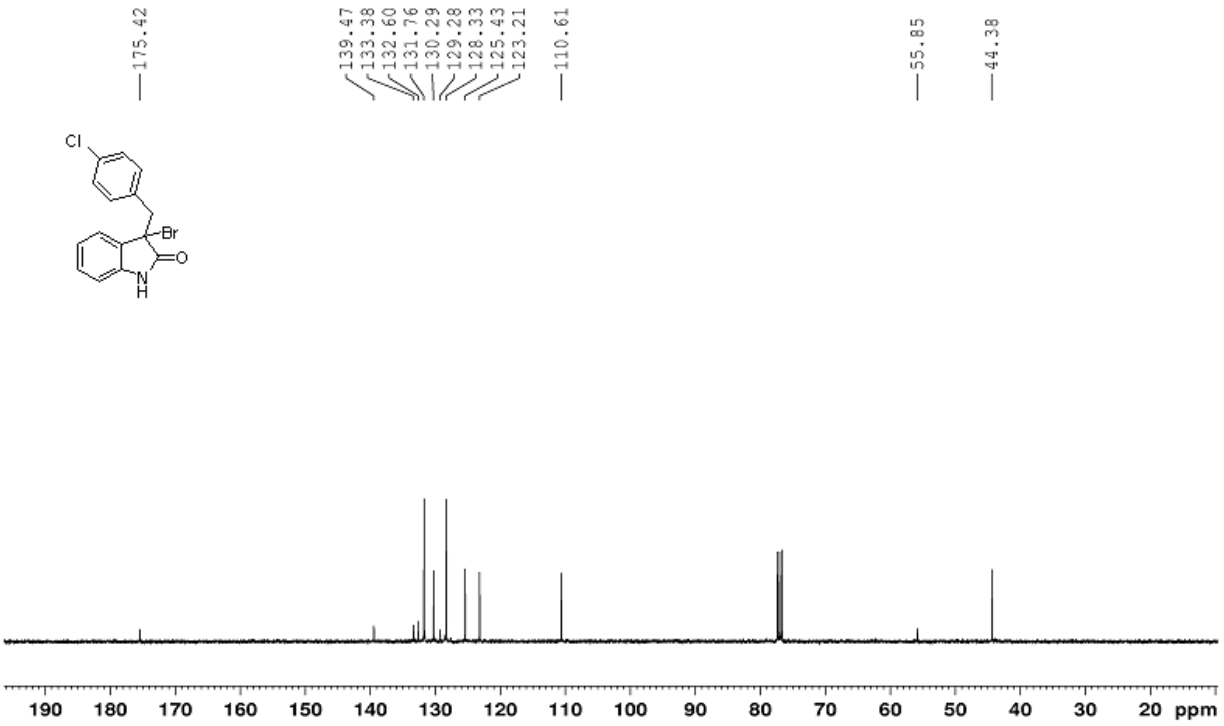
2i


8.45
8.24
7.40
7.38
7.24
7.22
7.20
7.14
7.12
7.11
7.09
7.07
6.95
6.93
6.78
6.77
6.76
6.75
3.68
1.21
Br
O
N
H
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
ppm
1.07
1.00
1.13
3.25
2.10
1.03
2.00
9.17

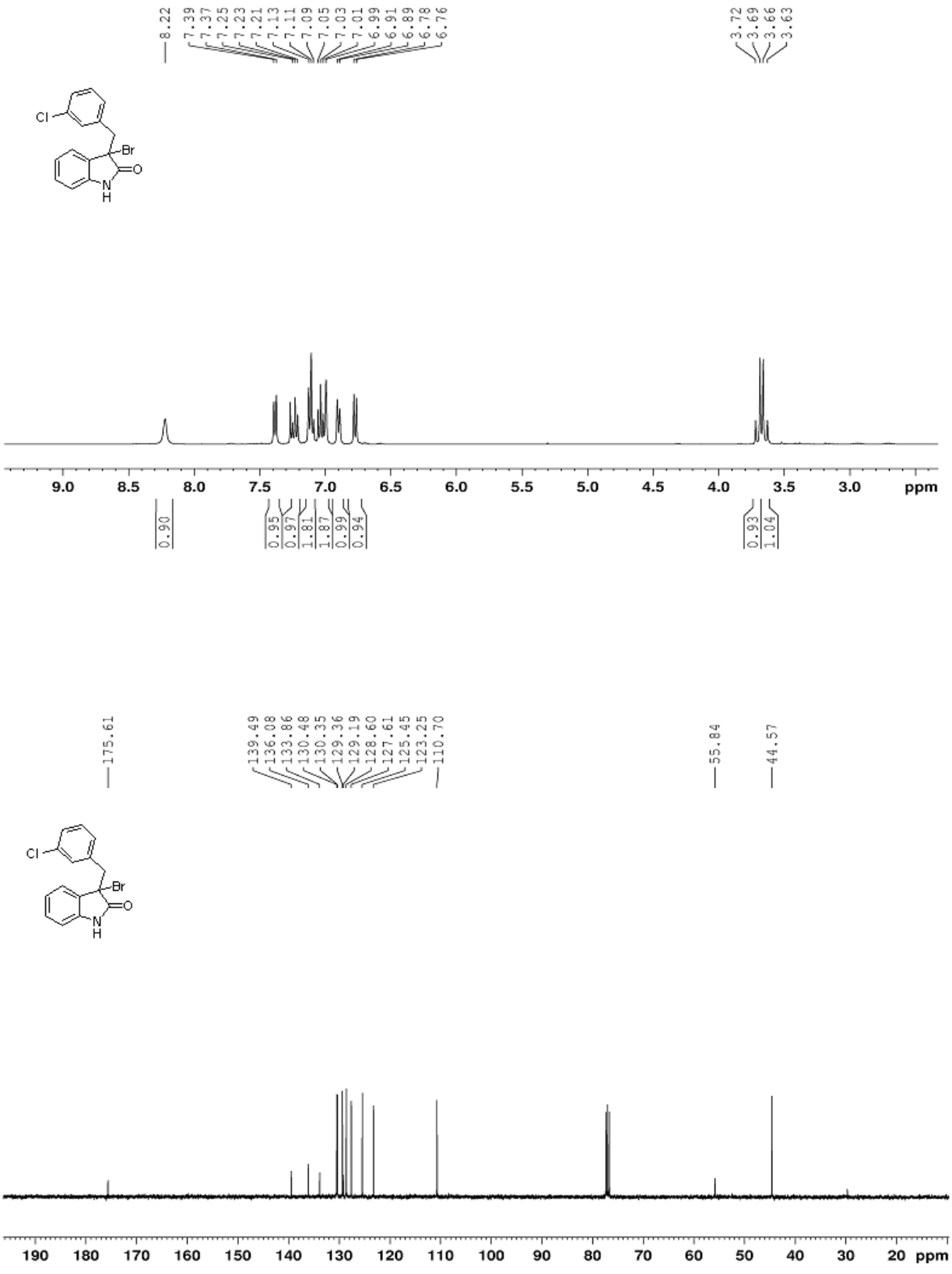

176.66
150.15
139.83
131.10
130.15
130.10
129.81
125.50
125.08
123.04
110.90
56.94
44.41
34.40
31.26
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

2j

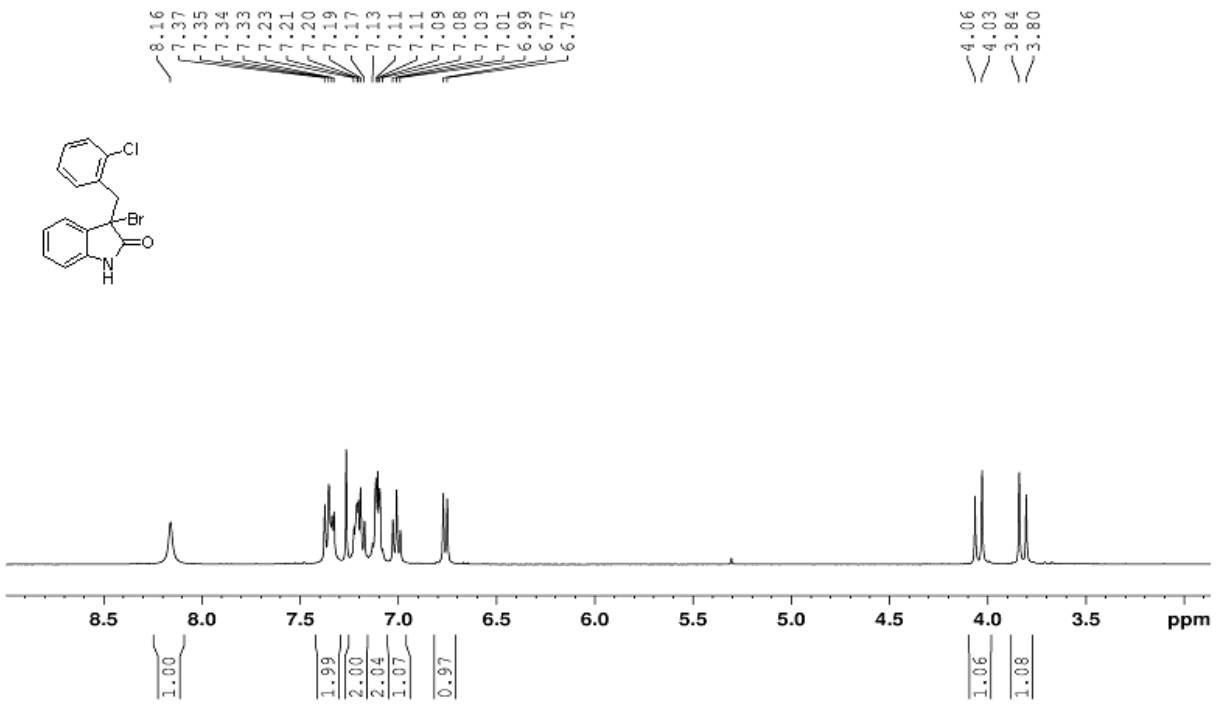

7.94
7.41
7.39
7.24
7.22
7.20
7.12
7.10
7.08
7.06
6.94
6.92
6.75
6.73
6.71
3.73
3.69
3.66
3.63
Cl
Br
O
N
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
0.91
0.94
1.29
2.81
1.97
0.92
0.90
1.03

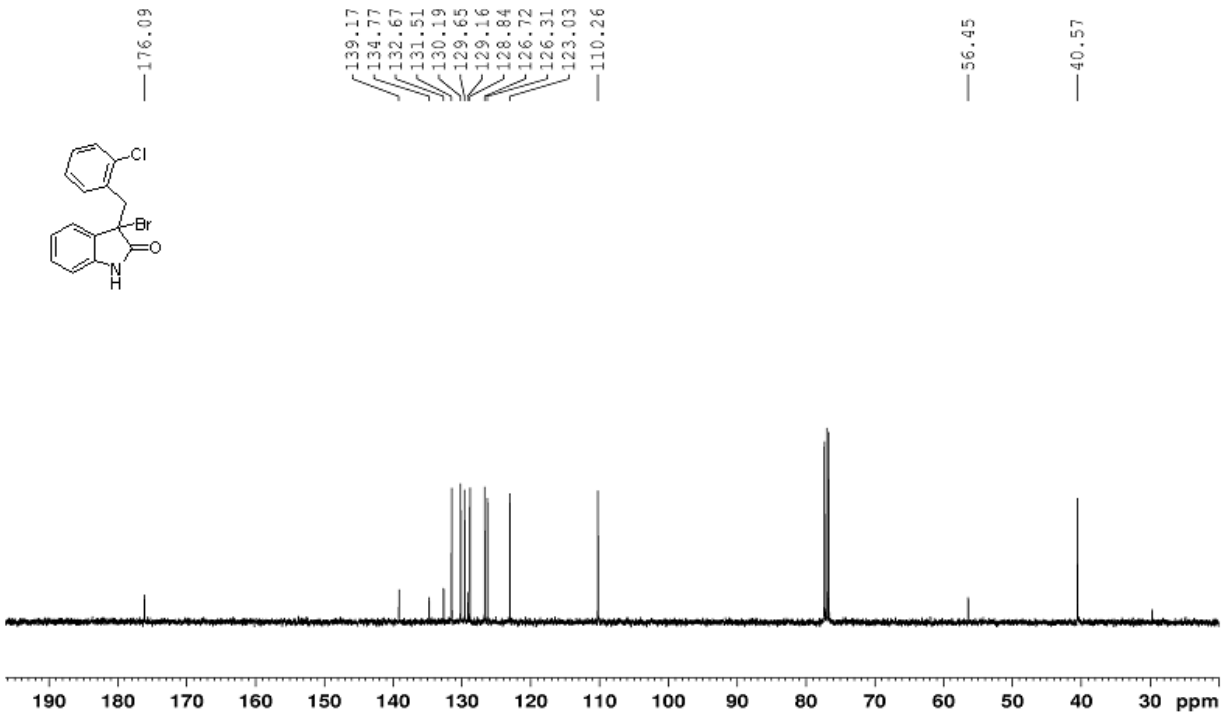

175.42
139.47
133.38
132.60
131.76
130.29
129.28
128.33
125.43
123.21
110.61
55.85
44.38
Cl
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

2k

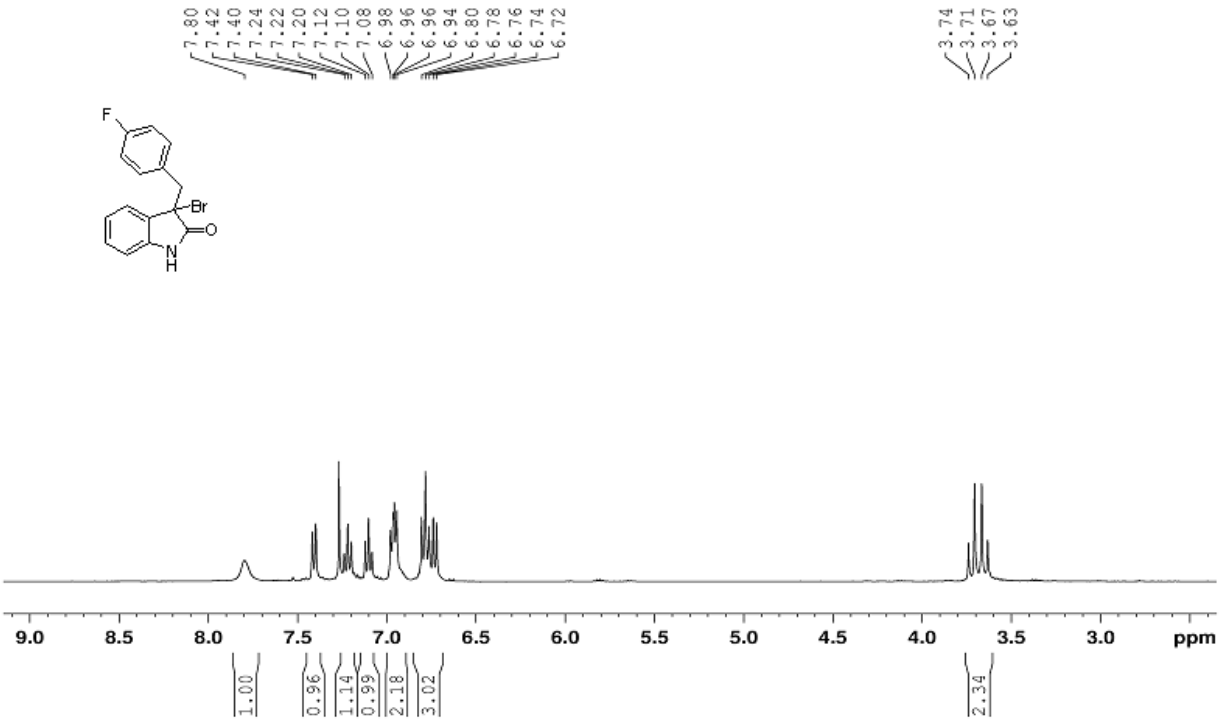

8.22
7.39
7.37
7.25
7.23
7.21
7.13
7.11
7.09
7.05
7.03
7.01
6.99
6.91
6.89
6.78
6.76
3.72
3.69
3.66
3.63
Cl
Br
O
N
H
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
0.90
0.95
0.97
1.81
1.87
0.99
0.94
0.93
1.04
175.61
139.49
136.08
133.86
130.48
130.35
129.36
129.19
128.60
127.61
125.45
123.25
110.70
55.84
44.57
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

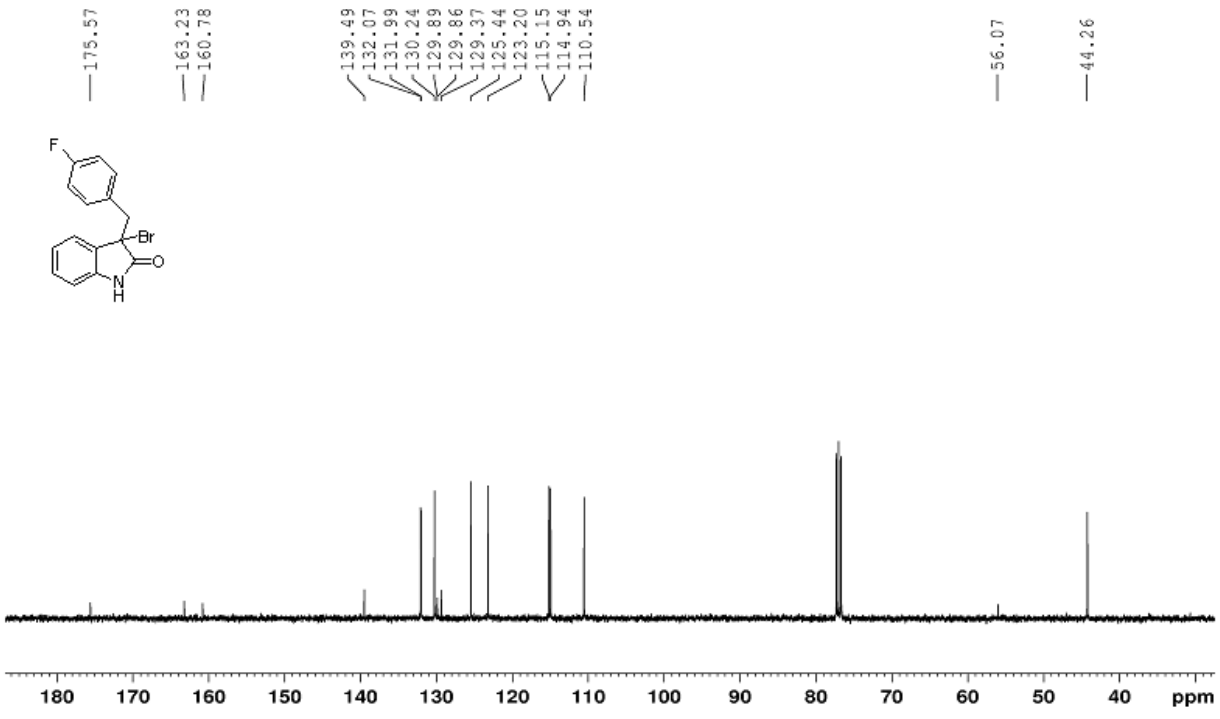
2l


8.16
7.37
7.35
7.34
7.33
7.23
7.21
7.20
7.19
7.17
7.13
7.11
7.11
7.09
7.08
7.03
7.01
6.99
6.77
6.75
4.06
4.03
3.84
3.80
Cl
Br
O
N
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
1.00
1.99
2.00
2.04
1.07
0.97
1.06
1.08

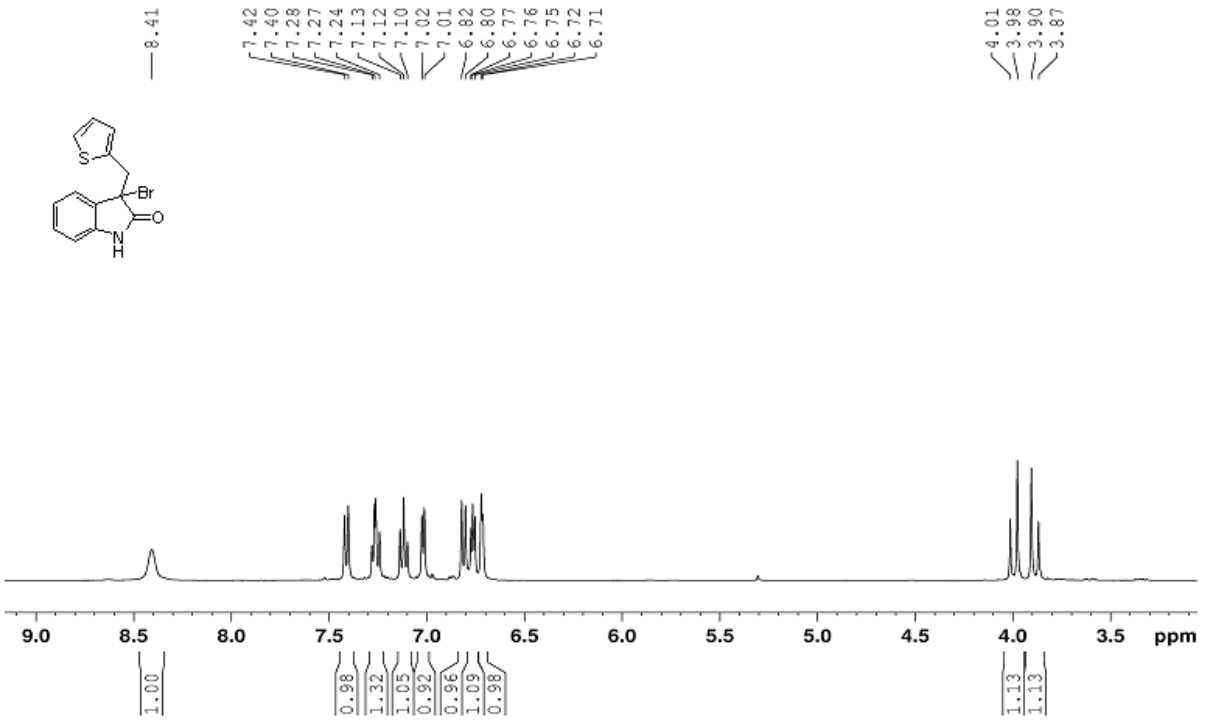

176.09
139.17
134.77
132.67
131.51
130.19
129.65
129.16
128.84
126.72
126.31
123.03
110.26
56.45
40.57
Cl
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

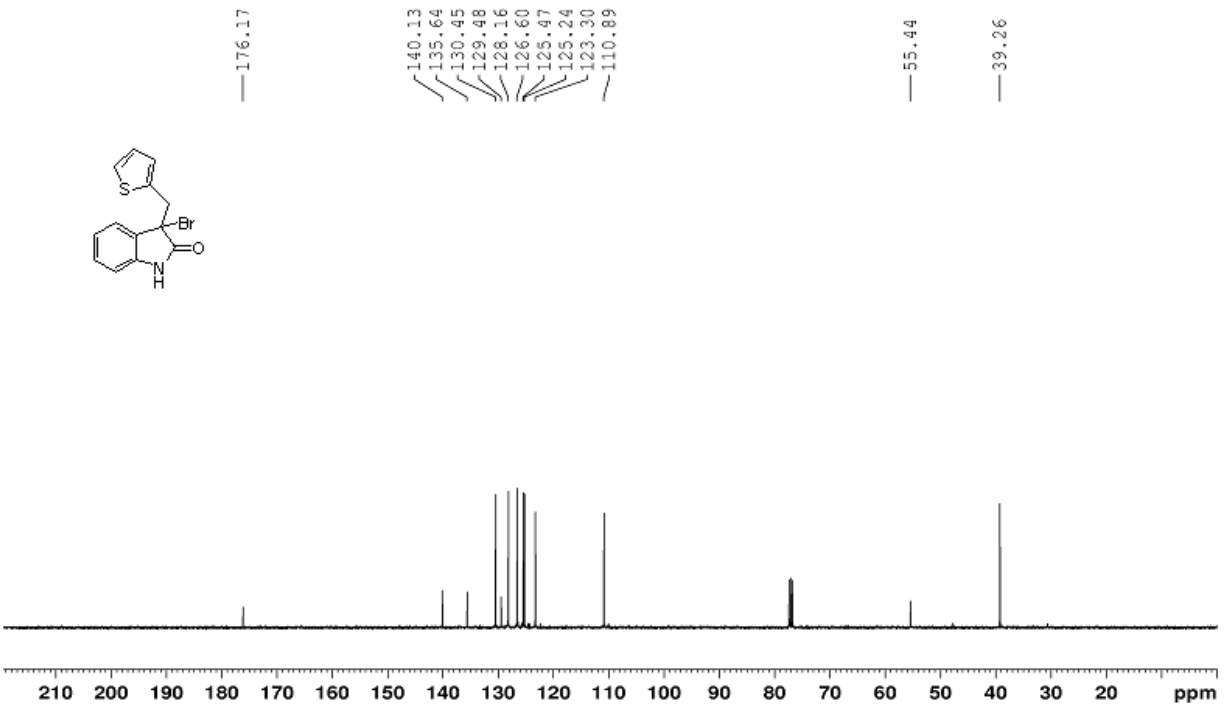
2m


7.80
7.42
7.40
7.24
7.22
7.20
7.12
7.10
7.08
6.98
6.96
6.96
6.94
6.80
6.78
6.76
6.74
6.72
3.74
3.71
3.67
3.63
F
Br
O
N
H
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
ppm
1.00
0.96
1.14
0.99
2.18
3.02
2.34

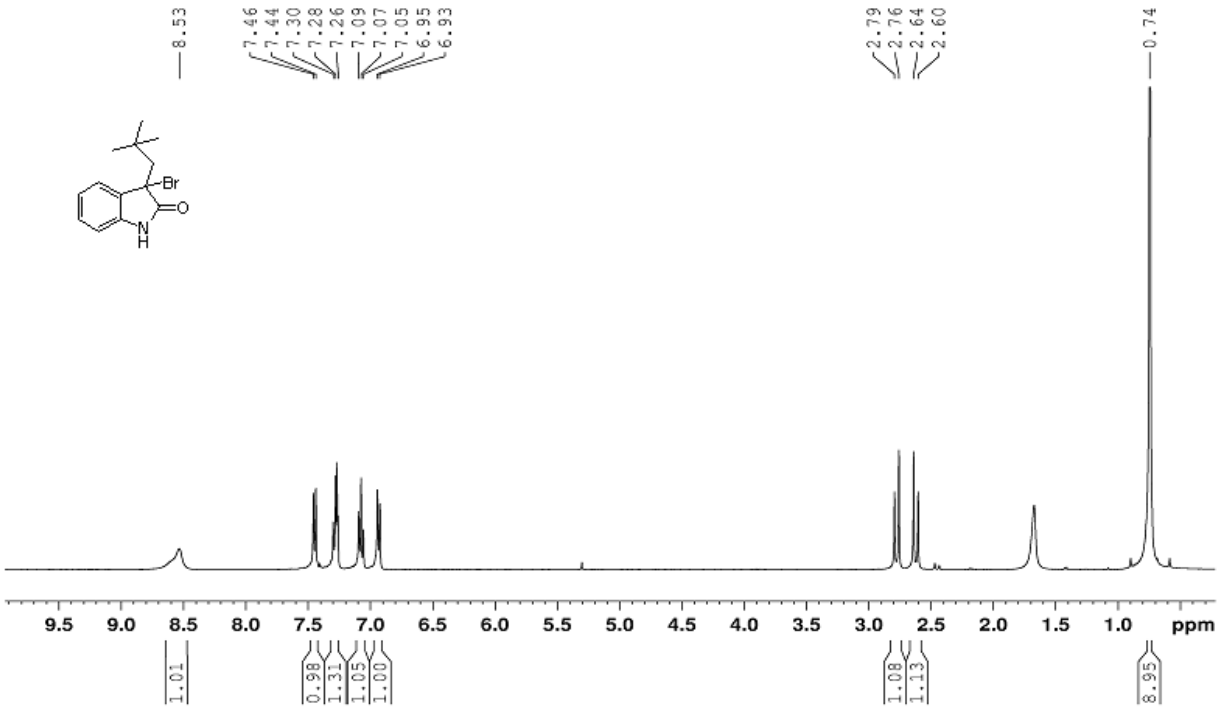

175.57
163.23
160.78
139.49
132.07
131.99
130.24
129.89
129.86
129.37
125.44
123.20
115.15
114.94
110.54
56.07
44.26
F
Br
O
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

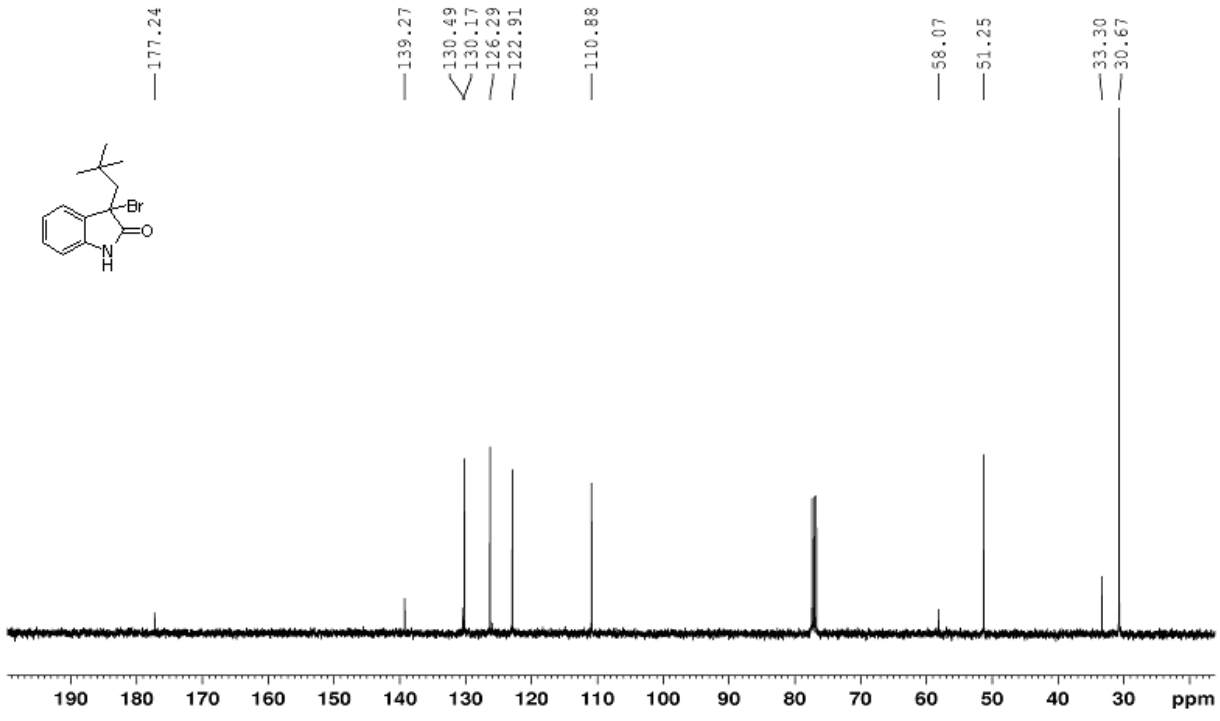
2n


8.41
7.42
7.40
7.28
7.27
7.24
7.13
7.12
7.10
7.02
7.01
6.82
6.80
6.77
6.76
6.75
6.72
6.71
4.01
3.98
3.90
3.87
Br
O
N
H
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
1.00
0.98
1.32
1.05
0.92
0.96
1.09
0.98
1.13
1.13

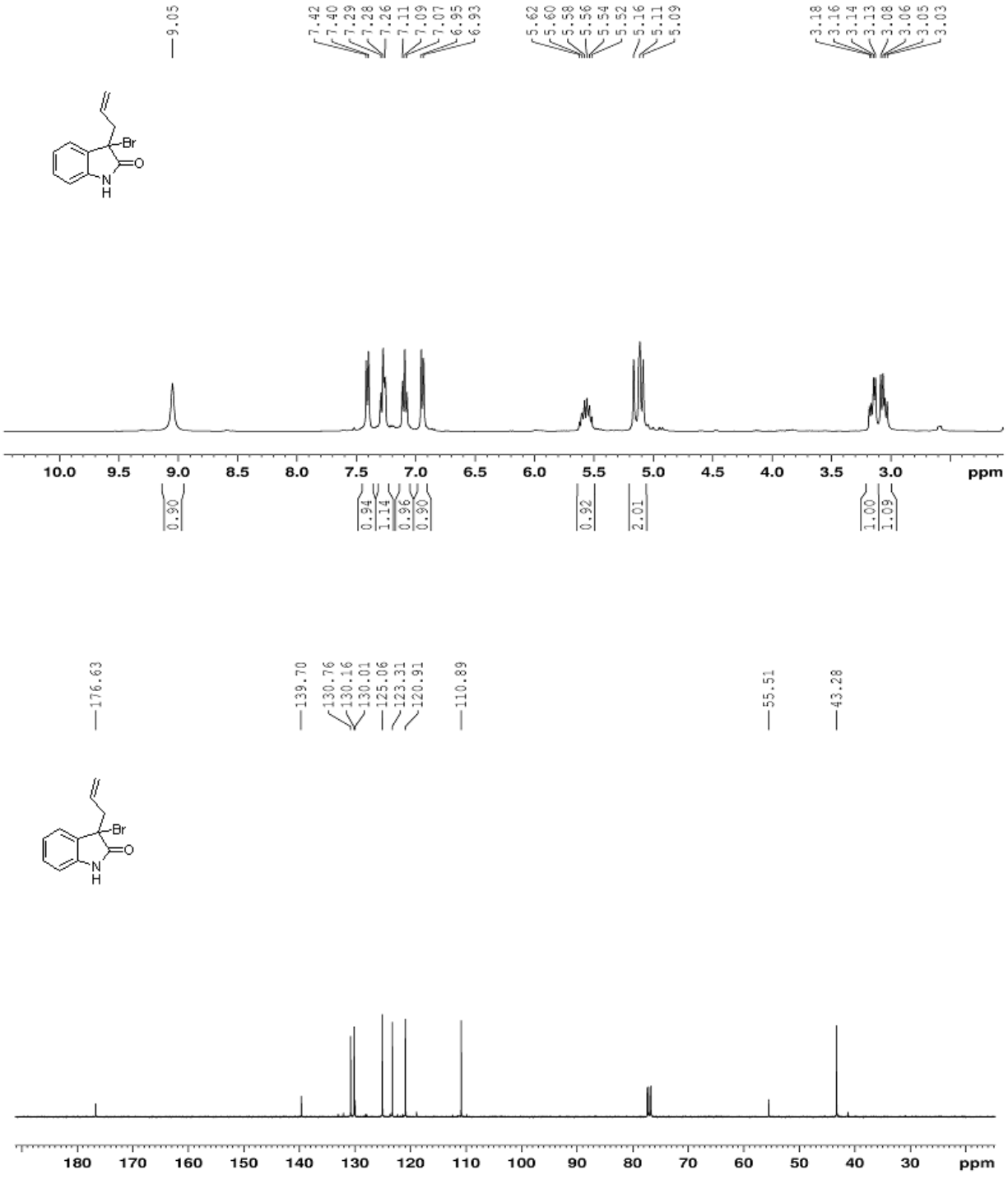

176.17
140.13
135.64
130.45
129.48
128.16
126.60
125.47
125.24
123.30
110.89
55.44
39.26
Br
O
N
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

2o

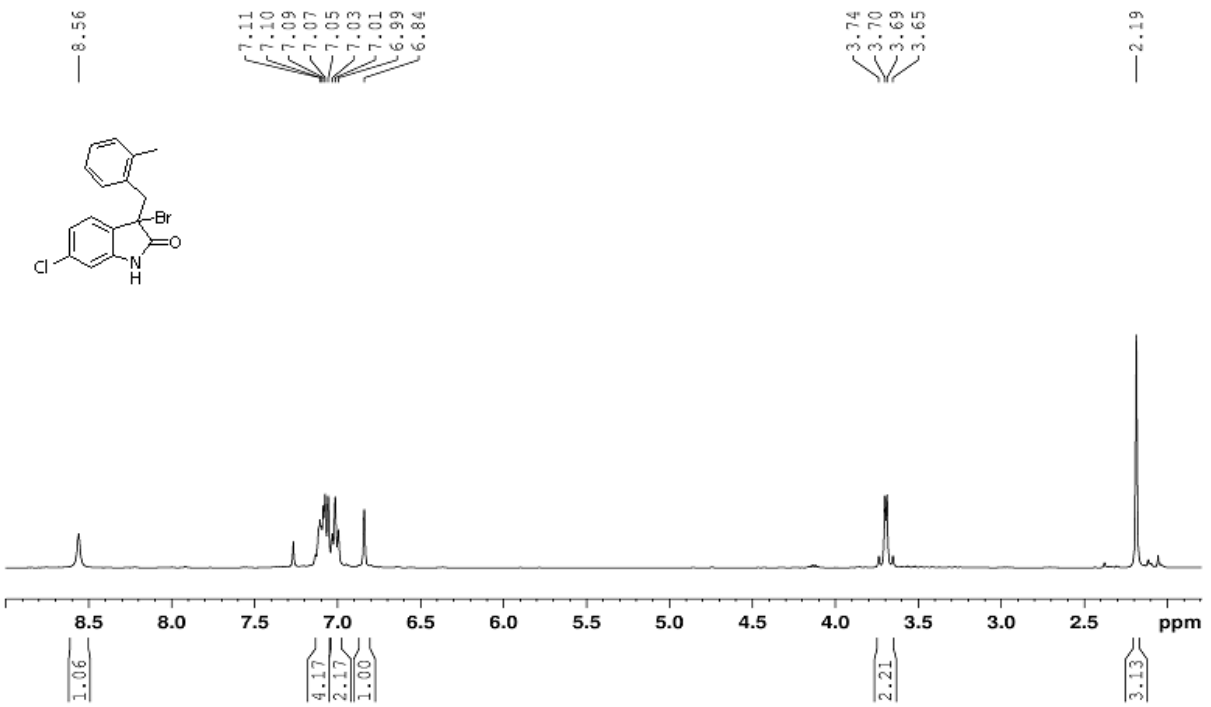

8.53
7.46
7.44
7.30
7.28
7.26
7.09
7.07
7.05
6.95
6.93
2.79
2.76
2.64
2.60
0.74
Br
O
N
H
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.01
0.98
1.31
1.05
1.00
1.08
1.13
8.95

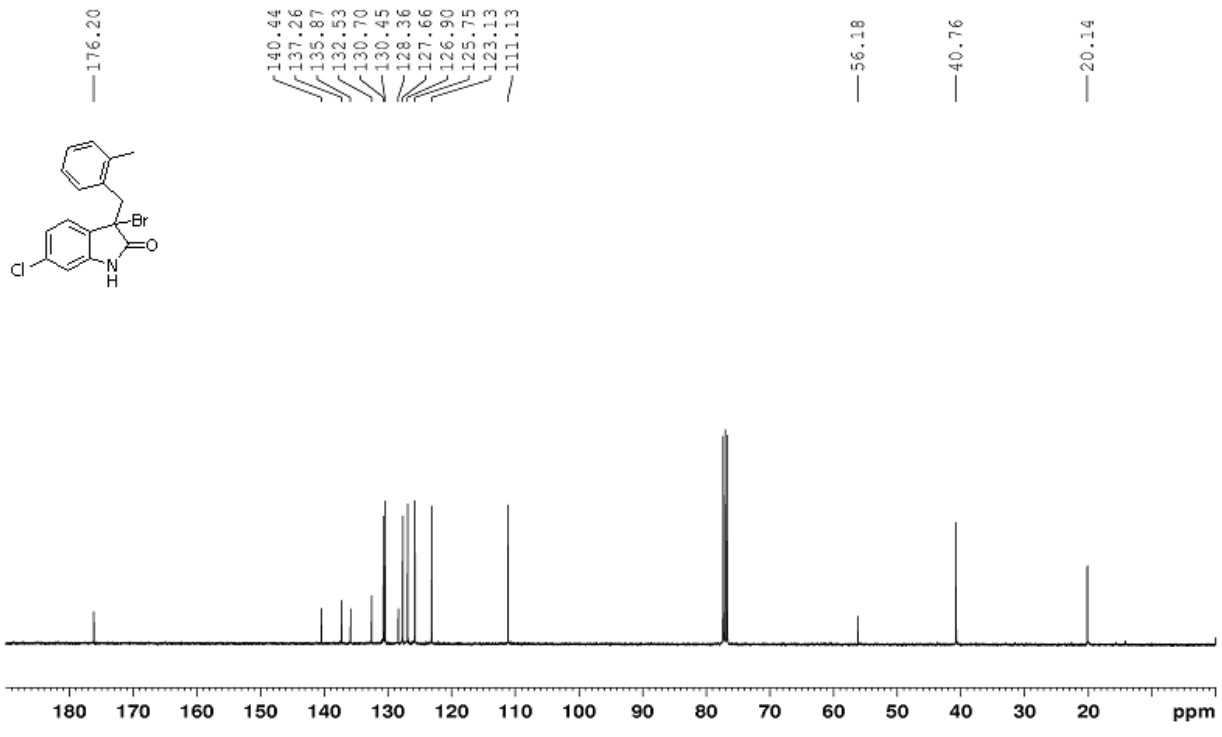

177.24
139.27
130.49
130.17
126.29
122.91
110.88
58.07
51.25
33.30
30.67
Br
O
N
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

2p

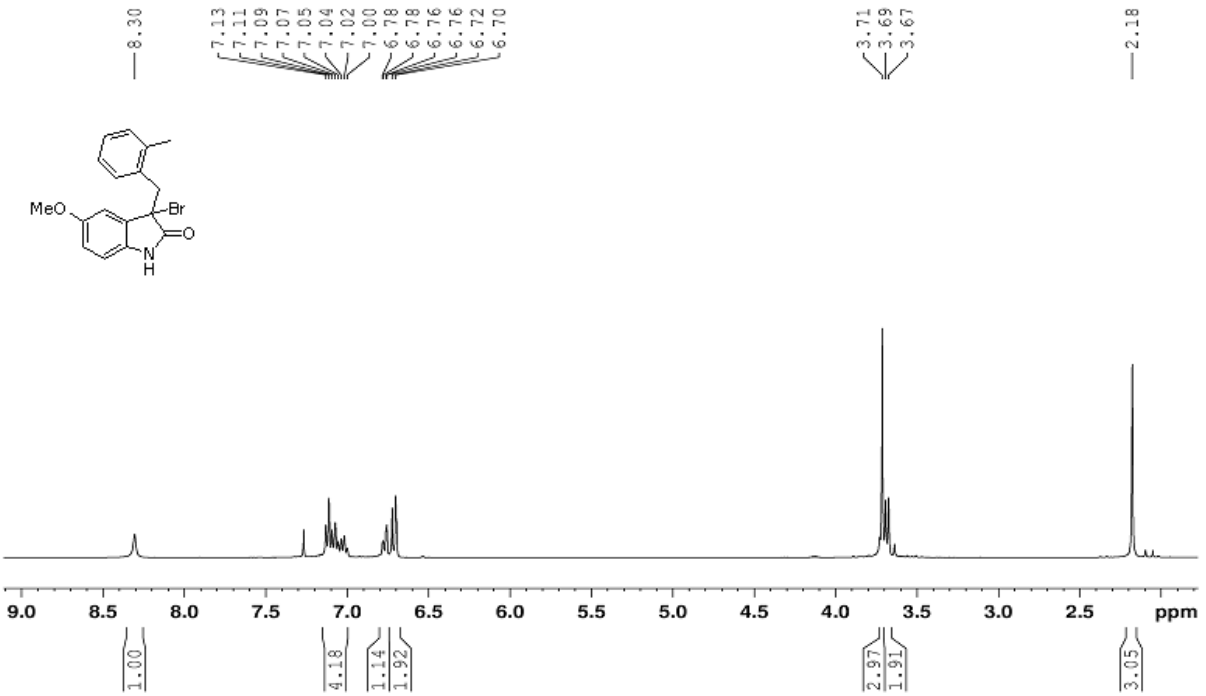

9.05
7.42
7.40
7.29
7.28
7.26
7.11
7.09
7.07
6.95
6.93
5.62
5.60
5.58
5.56
5.54
5.52
5.16
5.11
5.09
3.18
3.16
3.14
3.13
3.08
3.06
3.05
3.03
Br
O
N
H
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
0.90
0.94
1.14
0.96
0.90
0.92
2.01
1.00
1.09
176.63
139.70
130.76
130.16
130.01
125.06
123.31
120.91
110.89
55.51
43.28
Br
O
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

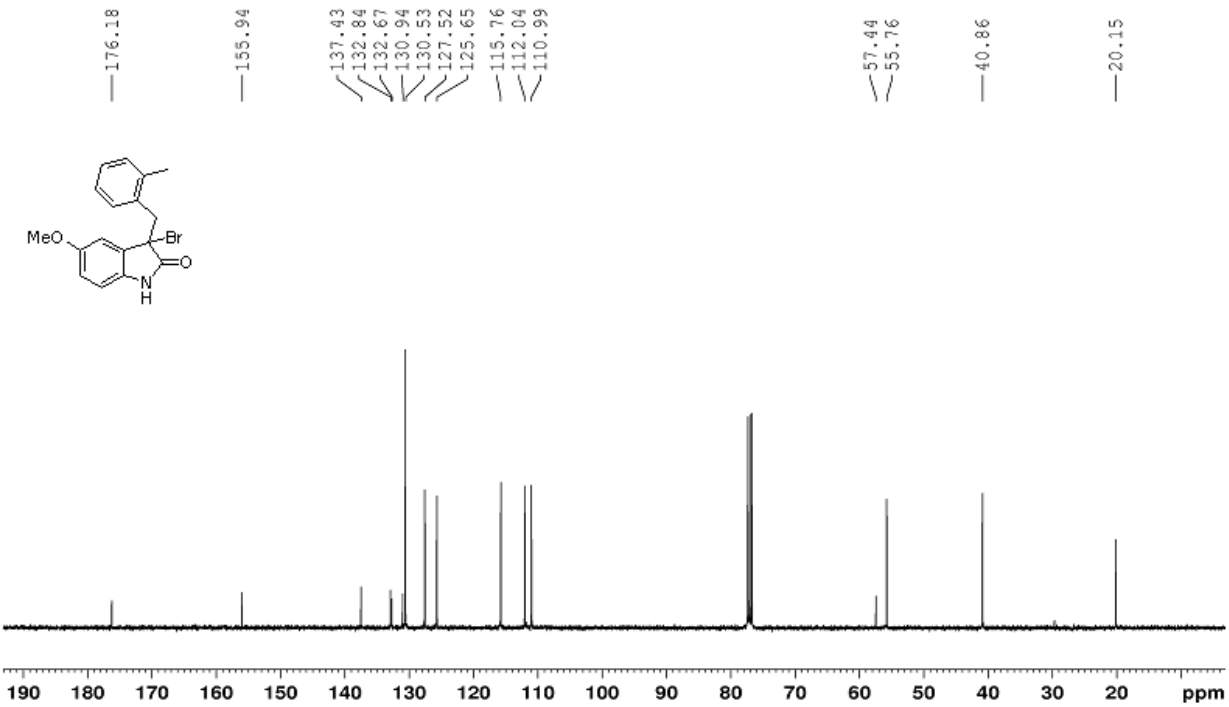
2q


8.56
7.11
7.10
7.09
7.07
7.05
7.03
7.01
6.99
6.84
3.74
3.70
3.69
3.65
2.19
Br
Cl
N
H
O
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
ppm
1.06
4.17
2.17
1.00
2.21
3.13

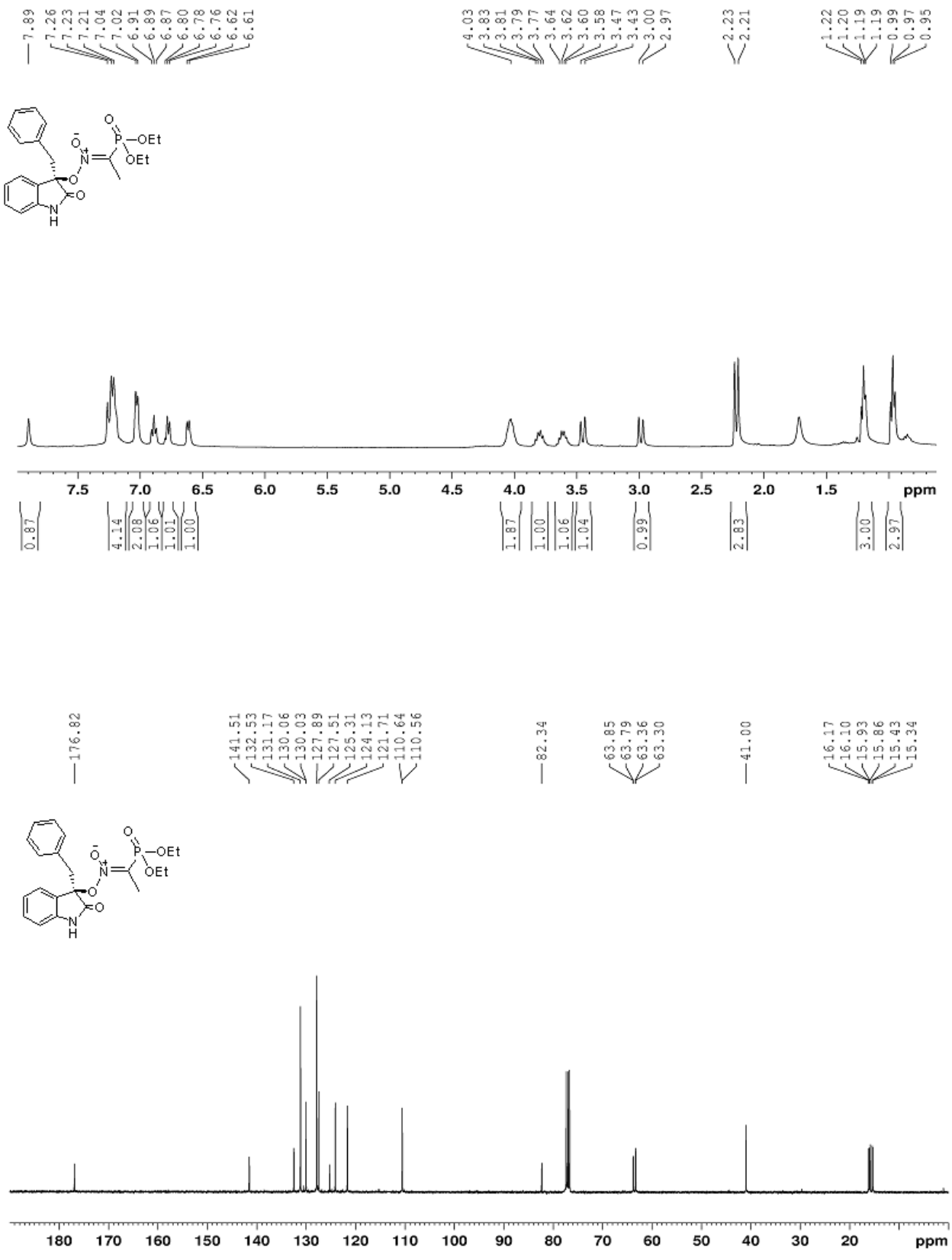

176.20
140.44
137.26
135.87
132.53
130.70
130.45
128.36
127.66
126.90
125.75
123.13
111.13
56.18
40.76
20.14
Br
Cl
N
H
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

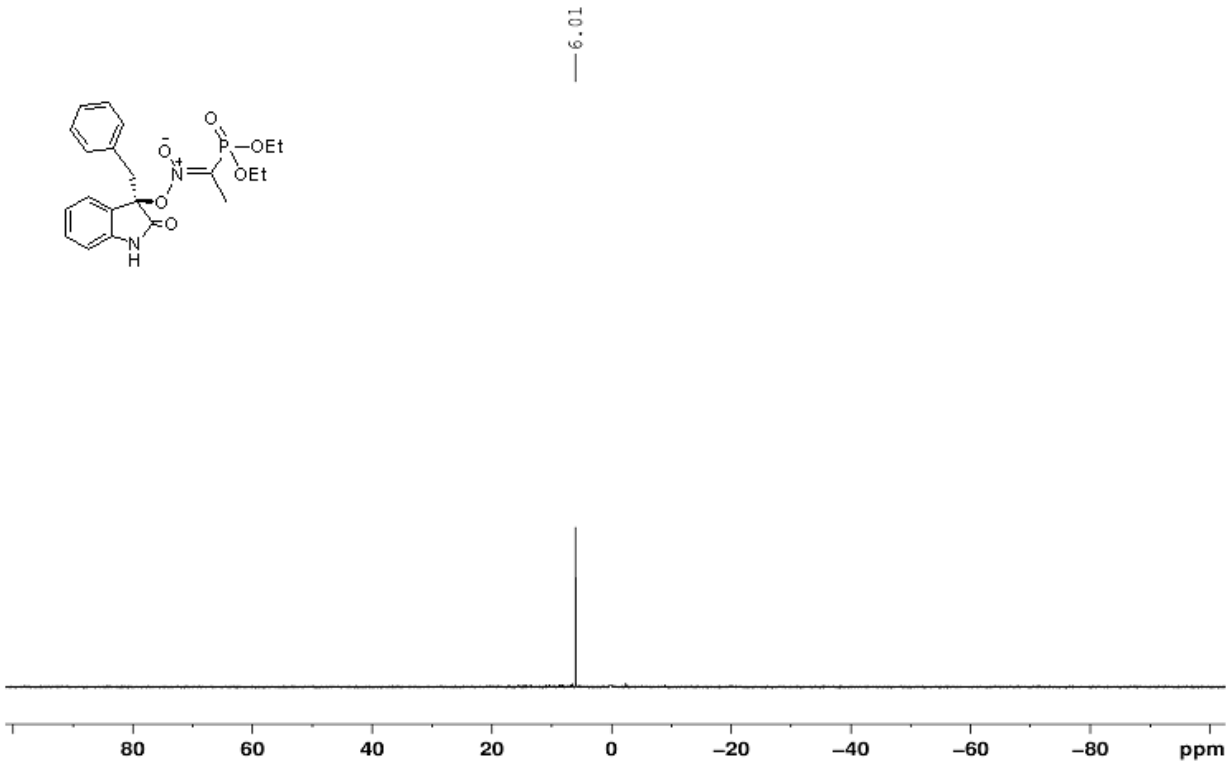
2r


8.30
7.13
7.11
7.09
7.07
7.05
7.04
7.02
7.00
6.78
6.78
6.76
6.76
6.72
6.70
3.71
3.69
3.67
2.18
MeO
Br
O
N
H
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
ppm
1.00
4.18
1.14
1.92
2.97
1.91
3.05

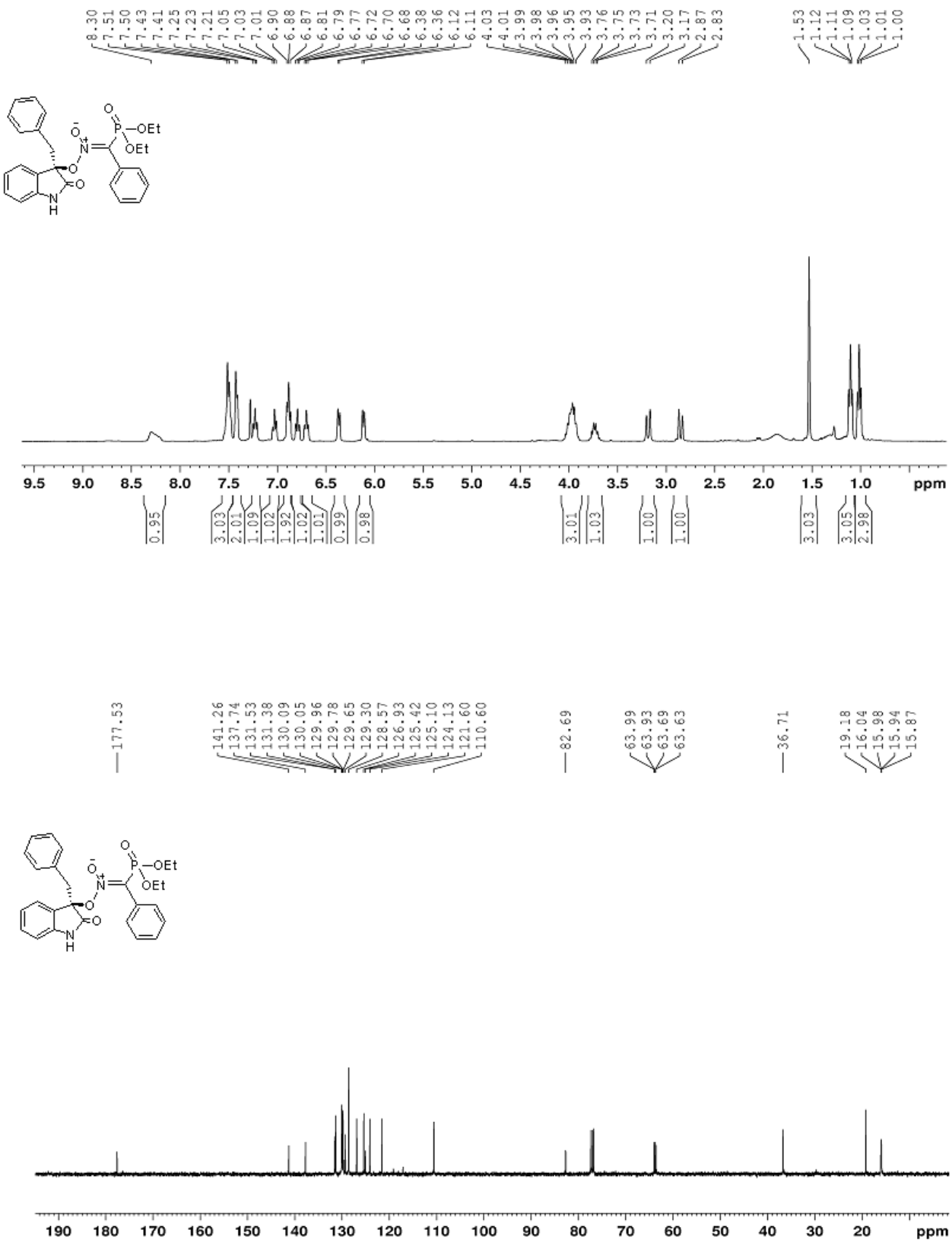

176.18
155.94
137.43
132.84
132.67
130.94
130.53
127.52
125.65
115.76
112.04
110.99
57.44
55.76
40.86
20.15
MeO
Br
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

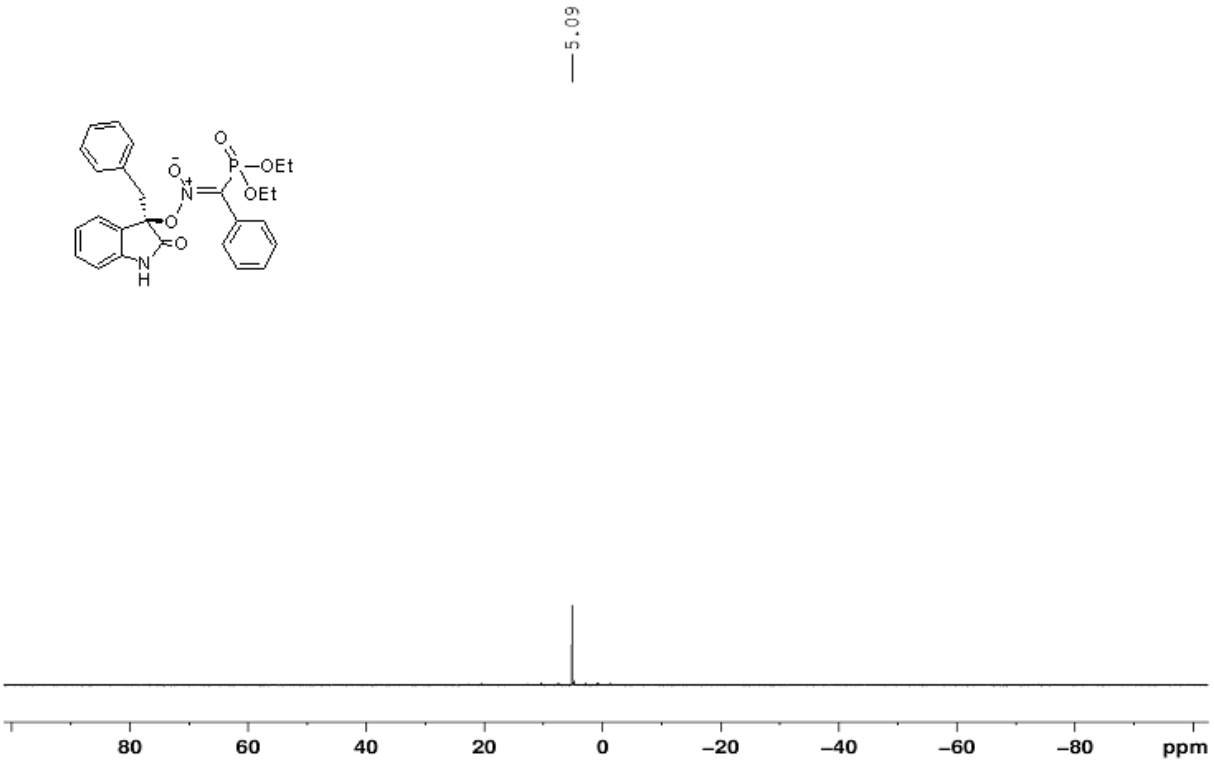
4a


7.89
7.26
7.23
7.21
7.04
7.02
6.91
6.89
6.87
6.80
6.78
6.76
6.62
6.61
4.03
3.83
3.81
3.79
3.77
3.64
3.62
3.60
3.58
3.47
3.43
3.00
2.97
2.23
2.21
1.22
1.20
1.19
1.19
0.99
0.97
0.95
OEt
OEt
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
ppm
0.87
4.14
2.08
1.06
1.01
1.00
1.87
1.00
1.06
1.04
0.99
2.83
3.00
2.97
176.82
141.51
132.53
131.17
130.06
130.03
127.89
127.51
125.31
124.13
121.71
110.64
110.56
82.34
63.85
63.79
63.36
63.30
41.00
16.17
16.10
15.93
15.86
15.43
15.34
OEt
OEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

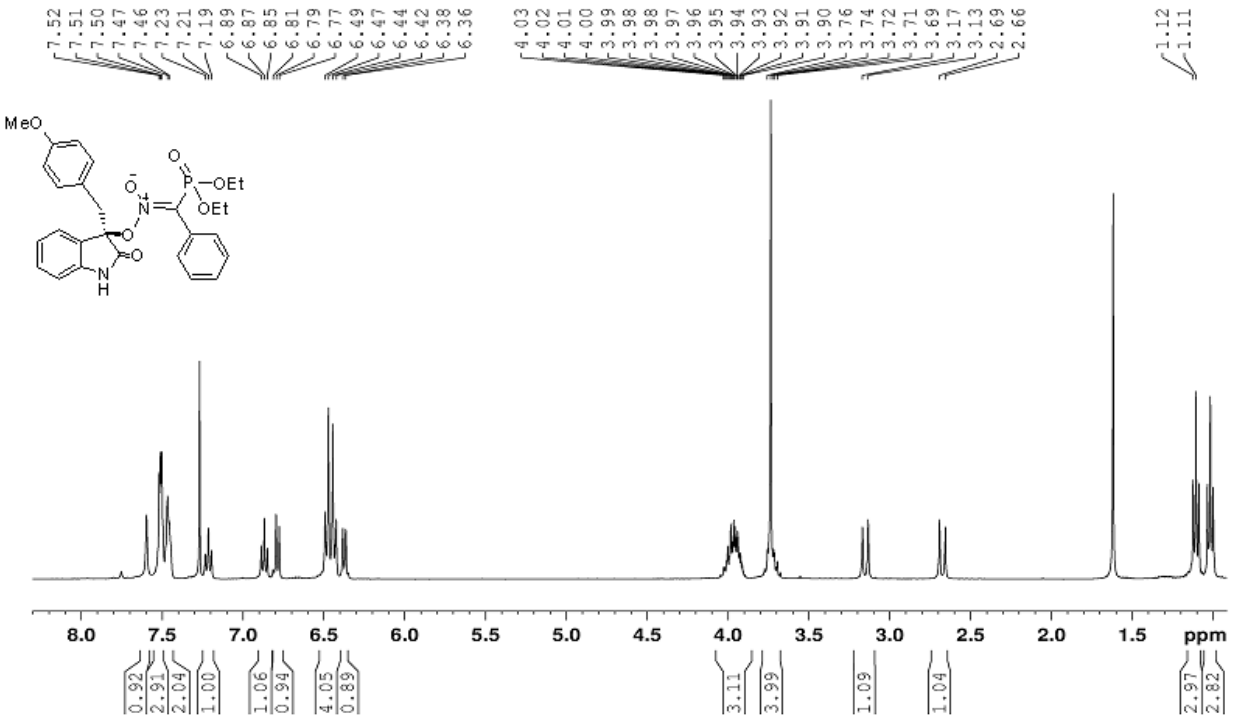

6.01
O
P
OEt
OEt
O
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

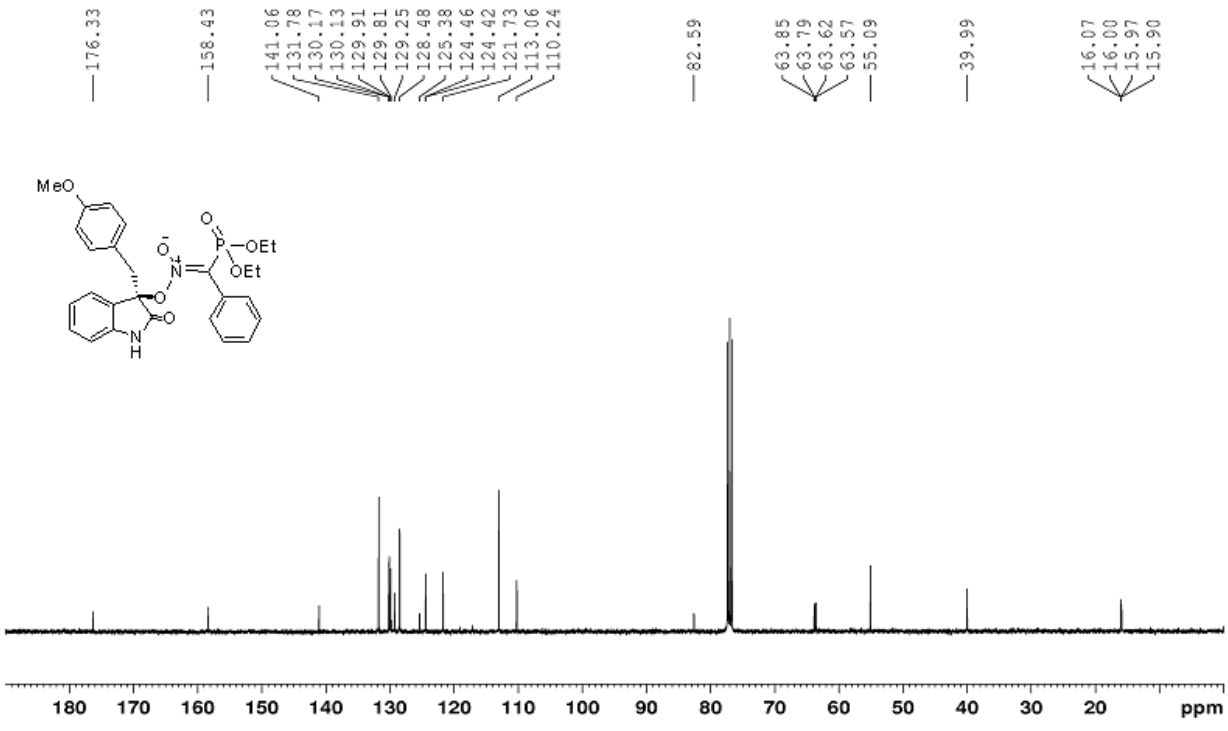
4b

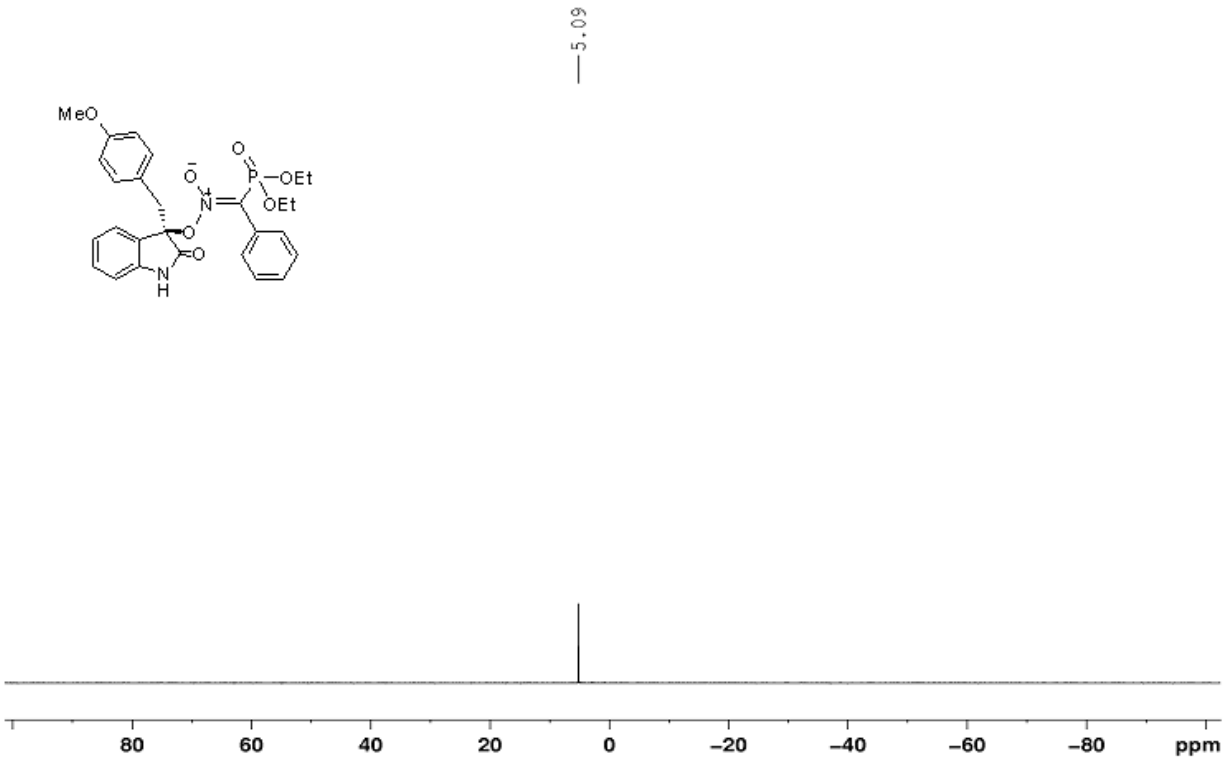

8.30
7.51
7.50
7.43
7.41
7.25
7.23
7.21
7.05
7.03
7.01
6.90
6.88
6.87
6.81
6.79
6.77
6.72
6.70
6.68
6.38
6.36
6.12
6.11
4.03
4.01
3.99
3.98
3.96
3.95
3.93
3.76
3.75
3.73
3.71
3.20
3.17
2.87
2.83
1.53
1.12
1.11
1.09
1.03
1.01
1.00
OEt
OEt
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.95
3.03
2.01
1.09
1.02
1.92
1.02
1.01
0.99
0.98
3.01
1.03
1.00
1.00
3.03
3.05
2.98
177.53
141.26
137.74
131.53
131.38
130.09
130.05
129.96
129.78
129.65
129.30
128.57
126.93
125.42
125.10
124.13
121.60
110.60
82.69
63.99
63.93
63.69
63.63
36.71
19.18
16.04
15.98
15.94
15.87
OEt
OEt
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


5.09
O
P
OEt
OEt
O
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

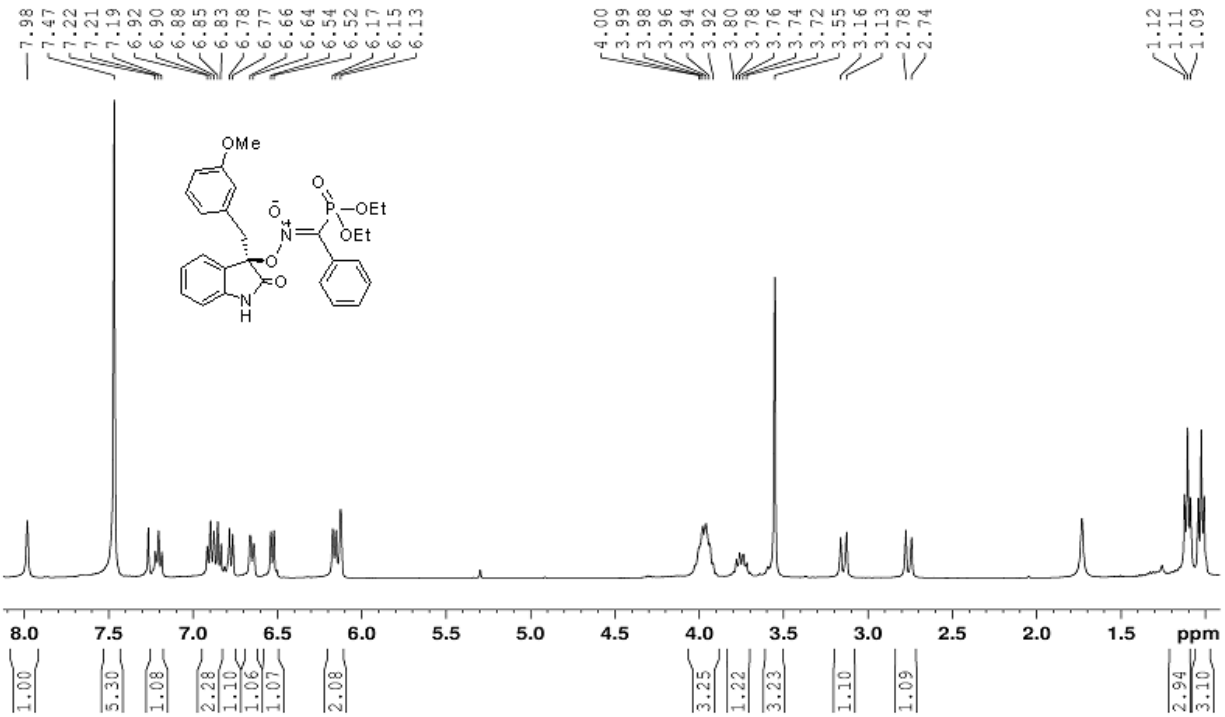
4c

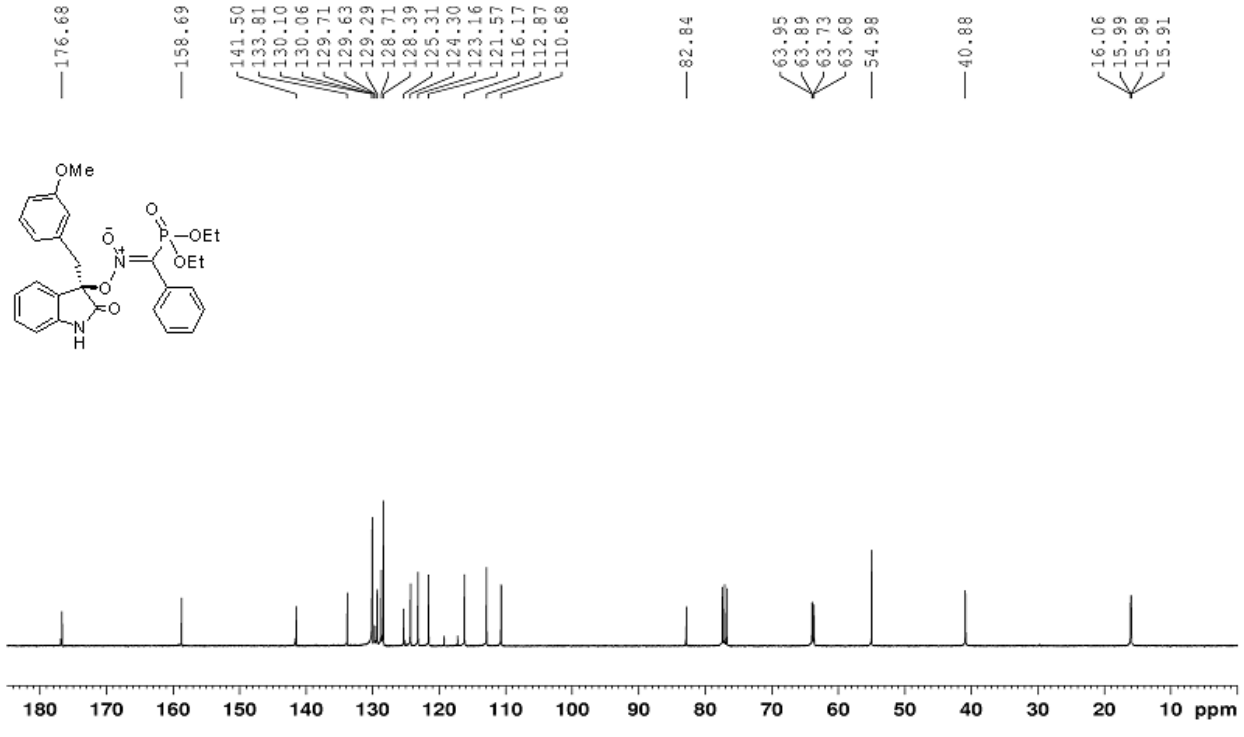

7.52
7.51
7.50
7.47
7.46
7.23
7.21
7.19
6.89
6.87
6.85
6.81
6.79
6.77
6.49
6.47
6.44
6.42
6.38
6.36
4.03
4.02
4.01
4.00
3.99
3.98
3.98
3.97
3.96
3.95
3.94
3.93
3.92
3.91
3.90
3.76
3.74
3.72
3.71
3.69
3.17
3.13
2.69
2.66
1.12
1.11
MeO
OEt
OEt
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.92
2.91
2.04
1.00
1.06
0.94
4.05
0.89
3.11
3.99
1.09
1.04
2.97
2.82

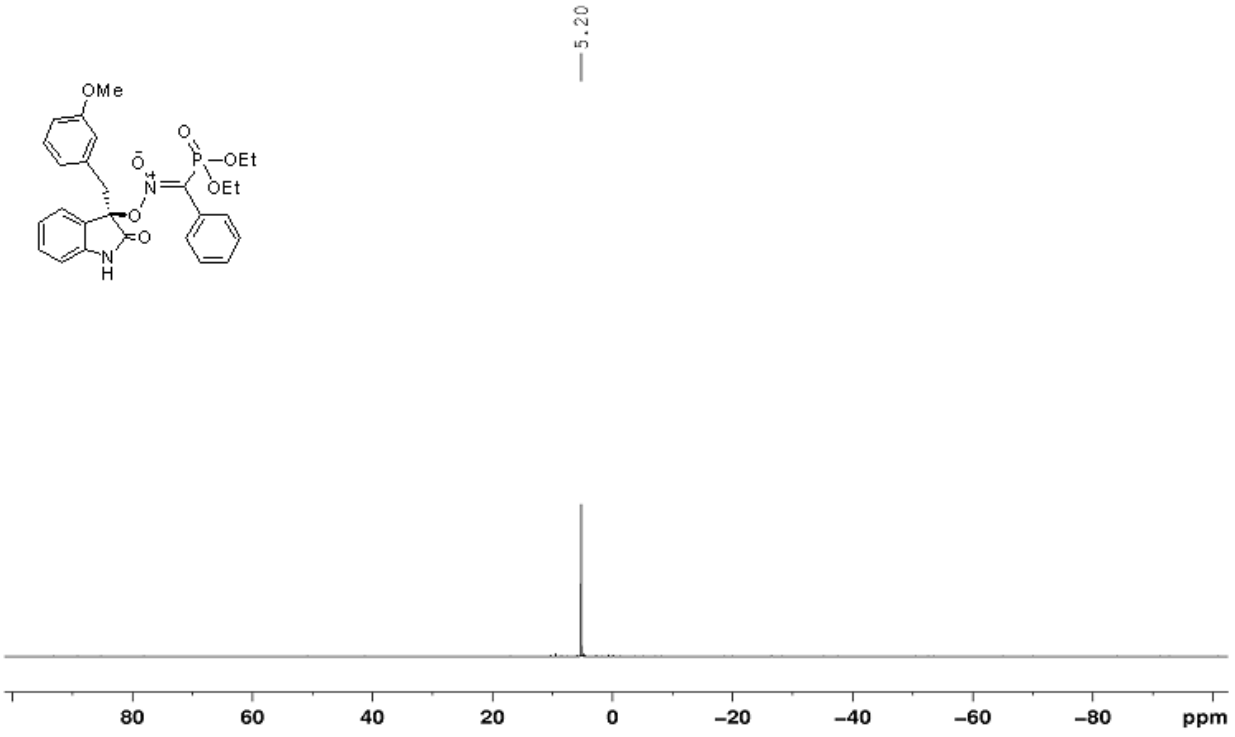

176.33
158.43
141.06
131.78
130.17
130.13
129.91
129.81
129.25
128.48
125.38
124.46
124.42
121.73
113.06
110.24
82.59
63.85
63.79
63.62
63.57
55.09
39.99
16.07
16.00
15.97
15.90
MeO
OEt
OEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


5.09
MeO
O
P
OEt
OEt
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

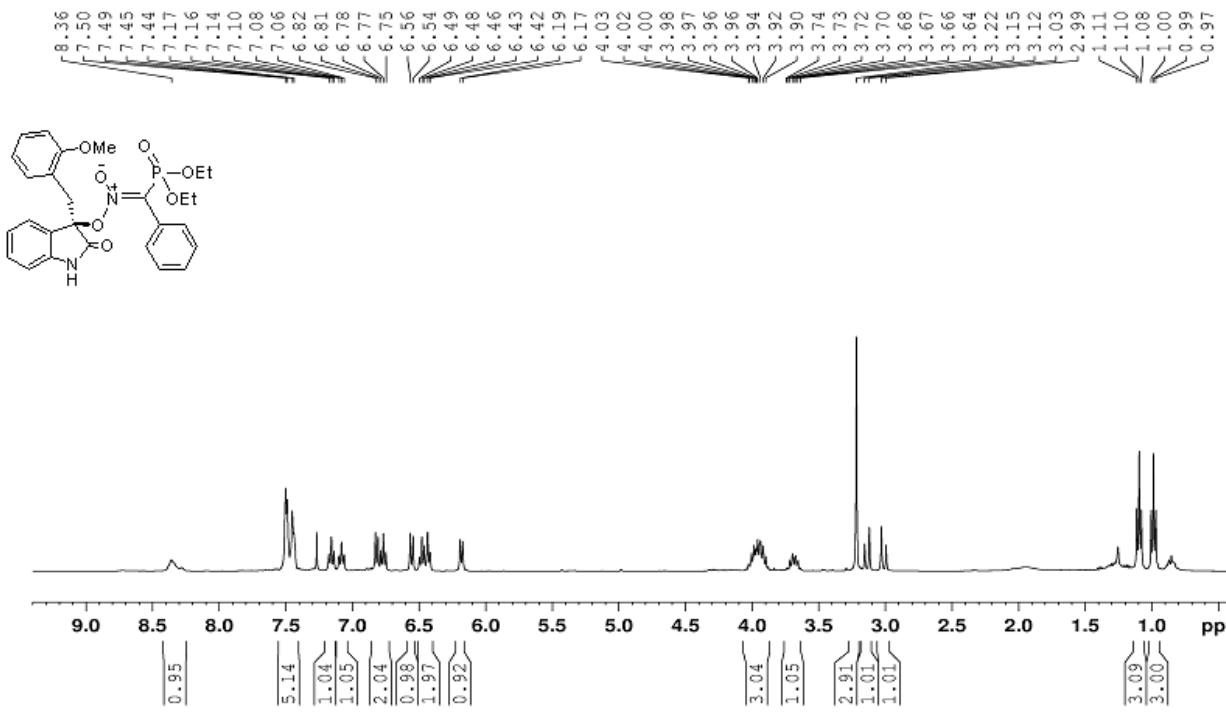
4d

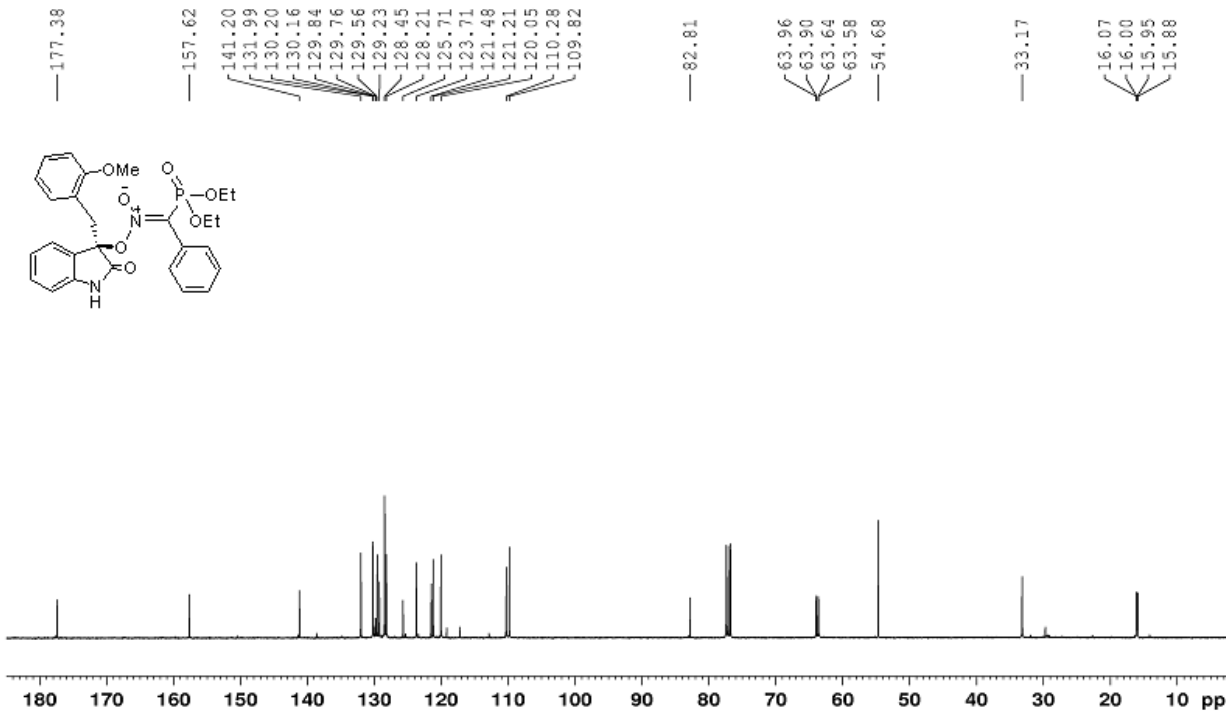

7.98
7.47
7.22
7.21
7.19
6.92
6.90
6.88
6.85
6.83
6.78
6.77
6.66
6.64
6.54
6.52
6.17
6.15
6.13
4.00
3.99
3.98
3.96
3.94
3.92
3.80
3.78
3.76
3.74
3.72
3.55
3.16
3.13
2.78
2.74
1.12
1.11
1.09
OMe
O
P—OEt
OEt
N
O
O
N
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
5.30
1.08
2.28
1.10
1.06
1.07
2.08
3.25
1.22
3.23
1.10
1.09
2.94
3.10

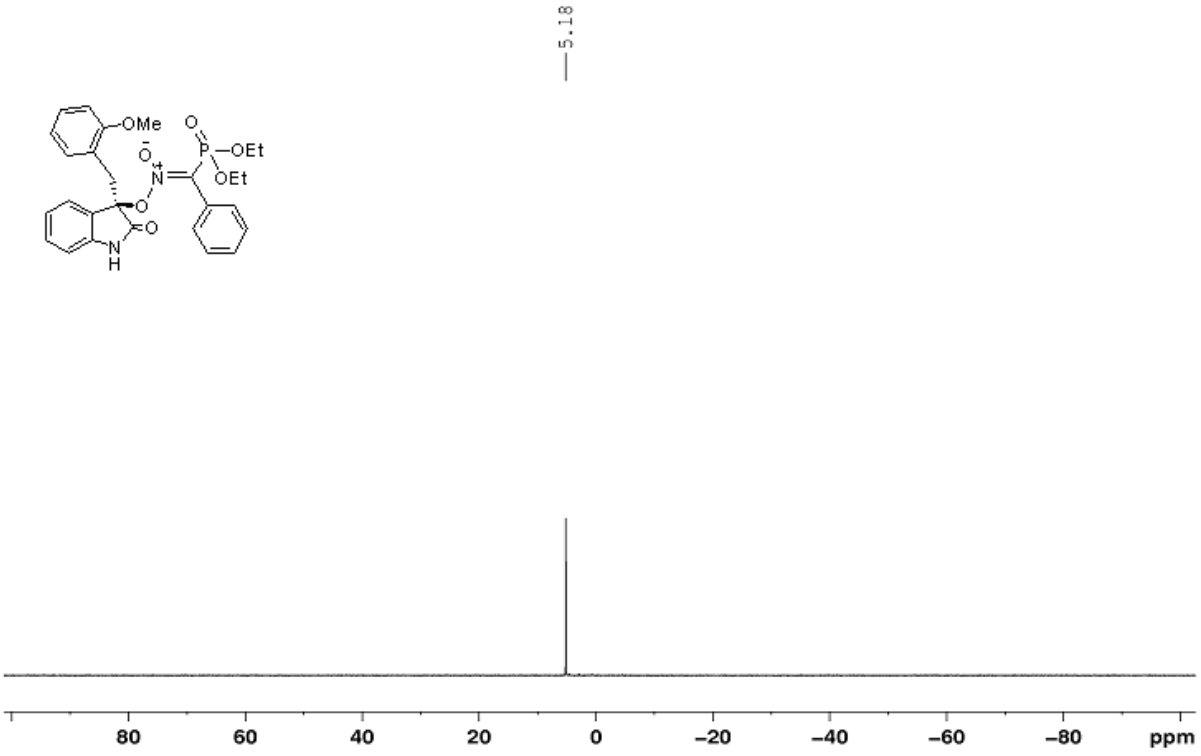

176.68
158.69
141.50
133.81
130.10
130.06
129.71
129.63
129.29
128.71
128.39
125.31
124.30
123.16
121.57
116.17
112.87
110.68
82.84
63.95
63.89
63.73
63.68
54.98
40.88
16.06
15.99
15.98
15.91
OMe
O
P—OEt
OEt
N
O
O
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


5.20
OMe
O
P
OEt
OEt
O
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

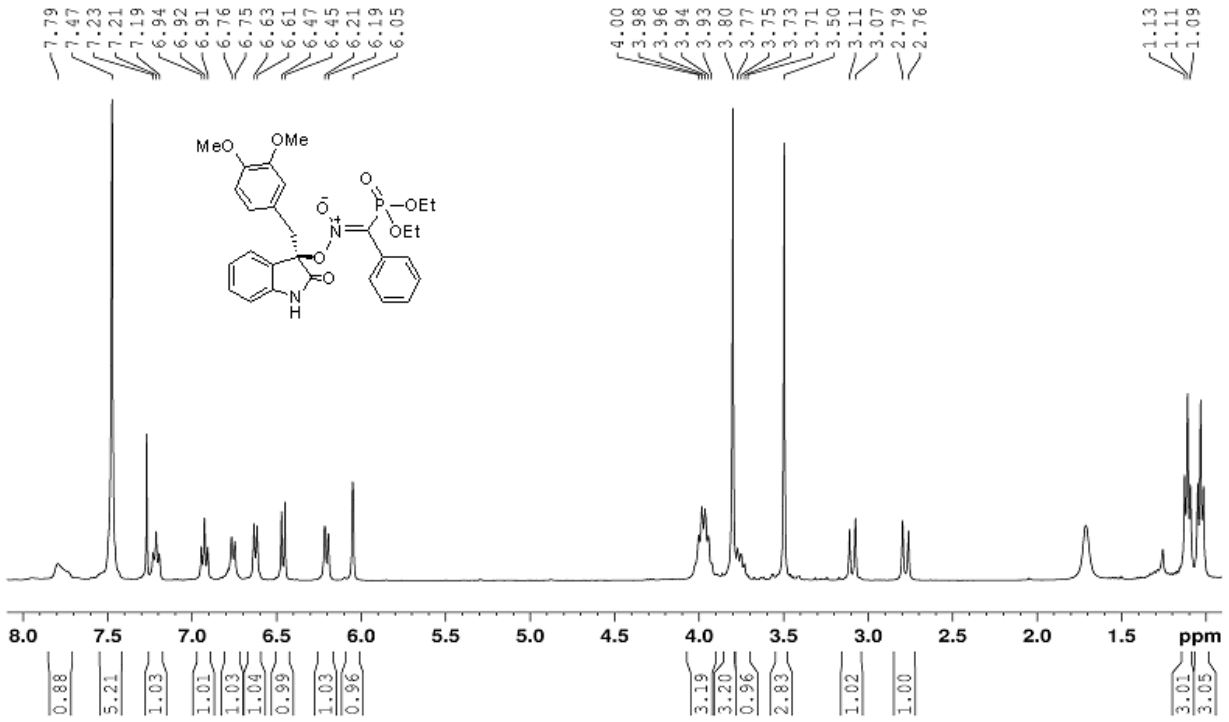
4e

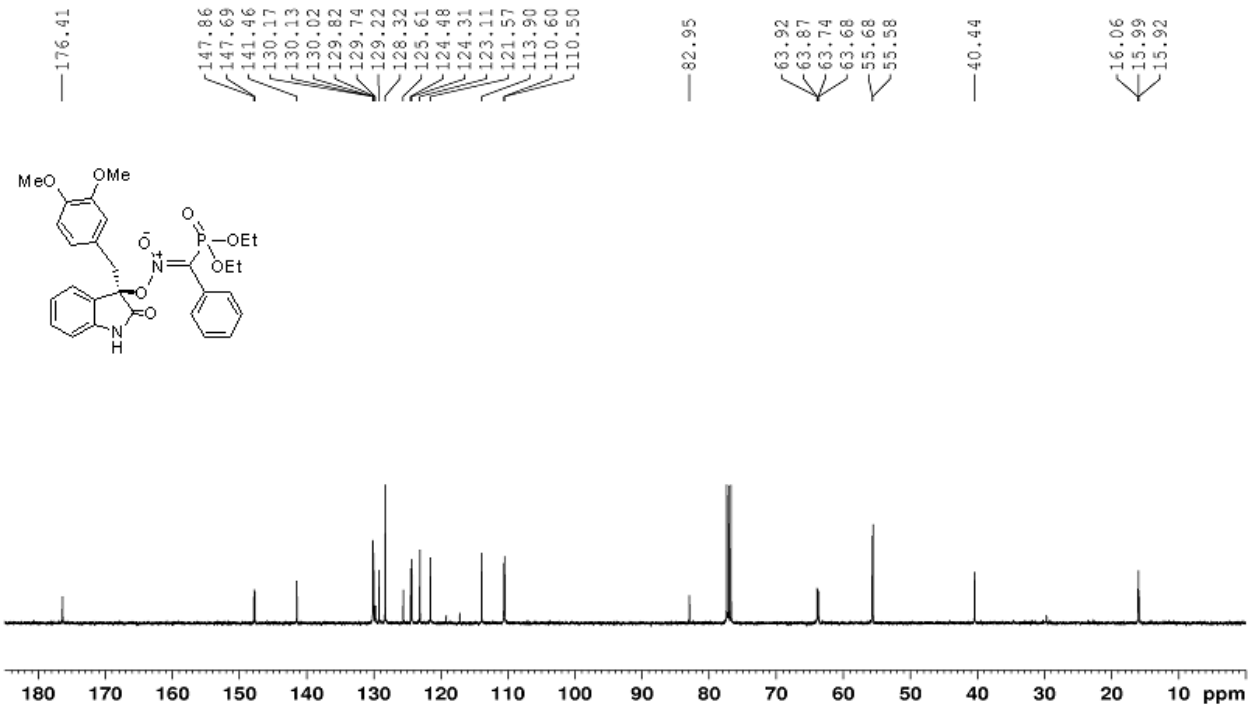

8.36 7.50 7.49 7.45 7.44 7.17 7.16 7.14 7.10 7.08 7.06 6.82 6.81 6.78 6.77 6.75 6.56 6.54 6.49 6.48 6.46 6.43 6.42 6.19 6.17 4.03 4.02 4.00 3.98 3.97 3.96 3.96 3.94 3.92 3.90 3.74 3.73 3.72 3.70 3.68 3.67 3.66 3.64 3.22 3.15 3.12 3.03 2.99 1.11 1.10 1.08 1.00 0.99 0.97
OMe
OEt
OEt
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.95 5.14 1.04 1.05 2.04 0.98 1.97 0.92 3.04 1.05 2.91 1.01 1.01 3.09 3.00

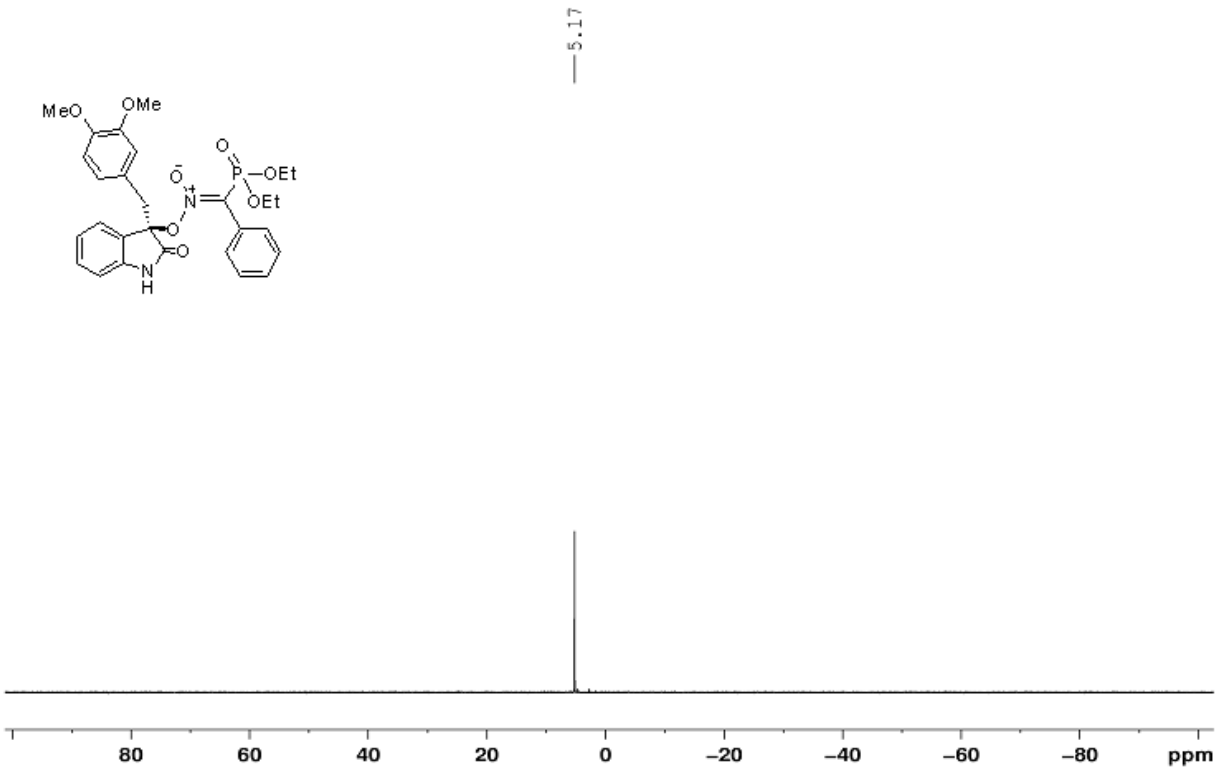

177.38 157.62 141.20 131.99 130.20 130.16 129.84 129.76 129.56 129.23 128.45 128.21 125.71 123.71 121.48 121.21 120.05 110.28 109.82 82.81 63.96 63.90 63.64 63.58 54.68 33.17 16.07 16.00 15.95 15.88
OMe
OEt
OEt
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


5.18
OMe
O
P
OEt
OEt
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

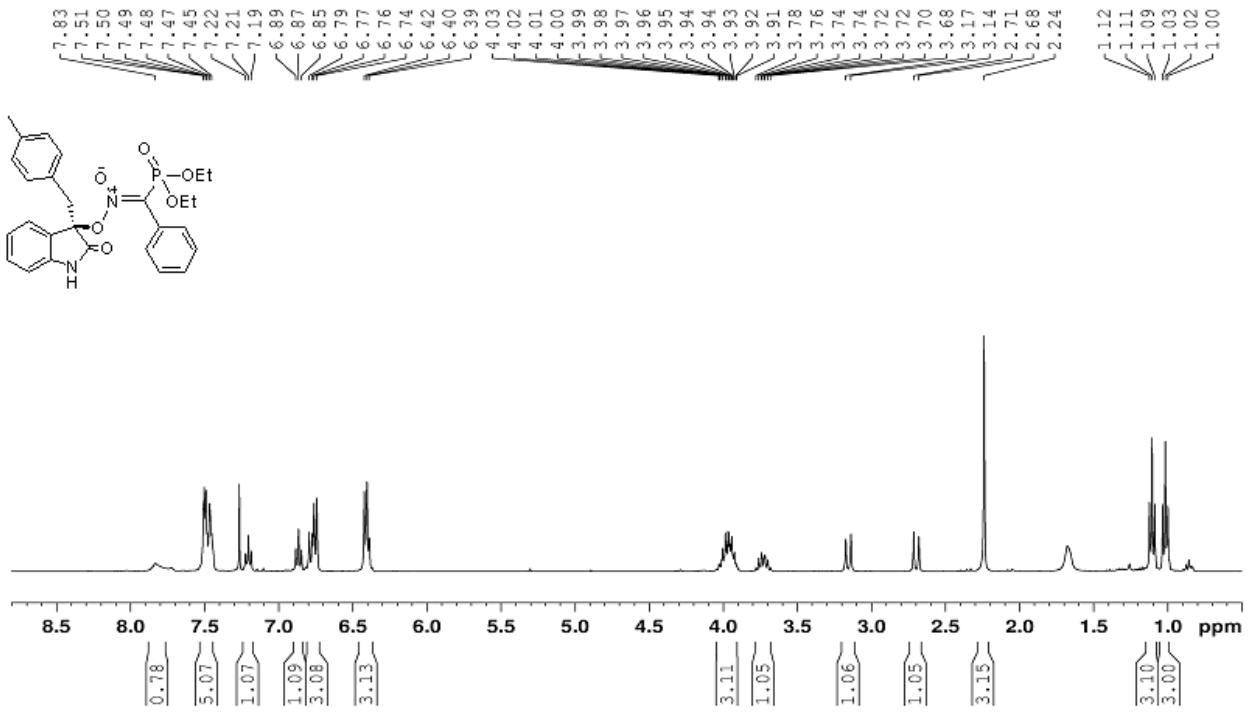
4f

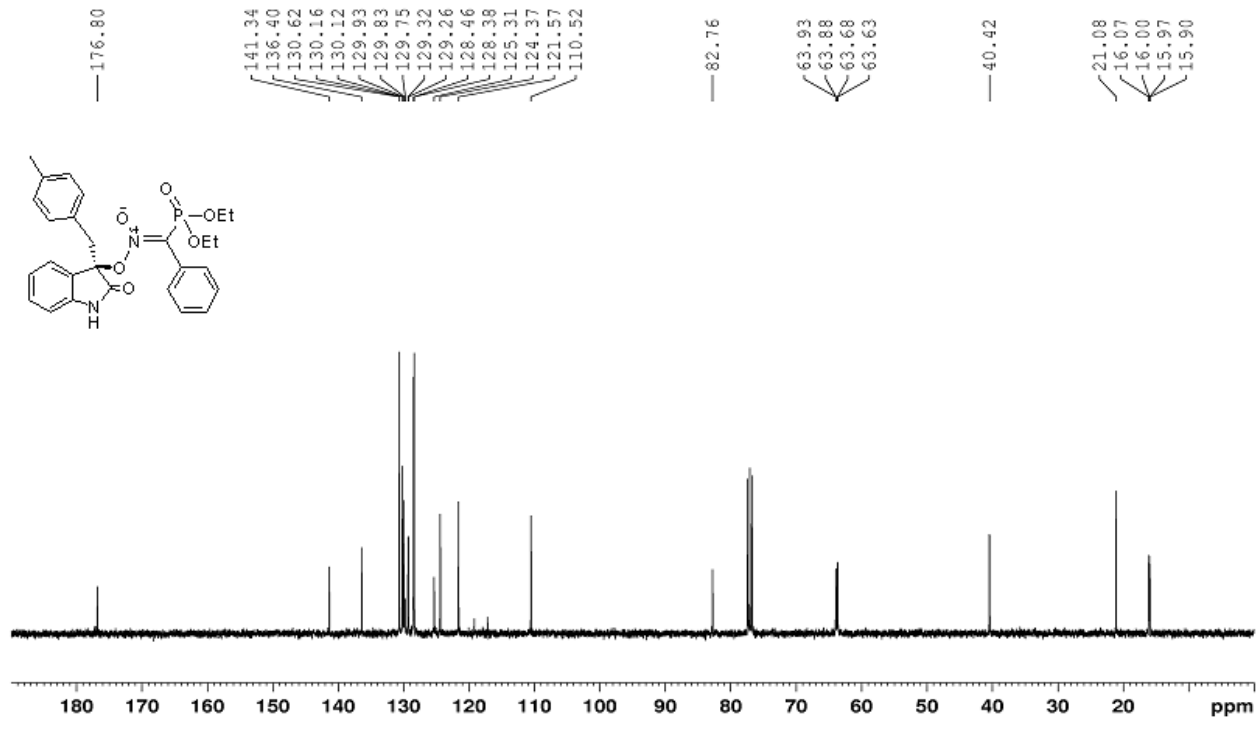

7.79
7.47
7.23
7.21
7.19
6.94
6.92
6.91
6.76
6.75
6.63
6.61
6.47
6.45
6.21
6.19
6.05
4.00
3.98
3.96
3.94
3.93
3.80
3.77
3.75
3.73
3.71
3.50
3.11
3.07
2.79
2.76
1.13
1.11
1.09
MeO
OMe
O
P
OEt
OEt
N
O
N
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.88
5.21
1.03
1.01
1.03
1.04
0.99
1.03
0.96
3.19
3.20
0.96
2.83
1.02
1.00
3.01
3.05

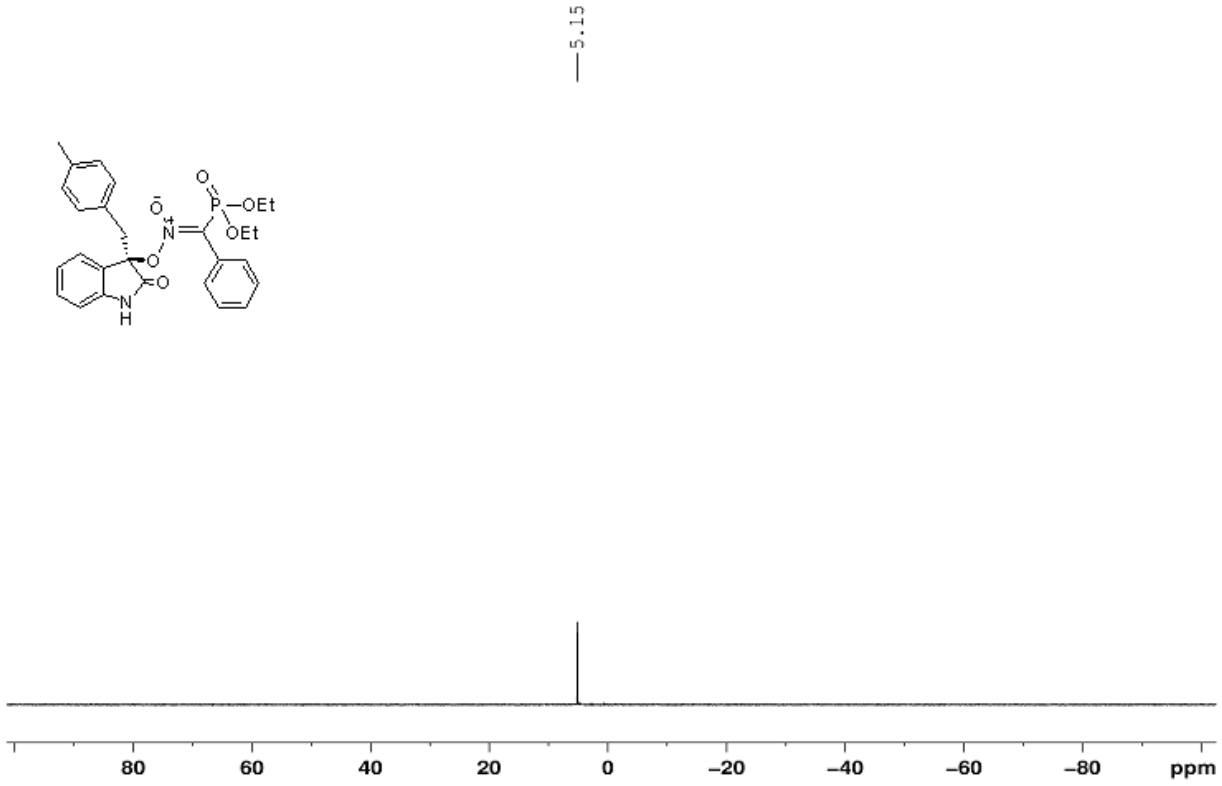

176.41
147.86
147.69
141.46
130.17
130.13
130.02
129.82
129.74
129.22
128.32
125.61
124.48
124.31
123.11
121.57
113.90
110.60
110.50
82.95
63.92
63.87
63.74
63.68
55.68
55.58
40.44
16.06
15.99
15.92
MeO
OMe
O
P
OEt
OEt
N
O
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


5.17
MeO
OMe
O
P
OEt
OEt
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

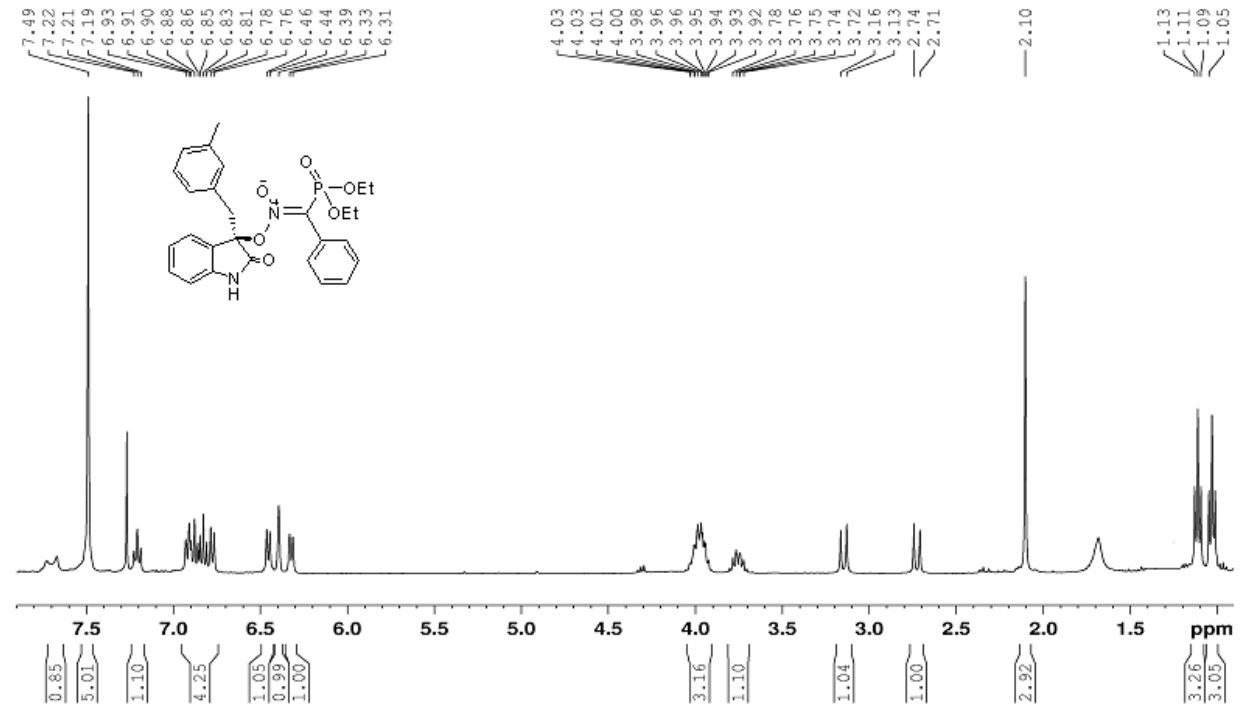
4g

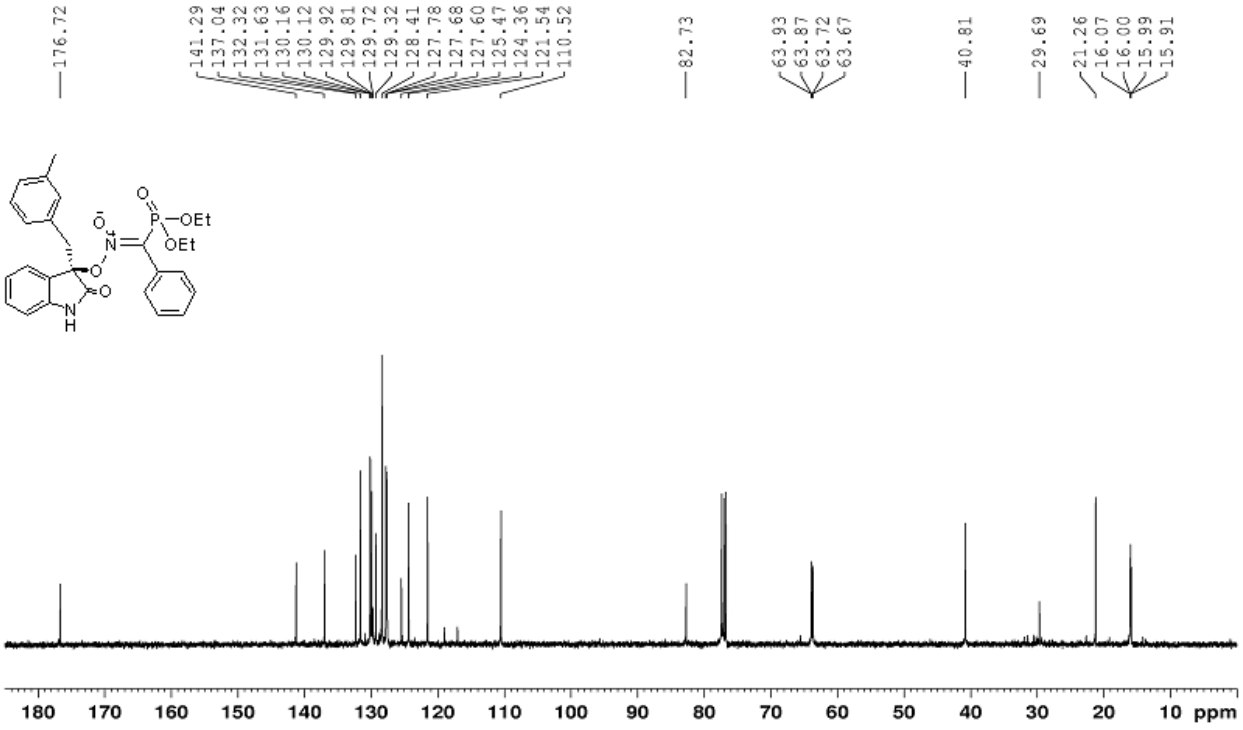

7.83 7.51 7.50 7.49 7.48 7.47 7.45 7.22 7.21 7.19 6.89 6.87 6.85 6.79 6.77 6.76 6.74 6.42 6.40 6.39 4.03 4.02 4.01 4.00 3.99 3.98 3.97 3.96 3.95 3.94 3.94 3.93 3.92 3.91 3.78 3.76 3.74 3.74 3.72 3.72 3.70 3.68 3.17 3.14 2.71 2.68 2.24 1.12 1.11 1.09 1.03 1.02 1.00
OEt
OEt
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.78 5.07 1.07 1.09 3.08 3.13 3.11 1.05 1.06 1.05 3.15 3.10 3.00

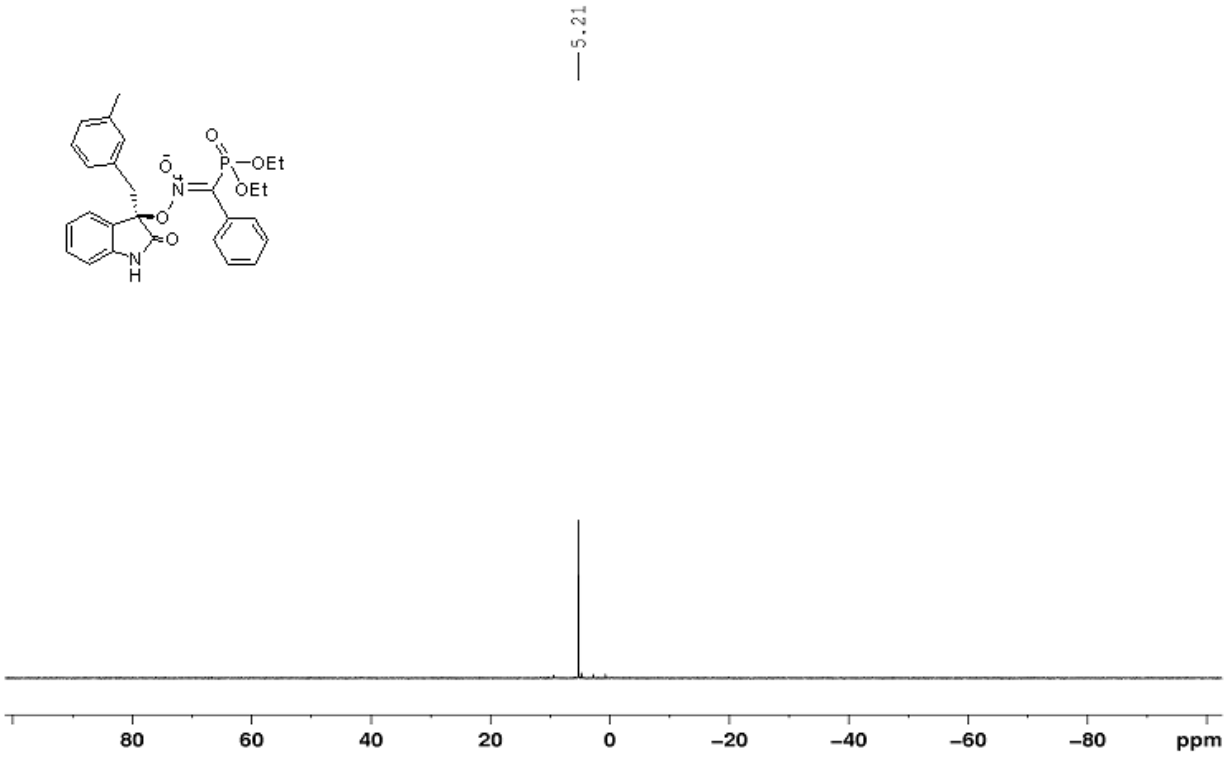

176.80
141.34 136.40 130.62 130.16 130.12 129.93 129.83 129.75 129.32 129.26 128.46 128.38 125.31 124.37 121.57 110.52
82.76
63.93 63.88 63.68 63.63
40.42
21.08 16.07 16.00 15.97 15.90
OEt
OEt
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


5.15
O
P
OEt
OEt
O
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

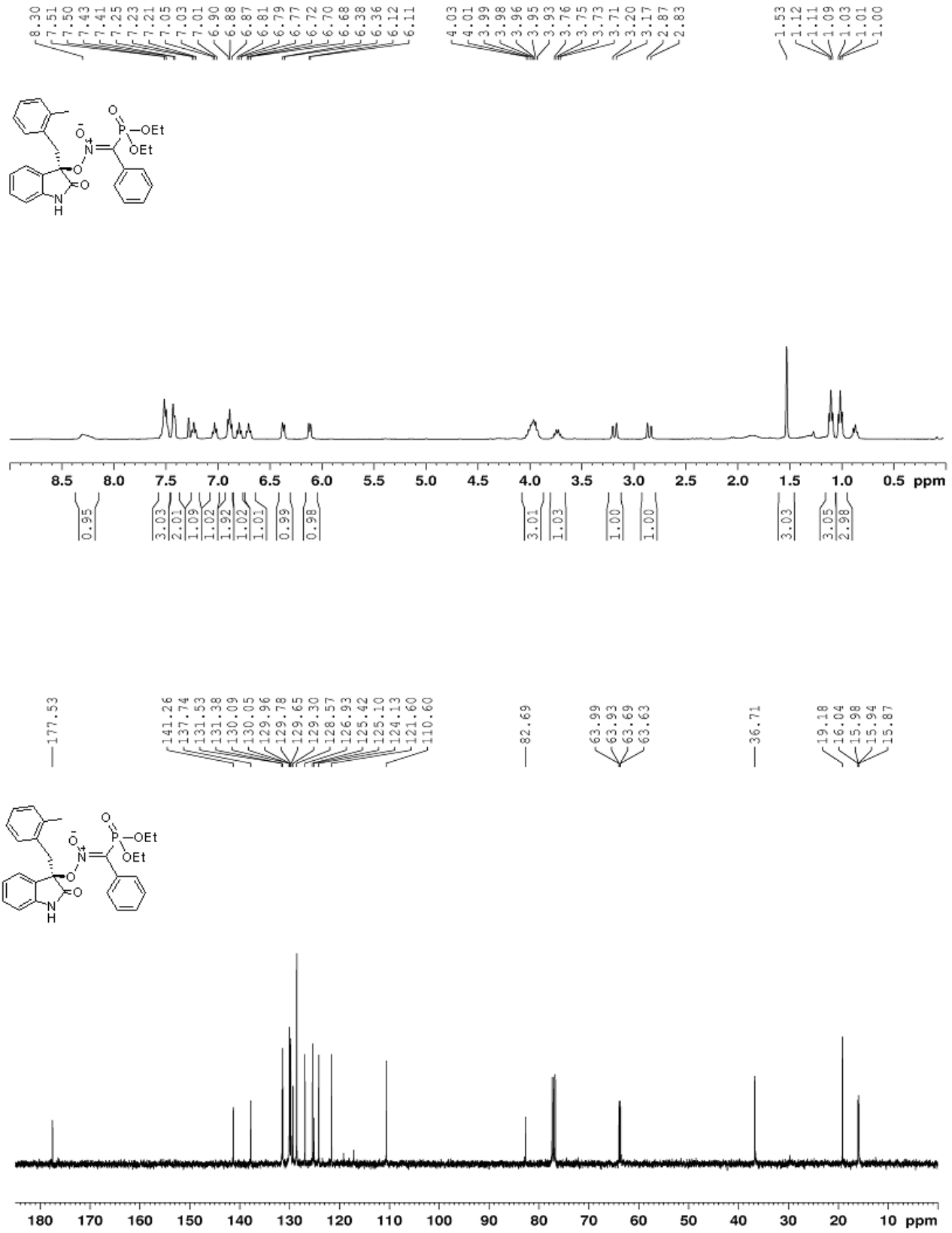
4h

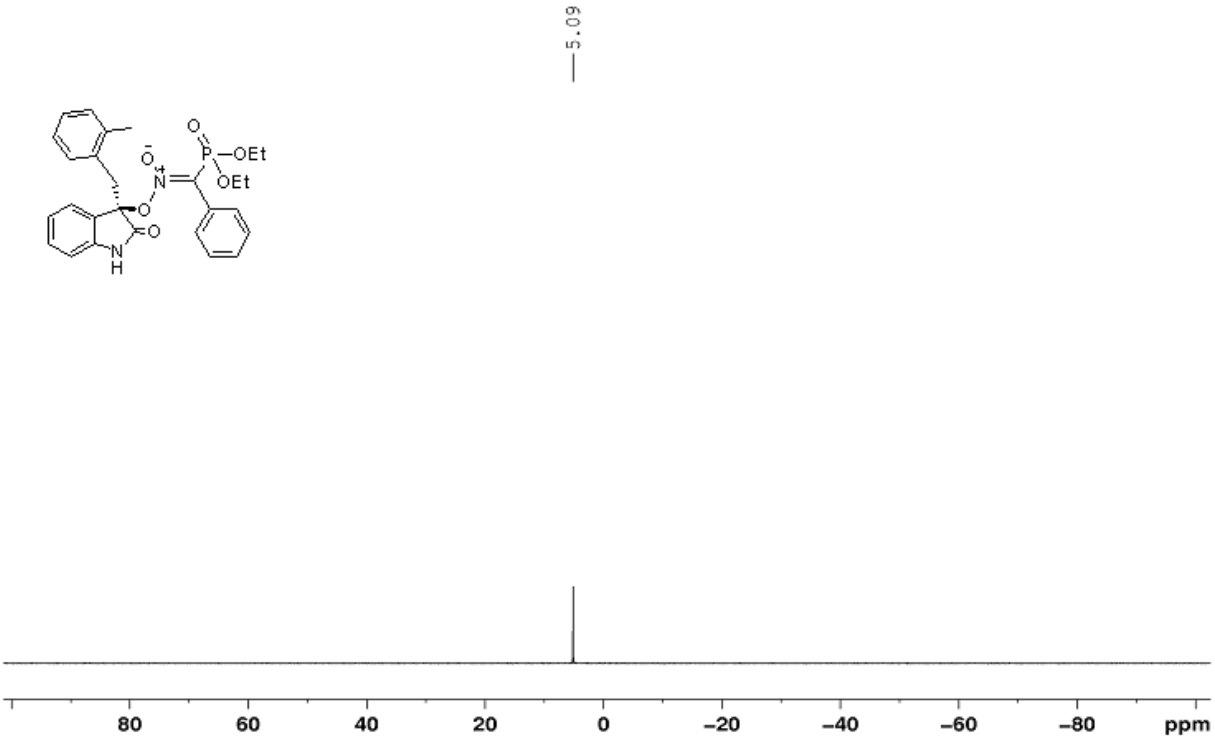

7.49
7.22
7.21
7.19
6.93
6.91
6.90
6.88
6.86
6.85
6.83
6.81
6.78
6.76
6.46
6.44
6.39
6.33
6.31
4.03
4.03
4.01
4.00
3.98
3.96
3.96
3.95
3.94
3.93
3.92
3.78
3.76
3.75
3.74
3.72
3.16
3.13
2.74
2.71
2.10
1.13
1.11
1.09
1.05
OEt
OEt
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.85
5.01
1.10
4.25
1.05
0.99
1.00
3.16
1.10
1.04
1.00
2.92
3.26
3.05


176.72
141.29
137.04
132.32
131.63
130.16
130.12
129.92
129.81
129.72
129.32
128.41
127.78
127.68
127.60
125.47
124.36
121.54
110.52
82.73
63.93
63.87
63.72
63.67
40.81
29.69
21.26
16.07
16.00
15.99
15.91
OEt
OEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

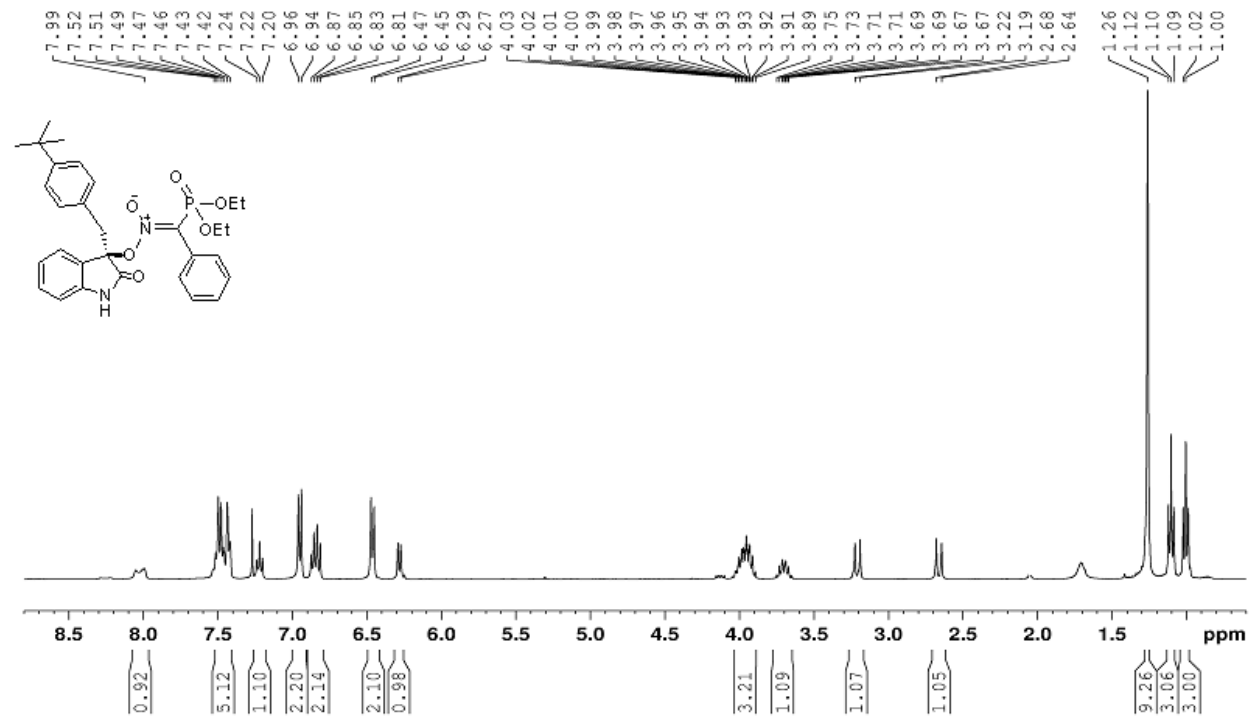

5.21
O
P
OEt
OEt
O
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

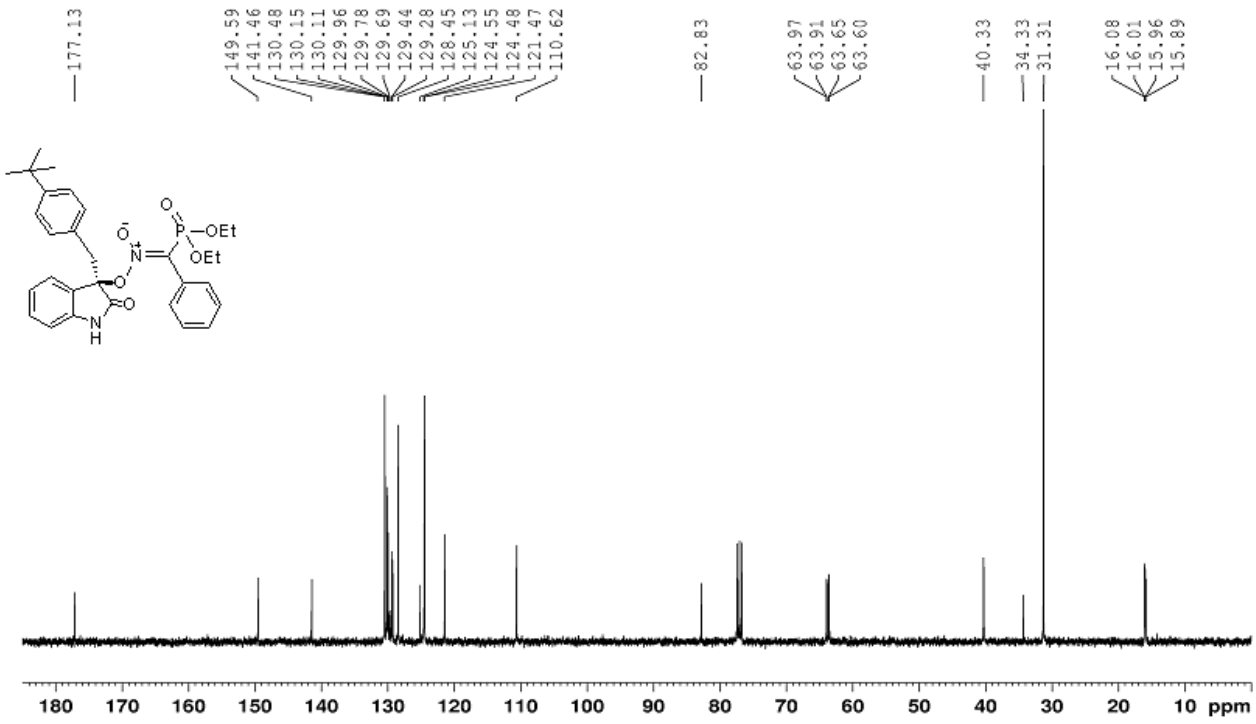
4i

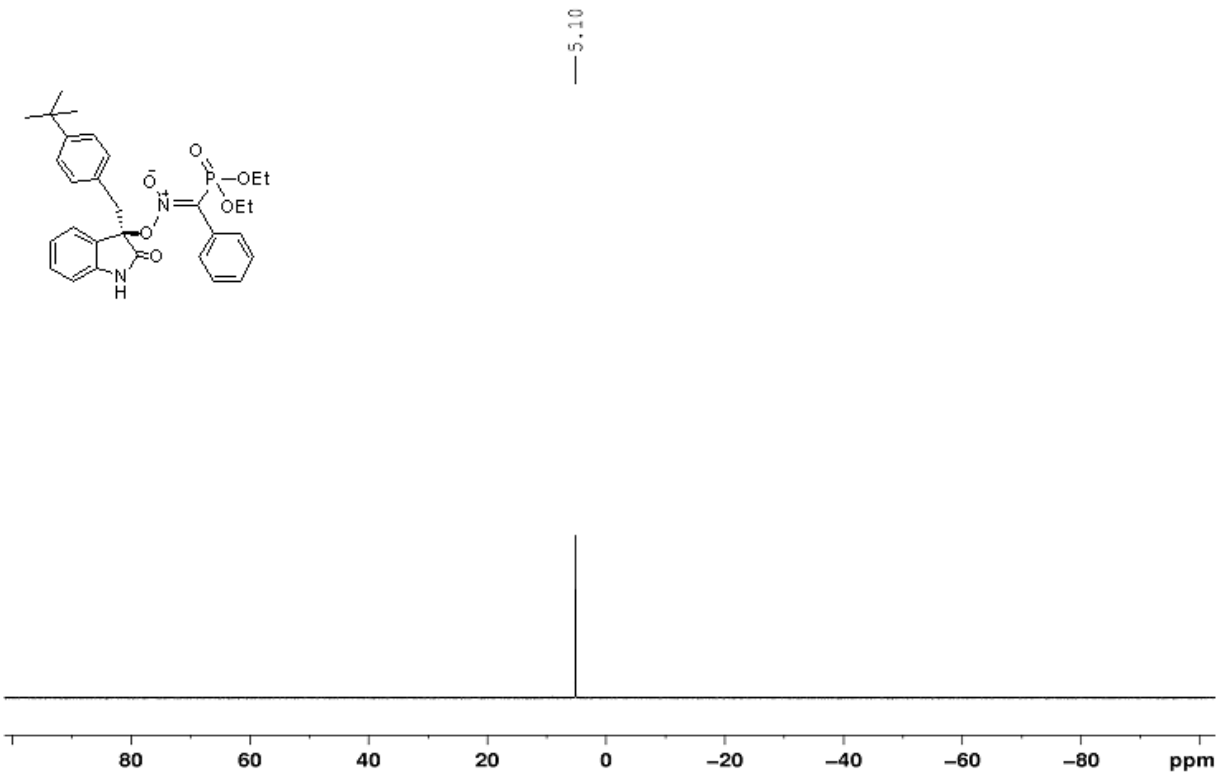

8.30
7.51
7.50
7.43
7.41
7.25
7.23
7.21
7.05
7.03
7.01
6.90
6.88
6.87
6.81
6.79
6.77
6.72
6.70
6.68
6.38
6.36
6.12
6.11
4.03
4.01
3.99
3.98
3.96
3.95
3.93
3.76
3.75
3.73
3.71
3.20
3.17
2.87
2.83
1.53
1.12
1.11
1.09
1.03
1.01
1.00
OEt
OEt
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.85
3.03
2.01
1.09
1.02
1.92
1.02
1.01
0.99
0.98
3.01
1.03
1.00
1.00
3.03
3.05
2.98
177.53
141.26
137.74
131.53
131.38
130.09
130.05
129.96
129.78
129.65
129.30
128.57
126.93
125.42
125.10
124.13
121.60
110.60
82.69
63.99
63.93
63.69
63.63
36.71
19.18
16.04
15.98
15.94
15.87
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


5.09
O
P—OEt
OEt
O
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

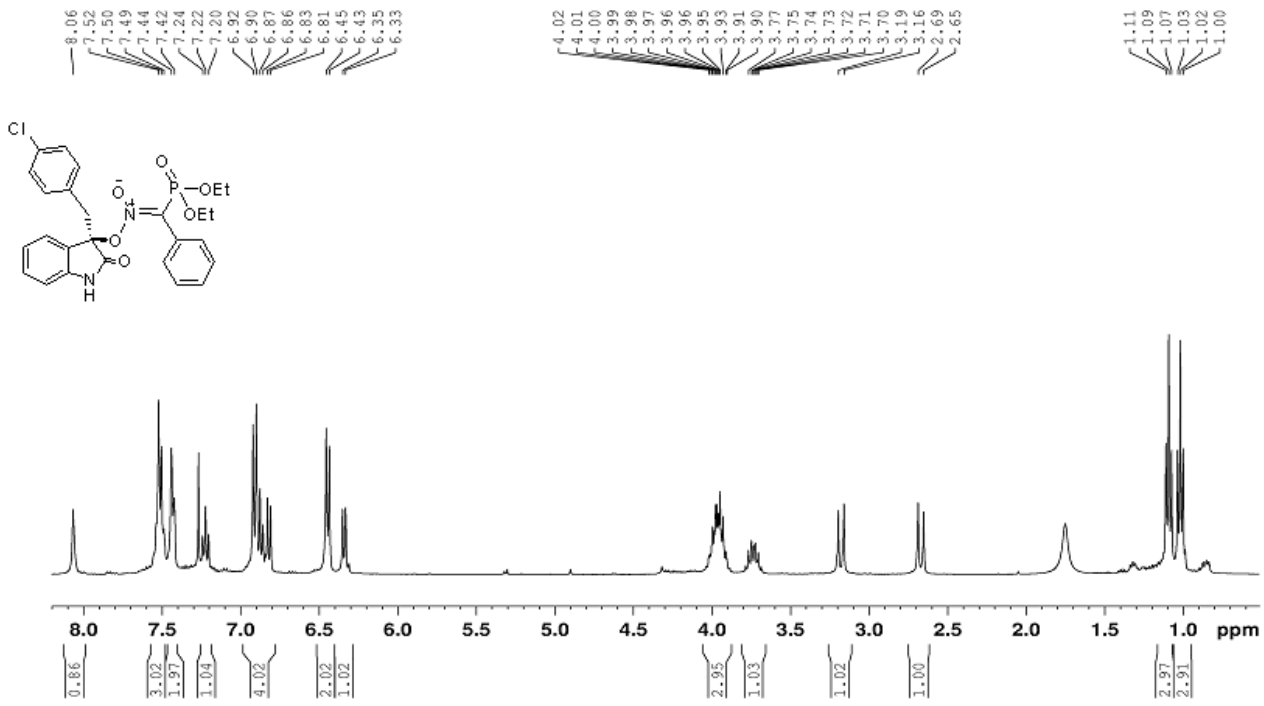
4j

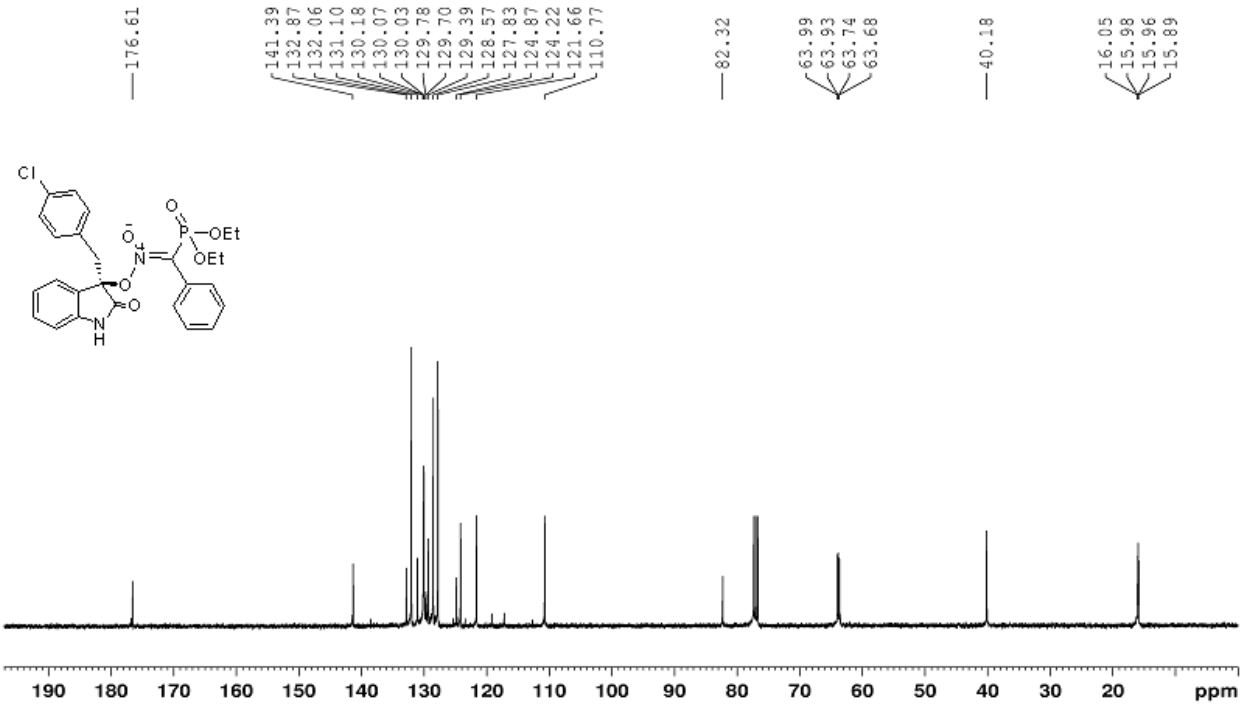

7.99
7.52
7.51
7.49
7.47
7.46
7.43
7.42
7.24
7.22
7.20
6.96
6.94
6.87
6.85
6.83
6.81
6.47
6.45
6.29
6.27
4.03
4.02
4.01
4.00
3.99
3.98
3.97
3.96
3.95
3.94
3.93
3.92
3.91
3.89
3.75
3.73
3.71
3.71
3.69
3.69
3.67
3.67
3.22
3.19
2.68
2.64
1.26
1.12
1.10
1.09
1.02
1.00
OEt
OEt
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.92
5.12
1.10
2.20
2.14
2.10
0.98
3.21
1.09
1.07
1.05
9.26
3.06
3.00

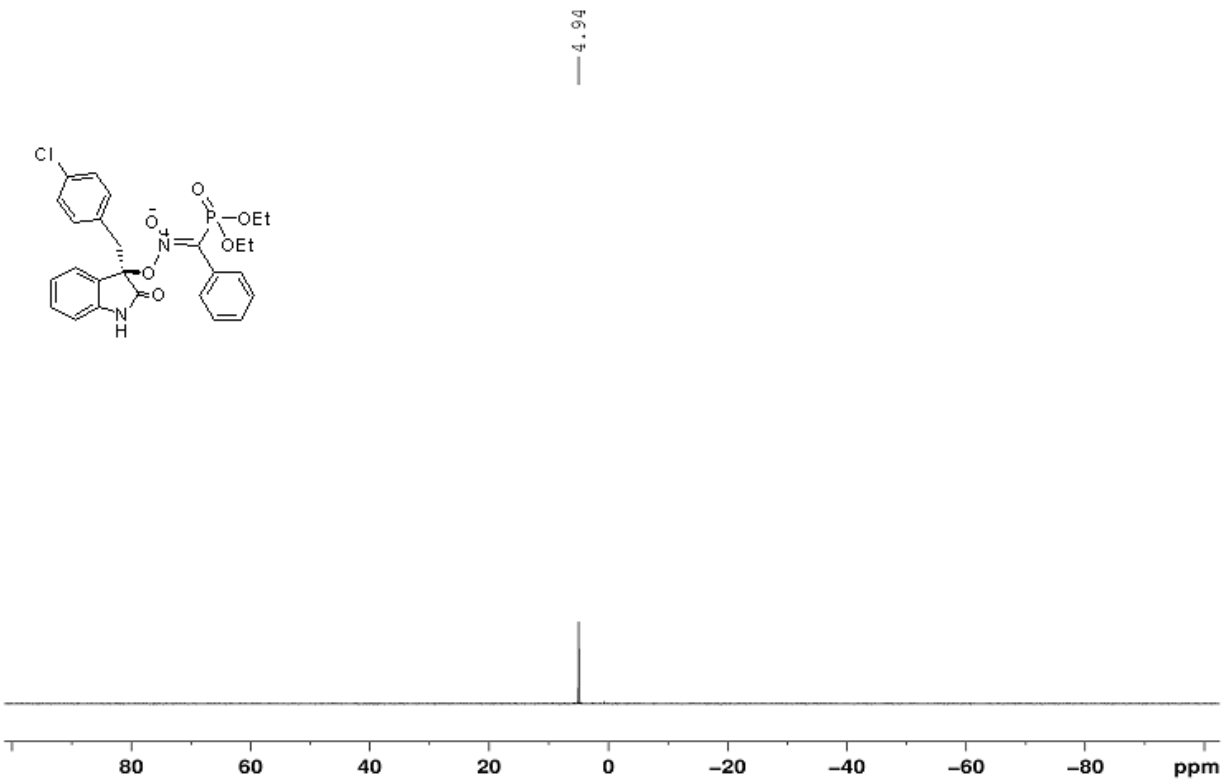

177.13
149.59
141.46
130.48
130.15
130.11
129.96
129.78
129.69
129.44
129.28
128.45
125.13
124.55
124.48
121.47
110.62
82.83
63.97
63.91
63.65
63.60
40.33
34.33
31.31
16.08
16.01
15.96
15.89
OEt
OEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


5.10
OEt
OEt
80
60
40
20
0
−20
−40
−60
−80
ppm

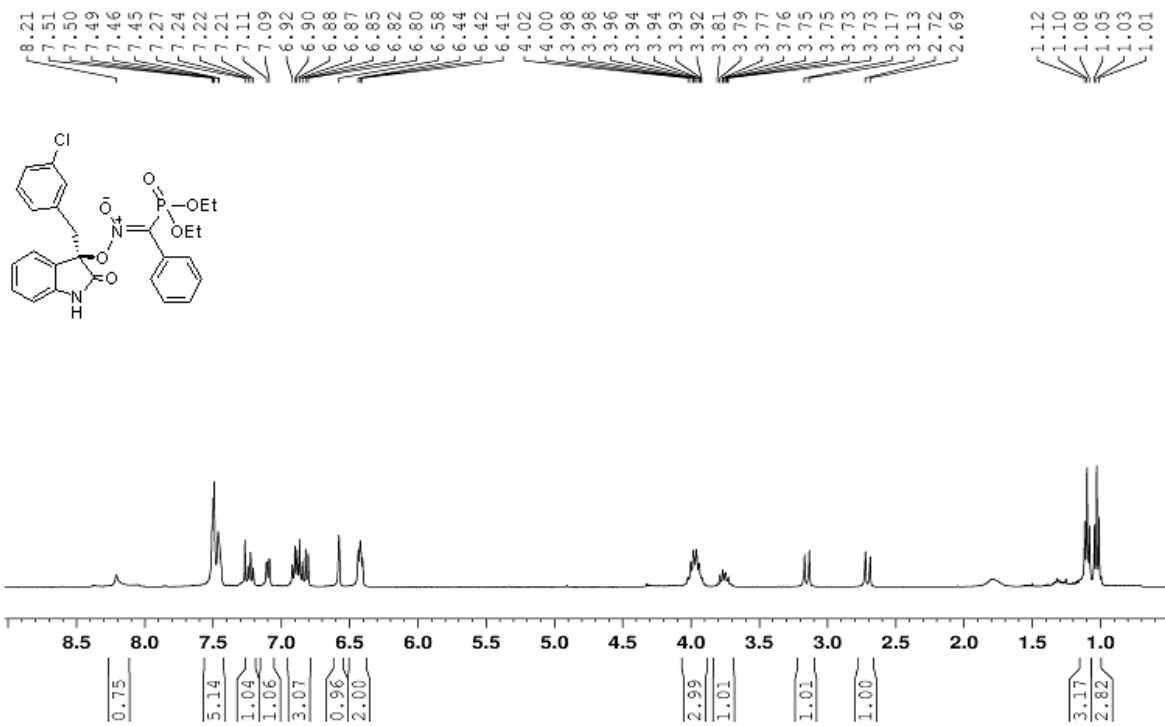
4k

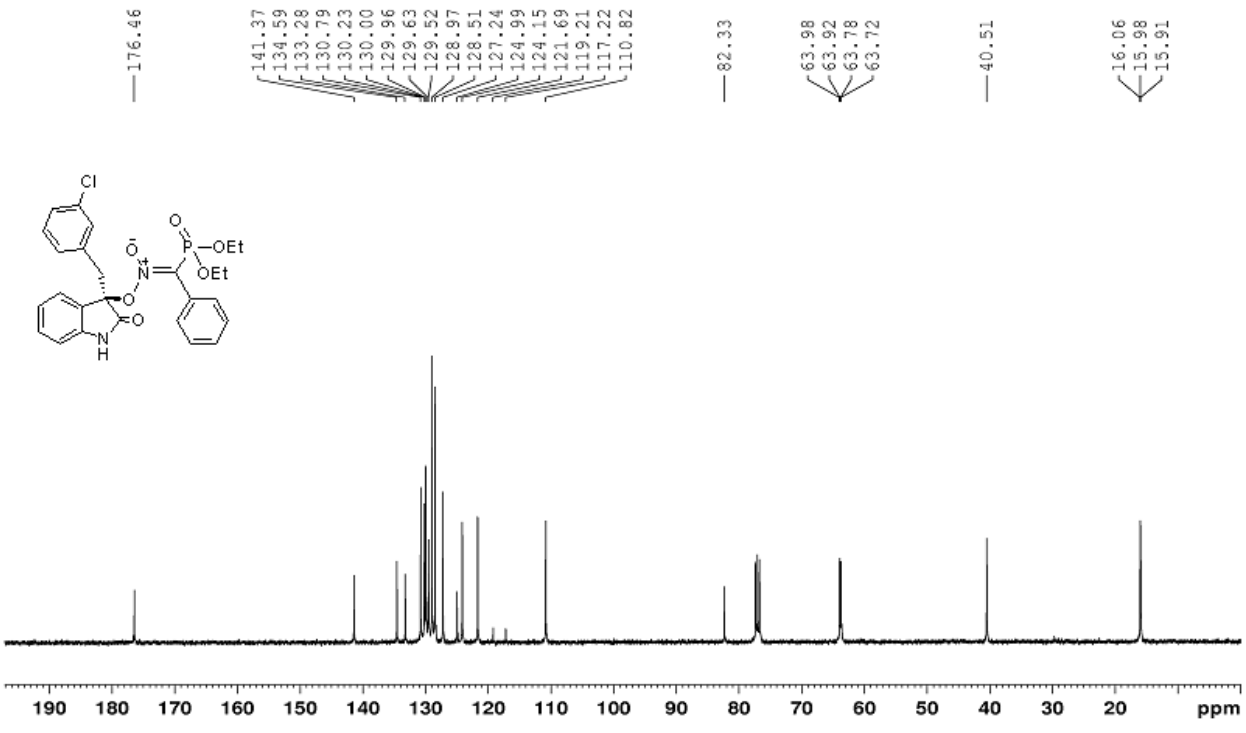

8.06
7.52
7.50
7.49
7.44
7.42
7.24
7.22
7.20
6.92
6.90
6.87
6.86
6.83
6.81
6.45
6.43
6.35
6.33
4.02
4.01
4.00
3.99
3.98
3.97
3.96
3.96
3.95
3.93
3.91
3.90
3.77
3.75
3.74
3.73
3.72
3.71
3.70
3.19
3.16
2.69
2.65
1.11
1.09
1.07
1.03
1.02
1.00
Cl
O
P
OEt
OEt
N
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.86
3.02
1.97
1.04
4.02
2.02
1.02
2.95
1.03
1.02
1.00
2.97
2.91

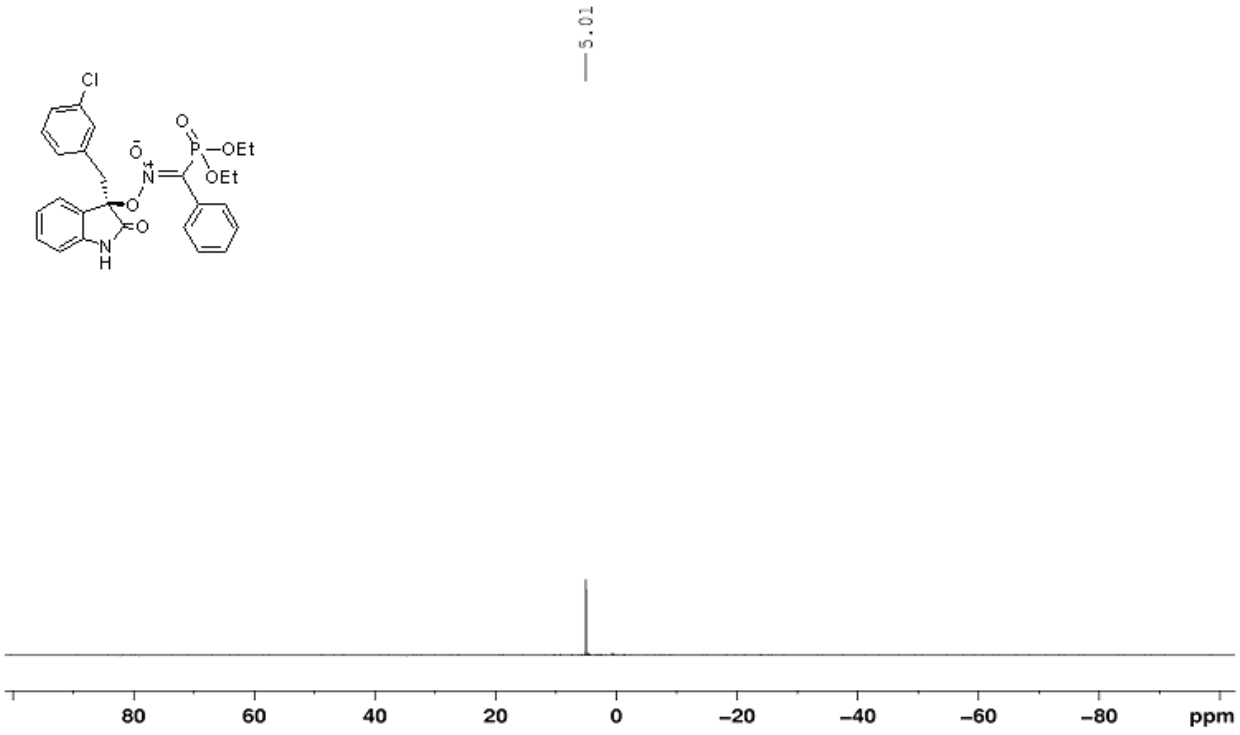

176.61
141.39
132.87
132.06
131.10
130.18
130.07
130.03
129.78
129.70
129.39
128.57
127.83
124.87
124.22
121.66
110.77
82.32
63.99
63.93
63.74
63.68
40.18
16.05
15.98
15.96
15.89
Cl
O
P
OEt
OEt
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


4.94
Cl
O
P
OEt
OEt
O
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

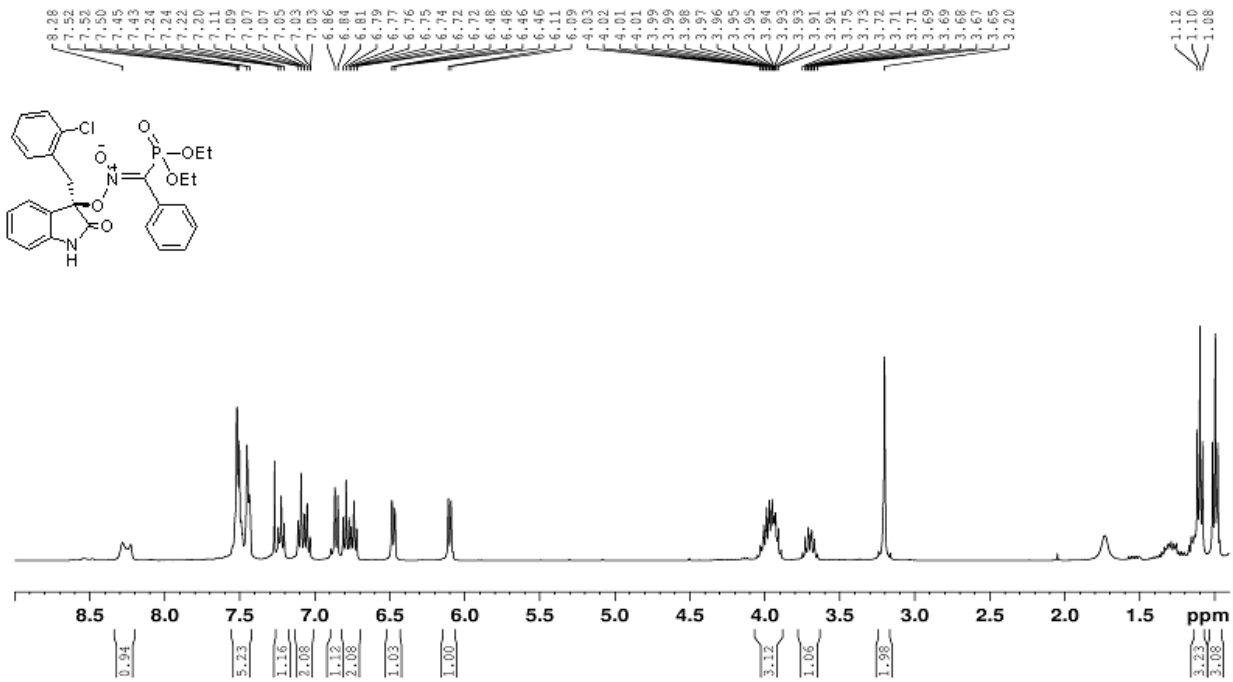
4l

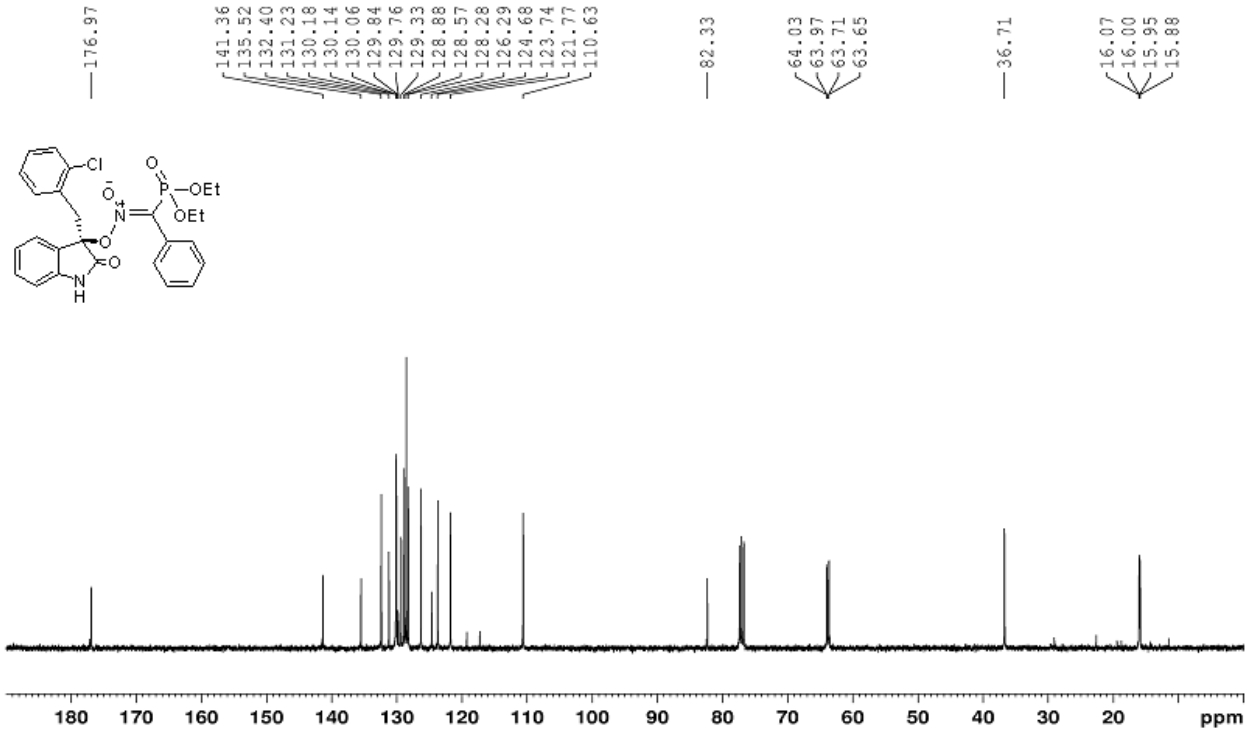

8.21
7.51
7.50
7.49
7.46
7.45
7.27
7.24
7.22
7.21
7.11
7.09
6.92
6.90
6.88
6.87
6.85
6.82
6.80
6.58
6.44
6.42
6.41
4.02
4.00
3.98
3.98
3.96
3.94
3.94
3.93
3.92
3.81
3.79
3.77
3.76
3.75
3.75
3.73
3.73
3.17
3.13
2.72
2.69
1.12
1.10
1.08
1.05
1.03
1.01
Cl
O
P
OEt
OEt
N
O
O
N
H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.75
5.14
1.04
1.06
3.07
0.96
2.00
2.99
1.01
1.01
1.00
3.17
2.82

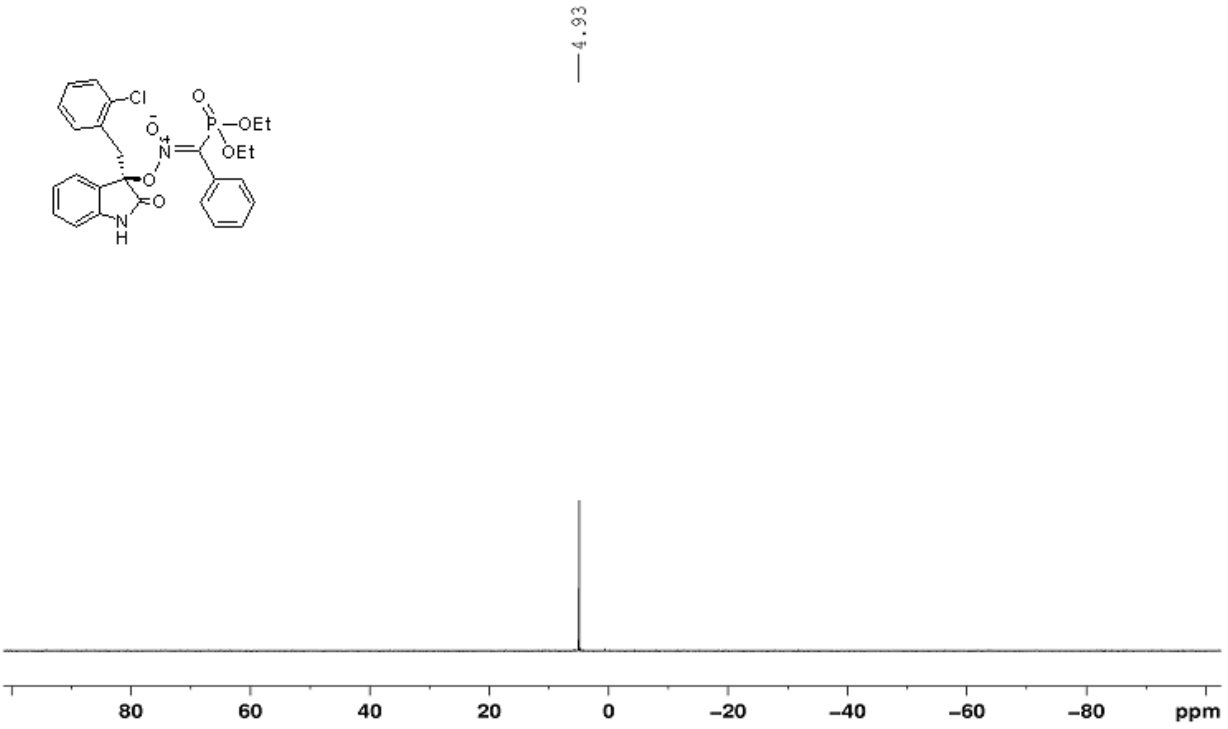

176.46
141.37
134.59
133.28
130.79
130.23
130.00
129.96
129.63
129.52
128.97
128.51
127.24
124.99
124.15
121.69
119.21
117.22
110.82
82.33
63.98
63.92
63.78
63.72
40.51
16.06
15.98
15.91
Cl
O
P
OEt
OEt
N
O
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


5.01
Cl
O
P
OEt
OEt
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

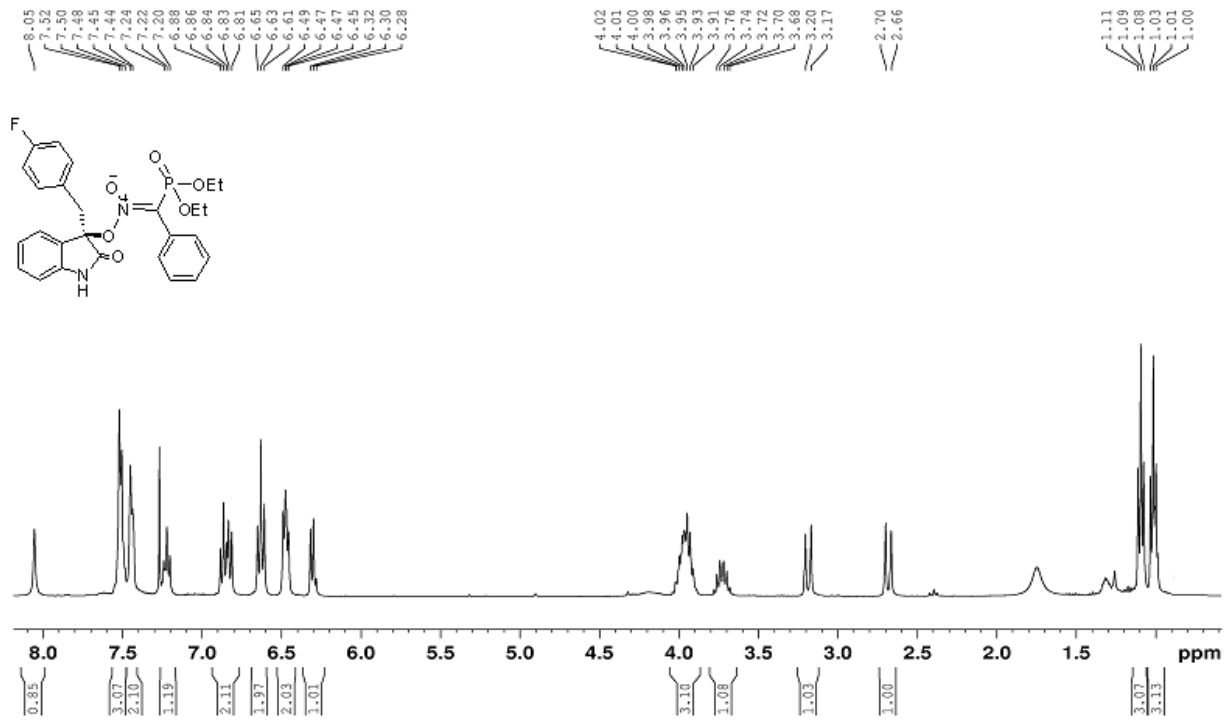
4m

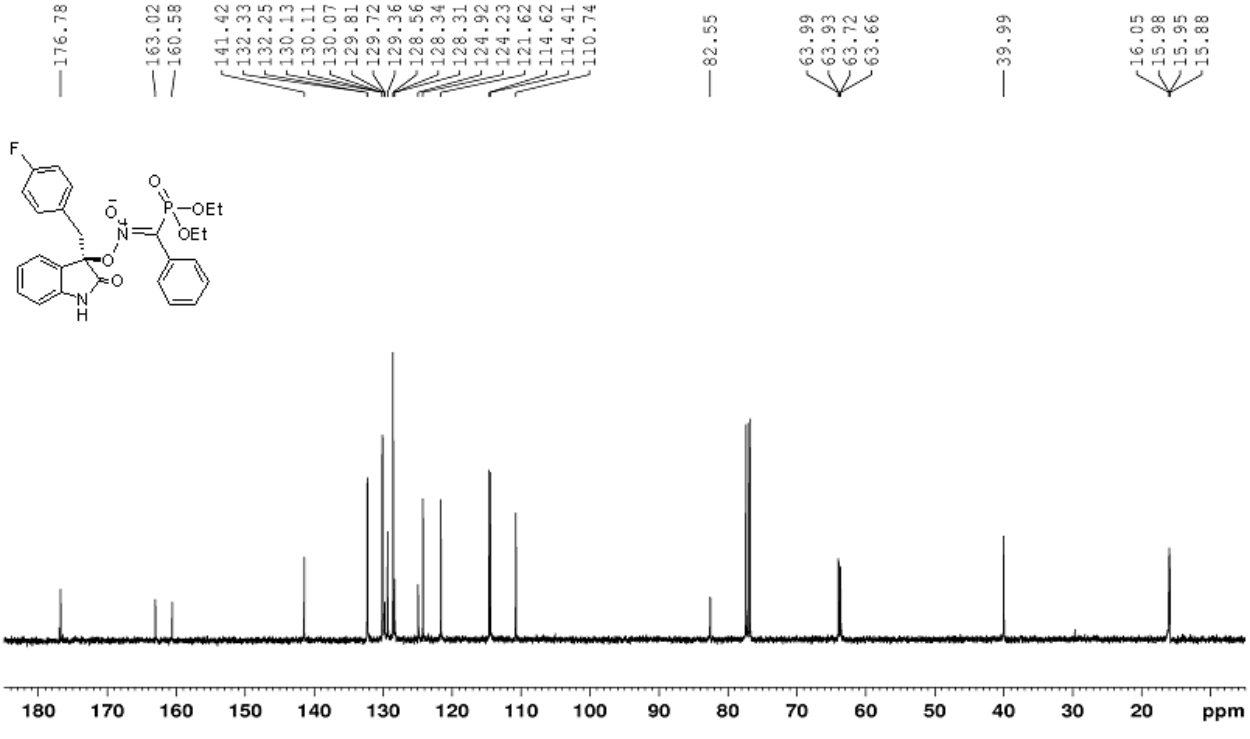

8.28
7.52
7.52
7.50
7.45
7.43
7.24
7.24
7.22
7.20
7.11
7.09
7.07
7.07
7.05
7.03
7.03
6.86
6.84
6.81
6.79
6.77
6.76
6.75
6.74
6.72
6.72
6.48
6.48
6.46
6.46
6.11
6.09
4.03
4.02
4.01
4.01
3.99
3.99
3.98
3.97
3.96
3.95
3.95
3.94
3.93
3.93
3.91
3.91
3.75
3.73
3.72
3.71
3.71
3.69
3.69
3.68
3.67
3.65
3.20
1.12
1.10
1.08
Cl
O
N
O
P
OEt
OEt
O
N
H
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
ppm
0.94
5.23
1.16
2.08
1.12
2.08
1.03
1.00
3.12
1.06
1.98
3.23
3.08

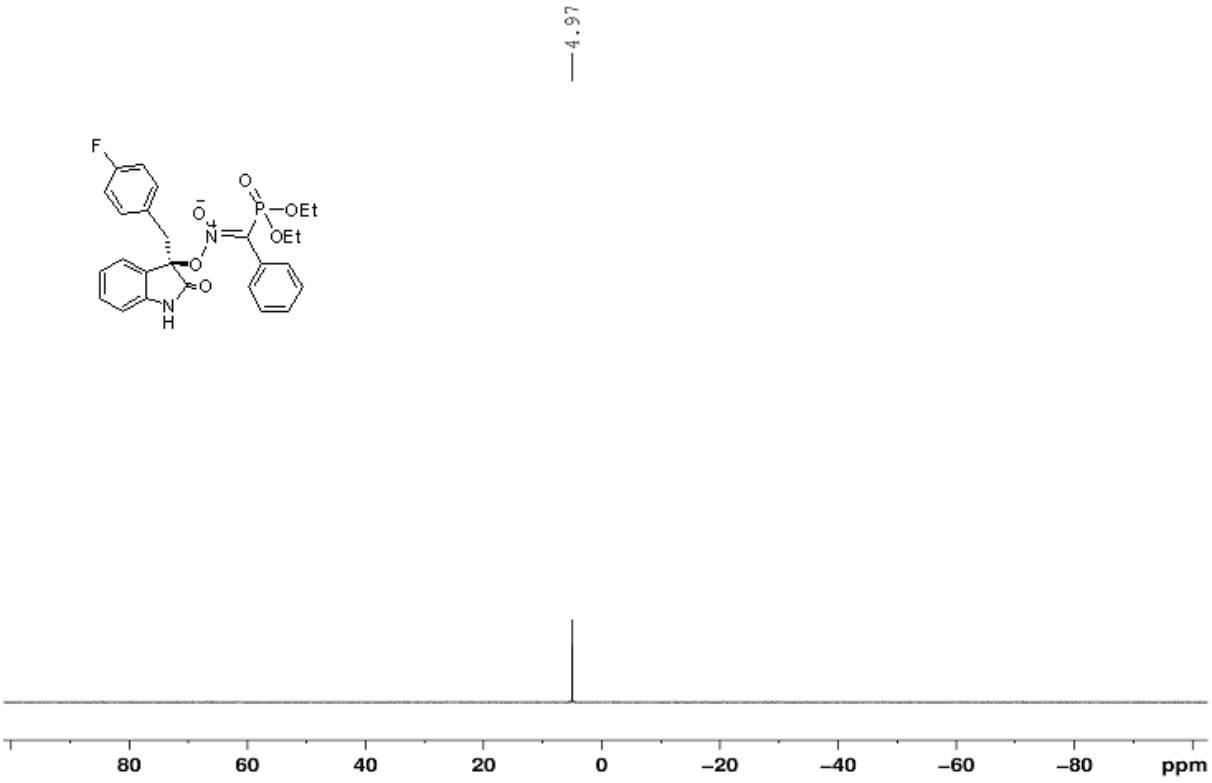

176.97
141.36
135.52
132.40
131.23
130.18
130.14
130.06
129.84
129.76
129.33
128.88
128.57
128.28
126.29
124.68
123.74
121.77
110.63
82.33
64.03
63.97
63.71
63.65
36.71
16.07
16.00
15.95
15.88
Cl
O
N
O
P
OEt
OEt
O
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


4.93
Cl
O
P
OEt
OEt
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

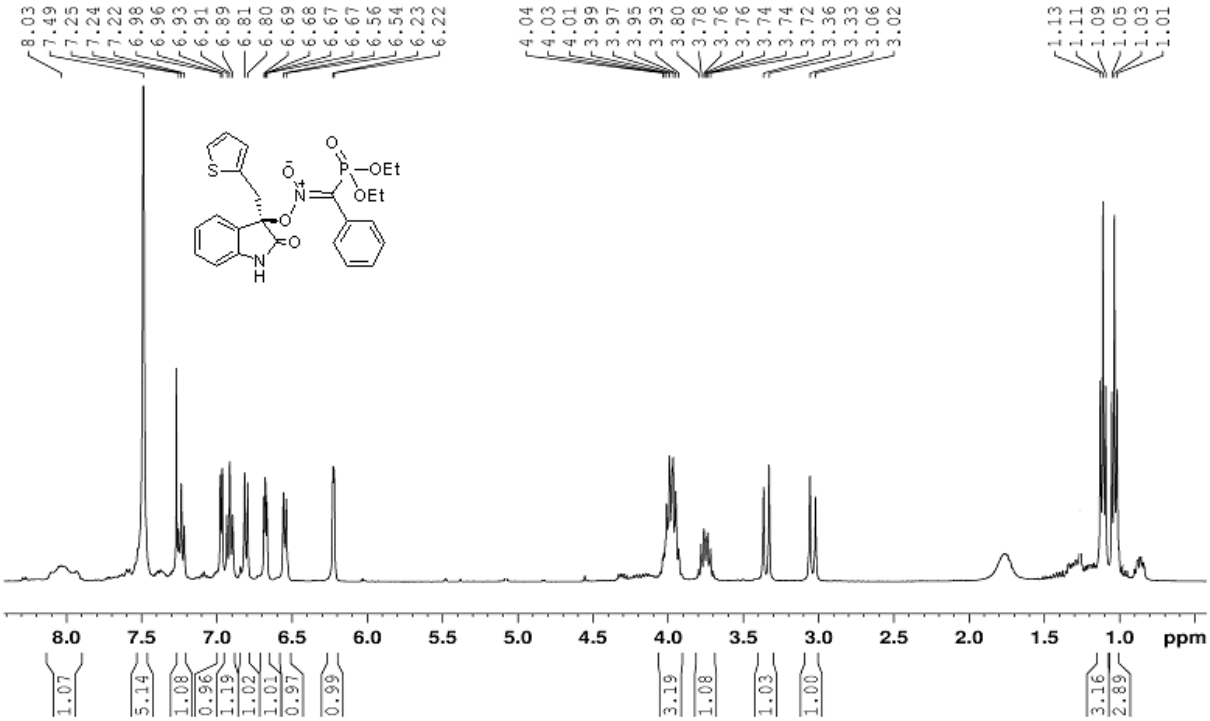
4n

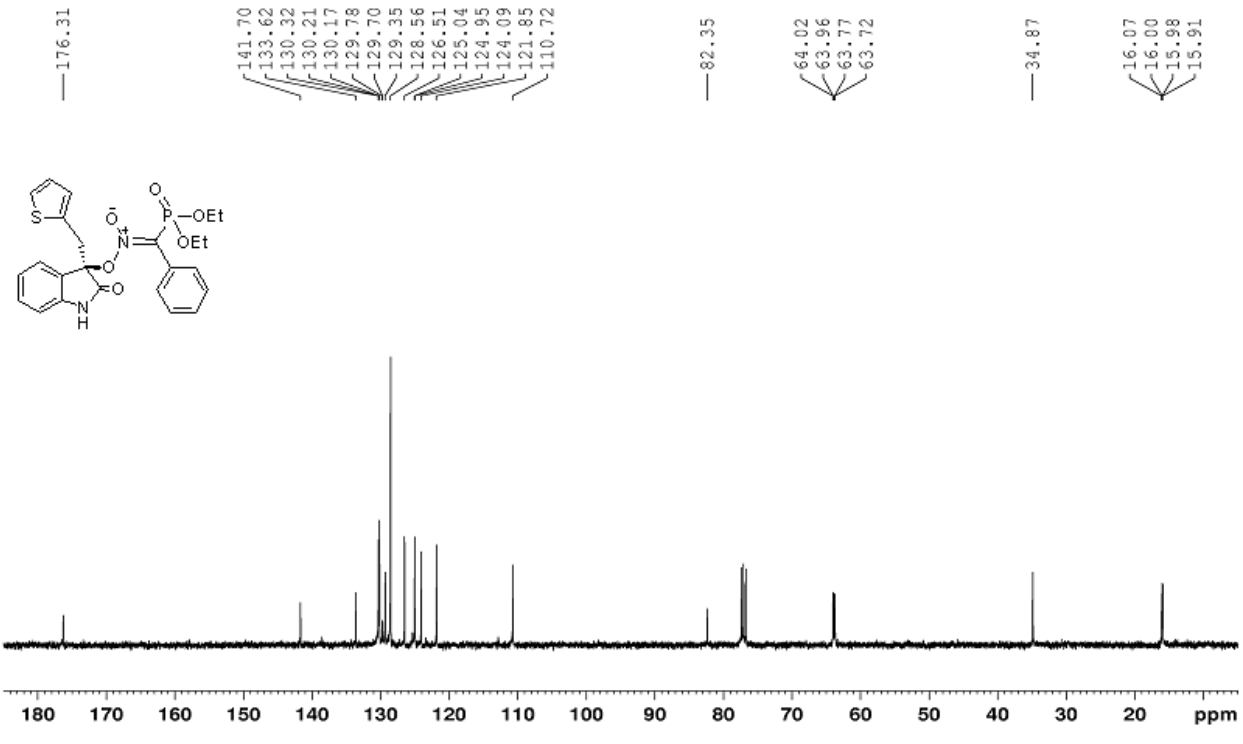

8.05
7.52
7.50
7.48
7.45
7.44
7.24
7.22
7.20
6.88
6.86
6.84
6.83
6.81
6.65
6.63
6.61
6.49
6.47
6.47
6.45
6.32
6.30
6.28
4.02
4.01
4.00
3.98
3.96
3.95
3.93
3.91
3.76
3.74
3.72
3.70
3.68
3.20
3.17
2.70
2.66
1.11
1.09
1.08
1.03
1.01
1.00
F
O
P
OEt
OEt
N
O
O
N
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.85
3.07
2.10
1.19
2.11
1.97
2.03
1.01
3.10
1.08
1.03
1.00
3.07
3.13

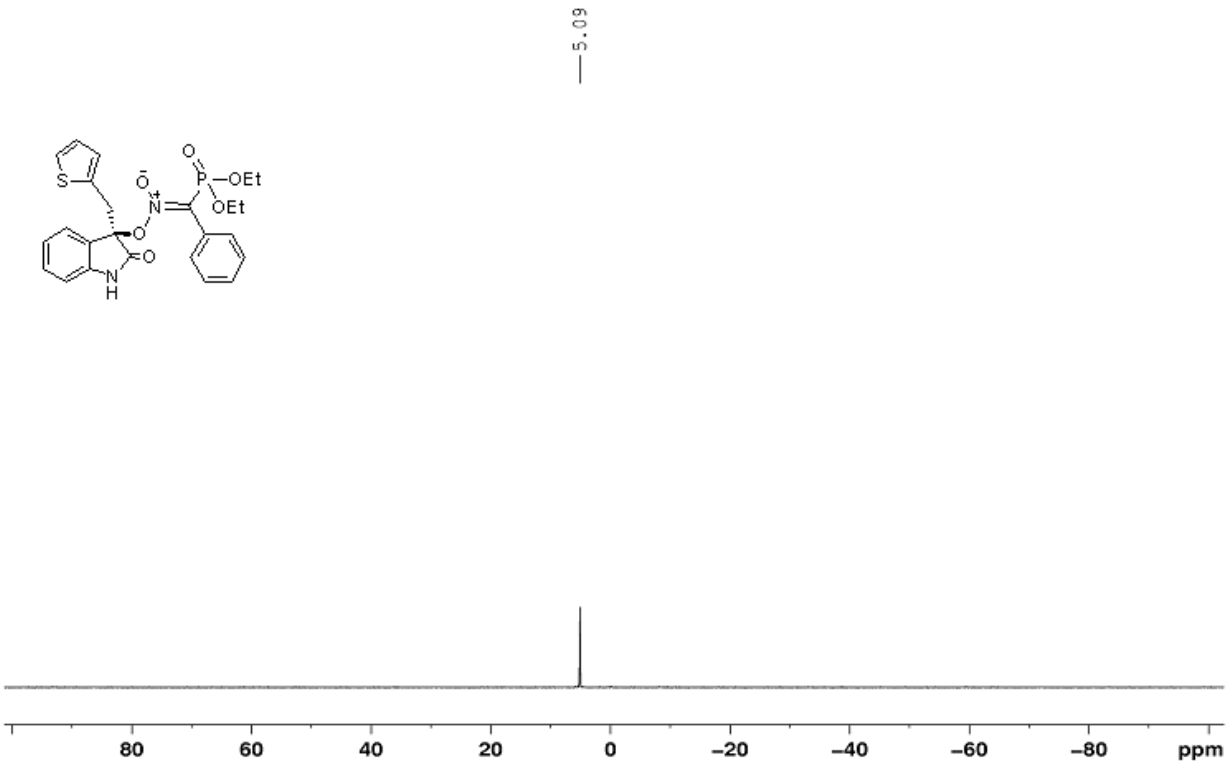

176.78
163.02
160.58
141.42
132.33
132.25
130.13
130.11
130.07
129.81
129.72
129.36
128.56
128.34
128.31
124.92
124.23
121.62
114.62
114.41
110.74
82.55
63.99
63.93
63.72
63.66
39.99
16.05
15.98
15.95
15.88
F
O
P
OEt
OEt
N
O
O
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


4.97
F
O
P
OEt
OEt
O
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

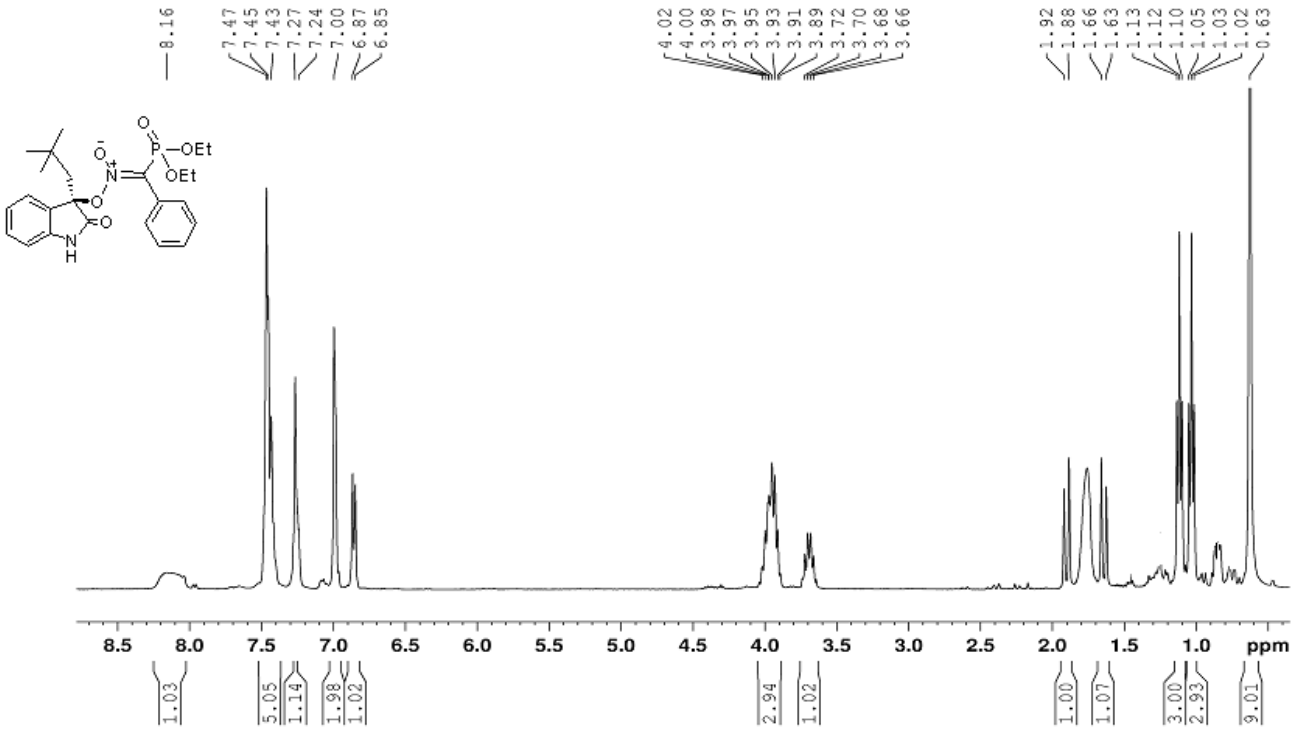
4o

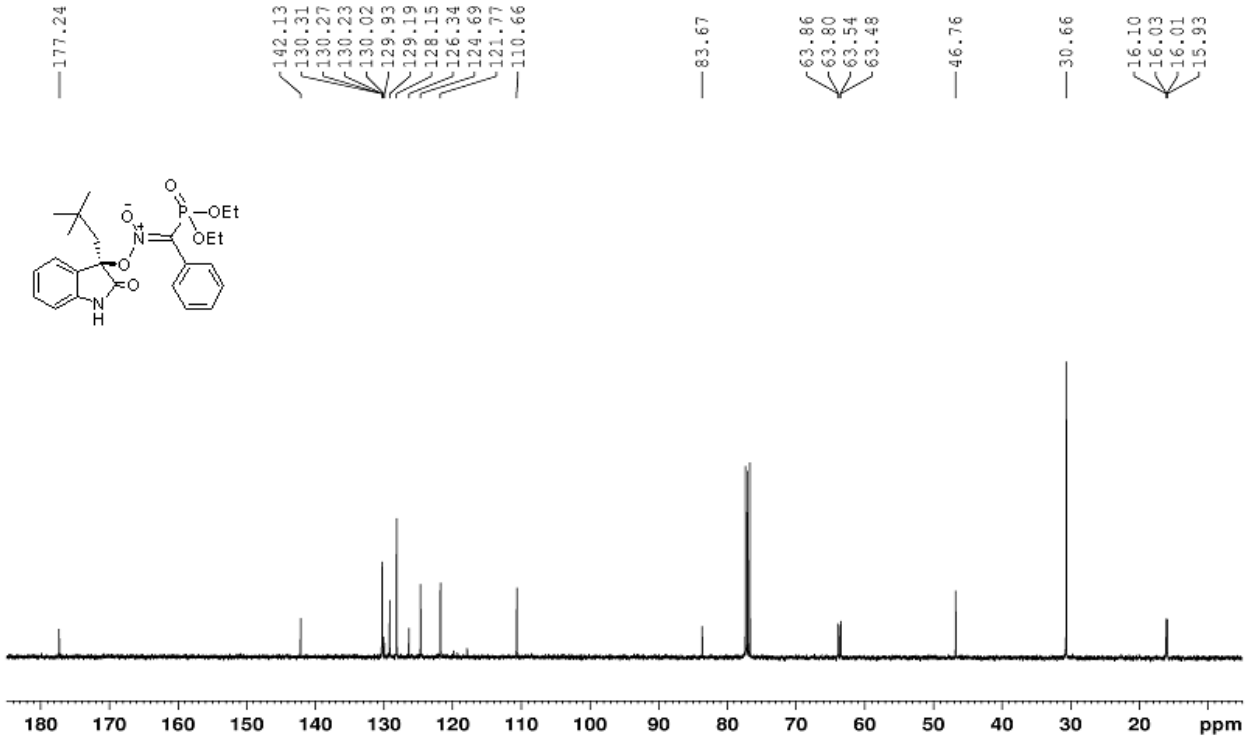

8.03
7.49
7.25
7.24
7.22
6.98
6.96
6.93
6.91
6.89
6.81
6.80
6.69
6.68
6.67
6.67
6.56
6.54
6.23
6.22
4.04
4.03
4.01
3.99
3.97
3.95
3.93
3.80
3.78
3.76
3.76
3.74
3.74
3.72
3.36
3.33
3.06
3.02
1.13
1.11
1.09
1.05
1.03
1.01
OEt
OEt
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.07
5.14
1.08
0.96
1.19
1.02
1.01
0.97
0.99
3.19
1.08
1.03
1.00
3.16
2.89

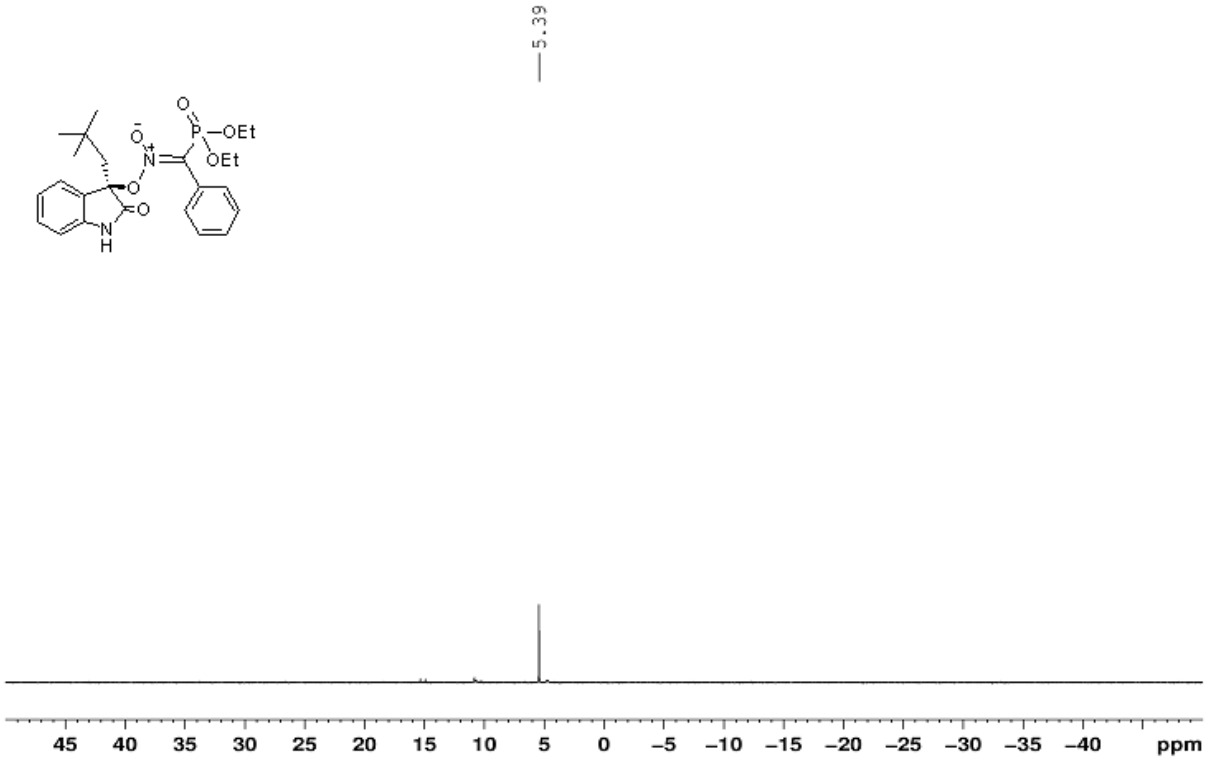

176.31
141.70
133.62
130.32
130.21
130.17
129.78
129.70
129.35
128.56
126.51
125.04
124.95
124.09
121.85
110.72
82.35
64.02
63.96
63.77
63.72
34.87
16.07
16.00
15.98
15.91
OEt
OEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


5.09
S
O
N
O
P
OEt
OEt
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

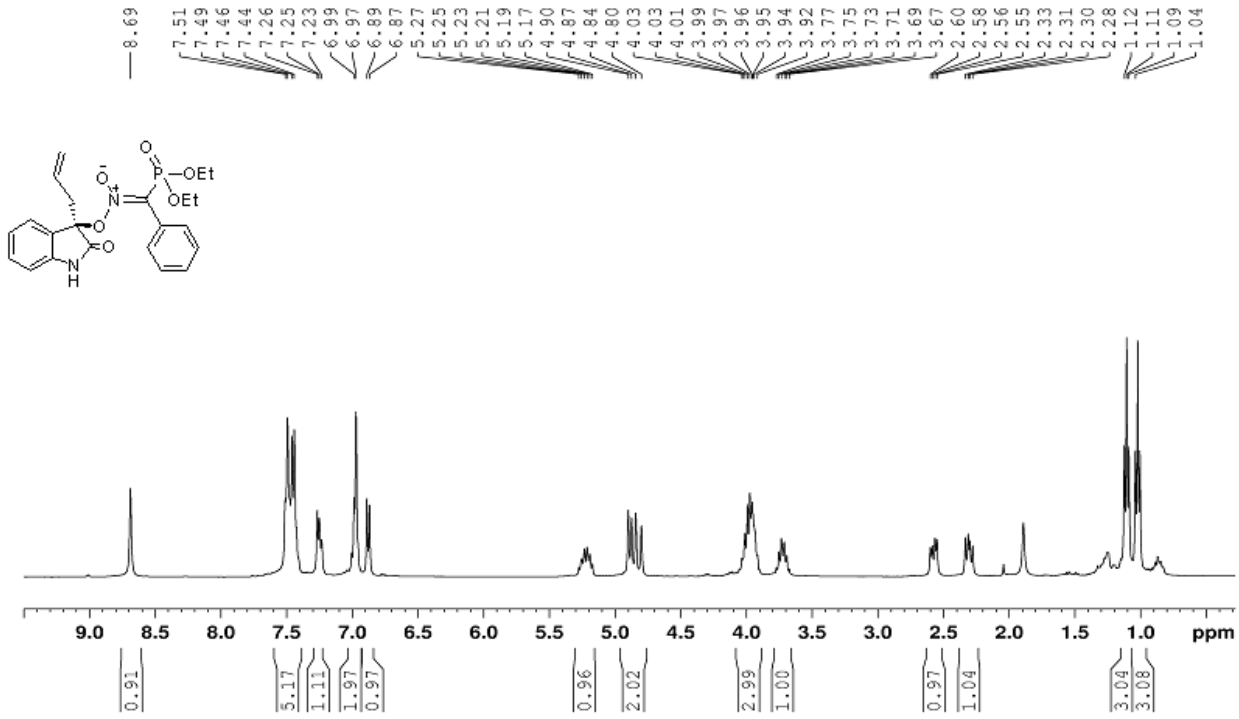
4p

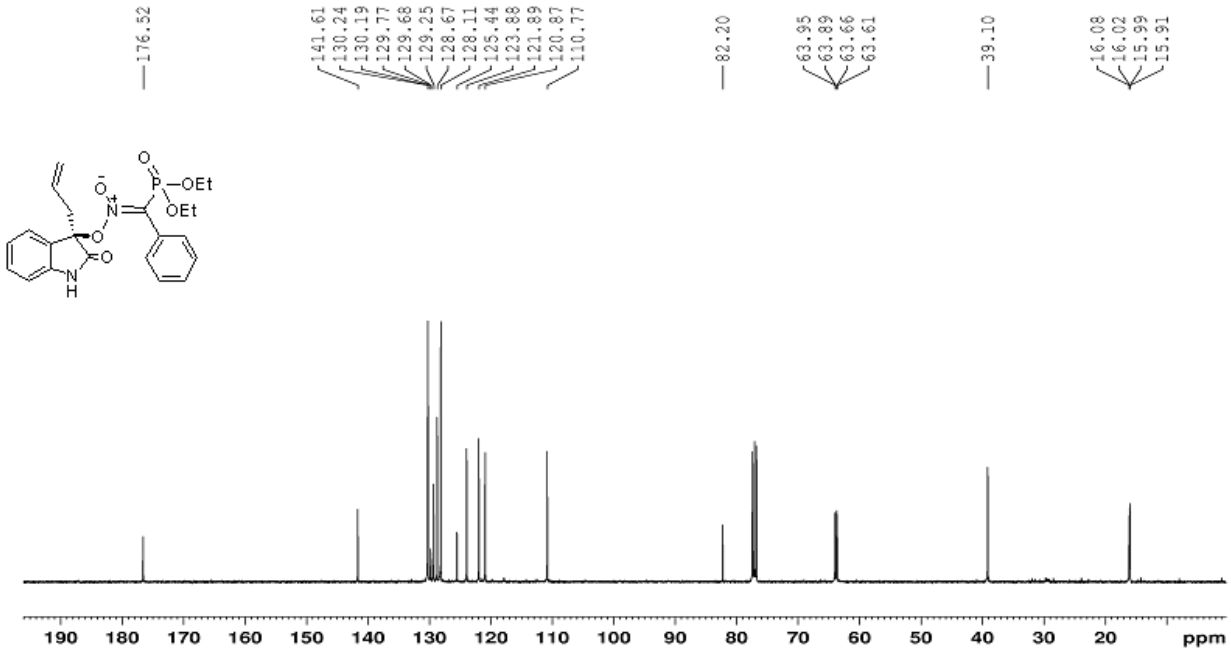

8.16
7.47
7.45
7.43
7.27
7.24
7.00
6.87
6.85
4.02
4.00
3.98
3.97
3.95
3.93
3.91
3.89
3.72
3.70
3.68
3.66
1.92
1.88
1.66
1.63
1.13
1.12
1.10
1.05
1.03
1.02
0.63
OEt
OEt
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.03
5.05
1.14
1.98
1.02
2.94
1.02
1.00
1.07
3.00
2.93
9.01

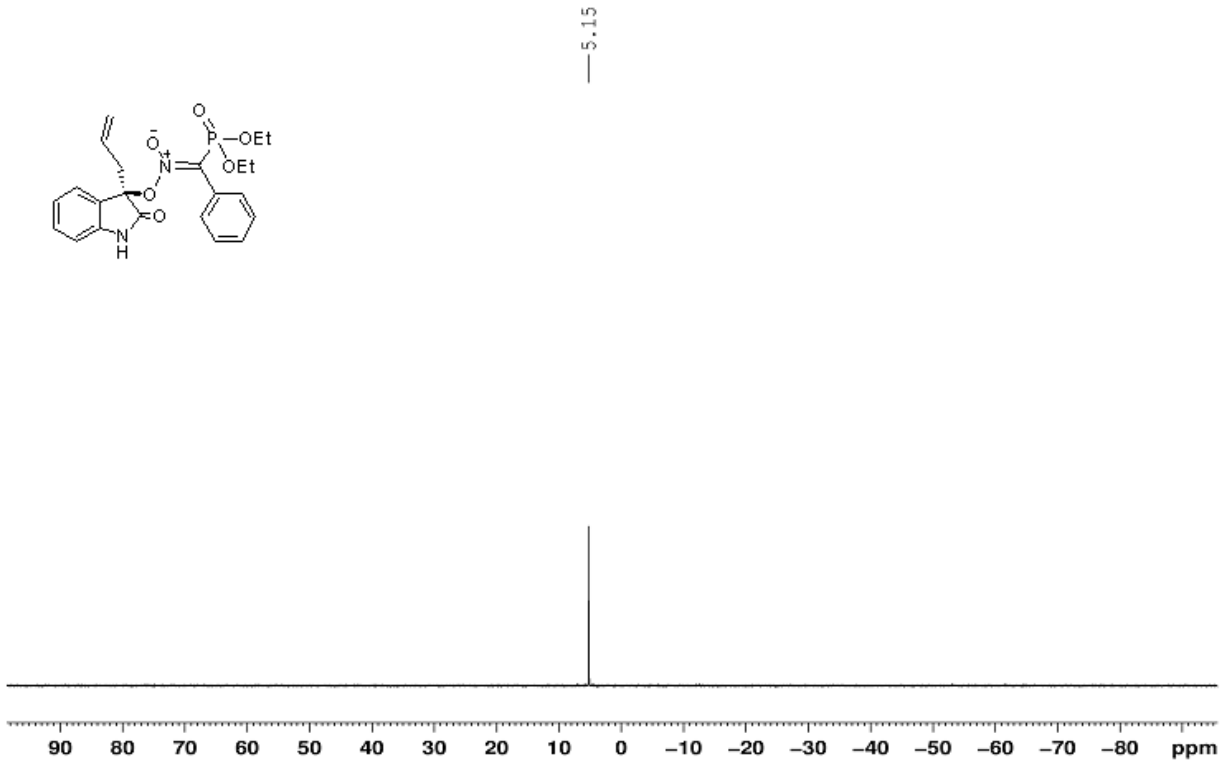

177.24
142.13
130.31
130.27
130.23
130.02
129.93
129.19
128.15
126.34
124.69
121.77
110.66
83.67
63.86
63.80
63.54
63.48
46.76
30.66
16.10
16.03
16.01
15.93
OEt
OEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


5.39
OEt
OEt
O
N
H
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
ppm

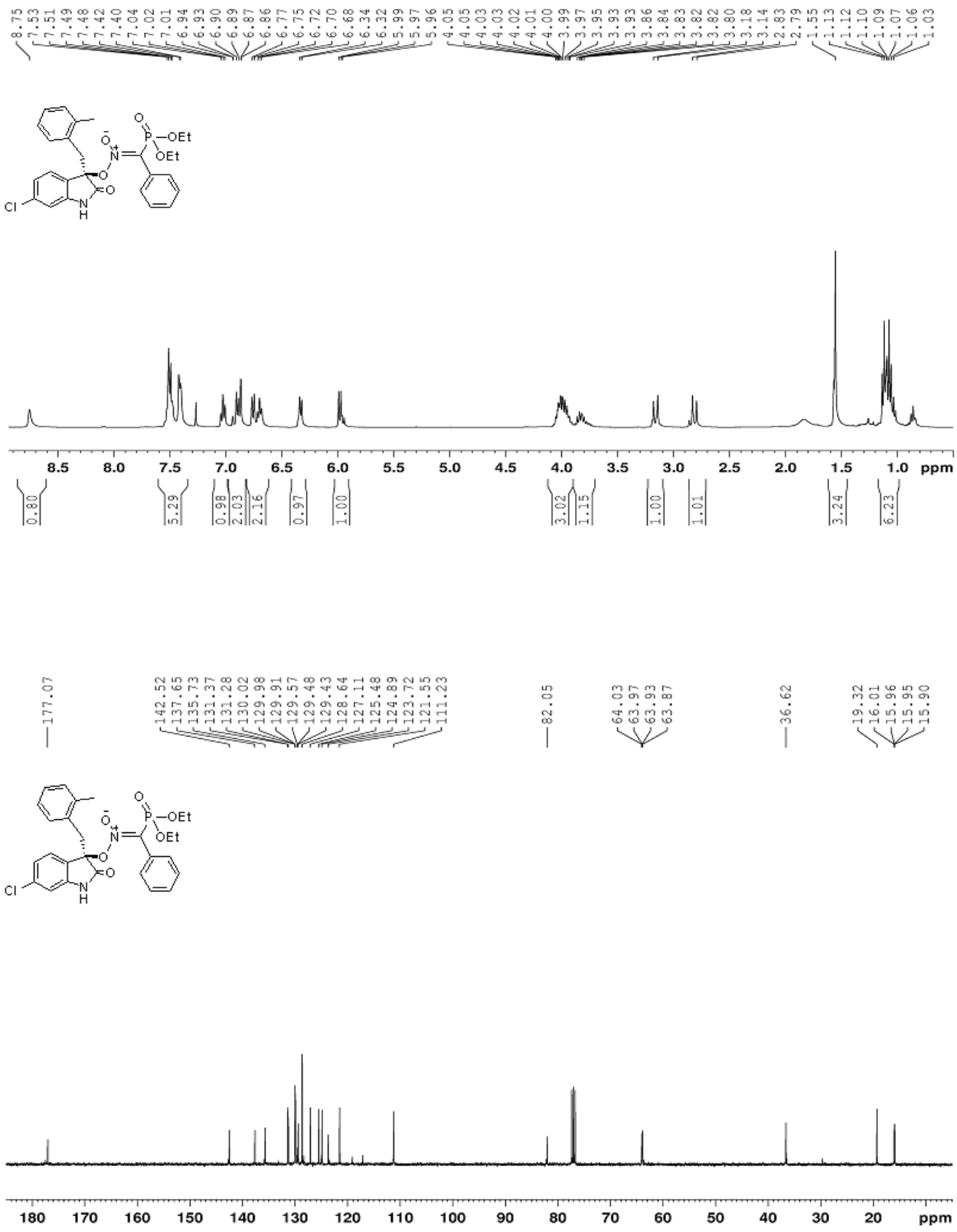
4q

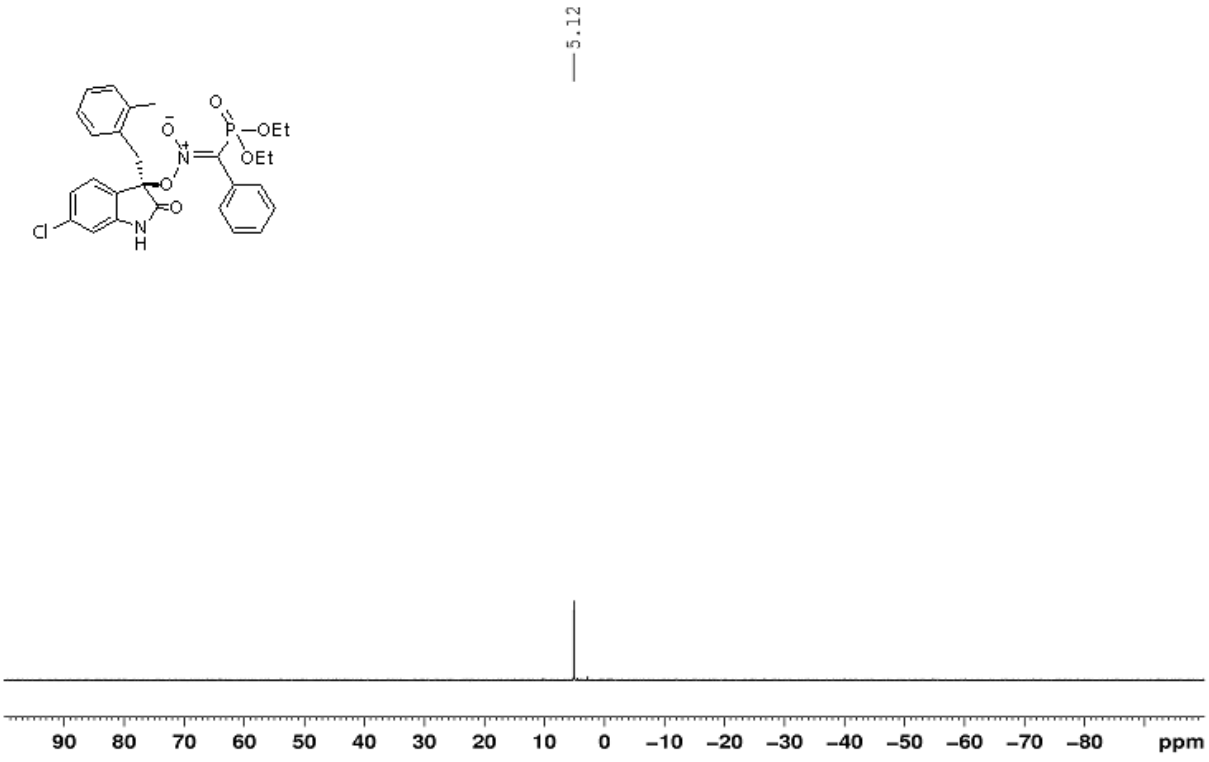

8.69
7.51
7.49
7.46
7.44
7.26
7.25
7.23
6.99
6.97
6.89
6.87
5.27
5.25
5.23
5.21
5.19
5.17
4.90
4.87
4.84
4.80
4.03
4.03
4.01
3.99
3.97
3.96
3.95
3.94
3.92
3.77
3.75
3.73
3.71
3.69
3.67
2.60
2.58
2.56
2.55
2.33
2.31
2.30
2.28
1.12
1.11
1.09
1.04
OEt
OEt
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.91
5.17
1.11
1.97
0.97
0.96
2.02
2.99
1.00
0.97
1.04
3.04
3.08


176.52
141.61
130.24
130.19
129.77
129.68
129.25
128.67
128.11
125.44
123.88
121.89
120.87
110.77
82.20
63.95
63.89
63.66
63.61
39.10
16.08
16.02
15.99
15.91
OEt
OEt
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

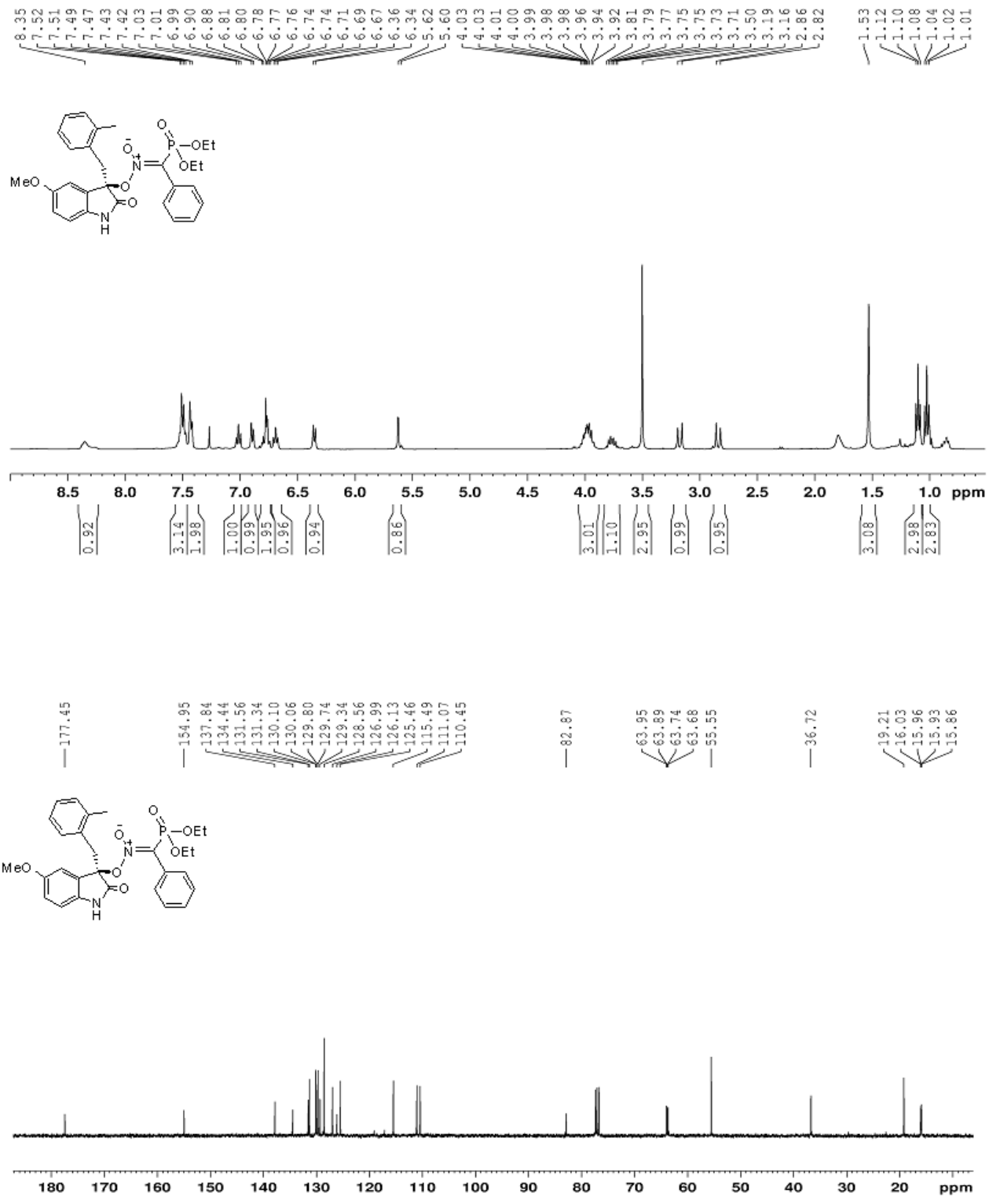

5.15
OEt
OEt
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

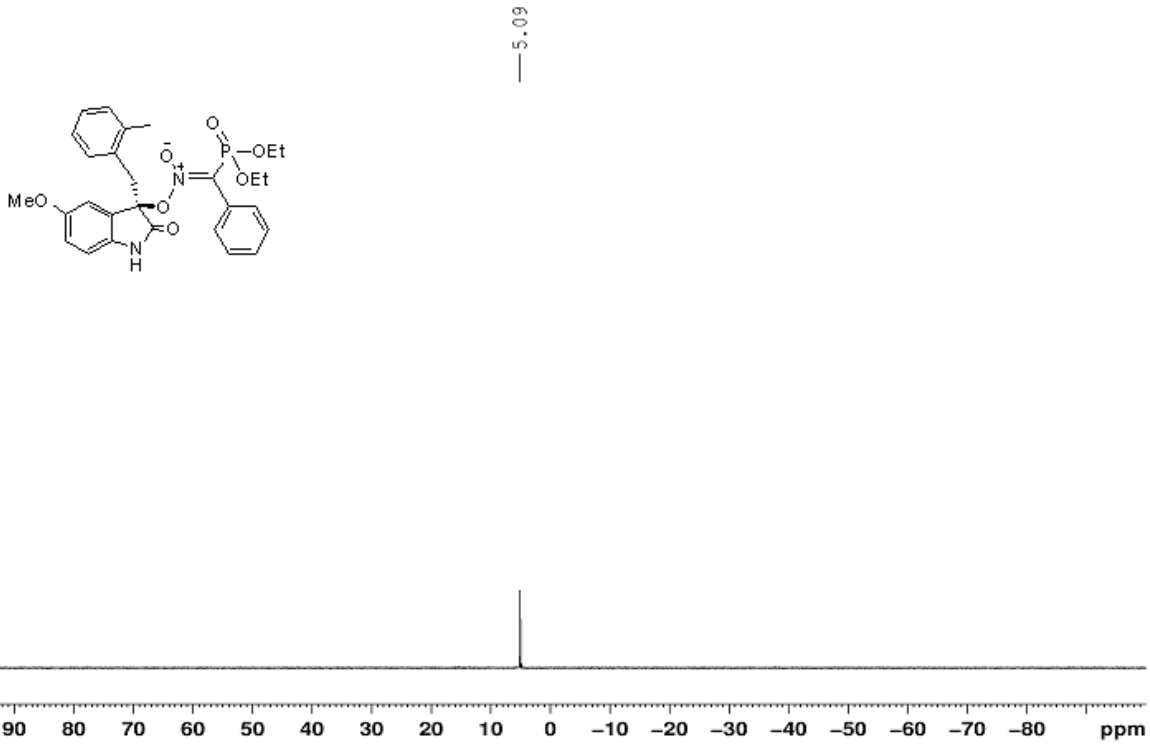
4r


8.75 7.53 7.51 7.49 7.48 7.42 7.40 7.04 7.02 7.01 6.94 6.93 6.90 6.89 6.87 6.86 6.77 6.75 6.72 6.70 6.68 6.34 6.32 5.99 5.97 5.96 4.05 4.05 4.03 4.03 4.02 4.01 4.00 3.99 3.97 3.95 3.93 3.93 3.86 3.84 3.83 3.82 3.82 3.80 3.18 3.14 2.83 2.79 1.55 1.13 1.12 1.10 1.09 1.07 1.06 1.03
OEt
OEt
Cl
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 ppm
0.80 5.29 0.98 2.03 2.16 0.97 1.00 3.02 1.15 1.00 1.01 3.24 6.23
177.07 142.52 137.65 135.73 131.37 131.28 130.02 129.98 129.91 129.57 129.48 129.43 128.64 127.11 125.48 124.89 123.72 121.55 111.23 82.05 64.03 63.97 63.93 63.87 36.62 19.32 16.01 15.96 15.95 15.90
OEt
OEt
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

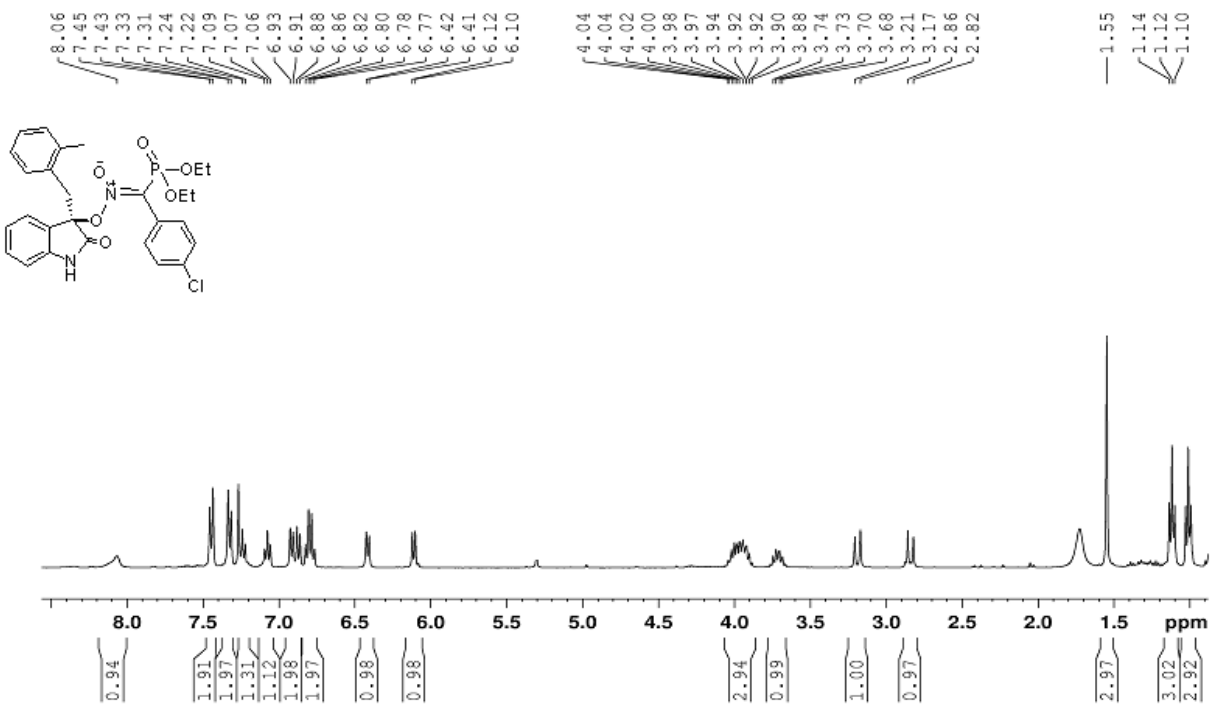

5.12
O
P—OEt
OEt
N
O
O
Cl
N
H
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

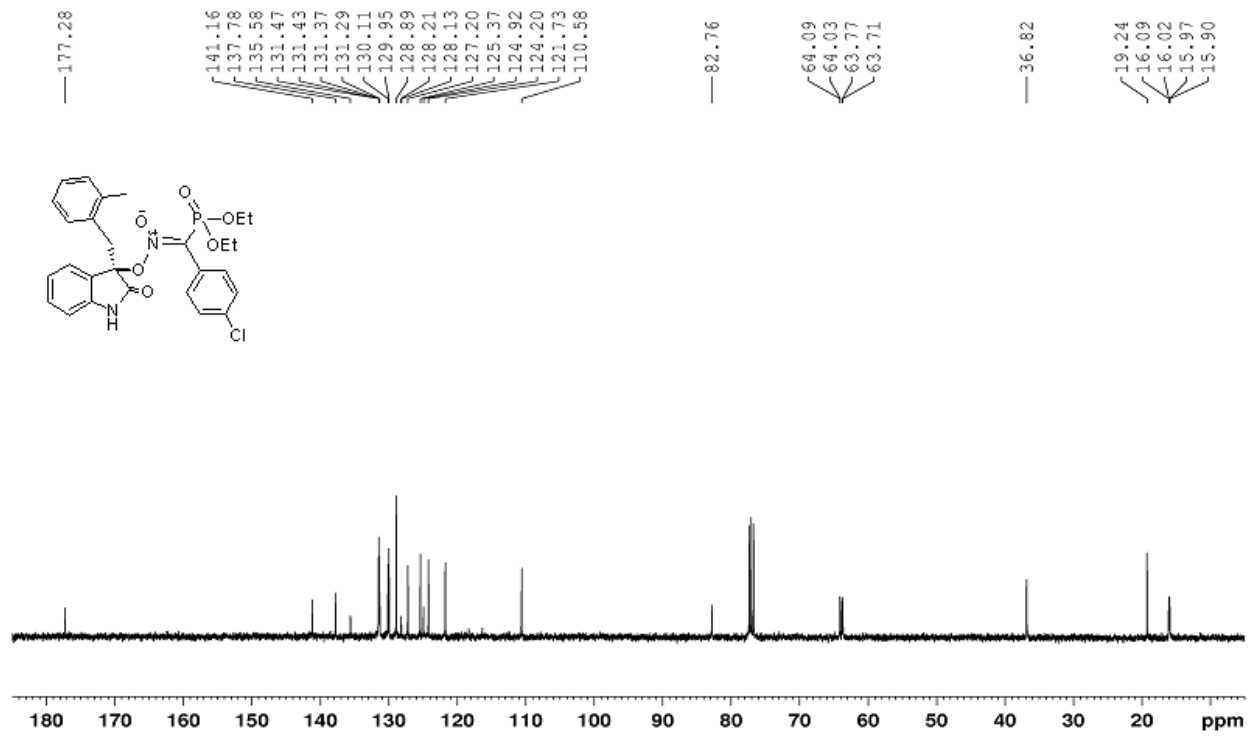
4s

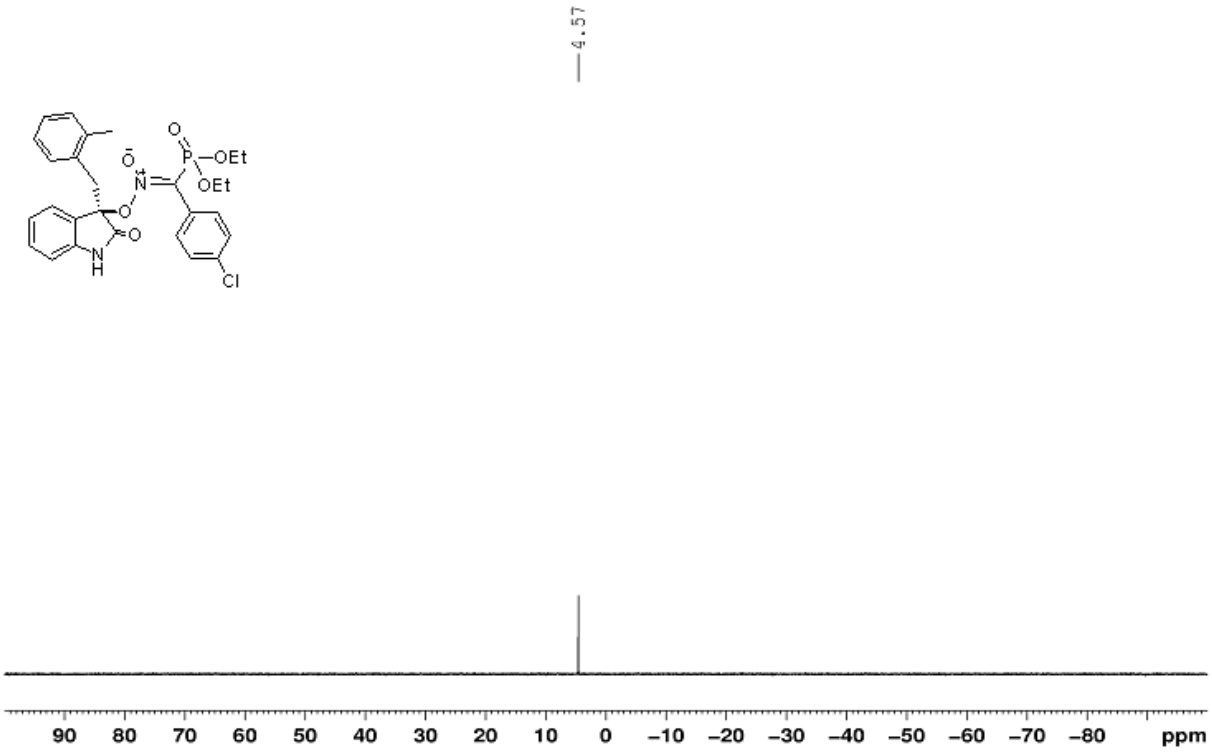

8.35 7.52 7.51 7.49 7.47 7.43 7.42 7.03 7.01 6.99 6.90 6.88 6.81 6.80 6.78 6.77 6.76 6.74 6.74 6.71 6.69 6.67 6.36 6.34 5.62 5.60 4.03 4.03 4.01 4.00 3.99 3.98 3.98 3.96 3.94 3.92 3.81 3.79 3.77 3.75 3.75 3.73 3.71 3.50 3.19 3.16 2.86 2.82 1.53 1.12 1.10 1.08 1.04 1.02 1.01
MeO
OEt
OEt
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.92 3.14 1.98 1.00 0.99 1.95 0.96 0.94 0.86 3.01 1.10 2.95 0.99 0.95 3.08 2.98 2.83
177.45 154.95 137.84 134.44 131.56 131.34 130.10 130.06 129.80 129.74 129.34 128.56 126.99 126.13 125.46 115.49 111.07 110.45 82.87 63.95 63.89 63.74 63.68 55.55 36.72 19.21 16.03 15.96 15.93 15.86
MeO
OEt
OEt
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


5.09
MeO
O
N
H
O
P
OEt
OEt
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

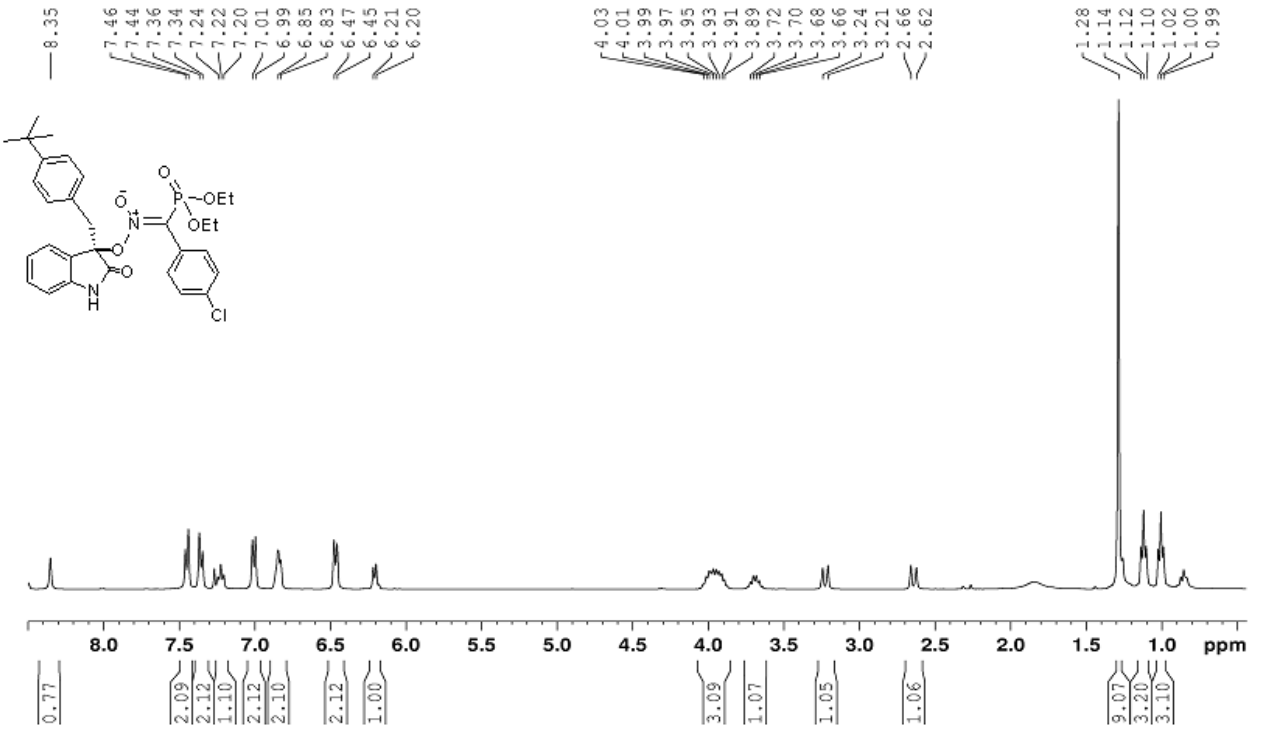
4t

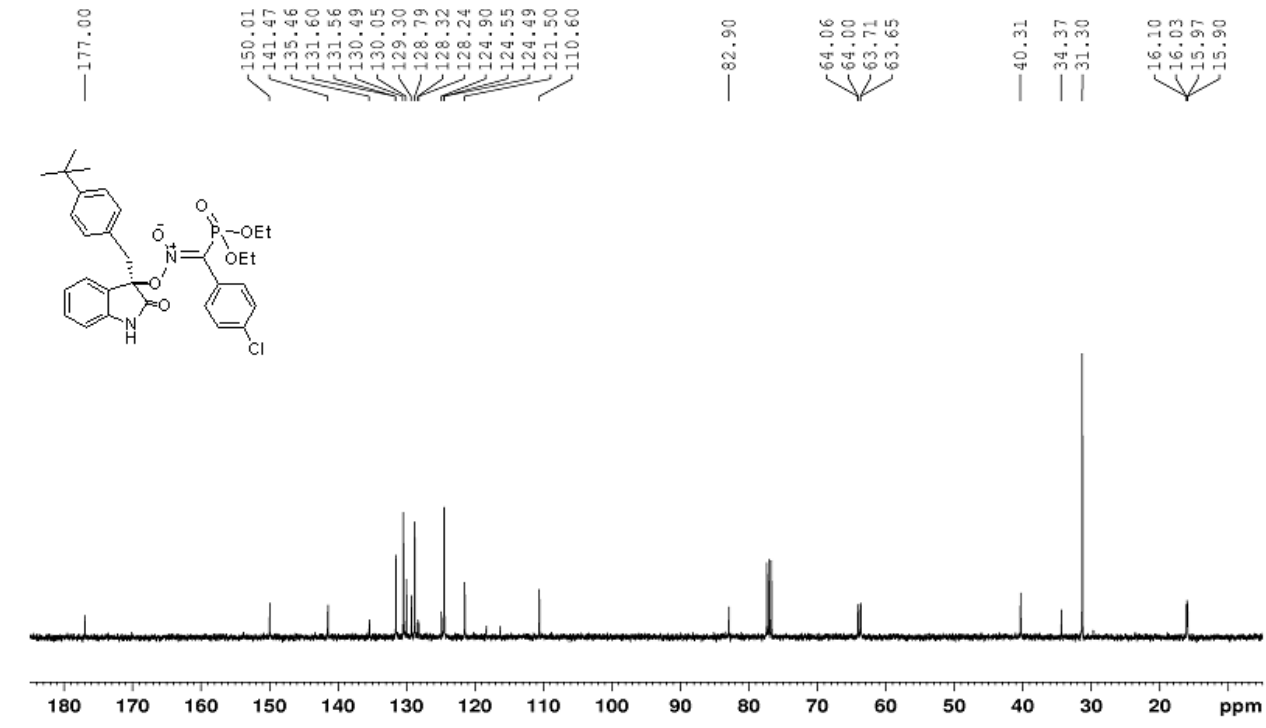

8.06
7.45
7.43
7.33
7.31
7.24
7.22
7.09
7.07
7.06
6.93
6.91
6.88
6.86
6.82
6.80
6.78
6.77
6.42
6.41
6.12
6.10
4.04
4.04
4.02
4.00
3.98
3.97
3.94
3.92
3.92
3.90
3.88
3.74
3.73
3.70
3.68
3.21
3.17
2.86
2.82
1.55
1.14
1.12
1.10
OEt
OEt
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.94
1.91
1.97
1.31
1.12
1.98
1.97
0.98
0.98
2.94
0.99
1.00
0.97
2.97
3.02
2.92

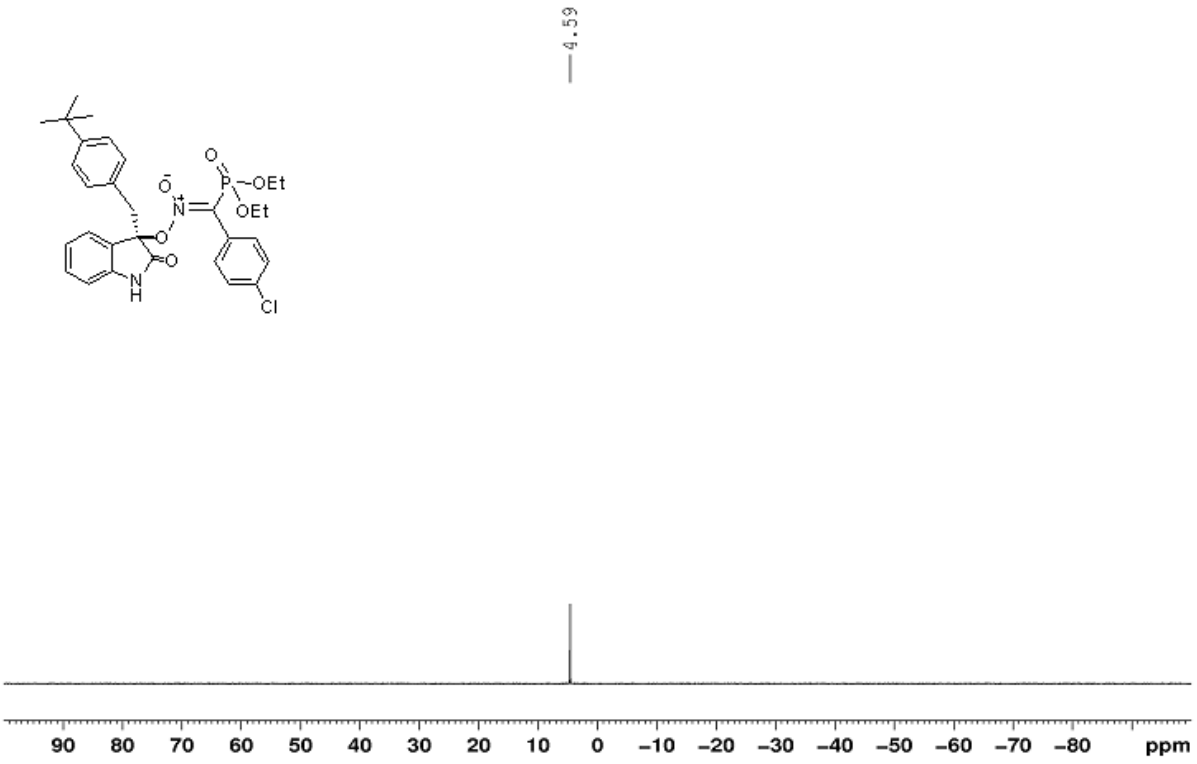

177.28
141.16
137.78
135.58
131.47
131.43
131.37
131.29
130.11
129.95
128.89
128.21
128.13
127.20
125.37
124.92
124.20
121.73
110.58
82.76
64.09
64.03
63.77
63.71
36.82
19.24
16.09
16.02
15.97
15.90
OEt
OEt
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


4.57
O
P
OEt
OEt
O
N
O
O
N
H
Cl
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
ppm

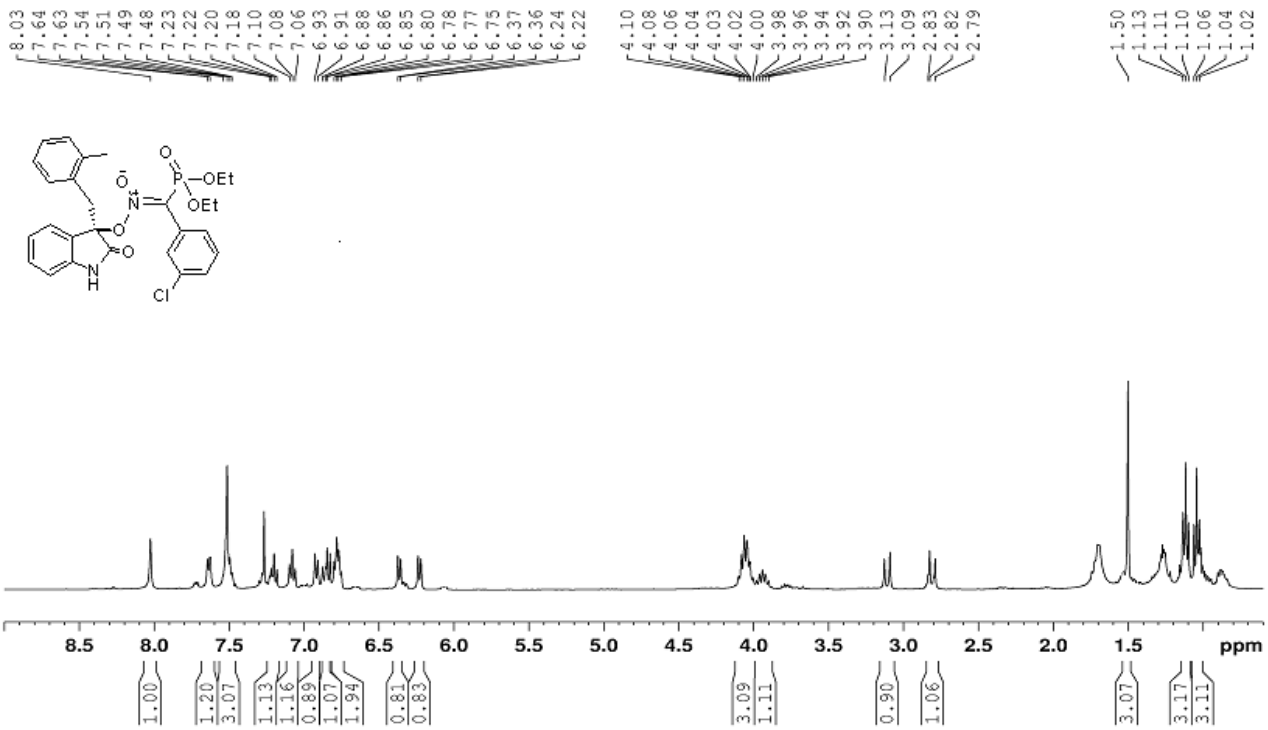
4u

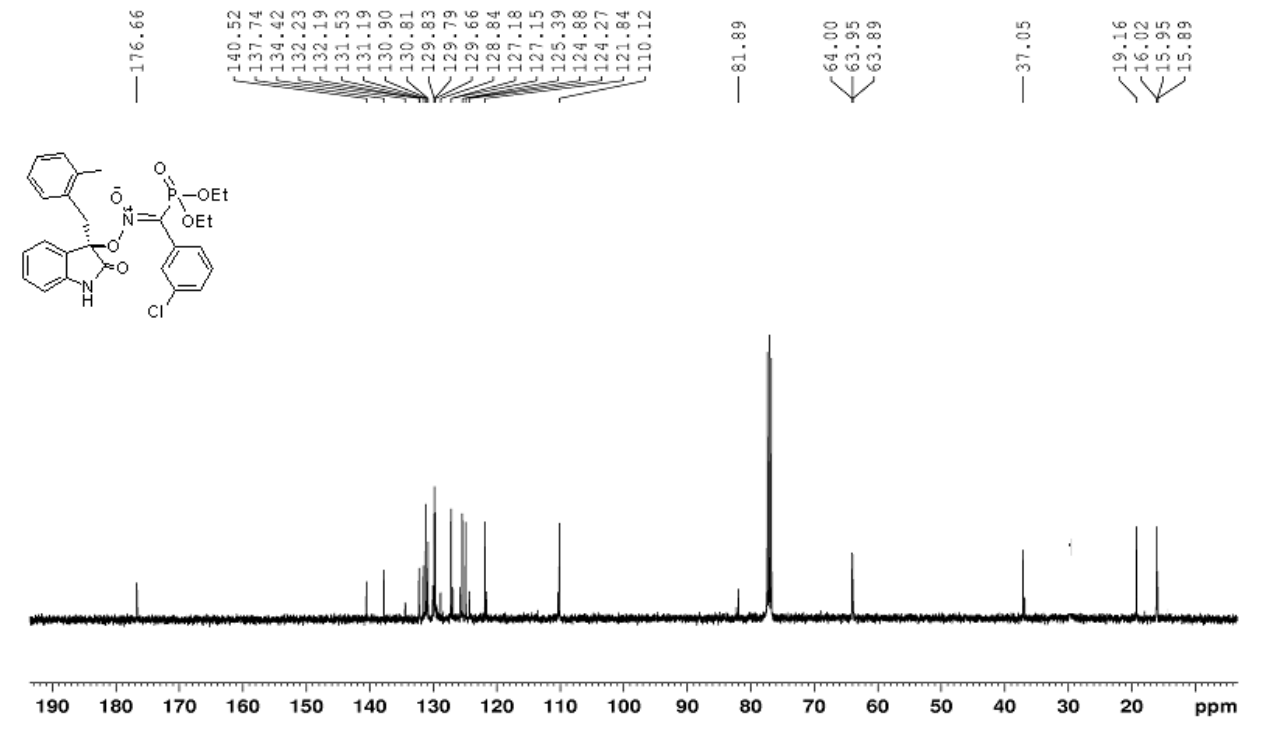

8.35
7.46
7.44
7.36
7.34
7.24
7.22
7.20
7.01
6.99
6.85
6.83
6.47
6.45
6.21
6.20
4.03
4.01
3.99
3.97
3.95
3.93
3.91
3.89
3.72
3.70
3.68
3.66
3.24
3.21
2.66
2.62
1.28
1.14
1.12
1.10
1.02
1.00
0.99
OEt
OEt
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.77
2.09
2.12
1.10
2.12
2.10
2.12
1.00
3.09
1.07
1.05
1.06
9.07
3.20
3.10

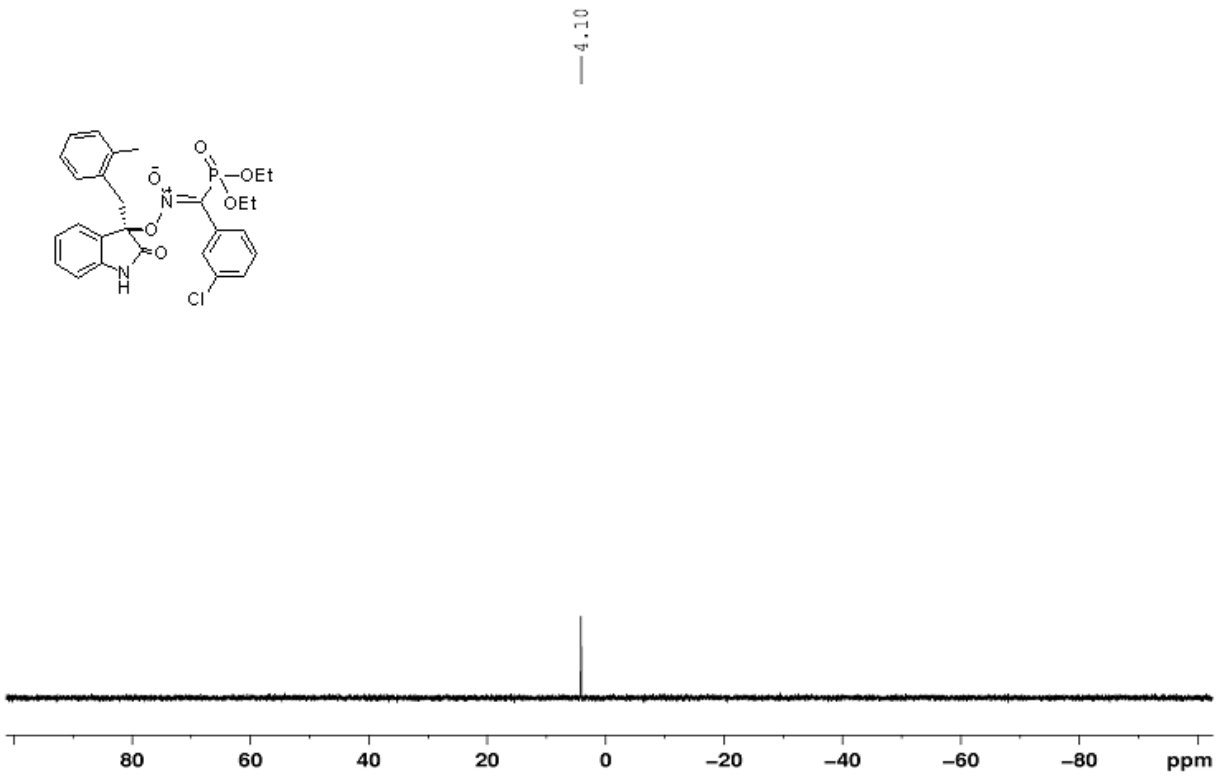

177.00
150.01
141.47
135.46
131.60
131.56
130.49
130.05
129.30
128.79
128.32
128.24
124.90
124.55
124.49
121.50
110.60
82.90
64.06
64.00
63.71
63.65
40.31
34.37
31.30
16.10
16.03
15.97
15.90
OEt
OEt
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


4.59
O
P
OEt
OEt
O
N
O
N
H
O
Cl
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 ppm

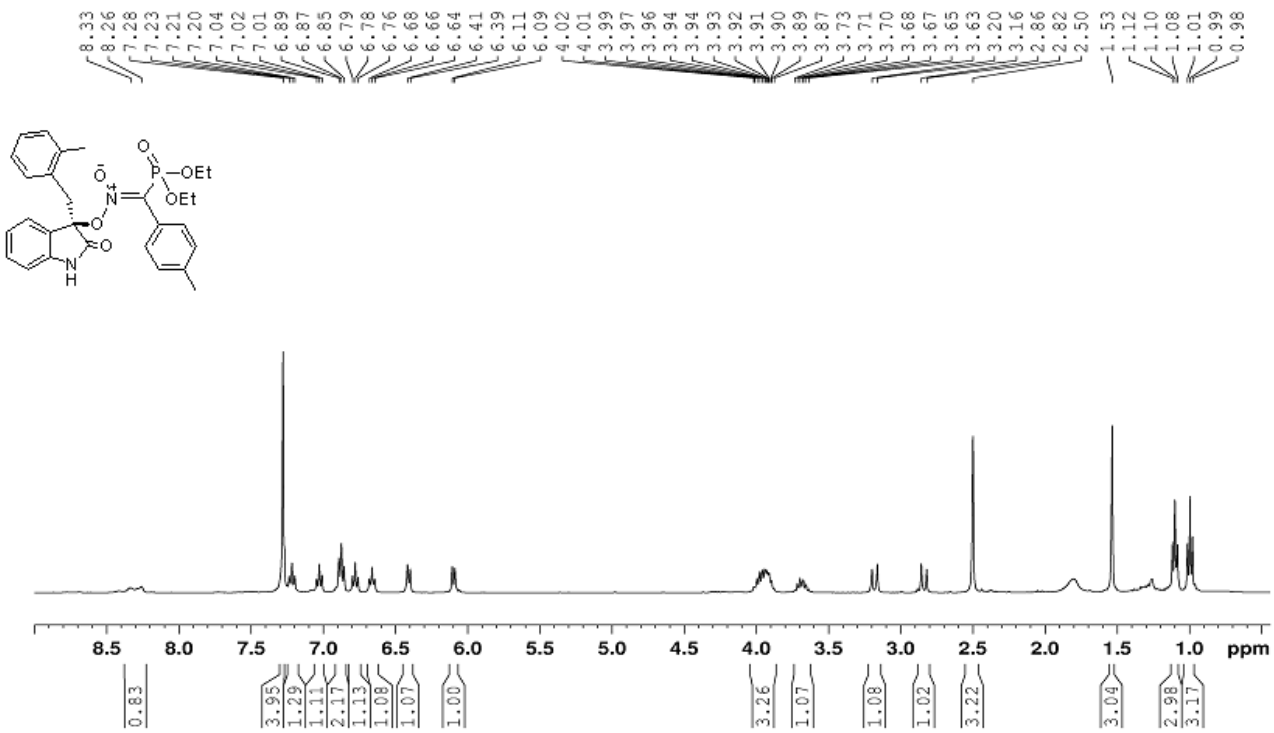
4v

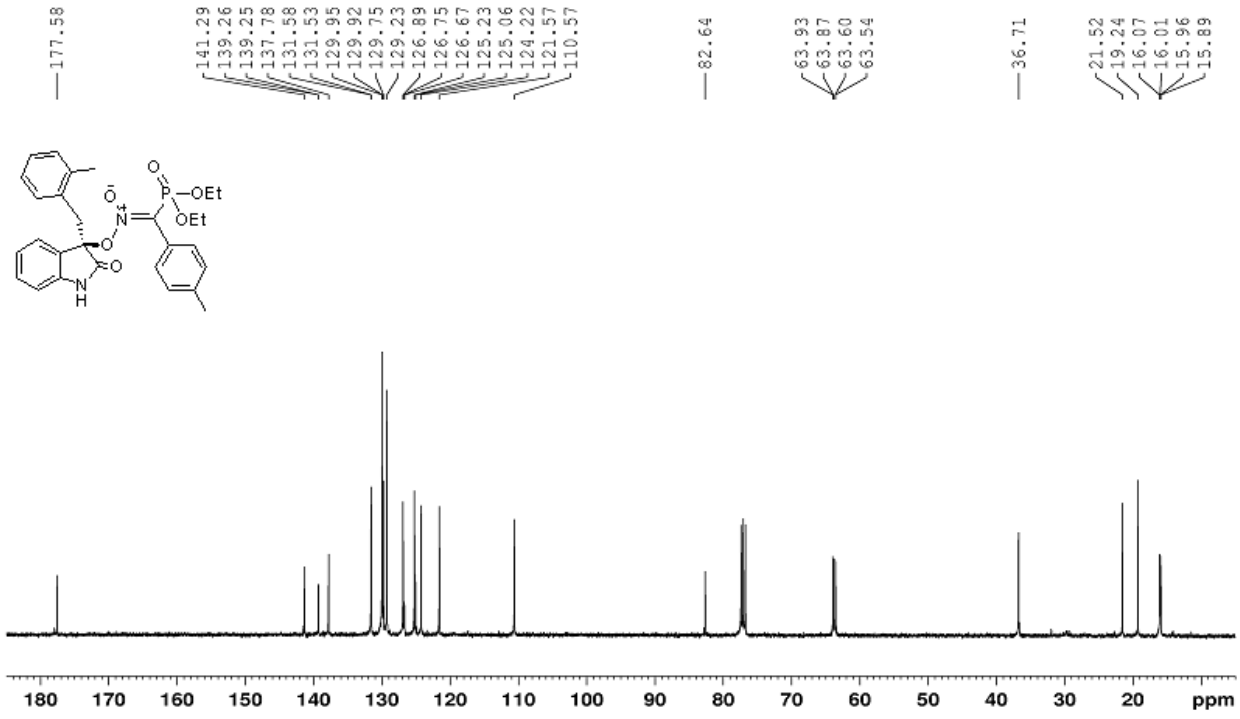

8.03
7.64
7.63
7.54
7.51
7.49
7.48
7.23
7.22
7.20
7.18
7.10
7.08
7.06
6.93
6.91
6.88
6.86
6.85
6.80
6.78
6.77
6.75
6.37
6.36
6.24
6.22
4.10
4.08
4.06
4.04
4.03
4.02
4.00
3.98
3.96
3.94
3.92
3.90
3.13
3.09
2.83
2.82
2.79
1.50
1.13
1.11
1.10
1.06
1.04
1.02
OEt
OEt
Cl
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
1.20
3.07
1.13
1.16
0.89
1.07
1.94
0.81
0.83
3.09
1.11
0.90
1.06
3.07
3.17
3.11

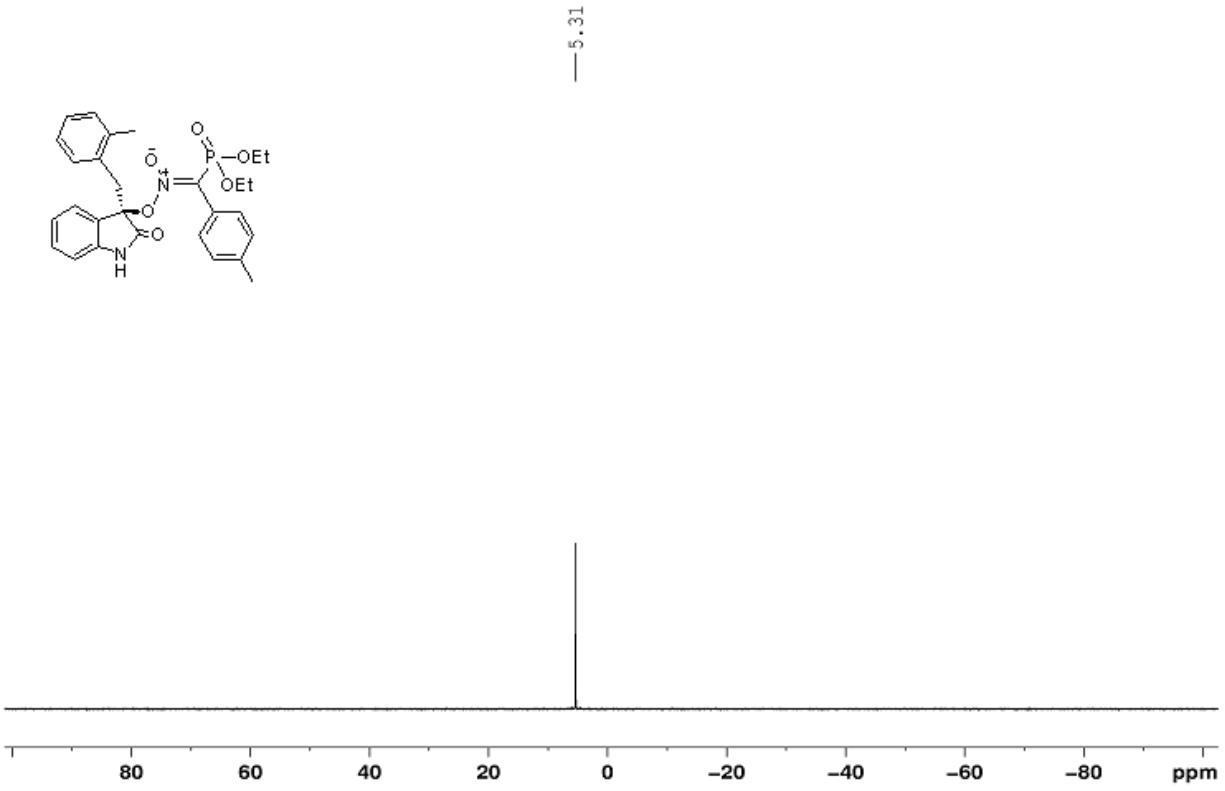

176.66
140.52
137.74
134.42
132.23
132.19
131.53
131.19
130.90
130.81
129.83
129.79
129.66
128.84
127.18
127.15
125.39
124.88
124.27
121.84
110.12
81.89
64.00
63.95
63.89
37.05
19.16
16.02
15.95
15.89
OEt
OEt
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


4.10
O
P
OEt
OEt
O
N
O
O
N
H
Cl
80
60
40
20
0
−20
−40
−60
−80
ppm

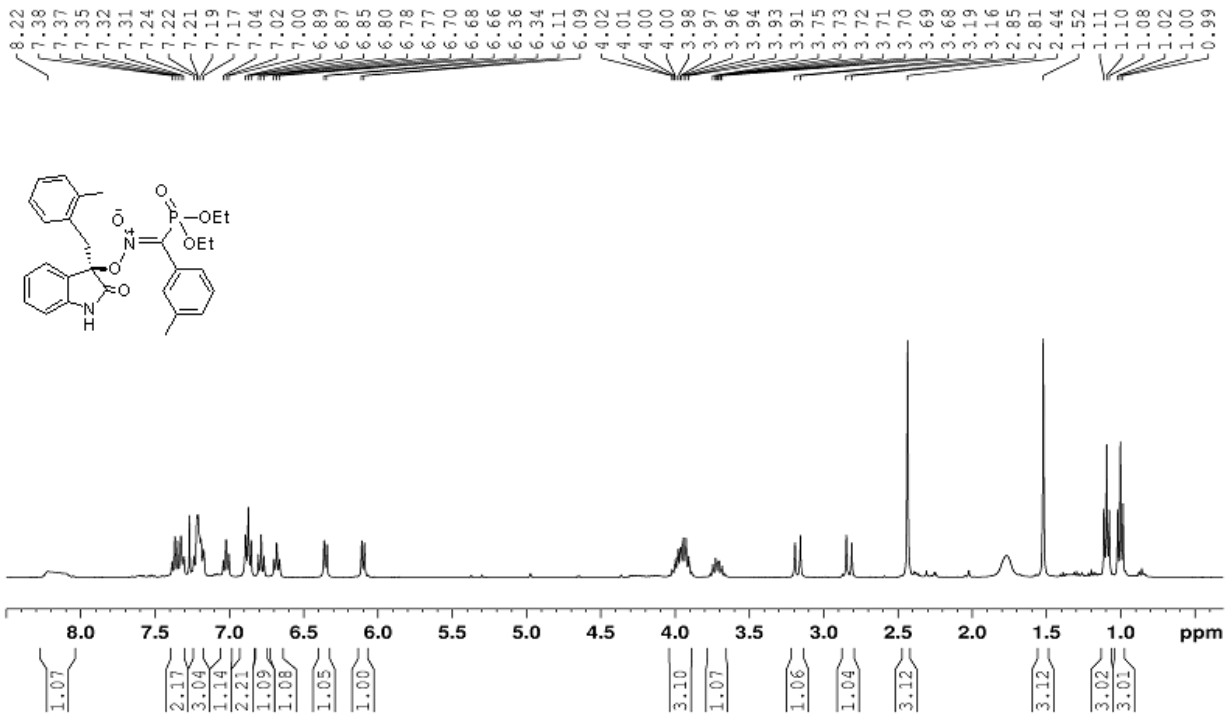
4w

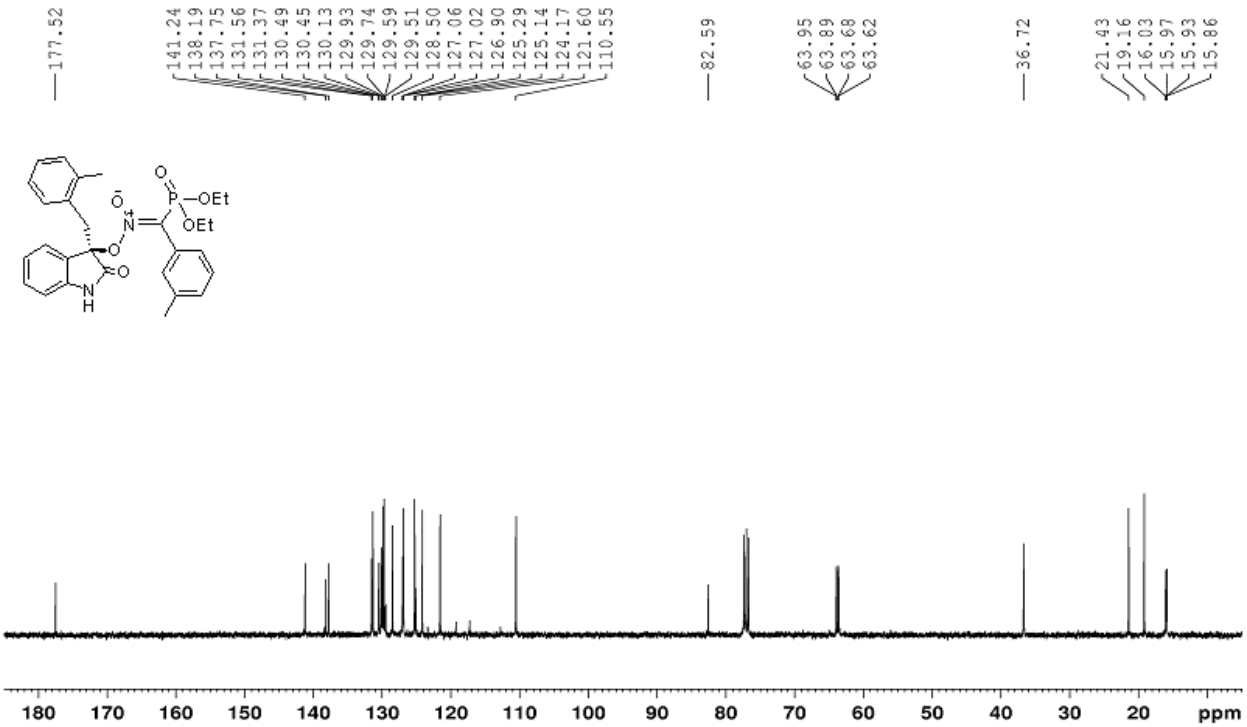

8.33
8.26
7.28
7.23
7.21
7.20
7.04
7.02
7.01
6.89
6.87
6.85
6.79
6.78
6.76
6.68
6.66
6.64
6.41
6.39
6.11
6.09
4.02
4.01
3.99
3.97
3.96
3.94
3.94
3.93
3.92
3.91
3.90
3.89
3.87
3.73
3.71
3.70
3.68
3.67
3.65
3.63
3.20
3.16
2.86
2.82
2.50
1.53
1.12
1.10
1.08
1.01
0.99
0.98
OEt
OEt
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.83
3.95
1.29
1.11
2.17
1.13
1.08
1.07
1.00
3.26
1.07
1.08
1.02
3.22
3.04
2.98
3.17

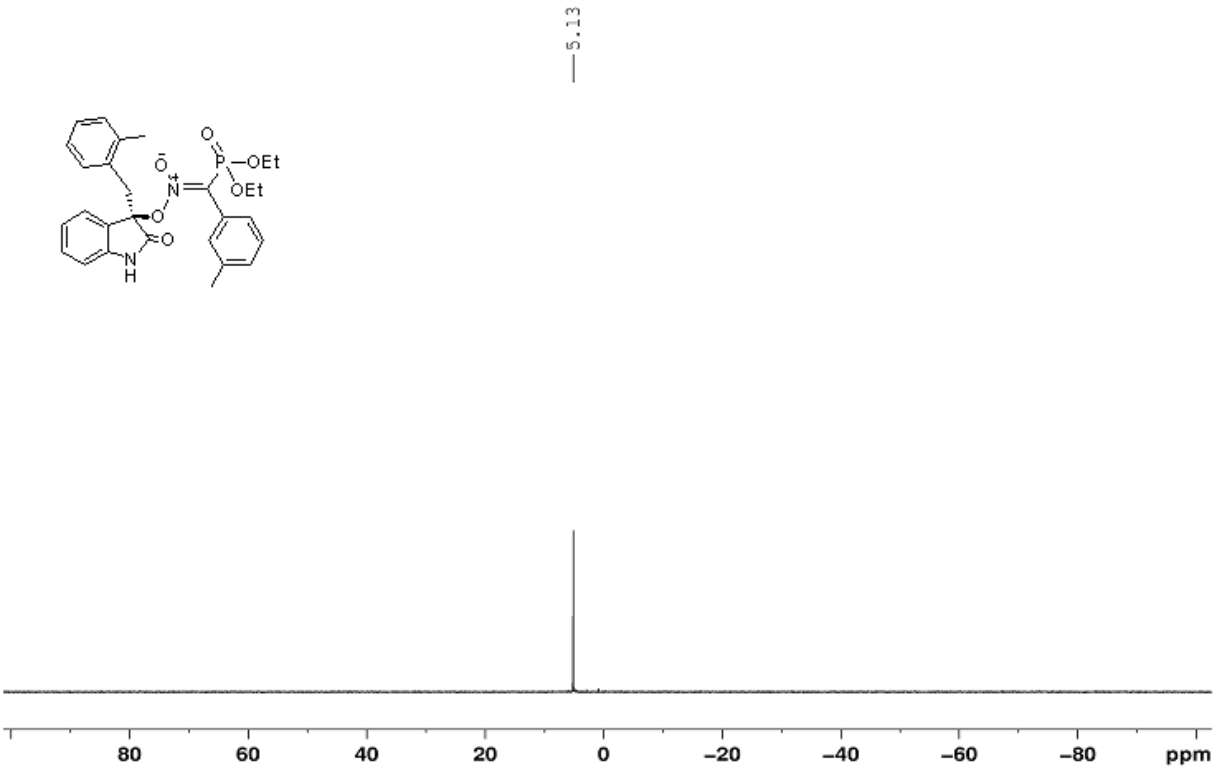

177.58
141.29
139.26
139.25
137.78
131.58
131.53
129.95
129.92
129.75
129.23
126.89
126.75
126.67
125.23
125.06
124.22
121.57
110.57
82.64
63.93
63.87
63.60
63.54
36.71
21.52
19.24
16.07
16.01
15.96
15.89
OEt
OEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


5.31
O
P
OEt
OEt
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

4x

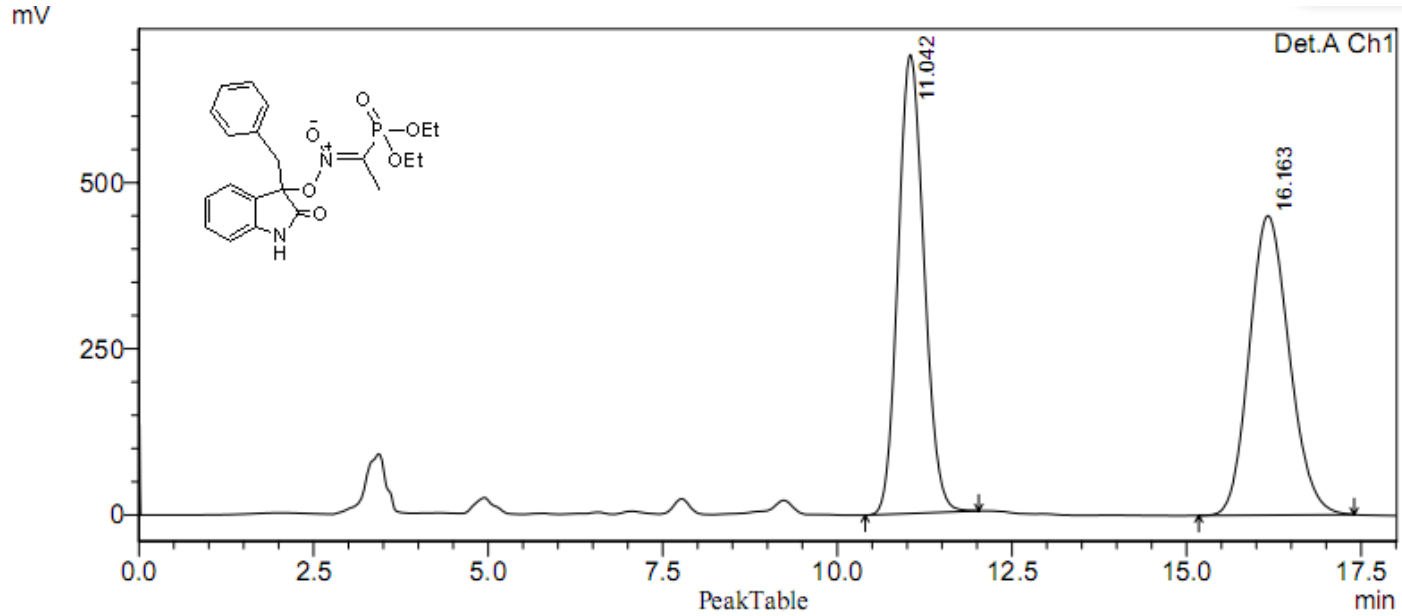

8.22
7.38
7.37
7.35
7.32
7.31
7.24
7.22
7.21
7.19
7.17
7.04
7.02
7.00
6.89
6.87
6.85
6.80
6.78
6.77
6.70
6.68
6.66
6.36
6.34
6.11
6.09
4.02
4.01
4.00
4.00
3.98
3.97
3.96
3.94
3.93
3.91
3.75
3.73
3.72
3.71
3.70
3.69
3.68
3.19
3.16
2.85
2.81
2.44
1.52
1.11
1.10
1.08
1.02
1.00
0.99
O
P
OEt
OEt
N
O
O
N
H
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
ppm
1.07
2.17
3.04
1.14
2.21
1.09
1.08
1.05
1.00
3.10
1.07
1.06
1.04
3.12
3.12
3.02
3.01


177.52
141.24
138.19
137.75
131.56
131.37
130.49
130.45
130.13
129.93
129.74
129.59
129.51
128.50
127.06
127.02
126.90
125.29
125.14
124.17
121.60
110.55
82.59
63.95
63.89
63.68
63.62
36.72
21.43
19.16
16.03
15.97
15.93
15.86
O
P
OEt
OEt
N
O
O
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


5.13
O
P
OEt
OEt
O
N
O
O
N
H
80
60
40
20
0
−20
−40
−60
−80
ppm

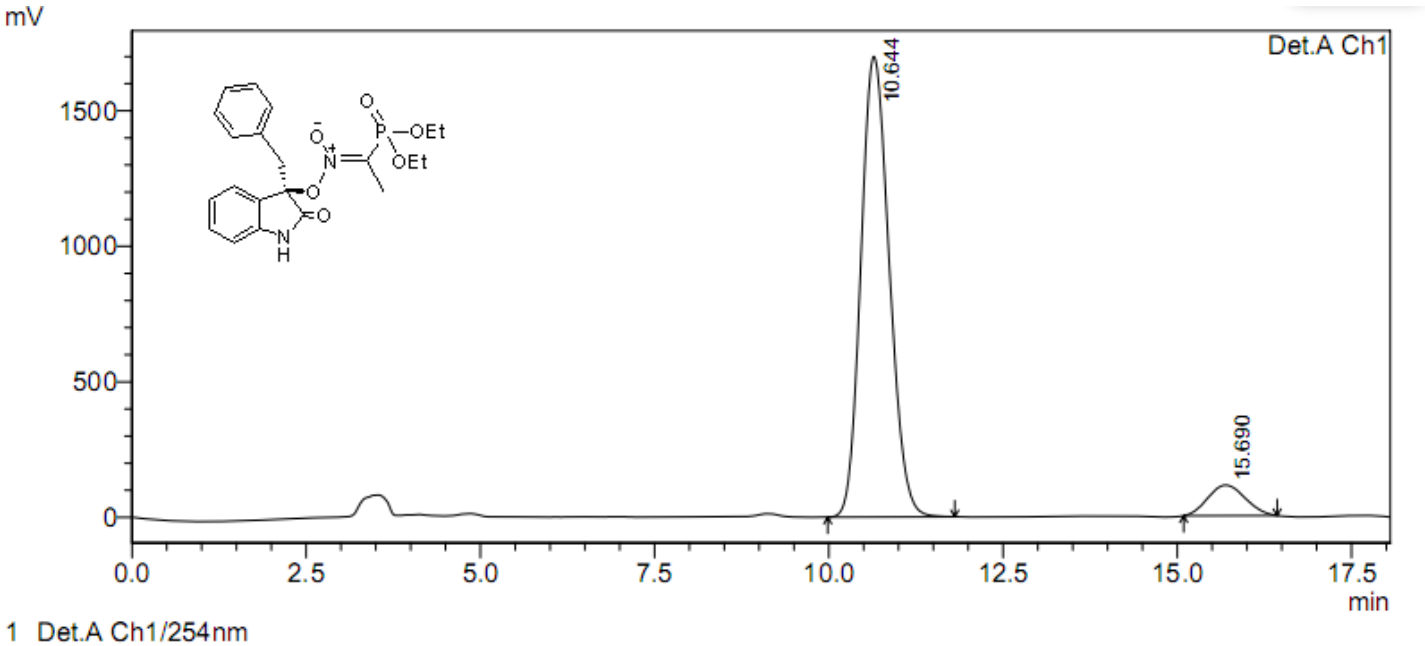
HPLC Spectra

4a



1 Det.A Ch1/21(Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %
1	11.042	17844128	690193	49.886
2	16.163	17925636	450535	50.114
Total		35769765	1140728	100.000



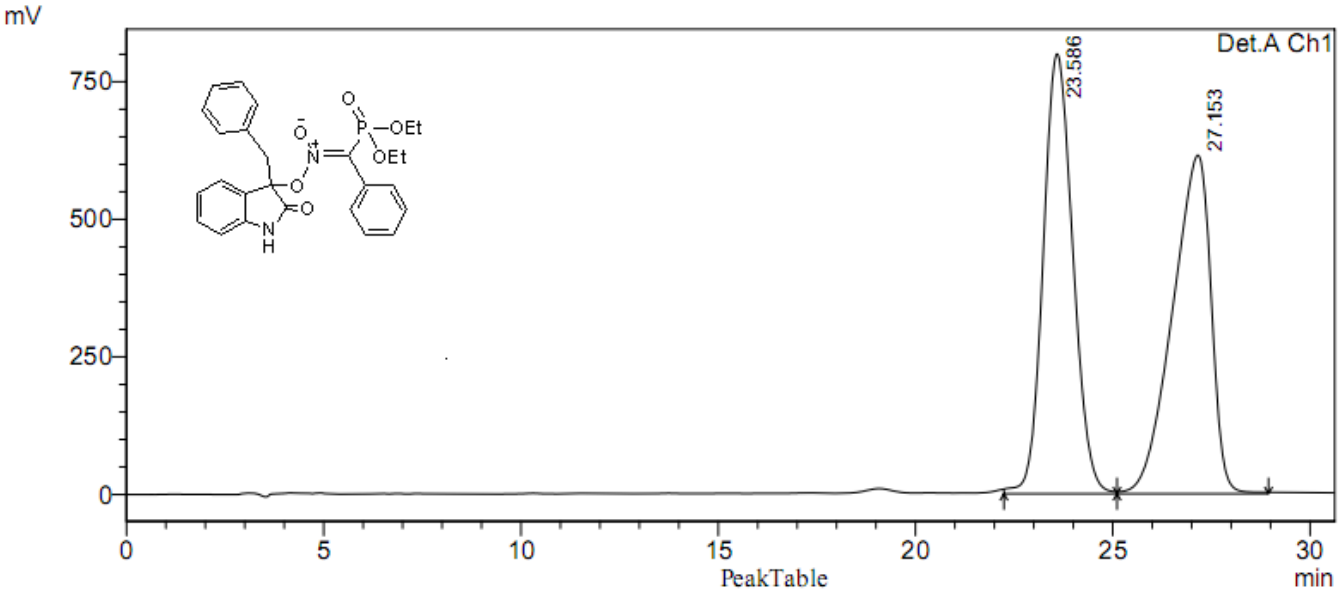
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

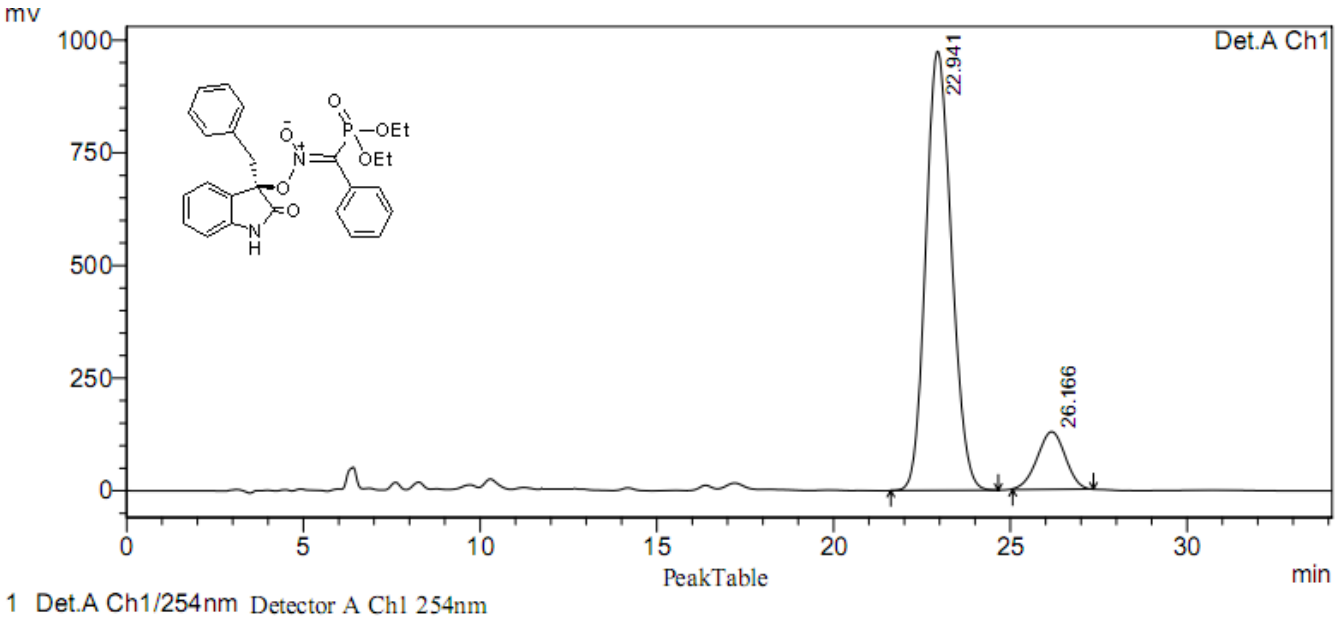
Peak#	Ret. Time	Area	Height	Area %
1	10.644	48024910	1699450	91.940
2	15.690	4209884	112998	8.060
Total		52234794	1812448	100.000

4b



1 Det.A Ch1/254nm Detector A Ch1 254nm

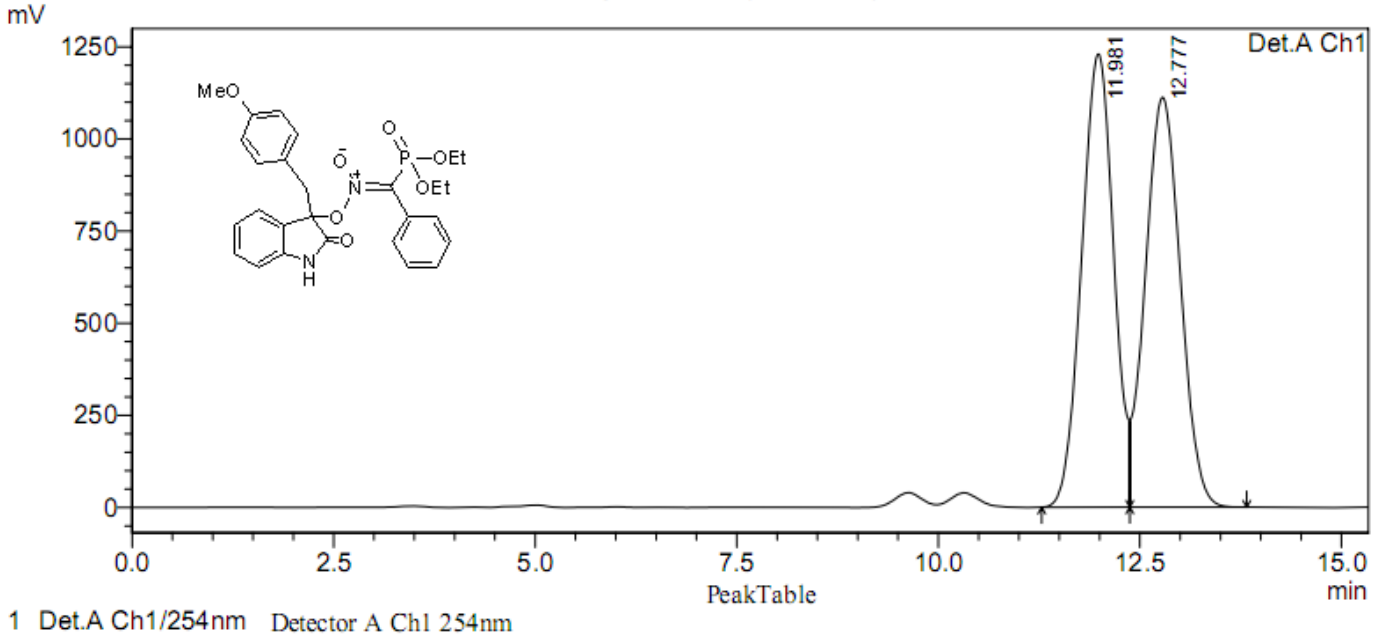
Peak#	Ret. Time	Area	Height	Area %
1	23.586	41855799	799341	50.002
2	27.153	41852997	615110	49.998
Total		83708796	1414451	100.000



1 Det.A Ch1/254nm Detector A Ch1 254nm

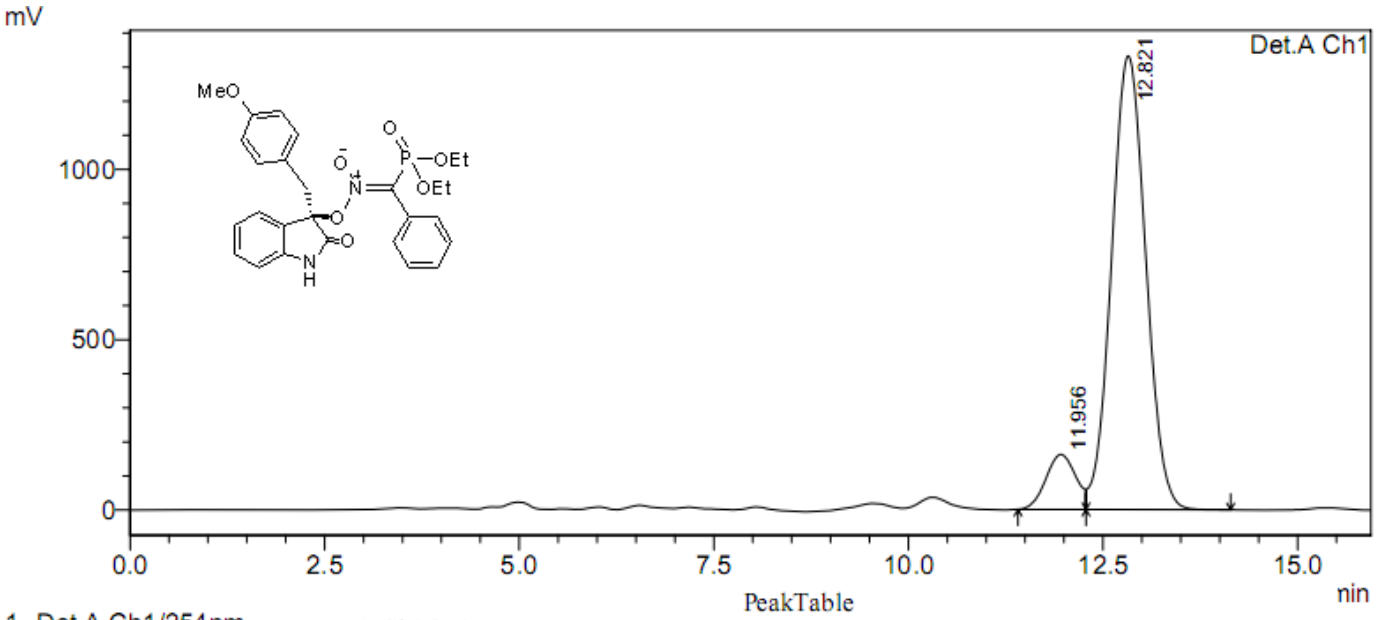
Peak#	Ret. Time	Area	Height	Area %
1	22.941	49499578	974816	87.466
2	26.166	7093345	127902	12.534
Total		56592923	1102718	100.000

4c



1 Det.A Ch1/254nm Detector A Ch1 254nm

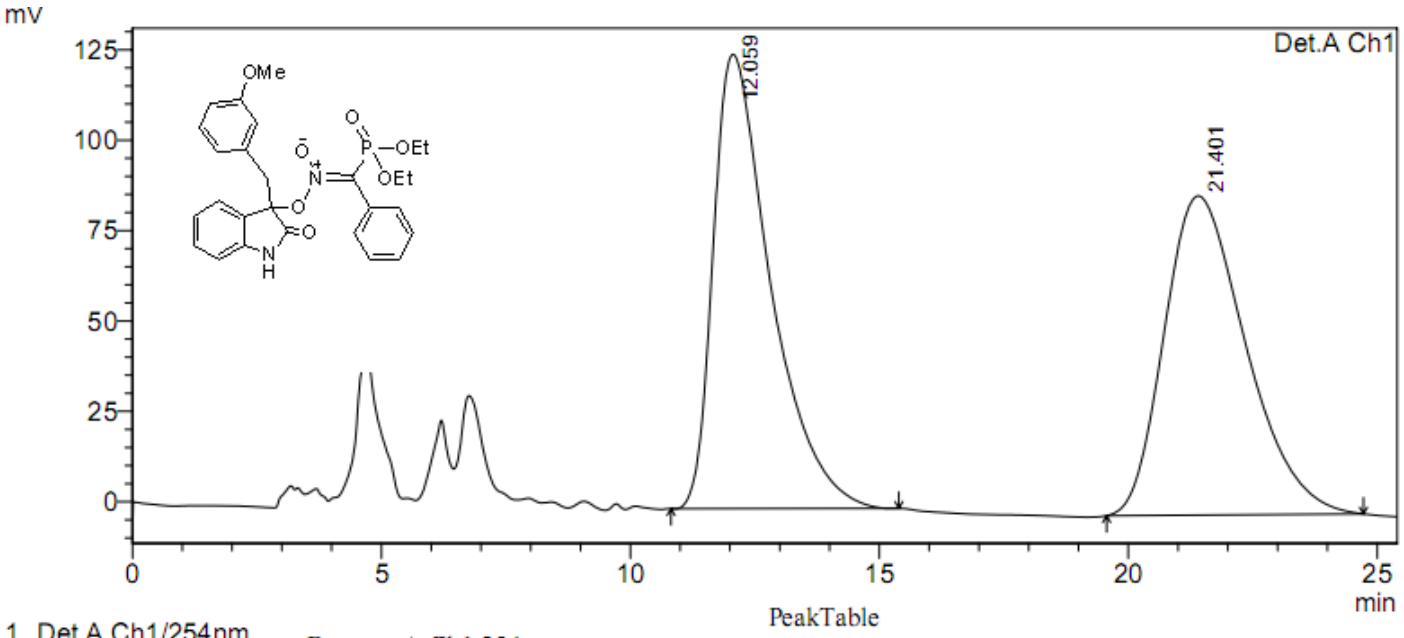
Peak#	Ret. Time	Area	Height	Area %
1	11.981	33961080	1230045	50.172
2	12.777	33728597	1112384	49.828
Total		67689677	2342429	100.000



1 Det.A Ch1/254nm Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.956	4306418	161563	9.559
2	12.821	40744072	1332365	90.441
Total		45050489	1493928	100.000

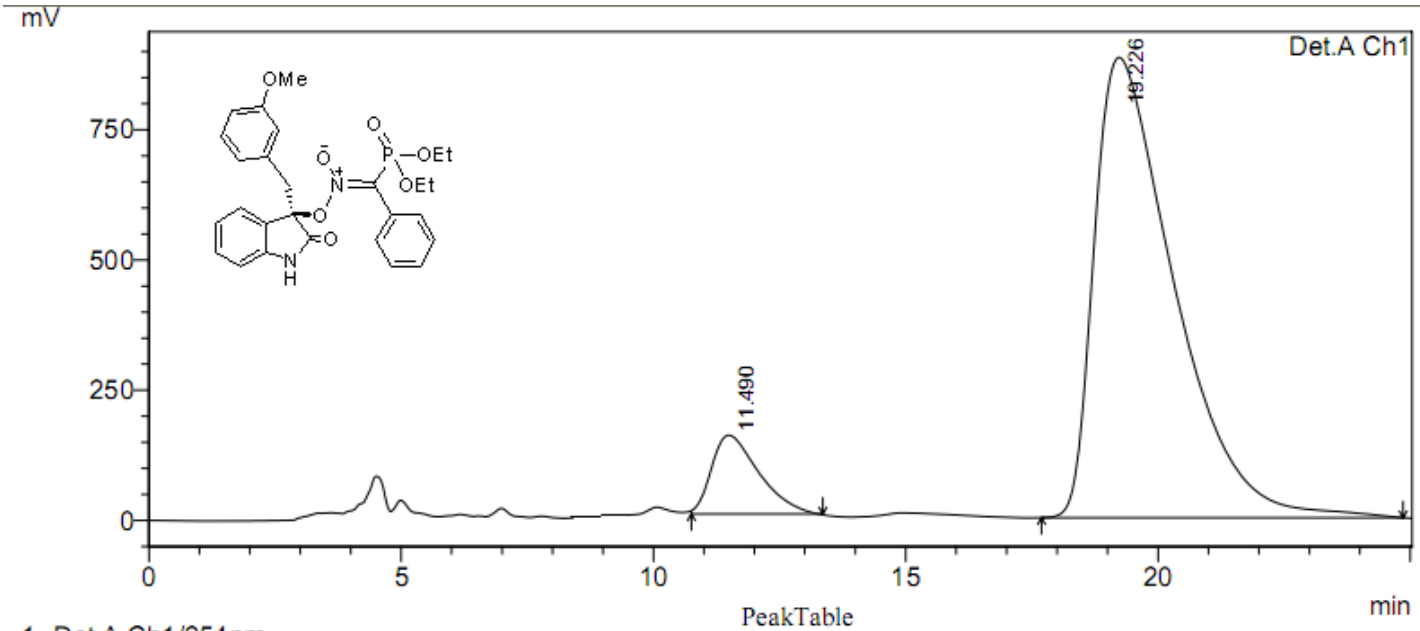
4d



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.059	10051436	125699	50.034	58.753
2	21.401	10037942	88244	49.966	41.247
Total		20089378	213943	100.000	100.000

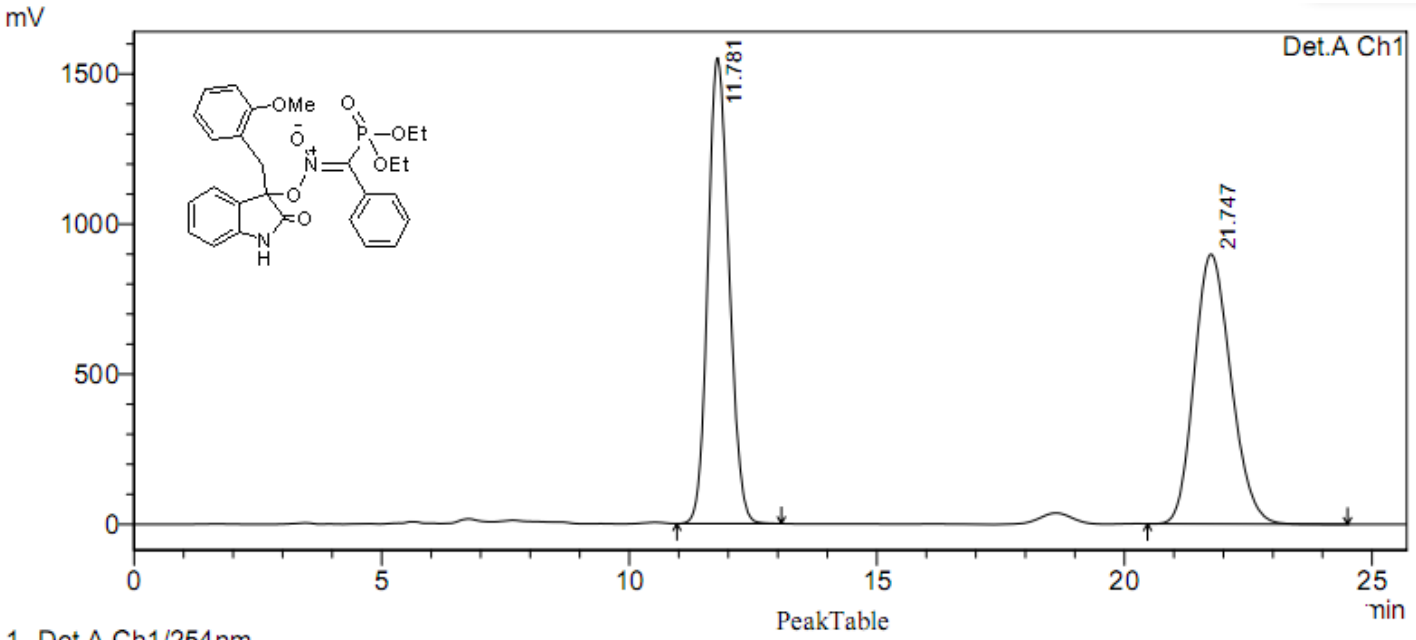


1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.490	9848568	151075	9.198
2	19.226	97224681	883562	90.802
Total		107073249	1034637	100.000

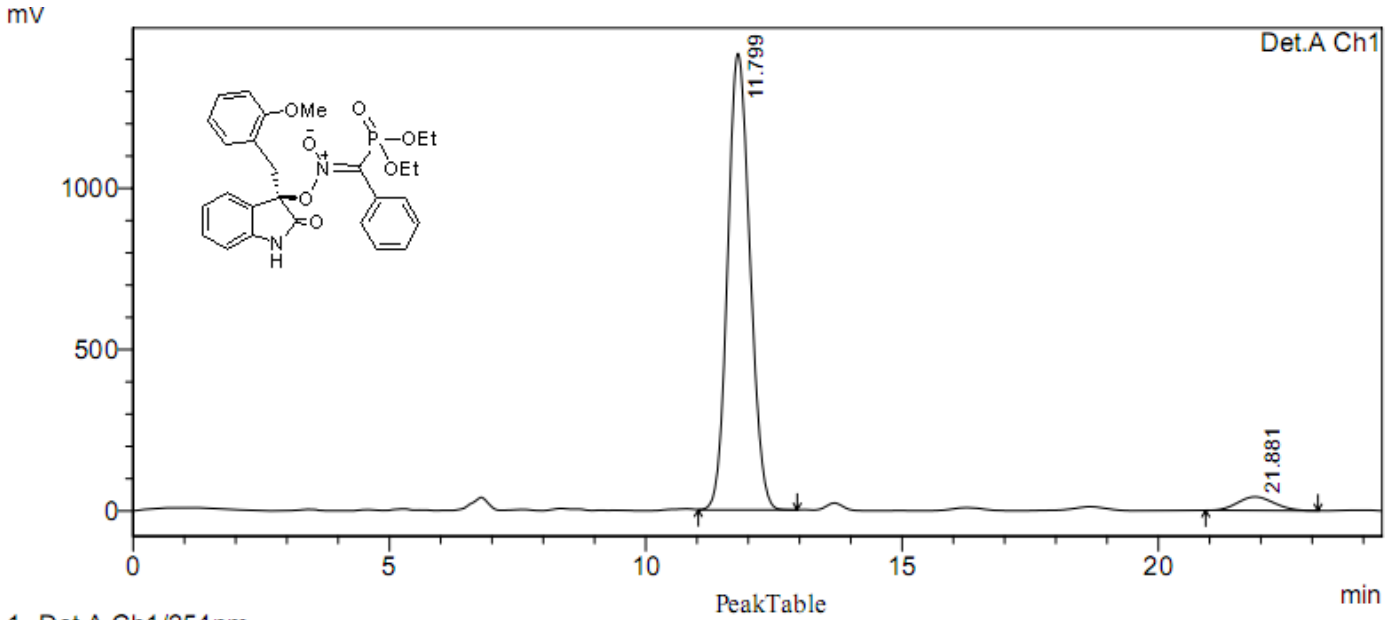
4e



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.781	46173491	1552023	49.971
2	21.747	46226823	898133	50.029
Total		92400314	2450156	100.000

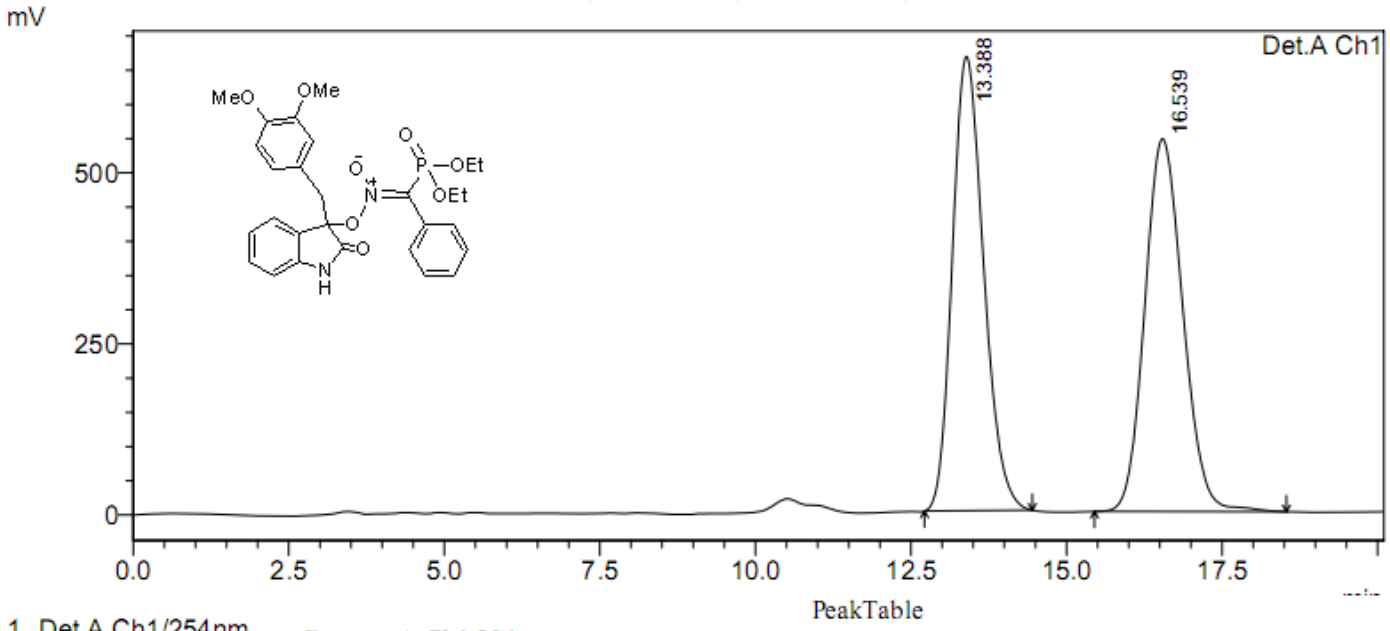


1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.799	42837882	1414917	95.338
2	21.881	2094735	42366	4.662
Total		44932617	1457283	100.000

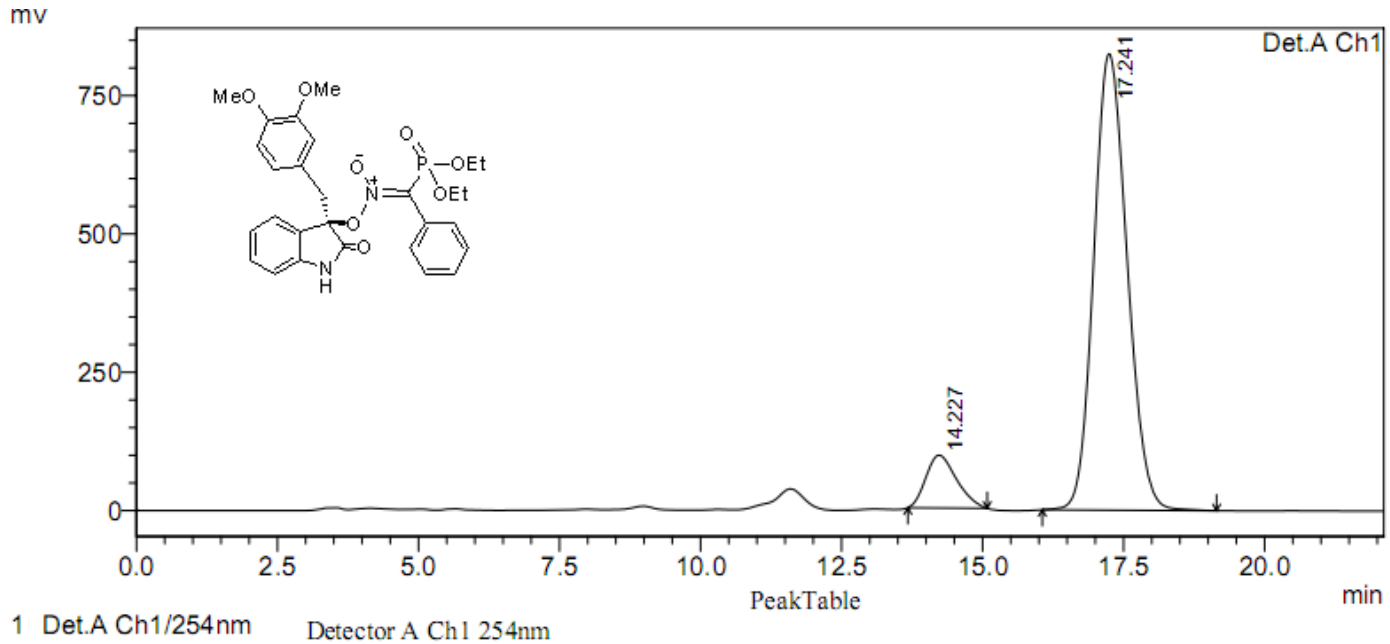
4f



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.388	23220645	663921	49.975
2	16.539	23243942	544851	50.025
Total		46464587	1208772	100.000

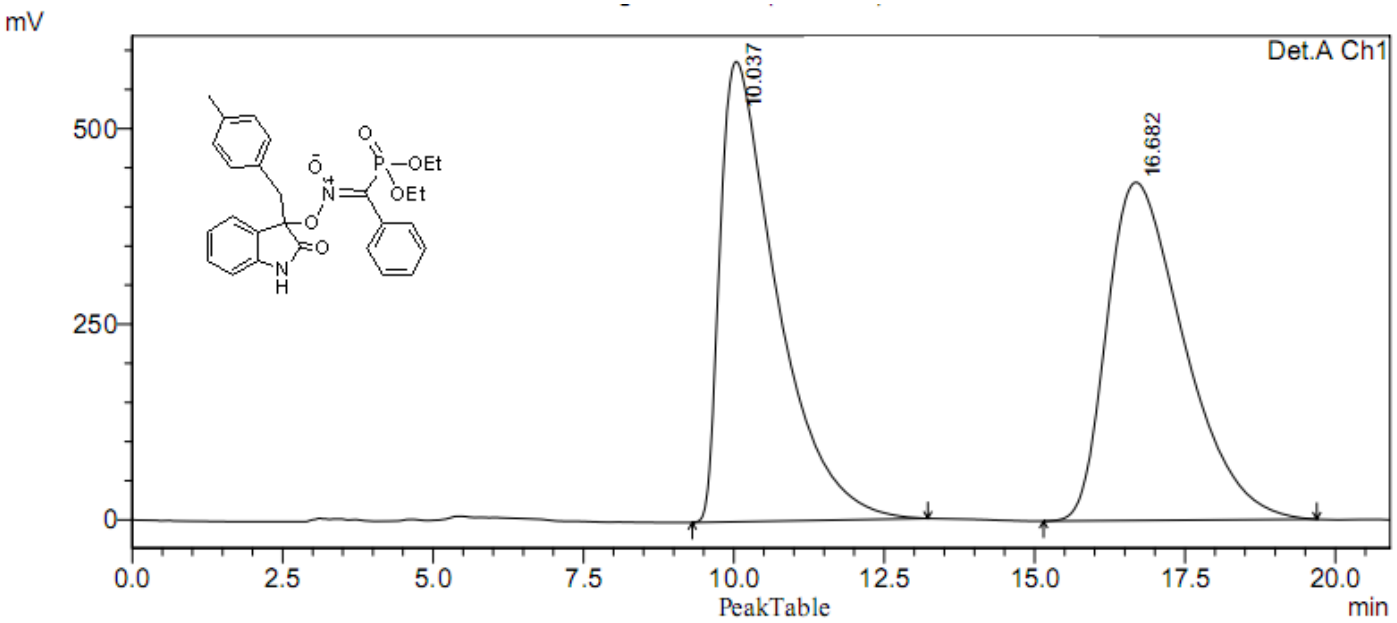


1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.227	3624116	95590	9.648
2	17.241	33940349	824928	90.352
Total		37564465	920517	100.000

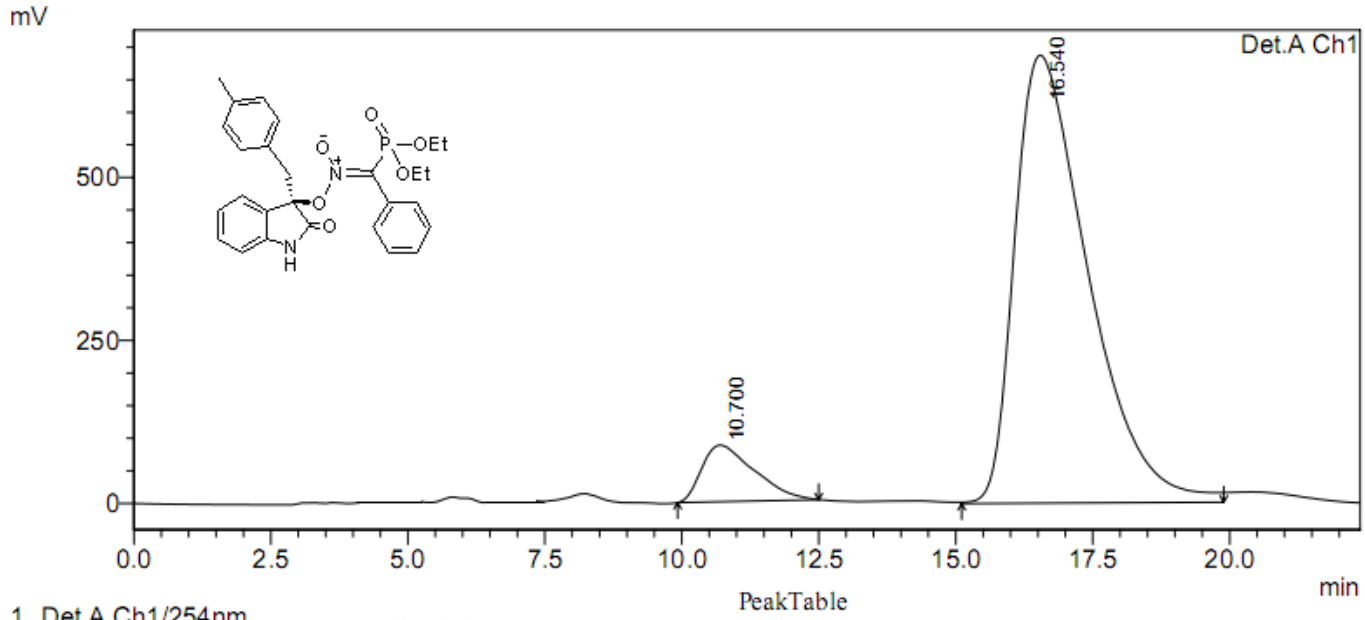
4g



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.037	38719201	587916	50.053
2	16.682	38637647	432101	49.947
Total		77356847	1020017	100.000

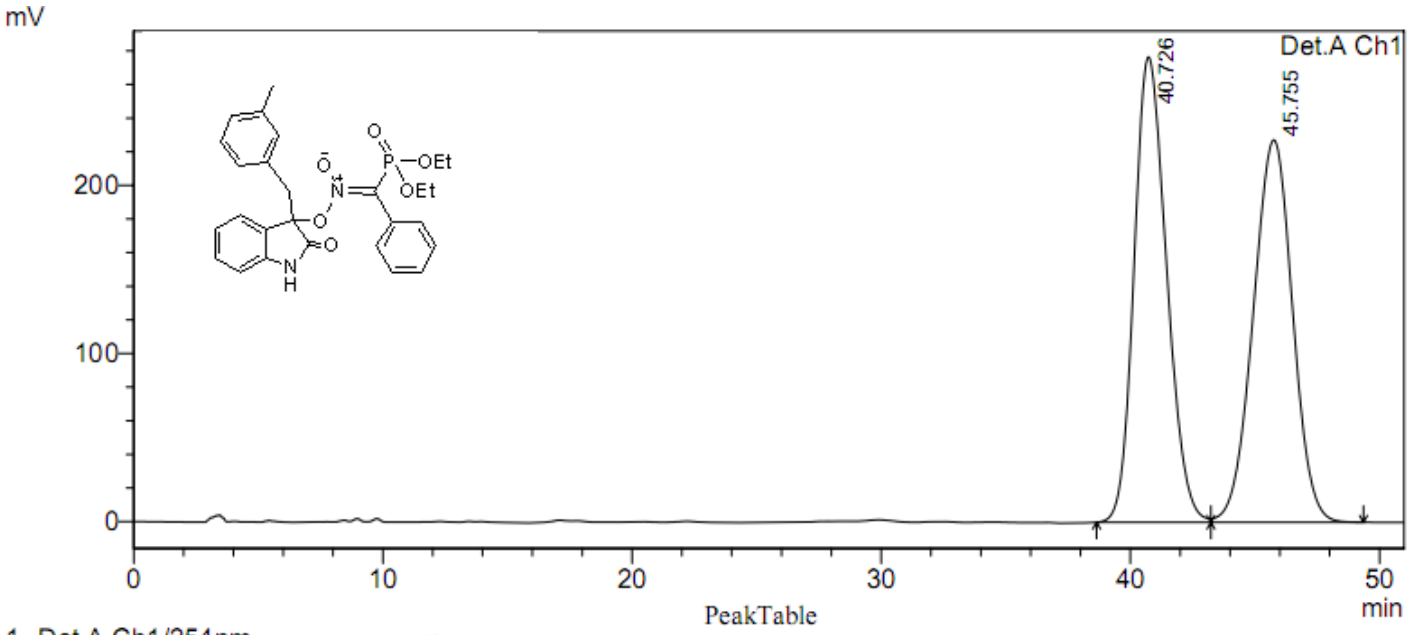


1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.700	5779909	86734	8.276
2	16.540	64057198	687333	91.724
Total		69837108	774067	100.000

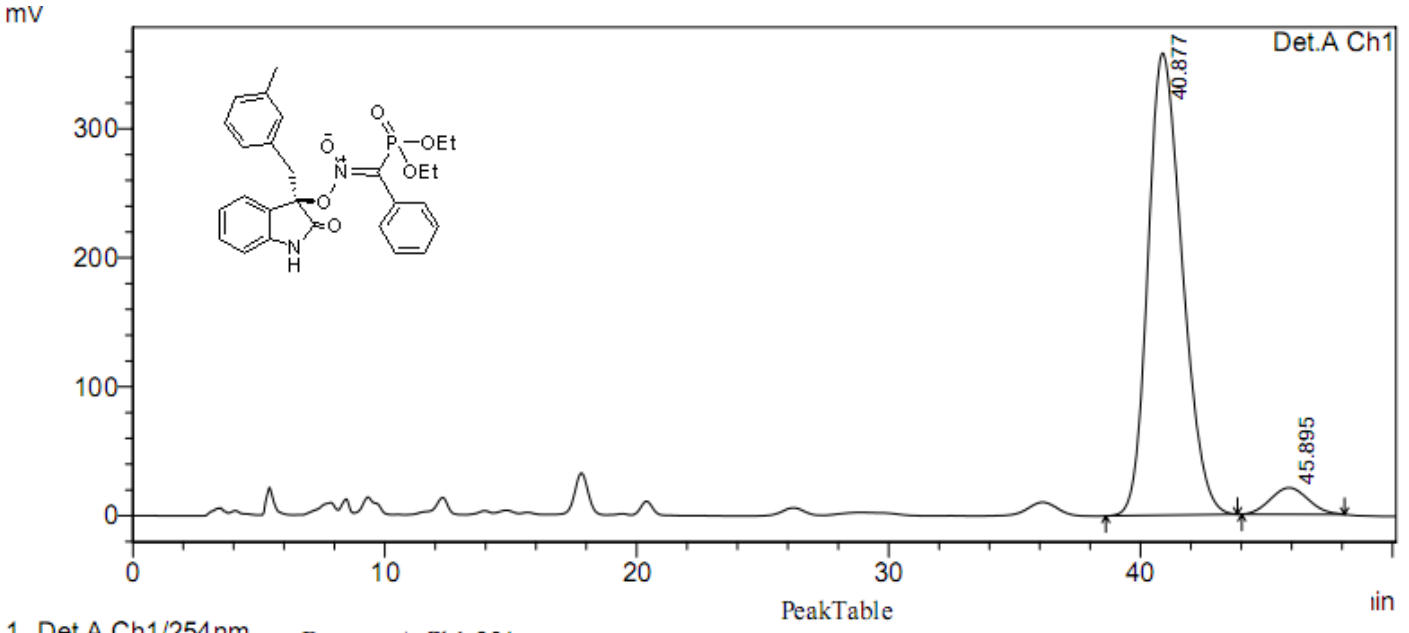
4h



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	40.726	25075665	276805	50.103
2	45.755	24972746	227386	49.897
Total		50048411	504191	100.000

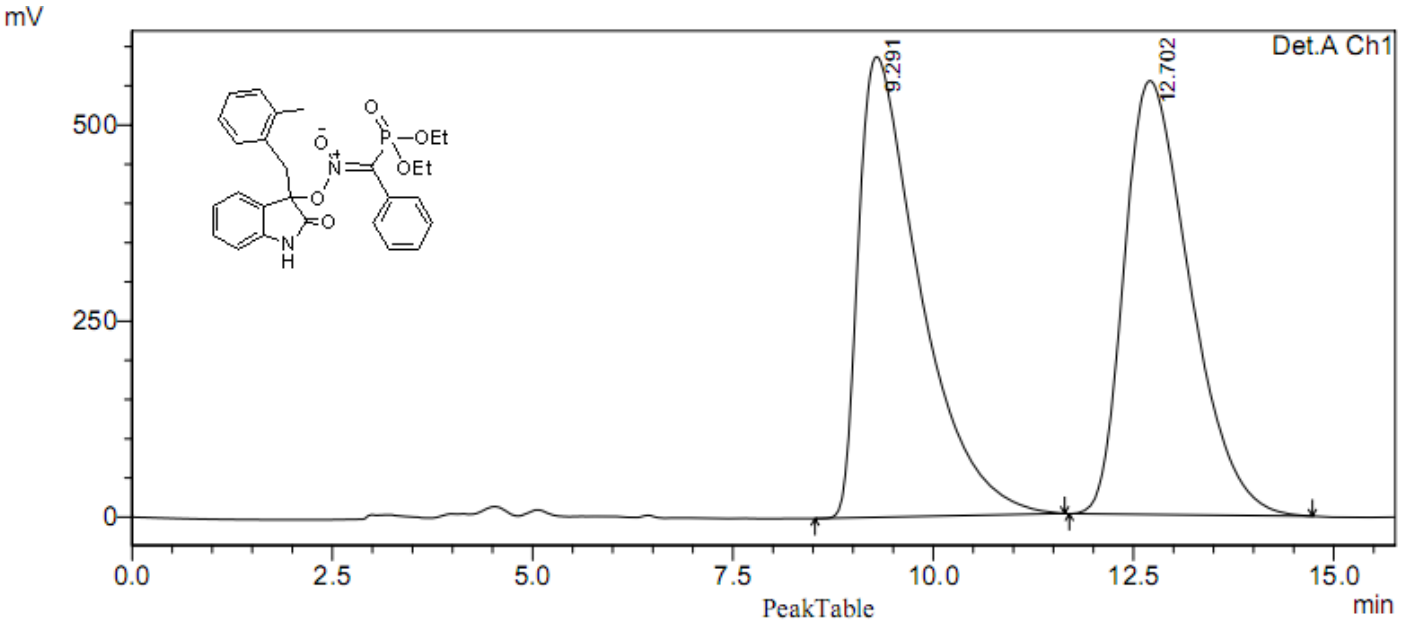


1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	40.877	33964099	358301	94.059
2	45.895	2145406	20555	5.941
Total		36109506	378856	100.000

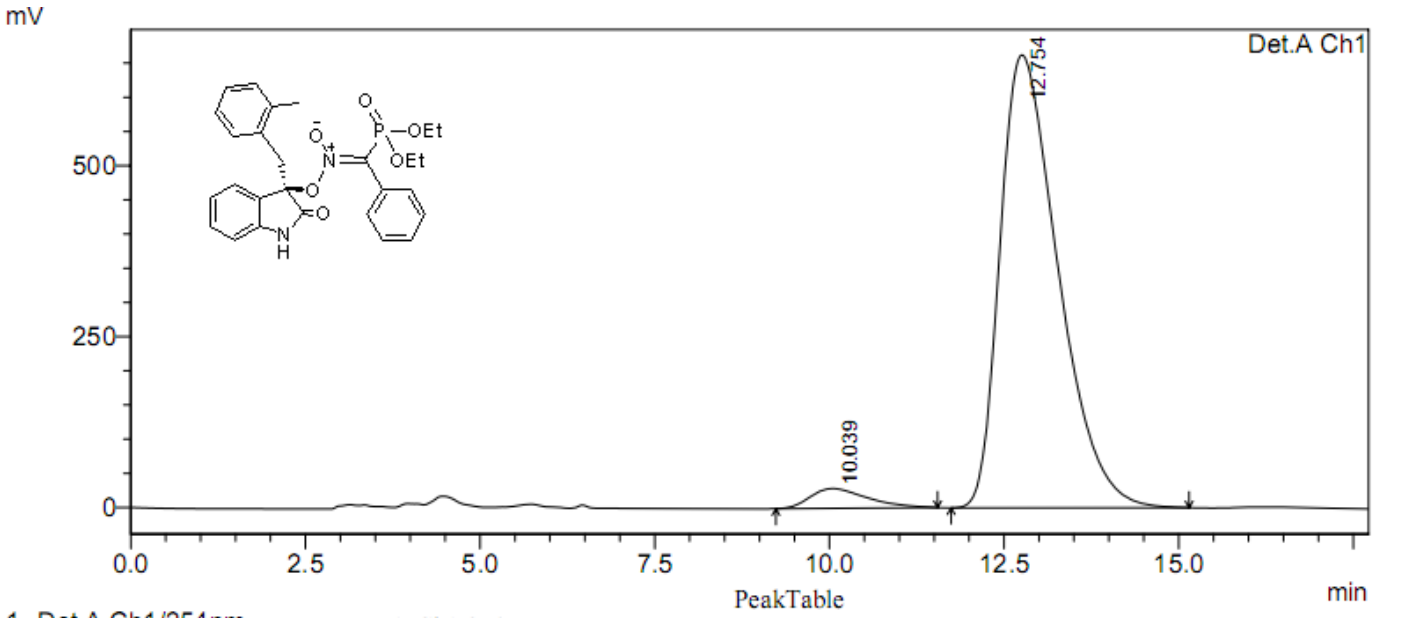
4i



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.291	31364618	587410	49.767
2	12.702	31658697	553032	50.233
Total		63023315	1140442	100.000

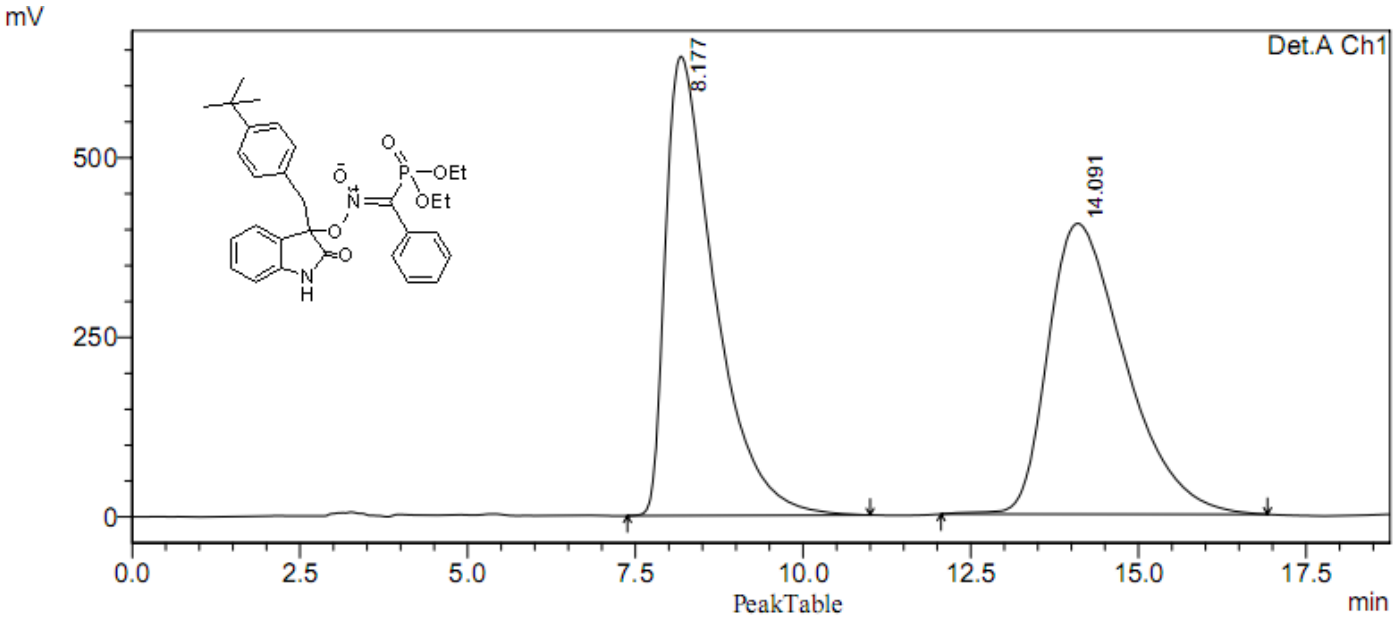


1 Det.A Ch1/254nm

Detector A Ch1 254nm

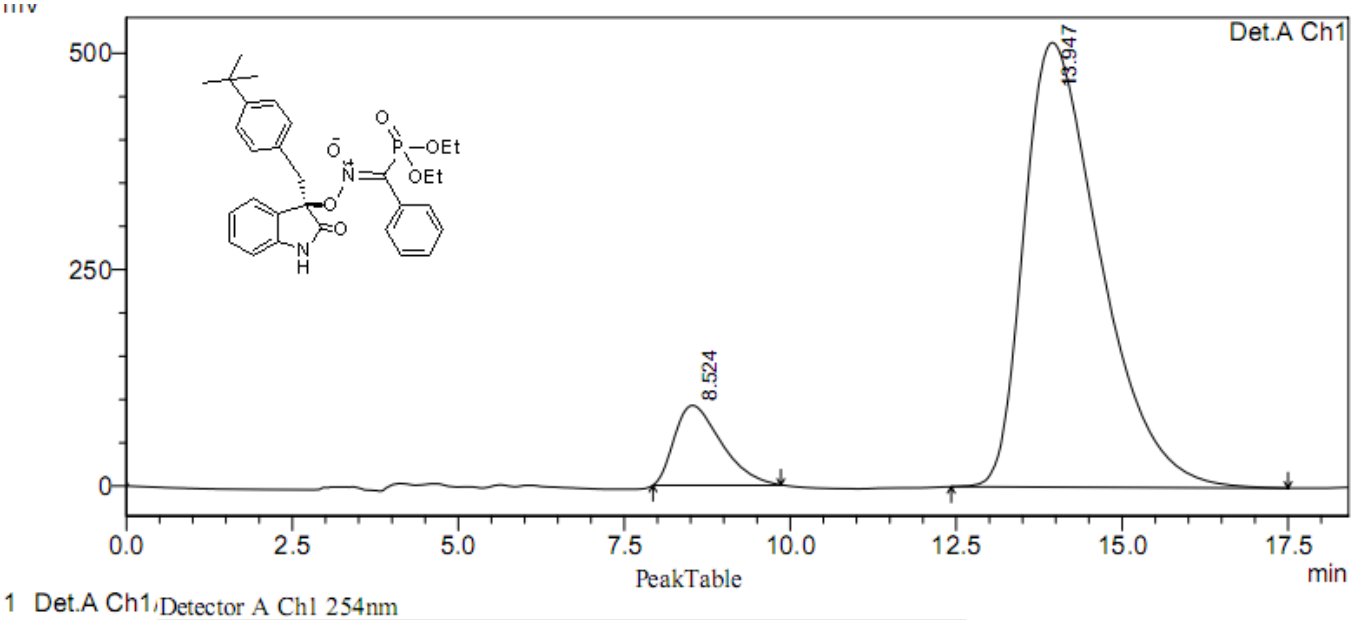
Peak#	Ret. Time	Area	Height	Area %
1	10.039	1641205	28889	4.108
2	12.754	38308941	662520	95.892
Total		39950147	691409	100.000

4j



1 Det.A Ch1/254nm Detector A Ch1 254nm

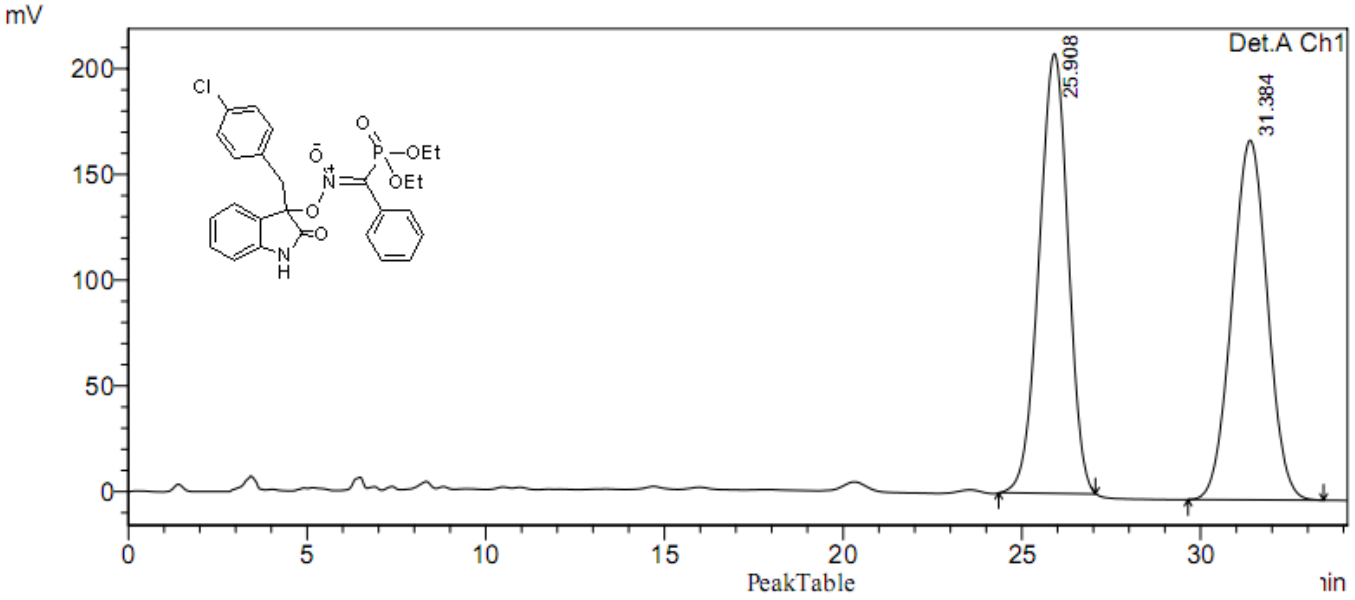
Peak#	Ret. Time	Area	Height	Area %
1	8.177	32593329	639236	50.036
2	14.091	32546827	404722	49.964
Total		65140156	1043957	100.000



1 Det.A Ch1/Detector A Ch1 254nm

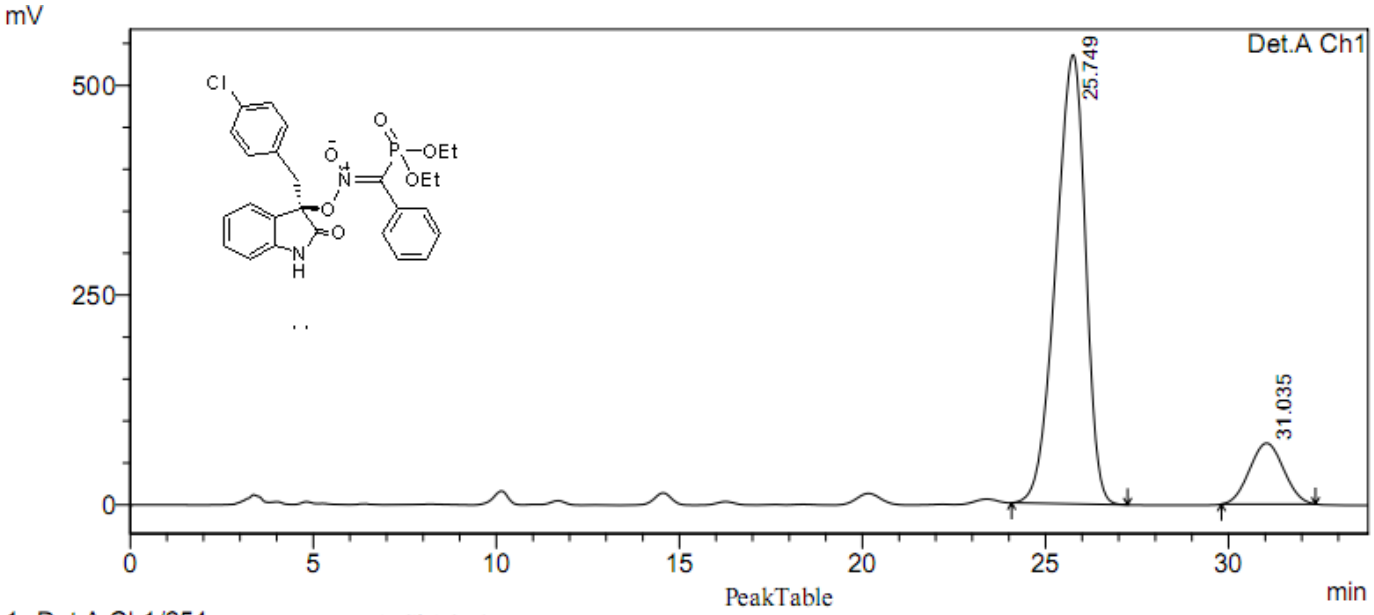
Peak#	Ret. Time	Area	Height	Area %
1	8.524	4543891	92206	9.967
2	13.947	41046585	513528	90.033
Total		45590476	605734	100.000

4k



1 Det.A Ch1/254nm Detector A Ch1 254nm

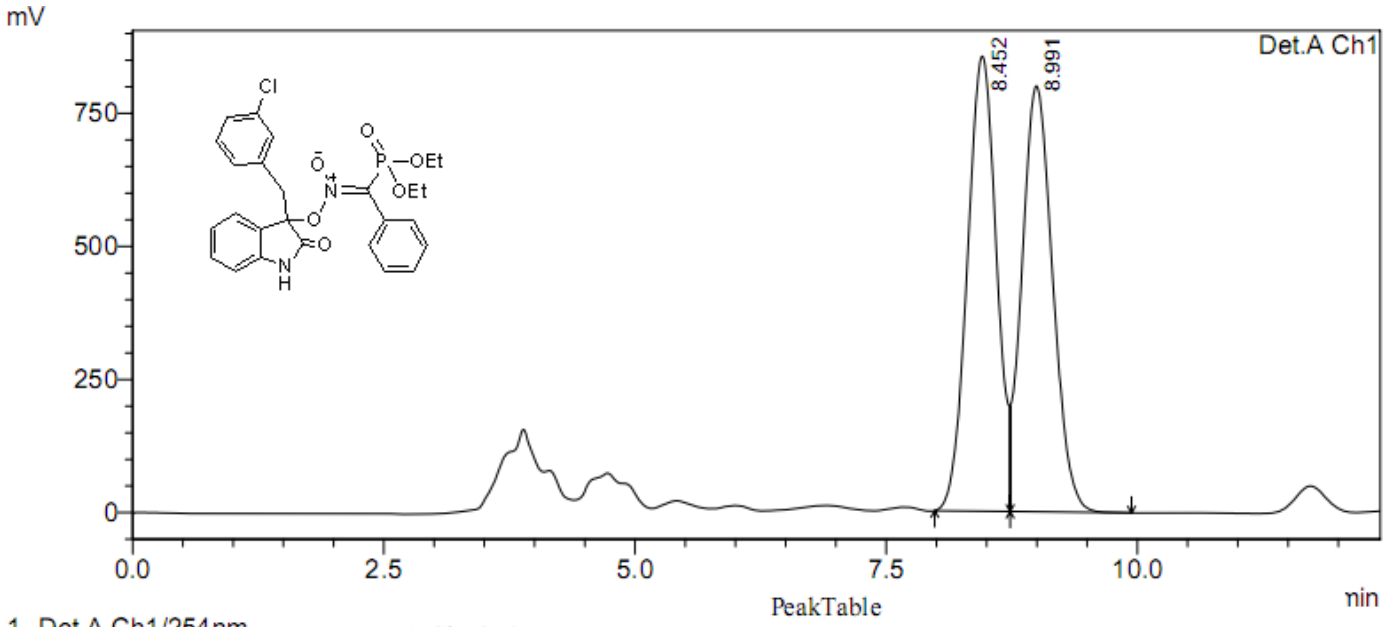
Peak#	Ret. Time	Area	Height	Area %
1	25.908	11754743	207994	50.029
2	31.384	11741267	170076	49.971
Total		23496010	378070	100.000



1 Det.A Ch1/254nm Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.749	30173247	535554	86.452
2	31.035	4728477	72653	13.548
Total		34901724	608207	100.000

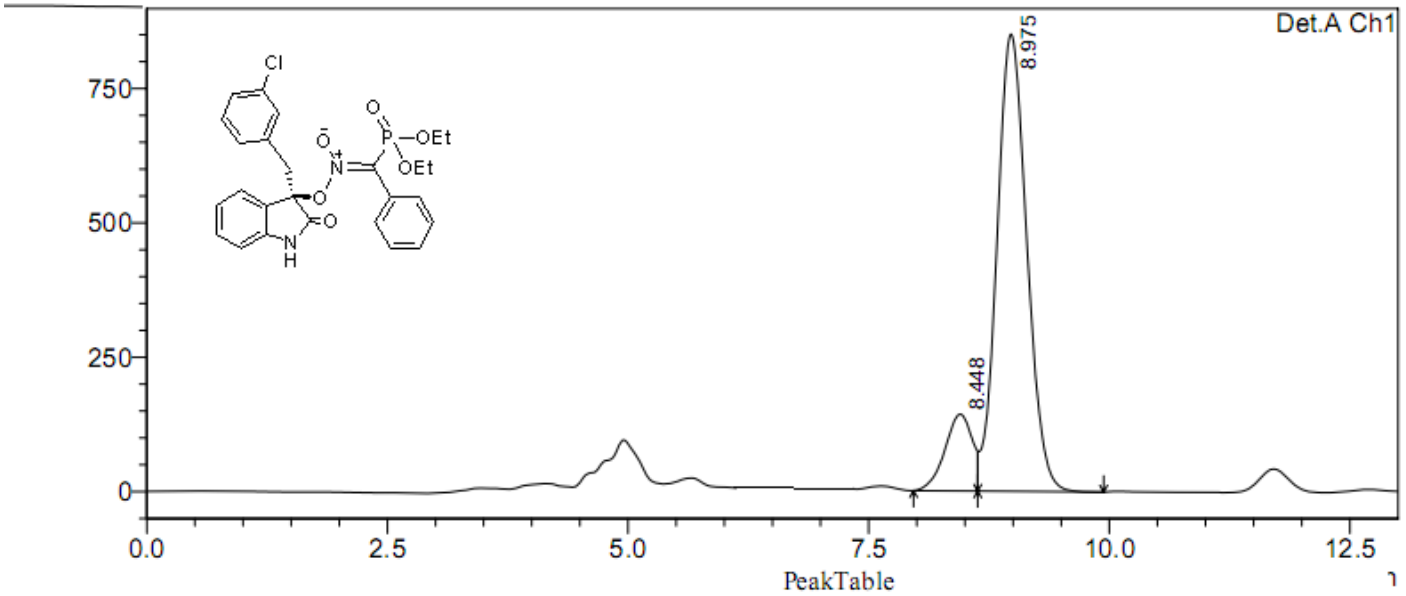
4l



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.452	17222676	855097	50.242
2	8.991	17056761	799891	49.758
Total		34279438	1654988	100.000

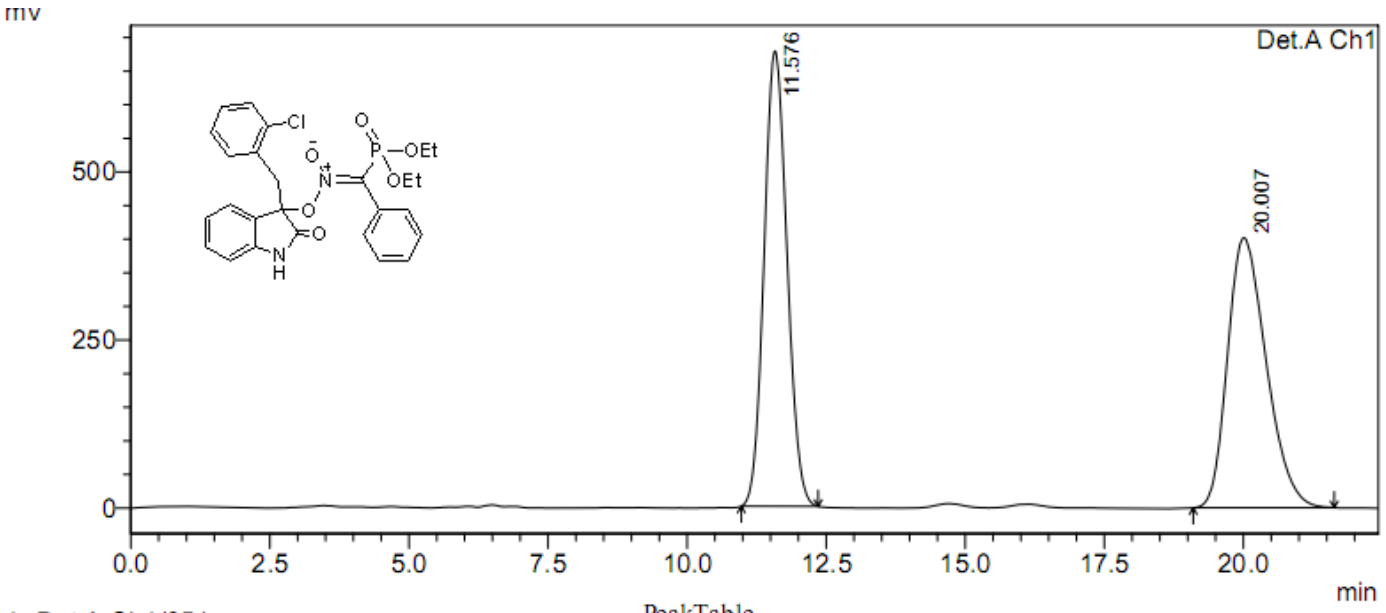


1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.448	2814329	142926	13.294
2	8.975	18354848	850422	86.706
Total		21169177	993348	100.000

4m

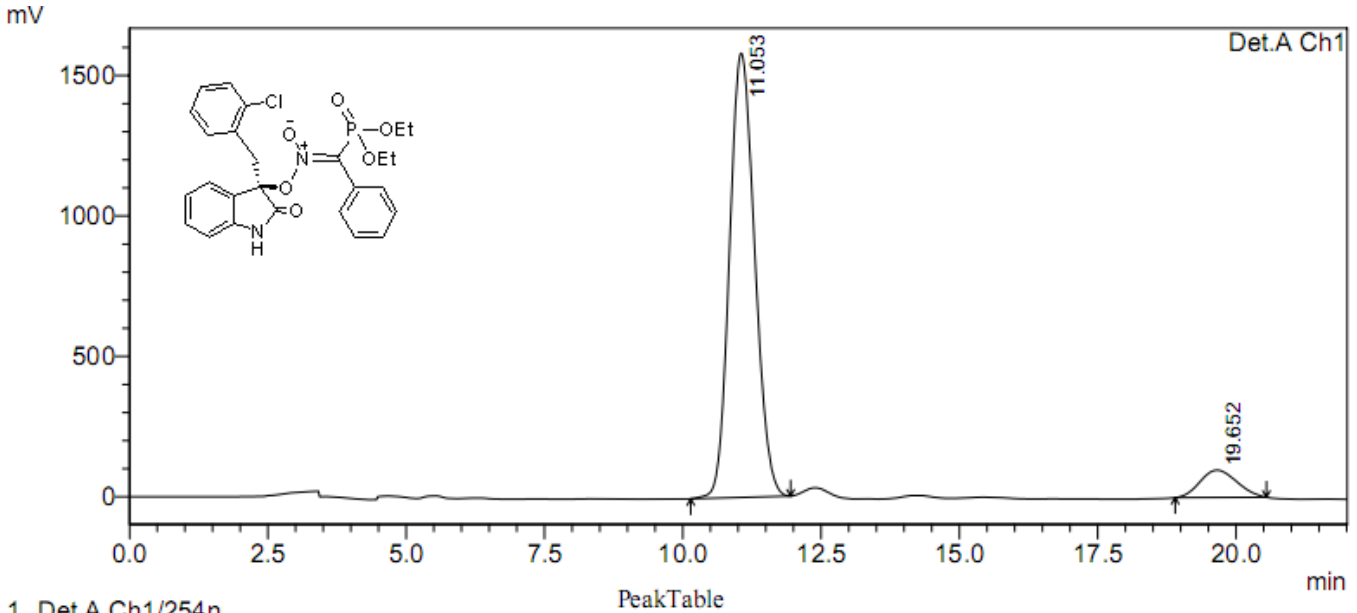


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.576	19388025	677420	49.935
2	20.007	19438312	401748	50.065
Total		38826337	1079168	100.000



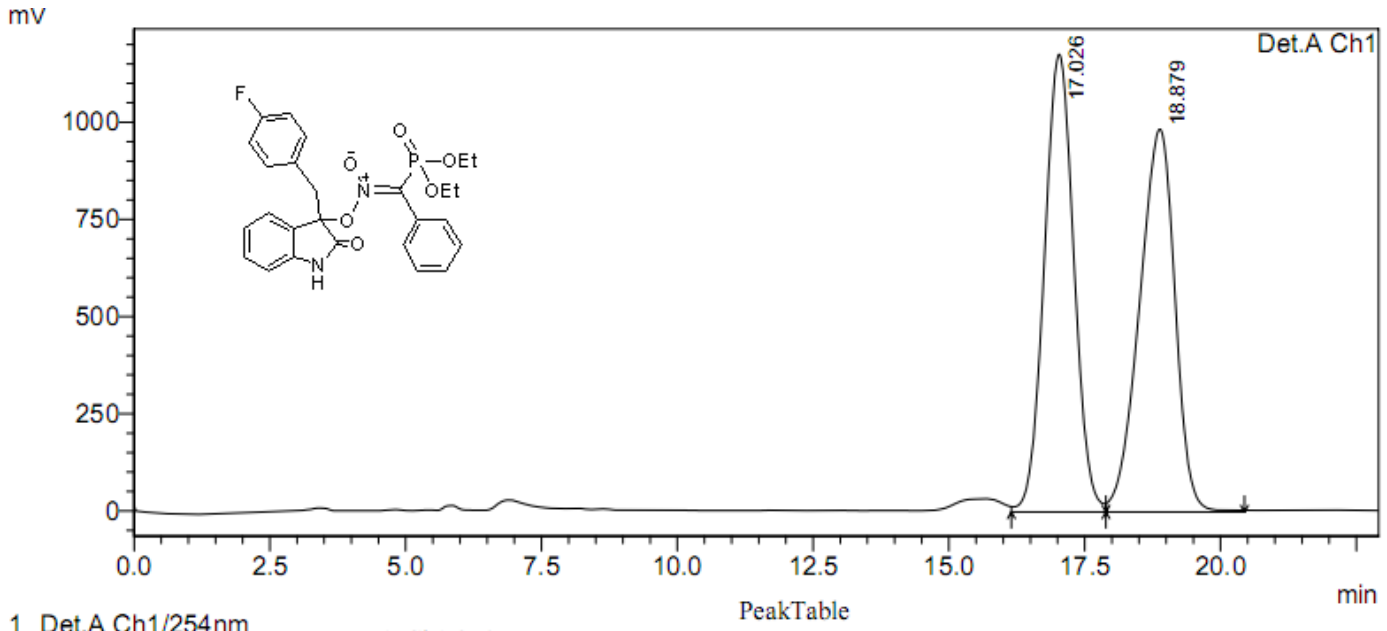
1 Det.A Ch1/254n

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.053	50162321	1581927	91.767
2	19.652	4500221	97420	8.233
Total		54662542	1679347	100.000

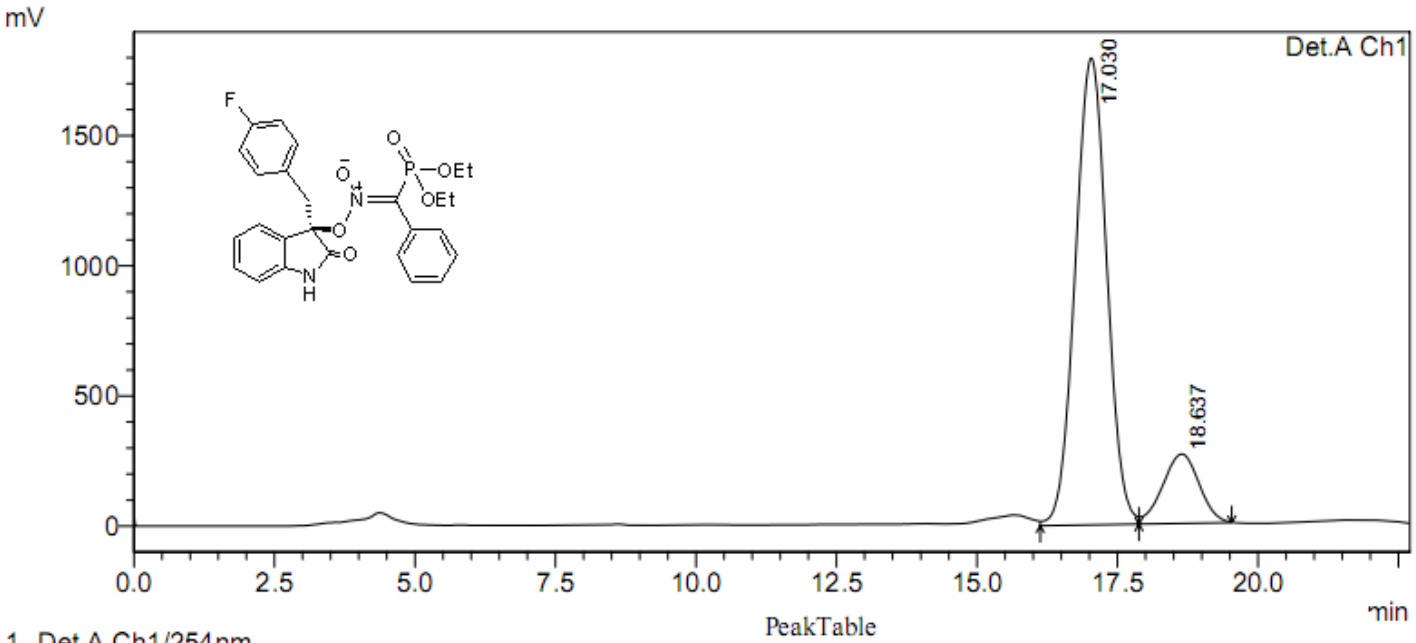
4n



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	17.026	44625422	1177156	49.946
2	18.879	44722370	984970	50.054
Total		89347792	2162126	100.000

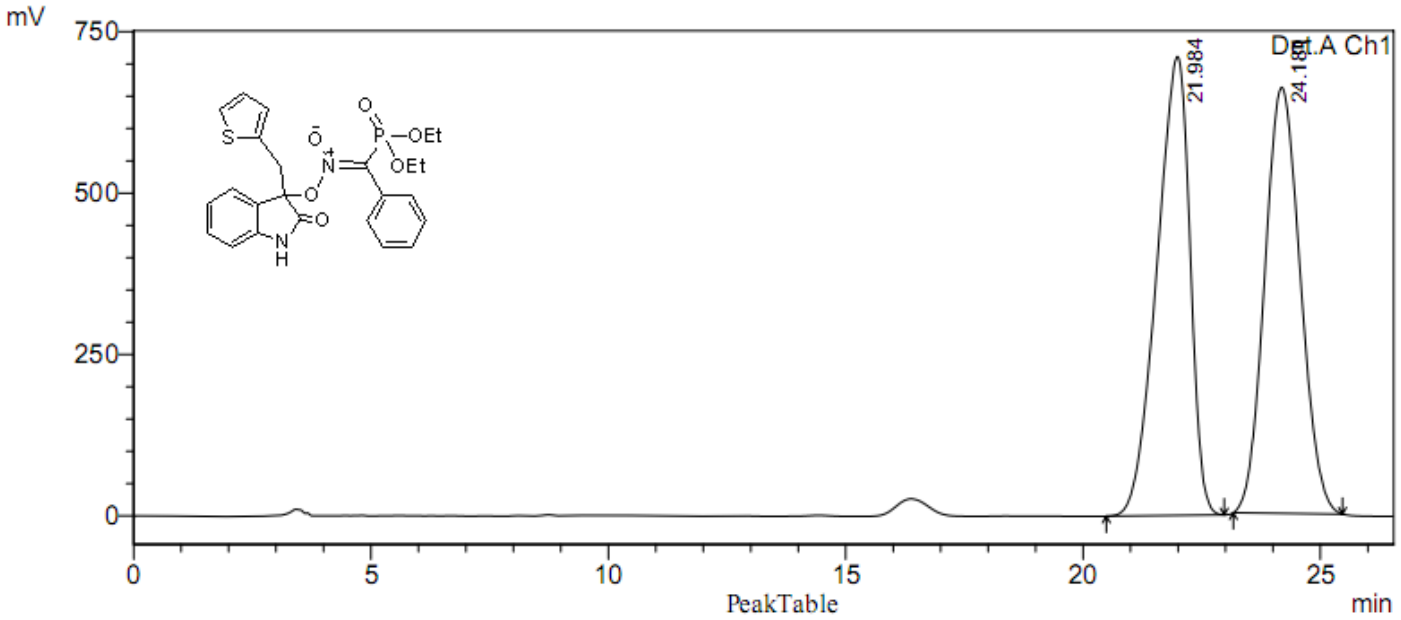


1 Det.A Ch1/254nm

Detector A Ch1 254nm

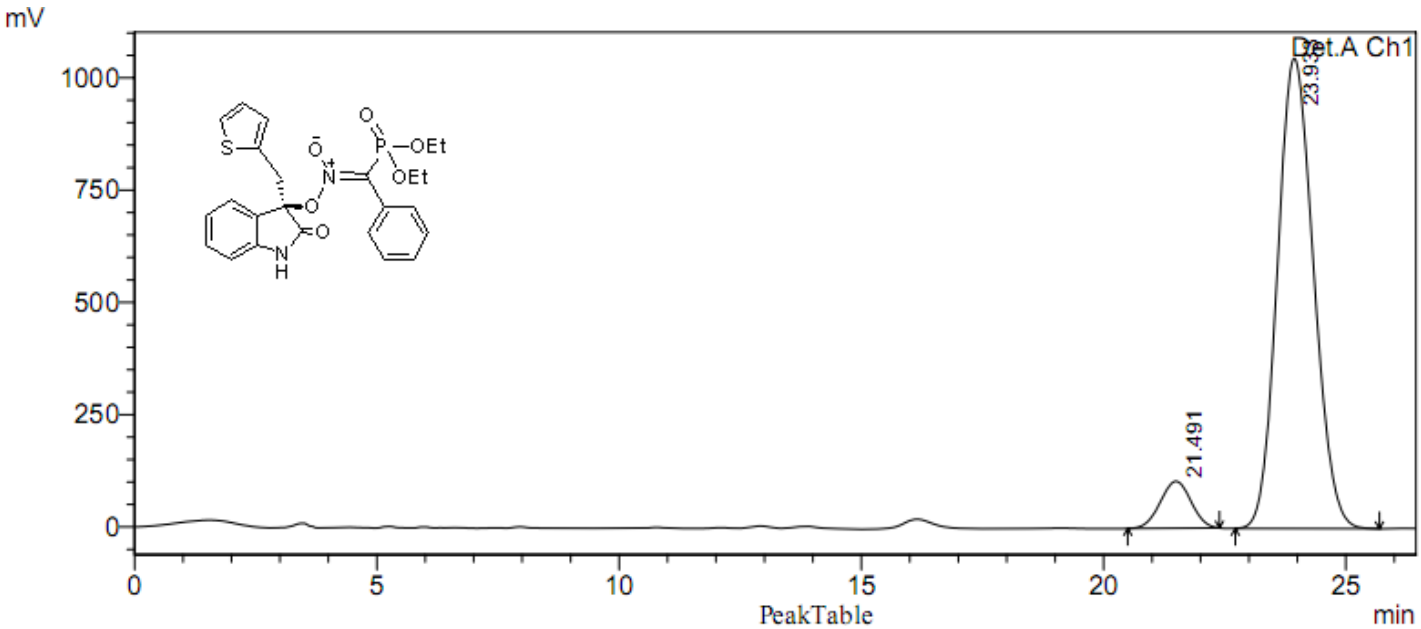
Peak#	Ret. Time	Area	Height	Area %
1	17.030	70003309	1793526	85.310
2	18.637	12054226	266783	14.690
Total		82057534	2060309	100.000

4o



1 Det.A Ch1/254nm Detector A Ch1 254nm

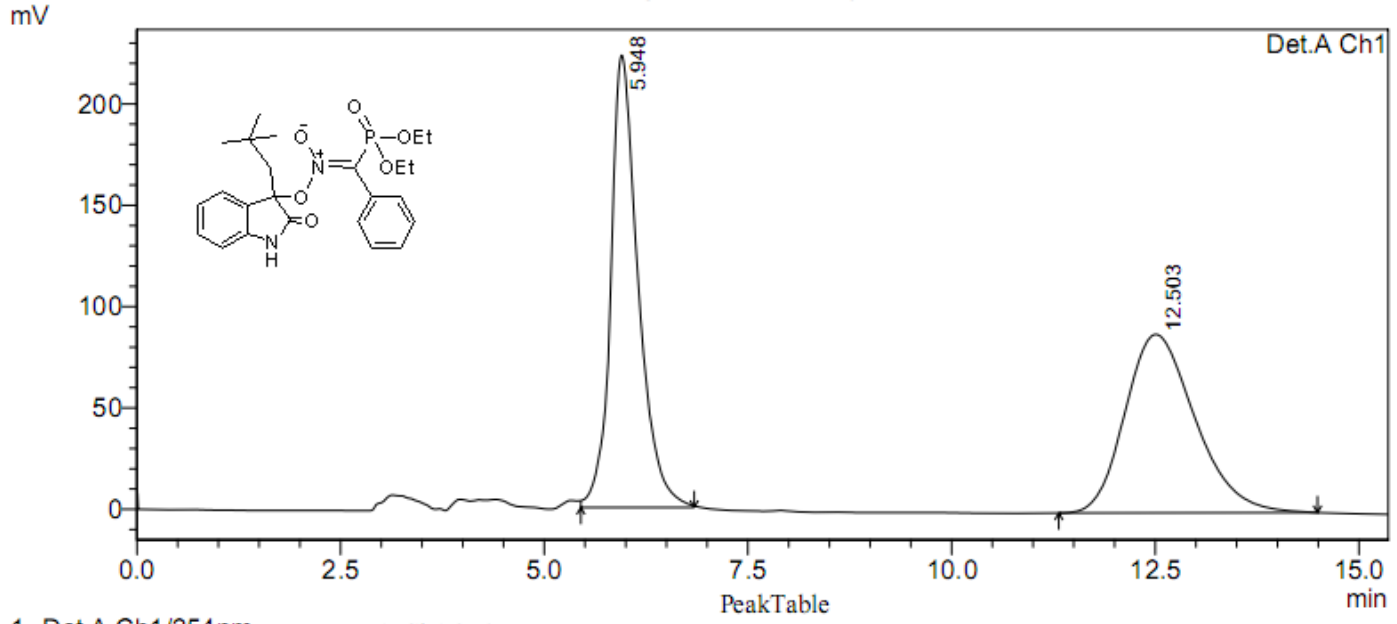
Peak#	Ret. Time	Area	Height	Area %
1	21.984	34383562	710848	49.973
2	24.181	34420624	659909	50.027
Total		68804186	1370757	100.000



1 Det.A Ch1/254nm Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	21.491	4630975	104553	7.863
2	23.933	54263274	1046677	92.137
Total		58894249	1151230	100.000

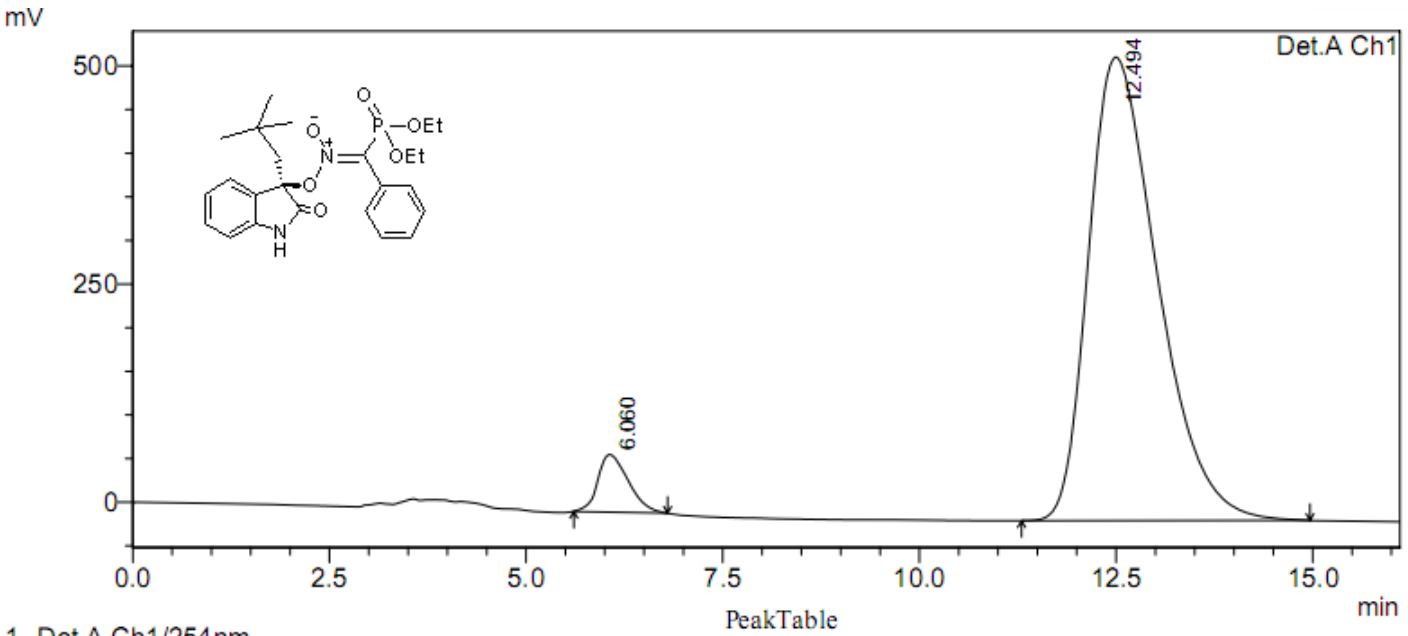
4p



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.948	5241182	223182	49.901
2	12.503	5261897	88051	50.099
Total		10503079	311233	100.000

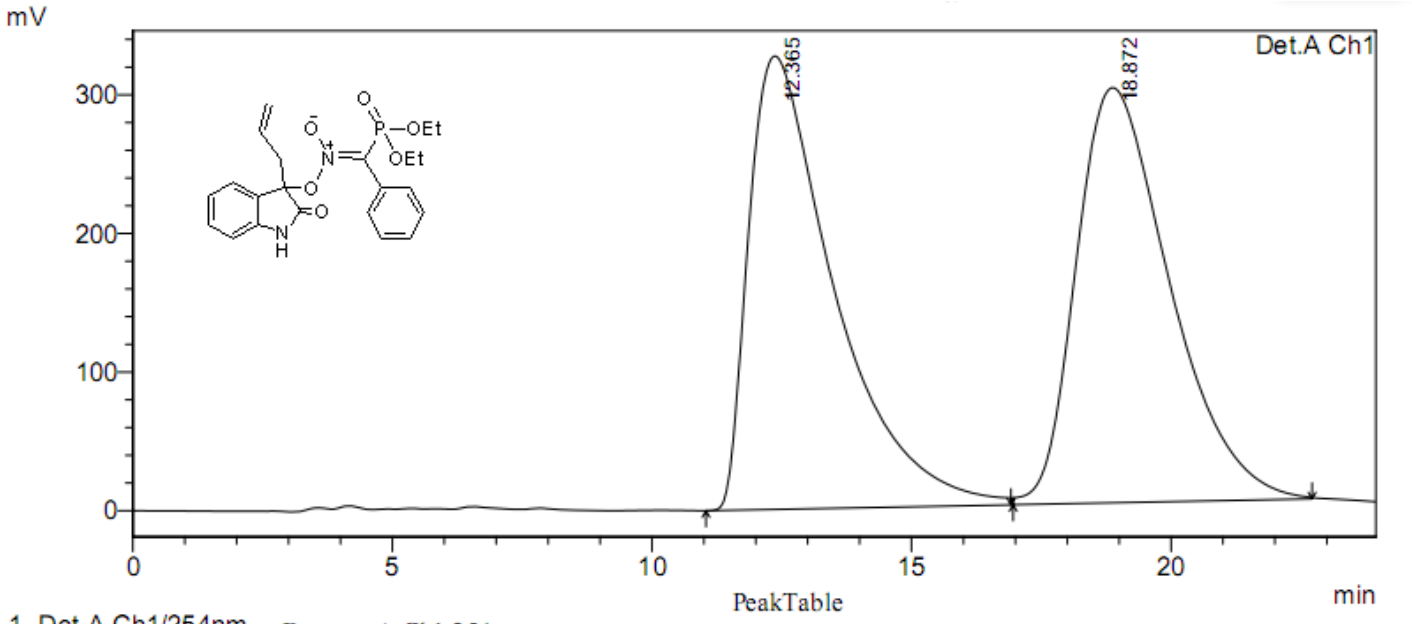


1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.060	1777751	66027	5.201
2	12.494	32402336	531242	94.799
Total		34180087	597270	100.000

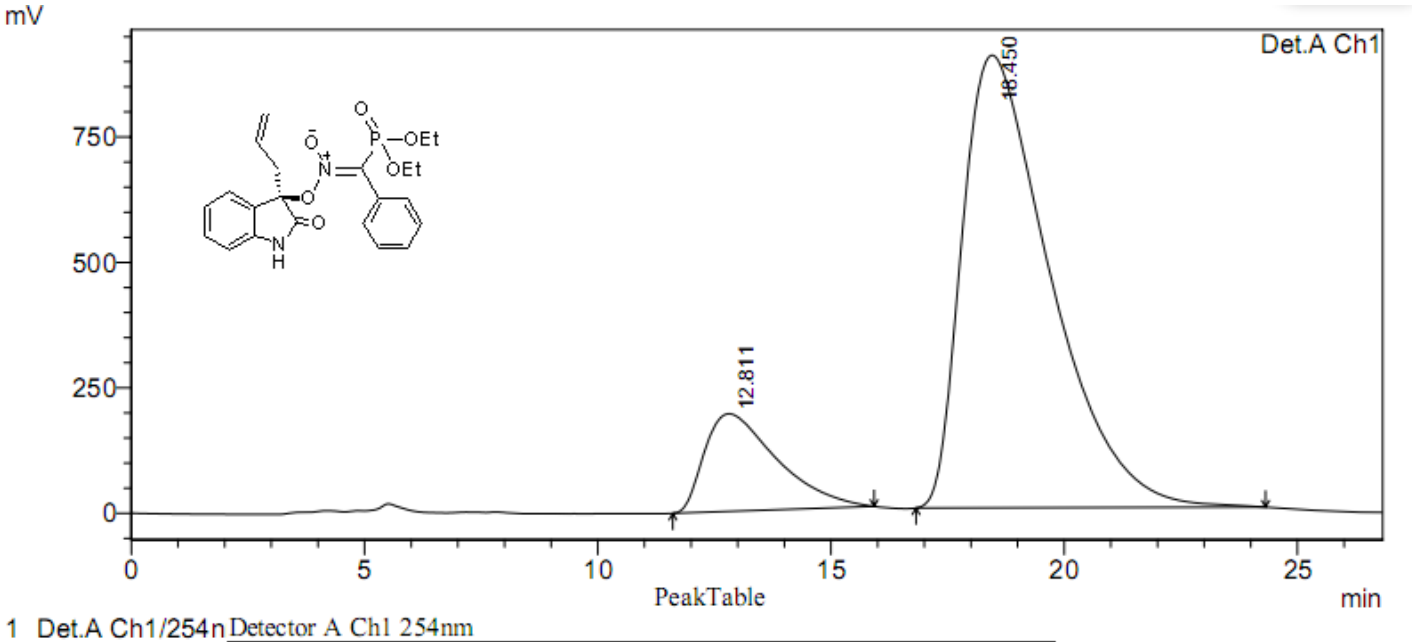
4q



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.365	37460536	326982	49.936
2	18.872	37557126	299485	50.064
Total		75017662	626467	100.000

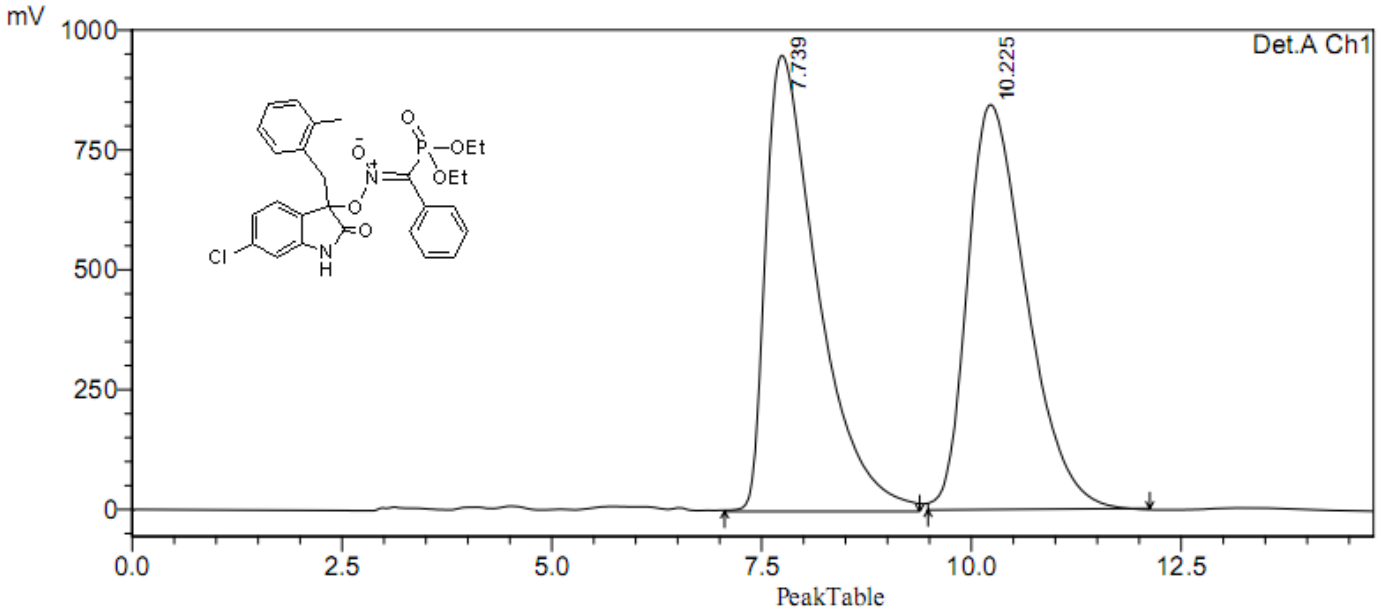


1 Det.A Ch1/254n

Detector A Ch1 254nm

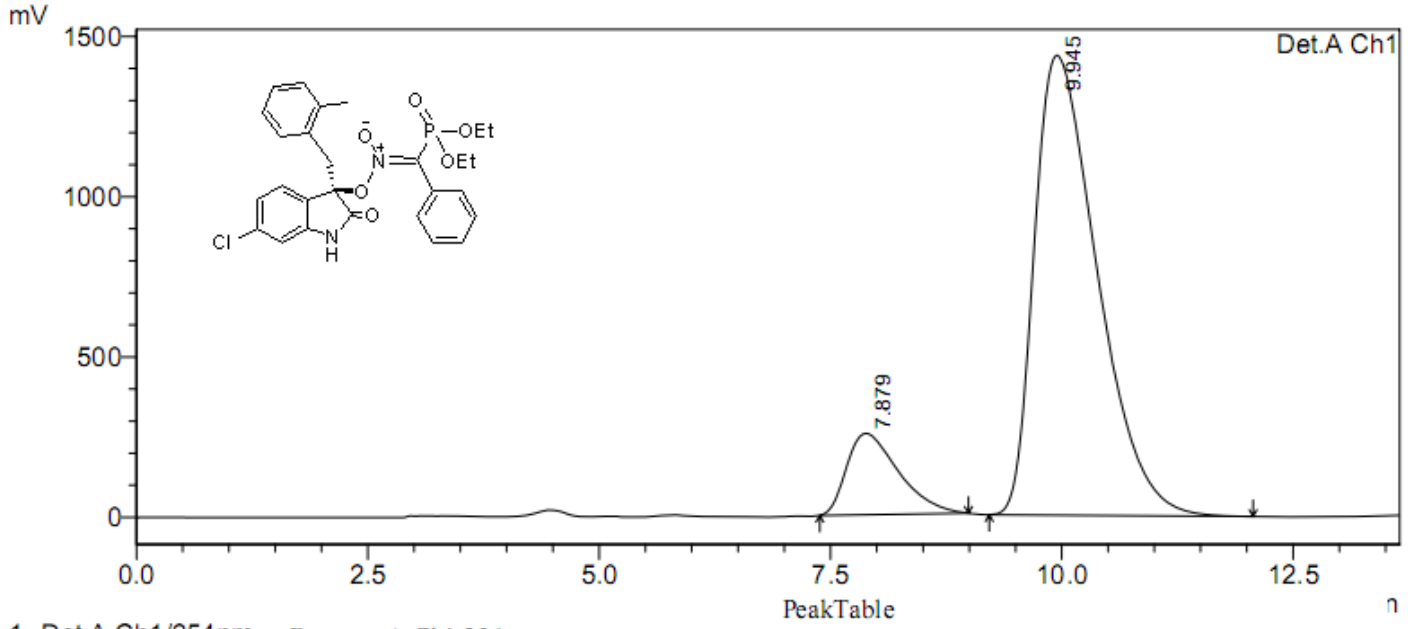
Peak#	Ret. Time	Area	Height	Area %
1	12.811	20976513	194572	15.035
2	18.450	118539274	902154	84.965
Total		139515787	1096726	100.000

4r



1 Det.A Ch1/254nm Detector A Ch1 254nm

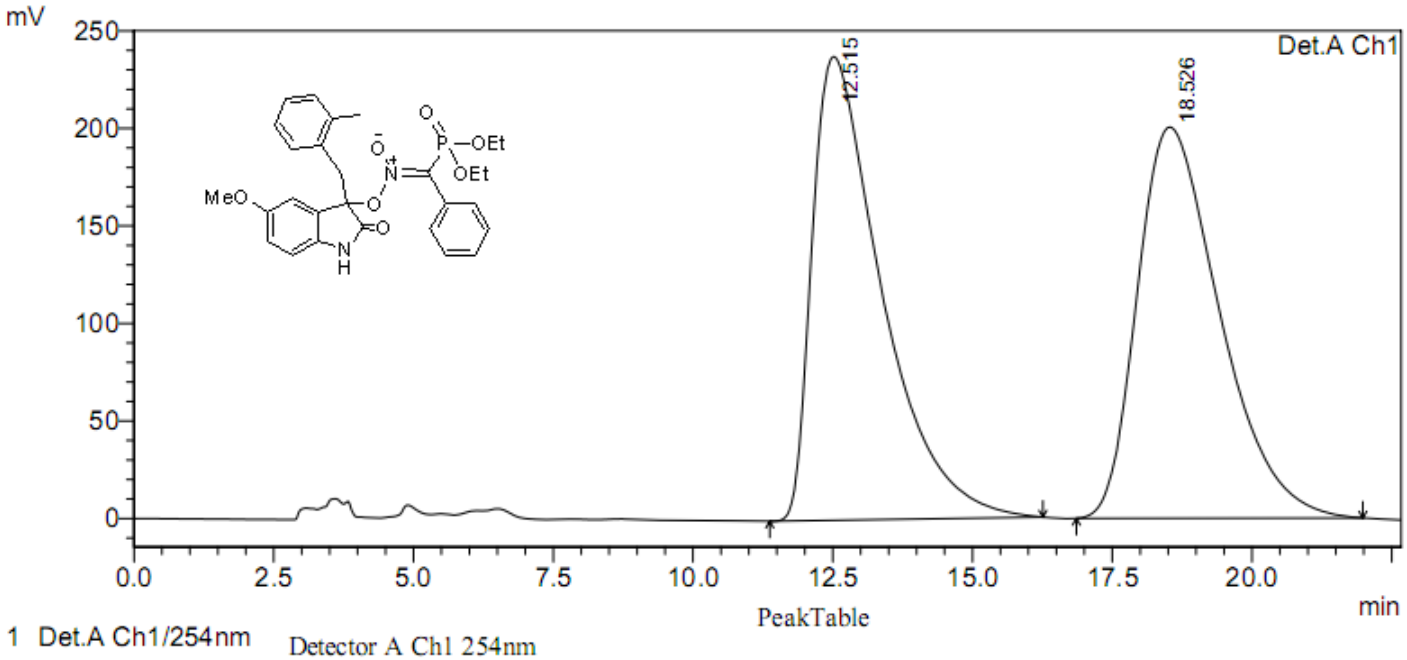
Peak#	Ret. Time	Area	Height	Area %
1	7.739	41048032	951248	49.872
2	10.225	41258803	844414	50.128
Total		82306835	1795661	100.000



1 Det.A Ch1/254nm Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.879	9877361	253694	12.716
2	9.945	67800940	1434812	87.284
Total		77678302	1688507	100.000

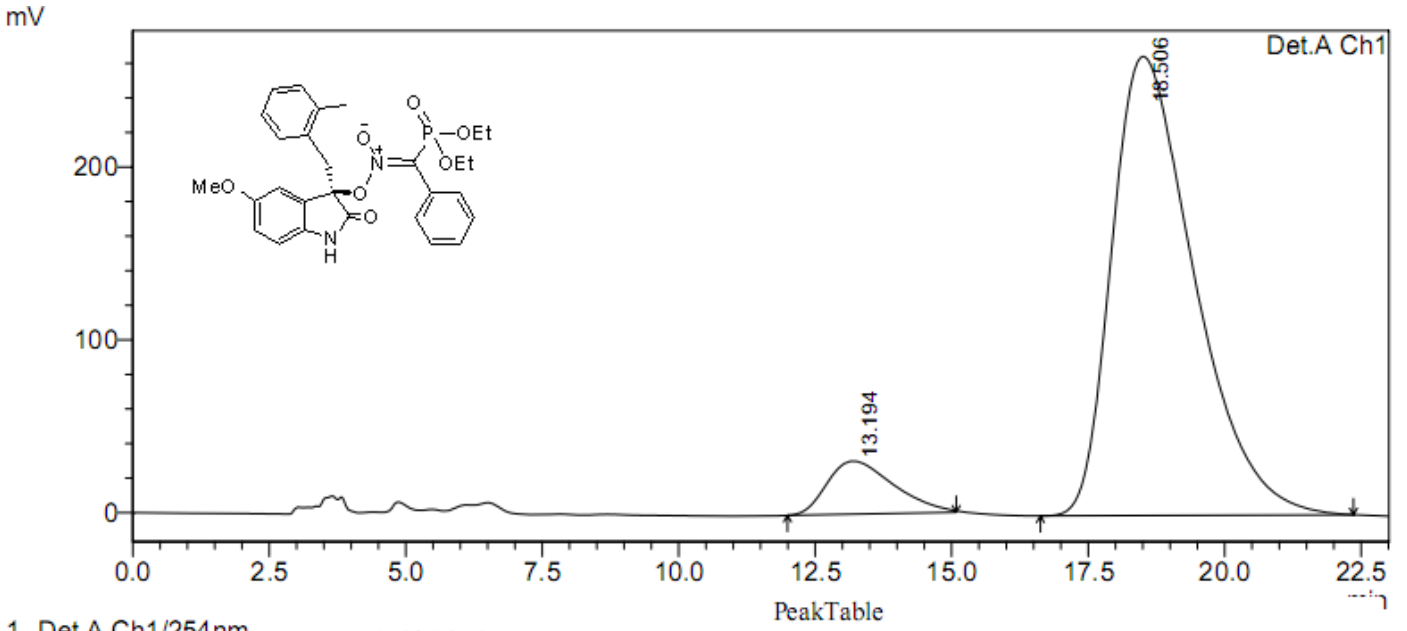
4s



1 Det.A Ch1/254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.515	20524779	237730	49.951
2	18.526	20565029	200553	50.049
Total		41089808	438283	100.000

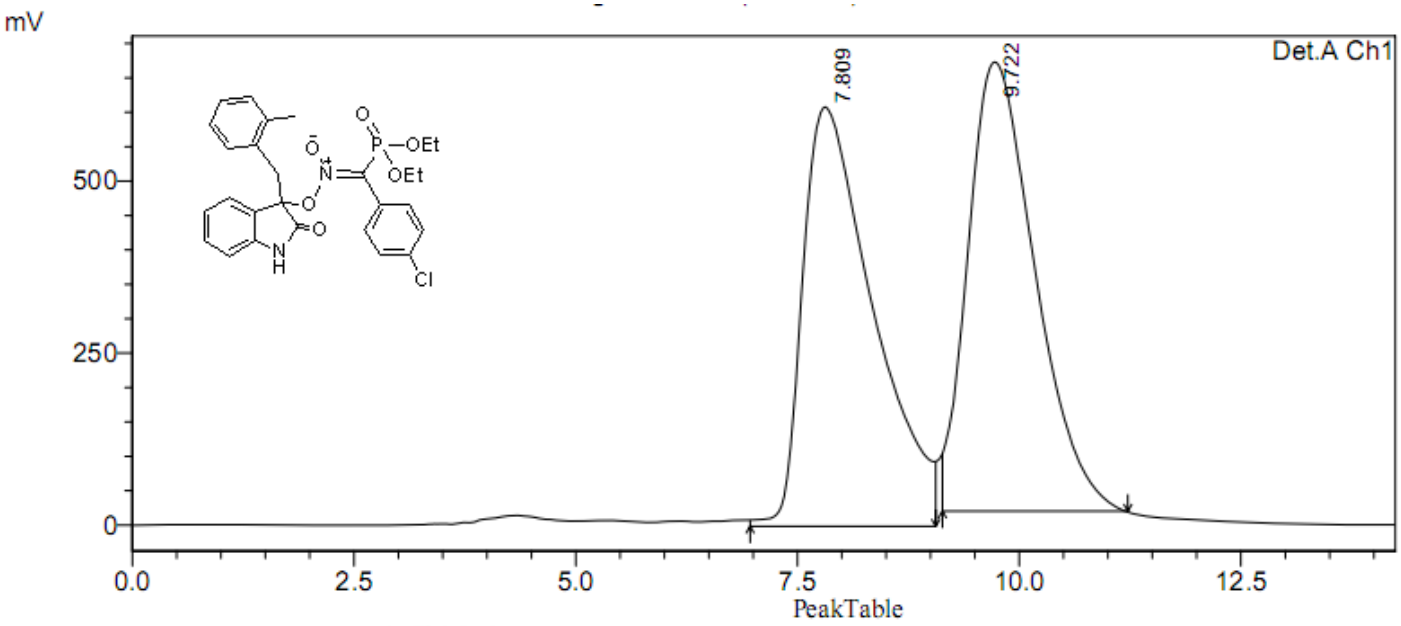


1 Det.A Ch1/254nm

Detector A Ch1 254nm

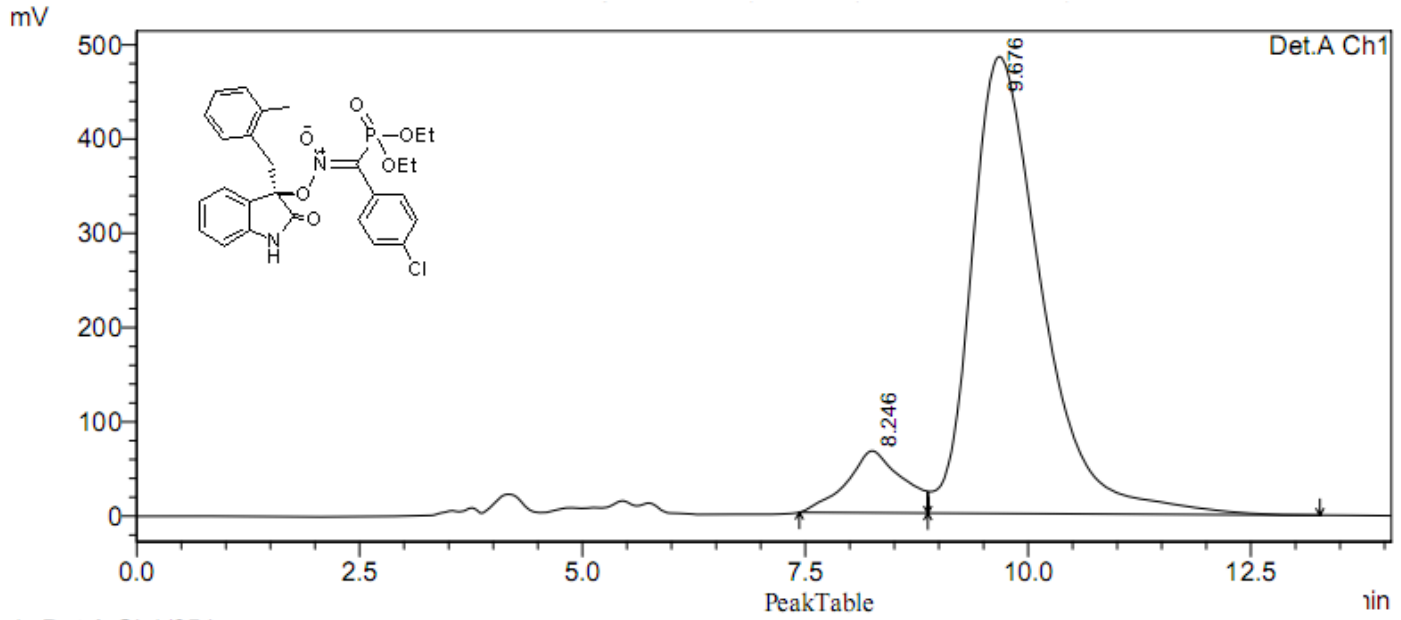
Peak#	Ret. Time	Area	Height	Area %
1	13.194	2597585	30715	8.510
2	18.506	27927966	265751	91.490
Total		30525551	296466	100.000

4t



1 Det.A Ch1/254nm Detector A Ch1 254nm

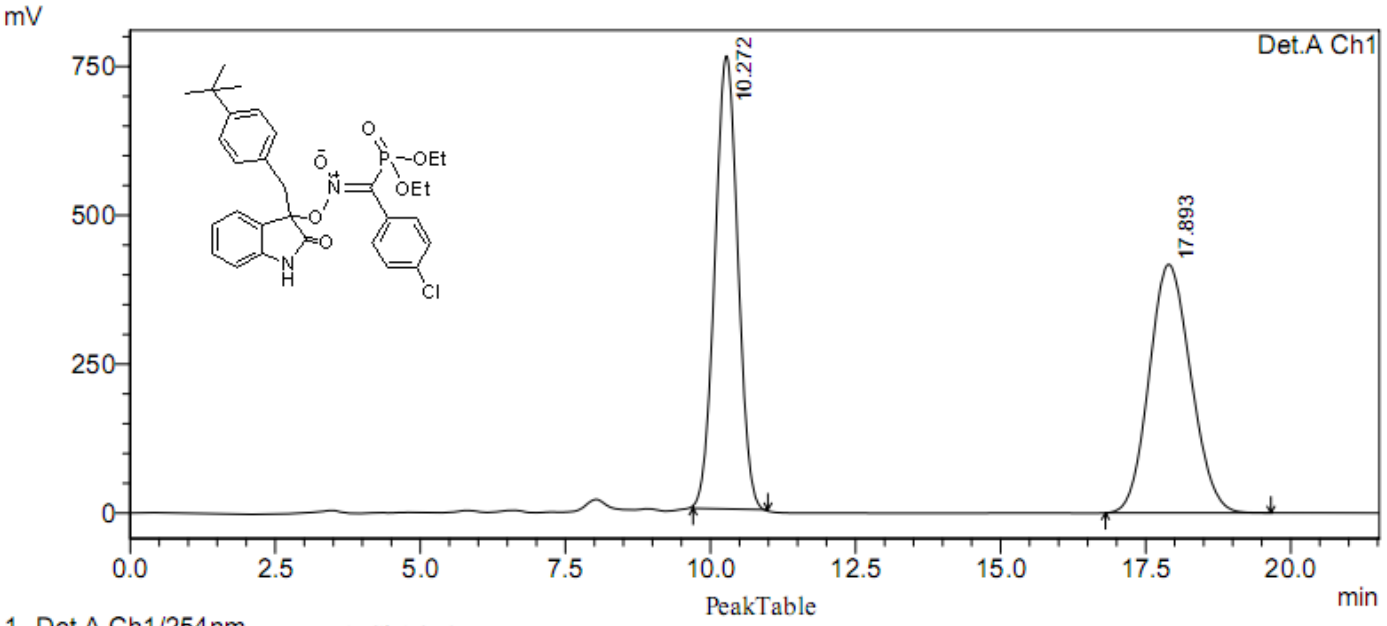
Peak#	Ret. Time	Area	Height	Area %
1	7.809	33579387	609256	49.410
2	9.722	34382000	652999	50.590
Total		67961387	1262255	100.000



1 Det.A Ch1/254nm Detector A Ch1 254nm

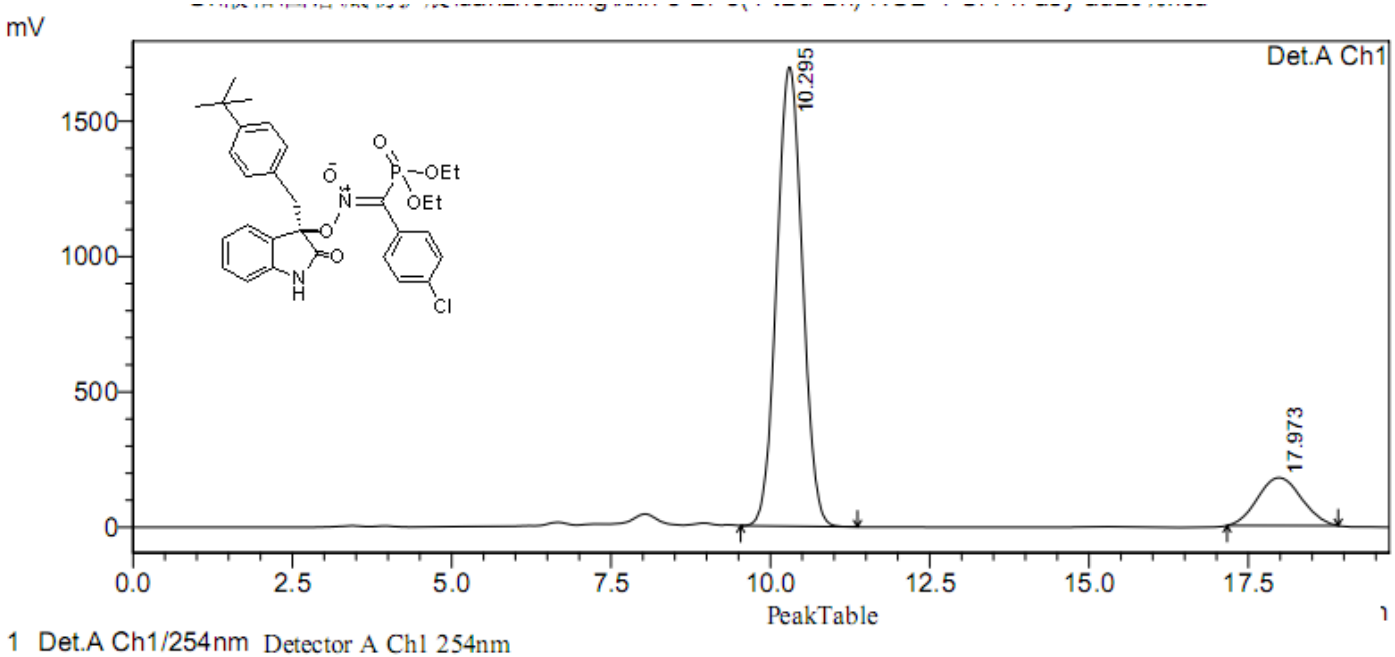
Peak#	Ret. Time	Area	Height	Area %
1	8.246	2851387	65634	9.704
2	9.676	26532671	484699	90.296
Total		29384058	550333	100.000

4u



1 Det.A Ch1/254nm Detector A Ch1 254nm

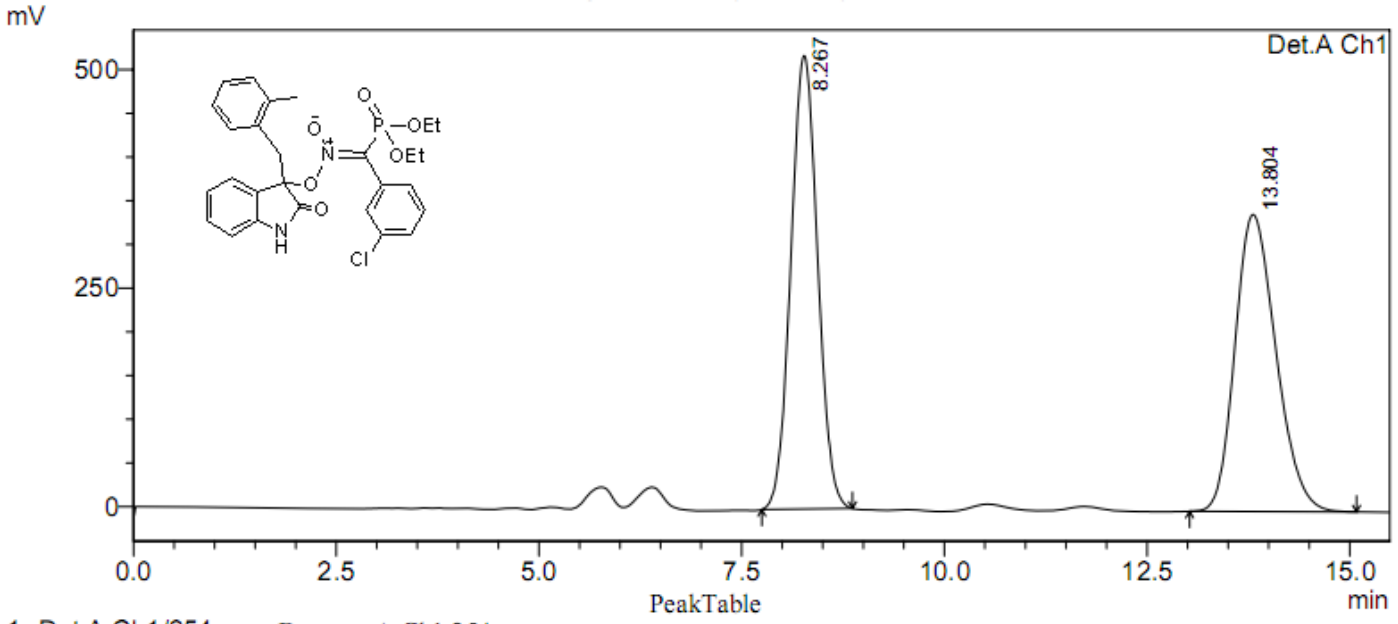
Peak#	Ret. Time	Area	Height	Area %
1	10.272	20928739	760965	50.098
2	17.893	20846800	417352	49.902
Total		41775538	1178317	100.000



1 Det.A Ch1/254nm Detector A Ch1 254nm

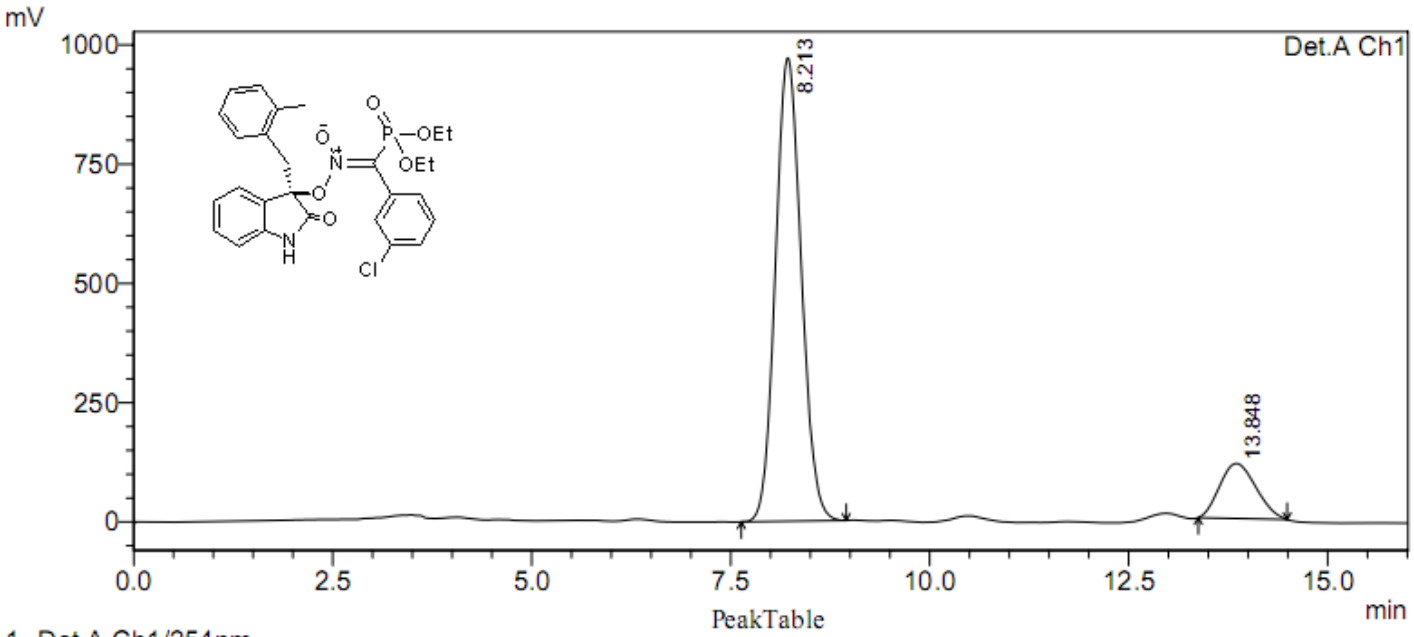
Peak#	Ret. Time	Area	Height	Area %
1	10.295	47683317	1697048	84.886
2	17.973	8489881	177527	15.114
Total		56173198	1874575	100.000

4v



1 Det.A Ch1/254nm Detector A Ch1 254nm

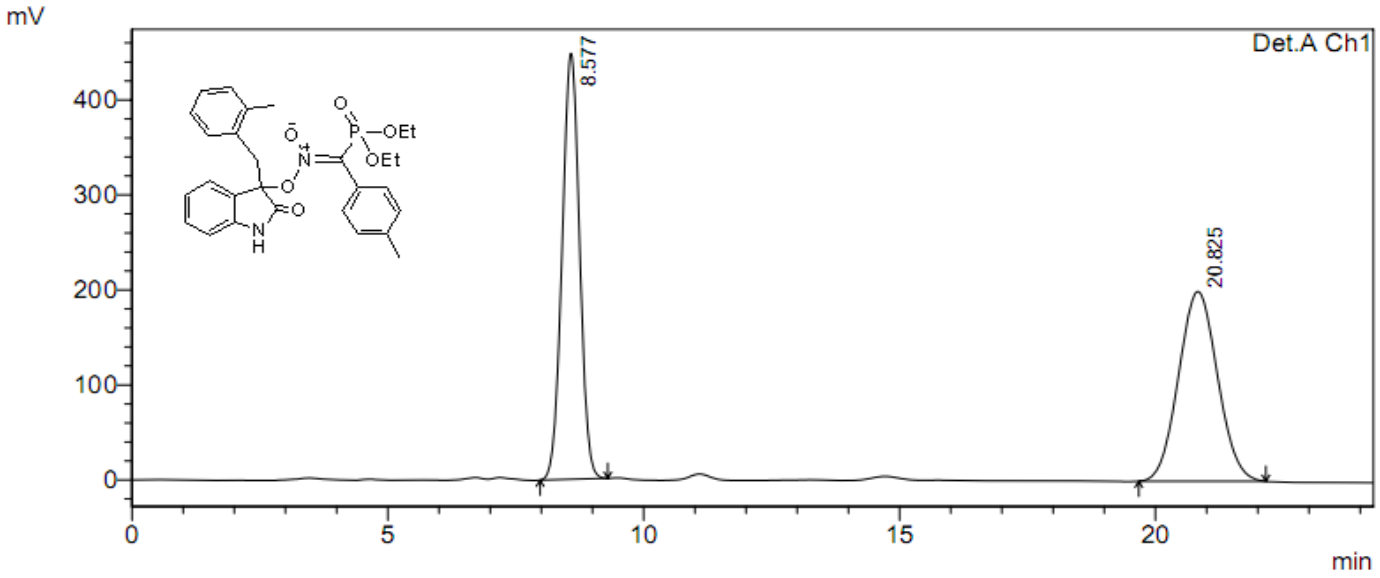
Peak#	Ret. Time	Area	Height	Area %
1	8.267	11897648	518751	49.918
2	13.804	11936866	339998	50.082
Total		23834515	858749	100.000



1 Det.A Ch1/254nm Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.213	21909051	971681	85.694
2	13.848	3657657	115158	14.306
Total		25566709	1086840	100.000

4w

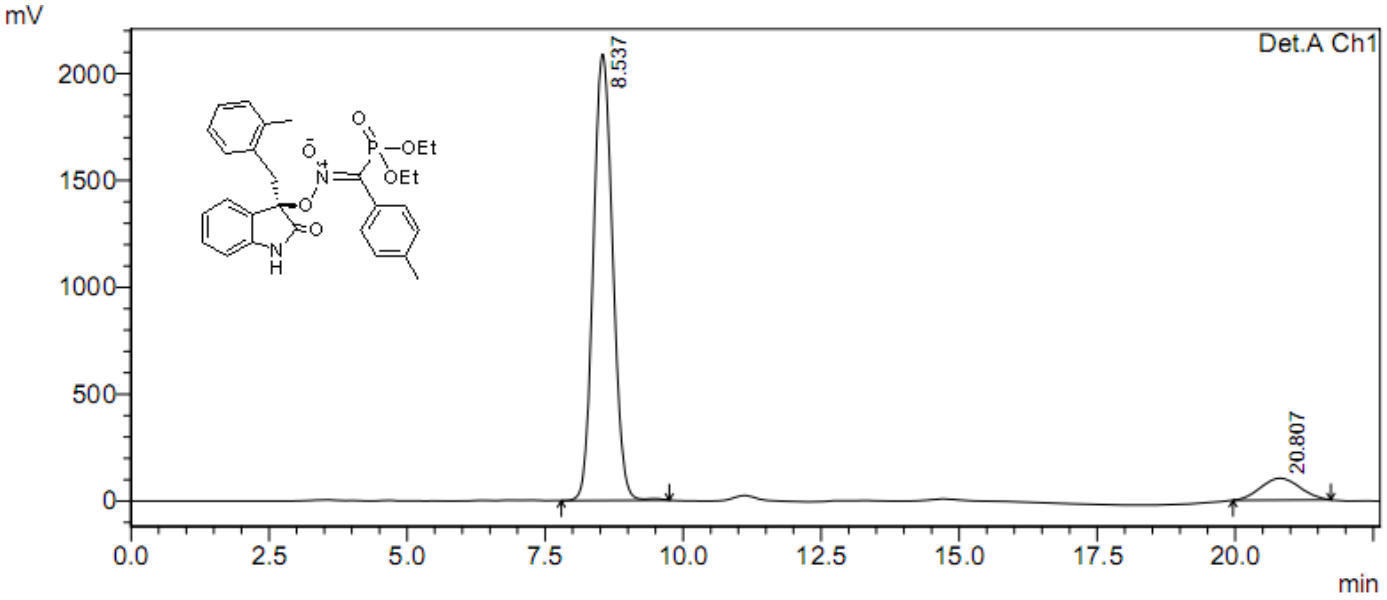


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.577	10617024	448346	50.068
2	20.825	10588183	199639	49.932
Total		21205207	647984	100.000



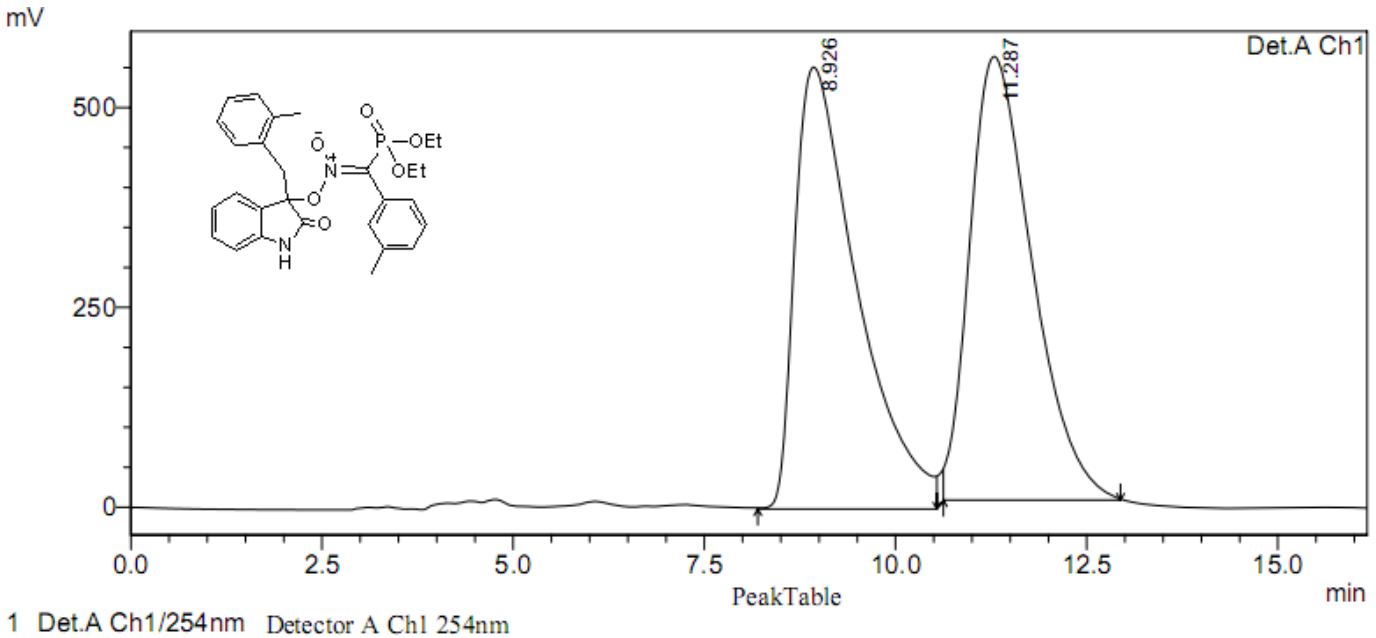
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

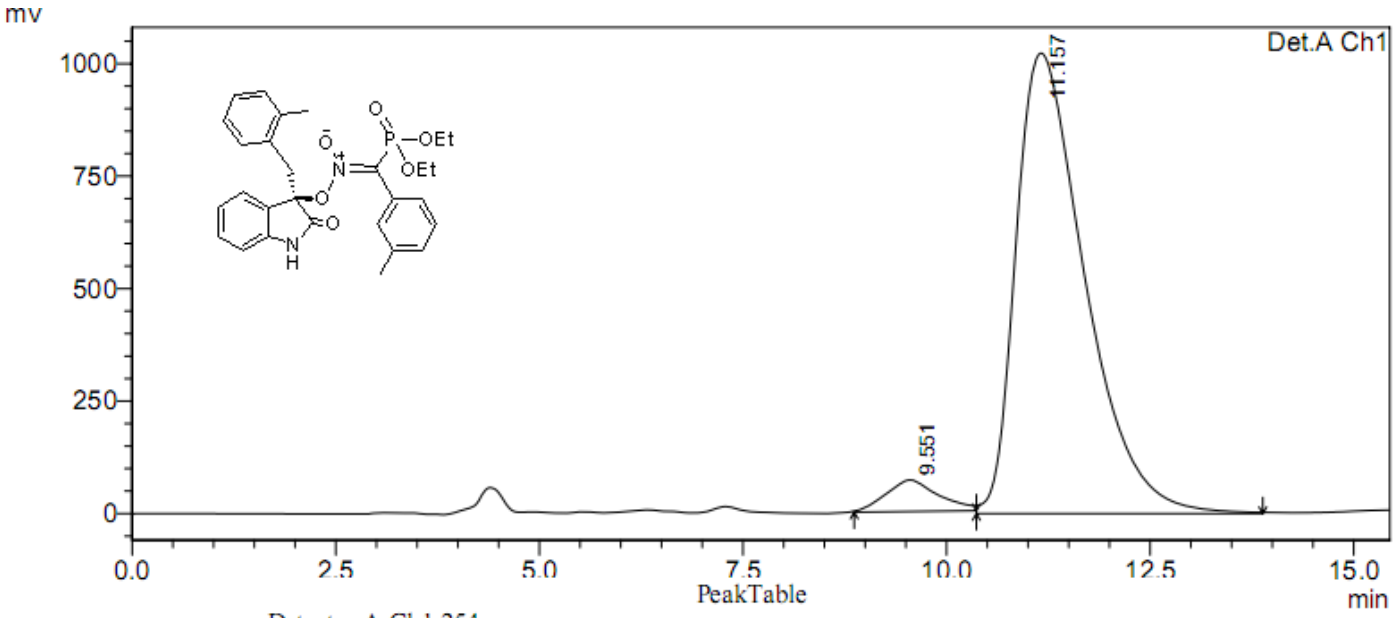
Peak#	Ret. Time	Area	Height	Area %
1	8.537	50917541	2088605	90.912
2	20.807	5090123	102368	9.088
Total		56007665	2190974	100.000

4x



1 Det.A Ch1/254nm Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.926	31266190	552728	49.835
2	11.287	31473480	554815	50.165
Total		62739670	1107543	100.000



1 Det.A Ch1/254nm Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.551	3136141	70050	4.944
2	11.157	60298846	1023590	95.056
Total		63434987	1093640	100.000