Supporting Information

Photoinduced Syntheses and Reactivities of Phosphorus-Containing Interelement Compounds

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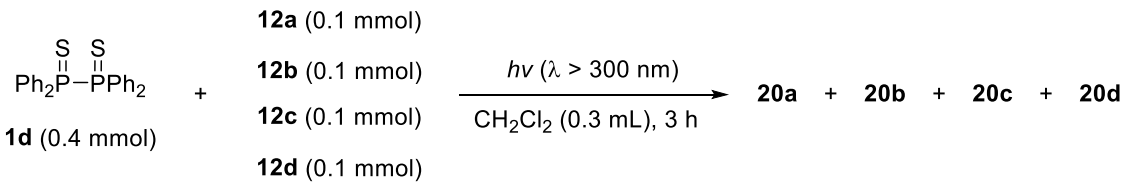
Table S1. Hammet linear free energy relationship study using **1d** and **20a**–**20d**



R	**20** (mmol)[a]	σ_p	$\log(k_R/k_H)$
p-H	0.0105	0	0
p-Cl	0.0073	+ 0.227	-0.162
p-F	0.0129	+0.062	0.093
p-CF_3	0.0130	+0.540	0.094

[a]Determined by ^{31}P NMR.

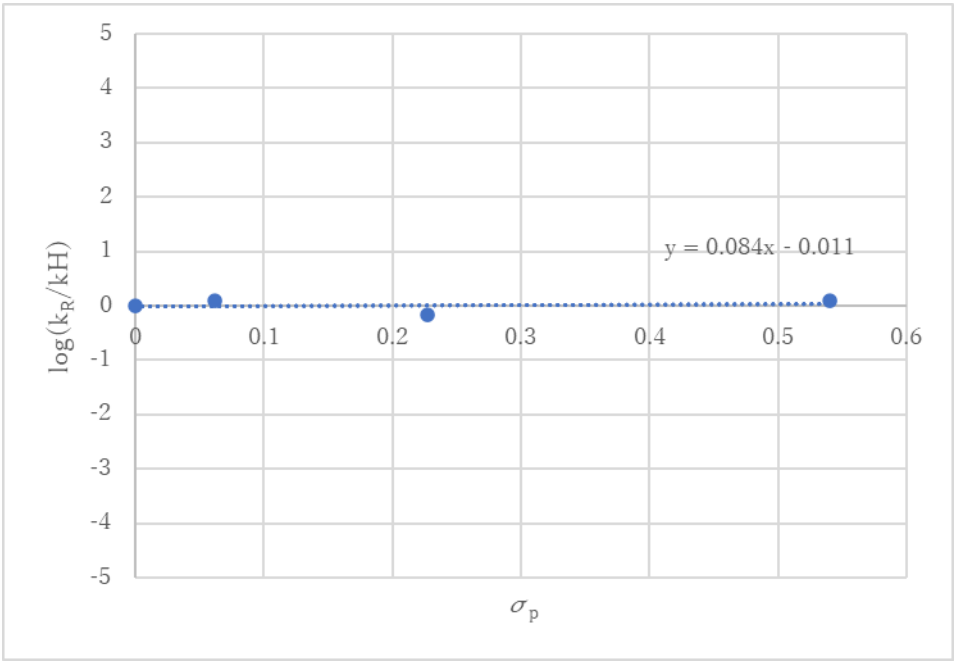
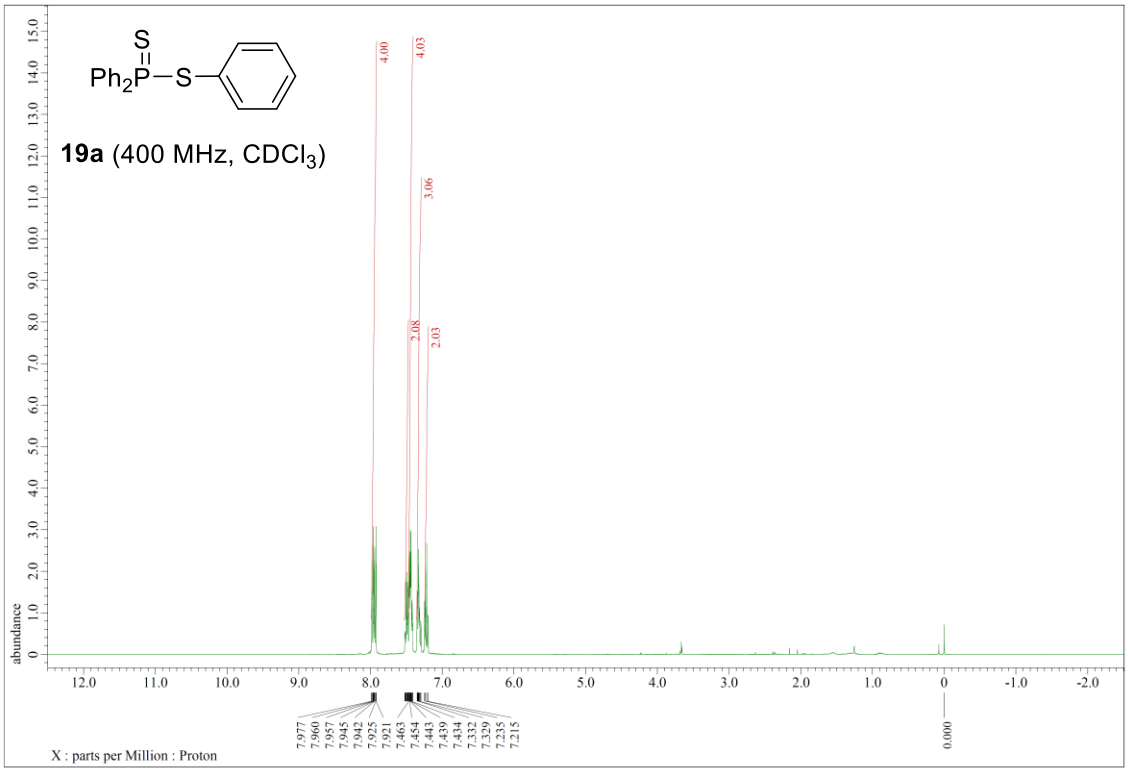
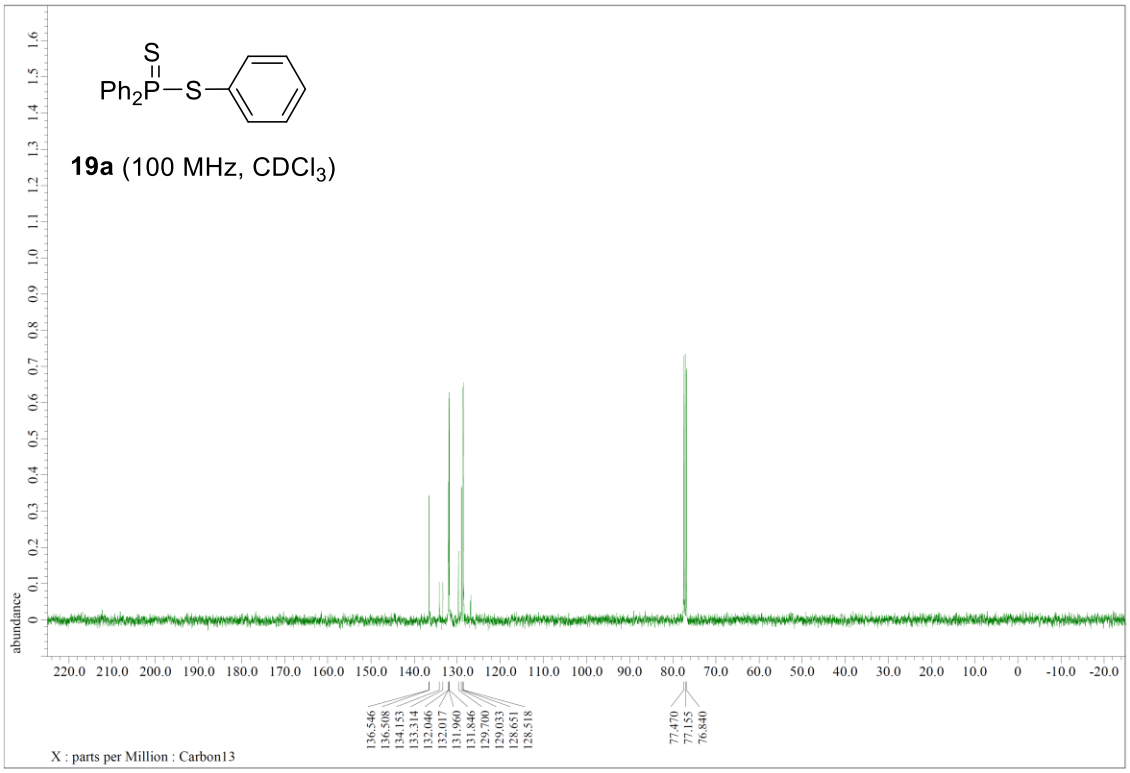


Figure S1 ^{1}H, ^{13}C, and ^{31}P NMR spectra of compound **19a**





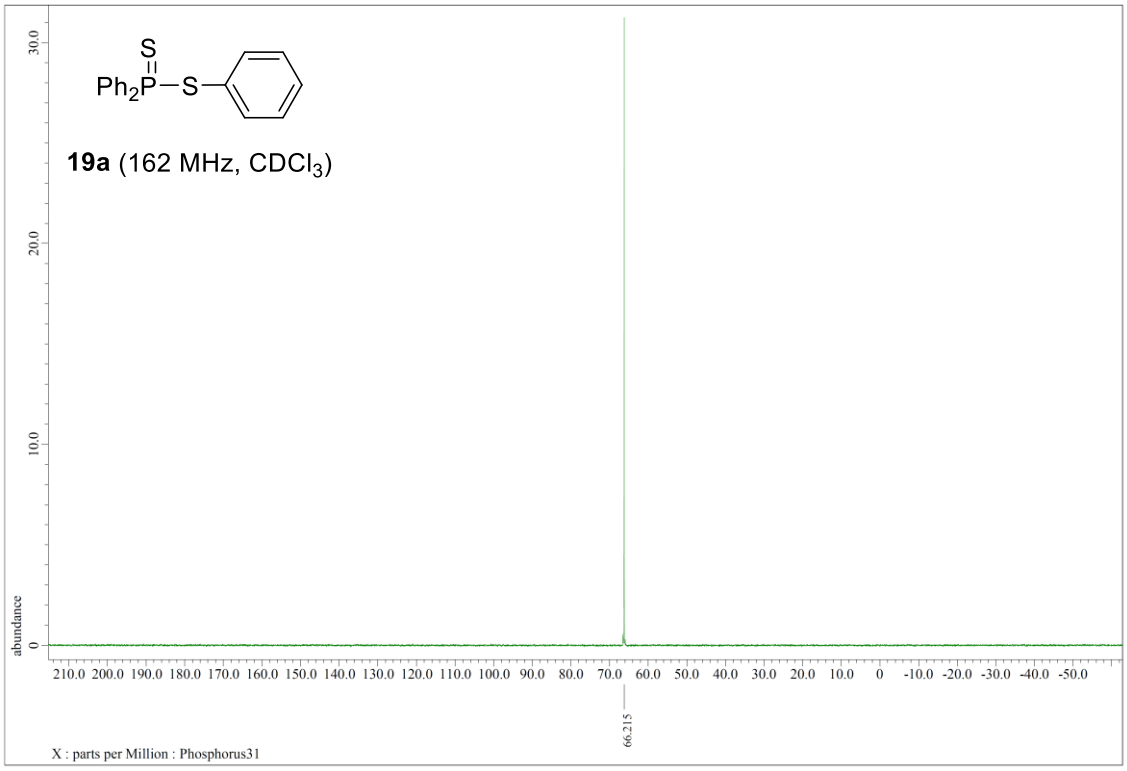
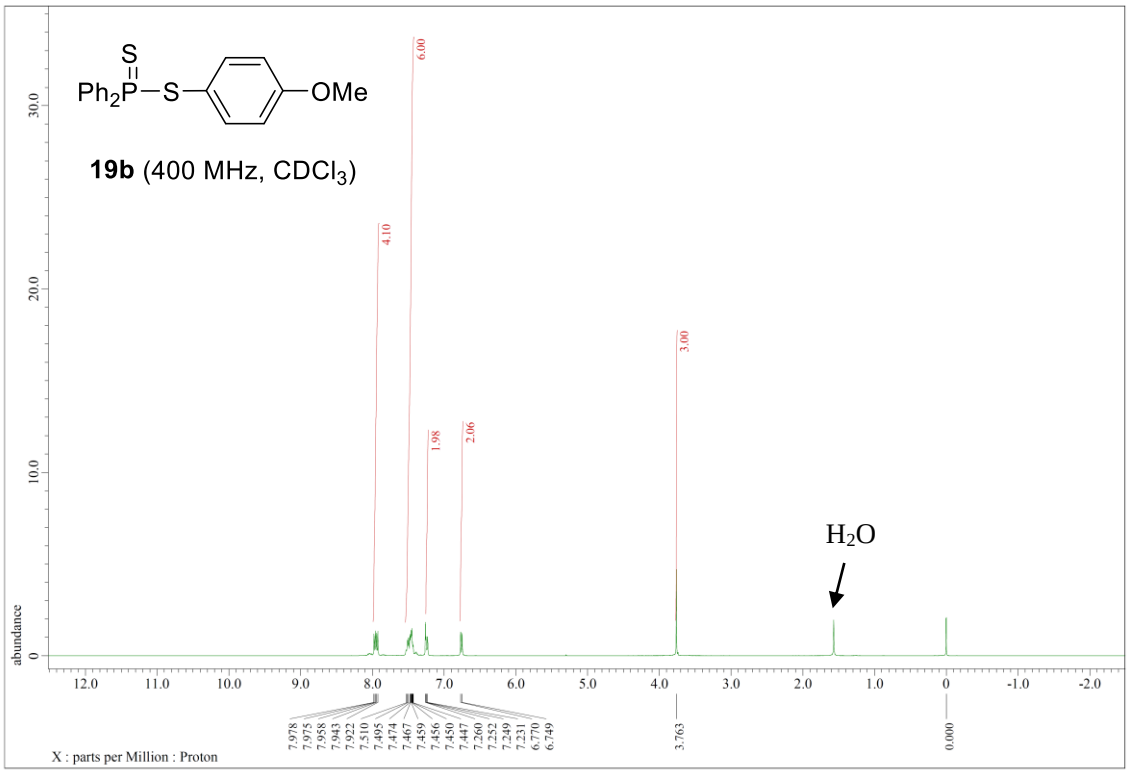
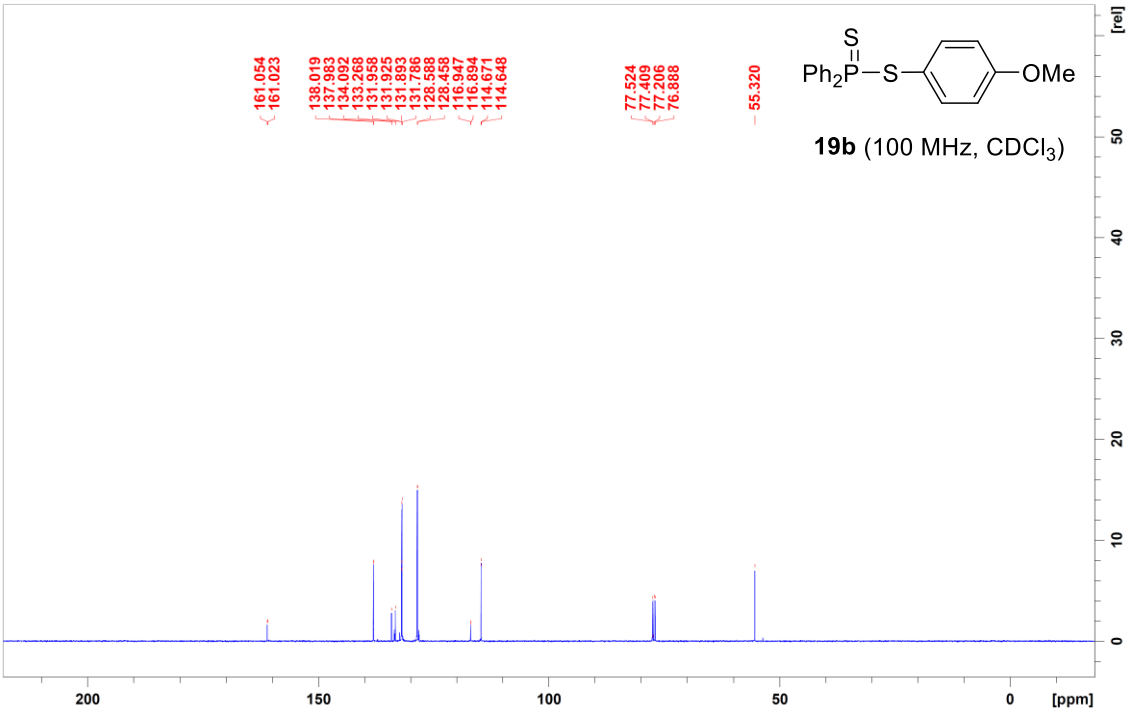

S
Ph2P—S
19a (162 MHz, CDCl3)
abundance
30.0
20.0
10.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0
66.215
X : parts per Million : Phosphorus31

Figure S2 ^{1}H, ^{13}C, and ^{31}P NMR spectra of compound **19b**





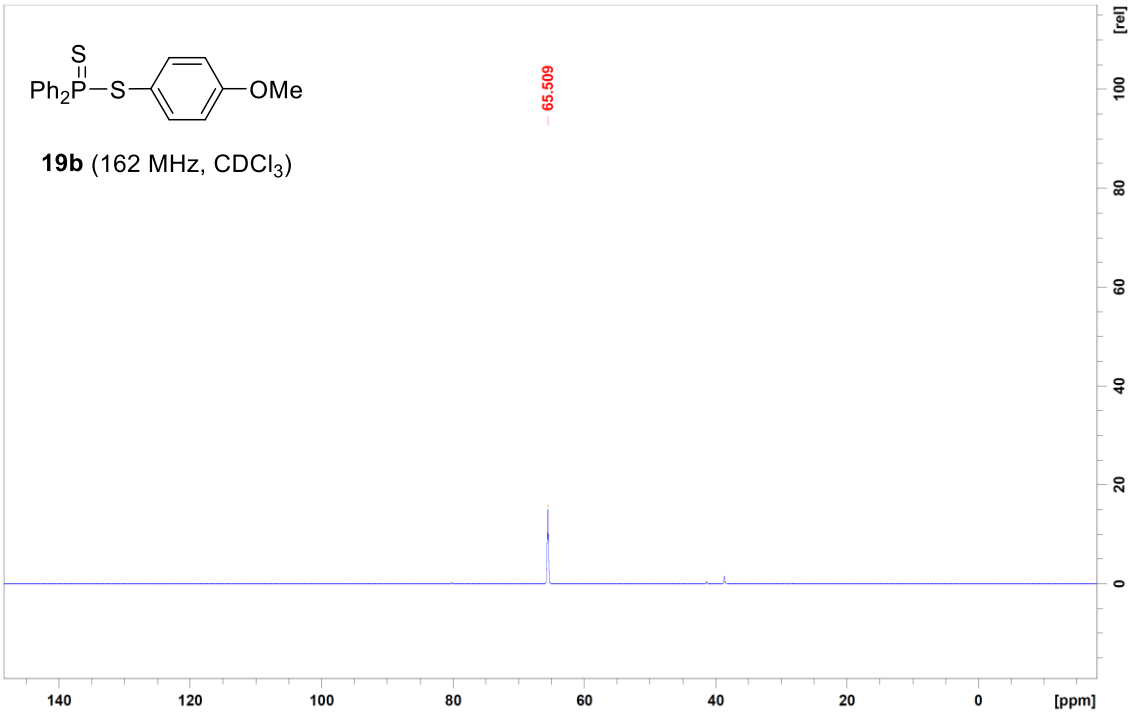
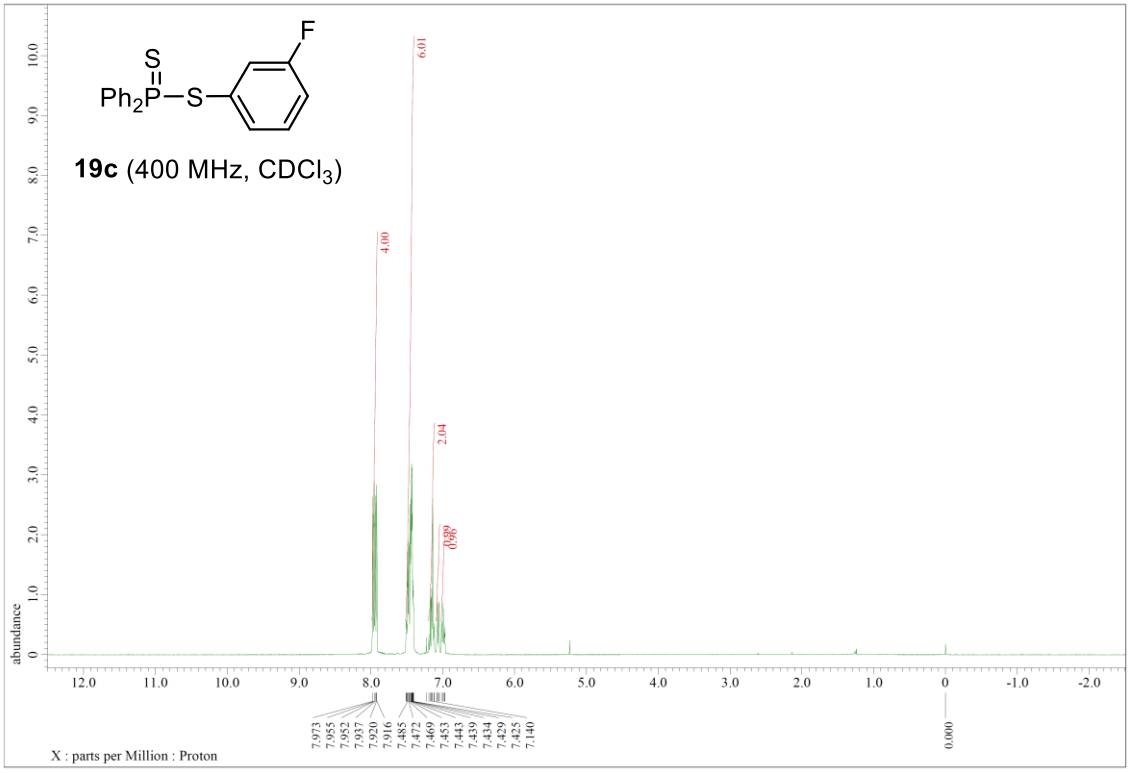
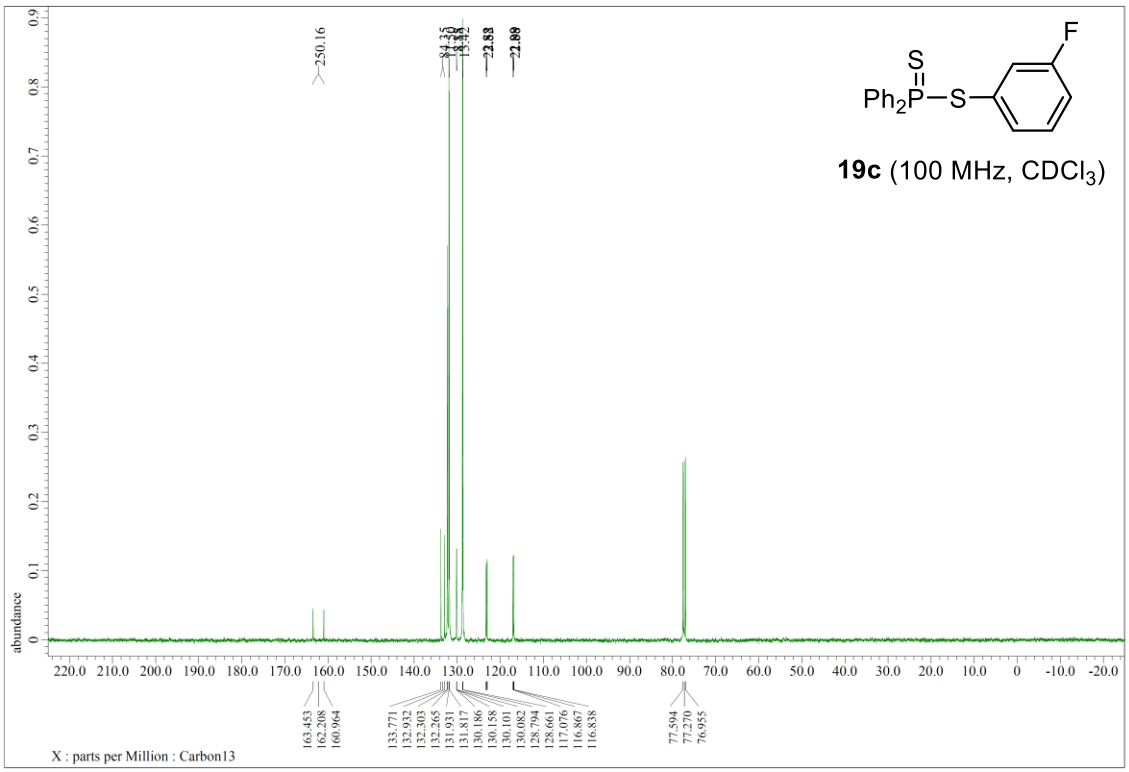

S
Ph2P
S
OMe
65.509
19b (162 MHz, CDCl3)
[rel]
100
80
60
40
20
0
140
120
100
80
60
40
20
0
[ppm]

Figure S3 ^{1}H, ^{13}C, and ^{31}P NMR spectra of compound **19c**





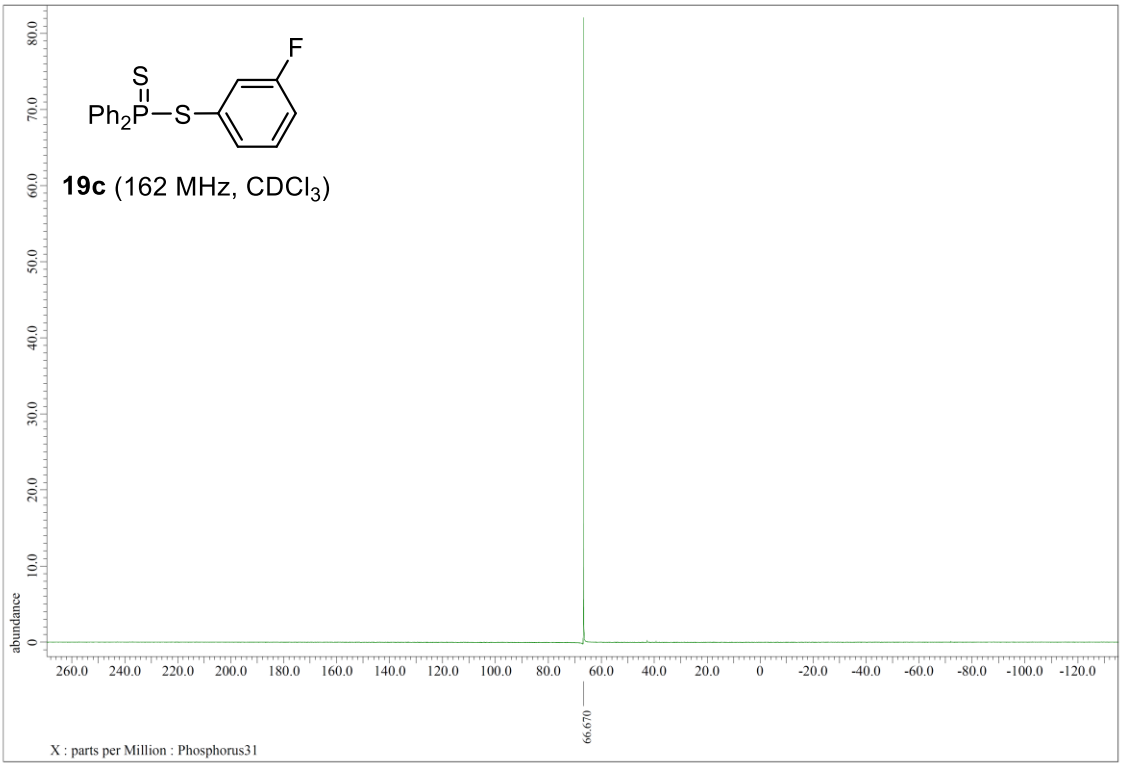
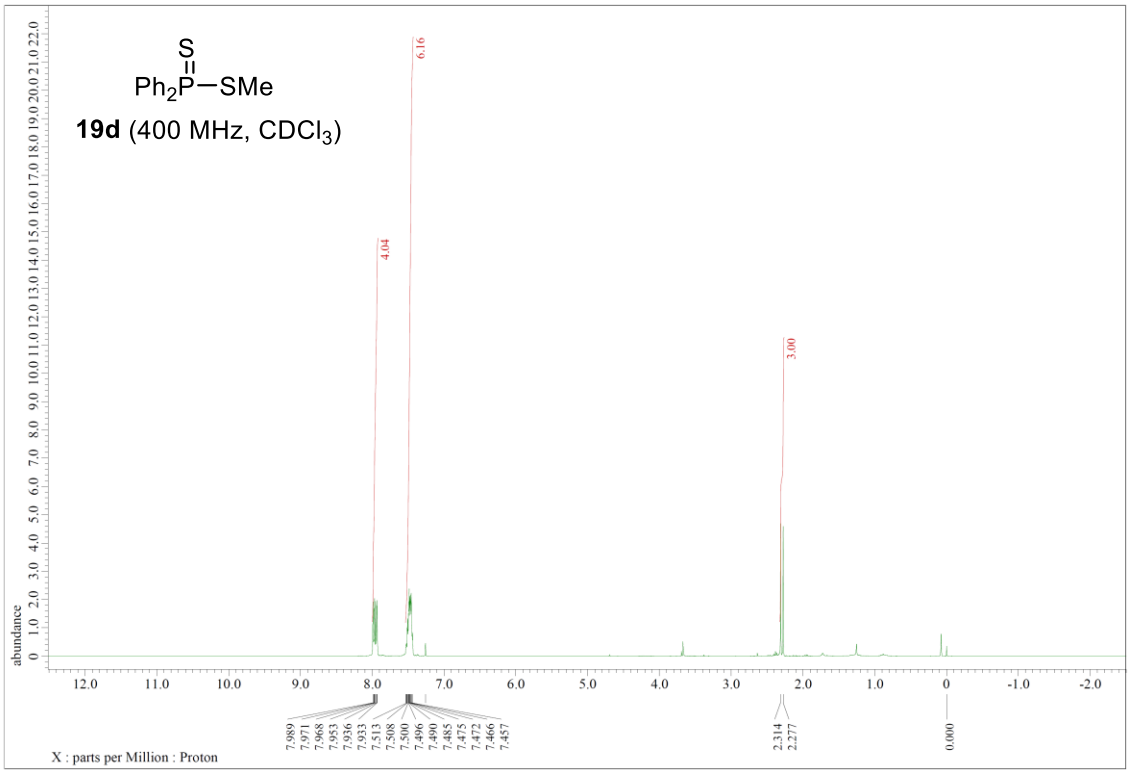
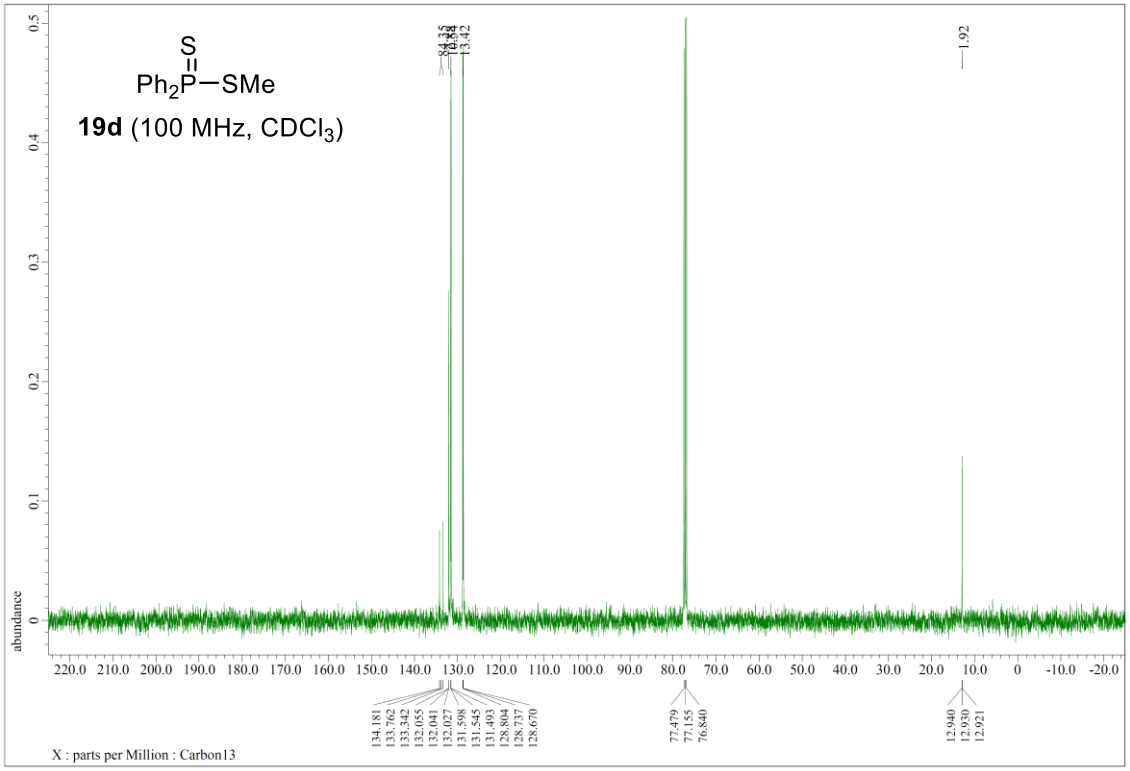

F
S
Ph2P
S
19c (162 MHz, CDCl3)
abundance
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
260.0 240.0 220.0 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0
66.670
X : parts per Million : Phosphorus31

Figure S4 ^{1}H, ^{13}C, and ^{31}P NMR spectra of compound **19d**





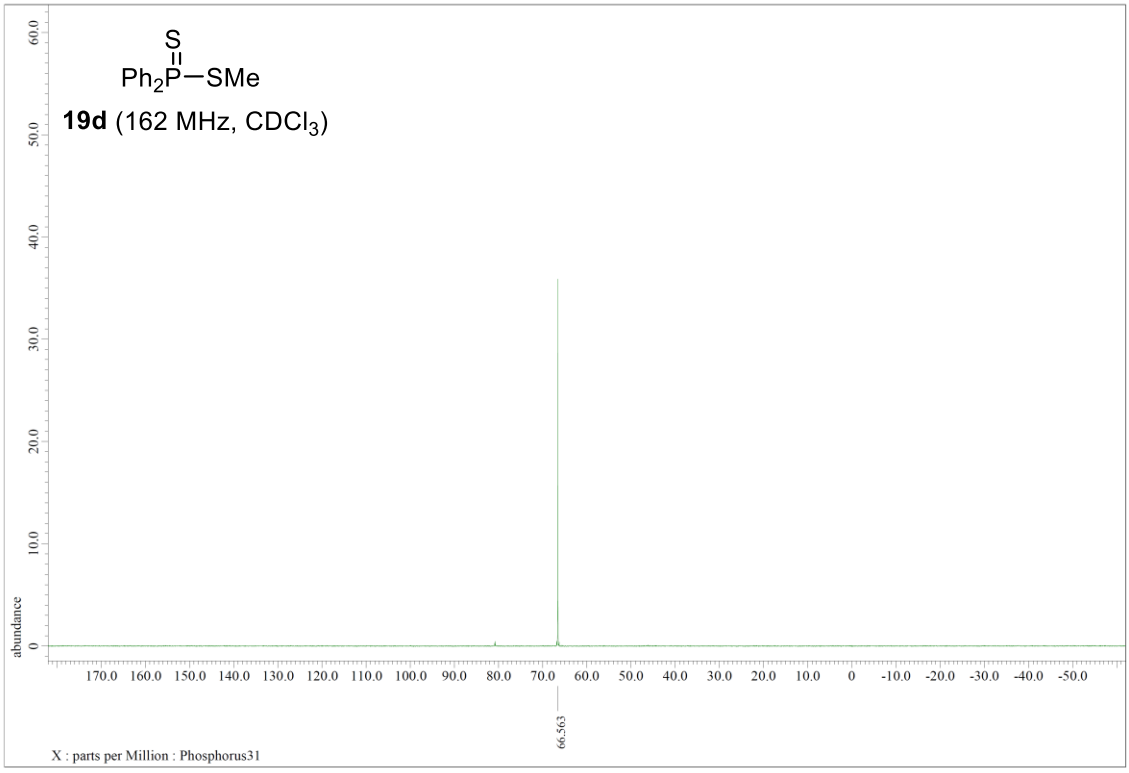
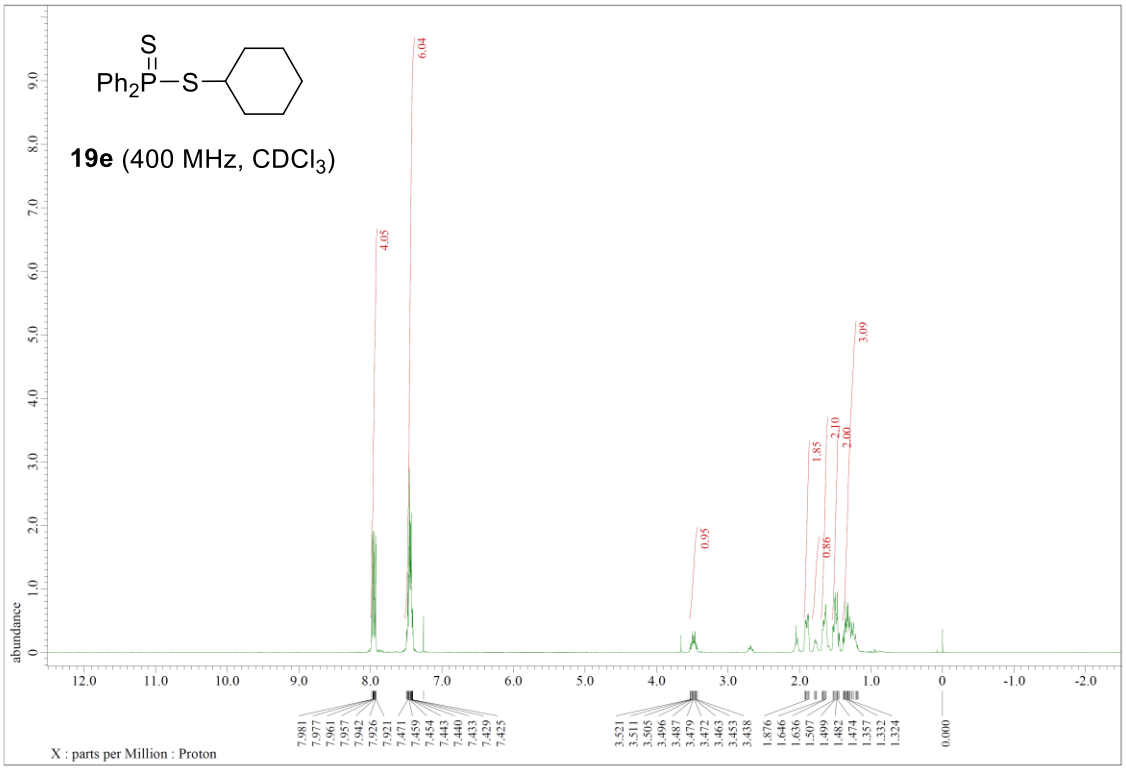
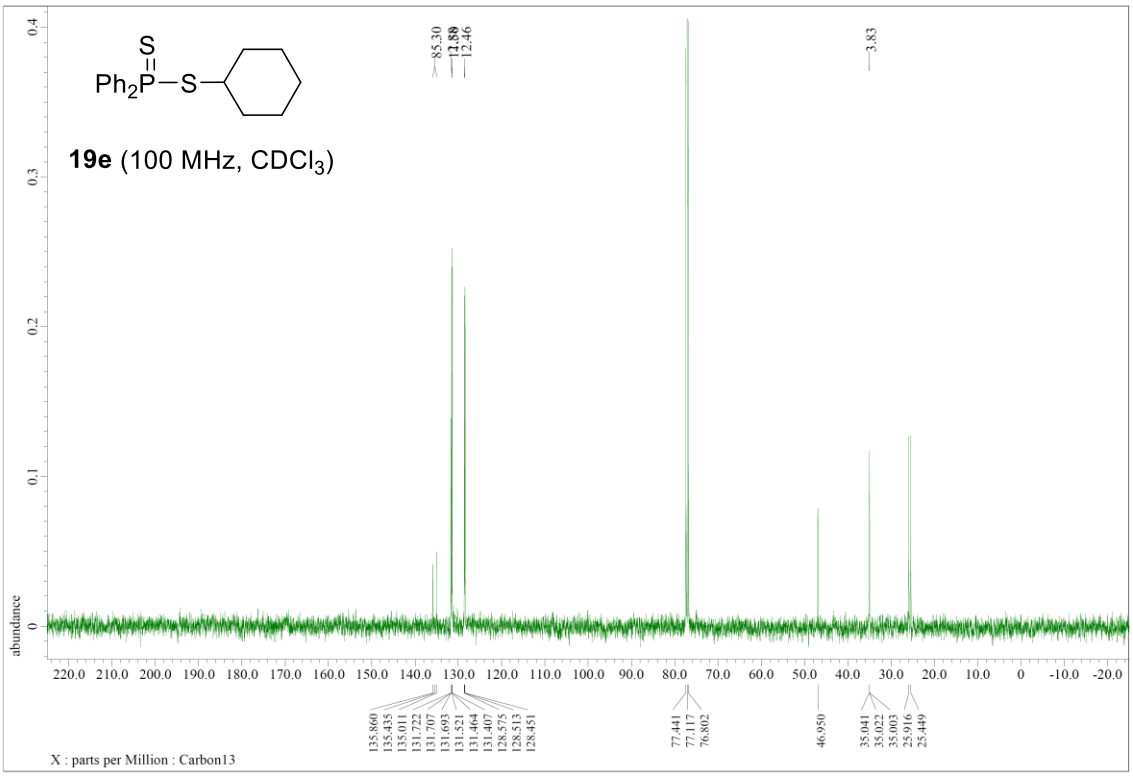

S
Ph2P—SMe
19d (162 MHz, CDCl3)
abundance
60.0
50.0
40.0
30.0
20.0
10.0
0
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0
66.563
X : parts per Million : Phosphorus31

Figure S5 ^{1}H, ^{13}C, and ^{31}P NMR spectra of compound **19e**





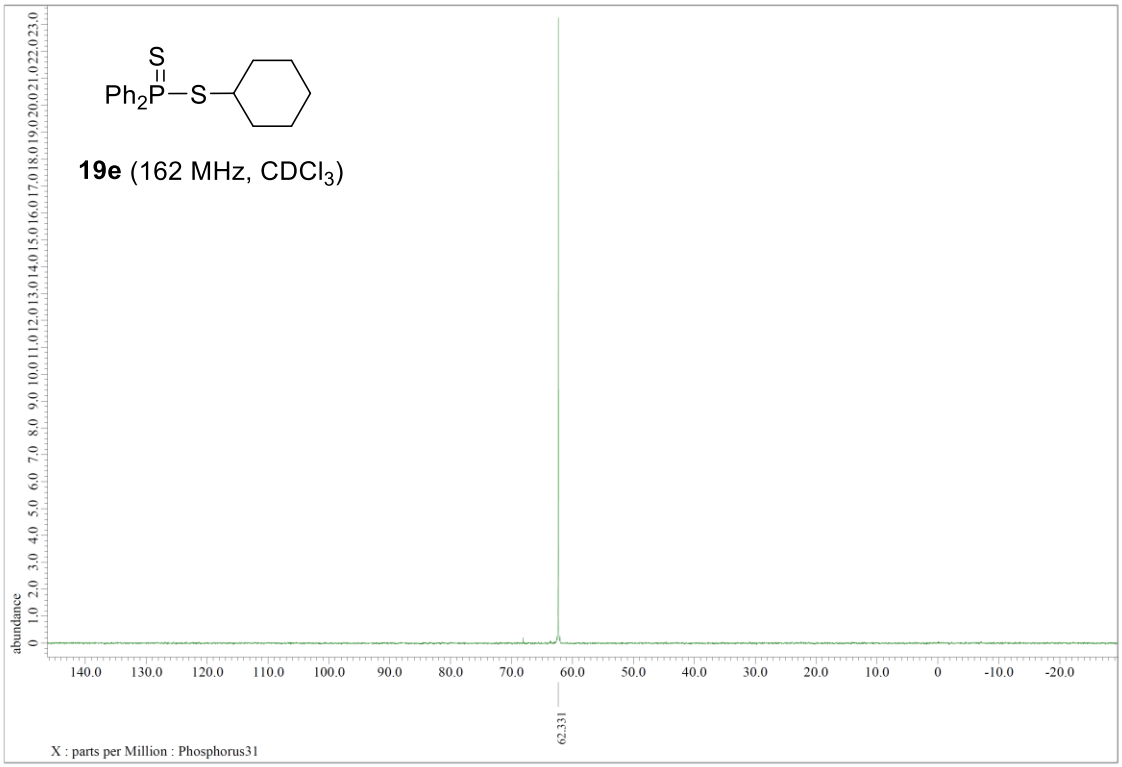
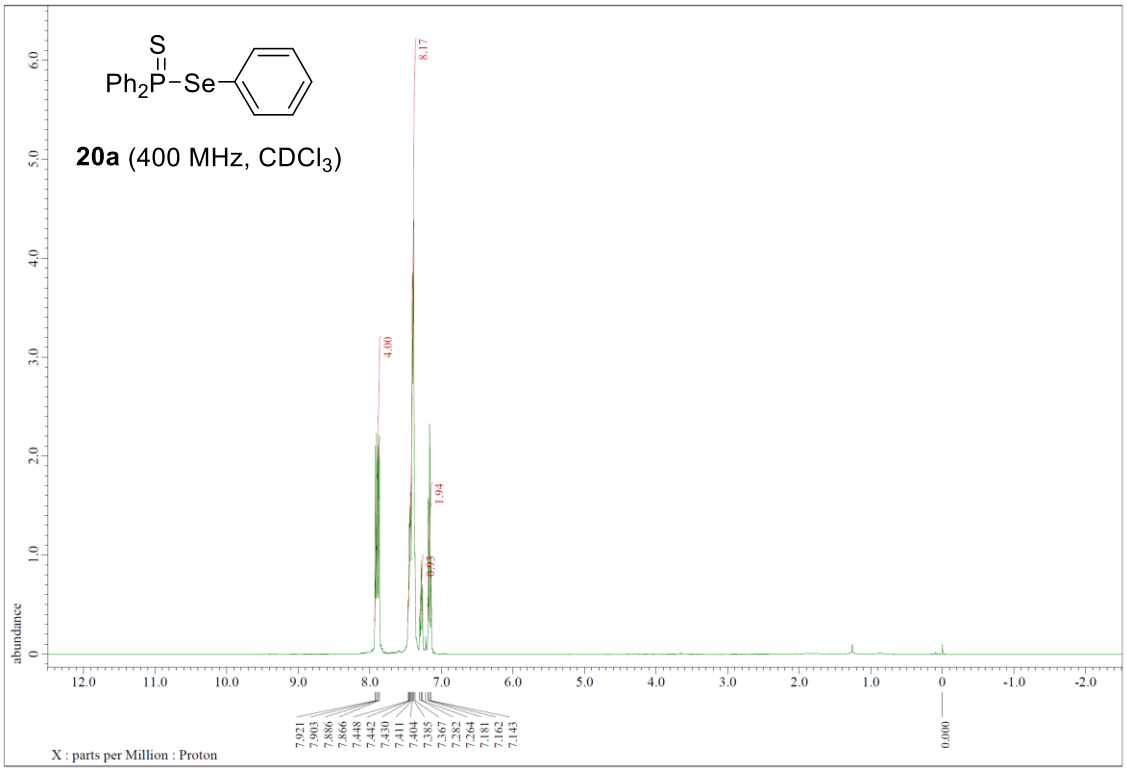
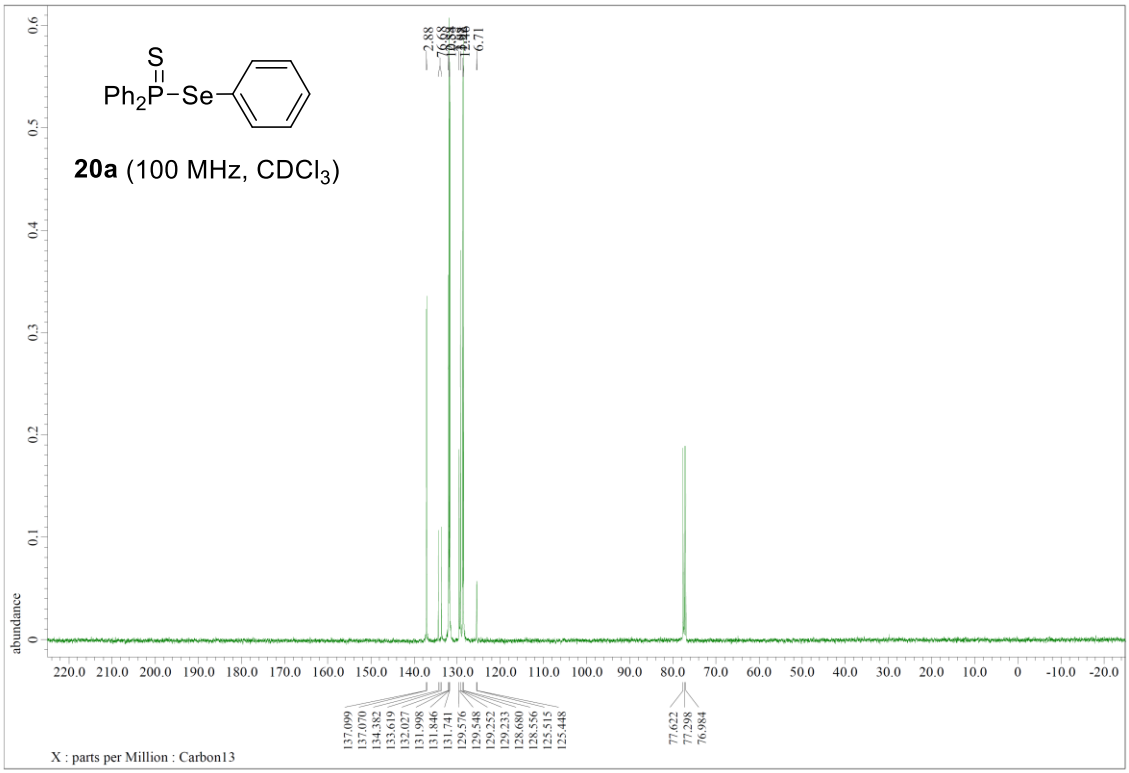
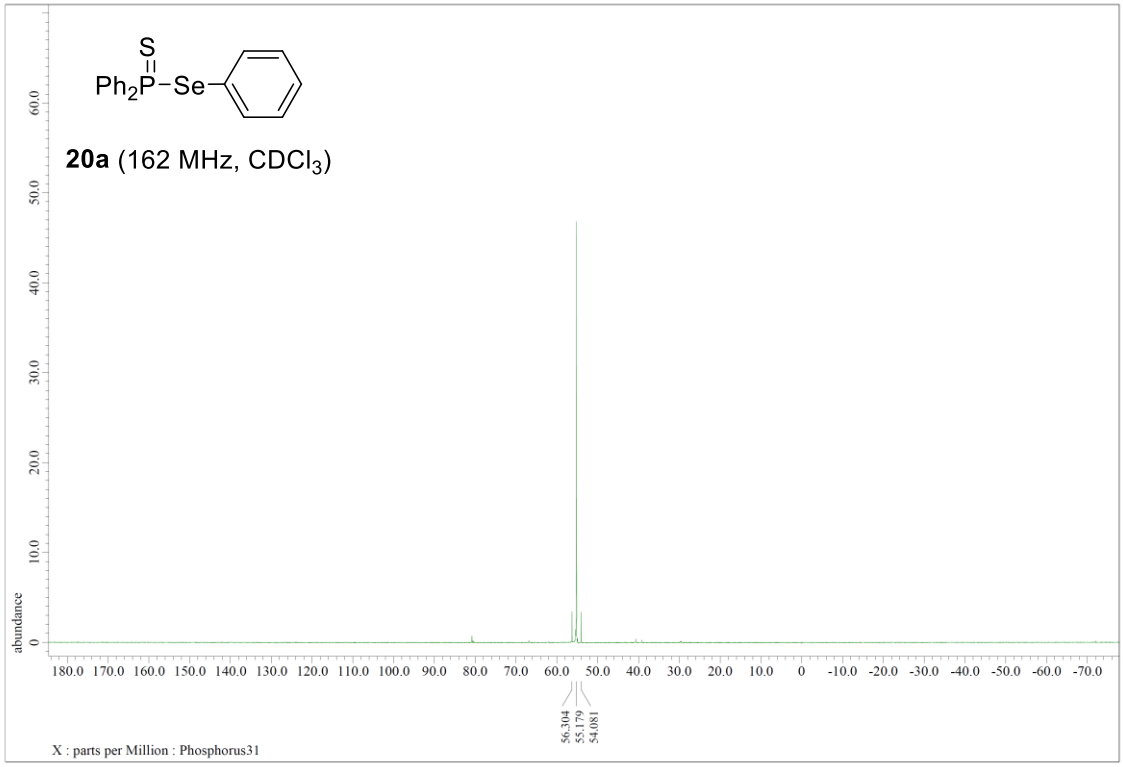

S
Ph2P—S
19e (162 MHz, CDCl3)
abundance
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
62.331
X : parts per Million : Phosphorus31

Figure S6 ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra of compound **20a**






S
Ph2P–Se
20a (162 MHz, CDCl3)
abundance
60.0
50.0
40.0
30.0
20.0
10.0
0
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0 -70.0
56.304
55.179
54.081
X : parts per Million : Phosphorus31

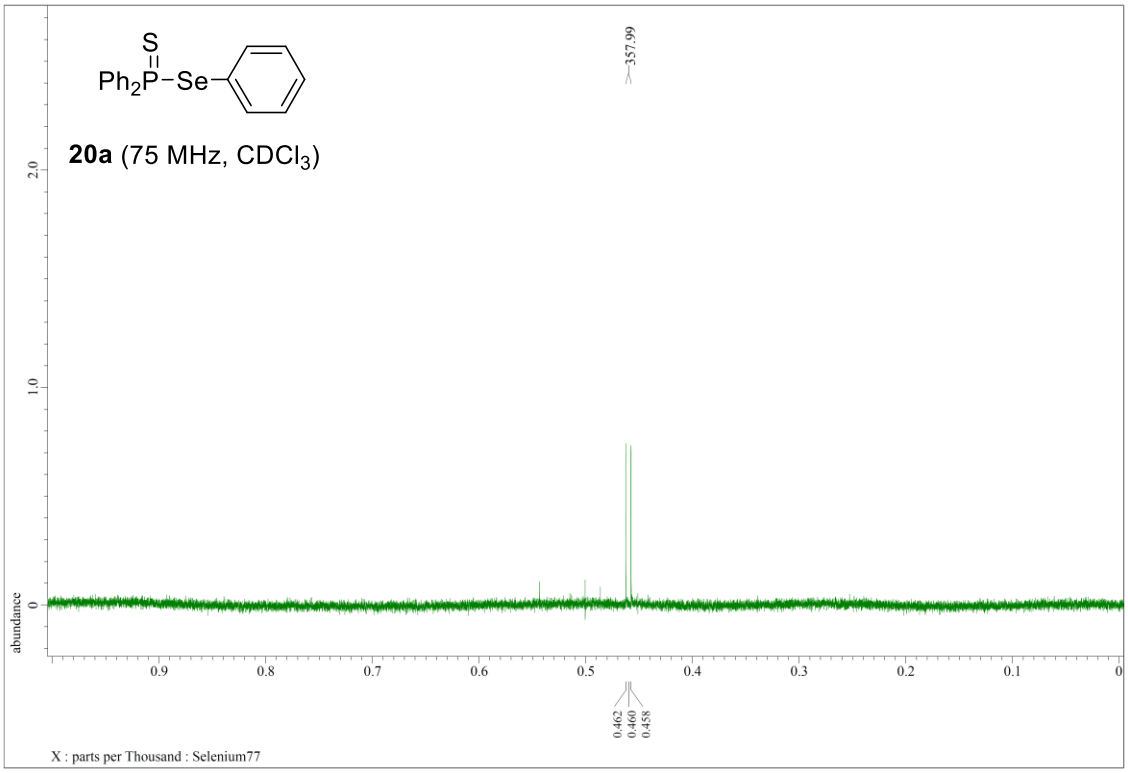
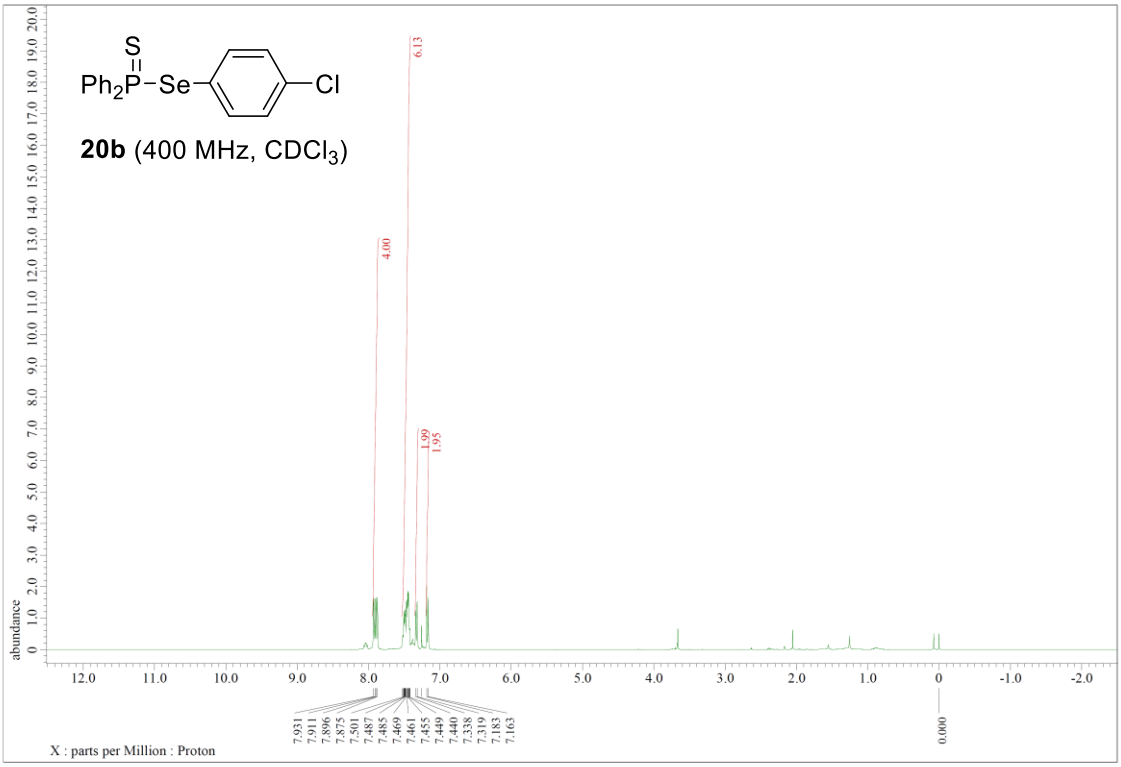
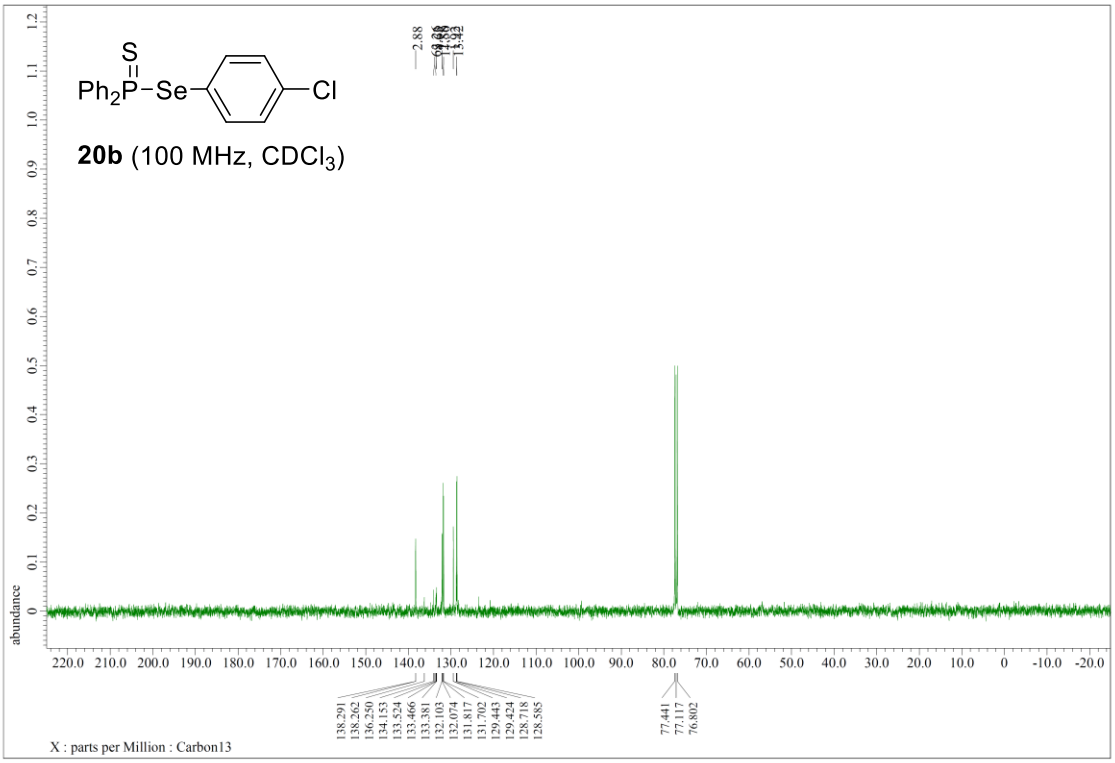
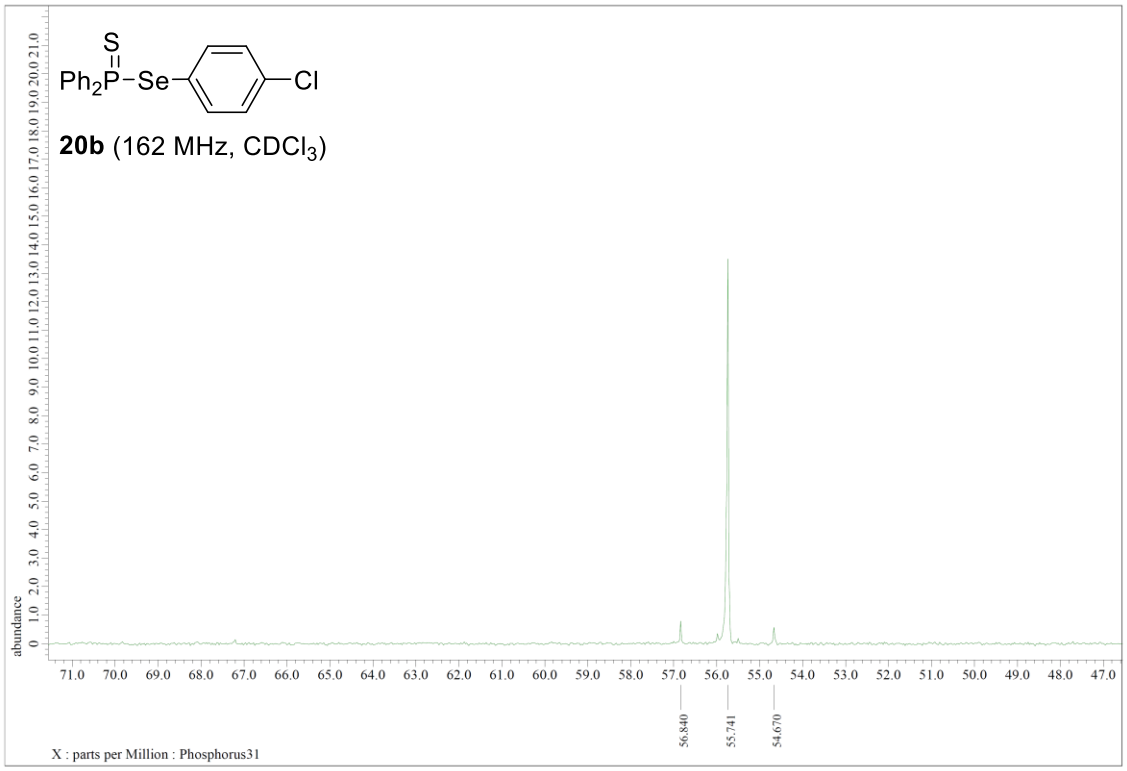

S
Ph2P–Se
20a (75 MHz, CDCl3)
357.99
abundance
2.0
1.0
0
0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
0.462
0.460
0.458
X : parts per Thousand : Selenium77

Figure S7 ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra of compound **20b**






S
Ph2P–Se
Cl
20b (162 MHz, CDCl3)
abundance
56.840
55.741
54.670
X : parts per Million : Phosphorus31

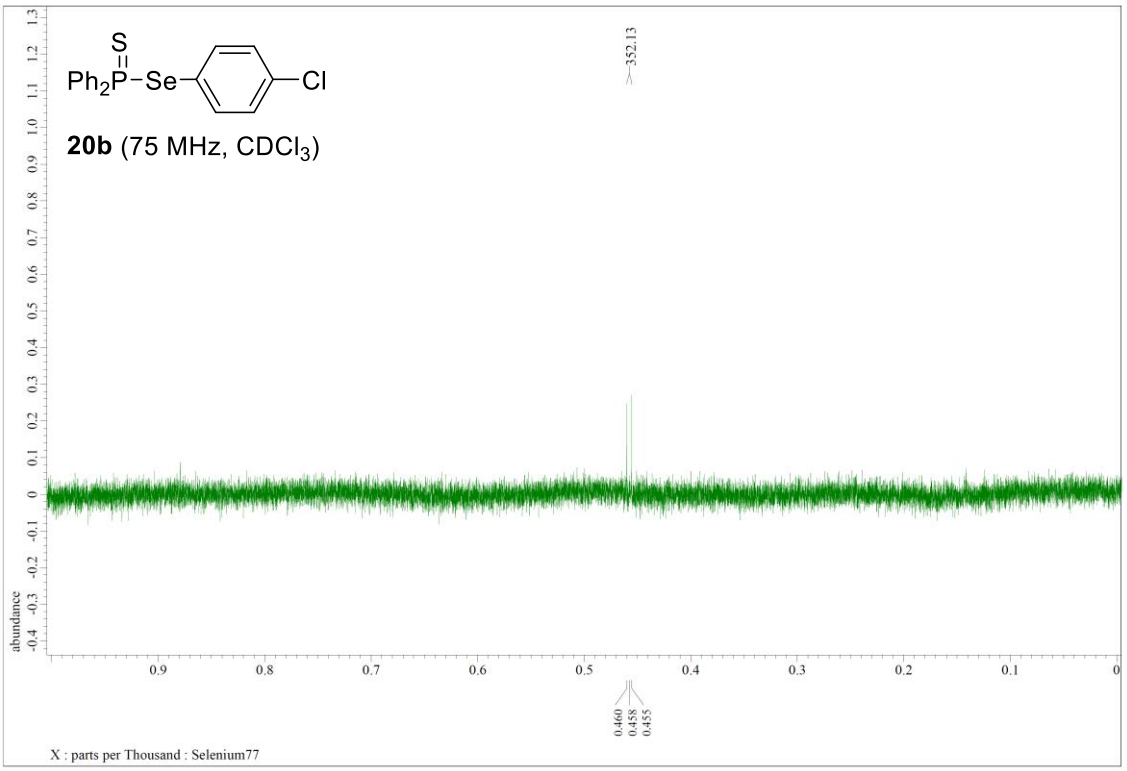
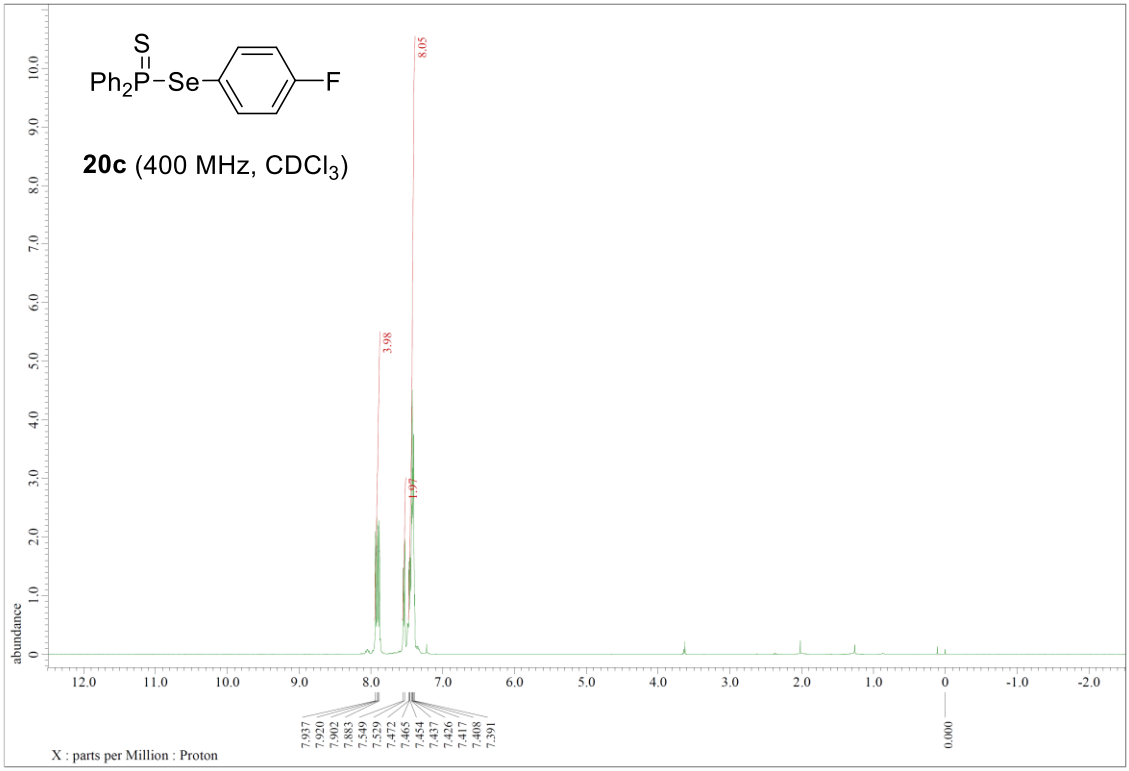
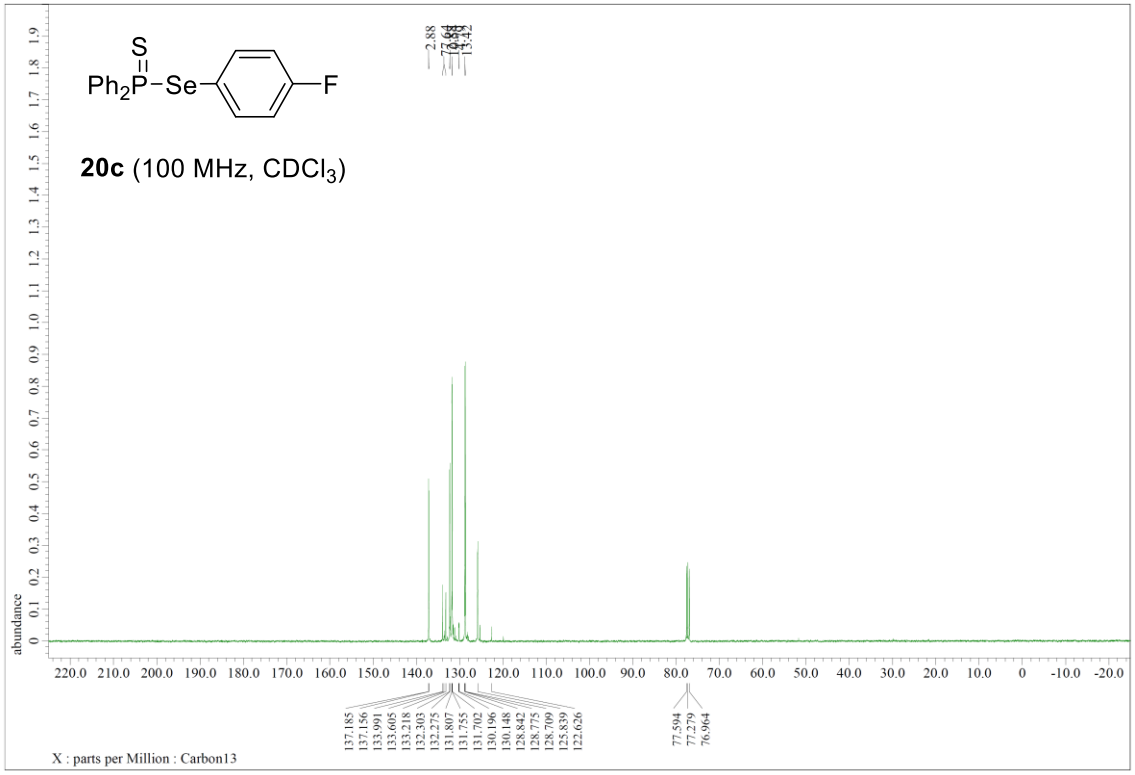
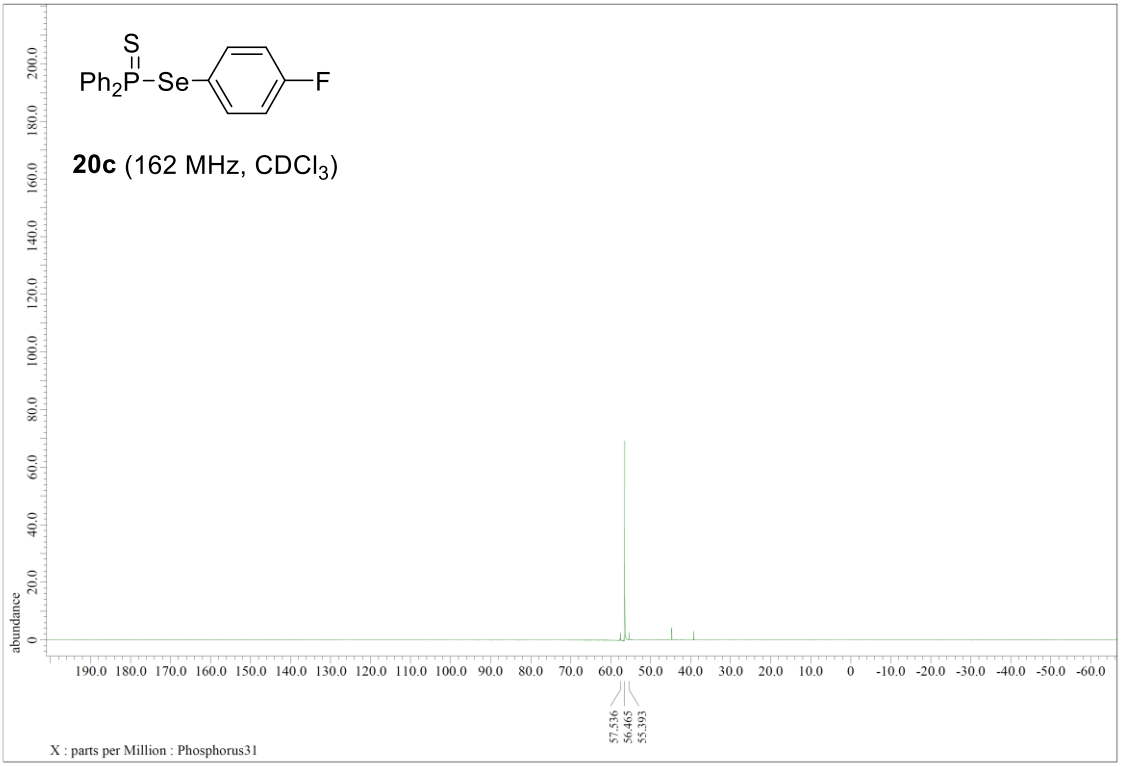

S
Ph2P–Se
Cl
20b (75 MHz, CDCl3)
>352.13
abundance
0.460
0.458
0.455
X : parts per Thousand : Selenium77

Figure S8 ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra of compound **20c**






S
Ph2P–Se
F
20c (162 MHz, CDCl3)
abundance
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0 -30.0 -40.0 -50.0 -60.0
57.536
56.465
55.393
X : parts per Million : Phosphorus31

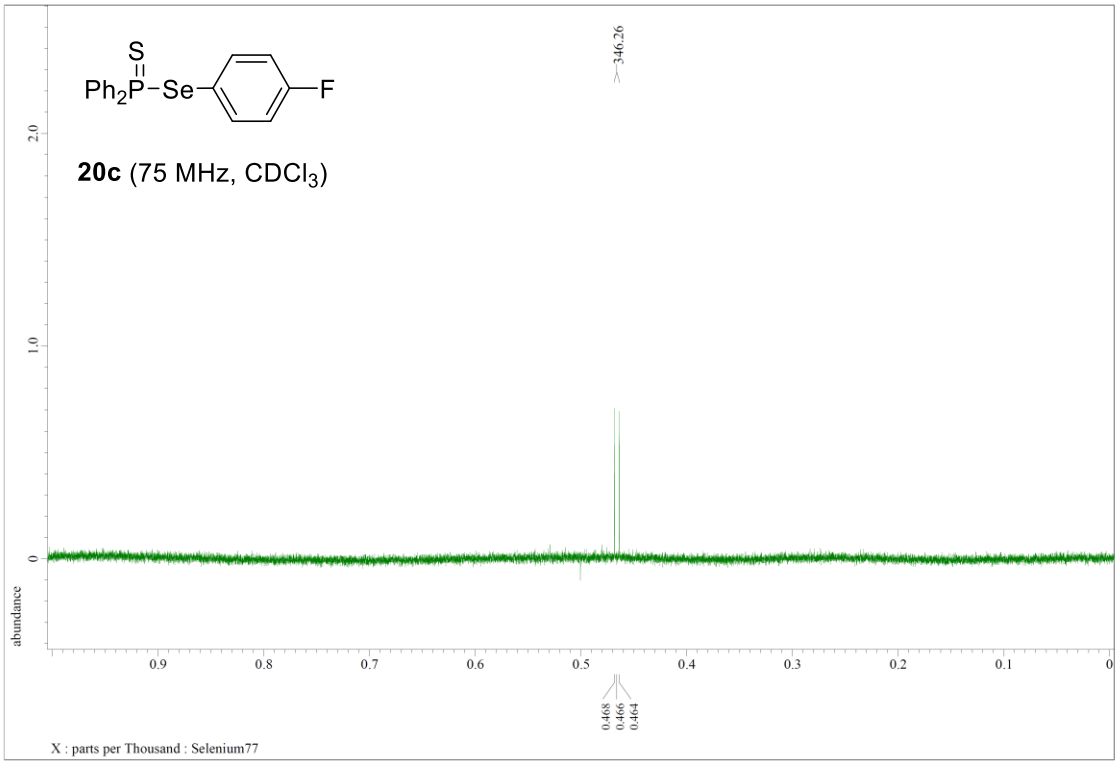
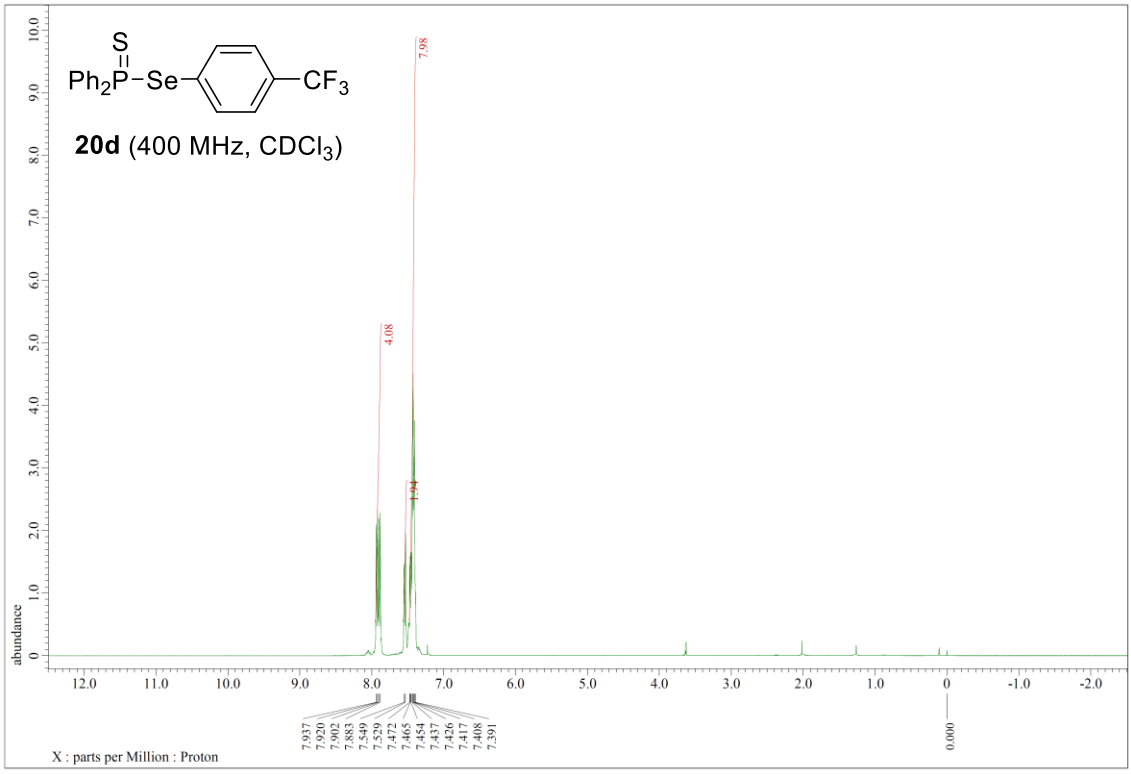
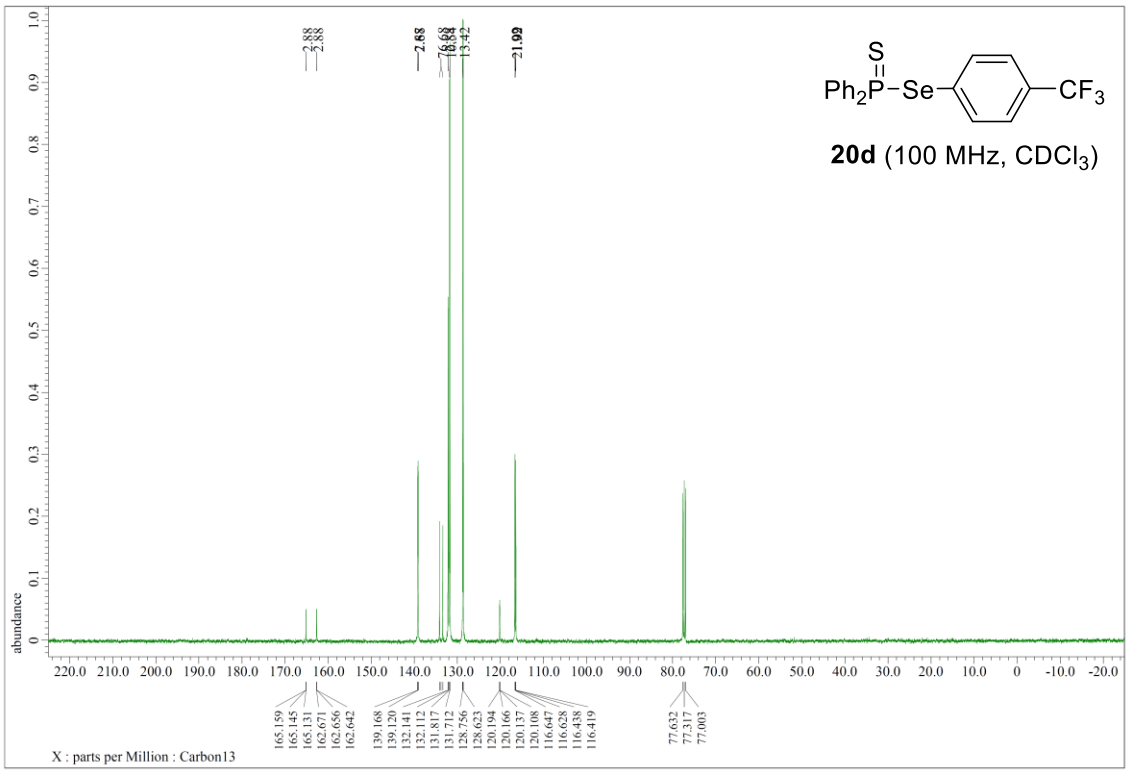
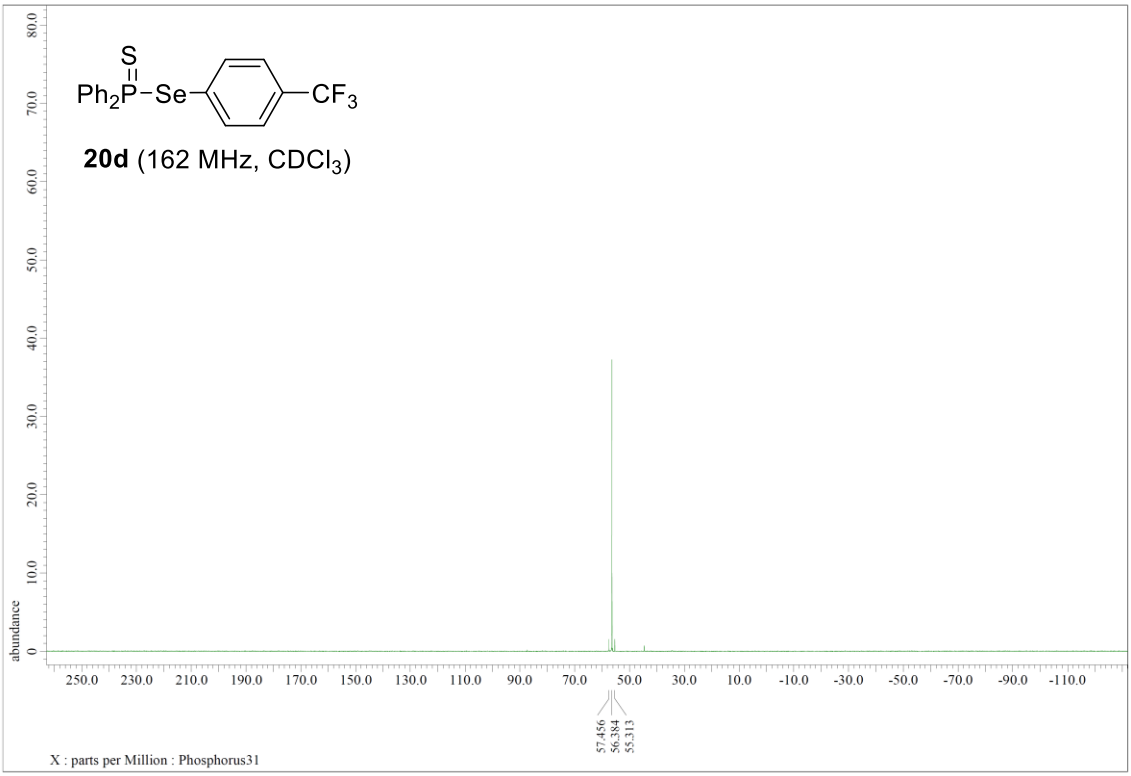

S
Ph2P–Se
F
346.26
20c (75 MHz, CDCl3)
abundance
2.0
1.0
0
0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
0.468
0.466
0.464
X : parts per Thousand : Selenium77

Figure S9 ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra of compound **20d**






S
Ph2P–Se
CF3
20d (162 MHz, CDCl3)
abundance
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
250.0 230.0 210.0 190.0 170.0 150.0 130.0 110.0 90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0
57.456
56.384
55.313
X : parts per Million : Phosphorus31

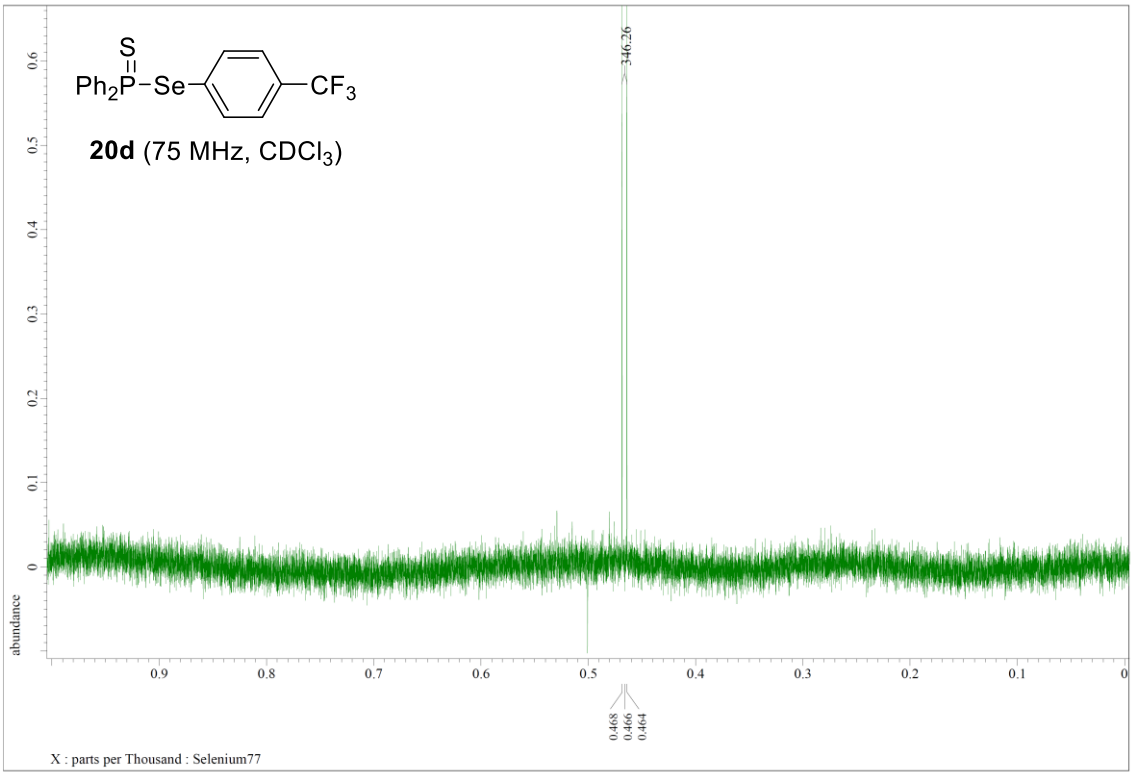
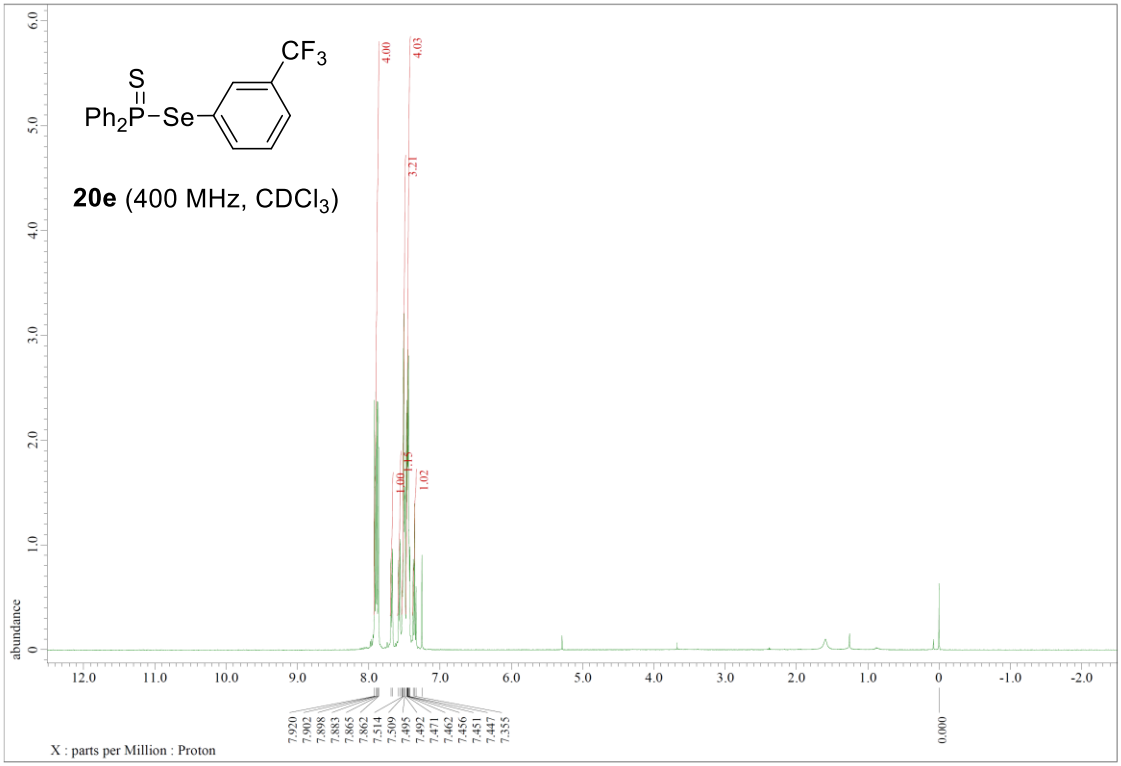
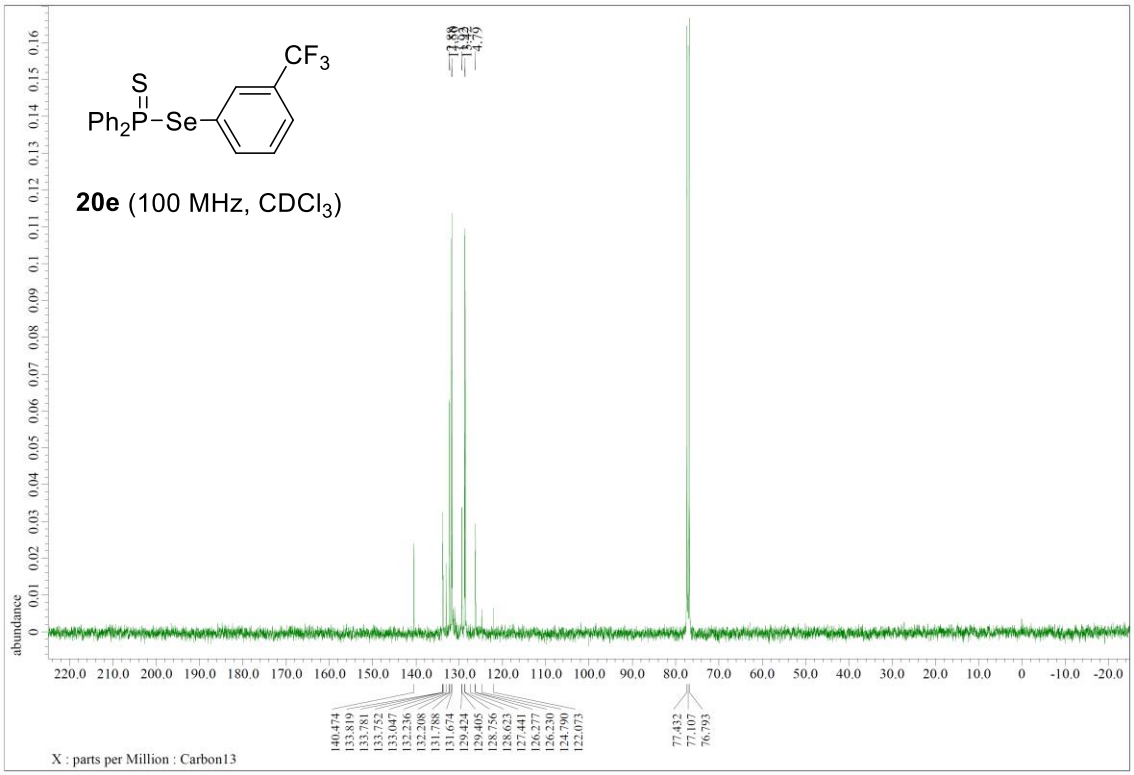
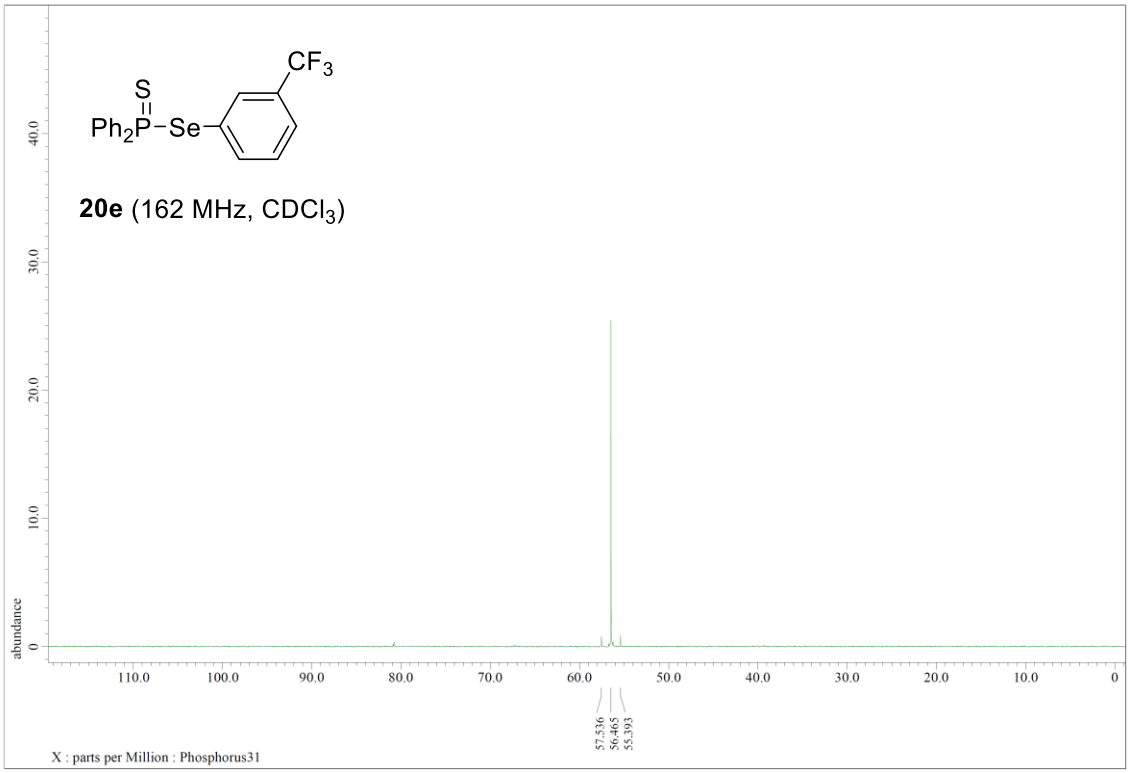

S
Ph2P–Se
CF3
20d (75 MHz, CDCl3)
346.26
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
0.468
0.466
0.464
X : parts per Thousand : Selenium77

Figure S10 ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra of compound **20e**






CF3
S
Ph2P–Se
20e (162 MHz, CDCl3)
abundance
40.0
30.0
20.0
10.0
0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
57.536
56.465
55.393
X : parts per Million : Phosphorus31

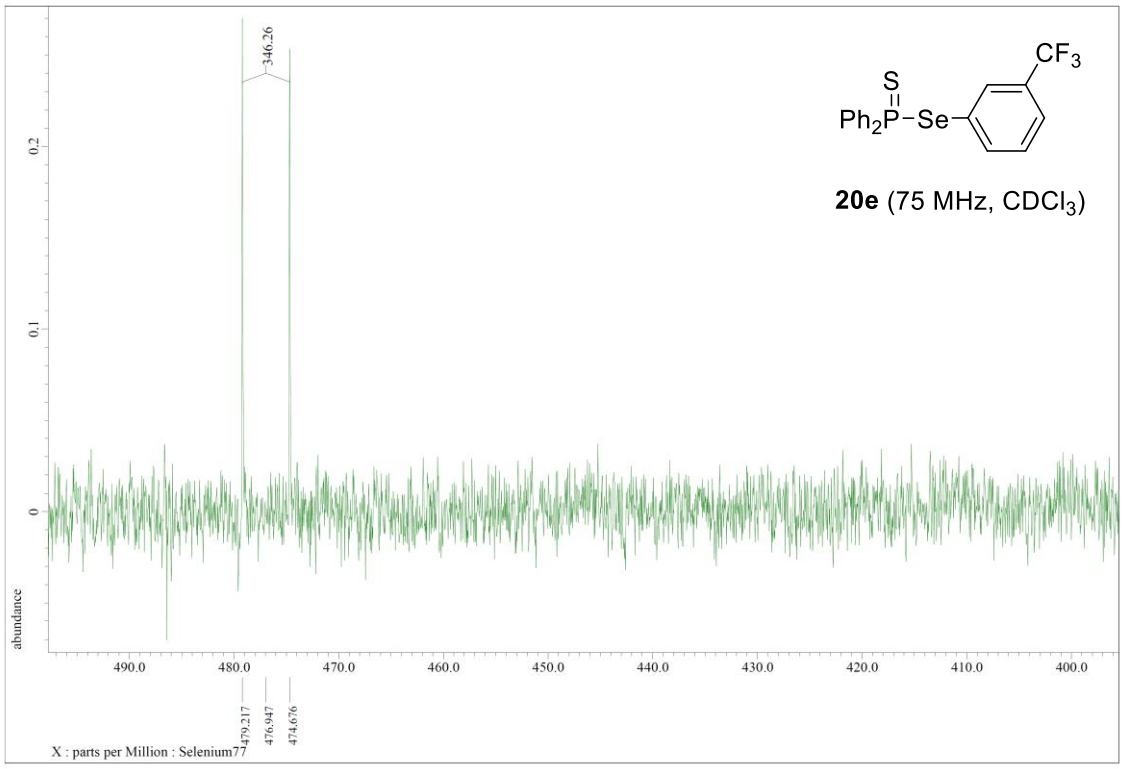
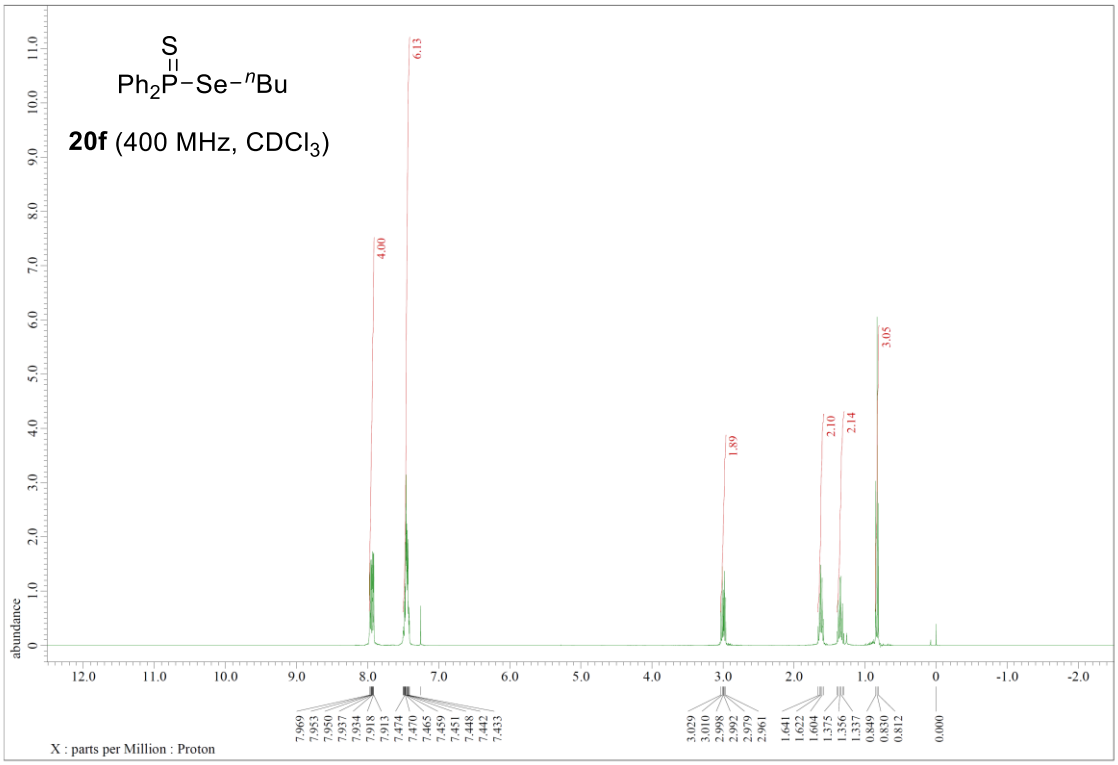
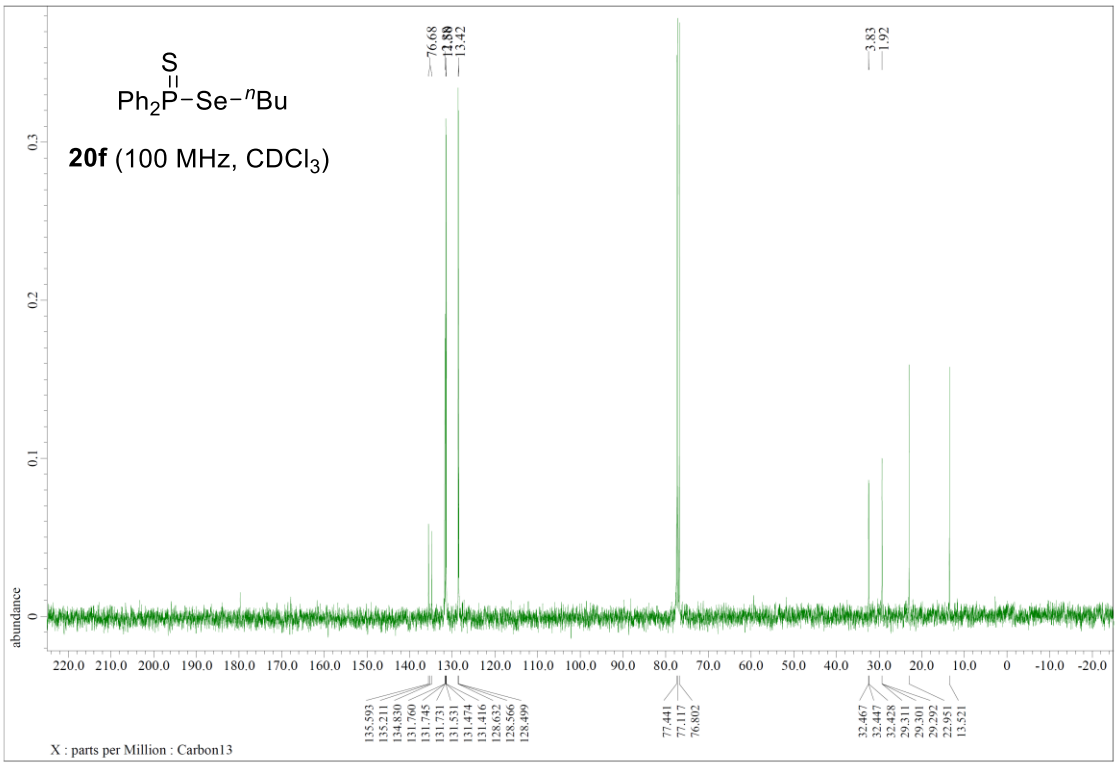
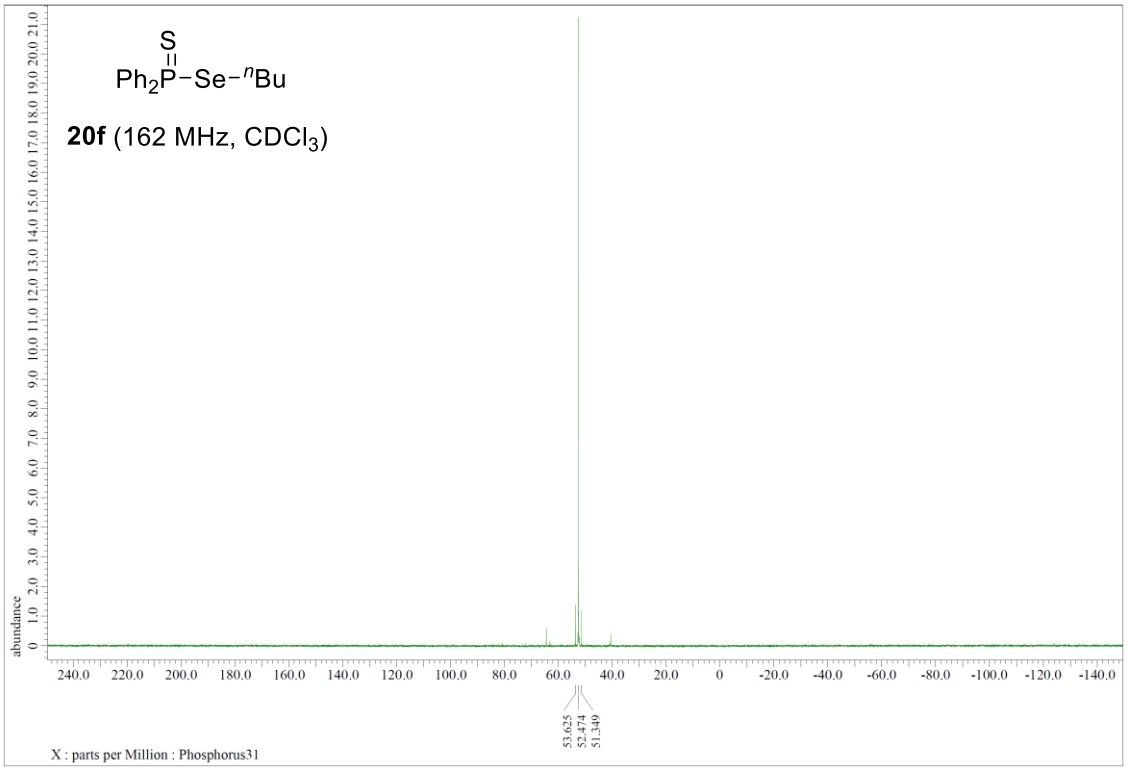

346.26
CF3
S
Ph2P–Se
20e (75 MHz, CDCl3)
abundance
0.2
0.1
0
490.0
480.0
470.0
460.0
450.0
440.0
430.0
420.0
410.0
400.0
479.217
476.947
474.676
X : parts per Million : Selenium77

Figure S11 ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra of compound **20f**






S
Ph2P–Se–nBu
20f (162 MHz, CDCl3)
abundance
X : parts per Million : Phosphorus31
53.625
52.474
51.349

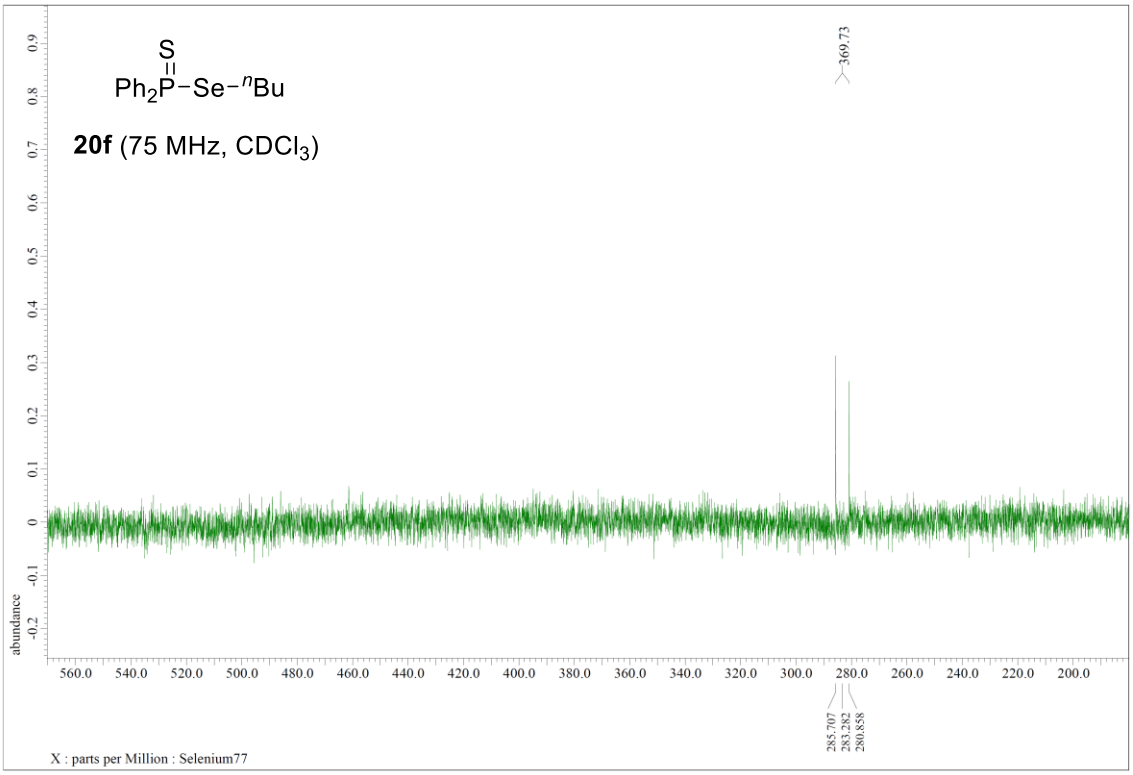
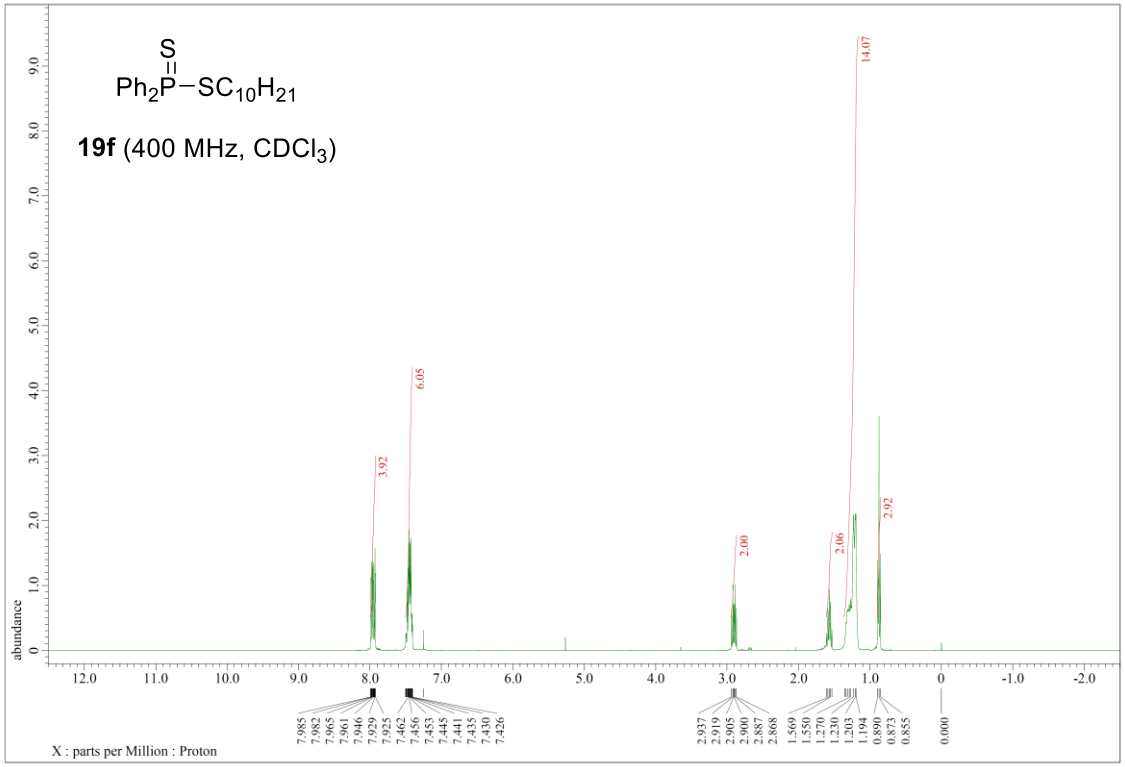
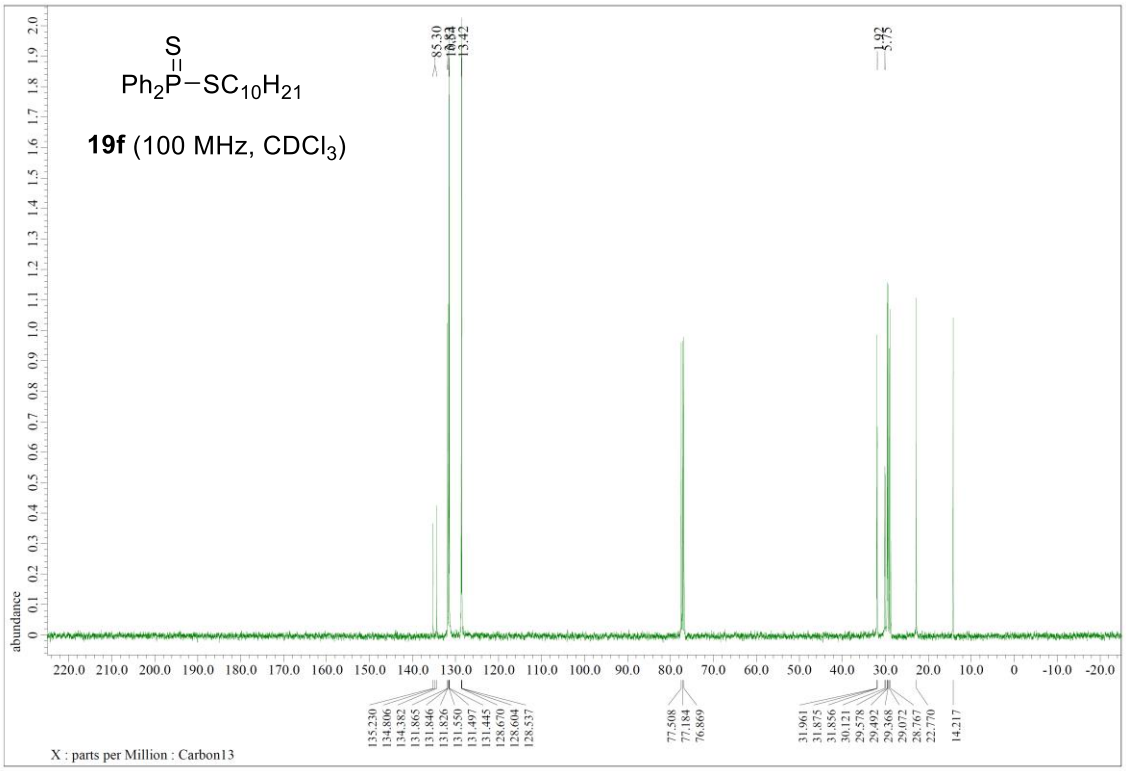

S
Ph2P–Se–nBu
20f (75 MHz, CDCl3)
369.73
abundance
X : parts per Million : Selenium77
285.707
283.282
280.858

Figure S12 ^{1}H, ^{13}C, and ^{31}P NMR spectra of compound **19f**





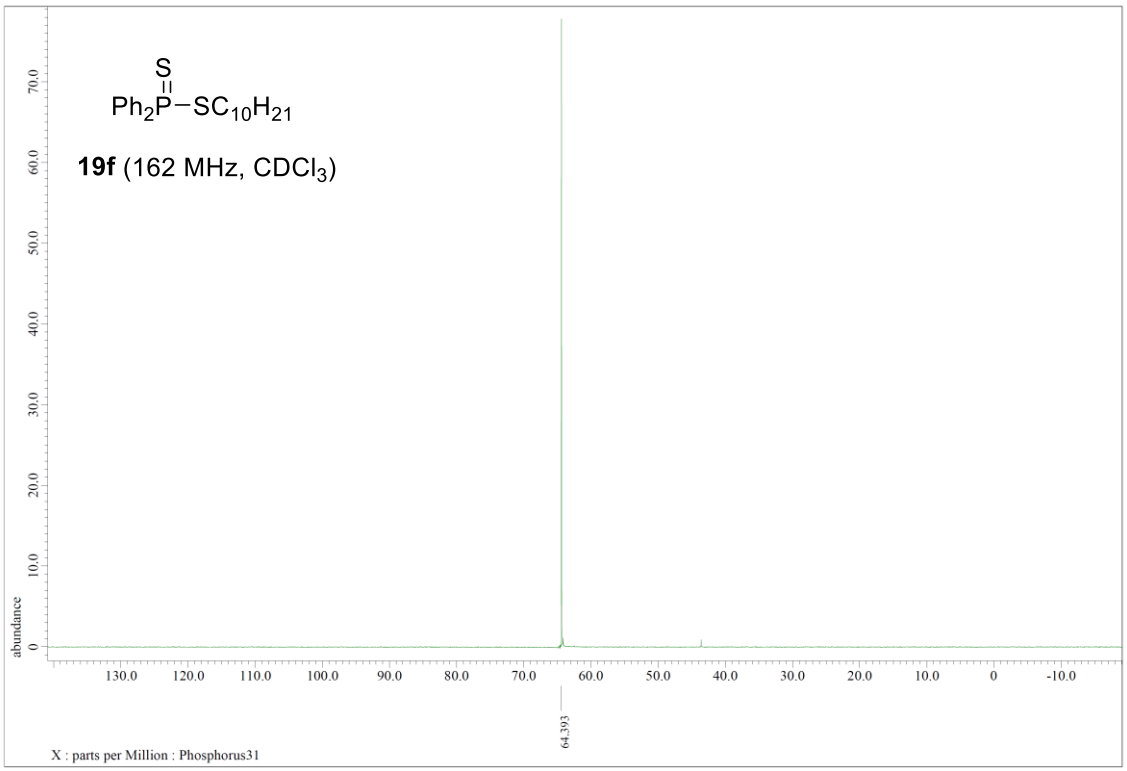
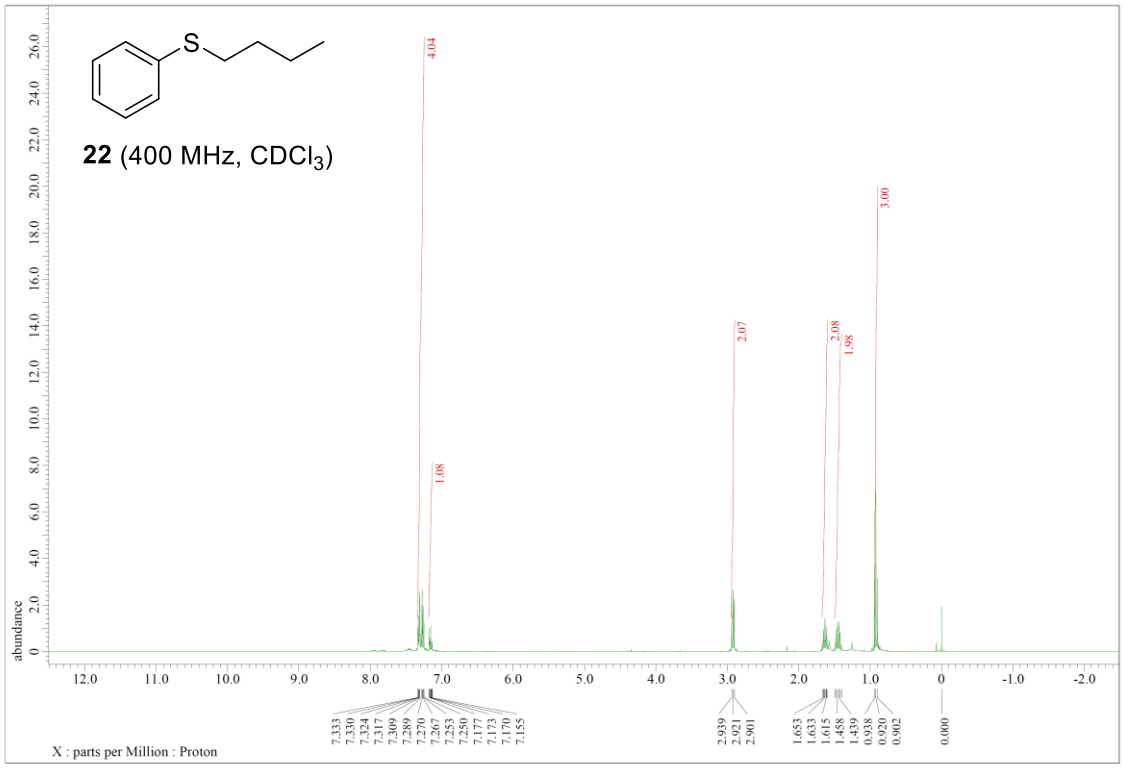

S
Ph2P−SC10H21
19f (162 MHz, CDCl3)
abundance
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
64.393
X : parts per Million : Phosphorus31

Figure S13 ^{1}H and ^{13}C NMR spectra of compound **22**



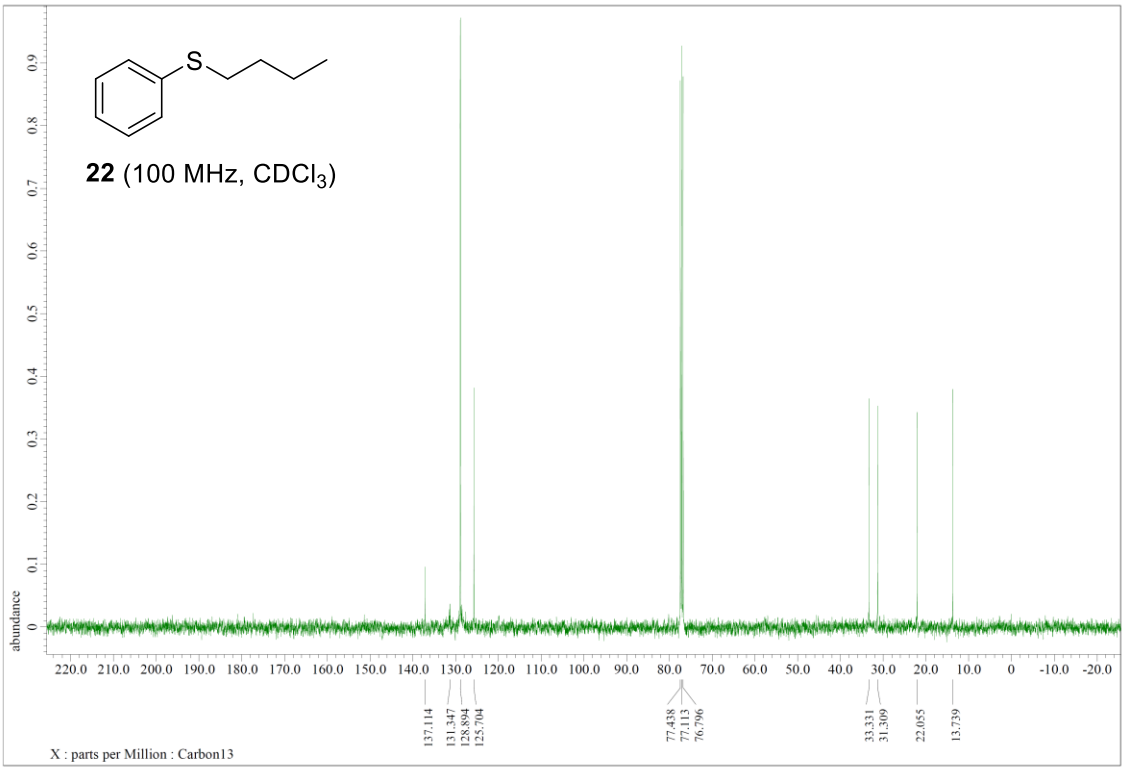
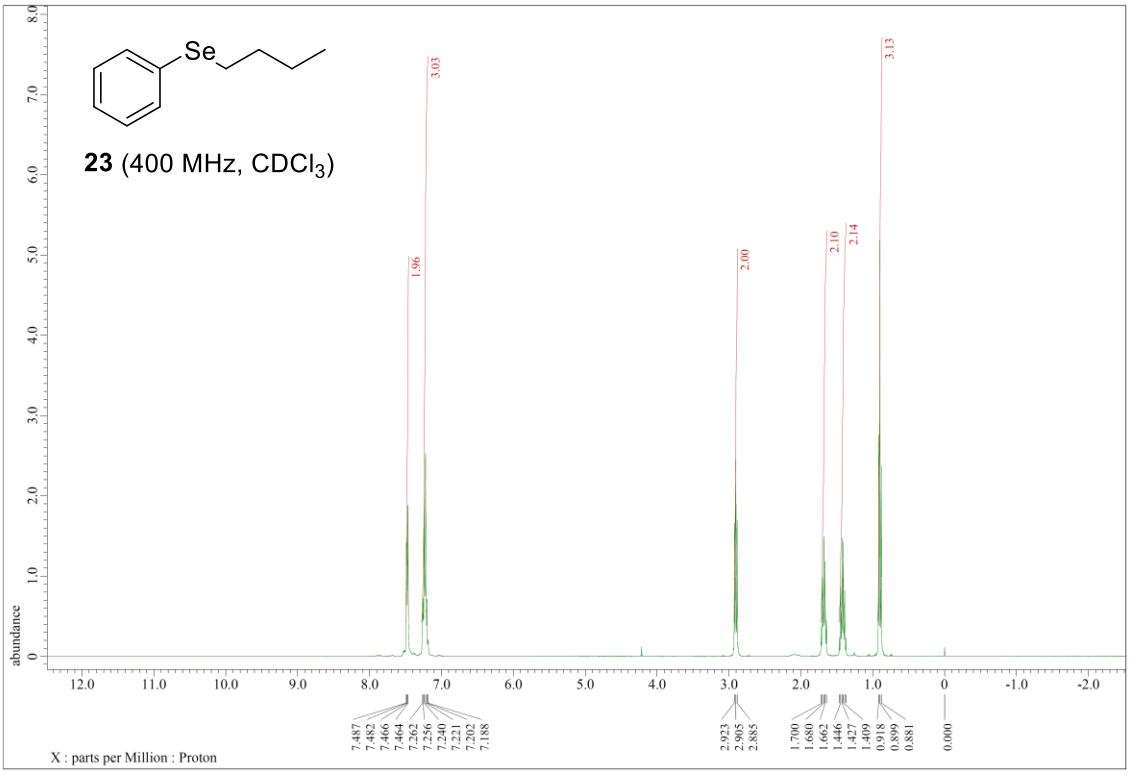
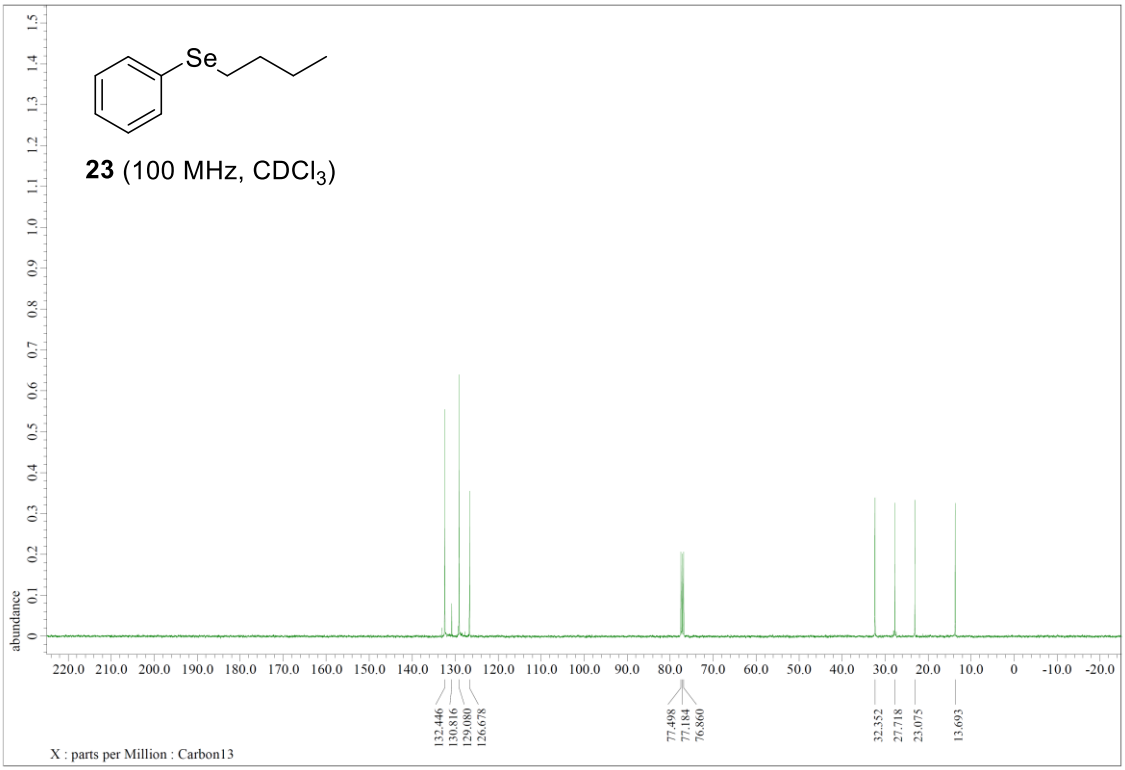
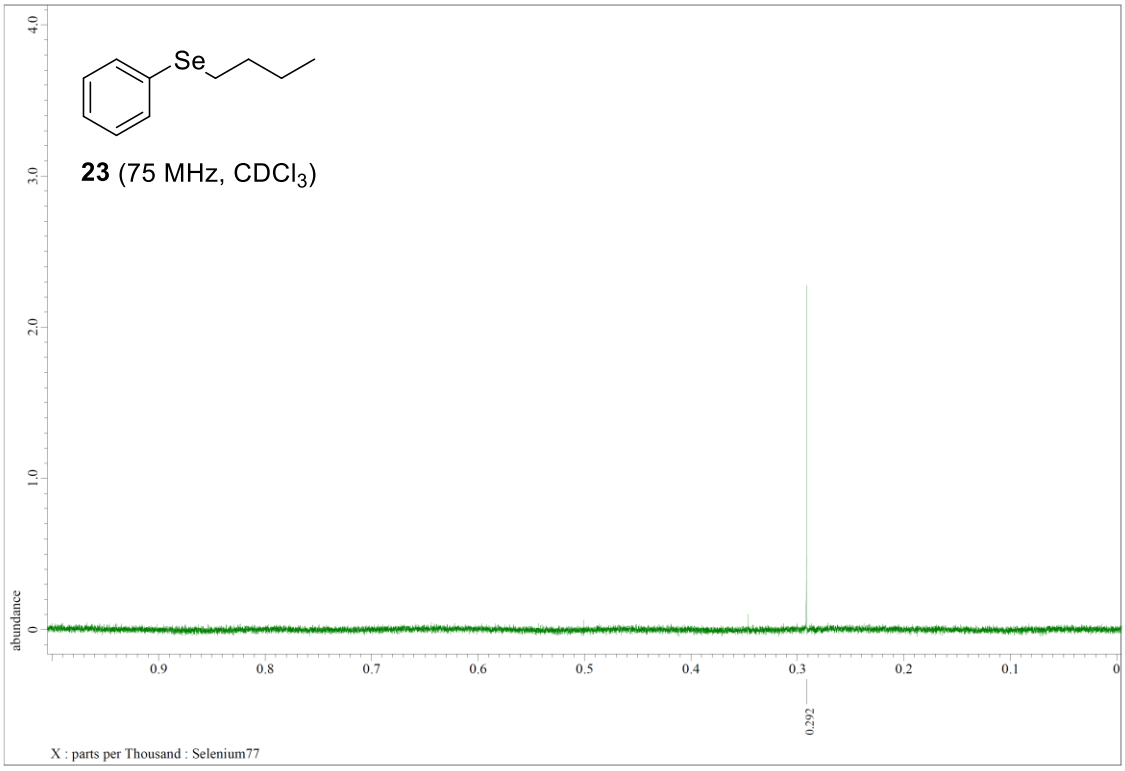


Figure S14 ^{1}H, ^{13}C, and ^{77}Se NMR spectra of compound **23**






Se
23 (75 MHz, CDCl3)
abundance
4.0
3.0
2.0
1.0
0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0,292
X : parts per Thousand : Selenium77