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Supporting Information

for

Access to cyclopropanes with geminal trifluoromethyl and difluoromethylphosphonate groups

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Experimental section and characterization of synthesized compounds

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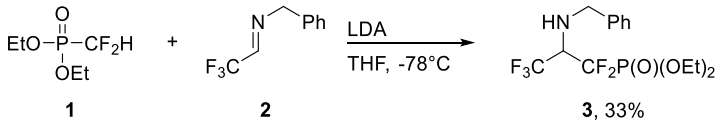
1. General information

All reactions were carried out under anhydrous conditions and under argon atmosphere. THF and toluene were freshly distilled from sodium benzophenone ketyl and DCM was distilled over calcium hydride before use. All reagents were purchased from commercial sources and used without further purification. Diethyl difluoromethylphosphonate (**1**) and *N*-benzyltrifluoroacetaldimine (**2**) were prepared according to the known procedures [1,2]. The products were purified by column chromatography over silica gel 60 (230−400 mesh ASTM). Analytical TLCs were performed with silica gel 60 F254 plates. Visualization was accomplished using UV light or by spraying with $Ce(SO_4)_2$ solution in 5% H_2SO_4. NMR spectra were recorded on a JEOL ECX400 instrument and the frequencies for ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR are 400, 100, 376 and 161 MHz, respectively. ^{31}P NMR spectra were broadband decoupled from hydrogen nuclei. All measurements were carried out in solution in $CDCl_3$. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. High-resolution mass spectra (HRMS) were recorded on an ESI-Qq-TOF mass spectrometer.

2. Synthesis of diethyl 2-(benzylamino)-1,1,3,3,3-pentafluoropropylphosphonate (3)

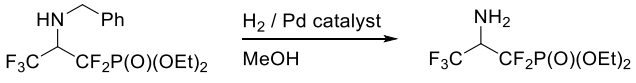


1 **2** **3**, 33%

To a solution of diisopropylamine (24.4 mL, 17.3 mmol) and *n*-butyllithium (71.3 mL, 17.3 mmol, 2.5 M solution in hexanes) in dry THF (150 mL) at −78 °C and under argon atmosphere diethyl difluoromethylphosphonate (**1**, 22.6 mL, 14.4 mmol) was added dropwise for 15 min and the mixture was stirred for 30 min at −78 °C. Then, a solution of *N*-benzyltrifluoroacetaldimine (**2**, 27.0 g, 14.4 mmol) in dry THF (200 mL) was added dropwise and the resultant mixture was stirred at −78 °C for the next 3 h. Afterwards, the solution was

warmed to RT with the addition of saturated aqueous NH_4Cl (200 mL) and it was stirred overnight. After dilution with H_2O (50 mL) the solution was extracted with EtOAc (3 × 200 mL), combined organic layers were washed with brine (200 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel, using DCM: EtOAc (9:1 ratio) to give compound **3** in 33% yield as a yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.37 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.31-7.22 (m, 3H), 4.33-4.13 (m, 4H), 4.12-3.93 (m, 2H), 3.91-3.77 (m, 1H), 1.91 (s, 1H), 1.34 (t, 3H, $^3J_{HH}$ = 8.0 Hz), 1.25 (t, 3H, $^3J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 138.6, 128.5 (d, $^1J_{CH}$ = 13.0 Hz),127.6, 123.4 (td, $^1J_{CF}$ = 285.0 Hz, $^1J_{CP}$ = 12.0 Hz), 118.7 (td, $^{,1}J_{CF}$ = 269.0 Hz, $^1J_{CP}$ = 213.0 Hz), 64.9 (dt, $^2J_{CP}$ = 7.0 Hz, $^2J_{CP}$ = 2.0 Hz), 61.8-60.3 (m), 53.0, 16.3 (dd, $^3J_{CP}$ = 13.0 Hz, $^3J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -68.8 (dq, 3F, $^4J_{FF}$ = 22.6 Hz, $^4J_{FP}$ = 3.8 Hz), -109.8 (ddqd, 1F, $^2J_{FF}$ = 304.6 Hz, $^2J_{FP}$ = 97.8 Hz, $^3J_{FH}$ = 15.0 Hz, $^4J_{FF}$ = 3.8 Hz), -123.1 (ddqd, 1F, $^2J_{FF}$ = 304.6 Hz, $^2J_{FP}$ = 97.8 Hz, $^3J_{FH}$ = 15.0 Hz, $^4J_{FF}$ = 3.8 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.6 (tq, 1P, $^2J_{PF}$ = 99.8 Hz, $^3J_{PH}$ = 3.2 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{14}H_{20}F_5NO_3P$ 376.1101; found 376.1095.

3. Synthesis of diethyl 2-amino-1,1,3,3,3-pentafluoropropylphosphonate (4)

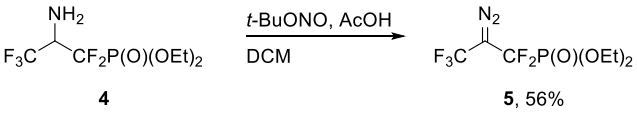


3 **4**, 90%

To a solution of **3** (11.6 g, 3.1 mmol) in MeOH (200 mL) Pd catalyst, Palladium 5 wt. % (dry basis) on activated carbon (2.0 g, 3.1 mmol) was added. Then, the reaction mixture was degassed for 10 min. Afterwards, H_2 was introduced into the reaction from a balloon and the mixture was left to stir overnight. The resulting suspension was filtered over Celite, washed with MeOH and evaporated under reduced pressure to furnish compound **4** in 90% yield as orange oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.28-4.16 (m, 4H), 3.86-3.73 (m, 1H), 1.85 (s, 2H),

1.29 (dt, 6H, $^{3}J_{HH}$ = 12.0, 4.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.7 (qd, $^{1}J_{CF}$ = 282.0 Hz, $^{1}J_{CP}$ = 12.0 Hz), 117.8 (td, $^{1}J_{CF}$ = 269.0 Hz, $^{1}J_{CP}$ = 213.0 Hz), 65.2-65.0 (m), 56.5-55.0 (m), 16.2 (dd, $^{3}J_{CP}$ = 6.0, $^{3}J_{CP}$ = 2.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -72.3 (dq, 3F, $^{4}J_{FF}$ = 22.6 Hz, $^{4}J_{FP}$ = 7.5 Hz), -113.1 (ddqd, 1F, $^{2}J_{FF}$ = 308.3 Hz, $^{2}J_{FP}$ = 97.8 Hz, $^{3}J_{FH}$ = 15.0 Hz, $^{4}J_{FF}$ = 3.8 Hz), -125.8 (ddqd, 1F, $^{2}J_{FF}$ = 308.3 Hz, $^{2}J_{FP}$ = 97.8 Hz, $^{3}J_{FH}$ = 15.0 Hz, $^{4}J_{FF}$ = 3.8 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.5 (t, 1P, $^{2}J_{PF}$ = 96.6 Hz). **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd. for $C_7H_{13}F_5NNaO_3P$ 308.0451; found 308.0446.

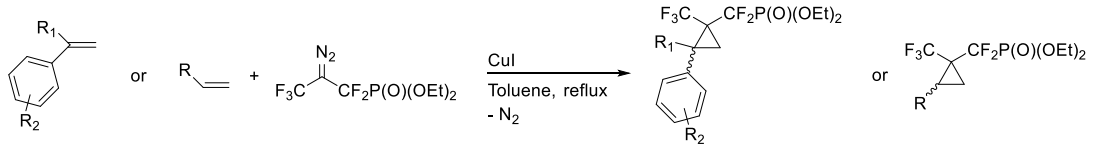
4. Synthesis of diethyl 2-diazo-1,1,3,3,3-pentafluoropropylphosphonate (5)



4 **5**, 56%

A solution of **4** (7.5 g, 2.6 mmol) in dry DCM (300 mL) under argon atmosphere was cooled down to 0 °C and *t*-BuONO (4.7 mL, 3.9 mmol) and AcOH (0.6 mL, 1.1 mmol) were added in one portion. The reaction mixture was stirred overnight at RT. The solvent was evaporated, and the crude product was purified via flash column chromatography on silica gel using DCM as eluent to give compound **5** in 56% yield as yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.33-4.20 (m, 4H), 1.32 (t, 6H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 123.7 (qd, $^{1}J_{CF}$ = 286.0 Hz, $^{1}J_{CP}$ = 5.0 Hz), 115.3 (dt, $^{1}J_{CF}$ = 264.0 Hz, $^{1}J_{CP}$ = 230.0 Hz), 65.6 (d, $^{2}J_{CP}$ = 7.0 Hz), 16.2 (d, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -55.1 (td, 3F, $^{4}J_{FF}$ = 7.5 Hz, $^{4}J_{FP}$ = 3.8 Hz), -104 (dq, 2F, $^{2}J_{FP}$ = 112.8 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 3.8 (tq, 1P, $^{2}J_{PF}$ = 111.1 Hz, $^{3}J_{PH}$ = 1.61 Hz).

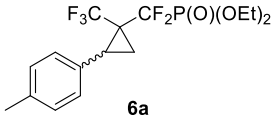
5. General procedure for the cyclopropanation of alkenes with diazo compound (5).



5 **6a-i** **7a-g**

In a manner similar to Ref. 3. To a solution of alkene (2.5 mmol) and CuI (0.17 mmol) in dry toluene under argon atmosphere, **5** (1.7 mmol) was added. The reaction mixture was stirred under reflux. After the time indicated, the solvent was evaporated under reduced pressure and the crude product was purified via flash chromatography on silica gel using DCM/EtOAc (10:1 ratio) as eluent.

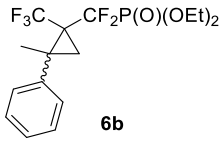
6. Characterization data



6a

Diethyl (2-(*p*-tolyl)-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**6a**) was prepared from 0.3 g (0.1 mmol) of **5**, 0.019 g (0.01 mmol) of CuI, 0.2 mL (0.15 mmol) of 4-methylstyrene and 5 mL of dry toluene. The reaction mixture was refluxed for 3.5 h to give compound **6a** in 74% yield as yellow oil. Mixture of isomers in 1:1 ratio. *Major isomer*: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.20-7.17 (m, 2H), 7.05-7.02 (m, 2H), 4.34-4.19 (m, 4H), 2.93 (t, 1H, $^{3}J_{HH}$ = 8.0 Hz), 1.72-1.69 (m, 2H), 1.34 (t, 6H, $^{3}J_{HH}$ = 8.0 Hz), 1.18 (t, 3H, $^{4}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 136.8, 130.3 (d, $^{3}J_{CH}$ = 11.0 Hz), 129.4, 123.3 (qd, $^{1}J_{CF}$ = 274.0 Hz, $^{1}J_{CP}$ = 4.0 Hz), 118.0 (td, $^{1}J_{CF}$ = 306.0 Hz, $^{1}J_{CP}$ = 217.0 Hz), 65.2-64.7 (m), 33.5-32.5 (m), 30.9, 29.7, 26.7, 16.3 (dt, $^{3}J_{CP}$ = 15.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -59.0 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -106.8 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz) -110.9 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR**

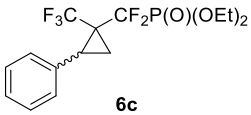
($CDCl_3$, 161 MHz): δ 4.9 (dd, 1P, $^2J_{PF}$ = 111.1 Hz, $^2J_{PF}$ = 106.3 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.21-7.13 (m, 2H), 7.04-7.01 (m, 2H), 4.22-4.07 (m, 4H), 2.84 (t, 1H, $^3J_{HH}$ = 8.0 Hz), 1.84-1.54 (m, 2H), 1.33 (t, 6H, $^3J_{HH}$ = 8.0 Hz), 1.17 (t, 3H, $^4J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 136.8, 130.3 (d, $^3J_{CH}$ = 11.0 Hz), 129.4, 123.3 (qd, $^1J_{CF}$ = 274.0 Hz, $^1J_{CP}$ = 4.0 Hz), 118.0 (td, $^1J_{CF}$ = 306.0 Hz, $^1J_{CP}$ = 217.0 Hz), 65.2-64.7 (m), 33.5-32.5 (m), 30.9, 29.7, 26.7, 16.3 (dt, $^3J_{CP}$ = 15.0 Hz, $^3J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.8 (t, 3F, $^4J_{FF}$ = 7.5 Hz), -105.1 (ddq, 1F, $^2J_{FF}$ = 312.1 Hz, $^2J_{FP}$ = 109.0 Hz, $^4J_{FF}$ = 7.5 Hz) -106.2 (ddq, 1F, $^2J_{FF}$ = 312.1 Hz, $^2J_{FP}$ = 109.0 Hz, $^4J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.8 (t, 1P, $^2J_{PF}$ = 107.9 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{16}H_{21}F_5O_3P$ 387.1148; found 387.1141.



6b

Diethyl (2-methyl-2-phenyl-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**6b**) was prepared from 0.5 g (0.2 mmol) of **5**, 0.032 g (0.02 mmol) of CuI, 0.3 mL (0.25 mmol) of α-methylstyrene and 7 mL of dry toluene. The reaction mixture was refluxed for 48 h to give compound **6b** in 50% yield as yellow oil. Mixture of isomers in 1.4:1 ratio. *Major isomer*: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.48 (d, 1H, $^3J_{HH}$ = 8.0 Hz), 7.23-7.04 (m, 4H), 4.31-4.14 (m, 4H), 1.95-1.61 (m, 2H), 1.56-1.48 (m, 3H), 1.31 (t, 6H, $^3J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 142.2, 129.9, 128.4, 126.9, 121.2 (qd, $^1J_{CF}$ = 275.0 Hz, $^1J_{CP}$ = 6.0 Hz), 118.4 (td, $^1J_{CF}$ = 288.0 Hz, $^1J_{CP}$ = 216.0 Hz), 65.1 (qd, $^2J_{CP}$ = 7.0 Hz, $^2J_{CP}$ = 2.0 Hz), 37.6-35.6 (m), 25.0 (q, $^1J_{CH}$ = 3.0 Hz), 19.6-19.5 (m), 16.3 (qd, $^3J_{CP}$ = 8.0 Hz, $^3J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -58.1 (dd, 3F, $^4J_{FF}$ = 15.0 Hz, $^4J_{FP}$ = 7.5 Hz), -98.3 (ddq, 1F, $^2J_{FF}$ = 319.6 Hz, $^2J_{FP}$ = 109.0 Hz, $^4J_{FF}$ = 15.0 Hz), -101.5 (ddq, 1F, $^2J_{FF}$ = 319.6 Hz, $^2J_{FP}$ = 109.0 Hz, $^4J_{FF}$ = 15.0 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.5 (dd, 1P, $^2J_{PF}$ = 107.8 Hz, $^2J_{PF}$ = 106.3 Hz).

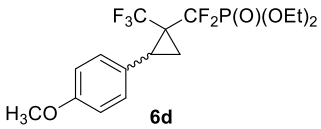
Minor isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.48 (d, 1H, $^{3}J_{HH}$ = 8.0 Hz), 7.23-7.04 (m, 4H), 4.14-3.88 (m, 4H), 1.95-1.61 (m, 2H), 1.56-1.48 (m, 3H), 1.18 (dt, 6H, $^{3}J_{HH}$ = 16.0 Hz, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 142.1, 129.6, 128.1, 126.7, 121.2 (qd, $^{1}J_{CF}$ = 275.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 118.4 (td, $^{1}J_{CF}$ = 288.0 Hz, $^{1}J_{CP}$ = 216.0 Hz), 64.7 (qd, $^{2}J_{CP}$ = 7.0 Hz, $^{2}J_{CP}$ = 2.0 Hz), 37.6-35.6 (m), 24.7 (dd, $^{1}J_{CH}$ = 10.0 Hz, $^{1}J_{CH}$ = 3.0 Hz), 18.0-17.8 (m), 16.3 (qd, $^{3}J_{CP}$ = 8.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -55.8 (td, 3F, $^{4}J_{FF}$ = 7.5 Hz, $^{4}J_{FP}$ = 3.8 Hz), -99.4 (ddq, 1F, $^{2}J_{FF}$ = 319.6 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 15.0 Hz) -104.8 (ddq, 1F, $^{2}J_{FF}$ = 319.6 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 15.0 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 6.1 (t, 1P, $^{2}J_{PF}$ = 109.5 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{16}H_{21}F_5O_3P$ 387.1149; found 387.1141.



6c

Diethyl (2-phenyl-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**6c**) was prepared from 0.84 g (0.3 mmol) of **5**, 0.053 g (0.03 mmol) of CuI, 0.49 mL (0.4 mmol) of styrene and 11 mL of dry toluene. The reaction mixture was refluxed for 4 h to give compound **6c** in 35% yield as yellow oil. Mixture of isomers in 1:3 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.30 (d, 2H, $^{3}J_{HH}$ = 8.0 Hz), 7.25-7.16 (m, 3H), 4.34-4.12 (m, 4H), 2.98 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.76-1.69 (m, 2H), 1.33 (t, 6H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 133.3, 129.4, 128.2, 127.5, 124.4 (qd, $^{1}J_{CF}$ = 275.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 117.4 (td, $^{1}J_{CF}$ = 260.0 Hz, $^{1}J_{CP}$ = 218.0 Hz), 65.2 (dd, $^{2}J_{CP}$ = 18.0 Hz, $^{2}J_{CP}$ = 8.0 Hz), 33.5-32.4 (m), 26.1 (t, $^{1}J_{CH}$ = 5.0 Hz), 24.7, 16.4 (dd, $^{3}J_{CP}$ = 8.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -59.1 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -106.9 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -111.0 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.9 (dd, 1P, $^{2}J_{PF}$ = 109.5 Hz, $^{2}J_{PF}$ = 106.3 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.30 (d, 2H, $^{3}J_{HH}$ = 8.0 Hz), 7.25-7.16 (m, 3H), 4.34-4.12 (m, 4H), 2.98 (t, 1H, $^{4}J_{HF}$ =

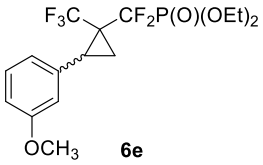
8.0 Hz), 1.76-1.69 (m, 2H), 1.33 (t, 6H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 133.3, 129.4, 128.2, 127.5, 124.4 (qd, $^{1}J_{CF}$ = 275.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 117.4 (dd, $^{1}J_{CF}$ = 260.0 Hz, $^{1}J_{CP}$ = 218.0 Hz), 65.2 (dd, $^{2}J_{CP}$ = 18.0 Hz, $^{2}J_{CP}$ = 8.0 Hz), 33.5-32.4 (m), 26.1 (t, $^{1}J_{CH}$ = 5.0 Hz), 24.7, 16.4 (dd, $^{3}J_{CP}$ = 8.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.8 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -104.6 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -106.5 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.7 (t, 1P, $^{2}J_{PF}$ = 106.3 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{15}H_{19}F_5O_3P$ 373.0992; found 373.0991.



6d

Diethyl (2-(4-methoxyphenyl)-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**6d**) was prepared from 0.3 g (0.1 mmol) of **5**, 0.019 g (0.01 mmol) of CuI, 0.2 mL (0.15 mmol) of 4-methoxystyrene and 5 mL of dry toluene. The reaction mixture was refluxed for 2.5 h to give compound **6d** in 67% yield as yellow oil. Mixture of isomers in 1:1.3 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.22-7.19 (m, 2H), 6.78-6.74 (m, 2H), 4.34-4.18 (m, 4H), 3.71 (s, 3H), 2.91 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.73-1.65 (m, 2H), 1.33 (t, 6H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.9, 130.5, 128.6, 124.3 (qd, $^{1}J_{CF}$ = 274.0 Hz, $^{1}J_{CP}$ = 5.0 Hz), 117.3 (dt, $^{1}J_{CF}$ = 260.0 Hz, $^{1}J_{CP}$ = 219.0 Hz), 65.2 (dd, $^{2}J_{CP}$ = 20.0 Hz, $^{2}J_{CP}$ = 7.0 Hz), 55.2, 39.9-39.3 (m), 33.3-32.3 (m), 25.4 (t, $^{1}J_{CH}$ = 4.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 9.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -59.0 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -106.7 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -111.1 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.9 (dd, 1P, $^{2}J_{PF}$ = 111.1 Hz, $^{2}J_{PF}$ = 106.3 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.23-7.16 (m, 2H), 6.78-6.74 (m, 2H), 4.19-3.98 (m, 4H), 3.71 (s, 3H), 2.83 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.80-1.55 (m, 2H), 1.23 (tdd, 6H, $^{3}J_{HH}$ = 8.0 Hz,

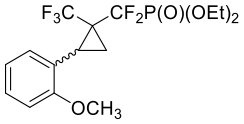
$^{4}J_{HP}$ = 4.0 Hz, $^{4}J_{HP}$ = 4.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 158.9, 130.5, 128.6, 124.3 (qd, $^{1}J_{CF}$ = 274.0 Hz, $^{1}J_{CP}$ = 5.0 Hz), 117.3 (td, $^{1}J_{CF}$ = 260.0 Hz, $^{1}J_{CP}$ = 219.0 Hz), 65.2 (dd, $^{2}J_{CP}$ = 20.0 Hz, $^{2}J_{CP}$ = 7.0 Hz), 55.2, 39.9-39.3 (m), 33.3-32.3 (m), 25.4 (t, $^{1}J_{CH}$ = 4.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 9.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.7 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -104.8 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -106.1 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.8 (t, 1P, $^{2}J_{PF}$ = 106.3 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{16}H_{21}F_5O_4P$ 403.1097; found 403.1092.



6e

Diethyl (2-(3-methoxyphenyl)-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**6e**) was prepared from 0.3 g (0.1 mmol) of **5**, 0.019 g (0.01 mmol) of CuI, 0.2 mL (0.15 mmol) of 3-methoxystyrene and 5 mL of dry toluene. The reaction mixture was refluxed for 7 h to give compound **6e** in 41% yield as yellow oil. Mixture of isomers in 1:1.9 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.16-7.11 (m, 1H), 6.90-6.84 (m, 2H), 6.74-6.70 (m, 1H), 4.32-4.20 (m, 4H), 3.71 (s, 3H), 2.96 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.80-1.66 (m, 2H), 1.33 (t, 6H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 159.5, 135.2, 129.2, 120.7 (qd, $^{1}J_{CF}$ = 274.0 Hz, $^{1}J_{CP}$ = 5.0 Hz), 117.3 (td, $^{1}J_{CF}$ = 260.0 Hz, $^{1}J_{CP}$ = 213.0 Hz), 65.2 (dd, $^{2}J_{CP}$ = 15.0 Hz, $^{2}J_{CP}$ = 7.0 Hz), 55.2 (d, $^{5}J_{CH}$ = 3.0 Hz), 33.3-32.5 (m), 26.1 (t, $^{1}J_{CH}$ = 4.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 7.0 Hz, $^{3}J_{CP}$ = 5.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -59.2 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -106.9 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -110.8 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.9 (dd, 1P, $^{2}J_{PF}$ = 109.5 Hz, $^{2}J_{PF}$ = 106.3 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.16-7.11 (m, 1H), 6.90-6.84 (m, 2H), 6.74-6.70 (m, 1H), 4.19-4.00 (m, 4H), 3.72 (s, 3H), 2.87 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.80-1.66 (m, 2H), 1.23 (td, 6H, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 4.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 159.4,

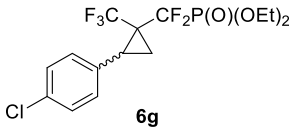
134.9, 129.0, 120.7 (qd, $^{1}J_{CF}$ = 274.0 Hz, $^{1}J_{CP}$ = 5.0 Hz), 117.5 (td, $^{1}J_{CF}$ = 260.0 Hz, $^{1}J_{CP}$ = 213.0 Hz), 64.8 (t, $^{2}J_{CP}$ = 6.0 Hz), 55.3 (d, $^{5}J_{CH}$ = 4.0 Hz), 33.3-32.5 (m), 27.1,16.2 (dd, $^{3}J_{CP}$ = 11.0 Hz, $^{3}J_{CP}$ = 5.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.8 (t, 3F, $^{4}J_{FF}$ = 3.8 Hz), -104.7 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -106.6 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.8 (t, 1P, $^{2}J_{PF}$ = 106.3 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{16}H_{21}F_5O_4P$ 403.1097; found 403.1092.



6f

Diethyl (2-(2-methoxyphenyl)-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**6f**) was prepared from 0.3 g (0.1 mmol) of **5**, 0.019 g (0.01 mmol) of CuI, 0.2 mL (0.15 mmol) of 2-methoxystyrene and 5 mL of dry toluene. The reaction mixture was refluxed for 7 h to give compound **6f** in 53% yield as yellow oil. Mixture of isomers in 1:1.4 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.19-7.14 (m, 1H), 7.07-7.02 (m, 1H), 6.82-6.76 (m, 2H), 4.31-4.17 (m, 4H), 3.75 (s, 3H), 2.97 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.83-1.70 (m, 2H), 1.31 (td, 6H, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 4.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 159.2, 129.5, 128.9, 124.0 (qd, $^{1}J_{CF}$ = 273.0 Hz, $^{1}J_{CP}$ = 4.0 Hz),118.4 (dt, $^{1}J_{CF}$ = 296.0 Hz, $^{1}J_{CP}$ = 269.0 Hz), 65.2-65.0 (m), 55.3, 33.1-33.7 (m), 29.8.29.2 (m), 23.2, 16.4 (dq, $^{3}J_{CP}$ = 6.0 Hz, $^{3}J_{CP}$ = 2.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -60.1 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -106.0 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -108.2 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.8 (t, 1P, $^{2}J_{PF}$ = 109.5 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.19-7.14 (m, 1H), 7.07-7.02 (m, 1H), 6.82-6.76 (m, 2H), 4.15-3.97 (m, 4H), 3.77 (s, 3H), 2.77 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.83-1.70 (m, 2H), 1.21 (dt, 6H, $^{3}J_{HH}$ = 12.0 Hz, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 159.1, 129.5, 128.6, 124.0 (qd, $^{1}J_{CF}$ = 273.0 Hz, $^{1}J_{CP}$ = 4.0 Hz), 118.1 (dt, $^{1}J_{CF}$ = 296.0 Hz, $^{1}J_{CP}$ = 269.0 Hz), 64.8 (dd, $^{2}J_{CP}$ = 14.0 Hz, $^{2}J_{CP}$ = 7.0 Hz),

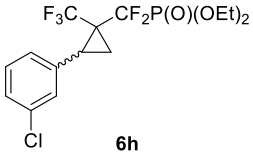
55.2, 33.1-33.7 (m), 29.8-29.2 (m), 22.8, 16.2 (dd, $^{3}J_{CP}$ = 6.0 Hz, $^{3}J_{CP}$ = 1.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.9 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -107.0 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -109.2 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.0 (t, 1P, $^{2}J_{PF}$ = 109.5 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{16}H_{21}F_5O_4P$ 403.1097; found 403.1092.



6g

Diethyl (2-(4-chlorophenyl)-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**6g**) was prepared from 0.3 g (0.1 mmol) of **5**, 0.019 g (0.01 mmol) of CuI, 0.2 mL (0.15 mmol) of 4-chlorstyrene and 5 mL of dry toluene. The reaction mixture was refluxed for 3 h to give compound **6g** in 45% yield as yellow oil. Mixture of isomers in 1:1.5 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.24-7.19 (m, 4H), 4.33-4.21 (m, 4H), 2.92 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.77-1.66 (m, 2H), 1.35 (tdd, 6H, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 4.0 Hz, $^{3}J_{HH}$ = 4.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 133.4, 131.9, 130.8, 123.6 (qd, $^{1}J_{CF}$ = 275.0 Hz, $^{1}J_{CP}$ = 5.0 Hz), 117.2 (td, $^{1}J_{CF}$ = 260.0 Hz, $^{1}J_{CP}$ = 217.0 Hz), 65.3 (dd, $^{2}J_{CP}$ = 20.0 Hz, $^{2}J_{CP}$ = 7.0 Hz), 33.5-32.5 (m), 30.3-29.4 (m), 25.4 (t, $^{1}J_{CH}$ = 5.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 12.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -59.1 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -107.0 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -111.7 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.7 (dd, 1P, $^{2}J_{PF}$ = 111.1 Hz, $^{2}J_{PF}$ = 104.7 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.26-7.19 (m, 4H), 4.20-3.99 (m, 4H), 2.83 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.81-1.54 (m, 2H), 1.24 (td, 6H, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 4.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 133.4, 131.9, 130.8, 123.6 (qd, $^{1}J_{CF}$ = 275.0 Hz, $^{1}J_{CP}$ = 5.0 Hz), 117.2 (td, $^{1}J_{CF}$ = 260.0 Hz, $^{1}J_{CP}$ = 217.0 Hz), 65.3 (dd, $^{2}J_{CP}$ = 20.0 Hz, $^{2}J_{CP}$ = 7.0 Hz), 33.5-32.5 (m), 30.3-29.4 (m), 25.4 (t, $^{1}J_{CH}$ = 5.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 12.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$,

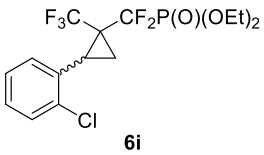
376 MHz): δ -64.9 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -104.3 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -106.3 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.5 (t, 1P, $^{2}J_{PF}$ = 106.3 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{15}H_{18}ClF_5O_3P$ 407.0602; found 407.0596.



6h

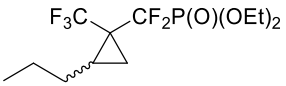
Diethyl (2-(3-chlorophenyl)-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**6h**) was prepared from 0.3 g (0.1 mmol) of **5**, 0.019 g (0.01 mmol) of CuI, 0.2 mL (0.15 mmol) of 3-chlorstyrene and 5 mL of dry toluene. The reaction mixture was refluxed for 5 h to give compound **6h** in 41% yield as yellow oil. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.24-7.08 (m, 4H), 4.35-4.22 (m, 4H), 2.93 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.78-1.68 (m, 2H), 1.35 (t, 6H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 135.5, 134.1, 129.5, 123.7 (qd, $^{1}J_{CF}$ = 274.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 117.1 (td, $^{1}J_{CF}$ = 261.0 Hz, $^{1}J_{CP}$ = 217.0 Hz), 65.3 (dd, $^{2}J_{CP}$ = 17.0 Hz, $^{2}J_{CP}$ = 8.0 Hz), 33.5-32.6 (m), 29.8, 25.6 (t, $^{1}J_{CH}$ = 4.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 9.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -59.2 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -107.2 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -111.4 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.7 (dd, 1P, $^{2}J_{PF}$ = 109.5 Hz, $^{2}J_{PF}$ = 106.3 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.29-7.27 (m, 2H), 7.18-7.16 (m, 2H), 4.20-4.03 (m, 4H), 2.85 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.82-1.59 (m, 2H), 1.25 (tdd, 6H, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 4.0 Hz, $^{3}J_{HH}$ = 4.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 135.5, 134.1, 129.5, 123.7 (qd, $^{1}J_{CF}$ = 274.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 117.1 (td, $^{1}J_{CF}$ = 261.0 Hz, $^{1}J_{CP}$ = 217.0 Hz), 65.3 (dd, $^{2}J_{CP}$ = 17.0 Hz, $^{2}J_{CP}$ = 8.0 Hz), 33.5-32.6 (m), 29.8, 25.6 (t, $^{1}J_{CH}$ = 4.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 9.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.9 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -104.3 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz, $^{4}J_{FF}$ = 7.5 Hz), -106.5 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 105.3 Hz,

$^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.6 (t, 1P, $^{2}J_{PF}$ = 106.3 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{15}H_{18}ClF_5O_3P$ 407.0602; found 407.0596.



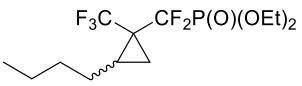
6i

Diethyl (2-(2-chlorophenyl)-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**6i**) was prepared from 0.3 g (0.1 mmol) of **5**, 0.019 g (0.01 mmol) of CuI, 0.2 mL (0.15 mmol) of 2-chlorstyrene and 5 mL of dry toluene. The reaction mixture was refluxed for 8 h to give compound **6i** in 53% yield as yellow oil. Mixture of isomers in 1:2.2 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.24-7.14 (m, 4H), 4.30-4.20 (m, 4H), 3.09 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.93-1.80 (m, 2H), 1.33 (td, 6H, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 4.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 136.2, 131.6, 130.3, 123.8 (qd, $^{1}J_{CF}$ = 275.0 Hz, $^{1}J_{CP}$ = 5.0 Hz), 117.8 (td, $^{1}J_{CF}$ = 262.0 Hz, $^{1}J_{CP}$ = 217.0 Hz), 65.0 (dd, $^{2}J_{CP}$ = 11.0 Hz, $^{2}J_{CP}$ = 6.0 Hz), 33.9-32.7 (m), 29.5, 24.4 (t, $^{1}J_{CH}$ = 4.0 Hz), 16.3 (dd, $^{3}J_{CP}$ = 11.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -59.8 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -105.2 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz), -109.0 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.5 (t, 1P, $^{2}J_{PF}$ = 106.3 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.34-7.31 (m, 1H), 7.20-7.10 (m, 3H), 4.20-4.01 (m, 4H), 2.88 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 1.95-1.64 (m, 2H), δ 1.25 (dt, 6H, $^{3}J_{HH}$ = 16.0 Hz, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 136.2, 131.6, 130.3, 123.8 (qd, $^{1}J_{CF}$ = 275.0 Hz, $^{1}J_{CP}$ = 5.0 Hz), 117.8 (td, $^{1}J_{CF}$ = 262.0 Hz, $^{1}J_{CP}$ = 217.0 Hz), 65.0 (dd, $^{2}J_{CP}$ = 11.0 Hz, $^{2}J_{CP}$ = 6.0 Hz), 33.9-32.7 (m), 29.5, 24.4 (t, $^{1}J_{CH}$ = 4.0 Hz), 16.3 (dd, $^{3}J_{CP}$ = 11.0 Hz, $^{3}J_{CP}$ = 6.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.8 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -105.6 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz), -108.5 (ddq, 1F, $^{2}J_{FF}$ = 315.8 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.5 (t, 1P, $^{2}J_{PF}$ = 107.9 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{15}H_{18}ClF_5O_3P$ 407.0602; found 407.0596.



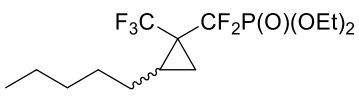
7a

Diethyl (2-propyl-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**7a**) was prepared from 0.3 g (0.1 mmol) of **5**, 0.019 g (0.01 mmol) of CuI, 0.16 mL (0.15 mmol) of 1-pentene and 5 mL of dry toluene. The reaction mixture was refluxed for 3.5 h to give compound **7a** in 48% yield as yellow oil. Mixture of isomers in 1:1.2 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.29-4.15 (m, 4H), 2.31-1.54 (m, 2H), 1.47-1.21 (m, 10H), 1.16-1.11 (3, 1H), 0.89 (t, 3H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.0 (qd, $^{1}J_{CF}$ = 274.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 117.9 (td, $^{1}J_{CF}$ = 309.0 Hz, $^{1}J_{CP}$ = 216.0 Hz), 65.1-64.8 (m), 31.0-30.5 (m), 28.7 (t, $^{2}J_{CF}$ = 5.0 Hz), 23.5 (q, $^{3}J_{CH}$ = 2.0 Hz), 23.0, 22.6, 22.2 (t, $^{3}J_{CH}$ = 4.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 10.0 Hz, $^{3}J_{CP}$ = 4.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -57.8 (s, 3F), -106.8 (ddq, 1F, $^{2}J_{FF}$ = 323.4 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz), -110.3 (ddq, 1F, $^{2}J_{FF}$ = 323.4 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.1 (t, 1P, $^{2}J_{PF}$ = 109.5 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.29-4.15 (m, 4H), 2.31-1.54 (m, 2H), 1.47-1.21 (m, 10H), 1.03 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 0.89 (t, 3H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.0 (qd, $^{1}J_{CF}$ = 274.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 117.9 (td, $^{1}J_{CF}$ = 309.0 Hz, $^{1}J_{CP}$ = 216.0 Hz), 65.1-64.8 (m), 31.0-30.5 (m), 28.7 (t, $^{2}J_{CF}$ = 5.0 Hz), 23.5 (q, $^{3}J_{CH}$ = 2.0 Hz), 23.0, 22.6, 22.2 (t, $^{3}J_{CH}$ = 4.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 10.0 Hz, $^{3}J_{CP}$ = 4.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.8 (t, 3F, $^{4}J_{FF}$ = 3.8 Hz), -102.1, (ddq, 1F, $^{2}J_{FF}$ = 323.4 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz), -104.2 (ddq, 1F, $^{2}J_{FF}$ = 323.4 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.2 (dd, 1P, $^{2}J_{PF}$ = 111.1 Hz, $^{2}J_{PF}$ = 109.5 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{12}H_{21}F_5O_3P$ 339.1148; found 339.1143.



7b

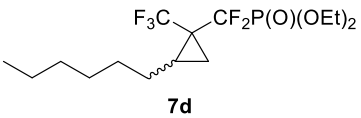
Diethyl (2-butyl-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**7b**) was prepared from 0.3 g (0.1 mmol) of **5**, 0.019 g (0.01 mmol) of CuI, 0.19 mL (0.15 mmol) of 1-hexene and 5 mL of dry toluene. The reaction mixture was refluxed for 3.5 h to give compound **7b** in 46% yield as yellow oil. Mixture of isomers in 1:1.3 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.29-4.15 (m, 4H), 2.31-1.48 (m, 2H), 1.47-1.21 (m, 12H), 1.21-1.11 (m, 1H), 0.84 (t, 3H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.3 (qd, $^{1}J_{CF}$ = 277.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 118.5 (td, $^{1}J_{CF}$ = 263.0 Hz, $^{1}J_{CP}$ = 218.0 Hz), 65.1-64.8 (m), 32.0, 31.6, 31.1-30.5 (m), 26.3 (t, $^{2}J_{CF}$ = 4.0 Hz), 23.7 (q, $^{3}J_{CH}$ = 2.0 Hz), 22.4 (t, $^{3}J_{CH}$ = 3.0 Hz), 16.3 (dd, $^{3}J_{CP}$ = 6.0 Hz, $^{3}J_{CP}$ = 4.0 Hz), 14.25; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -57.7 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -106.8 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz) -110.2 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.1 (t, 1P, $^{2}J_{PF}$ = 109.5 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.29-4.15 (m, 4H), 2.31-1.48 (m, 2H), 1.47-1.21 (m, 12H), 1.02 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 0.84 (t, 3H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.3 (qd, $^{1}J_{CF}$ = 277.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 118.5 (td, $^{1}J_{CF}$ = 263.0 Hz, $^{1}J_{CP}$ = 218.0 Hz), 65.1-64.8 (m), 32.0, 31.6, 31.1-30.5 (m), 26.3 (t, $^{2}J_{CF}$ = 4.0 Hz), 23.7 (q, $^{3}J_{CH}$ = 2.0 Hz), 22.4 (t, $^{3}J_{CH}$ = 3.0 Hz), 16.3 (dd, $^{3}J_{CP}$ = 6.0 Hz, $^{3}J_{CP}$ = 4.0 Hz), 14.25; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.7 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -102.2 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz) -104.1 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.3 (dd, 1P, $^{2}J_{PF}$ = 111.1 Hz, $^{2}J_{PF}$ = 109.5 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{13}H_{23}F_5O_3P$ 353.1304; found 353.1298.



7c

Diethyl (2-pentyl-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**7c**) was prepared from 0.5 g (0.2 mmol) of **5**, 0.032 g (0.02 mmol) of CuI, 0.33 mL (0.25 mmol) of 1-

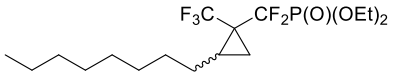
hepten and 10 mL of dry toluene. The reaction mixture was refluxed for 2.5 h to give compound **7c** in 42% yield as yellow oil. Mixture of isomers in 1:1.1 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.29-4.15 (m, 4H), 1.95-1.52 (m, 2H), 1.47-1.19 (m, 14H), 1.13 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 0.82 (t, 3H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.7 (qd, $^{1}J_{CF}$ = 274.0 Hz, $^{1}J_{CP}$ = 5.0 Hz), 118.5 (td, $^{1}J_{CF}$ = 263.0 Hz, $^{1}J_{CP}$ = 218.0 Hz), 65.2-64.8 (m), 31.5 (d, $^{2}J_{CH}$ = 3.0 Hz), 31.0-30.5 (m), 29.5, 29.1, 26.6 (q, $^{2}J_{CF}$ = 2.0 Hz), 23.7 (q, $^{3}J_{CH}$ = 2.0 Hz), 22.6 (d, $^{3}J_{CH}$ = 4.0 Hz), 22.5 (t, $^{3}J_{CH}$ = 4.0 Hz), 16.3 (dd, $^{3}J_{CP}$ = 6.0 Hz, $^{3}J_{CP}$ = 4.0 Hz), 14.1; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -57.8 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -106.8, (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz) -110.2 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.1 (t, 1P, $^{2}J_{PF}$ = 109.5 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.29-4.15 (m, 4H), 1.95-1.52 (m, 2H), 1.47-1.19 (m, 14H), 1.02 (t, 1H, $^{4}J_{HF}$ = 8.0 Hz), 0.82 (t, 3H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.3 (qd, $^{1}J_{CF}$ = 273.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 117.7 (td, $^{1}J_{CF}$ = 260.0 Hz, $^{1}J_{CP}$ = 218.0 Hz), 65.2-64.8 (m), 31.5 (d, $^{2}J_{CH}$ = 3.0 Hz), 31.0-30.5 (m), 29.5, 29.1, 26.6 (q, $^{2}J_{CF}$ = 2.0 Hz), 23.7 (q, $^{3}J_{CH}$ = 2.0 Hz), 22.6 (d, $^{3}J_{CH}$ = 4.0 Hz), 22.5 (t, $^{3}J_{CH}$ = 4.0 Hz), 16.3 (dd, $^{3}J_{CP}$ = 6.0 Hz, $^{3}J_{CP}$ = 4.0 Hz), 14.1; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.8 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -102.1 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz) -104.1 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.2 (dd, 1P, $^{2}J_{PF}$ = 111.1 Hz, $^{2}J_{PF}$ = 109.5 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{14}H_{25}F_5O_3P$ 367.1461; found 367.1455.



7d

Diethyl (2-hexyl-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**7d**) was prepared from 0.2 g (0.07 mmol) of **5**, 0.012 g (0.007 mmol) of CuI, 0.16 mL (0.1 mmol) of octene-1 and 4 mL of dry toluene. The reaction mixture was refluxed for 2.5 h to give compound **7d** in 34% yield as yellow oil. Mixture of isomers in 1:2.2 ratio. *Major isomer:* **^{1}H**

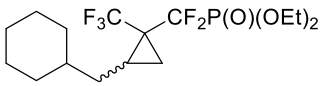
NMR ($CDCl_3$, 400 MHz): δ 4.29-4.14 (m, 4H), 1.96-1.47 (m, 2H), 1.43-1.28 (m, 10H), 1.28-1.17 (m, 6H), 1.15-1.01 (m, 1H), 0.81 (t, 3H, $^3J_{HH}$ = 4.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.7 (qd, $^1J_{CF}$ = 275.0 Hz, $^1J_{CP}$ = 5.0 Hz), 117.7 (td, $^1J_{CF}$ = 266.0 Hz, $^1J_{CP}$ = 219.0 Hz), 64.9 (m), 31.8 (d, $^2J_{CH}$ = 6.0 Hz), 29.8, 29.4, 29.0 (d, $^2J_{CH}$ = 5.0 Hz), 26.7, 23.7, 22.7, 22.5 (t, $^3J_{CH}$ = 4.0 Hz), 16.4 (dd, $^3J_{CP}$ = 6.0 Hz, $^3J_{CP}$ = 4.0 Hz), 14.1; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -57.7 (t, 3F, $^4J_{FF}$ = 7.5 Hz), -106.8 (ddq, 1F, $^2J_{FF}$ = 312.1 Hz, $^2J_{FP}$ = 109.0 Hz, $^4J_{FF}$ = 7.5 Hz) -110.2 (ddq, 1F, $^2J_{FF}$ = 312.1 Hz, $^2J_{FP}$ = 109.0 Hz, $^4J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.2 (t, 1P, $^2J_{PF}$ = 109.5 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.29-4.14 (m, 4H), 1.96-1.47 (m, 2H), 1.43-1.28 (m, 10H), 1.28-1.17 (m, 6H), 1.15-1.01 (m, 1H), 0.81 (t, 3H, $^3J_{HH}$ = 4.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): 124.7 (qd, $^1J_{CF}$ = 275.0 Hz, $^1J_{CP}$ = 5.0 Hz), 117.7 (td, $^1J_{CF}$ = 266.0 Hz, $^1J_{CP}$ = 219.0 Hz), 64.9 (m), 31.8 (d, $^2J_{CH}$ = 6.0 Hz), 29.8, 29.4, 29.0 (d, $^2J_{CH}$ = 5.0 Hz), 26.7, 23.7, 22.7, 22.5 (t, $^3J_{CH}$ = 4.0 Hz), 16.4 (dd, $^3J_{CP}$ = 6.0 Hz, $^3J_{CP}$ = 4.0 Hz), 14.1; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.7 (t, 3F, $^4J_{FF}$ = 7.5 Hz), -102.1 (ddq, 1F, $^2J_{FF}$ = 312.1 Hz, $^2J_{FP}$ = 109.0 Hz, $^4J_{FF}$ = 7.5 Hz) -104.1 (ddq, 1F, $^2J_{FF}$ = 312.1 Hz, $^2J_{FP}$ = 109.0 Hz, $^4J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.3 (dd, 1P, $^2J_{PF}$ = 109.5 Hz, $^2J_{PF}$ = 107.9 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{15}H_{27}F_5O_3P$ 381.1617; found 381.1613.



7e

Diethyl (2-octyl-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**7e**) was prepared from 0.3 g (0.1 mmol) of **5**, 0.019 g (0.01 mmol) of CuI, 0.3 mL (0.15 mmol) of 1-decene and 5 mL of dry toluene. The reaction mixture was refluxed for 5 h to give compound **7e** in 41% yield as yellow oil. Mixture of isomers in 1:1.2 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.30-4.13 (m, 4H), 1.82-1.54 (m, 1H), 1.52-1.01 (m, 22H), 0.80 (t, 3H, $^3J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.3 (qd, $^1J_{CF}$ = 272.0 Hz, $^1J_{CP}$ = 6.0 Hz), 117.6 (td, $^1J_{CF}$ = 261.0 Hz, $^1J_{CP}$ = 218.0 Hz), 65.0-64.8 (m), 31.9, 31.1-30.5 (m), 29.8, 29.5 (d,

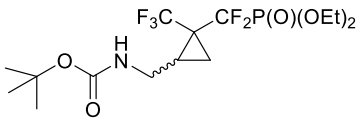
$^{2}J_{CH}$ = 7.0 Hz), 29.4 (d, $^{3}J_{CH}$ = 4.0 Hz), 29.3 (d, $^{3}J_{CH}$ = 4.0 Hz), 26.7 (dd, $^{3}J_{CH}$ = 6.0 Hz, $^{3}J_{CH}$ = 3.0 Hz), 23.7, 22.7, 22.5 (t, $^{3}J_{CH}$ = 4.0 Hz), 16.3 (dd, $^{3}J_{CP}$ = 7.0 Hz, $^{3}J_{CP}$ = 4.0 Hz), 14.1; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -57.8 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -106.8 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz) -110.1 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.1 (t, 1P, $^{2}J_{PF}$ = 109.5 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.30-4.13 (m, 4H), 1.82-1.54 (m, 1H), 1.52-1.01 (m, 22H), 0.80 (t, 3H, $^{3}J_{HH}$ = 8.0 Hz); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.3 (qd, $^{1}J_{CF}$ = 272.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 117.6 (td, $^{1}J_{CF}$ = 261.0 Hz, $^{1}J_{CP}$ = 218.0 Hz), 65.0-64.8 (m), 31.9, 31.1-30.5 (m), 29.8, 29.5 (d, $^{2}J_{CH}$ = 7.0 Hz), 29.4 (d, $^{3}J_{CH}$ = 4.0 Hz), 29.3 (d, $^{3}J_{CH}$ = 4.0 Hz), 26.7 (dd, $^{3}J_{CH}$ = 6.0 Hz, $^{3}J_{CH}$ = 3.0 Hz), 23.7, 22.7, 22.5 (t, $^{3}J_{CH}$ = 4.0 Hz), 16.3 (dd, $^{3}J_{CP}$ = 7.0 Hz, $^{3}J_{CP}$ = 4.0 Hz), 14.1; **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.7 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -102.1 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz) -103.9 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.3 (dd, 1P, $^{2}J_{PF}$ = 111.1 Hz, $^{2}J_{PF}$ = 109.5 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{17}H_{31}F_5O_3P$ 409.1930; found 409.1924.



7f

Diethyl (2-(cyclohexylmethyl)-1-(trifluoromethyl)cyclopropyl)difluoromethylphosphonate (**7f**) was prepared from 0.5 g (0.2 mmol) of **5**, 0.032 g (0.02 mmol) of CuI, 0.4 mL (0.25 mmol) of allylcyclohexane and 10 mL of dry toluene. The reaction mixture was refluxed for 5 h to give compound **7f** in 28% yield as yellow oil. Mixture of isomers in 1:1.3 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.30-4.13 (m, 4H), 2.10-1.69 (m, 2H), 1.65-1.06 (m, 17H), 1.05-0.97 (m, 1H), 0.92-0.81 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.7 (qd, $^{1}J_{CF}$ = 276.0 Hz, $^{1}J_{CP}$ = 4.0 Hz), 118.5 (td, $^{1}J_{CF}$ = 264.0 Hz, $^{1}J_{CP}$ = 218.0 Hz), 65.0-64.8 (m), 38.5, 38.1, 33.4, 33.0, 30.9-29.7 (m), 26.6 (d, $^{3}J_{CH}$ = 2.0 Hz), 26.3 (t, $^{3}J_{CH}$ = 3.0 Hz), 24.1, 21.9, 20.6

(t, $^{3}J_{CH}$ = 3.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 6.0 Hz, $^{3}J_{CP}$ = 4.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -57.7 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -106.7 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz) -109.9 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.1 (t, 1P, $^{2}J_{PF}$ = 109.5 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.30-4.13 (m, 4H), 2.10-1.69 (m, 2H), 1.65-1.06 (m, 17H), 1.05-0.97 (m, 1H), 0.92-0.81 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 124.4 (qd, $^{1}J_{CF}$ = 273.0 Hz, $^{1}J_{CP}$ = 6.0 Hz), 117.7 (td, $^{1}J_{CF}$ = 266.0 Hz, $^{1}J_{CP}$ = 219.0 Hz), 65.9-65.7 (m), 38.5, 38.1, 33.4, 33.0, 30.9-29.7 (m), 26.6 (d, $^{3}J_{CH}$ = 2.0 Hz), 26.3 (t, $^{3}J_{CH}$ = 3.0 Hz), 24.1, 21.9, 20.6 (t, $^{3}J_{CH}$ = 3.0 Hz), 16.4 (dd, $^{3}J_{CP}$ = 6.0 Hz, $^{3}J_{CP}$ = 4.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.6 (t, 3F, $^{4}J_{FF}$ = 7.5 Hz), -101.9 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz), -104.2 (ddq, 1F, $^{2}J_{FF}$ = 312.1 Hz, $^{2}J_{FP}$ = 109.0 Hz, $^{4}J_{FF}$ = 7.5 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 5.3 (dd, 1P, $^{2}J_{PF}$ = 111.1Hz, $^{2}J_{PF}$ = 109.5 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{16}H_{27}F_5O_3P$ 393.1617; found 393.1613.

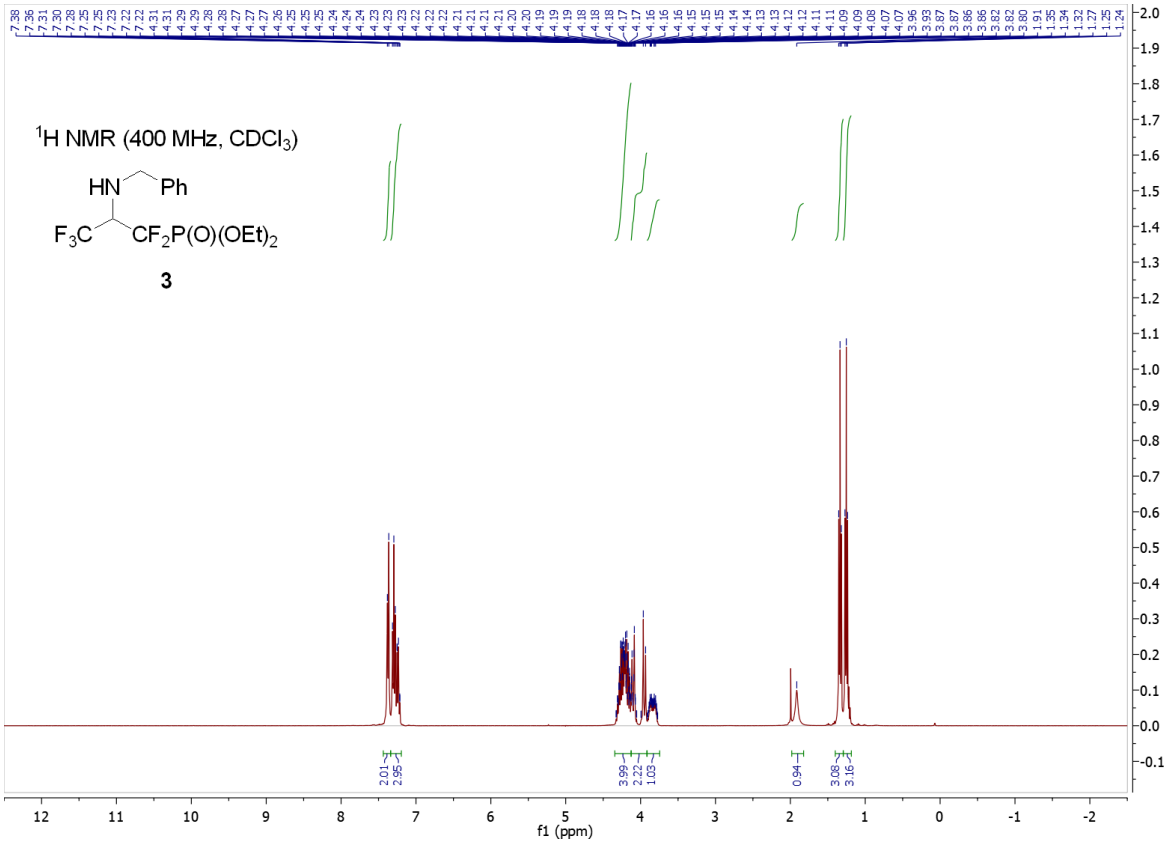


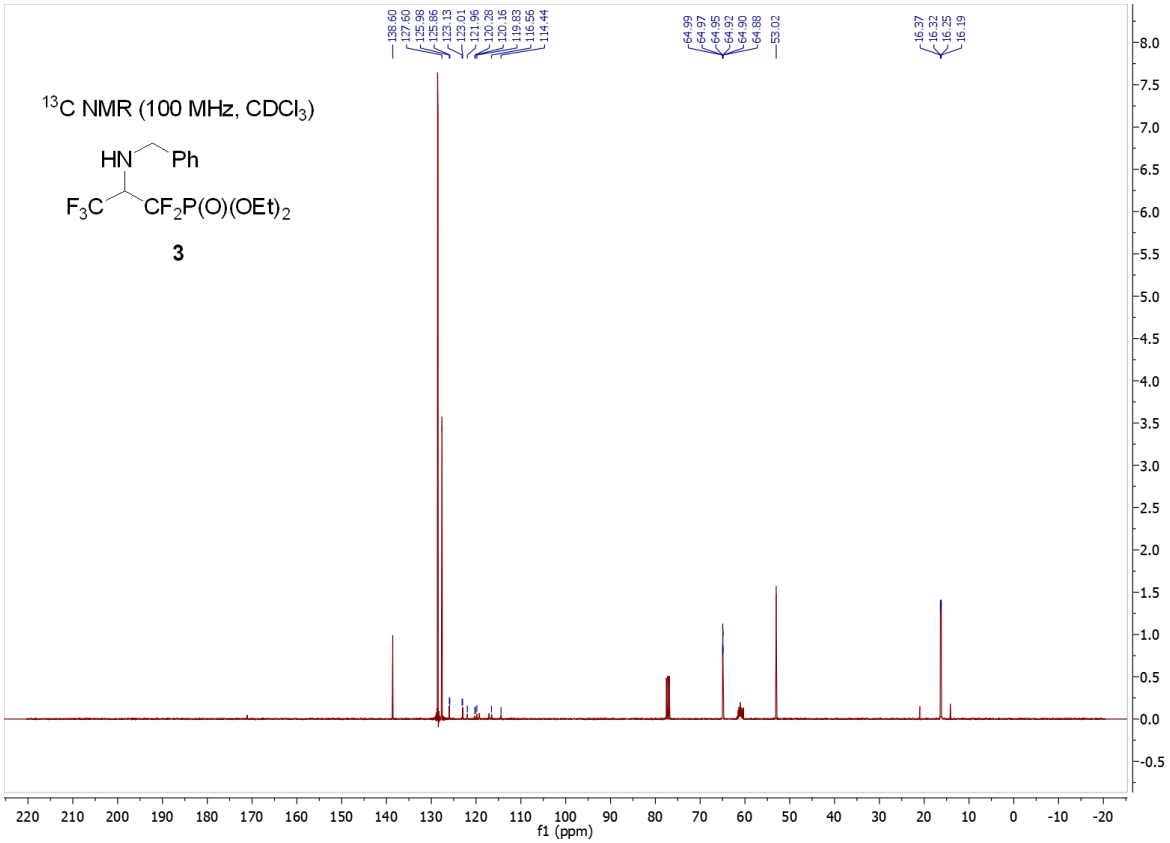
7g

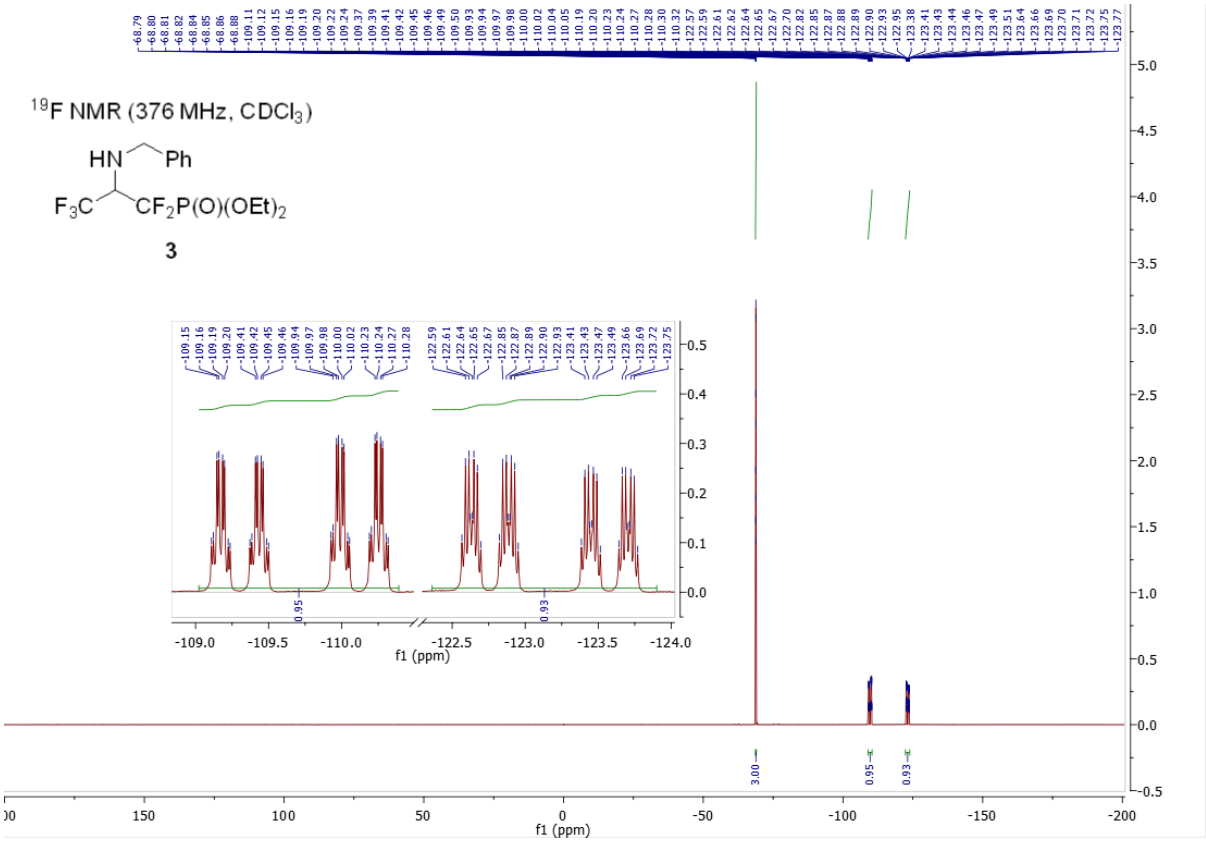
tert-Butyl ((2-((diethoxyphosphoryl)difluoromethyl)-2-(trifluoromethyl)cyclopropyl)methyl)carbamate (**7g**) was prepared from 0.5 g (0.2 mmol) of **5**, 0.032 g (0.02 mmol) of CuI, 0.4 g (0.25 mmol) of *tert*-butyl-*N*-allylcarbamate and 10 mL of dry toluene. The reaction mixture was refluxed for 5 h to give compound **7g** in 53% yield as yellow oil. Mixture of isomers in 1:6 ratio. *Major isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.27-4.16 (m, 8H), 1.97 (d, 1H, $^{4}J_{HF}$ = 4.0 Hz), 1.38 (s, 3H), 1.34-1.30 (m, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 151.9, 120.6 (td, $^{1}J_{CF}$ = 282.0 Hz, $^{1}J_{CP}$ = 11.0 Hz), 114.3 (td, $^{1}J_{CF}$ = 265.0 Hz, $^{1}J_{CP}$ = 215.0 Hz), 67.6-66.4 (m), 64.4 (dd, $^{2}J_{CH}$ = 13.0, $^{2}J_{CH}$ = 7.0 Hz), 42.8, 40.6, 36.5-36.4 (m), 28.7, 27.4, 27.2, 22.9, 15.3 (dd, $^{3}J_{CP}$ = 5.0, $^{3}J_{CP}$ = 2.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -71.4 (q, 3F, $^{4}J_{FF}$ = 11.3 Hz), -116.5 (ddtd, 1F, $^{2}J_{FF}$ = 319.6 Hz, $^{2}J_{FP}$ = 90.2 Hz, 11.3 Hz, $^{4}J_{FF}$

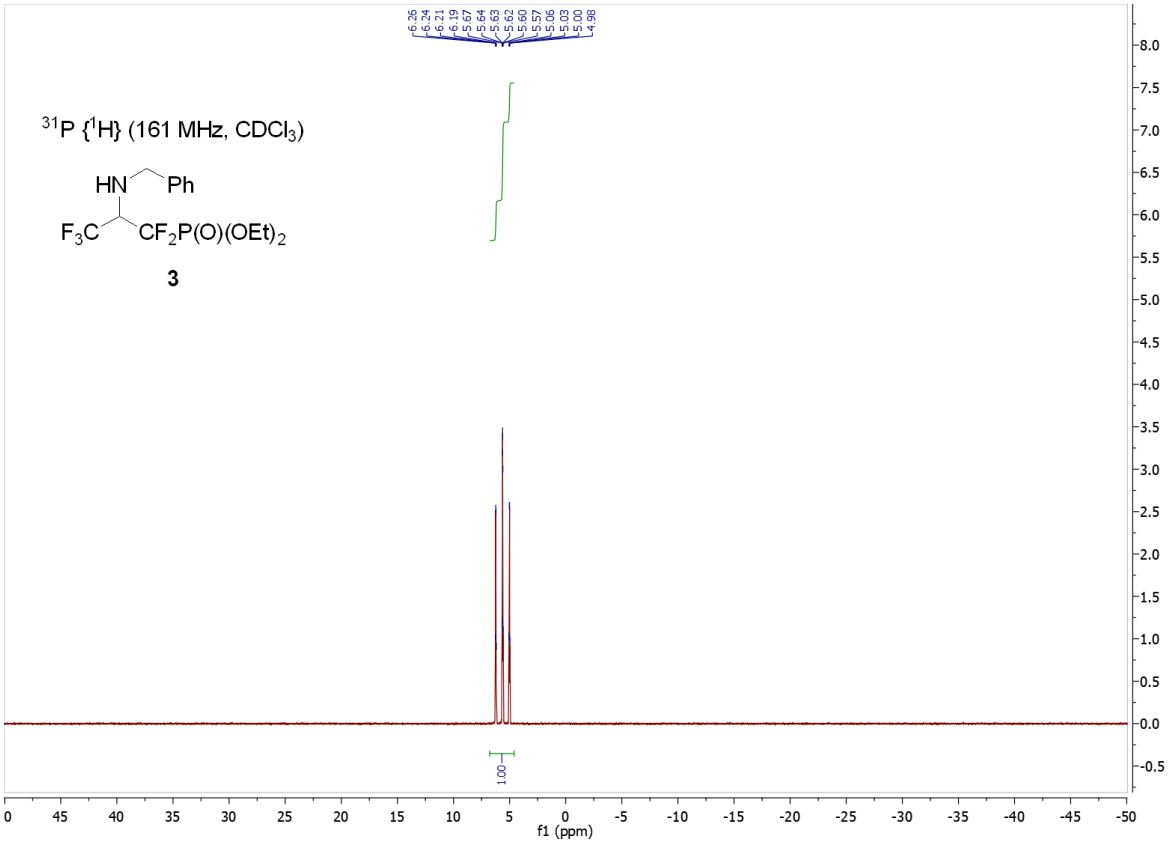
= 7.6 Hz), -123.6 (ddtd, 1F, $^{2}J_{FF}$ = 319.6 Hz, $^{2}J_{FP}$ = 90.2 Hz, 11.3 Hz, $^{4}J_{FF}$ = 7.6 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 3.6 (ddq, 1P, $^{2}J_{PF}$ = 103.0 Hz, $^{2}J_{PF}$ = 91.8 Hz, $^{4}J_{PF}$ = 3.2 Hz). *Minor isomer:* **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 4.27-4.16 (m, 8H), 1.98 (d, 1H, $^{4}J_{HF}$ = 4.0 Hz), 1.38 (s, 3H), 1.34-1.30 (m, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 151.9, 120.6 (td, $^{1}J_{CF}$ = 282.0 Hz, $^{1}J_{CP}$ = 11.0 Hz), 114.3 (td, $^{1}J_{CF}$ = 265.0 Hz, $^{1}J_{CP}$ = 215.0 Hz), 67.6-66.4 (m), 64.4 (dd, $^{2}J_{CH}$ = 13.0, $^{2}J_{CH}$ = 7.0 Hz), 42.8, 40.6, 36.5-36.4 (m), 28.7, 27.4, 27.2, 22.9, 15.3 (dd, $^{3}J_{CP}$ = 5.0, $^{3}J_{CP}$ = 2.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -64.9 (d, 3F, $^{4}J_{FF}$ = 3.8 Hz), -98.6 (ddtd, 1F, $^{2}J_{FF}$ = 319.6 Hz, $^{2}J_{FP}$ = 90.2 Hz, $^{4}J_{FF}$ = 11.3 Hz, $^{4}J_{FH}$ = 3.8 Hz), -106.2 (ddtd, 1F, $^{2}J_{FF}$ = 319.6 Hz, $^{2}J_{FP}$ = 90.2 Hz, $^{4}J_{FF}$ = 11.3 Hz, $^{4}J_{FH}$ = 3.8 Hz); **^{31}P {^{1}H} NMR** ($CDCl_3$, 161 MHz): δ 4.8 (dd, 1P, $^{2}J_{PF}$ = 111.1 Hz, $^{2}J_{PF}$ = 103.0 Hz). **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd. for $C_{15}H_{26}F_5NO_5P$ 426.1468; found 426.1464.

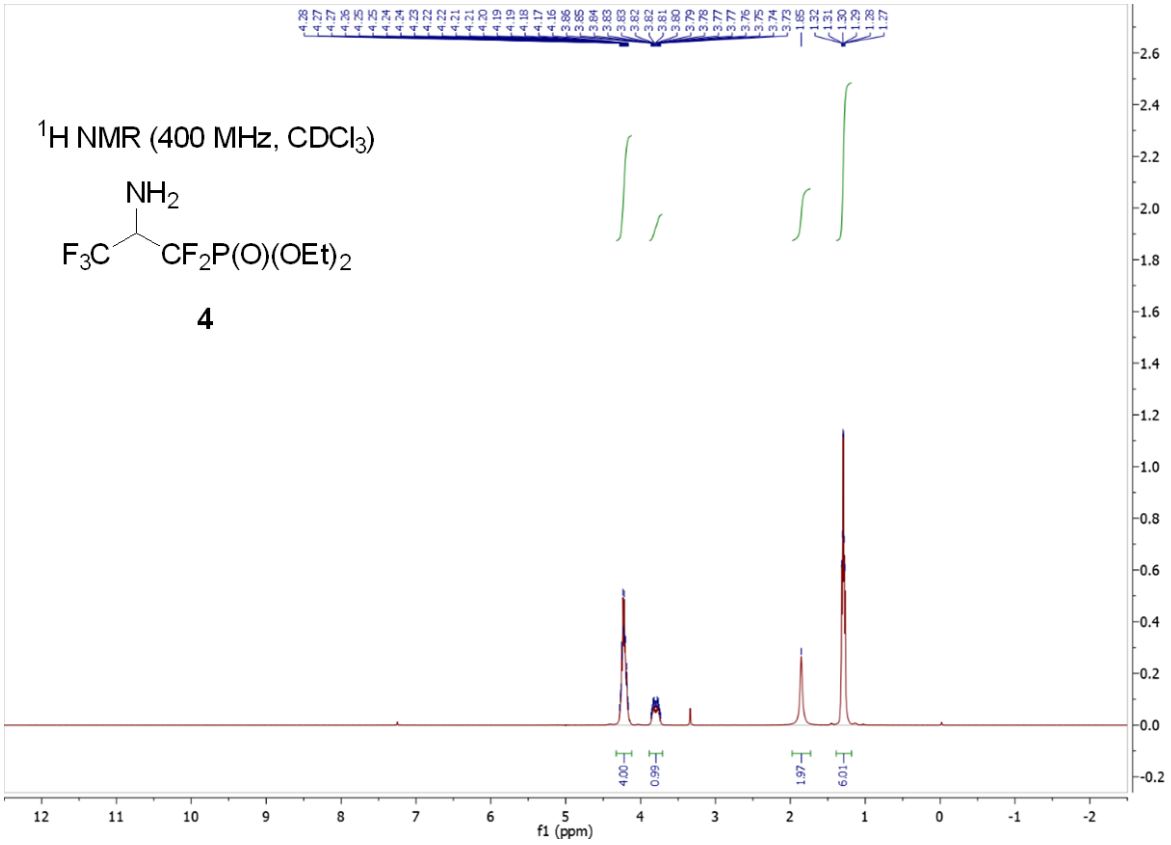
7. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{31}P NMR spectra for the compounds 3, 4, 5, 6a–i and 7a–g

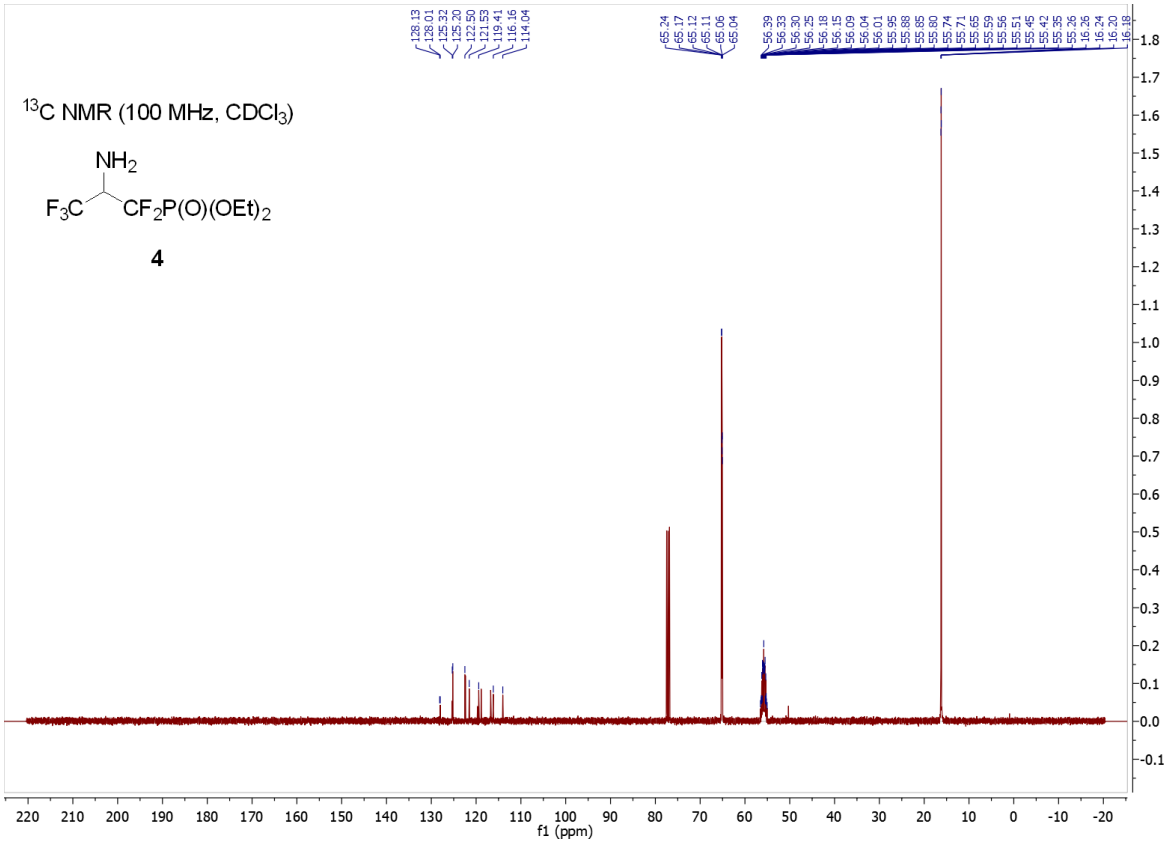


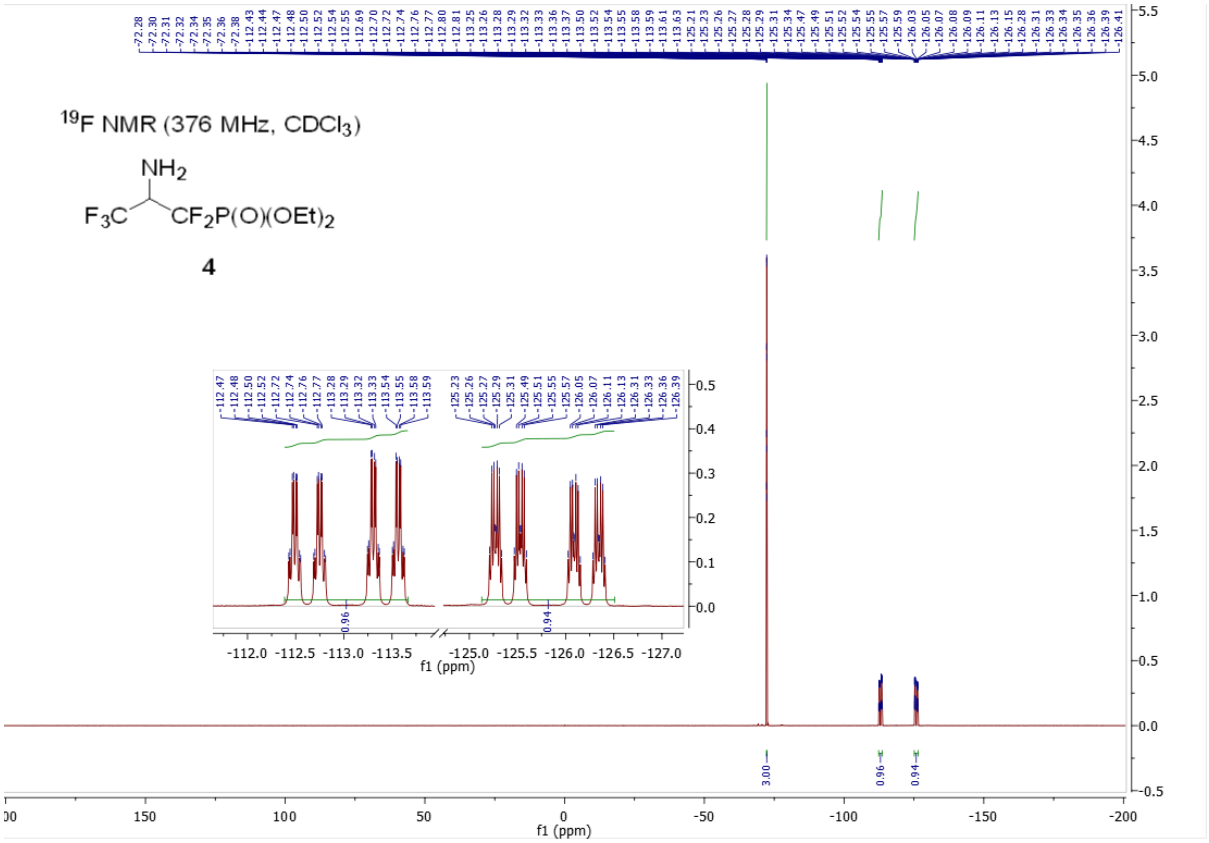

^{13}C NMR (100 MHz, $CDCl_3$)
HN
Ph
F_3C
$CF_2P(O)(OEt)_2$
3
f1 (ppm)

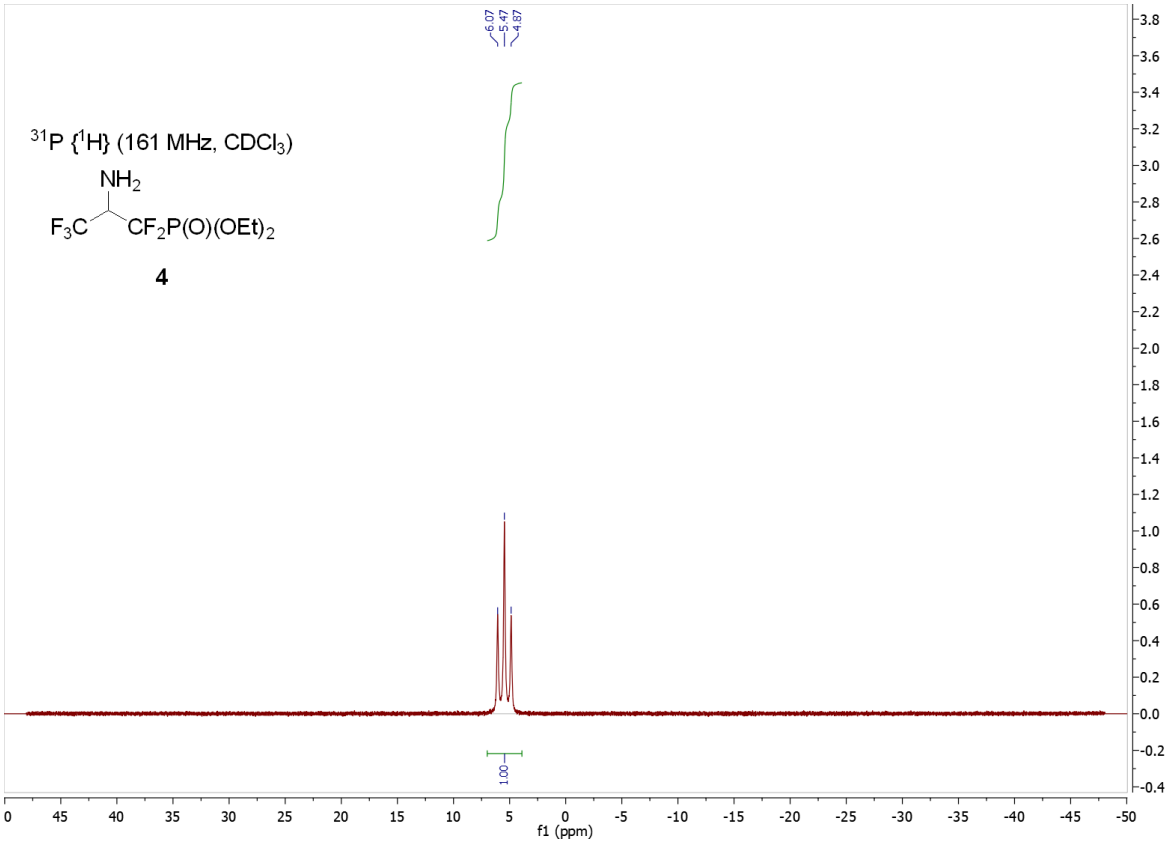

^{19}F NMR (376 MHz, $CDCl_3$)
HN
Ph
F_3C
$CF_2P(O)(OEt)_2$
3
f1 (ppm)

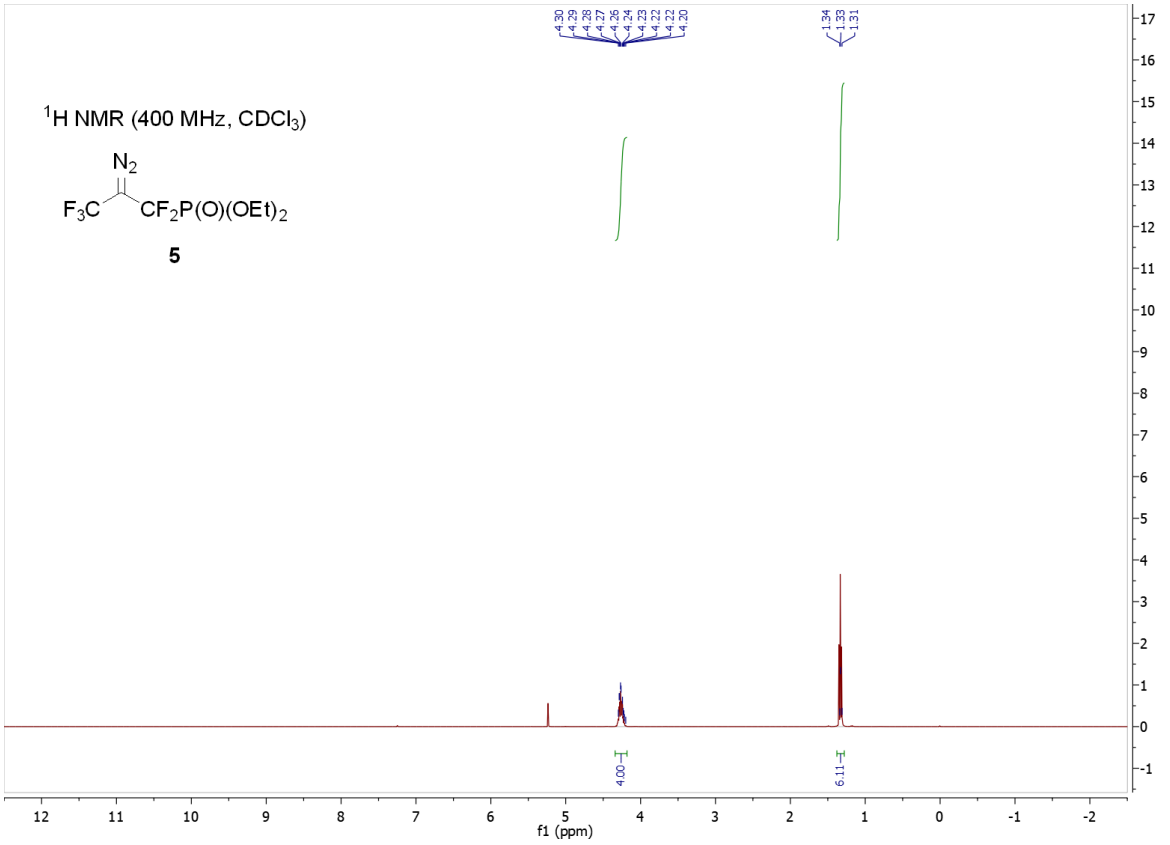

^{31}P {^{1}H} (161 MHz, CDCl$_3$)
HN
Ph
F$_3$C
CF$_2$P(O)(OEt)$_2$
3
f1 (ppm)

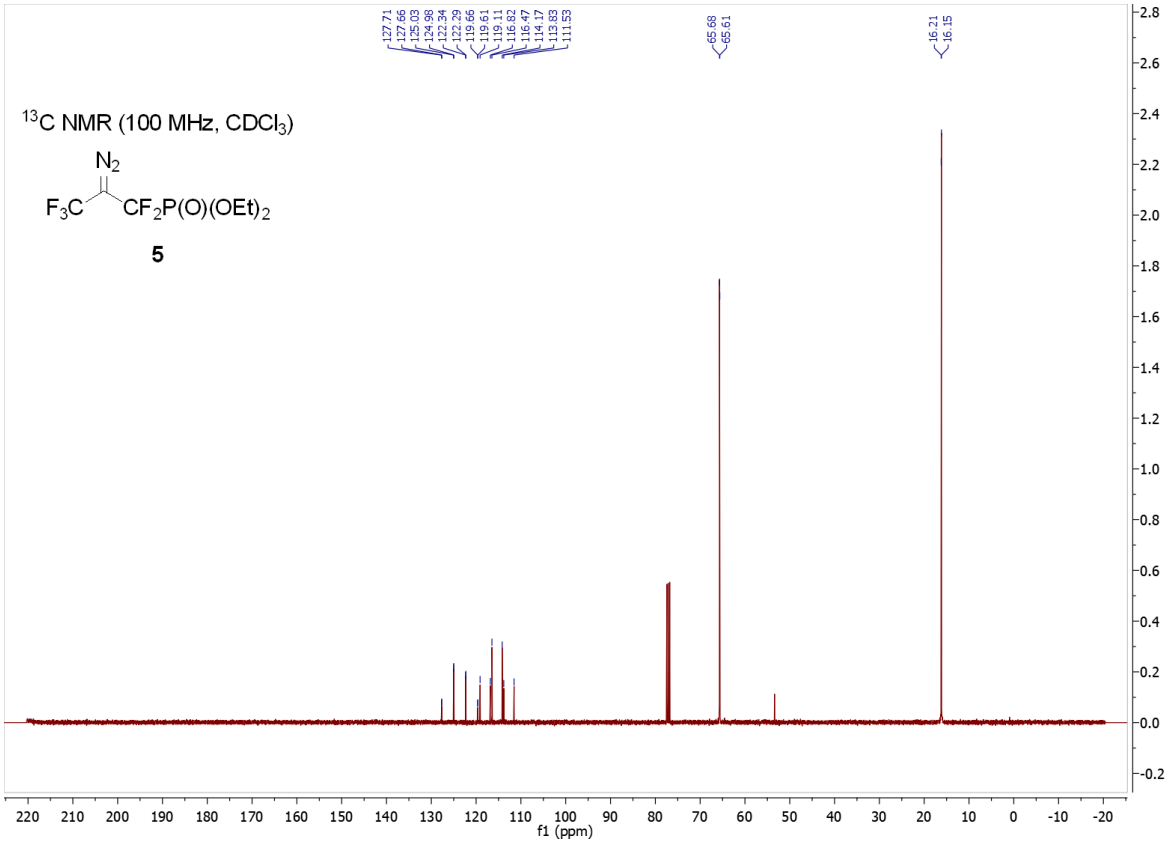

^{1}H NMR (400 MHz, CDCl$_3$)
NH$_2$
F$_3$C
CF$_2$P(O)(OEt)$_2$
4
f1 (ppm)

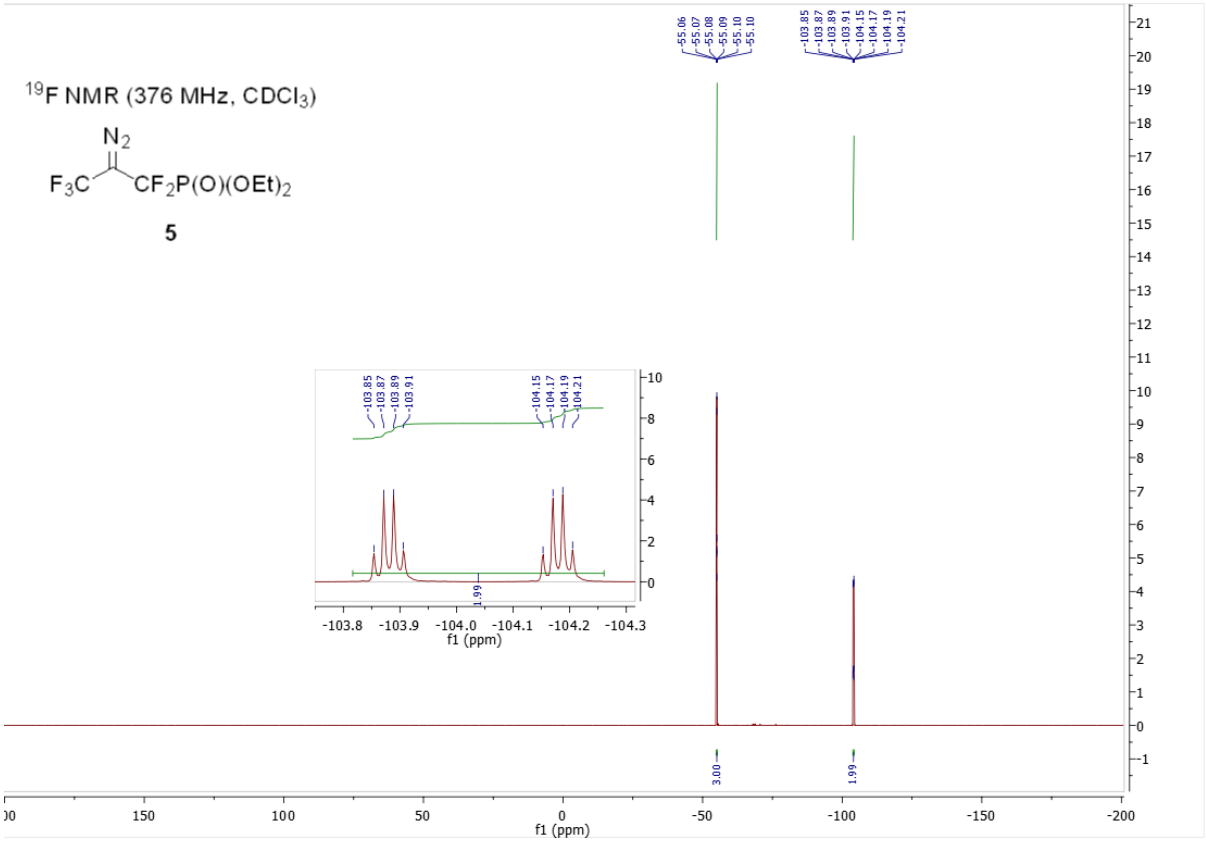

^{13}C NMR (100 MHz, $CDCl_3$)
NH_2
F_3C
$CF_2P(O)(OEt)_2$
4
f1 (ppm)

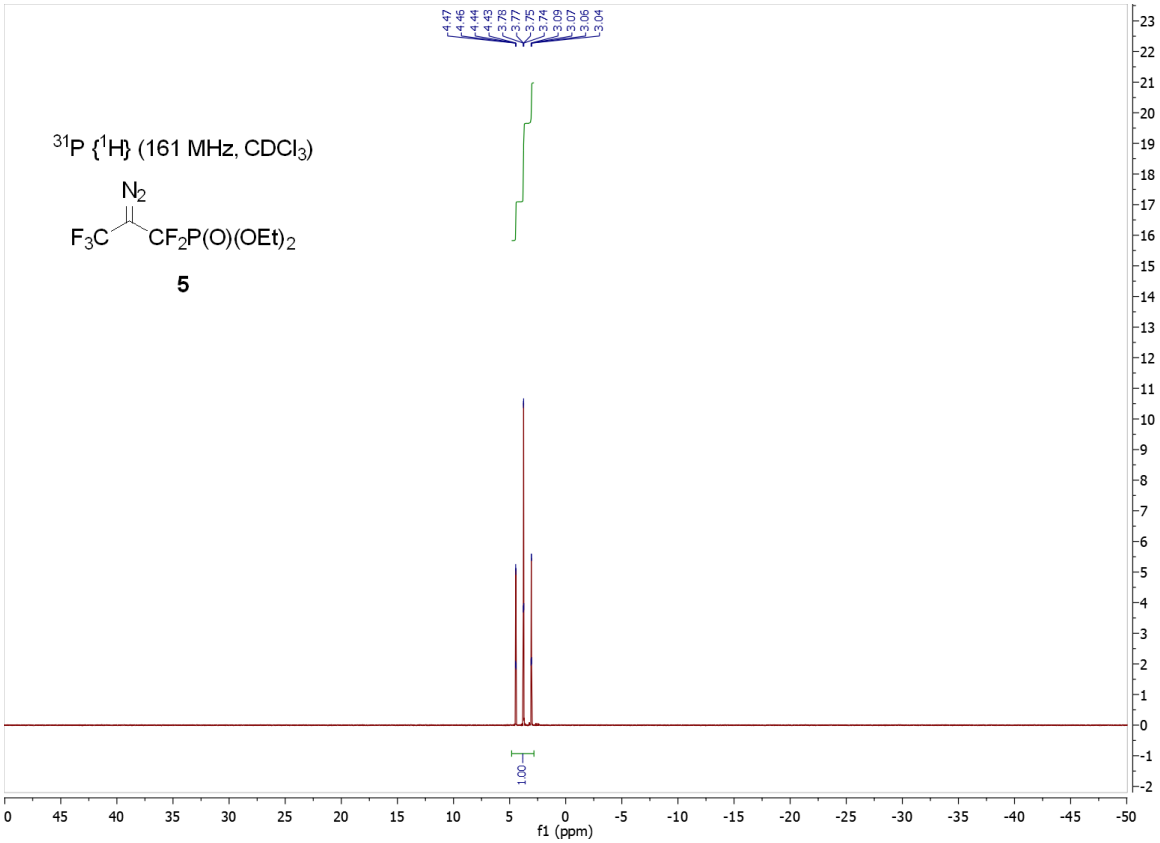

^{19}F NMR (376 MHz, $CDCl_3$)
NH_2
F_3C
$CF_2P(O)(OEt)_2$
4
f1 (ppm)

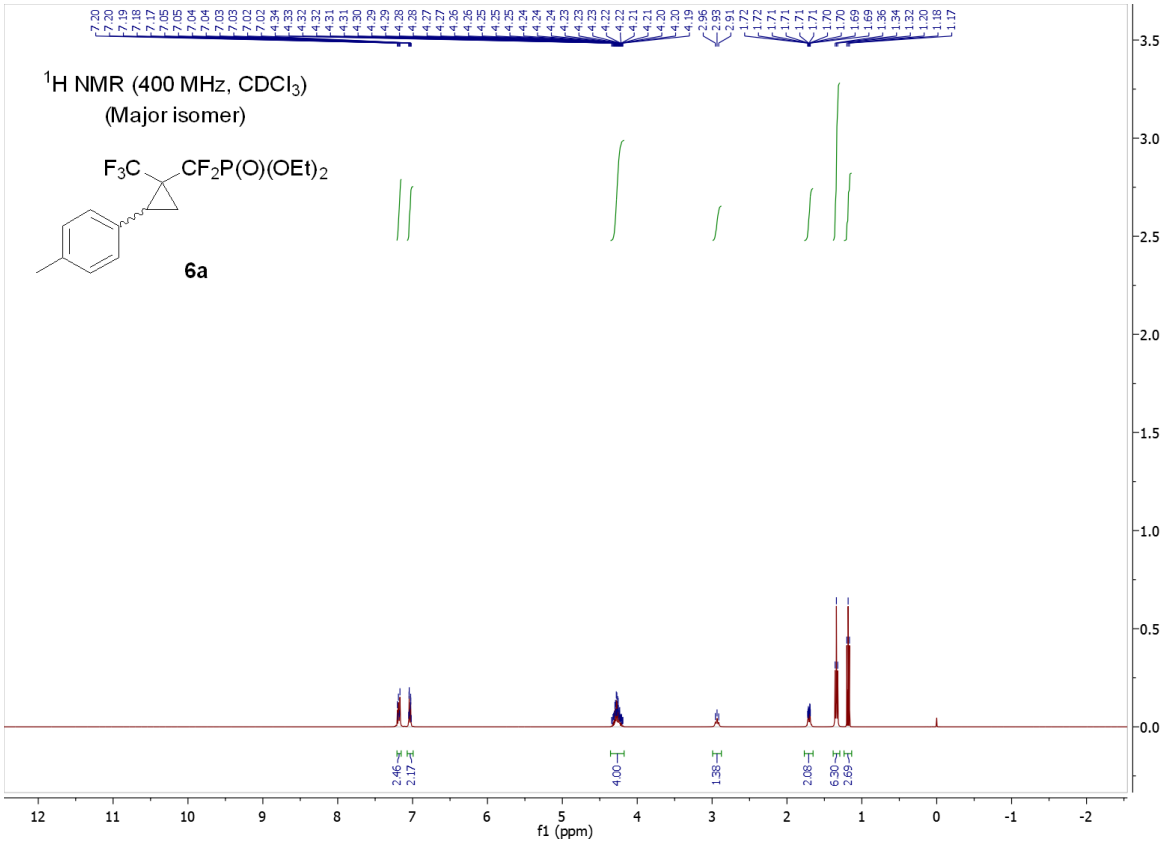

^{31}P {^{1}H} (161 MHz, $CDCl_3$)
NH_2
F_3C
$CF_2P(O)(OEt)_2$
4
6.07
5.47
4.87
1.00
f1 (ppm)

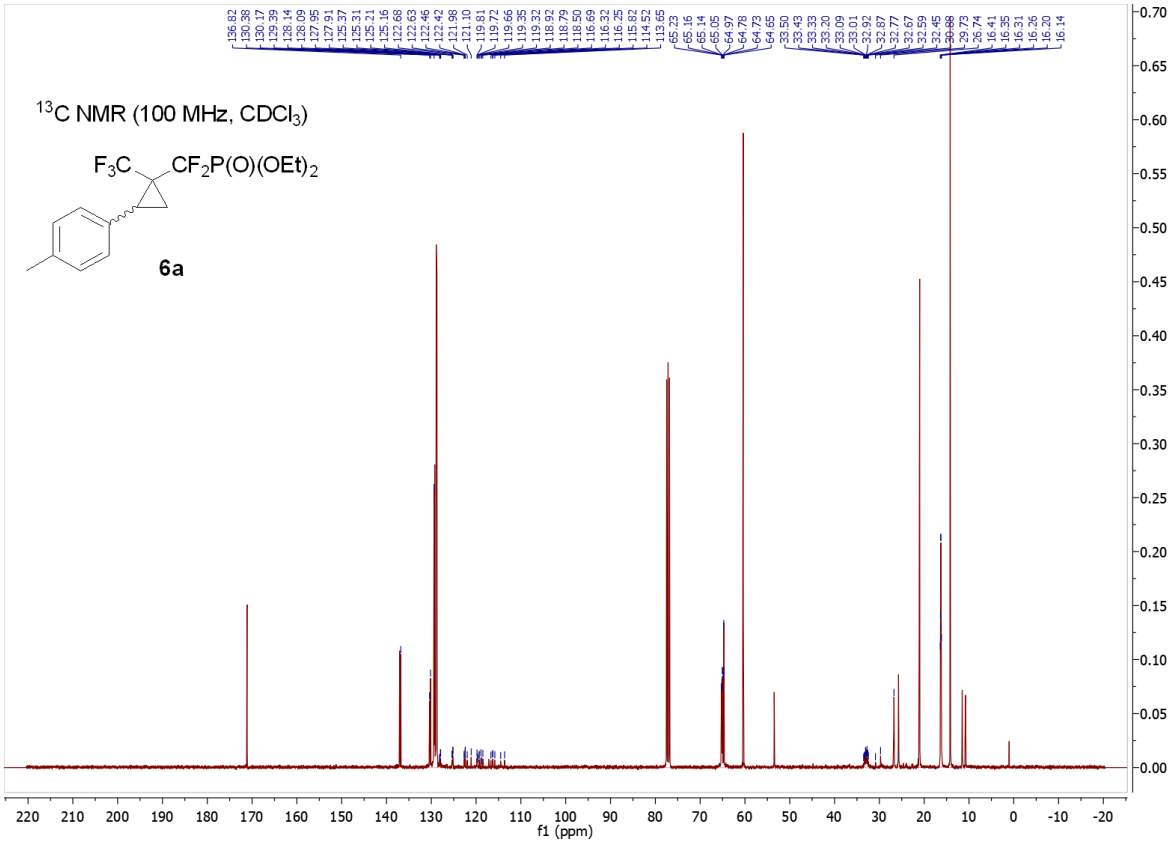

^{1}H NMR (400 MHz, $CDCl_3$)
N_2
F_3C
$CF_2P(O)(OEt)_2$
5
4.30
4.29
4.28
4.27
4.26
4.24
4.23
4.22
4.22
4.20
1.34
1.33
1.31
4.00
6.11
f1 (ppm)

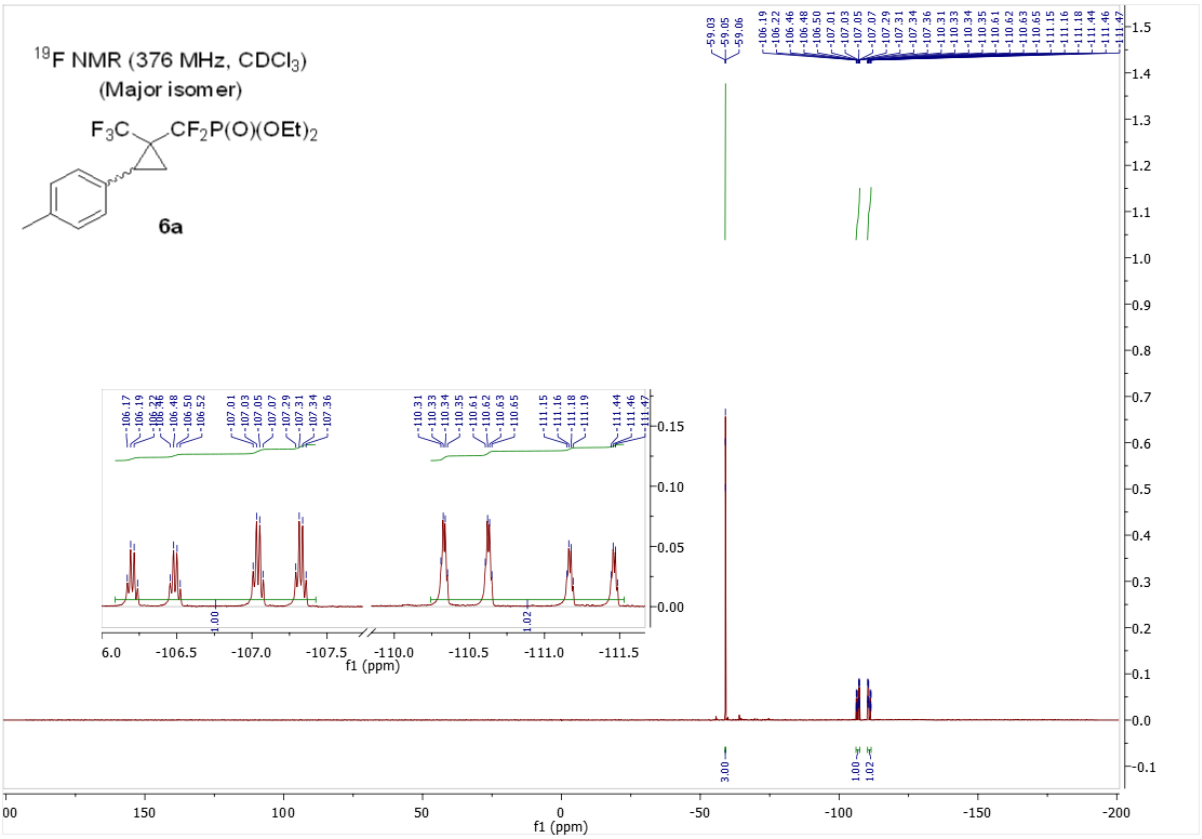

^{13}C NMR (100 MHz, $CDCl_3$)
N_2
F_3C $CF_2P(O)(OEt)_2$
5
f1 (ppm)

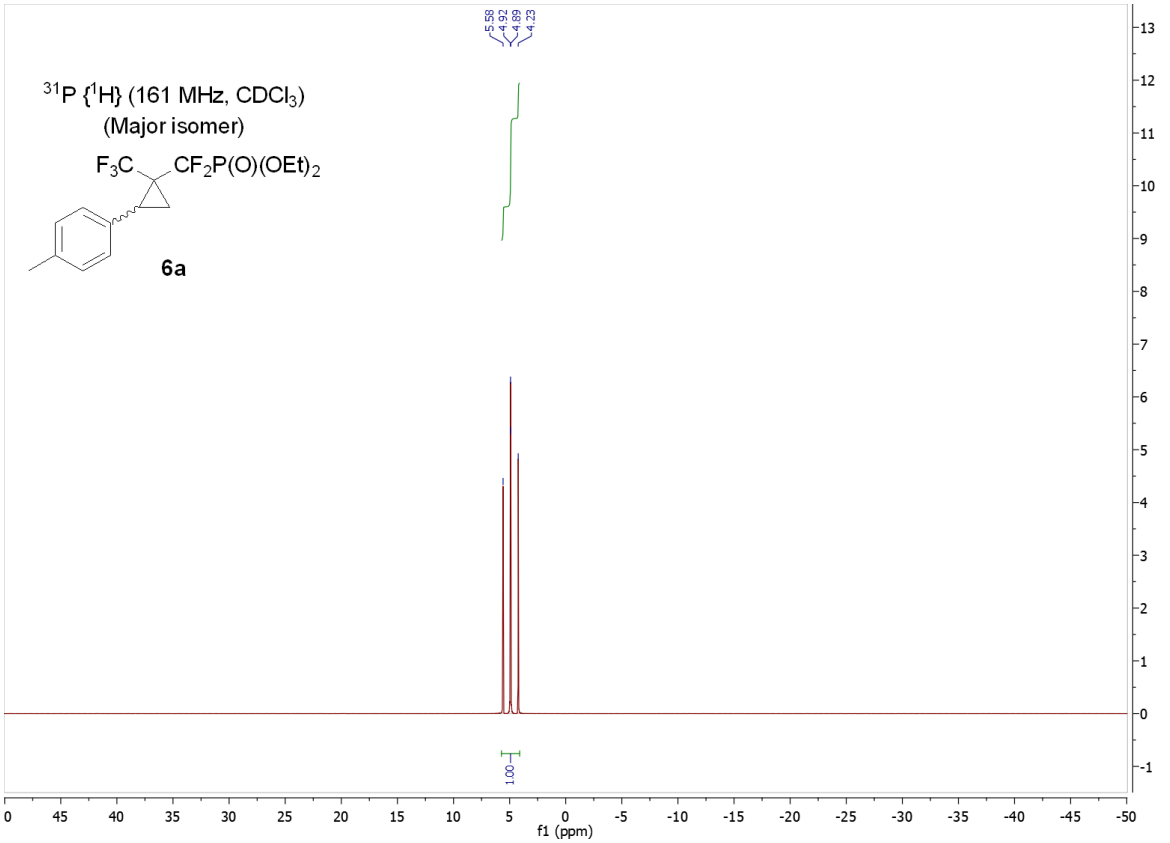

^{19}F NMR (376 MHz, $CDCl_3$)
N_2
F_3C $CF_2P(O)(OEt)_2$
5
3.00
1.99
f1 (ppm)

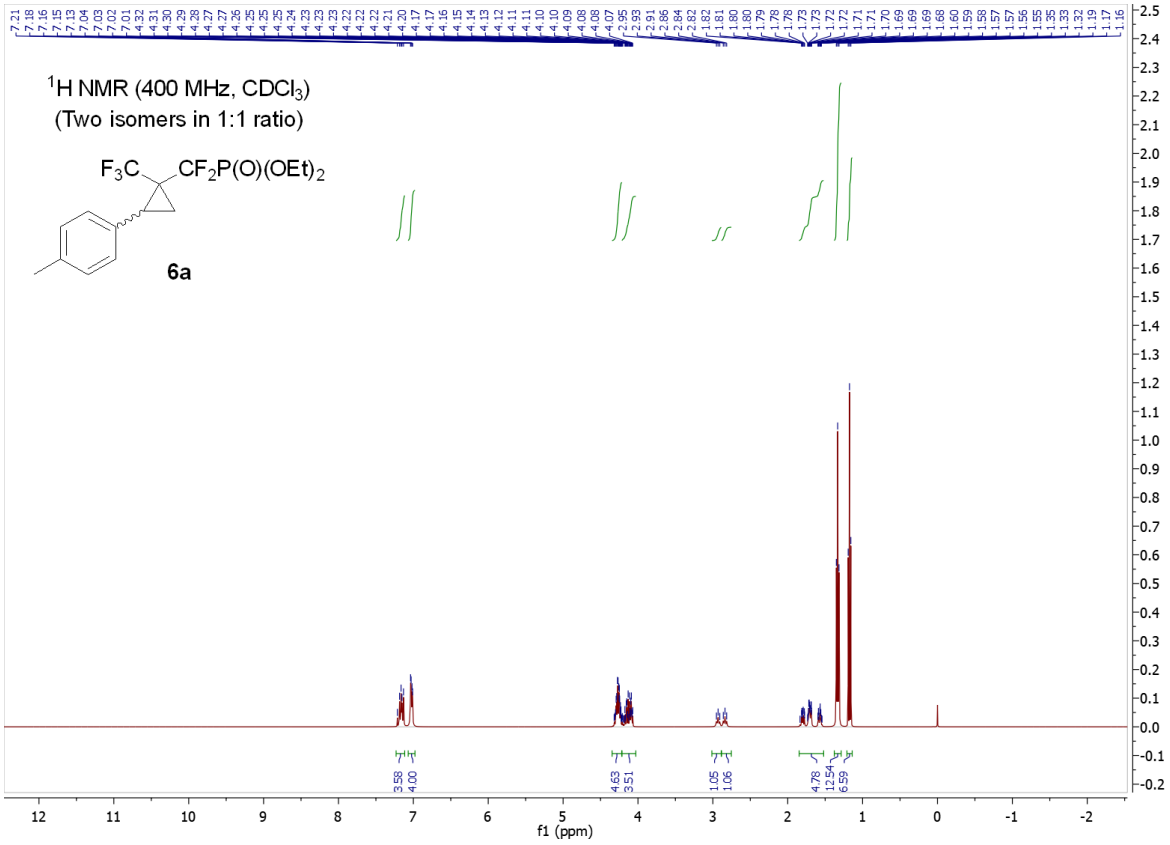

^{31}P {^{1}H} (161 MHz, CDCl$_3$)
N$_2$
F$_3$C
CF$_2$P(O)(OEt)$_2$
5
f1 (ppm)

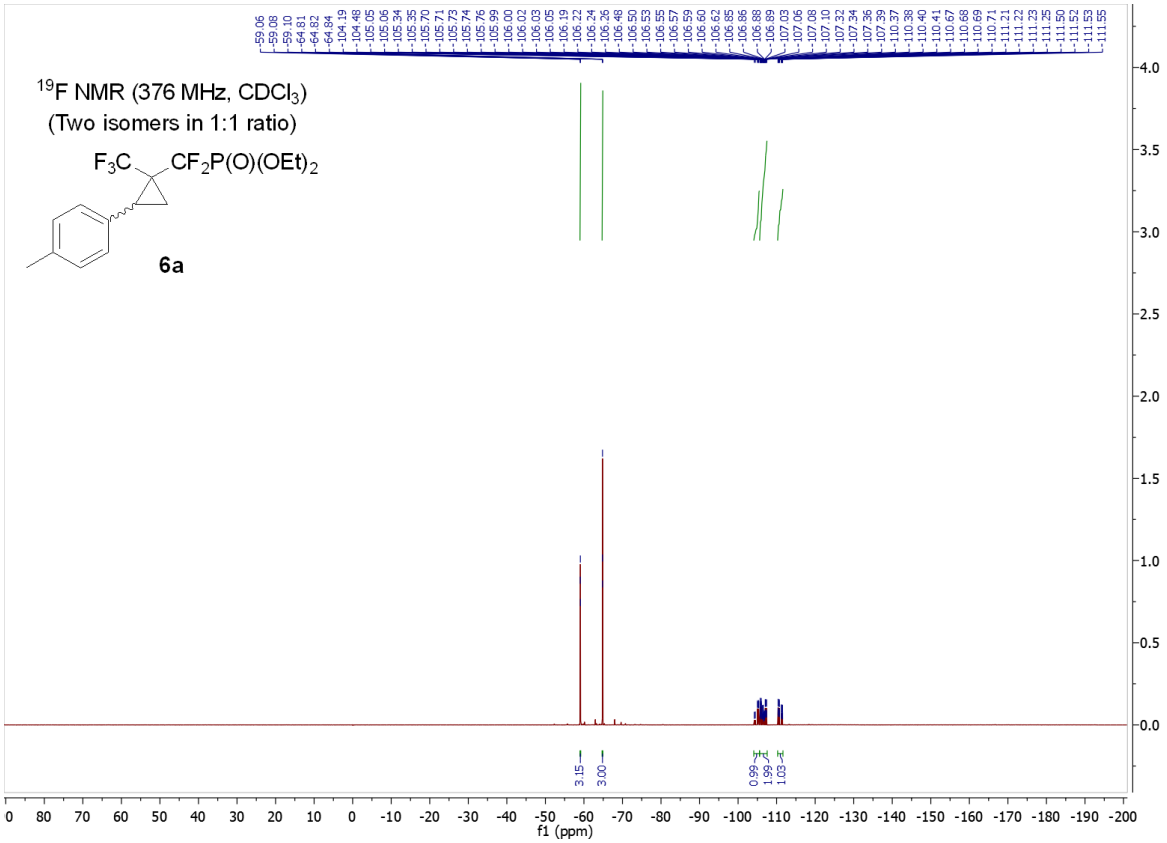

^{1}H NMR (400 MHz, CDCl$_3$)
(Major isomer)
F$_3$C
CF$_2$P(O)(OEt)$_2$
6a
f1 (ppm)

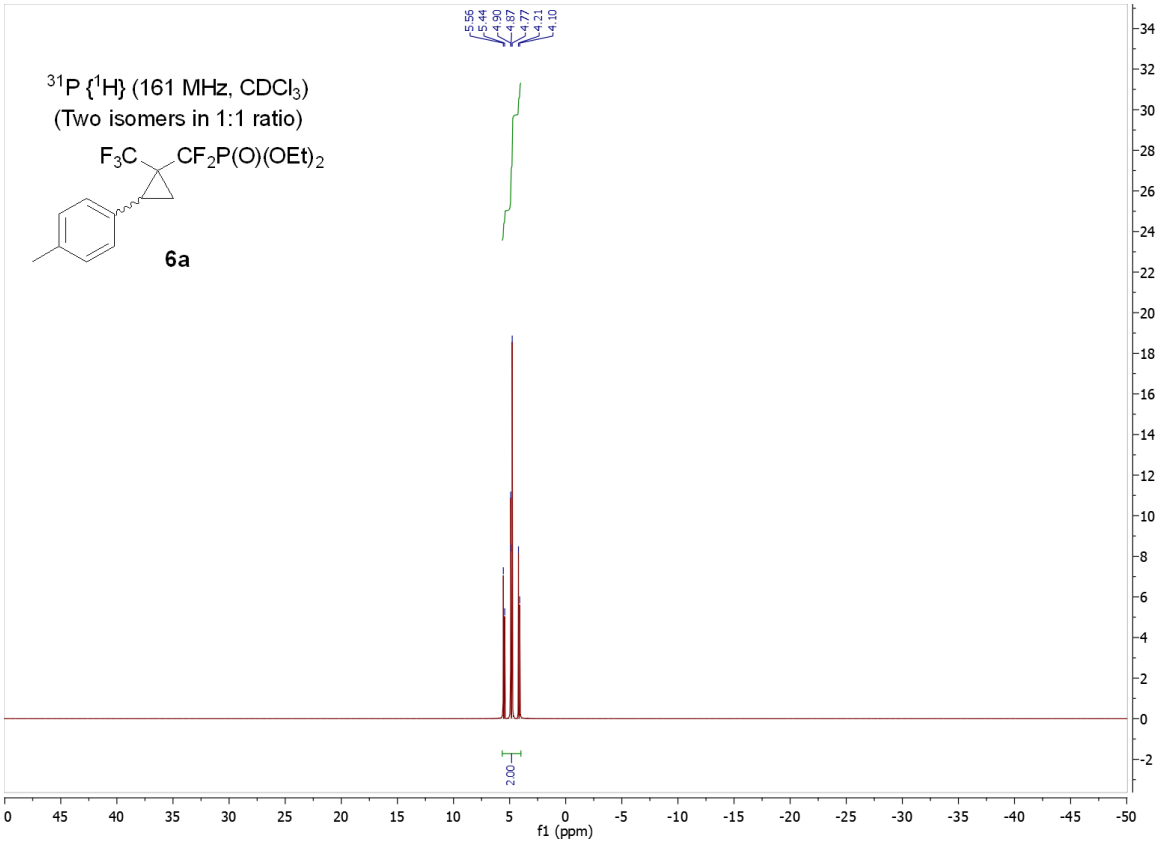

^{13}C NMR (100 MHz, $CDCl_3$)
F_3C $CF_2P(O)(OEt)_2$
6a
f1 (ppm)

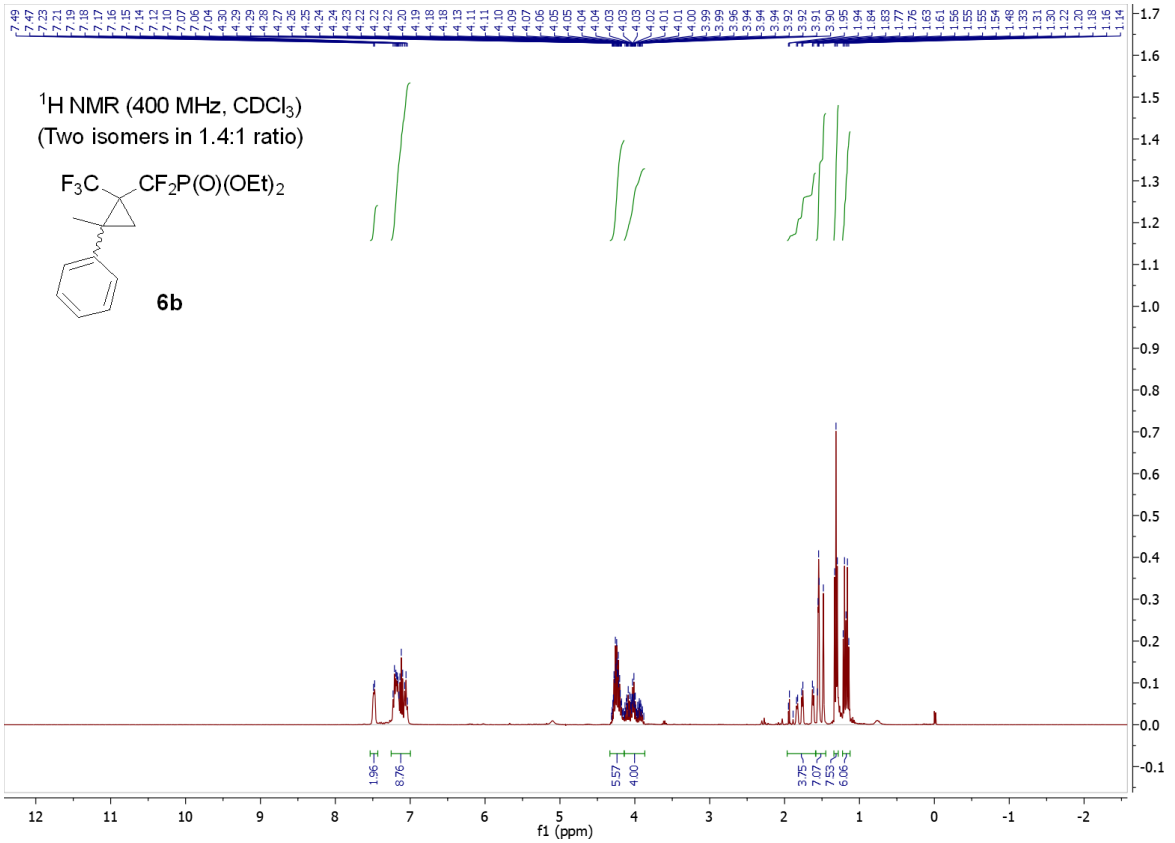

^{19}F NMR (376 MHz, $CDCl_3$)
(Major isomer)
F_3C $CF_2P(O)(OEt)_2$
6a
f1 (ppm)

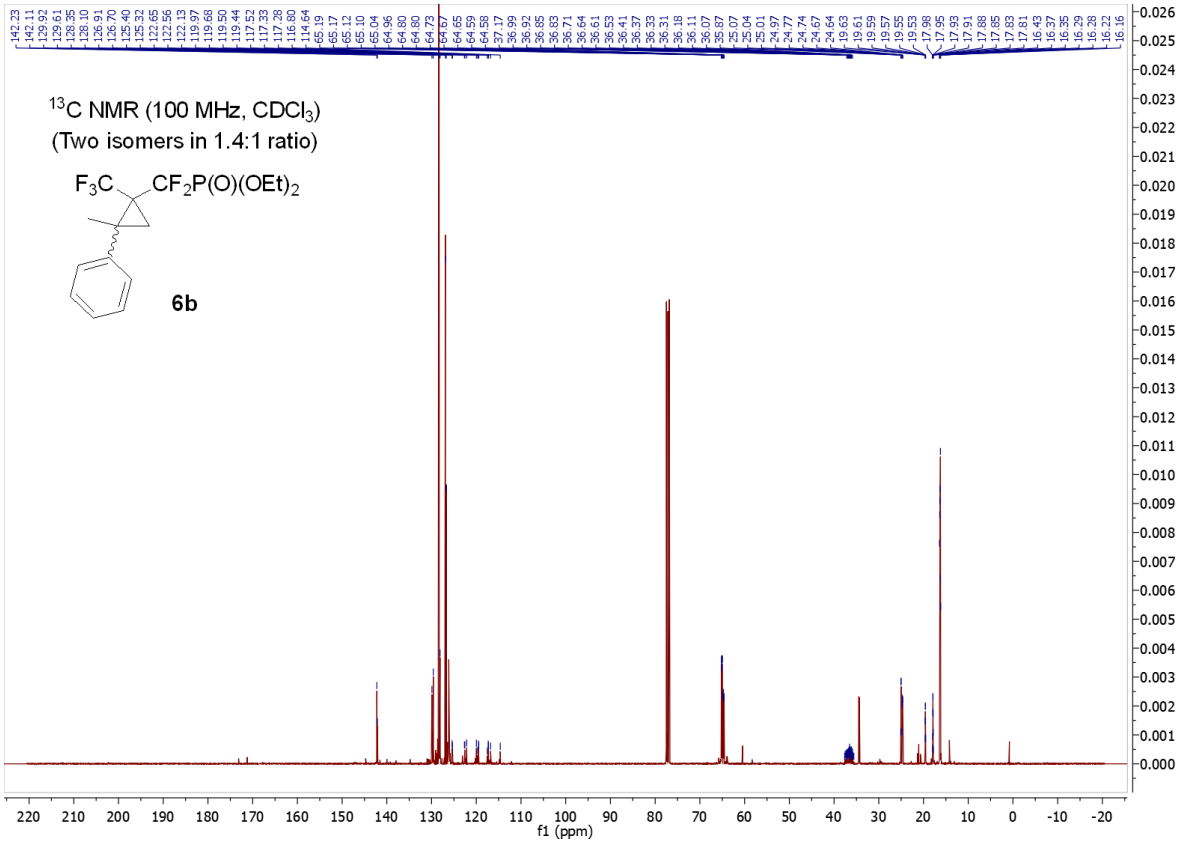

^{31}P {^{1}H} (161 MHz, CDCl$_3$)
(Major isomer)
F$_3$C
CF$_2$P(O)(OEt)$_2$
6a
f1 (ppm)

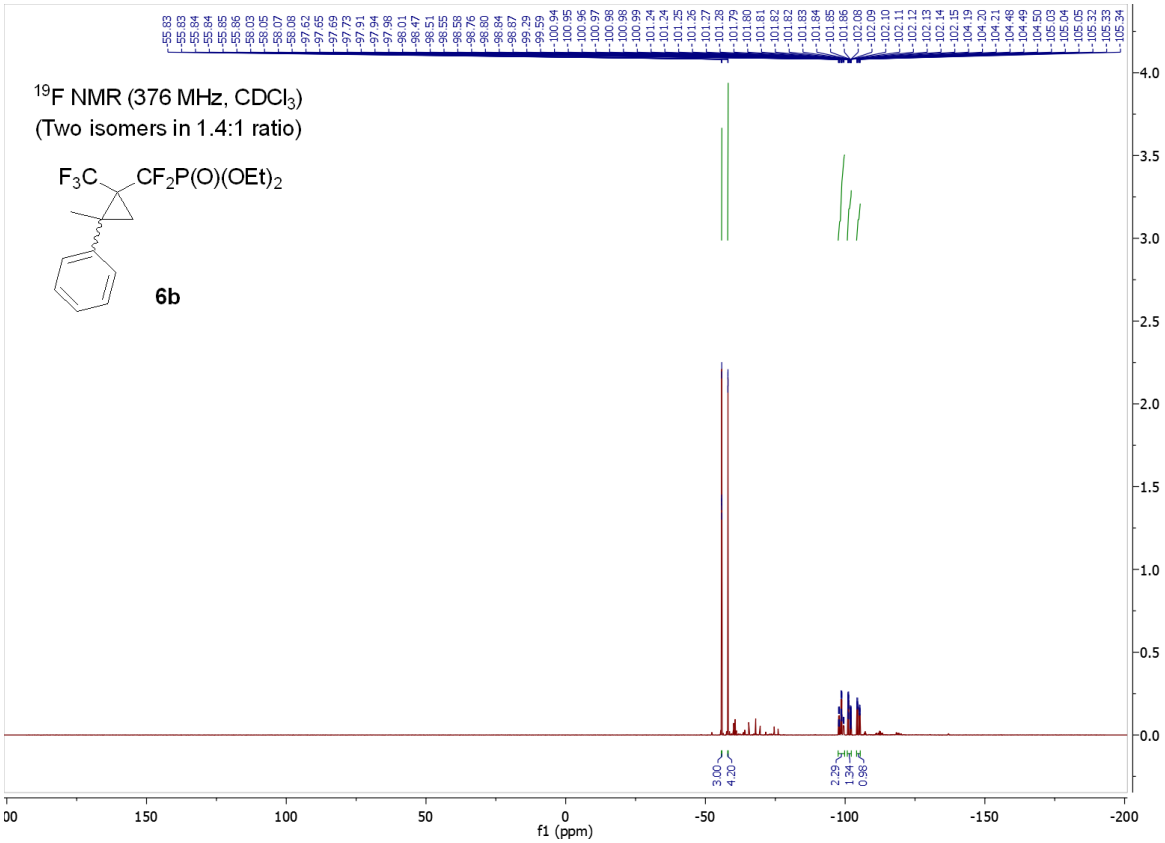

^{1}H NMR (400 MHz, CDCl$_3$)
(Two isomers in 1:1 ratio)
F$_3$C
CF$_2$P(O)(OEt)$_2$
6a
f1 (ppm)

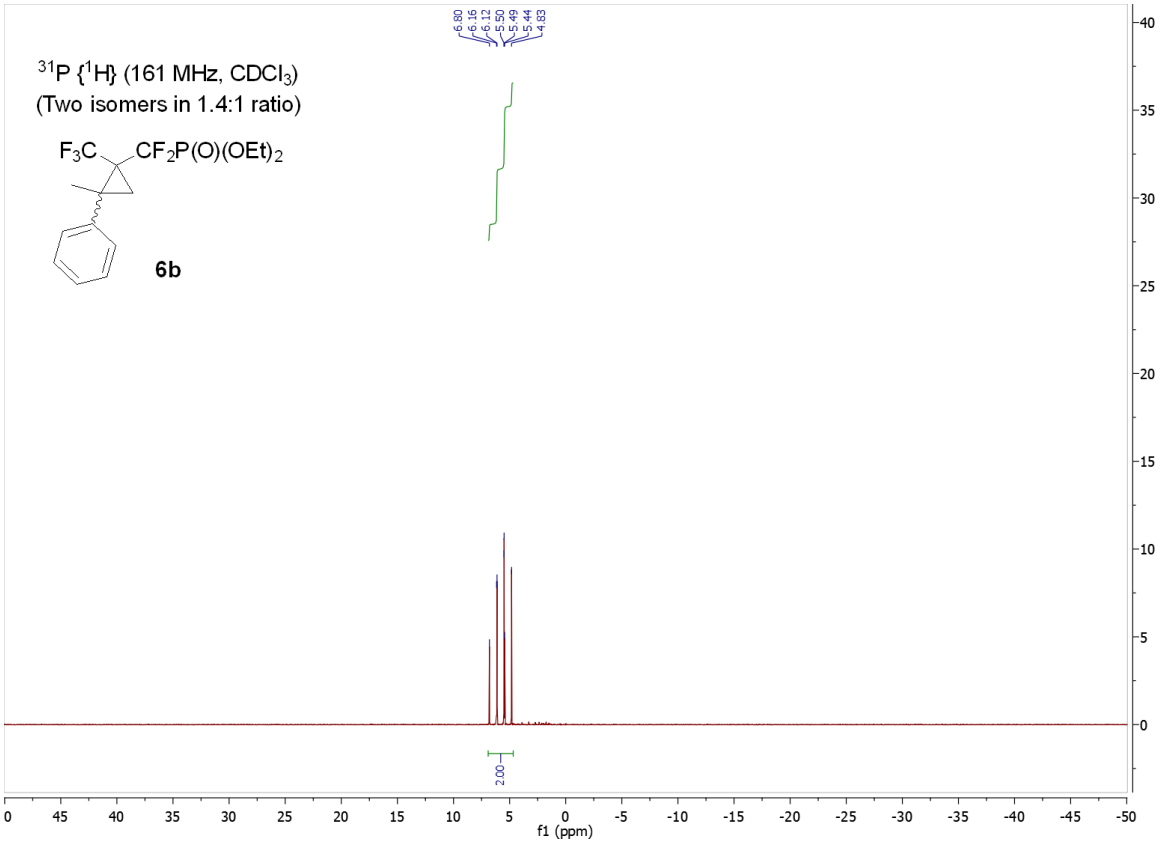

19F NMR (376 MHz, CDCl3)
(Two isomers in 1:1 ratio)
F3C
CF2P(O)(OEt)2
6a
f1 (ppm)

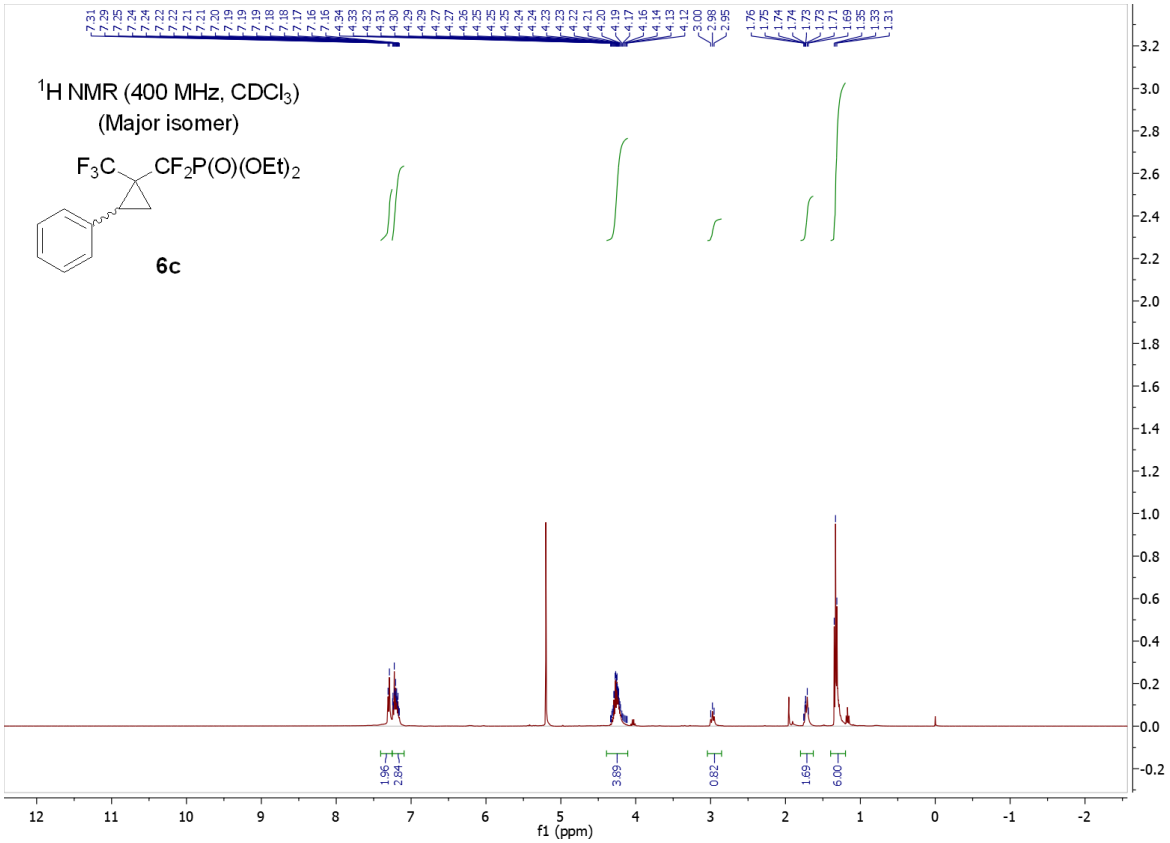

31P {1H} (161 MHz, CDCl3)
(Two isomers in 1:1 ratio)
F3C
CF2P(O)(OEt)2
6a
f1 (ppm)

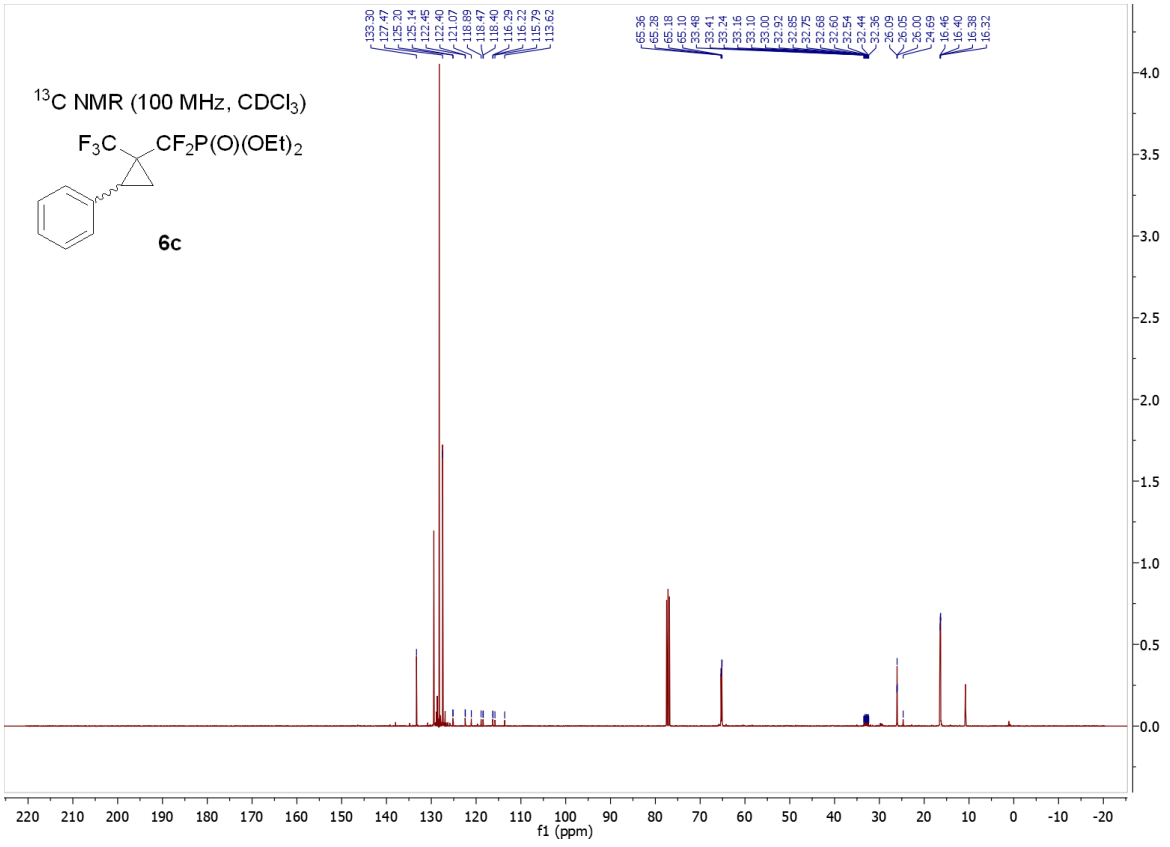

^{1}H NMR (400 MHz, $CDCl_3$)
(Two isomers in 1.4:1 ratio)
F_3C $CF_2P(O)(OEt)_2$
6b
f1 (ppm)

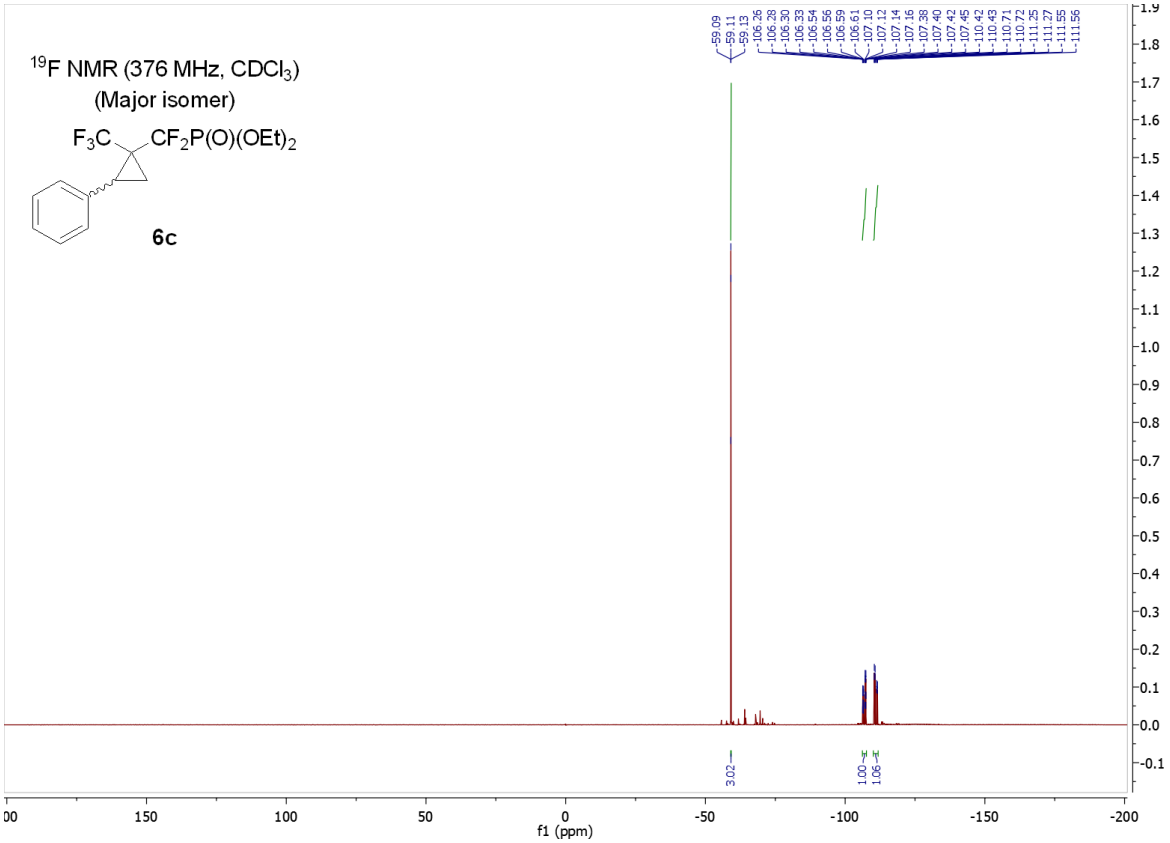

^{13}C NMR (100 MHz, $CDCl_3$)
(Two isomers in 1.4:1 ratio)
F_3C $CF_2P(O)(OEt)_2$
6b
f1 (ppm)

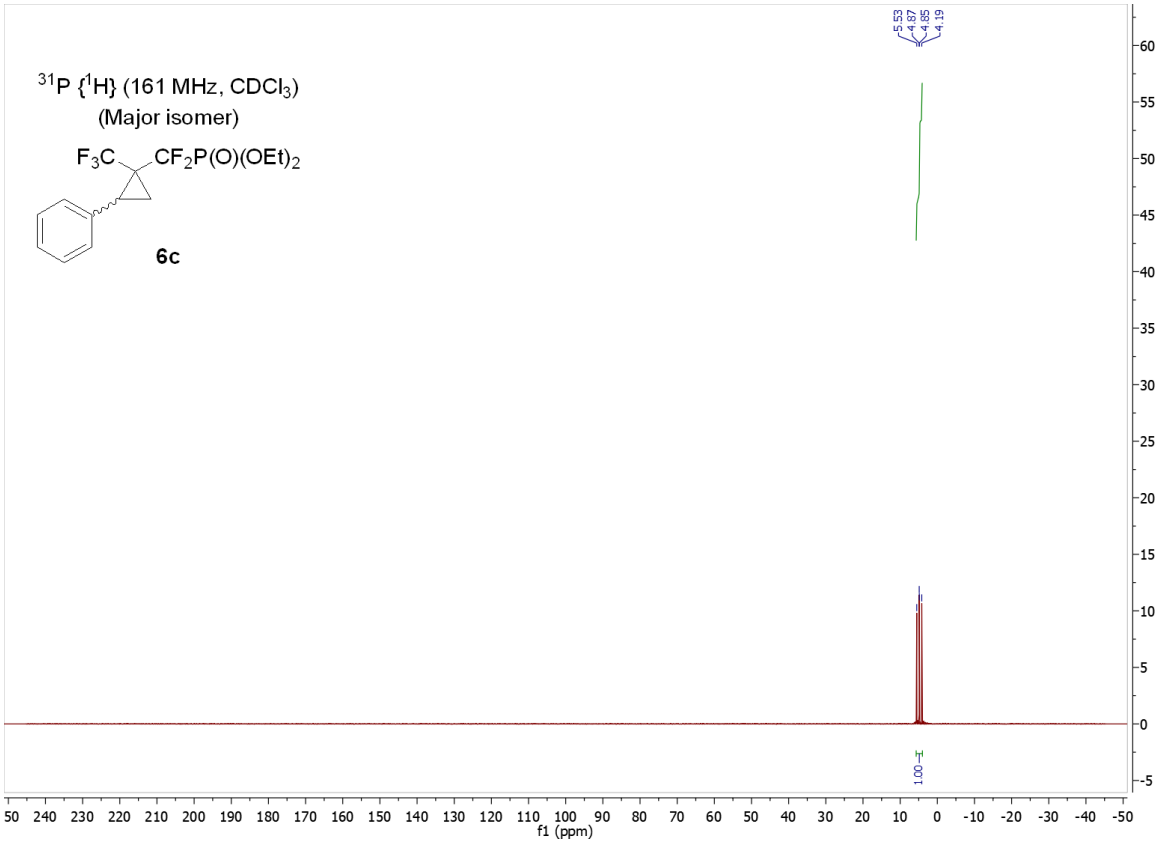

19F NMR (376 MHz, CDCl3)
(Two isomers in 1.4:1 ratio)
F3C
CF2P(O)(OEt)2
6b
f1 (ppm)

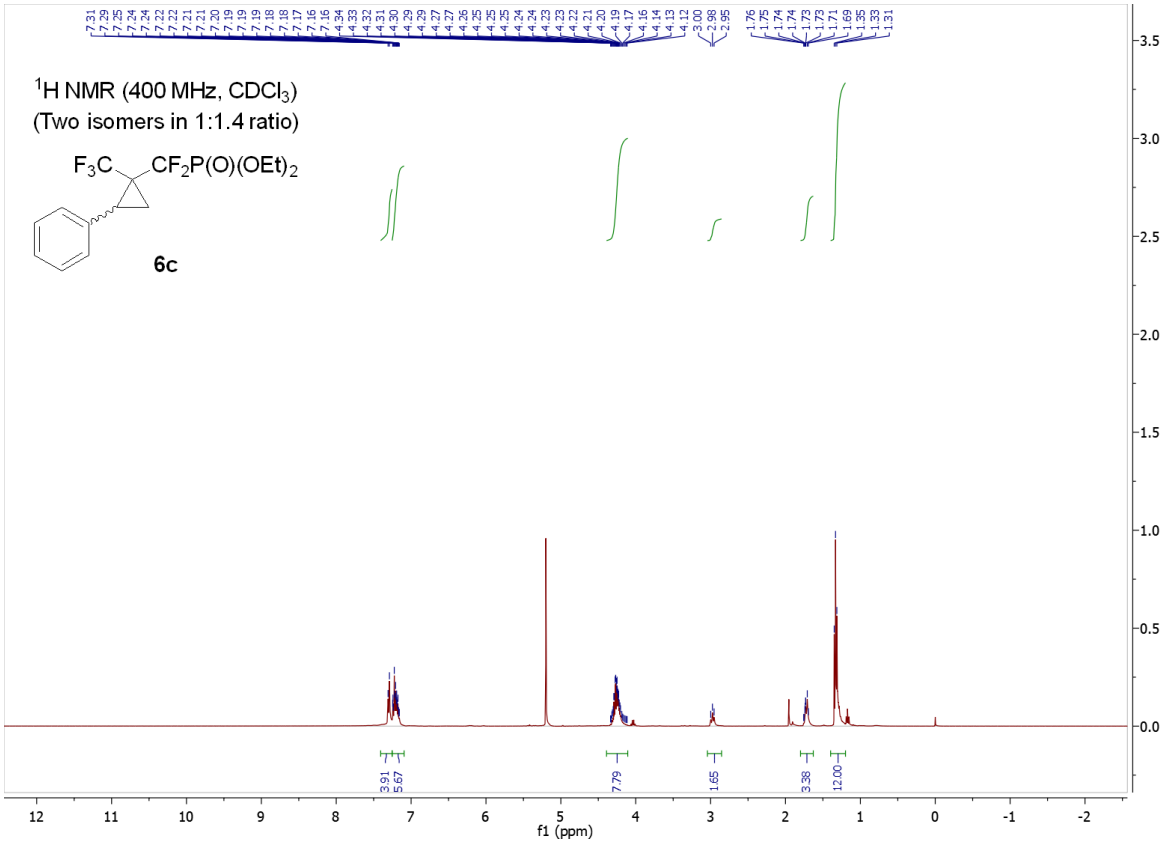

31P {1H} (161 MHz, CDCl3)
(Two isomers in 1.4:1 ratio)
F3C
CF2P(O)(OEt)2
6b
f1 (ppm)

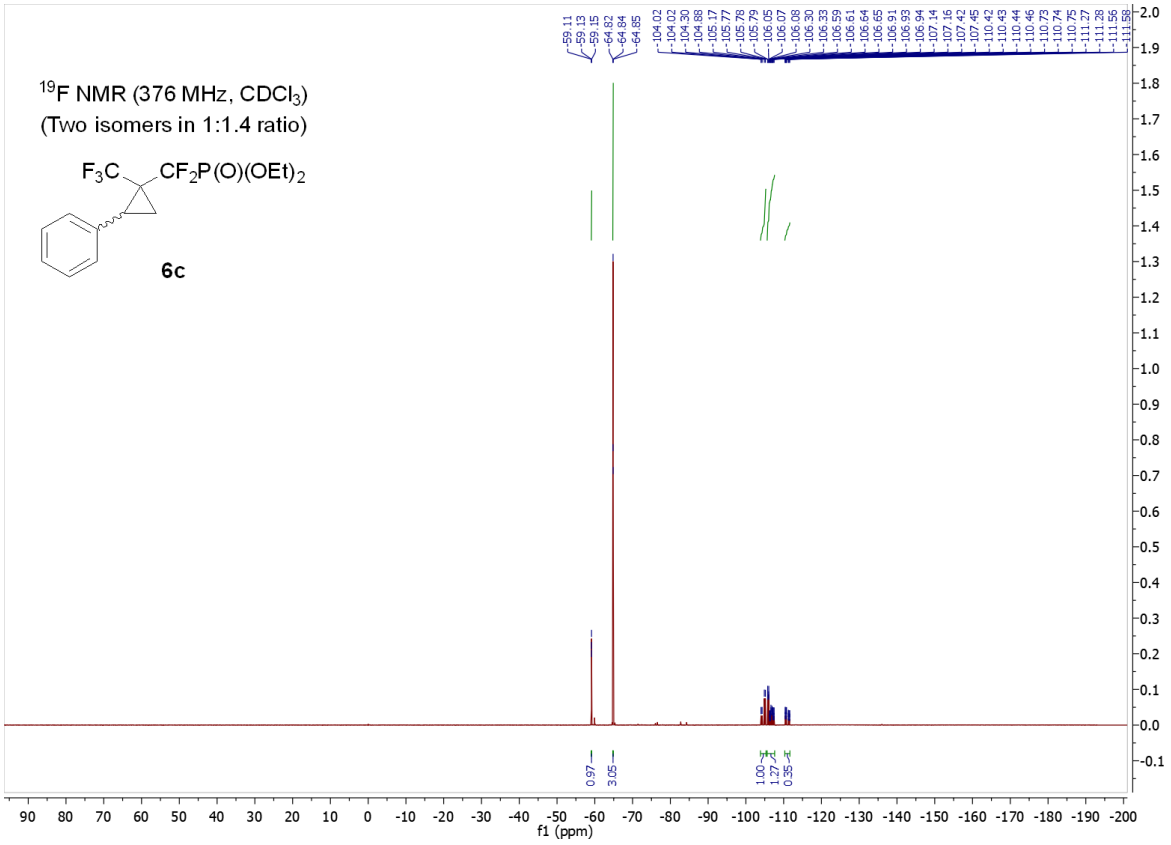

^{1}H NMR (400 MHz, $CDCl_3$)
(Major isomer)
F_3C $CF_2P(O)(OEt)_2$
6c
f1 (ppm)

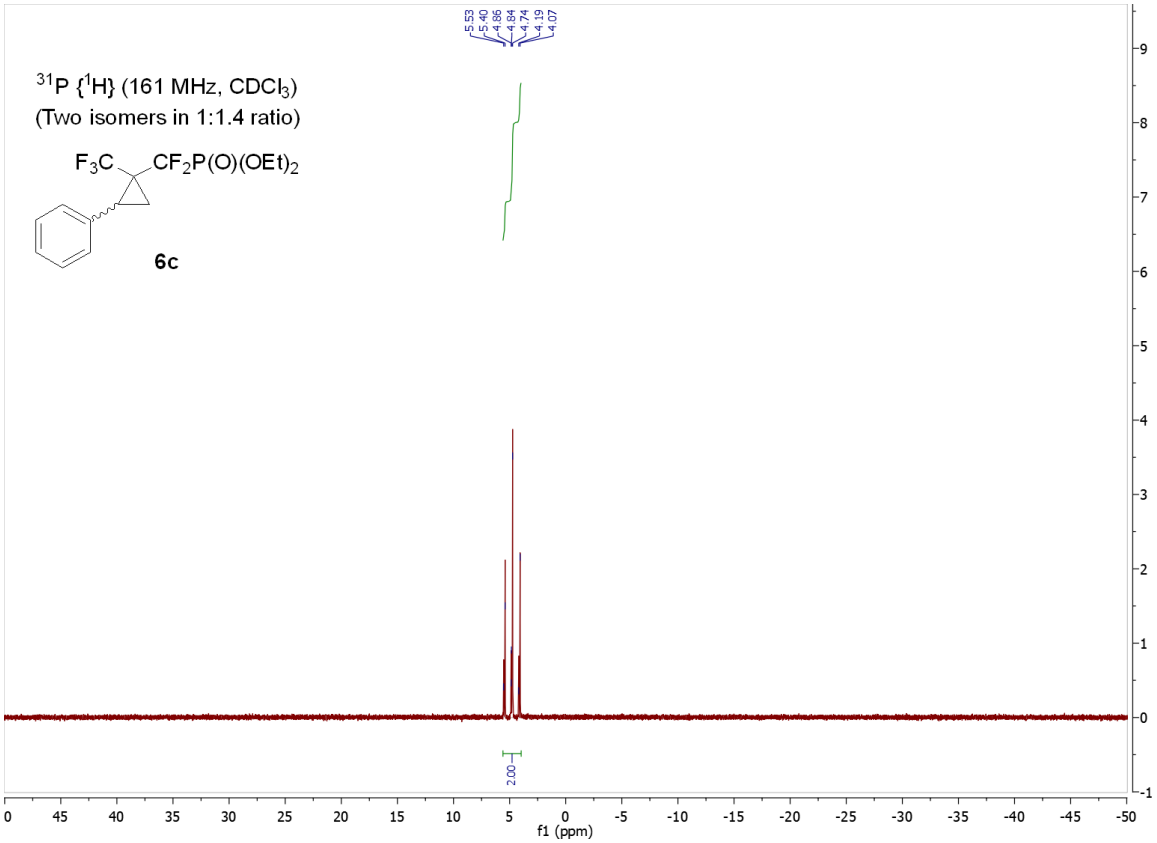

^{13}C NMR (100 MHz, $CDCl_3$)
F_3C $CF_2P(O)(OEt)_2$
6c
f1 (ppm)

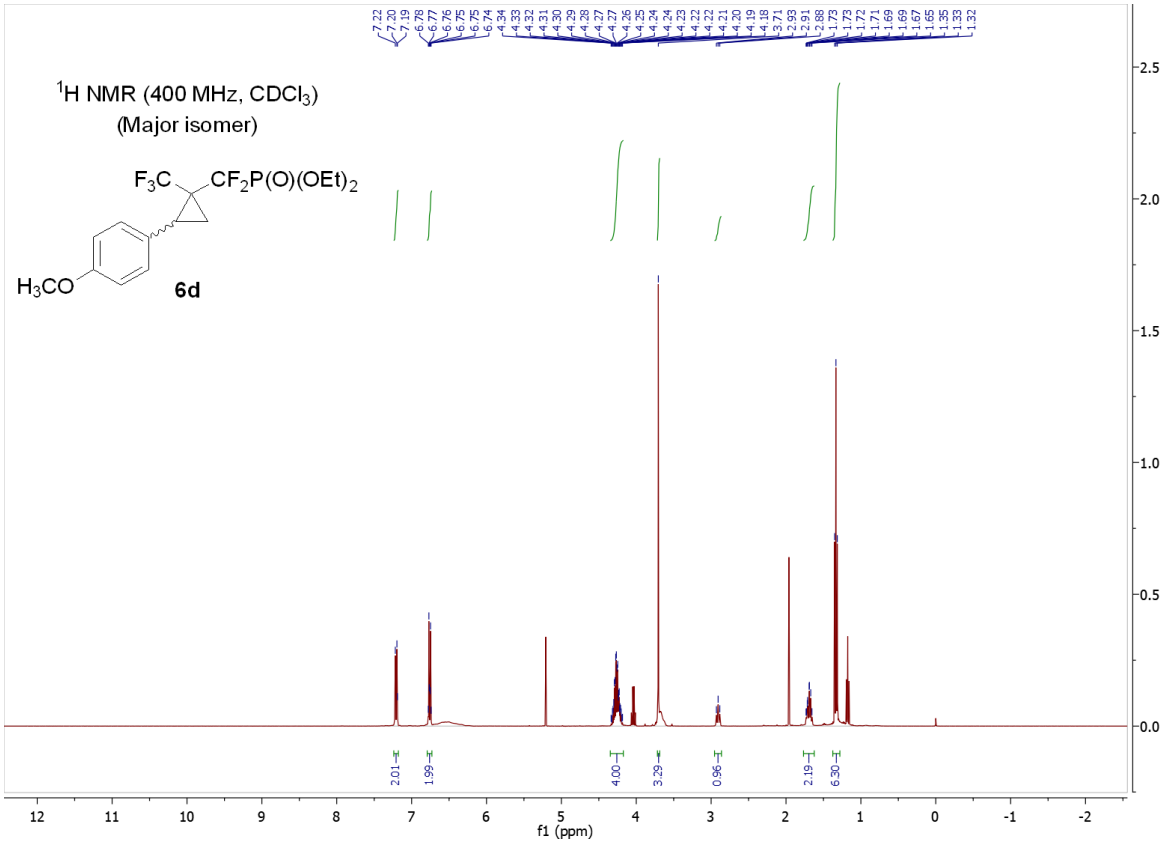

^{19}F NMR (376 MHz, $CDCl_3$)
(Major isomer)
F_3C
$CF_2P(O)(OEt)_2$
6c
f1 (ppm)

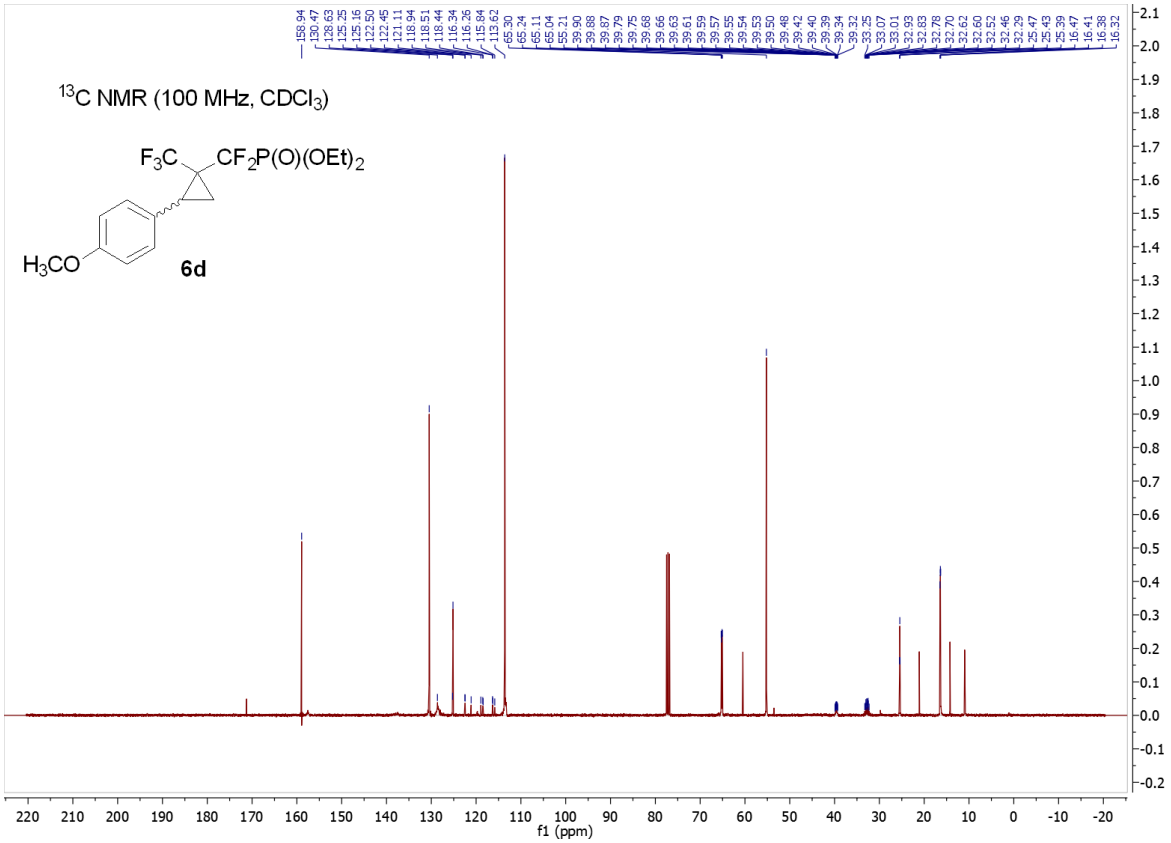

^{31}P {^{1}H} (161 MHz, $CDCl_3$)
(Major isomer)
F_3C
$CF_2P(O)(OEt)_2$
6c
f1 (ppm)


^{1}H NMR (400 MHz, $CDCl_3$)
(Two isomers in 1:1.4 ratio)
F_3C $CF_2P(O)(OEt)_2$
6c
f1 (ppm)


^{19}F NMR (376 MHz, $CDCl_3$)
(Two isomers in 1:1.4 ratio)
F_3C $CF_2P(O)(OEt)_2$
6c
f1 (ppm)


31P {1H} (161 MHz, CDCl3)
(Two isomers in 1:1.4 ratio)
F3C
CF2P(O)(OEt)2
6c
f1 (ppm)


1H NMR (400 MHz, CDCl3)
(Major isomer)
F3C
CF2P(O)(OEt)2
H3CO
6d
f1 (ppm)


158.94
130.47
128.63
125.25
125.16
122.50
122.45
121.11
118.94
118.51
118.44
116.34
116.26
115.84
113.62
65.30
65.24
65.11
65.04
55.21
39.90
39.88
39.87
39.79
39.75
39.68
39.66
39.63
39.61
39.59
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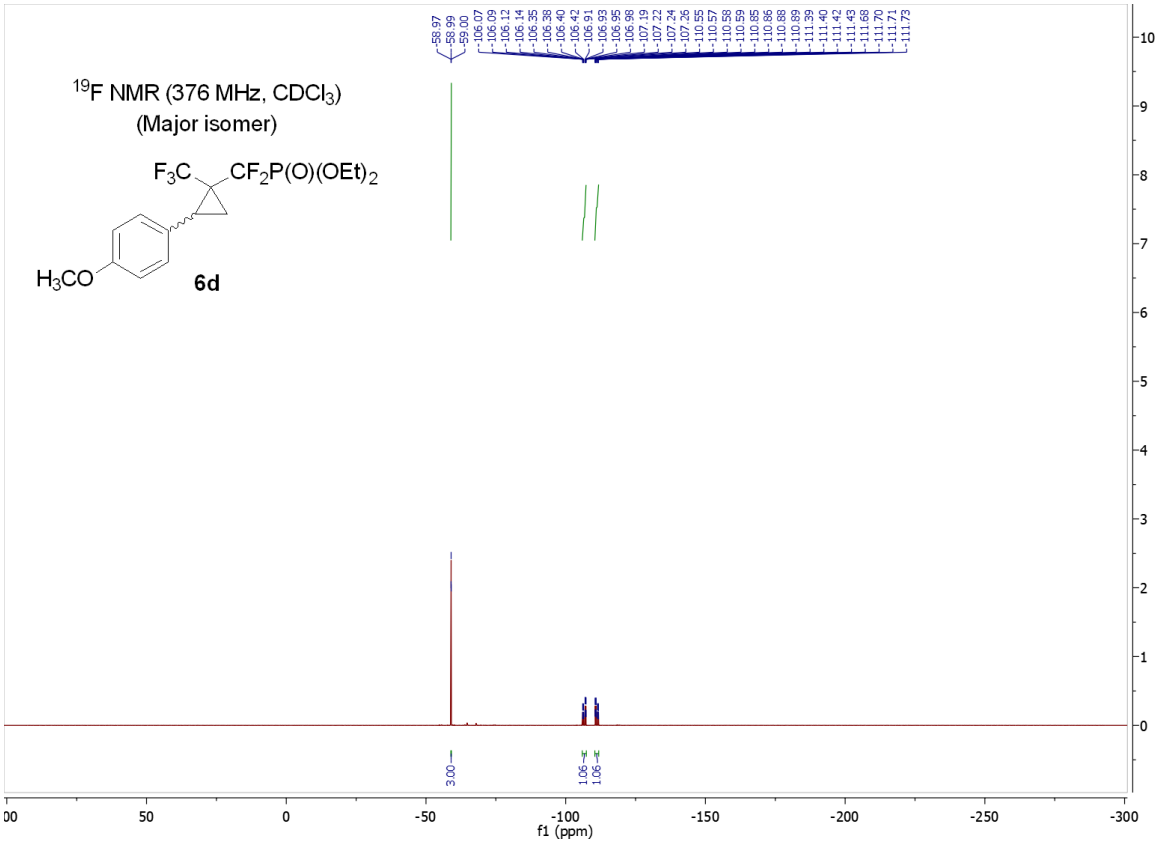
33.25
33.07
33.01
32.93
32.83
32.78
32.70
32.62
32.60
32.52
32.46
32.29
25.47
25.43
25.39
16.47
16.41
16.38
16.32
13C NMR (100 MHz, CDCl3)
F3C
CF2P(O)(OEt)2
H3CO
6d
f1 (ppm)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106.40
106.42
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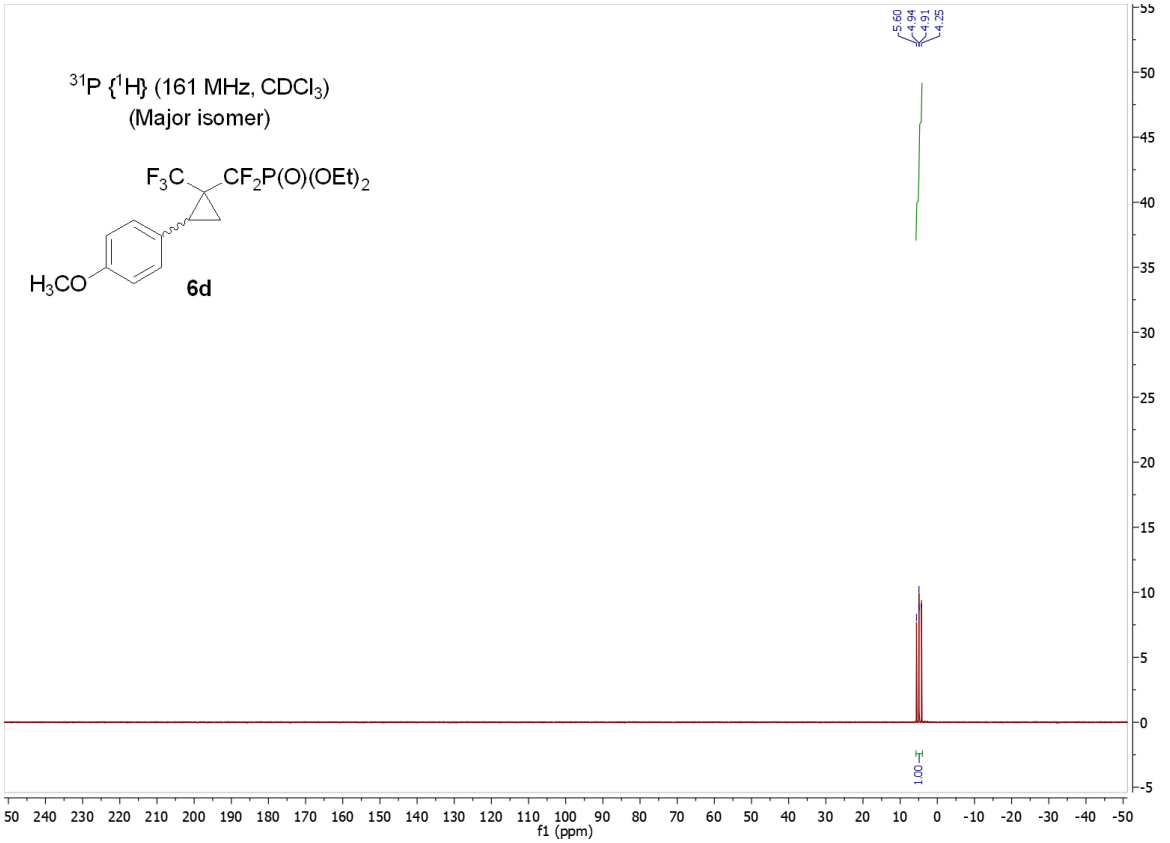
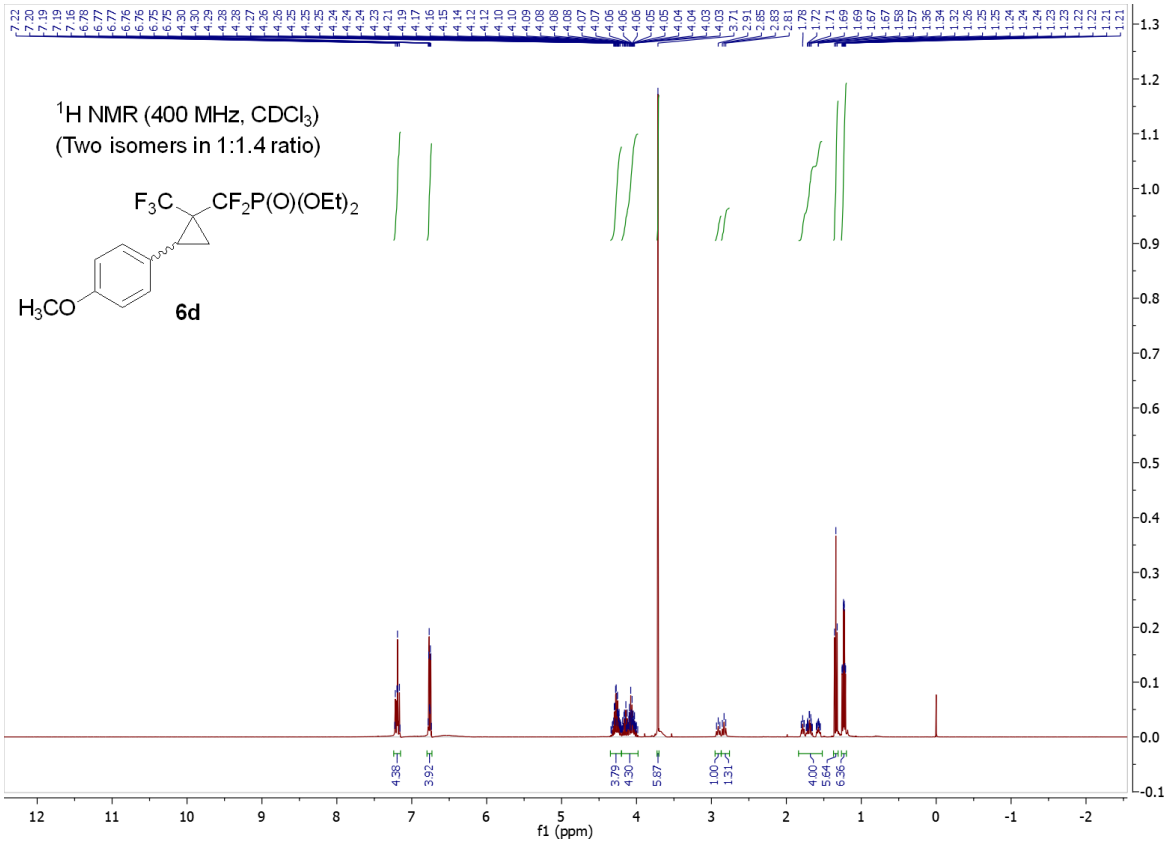
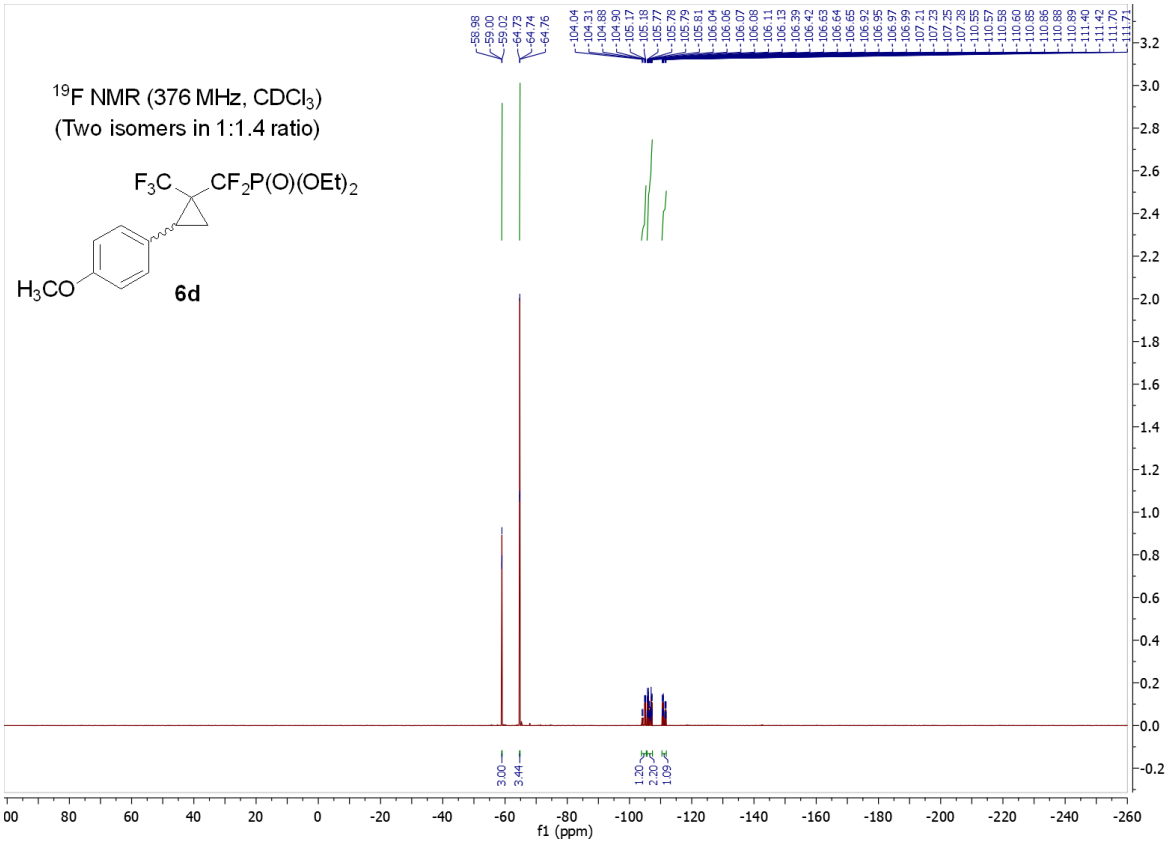
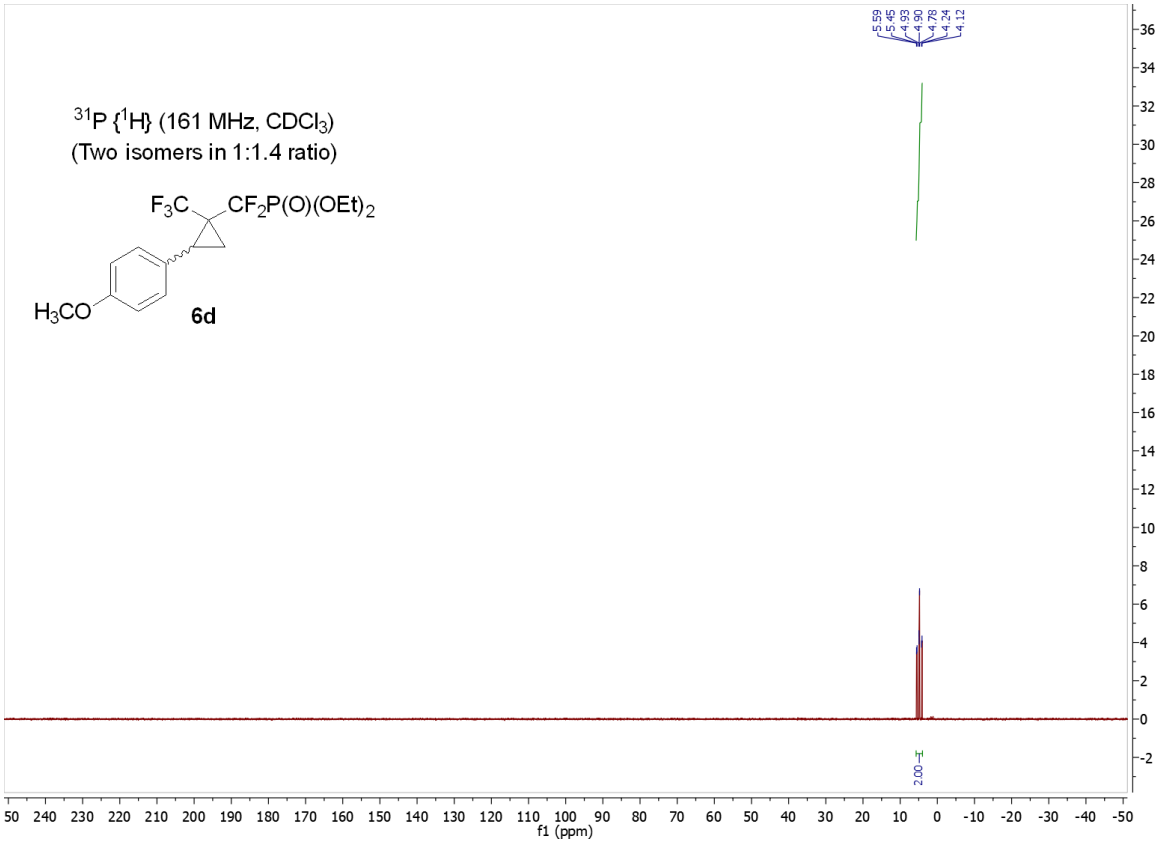
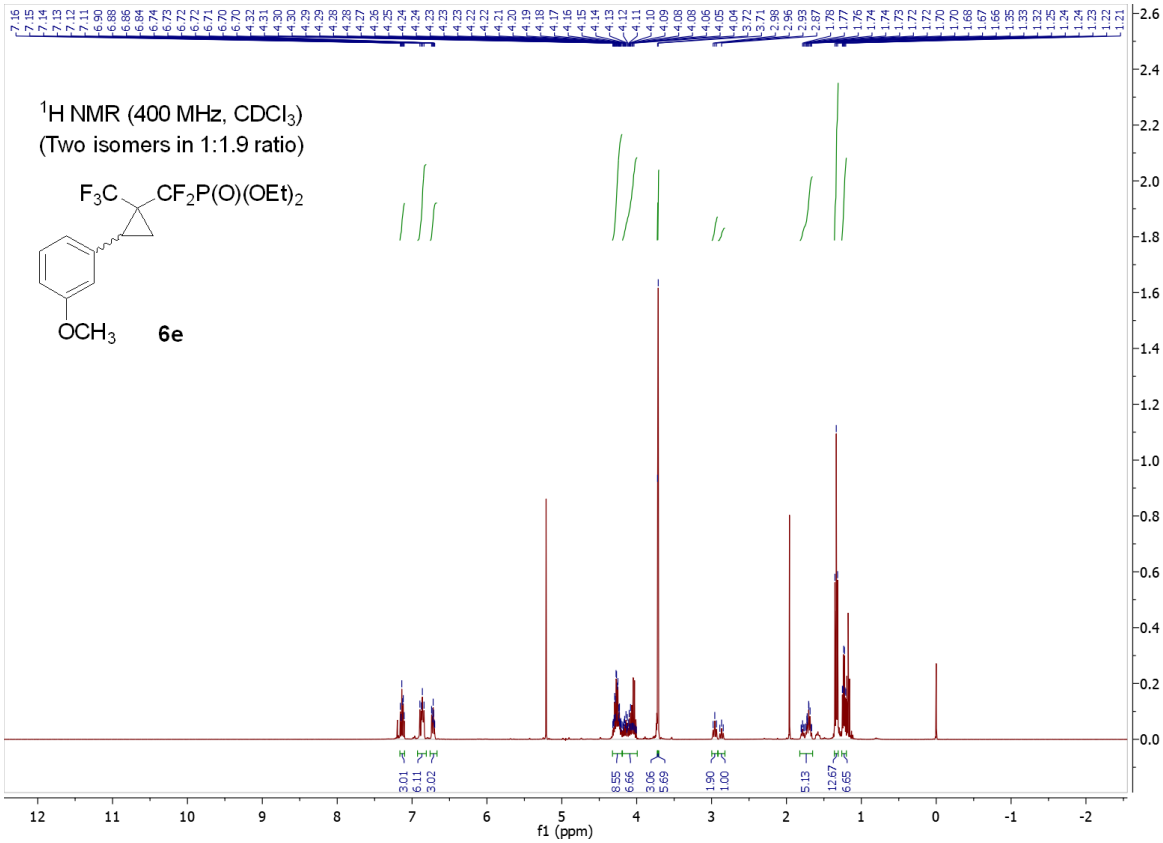
106.95
106.98
107.19
107.22
107.24
107.26
110.55
110.57
110.58
110.59
110.85
110.86
110.88
110.89
111.39
111.40
111.42
111.43
111.68
111.70
111.71
111.73
19F NMR (376 MHz, CDCl3)
(Major isomer)
F3C
CF2P(O)(OEt)2
H3CO
6d
3.00
1.06
1.06
f1 (ppm)

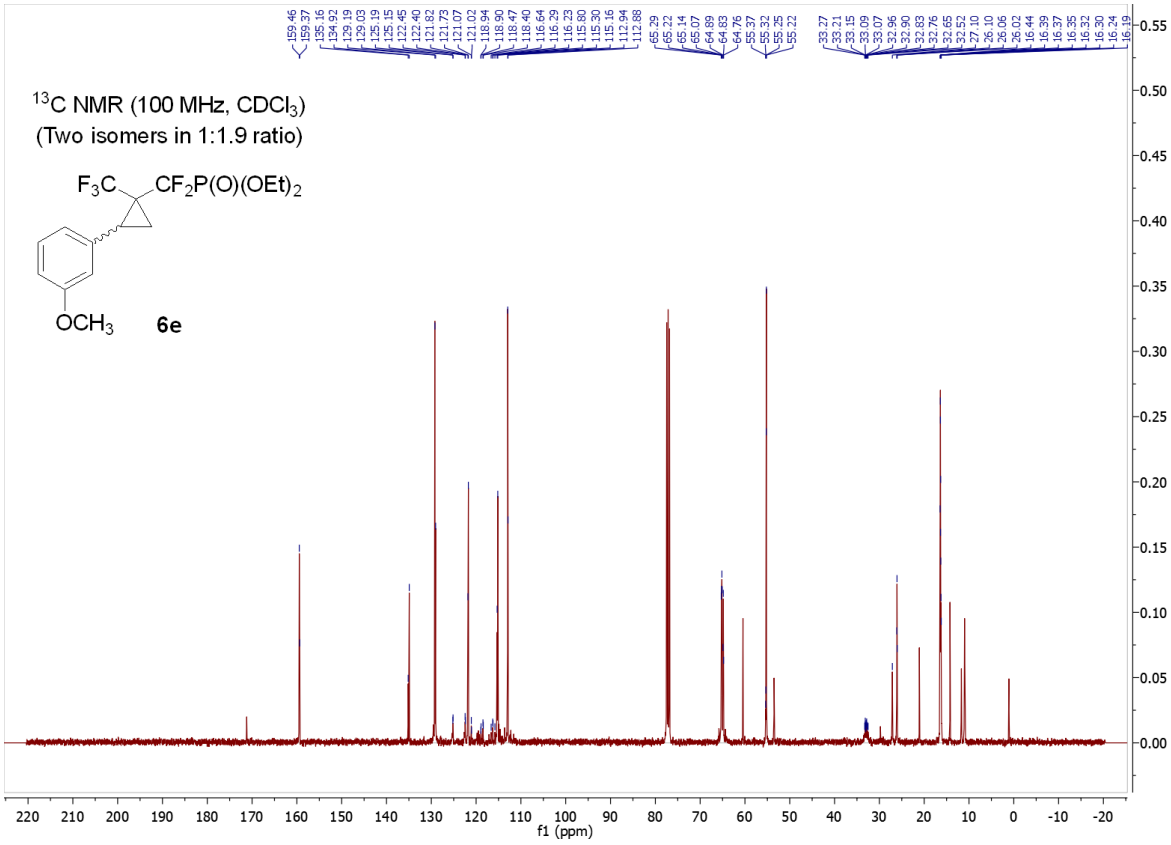

31P {1H} (161 MHz, CDCl3)
(Major isomer)
F3C
CF2P(O)(OEt)2
H3CO
6d
f1 (ppm)

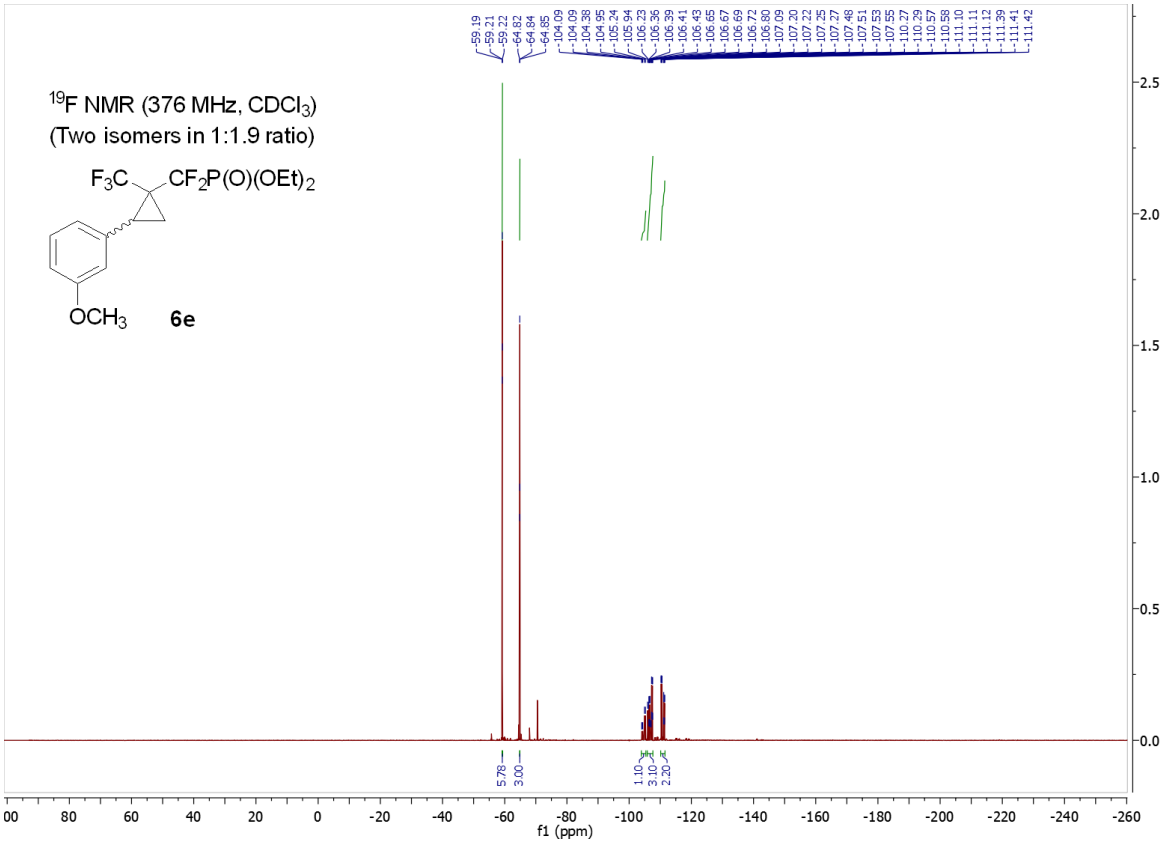

1H NMR (400 MHz, CDCl3)
(Two isomers in 1:1.4 ratio)
F3C
CF2P(O)(OEt)2
H3CO
6d
f1 (ppm)

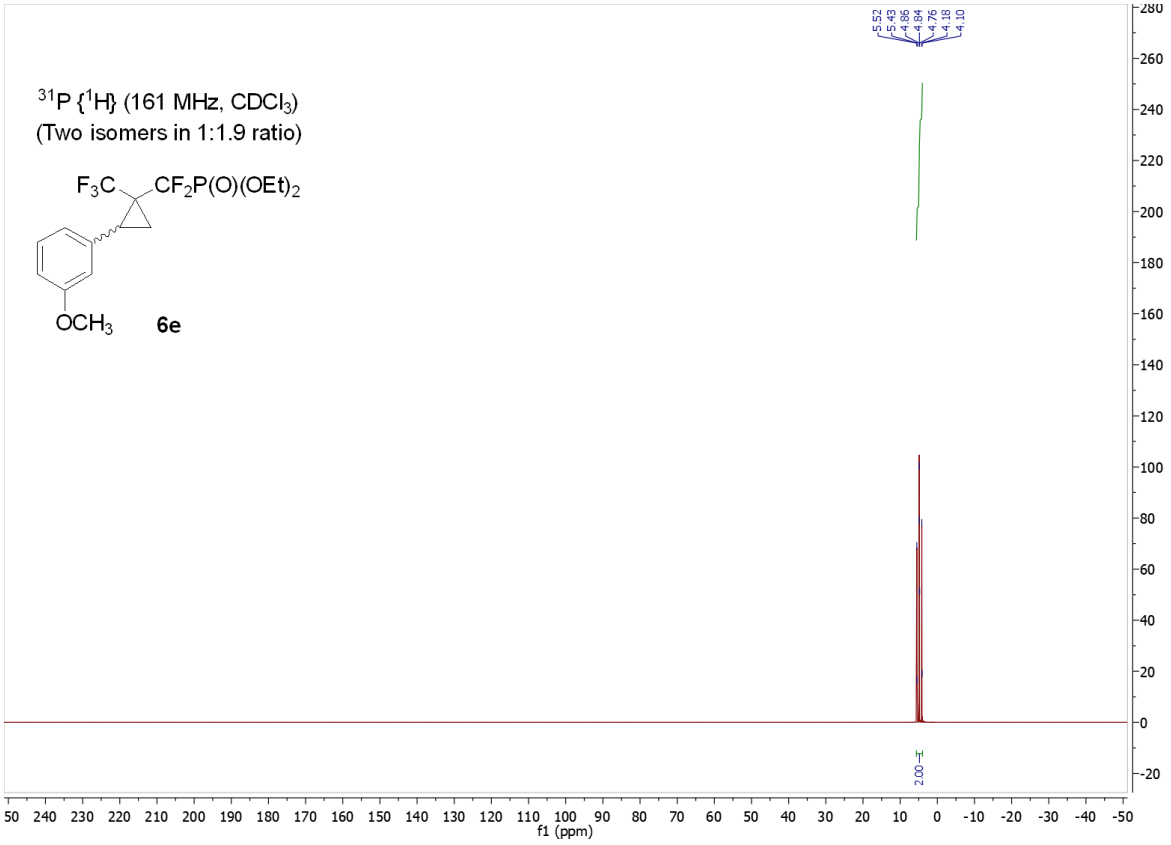

19F NMR (376 MHz, CDCl3)
(Two isomers in 1:1.4 ratio)
F3C
CF2P(O)(OEt)2
H3CO
6d
f1 (ppm)

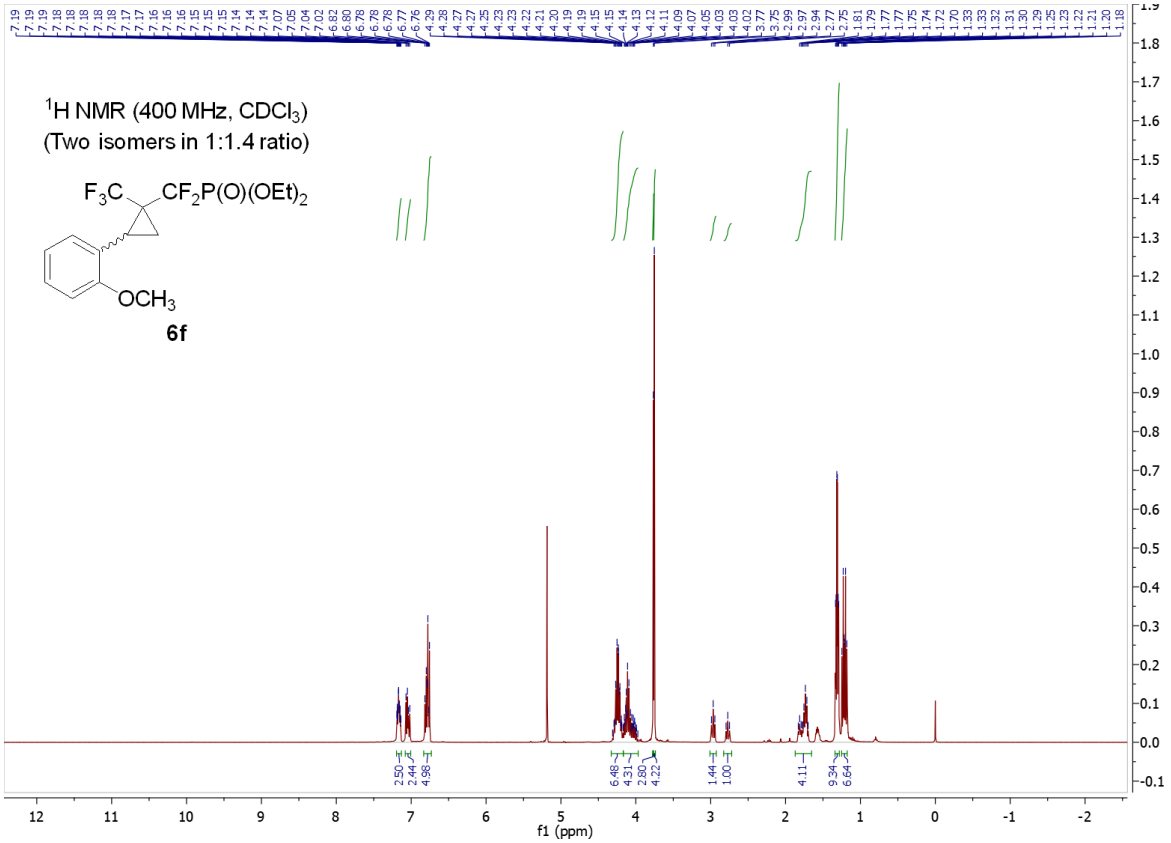

31P {1H} (161 MHz, CDCl3)
(Two isomers in 1:1.4 ratio)
F3C
CF2P(O)(OEt)2
H3CO
6d
f1 (ppm)

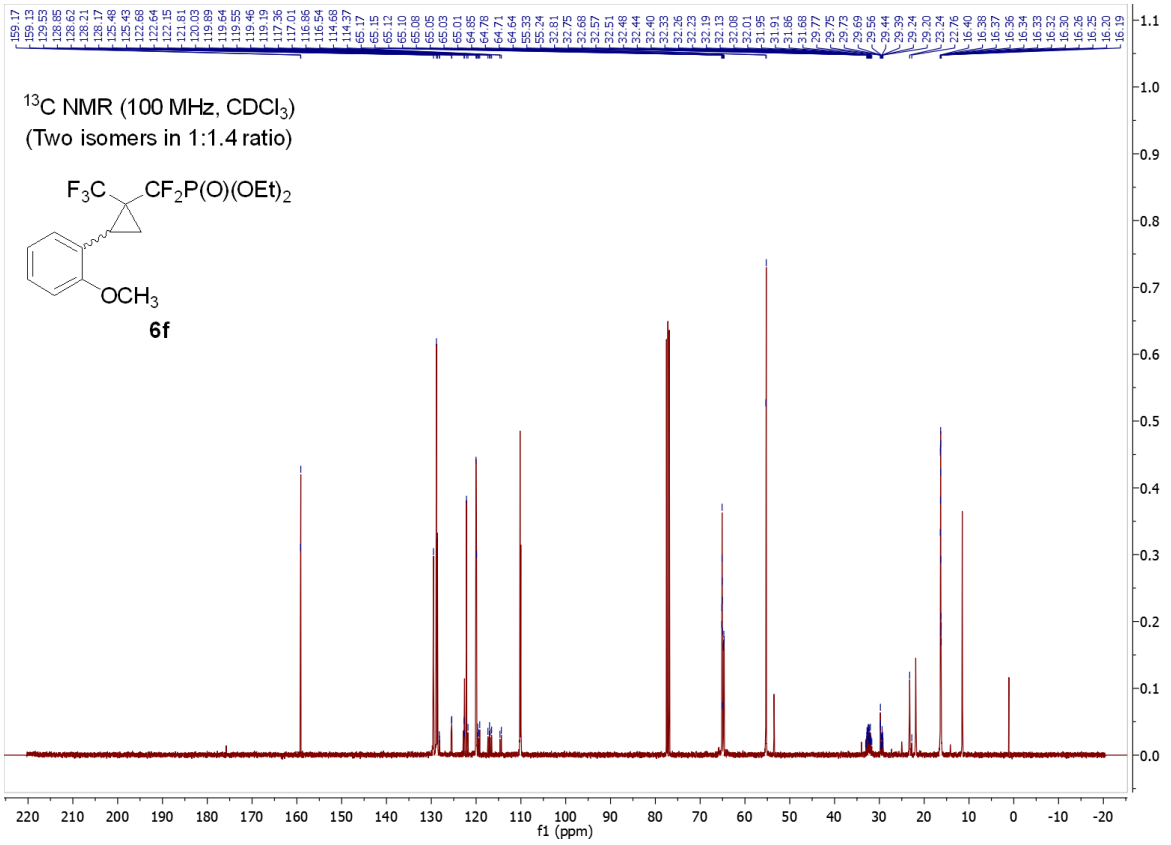

^{1}H NMR (400 MHz, $CDCl_3$)
(Two isomers in 1:1.9 ratio)
F_3C
$CF_2P(O)(OEt)_2$
OCH_3
6e
f1 (ppm)

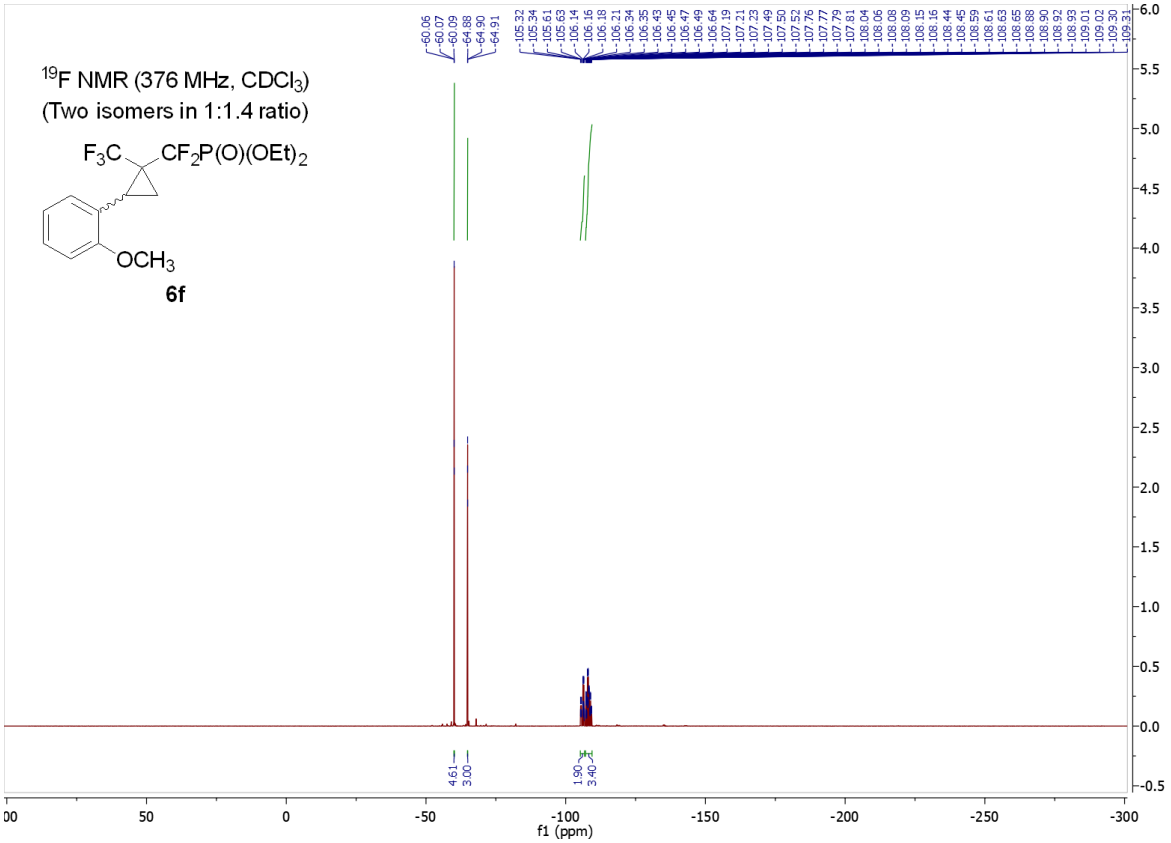

^{13}C NMR (100 MHz, $CDCl_3$)
(Two isomers in 1:1.9 ratio)
F_3C
$CF_2P(O)(OEt)_2$
OCH_3
6e
f1 (ppm)

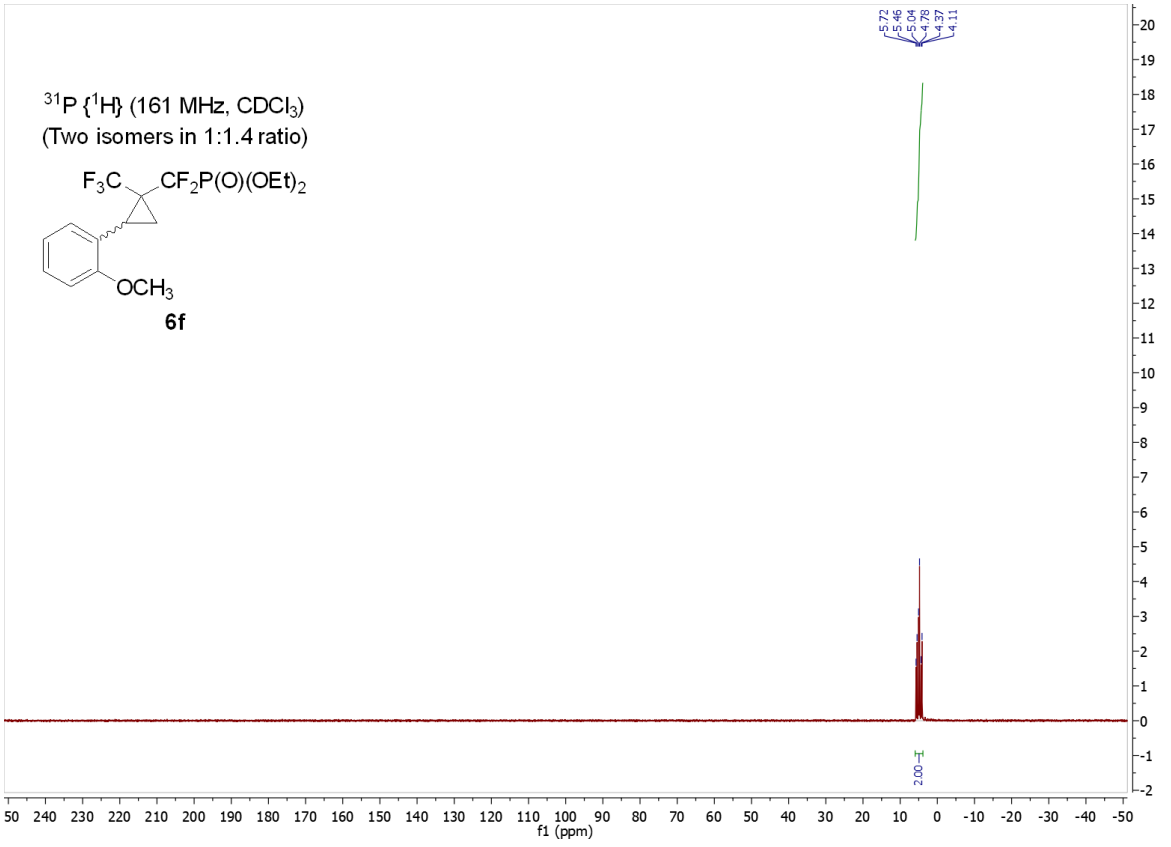

19F NMR (376 MHz, CDCl3)
(Two isomers in 1:1.9 ratio)
F3C
CF2P(O)(OEt)2
OCH3
6e
f1 (ppm)

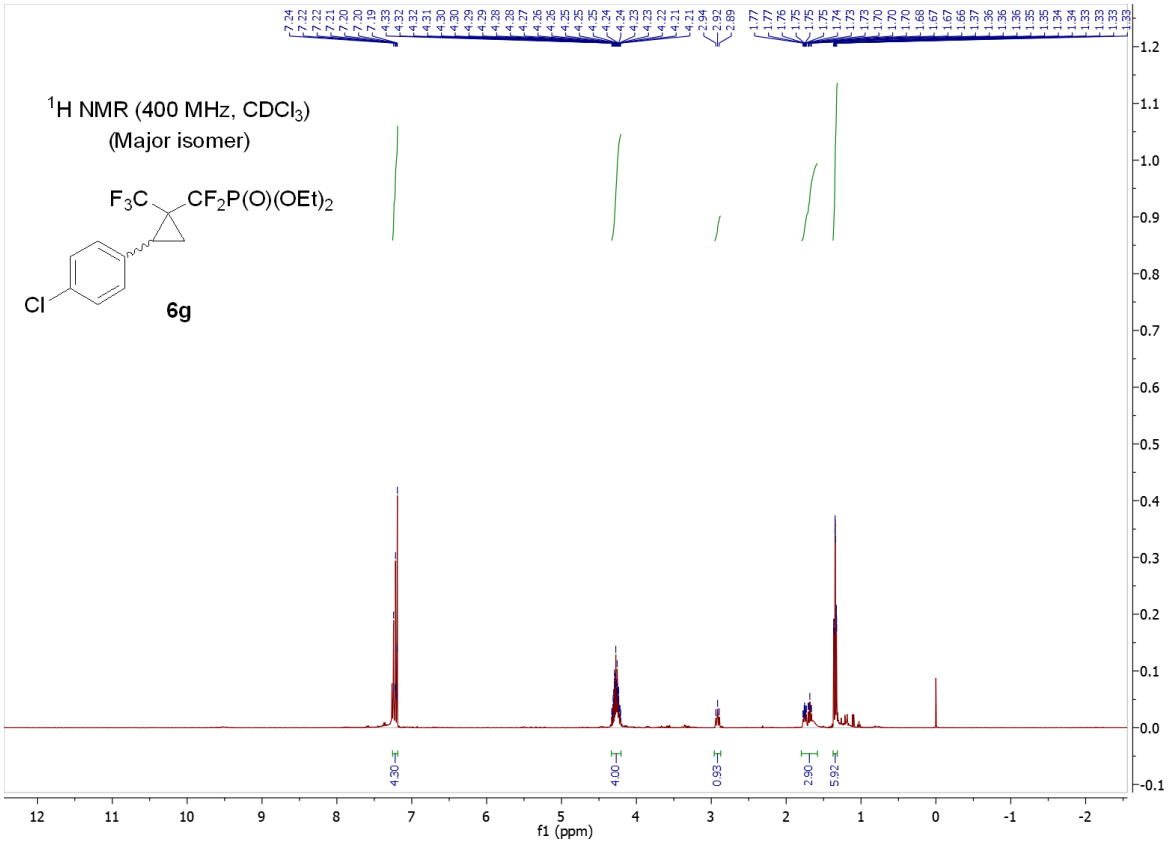

31P {1H} (161 MHz, CDCl3)
(Two isomers in 1:1.9 ratio)
F3C
CF2P(O)(OEt)2
OCH3
6e
f1 (ppm)

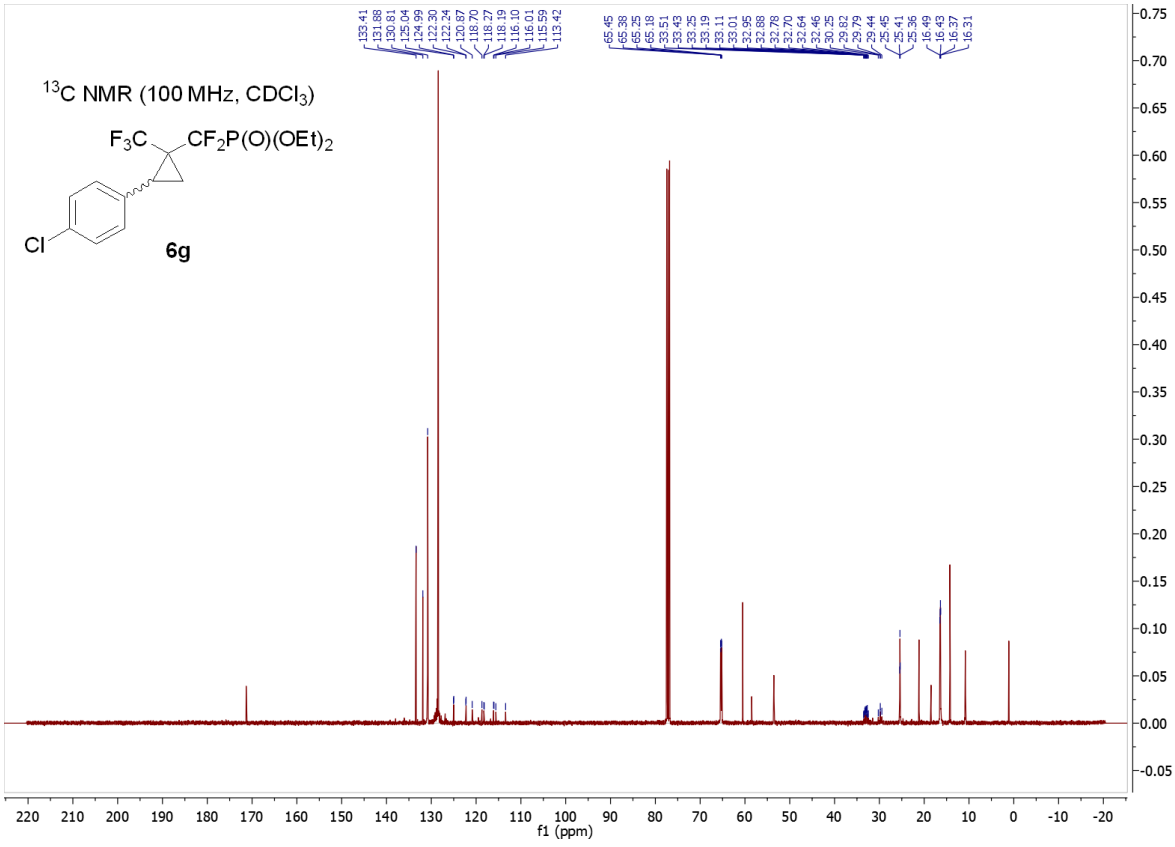

^{1}H NMR (400 MHz, $CDCl_3$)
(Two isomers in 1:1.4 ratio)
F_3C
$CF_2P(O)(OEt)_2$
OCH_3
6f
f1 (ppm)

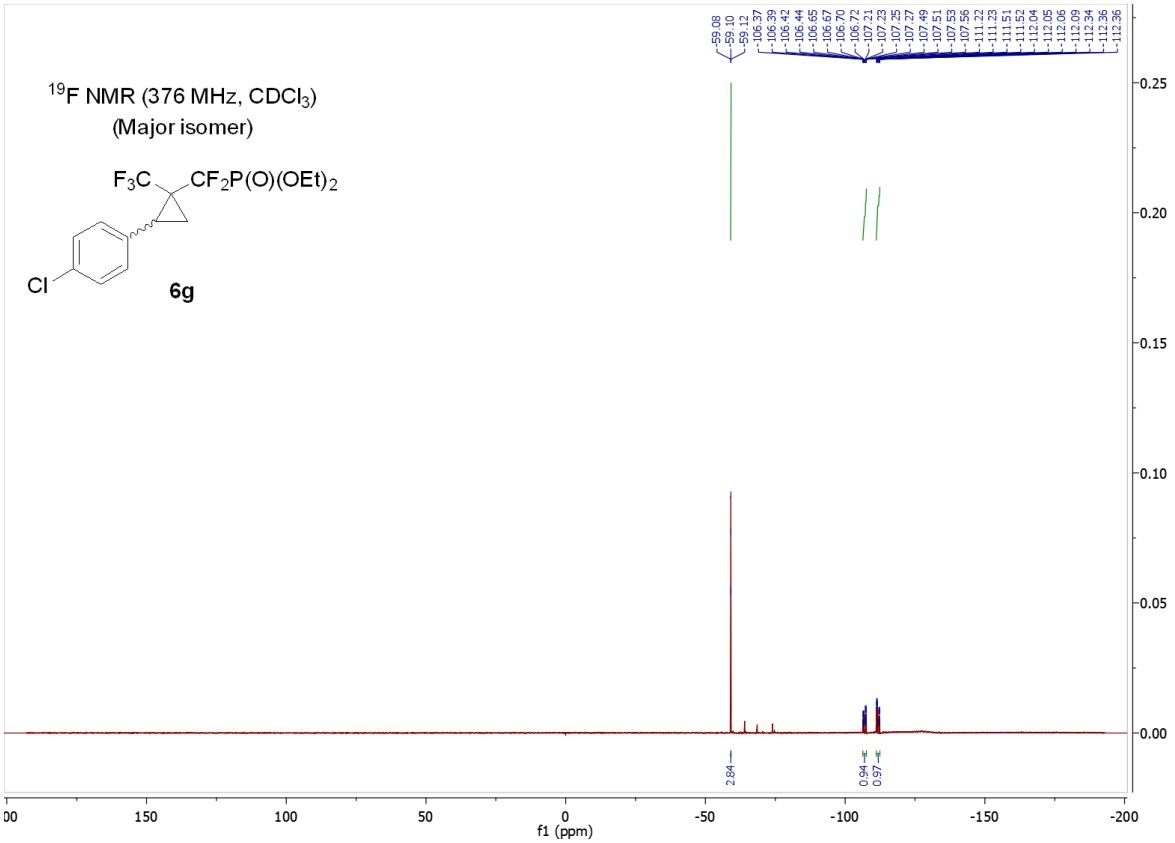

^{13}C NMR (100 MHz, $CDCl_3$)
(Two isomers in 1:1.4 ratio)
F_3C
$CF_2P(O)(OEt)_2$
OCH_3
6f
f1 (ppm)

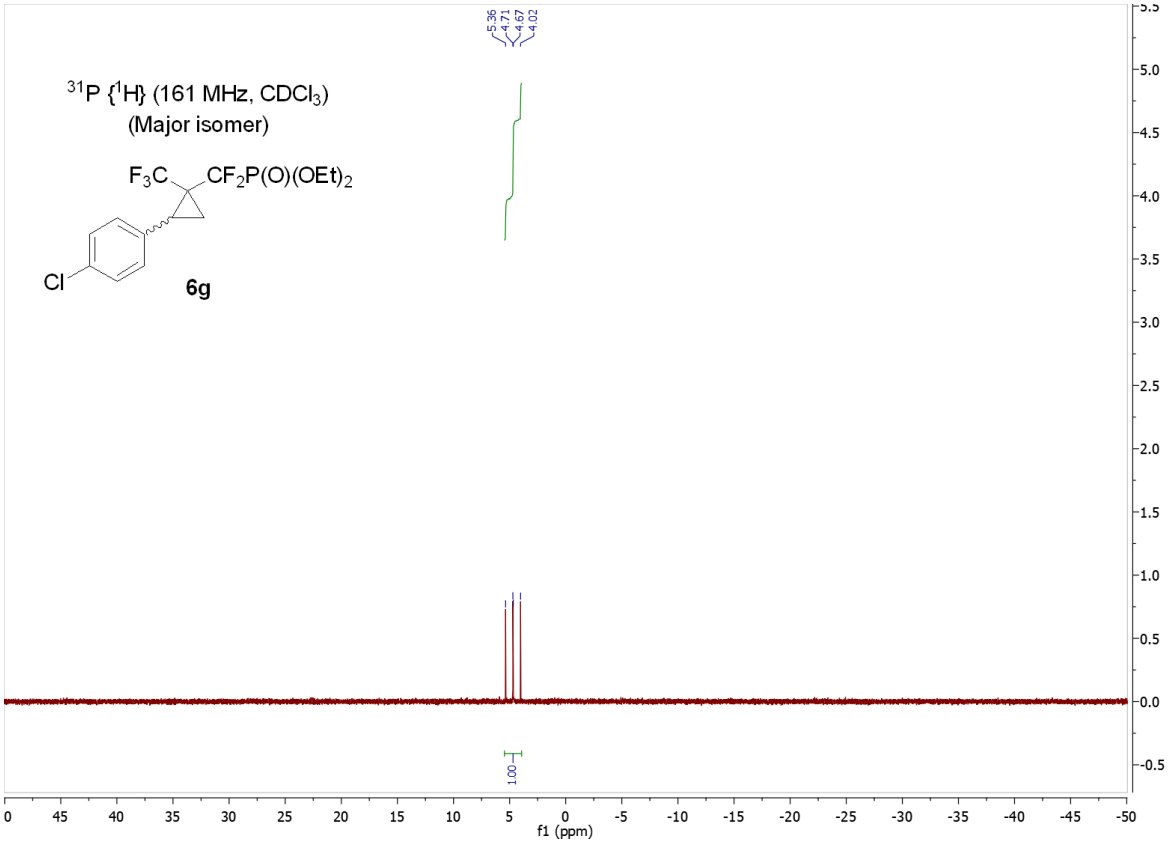

19F NMR (376 MHz, CDCl3)
(Two isomers in 1:1.4 ratio)
F3C
CF2P(O)(OEt)2
OCH3
6f
f1 (ppm)

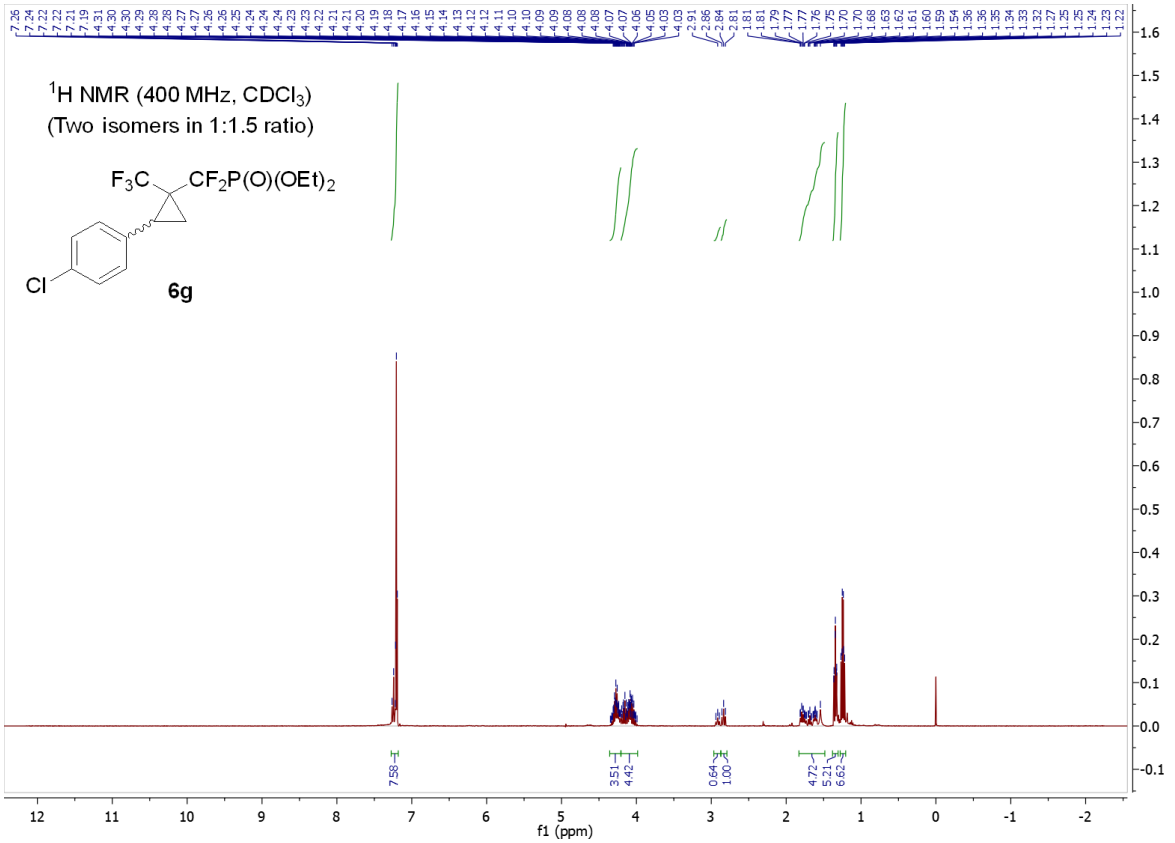

31P {1H} (161 MHz, CDCl3)
(Two isomers in 1:1.4 ratio)
F3C
CF2P(O)(OEt)2
OCH3
6f
f1 (ppm)

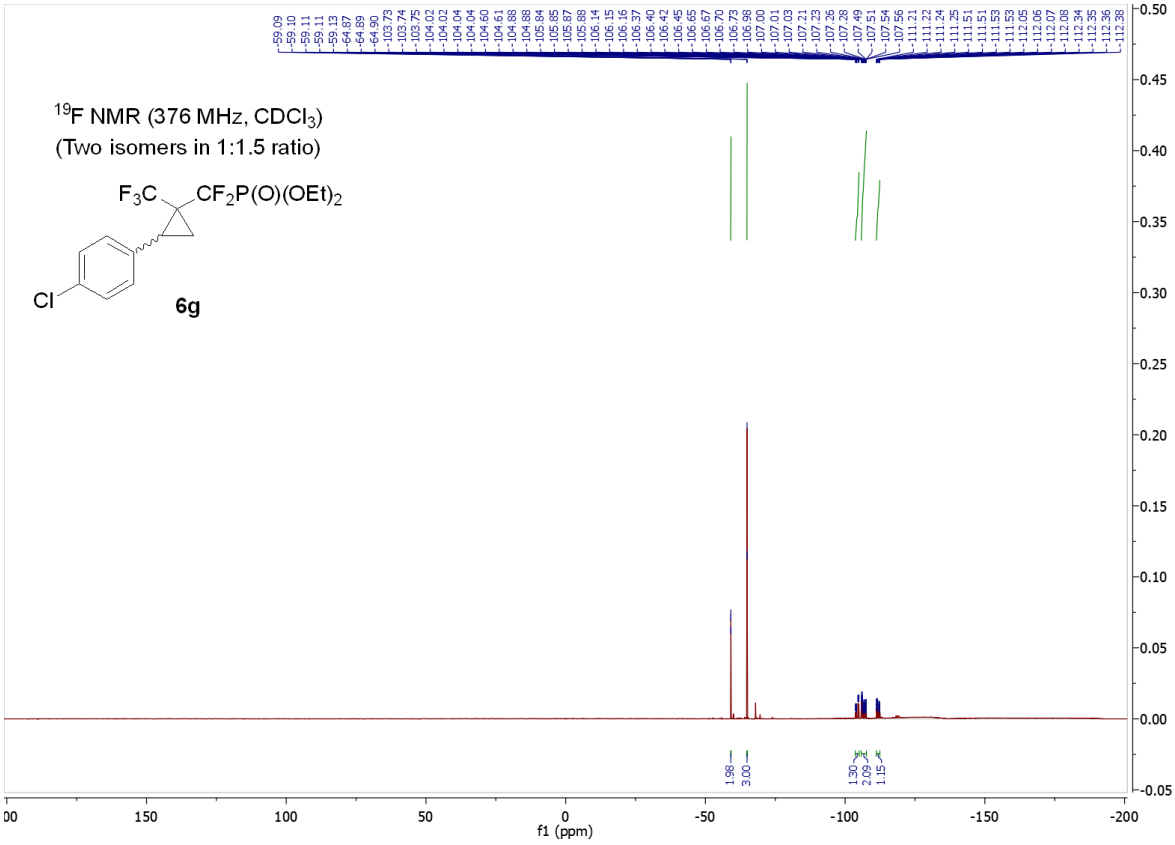

^{1}H NMR (400 MHz, $CDCl_3$)
(Major isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6g
f1 (ppm)

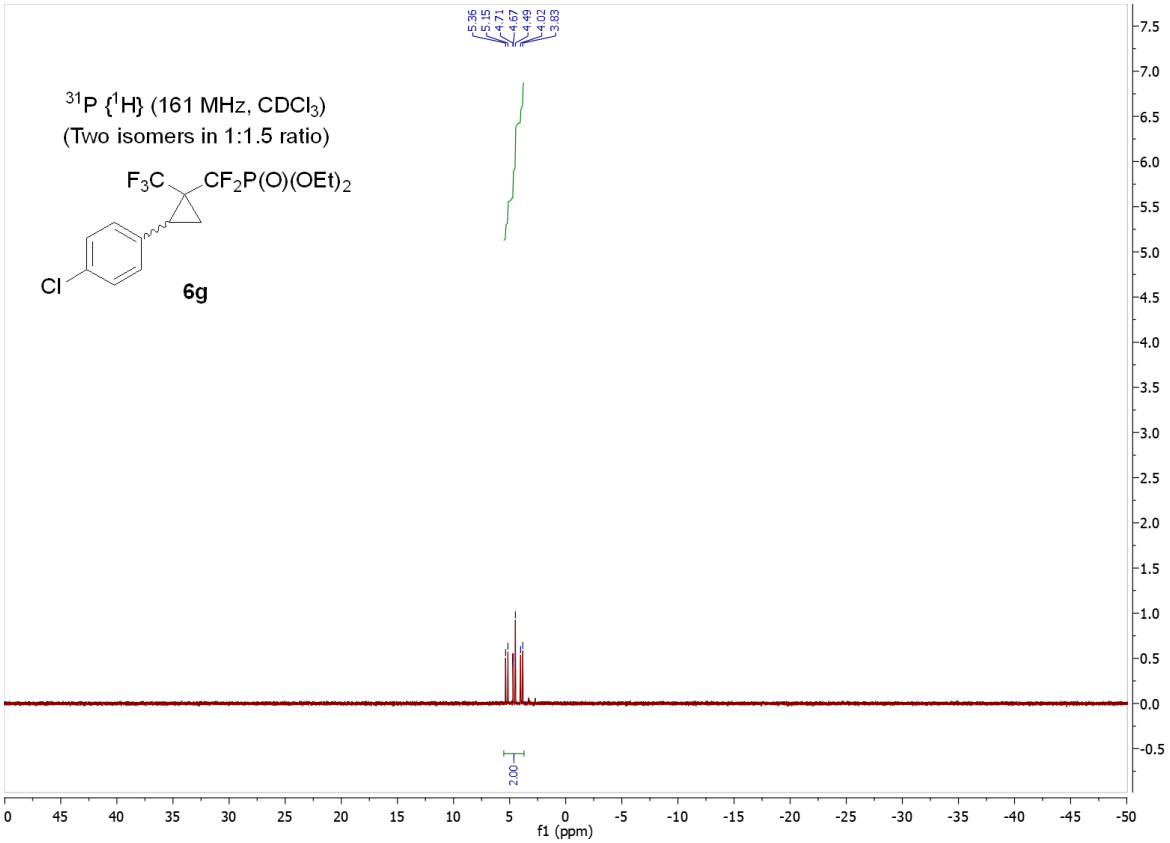

^{13}C NMR (100 MHz, $CDCl_3$)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6g
f1 (ppm)

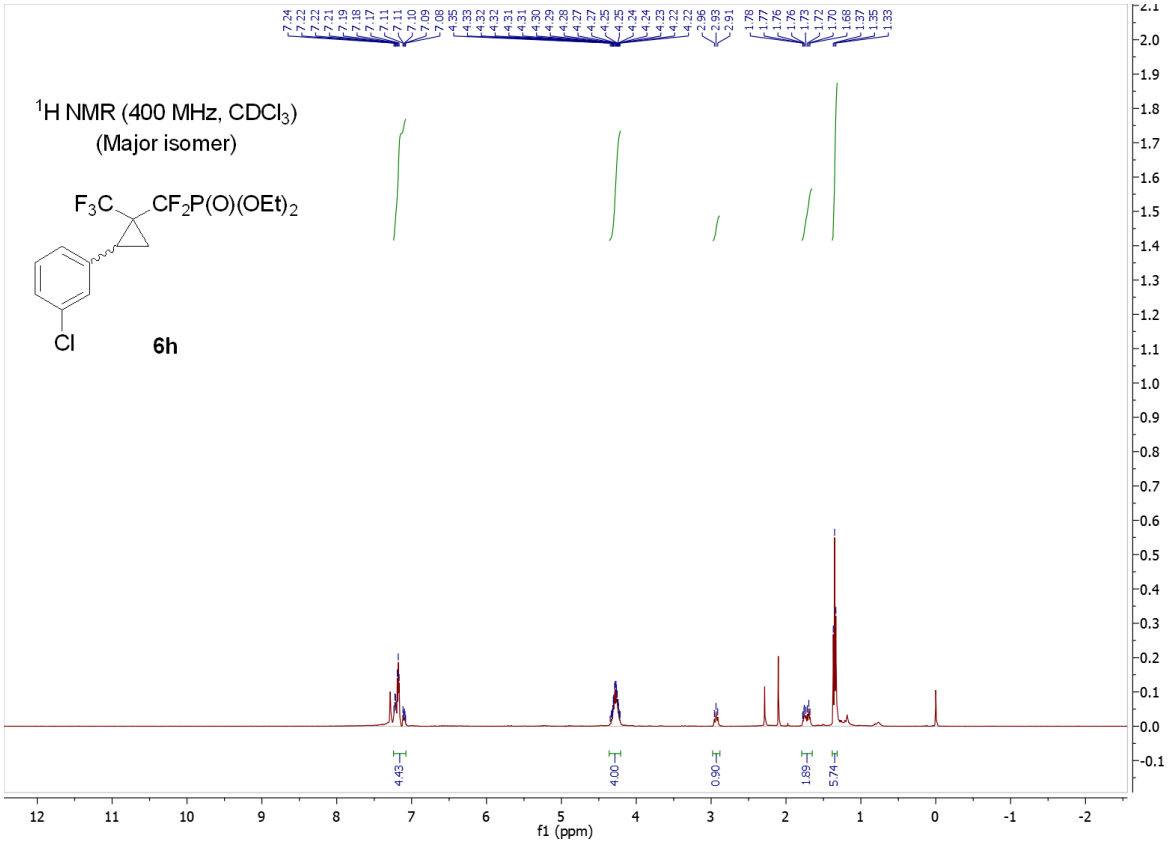

^{19}F NMR (376 MHz, $CDCl_3$)
(Major isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6g
f1 (ppm)

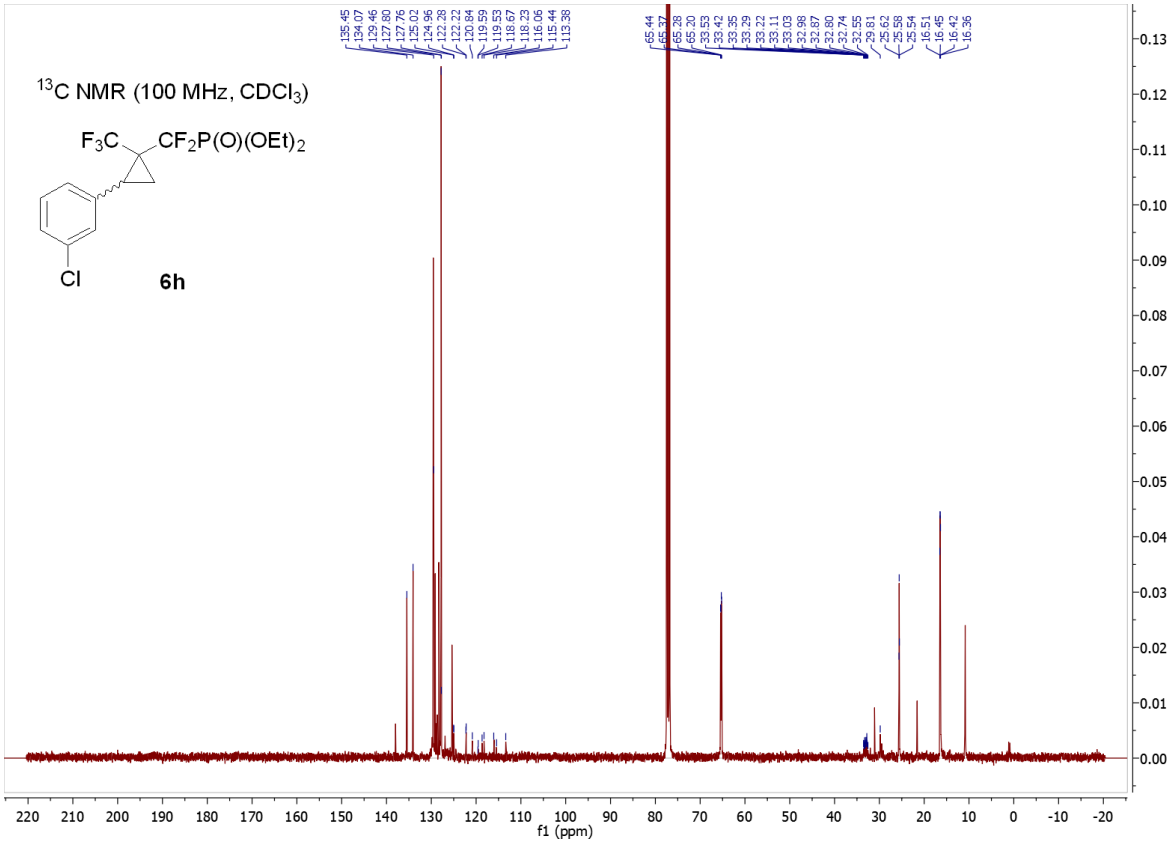

^{31}P {^{1}H} (161 MHz, $CDCl_3$)
(Major isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6g
f1 (ppm)

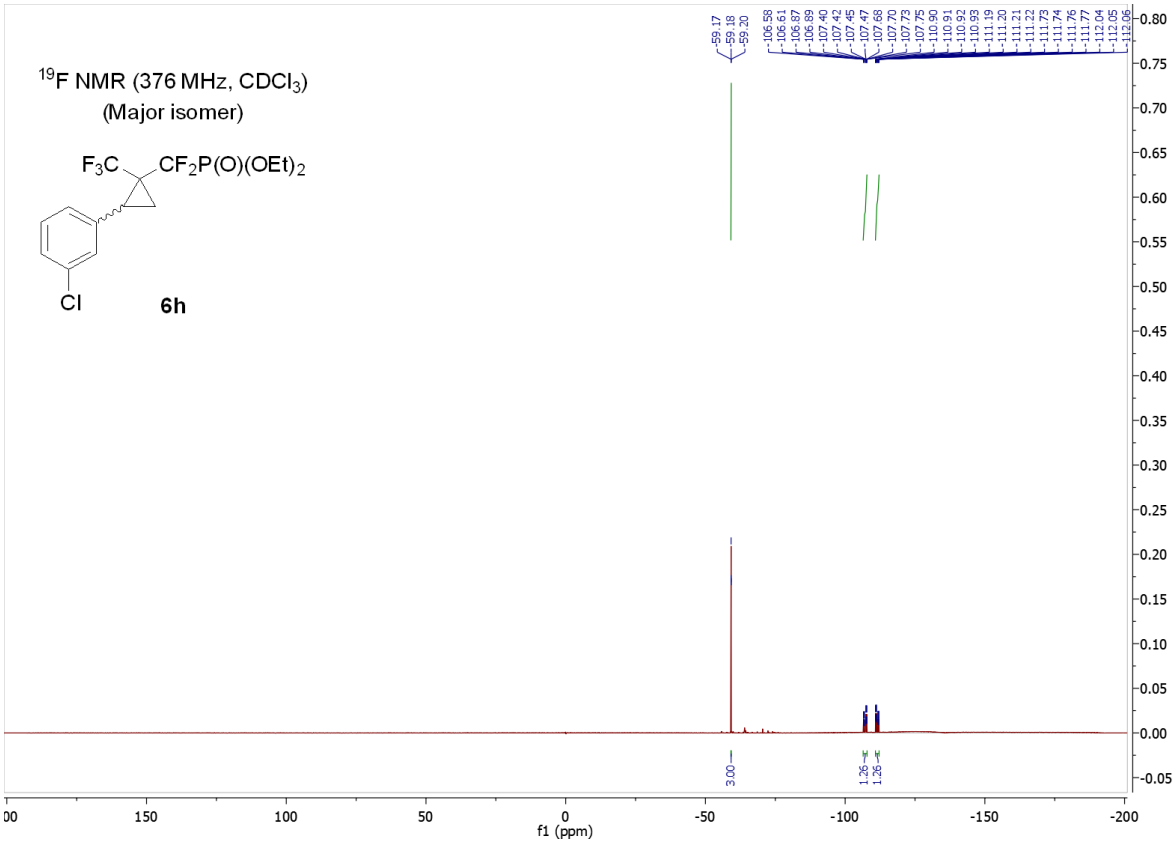

^{1}H NMR (400 MHz, $CDCl_3$)
(Two isomers in 1:1.5 ratio)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6g
f1 (ppm)

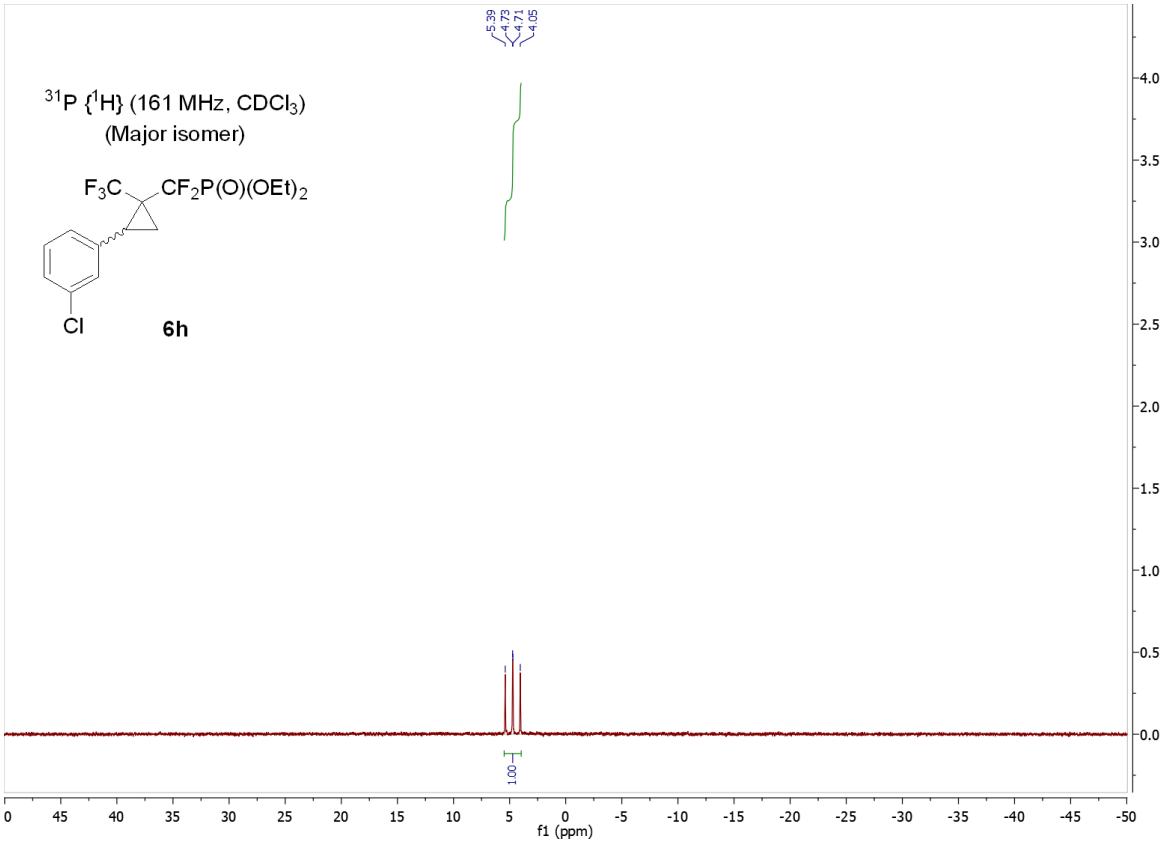

^{19}F NMR (376 MHz, $CDCl_3$)
(Two isomers in 1:1.5 ratio)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6g
f1 (ppm)

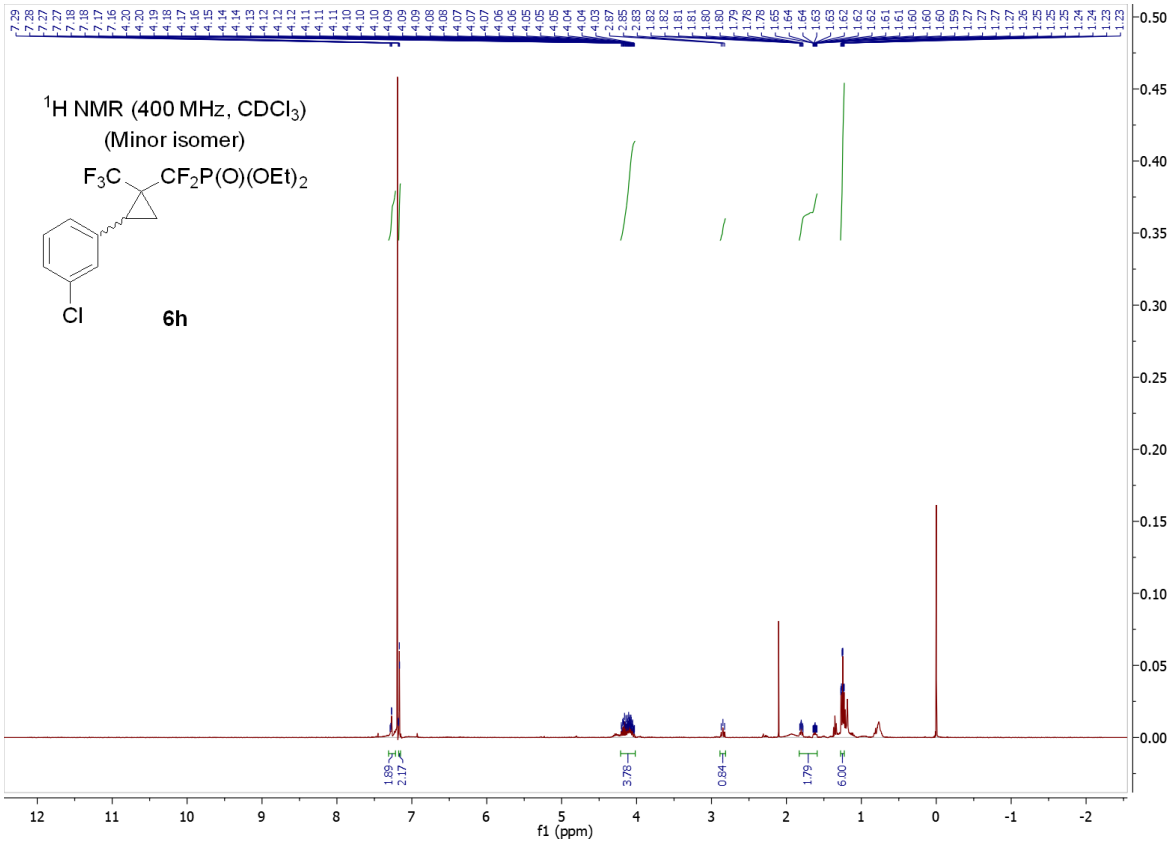

31P {1H} (161 MHz, CDCl3)
(Two isomers in 1:1.5 ratio)
F3C
CF2P(O)(OEt)2
Cl
6g
f1 (ppm)

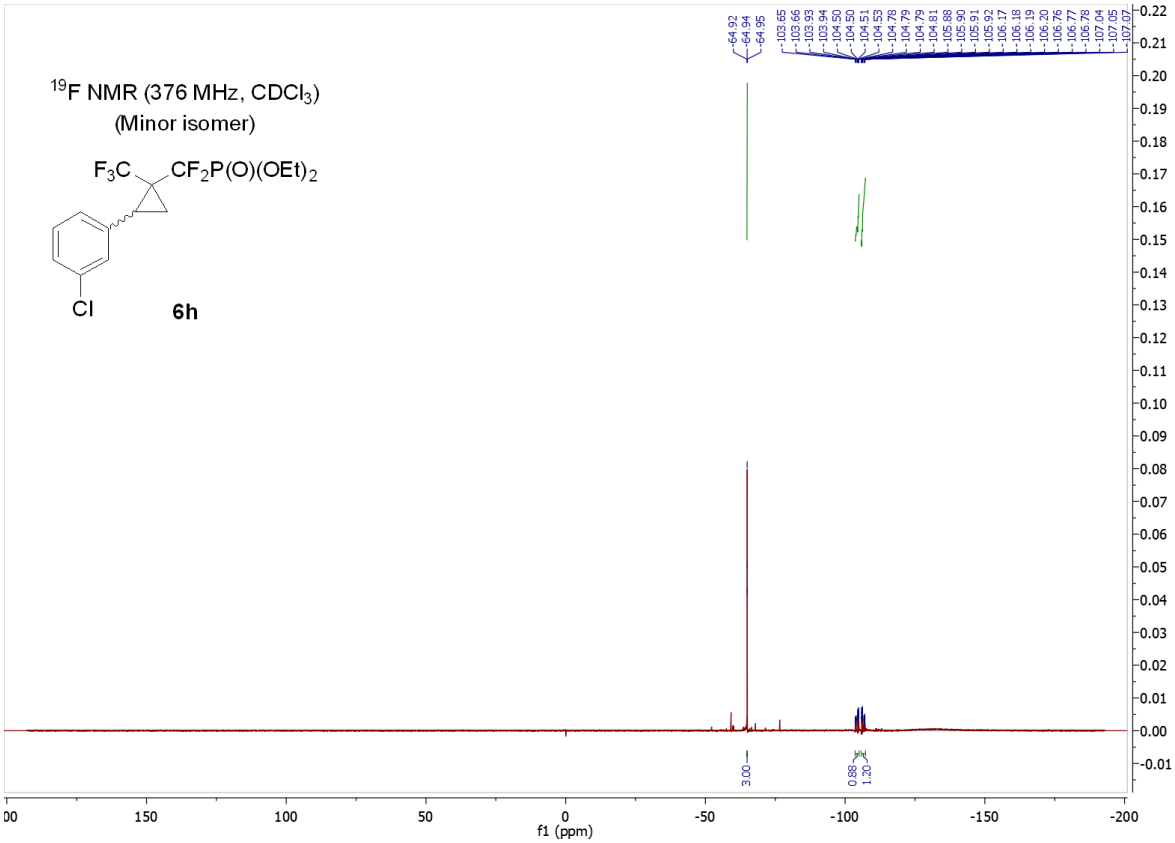

1H NMR (400 MHz, CDCl3)
(Major isomer)
F3C
CF2P(O)(OEt)2
Cl
6h
f1 (ppm)

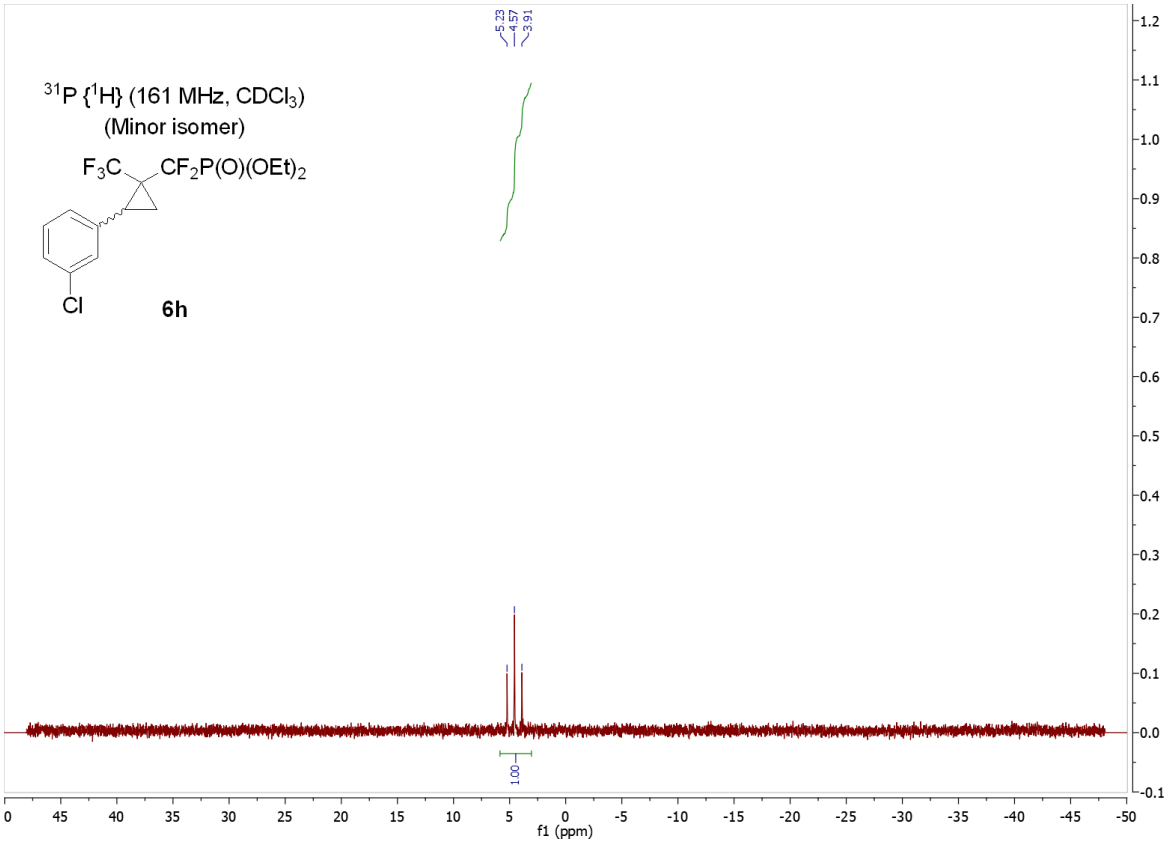

^{13}C NMR (100 MHz, $CDCl_3$)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6h
f1 (ppm)

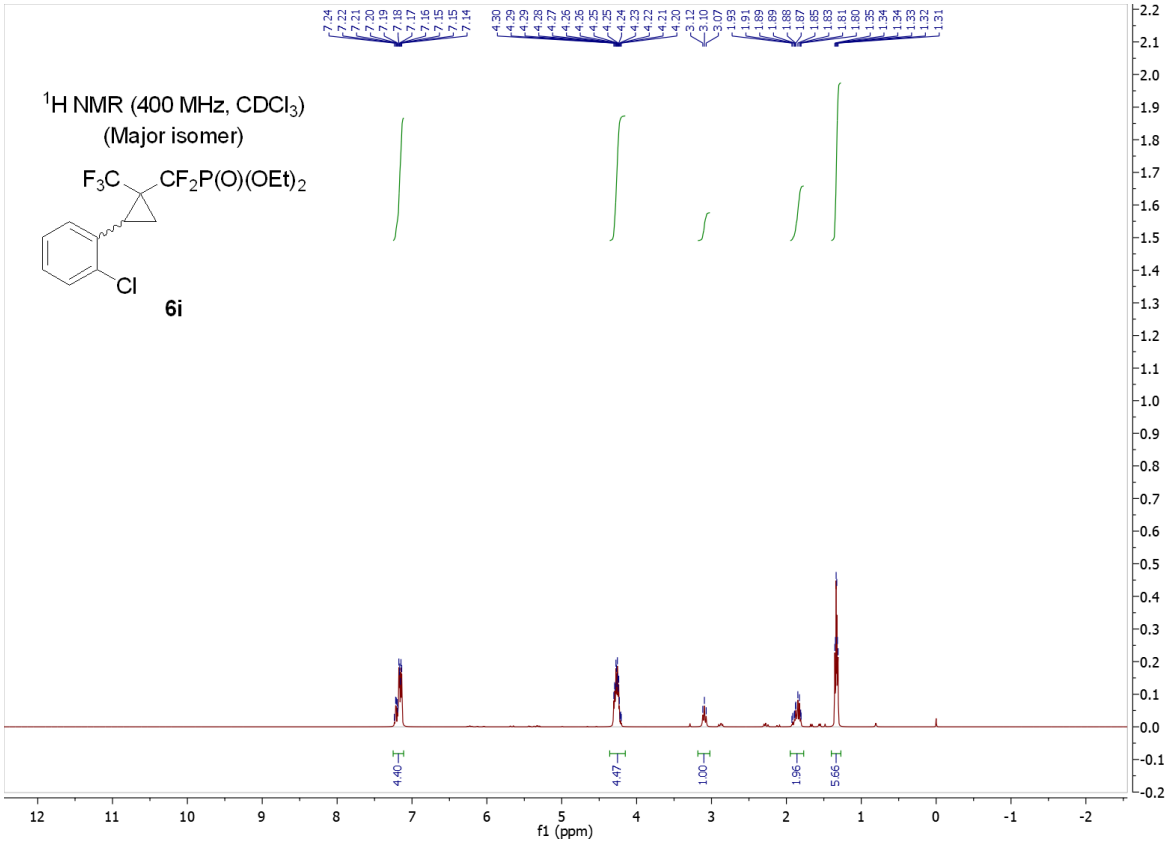

^{19}F NMR (376 MHz, $CDCl_3$)
(Major isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6h
3.00
1.26
1.26
f1 (ppm)

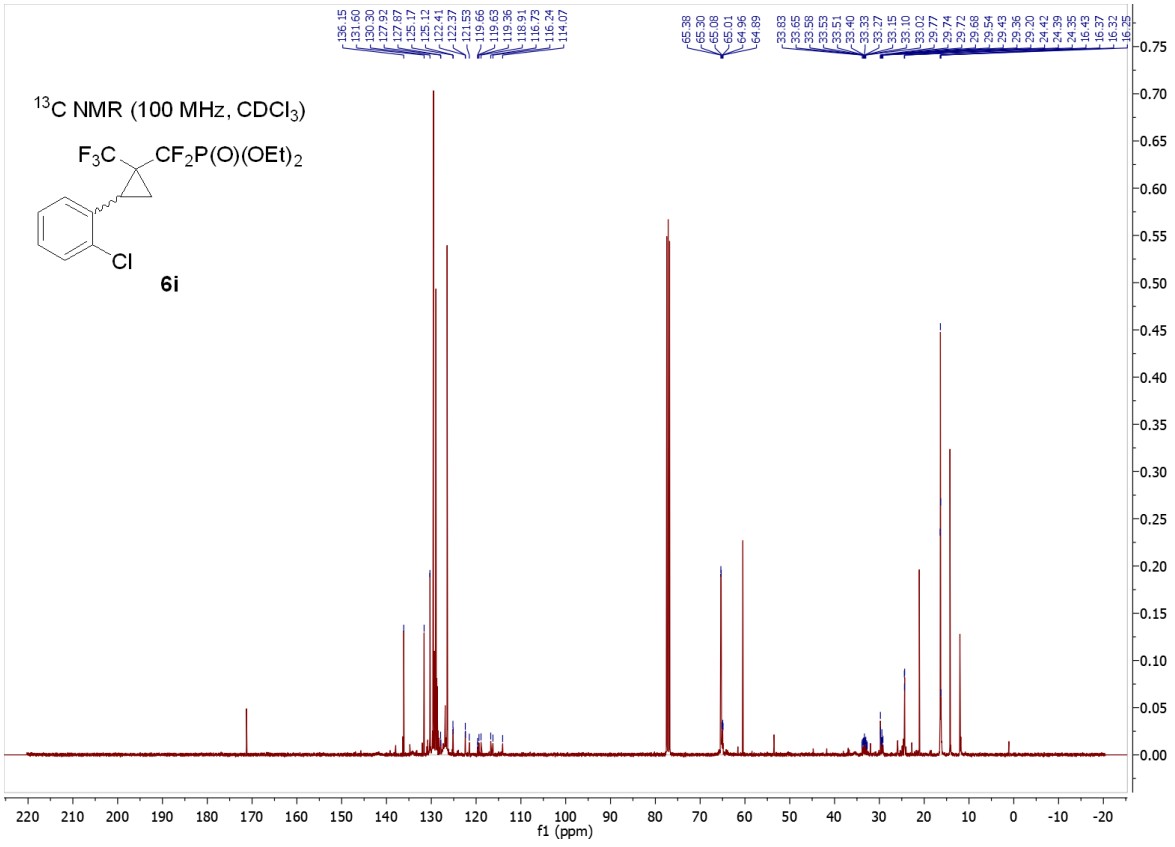

^{31}P {^{1}H} (161 MHz, $CDCl_3$)
(Major isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6h
5.39
4.73
4.71
4.05
1.00
f1 (ppm)

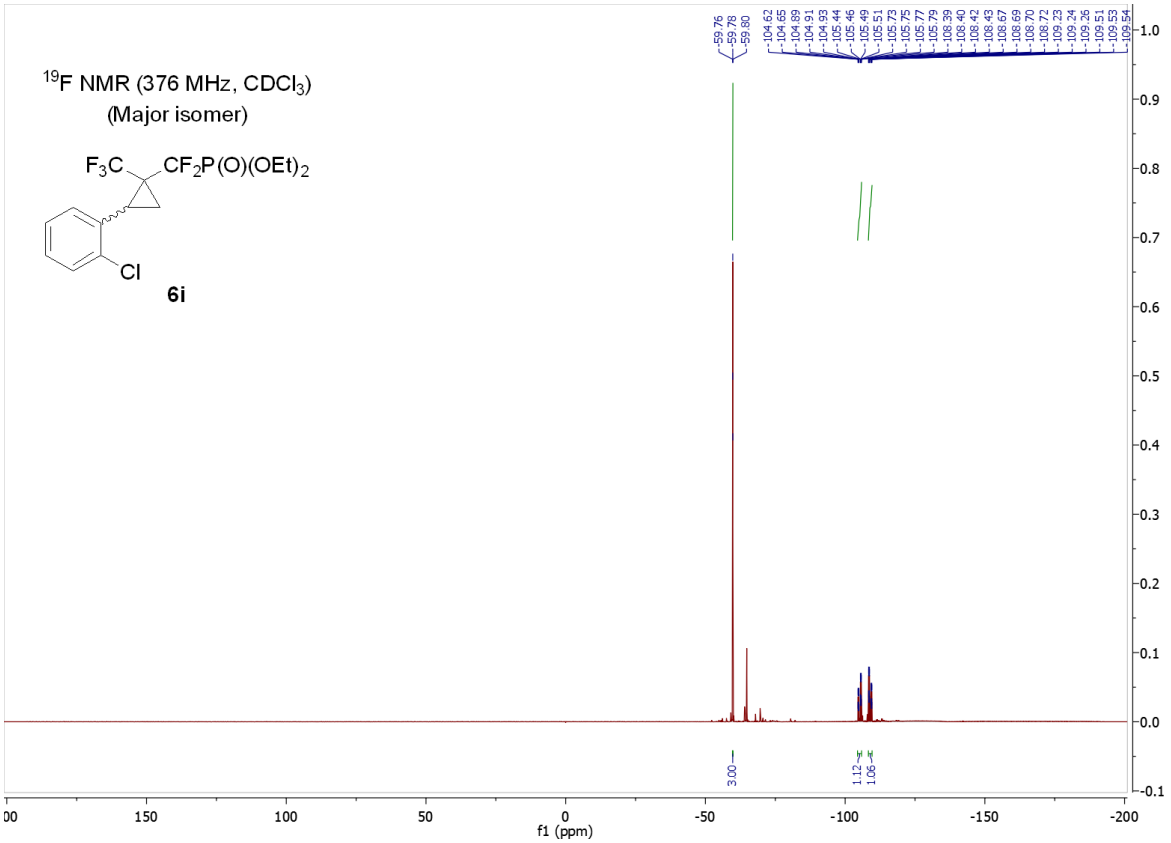

^{1}H NMR (400 MHz, $CDCl_3$)
(Minor isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6h
1.89
2.17
3.78
0.84
1.79
6.00
f1 (ppm)

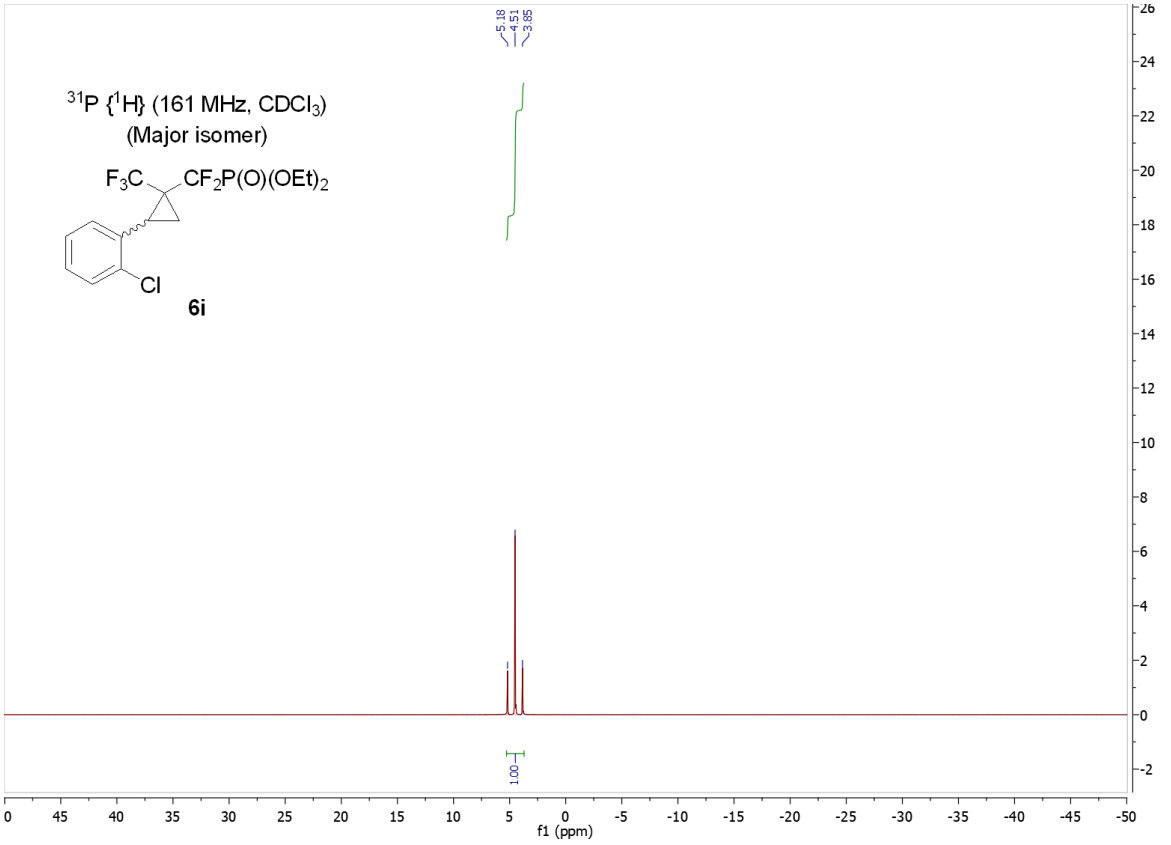

^{19}F NMR (376 MHz, $CDCl_3$)
(Minor isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6h
f1 (ppm)

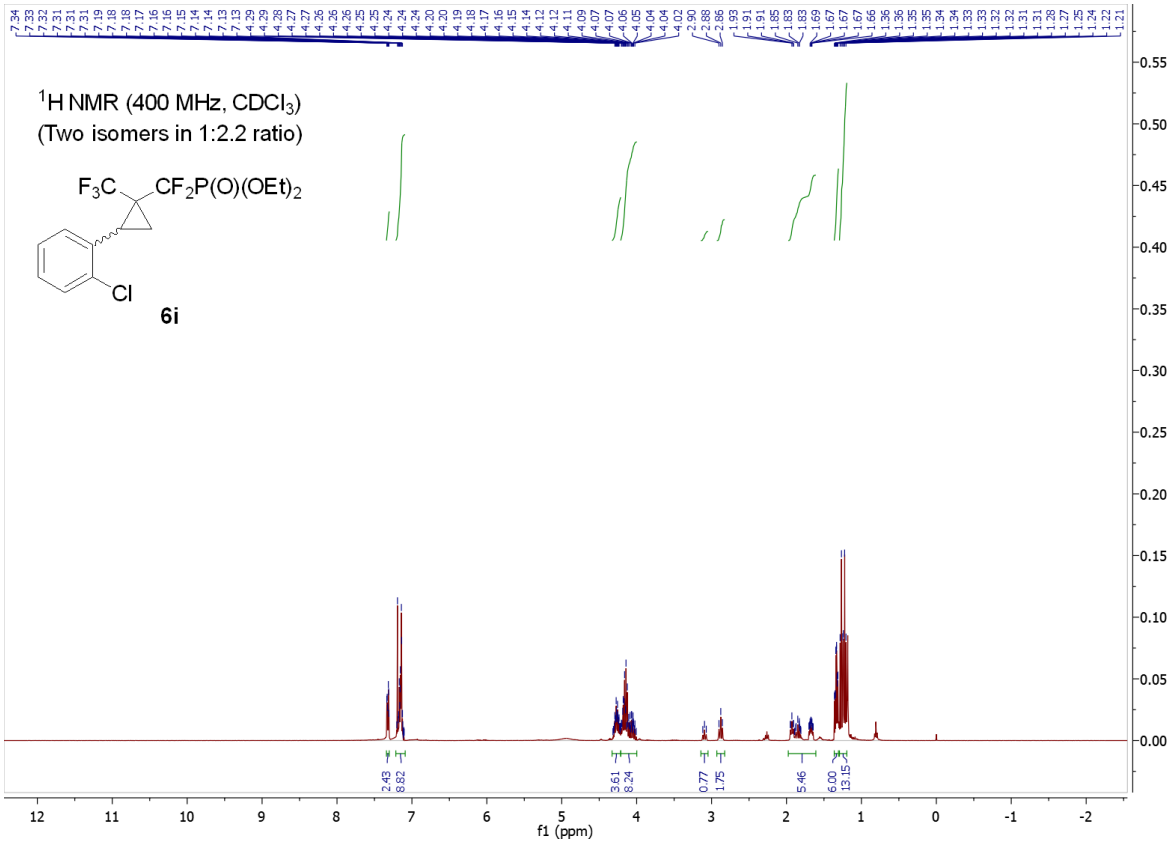

^{31}P {^{1}H} (161 MHz, $CDCl_3$)
(Minor isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6h
f1 (ppm)

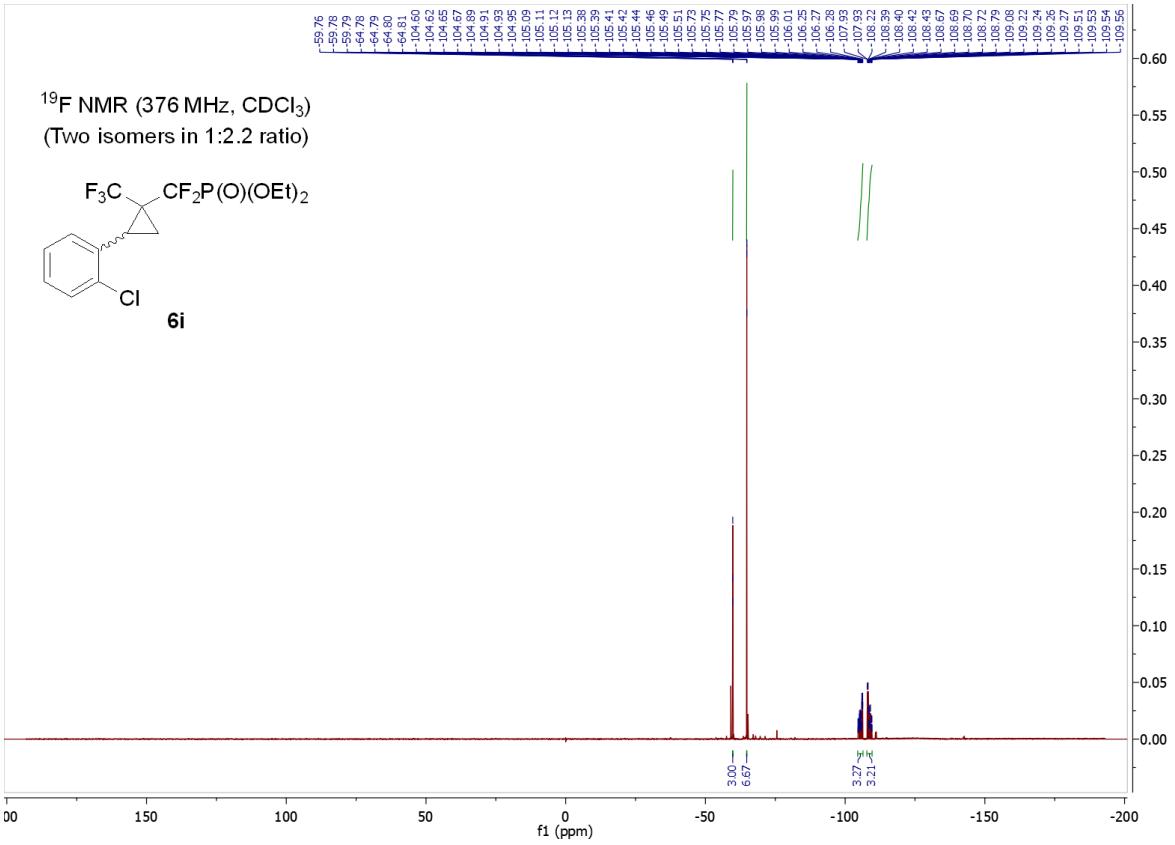

^{1}H NMR (400 MHz, $CDCl_3$)
(Major isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6i
4.40
4.47
1.00
1.96
5.66
f1 (ppm)

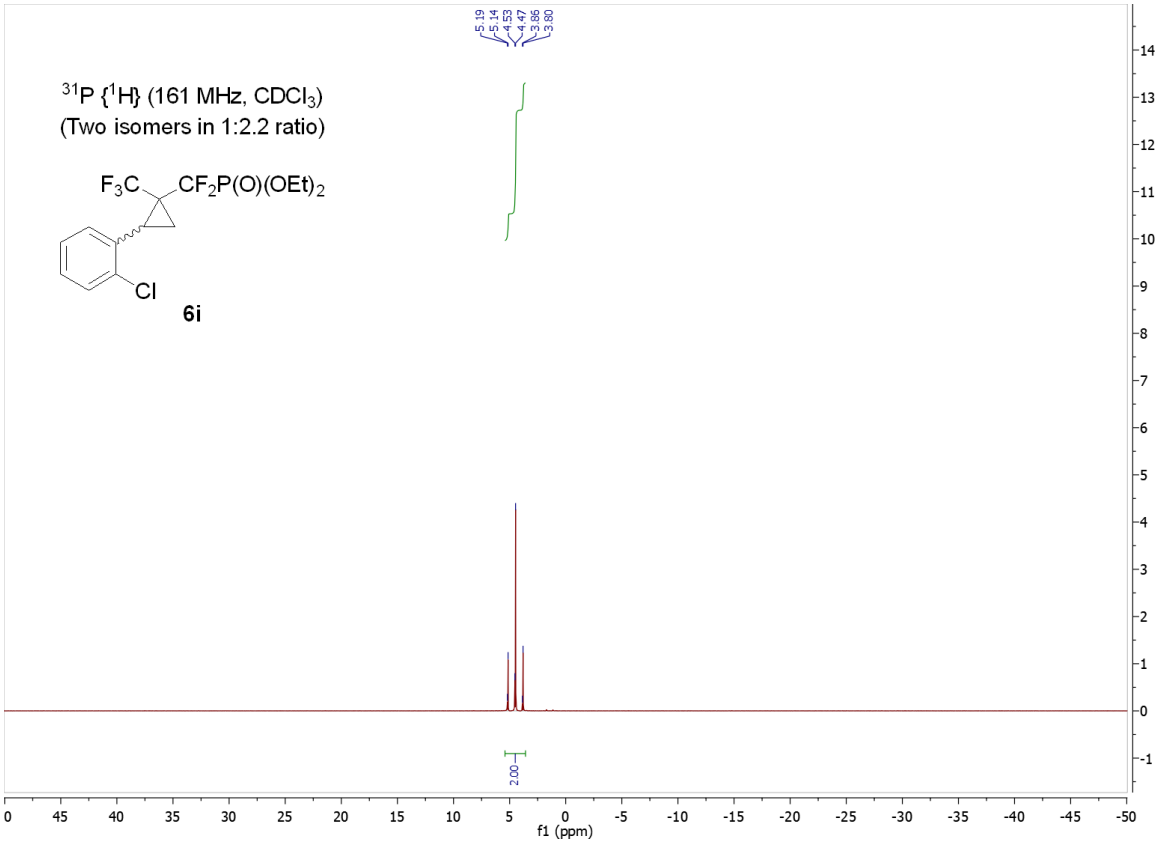

^{13}C NMR (100 MHz, $CDCl_3$)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6i
f1 (ppm)

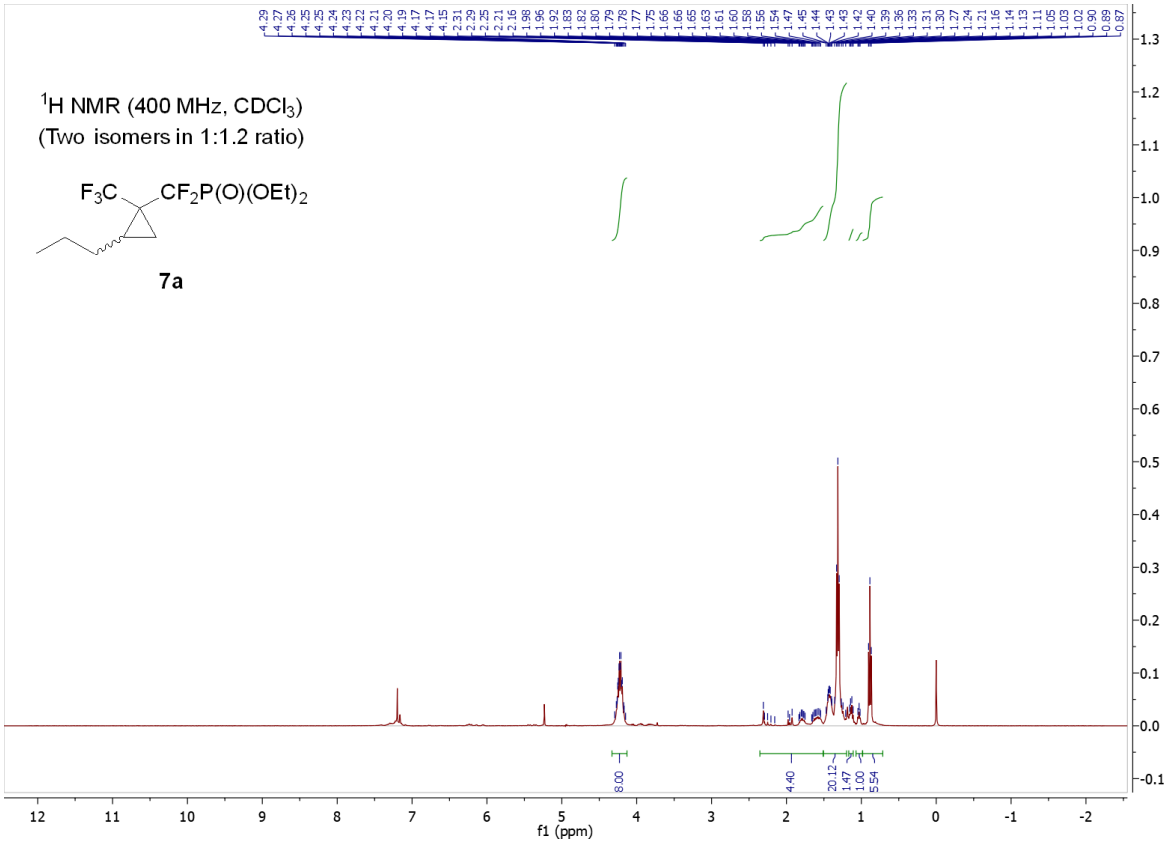

^{19}F NMR (376 MHz, $CDCl_3$)
(Major isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6i
f1 (ppm)

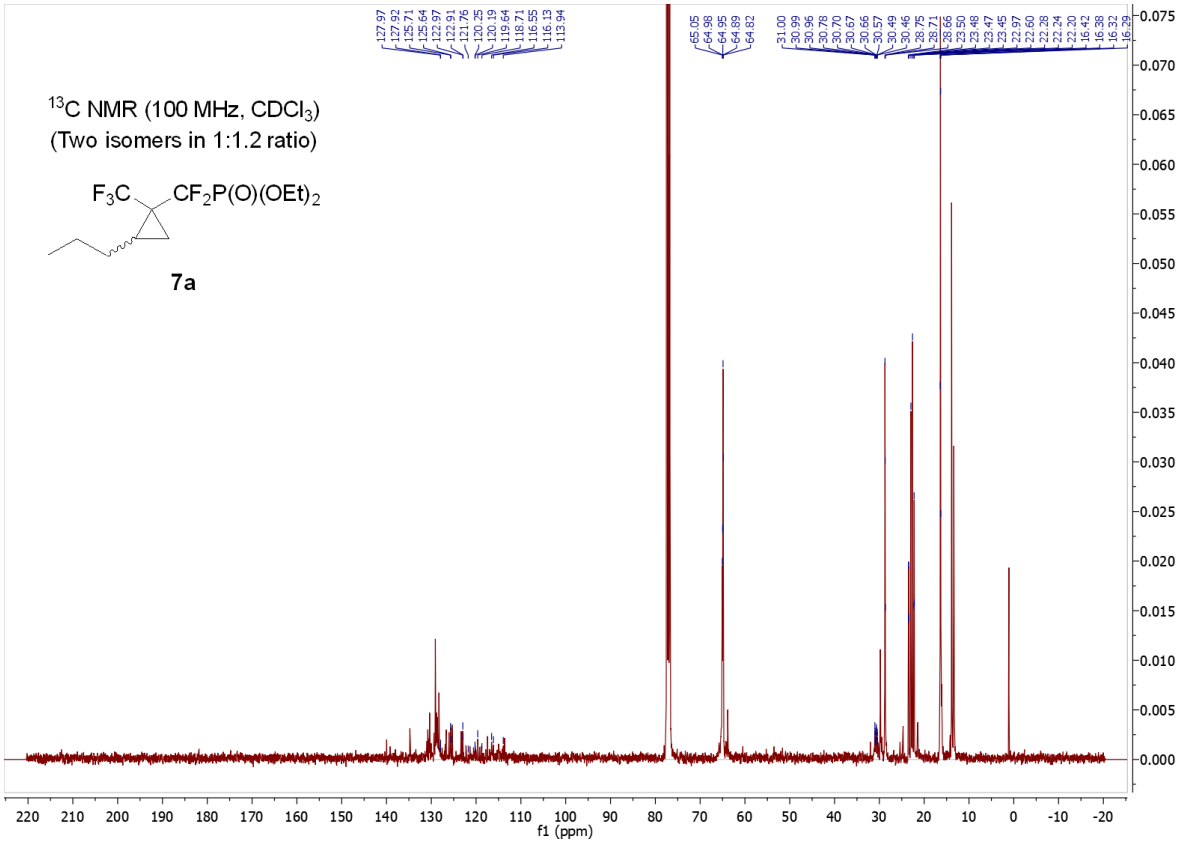

^{31}P {^{1}H} (161 MHz, $CDCl_3$)
(Major isomer)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6i
f1 (ppm)

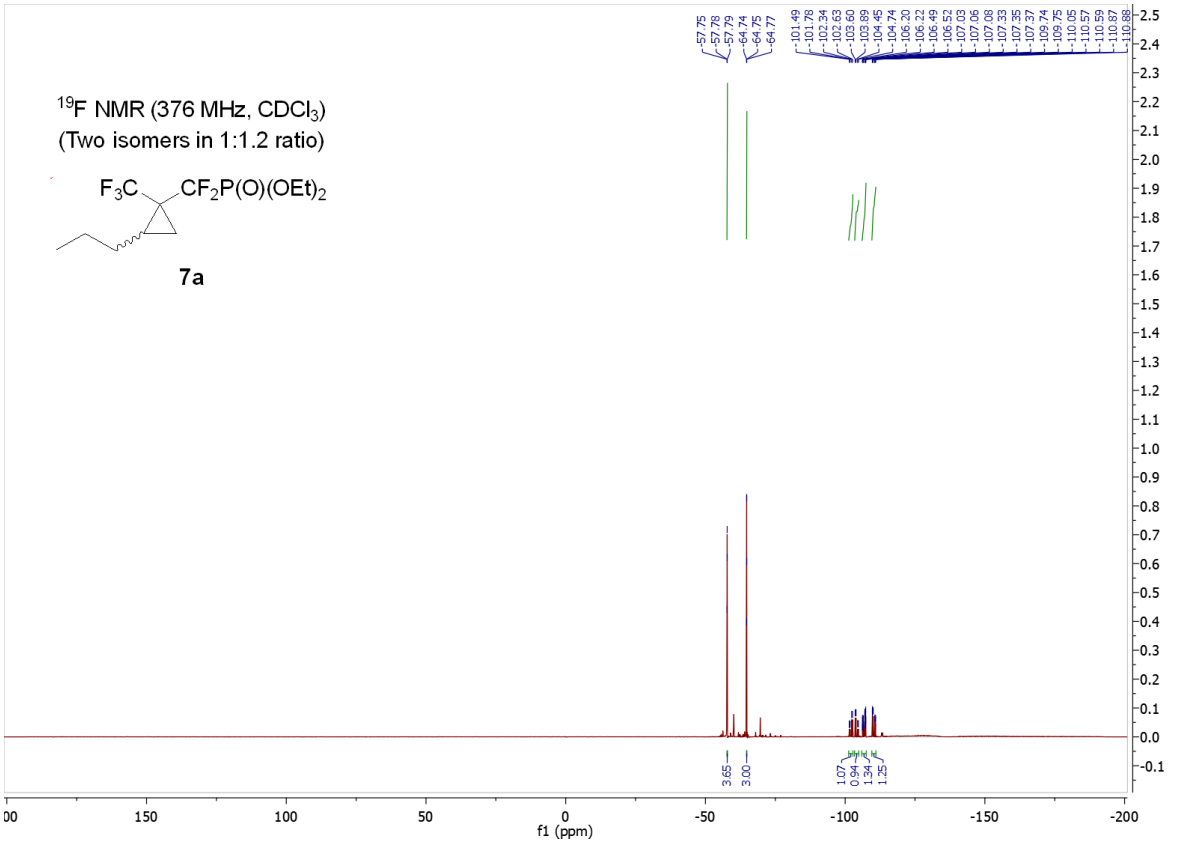

^{1}H NMR (400 MHz, $CDCl_3$)
(Two isomers in 1:2.2 ratio)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6i
f1 (ppm)

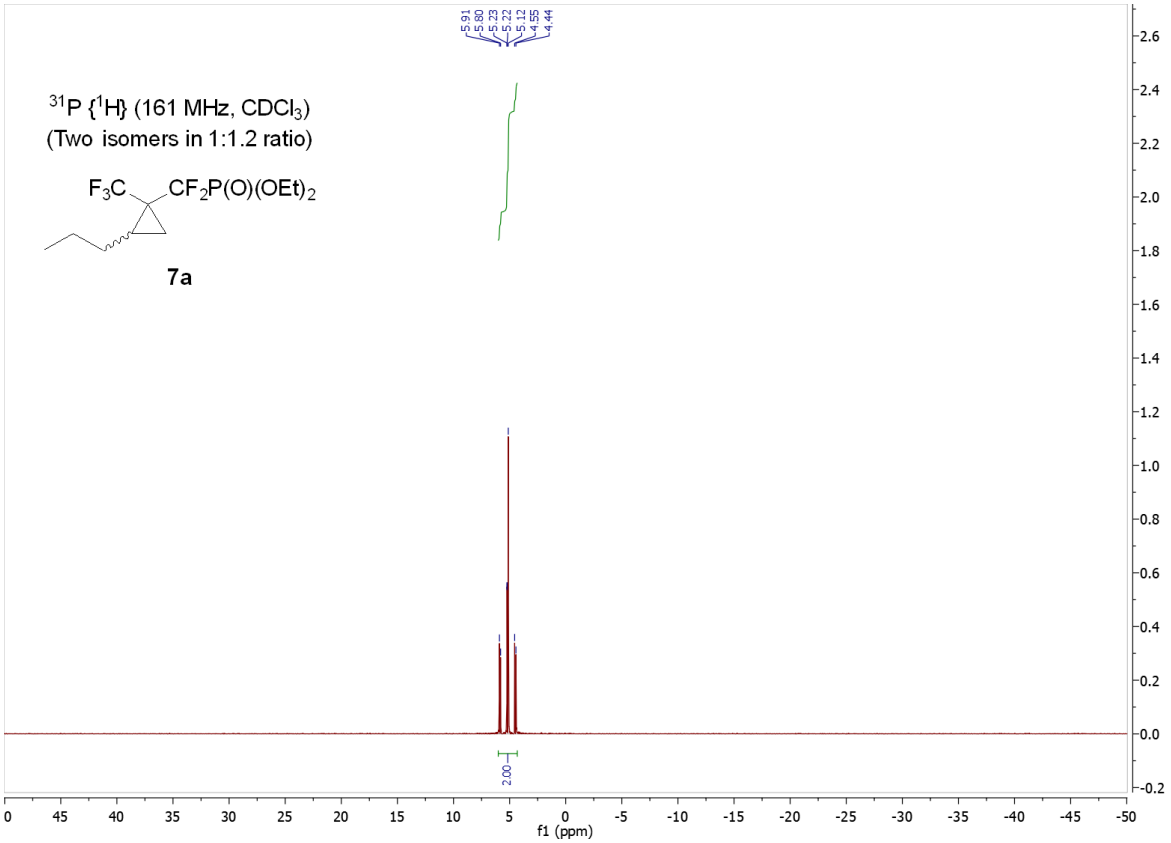

^{19}F NMR (376 MHz, $CDCl_3$)
(Two isomers in 1:2.2 ratio)
F_3C
$CF_2P(O)(OEt)_2$
Cl
6i
f1 (ppm)

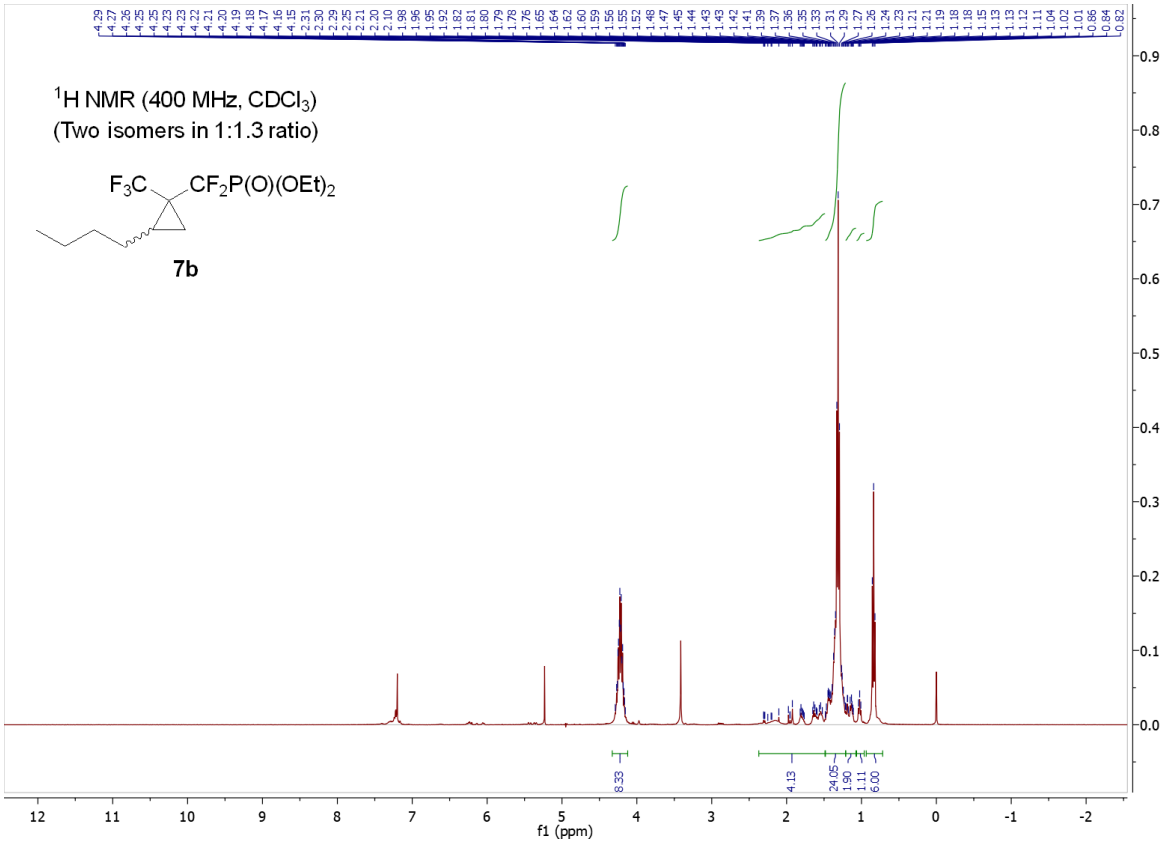

31P {1H} (161 MHz, CDCl3)
(Two isomers in 1:2.2 ratio)
F3C
CF2P(O)(OEt)2
Cl
6i
f1 (ppm)

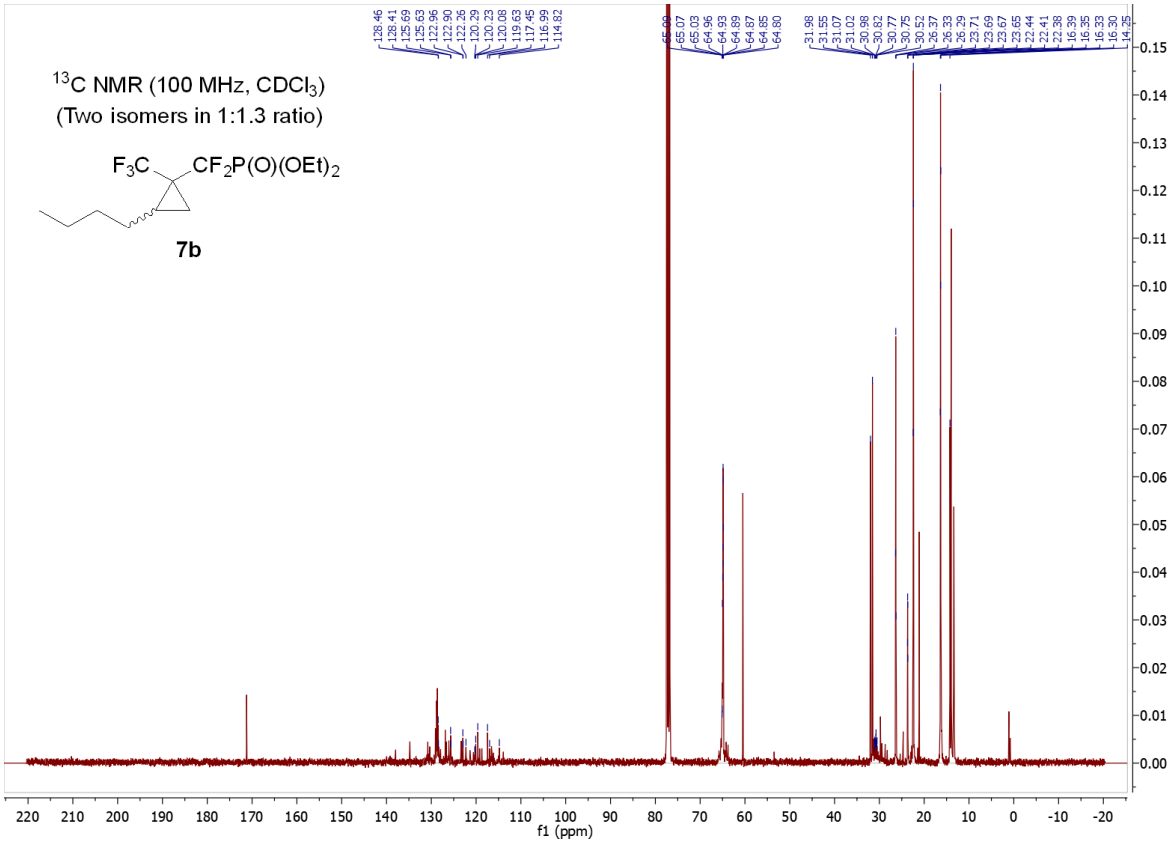

1H NMR (400 MHz, CDCl3)
(Two isomers in 1:1.2 ratio)
F3C
CF2P(O)(OEt)2
7a
f1 (ppm)

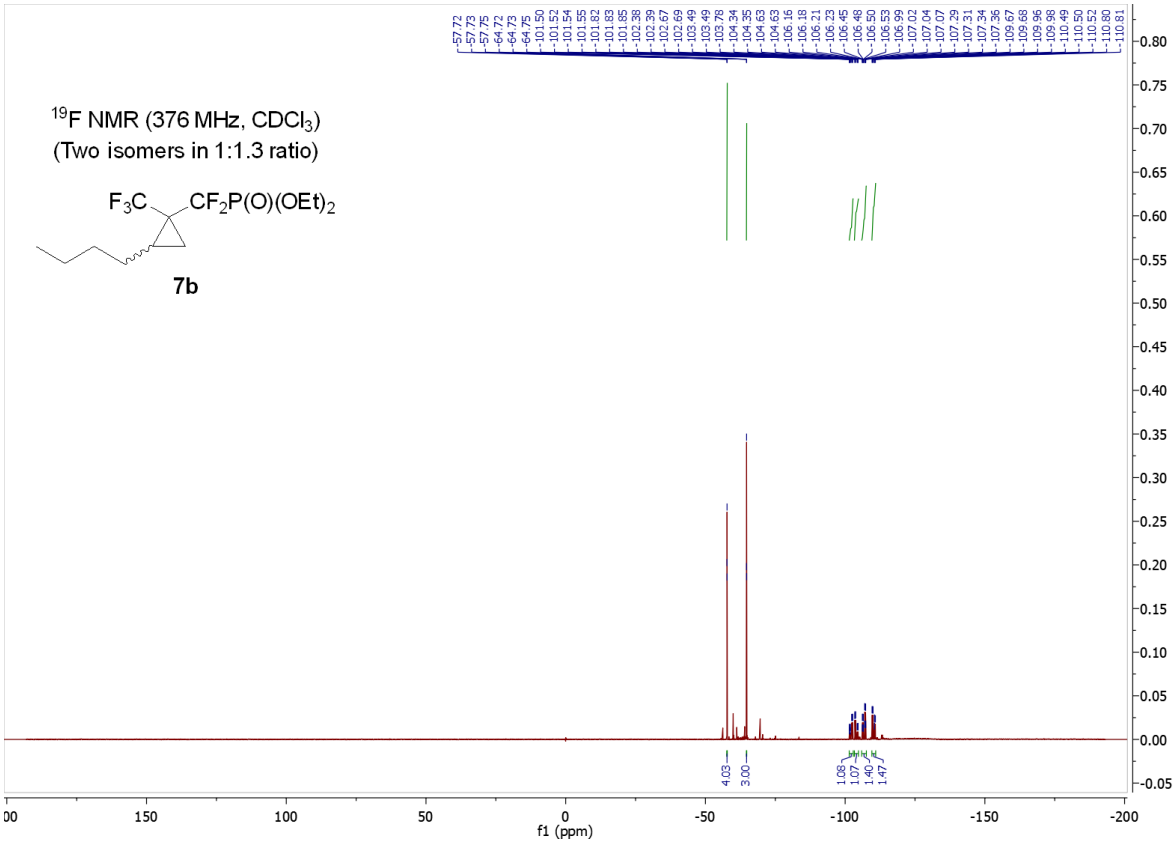

^{13}C NMR (100 MHz, $CDCl_3$)
(Two isomers in 1:1.2 ratio)
F_3C $CF_2P(O)(OEt)_2$
7a
f1 (ppm)

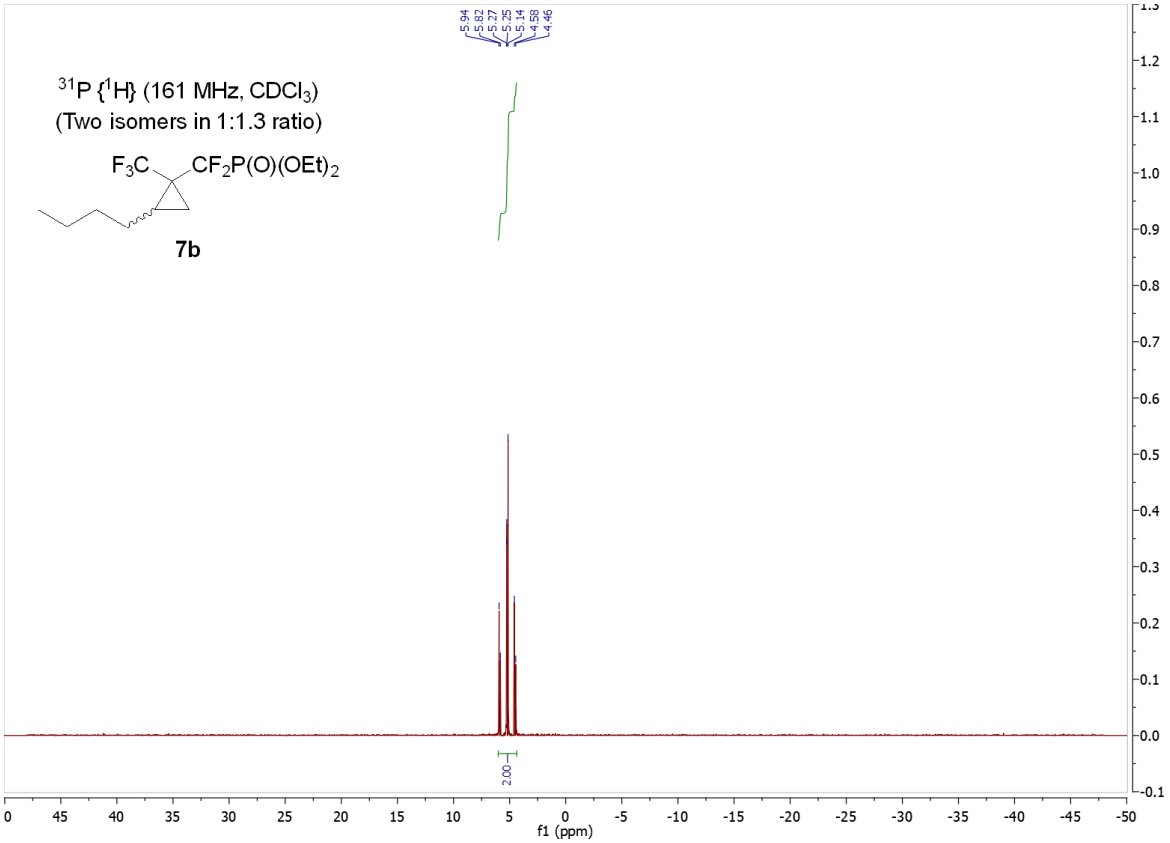

^{19}F NMR (376 MHz, $CDCl_3$)
(Two isomers in 1:1.2 ratio)
F_3C $CF_2P(O)(OEt)_2$
7a
f1 (ppm)

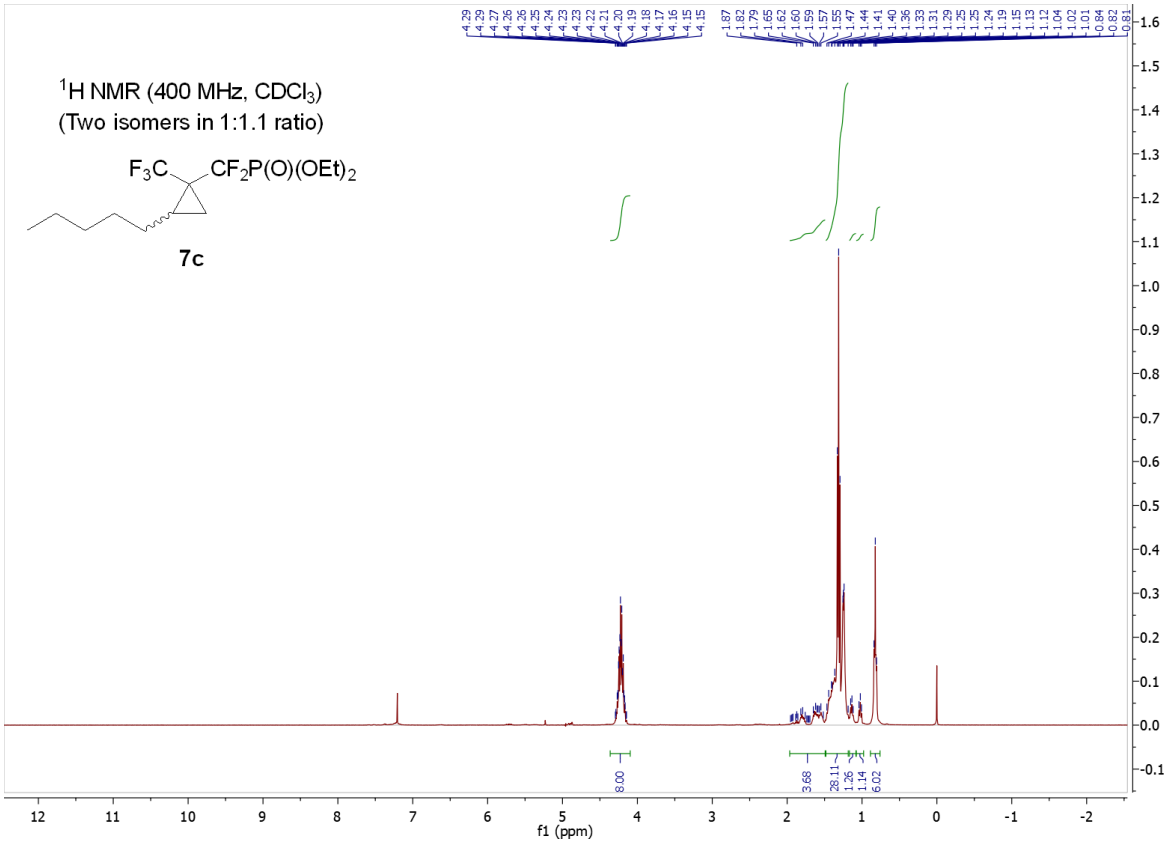

^{31}P {^{1}H} (161 MHz, CDCl$_3$)
(Two isomers in 1:1.2 ratio)
F$_3$C
CF$_2$P(O)(OEt)$_2$
7a
f1 (ppm)

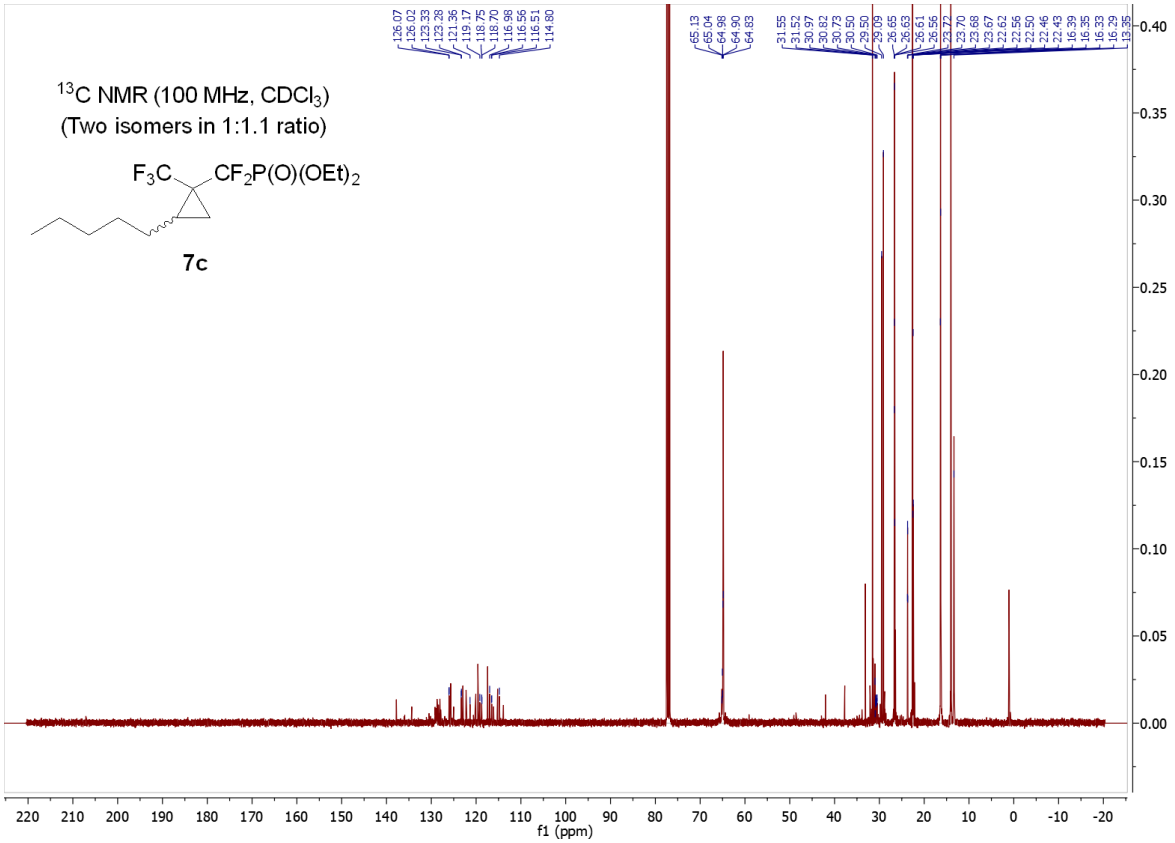

^{1}H NMR (400 MHz, CDCl$_3$)
(Two isomers in 1:1.3 ratio)
F$_3$C
CF$_2$P(O)(OEt)$_2$
7b
f1 (ppm)

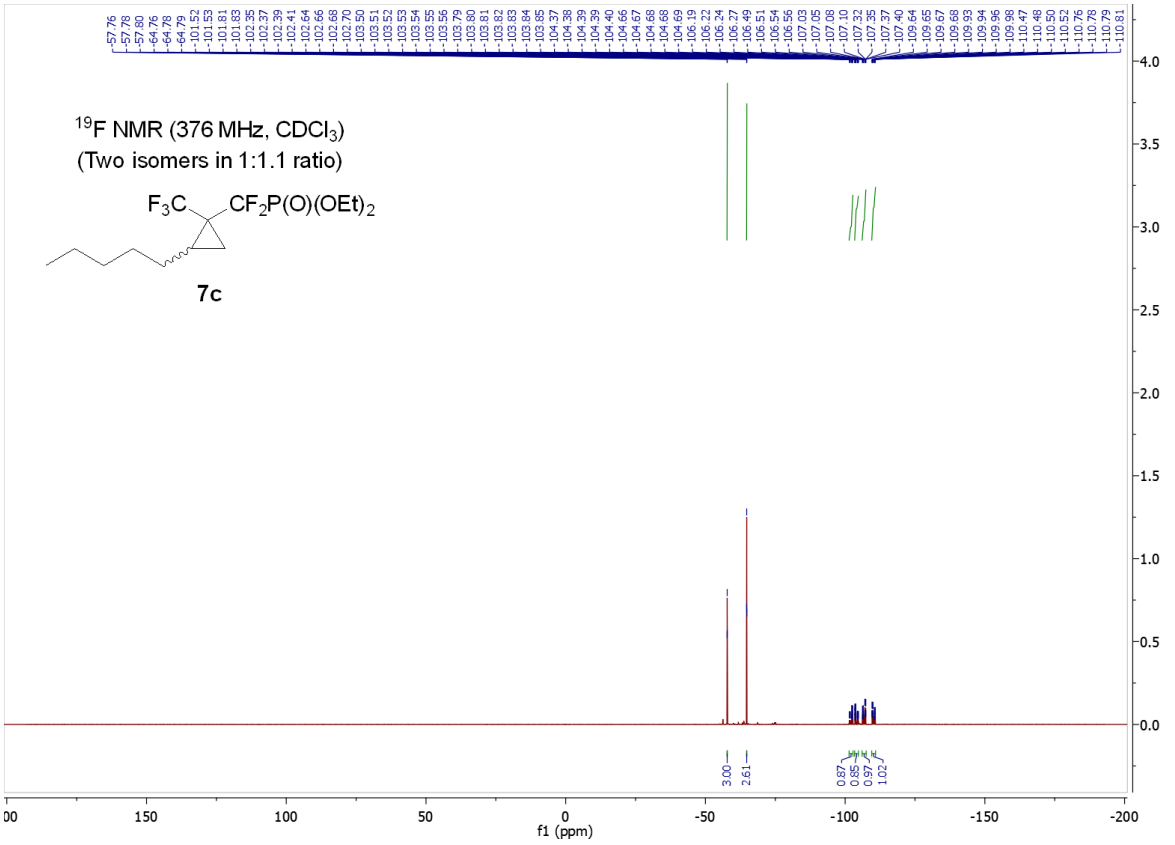

^{13}C NMR (100 MHz, $CDCl_3$)
(Two isomers in 1:1.3 ratio)
F_3C $CF_2P(O)(OEt)_2$
7b
f1 (ppm)

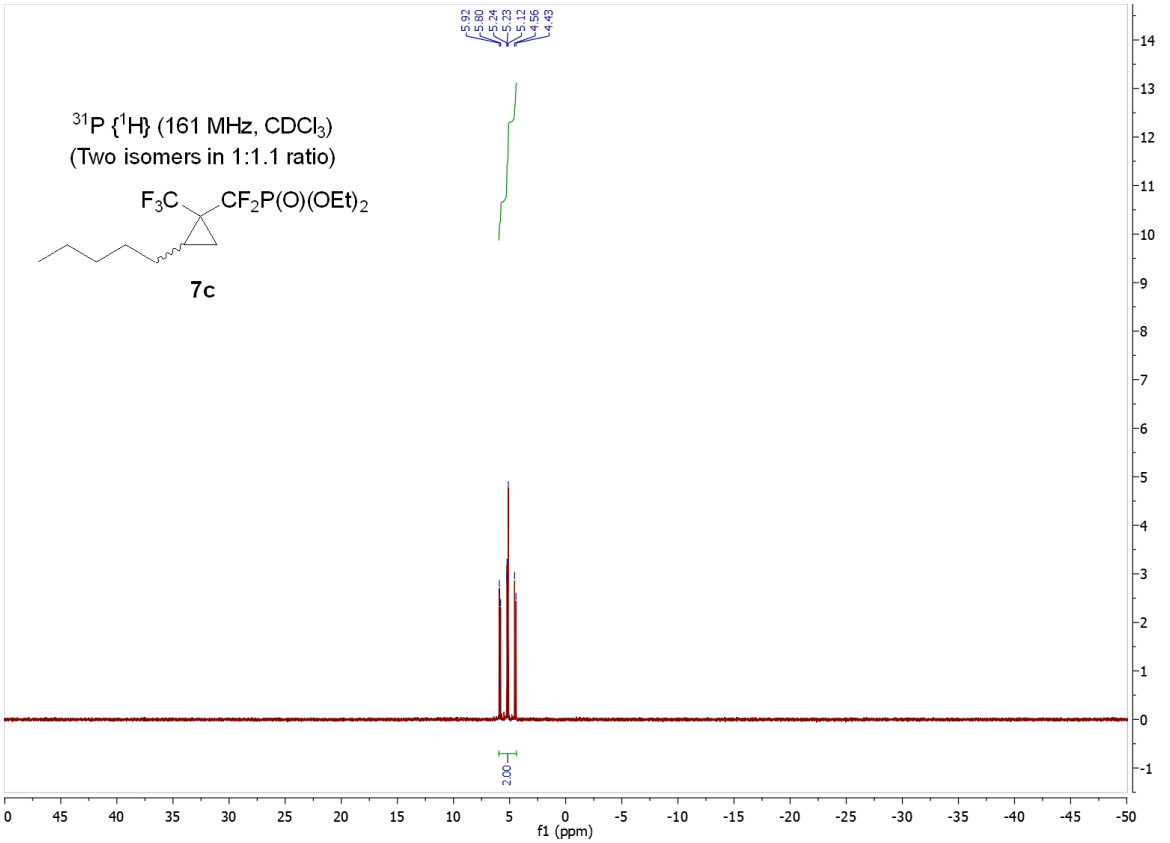

^{19}F NMR (376 MHz, $CDCl_3$)
(Two isomers in 1:1.3 ratio)
F_3C $CF_2P(O)(OEt)_2$
7b
4.03
3.00
1.08
1.07
1.40
1.47
f1 (ppm)

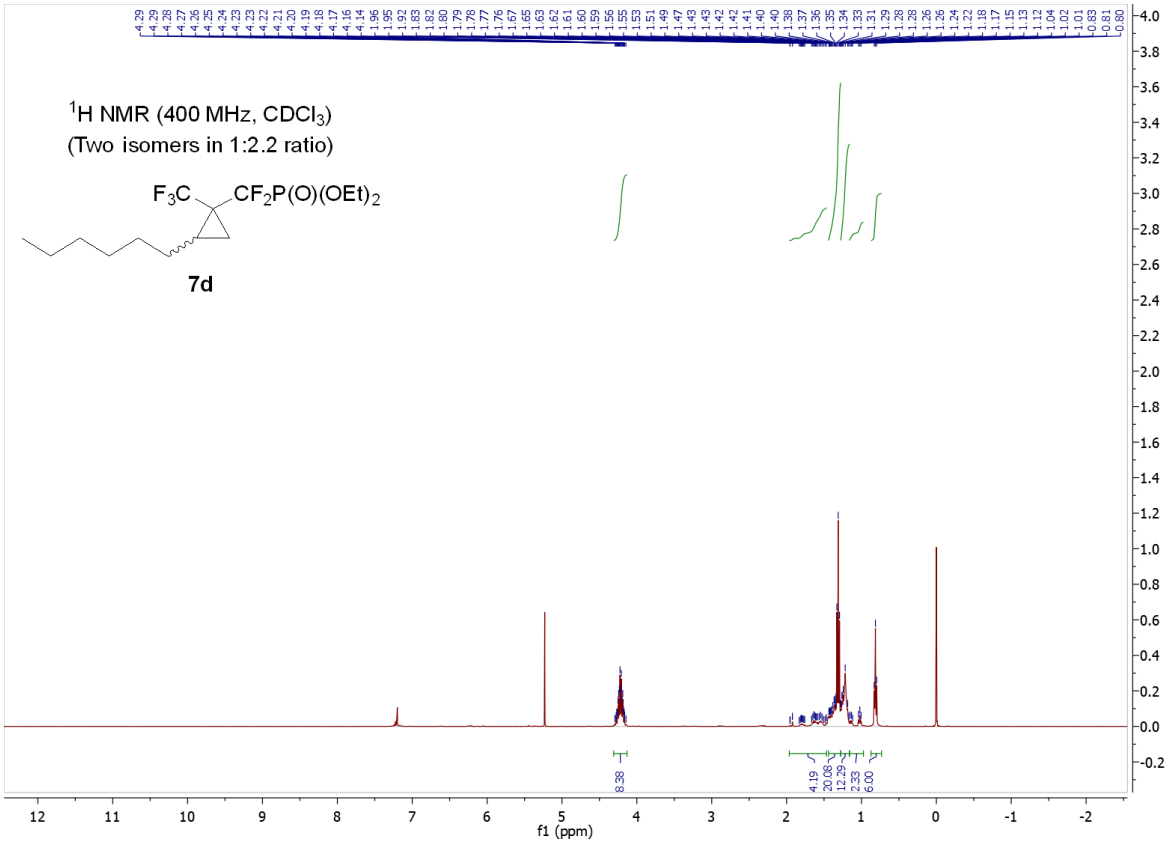

$^{31}P\{^{1}H\}$ (161 MHz, $CDCl_3$)
(Two isomers in 1:1.3 ratio)
F_3C $CF_2P(O)(OEt)_2$
7b
f1 (ppm)

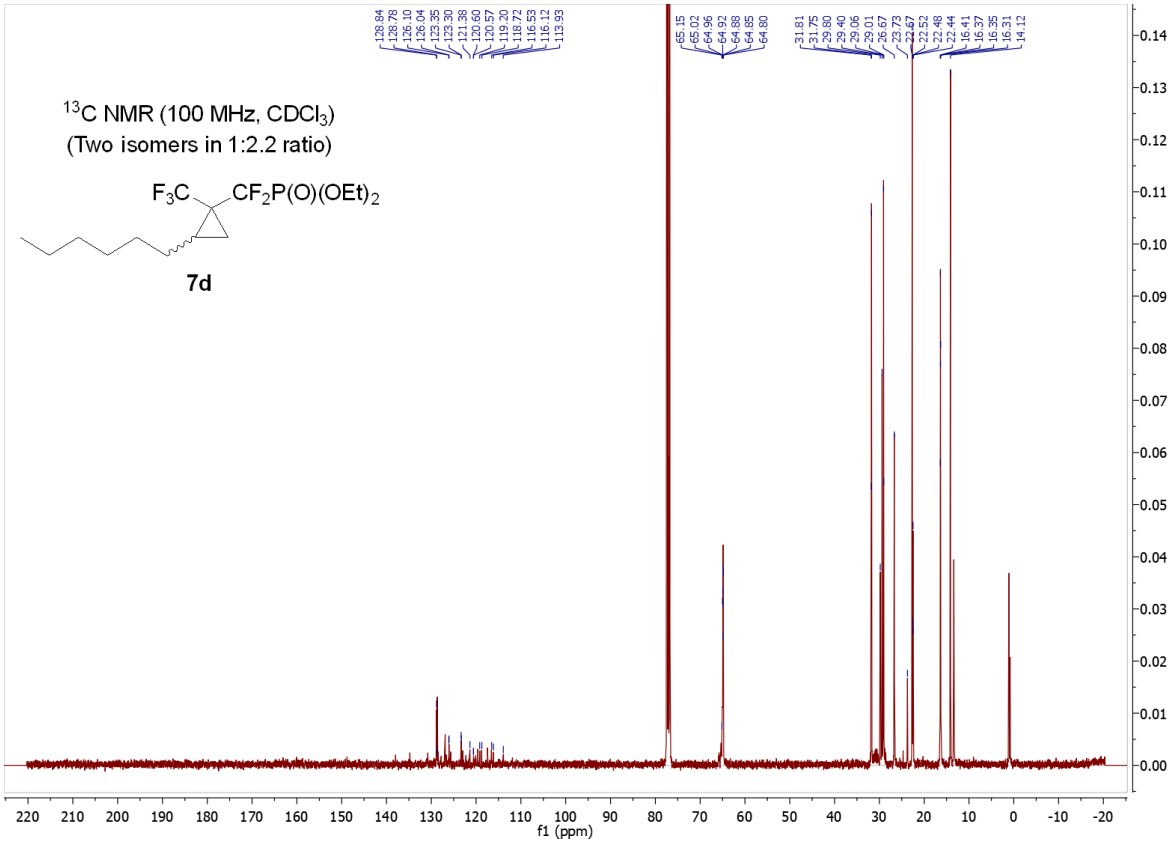

^{1}H NMR (400 MHz, $CDCl_3$)
(Two isomers in 1:1.1 ratio)
F_3C $CF_2P(O)(OEt)_2$
7c
f1 (ppm)

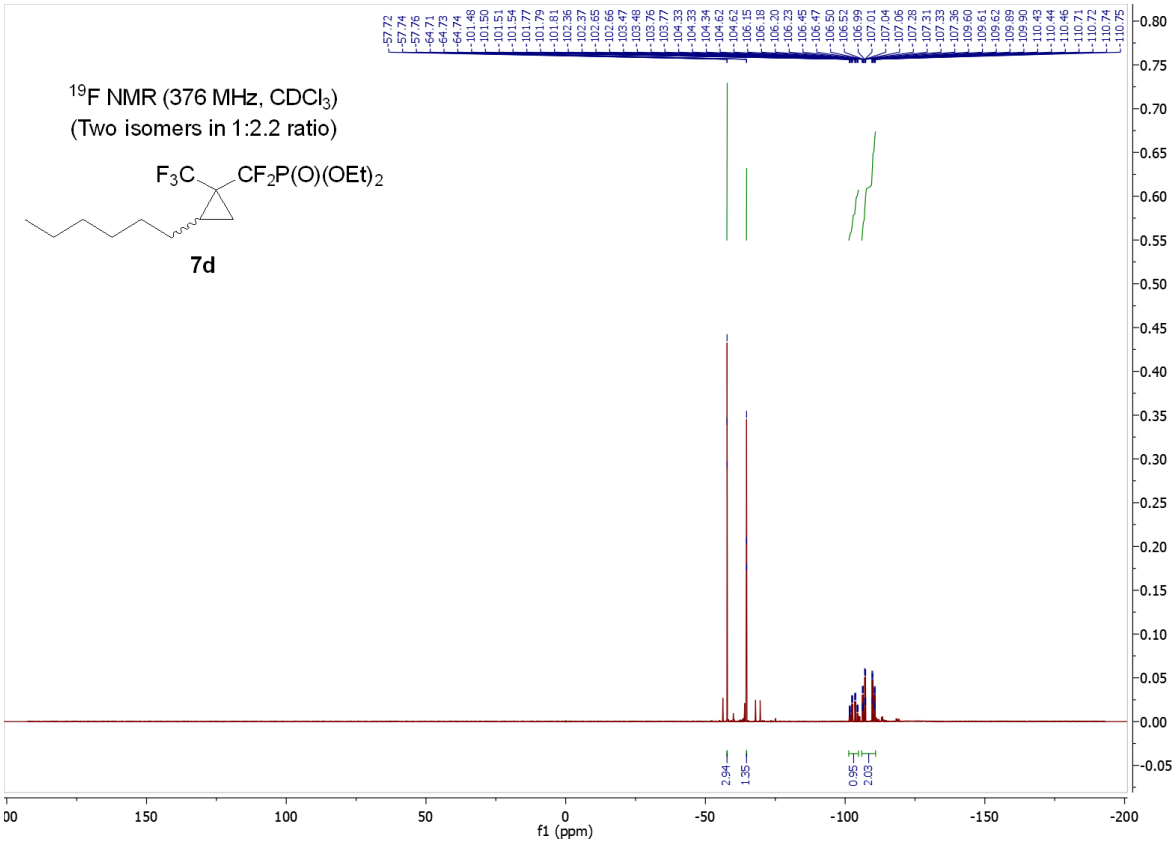

^{13}C NMR (100 MHz, $CDCl_3$)
(Two isomers in 1:1.1 ratio)
F_3C $CF_2P(O)(OEt)_2$
7c
f1 (ppm)

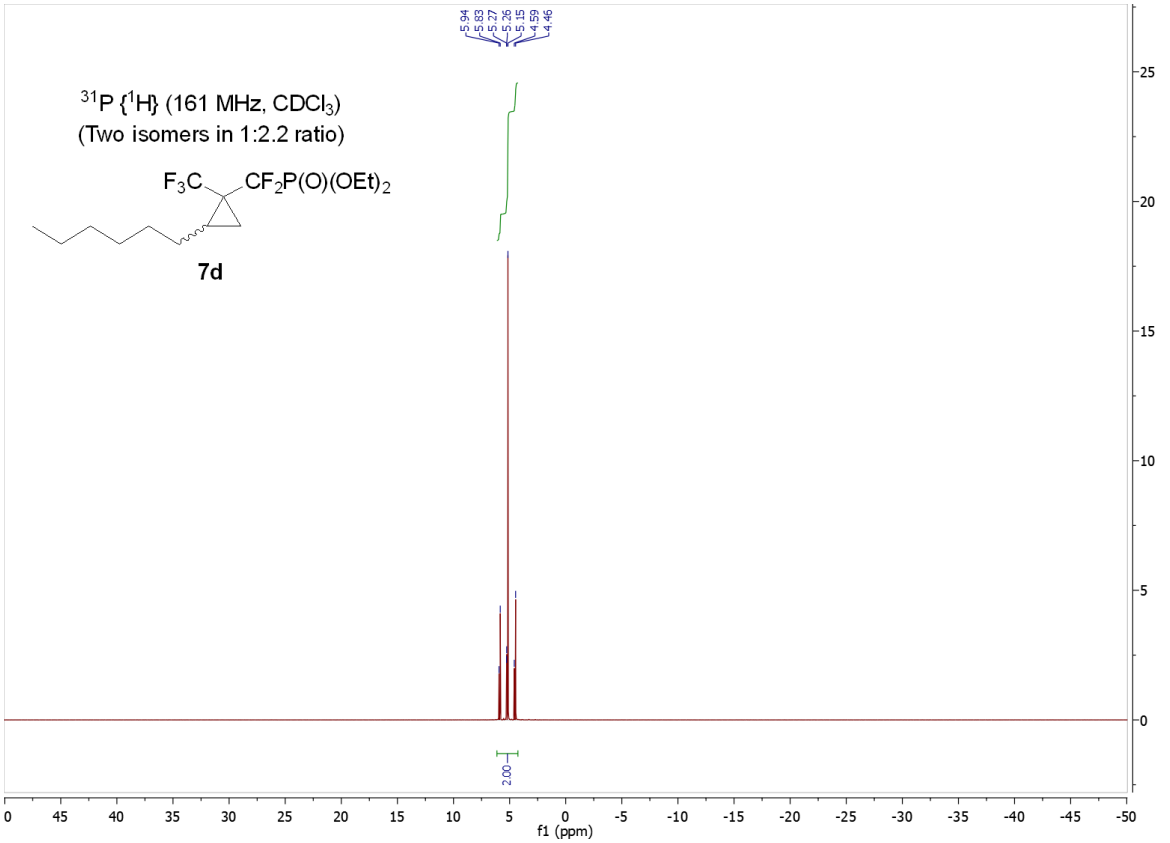

^{19}F NMR (376 MHz, $CDCl_3$)
(Two isomers in 1:1.1 ratio)
F_3C $CF_2P(O)(OEt)_2$
7c
f1 (ppm)

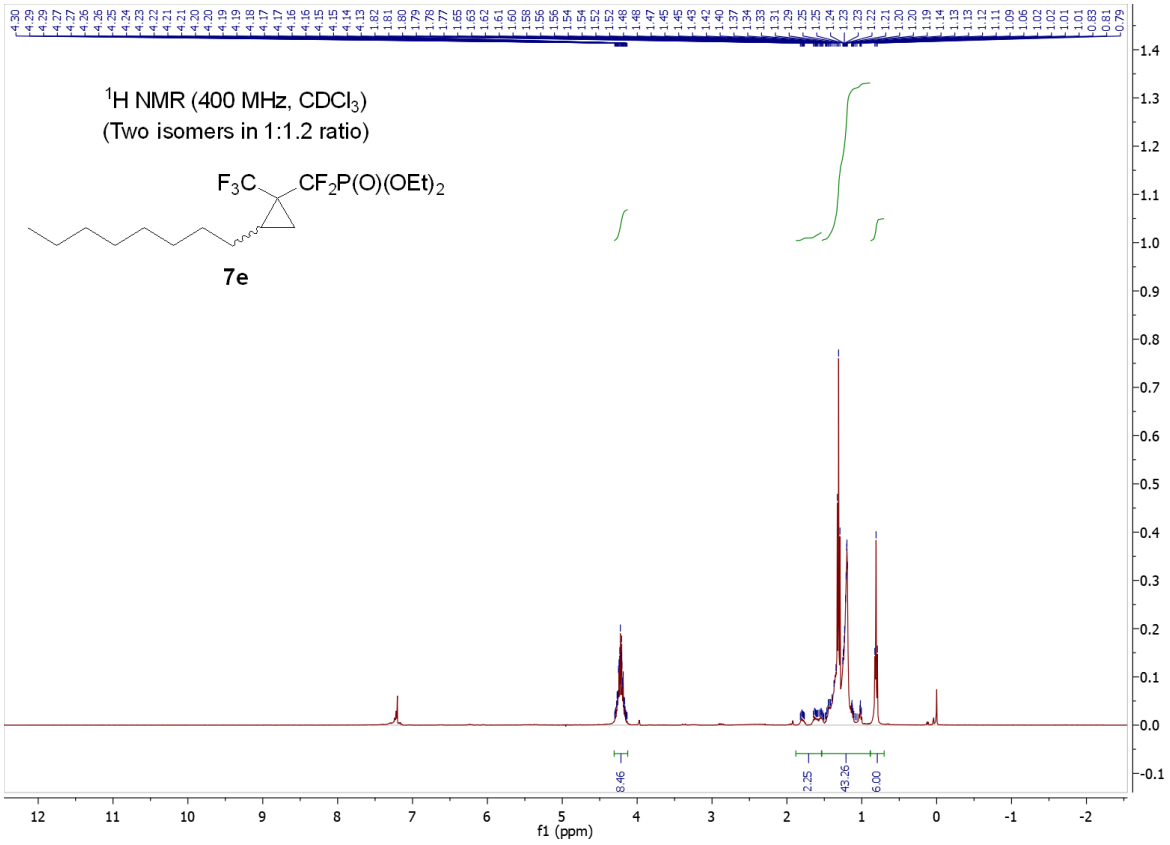

$^{31}P\{^{1}H\}$ (161 MHz, $CDCl_3$)
(Two isomers in 1:1.1 ratio)
F_3C
$CF_2P(O)(OEt)_2$
7c
f1 (ppm)

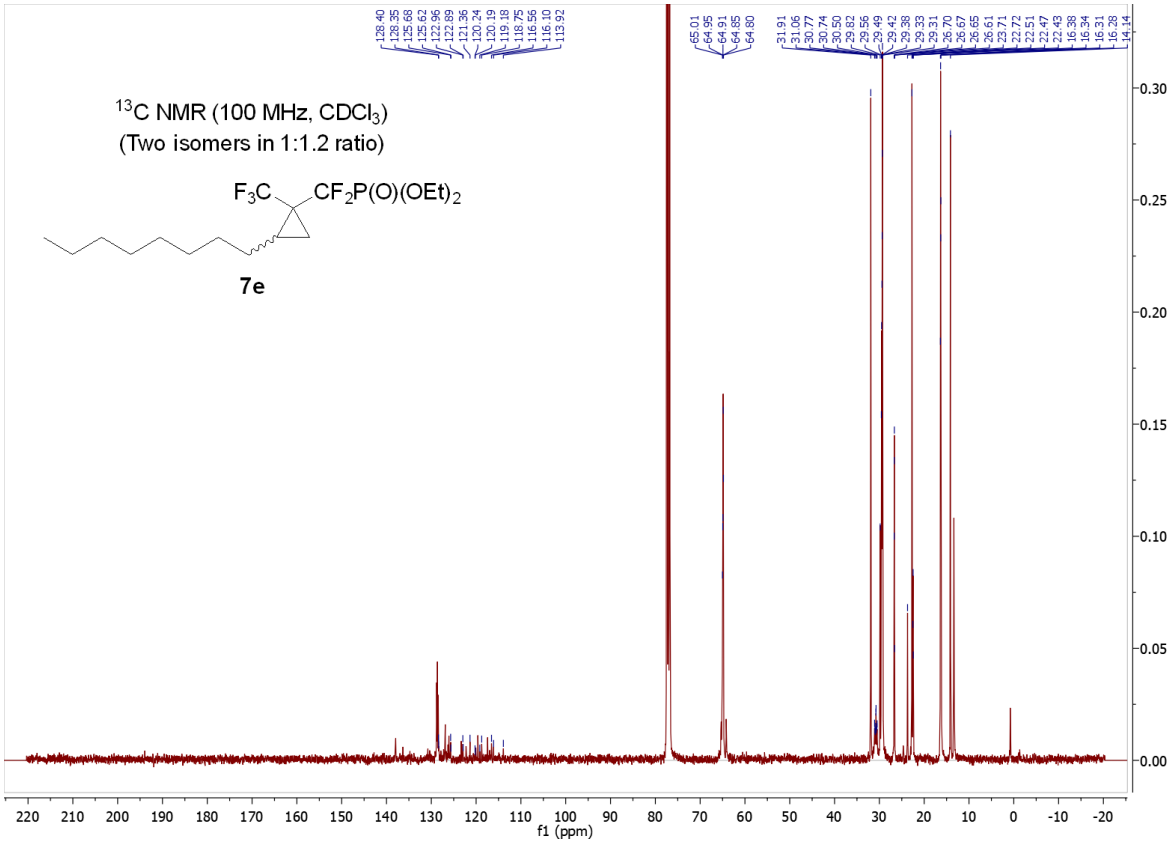

^{1}H NMR (400 MHz, $CDCl_3$)
(Two isomers in 1:2.2 ratio)
F_3C
$CF_2P(O)(OEt)_2$
7d
f1 (ppm)

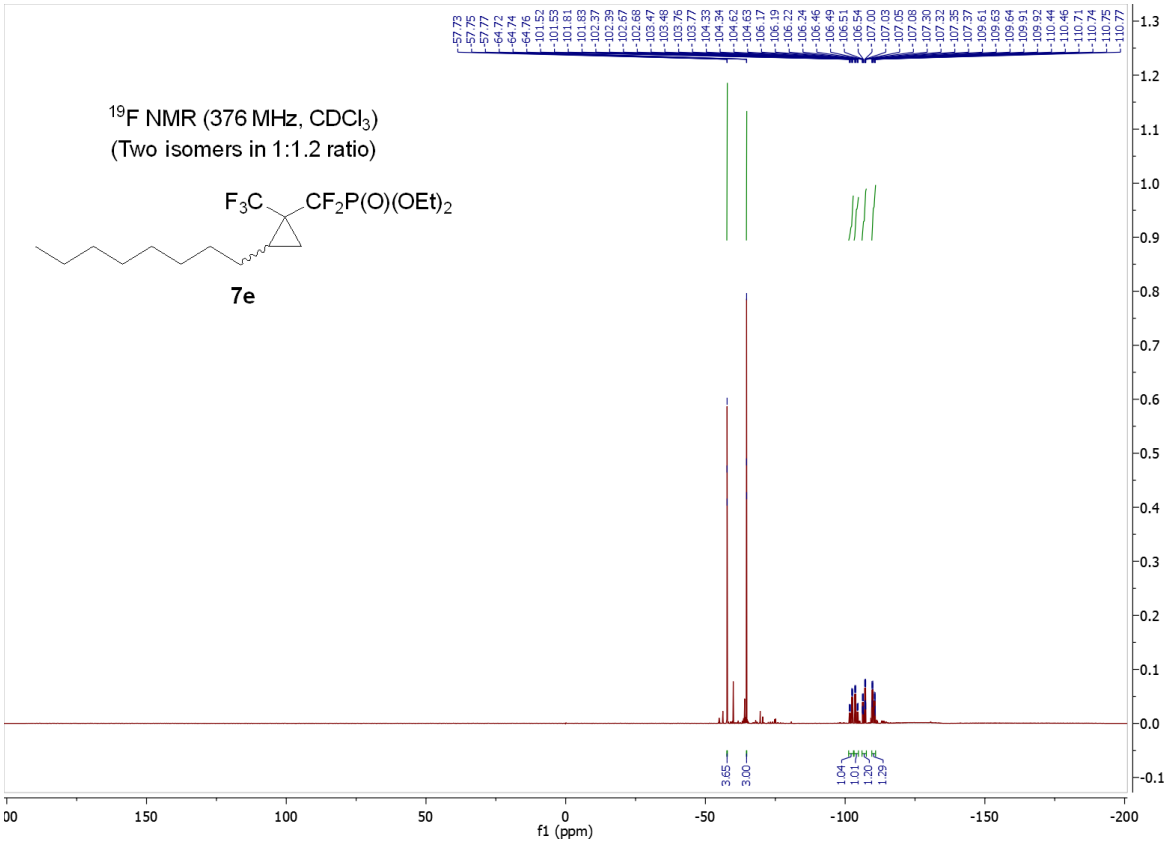

^{13}C NMR (100 MHz, $CDCl_3$)
(Two isomers in 1:2.2 ratio)
F_3C $CF_2P(O)(OEt)_2$
7d
f1 (ppm)

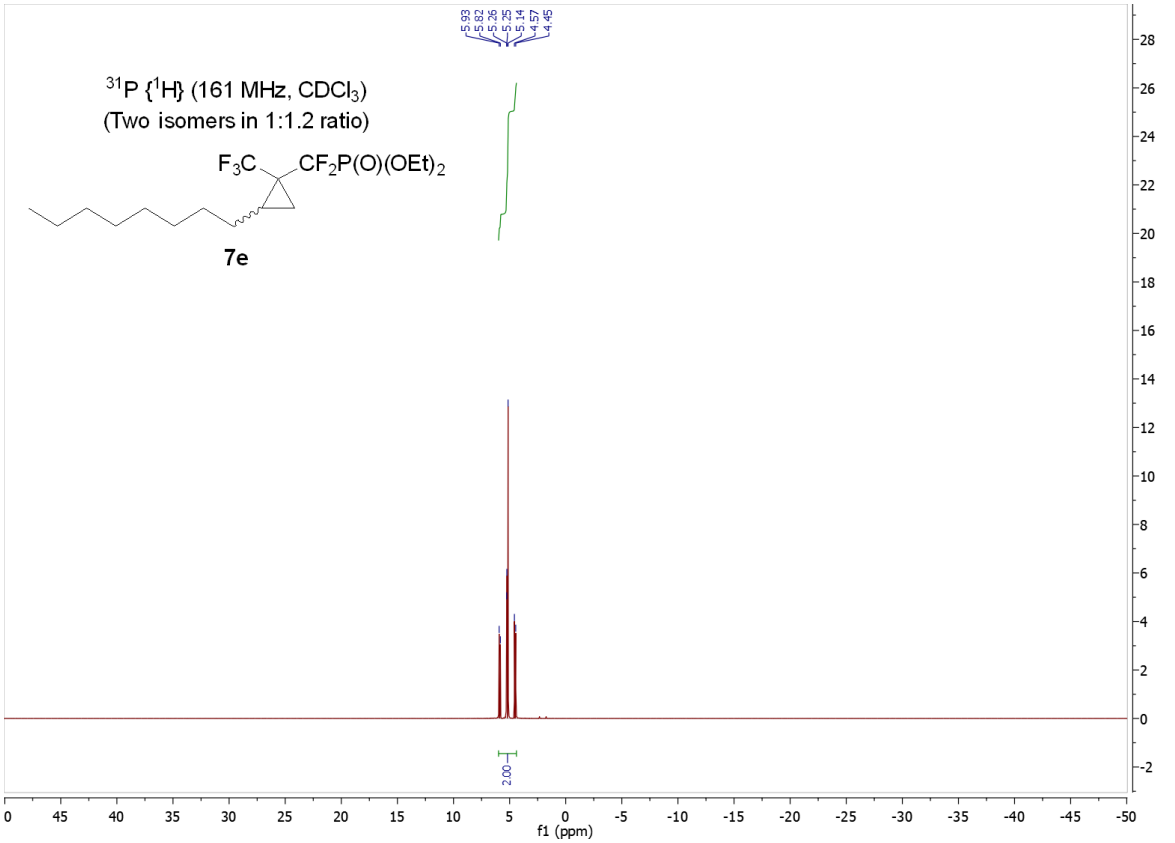

^{19}F NMR (376 MHz, $CDCl_3$)
(Two isomers in 1:2.2 ratio)
F_3C $CF_2P(O)(OEt)_2$
7d
2.94
1.35
0.95
2.03
f1 (ppm)

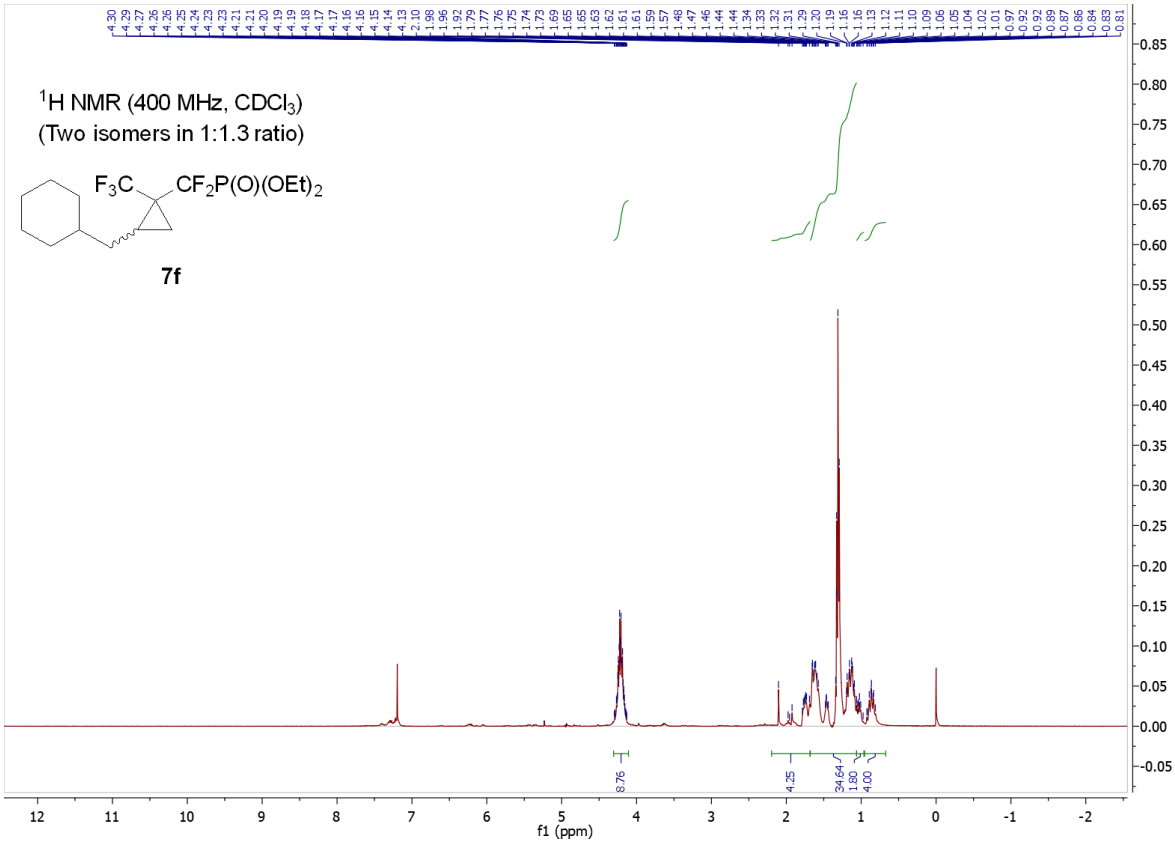

31P {1H} (161 MHz, CDCl3)
(Two isomers in 1:2.2 ratio)
F3C
CF2P(O)(OEt)2
7d
f1 (ppm)

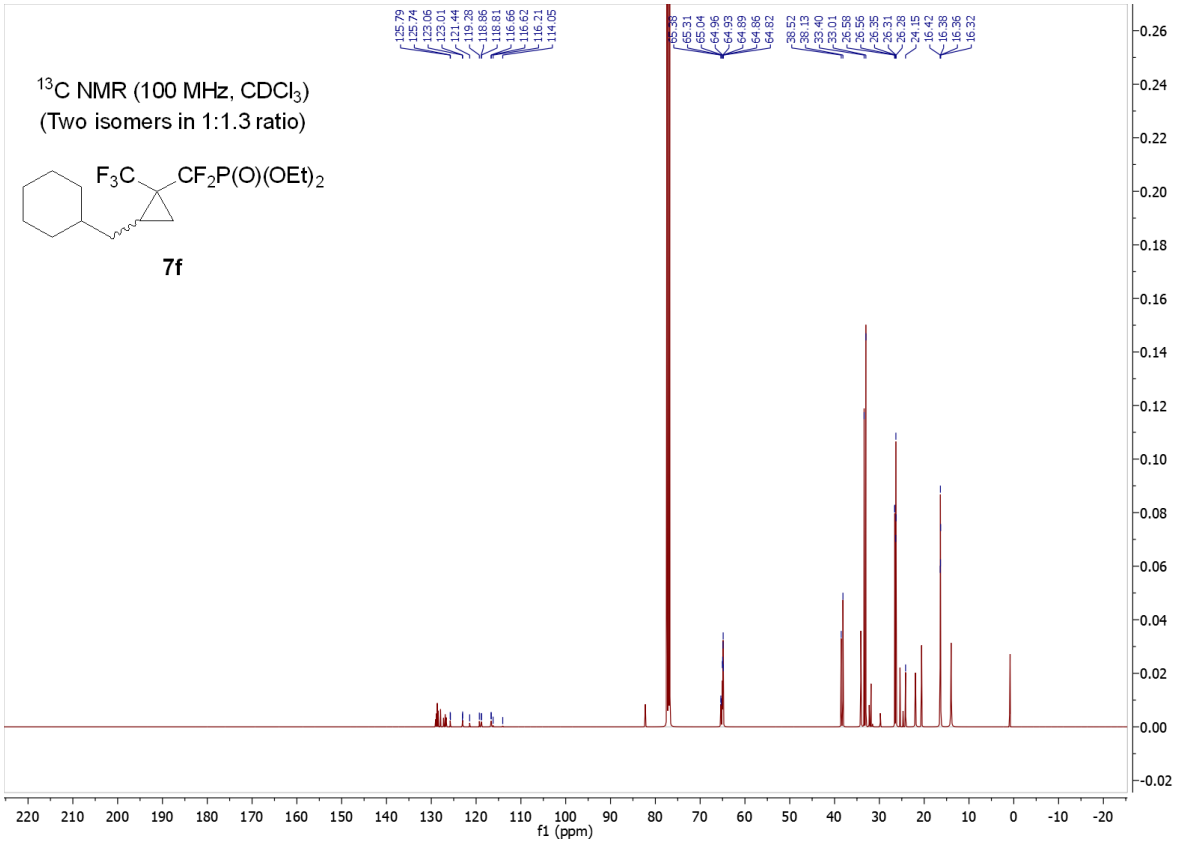

1H NMR (400 MHz, CDCl3)
(Two isomers in 1:1.2 ratio)
F3C
CF2P(O)(OEt)2
7e
f1 (ppm)

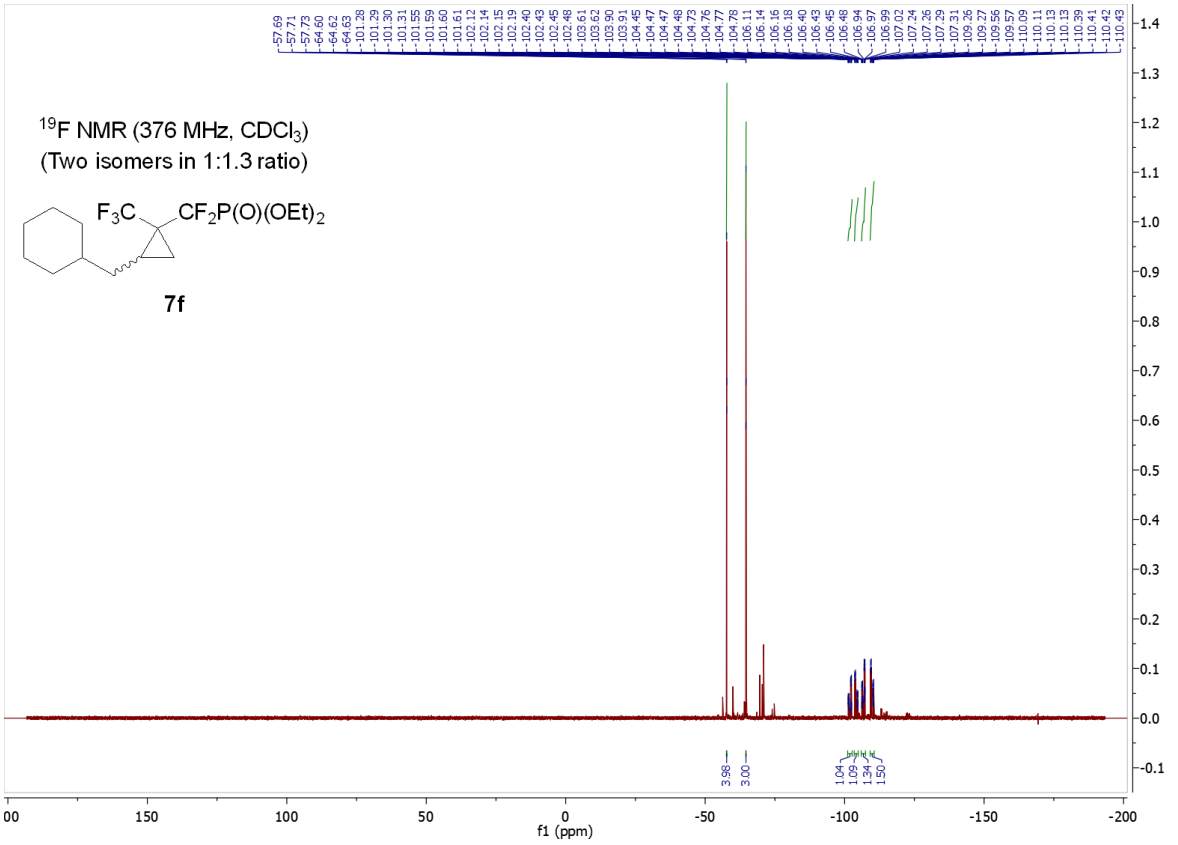

^{13}C NMR (100 MHz, $CDCl_3$)
(Two isomers in 1:1.2 ratio)
F_3C $CF_2P(O)(OEt)_2$
7e
f1 (ppm)

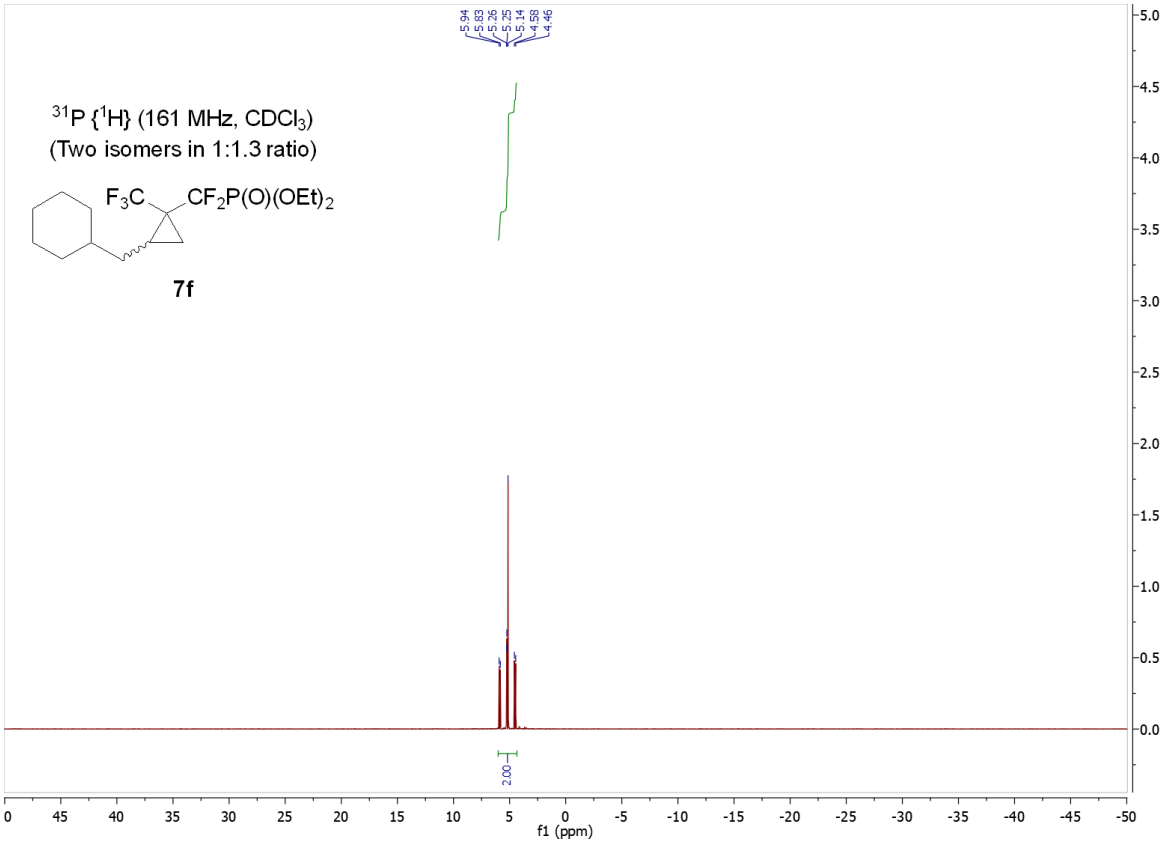

^{19}F NMR (376 MHz, $CDCl_3$)
(Two isomers in 1:1.2 ratio)
F_3C $CF_2P(O)(OEt)_2$
7e
3.65
3.00
1.04
1.01
1.20
1.29
f1 (ppm)

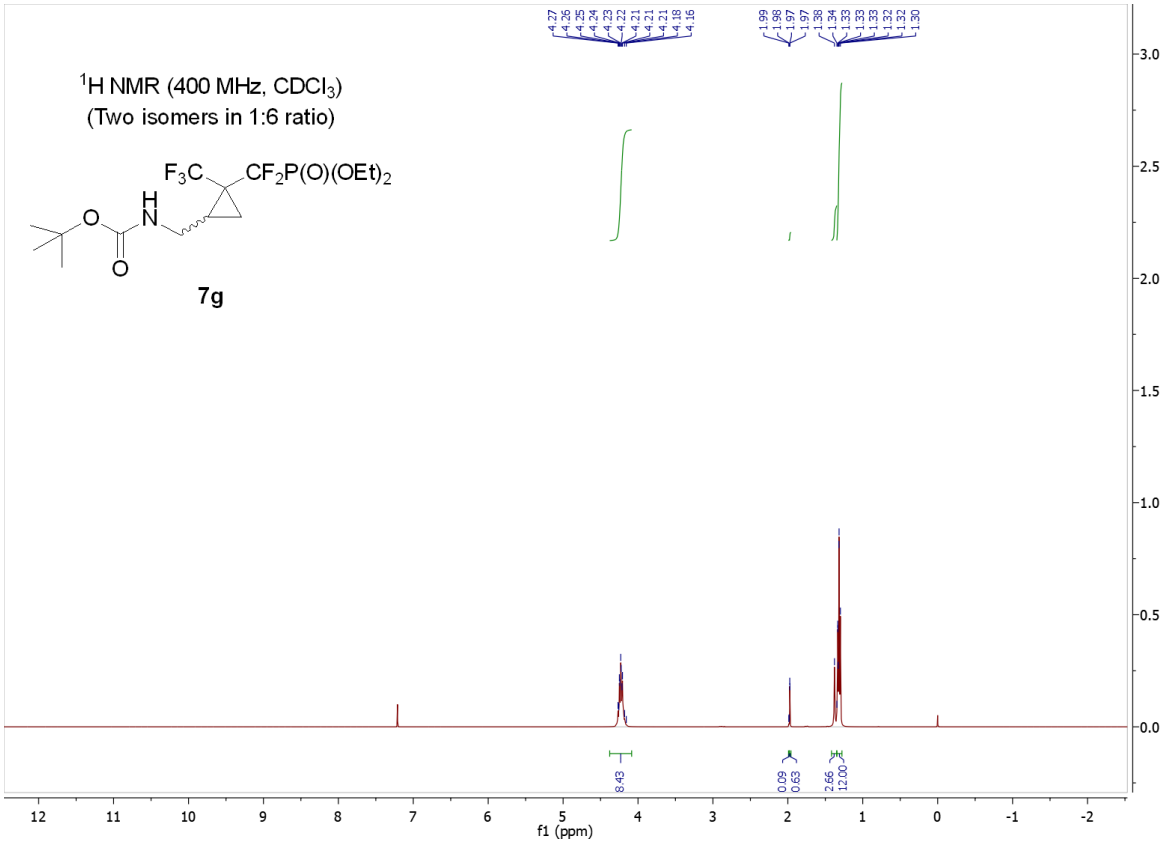

31P {1H} (161 MHz, CDCl3)
(Two isomers in 1:1.2 ratio)
F3C
CF2P(O)(OEt)2
7e
f1 (ppm)

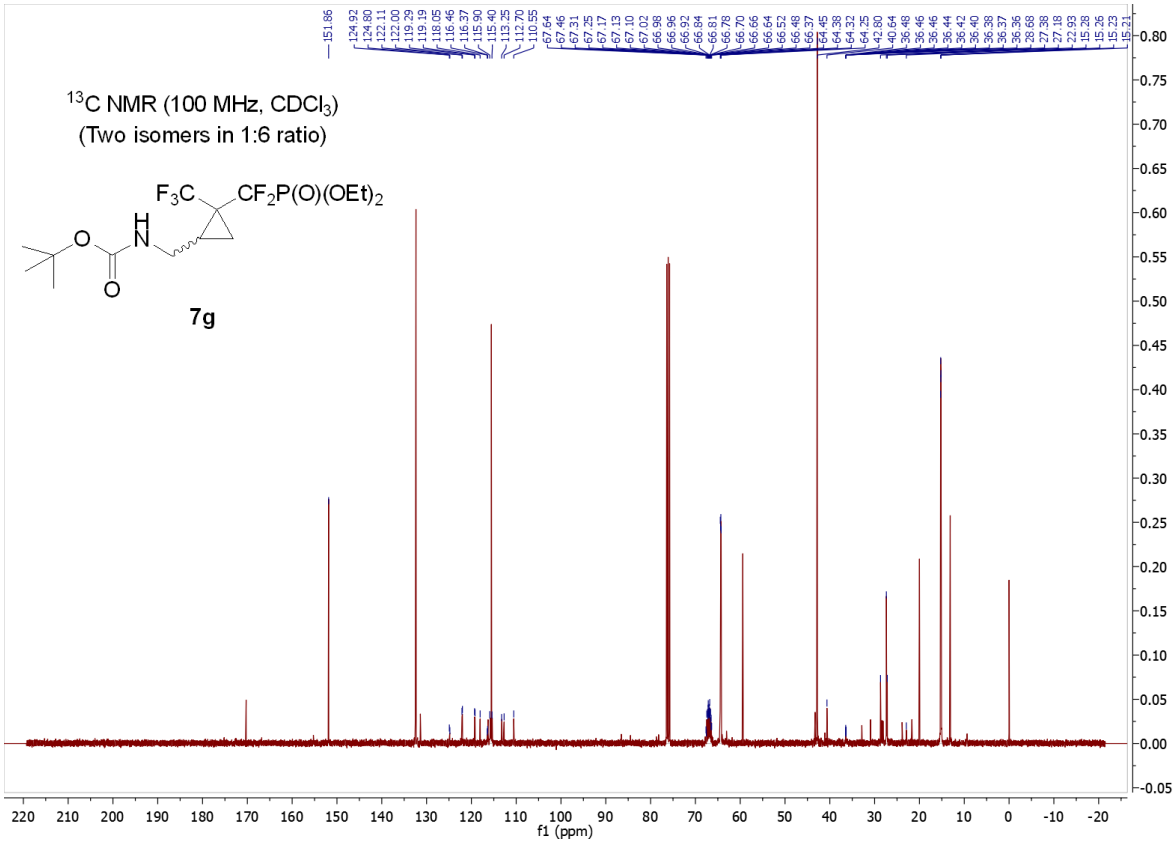

1H NMR (400 MHz, CDCl3)
(Two isomers in 1:1.3 ratio)
F3C
CF2P(O)(OEt)2
7f
f1 (ppm)

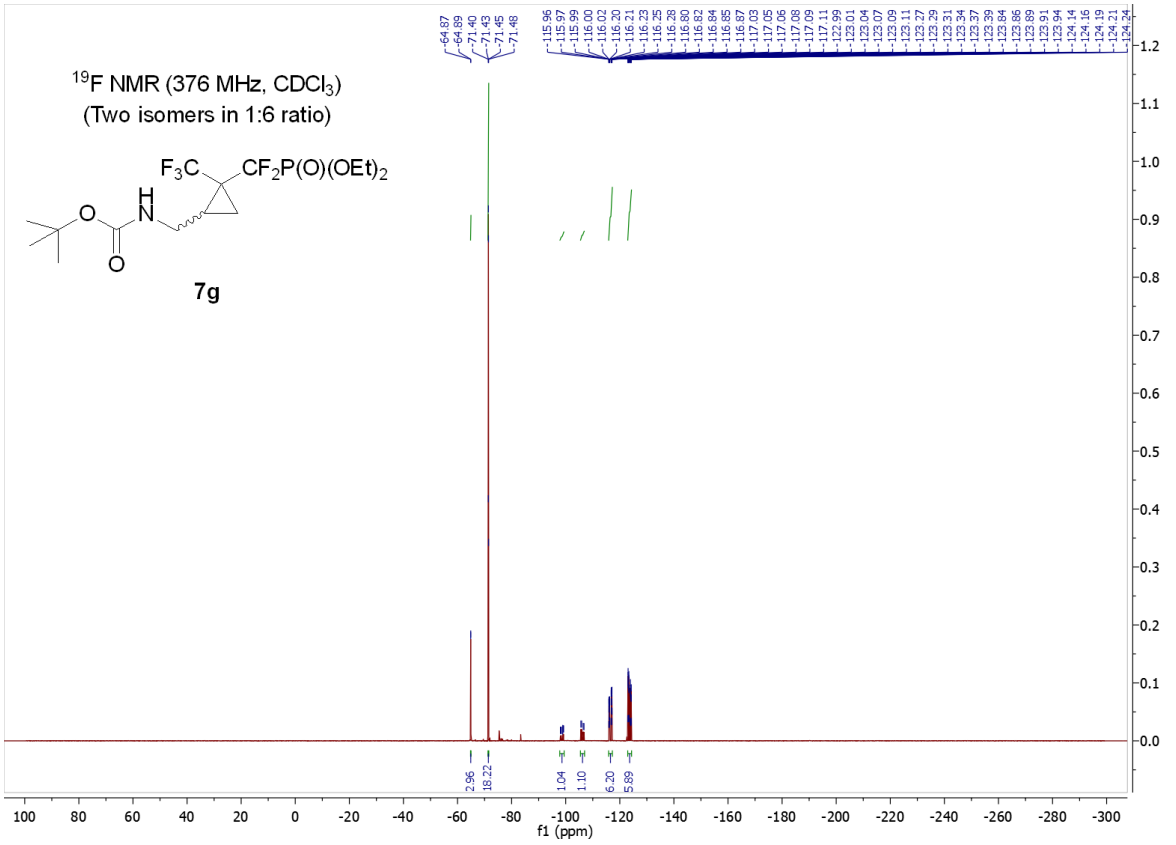

^{13}C NMR (100 MHz, $CDCl_3$)
(Two isomers in 1:1.3 ratio)
F_3C $CF_2P(O)(OEt)_2$
7f
f1 (ppm)

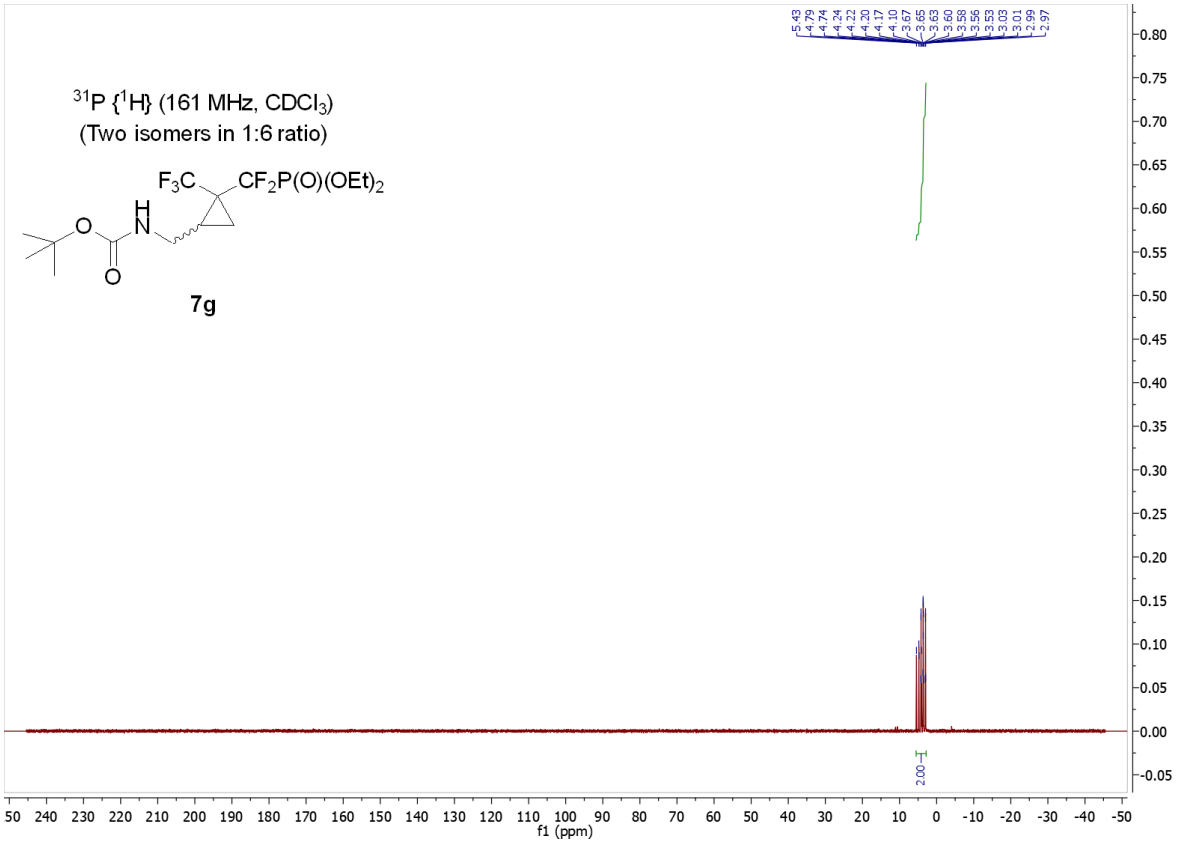

^{19}F NMR (376 MHz, $CDCl_3$)
(Two isomers in 1:1.3 ratio)
F_3C $CF_2P(O)(OEt)_2$
7f
f1 (ppm)


$^{31}P\{^{1}H\}$ (161 MHz, $CDCl_3$)
(Two isomers in 1:1.3 ratio)
F_3C
$CF_2P(O)(OEt)_2$
7f
5.94
5.83
5.26
5.25
5.14
4.58
4.46
2.00
f1 (ppm)


^{1}H NMR (400 MHz, $CDCl_3$)
(Two isomers in 1:6 ratio)
F_3C
$CF_2P(O)(OEt)_2$
H
N
O
O
7g
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.21
4.21
4.18
4.16
1.99
1.98
1.97
1.97
1.38
1.34
1.33
1.33
1.32
1.32
1.30
8.43
0.09
0.63
2.66
12.00
f1 (ppm)

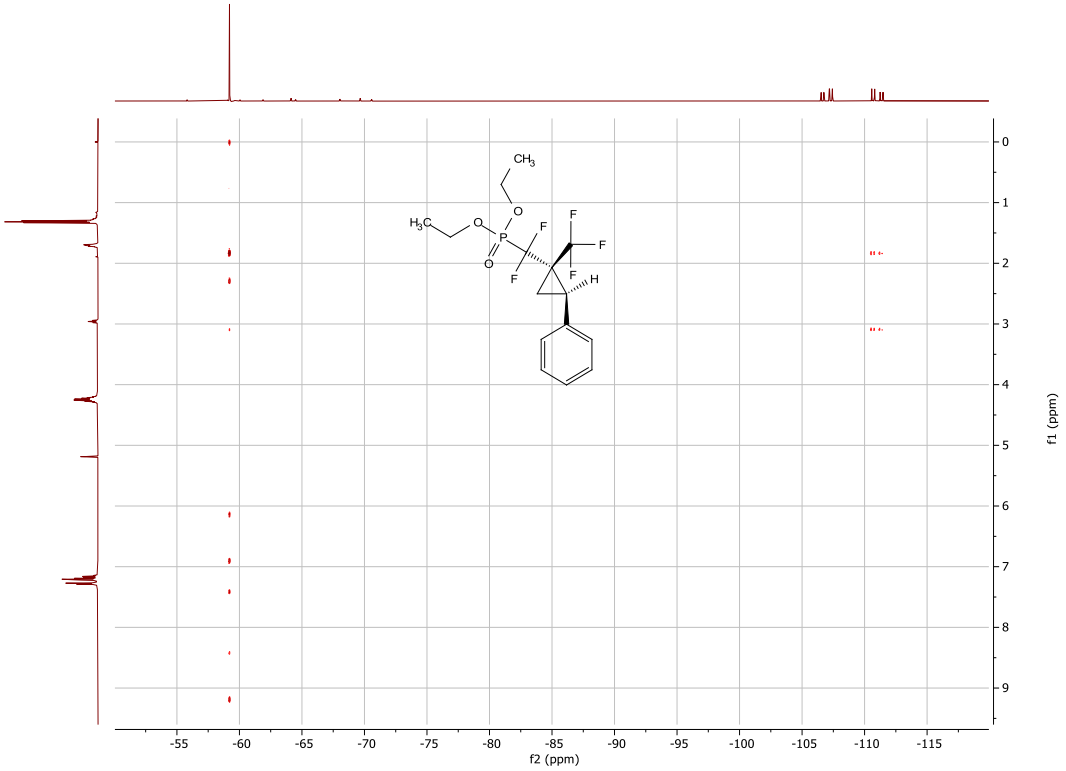

^{13}C NMR (100 MHz, $CDCl_3$)
(Two isomers in 1:6 ratio)
F_3C
$CF_2P(O)(OEt)_2$
H
N
O
O
7g
f1 (ppm)


^{19}F NMR (376 MHz, $CDCl_3$)
(Two isomers in 1:6 ratio)
F_3C
$CF_2P(O)(OEt)_2$
H
N
O
O
7g
2.96
18.22
1.04
1.10
6.20
5.89
f1 (ppm)

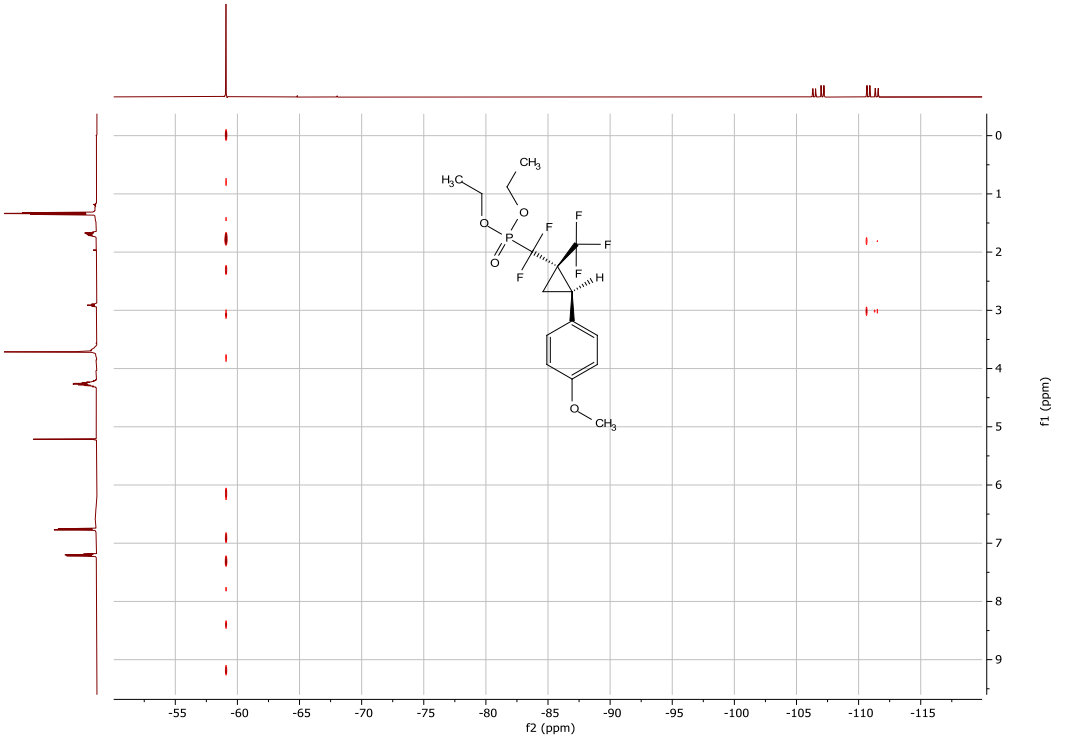

31P {1H} (161 MHz, CDCl3)
(Two isomers in 1:6 ratio)
F3C
CF2P(O)(OEt)2
H
N
O
O
7g
5.43
4.79
4.74
4.24
4.22
4.20
4.17
4.10
3.67
3.65
3.63
3.60
3.58
3.56
3.53
3.03
3.01
2.99
2.97
2.00
f1 (ppm)

8. Copies of HOESY ^{19}F, ^{1}H 2D NMR spectra

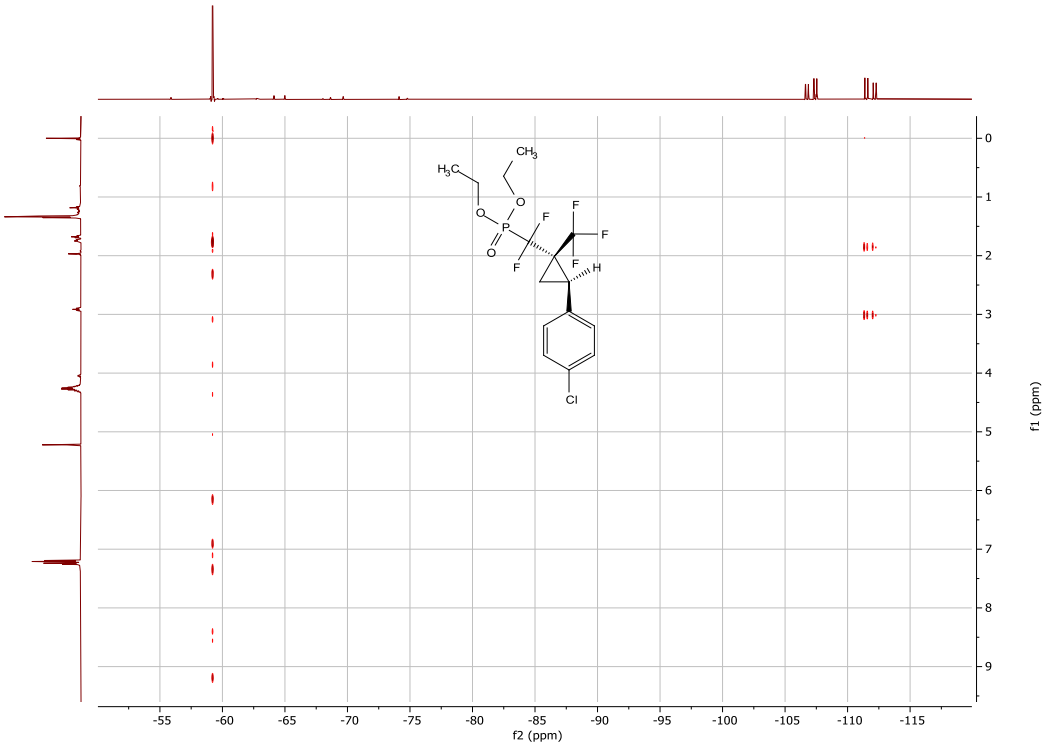
HOESY ^{19}F-^{1}H 2D NMR spectrum of **6c** (major isomer):



HOESY ^{19}F, ^{1}H 2D NMR spectrum of **6d** (major isomer):



HOESY ^{19}F, ^{1}H 2D NMR spectrum of **6g** (major isomer):



9. DFT calculations

Geometry optimizations were performed on the B3LYP/6-31G(d) (for H, C, F, N, O, P) and B3LYP/def2tzvp (for Cu and I) level of theory. More accurate energies were computed using 6-311+g(3d,p) instead of 6-31G(d). Solvation effects were considered by means of the default (SCRD) model of solvation with the solvent toluene. Thermochemical values refer to a temperature of 384 K. All calculations were carried out with an ultrafine integration grid (99,590). Transition structures were located either by a QST2 optimization or by directing the Berny geometry optimization algorithm towards a first order saddle point. Frequency calculations were conducted to characterize all stationary points.

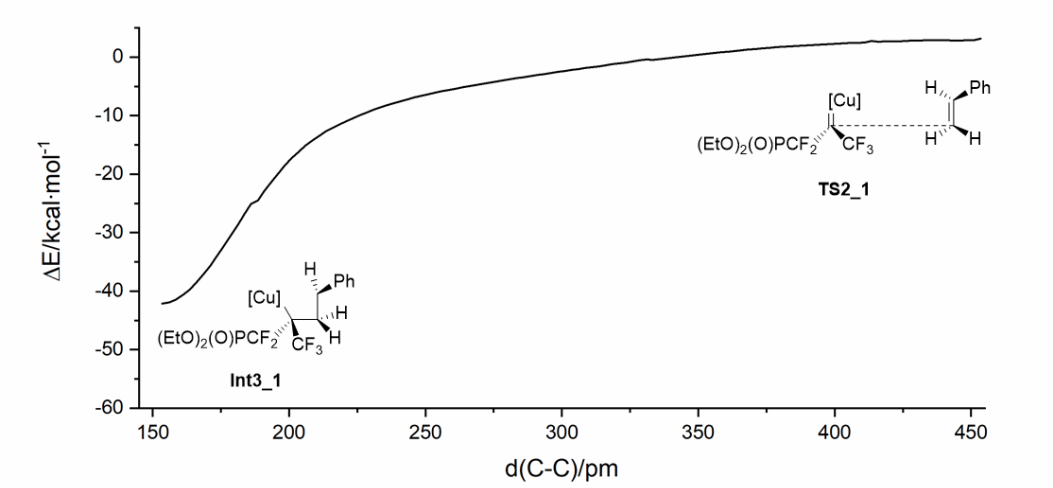


Figure 1. Change in electronic energy relative to **Int2** and styrene in dependence of the respective C-C bond that is formed along the reaction pathway leading to **Int3_1**.

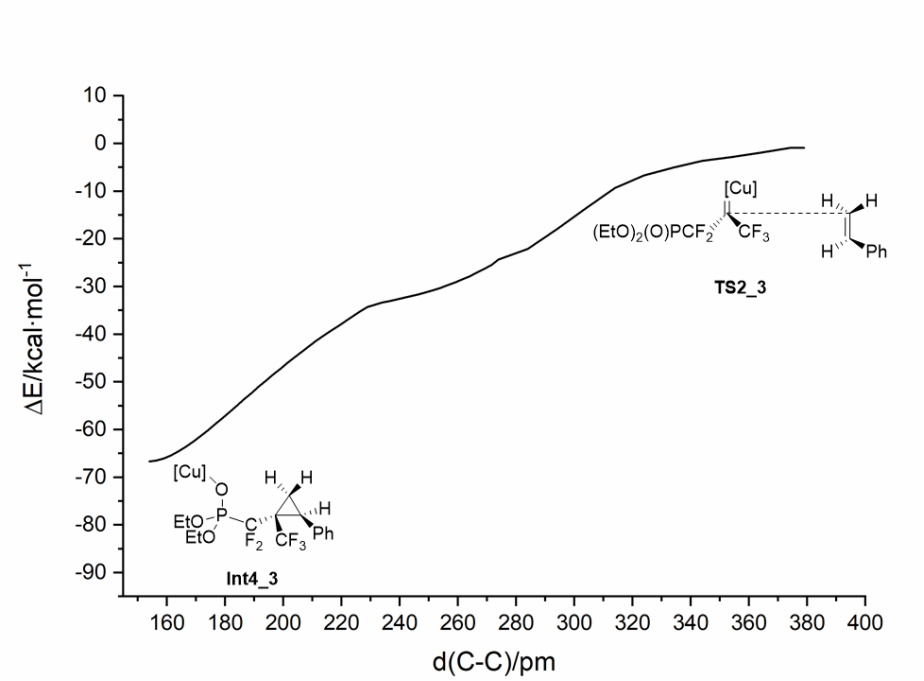


Figure 2. Change in electronic energy relative to **Int2** and styrene in dependence of the respective C-C bond that is formed along the reaction pathway leading directly to **Int4_4**.

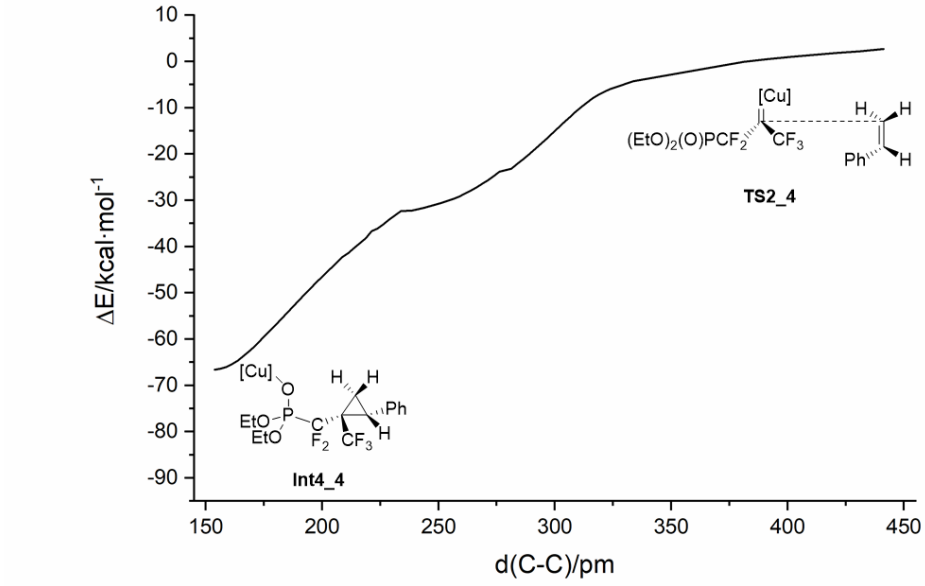
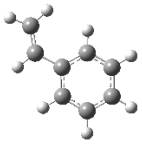
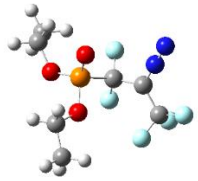
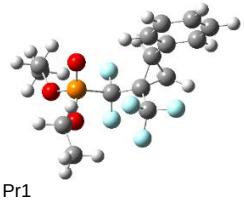
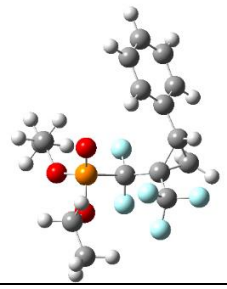
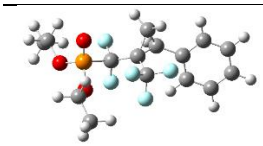


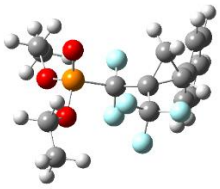
Figure 3. Change in electronic energy relative to Int2 and styrene in dependence of the respective C-C bond that is formed along the reaction pathway leading directly to Int4_4.

Table S3. Cartesian coordinates and calculated thermochemical values of substrates, catalyst, products, intermediates and transition states.

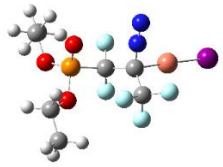
Molecule	Coordinates				Thermochemical values / Hartree
Substrates and Catalyst					
 CuI	Cu	0.00000000	0.00000000	-1.56964500	Sum of electronic and zero-point Energies= -1938.441800 Sum of electronic and thermal Energies= -1938.437992 Sum of electronic and thermal Enthalpies= -1938.436775 Sum of electronic and thermal Free Energies= -1938.475739
	I	0.00000000	0.00000000	0.85886200	
 Styrene	C	0.00000000	0.56045000	0.00000000	Sum of electronic and zero-point Energies= -309.615611 Sum of electronic and thermal Energies= -309.604921 Sum of electronic and thermal Enthalpies= -309.603705 Sum of electronic and thermal Free Energies= -309.657859
	C	1.33856100	0.13047200	0.00000000	
	C	1.66266100	-1.22604900	0.00000000	
	C	0.65031400	-2.18606800	0.00000000	
	C	-0.68690200	-1.77578000	0.00000000	
	C	-1.00866300	-0.42165000	0.00000000	
	H	2.13267900	0.87393700	0.00000000	
	H	2.70575900	-1.53168600	0.00000000	
	H	0.89764100	-3.24429600	0.00000000	
	H	-1.48235700	-2.51673000	0.00000000	
	H	-2.05330000	-0.12369100	0.00000000	
	C	-0.28181400	2.00610500	0.00000000	
	H	0.60685100	2.63777400	0.00000000	
	C	-1.47930100	2.60565200	0.00000000	
	H	-1.55872500	3.68913900	0.00000000	
	H	-2.41768400	2.05676000	0.00000000	
 Adduct 3	P	1.16959500	0.22765800	0.45381800	Sum of electronic and zero-point Energies= -1448.747538 Sum of electronic and thermal Energies= -1448.717522 Sum of electronic and thermal Enthalpies= -1448.716306 Sum of electronic and thermal Free Energies= -1448.818373
	O	1.23405300	-0.07076200	1.90832300	
	C	-0.11417800	-0.84814800	-0.38413700	
	C	-1.49104900	-0.76415900	0.21056900	
	N	-1.69550200	-1.27555800	1.39127700	
	N	-1.86745400	-1.73500300	2.41621600	
	C	-2.62837200	-0.06396500	-0.46231900	
	F	-3.70645100	-0.04732700	0.35039900	
	F	-2.32310600	1.21180600	-0.77651600	
	F	-2.99393400	-0.66495400	-1.61430200	
	F	0.35947500	-2.14127400	-0.26667200	
	F	-0.20251500	-0.55166300	-1.71038800	
	O	0.64411500	1.65650700	-0.02455300	
	O	2.52757800	0.04129700	-0.38058400	
	C	3.57214400	-0.90026500	0.02115300	
	H	4.49099800	-0.30897600	0.06586900	
	H	3.35229700	-1.27332500	1.02502300	
	C	1.28161300	2.88885300	0.43187100	
	H	2.30465000	2.90883700	0.04272100	
	H	1.31701600	2.87723900	1.52580100	
	C	3.67905300	-2.01990100	-0.99483400	
	H	3.88480600	-1.62250400	-1.99424400	
	H	4.50077300	-2.68947200	-0.71433900	
	H	2.75435600	-2.60289100	-1.03356200	
	C	0.46185000	4.04977600	-0.08841100	
	H	-0.56380900	4.00241300	0.29129800	
	H	0.91211100	4.99240600	0.24289800	

	H	0.43001700	4.04655900	-1.18272300	
Products					
 N_2	N	0.00000000	0.00000000	0.55259000	Sum of electronic and zero-point Energies=
	N	0.00000000	0.00000000	-0.55259000	-109.553048
					Sum of electronic and thermal Energies=
					-109.550006
					Sum of electronic and thermal Enthalpies=
					-109.548790
					Sum of electronic and thermal Free Energies=
					-109.577887
 Pr1	P	-1.84936700	0.05289600	-0.66611000	Sum of electronic and zero-point Energies=
	O	-1.05378800	-0.18913800	-1.89845100	-1648.891070
	C	-1.03733100	-0.67385300	0.86506100	Sum of electronic and thermal Energies=
	C	0.44905100	-0.41984600	1.07773900	-1648.853069
	C	0.83778500	1.03274100	1.24914900	Sum of electronic and thermal Enthalpies=
	F	2.09933600	1.17051000	1.70533100	-1648.851853
	F	0.77035400	1.71597400	0.07763300	Sum of electronic and thermal Free Energies=
	F	0.03048300	1.67554400	2.11968600	-1648.969463
	F	-1.22730000	-2.04150700	0.73557200	
	F	-1.74643900	-0.29868500	1.97383300	
	O	-2.11006500	1.55614200	-0.20054700	
	O	-3.32916800	-0.56929400	-0.63138800	
	C	-3.65513400	-1.83988500	-1.27258200	
	H	-4.30223500	-1.59527200	-2.12014400	
	H	-2.74552200	-2.30357000	-1.66326800	
	C	-2.01966500	2.67318700	-1.13663500	
	H	-2.92882700	2.67612900	-1.74684500	
	H	-1.15749000	2.51709000	-1.78994400	
	C	-4.36020300	-2.73341700	-0.27238400	
	H	-5.26268500	-2.24948400	0.11541800	
	H	-4.65391200	-3.67031100	-0.76047500	
	H	-3.70091600	-2.96942900	0.56813600	
	C	-1.88748000	3.94264100	-0.32286400	
	H	-0.98444200	3.91056800	0.29389400	
	H	-1.82085200	4.80376200	-0.99776900	
	H	-2.75441300	4.08200700	0.33126100	
	C	1.22095900	-1.45350000	1.87704300	
	H	1.99586300	-1.06928300	2.53164300	
	H	0.65709200	-2.28935800	2.27696900	
	C	1.42815500	-1.37569900	0.39317500	
	H	0.90367300	-2.14183400	-0.17209500	
	C	2.70088600	-0.92553800	-0.26443900	
	C	2.64480300	-0.34396000	-1.54030200	
	C	3.94894700	-1.12789100	0.33487900	
	C	3.81614600	0.03248900	-2.19617900	
	H	1.67736000	-0.18699800	-2.01048600	
	C	5.12192300	-0.75083300	-0.32251600	
	H	4.00557700	-1.58815300	1.31767700	
	C	5.05861500	-0.16871200	-1.58902500	
	H	3.75863100	0.48431900	-3.18312700	
	H	6.08407100	-0.91457500	0.15604400	
	H	5.97102500	0.12521100	-2.10138200	
	P	-1.05149000	1.18418800	0.34887400	Sum of electronic and zero-point Energies=
	O	-0.43842200	1.06146700	1.69611600	-1648.888421
	C	-0.29749800	0.04177500	-0.94831600	Sum of electronic and thermal Energies=
	C	-0.03881200	-1.41928200	-0.60675500	-1648.850513
	C	-1.25339100	-2.18303700	-0.12458400	Sum of electronic and thermal Enthalpies=
	F	-1.00282100	-3.50968900	-0.03377900	-1648.849297
	F	-1.65100900	-1.78273000	1.10900700	Sum of electronic and thermal Free Energies=
	F	-2.31378800	-2.03717200	-0.94531100	-1648.966130
	F	0.89742800	0.63166400	-1.30232200	

Pr2	F	-1.09380400	0.10059700	-2.06579200	
	O	-2.60147100	0.83571000	0.18868400	
	O	-0.95260700	2.62325900	-0.35684300	
	C	0.21821300	3.48179400	-0.19215800	
	H	-0.09109600	4.29999400	0.46519400	
	H	1.01969100	2.92977500	0.30536900	
	C	-3.50421500	0.84368300	1.33512300	
	H	-3.75599900	1.88559900	1.55919500	
	H	-2.98654000	0.41454800	2.19673200	
	C	0.64688400	3.98999900	-1.55337700	
	H	-0.16951200	4.53013400	-2.04432900	
	H	1.49479800	4.67564400	-1.43898800	
	H	0.95424100	3.15952600	-2.19582600	
	C	-4.73092500	0.04065900	0.95761100	
	H	-4.45566200	-0.99062900	0.71728800	
	H	-5.43400300	0.02925400	1.79848200	
	H	-5.23574900	0.47907400	0.09051300	
	C	0.91448600	-2.16877500	-1.51796900	
	H	0.63469200	-3.16959100	-1.82944600	
	H	1.39365600	-1.56805700	-2.28426200	
	C	1.31187600	-1.92964800	-0.09134000	
	H	1.18162000	-2.79261900	0.55915800	
	C	2.48136600	-1.07273900	0.30635400	
	C	2.47037000	-0.37355100	1.52159300	
	C	3.63582700	-1.03481400	-0.48518500	
	C	3.58796200	0.35684900	1.92647500	
	H	1.57566100	-0.37845200	2.13545000	
	C	4.75534200	-0.30619400	-0.07868400	
	H	3.66223600	-1.58393800	-1.42266100	
	C	4.73439400	0.39277100	1.12887600	
	H	3.56103300	0.89987200	2.86768600	
	H	5.64318400	-0.28823700	-0.70564900	
	H	5.60477800	0.96081100	1.44710400	
 Pr3	P	2.40333500	-0.01082900	0.32465600	Sum of electronic and zero-point Energies=
	O	2.57895500	0.06535200	1.79679300	-1648.890124
	C	0.73554500	-0.72023700	-0.18264600	Sum of electronic and thermal Energies=
	C	-0.54457900	-0.22145700	0.47479000	-1648.852113
	C	-0.78903900	1.26523200	0.36121300	Sum of electronic and thermal Enthalpies=
	F	-1.96069000	1.63420300	0.91436300	-1648.850897
	F	0.17301700	1.97946800	1.00207400	Sum of electronic and thermal Free Energies=
	F	-0.79507600	1.68400600	-0.92250700	-1648.968676
	F	0.85863900	-2.07423900	0.09166100	
	F	0.60981400	-0.61421400	-1.54429700	
	O	2.45156900	1.33159400	-0.53680800	
	O	3.43555200	-0.94689400	-0.47611000	
	C	3.97965300	-2.17172100	0.10060100	
	H	5.03251800	-1.96747900	0.31766400	
	H	3.47650000	-2.39545600	1.04492900	
	C	3.07979600	2.54530400	-0.02535600	
	H	4.16364300	2.43596200	-0.13757000	
	H	2.84494800	2.64533300	1.03740500	
	C	3.82603500	-3.29860300	-0.90070700	
	H	4.32832800	-3.05514400	-1.84283100	
	H	4.27565900	-4.21345100	-0.49683000	
	H	2.76903100	-3.49081600	-1.10749600	
	C	2.54879900	3.71134800	-0.83173100	
	H	1.46296600	3.78997800	-0.72262000	
	H	3.00549700	4.64153500	-0.47444800	
	H	2.78686400	3.59504600	-1.89415100	
	C	-1.06269700	-0.91419900	1.71617400	
	H	-0.43456100	-1.68115000	2.15595300	

	H	-1.57978300	-0.28103300	2.43031500	
	C	-1.72680100	-1.19385700	0.39932000	
	H	-1.42926500	-2.13698100	-0.05390500	
	C	-3.12802800	-0.78939400	0.04499100	
	C	-4.16449500	-0.86489600	0.98218200	
	C	-3.42679900	-0.39604200	-1.26742900	
	C	-5.47512600	-0.54981500	0.61737900	
	H	-3.94575600	-1.17507900	2.00069100	
	C	-4.73484700	-0.08025200	-1.63232400	
	H	-2.62497600	-0.32860700	-1.99856300	
	C	-5.76373400	-0.15633200	-0.69005300	
	H	-6.26976700	-0.61254800	1.35636100	
	H	-4.95050600	0.22795000	-2.65203400	
	H	-6.78340600	0.09047300	-0.97377000	
 Pr4	P	1.75184100	0.99571500	-0.38663500	Sum of electronic and zero-point Energies=
	O	2.07346800	0.90683500	-1.83348000	-1648.889257
	C	0.09069200	0.22135500	0.04803900	Sum of electronic and thermal Energies=
	C	-0.24303600	-1.16749200	-0.47684800	-1648.851304
	C	0.74505700	-2.25017500	-0.10228000	Sum of electronic and thermal Enthalpies=
	F	0.30795800	-3.47616500	-0.47181000	-1648.850088
	F	1.94433500	-2.08000800	-0.71345400	Sum of electronic and thermal Free Energies=
	F	0.98080800	-2.29301600	1.22484900	-1648.967355
	F	-0.82699000	1.11889100	-0.46394300	
	F	-0.05397100	0.24496700	1.41227000	
	O	2.71924900	0.28686900	0.66721800	
	O	1.62047800	2.47230800	0.23306000	
	C	1.07759900	3.59040600	-0.53197000	
	H	1.91991200	4.25840500	-0.73614700	
	H	0.68865800	3.23349700	-1.48919500	
	C	4.10518000	-0.02685800	0.33662400	
	H	4.68475700	0.90054600	0.39396200	
	H	4.14797200	-0.40476700	-0.68807800	
	C	0.00691500	4.27805900	0.29076400	
	H	0.41112900	4.62080400	1.24909300	
	H	-0.37238300	5.15021400	-0.25496300	
	H	-0.82751800	3.59803500	0.48578100	
	C	4.59318000	-1.05360700	1.33641900	
	H	3.98786100	-1.96318800	1.27840000	
	H	5.63575200	-1.31155900	1.11742500	
	H	4.54077000	-0.66287000	2.35793100	
	C	-0.91934700	-1.30120600	-1.82339700	
	H	-1.11770700	-0.37170200	-2.34614100	
	H	-0.60655100	-2.12401800	-2.45852800	
	C	-1.71122500	-1.60517600	-0.58522600	
	H	-1.82915900	-2.66674900	-0.37986700	
	C	-2.87668200	-0.78509300	-0.11045900	
	C	-3.11061500	-0.61890500	1.26202000	
	C	-3.79306200	-0.24711300	-1.02168000	
	C	-4.23277700	0.07632700	1.71105700	
	H	-2.40157500	-1.02465500	1.97825000	
	C	-4.91748700	0.44865600	-0.57328600	
	H	-3.62726500	-0.37678500	-2.08795800	
	C	-5.14042900	0.61281600	0.79443600	
	H	-4.39709200	0.20142400	2.77818000	
	H	-5.61896800	0.86058000	-1.29423400	
	H	-6.01480900	1.15498100	1.14475100	

Intermediates



Int1

P	-2.79870800	0.51772800	0.21971900
O	-3.00354800	0.32181800	1.67895400
C	-0.95504600	0.50597900	-0.14276500
C	-0.10151400	-0.59187000	0.52782300
N	-0.17174500	-0.49570800	1.89775600
N	-0.16859800	-0.41091500	3.01458200
C	-0.31404400	-2.04889400	0.10499000
F	0.58486200	-2.83834500	0.72287400
F	-1.53781700	-2.52175100	0.43464100
F	-0.16737300	-2.16701500	-1.21619300
F	-0.49590900	1.71014300	0.34896500
F	-0.70827700	0.47027800	-1.47271700
O	-3.30486900	-0.59396700	-0.79774000
O	-3.32834700	1.87605300	-0.43187400
C	-3.33194800	3.15464100	0.28681300
H	-4.38523200	3.41255800	0.42526200
H	-2.87844800	3.02242400	1.27244100
C	-4.55038100	-1.33078500	-0.56136100
H	-5.38233300	-0.65807100	-0.79127800
H	-4.59559800	-1.60552800	0.49611100
C	-2.60313400	4.19070000	-0.54345800
H	-3.06413100	4.29509200	-1.53104800
H	-2.65098800	5.16151600	-0.03647500
H	-1.55132600	3.91915500	-0.67362400
C	-4.54362000	-2.54670800	-1.46148700
H	-3.69403900	-3.19600500	-1.22860100
H	-5.46866100	-3.11430700	-1.30901900
H	-4.48635300	-2.25522300	-2.51512900
Cu	1.87696500	-0.09720400	0.12637200
I	4.23586800	0.37185600	-0.33343000

Sum of electronic and zero-point Energies=
-3387.204920
Sum of electronic and thermal Energies=
-3387.169262
Sum of electronic and thermal Enthalpies=
-3387.168046
Sum of electronic and thermal Free Energies=
-3387.285836

Int2

P	-2.17621800	-0.51848000	-0.83276000
O	-1.76876700	-1.53224000	-1.83378400
C	-1.19941000	-0.69644200	0.82864800
C	-0.12810800	0.30653000	0.78832100
C	-0.40243900	1.62854200	1.47251800
F	0.06722200	1.47981500	2.73392700
F	0.27340300	2.63354100	0.88798600
F	-1.68872800	2.00736000	1.55204500
F	-0.71078900	-1.97225900	0.84531200
F	-2.07374700	-0.59464100	1.87520900
O	-1.83259800	1.02168300	-1.08679700
O	-3.71412800	-0.49188700	-0.40299100
C	-4.55507500	-1.69328900	-0.46165400
H	-5.56525000	-1.29765000	-0.58716400
H	-4.28261600	-2.26366600	-1.35325300
C	-2.43918700	1.82559500	-2.15337900
H	-3.52084300	1.82908400	-1.99304300
H	-2.21391500	1.34667300	-3.11041300
C	-4.42984900	-2.51944400	0.80349200
H	-4.66815600	-1.92198100	1.68864500
H	-5.13343300	-3.35857800	0.75160800
H	-3.42137200	-2.93114000	0.91730100
C	-1.85158400	3.21732400	-2.06218000
H	-0.76920800	3.19852600	-2.22448600
H	-2.30533200	3.85040800	-2.83288700
H	-2.05431300	3.66220400	-1.08294000
Cu	1.55729700	-0.06936100	0.10023200
I	3.90882500	-0.54156400	-0.38386800

Sum of electronic and zero-point Energies=
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Sum of electronic and thermal Energies=
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Sum of electronic and thermal Enthalpies=
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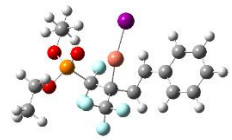

Int3_1

P	-2.59523300	-0.35283100	0.01961800
O	-1.56411400	-1.00090500	-0.86708200
C	-1.67028300	0.76612200	1.20923400
C	-0.37790300	1.31589100	0.63816100
C	-0.55397900	2.36811300	-0.42333100
F	0.62873800	2.70471200	-0.99444700
F	-1.37373900	1.98238100	-1.43320000
F	-1.07682800	3.51902400	0.07148100
F	-1.34340800	-0.05726100	2.27727200
F	-2.48737000	1.74100200	1.71792800
O	-3.68604400	0.58507000	-0.64684200
O	-3.47374800	-1.34932800	0.90301500
C	-2.95112500	-2.60782400	1.44759600
H	-3.40851400	-3.40355100	0.85387600
H	-1.86919600	-2.65223800	1.30303500
C	-4.09192200	0.44323500	-2.04920600
H	-4.82589600	-0.36684700	-2.09674800
H	-3.21570100	0.16605100	-2.64040000
C	-3.33530400	-2.70027100	2.90904400
H	-4.42165900	-2.64119900	3.03311000
H	-2.99363500	-3.66001300	3.31385900
H	-2.87132600	-1.89363800	3.48454100
C	-4.67817000	1.76546500	-2.49316300
H	-3.93029400	2.56141300	-2.42501400
H	-5.00664200	1.68324500	-3.53559100
H	-5.54233200	2.03903000	-1.87901200
Cu	0.46306300	-0.32384600	-0.19080300
I	1.73461000	-2.36450900	-1.06466300
C	0.66401500	1.71921300	1.69096000
H	1.03704200	2.73603500	1.55759900
H	0.29793200	1.62903700	2.71646300
C	1.66126100	0.64840500	1.34274600
H	1.54108500	-0.27479100	1.90895000
C	3.01398300	0.90651500	0.86442400
C	3.98487800	-0.11026400	1.01951600
C	3.42489100	2.15296800	0.34230700
C	5.31555200	0.11975800	0.69440100
H	3.67995300	-1.07859100	1.40349800
C	4.75644500	2.37244000	0.00474700
H	2.70147700	2.94308500	0.18220900
C	5.70588900	1.36119100	0.18155800
H	6.04796800	-0.67044800	0.83089400
H	5.05588400	3.33529900	-0.39920900
H	6.74452100	1.53792800	-0.08391800

Sum of electronic and zero-point Energies=
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Sum of electronic and thermal Energies=
-3587.283415
Sum of electronic and thermal Enthalpies=
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Sum of electronic and thermal Free Energies=
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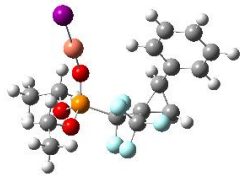
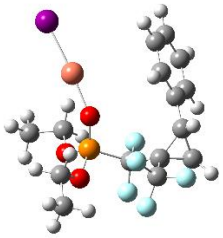
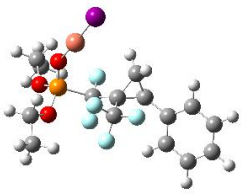
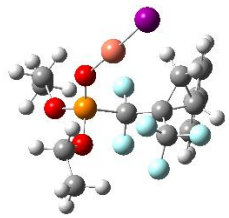
Int3_2

P	2.15561500	0.62425000	-0.83511600
O	1.11538900	-0.28692100	-1.43336400
C	1.49947100	1.19573900	0.82714200
C	0.61370500	0.17444800	1.51523200
C	1.34850900	-0.99131100	2.13021200
F	0.48062800	-1.90233400	2.63265600
F	2.14450900	-1.64895300	1.24967000
F	2.14594200	-0.61573600	3.16029800
F	0.73601400	2.31269700	0.52091000
F	2.51407500	1.64174900	1.63209400
O	3.58858000	0.03066800	-0.51489800
O	2.48776200	1.93535300	-1.68093400
C	1.48595200	2.63761900	-2.49055100
H	1.70711700	2.38444600	-3.53075900
H	0.48766500	2.26391900	-2.25109900
C	4.13276200	-1.14227900	-1.21027700
H	4.50253200	-0.80426600	-2.18292400

Sum of electronic and zero-point Energies=
-3587.328871
Sum of electronic and thermal Energies=
-3587.284853
Sum of electronic and thermal Enthalpies=
-3587.283637
Sum of electronic and thermal Free Energies=
-3587.418112

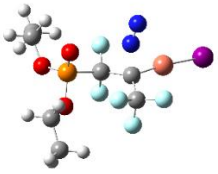
	H	3.32511200	-1.86171600	-1.36466200	
	C	1.61144400	4.12369200	-2.23074900	
	H	2.62079900	4.47854100	-2.46326900	
	H	0.90080900	4.66444900	-2.86664900	
	H	1.39016900	4.35485800	-1.18427500	
	C	5.23978000	-1.70912000	-0.34907700	
	H	4.84904900	-2.02488700	0.62304400	
	H	5.67576600	-2.58113000	-0.84975900	
	H	6.03176400	-0.97023600	-0.18898700	
	Cu	-0.51824700	-0.61383900	0.02526900	
	I	-1.97998400	-2.25587600	-1.30302300	
	C	-0.44793800	0.73932300	2.46618700	
	H	-0.38372300	0.34574800	3.48402100	
	H	-0.43350200	1.82736300	2.52052200	
	C	-1.60742200	0.18052400	1.68744200	
	H	-1.92715300	-0.81279500	1.99492900	
	C	-2.64167800	1.00517700	1.06207700	
	C	-3.88534500	0.40398800	0.76048000	
	C	-2.48871100	2.38846700	0.82221700	
	C	-4.94050000	1.16015500	0.26580800	
	H	-4.01008400	-0.66205900	0.92196600	
	C	-3.54500000	3.13758100	0.31261000	
	H	-1.54004500	2.87403700	1.01781900	
	C	-4.77330500	2.52972700	0.03575600	
	H	-5.89115500	0.68124400	0.05042600	
	H	-3.41088400	4.20029800	0.13123800	
	H	-5.59487800	3.11920600	-0.36161800	
 Int4_1	P	1.58348800	-1.51381700	-0.14650100	Sum of electronic and zero-point Energies=
	O	0.24661800	-1.28649800	-0.80634700	-3587.365284
	C	2.70559800	-0.02723200	-0.36838000	Sum of electronic and thermal Energies=
	C	2.20707300	1.36299000	-0.00491100	-3587.321275
	C	1.72925600	1.51848500	1.42237000	Sum of electronic and thermal Enthalpies=
	F	1.57996000	2.80809900	1.77159900	-3587.320059
	F	0.52664800	0.91358400	1.61206400	Sum of electronic and thermal Free Energies=
	F	2.58672400	0.96121000	2.30352600	-3587.457358
	F	3.01395700	-0.05388800	-1.71465500	
	F	3.86813900	-0.29868700	0.29821200	
	O	1.63291200	-1.74347500	1.41153500	
	O	2.38588200	-2.74298100	-0.75842500	
	C	2.38412100	-3.08922900	-2.18640300	
	H	1.42693700	-2.78831400	-2.61967600	
	H	3.18834200	-2.51580700	-2.65364100	
	C	0.62661600	-2.48387100	2.18542500	
	H	0.74152700	-3.54503500	1.94718500	
	H	-0.36708600	-2.14852100	1.87244500	
	C	2.60908200	-4.58076400	-2.30313700	
	H	1.79543800	-5.13951500	-1.82950200	
	H	2.64613800	-4.85622600	-3.36335800	
	H	3.55595600	-4.87324300	-1.83793000	
	C	0.88046000	-2.19053000	3.64686100	
	H	0.79483300	-1.11761600	3.84319500	
	H	0.13530100	-2.71763700	4.25301600	
	H	1.87706100	-2.52788400	3.94901600	
	Cu	-1.64467600	-1.09508600	-0.38632500	
	I	-4.03736300	-0.94629900	0.03253600	
	C	2.96835300	2.51633500	-0.63131400	
	H	3.12816000	3.38193300	0.00265300	
	H	3.80336000	2.26207400	-1.27589200	
	C	1.57842800	2.22306300	-1.10962400	
	H	1.53201400	1.68833400	-2.05511700	
	C	0.41032400	3.14179400	-0.88399100	

	C	-0.89165700	2.62085100	-0.85717900	
	C	0.58457900	4.52576200	-0.76216400	
	C	-1.99294500	3.46121600	-0.69887200	
	H	-1.04765600	1.54904500	-0.95811500	
	C	-0.51696100	5.37001200	-0.60658500	
	H	1.58509300	4.94814500	-0.79565200	
	C	-1.80786100	4.84033900	-0.57170300	
	H	-2.99221300	3.03534400	-0.67299900	
	H	-0.36367900	6.44202800	-0.51391200	
	H	-2.66492200	5.49695000	-0.44834500	
 Int4_2	P	-1.05278400	-1.26852000	0.50043800	Sum of electronic and zero-point Energies=
	O	-0.02124900	-0.79752900	-0.49345600	-3587.363156
	C	-2.19305000	0.12677100	1.03372300	Sum of electronic and thermal Energies=
	C	-2.85540100	1.02371400	0.00173200	-3587.319205
	C	-3.67408400	0.29435900	-1.04145100	Sum of electronic and thermal Enthalpies=
	F	-4.42452400	1.14806600	-1.77015500	-3587.317989
	F	-2.87861600	-0.36942500	-1.92098600	Sum of electronic and thermal Free Energies=
	F	-4.51084700	-0.61512900	-0.50518700	-3587.454622
	F	-1.41971600	0.89202100	1.87537600	
	F	-3.16024900	-0.45071800	1.81579100	
	O	-2.05742200	-2.36757000	-0.02494500	
	O	-0.49661800	-1.88791000	1.85355600	
	C	0.57043800	-1.30343700	2.67963900	
	H	1.27377100	-0.77337100	2.02885500	
	H	0.09550900	-0.58867100	3.35488000	
	C	-1.75769800	-3.26806800	-1.14652600	
	H	-1.01775600	-3.99503700	-0.79984100	
	H	-1.32859300	-2.67644500	-1.95806400	
	C	1.24983800	-2.43072500	3.42428200	
	H	1.72479200	-3.13089000	2.72972900	
	H	2.02591000	-2.01142200	4.07452100	
	H	0.53456300	-2.97803700	4.04700700	
	C	-3.05708400	-3.92770000	-1.55133600	
	H	-3.78862300	-3.17681400	-1.86440800	
	H	-2.86957300	-4.60621000	-2.39122200	
	H	-3.47836500	-4.50820600	-0.72438400	
	Cu	1.91318700	-0.54551500	-0.53594400	
	I	4.34616700	-0.38916400	-0.56763400	
	C	-3.40203700	2.34146300	0.51754500	
	H	-4.38742600	2.64420700	0.17932200	
	H	-3.19548400	2.55466700	1.56123600	
	C	-2.26327100	2.36976300	-0.45536400	
	C	-0.88161300	2.87471600	-0.15539700	
	C	-0.59347300	3.65199200	0.97286200	
	C	0.14273200	2.62722100	-1.08235900	
	C	0.69377300	4.15121700	1.18286600	
	H	-1.37774000	3.87900400	1.68885400	
	C	1.42973500	3.12437200	-0.87416800	
	H	-0.07208700	2.04187700	-1.97288800	
	C	1.70991300	3.88598800	0.26366200	
	H	0.89929200	4.75262600	2.06450300	
	H	2.21199200	2.91978000	-1.59944100	
	H	2.71192900	4.27257900	0.42700000	
	H	-2.56405400	2.58468700	-1.47828600	
	P	0.54038800	2.24366800	0.07423800	Sum of electronic and zero-point Energies=
	O	1.73353800	1.39361900	-0.27278600	-3587.363978
	C	-1.07595500	1.53132300	-0.56978300	Sum of electronic and thermal Energies=
	C	-1.45088900	0.08011500	-0.31903800	-3587.320033
	C	-1.40207700	-0.35438300	1.12703400	Sum of electronic and thermal Enthalpies=
	F	-1.80435100	-1.62245900	1.29715600	-3587.318817
	F	-0.12825900	-0.28653600	1.61408700	Sum of electronic and thermal Free Energies=

Int4_3	F	-2.15867100	0.43216000	1.91990900	-3587.455471
	F	-0.99265600	1.73674200	-1.93382500	
	F	-2.07560600	2.34696300	-0.11109100	
	O	0.22700700	2.50461500	1.59805500	
	O	0.61376300	3.69765200	-0.56136600	
	C	1.17751300	3.98081400	-1.88932100	
	H	2.12188400	4.49883500	-1.70515900	
	H	1.39192700	3.04234100	-2.40527900	
	C	1.22638400	2.41726500	2.67236200	
	H	1.84794900	3.31536100	2.61644400	
	H	1.84899200	1.53671100	2.49713400	
	C	0.19720100	4.84037500	-2.65781800	
	H	-0.01825100	5.76776400	-2.11740800	
	H	0.63021600	5.10029700	-3.63071900	
	H	-0.74131500	4.30369500	-2.82628300	
	C	0.47281700	2.32392200	3.98011700	
	H	-0.16495600	1.43512400	3.99334000	
	H	1.19118300	2.25188800	4.80448100	
	H	-0.15064100	3.20950300	4.13949200	
	Cu	2.51029500	-0.38785700	-0.21545400	
	I	3.55475000	-2.58923700	-0.21439500	
	C	-1.15769700	-0.97048100	-1.37182100	
	H	-0.57281800	-0.66701400	-2.23344300	
	H	-0.93310500	-1.96372700	-0.99600000	
	C	-2.55794100	-0.45126900	-1.23856400	
	H	-2.82876600	0.28641500	-1.99133100	
	C	-3.73020700	-1.25237800	-0.75211300	
	C	-3.87053000	-2.60723400	-1.07297700	
	C	-4.74195500	-0.61755400	-0.01683500	
	C	-5.00133000	-3.31767900	-0.66376700	
	H	-3.09507900	-3.10731400	-1.64703900	
	C	-5.87066000	-1.32671000	0.39244300	
	H	-4.63481200	0.43342600	0.24056400	
	C	-6.00332600	-2.67996800	0.06949500	
	H	-5.09733200	-4.36968700	-0.91892300	
	H	-6.64535400	-0.82379000	0.96521300	
	H	-6.88248300	-3.23330400	0.38862400	
 Int 4_4	P	-0.27445900	1.89525100	-0.48617300	Sum of electronic and zero-point Energies=
	O	0.95434800	1.30388800	-1.12997500	-3587.363608
	C	-1.51022800	0.59362100	0.08313800	Sum of electronic and thermal Energies=
	C	-1.05484800	-0.56027500	0.95960600	-3587.319578
	C	-0.32689800	-0.15615500	2.22301800	Sum of electronic and thermal Enthalpies=
	F	-0.09429500	-1.21068300	3.02816400	-3587.318362
	F	0.88990500	0.39130800	1.94839800	Sum of electronic and thermal Free Energies=
	F	-1.01296200	0.75842500	2.93663500	-3587.455821
	F	-2.00230200	0.09643300	-1.10346900	
	F	-2.53208700	1.27213600	0.69051000	
	O	-0.08123600	2.78026100	0.80593000	
	O	-1.09973100	2.82135700	-1.47809200	
	C	-1.26794500	2.54421700	-2.91225900	
	H	-0.70310100	3.32420100	-3.42870900	
	H	-0.82229900	1.57647700	-3.15276700	
	C	1.13628400	3.54981900	1.09720600	
	H	1.15577100	4.40780200	0.41891800	
	H	2.00308700	2.91420100	0.89968000	
	C	-2.74297300	2.59171100	-3.24828900	
	H	-3.17324600	3.56370300	-2.98637500	
	H	-2.87263600	2.43595000	-4.32565800	
	H	-3.28902600	1.80813600	-2.71484400	
	C	1.06468000	3.96980700	2.54816100	
	H	1.01337100	3.09241900	3.19983600	

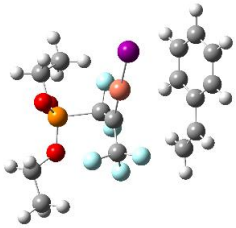
	H	1.96398800	4.54208400	2.80212200	
	H	0.18852000	4.59951400	2.73282800	
	Cu	2.36759400	-0.00086400	-0.80471800	
	I	4.14801400	-1.62323900	-0.44177400	
	C	-0.63727400	-1.86594200	0.31226800	
	H	-0.67313900	-1.89108200	-0.77176700	
	H	0.20358100	-2.39285600	0.75198200	
	C	-1.93613400	-1.81639700	1.05909100	
	H	-1.89753900	-2.25085900	2.05543700	
	C	-3.28153400	-1.95688100	0.40561500	
	C	-4.39093700	-1.26894400	0.91860600	
	C	-3.46762500	-2.83652300	-0.66765600	
	C	-5.65685500	-1.45105900	0.36237700	
	H	-4.25828900	-0.58165800	1.74963500	
	C	-4.73511500	-3.02027600	-1.22452200	
	H	-2.61812600	-3.38583600	-1.06445600	
	C	-5.83286000	-2.32713700	-0.71201800	
	H	-6.50627700	-0.90770700	0.76788500	
	H	-4.86291300	-3.70763700	-2.05663200	
	H	-6.81958200	-2.46904600	-1.14476000	

Transition states



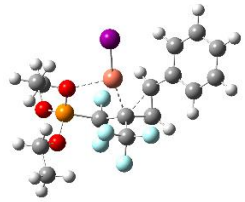
TS1

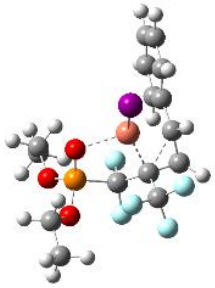
P	-2.78393500	0.50023700	0.19884700	Sum of electronic and zero-point Energies=
O	-3.01075200	0.31963600	1.65608800	-3387.187169
C	-0.94828100	0.53391600	-0.21143600	Sum of electronic and thermal Energies=
C	0.04005100	-0.52869800	0.26848000	-3387.151373
N	-0.29991000	-0.38432300	2.19748800	Sum of electronic and thermal Enthalpies=
N	-0.08132300	-0.23900200	3.27149000	-3387.150157
C	-0.37317500	-1.99152600	0.12587200	Sum of electronic and thermal Free Energies=
F	0.55009300	-2.79822000	0.67653400	-3387.268033
F	-1.55672600	-2.32001700	0.68400900	
F	-0.43995900	-2.24675900	-1.19197800	
F	-0.49851100	1.74207500	0.27180000	
F	-0.77922100	0.53141500	-1.56791000	
O	-3.26877000	-0.62144900	-0.81955100	
O	-3.33095200	1.84574500	-0.46870400	
C	-3.38178500	3.12118300	0.25149000	
H	-4.44379800	3.34632400	0.38138600	
H	-2.93317300	3.00245900	1.24113300	
C	-4.41986900	-1.48118500	-0.53974600	
H	-5.32607200	-0.88526500	-0.68640500	
H	-4.37034300	-1.80236300	0.50399700	
C	-2.67867700	4.18198700	-0.56981700	
H	-3.13283100	4.27332100	-1.56189700	
H	-2.76312500	5.14988600	-0.06191400	
H	-1.61764500	3.94389900	-0.68975100	
C	-4.35599700	-2.65205300	-1.49656600	
H	-3.43215000	-3.22043700	-1.35057400	
H	-5.20751700	-3.31743800	-1.31442000	
H	-4.39840200	-2.31201200	-2.53631600	
Cu	1.88646100	-0.11342700	0.10634200	
I	4.25385700	0.34605800	-0.34036100	



TS2_2

P	-2.78702200	-0.70809500	0.70132700	Sum of electronic and zero-point Energies=
O	-2.33557500	-2.11905400	0.65815000	-3587.266340
C	-1.33201200	0.54934100	0.50899400	Sum of electronic and thermal Energies=
C	-0.49334900	0.16556500	-0.63432700	-3587.221887
C	-0.98763700	0.51084500	-2.02564400	Sum of electronic and thermal Enthalpies=
F	0.05374100	0.73747200	-2.84243900	-3587.220671
F	-1.64997000	-0.58437100	-2.48376500	Sum of electronic and thermal Free Energies=
F	-1.81981400	1.55783800	-2.12695400	-3587.360569
F	-0.63437900	0.44374900	1.69109900	
F	-1.85930100	1.80729200	0.47774900	

	O	-3.76019500	-0.16316100	-0.43053400	
	O	-3.46488200	-0.17786000	2.04574600	
	C	-3.08912400	-0.69012700	3.36862500	
	H	-3.96128600	-1.24563200	3.72250900	
	H	-2.25450300	-1.38719600	3.26405700	
	C	-4.59944700	-1.06896200	-1.22516700	
	H	-5.41771400	-1.41021900	-0.58496800	
	H	-3.99408200	-1.92863400	-1.52114100	
	C	-2.75515800	0.47823500	4.27419900	
	H	-3.59988500	1.17028400	4.34511200	
	H	-2.52795800	0.10493200	5.27892300	
	H	-1.88372800	1.02064900	3.89792100	
	C	-5.10327500	-0.28555700	-2.41916800	
	H	-4.26565500	0.06535600	-3.02797100	
	H	-5.73783000	-0.93236000	-3.03473300	
	H	-5.69427000	0.57809800	-2.09967100	
	Cu	1.00420500	-0.91123600	-0.41166500	
	I	2.96634300	-2.30788800	-0.15003100	
	C	0.12631800	3.92193000	-1.17772300	
	H	-0.37967600	4.29789800	-2.06150900	
	H	-0.42414400	3.99160600	-0.24414500	
	C	1.36105700	3.40601800	-1.26248000	
	H	1.84299700	3.38842700	-2.23983800	
	C	2.17854700	2.85043300	-0.16882800	
	C	3.51228700	2.49322200	-0.43233100	
	C	1.68462600	2.65188200	1.13568100	
	C	4.33006000	1.96526900	0.56779100	
	H	3.91002100	2.63370000	-1.43467600	
	C	2.50006800	2.12337300	2.13433800	
	H	0.65369400	2.90006800	1.36847800	
	C	3.82708000	1.77956500	1.85696800	
	H	5.35743100	1.69657000	0.33862200	
	H	2.09736300	1.97399700	3.13252600	
	H	4.45892300	1.36441500	2.63687200	
 TS3_1	P	-2.58010700	-0.40116000	0.13704000	Sum of electronic and zero-point Energies=
	O	-1.54817700	-1.42778600	-0.22051300	-3587.319246
	C	-1.70002100	1.02898500	0.95786200	Sum of electronic and thermal Energies=
	C	-0.36403500	1.48426300	0.35905600	-3587.275684
	C	-0.42520100	1.97809600	-1.07651300	Sum of electronic and thermal Enthalpies=
	F	0.76010800	2.47082300	-1.48406800	-3587.274468
	F	-0.76742300	1.00307200	-1.95587300	Sum of electronic and thermal Free Energies=
	F	-1.33808400	2.96244600	-1.21700700	-3587.409239
	F	-1.45006400	0.58498000	2.24767700	
	F	-2.54223400	2.09762800	1.08218700	
	O	-3.39325200	0.31067900	-1.02206000	
	O	-3.71071200	-0.86329900	1.16028400	
	C	-3.49568900	-1.89348000	2.18325100	
	H	-4.12990600	-2.73325100	1.88984400	
	H	-2.45393000	-2.22059900	2.15350200	
	C	-3.66254200	-0.33990700	-2.31083200	
	H	-4.52167600	-1.00111100	-2.16821700	
	H	-2.79006300	-0.93720700	-2.58536900	
	C	-3.88677100	-1.33436500	3.53678200	
	H	-4.92841200	-0.99885800	3.53352000	
	H	-3.77742800	-2.11530800	4.29754700	
	H	-3.24568600	-0.49082300	3.80709500	
	C	-3.94547000	0.75257000	-3.32069200	
	H	-3.07929200	1.41242000	-3.42183200	
	H	-4.15660100	0.29919000	-4.29518400	
	H	-4.81208800	1.34921600	-3.01992400	
	Cu	0.51535000	-0.53186000	-0.02976100	

	I	1.98953400	-2.41829400	-0.80145800	
	C	0.33435500	2.44670100	1.30449800	
	H	0.75764300	3.33314700	0.83999800	
	H	-0.21087800	2.68366900	2.21490400	
	C	1.19630800	1.24492600	1.33181700	
	H	0.94689700	0.54888000	2.12893300	
	C	2.63019200	1.24890000	0.94916900	
	C	3.44870800	0.24717500	1.50458300	
	C	3.23474100	2.27292100	0.19928000	
	C	4.82804700	0.27107100	1.32292100	
	H	2.99694700	-0.55313700	2.08239800	
	C	4.61441100	2.28430300	0.00541400	
	H	2.63743000	3.05994300	-0.24333900	
	C	5.41602600	1.28712700	0.56629100	
	H	5.44056600	-0.50964200	1.76364000	
	H	5.06421300	3.07928500	-0.58231200	
	H	6.49144300	1.30208600	0.41428500	
 TS3_2	P	2.05751300	0.49582600	-0.84361700	Sum of electronic and zero-point Energies=
	O	0.88066100	-0.10608800	-1.55780800	-3587.323182
	C	1.49077500	1.07456800	0.85072700	Sum of electronic and thermal Energies=
	C	0.44421900	0.22714400	1.56854200	-3587.280298
	C	0.94859900	-1.10594200	2.09461300	Sum of electronic and thermal Enthalpies=
	F	-0.05857200	-1.82745900	2.63035000	-3587.279082
	F	1.53208400	-1.86817600	1.13958100	Sum of electronic and thermal Free Energies=
	F	1.87054900	-0.93754600	3.06940200	-3587.409991
	F	0.95152400	2.32341200	0.60699900	
	F	2.57345400	1.27806700	1.66380800	
	O	3.30616200	-0.42583800	-0.53246900	
	O	2.71010800	1.77464900	-1.53703200	
	C	1.92877400	2.76632900	-2.28548400	
	H	2.14806500	2.58689800	-3.34122500	
	H	0.86219500	2.59684600	-2.12098200	
	C	3.63144900	-1.60541900	-1.34805500	
	H	4.10009100	-1.24680400	-2.26935000	
	H	2.70218000	-2.12385800	-1.59578000	
	C	2.35698700	4.15024800	-1.84577800	
	H	3.43042000	4.29735100	-2.00362300	
	H	1.81611400	4.90133600	-2.43329000	
	H	2.13251100	4.30804800	-0.78650600	
	C	4.56671600	-2.47471200	-0.53763900	
	H	4.08260800	-2.80667500	0.38584200	
	H	4.83585500	-3.35889600	-1.12660100	
	H	5.48497900	-1.93556600	-0.28288400	
	Cu	-0.73112800	-0.53581000	-0.12207100	
	I	-2.08108300	-2.52773200	-1.00546800	
	C	-0.34716700	0.97706700	2.62651800	
	H	-0.39871400	0.49133100	3.59943500	
	H	-0.10094400	2.03086200	2.72356400	
	C	-1.42344400	0.62157100	1.67054900	
	H	-1.94508400	-0.30059700	1.91309200	
	C	-2.20922900	1.60021000	0.88075700	
	C	-3.36496700	1.14181800	0.21269500	
	C	-1.92773300	2.98026000	0.86186500	
	C	-4.20207400	2.03031300	-0.45683900	
	H	-3.60386400	0.08271000	0.22513400	
	C	-2.76729700	3.86390000	0.18777500	
	H	-1.05894500	3.37204700	1.37618300	
	C	-3.90366800	3.39447200	-0.47657500	
	H	-5.08692100	1.65406500	-0.96175500	
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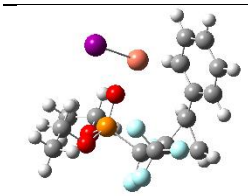
	H	-4.55495300	4.08875700	-1.00020300	



TS4_1

P	2.09734600	-0.83797000	-0.28771700
O	0.87901900	-0.75957400	-1.14808200
C	2.70162800	0.87330000	0.21071000
C	1.60425900	1.86657100	0.57466300
C	0.82375100	1.52143700	1.82929900
F	0.07538800	2.55693700	2.26572000
F	-0.02872500	0.48449000	1.63030000
F	1.63607300	1.16985500	2.84318800
F	3.36995600	1.35156500	-0.90312100
F	3.63496100	0.77610900	1.19921000
O	2.00065800	-1.53899600	1.13210500
O	3.37589900	-1.54013200	-0.95516500
C	3.67444200	-1.42901500	-2.38019200
H	2.73535400	-1.33575800	-2.93294400
H	4.26392500	-0.51858000	-2.52169800
C	1.15242000	-2.71220600	1.37438500
H	1.64311900	-3.57538000	0.91384300
H	0.18307900	-2.54991300	0.89657200
C	4.44504500	-2.66432500	-2.79710600
H	3.84355100	-3.56784400	-2.65332500
H	4.70796400	-2.58864900	-3.85865700
H	5.36996400	-2.76319000	-2.21931700
C	1.01723100	-2.87015700	2.87278100
H	0.54869100	-1.98332400	3.31078600
H	0.38430200	-3.73826900	3.08826000
H	1.99358000	-3.02434300	3.34438700
Cu	-1.80265900	-0.07965800	-0.77927700
I	-3.08165400	-1.99124700	0.19083300
C	1.79352800	3.33456100	0.25213300
H	1.35653100	4.03793500	0.95243400
H	2.75037000	3.63710500	-0.16007500
C	0.89486000	2.51100700	-0.62476200
H	1.37209400	2.20502500	-1.55017400
C	-0.58835100	2.59578600	-0.78892300
C	-1.16297900	1.75249600	-1.77942500
C	-1.42566100	3.45833800	-0.08204700
C	-2.55299200	1.76542200	-2.01127600
H	-0.50525400	1.19441400	-2.44307100
C	-2.80898200	3.46696700	-0.31624000
H	-1.01068700	4.13720500	0.65455800
C	-3.37915500	2.62056900	-1.25972000
H	-2.97204100	1.18227500	-2.82680100
H	-3.43781000	4.14859900	0.24953000
H	-4.44990400	2.63289000	-1.43785800

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Sum of electronic and thermal Energies=
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Sum of electronic and thermal Enthalpies=
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Sum of electronic and thermal Free Energies=
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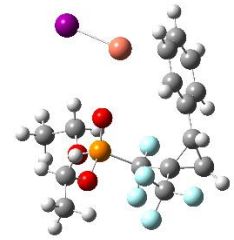

TS4_2

P	-1.14512200	-1.34031800	0.15554000
O	-0.14896800	-0.71740600	-0.75884600
C	-2.11113800	-0.06287200	1.13613300
C	-2.83868900	1.06476100	0.41435600
C	-3.92330200	0.62484700	-0.54948000
F	-4.71993300	1.66270500	-0.89809300
F	-3.39326700	0.14843200	-1.70462900
F	-4.71884400	-0.33516900	-0.04843600
F	-1.16932700	0.49179500	1.98373500
F	-3.00574500	-0.71880200	1.93969600
O	-2.32791000	-2.19483800	-0.48578900
O	-0.59078300	-2.32906600	1.28621700
C	0.67712600	-2.11057700	1.98314800
H	1.42297100	-1.76362000	1.26343100
H	0.51383900	-1.33419200	2.73635300
C	-2.17142500	-2.86189000	-1.77551800
H	-1.47664200	-3.69773300	-1.64526500

Sum of electronic and zero-point Energies=
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Sum of electronic and thermal Energies=
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Sum of electronic and thermal Enthalpies=
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Sum of electronic and thermal Free Energies=
-3587.441052

	H	-1.73934300	-2.15256800	-2.48639900	
	C	1.08832500	-3.42272700	2.61645800	
	H	1.24636300	-4.19143500	1.85308100	
	H	2.02866100	-3.28098400	3.16118500	
	H	0.32827300	-3.77675100	3.32122900	
	C	-3.54130400	-3.33530400	-2.21270400	
	H	-4.22665400	-2.48831700	-2.31455400	
	H	-3.46049500	-3.83962600	-3.18246100	
	H	-3.96162400	-4.04168900	-1.48936900	
	Cu	2.38757600	0.93098600	-0.51368200	
	I	4.17155600	-0.78744100	-0.38468900	
	C	-3.07253600	2.33337300	1.21031500	
	H	-4.04233500	2.81198400	1.12886100	
	H	-2.64144500	2.34495400	2.20542900	
	C	-2.15483900	2.38306300	0.02467500	
	C	-0.67836800	2.63927800	0.05536800	
	C	0.00152100	3.08299000	1.20263800	
	C	0.03933200	2.49066000	-1.13559000	
	C	1.36868800	3.34137100	1.17156200	
	H	-0.54526000	3.23048300	2.12845300	
	C	1.41669800	2.77315000	-1.19270900	
	H	-0.47395700	2.16439900	-2.03503000	
	C	2.09206300	3.19258000	-0.02423400	
	H	1.87633500	3.68344400	2.06849100	
	H	1.92643800	2.77860000	-2.15419500	
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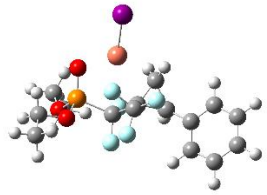 TS4_3	P	-1.99075800	2.00105900	-0.17907400	Sum of electronic and zero-point Energies=
	O	-0.92973900	2.38014700	-1.14826700	-3587.339242
	C	-2.42932100	0.17354500	-0.27478600	Sum of electronic and thermal Energies=
	C	-1.31728600	-0.86583400	-0.38039200	-3587.296077
	C	-0.31364900	-0.85772900	0.73649700	Sum of electronic and thermal Enthalpies=
	F	0.62651900	-1.80118000	0.62150300	-3587.294861
	F	0.41581200	0.36236200	0.72954300	Sum of electronic and thermal Free Energies=
	F	-0.85246100	-0.92651900	1.95105400	-3587.431380
	F	-3.19549700	0.08195600	-1.42170800	
	F	-3.24724100	-0.15269200	0.77141700	
	O	-1.71442400	2.13492400	1.38707100	
	O	-3.40385800	2.74068400	-0.35007500	
	C	-3.85705200	3.28339000	-1.62840600	
	H	-3.90598800	4.36731300	-1.49292300	
	H	-3.11147000	3.06771200	-2.39774000	
	C	-1.35351800	3.42196700	1.97636100	
	H	-2.17783500	4.11969500	1.80003300	
	H	-0.45676800	3.79407500	1.47186800	
	C	-5.21635600	2.70049600	-1.96641800	
	H	-5.94220400	2.92247100	-1.17783200	
	H	-5.57960100	3.13781400	-2.90327900	
	H	-5.15210400	1.61581700	-2.08779300	
	C	-1.11519500	3.20039500	3.45626200	
	H	-0.30106200	2.48680600	3.61672600	
	H	-0.84147700	4.15013200	3.92828500	
	H	-2.01782000	2.81782100	3.94248000	
	Cu	2.39943700	0.56956300	0.14397500	
	I	4.71580500	0.82745900	-0.47042100	
	C	-0.83710900	-1.31805800	-1.74550300	
	H	-1.23075900	-0.78471300	-2.60317400	
	H	0.21110200	-1.58965000	-1.81995700	
	C	-1.75183300	-2.21763800	-0.97223000	
	H	-2.78973900	-2.17905000	-1.29524000	
	C	-1.35810700	-3.54593300	-0.39676700	

	C	-0.46739300	-4.39358200	-1.06479900	
	C	-1.94309800	-3.97845800	0.80239400	
	C	-0.16033000	-5.65126400	-0.54058900	
	H	-0.01633200	-4.07210300	-1.99963600	
	C	-1.63588600	-5.23359900	1.32670900	
	H	-2.63546900	-3.32319100	1.32552700	
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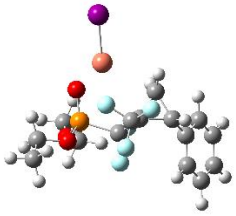 TS4_4	P	-0.92831400	2.01486700	-0.43558800	Sum of electronic and zero-point Energies=
	O	0.13263800	1.70773700	-1.43111500	-3587.338445
	C	-1.86570300	0.47491600	0.11080100	Sum of electronic and thermal Energies=
	C	-1.07200500	-0.79005700	0.41873500	-3587.295206
	C	-0.02088900	-0.64538000	1.48381300	Sum of electronic and thermal Enthalpies=
	F	0.58695500	-1.80205100	1.78225200	-3587.293989
	F	1.02975700	0.20199100	1.04862300	Sum of electronic and thermal Free Energies=
	F	-0.46223300	-0.08871100	2.60855200	-3587.431319
	F	-2.69942600	0.21305000	-0.95390900	
	F	-2.66027700	0.79068400	1.17832900	
	O	-0.51800600	2.61507800	0.98555000	
	O	-2.08712300	3.01377800	-0.91547800	
	C	-2.49742800	3.12888300	-2.31297100	
	H	-2.20177200	4.13220700	-2.63169000	
	H	-1.94580400	2.40243800	-2.91482800	
	C	0.25327100	3.85205700	1.07929000	
	H	-0.35433800	4.66239700	0.66514400	
	H	1.15997400	3.74238700	0.47666900	
	C	-3.99841600	2.93020500	-2.40803000	
	H	-4.52759500	3.66284200	-1.79056900	
	H	-4.31983700	3.05835100	-3.44784700	
	H	-4.27620100	1.92619800	-2.07614200	
	C	0.57506300	4.08442500	2.54166100	
	H	1.16694100	3.25719100	2.94561500	
	H	1.15379800	5.00847400	2.64621900	
	H	-0.34190400	4.17994900	3.13119200	
	Cu	2.85227500	-0.32264800	0.18605600	
	I	5.00133900	-0.96315900	-0.69752100	
	C	-0.80319000	-1.78433000	-0.69384500	
	H	-1.19133300	-1.50433200	-1.66672400	
	H	0.16488600	-2.27429600	-0.71533400	
	C	-1.77845800	-2.15948500	0.37931300	
	H	-1.37839300	-2.84225100	1.12615400	
	C	-3.25177200	-2.33756700	0.15051600	
	C	-4.16980300	-1.98703400	1.15035200	
	C	-3.72170600	-2.93935700	-1.02268500	
	C	-5.53249200	-2.22609800	0.97451000	
	H	-3.81521300	-1.51357500	2.06150100	
	C	-5.08591300	-3.18019400	-1.19896000	
	H	-3.01721100	-3.22574300	-1.79888400	
	C	-5.99474900	-2.82359200	-0.20126300	
	H	-6.23371300	-1.94451100	1.75528800	
	H	-5.43605100	-3.64812800	-2.11499400	
	H	-7.05640000	-3.01015200	-0.33762800	

10. References

1. Bergstrom, D. E.; Shum, P. W. *J. Org. Chem.* **1988**, *53*, 3953–3958. doi:10.1021/jo00252a014
2. Yang, S.; Zhu, S.; Lu, D.; Gong, Y. *Org. Lett.* **2019**, *21*, 2019–2024. doi:10.1021/acs.orglett.9b00128
3. Titaniuk, I. G.; Beletskaya, I. P.; Peregudov, A. S.; Osipov, S. N. J. Fluorine Chem. 2007, 128, 723-728. doi.org/10.1016/j.jfluchem.2007.02.003