Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A General Photochemical Strategy for the Oximation of Activated Alkenes without a Catalyst

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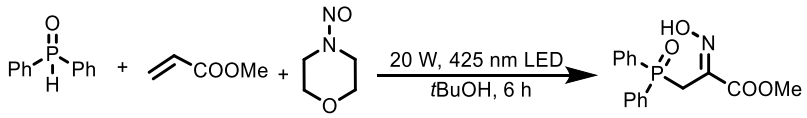
1. General Experimental Details

Catalytic reactions were performed under a N_2 atmosphere in pre-dried glassware using a Kessil PR160L photoreactor with 425 nm irradiation. The reaction temperature was measured by digital thermometer PCE-T 390, which was in the range of 30 to 32 °C (Room temperature: 22 to 25 °C). Methanol, dichloromethane, ethyl acetate, *n*-hexane and *n*-pentane were distilled prior to use. Other chemicals were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, TCI, or BLD Pharmatech GmbH) and used without further purification. Reactions were monitored by thin layer chromatography (TLC), using Merck silica gel 60 F254 glass plates (0.25 mm thick). Chromatography was carried out on Merck silica gel 60 (40–63 μm). Data for ^{1}H NMR are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p= quintet, m = multiplet, dd =doublet of doublets, ddd= doublet of double doublets, dt = doublet of triplets), coupling constants (J) were reported in Hertz (Hz). EI-MS was recorded on *Jeol AccuTOF* at 70 eV; ESI-MS was recorded on Bruker Daltonik *micrOTOF* and *maXis*. The ratios of mass to charge (*m/z*) are reported and the intensity relative to the base peak (I = 100) is given in parenthesis. All IR spectra were recorded on a Bruker FT-IR Alpha-P device.

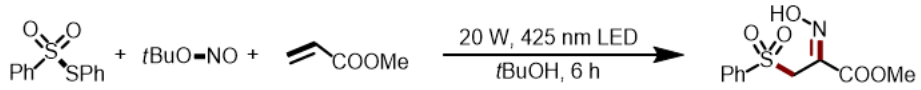
2. Optimization of the Reaction Condition



1 2 3 4

Entry[a]	**1** (equiv.)	**2** (equiv.)	**3** (equiv.)	Solvent (mL)	Yield[b] (%)	Wavelenght (nm)
1	1	2	2	MeCN (1.0)	26	420
2	1	2	2	DMSO (1.0)	0	420
3	1	2	2	DMF (1.0)	0	420
4	1	2	2	DMA (1.0)	0	420
5	1	2	2	DCM (1.0)	23	420
6	1	2	2	EtOAc (1.0)	18	420
7	1	2	2	Acetone (1.0)	37	420
8	3	2	3	EtOH (1.0)	51	420
9	1	2	2	*t*BuOH (1.0)	42	420
10	2	1	2	*t*BuOH (1.0)	54	420
11	2	1	3	*t*BuOH (1.0)	58	420
12	3	2	1	*t*BuOH (1.0)	60	420
13	3	1	2	*t*BuOH (1.0)	67	420
14	3	1	3	*t*BuOH (1.0)	89	420
15	3	1	3	*t*BuOH (1.0)	61	390
16	3	1	3	*t*BuOH (1.0)	59	455

[a]Reaction conditions: **1** (0.6 mmol), **2** (0.2 mmol), **3** (0.6 mmol), in *t*BuOH at room temperature under irradiation of LEDs (20 W, λ = 425 nm) for 6 hours. [b]Isolated yield.



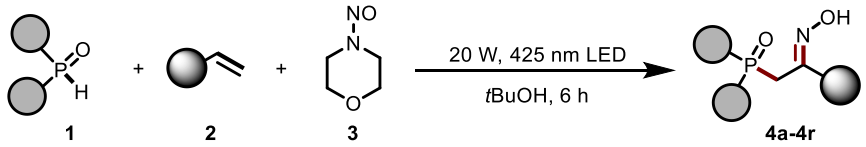
5 **3b** **2a** **6a**

Entry[a]	**5** (equiv.)	**3b** (equiv.)	**2a** (equiv.)	Solvent (mL)	Alkali	Yield [b] (%)	Wavelenght (nm)
1	3	3	1	*t*BuOH (1.0)	\	22	420
2	3	3	1	*t*BuOH (1.0)	K_2HPO_4	16	420
3	3	3	1	*t*BuOH (1.0)	NaH_2PO_4	15	420
4	3	3	1	*t*BuOH (1.0)	Na_3PO_4	15	420
5	3	3	1	*t*BuOH (1.0)	$NaHCO_3$	10	420
6	3	3	1	*t*BuOH (1.0)	NaOH	12	420
7	3	3	1	*t*BuOH(1.0)	KOH	15	420
8	3	3	1	*t*BuOH(1.0)	NaOMe	14	420
9	3	3	1	*t*BuOH (1.0)	NaOPiv	20	420
10	3	4	1	*t*BuOH (1.0)	\	33	420
11	3	5	1	*t*BuOH (1.0)	\	44	420
12	3	6	1	*t*BuOH (1.0)	\	60	420
13	3	7	1	*t*BuOH (1.0)	\	67	420
14	3	8	1	*t*BuOH (1.0)	\	80	420
15	3	1	2	*t*BuOH (1.0)	\	30	420
16	3	1	3	*t*BuOH (1.0)	\	38	420

[a]Reaction conditions: **5** (0.6 mmol), **2a** (0.2 mmol), **3b** (1.6 mmol), in *t*BuOH at room temperature under irradiation of LEDs (20 W, λ = 425 nm) for 6 hours.

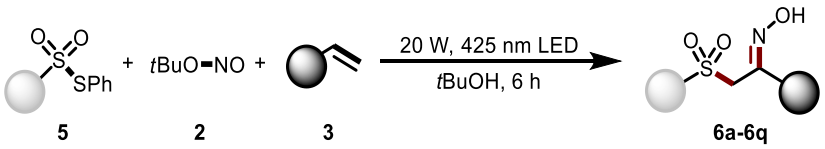
3. General Procedures

General Procedure 1



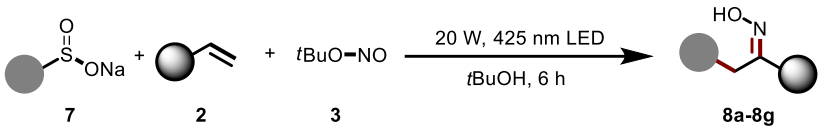
In an oven-dried tube, diphenylphosphine oxide (121.0 mg, 0.6 mmol 3.0 equiv.), 4-nitrosomorpholine (70.0 mg, 0.6 mmol 3.0 equiv.), and alkene (0.20 mmol, 1.0 equiv.), were dissolved in *t*BuOH (1.0 mL). The reaction mixture was stirred and irradiated using a 425 nm LED lamp under N_2 for 6 h. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel afforded the desired products **4a-4r.**

General Procedure 2



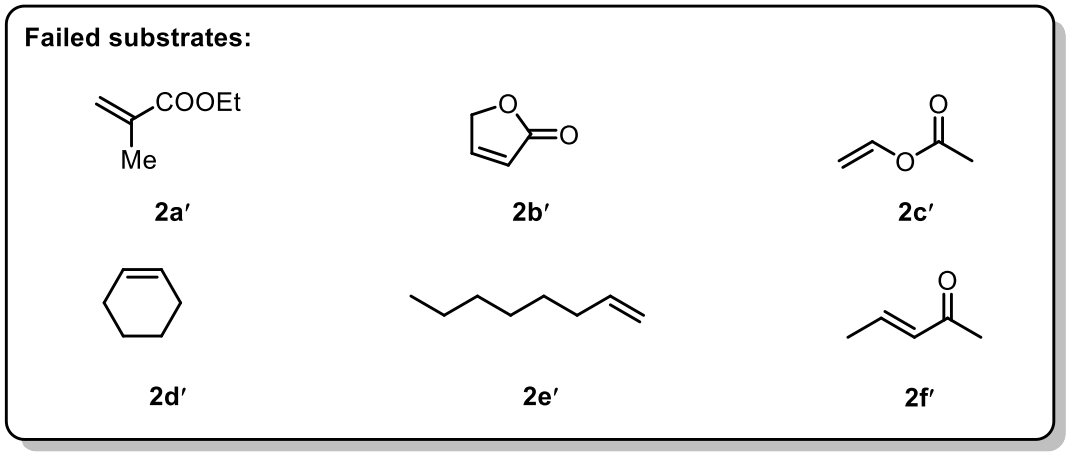
In an oven-dried tube, S-phenyl benzenesulfonothioate (150.0 mg, 0.6 mmol, 3.0 equiv), tert-butyl nitrite (165.0 mg, 1.6 mmol, 8.0 equiv.), and alkene (0.20 mmol, 1.0 equiv.), were dissolved in *t*BuOH (1.0 mL). The reaction mixture was stirred and irradiated using a 425-nm LED lamp under N_2 for 6 h. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel afforded the desired products **6a-6q.**

General Procedure 3



In an oven-dried tube, sodium trifluoromethanesulfinate (94.0 mg, 0.6 mmol 3.0 equiv), tert-butyl nitrite (165.0 mg, 1.6 mmol, 8.0 equiv.), and alkene (0.20 mmol, 1.0 equiv.), were dissolved in *t*BuOH (1.0 mL). The reaction mixture was stirred and irradiated using a 425-nm LED lamp under N_2 for 6h. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel afforded the desired products **8a-8g**

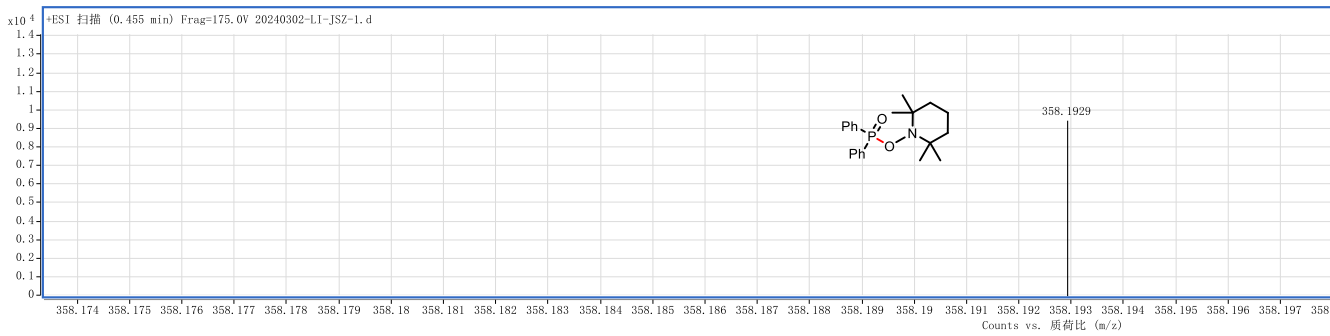
Failed substrates

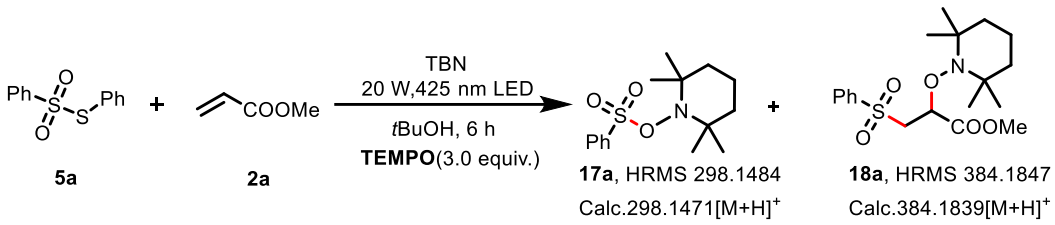


Mechanistic Studies

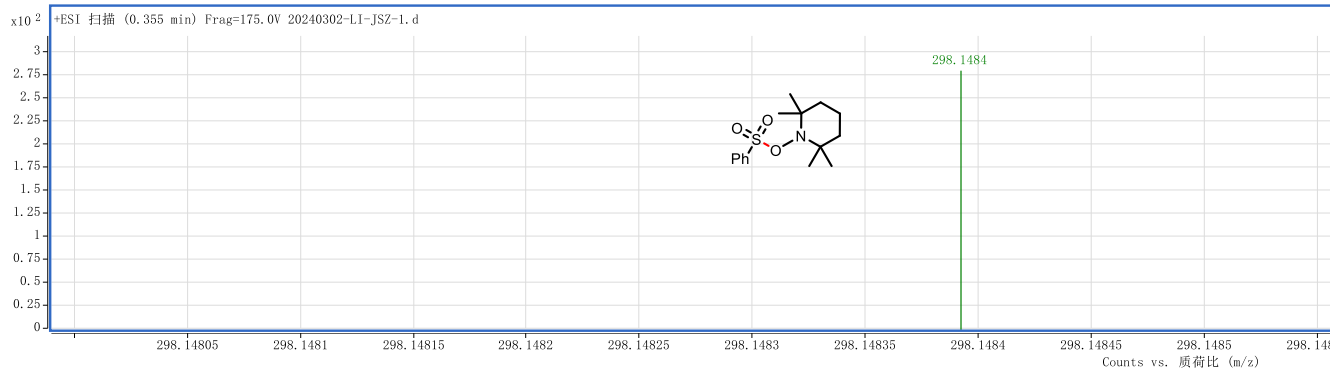
In an oven-dried tube, **1a** (0.6 mmol, 3.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.), **3** (0.6

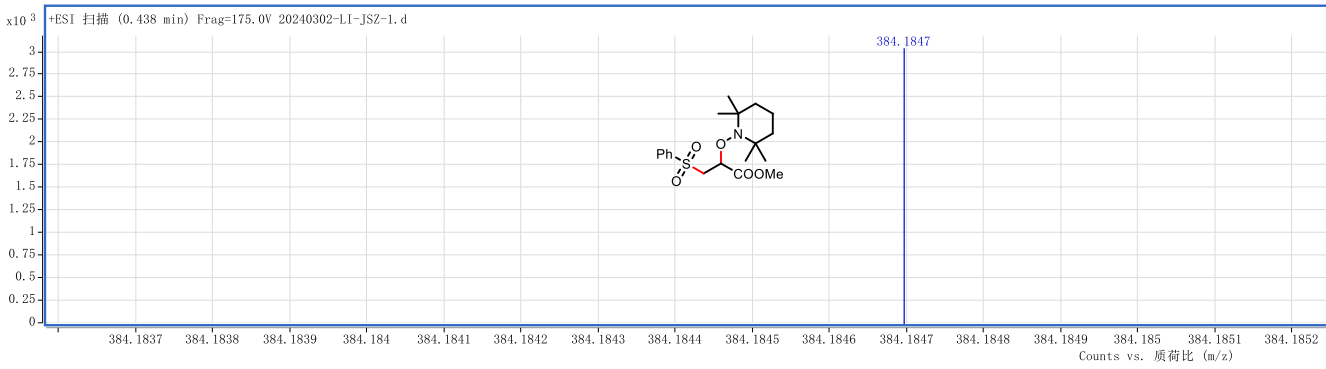
mmol, 3.0 equiv.), and 2,2,6,6-Tetramethylpiperidinooxy (93.6 mg, 0.6 mmol) were dissolved in *t*BuOH (1.0 mL). The tube was positioned approximately 5 cm away from a 20 W blue LEDs lamp (λ max = 425 nm). After being stirred at 25 °C for 6 h, the reaction mixture was analyzed by HR-MS.

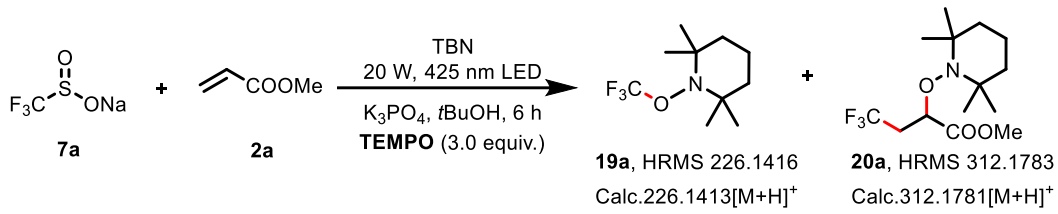




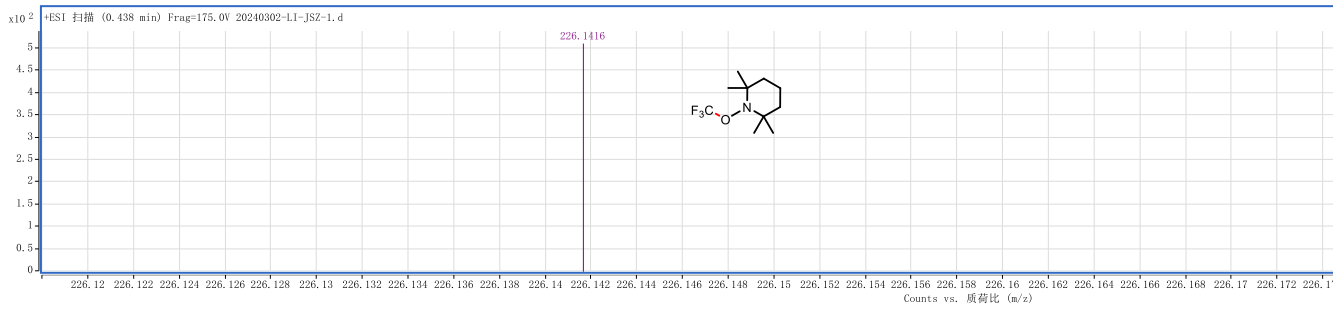
In an oven-dried tube, **5a** (0.6 mmol, 3.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.), TBN (1.6 mmol, 8.0 equiv.), and 2,2,6,6-Tetramethylpiperidinooxy (93.6 mg, 0.6 mmol) were dissolved in *t*BuOH (1.0 mL). The tube was positioned approximately 5 cm away from a 20 W blue LEDs lamp (λ max = 425 nm). After being stirred at 25 °C for 6 h, the reaction mixture was analyzed by HR-MS.

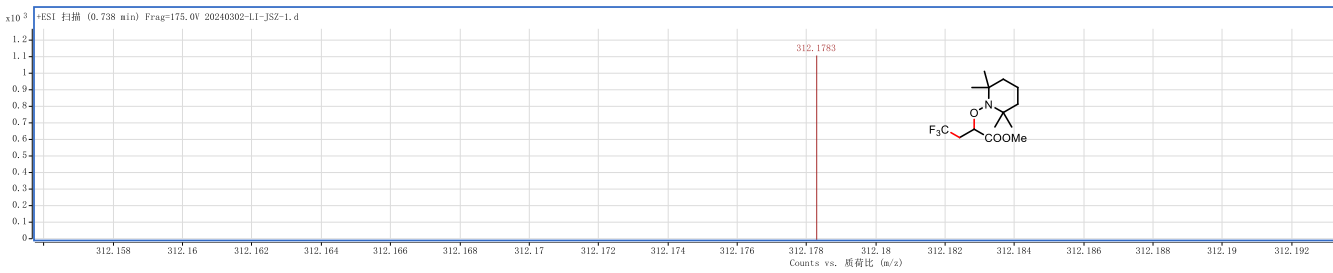


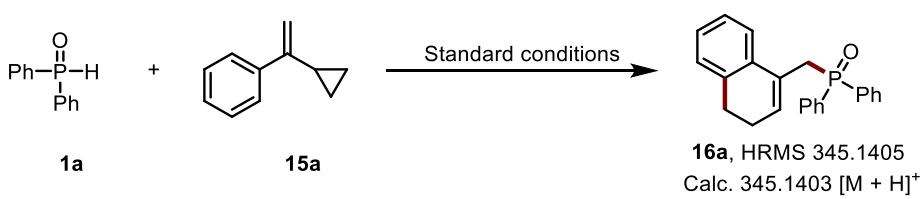




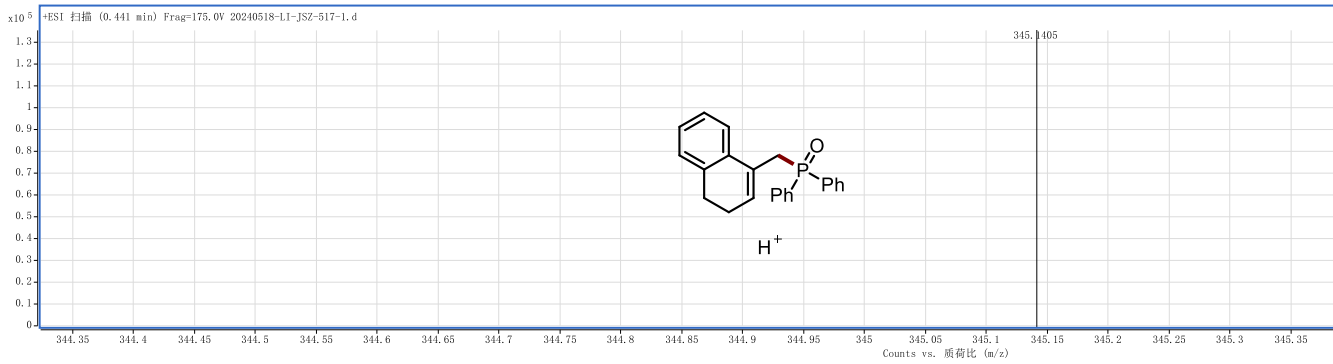
In an oven-dried tube, **7a** (0.6 mmol, 3.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.), TBN (1.6 mmol, 8.0 equiv.), K_3PO_4 (0.4 mmol, 2.0 equiv.) and 2,2,6,6-Tetramethyl piperidinooxy (93.6 mg, 0.6 mmol) were dissolved in *t*BuOH (1.0 mL). The tube was positioned approximately 5 cm away from a 20 W blue LEDs lamp (λ max = 425 nm). After being stirred at 25 °C for 6 h, the reaction mixture was analyzed by HR-MS.

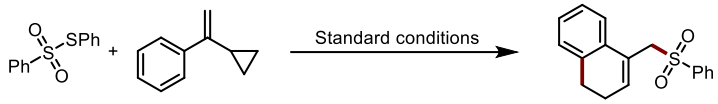






In an oven-dried tube, **1a** (0.6 mmol, 3.0 equiv.), **15a** (0.2 mmol, 1.0 equiv.), and 4-nitrosomorpholine (0.6 mmol, 3.0 equiv.) were dissolved in *t*BuOH (1.0 mL). The tube was positioned approximately 5 cm away from a 20 W blue LEDs lamp (λ max = 425 nm). After being stirred at 25 °C for 6 h, the reaction mixture was analyzed by HR-MS.

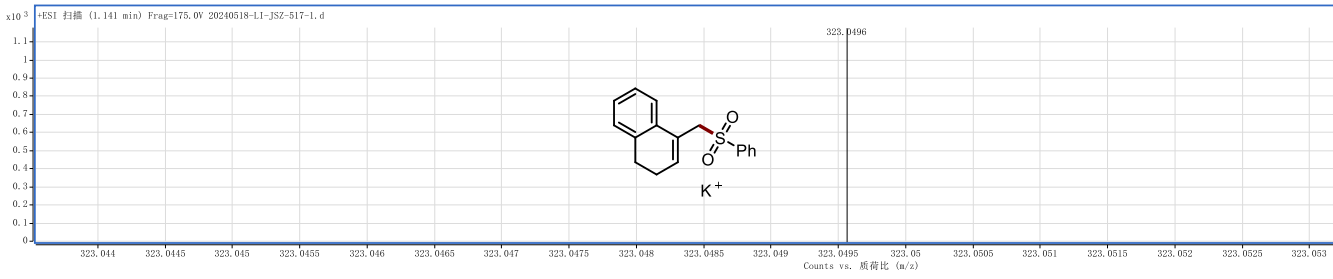


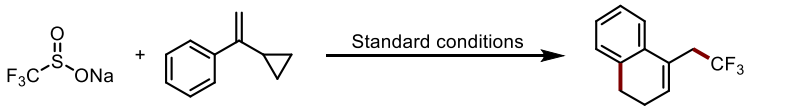


5a **15a**

17a, HRMS 323.0496
Calc. 323.0503 $[M + K]^+$

In an oven-dried tube, **5a** (0.6 mmol, 3.0 equiv.), **15a** (0.2 mmol, 1.0 equiv.) and TBN (1.6 mmol, 8.0 equiv.) were dissolved in *t*BuOH (1.0 mL). The tube was positioned approximately 5 cm away from a 20 W blue LEDs lamp (λ max = 425 nm). After being stirred at 25 °C for 6 h, the reaction mixture was analyzed by HR-MS.



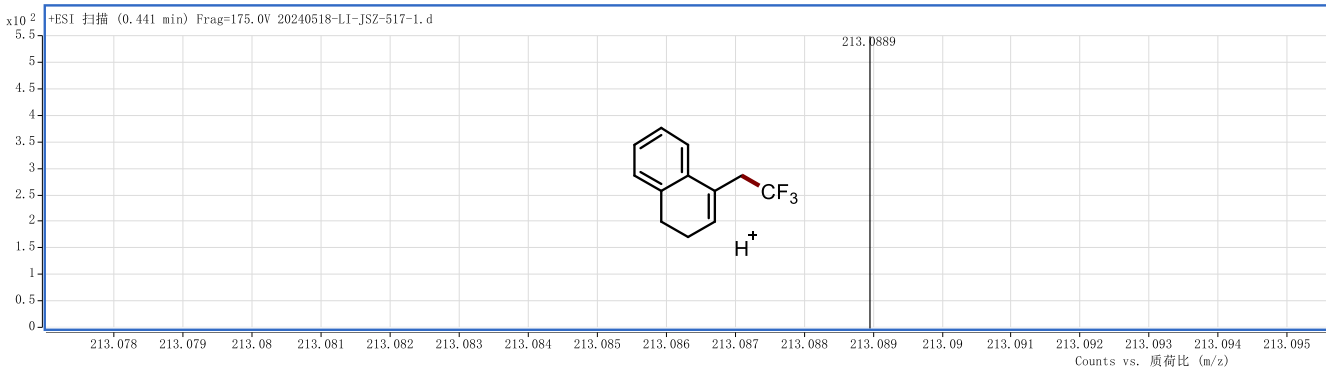


7a **15a**

18a, HRMS 213.0889
Calc. 213.0886 $[M + H]^+$

In an oven-dried tube, **7a** (0.6 mmol, 3.0 equiv.), **15a** (0.2 mmol, 1.0 equiv.), TBN (1.6 mmol, 8.0 equiv.) and K_3PO_4 (0.4 mmol, 2.0 equiv.) were dissolved in *t*BuOH (1.0 mL). The tube was positioned approximately 5 cm away from a 20 W blue LEDs lamp (λ max = 425 nm). After being stirred at 25 °C for 6 h, the reaction mixture was analyzed

by HR-MS.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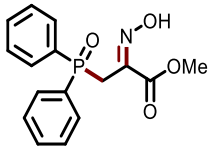
x10 2
213.0889
CF3
H+
213.078 213.079 213.08 213.081 213.082 213.083 213.084 213.085 213.086 213.087 213.088 213.089 213.09 213.091 213.092 213.093 213.094 213.095
Counts vs. 质荷比 (m/z)

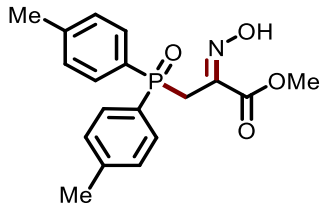
4. Characterization Data of Products

Methyl (E)-3-(diphenylphosphoryl)-2-(hydroxyimino)propanoate (4a)



The general procedure 1 was followed using diphenylphosphine oxide (121 mg, 0.6 mmol), 4-nitrosomorpholine (70 mg, 0.6 mmol), methyl acrylate (17.2 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4a** as colorless oil (56.4 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.99 (s, 1H), 7.88 – 7.80 (m, 4H), 7.56 – 7.52 (m, 2H), 7.50 – 7.41 (m, 4H), 3.93 (d, J = 14.6 Hz, 2H), 3.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.5 (d, J = 2.5 Hz), 142.6 (d, J = 9.8 Hz), 132.2 (d, J = 2.9 Hz), 132.2 (d, J = 103.1 Hz),131.4 (d, J = 9.9 Hz), 128.7 (d, J = 12.3 Hz), 52.5, 28.7 (d, J = 64.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.1. **ATR-FTIR (cm^{-1}):** 3175, 2850, 1821, 1361, 1211, 863, 774, 601. **HR-MS** (ESI) $C_{16}H_{17}NO_4P$ $[M+H]^+$: 318.0890, found: 318.0888.

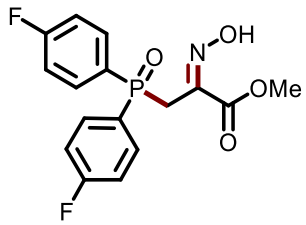
Methyl (E)-3-(di-p-tolylphosphoryl)-2-(hydroxyimino)propanoate (4b)



The general procedure 1 was followed using di-p-tolylphosphine oxide(138mg, 0.6 mmol), 4-nitrosomorpholine (70 mg, 0.6 mmol), methyl acrylate (32.8mg, 0.2mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4b** as colorless oil (55.9 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.98 (s, 1H), 7.71 (m, J = 11.9, 7.8 Hz, 4H), 7.34 – 7.11 (m, 4H), 3.89 (d, J = 14.9 Hz, 2H), 3.62 (s, 3H), 2.39 (s, 6H). **^{13}C NMR**

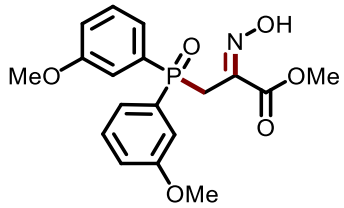
(101 MHz, $CDCl_3$): δ = 164.7 (d, J = 2.6 Hz), 142.9 (d, J = 9.8 Hz), 142.6 (d, J = 2.8 Hz), 131.4 (d, J = 10.2 Hz), 129.4 (d, J = 12.6 Hz), 129.1 (d, J = 105.7 Hz), 52.6, 29.0 (d, J = 64.6 Hz), 21.8. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.4. **ATR-FTIR (cm^{-1}):** 3312, 2960, 1736, 1365, 1069, 858, 787, 620. **HR-MS** (ESI) $C_{18}H_{21}NO_4P$ $[M+H]^+$: 346.1203, found: 346.1204.

Methyl (E)-3-(bis(4-fluorophenyl)phosphoryl)-2-(hydroxyimino)propanoate (4c)



The general procedure 1 was followed using bis(4-fluorophenyl) (methylene)-l5-phosphane(121 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), methyl acrylate (33.6 mg, 0.2mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4c** as colorless oil (54.4 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ =12.80 (s, 1H), 7.90 – 7.76 (m, 4H), 7.21 – 7.11 (m, 4H), 3.89 (d, J = 14.7 Hz, 2H), 3.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.5 (d, J = 6.0 Hz), 164.2, 142.6, 133.9 (dd, J = 11.5, 8.9 Hz), 128.4, 116.3 (dd, J = 21.4, 13.5 Hz), 52.9, 28.9 (d, J = 66.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 28.1. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -105.9. **ATR-FTIR (cm^{-1}):** 3205, 2956, 1826, 1148, 1052, 823, 732, 710. **HR-MS** (ESI) $C_{18}H_{21}NO_4P$ $[M+H]^+$: 354.0701, found: 354.0696.

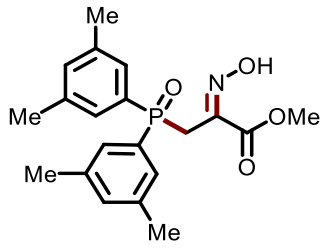
Methyl(E)-3-(bis(3-methoxyphenyl)phosphoryl)-2-(hydroxyimino)propanoate (4d)



The general procedure 1 was followed using bis(3-methoxyphenyl)phosphine oxide (157mg, 0.6 mmol), 4-nitrosomorpholine (70 mg, 0.6 mmol), methyl acrylate (17.2mg,

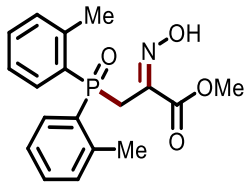
0.2mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4d** as colorless oil (61.1 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 13.13 (s, 1H), 7.43 – 7.31 (m, 6H), 7.08 – 6.99 (m, 2H), 3.90 (d, *J* = 14.9 Hz, 2H), 3.77 (s, 6H), 3.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.4 (d, *J* = 2.6 Hz), 159.6 (d, *J* = 14.9 Hz), 142.7 (d, *J* = 9.7 Hz), 133.2 (d, *J* = 102.4 Hz), 129.8 (d, *J* = 14.6 Hz), 123.2 (d, *J* = 10.2 Hz), 118.8 (d, *J* = 2.7 Hz), 115.7 (d, *J* = 10.7 Hz), 55.6, 52.5, 28.8 (d, *J* = 65.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.6. **ATR-FTIR (cm^{-1}):** 3240, 2955, 1725, 1429, 1302, 920, 774, 692. **HR-MS** (ESI) $C_{18}H_{21}NO_6P$ $[M+H]^+$: 378.1101, found: 378.1105.

Methyl (E)-3-(bis(3,5-dimethylphenyl)phosphoryl)-2-(hydroxyimino)propanoate (4e)



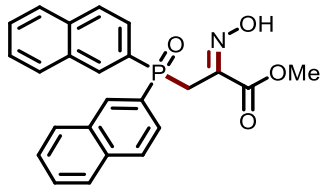
The general procedure 1 was followed using bis(3,5-dimethylphenyl)phosphine oxide (150 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), methyl acrylate (17.2 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4e** as colorless oil (59.0 mg, 79% yield) **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.78 (s, 1H), 7.42 (d, *J* = 12.4 Hz, 4H), 7.12 (s, 2H), 3.90 – 3.86 (m, 4H), 3.61 – 3.60 (m, 3H), 2.32 (d, *J* = 3.3 Hz, 12H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.7, 143.1 (d, *J* = 9.3 Hz), 138.3 (d, *J* = 12.9 Hz), 133.9 (d, *J* = 3.0 Hz), 132.1 (d, *J* = 102.0 Hz), 128.8 (d, *J* = 9.8 Hz), 52.4, 28.8 (d, *J* = 64.1 Hz), 21.4.**^{31}P NMR** (162 MHz, $CDCl_3$) δ = 29.4. **ATR-FTIR (cm^{-1}):** 3023, 2838, 1740, 1366, 1225, 991, 875, 597. **HR-MS** (ESI) $C_{20}H_{25}NO_4P$ $[M+H]^+$: 374.1516, found: 374.1513.

Methyl (E)-3-(di-o-tolylphosphoryl)-2-(hydroxyimino)propanoate (4f)



The general procedure 1 was followed using di-o-tolylphosphine oxide (138 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), methyl acrylate (17.2 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4f** as colorless oil (53.1 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.89 (s, 1H), 7.89 – 7.84 (m, 2H), 7.43 – 7.39 (m, 2H), 7.32 – 7.25 (m, 2H), 7.21 – 7.14 (m, 2H), 4.06 (d, *J* = 14.4 Hz, 2H), 3.47 (s, 3H), 2.23 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.3 (d, *J* = 2.2 Hz), 142.4 (d, *J* = 8.8 Hz), 141.9 (d, *J* = 9.3 Hz), 132.3, 132.2 (d, *J* = 9.0 Hz), 131.8 (d, *J* = 11.0 Hz), 130.8 (d, *J* = 100.3 Hz), 125.9 (d, *J* = 12.2 Hz), 52.5, 26.8 (d, *J* = 65.4 Hz), 21.5 (d, *J* = 4.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.3. **ATR-FTIR (cm^{-1}):** 3459, 2790, 1776, 1435, 1295, 1123, 894, 797. **HR-MS** (ESI) $C_{18}H_{21}NO_4P$ $[M+H]^+$: 346.1203, found: 346.1198.

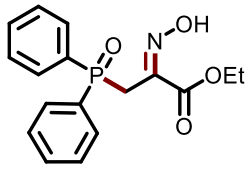
Methyl (E)-3-(di(naphthalen-2-yl)phosphoryl)-2-(hydroxyimino)propanoate (4g)



The general procedure 1 was followed using di(naphthalen-2-yl)phosphine oxide(181 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), methyl acrylate (17.2 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4g** as colorless oil (58.4 mg, 70% yield) **^{1}H NMR** (400 MHz, $CDCl_3$): δ =13.18 (s, 1H), 8.51 (d, *J* = 13.9 Hz, 2H), 7.94 – 7.85 (m, 6H), 7.82 (d, *J* = 10.2 Hz, 2H), 7.64 – 7.45 (m, 4H), 4.14 (d, *J* = 14.6 Hz, 2H), 3.49 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.5 (d, *J* = 2.6 Hz), 142.7 (d, *J* = 9.9 Hz), 134.8 (d, *J* = 2.5 Hz), 133.4 (d, *J* = 9.0 Hz), 132.5 (d, *J* = 13.2 Hz), 129.2, 129.1 (d, *J* = 103.6 Hz), 128.5, 128.3 (d, *J* = 5.8 Hz), 127.8, 126.9, 125.9 (d, *J* = 11.1 Hz), 52.4, 28.6

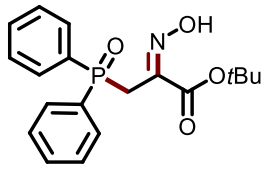
(d, J = 64.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 29.4. **ATR-FTIR (cm^{-1}):** 3302, 2947, 1961, 1864, 1567, 1221, 1055, 940. **HR-MS** (ESI) $C_{24}H_{21}NO_4P[M+H]^+$: 418.1203, found: 418.1205.

Ethyl (E)-3-(diphenylphosphoryl)-2-(hydroxyimino)propanoate (4h)[1]



The general procedure 1 was followed using diphenylphosphine oxide (121 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), ethyl acrylate (20.0 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4h** as colorless oil (53.6 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 13.07 (s, 1H), 7.86 – 7.81 (m, 4H), 7.53 – 7.5 (m, 2H), 7.45 – 7.42 (m , 4H), 4.08 – 4.03 (m, 2H), 3.93 (d, J = 14.9 Hz, 2H), 1.14 (t, J = 7.1 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.0 (d, J = 2.6 Hz), 142.8 (d, J = 9.7 Hz), 132.0 (d, J = 102.8 Hz),132.2 (d, J = 2.8 Hz), 131.3 (d, J = 9.9 Hz), 128.6 (d, J = 12.4 Hz), 61.7, 28.7 (d, J = 64.9 Hz), 14.2. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.3. **ATR-FTIR (cm^{-1}):** 3044, 2979, 1661, 1535, 1371, 1298, 1002, 898. **HR-MS** (ESI) $C_{17}H_{19}NO_4P$ $[M+H]^+$: 332.1046, found: 332.1047.

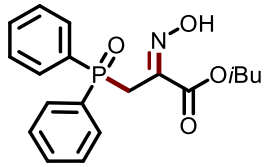
Tert-butyl (E)-3-(diphenylphosphoryl)-2-(hydroxyimino)propanoate (4i)



The general procedure 1 was followed using diphenylphosphine oxide (121.0 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), tert-butyl acrylate (25.6 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4i** as colorless oil (55.3 mg, 77% yield) **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 11.88 (s, 1H), 7.85 (m, 4H), 7.60 – 7.38 (m, 6H), 3.91 (d, J = 15.2 Hz, 2H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.8 (d, J =

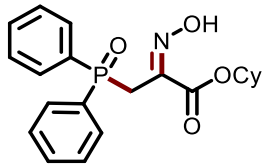
2.2 Hz), 144.6 (d, *J* = 10.8 Hz), 132.3 (d, *J* = 102.4 Hz), 132.1 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 9.8 Hz), 128.7 (d, *J* = 12.3 Hz), 82.5, 28.8 (d, *J* = 64.7 Hz), 28.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 28.7. **ATR-FTIR (cm^{-1}):** 3268, 2997, 1936, 1568, 1414, 1274, 998, 731. **HR-MS** (ESI) $C_{19}H_{23}NO_4P$ $[M+H]^+$: 360.1359, found: 360.1359.

Isobutyl (E)-3-(diphenylphosphoryl)-2-(hydroxyimino)propanoate (4j)



The general procedure 1 was followed using diphenylphosphine oxide (157.0 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), isobutyl acrylate (17.2 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4j** as colorless oil (60.3 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.92 (s, 1H), 7.87 – 7.82 (m, 4H), 7.54 – 7.50 (m, 2H), 7.48 – 7.42 (m, 4H), 3.94 (d, *J* = 15.0 Hz, 2H), 3.80-3.78 (m, 2H), 1.94 – 1.74 (m, 1H), 0.83 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.1 (d, *J* = 2.6 Hz), 142.9 (d, *J* = 9.7 Hz), 132.2 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 102.9 Hz), 131.3 (d, *J* = 9.9 Hz), 128.7 (d, *J* = 12.4 Hz), 71.7, 28.9 (d, *J* = 64.7 Hz), 27.7, 19.2. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.2. **ATR-FTIR (cm^{-1}):** 3125, 2955, 1947, 1661, 1465, 1375, 829, 772. **HR-MS** (ESI) $C_{19}H_{23}NO_4P$ $[M+H]^+$: 360.1359, found: 360.1360.

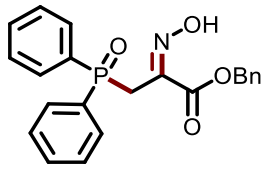
Cyclohexyl (E)-3-(diphenylphosphoryl)-2-(hydroxyimino)propanoate (4k)



The general procedure 1 was followed using diphenylphosphine oxide (121.0 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), cyclohexyl acrylate (30.8 mg, 0.2mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4k** as colorless oil (61.7 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.30 (s, 1H), 7.87-7.82 (m, 4H), 7.56 – 7.50

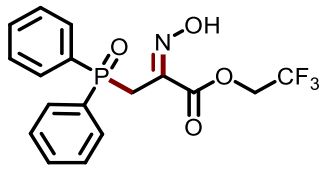
(m, 2H), 7.48 – 7.43 (m, 4H), 4.68 – 4.64 (m, 1H), 3.95 – 3.92 (m, 2H), 1.80 (s, 2H), 1.77 – 1.63 (m, 4H), 1.42 – 1.25 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.4, 143.6, 132.19 (d, J = 2.8 Hz), 132.22 (d, J = 102.1 Hz), 131.4 (d, J = 9.9 Hz), 128.7 (d, J = 12.4 Hz), 74.8, 31.5, 29.0 (d, J = 64.9 Hz), 25.4, 24.0. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.1. **ATR-FTIR (cm^{-1}):** 3300, 2871, 1756, 1472, 1311, 994, 857, 772. **HR-MS** (ESI) $C_{21}H_{25}NO_4P$ $[M+H]^+$: 386.1516, found:386.1519.

Benzyl (E)-3-(diphenylphosphoryl)-2-(hydroxyimino)propanoate (4l)



The general procedure 1 was followed using diphenylphosphine oxide (121.0 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), benzyl acrylate(32.4 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4l** as colorless oil (56.6 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.95 (s, 1H), 7.88 – 7.75 (m, 4H), 7.49 – 7.45 (m, Hz, 2H), 7.38 – 7.34 (m, 4H), 7.33 – 7.26 (m, 5H), 5.06 (s, 2H), 3.93 (d, J = 14.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.8 (d, J = 2.6 Hz), 142.6 (d, J = 9.8 Hz), 135.5, 132.0 (d, J = 2.8 Hz), 131.9 (d, J = 103.1 Hz),131.2 (d, J = 10.0 Hz), 128.6, 128.5 (d, J = 3.9 Hz), 128.3, 128.2, 67.11, 28.77 (d, J = 64.7 Hz).**^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.2. **ATR-FTIR (cm^{-1}):** 3256, 2842, 1792, 1398, 1205, 874, 769, 704. **HR-MS** (ESI) $C_{22}H_{21}NO_4P$ $[M+H]^+$: 394.1203, found: 394.1197.

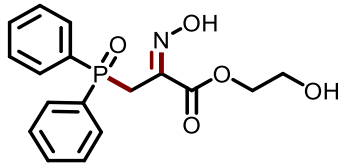
2,2,2-Trifluoroethyl (E)-3-(diphenylphosphoryl)-2-(hydroxyimino)propanoate (4m)



The general procedure 1 was followed using diphenylphosphine oxide (121.0 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), 2,2,2-trifluoroethyl acrylate (31.0

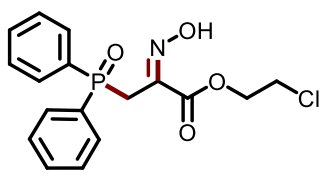
mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4m** as colorless oil (56.2 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 13.53 (s, 1H), 7.89 – 7.77 (m, 4H), 7.58 – 7.53(m, 2H), 7.50 – 7.45 (m, 4H), 4.40 – 4.34 (m, 2H), 3.94 (d, *J* = 14.5 Hz, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.7 (d, *J* = 2.6 Hz), 141.3 (d, *J* = 9.8 Hz), 132.5 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 103.5 Hz), 131.3 (d, *J* = 9.9 Hz), 128.8 (d, *J* = 12.3 Hz), 122.8 (d, *J* = 277.5 Hz), 61.0 (q, *J* = 36.9 Hz), 28.8 (d, *J* = 64.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -73.3. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.4. **ATR-FTIR (cm^{-1}):** 3295, 2875, 1927, 1442, 1367, 1109, 962, 812. **HR-MS** (ESI) $C_{17}H_{16}F_3NO_4P$ $[M+H]^+$: 386.0764, found: 386.0760.

2-hydroxyethyl (E)-3-(diphenylphosphoryl)-2-(hydroxyimino)propanoate (4n)



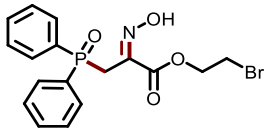
The general procedure 1 was followed using diphenylphosphine oxide (121.0 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), 2-hydroxyethyl acrylate (23.1 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 10/1) to obtain **4n** as colorless oil (49.3 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.43 (s, 1H), 7.84 – 7.70 (m, 4H), 7.49 – 7.42 (m, 2H), 7.39 – 7.37(m, 4H), 5.36 (s, 1H), 4.27 – 4.11 (m, 2H), 3.88 (d, *J* = 14.9 Hz, 2H), 3.76 – 3.59 (m, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.9, 143.6 (d, *J* = 9.3 Hz), 132.4 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 102.9 Hz), 128.7 (d, *J* = 12.2 Hz), 67.7, 60.1, 28.5 (d, *J* = 64.6 Hz).**^{31}P NMR** (162 MHz, $CDCl_3$): δ = 30.1. **ATR-FTIR (cm^{-1}):** 3359, 2996, 2362, 1865, 1312, 1247, 1129, 883. **HR-MS** (ESI) $C_{17}H_{19}NO_5P$ $[M+H]^+$: 348.0995, found: 348.0992.

2-chloroethyl (E)-3-(diphenylphosphoryl)-2-(hydroxyimino)propanoate (4o)



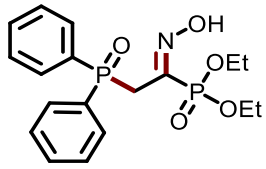
The general procedure 1 was followed using diphenylphosphine oxide (121.0 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), 2-chloroethyl acrylate (26.8 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4o** as colorless oil (43.8 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 13.13 (s, 1H), 7.87 – 7.81 (m, 4H), 7.54 – 7.51 (m, 2H), 7.49 – 7.44 (m, 4H), 4.24 (t, *J* = 6.1 Hz, 2H), 3.93 (d, *J* = 14.7 Hz, 2H), 3.51 (t, *J* = 6.2 Hz, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.3, 142.2 (d, J = 9.8 Hz), 132.3, 132.1 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 9.7 Hz), 128.6 (d, *J* = 12.3 Hz), 64.7, 40.7, 28.6 (d, *J* = 64.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.1. **ATR-FTIR (cm^{-1}):** 3023, 2901, 1973, 1882, 1569, 1241, 956, 872. **HR-MS** (ESI) $C_{17}H_{17}ClNO_4P$ $[M+H]^+$: 366.0656, found:366.0656.

2-Bromoethyl (E)-2-(diphenylphosphoryl)-3-(hydroxyimino)propanoate (4p)



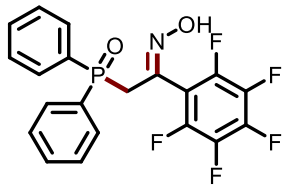
The general procedure 1 was followed using diphenylphosphine oxide (121.0 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), 2-bromoethyl acrylate (35.6 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4p** as colorless oil (59.9 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 13.22 (s, 1H), 7.86 – 7.80 (m, 4H), 7.56 – 7.51 (m, 2H), 7.49 – 7.44 (m, 4H), 4.27 (t, *J* = 6.7 Hz, 2H), 3.93 (d, *J* = 14.7 Hz, 2H), 3.31 (t, *J* = 6.7 Hz, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.3 (d, *J* = 2.5 Hz), 142.3 (d, *J* = 9.8 Hz), 132.3 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 103.2 Hz), 131.3 (d, *J* = 9.8 Hz), 128.7 (d, *J* = 12.3 Hz), 64.7, 28.7 (d, *J* = 64.6 Hz), 27.9. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = 29.4. **ATR-FTIR (cm^{-1}):** 3248, 2796, 1922, 1658, 1561, 1347, 1207, 991. **HR-MS** (ESI) $C_{16}H_{16}BrNO_4P$ $[M+H]^+$: 410.0151, found: 410.0153.

Diethyl (Z)-(2-(diphenylphosphoryl)-1-(hydroxyimino)ethyl)phosphonate (4q)



The general procedure 1 was followed using diphenylphosphine oxide (157.0 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), diethyl vinylphosphonate (32.8 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4q** as colorless oil (59.3 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 13.14 (s, 1H), 7.93 – 7.81 (m, 4H), 7.57 – 7.49 (m, 2H), 7.49 – 7.41 (m, 4H), 4.06 – 3.88 (m, 4H), 3.85 – 3.79 (m, 2H), 1.19 – 1.15 (m, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 144.7 (d, J = 10.6 Hz), 142.5 (d, J = 10.3 Hz), 132.9 (d, J = 103.1 Hz), 132.1 (d, J = 2.8 Hz), 131.3 (d, J = 9.9 Hz), 128.7 (d, J = 12.2 Hz), 63.3 (d, J = 6.1 Hz), 30.2 (dd, J = 63.9, 18.3 Hz), 16.2 (d, J = 6.5 Hz).**^{31}P NMR** (162 MHz, $CDCl_3$) δ = 28.7, 9.2. **ATR-FTIR (cm^{-1}):** 3062, 2991, 2364, 1584, 1336, 1270, 774, 720. **HR-MS** (ESI) $C_{18}H_{24}NO_5P_2$ $[M+H]^+$: 396.1124, found: 396.1133.

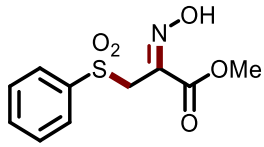
(E)-(2-(hydroxyimino)-2-(perfluorophenyl)ethyl)diphenylphosphine oxide (4r)



The general procedure 1 was followed using diphenylphosphine oxide (121.0 mg, 0.6 mmol), 4-nitrosomorpholine (70.0 mg, 0.6 mmol), 1,2,3,4,5-pentafluoro-6-vinylbenzene (39.0 mg, 0.2 mmol), and 2-methylpropan-2-ol (1.0 mL), and was purified by silica gel column chromatography (DCM/MeOH = 20/1) to obtain **4r** as colorless oil (58.7 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 11.28 (s, 1H), 7.77 – 7.68 (m, 4H), 7.54 – 7.45 (m, 2H), 7.42 – 7.37 (m, 4H), 4.00 (d, J = 14.3 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 171.5, 138.8, 132.4 (d, J = 2.7 Hz), 131.6 (d, J = 102.3 Hz), 131.0 (d, J = 9.8 Hz), 128.7 (d, J = 12.3 Hz), 31.0 (d, J = 65.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -139.9, -148.0, -160.0. **^{31}P NMR** (162 MHz, $CDCl_3$): δ

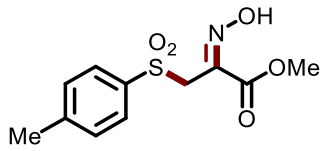
= 28.0. **ATR-FTIR (cm^{-1}):** 3069, 2900, 1892, 1311, 1255, 874, 796, 710. **HR-MS** (ESI) $C_{20}H_{14}F_5NO_2P[M+H]^+$: 426.0677, found: 426.0679.

Methyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6a)



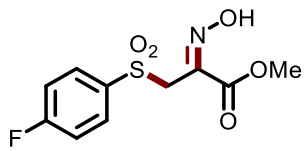
The general procedure 2 was followed using sodium benzenesulfinate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), methyl acrylate (17.2 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain **6a** as colorless oil (41.2 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.01 (s, 1H), 7.93 – 7.87 (m, 2H), 7.67 – 7.63 (m, 1H), 7.56 – 7.53 (m, 2H), 4.59 (s, 2H), 3.75 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.6, 141.3, 139.5, 134.3, 129.3, 128.4, 53.3, 51.5. **ATR-FTIR (cm^{-1}):** 3331, 2279, 1864, 1556, 1355, 1137, 1005, 887. **HR-MS** (ESI) $C_{10}H_{12}NO_5S$ $[M+H]^+$: 258.0431, found: 258.0431.

Methyl (E)-2-(hydroxyimino)-3-tosylpropanoate (6b)[2]



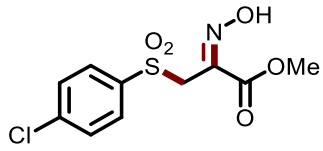
The general procedure 2 was followed using S-phenyl 4-methylbenzenesulfonothioate (159.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), methyl acrylate (17.2 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain **6b** as colorless oil (45.0 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 4.58 (s, 2H), 3.77 (t, J = 1.0 Hz, 3H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.7, 145.4, 141.7, 136.7, 130.0, 128.5, 53.3, 51.6, 21.8. **ATR-FTIR (cm^{-1}):** 3225, 2980, 1782, 1641, 1355, 1027, 997, 812. **HR-MS** (ESI) $C_{11}H_{14}NO_5S$ $[M+H]^+$: 272.0587, found: 272.0585.

Methyl (E)-3-((4-fluorophenyl)sulfonyl)-2-(hydroxyimino)propanoate (6c)



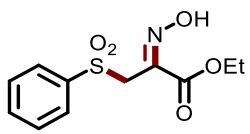
The general procedure 2 was followed using S-phenyl 4-fluorobenzenesulfonothioate (160.8 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), methyl acrylate (17.2 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain **6c** as colorless oil (45.1 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.04 – 7.76 (m, 2H), 7.25 – 7.19 (m, 2H), 4.59 (s, 2H), 3.79 (d, J = 0.9 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 166.3 (d, J = 257.1 Hz), 162.7, 141.4, 135.6 (d, J = 3.0 Hz), 131.5 (d, J = 9.8 Hz), 116.7 (d, J = 22.8 Hz), 53.5, 51.7. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -102.6. **ATR-FTIR (cm^{-1}):** 3307, 2957, 1980, 1755, 1623, 1447, 1057, 847. **HR-MS** (ESI) $C_{10}H_{11}FNO_5S$ $[M+H]^+$: 276.0336, found: 276.0337.

Methyl (E)-3-((4-chlorophenyl)sulfonyl)-2-(hydroxyimino)propanoate (6d)



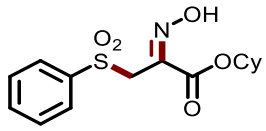
The general procedure 2 was followed using S-phenyl 4-chlorobenzenesulfonothioate (171.0mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), methyl acrylate (17.2 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain **6d** as colorless oil (47.1 mg, 81% yield) **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.47 (s, 1H), 7.84 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 4.60 (s, 2H), 3.82 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.4, 141.5, 141.0, 137.9, 129.9, 129.5, 53.4, 51.4. **ATR-FTIR (cm^{-1}):** 3047, 2767, 1929, 1623, 1544, 1277, 1002, 774. **HR-MS** (ESI) $C_{10}H_{11}ClNO_5S$ $[M+H]^+$: 292.0041, found: 292.0041.

Ethyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6e)



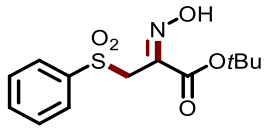
The general procedure 2 was followed using S-phenyl benzenesulfonothioate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), ethyl acrylate (20 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain **6e** as colorless oil (42.3 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.05 (s, 1H), 7.93 – 7.91 (m, 2H), 7.68 – 7.65 (m, 1H), 7.58 – 7.54 (m, 2H), 4.61 (s, 2H), 4.25 – 4.20 (m, 2H), 1.30 – 1.27 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.1, 141.6, 139.6, 134.2, 129.3, 128.5, 62.8, 51.5, 14.1. **ATR-FTIR (cm^{-1}):** 3185, 2462, 1980, 1773, 1596, 1244, 1129, 990. **HR-MS** (ESI) $C_{11}H_{14}NO_5S$ $[M+H]^+$: 272.0587, found: 272.0590.

Cyclohexyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6f)



The general procedure 2 was followed using sodium benzenesulfinate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), cyclohexyl acrylate (30.8 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **6f** as colorless oil (52.0 mg, 80% yield) **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.12 (s, 1H), 7.91 (d, J = 7.1 Hz, 2H), 7.68 – 7.64 (m, 1H), 7.59 – 7.46 (m, 2H), 4.86 – 4.80 (m, 1H), 4.60 (s, 2H), 1.87 – 1.73 (m, 4H), 1.58 – 1.22 (m, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 161.5, 141.8, 139.7, 134.2, 129.4, 128.5, 75.8, 51.6, 31.4, 25.3, 23.8. **ATR-FTIR (cm^{-1}):** 3205, 2847, 1772, 1651, 1549, 1263, 1180, 921. **HR-MS** (ESI) $C_{15}H_{20}NO_5S$ $[M+H]^+$: 326.1057, found:326.1049.

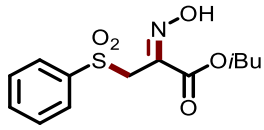
Tert-butyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6g)



The general procedure 2 was followed using S-phenyl benzenesulfonothioate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), tert-butyl acrylate (25.7 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **6g** as colorless oil (44.9 mg, 75% yield).

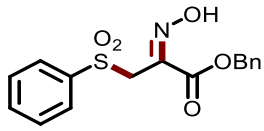
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.56–7.52 (m, 2H), 4.56 (s, 2H), 1.50–1.28 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 160.8, 142.3, 139.7, 134.2, 129.3, 128.5, 84.1, 51.4, 27.9. **ATR-FTIR (cm^{-1}):** 3209, 2980, 1944, 1722, 1623, 1472, 1330, 1024. **HR-MS** (ESI) $C_{13}H_{18}NO_5S$ $[M+H]^+$: 300.0900, found: 300.0908.

Isobutyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6h)



The general procedure 2 was followed using S-phenyl benzenesulfonothioate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), isobutyl acrylate (25.6 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **6 h** as colorless oil (45.4 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 9.50 (s, 1H), 7.97 – 7.86 (m, 2H), 7.73 – 7.62 (m, 1H), 7.55 (m, 2H), 4.60 (s, 2H), 3.97 (m, 2H), 1.98 (m, 1H), 0.95 m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 162.1, 142.0, 139.5, 134.2, 129.3, 128.5, 51.6, 27.8, 19.2. **ATR-FTIR (cm^{-1}):** 3030, 2771, 1905, 1672, 1553, 1238, 1059, 956. **HR-MS** (ESI) $C_{13}H_{18}NO_5S$ $[M+H]^+$: 300.0900, found: 300.0901.

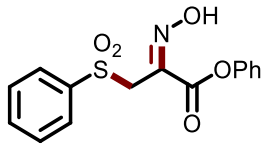
Benzyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6i)



The general procedure 2 was followed using S-phenyl benzenesulfonothioate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), benzyl acrylate (32.4 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **6i** as colorless oil (44.9 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 7.96 – 7.80 (m, 2H), 7.65 – 7.56 (m, 1H), 7.47 (m, 2H), 7.35 (m, 5H), 5.17 (s, 2H), 4.56 (s, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 162.0, 141.4, 139.5, 134.8, 134.3, 129.3, 128.9, 128.8, 128.4, 68.3, 51.6. **ATR-FTIR (cm^{-1}):** 3120, 2750, 1664, 1579, 1432, 1288, 1159, 836. **HR-MS** (ESI) $C_{16}H_{16}NO_5S$ $[M+H]^+$:

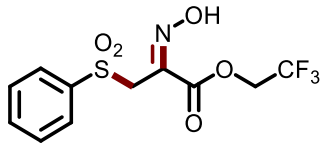
334.0744, found: 334.0749.

Phenyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6j)



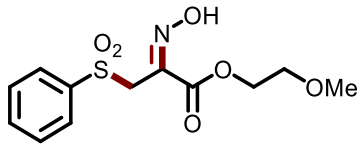
The general procedure 2 was followed using S-phenyl benzenesulfonothioate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), phenyl acrylate (30.0 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **6j** as colorless oil (43.4 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.68 (s, 1H), 8.04 – 7.87 (m, 2H), 7.72 – 7.60 (m, 1H), 7.52 (m, 2H), 7.38 (m, 2H), 7.27 (m, 1H), 7.07 (m, 2H), 4.68 (m , 2H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 161.0, 150.2, 141.2, 139.3, 134.4, 129.7, 129.5, 128.4, 126.6, 121.4, 51.6. **ATR-FTIR (cm^{-1}):** 3286, 2910, 1755, 1432, 1159, 752, 662, 574. **HR-MS** (ESI) $C_{15}H_{14}NO_5S$ $[M+H]^+$: 320.0587, found: 320.0589.

2,2,2-trifluoroethyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6k)



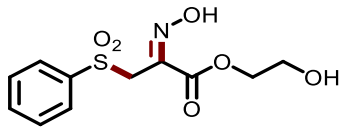
The general procedure 2 was followed using S-phenyl benzenesulfonothioate(150.0mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), 2,2,2-trifluoroethyl acrylate (31.0 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **6k** as colorless oil (48.1 mg, 74% yield) **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.51 (s, 0.5H), 7.96 – 7.89 (m, 2H), 7.75 – 7.64 (m, 1H), 7.58 – 7.55 (m, 2H), 4.65 – 4.50 (m, 4H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.7, 143.1 (d, J = 9.3 Hz), 138.3 (d, J = 12.9 Hz), 133.9 (d, J = 3.0 Hz), 132.1 (d, J = 102.0 Hz), 128.8 (d, J = 9.8 Hz), 52.4, 28.8 (d, J = 64.1 Hz), 21.4.**^{19}F NMR** (376 MHz, $CDCl_3$): δ = -73.5. **ATR-FTIR (cm^{-1}):** 3112, 2750, 1844, 1659, 1412, 1285, 1002, 993. **HR-MS** (ESI) $C_{11}H_{11}F_3NO_5S$ $[M+H]^+$: 326.0305, found: 326.0311.

2-methoxyethyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6l)



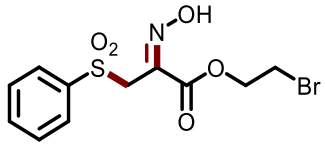
The general procedure 2 was followed using S-phenyl benzenesulfonothioate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), 2-methoxyethyl acrylate (26.0 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain **6l** as colorless oil (42.8 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): 10.70 (s, 1H), 7.97 – 7.85 (m, 2H), 7.67 – 7.63 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 4.60 (s, 2H), 4.33 – 4.22 (m, 2H), 3.69 – 3.60 (m, 2H), 3.38 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.2, 141.1, 139.7, 134.2, 129.3, 128.4, 70.0, 65.0, 59.0, 51.5. **ATR-FTIR (cm^{-1}):** 3127, 2865, 1856, 1725, 1328, 1025, 997, 834. **HR-MS** (ESI) $C_{12}H_{16}NO_6S$ $[M+H]^+$: 302.0693, found: 302.0687.

2-Hydroxyethyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6m)



The general procedure 2 was followed using S-phenyl benzenesulfonothioate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), 2-hydroxyethyl acrylate (23.0 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **6m** as colorless oil (41.4 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 11.47 (s, 1H), 7.95 – 7.86 (m, 2H), 7.72 – 7.62 (m, 1H), 7.55 (m, 2H), 4.61 (s, 2H), 4.32 – 4.22 (m, 2H), 3.89 – 3.79 (m, 2H), 2.82 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.2, 141.1, 139.4, 134.5, 129.5, 128.3, 68.0, 60.4, 51.6. **ATR-FTIR (cm^{-1}):** 3302, 2986, 1977, 1754, 1528, 1322, 1154, 1026. **HR-MS** (ESI) $C_{11}H_{14}NO_6S$ $[M+H]^+$: 288.0536, found: 288.0540.

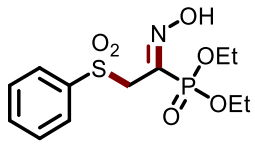
2-bromoethyl (E)-2-(hydroxyimino)-3-(phenylsulfonyl)propanoate (6n)



The general procedure 2 was followed using S-phenyl benzenesulfonothioate (150.0

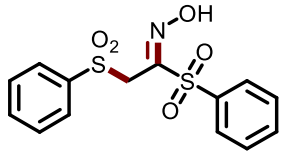
mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), 2-bromoethyl acrylate (35.6 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 1/1) to obtain **6n** as colorless oil (52.3 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 8.09 – 7.82 (m, 2H), 7.77 – 7.63 (m, 1H), 7.57 (m , 2H), 4.61 (s, 2H), 4.48 (m , 2H), 3.52 (m, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 161.6, 141.4, 139.5, 134.3, 129.4, 128.5, 65.6, 51.5, 27.9. **ATR-FTIR (cm^{-1}):** 3145, 2750, 1836, 1642, 1229, 1054, 992, 881. **HR-MS** (ESI) $C_{11}H_{13}BrNO_5S$ $[M+H]^+$: 349.9692, found:349.9692 .

Diethyl (Z)-(1-(hydroxyimino)-2-(phenylsulfonyl)ethyl)phosphonate (6o)



The general procedure 2 was followed using S-phenyl benzenesulfonothioate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), diethyl vinylphosphonate (23.0 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **6o** as colorless oil (43.6 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.94 (s, 1H), 8.02 – 7.91 (m, 2H), 7.70 – 7.60 (m, 1H), 7.54 (m, 2H), 4.46 (d, J = 12.3 Hz, 2H), 4.30 – 4.08 (m, 4H), 1.35 (t, J = 7.1 Hz, 7H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 143.9, 140.4, 134.1, 129.2, 128.4, 64.0, 63.9, 53.3, 53.1, 16.4, 16.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ = 7.0. **ATR-FTIR (cm^{-1}):** 3005, 2647, 1754, 1625, 1522, 1325, 1205, 1100. **HR-MS** (ESI) $C_{12}H_{19}NO_6SP$ $[M+H]^+$: 336.0665, found: 336.0667.

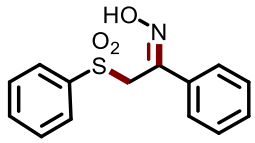
(Z)-1,2-bis(phenylsulfonyl)ethan-1-one oxime (6p)



The general procedure 2 was followed using S-phenyl benzenesulfonothioate (150.0 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), (vinylsulfonyl)benzene (33.6 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain **6p** as colorless oil (30.5 mg, 45%

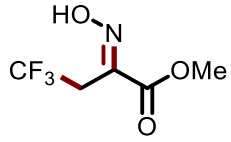
yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.36 (s, 1H), 8.04 – 7.97 (m, 2H), 7.88 – 7.82 (m, 2H), 7.74 – 7.64 (m, 2H), 7.56 (m, 4H), 4.66 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 152.1, 139.8, 137.7, 134.8, 134.6, 129.6, 129.5, 129.4, 128.5, 52.1. **ATR-FTIR (cm^{-1}):** 3112, 2870, 1625, 1442, 1256, 1102, 1007, 884. **HR-MS** (ESI) $C_{14}H_{14}NO_5S_2$ $[M+H]^+$: 340.0308, found: 340.0310.

(Z)-1-phenyl-2-(phenylsulfonyl)ethan-1-one oxime (6q)[2]



The general procedure 2 was followed using sodium benzenesulfinate (98.4 mg, 0.6 mmol), tert-butyl nitrite (165.0 mg, 1.6 mmol), styrene (20.8 mg, 0.2 mmol), and 2-methylpropan-2-ol (0.5 mL), and was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain **6q** as colorless oil (20.9 mg, 38% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = δ = 7.85 – 7.83 (m, 2H), 7.66 – 7.60 (m, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.41 – 7.32 (m, 3H), 4.75 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 148.1, 139.6, 134.0, 133.7, 130.2, 129.0, 128.8, 128.7, 126.8, 52.8. **ATR-FTIR (cm^{-1}):** 3105, 2871, 1654, 1446, 1239, 1100, 997, 853. **HR-MS** (ESI) $C_{14}H_{14}NO_3S$ $[M+H]^+$: 276.0689, found: 276.0683.

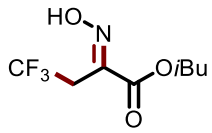
Methyl (Z)-4,4,4-trifluoro-2-(hydroxyimino)butanoate (8a)



The general procedure 3 was followed using sodium trifluoromethanesulfinate (93.3 mg, 0.6 mmol), tert-butyl nitrite (160.0 mg, 1.6 mmol), methyl acrylate (17.2 mg, 0.2 mmol), 2-methylpropan-2-ole (0.5 mL), and K_3PO_4 (84.8 mg, 0.4 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **8a** as colorless oil (26.7 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.84 (s, 1H), 3.91 (s, 3H), 3.60 (d, J = 10.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.0, 143.1, 124.2 (d, J = 278.2 Hz), 53.4, 29.4 (d, J = 32.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -62.4. **ATR-FTIR (cm^{-1}):** 3255, 2930, 1551, 1476, 1328, 1100, 896, 794. **HR-MS** (ESI)

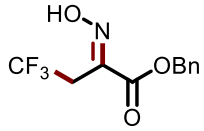
$C_5H_7F_3NO_3$ $[M+H]^+$: 186.0373, found: 186.0377.

Isobutyl (Z)-4,4,4-trifluoro-2-(hydroxyimino)butanoate (8b)[3]



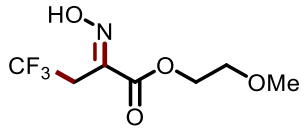
The general procedure 3 was followed using sodium trifluoromethanesulfinate (93.3 mg, 0.6 mmol), tert-butyl nitrite (160.0 mg, 1.6 mmol), isobutyl acrylate (25.6 mg, 0.2 mmol), 2-methylpropan-2-ole (0.5 mL), and K_3PO_4 (84.8 mg, 0.4 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **8c** as colorless oil (20.9 mg, 46% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.84 (s, 1H), 4.08 (d, J = 6.7 Hz, 2H), 3.60 – 3.55 (m, 2H), 0.97 (d, J = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.5, 142.7, 128.8 – 118.9 (m), 72.7, 29.4 (q, J = 32.4 Hz), 27.8, 19.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.3. **ATR-FTIR (cm^{-1}):** 3059, 2881, 1960, 1744, 1671, 1551, 1372, 996. **HR-MS** (ESI) $C_8H_{13}F_3NO_3$ $[M+H]^+$: 228.0842, found:228.0842 .

Benzyl (Z)-4,4,4-trifluoro-2-(hydroxyimino)butanoate (8c)



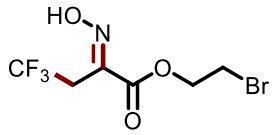
The general procedure 3 was followed using sodium trifluoromethanesulfinate (93.3 mg, 0.6 mmol), tert-butyl nitrite (160.0 mg, 1.6 mmol), benzyl acrylate (32.4 mg, 0.2 mmol), 2-methylpropan-2-ole (0.5 mL), and K_3PO_4 (84.8 mg, 0.4 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **8d** as colorless oil (18.8 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.39 (s, 1H), 7.40 – 77.26 (m, 5H), 5.31 (s, 2H), 3.59 – 3.52 (m, 2H). **^{13}C N**MR (101 MHz, $CDCl_3$): δ = 162.3, 142.7, 134.8, 129.1, 128.9, 128.8, 124.2 (d, J = 278.0 Hz), 68.4, 29.4 (q, J = 32.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.3. **ATR-FTIR (cm^{-1}):** 3271, 2997, 2368, 1697, 1528, 1427, 1334, 1265. **HR-MS** (ESI) $C_{11}H_{11}F_3NO_3$ $[M+H]^+$: 262.0686, found: 262.0688.

2-Methoxyethyl (Z)-4,4,4-trifluoro-2-(hydroxyimino)butanoate (8d)



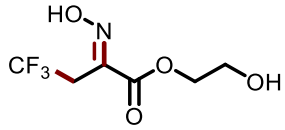
The general procedure 3 was followed using sodium trifluoromethanesulfinate (93.3 mg, 0.6 mmol), *tert*-butyl nitrite (160.0 mg, 1.6 mmol), 2-methoxyethyl acrylate (26.0 mg, 0.2 mmol), 2-methylpropan-2-ol (0.5 mL), and K_3PO_4 (84.8 mg, 0.40 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 2/1) to obtain **8b** as colorless oil (23.4 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.8 (s, 1H), 4.8 – 4.2 (m, 2H), 3.8 – 3.7 (m, 2H), 3.6 (q, J = 10.2 Hz, 2H), 3.4 (s, 3H). **^{13}C** N**MR** (101 MHz, $CDCl_3$): δ = 162.5, 142.3 (d, J = 2.5 Hz), 124.2 (q, J = 278.3 Hz), 70.1, 65.0, 59.0, 29.3 (q, J = 32.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.3. **ATR-FTIR (cm^{-1}):** 3258, 2910, 1773, 1641, 1596, 1238, 1160, 942. **HR-MS** (ESI) $C_7H_{11}F_3NO_3$ $[M+H]^+$: 230.0635, found: 230.0641.

2-Bromoethyl (Z)-4,4,4-trifluoro-2-(hydroxyimino)butanoate (8e)



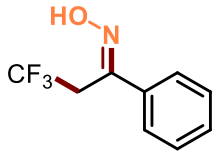
The general procedure 3 was followed using sodium trifluoromethanesulfinate (93.3 mg, 0.6 mmol), tert-butyl nitrite (160.0 mg, 1.6 mmol), 2-bromoethyl acrylate (35.6 mg, 0.2 mmol), 2-methylpropan-2-ole (0.5 mL), and K_3PO_4 (84.8 mg, 0.40 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **8e** as colorless oil (23.5 mg, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.12 (s, 1H), 4.62 – 4.59 (m, 2H), 3.89 – 3.35 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.0, 142.6, 124.1 (d, J = 278.4 Hz), 65.6, 30.4, 27.8. **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.3. **ATR-FTIR (cm^{-1}):** 3075, 2776, 1922, 1514, 1322, 1255, 1036, 997. **HR-MS** (ESI) $C_6H_8BrF_3NO_3$ $[M+H]^+$: 277.9634, found: 277.9635.

2-Hydroxyethyl (Z)-4,4,4-trifluoro-2-(hydroxyimino)butanoate(8f)



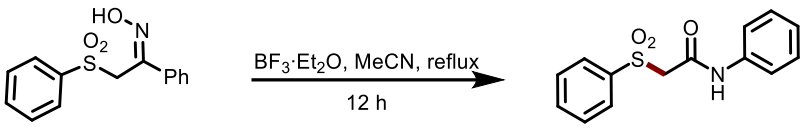
The general procedure 3 was followed using sodium trifluoromethanesulfinate (93.3 mg, 0.6 mmol), tert-butyl nitrite (160.0 mg, 1.6 mmol), 2-hydroxyethyl acrylate (25.6 mg, 0.2 mmol), 2-methylpropan-2-ole (0.5 mL), and K_3PO_4 (84.8 mg, 0.40 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 1/1) to obtain **8f** as colorless oil (15.7 mg, 35% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 11.08 (s, 1H), 4.41 – 4.39 (m, 2H), 3.9 – 3.92 (m, 2H), 3.64 – 3.56 (m, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.5, 142.8, 124.2 (d, J = 278.3 Hz), 67.8, 60.6, 32.9 – 25.6 (m). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -62.3. **ATR-FTIR (cm^{-1}):** 3017, 2912, 1963, 1845, 1533, 1227, 1008, 921. **HR-MS** (ESI) $C_6H_9F_3NO_4$ $[M+H]^+$: 216.0478, found:216.0479.

(E)-3,3,3-trifluoro-1-phenylpropan-1-one oxime (8g)[3]



The general procedure 3 was followed using sodium trifluoromethanesulfinate (93.3 mg, 0.6 mmol), tert-butyl nitrite (160.0 mg, 1.6 mmol), styrene (20.8 mg, 0.2 mmol), 2-methylpropan-2-ole (0.5 mL), and K_3PO_4 (84.8 mg, 0.40 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **8g** as colorless oil (18.7 mg, 46% yield). **^{1}H NMR** (400 MHz, DMSO-*d6*): δ = 11.14 (s, 1H), 6.88 – 6.86 (m, 2H), 6.57– 6.55 (m, 3H), 3.09 (q, J = 11.3 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*): δ = 146.9, 134.9, 129.2, 128.4, 126.0, 125.1 (d, J = 278.3 Hz), 28.7 (q, J = 29.9 Hz).**^{19}F NMR** (376 MHz, DMSO-*d6*): δ = -60.3. **ATR-FTIR (cm^{-1}):** 3028, 2900, 1872, 1673, 1455, 1369, 1215, 883. **HR-MS** (ESI) $C_9H_9F_3NO$ $[M+H]^+$: 204.0631, found: 204.0632.

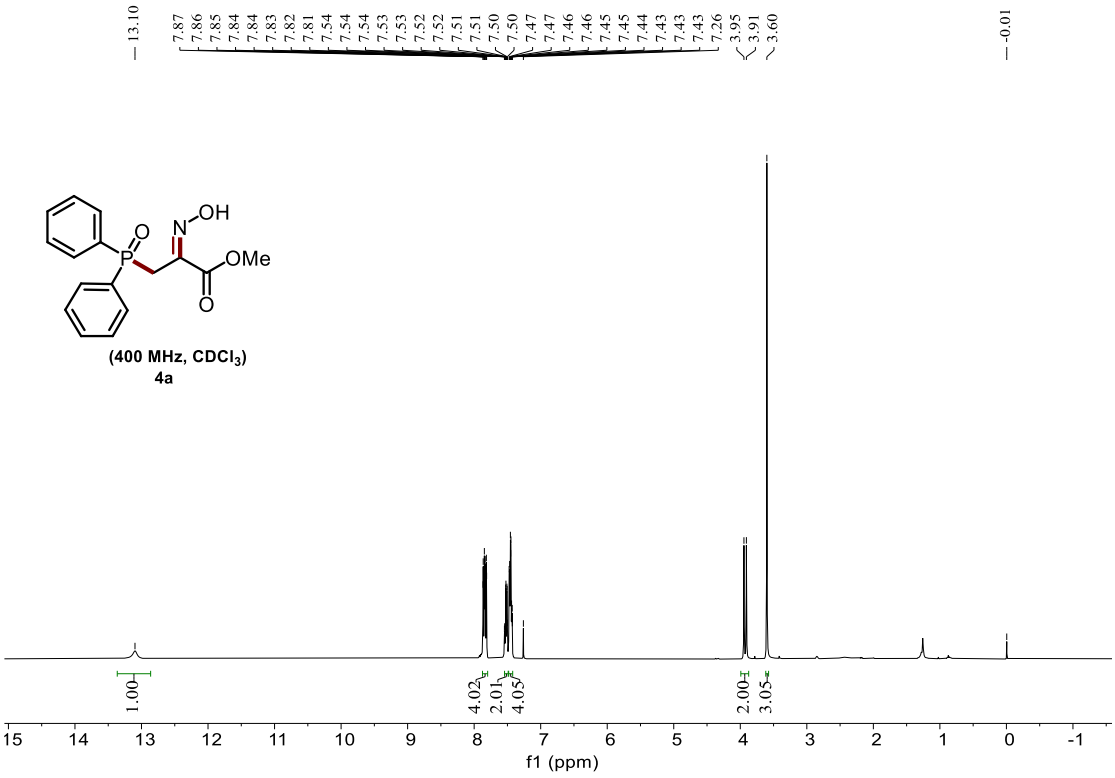
N-phenyl-2-(phenylsulfonyl)acetamide (9a)

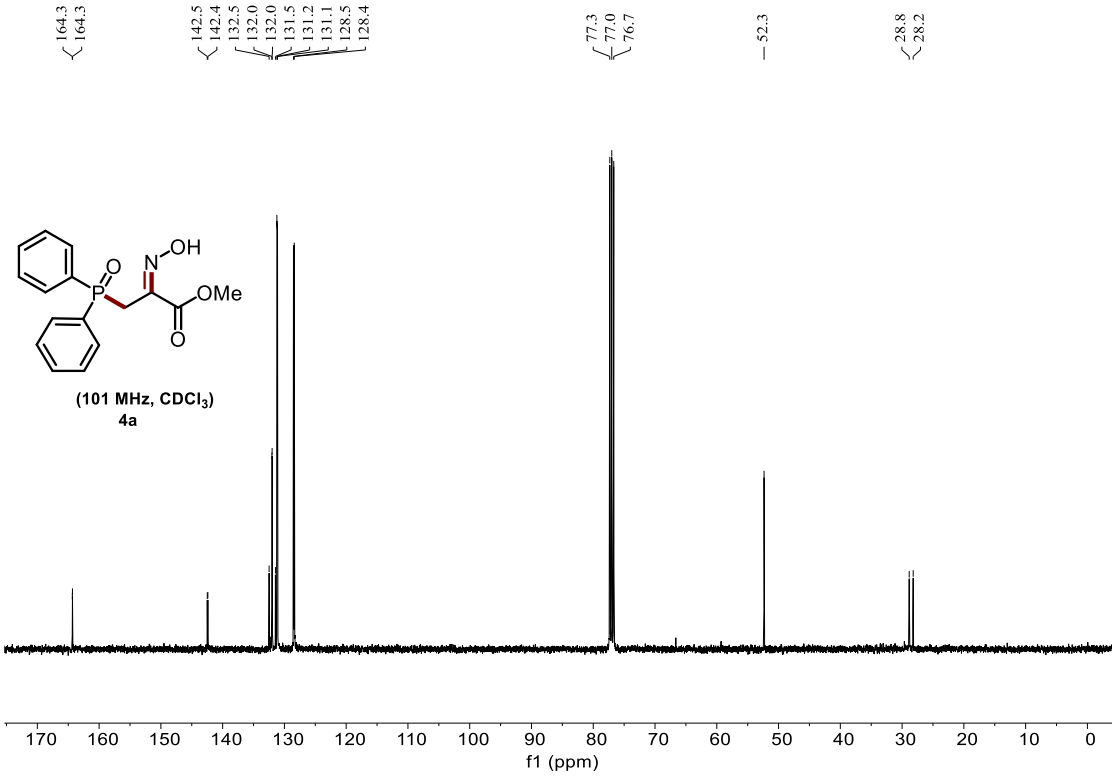


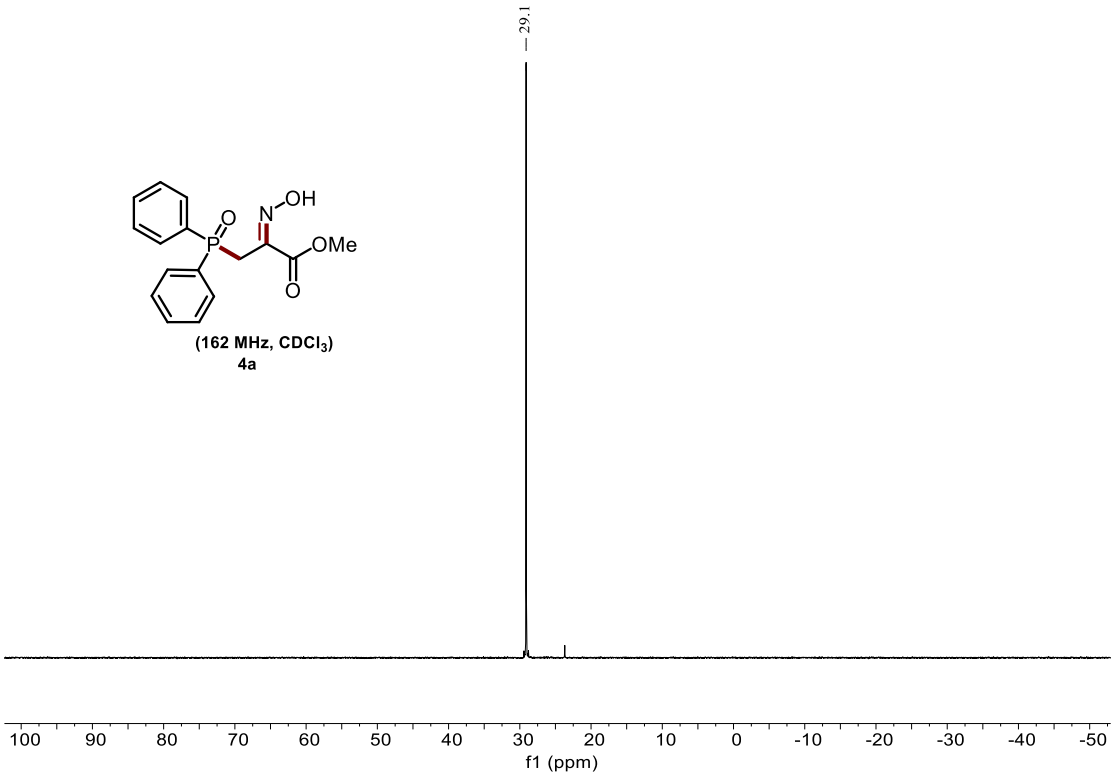
(*Z*)-1-phenyl-2-(phenylsulfonyl)ethan-1-one oxime (55.0 mg, 0.2 mmol, 1 equiv.), Boron trifluoride diethyl etherate (85.0 mg, 0.6 mmol, 3 equiv.) were dissolved in Acetonitrile(1.0 mL) and reflux for 12 h in an nitrogen atmosphere. The resulting mixture was concentrated under vacuum and the crude product was purified by silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent and 2-(diphenylphosphoryl)-1-phenylethan-1-one(253.0 mg, 92% yield) was isolated as colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 1H), 7.98 – 7.88 (m, 2H), 7.73 – 7.65 (m, 1H), 7.58 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.21 – 7.13 (m, 1H), 4.18 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 158.5, 137.9, 137.0, 134.6, 129.5, 129.1, 128.1, 125.2, 120.2, 62.9. **HR-MS** (ESI) $C_{14}H_{14}NO_3S$ $[M+H]^+$: 276.0689, found:276.0690.

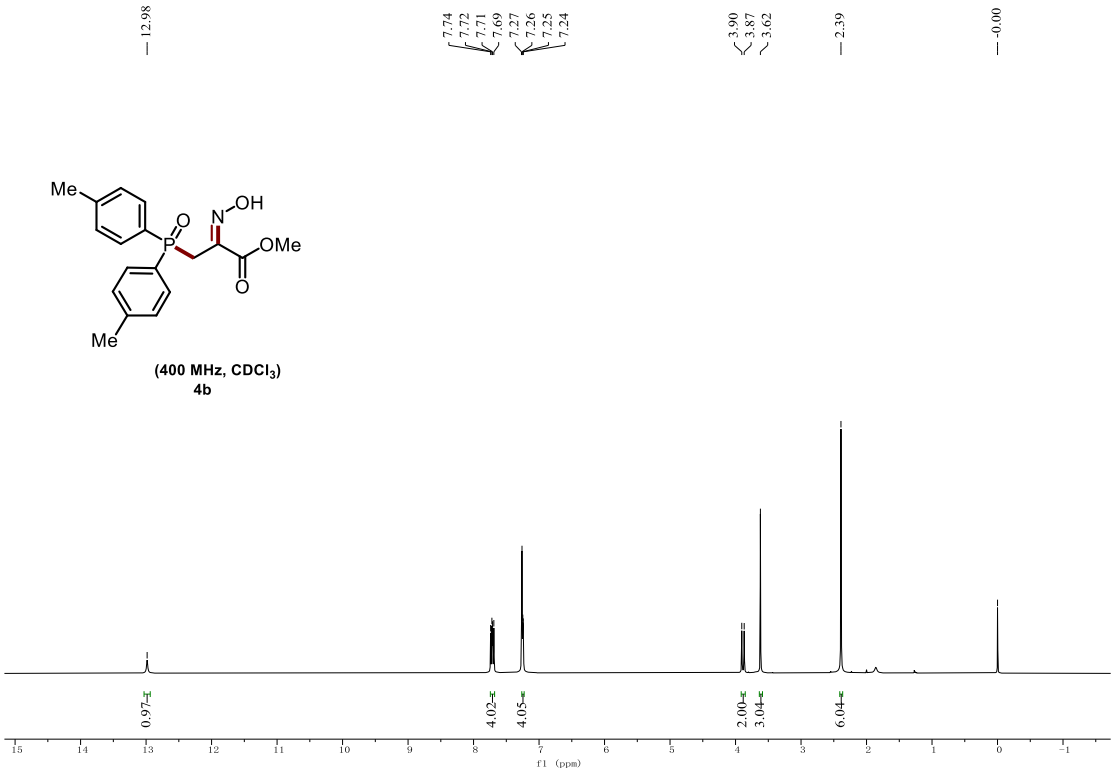
5. NMR Spectra



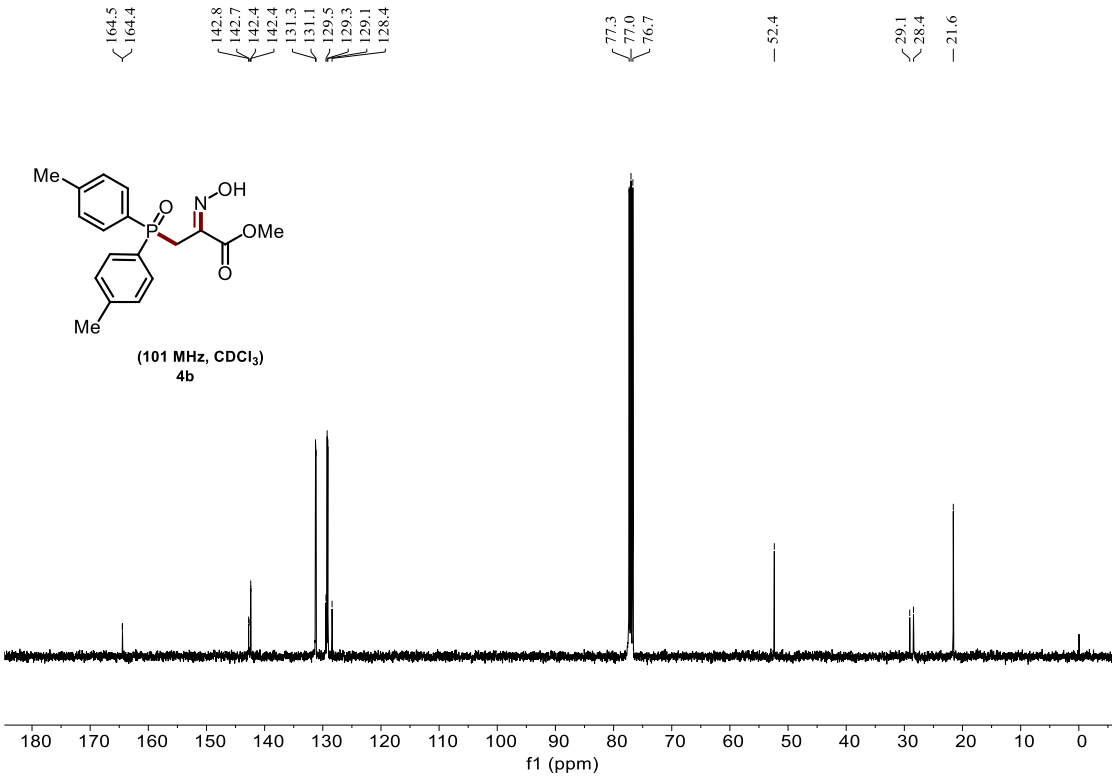


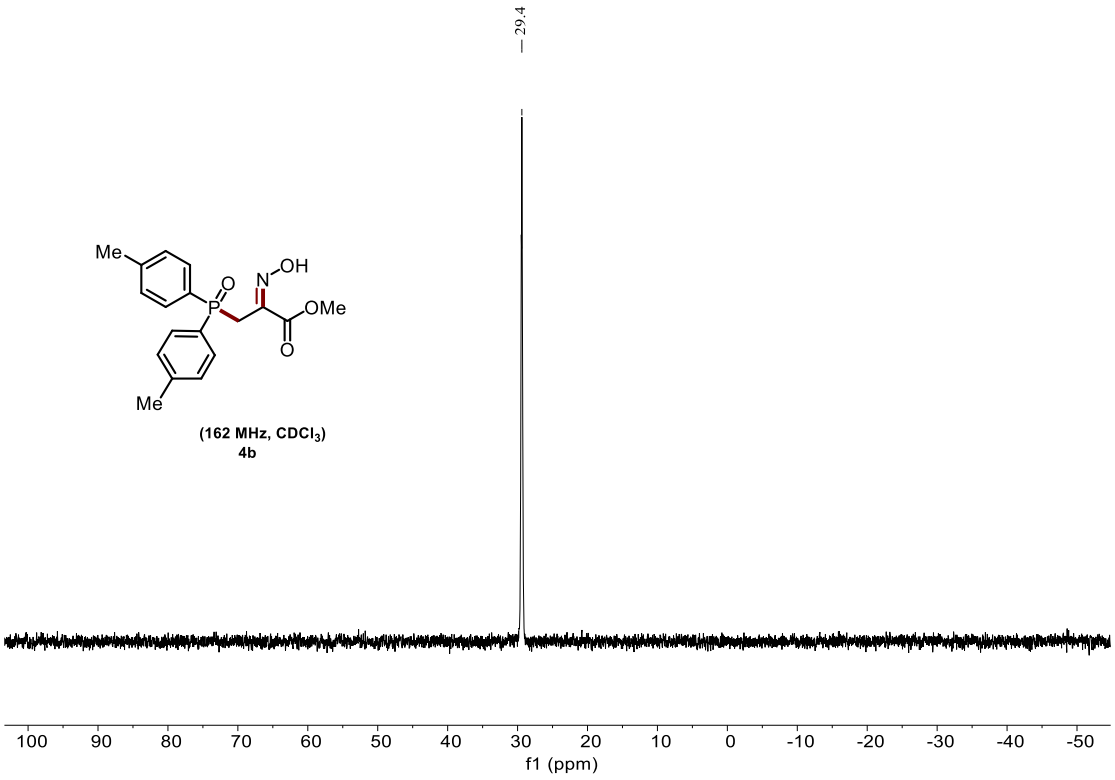


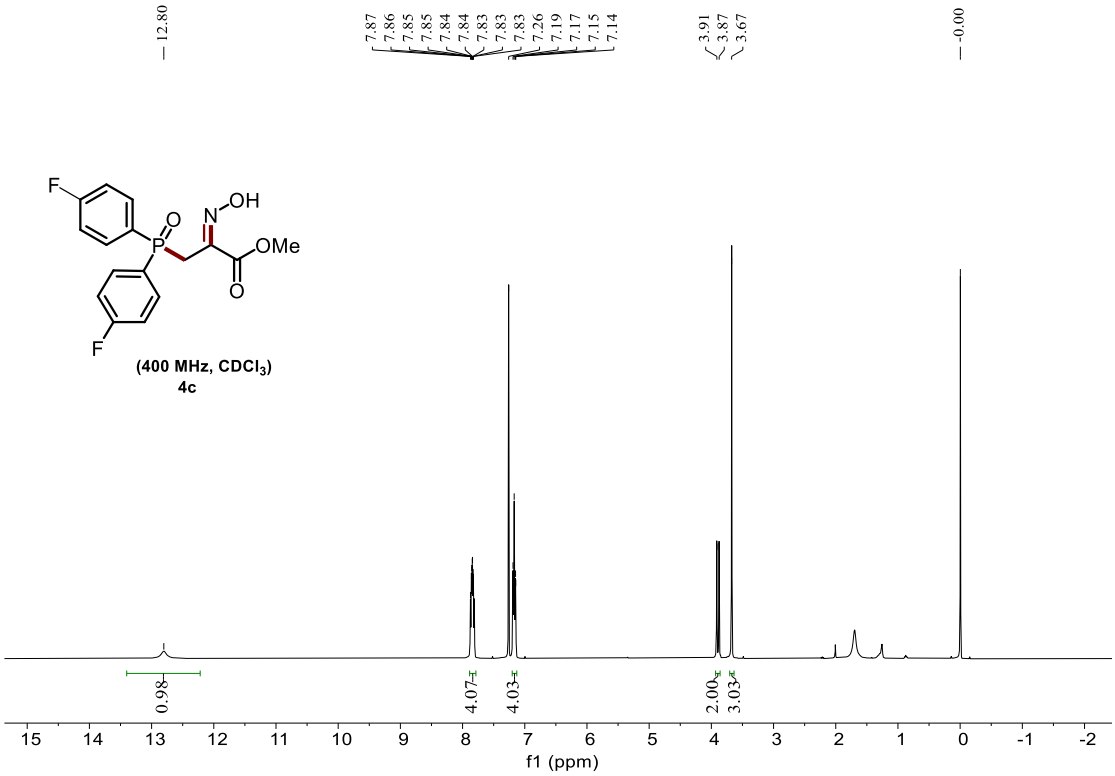
(162 MHz, $CDCl_3$)
4a

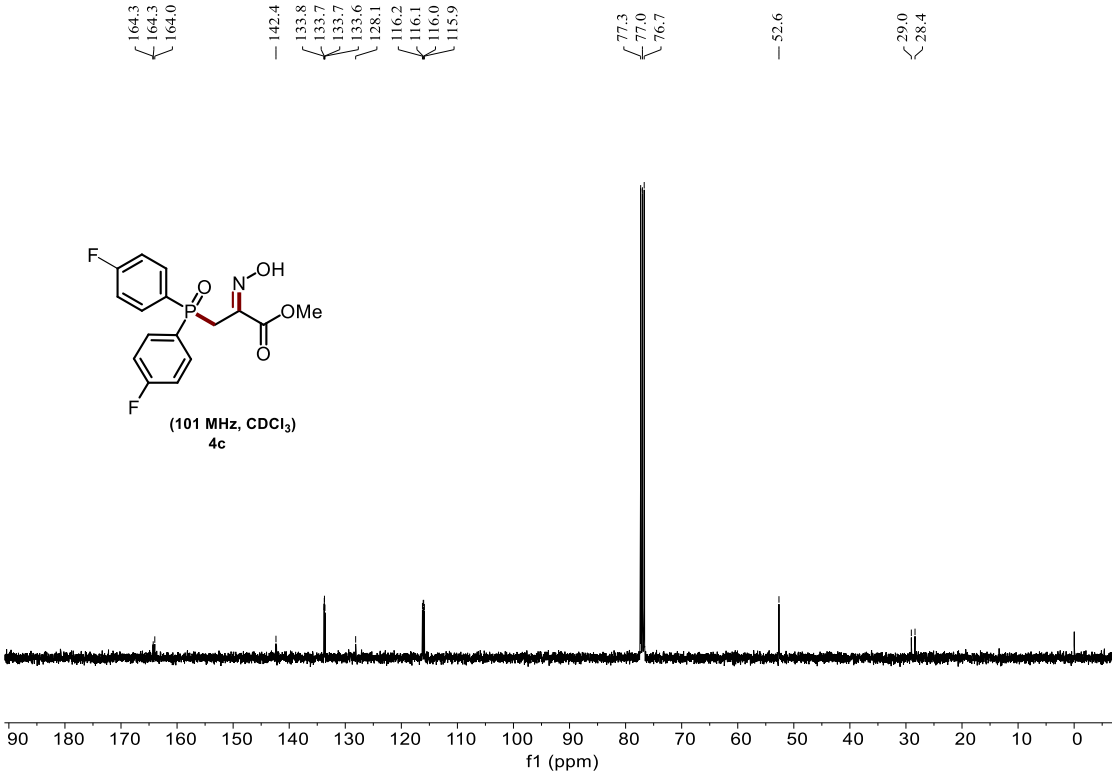


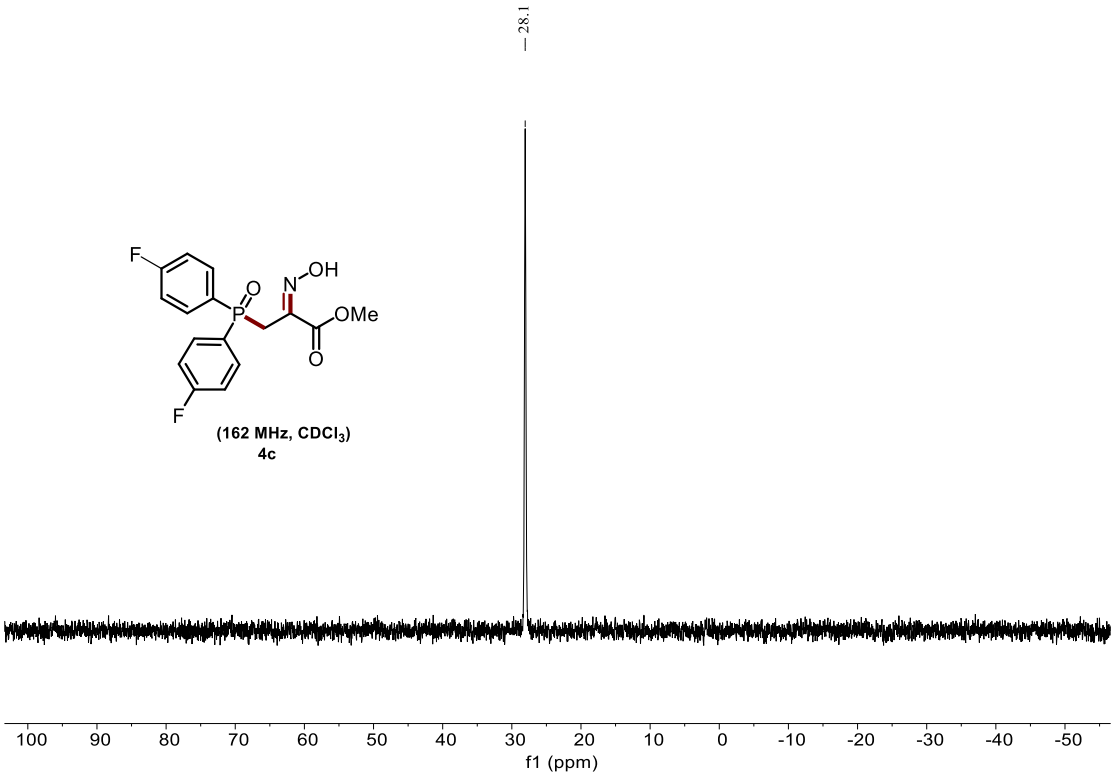
(400 MHz, $CDCl_3$)
4b


164.5
164.4
142.8
142.7
142.4
142.4
131.3
131.1
129.5
129.3
129.1
128.4
77.3
77.0
76.7
52.4
29.1
28.4
21.6
Me
N
OH
O
P
OMe
O
Me
(101 MHz, CDCl3)
4b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

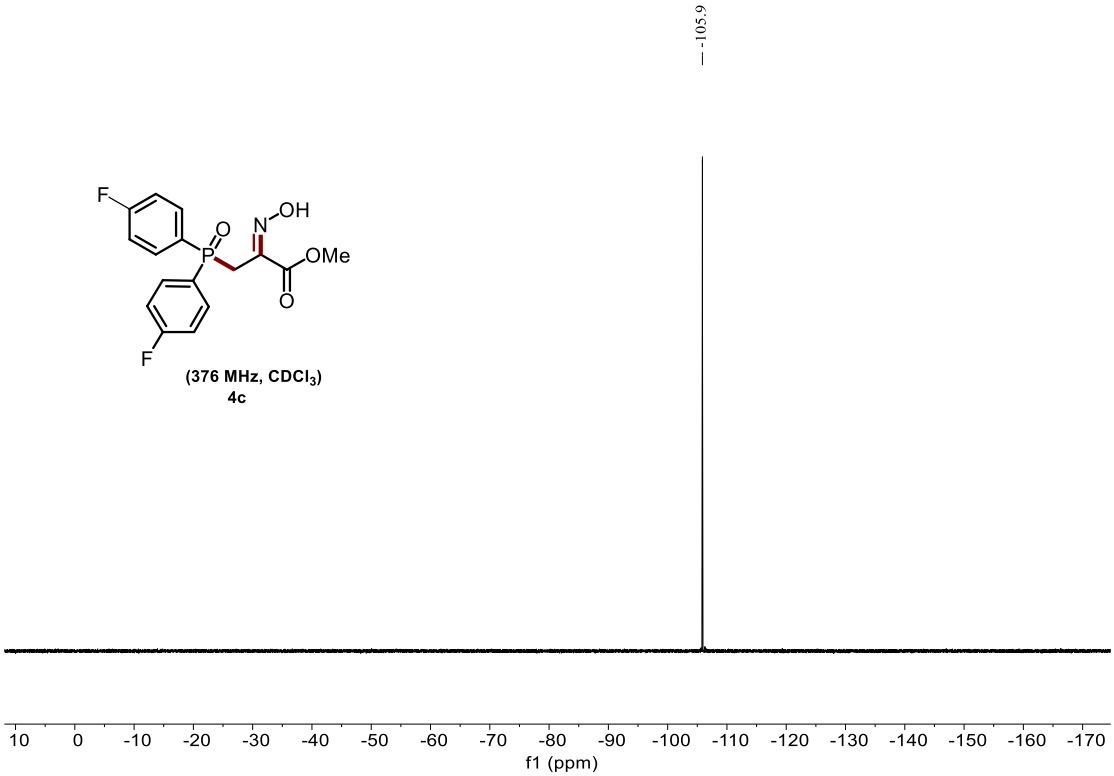

29.4
Me
N
OH
O
P
OMe
O
Me
(162 MHz, CDCl3)
4b
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)


12.80
7.87
7.86
7.85
7.85
7.84
7.84
7.83
7.83
7.83
7.26
7.19
7.17
7.15
7.14
3.91
3.87
3.67
-0.00
F
O
N
OH
P
OMe
O
F
(400 MHz, CDCl3)
4c
0.98
4.07
4.03
2.00
3.03
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

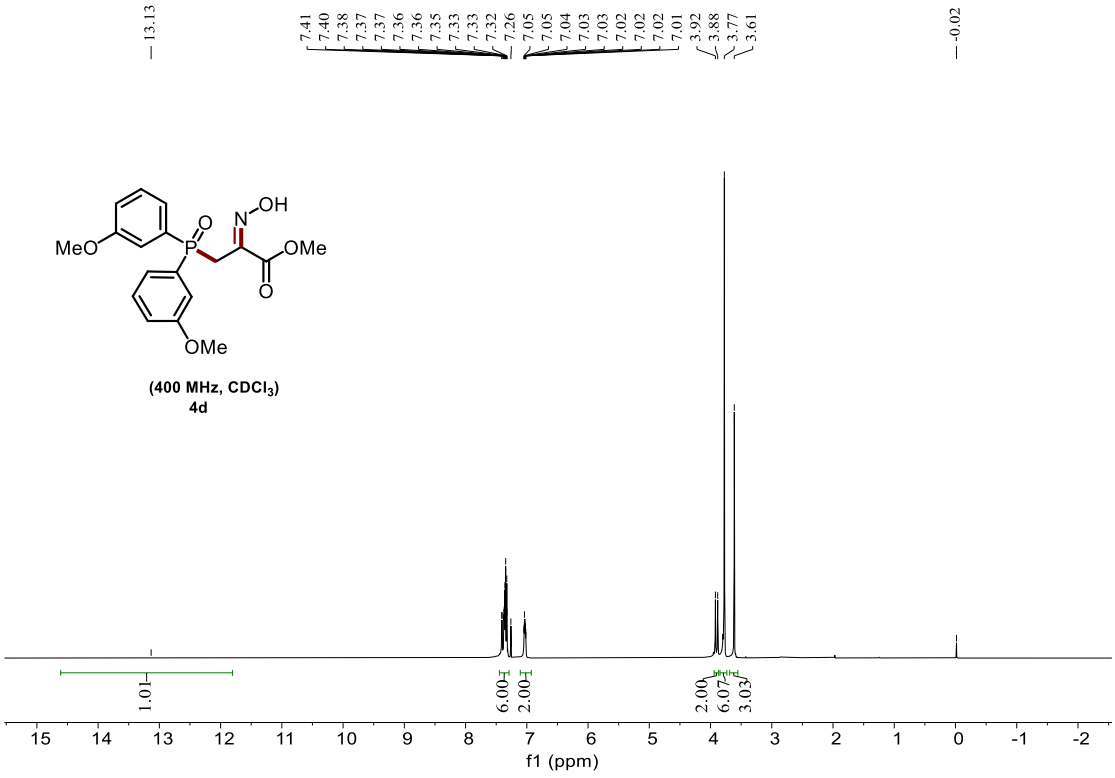

164.3
164.3
164.0
142.4
133.8
133.7
133.7
133.6
128.1
116.2
116.1
116.0
115.9
77.3
77.0
76.7
52.6
29.0
28.4
F
O
N
OH
P
OMe
O
F
(101 MHz, CDCl3)
4c
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

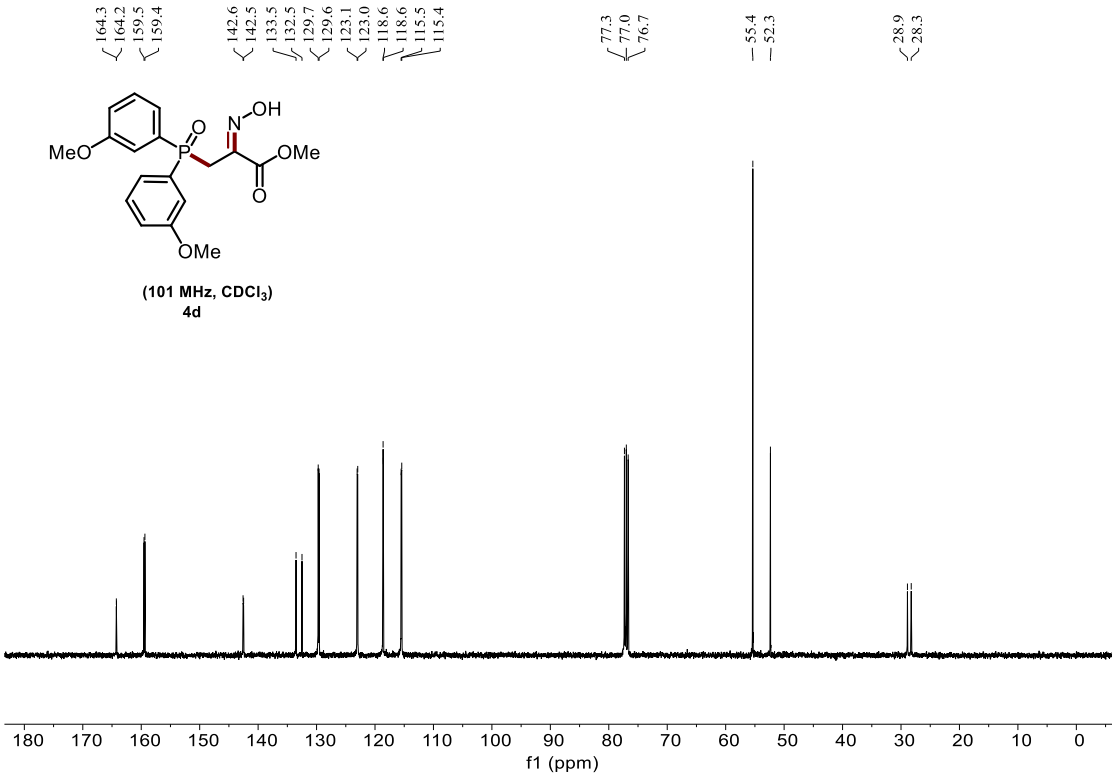


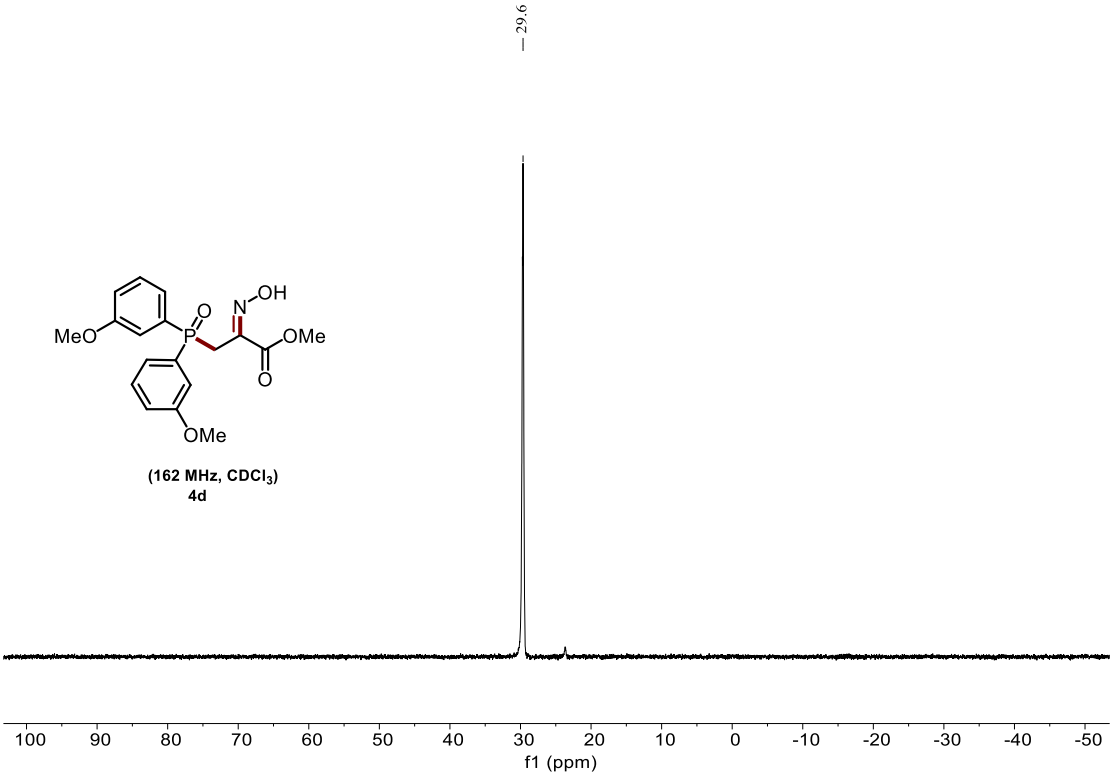
(162 MHz, $CDCl_3$)
4c



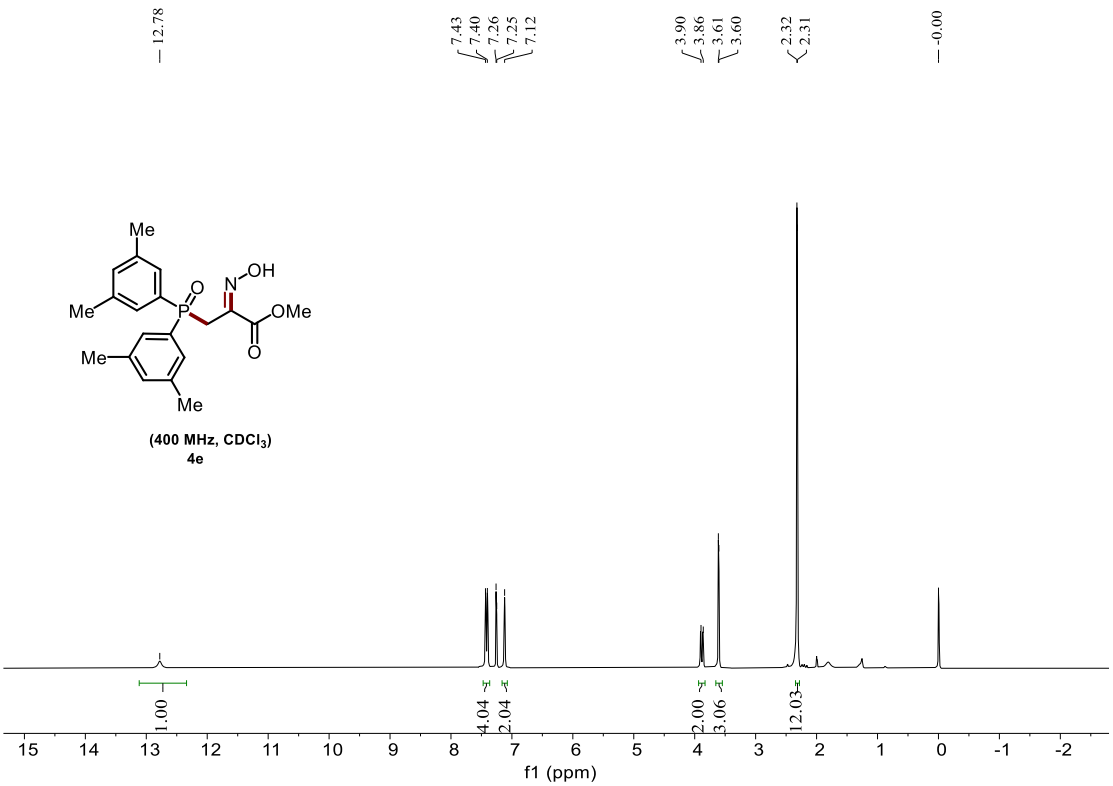
(376 MHz, $CDCl_3$)
4c


13.13
7.41
7.40
7.38
7.37
7.37
7.36
7.36
7.35
7.33
7.33
7.32
7.26
7.05
7.05
7.04
7.03
7.03
7.02
7.02
7.02
7.01
3.92
3.88
3.77
3.61
-0.02
MeO
P
O
N
OH
OMe
O
OMe
(400 MHz, CDCl3)
4d
1.01
6.00
2.00
2.00
6.07
3.03
f1 (ppm)

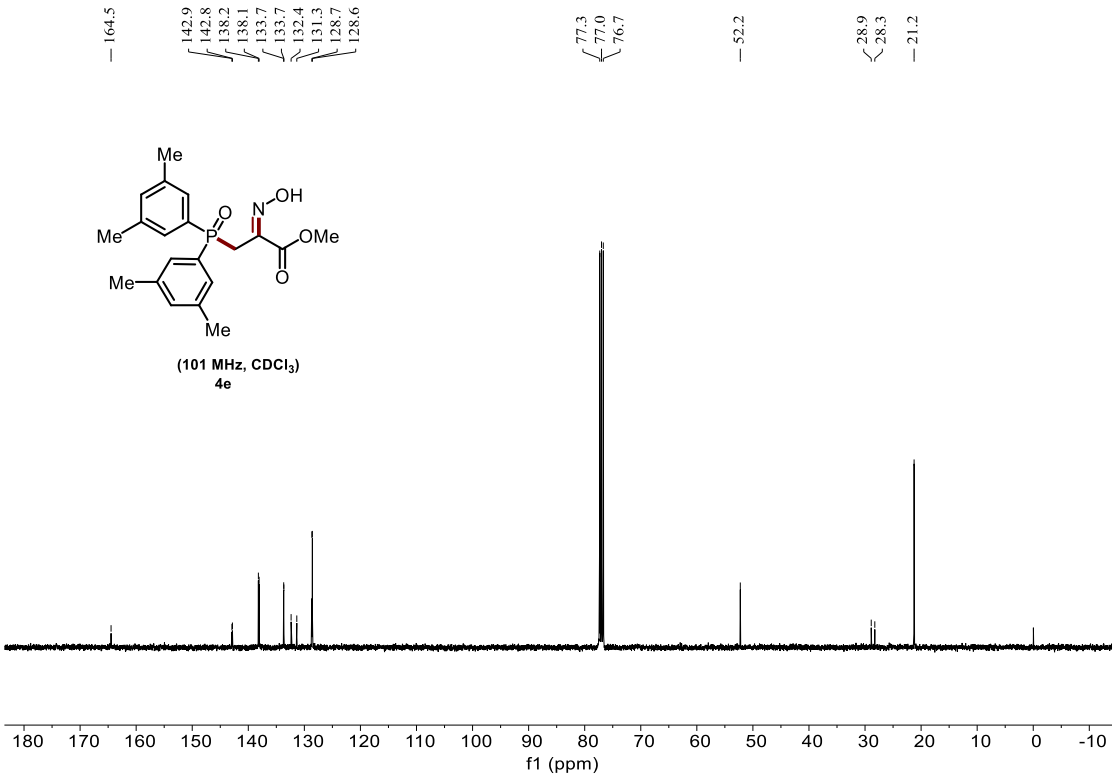

164.3
164.2
159.5
159.4
142.6
142.5
133.5
132.5
129.7
129.6
123.1
123.0
118.6
118.6
115.5
115.4
77.3
77.0
76.7
55.4
52.3
28.9
28.3
MeO
P
O
N
OH
OMe
O
OMe
(101 MHz, CDCl3)
4d
f1 (ppm)

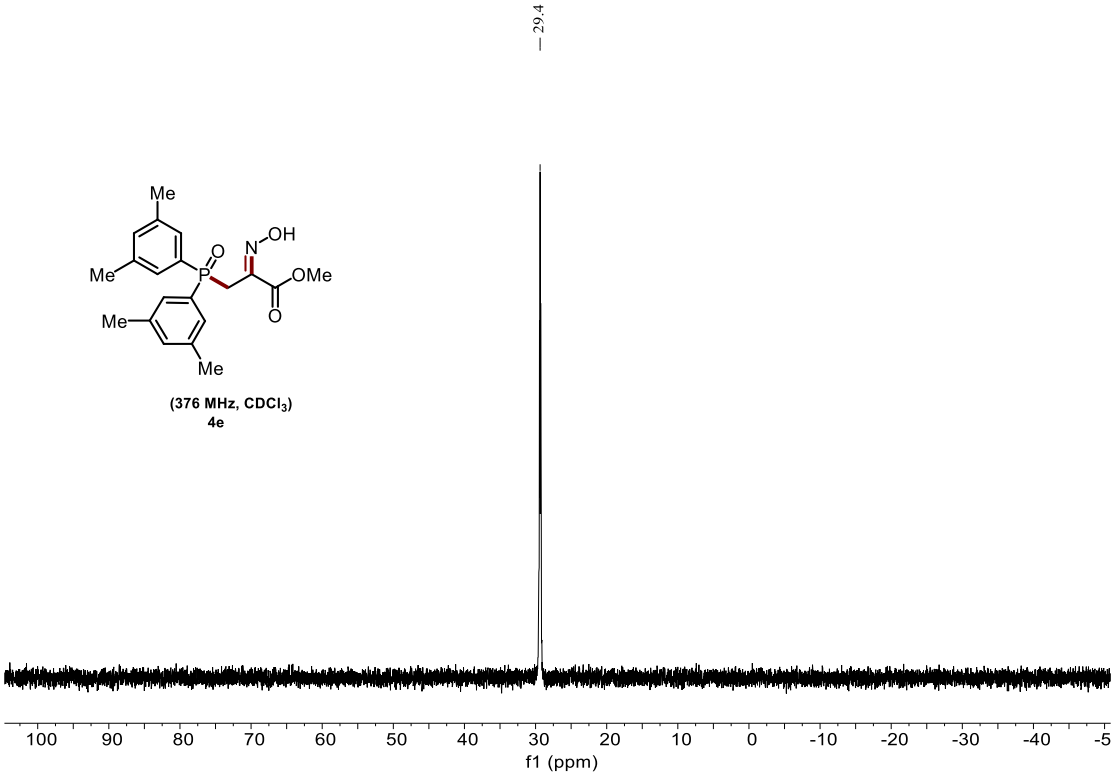


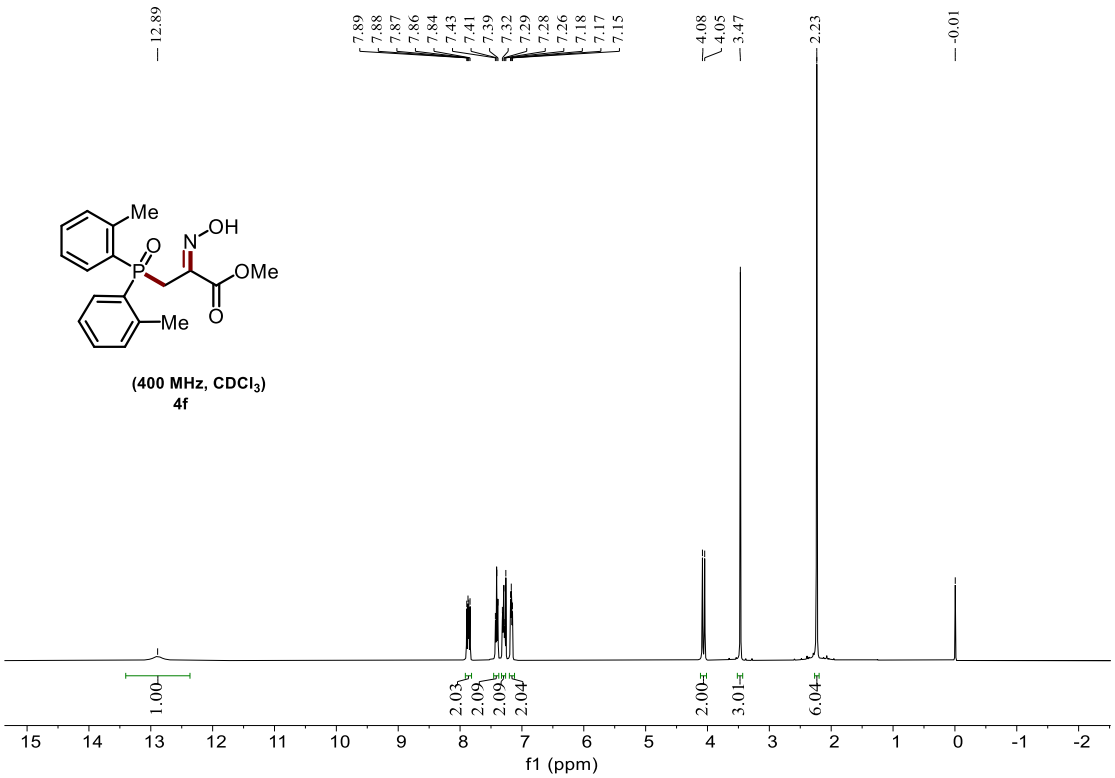
(162 MHz, $CDCl_3$)
4d



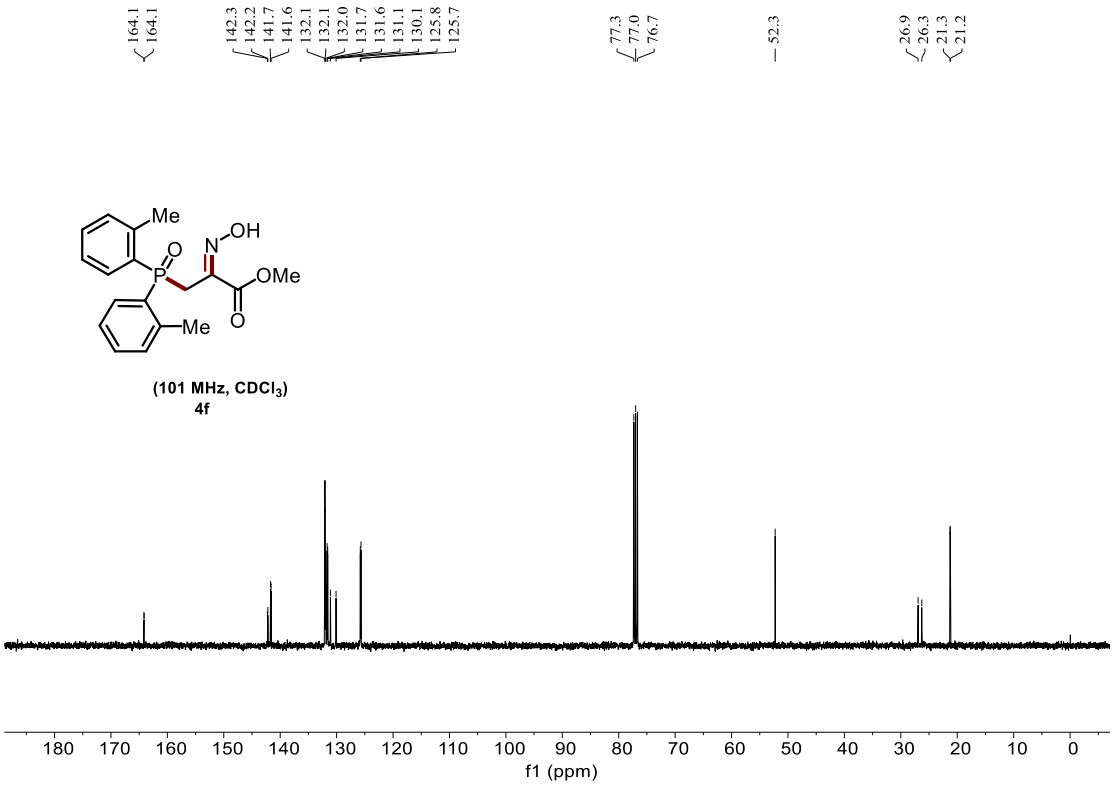
(400 MHz, $CDCl_3$)
4e


164.5
142.9
142.8
138.2
138.1
133.7
133.7
132.4
131.3
128.7
128.6
77.3
77.0
76.7
52.2
28.9
28.3
21.2
Me
Me
Me
Me
P
O
N
OH
OMe
O
(101 MHz, CDCl3)
4e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

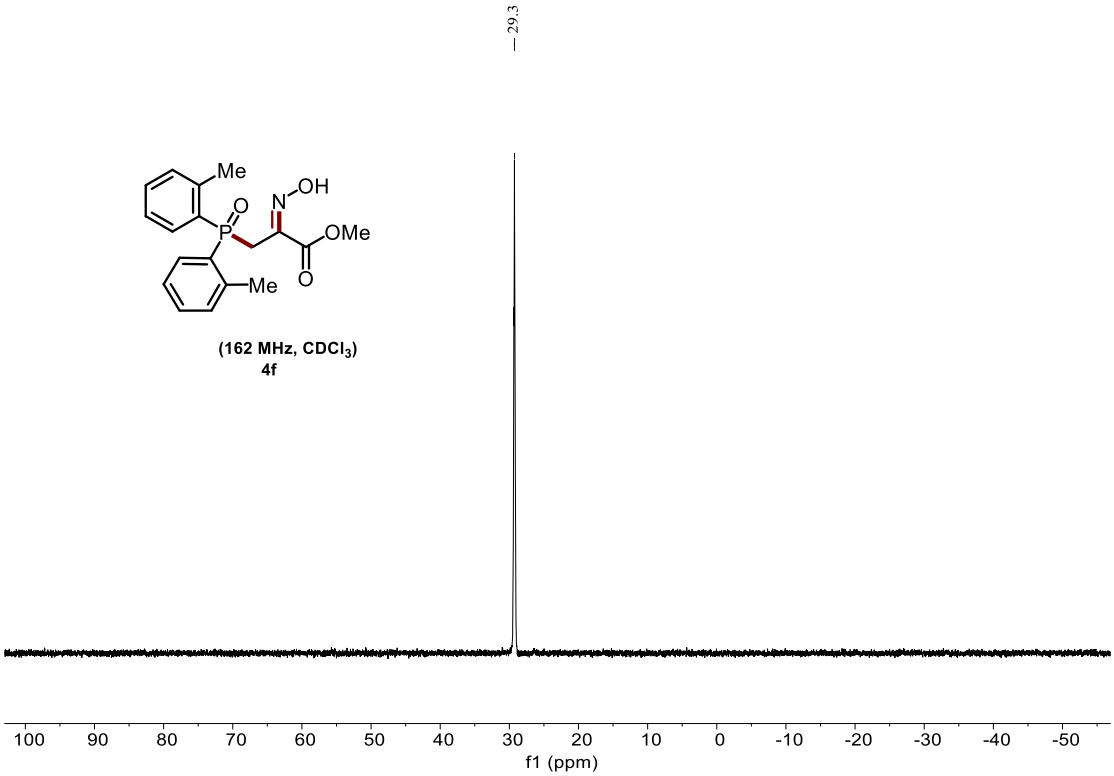

29.4
Me
Me
Me
Me
P
O
N
OH
OMe
O
(376 MHz, CDCl3)
4e
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5
f1 (ppm)



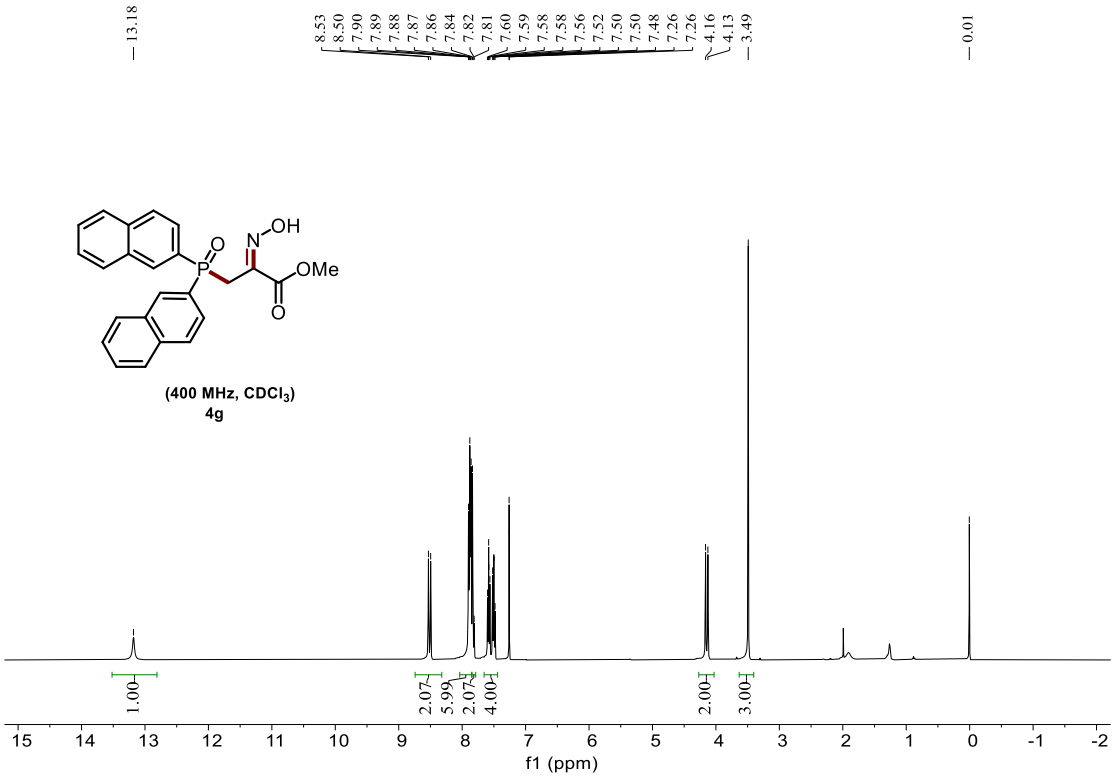
(400 MHz, $CDCl_3$)
4f



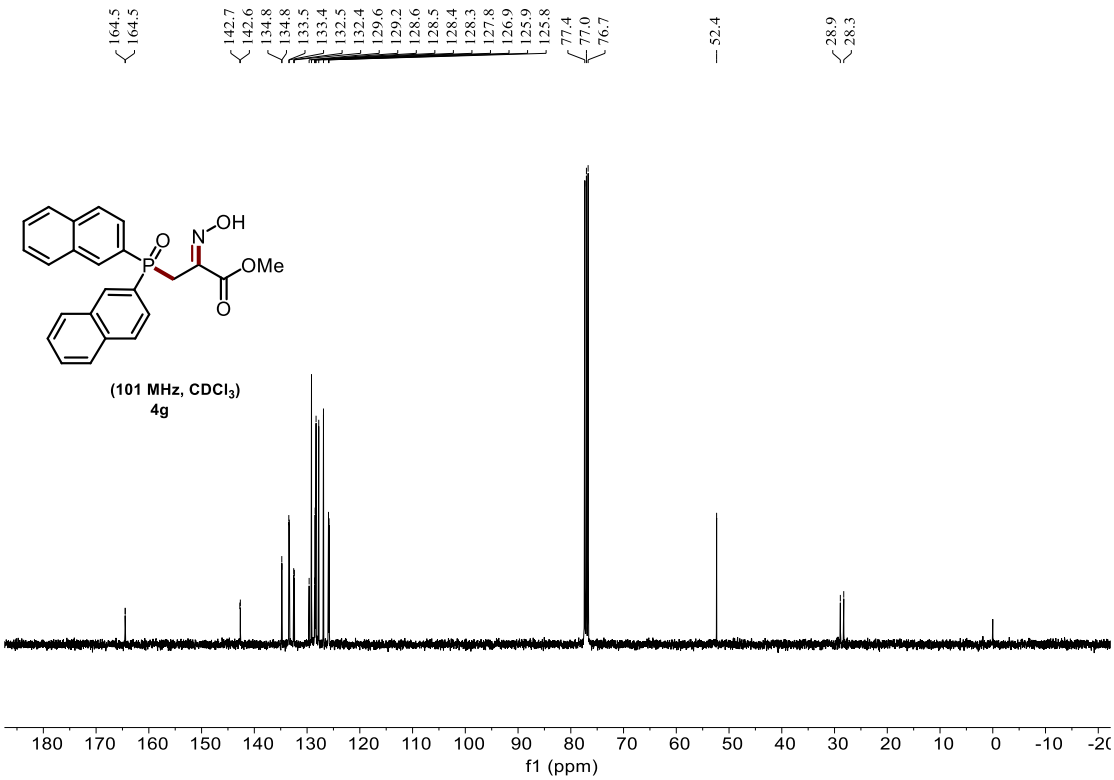
(101 MHz, $CDCl_3$)
4f

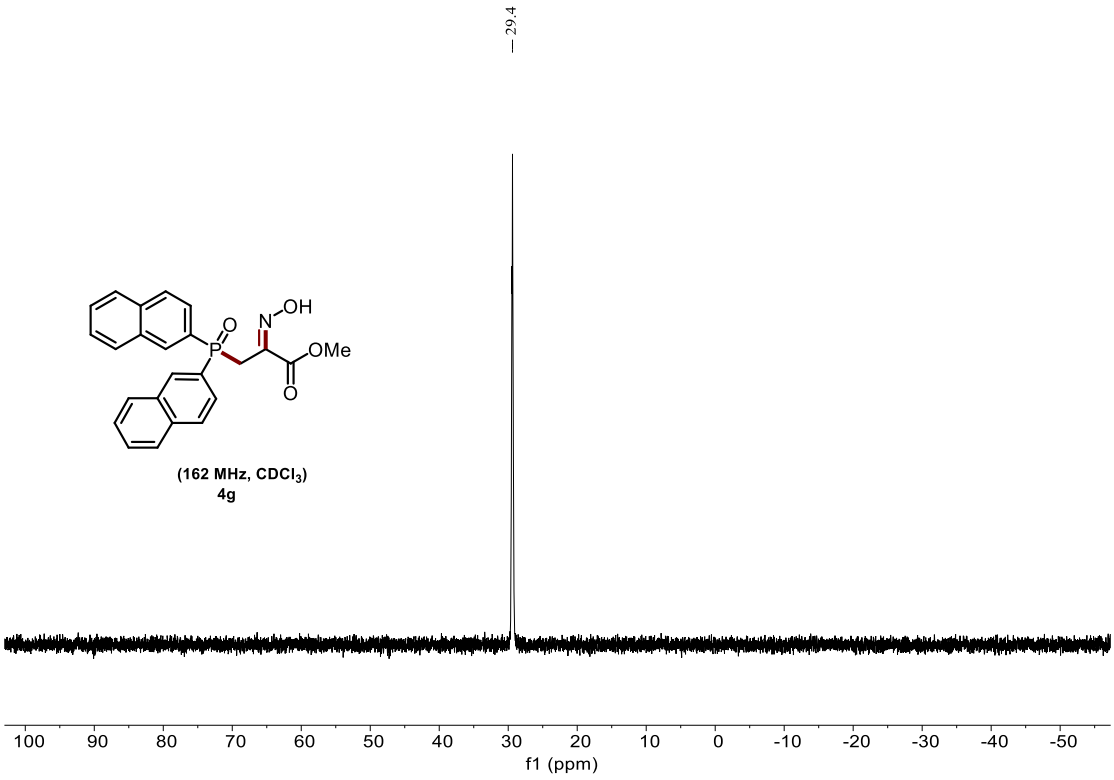


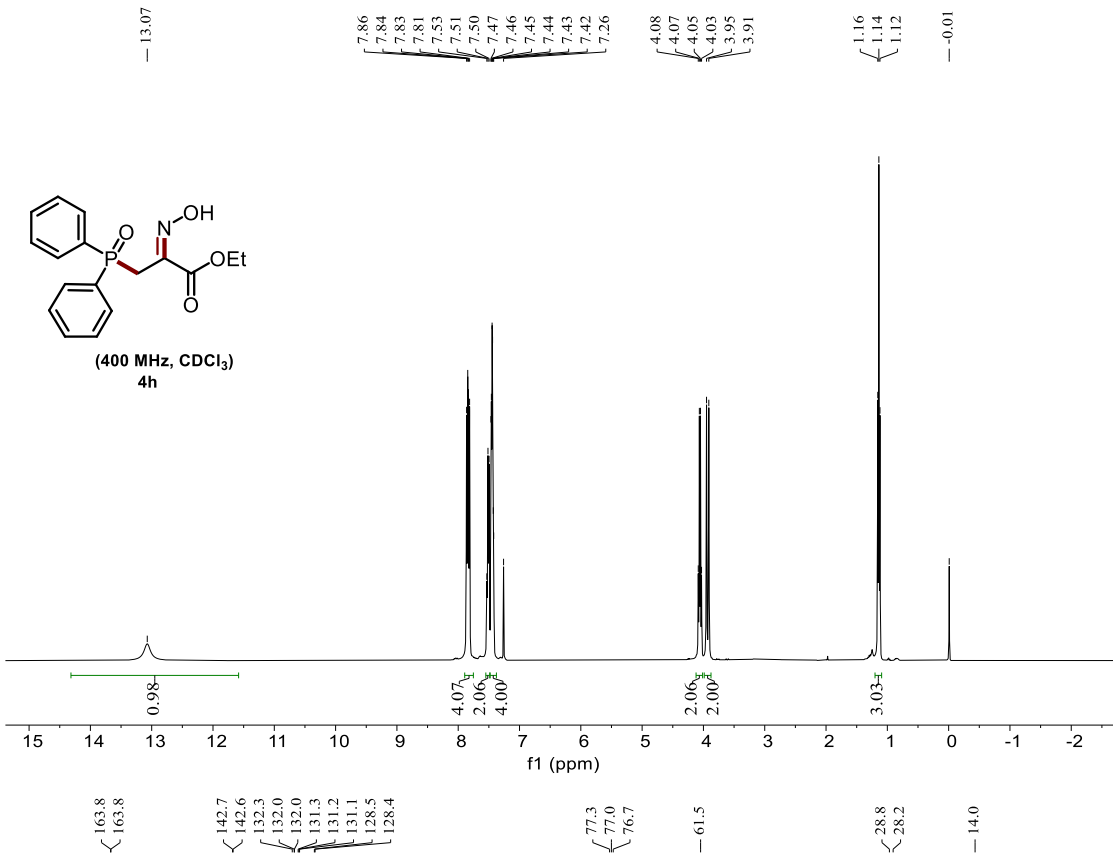
(162 MHz, $CDCl_3$)
4f

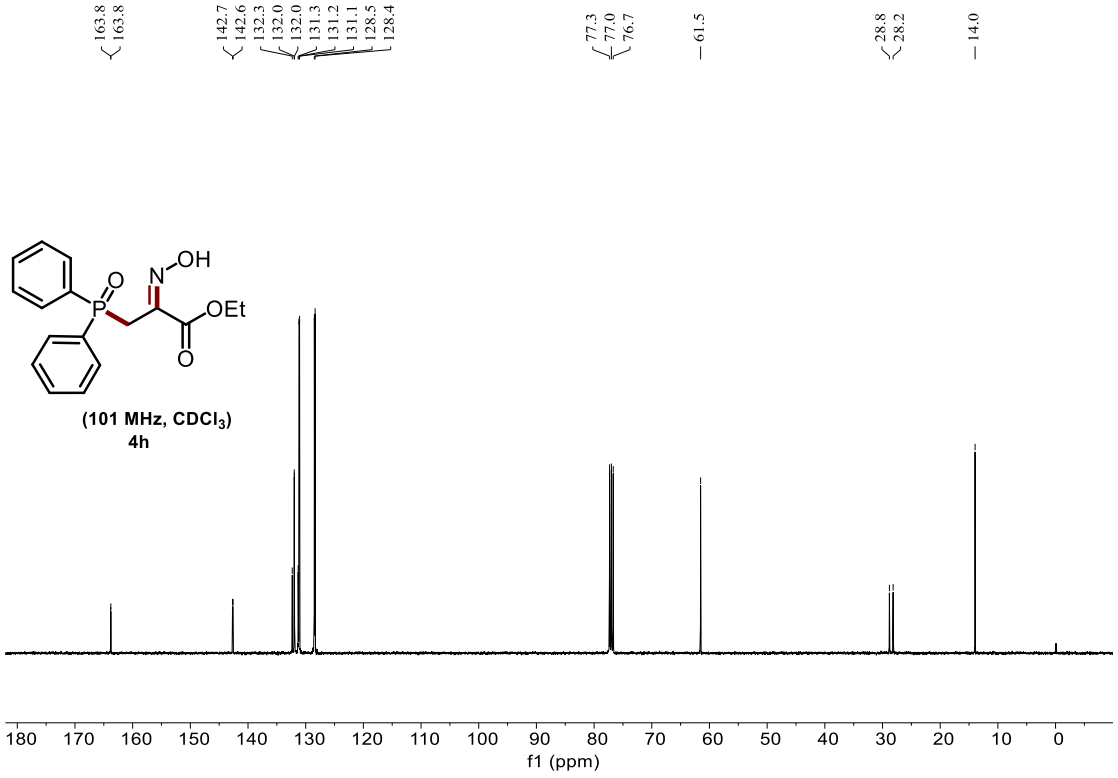


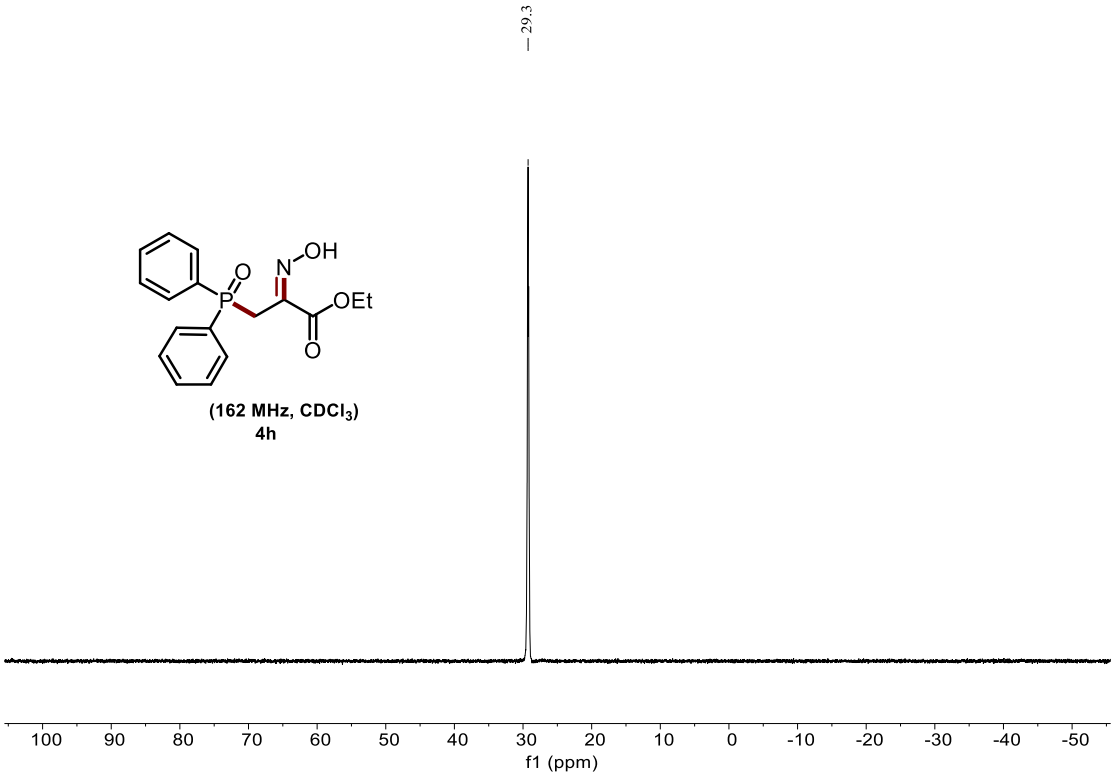
(400 MHz, $CDCl_3$)
4g


164.5
164.5
142.7
142.6
134.8
134.8
133.5
133.4
132.5
132.4
129.6
129.2
128.6
128.5
128.4
128.3
127.8
126.9
125.9
125.8
77.4
77.0
76.7
52.4
28.9
28.3
OH
N
O
P
OMe
O
(101 MHz, CDCl3)
4g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

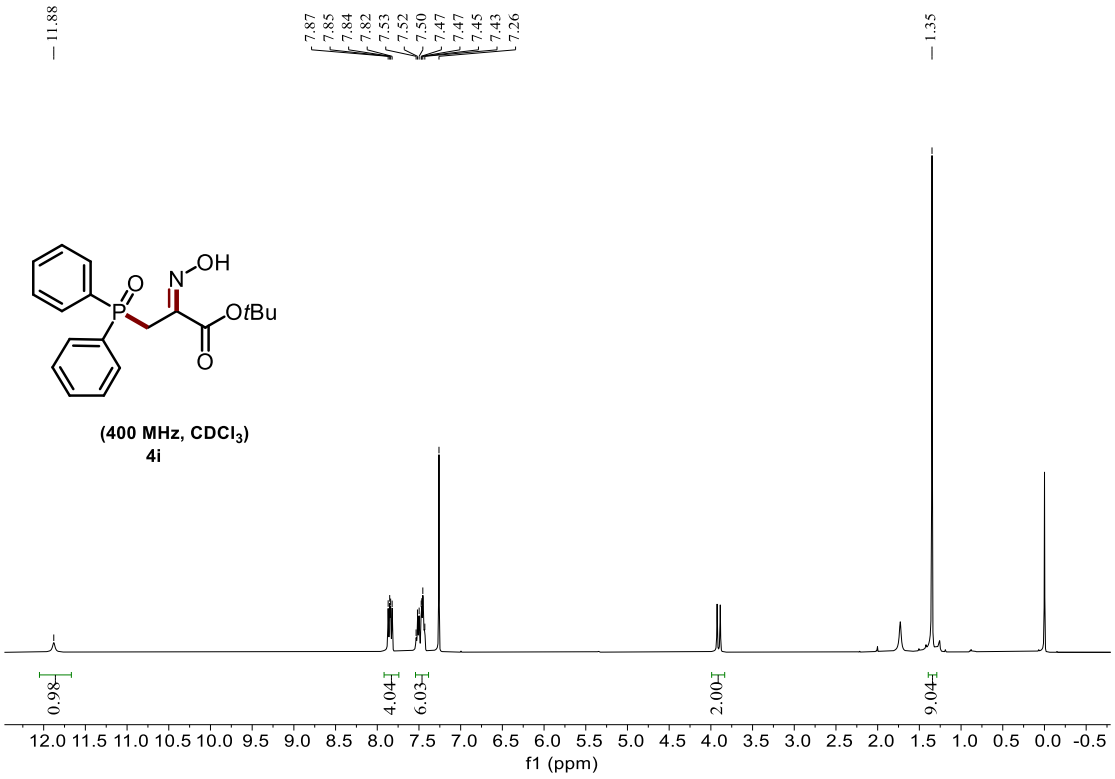

29.4
OH
N
O
P
OMe
O
(162 MHz, CDCl3)
4g
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)


13.07
7.86
7.84
7.83
7.81
7.53
7.51
7.50
7.47
7.46
7.45
7.44
7.43
7.42
7.26
4.08
4.07
4.05
4.03
3.95
3.91
1.16
1.14
1.12
-0.01
OH
N
O
P
OEt
O
(400 MHz, CDCl3)
4h
0.98
4.07
2.06
4.00
2.06
2.00
3.03
f1 (ppm)

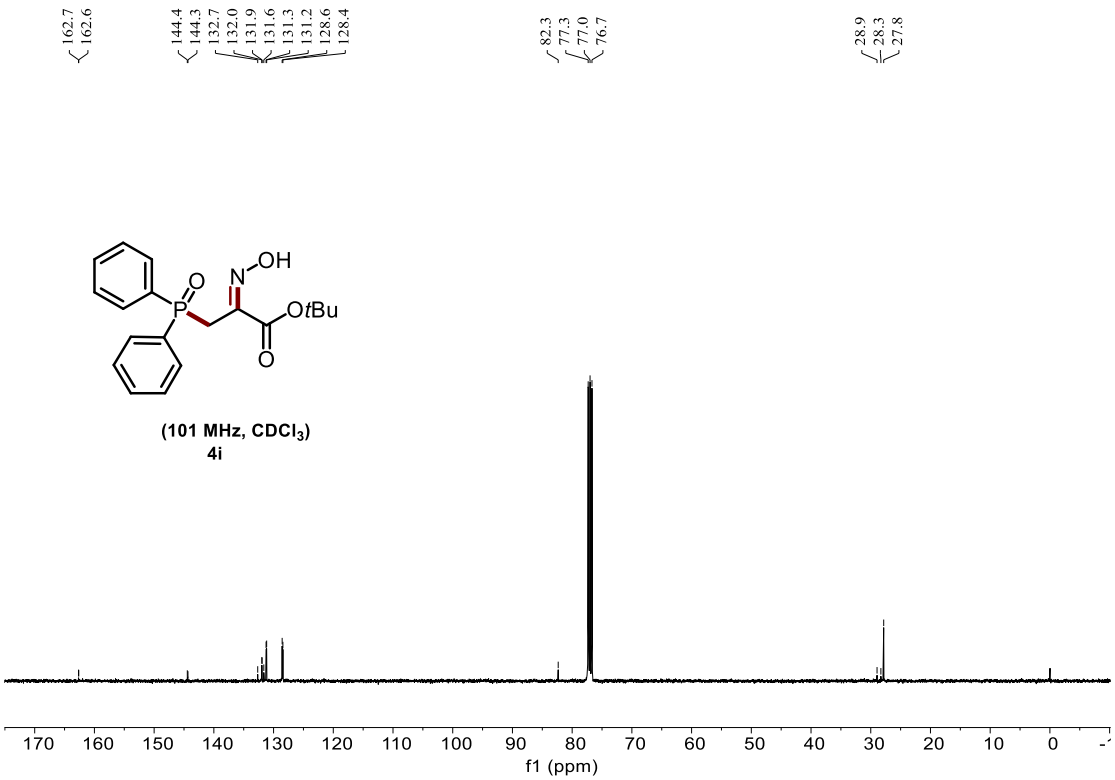

163.8
163.8
142.7
142.6
132.3
132.0
132.0
131.3
131.2
131.1
128.5
128.4
77.3
77.0
76.7
61.5
28.8
28.2
14.0
OH
N
O
P
OEt
O
(101 MHz, CDCl3)
4h
f1 (ppm)



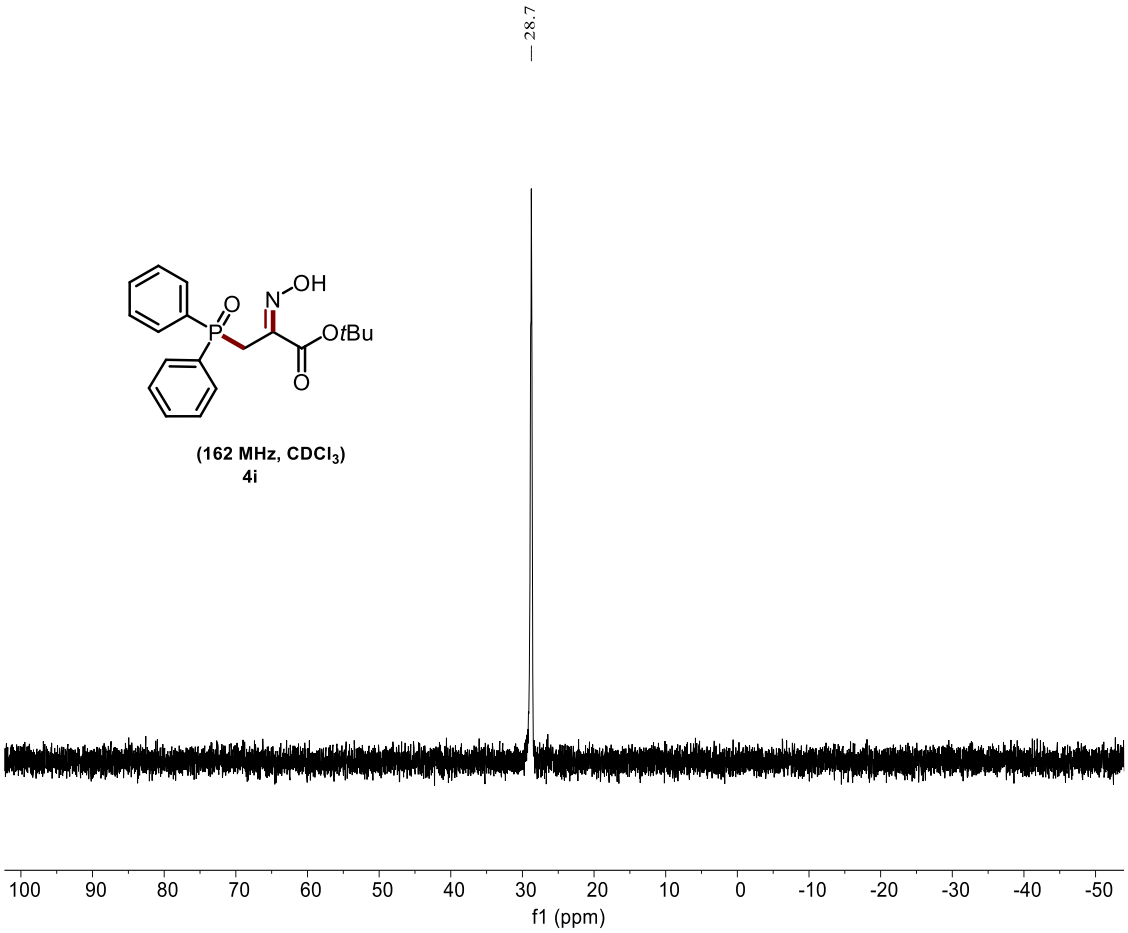
(162 MHz, $CDCl_3$)
4h



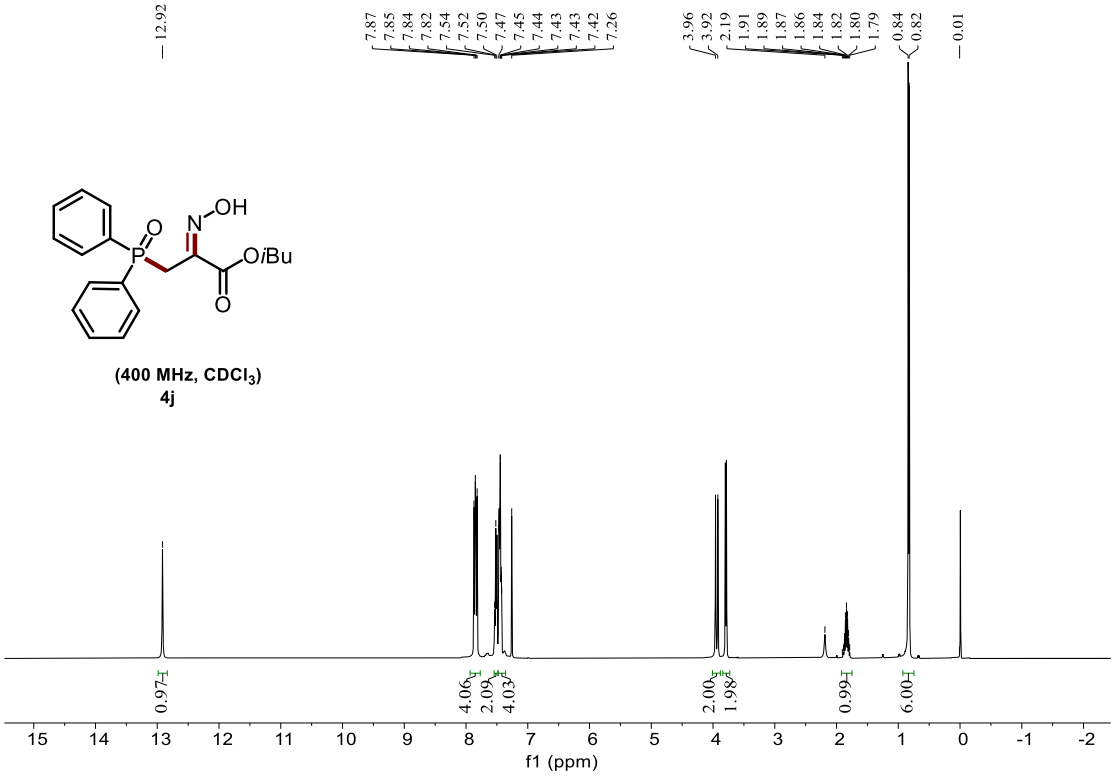
(400 MHz, $CDCl_3$)
4i



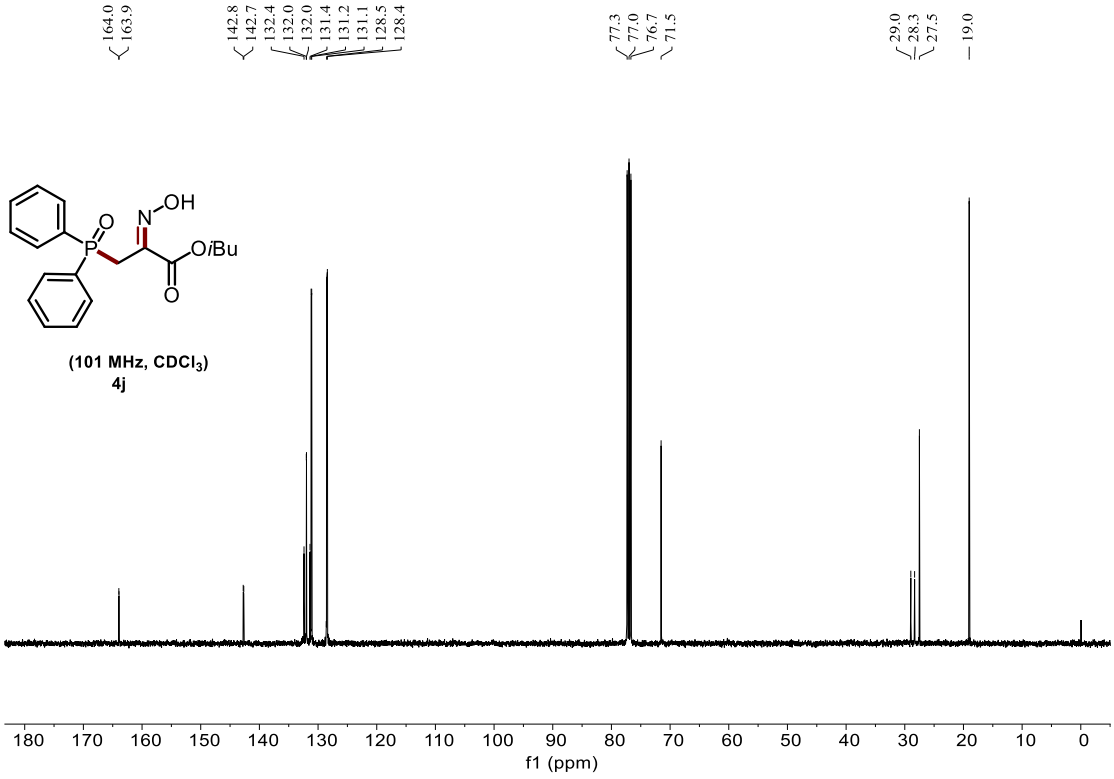
(101 MHz, $CDCl_3$)
4i



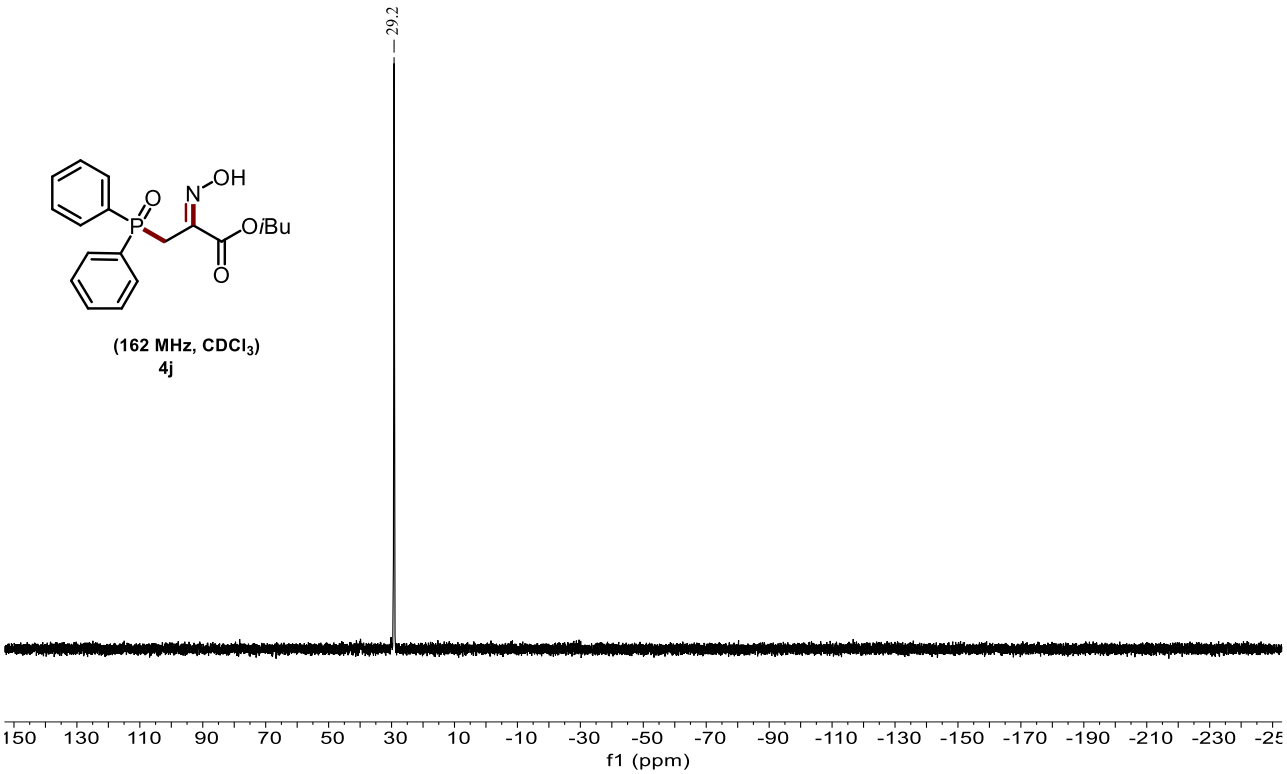
(162 MHz, $CDCl_3$)
4i



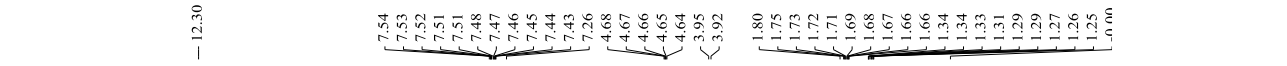
(400 MHz, $CDCl_3$)
4j

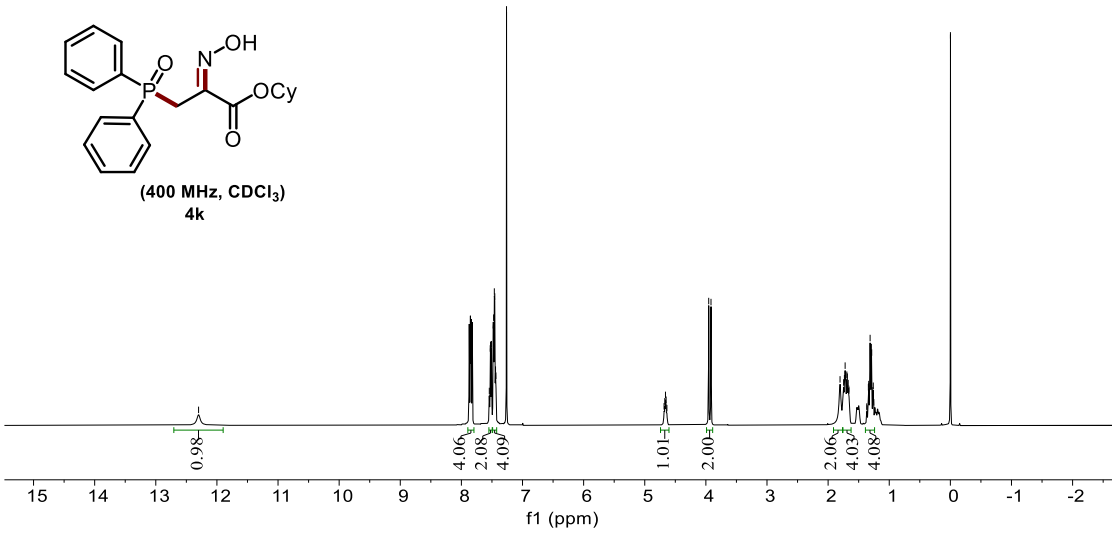


(101 MHz, $CDCl_3$)
4j

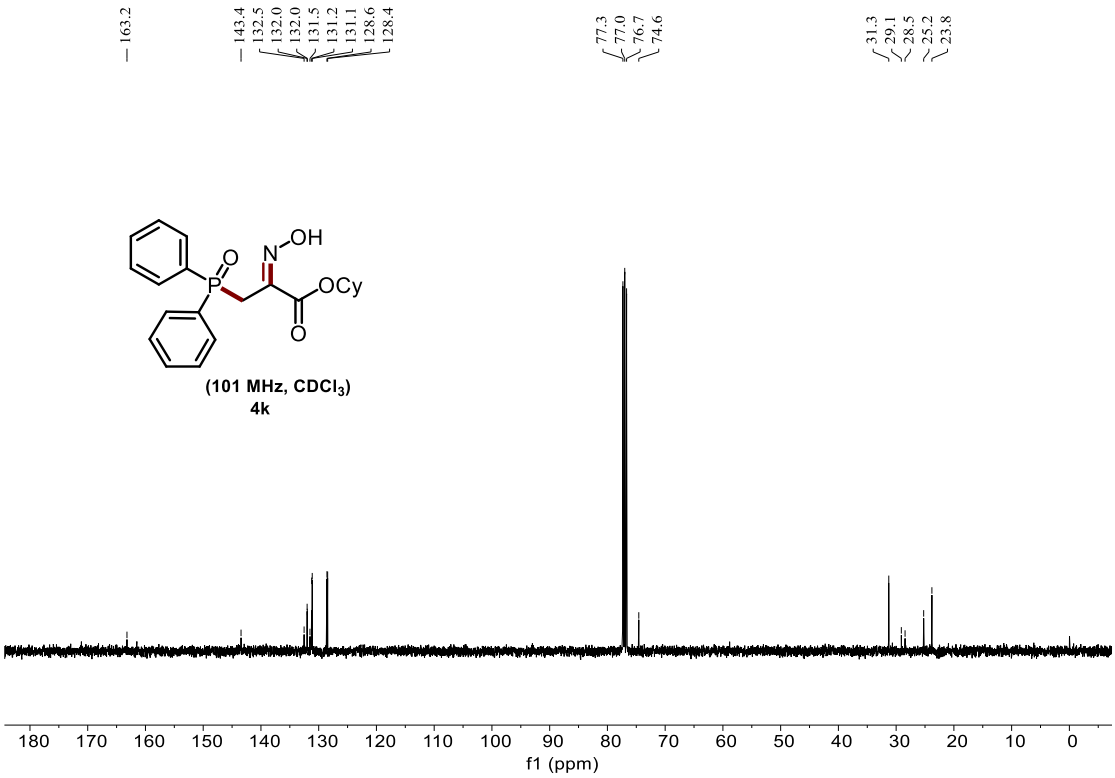


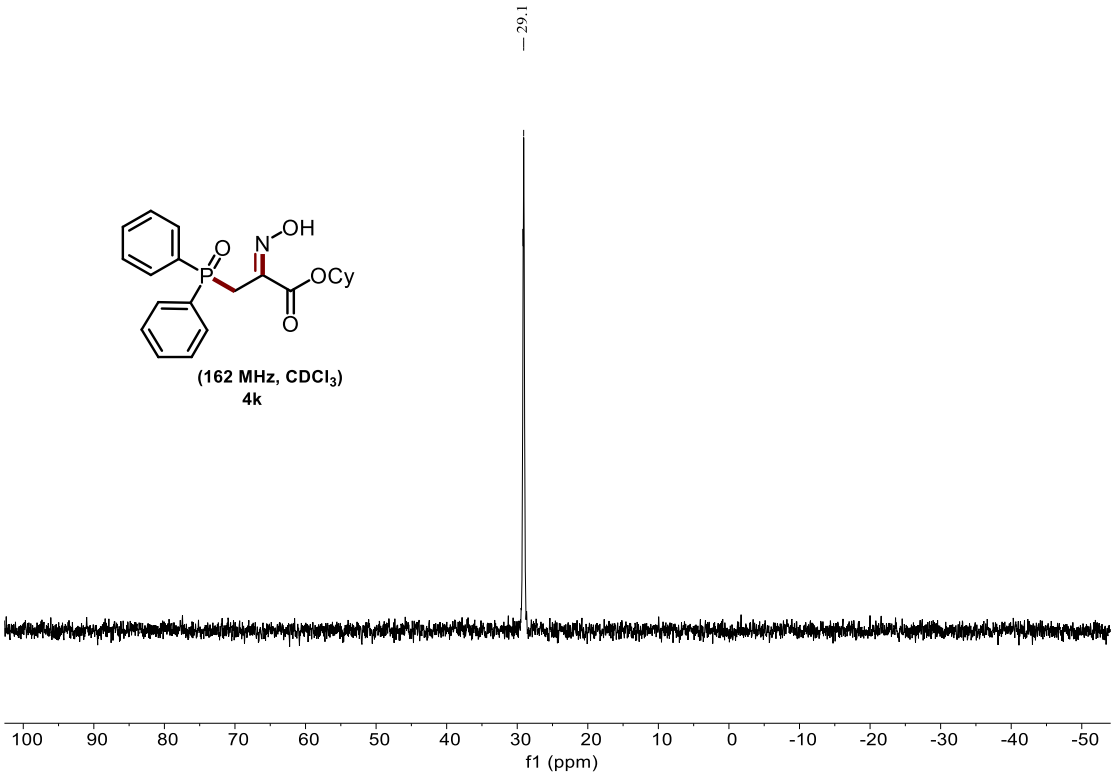
(162 MHz, $CDCl_3$)
4j

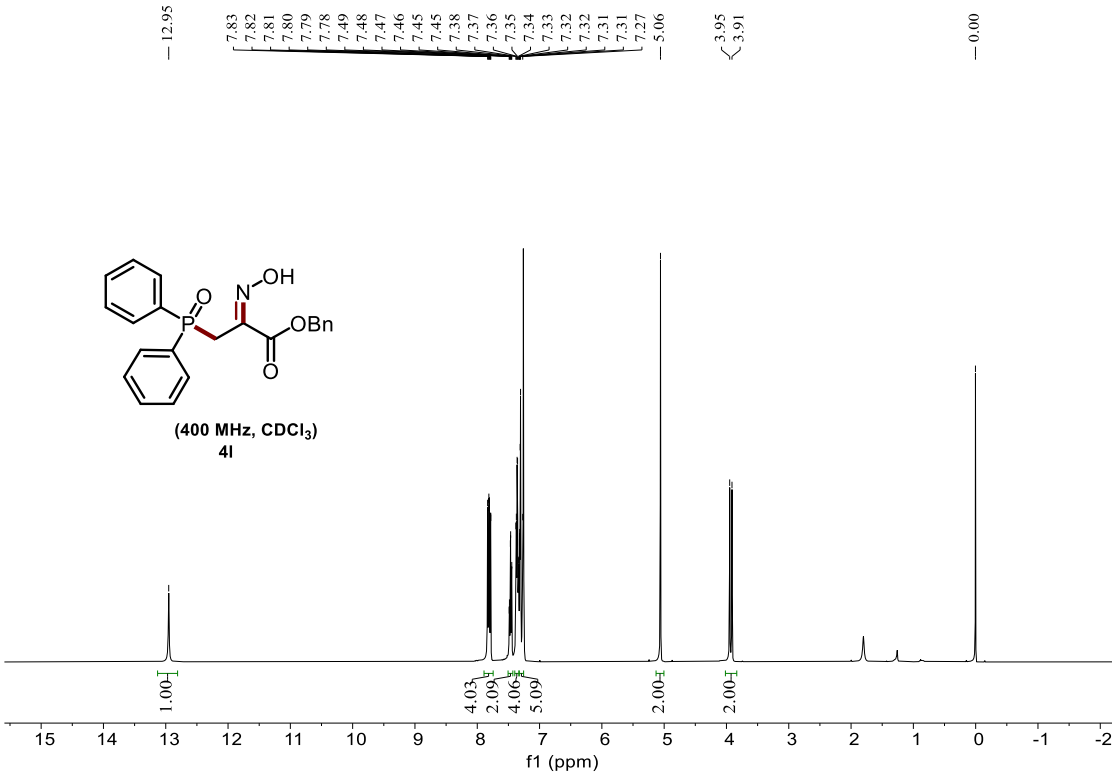


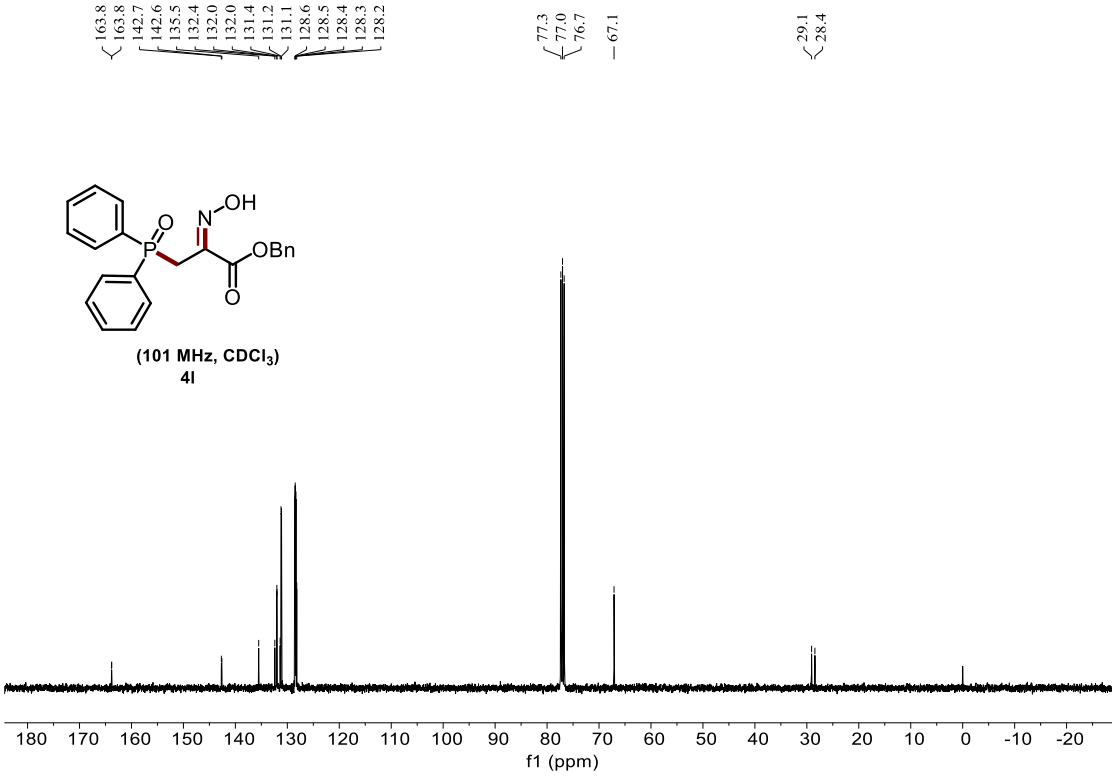


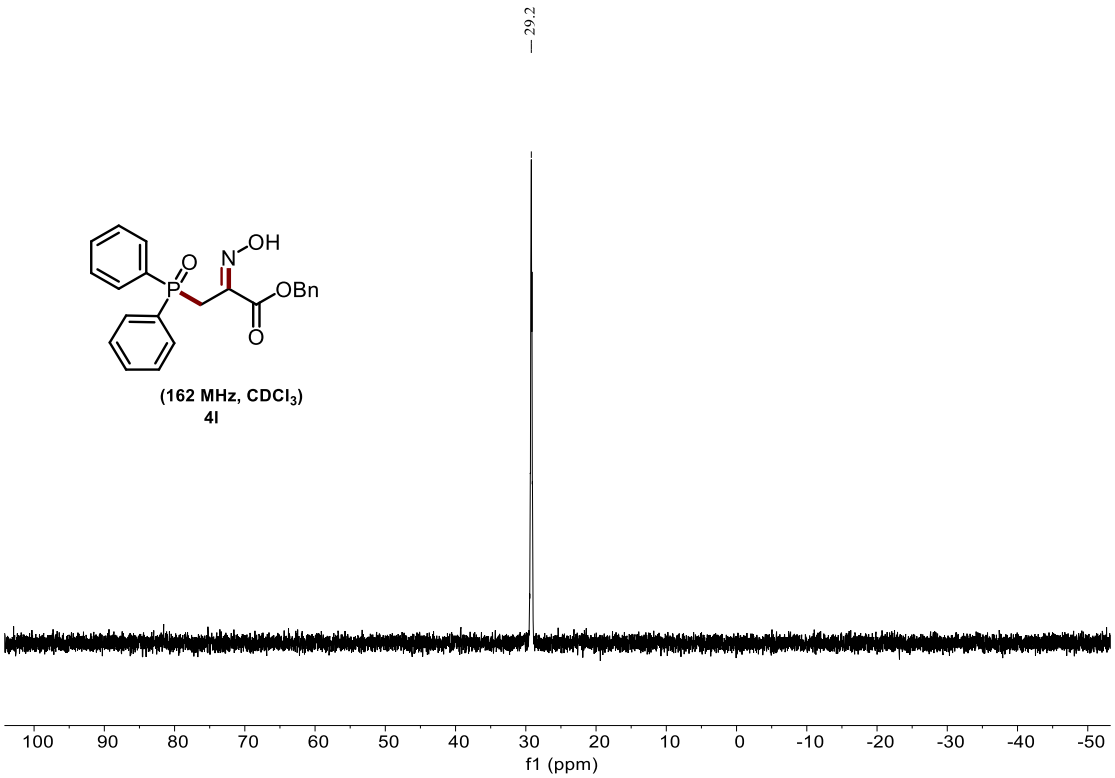
(400 MHz, $CDCl_3$)
4k


163.2
143.4
132.5
132.0
132.0
131.5
131.2
131.1
128.6
128.4
77.3
77.0
76.7
74.6
31.3
29.1
28.5
25.2
23.8
OH
N
O
P
OCy
O
(101 MHz, CDCl3)
4k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

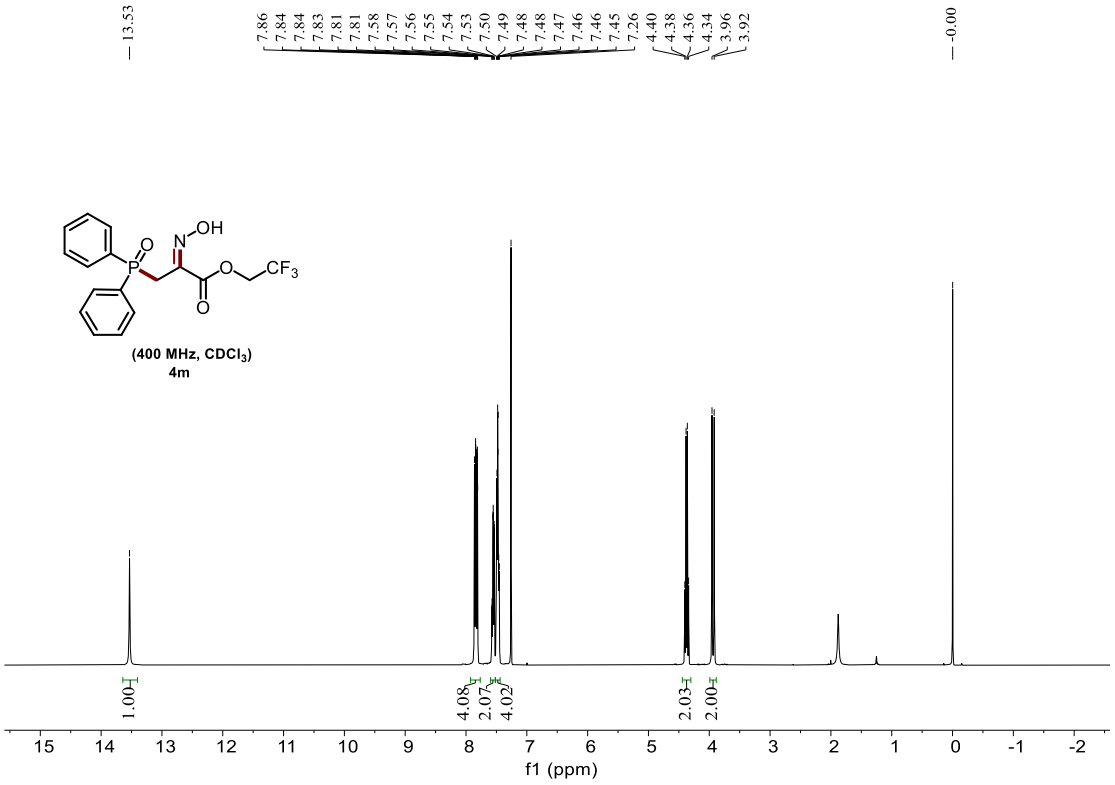

29.1
OH
N
O
P
OCy
O
(162 MHz, CDCl3)
4k
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)


12.95
7.83
7.82
7.81
7.80
7.79
7.78
7.49
7.48
7.47
7.46
7.45
7.45
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.27
5.06
3.95
3.91
0.00
OH
N
O
P
OBn
O
(400 MHz, CDCl3)
4l
1.00
4.03
2.09
4.06
5.09
2.00
2.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

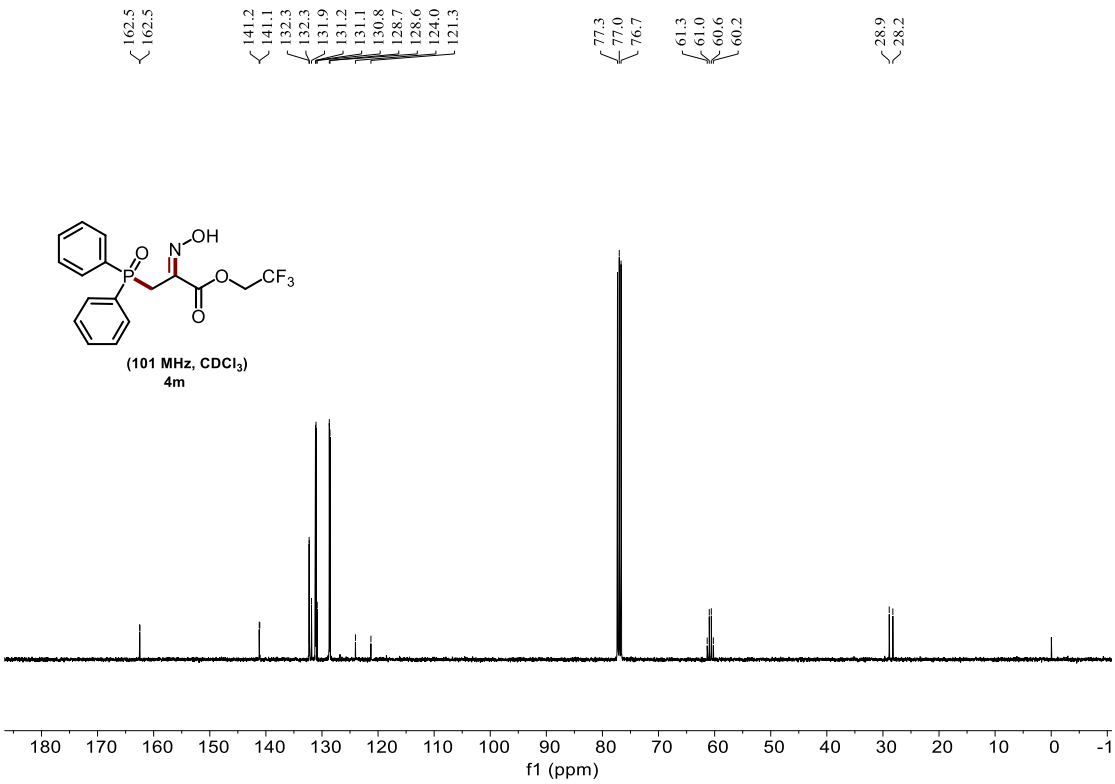

163.8
163.8
142.7
142.6
135.5
132.4
132.0
132.0
131.4
131.2
131.1
128.6
128.5
128.4
128.3
128.2
77.3
77.0
76.7
67.1
29.1
28.4
OH
N
O
P
OBn
O
(101 MHz, CDCl3)
4l
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

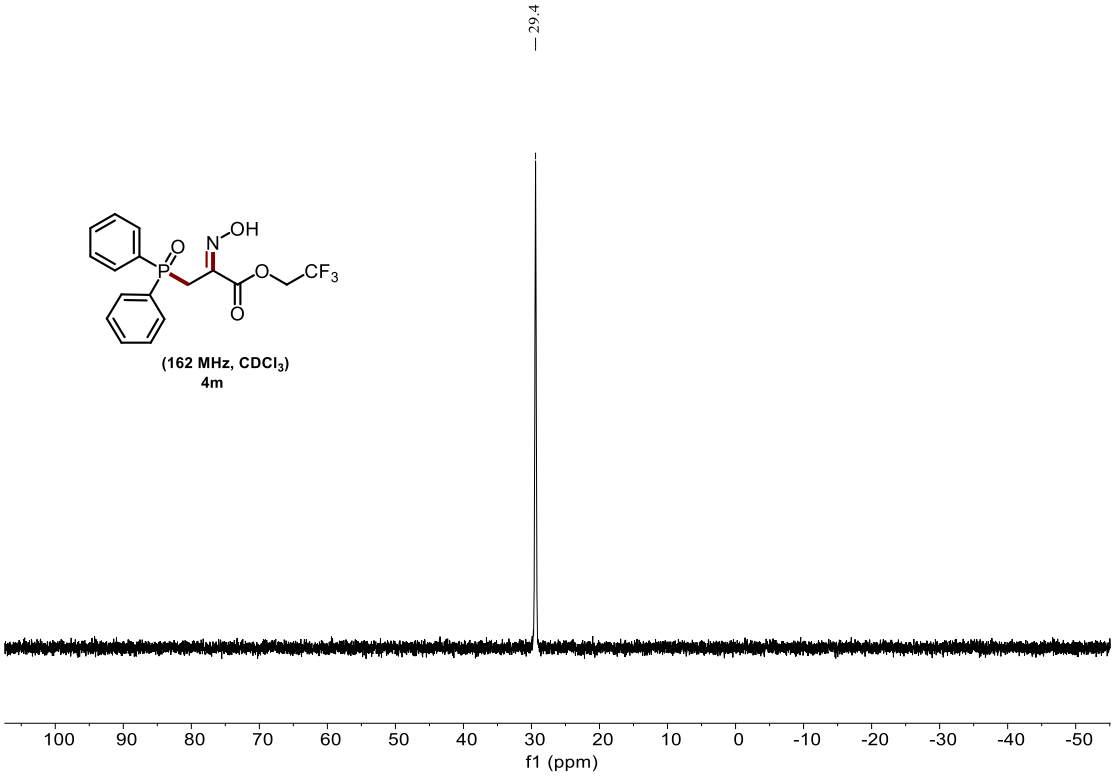


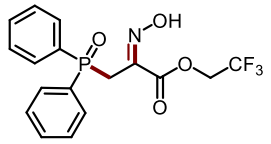
(162 MHz, $CDCl_3$)
4l



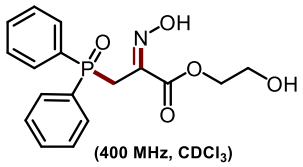
(400 MHz, $CDCl_3$)
4m


162.5
162.5
141.2
141.1
132.3
132.3
131.9
131.2
131.1
130.8
128.7
128.6
124.0
121.3
77.3
77.0
76.7
61.3
61.0
60.6
60.2
28.9
28.2
OH
N
O
P
O
O
CF3
O
(101 MHz, CDCl3)
4m
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

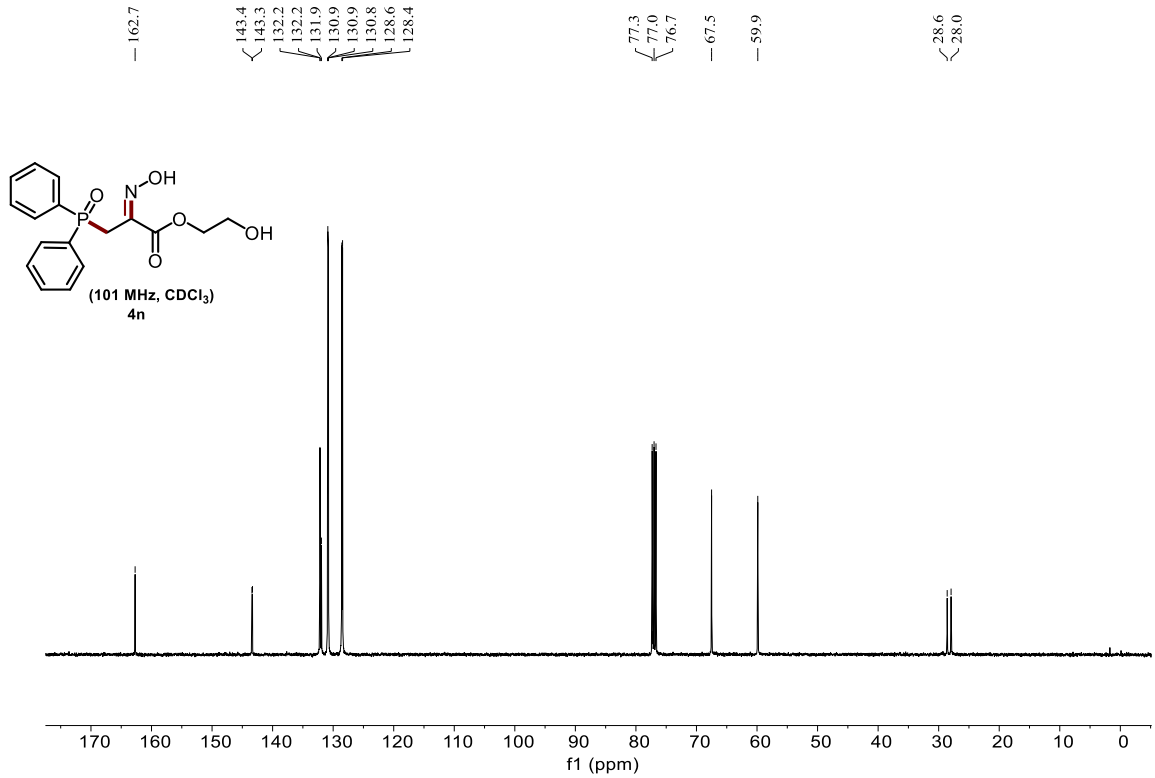

29.4
OH
N
O
P
O
O
CF3
O
(162 MHz, CDCl3)
4m
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

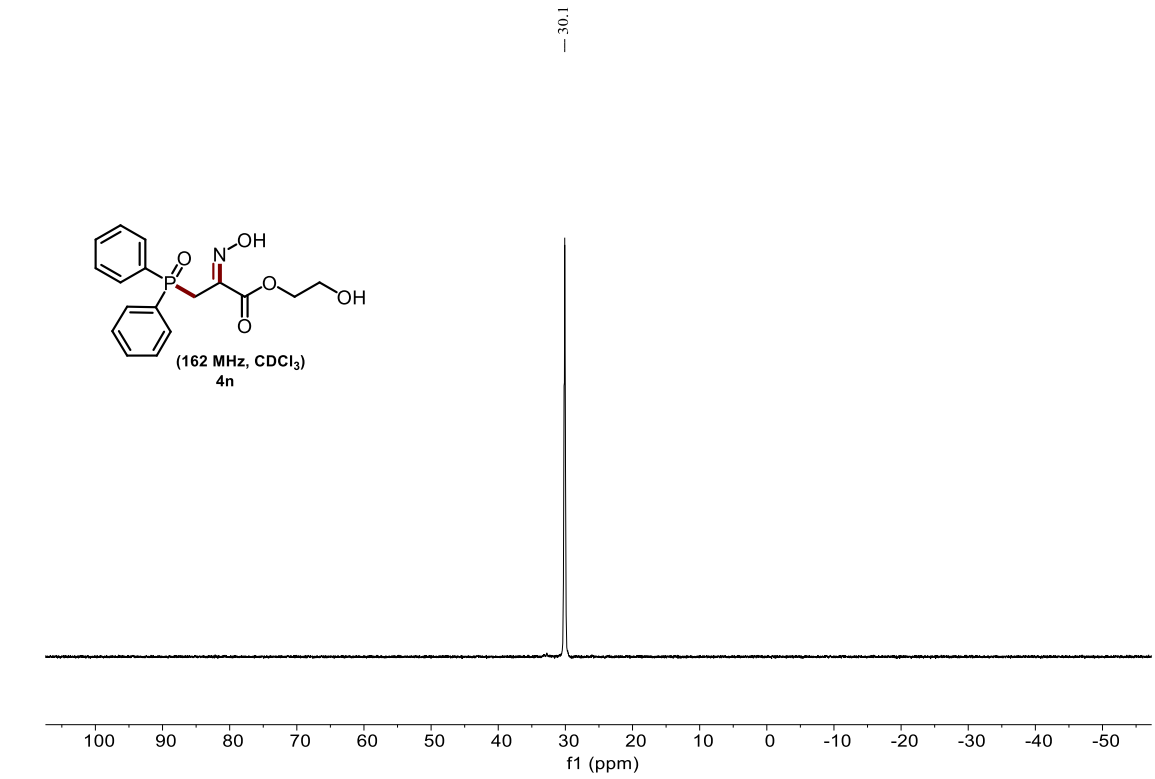


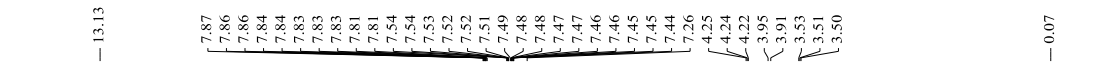
(376 MHz, $CDCl_3$)
4m

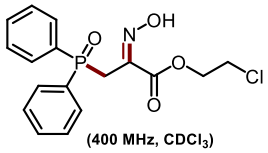


(400 MHz, $CDCl_3$)
4n

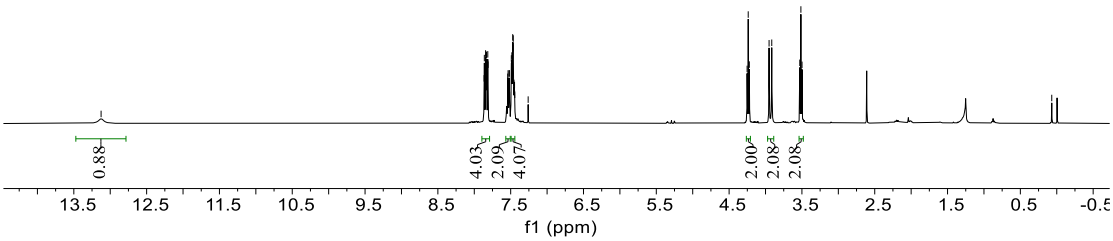

162.7
143.4
143.3
132.2
132.2
131.9
130.9
130.9
130.8
128.6
128.4
77.3
77.0
76.7
67.5
59.9
28.6
28.0
OH
N
OH
O
P
O
O
O
OH
(101 MHz, CDCl3)
4n
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

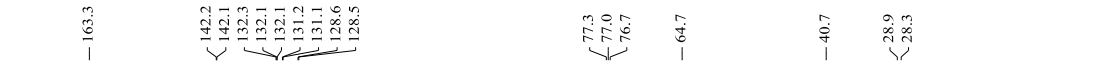

30.1
OH
N
OH
O
P
O
O
O
OH
(162 MHz, CDCl3)
4n
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

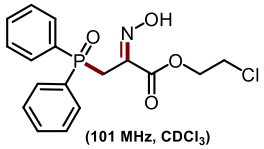




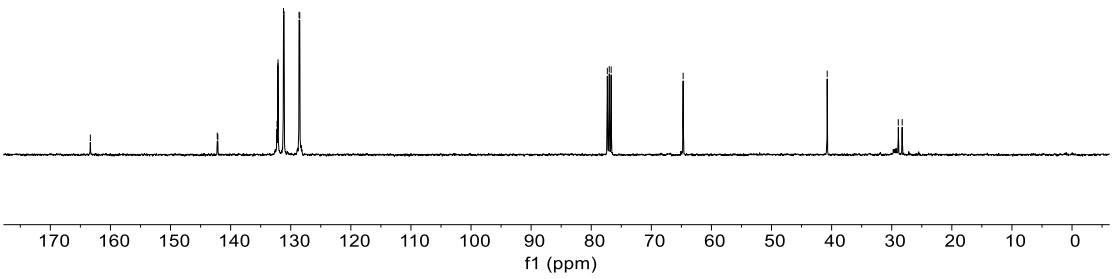
(400 MHz, $CDCl_3$)
4o

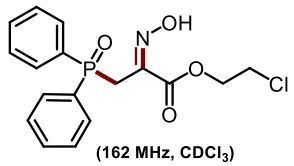




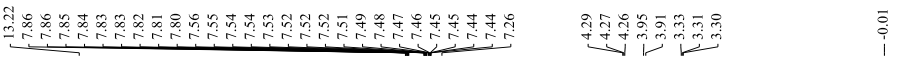


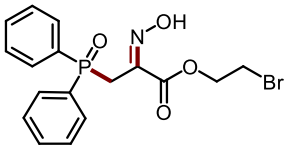
(101 MHz, $CDCl_3$)
4o



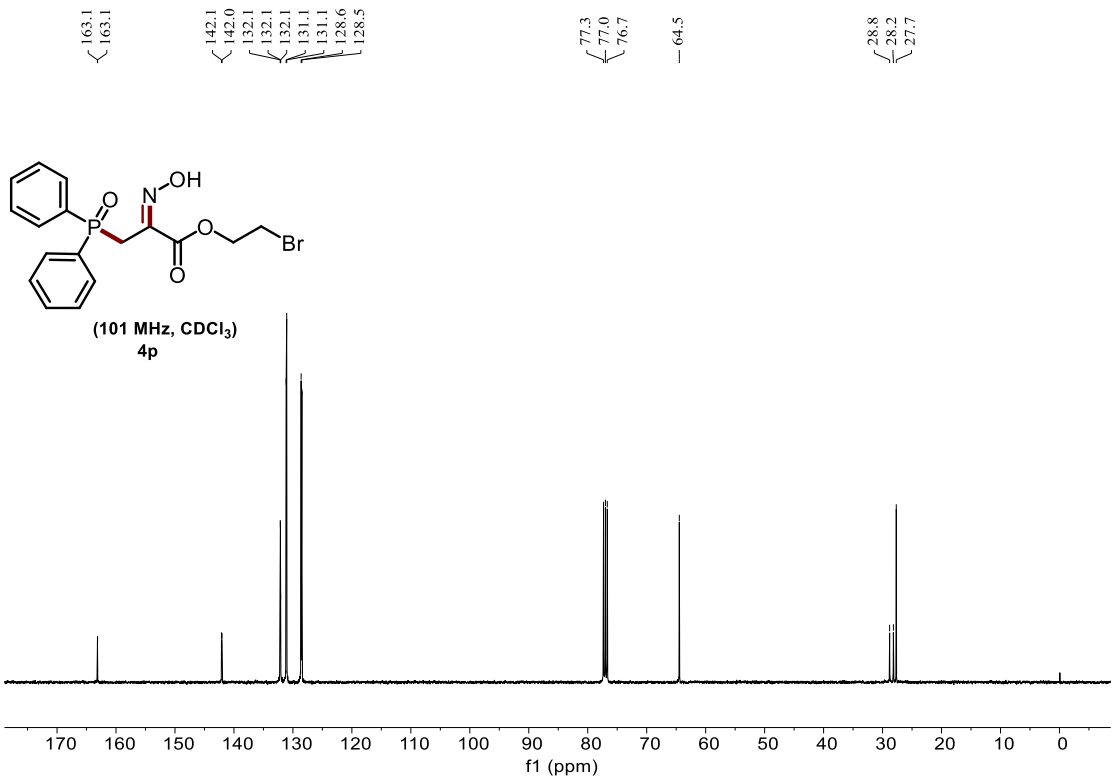


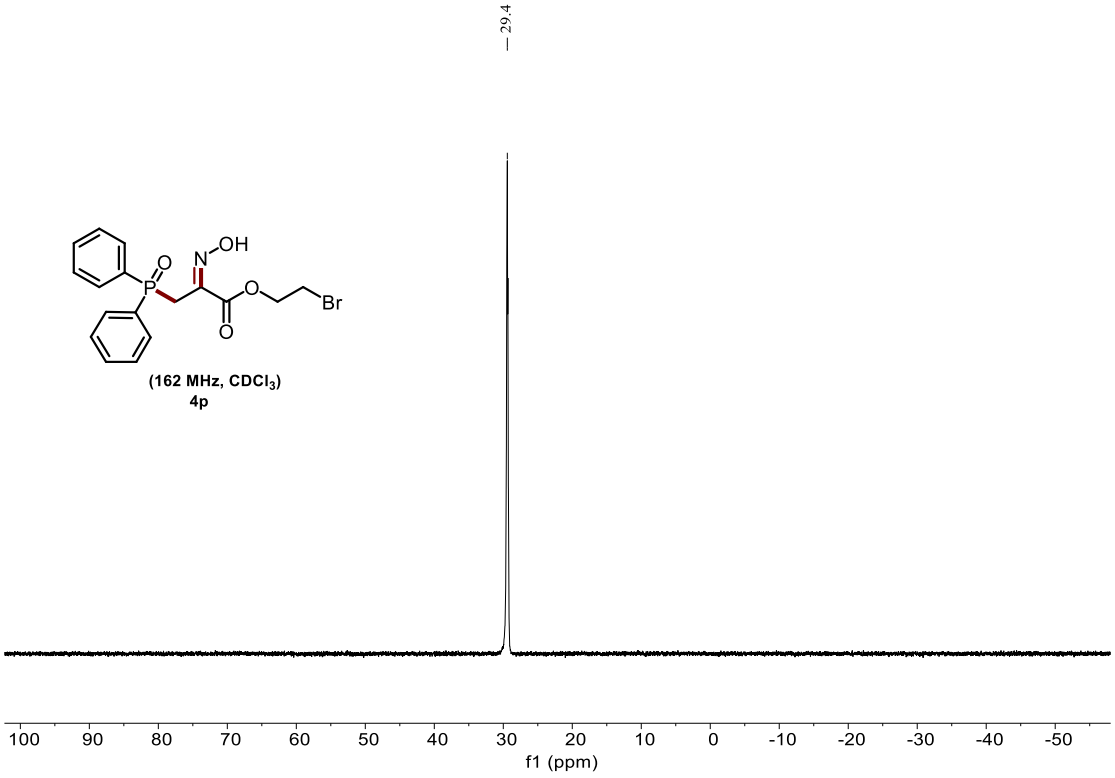
(162 MHz, $CDCl_3$)
4o

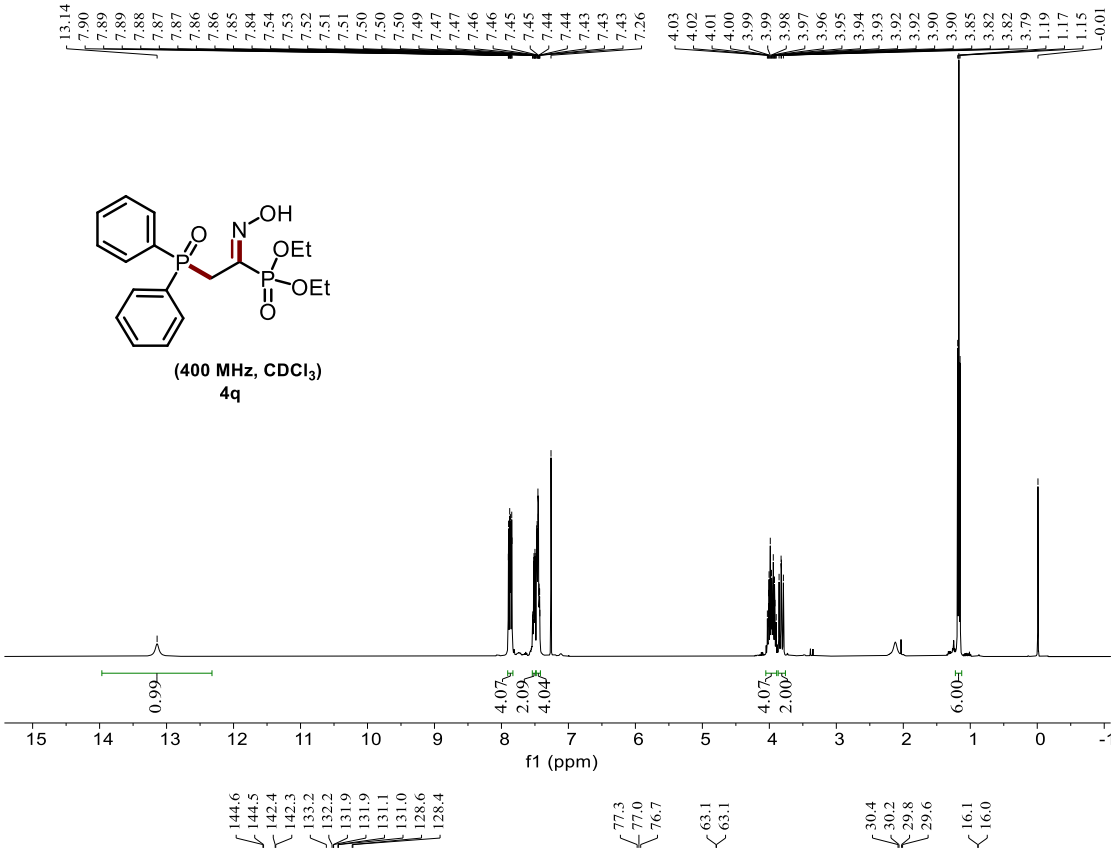


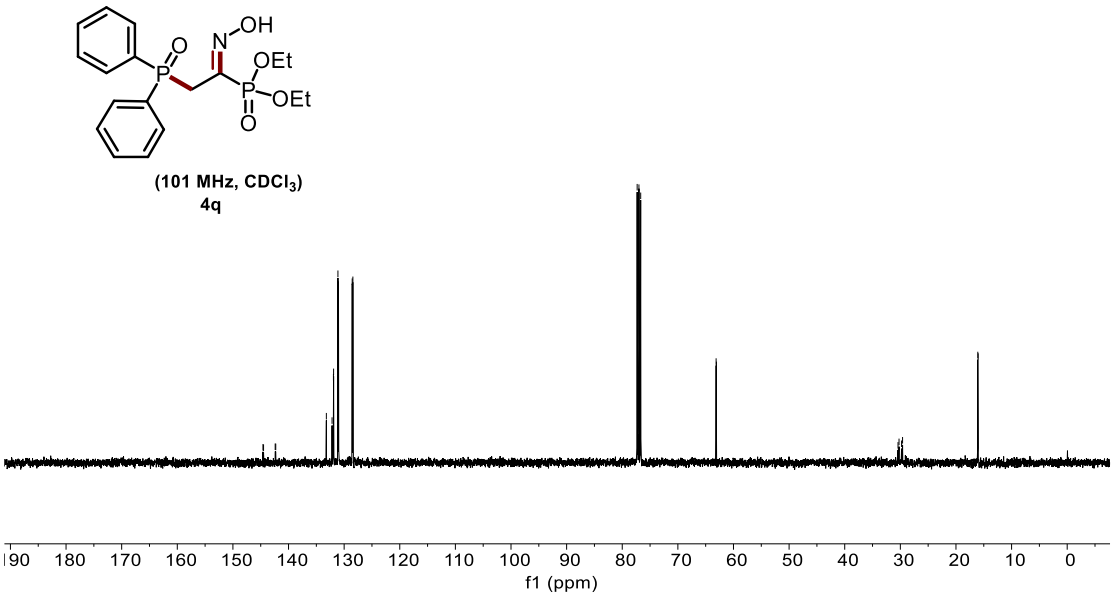


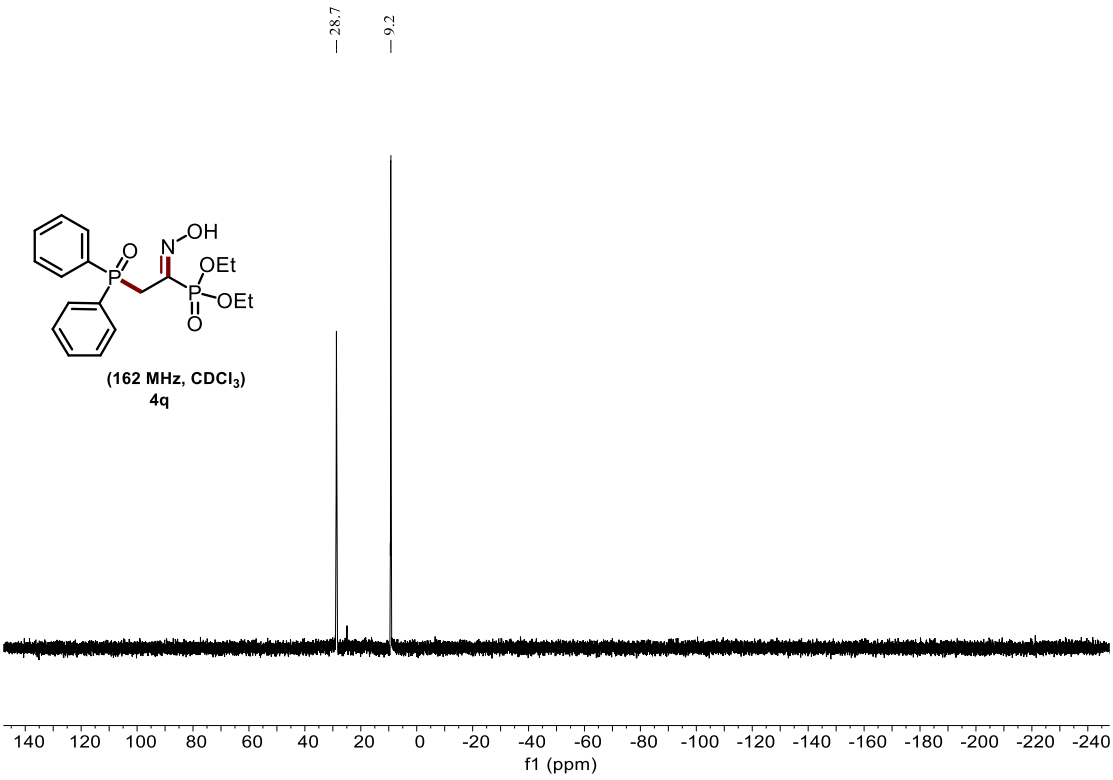
(400 MHz, $CDCl_3$)
4p

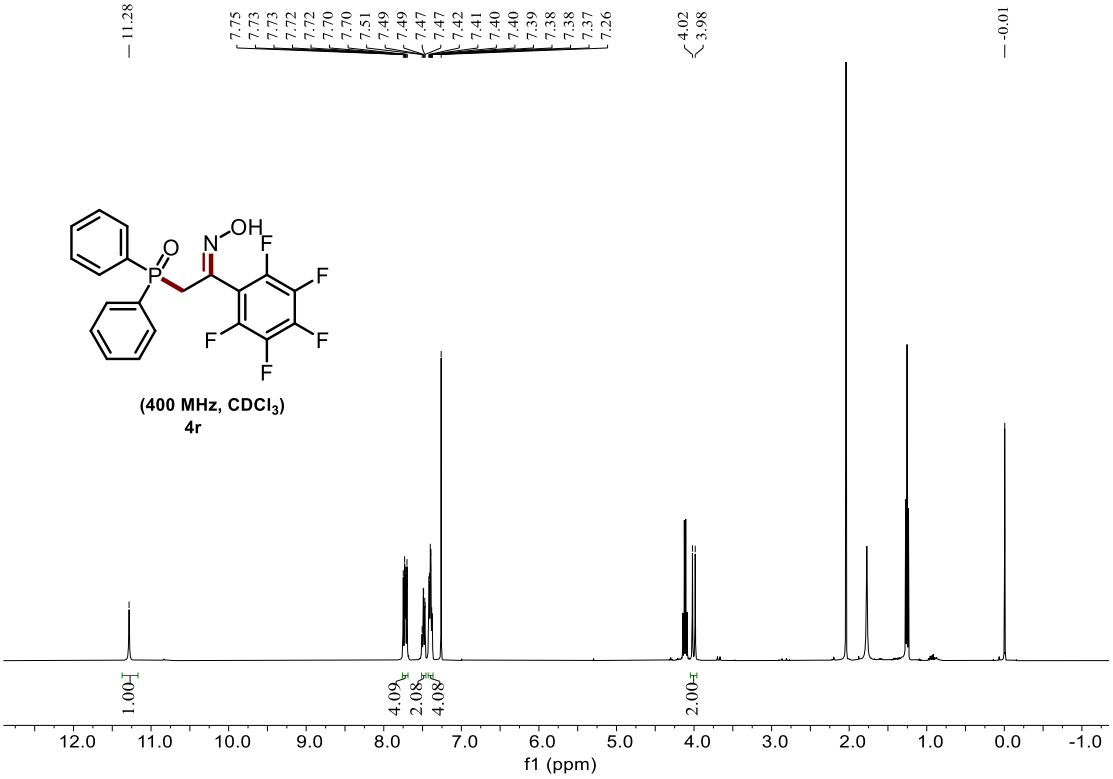

163.1
163.1
142.1
142.0
132.1
132.1
132.1
131.1
131.1
128.6
128.5
77.3
77.0
76.7
64.5
28.8
28.2
27.7
OH
N
O
P
O
O
Br
O
(101 MHz, CDCl3)
4p
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

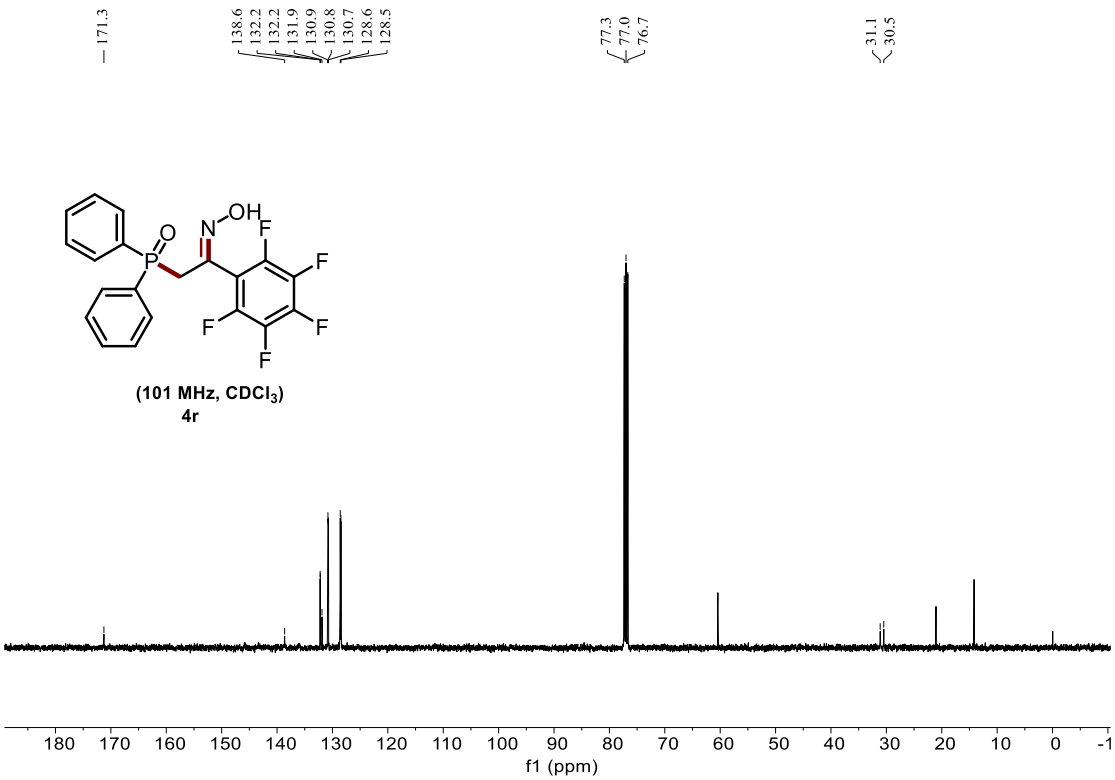

29.4
OH
N
O
P
O
O
Br
O
(162 MHz, CDCl3)
4p
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

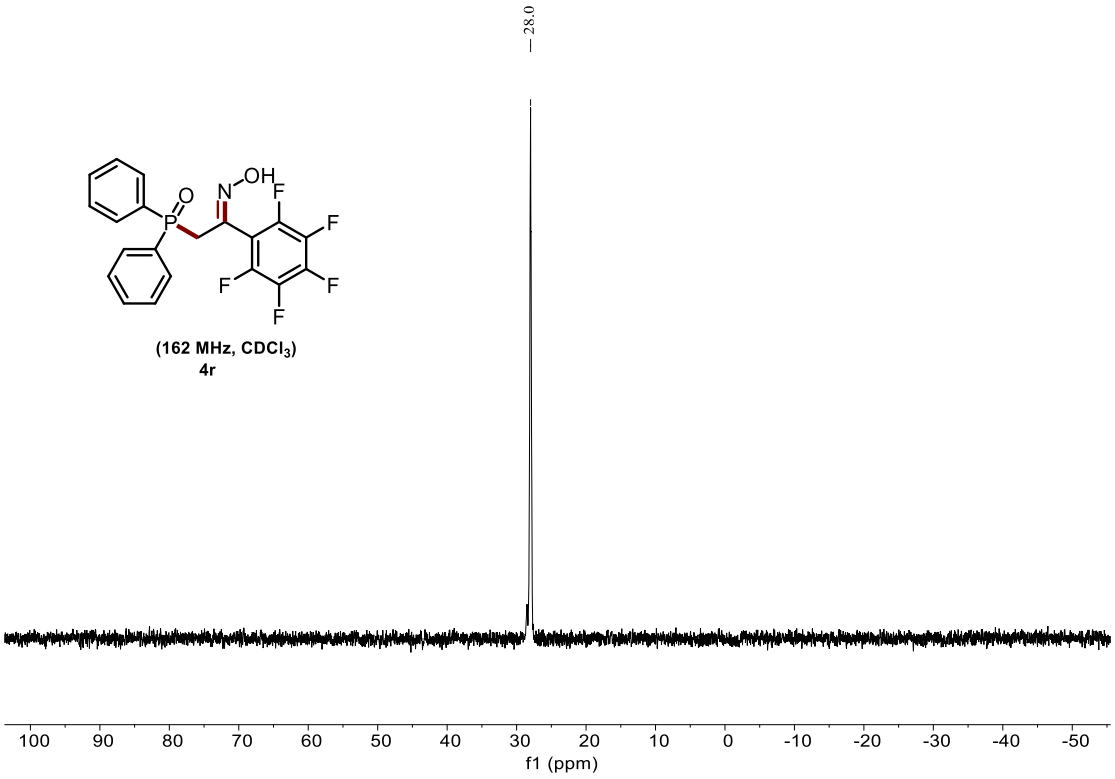

13.14
7.90
7.89
7.89
7.88
7.87
7.87
7.86
7.86
7.85
7.84
7.54
7.53
7.52
7.51
7.51
7.50
7.50
7.50
7.49
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.43
7.26
4.03
4.02
4.01
4.00
3.99
3.99
3.98
3.97
3.96
3.95
3.94
3.93
3.92
3.90
3.90
3.85
3.82
3.82
3.79
1.19
1.17
1.15
-0.01
OH
N
O
P
OEt
P
OEt
O
(400 MHz, CDCl3)
4q
0.99
4.07
2.09
4.04
4.07
2.00
6.00
f1 (ppm)
144.6
144.5
142.4
142.3
133.2
132.2
131.9
131.9
131.1
131.0
128.6
128.4
77.3
77.0
76.7
63.1
63.1
30.4
30.2
29.8
29.6
16.1
16.0

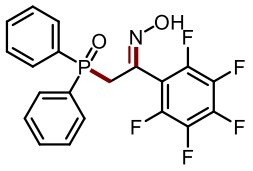

OH
N
O
P
OEt
P
OEt
O
(101 MHz, CDCl3)
4q
f1 (ppm)


28.7
9.2
OH
N
O
OEt
P
OEt
O
(162 MHz, CDCl3)
4q
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

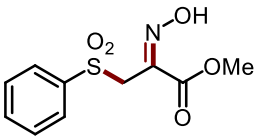

11.28
7.75 7.73 7.73 7.72 7.72 7.70 7.70 7.51 7.49 7.49 7.47 7.47 7.42 7.41 7.40 7.40 7.39 7.38 7.38 7.37 7.26
4.02
3.98
-0.01
OH
N
O
F
F
F
F
F
(400 MHz, CDCl3)
4r
1.00
4.09
2.08
4.08
2.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


171.3
138.6
132.2
132.2
131.9
130.9
130.8
130.7
128.6
128.5
77.3
77.0
76.7
31.1
30.5
O
P
N
OH
F
F
F
F
F
(101 MHz, CDCl3)
4r
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

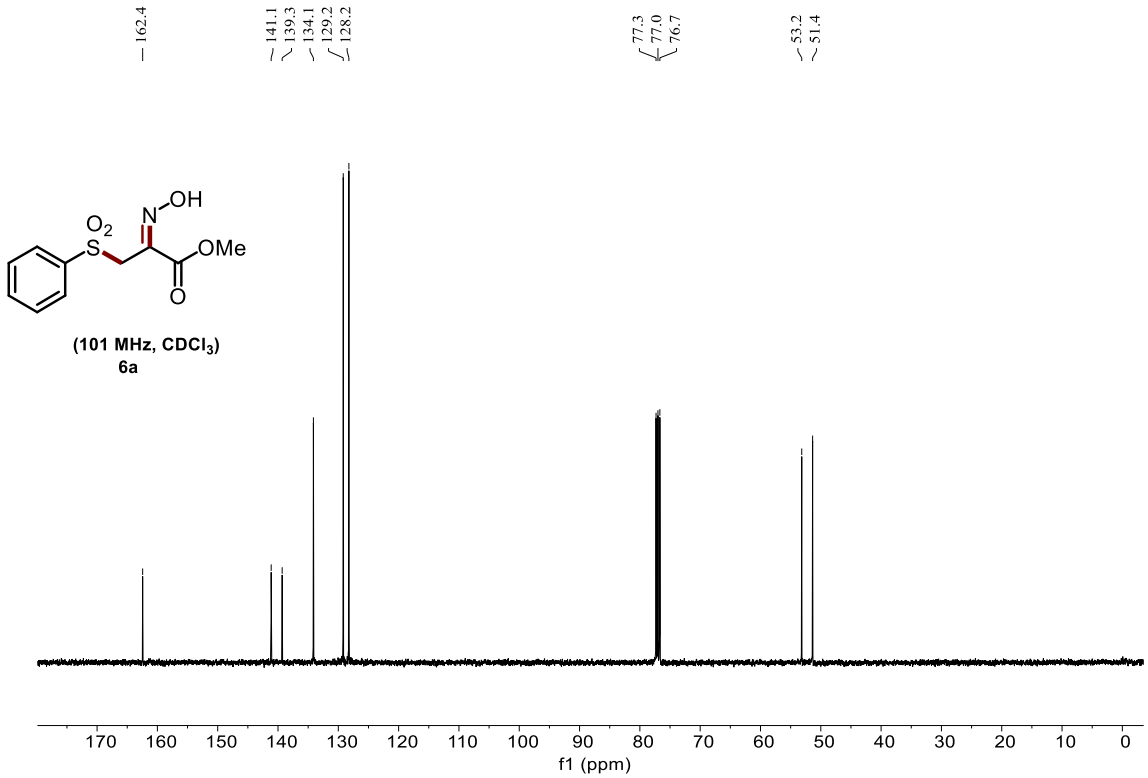

28.0
O
P
N
OH
F
F
F
F
F
(162 MHz, CDCl3)
4r
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)



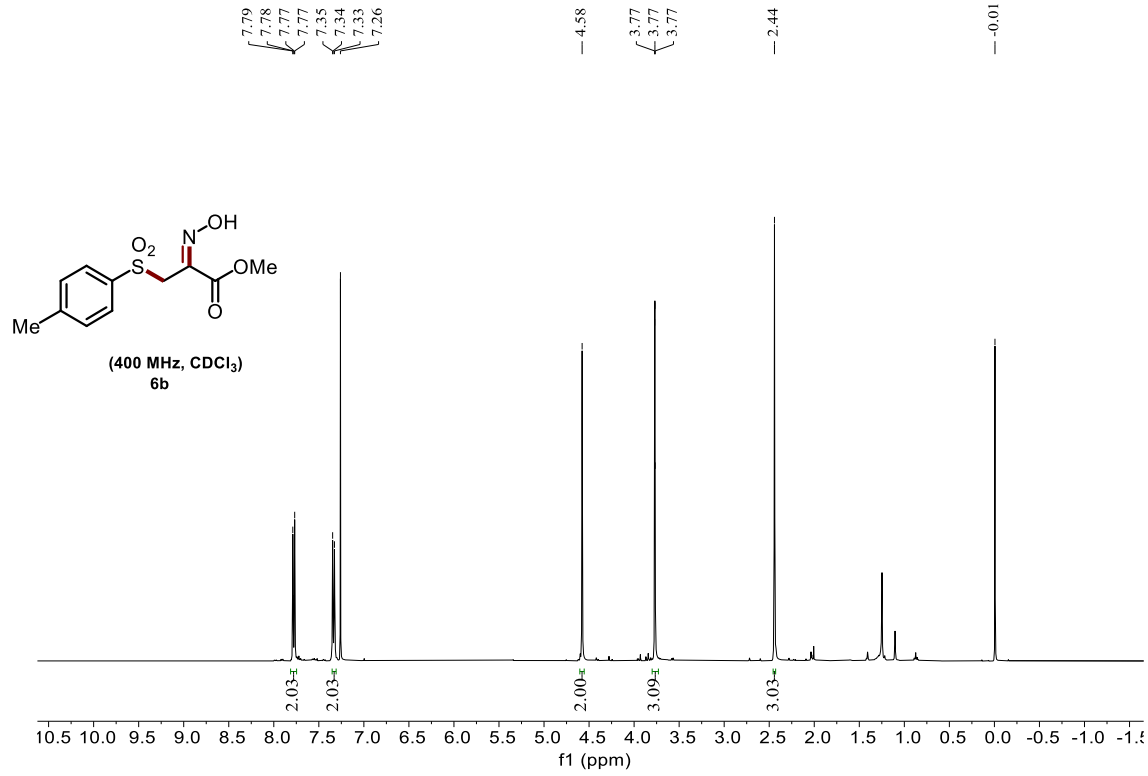
(376 MHz, $CDCl_3$)
4r



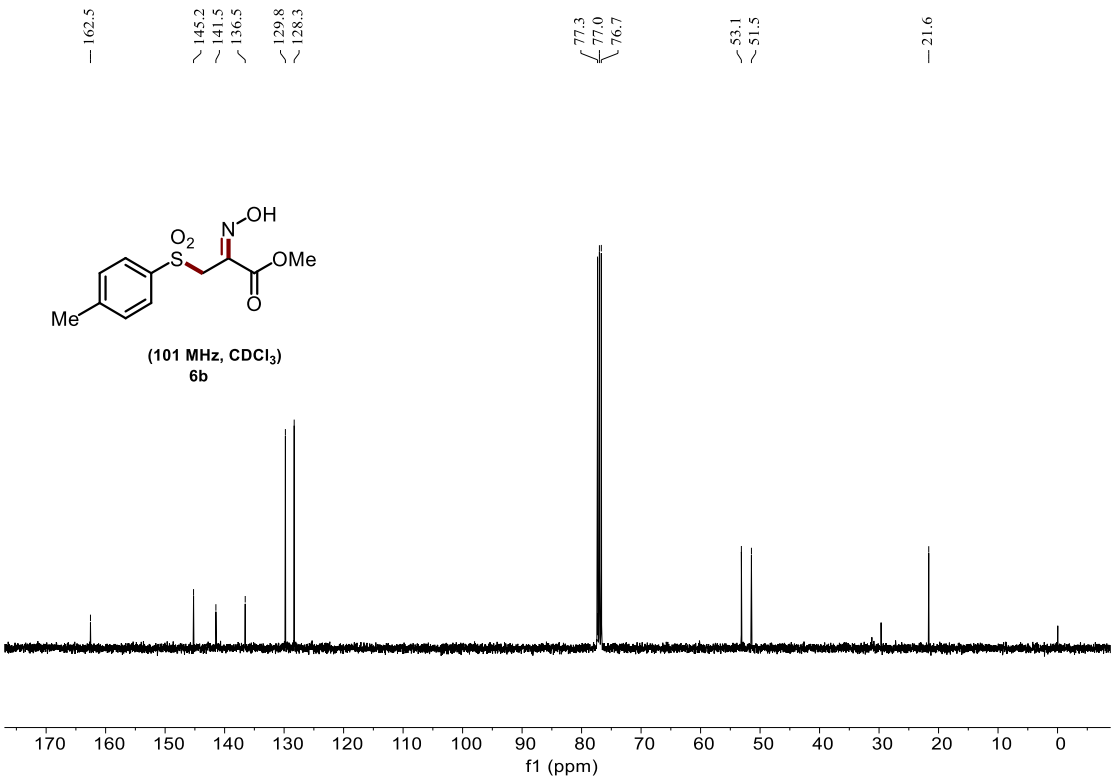
(400 MHz, $CDCl_3$)
6a

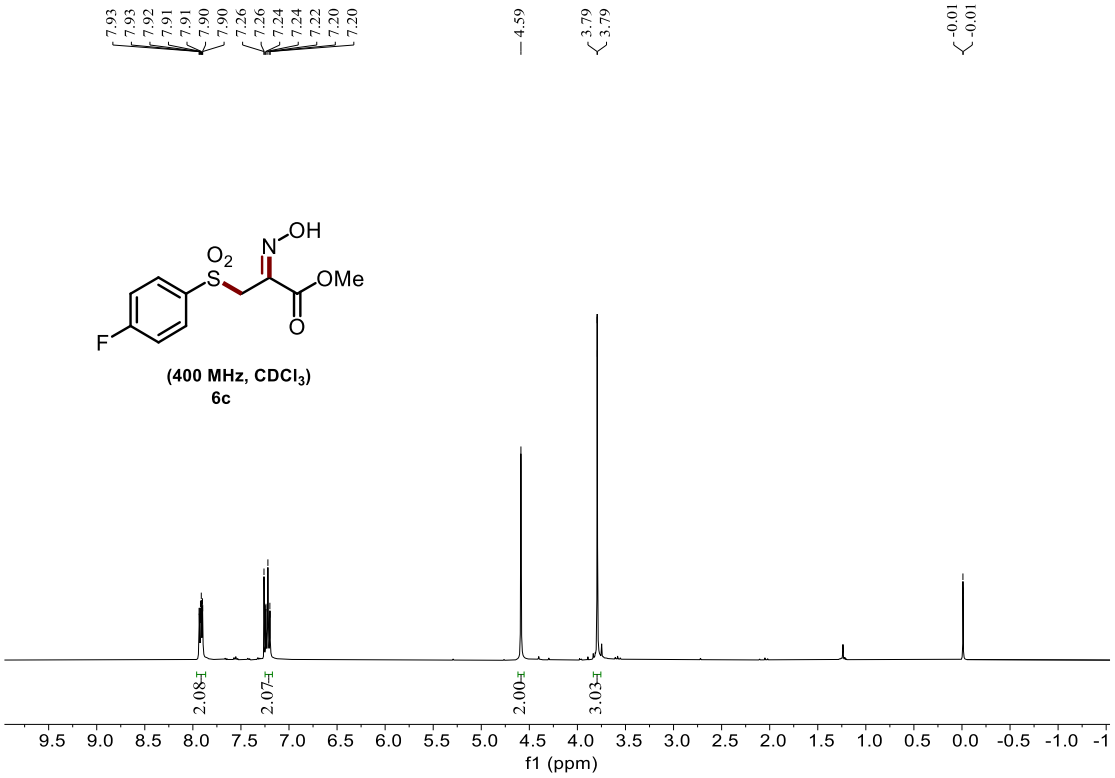


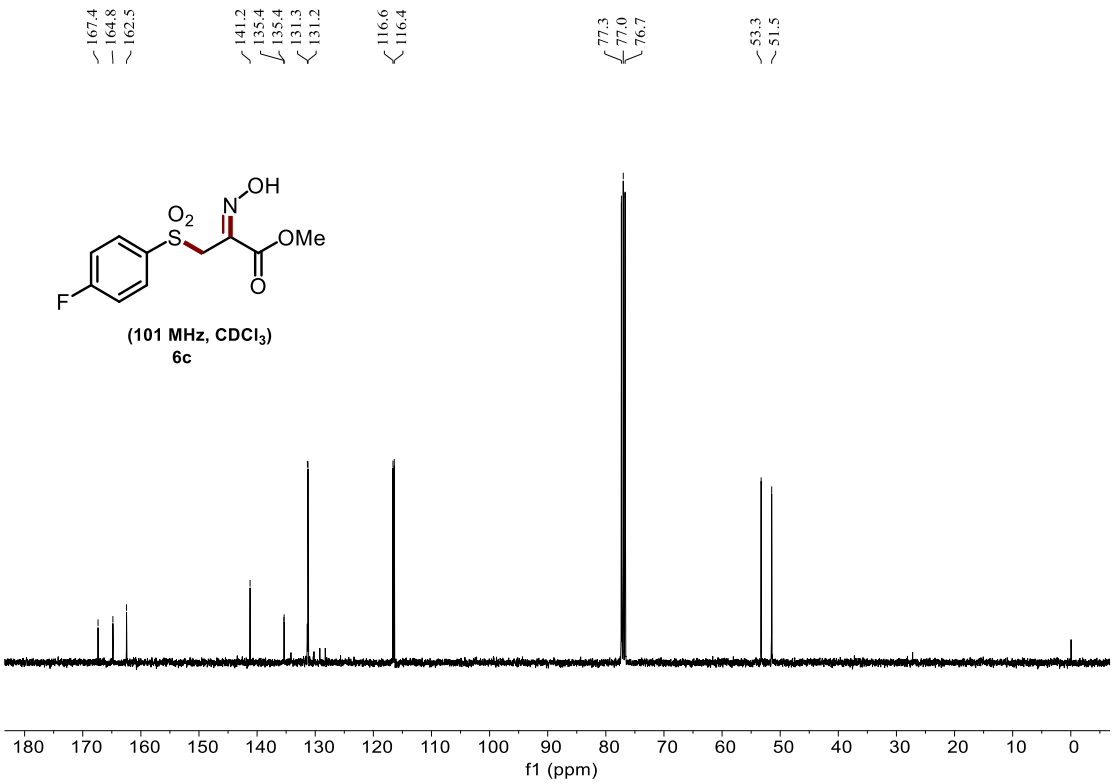
(101 MHz, $CDCl_3$)
6a



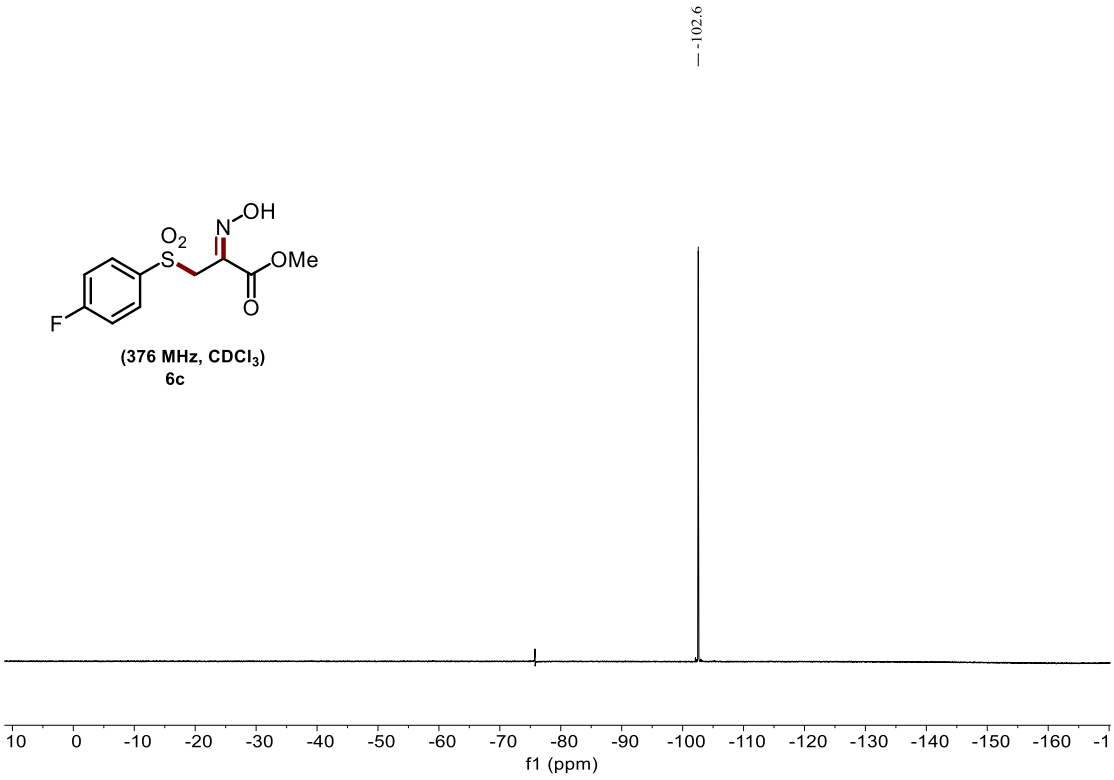
(400 MHz, $CDCl_3$)
6b


162.5
145.2
141.5
136.5
129.8
128.3
77.3
77.0
76.7
53.1
51.5
21.6
OH
N
O2
S
OMe
O
Me
(101 MHz, CDCl3)
6b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

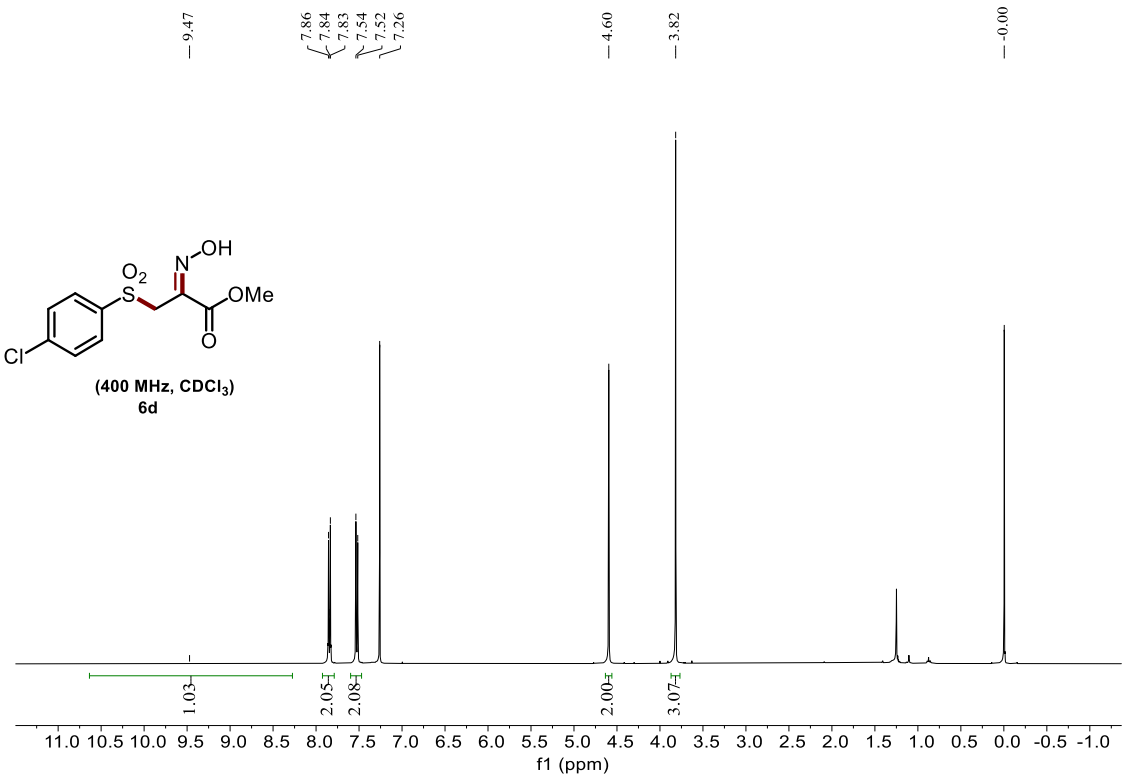

7.93
7.93
7.92
7.91
7.91
7.90
7.90
7.26
7.26
7.24
7.24
7.22
7.20
7.20
4.59
3.79
3.79
0.01
0.01
OH
N
O2
S
OMe
O
F
(400 MHz, CDCl3)
6c
2.08
2.07
2.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

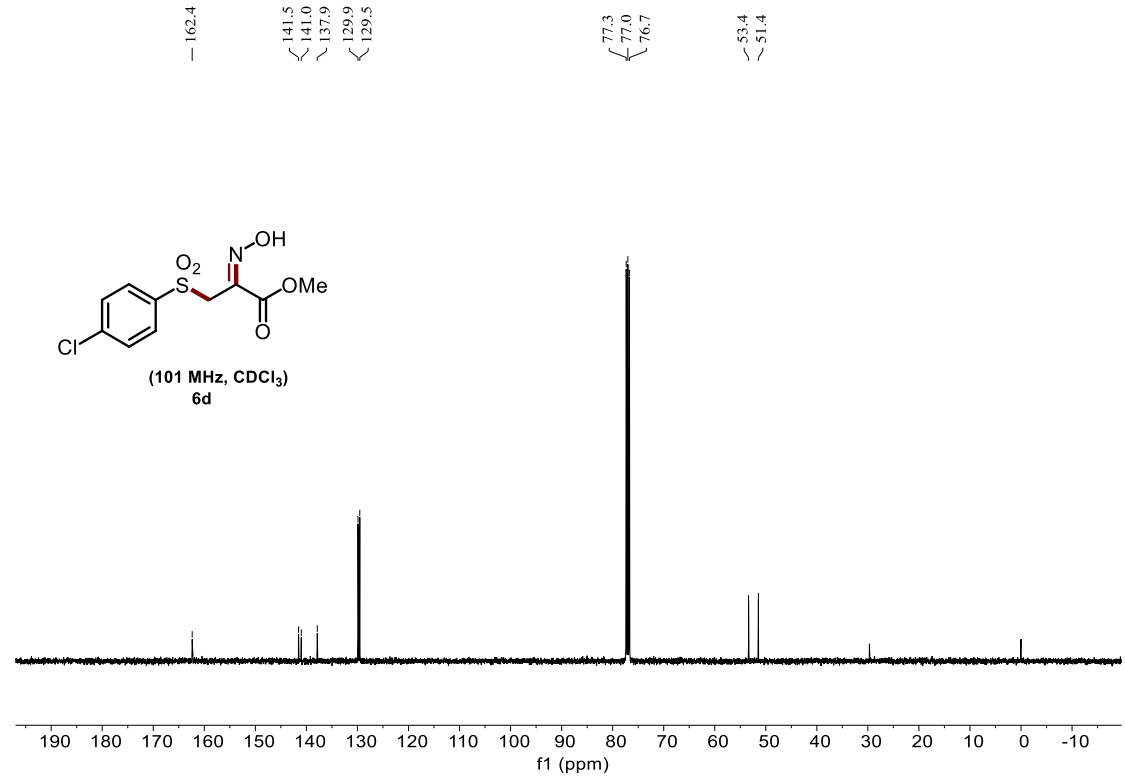


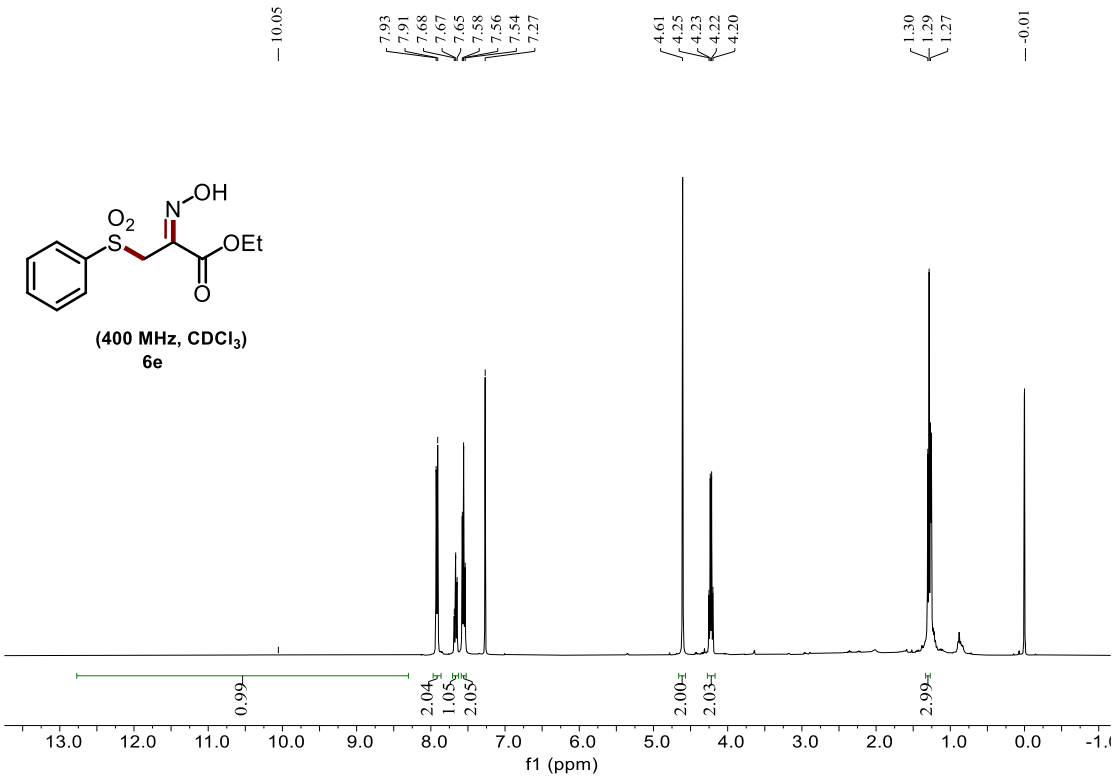
(101 MHz, $CDCl_3$)
6c

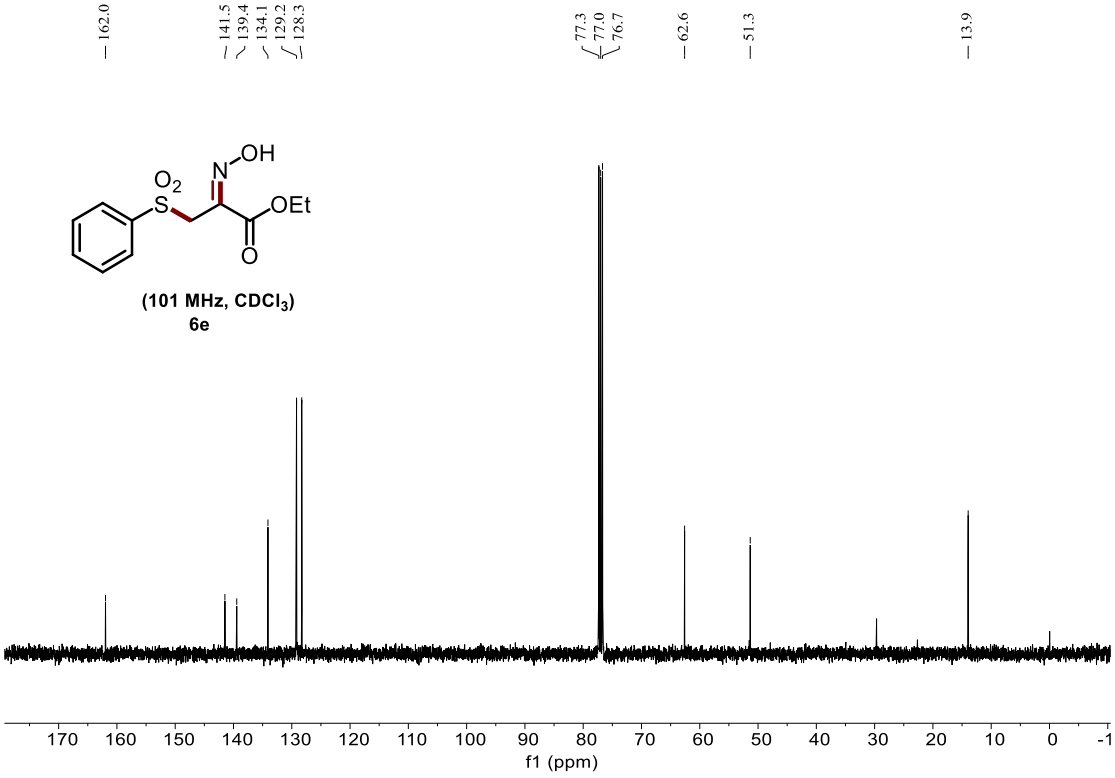


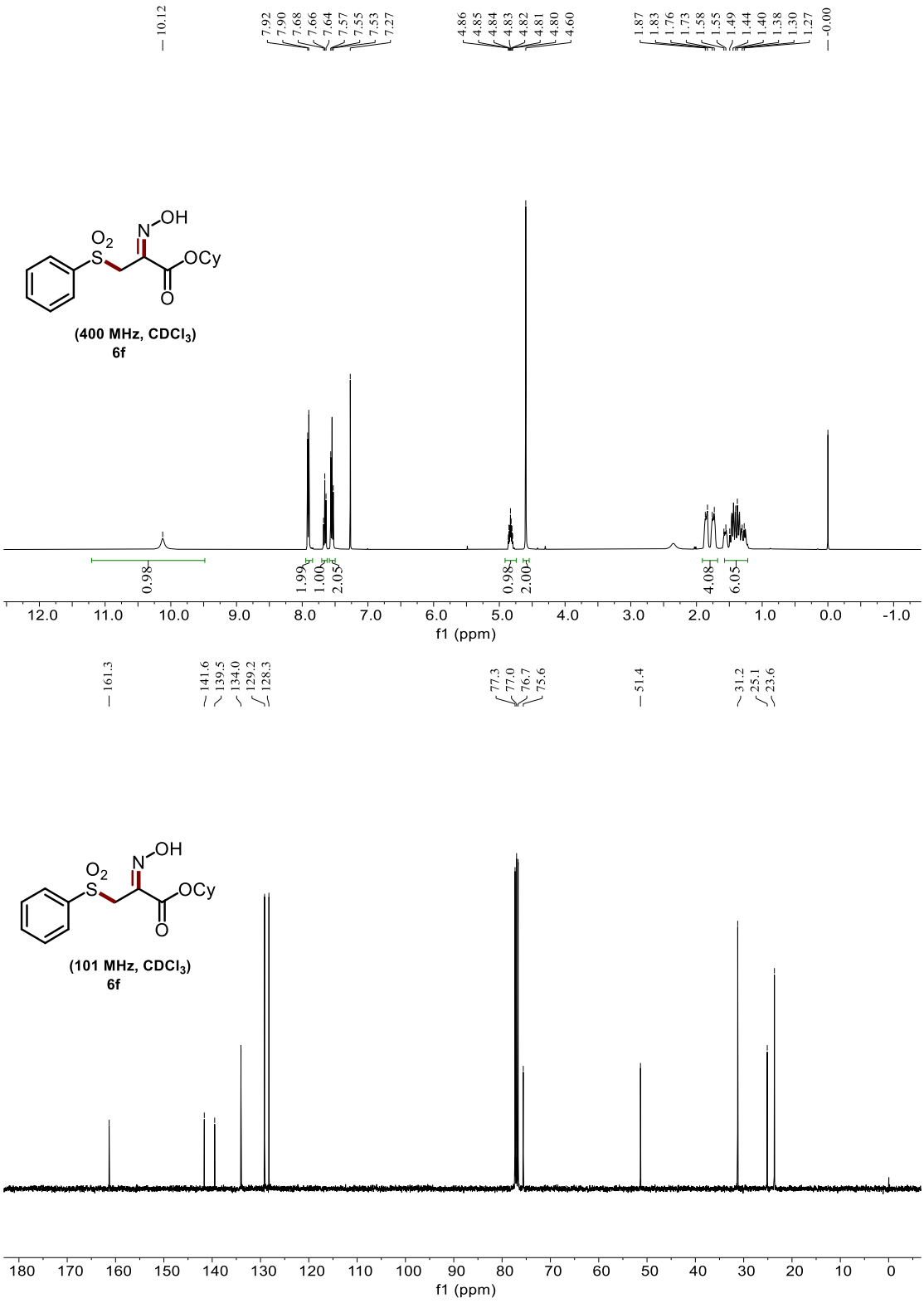
(376 MHz, $CDCl_3$)
6c

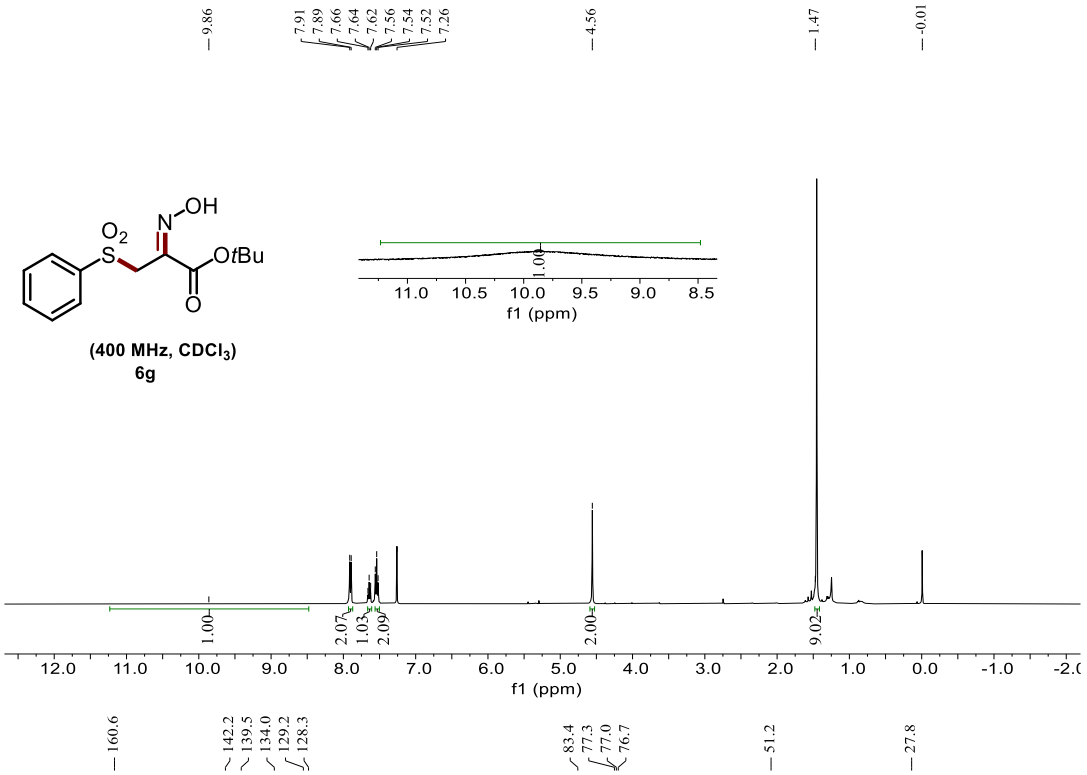

9.47
7.86
7.84
7.83
7.54
7.52
7.26
4.60
3.82
-0.00
OH
N
O2
S
OMe
O
Cl
(400 MHz, CDCl3)
6d
1.03
2.05
2.08
2.00
3.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

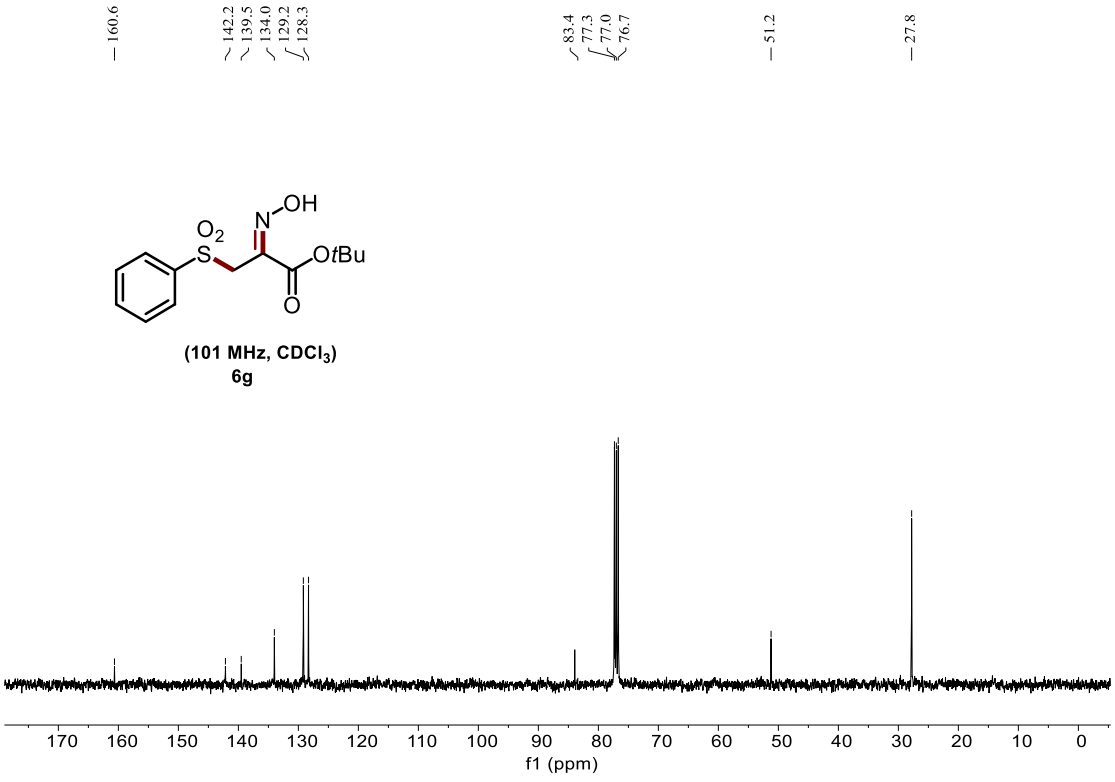

162.4
141.5
141.0
137.9
129.9
129.5
77.3
77.0
76.7
53.4
51.4
OH
N
O2
S
OMe
O
Cl
(101 MHz, CDCl3)
6d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

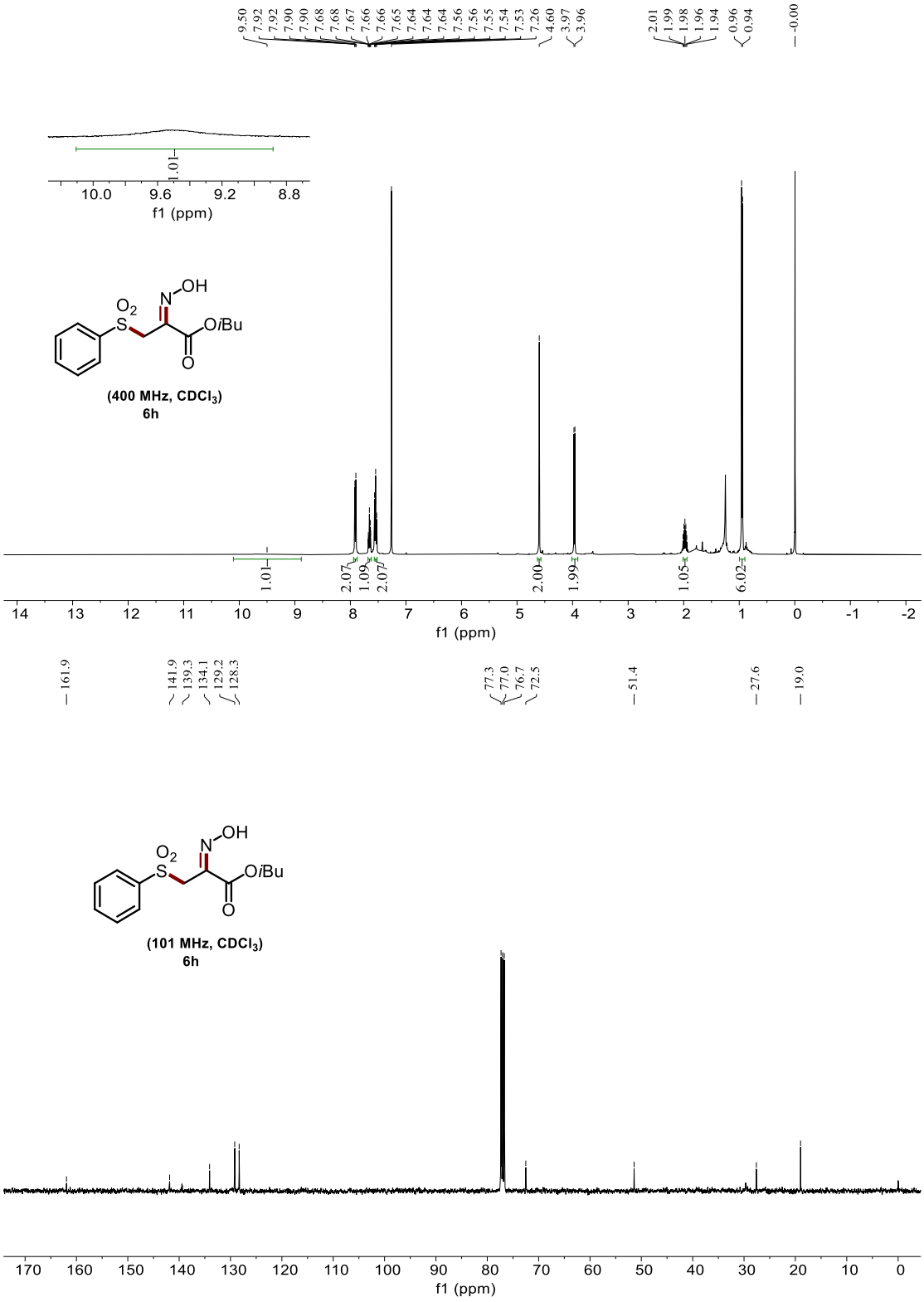

10.05
7.93
7.91
7.68
7.67
7.65
7.58
7.56
7.54
7.27
4.61
4.25
4.23
4.22
4.20
1.30
1.29
1.27
-0.01
OH
N
O2
S
OEt
O
(400 MHz, CDCl3)
6e
0.99
2.04
1.05
2.05
2.00
2.03
2.99
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

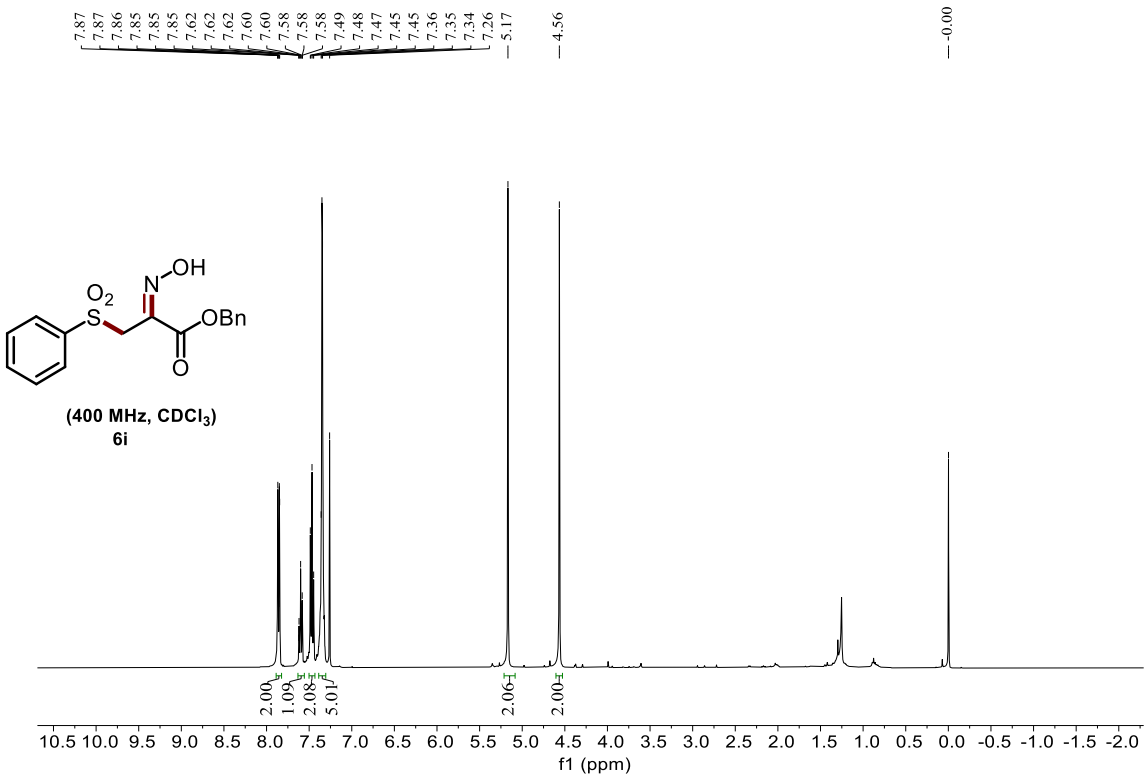

162.0
141.5
139.4
134.1
129.2
128.3
77.3
77.0
76.7
62.6
51.3
13.9
OH
N
O2
S
OEt
O
(101 MHz, CDCl3)
6e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

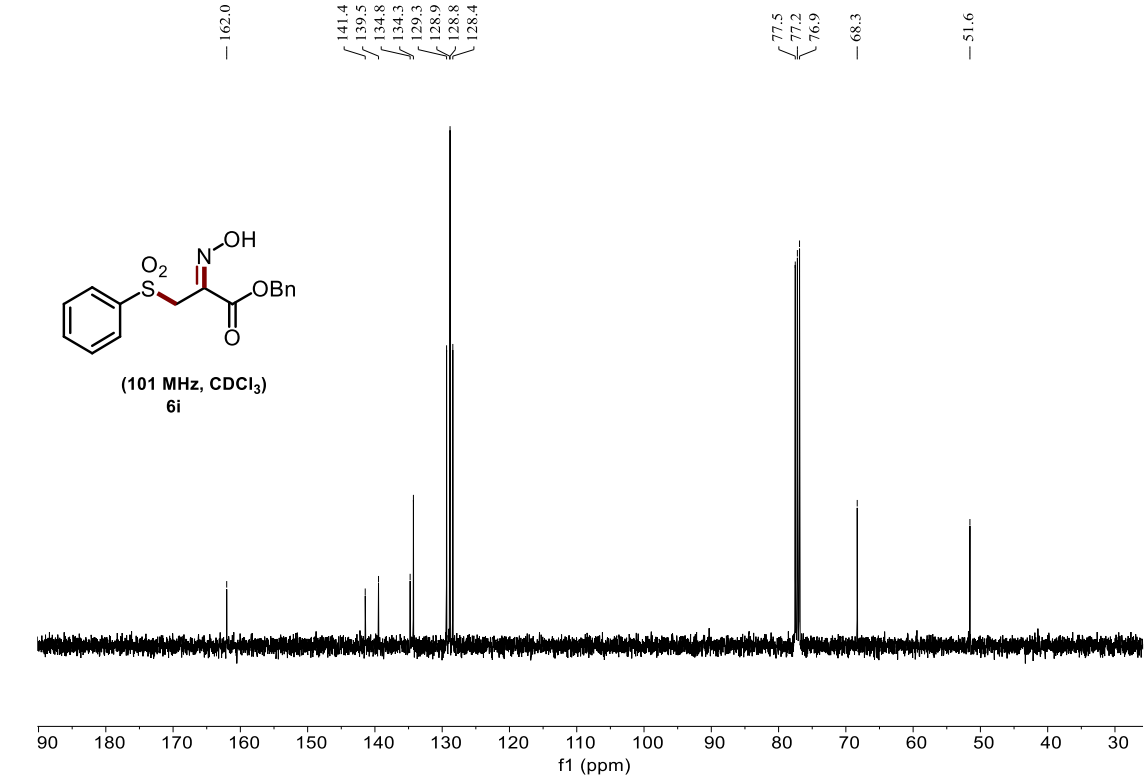

10.12
7.92
7.90
7.68
7.66
7.64
7.57
7.55
7.53
7.27
4.86
4.85
4.84
4.83
4.82
4.81
4.80
4.60
1.87
1.83
1.76
1.73
1.58
1.55
1.49
1.44
1.40
1.38
1.30
1.27
0.00
OH
N
O2
S
OCy
O
(400 MHz, CDCl3)
6f
0.98
1.99
1.00
2.05
0.98
2.00
4.08
6.05
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)
161.3
141.6
139.5
134.0
129.2
128.3
77.3
77.0
76.7
75.6
51.4
31.2
25.1
23.6
(101 MHz, CDCl3)
6f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

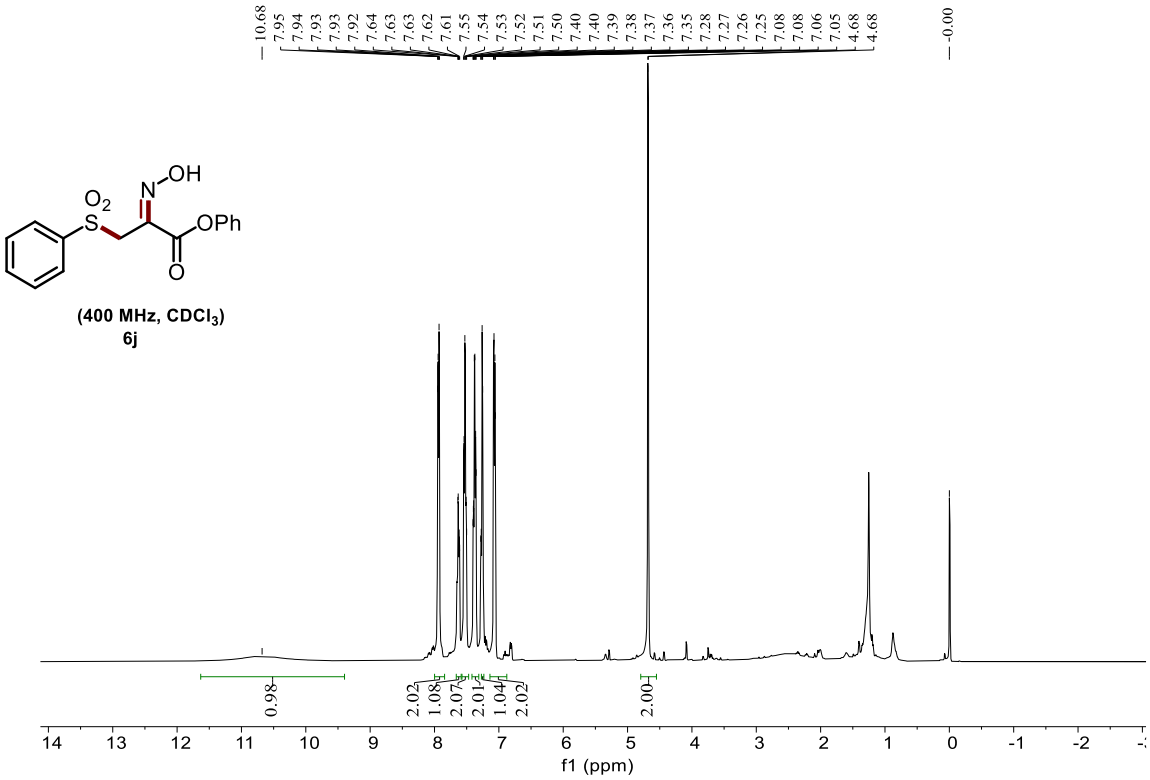

9.86
7.91
7.89
7.66
7.64
7.62
7.56
7.54
7.52
7.26
4.56
1.47
-0.01
OH
N
O2
S
OtBu
O
(400 MHz, CDCl3)
6g
1.00
11.0
10.5
10.0
9.5
9.0
8.5
f1 (ppm)
1.00
2.07
1.03
2.09
2.00
9.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


160.6
142.2
139.5
134.0
129.2
128.3
83.4
77.3
77.0
76.7
51.2
27.8
OH
N
O2
S
OtBu
O
(101 MHz, CDCl3)
6g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

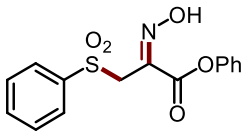

9.50
7.92
7.92
7.90
7.90
7.68
7.68
7.67
7.66
7.66
7.65
7.64
7.64
7.64
7.56
7.56
7.55
7.54
7.53
7.26
4.60
3.97
3.96
2.01
1.99
1.98
1.96
1.94
0.96
0.94
-0.00
1.01
10.0
9.6
9.2
8.8
f1 (ppm)
O2
S
N
OH
OiBu
O
(400 MHz, CDCl3)
6h
1.01
2.07
1.09
2.07
2.00
1.99
1.05
6.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
161.9
141.9
139.3
134.1
129.2
128.3
77.3
77.0
76.7
72.5
51.4
27.6
19.0
O2
S
N
OH
OiBu
O
(101 MHz, CDCl3)
6h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.87
7.87
7.86
7.85
7.85
7.85
7.62
7.62
7.62
7.60
7.60
7.58
7.58
7.58
7.49
7.48
7.47
7.45
7.45
7.36
7.35
7.34
7.26
5.17
4.56
0.00
OH
N
O2
S
OBn
O
(400 MHz, CDCl3)
6i
2.00
1.09
2.08
5.01
2.06
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

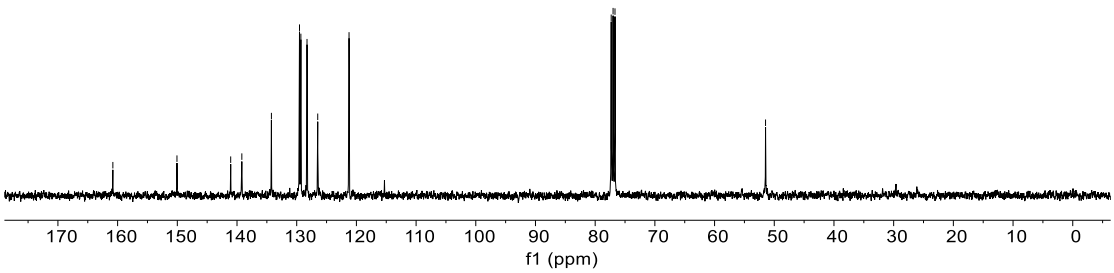

162.0
141.4
139.5
134.8
134.3
129.3
128.9
128.8
128.4
77.5
77.2
76.9
68.3
51.6
OH
N
O2
S
OBn
O
(101 MHz, CDCl3)
6i
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)

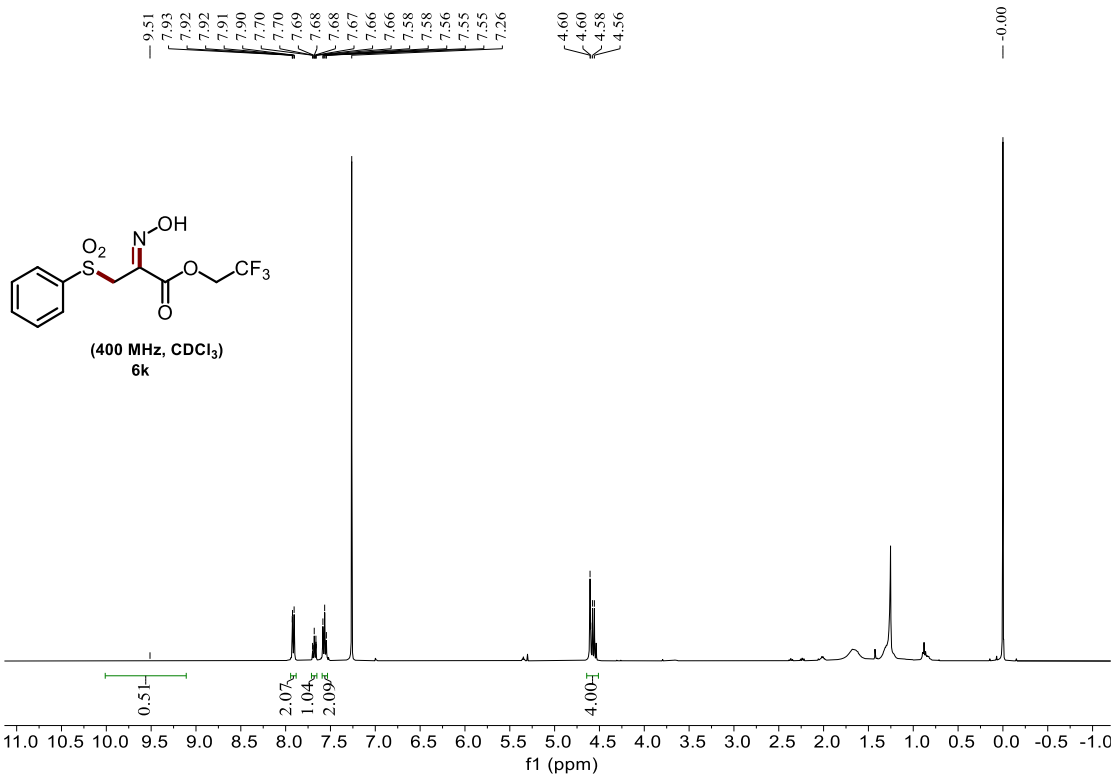


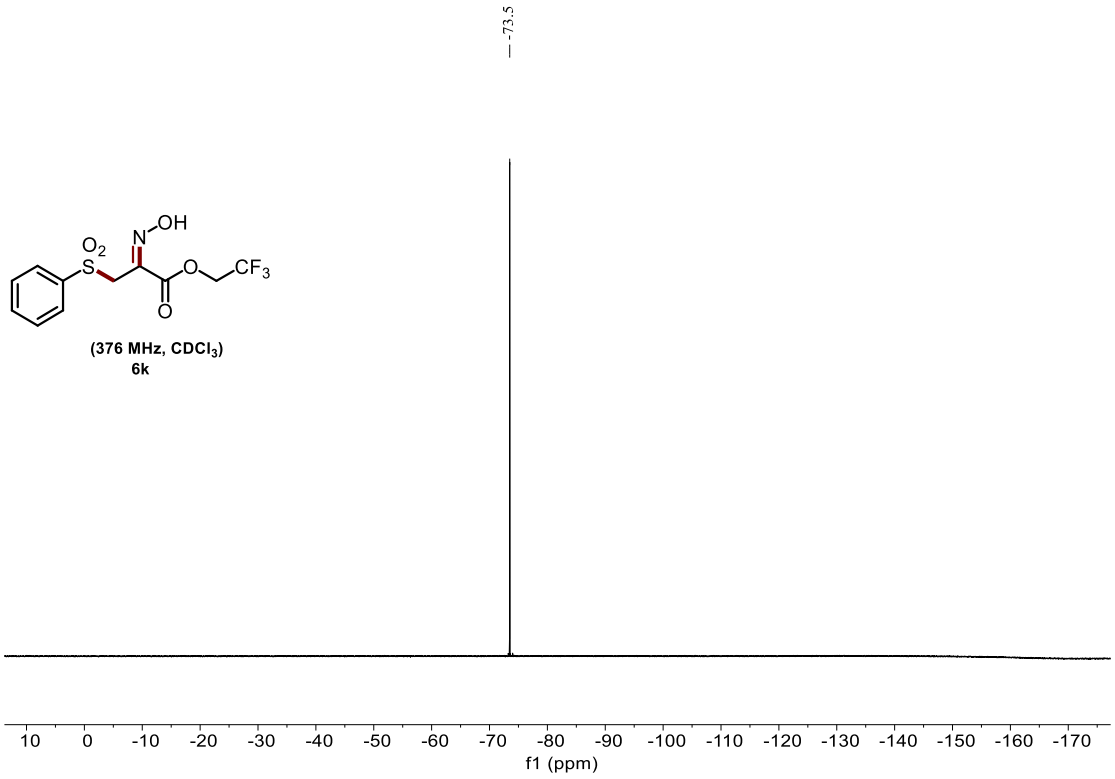
(400 MHz, $CDCl_3$)
6j

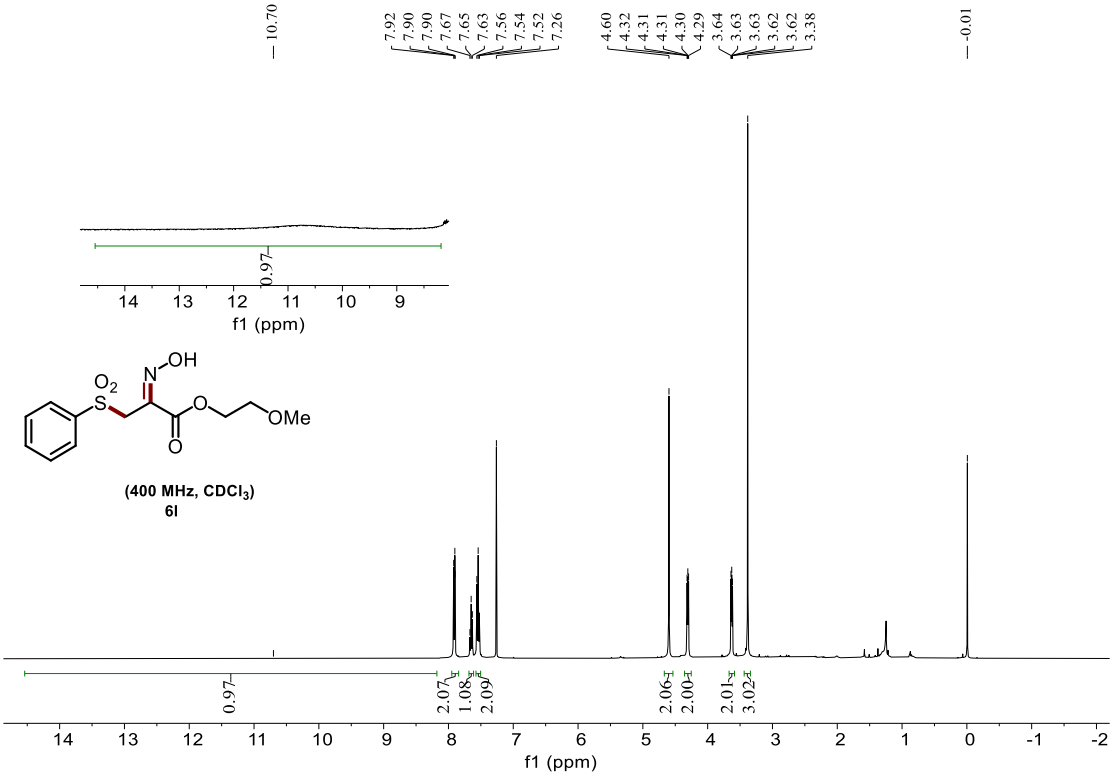


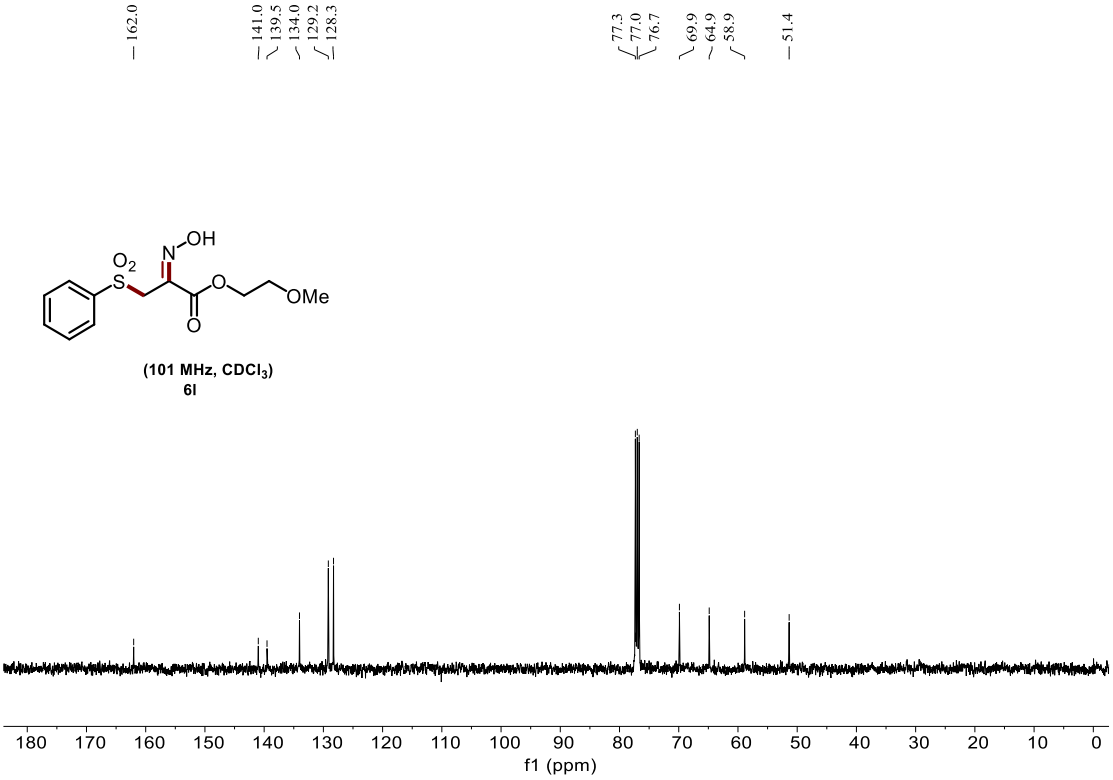
(101 MHz, $CDCl_3$)
6j

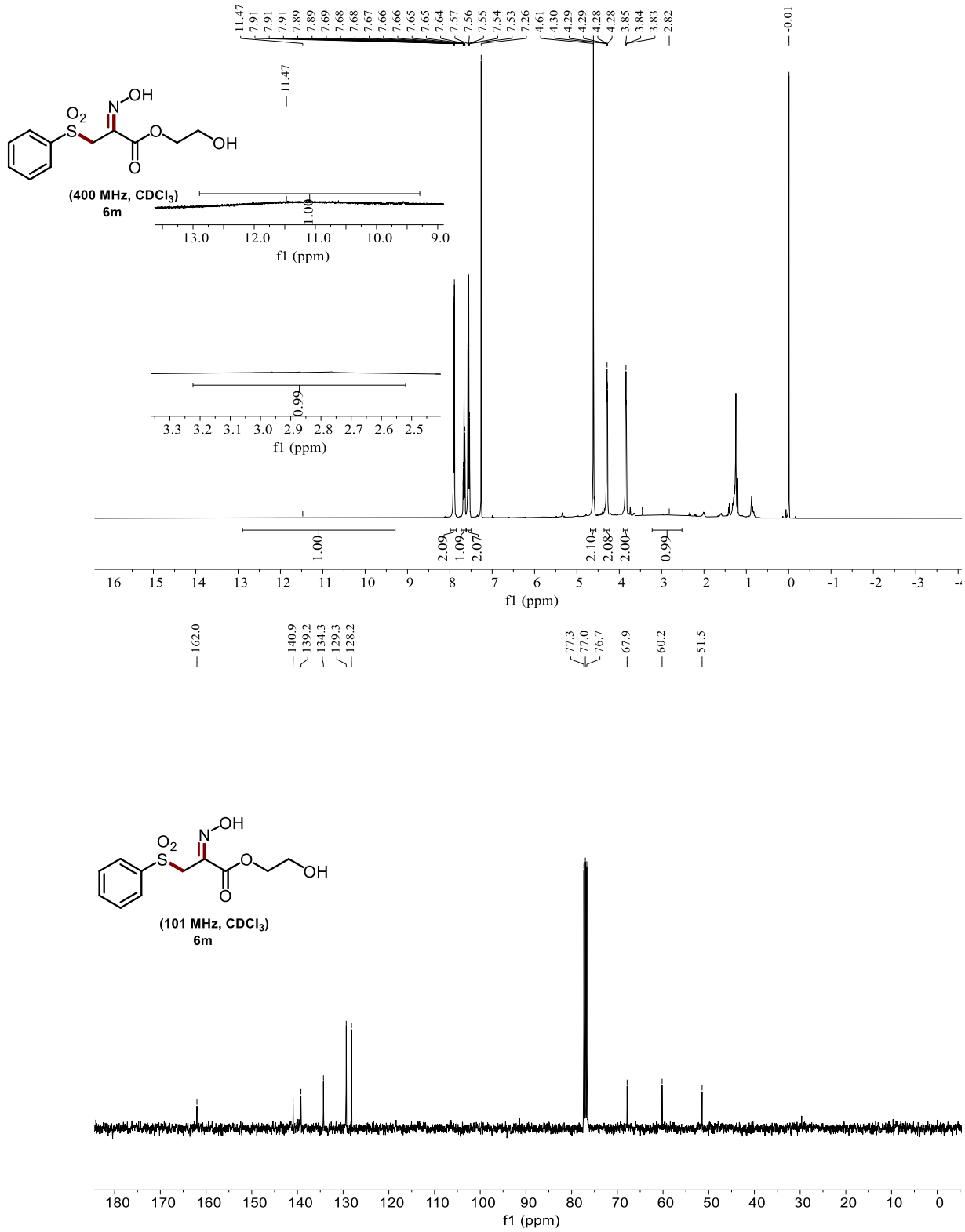


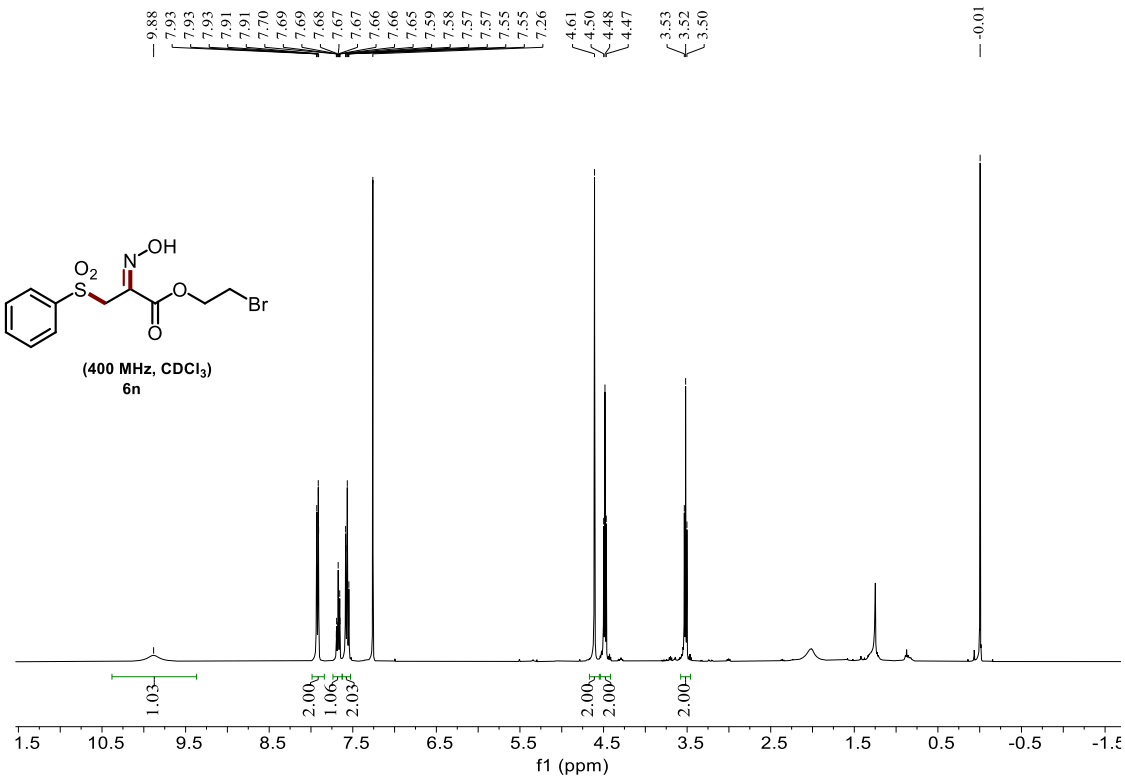

9.51
7.93
7.92
7.92
7.91
7.90
7.70
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.58
7.58
7.56
7.55
7.55
7.26
4.60
4.60
4.58
4.56
-0.00
OH
N
O2
S
O
CF3
O
(400 MHz, CDCl3)
6k
0.51
2.07
1.04
2.09
4.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

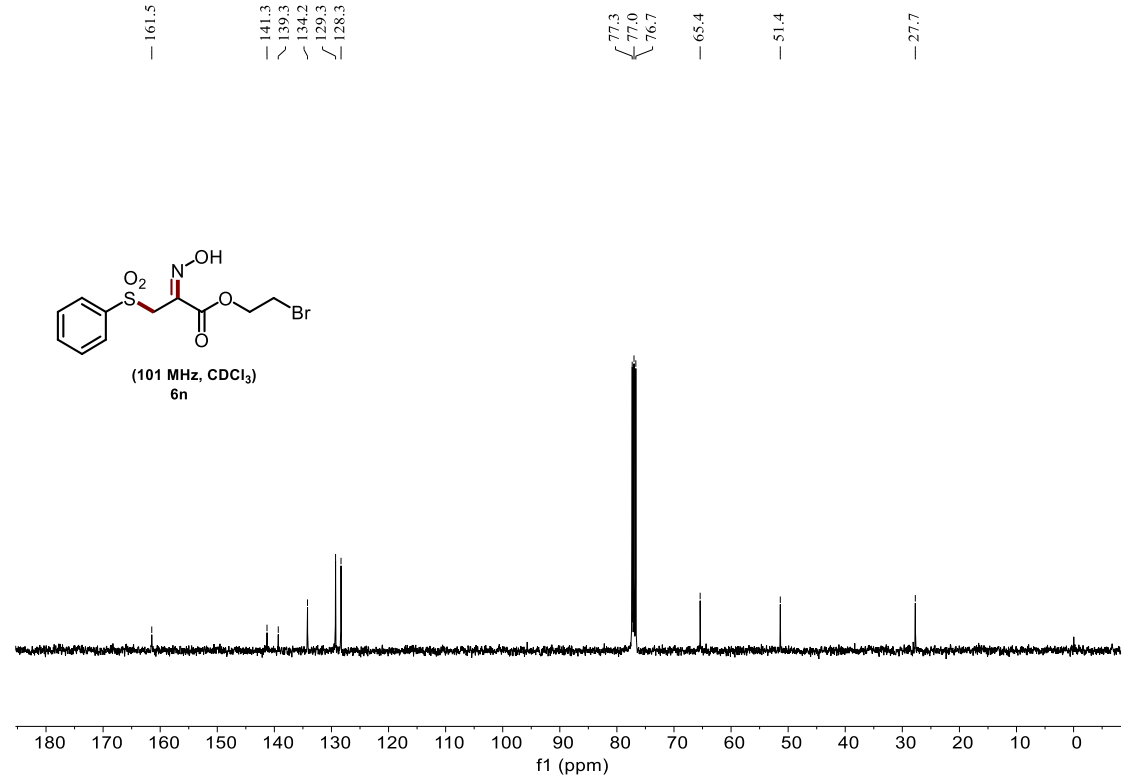

-73.5
OH
N
O2
S
O
CF3
O
(376 MHz, CDCl3)
6k
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

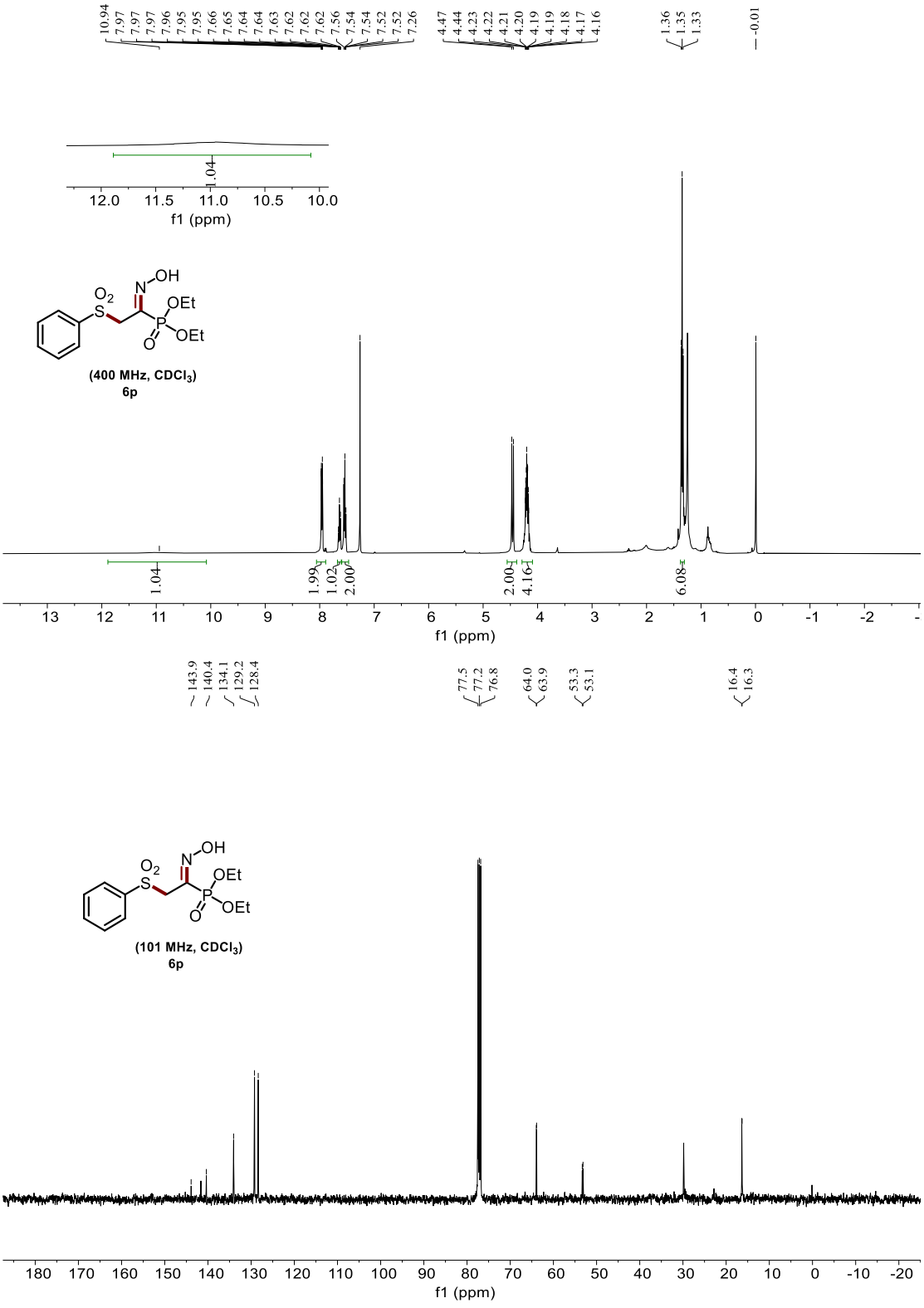

10.70
7.92
7.90
7.90
7.67
7.65
7.63
7.56
7.54
7.52
7.26
4.60
4.32
4.31
4.31
4.30
4.29
3.64
3.63
3.63
3.62
3.62
3.38
-0.01
0.97
f1 (ppm)
O2
S
N
OH
O
O
OMe
(400 MHz, CDCl3)
6l
0.97
2.07
1.08
2.09
2.06
2.00
2.01
3.02
f1 (ppm)

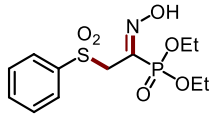

162.0
141.0
139.5
134.0
129.2
128.3
77.3
77.0
76.7
69.9
64.9
58.9
51.4
O2
S
N
OH
O
O
OMe
(101 MHz, CDCl3)
6l
f1 (ppm)


(400 MHz, CDCl3)
6m
f1 (ppm)
(101 MHz, CDCl3)
6m
f1 (ppm)

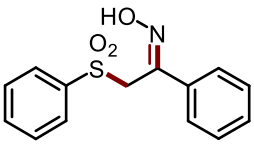

9.88
7.93
7.93
7.93
7.91
7.91
7.70
7.69
7.69
7.68
7.67
7.67
7.66
7.66
7.65
7.59
7.58
7.57
7.57
7.55
7.55
7.26
4.61
4.50
4.48
4.47
3.53
3.52
3.50
-0.01
OH
N
O2
S
O
Br
O
(400 MHz, CDCl3)
6n
1.03
2.00
1.06
2.03
2.00
2.00
2.00
1.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


161.5
141.3
139.3
134.2
129.3
128.3
77.3
77.0
76.7
65.4
51.4
27.7
OH
N
O2
S
O
Br
O
(101 MHz, CDCl3)
6n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

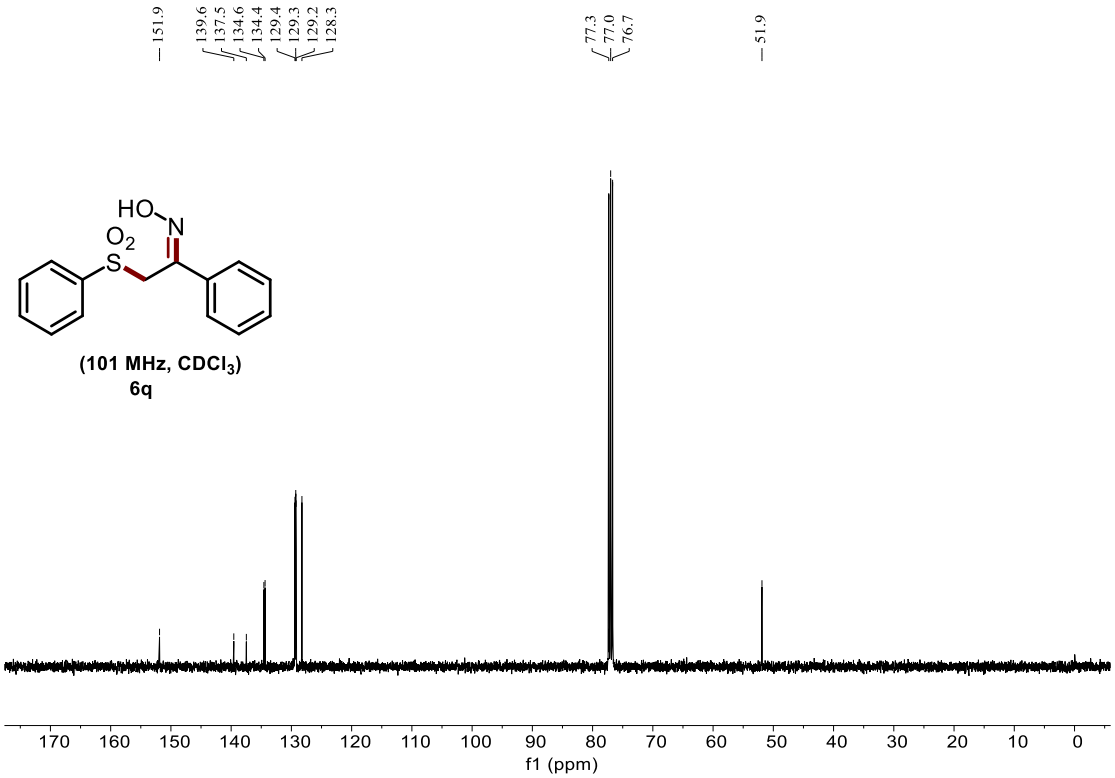

10.94
7.97
7.97
7.97
7.96
7.95
7.95
7.66
7.65
7.64
7.64
7.63
7.62
7.62
7.62
7.56
7.54
7.54
7.52
7.52
7.26
4.47
4.44
4.23
4.22
4.21
4.20
4.19
4.19
4.18
4.17
4.16
1.36
1.35
1.33
-0.01
1.04
12.0
11.5
11.0
10.5
10.0
f1 (ppm)
OH
N
O2
S
OEt
P
OEt
O
(400 MHz, CDCl3)
6p
1.04
1.99
1.02
2.00
2.00
4.16
6.08
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
143.9
140.4
134.1
129.2
128.4
77.5
77.2
76.8
64.0
63.9
53.3
53.1
16.4
16.3
OH
N
O2
S
OEt
P
OEt
O
(101 MHz, CDCl3)
6p
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

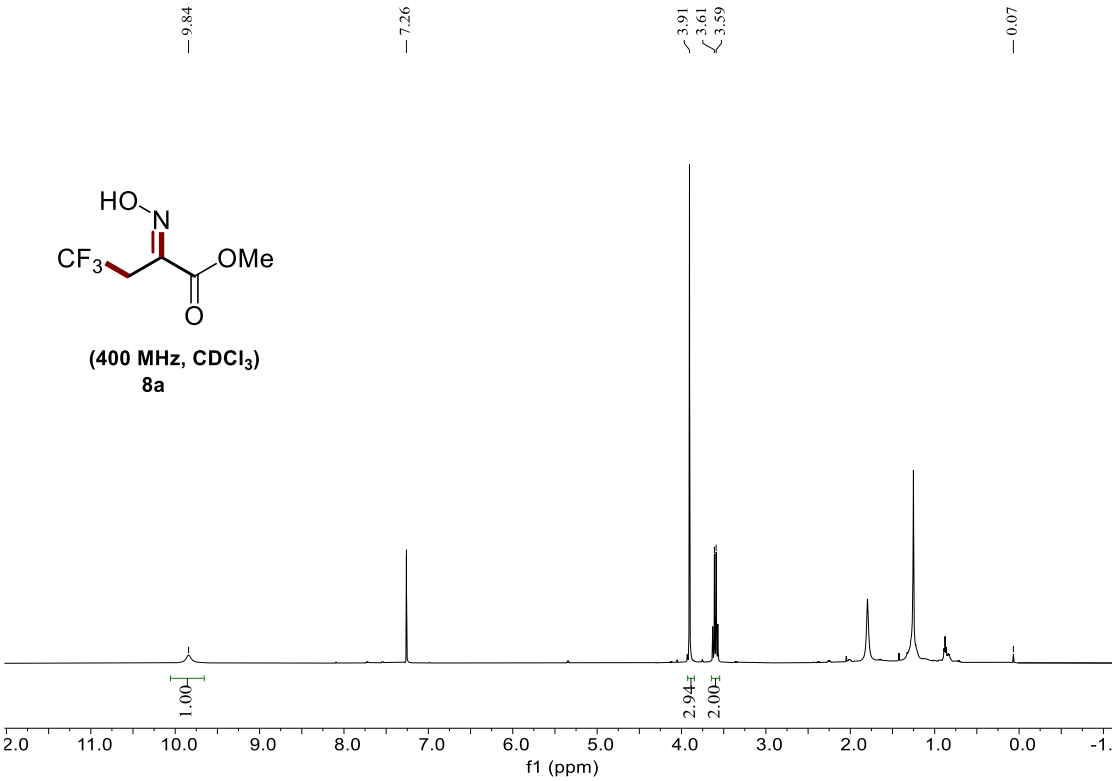


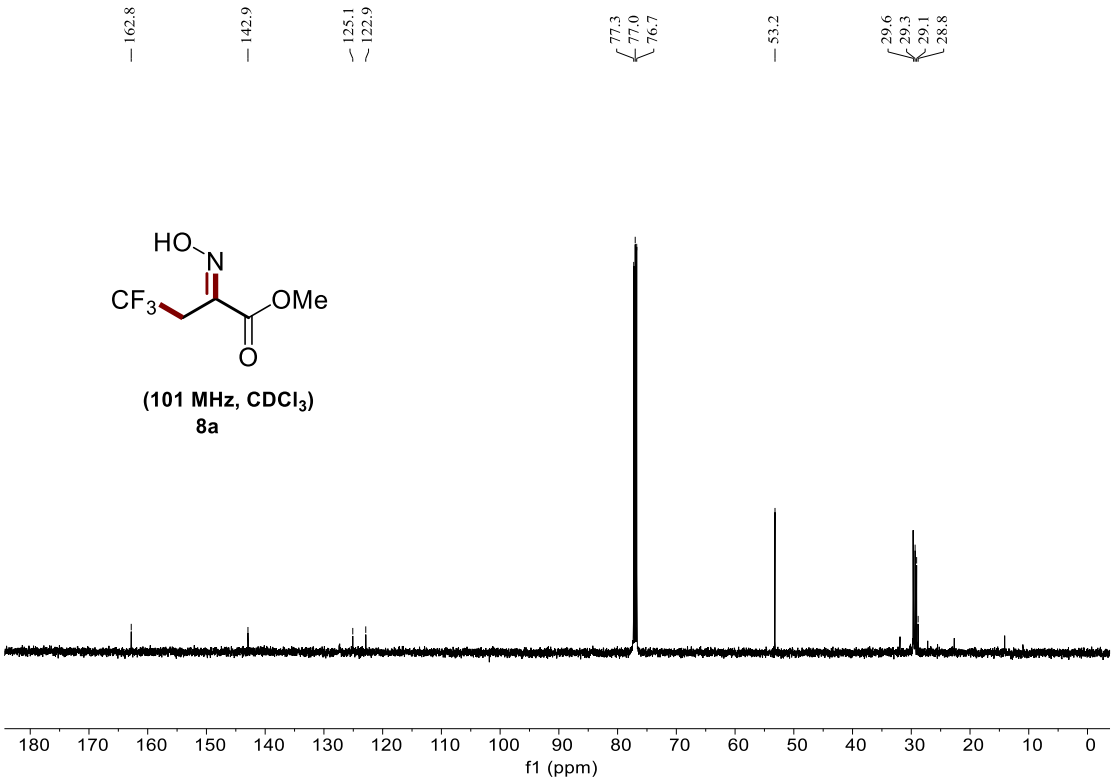
(162 MHz, $CDCl_3$)
6p



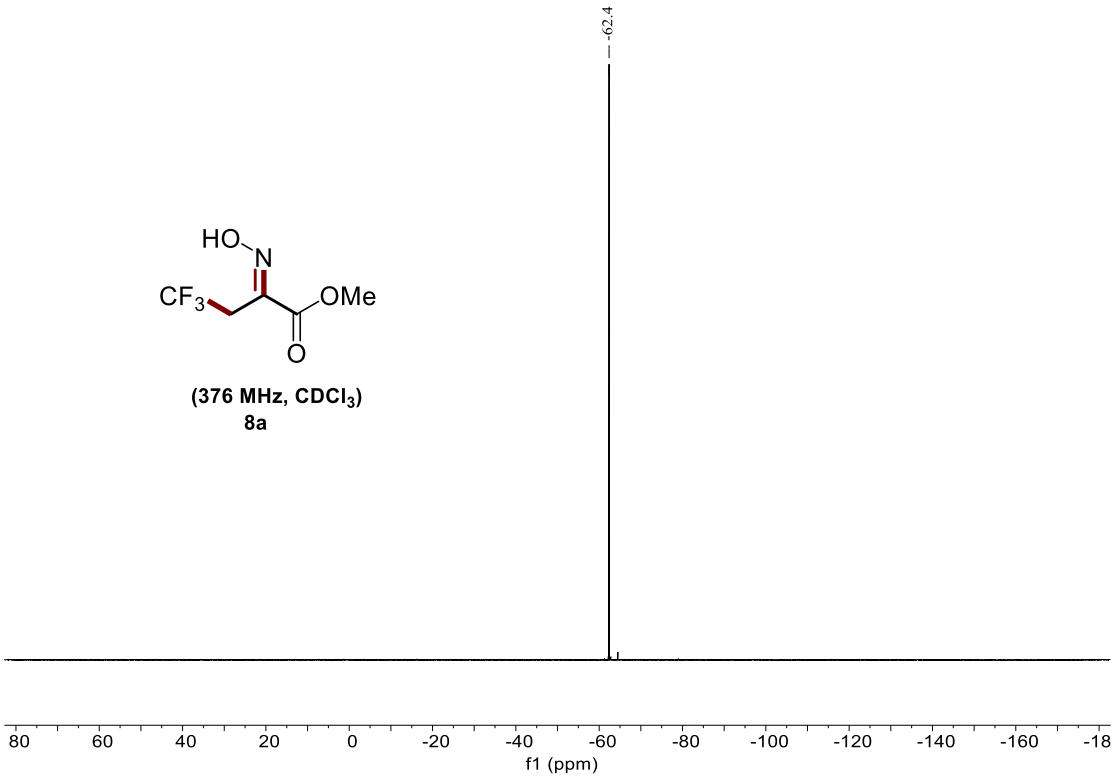
(400 MHz, $CDCl_3$)
6q


151.9
139.6
137.5
134.6
134.4
129.4
129.3
129.2
128.3
77.3
77.0
76.7
51.9
HO
N
O2
S
(101 MHz, CDCl3)
6q
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

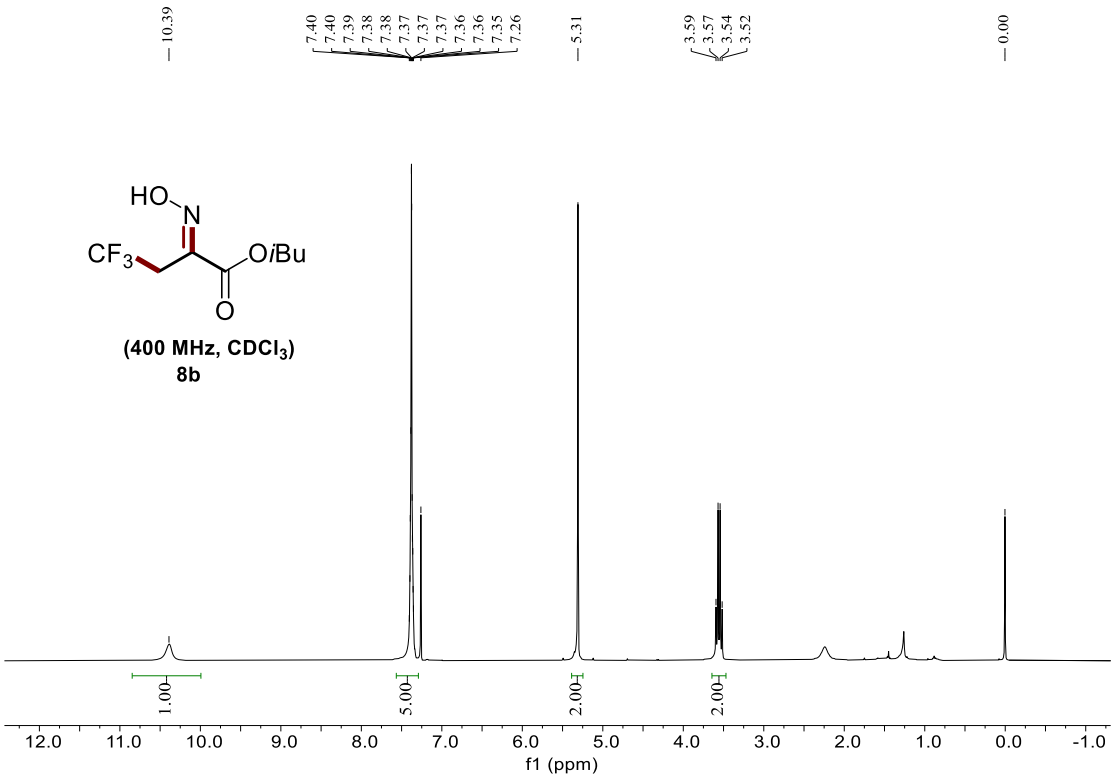

9.84
7.26
3.91
3.61
3.59
0.07
HO
N
CF3
OMe
O
(400 MHz, CDCl3)
8a
1.00
2.94
2.00
2.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.
f1 (ppm)

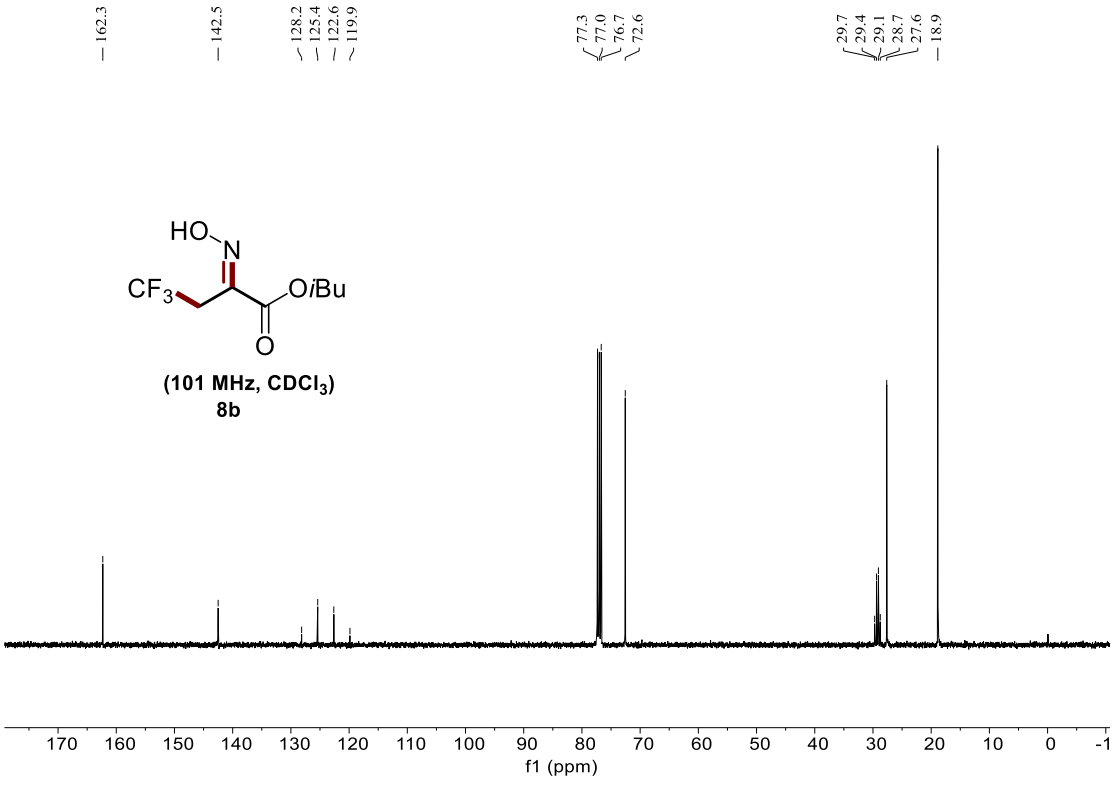


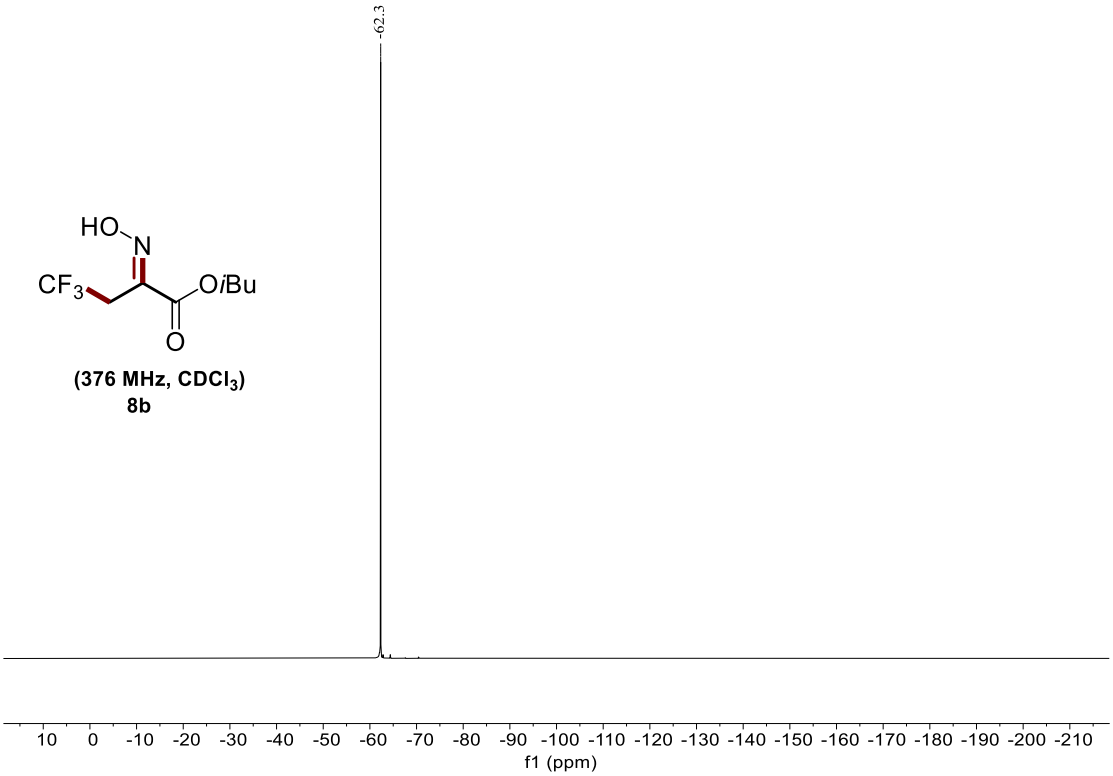
(101 MHz, $CDCl_3$)
8a



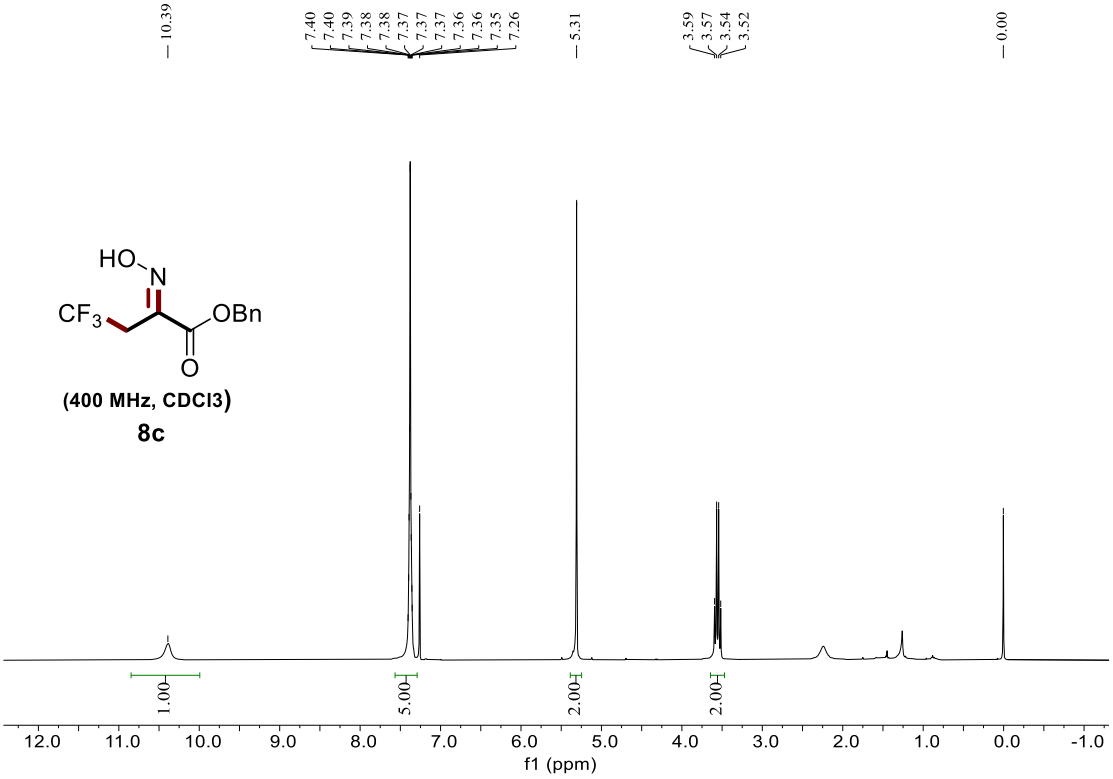
(376 MHz, $CDCl_3$)
8a


10.39
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.26
5.31
3.59
3.57
3.54
3.52
0.00
HO
N
CF3
OiBu
O
(400 MHz, CDCl3)
8b
1.00
5.00
2.00
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

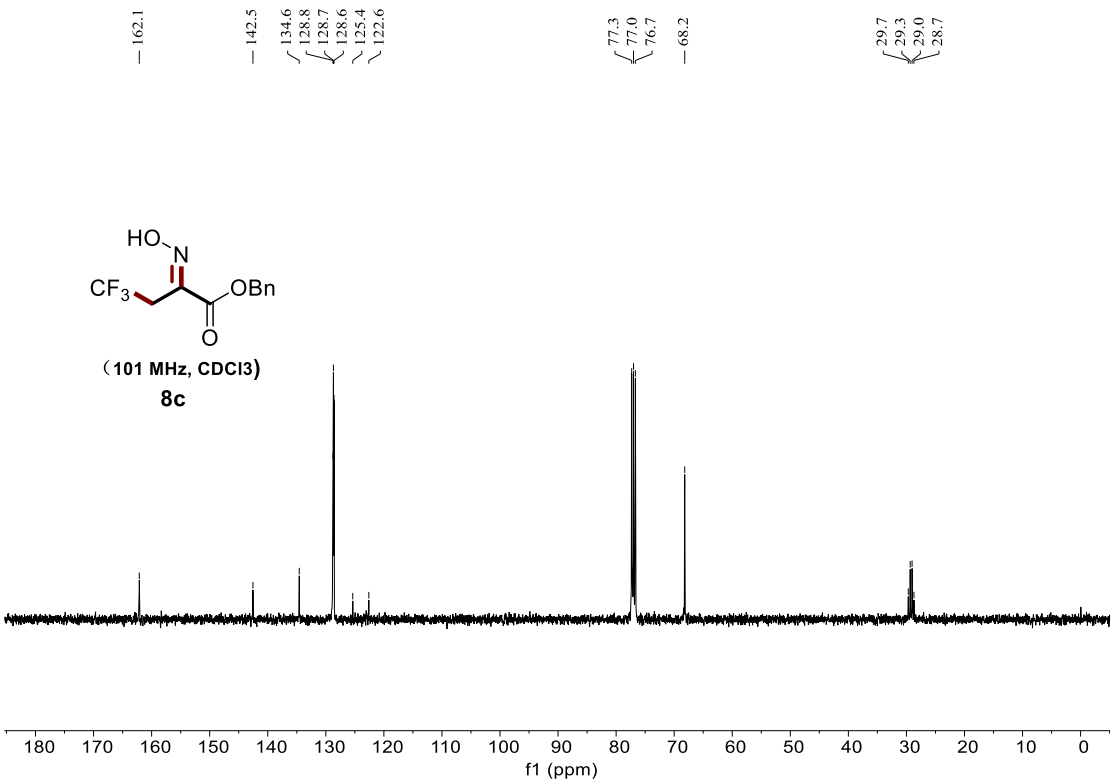

162.3
142.5
128.2
125.4
122.6
119.9
77.3
77.0
76.7
72.6
29.7
29.4
29.1
28.7
27.6
18.9
HO
N
CF3
OiBu
O
(101 MHz, CDCl3)
8b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



(376 MHz, $CDCl_3$)
8b

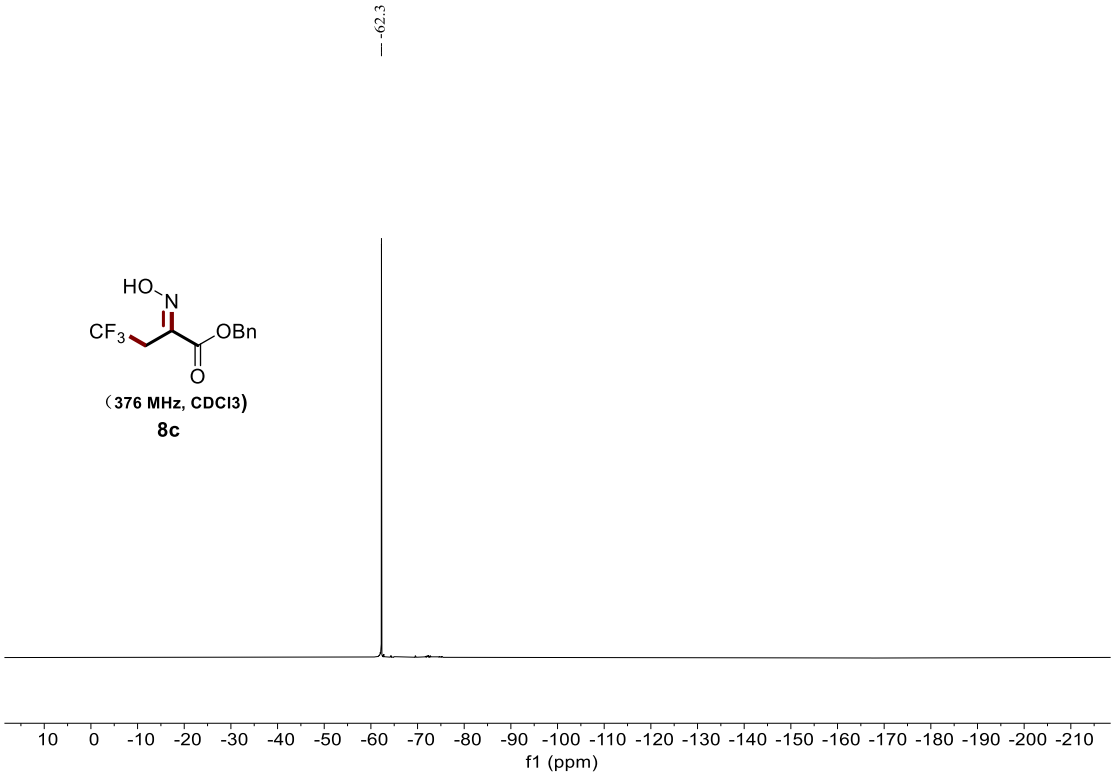


(400 MHz, CDCl3)
8c



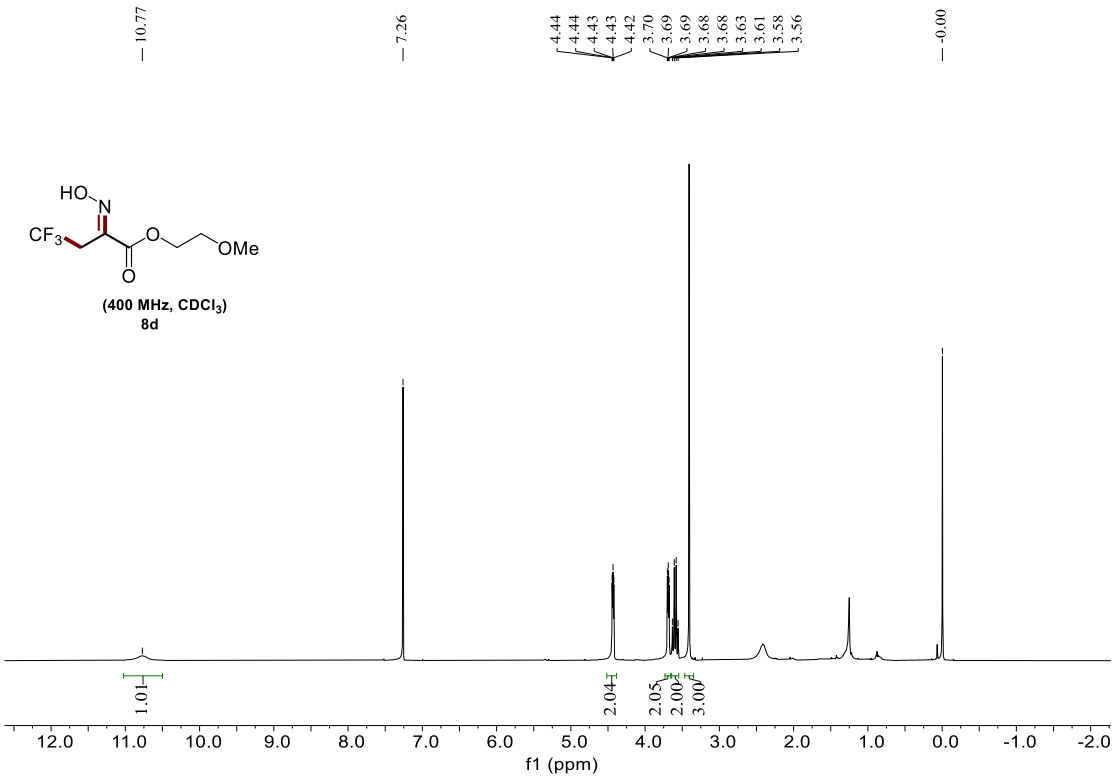
（101 MHz, CDCl3）

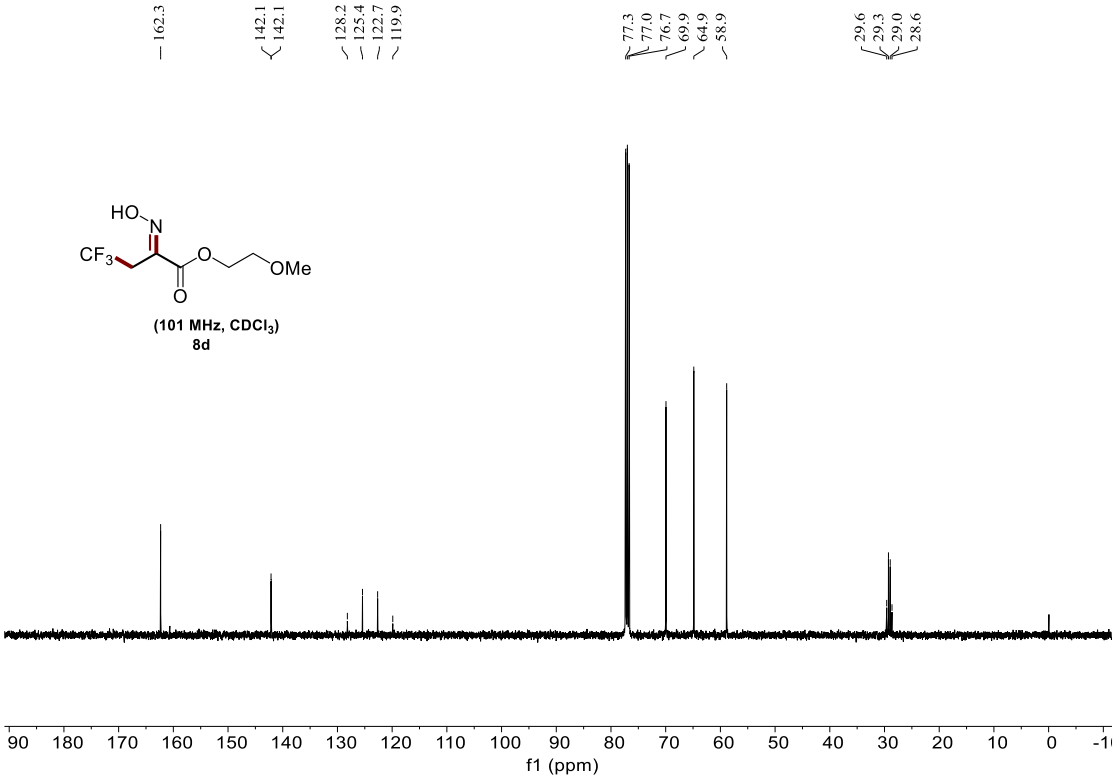
8c

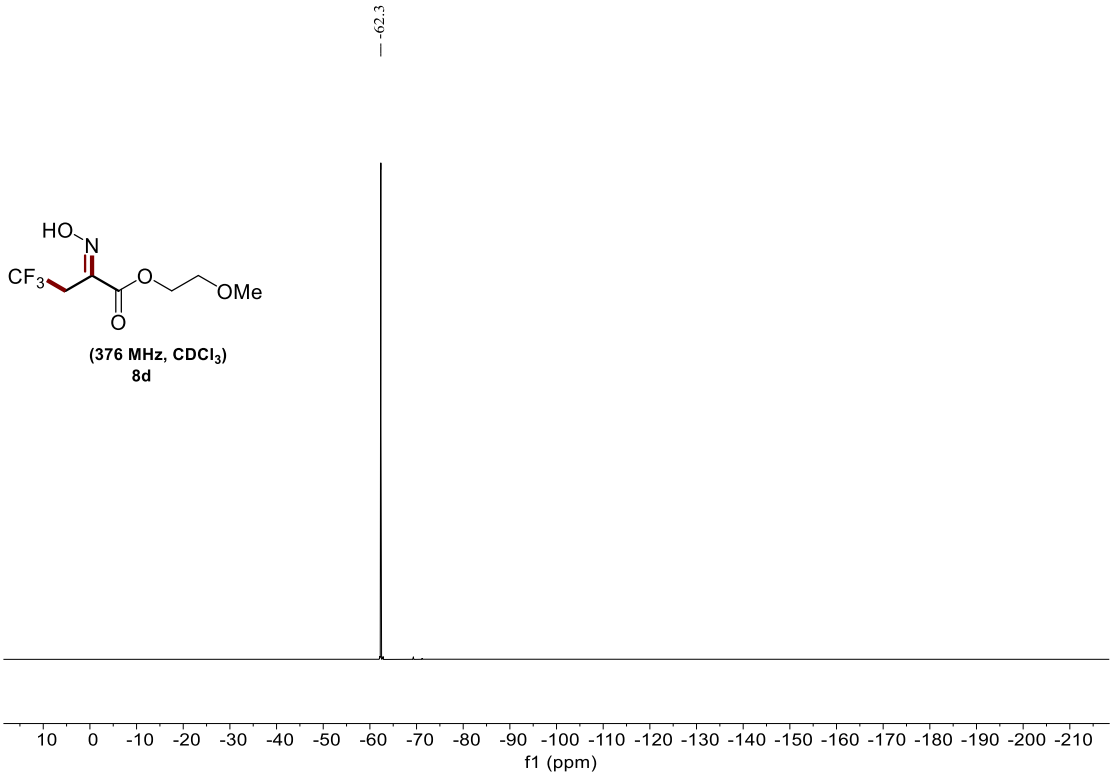


（376 MHz, CDCl3）

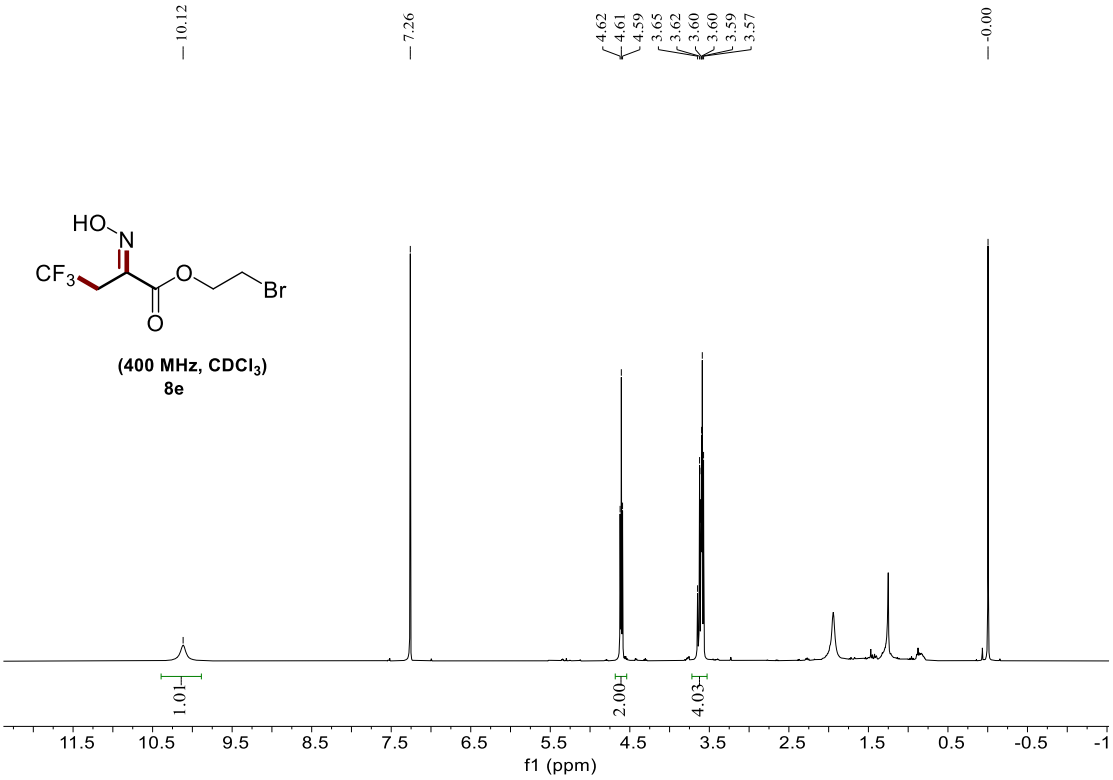
8c


10.77
7.26
4.44
4.44
4.43
4.43
4.42
3.70
3.69
3.69
3.68
3.68
3.63
3.61
3.58
3.56
0.00
HO
N
CF3
O
O
OMe
O
(400 MHz, CDCl3)
8d
1.01
2.04
2.05
2.00
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)

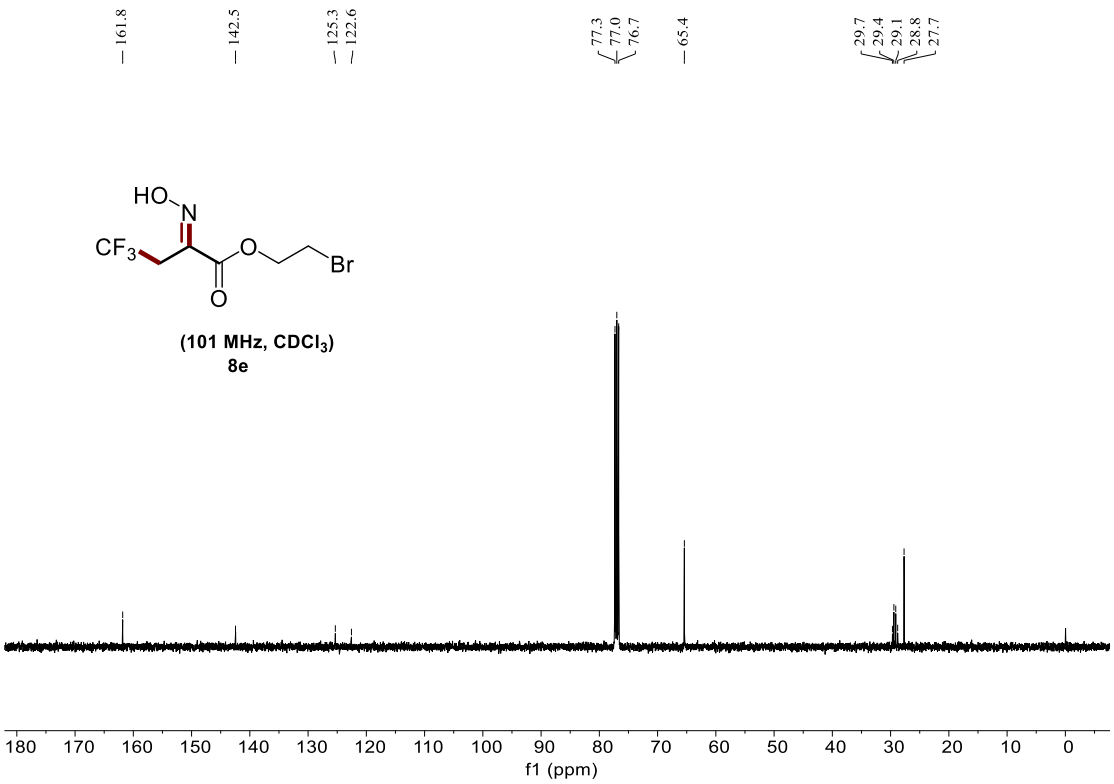

162.3
142.1
142.1
128.2
125.4
122.7
119.9
77.3
77.0
76.7
69.9
64.9
58.9
29.6
29.3
29.0
28.6
HO
N
CF3
O
O
OMe
O
(101 MHz, CDCl3)
8d
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



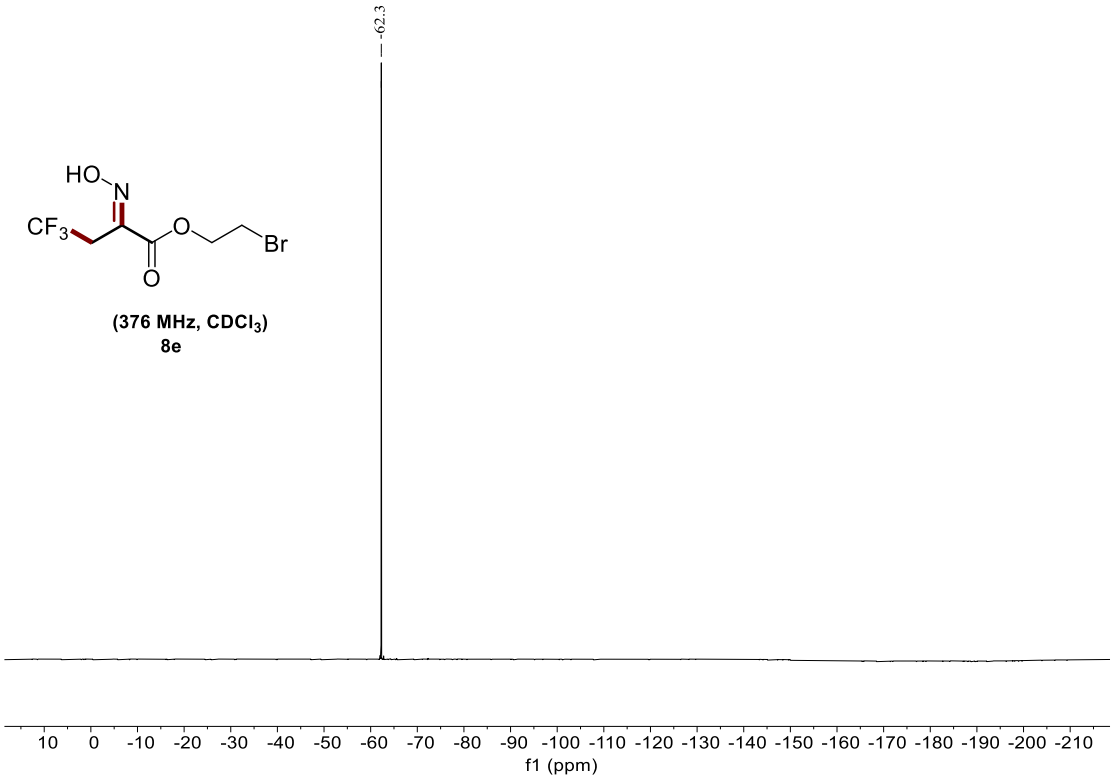
(376 MHz, $CDCl_3$)
8d



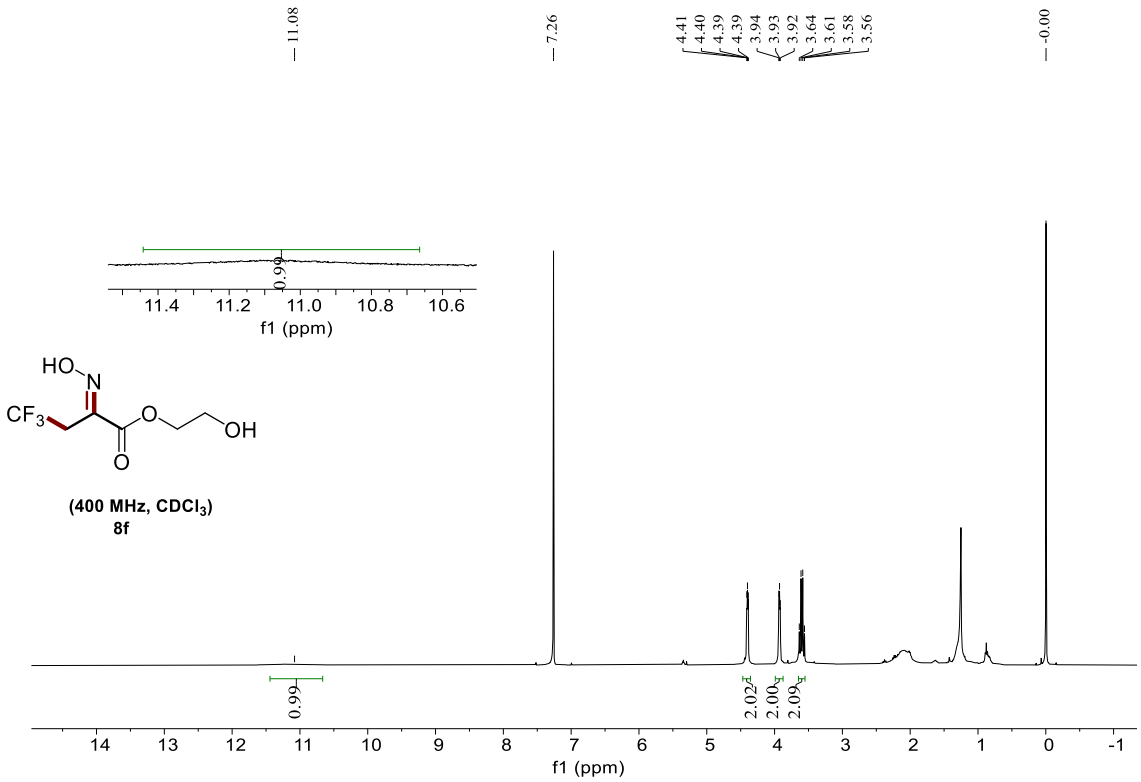
(400 MHz, $CDCl_3$)
8e

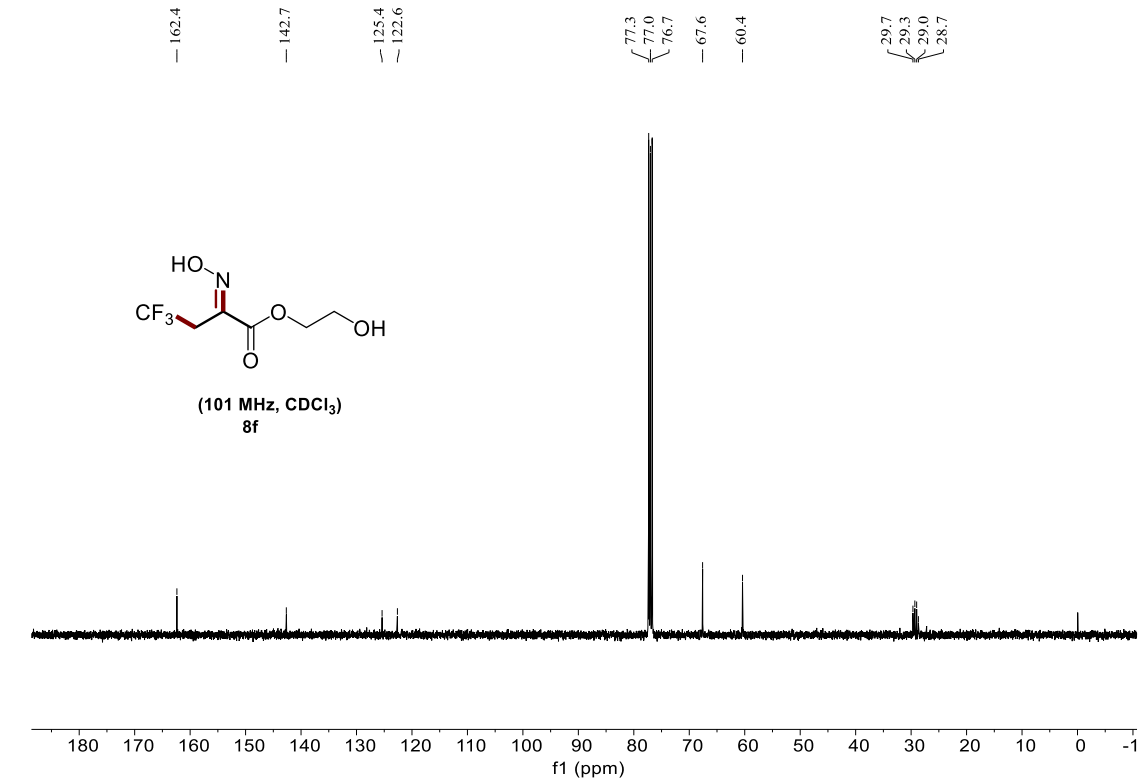


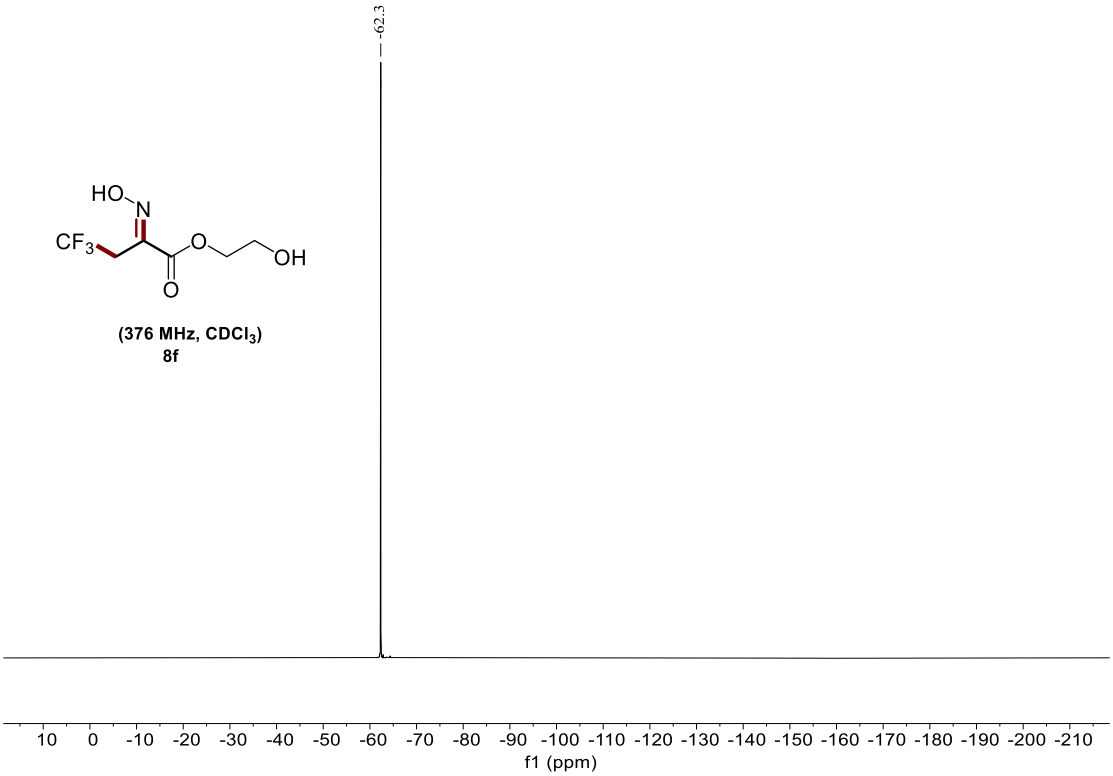
(101 MHz, $CDCl_3$)
8e



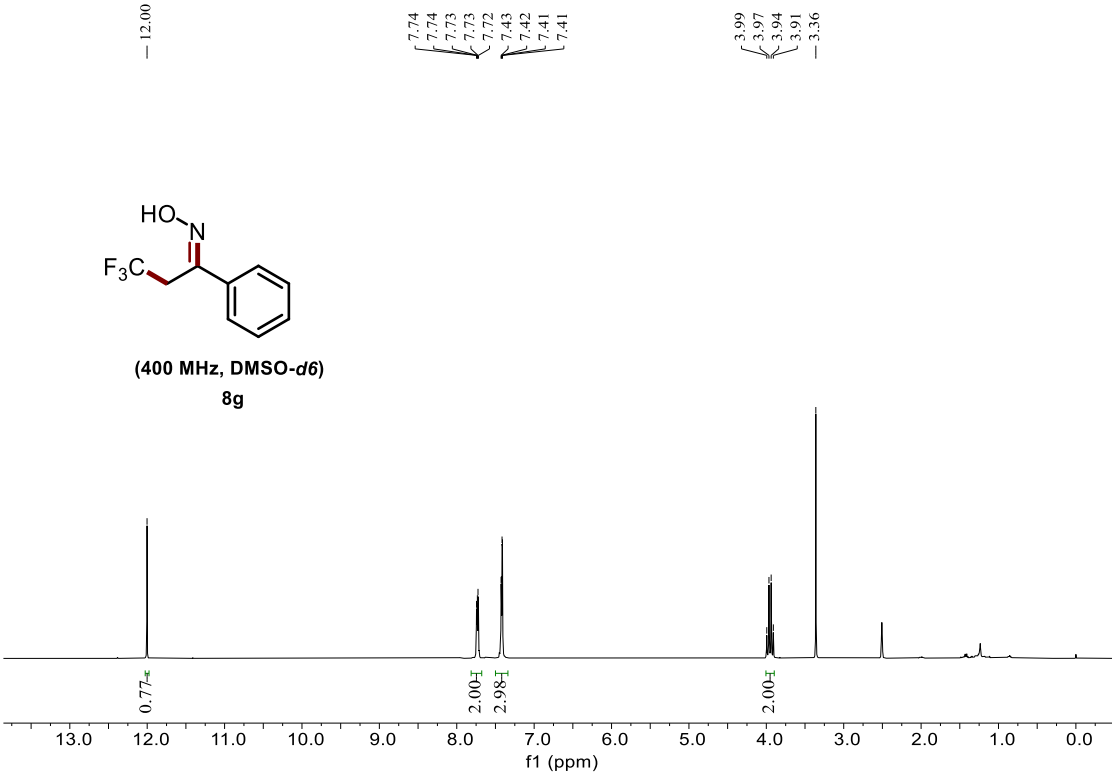
(376 MHz, $CDCl_3$)
8e


11.08
7.26
4.41
4.40
4.39
4.39
3.94
3.93
3.92
3.64
3.61
3.58
3.56
-0.00
0.99
11.4
11.2
11.0
10.8
10.6
f1 (ppm)
HO
N
CF3
O
OH
O
(400 MHz, CDCl3)
8f
0.99
2.02
2.00
2.09
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

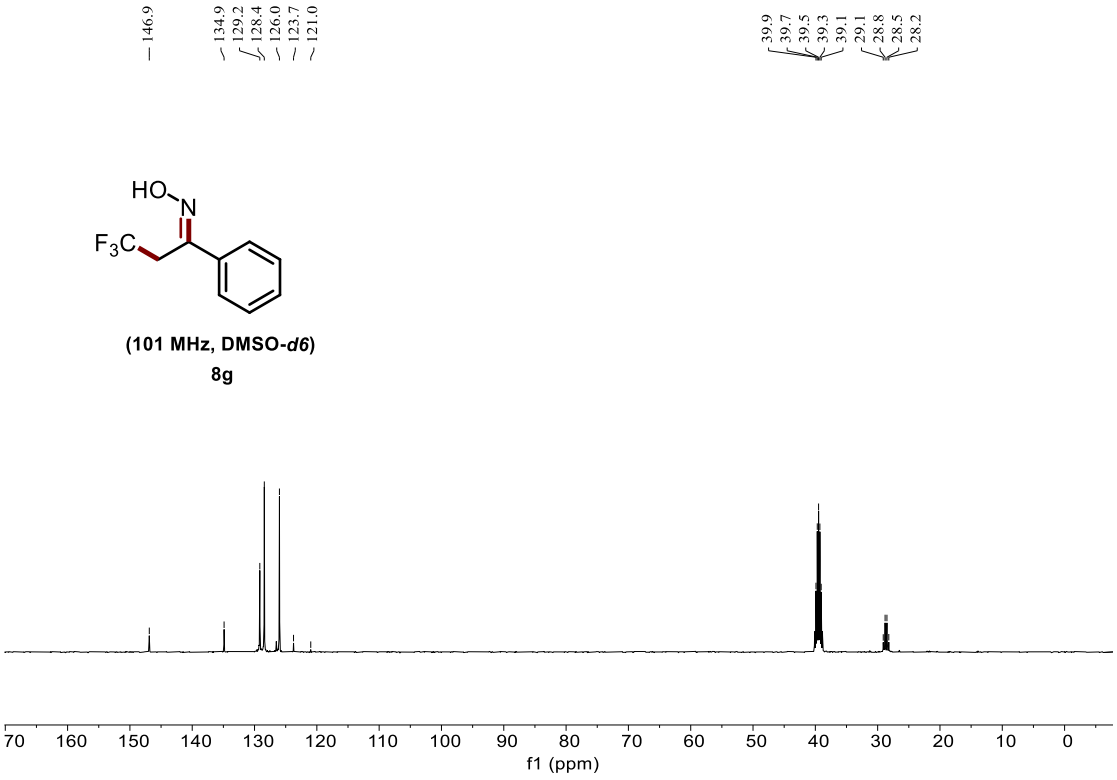

162.4
142.7
125.4
122.6
77.3
77.0
76.7
67.6
60.4
29.7
29.3
29.0
28.7
HO
N
CF3
O
OH
O
(101 MHz, CDCl3)
8f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

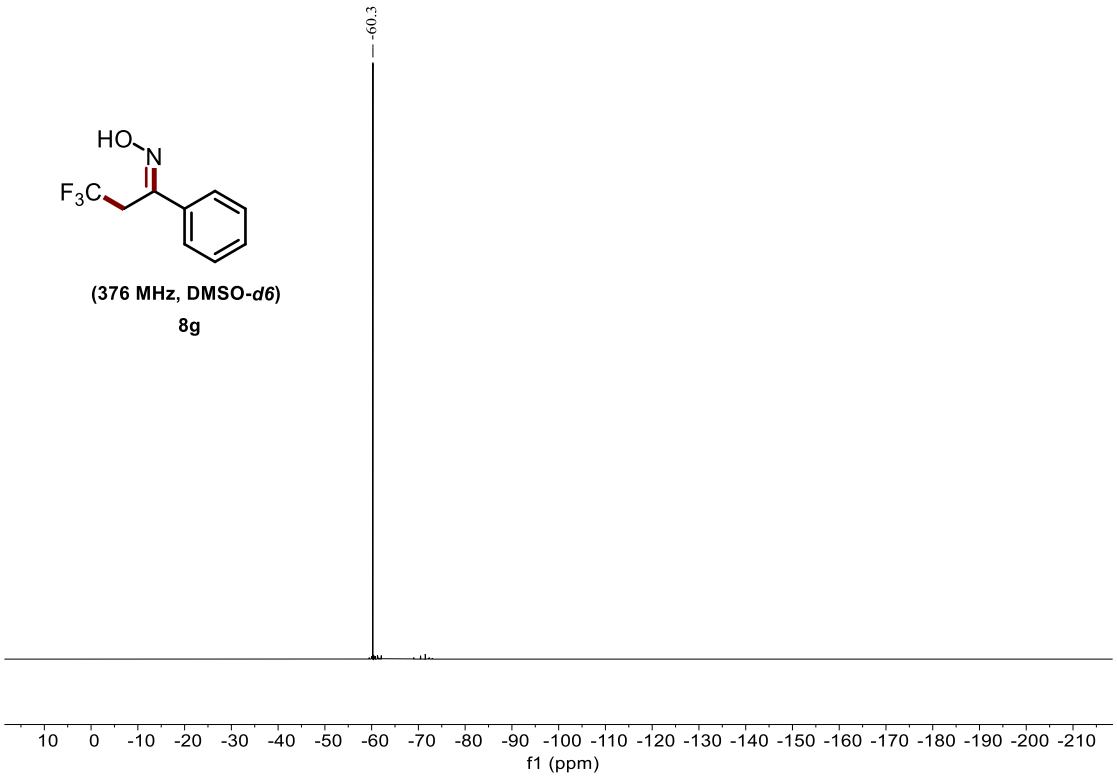


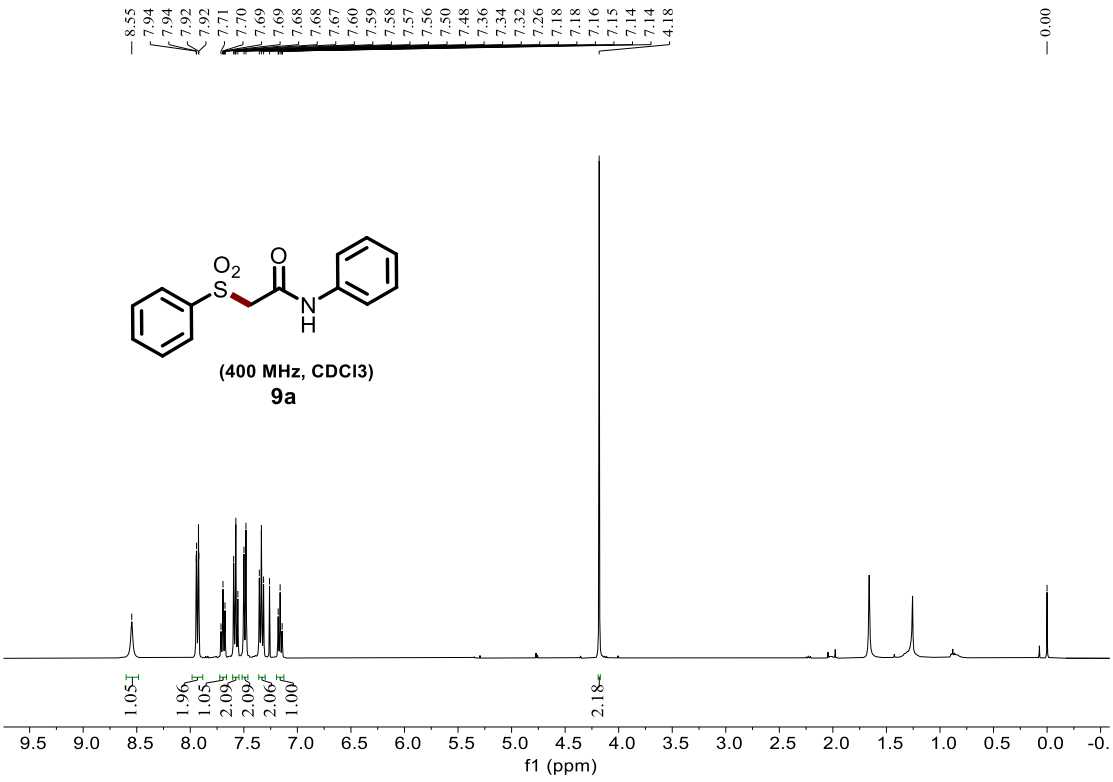
(376 MHz, $CDCl_3$)
8f

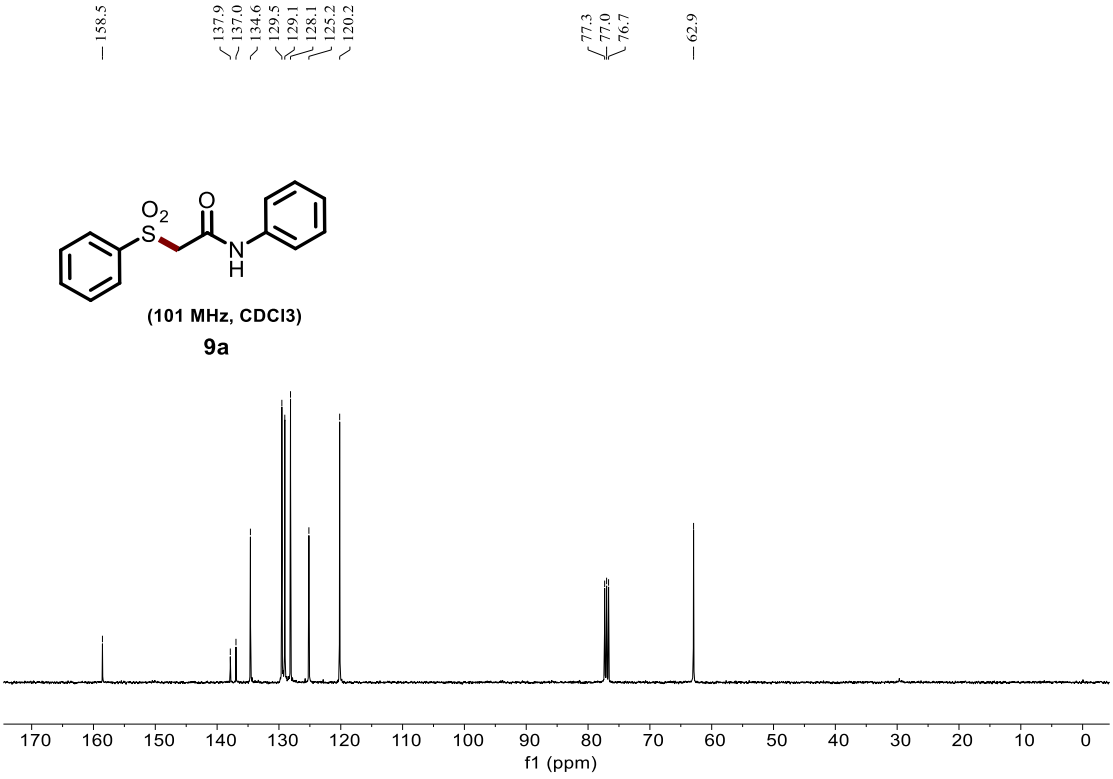


(400 MHz, DMSO-*d6*)
8g


146.9
134.9
129.2
128.4
126.0
123.7
121.0
39.9
39.7
39.5
39.3
39.1
29.1
28.8
28.5
28.2
HO
N
F3C
(101 MHz, DMSO-d6)
8g
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-60.3
HO
N
F3C
(376 MHz, DMSO-d6)
8g
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.55
7.94
7.94
7.92
7.92
7.71
7.70
7.69
7.69
7.68
7.68
7.67
7.60
7.59
7.58
7.57
7.56
7.50
7.48
7.36
7.34
7.32
7.26
7.18
7.18
7.16
7.15
7.14
7.14
4.18
0.00
O2
S
O
N
H
(400 MHz, CDCl3)
9a
1.05
1.96
1.05
2.09
2.09
2.06
1.00
2.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


158.5
137.9
137.0
134.6
129.5
129.1
128.1
125.2
120.2
77.3
77.0
76.7
62.9
O2
S
O
N
H
(101 MHz, CDCl3)
9a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

6. References

(1) Y. A. Naumovich, S. L. Ioffe, and A. Y. Sukhorukov, Michael Addition of P-Nucleophiles to Conjugated Nitrosoalkenes, *J. Org. Chem.* **2019**, *84*, 7244.

(2) Y. A. Naumovich, S. L. Ioffe, and A. Y. Sukhorukov, Michael Addition of P-Nucleophiles to Conjugated Nitrosoalkenes, *Org. Chem. Front*., **2017**, *4*, 135.

(3) Y. Wu, Y. Zhang, Z. Yang, J. Jiao, X. Zheng, W. Feng, M. Zhang, H. Cheng, and L. Tang, Dual Role softer t-Butyl Nitritein the Transition Metal – and External Oxidant-Free Trifluoromethyloximation of Alkenes. *ChemSusChem*., 2019, 12, 3960.