Supporting Information

Cascade heteroarylation/annulation of arylphosphonic acid monoesters with benzothiophenes: access to benzothieno-fused oxaphosphacycles

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General Information. $[RuCl_2(p\text{-cymene})]_2$ (>97%), $RuCl_3{\bullet}3H_2O$ (>98%), $[IrCp^*Cl_2]_2$ (96%), $Pd(OAc)_2$ (98%), $Cu(OAc)_2{\cdot}H_2O$ (>98%), AgOAc (≥99.99%), Ag_2CO_3 (98%), Ag_2O (99%), $Cu(OAc)_2$ (98%), $K_2S_2O_8$ (≥99.0%), $AgSbF_6$ (>98%), 1,1,1,3,3,3-hexafluoro-2-propanol, 2,2,2-trifluoroethanol, 2-methyltetrahydrofuran, diphenylphosphinic acid **1j**, benzothiophenes **2a-d**, **2f-g** and **2i**, 2,3-benzofuran **2A** and 1-methyl-1*H*-indole **2B** of Aldrich and TCI Chemicals were used as received, whereas $[Ru(O_2CAd)_2(p\text{-cymene})]$ was prepared according to literature.[1a] Methanol, 1,4-dioxane, 1,2-dichloroethane, toluene and dimethylformamide (DMF) were dried prior to use as per the standard procedure. Merck silica gel G/GF254 plates were used for analytical thin-layer chromatography (TLC). Column chromatography was carried out using Rankem silica gel (60-120 mesh). Bruker Avance III 400, 500 and 600 MHz NMR spectrometers were used to record spectra using $CDCl_3$ as the solvent and tetramethylsilane (Me_4Si) as an internal standard. Chemical shifts (δ) and spin-spin coupling constant (*J*) are reported in parts per million and hertz (Hz), respectively, and to describe peak patterns following abbreviations were used when appropriate: s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet. Melting points were determined using a Büchi B-540 apparatus and are uncorrected. FT-IR spectra were recorded on a PerkinElmer FT-IR spectrometer. Quadrupole time-of-flight electrospray ionization (ESI) mass spectrometer (Agilent 6546) was used for recording HRMS. Single crystal X-ray data was collected on a Bruker SMART APEX equipped with a CCD area detector using Mo/Kα radiation and the structure was solved by direct method using SHELXL-2018/3 (Göttingen, Germany). HPLC analysis was performed on Waters-2489 system with spherisorb ODS2 column using iso-propanol and hexane as an eluent.

Scheme S1: Tandem C-H Heteroarylation and Annulation

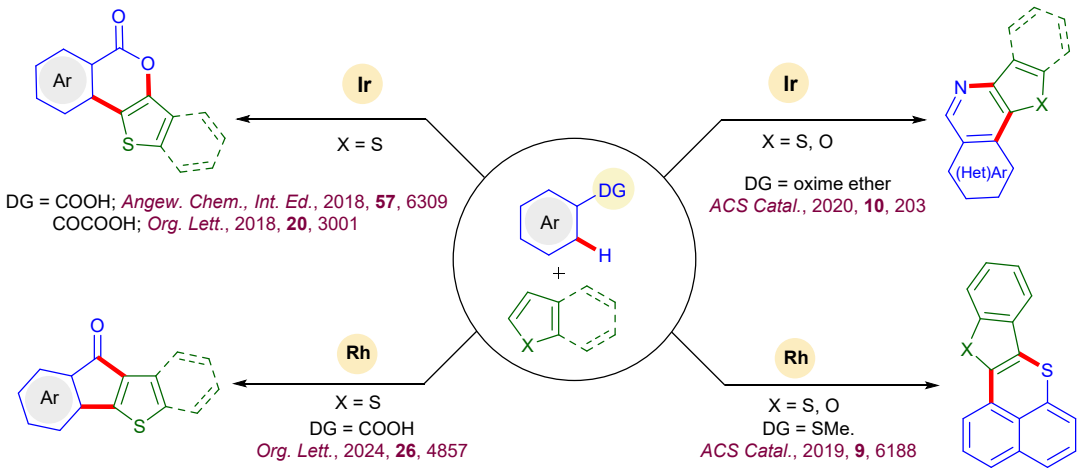
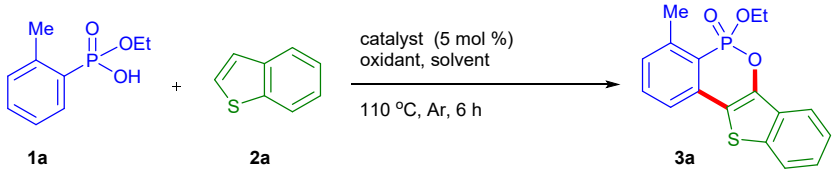


Table S1. Optimization of the Reaction Conditions[a]



1a 2a 3a

entry	catalyst	oxidant	solvent	yield[b] (%)
1	$[RuCl_2(p\text{-cymene})]_2$	AgOAc	HFIP	21
2	$[RuCl_2(p\text{-cymene})]_2$	Ag_2CO_3	HFIP	66
3	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	HFIP	86
4	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2$	HFIP	n.d.
5	$[RuCl_2(p\text{-cymene})]_2$	$K_2S_2O_8$	HFIP	n.d.
6	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	TFE	52
7	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	MeOH	trace
8	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	H_2O	n.d.
9	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	2-methyltetrahydrofuran	n.d.
10	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	1,4-dioxane	n.d.
11	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	$(CH_2Cl)_2$	trace
12	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	toluene	n.d.
13	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	DMF	n.d.
14	$[RuCl_2(p\text{-cymene})]_2$/ $AgSbF_6$ (20 mol %)	Ag_2O	HFIP	43
15	$[Ru(O_2CAd)_2(p\text{-cymene})]$	Ag_2O	HFIP	79
16	$RuCl_3 \cdot 3H_2O$	Ag_2O	HFIP	n.d.
17	$[IrCp^*Cl_2]_2$	Ag_2O	HFIP	72
18[c]	$Pd(OAc)_2$	Ag_2O	HFIP	n.d.
19	---	Ag_2O	HFIP	n.d.
20	$[RuCl_2(p\text{-cymene})]_2$	---	HFIP	n.d.
21[d]	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	HFIP	43
22[e]	$[RuCl_2(p\text{-cymene})]_2$	Ag_2O	HFIP	61

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (5 mol %), oxidant (3 equiv), solvent (1.0 mL), 110 °C, 6 h, Ar, pressure tube. [b]Isolated yield. [c]Using 10 mol% $Pd(OAc)_2$ [d]Using 1 equiv Ag_2O. [e]Using 2 equiv Ag_2O. n.d. = not detected.

Reaction-Condition-Based Sensitivity Assessment

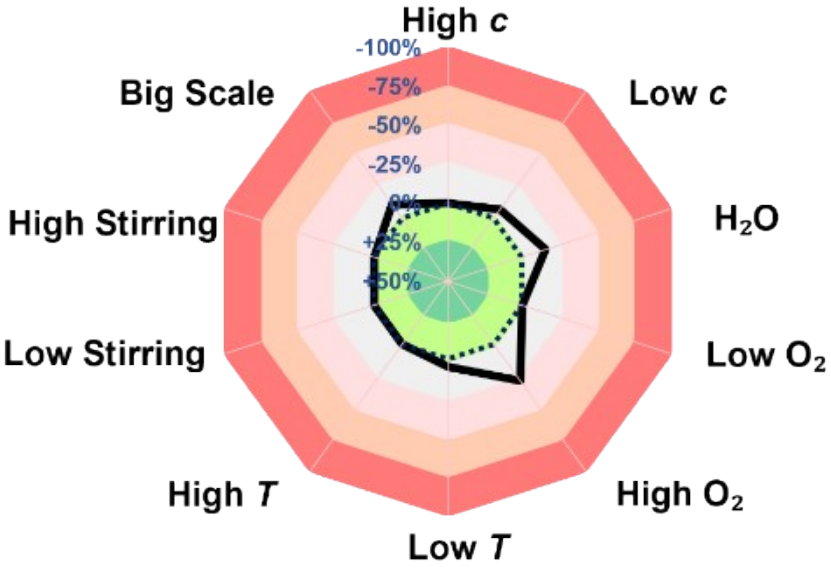
A reaction-condition-based sensitivity assessment,[1b-d] has been performed to examine the sensitivity of the reaction for synthesis of benzothieno-fused oxaphosphacycles. The standard reaction was performed under varied conditions: temperature, concentration, stirring rate, content of oxygen and water.

Standard reaction conditions: **1a** (20 mg, 0.1 mmol), **2a** (26.8 mg, 0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3 mg, 5 mol %, 0.005 mmol), Ag_2O (69.5 mg, 0.3 mmol, 3 equiv), HFIP (1 mL), 110 °C, 6 h, Ar, pressure tube. Thereafter, 10 reaction sets were prepared and stirred at indicated stir rate in a preheated oil bath with specified temperature for 6 h. Upon completion, the reaction mixtures were cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and passed through a short celite pad. The purification was performed as described in the general procedure to afford **3a**.

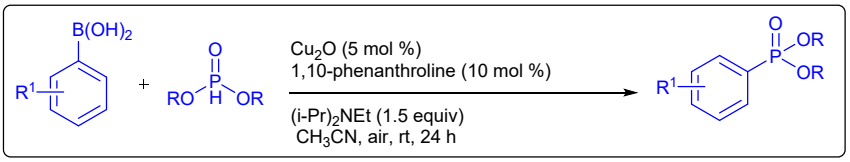
Preparation of Reaction Sets

entry	experiment	preparation	yield (%)	deviation (%)
0	standard	stand. cond.	86	-
1	high conc.	stand. cond., V (HFIP) = 0.5 mL	86	0
2	low conc.	stand. cond., V (HFIP) = 1.5 mL	80	-7
3	H_2O	stand. cond. + 3 μL H_2O	72	-16
4	low oxygen	stand. cond. + degassed then Ar	86	0
5	high oxygen	stand. cond. + purged with O_2 gas	61	-29
6	low temp.	stand. cond. + 100 °C	82	-5
7	high temp.	stand. cond. + 120 °C	86	0
8	low stirring	stand. cond. + stirring rate 500 r/min	86	0
9	high stirring	stand. cond. + stirring rate 1000 r/min	86	0
10	big scale	‘gram scale’ conditions	76	-11

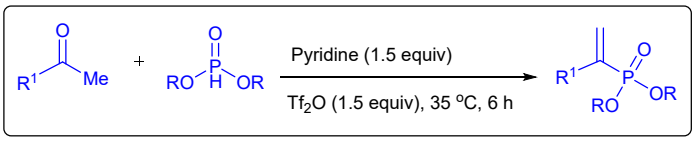
Radar Diagram:



General Procedure for the Preparation of Aryl/Vinyl Phosphonic Acid Monoesters 1a-l and 1A-E.

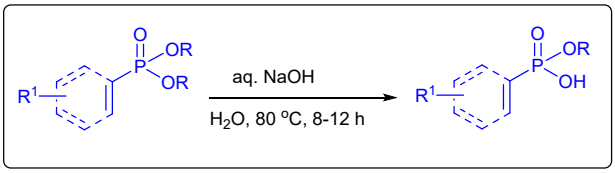


Step-1 **(For Aryl Phosphonates):**[2a] A mixture of arylboronic acid (4.0 mmol, 1 equiv), *H*-phosphonate diester (2 mmol, 0.5 equiv), 1,10-phenanthroline (36.0 mg, 0.2 mmol, 5 mol %) and Cu_2O (14.3 mg, 0.1 mmol, 2.5 mol %) was stirred in CH_3CN for 24 h under air. Upon completion (monitored by TLC), the reaction mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford dialkyl aryl phosphonates.



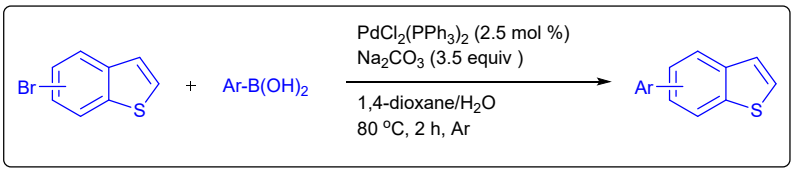
Step-1 **(For Vinyl Phosphonates):** [2e] To a stirred solution of ketone (0.4 mmol, 1 equiv) and *H*-phosphonate diester (0.8 mmol, 2 equiv), Tf_2O (0.6 mmol, 1.5 equiv, 101 μL) and pyridine (0.6 mmol, 1.5 equiv, 48 µL) were added. The mixture was stirred at 35 °C for 6 h. Upon

completion (monitored by TLC), ethyl acetate (20 mL) and saturated sodium bicarbonate (20 mL) were added. The solution was extracted with ethyl acetate (3 x 20 mL) and combined organic layer was washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate to afford dialkyl vinyl phosphonates.



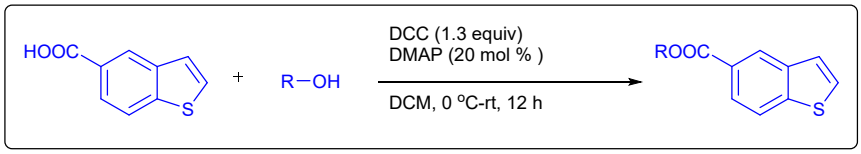
Step-2 **(Hydrolysis):** [2b] A mixture of dialkyl aryl/vinyl phosphonate (2.0 mmol, 1 equiv) and NaOH (160 mg, 4.0 mmol, 2 equiv) was stirred in water (10 mL) at 80 °C in a preheated oil bath for an appropriate time (8-12 h). Upon completion (monitored by TLC), the reaction mixture was allowed to cool to room temperature and neutralized with conc. HCl. The reaction mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using methanol and CH_2Cl_2 as an eluent to afford the products **1a-l** and **1A-E**.

Substrates **1c**, **1d**, **1g**, **1i**, **1k** and **1B-E** are new, whose characterization data are provided, whereas **1a-b**,[2b] **1e**,[2c] **1f**,[2d] **1h**,[2b] **1l**[2b] and **1A**[2c] are known, synthesized according to the reported procedure.



General Procedure for the Preparation of Substituted Benzothiophenes 2e and **2h (Suzuki Reaction).**[3a] A mixture of bromobenzothiophene (213 mg, 1 mmol, 1 equiv), Na_2CO_3 (371 mg, 3.5 mmol, 3.5 equiv), $PdCl_2(PPh_3)_2$ (17.5 mg, 2.5 mol %) and arylboronic acid (1.3 mmol, 1.3 equiv) was stirred in 1,4-dioxane:H_2O (1:1, v/v, 10 mL) under Ar atmosphere for 2 h at 80 °C. After completion, the reaction mixture was cooled to room temperature and added aqueous NH_4Cl solution (15 mL). The mixture was extracted with ethyl acetate (20 mL x 3) and washed with brine (2 x 20 mL) and water (1 x 20 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate/*n*-hexane as an eluent to provide substituted benzothiophenes **2e** and **2h**.

Substrate **2e**[3c] is known, synthesized according to the reported procedure, whereas **2h** is new, whose characterization data is provided.



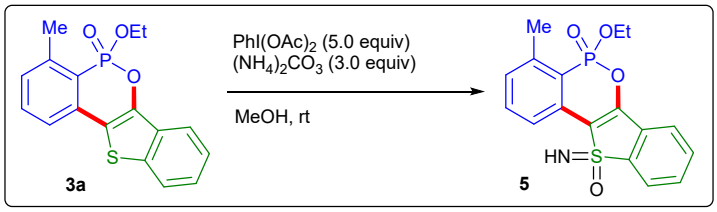
General Procedure for the Preparation of Substituted Benzothiophenes 2j-l .[3b] To a stirred solution of benzothiophene-5-carboxylic acid (196.02 mg, 1.1 mmol, 1.1 equiv) in CH_2Cl_2 (5 mL), alcohol (1 mmol, 1 equiv), DMAP (25 mg, 0.2 mmol, 20 mol %) and DCC (268 mg, 1.3 mmol, 1.3 equiv) were added sequentially at 0 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred for 12 h at the same temperature. Upon completion, as monitored by TLC, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and passed through a short pad of celite. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate and *n*-hexane as an eluent to give substituted benzothiophenes **2j-l**.

Substrates **2j-l** are new, whose characterization data are provided.

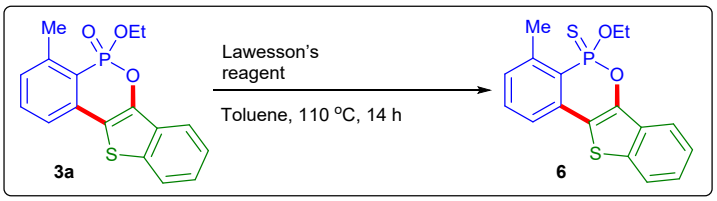
General Procedure for Ru(II)-Catalyzed Annulation of Aryl/Vinyl Phosphonic Acid Monoesters with Benzothiophenes. In an oven-dried pressure tube, a mixture of aryl/vinyl phosphonic acid monoester **1** (0.1 mmol), benzothiophene **2** (0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3 mg, 5 mol %, 0.005 mmol) and Ag_2O (69.5 mg, 0.3 mmol, 3 equiv) was stirred in HFIP (1.0 ml) at 110 °C in a preheated oil bath for 6 h under Ar atmosphere. The progress of the reaction was monitored by TLC utilizing ethyl acetate and hexane as an eluent. Upon completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and passed through a short celite pad. The filtrate was concentrated under reduced pressure and the residue was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent to afford **3**.

Scale-up Synthesis of 3a. In an oven-dried pressure tube, a mixture of ethyl hydrogen *o*-tolylphosphonate **1a** (5 mmol, 1.0 g), benzo[*b*]thiophene **2a** (10 mmol, 1.34 g), $[RuCl_2(p\text{-cymene})]_2$ (5 mol %, 0.25 mmol, 153 mg) and Ag_2O (3 equiv, 3.4 g) was stirred in HFIP (10.0 ml) at 110 °C in a preheated oil bath for 6 h under Ar atmosphere. The reaction mixture was cooled to room temperature and diluted with CH_2Cl_2 (20 mL) and passed through a celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent (70/30, v/v) to afford **3a** in 75% (1.24 g) yield.

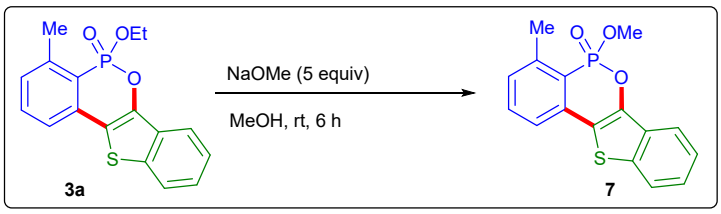
Procedures for the Post-Synthetic Modifications



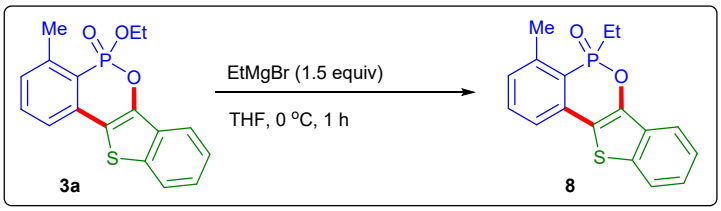
Synthesis of 5.[4a] Compound **3a** (33.0 mg, 0.1 mmol, 1 equiv), $PhI(OAc)_2$ (161.0 mg, 0.50 mmol, 5.0 equiv) and $(NH_4)_2CO_3$ (28.8 mg, 0.30 mmol, 3.0 equiv) were stirred in methanol (1 mL) at room temperature for overnight. After completion (monitored by TLC), the reaction mixture was diluted with ethyl acetate (10 mL) and passed through a short celite pad. Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate/*n*-hexane as the eluent (40/60, v/v) to provide **5** in 77% (27.8 mg) yield.



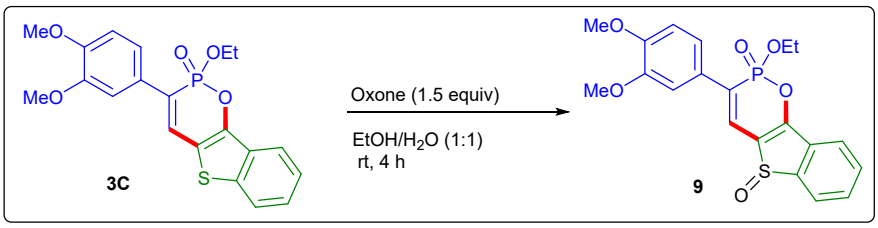
Synthesis of 6.[4b] Compound **3a** (33.0 mg, 0.1 mmol, 1 equiv) and Lawesson's reagent (81.0 mg, 0.2 mmol, 0.2 equiv) were stirred in toluene (1 mL) at 110 °C for 14 h under N_2 atmosphere. After completion (monitored by TLC), the reaction mixture diluted with ethyl acetate (10 mL) and passed through a short celite pad. Evaporation of solvent gave a residue that was purified on silica gel column chromatography using ethyl acetate/*n*-hexane as the eluent (10/90, v/v) to provide **6** in 82% (28.4 mg) yield.



Synthesis of 7.[5b] Compound **3a** (33.0 mg, 0.1 mmol, 1 equiv) and NaOMe (5 equiv, 27 mg) were stirred in MeOH (1 mL) at room temperature for 6 h. After completion (monitored by TLC), the reaction mixture was extracted with ethyl acetate (10 mL x 3) and washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using ethyl acetate/*n*-hexane (30/70, v/v) as an eluent to provide **7** in 86% (27.2 mg) yield.



Synthesis of 8.[4b] To a stirred solution of **3a** (33.0 mg, 0.1 mmol, 1 equiv) in THF (1 mL), EtMgBr (3 M in Et_2O, 50 μL, 0.15 mmol, 1.5 equiv) was added dropwise at 0 °C and continued the stirring at the same temperature for additional 1 h. After completion (monitored by TLC), saturated aqueous solution of NH_4Cl (10 mL) was added to the reaction mixture and extracted with ethyl acetate (10 mL x 3), washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using ethyl acetate/*n*-hexane (70/30, v/v) as an eluent to provide **8** in 84% (26.4 mg) yield.



Synthesis of 9.[5a] Compound **3C** (40.0 mg, 0.1 mmol, 1 equiv) and oxone (46.1 mg, 1.5 equiv, 0.15 mmol) were stirred in EtOH/H_2O (1 mL, 1:1, v/v) at room temperature for 4 h. After completion (monitored by TLC), the reaction mixture was filtered and the residue was washed with CH_2Cl_2/acetone (10 mL, 1:1, v/v), followed by CH_2Cl_2 (10 mL). Evaporation of the filtrate gave a residue that was purified by silica gel column chromatography using ethyl acetate/*n*-hexane as the eluent (70/30, v/v) to provide **9** in 73% (30.5 mg) yield.

Photophysical Experiment Details: Absorption and emission spectra of some synthesized compounds were recorded in CH_2Cl_2 (1.0 x 10^{-5} M) at ambient temperature. The absorption and emission wavelengths are listed in the following.

entry	compound	λ_{abs} (nm)	λ_{em} (nm)
1	**3i**	326	384
2	**3s**	343	397
3	**3h**	330, 346	420

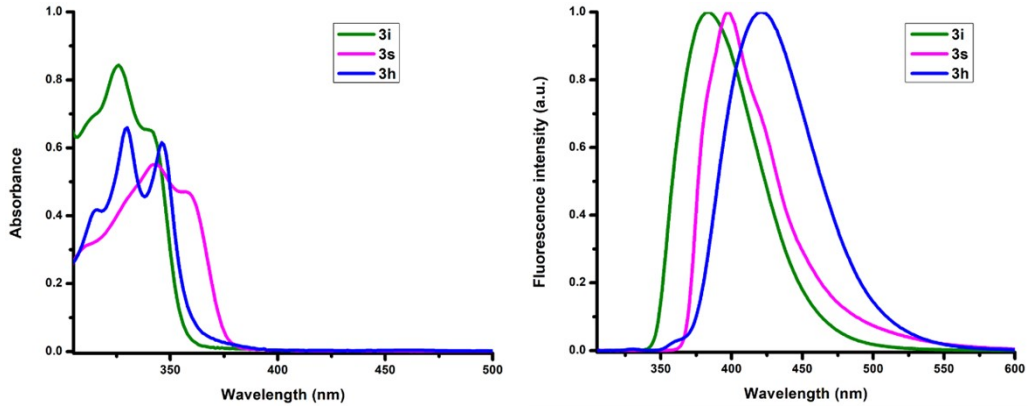


Figure S1: Absorption (left) and normalized emission (right) spectra of **3i**, **3s** and **3h** in CH_2Cl_2 (1.0×10^{-5} M)

under ambient light under UV light

Figure S2: Fluorescence behaviour

Sample Preparation for Crystal Growth. The compound **3m** was dissolved in minimum volume of acetonitrile and kept at room temperature for slow evaporation (3 days). The block shaped crystal was then subjected to X-ray diffraction.

Crystal Data and Structure Refinement for 3m

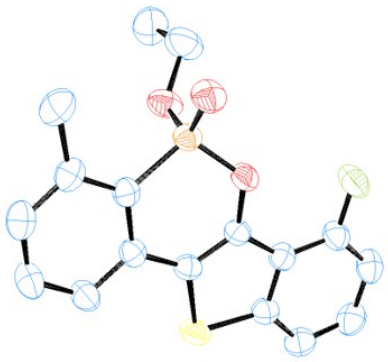
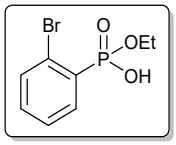


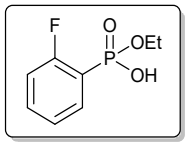
Figure S3. ORTEP diagram of **3m** with 50% ellipsoid (CCDC 2388928). H-Atoms are omitted for clarity.

Identification code	**3m**
Empirical formula	$C_{17}H_{14}FO_3PS$
Solvent for crystal growth	Acetonitrile
Formula weight	348.31
Crystal habit, colour	block and yellow
Temperature, *T*/K	301 K
Wavelength, λ/Å	0.71073
Crystal system	orthorhombic
Space group	'P 21 21 21'
Unit cell dimensions	a = 7.7392(9) Å b = 13.4287(15) Å c = 15.1509(17) Å α = 90 β = 90 γ = 90
Volume, *V*/Å^3	1574.6(3)
Z	4
Calculated density, g·cm^{-3}	1.469
Absorption coefficient, μ/mm^{-1}	0.329
F(000)	720
θ range for data collection	2.026 to 26.365°
Limiting indices	-9≤ h ≤ 9, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflection collected / unique	3220 / 3032
Completeness to θ	99.60% (θ = 26.36°)
Absorption correction	none
Refinement method	'SHELXL-2018/3 (Sheldrick, 2015) '
Data / restraints / parameters	3220/0/211
Goodness-of-fit on F^2	1.073
Final *R* indices [I >2sigma(I)]	R1 = 0.0348, wR2 = 0.0790
R indices (all data)	R1 = 0.0306, wR2 = 0.0740

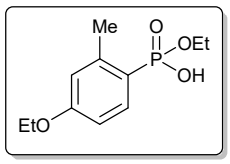
Characterization Data of Aryl Phosphonic Acid Monoesters



Ethyl hydrogen (2-bromophenyl)phosphonate 1c. Analytical TLC on silica gel, 1:2 methanol/ CH_2Cl_2 R_f = 0.52; brown liquid; yield 82% (434.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.96 (bs, 1H), 7.96-7.92 (m, 1H), 7.63-7.60 (m, 1H), 7.33-7.31 (m, 2H), 4.14-4.09 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.5 (d, *J* = 8.2 Hz), 134.2 (d, *J* = 11.4 Hz), 133.5, 130.7 (d, *J* = 198.6 Hz), 126.9 (d, *J* = 13.8 Hz), 125.3 (d, *J* = 4.2 Hz), 62.6 (d, *J* = 6.0 Hz), 16.2 (d, *J* = 6.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 15.8; FT-IR (neat) 3328, 2949, 2865, 1706, 1453, 1326, 1269, 1184, 1093, 1013, 968, 754 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_8H_{11}BrO_3P$: 264.9624, found 264.9621.

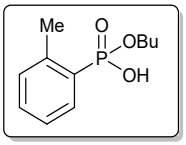


Ethyl hydrogen (2-fluorophenyl)phosphonate 1d. Analytical TLC on silica gel, 1:2 methanol/ CH_2Cl_2 R_f = 0.50; yellow liquid; yield 79% (322.5 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (bs, 1H), 7.81-7.76 (m, 1H), 7.52-7.49 (m, 1H), 7.18-7.16 (m, 1H), 7.11-7.07 (m, 1H), 4.15-4.11 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4 (d, *J* = 251.2 Hz), 134.7 (d, *J* = 8.2 Hz), 134.1 (q, *J* = 2.1 Hz), 124.1 (dd, *J* = 13.9 Hz, *J* = 3.3 Hz), 117.6 (d, *J* = 193.2 Hz), 116.1 (dd, *J* = 21.9 Hz, *J* = 7.8 Hz), 62.5 (d, *J* = 5.7 Hz), 16.2 (d, *J* = 6.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 14.34; ^{19}F NMR (565 MHz, $CDCl_3$) δ -103.82; FT-IR (neat) 2922, 2857, 1710, 1606, 1574, 1476, 1445, 1222, 1137, 1089, 1032, 993, 826, 763 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_8H_{11}FO_3P$: 205.0425, found 205.0422.

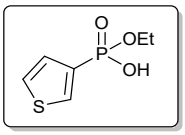


Ethyl hydrogen (4-ethoxy-2-methylphenyl)phosphonate 1g. Analytical TLC on silica gel, 1:2 methanol/ CH_2Cl_2 R_f = 0.52; brown solid; mp 82-83 °C; yield 81% (395.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.76 (m, 1H), 6.81 (bs, 1H), 6.74-6.73 (m, 1H), 6.70-6.67 (m, 1H), 4.05-4.00 (m, 4H), 2.53 (m, 3H), 1.40 (t, *J* = 7.5 Hz, 3H), 1.28 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (d, *J* = 3.1 Hz), 144.0 (d, *J* = 12.0 Hz), 135.5 (d, *J* = 12.0 Hz), 119.4 (d, *J* = 196.7 Hz), 117.6 (d, *J* = 16.0 Hz), 110.8 (d, *J* = 16.0 Hz), 63.5, 61.6 (d, *J* = 5.7 Hz), 21.5 (d, *J* = 3.5 Hz), 16.3 (d, *J* = 6.7 Hz), 14.8; ^{31}P NMR (202 MHz, $CDCl_3$) δ

22.52; FT-IR (KBr) 2980, 2929, 1737, 1598, 1483, 1304, 1200, 1086, 1040, 978 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{11}H_{18}O_4P$: 245.0938, found 245.0939.

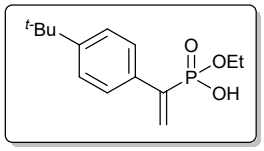


Butyl hydrogen *o*-tolylphosphonate 1i. Analytical TLC on silica gel, 1:2 methanol/ CH_2Cl_2 R_f = 0.82; brown liquid; yield 84% (383.4 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.88-7.84 (m, 1H), 7.56 (s, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.23-7.20 (m, 2H), 3.98-3.94 (m, 2H), 2.56 (s, 3H), 1.61-1.56 (m, 2H), 1.36-1.30 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.9 (d, *J* = 11.2 Hz), 133.4 (d, *J* = 10.2 Hz), 132.5, 131.2 (d, *J* = 15.3 Hz), 127.7 (d, *J* = 189.3 Hz), 125.4 (d, *J* = 15.1 Hz), 65.6 (d, *J* = 5.8 Hz), 32.4 (d, *J* = 6.6 Hz), 21.3 (d, *J* = 3.1 Hz), 18.8, 13.6; ^{31}P NMR (243 MHz, $CDCl_3$) δ 21.44; FT-IR (neat) 2958, 2875, 2314, 1665, 1457, 1193, 1149, 1024, 978, 755 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{11}H_{18}O_3P$: 229.0989, found 229.0981.



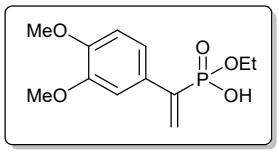
Ethyl hydrogen thiophen-3-ylphosphonate 1k. Analytical TLC on silica gel, 1:2 methanol/ CH_2Cl_2 R_f = 0.40; brown liquid; yield 75% (228.2 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.38-7.32 (m, 2H), 6.46 (bs, 1H), 4.05-4.01 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.9 (d, *J* = 18.7 Hz), 131.0 (d, *J* = 198.6 Hz), 129.1 (d, *J* = 17.5 Hz), 127.1 (d, *J* = 19.2 Hz), 62.2 (d, *J* = 5.1 Hz), 16.3 (d, *J* = 6.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 14.72; FT-IR (neat) 3100, 2983, 2249, 1657, 1502, 1407, 1213, 1162, 1099, 983, 719 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_6H_{10}O_3PS$: 193.0083, found 193.0081.

Characterization Data of Vinyl Phosphonic Acid Monoesters

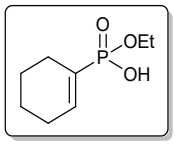


Ethyl hydrogen (1-(4-(*tert*-butyl)phenyl)vinyl)phosphonate 1B. Analytical TLC on silica gel, 1:2 methanol/ CH_2Cl_2 R_f = 0.80; yellow liquid; yield 70% (375.6 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 9.73 (bs, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 6.30 (d, *J* = 22.8 Hz, 1H), 6.14 (d, *J* = 46.2 Hz, 1H), 4.08-4.03 (m, 2H), 1.32 (s, 9H), 1.26

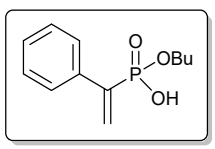
(t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.3, 140.2 (d, J = 178.8 Hz), 133.6 (d, J = 12.3 Hz), 130.4 (d, J = 8.1 Hz), 127.2 (d, J = 6.0 Hz), 125.4, 62.2 (d, J = 6.0 Hz), 34.6, 31.3, 16.3 (d, J = 6.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.48; FT-IR (neat) 2960, 2298, 1667, 1509, 1467, 1393, 1193, 1033, 983, 838, 775 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{14}H_{22}O_3P$: 269.1302, found 269.1296.



Ethyl hydrogen (1-(3,4-dimethoxyphenyl)vinyl)phosphonate 1C. Analytical TLC on silica gel, 1:2 methanol/ CH_2Cl_2 R_f = 0.70; brown liquid; yield 72% (392 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11-7.10 (m, 2H), 7.04 (bs, 1H), 6.82 (d, J = 9.0 Hz, 1H), 6.23 (d, J = 22.2 Hz, 1H), 6.08 (d, J = 46.8 Hz, 1H), 4.04-3.99 (m, 2H), 3.86 (s, 6H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.3, 148.7, 140.0 (d, J = 178.5 Hz), 129.6 (d, J = 8.2 Hz), 129.4 (d, J = 12.6 Hz), 120.3 (d, J = 6.3 Hz), 111.1, 110.8 (d, J = 5.1 Hz), 62.2 (d, J = 5.8 Hz), 55.9 (d, J = 3.0 Hz), 16.3 (d, J = 6.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.89; FT-IR (neat) 2939, 1598, 1512, 1456, 1325, 1253, 1214, 1143, 1024, 981, 810, 728 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{12}H_{18}O_5P$: 273.0887, found 273.0888.



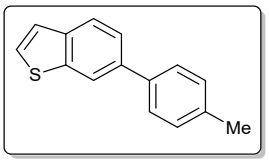
Ethyl hydrogen cyclohex-1-en-1-ylphosphonate 1D. Analytical TLC on silica gel, 1:2 methanol/ CH_2Cl_2 R_f = 0.62; yellow liquid; yield 68% (258.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, J = 22.8 Hz, 1H), 5.78 (s, 1H), 4.08-4.01 (m, 2H), 2.20-2.15 (m, 4H), 1.68-1.59 (m, 4H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.3 (d, J = 8.8 Hz), 128.6 (d, J = 185.2 Hz), 61.5 (d, J = 5.8 Hz), 26.0 (d, J = 18.3 Hz), 24.0 (d, J = 9.7 Hz), 22.0 (d, J = 10.5 Hz), 21.4, 16.4 (d, J = 6.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 22.39; FT-IR (neat) 3428, 2932, 1636, 1445, 1391, 1159, 1021, 956, 787 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_8H_{16}O_3P$: 191.0832, found 191.0830.



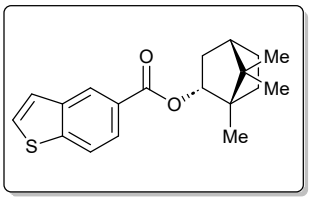
Butyl hydrogen (1-phenylvinyl)phosphonate 1E. Analytical TLC on silica gel, 1:3 methanol/ CH_2Cl_2 R_f = 0.82; brown liquid; yield 73% (350.7 mg); ^{1}H NMR (600 MHz,

$CDCl_3$) δ 10.42 (bs, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.35-7.30 (m, 3H), 6.33 (d, *J* = 22.2 Hz, 1H), 6.15 (d, *J* = 46.2 Hz, 1H), 3.99-3.96 (m, 2H), 1.59-1.54 (m, 2H), 1.31-1.26 (m, 2H), 0.85 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.5 (d, *J* = 179.5 Hz), 136.6 (d, *J* = 12.1 Hz), 131.0 (d, *J* = 7.8 Hz), 128.5, 128.3, 127.6 (d, *J* = 5.7 Hz), 66.0 (d, *J* = 6.1 Hz), 32.3 (d, *J* = 6.6 Hz), 18.7, 13.6; ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.70; FT-IR (neat) 2958, 2309, 1668, 1491, 1460, 1389, 1191, 977, 847, 776, 700 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{12}H_{18}O_3P$: 241.0989, found 241.0980.

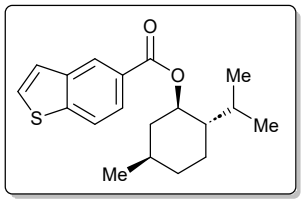
Characterization Data of Benzothiophenes



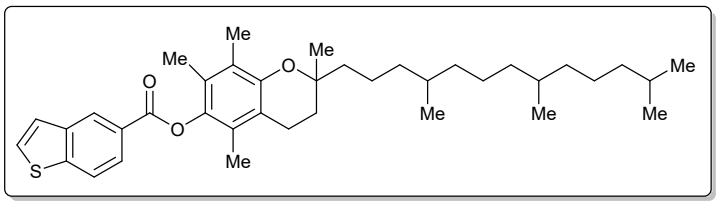
6-(*p*-Tolyl)benzo[*b*]thiophene 2h. Analytical TLC on silica gel, 1:20 ethyl acetate/hexane R_f = 0.70; colorless solid; yield 84% (188.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.10 (m, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.64-7.58 (m, 3H), 7.46 (d, *J* = 5.2 Hz, 1H), 7.38-7.36 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.6, 138.6, 138.3, 137.6, 137.1, 129.7, 127.3, 126.6, 123.9, 123.8, 123.7, 120.6, 21.2; FT-IR (KBr) 3022, 2916, 1907, 1758, 1598, 1454, 1381, 1299, 1046, 877, 806, 753 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{13}S$: 225.0733, found 225.0729.



(1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl benzo[*b*]-thiophene-5-carboxylate 2j. Analytical TLC on silica gel, 1:20 ethyl acetate/hexane R_f = 0.60; yellow liquid; yield 75% (235.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.538-8.536 (m, 1H), 8.03-8.01 (m, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 6.0 Hz, 1H), 7.45 (d, *J* = 6.0 Hz, 1H), 5.17-5.15 (m, 1H), 2.53-2.47 (m, 1H), 2.21-2.17 (m, 1H), 1.86-1.80 (m, 1H), 1.75 (t, *J* = 4.8 Hz, 1H), 1.47-1.41 (m, 1H), 1.36-1.32 (m, 1H), 1.17-1.14 (m, 1H), 0.98 (s, 3H), 0.94 (d, *J* = 4.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 139.5, 128.4, 127.7, 127.4, 125.5, 124.8, 124.6, 122.4, 80.7, 49.3, 48.0, 45.2, 37.1, 28.3, 27.6, 19.9, 19.1, 13.8; FT-IR (neat) 2952, 1712, 1601, 1455, 1375, 1326, 1270, 1187, 1094, 1017, 798, 757 cm^{-1}; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{19}H_{22}NaO_2S$: 337.1233, found 337.1226.

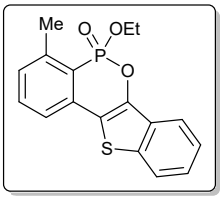


(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl benzo[*b*]thiophene-5-carboxylate 2k. Analytical TLC on silica gel, 1:20 ethyl acetate/hexane R_f = 0.60; yellow liquid; yield 78% (246.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.553-8.551 (m, 1H), 8.04-8.02 (m, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 5.4 Hz, 1H), 7.41 (d, *J* = 5.4 Hz, 1H), 5.03-4.98 (m, 1H), 2.19-2.16 (m, 1H), 2.04-1.99 (m, 1H), 1.75-1.70 (m, 2H), 1.61-1.53 (m, 2H), 1.17-1.11 (m, 2H), 0.97-0.92 (m, 7H), 0.83 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 143.9, 139.3, 127.5, 127.2, 125.4, 124.7, 124.4, 122.2, 74.8, 47.3, 41.1, 34.4, 31.5, 26.6, 23.7, 22.1, 20.8, 16.6; FT-IR (neat) 2927, 2277, 1705, 1581, 1424, 1192, 1145, 1033, 989, 757 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{25}O_2S$: 317.1570, found 317.1564.

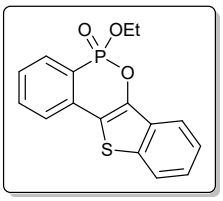


2,5,7,8-Tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl benzo[*b*]thiophene-5-carboxylate 2l. Analytical TLC on silica gel, 1:20 ethyl acetate/hexane R_f = 0.64; yellow liquid; yield 72% (425.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 5.4 Hz, 1H), 7.49 (d, *J* = 5.4 Hz, 1H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.17 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 1.89-1.77 (m, 2H), 1.68-1.62 (m, 2H), 1.60-1.52 (m, 2H), 1.46-1.41 (m, 2H), 1.37-1.24 (m, 12H), 1.19-1.07 (m, 6H), 0.91-0.88 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 149.6, 144.7, 140.8, 139.6, 127.9, 127.0, 126.2, 126.0, 125.29, 125.21, 124.5, 123.2, 122.6, 117.5, 75.1, 39.5, 37.59, 37.52, 37.4, 32.9, 28.1, 24.95, 24.93, 24.5, 24.3, 23.8, 22.8, 22.7, 21.1, 20.7, 19.89, 19.83, 19.78, 19.74, 13.2, 12.3, 12.0; FT-IR (neat) 2925, 2863, 1730, 1600, 1456, 1454, 1376, 1326, 1234, 1174, 1087, 918, 752 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{38}H_{55}O_3S$: 591.3867, found 591.3869.

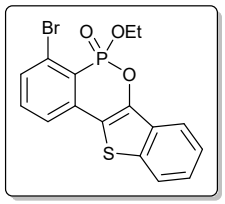
Characterization Data of the Products



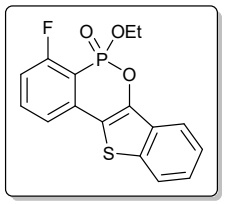
5-Ethoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3a. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.48; brown solid; mp 129-130 °C; yield 86% (28.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.87 (m, 1H), 7.81-7.77 (m, 1H), 7.57-7.53 (m, 1H), 7.47-7.37 (m, 3H), 7.29-7.27 (m, 1H), 4.35-4.20 (m, 2H), 2.78 (d, *J* = 1.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7 (d, *J* = 9.6 Hz), 141.0 (d, *J* = 7.8 Hz), 135.7, 135.3 (d, *J* = 7.6 Hz), 133.4, 131.4 (d, *J* = 6.3 Hz), 130.8 (d, *J* = 14.8 Hz), 126.6, 125.2, 123.0, 122.1 (d, *J* = 10.8 Hz), 121.0, 119.0 (d, *J* = 178.2 Hz), 117.9 (d, *J* = 13.6 Hz), 63.2 (d, *J* = 6.9 Hz), 21.6 (d, *J* = 4.3 Hz), 16.5 (d, *J* = 6.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.48; FT-IR (KBr) 3060, 2972, 2924, 1715, 1590, 1458, 1370, 1263, 1153, 1029, 960, 853, 759 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}O_3PS$: 331.0553, found 331.0556.



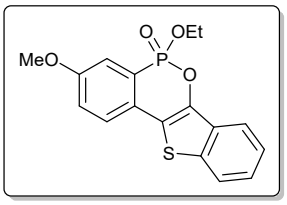
5-Ethoxybenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3b. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.40; brown solid; mp 98-99 °C; yield 72% (22.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99-7.96 (m, 1H), 7.90-7.87 (m, 1H), 7.80-7.79 (m, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.50-7.47 (m, 1H), 7.46-7.42 (m, 2H), 4.28-4.23 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.5 (d, *J* = 7.9 Hz), 135.7, 134.7 (d, *J* = 7.0 Hz), 133.8 (d, *J* = 2.4 Hz), 131.5 (d, *J* = 6.3 Hz), 130.7 (d, *J* = 9.1 Hz), 128.3 (d, *J* = 15.4 Hz), 126.8, 125.3, 124.3 (d, *J* = 10.8 Hz), 123.1, 121.0, 120.5 (d, *J* = 182.5 Hz), 117.9 (d, *J* = 13.8 Hz), 63.4 (d, *J* = 6.6 Hz), 16.5 (d, *J* = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 13.29; FT-IR (KBr) 3427, 2922, 2854, 1728, 1591, 1467, 1371, 1266, 1159, 1093, 1025, 961, 854, 757 cm^{-1}; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{16}H_{13}NaO_3PS$: 339.0216, found 339.0218.



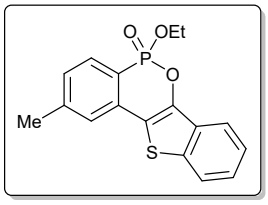
4-Bromo-5-ethoxybenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3c. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.47; brown solid; mp 135-136 °C yield 63% (24.9 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90-7.87 (m, 1H), 7.79-7.76 (m, 1H), 7.65-7.62 (m, 1H), 7.49-7.42 (m, 4H), 4.47-4.38 (m, 2H), 1.44 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.6 (d, *J* = 7.9 Hz), 137.3 (d, *J* = 6.1 Hz), 135.8, 134.2 (d, *J* = 1.8 Hz), 133.3 (d, *J* = 11.4 Hz), 131.2 (d, *J* = 6.6 Hz), 127.2, 125.7 (d, *J* = 3.3 Hz), 125.3, 123.4 (d, *J* = 10.0 Hz), 123.0, 121.7 (d, *J* = 187.2 Hz), 121.4, 116.4 (d, *J* = 13.2 Hz), 64.7 (d, *J* = 7.0 Hz), 16.5 (d, *J* = 4.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 8.37; FT-IR (KBr) 3424, 2921, 2860, 1723, 1583, 1450, 1371, 1266, 1194, 1156, 1104, 1033, 968, 852, 760 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{13}BrO_3PS$: 394. 9501, found 394. 9502.



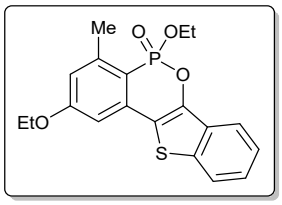
5-Ethoxy-4-fluorobenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3d. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.46; brown solid; mp 123-124 °C; yield 59% (19.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89-7.88 (m, 1H), 7.79-7.78 (m, 1H), 7.66-7.63 (m, 1H), 7.45-7.44 (m, 2H), 7.34-7.32 (m, 1H), 7.16-7.12 (m, 1H), 4.45-4.40 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.5 (d, *J* = 252.0 Hz), 141.9 (d, *J* = 7.5 Hz), 136.4 (d, *J* = 3.9 Hz), 135.8, 135.6 (d, *J* = 9.6 Hz), 131.2 (d, *J* = 6.7 Hz), 127.2, 125.4, 123.0, 121.3, 120.1 (dd, *J* = 10.0 Hz, *J* = 3.0 Hz), 116.3 (dd, *J* = 13.9 Hz, *J* = 3.3 Hz), 115.2 (dd, *J* = 22.0 Hz, *J* = 7.9 Hz), 109.0 (d, *J* = 181.0 Hz), 64.6 (d, *J* = 6.4 Hz), 16.5 (d, *J* = 6.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 7.10; ^{19}F NMR (565 MHz, $CDCl_3$) δ -103.09; FT-IR (KBr) 3403, 2919, 2853, 1732, 1601, 1539, 1463, 1371, 1263, 1174, 1114, 1028, 967, 859, 794 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{13}FO_3PS$: 335.0302, found 335.0299.



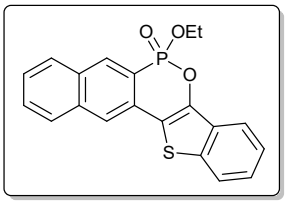
5-Ethoxy-3-methoxybenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3e. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.39; brown solid; mp 142-143 °C; yield 82% (28.4 mg,); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91-7.90 (m, 1H), 7.81- 7.80 (m, 1H), 7.64-7.61 (m, 1H), 7.49-7.45 (m, 1H), 7.44-7.40 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 1H), 4.25-4.20 (m, 2H), 4.06 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.1 (d, *J* = 15.9 Hz), 141.0 (d, *J* = 7.9 Hz), 137.7, 130.2 (d, *J* = 6.0 Hz), 129.0 (d, *J* = 18.1 Hz), 126.1, 124.7, 124.3 (d, *J* = 7.6 Hz), 122.7 (d, *J* = 8.2 Hz), 122.4, 121.5 (d, *J* = 180.7 Hz), 120.5, 115.7 (d, *J* = 2.8 Hz), 114.4 (d, *J* = 14.2 Hz), 63.3 (d, *J* = 6.6 Hz), 56.1, 16.5 (d, *J* = 6.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 13.14; FT-IR (KBr) 3463, 2924, 2854, 1727, 1600, 1490, 1371, 1270, 1083, 1028, 964, 853, 760 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}O_4PS$: 347.0502, found 347.0495.



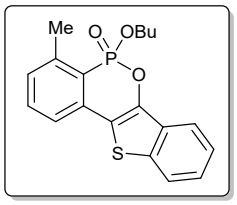
5-Ethoxy-2-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3f. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.48; brown solid; mp 140-141 °C; yield 75% (24.8 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88-7.84 (m, 2H), 7.80-7.79 (m, 1H), 7.46-7.41 (m, 2H), 7.34 (d, *J* = 5.4 Hz, 1H), 7.31-7.29 (s, 1H), 4.26-4.21 (m, 2H), 2.49 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7 (d, *J* = 2.4 Hz), 141.6 (d, *J* = 7.6 Hz), 135.6, 134.7 (d, *J* = 7.3 Hz), 131.6 (d, *J* = 6.1 Hz), 130.7 (d, *J* = 9.6 Hz), 129.2 (d, *J* = 15.9 Hz), 126.7, 125.2, 124.8 (d, *J* = 11.2 Hz), 123.1, 121.0, 117.9 (d, *J* = 13.5 Hz), 117.4 (d, *J* = 185.1 Hz), 63.2 (d, *J* = 6.6 Hz), 22.0, 16.5 (d, *J* = 6.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 14.10; FT-IR (KBr) 3452, 2920, 2854, 1734, 1602, 1460, 1372, 1265, 1161, 1093, 1030, 964, 854, 756 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}O_3PS$: 331.0553, found 331.0556.



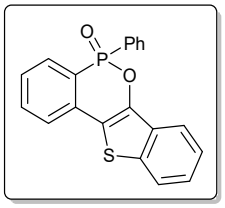
2,5-Diethoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3g. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.35; brown solid; mp 159-160 °C; yield 81% (30.3 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87-7.85 (m, 1H), 7.77-7.75 (m, 1H), 7.44-7.40 (m, 2H), 6.829-6.822 (m, 1H), 6.76 (s, 1H), 4.27-4.16 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.70 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.6 (d, *J* = 2.8 Hz), 145.0 (d, *J* = 10.9 Hz), 141.3 (d, *J* = 7.8 Hz), 137.3 (d, *J* = 9.1 Hz), 135.6, 131.4 (d, *J* = 6.4 Hz), 126.7, 125.2, 123.0, 121.0, 117.7 (d, *J* = 13.3 Hz), 117.1 (d, *J* = 15.6 Hz), 110.5 (d, *J* = 186.1 Hz), 107.6 (d, *J* = 11.8 Hz), 63.9, 63.1 (d, *J* = 7.0 Hz), 21.8 (d, *J* = 4.2 Hz), 16.4 (d, *J* = 6.3 Hz), 14.7; ^{31}P NMR (243 MHz, $CDCl_3$) δ 14.09; FT-IR (KBr) 3452, 2924, 2857, 1731, 1596, 1454, 1377, 1263, 1197, 1100, 1030, 959, 850, 761 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{20}O_4PS$: 375.0815, found 375.0817.



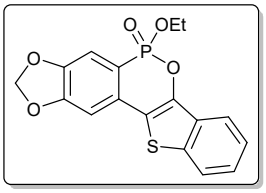
6-Ethoxybenzo[4,5]thieno[2,3-*e*]naphtho[2,3-*c*][1,2]oxaphosphinine 6-oxide 3h. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.46; brown solid; mp 209-210 °C; yield 73% (26.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 16.2 Hz, 1H), 7.97-7.93 (m, 3H), 7.89-7.88 (m, 1H), 7.82-7.81 (m, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.47-7.43 (m, 2H), 4.30-4.25 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.3 (d, *J* = 7.6 Hz), 135.7, 135.6 (d, *J* = 2.1 Hz), 133.1 (d, *J* = 9.4 Hz), 132.1 (d, *J* = 16.8 Hz), 131.8 (d, *J* = 6.3 Hz), 129.8 (d, *J* = 7.3 Hz), 129.5, 129.2, 128.2, 127.3, 126.8, 125.3, 123.1, 122.8 (d, *J* = 10.5 Hz), 120.9 (d, *J* = 7.6 Hz), 119.1 (d, *J* = 183.0 Hz), 118.7 (d, *J* = 12.3 Hz), 63.4 (d, *J* = 6.6 Hz), 16.5 (d, *J* = 6.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 13.13; FT-IR (KBr) 3454, 2921, 2857, 1731, 1594, 1460, 1372, 1274, 1098, 1028, 958, 863, 757 cm^{-1}; HRMS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{20}H_{15}NaO_3PS$: 389.0372, found 389.0374.



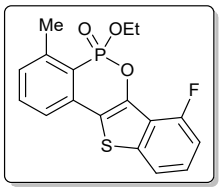
5-Butoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3i. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.80; yellow liquid; yield 84% (30.1 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 -7.87 (m, 1H), 7.79-7.78 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.46-7.41 (m, 2H), 7.39-7.37 (m, 1H), 7.28-7.27 (m, 1H), 4.24-4.15 (m, 2H), 2.77 (s, 3H), 1.69-1.64 (m, 2H), 1.37-1.31 (m, 2H), 0.85 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7 (d, *J* = 9.6 Hz), 141.0 (d, *J* = 7.9 Hz), 135.7, 135.3 (d, *J* = 7.6 Hz), 133.4, 131.4 (d, *J* = 6.3 Hz), 130.8 (d, *J* = 15.0 Hz), 126.6, 125.1, 123.0, 122.1 (d, *J* = 10.8 Hz), 121.0, 119.1 (d, *J* = 178.2 Hz), 117.9 (d, *J* = 13.8 Hz), 66.9 (d, *J* = 7.3 Hz), 32.5 (d, *J* = 6.1 Hz), 21.7 (d, *J* = 4.3 Hz), 18.7, 13.5; ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.48; FT-IR (neat) 3449, 2957, 2871, 1728, 1589, 1460, 1369, 1268, 1065, 1022, 852, 756 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{20}O_3PS$: 359.0866, found 359.0867.



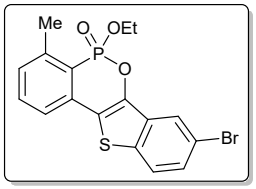
5-Phenylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3j. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.41; brown solid; mp 245-246 °C; yield 64% (22.3 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88-7.84 (m, 3H), 7.80-7.79 (m, 1H), 7.67-7.63 (m, 2H), 7.62-7.56 (m, 2H), 7.51-7.48 (m, 2H), 7.43-7.38 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.3 (d, *J* = 9.0 Hz), 135.9, 133.8 (d, *J* = 5.5 Hz), 133.5, 133.3, 132.1 (d, *J* = 11.2 Hz), 131.8 (d, *J* = 5.5 Hz), 131.6 (d, *J* = 12.1 Hz), 130.7 (d, *J* = 144.1 Hz), 128.8 (d, *J* = 14.1 Hz), 128.3 (d, *J* = 14.2 Hz), 126.8, 125.2, 124.0 (d, *J* = 8.5 Hz), 123.2 (d, *J* = 127.6 Hz), 123.0, 121.4, 117.6 (d, *J* = 12.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 28.70; FT-IR (KBr) 3425, 2922, 2855, 1727, 1591, 1461, 1372, 1241, 1124, 1092, 979, 839, 754 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{14}O_2PS$: 349.0447, found 349.0445.



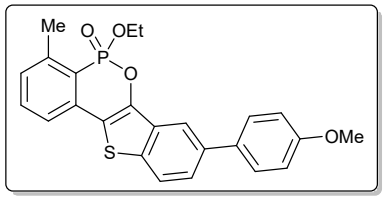
5-Ethoxy-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*]benzo[4,5]thieno-[2,3-*e*][1,2]oxaphosphinine 5-oxide 3l. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.36; colorless solid; mp 243-244 °C; yield 79% (28.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.58-7.54 (m, 1H), 7.47-7.42 (m, 2H), 6.95 (dd, *J* = 7.8 Hz, 3.0 Hz, 1H), 6.23 (d, *J* = 5.4 Hz, 2H), 4.25-4.20 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.9 (d, *J* = 3.3 Hz), 142.1 (d, *J* = 18.3 Hz), 141.8 (d, *J* = 7.8 Hz), 137.3, 130.5 (d, *J* = 6.0 Hz), 126.5, 126.4 (d, *J* = 10.3 Hz), 125.1, 122.9, 120.8, 117.2 (d, *J* = 9.4 Hz), 113.5 (d, *J* = 189.4 Hz), 113.2 (d, *J* = 13.3 Hz), 108.5 (d, *J* = 19.0 Hz), 102.6, 63.2 (d, *J* = 6.6 Hz), 16.5 (d, *J* = 5.8 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 13.09; FT-IR (KBr) 3490, 2983, 2917, 1764, 1624, 1453, 1372, 1260, 1120, 1028, 964, 909, 854, 758 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}O_5PS$: 361.0295, found 361.0296.



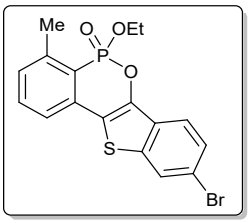
5-Ethoxy-7-fluoro-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3m. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.46; yellow solid; mp 160-161 °C; yield 68% (23.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.35-7.32 (m, 2H), 7.28-7.27 (m, 1H), 7.05 (t, *J* = 9.6, 1H), 4.34-4.29 (m, 2H), 2.75 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2 (d, *J* = 255.3 Hz), 142.7 (d, *J* = 9.4 Hz), 139.2 (dd, *J* = 7.8 Hz, 3.0 Hz), 137.7 (d, *J* = 4.8 Hz), 134.7 (d, *J* = 7.6 Hz), 133.4 (d, *J* = 2.1 Hz), 131.1 (d, *J* = 15.0 Hz), 127.4 (d, *J* = 7.0 Hz), 122.3 (d, *J* = 10.8 Hz), 120.5 (dd, *J* = 16.0 Hz, 5.8 Hz), 119.0 (d, *J* = 179.1 Hz), 118.9 (d, *J* = 4.2 Hz), 118.2 (d, *J* = 14.2 Hz), 111.3 (d, *J* = 18.4 Hz), 63.4 (d, *J* = 7.0 Hz), 21.6 (d, *J* = 4.2 Hz), 16.4 (d, *J* = 5.8 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.59; ^{19}F NMR (565 MHz, $CDCl_3$) δ -119.16; FT-IR (KBr) 3474, 2921, 2857, 1731, 1587, 1459, 1359, 1262, 1026, 959, 848, 779 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}FO_3PS$: 349.0459, found 349.0451.



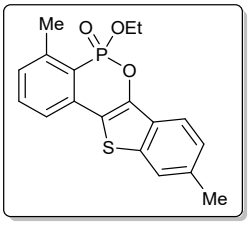
8-Bromo-5-ethoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3n. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.46; brown solid; mp 189-190 °C; yield 75% (30.7 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.54-7.48 (m, 2H), 7.35-7.33 (m, 1H), 7.28-7.27 (m, 1H), 4.34-4.22 (m, 2H), 2.75 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.8 (d, *J* = 9.6 Hz), 139.8 (d, *J* = 7.8 Hz), 134.7 (d, *J* = 7.6 Hz), 134.1, 133.5 (d, *J* = 2.1 Hz), 132.9 (d, *J* = 6.1 Hz), 131.2 (d, *J* = 15.0 Hz), 129.7, 124.4, 123.6, 122.2 (d, *J* = 10.8 Hz), 119.5 (d, *J* = 13.8 Hz), 119.3, 119.2 (d, *J* = 178.2 Hz), 63.4 (d, *J* = 7.0 Hz), 21.6 (d, *J* = 4.5 Hz), 16.5 (d, *J* = 6.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.10; FT-IR (KBr) 3442, 2923, 2853, 1731, 1588, 1455, 1346, 1262, 1066, 1026, 961, 851, 788 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}BrO_3PS$: 408.9658, found 408.9659.



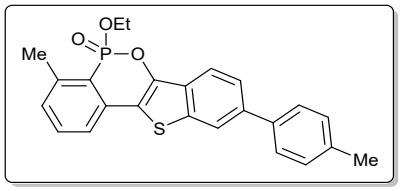
5-Ethoxy-8-(4-methoxyphenyl)-4-methylbenzo-[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3p. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.44; green liquid; yield 81% (35.3 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.63-7.61 (m, 3H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.27 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 2H), 4.33-4.20 (m, 2H), 3.87 (s, 3H), 2.77 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 142.7 (d, *J* = 9.6 Hz), 141.0 (d, *J* = 7.9 Hz), 138.3, 135.3 (d, *J* = 7.6 Hz), 134.0, 133.5 (d, *J* = 1.5 Hz), 133.0, 132.0 (d, *J* = 6.3 Hz), 130.8 (d, *J* = 15.0 Hz), 128.4, 125.9, 123.3, 122.1 (d, *J* = 10.8 Hz), 118.9 (d, *J* = 178.2 Hz), 118.5, 118.4 (d, *J* = 13.6 Hz), 114.5, 63.3 (d, *J* = 7.0 Hz), 55.5, 21.6 (d, *J* = 4.3 Hz), 16.5 (d, *J* = 6.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.55; FT-IR (neat) 3402, 2919, 2852, 1731, 1597, 1515, 1452, 1362, 1252, 1179, 1028, 963, 851, 795 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}O_4PS$: 437.0971, found 437.0969.



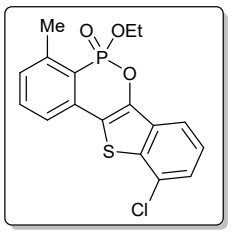
9-Bromo-5-ethoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3q. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.46; colorless solid; mp 155-156 °C; yield 73% (29.9 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.54-7.51 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.28-7.27 (m, 1H), 4.33-4.22 (m, 2H), 2.75 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H);^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7 (d, *J* = 9.6 Hz), 140.5 (d, *J* = 7.8 Hz), 136.8, 134.8 (d, *J* = 7.8 Hz), 133.5 (d, *J* = 1.9 Hz), 131.1 (d, *J* = 15.0 Hz), 130.1 (d, *J* = 6.3 Hz), 128.7, 125.6, 122.1 (d, *J* = 10.9 Hz), 121.9, 120.6, 118.7 (d, *J* = 178.8 Hz), 118.3 (d, *J* = 13.8 Hz), 63.4 (d, *J* = 7.0 Hz), 21.6 (d, *J* = 4.3 Hz), 16.4 (d, *J* = 6.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.40; FT-IR (KBr) 3471, 2921, 2857, 1734, 1586, 1456, 1367, 1265, 1075, 1026, 961, 852, 764 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}BrO_3PS$: 408.9658, found 408.9658.



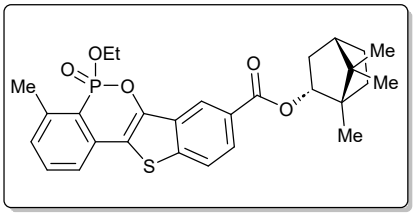
5-Ethoxy-4,9-dimethylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3r. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.47; pink solid; mp 189-190 °C; yield 82% (28.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.279-7.275 (m, 1H), 7.25-7.23 (m, 1H), 4.30-4.21 (m, 2H), 2.77 (s, 3H), 2.50 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.6 (d, *J* = 9.6 Hz), 141.0 (d, *J* = 8.1 Hz), 137.1, 136.0, 135.5 (d, *J* = 7.6 Hz), 133.4 (d, *J* = 2.2 Hz), 130.5 (d, *J* = 14.8 Hz), 129.2 (d, *J* = 6.4 Hz), 126.9, 122.9, 121.9 (d, *J* = 10.8 Hz), 120.6, 118.7 (d, *J* = 178.0 Hz), 116.7 (d, *J* = 13.8 Hz), 63.1 (d, *J* = 7.0 Hz), 21.9, 21.6 (d, *J* = 4.3 Hz), 16.4 (d, *J* = 6.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.60; FT-IR (KBr) 3474, 2922, 2857, 1734, 1589, 1537, 1457, 1369, 1266, 1028, 961, 838, 756 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{18}O_3PS$: 345.0709, found 345.0710.



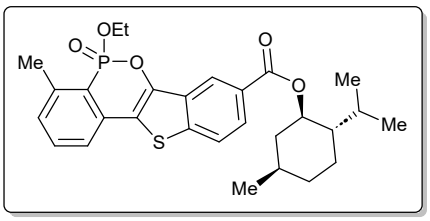
5-Ethoxy-4-methyl-9-(*p*-tolyl)benzo[*c*]benzo[4,5]-thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3s. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.45; brown solid; mp 195-196 °C; yield 79% (33.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.57-7.53 (m, 3H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.30-7.27 (m, 3H), 4.34-4.23 (m, 2H), 2.78 (s, 3H), 2.43 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7 (d, *J* = 9.6 Hz), 140.9 (d, *J* = 7.9 Hz), 140.0, 137.7 (d, *J* = 7.6 Hz), 136.4, 135.4 (d, *J* = 7.6 Hz), 133.4 (d, *J* = 2.2 Hz), 130.7 (d, *J* = 15.0 Hz), 130.2 (d, *J* = 6.4 Hz), 129.8, 127.3, 124.8, 122.1 (d, *J* = 10.8 Hz), 121.1 (d, *J* = 10.9 Hz), 118.9 (d, *J* = 178.2 Hz), 117.9 (d, *J* = 13.8 Hz), 63.2 (d, *J* = 7.0 Hz), 21.6 (d, *J* = 4.3 Hz), 21.2, 16.5 (d, *J* = 6.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.50; FT-IR (KBr) 3472, 2921, 2863, 1731, 1588, 1457, 1372, 1265, 1027, 961, 855, 807 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{24}H_{22}O_3PS$: 421.1022, found 421.1024.



10-Chloro-5-ethoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]-oxaphosphinine 5-oxide 3t. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.47; brown solid; mp 145-146 °C; yield 72% (26.3 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79-7.78 (m, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.42-7.38 (m, 3H), 7.29-7.27 (m, 1H), 4.32-4.21 (m, 2H), 2.76 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.8 (d, *J* = 9.6 Hz), 140.9 (d, *J* = 7.8 Hz), 134.8 (d, *J* = 7.6 Hz), 134.6, 133.5 (d, *J* = 2.1 Hz), 132.9 (d, *J* = 6.9 Hz), 131.2 (d, *J* = 15.0 Hz), 128.4, 126.5, 126.2, 122.2 (d, *J* = 10.8 Hz), 119.4, 119.27 (d, *J* = 13.8 Hz), 119.23 (d, *J* = 178.5 Hz), 63.3 (d, *J* = 7.0 Hz), 21.6 (d, *J* = 4.3 Hz), 16.4 (d, *J* = 6.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.20; FT-IR (KBr) 3465, 2922, 2857, 1734, 1591, 1460, 1372, 1267, 1028, 964, 854, 755 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{15}ClO_3PS$: 365.0163, found 365.0162.

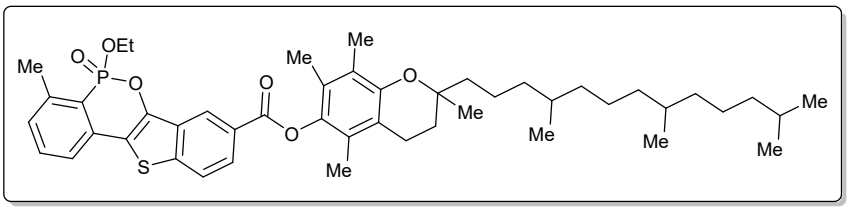


(1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 5-ethoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine-8-carboxylate 5-oxide 3w. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.58; colorless solid; mp 152-153 °C; yield 66% (33.7 mg); An inseparable mixture of diasteroisomers (dr = 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55-8.54 (m, 2H), 8.10 (s, 1H), 8.08 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 6.6 Hz, 2H), 7.30-7.28 (m, 2H), 5.19-5.17 (m, 2H), 4.37-4.25 (m, 4H), 2.77 (s, 6H), 2.54-2.48 (m, 2H), 2.21-2.15 (m, 2H), 1.88-1.81 (m, 2H), 1.77-1.76 (m, 2H), 1.49-1.44 (m, 2H), 1.40-1.34 (m, 8H), 1.19-1.16 (m, 2H), 0.99 (s, 6H), 0.96-0.95 (m, 6H), 0.94 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.66, 166.65, 142.8 (d, *J* = 9.6 Hz), 141.19 (d, *J* = 7.3 Hz), 141.18 (d, *J* = 7.8 Hz), 139.7, 139.6, 134.8 (d, *J* = 7.6 Hz), 133.56, 133.55, 131.3 (d, *J* = 6.4 Hz), 131.2 (d, *J* = 15.0 Hz), 128.3, 128.2, 127.1 (d, *J* = 3.6 Hz), 123.0, 122.58, 122.56, 122.1 (d, *J* = 10.8 Hz), 119.2 (d, *J* = 178.5 Hz), 119.1 (d, *J* = 178.5 Hz), 119.08 (d, *J* = 13.8 Hz), 119.06 (d, *J* = 13.8 Hz), 81.1, 63.5 (d, *J* = 6.9 Hz), 49.3 (d, *J* = 8.2 Hz), 48.1, 48.0, 45.12, 45.10, 37.0, 28.29, 28.27, 27.6 (d, *J* = 5.5 Hz), 21.6 (d, *J* = 4.3 Hz), 19.9, 19.0, 16.5 (d, *J* = 6.1 Hz), 13.85, 13.84; ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.31, 12.28; FT-IR (KBr) 3427, 2923, 2855, 1714, 1591, 1457, 1359, 1264, 1122, 1026, 964, 846, 755 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{32}O_5PS$: 511.1703, found 511.1697.

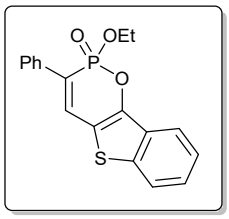


(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 5-ethoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine-8-carboxylate 5-oxide 3x. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.56; colorless solid; mp 160-161 °C; yield 61% (31.2 mg); An inseparable mixture of diasteroisomers (dr = 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (s, 1H), δ 8.55 (s, 1H), 8.10-8.07 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.30-7.28 (m, 2H), 5.04-4.96 (m, 2H), 4.38-4.22 (m, 4H), 2.77 (s, 6H), 2.17-2.14 (m, 2H), 2.04-1.96 (m, 2H), 1.79-1.74 (m, 4H), 1.67-1.61 (m, 4H), 1.36 (t, *J* = 7.2 Hz, 6H), 1.20-1.15 (m, 4H), 0.99-0.93 (m, 14H), 0.83-0.80 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.88, 165.86, 142.89 (d, *J* = 9.7 Hz), 142.86 (d, *J* = 9.6 Hz),

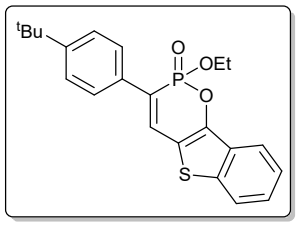
141.26 (d, *J* = 6.9 Hz), 141.21 (d, *J* = 6.6 Hz), 139.66, 139.65, 134.9 (d, *J* = 7.6 Hz), 133.56, 133.54, 131.35 (d, *J* = 6.1 Hz), 131.33 (d, *J* = 6.1 Hz), 131.2 (d, *J* = 15.0 Hz), 128.29, 128.25, 127.2 (d, *J* = 11.1 Hz), 122.9, 122.7 (d, *J* = 10.2 Hz), 122.2 (d, *J* = 10.8 Hz), 119.27 (d, *J* = 172.5 Hz), 119.23 (d, *J* = 171.9 Hz), 119.09 (d, *J* = 12.1 Hz), 119.06 (d, *J* = 13.9 Hz), 75.4, 75.3, 63.47 (d, *J* = 6.9 Hz), 63.45 (d, *J* = 6.9 Hz), 47.37, 47.33, 41.18, 41.12, 34.4, 31.67, 31.64, 29.8, 26.8, 26.4, 23.9, 23.5, 22.2 (d, *J* = 3.9 Hz), 21.6 (d, *J* = 4.2 Hz), 21.0, 20.8, 16.8, 16.5 (d, *J* = 5.2 Hz), 16.4 (d, *J* = 6.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.37, 12.23; FT-IR (KBr) 3430, 2923, 2855, 1716, 1591, 1459, 1371, 1266, 1122, 1032, 844, 755 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{28}H_{34}O_5PS$: 513.1860, found 513.1844.



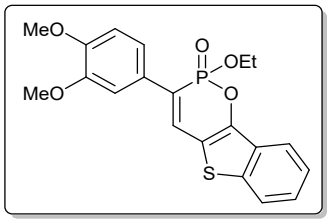
2,5,7,8-Tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 5-ethoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine-8-carboxylate 5-oxide 3y. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.60; yellow liquid; yield 59% (46.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 6.6 Hz, 1H), 7.31-7.29 (m, 1H), 4.39-4.27 (m, 2H), 2.77 (s, 3H), 2.64-2.62 (m, 2H), 2.13 (s, 3H), 2.09 (d, *J* = 9.0 Hz, 3H), 2.05 (d, *J* = 9.6 Hz, 3H), 1.88-1.78 (m, 2H), 1.53-1.50 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 5H), 1.28-1.25 (m, 14H), 1.15-1.04 (m, 6H), 0.87-0.84 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.0, 149.7, 142.8 (d, *J* = 9.1 Hz), 141.2 (d, *J* = 6.9 Hz), 140.8, 140.2, 134.8 (d, *J* = 7.2 Hz), 133.5, 131.6 (d, *J* = 7.5 Hz), 131.3 (d, *J* = 15.0 Hz), 127.5, 127.0, 125.2, 123.3, 123.2, 122.2 (d, *J* = 10.9 Hz), 119.4 (d, *J* = 178.2 Hz), 119.2 (d, *J* = 14.1 Hz), 117.7, 75.2, 63.5 (d, *J* = 6.3 Hz), 39.5, 37.6, 37.5, 37.4, 32.9, 32.8, 29.8, 28.1, 24.9, 24.6, 22.8 (d, *J* = 13.5 Hz), 21.6 (d, *J* = 3.9 Hz), 21.2, 20.8, 19.9, 19.8, 19.79, 19.76, 16.5 (d, *J* = 5.85 Hz), 13.2, 12.4, 12.0; ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.14; FT-IR (neat) 3432, 2923, 2858, 1732, 1591, 1456, 1372, 1222, 1084, 1028, 962, 849, 753 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{47}H_{64}O_6PS$: 787.4156, found 787.4153.



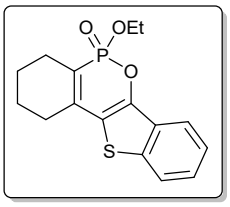
2-Ethoxy-3-phenylbenzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 2-oxide 3A. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.60; brown sticky liquid; yield 63% (21.5 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 37.8 Hz, 1H), 7.46-7.42 (m, 4H), 7.39-7.37 (m, 1H), 4.26-4.17 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.9 (d, *J* = 9.1 Hz), 137.6, 134.8 (d, *J* = 10.5 Hz), 132.6 (d, *J* = 5.1 Hz), 130.4 (d, *J* = 6.3 Hz), 129.1, 128.9, 127.4 (d, *J* = 7.0 Hz), 126.9, 125.3, 125.0 (d, *J* = 170.2 Hz), 123.2, 121.2, 116.1 (d, *J* = 19.6 Hz), 64.1 (d, *J* = 7.0 Hz), 16.4 (d, *J* = 6.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.65; FT-IR (neat) 3425, 3063, 2921, 2853, 1727, 1584, 1521, 1451, 1381, 1336, 1265, 1030, 967, 844, 759 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{16}O_3PS$: 343.0553, found 343.0552.



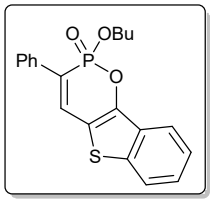
3-(4-(*tert*-Butyl)phenyl)-2-ethoxybenzo[4,5]thieno[2,3-*e*][1,2]-oxaphosphinine 2-oxide 3B. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.40; brown sticky liquid; yield 68% (27.1 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 31.8 Hz, 1H), 7.44-7.39 (m, 4H), 4.27-4.17 (m, 2H), 1.33 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.1, 143.6 (d, *J* = 9.3 Hz), 137.4, 131.8 (d, *J* = 5.4 Hz), 131.6, 130.3 (d, *J* = 6.3 Hz), 128.5, 126.9 (d, *J* = 7.2 Hz), 126.7, 126.0, 125.2, 124.7 (d, *J* = 169.6 Hz), 123.1, 121.0, 119.1, 116.2 (d, *J* = 19.5 Hz), 63.8 (d, *J* = 7.0 Hz), 34.7, 31.2, 16.4 (d, *J* = 6.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.94; FT-IR (neat) 3454, 2958, 2868, 1690, 1585, 1517, 1461, 1376, 1263, 1025, 968, 839, 757 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{22}H_{24}O_3PS$: 399.1179, found 399.1174.



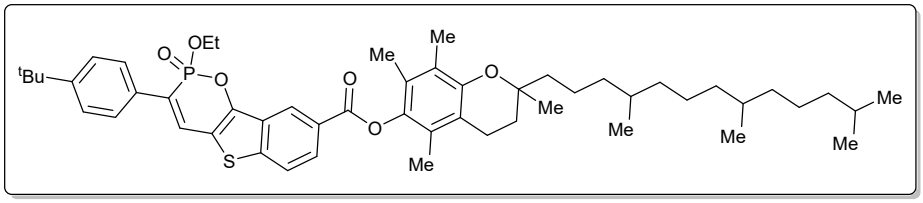
3-(3,4-Dimethoxyphenyl)-2-ethoxybenzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 2-oxide 3C. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.30; brown sticky liquid; yield 70% (28.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.44-7.38 (m, 3H), 7.34-7.32 (m, 1H), 7.27-7.26 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.24-4.14 (m, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.9, 149.3, 143.4 (d, *J* = 9.0 Hz), 137.3, 131.0 (d, *J* = 5.4 Hz), 130.3 (d, *J* = 6.3 Hz), 127.5 (d, *J* = 10.8 Hz), 126.7, 125.2, 124.7 (d, *J* = 169.3 Hz), 123.1, 121.0, 120.3 (d, *J* = 7.3 Hz), 116.1 (d, *J* = 19.3 Hz), 111.4, 110.2 (d, *J* = 7.3 Hz), 63.9 (d, *J* = 7.0 Hz), 56.1 (d, *J* = 9.9 Hz), 16.4 (d, *J* = 6.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.76; FT-IR (neat) 3467, 2925, 2850, 1719, 1590, 1515, 1459, 1378, 1259, 1155, 1026, 964, 851, 761 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}O_5PS$: 403.0764, found 403.0758.



5-Ethoxy-1,2,3,4-tetrahydrobenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 3D. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.56; yellow liquid; yield 52% (16.6 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.43-7.37 (m, 2H), 4.26-4.21 (m, 2H), 2.71-2.66 (m, 1H), 2.57 (s, 2H), 2.48-2.43 (m, 1H), 1.88-1.79 (m, 4H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.2 (d, *J* = 5.1 Hz), 141.4 (d, *J* = 8.1 Hz), 135.6, 130.9 (d, *J* = 6.6 Hz), 126.3, 125.1, 123.0, 120.9, 117.9 (d, *J* = 173.2 Hz), 63.2 (d, *J* = 6.9 Hz), 29.8, 28.3 (d, *J* = 13.5 Hz), 23.4 (d, *J* = 8.5 Hz), 21.7 (d, *J* = 10.5 Hz), 21.6, 16.6 (d, *J* = 5.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 15.82; FT-IR (neat) 3391, 2922, 2863, 1720, 1591, 1455, 1375, 1239, 1090, 1034, 958, 860, 756 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{18}O_3PS$: 321.0709, found 321.0697.

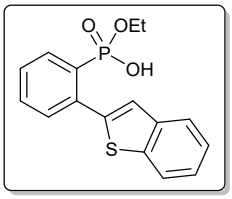


2-Butoxy-3-phenylbenzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 2-oxide 3E. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.84; brown solid; mp 145-146 °C; yield 72% (26.6 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91-7.89 (m, 1H), 7.78-7.70 (m, 1H), 7.74-7.73 (m, 2H), 7.52-7.45 (m, 2H), 7.44-7.42 (m, 3H), 7.39-7.37 (t, *J* = 7.3 Hz, 1H), 4.18-4.10 (m, 2H), 1.60-1.55 (m, 2H), 1.29-1.23 (m, 2H), 0.79 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.9 (d, *J* = 9.3 Hz), 137.6, 134.9 (d, *J* = 10.3 Hz), 132.5 (d, *J* = 4.9 Hz), 130.4 (d, *J* = 6.3 Hz), 129.1, 128.9, 127.4 (d, *J* = 7.0 Hz), 126.9, 125.3, 125.1 (d, *J* = 169.9 Hz), 123.2, 121.2, 116.1 (d, *J* = 19.5 Hz), 67.7 (d, *J* = 7.3 Hz), 32.4 (d, *J* = 6.0 Hz), 18.6, 13.5; ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.56; FT-IR (KBr) 3449, 2923, 2865, 1734, 1580, 1520, 1460, 1380, 1337, 1267, 1025, 986, 843, 758 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}O_3PS$: 371.0866, found 371.0862.

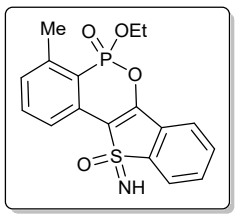


2,5,7,8-Tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 3-(4-(*tert*-butyl)phenyl)-2-ethoxybenzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine-8-carboxylate 2-oxide 3G. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.80; yellow liquid; yield 54% (46.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.26-8.25 (m, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.52-7.45 (m, 3H), 4.33-4.23 (m, 2H), 2.65-2.62 (m, 2H), 2.14 (s, 3H), 2.09 (d, *J* = 6.0 Hz, 3H), 2.05 (d, *J* = 6.6 Hz, 3H), 1.87-1.80 (m, 2H), 1.54-1.49 (m, 2H), 1.35 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 5H), 1.28-1.24 (m, 12H), 1.15-1.08 (m, 8H), 0.87-0.84 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 152.5, 149.7, 143.8 (d, *J* = 8.8 Hz), 141.8, 140.7, 131.6 (d, *J* = 169.6 Hz), 131.1 (d, *J* = 4.9 Hz), 127.5, 127.1, 127.07, 127.01 (d, *J* = 6.6 Hz), 126.1, 125.2 (d, *J* = 4.2 Hz), 125.0, 123.5, 123.4, 123.3 (d, *J* = 8.4 Hz), 117.7 (d, *J* = 6.7 Hz),117.6, 117.5 (d, *J* = 19.6 Hz), 75.2, 64.3 (d, *J* = 7.0 Hz), 39.5, 37.7, 37.6, 37.5, 37.4, 34.8, 32.9 (d, *J* = 1.9 Hz), 31.3, 31.1, 28.1, 24.9 (d, *J* = 1.9 Hz), 24.5, 24.3, 23.8, 22.8, 22.7, 21.2, 20.7, 19.9 (d, *J* = 9.7 Hz), 19.7 (d, *J* = 5.2 Hz), 16.4 (d, *J* = 6.1 Hz), 13.2, 12.4, 12.0; ^{31}P NMR (243 MHz, $CDCl_3$) δ

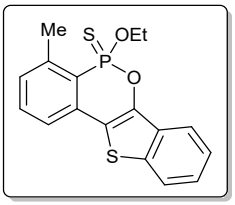
11.40; FT-IR (neat) 2927, 2863, 1733, 1458, 1371, 1326, 1269, 1224, 1090, 1029, 967, 837, 752 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{52}H_{72}O_6PS$: 855.4782, found 855.4753.



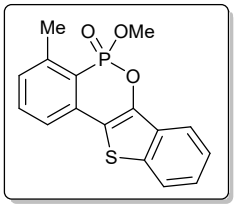
Ethyl hydrogen (2-(benzo[*b*]thiophen-2-yl)phenyl)phosphonate 3b′. Analytical TLC on silica gel, 1:2 methanol/ CH_2Cl_2 R_f = 0.70; colorless solid; yield 84% (534.0 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 8.87 (bs, 1H), 8.09-8.05 (m, 1H), 7.80 (dd, *J* = 25.8 Hz, 7.8 Hz, 2H), 7.58-7.55 (m, 3H), 7.45-7.42 (m, 1H), 7.34-7.30 (m, 2H), 3.81-3.77 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.5 (d, *J* = 4.6 Hz), 140.4, 140.1, 138.2 (d, *J* = 8.8 Hz), 134.1 (d, *J* = 9.6 Hz), 132.4 (d, *J* = 13.5 Hz), 132.0 (d, *J* = 2.4 Hz), 128.9 (d, *J* = 192.3 Hz), 128.5 (d, *J* = 15.1 Hz), 128.0 (d, *J* = 14.5 Hz), 125.5, 124.4 (d, *J* = 6.6 Hz), 124.1, 121.9, 62.0 (d, *J* = 6.1 Hz), 15.9 (d, *J* = 6.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.86; FT-IR (KBr) 3386, 2920, 2857, 2323, 1732, 1591, 1460, 1378, 1196, 1041, 986, 758 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{16}O_3PS$: 319.0553, found 319.0545.



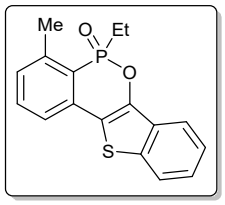
5-Ethoxy-11-imino-4-methyl-11*H*-11λ^4-benzo[*c*]benzo[4,5]thieno-[2,3-*e*][1,2]oxaphosphinine 5,11-dioxide 5. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.37; yellow solid; mp 192-193 °C; yield 77% (27.8 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.90-7.88 (m, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.67-7.61 (m, 3H), 7.37-7.35 (m, 1H), 4.36-4.26 (m, 2H), 3.48 (bs, 1H), 2.73 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.4 (d, *J* = 8.1 Hz), 143.1 (d, *J* = 9.3 Hz), 141.7, 133.8 (d, *J* = 2.1 Hz), 133.1, 131.9 (d, *J* = 15.1 Hz), 131.7, 130.0 (d, *J* = 29.7 Hz), 127.3 (d, *J* = 6.3 Hz), 121.4 (d, *J* = 10.8 Hz), 121.3, 120.5, 118.8 (d, *J* = 187.0 Hz), 118.7 (d, *J* = 4.8 Hz), 64.2 (d, *J* = 7.2 Hz), 21.6 (d, *J* = 4.5 Hz), 16.4 (d, *J* = 6.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.95; FT-IR (KBr) 3466, 3247, 2922, 2855, 1722, 1624, 1586, 1459, 1364, 1248, 1112, 1022, 965, 804 cm^{-1}. HPLC: spherisorb ODS2, hexane/^{i}PrOH = 95:5, flow rate: 1 mL/min, λ= 254 nm, t_R = 26.73 min; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{17}NO_4PS$: 362.0611, found 362.0610.



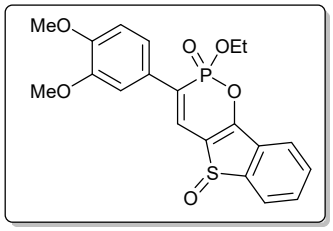
5-Ethoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-sulfide 6. Analytical TLC on silica gel, 1:10 ethyl acetate/hexane R_f = 0.48; yellow solid; mp 102-103 °C; yield 82% (28.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87-7.86 (m, 1H), 7.77-7.76 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.43-7.39 (m, 2H), 7.36-7.34 (m, 1H), 7.25-7.23 (m, 1H), 4.43-4.32 (m, 2H), 2.76 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.5 (d, *J* = 11.2 Hz), 140.4 (d, *J* = 9.7 Hz), 135.8, 133.2 (d, *J* = 7.3 Hz), 132.8 (d, *J* = 2.2 Hz), 131.6 (d, *J* = 13.9 Hz), 126.6, 125.1, 123.4 (d, *J* = 140.4 Hz), 123.0, 122.3, 122.2, 121.0, 118.0 (d, *J* = 14.2 Hz), 64.0 (d, *J* = 7.9 Hz), 21.9 (d, *J* = 4.9 Hz), 16.3 (d, *J* = 7.2 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 76.13; FT-IR (KBr) 3465, 2920, 2857, 1733, 1588, 1457, 1367, 1247, 1022, 961, 836, 754 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}O_2PS_2$: 347.0324, found 347.0324.



5-Methoxy-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 5-oxide 7. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.48; colorless solid; mp 125-126 °C; yield 86% (27.2 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90-7.88 (m, 1H), 7.78-7.77 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.46-7.41 (m, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.28-7.26 (m, 1H), 3.87 (d, *J* = 12.0 Hz, 3H), 2.76 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.8 (d, *J* = 9.7 Hz), 141.0 (d, *J* = 7.9 Hz), 135.7, 135.4 (d, *J* = 7.6 Hz), 133.5 (d, *J* = 2.2 Hz), 131.3 (d, *J* = 6.3 Hz), 130.8 (d, *J* = 15.0 Hz), 126.7, 125.2, 123.0, 122.2 (d, *J* = 10.9 Hz), 121.0, 118.5 (d, *J* = 177.9 Hz), 117.9 (d, *J* = 13.6 Hz), 53.2 (d, *J* = 6.9 Hz), 21.6 (d, *J* = 4.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 13.82; FT-IR (KBr) 3467, 2921, 2853, 1726, 1589, 1458, 1370, 1261, 1030, 858, 795, 732 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{14}O_3PS$: 317.0396, found 317.0393.



5-Ethyl-4-methylbenzo[*c*]benzo[4,5]thieno[2,3-*e*][1,2]oxaphosphi-nine 5-oxide 8. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.30; yellow liquid; yield 84% (26.4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87-7.86 (m, 1H), 7.76-7.75 (m, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.44-7.39 (m, 2H), 7.35-7.33 (m, 1H), 7.24-7.22 (m, 1H), 2.76 (s, 3H), 2.28-2.13 (m, 2H), 1.15-1.09 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.2 (d, *J* = 11.4 Hz), 140.9 (d, *J* = 8.7 Hz), 135.8, 134.4 (d, *J* = 5.8 Hz), 133.2 (d, *J* = 1.9 Hz), 131.5 (d, *J* = 5.2 Hz), 131.2 (d, *J* = 12.3 Hz), 126.6, 125.1, 123.0, 122.2 (d, *J* = 8.1 Hz), 121.1, 120.5 (d, *J* = 113.4 Hz), 117.8 (d, *J* = 12.1 Hz), 24.7 (d, *J* = 97.6 Hz), 21.6 (d, *J* = 3.9 Hz), 5.8 (d, *J* = 5.5 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 45.12; FT-IR (neat) 3446, 2922, 1715, 1587, 1456, 1368, 1218, 1108, 1067, 836, 753 cm^{-1}; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}O_2PS$: 315.0604, found 315.0602.



3-(3,4-Dimethoxyphenyl)-2-ethoxybenzo[4,5]thieno[2,3-*e*][1,2]oxaphosphinine 2,5-dioxide 9. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.30; yellow liquid; yield 73% (30.5 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.70-7.68 (m, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.61-7.58 (m, 1H), 7.53-7.45 (m, 1H), 7.38-7.34 (m, 1H), 7.23 (s, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.32-4.16 (m, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.0 (d, *J* = 9.4 Hz), 150.5, 149.5, 144.4, 132.9, 131.5 (d, *J* = 6.6 Hz), 131.1, 128.5 (d, *J* = 5.5 Hz), 128.4 (d, *J* = 4.9 Hz), 127.0, 126.7 (d, *J* = 11.1 Hz), 126.3 (d, *J* = 168.7 Hz), 123.3 (d, *J* = 19.8 Hz), 122.1, 120.7 (d, *J* = 7.2 Hz), 111.5, 110.0 (d, *J* = 8.1 Hz), 65.0 (d, *J* = 7.2 Hz), 56.2 (d, *J* = 17.1 Hz), 16.3 (d, *J* = 6.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.46; FT-IR (neat) 2922, 2855, 1718, 1591, 1514, 1458, 1374, 1264, 1162, 1027, 867, 762 cm^{-1}; HPLC: spherisorb ODS2, hexane/^{i}PrOH = 85:15, flow rate: 1 mL/min, λ= 254 nm, t_R = 7.75 min; HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{20}H_{20}O_6PS$: 419.0713, found 419.0699.

Mechanistic Investigations

H/D Exchange Experiment of 1b with D_2O in Absence of 2a. In an oven-dried pressure tube, a mixture of ethyl hydrogen phenylphosphonate **1b** (18.6 mg, 0.1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3 mg, 5 mol %, 0.005 mmol), Ag_2O (69.5 mg, 3 equiv, 0.3 mmol) and D_2O (1.0 mmol, 0.2 mL) was stirred in HFIP (1.0 ml) at 110 °C in a preheated oil bath for 6 h under Ar atmosphere. The resulting mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and passed through a short pad of celite. The purification was performed as described in the general procedure to give $[D_n]$-**1b**. No deuterium incorporation was observed at the *ortho*-position of aryl ring based on 600 MHz ^1H NMR spectrum.

H/D Exchange Experiment of 1b with D_2O in Presence of 2a. In an oven-dried pressure tube, a mixture of ethyl hydrogen phenylphosphonate **1b** (18.6 mg, 0.10 mmol), benzothiophene **2a** (0.20 mmol, 26.8 mg), $[RuCl_2(p\text{-cymene})]_2$ (3 mg, 5 mol %, 0.005 mmol), Ag_2O (69.5 mg, 3 equiv, 0.3 mmol) and D_2O (1.0 mmol, 0.2 mL) was stirred in HFIP (1.0 ml) at 110 °C in a preheated oil bath for 6 h under Ar atmosphere. The resulting mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and passed through a short pad of celite. The purification was performed as described in the general procedure to give $[D_n]$-**1b** and $[D_n]$-**3b**. The starting **1b** was analyzed using 600 MHz ^1H NMR and no deuterium incorporation was observed at the *ortho*-position of aryl ring.

Preparation of Ethyl hydrogen (phenyl-d_5)phosphonate $[D_5]$-**1b.**

Step-I:[6] To a stirred solution of sulfuric acid (0.6 mL) in water (2 mL), benzene-d_6 (0.3 mL, 3 mmol, 1 equiv) was added dropwise at 0 °C. Then, $NaBrO_3$ (497 mg, 3.3 mmol, 1.1 equiv) was added to the reaction mixture at the same temperature in two portions with an interval of 1 h and allowed to stir for 10 h at room temperature. After completion, ice water was added into the mixture and extracted using diethyl ether (3 x 20 mL). The combined organic layer was washed with brine (1 x 20 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was used for the next step without further purification (75% yield, 364 mg).

Step-II:[6] A solution of 1-bromobenzene-d_5 (0.2 mL, 2.0 mmol, 1 equiv) in THF (10 mL) under N_2 atmosphere was cooled to -78 °C. Thereafter, *n*-BuLi (1 mL, 2 M in cyclohexane, 2.0 mmol) was added dropwise over 30 min. The mixture was then stirred at the same temperature and

after 2 h triisopropyl borate (0.7 mL, 3.0 mmol, 1.5 equiv) dissolved in 1 mL of THF was added drop wise to the mixture. The solution was allowed to warm up to room temperature and stirred for 12 h. After completion (monitored by TLC), the reaction mixture was quenched with dilute HCl (20%, 4 mL) and stirred for 3 h at room temperature. The solution was extracted using diethyl ether (3 x 20 mL) and the combined organic layer was washed with brine (1 x 20 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue, which was treated with 10 mL *n*-hexane. The white solid (phenyl-d_5)boronic acid was precipitated, which was used for the next step without further purification (78% yield, 198 mg).

Step-III: [2a] A mixture of (phenyl-d_5)boronic acid (127 mg, 1.0 mmol, 1 equiv), diethyl phosphite (64 μL, 0.5 mmol, 0.5 equiv), 1,10-phenanthroline (9.0 mg, 0.05 mmol, 5 mol %) and Cu_2O (3.6 mg, 0.025 mmol, 2.5 mol %) was stirred in CH_3CN (10 mL) for 24 h under air. Upon completion, the reaction mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using *n*-hexane and ethyl acetate as an eluent (70/30, v/v) to afford diethyl (phenyl-d_5)phosphonate in 79% (173 mg) yield.

***Step-IV*:** [2b] A mixture of diethyl(phenyl-d_5)phosphonate (109.5 mg, 0.50 mmol, 1 equiv) and NaOH (40 mg, 1.0 mmol, 2 equiv) was stirred in water (10 mL) at 80 °C in a preheated oil bath for 12 h. Upon completion, (as monitored by TLC), the reaction mixture was allowed to cool to room temperature and neutralized with cooled conc. HCl (2 mL). The reaction mixture was then extracted using ethyl acetate (3 x 10 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave ethyl hydrogen (phenyl-d_5)phosphonate [D_5]-**1b** in 82% (78.3 mg) yield.

Kinetic Isotope Effect Experiment. In an oven-dried pressure tube, a mixture of ethyl hydrogen phenylphosphonate **1b** (0.1 mmol, 18.6 mg) and ethyl hydrogen (phenyl-d_5)phosphonate [D_5]-**1b** (0.1 mmol, 19.1 mg) was reacted with benzo[*b*]thiophene **2a** (0.40 mmol, 53.6 mg) for 0.5 h under standard reaction conditions. The resulting mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and passed through a short pad of celite. The purification was performed as described in the general procedure to afford a mixture of **3b** and [D_4]-**3b**. The intermolecular k_H/k_D was found to be 5.6, based on 600 MHz ^{1}H NMR of the product **3b** and [D_4]-**3b**.

Preparation of the Intermediate 3b′

Step-I: [3b] A mixture of diethyl (2-bromophenyl)phosphonate (586 mg, 2 mmol, 1 equiv), Na_2CO_3 (742 mg, 7.0 mmol, 3.5 equiv), $PdCl_2(PPh_3)_2$ (35 mg, 2.5 mol %) and benzothiophen-2-ylboronic acid (463 mg, 2.6 mmol, 1.3 equiv) was stirred in 1,4-dioxane : H_2O (1:1, v/v, 10 mL) under Ar atmosphere for 2 h at 80 °C. After completion, the reaction mixture was cooled to room temperature and added aqueous NH_4Cl solution (15 mL). The mixture was extracted using ethyl acetate (20 mL x 3), washed with brine (2 x 20 mL) and water (1 x 20 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography using ethyl acetate/*n*-hexane as an eluent (70/30, v/v) to provide diethyl (2-(benzo[*b*]thiophen-2-yl)phenyl)phosphonate in 73% (506 mg) yield.

Step-II: [2b] A mixture of diethyl (2-(benzo[*b*]thiophen-2-yl)phenyl)phosphonate (692 mg, 2.0 mmol, 1 equiv) and NaOH (80 mg, 4.0 mmol, 2 equiv) was stirred in water (10 mL) at 80 °C in a preheated oil bath for 12 h. Upon completion (as monitored by TLC), the reaction mixture was allowed to cool to room temperature and neutralized with conc. HCl (5 mL). The reaction mixture was extracted using ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine (2 x 10 mL) and water (1 x 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave ethyl hydrogen (2-(benzo[*b*]thiophen-2-yl)phenyl)phosphonate **3b′** in 84% (534 mg) yield.

Intramolecular Lactonization of 3b′.

i. In an oven-dried pressure tube, a mixture of **3b′** (31.8 mg, 0.1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3 mg, 5 mol %, 0.005 mmol) and Ag_2O (69.5 mg, 3 equiv, 0.3 mmol) was stirred in HFIP (1.0 ml) at 110 °C in a preheated oil bath for 6 h under Ar. The resulting mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and passed through a short pad of celite. The purification was performed as described in the general procedure to give **3b** in 68% (21.6 mg) yield.
ii. In an oven-dried pressure tube, a mixture of **3b′** (31.8 mg, 0.1 mmol) and Ag_2O (69.5 mg, 3 equiv, 0.3 mmol) was stirred in HFIP (1.0 ml) at 110 °C in a preheated oil bath for 6 h under Ar. The resulting mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and passed through a short pad of celite. The purification was performed as described in the general procedure to give **3b** in 52% (16.5 mg) yield.

iii. In an oven-dried pressure tube, **3b′** (31.8 mg, 0.1 mmol) was stirred in HFIP (1.0 ml) at 110 °C in a preheated oil bath for 6 h under Ar. The resulting mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and passed through a short pad of celite. No product was detected except for the recovery of **3b′**.

Radical Trapping Experiment. In an oven-dried pressure tube, a mixture of **3b′** (31.8 mg, 0.1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3 mg, 5 mol %, 0.005 mmol), Ag_2O (69.5 mg, 3 equiv, 0.3 mmol) and BHT (0.3 mmol, 66 mg) was stirred in HFIP (1.0 ml) at 110 °C in a preheated oil bath for 6 h under Ar. The resulting mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and passed through a short pad of celite. The formation of BHT adduct **4** was confirmed by high-resolution mass spectrometry (HRMS) analysis of crude reaction mixture. HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{31}H_{38}O_4PS$: 537.2223, found 537.2211.

Sample Name	TPS-568	**Position**	P1-A1	**Instrument Name**	QTOF
User Name	SYSTEM (SYSTEM)	**Inj Vol**	5	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	TPS-568.d
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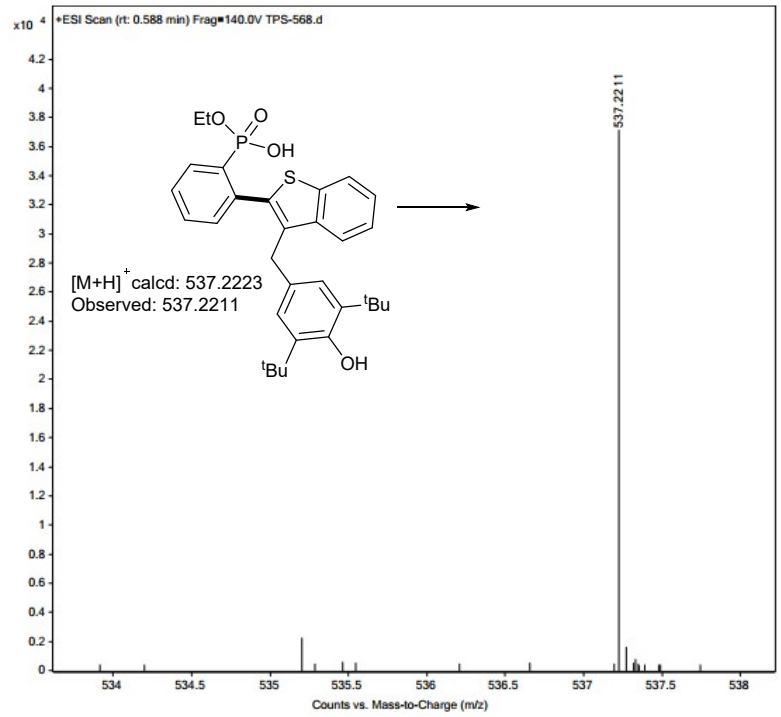

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5. (*a*) J. A. Ivie, N. D. Bamberger, K. N. Parida, S. Shepard, D. Dyer, A. Saraiva-Souza, R. Himmelhuber, D. V. McGrath, M. Smeu and O. L. A. Monti, *ACS Appl. Mater. Interfaces*, 2021, **13**, 4267; (*b*) X. Yuan, X. Ke and J. Xu, *Org. Lett.*, 2022, **24**, 9141.
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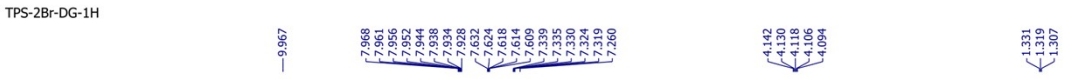
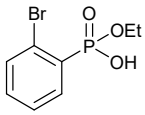
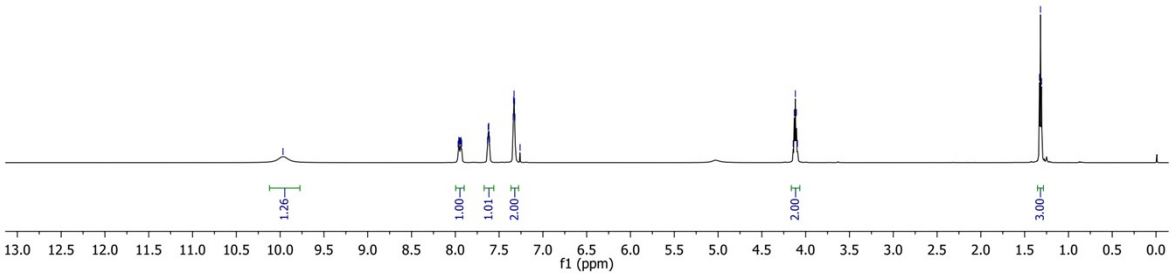
TPS-2Br-DG-1H





1c

^{1}H NMR (600 MHz, $CDCl_3$)



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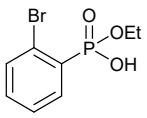

1c

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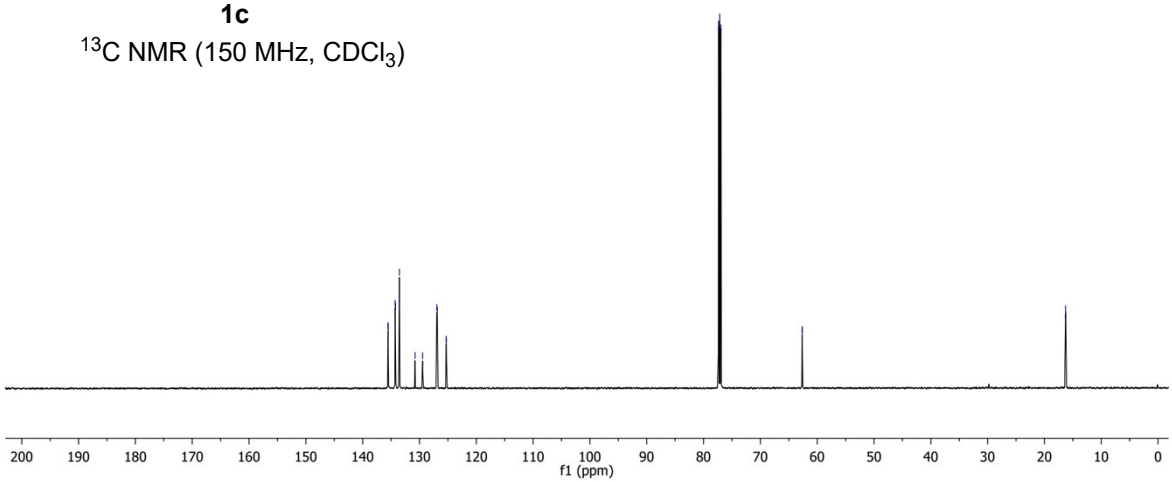

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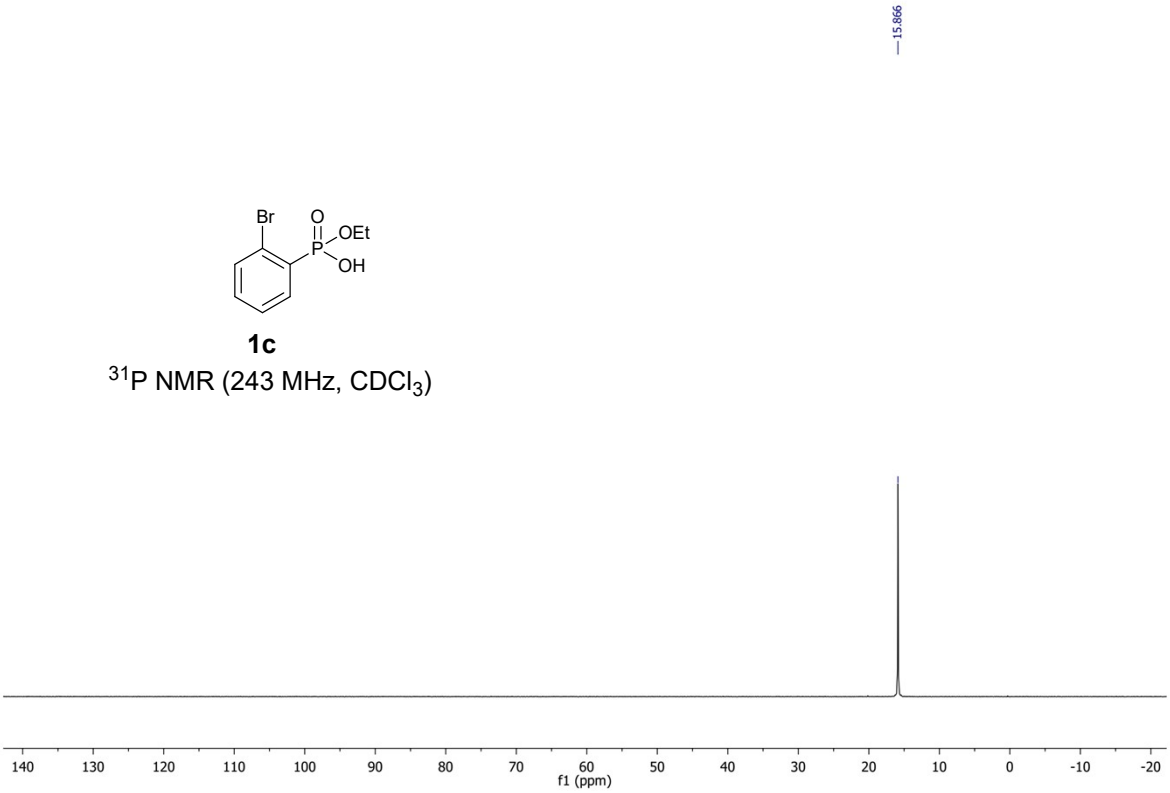
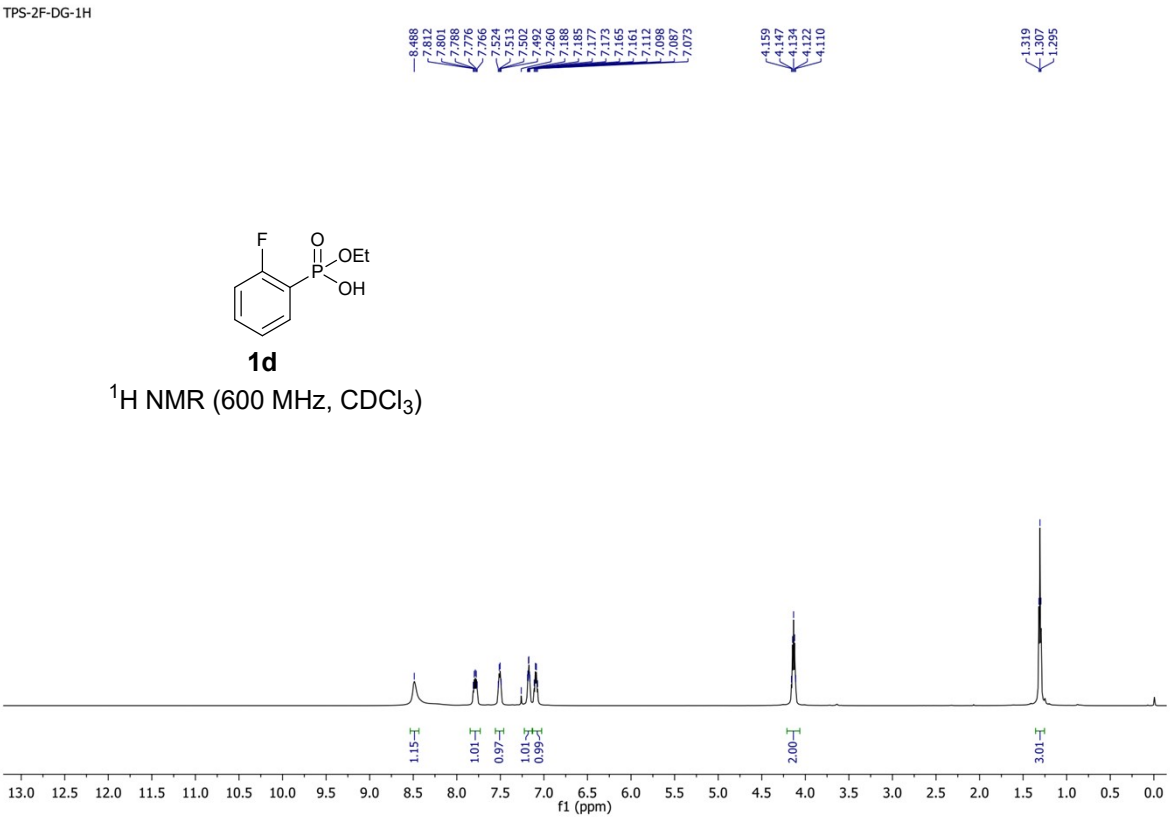


1c

^{31}P NMR (243 MHz, $CDCl_3$)

TPS-2F-DG-1H



1d

^{1}H NMR (600 MHz, $CDCl_3$)

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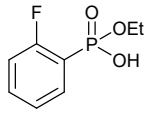
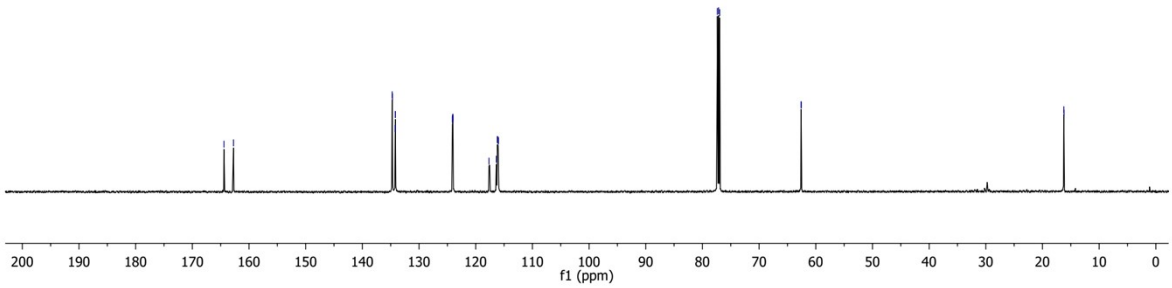


1d

^{13}C NMR (150 MHz, $CDCl_3$)



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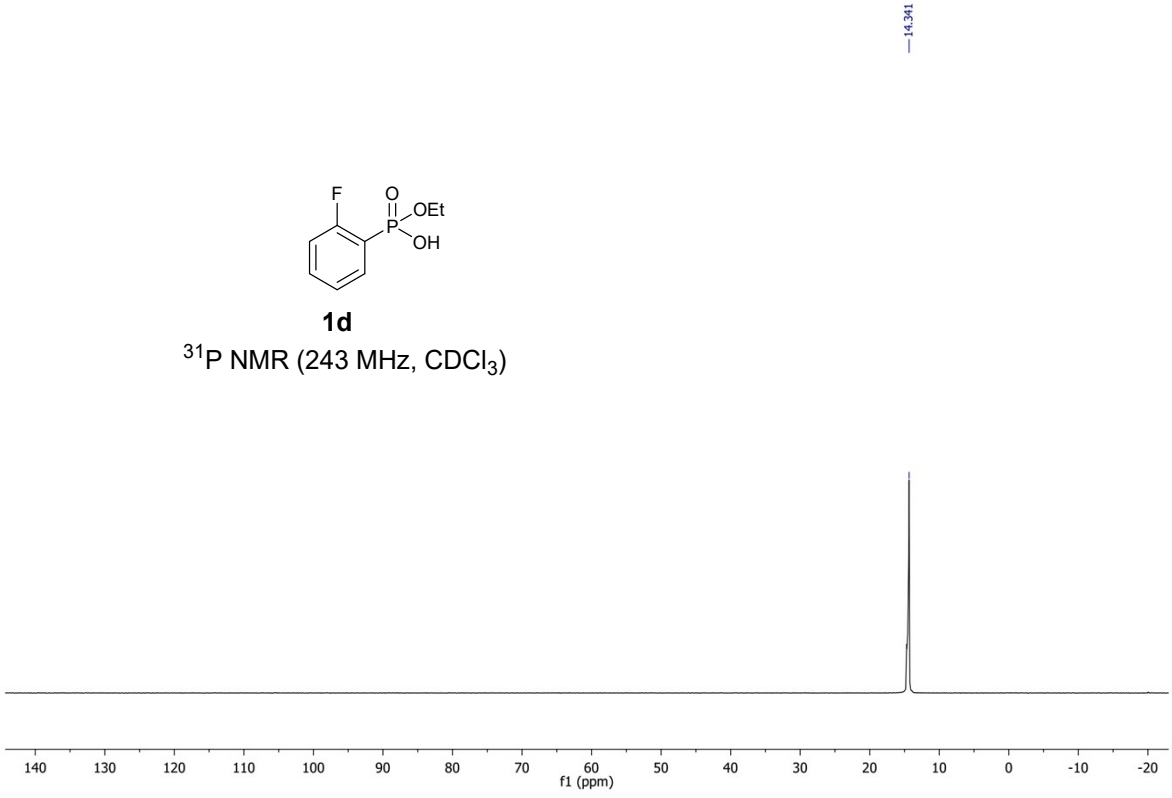
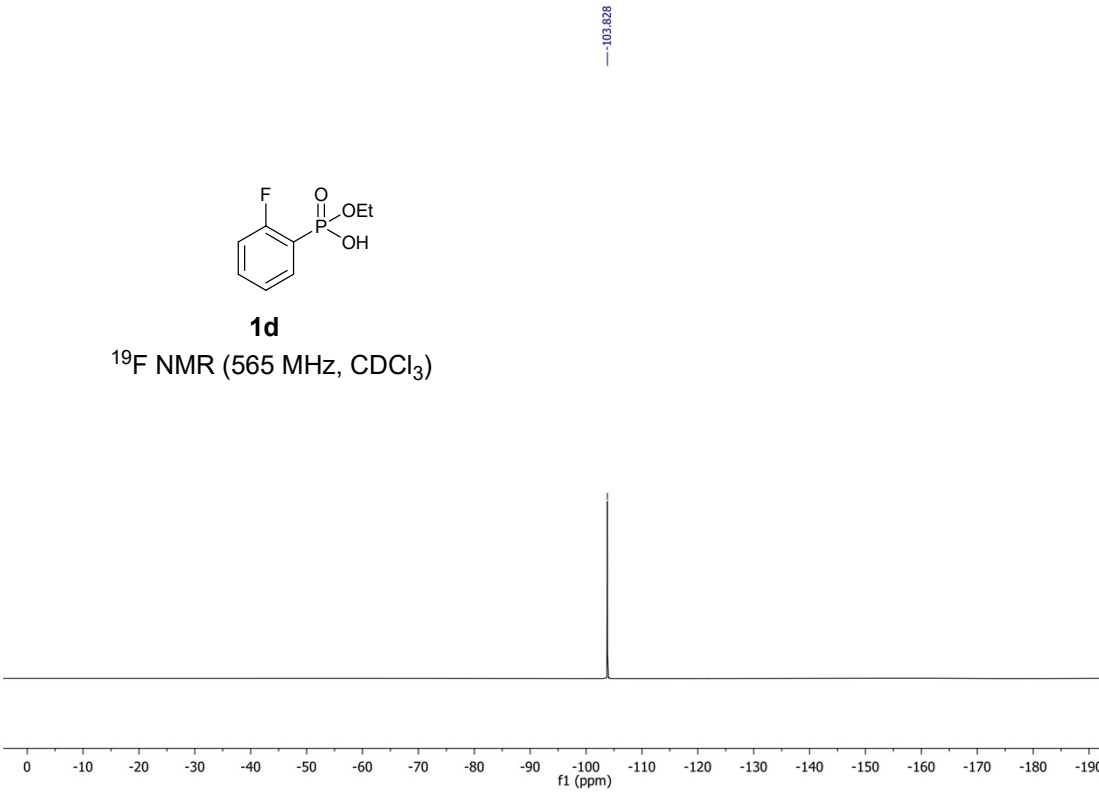


1d

^{31}P NMR (243 MHz, $CDCl_3$)

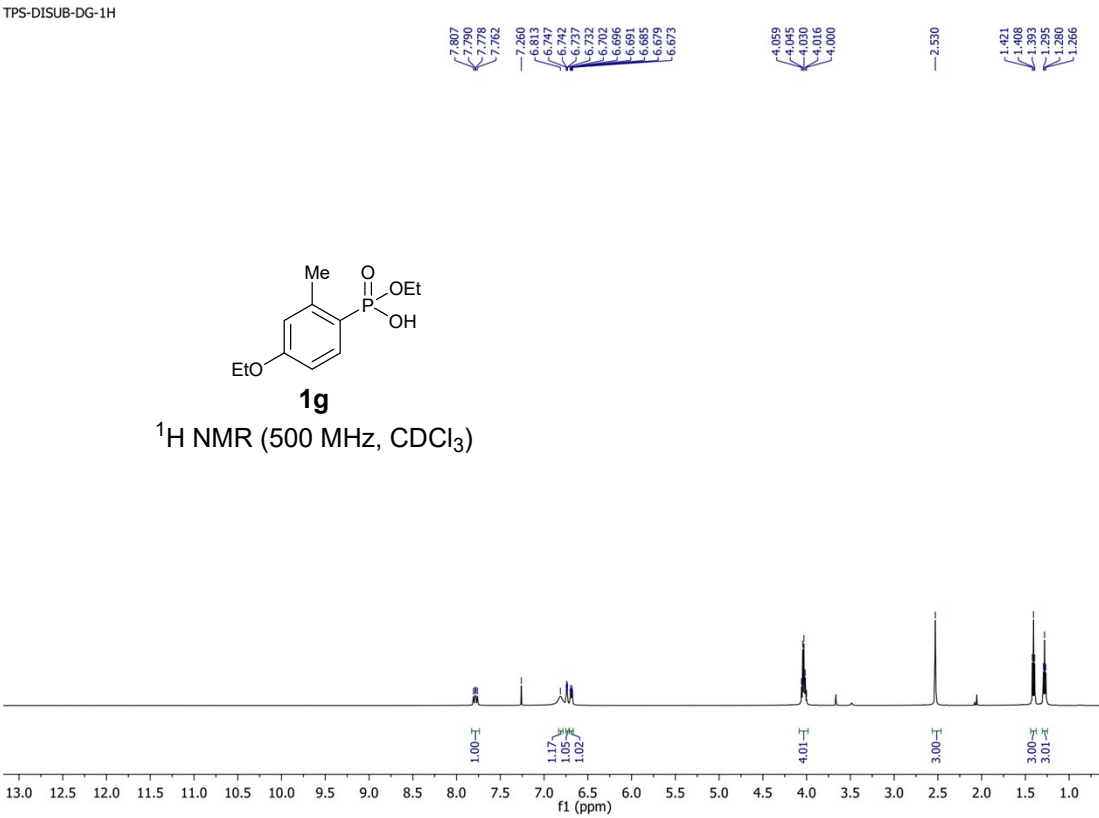
TPS-2F DG-19F



1d

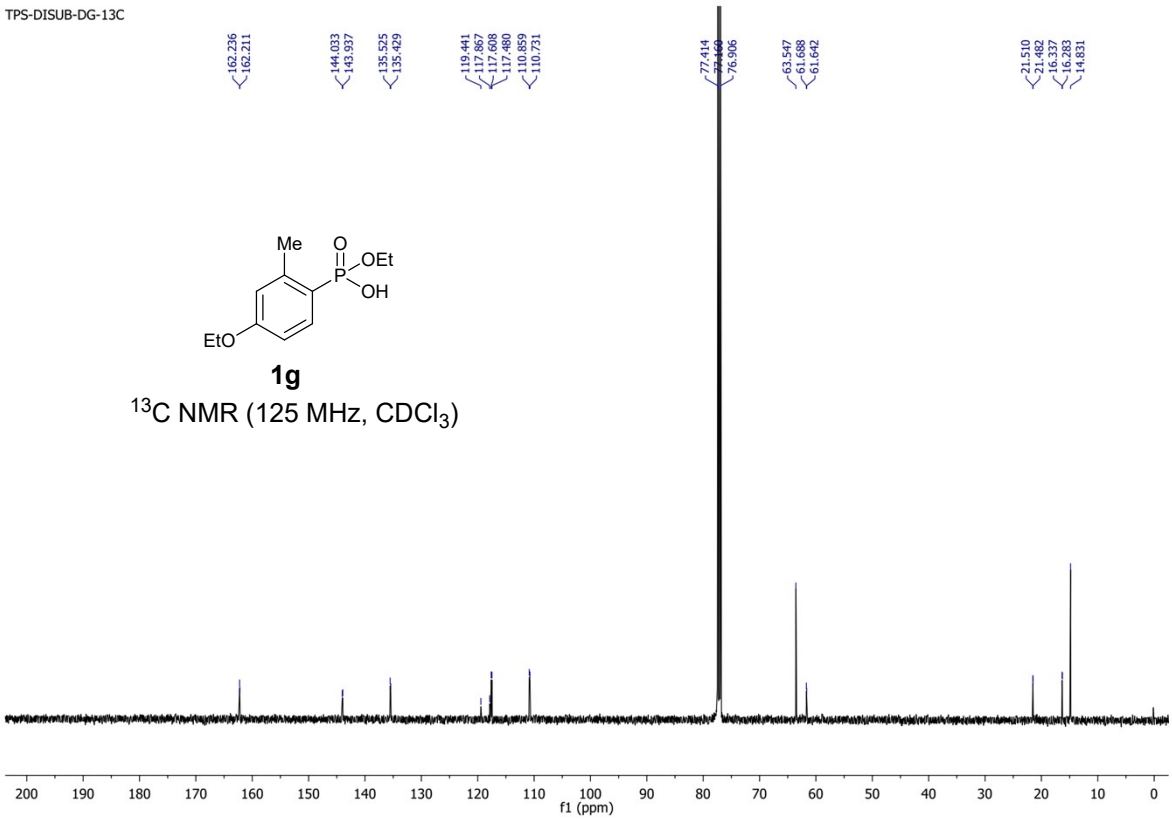
^{19}F NMR (565 MHz, $CDCl_3$)

TPS-DISUB-DG-1H



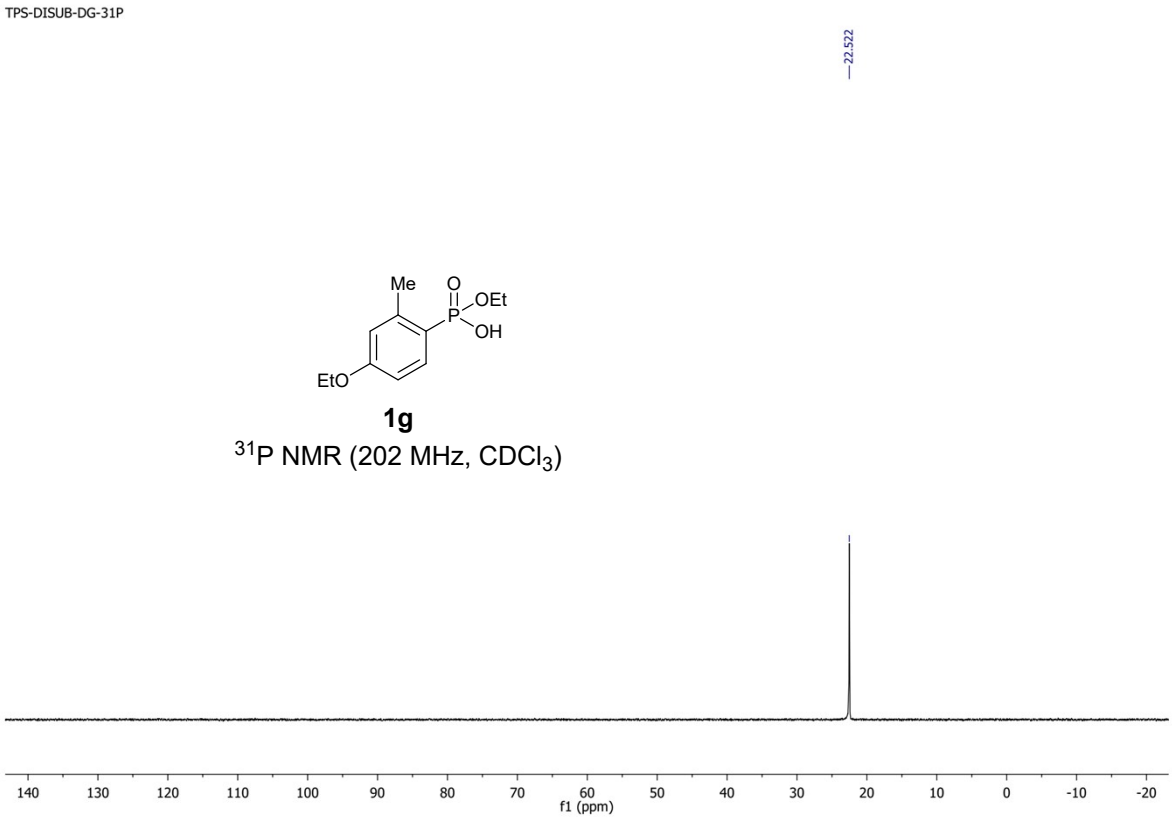
1g

^{1}H NMR (500 MHz, $CDCl_3$)



1g

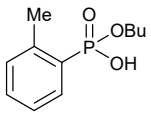
^{13}C NMR (125 MHz, $CDCl_3$)



1g

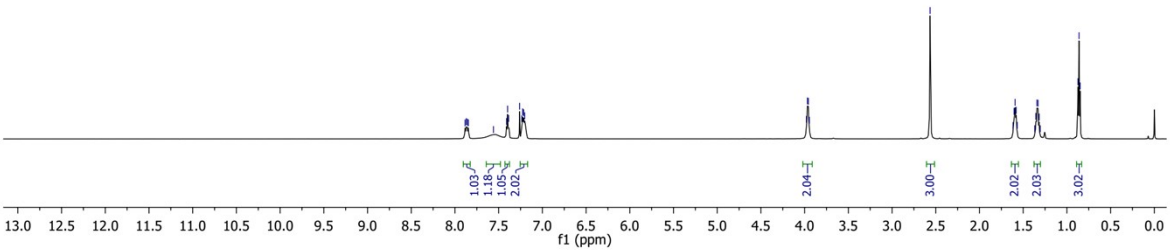
^{31}P NMR (202 MHz, $CDCl_3$)

TPS-OBu DG-1H

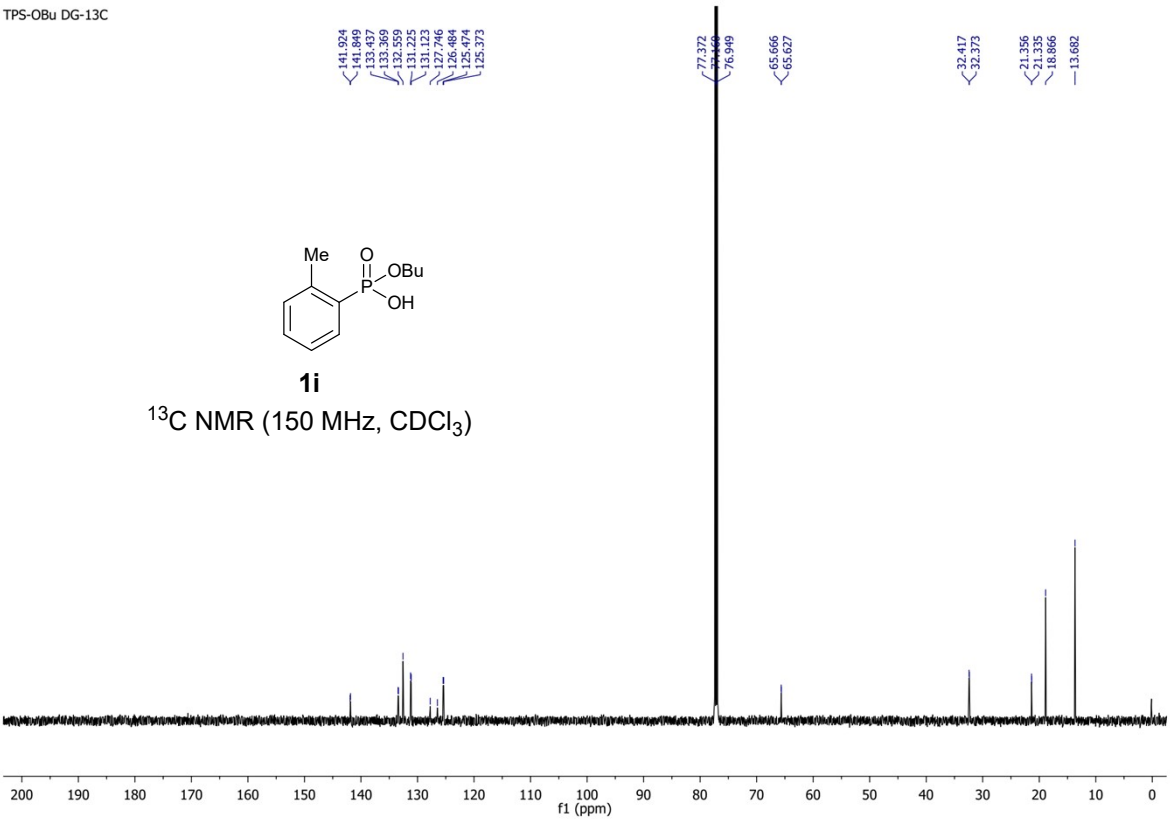


1i

^{1}H NMR (600 MHz, $CDCl_3$)



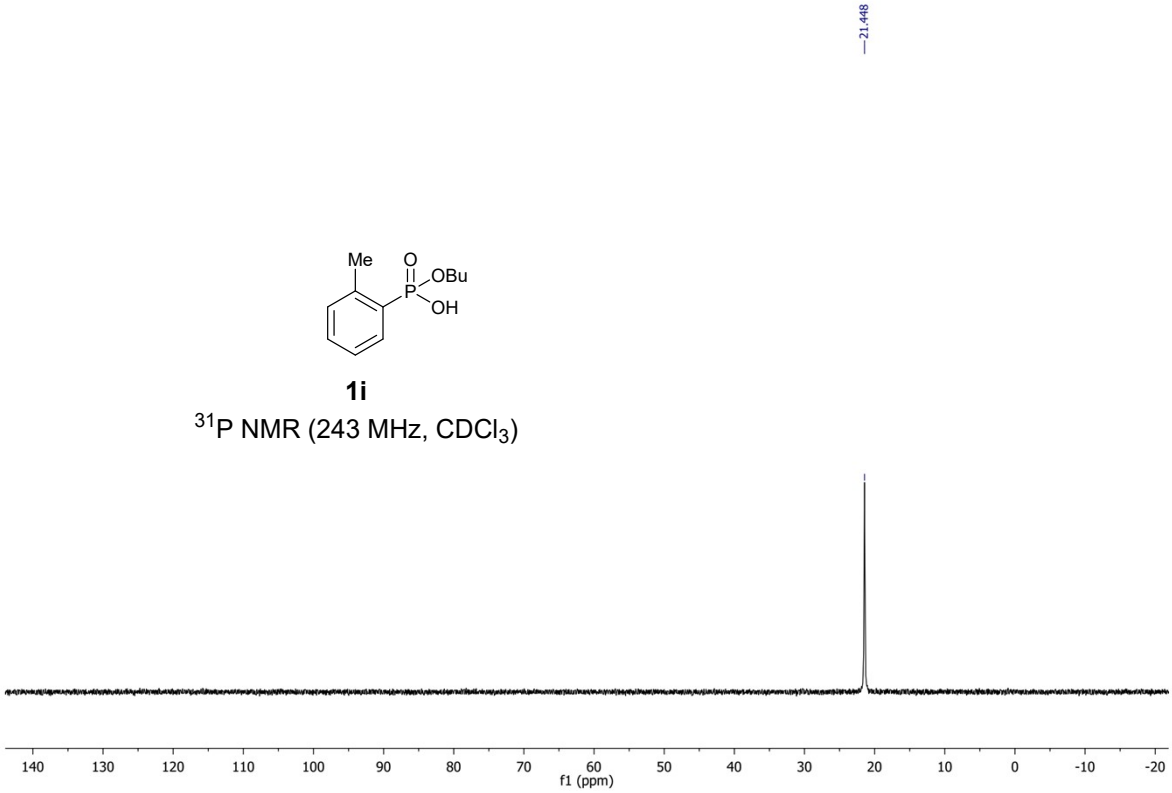
TPS-OBu DG-13C



1i

^{13}C NMR (150 MHz, $CDCl_3$)

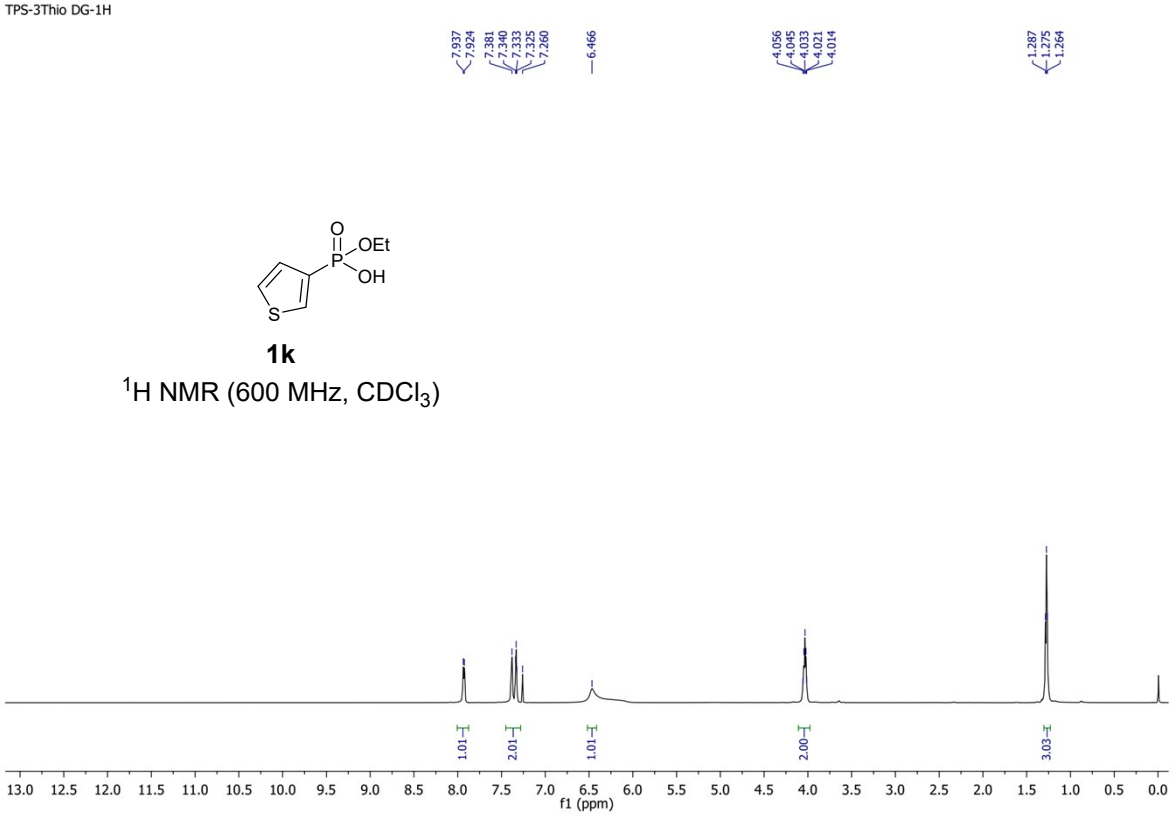
TPS-OBu DG-31P



1i

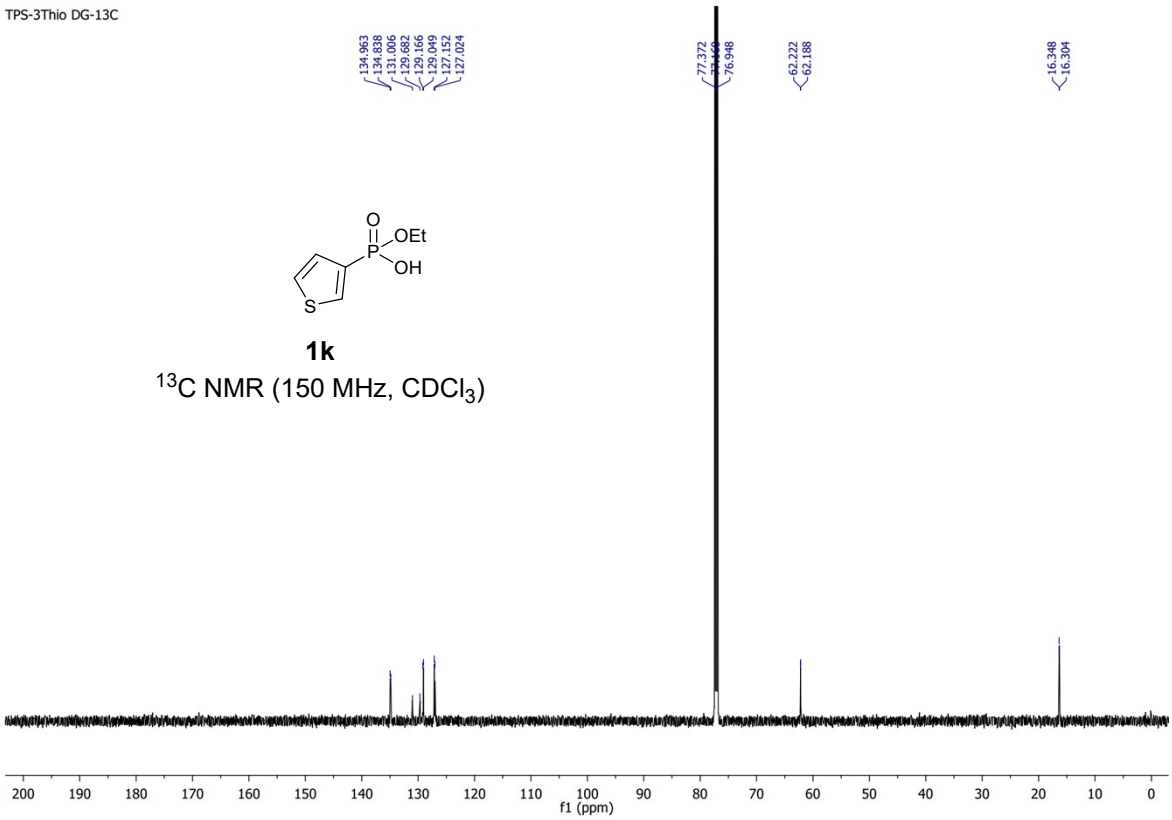
^{31}P NMR (243 MHz, $CDCl_3$)

TPS-3Thio DG-1H



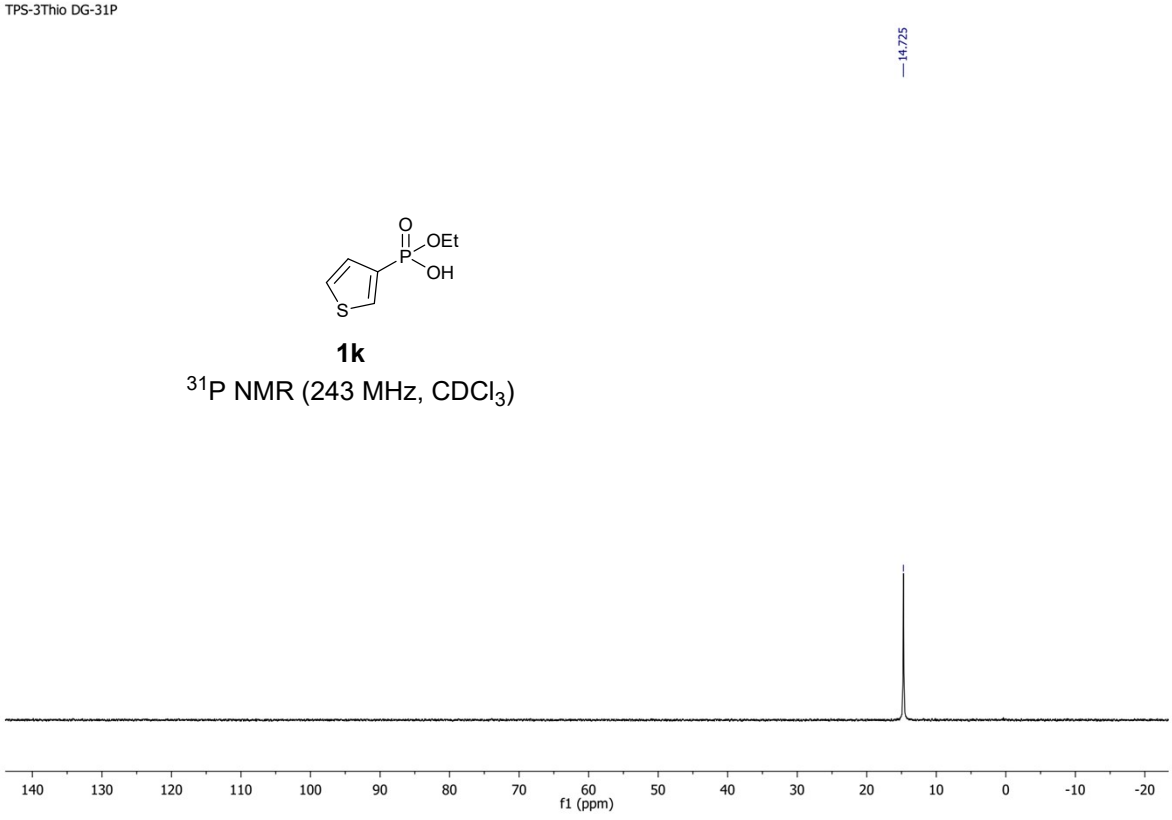
1k

^{1}H NMR (600 MHz, $CDCl_3$)



1k

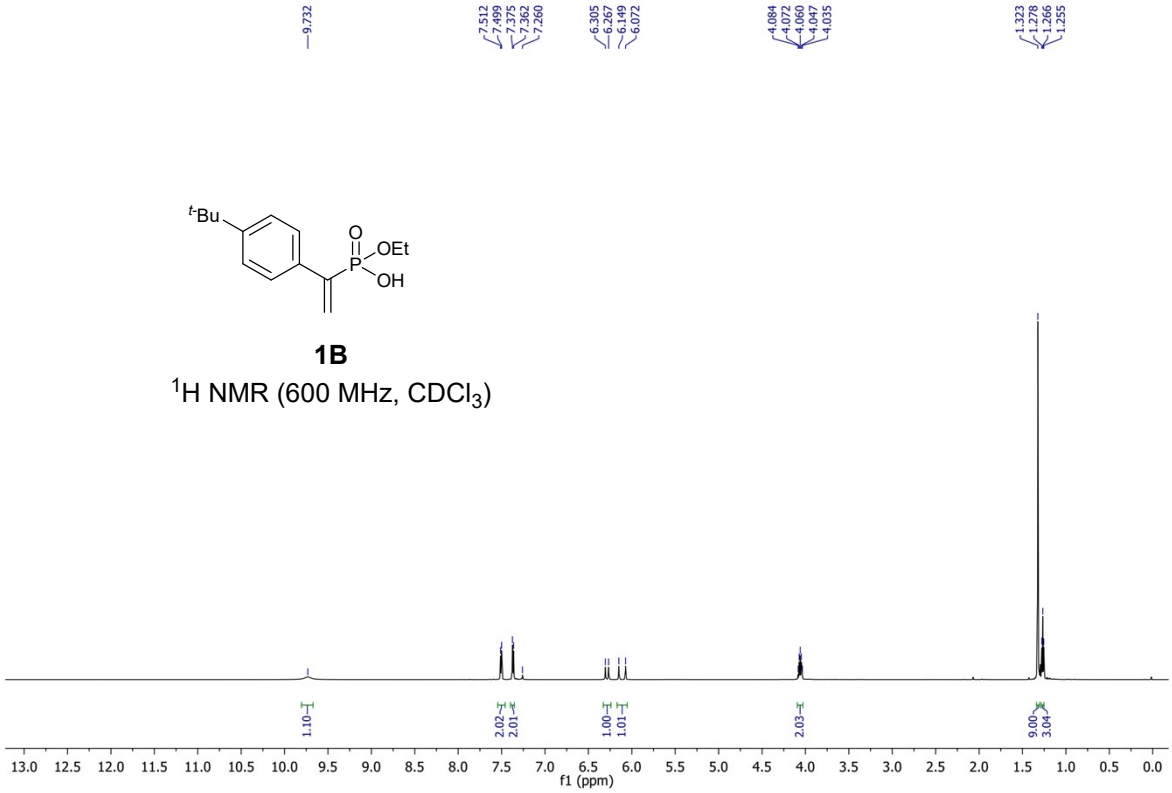
^{13}C NMR (150 MHz, $CDCl_3$)



1k

^{31}P NMR (243 MHz, $CDCl_3$)

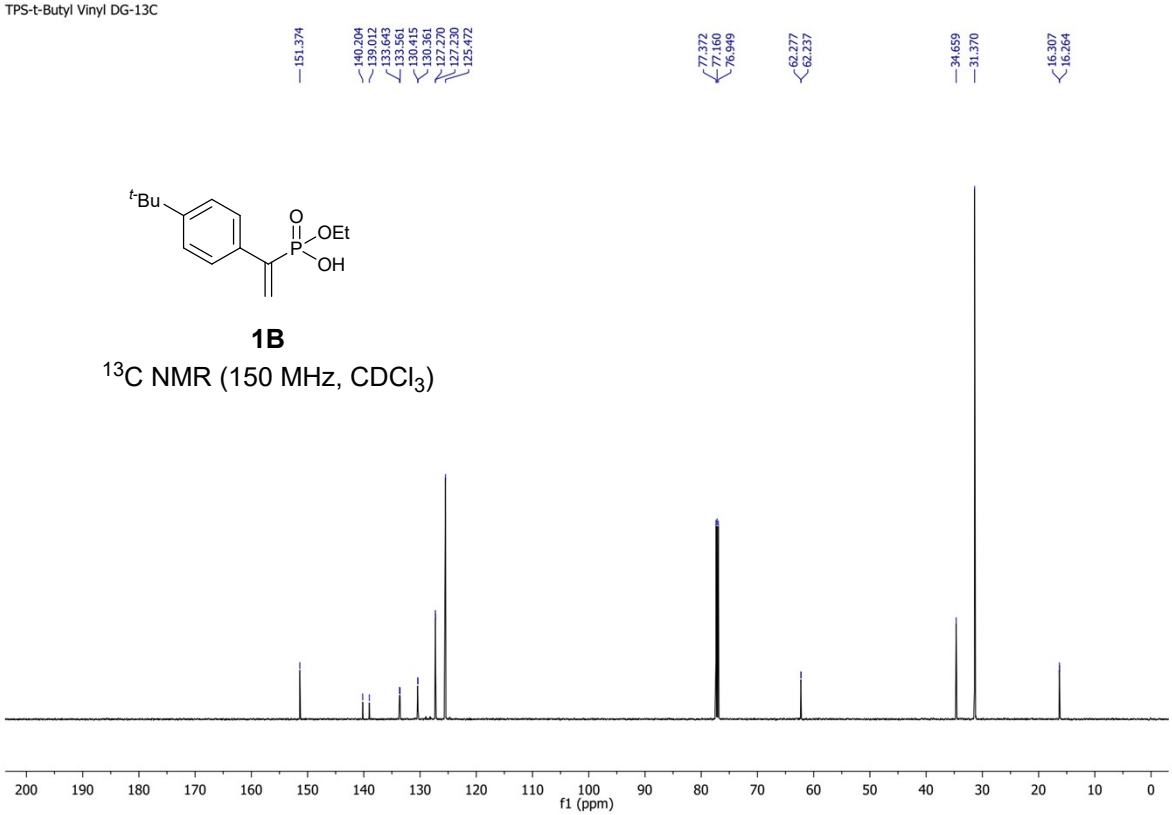
TPS-t-Butyl Vinyl DG-1H



1B

^{1}H NMR (600 MHz, $CDCl_3$)

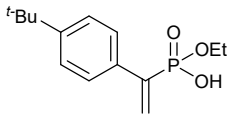
TPS-t-Butyl Vinyl DG-13C



1B

^{13}C NMR (150 MHz, $CDCl_3$)

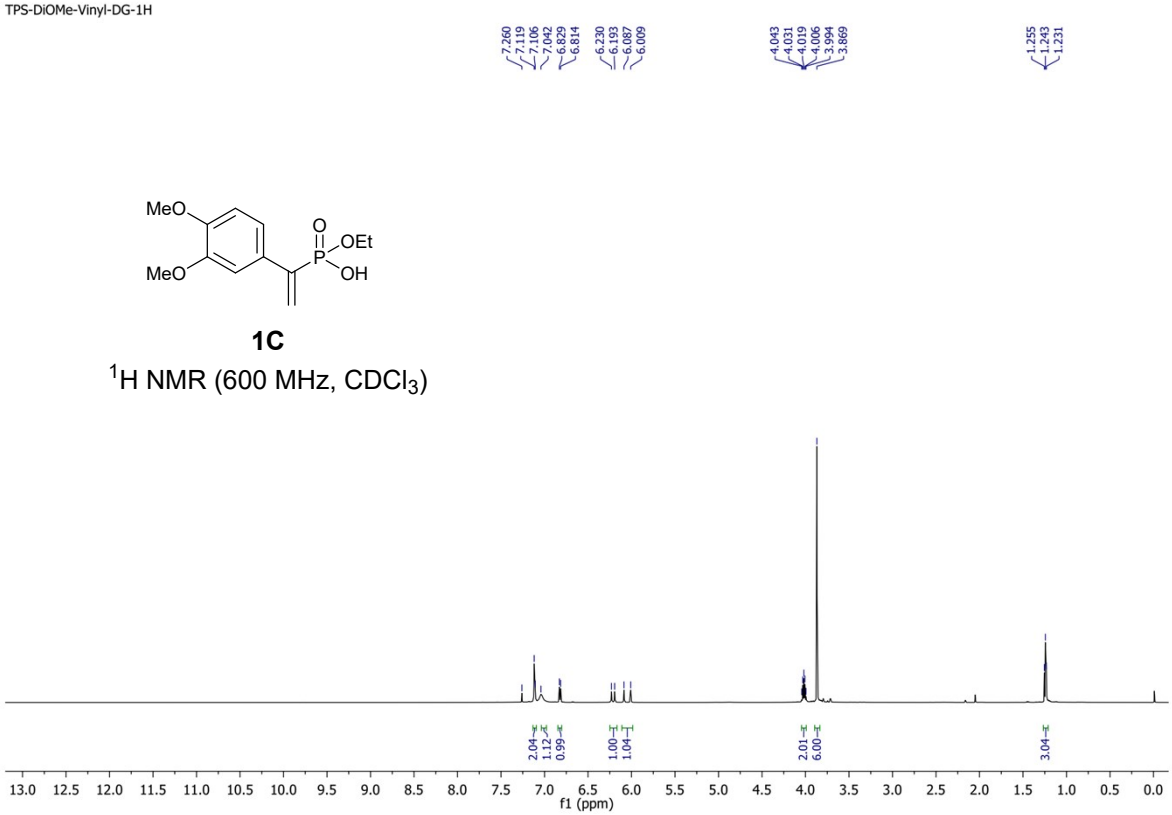
TPS-t-Butyl Vinyl DG-31P



1B

^{31}P NMR (243 MHz, $CDCl_3$)

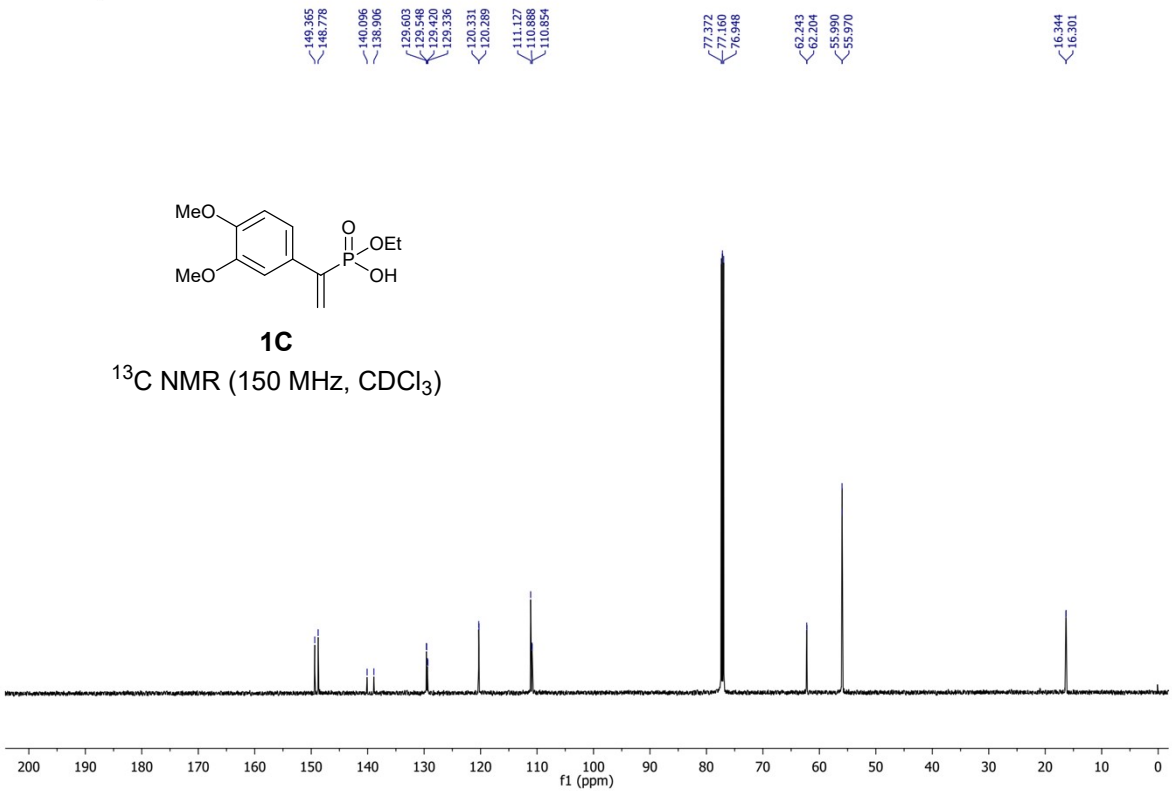
TPS-DiOMe-Vinyl-DG-1H



1C

^{1}H NMR (600 MHz, $CDCl_3$)

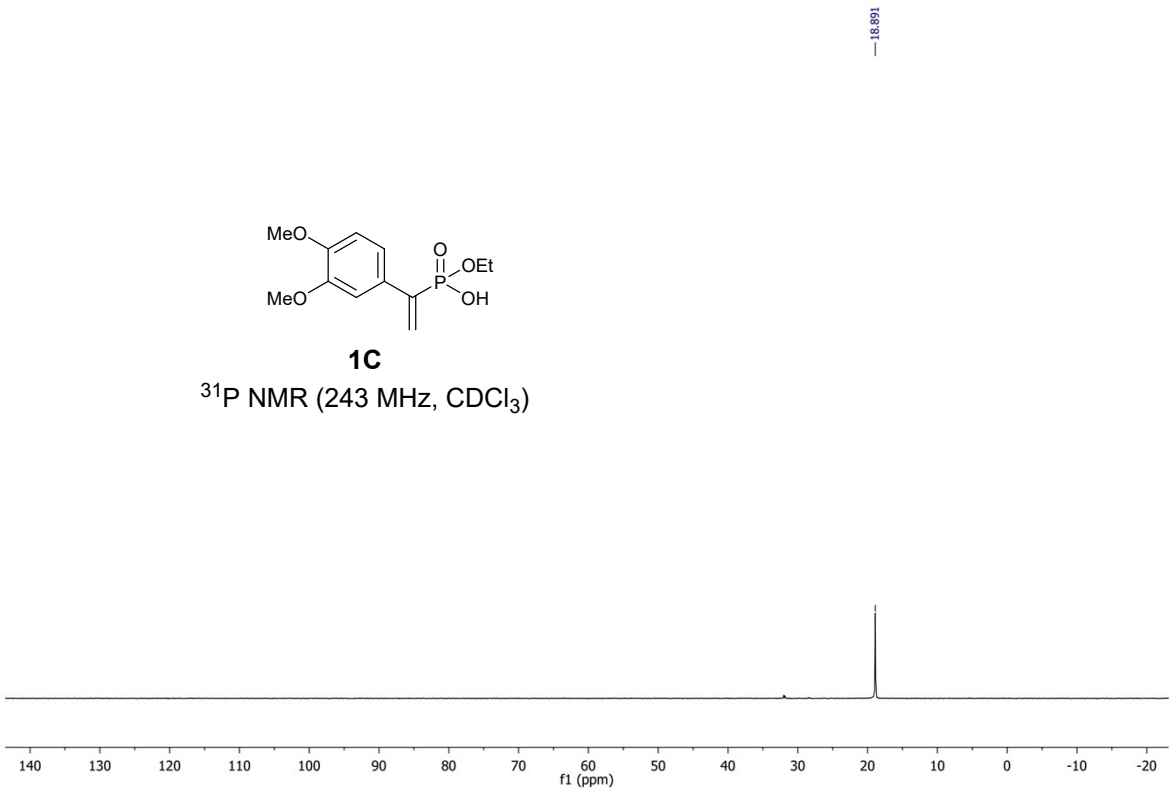
TPS-DiOMe-Vinyl-DG-13C



1C

^{13}C NMR (150 MHz, $CDCl_3$)

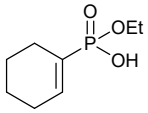
TPS-DiOMe-Vinyl-DG-31P



1C

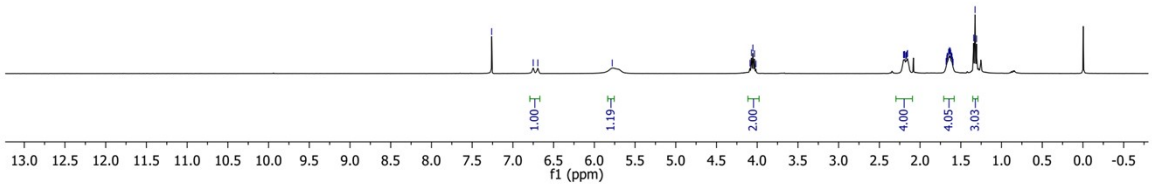
^{31}P NMR (243 MHz, $CDCl_3$)

TPS-Cyclohexene DG-1H

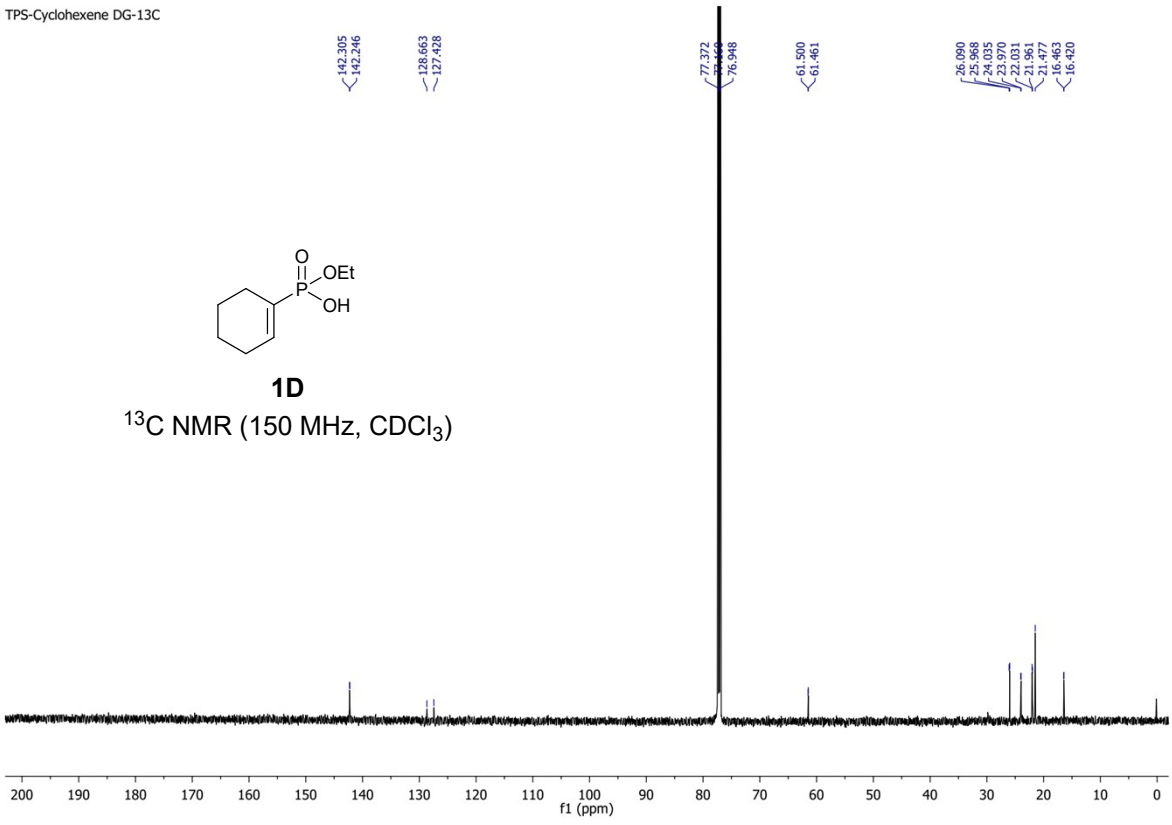


1D

^{1}H NMR (400 MHz, $CDCl_3$)



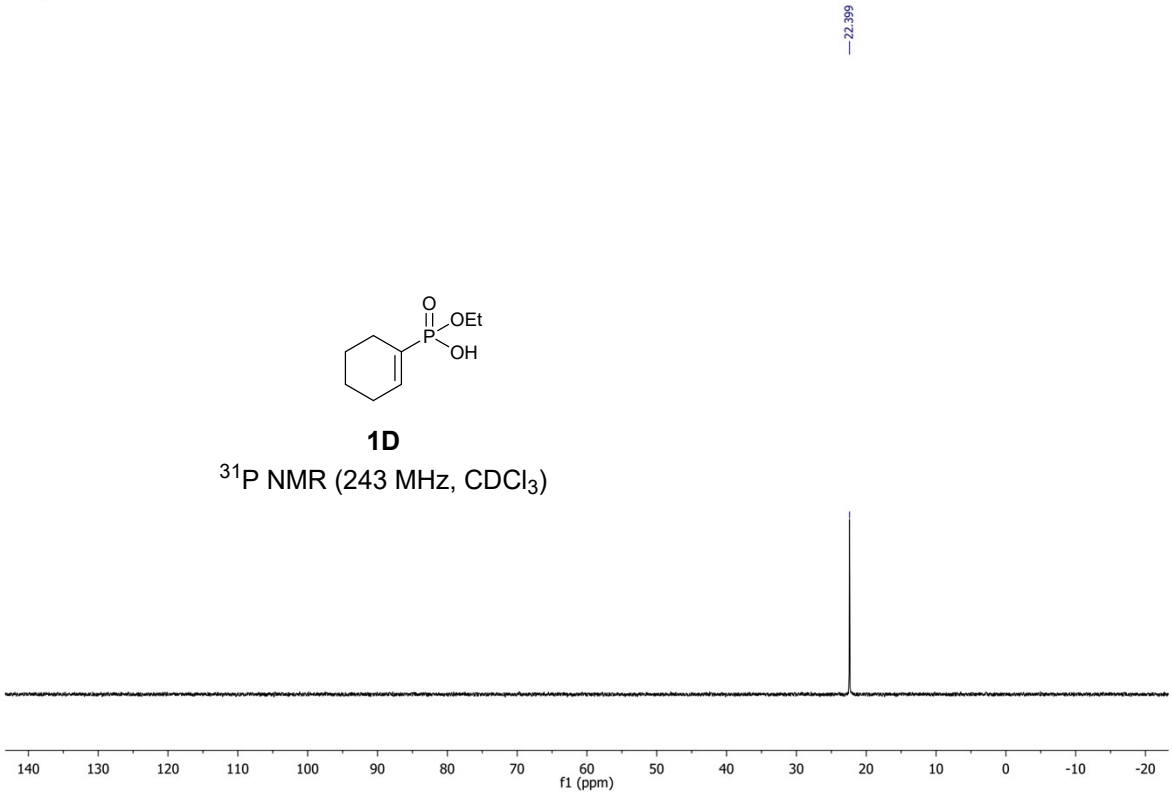
TPS-Cyclohexene DG-13C



1D

^{13}C NMR (150 MHz, $CDCl_3$)

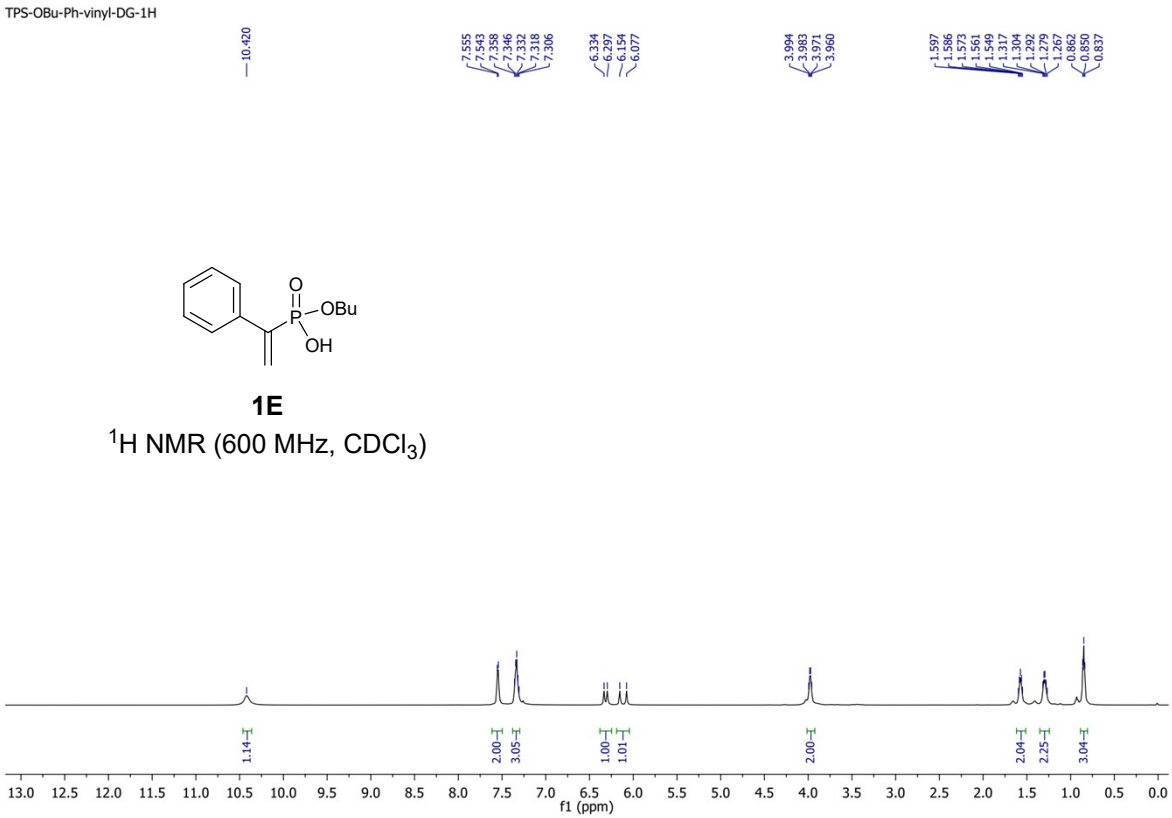
TPS-Cyclohexene DG-31P



1D

^{31}P NMR (243 MHz, $CDCl_3$)

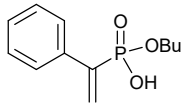
TPS-OBu-Ph-vinyl-DG-1H



1E

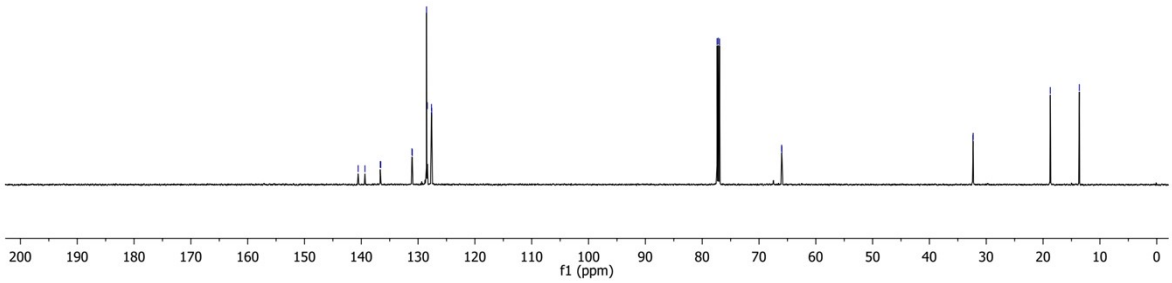
^{1}H NMR (600 MHz, $CDCl_3$)

TPS-OBu-Ph-vinyl-DG-13C

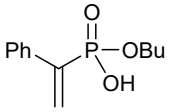


1E

^{13}C NMR (150 MHz, $CDCl_3$)

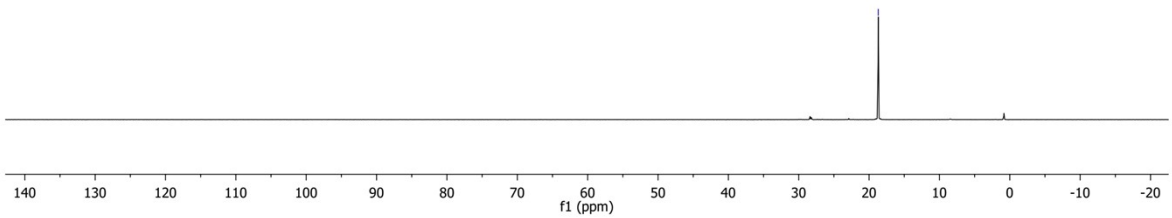


TPS-OBu-Ph-vinyl-DG-31P

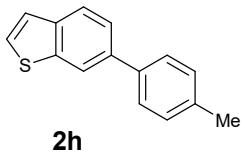


1E

^{31}P NMR (243 MHz, $CDCl_3$)

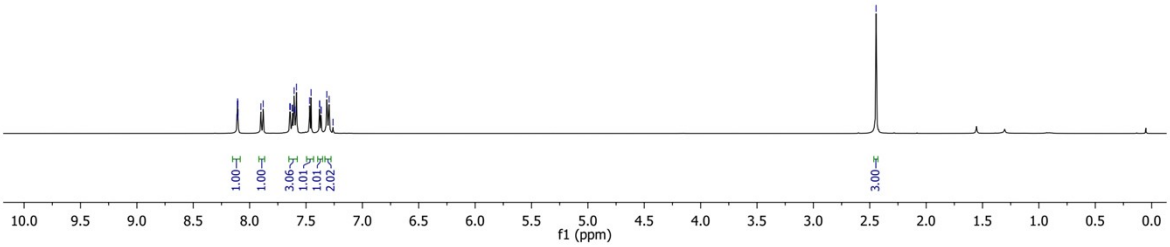


TPS-6 p-Tolyl BT-1H

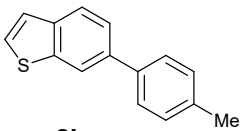


2h

^{1}H NMR (400 MHz, $CDCl_3$)

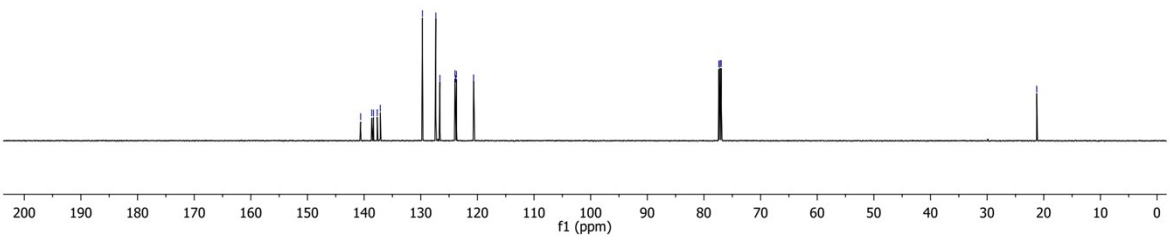


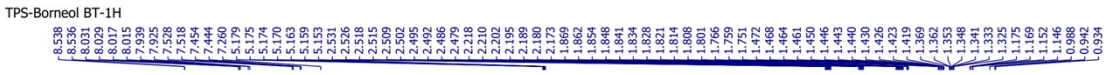
TPS-6 p-Tolyl BT-13C

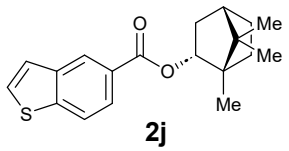


2h

^{13}C NMR (150 MHz, $CDCl_3$)

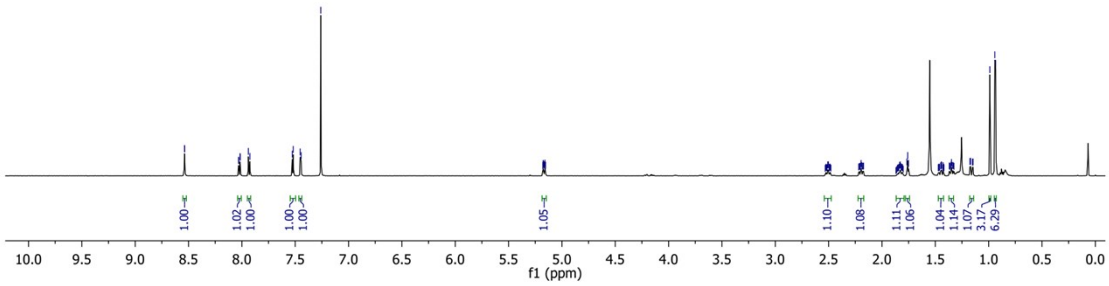


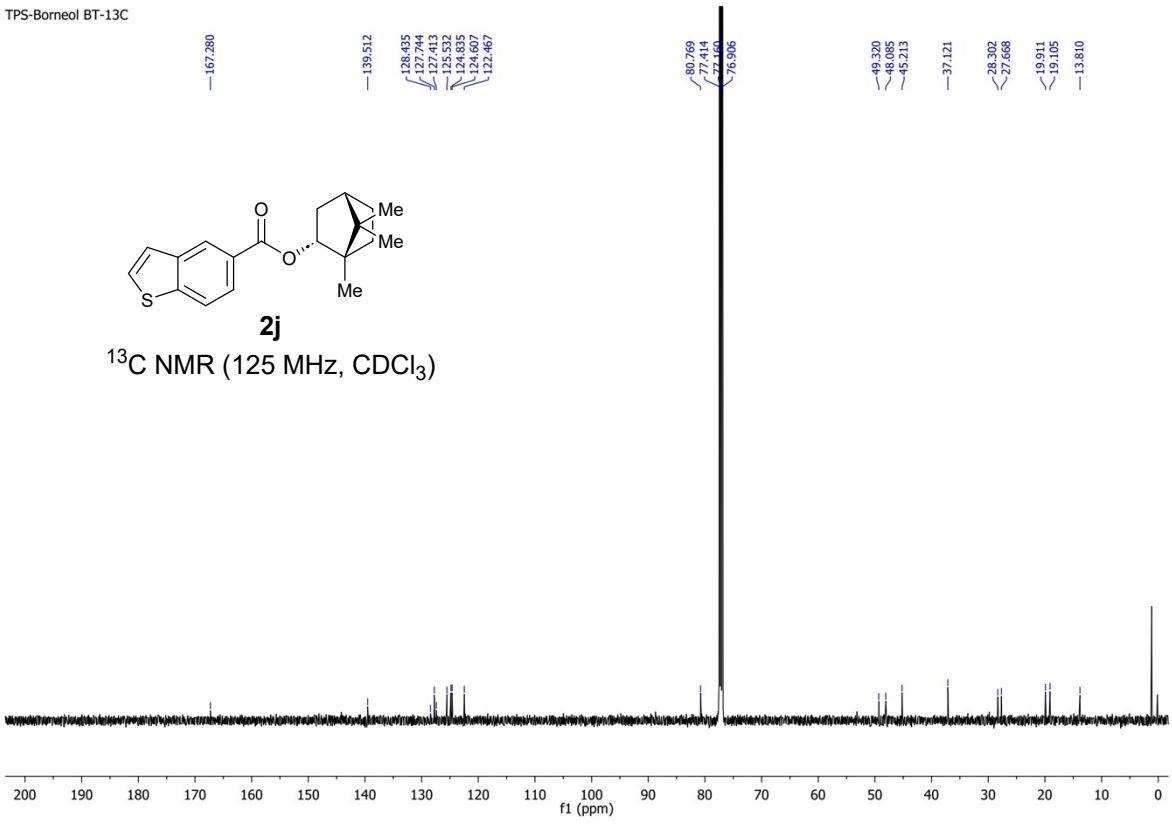




2j

^{1}H NMR (600 MHz, $CDCl_3$)

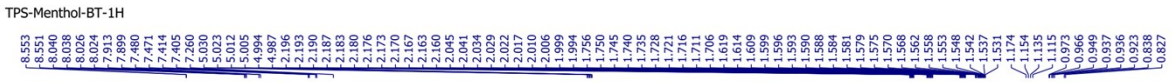


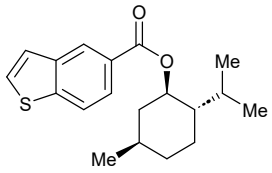


2j

^{13}C NMR (125 MHz, $CDCl_3$)

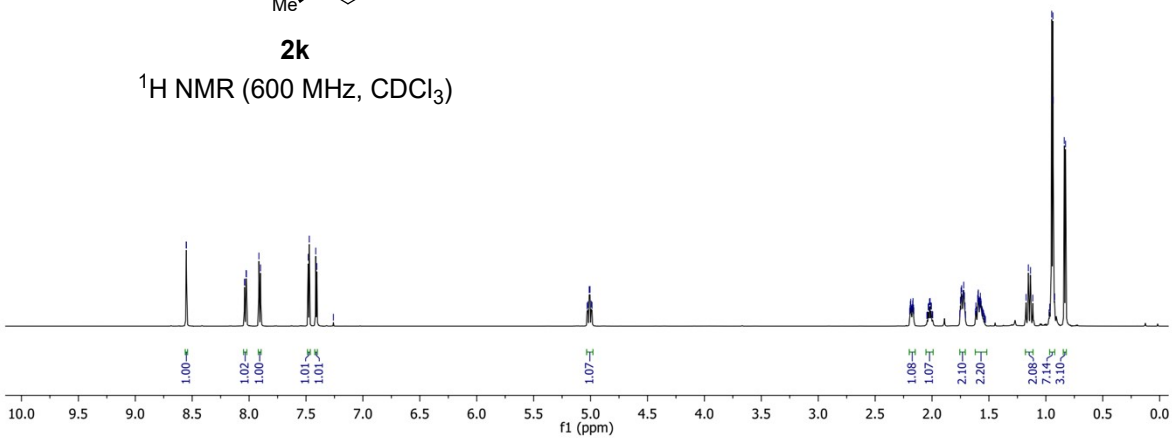
TPS-Menthol-BT-1H



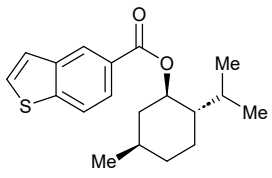


2k

^{1}H NMR (600 MHz, $CDCl_3$)

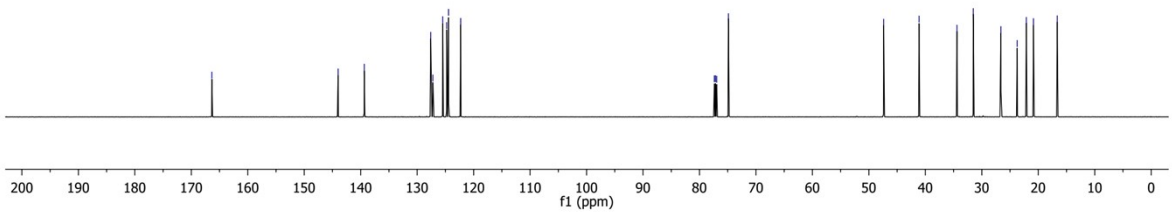


TPS-Menthol-BT-13C

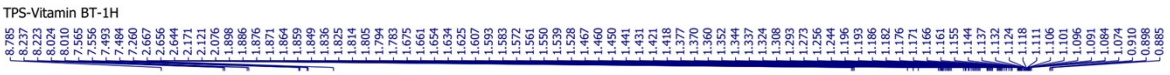


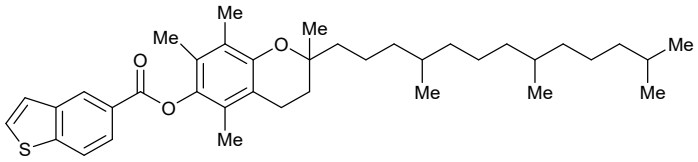
2k

^{13}C NMR (150 MHz, $CDCl_3$)



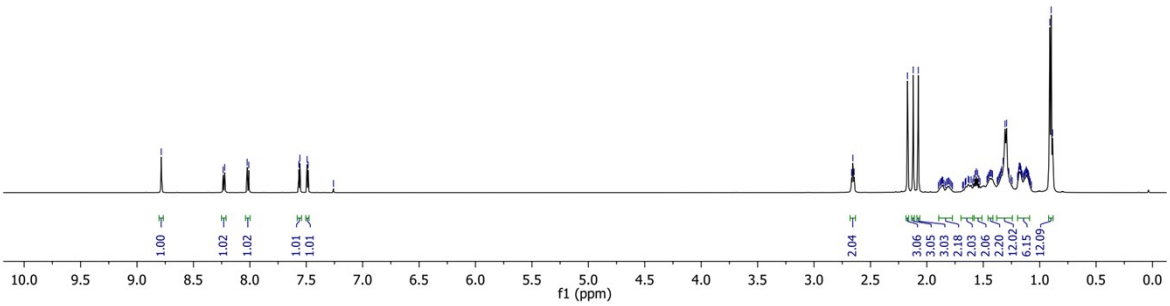
TPS-Vitamin BT-1H



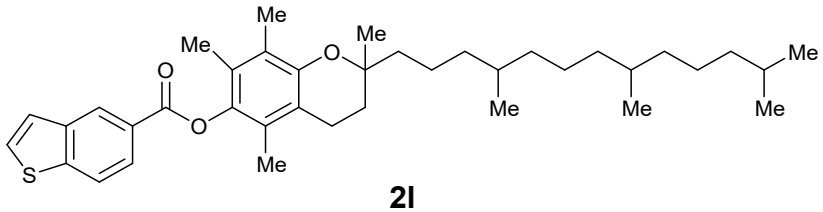


2l

^{1}H NMR (600 MHz, $CDCl_3$)

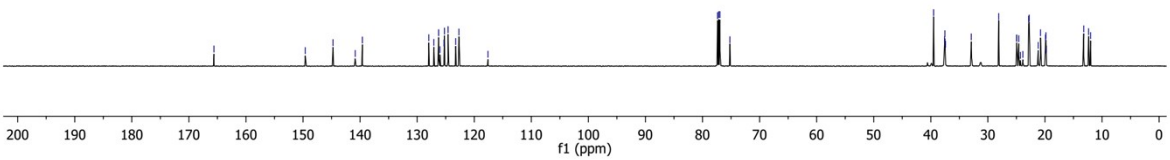


TPS-Vitamin BT-13C

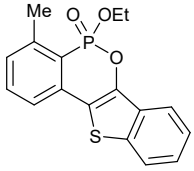


2l

^{13}C NMR (150 MHz, $CDCl_3$)

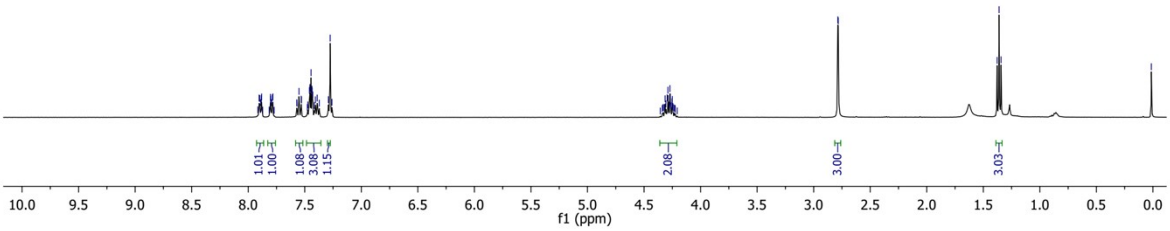


TPS-2 Me Phos-BT-1H

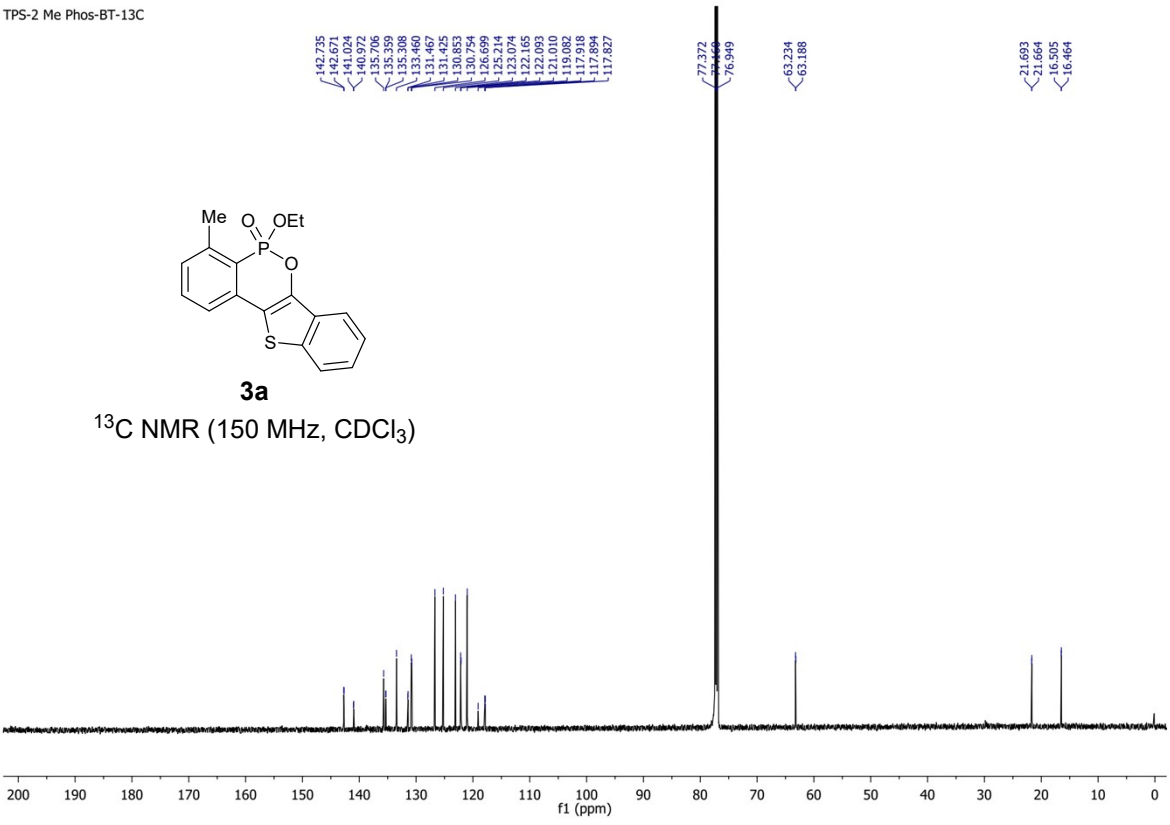


3a

^{1}H NMR (400 MHz, $CDCl_3$)



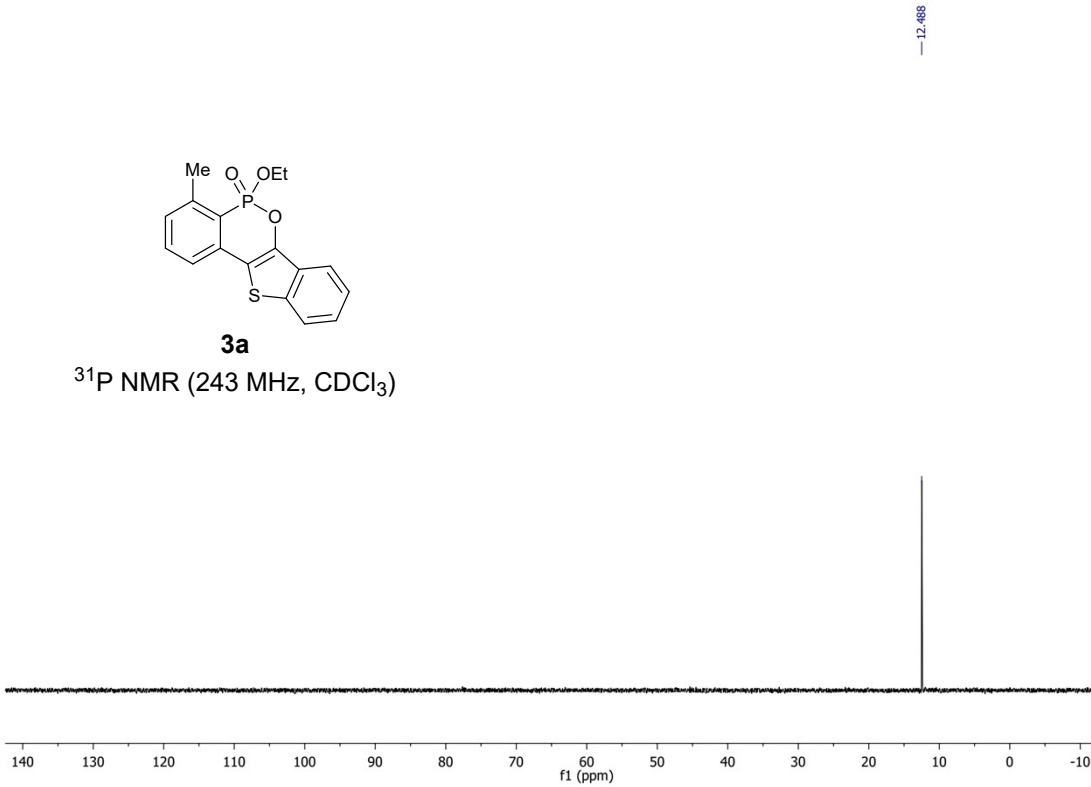
TPS-2 Me Phos-BT-13C



3a

^{13}C NMR (150 MHz, $CDCl_3$)

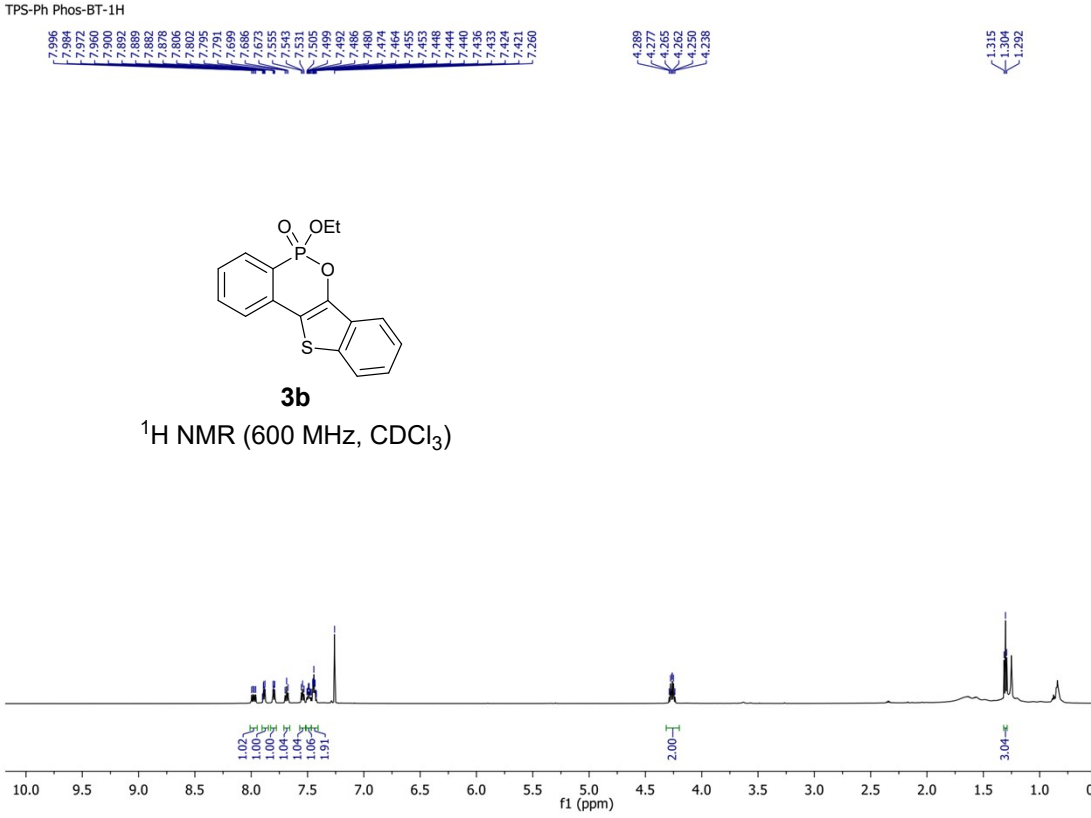
TPS-2 Me Phos-BT-31P



3a

^{31}P NMR (243 MHz, $CDCl_3$)

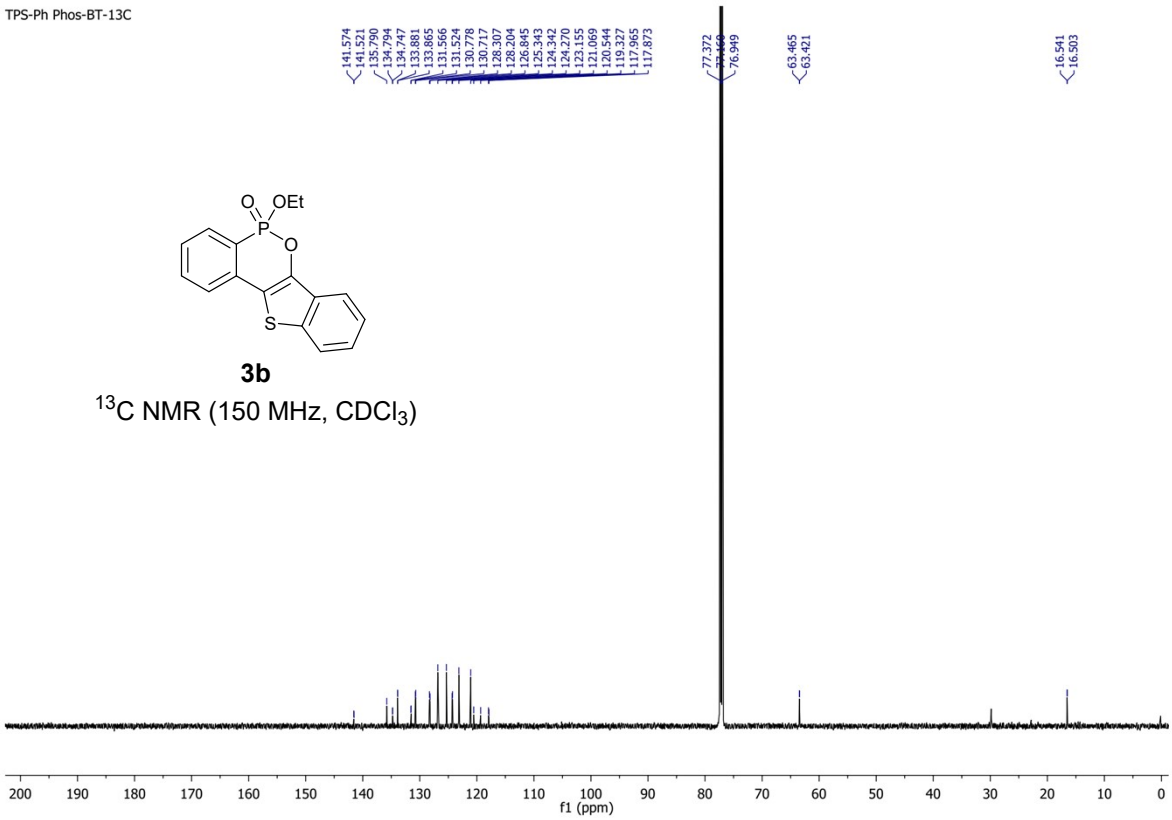
TPS-Ph Phos-BT-1H



3b

^{1}H NMR (600 MHz, $CDCl_3$)

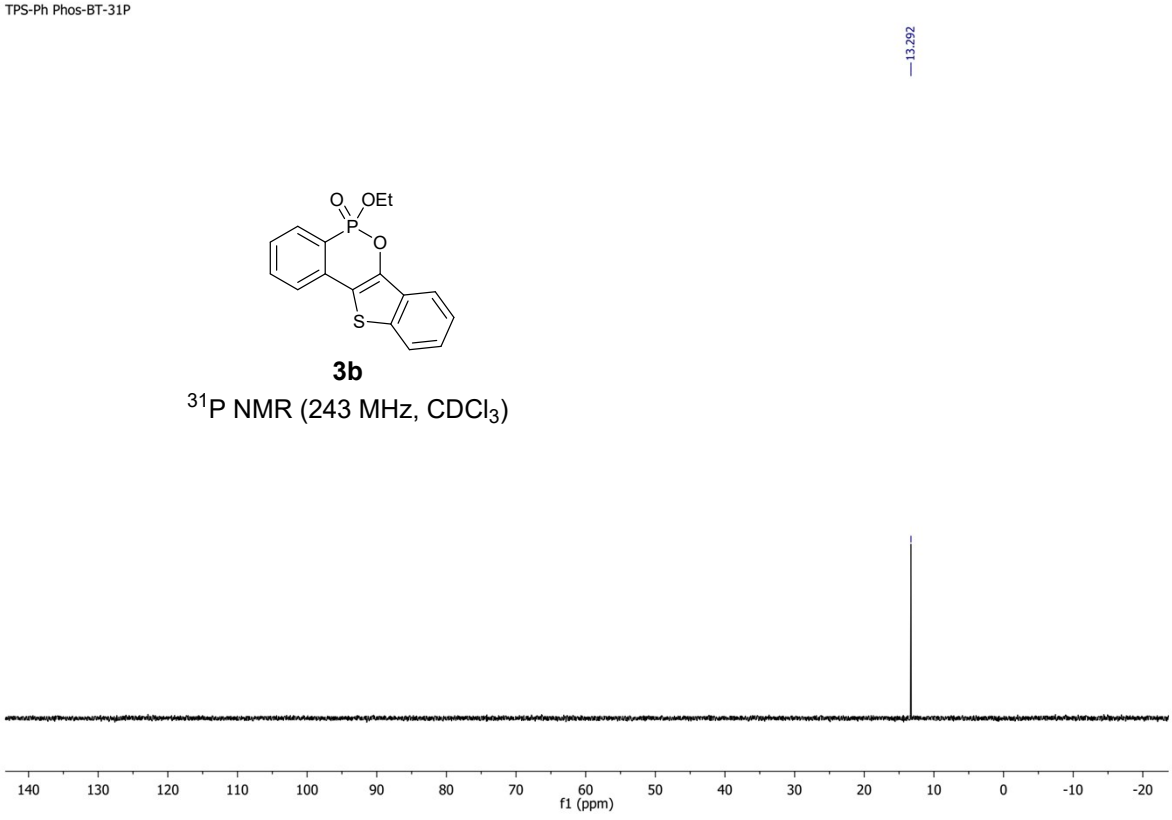
TPS-Ph Phos-BT-13C



3b

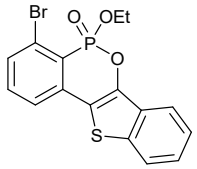
^{13}C NMR (150 MHz, $CDCl_3$)

TPS-Ph Phos-BT-31P



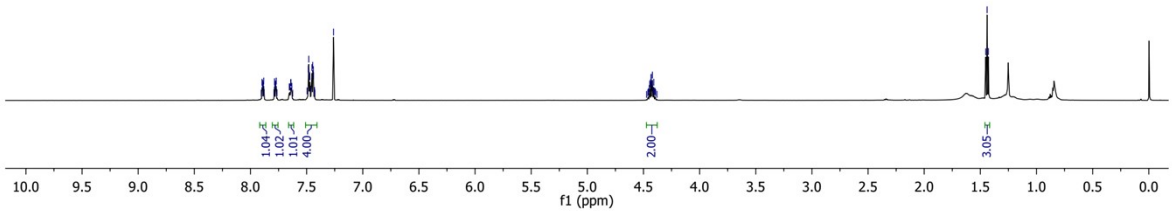
3b

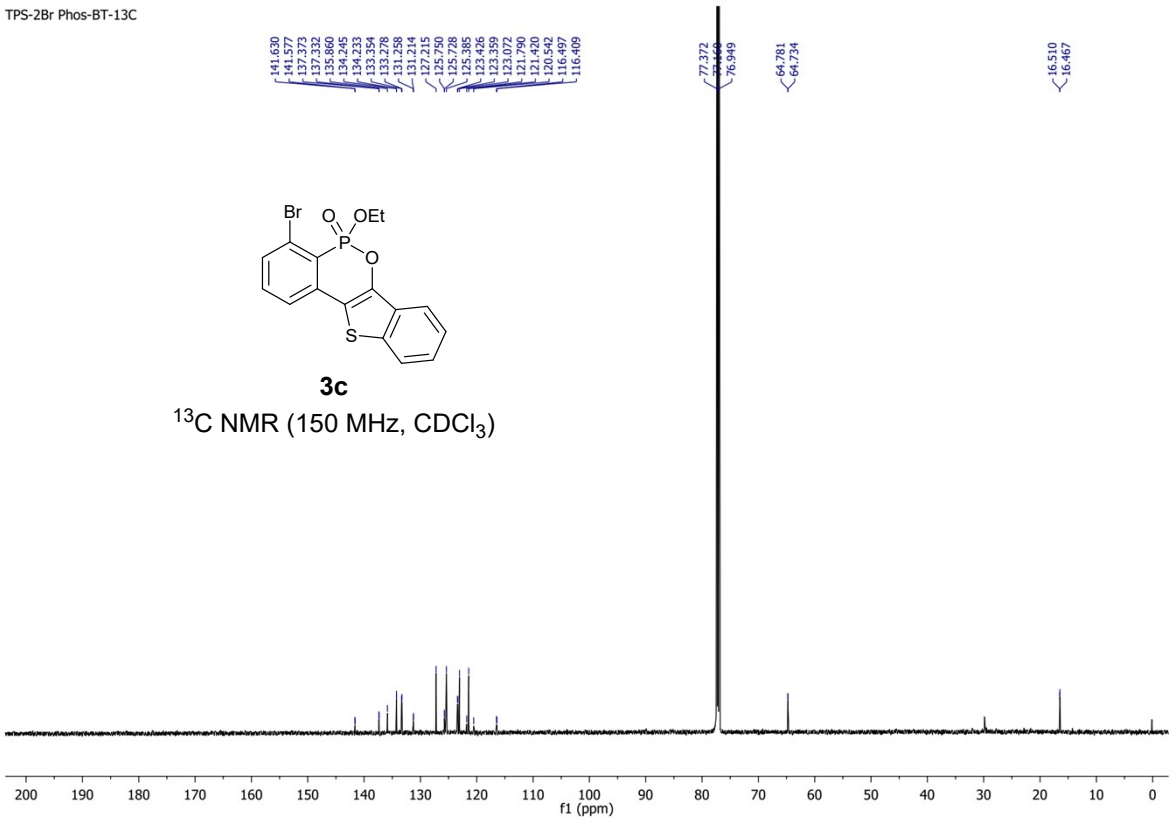
^{31}P NMR (243 MHz, $CDCl_3$)



3c

^{1}H NMR (600 MHz, $CDCl_3$)

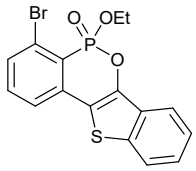




3c

^{13}C NMR (150 MHz, $CDCl_3$)

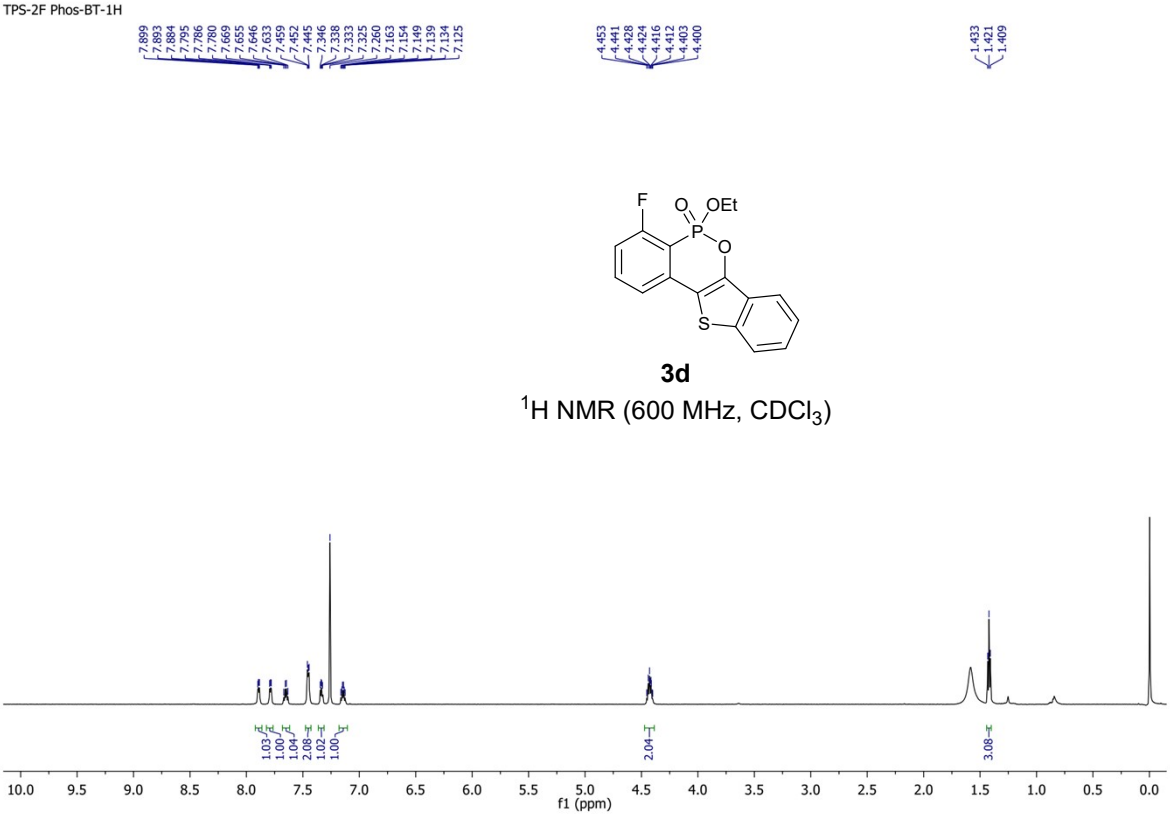
TPS-2Br Phos-BT-31P



3c

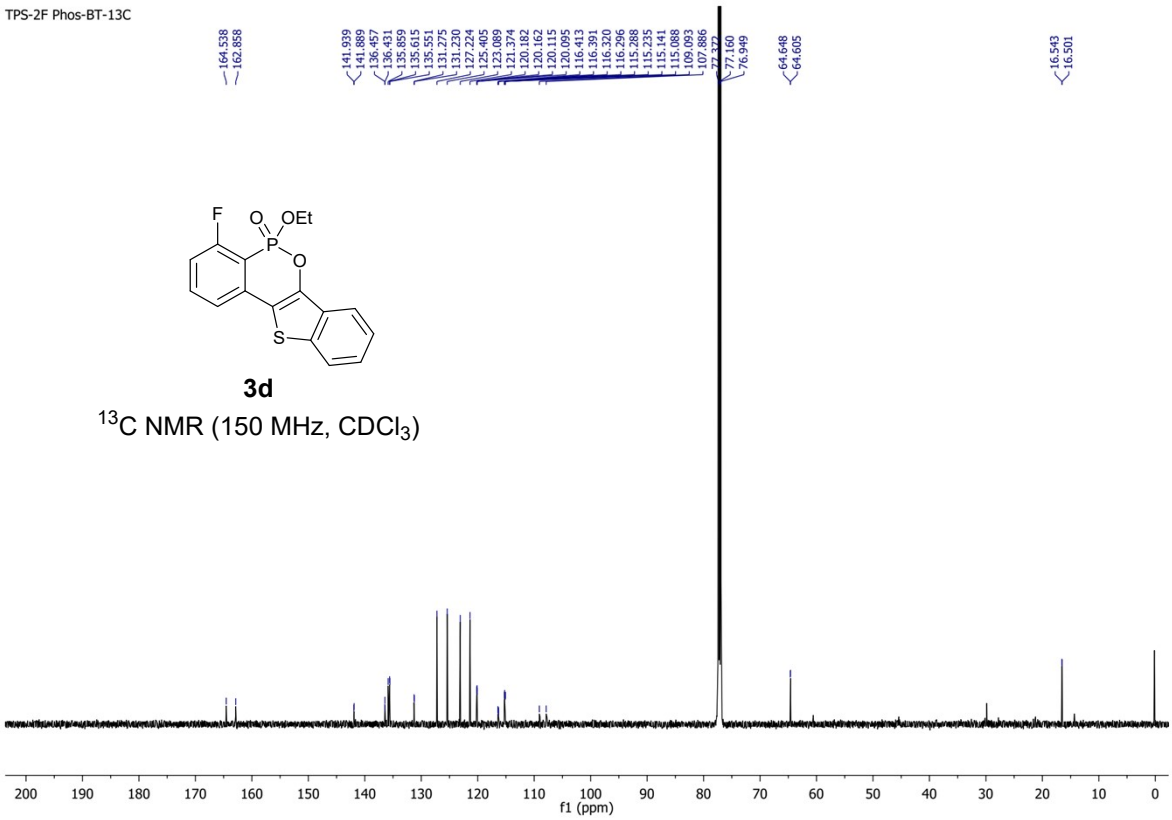
^{31}P NMR (243 MHz, $CDCl_3$)

TPS-2F Phos-BT-1H



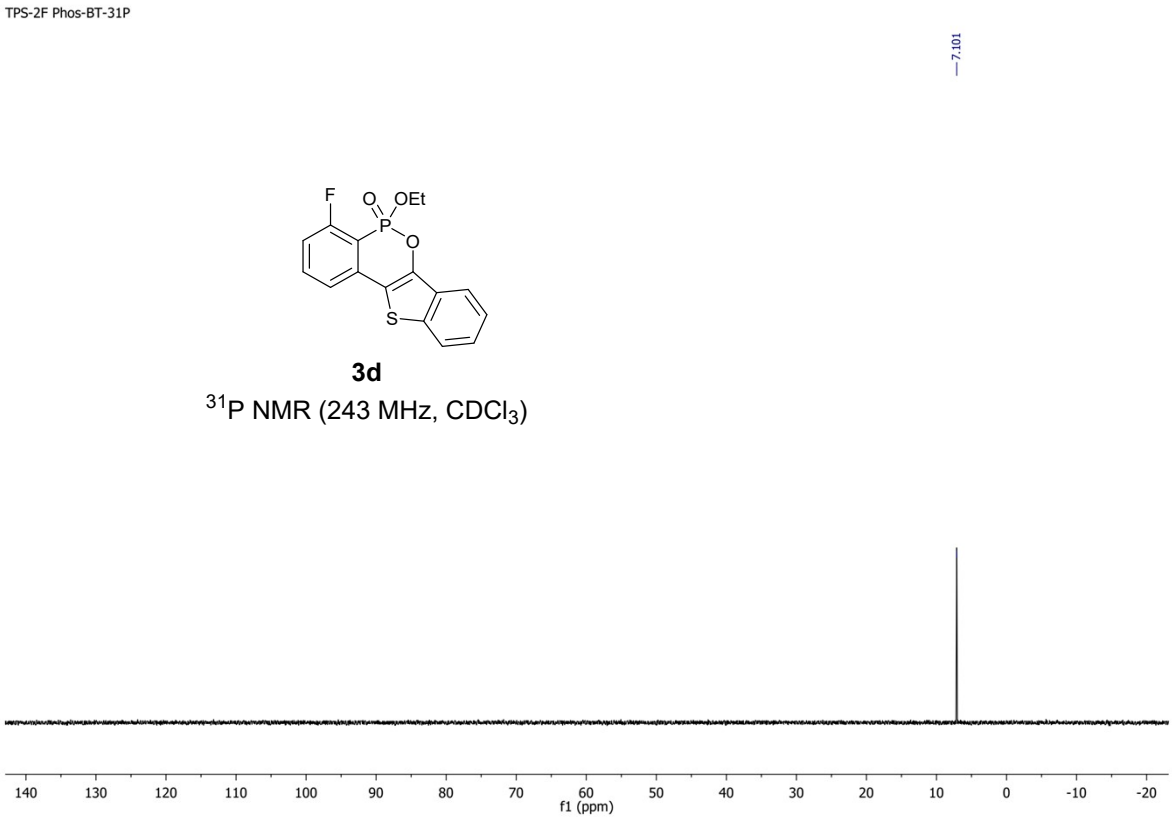
3d

^{1}H NMR (600 MHz, $CDCl_3$)



3d

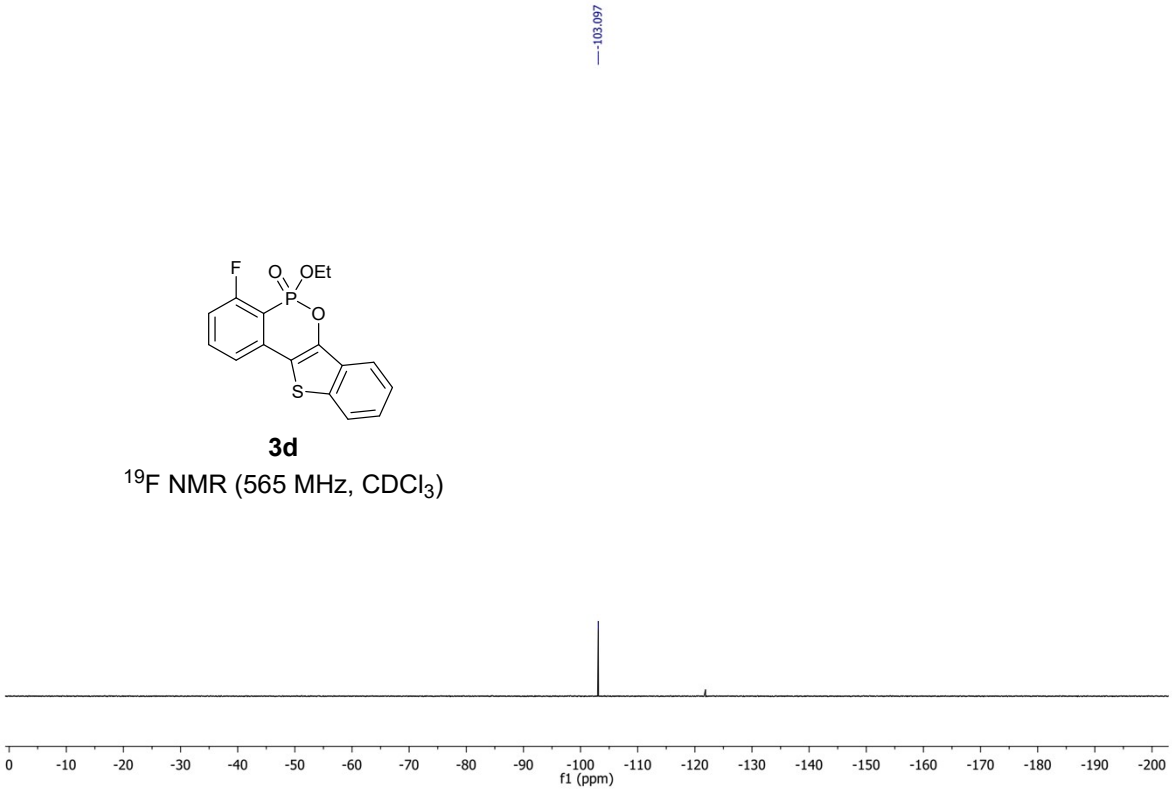
^{13}C NMR (150 MHz, $CDCl_3$)



3d

^{31}P NMR (243 MHz, $CDCl_3$)

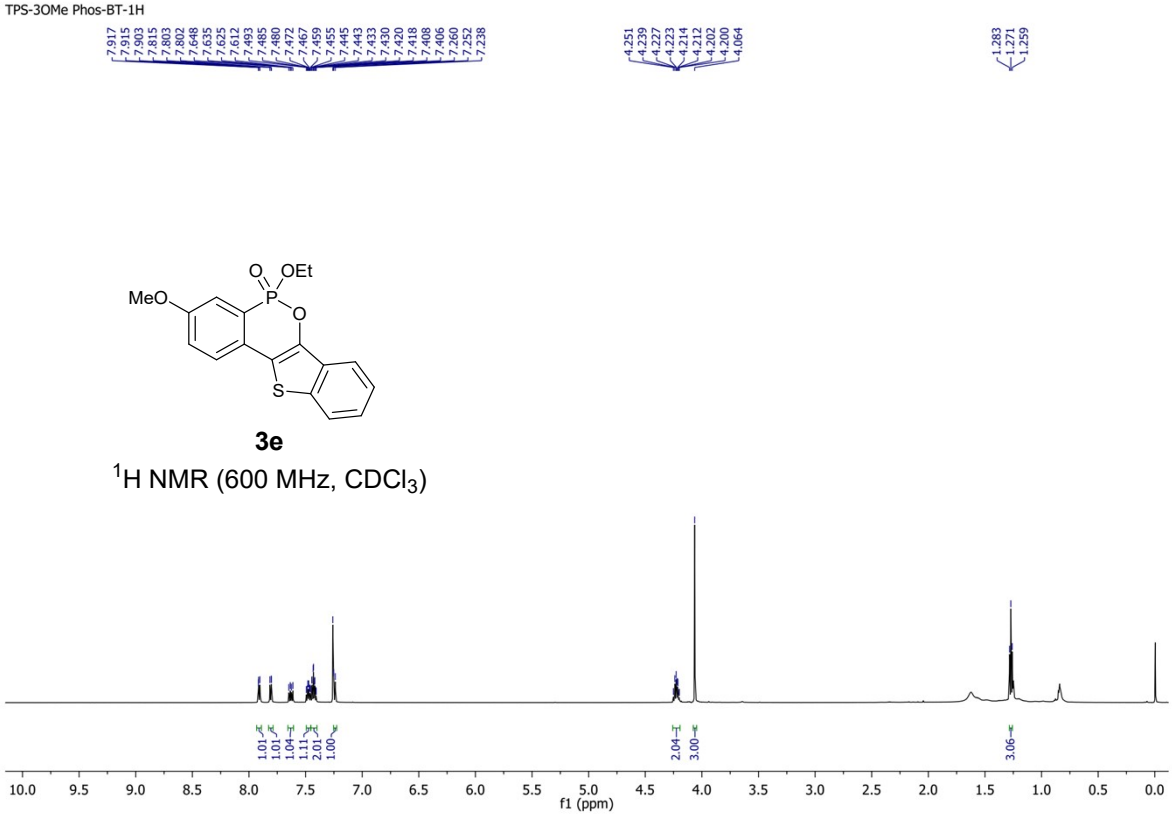
TPS-2F Phos-BT-19F



3d

^{19}F NMR (565 MHz, $CDCl_3$)

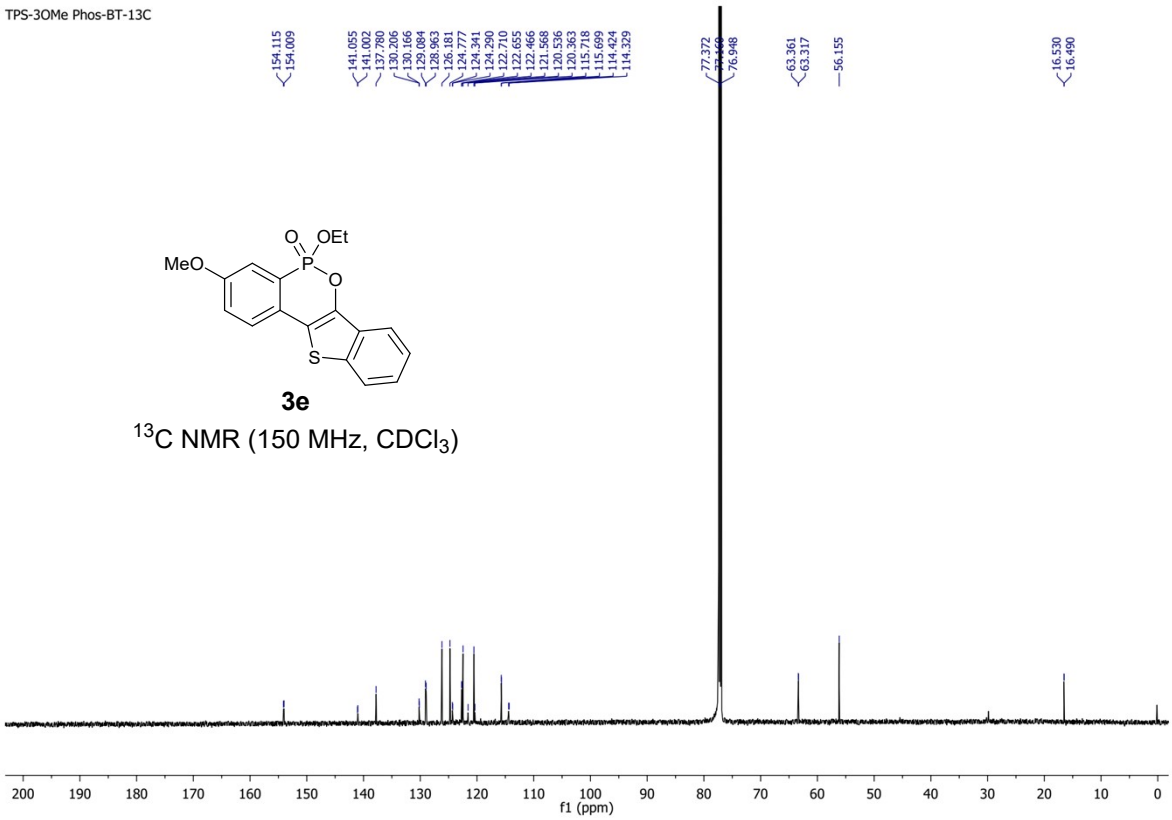
TPS-3OMe Phos-BT-1H



3e

^{1}H NMR (600 MHz, $CDCl_3$)

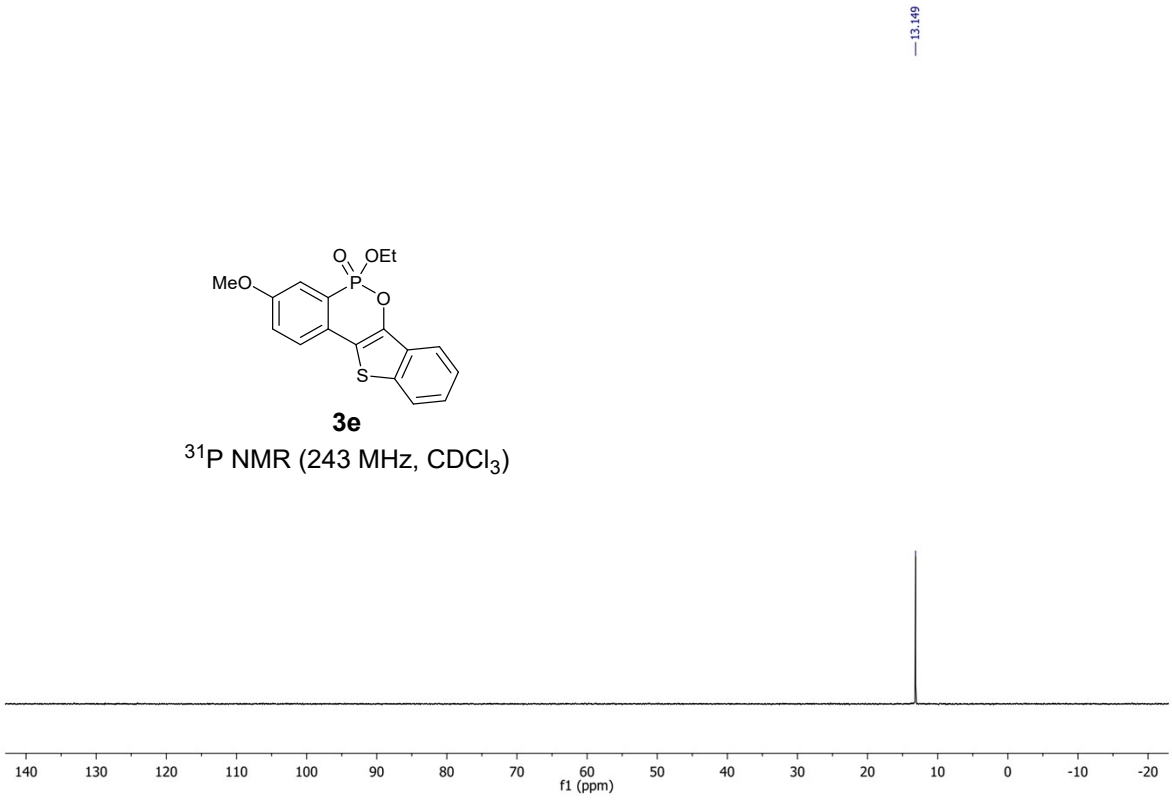
TPS-3OMe Phos-BT-13C



3e

^{13}C NMR (150 MHz, $CDCl_3$)

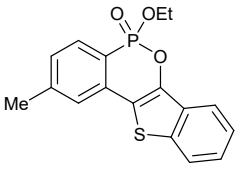
TPS-3OMe Phos-BT-31P



3e

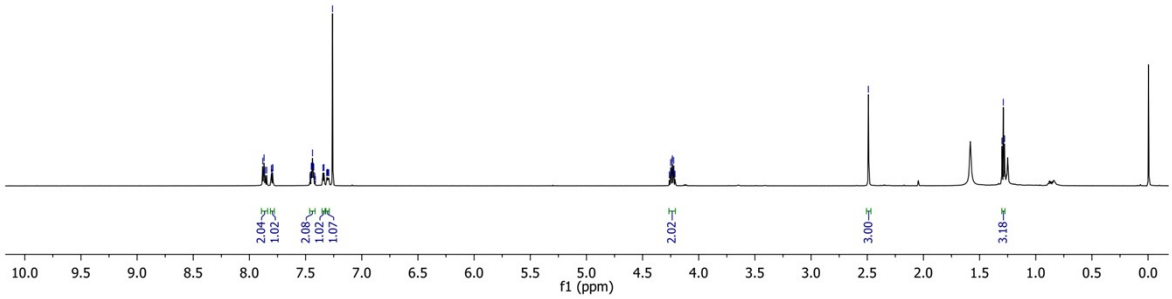
^{31}P NMR (243 MHz, $CDCl_3$)

TPS-4Me Phos-BT-1H

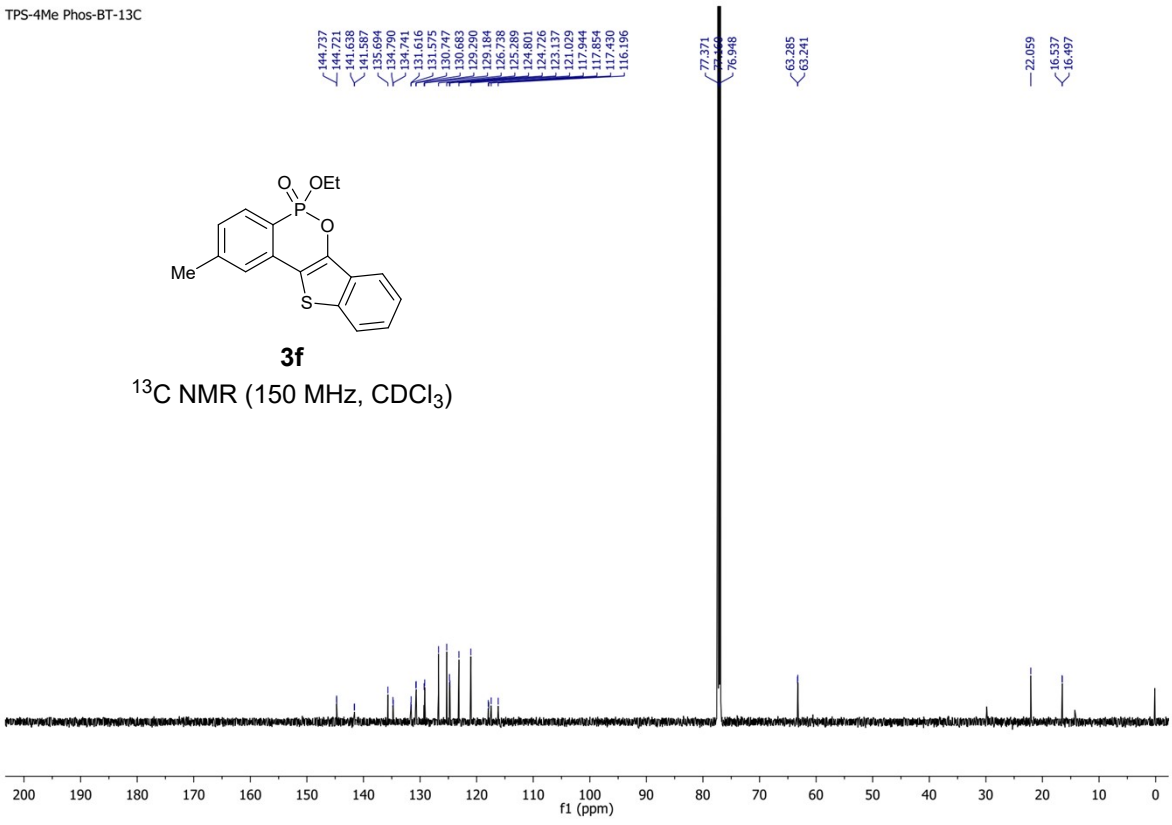


3f

^{1}H NMR (600 MHz, $CDCl_3$)



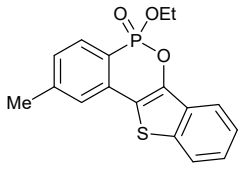
TPS-4Me Phos-BT-13C



3f

^{13}C NMR (150 MHz, $CDCl_3$)

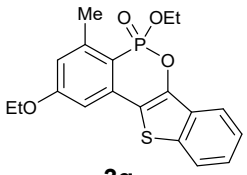
TPS-4Me Phos-BT-31P



3f

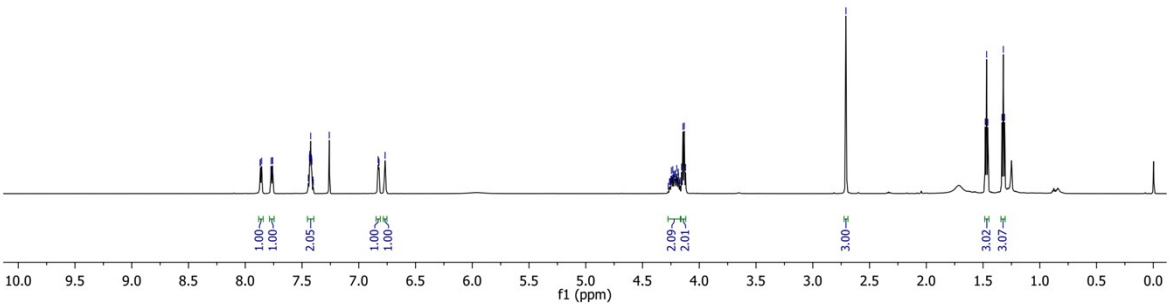
^{31}P NMR (243 MHz, $CDCl_3$)

TPS-Disub Phos-BT-1H

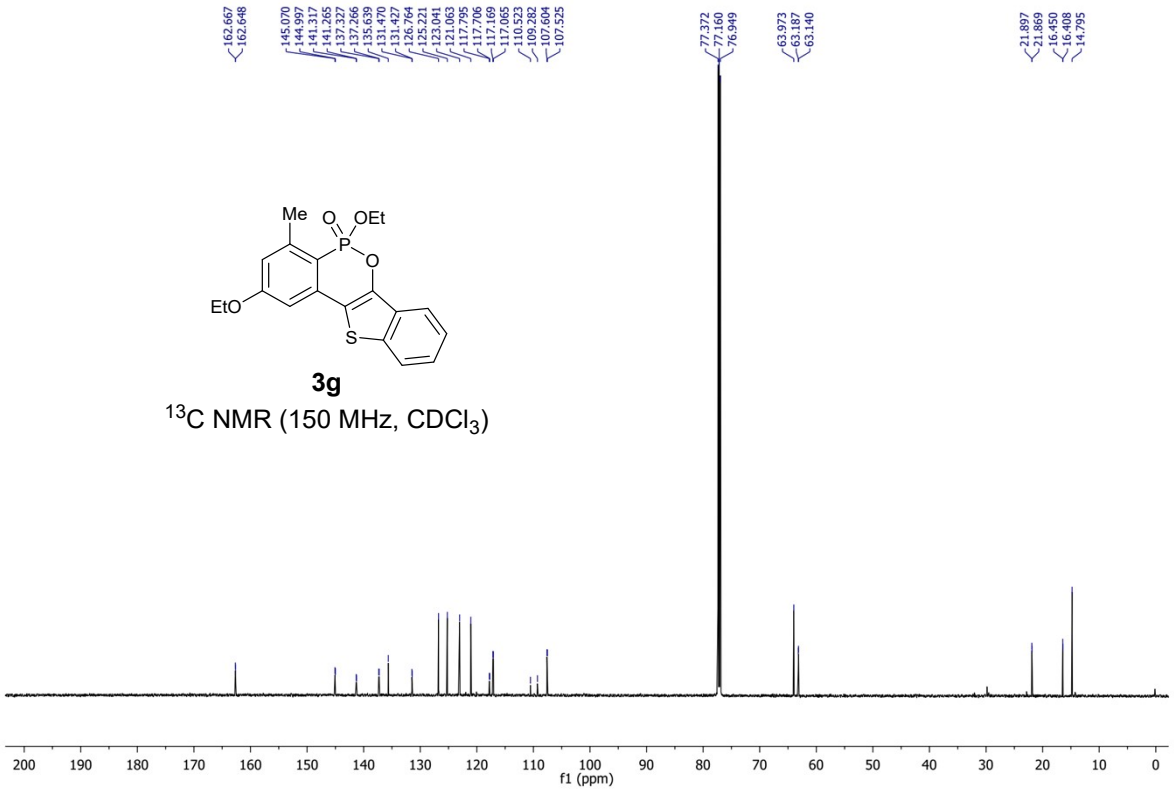


3g

^{1}H NMR (600 MHz, $CDCl_3$)



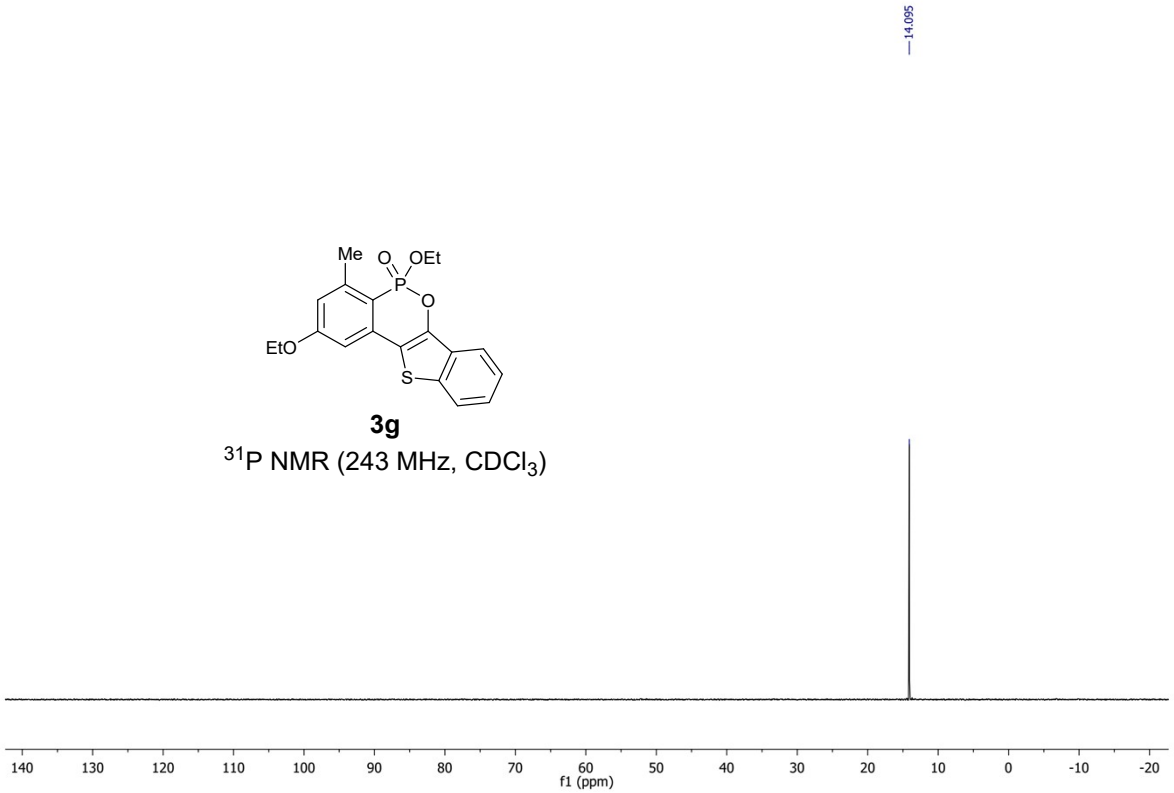
TPS-Disub Phos-BT-13C



3g

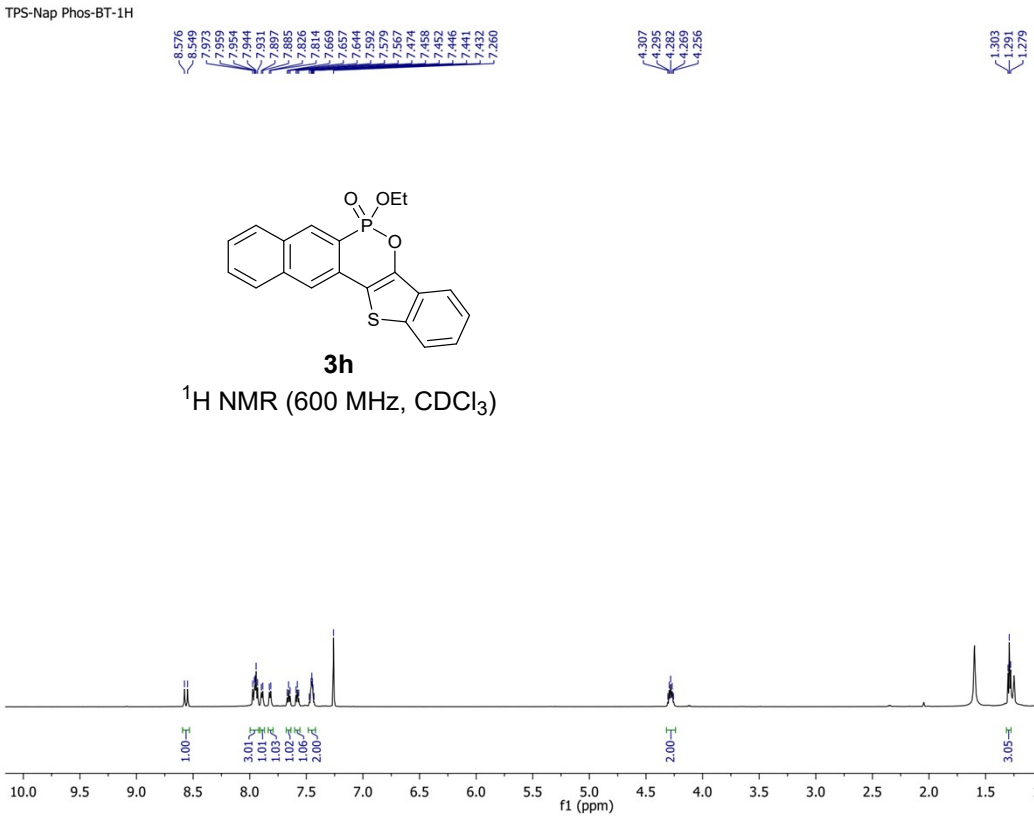
^{13}C NMR (150 MHz, $CDCl_3$)

TPS-Disub Phos-BT-31P



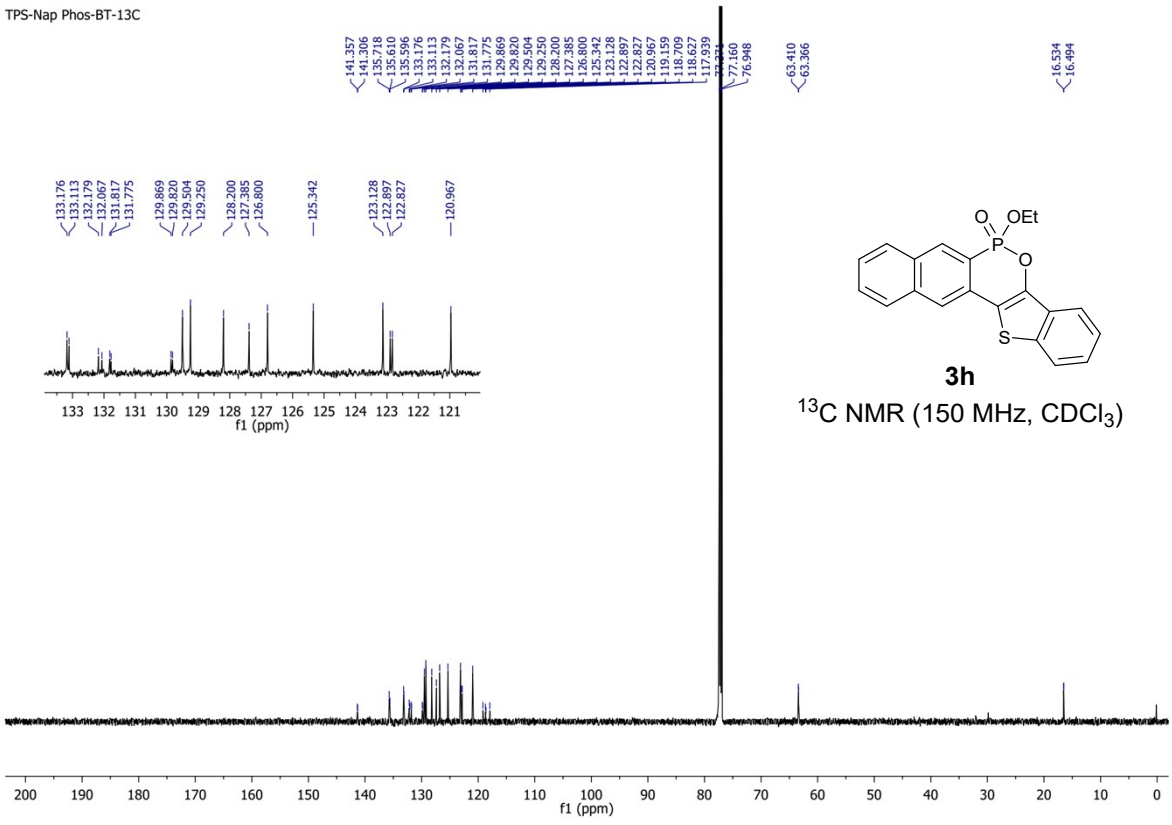
3g

^{31}P NMR (243 MHz, $CDCl_3$)



3h

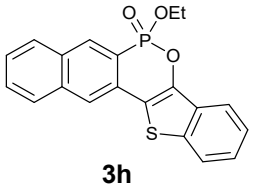
^{1}H NMR (600 MHz, $CDCl_3$)



3h

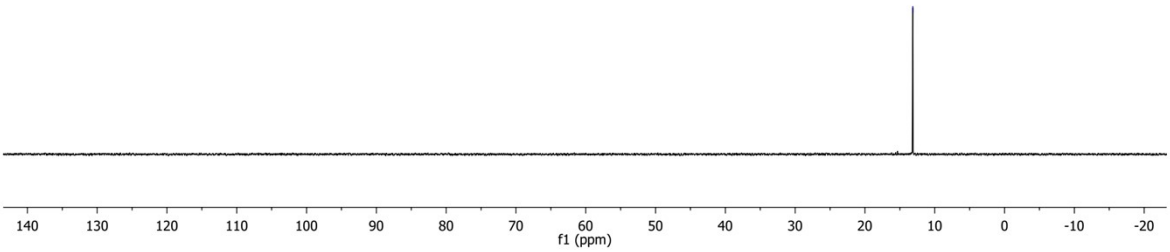
^{13}C NMR (150 MHz, $CDCl_3$)

TPS-Nap Phos-BT-31P

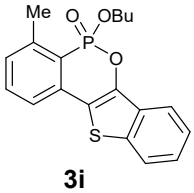


3h

^{31}P NMR (243 MHz, $CDCl_3$)

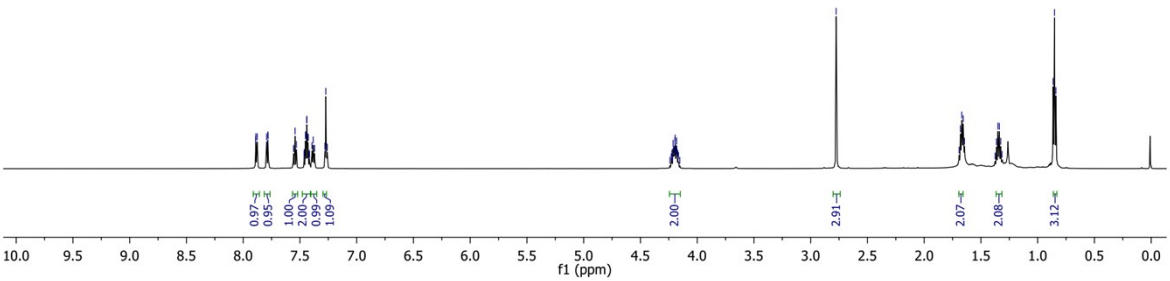


TPS-OBu Phos-BT-1H

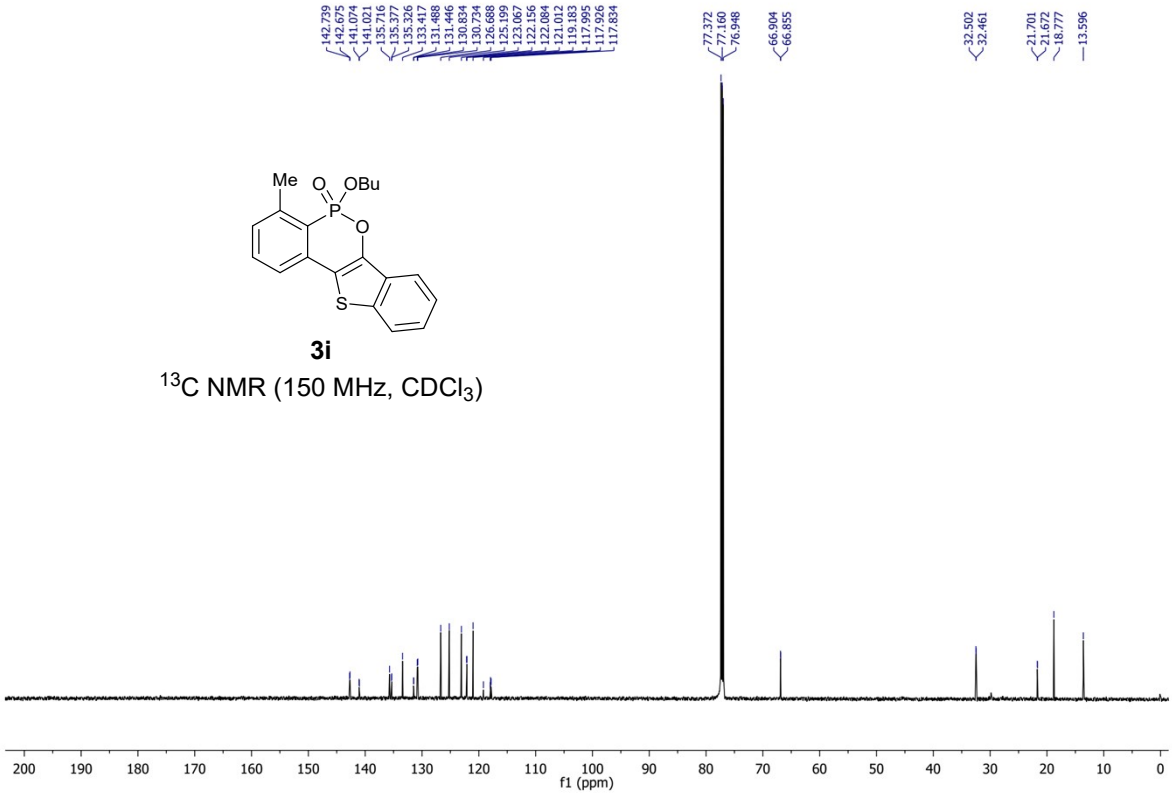


3i

^{1}H NMR (600 MHz, $CDCl_3$)



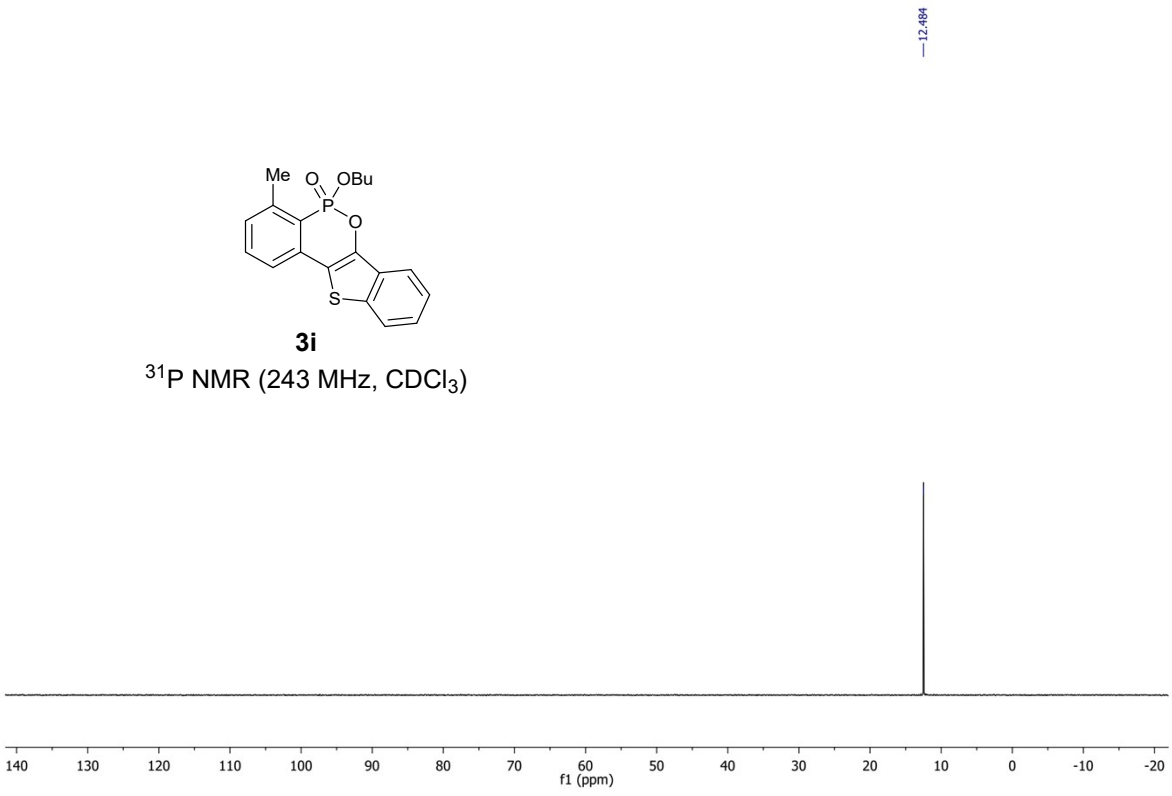
TPS-OBu Phos-BT-13C



3i

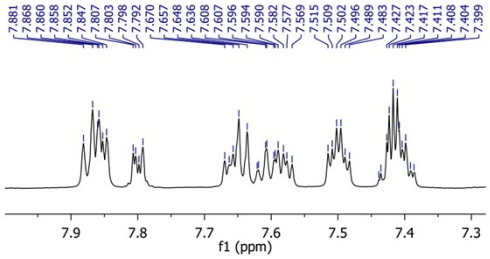
^{13}C NMR (150 MHz, $CDCl_3$)

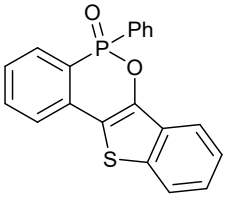
TPS-OBu Phos-BT-31P



3i

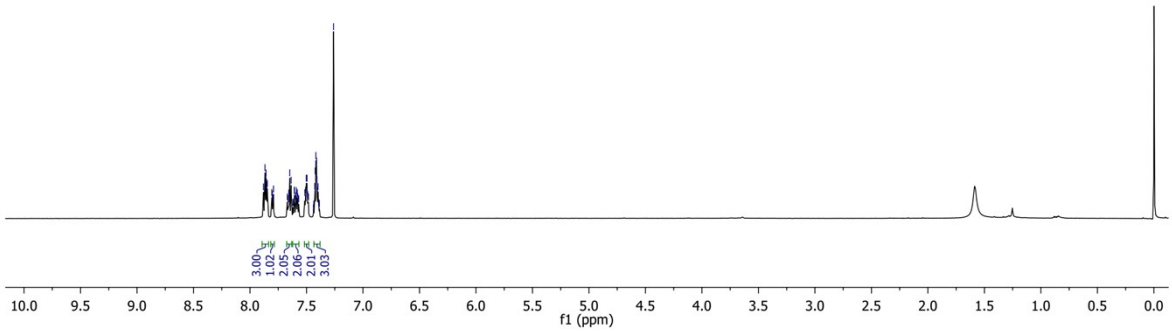
^{31}P NMR (243 MHz, $CDCl_3$)

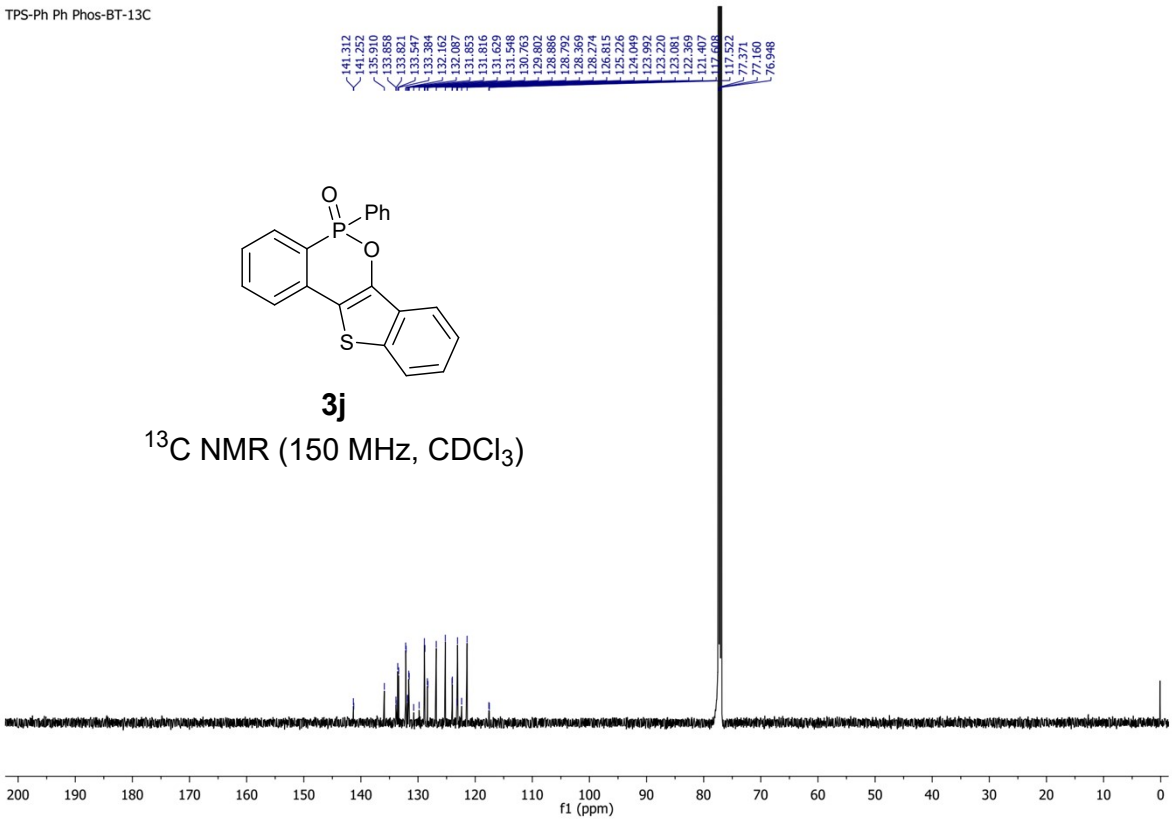




3j

^{1}H NMR (600 MHz, $CDCl_3$)

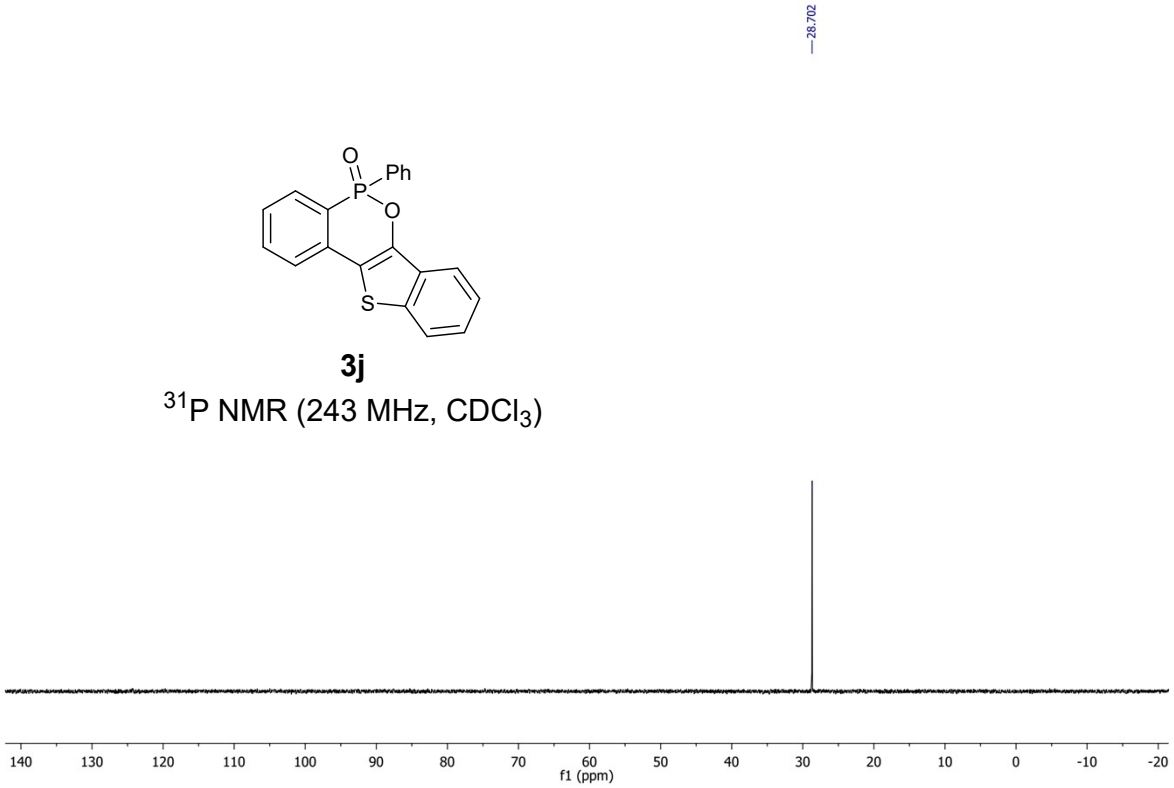




3j

^{13}C NMR (150 MHz, $CDCl_3$)

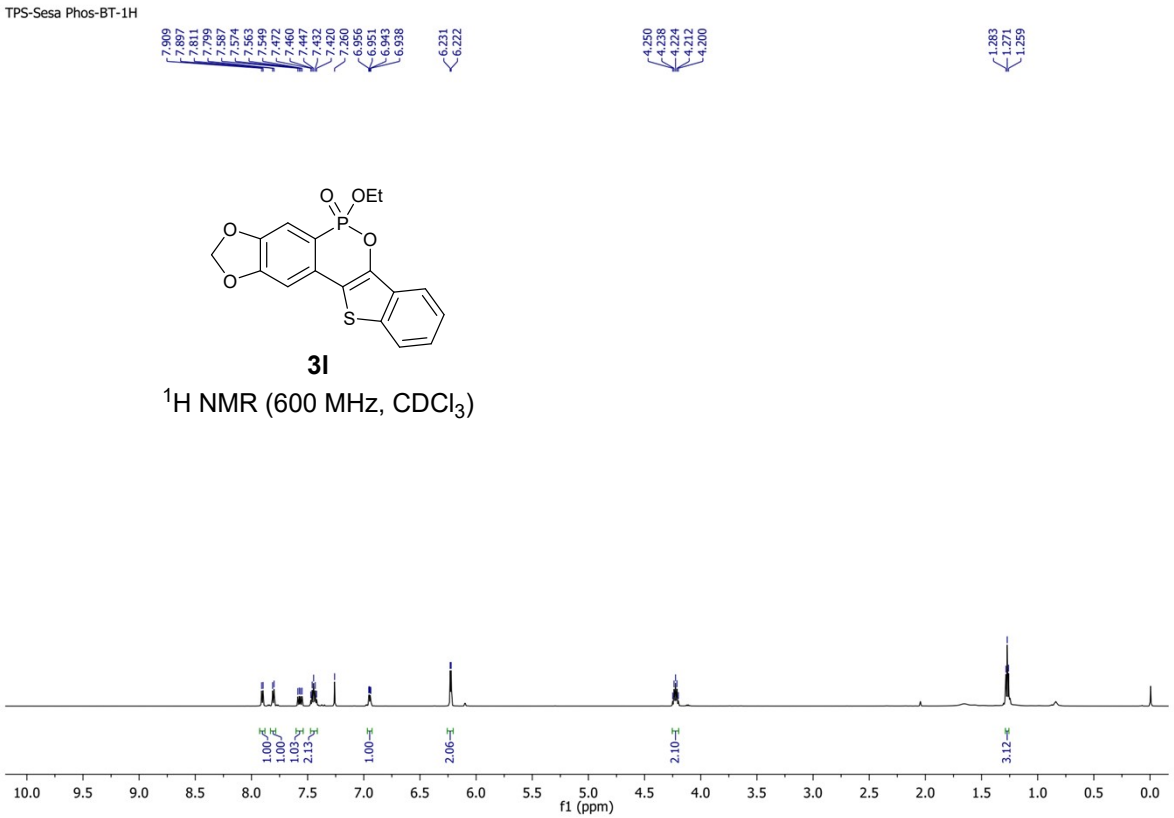
TPS-Ph Ph Phos-BT-31P



3j

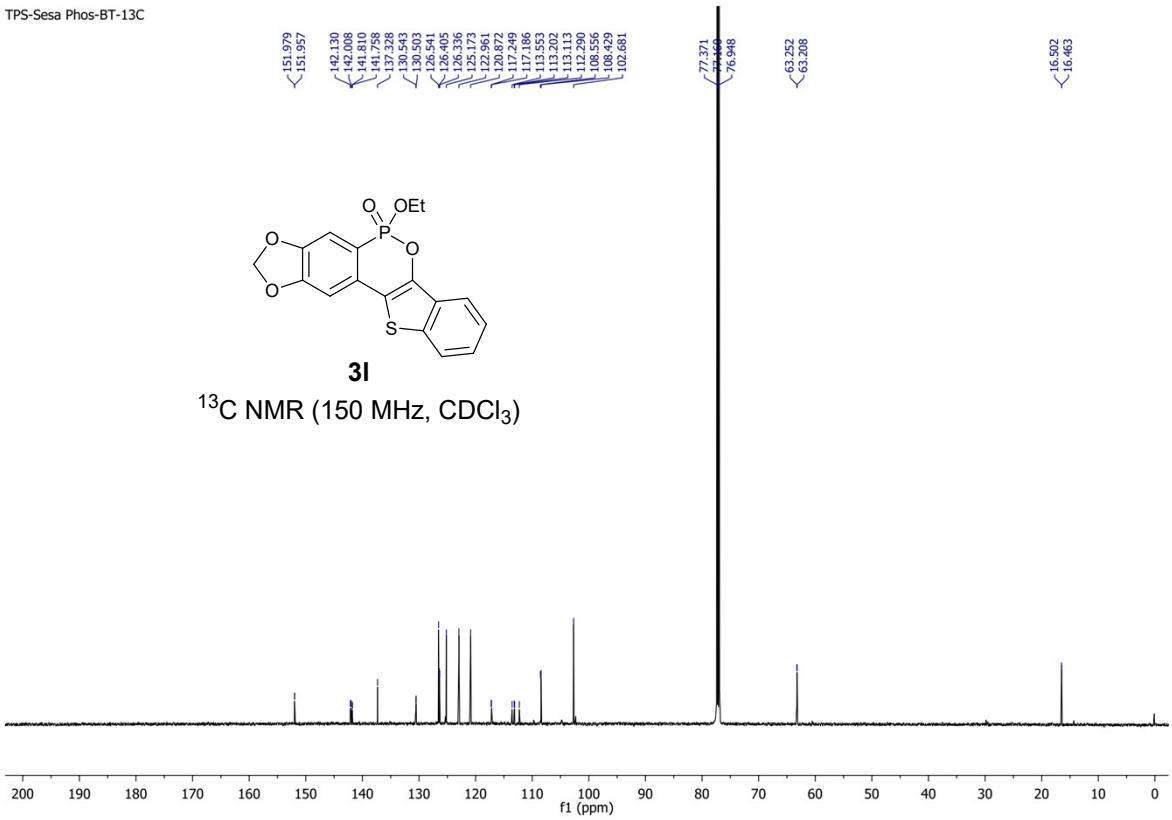
^{31}P NMR (243 MHz, $CDCl_3$)

TPS-Sesa Phos-BT-1H



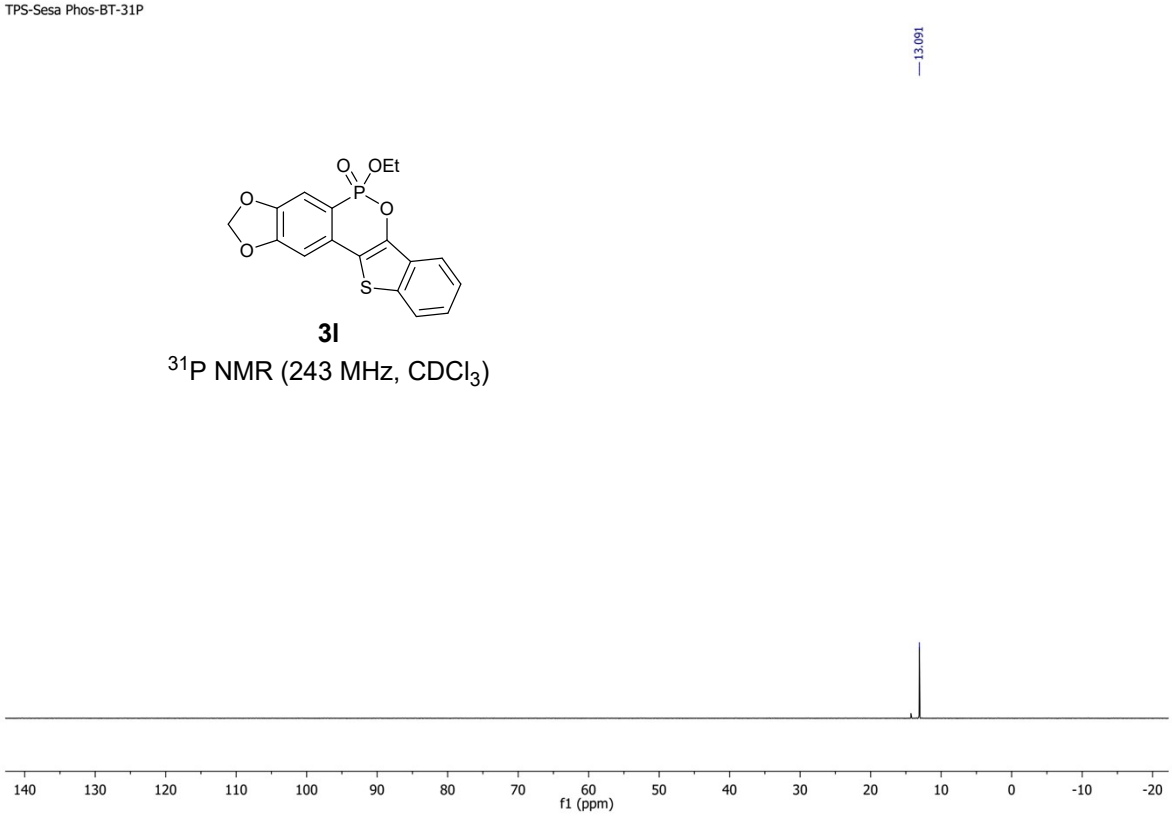
3l

^{1}H NMR (600 MHz, $CDCl_3$)



3l

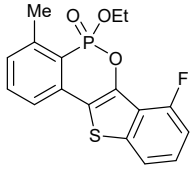
^{13}C NMR (150 MHz, $CDCl_3$)



3l

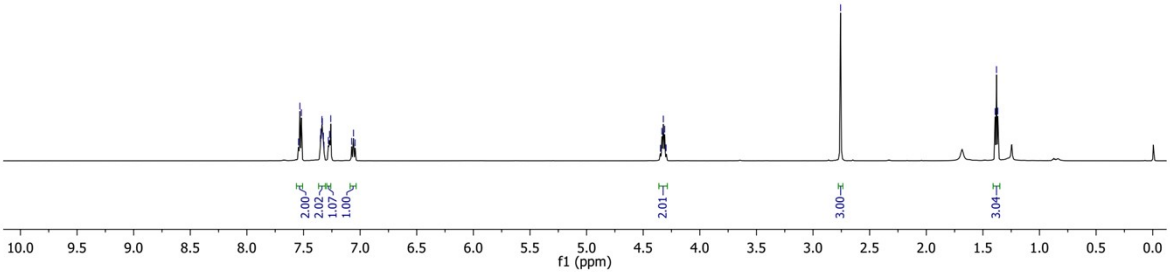
^{31}P NMR (243 MHz, $CDCl_3$)

TPS-Phos-4F BT-1H

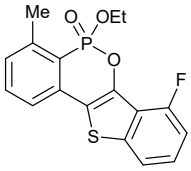


3m

^{1}H NMR (600 MHz, $CDCl_3$)



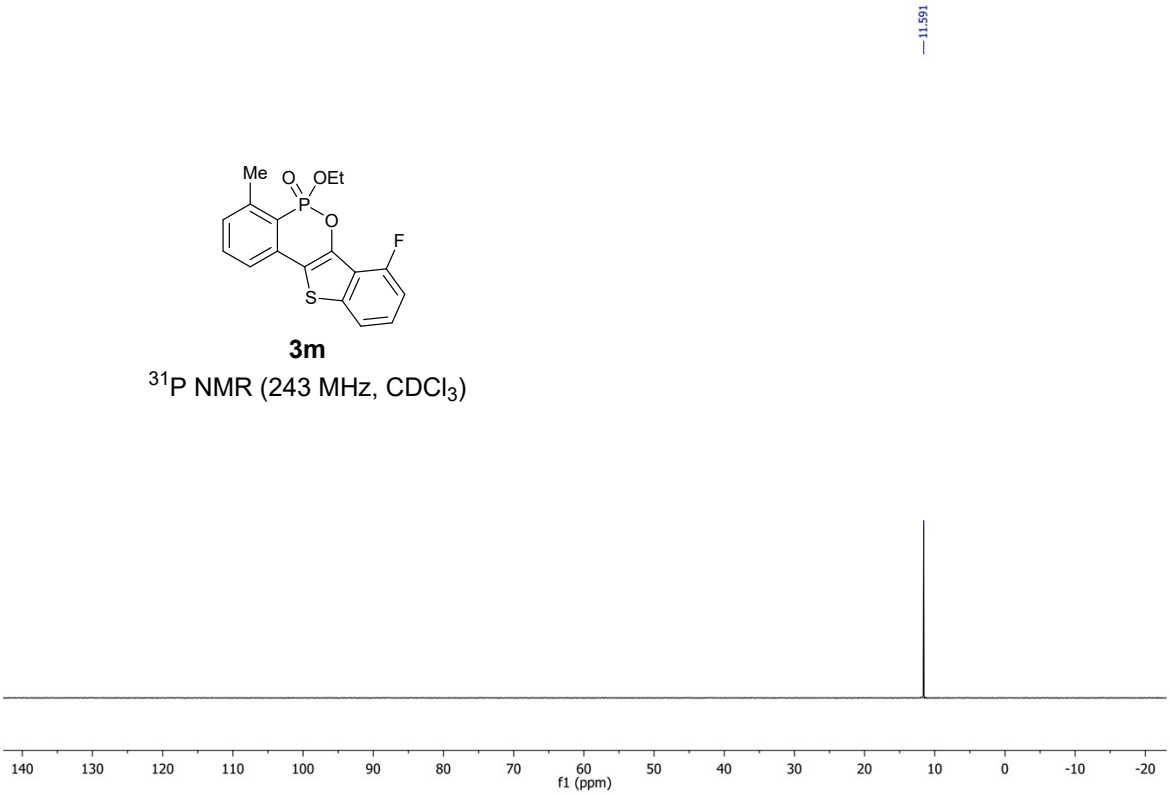
TPS-Phos-4F BT-13C



3m

^{13}C NMR (150 MHz, $CDCl_3$)

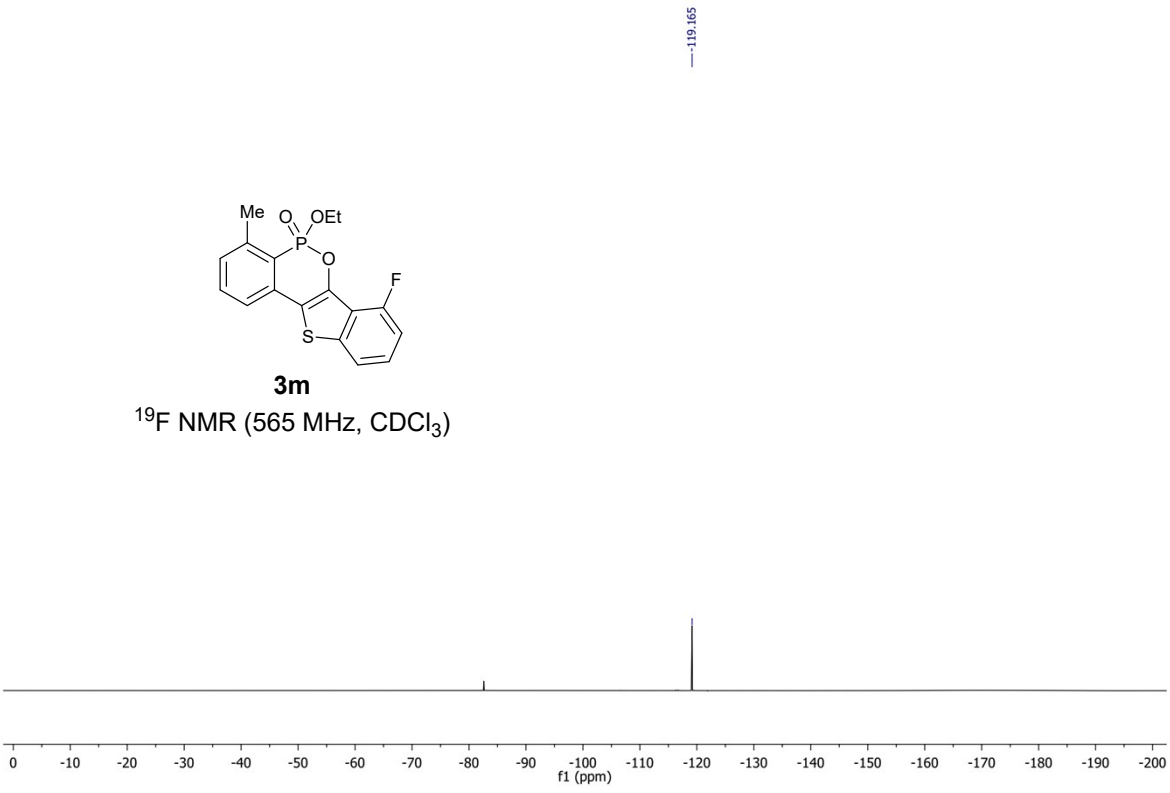
TPS-Phos-4F BT-31P



3m

^{31}P NMR (243 MHz, $CDCl_3$)

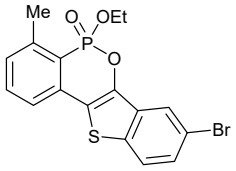
TPS-Phos-4F BT-19F



3m

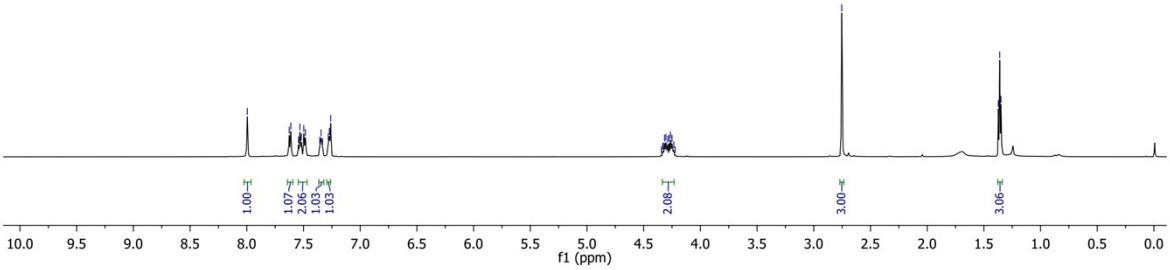
^{19}F NMR (565 MHz, $CDCl_3$)

TPS-Phos-5Br BT-1H

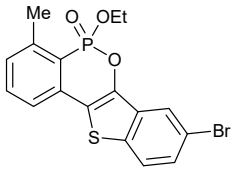


3n

^{1}H NMR (600 MHz, $CDCl_3$)



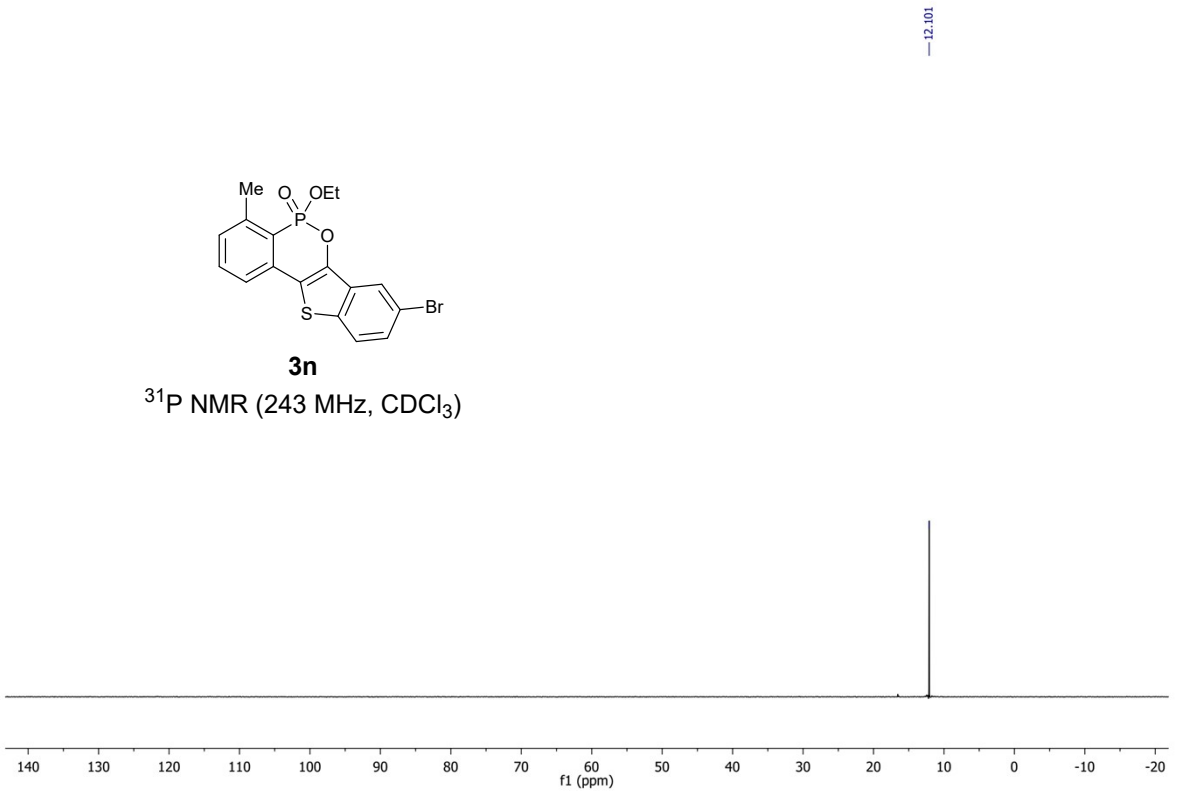
TPS-Phos-5Br BT-13C



3n

^{13}C NMR (150 MHz, $CDCl_3$)

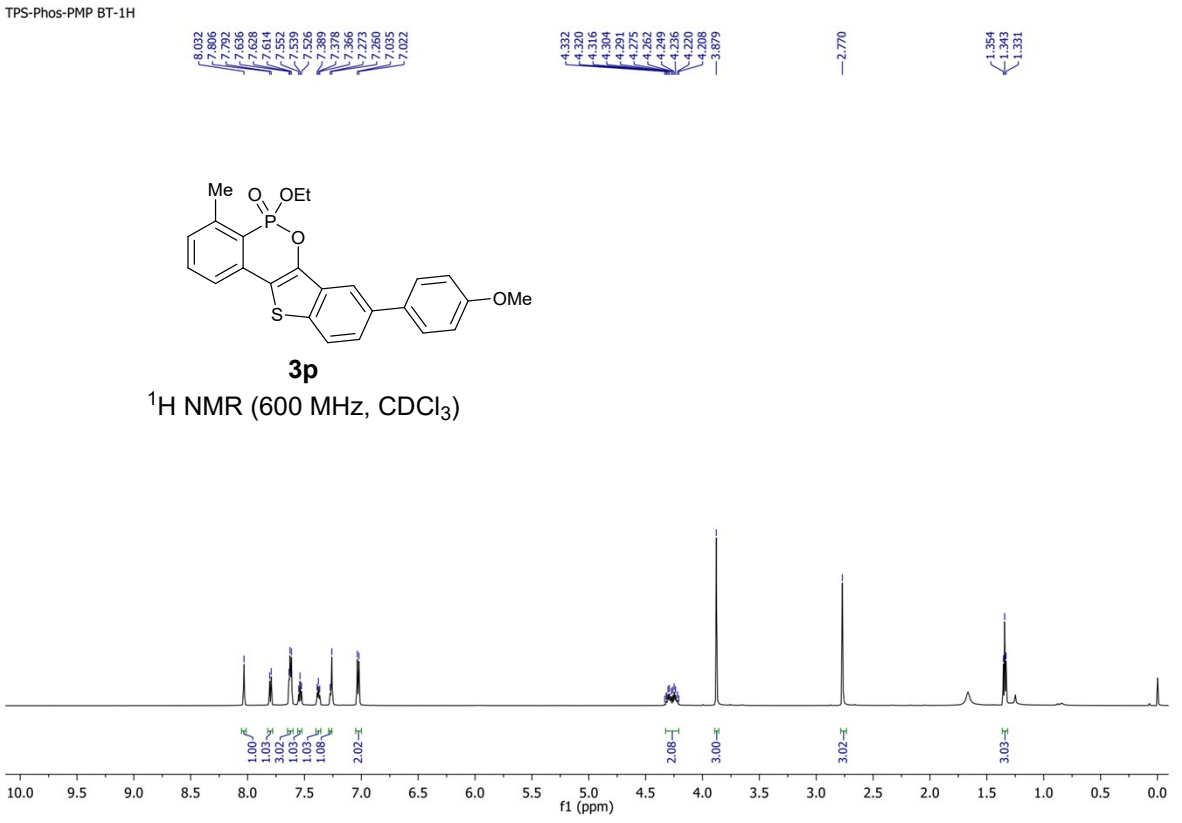
TPS-Phos-5Br BT-31P



3n

^{31}P NMR (243 MHz, $CDCl_3$)

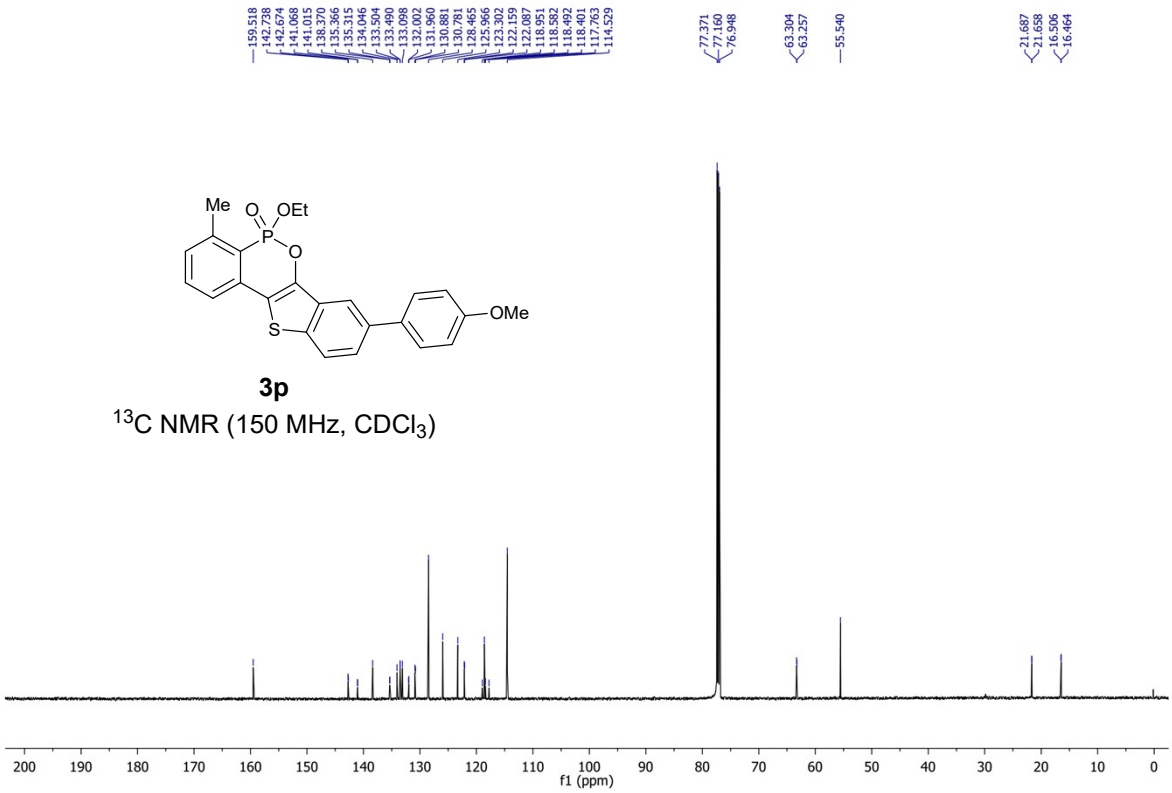
TPS-Phos-PMP BT-1H



3p

^{1}H NMR (600 MHz, $CDCl_3$)

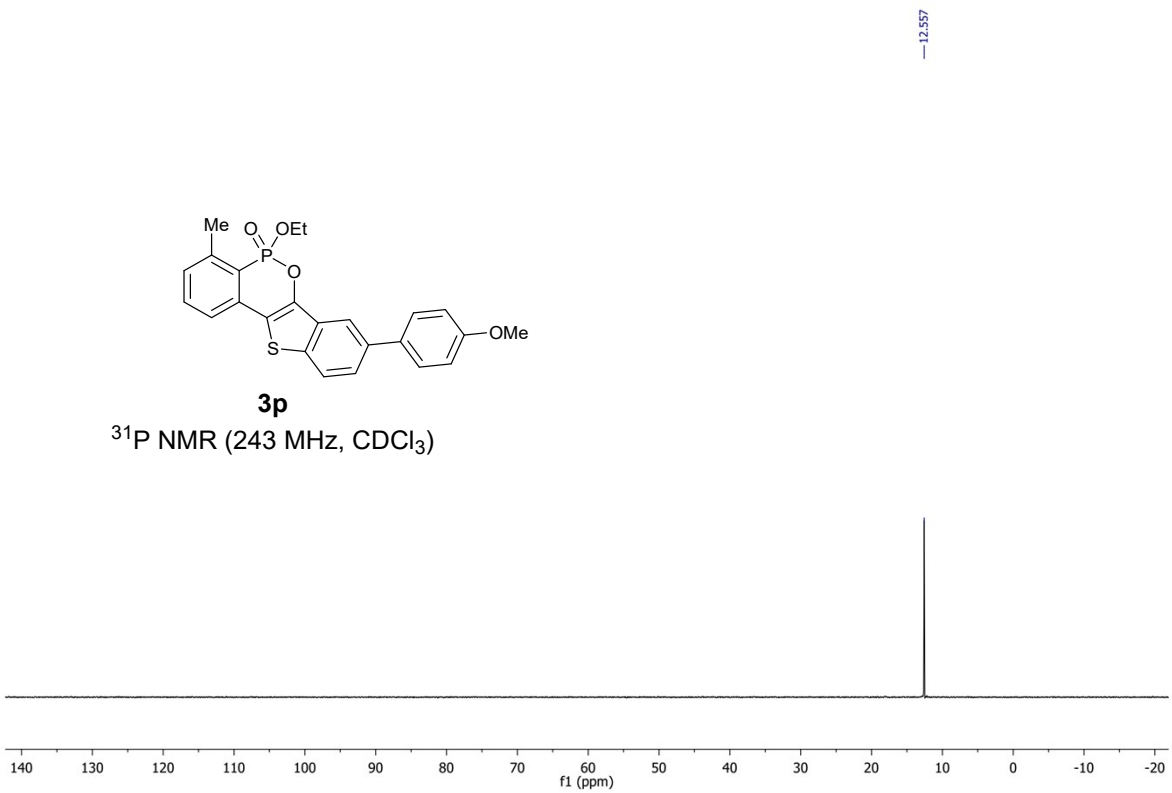
TPS-Phos-PMP BT-13C



3p

^{13}C NMR (150 MHz, $CDCl_3$)

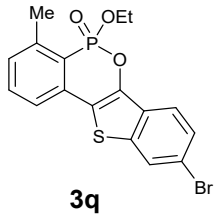
TPS-Phos-PMP BT-31P



3p

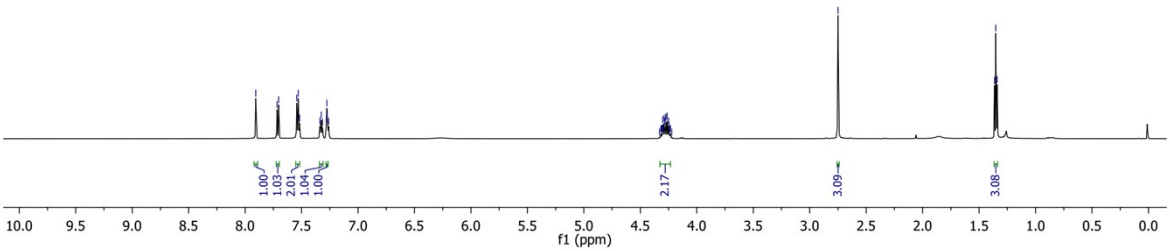
^{31}P NMR (243 MHz, $CDCl_3$)

TPS-Phos-6Br BT-1H

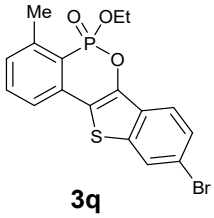


3q

^{1}H NMR (600 MHz, $CDCl_3$)

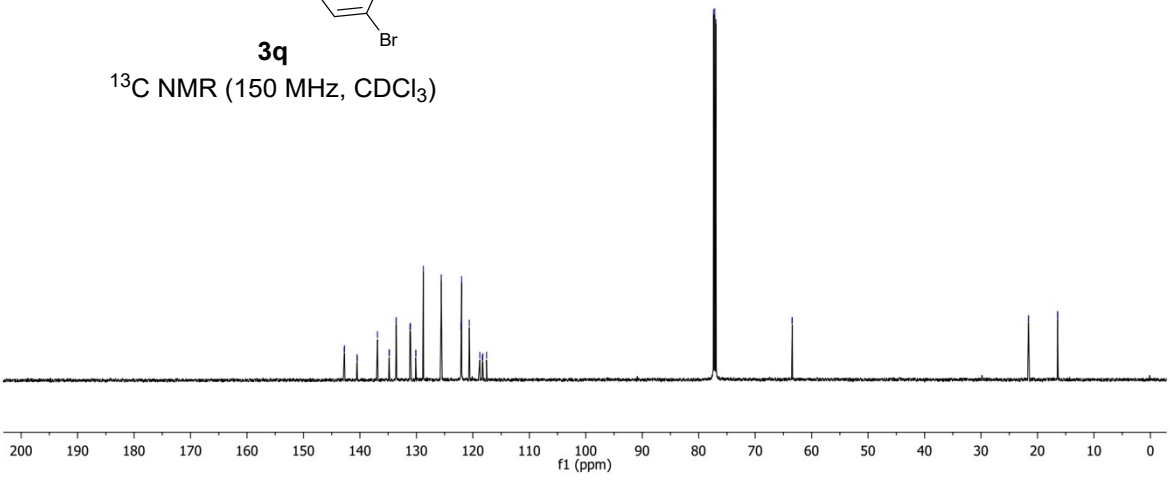


TPS-Phos-6Br BT-13C

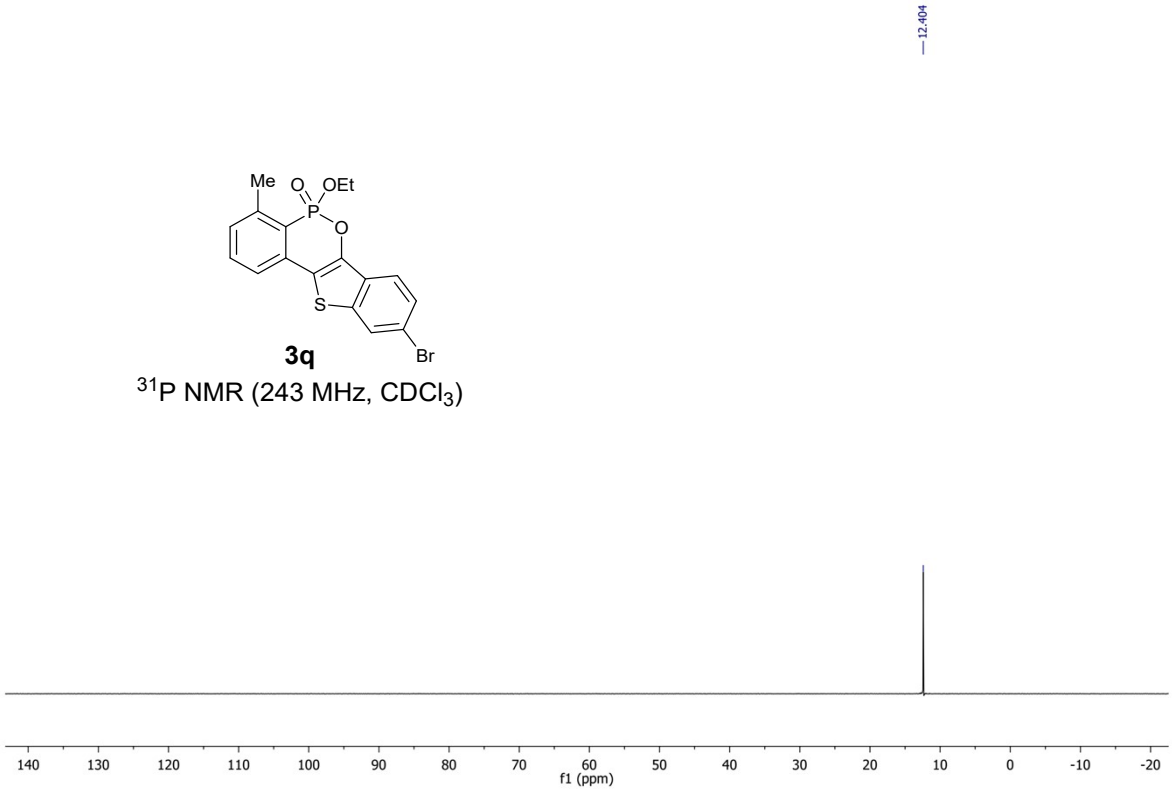


3q

^{13}C NMR (150 MHz, $CDCl_3$)



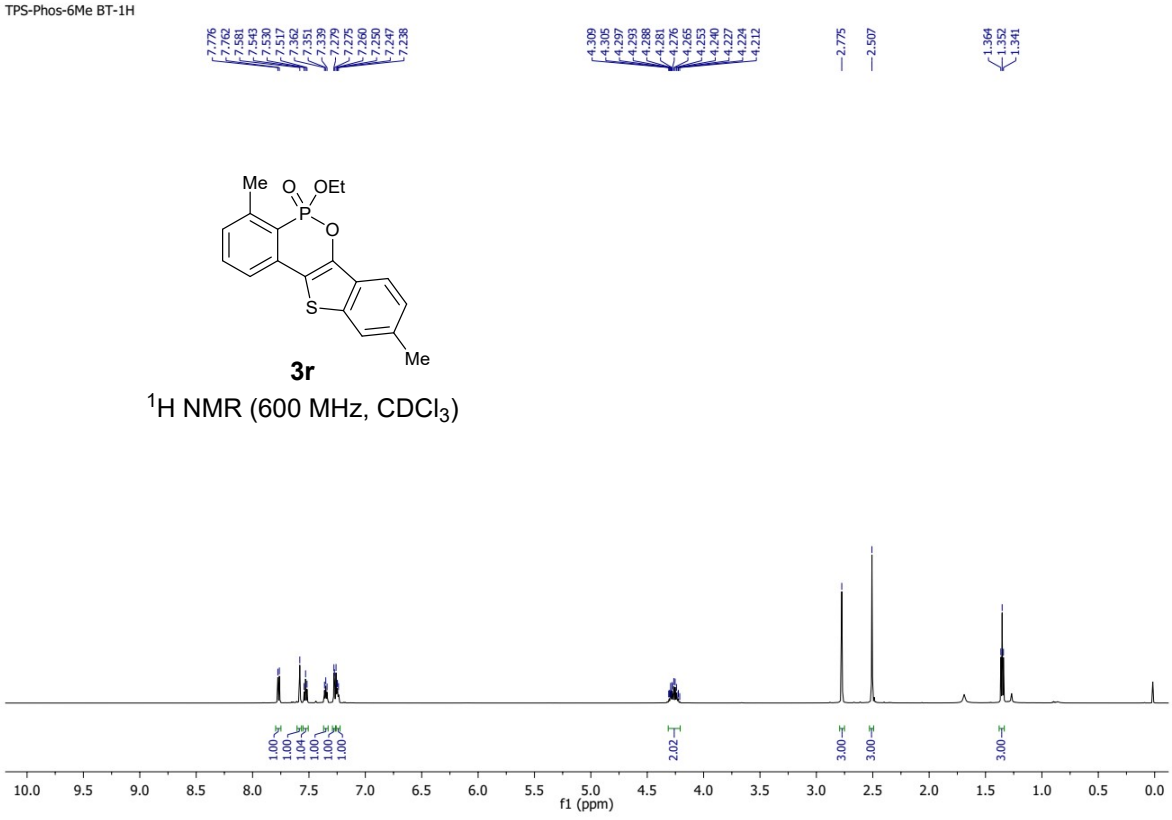
TPS-Phos-6Br BT-31P



3q

^{31}P NMR (243 MHz, $CDCl_3$)

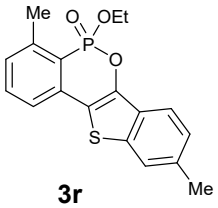
TPS-Phos-6Me BT-1H



3r

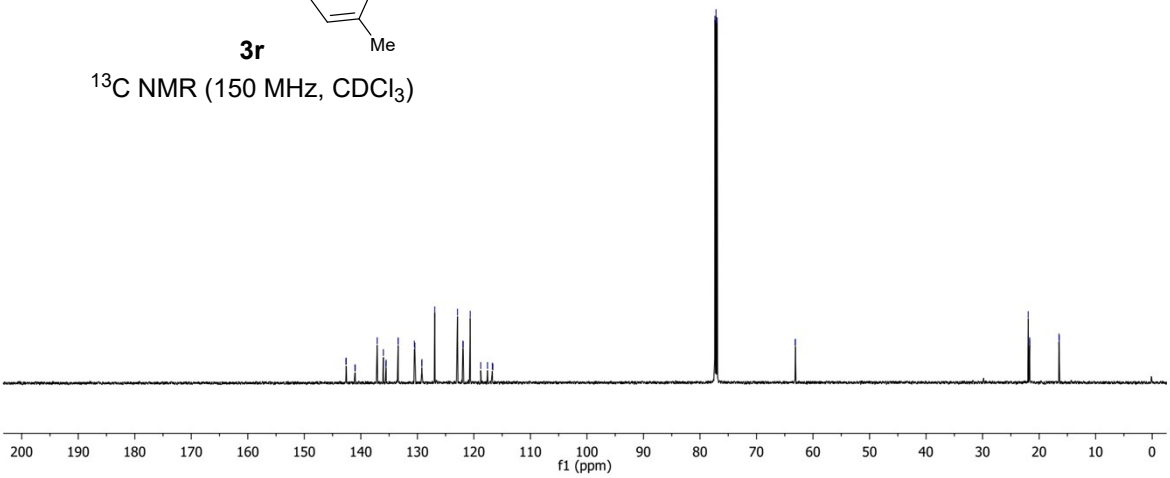
^{1}H NMR (600 MHz, $CDCl_3$)

TPS-Phos-6Me BT-13C

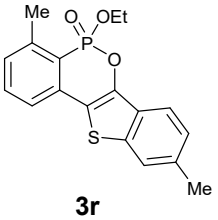


3r

^{13}C NMR (150 MHz, $CDCl_3$)

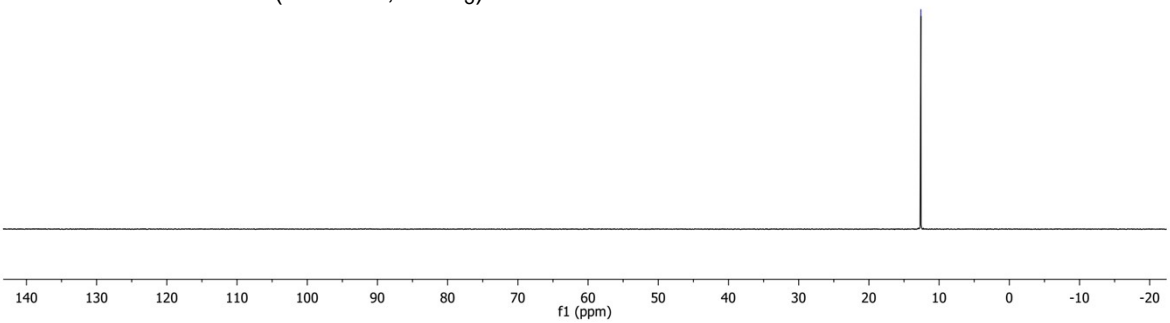


TPS-Phos-6Me BT-31P

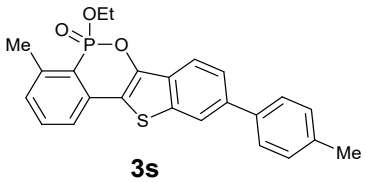


3r

^{31}P NMR (243 MHz, $CDCl_3$)

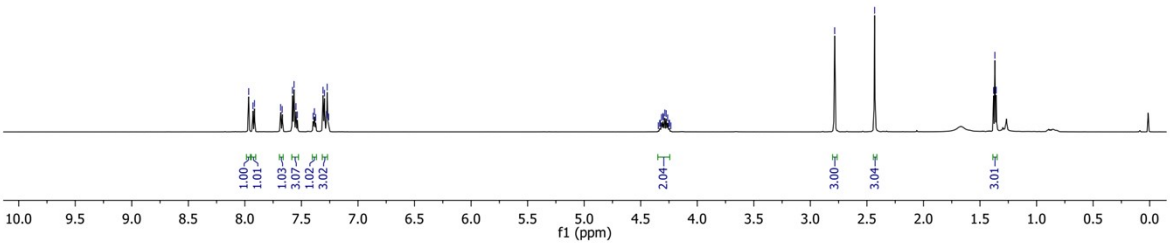


TPS-Phos-6Tolyl BT-1H

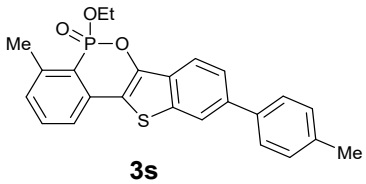


3s

^{1}H NMR (600 MHz, $CDCl_3$)



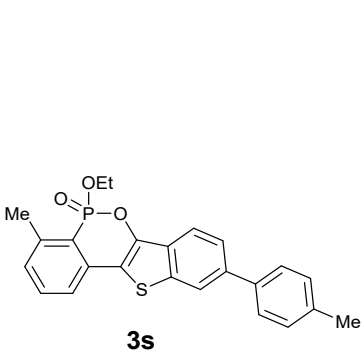
TPS-Phos-6Tolyl BT-13C



3s

^{13}C NMR (150 MHz, $CDCl_3$)

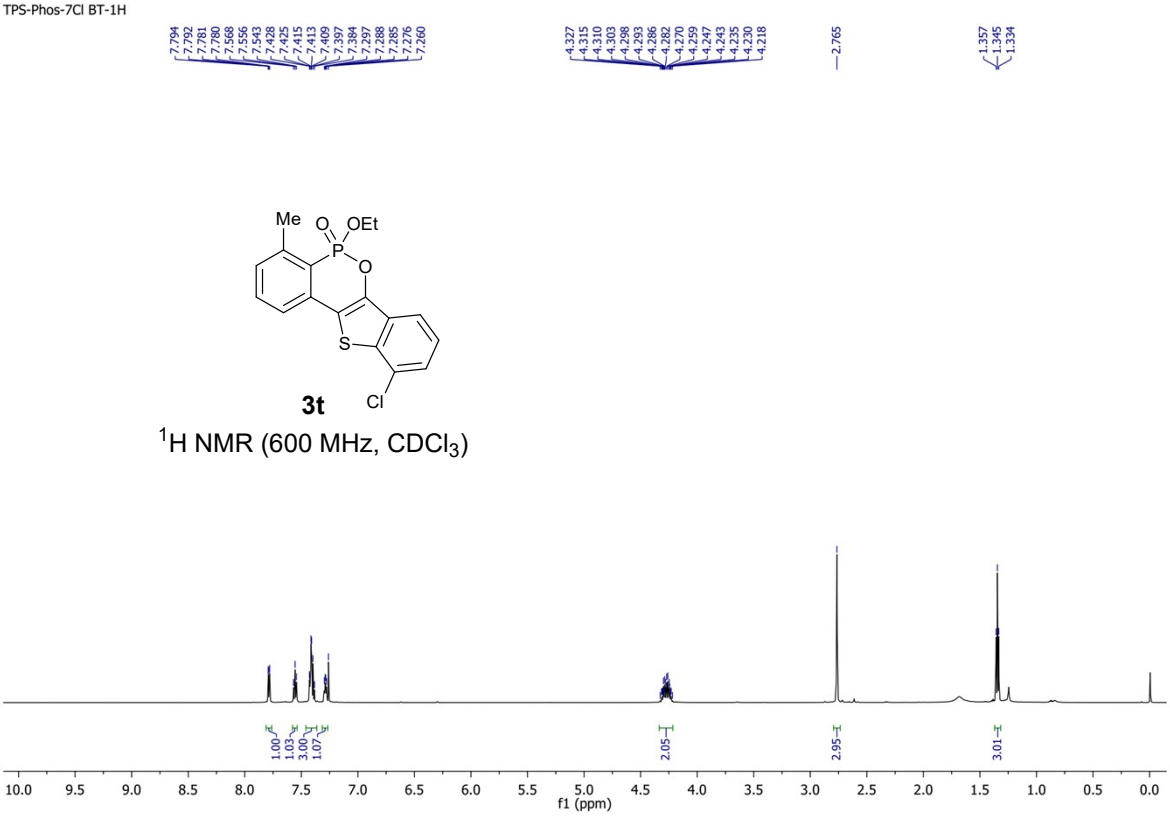
TPS-Phos-6Tolyl BT-31P



3s

^{31}P NMR (243 MHz, $CDCl_3$)

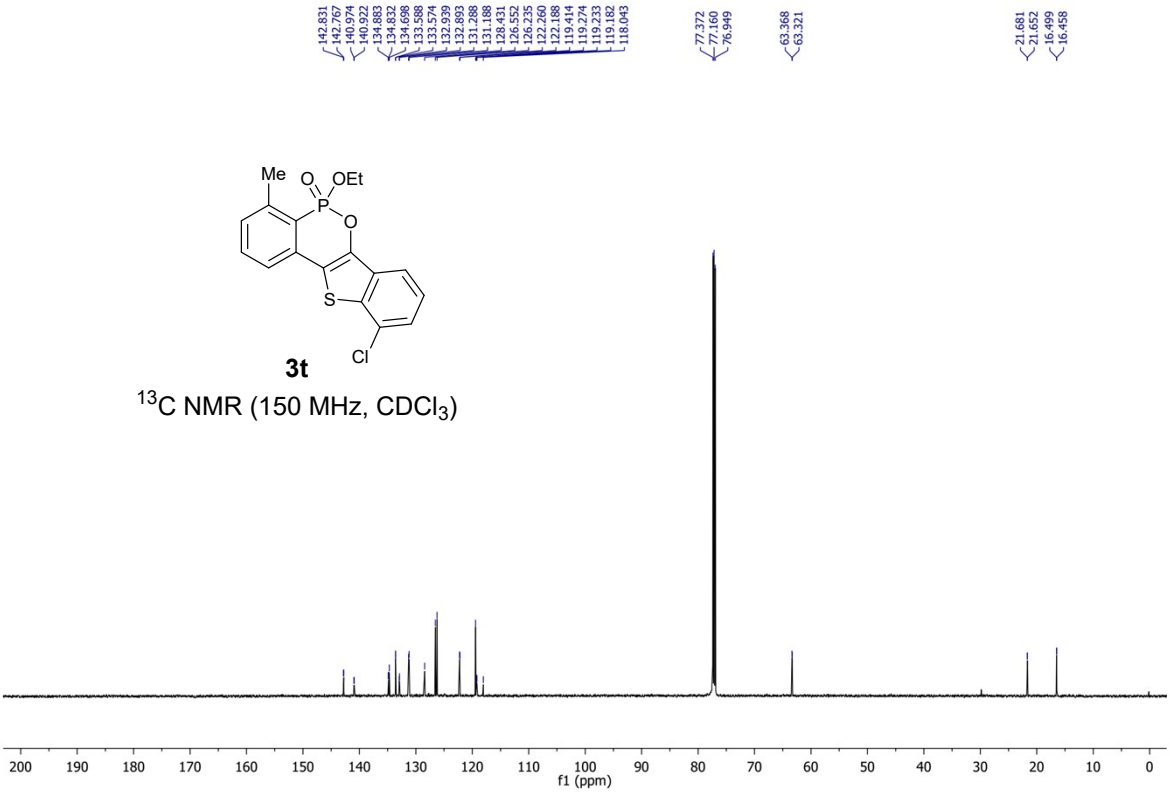
TPS-Phos-7Cl BT-1H



3t

^{1}H NMR (600 MHz, $CDCl_3$)

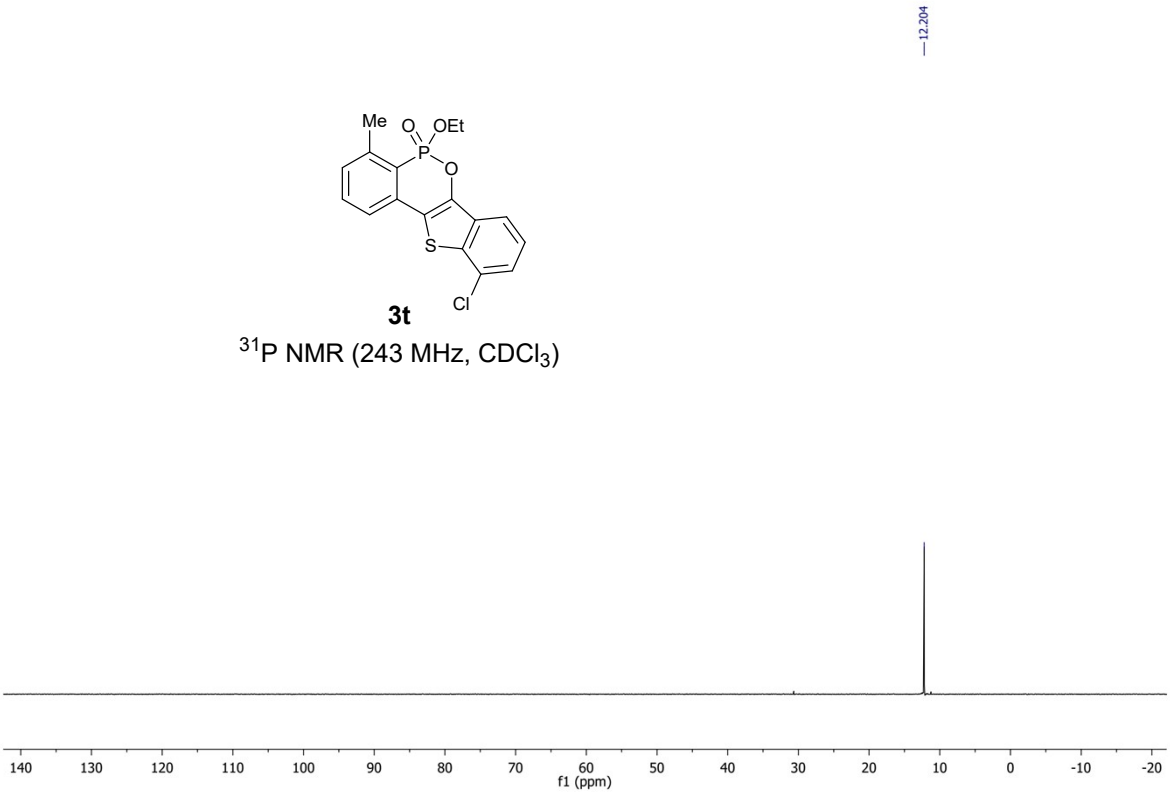
TPS-Phos-7Cl BT-13C



3t

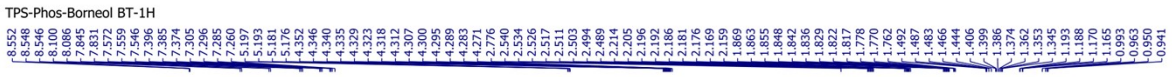
^{13}C NMR (150 MHz, $CDCl_3$)

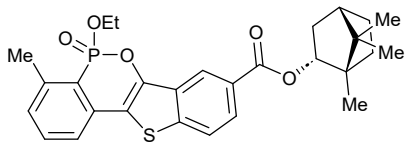
TPS-Phos-7Cl BT-31P



3t

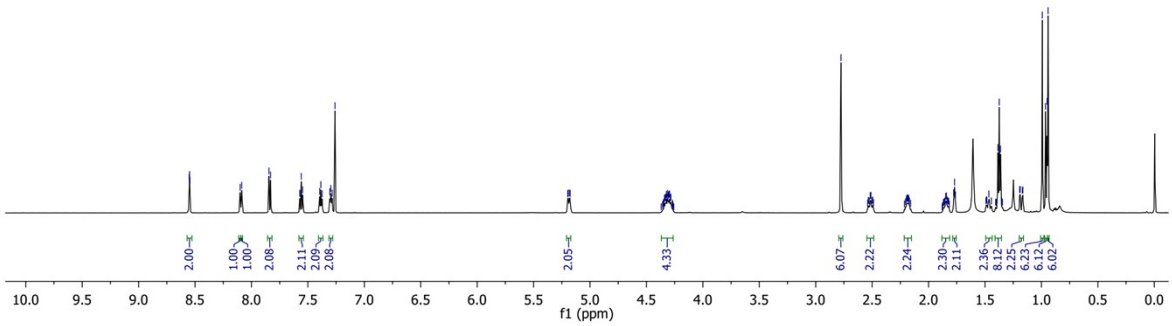
^{31}P NMR (243 MHz, $CDCl_3$)

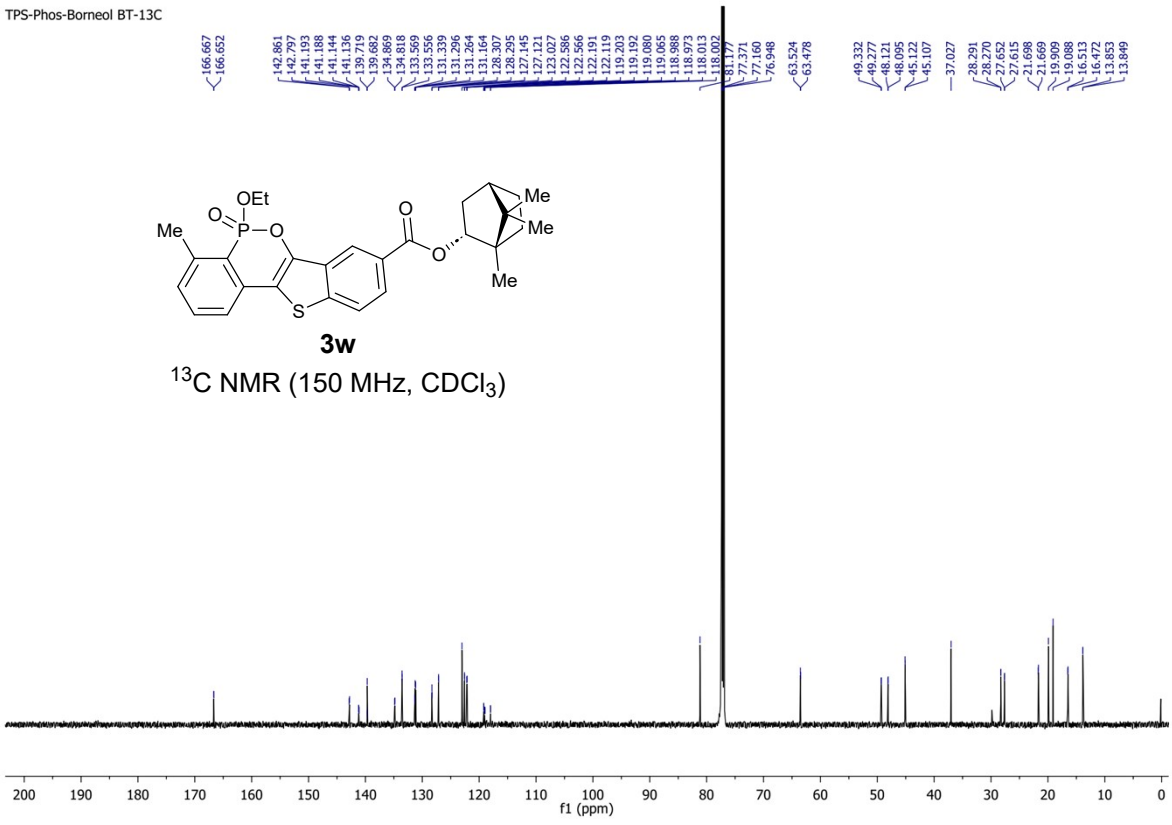




3w

^{1}H NMR (600 MHz, $CDCl_3$)

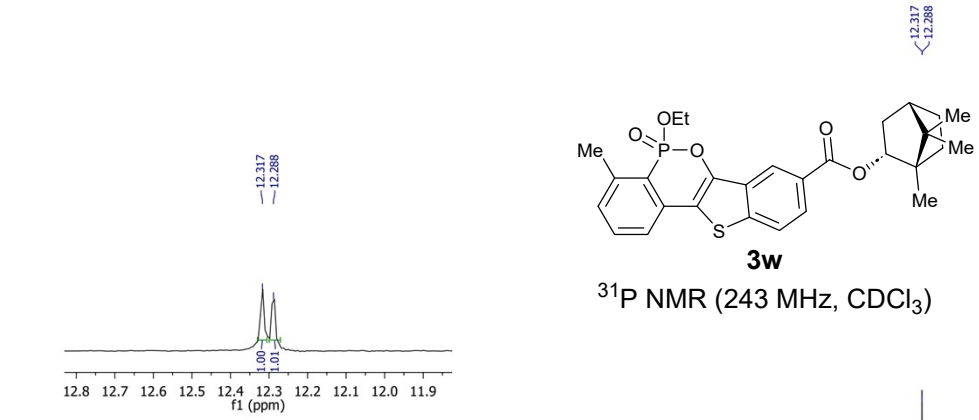




3w

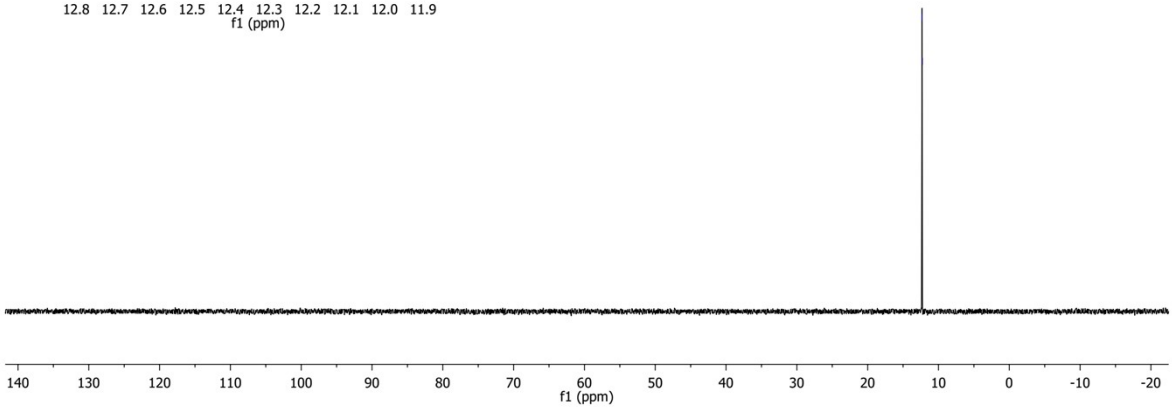
^{13}C NMR (150 MHz, $CDCl_3$)

TPS-Phos-Borneol BT-31P

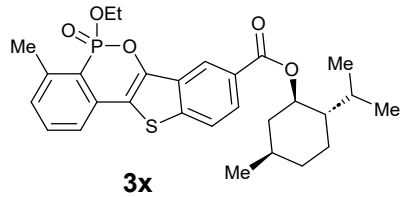


3w

^{31}P NMR (243 MHz, $CDCl_3$)

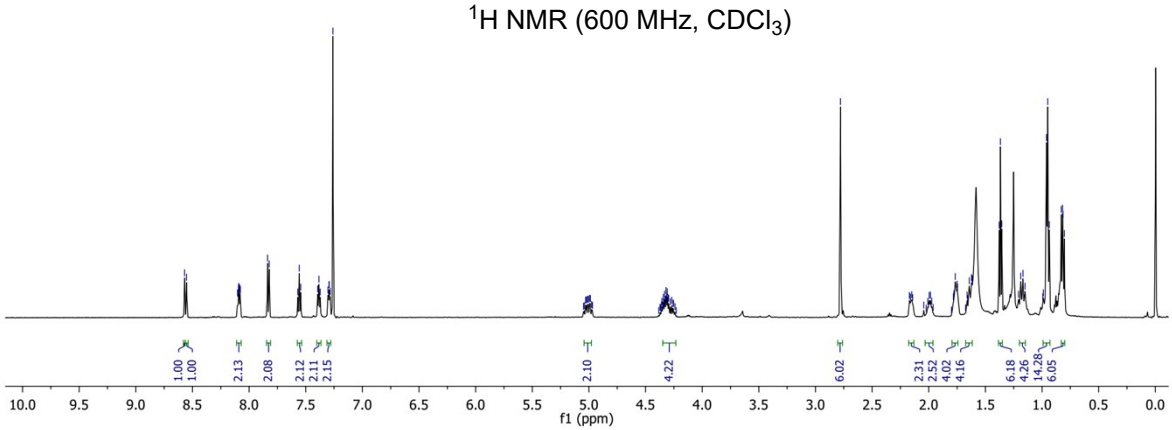


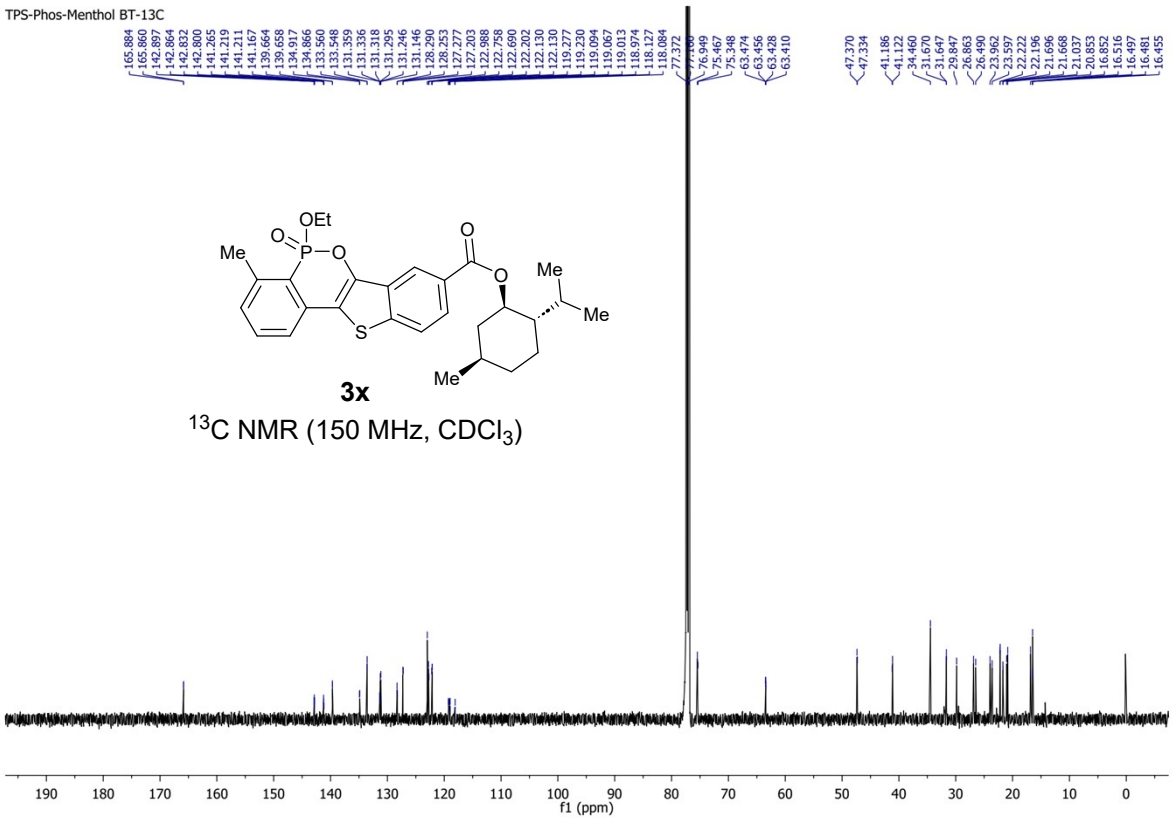
TPS-Phos-Menthol BT-1H



3x

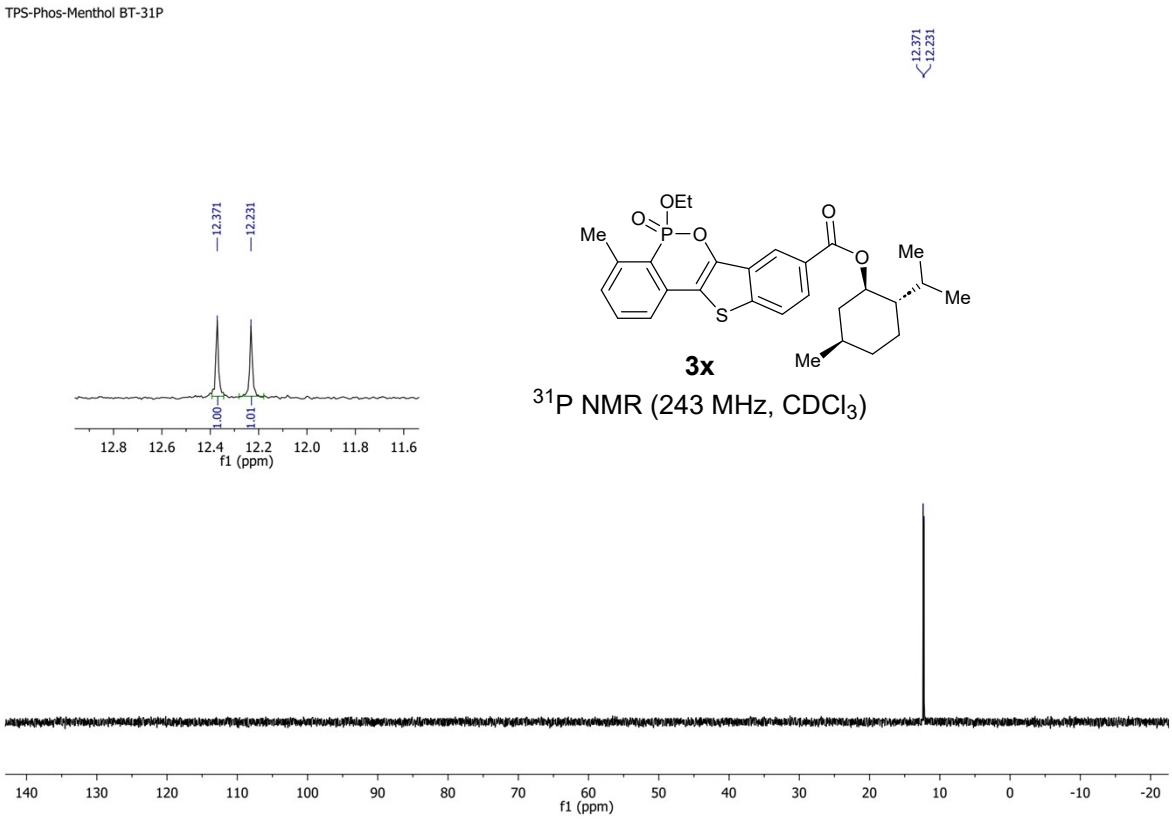
^{1}H NMR (600 MHz, $CDCl_3$)





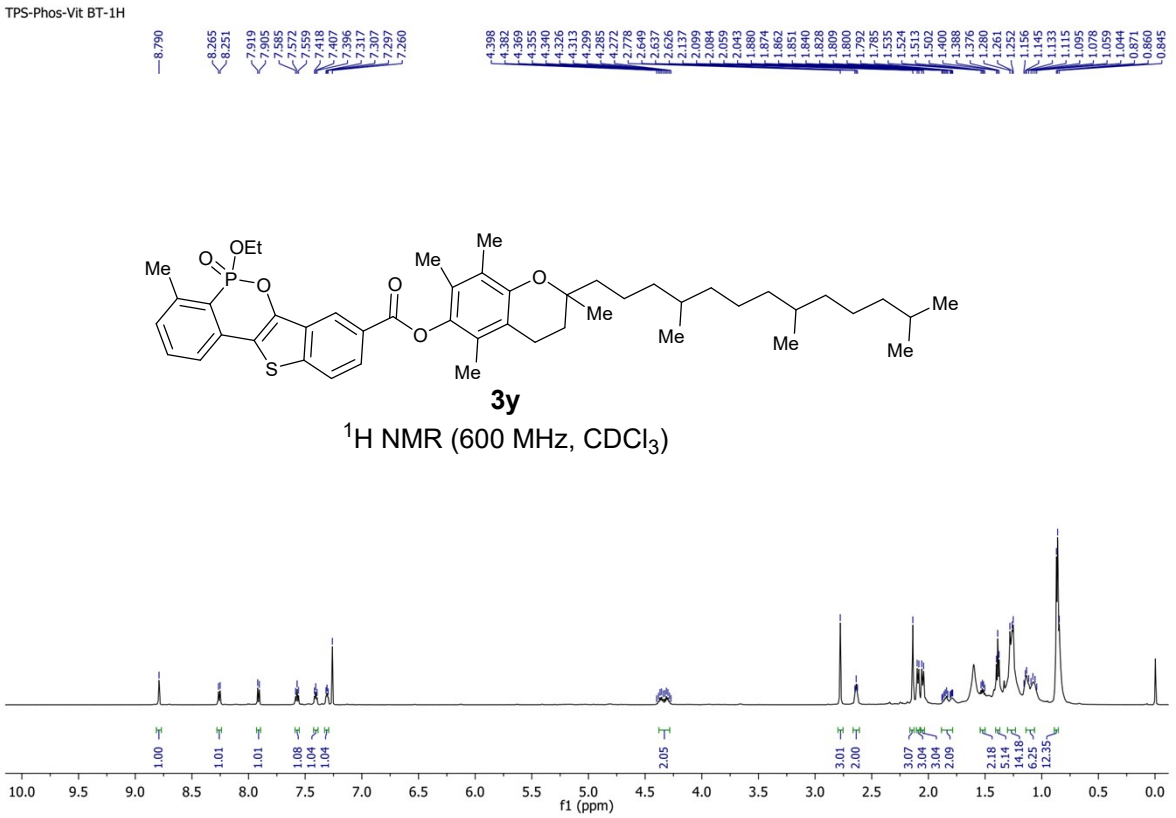
3x

^{13}C NMR (150 MHz, $CDCl_3$)



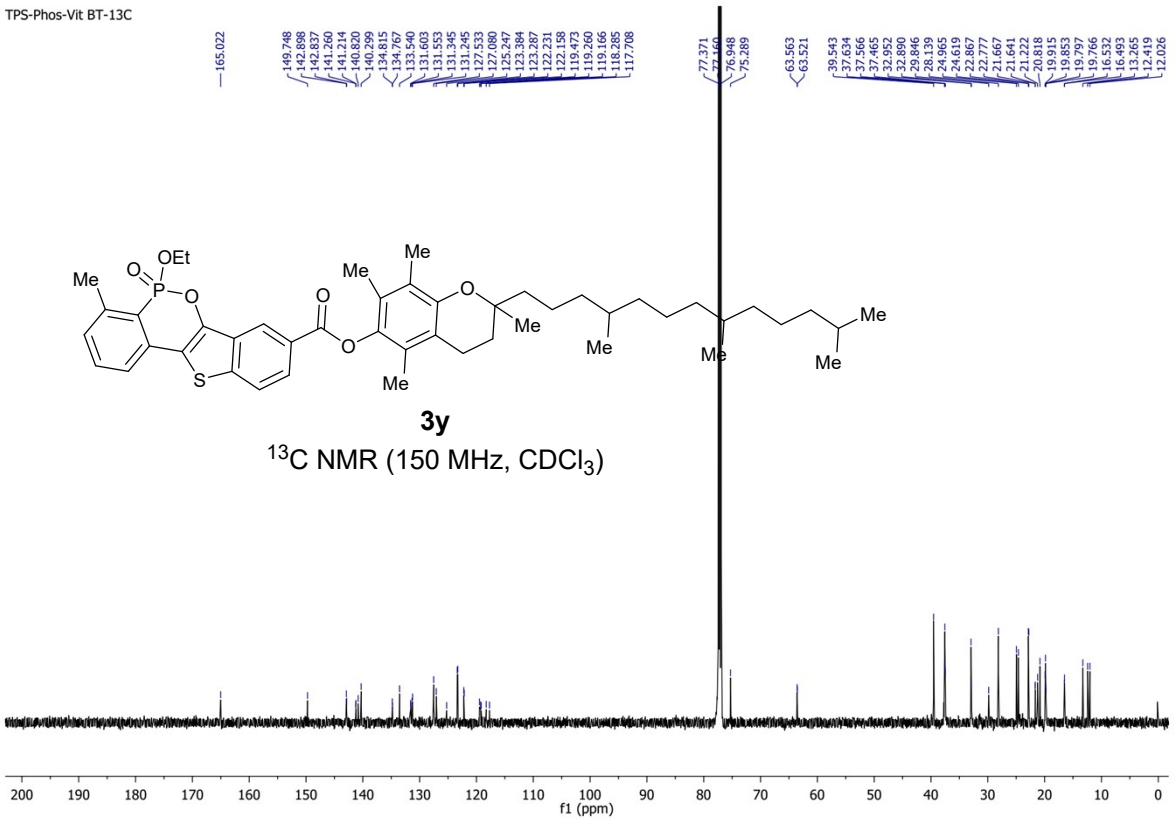
3x

^{31}P NMR (243 MHz, $CDCl_3$)



3y

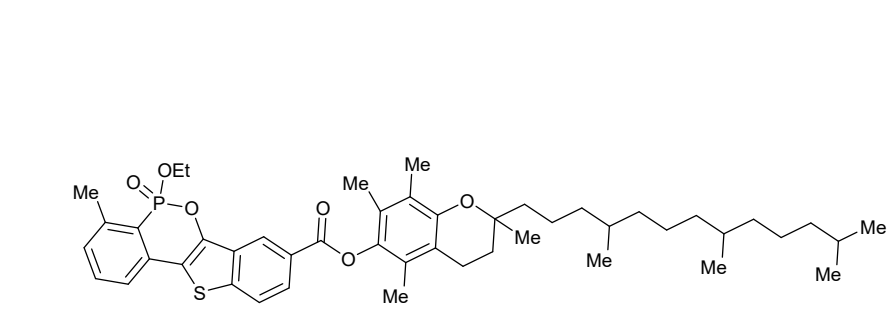
^{1}H NMR (600 MHz, $CDCl_3$)



3y

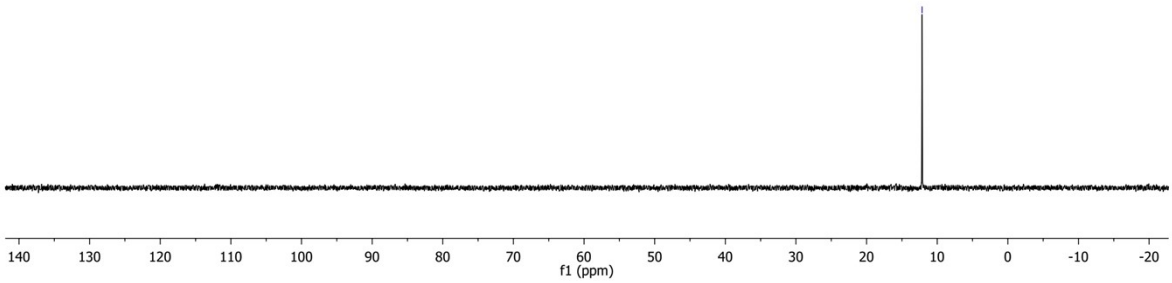
^{13}C NMR (150 MHz, $CDCl_3$)

TPS-Phos-Vit BT-31P

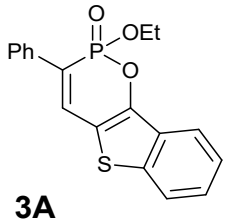


3y

^{31}P NMR (243 MHz, $CDCl_3$)

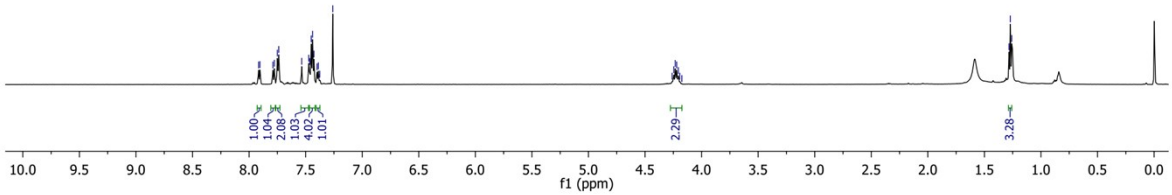


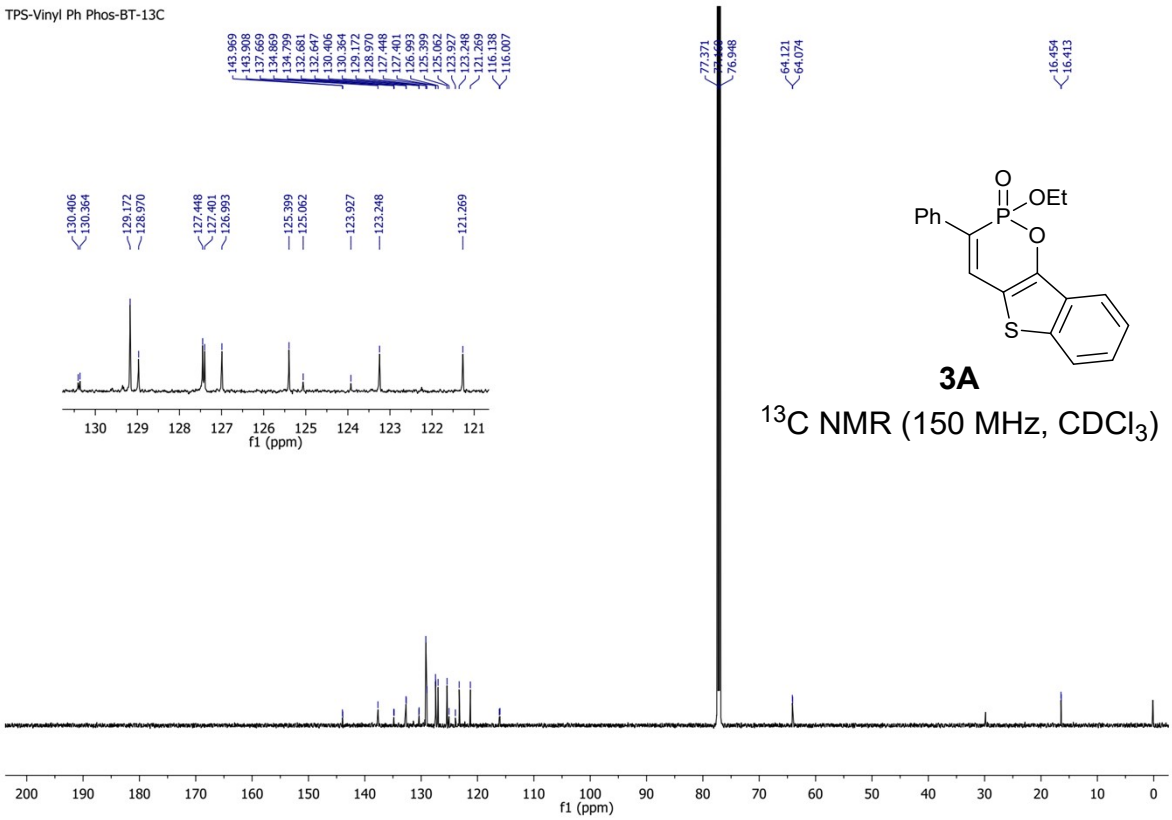
TPS-Vinyl Ph Phos-BT-1H



3A

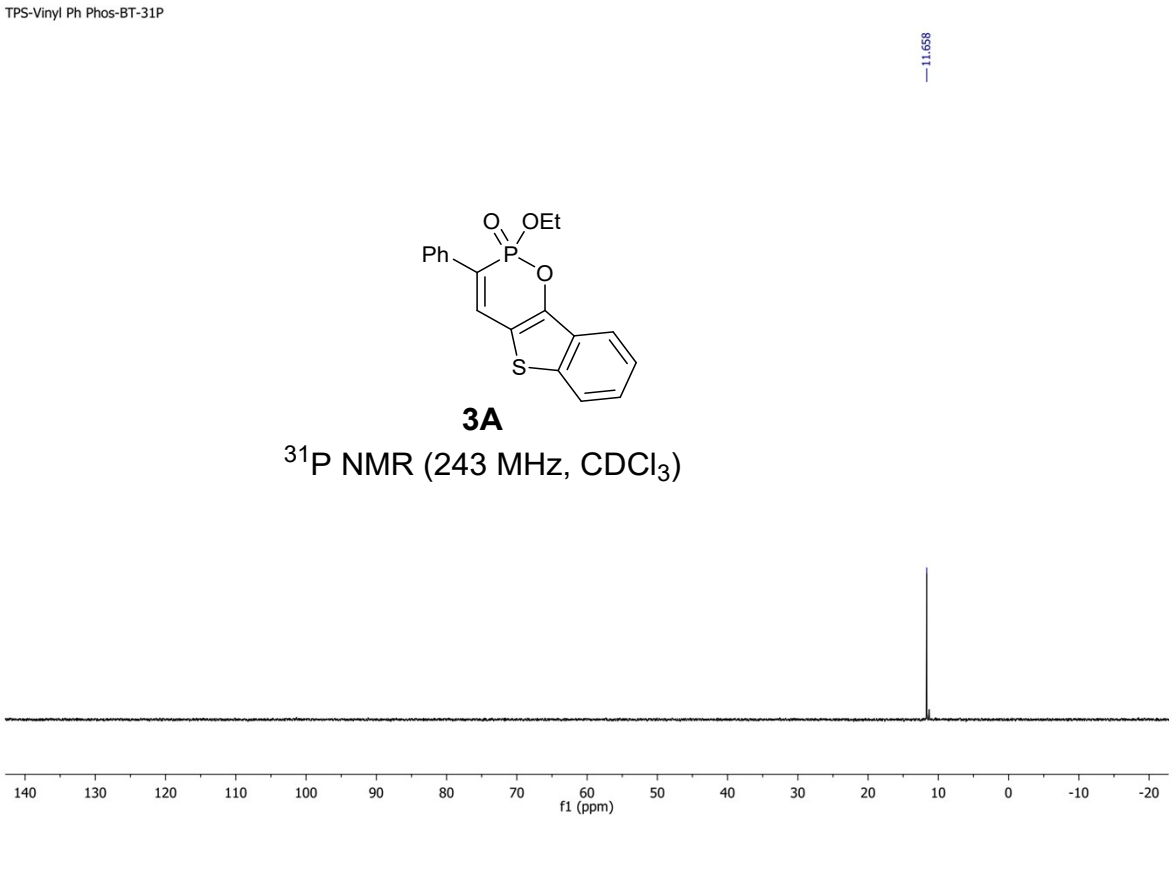
^{1}H NMR (600 MHz, $CDCl_3$)





3A

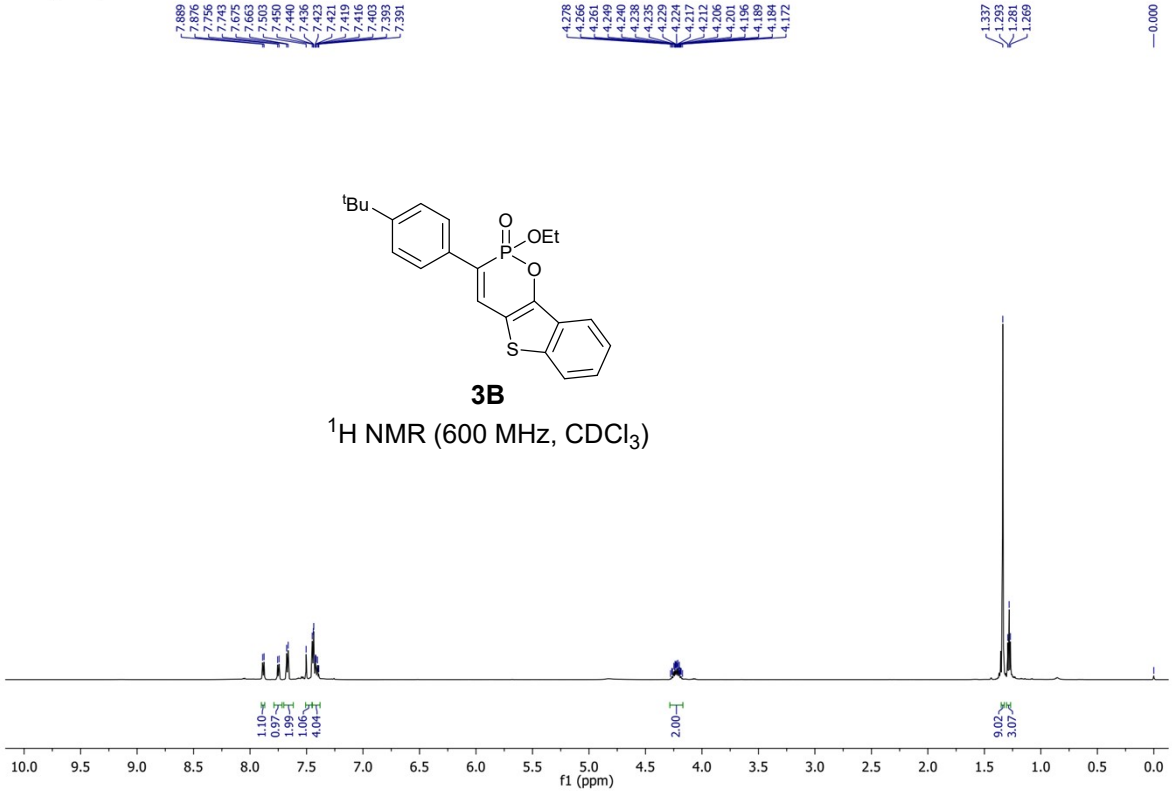
^{13}C NMR (150 MHz, $CDCl_3$)



3A

^{31}P NMR (243 MHz, $CDCl_3$)

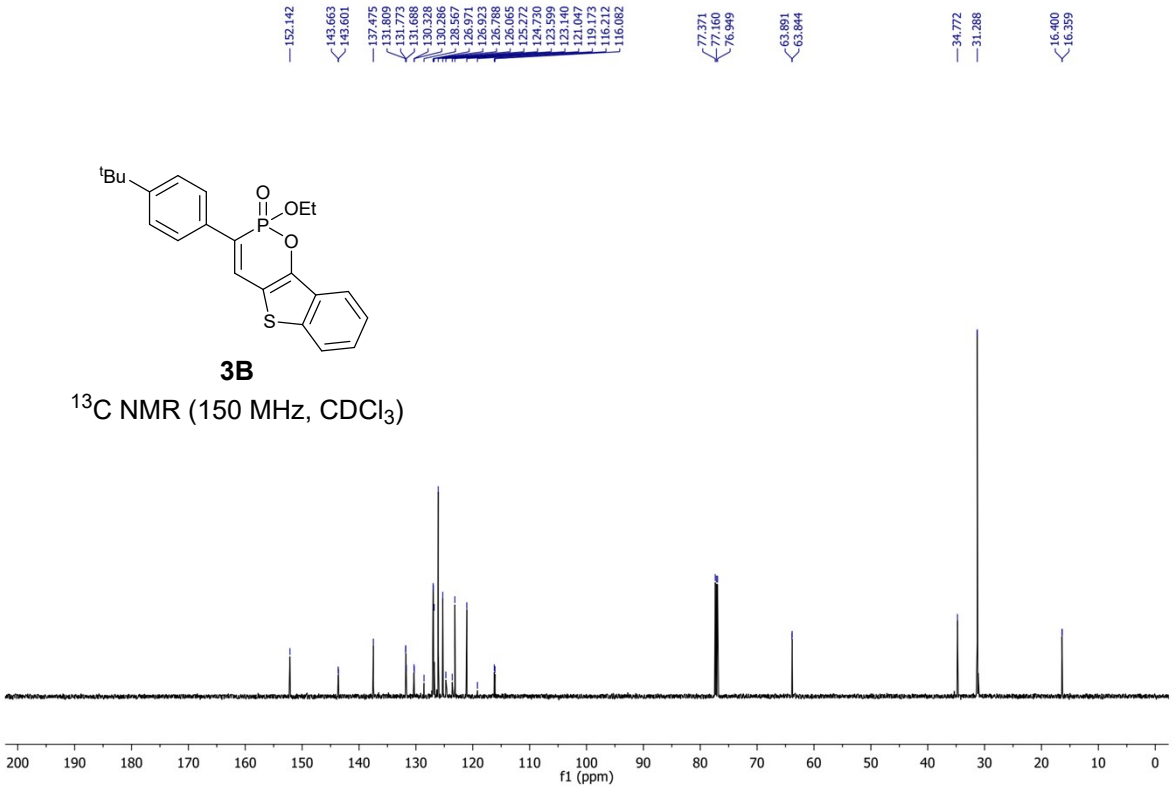
TPS-Vinyl t-Butyl Phos-BT-1H



3B

^{1}H NMR (600 MHz, $CDCl_3$)

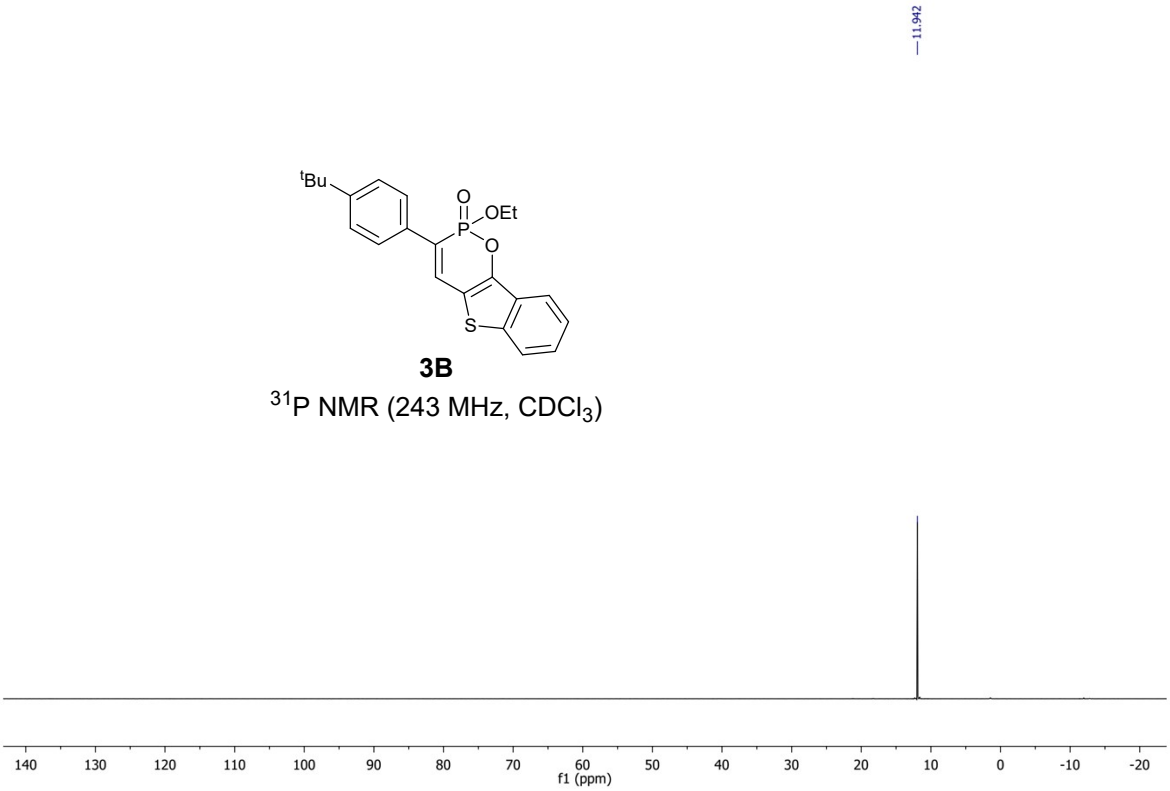
TPS-Vinyl t-Butyl Phos-BT-13C



3B

^{13}C NMR (150 MHz, $CDCl_3$)

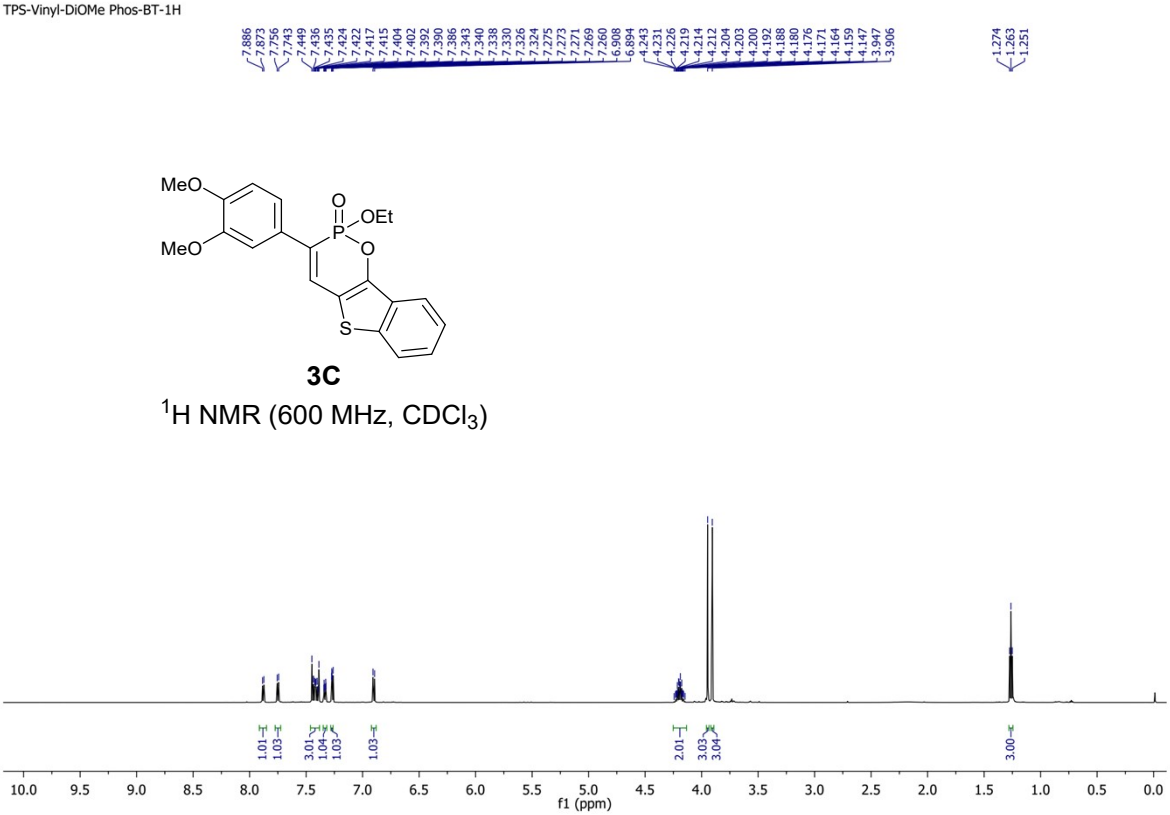
TPS-Vinyl t-Butyl Phos-BT-31P



3B

^{31}P NMR (243 MHz, $CDCl_3$)

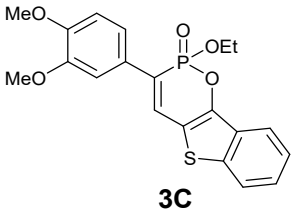
TPS-Vinyl-DiOMe Phos-BT-1H



3C

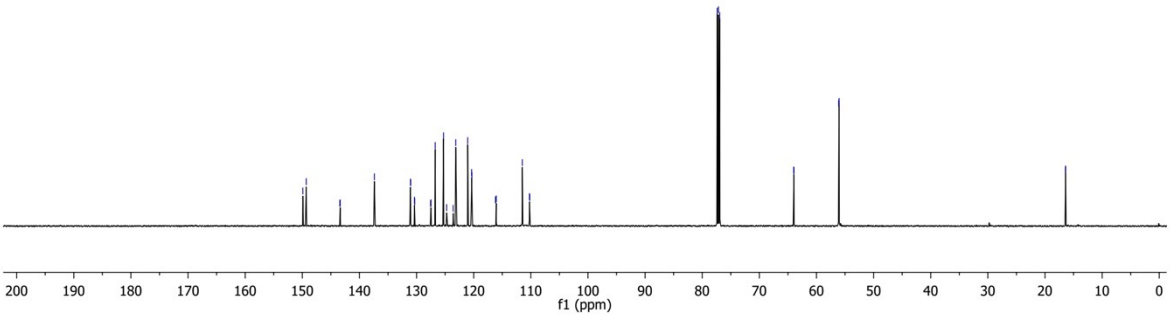
^{1}H NMR (600 MHz, $CDCl_3$)

TPS-Vinyl-DiOMe Phos-BT-13C

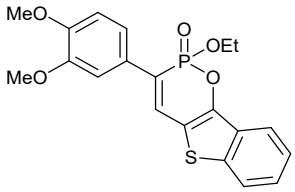


3C

^{13}C NMR (150 MHz, $CDCl_3$)

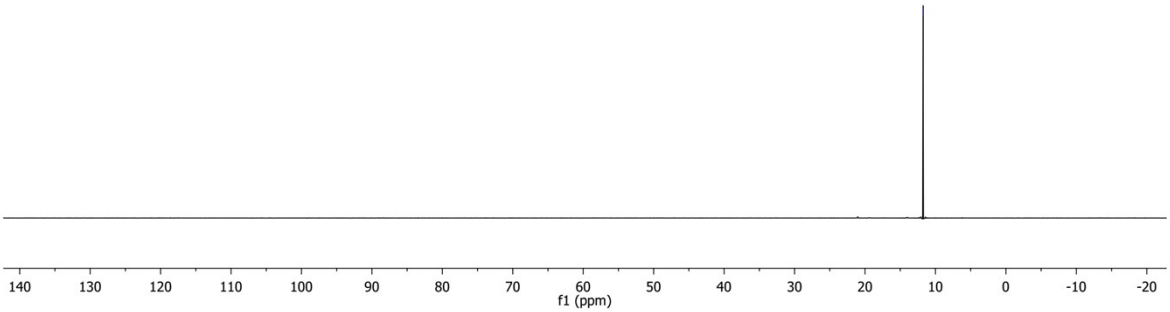


TPS-Vinyl-DiOMe Phos-BT-31P

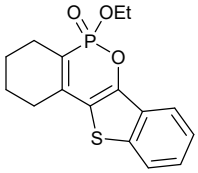


3C

^{31}P NMR (243 MHz, $CDCl_3$)

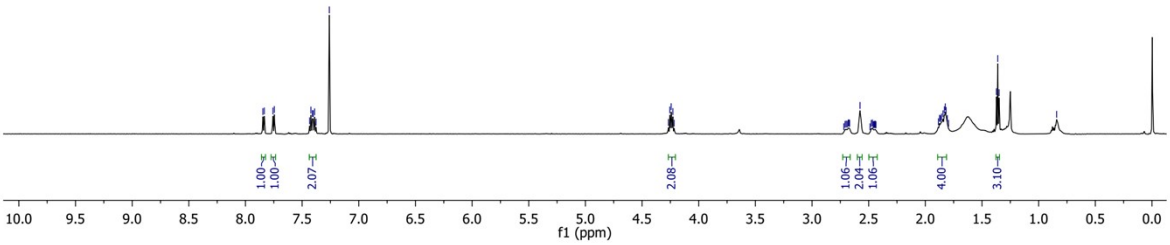


TPS-Hexanone Phos-BT-1H

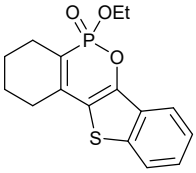


3D

^{1}H NMR (600 MHz, $CDCl_3$)



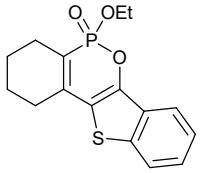
TPS-Hexanone Phos-BT-13C



3D

^{13}C NMR (150 MHz, $CDCl_3$)

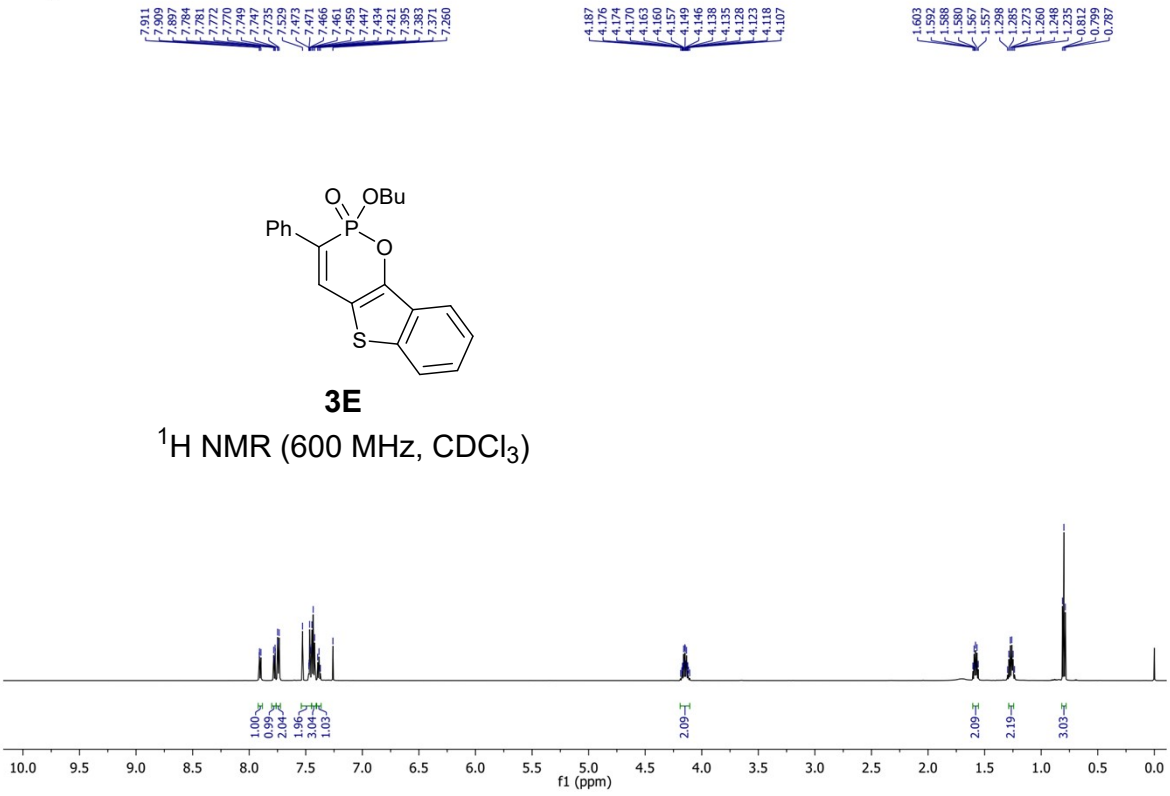
TPS-Hexanone Phos-BT-31P



3D

^{31}P NMR (243 MHz, $CDCl_3$)

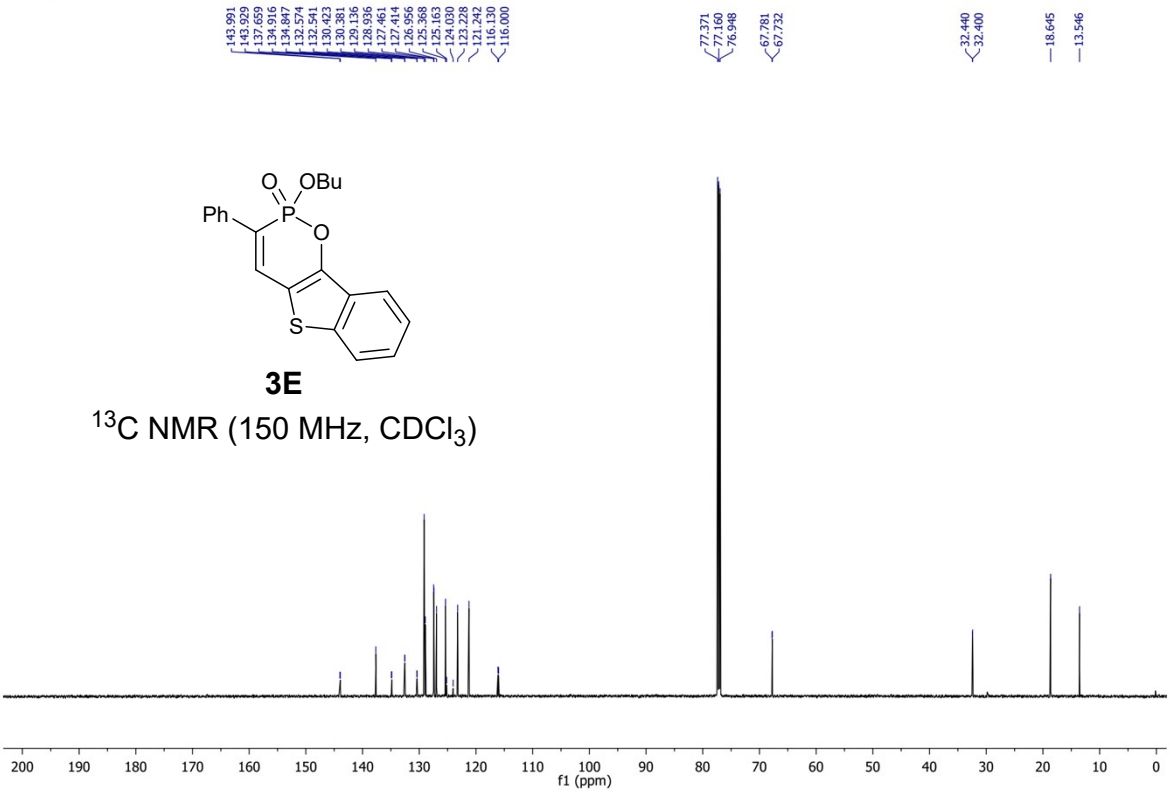
TPS-Vinyl OBu Phos-BT-1H



3E

^{1}H NMR (600 MHz, $CDCl_3$)

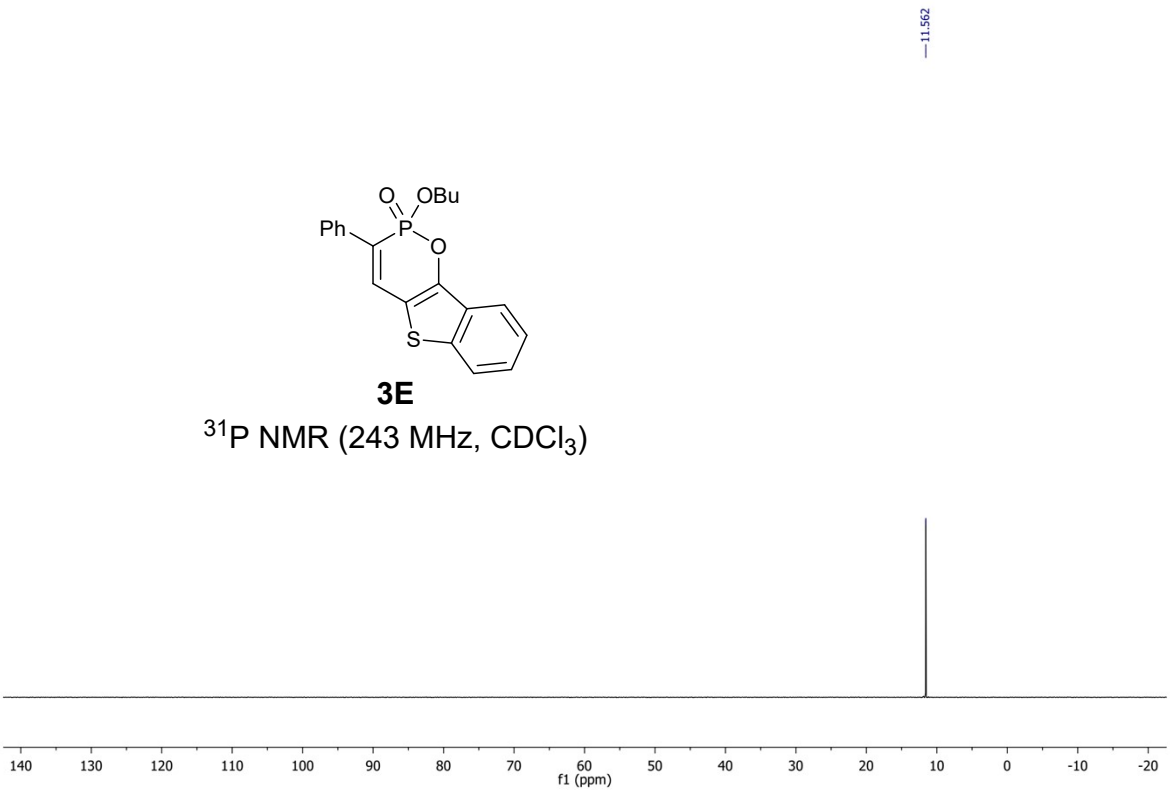
TPS-Vinyl OBu Phos-BT-13C



3E

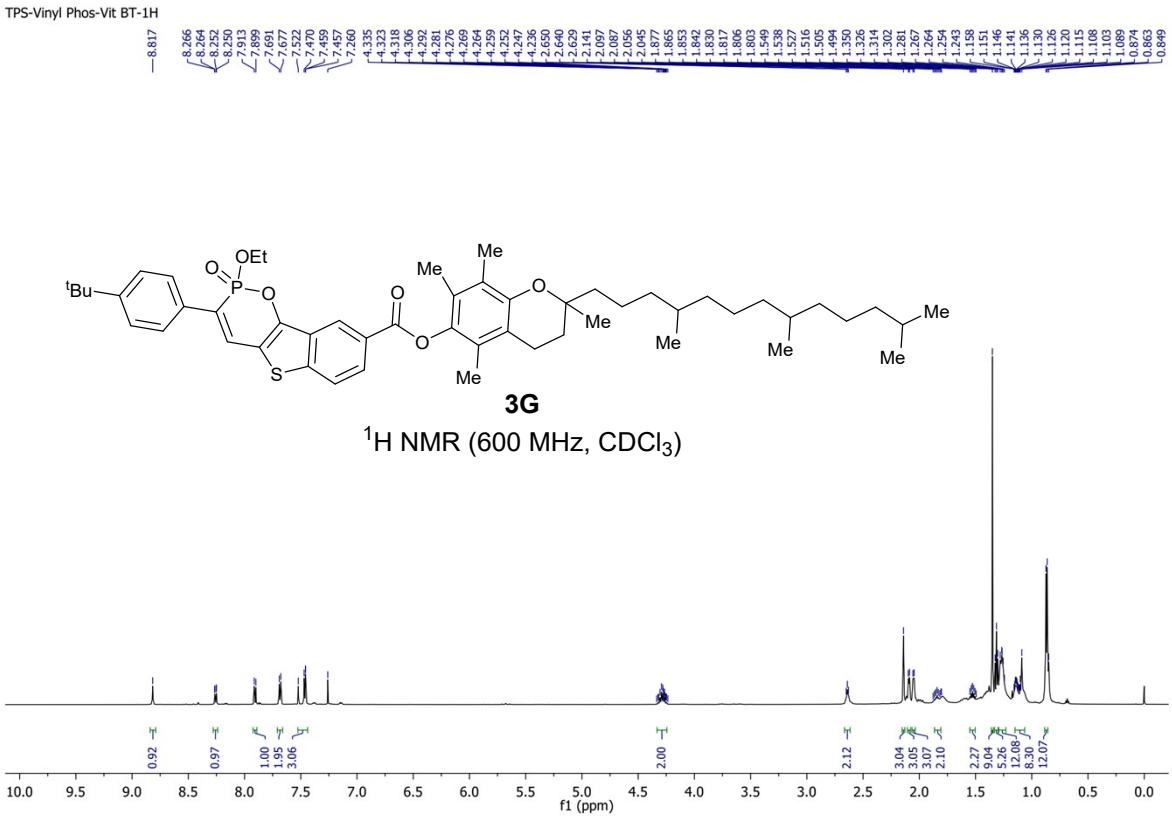
^{13}C NMR (150 MHz, $CDCl_3$)

TPS-Vinyl OBu Phos-BT-31P



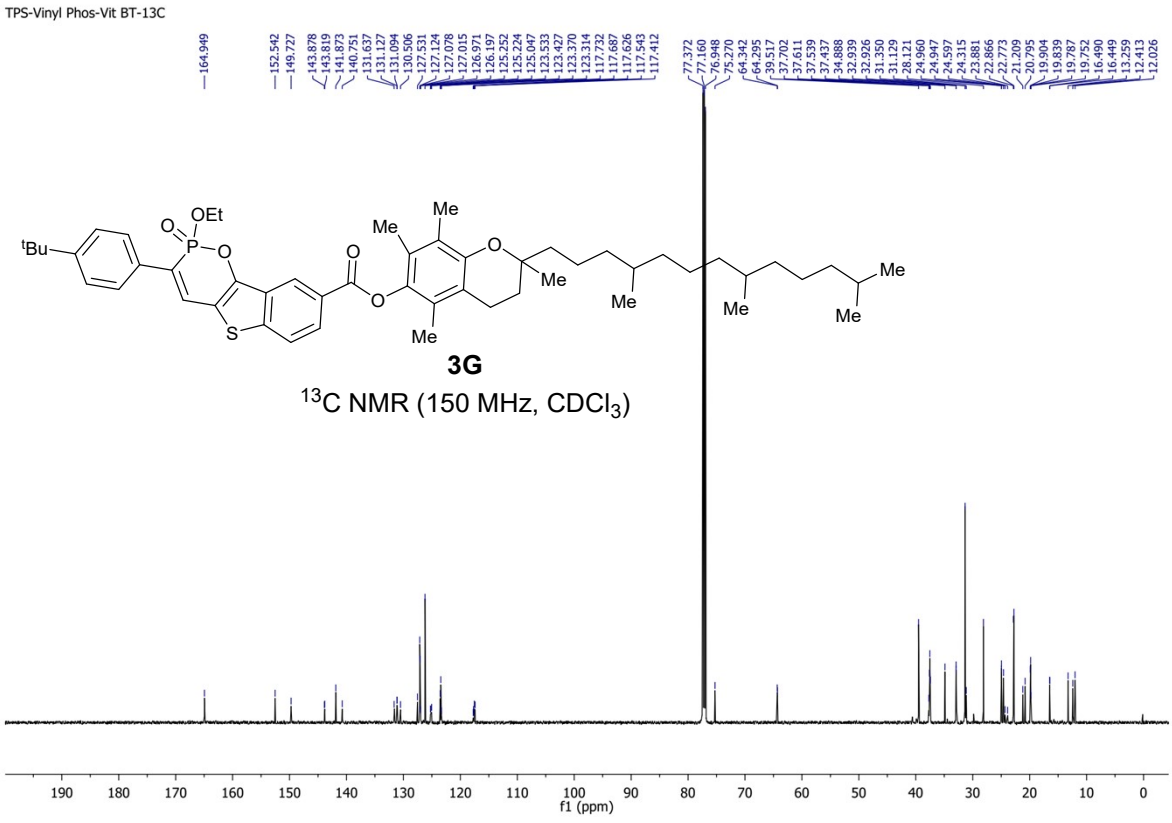
3E

^{31}P NMR (243 MHz, $CDCl_3$)



3G

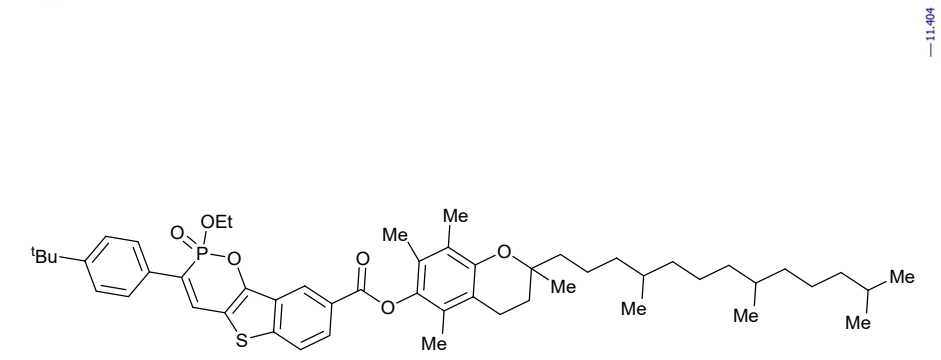
^{1}H NMR (600 MHz, $CDCl_3$)



3G

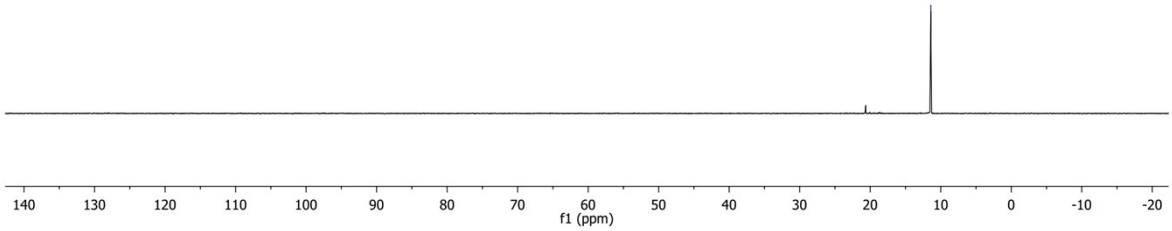
^{13}C NMR (150 MHz, $CDCl_3$)

TPS-Vinyl Phos-Vit BT-31P

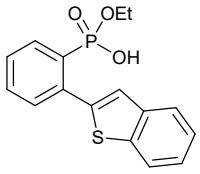


3G

^{31}P NMR (243 MHz, $CDCl_3$)

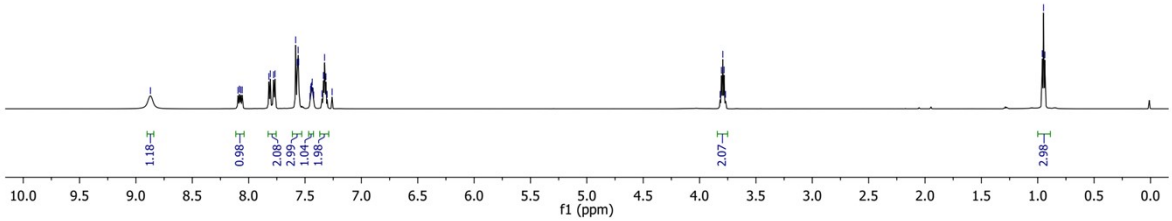


TPS-Het Ar-1H

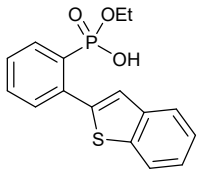


3b'

^{1}H NMR (600 MHz, $CDCl_3$)

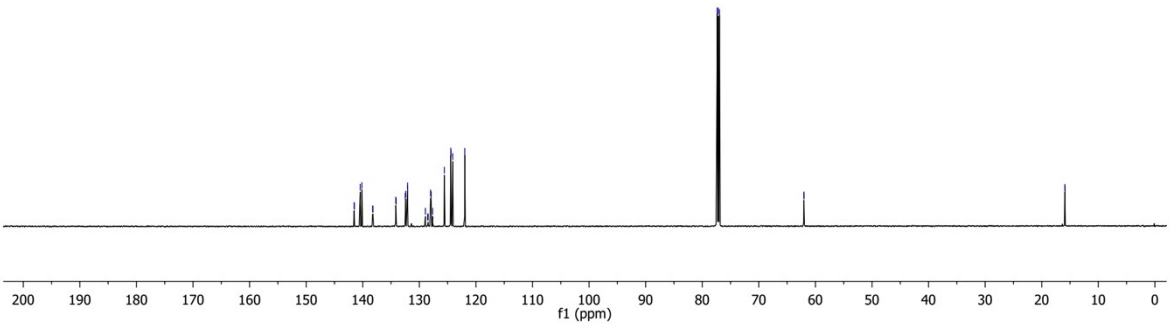


TPS-Het Ar-13C

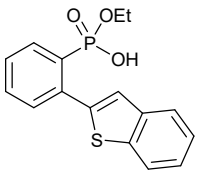


3b'

^{13}C NMR (150 MHz, $CDCl_3$)

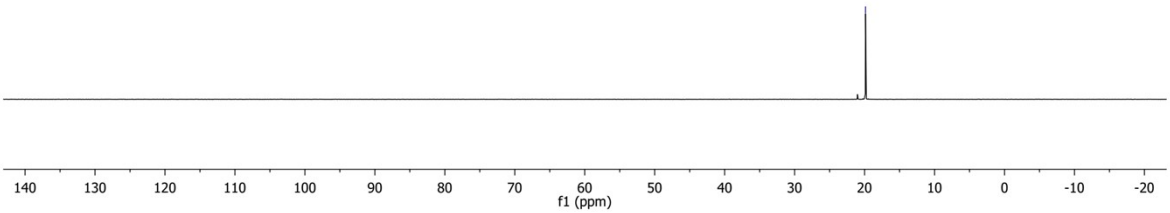


TPS-Het Ar-31P

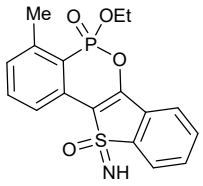


3b'

^{31}P NMR (243 MHz, $CDCl_3$)

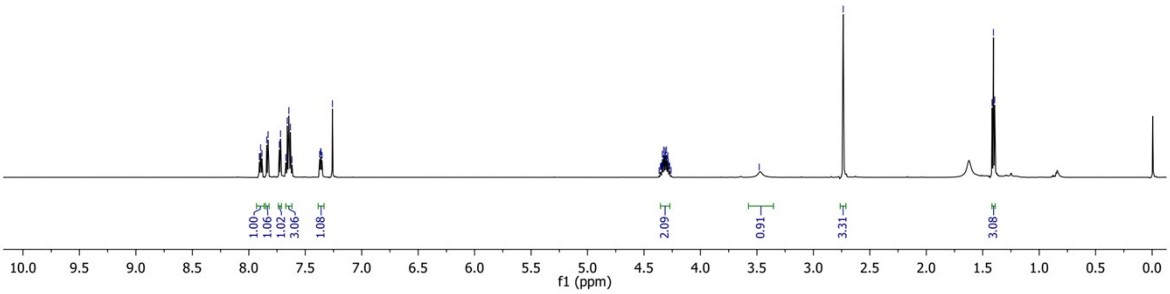


TPS-App SONH-BT-1H

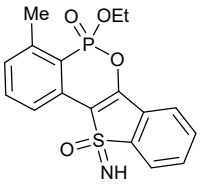


5

^{1}H NMR (600 MHz, $CDCl_3$)



TPS-App SONH-BT-13C

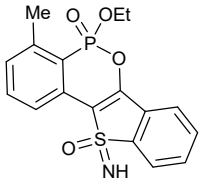


5

^{13}C NMR (150 MHz, $CDCl_3$)

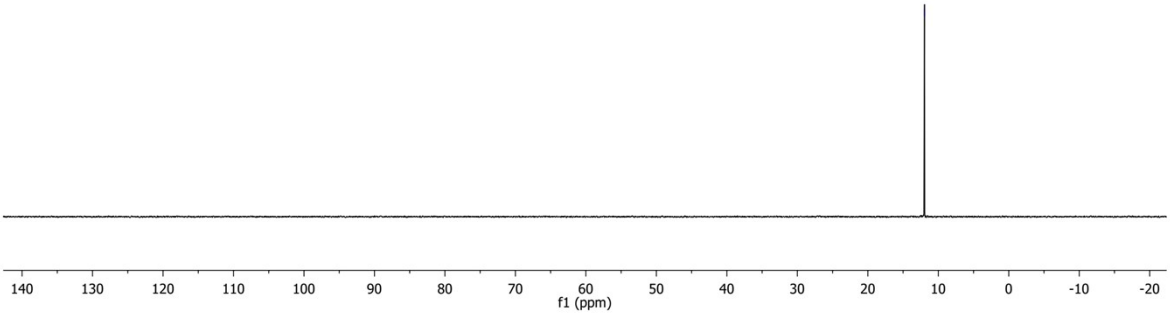
TPS-App SONH-BT-31P

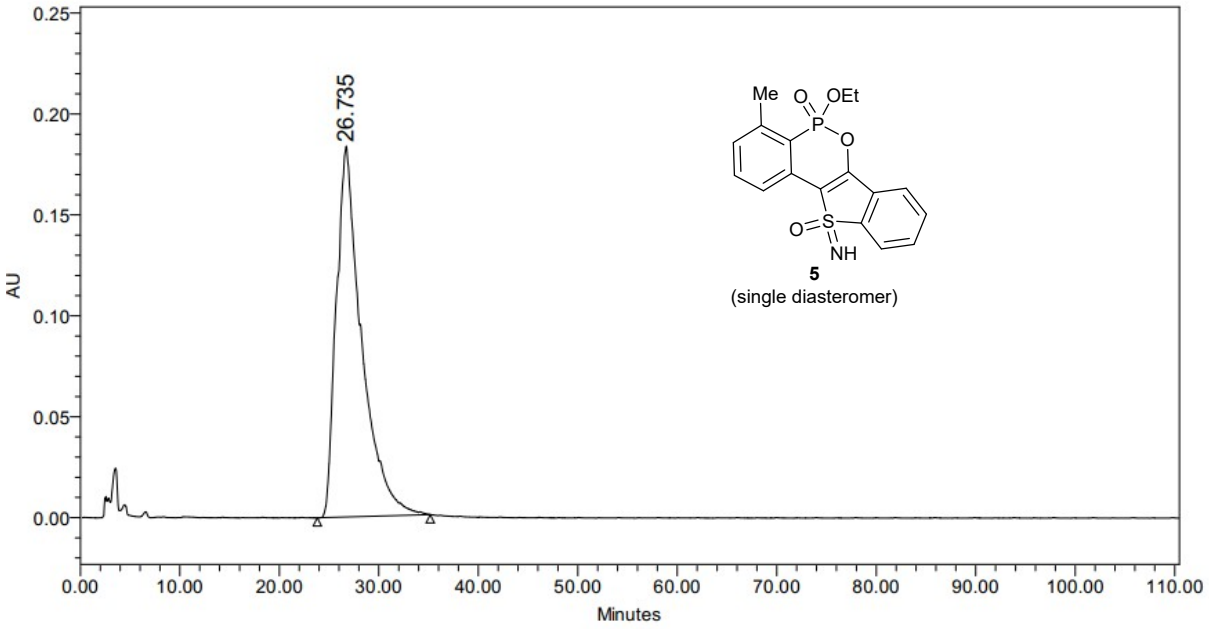
11.959



5

^{31}P NMR (243 MHz, $CDCl_3$)





5
(single diasteromer)

	RT	Area	% Area	Height
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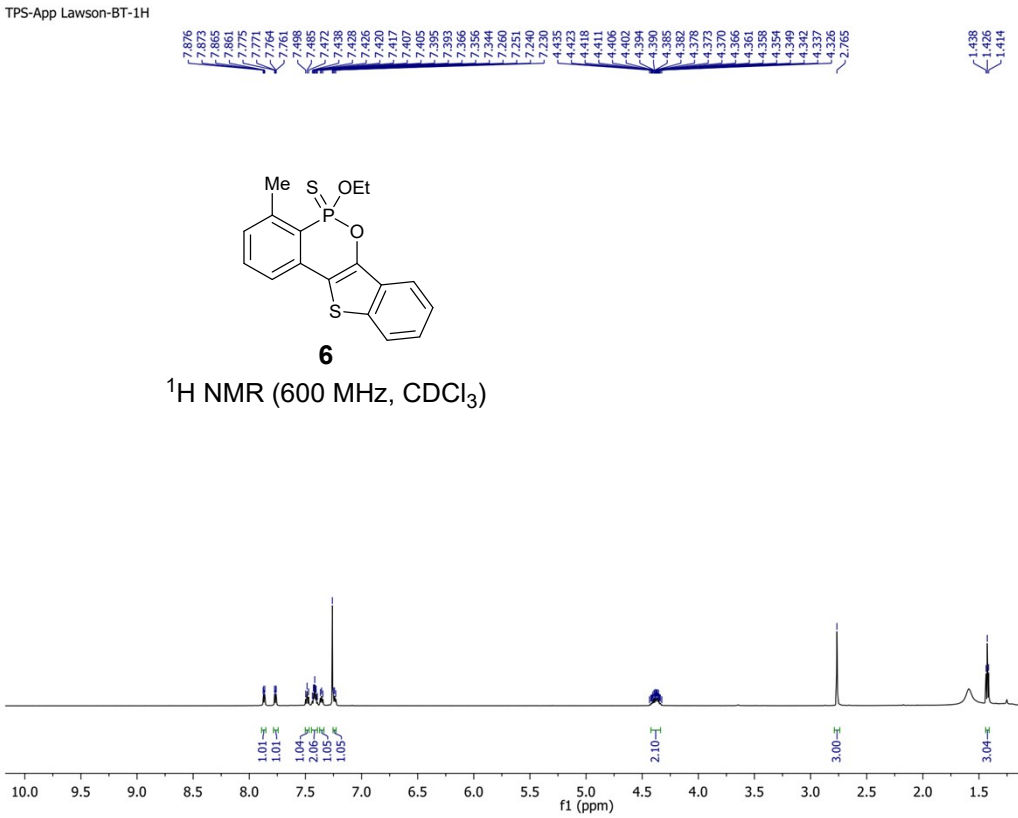
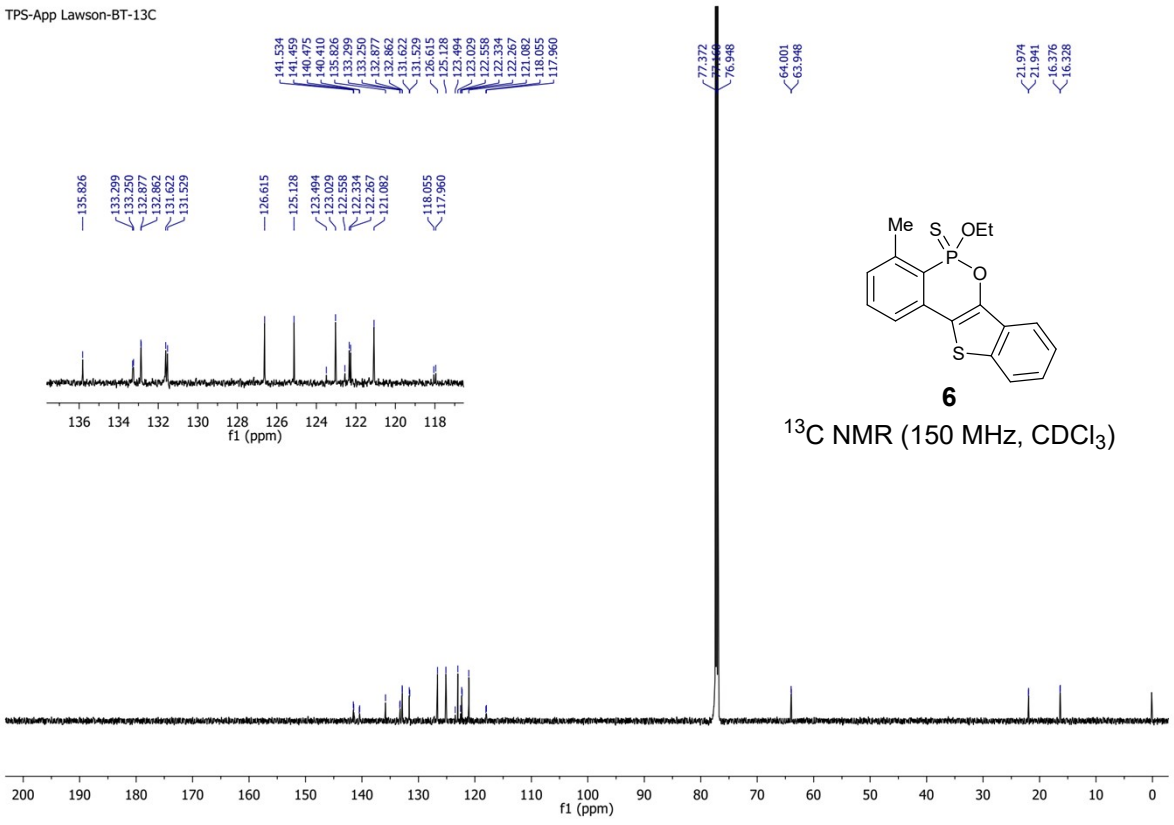
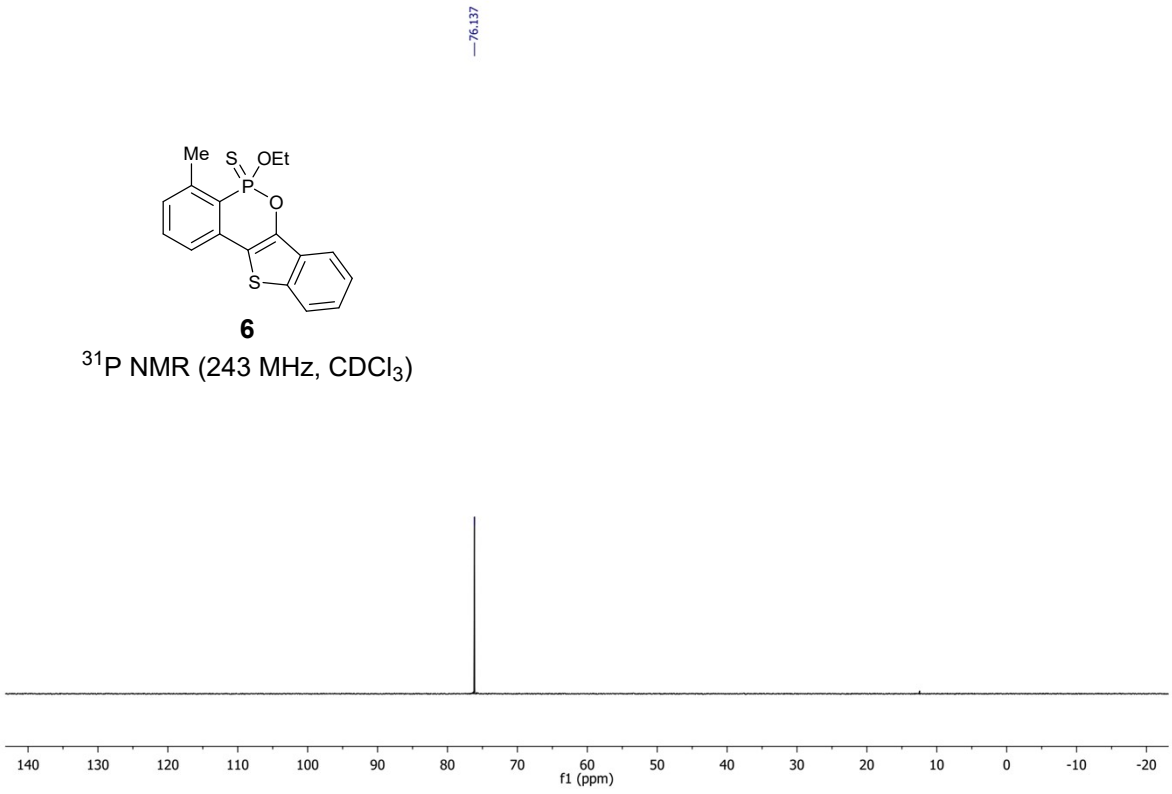

TPS-App Lawson-BT-1H
7.876
7.873
7.865
7.861
7.775
7.771
7.764
7.761
7.498
7.485
7.472
7.438
7.428
7.426
7.420
7.417
7.407
7.405
7.395
7.393
7.366
7.356
7.344
7.260
7.251
7.240
7.230
4.435
4.423
4.418
4.411
4.406
4.402
4.394
4.390
4.385
4.382
4.378
4.373
4.370
4.366
4.361
4.358
4.354
4.349
4.342
4.337
4.326
2.765
1.438
1.426
1.414
Me
S
OEt
P
O
S
6
1H NMR (600 MHz, CDCl3)
1.01
1.01
1.04
2.06
1.05
1.05
2.10
3.00
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


TPS-App Lawson-BT-13C
141.534
141.459
140.475
140.410
135.826
133.299
133.250
132.877
132.862
131.622
131.529
126.615
125.128
123.494
123.029
122.558
122.334
122.267
121.082
118.055
117.960
77.372
77.160
76.948
64.001
63.948
21.974
21.941
16.376
16.328
Me
S
OEt
P
O
S
6
13C NMR (150 MHz, CDCl3)
136
134
132
130
128
126
124
122
120
118
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

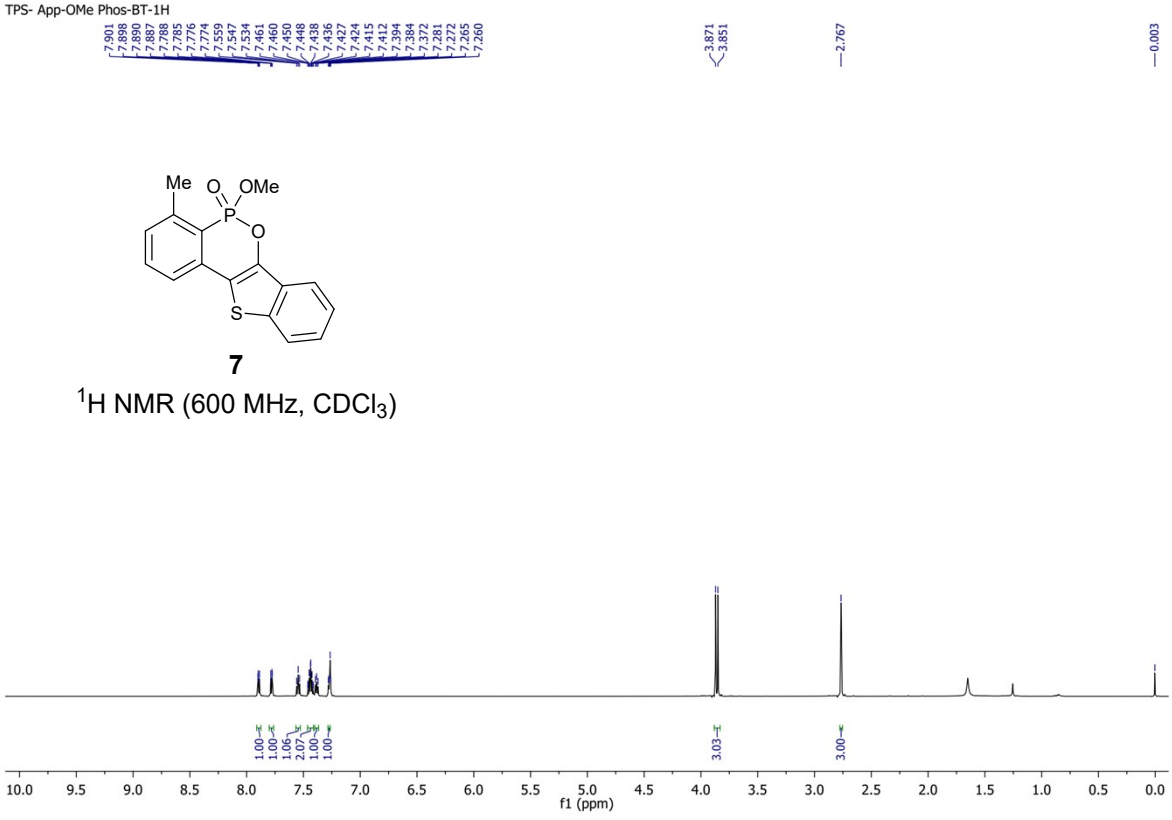
TPS-App Lawson-BT-31P



6

^{31}P NMR (243 MHz, $CDCl_3$)

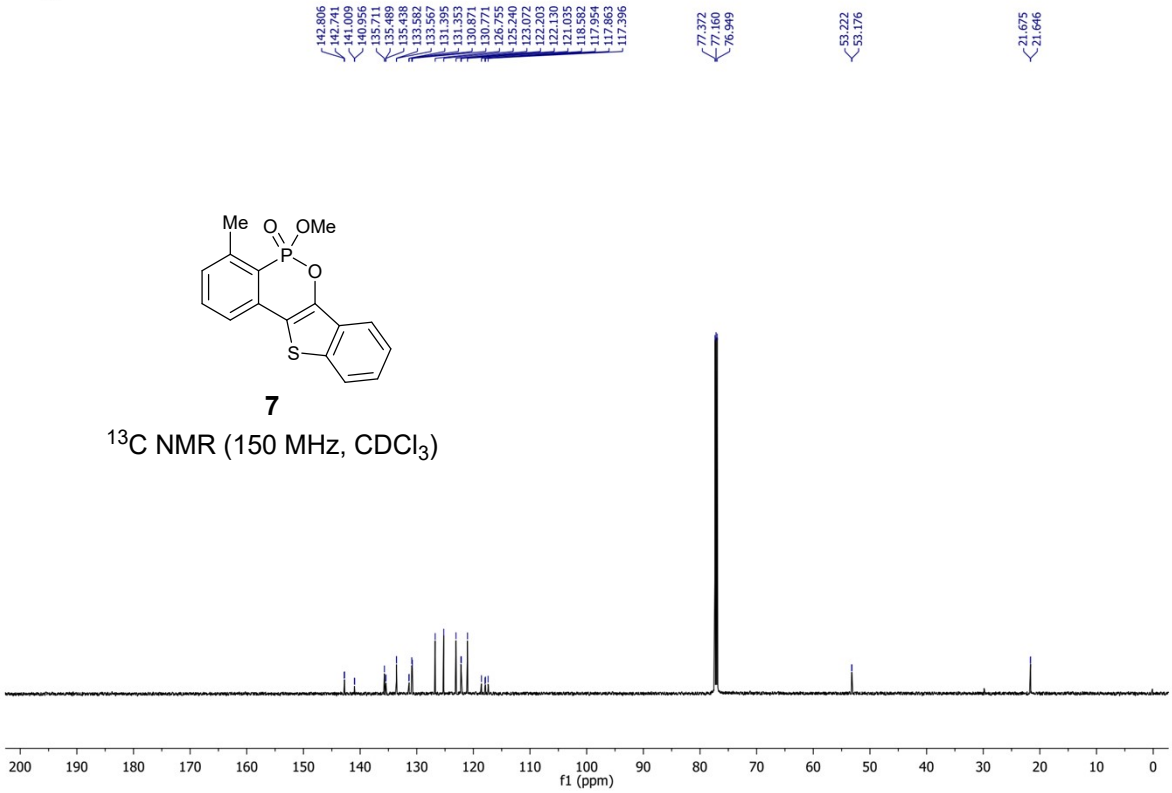
TPS- App-OMe Phos-BT-1H



7

^{1}H NMR (600 MHz, $CDCl_3$)

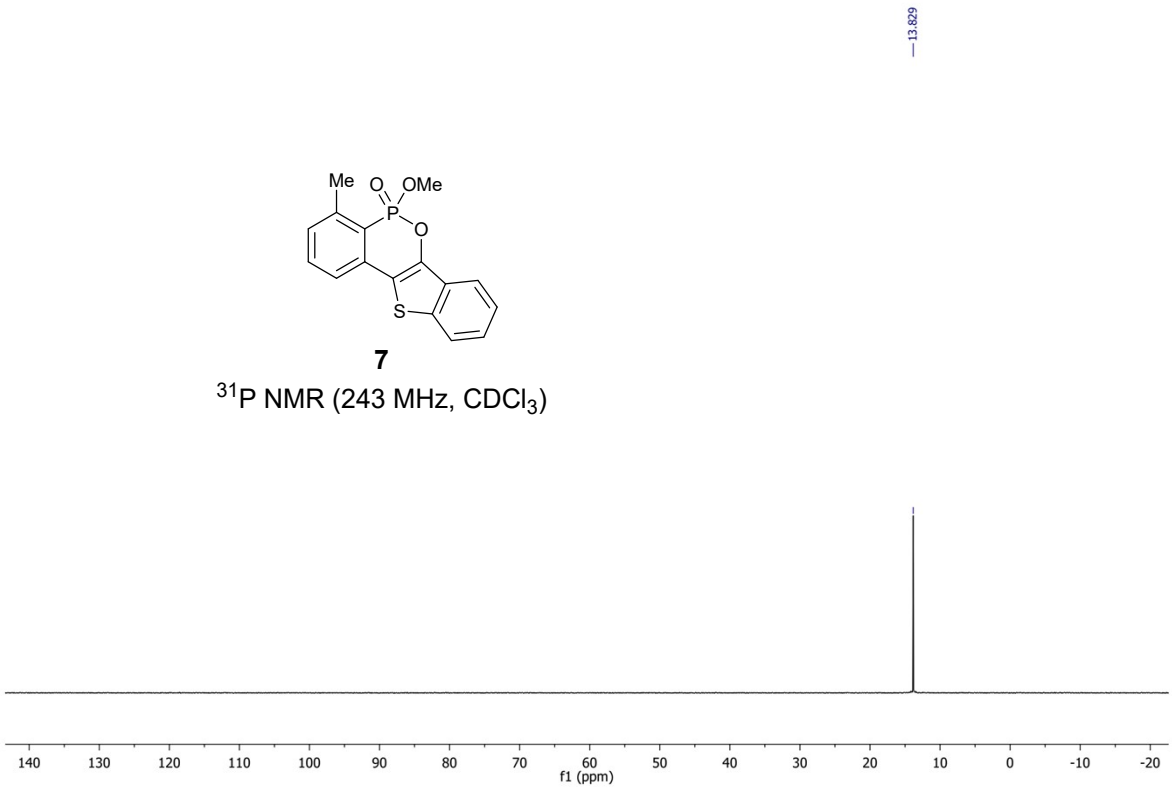
TPS- App-OMe Phos-BT-13C



7

^{13}C NMR (150 MHz, $CDCl_3$)

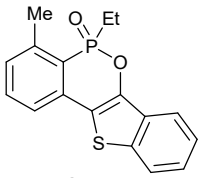
TPS- APP-OMe Phos-BT-31P



7

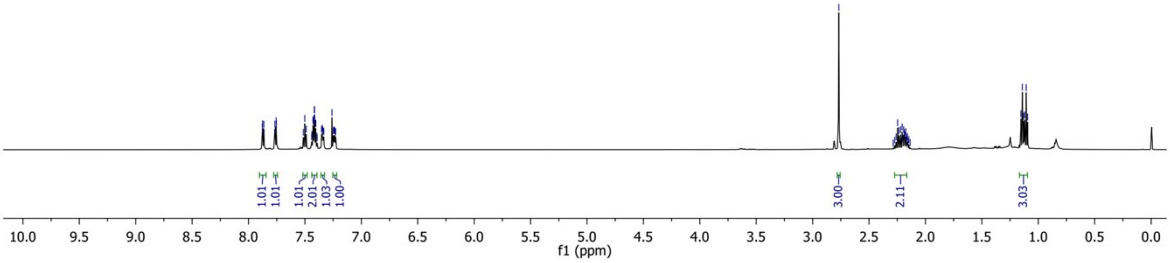
^{31}P NMR (243 MHz, $CDCl_3$)

TPS-App Et Phos-BT-1H

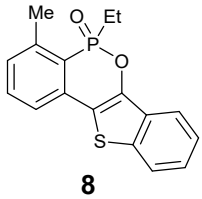


8

^{1}H NMR (600 MHz, $CDCl_3$)



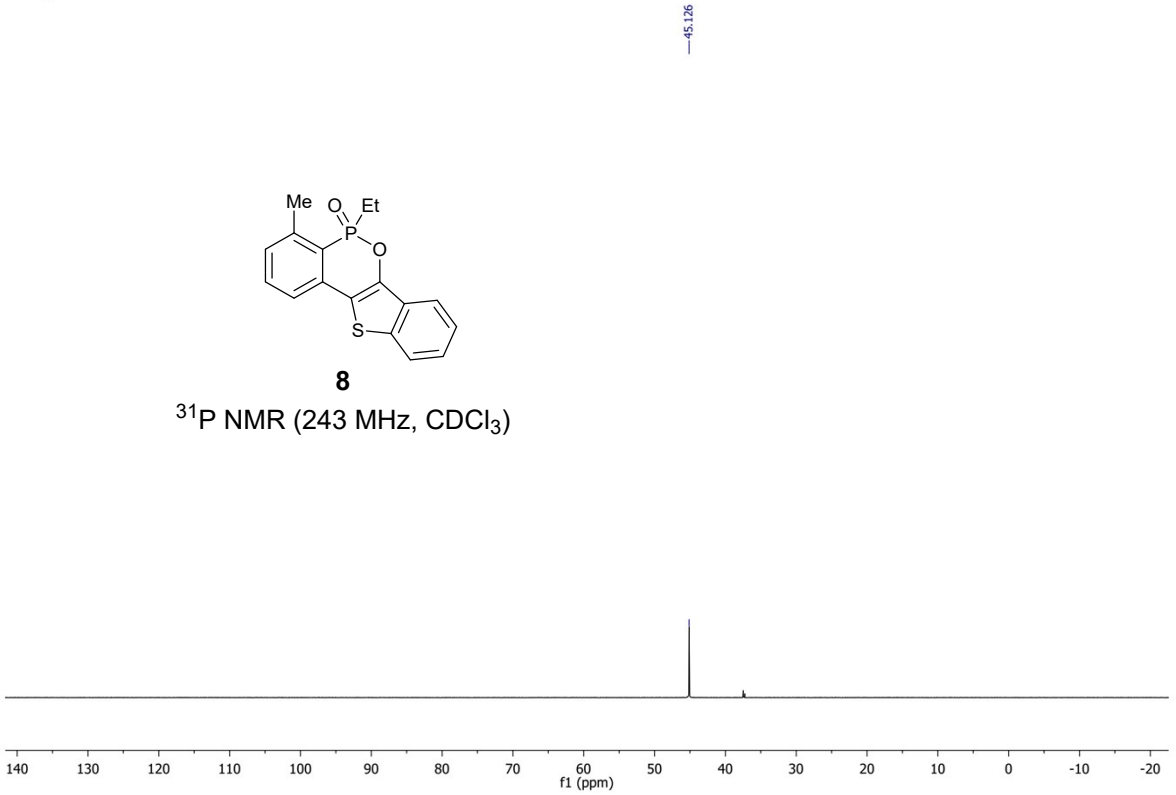
TPS-App Et Phos-BT-13C



8

^{13}C NMR (150 MHz, $CDCl_3$)

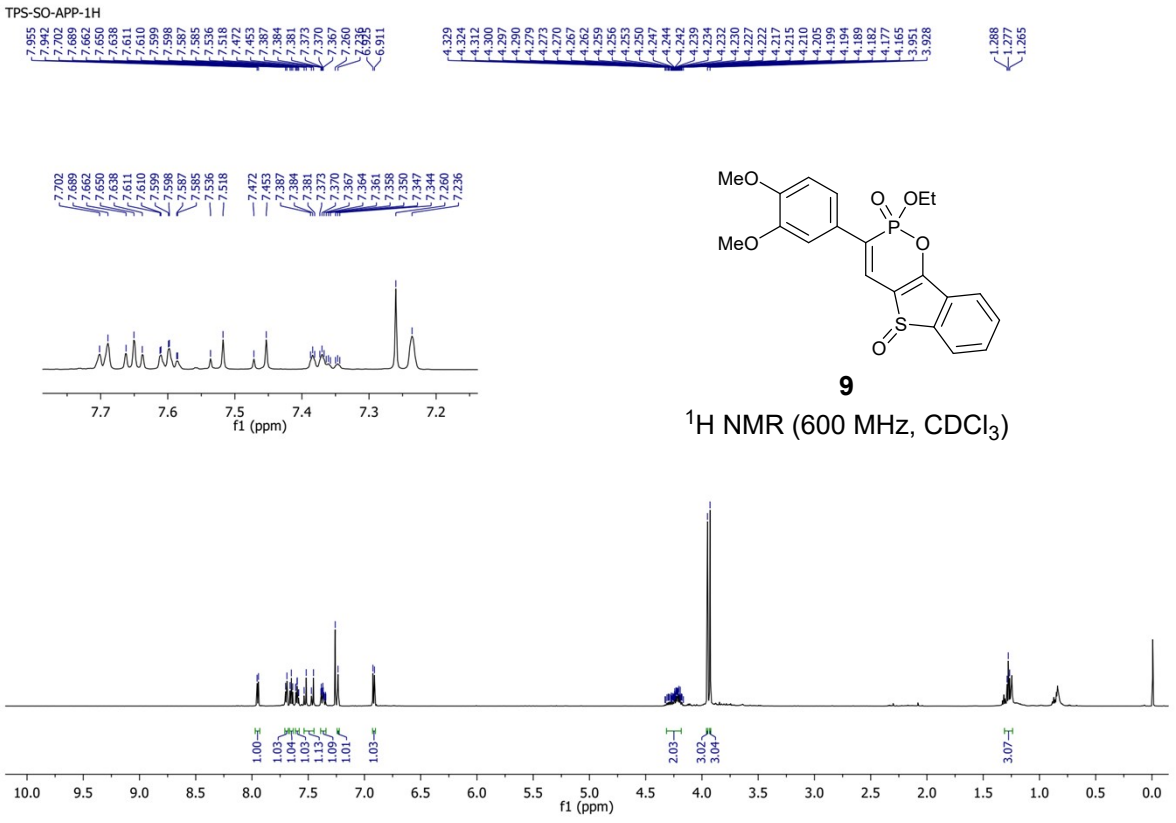
TPS-App Et Phos-BT-31P



8

^{31}P NMR (243 MHz, $CDCl_3$)

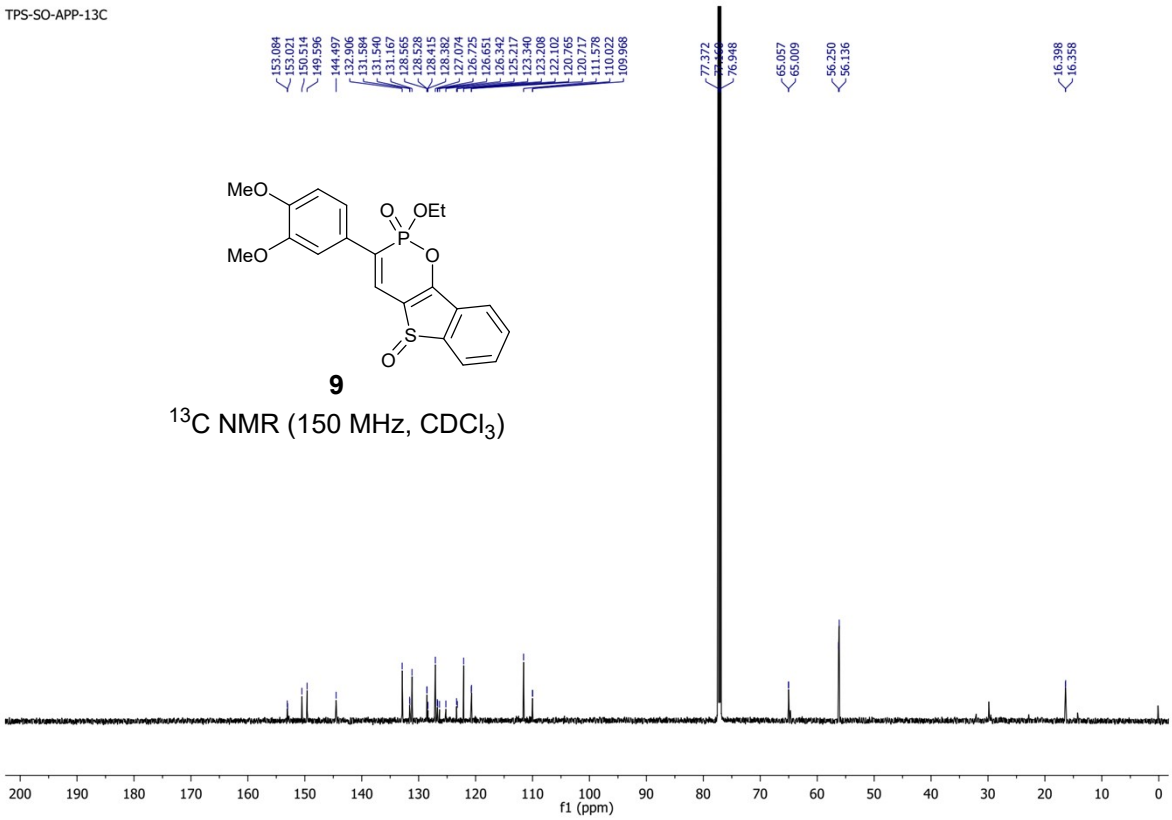
TPS-SO-APP-1H



9

^{1}H NMR (600 MHz, $CDCl_3$)

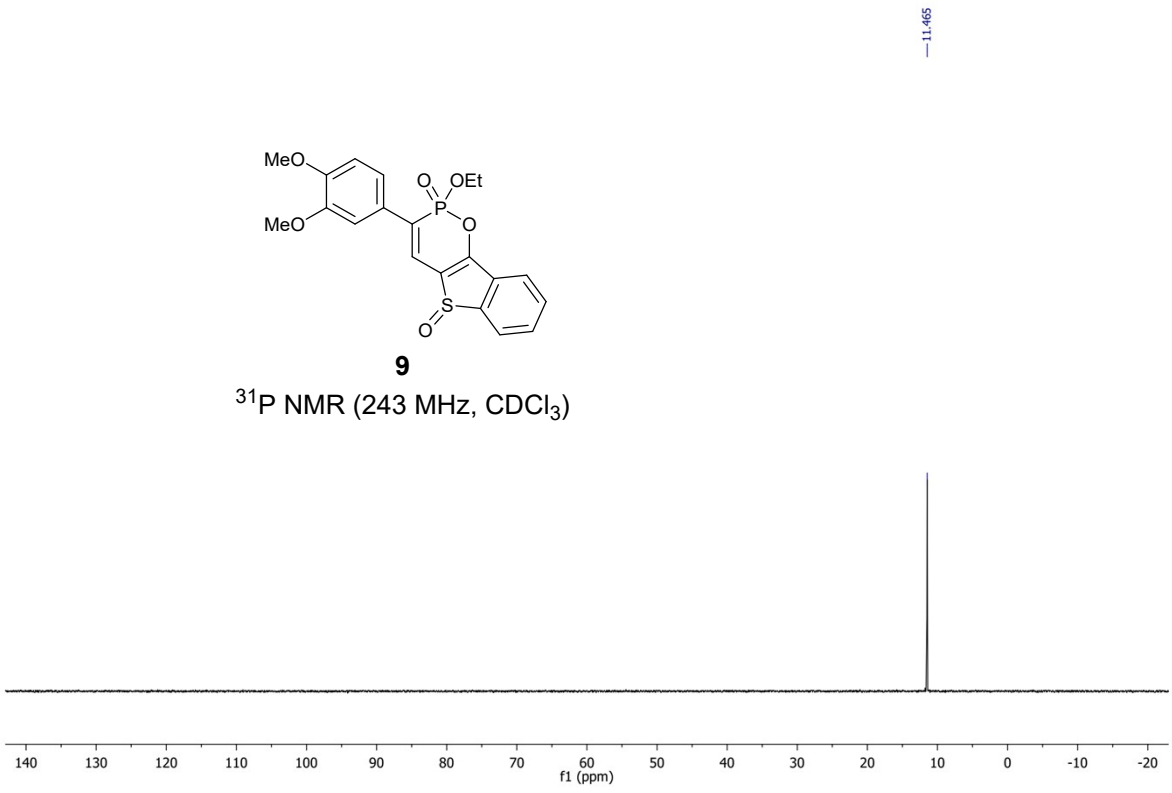
TPS-SO-APP-13C



9

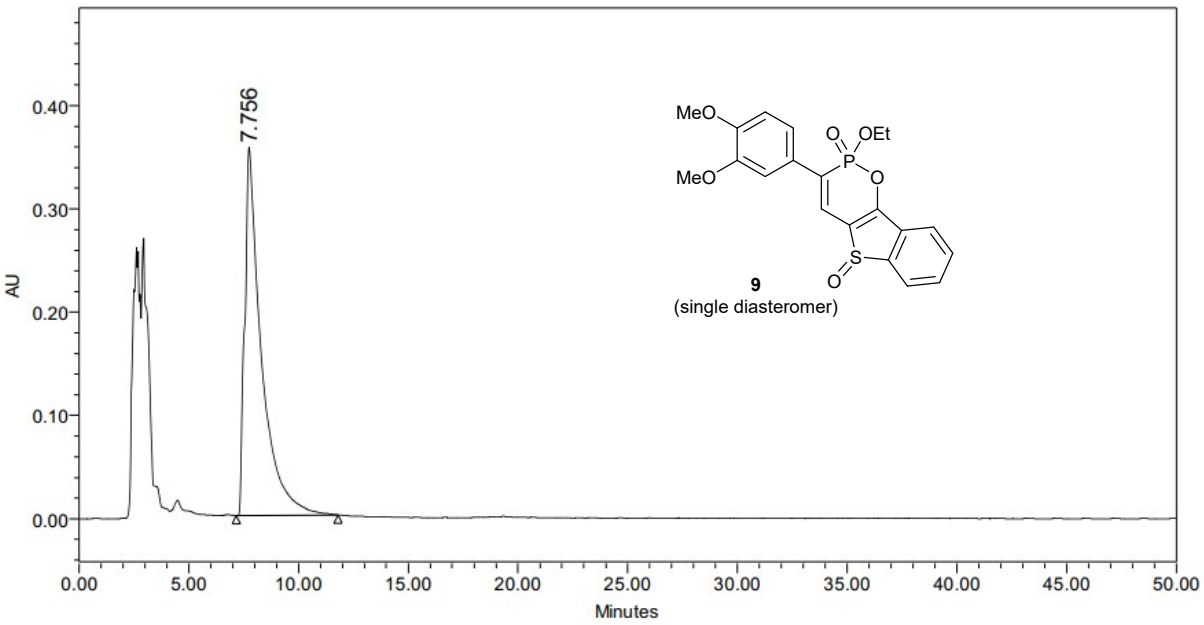
^{13}C NMR (150 MHz, $CDCl_3$)

TPS-SO-APP-31P

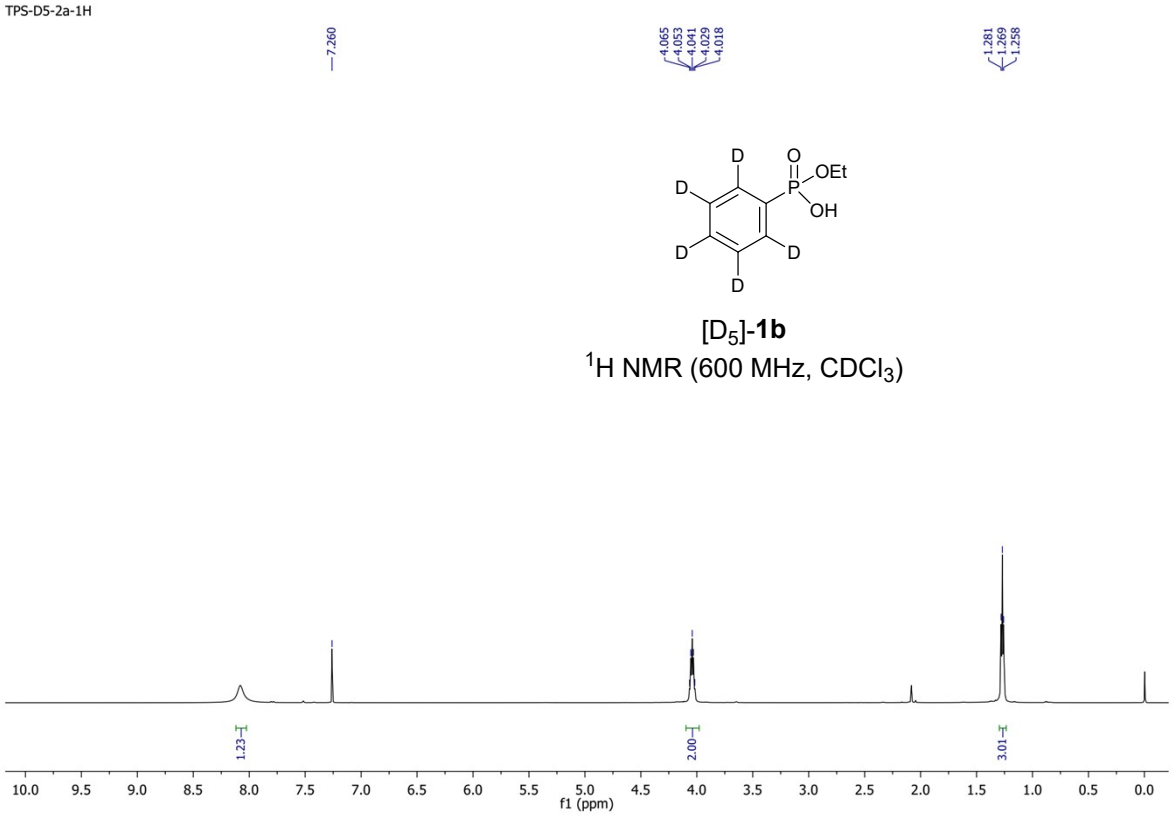


9

^{31}P NMR (243 MHz, $CDCl_3$)



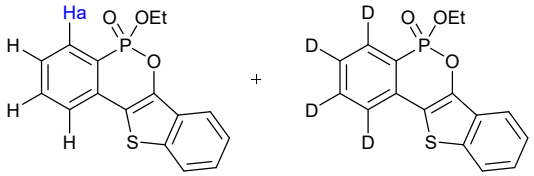
	RT	Area	% Area	Height
1	7.756	18727690	100.00	356569



$[D_5]$-**1b**

^{1}H NMR (600 MHz, $CDCl_3$)

TPS-KH/KD



^{1}H NMR (600 MHz, $CDCl_3$)

k_H/k_D = 5.6