Photoelectrochemical-Induced Heterogeneous Catalytic Selective Dehalogenation Coupling of Alkyl Halides with Thiophenols via Interfacial Charge Transfer

Lulu Zhao,[a] Jianjing Yang,[a]* Kelu Yan,[a] Xingda Cheng,[a] Zongzhao Sun,[b] * Jiangwei Wen [a]*

[a] Key Laboratory of Green Natural Products and Pharmaceutical Intermediates in Colleges and Universities of Shandong Province, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, 273165, Shandong, China. E-mail: jjyang@whu.edu.cn, wenjy@qfnu.edu.cn

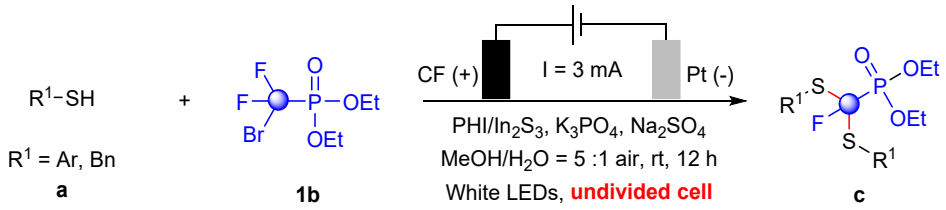
[b] College of Chemistry and Chemical Engineering, Linyi University, Linyi, 276000, Shandong, China. E-mail: sunzongzhao@lyu.edu.cn

Content

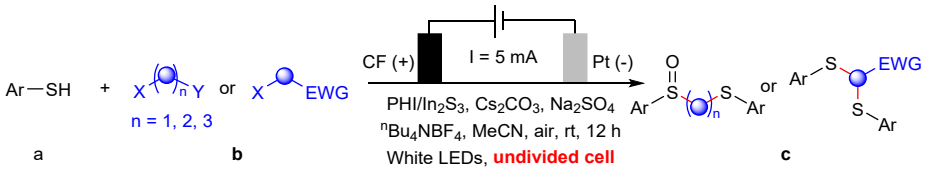
1. General information

All glassware was oven-dried at 100 ^{o}C for 3 hours and cooled down under vacuum All of the reaction solvents of methanol (AR) and acetonitrile (AR) was purchased from Greagent. Others were purchased from Adamas. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). X-ray diffraction (XRD) patterns were recorded on a Rigaku smartlab system at 45 kV and 200 mA with Cu-Kα radiation. Fourier transform infrared (FT-IR) were measured using Bruker VERTEX 70 spectrophotometers. The spherical aberration corrected Transmission Electron Microscope (ACTEM) was carried out on a FEI Themis G2 microscope at 100 KV. The elemental composition was characterized with an energy dispersive X-ray spectroscope (EDX, EMAX-5770, HORIBA). UV–vis absorbance spectra were obtained on a Scan UV–vis spectrophotometer (PerkinElmer, Lambda 750S) at the range of 200 – 800 nm. Inductively coupled plasma mass spectrometry (ICP-MS) result was obtained on a GSE200plus. X ray photoelectron spectroscopy (XPS) data were collected using the AXIS Nova spectrometer (Kratos Analytical) equipped with a monochromatic Al Kα X-ray source. The Al anode was powered at 10 mA and 15 kV. The thin-layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (b. p. 60-90 ^{o}C). ^{1}H, ^{13}C and ^{19}F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform).

2. General procedure



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, K_3PO_4 (1.0 mmol), Na_2SO_4(1.0 mmol) and PHI/In_2S_3 (2.5 mg) were combined. The flask was equipped with a carbon felt (1.0 × 1.0 cm^2) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, **a** (0.5 mmol), **1b** (1.5 mmol), and MeOH/H_2O (5.0 mL/1.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 3 mA under RT for 12 h under white light conditions.



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, Cs_2CO_3 (1.0 mmol), Na_2SO_4 (1.0 mmol), $^nBu_4NBF_4$ (1.0 mmol) and PHI/In_2S_3 (2.5 mg) were combined. The flask was equipped with a carbon felt (1.0 × 1.0 cm^2) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, **a** (1.5 mmol), **b** (0.5 mmol), and MeCN (6.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under RT for 12 h under white light conditions.

3. Photocatalyst characterization

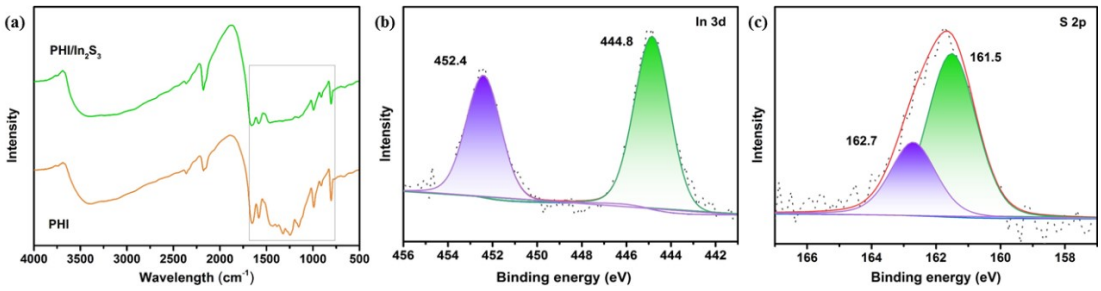


Figure S1. (a) FT-IR results. (b) (c) XPS results of PHI/In_2S_3.

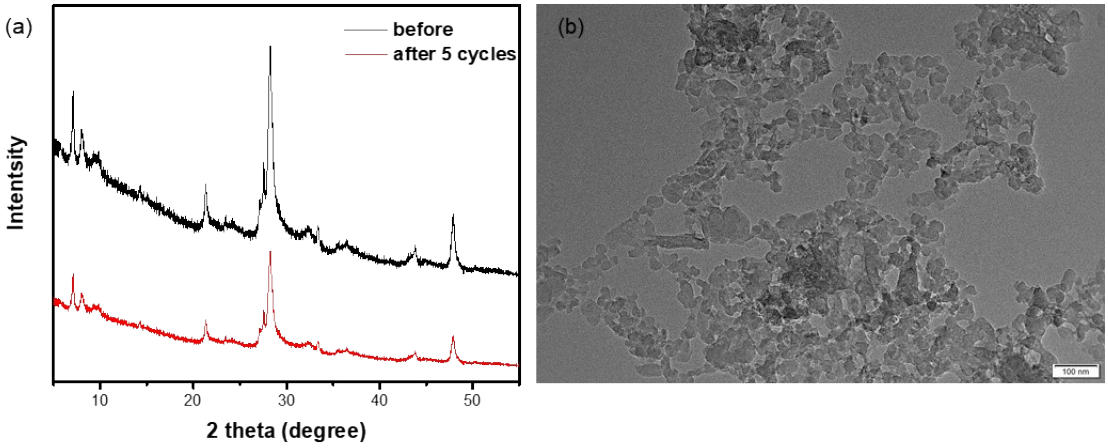
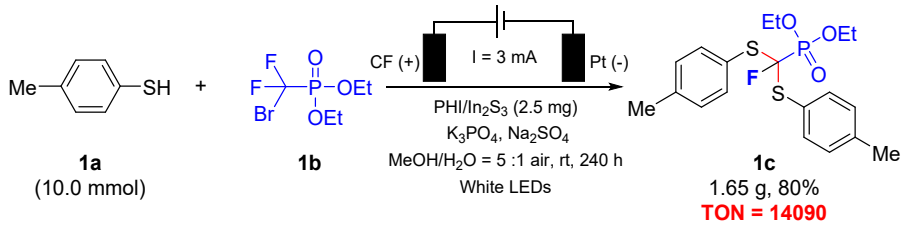


Figure S2. (a) XRD results of PHI/In_2S_3. (b) TEM results of PHI/In_2S_3 after 5 cycles

Table S1. ICP-MS results of PHI/In_2S_3.

Sample	Sampling Quality/g	Constant Volume/mL	Coefficient Dilution	Element	Swot (mg/mL)	Content mg/kg	Mass Fraction
PHI/In_2S_3	0.07419	25	50	In	5.9285	103068.5	10.3%

4. Gram-scale experiments



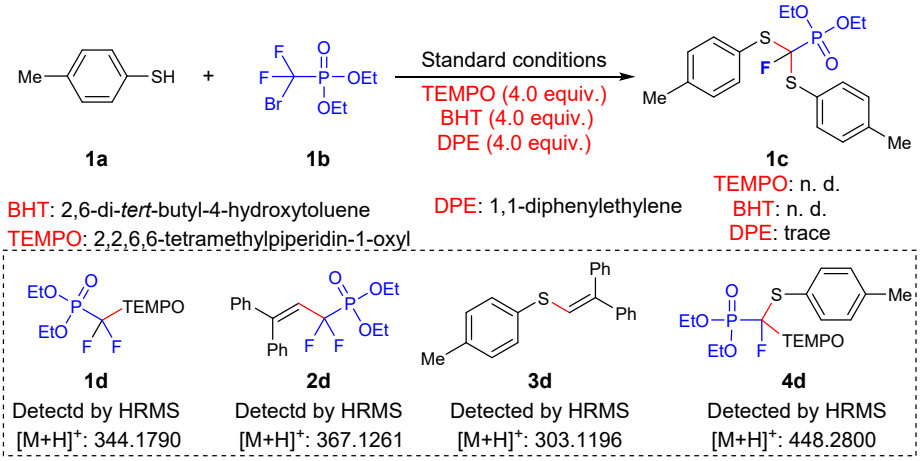
1a (10.0 mmol) **1b** **1c** 1.65 g, 80% TON = 14090

In an oven-dried undivided three-necked flask (250 mL) equipped with a stir bar, K_3PO_4 (20.0 mmol), Na_2SO_4(20.0 mmol), and PHI/In_2S_3(2.5 mg) were combined. The flask was equipped with a carbon felt (1.0 × 1.0 cm^2) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, 4-methylbenzenethiol **1a** (10.0 mmol), diethyl(bromodifluoromethyl) phosphonate **1b** (30.0 mmol), and MeOH/H_2O (100.0 mL/20.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 3 mA under RT for 240 h under white light. The desired product **1c** was subjected to column chromatography on silica gel (1.65 g, 80% yield, TON=14090).

5. Mechanistic exploration experiments

5.1. Radical trapping experiments

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, K_3PO_4 (1.0 mmol), Na_2SO_4 (1.0 mmol), PHI/In_2S_3 (2.5 mg), and TEMPO (1.0 mmol) or BHT (1.0 mmol) or DPE (1.0 mmol) were combined. The flask was equipped with a carbon felt (1.0 × 1.0 cm^2) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, 4-methylbenzenethiol **1a** (0.5 mmol), diethyl (bromodifluoromethyl)phosphonate **1b** (1.5 mmol), and MeOH/H_2O (6.0 mL, v = 5 : 1) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 3 mA under RT for 12 h under white light. Upon completion, we did not observe the target product. The radical intermediates shown in **1d** – **4d** were captured by high-resolution mass spectrometry (HRMS), further validating that the conversion should involve the free radical pathway.



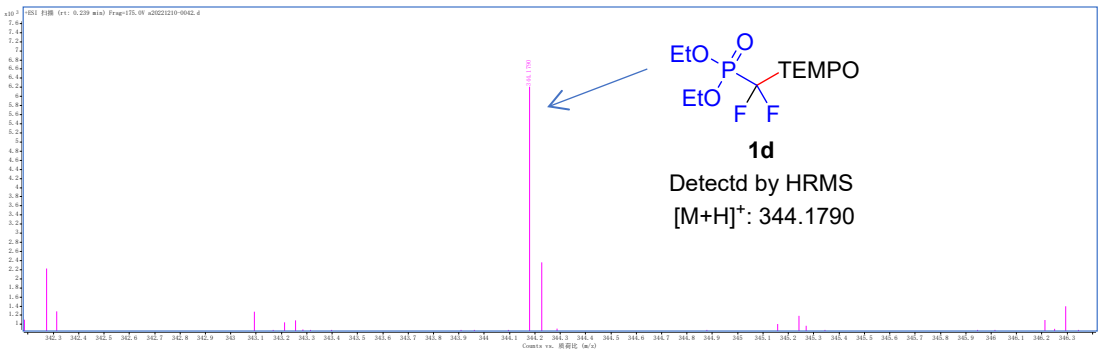


Figure S3. HRMS results of **1d**.

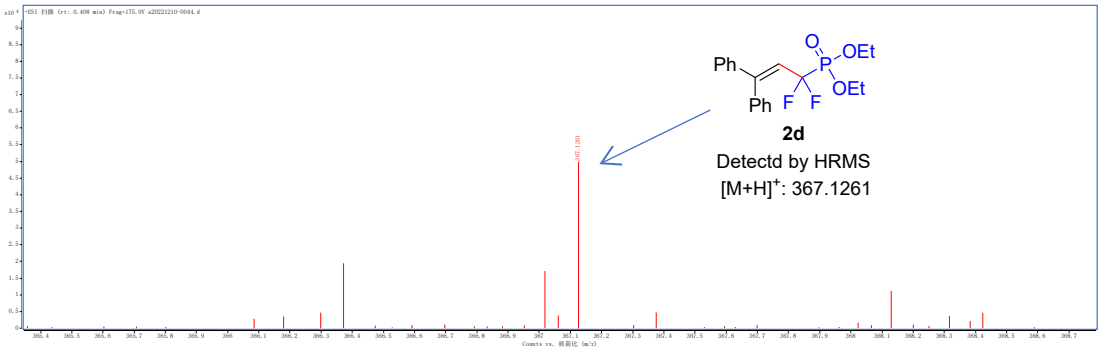


Figure S4. HRMS results of **2d**.

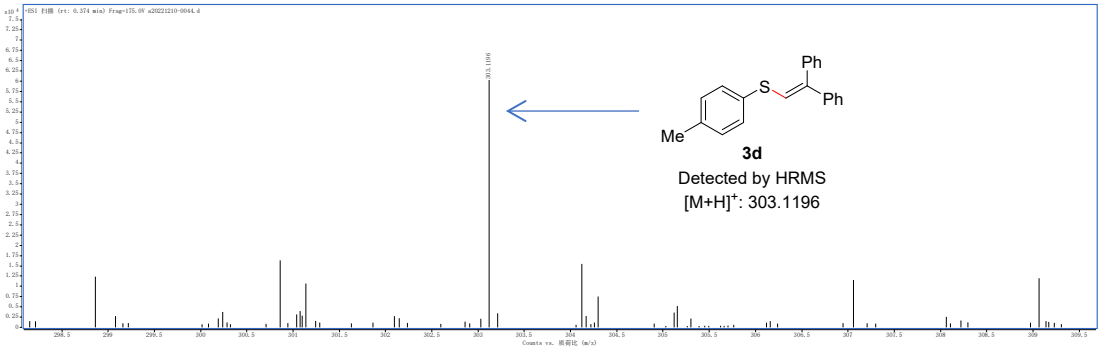


Figure S5. HRMS results of **3d**.

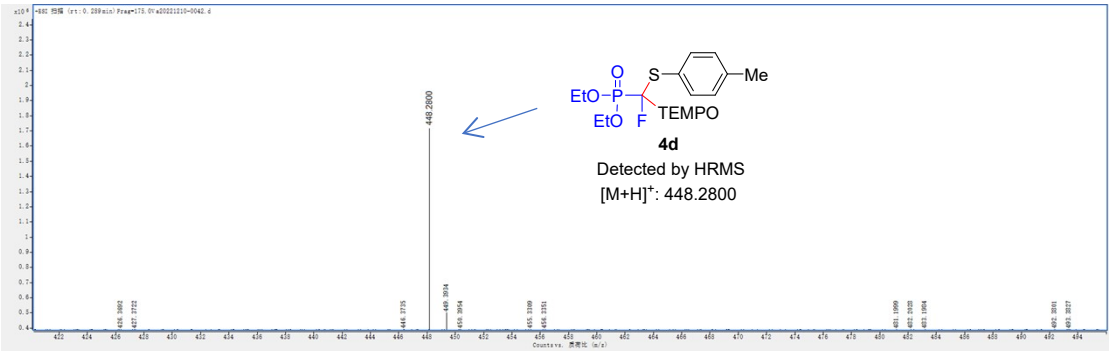
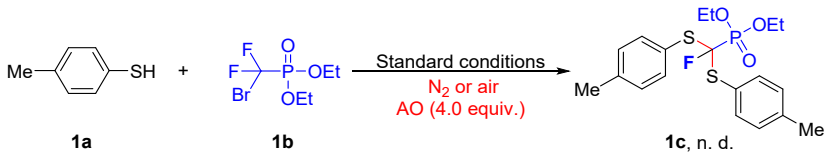


Figure S6. HRMS results of **4d**.

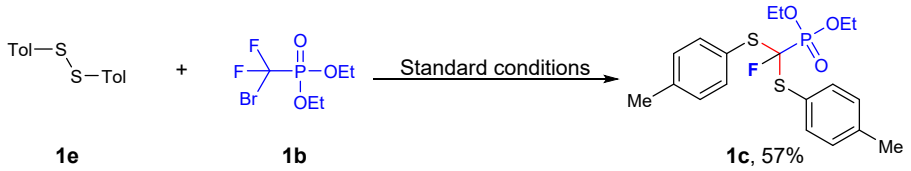
5.2 Active species trapping experiments



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, K_3PO_4 (1.0 mmol), Na_2SO_4 (1.0 mmol), PHI/In_2S_3 (2.5 mg), and AO (1.0 mmol) were combined. The flask was equipped with a carbon felt (1.0 × 1.0 cm^2) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the N_2 or air conditions, **1a** (0.5 mmol), **1b** (1.5 mmol), and MeOH/H_2O (5.0 mL/1.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 3 mA under RT for 12 h under white light. Upon completion, we did not observe

the desired product.

5.3 Intermediate experiments



1e **1b** **1c**, 57%

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, K_3PO_4 (1.0 mmol), Na_2SO_4 (1.0 mmol), and PHI/In_2S_3 (2.5 mg) were combined. The flask was equipped with a carbon felt (1.0 × 1.0 cm^2) as the anode and Pt plates (1.0 × 1.0 cm^2) as the cathode. Under the air, **1e** (0.5 mmol), diethyl (bromodifluoromethyl)phosphonate **1b** (1.5 mmol), and MeOH/H_2O (5.0 mL/1.0 mL) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 3 mA under RT for 12 h under white light. The desired product **1c** was subjected to column chromatography on silica gel (57% yield).

5.4 Photocurrent test

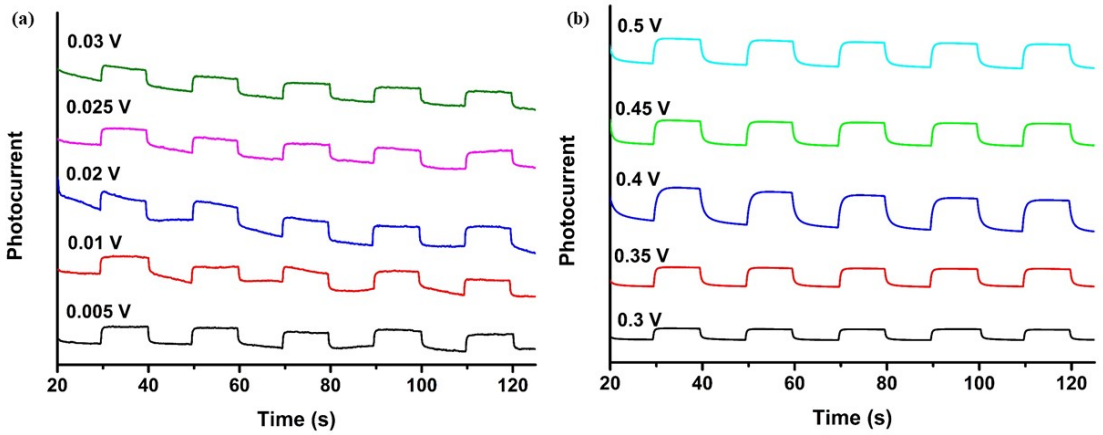
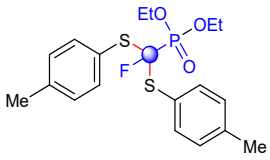
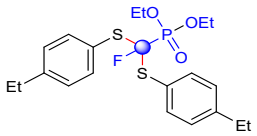


Figure S7. Photocurrent test, PHI/In_2S_3 (2.5 mg/mL) and Nafion (10.0 μL) were mixed and ultrasonically dispersed into DCM ink and take 10.0 μL and drop it onto the surface of the glassy carbon (d = 0.6 cm) electrode, allowing it to dry naturally. In a 25.0 mL three-necked flask, set up glassy carbon as work electrode, Pt (1.5 x 1.5 cm^2) as the counter electrode and Ag/AgCl as the reference electrode, and place it in a completely dark environment, MeOH (10.0 mL) as the solvent. Use the i-t technique to conduct photocurrent testing. (a) Standard reaction system. (b) PHI/In_2S_3.

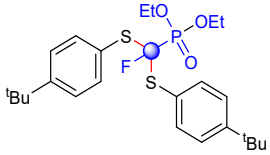
6. Detail descriptions for products



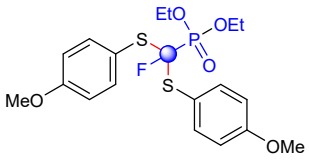
Diethyl (fluorobis(p-tolylthio)methyl)phosphonate (1c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 80% isolated yield (82.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 4H), 7.32 (d, *J* = 8.1 Hz, 4H), 2.92 (m, 2H), 2.81 (m, 2H), 2.42 (s, 6H), 1.19 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 140.0, 129.8, 124.2, 50.3, 21.3, 6.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.2 (d, *J* = 91.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -0.06. HRMS (ESI) m/z: [M+H] + calcd for $C_{19}H_{25}FO_3PS_2$: 415.0961; found: 415.0972.



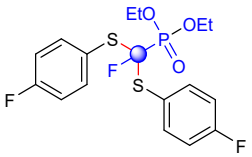
Diethyl (bis((4-ethylphenyl)thio)fluoromethyl)phosphonate (2c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 62% isolated yield (68.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 4H), 7.33 (d, *J* = 8.2 Hz, 4H), 2.89 (m, 2H), 2.80 (m, 2H), 2.70 (q, *J* = 7.7 Hz, 4H), 1.25 (t, *J* = 7.6 Hz, 6H), 1.18 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 140.2, 128.6, 124.3, 50.3, 28.7, 15.3, 6.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.1 (d, *J* = 91.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -0.06. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{21}H_{29}FO_3PS_2$: 443.1274; found: 443.1251.



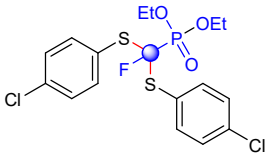
Diethyl (bis((4-(*tert*-butyl)phenyl)thio)fluoromethyl)phosphonate (3c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 63% isolated yield (78.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 8H), 2.90 (m, 2H), 2.79 (m, 2H), 1.31 (s, 18H), 1.17 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 139.9, 126.1, 124.0, 50.2, 34.9, 31.2, 6.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.4 (d, *J* = 91.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -0.06. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{25}H_{37}FO_3PS_2$: 499.1900; found: 499.1907.



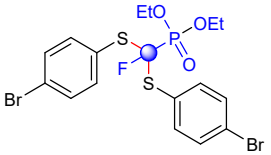
Diethyl (fluorobis((4-methoxyphenyl)thio)methyl)phosphonate (4c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 53% isolated yield (59.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 4H), 7.00 (d, J = 8.5 Hz, 4H), 3.82 (s, 6H), 2.85 (m, 4H), 1.14 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 134.1, 126.1, 114.6, 55.5, 50.4, 6.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -119.4 (d, J = 92.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -19.98. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{19}H_{25}FO_5PS_2$: 447.0860; found: 447.0860



Diethyl (fluorobis((4-fluorophenyl)thio)methyl)phosphonate (5c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 61% isolated yield (64.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (m, 4H), 7.24 (m, 4H), 2.91 (m, 2H), 2.79 (m, 2H), 1.17 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.30 (d, J = 251.2 Hz), 138.74 (d, J = 3.1 Hz), 126.45 (d, J = 8.8 Hz), 116.47 (d, J = 22.5 Hz), 50.4, 5.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ-135.2 (d, J = 91.0 Hz), -108.7. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{19}F_3O_3PS_2$: 423.0460; found: 423.0469.

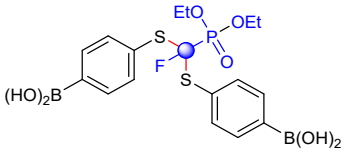


Diethyl (bis((4-chlorophenyl)thio)fluoromethyl)phosphonate (6c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 54% isolated yield (61.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 4H), 7.52 (m, 4H), 2.94 (m, 2H), 2.79 (m, 2H), 1.19 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 137.1, 129.4, 125.6, 50.3, 5.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.2 (d, J = 91.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -0.11. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{19}Cl_2FO_3PS_2$: 454.9869; found: 454.9873.

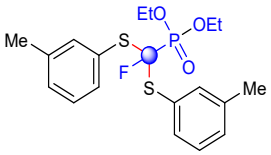


Diethyl (bis((4-bromophenyl)thio)fluoromethyl)phosphonate (7c): yellow oil was obtained by

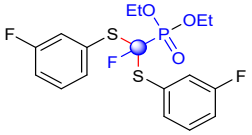
column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 77% isolated yield (104.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 4H), 7.47 (d, *J* = 8.5 Hz, 4H), 2.93 (m, 2H), 2.78 (m, 2H), 1.18 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 132.3, 125.8, 125.3, 50.2, 5.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.2 (d, *J* = 91.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -0.12. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{19}Br_2FO_3PS_2$: 544.8838; found: 544.8841.



((((Diethoxyphosphoryl)fluoromethylene)bis(sulfanediyl))bis(4,1-phenylene))diboronic acid (8c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 30% isolated yield (35.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 4H), 7.35 (d, *J* = 8.1 Hz, 4H), 3.02 (q, *J* = 7.4 Hz, 4H), 1.38 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 135.9, 129.0, 128.8, 126.4, 26.2, 14.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -90.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ -20.01. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{23}B_2FO_7PS_2$: 475.0787; found: 475.0781.

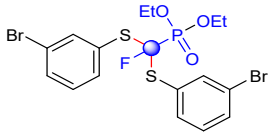


Diethyl (fluorobis(*m*-tolylthio)methyl)phosphonate (9c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 70% isolated yield (72.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.41 (m, 4H), 7.29 (d, *J* = 7.0 Hz, 2H), 2.93 (m, 2H), 2.82 (m, 2H), 2.42 (s, 6H), 1.20 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 139.3, 131.7, 128.9, 124.4, 121.3, 50.3, 21.4, 6.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.6 (d, *J* = 91.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 0.03. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{19}H_{25}FO_3PS_2$: 415.0961; found: 415.0970.

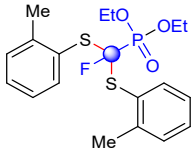


Diethyl (fluorobis((3-fluorophenyl)thio)methyl)phosphonate (10c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 62% isolated yield (65.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 2H), 7.40 (m, 4H), 7.22 (m, 2H), 2.99 (m, 2H), 2.8 (m, 2H),

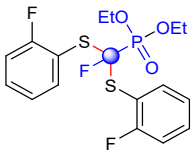
1.21 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.08 (d, J = 251.8 Hz), 130.82 (d, J = 7.7 Hz), 119.81 (d, J = 3.3 Hz), 118.05 (d, J = 21.5 Hz), 111.53 (d, J = 23.9 Hz), 50.2, 5.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.8, -135.2 (d, J = 91.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 0.04. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{17}H_{19}F_3O_3PS_2$: 423.0460; found: 423.0452.



Diethyl (bis((3-bromophenyl)thio)fluoromethyl)phosphonate (11c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 67% isolated yield (91.1 mg). H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.60 (m, 2H), 7.50 (m, 2H), 7.36 (t, J = 7.8 Hz, 2H), 2.95 (m, 2H), 2.79 (m, 2H), 1.18 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 134.0, 130.6, 127.1, 123.5, 122.7, 50.2, 5.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.1 (d, J = 91.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -20.03. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{17}H_{19}Br_2FO_3PS_2$: 544.8838; found: 544.8844.

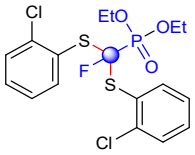


Diethyl (fluorobis(o-tolylthio)methyl)phosphonate (12c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 47% isolated yield (48.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (m, 2H), 7.44 (m, 4H), 7.19 (d, J = 7.4 Hz, 2H), 2.93 (m, 2H), 2.75 (m, 2H), 2.36 (s, 6H), 1.22 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 134.6, 130.7, 130.7, 127.1, 124.2, 48.2, 18.3, 6.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.0 (d, J = 91.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 0.17. HRMS (ESI) *m/z:* [M+H] $^+$ calcd for $C_{19}H_{25}FO_3PS_2$: 415.0961; found: 415.0957.

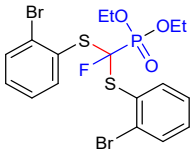


Diethyl (fluorobis((2-fluorophenyl)thio)methyl)phosphonate (13c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 51% isolated yield (53.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (t, J = 6.7 Hz, 2H), 7.46 (dd, J = 13.4, 6.0 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.08 (t, J = 8.9 Hz, 2H), 3.12 (m, 2H), 2.91 (m, 2H), 1.20 (t, J = 7.4 Hz, 6H). ^{13}C NMR

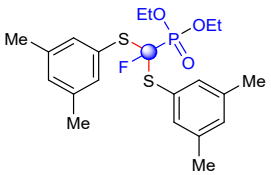
(126 MHz, $CDCl_3$) δ 157.79 (d, *J* = 246.7 Hz), 132.70 (d, *J* = 7.6 Hz), 130.18 (d, *J* = 16.6 Hz), 126.71 (d, *J* = 2.4 Hz), 125.29 (d, *J* = 3.3 Hz), 115.65 (d, *J* = 20.4 Hz), 48.0, 5.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.2 (d, *J* = 91.0 Hz), -114.4. ^{31}P NMR (202 MHz, $CDCl_3$) δ -19.98. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{19}F_3O_3PS_2$: 423.0460; found: 423.0460.



Diethyl (bis((2-chlorophenyl)thio)fluoromethyl)phosphonate (14c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 51% isolated yield (58.0 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.53 (m, 2H), 7.45 (m, 4H), 3.17 (m, 2H), 2.89 (m, 2H), 1.23 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 132.0, 130.2, 129.9, 127.8, 126.7, 47.2, 5.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.1 (d, *J* = 91.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -0.01. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{19}Cl_2FO_3PS_2$: 454.9869; found: 454.9872.

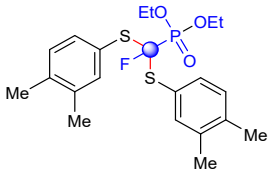


Diethyl (bis((2-bromophenyl)thio)fluoromethyl)phosphonate (15c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 62% isolated yield (84.3 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 4H), 7.37 (m, 2H), 3.15 (m, 2H), 2.87 (m, 2H), 1.21 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 132.9, 132.2, 128.2, 126.9, 118.7, 47.3, 5.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.6 (d, *J* = 89.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -20.03. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{19}Br_2FO_3PS_2$: 544.8838; found: 544.8841.

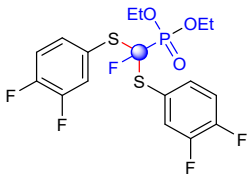


Diethyl (bis((3,5-dimethylphenyl)thio)fluoromethyl)phosphonate (16c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 45% isolated yield (49.7 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.19 (s, 4H), 7.09 (s, 2H), 2.91 (m, 2H), 2.79 (m, 2H),

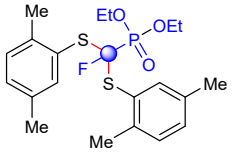
2.36 (s, 12H), 1.19 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 140.1, 133.6, 122.6, 51.2, 22.2, 7.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -100.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ -19.98. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{29}FO_3PS_2$: 443.1274; found: 443.1269.



Diethyl (bis((3,4-dimethylphenyl)thio)fluoromethyl)phosphonate (17c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 38% isolated yield (41.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 2H), 7.28 (dd, J = 7.8, 1.6 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 2.90 (m, 2H), 2.78 (m, 2H), 2.29 (d, J = 6.7 Hz, 12H), 1.16 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 140.0, 137.9, 130.2, 124.9, 121.7, 50.3, 19.8, 19.7, 6.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ -19.97. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{29}FO_3PS_2$: 443.1274; found: 443.1270.

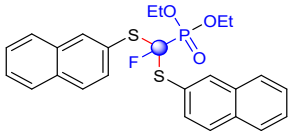


Diethyl (bis((3,4-difluorophenyl)thio)fluoromethyl)phosphonate (18c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 54% isolated yield (61.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.32 (dd, J = 7.9, 4.0 Hz, 4H), 2.93 (m, 2H), 2.77 (m, 2H), 1.18 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.96 (d, J = 253.4 Hz), 151.86 (d, J = 253.3 Hz), 151.02 (d, J = 254.7 Hz), 150.91 (d, J = 254.7 Hz), 140.13 (d, J = 7.1 Hz), 120.70 (d, J = 4.1 Hz), 120.65 (d, J = 4.1 Hz), 118.30 (d, J = 18.5 Hz), 113.84 (d, J = 19.5 Hz), 50.4, 5.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -132.9 (d, J = 1.9 Hz), -133.0 (d, J = 2.2 Hz), -133.8 (d, J = 1.5 Hz), -133.9 (d, J = 1.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -0.12. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{17}H_{17}F_5O_3PS_2$: 459.0271; found: 459.0286.

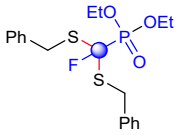


Diethyl (bis((2,5-dimethylphenyl)thio)fluoromethyl)phosphonate (19c): yellow oil was

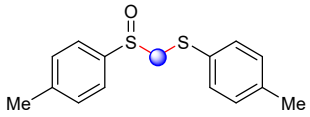
obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 66% isolated yield (72.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.16 (d, J = 7.7 Hz, 2H), 7.07 (d, J = 7.7 Hz, 2H), 2.92 (m, 2H), 2.75 (m, 2H), 2.34 (d, J = 35.3 Hz, 12H), 1.23 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 137.0, 131.4, 131.3, 130.5, 124.3, 48.4, 21.0, 17.7, 6.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -135.4 (d, J = 91.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -19.97. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{21}H_{29}FO_3PS_2$: 443.1274; found: 443.1270.



Diethyl (fluorobis(naphthalen-2-ylthio)methyl)phosphonate (20c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 84% isolated yield (102.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.99 (m, 6H), 7.61 (m, 6H), 3.04 (m, 2H), 2.88 (m, 2H), 1.21 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.3, 134.4, 132.8, 129.3, 128.4, 128.0, 127.7, 127.2, 125.0, 119.9, 49.9, 5.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.7. ^{31}P NMR (202 MHz, $CDCl_3$) δ 0.14. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{25}H_{25}FO_3PS_2$: 487.0961; found: 487.0970.

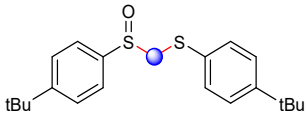


Diethyl (bis(benzylthio)fluoromethyl)phosphonate(21c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/1) with 45% isolated yield (93.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 10H), 3.97 (q, J = 12.9 Hz, 4H), 2.73 (m, 4H), 1.32 (t, J = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.9, 128.9, 128.3, 57.5, 44.0, 6.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.3. ^{31}P NMR (202 MHz, $CDCl_3$) δ -20.02. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{19}H_{25}FO_3PS_2$: 415.0961; found: 415.0952.

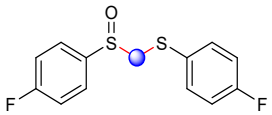


***p*-Tolyl((p-tolylsulfinyl)methyl)sulfane (25c):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 40% isolated yield (55.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 4.15 (d, J = 13.3 Hz, 1H), 4.01 (d, J = 13.3 Hz, 1H), 2.41 (s, 3H), 2.34 (s,

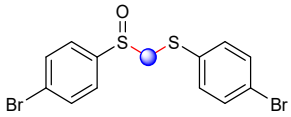
3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 139.5, 138.1, 131.6, 130.0, 129.8, 125.0, 61.5, 21.4, 21.1. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{15}H_{17}OS_2$: 277.0715; found: 277.0715.



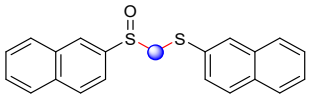
(4-(*Tert*-butyl)phenyl)(((4-(*tert*-butyl)phenyl)sulfinyl)methyl)sulfane (26c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 36% isolated yield (64.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.17 (d, *J* = 13.3 Hz, 1H), 4.04 (d, *J* = 13.3 Hz, 1H), 1.34 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 151.2, 139.5, 131.1, 130.1, 126.4, 126.3, 126.1, 124.8, 124.7, 61.3, 35.0, 34.6, 31.2. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{29}OS_2$: 361.1654; found: 361.1655.



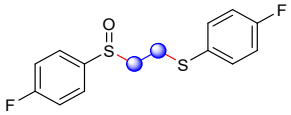
(4-Fluorophenyl)(((4-fluorophenyl)sulfinyl)methyl)sulfane (27c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 49% isolated yield (69.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.45 (dd, *J* = 8.7, 5.2 Hz, 2H), 7.19 (t, *J* = 8.5 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 4.07 (dd, *J* = 46.4, 13.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.82 (d, *J* = 252.7 Hz), 162.75 (d, *J* = 249.5 Hz), 138.01 (d, *J* = 3.2 Hz), 134.23 (d, *J* = 8.3 Hz), 128.48 (d, *J* = 3.3 Hz), 127.27 (d, *J* = 9.0 Hz), 116.53 (d, *J* = 22.6 Hz), 116.51 (d, *J* = 22.1 Hz), 61.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.3, -112.5. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{13}H_{11}F_2OS_2$: 285.0214; found: 285.0219.



(4-Bromophenyl)(((4-bromophenyl)sulfinyl)methyl)sulfane (28c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 41% isolated yield (83.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 4.15 (d, *J* = 13.7 Hz, 1H), 4.07 (d, *J* = 13.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 132.6, 132.4, 132.3, 129.2, 126.4, 124.8, 122.2, 60.6. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{13}H_{11}Br_2OS_2$: 406.8592; found: 406.8598.

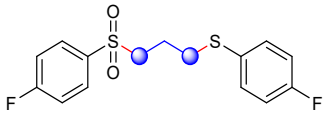


Naphthalen-2-yl((naphthalen-2-ylsulfinyl)methyl)sulfane (29c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 35% isolated yield (60.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.90 (dd, *J* = 5.9, 3.5 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.78 (s, 2H), 7.74 (dd, *J* = 6.0, 3.4 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.65 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.61 (dd, *J* = 6.0, 3.4 Hz, 1H), 7.57 (m, 2H), 7.47 (m, 3H), 4.37 (d, *J* = 13.6 Hz, 1H), 4.28 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 134.8, 130.5, 130.0, 129.3, 128.9, 128.5, 128.0, 128.0, 127.6, 127.3, 127.3, 126.8, 126.5, 126.2, 120.1, 60.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{21}H_{17}OS_2$: 349.0715; found: 349.0722.



(4-Fluorophenyl)(2-((4-fluorophenyl)sulfinyl)ethyl)sulfane (30c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 70% isolated yield (104.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (m, 2H), 7.34 (m, 2H), 7.24 (m, 2H), 7.02 (m, 2H), 3.24 (m, 1H), 3.04 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.42 (d, *J* = 252.0 Hz), 162.34 (d, *J* = 248.0 Hz), 138.35 (d, *J* = 3.1 Hz), 133.39 (d, *J* = 8.2 Hz), 128.97 (d, *J* = 3.4 Hz), 126.26 (d, *J* = 8.9 Hz), 116.76 (d, *J* = 22.6 Hz), 116.42 (d, *J* = 22.0 Hz), 55.9, 27.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.1, -113.7. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{14}H_{13}F_2OS_2$: 299.0370; found: 299.0377.

(4-Fluorophenyl)(2-((4-fluorophenyl)sulfinyl)ethyl)sulfane (30c) was synthesized from 4-fluorobenzenethiol and 1-bromo-2-fluoroethane as the starting materials: yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 34% isolated yield (50.7 mg).

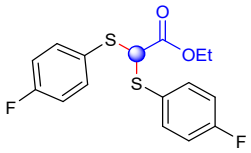


(4-Fluorophenyl)(3-((4-fluorophenyl)sulfinyl)propyl)sulfane (31c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 58% isolated yield (95.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.6, 5.1 Hz, 2H), 7.30 (dd, *J* = 8.3, 5.2 Hz, 2H), 7.20 (t, *J* = 8.5 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 3.01 (m, 3H), 2.88 (m, 1H), 2.10 (m, 1H), 1.90 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.35 (d, *J* = 251.6 Hz), 162.10 (d, *J* = 247.3 Hz), 139.03 (d, *J* = 2.9

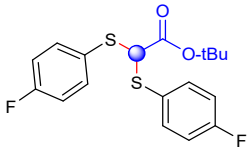
Hz), 133.14 (d, J = 8.0 Hz), 129.93 (d, J = 3.4 Hz), 126.27 (d, J = 8.8 Hz), 116.62 (d, J = 22.6 Hz), 116.19 (d, J = 21.9 Hz), 55.3, 34.1, 21.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.4, -114.5. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{15}H_{15}F_2O_2S_2$: 329.0476; found: 329.0473.

(4-Fluorophenyl)(3-((4-fluorophenyl)sulfinyl)propyl)sulfane (31c) was synthesized from (4-fluorobenzenethiol and 1-bromo-3-fluoropropane as the starting materials: yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 50% isolated yield (82.0 mg).

(4-Fluorophenyl)(3-((4-fluorophenyl)sulfinyl)propyl)sulfane (31c) was synthesized from (4-fluorobenzenethiol and 1-chloro-3-fluoropropane as the starting materials: yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/3) with 54% isolated yield (88.7 mg).

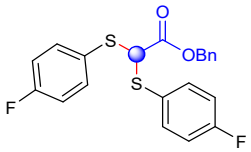


Ethyl 2,2-bis((4-fluorophenyl)thio)acetate (32c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/50) with 68% isolated yield (115.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (m, 4H), 7.06 (m, 4H), 4.67 (s, 1H), 4.18 (m, 2H), 1.23 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 163.36 (d, J = 249.9 Hz), 162.43 (d, J = 247.6 Hz), 137.94 (d, J = 8.4 Hz), 136.39 (d, J = 8.5 Hz), 133.49 (d, J = 8.2 Hz), 129.78 (d, J = 3.2 Hz), 127.50 (d, J = 3.4 Hz), 116.27 (d, J = 21.9 Hz), 116.17 (d, J = 21.9 Hz), 62.2, 59.4, 13.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.4. HRMS (ESI) *m/z:* $[M+H]^+$ calcd for $C_{16}H_{15}F_2O_2S_2$: 341.0476; found: 341.0491.

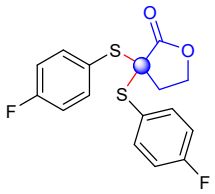


***Tert*-butyl 2,2-bis((4-fluorophenyl)thio)acetate (33c):** yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/50) with 82% isolated yield (150.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (m, 4H), 7.02 (dd, J = 9.6, 7.7 Hz, 4H), 4.59 (s, 1H), 1.37 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 163.23 (d, J = 249.6 Hz), 137.58 (d, J = 8.5 Hz), 136.17 (d, J = 8.4 Hz), 133.19 (d, J = 8.2 Hz), 127.92 (d, J = 3.4 Hz), 116.14 (d, J = 21.9 Hz), 116.03 (d, J = 21.9 Hz), 115.71 (d, J = 21.8 Hz), 83.0, 60.1, 27.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.8. HRMS

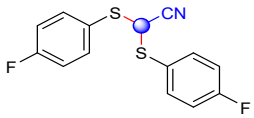
(ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{18}H_{19}F_2O_2S_2$: 369.0789; found: 369.0789.



Benzyl 2,2-bis((4-fluorophenyl)thio)acetate (34c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/50) with 53% isolated yield (106.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (m, 3H), 7.31 (m, 4H), 7.08 (dd, *J* = 7.5, 1.6 Hz, 3H), 6.95 (m, 3H), 4.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.12 (d, *J* = 249.7 Hz), 162.6, 137.4, 135.15 (d, *J* = 8.5 Hz), 134.6, 128.6, 128.4, 125.98 (d, *J* = 3.3 Hz), 116.28 (d, *J* = 22.1 Hz), 67.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.5. HRMS (ESI) *m/z:* [M+Na] $^{+}$ calcd for $C_{21}H_{16}F_2NaO_2S_2$: 425.0452; found: 425.0451.



3,3-Bis((4-fluorophenyl)thio)dihydrofuran-2(3*H*)-one (35c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/50) with 66% isolated yield (111.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (m, 4H), 7.10 (m, 4H), 4.25 (t, *J* = 6.6 Hz, 2H), 2.43 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 164.18 (d, *J* = 251.7 Hz), 138.87 (d, *J* = 8.7 Hz), 124.85 (d, *J* = 3.4 Hz), 116.42 (d, *J* = 21.9 Hz), 64.7, 61.7, 36.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.5. HRMS (ESI) *m/z:* [M+H] $^{+}$ calcd for $C_{16}H_{13}F_2O_2S_2$: 339.0320; found: 339.0318.



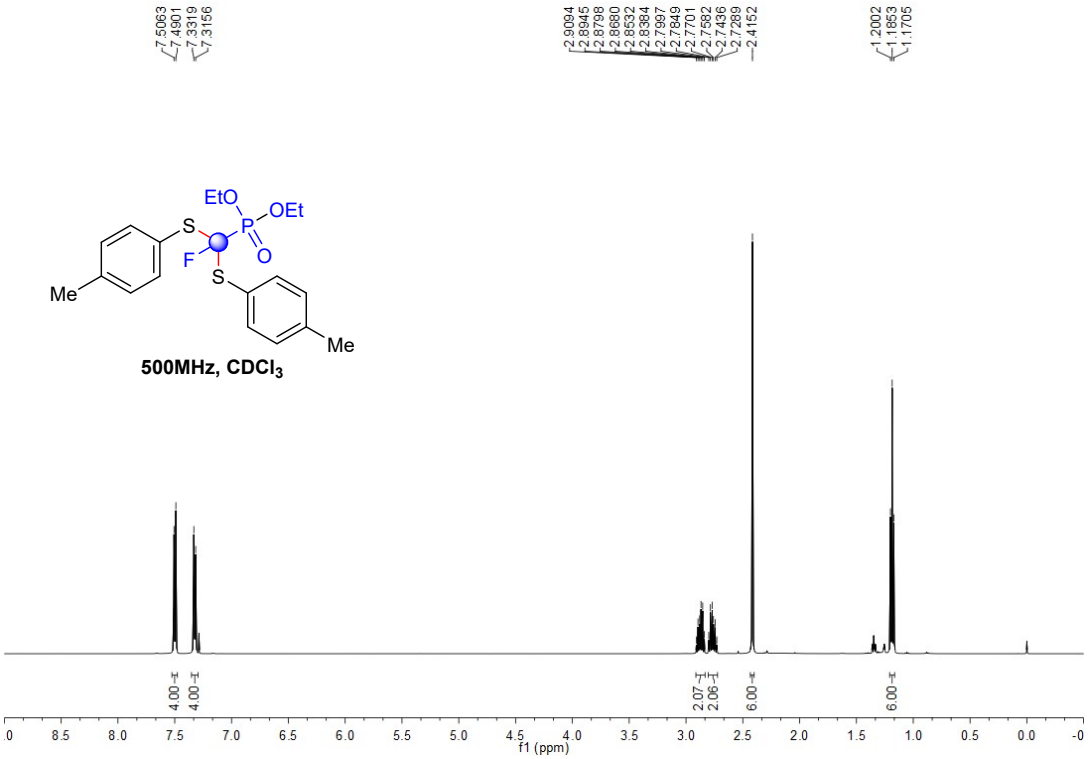
2,2-Bis((4-fluorophenyl)thio)acetonitrile (36c): yellow oil was obtained by column chromatography (eluent: EtOAc/petroleum ether = 1/50) with 45% isolated yield (65.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (m, 4H), 7.14 (m, 4H), 4.72 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.25 (d, *J* = 252.1 Hz), 163.60 (d, *J* = 250.5 Hz), 137.93 (d, *J* = 8.8 Hz), 135.91 (d, *J* = 8.6 Hz), 124.98 (d, *J* = 3.4 Hz), 116.90 (d, *J* = 22.1 Hz), 116.86 (d, *J* = 22.1 Hz), 115.5, 42.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -109.0. HRMS (ESI) *m/z:* [M+Na] $^{+}$ calcd for $C_{14}H_9F_2NNaS_2$: 316.0037; found: 316.0029.

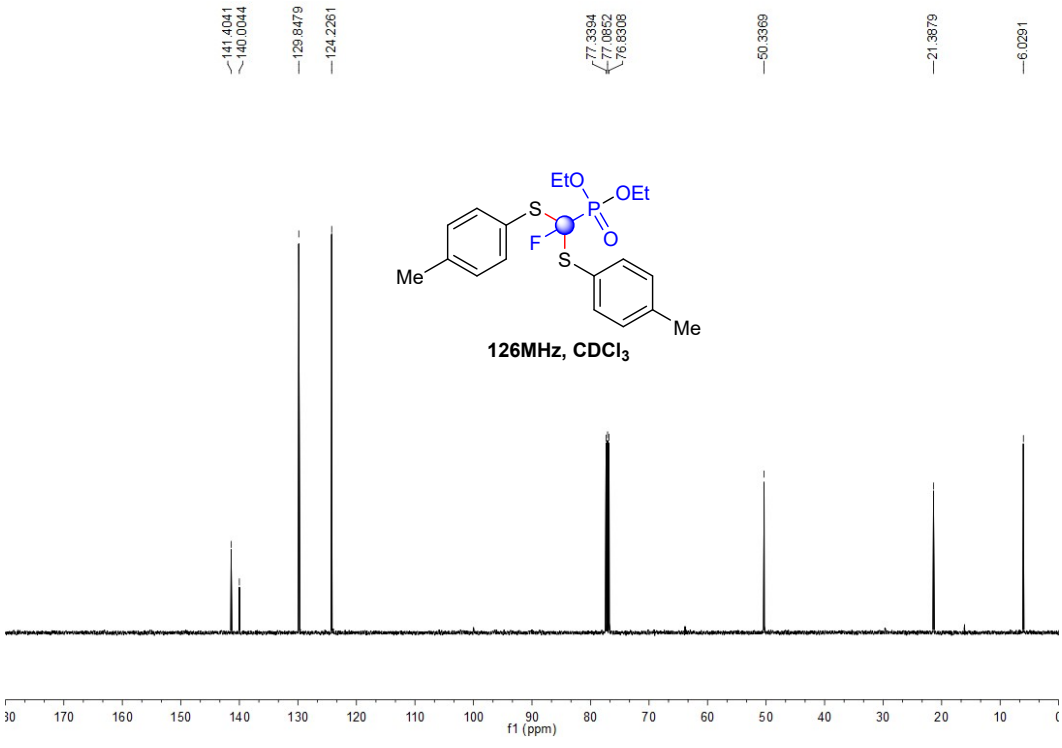
7. Copies of product NMR Spectra

1c

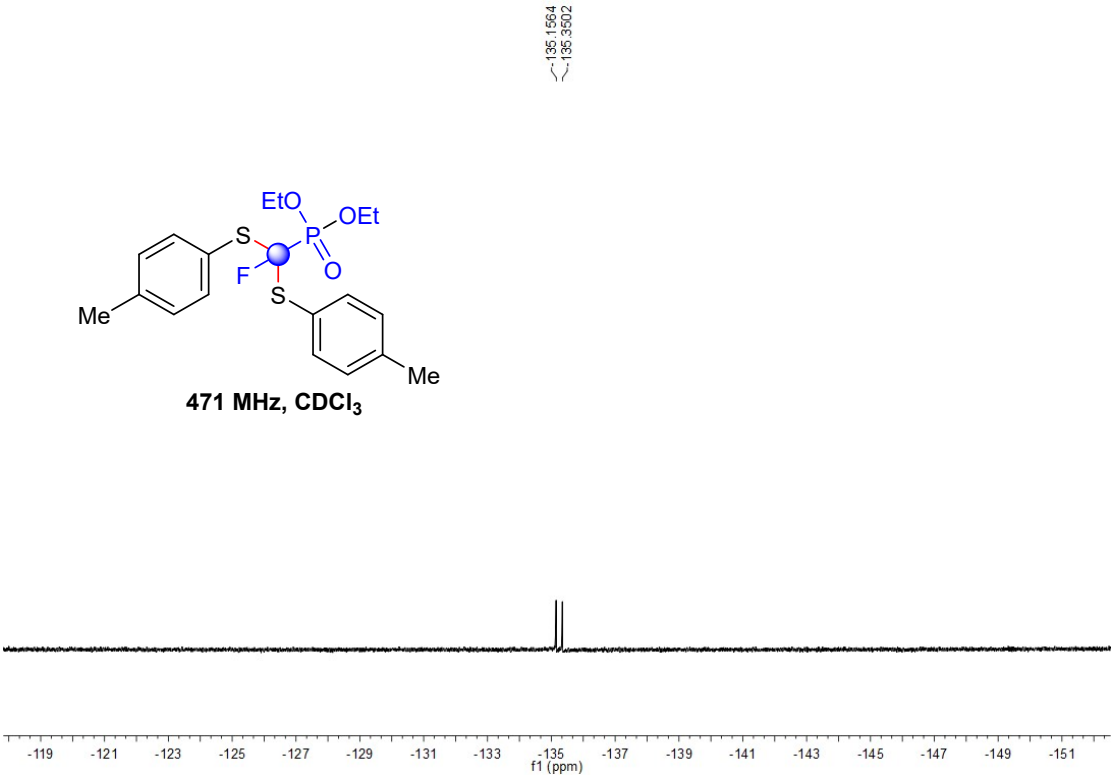
^{1}H NMR



^{13}C NMR

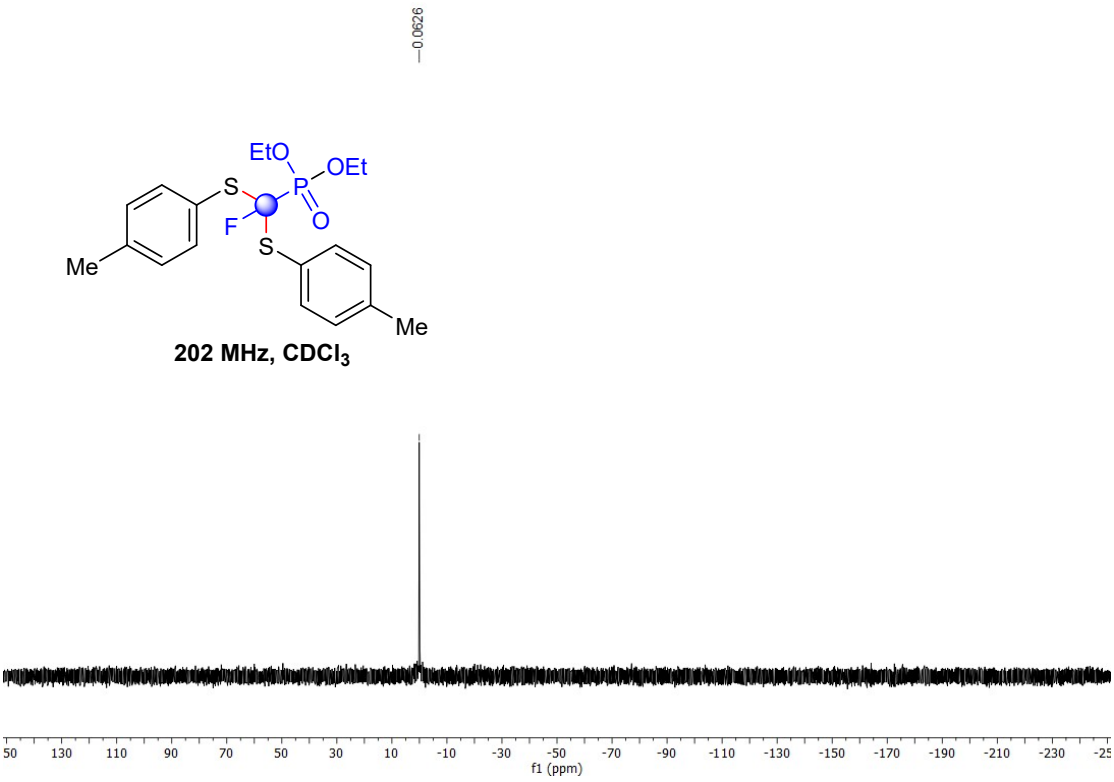


^{19}F NMR



471 MHz, $CDCl_3$

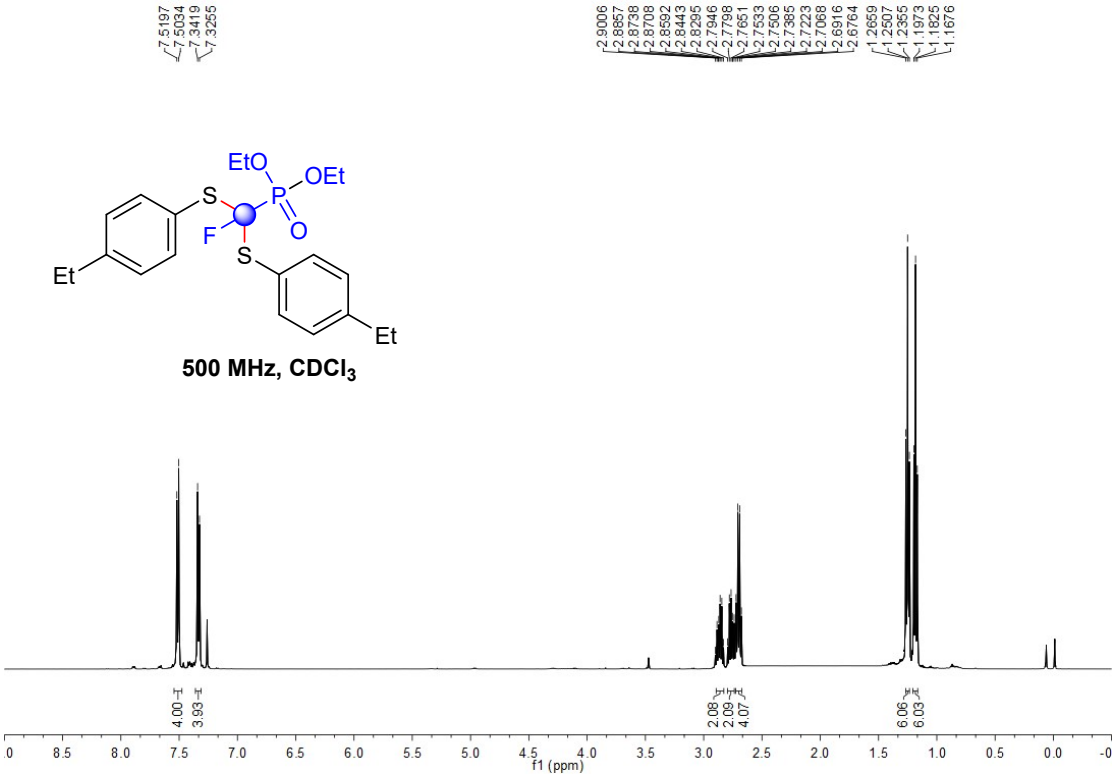
^{31}P NMR



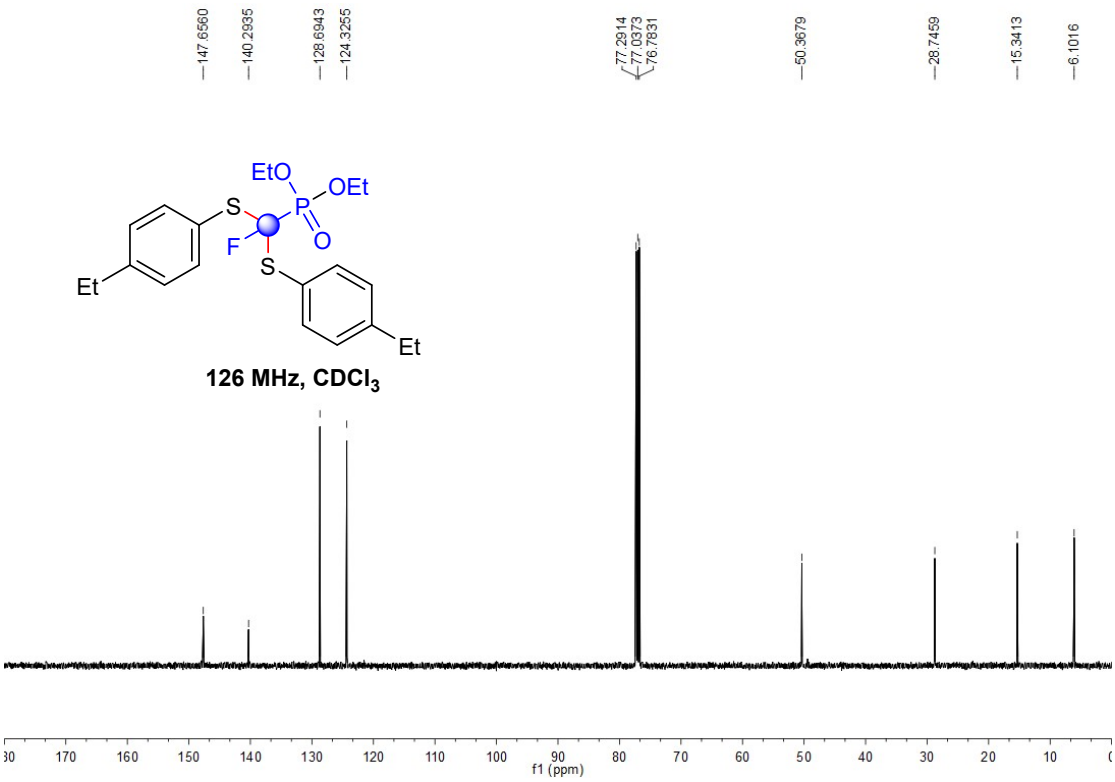
202 MHz, $CDCl_3$

2c

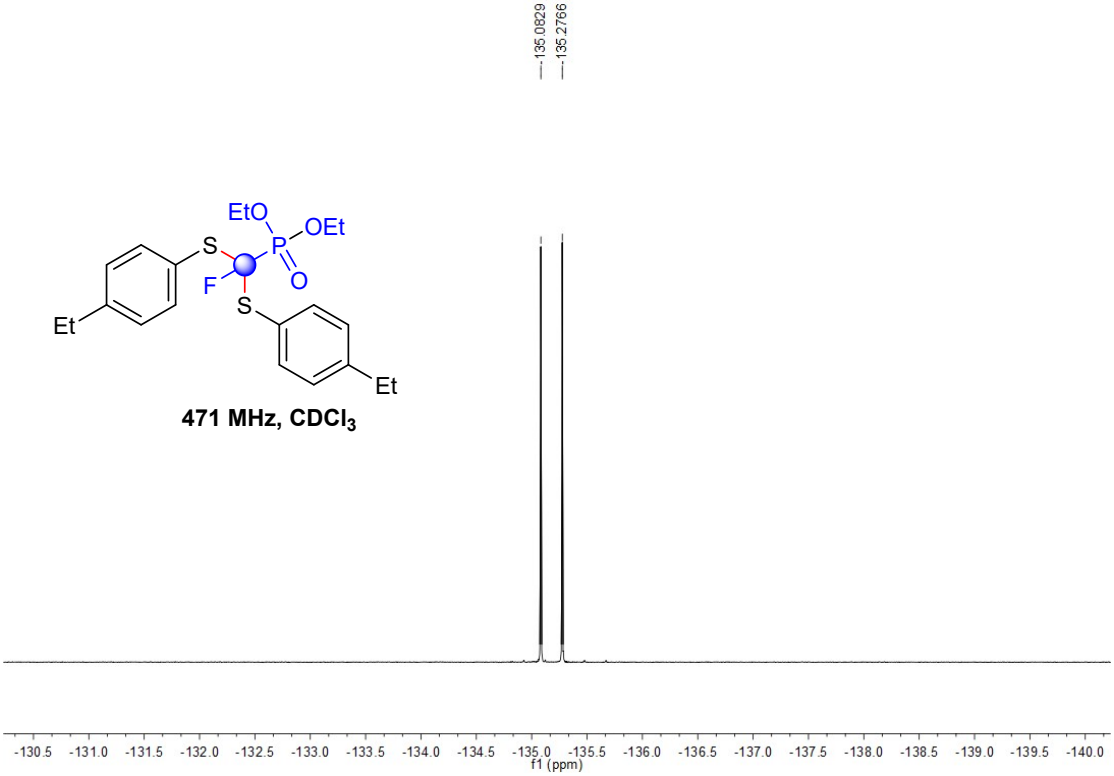
^{1}H NMR



^{13}C NMR

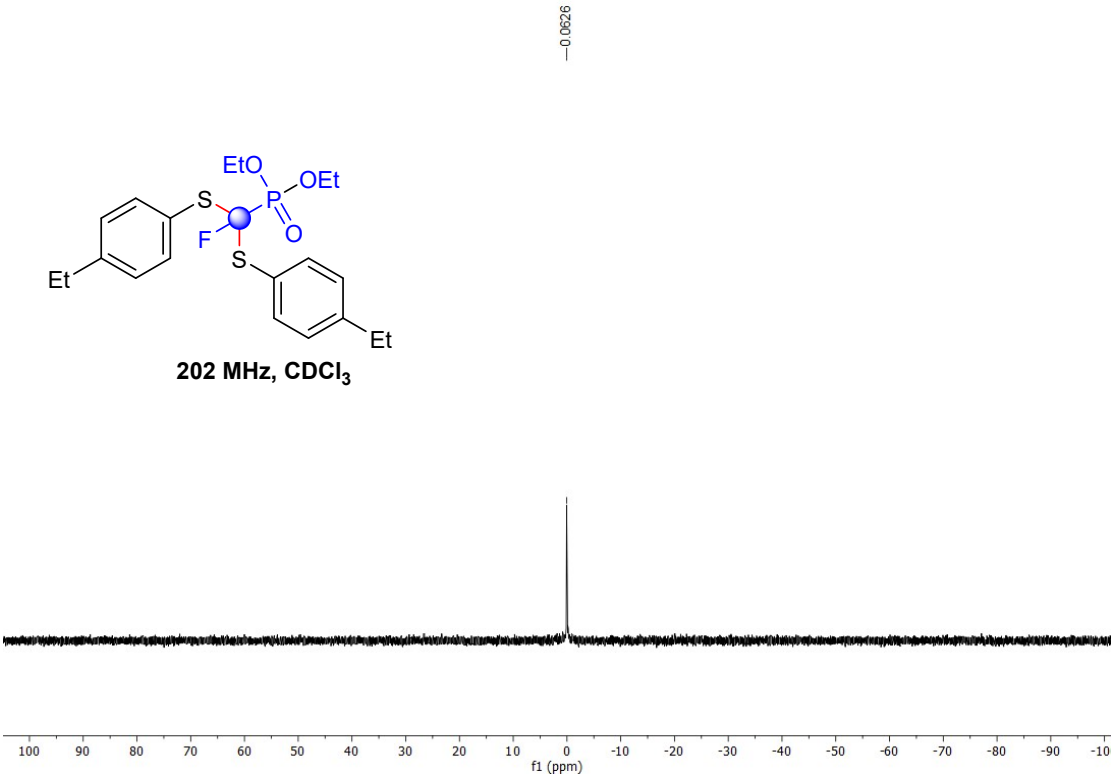


^{19}F NMR



471 MHz, $CDCl_3$

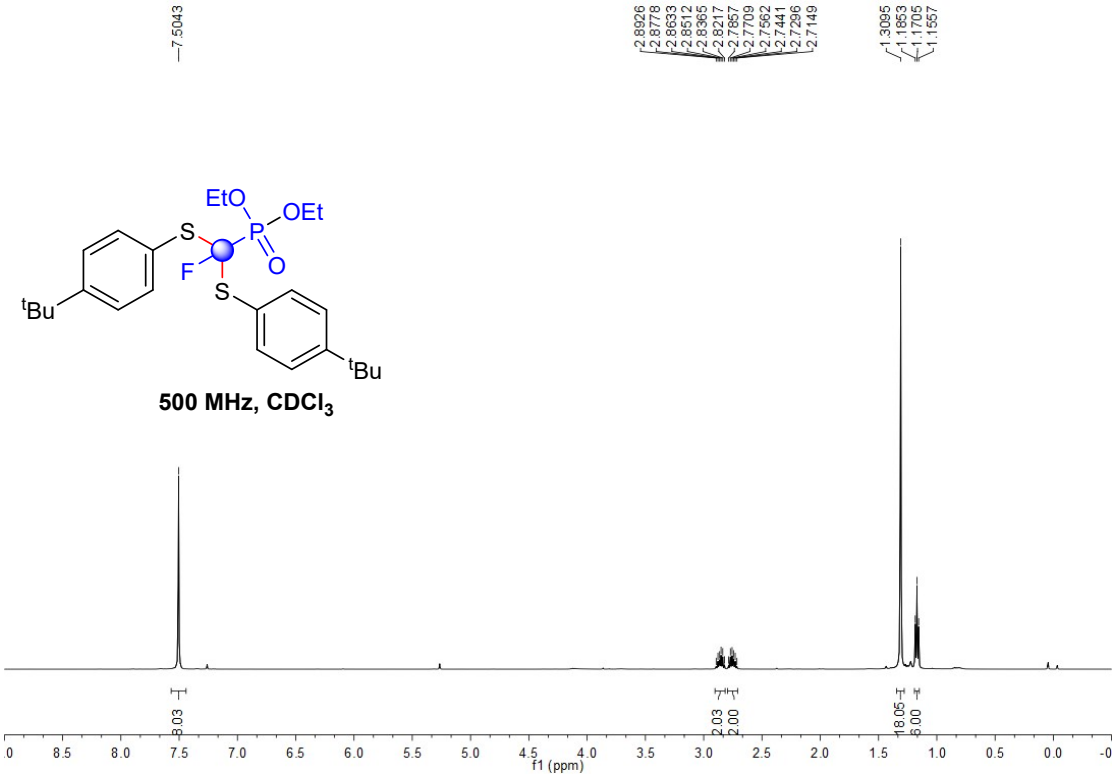
^{31}P NMR



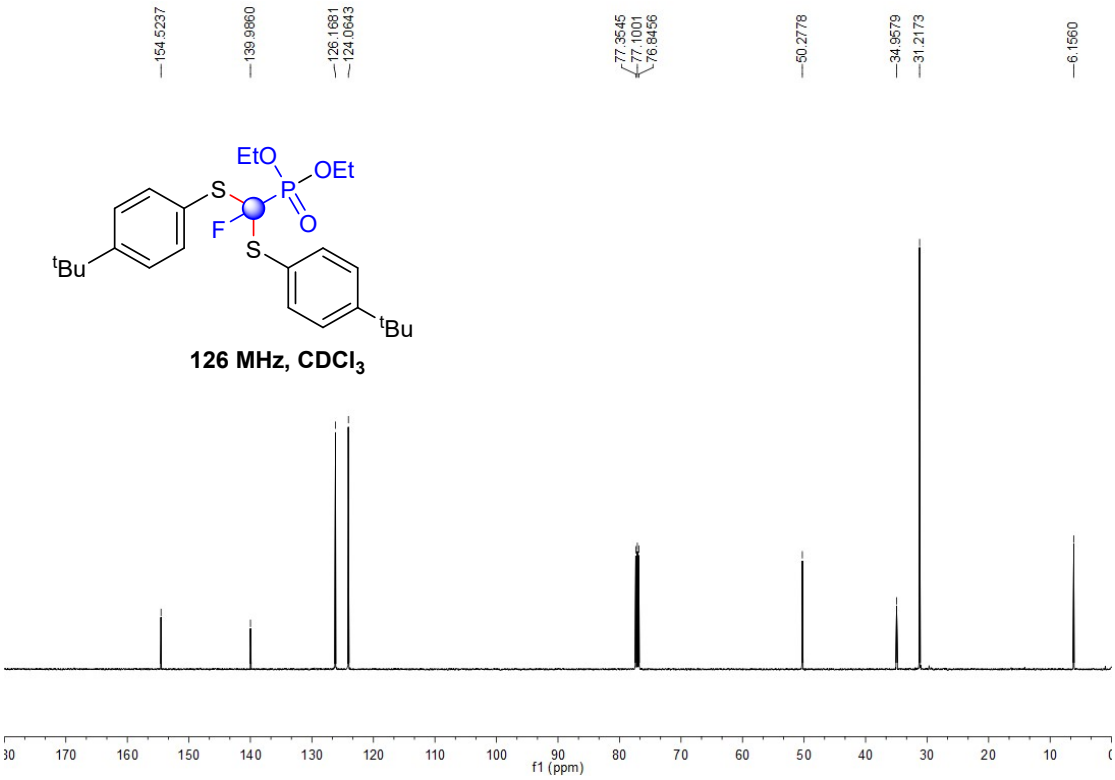
202 MHz, $CDCl_3$

3c

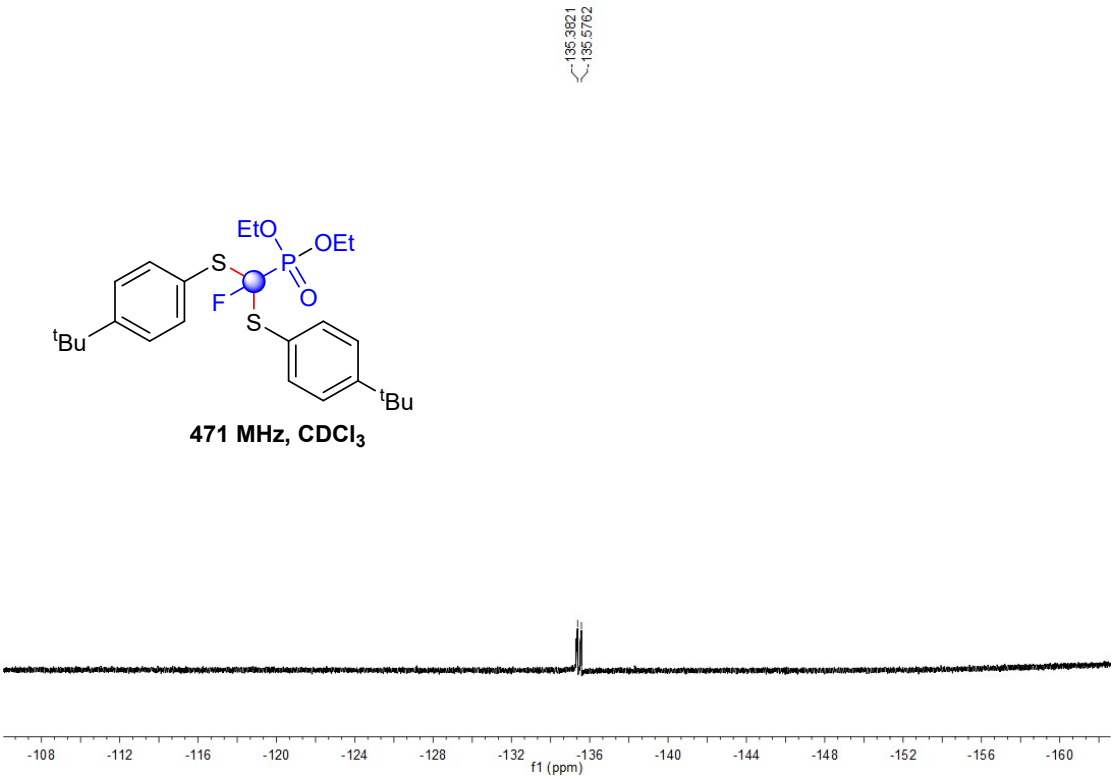
^{1}H NMR



^{13}C NMR

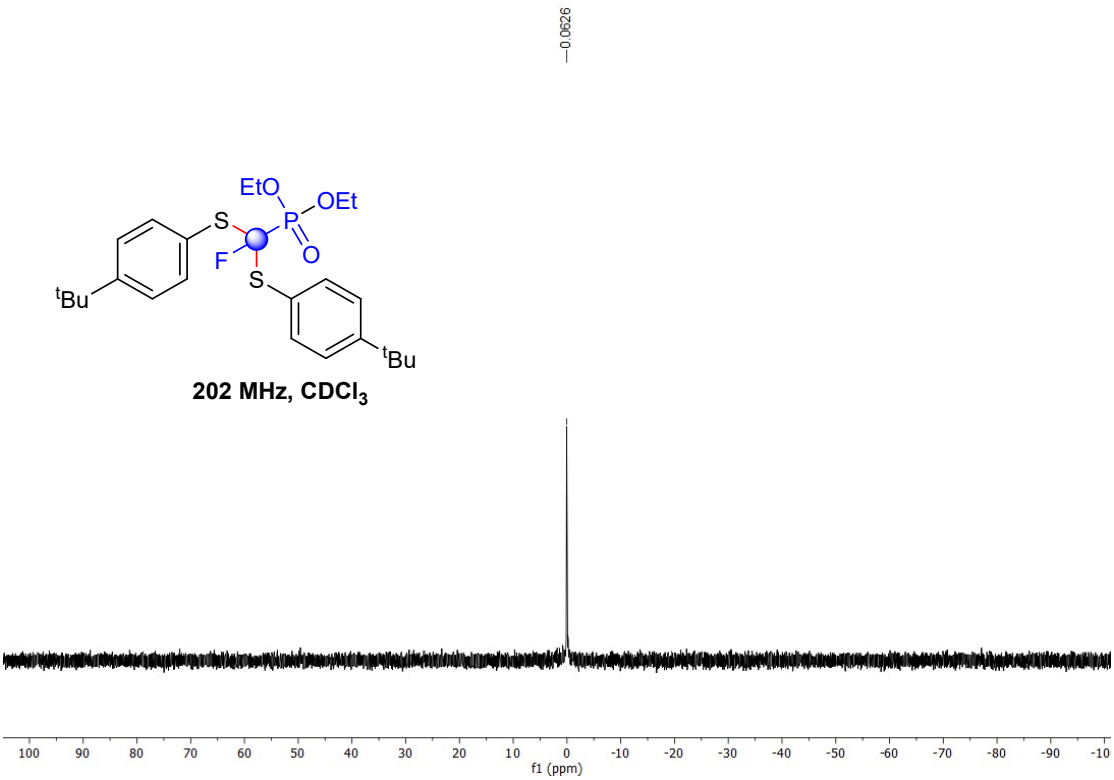


^{19}F NMR



471 MHz, $CDCl_3$

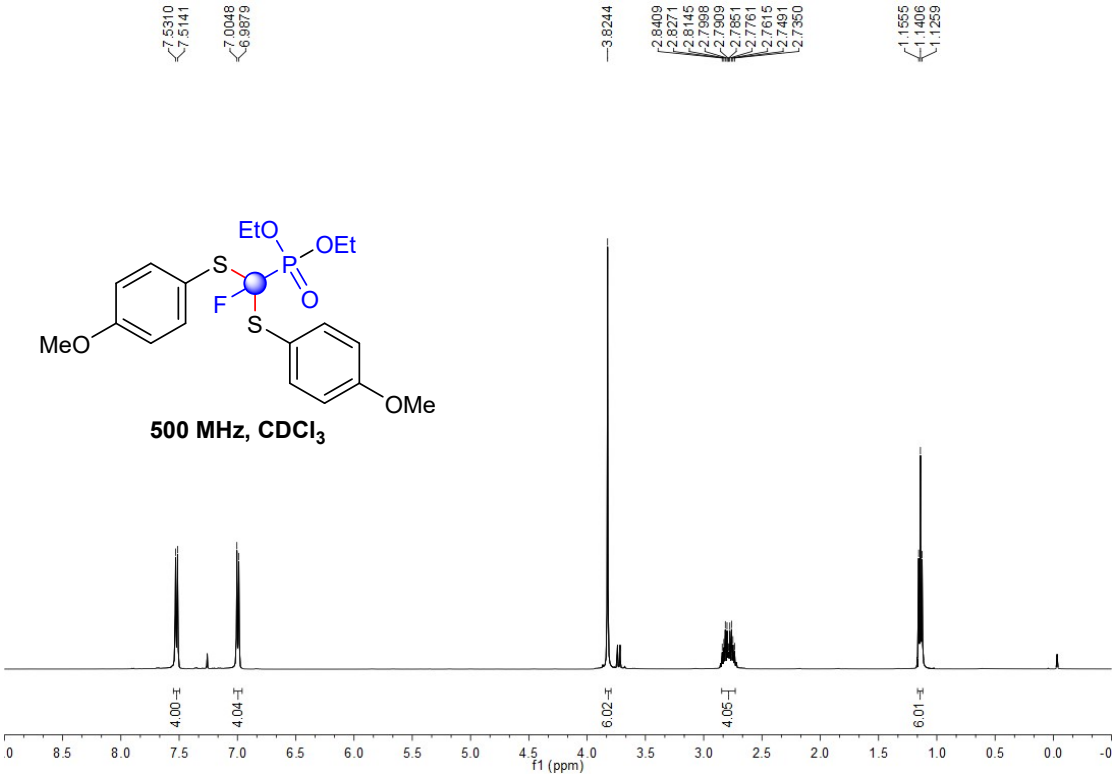
^{31}P NMR



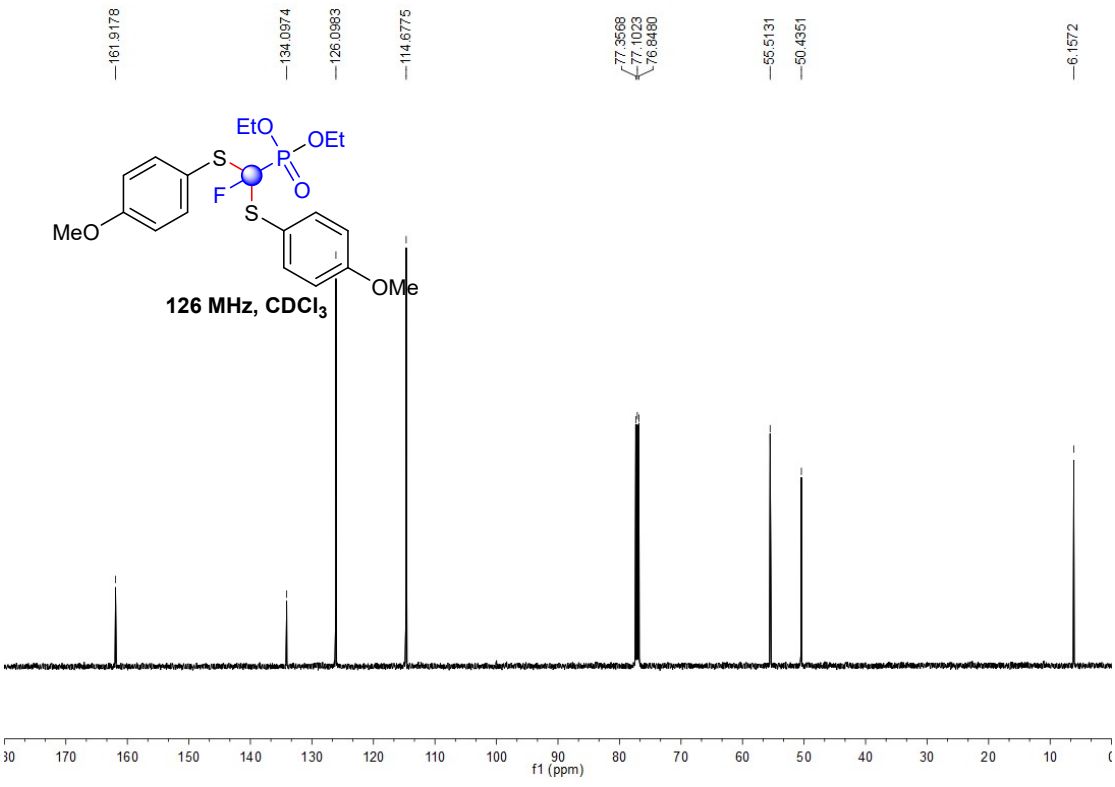
202 MHz, $CDCl_3$

4c

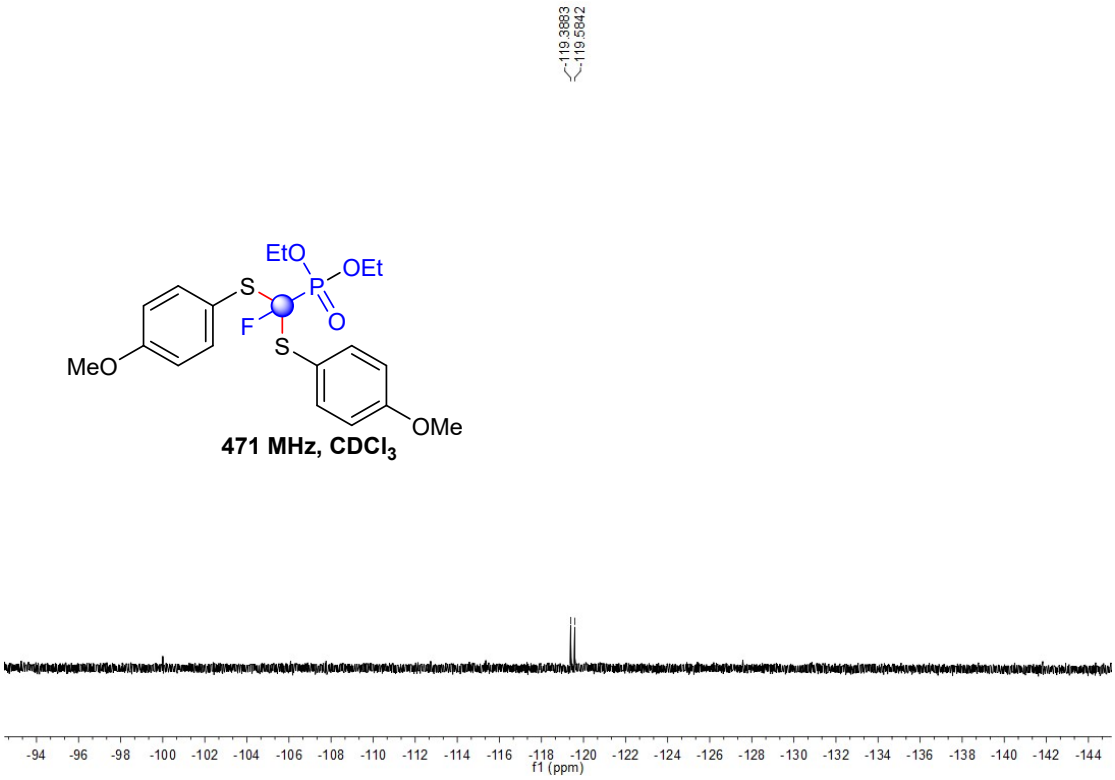
^{1}H NMR



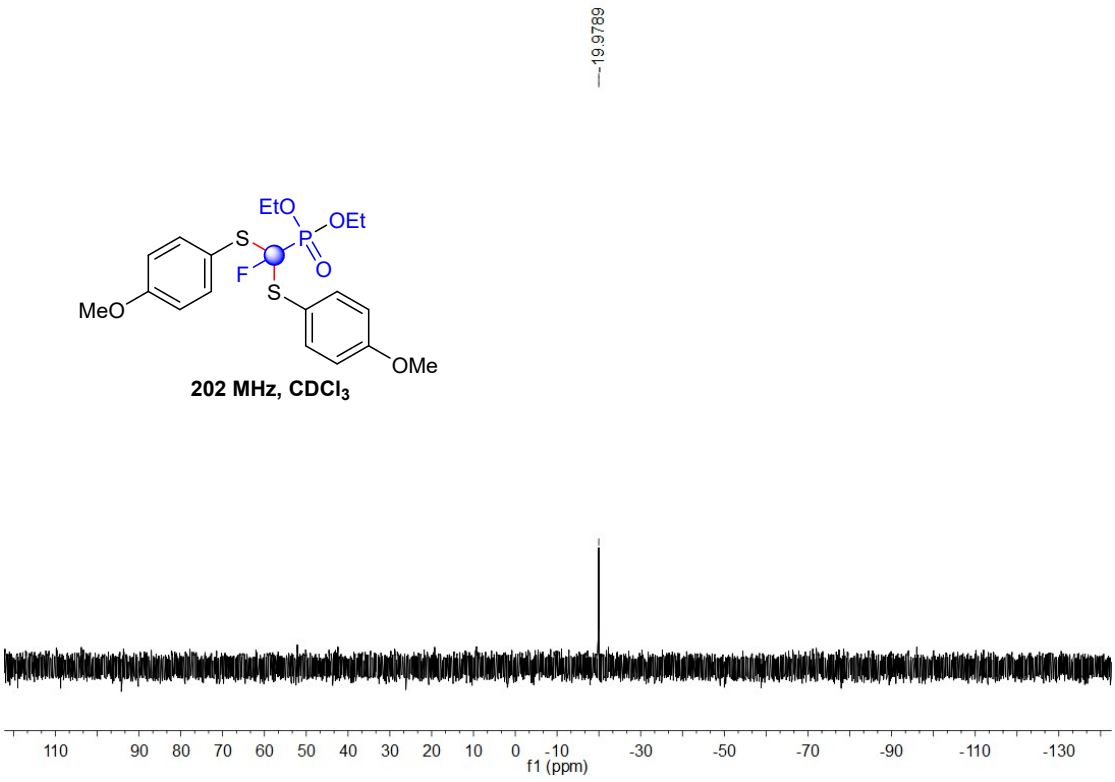
^{13}C NMR



^{19}F NMR

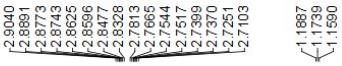


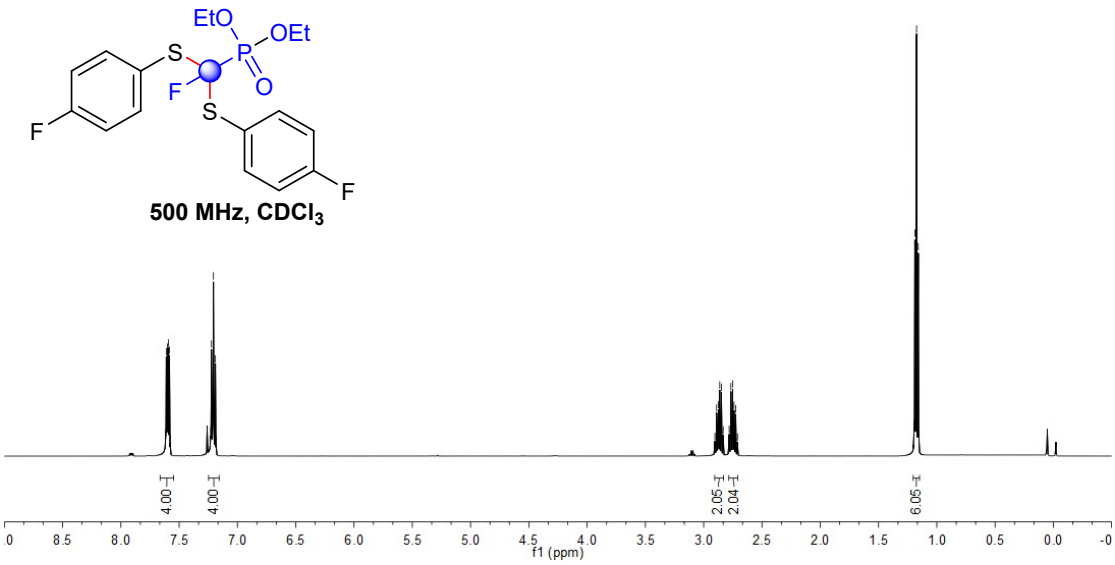
^{31}P NMR



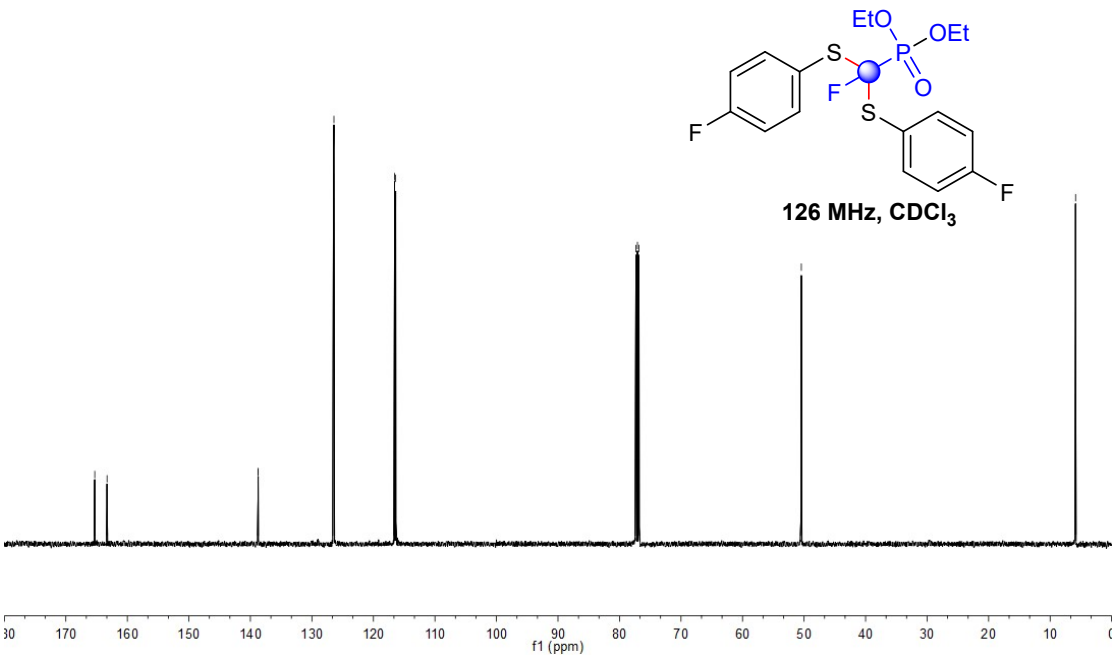
5c

^{1}H NMR

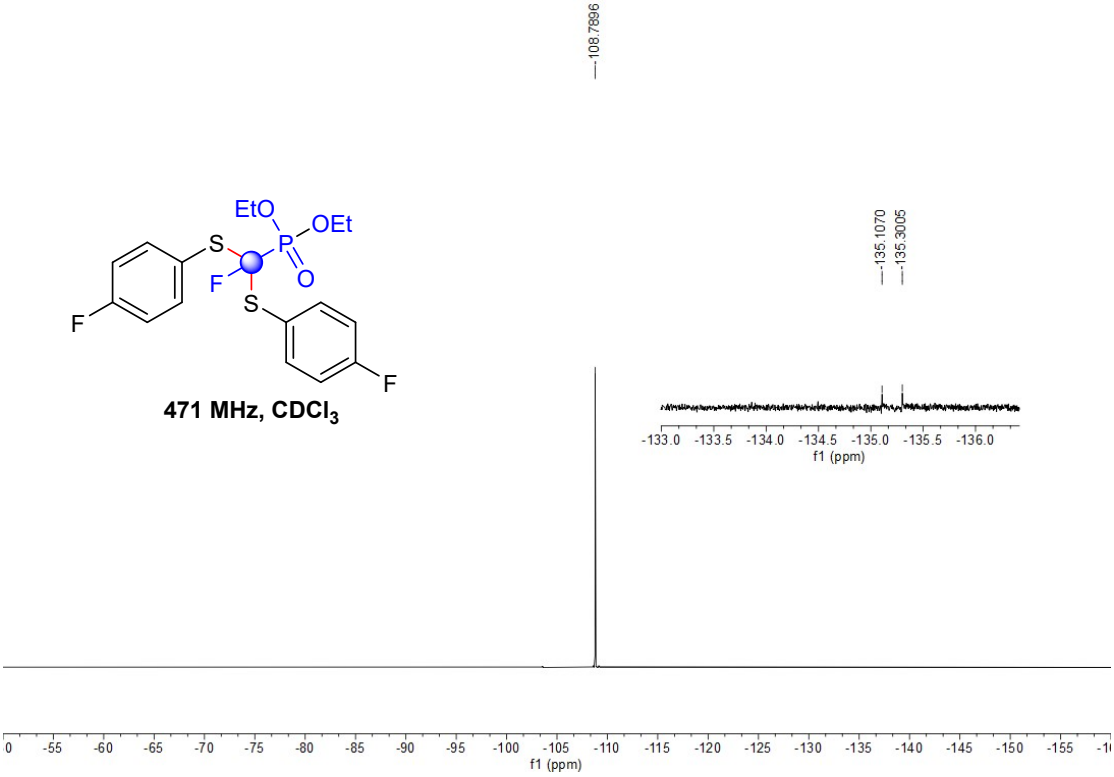




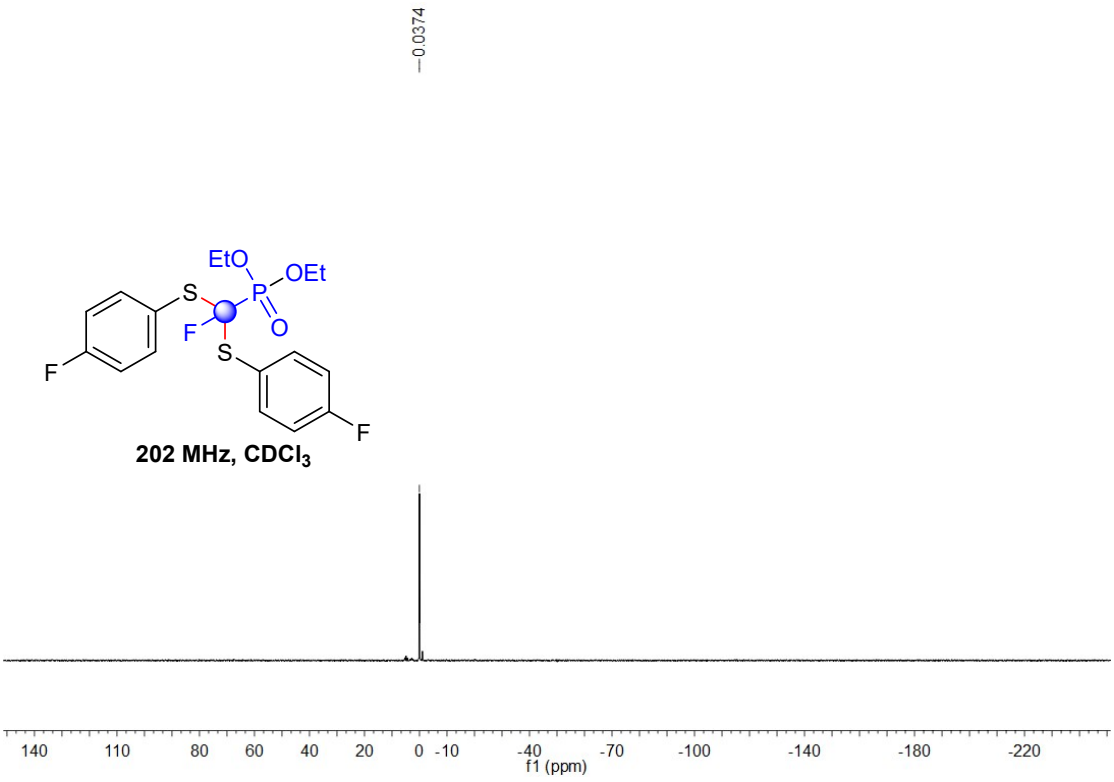
^{13}C NMR



^{19}F NMR

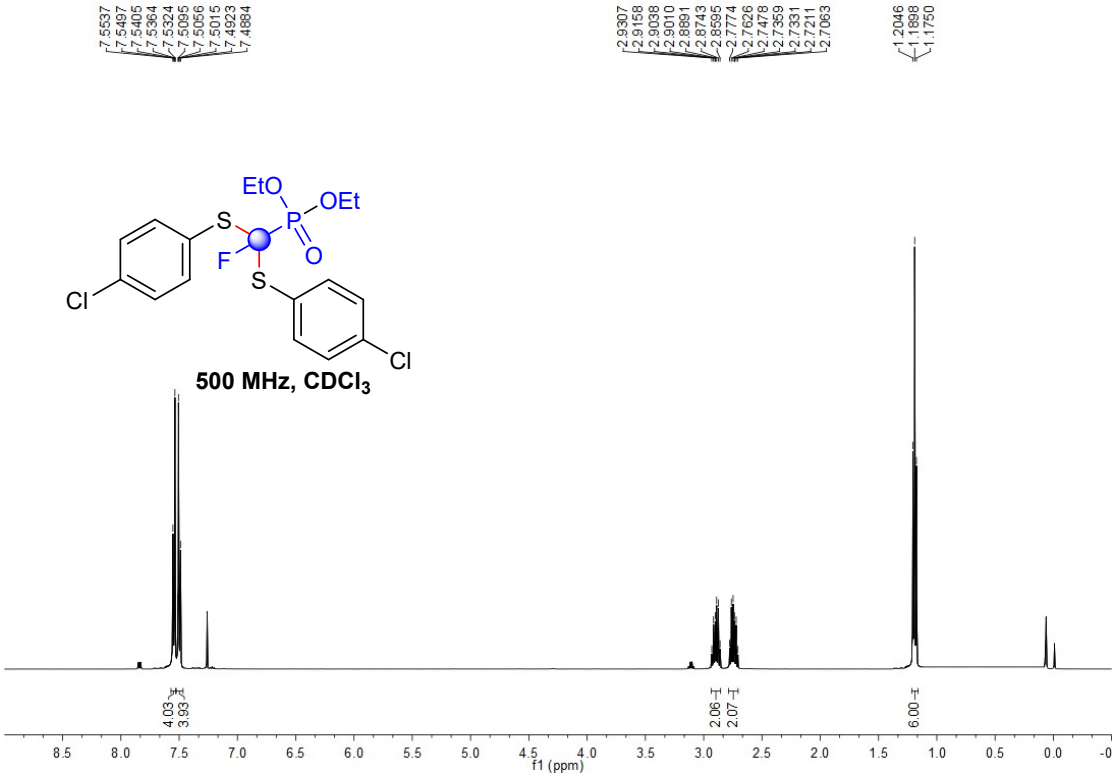


^{31}P NMR

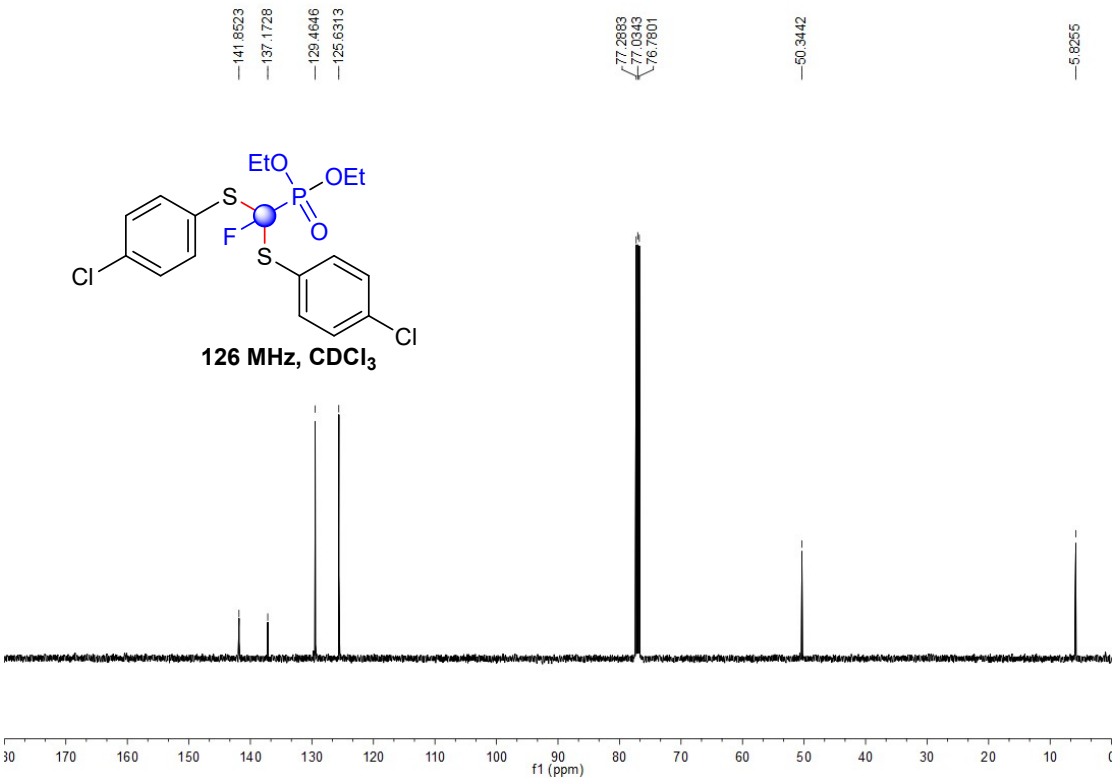


6c

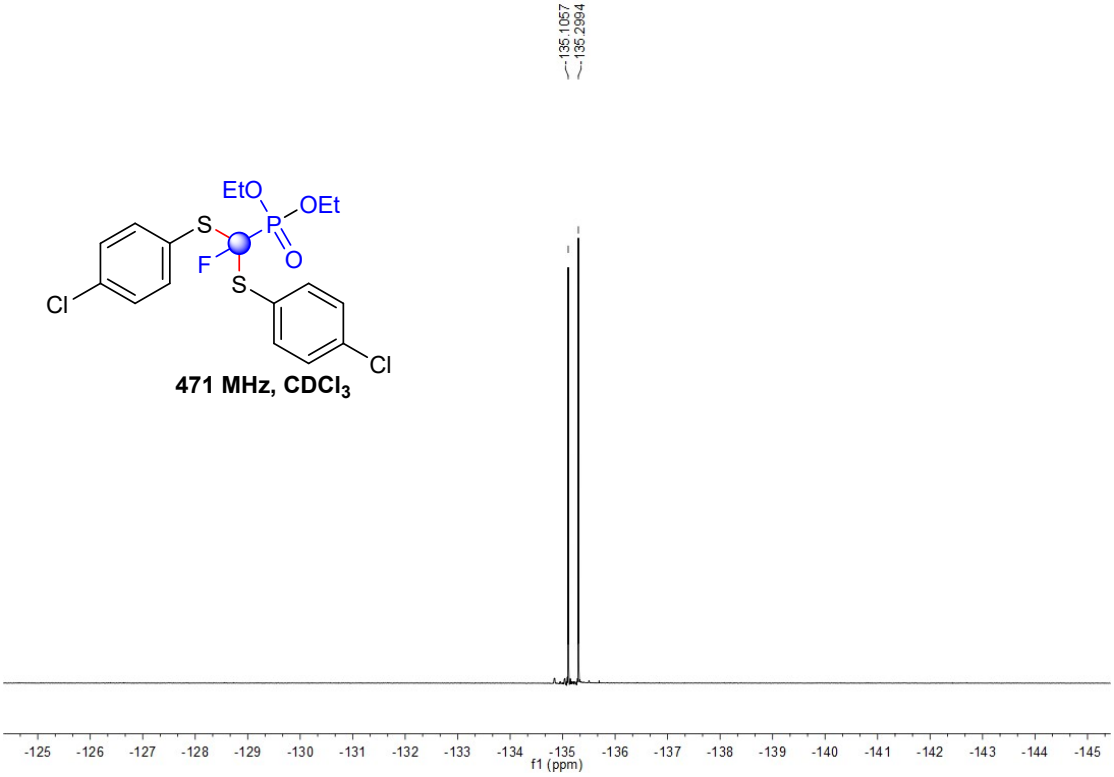
^{1}H NMR



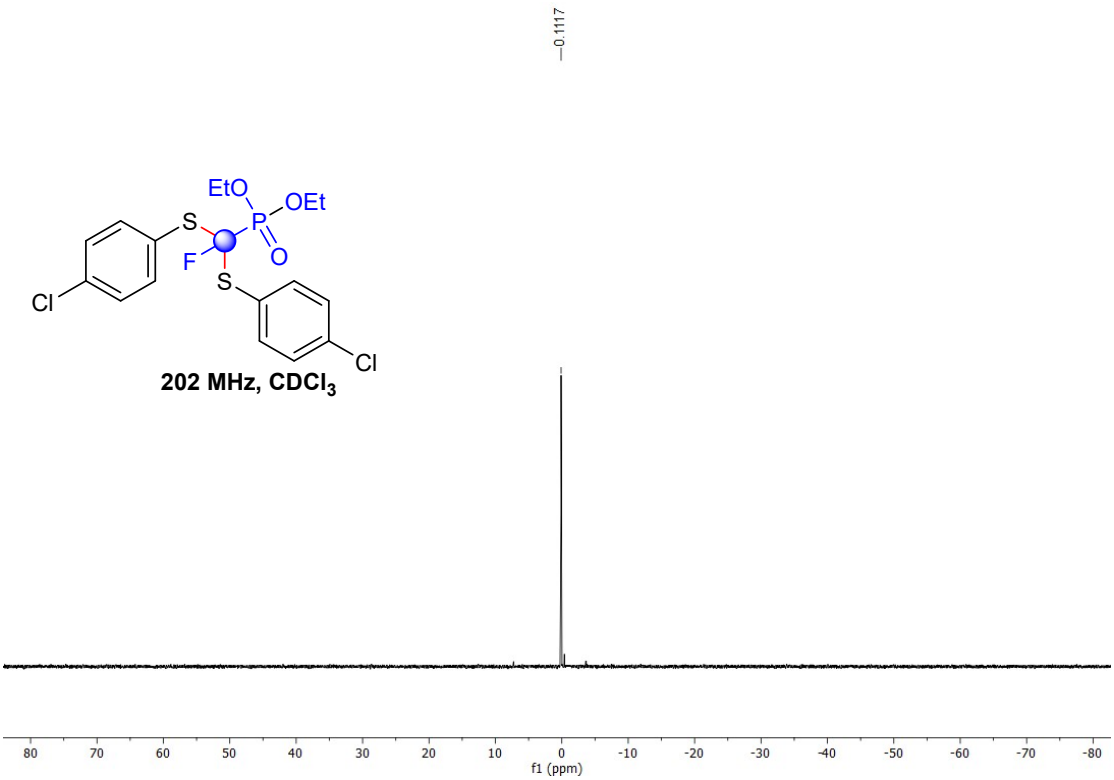
^{13}C NMR



^{19}F NMR

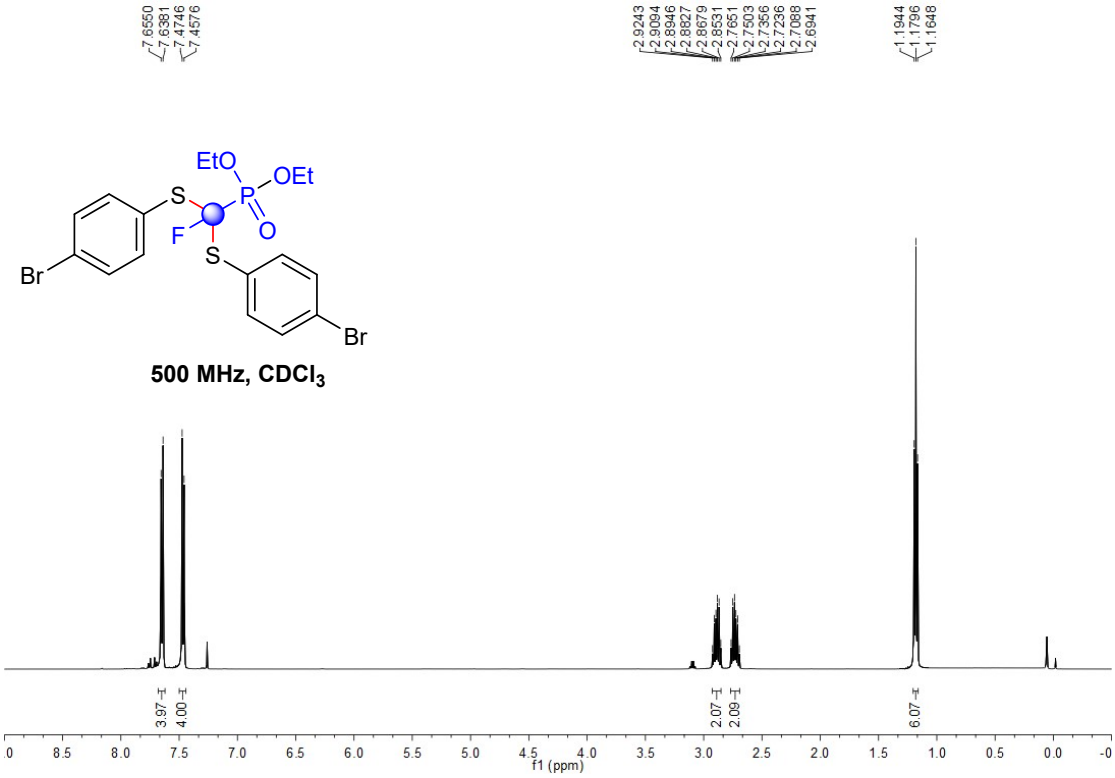


^{31}P NMR

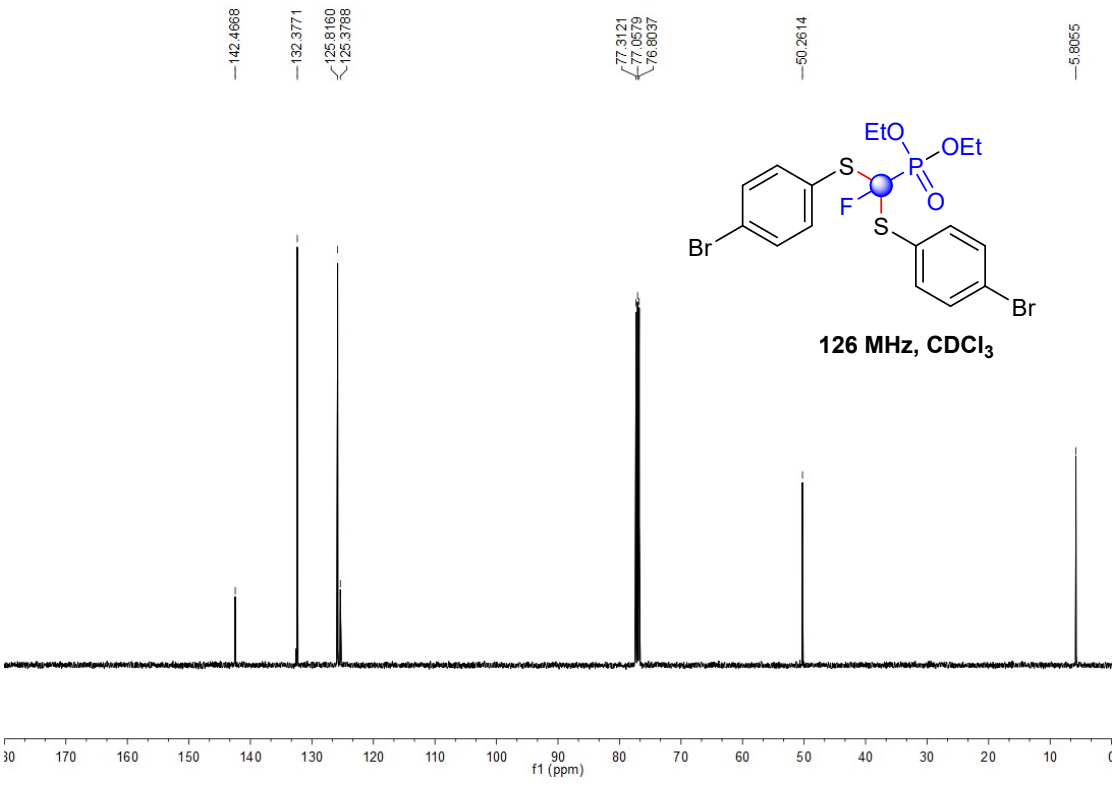


7c

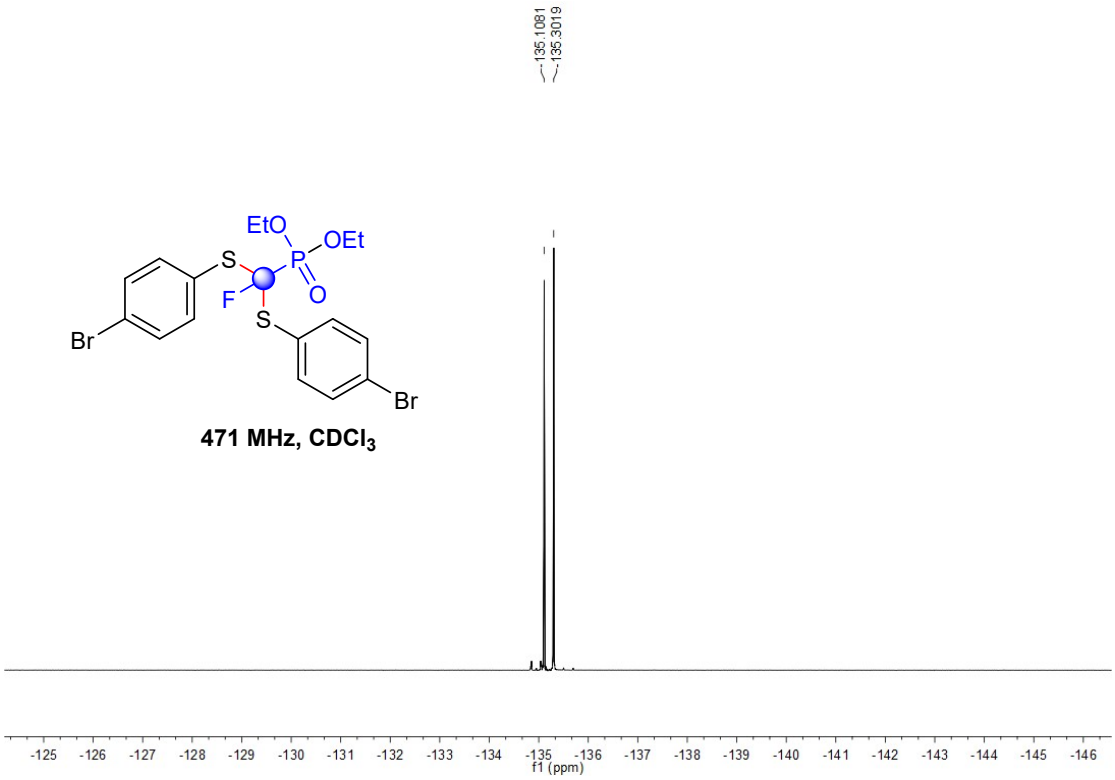
^{1}H NMR



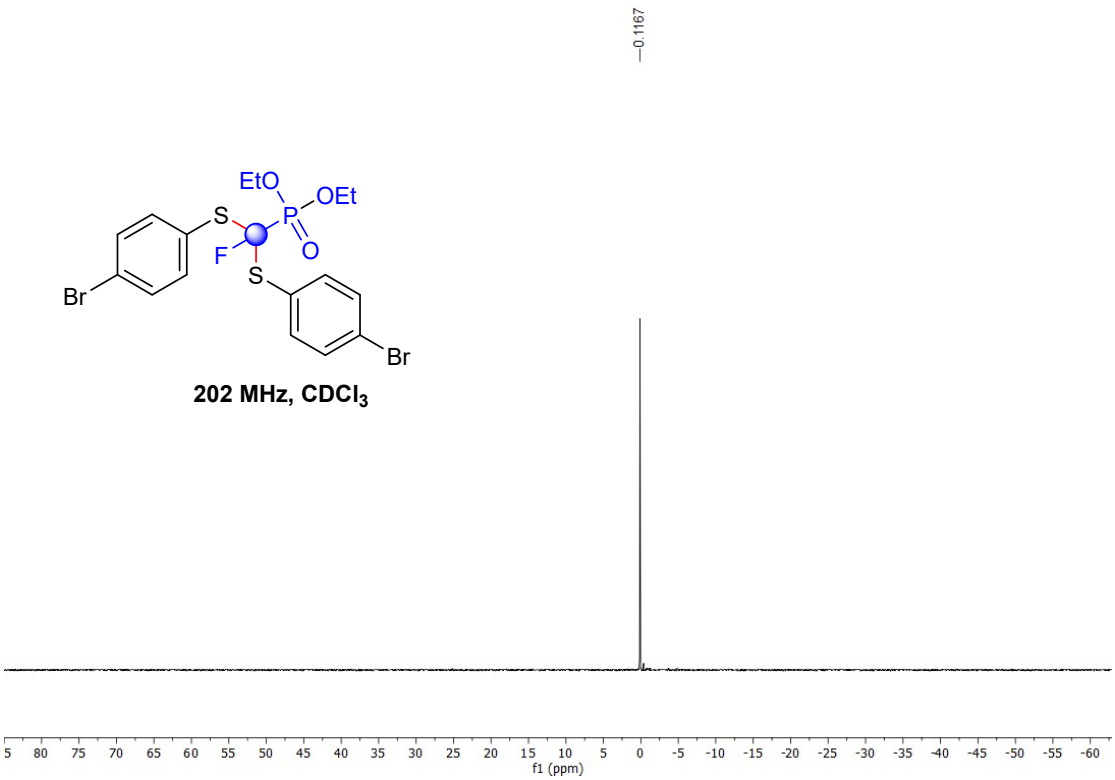
^{13}C NMR



^{19}F NMR

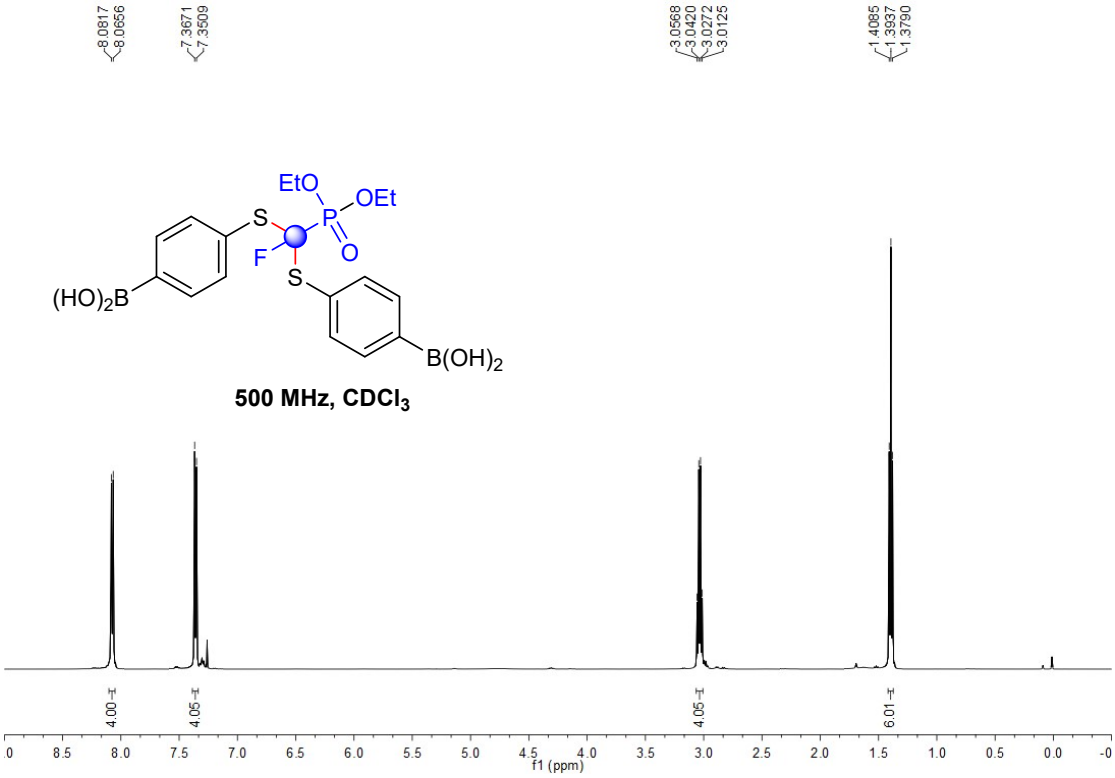


^{31}P NMR

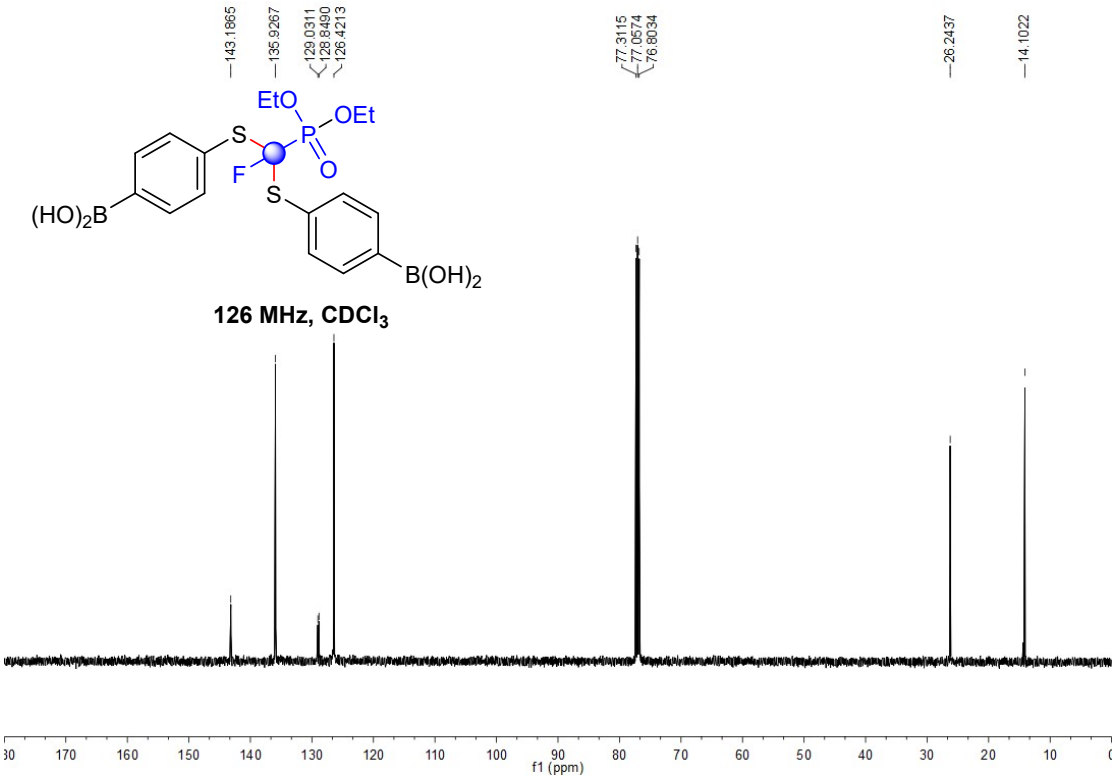


8c

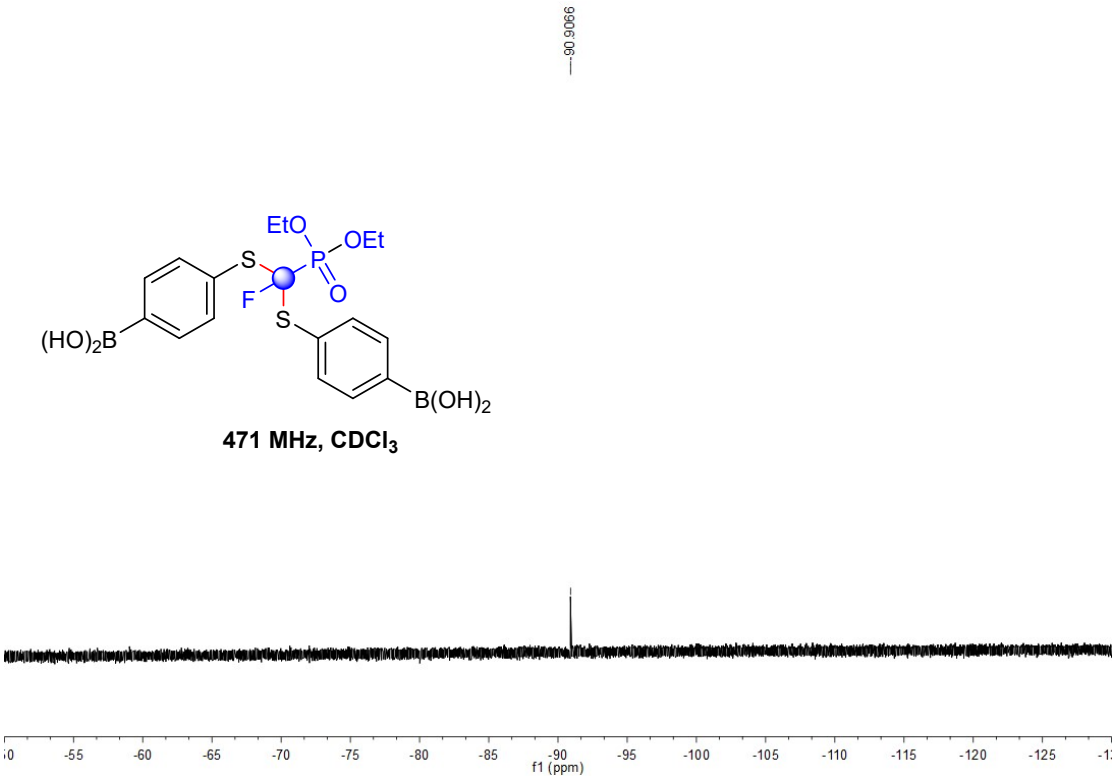
^{1}H NMR



^{13}C NMR

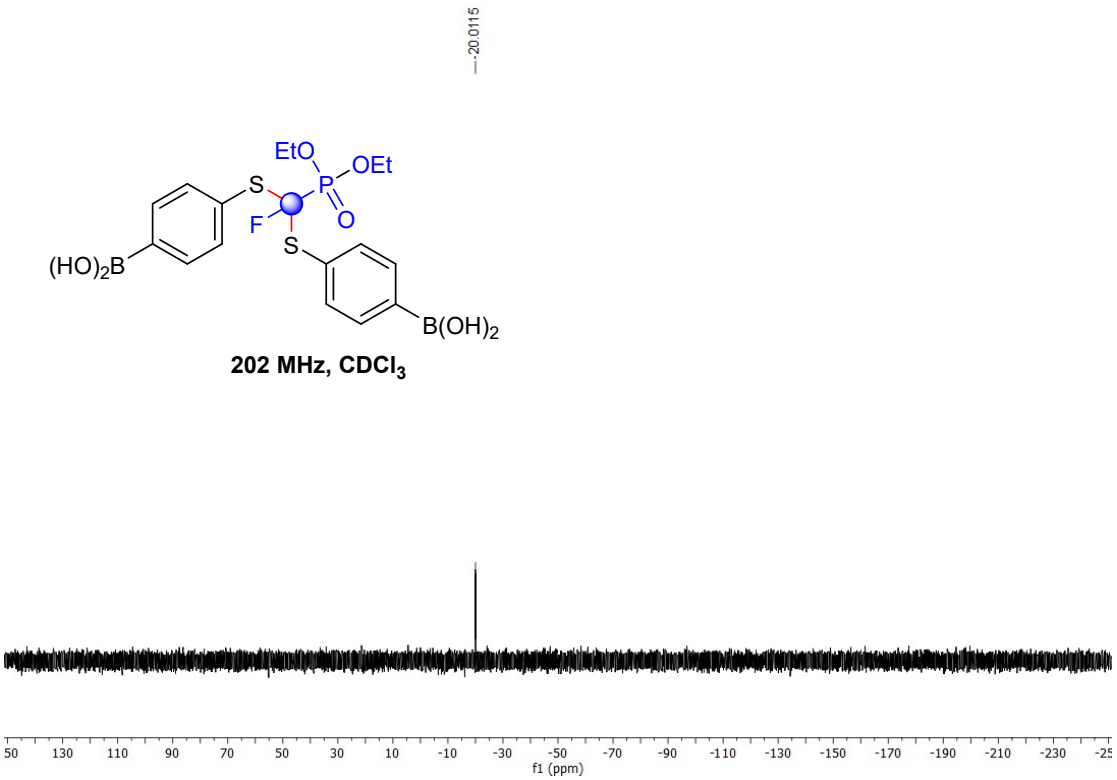


^{19}F NMR



471 MHz, $CDCl_3$

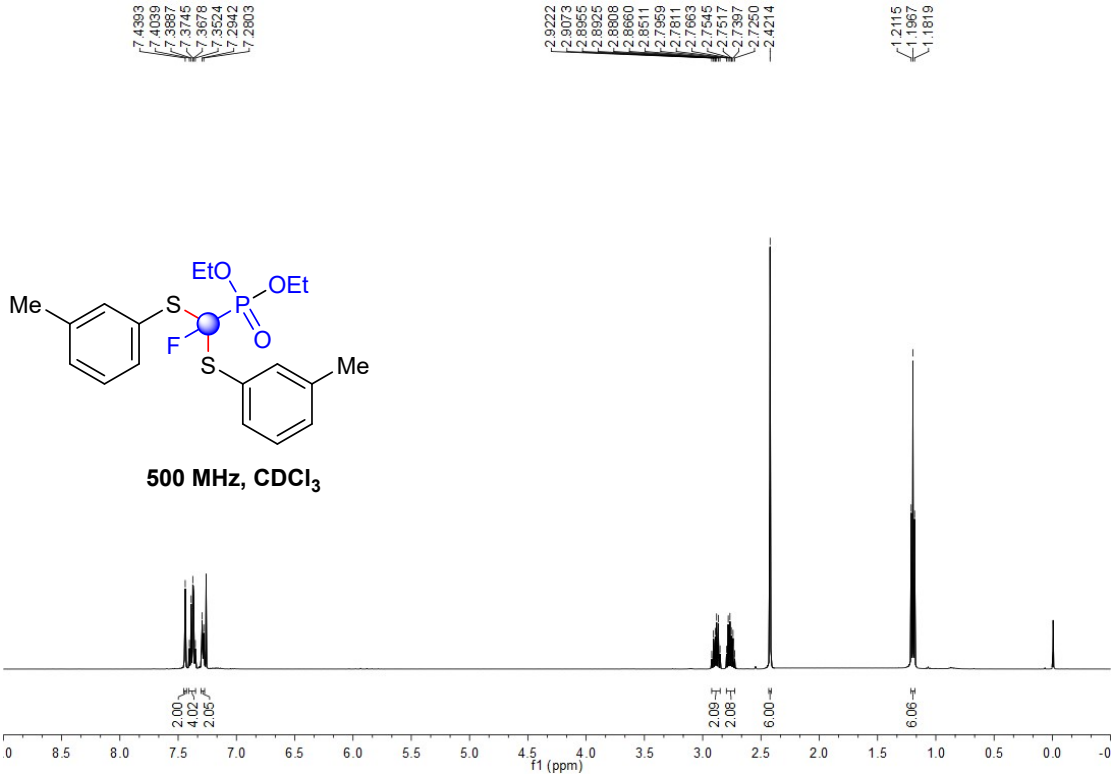
^{31}P NMR



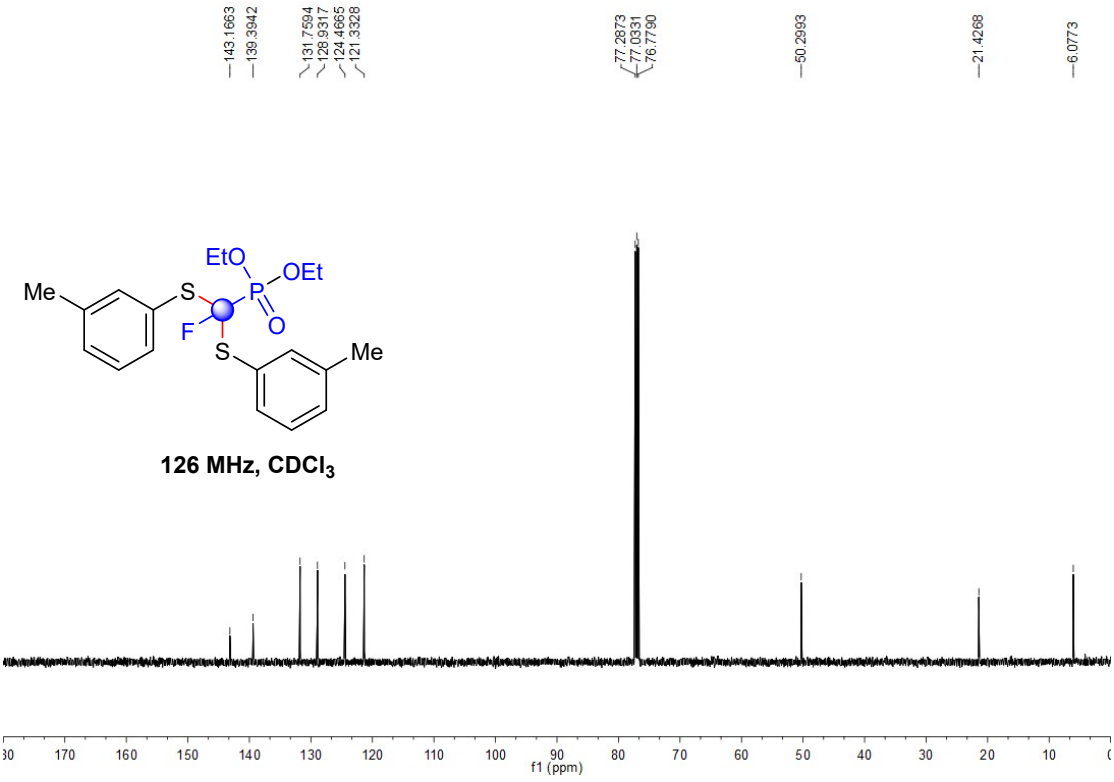
202 MHz, $CDCl_3$

9c

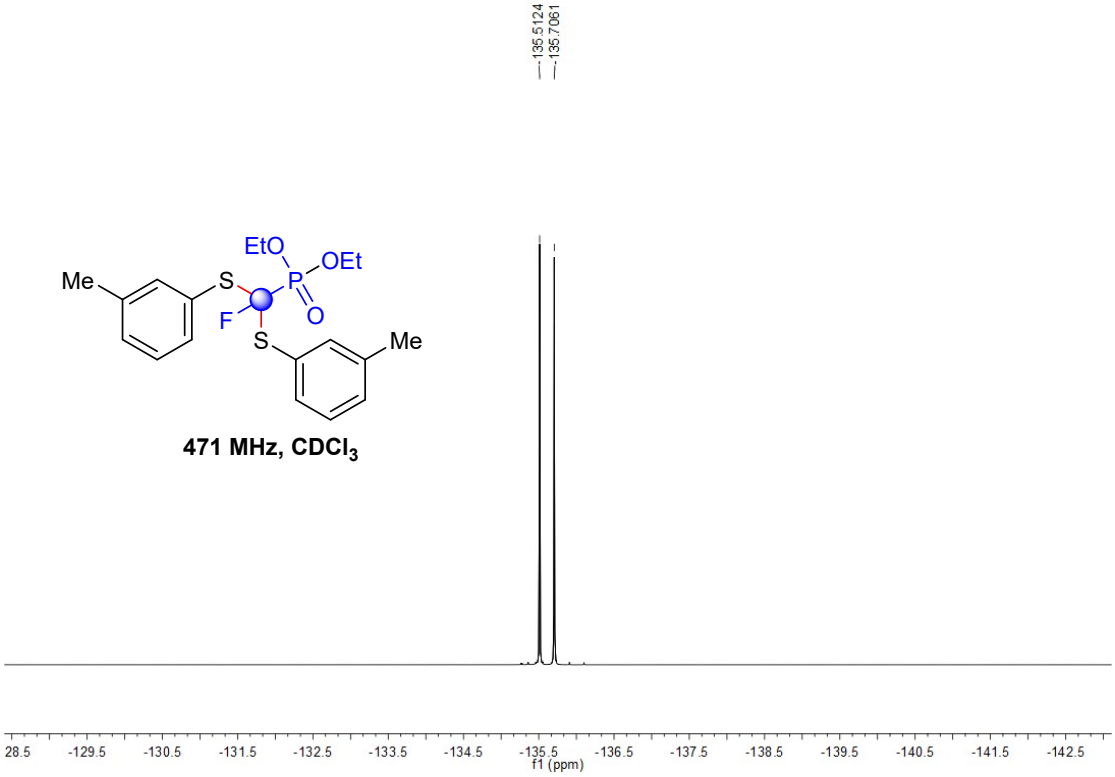
^{1}H NMR



^{13}C NMR

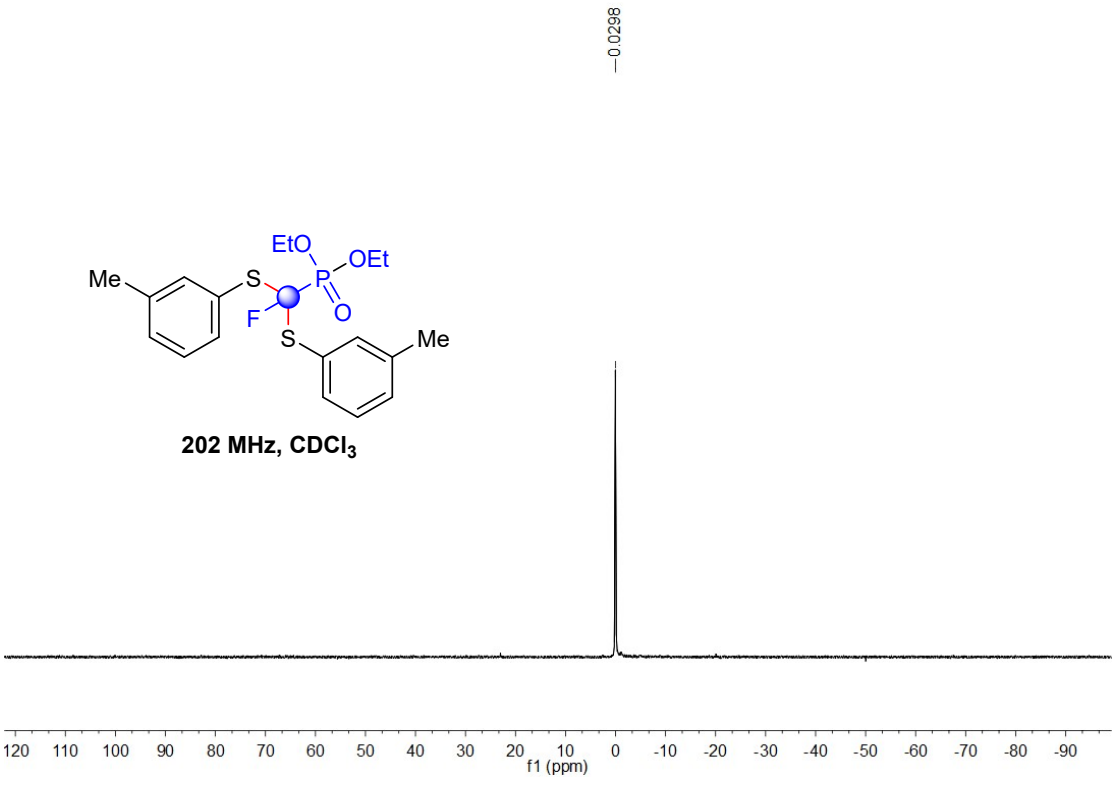


^{19}F NMR



471 MHz, $CDCl_3$

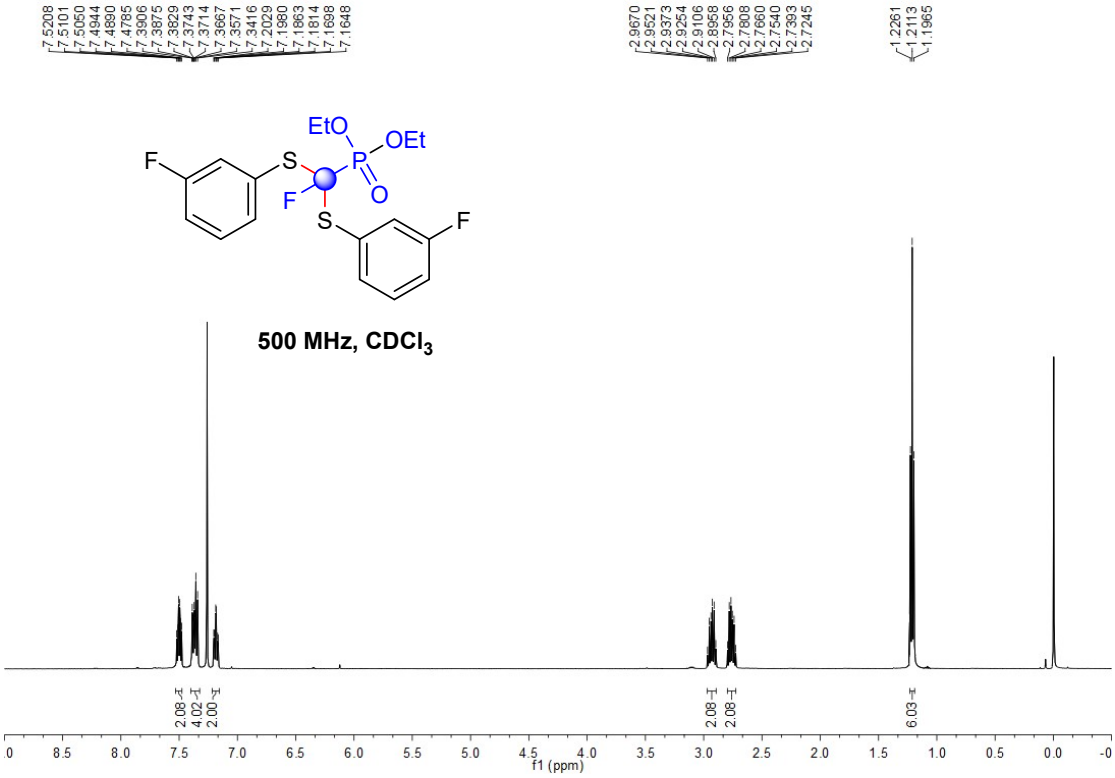
^{31}P NMR



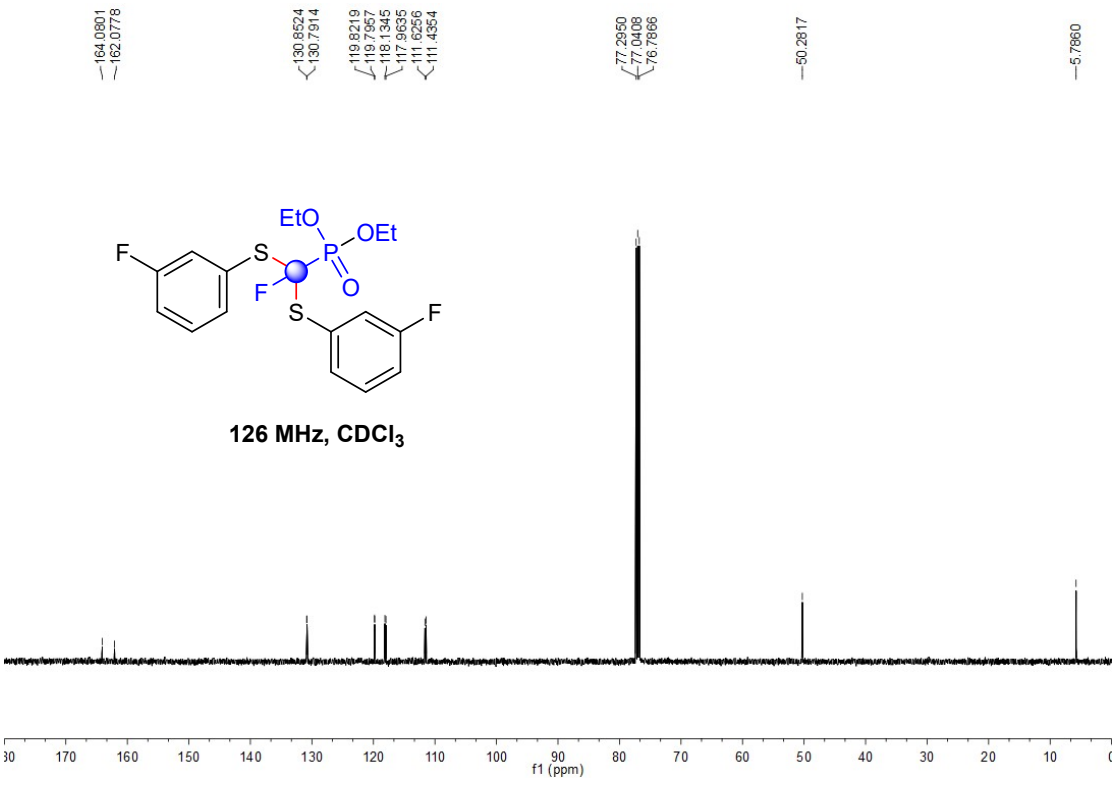
202 MHz, $CDCl_3$

10c

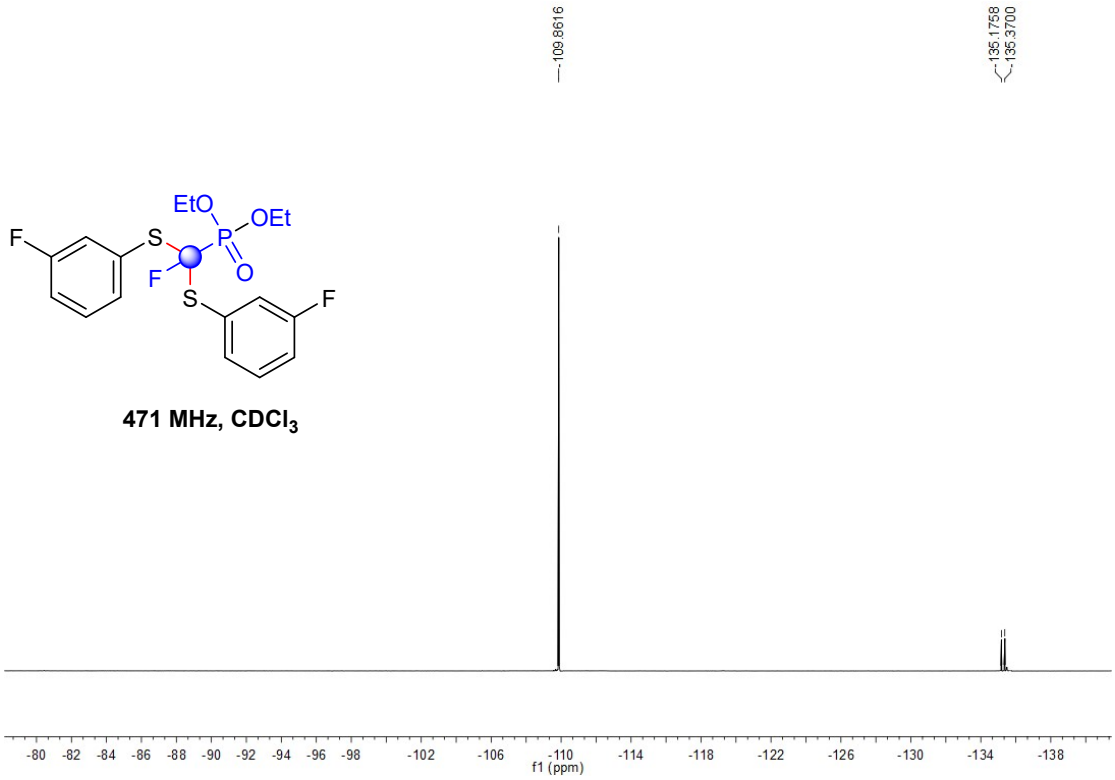
^{1}H NMR



^{13}C NMR

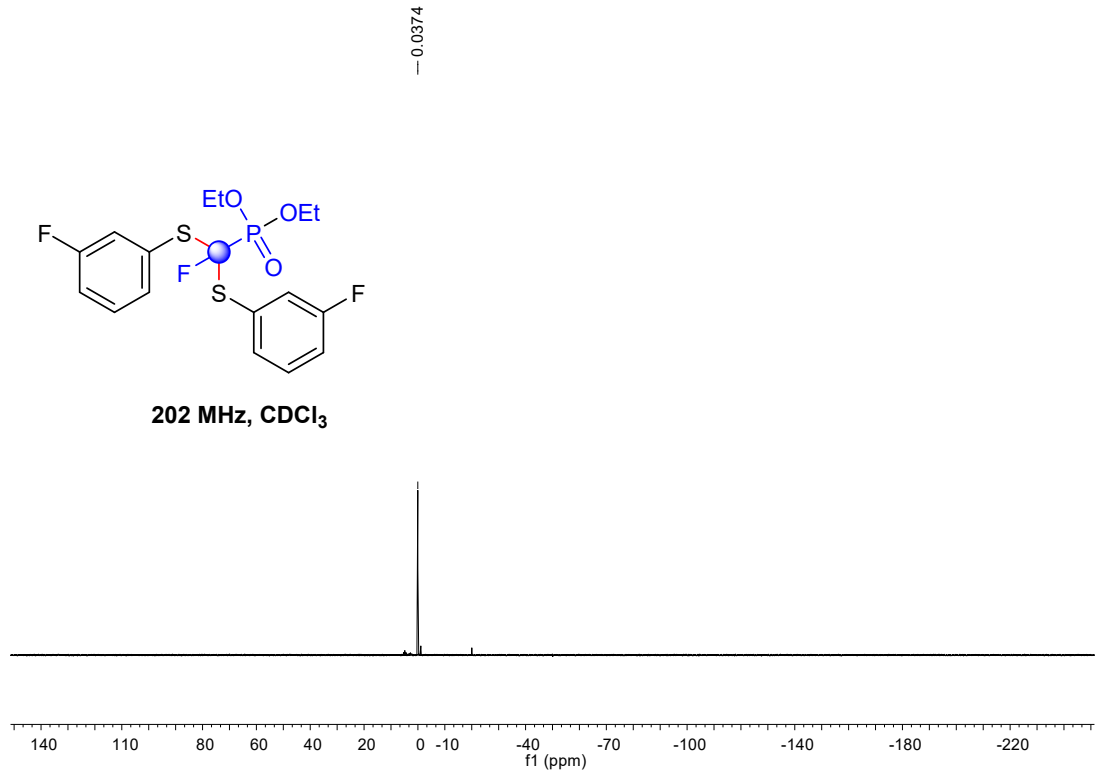


^{19}F NMR



471 MHz, $CDCl_3$

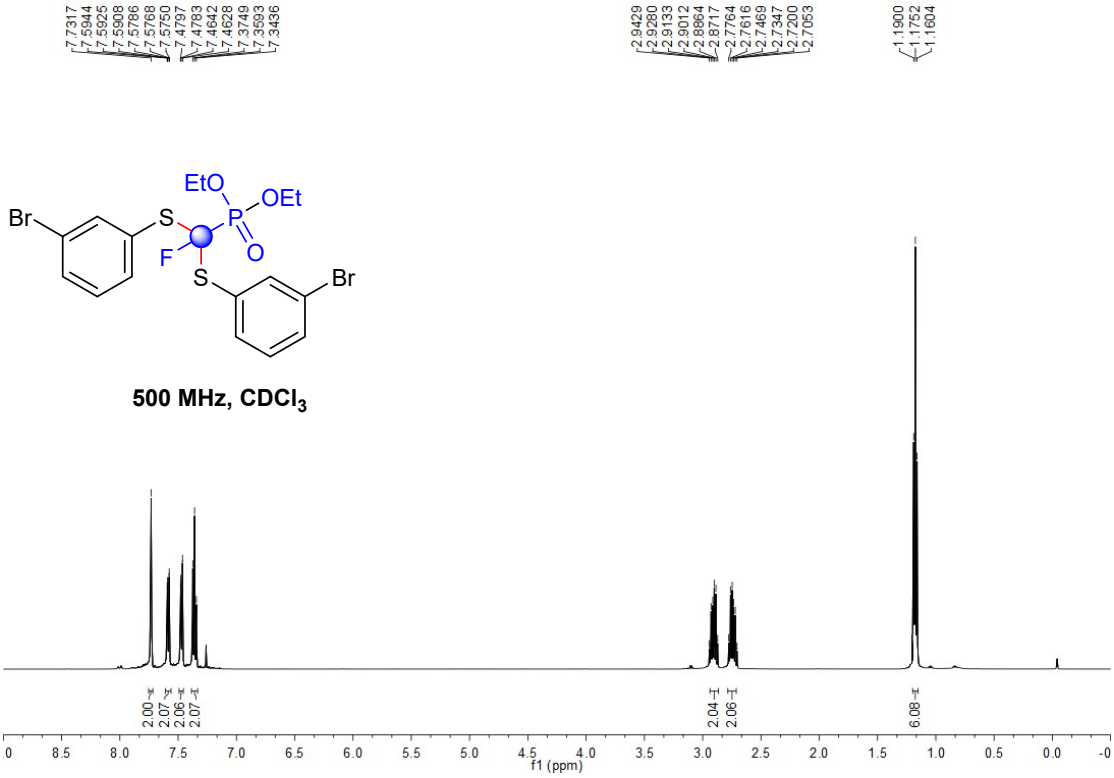
^{31}P NMR



202 MHz, $CDCl_3$

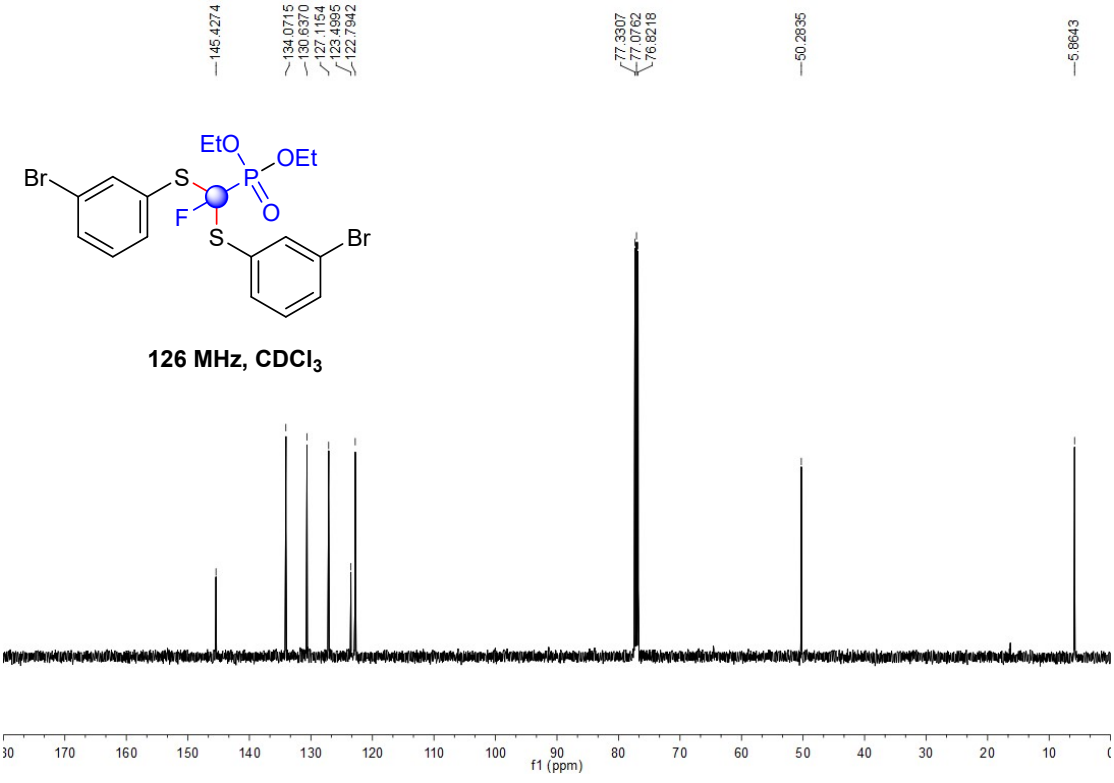
11c

^{1}H NMR



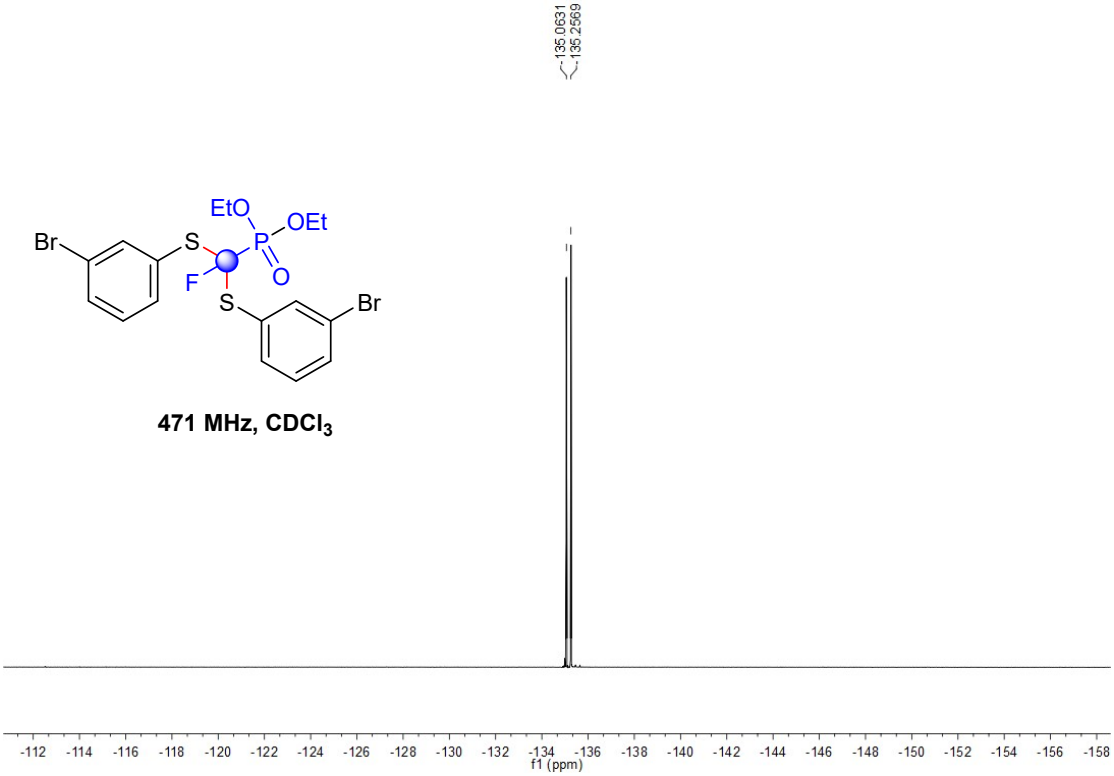
500 MHz, $CDCl_3$

^{13}C NMR



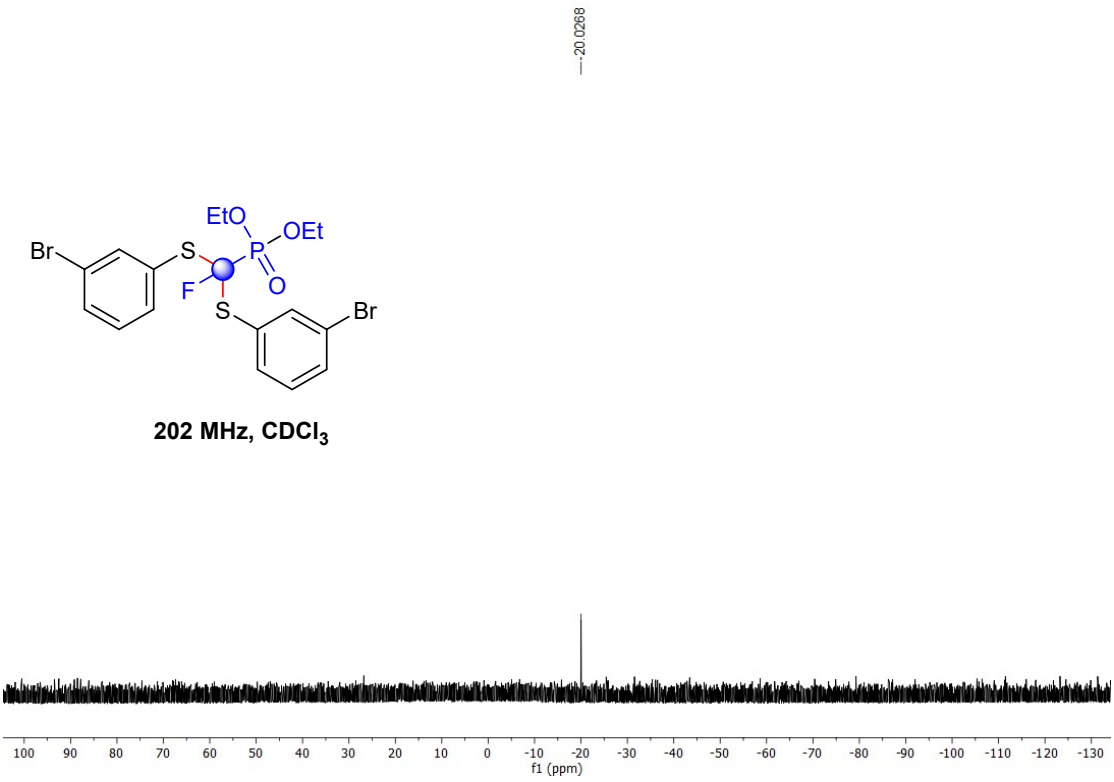
126 MHz, $CDCl_3$

^{19}F NMR



471 MHz, $CDCl_3$

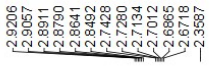
^{31}P NMR

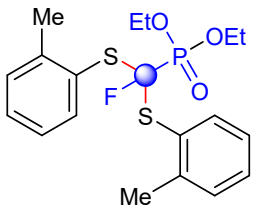


202 MHz, $CDCl_3$

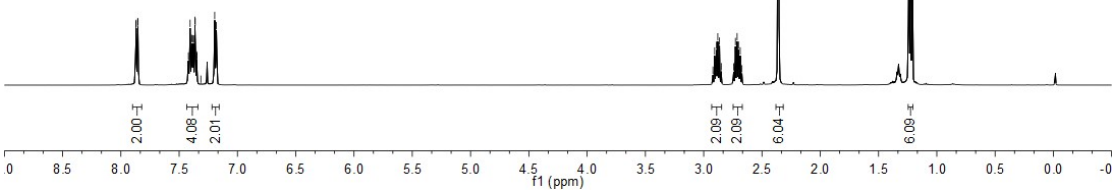
12c

^{1}H NMR

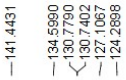


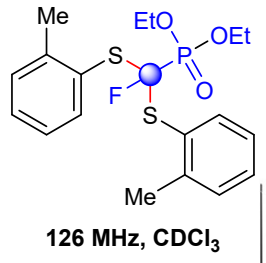


500 MHz, $CDCl_3$



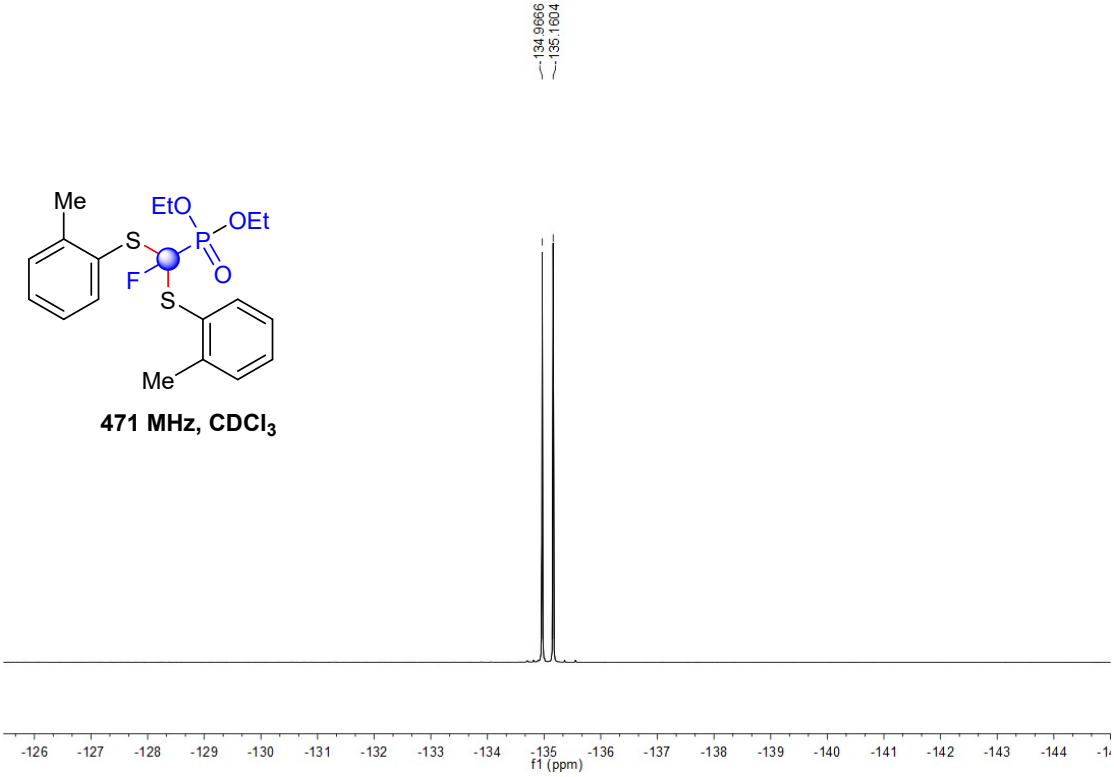
^{13}C NMR





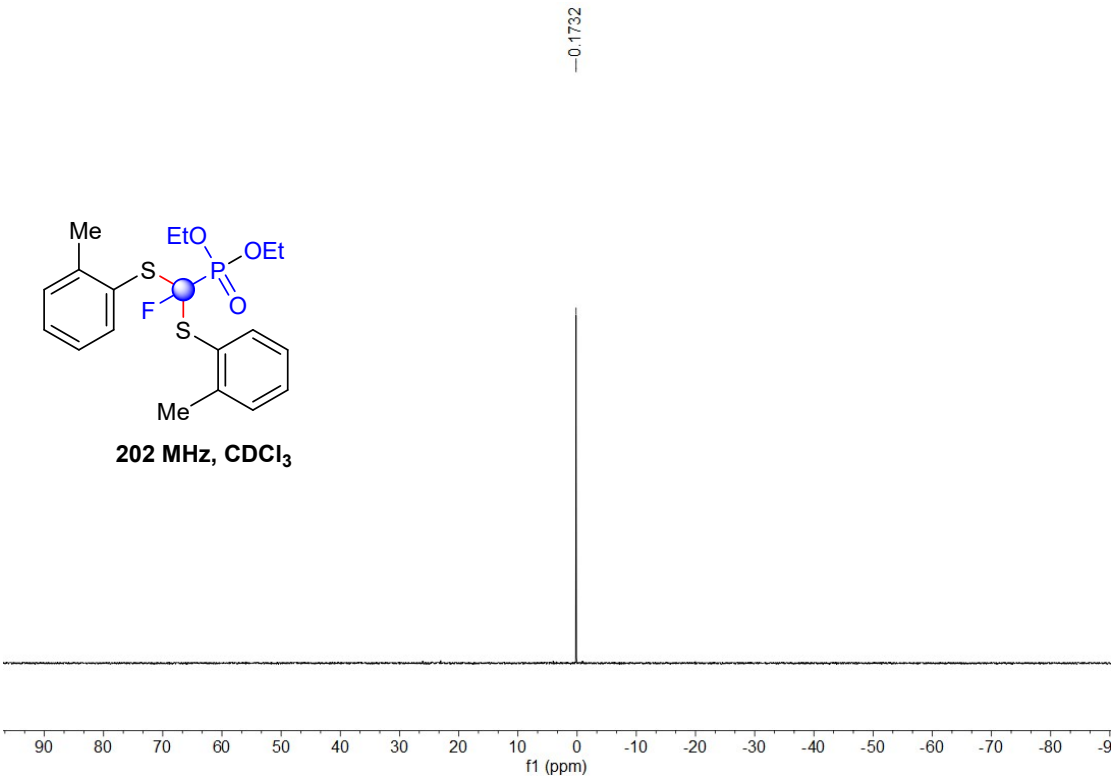
126 MHz, $CDCl_3$

^{19}F NMR



471 MHz, $CDCl_3$

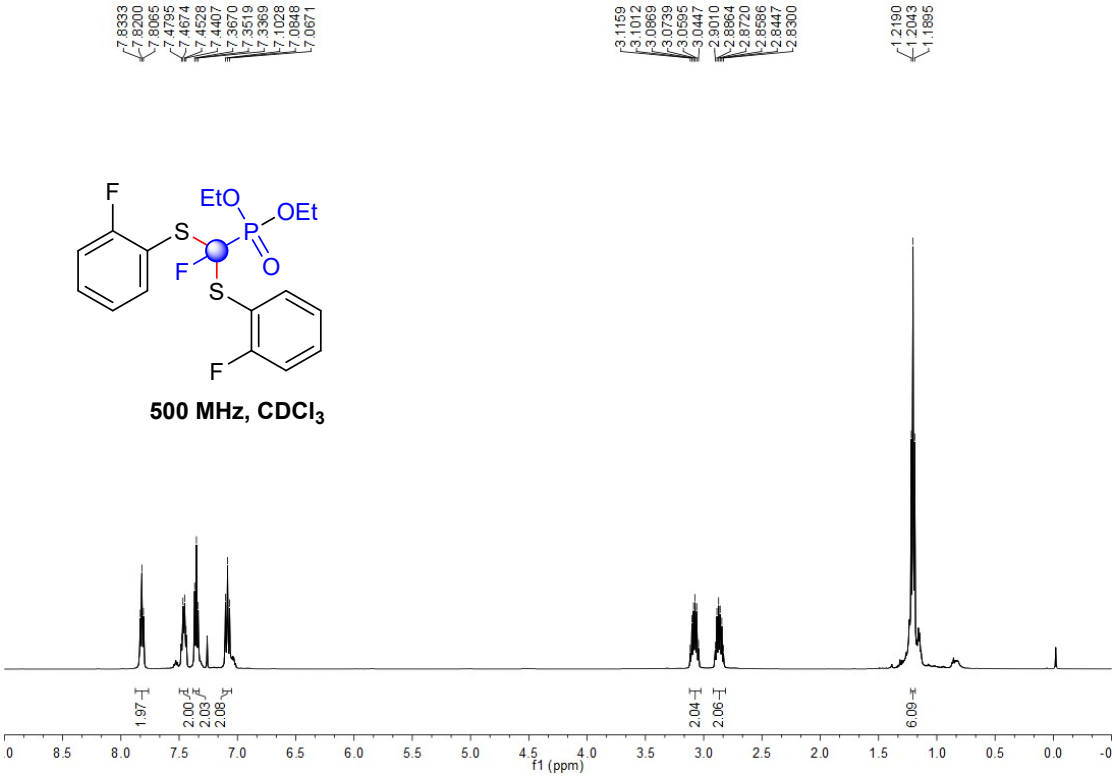
^{31}P NMR



202 MHz, $CDCl_3$

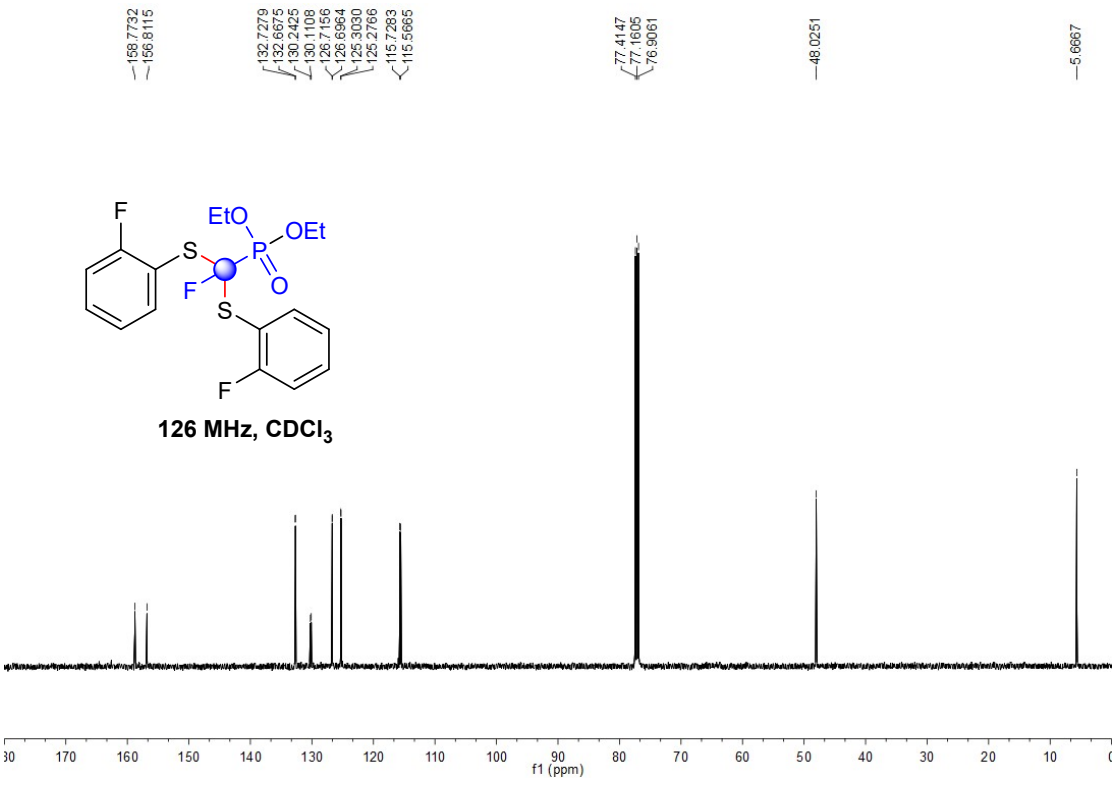
13c

^{1}H NMR



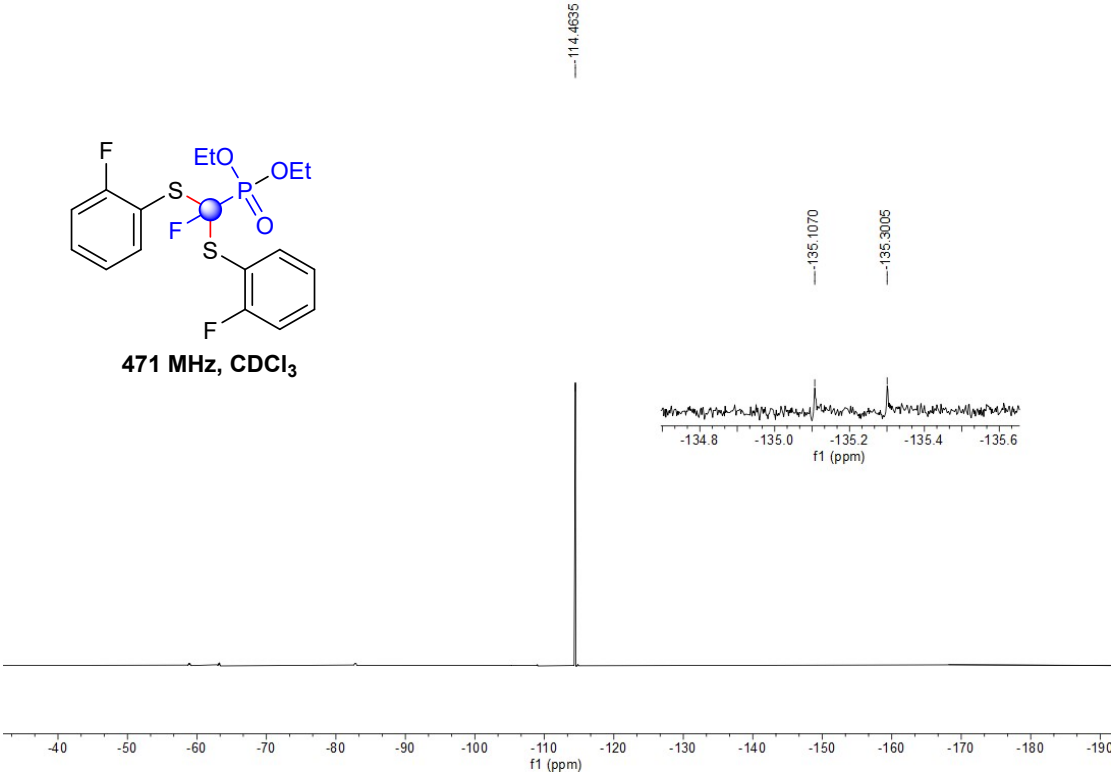
500 MHz, $CDCl_3$

^{13}C NMR



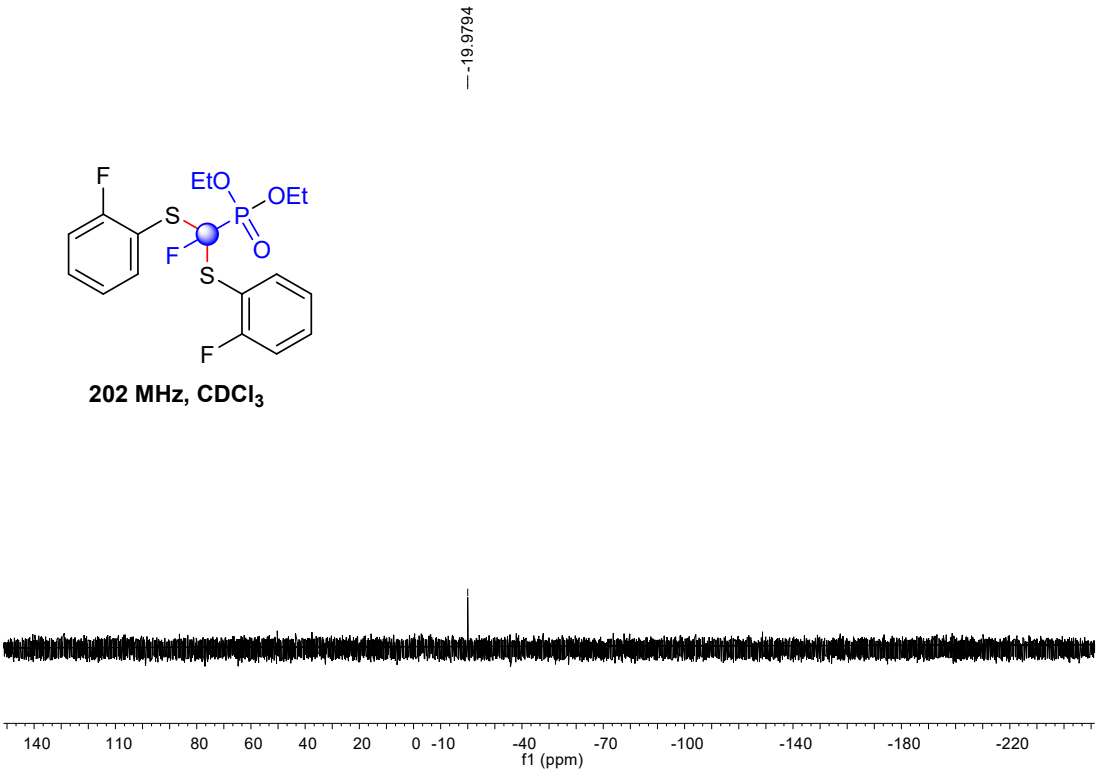
126 MHz, $CDCl_3$

^{19}F NMR



471 MHz, $CDCl_3$

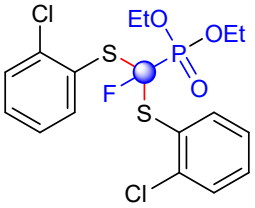
^{31}P NMR



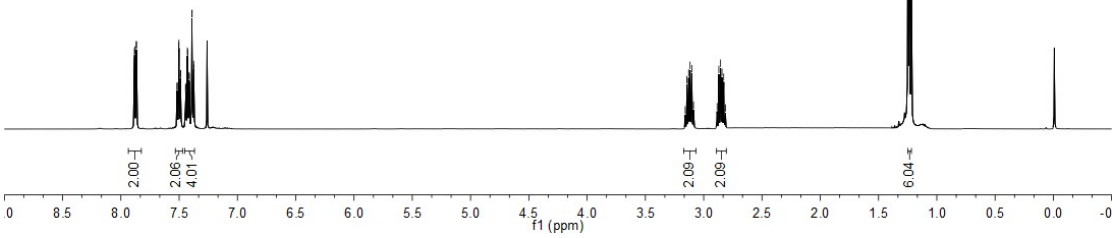
202 MHz, $CDCl_3$

14c

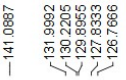
^{1}H NMR

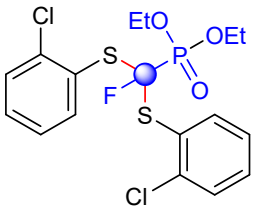


500 MHz, $CDCl_3$

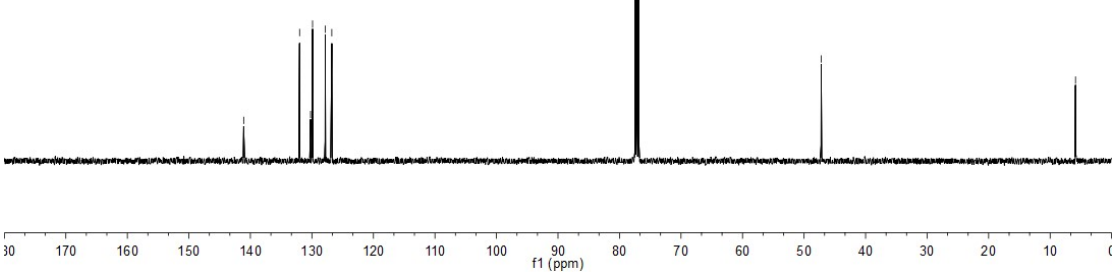


^{13}C NMR

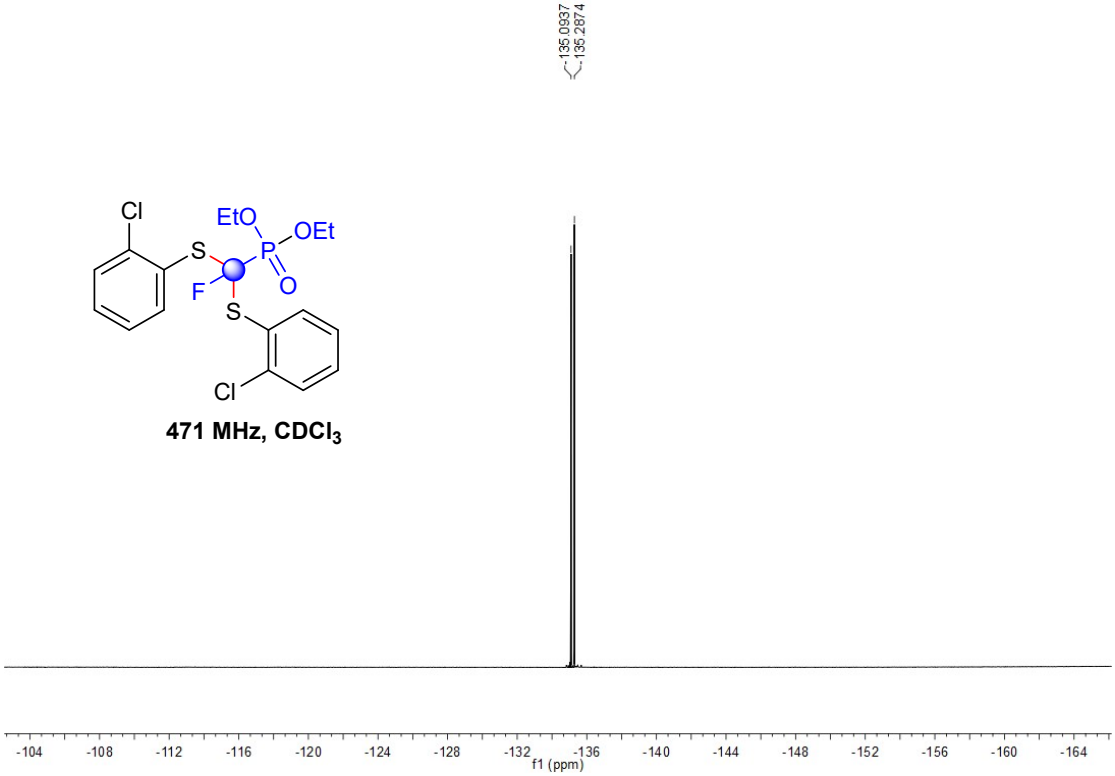




126 MHz, $CDCl_3$

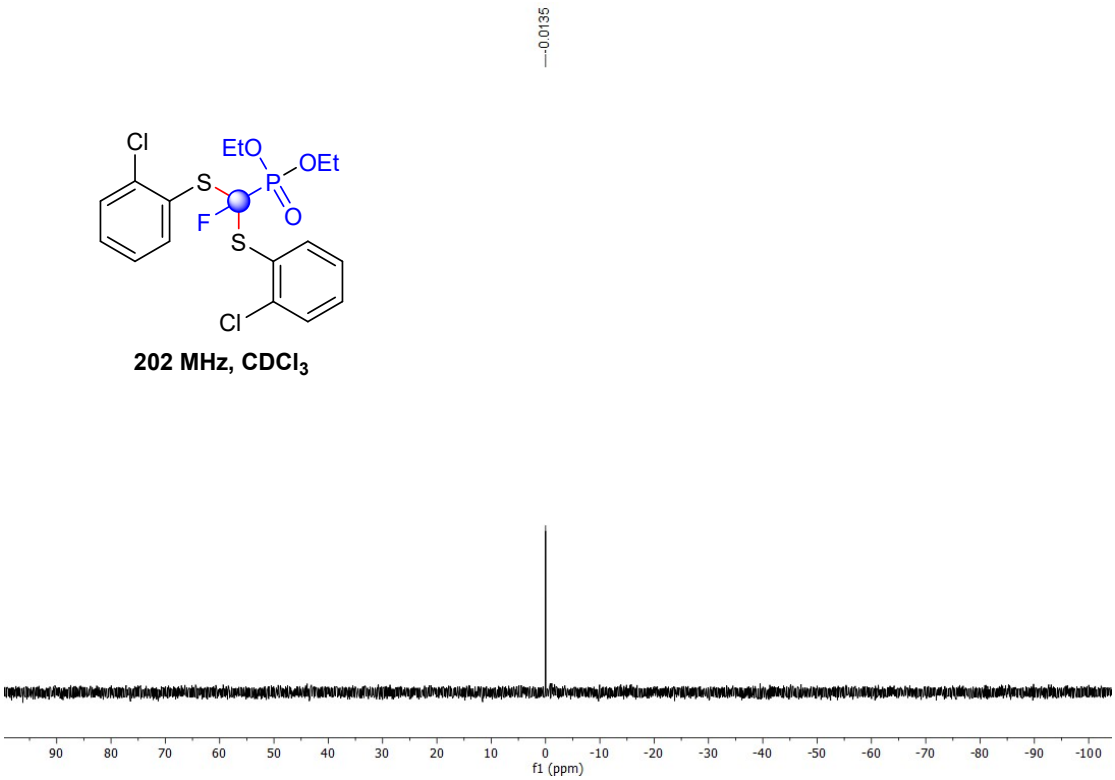


^{19}F NMR



471 MHz, $CDCl_3$

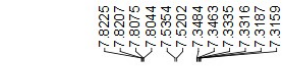
^{31}P NMR

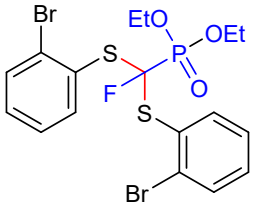


202 MHz, $CDCl_3$

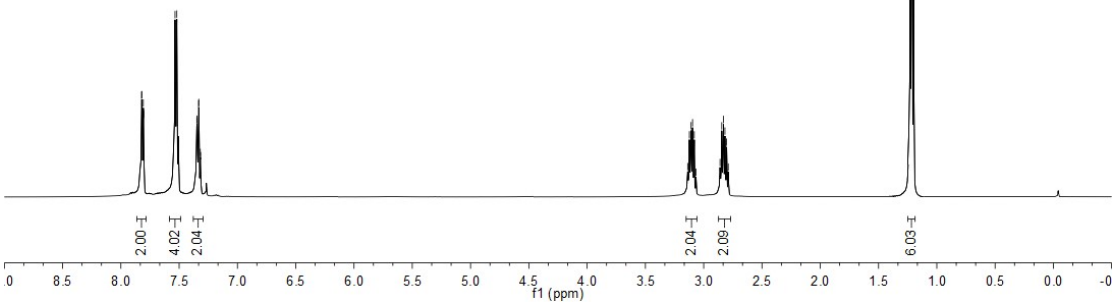
15c

^{1}H NMR

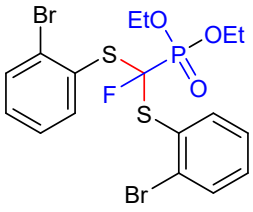




500 MHz, $CDCl_3$

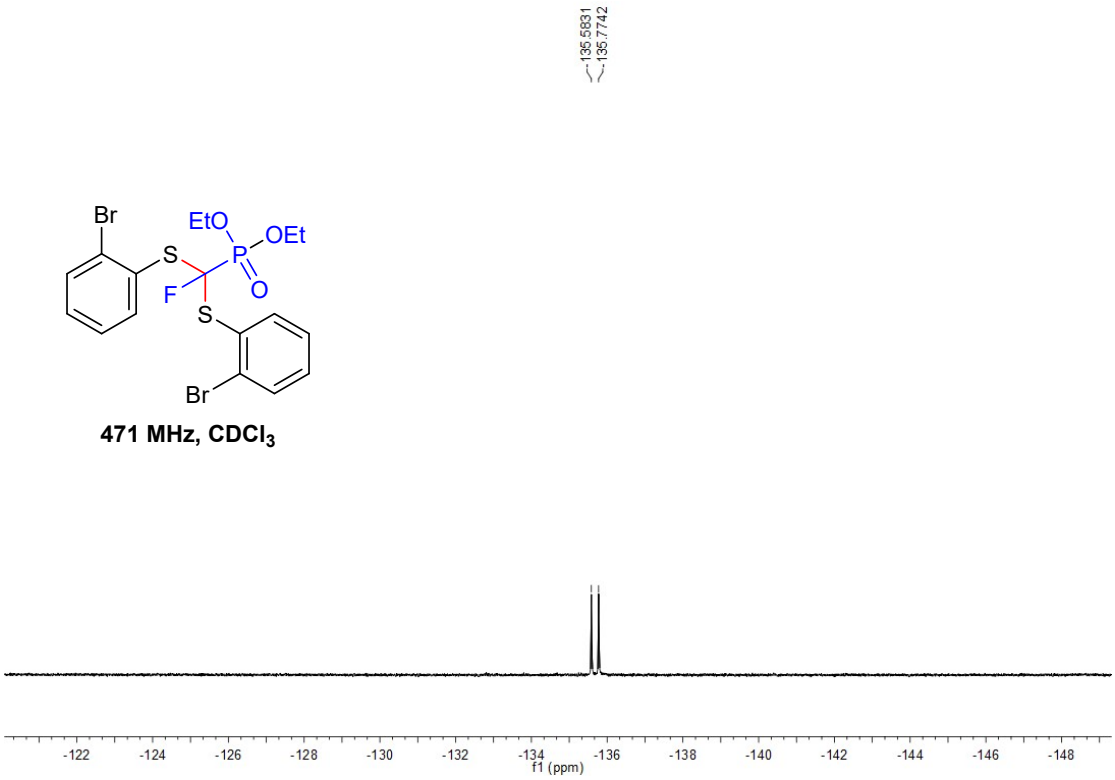


^{13}C NMR



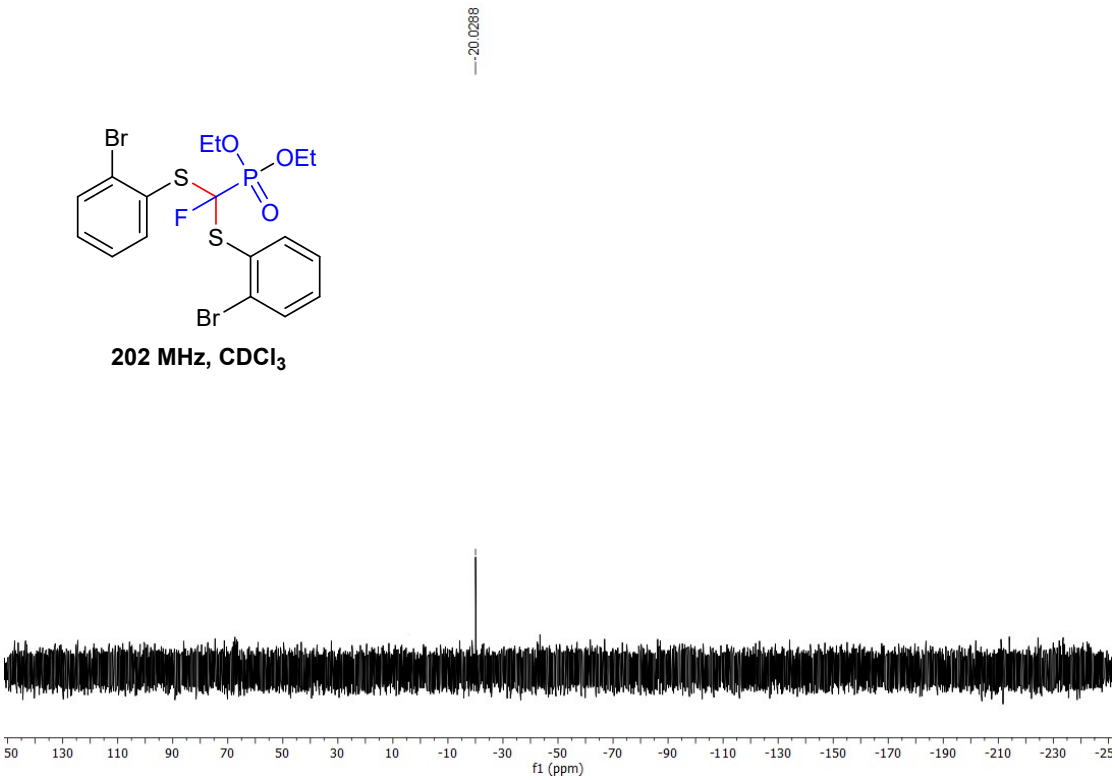
126 MHz, $CDCl_3$

^{19}F NMR



471 MHz, $CDCl_3$

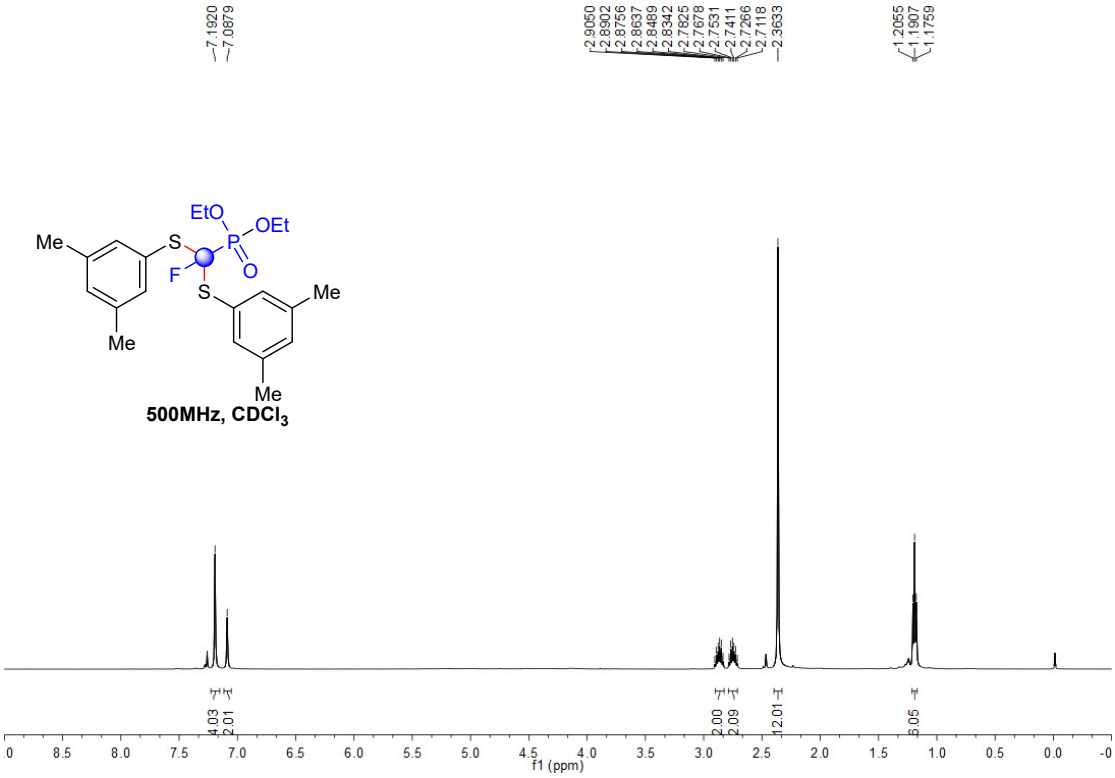
^{31}P NMR



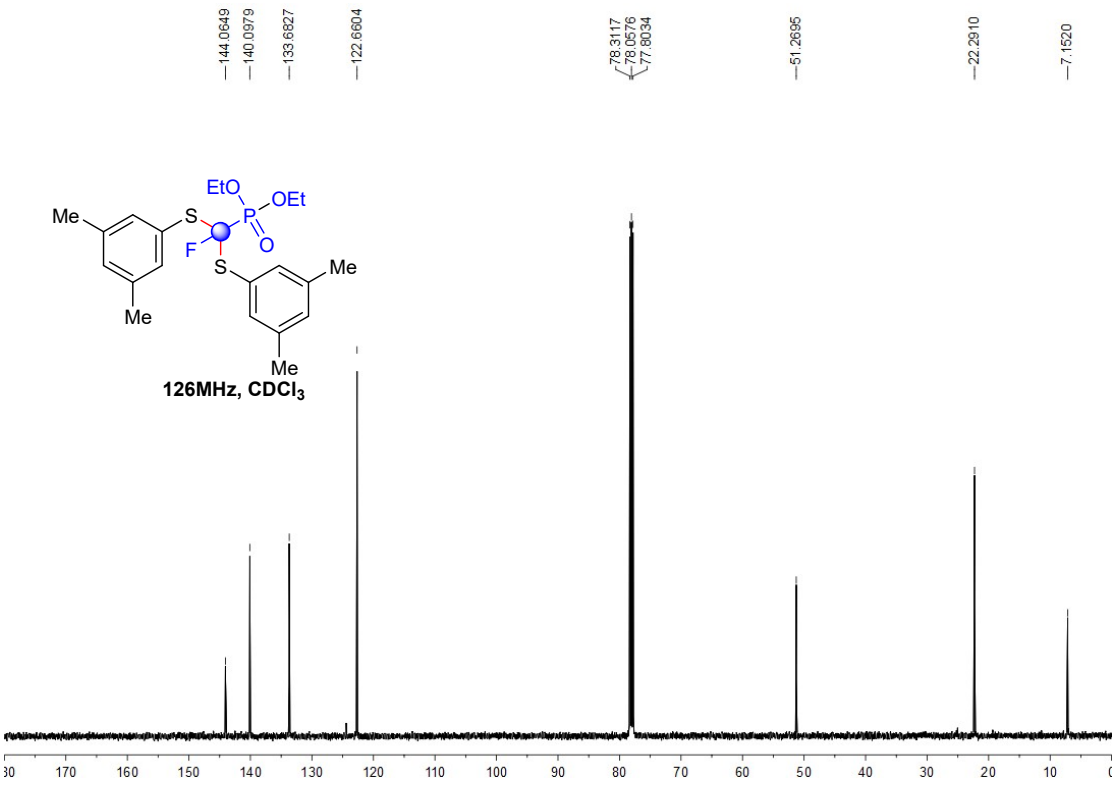
202 MHz, $CDCl_3$

16c

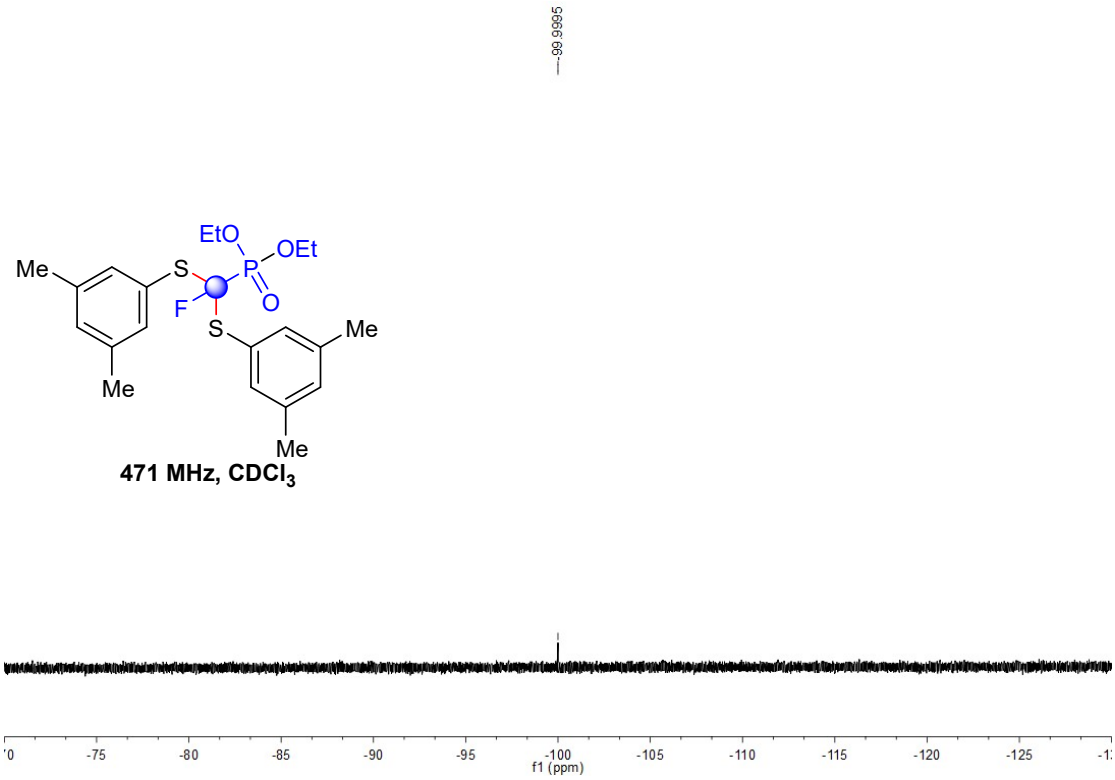
^{1}H NMR



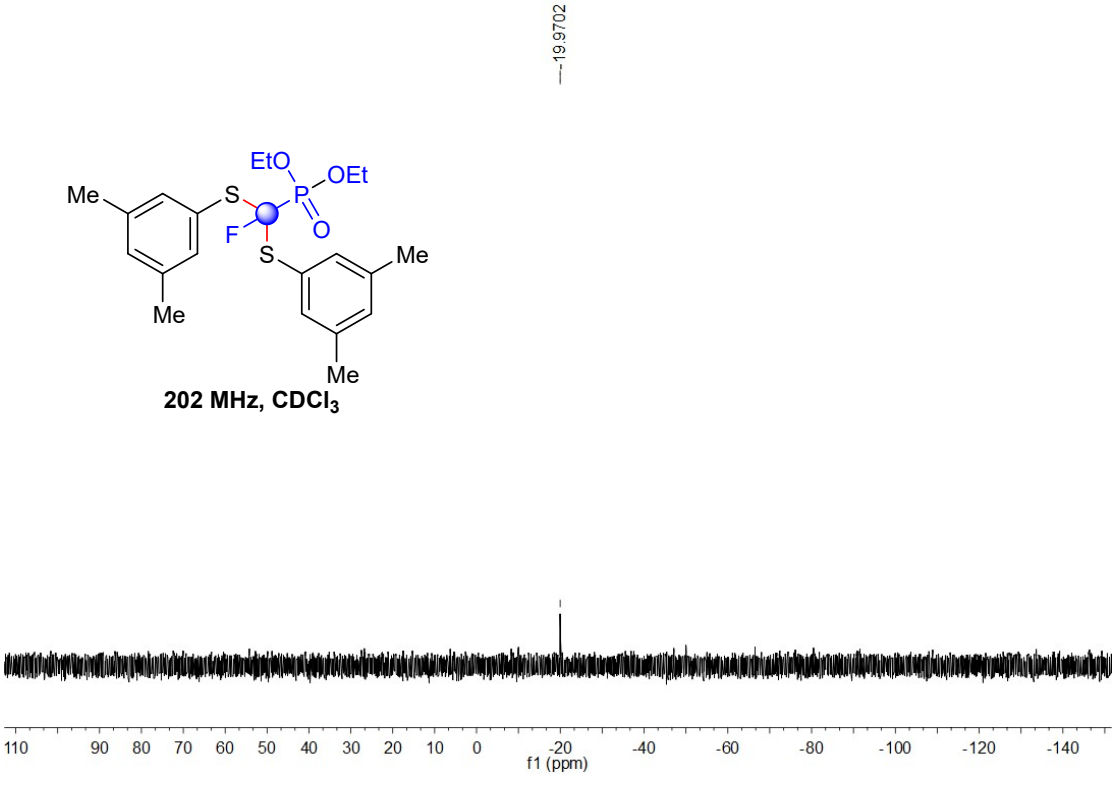
^{13}C NMR



^{19}F NMR

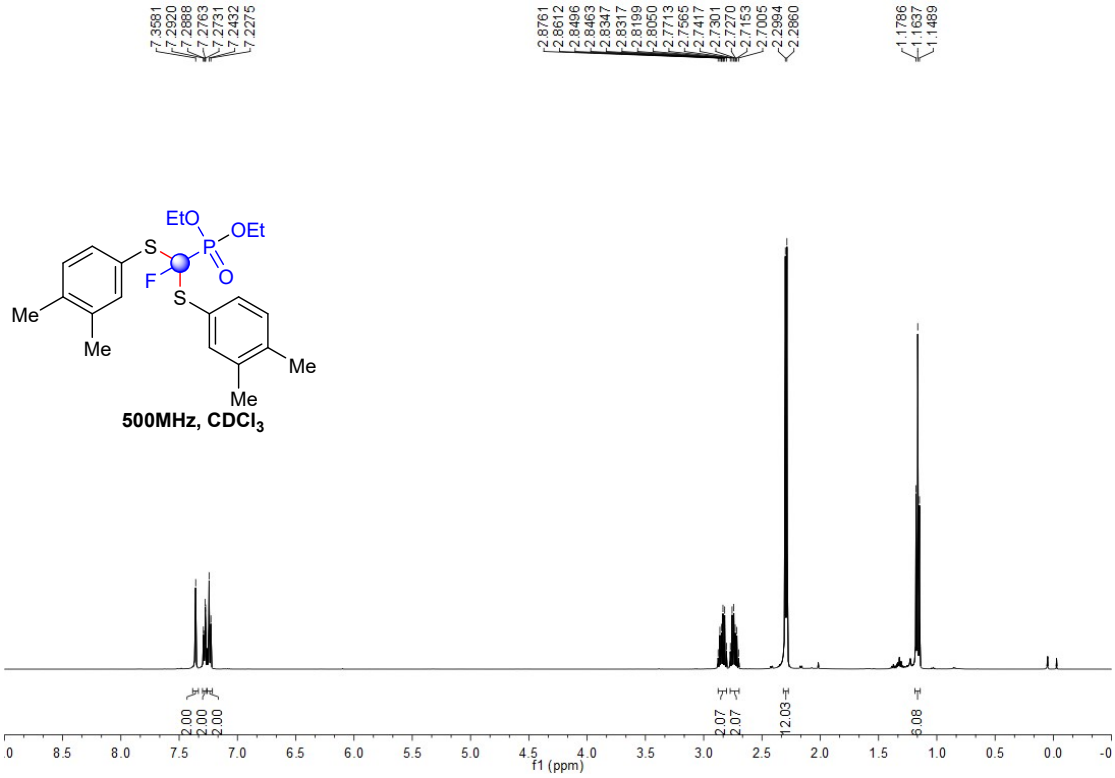


^{31}P NMR

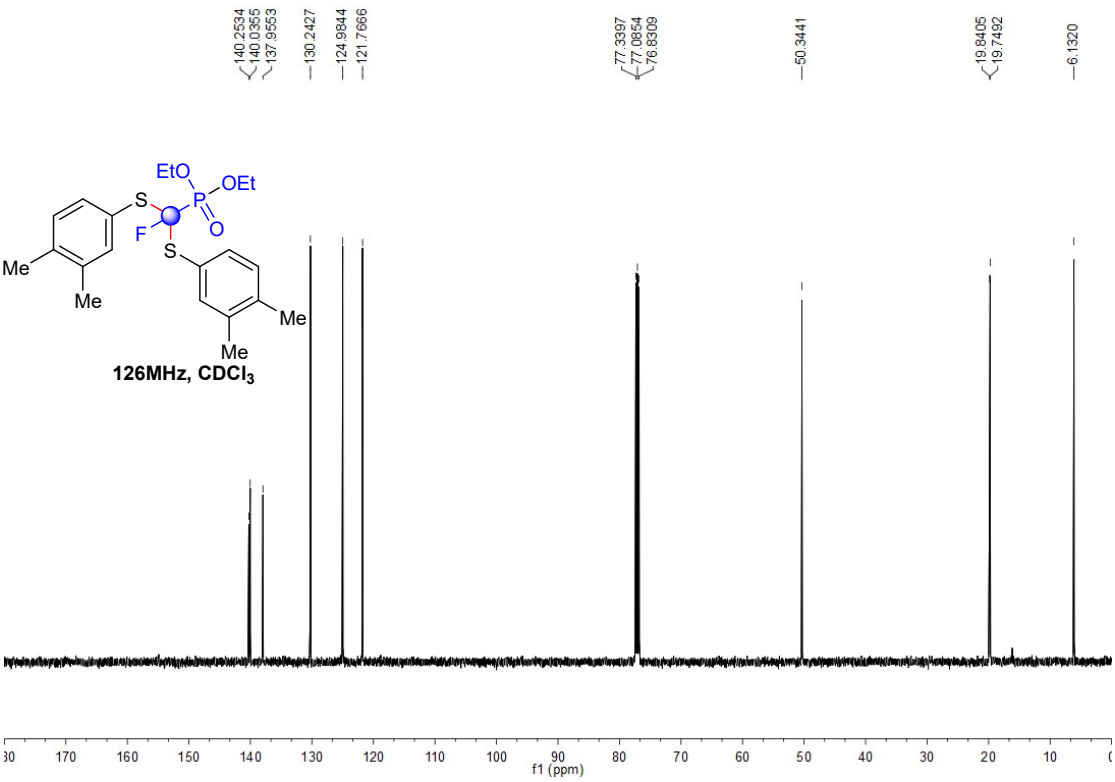


17c

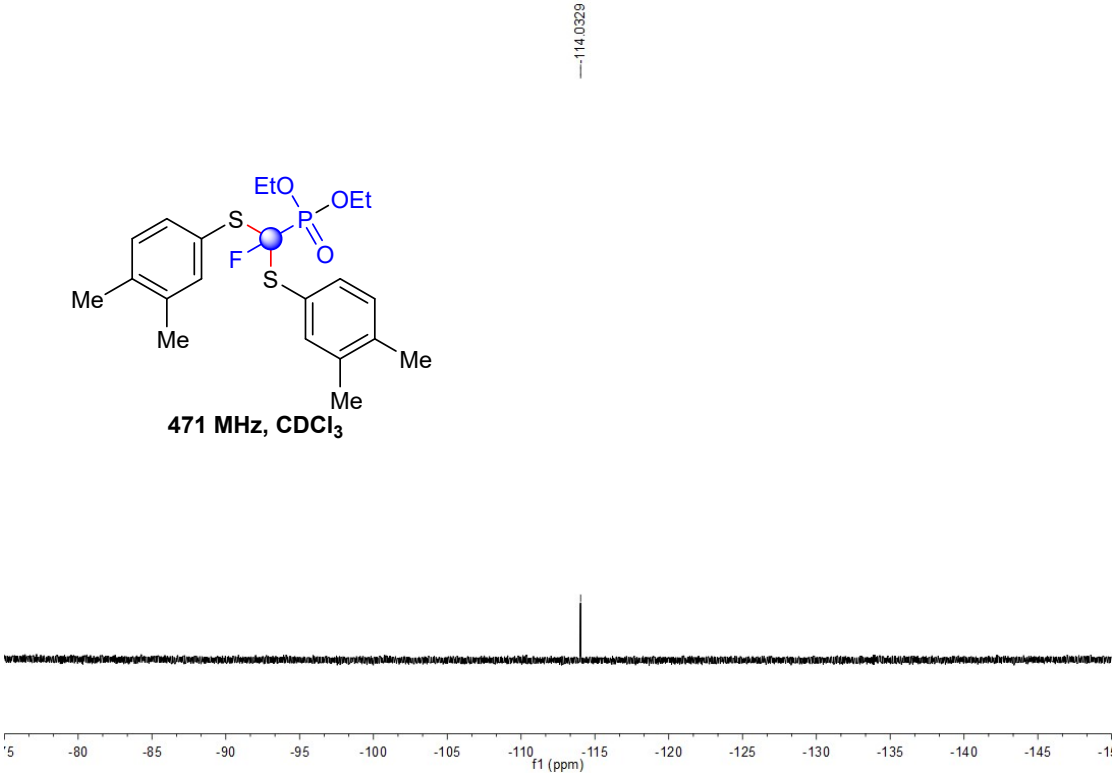
^{1}H NMR



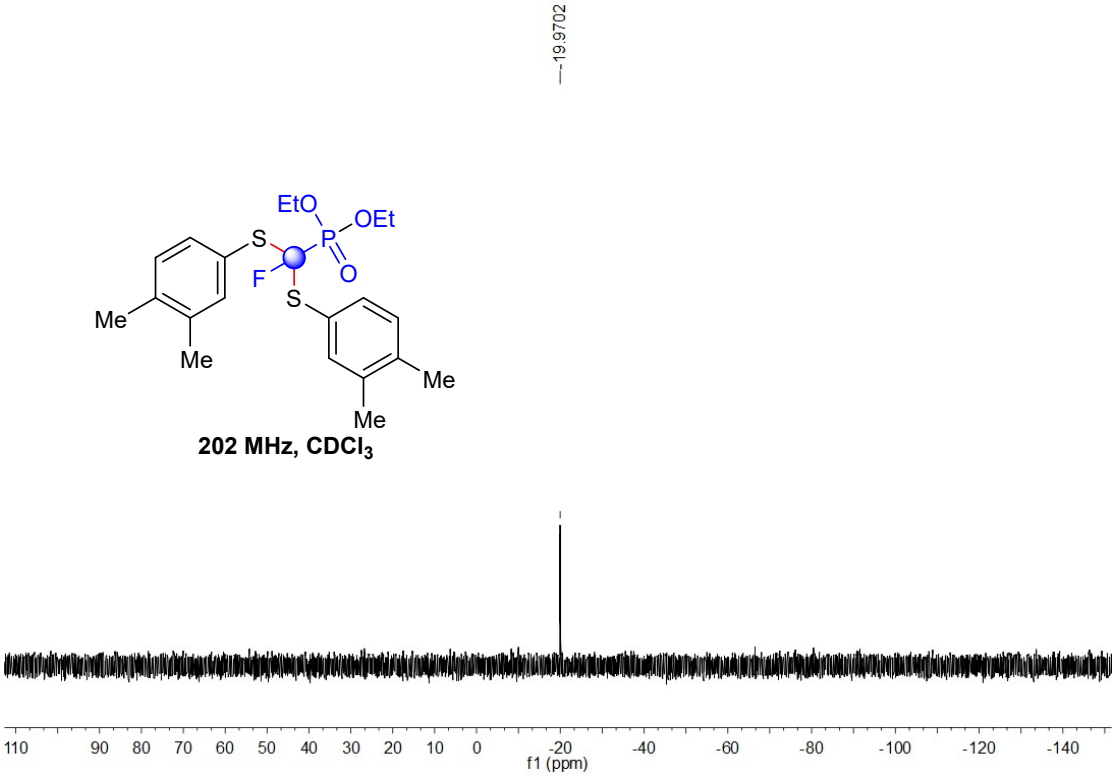
^{13}C NMR



^{19}F NMR

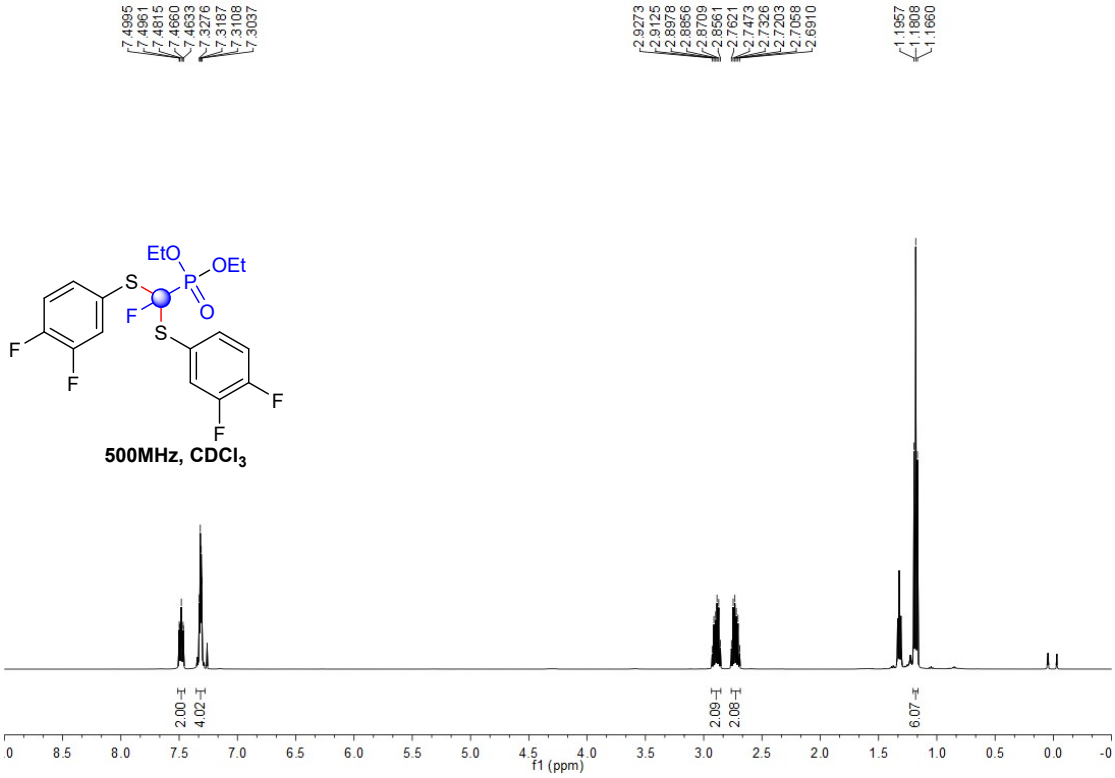


^{31}P NMR

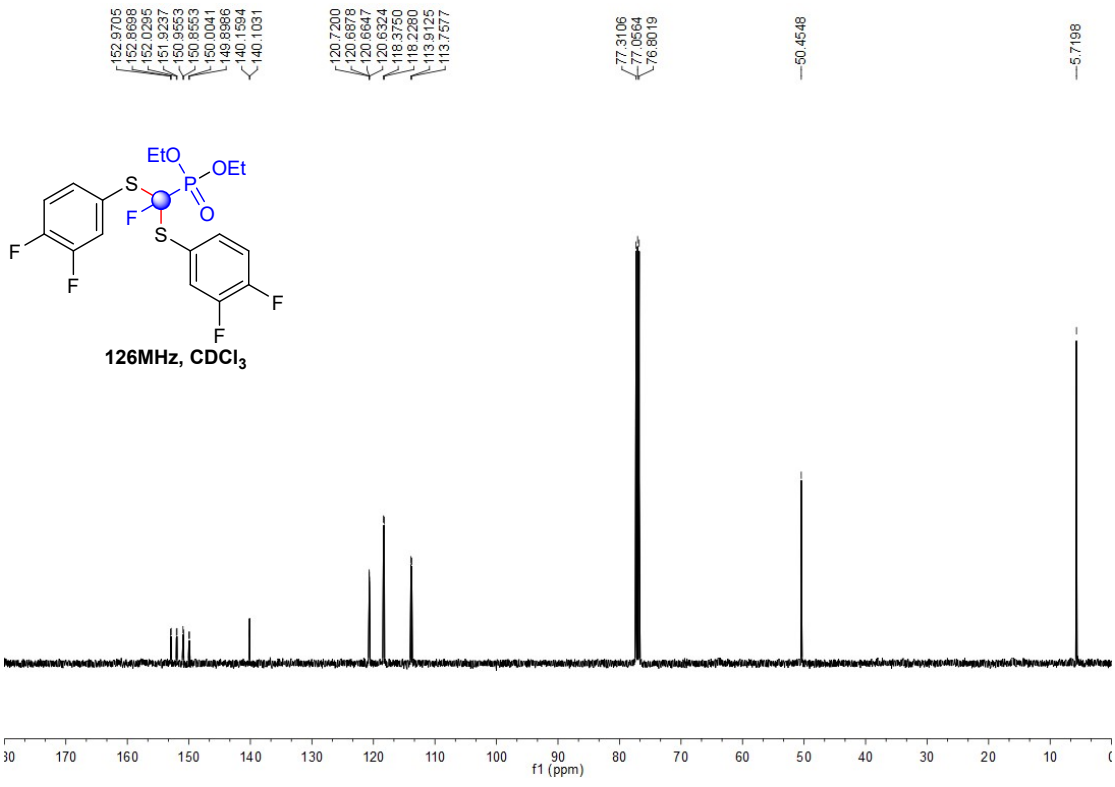


18c

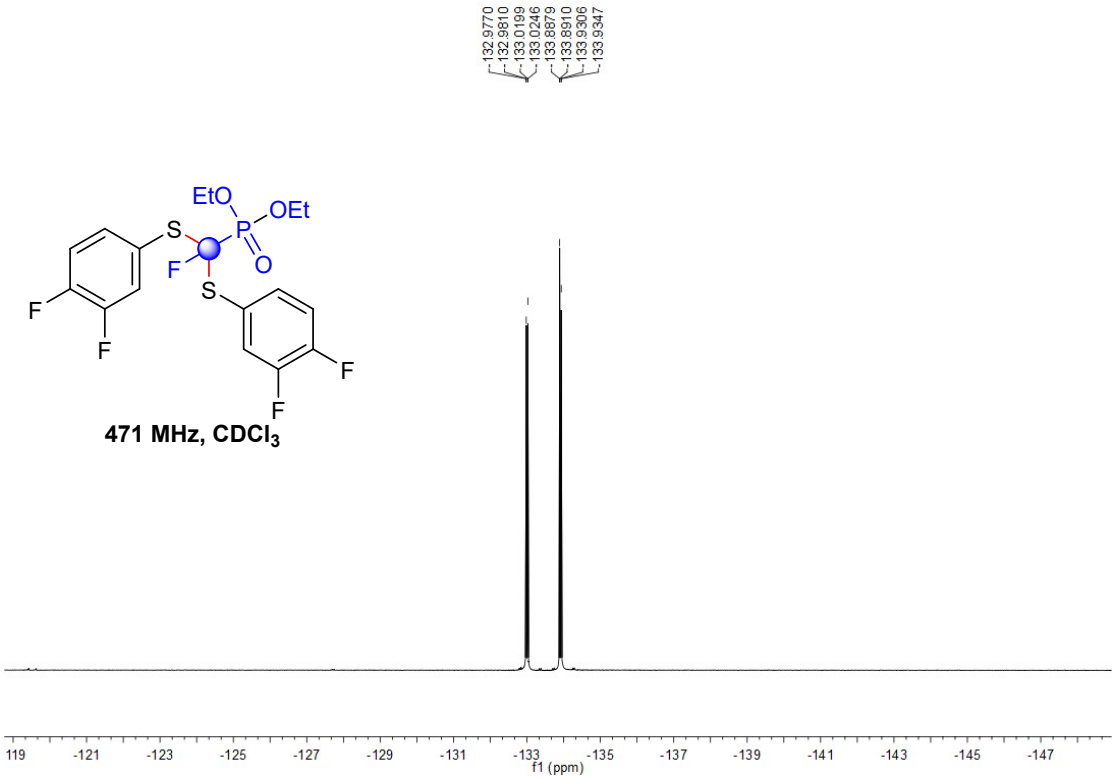
^{1}H NMR



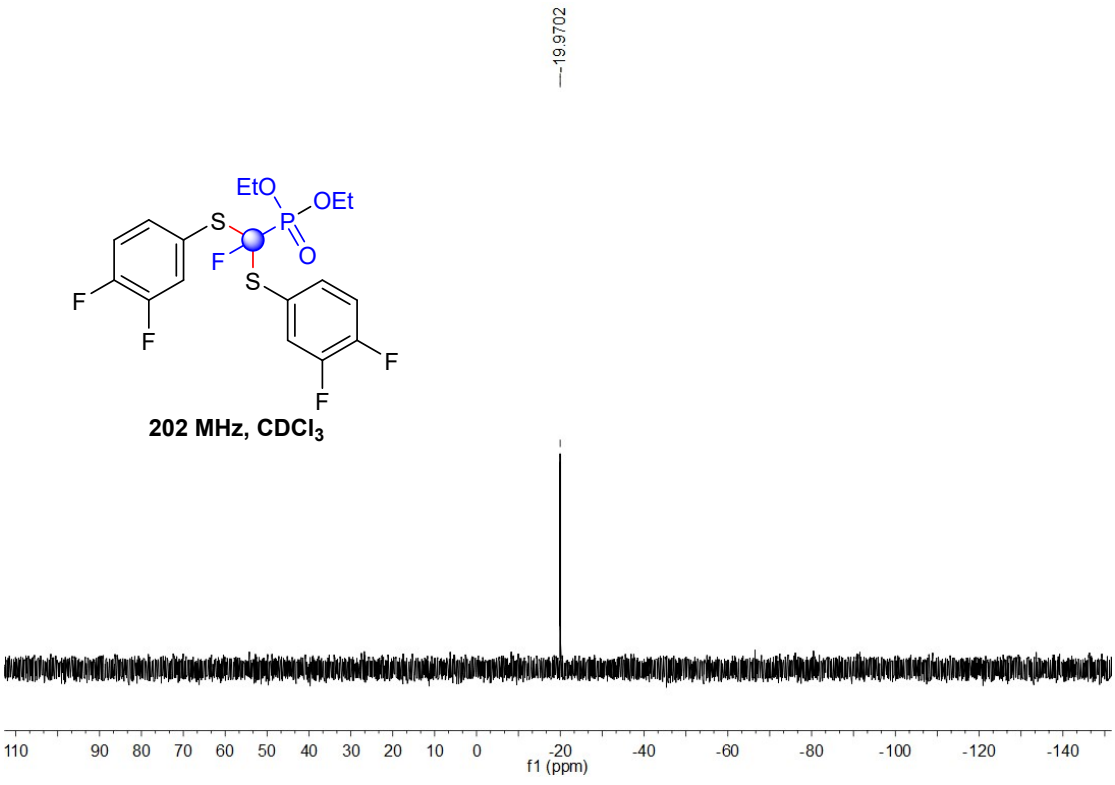
^{13}C NMR



^{19}F NMR

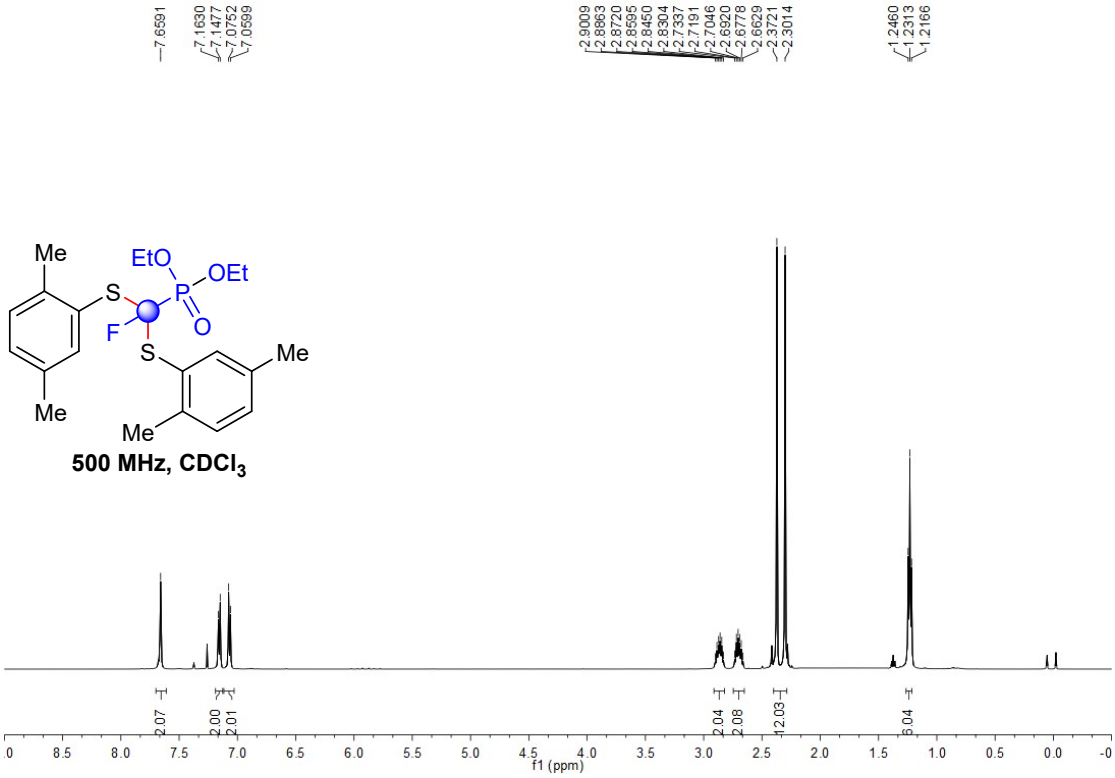


^{31}P NMR

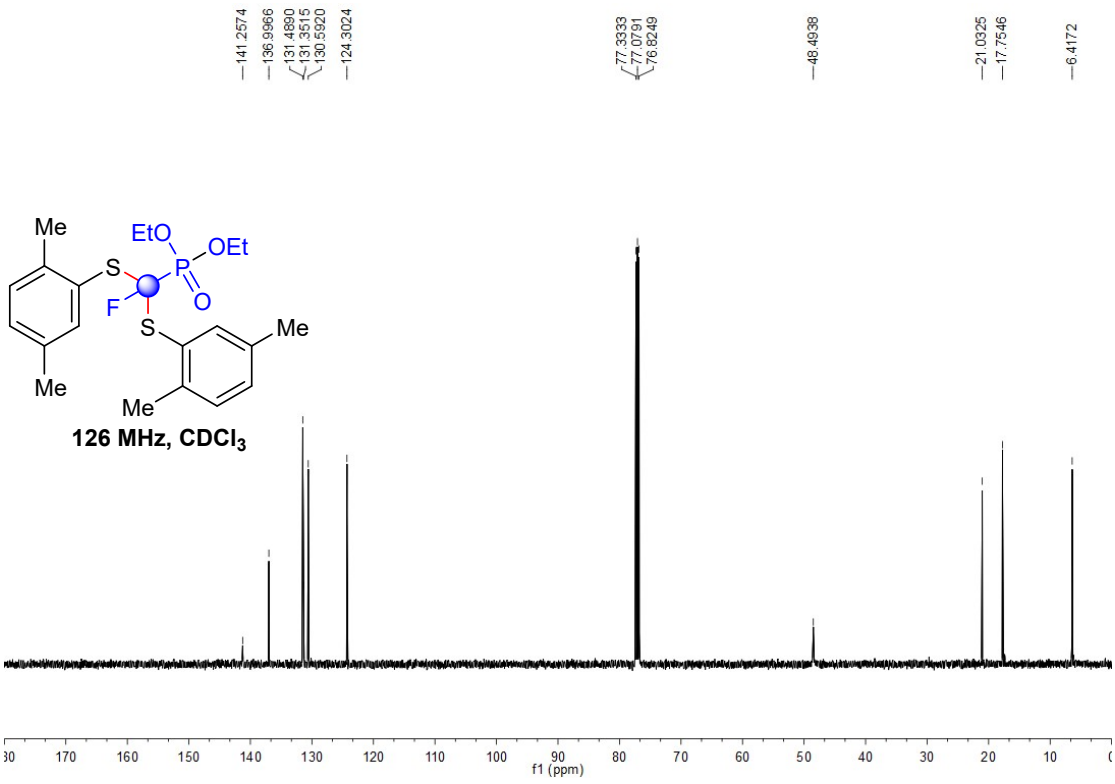


19c

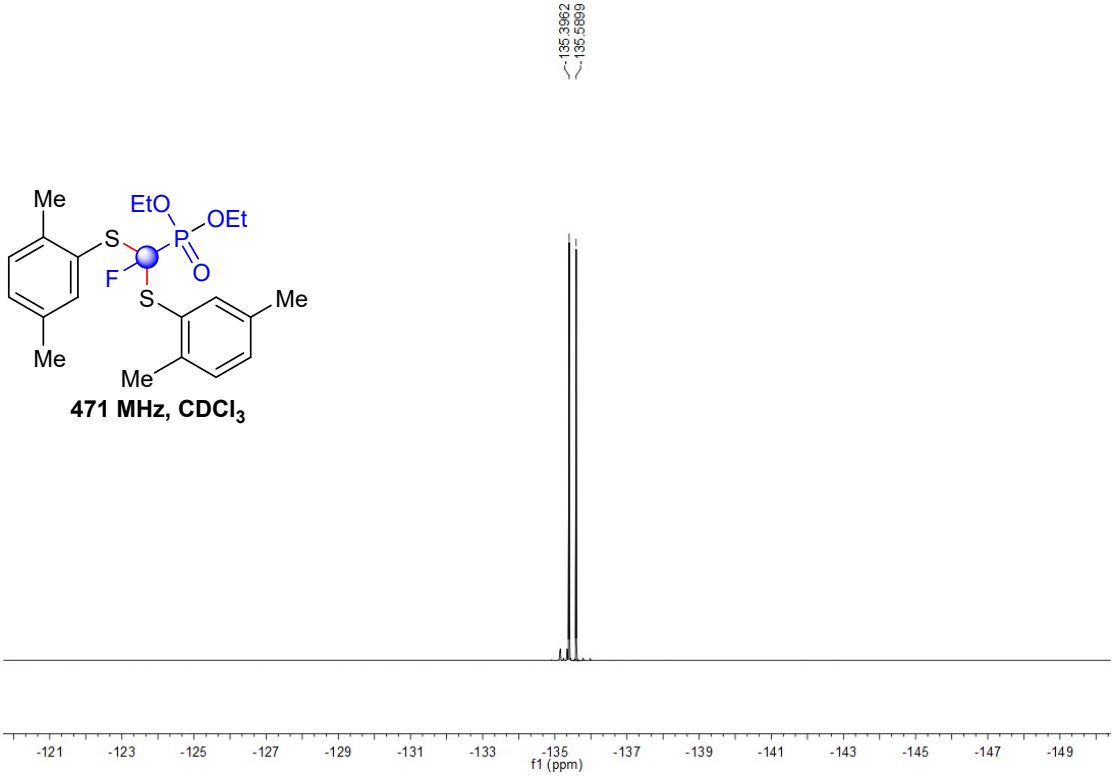
^{1}H NMR



^{13}C NMR

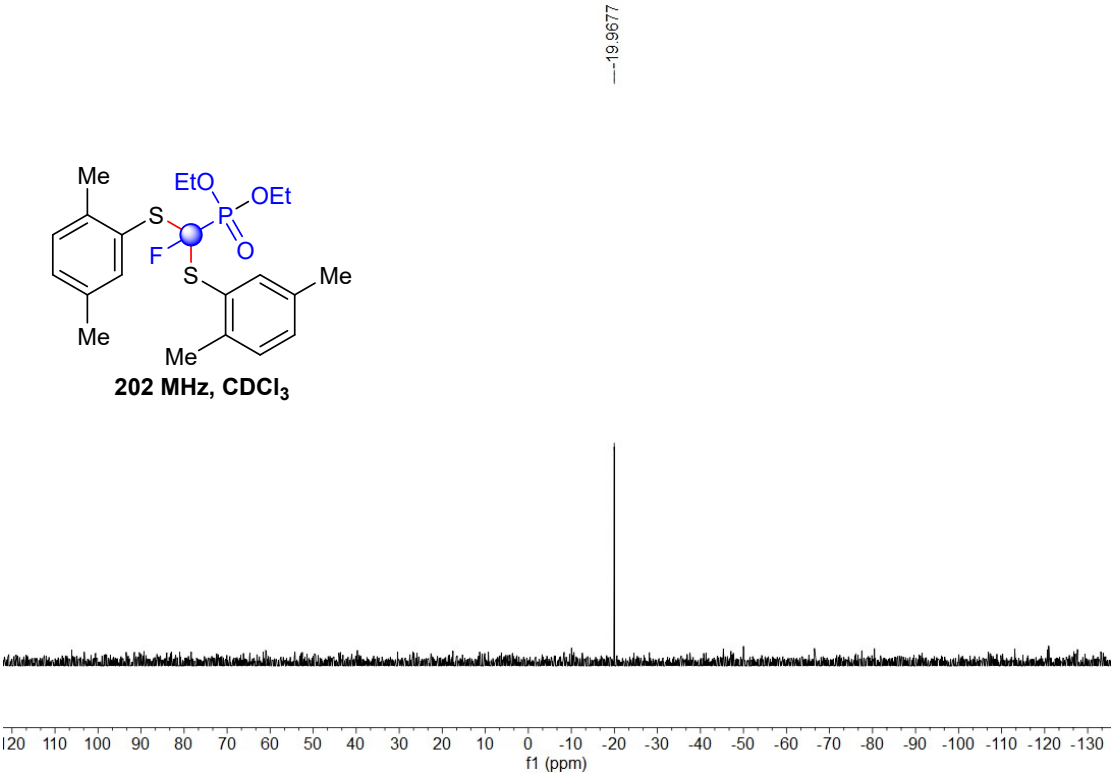


^{19}F NMR



471 MHz, $CDCl_3$

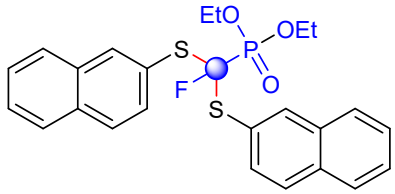
^{31}P NMR



202 MHz, $CDCl_3$

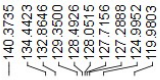
20c

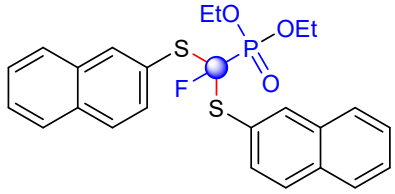
^{1}H NMR



500 MHz, $CDCl_3$

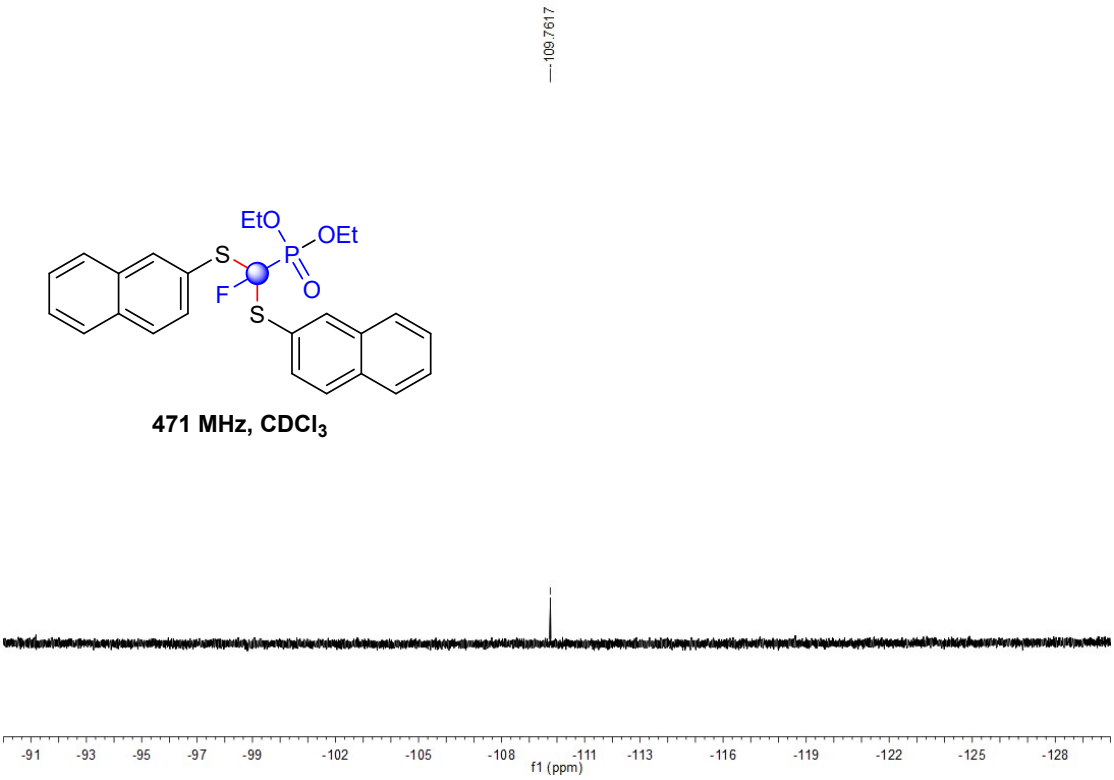
^{13}C NMR





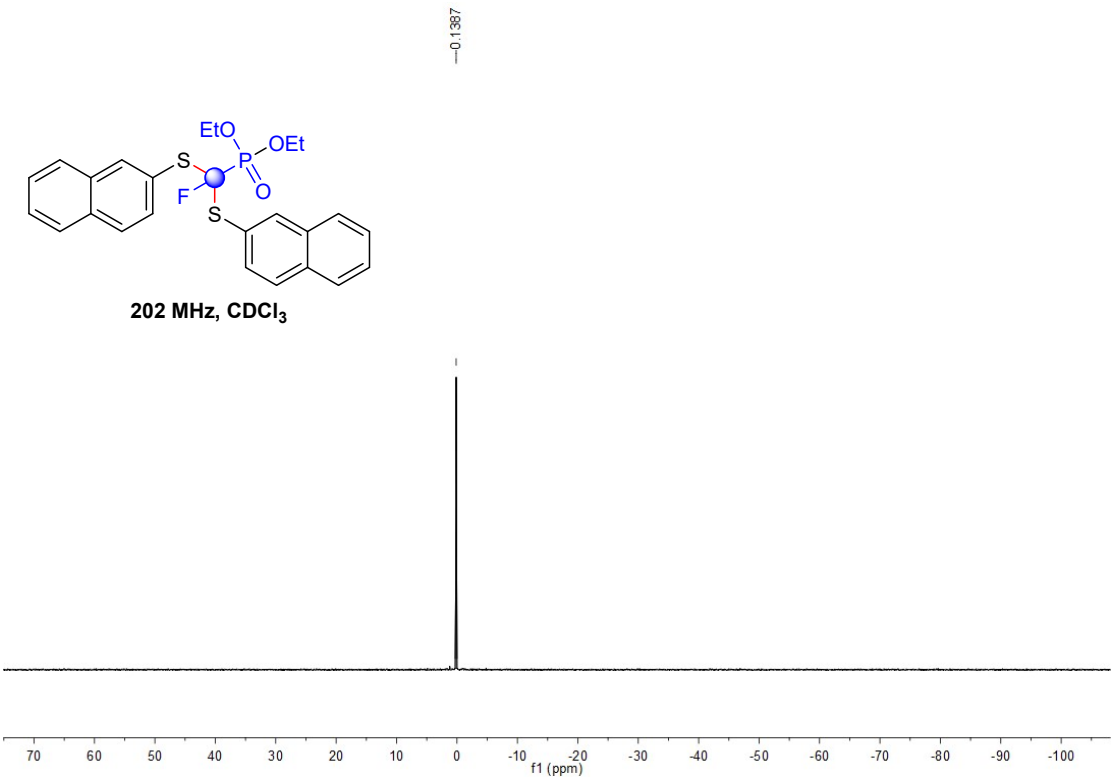
126 MHz, $CDCl_3$

^{19}F NMR



471 MHz, $CDCl_3$

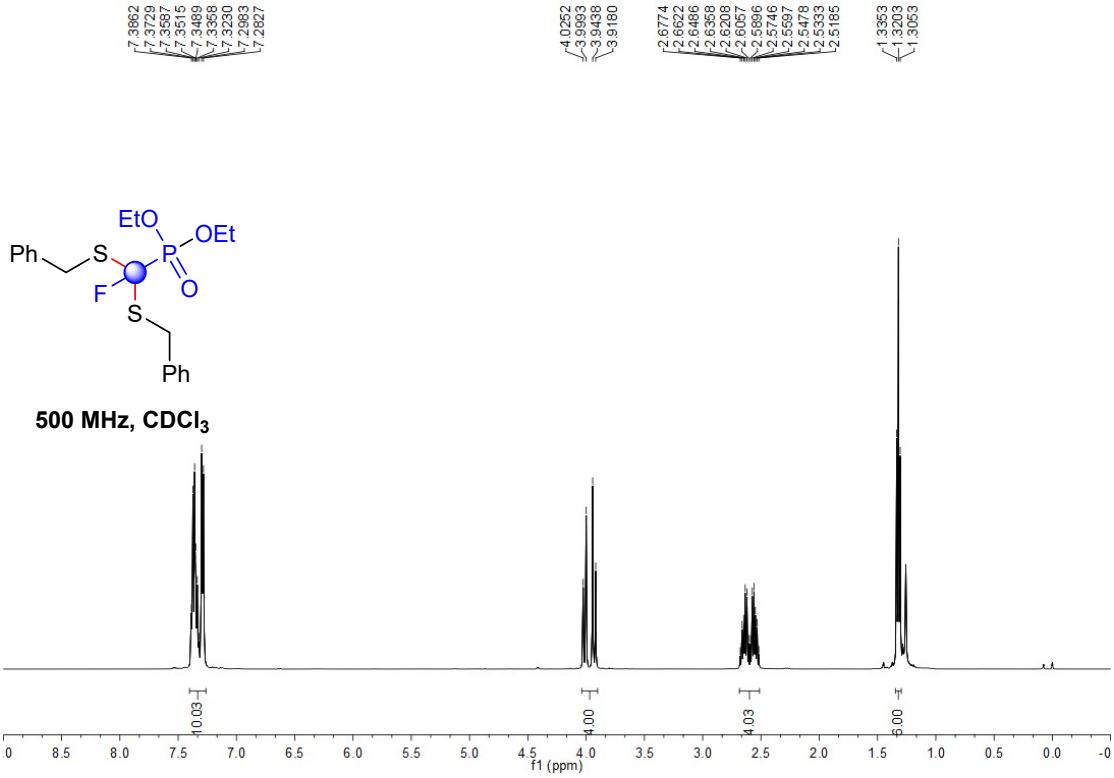
^{31}P NMR



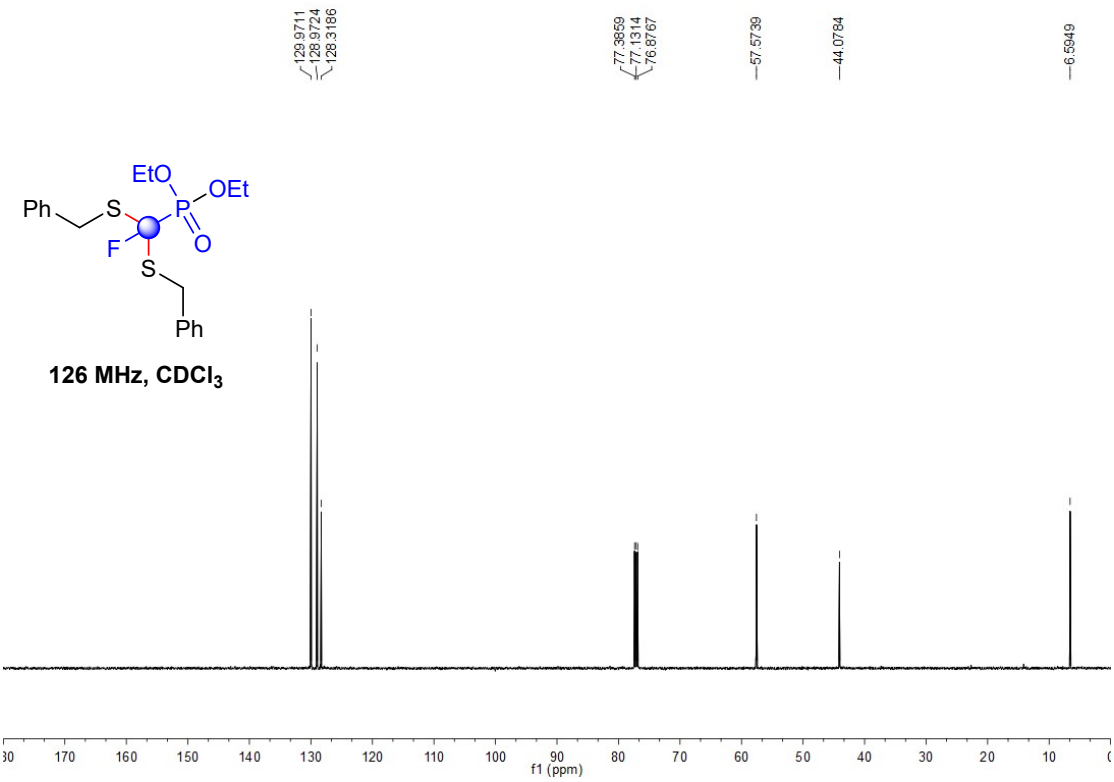
202 MHz, $CDCl_3$

21c

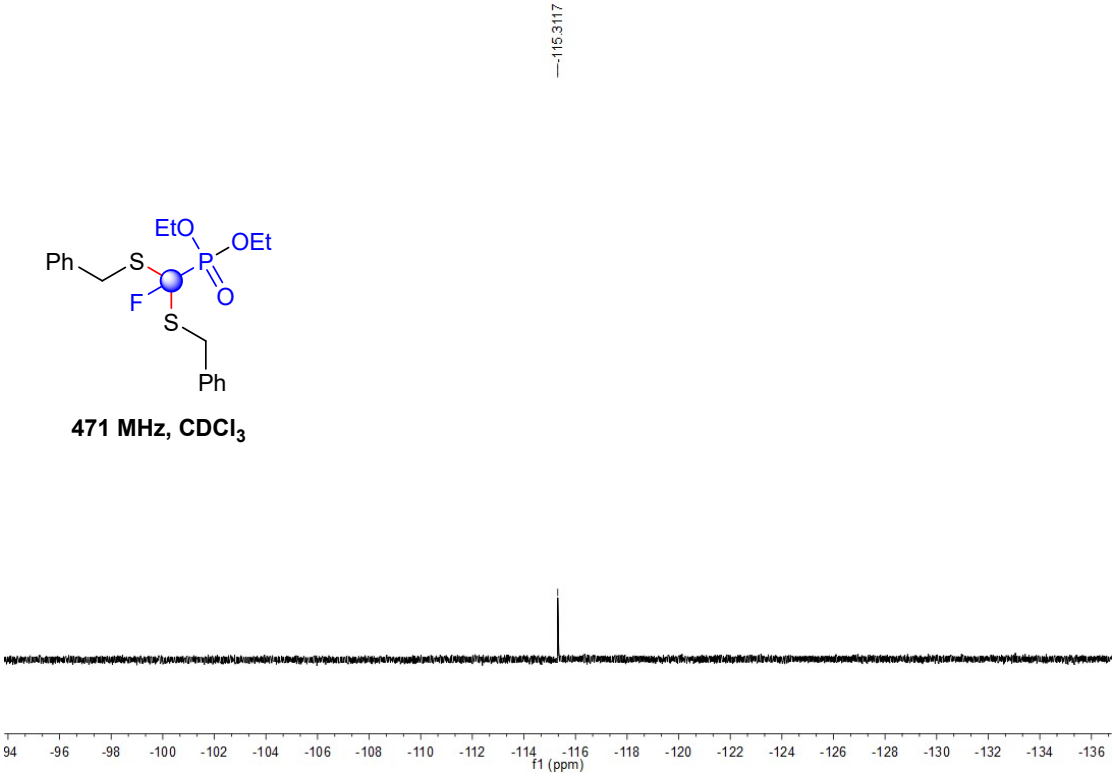
^{1}H NMR



^{13}C NMR

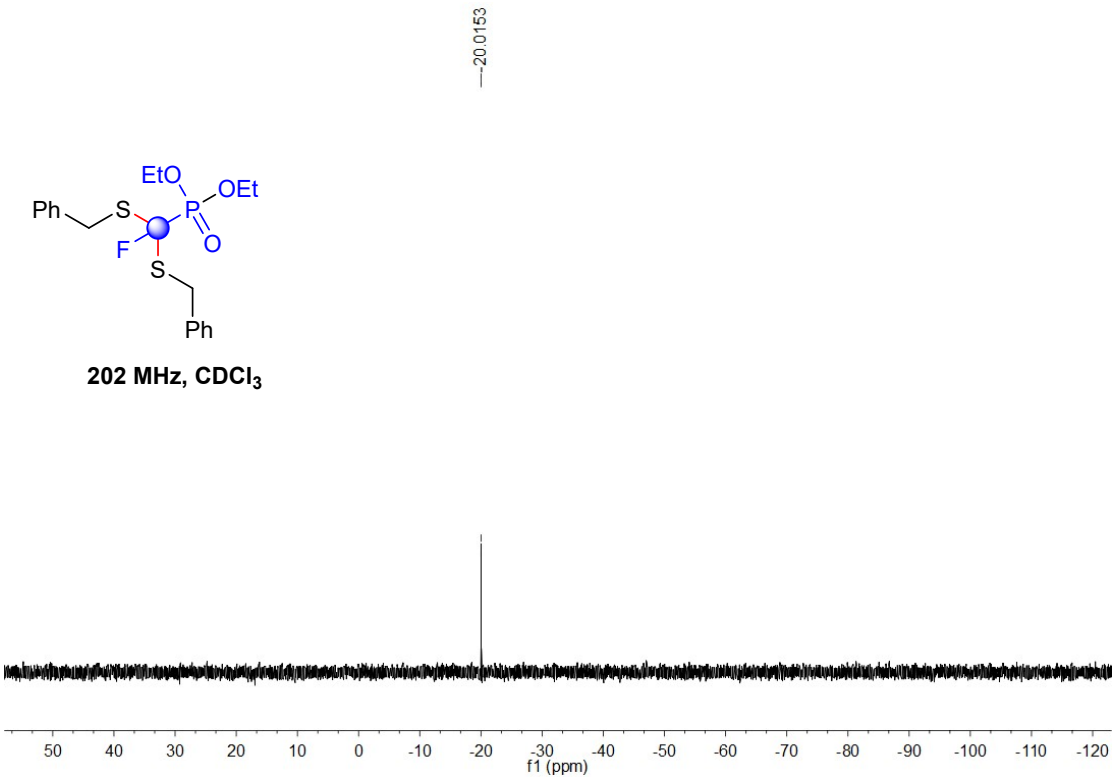


^{19}F NMR



471 MHz, $CDCl_3$

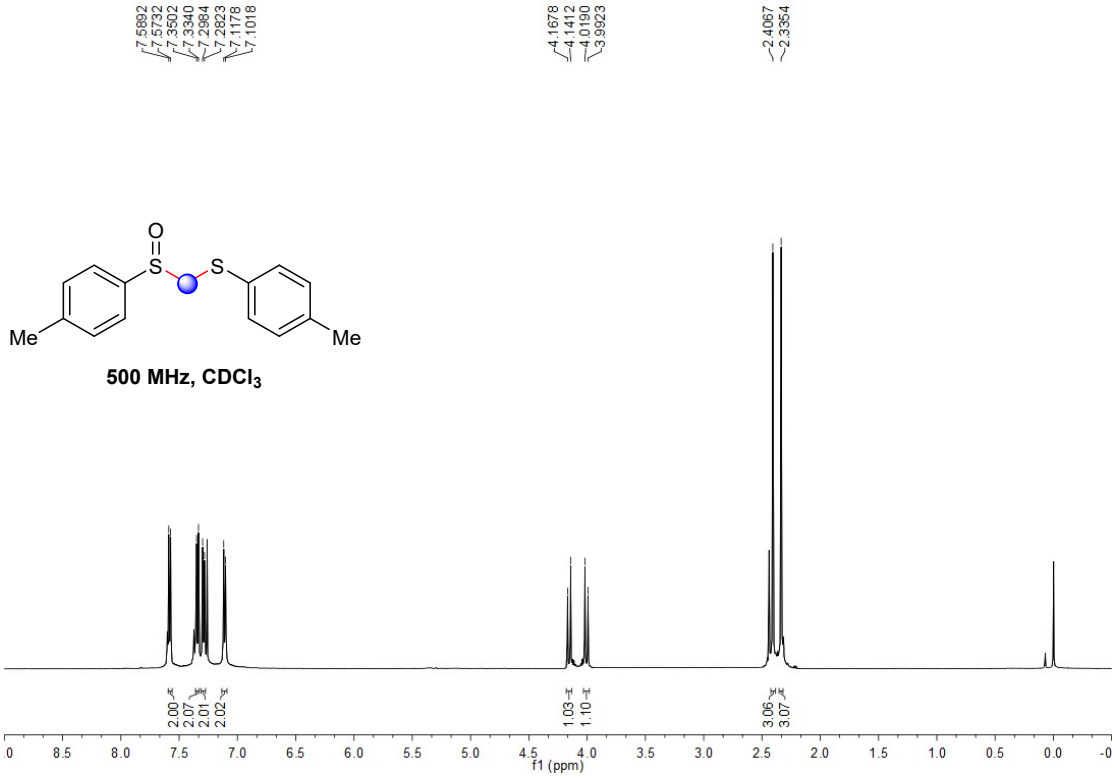
^{31}P NMR



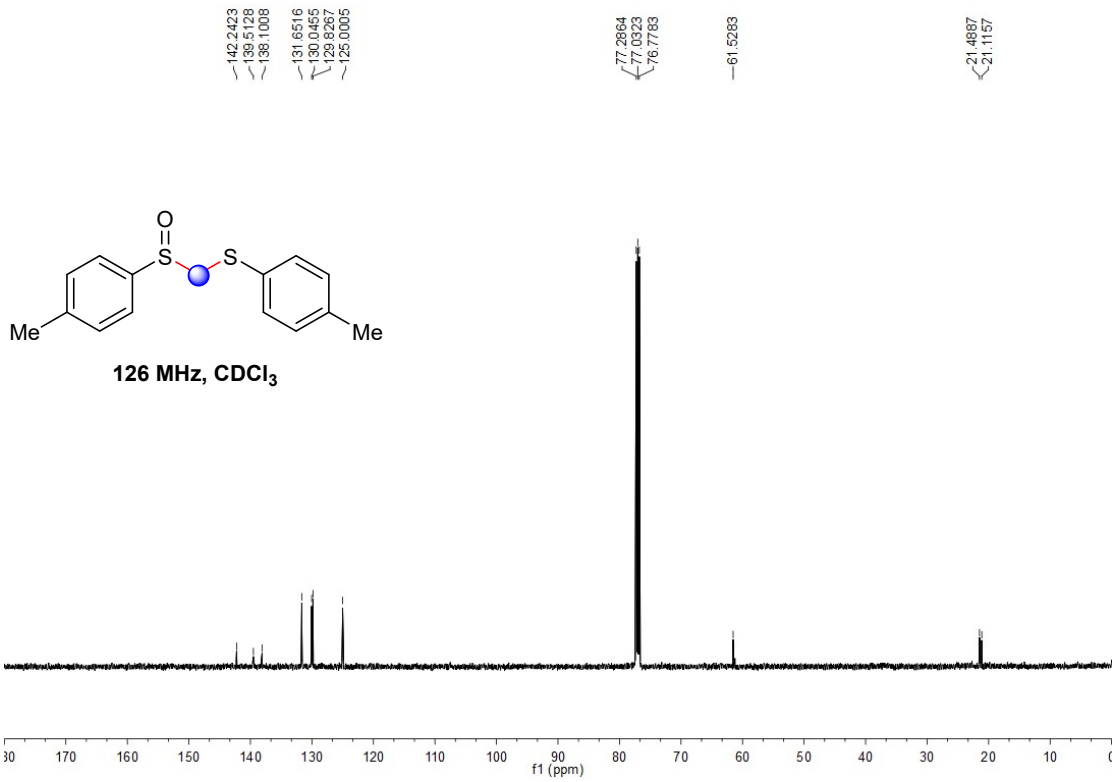
202 MHz, $CDCl_3$

25c

^{1}H NMR

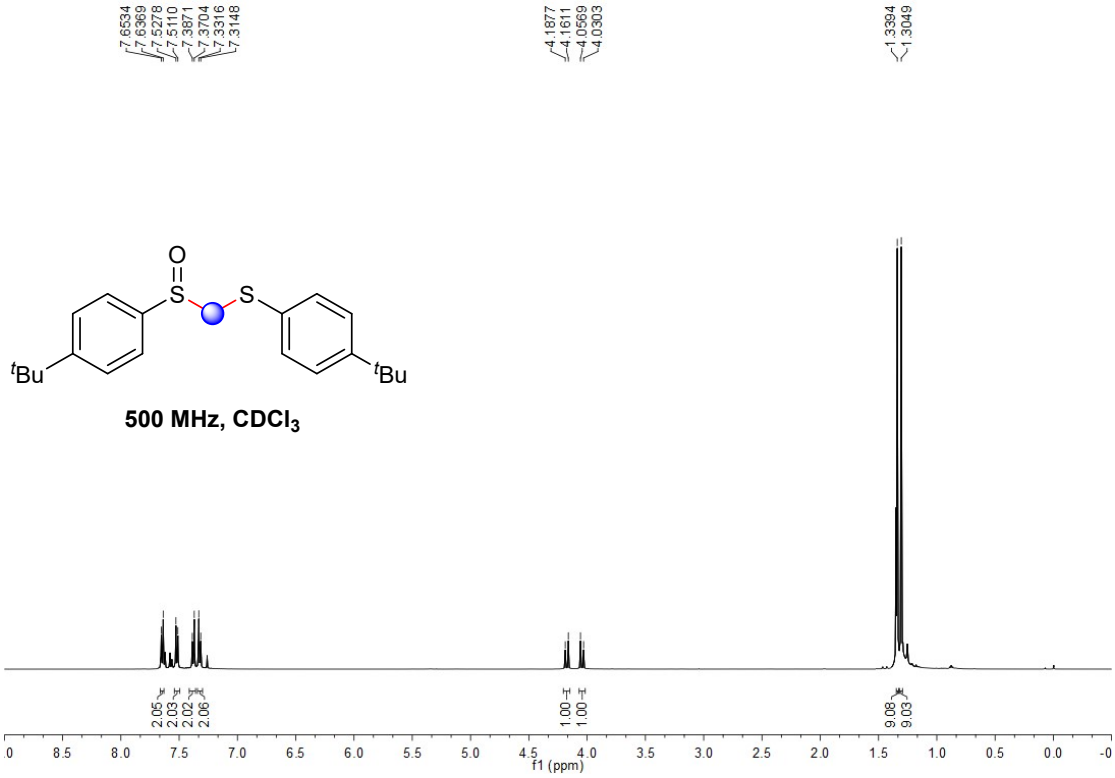


^{13}C NMR

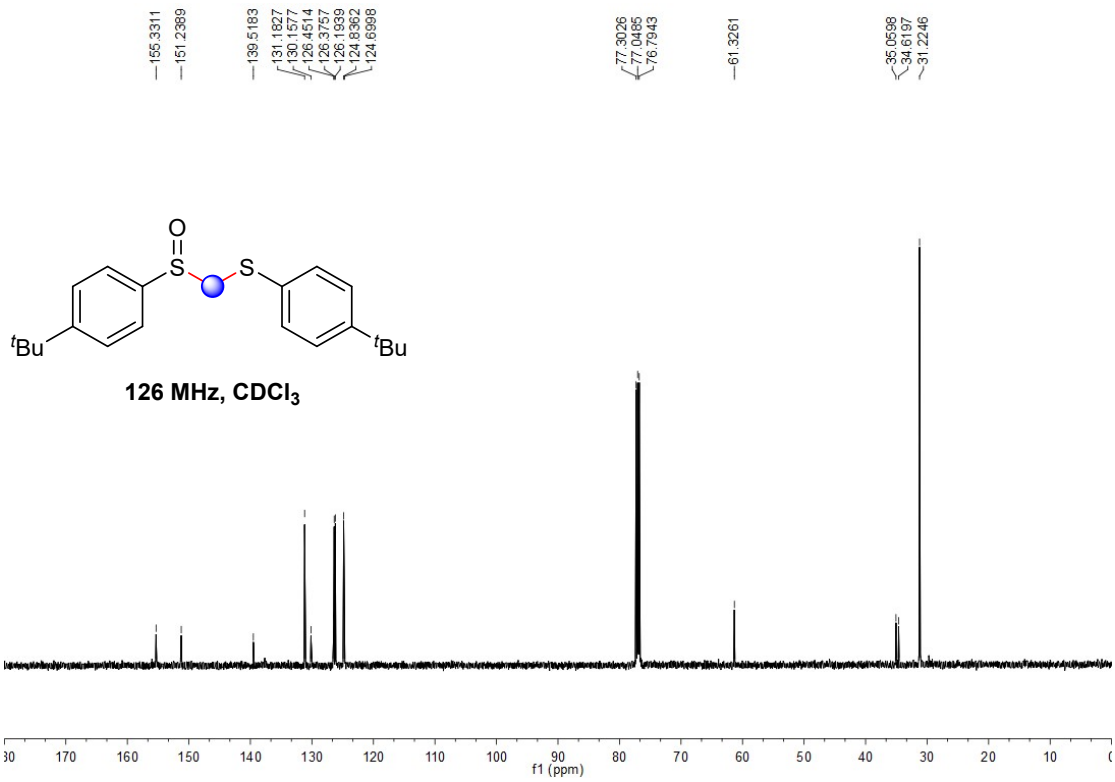


26c

^{1}H NMR

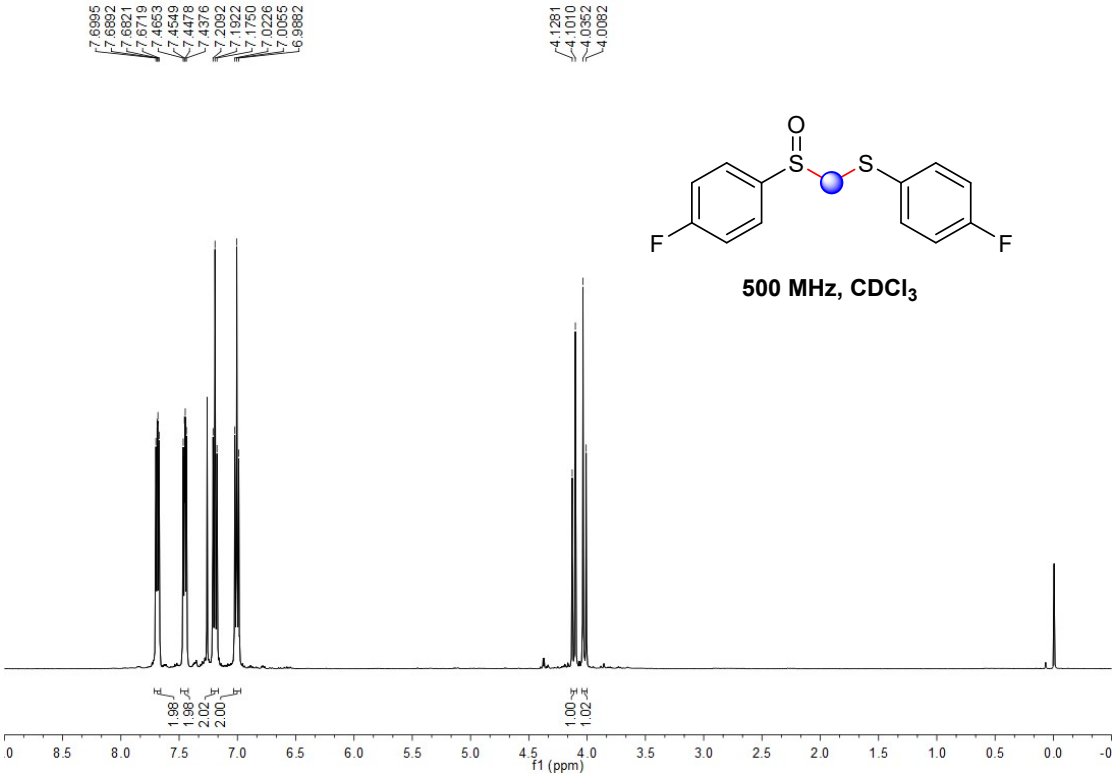


^{13}C NMR

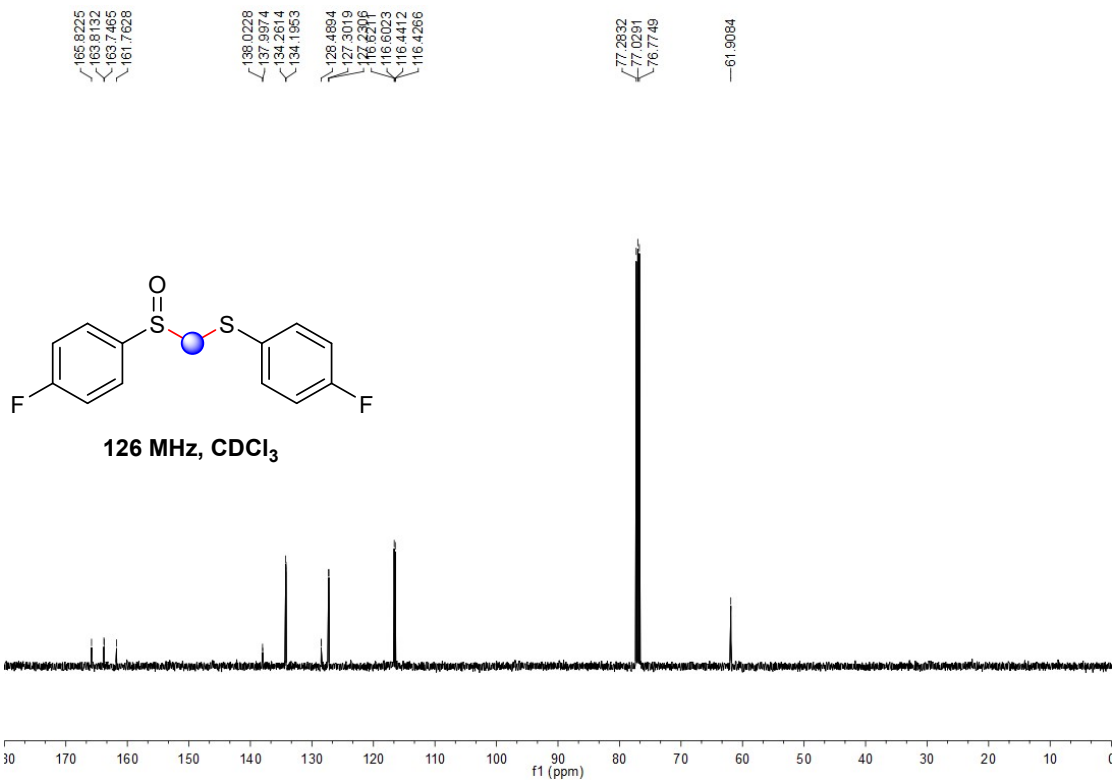


27c

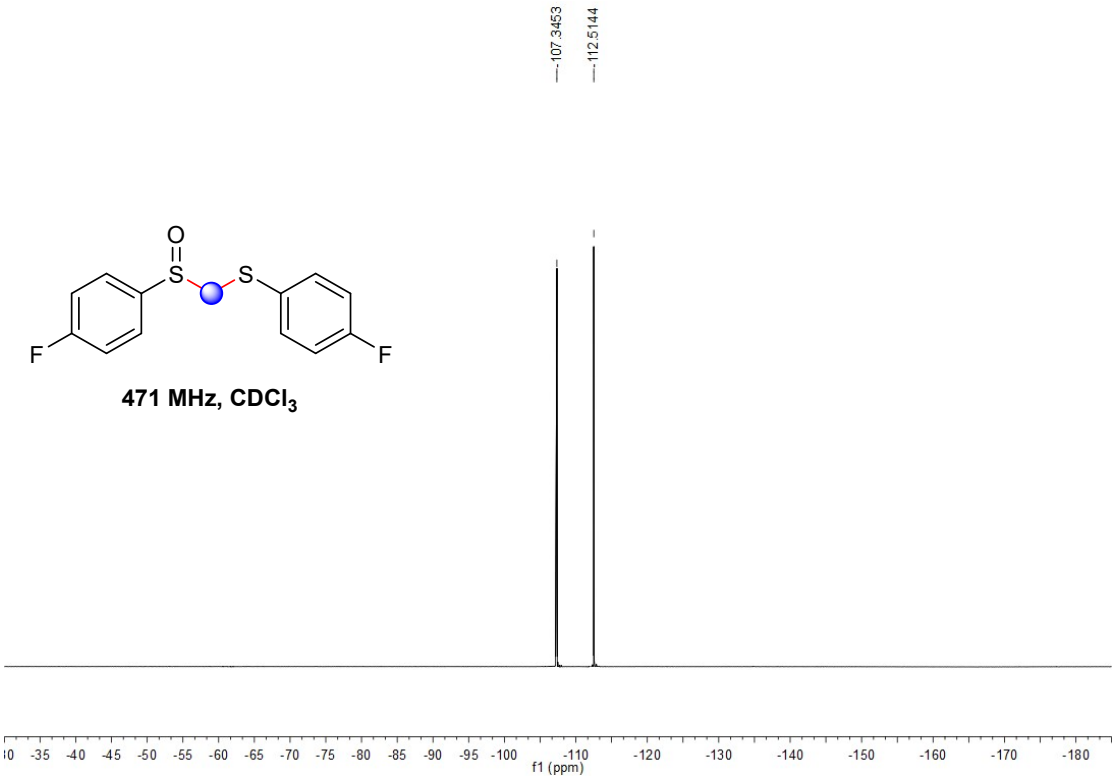
^{1}H NMR



^{13}C NMR

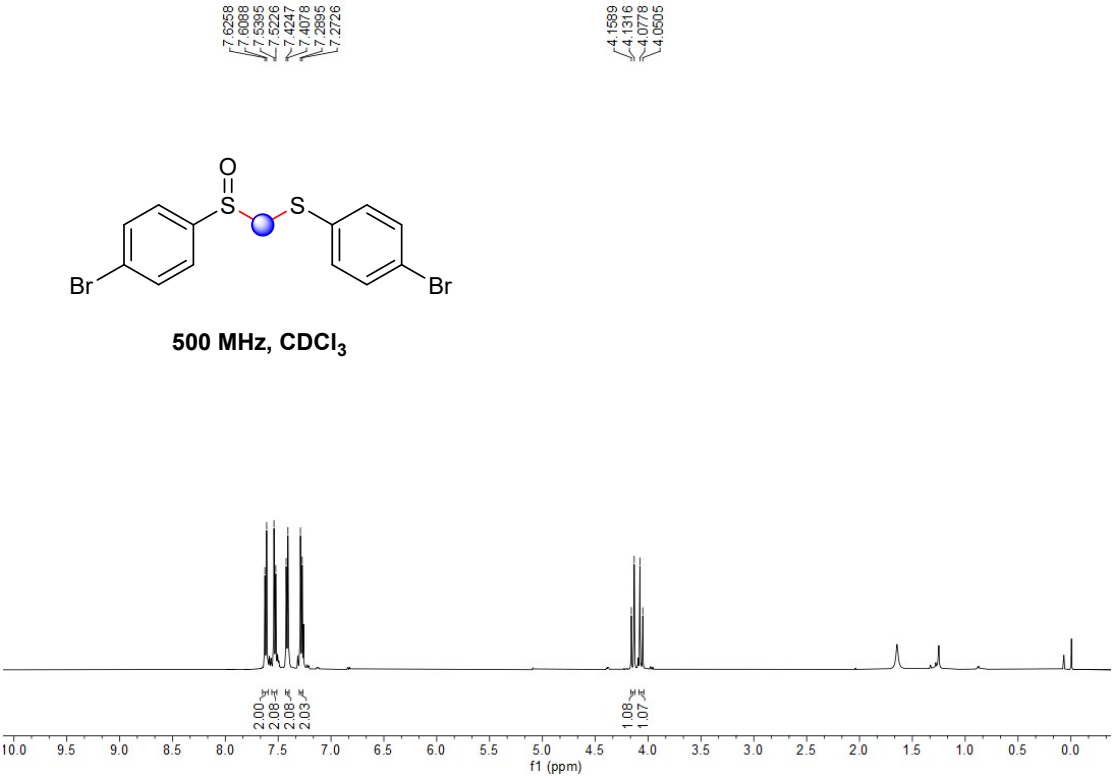


^{19}F NMR


-107.3453
-112.5144
O
S
S
F
F
471 MHz, CDCl3
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

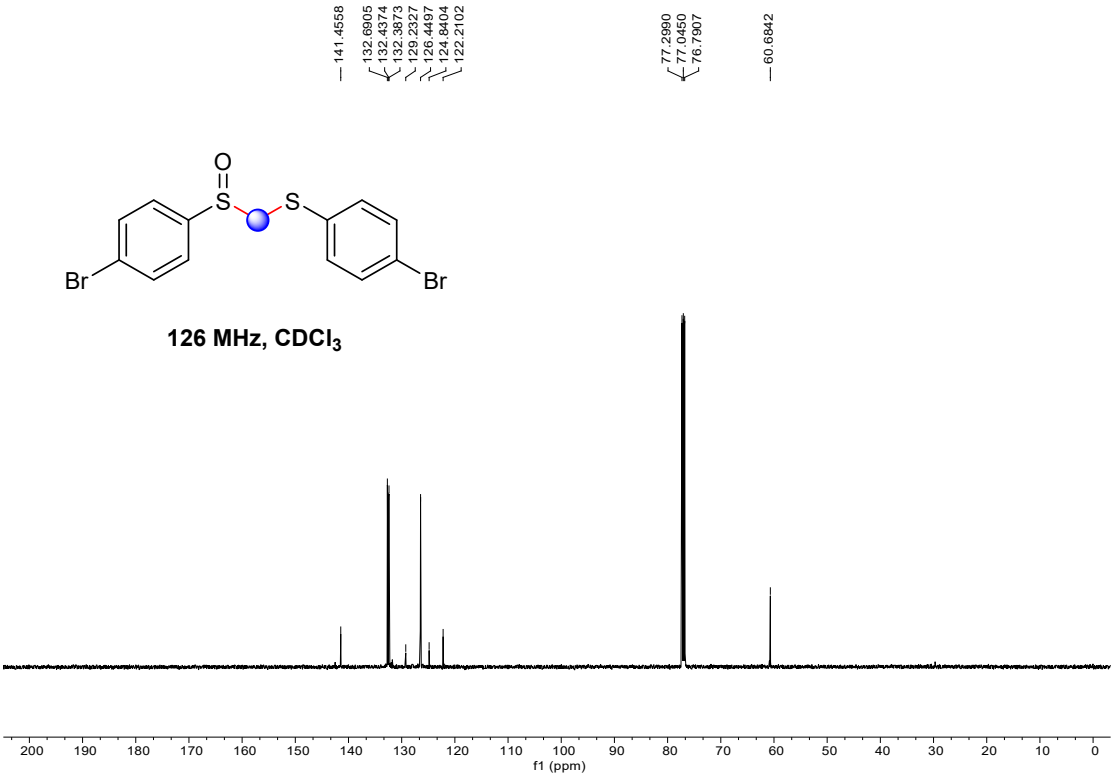
28c

^{1}H NMR



500 MHz, $CDCl_3$

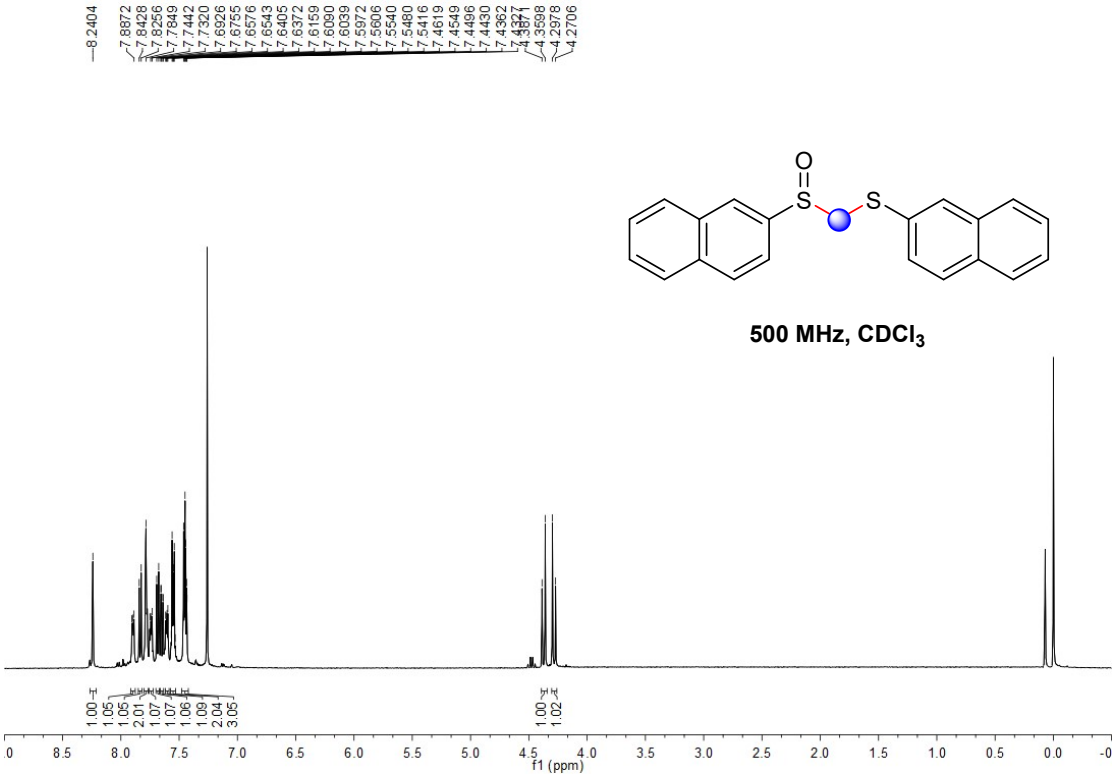
^{13}C NMR



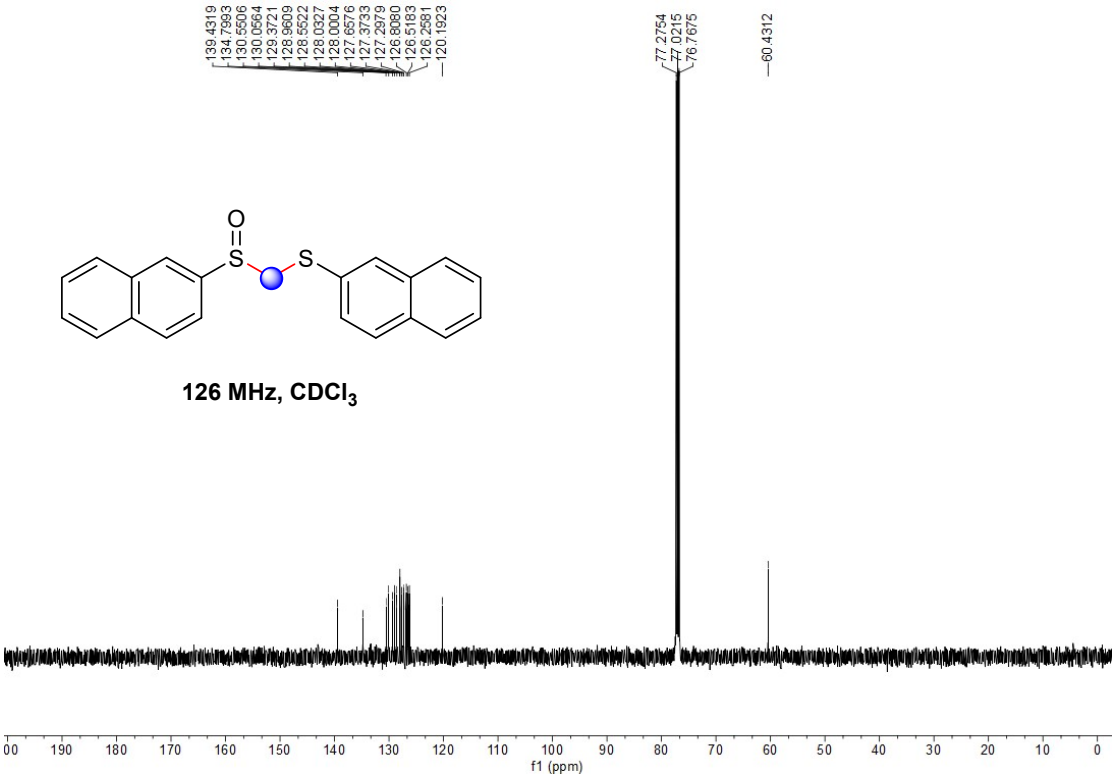
126 MHz, $CDCl_3$

29c

^{1}H NMR

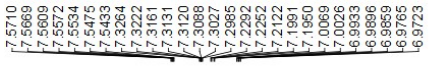


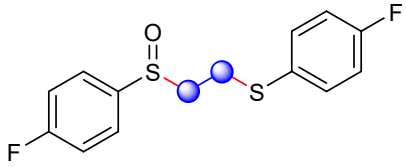
^{13}C NMR



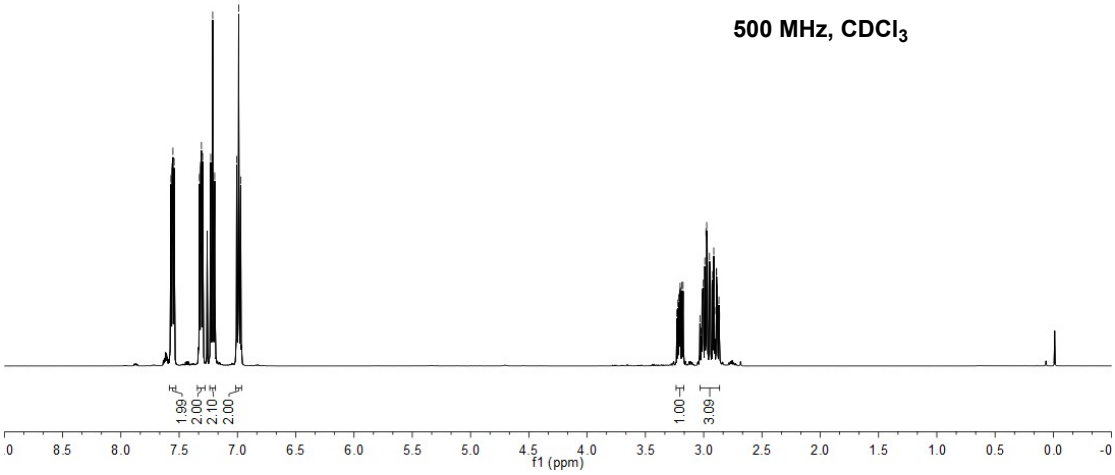
30c

^{1}H NMR

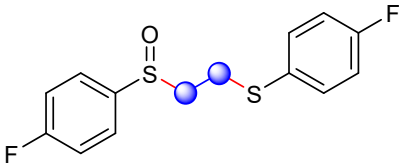




500 MHz, $CDCl_3$

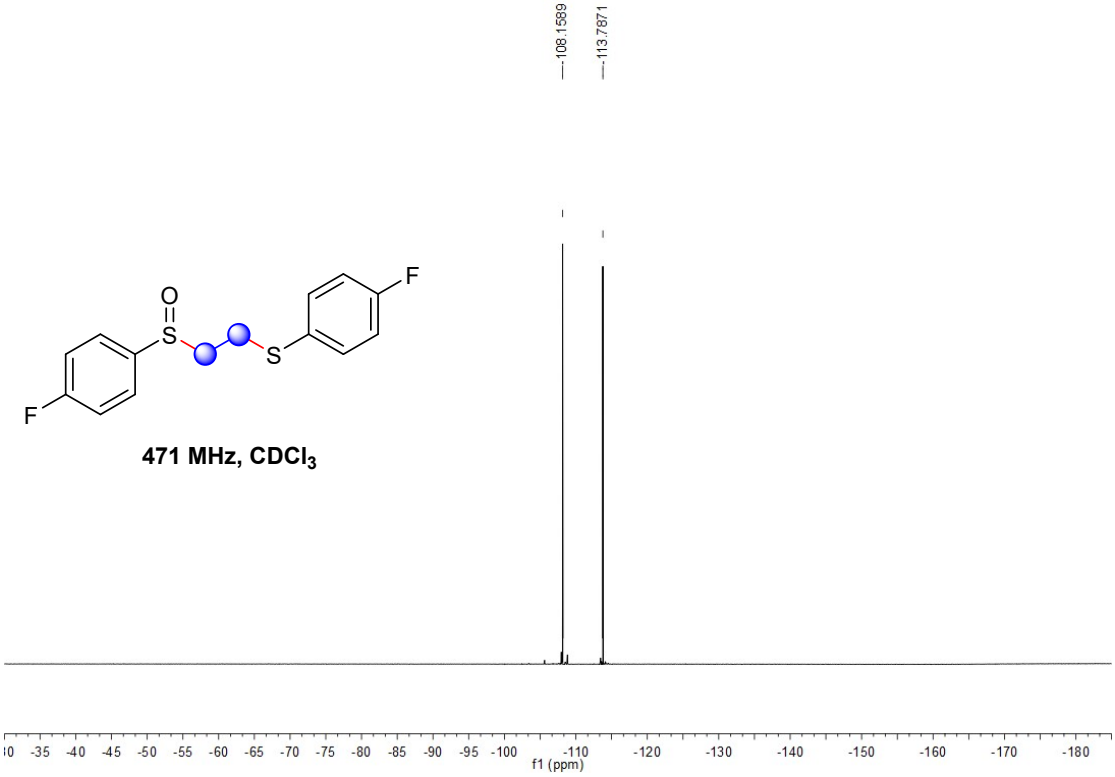


^{13}C NMR



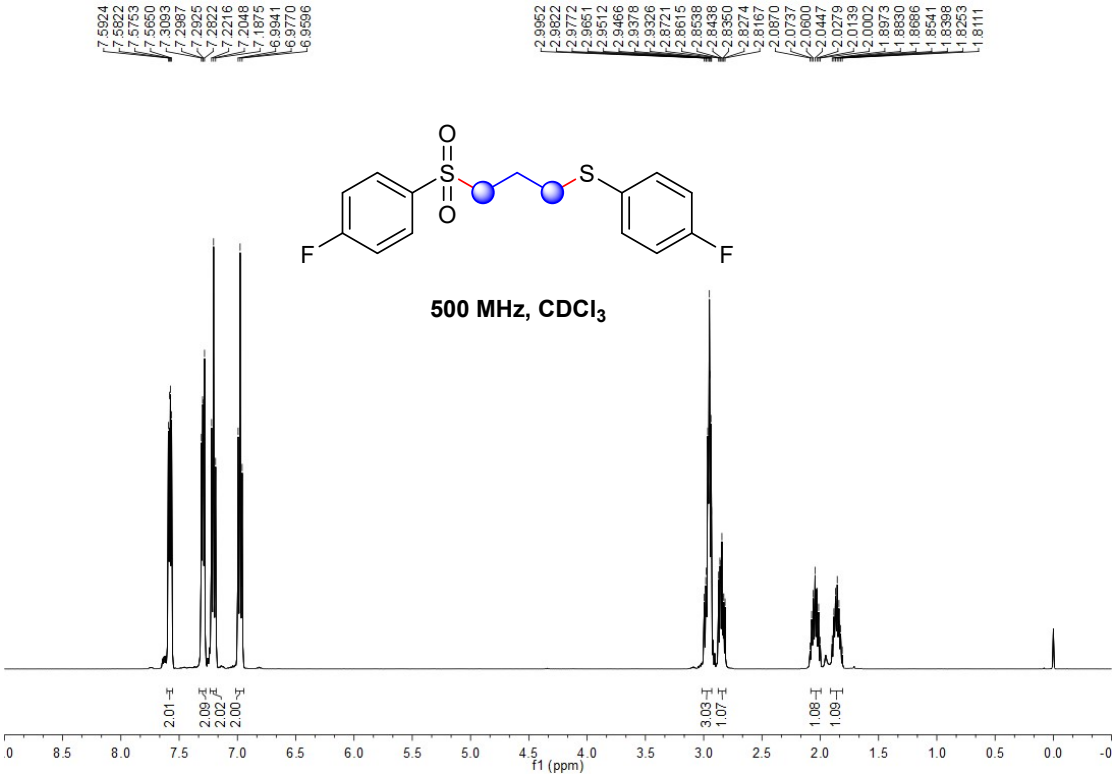
126 MHz, $CDCl_3$

^{19}F NMR

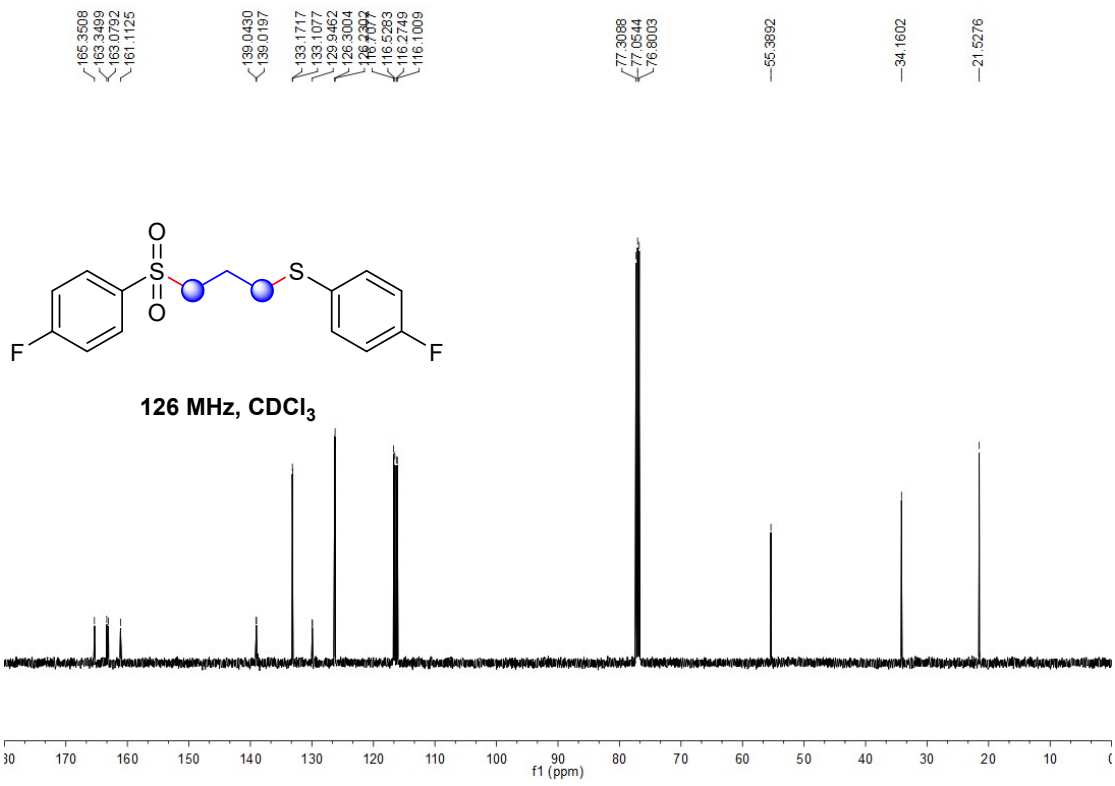

-108.1589
-113.7871
O
S
S
F
F
471 MHz, CDCl3
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

31c

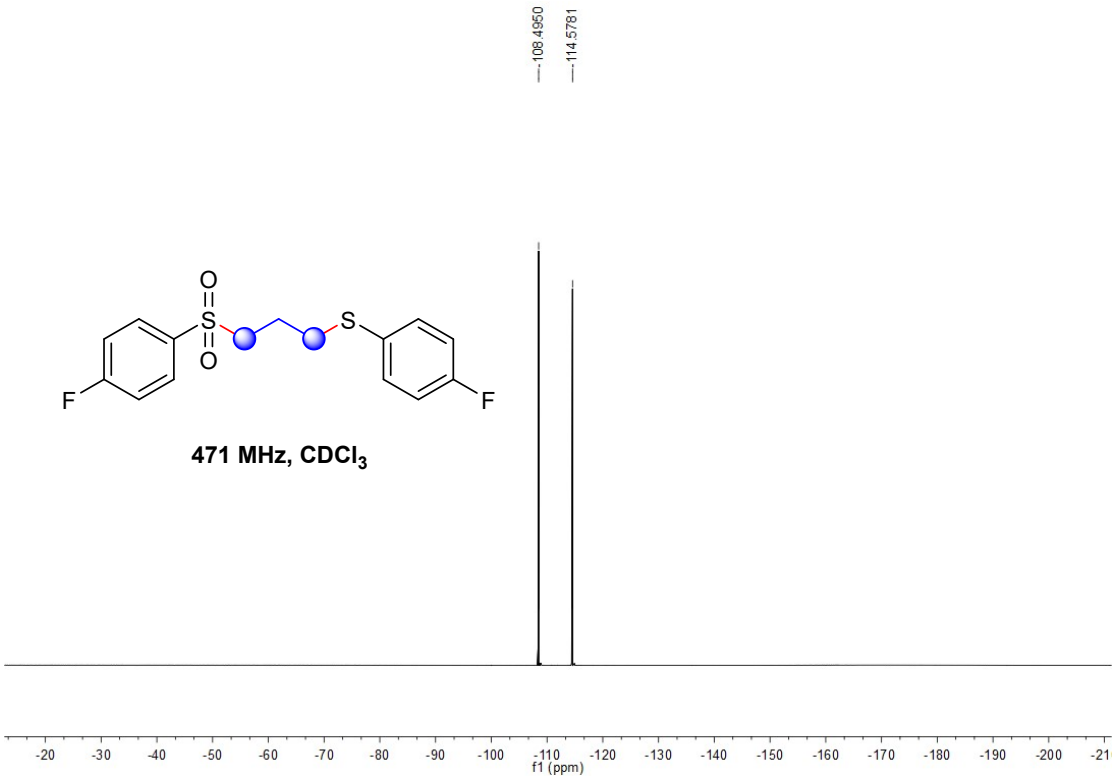
^{1}H NMR



^{13}C NMR

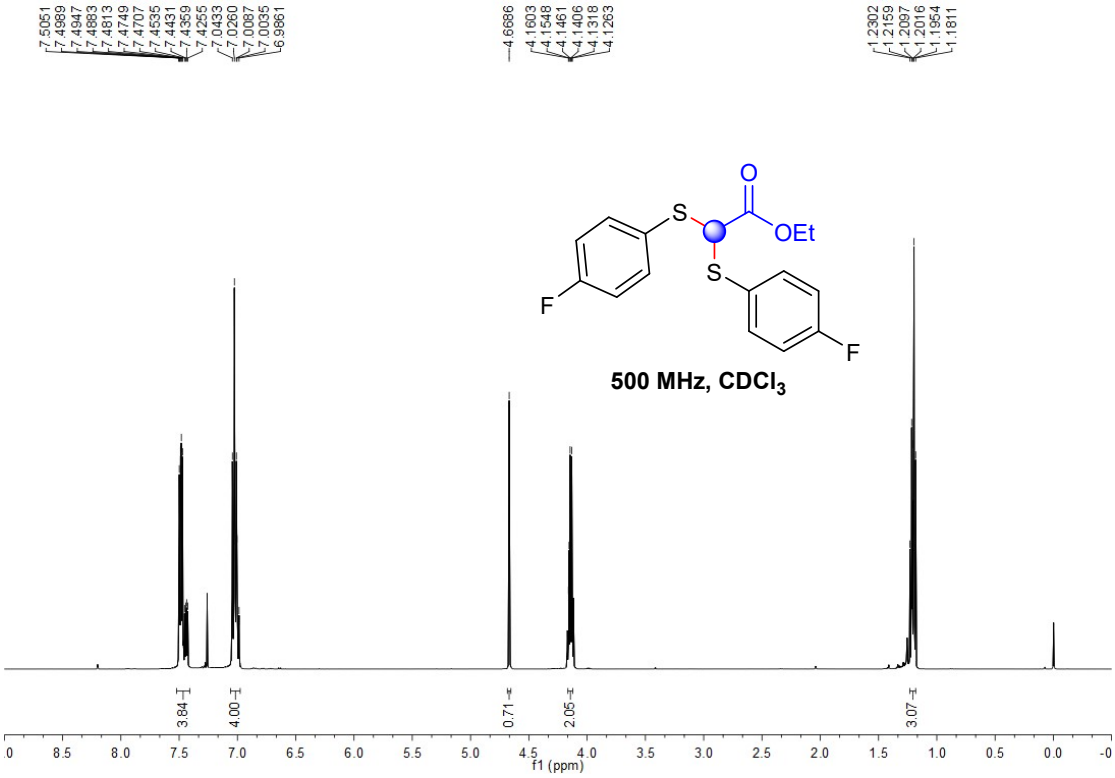


^{19}F NMR

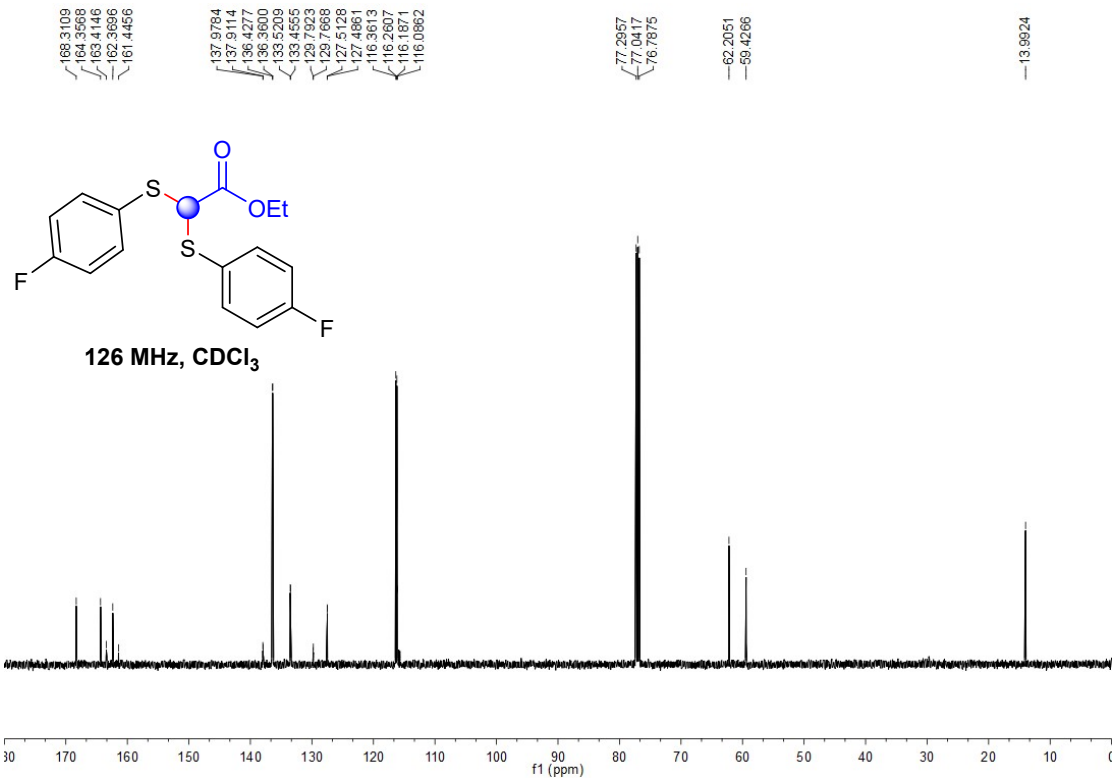

-108.4950
-114.5781
O
S
O
S
F
F
471 MHz, CDCl3
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

32c

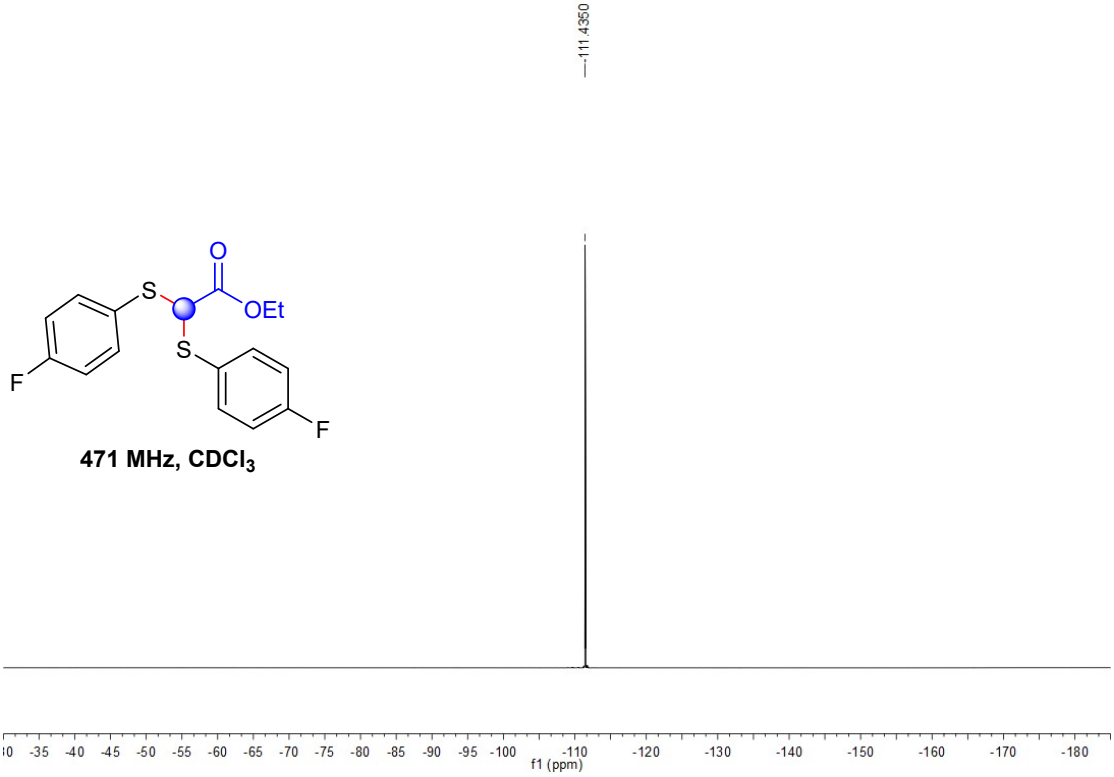
^{1}H NMR



^{13}C NMR

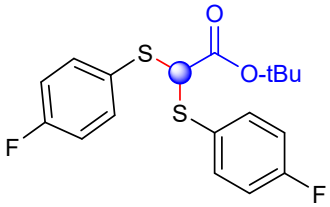


^{19}F NMR

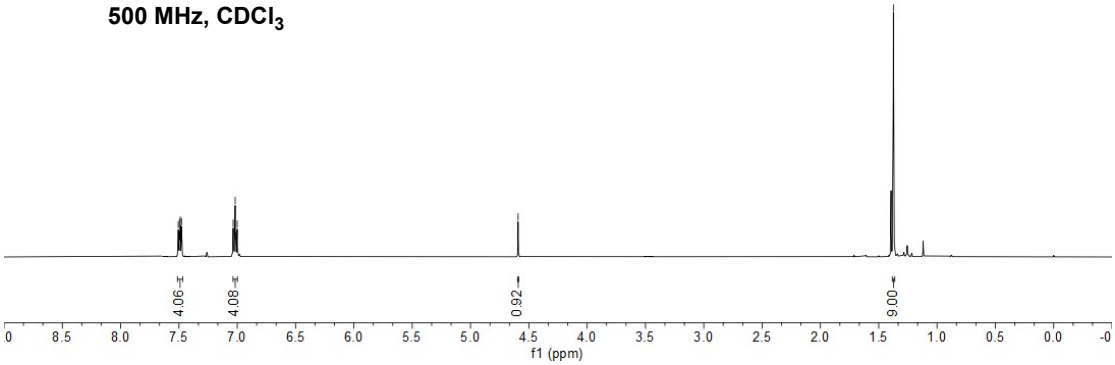

-111.4350
O
OEt
S
S
F
F
471 MHz, CDCl3
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

33c

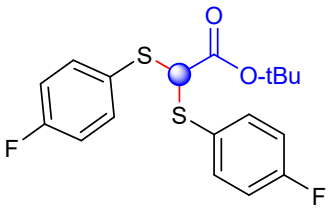
^{1}H NMR



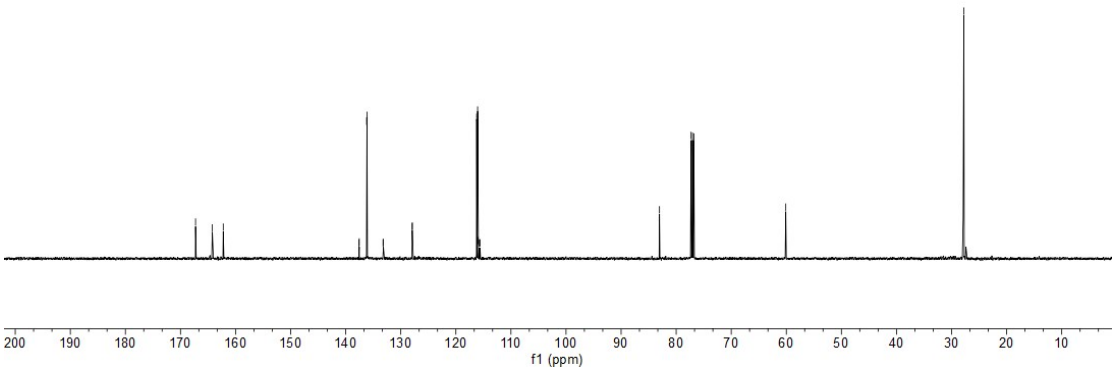
500 MHz, $CDCl_3$



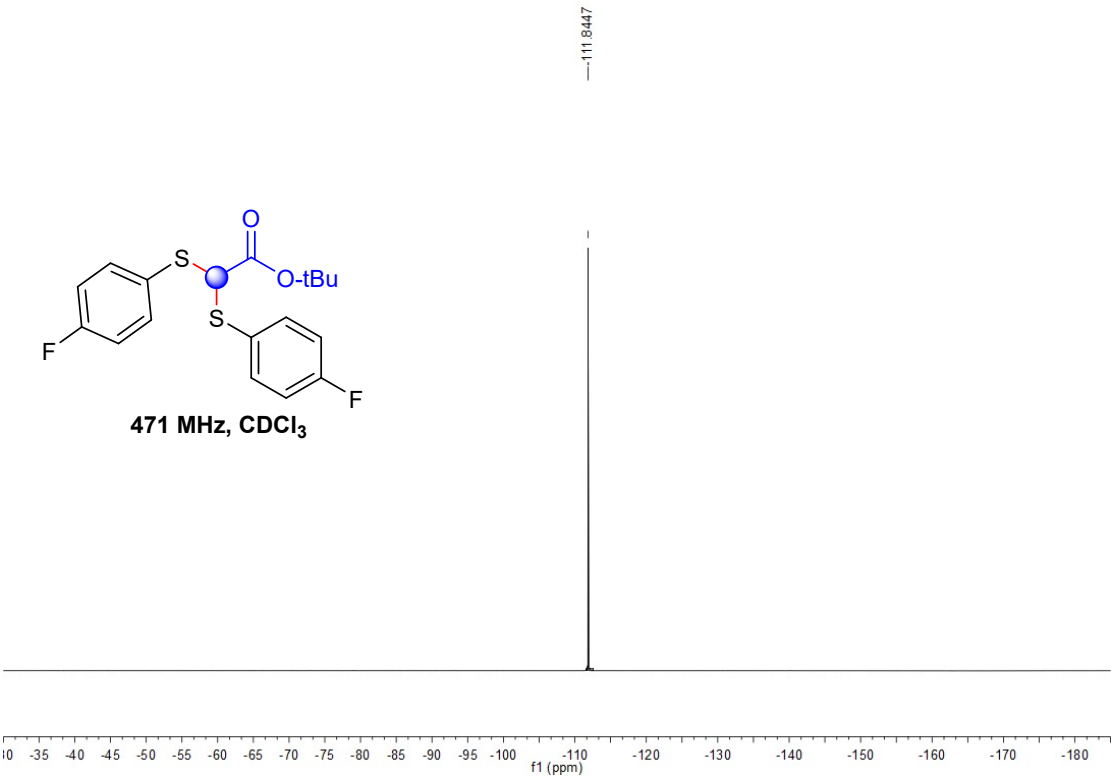
^{13}C NMR



126 MHz, $CDCl_3$

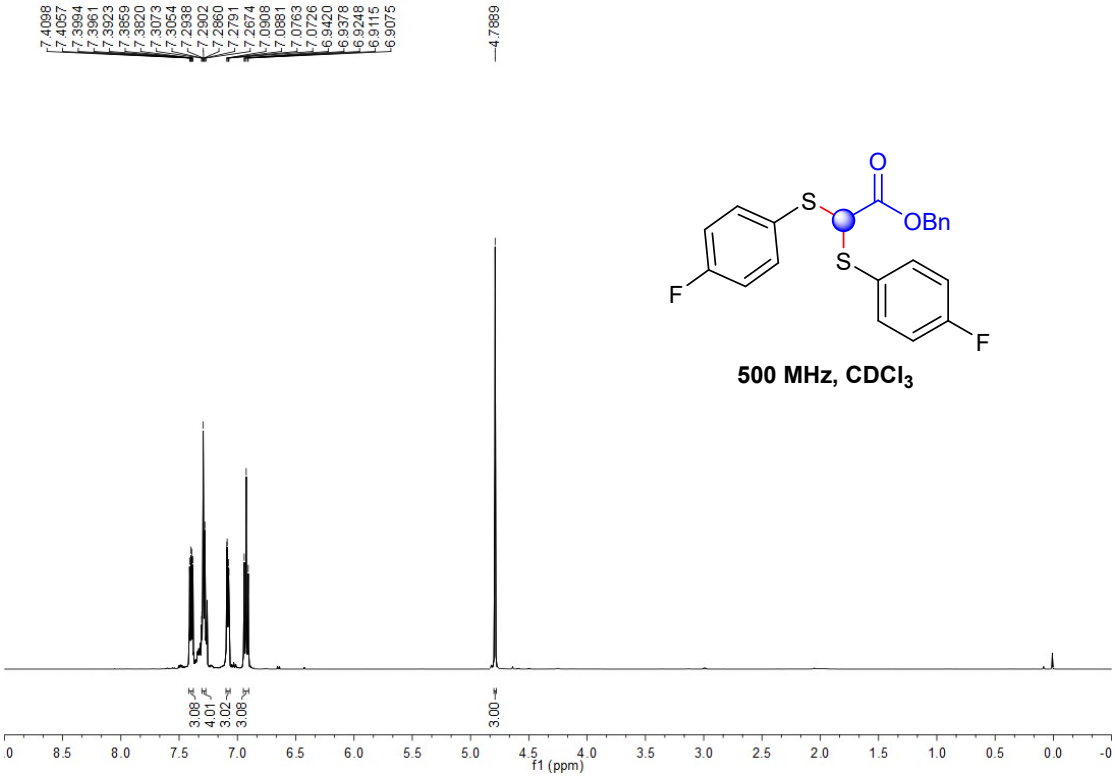


^{19}F NMR


-111.8447
O
S
O-tBu
S
F
F
471 MHz, CDCl3
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

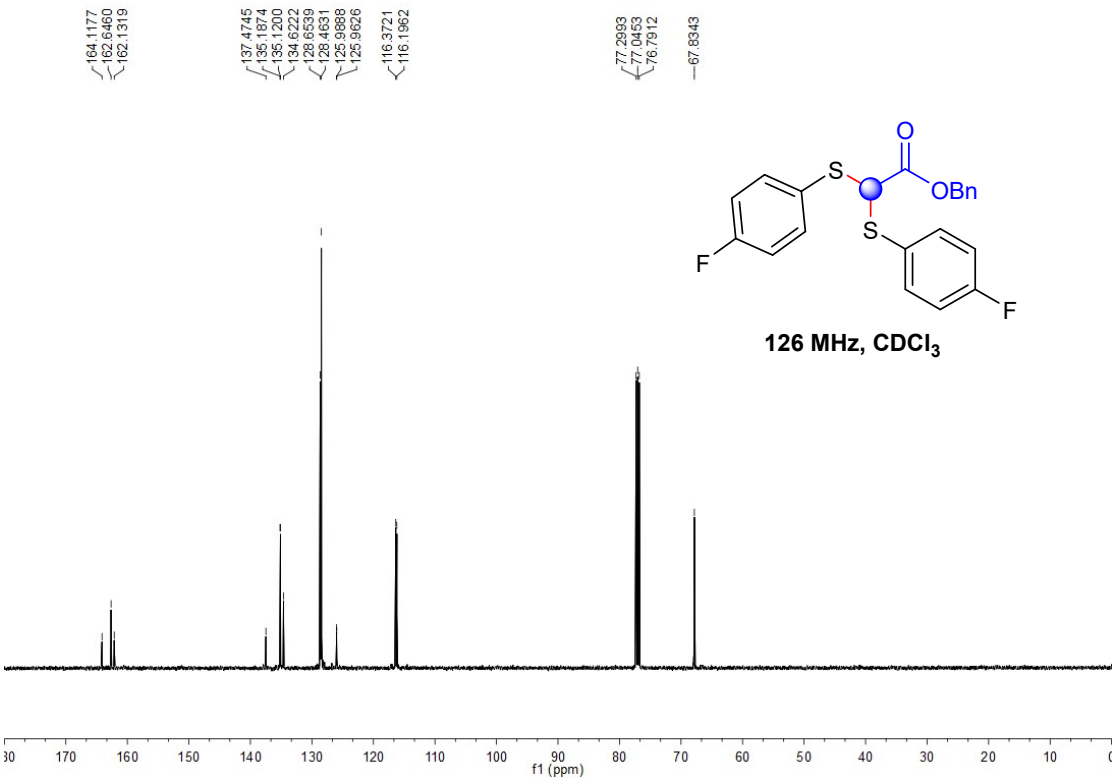
34c

^{1}H NMR



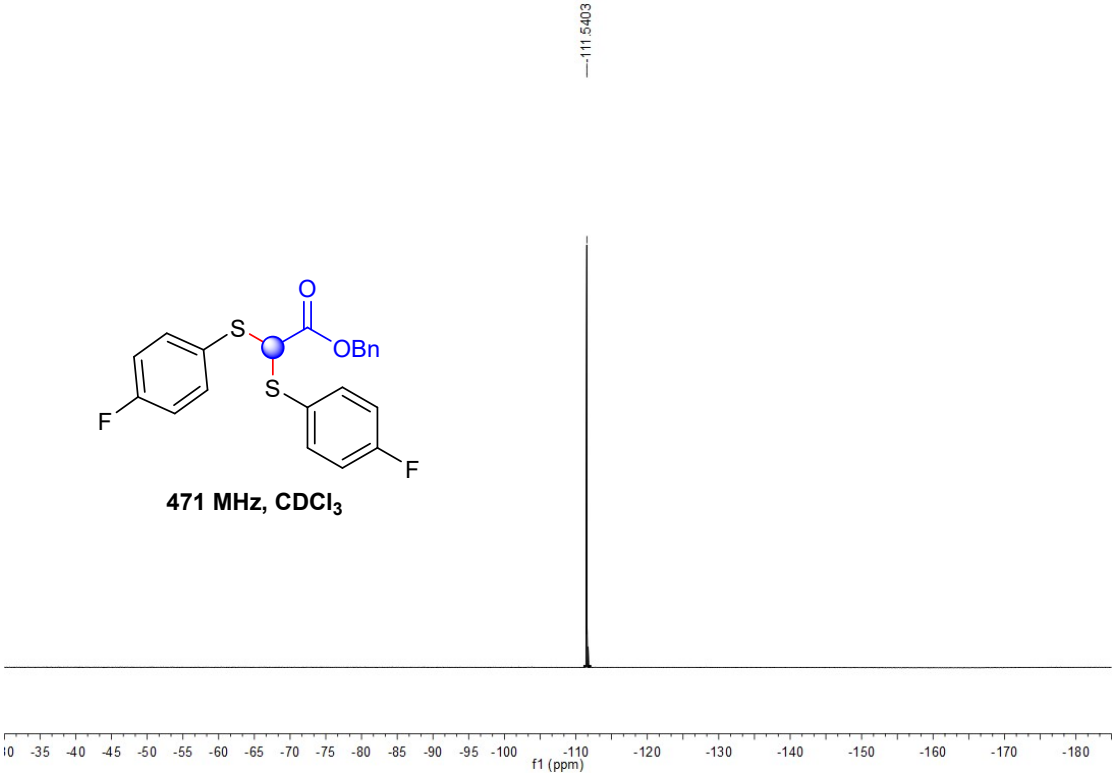
500 MHz, $CDCl_3$

^{13}C NMR



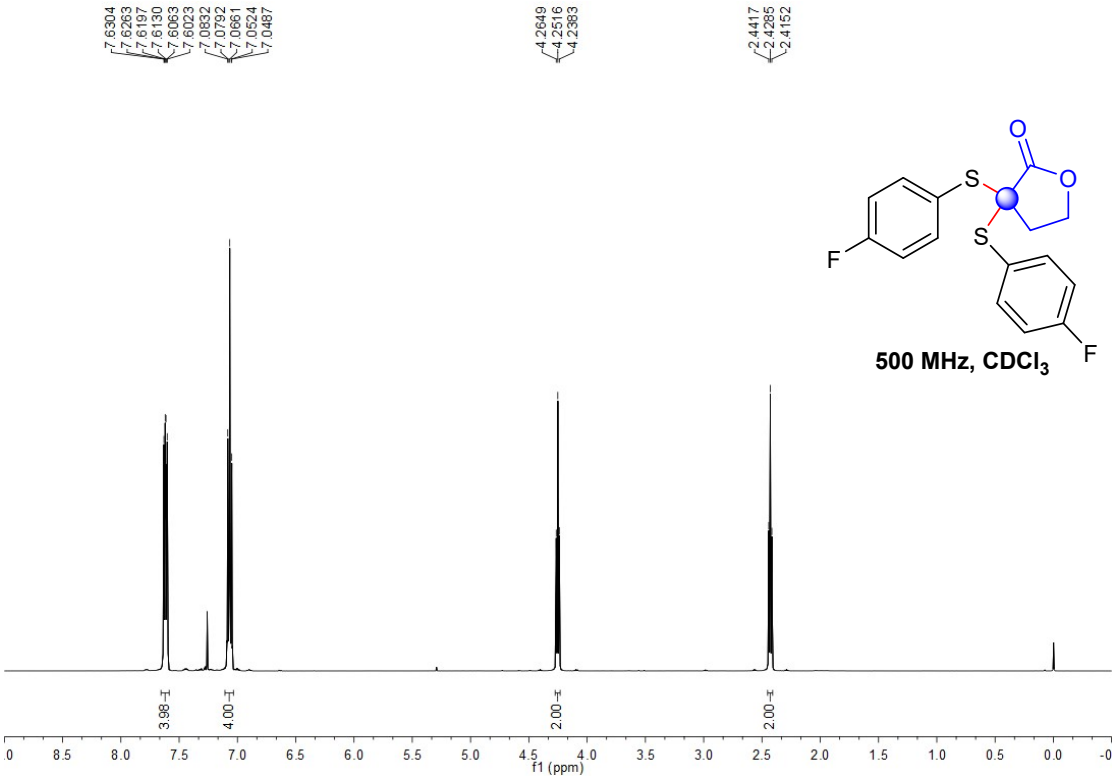
126 MHz, $CDCl_3$

^{19}F NMR

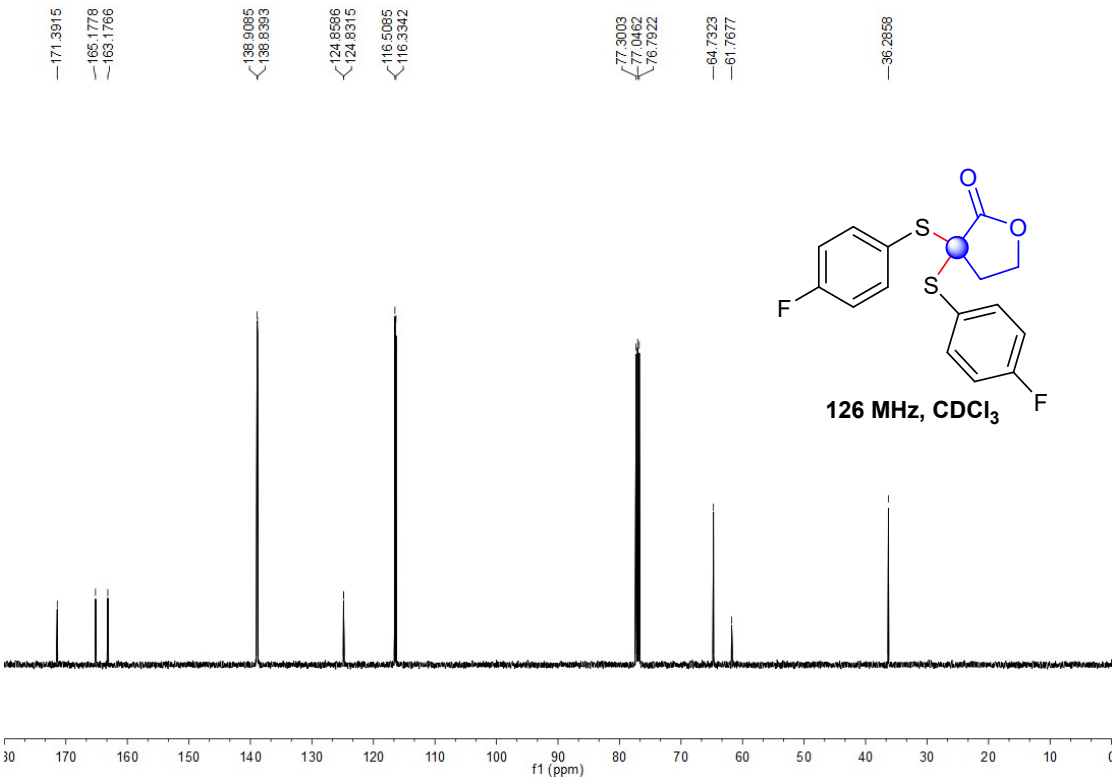

-111.5403
O
S
OBn
S
F
F
471 MHz, CDCl3
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

35c

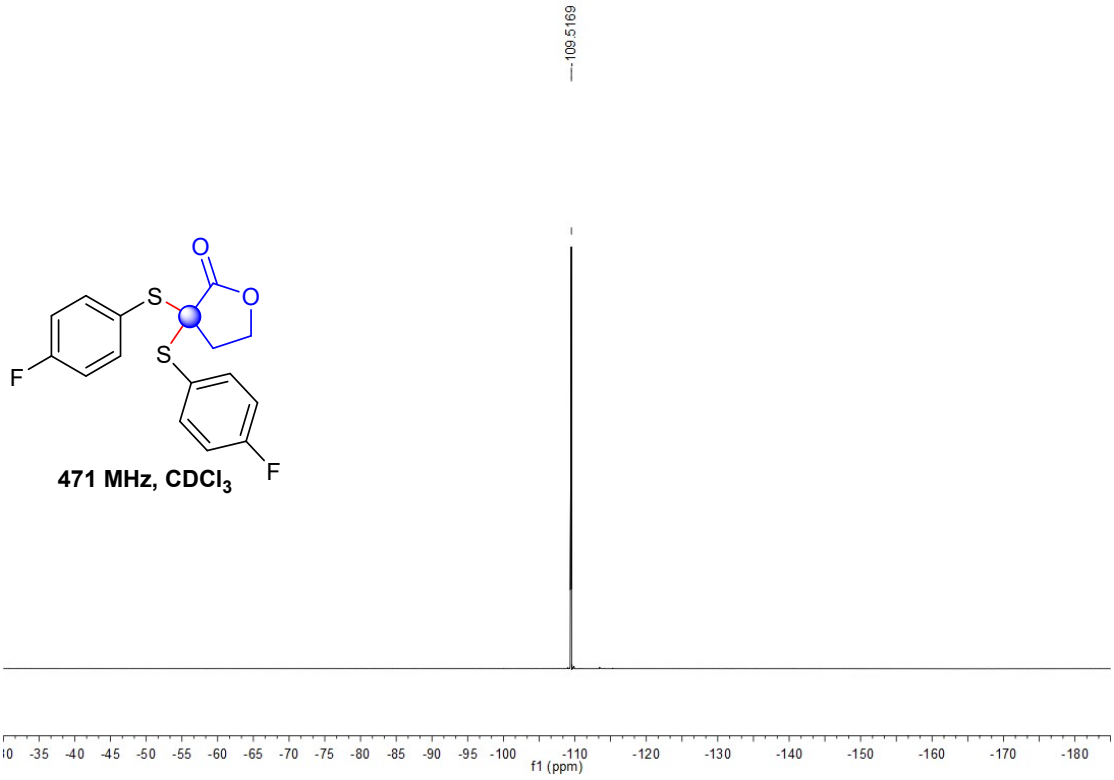
^{1}H NMR



^{13}C NMR

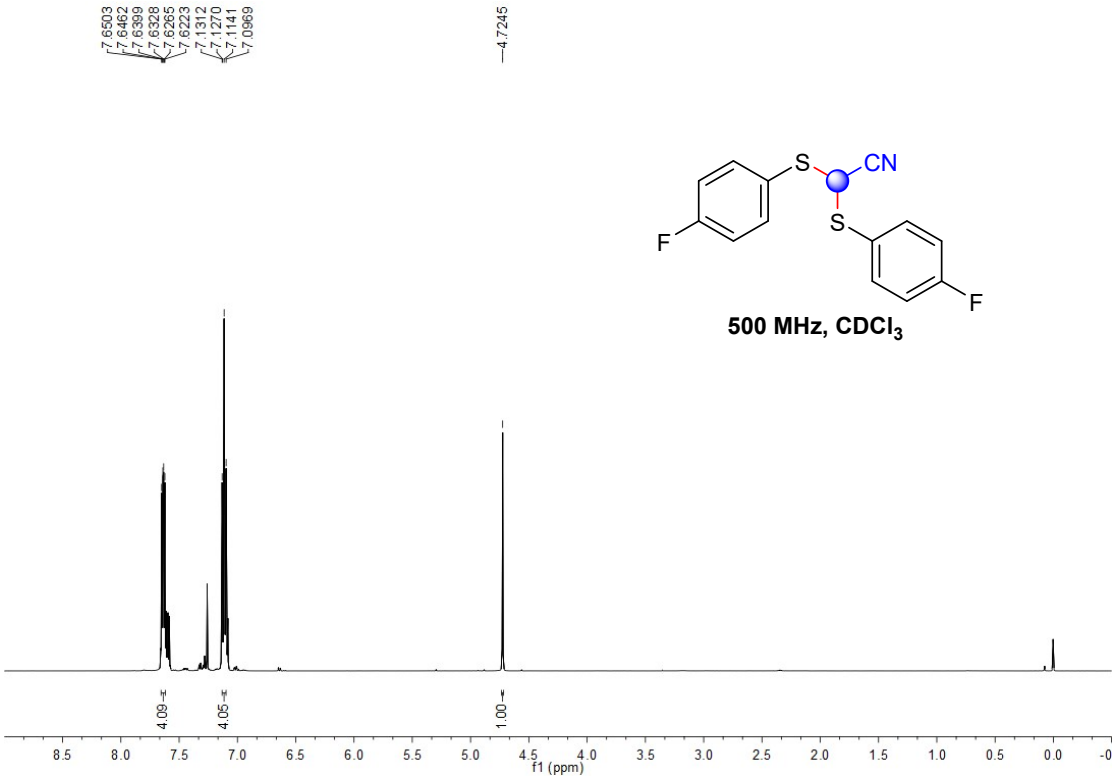


^{19}F NMR

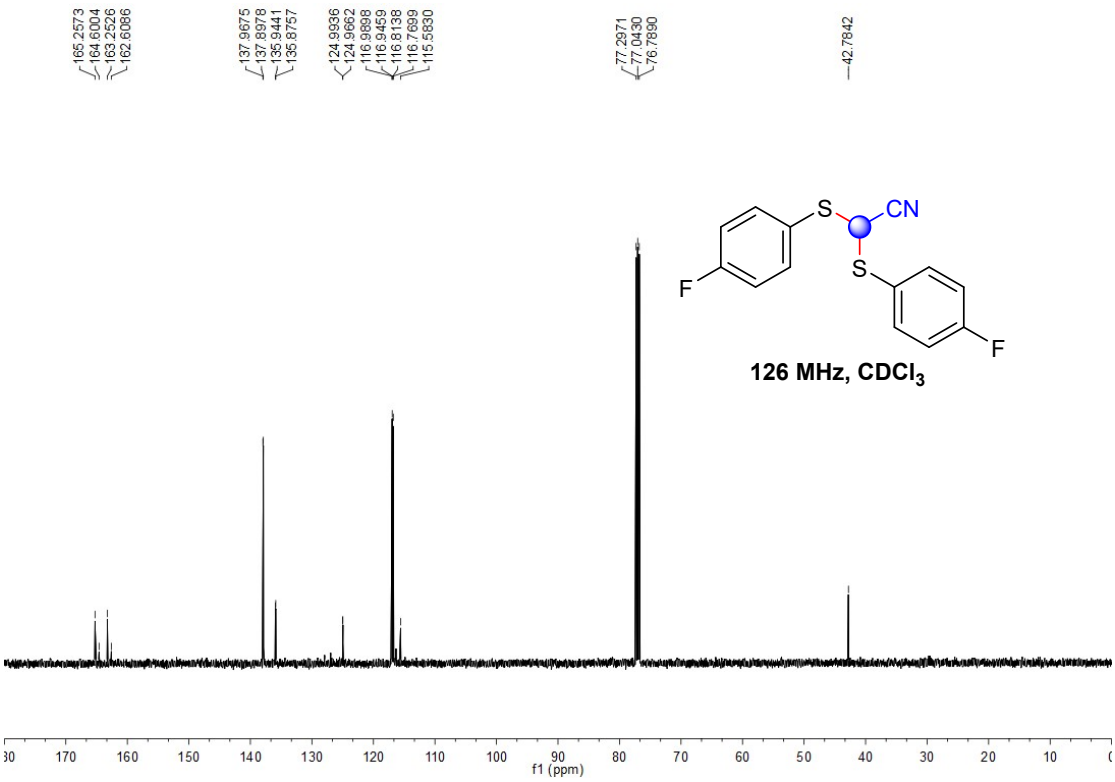

-109.5169
O
O
S
S
F
F
471 MHz, CDCl3
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

36c

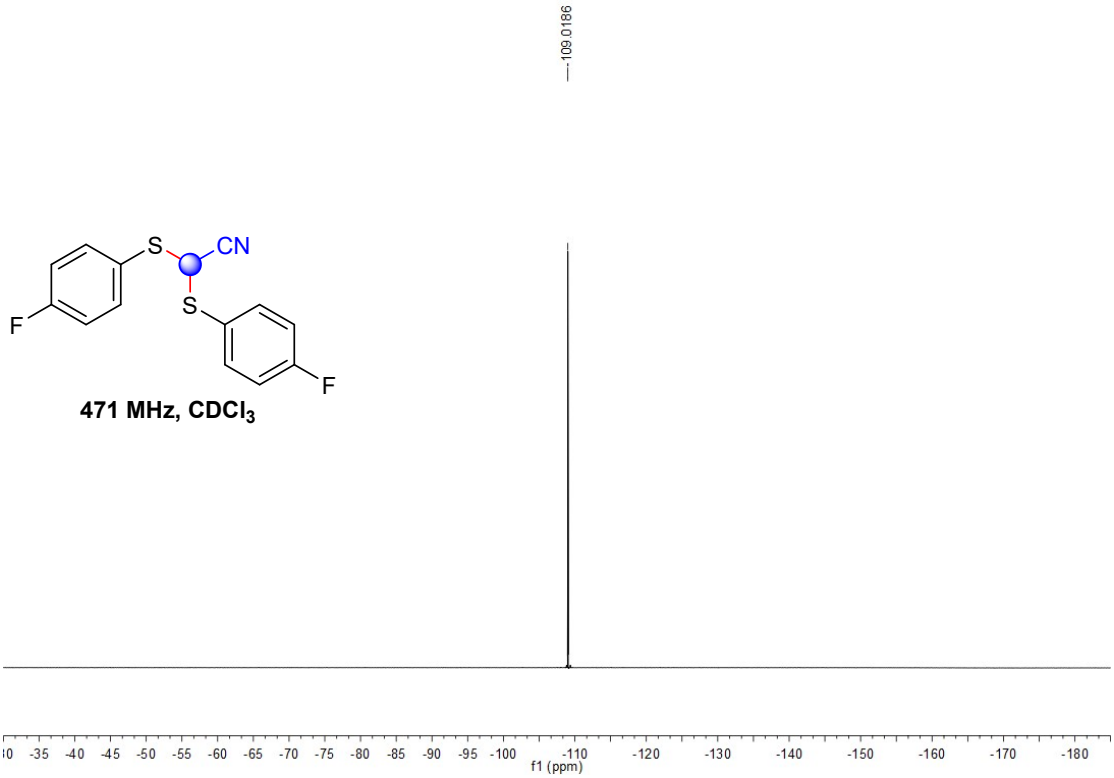
^{1}H NMR



^{13}C NMR



^{19}F NMR


-109.0186
S
CN
S
F
F
471 MHz, CDCl3
-35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)