Supporting Information

Batch and Flow Synthesis of Pyrrolo[1,2-*a*]quinolines via an Allene-based Reaction Cascade

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1. Materials and methods:

Unless otherwise stated, all solvents, substrates and reagentswere used as purchased without further purification.

^{1}H-NMR spectra were recorded on either 400 MHz, 600 MHz or 700 MHz instruments and are reported relative to residual solvent: $CHCl_3$ (δ 7.26 ppm). ^{13}C-NMR spectra were recorded on the same instruments and are reported relative to $CHCl_3$ (δ 77.16 ppm). Data for ^{1}H-NMR are reported as follows: chemical shift (δ/ ppm) (integration, multiplicity, coupling constant (Hz)). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br. s = broad singlet, app = apparent. Data for ^{13}C-NMR are reported in terms of chemical shift (δ/ ppm) and multiplicity (C, CH, CH_2 or CH_3). Data for ^{19}F-NMR were recorded on the above instruments at a frequency of 376 MHz using $CFCl_3$ as external standard. Data for ^{31}P-NMR were recorded on the above instruments at a frequency of 162 MHz. DEPT-135, COSY, HSQC, HMBC and NOESY experiments were used in the structural assignment. IR spectra were recorded neat (ATR sampling) with the intensities of the characteristic signals being reported as weak (w, <20% of tallest signal), medium (m, 21-70% of tallest signal) or strong (s, >71% of tallest signal). Low and high resolution mass spectrometry was performed using the indicated techniques on instruments equipped with Acquity UPLC and a lock-mass electrospray ion source. For accurate mass measurements the deviation from the calculated formula is reported in ppm. Melting points were recorded on an automated melting point system with a heating rate of 1 °C/min and are uncorrected.

The X-ray single crystal data for both compounds (**1e** and **2f**) have been collected using λMoKα radiation (λ =0.71073Å,Photon100 CMOS detector, IμS-microsource, focusing mirrors) with the diffractometer being equipped with a Cryostream open-flow nitrogen cryostat at the temperature

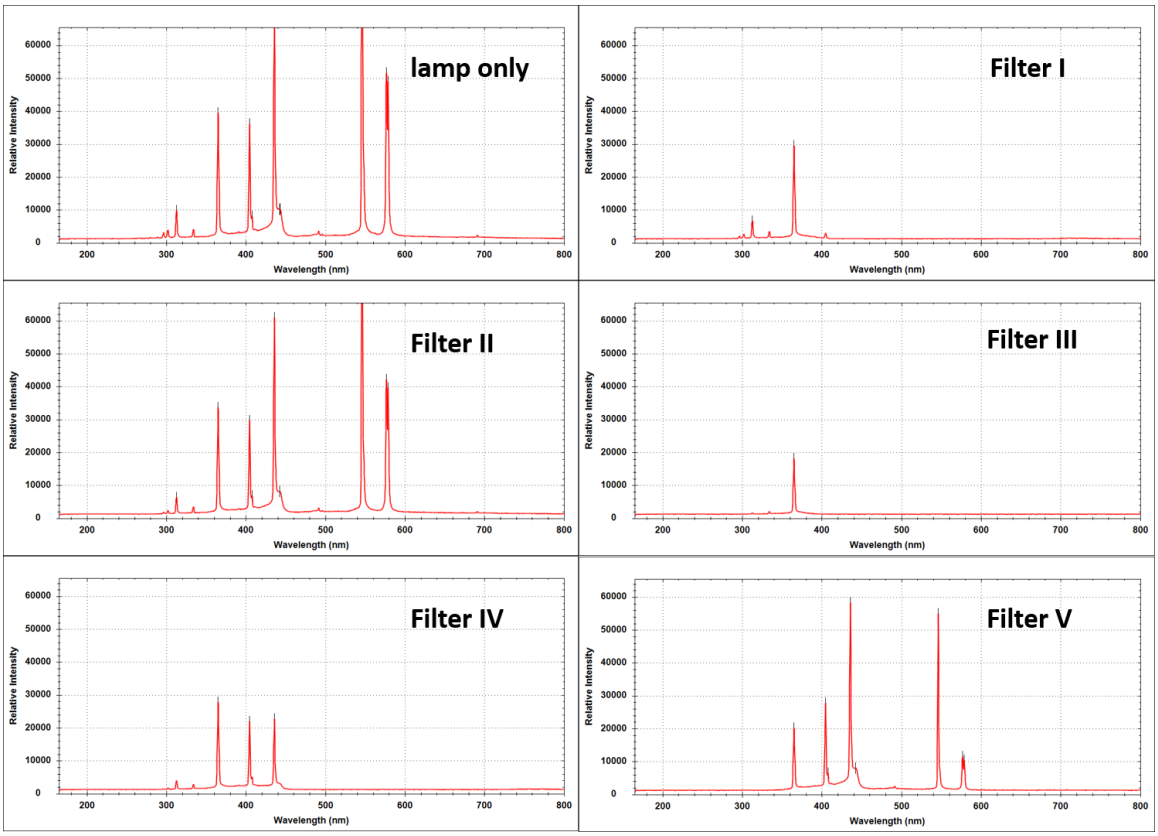
120.0(2)K. Both structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2 [1] and SHELXTL [2] software. All non-disordered non-hydrogen atoms were refined anisotropically, the hydrogen atoms of disordered Et-group in **2f** and in molecule **1e** were placed in the calculated positions and refined in riding mode, the remaining hydrogen atoms in structure **2f** were refined isotropically. Disordered atoms in both structures were refined isotropically with fixed SOF = 0.5. Crystal data and parameters of refinement are listed in Tables 1-17. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1411501-1411502. For microwave experiments a Biotage Initiator system was used and flow experiments were performed using a Vapourtec E-Series module with its UV150 extension for photochemical experiments.

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Cryst. (2009), 42, 339-341.

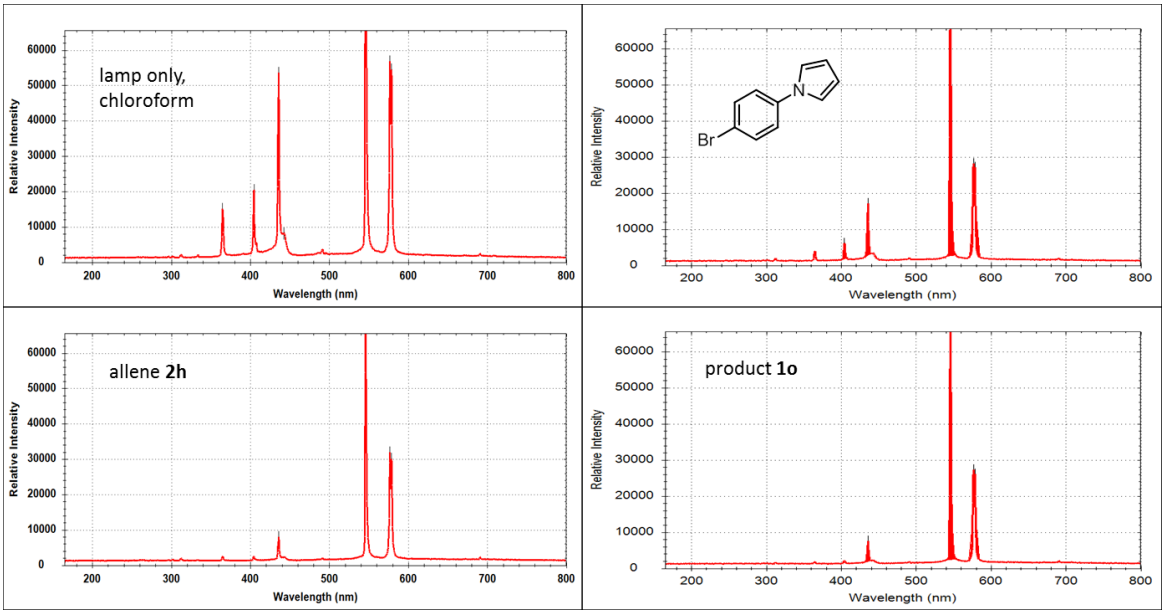
[2] G.M. Sheldrick, Acta Cryst. (2008), A64, 112-122

2. Commentary on Photo-Flow Reactions and the Use of the Photo-Spectrometer

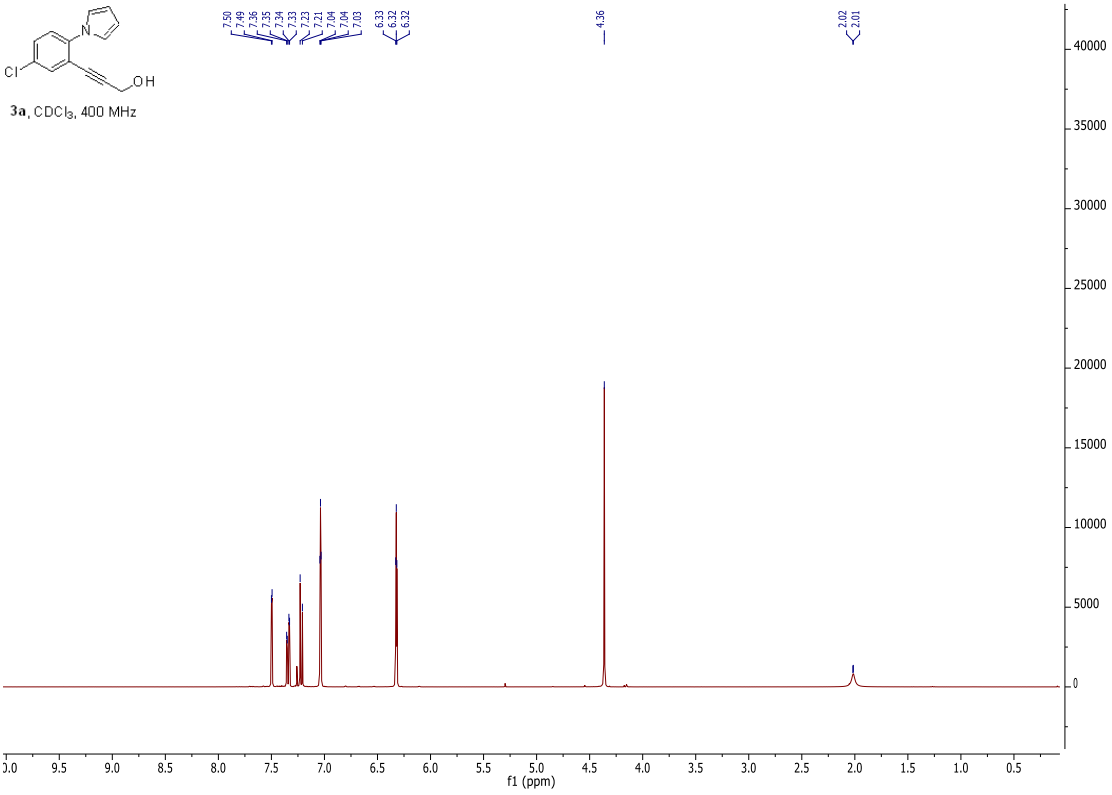
When using a selection of filters (see figures below) placed in between the high power medium pressure lamp and the coiled reactor (filled with water) it was established that filters **I**, **III** and **IV** worked best for increasing the conversion of allene intermediate into the desired cyclized product. A portable ExemplarLS photo-spectrometer was used to record real-time emission spectra of the different flow reactions (in chloroform).

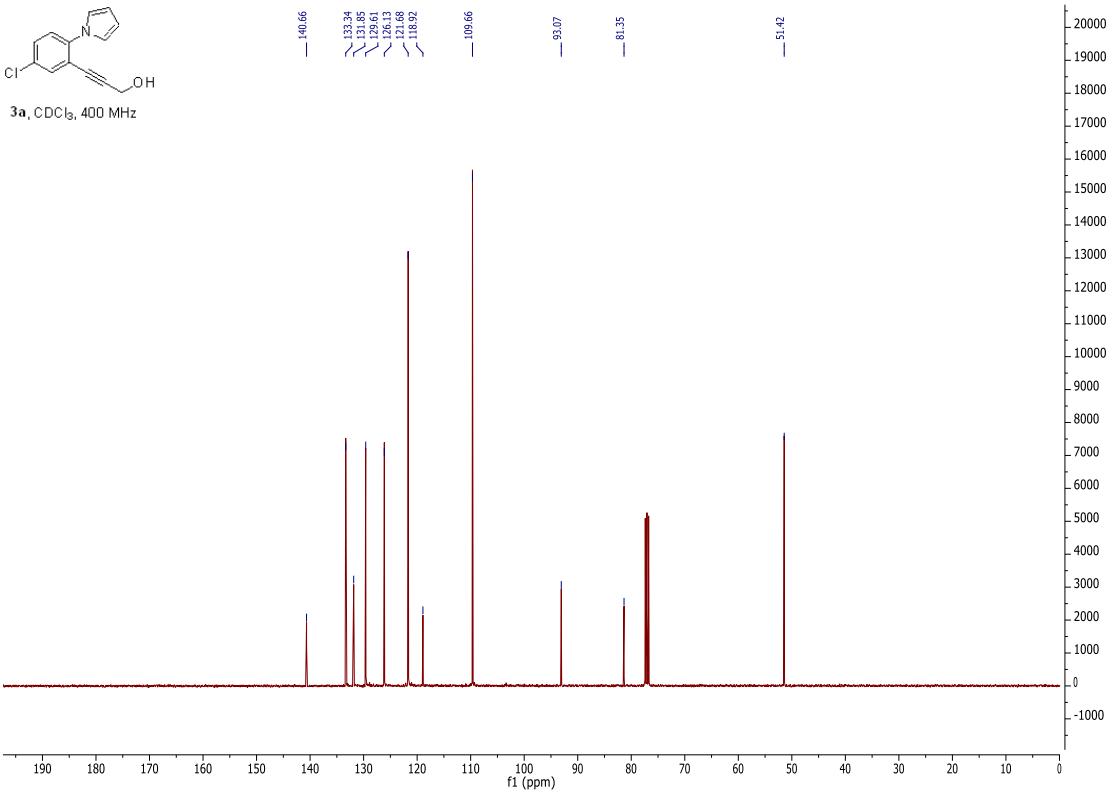


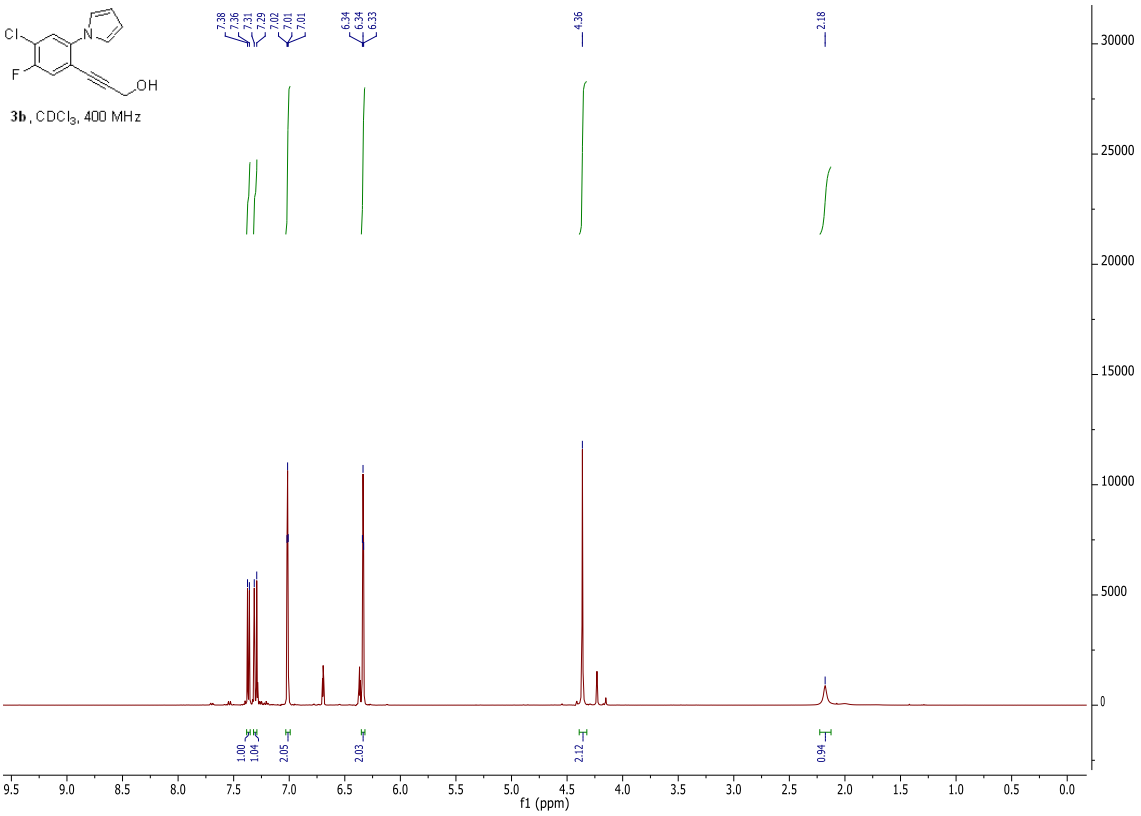
This established that the allene substrate absorbs light primarily below 440 nm, although both the desired product as well as a modified building block lacking the allene portion do absorb at similar wavelengths. In-line analysis (spectrometer) together with off-line analysis (^{1}H-NMR) thus indicated that the available wavelength range emitted by the lamp is suitable in activating the allene moiety, but decomposition of intermediate and reaction product(s) does occur concomitantly explaining the observed results.

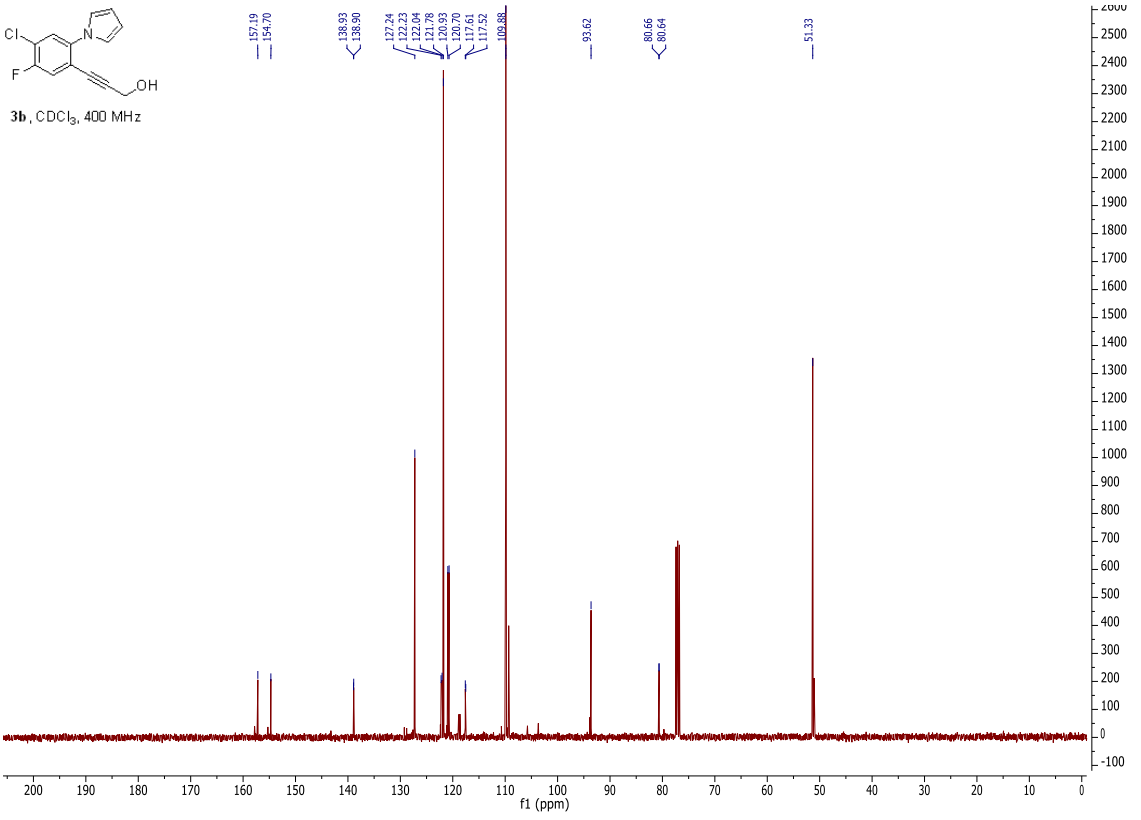

lamp only,
chloroform
Relative Intensity
Wavelength (nm)
Br
N
allene 2h
product 1o

3. Copies of ^{1}H- and ^{13}C-NMR spectra






3b, CDCl3, 400 MHz
7.38
7.36
7.31
7.29
7.02
7.01
7.01
6.34
6.34
6.33
4.36
2.18
1.00
1.04
2.05
2.03
2.12
0.94
f1 (ppm)


3b, CDCl3, 400 MHz
157.19
154.70
138.93
138.90
127.24
122.23
122.04
121.78
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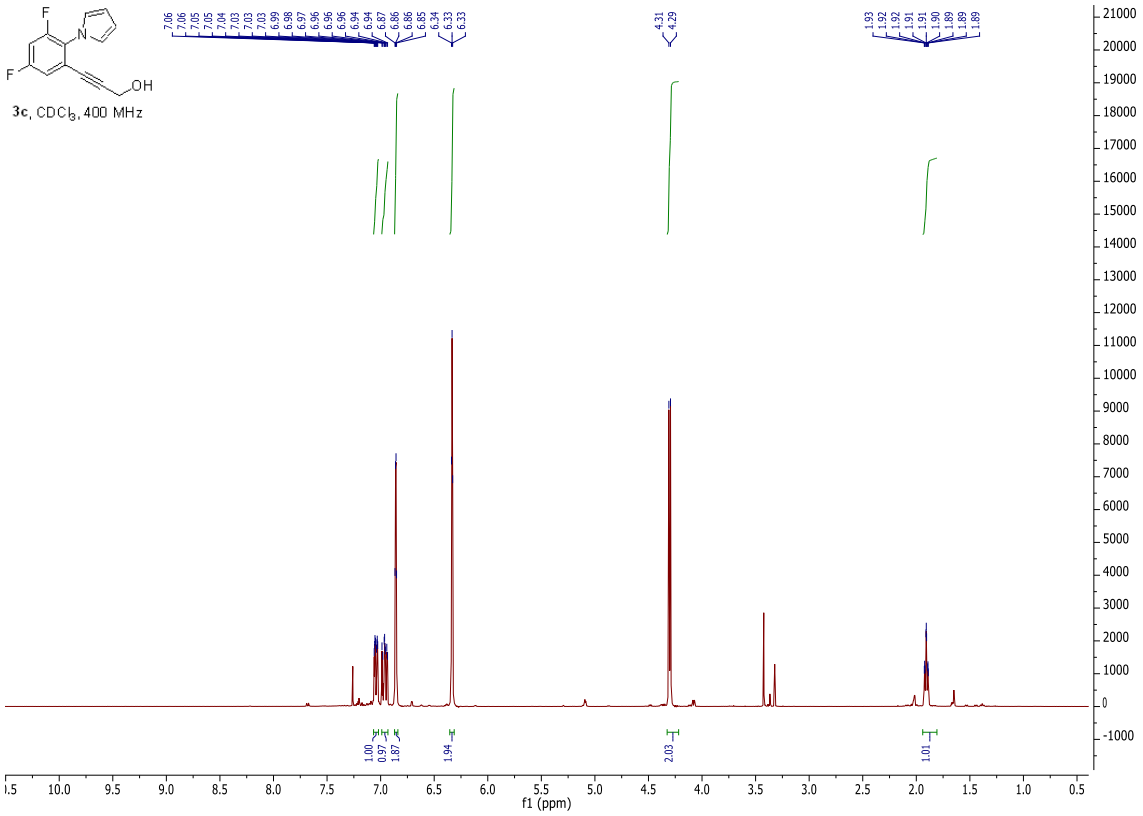
120.70
117.61
117.52
109.88
93.62
80.66
80.64
51.33
f1 (ppm)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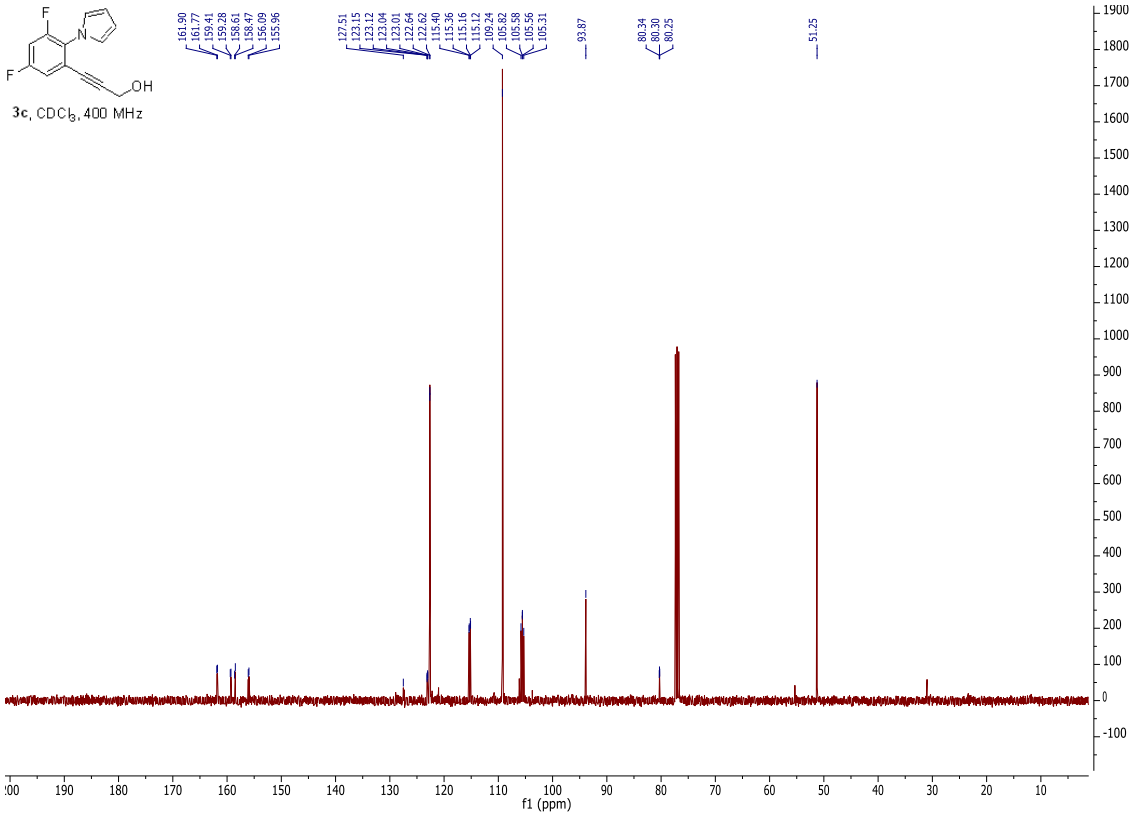
f1 (ppm)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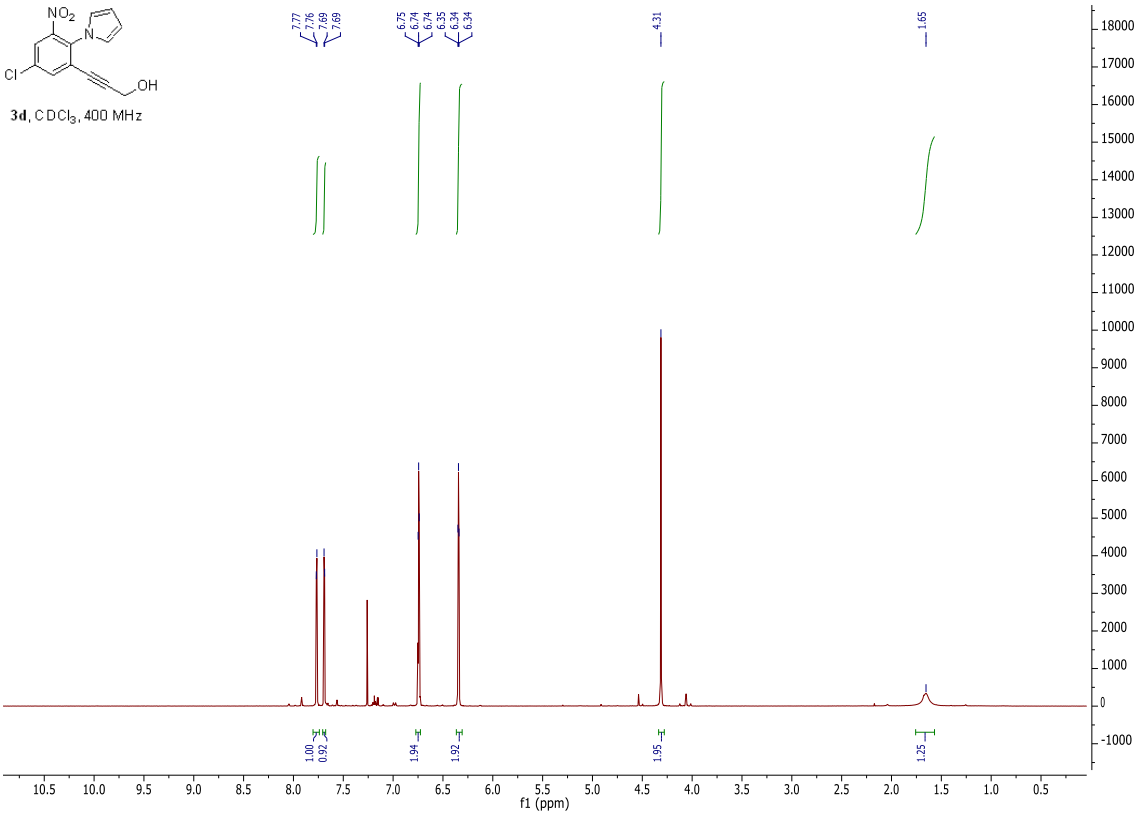
NO2
Cl
OH
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7.76
7.69
7.69
6.75
6.74
6.74
6.35
6.34
6.34
4.31
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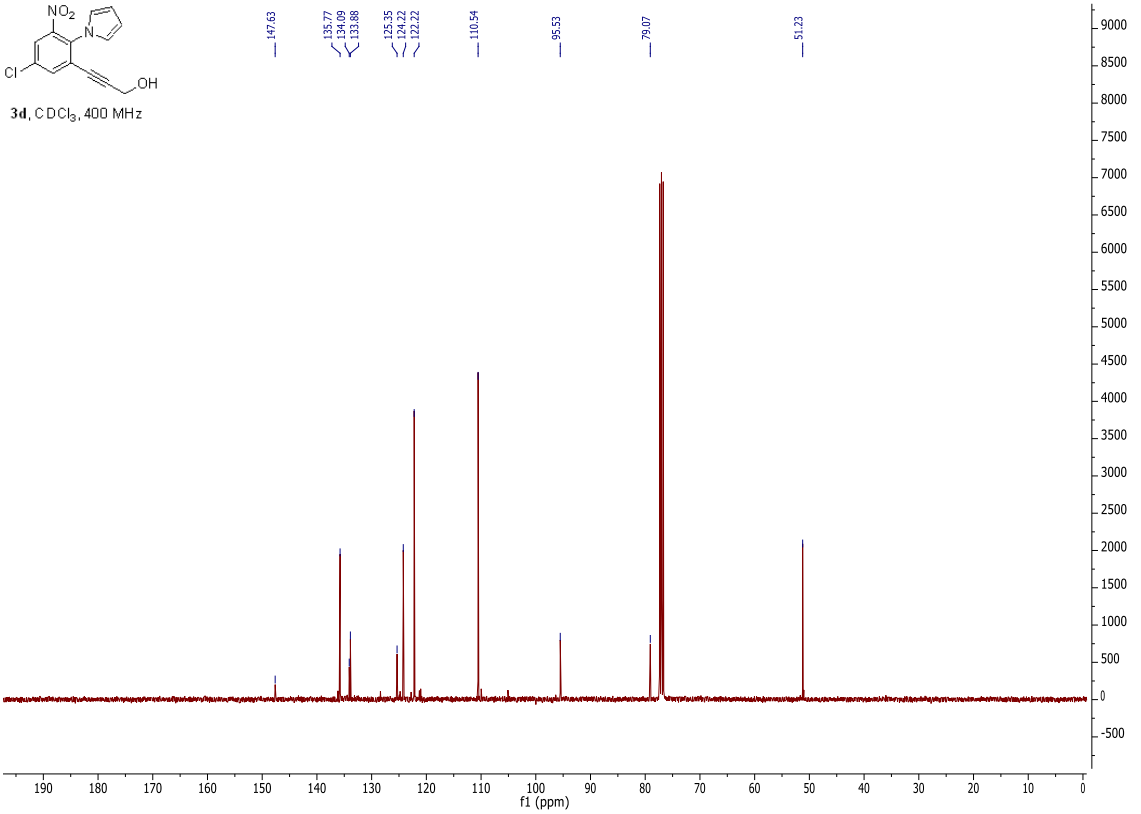
1.00
0.92
1.94
1.92
1.95
1.25
f1 (ppm)


NO2
Cl
OH
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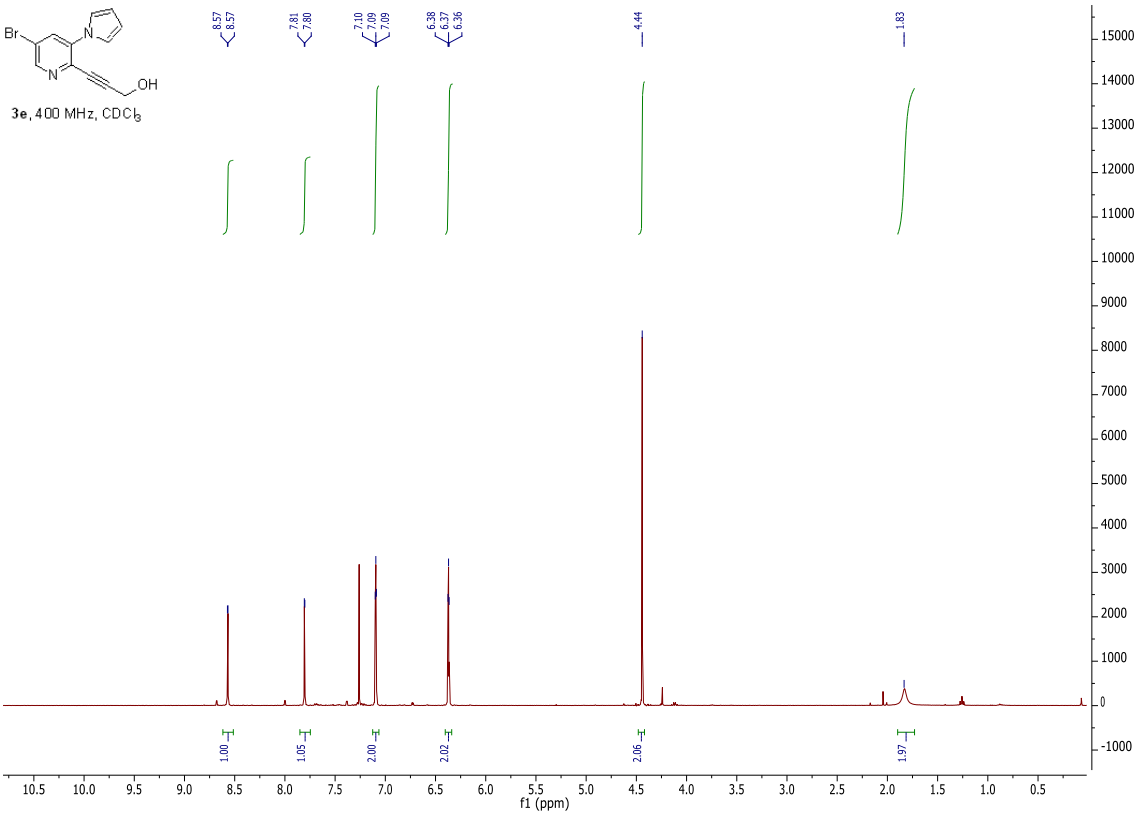
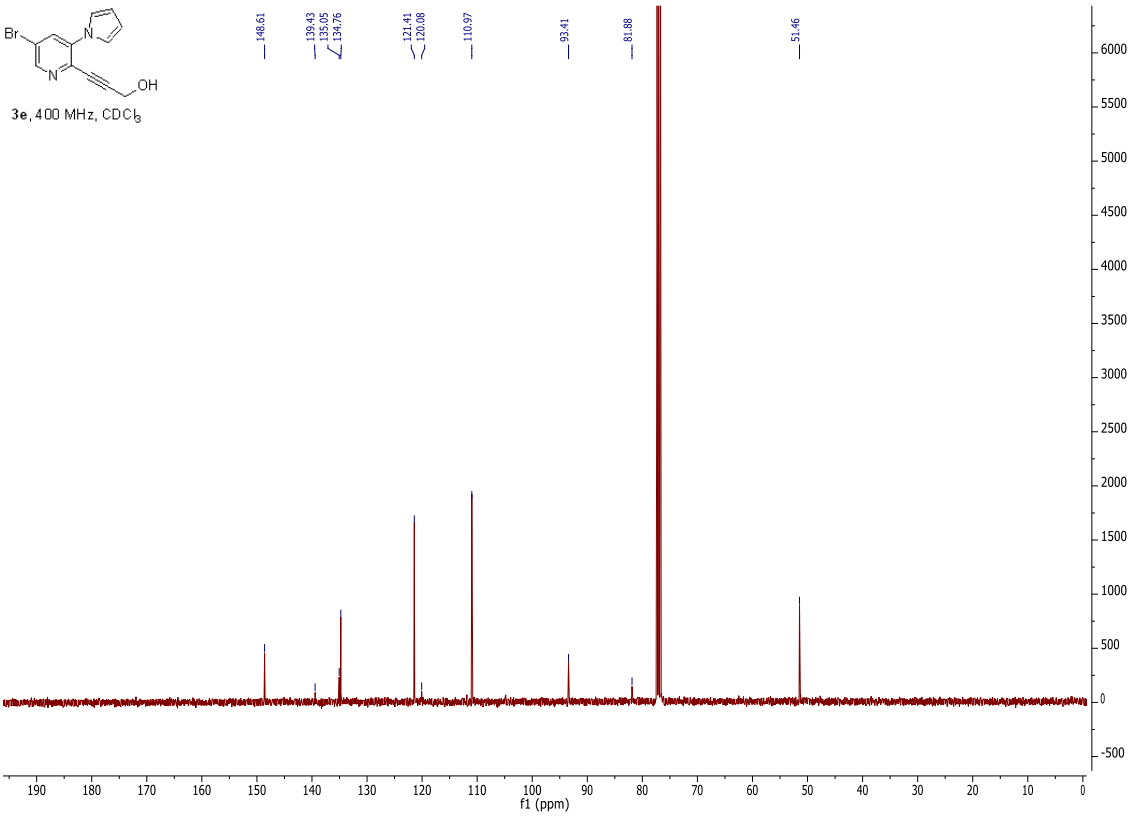
95.53
79.07
51.23
f1 (ppm)


Br
N
N
OH
3e, 400 MHz, CDCl3
8.57
8.57
7.81
7.80
7.10
7.09
7.09
6.38
6.37
6.36
4.44
1.83
1.00
1.05
2.00
2.02
2.06
1.97
f1 (ppm)


Br
N
N
OH
3e, 400 MHz, CDCl3
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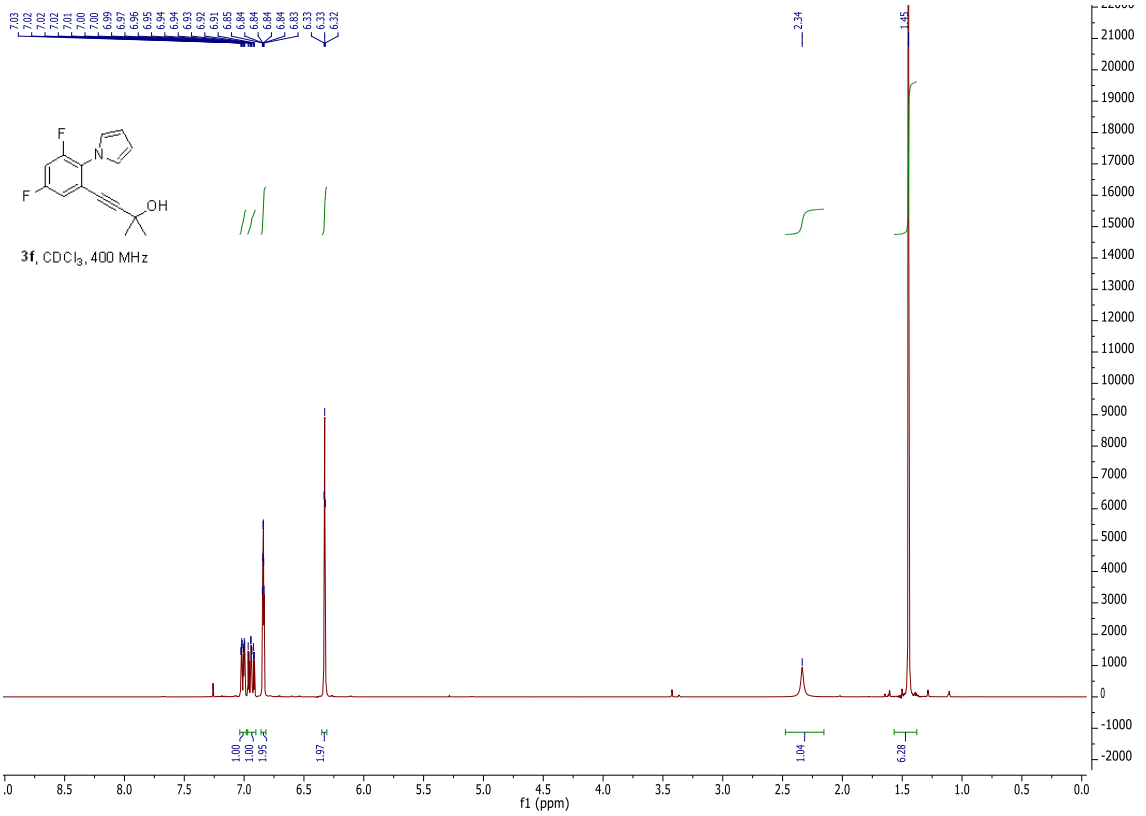
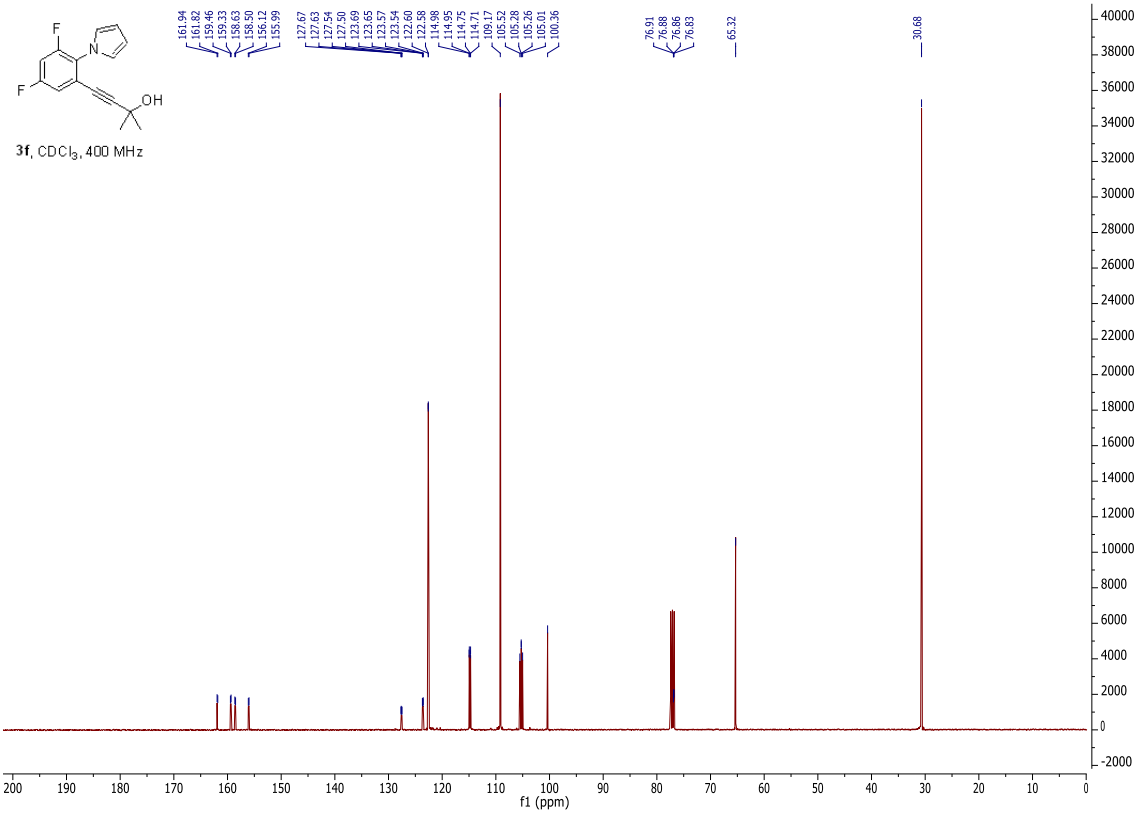
139.43
135.05
134.76
121.41
120.08
110.97
93.41
81.88
51.46
f1 (ppm)


7.03
7.02
7.02
7.02
7.01
7.00
7.00
6.99
6.97
6.96
6.95
6.94
6.93
6.92
6.91
6.85
6.84
6.84
6.84
6.84
6.83
6.33
6.32
2.34
1.45
F
N
F
OH
3f, CDCl3, 400 MHz
1.00
1.00
1.95
1.97
1.04
6.28
f1 (ppm)


161.94
161.82
159.46
159.33
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158.50
156.12
155.99
127.67
127.63
127.54
127.50
123.69
123.65
123.57
123.54
122.60
122.58
114.98
114.95
114.75
114.71
109.17
105.52
105.28
105.26
105.01
100.36
76.91
76.88
76.86
76.83
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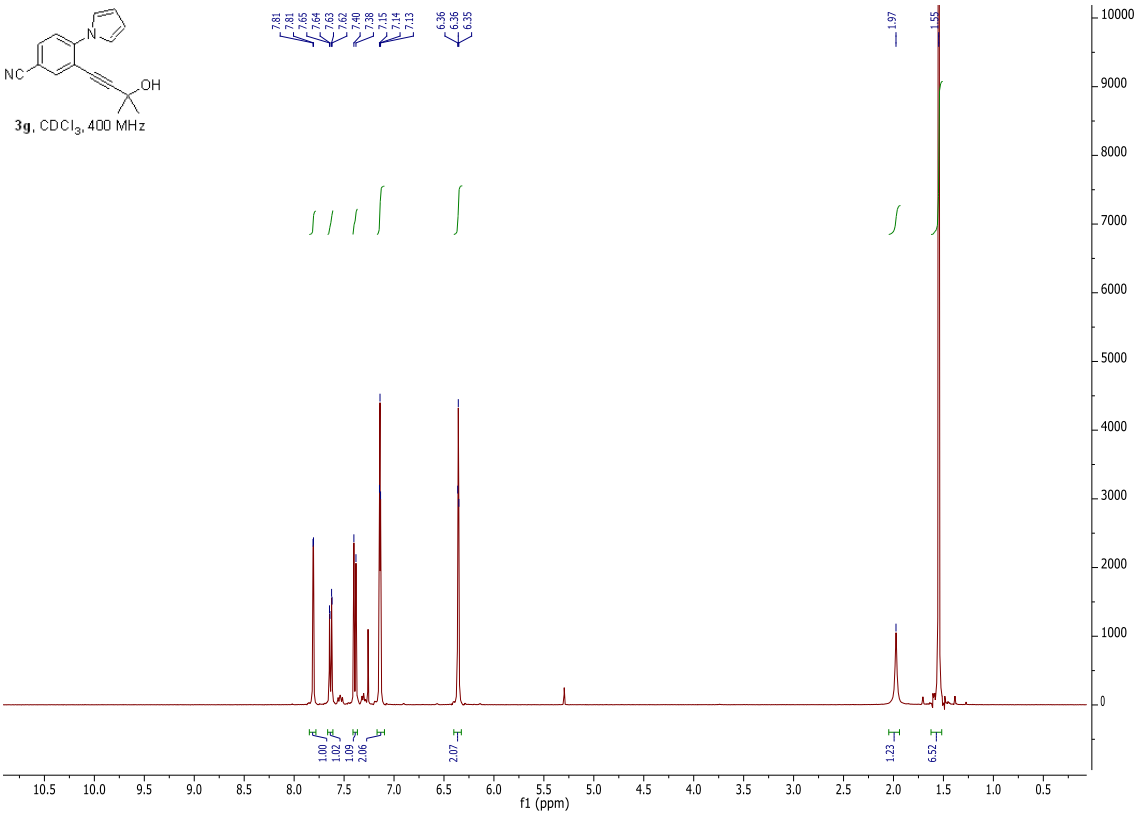
F
N
F
OH
3f, CDCl3, 400 MHz
f1 (ppm)


NC
OH
3g, CDCl3, 400 MHz
7.81
7.81
7.65
7.64
7.63
7.62
7.40
7.38
7.15
7.14
7.13
6.36
6.36
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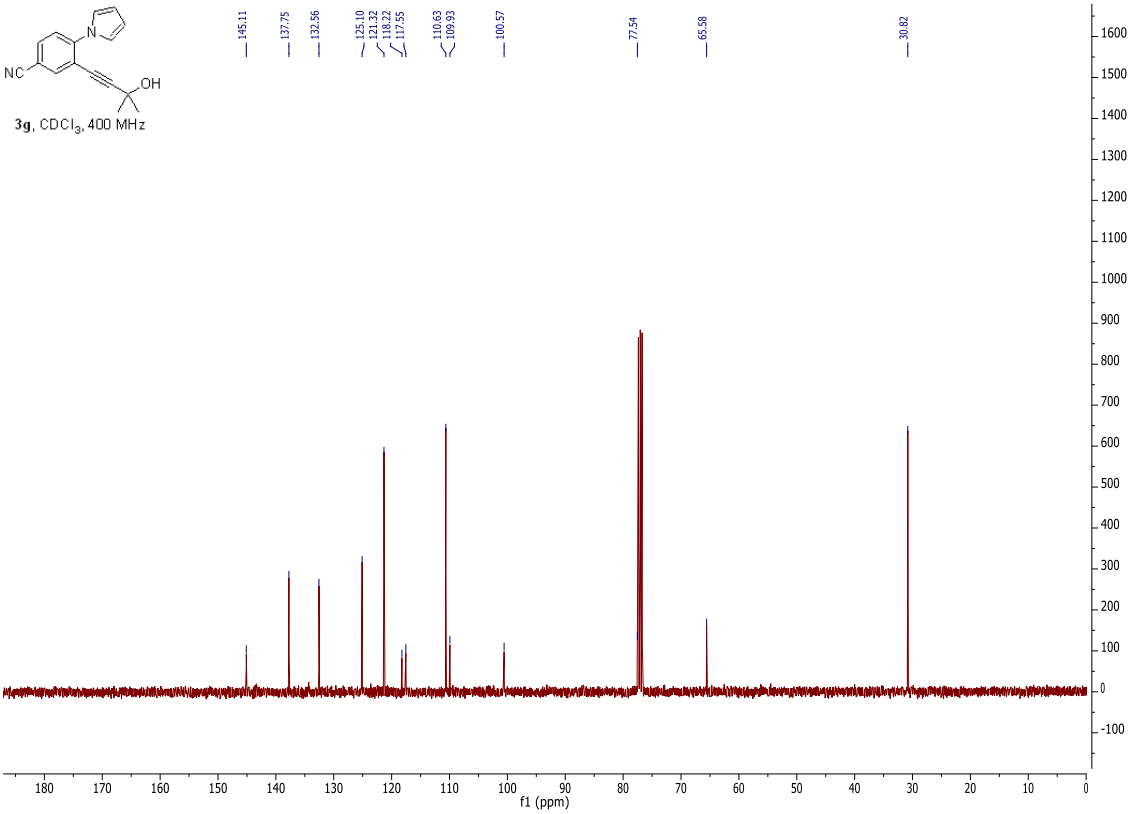
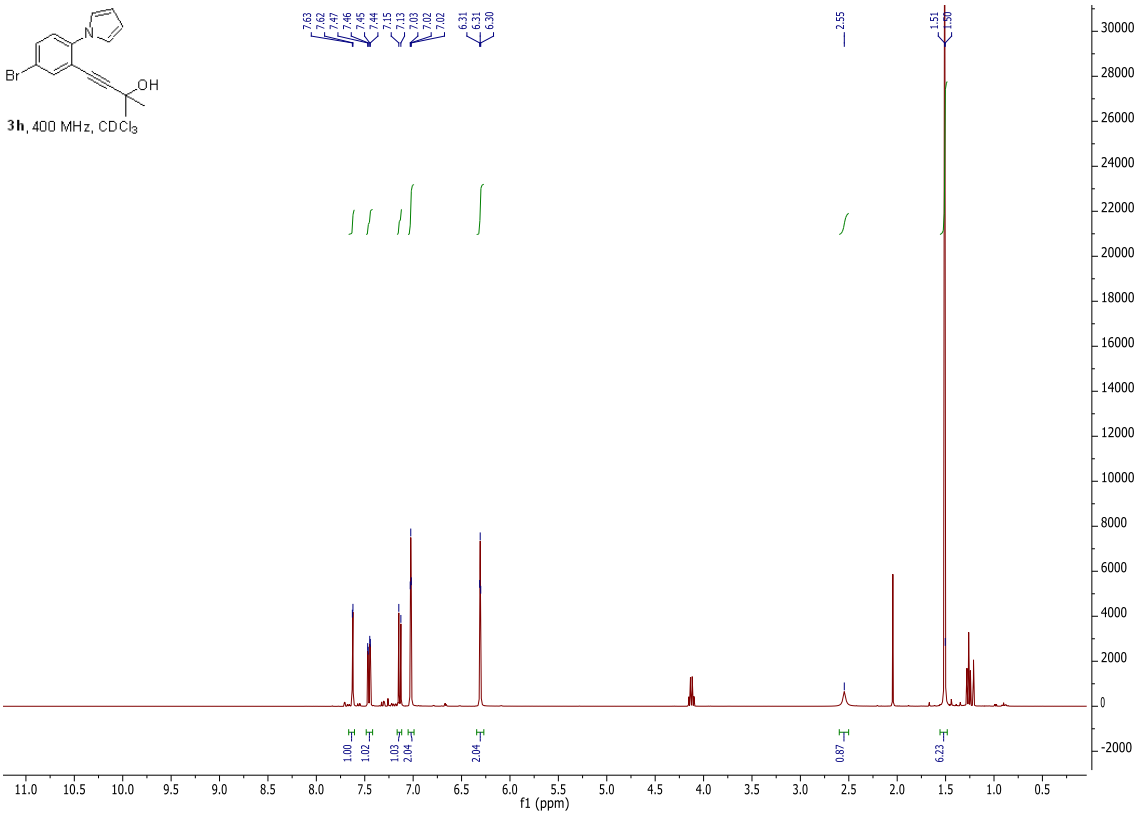
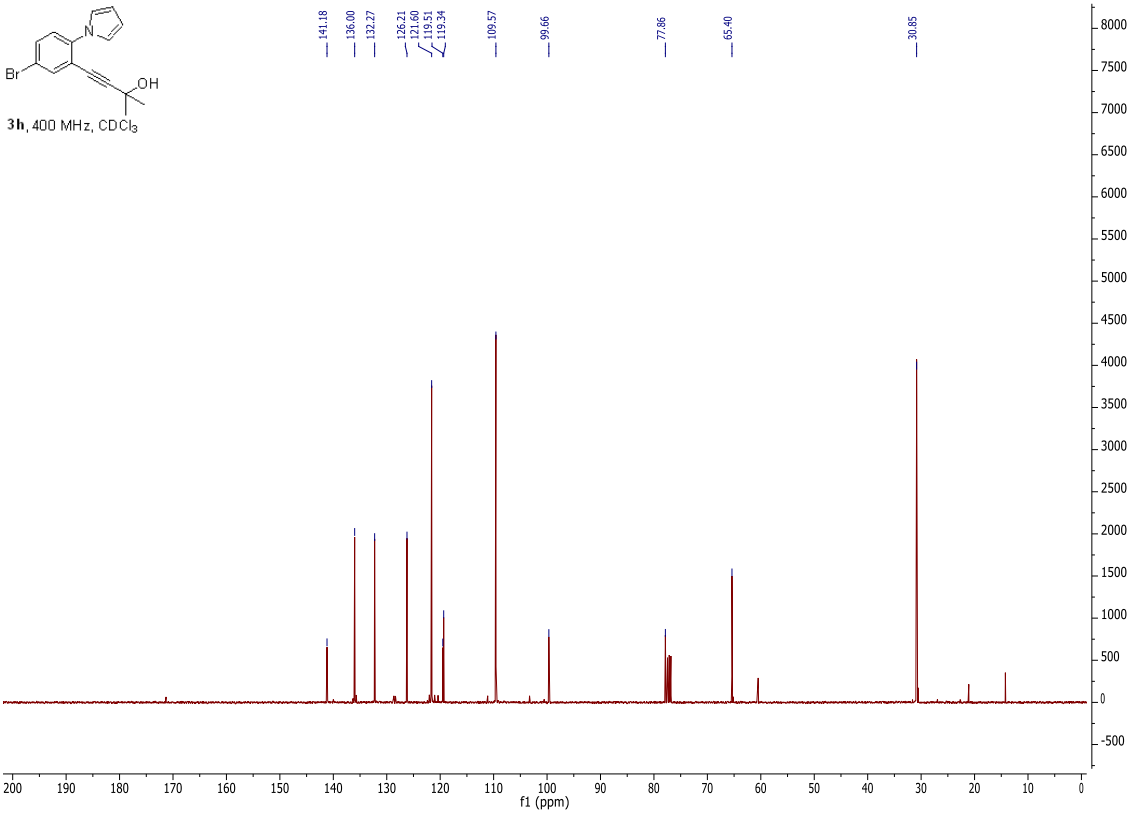
1.09
2.06
2.07
1.23
6.52
f1 (ppm)


NC
OH
3g, CDCl3, 400 MHz
145.11
137.75
132.56
125.10
121.32
118.22
117.55
110.63
109.93
100.57
77.54
65.58
30.82
f1 (ppm)


Br
OH
3h, 400 MHz, CDCl3
7.63
7.62
7.47
7.46
7.45
7.44
7.15
7.13
7.03
7.02
7.02
6.31
6.31
6.30
2.55
1.51
1.50
1.00
1.02
1.03
2.04
2.04
0.87
6.23
f1 (ppm)


Br
OH
3h, 400 MHz, CDCl3
141.18
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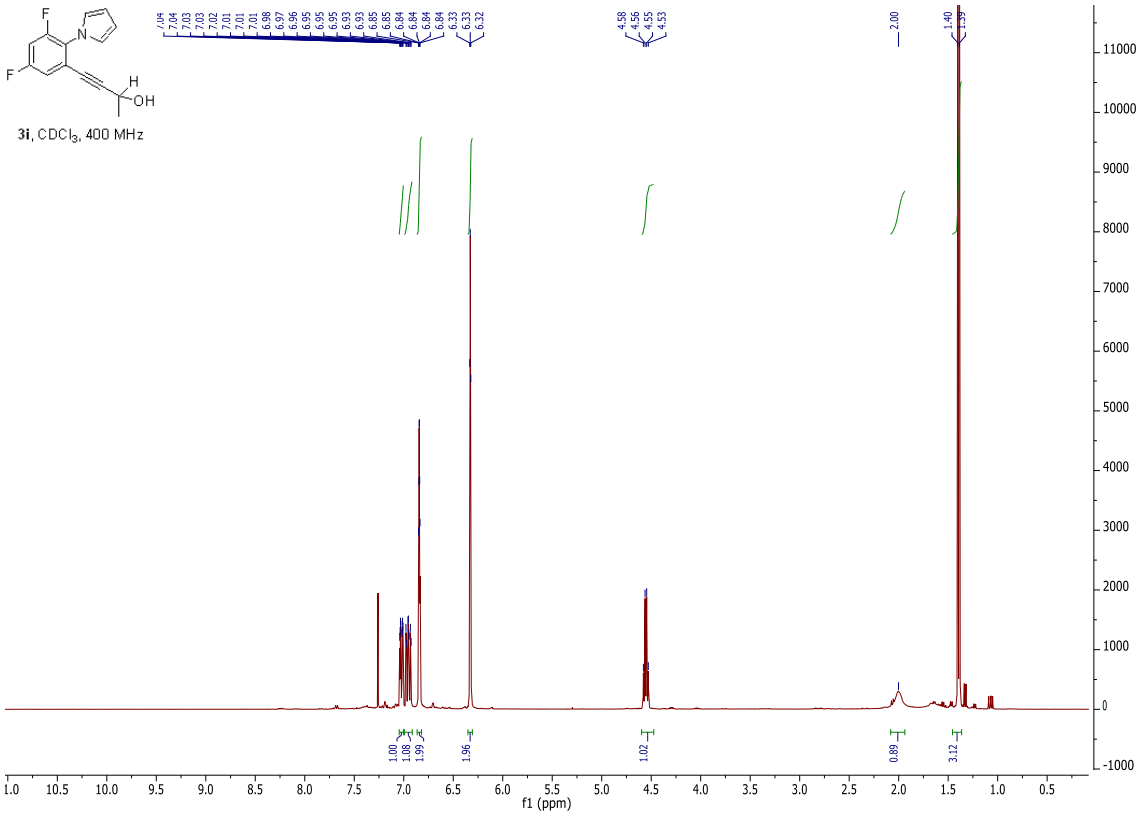
121.60
119.51
119.34
109.57
99.66
77.86
65.40
30.85
f1 (ppm)


3i, CDCl3, 400 MHz
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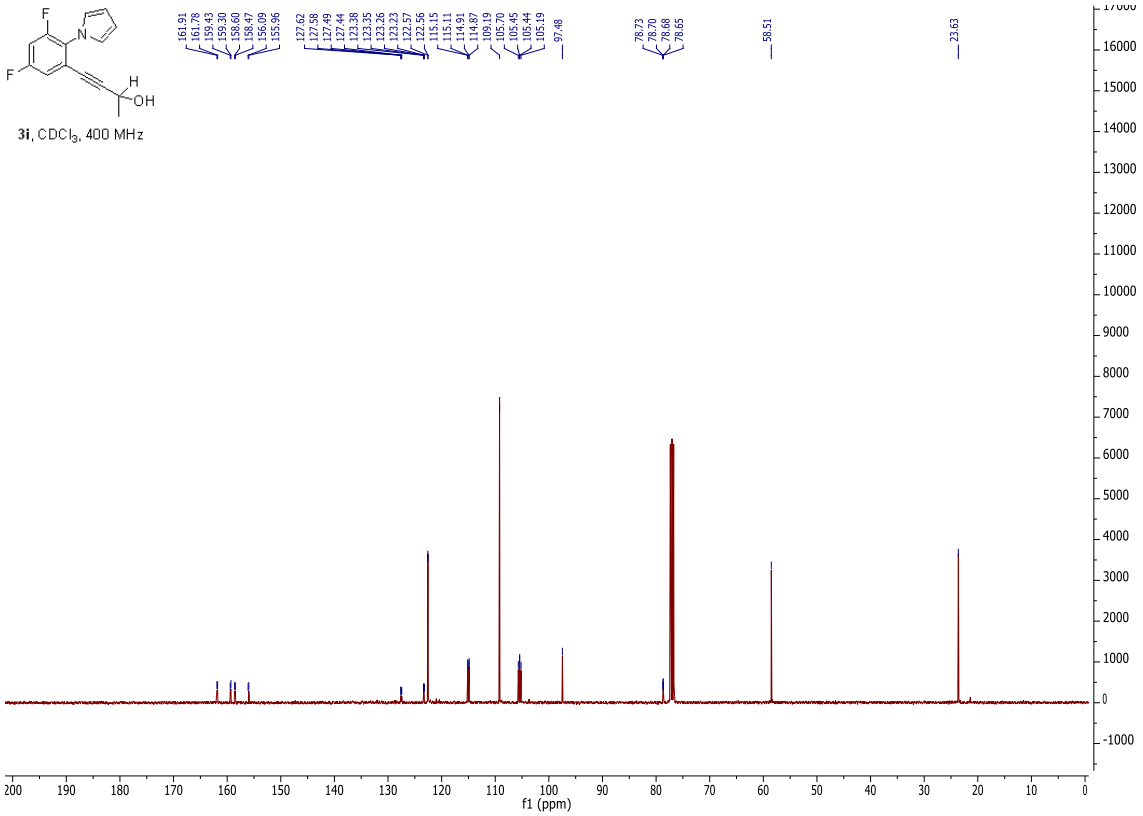
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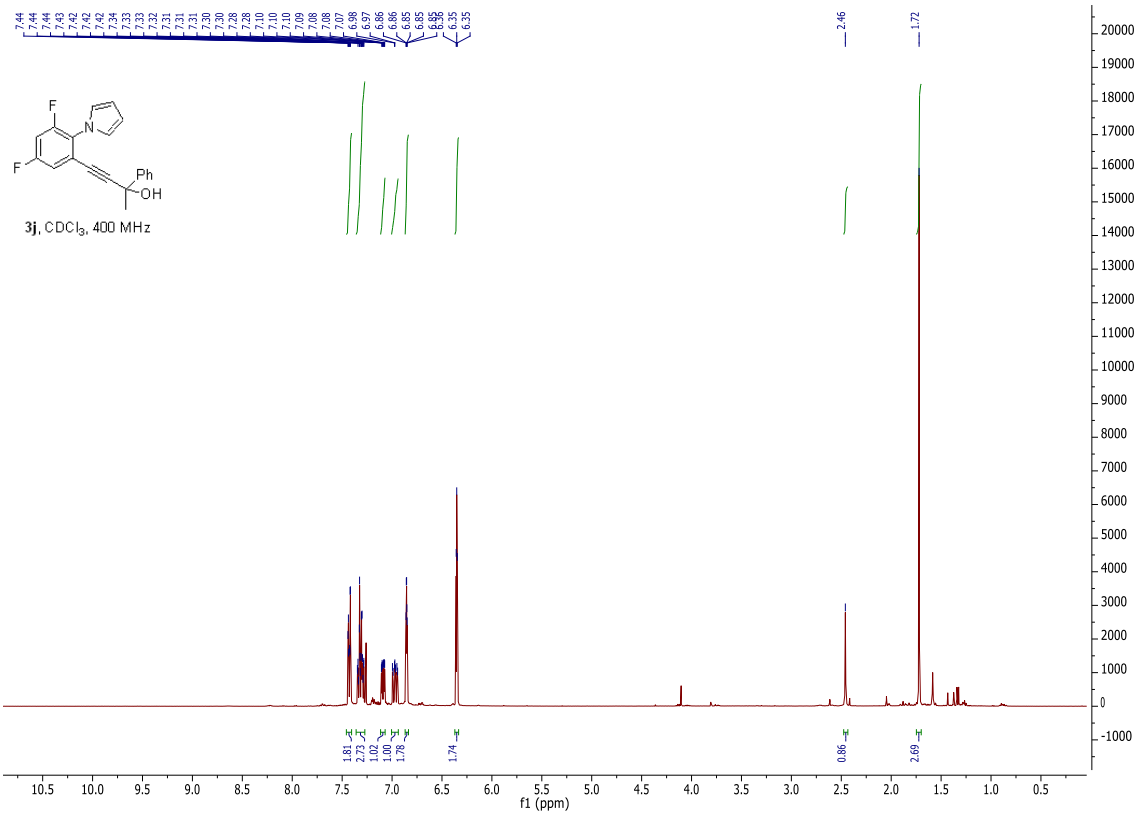
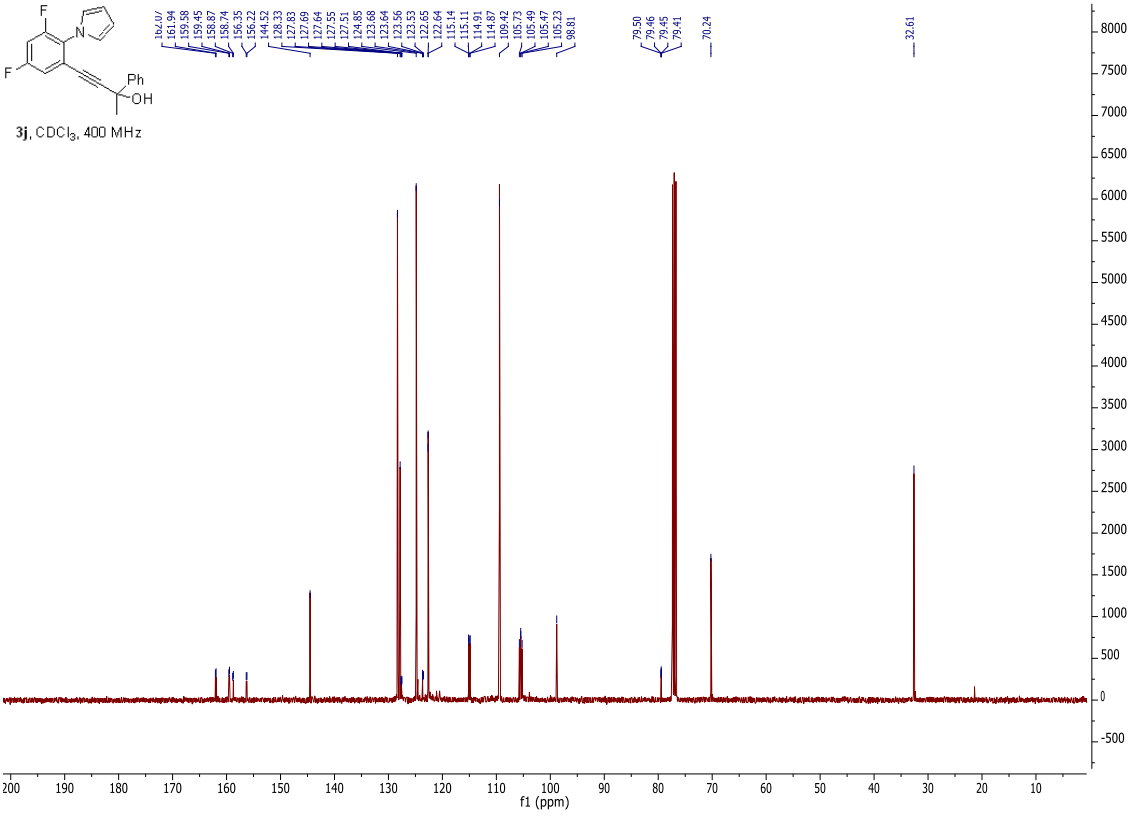
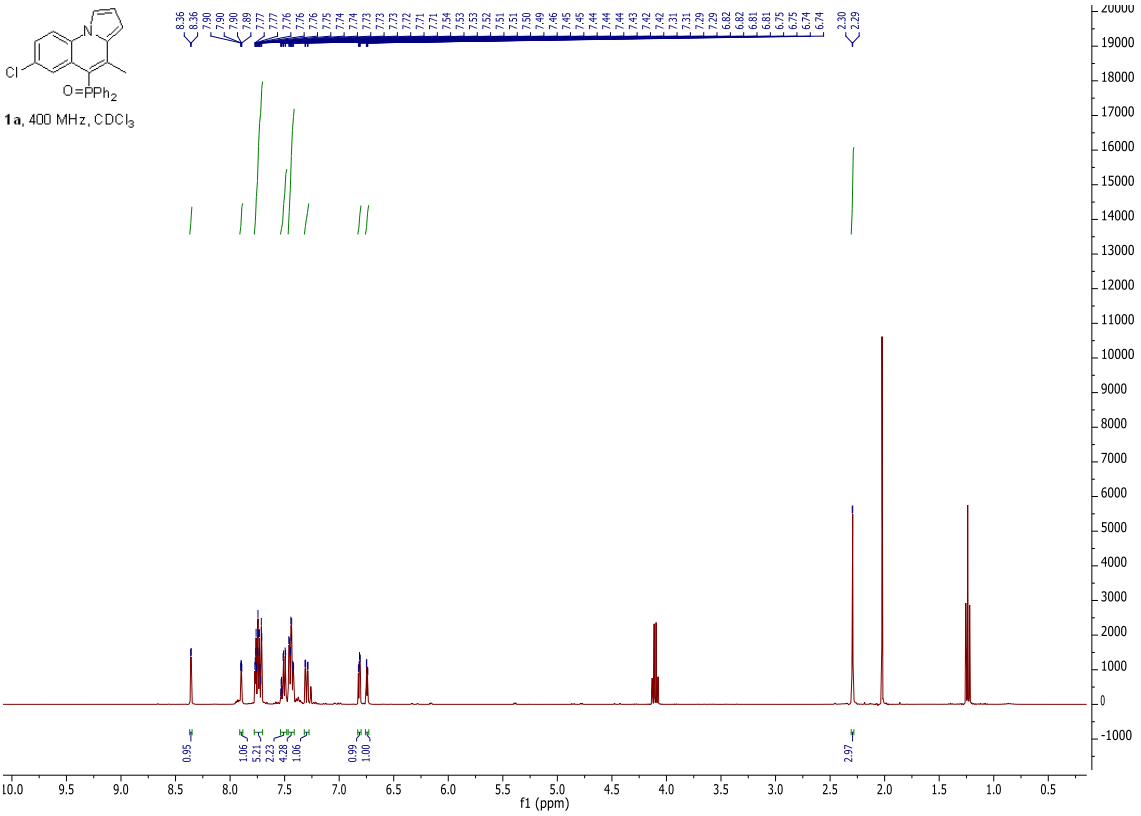
f1 (ppm)


F
N
F
Ph
OH
3j, CDCl3, 400 MHz
f1 (ppm)


F
N
F
Ph
OH
3j, CDCl3, 400 MHz
f1 (ppm)


Cl
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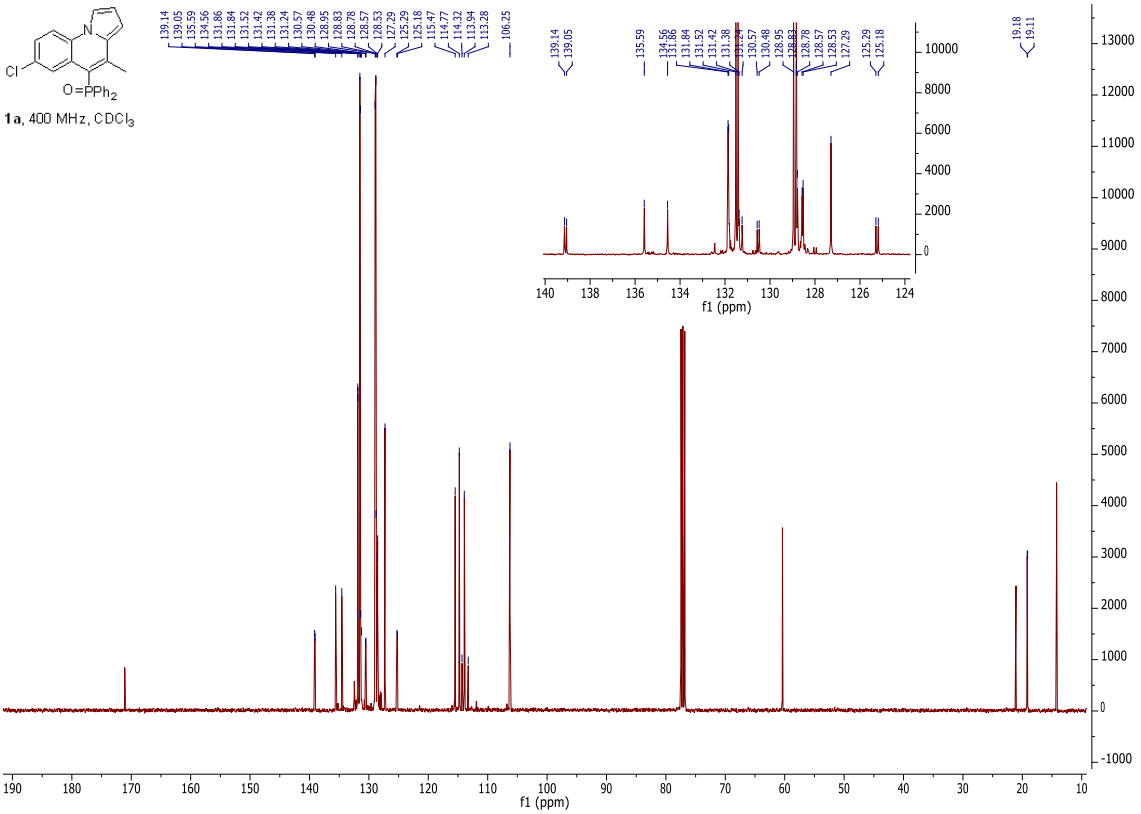
1a, 400 MHz, CDCl3
f1 (ppm)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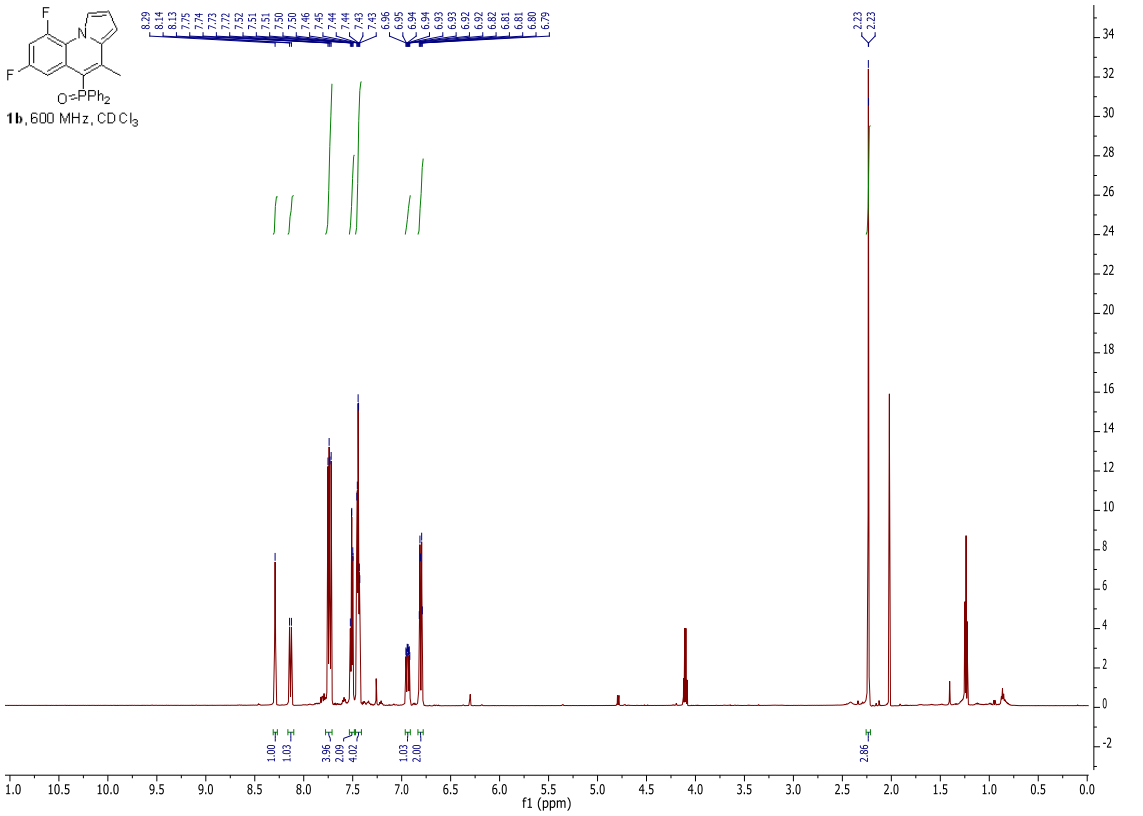
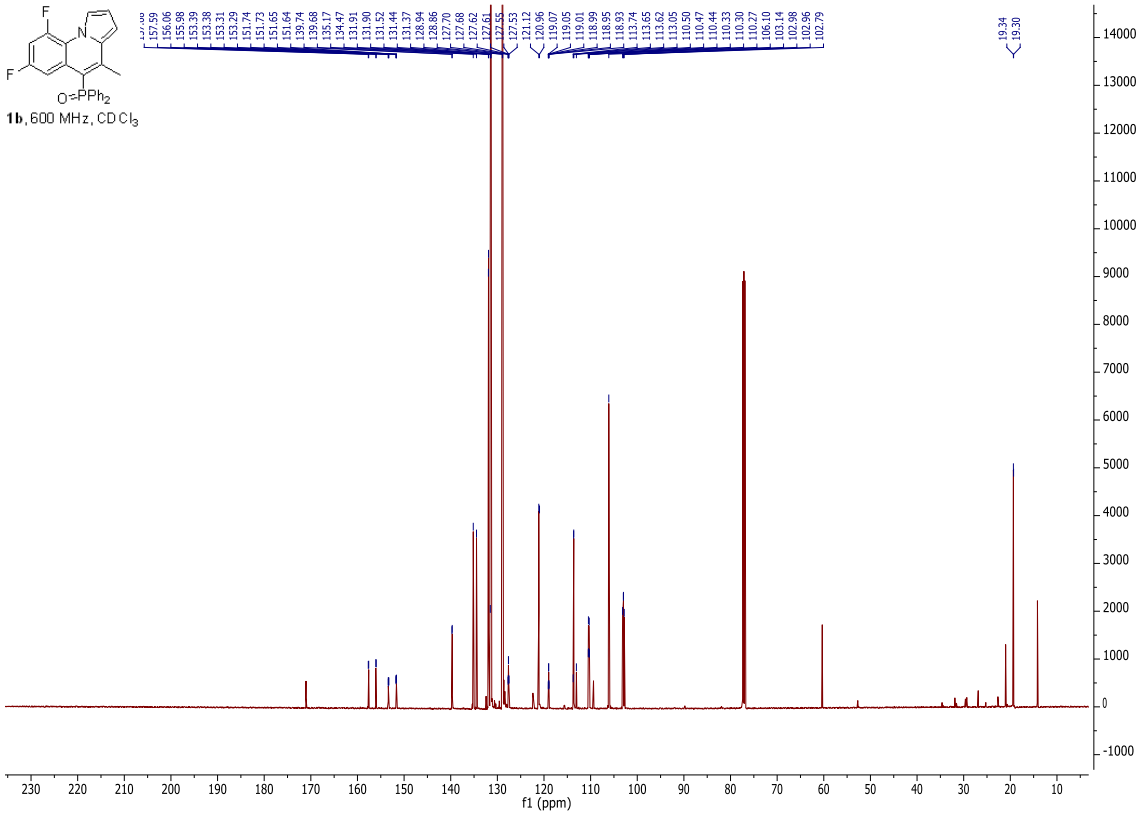
1a, 400 MHz, CDCl3
f1 (ppm)


F
F
N
O=PPh2
1b, 600 MHz, CDCl3
f1 (ppm)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F
N
O=PPh2
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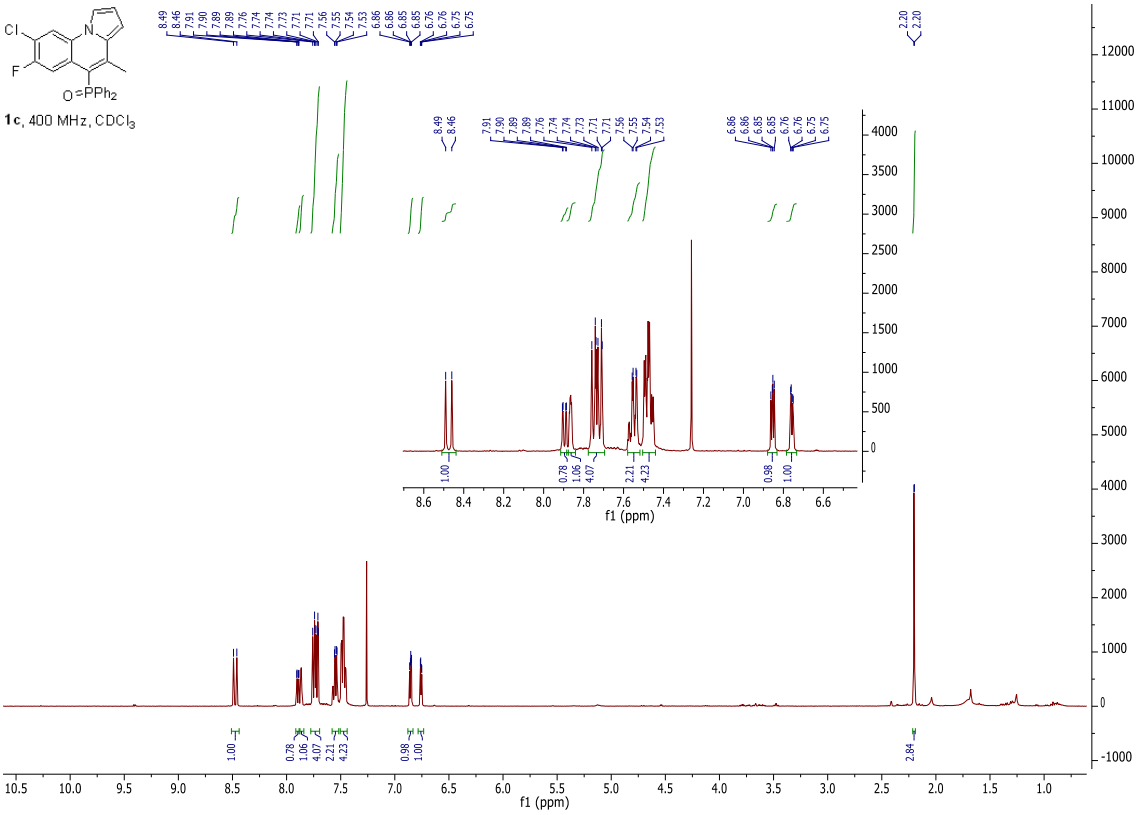
f1 (ppm)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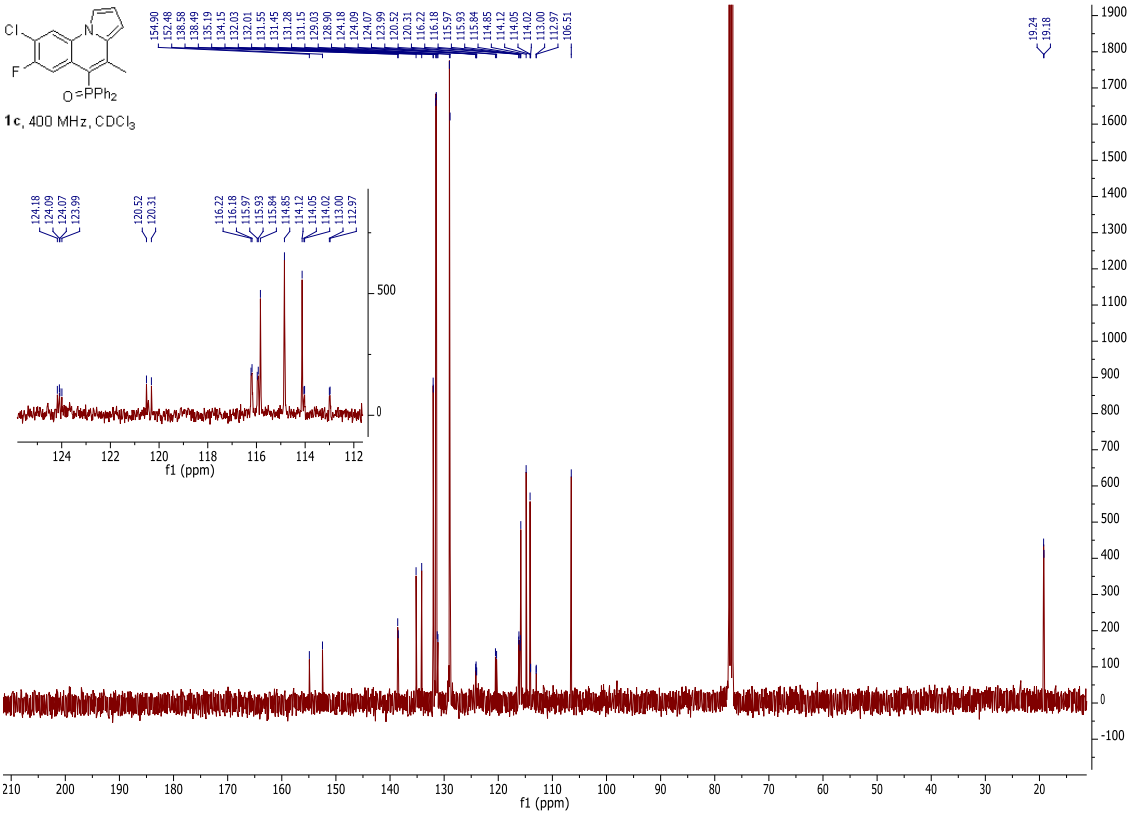
f1 (ppm)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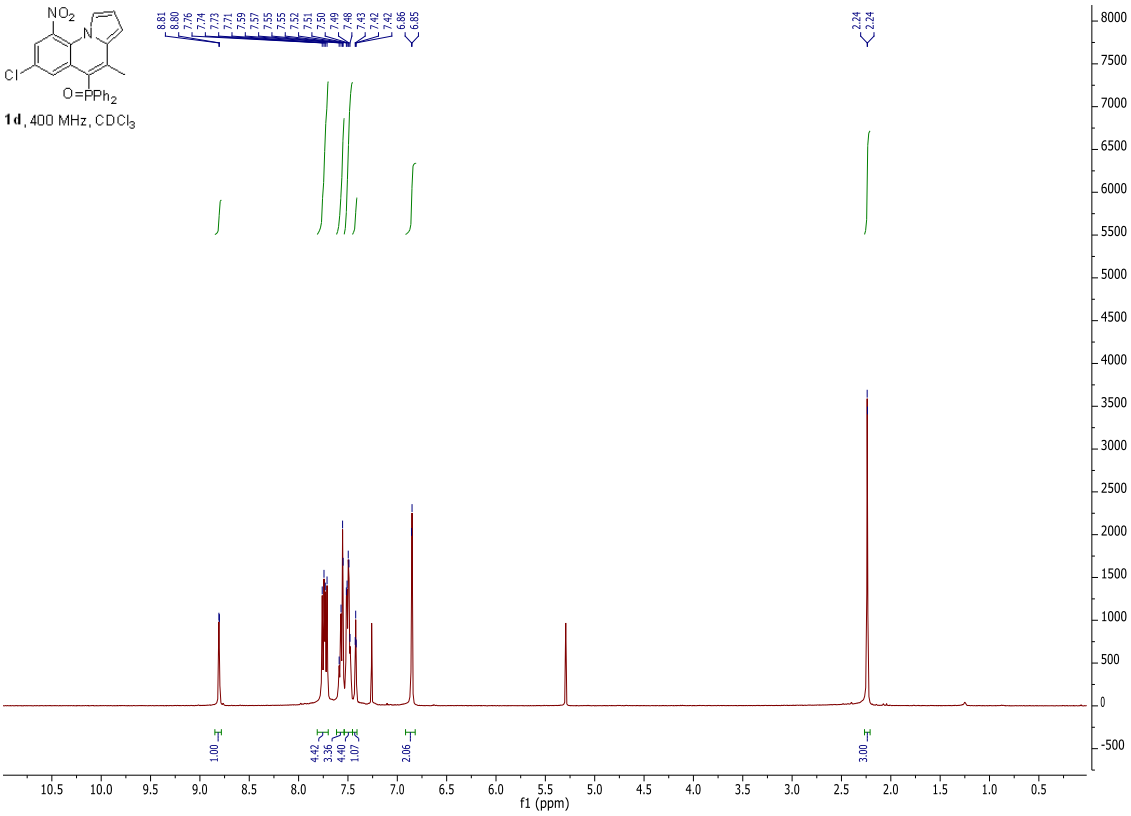
f1 (ppm)


NO2
N
Cl
O=PPh2
1d, 400 MHz, CDCl3
8.81
8.80
7.76
7.74
7.73
7.71
7.59
7.57
7.55
7.55
7.52
7.51
7.50
7.49
7.48
7.43
7.42
7.42
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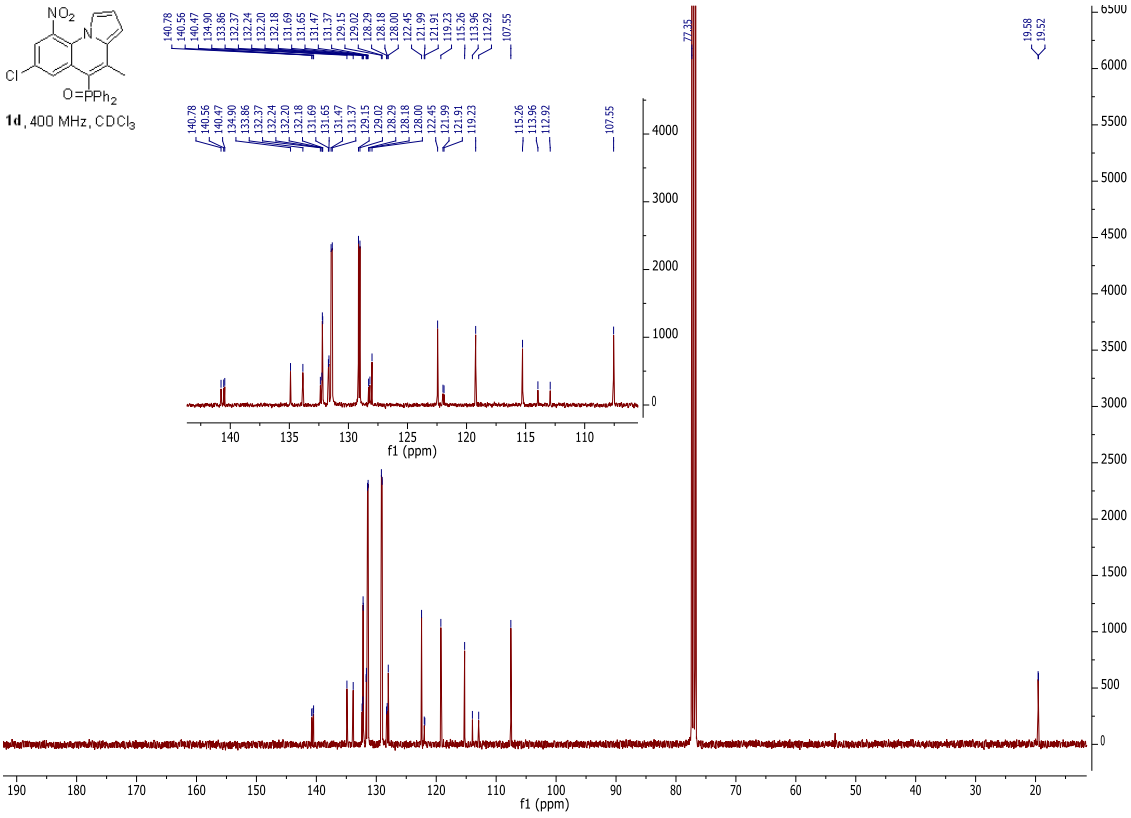
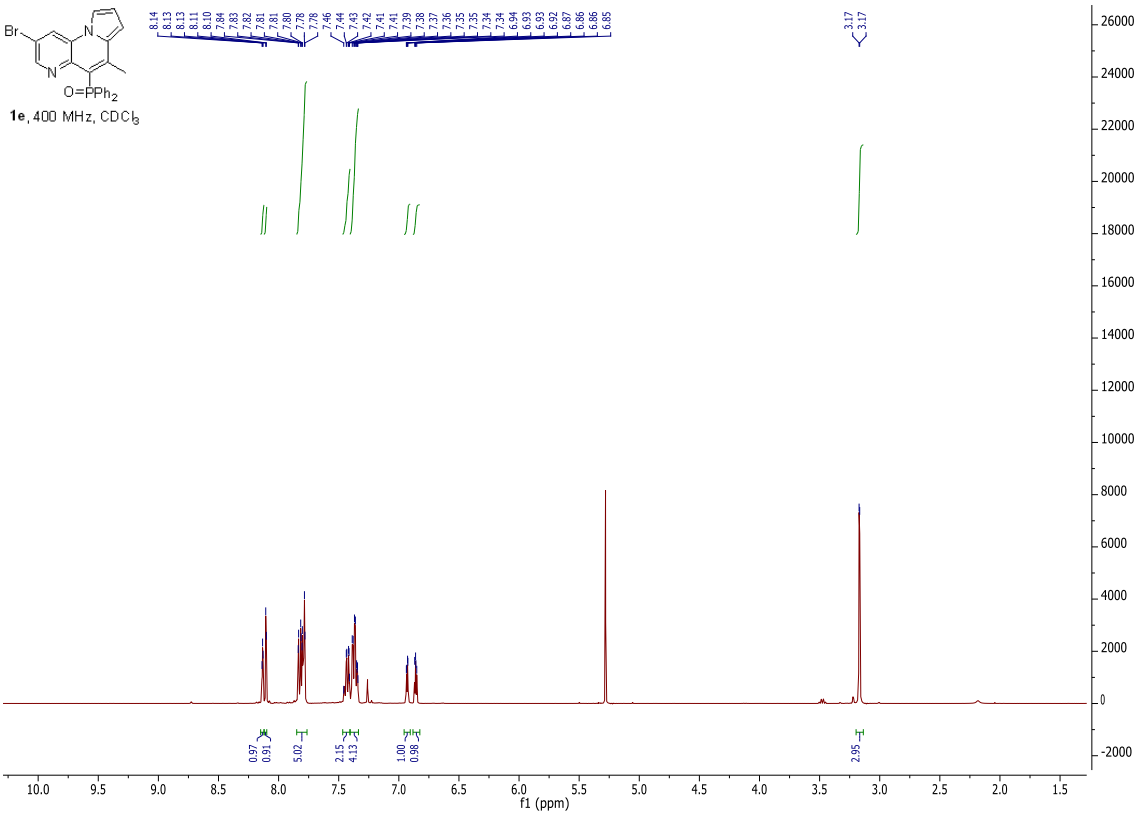
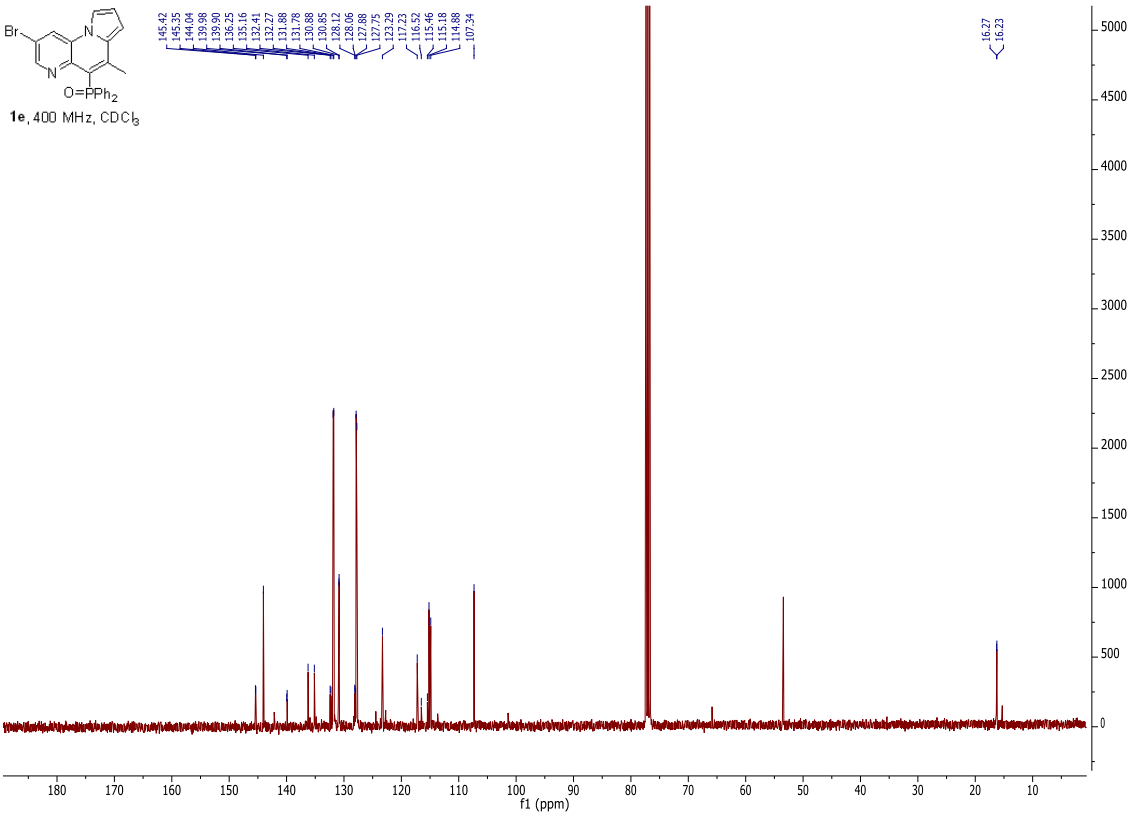
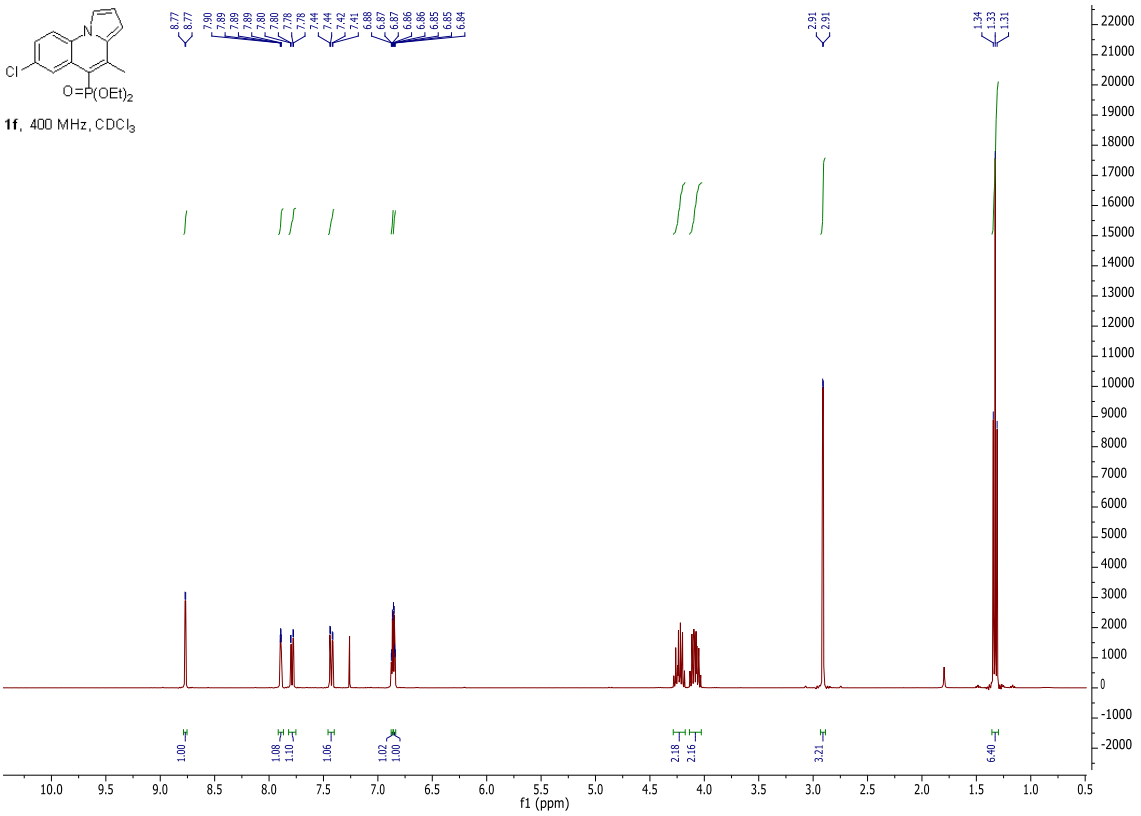
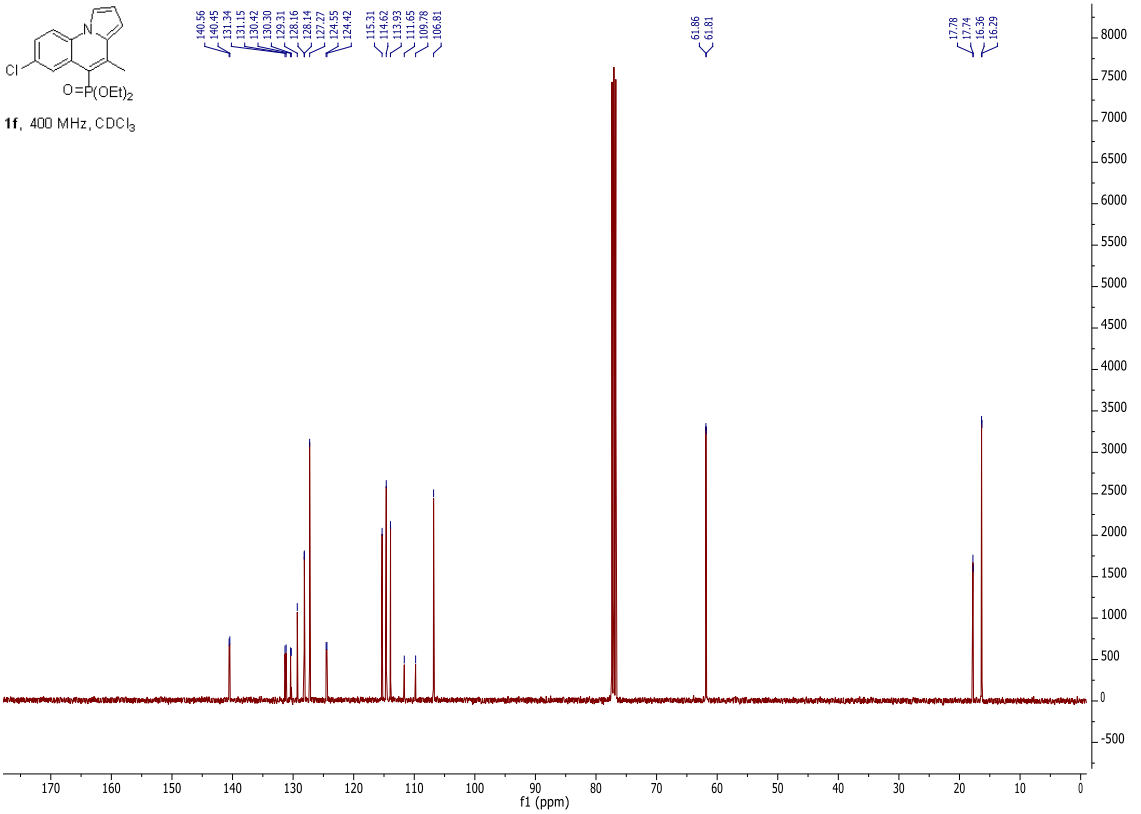
4.40
1.07
2.06
3.00
f1 (ppm)

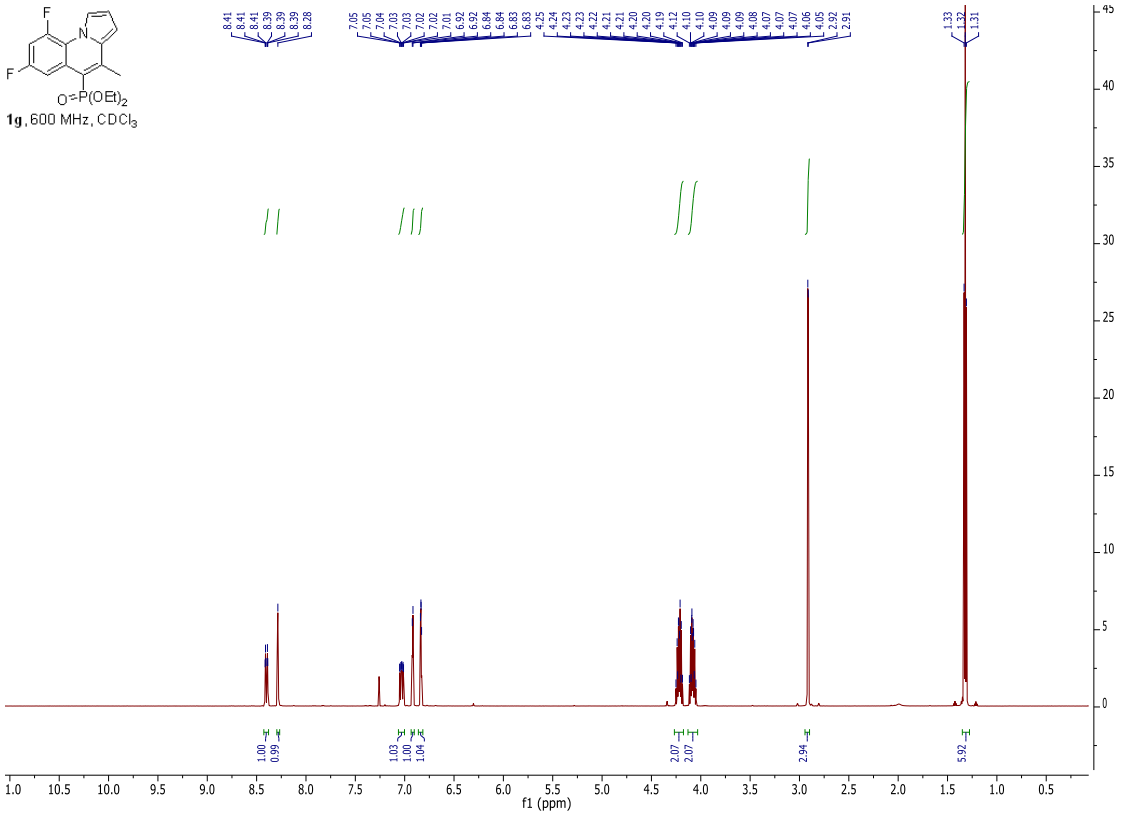

NO2
N
Cl
O=PPh2
1d, 400 MHz, CDCl3
140.78
140.56
140.47
134.90
133.86
132.37
132.24
132.20
132.18
131.69
131.65
131.47
131.37
129.15
129.02
128.29
128.18
128.00
122.45
121.99
121.91
119.23
115.26
113.96
112.92
107.55
77.35
19.58
19.52
f1 (ppm)

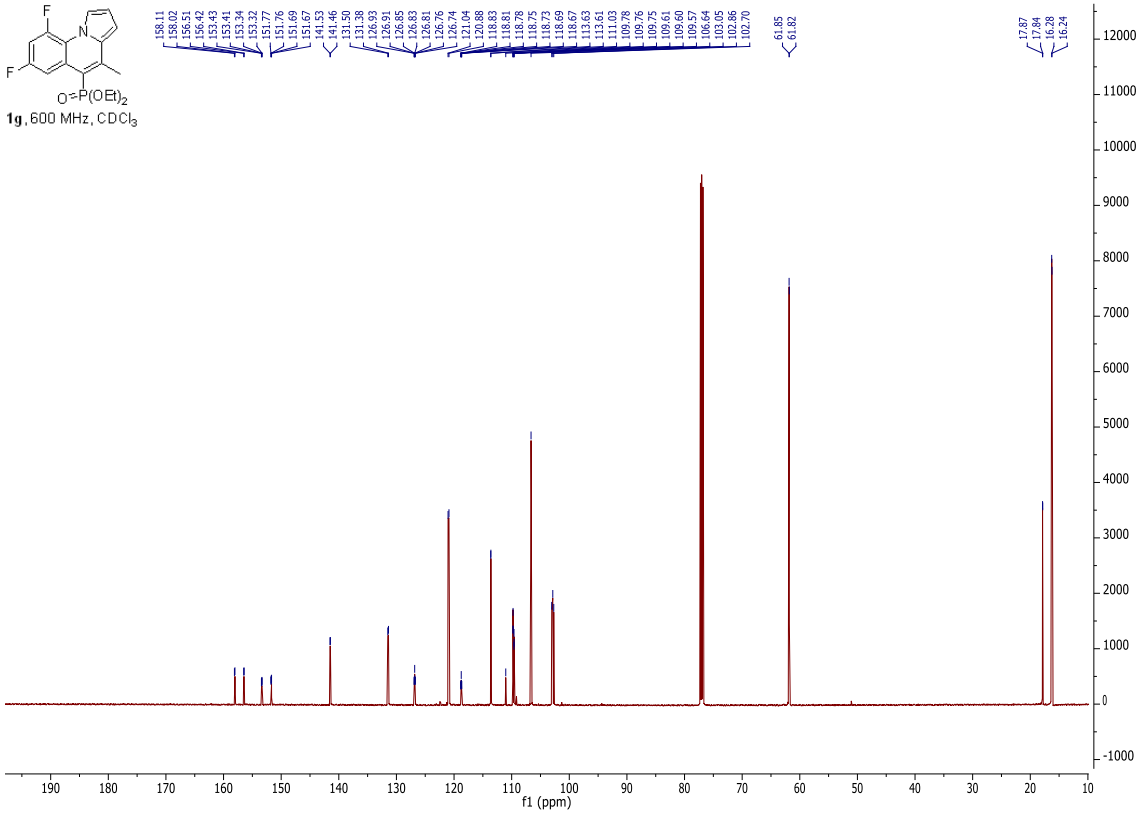

Br
N
N
O=PPh2
1e, 400 MHz, CDCl3
8.14
8.13
8.13
8.11
8.10
7.84
7.83
7.82
7.81
7.81
7.80
7.78
7.78
7.46
7.44
7.43
7.42
7.41
7.41
7.39
7.38
7.37
7.36
7.35
7.35
7.34
7.34
6.94
6.93
6.93
6.92
6.87
6.86
6.86
6.85
3.17
3.17
0.97
0.91
5.02
2.15
4.13
1.00
0.98
2.95
f1 (ppm)

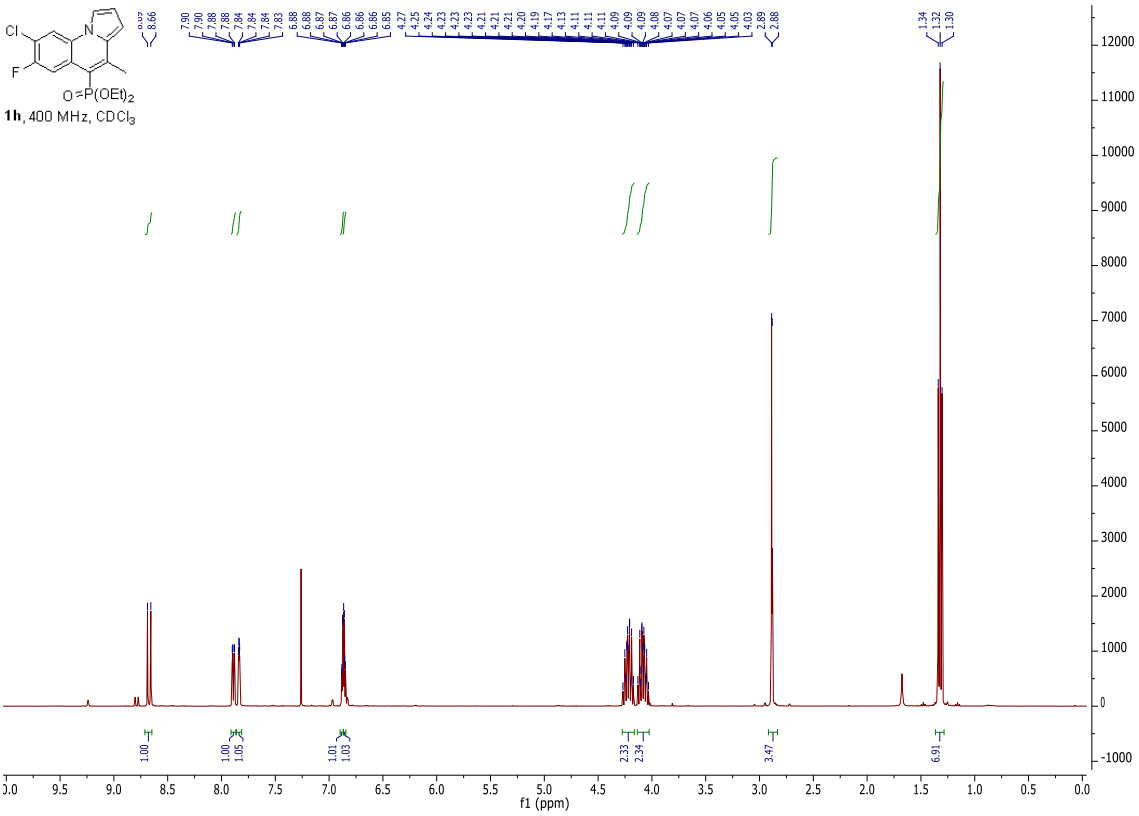

Br
N
N
O=PPh2
1e, 400 MHz, CDCl3
145.42
145.35
144.04
139.98
139.90
136.25
135.16
132.41
132.27
131.88
131.78
130.88
130.85
128.12
128.06
127.88
127.75
123.29
117.23
116.52
115.46
115.18
114.88
107.34
16.27
16.23
f1 (ppm)

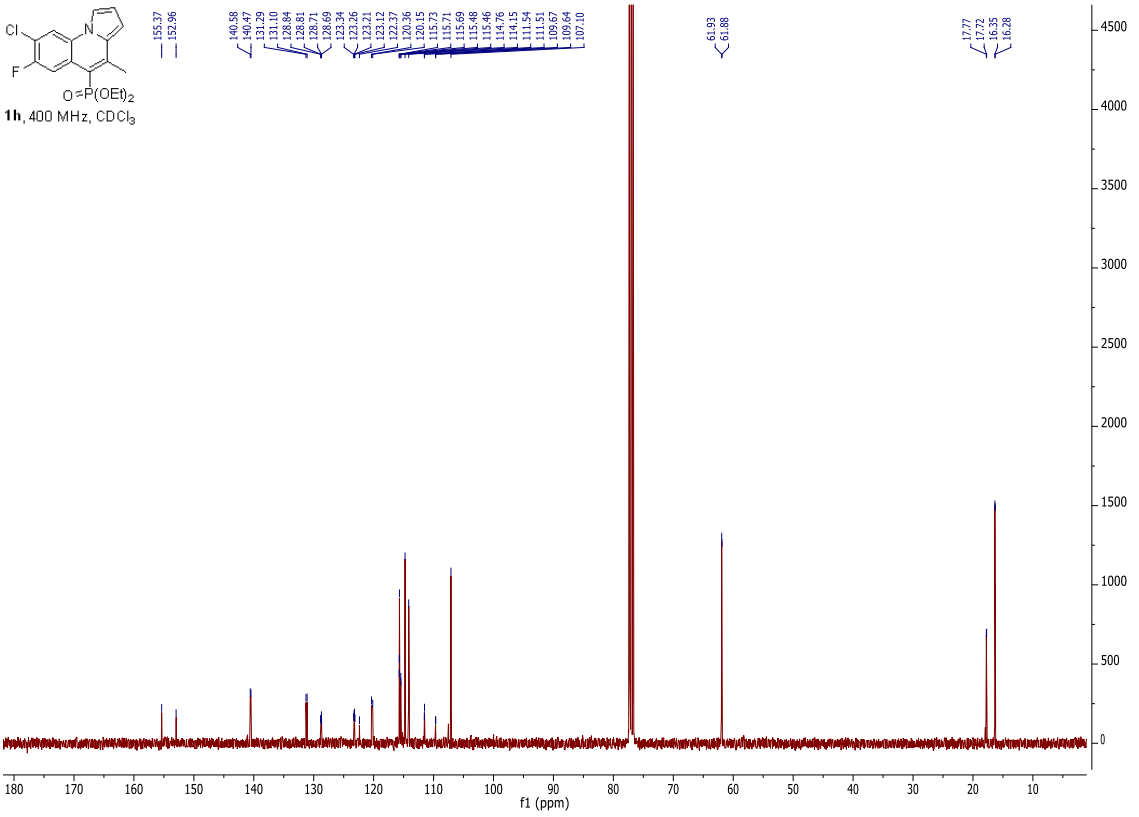

1f, 400 MHz, CDCl3
f1 (ppm)

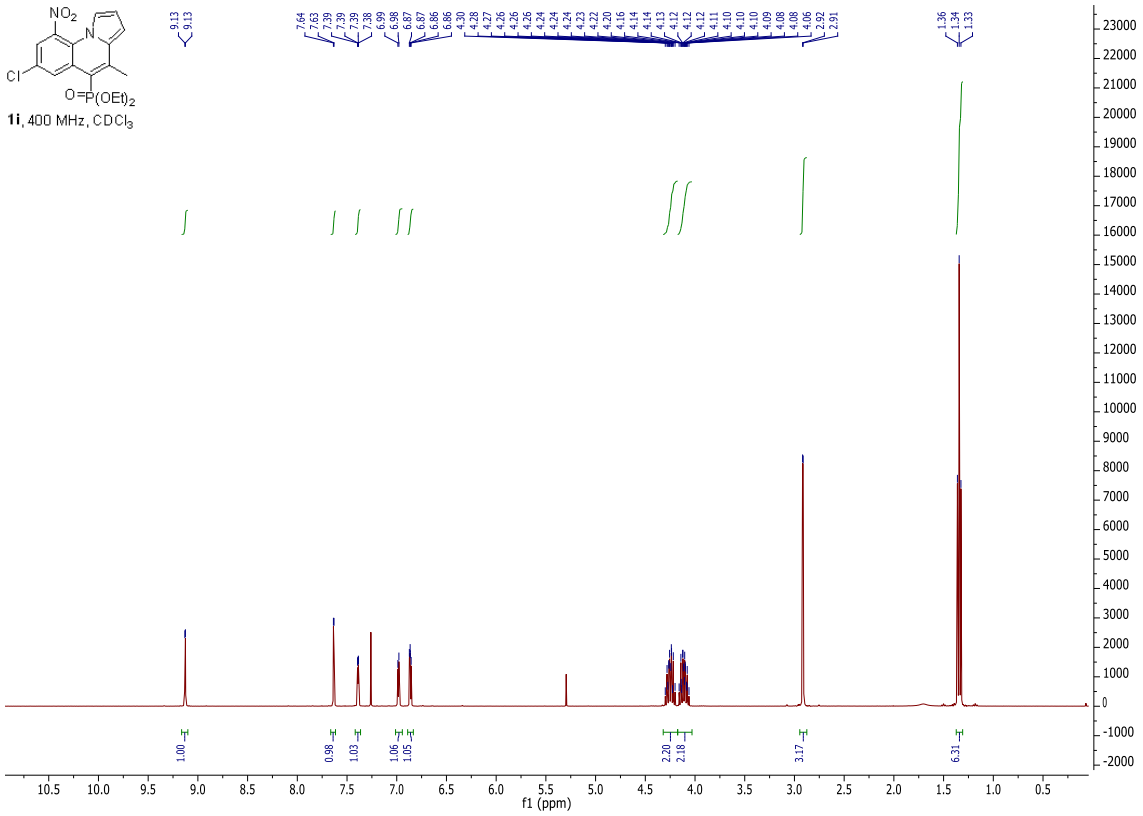

1f, 400 MHz, CDCl3
f1 (ppm)

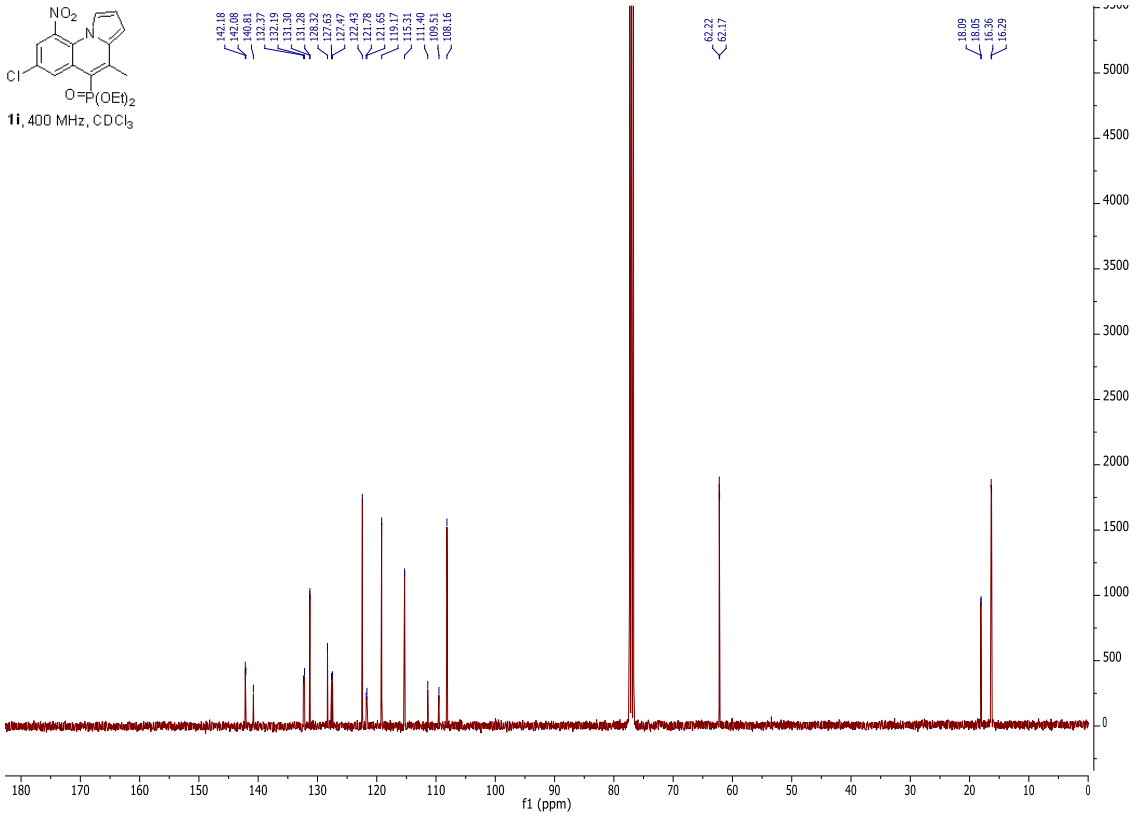

F
F
N
O=P(OEt)2
1g, 600 MHz, CDCl3
f1 (ppm)

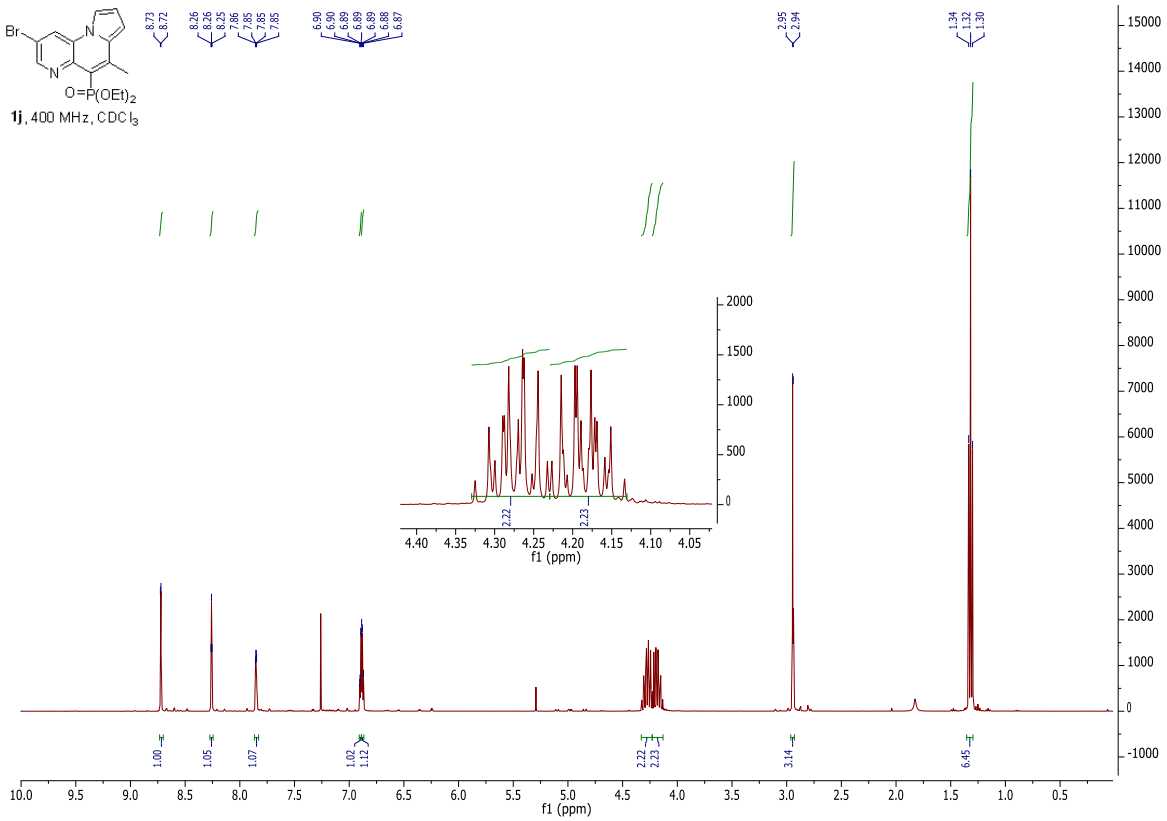

F
F
N
O=P(OEt)2
1g, 600 MHz, CDCl3
f1 (ppm)

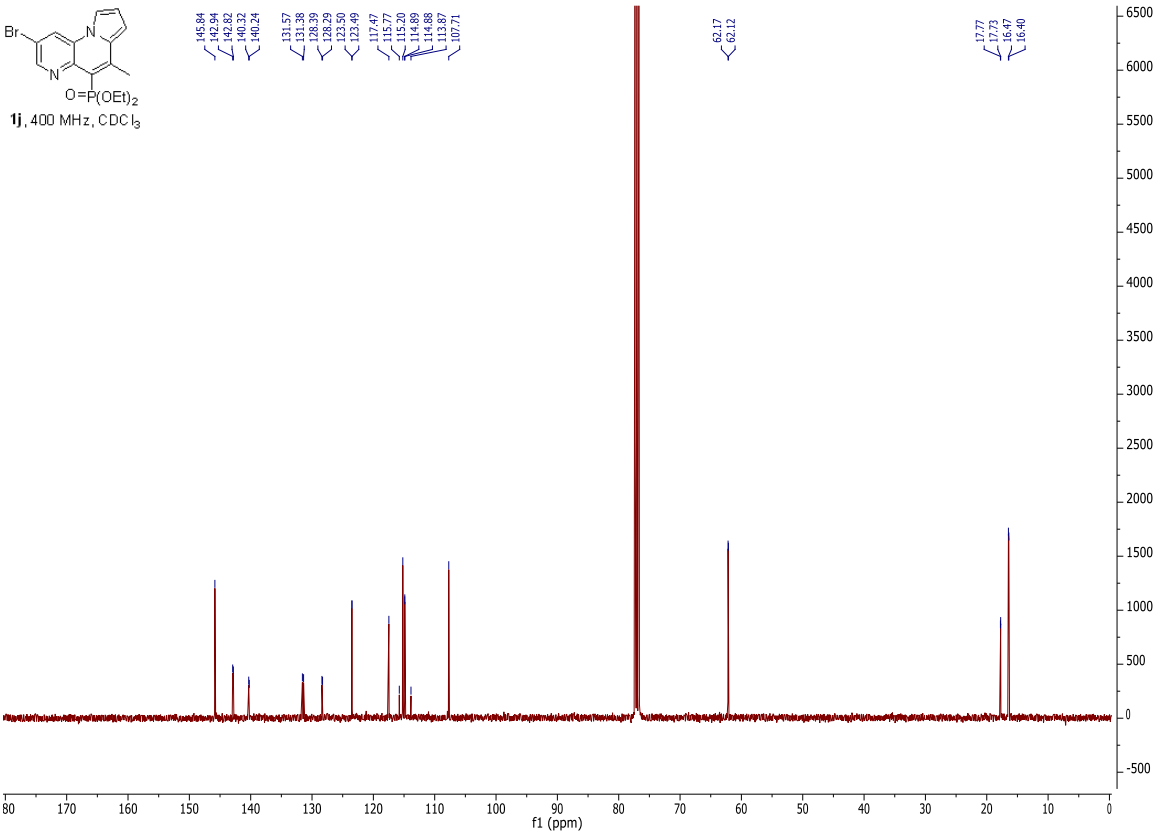

Cl
F
N
O=P(OEt)2
1h, 400 MHz, CDCl3
f1 (ppm)

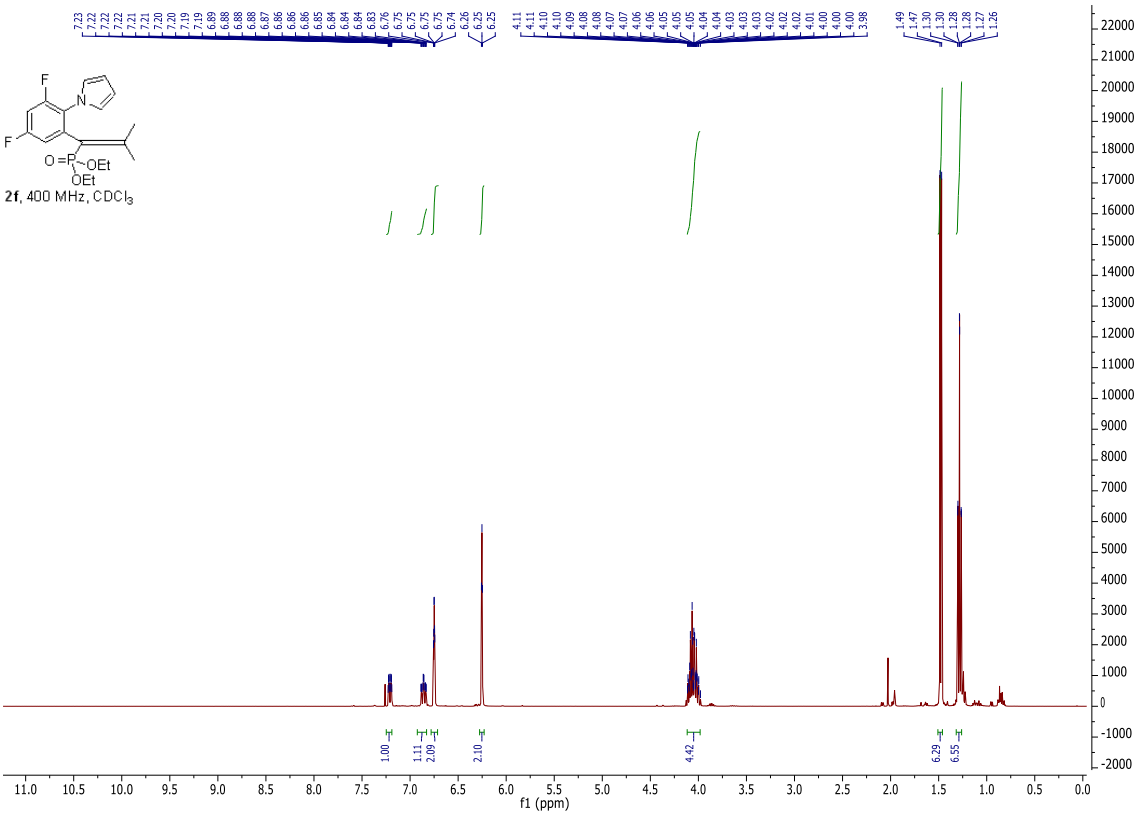

Cl
F
N
O=P(OEt)2
1h, 400 MHz, CDCl3
f1 (ppm)

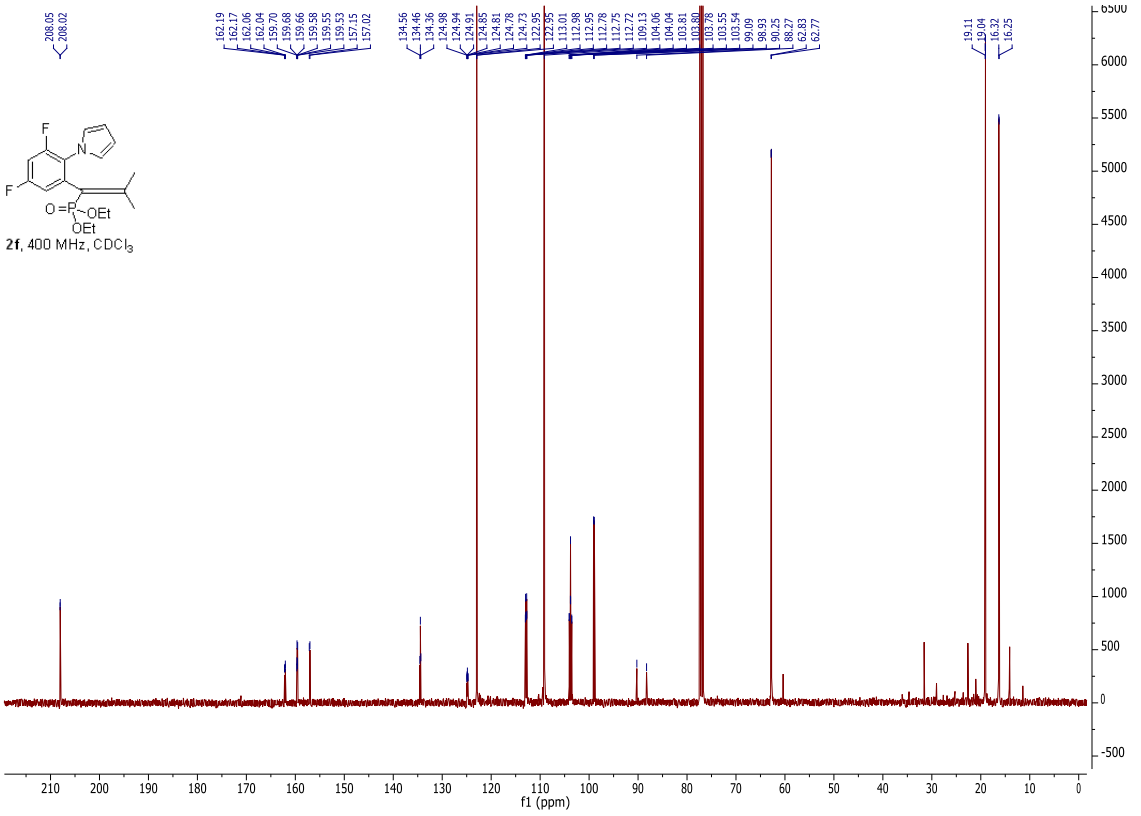

1i, 400 MHz, CDCl3
f1 (ppm)

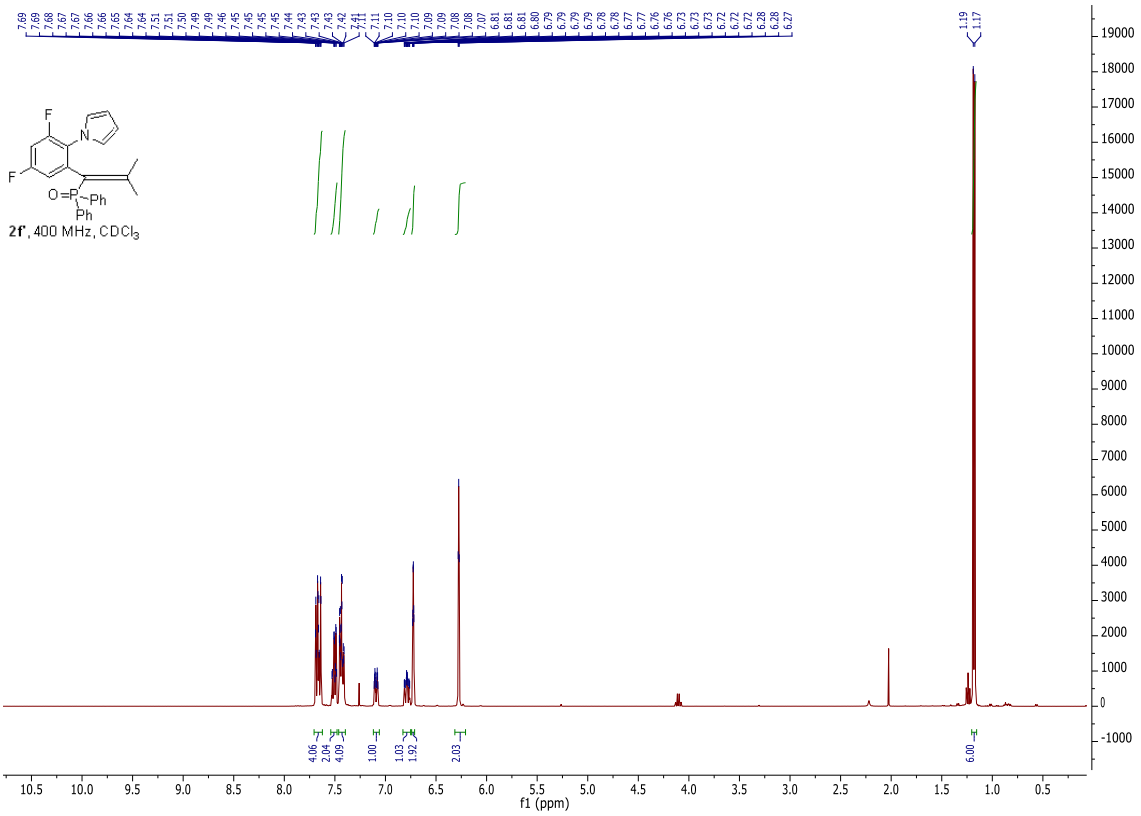

1i, 400 MHz, CDCl3
f1 (ppm)

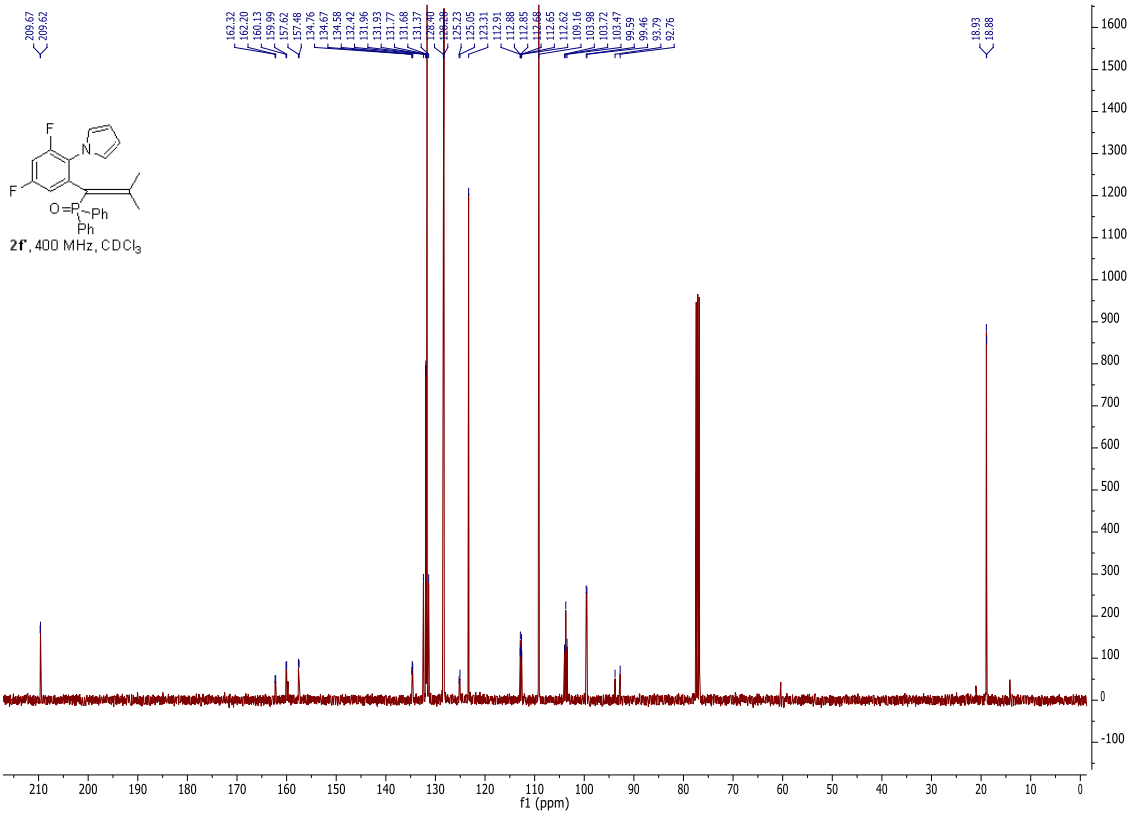

Br
N
N
O=P(OEt)2
1j, 400 MHz, CDCl3
8.73
8.72
8.26
8.26
8.25
7.86
7.85
7.85
7.85
6.90
6.90
6.89
6.89
6.88
6.88
6.87
2.95
2.94
1.34
1.32
1.30
1.00
1.05
1.07
1.02
1.12
2.22
2.23
3.14
6.45
f1 (ppm)

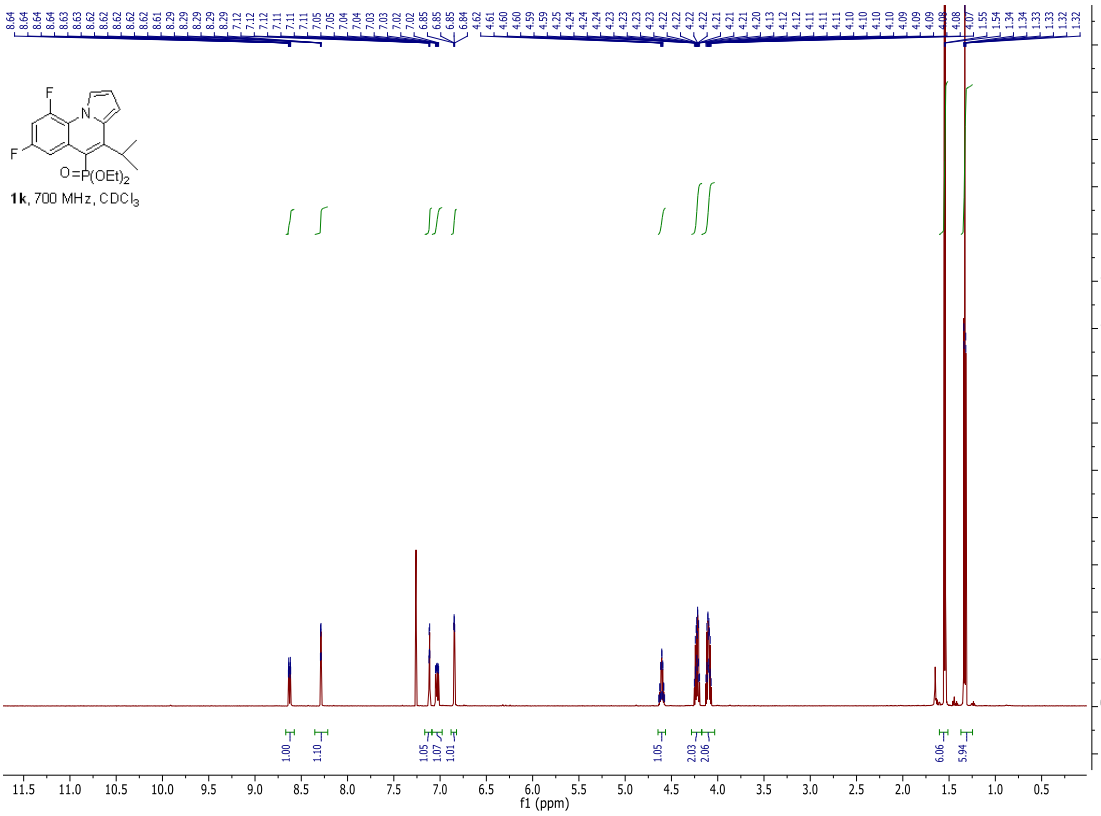

Br
N
N
O=P(OEt)2
1j, 400 MHz, CDCl3
145.84
142.94
142.82
140.32
140.24
131.57
131.38
128.39
128.29
123.50
123.49
117.47
115.77
115.20
114.89
114.88
113.87
107.71
62.17
62.12
17.77
17.73
16.47
16.40
f1 (ppm)

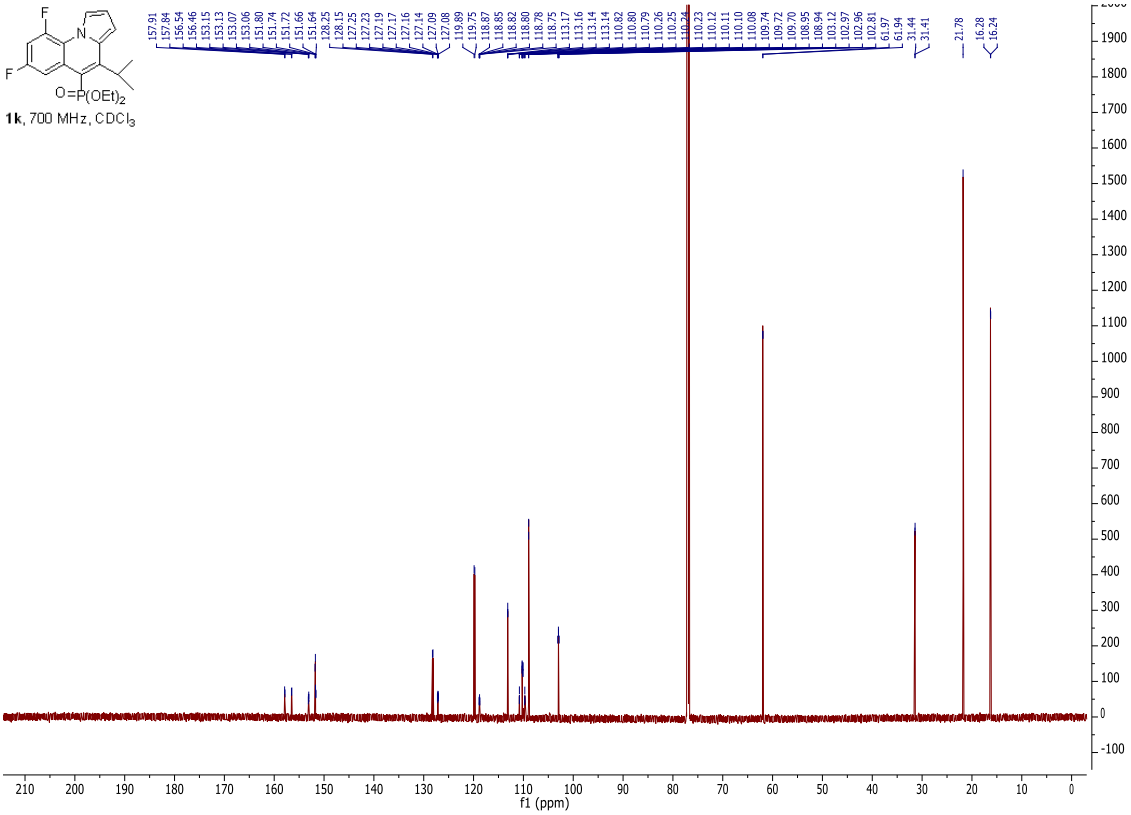

F
F
N
O=P
OEt
OEt
2f, 400 MHz, CDCl3
f1 (ppm)

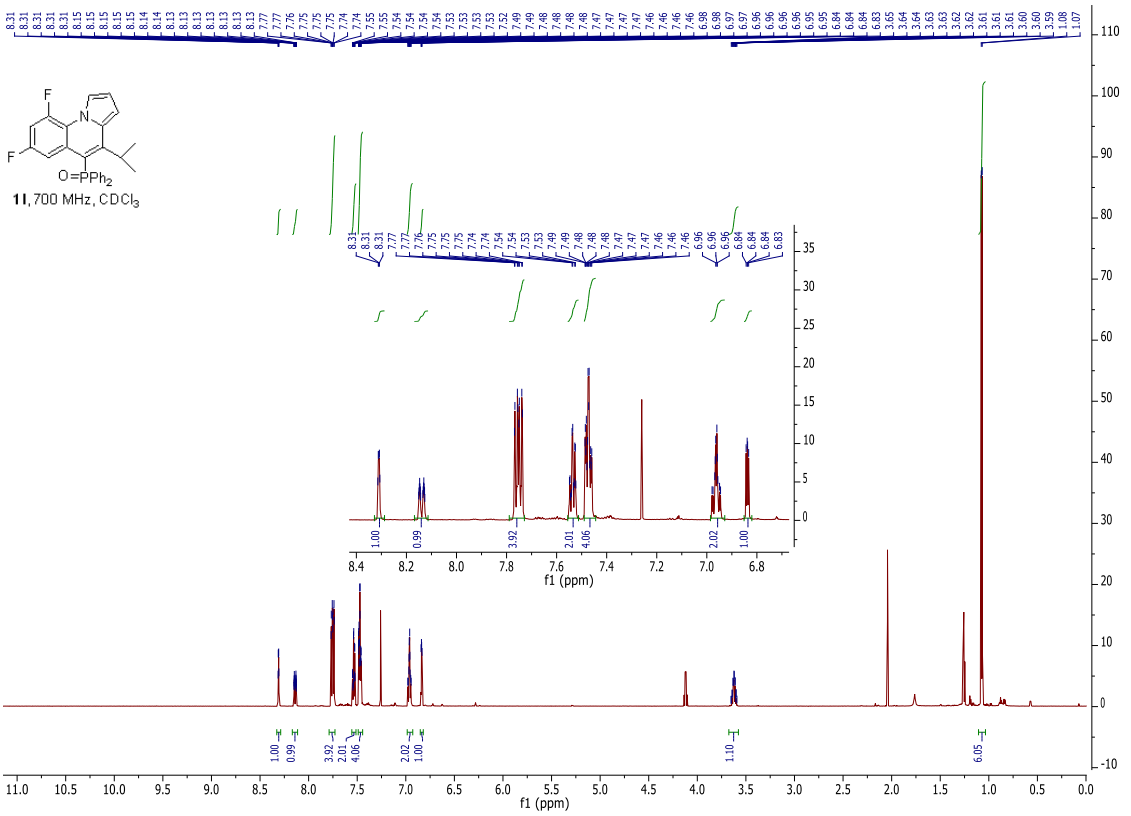

F
F
N
O=P
OEt
OEt
2f, 400 MHz, CDCl3
f1 (ppm)

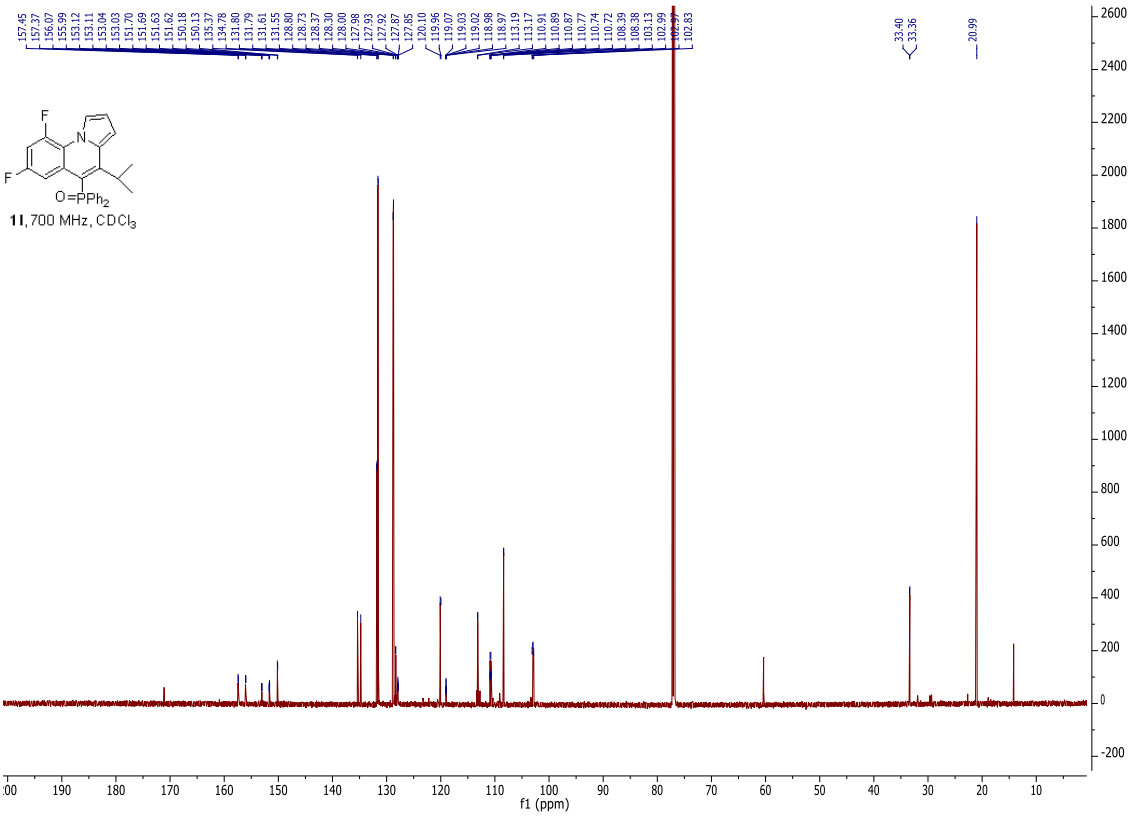

F
N
F
O=P
Ph
Ph
2f', 400 MHz, CDCl3
f1 (ppm)

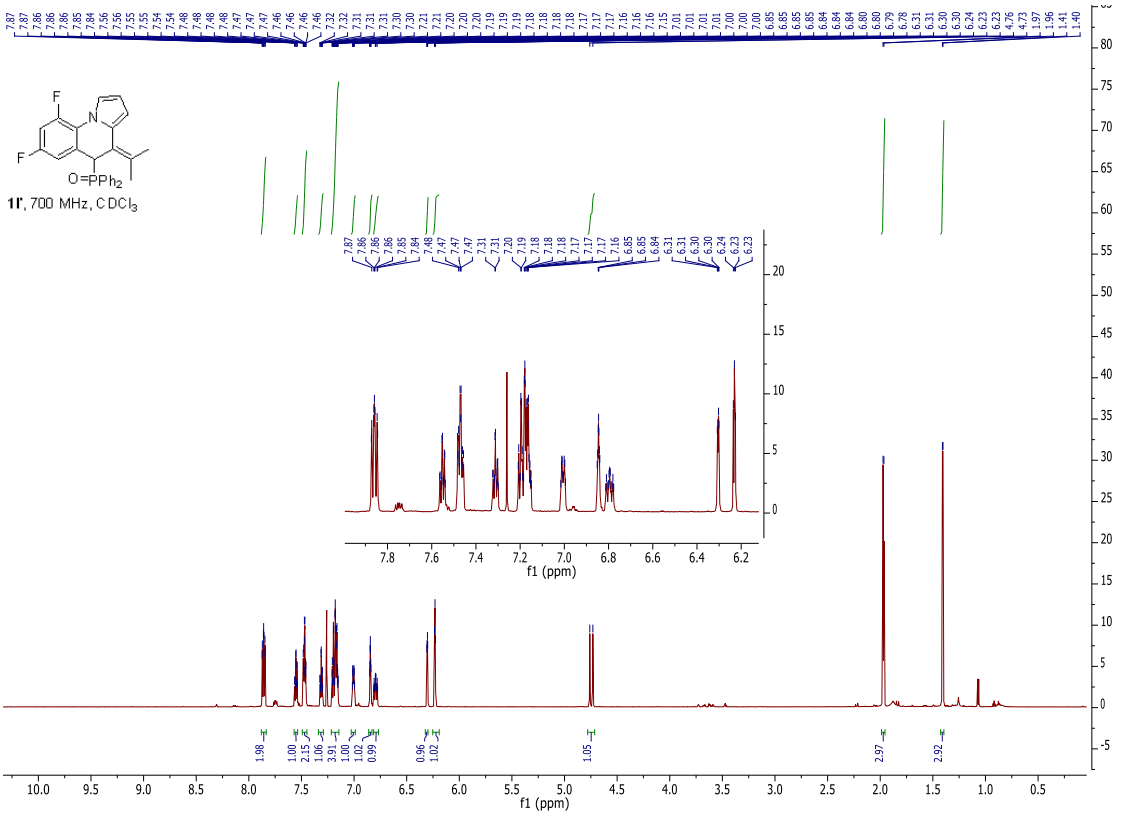

F
N
F
O=P
Ph
Ph
2f', 400 MHz, CDCl3
f1 (ppm)

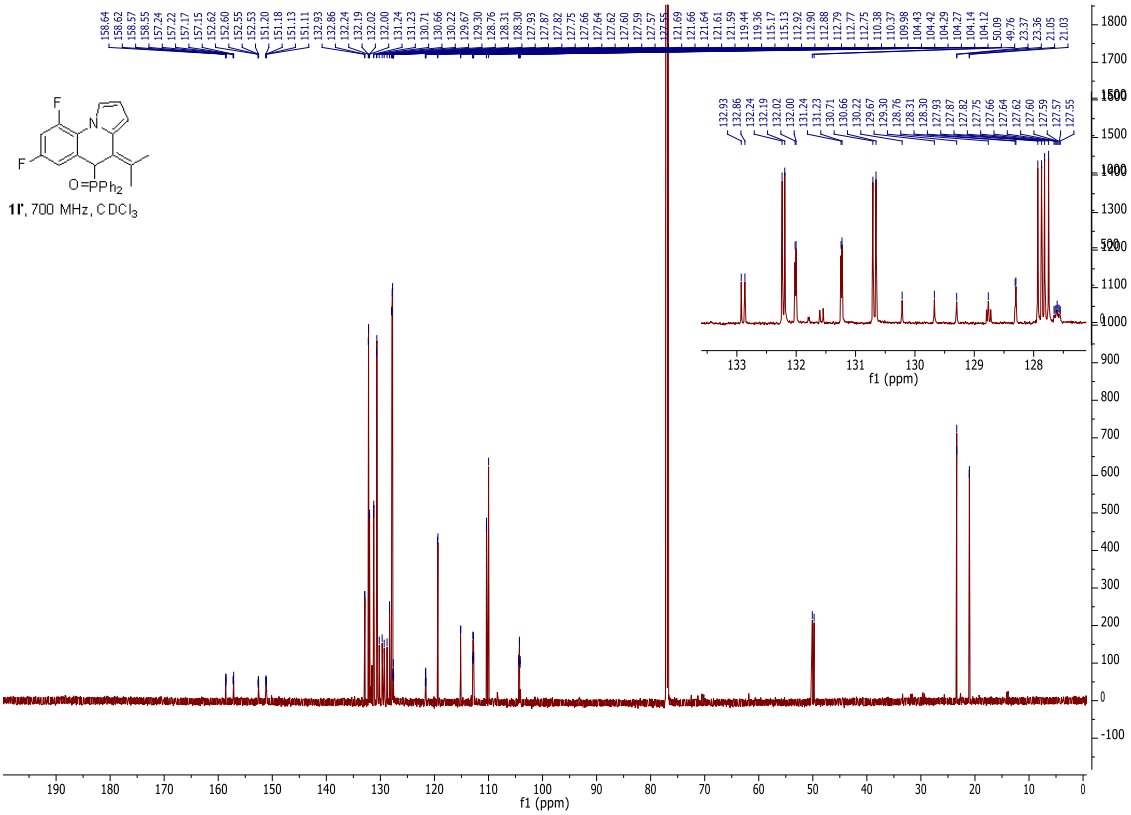

F
N
F
O=P(OEt)2
1k, 700 MHz, CDCl3
f1 (ppm)

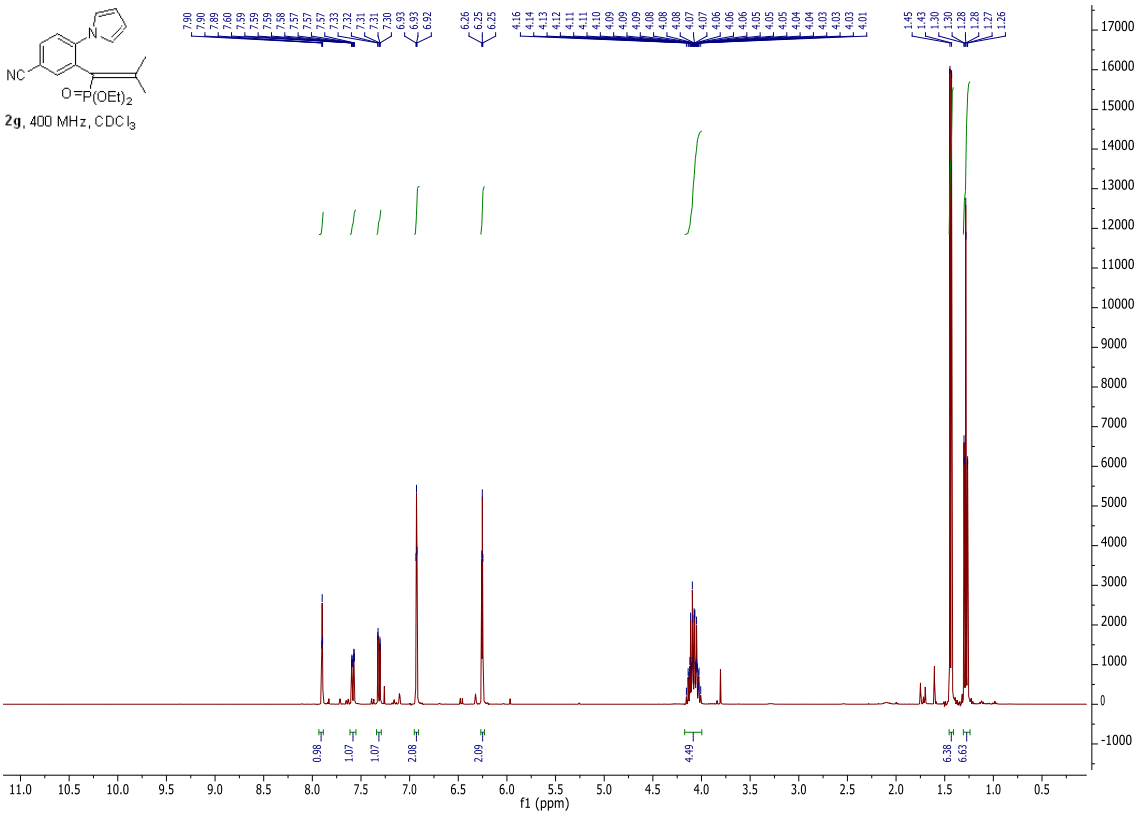

F
N
F
O=P(OEt)2
1k, 700 MHz, CDCl3
f1 (ppm)

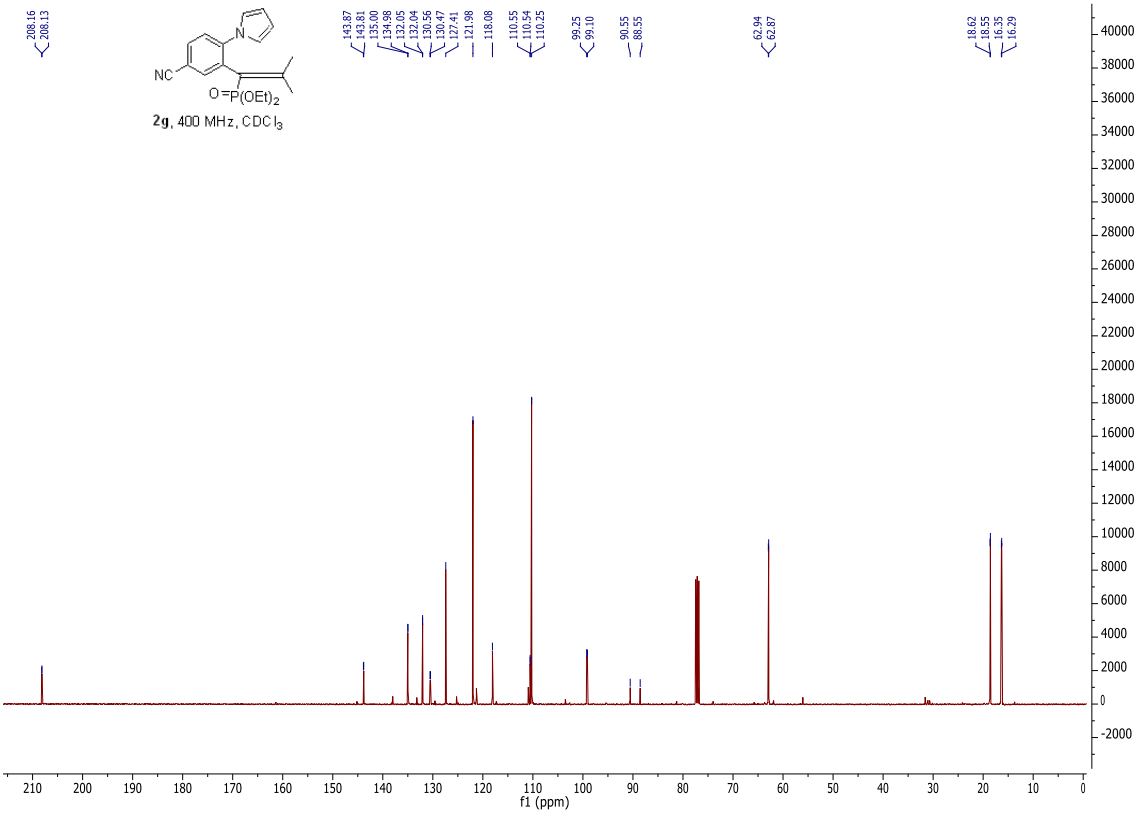

F
N
F
O=PPh2
1l, 700 MHz, CDCl3
f1 (ppm)

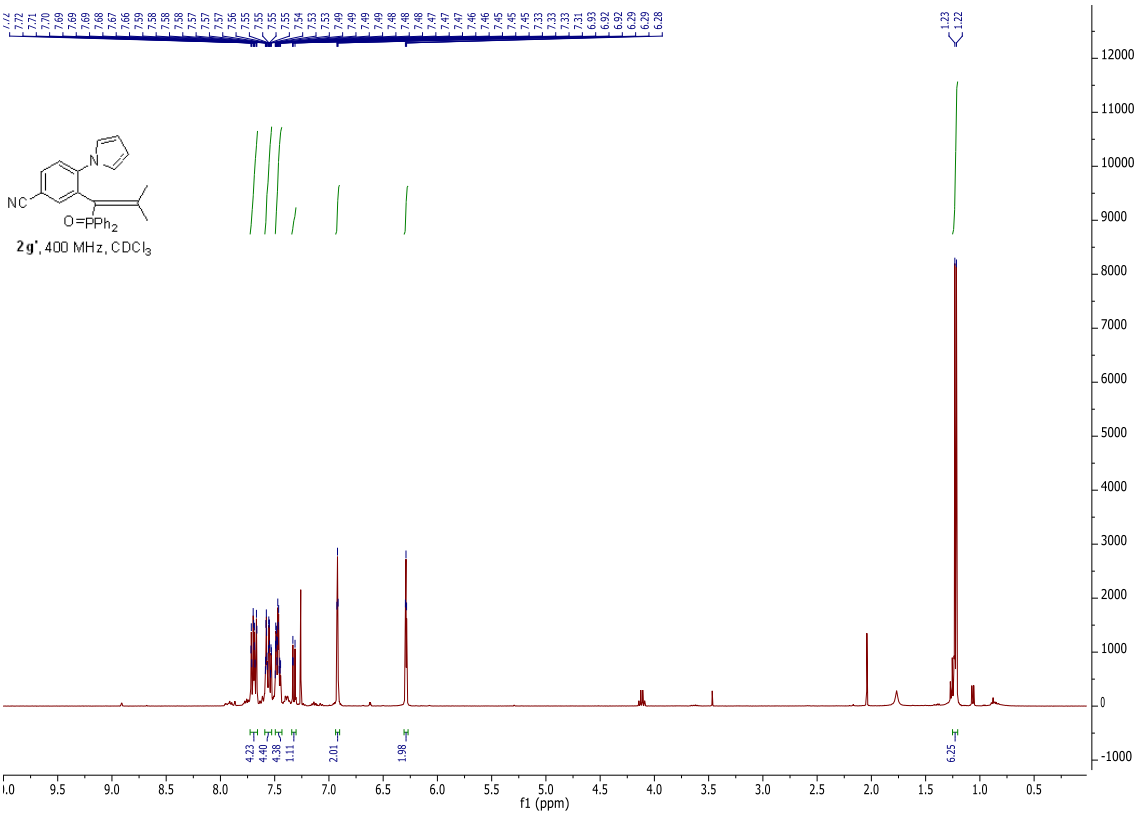

F
N
F
O=PPh2
1l, 700 MHz, CDCl3
f1 (ppm)

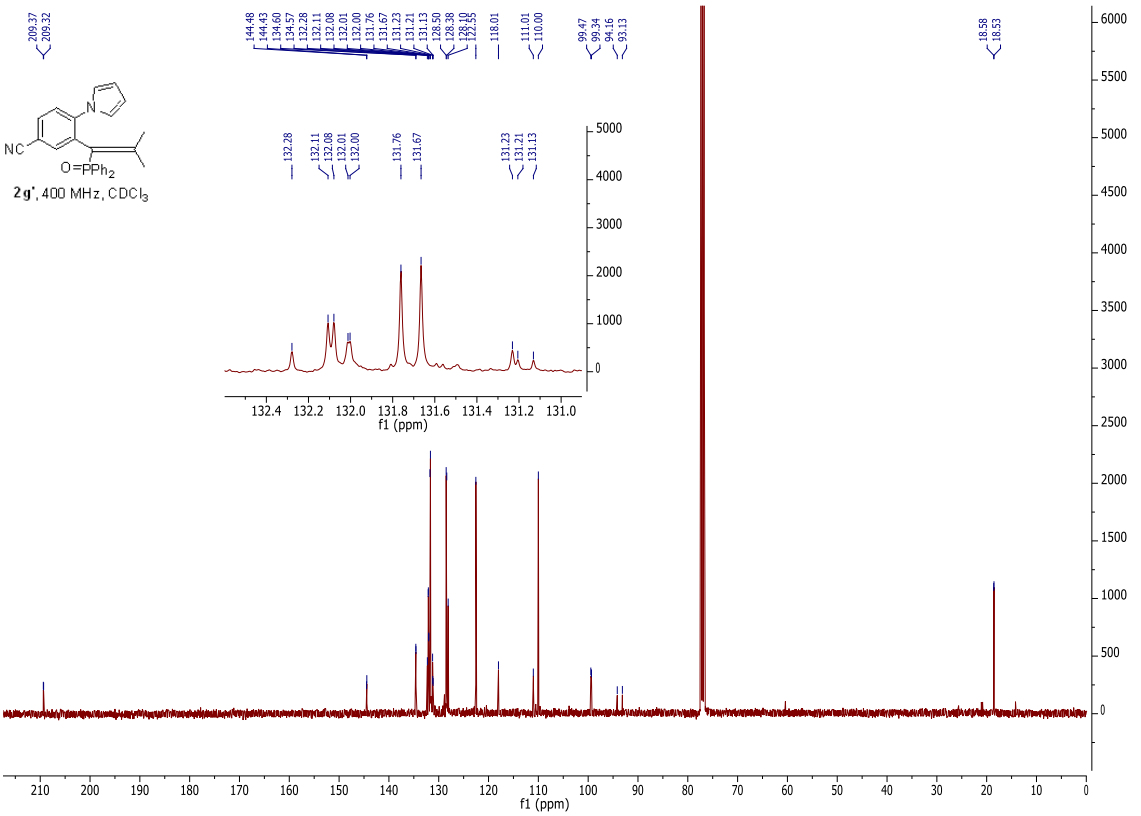

F
N
F
O=PPh2
1l', 700 MHz, CDCl3
f1 (ppm)

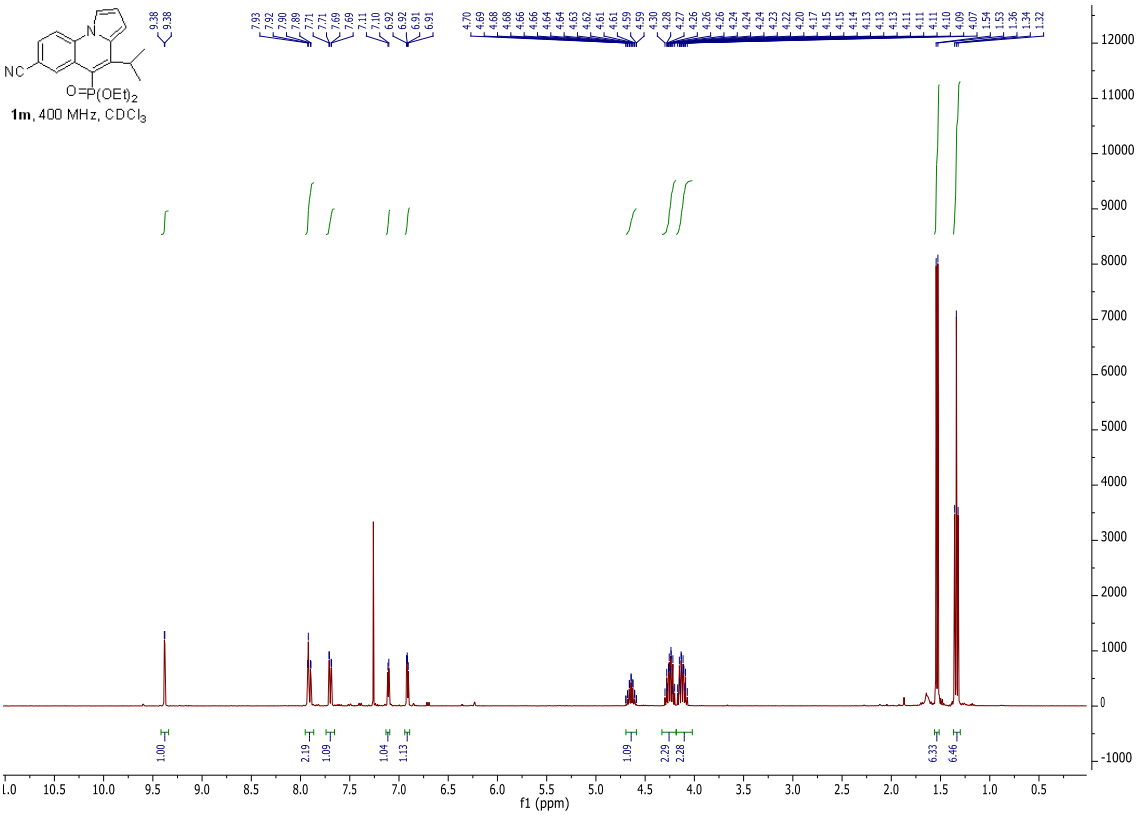

F
N
F
O=PPh2
1l', 700 MHz, CDCl3
f1 (ppm)

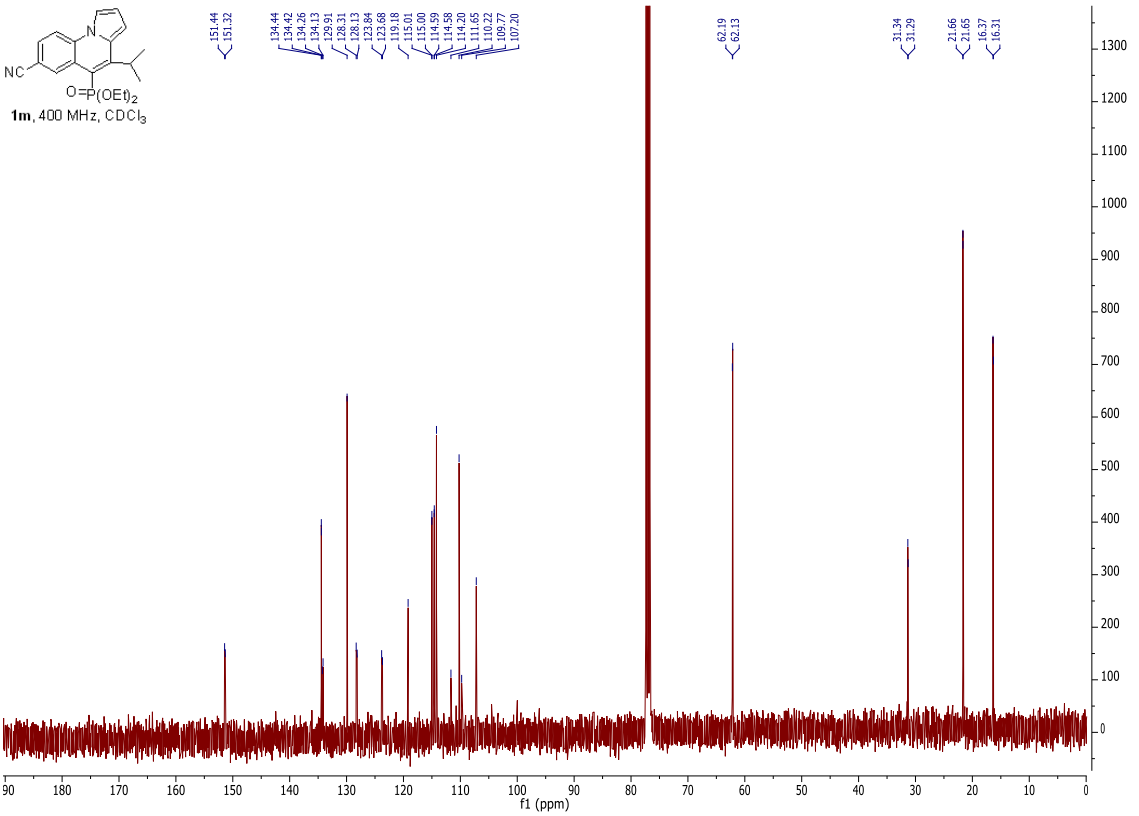

NC
O=P(OEt)2
2g, 400 MHz, CDCl3
f1 (ppm)

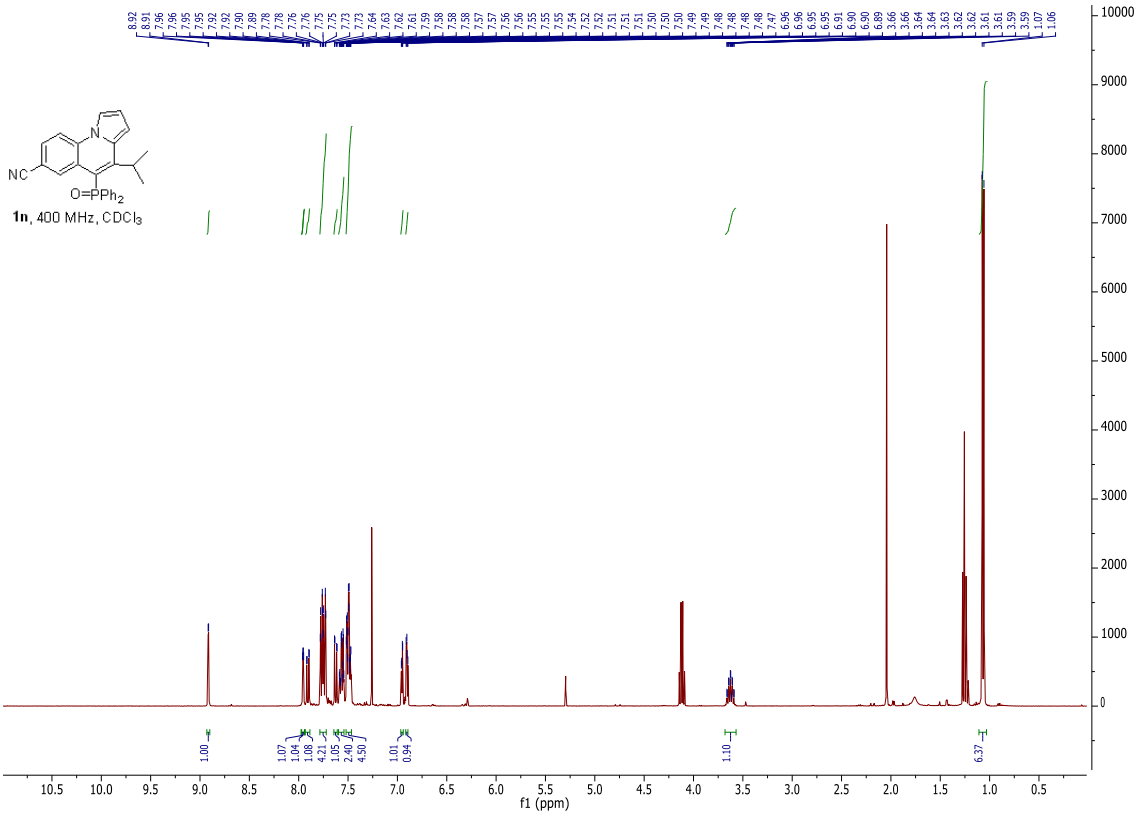

NC
O=P(OEt)2
2g, 400 MHz, CDCl3
f1 (ppm)

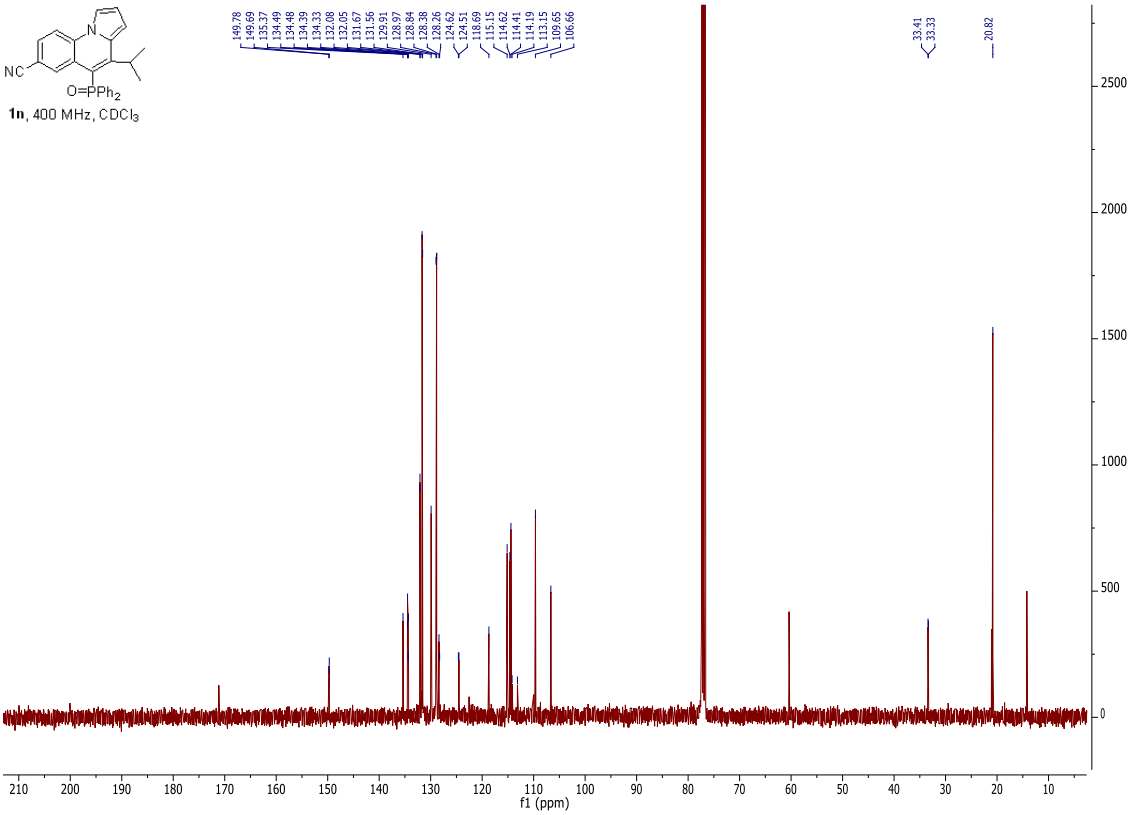

NC
O=PPh2
2g', 400 MHz, CDCl3
f1 (ppm)

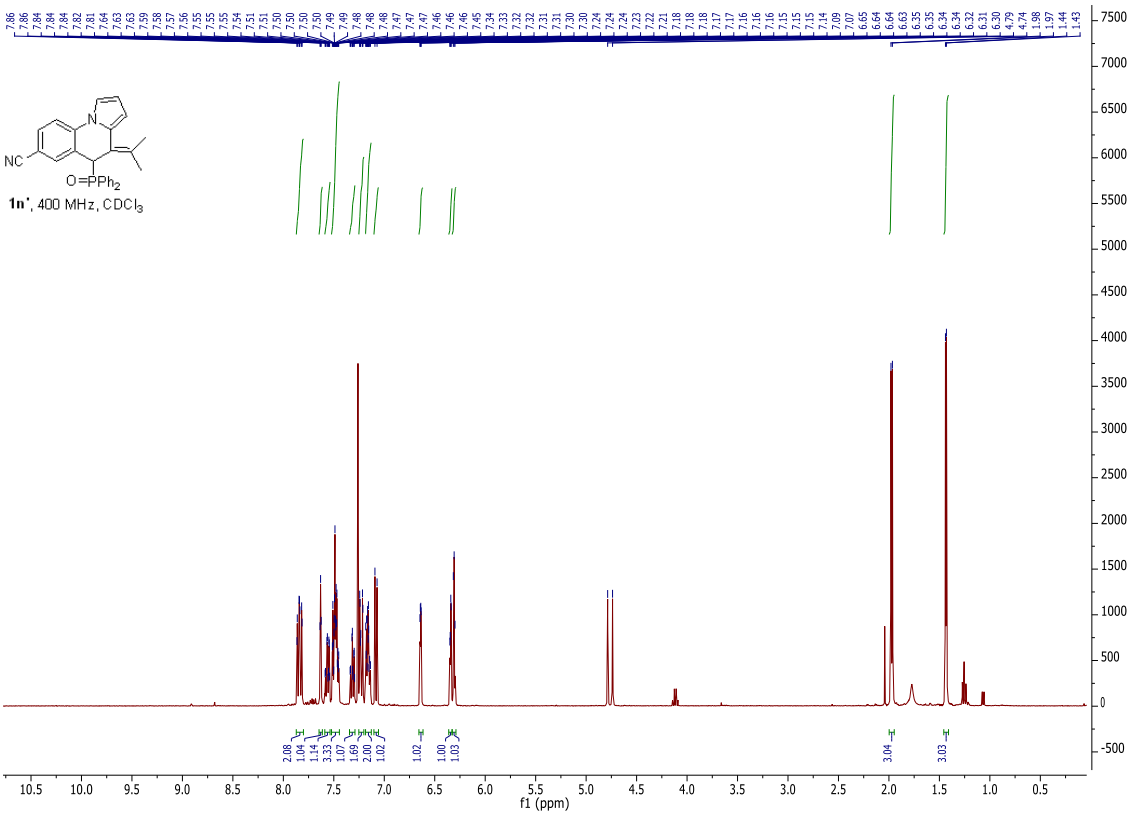

NC
O=PPh2
2g', 400 MHz, CDCl3
f1 (ppm)
f1 (ppm)

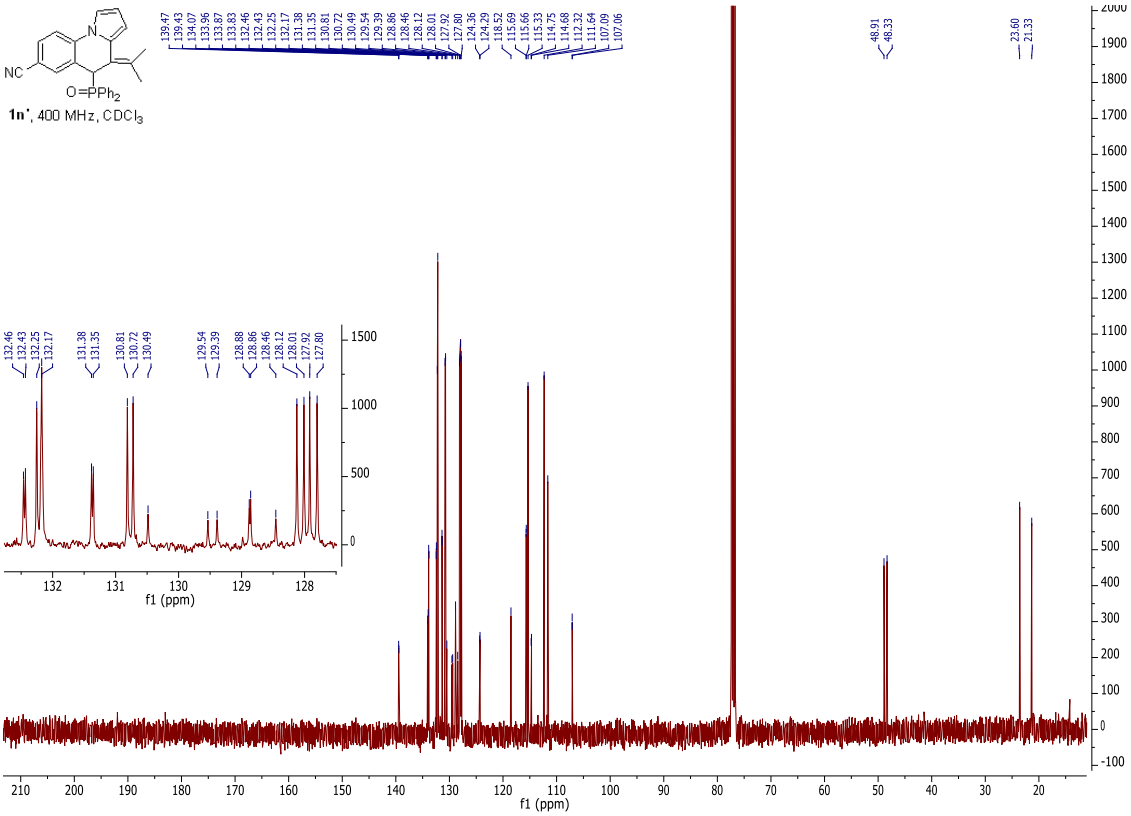

NC
O=P(OEt)2
1m, 400 MHz, CDCl3
f1 (ppm)

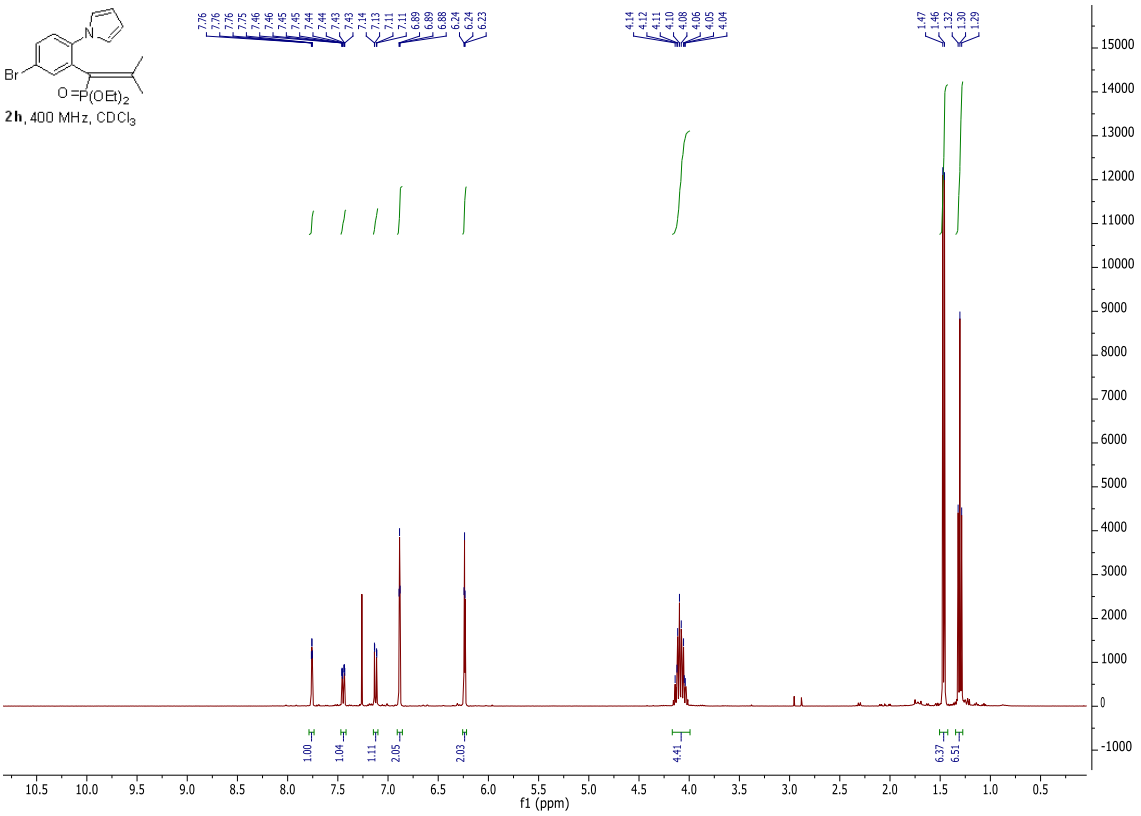

NC
O=P(OEt)2
1m, 400 MHz, CDCl3
f1 (ppm)

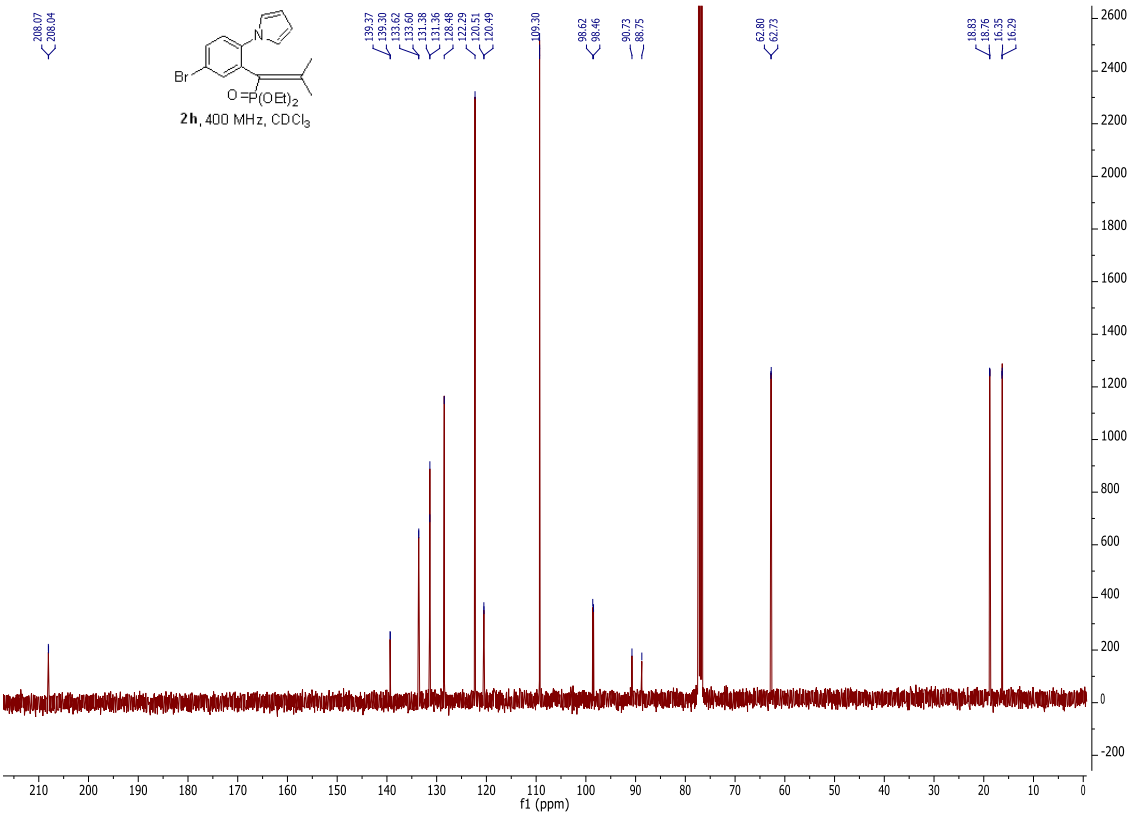

NC
O=PPh2
1n, 400 MHz, CDCl3
f1 (ppm)

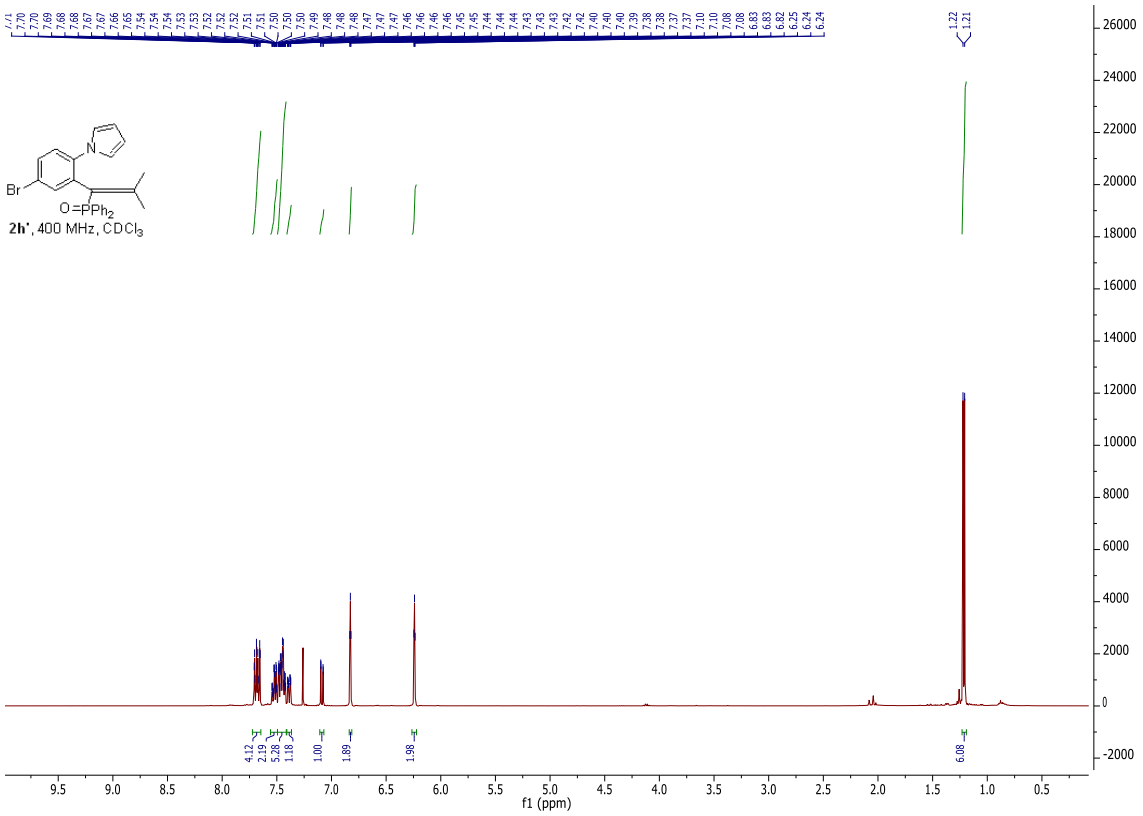

NC
O=PPh2
1n, 400 MHz, CDCl3
f1 (ppm)

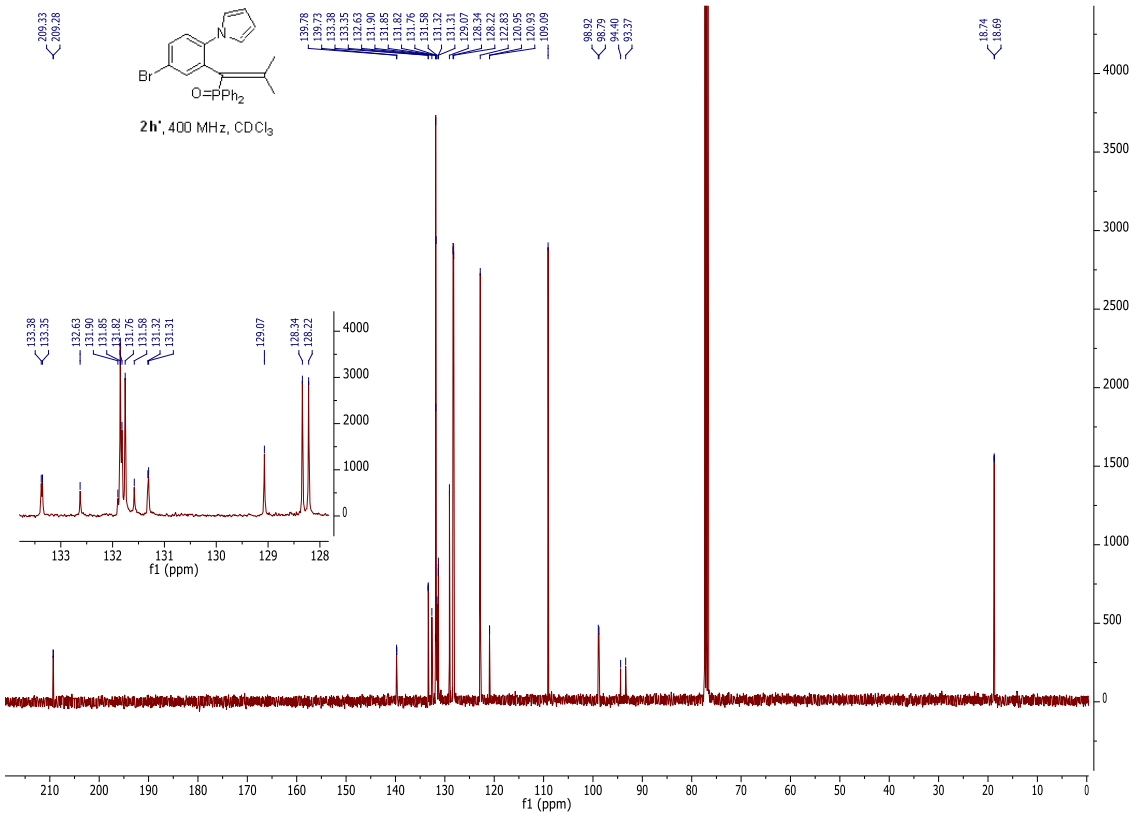

NC
O=PPh2
1n', 400 MHz, CDCl3
f1 (ppm)

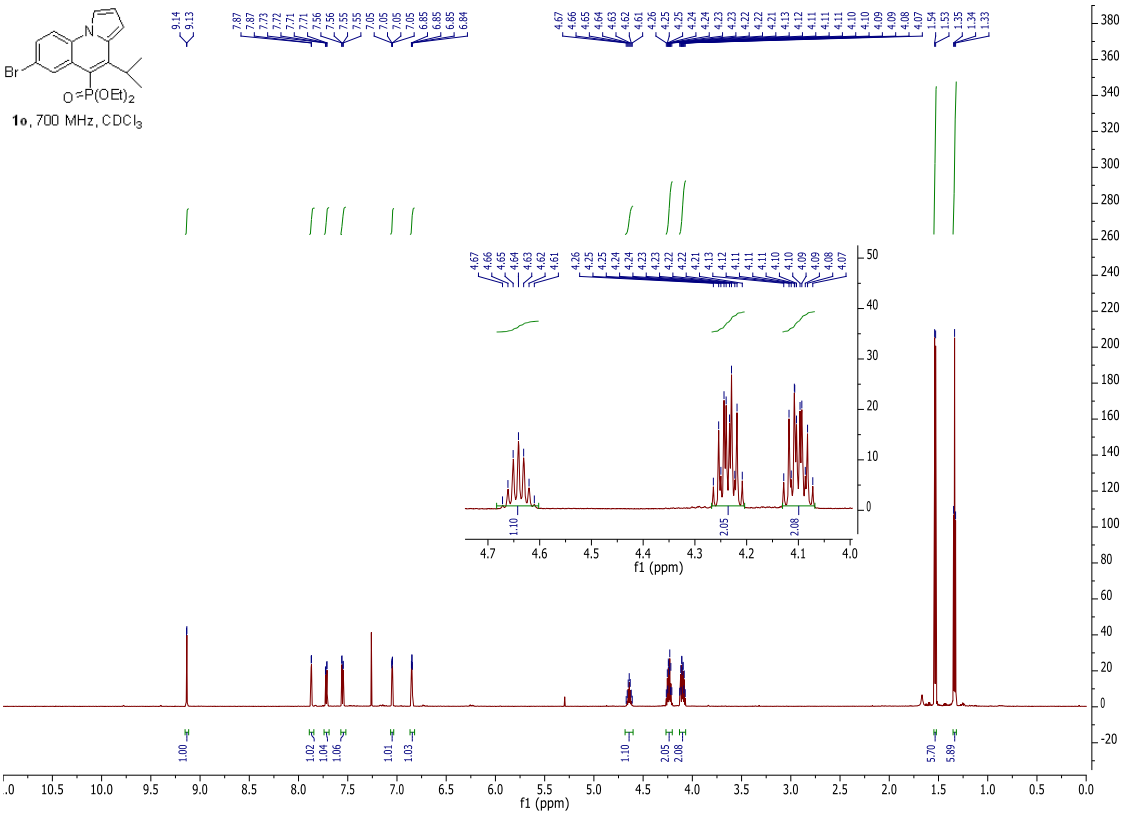

NC
O=PPh2
1n', 400 MHz, CDCl3
f1 (ppm)

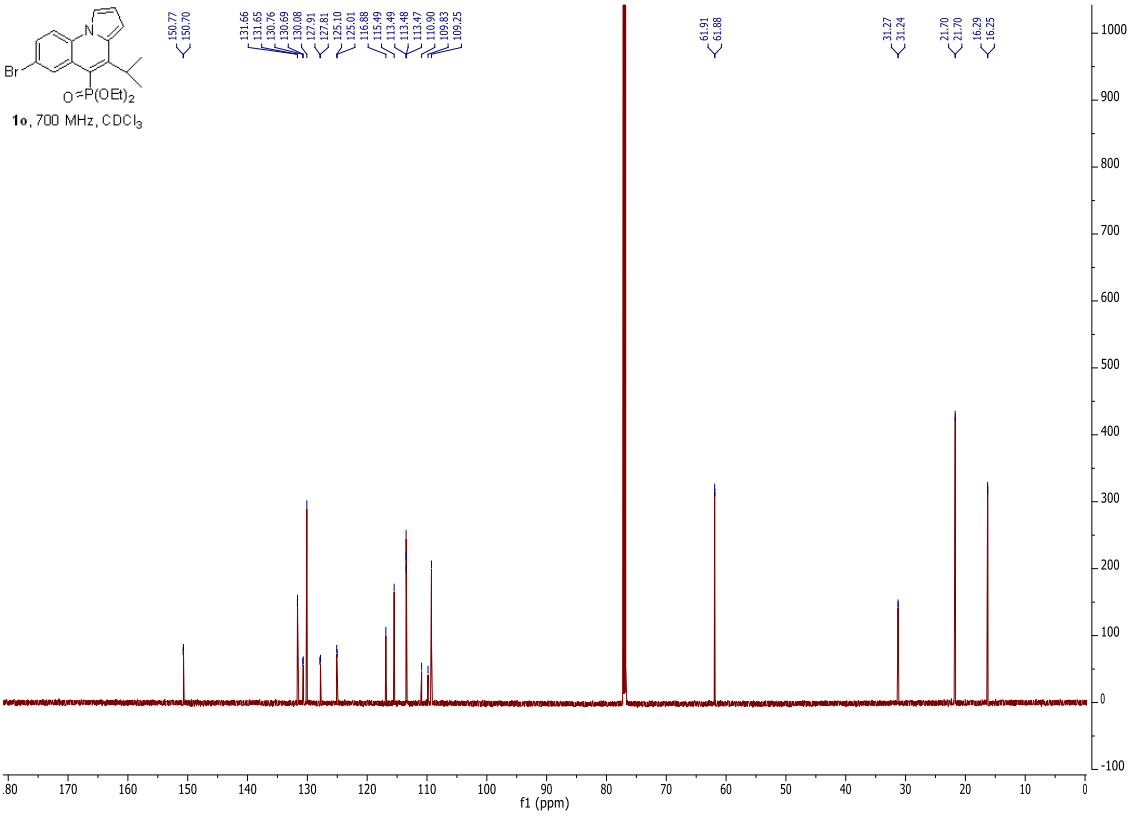

Br
O=P(OEt)2
2h, 400 MHz, CDCl3
f1 (ppm)

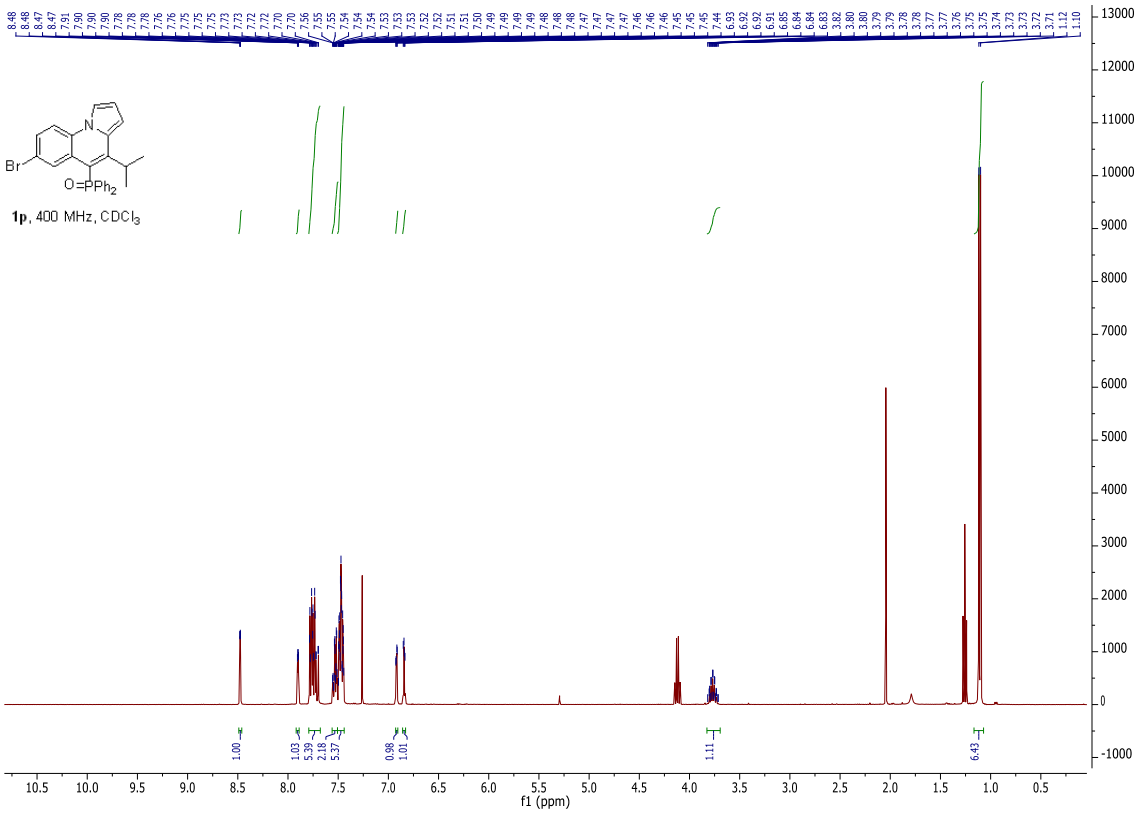

Br
O=P(OEt)2
2h, 400 MHz, CDCl3
f1 (ppm)

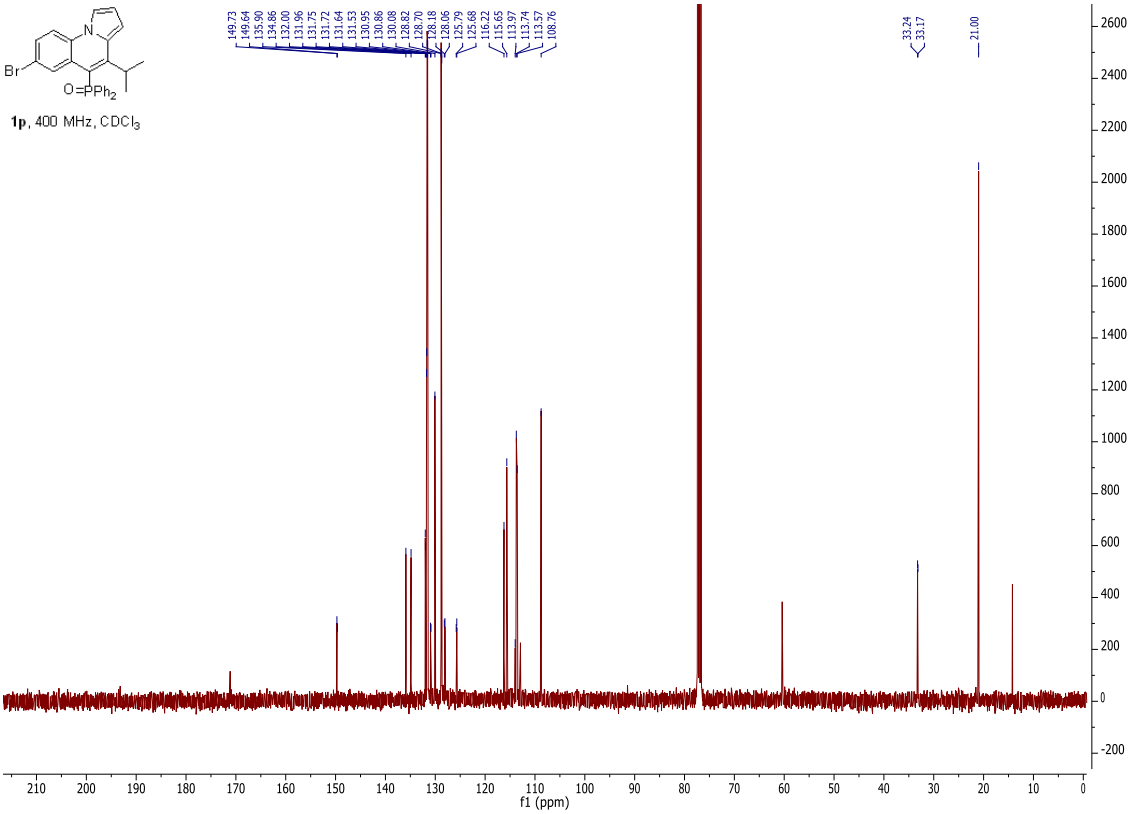

Br
O=PPh2
2h', 400 MHz, CDCl3
f1 (ppm)

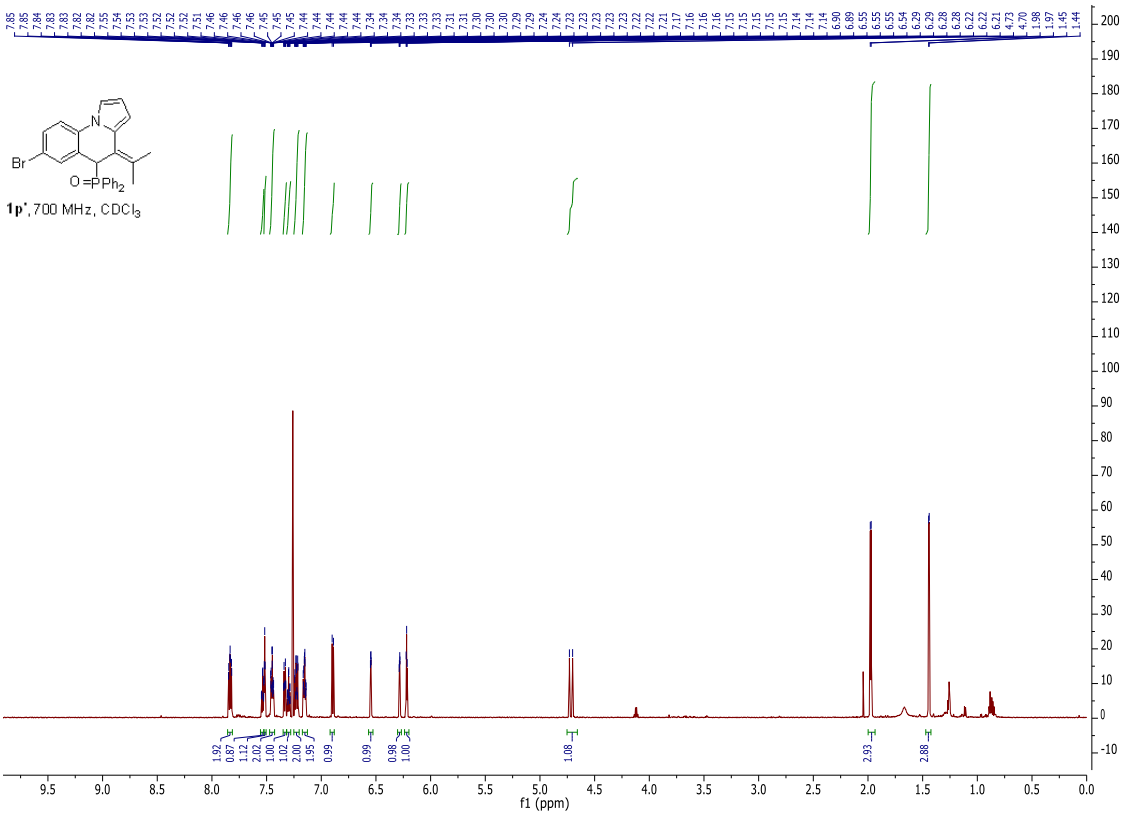

Br
O=PPh2
2h', 400 MHz, CDCl3
f1 (ppm)

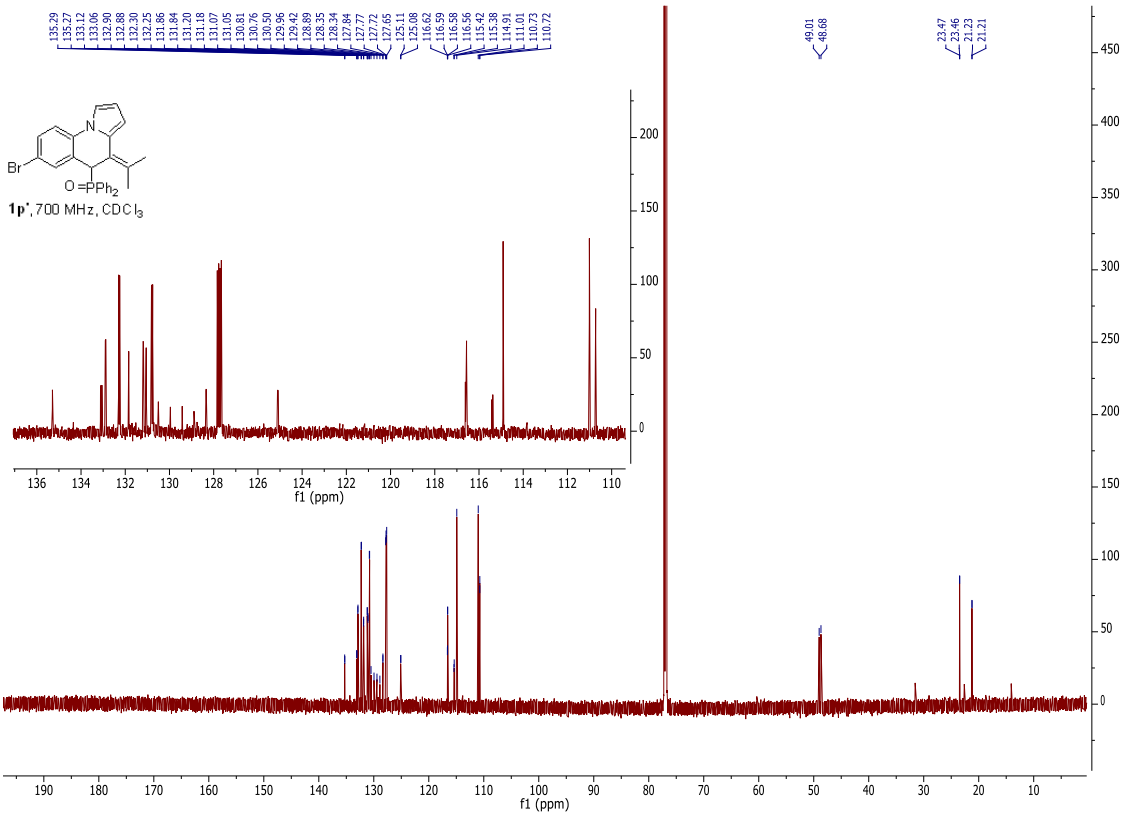

Br
O=P(OEt)2
1o, 700 MHz, CDCl3
f1 (ppm)

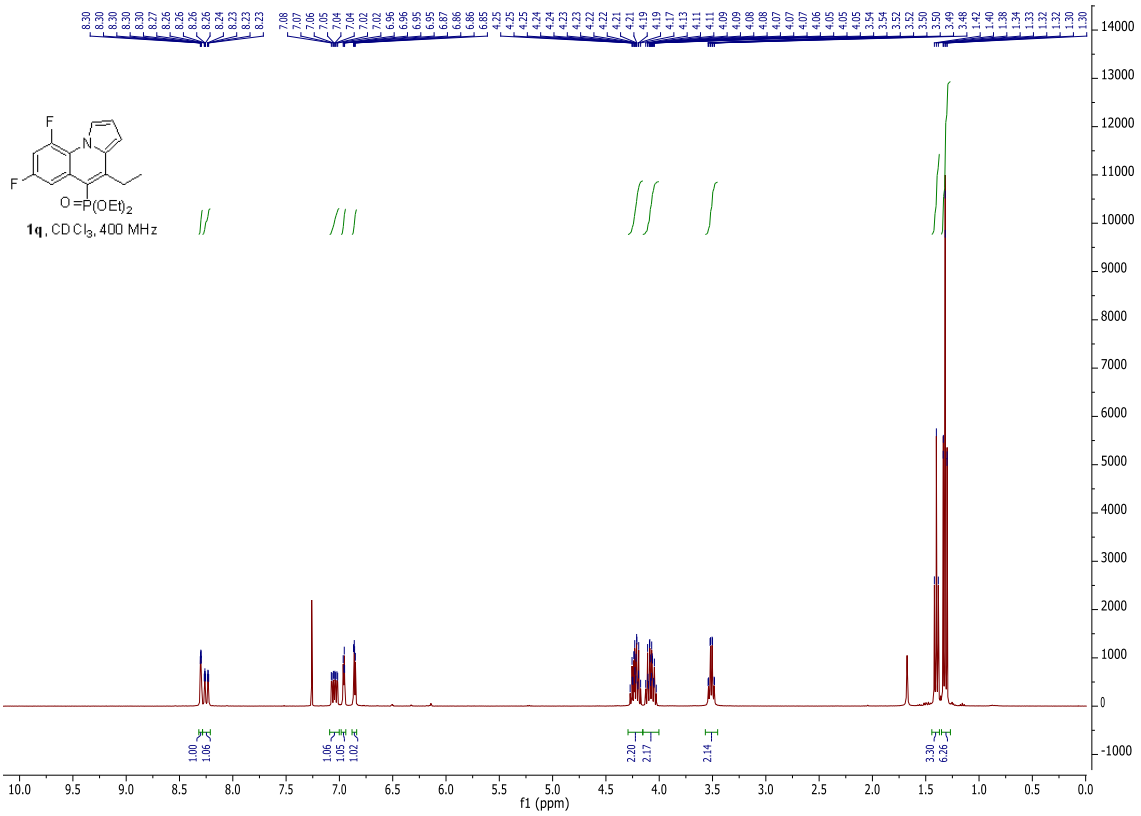

Br
O=P(OEt)2
1o, 700 MHz, CDCl3
f1 (ppm)

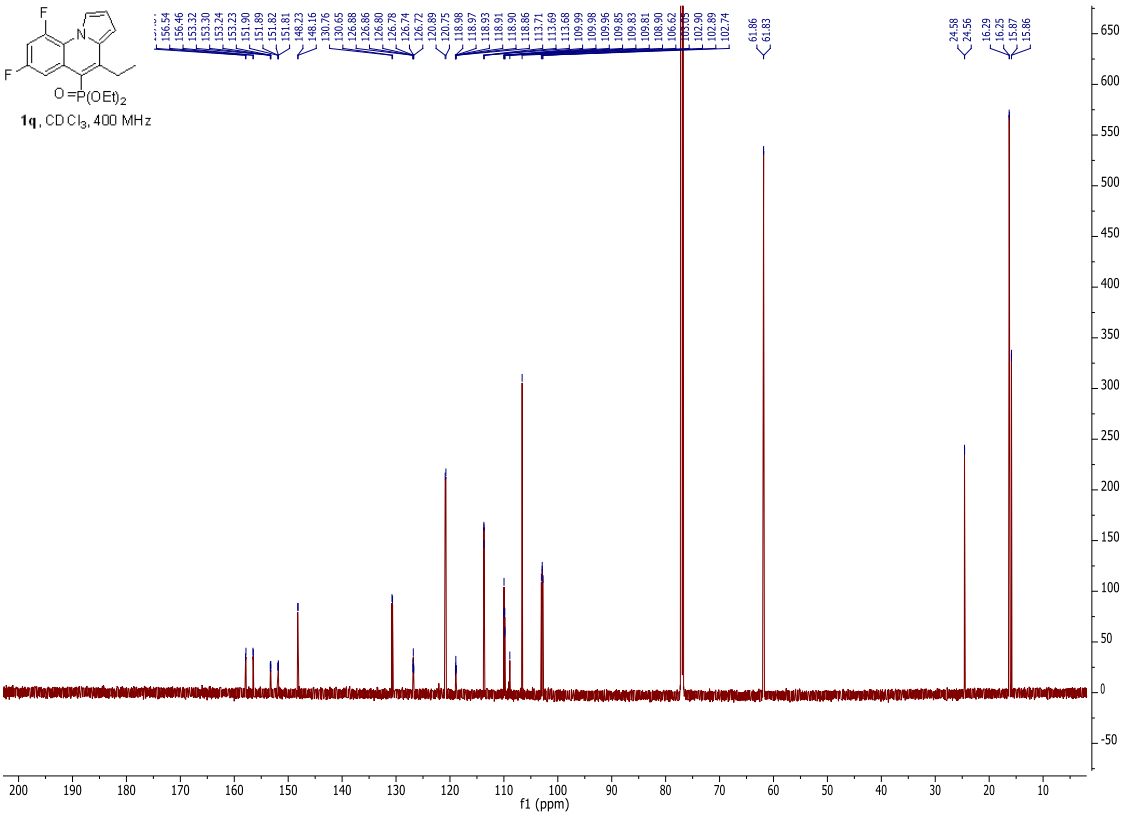

Br
O=PPh2
1p, 400 MHz, CDCl3
f1 (ppm)

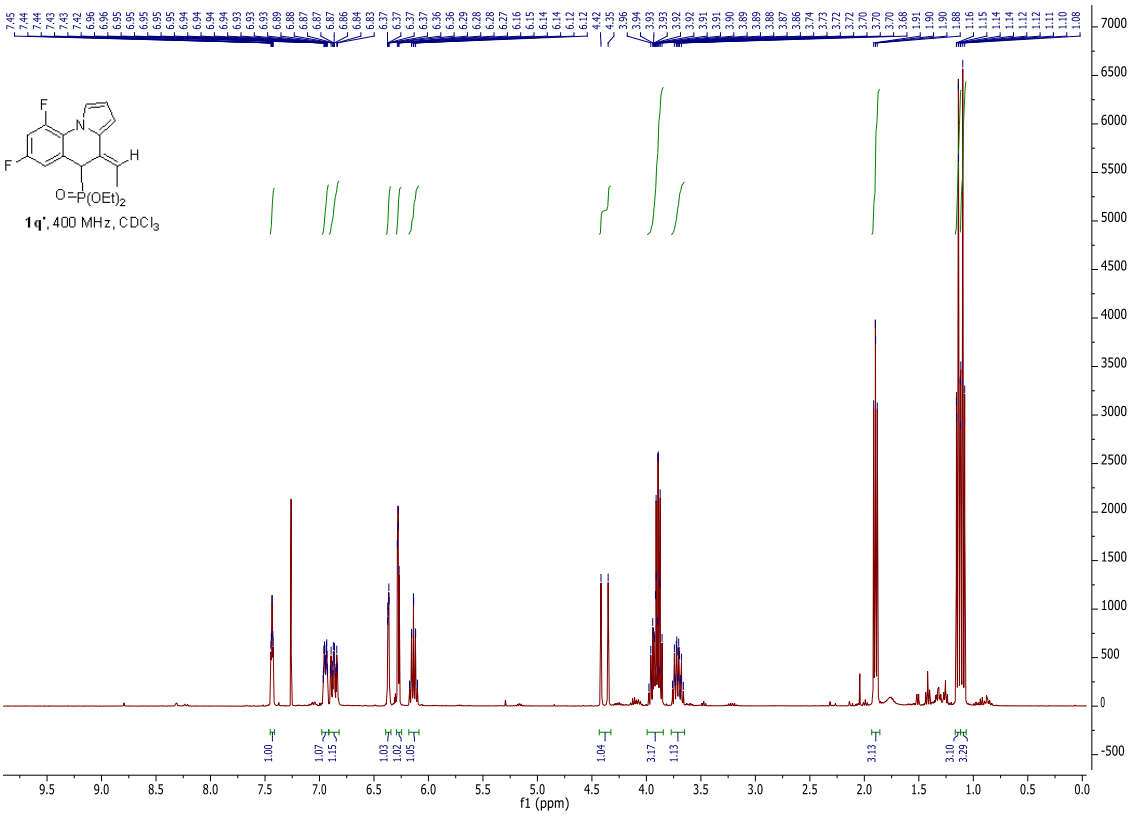

Br
O=PPh2
1p, 400 MHz, CDCl3
f1 (ppm)

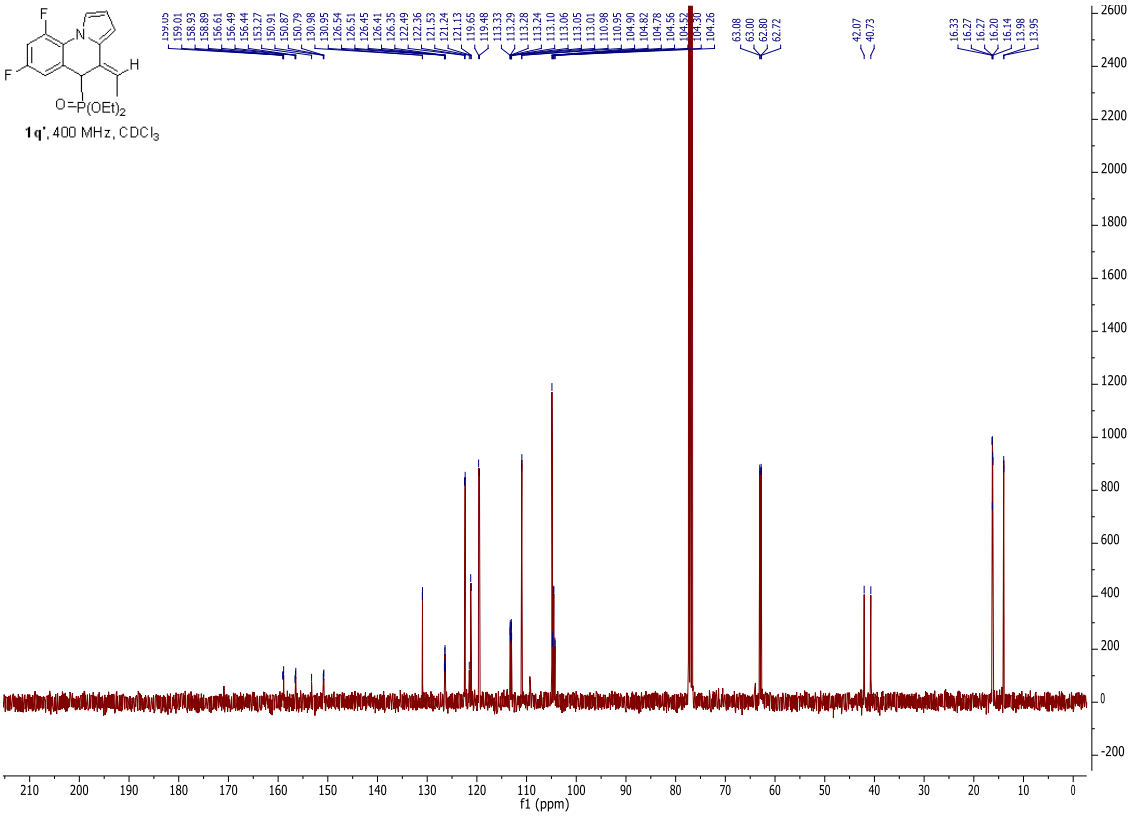

Br
O=PPh2
1p', 700 MHz, CDCl3
f1 (ppm)

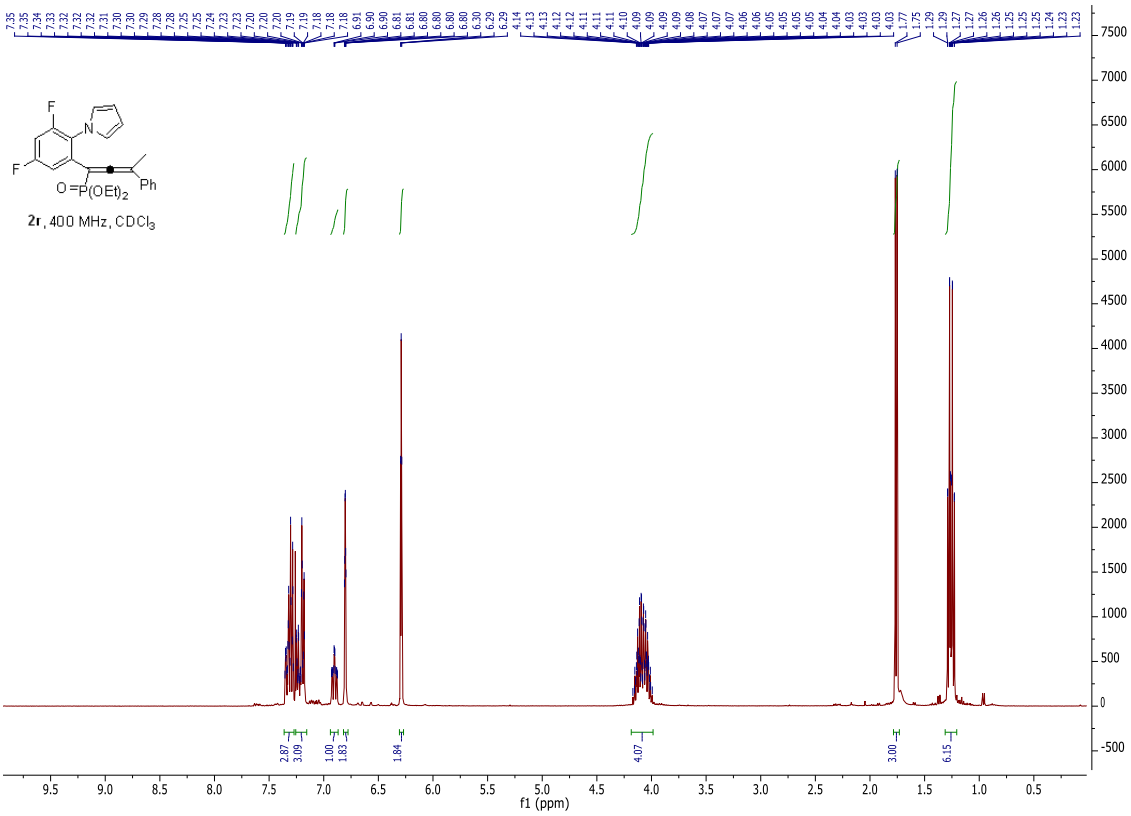

Br
O=PPh2
1p', 700 MHz, CDCl3
f1 (ppm)

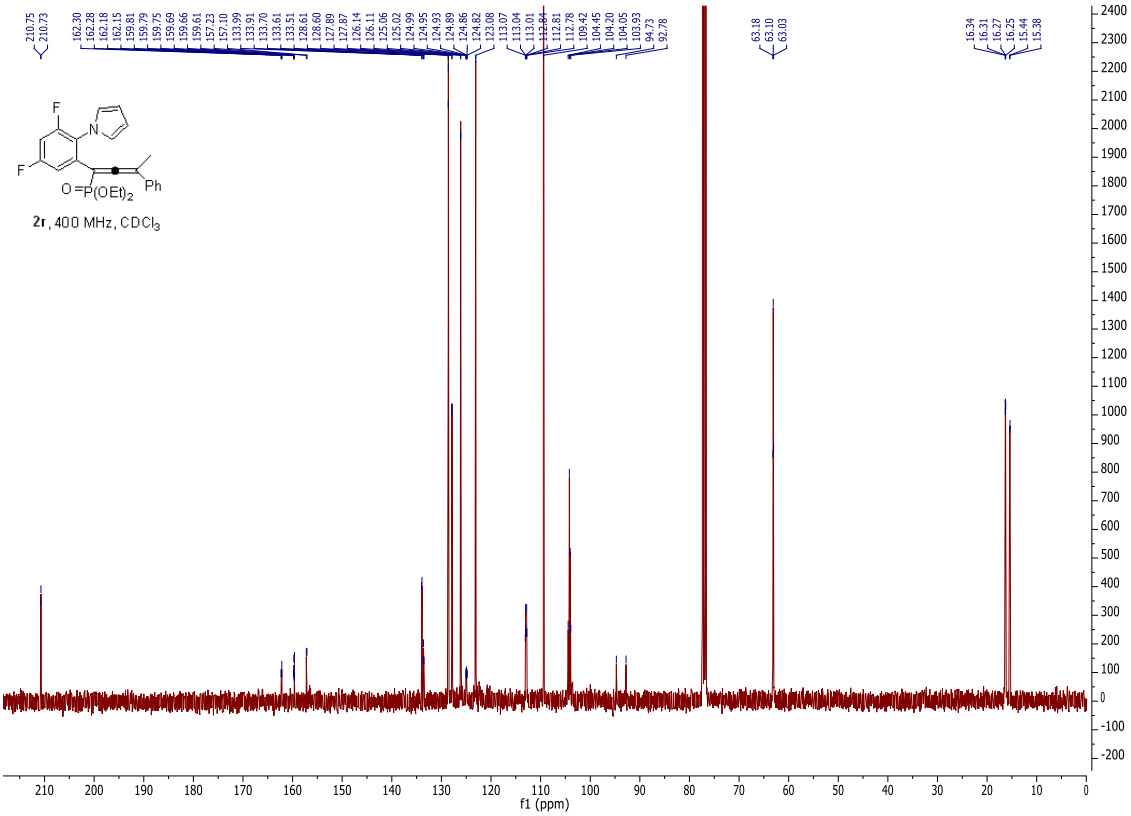

F
N
F
O=P(OEt)2
1q, CDCl3, 400 MHz
f1 (ppm)

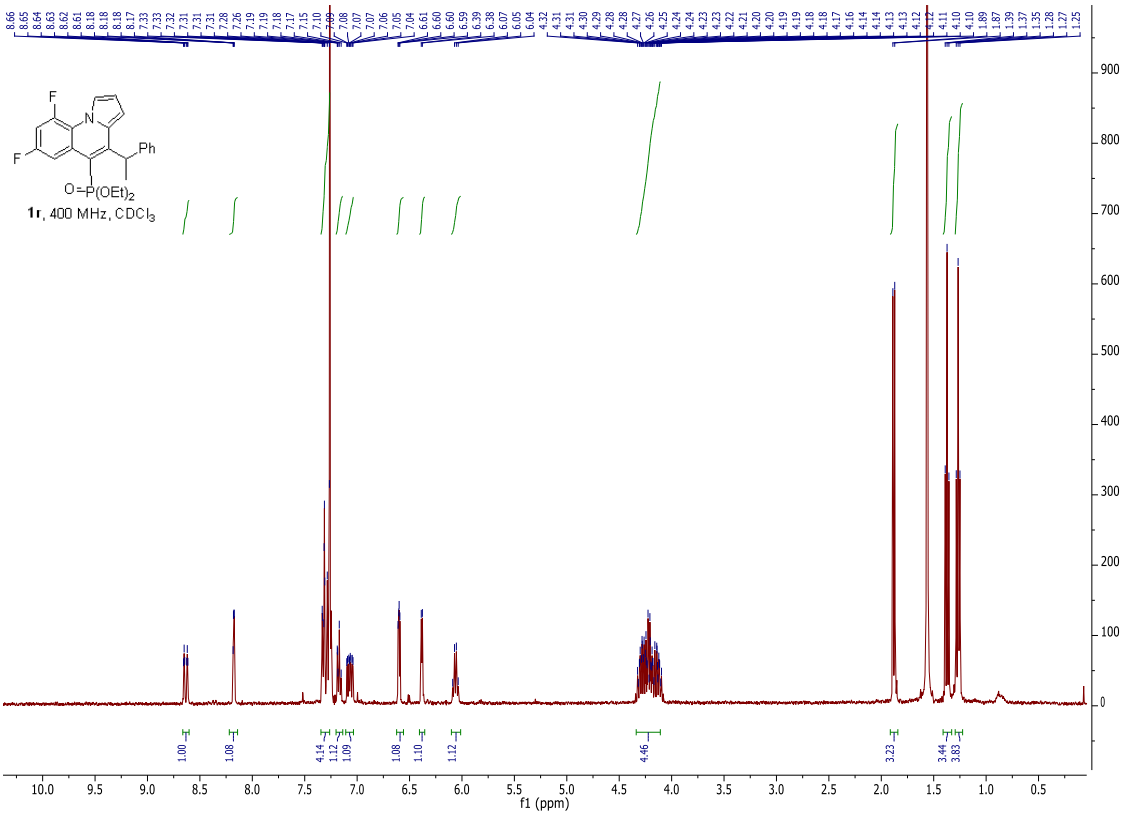

F
N
F
O=P(OEt)2
1q, CDCl3, 400 MHz
f1 (ppm)

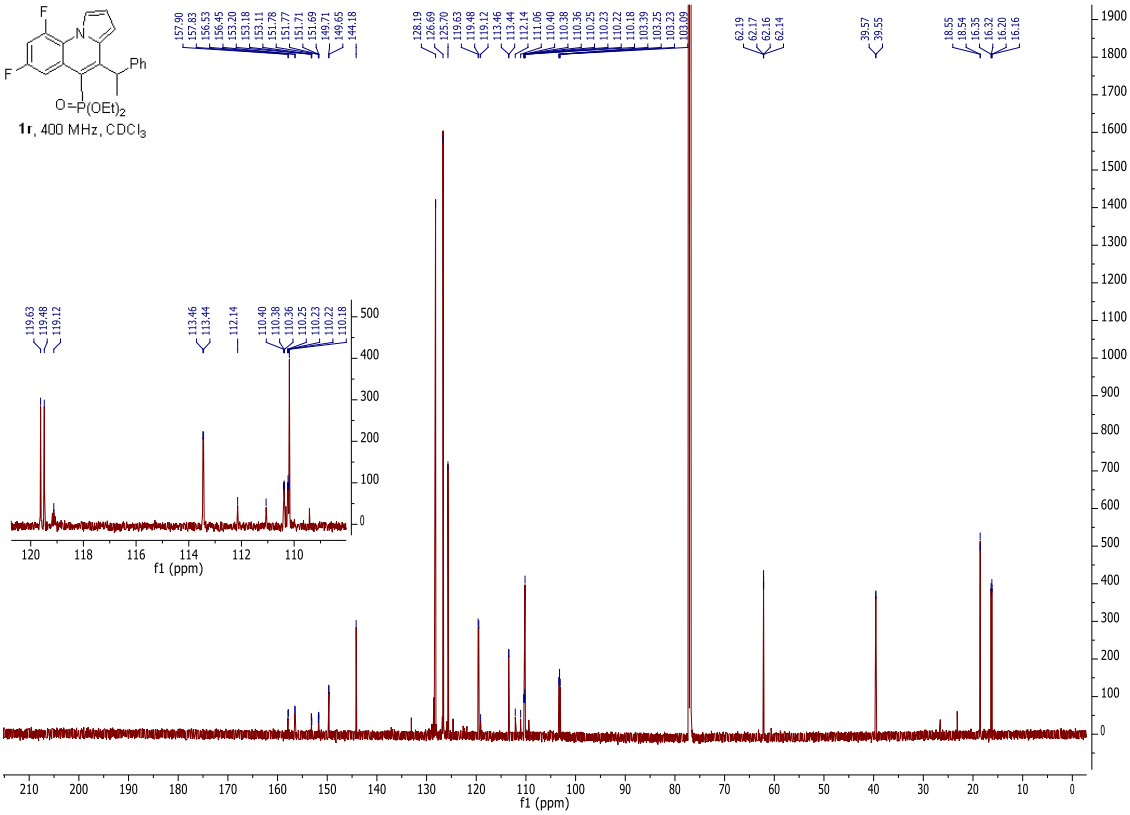

F
N
F
H
O=P(OEt)2
1q', 400 MHz, CDCl3
f1 (ppm)

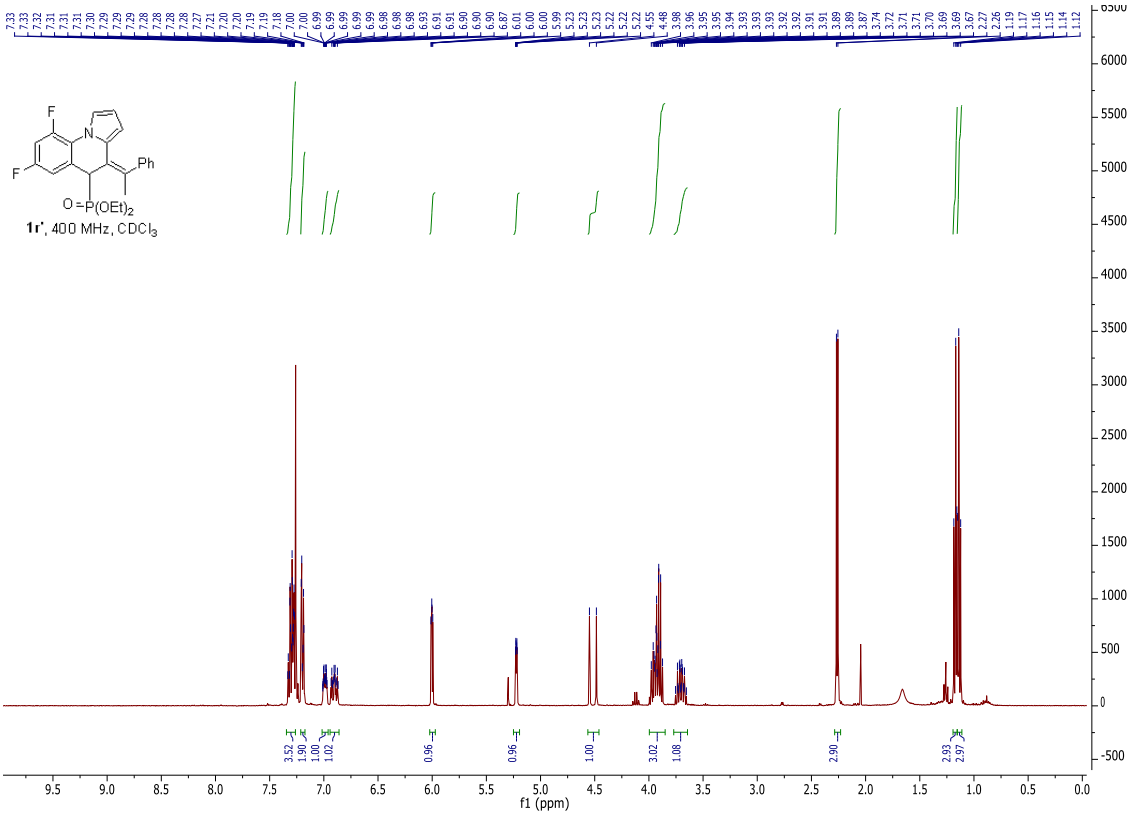

F
N
F
H
O=P(OEt)2
1q', 400 MHz, CDCl3
f1 (ppm)

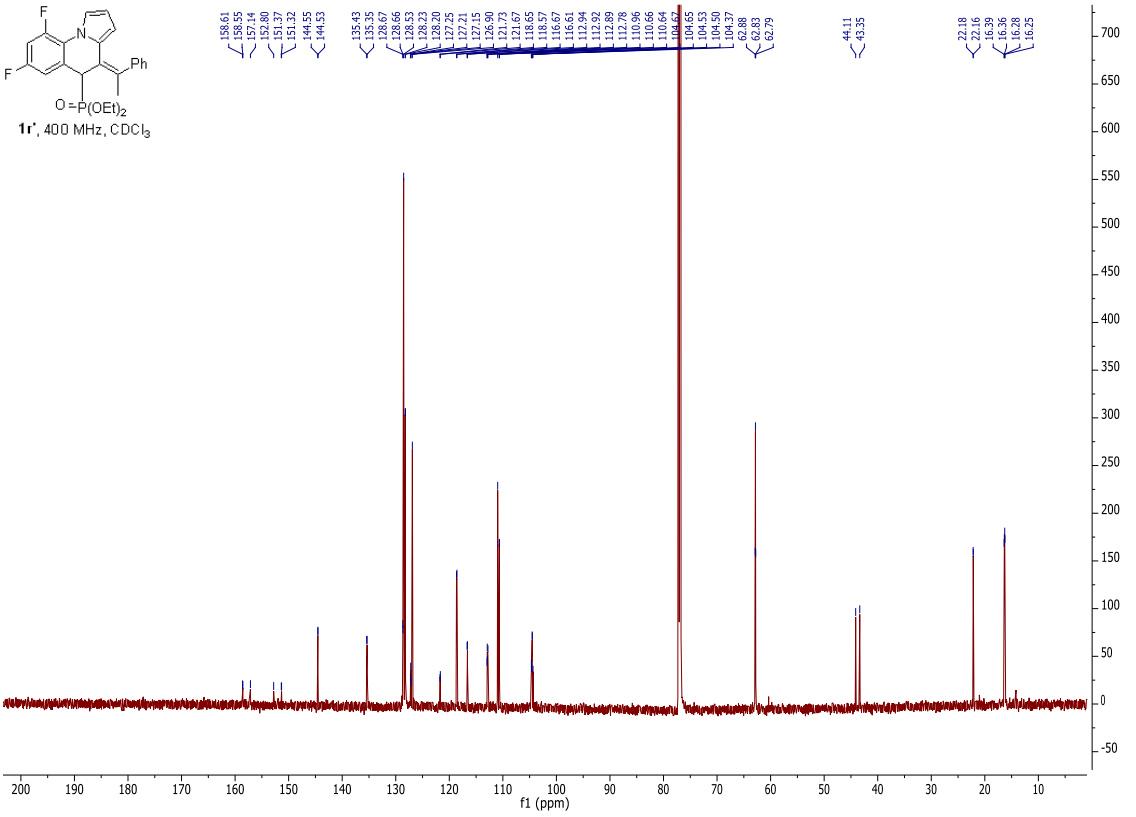

F
N
F
O=P(OEt)2
Ph
2r, 400 MHz, CDCl3
f1 (ppm)


F
N
F
O=P(OEt)2
Ph
2r, 400 MHz, CDCl3
f1 (ppm)

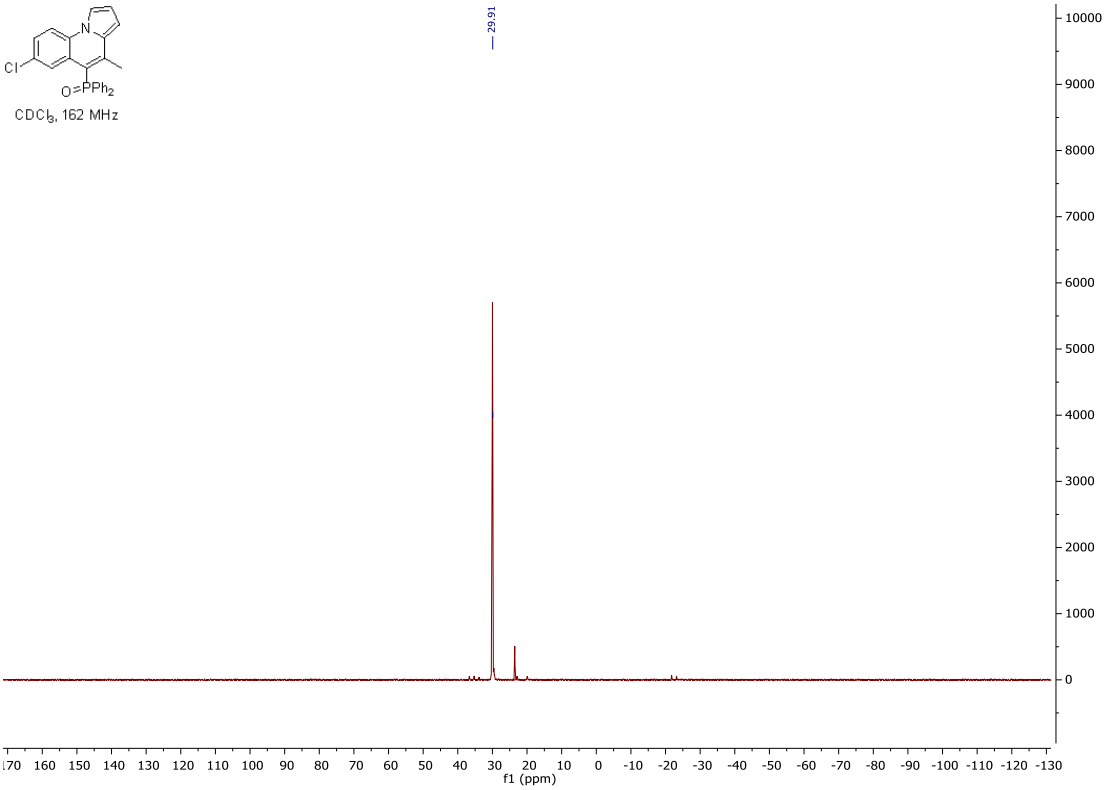

F
N
F
Ph
O=P(OEt)2
1r, 400 MHz, CDCl3
f1 (ppm)

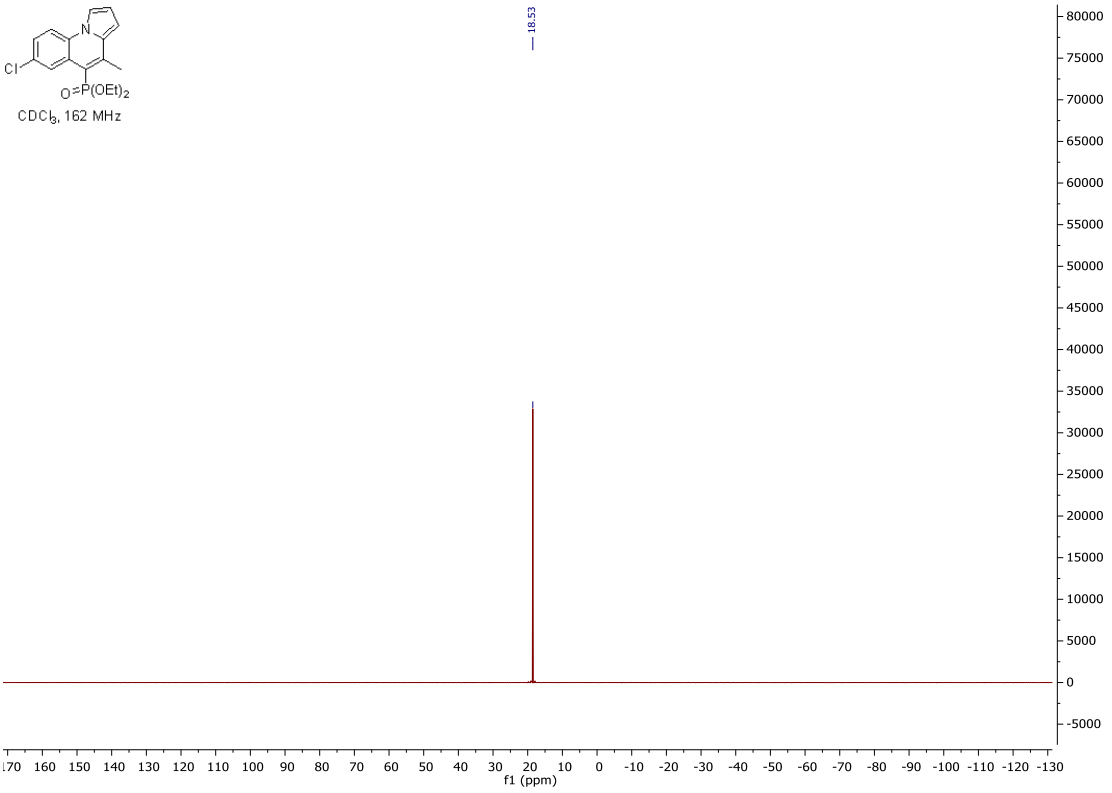

F
N
F
Ph
O=P(OEt)2
1r, 400 MHz, CDCl3
f1 (ppm)

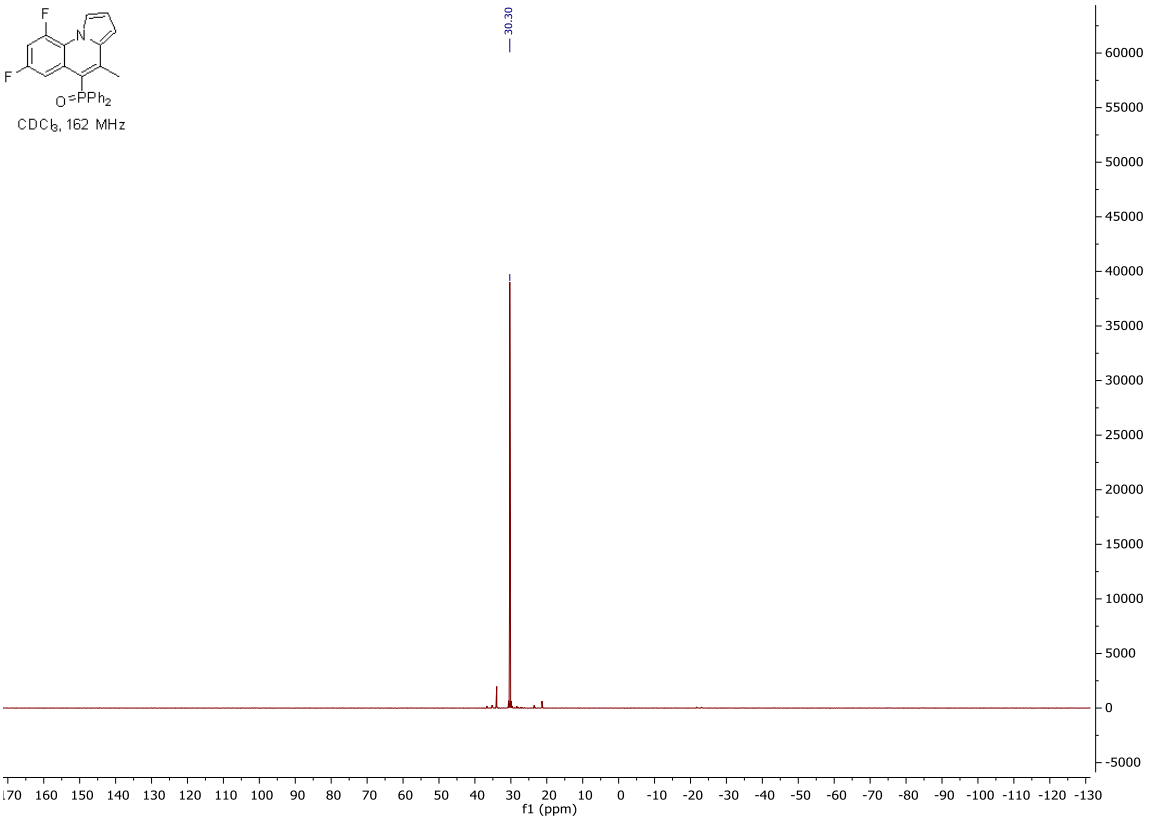

F
N
F
Ph
O=P(OEt)2
1r', 400 MHz, CDCl3
f1 (ppm)

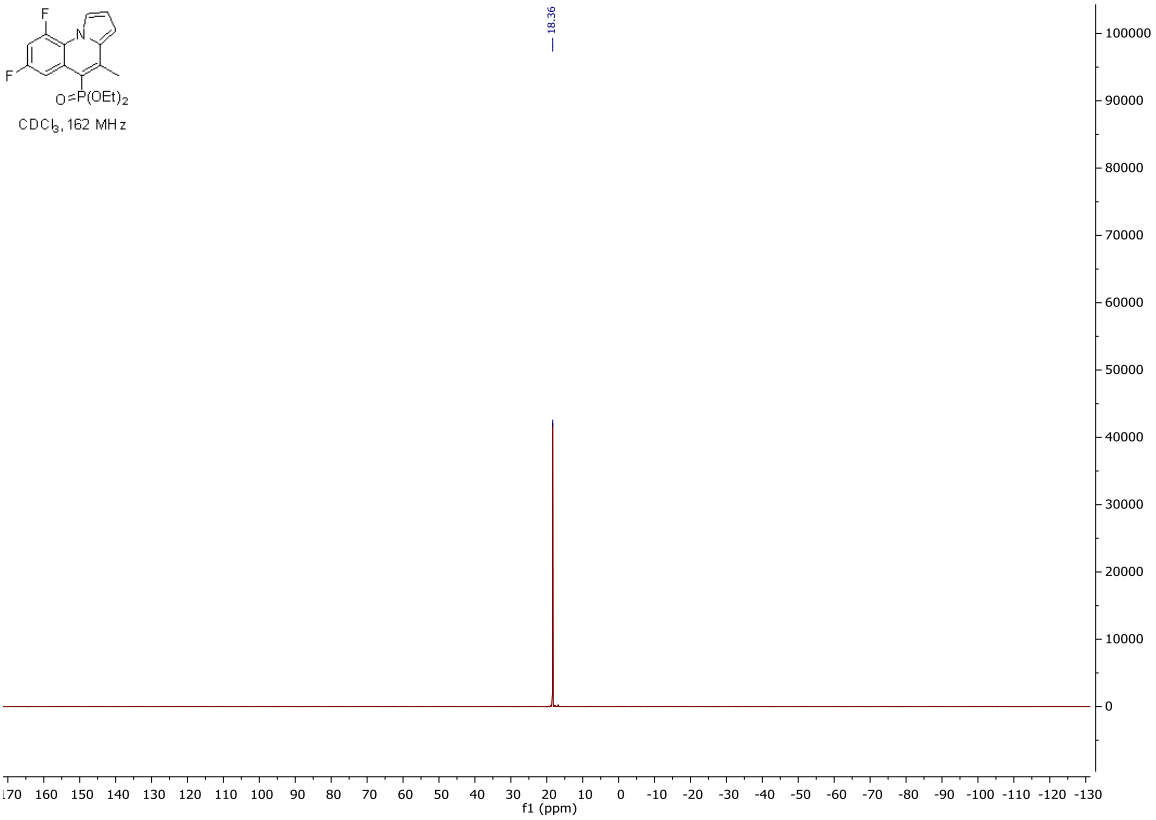

F
N
F
Ph
O=P(OEt)2
1r', 400 MHz, CDCl3
f1 (ppm)

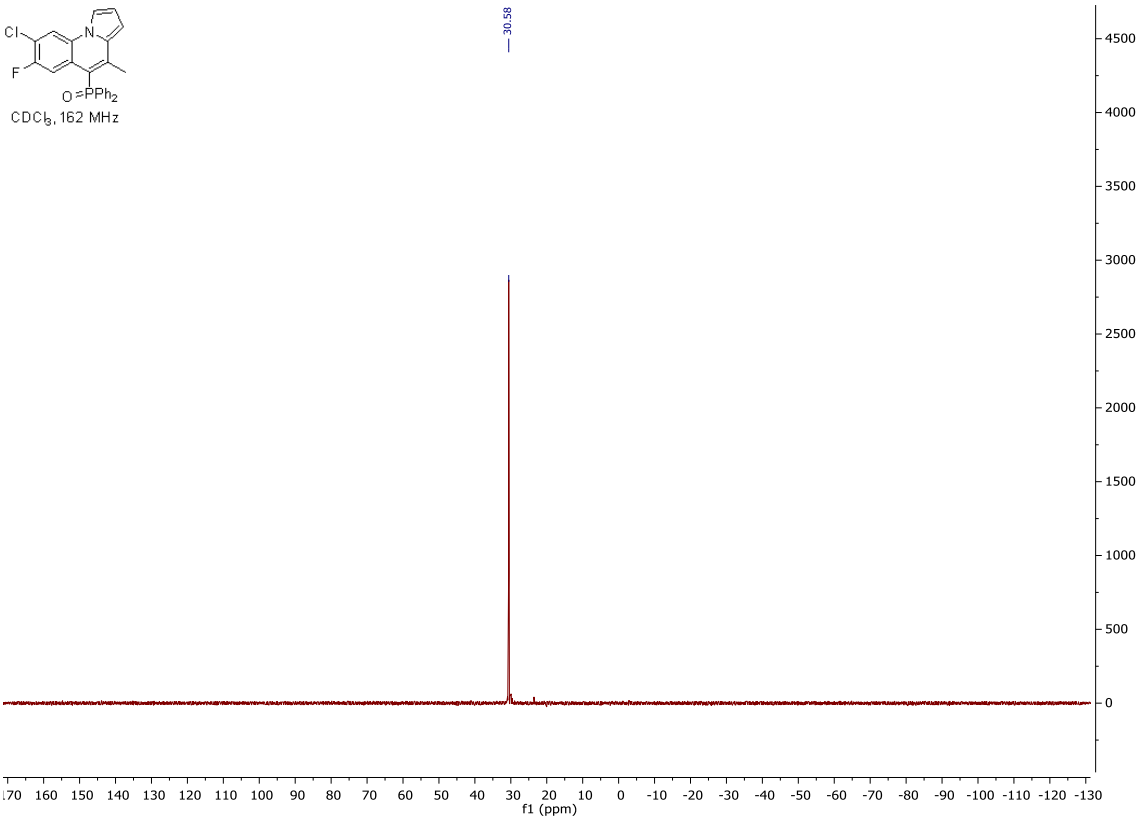
4. Copies of ^{31}P-NMR spectra:

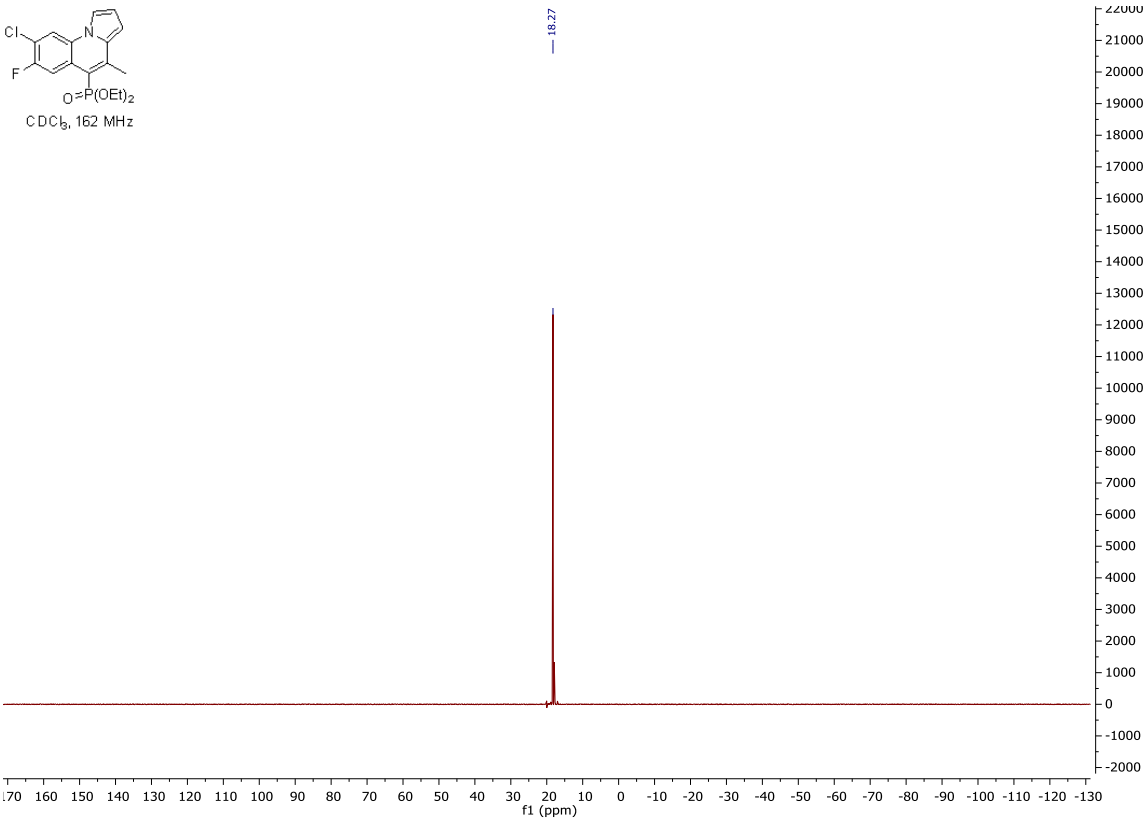


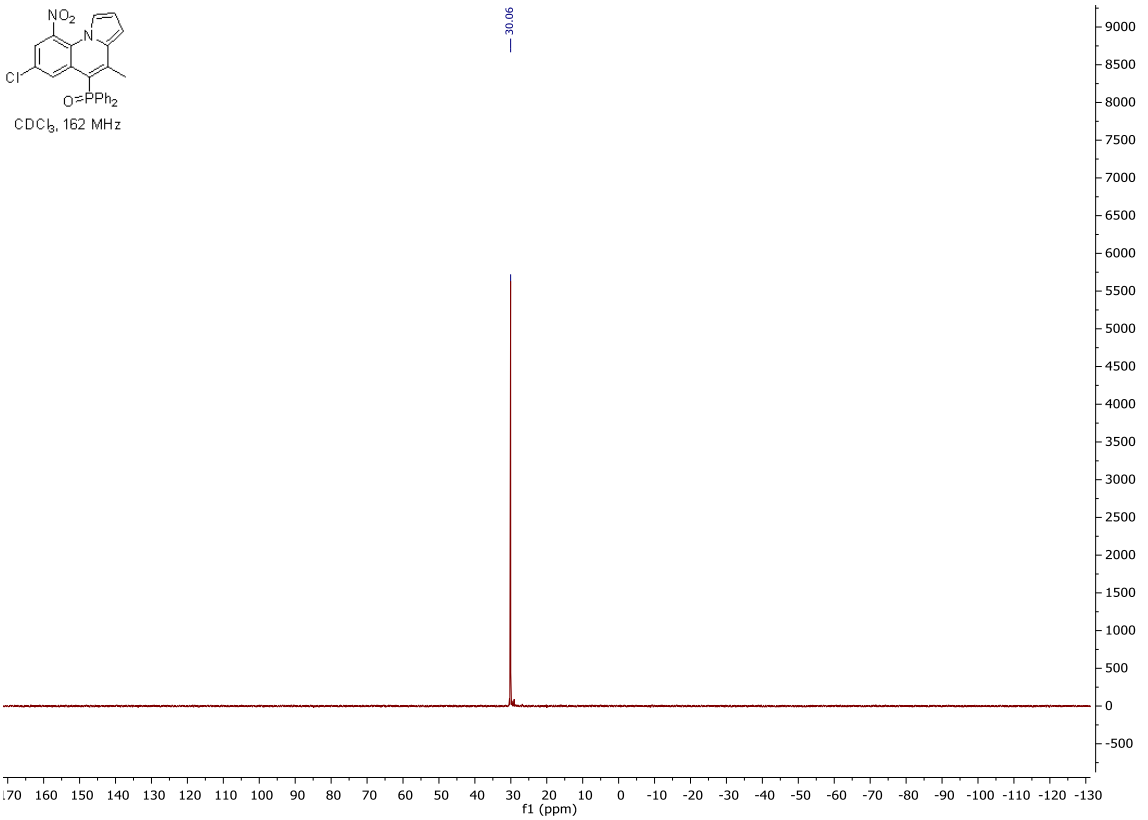


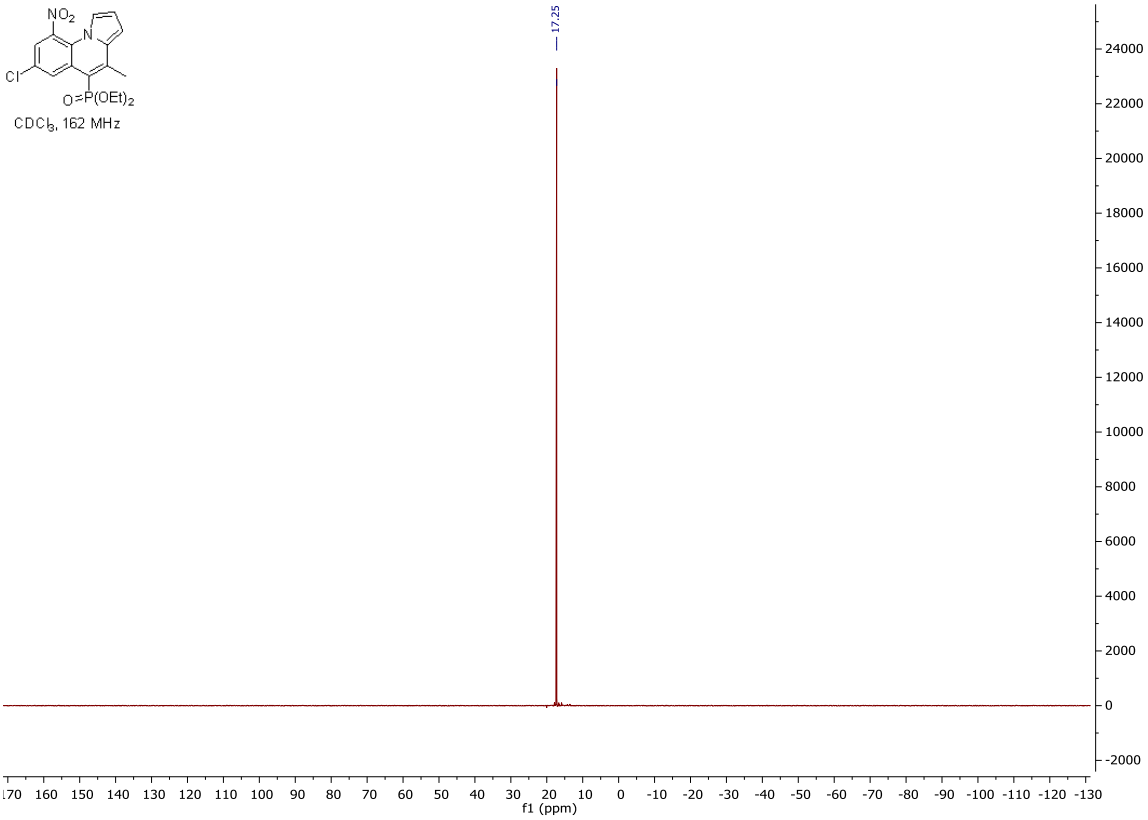

F
N
F
O=PPh2
CDCl3, 162 MHz
30.30
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

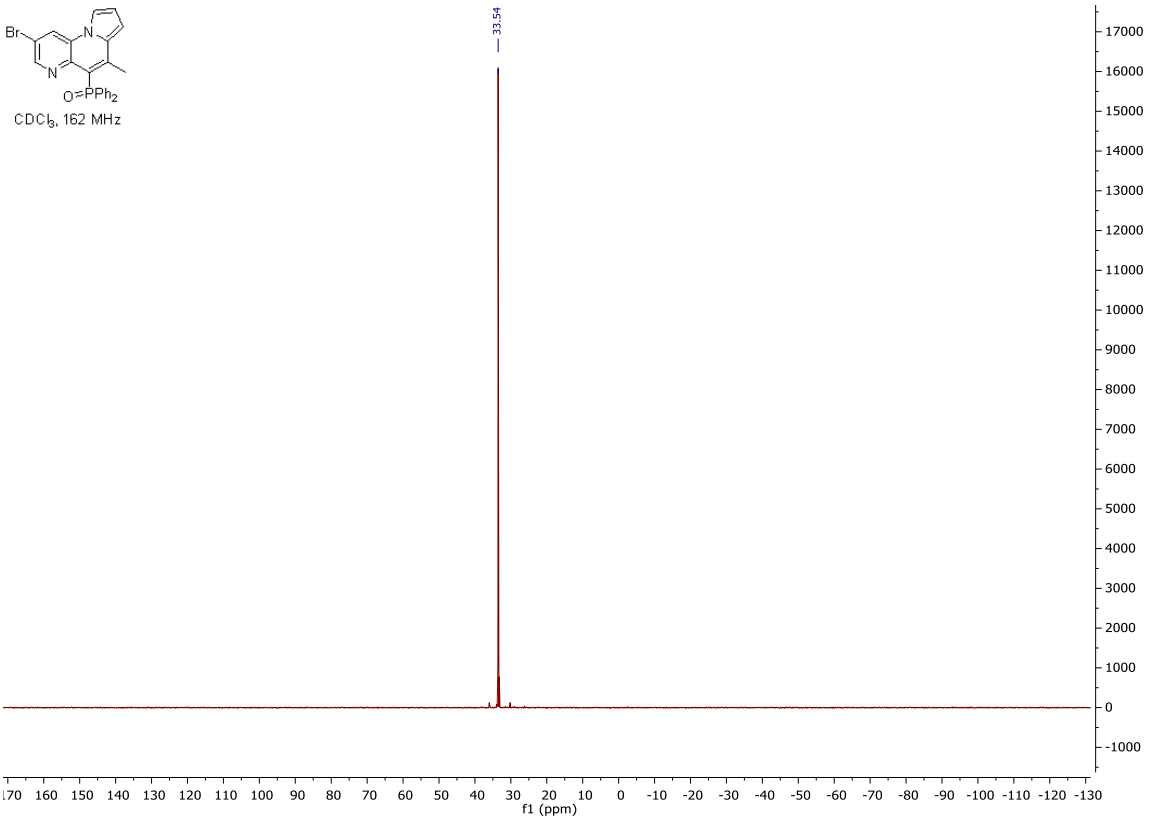

F
N
F
O=P(OEt)2
CDCl3, 162 MHz
18.36
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

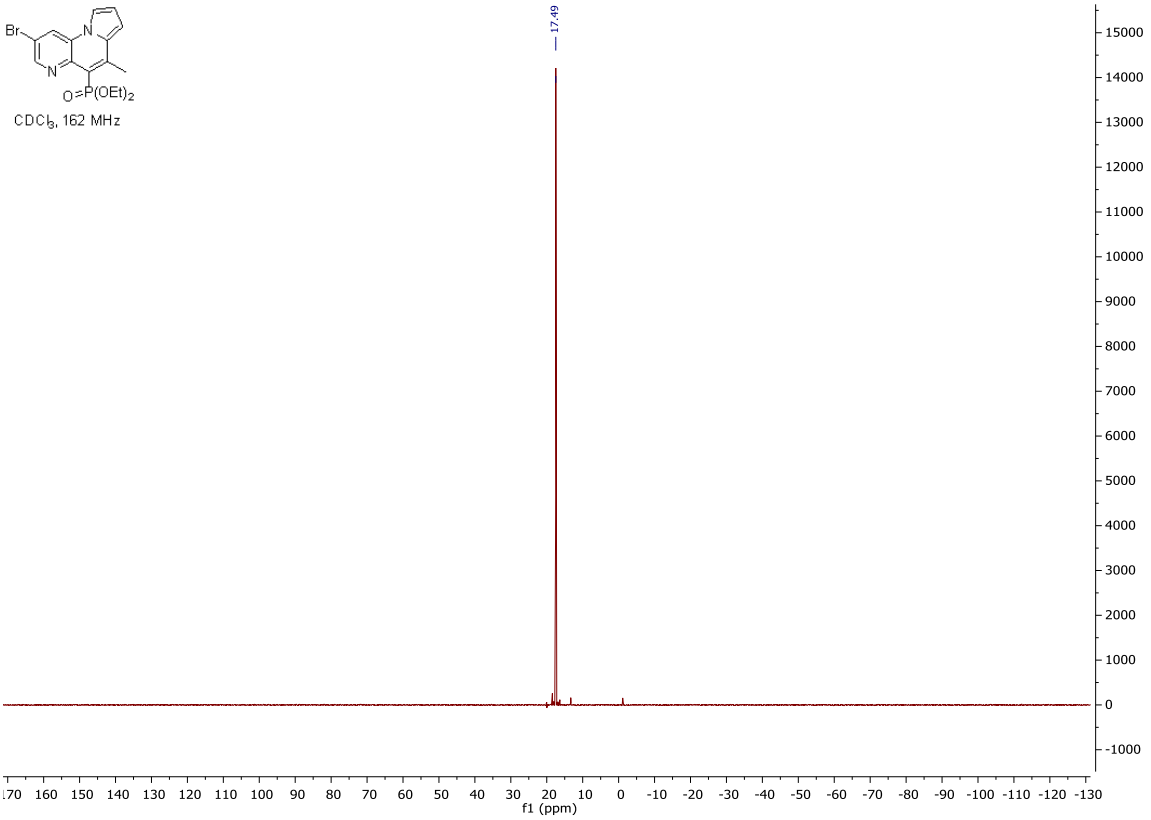

Cl
F
N
O=PPh2
CDCl3, 162 MHz
30.58
4500
4000
3500
3000
2500
2000
1500
1000
500
0
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

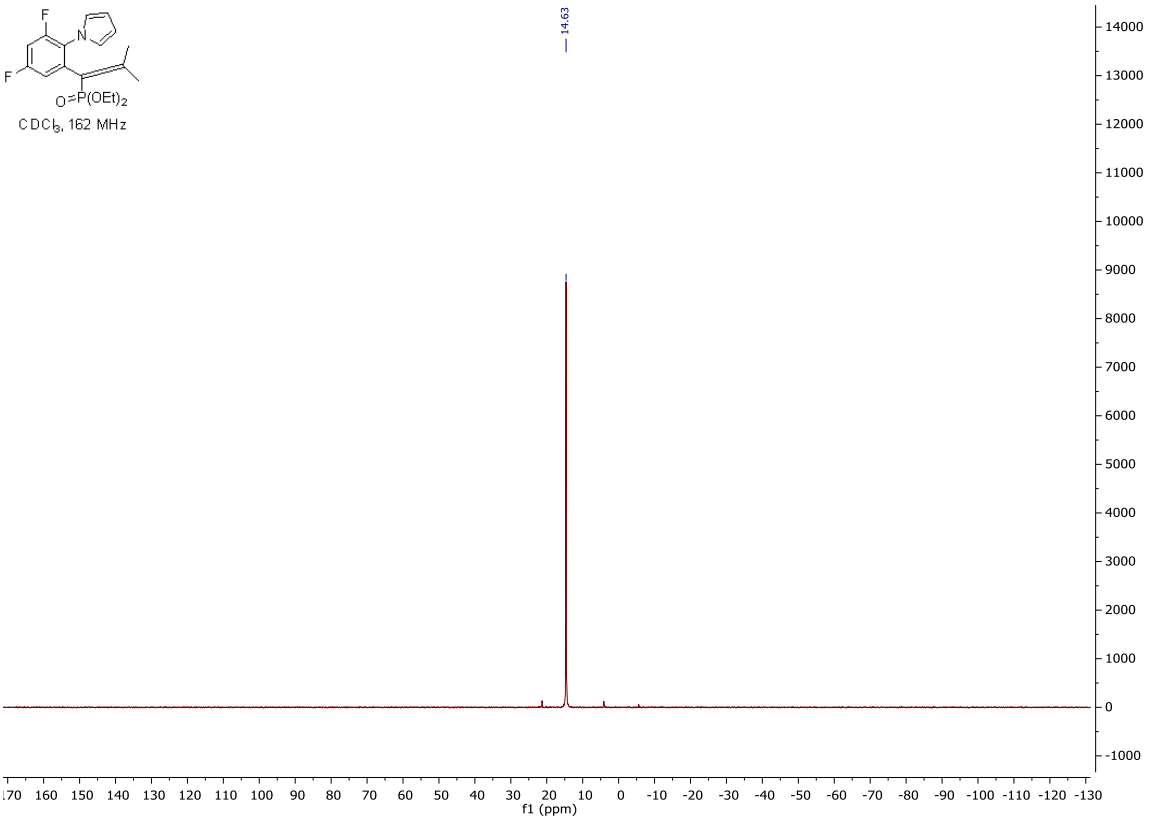

Cl
F
N
O=P(OEt)2
CDCl3, 162 MHz
18.27
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

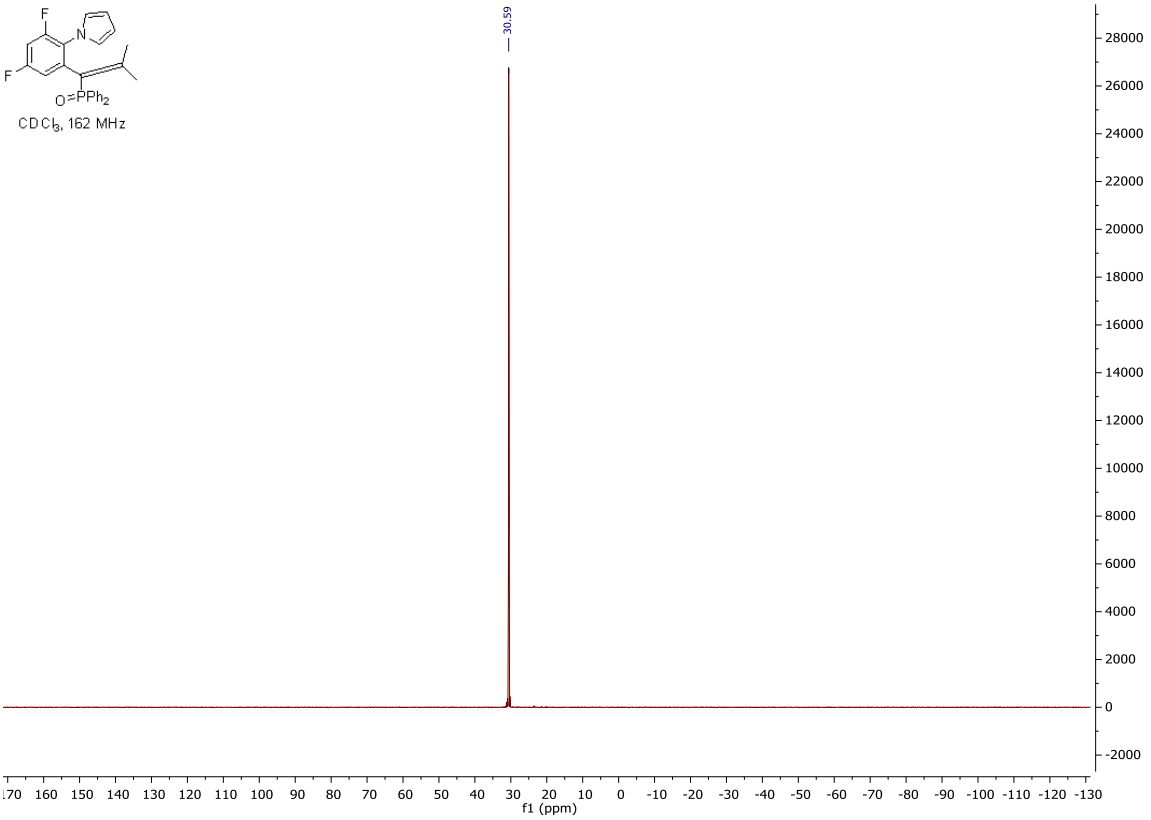

NO2
N
Cl
O=PPh2
CDCl3, 162 MHz
30.06
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

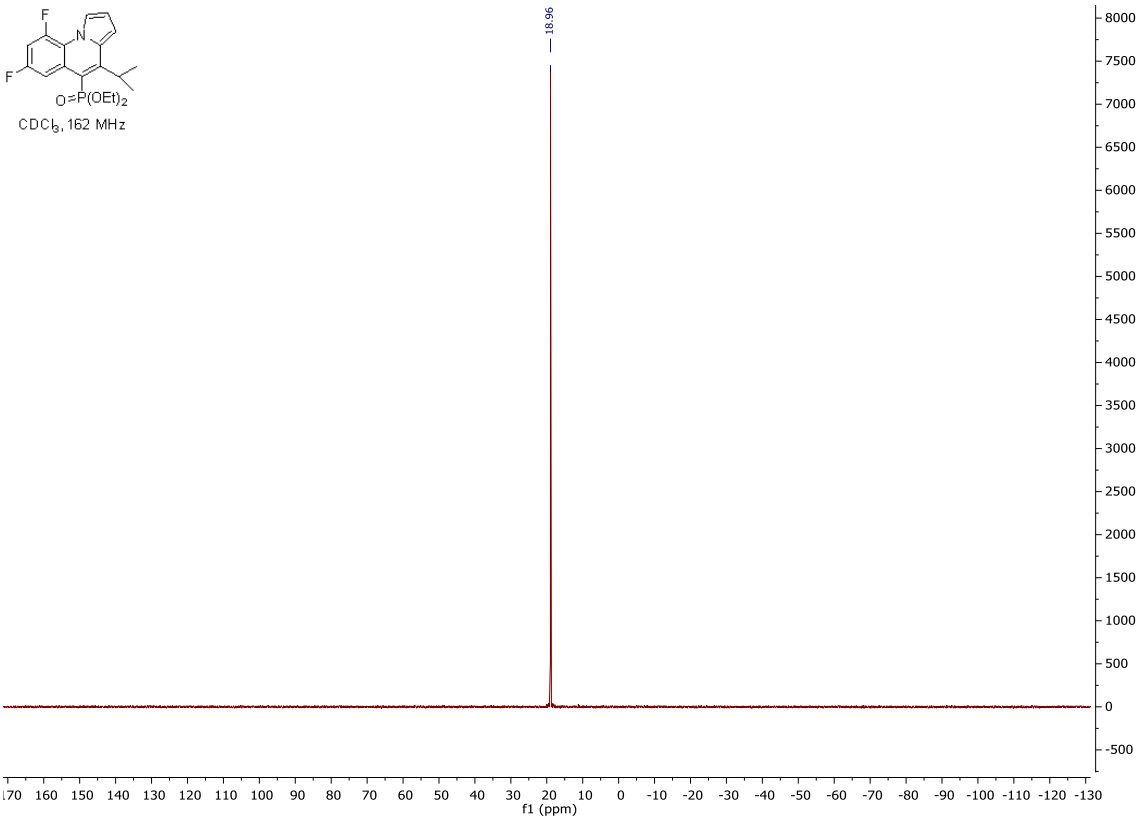

NO2
N
Cl
O=P(OEt)2
CDCl3, 162 MHz
17.25
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

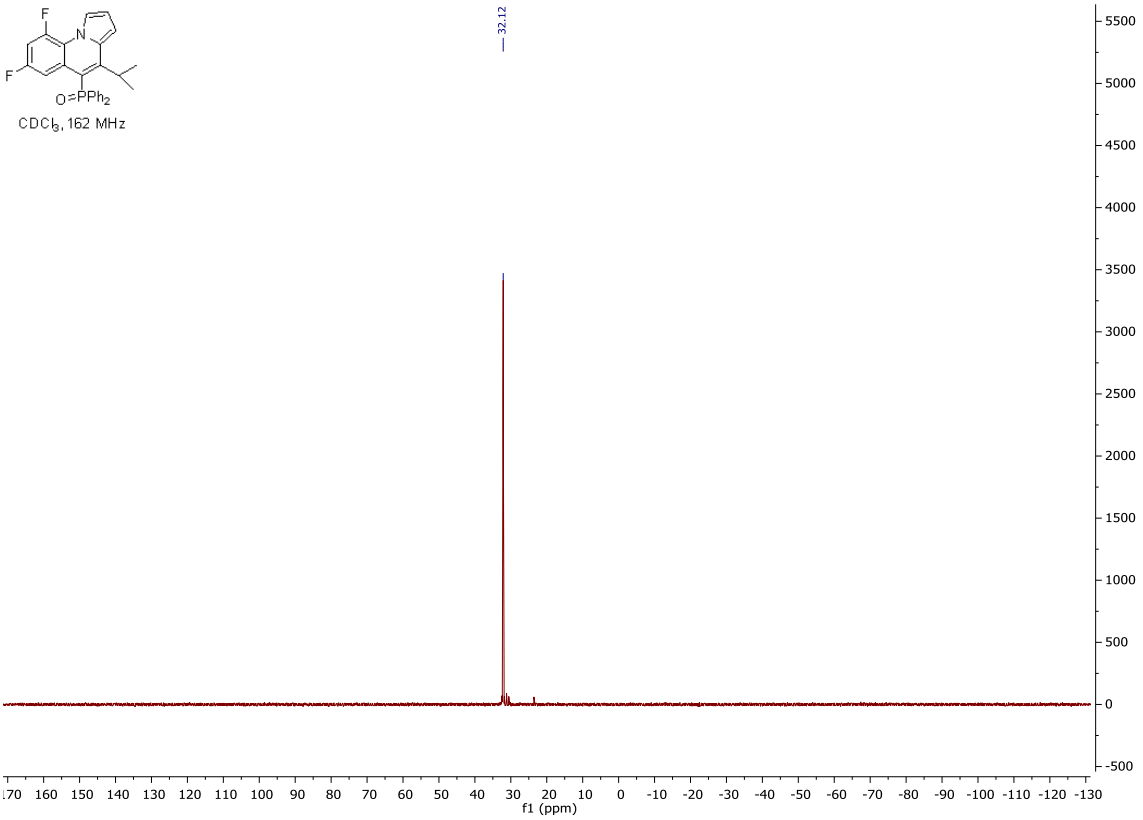

Br
N
N
O=PPh2
CDCl3, 162 MHz
33.54
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

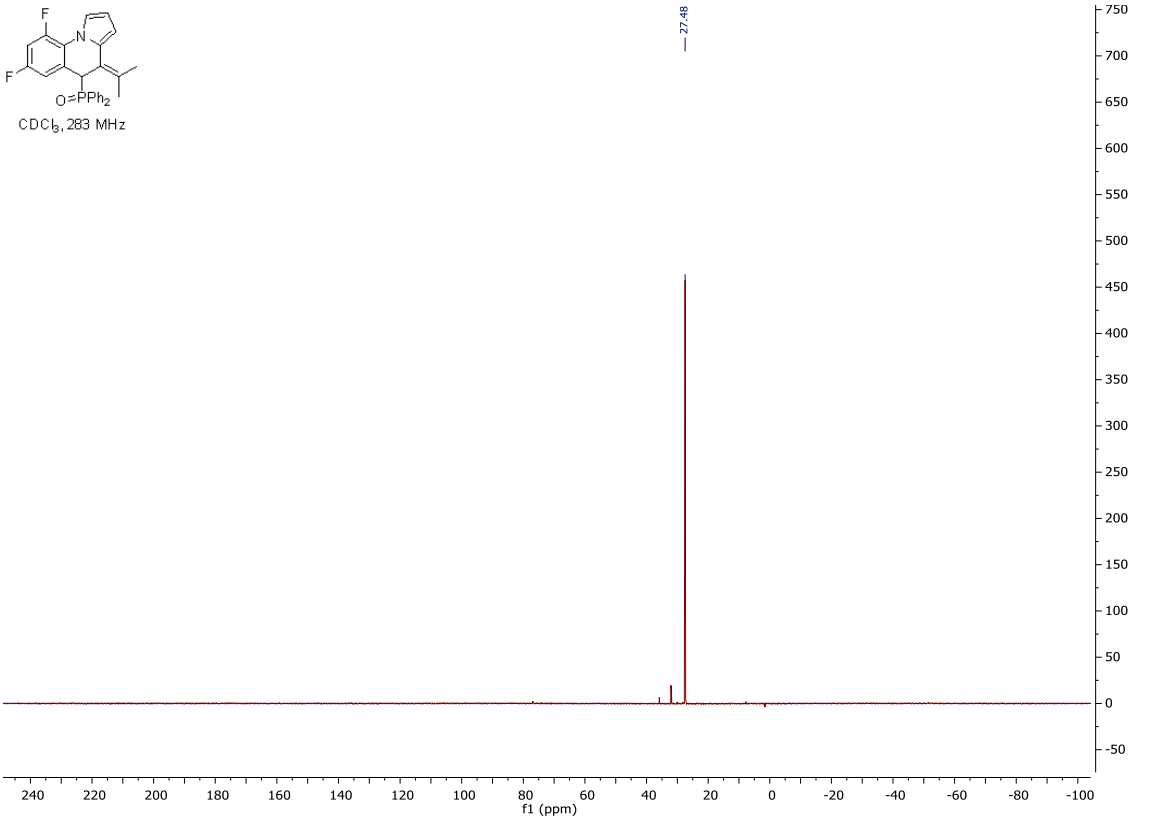

Br
N
N
O=P(OEt)2
CDCl3, 162 MHz
17.49
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

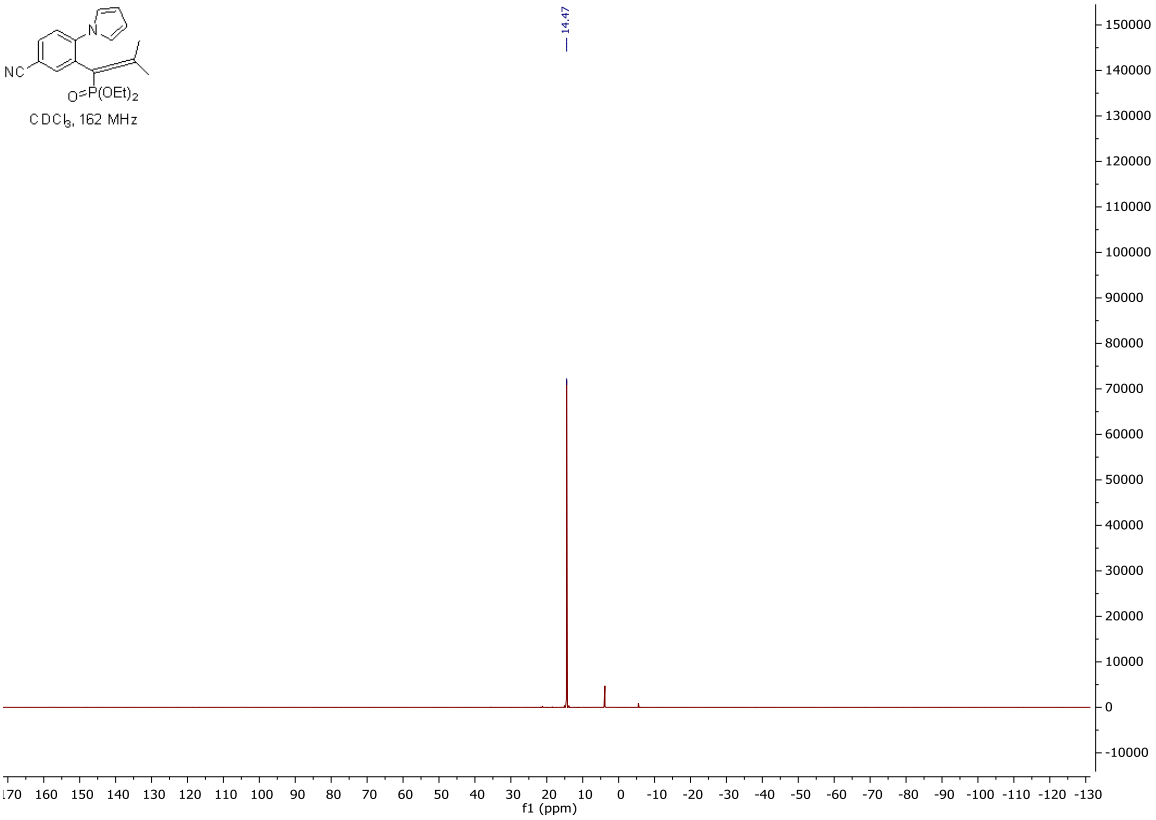

F
N
F
O=P(OEt)2
CDCl3, 162 MHz
14.63
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

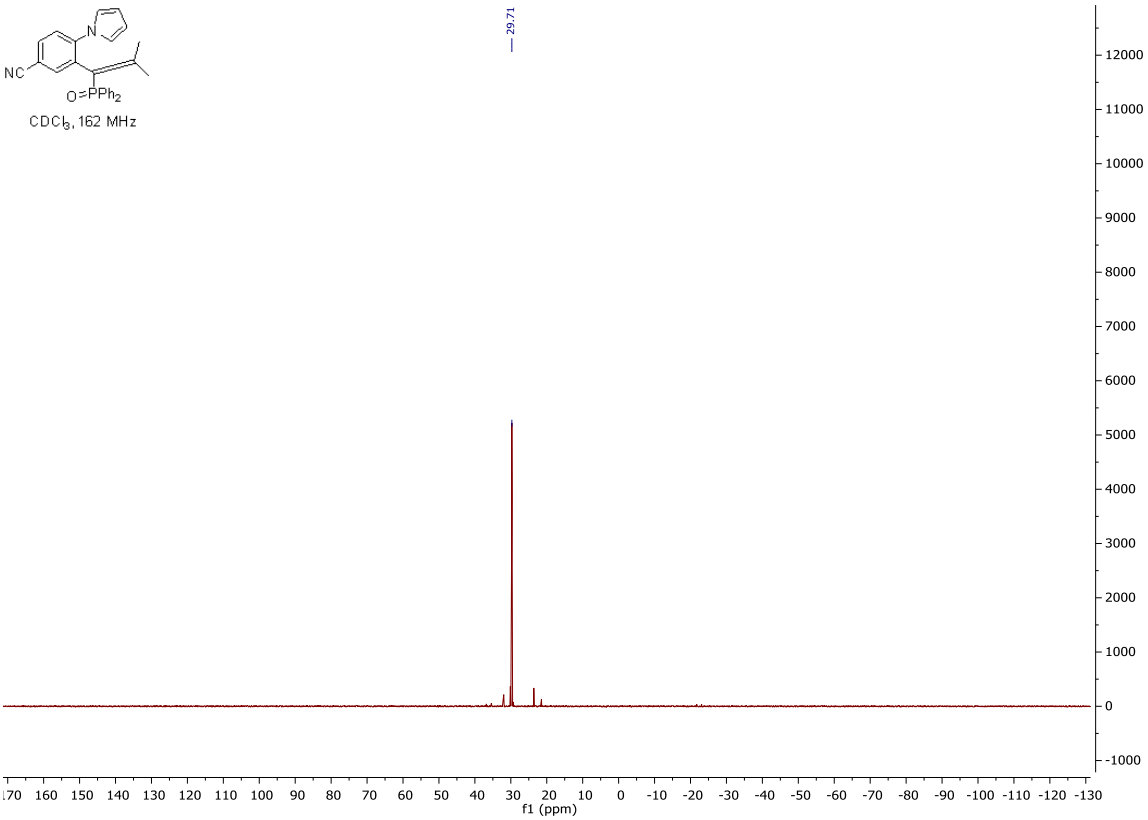

F
N
F
O=PPh2
CDCl3, 162 MHz
30.59
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

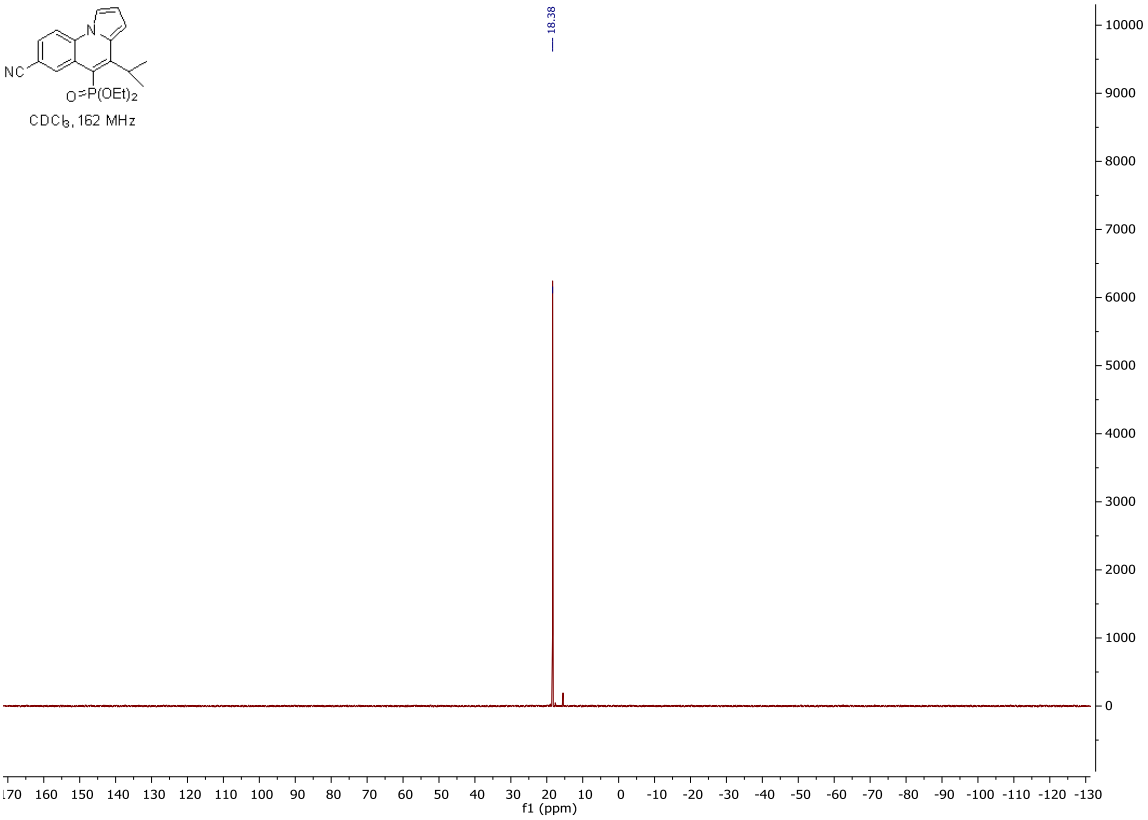

F
N
F
O=P(OEt)2
CDCl3, 162 MHz
18.96
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

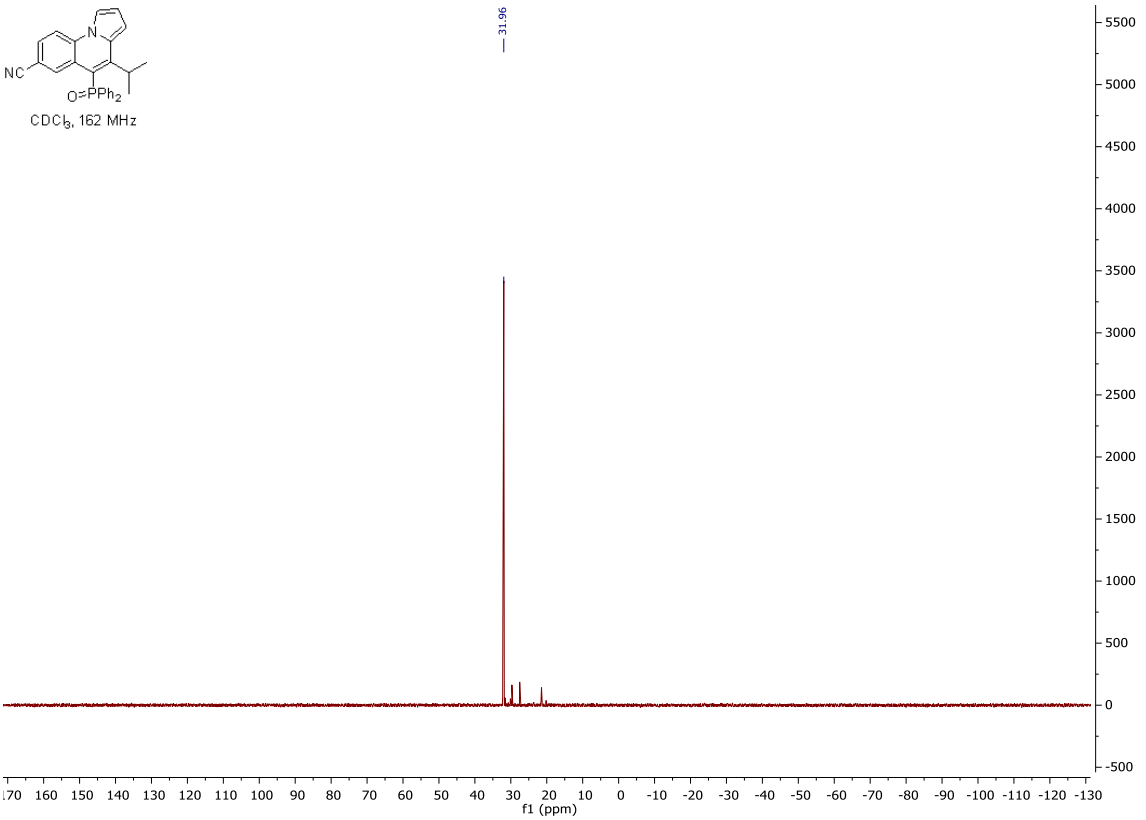

F
N
F
O=PPh2
CDCl3, 162 MHz
32.12
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

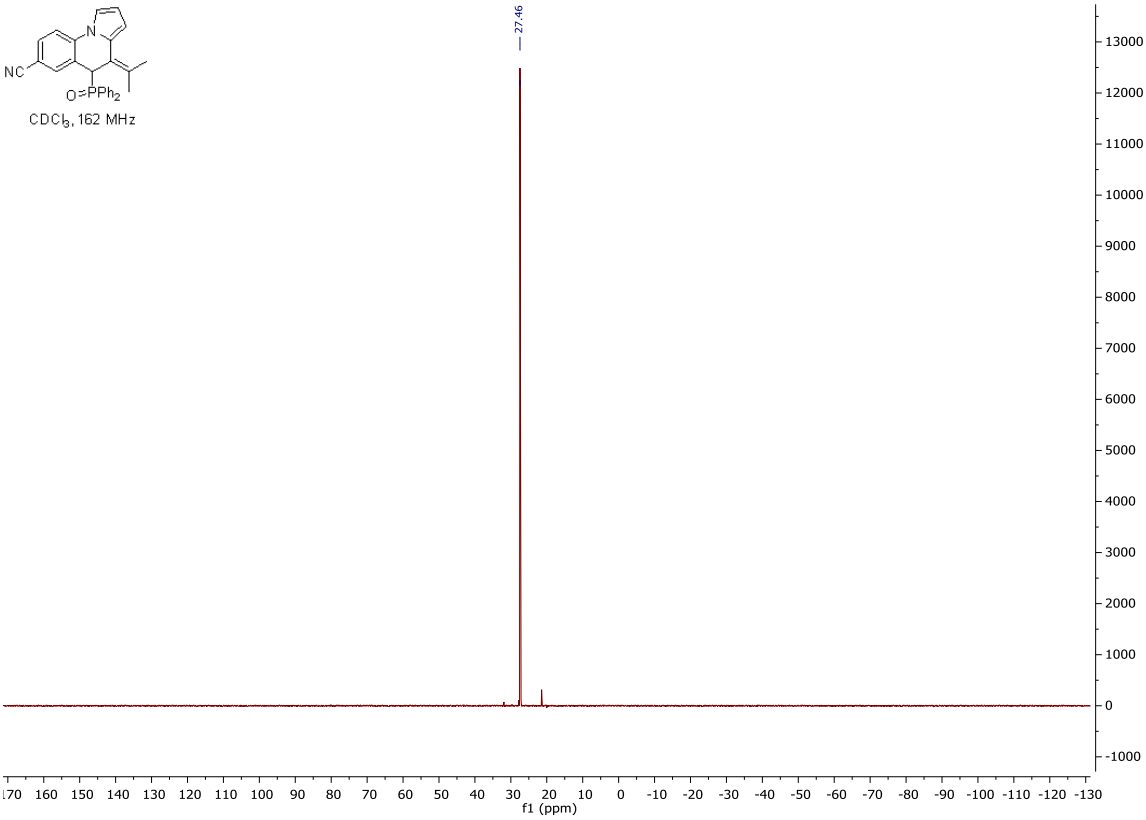

F
N
F
O=PPh2
CDCl3, 283 MHz
27.48
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100
f1 (ppm)

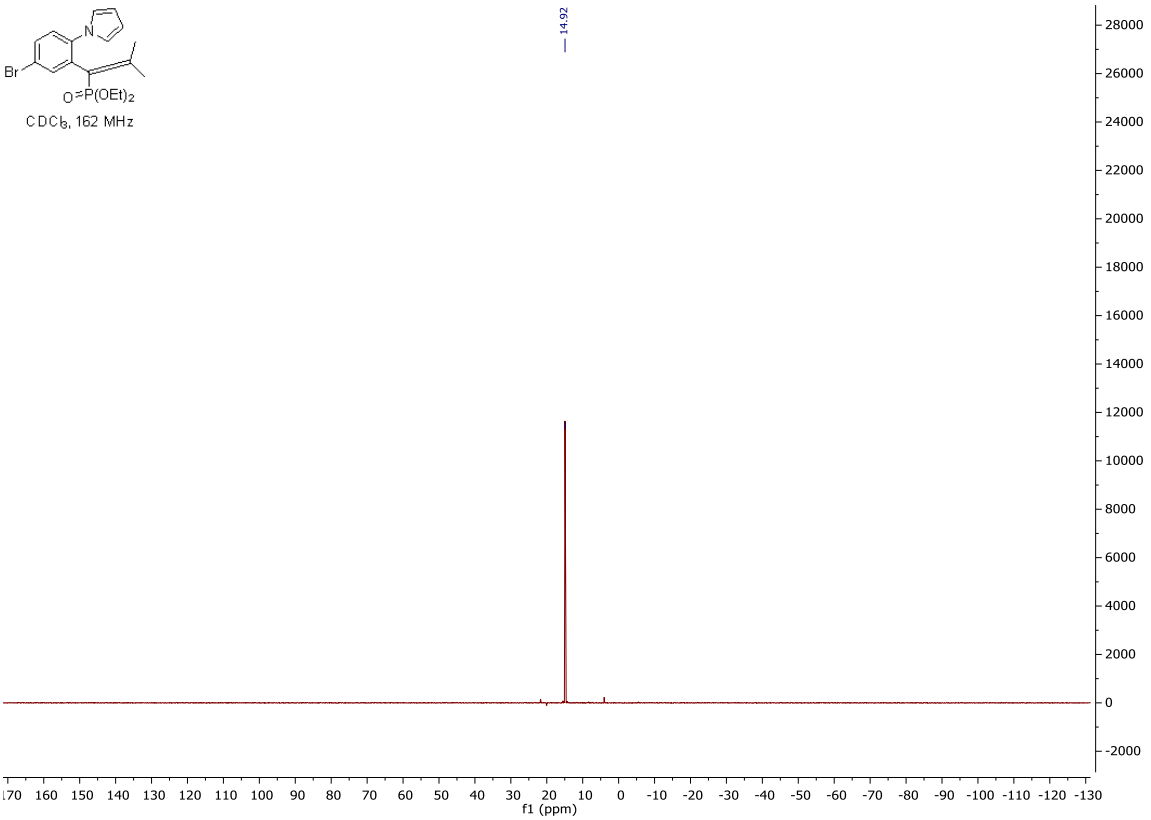

N
NC
O=P(OEt)2
CDCl3, 162 MHz
14.47
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

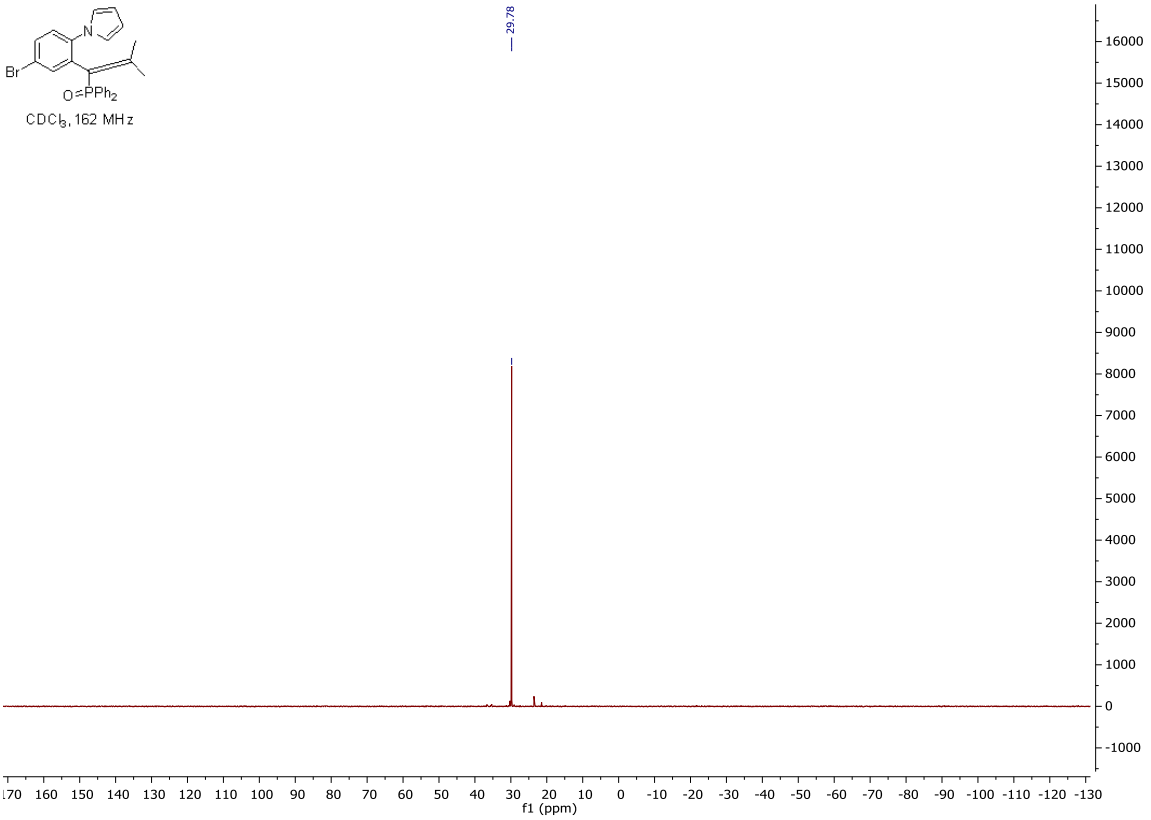

NC
O=PPh2
CDCl3, 162 MHz
29.71
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

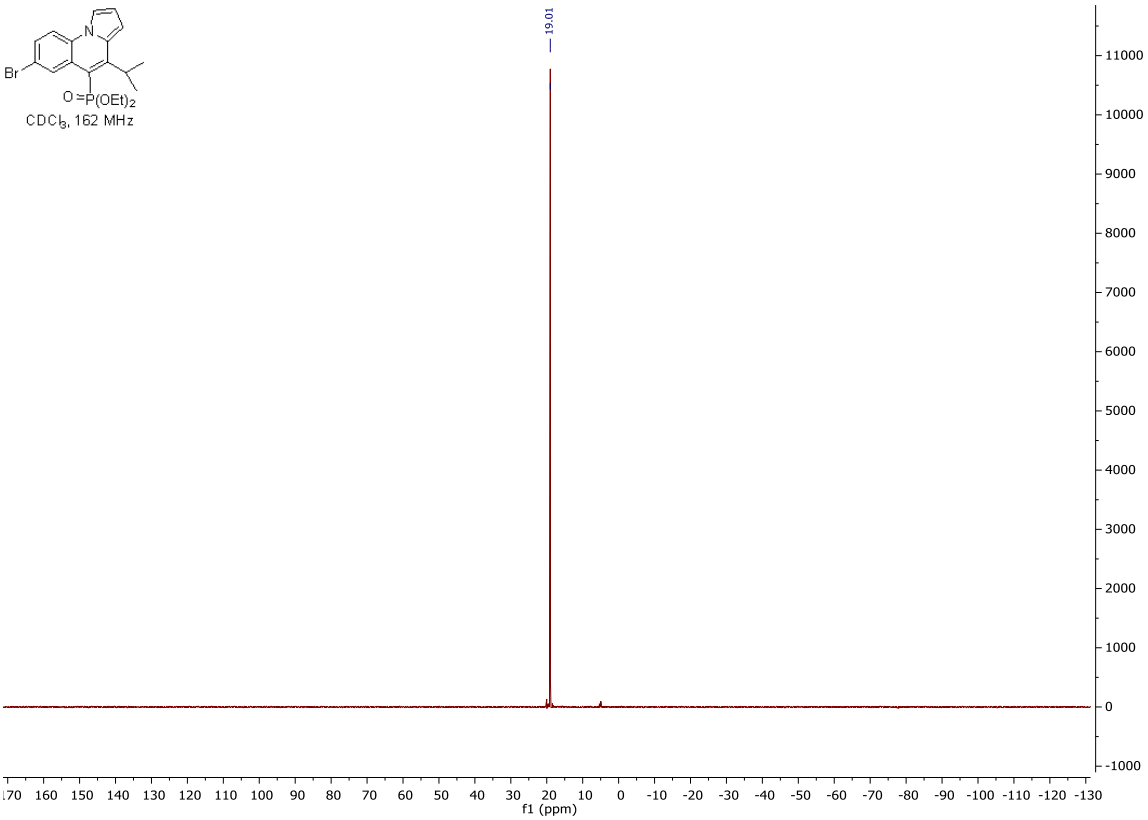

NC
O=P(OEt)2
CDCl3, 162 MHz
18.38
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

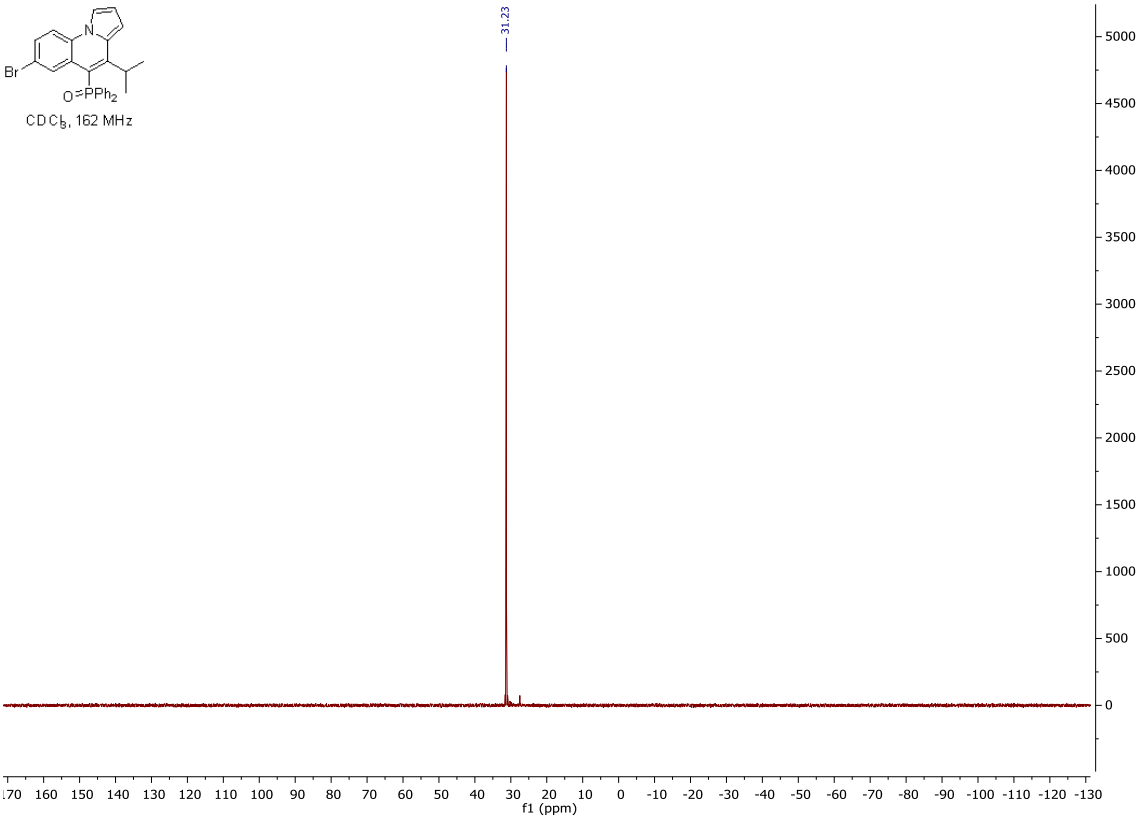

NC
O=PPh2
CDCl3, 162 MHz
31.96
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

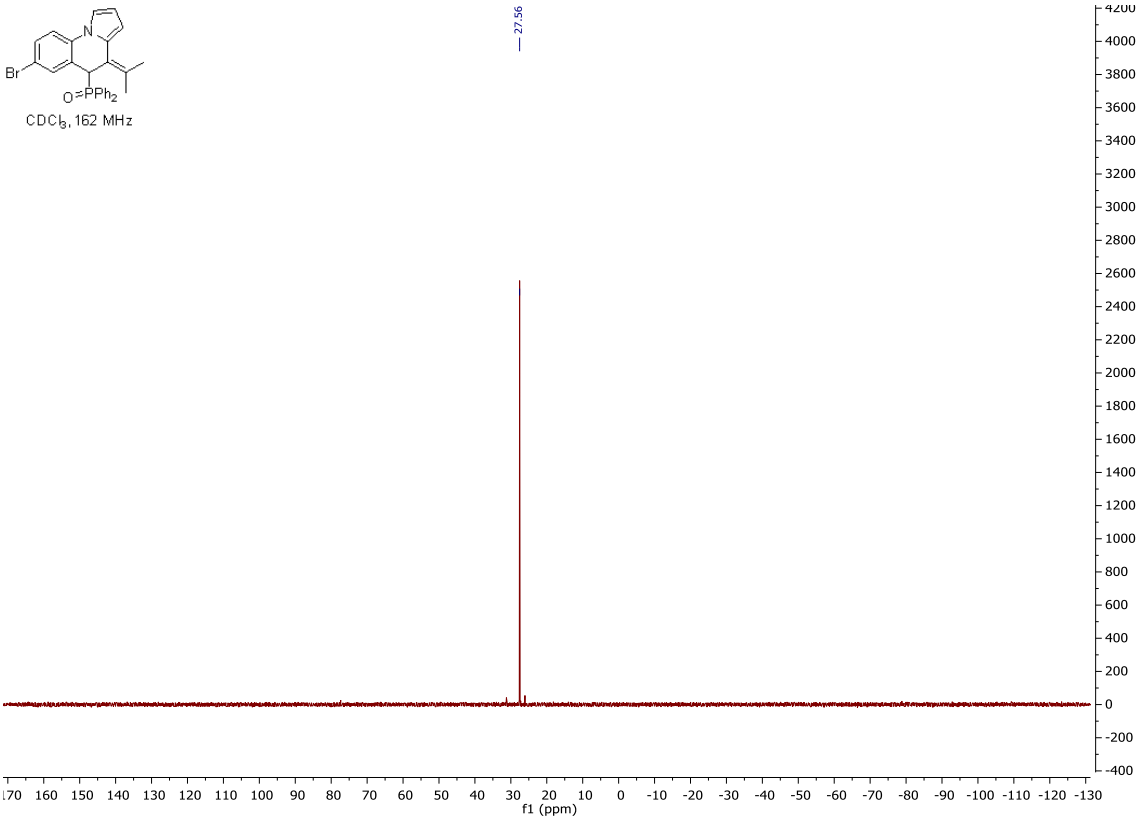

NC
O=PPh2
CDCl3, 162 MHz
27.46
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

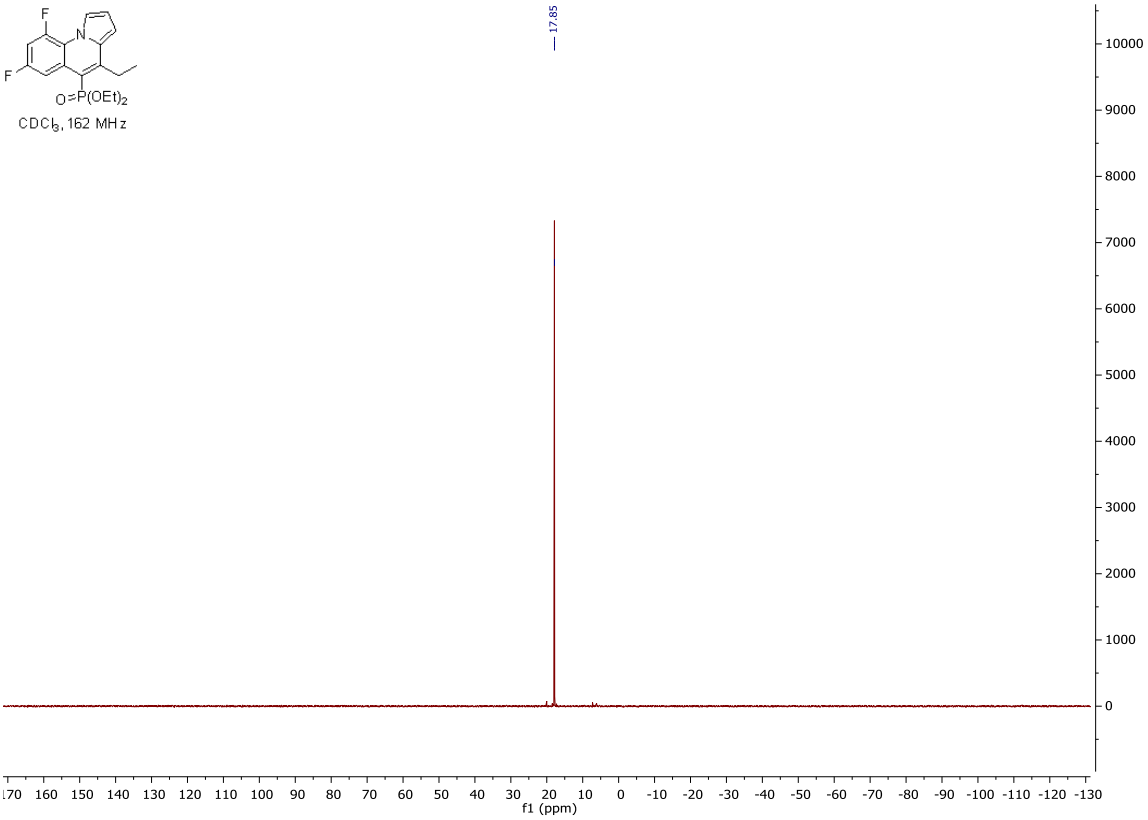

Br
O=P(OEt)2
CDCl3, 162 MHz
14.92
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

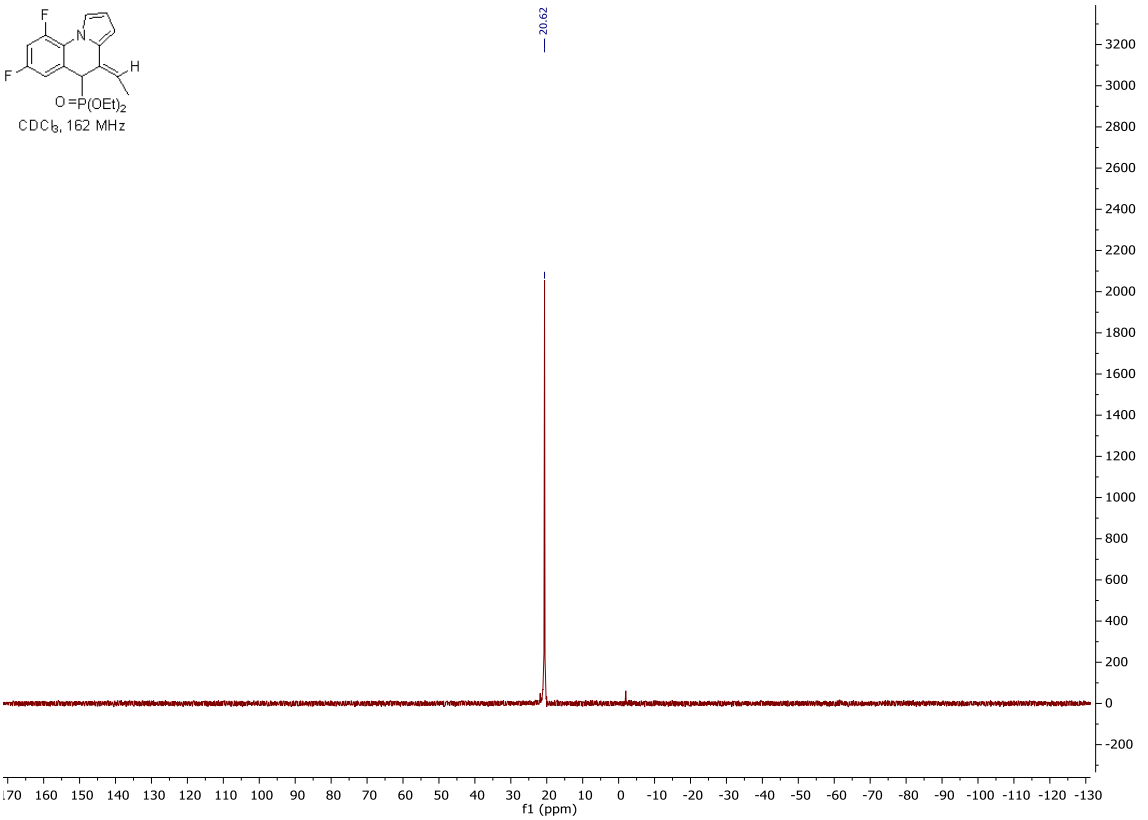

Br
O=PPh2
CDCl3, 162 MHz
29.78
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

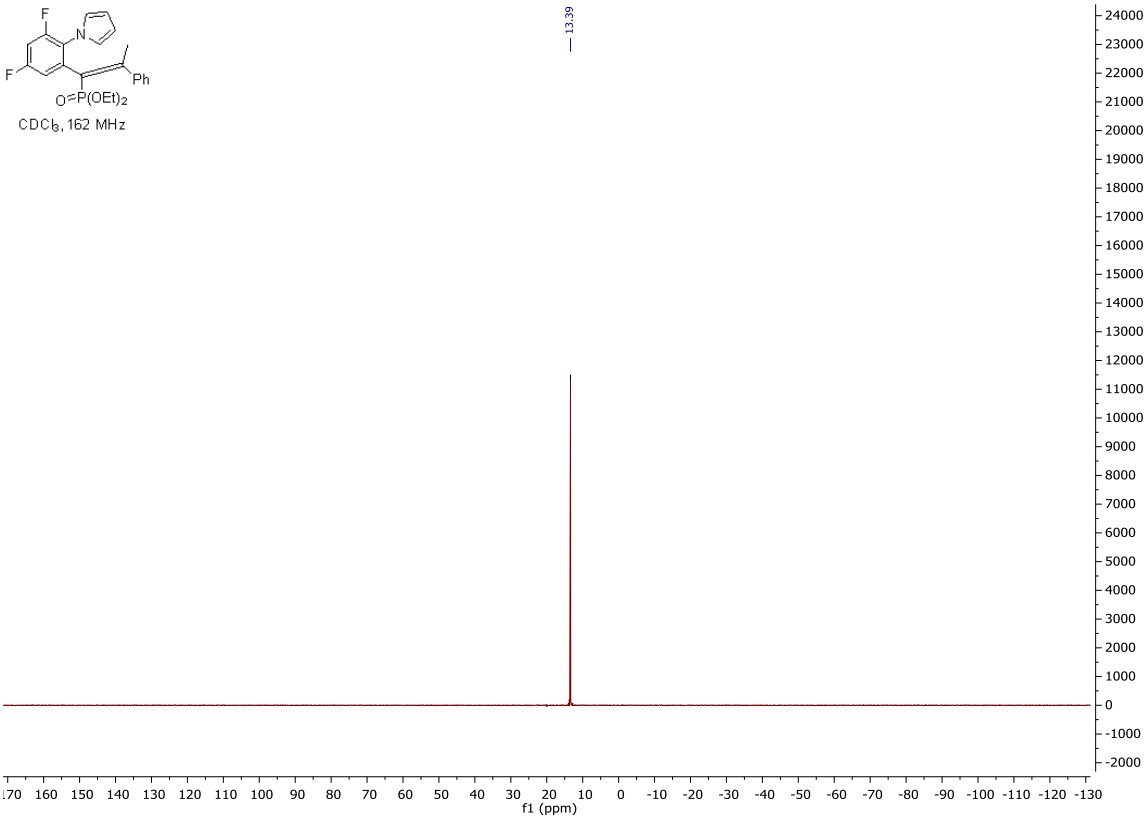

Br
O=P(OEt)2
CDCl3, 162 MHz
19.01
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

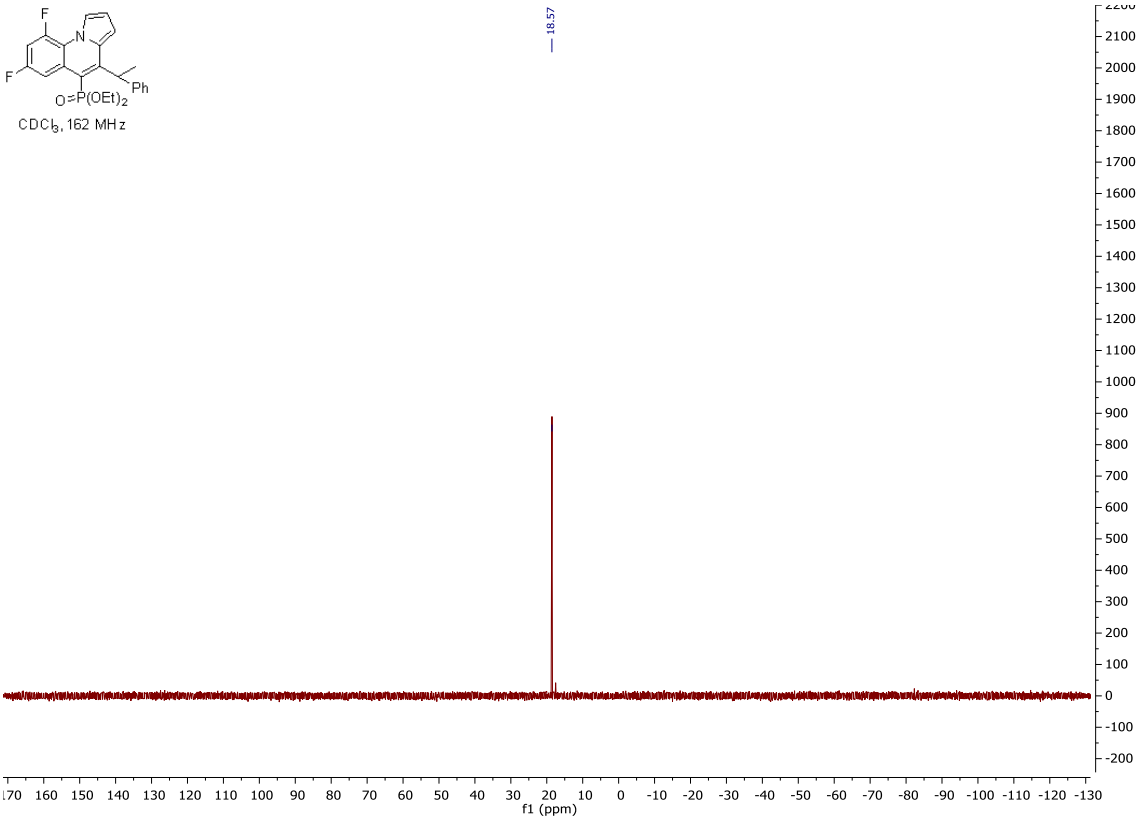

Br
O=PPh2
CDCl3, 162 MHz
31.23
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

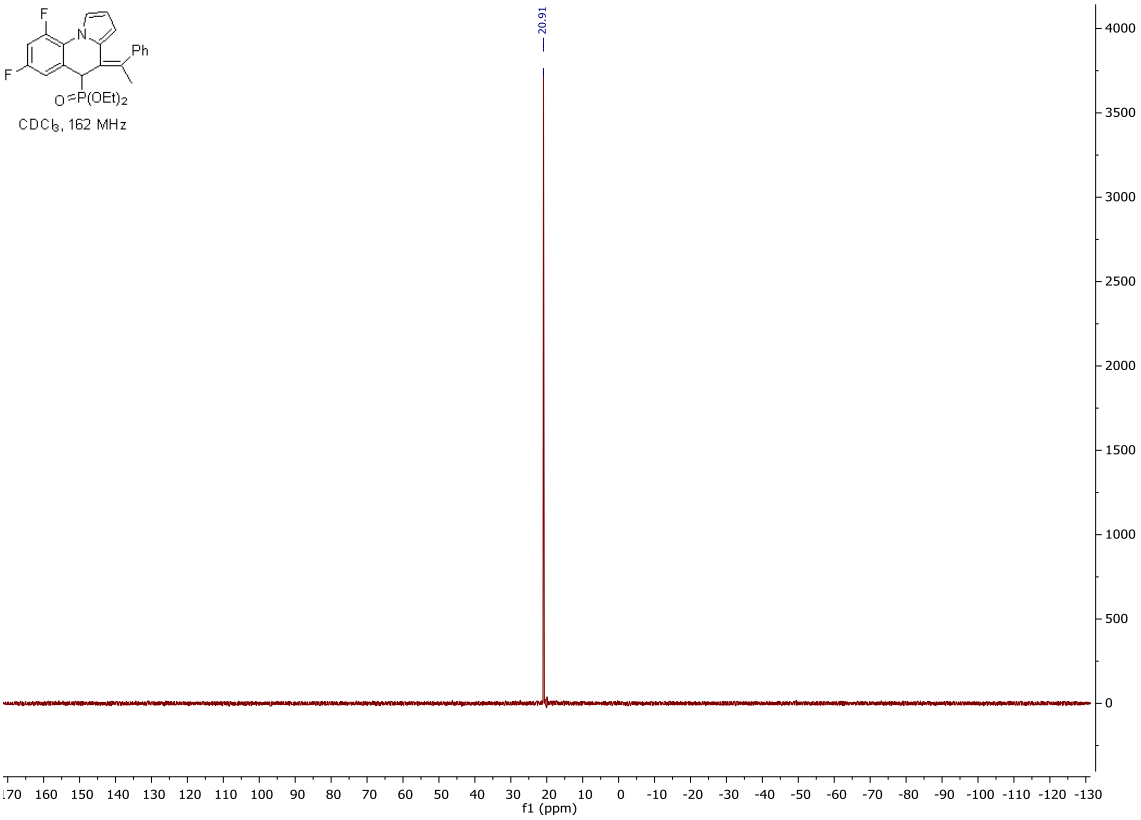

Br
O=PPh2
CDCl3, 162 MHz
27.56
f1 (ppm)


F
F
O=P(OEt)2
CDCl3, 162 MHz
17.85
f1 (ppm)


F
N
F
H
O=P(OEt)2
CDCl3, 162 MHz
20.62
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

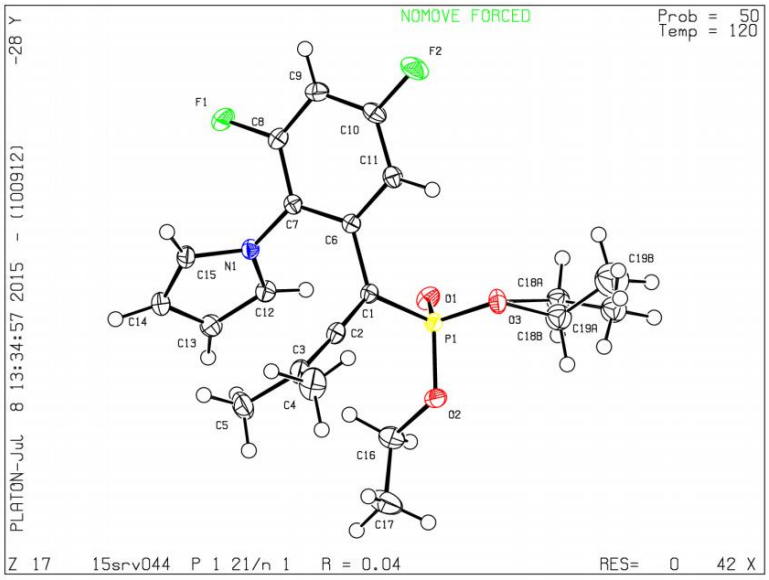

F
N
F
Ph
O=P(OEt)2
CDCl3, 162 MHz
13.39
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)


F
N
F
Ph
O=P(OEt)2
CDCl3, 162 MHz
18.57
f1 (ppm)


F
N
Ph
F
O=P(OEt)2
CDCl3, 162 MHz
20.91
f1 (ppm)

5. Single crystal X-ray diffraction data:

Diethyl (1-(3,5-difluoro-2-(1H-pyrrol-1-yl)phenyl)-3-methylbuta-1,2-dien-1-yl)phosphonate, 2f:



X-ray Structure of 2f *(shown at 50% probability level).*

Table 1 Crystal data and structure refinement for **2f**.	
Identification code	15srv044
Empirical formula	$C_{19}H_{22}F_2NO_3P$
Formula weight	381.35
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.01820(10)
b/Å	14.4498(2)
c/Å	16.8318(2)

α/°	90.00
β/°	100.2909(17)
γ/°	90.00
Volume/Å^3	1918.78(4)
Z	4
ρ_{calc}g/cm^3	1.320
μ/mm^{-1}	0.180
F(000)	800.0
Crystal size/mm^3	0.33 × 0.3 × 0.19
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.92 to 60
Index ranges	-11 ≤ h ≤ 11, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23
Reflections collected	41798
Independent reflections	5596 [R_{int} = 0.0319, R_{sigma} = 0.0194]
Data/restraints/parameters	5596/1/303
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0440, wR_2 = 0.1160
Final R indexes [all data]	R_1 = 0.0527, wR_2 = 0.1220
Largest diff. peak/hole / e Å^{-3}	0.70/-0.77

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 15srv044. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
P1	7158.7(4)	7358.0(2)	4274.5(2)	15.27(9)

F1	1317.3(12)	10049.1(6)	4082.4(6)	28.0(2)
F2	4730.9(13)	9520.0(7)	6598.1(5)	31.1(2)
O1	7521.1(13)	8200.4(7)	3844.3(6)	21.4(2)
O2	7471.2(13)	6420.7(7)	3846.5(6)	20.6(2)
O3	8282.5(12)	7231.9(8)	5134.8(6)	21.5(2)
N1	2537.7(14)	8514.5(8)	3414.5(7)	16.0(2)
C1	5026.5(16)	7338.6(9)	4447.7(8)	15.2(2)
C2	4059.2(17)	6609.4(10)	4267.4(8)	18.0(3)
C3	3043.6(18)	5912.8(10)	4059.6(10)	23.3(3)
C4	2765(2)	5166.3(13)	4646.3(13)	35.7(4)
C5	2081(2)	5830.6(12)	3206.5(12)	34.0(4)
C6	4334.3(16)	8214.7(9)	4741.3(8)	14.8(2)
C7	3115.3(16)	8744.6(9)	4235.7(8)	15.4(2)
C8	2467.5(17)	9522.4(10)	4565.2(8)	18.8(3)
C9	2958.5(18)	9796.9(10)	5356.5(9)	20.7(3)
C10	4192.1(18)	9265(1)	5823.2(8)	20.5(3)
C11	4899.7(17)	8491.5(10)	5537.3(8)	18.5(3)
C12	3542.3(17)	8427.8(10)	2832.0(8)	18.6(3)
C13	2506.1(19)	8214.6(10)	2117.5(8)	21.7(3)
C14	819.6(18)	8169.4(11)	2268.8(9)	23.2(3)
C15	870.5(17)	8357.9(10)	3066.8(9)	19.9(3)
C16	6928(2)	6333.9(12)	2976.2(9)	27.7(3)
C17	6771(3)	5326.2(14)	2772.3(13)	41.0(4)
C18A	10093(4)	7514(3)	5222(2)	23.5(8)
C18B	10126(5)	7262(3)	5164(2)	29.5(9)

C19B	10954(6)	7364(4)	6037(3)	51.4(11)
C19A	11041(4)	6941(3)	5929(2)	29.2(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 15srv044. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P1	13.62(16)	15.76(16)	16.38(16)	0.00(11)	2.51(11)	0.58(11)
F1	28.7(5)	24.5(4)	28.5(5)	-0.3(4)	-1.2(4)	12.1(4)
F2	41.8(6)	34.7(5)	15.4(4)	-7.7(4)	1.4(4)	1.1(4)
O1	19.4(5)	19.5(5)	26.9(5)	3.6(4)	8.6(4)	1.0(4)
O2	22.6(5)	18.8(5)	20.3(5)	-2.4(4)	3.7(4)	3.6(4)
O3	14.6(4)	29.6(5)	18.9(5)	-0.2(4)	-0.7(3)	-0.9(4)
N1	14.5(5)	18.8(5)	14.2(5)	0.8(4)	1.2(4)	1.1(4)
C1	14.5(5)	16.0(6)	14.8(5)	1.5(4)	2.2(4)	1.2(4)
C2	16.5(6)	18.6(6)	18.3(6)	3.1(5)	1.9(4)	2.8(5)
C3	18.0(6)	17.7(6)	32.2(7)	2.5(5)	-0.9(5)	-0.5(5)
C4	30.8(9)	25.1(8)	49.7(11)	10.9(7)	3.0(8)	-6.7(6)
C5	30.1(8)	25.2(8)	39.8(9)	-3.8(7)	-12.1(7)	-3.1(6)
C6	14.4(5)	15.1(5)	15.2(5)	0.8(4)	3.9(4)	-1.1(4)
C7	14.5(5)	17.3(6)	14.6(5)	0.2(4)	3.1(4)	-1.6(4)
C8	17.5(6)	18.1(6)	20.7(6)	2.1(5)	3.4(5)	2.7(5)
C9	22.6(6)	18.7(6)	22.0(6)	-3.5(5)	7.7(5)	-0.2(5)
C10	25.3(7)	23.0(7)	13.8(6)	-3.4(5)	4.9(5)	-4.4(5)
C11	19.3(6)	21.0(6)	14.7(6)	1.1(5)	1.7(5)	-0.6(5)
C12	17.8(6)	20.9(6)	17.5(6)	1.6(5)	4.1(5)	0.8(5)
C13	24.1(7)	24.4(7)	16.2(6)	0.8(5)	2.9(5)	2.7(5)
C14	20.0(6)	26.3(7)	20.9(6)	-1.6(5)	-3.1(5)	2.9(5)
C15	14.3(6)	23.4(7)	21.2(6)	-0.3(5)	1.0(5)	0.7(5)

C16	31.4(8)	31.1(8)	20.8(7)	-5.6(6)	5.3(6)	1.2(6)
C17	48.2(11)	36.7(10)	39.8(10)	-17.7(8)	11.9(9)	-12.4(9)

Table 4 Bond Lengths for 15srv044.

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
P1	O1	1.4716(10)		C3	C4	1.506(2)
P1	O2	1.5751(10)		C3	C5	1.509(2)
P1	O3	1.5734(10)		C6	C7	1.4030(17)
P1	C1	1.7852(13)		C6	C11	1.3942(18)
F1	C8	1.3499(16)		C7	C8	1.3941(18)
F2	C10	1.3499(15)		C8	C9	1.3780(19)
O2	C16	1.4570(18)		C9	C10	1.382(2)
O3	C18A	1.489(4)		C10	C11	1.378(2)
O3	C18B	1.471(4)		C12	C13	1.3692(19)
N1	C7	1.4167(16)		C13	C14	1.422(2)
N1	C12	1.3813(17)		C14	C15	1.364(2)
N1	C15	1.3789(17)		C16	C17	1.496(3)
C1	C2	1.3115(19)		C18A	C19A	1.536(4)
C1	C6	1.5010(18)		C18B	C19B	1.508(4)
C2	C3	1.303(2)				

Table 5 Bond Angles for 15srv044.

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
O1	P1	O2	115.12(6)		C11	C6	C1	118.85(11)

O1	P1	O3	114.69(6)		C11	C6	C7	119.87(12)
O1	P1	C1	111.86(6)		C6	C7	N1	122.31(12)
O2	P1	C1	107.24(6)		C8	C7	N1	119.82(12)
O3	P1	O2	102.10(6)		C8	C7	C6	117.86(12)
O3	P1	C1	104.81(6)		F1	C8	C7	118.56(12)
C16	O2	P1	119.38(9)		F1	C8	C9	117.78(12)
C18A	O3	P1	116.53(14)		C9	C8	C7	123.65(13)
C18B	O3	P1	115.73(15)		C8	C9	C10	116.19(13)
C18B	O3	C18A	14.7(2)		F2	C10	C9	118.06(13)
C12	N1	C7	125.69(11)		F2	C10	C11	118.55(13)
C15	N1	C7	125.16(11)		C11	C10	C9	123.38(13)
C15	N1	C12	109.14(11)		C10	C11	C6	118.98(12)
C2	C1	P1	121.26(10)		C13	C12	N1	107.73(12)
C2	C1	C6	121.04(12)		C12	C13	C14	107.48(12)
C6	C1	P1	117.50(9)		C15	C14	C13	107.77(12)
C3	C2	C1	176.85(14)		C14	C15	N1	107.88(12)
C2	C3	C4	122.43(15)		O2	C16	C17	108.20(15)
C2	C3	C5	120.36(14)		O3	C18A	C19A	105.5(3)
C4	C3	C5	117.21(14)		O3	C18B	C19B	107.5(3)
C7	C6	C1	121.27(11)					

Table 6 Selected Torsion Angles for 15srv044.

A	**B**	**C**	**D**	**Angle/°**		**A**	**B**	**C**	**D**	**Angle/°**
C2	C1	P1	O1	130.77(11)		C8	C7	N1	C15	-56.92(18)
C2	C1	P1	O2	3.65(13)		C11	C6	C1	P1	-73.02(14)
C2	C1	P1	O3	-104.36(12)		C16	O2	P1	O1	-42.46(12)

C2	C1	C6	C7	-66.79(17)		C16	O2	P1	O3	-167.38(11)
C2	C1	C6	C11	112.02(15)		C16	O2	P1	C1	82.72(11)
C6	C1	P1	O1	-44.18(11)		C18A	O3	P1	O1	-38.2(2)
C6	C1	P1	O2	-171.30(9)		C18A	O3	P1	O2	87.0(2)
C6	C1	P1	O3	80.69(10)		C18A	O3	P1	C1	-161.3(2)
C6	C7	N1	C12	-58.14(19)		C18B	O3	P1	O1	-54.6(2)
C6	C7	N1	C15	123.13(15)		C18B	O3	P1	O2	70.7(2)
C7	C6	C1	P1	108.17(12)		C18B	O3	P1	C1	-177.6(2)
C8	C7	N1	C12	121.80(15)						

Table 7 Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 15srv044.

Atom	***x***	***y***	***z***	**U(eq)**
H18A	10222	8184	5339	28
H18B	10533	7379	4721	28
H18C	10427	7792	4844	35
H18D	10514	6685	4936	35
H19A	12156	7515	6069	77
H19B	10848	6783	6323	77
H19C	10395	7862	6285	77
H19D	10719	6288	5852	44
H19E	10744	7164	6436	44
H19F	12266	7004	5952	44
H4A	3360(30)	5296(15)	5182(13)	36(6)

H4B	3120(30)	4571(18)	4461(15)	49(7)
H4C	1490(30)	5154(18)	4653(15)	54(7)
H5A	2420(30)	5304(19)	2955(15)	53(7)
H5B	2320(30)	6370(18)	2844(14)	47(7)
H5C	880(40)	5800(18)	3209(15)	59(8)
H9	2480(30)	10305(15)	5559(13)	34(5)
H11	5730(20)	8140(13)	5880(11)	23(5)
H12	4660(20)	8548(13)	2967(11)	18(4)
H13	2880(20)	8133(14)	1608(12)	27(5)
H14	-220(30)	8031(15)	1876(12)	32(5)
H15	20(20)	8406(13)	3363(12)	25(5)
H16A	7780(30)	6629(14)	2715(12)	32(5)
H16B	5840(30)	6675(15)	2816(12)	31(5)
H17A	7850(30)	5008(17)	2966(14)	44(6)
H17B	5940(30)	5049(18)	3056(16)	54(7)
H17C	6430(30)	5245(19)	2185(17)	60(8)

Table 8 Atomic Occupancy for 15srv044.

Atom	***Occupancy***		**Atom**	***Occupancy***		**Atom**	***Occupancy***
C18A	0.50		H18A	0.50		H18B	0.50
C18B	0.50		H18C	0.50		H18D	0.50
C19B	0.50		H19A	0.50		H19B	0.50
H19C	0.50		C19A	0.50		H19D	0.50
H19E	0.50		H19F	0.50			

Refinement model description

Number of restraints - 1, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H,H) groups

At 1.5 times of:

All C(H,H,H) groups

2. Restrained distances

C19A-C18A ≈ C19B-C18B

with sigma of 0.005

3. Others

Fixed Sof: C18A(0.5) H18A(0.5) H18B(0.5) C18B(0.5) H18C(0.5) H18D(0.5)

C19B(0.5) H19A(0.5) H19B(0.5) H19C(0.5) C19A(0.5) H19D(0.5) H19E(0.5) H19F(0.5)

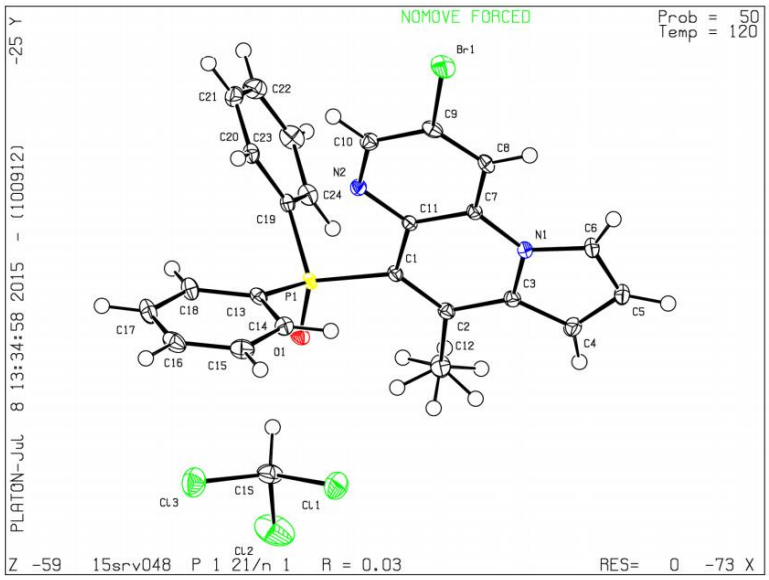
4.a Secondary CH2 refined with riding coordinates:

C18A(H18A,H18B), C18B(H18C,H18D)

4.b Idealised Me refined as rotating group:

C19B(H19A,H19B,H19C), C19A(H19D,H19E,H19F)

(2-Bromo-6-methylpyrrolo[1,2-a][1,5]naphthyridin-5-yl)diphenyl phosphine oxide, 1e:



X-ray Structure of 1e *(shown at 50% probability level).*

Table 9 Crystal data and structure refinement for **1e**.	
Identification code	15srv048
Empirical formula	$C_{24}H_{18}BrN_2OP$ x $CHCl_3$
Formula weight	580.65
Temperature/K	120.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.8026(2)

b/Å	11.7519(2)
c/Å	17.7173(3)
α/°	90.00
β/°	98.8047(17)
γ/°	90.00
Volume/Å^3	2428.48(7)
Z	4
ρ_{calc}g/cm^3	1.588
μ/mm^{-1}	2.111
F(000)	1168.0
Crystal size/mm^3	0.28 × 0.25 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.18 to 60
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -24 ≤ l ≤ 24
Reflections collected	39547
Independent reflections	7088 [R_{int} = 0.0347, R_{sigma} = 0.0264]
Data/restraints/parameters	7088/0/301
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0290, wR_2 = 0.0652
Final R indexes [all data]	R_1 = 0.0410, wR_2 = 0.0701
Largest diff. peak/hole / e Å^{-3}	0.67/-0.66

Table 10 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 15srv048. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	9241.88(15)	8720.46(13)	4705.01(10)	23.03(5)
Cl1	4110.7(4)	2674.3(5)	4941.1(3)	31.46(11)
Cl2	3730.2(5)	534.0(4)	4138.4(4)	48.25(15)
Cl3	2780.7(4)	2606.8(4)	3431.6(3)	31.52(11)
P1	6807.7(3)	3419.4(3)	3564.7(2)	10.20(7)
O1	6359.4(9)	2228.7(9)	3552.9(6)	15.0(2)
N1	8923.5(10)	4600.1(11)	5845.0(7)	11.7(2)
N2	7799.3(10)	5677.8(10)	3950.5(7)	11.5(2)
C1	7597.1(12)	3824.8(12)	4485.9(8)	10.5(3)
C1S	3940.7(15)	2002.5(15)	4042.2(10)	22.2(3)
C2	7826.8(12)	3091.3(12)	5097.5(8)	11.9(3)
C3	8502.8(12)	3486.5(12)	5786.3(8)	12.1(3)
C4	8881.9(13)	2958.9(14)	6477.4(9)	15.8(3)
C5	9544.2(13)	3748.7(14)	6951.9(9)	17.5(3)
C6	9552.8(13)	4752.9(14)	6556.9(8)	15.7(3)
C7	8697.8(12)	5364.0(12)	5242.3(8)	10.6(3)
C8	9090.2(12)	6488.5(13)	5297.7(9)	13.3(3)
C9	8809.7(13)	7170.1(12)	4666.4(9)	13.6(3)
C10	8173.9(12)	6741.4(13)	4000.1(9)	13.5(3)
C11	8041.8(12)	4980.1(12)	4559.7(8)	10.0(3)
C12	7414.8(15)	1880.7(13)	5128.1(10)	20.8(3)
C13	5622.6(12)	4384.4(12)	3322.9(9)	12.3(3)
C14	5145.5(13)	4946.7(13)	3888.9(9)	15.2(3)
C15	4107.3(14)	5512.8(14)	3711.5(10)	18.9(3)

C16	3540.1(13)	5525.2(14)	2966.9(10)	20.0(3)
C17	4016.9(14)	4982.9(14)	2395.1(10)	19.9(3)
C18	5050.7(13)	4406.6(13)	2571.0(9)	16.2(3)
C19	7786.5(12)	3551.9(12)	2878.4(8)	11.5(3)
C20	7820.9(13)	4466.3(13)	2381.7(9)	14.1(3)
C21	8576.1(14)	4452.7(14)	1850.4(9)	18.6(3)
C22	9314.8(15)	3539.1(15)	1827.9(10)	21.7(3)
C23	9299.5(14)	2632.5(15)	2328(1)	21.1(3)
C24	8531.4(13)	2632.0(13)	2849.0(9)	15.7(3)

Table 11 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 15srv048. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	27.36(9)	10.34(7)	29.55(10)	-0.93(6)	-1.53(7)	-5.96(6)
Cl1	32.6(2)	42.6(3)	19.2(2)	-3.97(18)	4.36(17)	-2.6(2)
Cl2	44.4(3)	19.7(2)	79.9(4)	2.1(2)	7.1(3)	-5.9(2)
Cl3	36.2(2)	34.5(2)	22.7(2)	-3.88(18)	0.68(18)	-1.47(19)
P1	9.84(16)	8.77(16)	11.28(17)	-1.08(13)	-0.68(13)	-1.12(12)
O1	15.9(5)	10.7(5)	17.6(5)	-2.0(4)	0.1(4)	-3.8(4)
N1	10.9(5)	12.9(6)	10.8(6)	0.4(4)	0.0(4)	-1.0(4)
N2	12.4(6)	10.9(6)	10.9(6)	0.1(4)	0.9(4)	-0.9(4)
C1	9.8(6)	10.0(6)	11.3(6)	-0.5(5)	0.0(5)	-1.1(5)
C1S	22.6(8)	19.7(8)	25.6(9)	-3.5(6)	8.1(7)	-6.5(6)
C2	10.6(6)	10.4(6)	14.2(7)	0.7(5)	0.6(5)	-0.5(5)

C3	10.0(6)	12.5(7)	13.7(7)	1.9(5)	1.2(5)	0.6(5)
C4	14.9(7)	17.9(7)	14.4(7)	4.2(6)	1.4(6)	1.4(6)
C5	14.3(7)	25.3(8)	11.9(7)	2.6(6)	-1.3(6)	0.4(6)
C6	13.4(7)	21.3(8)	11.1(7)	-0.5(6)	-1.8(5)	-1.4(6)
C7	9.0(6)	11.4(6)	11.3(7)	0.1(5)	1.0(5)	0.0(5)
C8	11.4(6)	13.7(7)	14.0(7)	-3.2(5)	-0.7(5)	-2.3(5)
C9	13.1(7)	8.5(6)	19.2(7)	-2.2(5)	2.5(6)	-2.5(5)
C10	13.6(7)	12.1(7)	14.6(7)	1.2(5)	2.1(5)	-0.2(5)
C11	8.4(6)	11.0(6)	10.6(6)	-0.7(5)	1.2(5)	-0.7(5)
C12	25.3(8)	12.0(7)	22.6(8)	4.5(6)	-4.5(7)	-4.4(6)
C13	10.4(6)	10.3(6)	15.5(7)	-1.1(5)	0.1(5)	-1.6(5)
C14	14.6(7)	16.4(7)	14.6(7)	0.5(6)	2.3(6)	-0.2(5)
C15	14.9(7)	19.6(8)	23.7(8)	-0.5(6)	7.7(6)	2.2(6)
C16	11.5(7)	16.7(7)	30.7(9)	3.4(6)	0.1(6)	1.7(6)
C17	16.6(7)	18.3(8)	21.6(8)	-0.1(6)	-6.7(6)	0.8(6)
C18	15.8(7)	15.7(7)	15.9(7)	-3.4(6)	-1.7(6)	0.6(6)
C19	12.0(6)	11.4(6)	10.3(6)	-2.5(5)	-0.7(5)	-0.7(5)
C20	15.0(7)	12.6(7)	13.4(7)	-1.0(5)	-1.6(5)	-0.4(5)
C21	22.1(8)	20.1(8)	12.9(7)	0.0(6)	0.4(6)	-5.1(6)
C22	21.2(8)	26.3(9)	19.1(8)	-7.3(6)	8.4(6)	-5.1(6)
C23	18.7(8)	19.3(8)	26.2(9)	-6.6(6)	5.6(7)	2.9(6)
C24	16.2(7)	12.0(7)	18.3(7)	-2.1(6)	0.6(6)	1.1(5)

Table 12 Bond Lengths for 15srv048.						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Br1	C9	1.8904(14)		C4	C5	1.407(2)
Cl1	C1S	1.7613(18)		C5	C6	1.373(2)
Cl2	C1S	1.7555(18)		C7	C8	1.399(2)
Cl3	C1S	1.7594(19)		C7	C11	1.4067(19)
P1	O1	1.4950(11)		C8	C9	1.374(2)
P1	C1	1.8148(14)		C9	C10	1.393(2)
P1	C13	1.8007(15)		C13	C14	1.390(2)
P1	C19	1.8075(15)		C13	C18	1.398(2)
N1	C3	1.3980(19)		C14	C15	1.387(2)
N1	C6	1.3740(19)		C15	C16	1.385(2)
N1	C7	1.3892(18)		C16	C17	1.387(2)
N2	C10	1.3243(19)		C17	C18	1.389(2)
N2	C11	1.3508(18)		C19	C20	1.394(2)
C1	C2	1.379(2)		C19	C24	1.399(2)
C1	C11	1.4543(19)		C20	C21	1.392(2)
C2	C3	1.430(2)		C21	C22	1.388(2)
C2	C12	1.507(2)		C22	C23	1.388(3)
C3	C4	1.384(2)		C23	C24	1.389(2)

Table 13 Bond Angles for 15srv048.								
Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**

O1	P1	C1	112.96(6)		N1	C7	C11	117.98(13)
O1	P1	C13	109.01(7)		C8	C7	C11	119.74(13)
O1	P1	C19	109.42(6)		C9	C8	C7	117.24(13)
C13	P1	C1	108.77(7)		C8	C9	Br1	120.15(11)
C13	P1	C19	109.81(7)		C8	C9	C10	120.69(13)
C19	P1	C1	106.82(7)		C10	C9	Br1	119.13(11)
C6	N1	C3	109.05(12)		N2	C10	C9	121.93(14)
C6	N1	C7	129.37(13)		N2	C11	C1	117.73(12)
C7	N1	C3	121.57(12)		N2	C11	C7	120.92(13)
C10	N2	C11	119.47(13)		C7	C11	C1	121.35(13)
C2	C1	P1	123.70(11)		C14	C13	P1	120.90(12)
C2	C1	C11	119.22(13)		C14	C13	C18	119.25(14)
C11	C1	P1	117.03(10)		C18	C13	P1	118.84(11)
Cl2	C1S	Cl1	110.56(10)		C15	C14	C13	120.38(15)
Cl2	C1S	Cl3	110.37(9)		C16	C15	C14	120.14(15)
Cl3	C1S	Cl1	110.20(10)		C15	C16	C17	119.99(15)
C1	C2	C3	119.00(13)		C16	C17	C18	120.07(15)
C1	C2	C12	126.35(13)		C17	C18	C13	120.15(15)
C3	C2	C12	114.64(13)		C20	C19	P1	125.08(11)
N1	C3	C2	120.87(13)		C20	C19	C24	119.53(14)
C4	C3	N1	106.89(13)		C24	C19	P1	115.37(11)
C4	C3	C2	132.24(14)		C21	C20	C19	120.12(14)
C3	C4	C5	107.94(14)		C22	C21	C20	119.90(15)
C6	C5	C4	108.02(14)		C21	C22	C23	120.41(15)
C5	C6	N1	108.10(14)		C22	C23	C24	119.88(15)

N1	C7	C8	122.28(13)		C23	C24	C19	120.13(15)

Table 14 Hydrogen Bonds for 15srv048.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C1S	H1S	O1	1.00	2.14	3.119(2)	167.5

Table 15 Selected Torsion Angles for 15srv048.

A	B	C	D	Angle/°		A	B	C	D	Angle/°
C2	C1	P1	O1	4.04(15)		C18	C13	P1	O1	-70.89(13)
C2	C1	P1	C13	125.22(13)		C18	C13	P1	C1	165.54(12)
C2	C1	P1	C19	-116.31(13)		C18	C13	P1	C19	48.97(14)
C11	C1	P1	O1	-178.42(10)		C20	C19	P1	O1	137.21(12)
C11	C1	P1	C13	-57.25(12)		C20	C19	P1	C1	-100.20(13)
C11	C1	P1	C19	61.22(12)		C20	C19	P1	C13	17.59(15)
C14	C13	P1	O1	97.52(13)		C24	C19	P1	O1	-41.02(13)
C14	C13	P1	C1	-26.04(14)		C24	C19	P1	C1	81.58(12)
C14	C13	P1	C19	-142.61(12)		C24	C19	P1	C13	-160.64(11)

Table 16 Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 15srv048.

Atom	*x*	*y*	*z*	U(eq)
H1S	4655	2122	3813	27
H4	8723	2198	6608	19

H5	9920	3611	7457	21
H6	9928	5435	6743	19
H8	9532	6769	5753	16
H10	8004	7226	3569	16
H12A	7327	1547	4616	31
H12B	6674	1870	5314	25(11)
H12C	7975	1438	5475	37
H12D	7324	1690	5654	43(14)
H12E	7977	1367	4956	65
H12F	6676	1799	4795	18(10)
H14	5533	4943	4400	18
H15	3785	5893	4102	23
H16	2825	5905	2848	24
H17	3636	5006	1883	24
H18	5370	4027	2180	19
H20	7328	5100	2406	17
H21	8586	5068	1504	22
H22	9834	3534	1468	26
H23	9813	2013	2314	25
H24	8512	2006	3186	19

Table 17 Atomic Occupancy for 15srv048.

Atom	***Occupancy***		**Atom**	***Occupancy***		**Atom**	***Occupancy***
H12A	0.50		H12B	0.50		H12C	0.50
H12D	0.50		H12E	0.50		H12F	0.50

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.5 times of:

All H(H) groups, H12A of C12

At 1.2 times of:

H4 of C4, H6 of C6, H5 of C5, H1S of C1S, H10 of C10, H8 of C8, H22 of C22, H23 of C23, H14 of C14, H15 of C15, H16 of C16, H24 of C24, H18 of C18, H17 of C17, H21 of C21, H20 of C20

2. Others

Fixed Sof: H12A(0.5) H12B(0.5) H12C(0.5) H12D(0.5) H12E(0.5) H12F(0.5)

3.a Ternary CH refined with riding coordinates:

C1S(H1S)

3.b Aromatic/amide H refined with riding coordinates:

C4(H4), C5(H5), C6(H6), C8(H8), C10(H10), C14(H14), C15(H15), C16(H16), C17(H17), C18(H18), C20(H20), C21(H21), C22(H22), C23(H23), C24(H24)

3.c Disordered Me refined with riding coordinates:

C12(H12A,H12B,H12C,H12D,H12E,H12F)