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Visible-light-mediated difluoromethylphosphonation of alkenes for the synthesis of CF_2P-containing heterocycles

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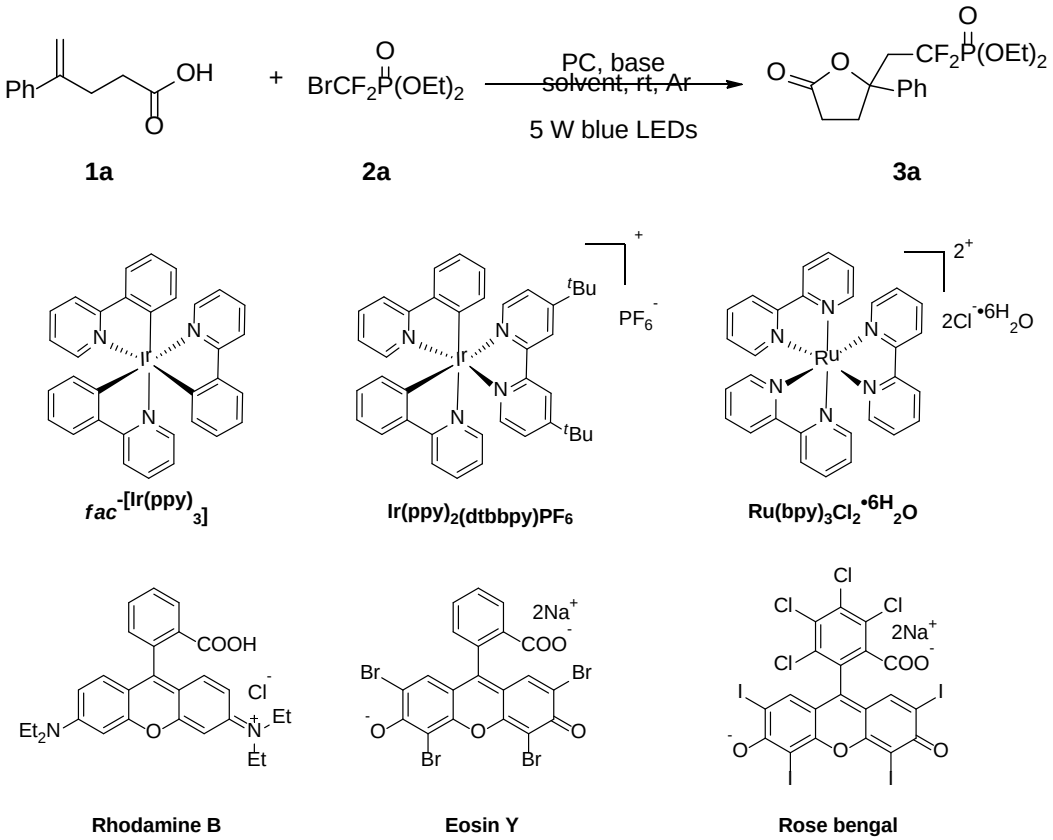
1. General information.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 400 spectrometer (400 MHz for ^{1}H and 101 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for 1H, or to chloroform δ = 77.0 for ^{13}C as internal tandard.^{31}P and ^{19}F NMR were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants are reported in Hertz (Hz). High resolution mass spectroscopic (HRMS) and mass spectra were measured using Bruker micro TOF-Q mass spectrometer and Thermo Scientific DS II mass spectrometer. Analytical thin layer chromatography (TLC) was carried out using commercial silica-gel plates, spots were detected with UV light (254 nm) and revealed with phosphomolybdic acid solutions. The starting materials were purchased from Aldrich, Across Organics, J&K Chemicals or TCI and used without further purification. Substrates **1**, **2** and **4** were prepared according to the reported procedure.[1-2] Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. Optimization of the reaction conditions.

Table S1. Optimization of the reaction conditions.

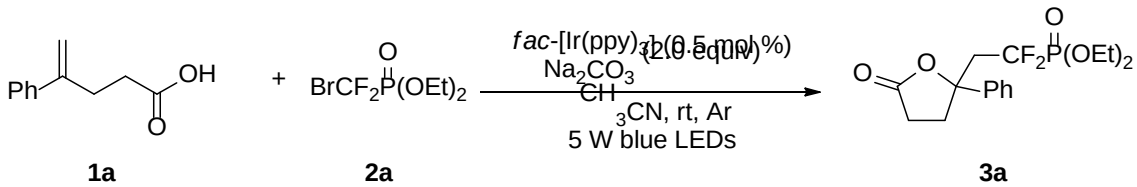


Entry	Photocat (mol %)	Base (2.0 equiv)	Solvent	Yield[b] %

1	*fac*-[Ir(ppy)$_3$] (1)	Na_2CO_3	CH_2Cl_2	62
2	Ir(ppy)$_2$(dtbbpy)PF_6 (1)	Na_2CO_3	CH_2Cl_2	trace
3	Ru(bpy)$_3Cl_2 \cdot 6H_2O$ (1)	Na_2CO_3	CH_2Cl_2	n.r.
4	Eosin Y (10)	Na_2CO_3	CH_2Cl_2	n.r.
5	Rhodamine B (10)	Na_2CO_3	CH_2Cl_2	n.r.
6	Rose bengal (10)	Na_2CO_3	CH_2Cl_2	n.r.
7	*fac*-[Ir(ppy)$_3$] (1)	Na_2CO_3	DCE	52
8	*fac*-[Ir(ppy)$_3$] (1)	Na_2CO_3	CH_3CN	80
9	*fac*-[Ir(ppy)$_3$] (1)	Na_2CO_3	DMF	15
10	*fac*-[Ir(ppy)$_3$] (1)	Na_2CO_3	toluene	56
11	*fac*-[Ir(ppy)$_3$] (1)	Na_2CO_3	dioxane	32
12	*fac*-[Ir(ppy)$_3$] (1)	Na_2CO_3	DME	51
13	*fac*-[Ir(ppy)$_3$] (1)	K_2CO_3	CH_3CN	46
14	*fac*-[Ir(ppy)$_3$] (1)	Cs_2CO_3	CH_3CN	n.r.
15	*fac*-[Ir(ppy)$_3$] (1)	NaOAc	CH_3CN	78
16	*fac*-[Ir(ppy)$_3$] (1)	$NaHCO_3$	CH_3CN	70
17	*fac*-[Ir(ppy)$_3$] (1)	K_3PO_4	CH_3CN	38
18	*fac*-[Ir(ppy)$_3$] (1)	NaI	CH_3CN	n.r.
19	*fac*-[Ir(ppy)$_3$] (1)	$Na_3PO_4 \cdot 12H_2O$	CH_3CN	57
20	*fac*-[Ir(ppy)$_3$] (1)	$NaPF_6$	CH_3CN	n.d.
21	*fac*-[Ir(ppy)$_3$] (1)	$PhCO_2Na$	CH_3CN	42
22[a]	***fac*-[Ir(ppy)$_3$] (0.5)**	**Na_2CO_3**	**CH_3CN**	**82**
23	*fac*-[Ir(ppy)$_3$] (1.5)	Na_2CO_3	CH_3CN	80
24[c]	*fac*-[Ir(ppy)$_3$] (0.5)	Na_2CO_3	CH_3CN	n.r.
25		Na_2CO_3	CH_3CN	n.r.

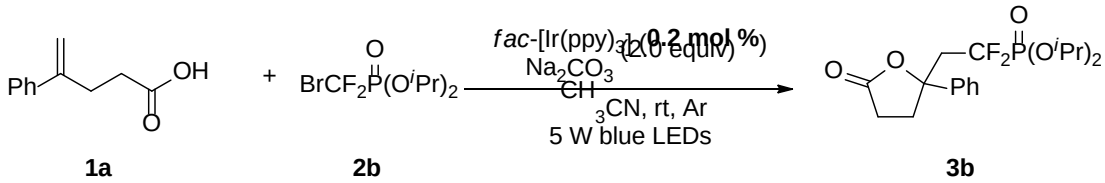
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), *fac*-[Ir(ppy)$_3$] (0.5 mol %), Na_2CO_3 (0.4 mmol), CH_3CN (2 mL), 24 h. [b] Isolated yields based on **1a**. [c] In a dark environment.

3. General procedure for photocatalyzed nucleophilic cyclization of alkenes



In a 10 ml Schlenk tube charged with a magnetic stir bar, **1a** (0.2 mmol), **2a** (0.4 mmol), *fac*-[Ir(ppy)$_3$] (0.5 mol %), Na_2CO_3 (0.4 mmol) were added. The tube was evacuated and backfilled with Ar for 3 times. 2 mL CH_3CN was then added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 5 W blue LEDs lamb, and the resulting solution was stirred at ambient temperature under visible-light irradiation for 24h. After the reaction completed, the mixture was concentrated under vacuum, and the residue was purified by flash chromatography on silica gel to afford the product **3a**.

Gram-scale (20 mmol) reaction:

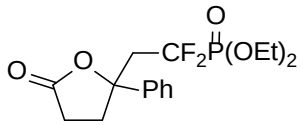


20 mmol, 3.52 g

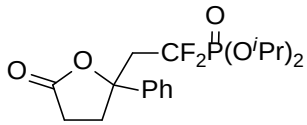
5.85 g, 75%

In a 500 mL flask charged with a magnetic stir bar, **1a** (20 mmol), **2a** (40 mmol), *fac*-[Ir(ppy)$_3$] (0.04 mmol), Na_2CO_3 (40 mmol) were added. The flask was evacuated and backfilled with Ar for 3 times. 300 mL CH_3CN was then added under Ar. The tube flask placed at a distance (app.5 cm) from 5 W blue LEDs lamb, and the resulting solution was stirred at ambient temperature under visible-light irradiation for 36h. After the reaction completed, the solvent CH_3CN was recovered by distillation under reduced pressure. The remaining solid residue was diluted with CH_2Cl_2 (200 mL) and washed with H_2O (150 mL). The aqueous phase was extracted twice with CH_2Cl_2 (100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the product **3b**.

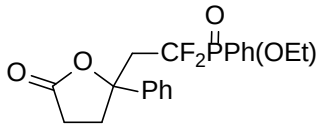
4. Characterization data of products



Diethyl (1,1-difluoro-2-(5-oxo-2-phenyltetrahydrofuran-2-yl)ethyl)phosphonate (**3a**)[3] Flash silica gel chromatography (PE: EA = 1:1) gave 60 mg of **3a** as a colorless oil in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 4H), 7.34 – 7.30 (m, 1H), 4.30 – 4.17 (m, 4H), 2.93 – 2.57 (m, 5H), 2.51 – 2.39 (m, 1H), 1.39 – 1.31 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 142.4, 128.4, 127.8, 124.4, 119.4 (td, *J* = 262.7, 216.0 Hz), 85.4 (d, *J* = 9.3 Hz), 64.6 (t, *J* = 7.4 Hz), 43.9 (td, *J* = 18.9, 14.7 Hz), 33.8, 28.0, 16.1 (dd, *J* = 5.2, 1.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.67 (ddd, *J* = 663.5, 300.1, 104.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.73 (t, *J* = 104.2 Hz). HRMS Calculated for $C_{16}H_{21}F_2NaO_5P$ $[M+Na]^+$: 385.0987, found: 385.0986.

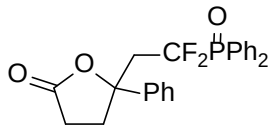


Diisopropyl (1,1-difluoro-2-(5-oxo-2-phenyltetrahydrofuran-2-yl)ethyl)phosphonate (**3b**) Flash silica gel chromatography (PE: EA = 1:1) gave 67 mg of **3b** as a colorless oil in 85% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 7.31 (t, *J* = 7.0 Hz, 1H), 4.88 – 4.75 (m, 2H), 2.92 – 2.53 (m, 5H), 2.53 – 2.30 (m, 1H), 1.37 – 1.31 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6 , 142.6, 128.4, 127.9, 124.5, 119.2 (td, *J* = 262.5, 217.6 Hz), 85.6 (d, *J* = 9.6 Hz), 73.9 (t, *J* = 7.1 Hz), 43.9 (td, *J* = 18.9, 14.6 Hz), 33.7 (s), 28.1 (s), 23.9 (dd, *J* = 5.7, 3.5 Hz), 23.5 (dd, *J* = 4.8, 2.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.74 (ddd, *J* = 746.6, 298.0, 104.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.91 (t, *J* = 104.1 Hz). HRMS Calculated for $C_{18}H_{26}F_2O_5P$ $[M+H]^+$: 391.1480, found: 391.1478.

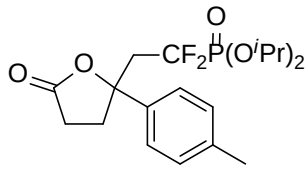


Ethyl (1,1-difluoro-2-(5-oxo-2-phenyltetrahydrofuran-2-yl)ethyl)(phenyl)phosphinate (**3c**) Flash silica gel chromatography (PE: EA = 2:3) gave 52 mg of **3c** as a colorless oil in 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (td, *J* = 13.0, 7.8 Hz, 2H), 7.64 (dd, *J* = 15.6, 7.9 Hz, 1H), 7.51 (dtd, *J* = 11.3, 7.6, 3.9 Hz, 2H), 7.40 – 7.27 (m, 5H), 4.32 – 4.11 (m, 2H), 2.97 – 2.68 (m, 3H), 2.68 – 2.52 (m, 2H), 2.47 – 2.33 (m, 1H), 1.37 (dt, *J* = 12.6, 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6 (d, *J* = 2.4 Hz), 142.6 (d, *J* = 49.5 Hz), 133.8 (dd, *J* = 4.9, 2.9 Hz), 133.1 (t, *J* = 9.3 Hz), 128.7 (d, *J* = 13.3 Hz), 128.5 (d, *J* = 6.5 Hz), 127.9 (d, *J* = 2.3 Hz), 124.5 (d, *J* = 11.5 Hz), 124.3 (dd, *J* = 133.1, 10.6 Hz), 120.9 (dddd, *J* = 268.0, 264.2, 153.0, 11.7 Hz), 85.7 (dd, *J* = 8.4, 4.1 Hz), 63.0 (dd, *J* = 8.4, 7.3 Hz), 43.14 – 42.39 (m), 33.9 (d, *J* = 42.9 Hz), 28.1 (d, *J* = 4.9 Hz), 16.4 (dd, *J* = 5.7, 3.0 Hz). ^{19}F NMR (376 MHz,

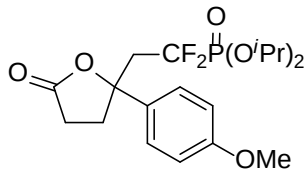
$CDCl_3$) δ -109.82 – -112.49 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.30 (ddd, *J* = 96.7, 88.5, 9.1 Hz). HRMS Calculated for $C_{20}H_{22}F_2O_4P$ $[M+H]^+$: 395.1218, found: 395.1217.



5-(2-(Diphenylphosphoryl)-2,2-difluoroethyl)-5-phenyldihydrofuran-2(3H)-one (**3d**) Flash silica gel chromatography (PE: EA = 2:3) gave 73 mg of **3d** as a colorless oil in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 19.7, 10.0 Hz, 4H), 7.58 (dd, *J* = 15.8, 7.7 Hz, 2H), 7.49 (dd, *J* = 16.4, 8.8 Hz, 4H), 7.32 – 7.25 (m, 5H), 2.85 (dd, *J* = 23.8, 16.8 Hz, 2H), 2.77 – 2.68 (m, 1H), 2.61 – 2.54 (m, 2H), 2.43 – 2.32 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 142.2, 133.0, 131.8 (dd, *J* = 9.3, 3.9 Hz), 128.7 (d, *J* = 12.2 Hz), 128.3 (s), 127.74 (s), 126.7 (d, *J* = 6.1 Hz), 124.7 (dt, *J* = 270.4, 76.8 Hz), 124.3, 85.6 (d, *J* = 7.7 Hz), 42.5 (dd, *J* = 31.6, 18.2 Hz), 34.2, 27.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.98 – -108.95 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.43 (t, *J* = 84.7 Hz). HRMS Calculated for $C_{24}H_{22}F_2O_3P$ $[M+H]^+$: 427.1269, found: 427.1264.

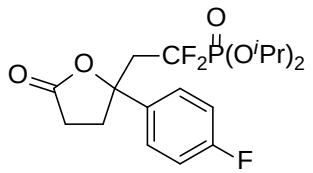


Diisopropyl (1,1-difluoro-2-(5-oxo-2-(p-tolyl)tetrahydrofuran-2-yl)ethyl)phosphonate (**3e**) Flash silica gel chromatography (PE: EA = 1:1) gave 70 mg of **3e** as a colorless oil in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 4.89 – 4.74 (m, 2H), 2.90 – 2.58 (m, 5H), 2.50 – 2.39 (m, 1H), 2.34 (s, 3H), 1.37 – 1.32 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 139.6, 137.6, 129.1, 124.5, 119.3(td, *J* = 262.6, 217.7 Hz), 85.7(d, *J* = 9.6 Hz), 73.9(t, *J* = 7.5 Hz), 43.9 (dd, *J* = 33.4, 18.9 Hz), 33.6, 28.2, 23.9 (dd, *J* = 5.2, 3.5 Hz), 23.5 (dd, *J* = 4.8, 2.1 Hz), 20.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.67 (ddd, *J* = 772.2, 298.0, 104.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.96 (t, *J* = 104.2 Hz). HRMS Calculated for $C_{19}H_{28}F_2O_5P$ $[M+H]^+$: 405.1637, found: 405.1637.

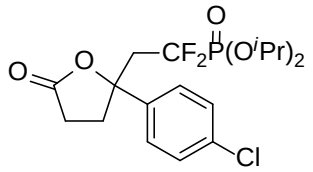


Diisopropyl (1,1-difluoro-2-(2-(4-methoxyphenyl)-5-oxotetrahydrofuran-2-yl)ethyl)phosphonate (**3f**) Flash silica gel chromatography (PE: EA = 1:1) gave 60 mg of **3f** as a colorless oil in 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.90 – 4.74 (m, 2H), 3.80 (s, 3H), 2.89 – 2.68 (m, 3H), 2.67 – 2.60 (m, 2H), 2.49 – 2.39 (m, 1H), 1.37 – 1.32 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 159.1, 134.4, 125.9, 119.2 (td, *J* = 262.5, 217.8 Hz), 113.7, 85.6 (d, *J* = 9.8 Hz), 73.9 (t, *J* = 6.8 Hz), 55.1, 44.0 (dd, *J* = 33.3, 18.8 Hz), 33.6, 28.3, 23.9 (t, *J* = 3.7 Hz), 23.5 (d, *J* = 4.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.82 (ddd, *J* = 761.2, 298.0, 104.3 Hz, 2F). ^{31}P NMR

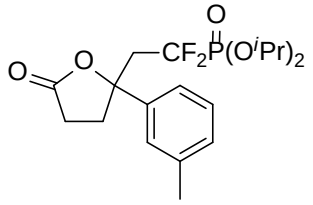
(162 MHz, $CDCl_3$) δ 3.97 (t, *J* = 104.2 Hz). HRMS Calculated for $C_{19}H_{28}F_2O_6P$ $[M+H]^+$: 421.1586, found: 421.1585.



Diisopropyl (1,1-difluoro-2-(2-(4-fluorophenyl)-5-oxotetrahydrofuran-2-yl)ethyl)phosphonate (**3g**) Flash silica gel chromatography (PE: EA = 1:1) gave 74 mg of **3g** as a colorless oil in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.10 – 7.04 (m, 2H), 4.87– 4.76 (m, 2H), 2.90 – 2.56 (m, 5H), 2.49 – 2.39 (m, 1H), 1.38 – 1.32 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 162.1 (d, *J* = 247.3 Hz), 138.2 (d, *J* = 3.2 Hz), 126.5 (d, *J* = 8.2 Hz), 119.8 (dt, *J* = 262.6, 217.3 Hz), 115.3(d, *J* = 21.6 Hz), 85.2 (d, *J* = 9.7 Hz), 73.9 (dd, *J* = 7.1, 4.7 Hz), 44.0 (td, *J* = 18.9, 14.6 Hz), 33.9, 28.0, 23.8 (t, *J* = 3.3 Hz), 23.5(d, *J* = 4.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.83 (ddd, *J* = 673.2, 298.0, 103.7 Hz), -114.18. ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.77 (t, *J* = 103.7 Hz). HRMS Calculated for $C_{18}H_{28}NF_3O_5P$ $[M+NH_4]^+$: 426.1652, found: 426.1653.

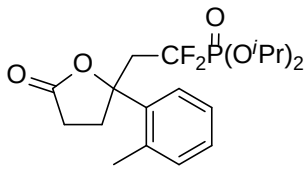


Diisopropyl (2-(2-(4-chlorophenyl)-5-oxotetrahydrofuran-2-yl)-1,1-difluoroethyl)phosphonate (**3h**) Flash silica gel chromatography (PE: EA = 1:1) gave 68 mg of **3h** as a colorless oil in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 4H), 4.85 – 4.76 (m, 2H), 2.90 – 2.58 (m, 5H), 2.44 (dt, *J* = 20.6, 9.4 Hz, 1H), 1.37 – 1.32 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 1410, 133.7, 128.5, 126.1, 119.0 (td, *J* = 262.7, 217.8 Hz), 85.0 (d, *J* = 9.6 Hz), 73.9 (dd, *J* = 6.5, 5.4 Hz), 43.8 (dd, *J* = 33.6, 18.8 Hz), 33.9, 27.9, 23.8 (t, *J* = 3.3 Hz), 23.4 (d, *J* = 4.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.67 (qd, *J* = 297.9, 103.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.73 (t, *J* = 103.5 Hz). HRMS Calculated for $C_{18}H_{28}NF_2O_5ClP$ $[M+NH_4]^+$: 442.1356, found: 442.1355.

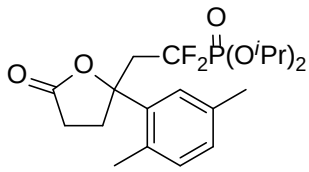


Diisopropyl (1,1-difluoro-2-(5-oxo-2-(m-tolyl)tetrahydrofuran-2-yl)ethyl)phosphonate (**3i**) Flash silica gel chromatography (PE: EA = 2:1) gave 63 mg of **3i** as a colorless oil in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 3H), 7.12 (d, *J* = 7.3 Hz, 1H), 4.82 (ddq, *J* = 19.1, 12.6, 6.3 Hz, 2H), 2.90 – 2.57 (m, 5H), 2.48– 2.41 (m, 1H), 2.36 (s, 3H), 1.38 – 1.32 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 142.9, 138.3, 128.7, 128.4, 125.2, 121.6, 1119.4 (td, *J* = 263.1, 218.6 Hz), 85.8 (d, *J* = 9.5 Hz), 74.0 (dd, *J* = 8.9, 7.4 Hz), 44.0 (td, *J* = 19.0, 14.5 Hz), 33.6, 28.3, 24.0 (dd, *J* = 7.7, 3.5 Hz), 23.6 (t, *J* = 4.5 Hz), 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.62 (ddd, *J* = 771.2, 297.9, 104.2 Hz). ^{31}P

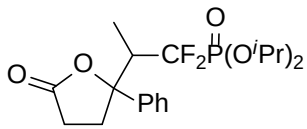
NMR (162 MHz, $CDCl_3$) δ 3.94 (t, *J* = 104.2 Hz). HRMS Calculated for $C_{19}H_{28}F_2O_5P$ $[M+H]^+$: 405.1637, found: 405.1636.



Diisopropyl (1,1-difluoro-2-(5-oxo-2-(o-tolyl)tetrahydrofuran-2-yl)ethyl)phosphonate (**3j**) Flash silica gel chromatography (PE: EA = 1:1) gave 67 mg of **3j** as a colorless oil in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.53 (m, 1H), 7.23 – 7.19 (m, 3H), 4.89 – 4.77 (m, 2H), 3.00 (ddd, *J* = 12.6, 9.6, 6.5 Hz, 1H), 2.89 – 2.77 (m, 2H), 2.77 – 2.67 (m, 1H), 2.67 – 2.56 (m, 1H), 2.50 (dd, *J* = 15.3, 5.5 Hz, 1H), 2.45 (s, 3H), 1.38 – 1.33 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 141.2, 133.2, 132.4, 128.0, 126.0, 124.8, 119.7 (dt, *J* = 261.6, 215.7 Hz), 86.3 (d, *J* = 9.5 Hz), 73.9 (dd, *J* = 9.5, 7.2 Hz), 41.8 (td, *J* = 18.9, 14.3 Hz), 32.8, 28.1, 23.9 (dd, *J* = 8.1, 3.5 Hz), 23.6 (t, *J* = 5.2 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.96 (ddd, *J* = 400.9, 297.0, 104.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.85 (t, *J* = 104.4 Hz). HRMS Calculated for $C_{19}H_{28}F_2O_5P$ $[M+H]^+$: 405.1637, found: 405.1635.

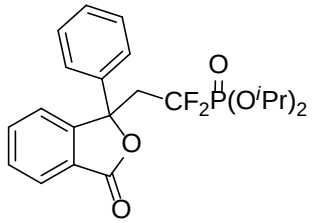


Diisopropyl (2-(2-(2,5-dimethylphenyl)-5-oxotetrahydrofuran-2-yl)-1,1-difluoroethyl)phosphonate (**3k**) Flash silica gel chromatography (PE: EA = 1:1) gave 63 mg of **3k** as a colorless oil in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.36 (m, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 4.90 – 4.77 (m, 2H), 3.05 – 2.93 (m, 1H), 2.87 – 2.68 (m, 3H), 2.64 – 2.43 (m, 2H), 2.39 (s, 3H), 2.32 (s, 3H), 1.38 – 1.33 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 141.2, 135.5, 132.4, 129.8, 128.6, 125.3, 119.7 (td, *J* = 263.7, 216.8 Hz), 86.3 (d, *J* = 9.4 Hz), 73.9 (dd, *J* = 10.8, 7.2 Hz), 41.8 (td, *J* = 18.9, 14.1 Hz), 32.6 (d, *J* = 2.5 Hz), 28.1, 23.9 (dd, *J* = 9.4, 3.4 Hz), 23.5 (dd, *J* = 7.5, 5.0 Hz), 20.9, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.00 (ddd, *J* = 400.8, 296.8, 104.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.88 (t, *J* = 104.6 Hz). HRMS Calculated for $C_{20}H_{30}F_2O_5P$ $[M+H]^+$: 419.1793, found: 419.1795.

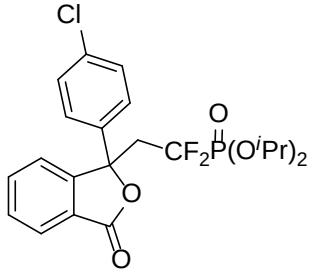


Diisopropyl (1,1-difluoro-2-(5-oxo-2-phenyltetrahydrofuran-2-yl)propyl)phosphonate (**3l**) Flash silica gel chromatography (PE: EA = 2:1) gave 29 mg of **3l** as a colorless oil in 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 4H), 7.32 – 7.28 (m, 1H), 4.92 – 4.78 (m, 2H), 3.02 – 2.83 (m, 2H), 2.62 – 2.48 (m, 2H), 2.38– 2.29 (m, 1H), 1.36 (dt, *J* = 7.9, 6.2 Hz, 12H), 1.15 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 143.1, 128.5, 127.8, 125.1, 121.9 (td, *J* = 267.8, 215.4 Hz), 88.7 (d, *J* = 6.5 Hz), 73.9 (d, *J* = 22.7 Hz), 47.2 (dd, *J* = 34.4, 16.7 Hz), 32.8, 28.4, 24.1(dd, *J* = 17.3, 2.8 Hz),

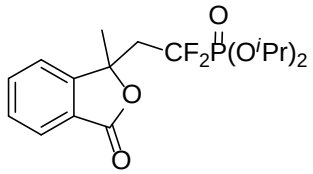
23.65 (t, J = 2.2 Hz), 10.84 (t, J = 5.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.35 (ddd, J = 411.7, 303.1, 106.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.49 (dd, J = 108.5, 104.5 Hz). HRMS Calculated for $C_{19}H_{28}F_2O_5P$ $[M+H]^+$: 405.1637, found: 405.1634.



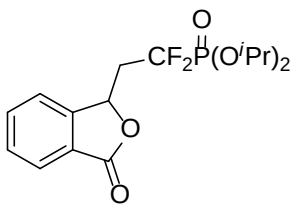
Diisopropyl (1,1-difluoro-2-(3-oxo-1-phenyl-1,3-dihydroisobenzofuran-1-yl)ethyl)phosphonate (**3m**) Flash silica gel chromatography (PE: EA = 1:1) gave 84 mg of **3m** as a colorless oil in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.6 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.58 – 7.53 (m, 2H), 7.50 (ddd, J = 13.3, 6.7, 3.9 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.30 (qd, J = 5.2, 2.8 Hz, 1H), 4.83 – 4.75 (m, 2H), 3.40 – 3.11 (m, 2H), 1.36 – 1.29 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 151.1, 140.0, 133.9, 129.2, 128.6, 128.3, 125.6, 124.9, 124.4, 122.9, 118.7 (td, J = 263.6, 218.2 Hz), 85.9 (d, J = 9.3 Hz), 73.9 (dd, J = 7.2, 3.1 Hz), 41.7 (dd, J = 34.2, 18.7 Hz), 23.6 (ddd, J = 14.5, 7.9, 4.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.08 (ddd, J = 400.7, 298.2, 103.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.71 (t, J = 102.1 Hz). HRMS Calculated for $C_{22}H_{26}F_2O_5P$ $[M+H]^+$: 439.1480, found: 439.1479.



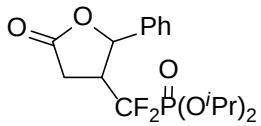
Diisopropyl (2-(1-(4-chlorophenyl)-3-oxo-1,3-dihydroisobenzofuran-1-yl)-1,1-difluoroethyl)phosphonate (**3n**) Flash silica gel chromatography (PE: EA = 2:1) gave 81 mg of **3n** as a colorless oil in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.53 (dd, J = 17.2, 7.9 Hz, 3H), 7.33 (d, J = 8.6 Hz, 2H), 4.79 (qd, J = 12.5, 6.2 Hz, 2H), 3.35 – 3.06 (m, 2H), 1.33 (dt, J = 8.4, 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 150.8, 138.6, 134.4, 134.2, 129.5, 128.8 126.1, 125.8, 124.9, 122.8, 118.7 (dt, J = 118.6, 84.4 Hz), 85.45 (d, J = 9.4 Hz), 74.09 (d, J = 6.9 Hz), 42.69 – 23.86 (m), 23.84 (t, J = 3.9 Hz), 23.54 (dd, J = 8.2, 4.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.84 (ddd, J = 400.6, 298.4, 102.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.60 (t, J = 102.8 Hz). HRMS Calculated for $C_{22}H_{28}NF_2O_5ClP$ $[M+NH_4]^+$: 490.1356, found: 490.1355.



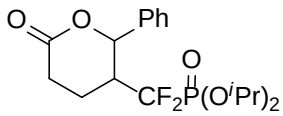
Diisopropyl (1,1-difluoro-2-(1-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)ethyl)phosphonate (**3o**) Flash silica gel chromatography (PE: EA = 2:1) gave 69 mg of **3o** as a colorless oil in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 6.8, 4.1 Hz, 1H), 7.69 (dd, *J* = 10.7, 4.3 Hz, 1H), 7.55 (ddd, *J* = 16.6, 8.2, 5.1 Hz, 2H), 4.86 – 4.76 (m, 2H), 2.91 – 2.68 (m, 2H), 1.77 (s, 3H), 1.39 – 1.32 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 152.6, 134.0, 129.1, 125.5, 125.2, 121.6, 119.1 (td, *J* = 262.8, 217.8 Hz), 84.0 (d, *J* = 9.9 Hz), 73.9 (d, *J* = 6.7 Hz), 41.5 (dd, *J* = 34.2, 19.3 Hz), 26.9, 23.9 (d, *J* = 3.2 Hz), 23.5 (t, *J* = 4.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.49 (qd, *J* = 297.2, 103.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.79 (t, *J* = 103.8 Hz). HRMS Calculated for $C_{17}H_{24}F_2O_5P$ $[M+H]^+$: 377.1324, found: 377.1322.



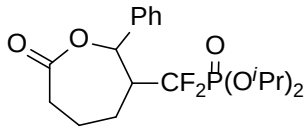
Diisopropyl (1,1-difluoro-2-(3-oxo-1,3-dihydroisobenzofuran-1-yl)ethyl)phosphonate (**3p**) Flash silica gel chromatography (PE: EA = 1:1) gave 33 mg of **3p** as a colorless oil in 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (t, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.58 (dd, *J* = 12.4, 7.6 Hz, 2H), 5.89 (dd, *J* = 7.4, 4.2 Hz, 1H), 4.96 – 4.86 (m, 2H), 2.80 – 2.51 (m, 2H), 1.44 – 1.39 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 148.7, 134.3, 129.5, 125.6, 122.2, 118.5 (td, *J* = 264.6, 218.2 Hz), 74.5 (dd, *J* = 11.4, 4.9 Hz), 74.2 (dd, *J* = 13.3, 7.1 Hz), 39.4 (td, *J* = 20.7, 15.1 Hz), 24.0 (dd, *J* = 5.7, 3.6 Hz), 23.6 (t, *J* = 4.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.52 (qd, *J* = 298.8, 103.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.98 (dd, *J* = 104.7, 102.3 Hz). HRMS Calculated for $C_{16}H_{25}NF_2O_5P$ $[M+NH_4]^+$: 380.1433, found: 380.1434.



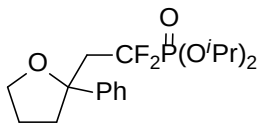
Diisopropyl (difluoro(5-oxo-2-phenyltetrahydrofuran-3-yl)methyl)phosphonate (**3q**) Flash silica gel chromatography (PE: EA = 1:1) gave 61 mg of **3q** as a colorless oil in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 5H), 5.88 (d, *J* = 4.5 Hz, 1H), 4.91 – 4.82 (m, 2H), 3.29 – 3.15 (m, 1H), 2.92 (ddd, *J* = 28.6, 18.5, 7.9 Hz, 2H), 1.39 – 1.37 (m, 9H), 1.34 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 138.7, 128.7, 1286, 125.2, 118.8 (ddd, *J* = 265.6, 262.3, 215.3 Hz), 78.6 (d, *J* = 4.8 Hz), 74.5 (dd, *J* = 20.2, 7.2 Hz), 47.2 (td, *J* = 20.8, 15.3 Hz), 28.1 (t, *J* = 4.3 Hz), 23.9 (t, *J* = 3.9 Hz), 23.5 (d, *J* = 3.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.77 (ddd, *J* = 404.2, 302.2, 103.7 Hz, 2F). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.37 (dd, *J* = 105.1, 102.1 Hz). HRMS Calculated for $C_{17}H_{27}NF_2O_5P$ $[M+NH_4]^+$: 394.1589, found: 394.1592.



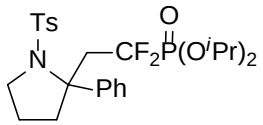
Diisopropyl (difluoro(6-oxo-2-phenyltetrahydro-2H-pyran-3-yl)methyl)phosphonate (**3r**) Flash silica gel chromatography (PE: EA = 2:1) gave 47 mg of **3r** as a colorless oil in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.39 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 6.0 Hz, 3H), 5.99 (d, *J* = 3.8 Hz, 1H), 4.92 – 4.84 (m, 2H), 2.96 – 2.82 (m, 1H), 2.79 – 2.70 (m, 1H), 2.55 (dt, *J* = 17.9, 5.7 Hz, 1H), 2.28 (td, *J* = 11.5, 5.5 Hz, 1H), 2.08 (dt, *J* = 15.8, 6.5 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 139.4, 128.6, 128.1, 125.5, 120.3 (dt, *J* = 265.6, 215.1 Hz), 77.8 (q, *J* = 4.5 Hz), 74.4 (t, *J* = 6.7 Hz), 42.1 (td, *J* = 19.0, 15.3 Hz), 27.2, 23.9 (dd, *J* = 6.9, 3.6 Hz), 23.6 (dd, *J* = 8.6, 4.9 Hz), 16.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.66 (ddd, *J* = 2146.5, 304.5, 104.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.67 (t, *J* = 104.7 Hz). HRMS Calculated for $C_{18}H_{29}NF_2O_5P$ $[M+NH_4]^+$: 408.1746, found: 408.1745.



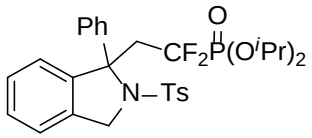
Diisopropyl (difluoro(7-oxo-2-phenyloxepan-3-yl)methyl)phosphonate (**3s**) Flash silica gel chromatography (PE: EA = 1:1) gave 26 mg of **3s** as a colorless oil in 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 5.66 (d, *J* = 8.5 Hz, 1H), 4.85 – 4.72 (m, 2H), 3.22 – 3.11 (m, 1H), 2.92 (dt, *J* = 13.7, 8.7 Hz, 1H), 2.54 (ddd, *J* = 13.6, 7.8, 3.1 Hz, 1H), 2.43 – 2.38 (m, 1H), 2.15 – 2.01 (m, 2H), 1.88 – 1.81 (m, 1H), 1.36 (t, *J* = 6.2 Hz, 3H), 1.31 (dd, *J* = 9.3, 4.0 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 139.6, 128.4 (d, *J* = 5.4 Hz), 127.2 (d, *J* = 1.2 Hz), 121.6 (td, *J* = 268.7, 215.1 Hz), 77.6 – 77.5 (m), 74.07 (dd, *J* = 18.9, 7.3 Hz), 46.4 (dd, *J* = 33.6, 16.4 Hz), 31.9, 23.9 (dd, *J* = 9.2, 3.5 Hz), 23.6 (dd, *J* = 8.9, 5.0 Hz), 23.1 (d, *J* = 5.9 Hz), 18.1 (d, *J* = 2.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.59 (ddd, *J* = 412.1, 306.0, 104.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.71 (dd, *J* = 105.8, 103.7 Hz). HRMS Calculated for $C_{19}H_{28}F_2O_5P$ $[M+H]^+$: 405.1637, found: 405.1638.



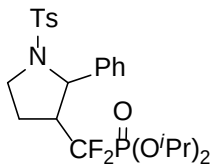
Diisopropyl (1,1-difluoro-2-(2-phenyltetrahydrofuran-2-yl)ethyl)phosphonate (**5a**) Flash silica gel chromatography (PE: EA = 3:1) gave 45 mg of **5a** as a colorless oil in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 4.85 – 4.70 (m, 2H), 4.02 (q, *J* = 7.6 Hz, 1H), 3.86 (td, *J* = 8.2, 5.5 Hz, 1H), 2.78 – 2.56 (m, 2H), 2.37 – 2.25 (m, 2H), 2.02 – 1.93 (m, 1H), 1.80 – 1.69 (m, 1H), 1.32 (dt, *J* = 6.1, 5.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 127.8, 126.5, 125.1, 119.9 (td, *J* = 262.3, 217.6 Hz), 83.9 (d, *J* = 9.7 Hz), 73.4 (t, *J* = 7.0 Hz), 67.1, 43.7 (td, *J* = 18.7, 13.8 Hz), 37.9, 25.0, 23.9 (dd, *J* = 6.7, 3.4 Hz), 23.5 (t, *J* = 5.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.49 (ddd, *J* = 716.9, 297.1, 106.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.88 (t, *J* = 107.0 Hz). HRMS Calculated for $C_{18}H_{28}F_2O_4P$ $[M+H]^+$: 377.1688, found: 377.1689.



Diisopropyl (1,1-difluoro-2-(2-phenyl-1-tosylpyrrolidin-2-yl)ethyl)phosphonate (**5b**) Flash silica gel chromatography (PE: EA = 2:1) gave 50 mg of **5b** as a colorless oil in 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 2H), 7.22 – 7.19 (m, 5H), 7.08 (d, *J* = 8.2 Hz, 2H), 4.94 – 4.85 (m, 2H), 3.80 – 3.65 (m, 2H), 3.51 – 3.46 (m, 1H), 3.19 – 3.04 (m, 1H), 2.62 (dt, *J* = 13.9, 7.1 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.35 (s, 3H), 2.15 – 2.04 (m, 1H), 2.00 – 1.90 (m, 1H), 1.39 (dd, *J* = 10.8, 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 142.3, 137.7, 128.9, 127.8, 127.0, 127.0, 126.8, 120.1 (td, *J* = 262.6, 219.4 Hz), 73.8 (dd, *J* = 6.8, 5.7 Hz), 69.9 (d, *J* = 10.8 Hz), 49.2, 40.9, 40.4 (dd, *J* = 33.2, 18.5 Hz), 24.1 (d, *J* = 3.4 Hz), 23.7 (dd, *J* = 4.9, 2.7 Hz), 23.2, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.17 (qd, *J* = 295.7, 108.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.93 (t, *J* = 108.3 Hz). HRMS Calculated for $C_{25}H_{35}NF_2O_5PS$ $[M+NH_4]^+$: 530.1936, found: 530.1933.



Diisopropyl (1,1-difluoro-2-(1-phenyl-2-tosylisoindolin-1-yl)ethyl)phosphonate (**5c**) Flash silica gel chromatography (PE: EA = 2:1) gave 87 mg of **5c** as a colorless oil in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.24 (m, 2H), 7.20 – 7.13 (m, 2H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 5H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.02 (d, *J* = 12.8 Hz, 1H), 4.86 (ddq, *J* = 28.2, 12.6, 6.2 Hz, 2H), 4.69 (d, *J* = 12.8 Hz, 1H), 4.25 – 4.11 (m, 1H), 3.19 (dddd, *J* = 32.6, 15.4, 5.1, 1.8 Hz, 1H), 2.28 (s, 3H), 1.43 (dd, *J* = 14.5, 6.2 Hz, 6H), 1.36 (dd, *J* = 6.1, 4.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 142.5 (d, *J* = 1.8 Hz), 142.2, 137.2, 134.6, 128.7, 127.9, 127.8, 127.8, 127.4, 126.7, 123.8, 123.7, 121.9, 120.2 (ddd, *J* = 266.1, 262.1, 218.7 Hz), 74.0 (dd, *J* = 11.5, 7.3 Hz), 72.6 (d, *J* = 10.4 Hz), 53.6 (d, *J* = 2.8 Hz), 39.3 (dd, *J* = 32.4, 16.6 Hz), 24.1 (dd, *J* = 11.4, 3.5 Hz), 23.8 (dd, *J* = 23.2, 4.9 Hz), 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.02 (ddd, *J* = 398.1, 295.1, 106.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.27 (dd, *J* = 109.3, 102.9 Hz). HRMS Calculated for $C_{29}H_{38}N_2F_2O_5PS$ $[M+NH_4]^+$: 595.2202, found: 595.2197.

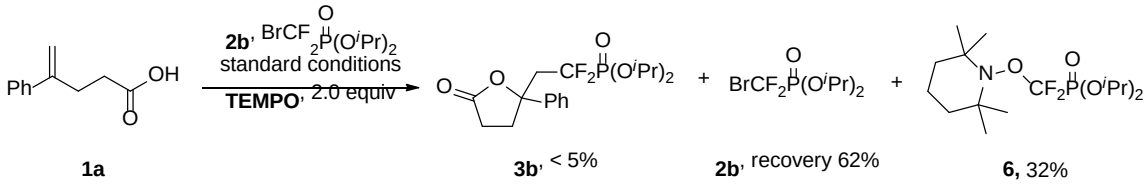


Diisopropyl (difluoro(2-phenyl-1-tosylpyrrolidin-3-yl)methyl)phosphonate (**5d**) Flash silica gel chromatography (PE: EA = 2:1) gave 51 mg of **5d** as a colorless oil in 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 3H), 5.20 (d, *J* = 3.4 Hz, 1H), 4.73 (dp, *J* = 12.7, 6.3 Hz, 2H), 3.69 (dd, *J* = 15.6, 6.3 Hz, 1H), 3.49 (q, *J* = 8.1 Hz, 1H), 2.80 – 2.70 (m, 1H), 2.39 (s, 3H), 2.19 – 2.14 (m, 2H), 1.31 (dd, *J* = 6.1, 3.4 Hz, 6H), 1.25 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 142.8, 134.8, 129.2, 128.3, 127.6, 127.2, 126.3, 119.6 (td, *J* = 266.7, 212.7 Hz), 73.9 (dd, *J* = 14.4, 7.2 Hz), 61.9 (d, *J* = 3.9 Hz), 52.3 (dd, *J* = 34.6, 19.5 Hz), 48.6, 24.3, 23.9 (dd, *J* = 8.8, 3.5 Hz), 23.5(t, *J* = 4.4 Hz), 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.66 (ddd, *J* = 405.7, 300.5, 106.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.05 (t, *J* = 105.8 Hz). HRMS Calculated for $C_{24}H_{36}N_2F_2O_5PS$ $[M+NH_4]^+$: 533.2045, found: 533.2040.

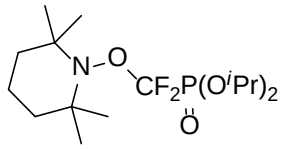
5. Mechanistic investigation

(1). Radical trapping experiments

a) Radical trapping experiment with TEMPO

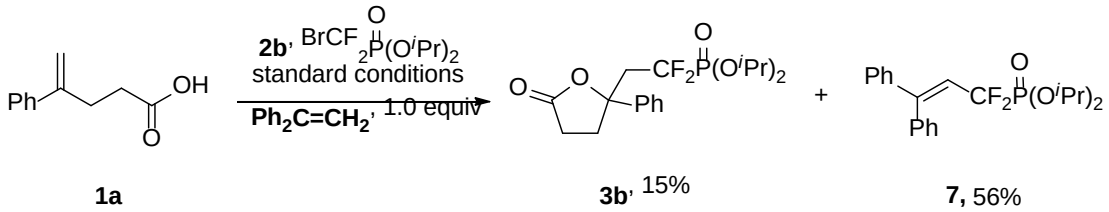


Under the standard reaction conditions, two equivalents of radical scavenger TEMPO were added into the reaction. Then the tube was placed at a distance (app.5 cm) from 5 W blue LEDs lamb, and the resulting solution was stirred at ambient temperature under visible-light irradiation for 24h. After the reaction was finished, the mixture was concentrated under vacuum, and the residue was purified by flash chromatography on silica gel to afford the product **3b**, **2b** and **6**. Since the polarities of the products **2b** and **6** were very close, it was difficult to separate **2b** and **6** apart. However, the respective yields could be calculated by the ^{1}H NMR.



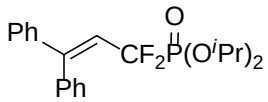
Diisopropyl (difluoro((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)phosphonate (**6**) Flash silica gel chromatography (PE: EA = 5:1) gave **6** as a colorless oil in 36% yield. Pick the **TEMPO-CF$_2$P(O)(O^{i}Pr)$_2$** peak. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (ddq, *J* = 19.1, 12.6, 6.3 Hz, 2H), 1.59 (dd, *J* = 12.9, 8.0 Hz, 6H), 1.41 (dd, *J* = 14.0, 6.7 Hz, 12H), 1.20 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 118.7 (dd, *J* = 576.9, 293.3 Hz), 73.6 (d, *J* = 6.7 Hz), 61.1, 40.3, 33.6 (t, *J* = 5.1 Hz), 24.1 (d, *J* = 3.2 Hz), 23.6 (d, *J* = 5.4 Hz), 20.7, 16.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.78 (d, *J* = 132.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 0.13 (t, *J* = 132.0 Hz). HRMS Calculated for $C_{16}H_{33}NF_2O_4P$ $[M+H]^+$: 372.2110, found: 372.2113.

b) Radical trapping experiment with 1,1-Diphenylethylene



Under the standard reaction conditions, one equivalent of radical scavenger 1,1-diphenylethylene was added into the reaction. After that, the tube was placed at a distance (app.5 cm) from 5 W blue LEDs lamb, and the resulting solution was stirred at ambient temperature under visible-light irradiation for

24h. After the reaction completed, the mixture was concentrated under vacuum, and the residue was purified by flash chromatography on silica gel to afford the product **3b** and **7**.



Diisopropyl (1,1-difluoro-3,3-diphenylallyl)phosphonate (**7**) Flash silica gel chromatography (PE: EA = 5:1) gave **7** as a colorless oil in 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 8H), 7.24 (dt, *J* = 4.5, 3.0 Hz, 2H), 6.16 (td, *J* = 16.1, 2.1 Hz, 1H), 4.84 (dq, *J* = 12.5, 6.2 Hz, 2H), 1.35 (dd, *J* = 10.7, 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7 (dt, *J* = 8.4, 5.8 Hz), 141.6, 138.2 (d, *J* = 1.3 Hz), 129.5 (d, *J* = 1.2 Hz), 128.7, 128.2, 127.9, 127.8, 127.4, 117.1 (td, *J* = 19.3, 14.1 Hz), 117.0 (td, *J* = 260.8, 222.4 Hz), 73.6(d, *J* = 7.1 Hz), 24.0 (d, *J* = 3.5 Hz), 23.7(d, *J* = 4.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.22 (d, *J* = 112.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.08 (t, *J* = 112.9 Hz). RMS Calculated for $C_{21}H_{26}F_2O_3P$ $[M+H]^+$: 395.1582, found: 395.1581.

(2) Emission quenching experiments

Emission intensities were surveyed on a HORIBA AquaLog fluorescence spectrometer and equipped with a 1-cm quartz cell. Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 0.1 mM *fac*-Ir(ppy)$_3$ in acetonitrile at room temperature. The solutions were irradiated at 390nm and fluorescence was measured from 400 nm to 700 nm. Control experiments showed that excited state of *fac*-Ir(ppy)$_3$ was quenched by $BrCF_2PO(O^iPr)_2$.

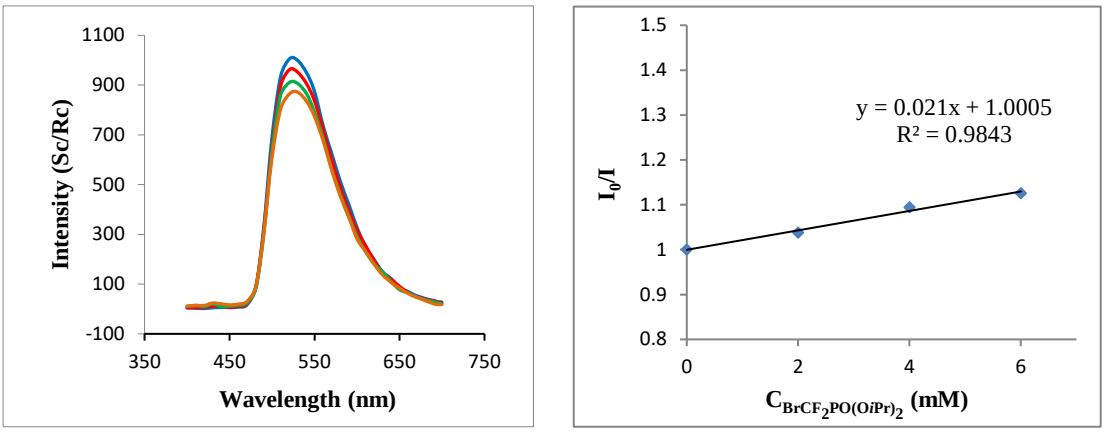


Figure S1. The Emission Quenching of *fac*-Ir(ppy)$_3$ by $BrCF_2PO(O^iPr)_2$.

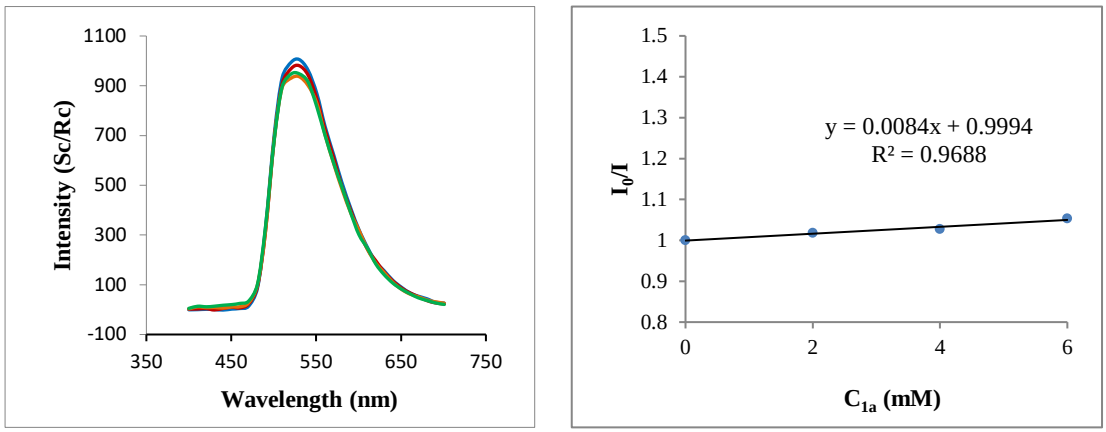


Figure S2. The Emission Quenching of *fac*-Ir(ppy)$_3$ by substrate **1a**.

(3). Electrochemistry experiments

Electrochemical investigation was studied on a Chi 660e electrochemical workstation. Cyclic voltammograms were obtained using a standard three electrode cell under argon at room temperature with a glassy carbon working electrode and a platinum wire auxiliary electrode. Ag/AgCl (0.01 mmol/L) reference electrode was used and the supporting electrolyte solution was 0.05 M (^{n}Bu)$_4$NPF$_6$. Measurement conditions: solvent, CH_3CN; concentration, 2×10^{-4} mol/L; supporting electrolyte, (^{n}Bu)$_4$NPF$_6$; work electrode, Pt/C; counter electrode, Pt; reference electrode, Ag/AgCl; scan speed, 0.1 V s^{-1}; temperature, room temperature.

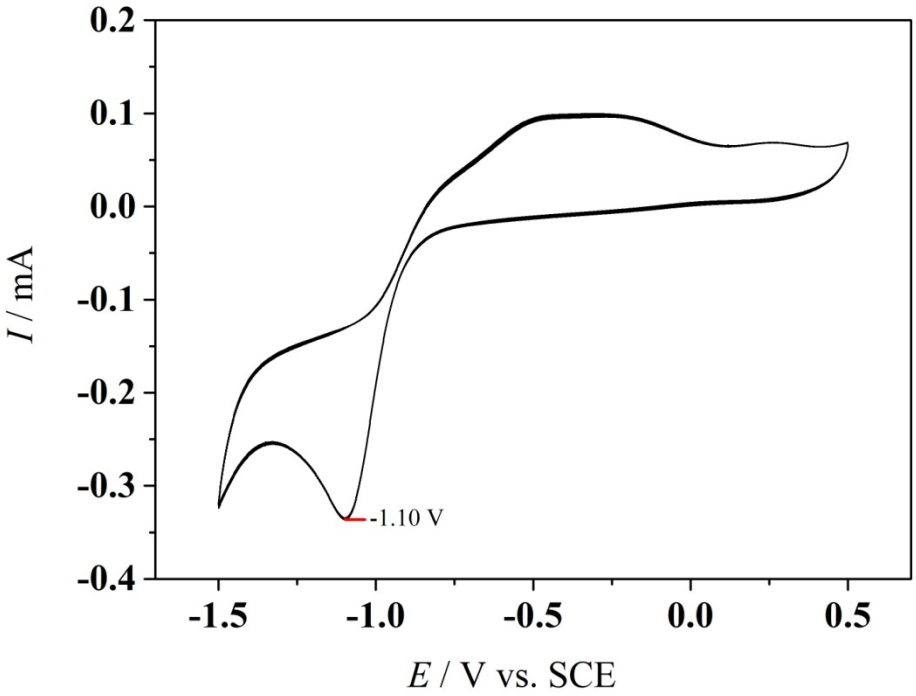


Figure S3. Cyclic voltammetry of **2b**.

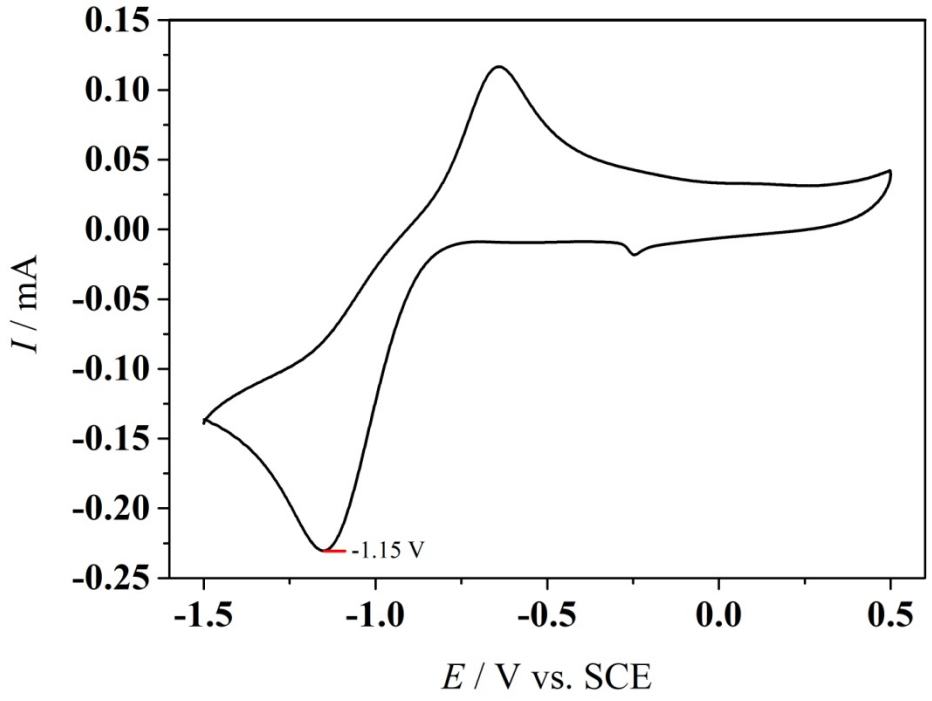


Figure S4. Cyclic voltammetry of **2d**.

The potential of diisopropyl bromodifluoromethylphosphate (**2b**) and (bromodifluoromethyl)diphenylphosphine oxide (**2d**) were investigated by cyclic voltammograms. Compound **2b** shows an irreversible reduction event at -1.10 V (vs. SCE) in acetonitrile; and Compound **2d** shows an irreversible reduction event at -1.15 V (vs. SCE) in acetonitrile.

6. References

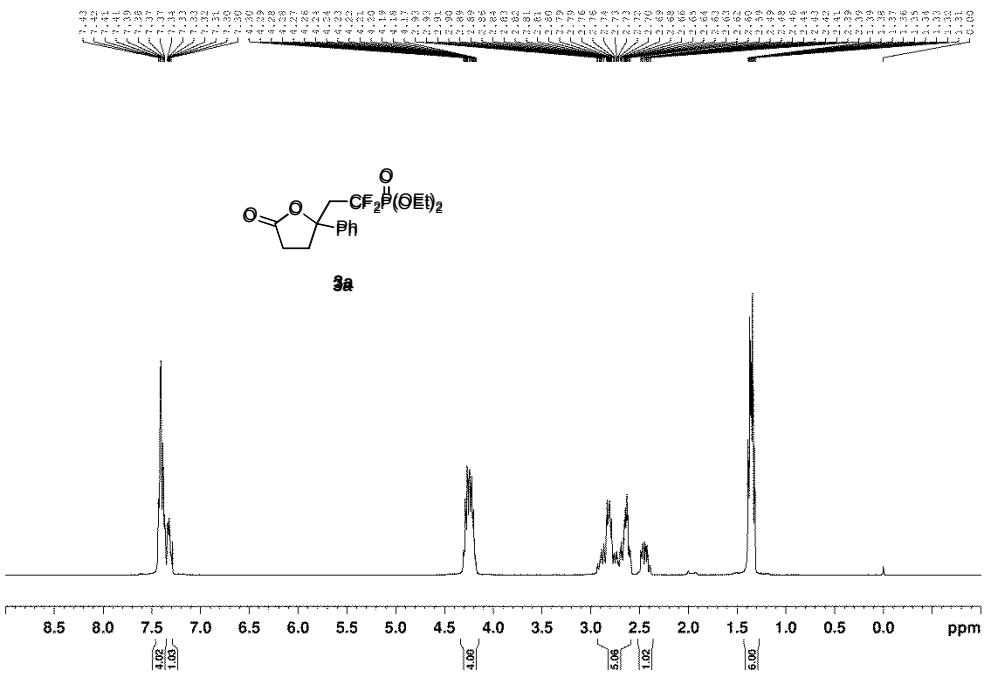
s1. (a) R. Zhu and S. L. Buchwald, *J. Am. Chem. Soc.*, 2012, **134**, 12462; (b) G. C. Geary, E. G. Hope and A. M. Stuart, *Angew. Chem., Int. Ed.*, 2015, **54**, 14911; (c) C. Li, Z.-C. Qi, Q. Yang, X.-Y. Qiang and S.-D. Yang, *Chin. J. Chem.*, 2018, **36**, 1052.

s2. R. M. Flynn and D. J. Burton, *J. Fluorine Chem.*, 2011, **132**, 815.

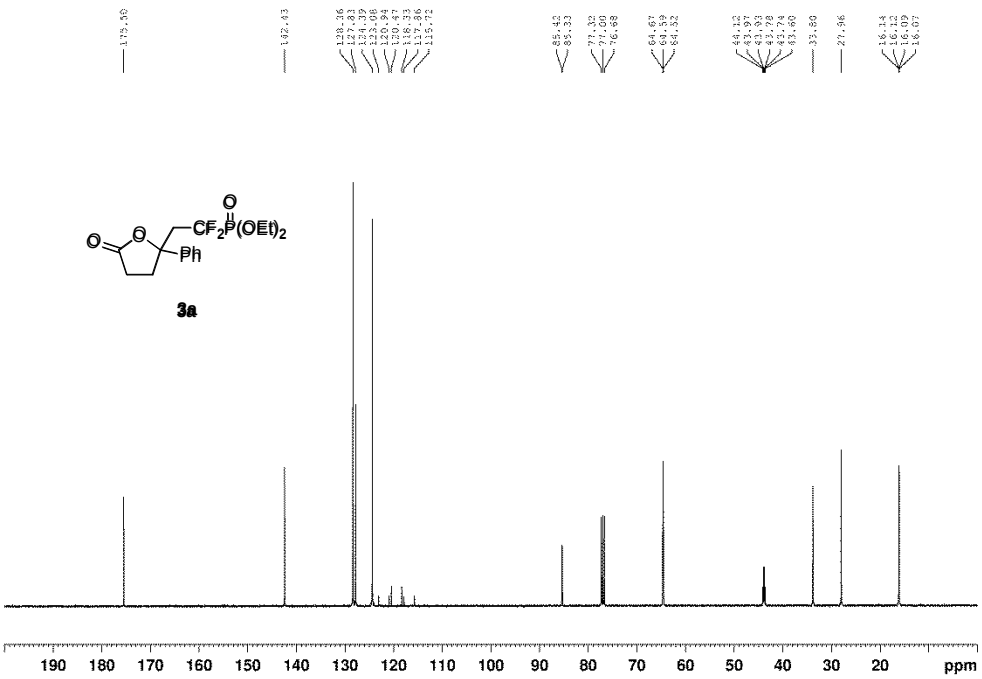
s3. W. Sha, W. Zhang, S. Ni, H. Mei, J. Han and Y. Pan, *J. Org. Chem.*, 2017, **82**, 9824.

7. Copies of NMR spectra

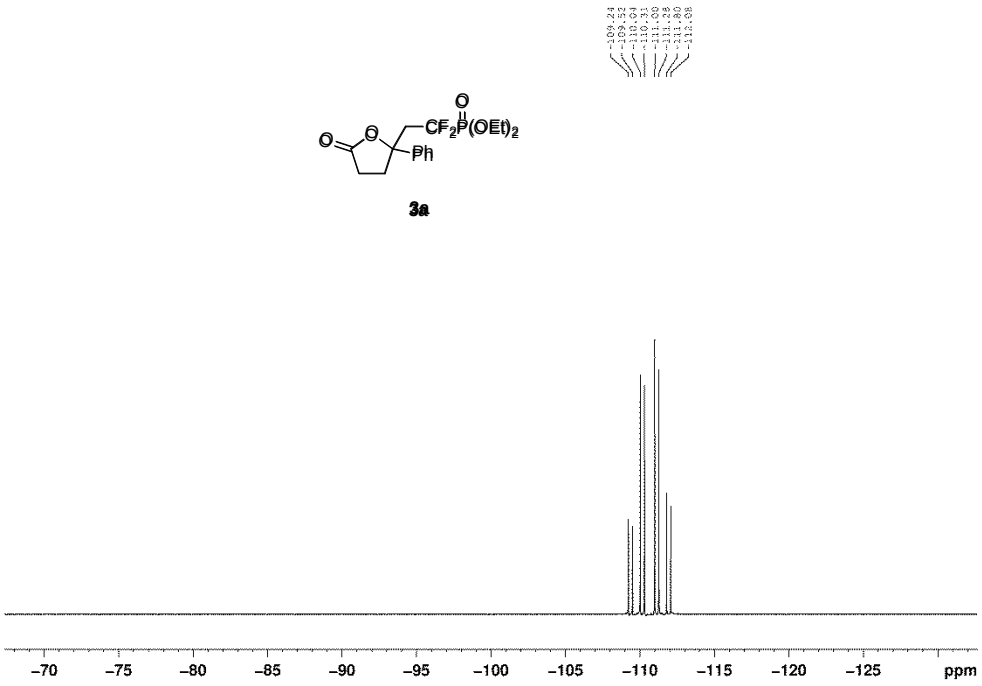
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3a



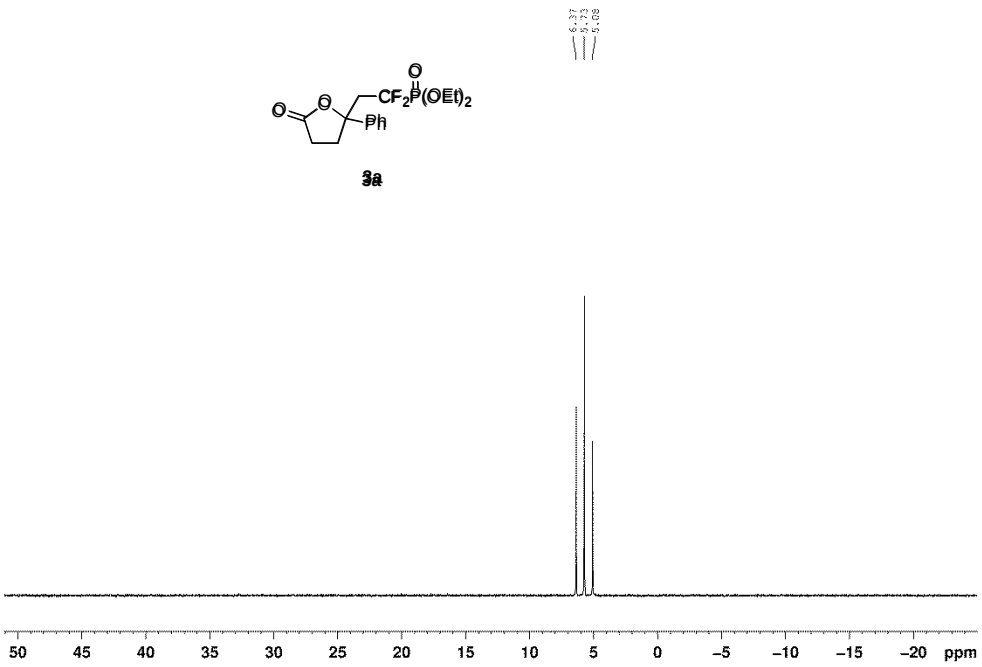
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3a



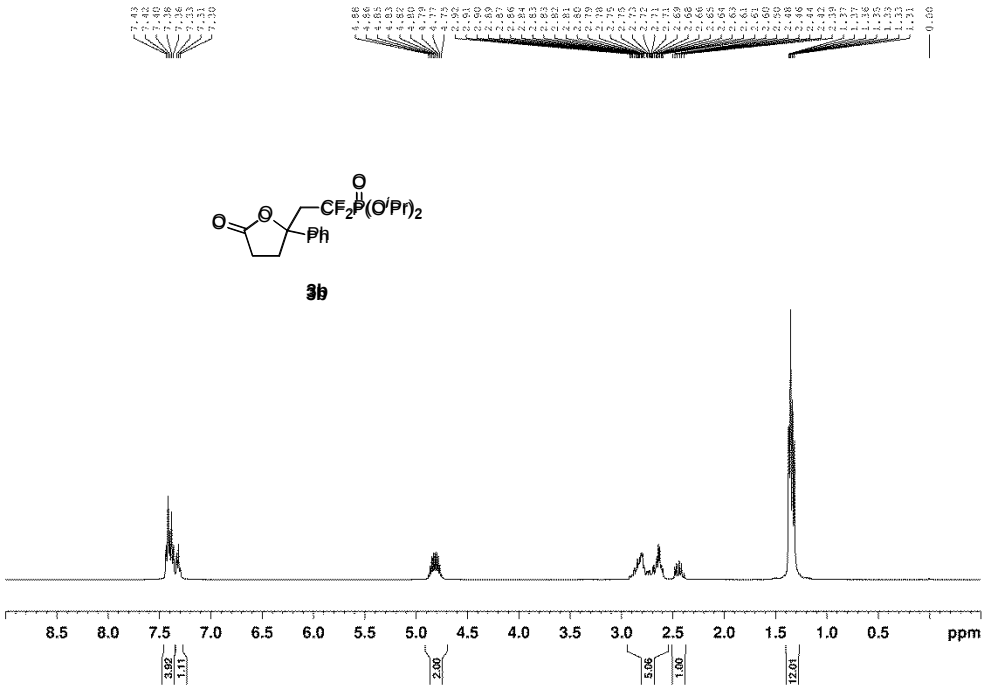
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3a



^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3a



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3b



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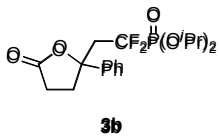
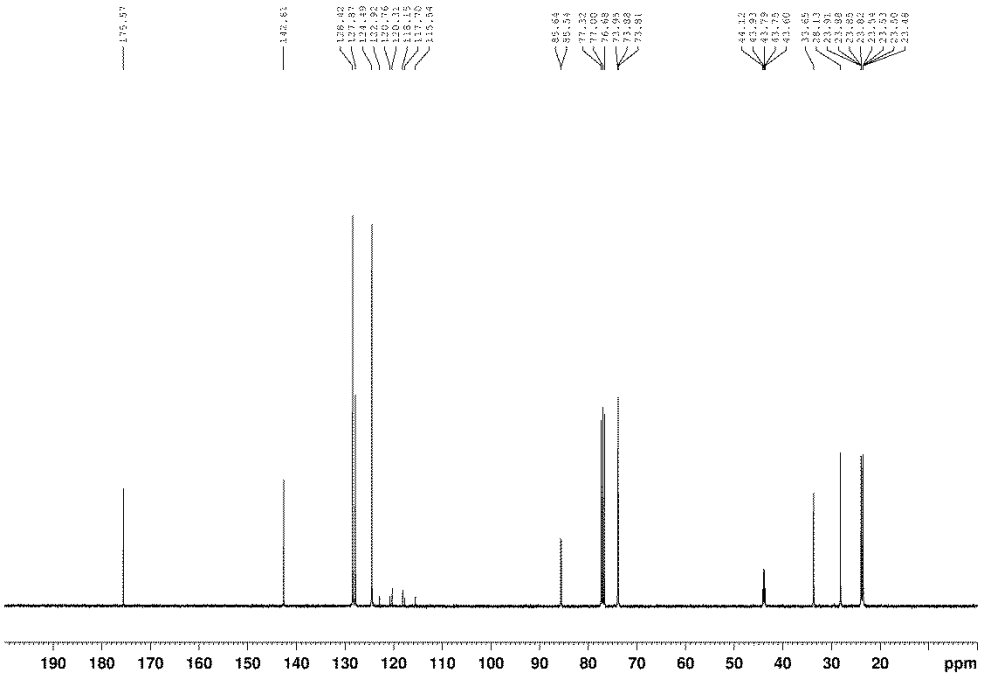
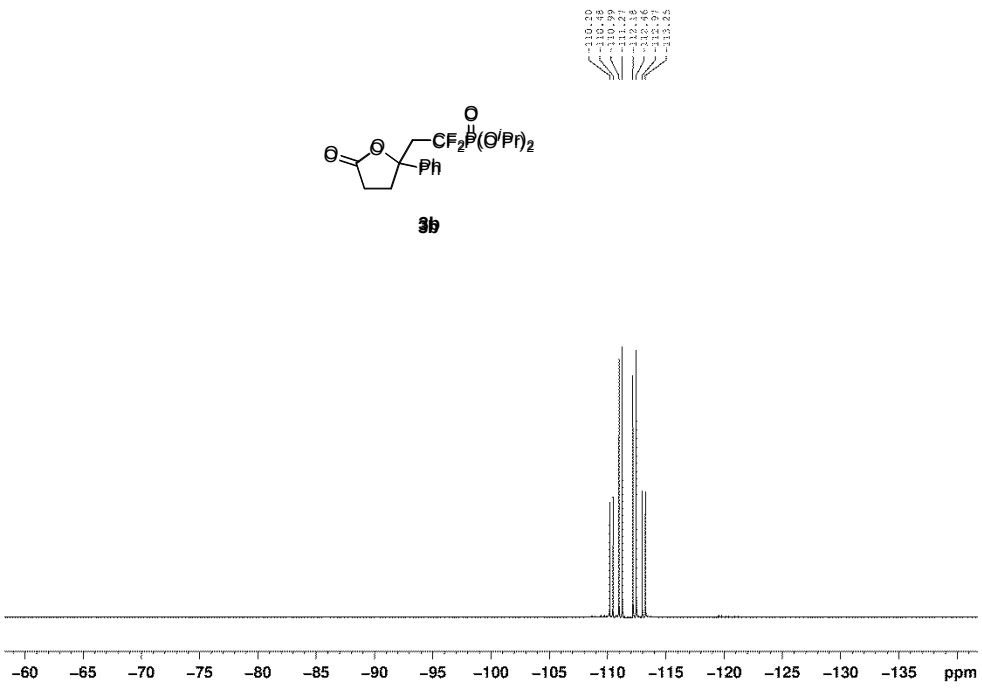
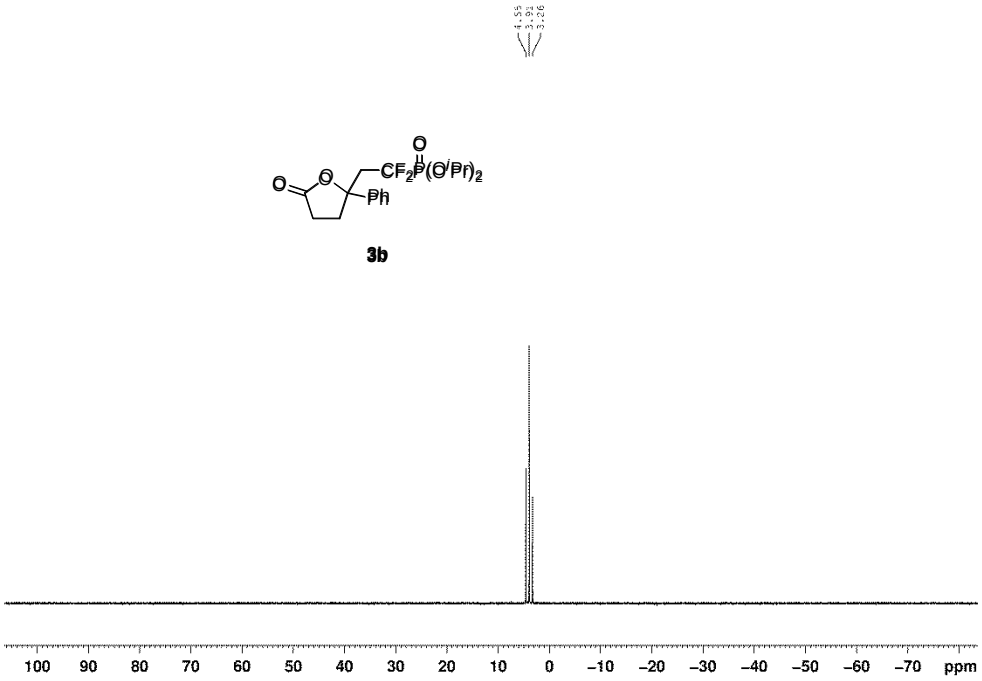




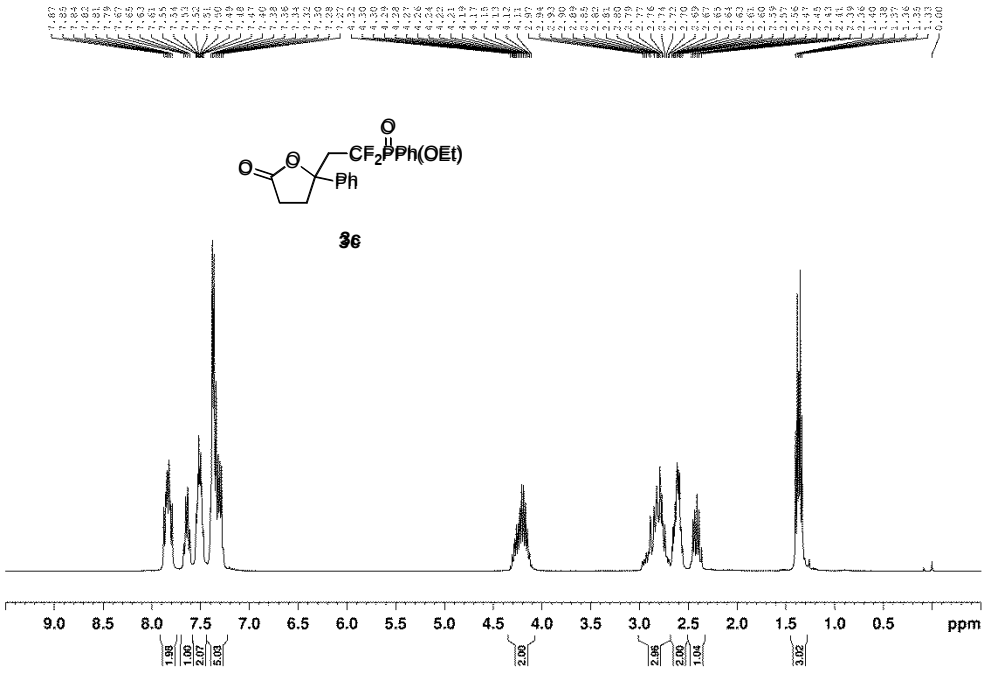
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3b



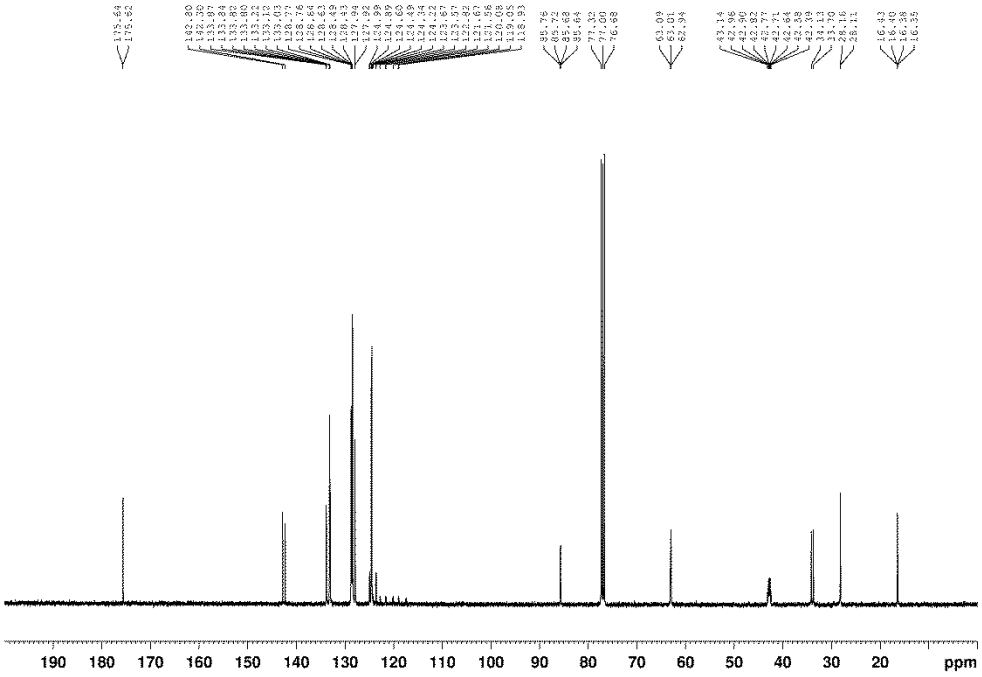
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3b



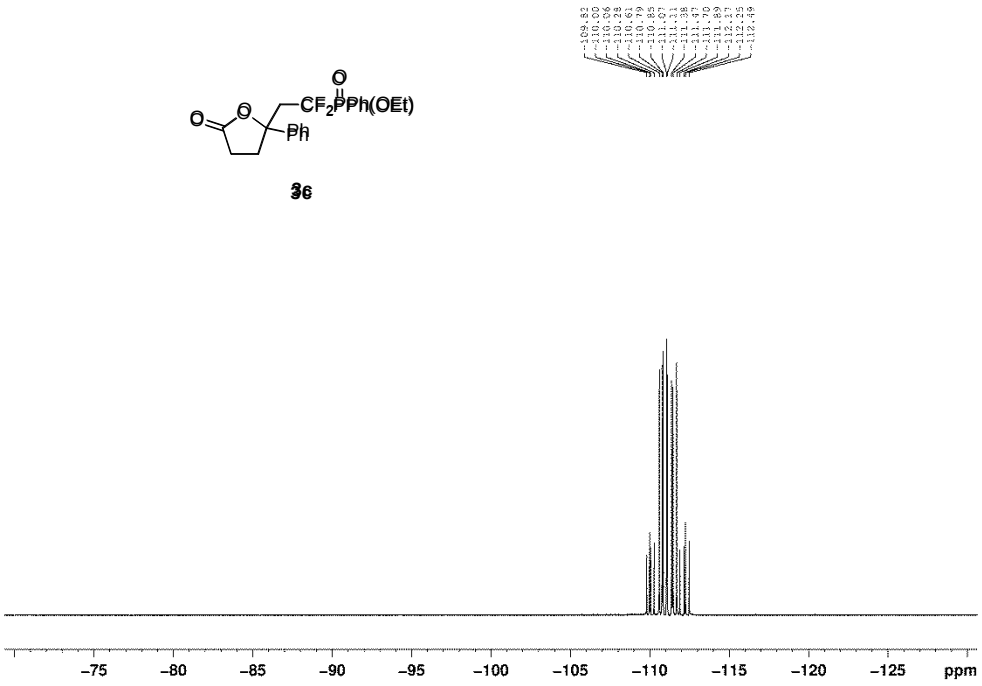
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3c



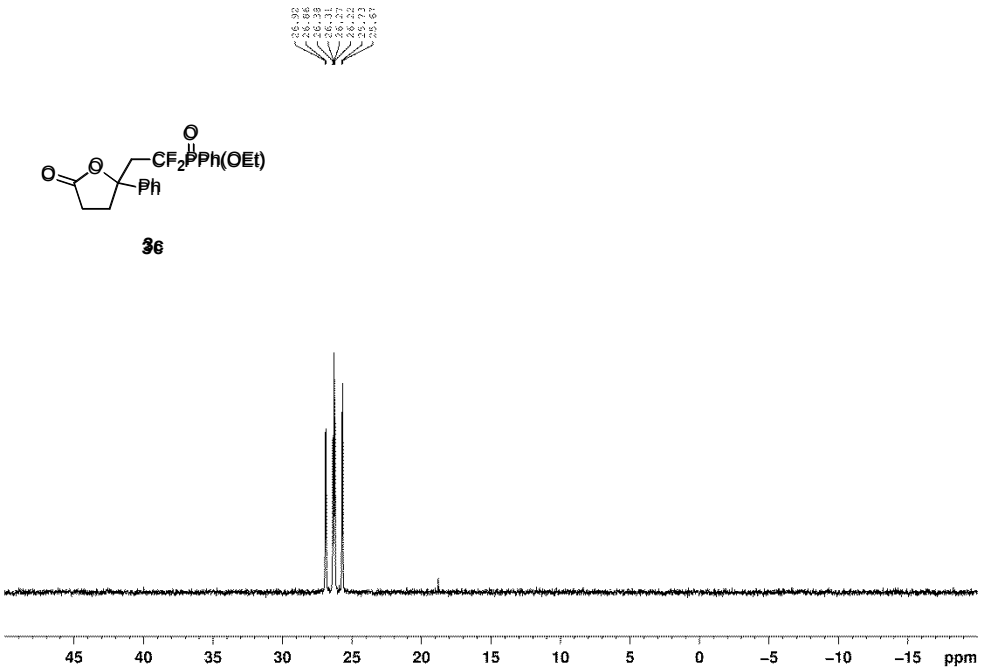
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3c



^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3c



^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3c



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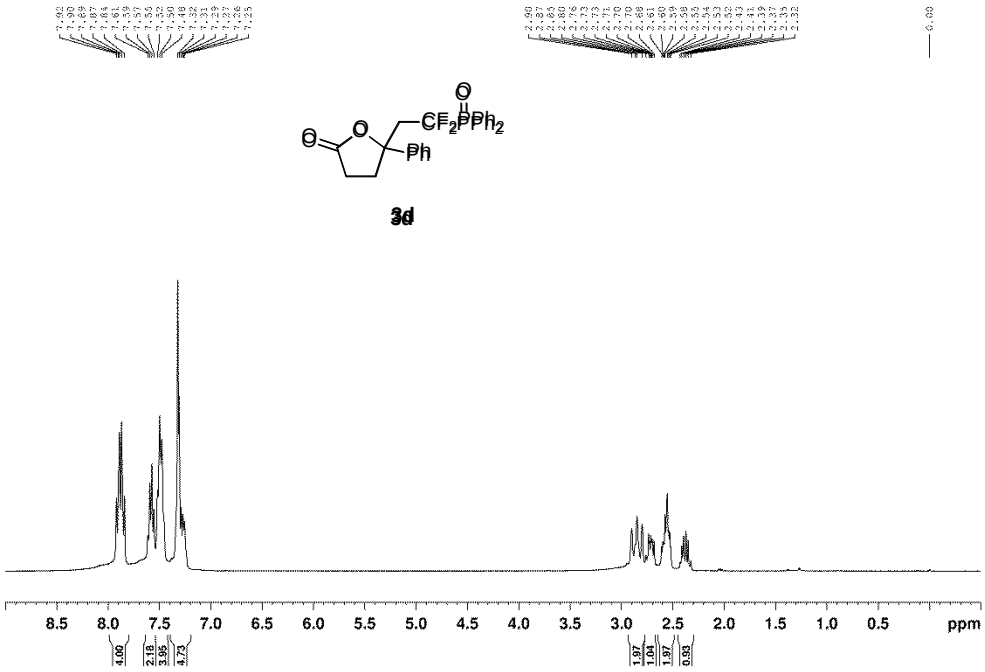
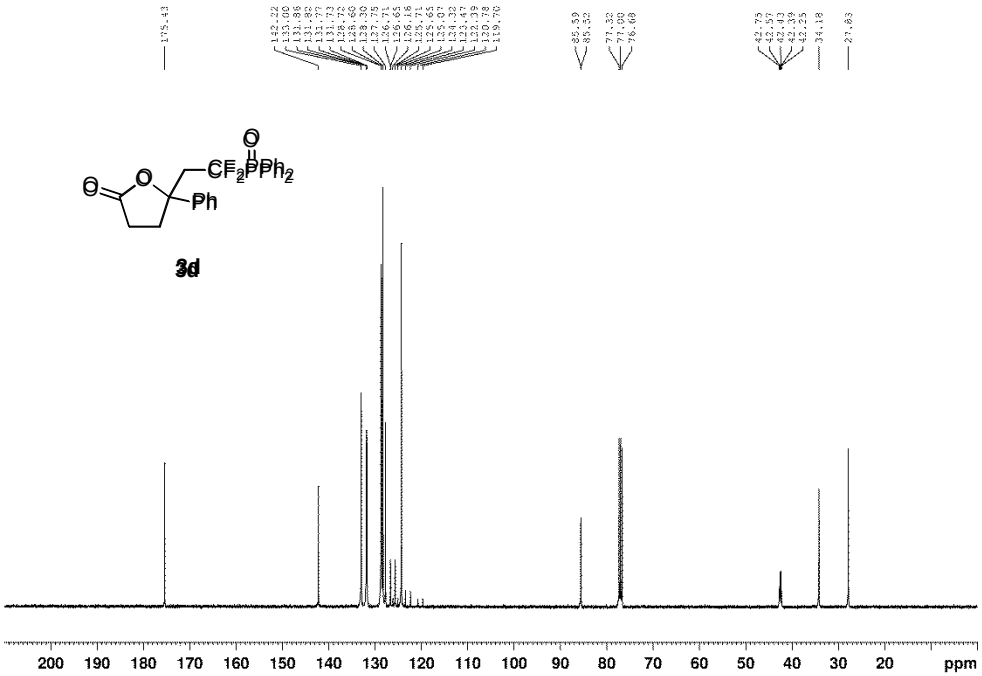
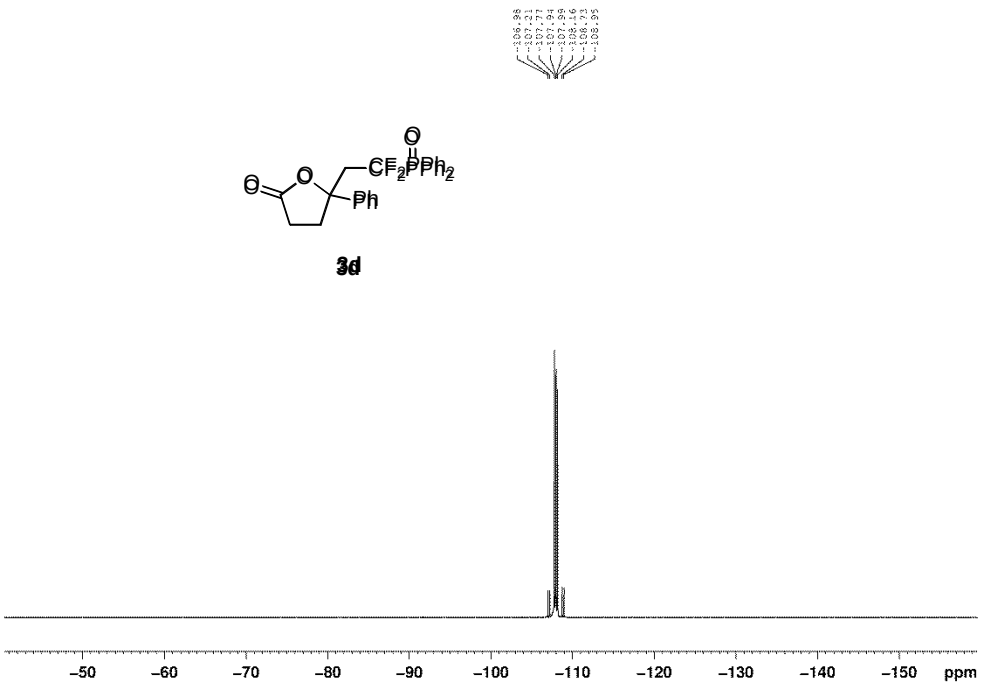


^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3d

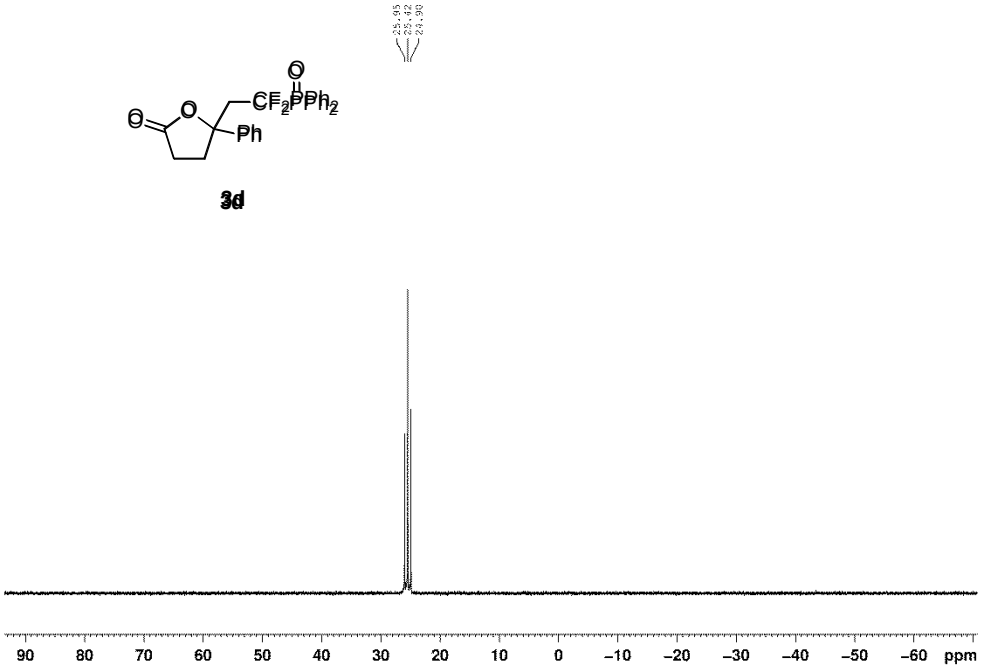


^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3d

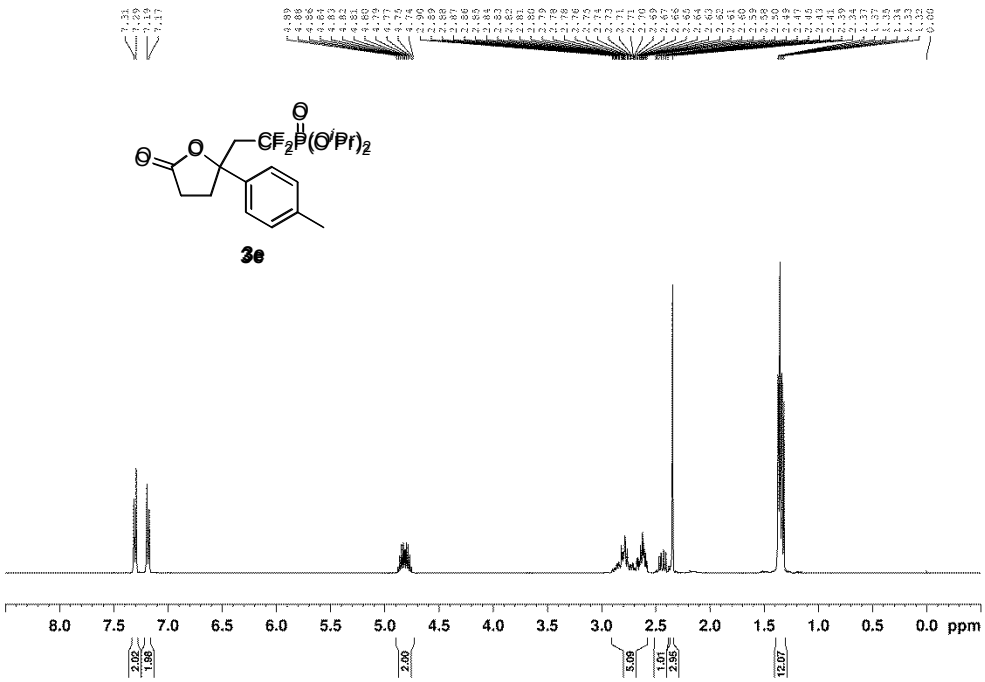


^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3d

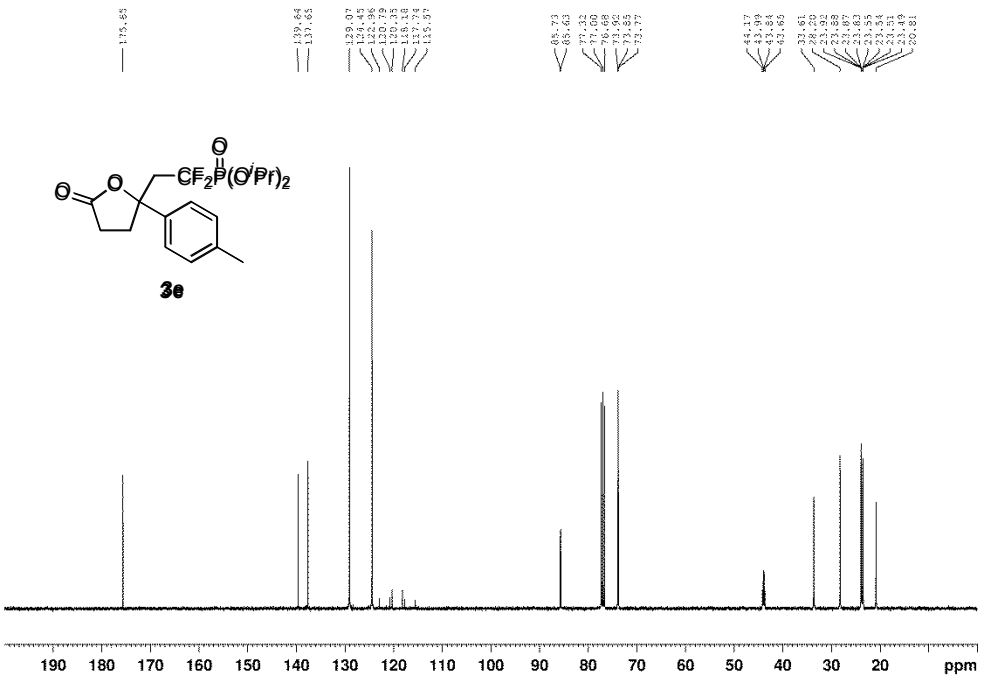
3d



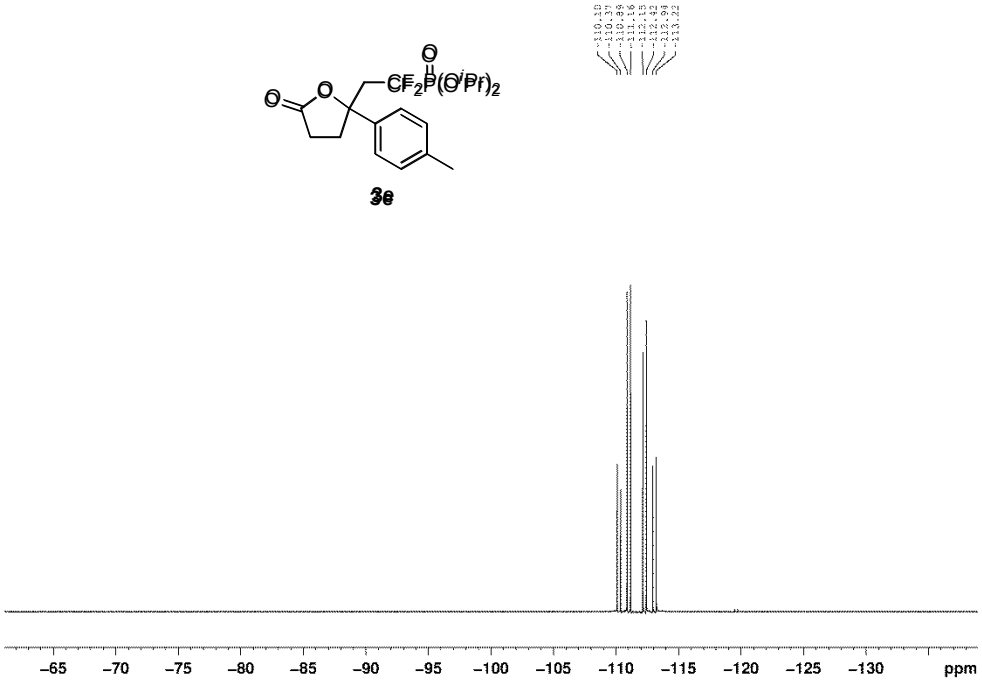
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3e



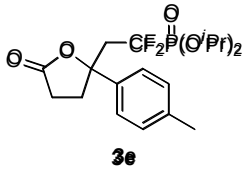
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3e

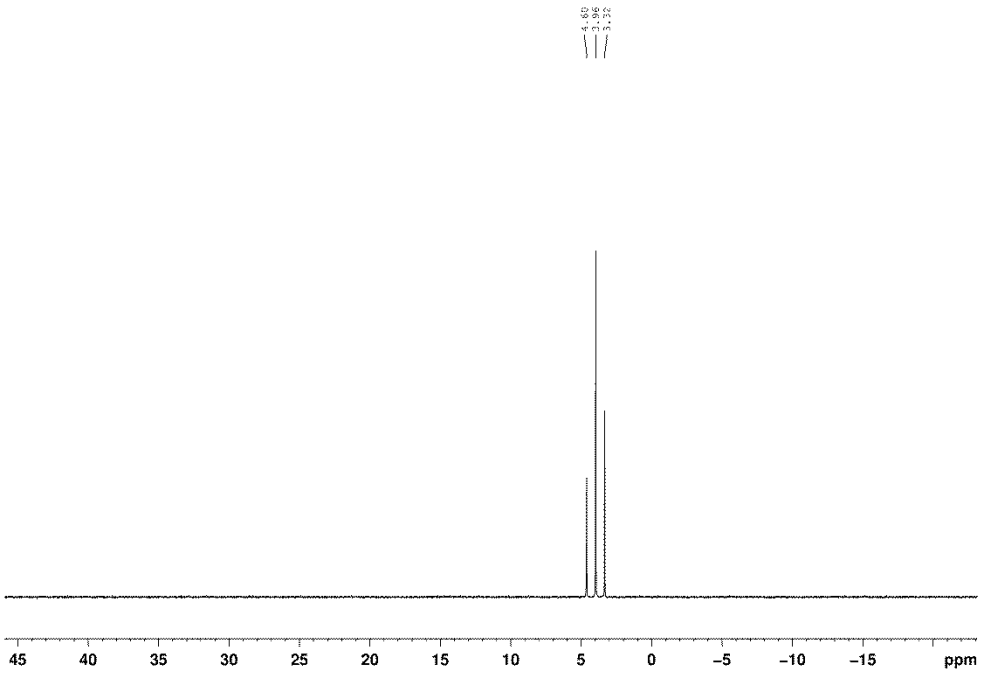


^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3e

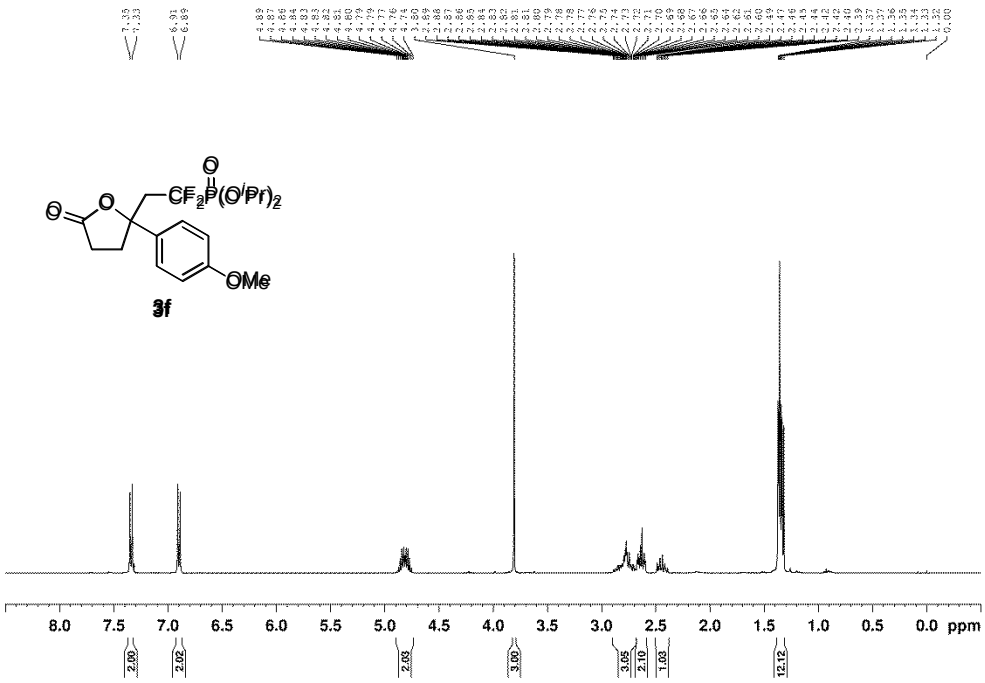


^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3e

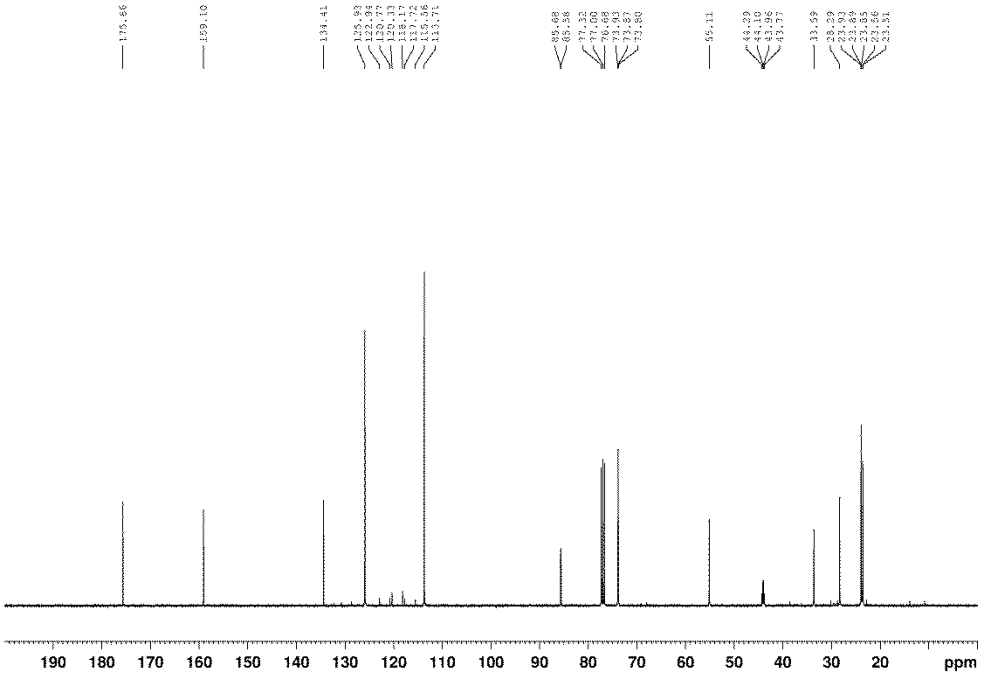




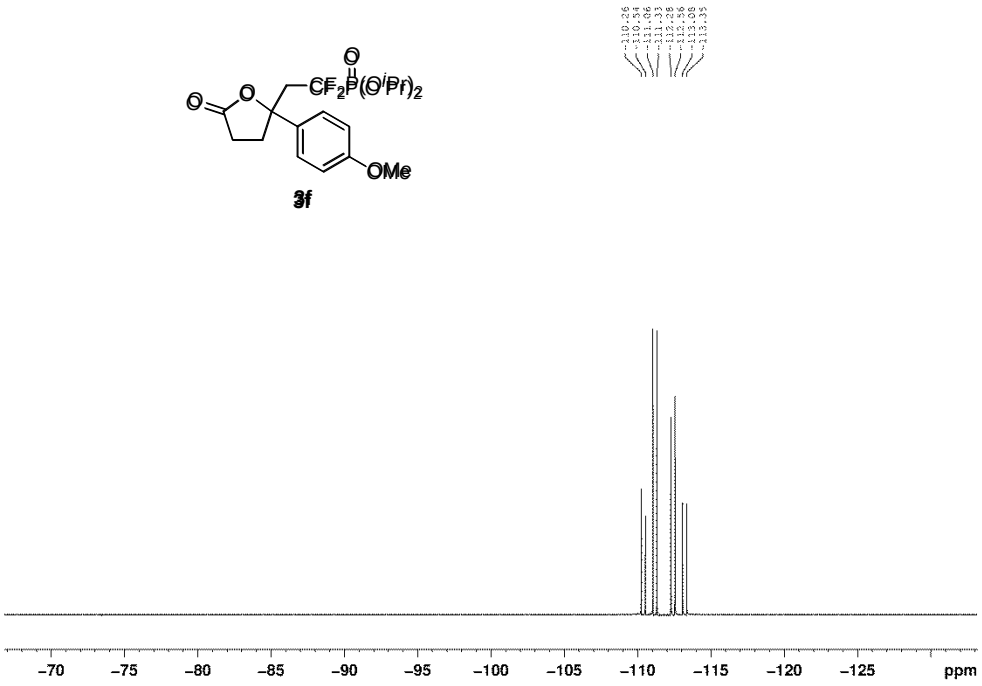
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3f



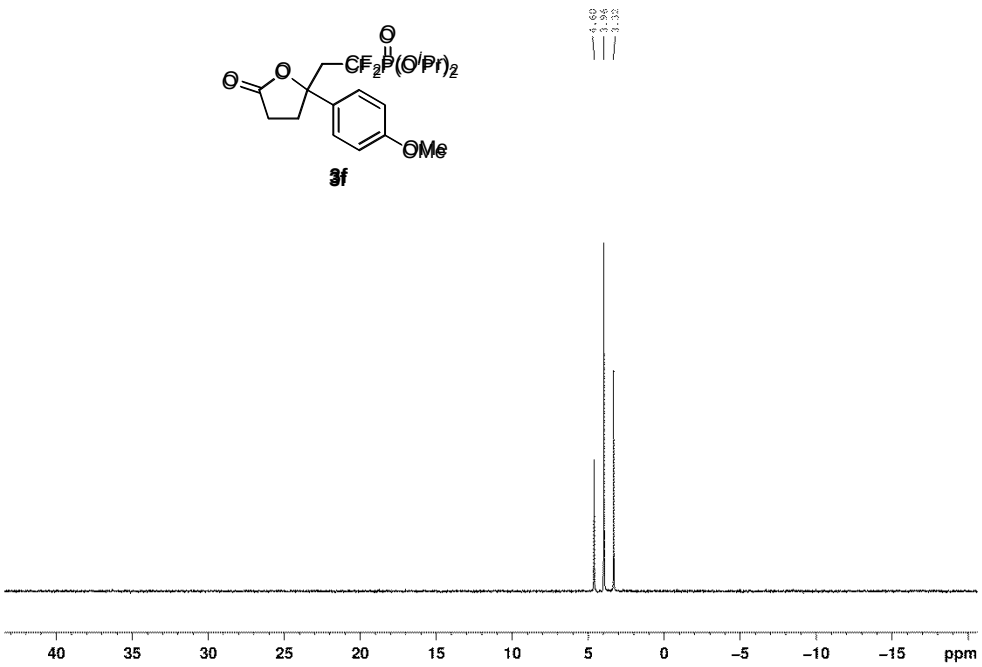
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3f



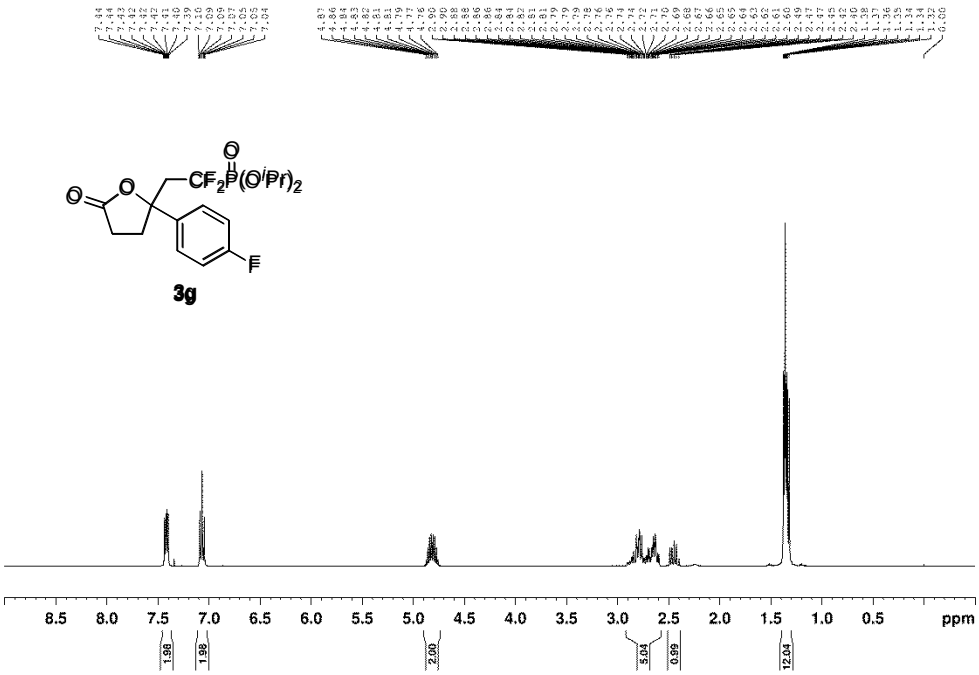
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3f



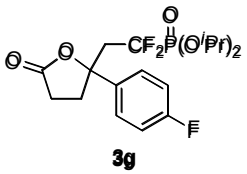
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3f

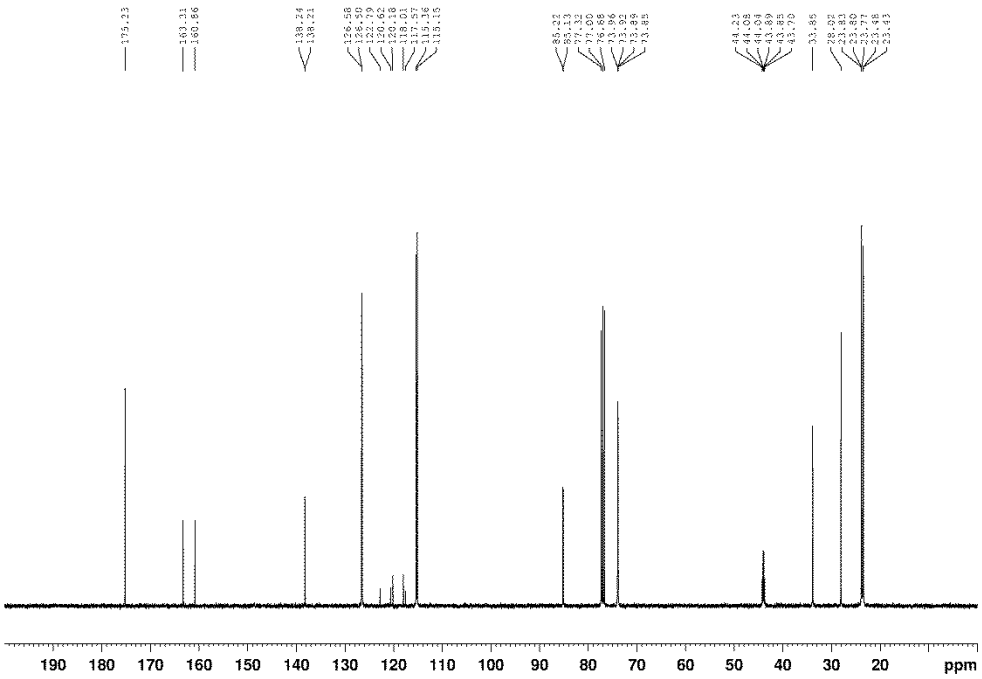


^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3g

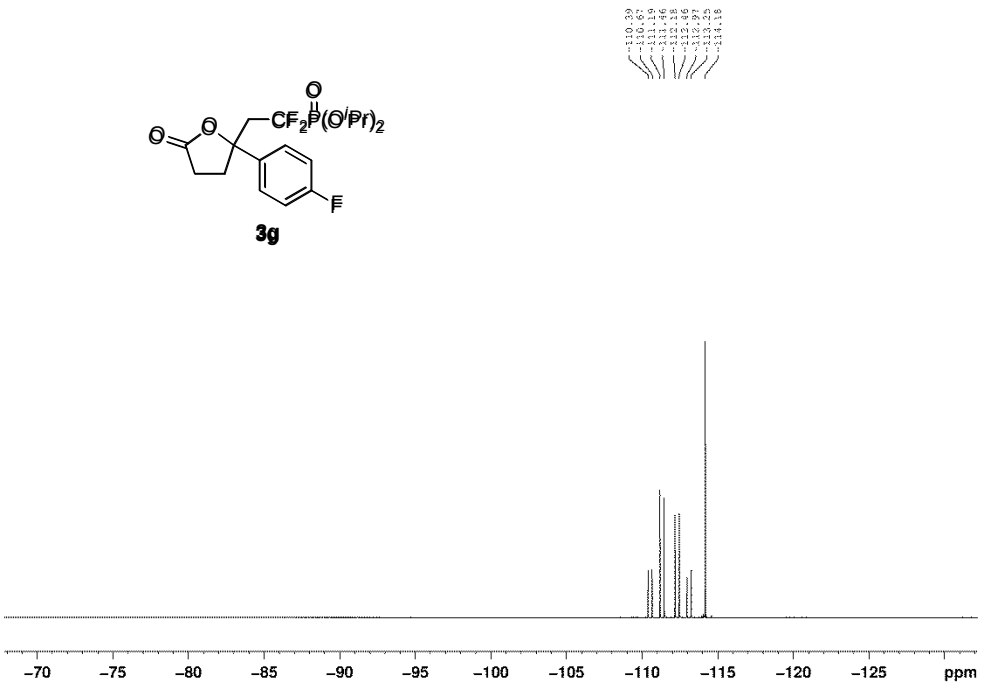


^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3g

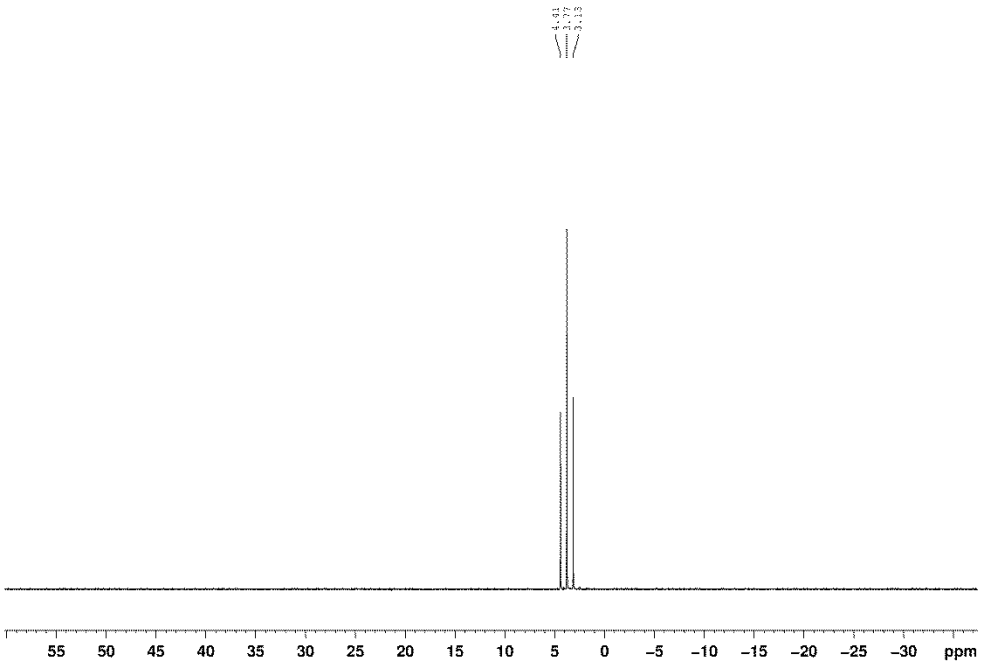




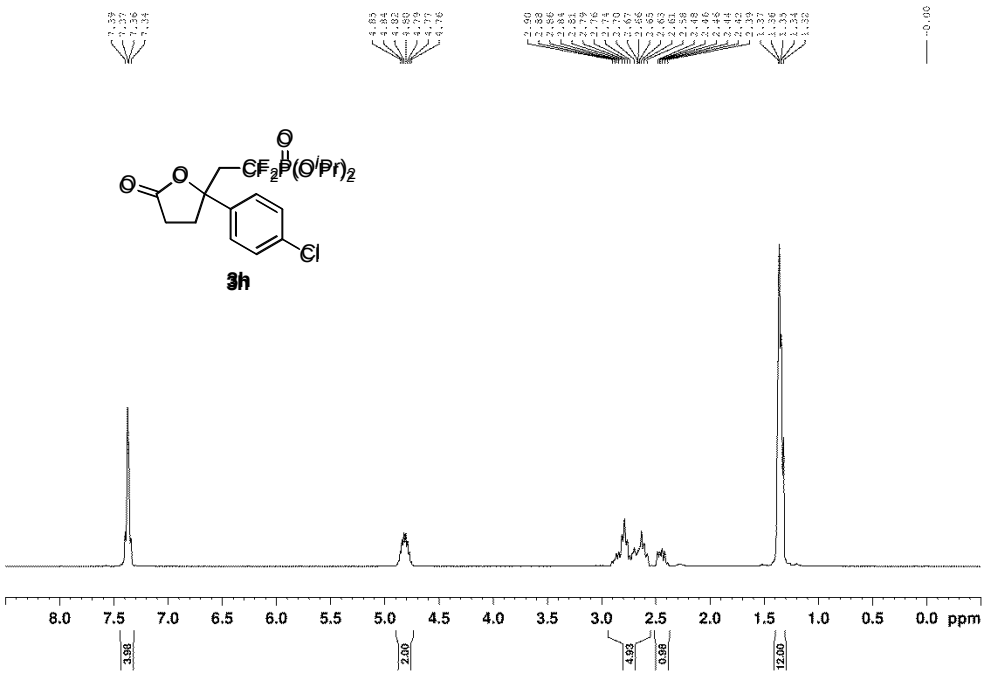
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3g



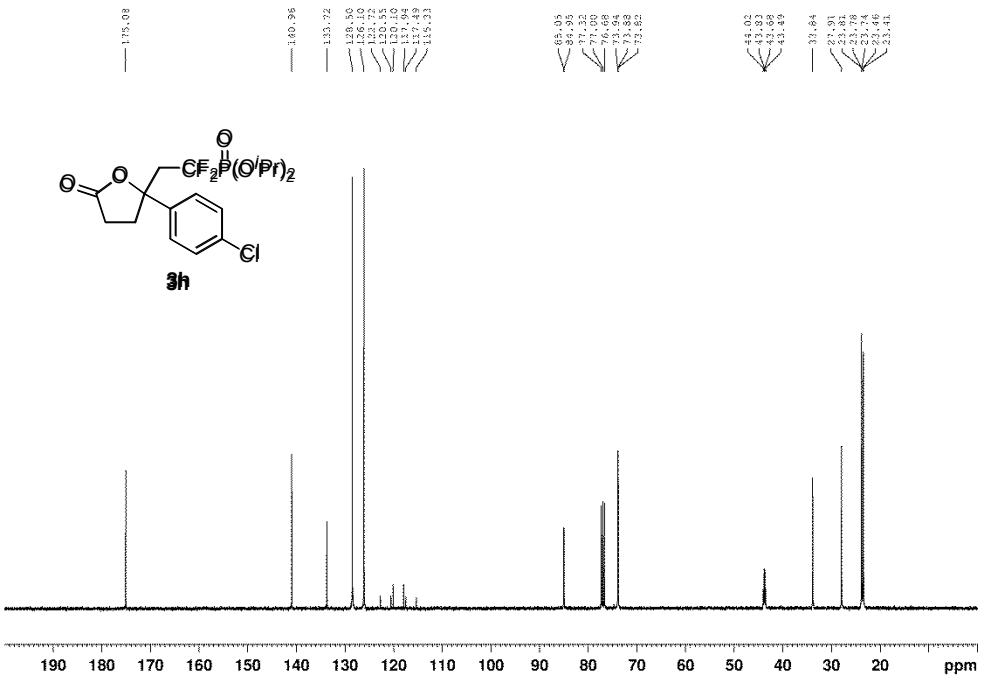
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3g



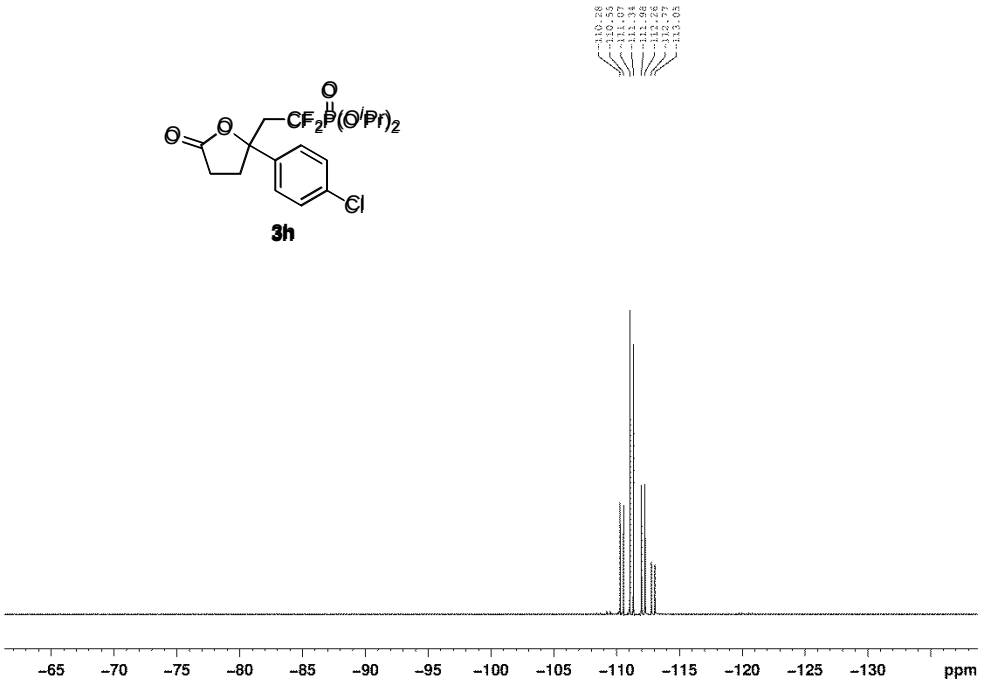
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3h



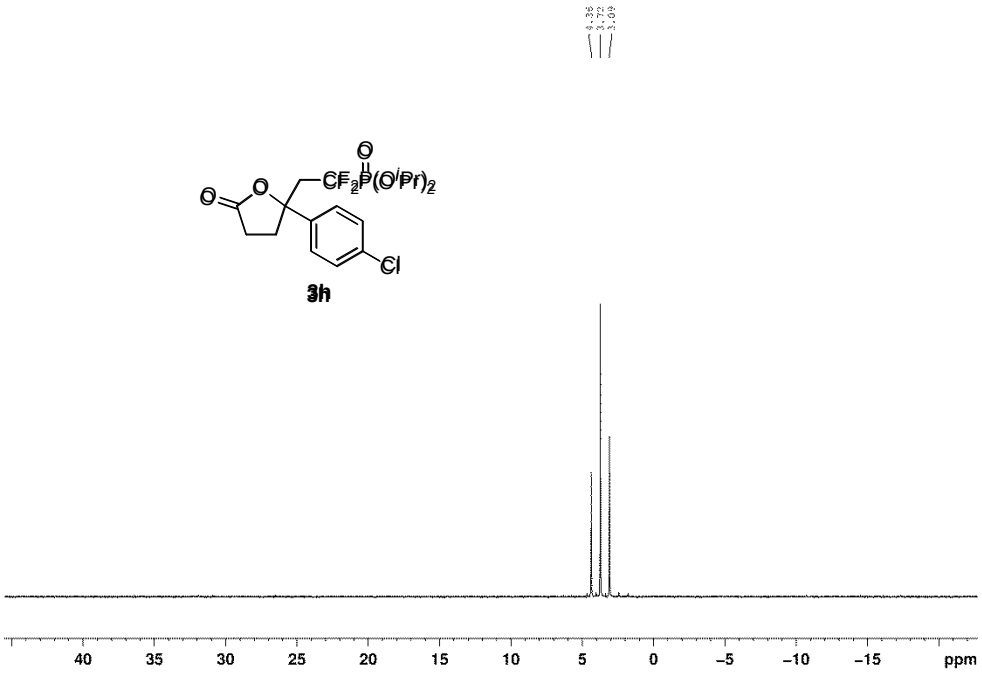
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3h



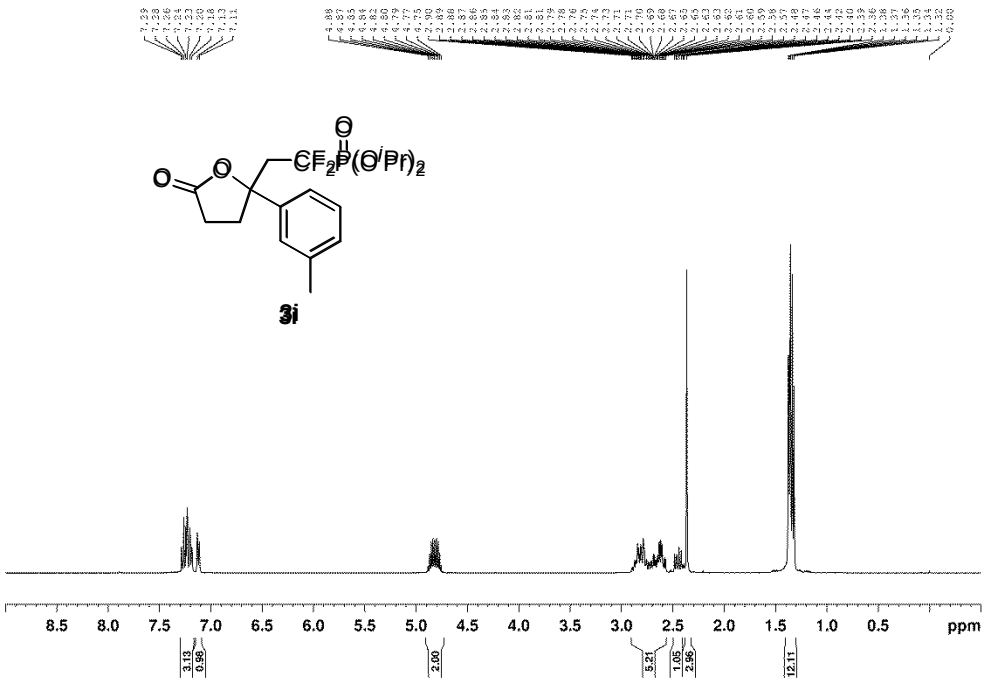
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3h



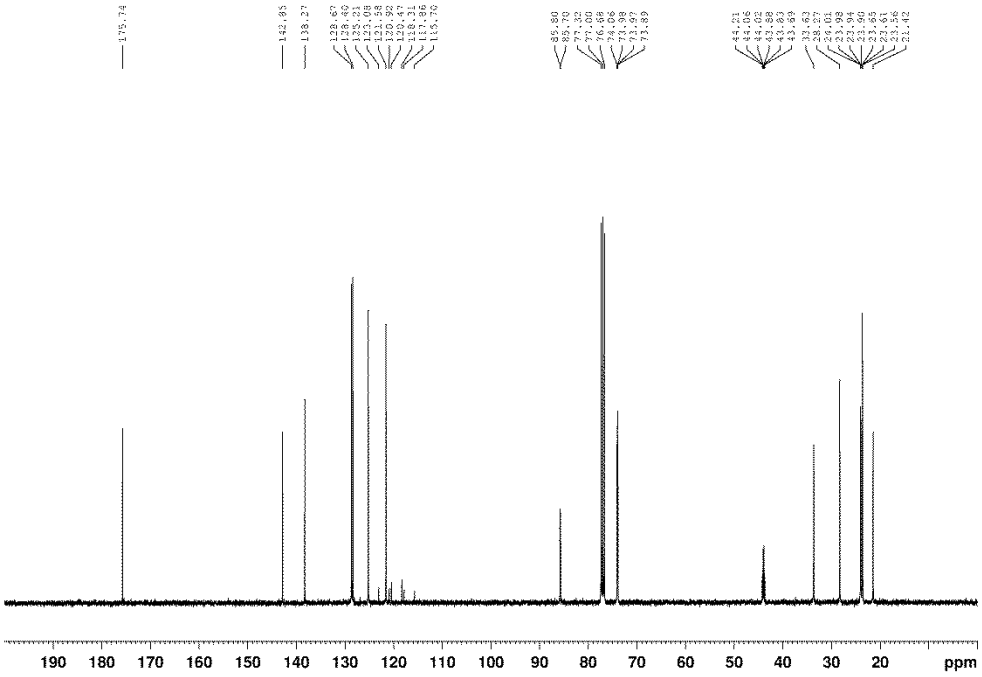
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3h



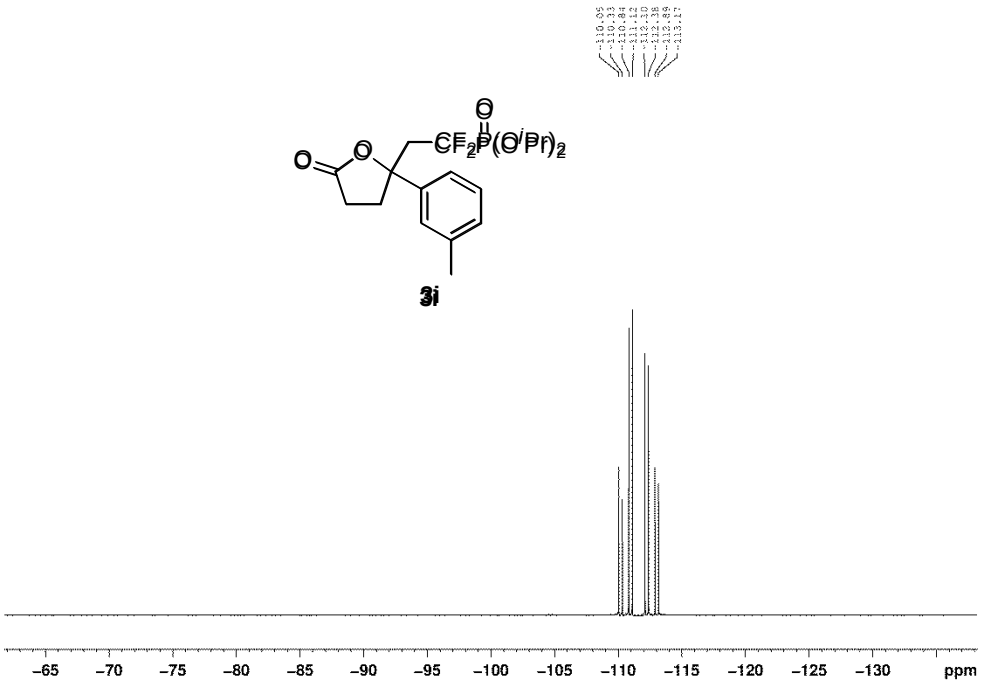
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3i



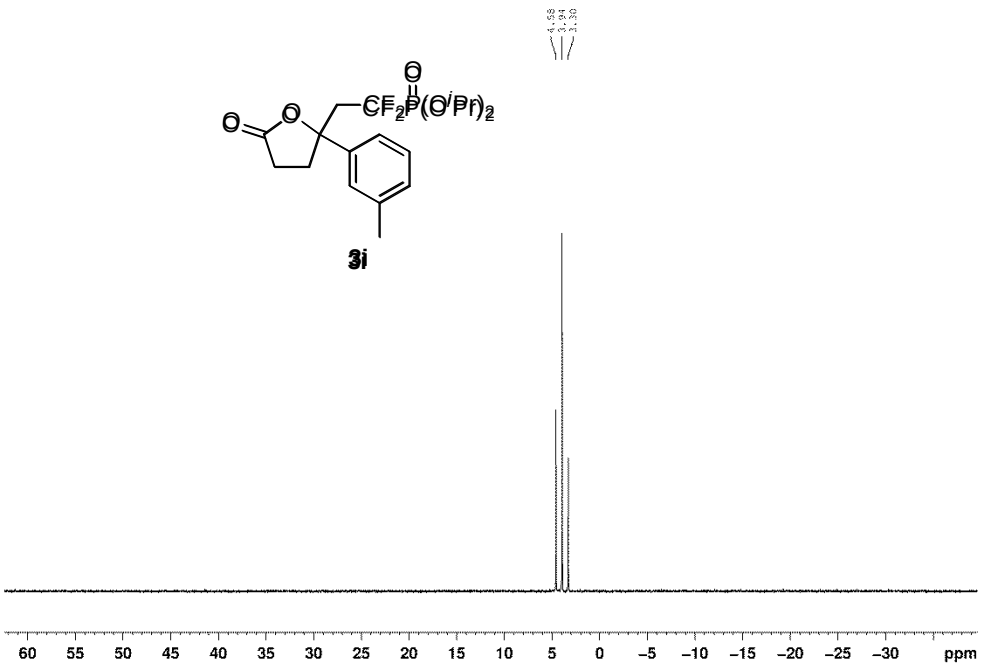
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3i



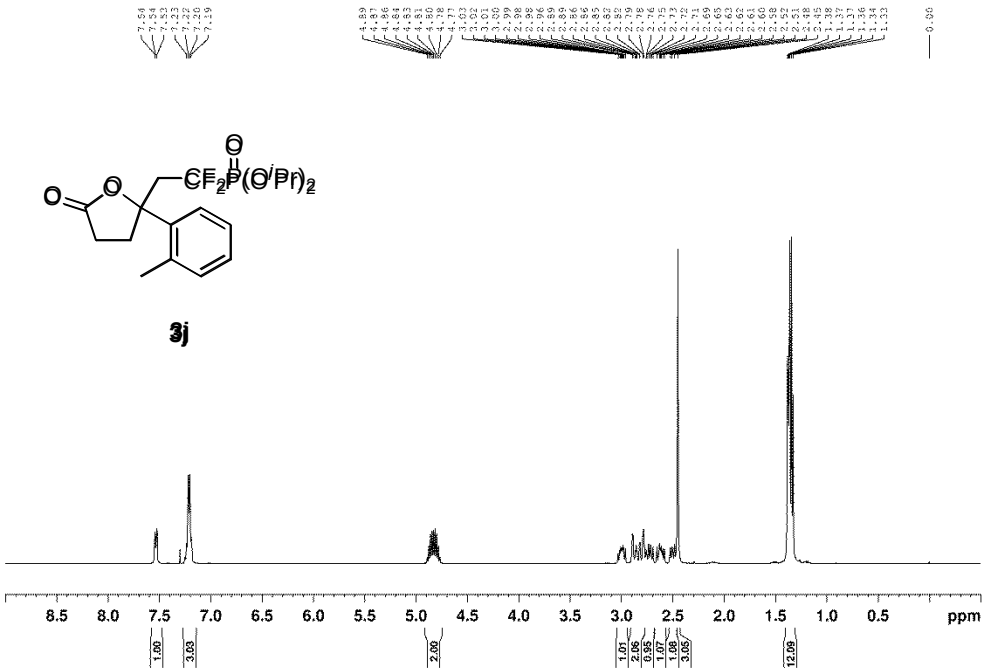
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3i



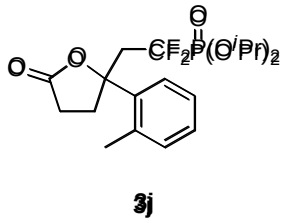
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3i

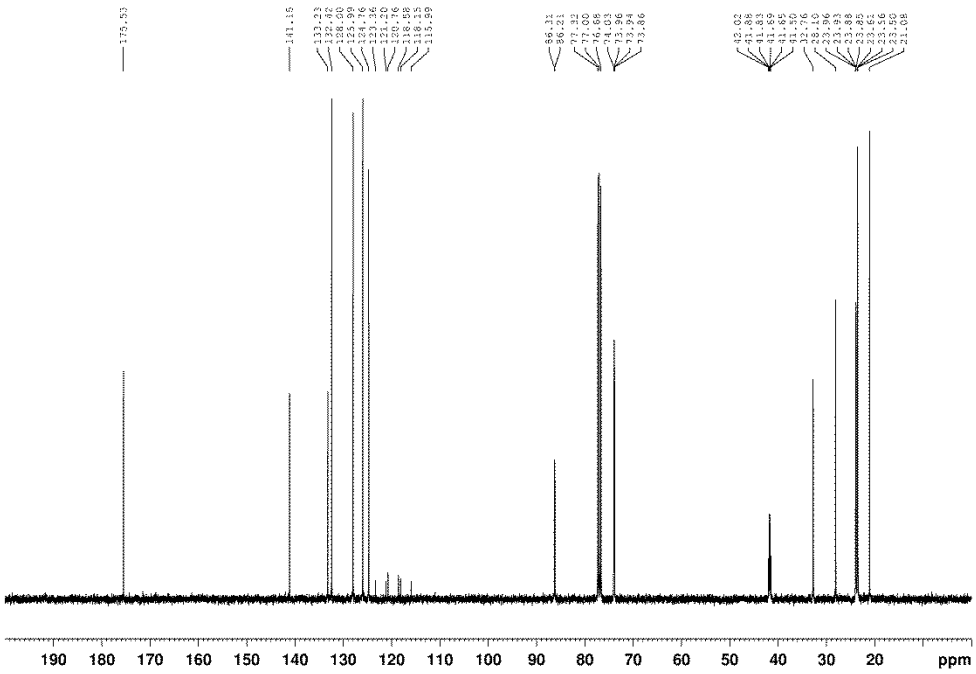


^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3j

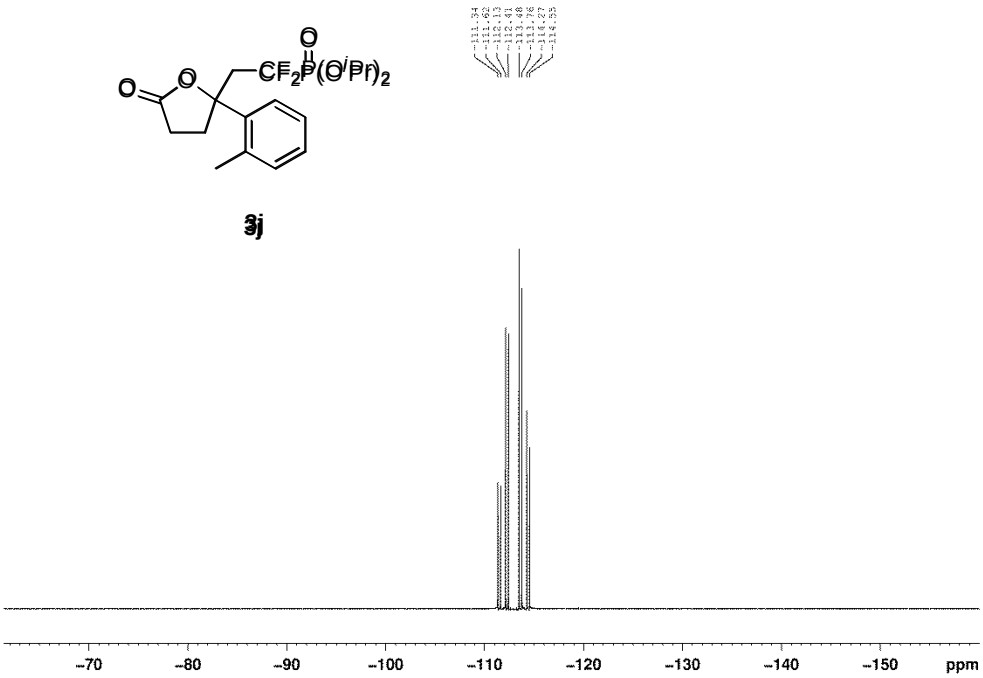


^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3j

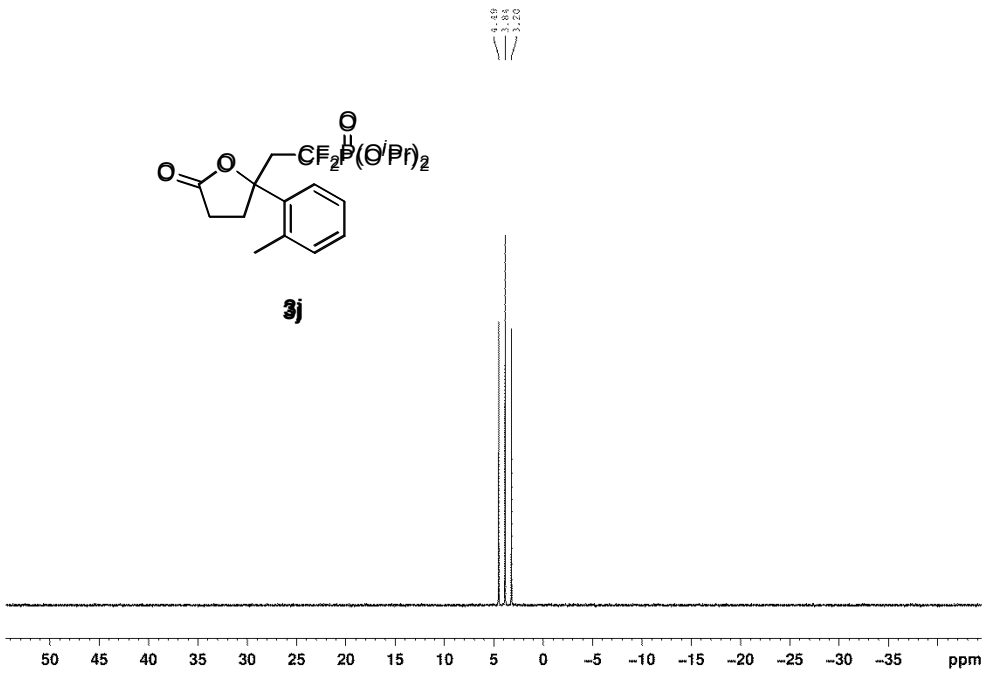




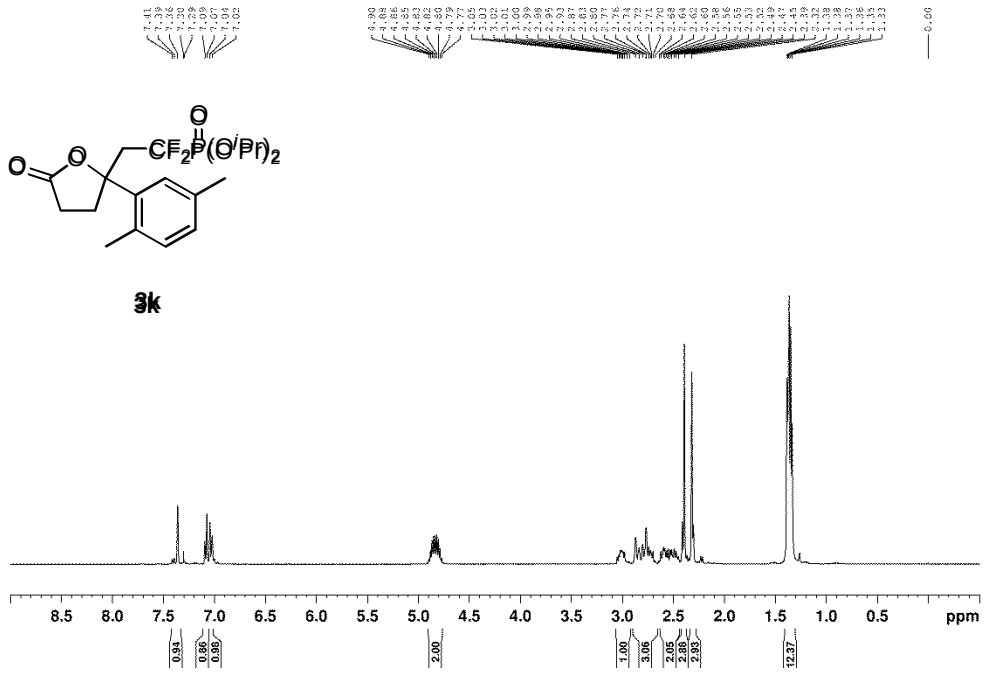
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3j



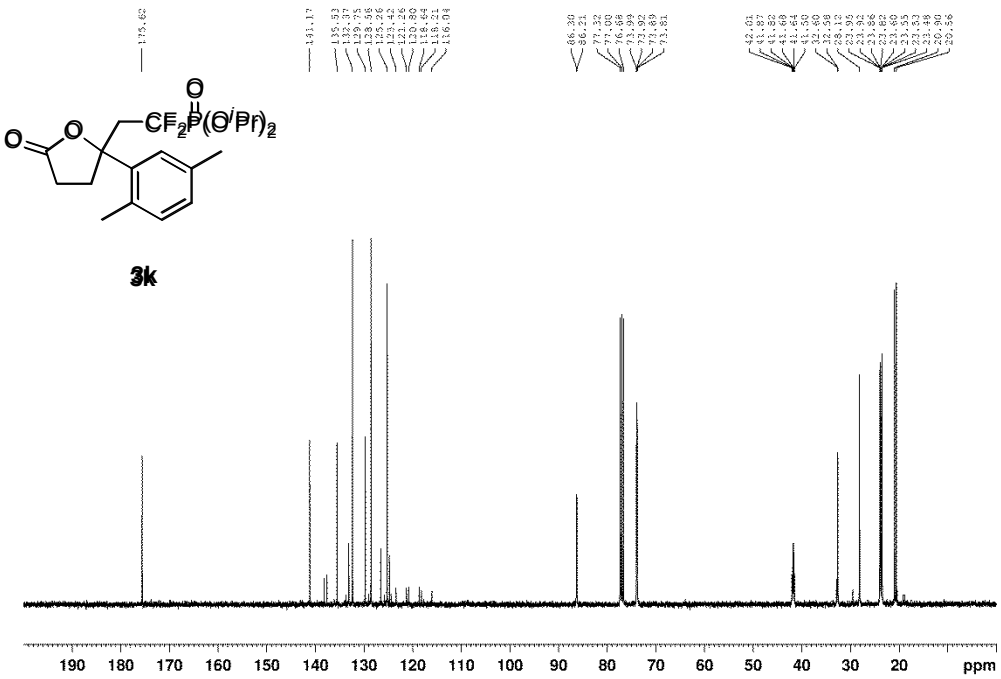
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3j



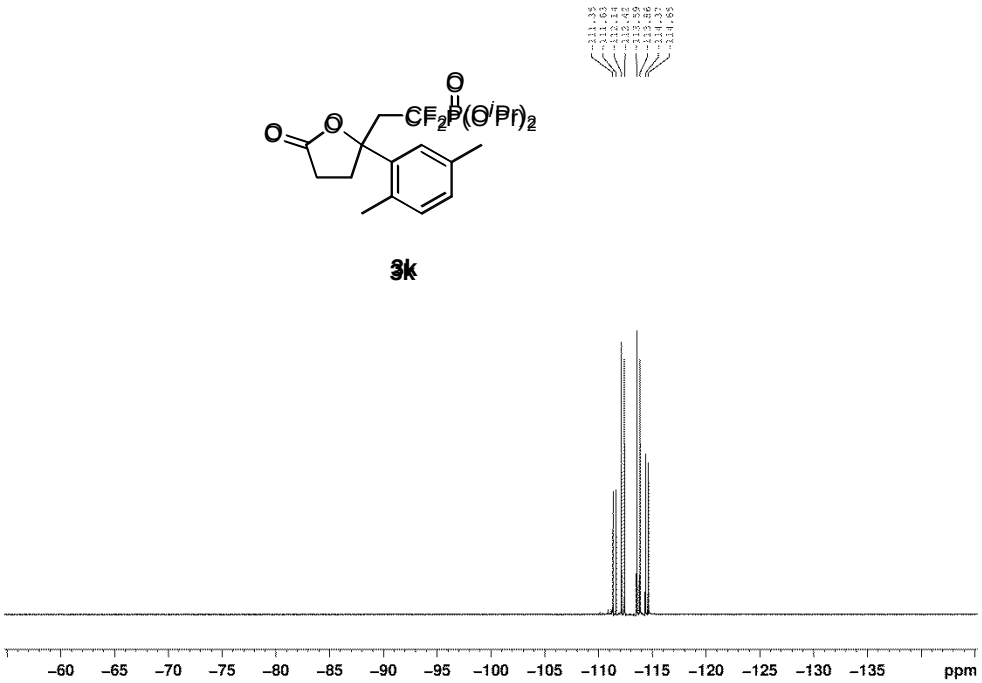
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3k



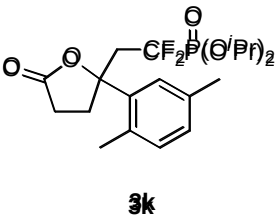
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3k

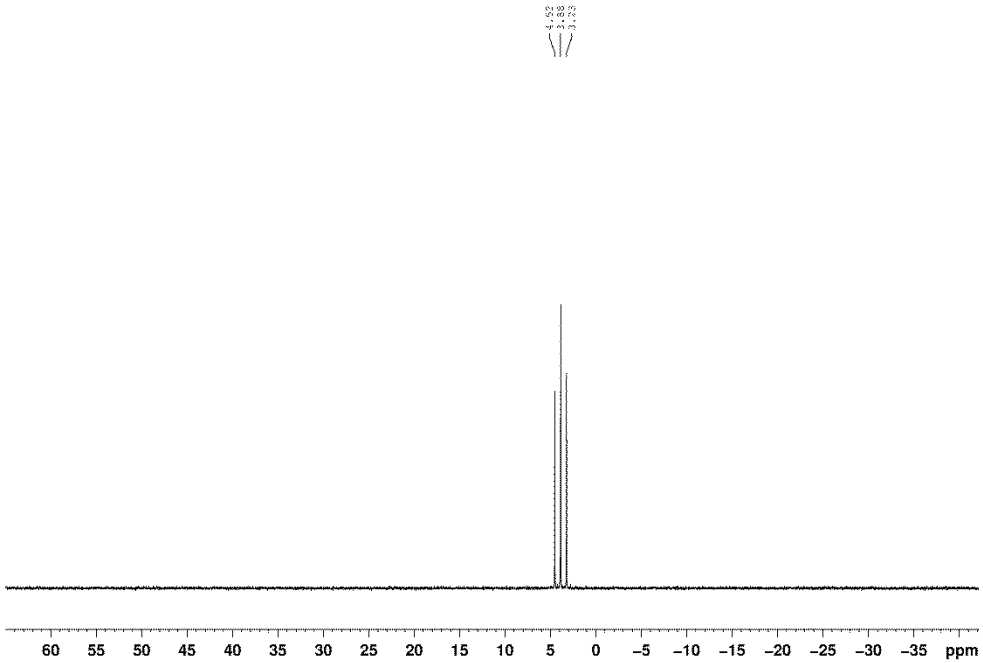


^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3k

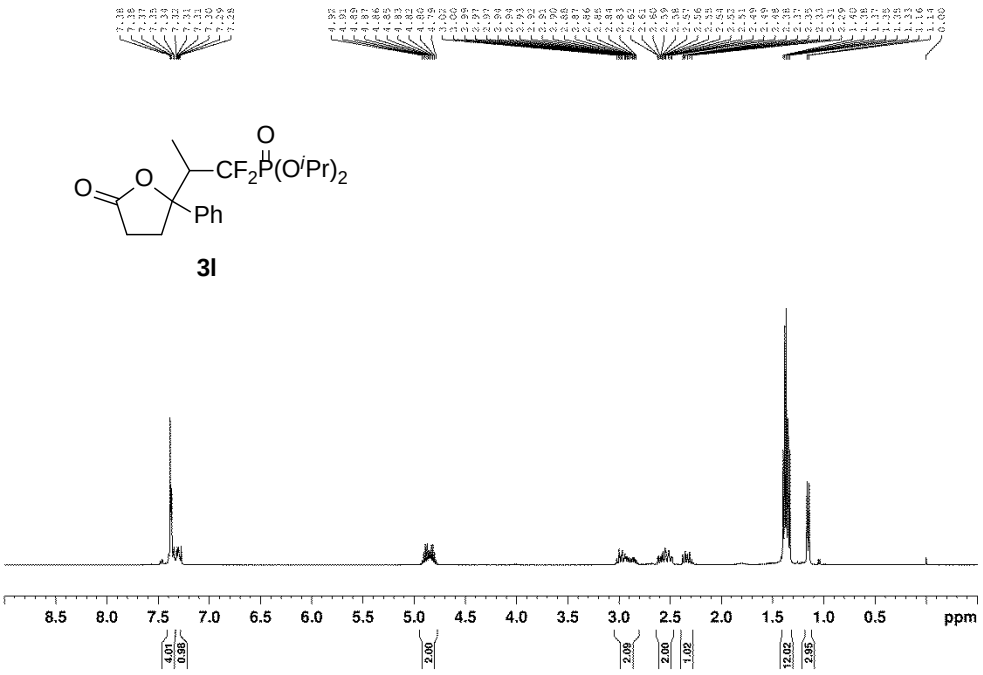


^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3k

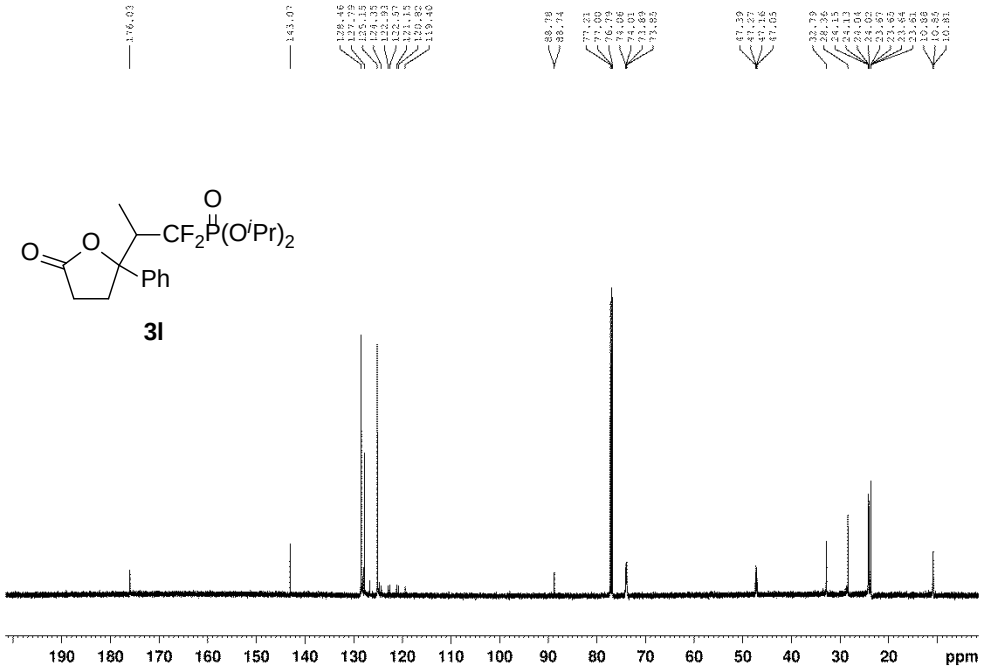




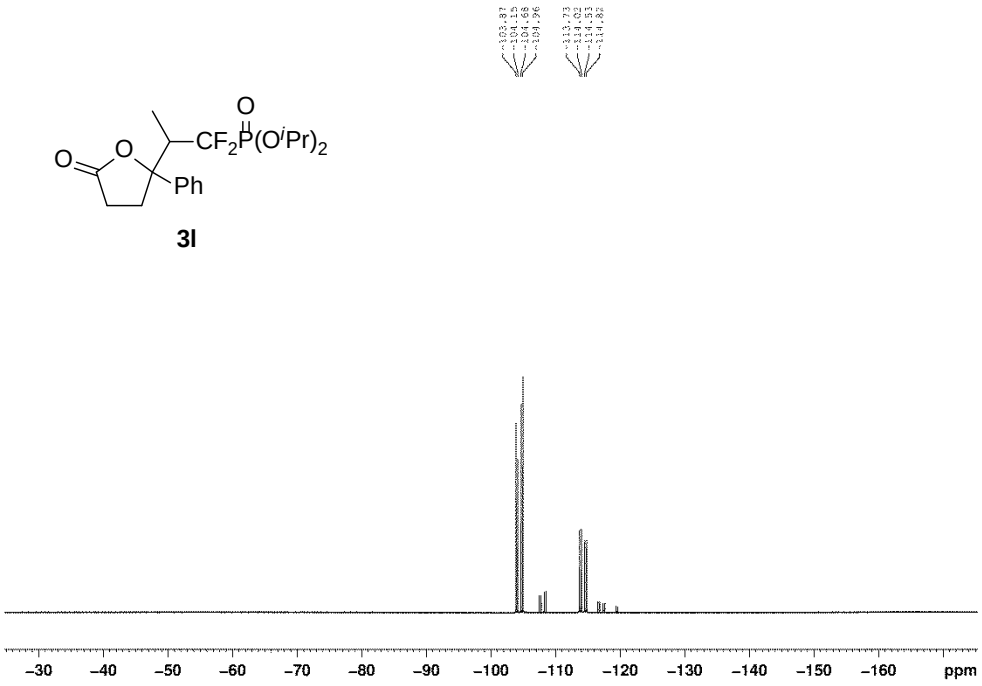
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3l



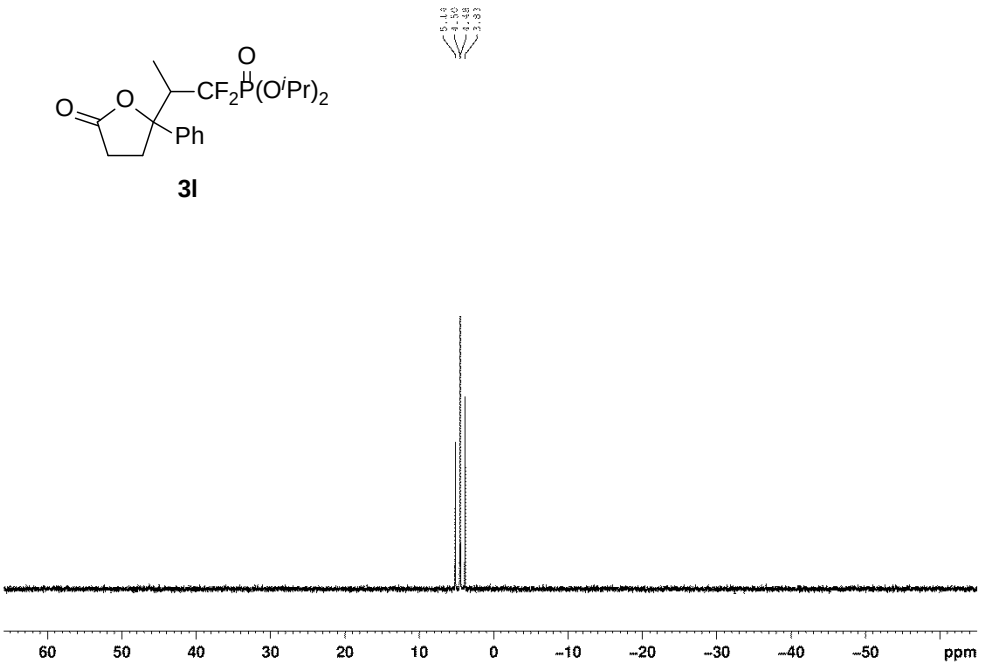
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3l



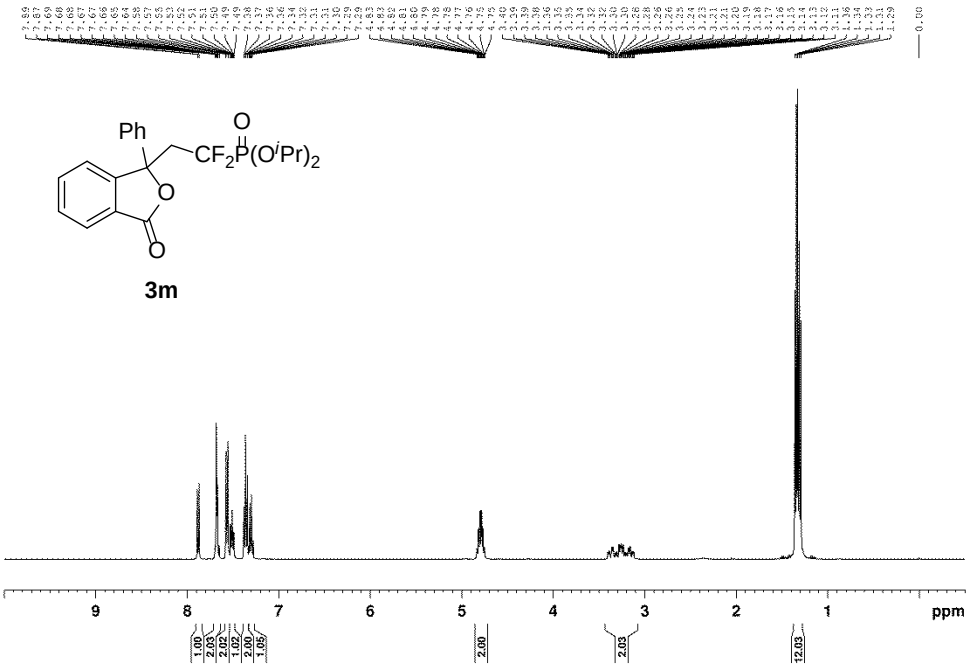
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3l



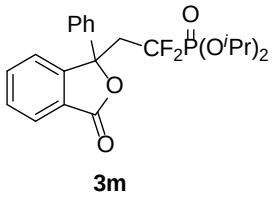
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3l

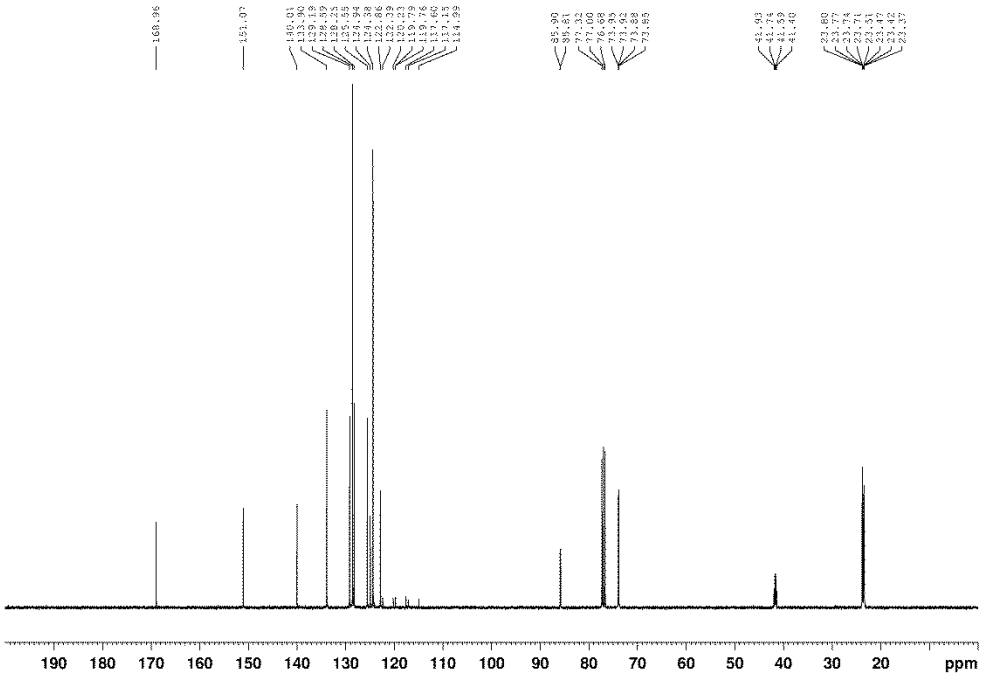


^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3m

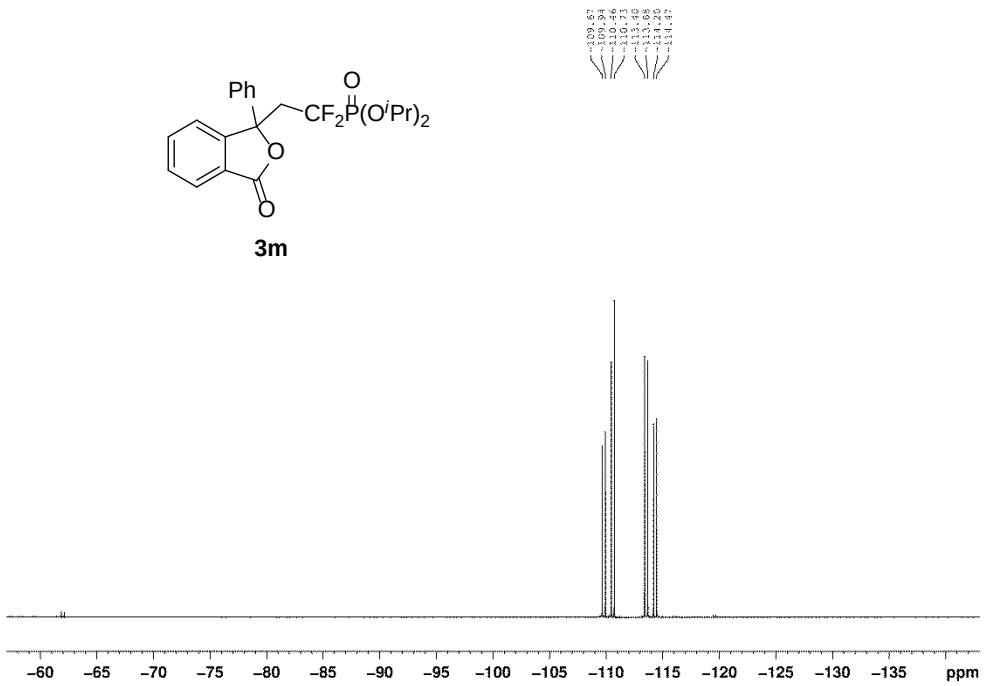


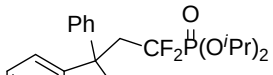
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3m



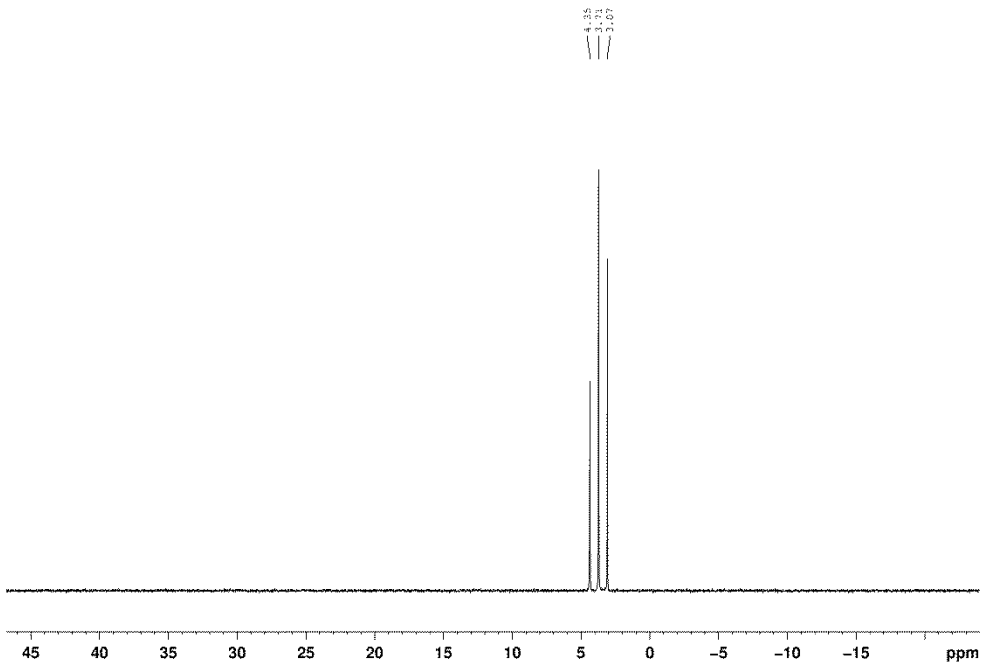


^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3l

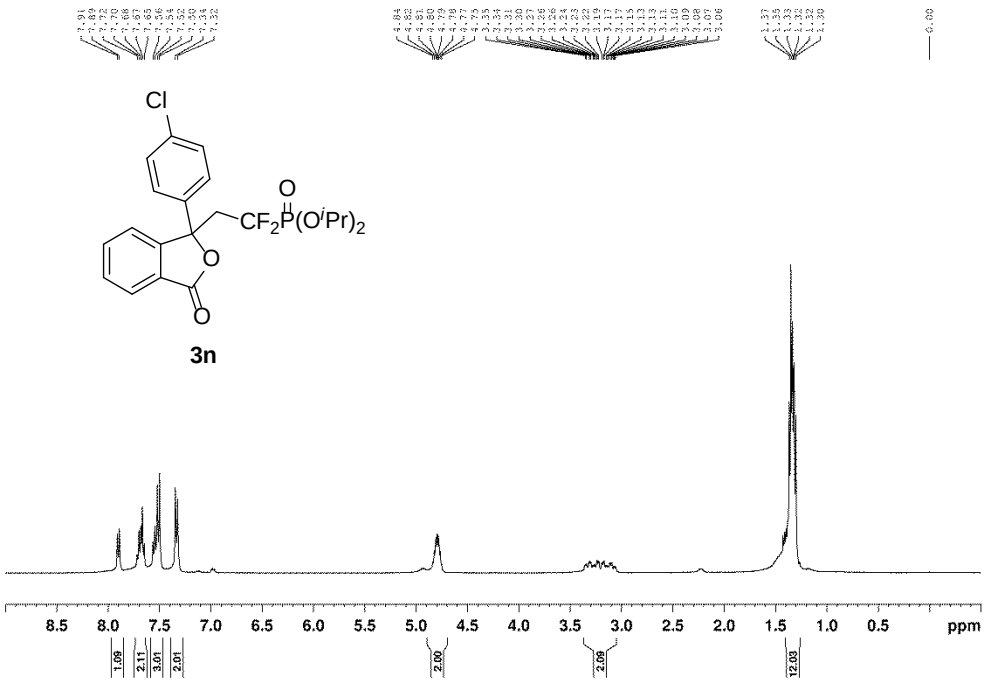




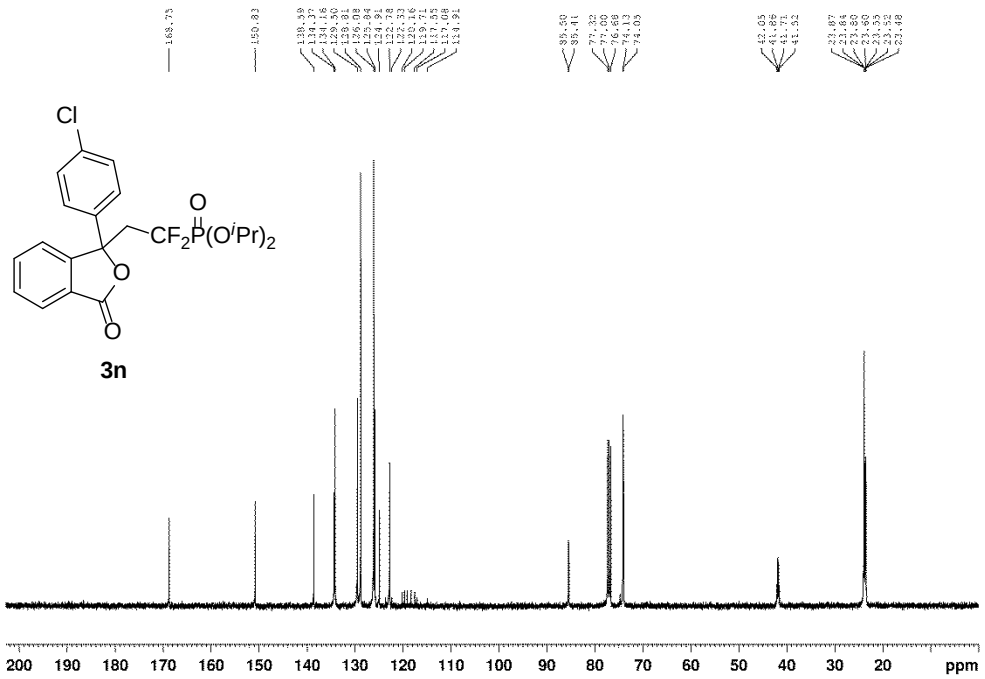
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3l



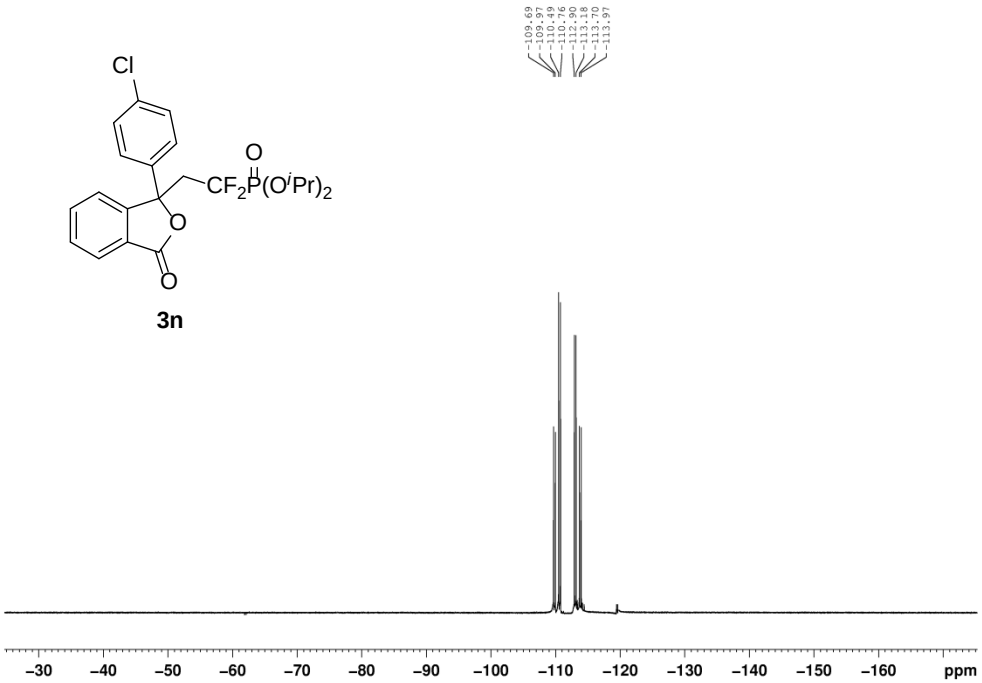
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3n



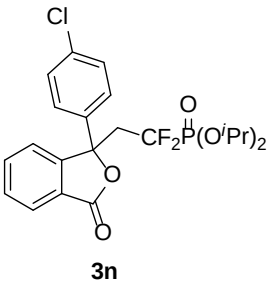
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3n

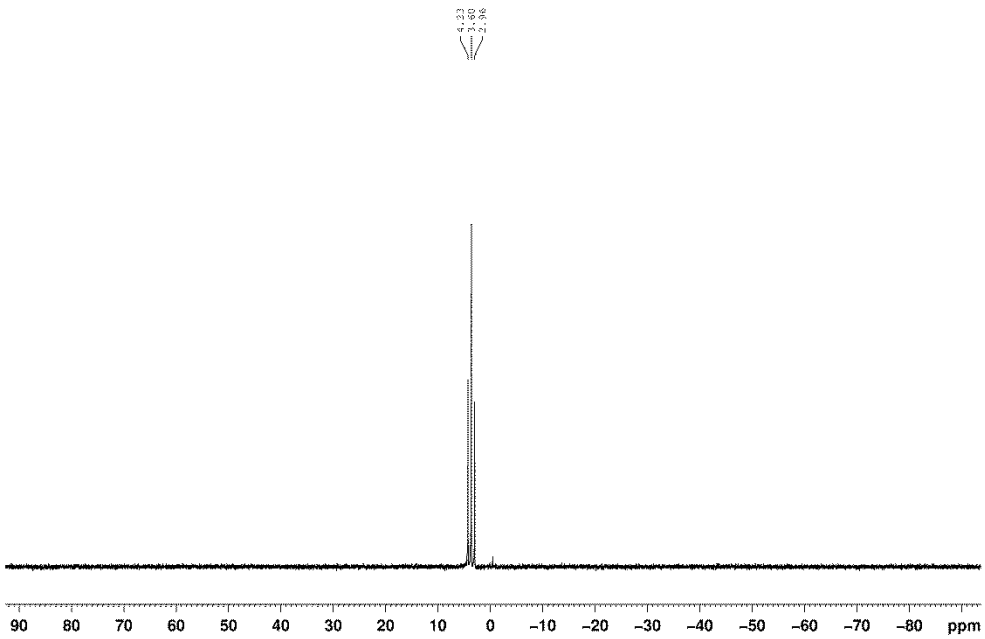


^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3n

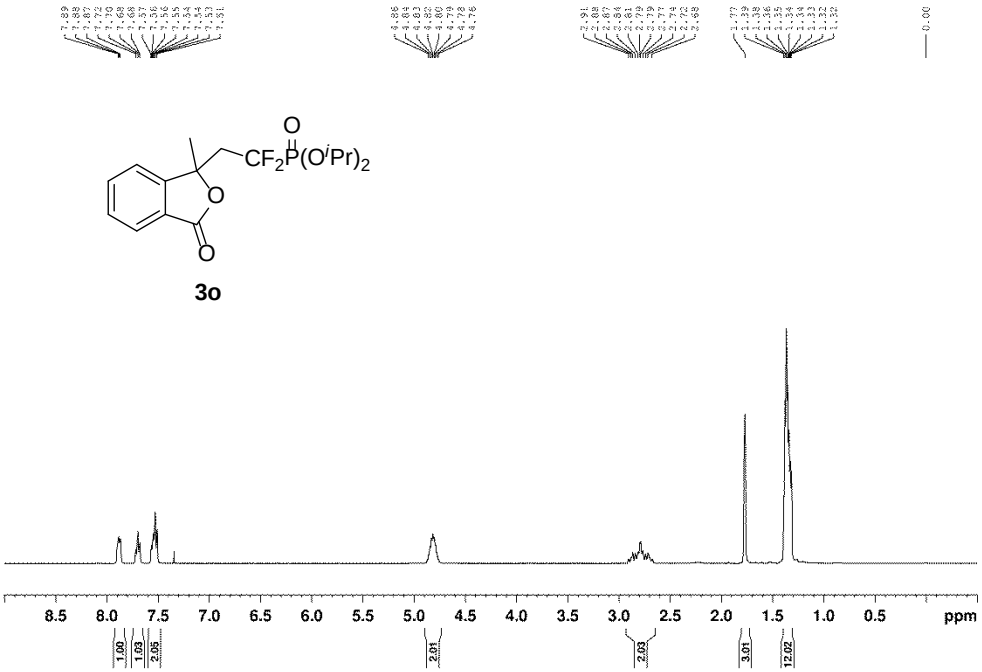


^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3n

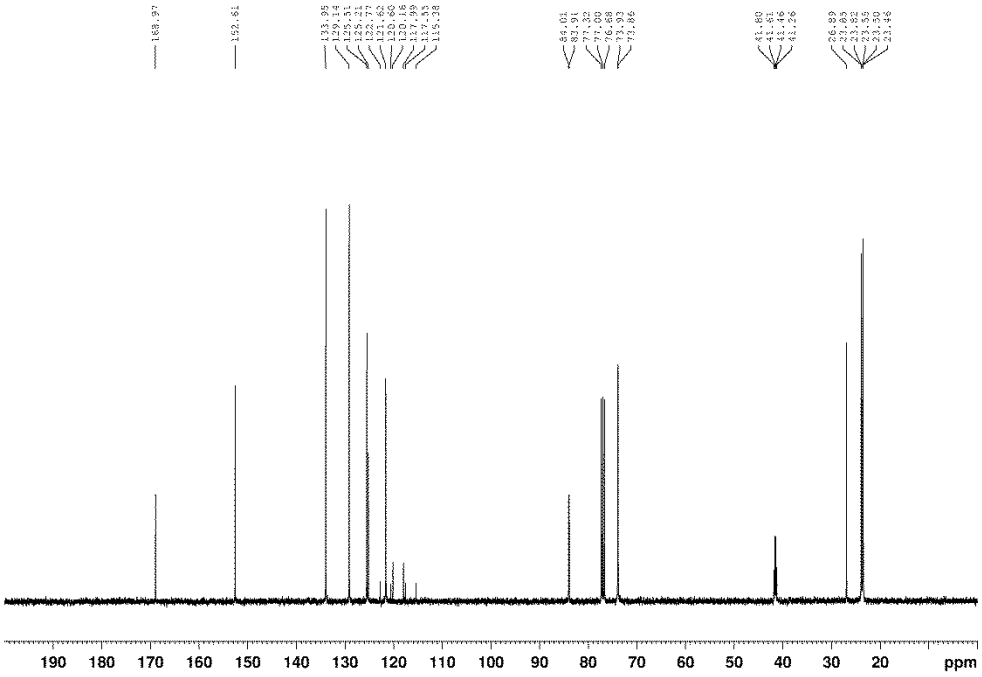




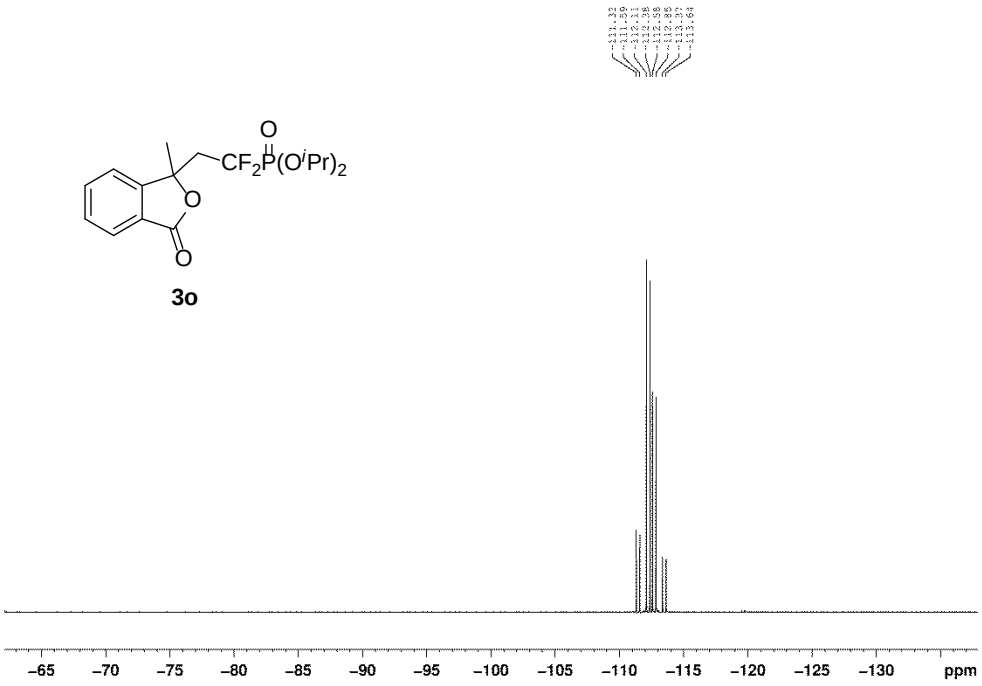
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3o



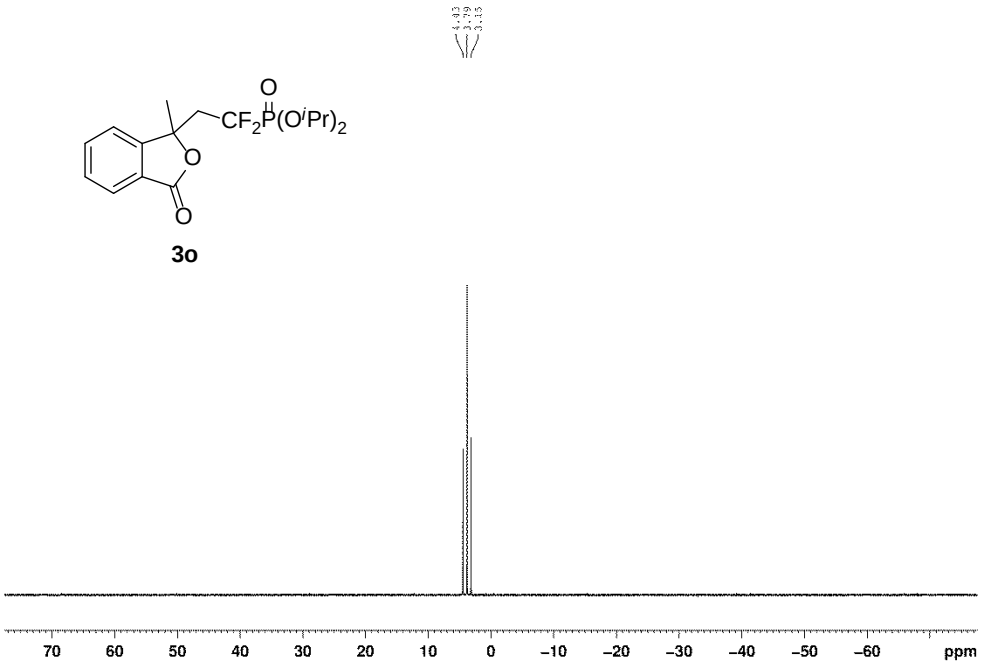
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3o



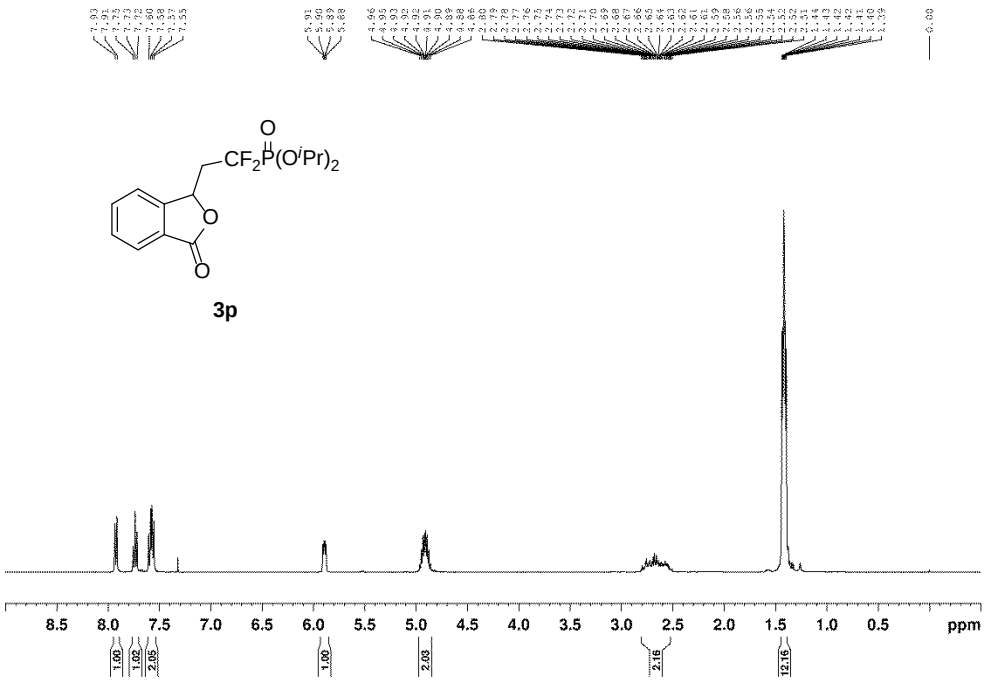
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3o



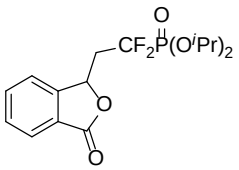
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3o



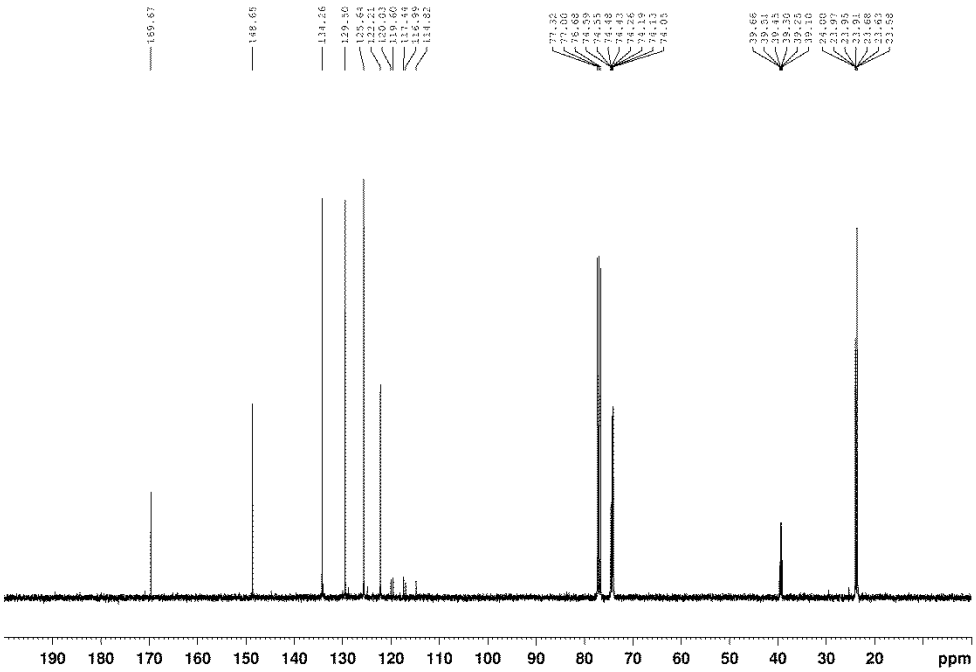
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3p



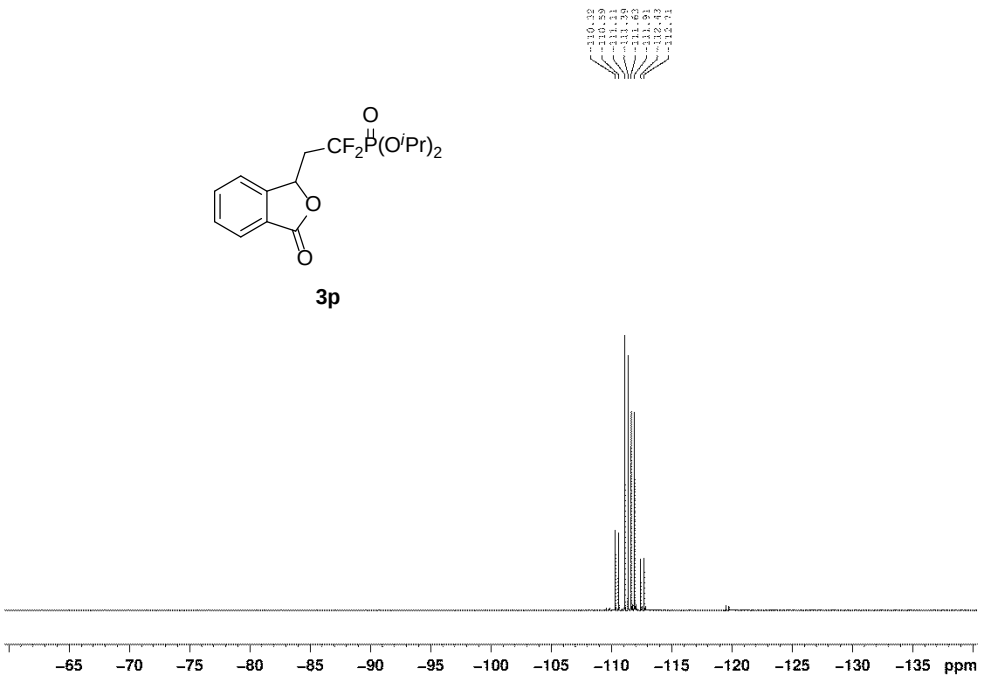
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3p

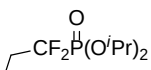


3p

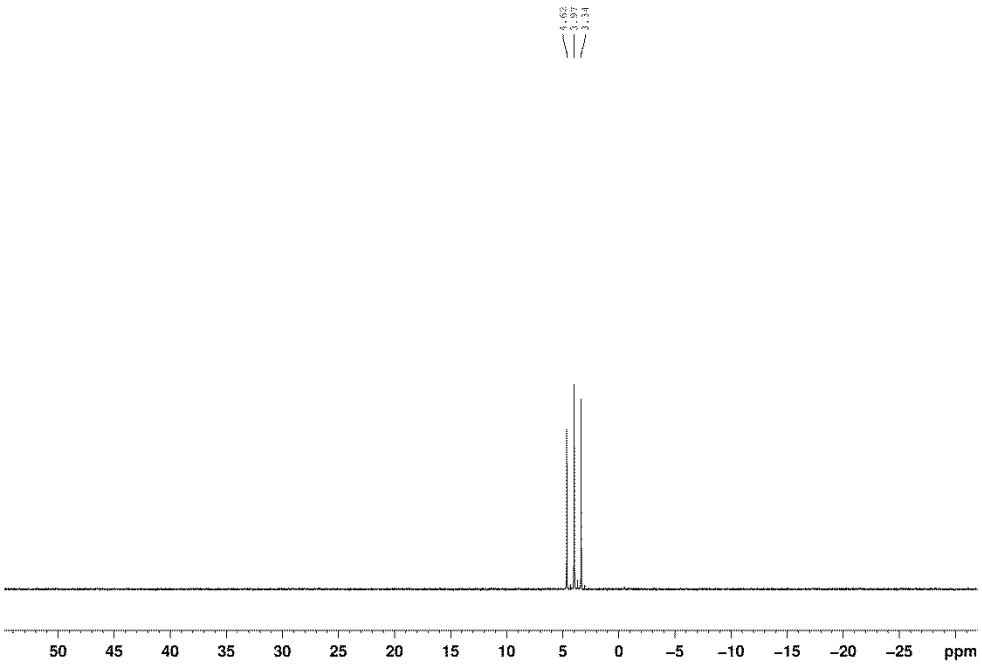


^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3p

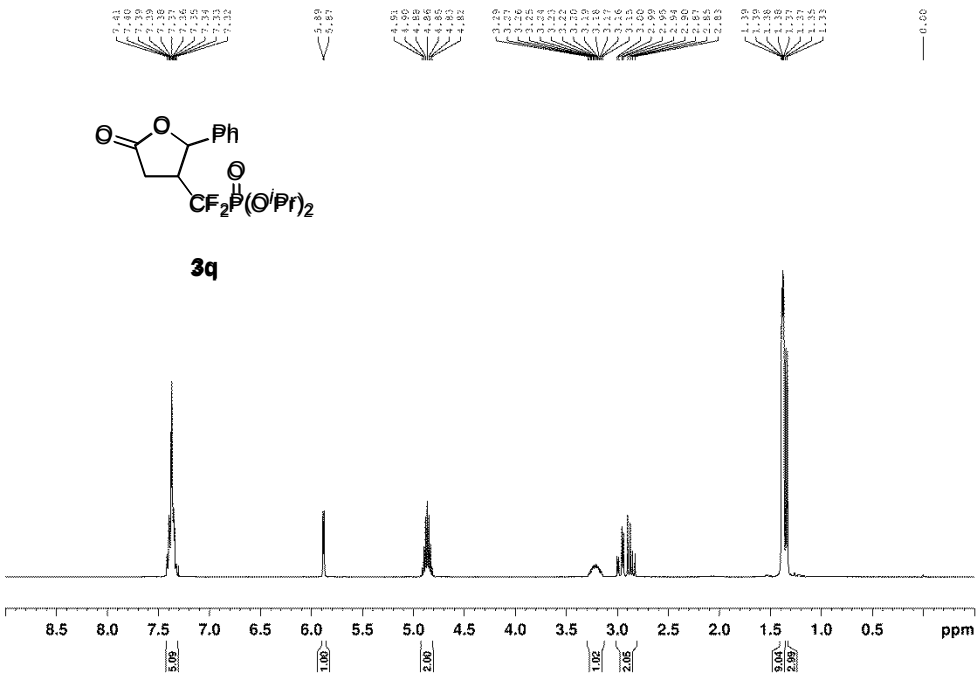




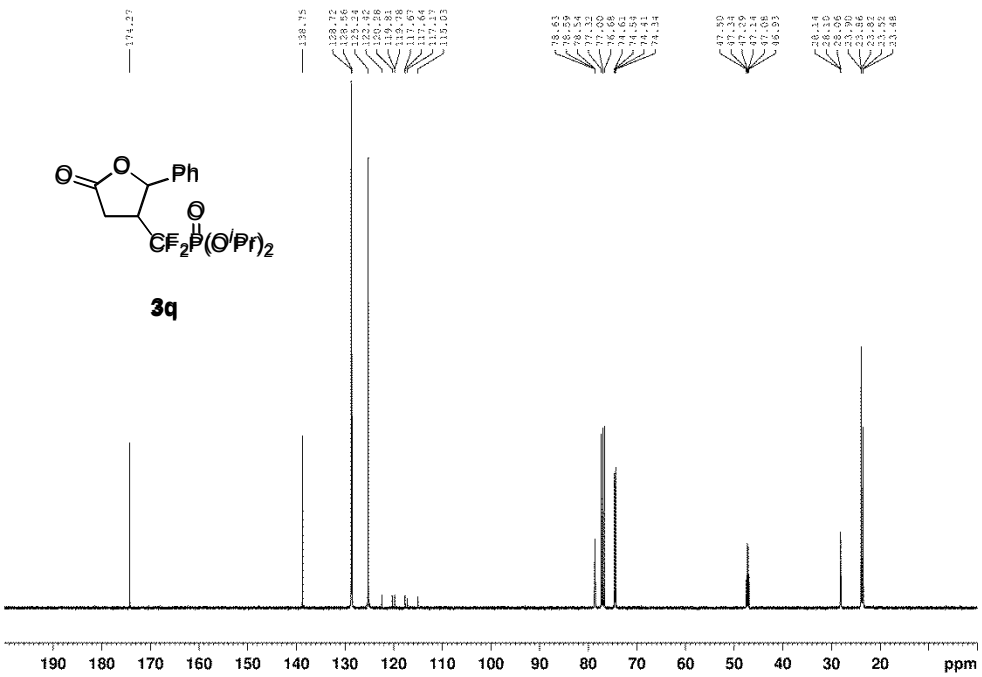
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3p



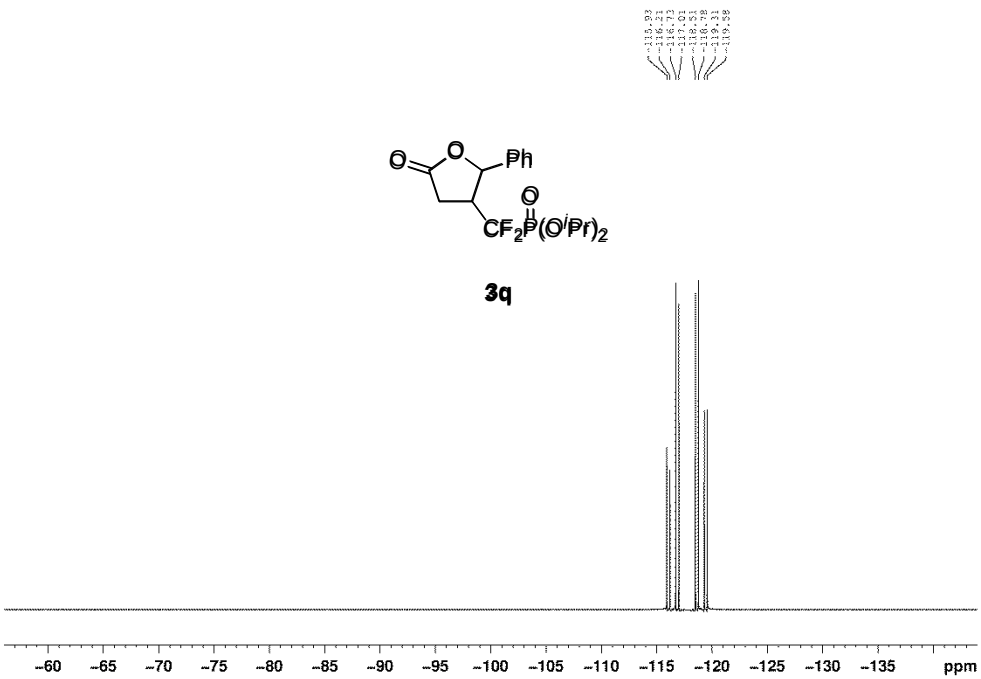
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3q



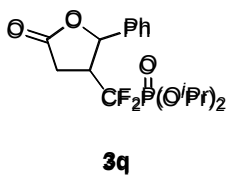
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3q

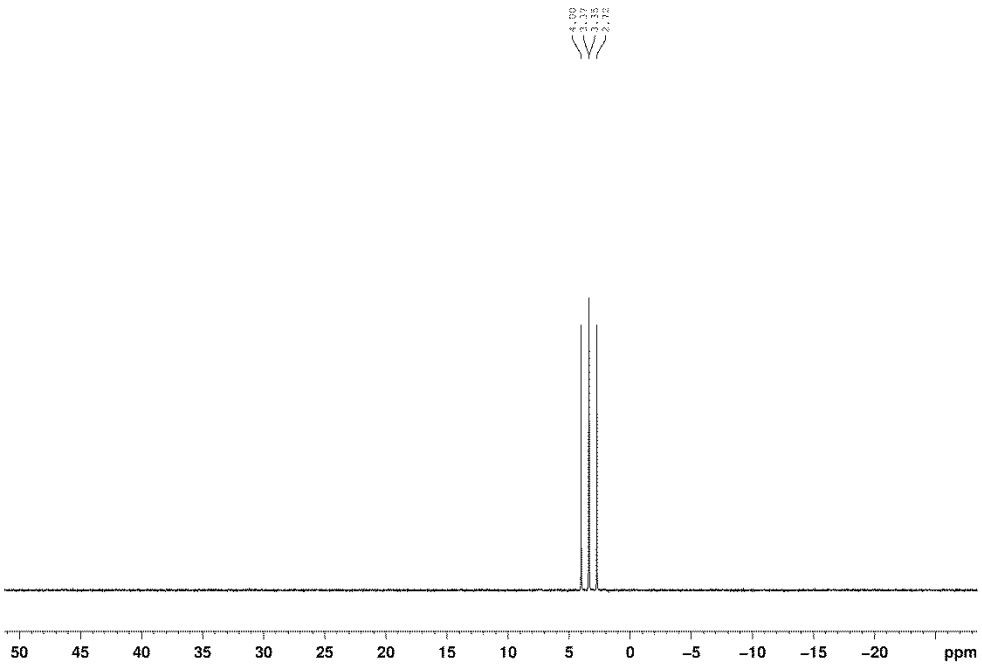


^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3q

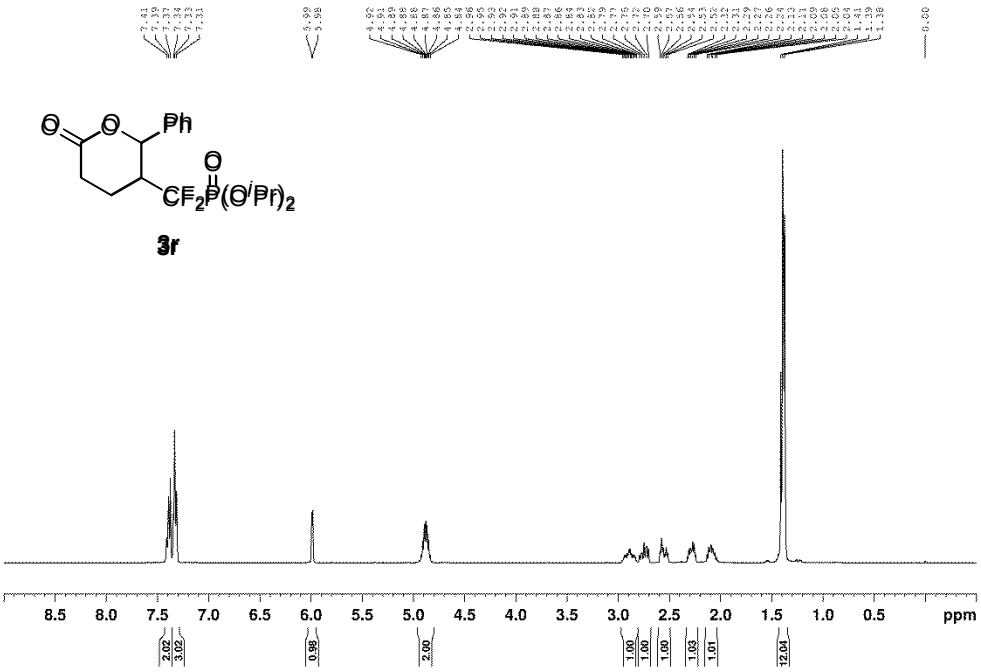


^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3q

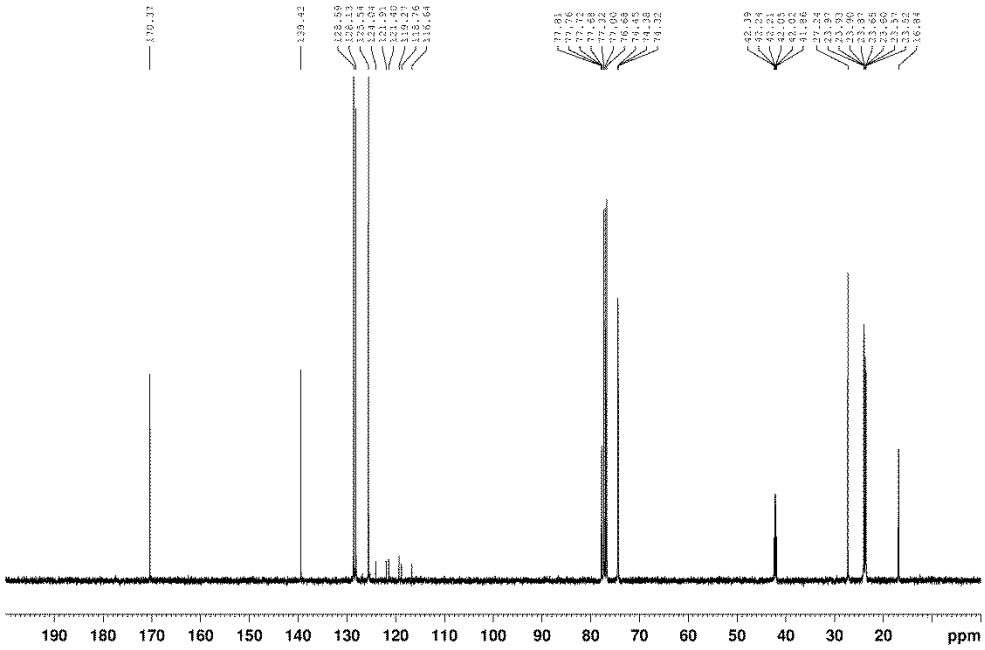




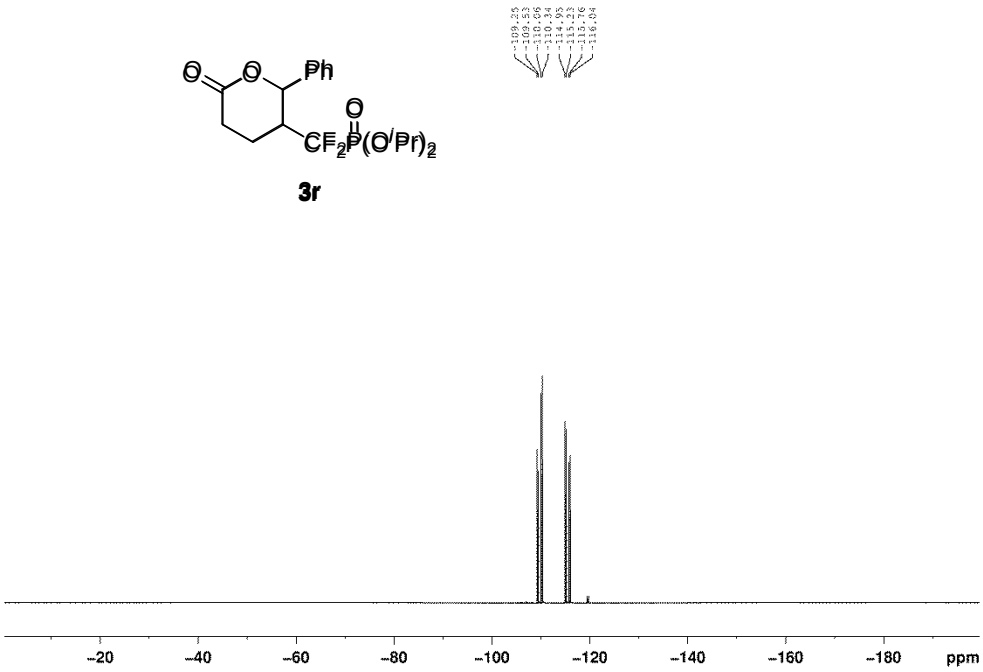
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3r



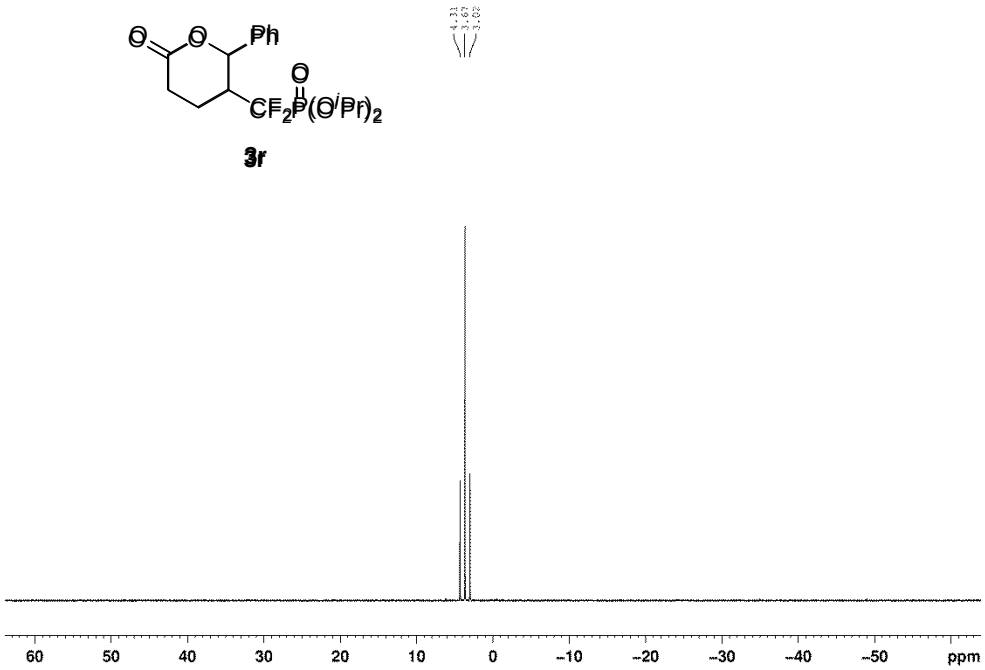
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3r



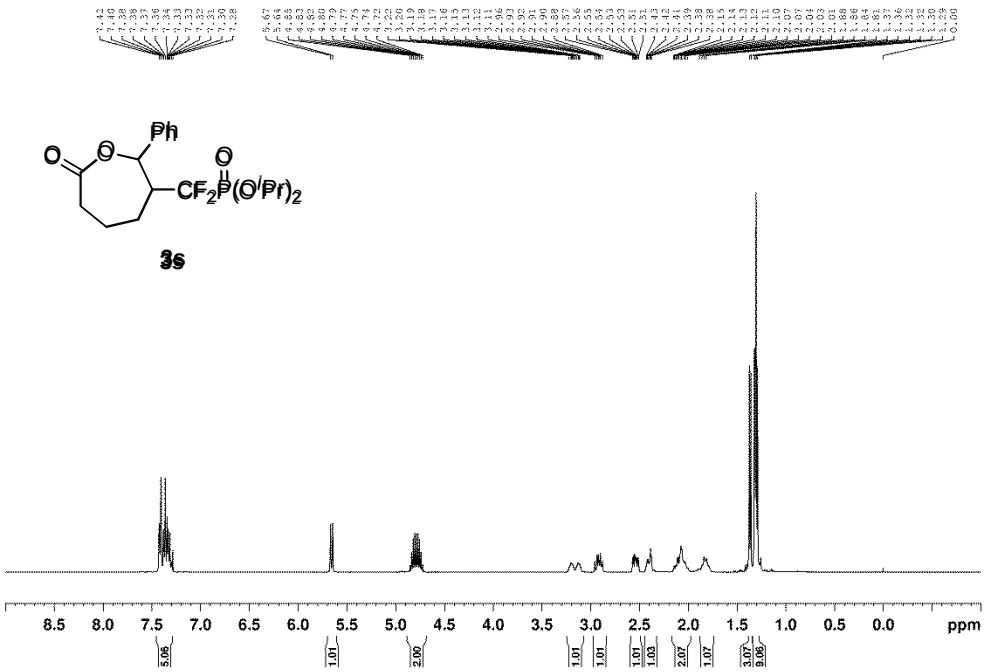
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3r



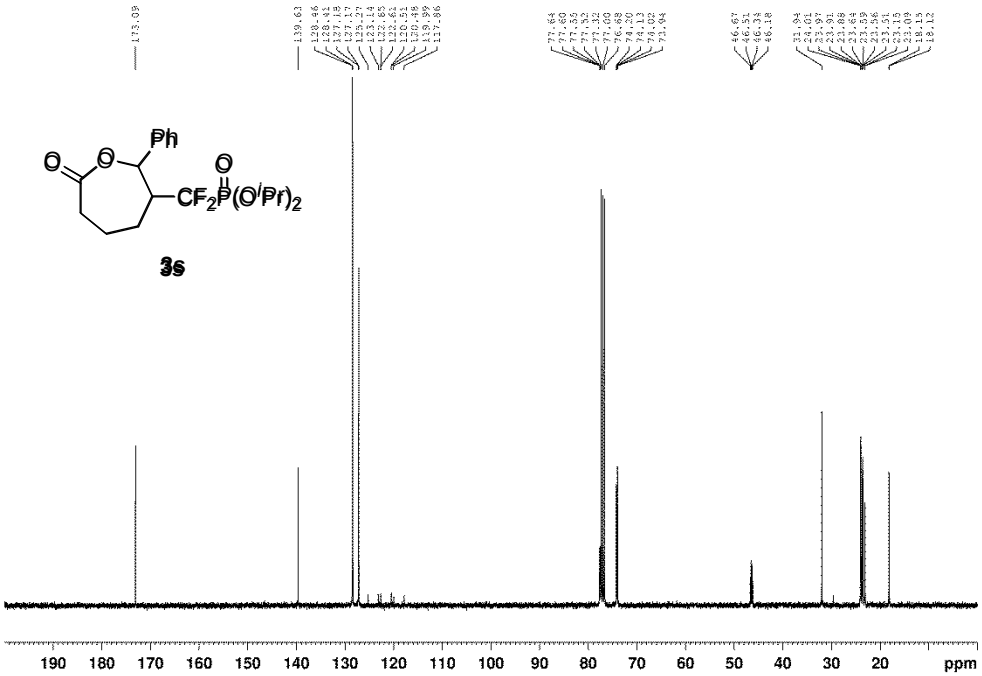
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3r



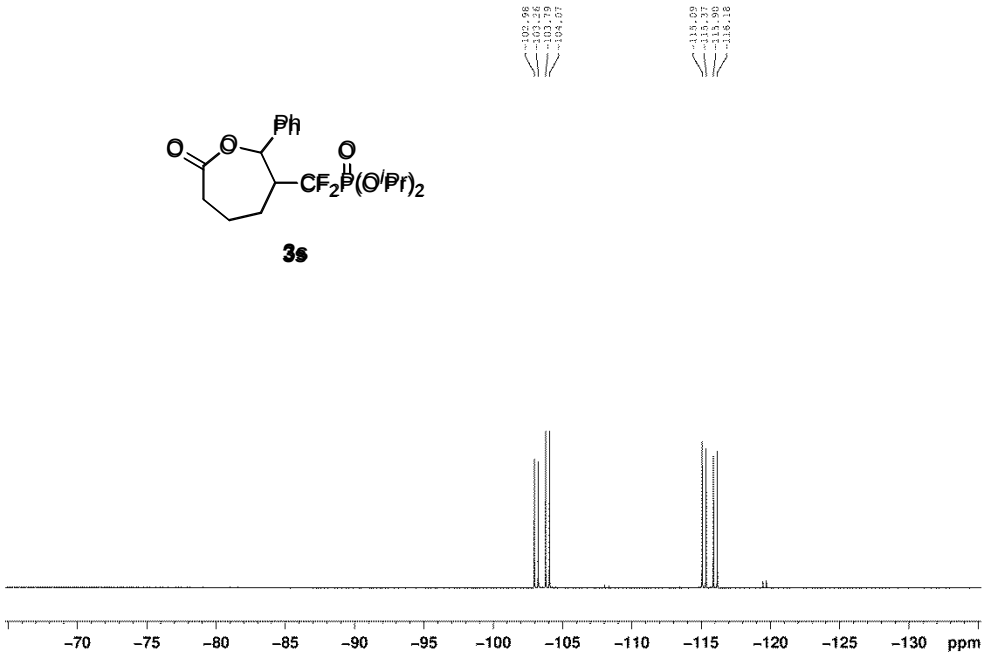
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 3s



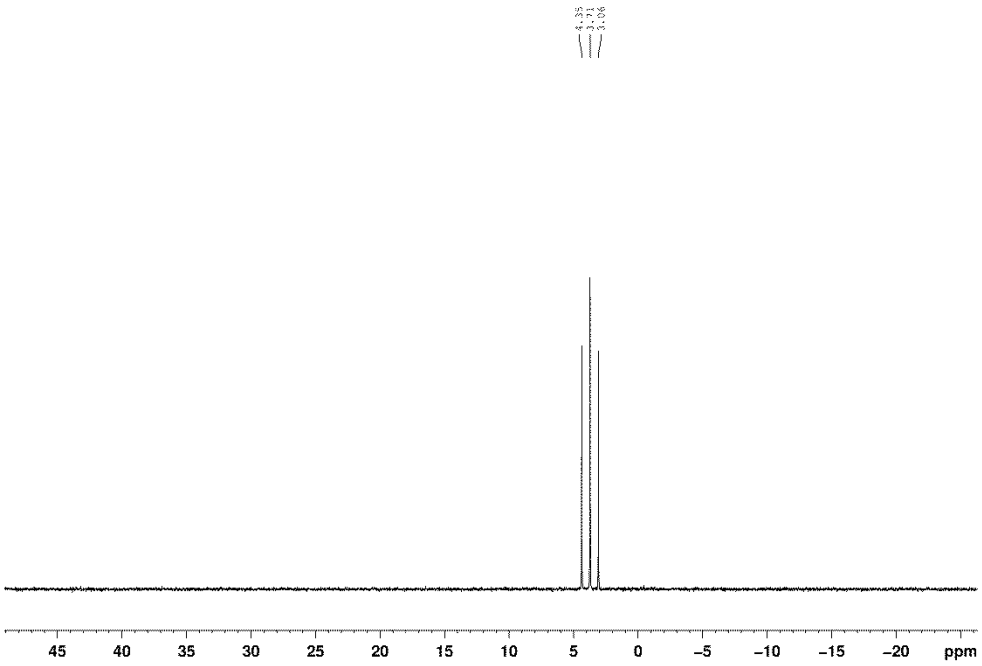
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 3s



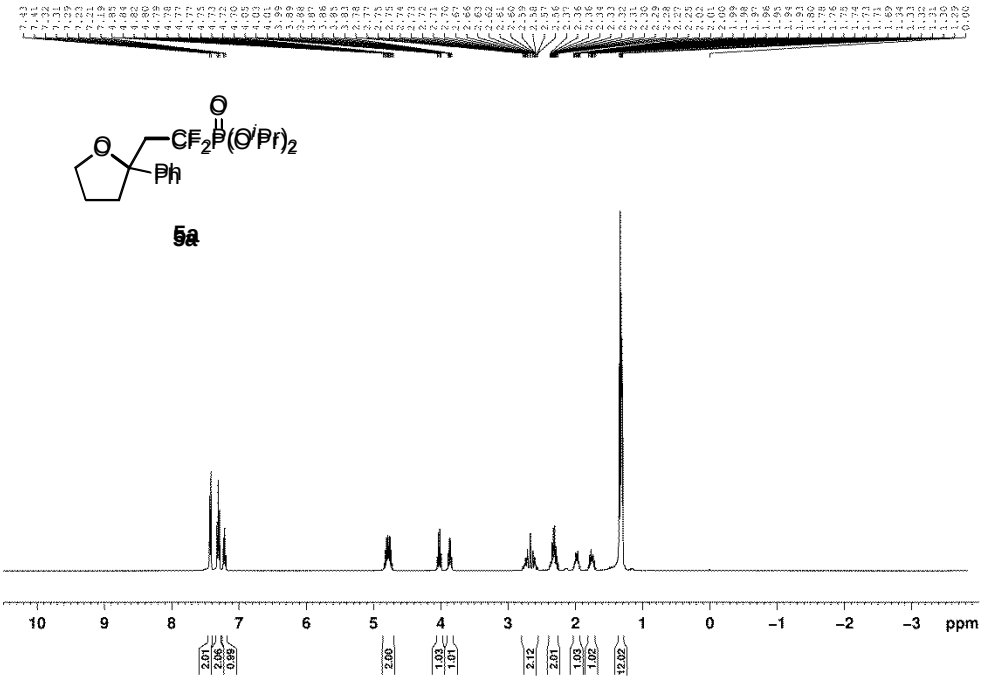
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 3s



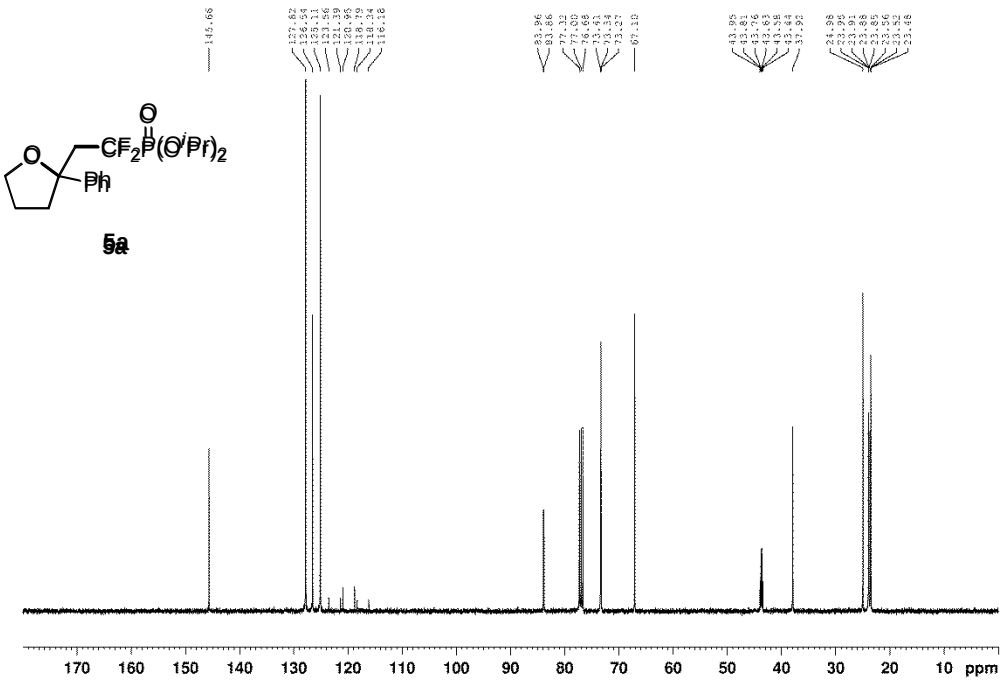
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 3s



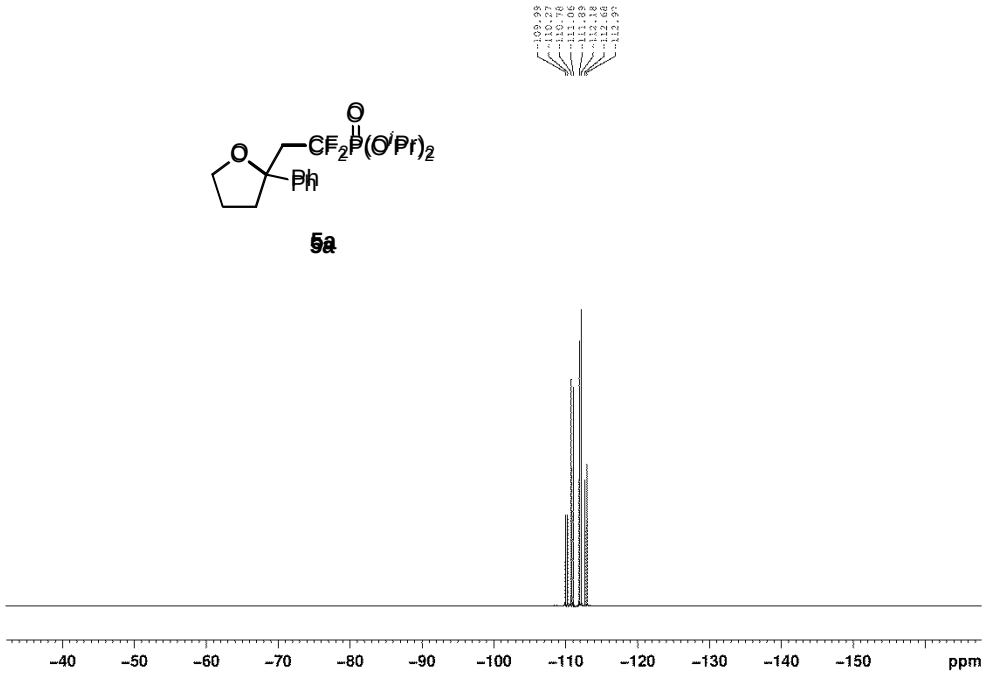
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5a



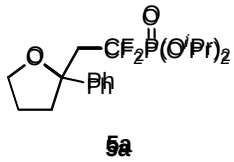
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5a

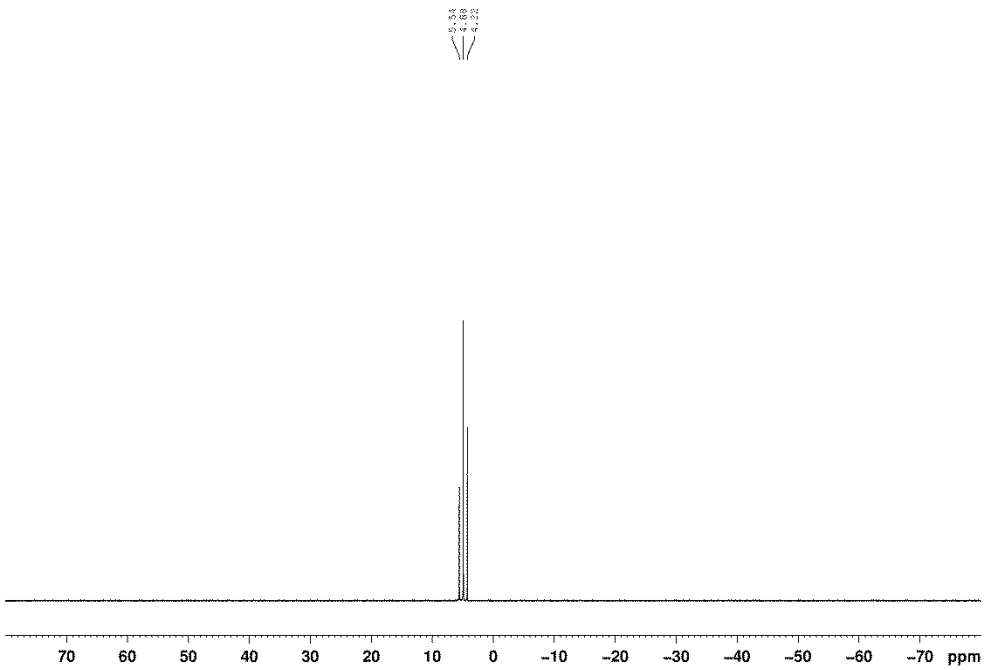


^{19}F NMR (376 MHz, CDCl$_3$) spectrum for 5a

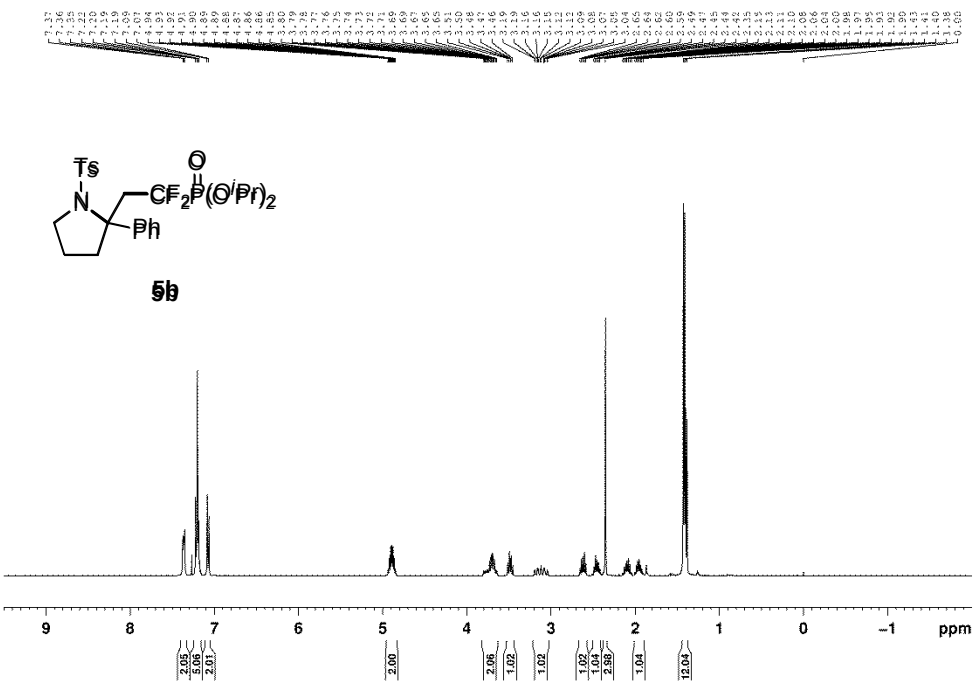


^{31}P NMR (162 MHz, CDCl$_3$) spectrum for 5a

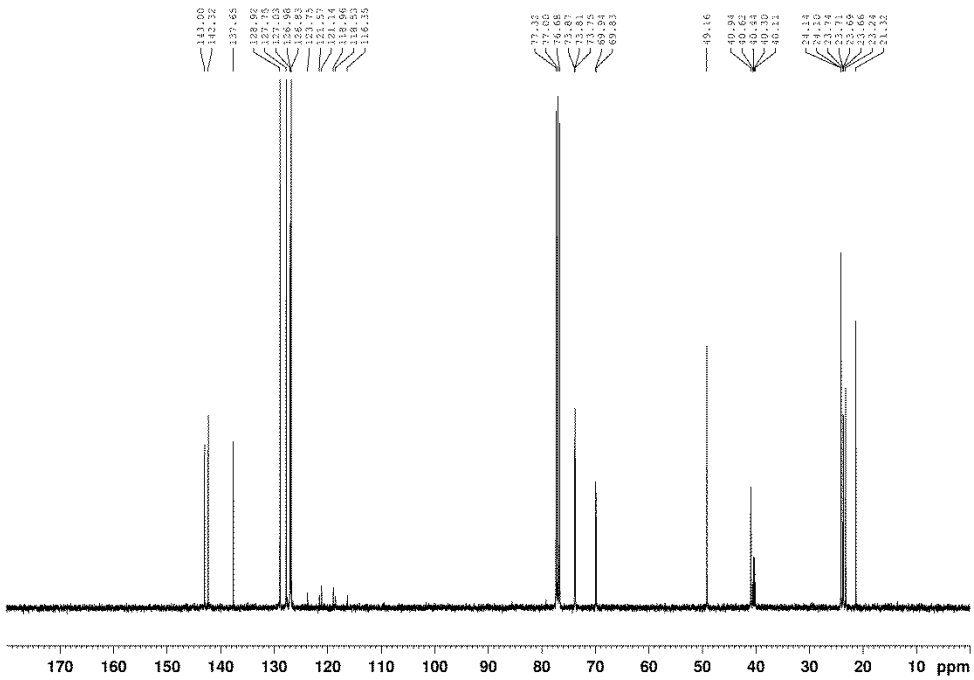




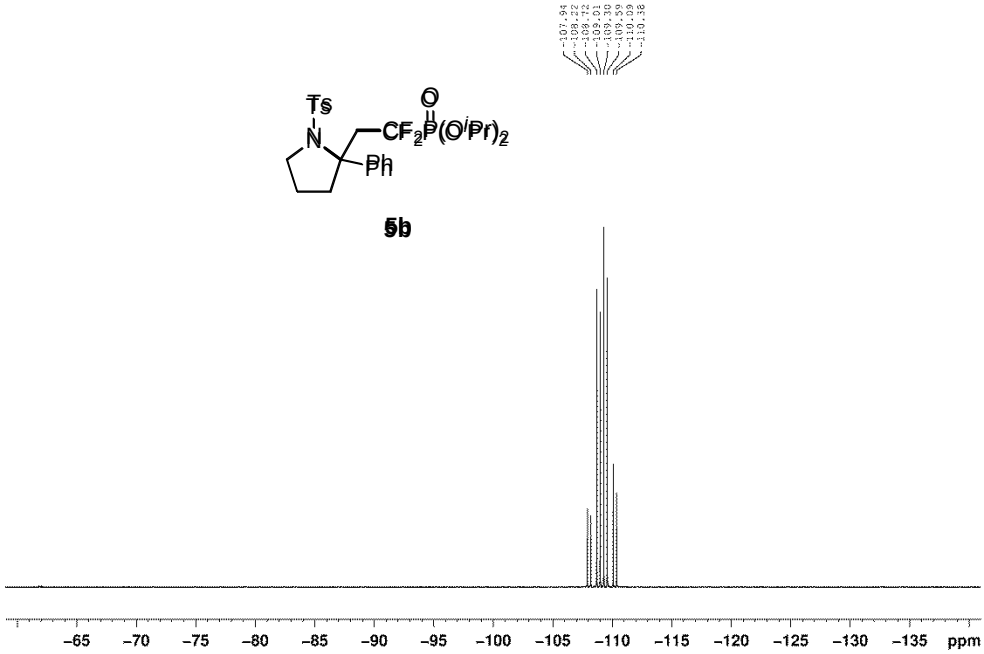
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5b



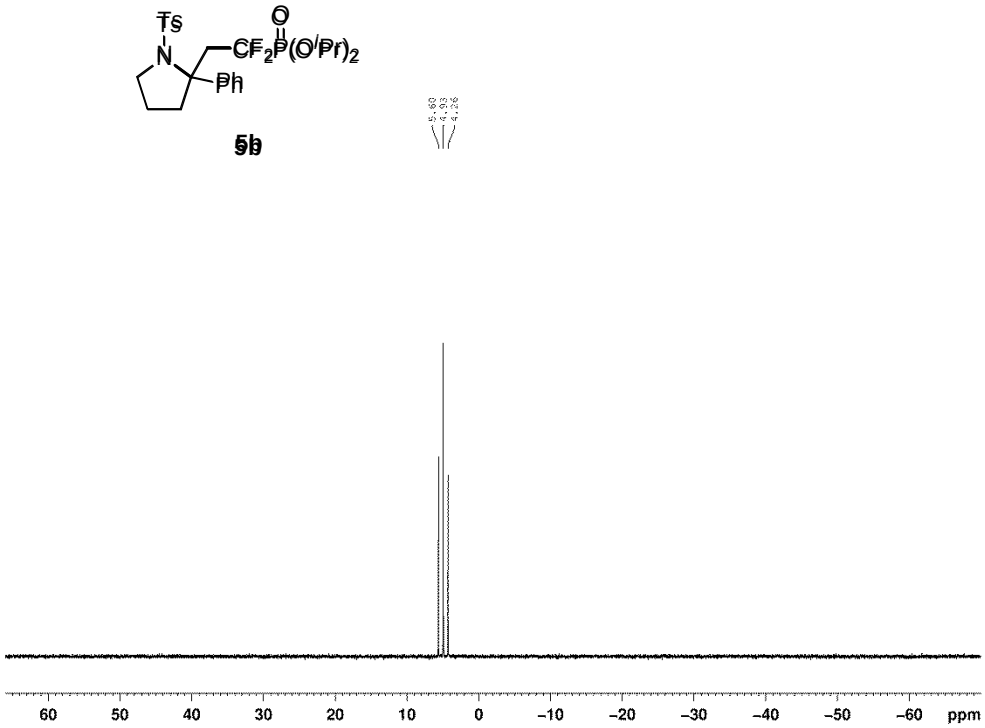
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5b



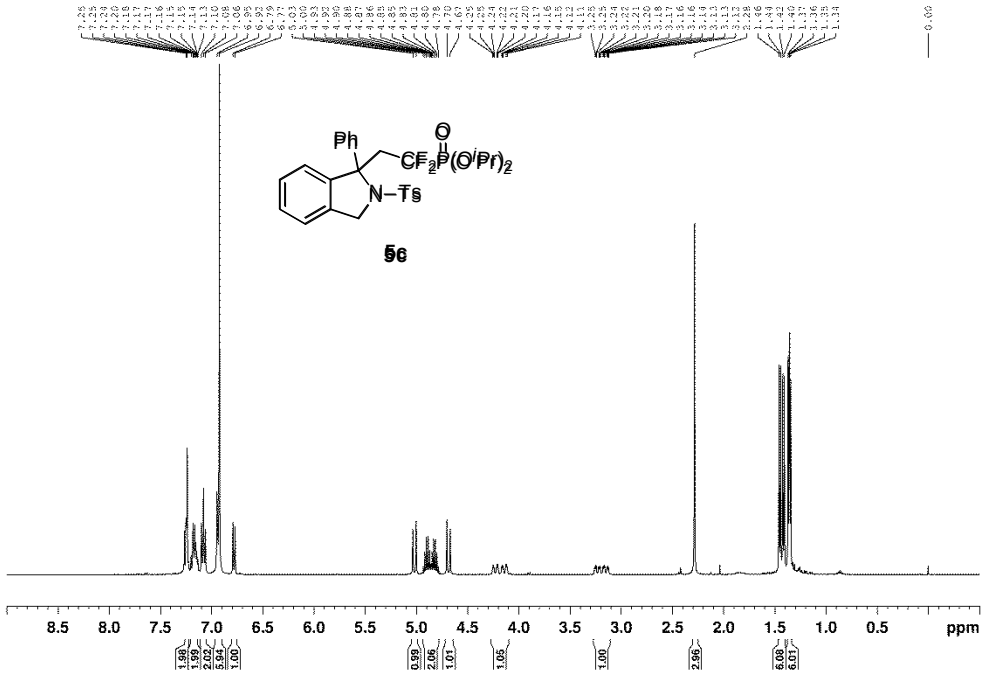
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 5b



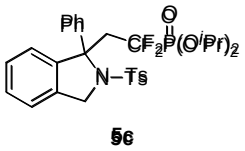
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 5b

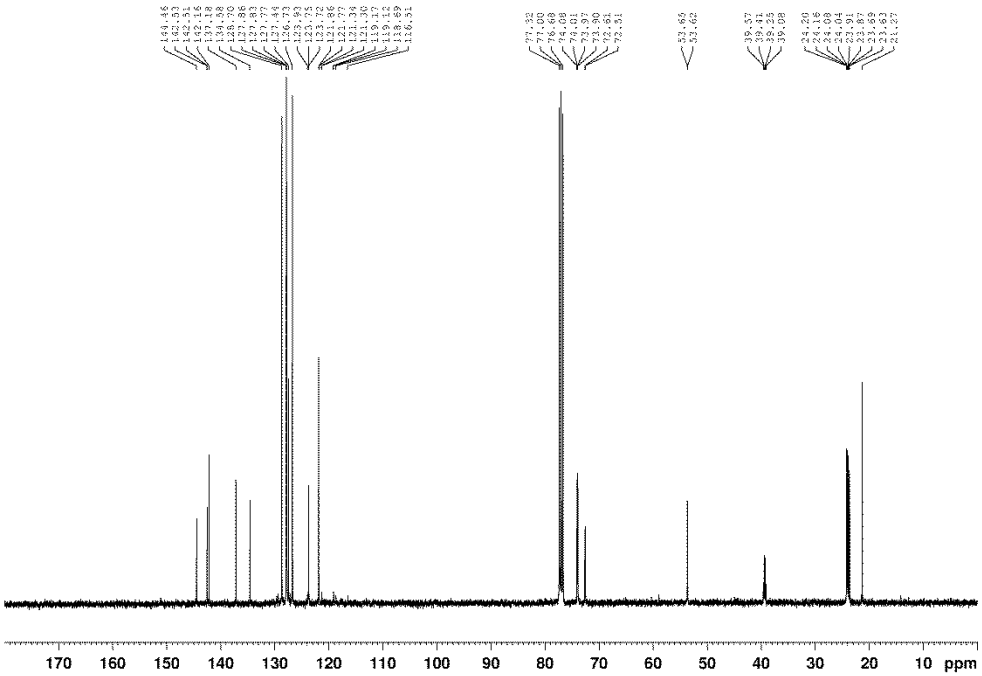


^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5c

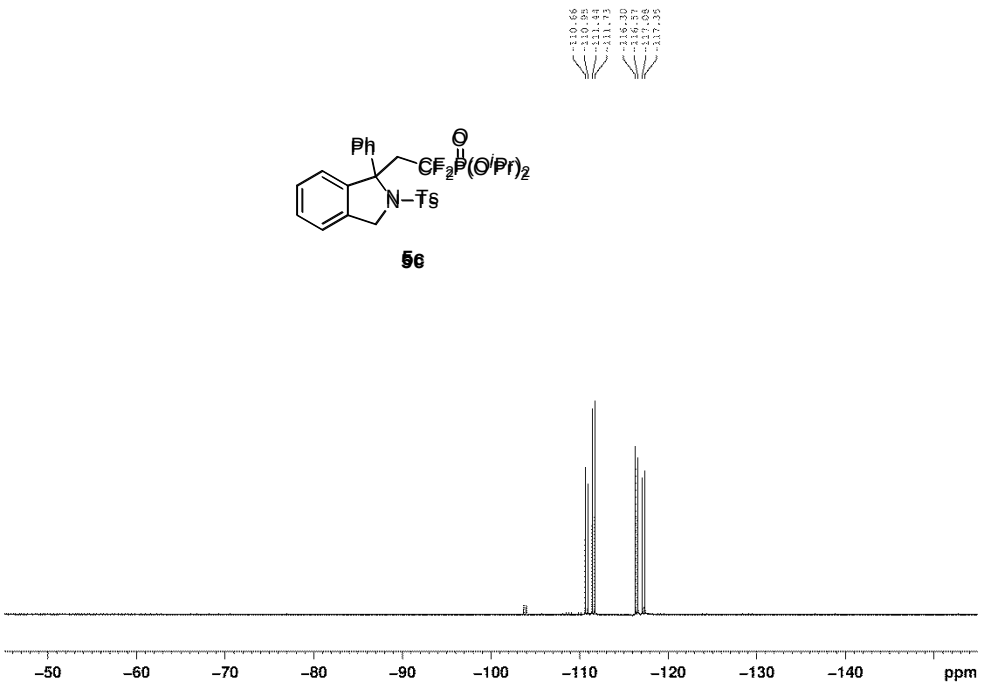


^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5c

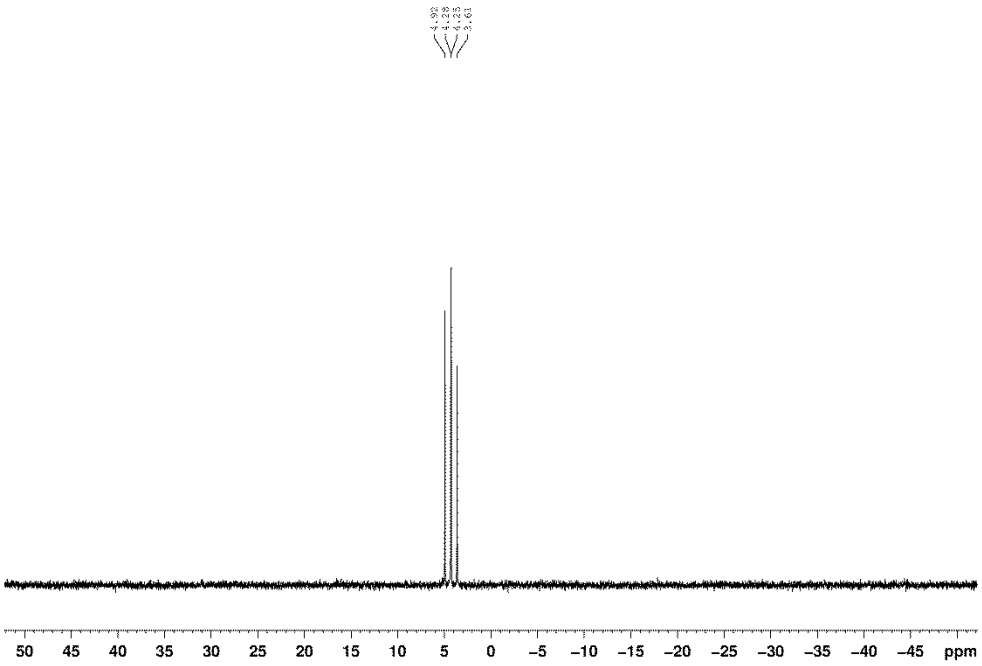




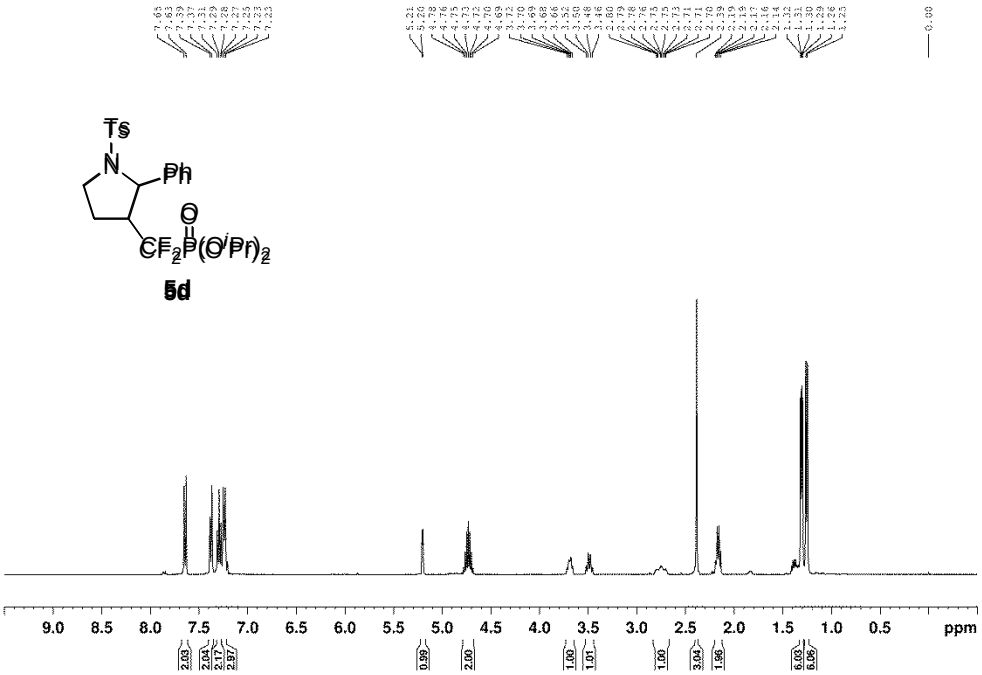
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 5c



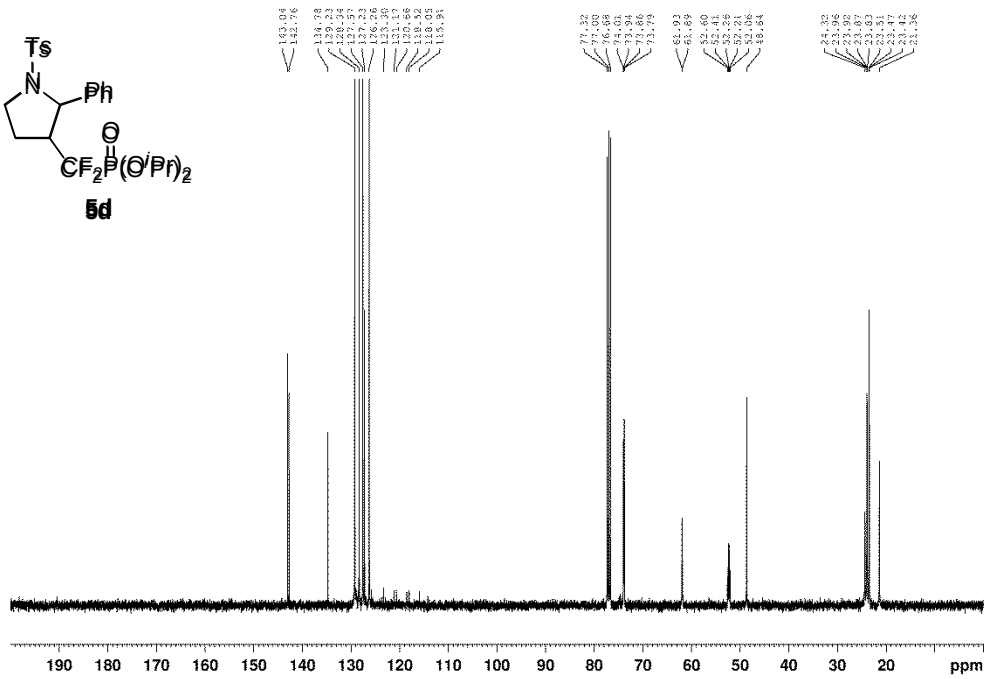
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 5c



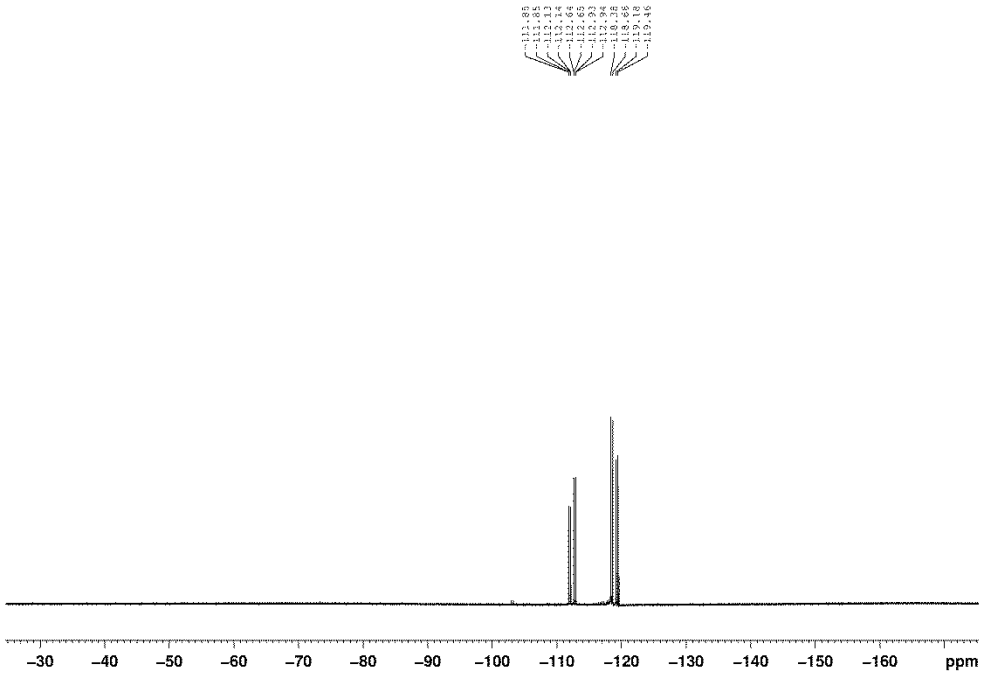
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 5d



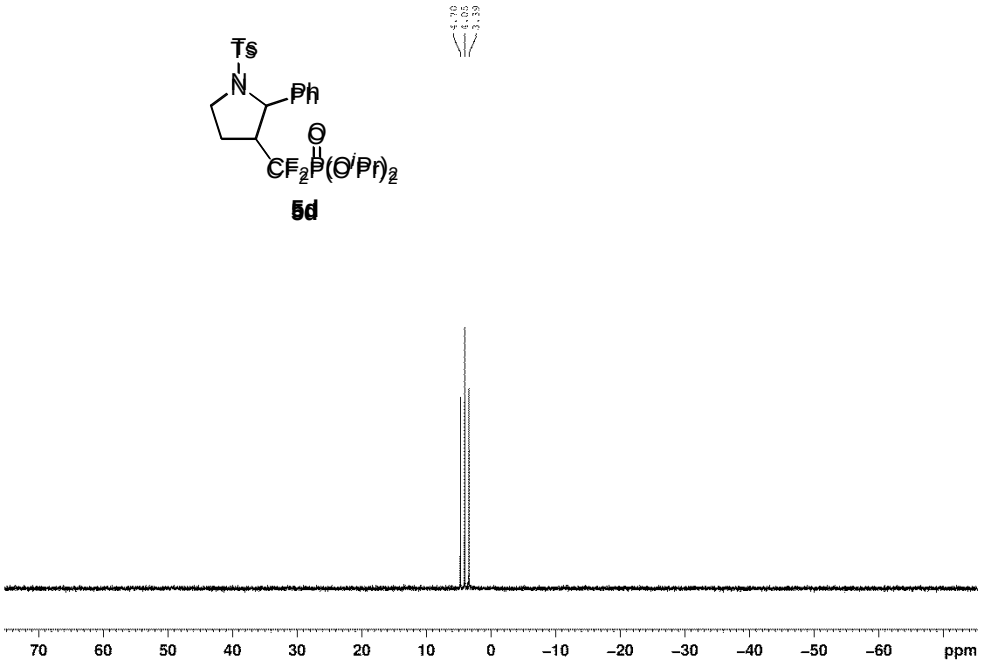
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 5d



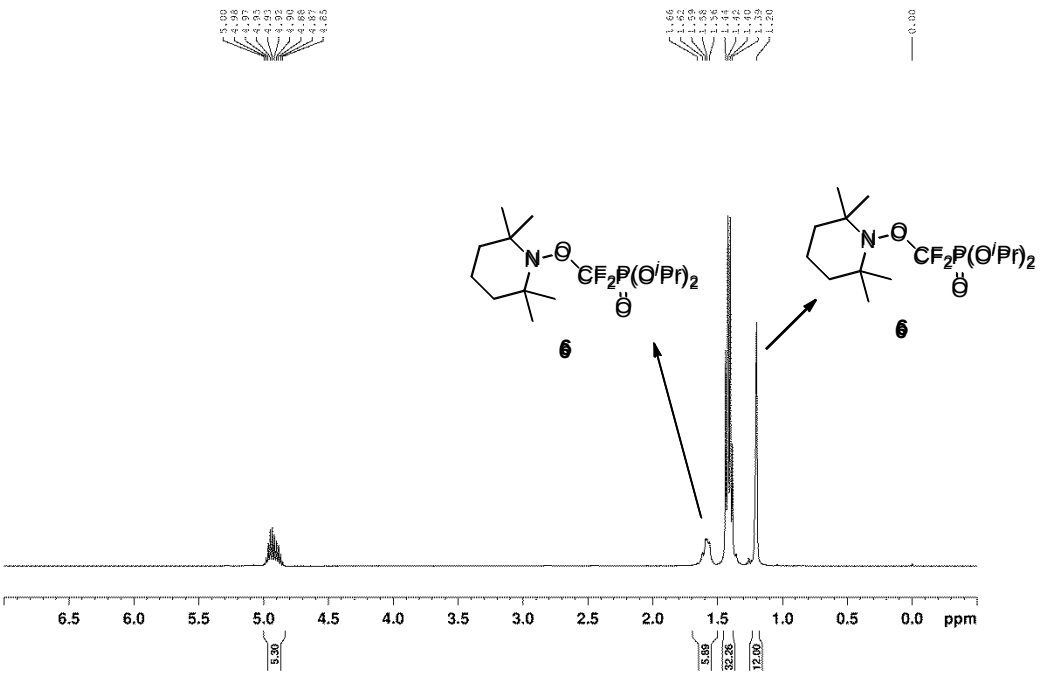
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 5d



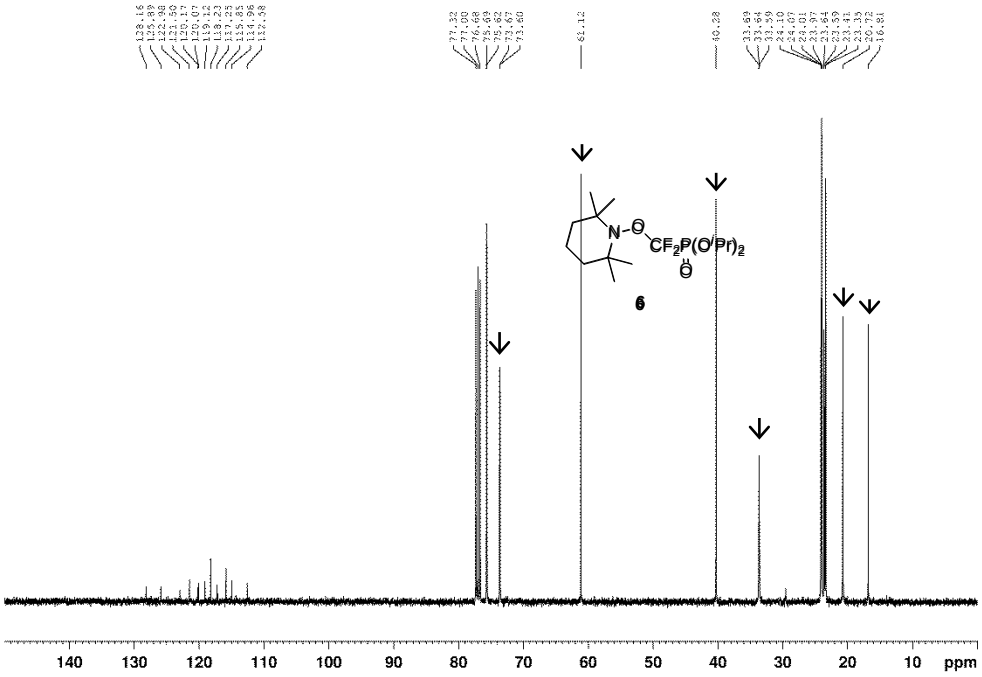
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 5d



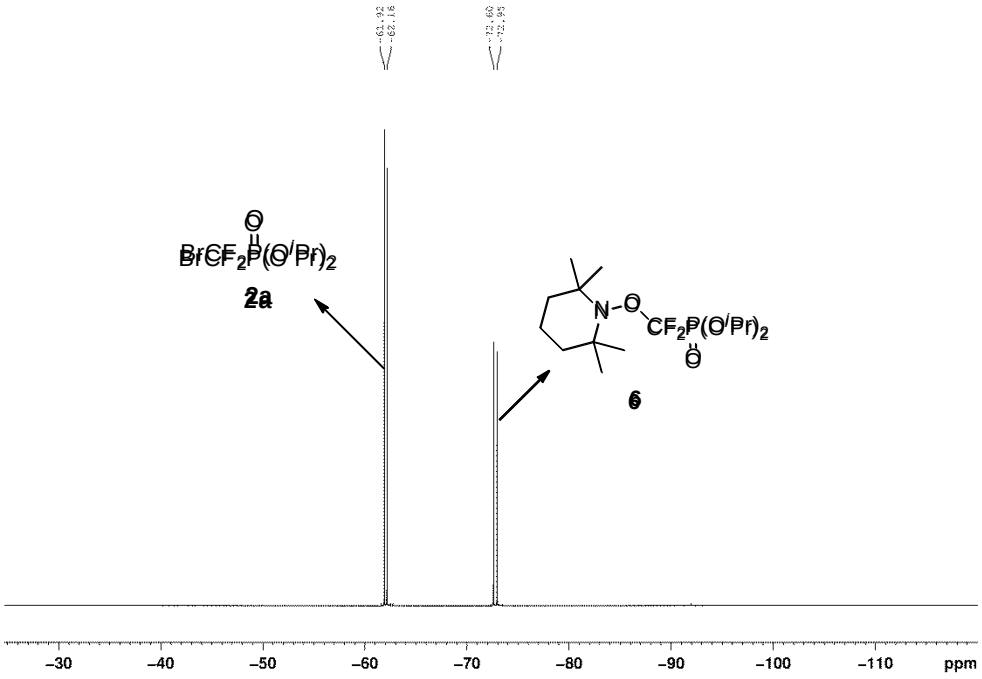
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 2a and **6**



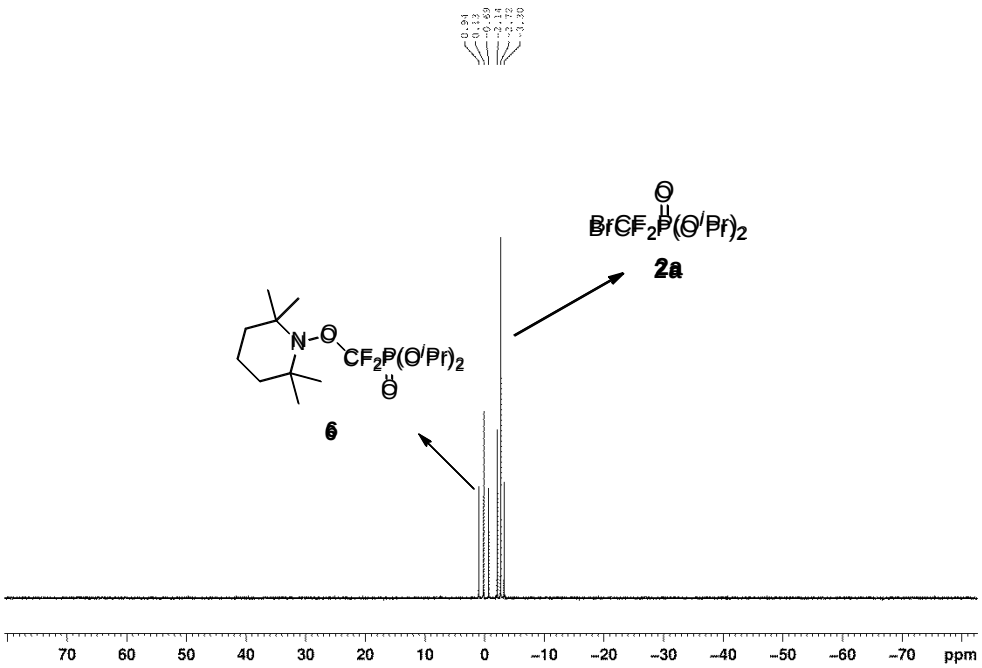
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 2a and **6**



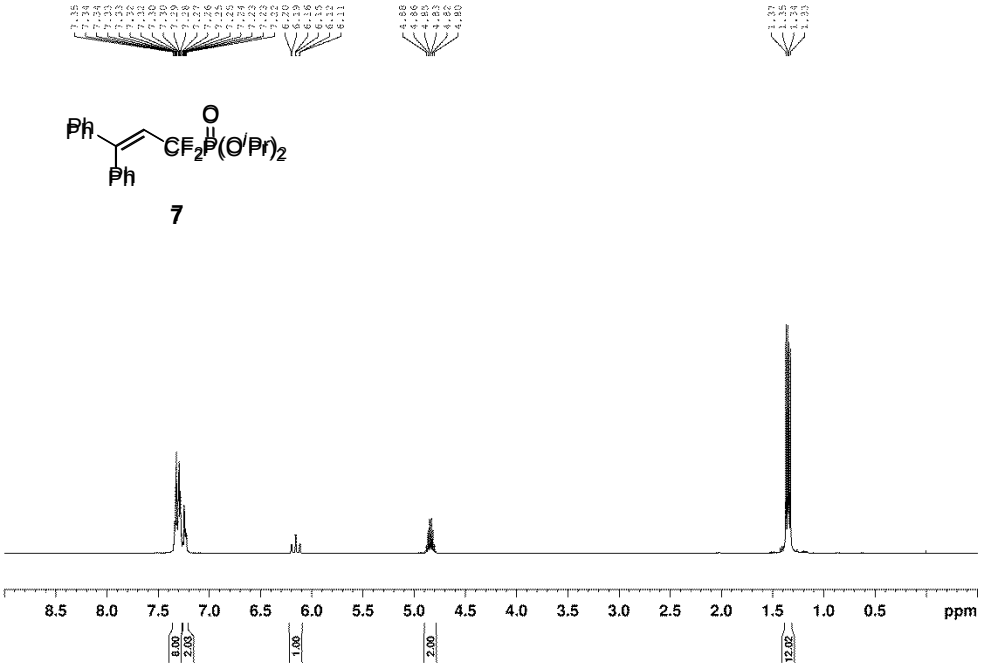
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 2a and **6**



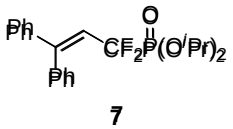
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 2a and **6**

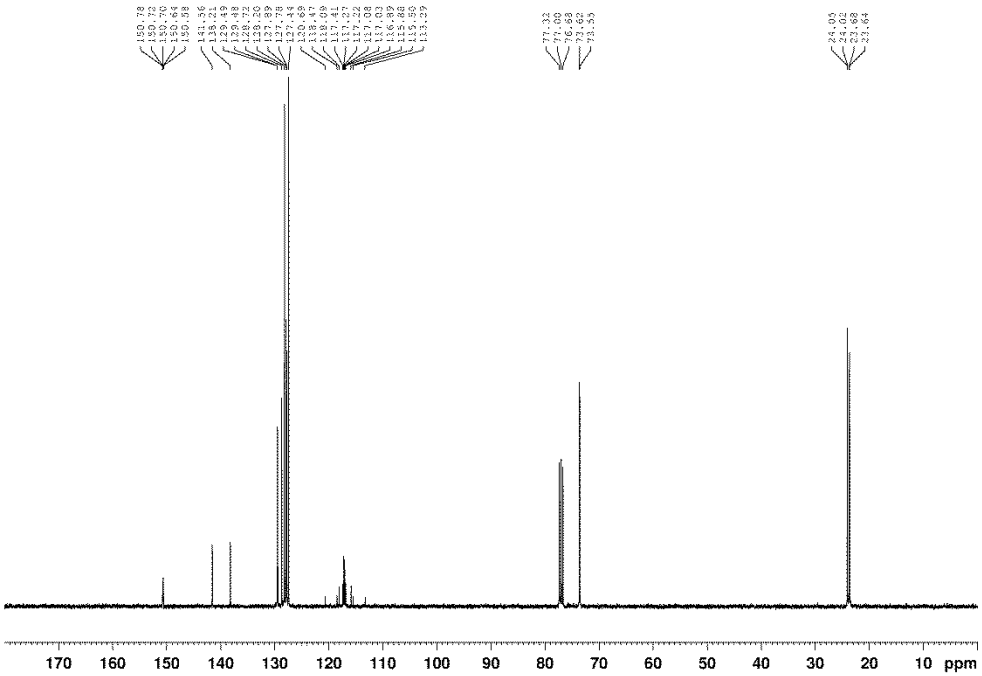


^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 7

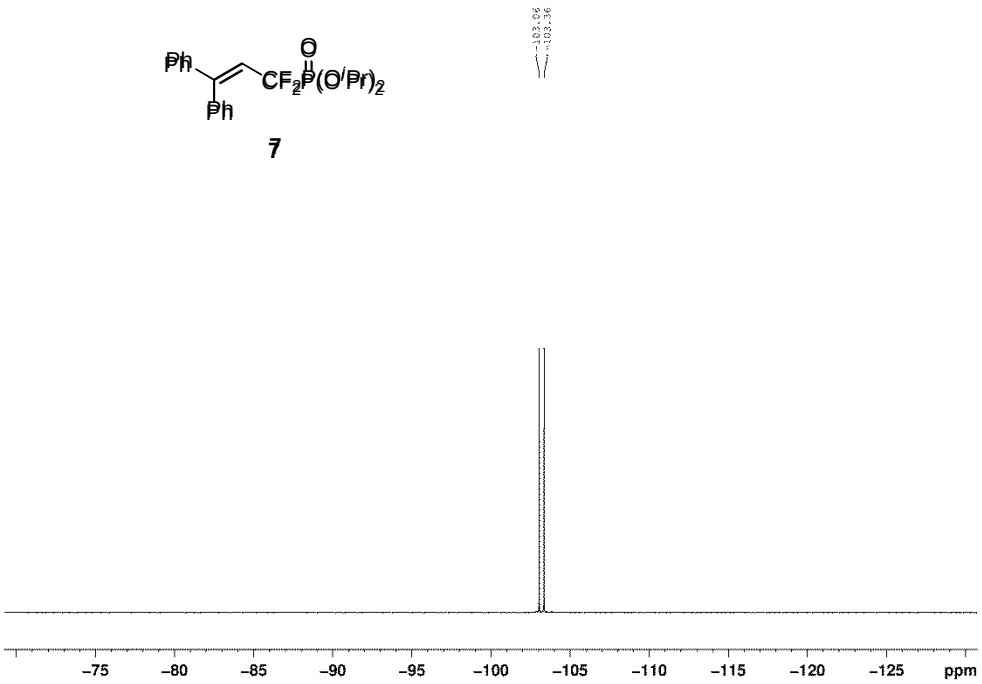


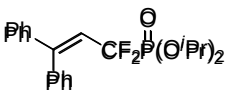
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 7





^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 7





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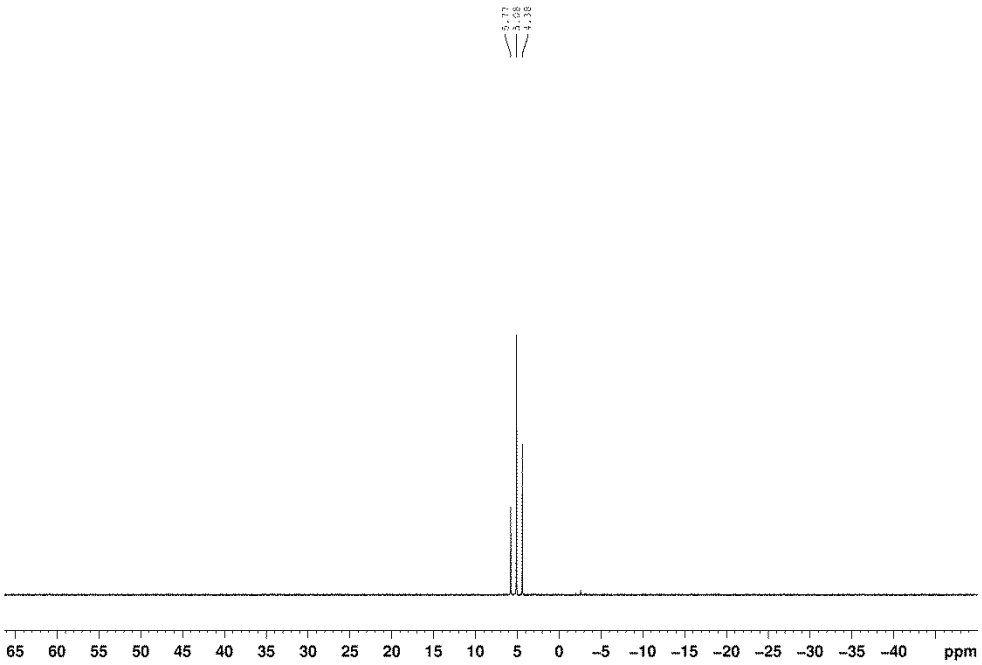
^{31}P NMR (162 MHz, $CDCl_3$) spectrum for 7