Synthesis and Structural Elucidation of *P*-stereogenic Coumarins

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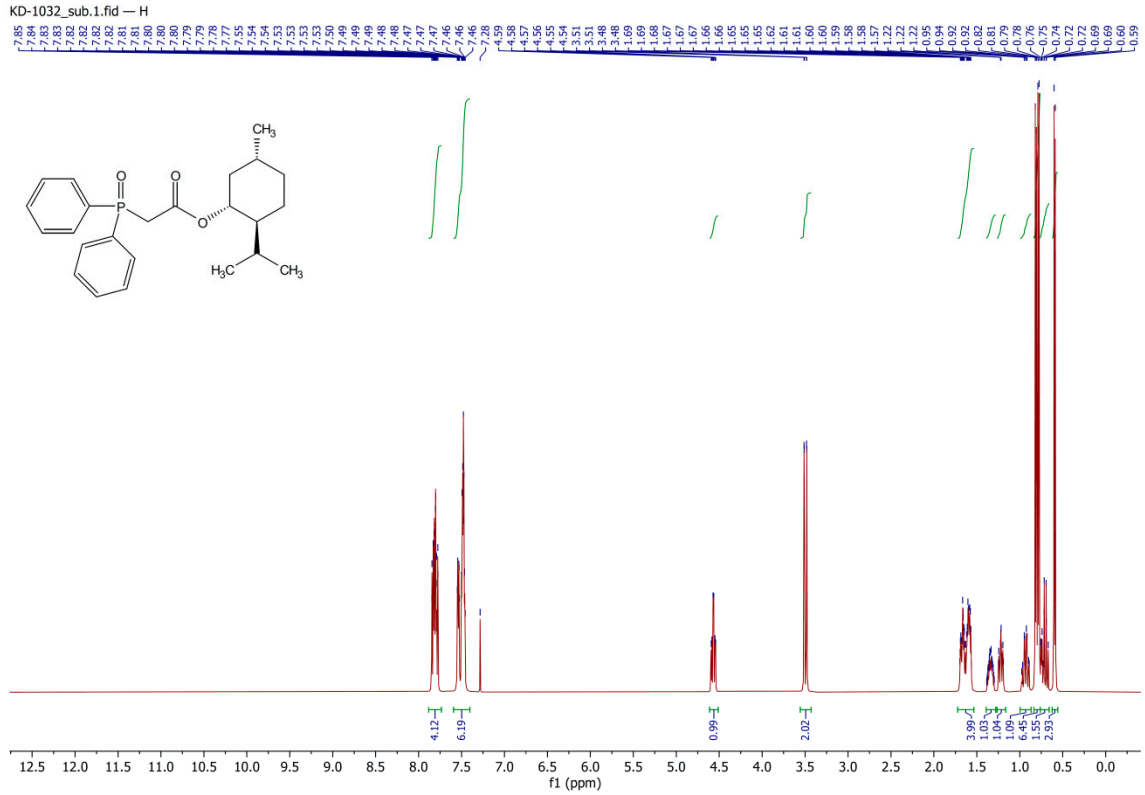
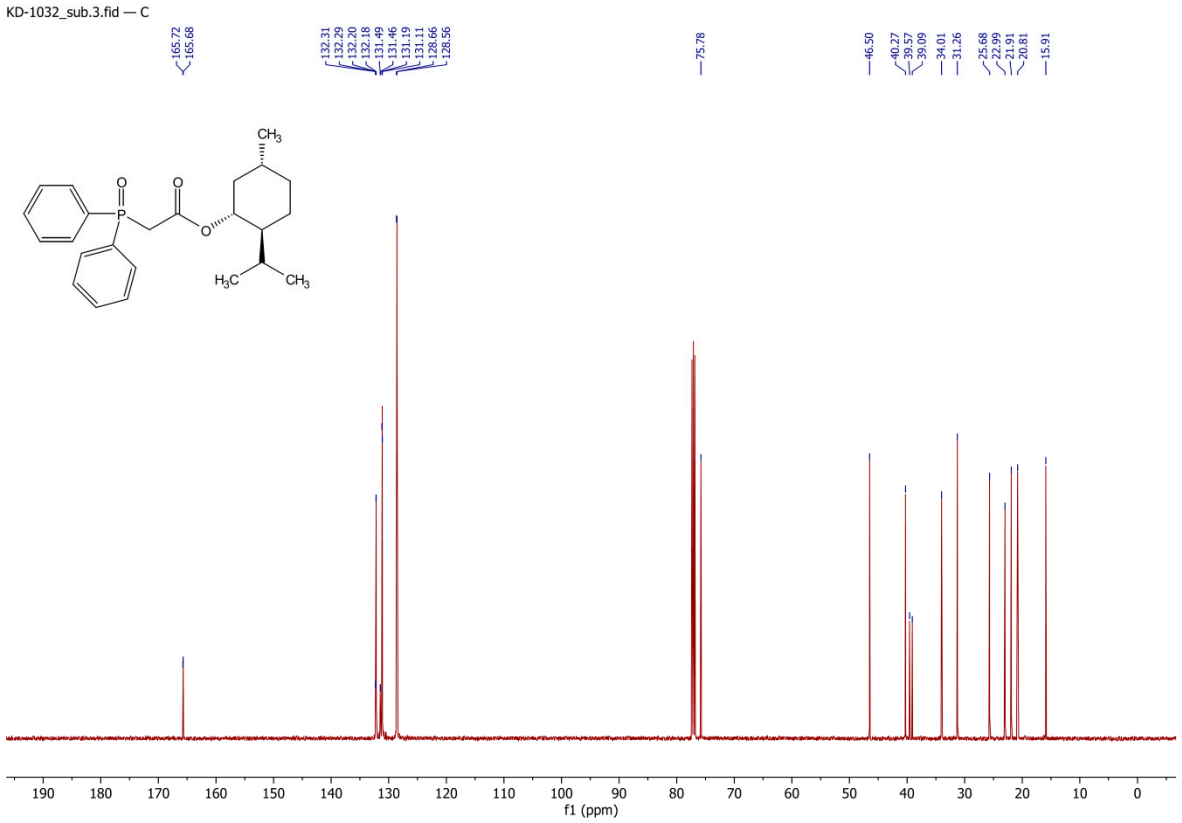
1. NMR spectra of compounds





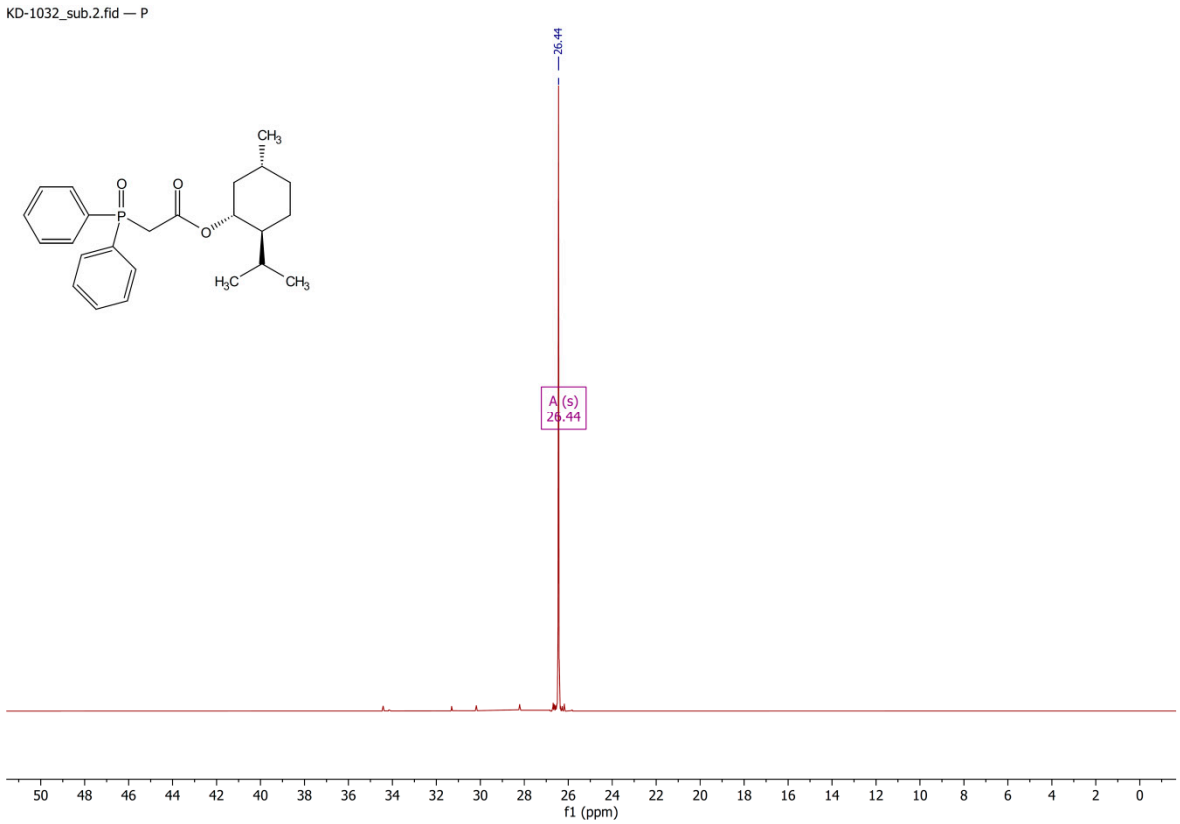


Figure S-1. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of L-menthyl diphenylphosphinylacetate (**1**) in $CDCl_3$.

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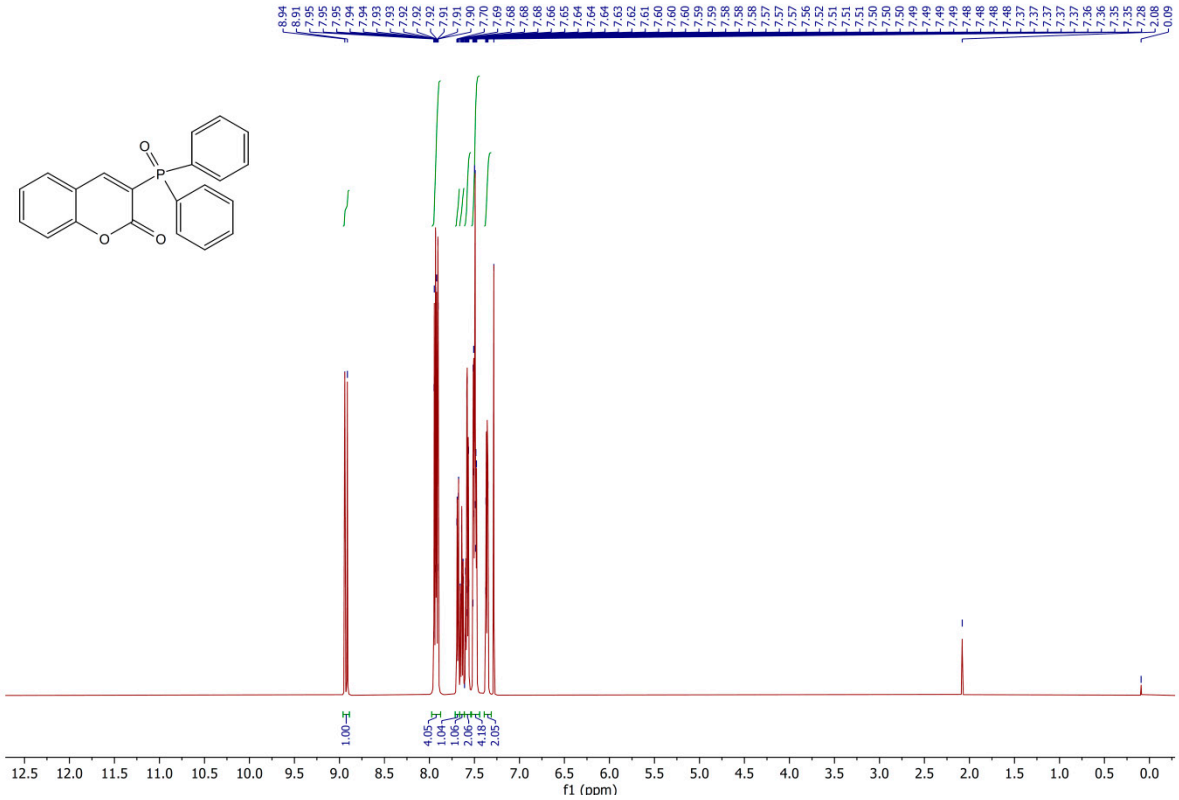

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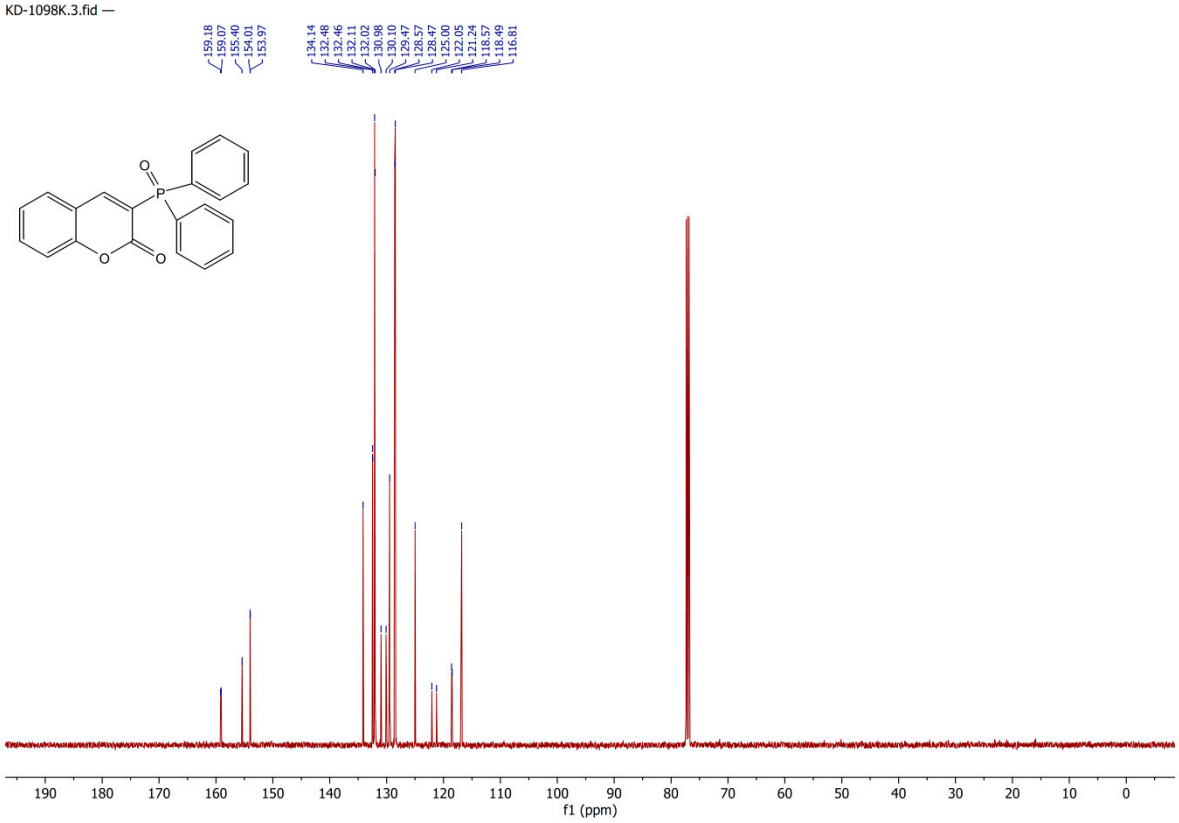


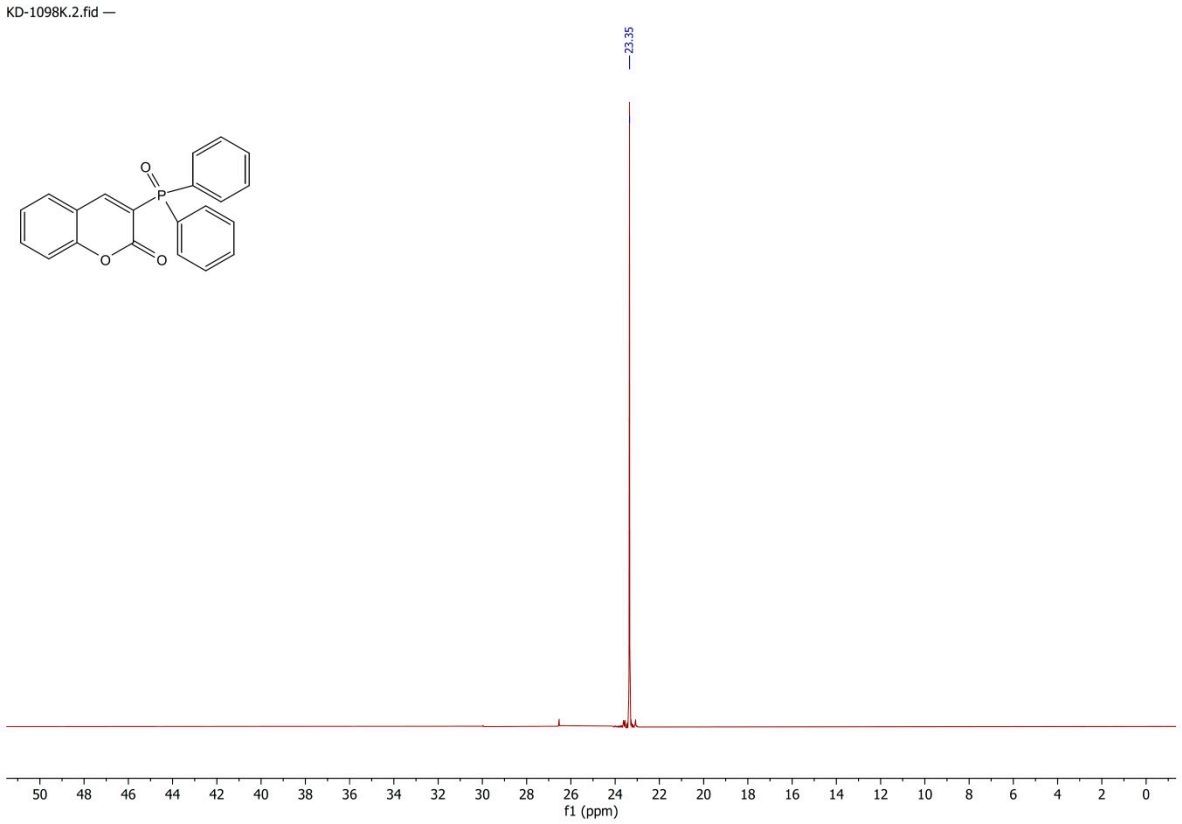
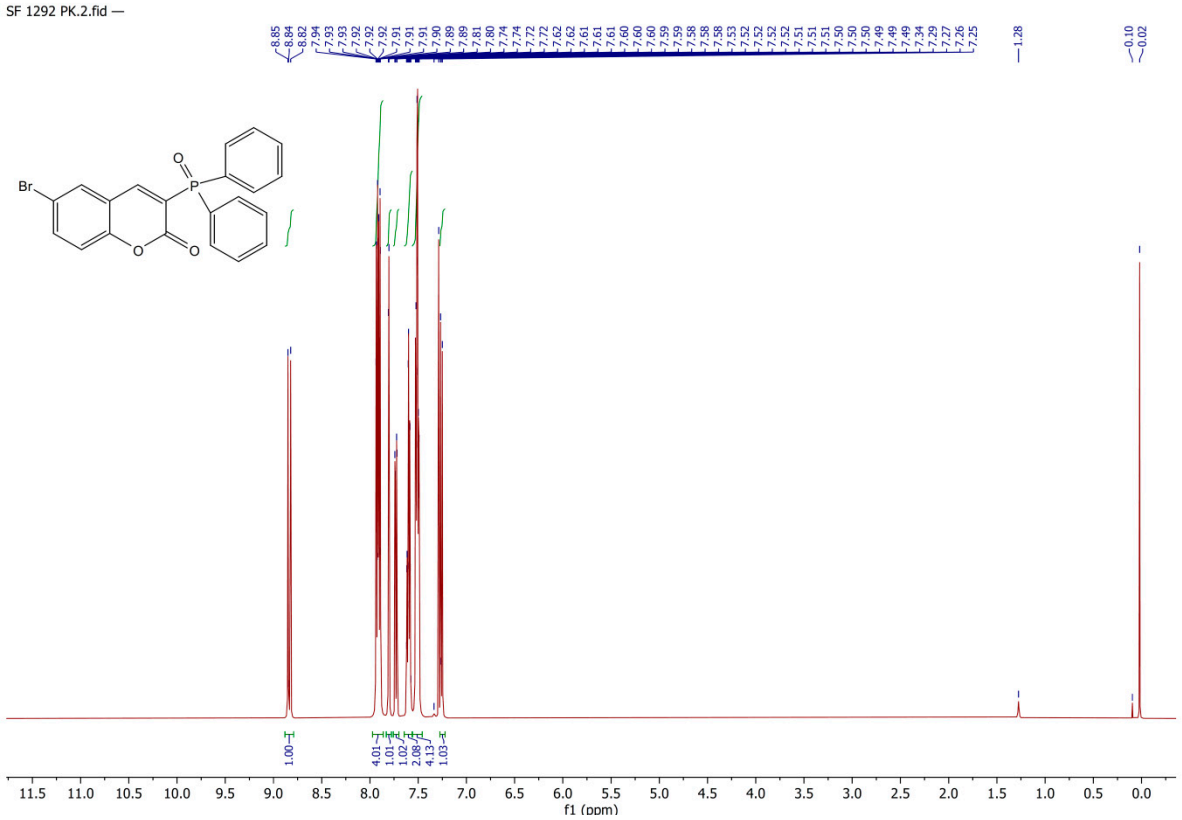


Figure S-2. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(Diphenylphosphinyl)-2*H*-chromen-2-one (**2a**) in $CDCl_3$.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7.89
7.81
7.80
7.74
7.74
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7.72
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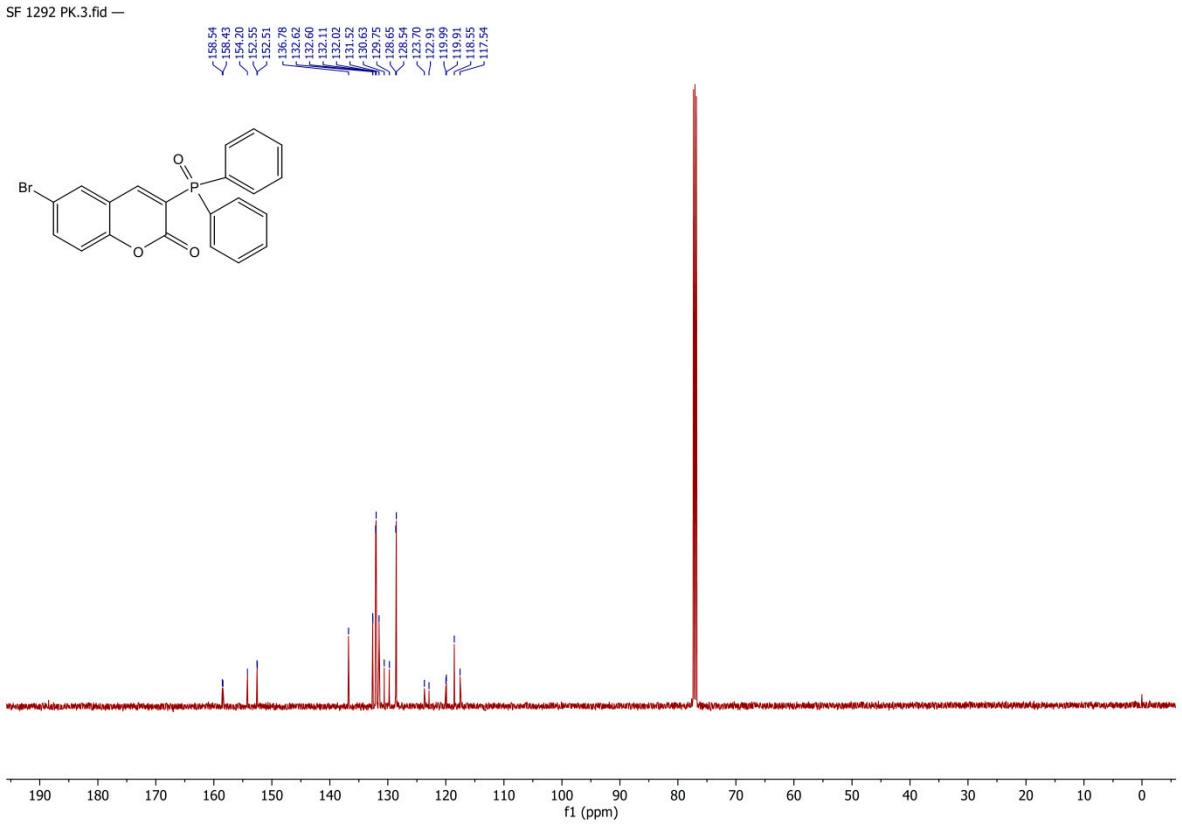
7.50
7.50
7.50
7.49
7.49
7.49
7.34
7.29
7.27
7.26
7.25
1.28
0.10
0.02
Br
O
P
O
O
O
1.00
4.01
1.01
1.02
2.08
4.13
1.03
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.52
130.63
129.75
128.65
128.54
123.70
122.91
119.99
119.91
118.55
117.54
Br
O
P
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

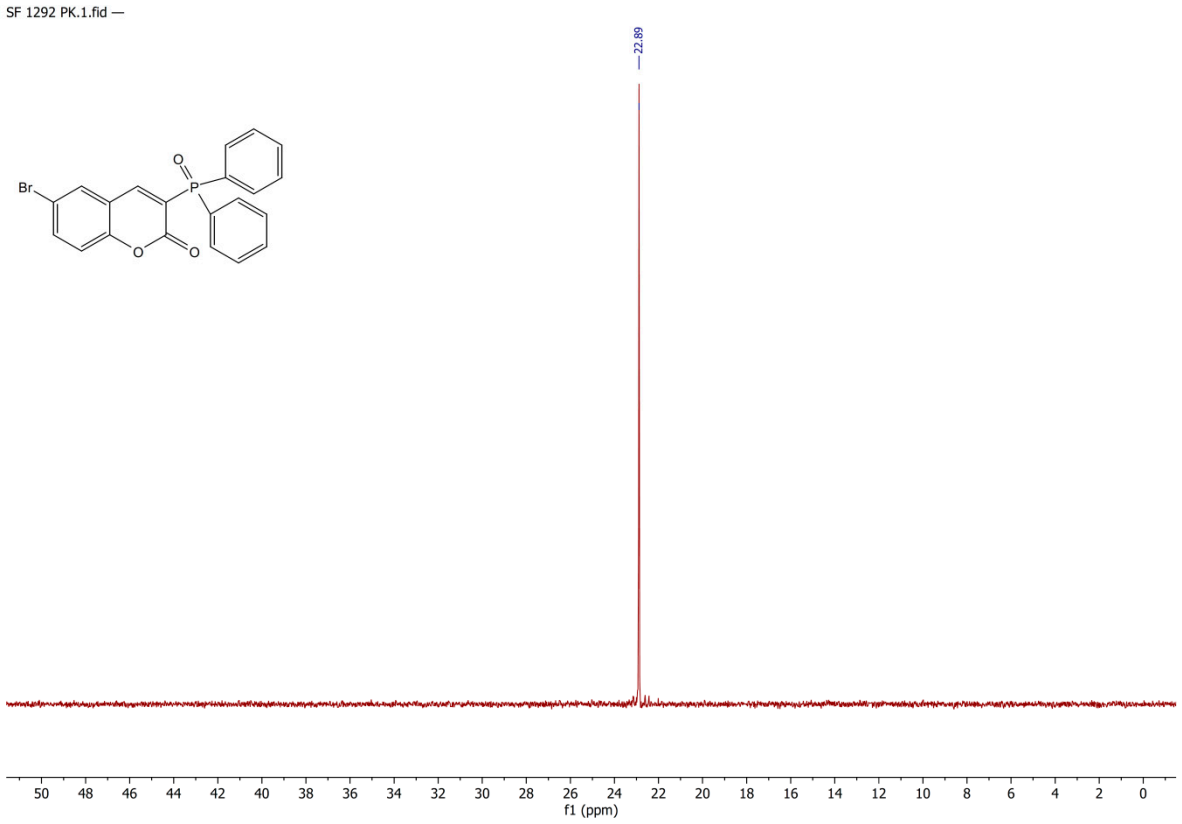
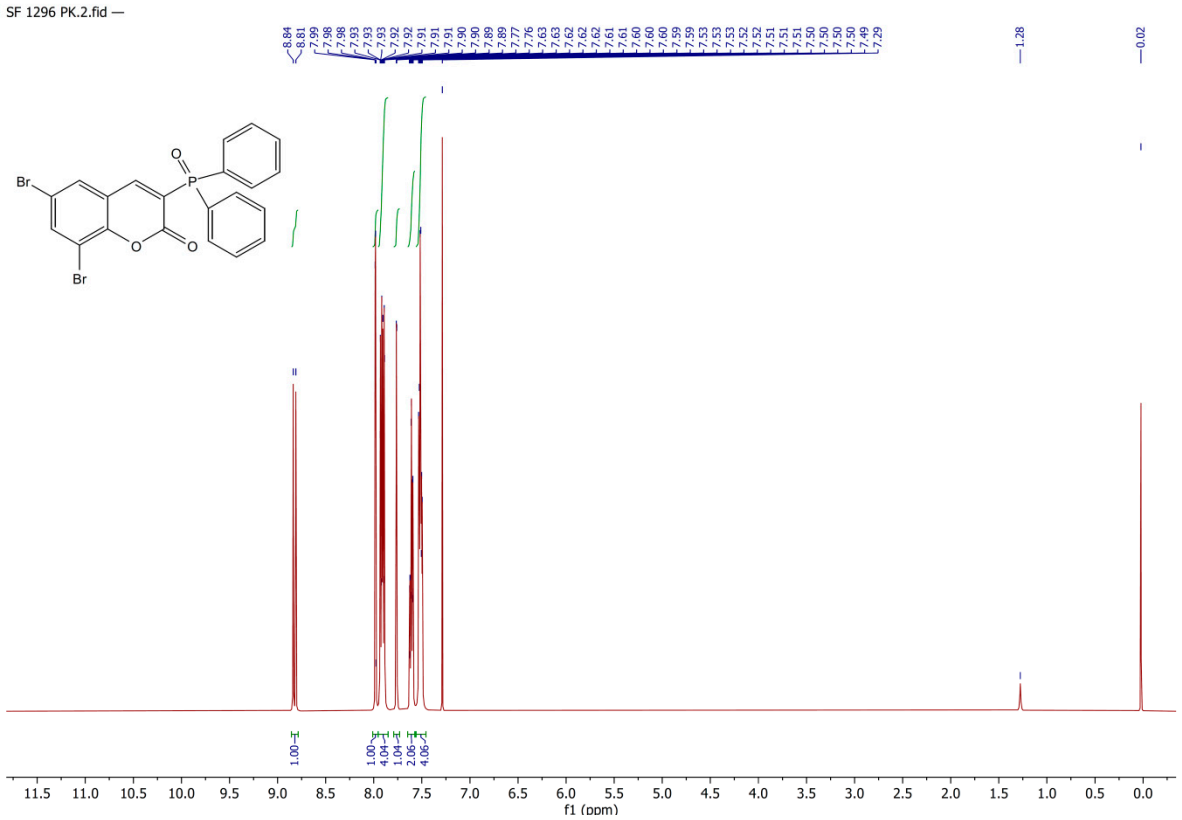


Figure S-3. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 6-(Bromo)-3-(diphenylphosphinyl)-2H-chromen-2-one (**2b**) in $CDCl_3$.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7.90
7.90
7.89
7.89
7.77
7.76
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7.60
7.60
7.60
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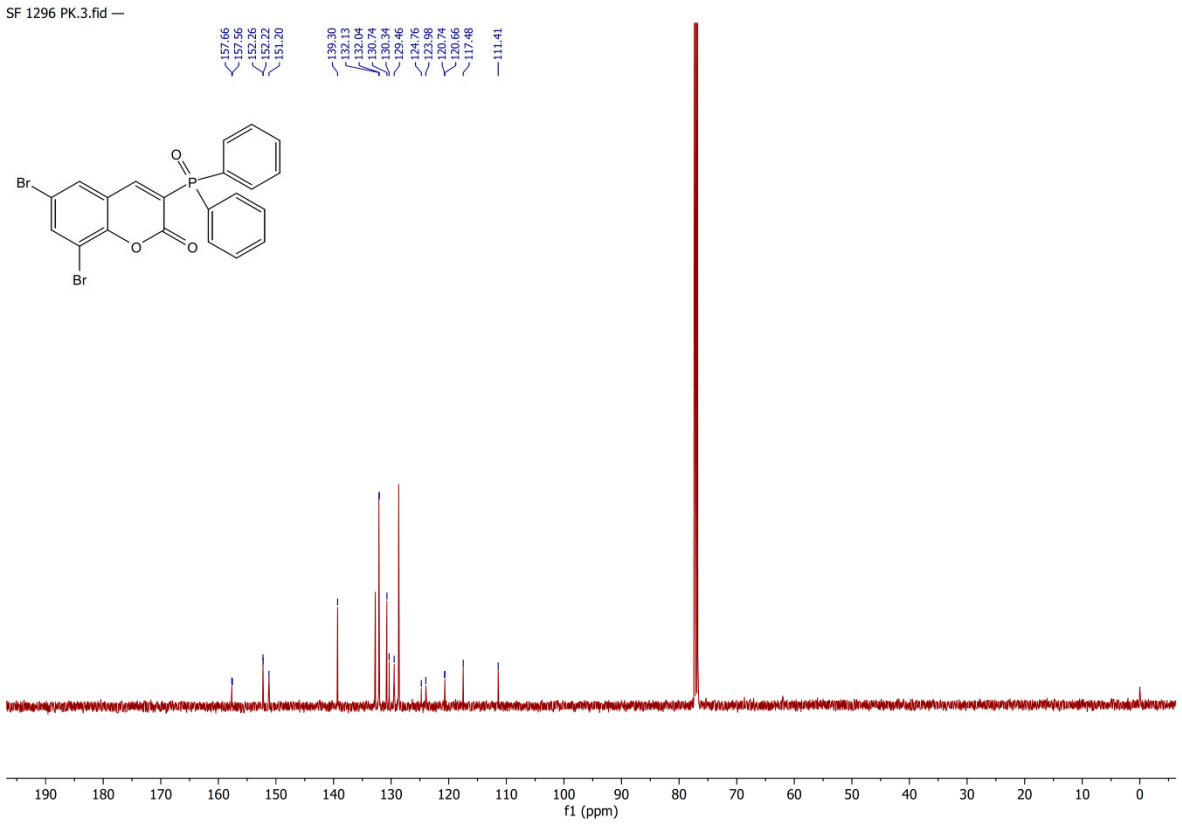
7.52
7.52
7.51
7.51
7.51
7.50
7.50
7.50
7.50
7.49
7.29
1.28
0.02
Br
O
P
O
O
Br
1.00
4.04
1.04
2.06
4.06
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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152.26
152.22
151.20
139.30
132.13
132.04
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130.34
129.46
124.76
123.98
120.74
120.66
117.48
111.41
Br
O
P
O
O
Br
190
180
170
160
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130
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50
40
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10
0
f1 (ppm)

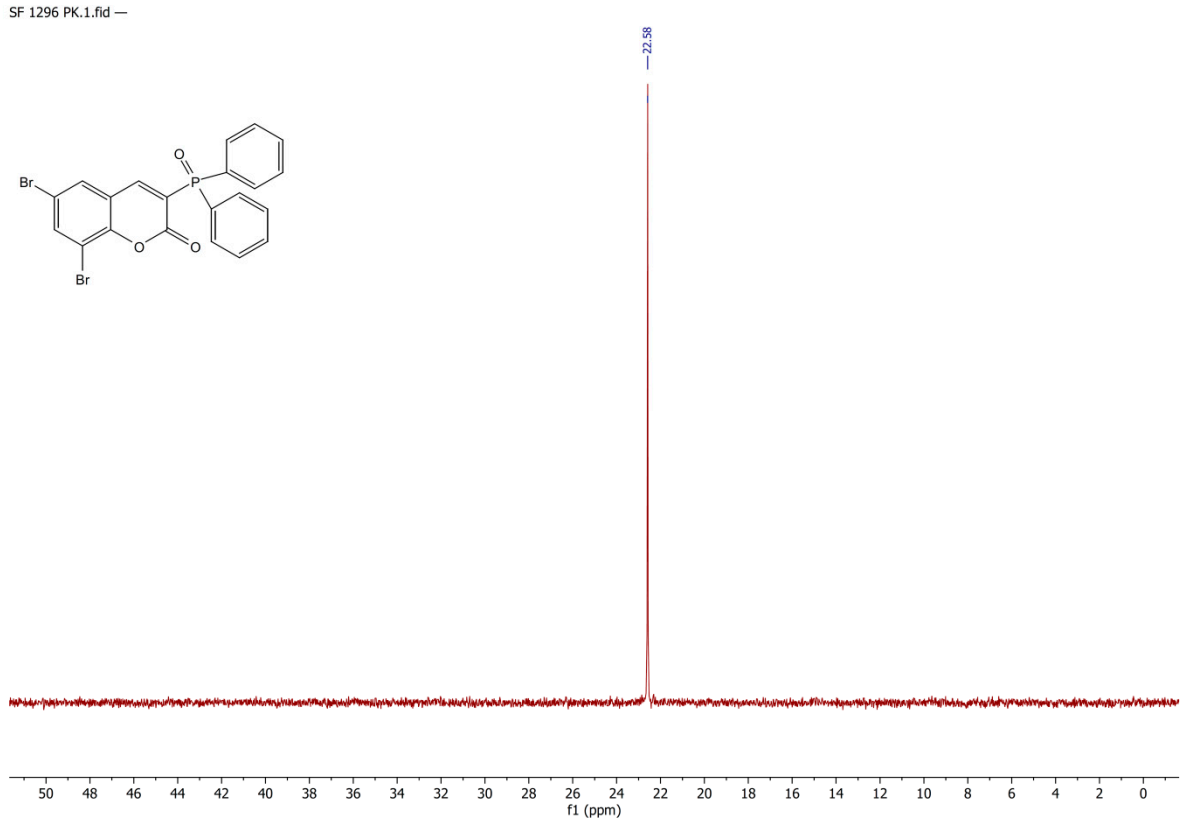
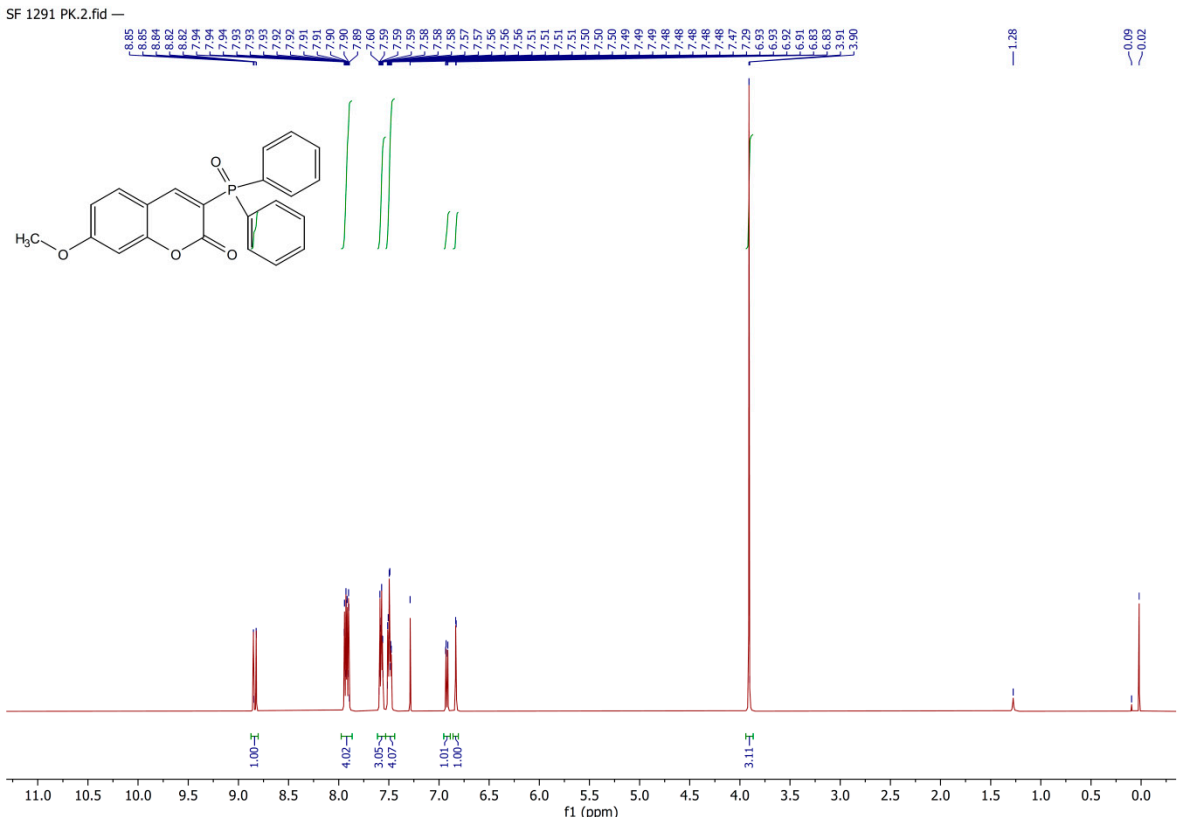


Figure S-4. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 6,8-(Dibromo)-3-(diphenylphosphinyl)-2*H*-chromen-2-one (**2c**) in $CDCl_3$.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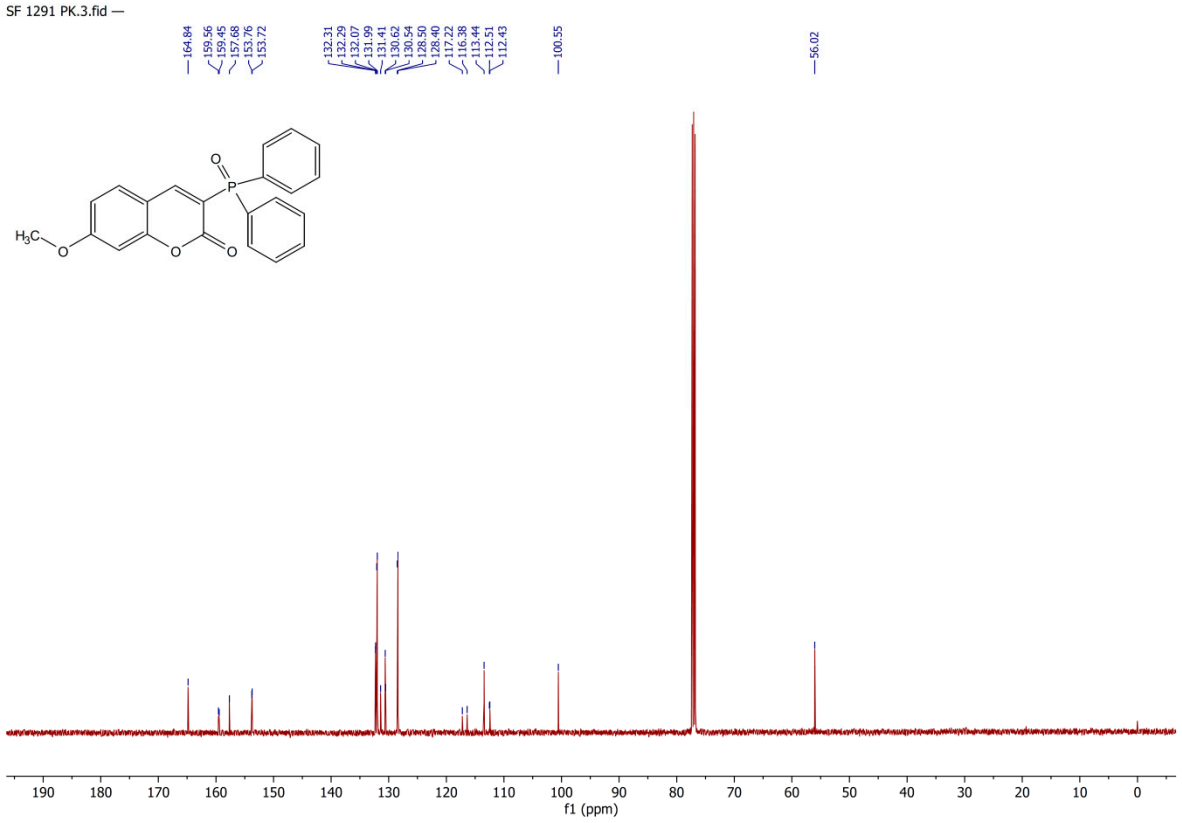
1.28
0.09
0.02
O
P
H3C
O
O
O
1.00 4.02 3.05 4.07 1.01 1.00 3.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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100.55
56.02
O
P
H3C
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

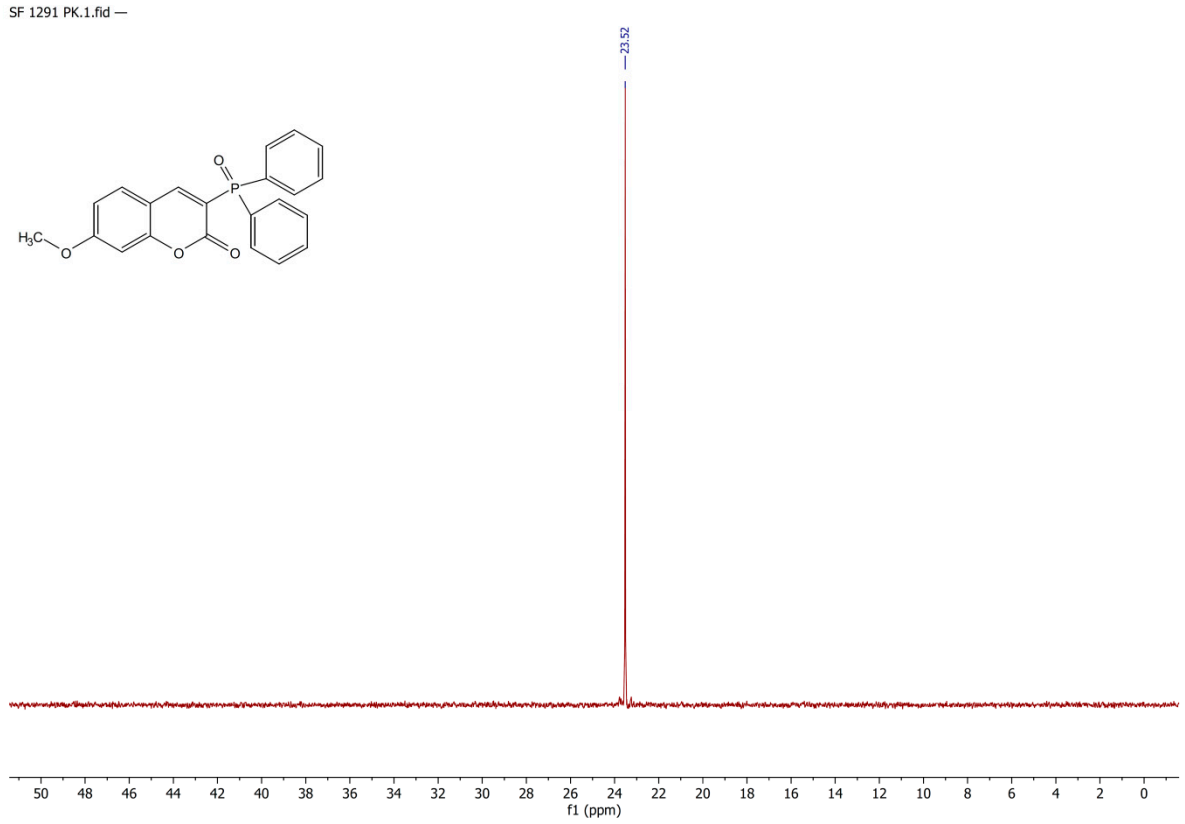
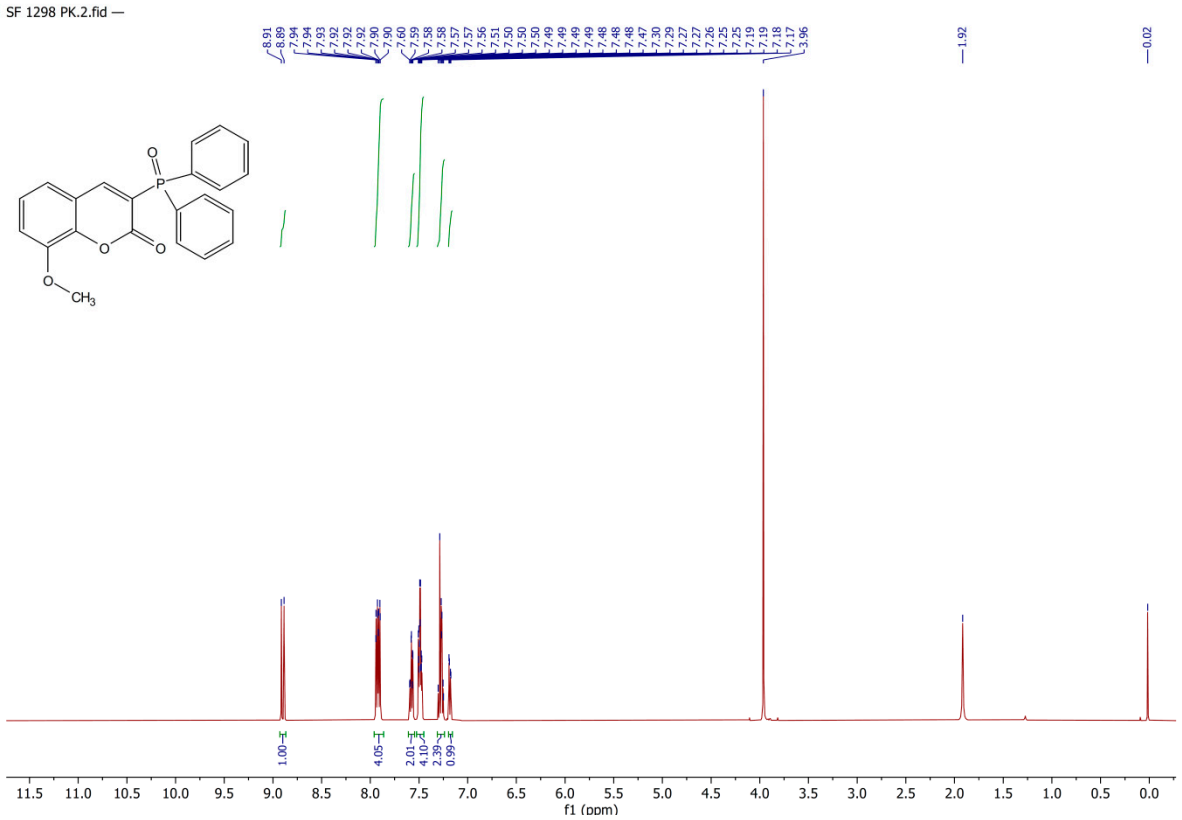


Figure S-5. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(Diphenylphosphinyl)-7-methoxy-2*H*-chromen-2-one (**2d**) in $CDCl_3$.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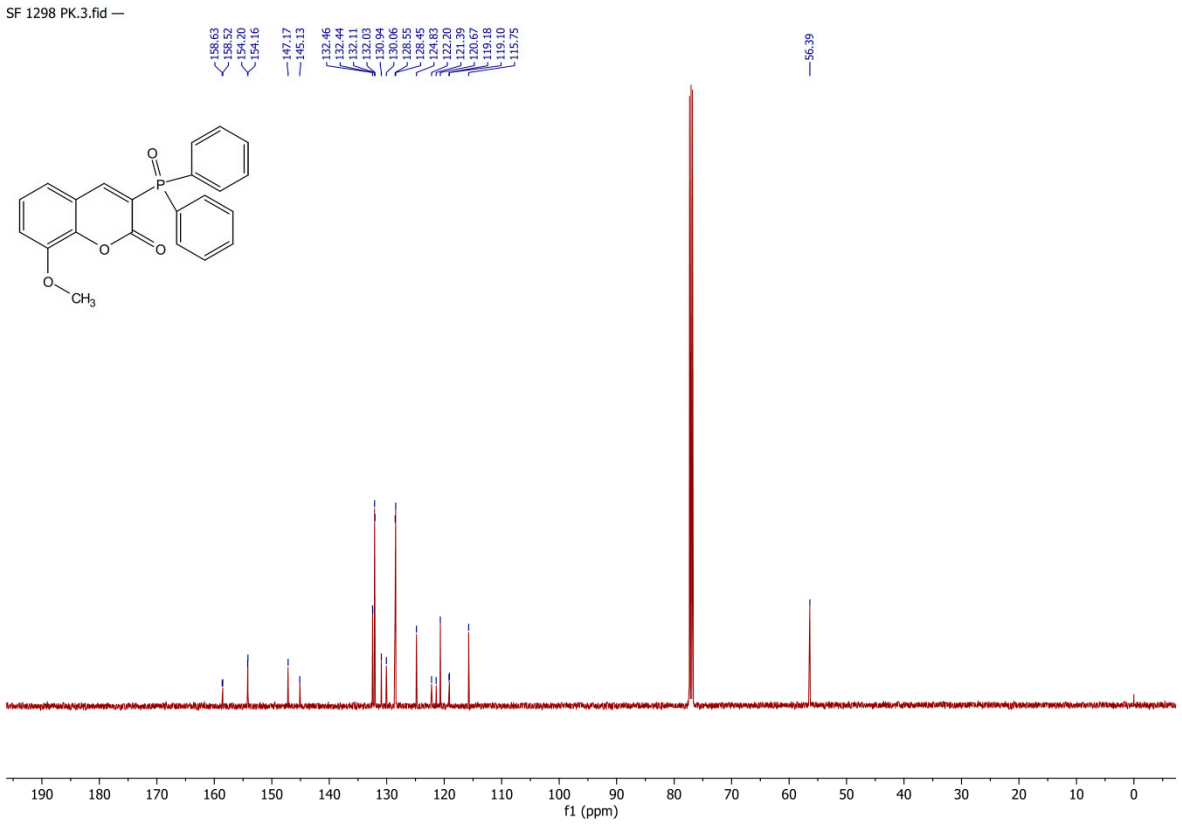
7.29
7.27
7.27
7.26
7.25
7.25
7.19
7.19
7.18
7.17
3.96
1.92
0.02
O
P
O
O
O
CH3
1.00
4.05
2.01
4.10
2.39
0.99
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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154.16
147.17
145.13
132.46
132.44
132.11
132.03
130.94
130.06
128.55
128.45
124.83
122.20
121.39
120.67
119.18
119.10
115.75
56.39
O
P
O
O
O
CH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

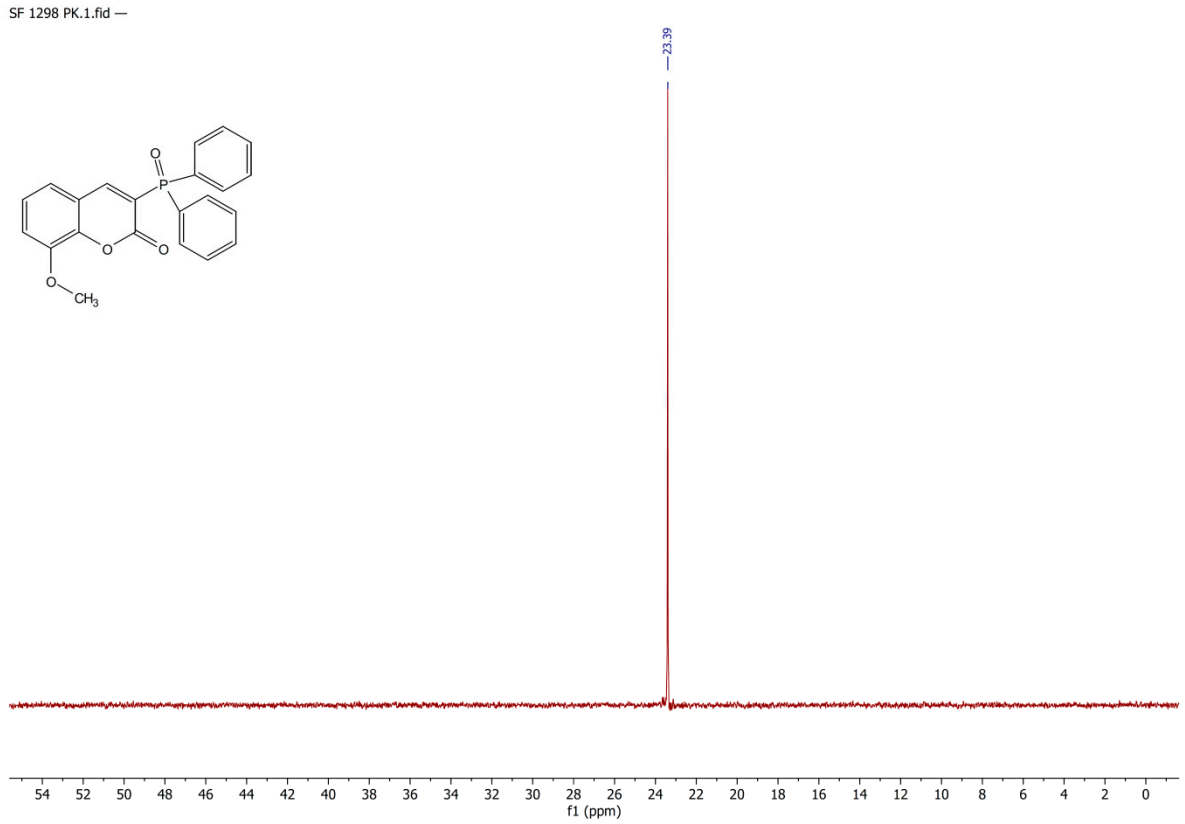
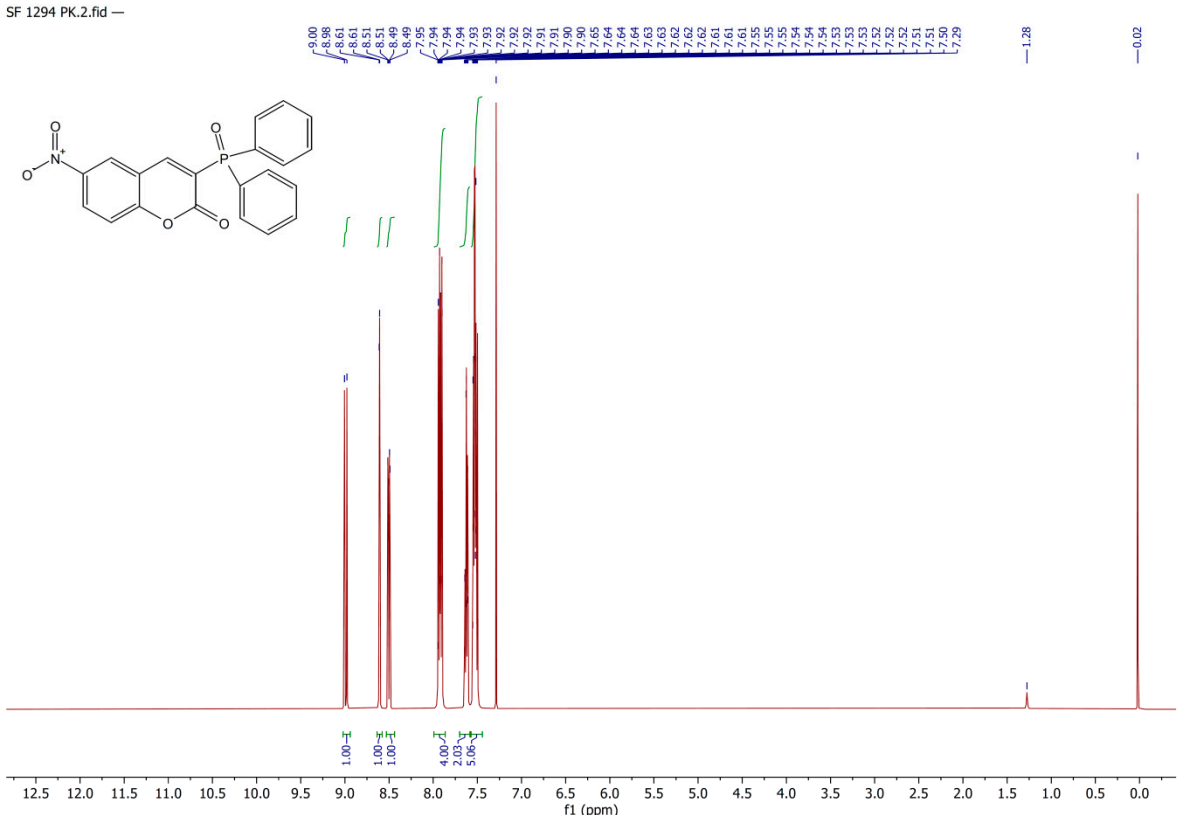


Figure S-6. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(Diphenylphosphinyl)-8-methoxy-2*H*-chromen-2-one (**2e**) in $CDCl_3$.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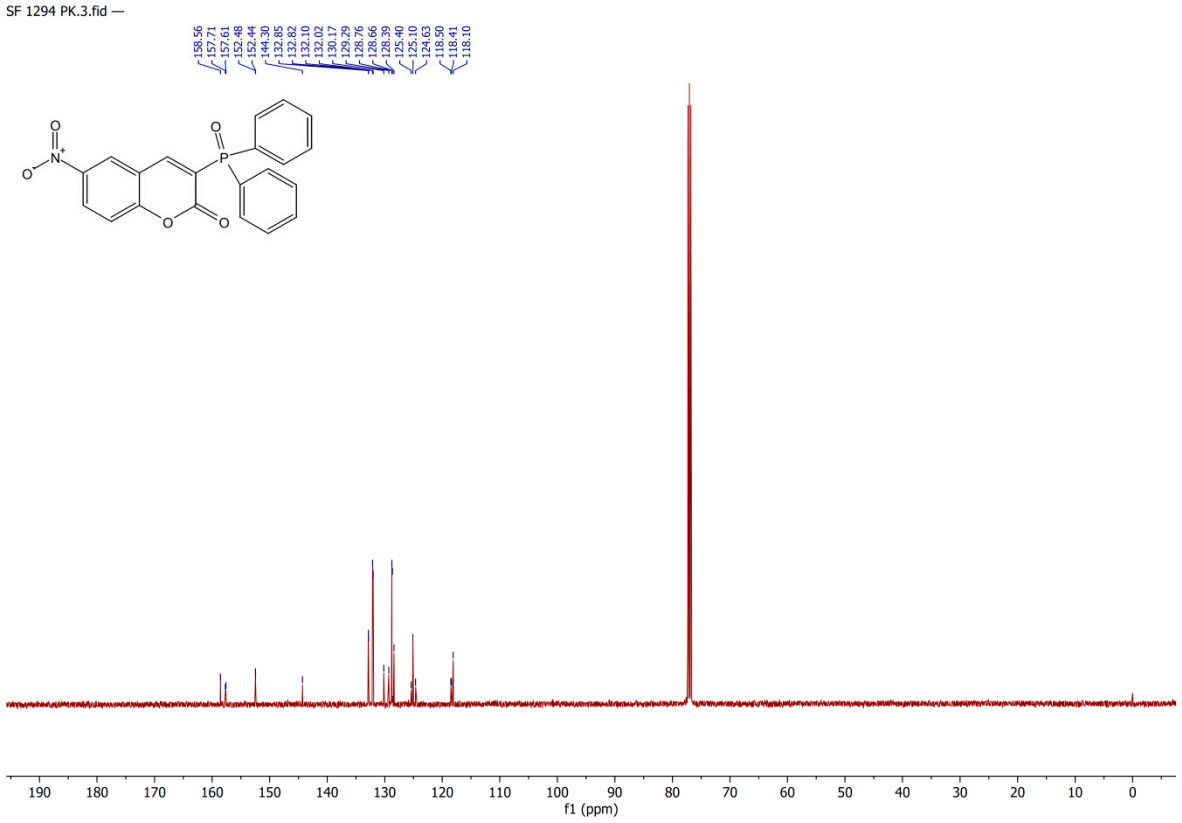
7.53
7.53
7.52
7.52
7.52
7.51
7.51
7.50
7.29
1.28
0.02
1.00
1.00
1.00
4.00
2.03
5.06
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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157.61
152.48
152.44
144.30
132.85
132.82
132.10
132.02
130.17
129.29
128.76
128.66
128.39
125.40
125.10
124.63
118.50
118.41
118.10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

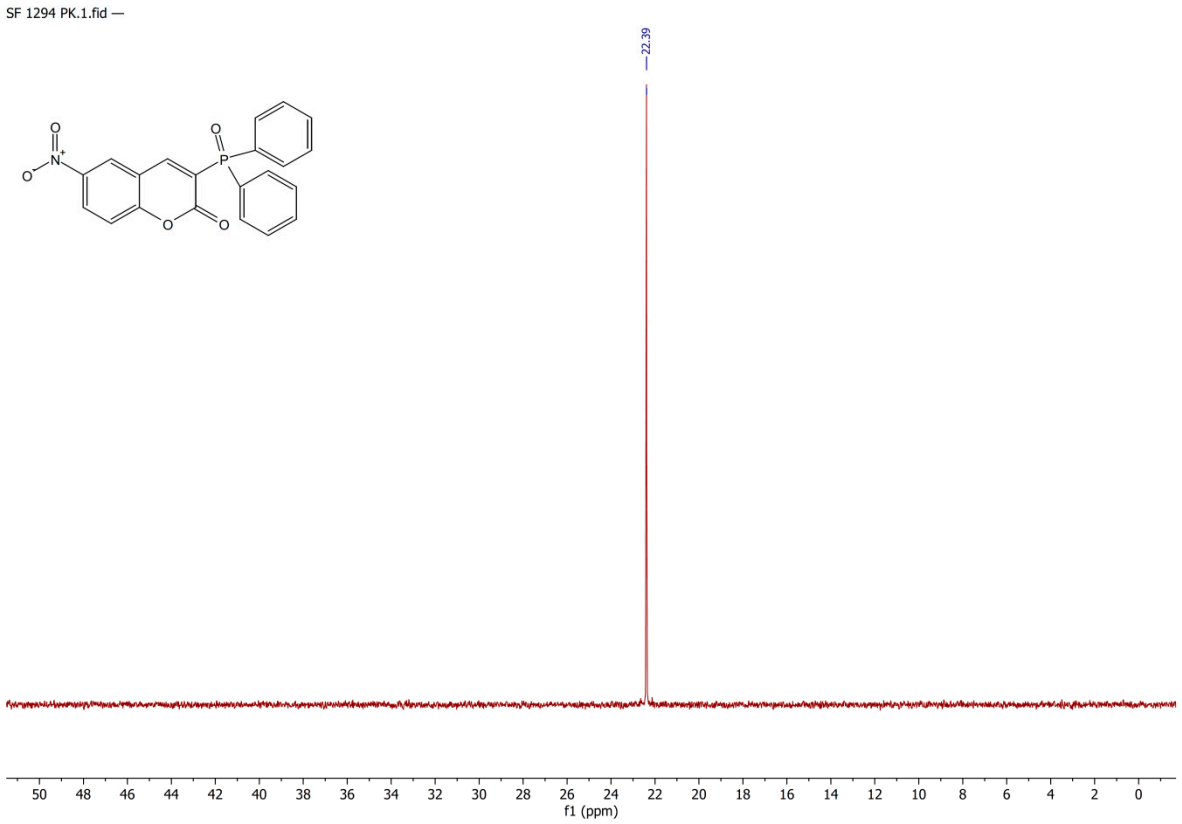
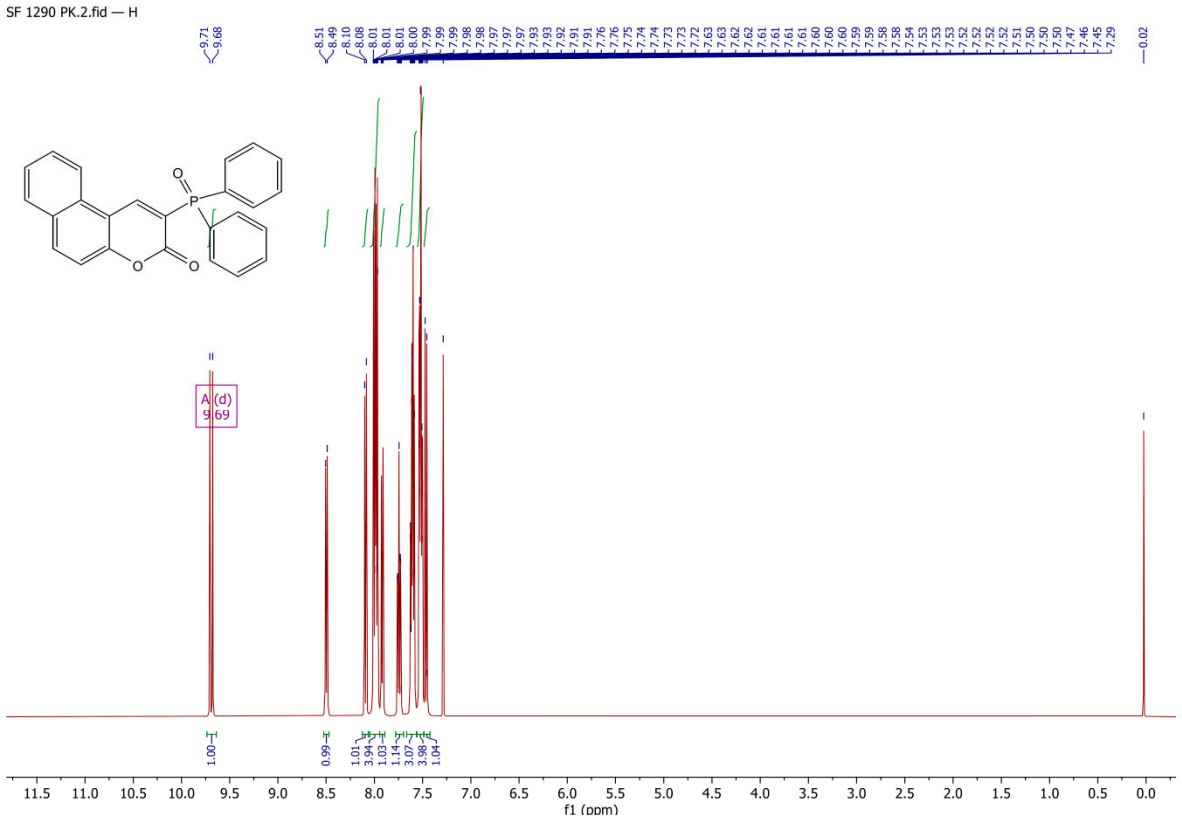


Figure S-7. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(Diphenylphosphinyl)-6-nitro-2*H*-chromen-2-one (**2f**) in $CDCl_3$.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A (d)
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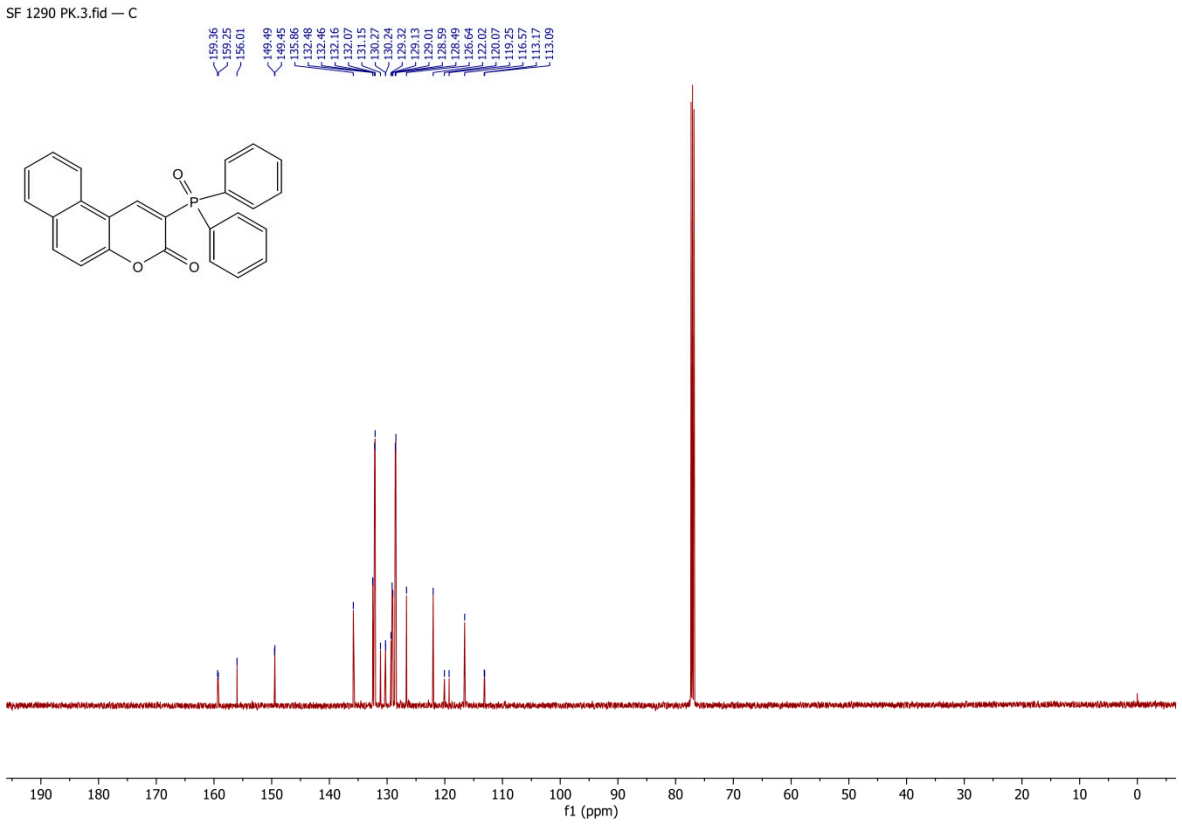
f1 (ppm)


SF 1290 PK.3.fid — C
f1 (ppm)

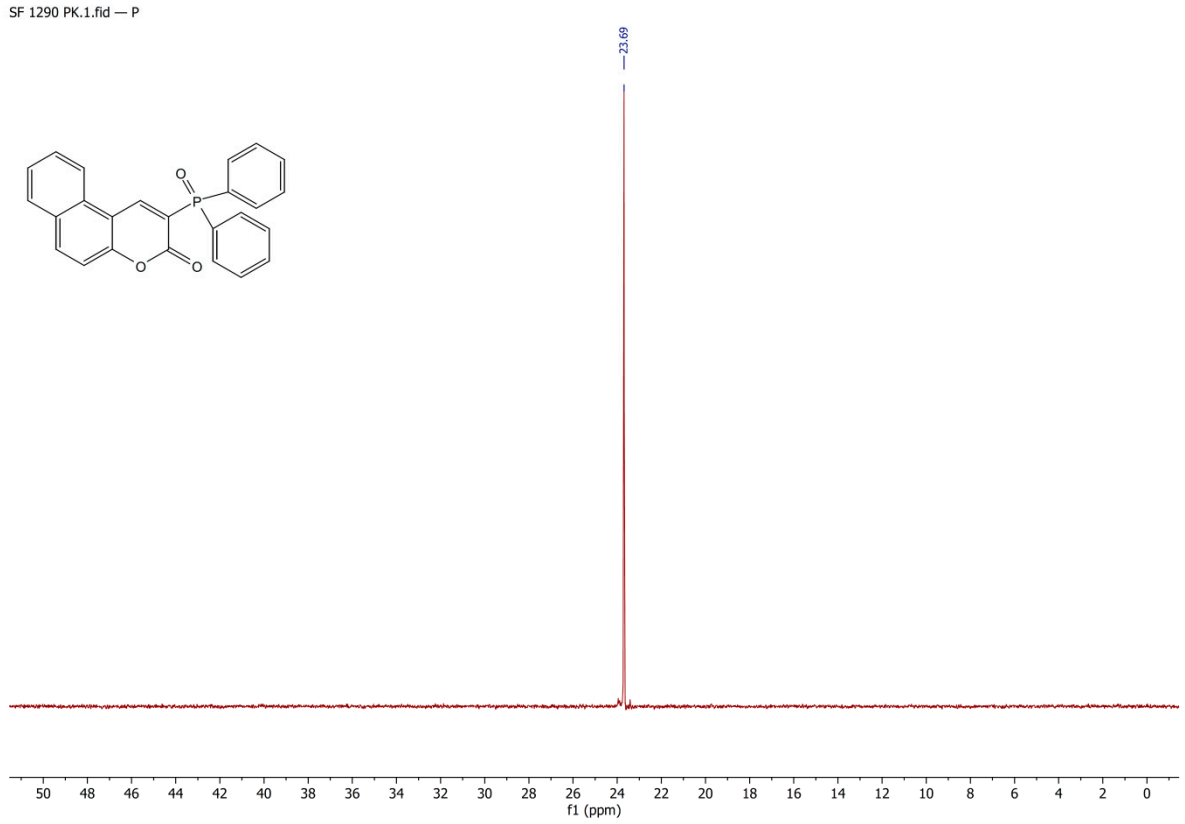
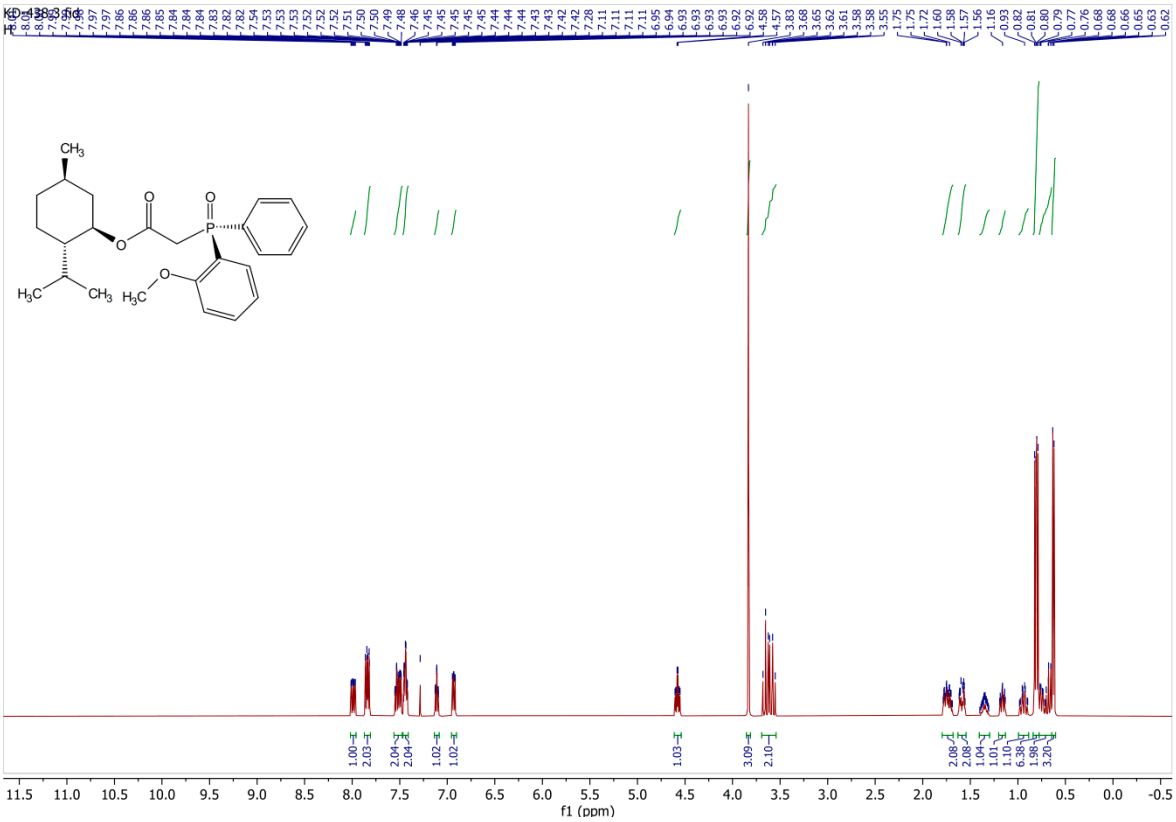


Figure S-8. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(Diphenylphosphinyl)-2*H*-benzo[h]chromen-2-one (**2g**) in $CDCl_3$.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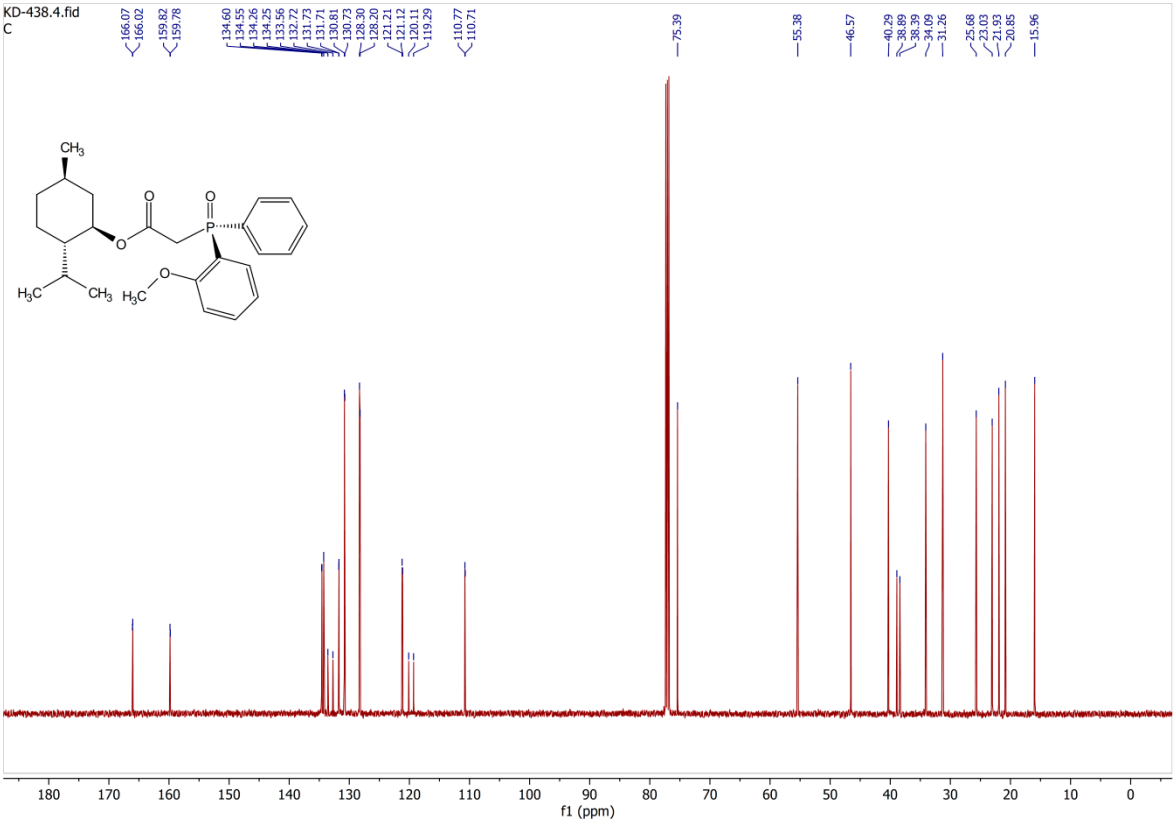
f1 (ppm)


KD-438.4.fid
C
f1 (ppm)

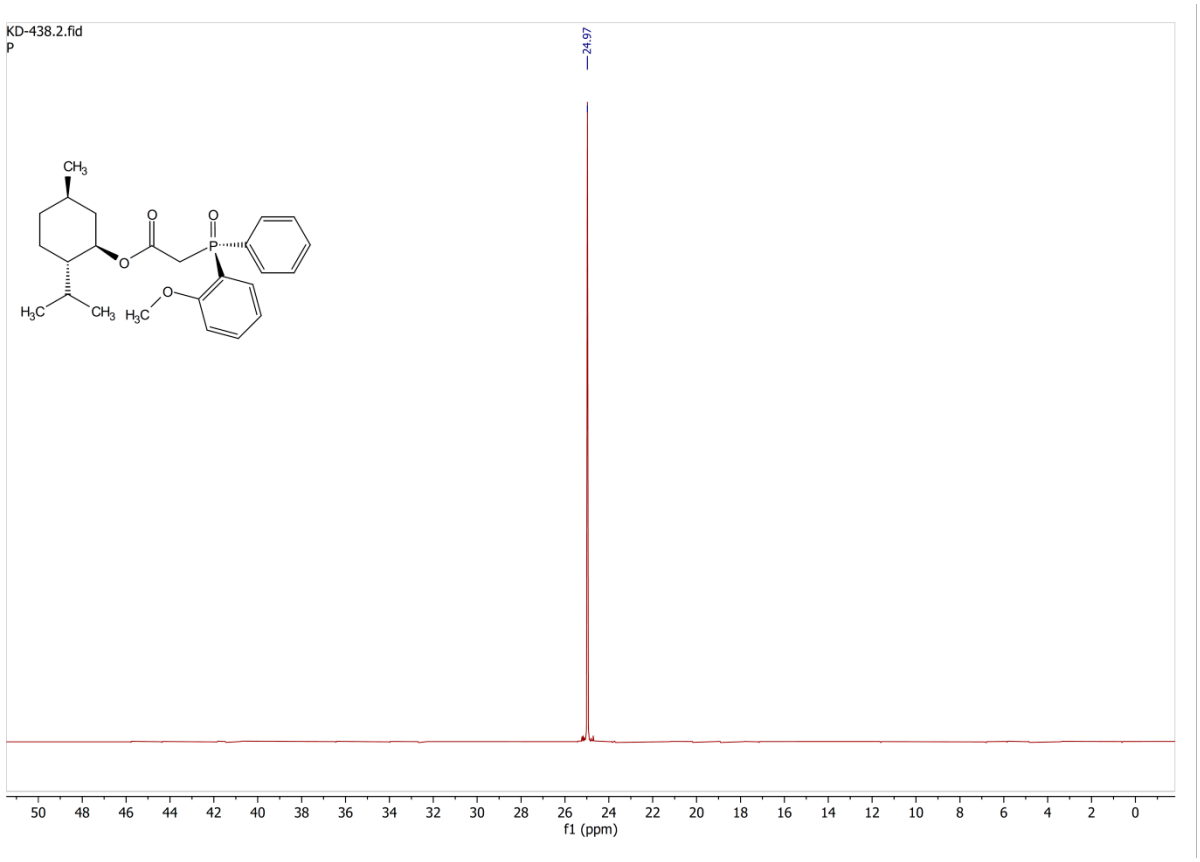
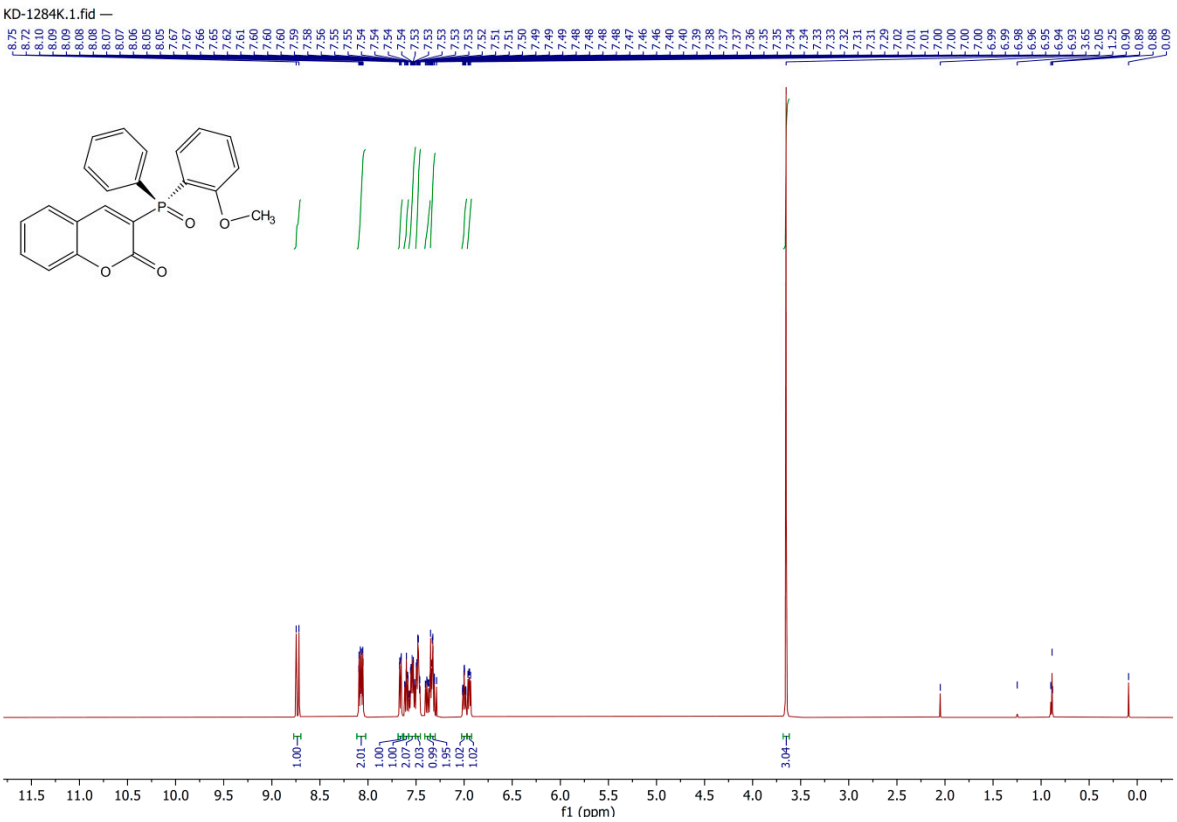


Figure S-9. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of *(S$_P$)-L-Menthyl (2-methoxyphenyl)phenylphosphinylacetate (***3**) in $CDCl_3$.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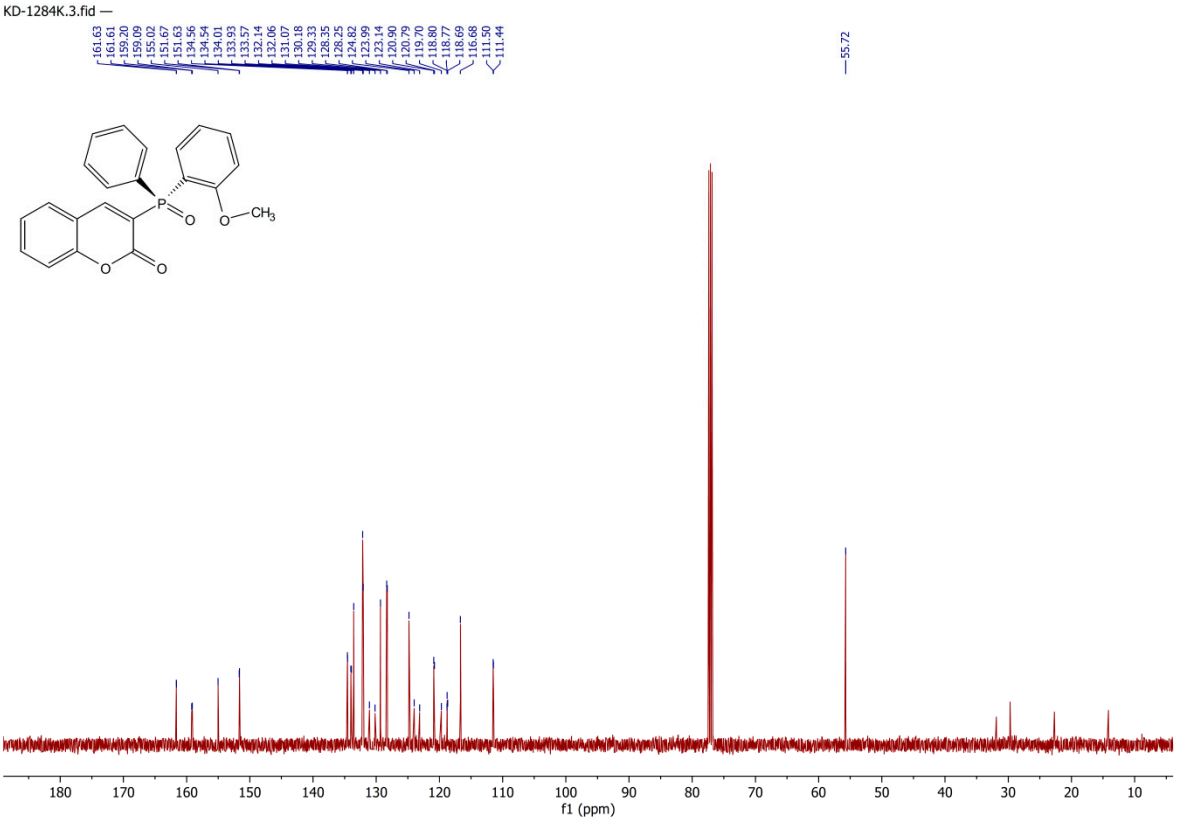
f1 (ppm)


KD-1284K.3.fid
55.72
f1 (ppm)

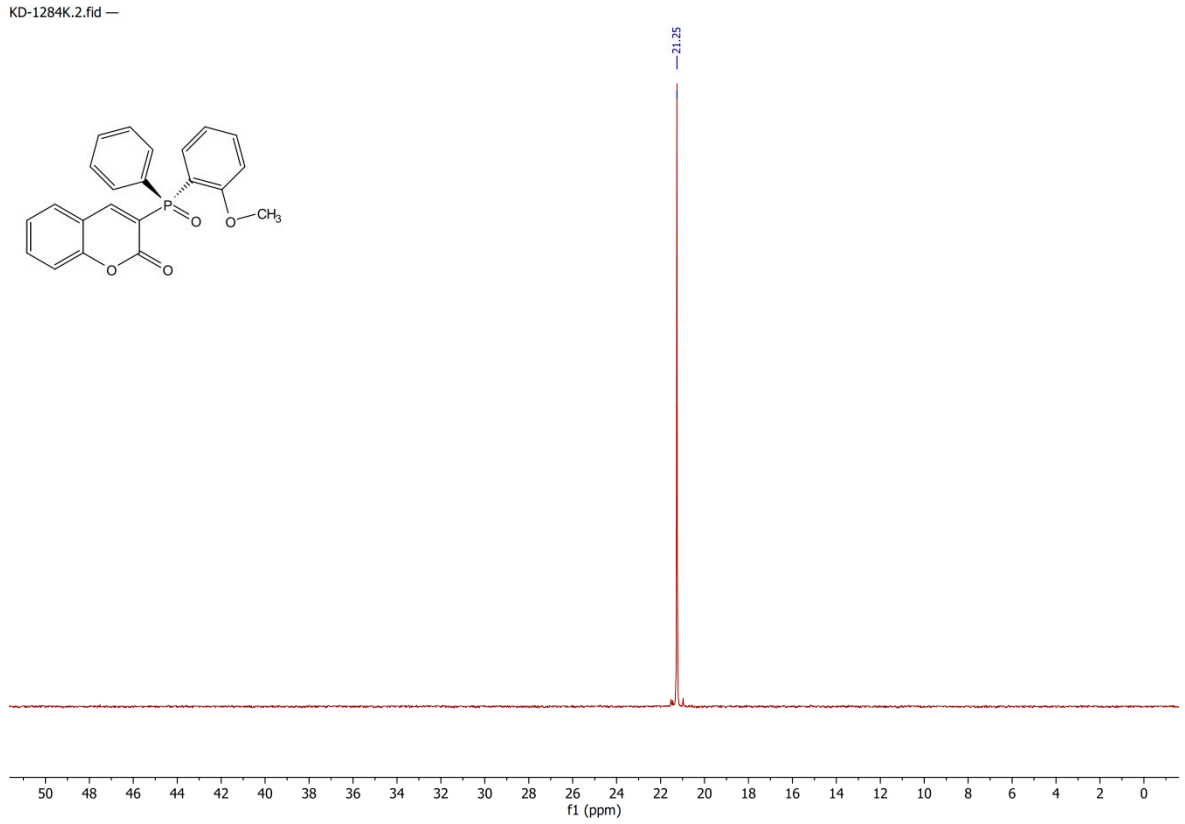
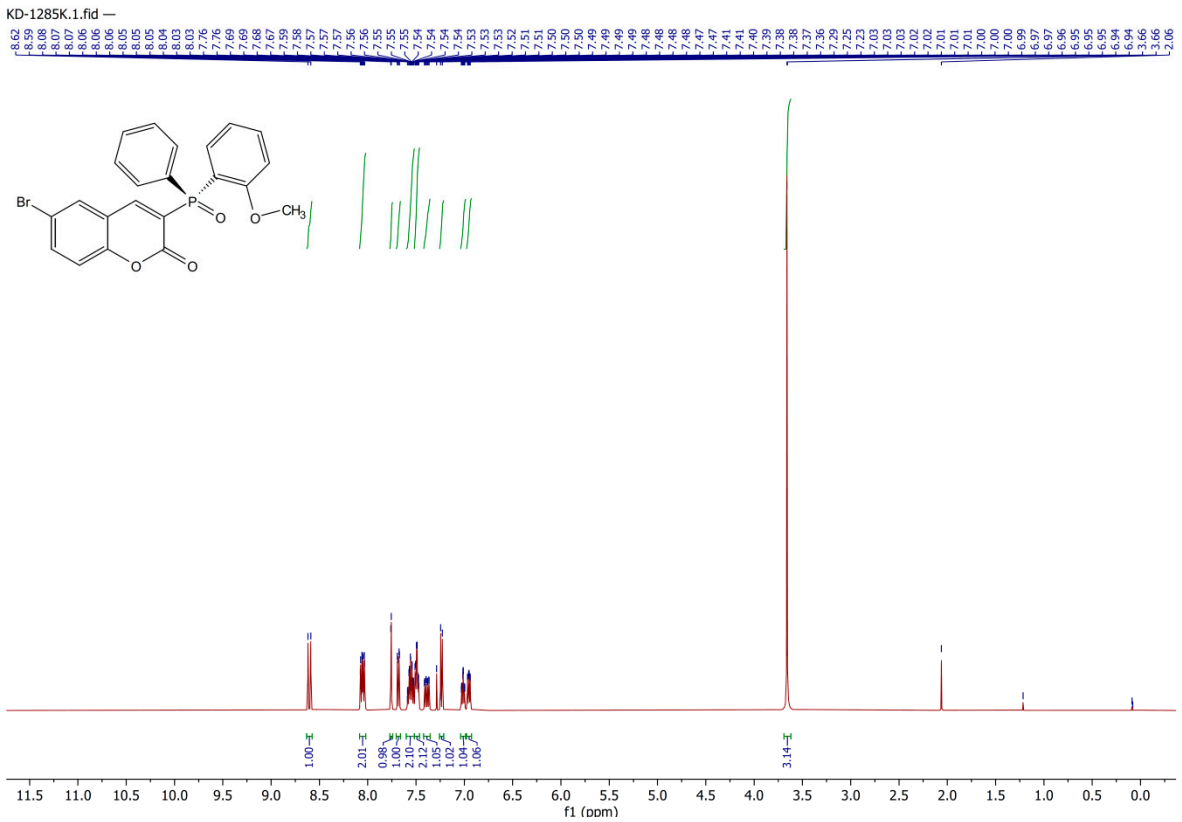
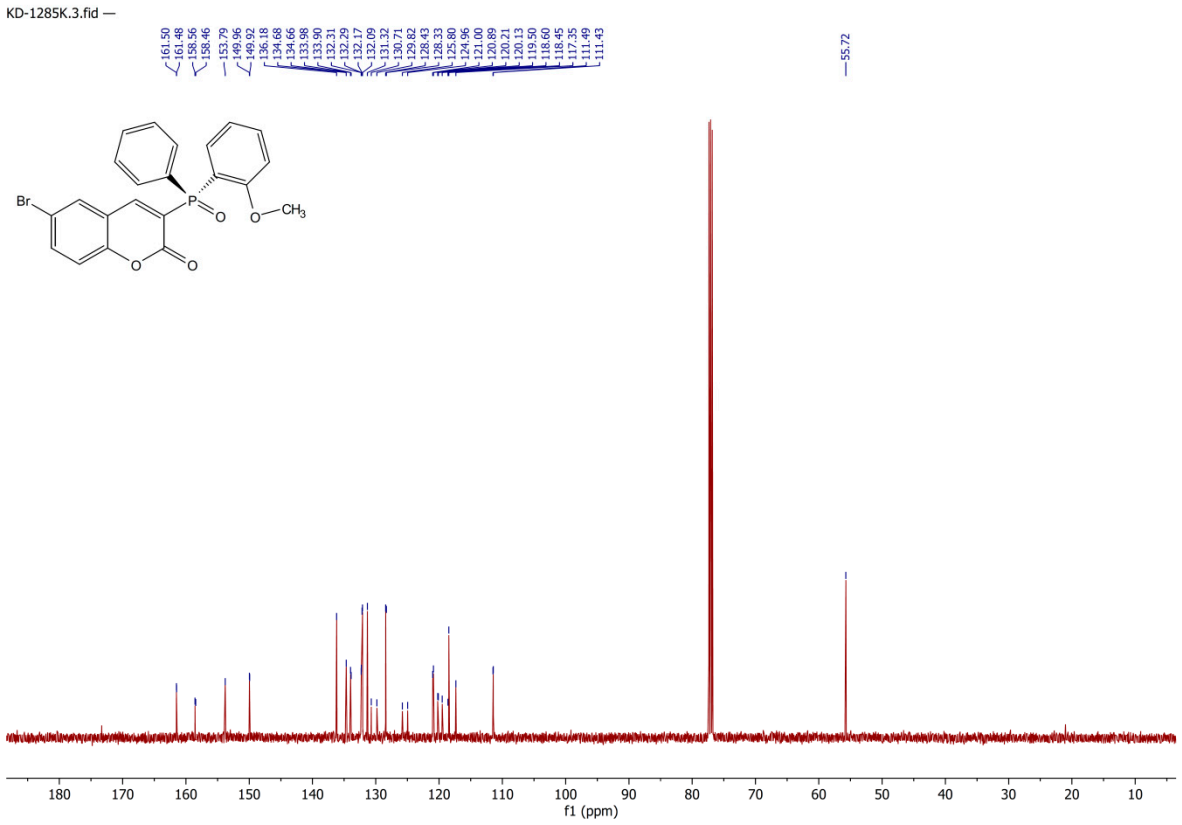


Figure S-10. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(S_P)-(2-Methoxyphenyl)phenylphosphinyl)-2*H*-chromen-2-one (**4a**) in $CDCl_3$.


KD-1285K.1.fid
Br
P
O
O
CH3
O
O
1.00
2.01
0.98
1.00
2.10
2.12
1.05
1.02
1.04
1.06
3.14
11.5 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
f1 (ppm)


KD-1285K.3.fid
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161.48
158.56
158.46
153.79
149.96
149.92
136.18
134.68
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133.98
133.90
132.31
132.29
132.17
132.09
131.23
130.71
129.82
128.43
128.33
125.80
124.96
121.00
120.89
120.21
120.13
119.50
118.60
118.45
117.35
111.49
111.43
55.72
Br
P
O
O
CH3
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

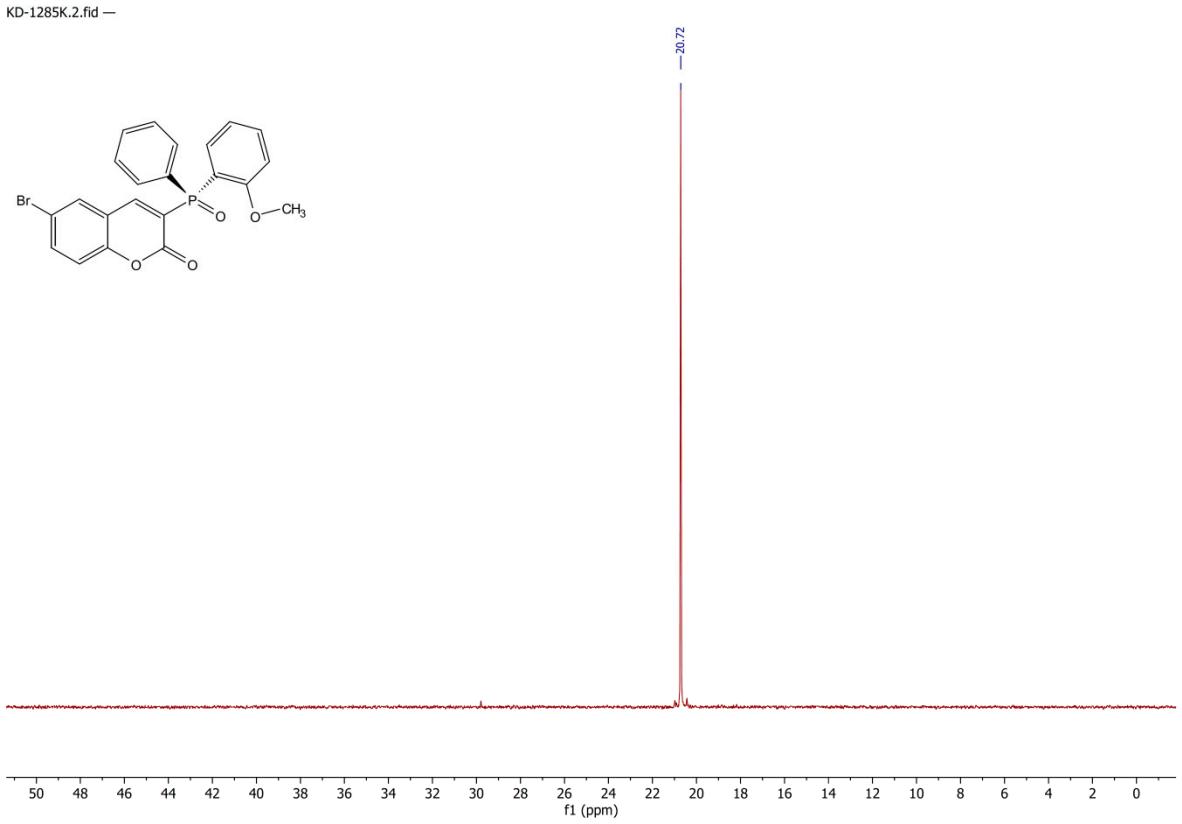
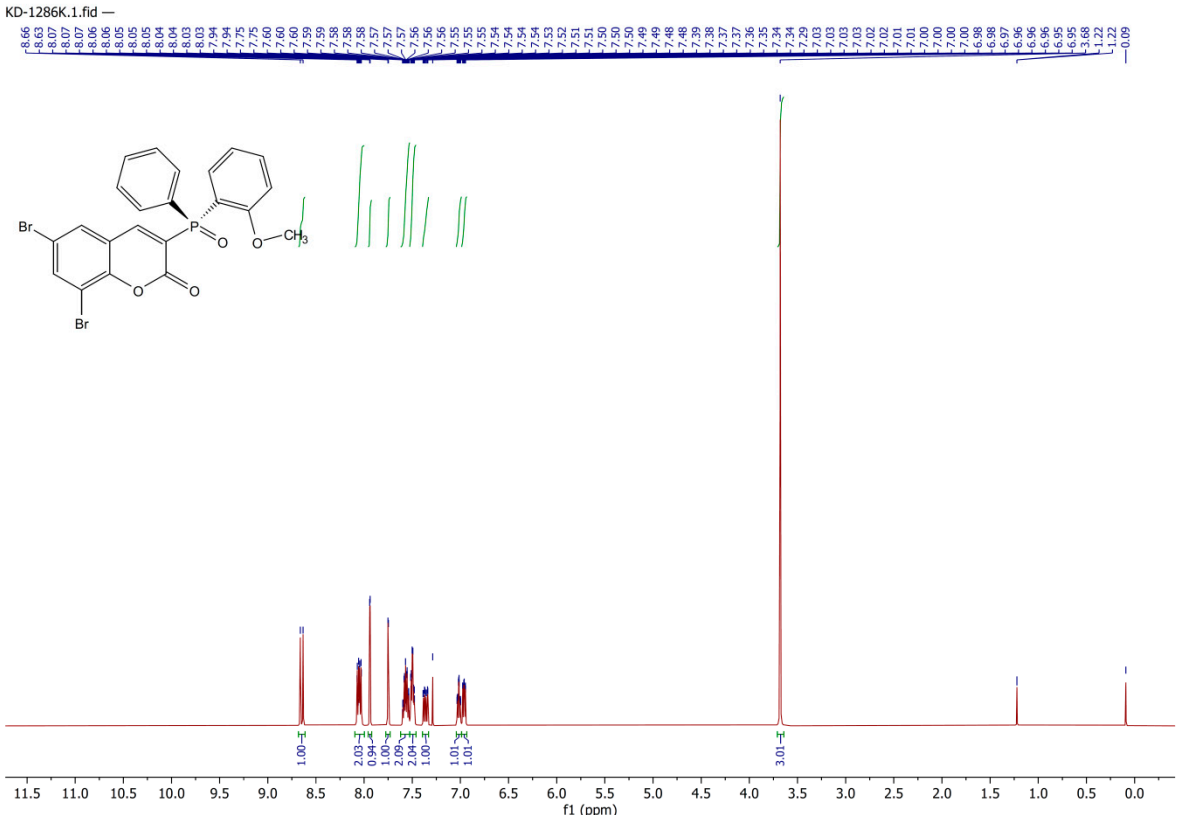
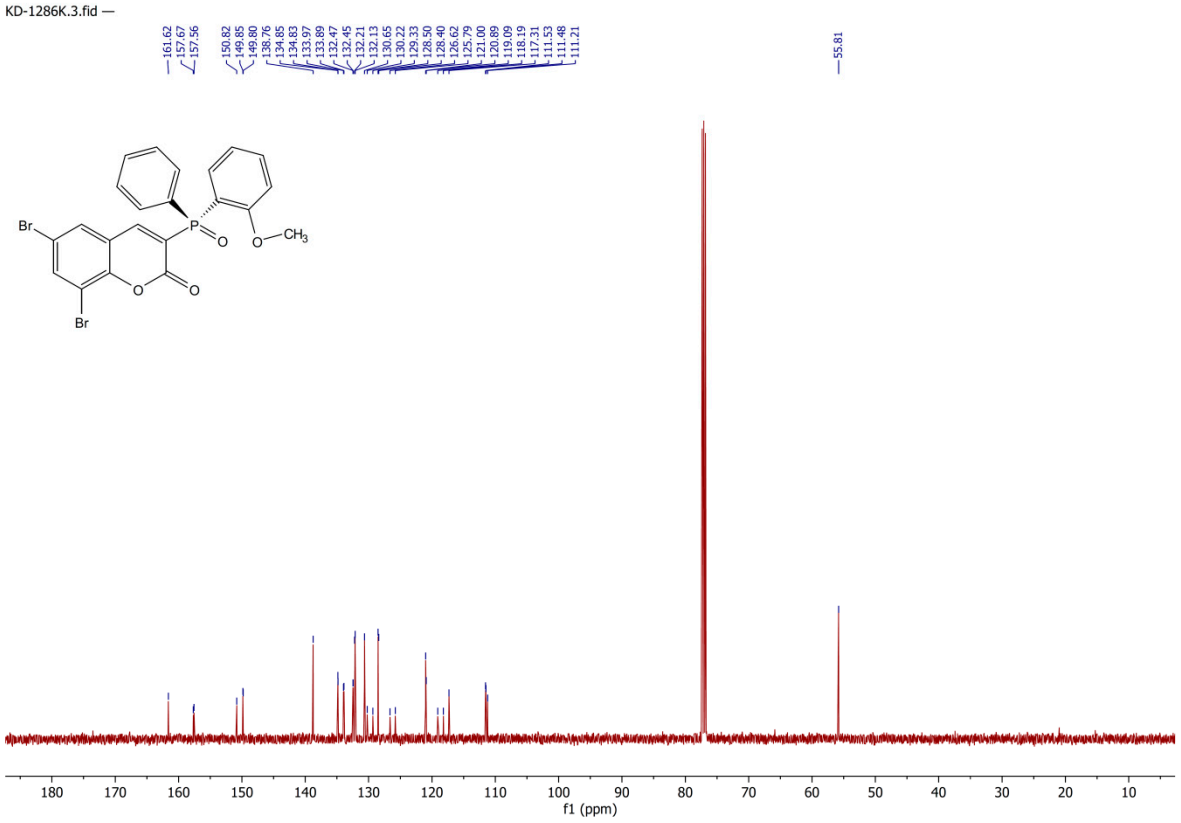


Figure S-11. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 6-(Bromo)-3-(*S*$_P$)-(2-methoxyphenyl)phenylphosphinyl)-2*H*-chromen-2-one (**4b**) in $CDCl_3$.


KD-1286K.1.fid
Br
P
O
O
CH3
O
O
Br
1.00
2.03
0.94
1.00
2.09
2.04
1.00
1.01
1.01
3.01
f1 (ppm)


KD-1286K.3.fid
161.62
157.67
157.56
150.82
149.85
149.80
138.76
134.85
134.83
133.97
133.89
132.47
132.45
132.21
132.13
130.65
130.22
129.33
128.50
128.40
126.62
125.79
121.00
120.89
119.09
118.19
117.31
111.53
111.48
111.21
55.81
Br
P
O
O
CH3
O
O
Br
f1 (ppm)

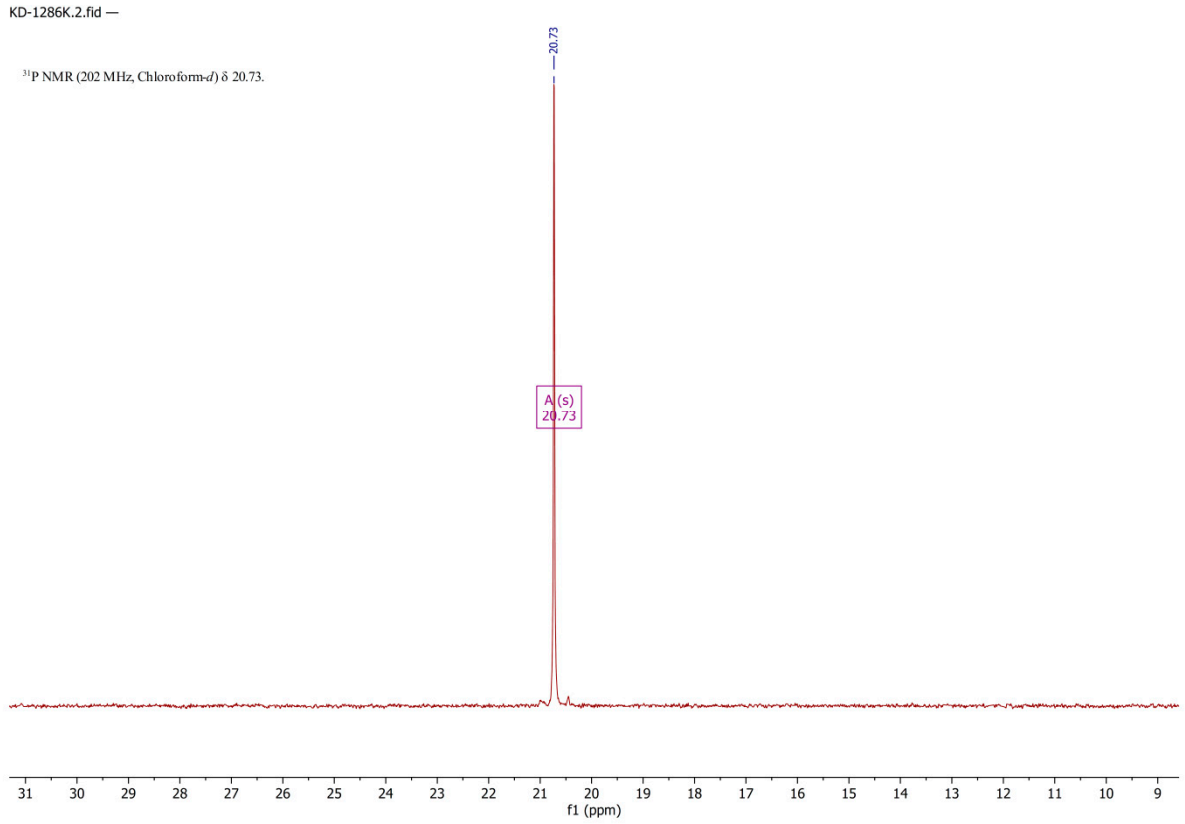
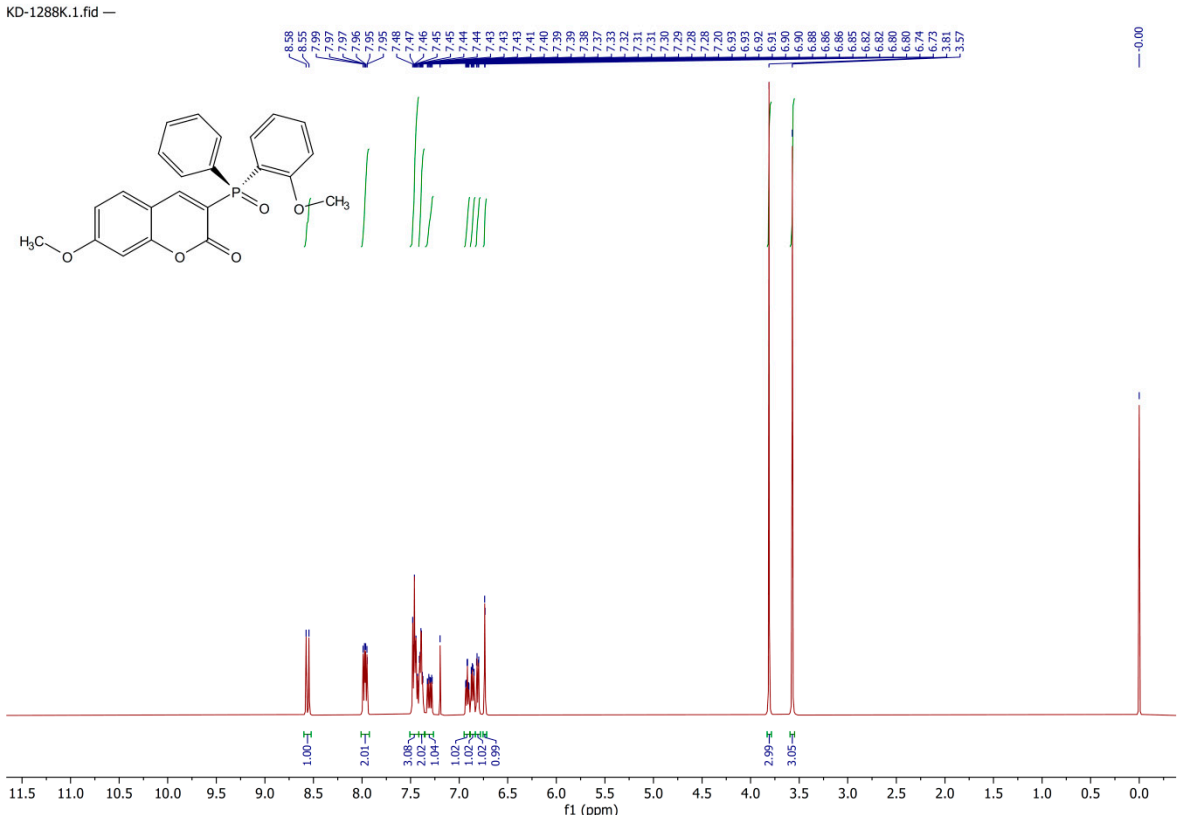
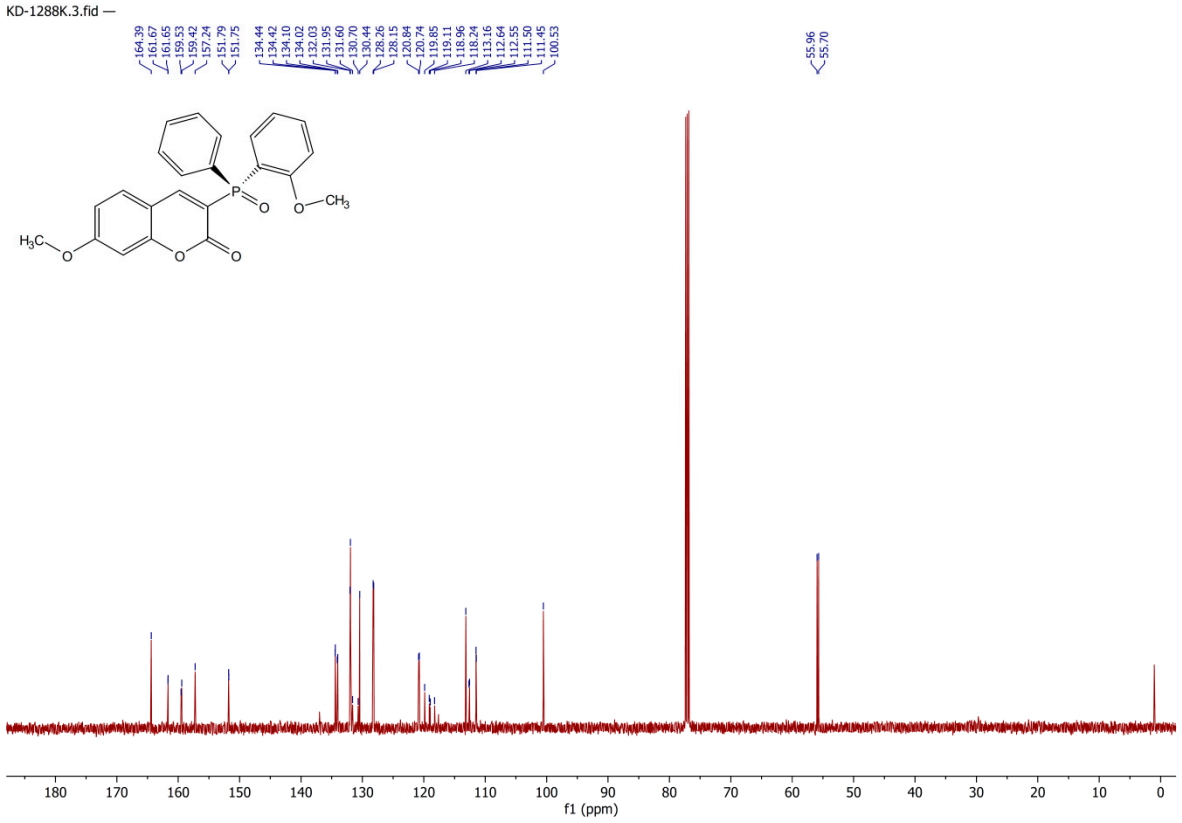


Figure S-11. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 6,8-(Dibromo)-3-(*S*$_P$)-(2-methoxyphenyl)phenylphosphinyl)-2*H*-chromen-2-one (**4c**) in $CDCl_3$.


KD-1288K.1.fid
f1 (ppm)


KD-1288K.3.fid
f1 (ppm)

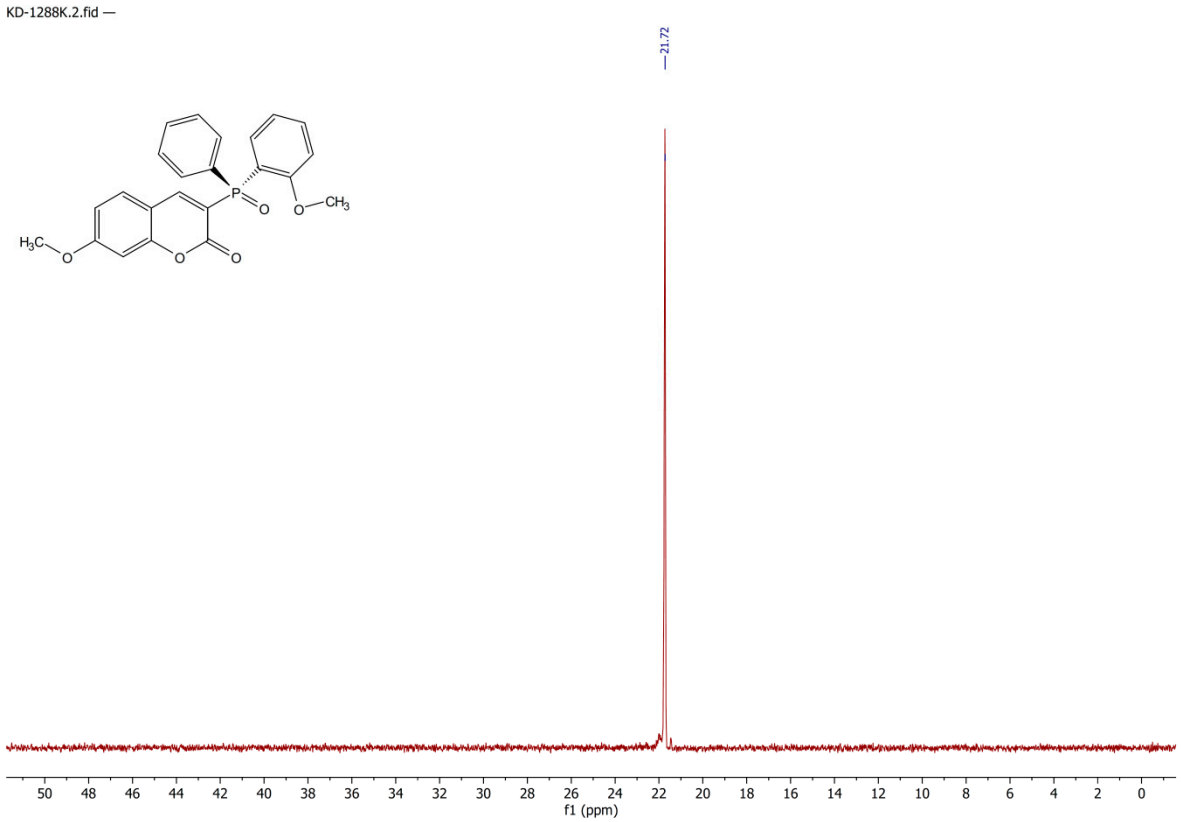
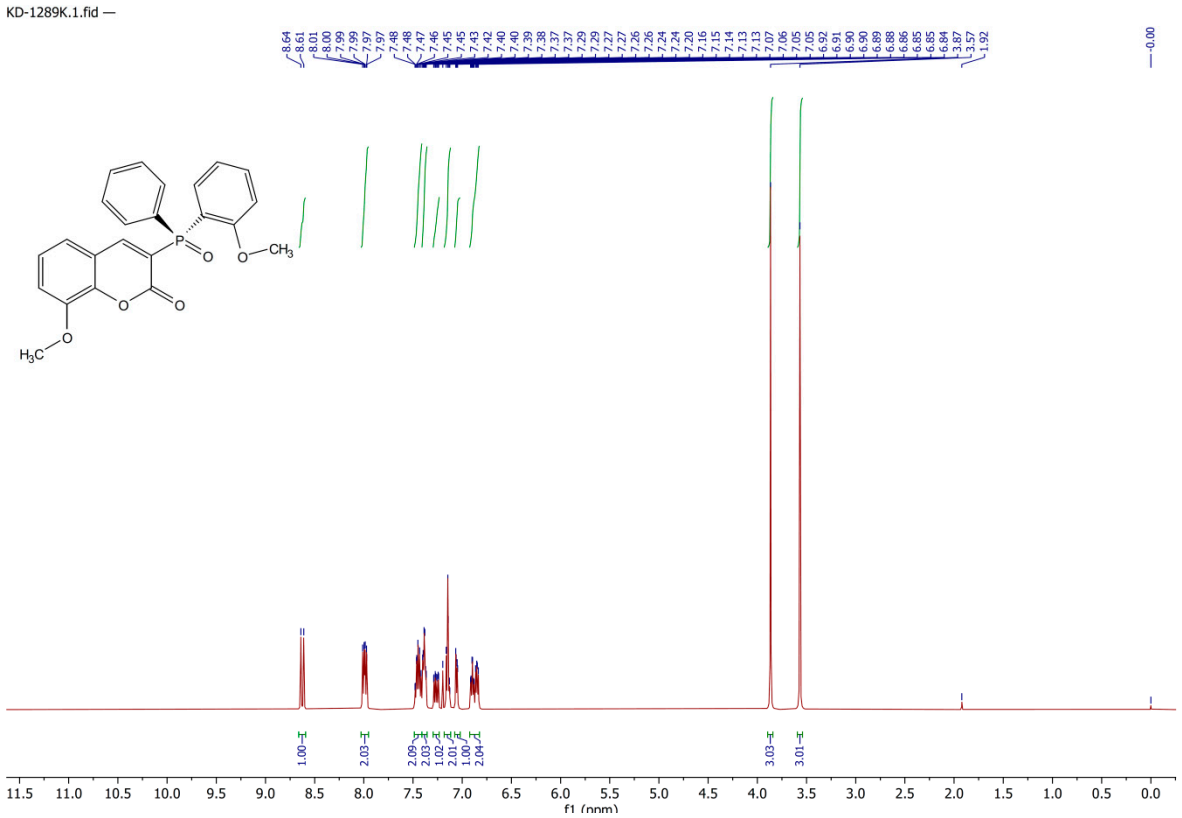
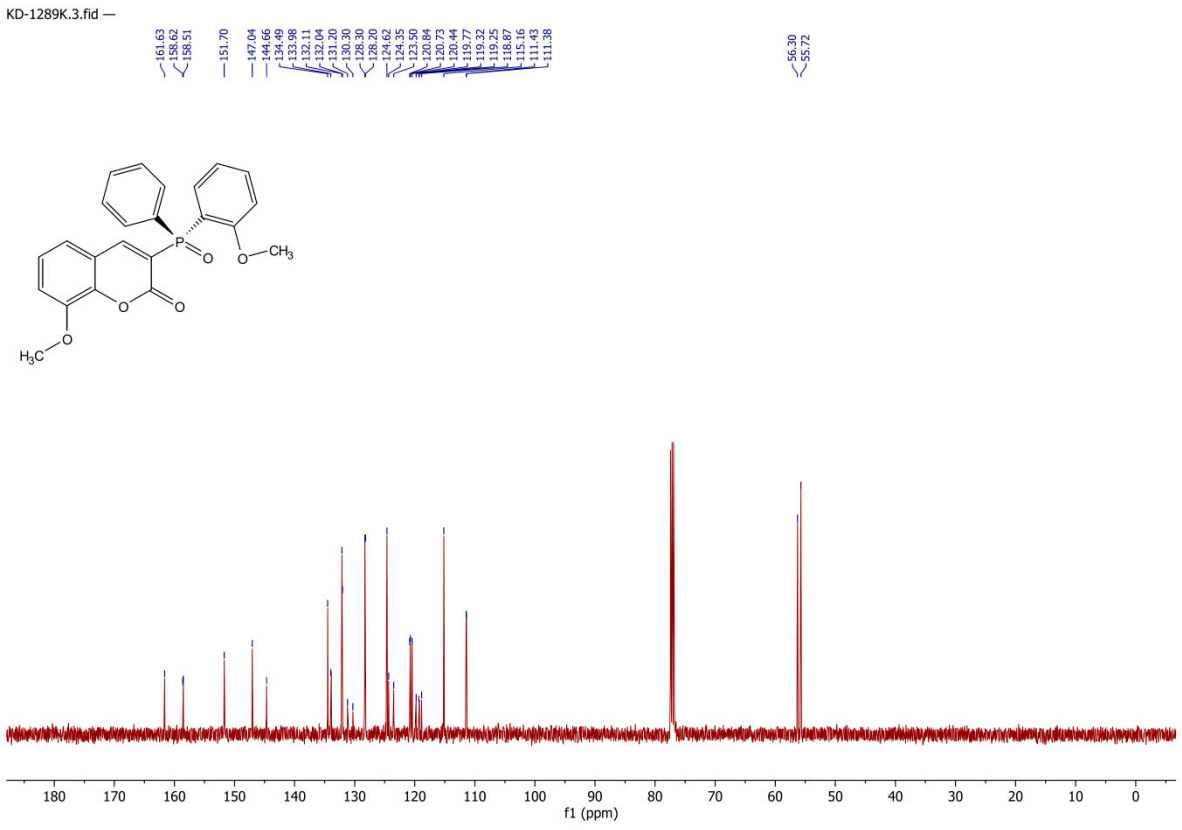


Figure S-12. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(S_P)-(2-Methoxyphenyl)phenylphosphinyl)-7-methoxy-2*H*-chromen-2-one (**4d**) in $CDCl_3$.


KD-1289K.1.fid
8.64
8.61
8.01
8.00
7.99
7.99
7.97
7.97
7.48
7.47
7.46
7.45
7.45
7.43
7.42
7.40
7.40
7.39
7.38
7.37
7.37
7.29
7.29
7.27
7.27
7.26
7.26
7.24
7.24
7.20
7.16
7.15
7.14
7.13
7.13
7.07
7.06
7.05
7.05
6.92
6.91
6.90
6.90
6.89
6.88
6.86
6.85
6.85
6.84
3.87
3.57
1.92
0.00
1.00
2.03
2.09
2.03
1.02
2.01
1.00
2.04
3.03
3.01
11.5
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
f1 (ppm)


KD-1289K.3.fid
161.63
158.62
158.51
151.70
147.04
144.66
134.49
133.98
132.11
132.04
131.20
130.30
128.30
128.20
124.62
124.35
123.50
123.04
120.73
120.44
119.77
119.32
119.25
118.87
115.16
111.43
111.38
56.30
55.72
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

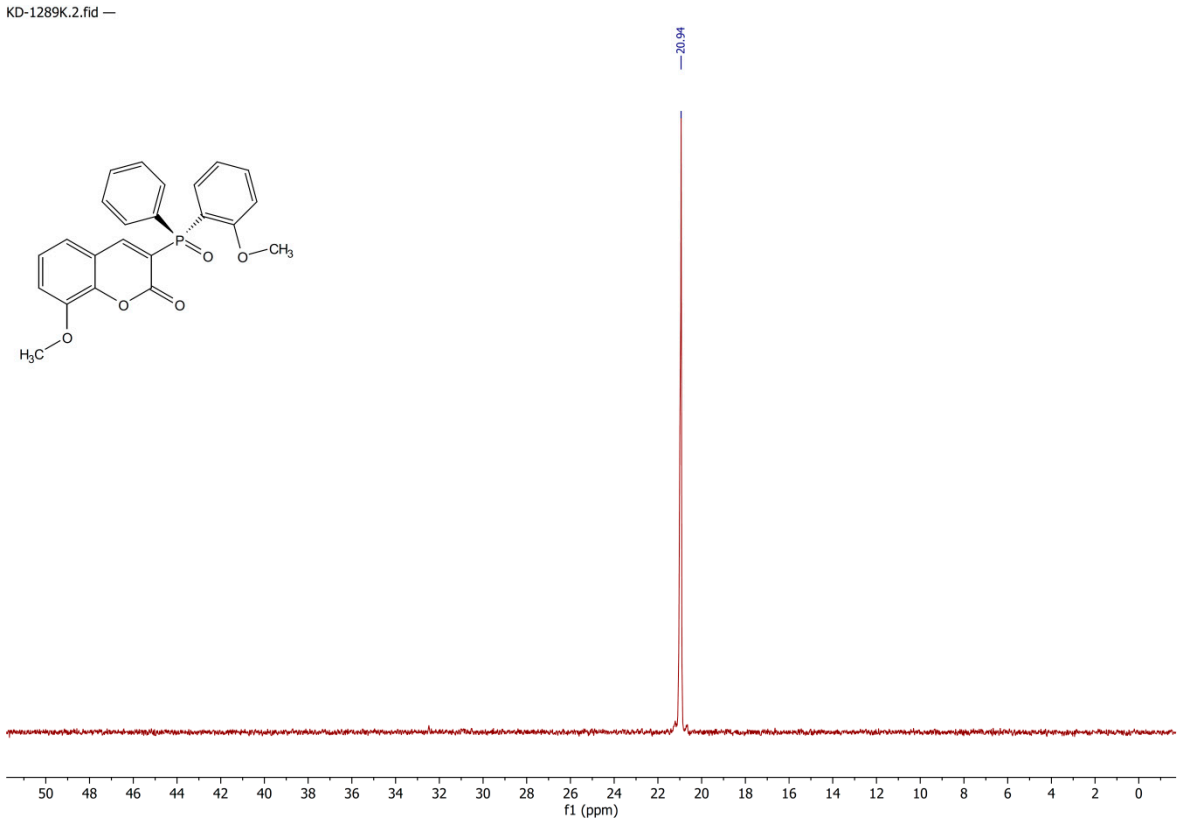
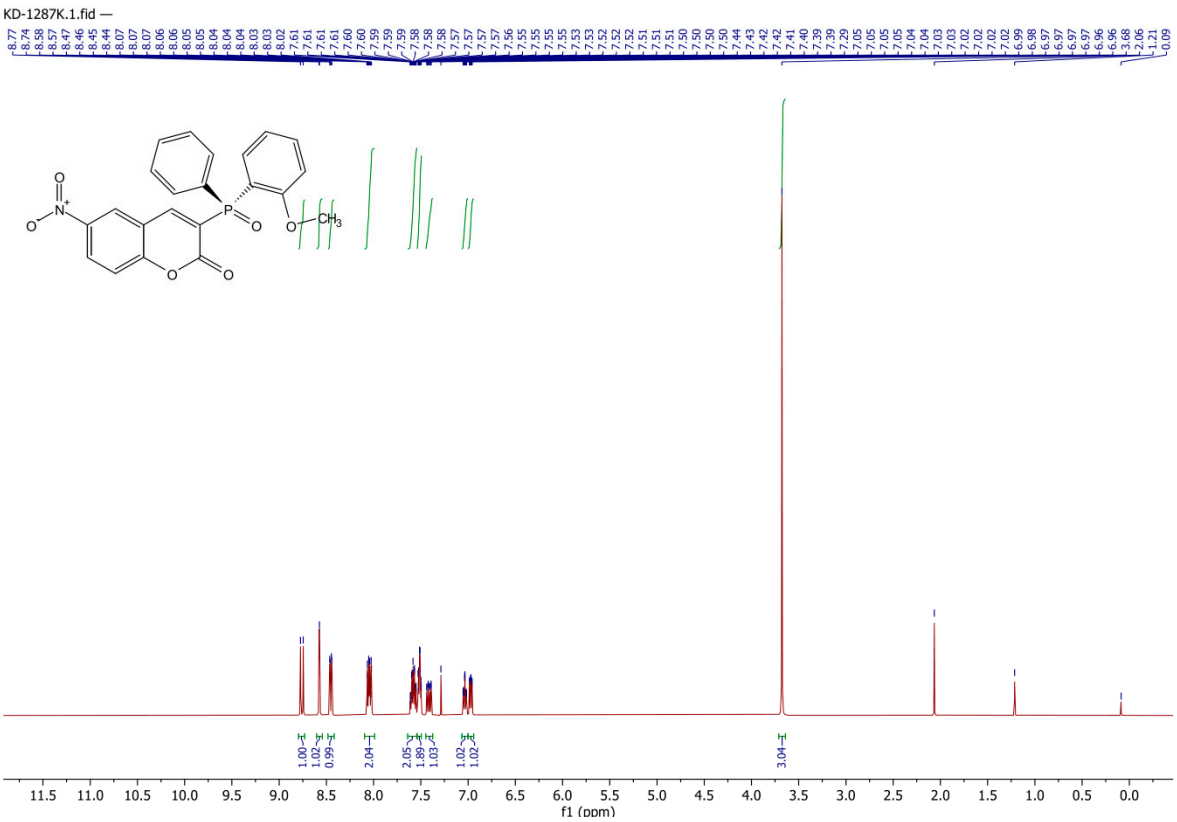
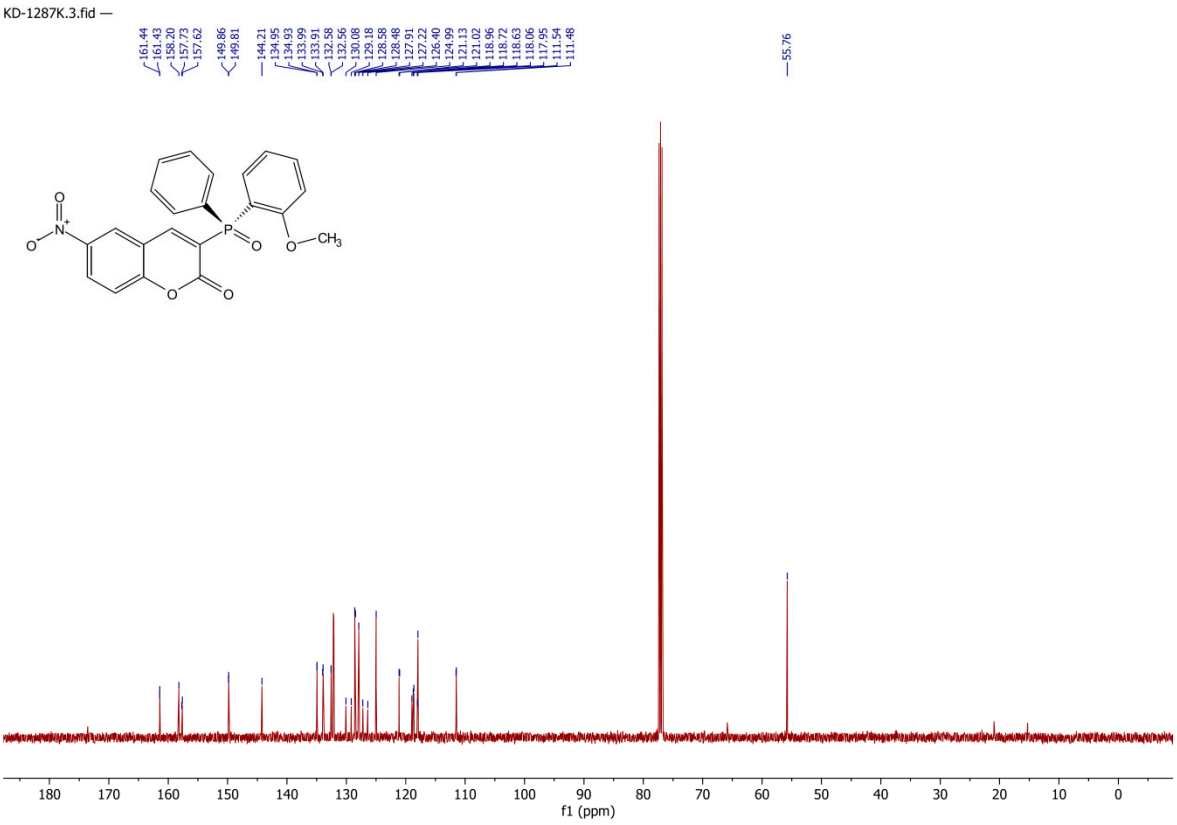


Figure S-13. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(S_P)-(2-Methoxyphenyl)phenylphosphinyl)-8-methoxy-2*H*-chromen-2-one (**4d**) in $CDCl_3$.


KD-1287K.1.fid
f1 (ppm)


KD-1287K.3.fid
f1 (ppm)

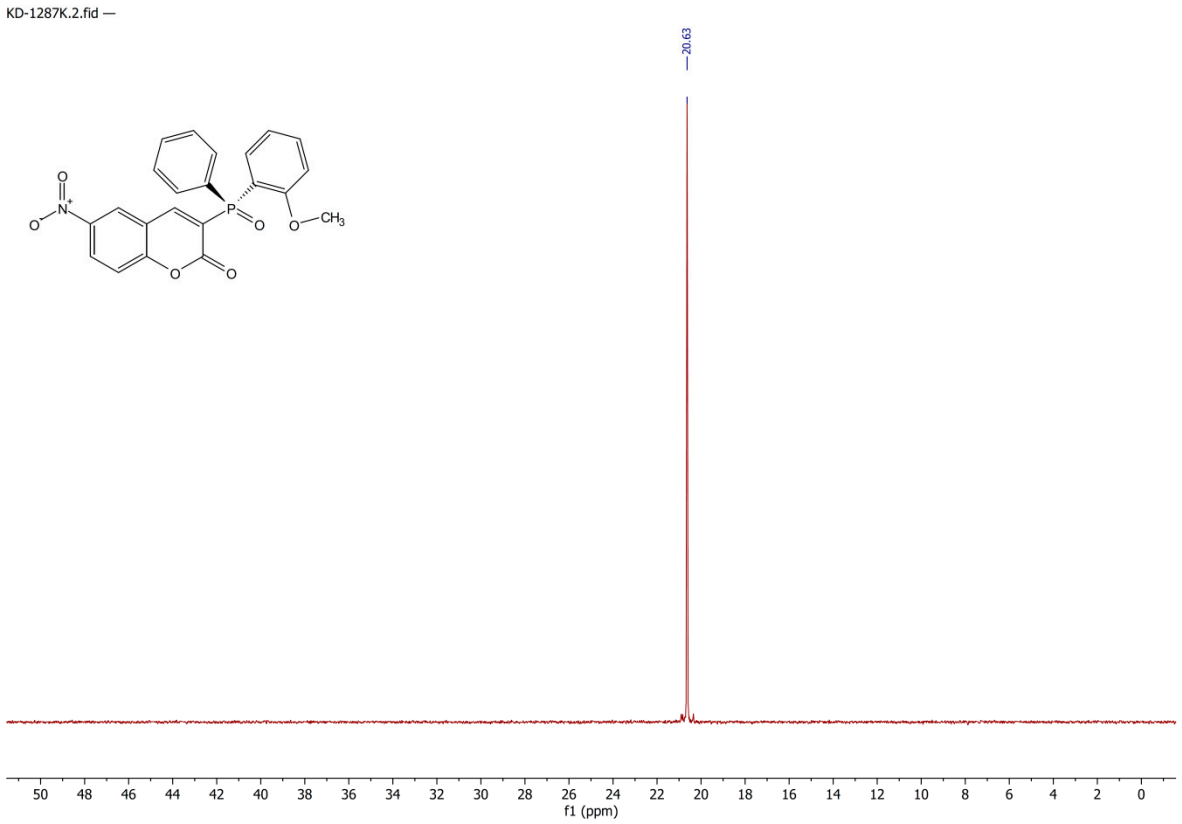
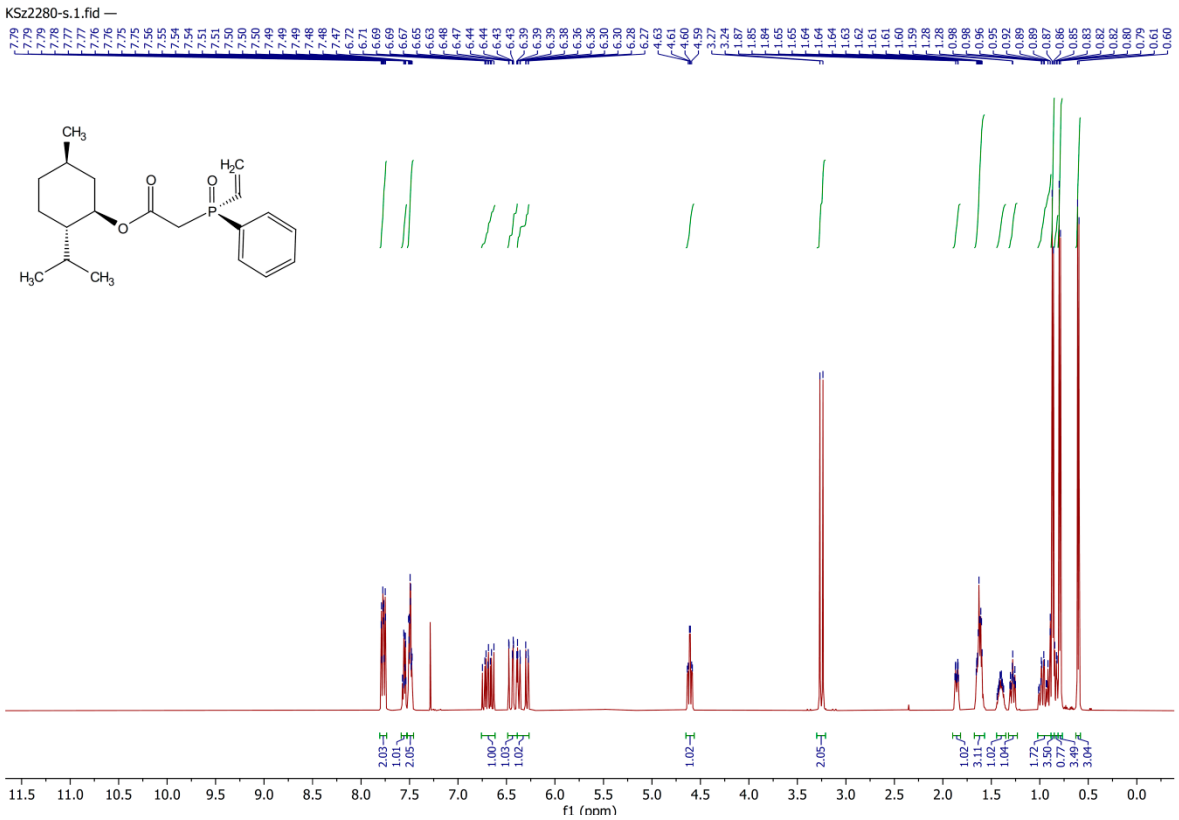
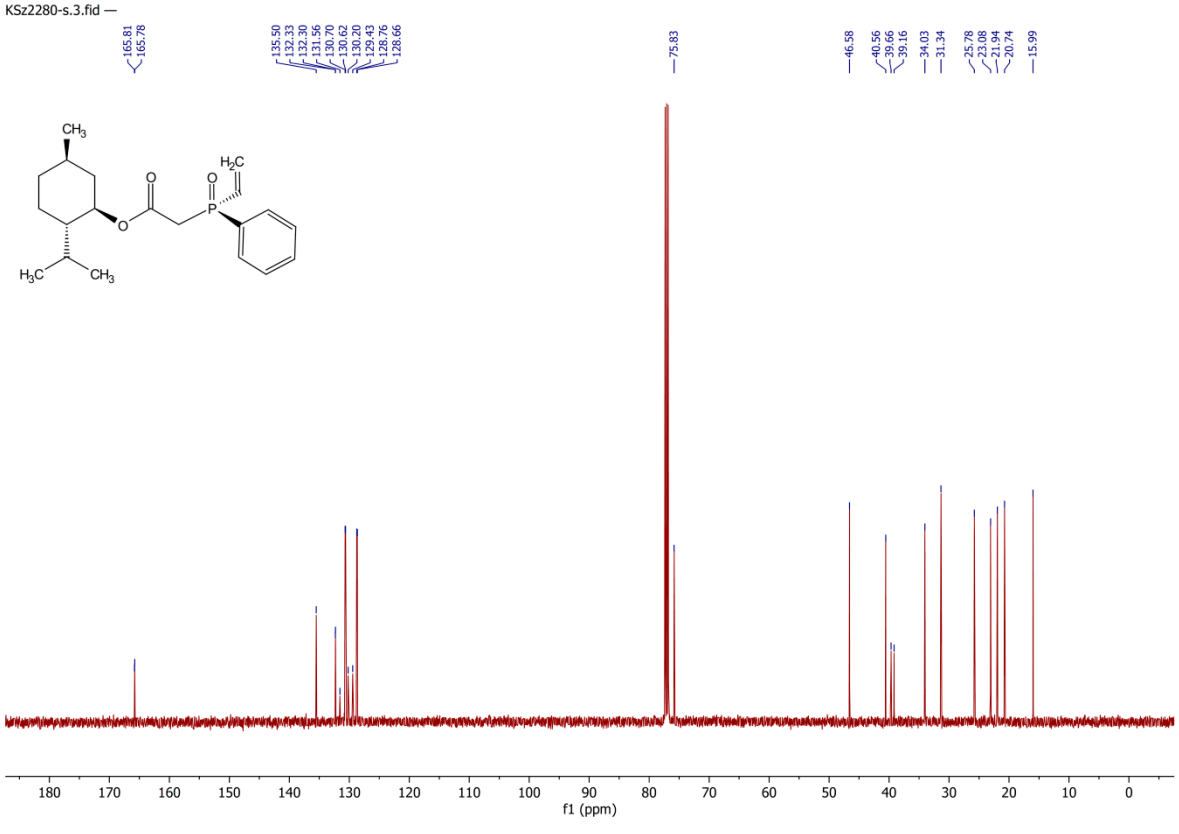


Figure S-14. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(*S*$_P$)-(2-Methoxyphenyl)phenylphosphinyl)-6-nitro-2*H*-chromen-2-one (**4f**) in $CDCl_3$.


KSz2280-s.1.fid
CH3
H2C
O
O
P
O
H3C
CH3
f1 (ppm)


KSz2280-s.3.fid
CH3
H2C
O
O
P
O
H3C
CH3
f1 (ppm)

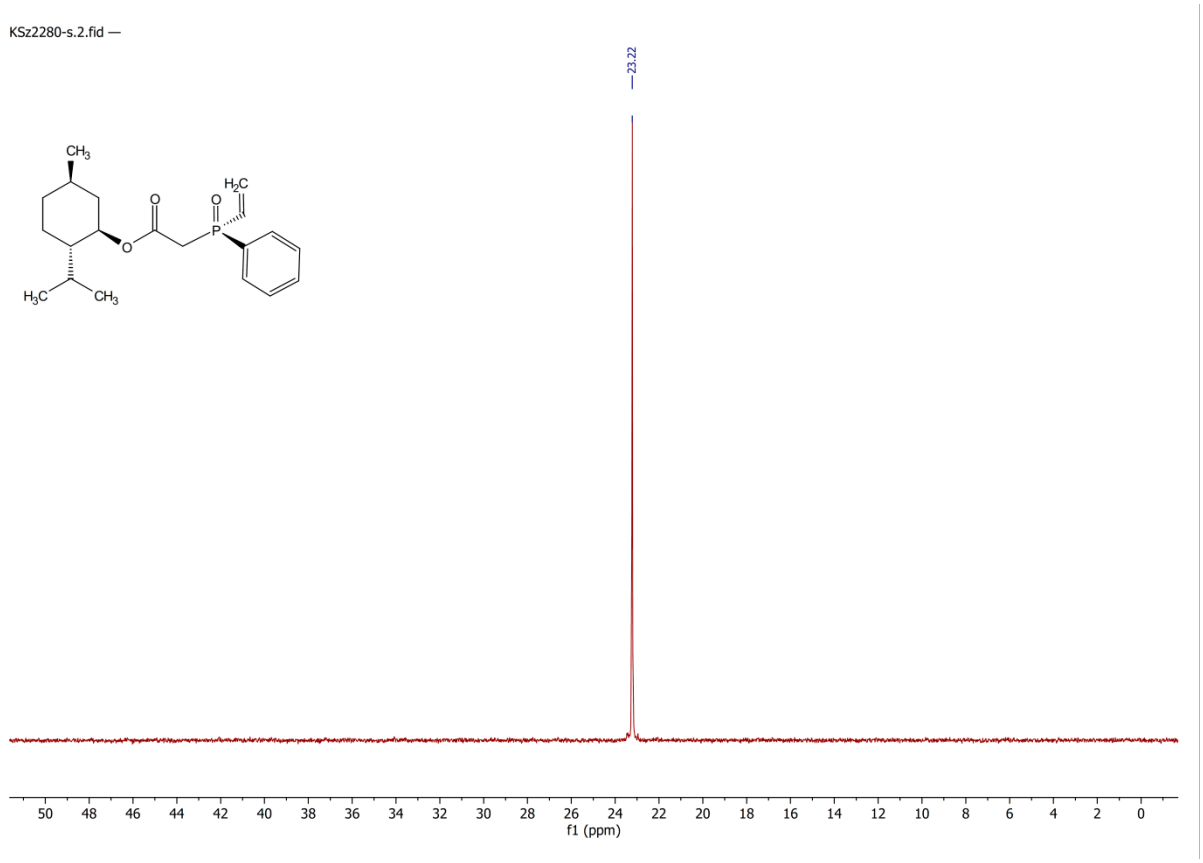
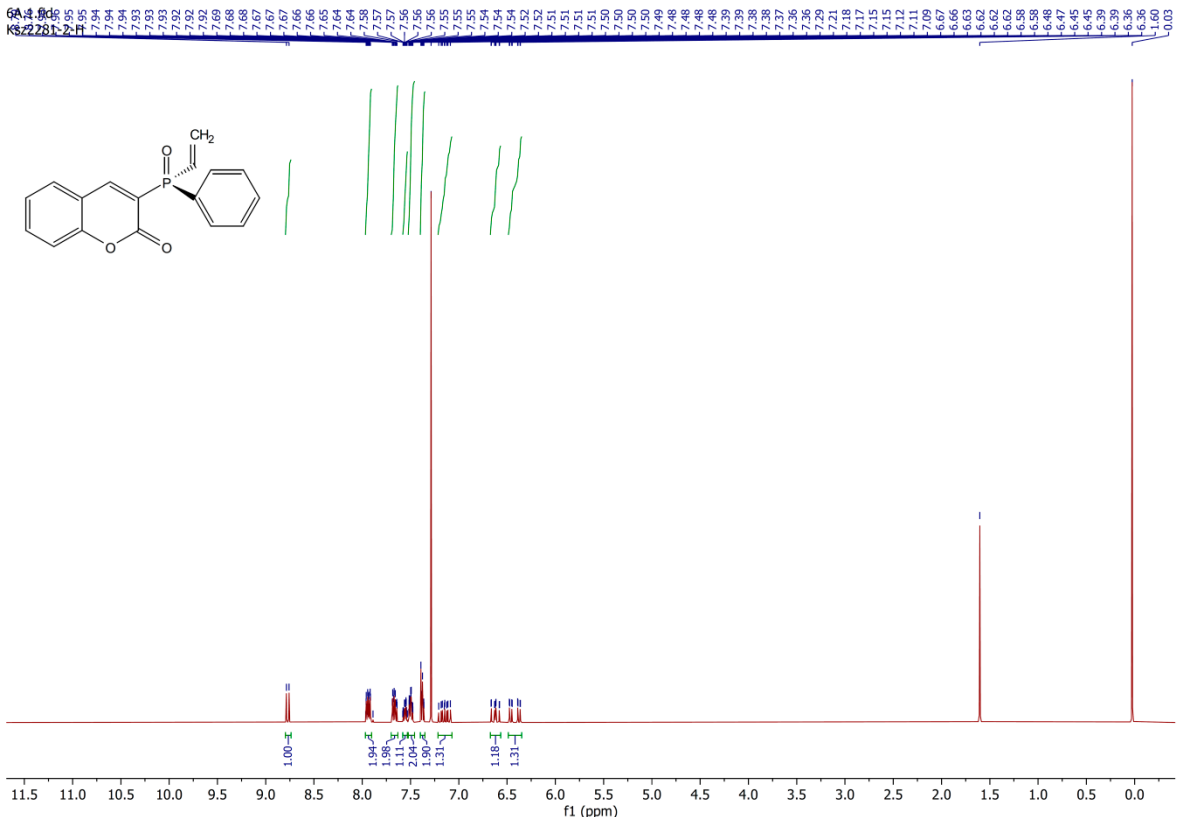
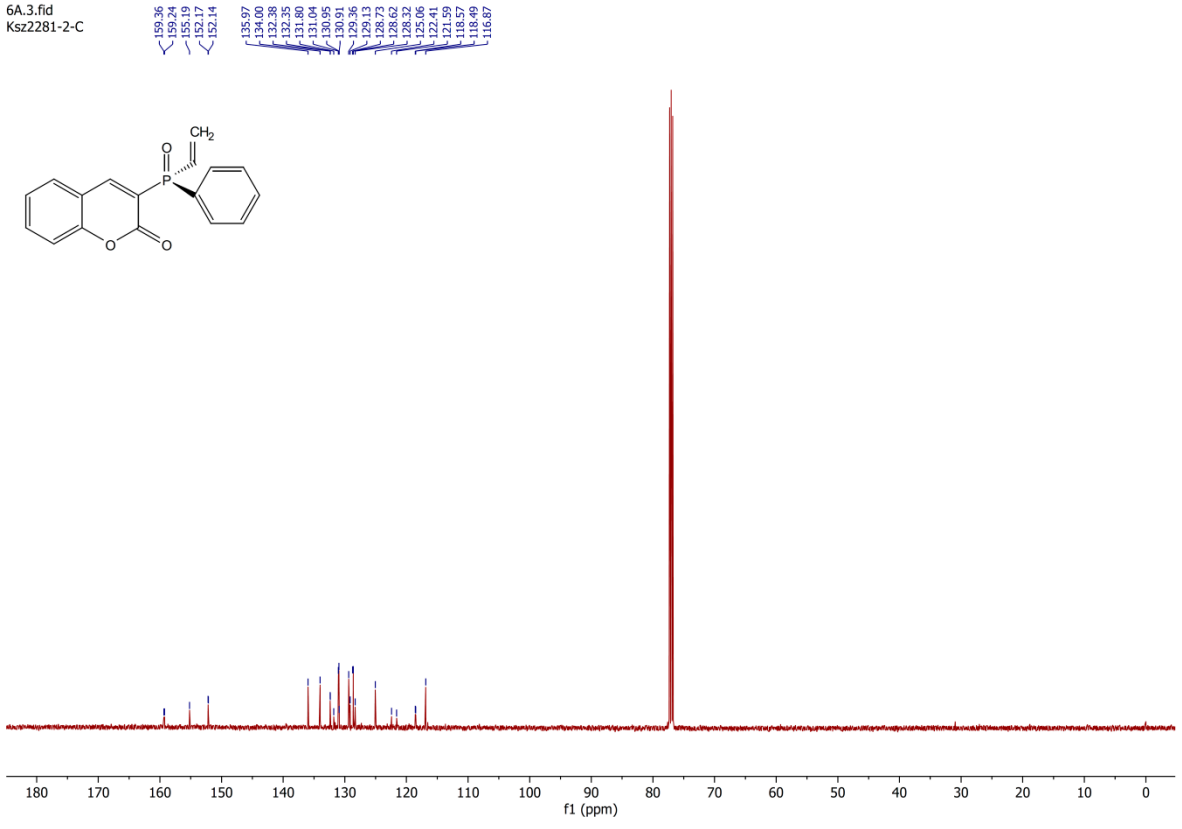


Figure S-15. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of *(S$_P$)-L-menthyl phenylvinylphosphinylacetate* (**5**) in $CDCl_3$.



6A.3.fid
Ksz2281-2-C



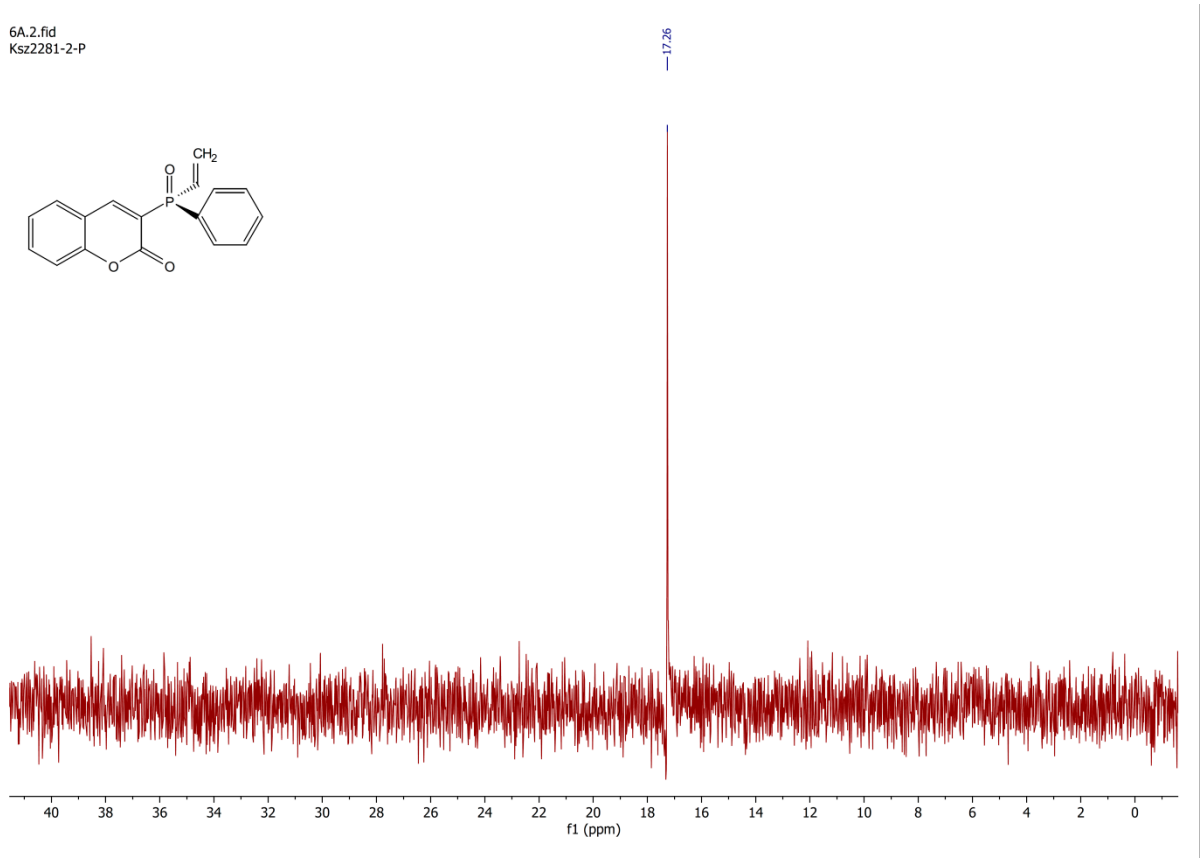
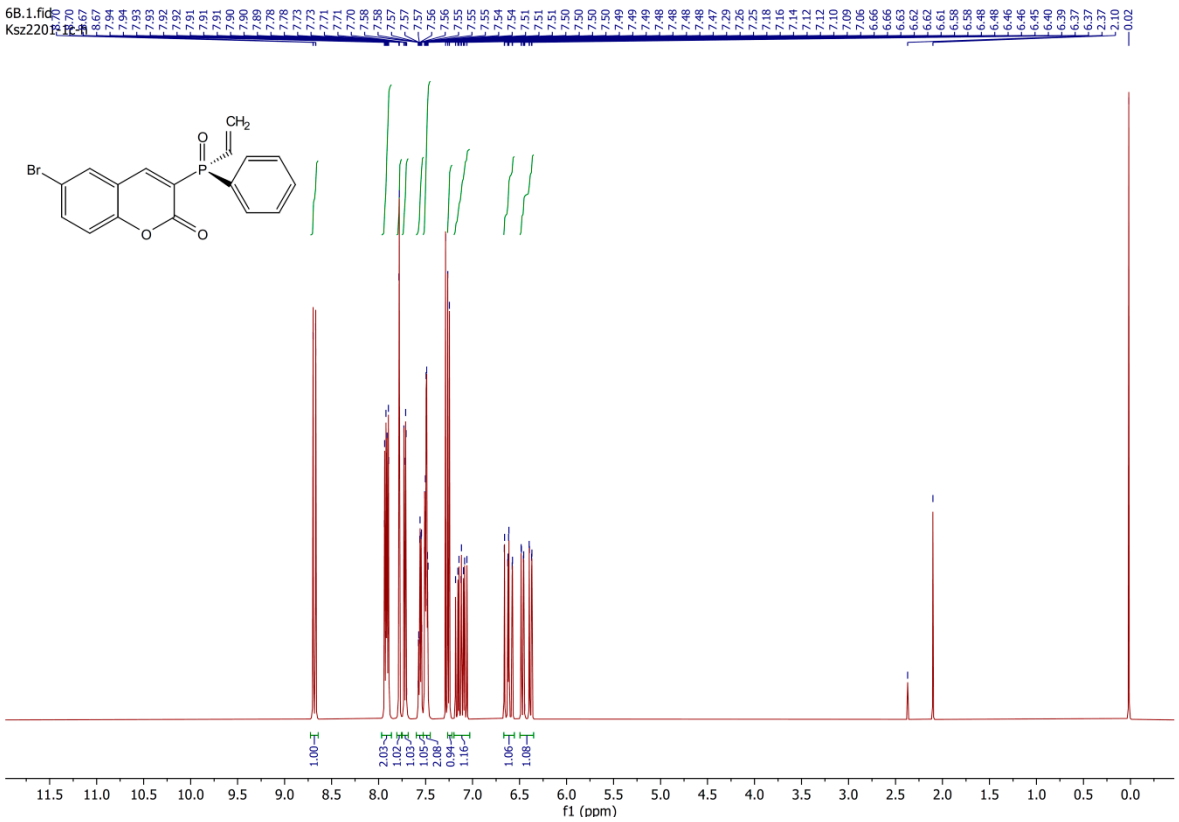
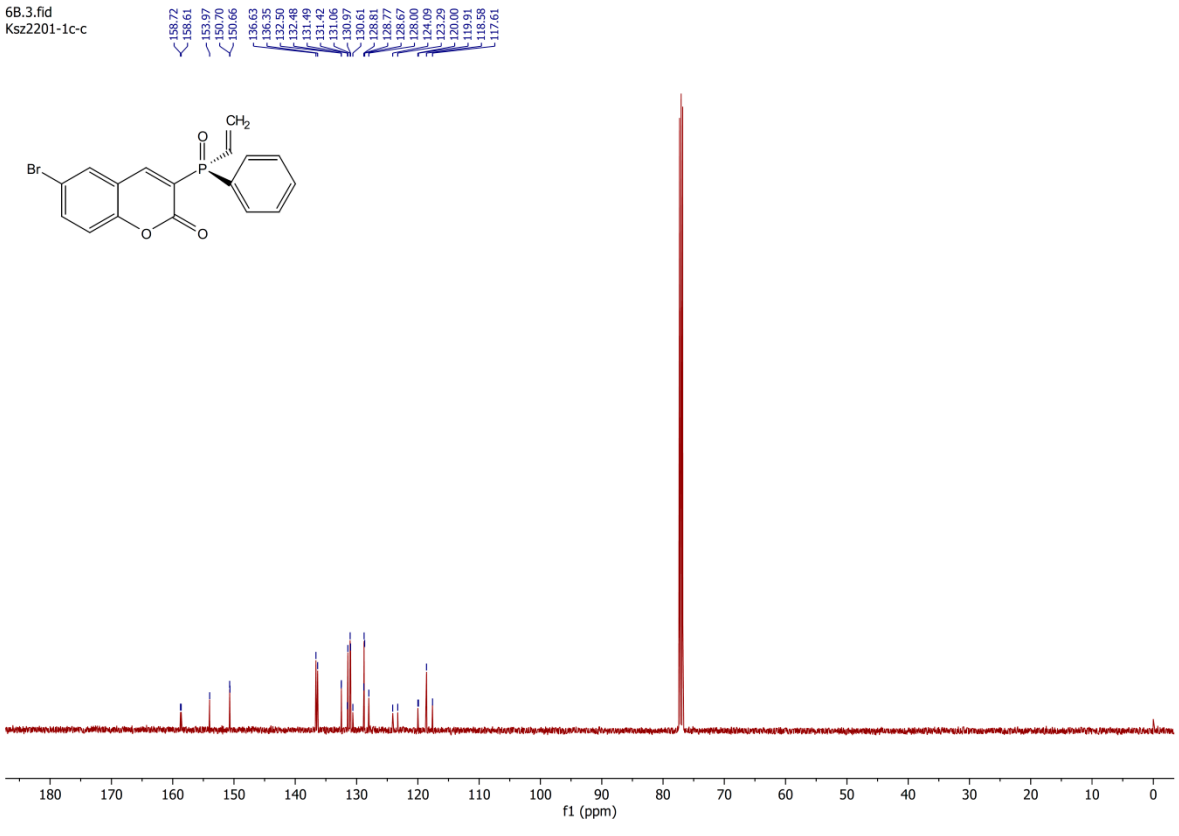


Figure S-16. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(S_P)-(Phenyl(vinyl)phosphinyl)-2*H*-chromen-2-one (**6a**) in $CDCl_3$.


6B.1.fid
Ksz2201-1c-H
Br
O
P
CH2
O
O
1.00
2.03
1.02
1.03
1.05
2.08
0.94
1.16
1.06
1.08
f1 (ppm)


6B.3.fid
Ksz2201-1c-c
158.72
158.61
153.97
150.70
150.66
136.63
136.35
132.50
132.48
131.49
131.42
131.06
130.97
130.61
128.81
128.77
128.67
128.00
124.09
123.29
120.00
119.91
118.58
117.61
Br
O
P
CH2
O
O
f1 (ppm)

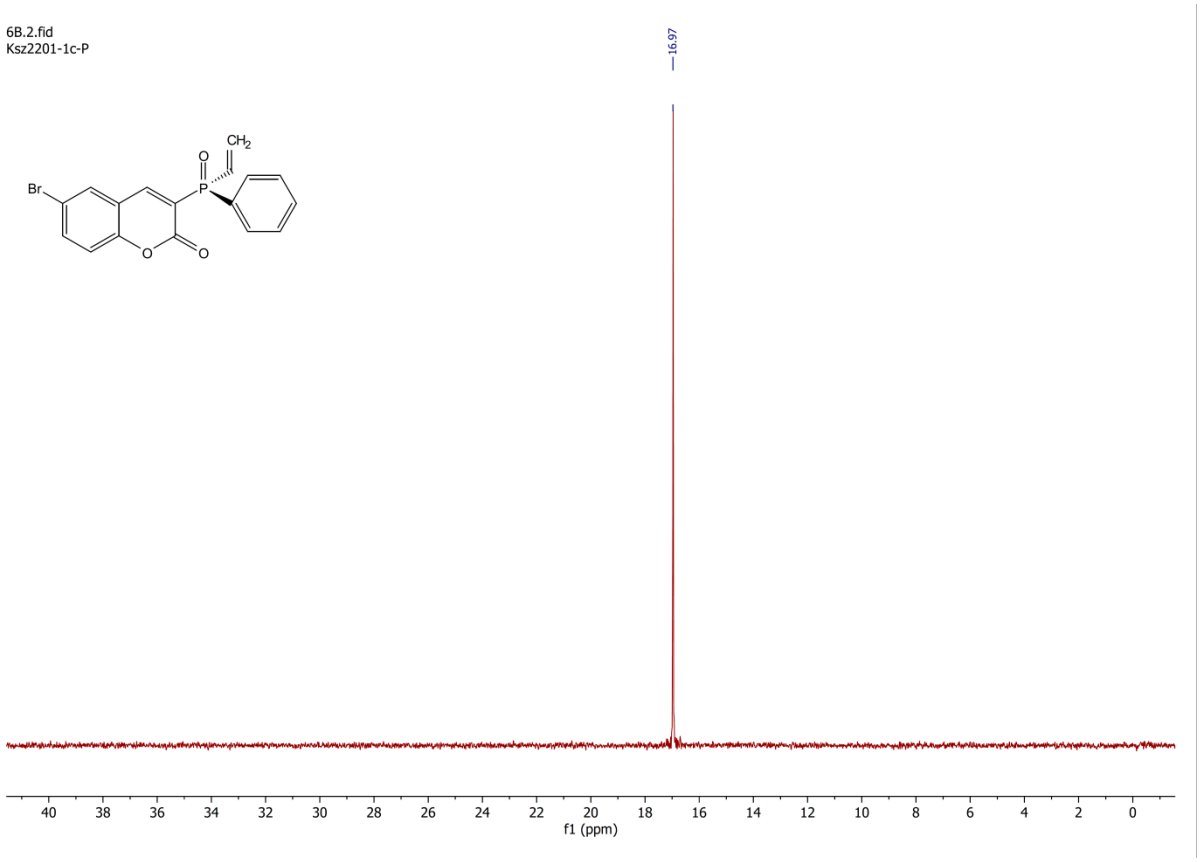
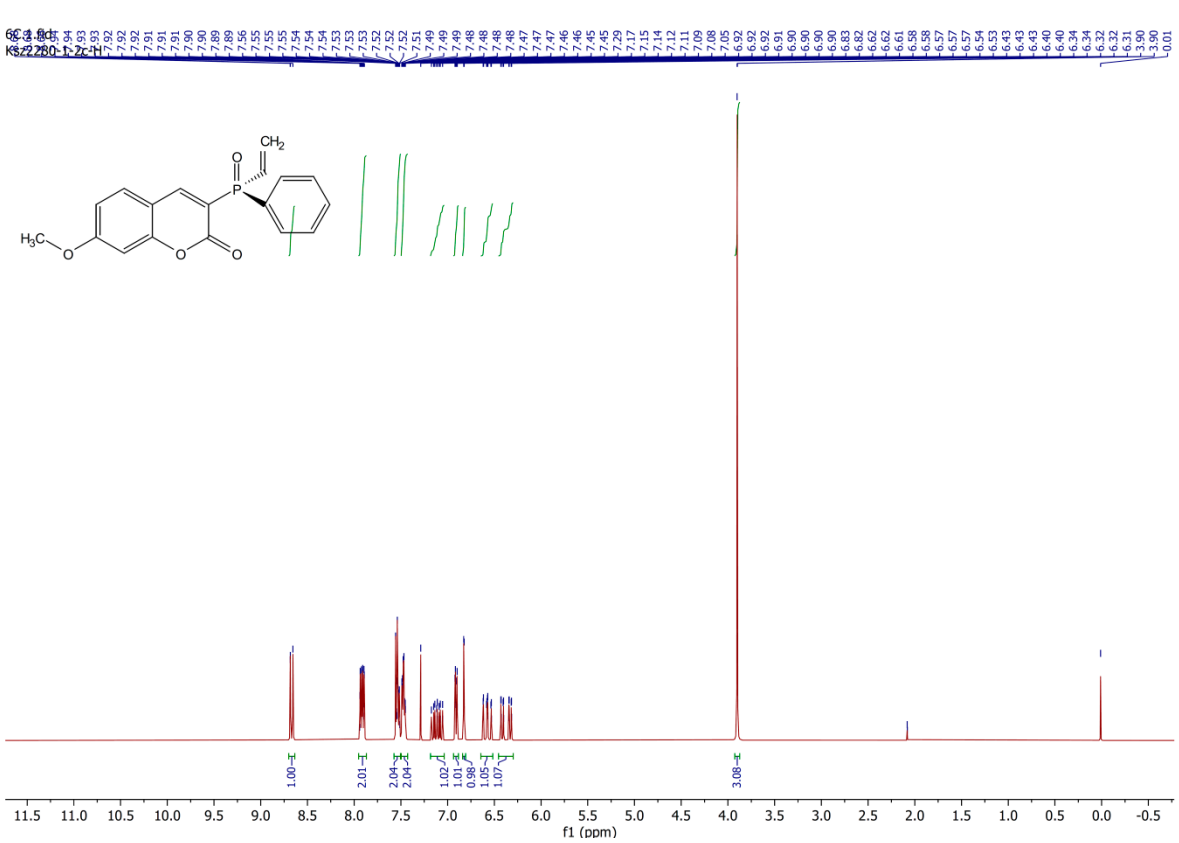
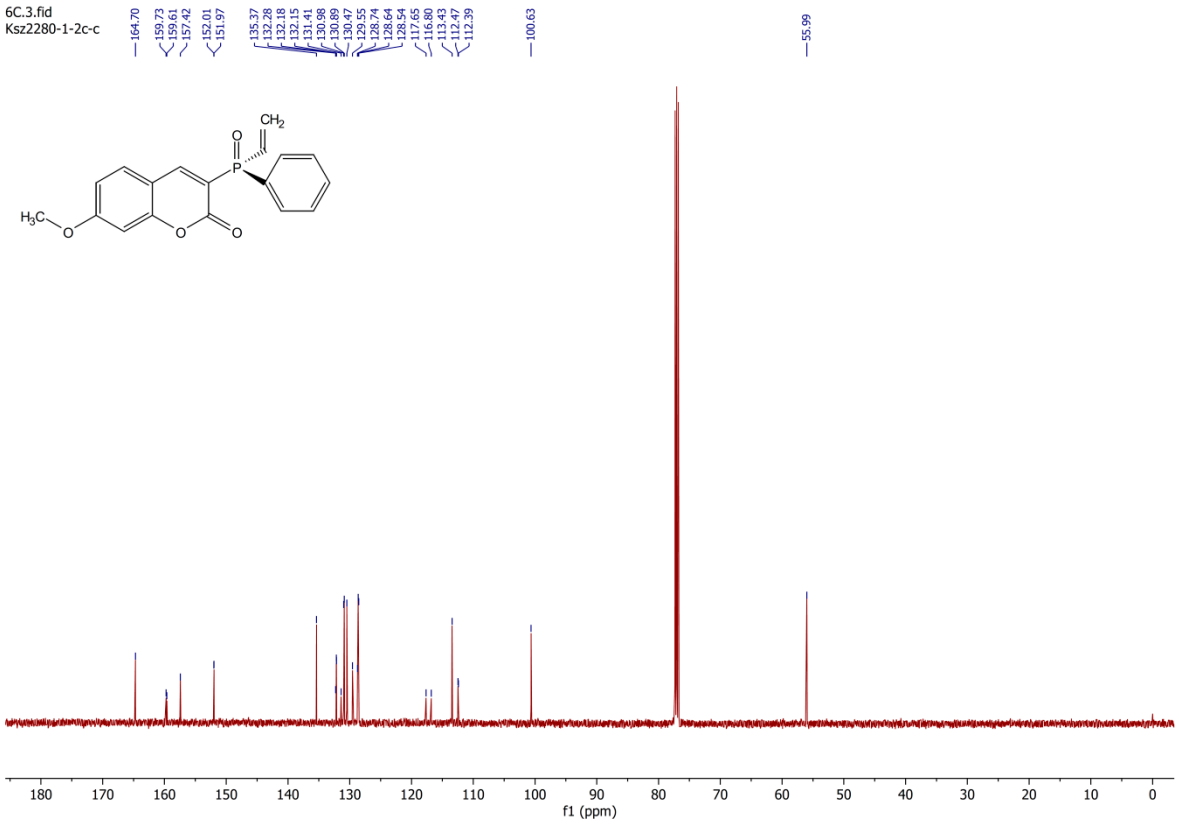


Figure S-17. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 6-(Bromo)-3-(*S*$_P$)-(phenyl(vinyl)phosphinyl)-2*H*-chromen-2-one (**6b**) in $CDCl_3$.


6C.4.fid
Ksz2280-1-2c-H
CH2
O
P
H3C
O
O
O
1.00
2.01
2.04
2.04
1.02
1.01
0.98
1.05
1.07
3.08
11.5 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
f1 (ppm)


6C.3.fid
Ksz2280-1-2c-c
164.70
159.73
159.61
157.42
152.01
151.97
135.37
132.28
132.18
132.15
131.41
130.98
130.89
130.47
129.55
128.74
128.64
128.54
117.65
116.80
113.43
112.47
112.39
100.63
55.99
CH2
O
P
H3C
O
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

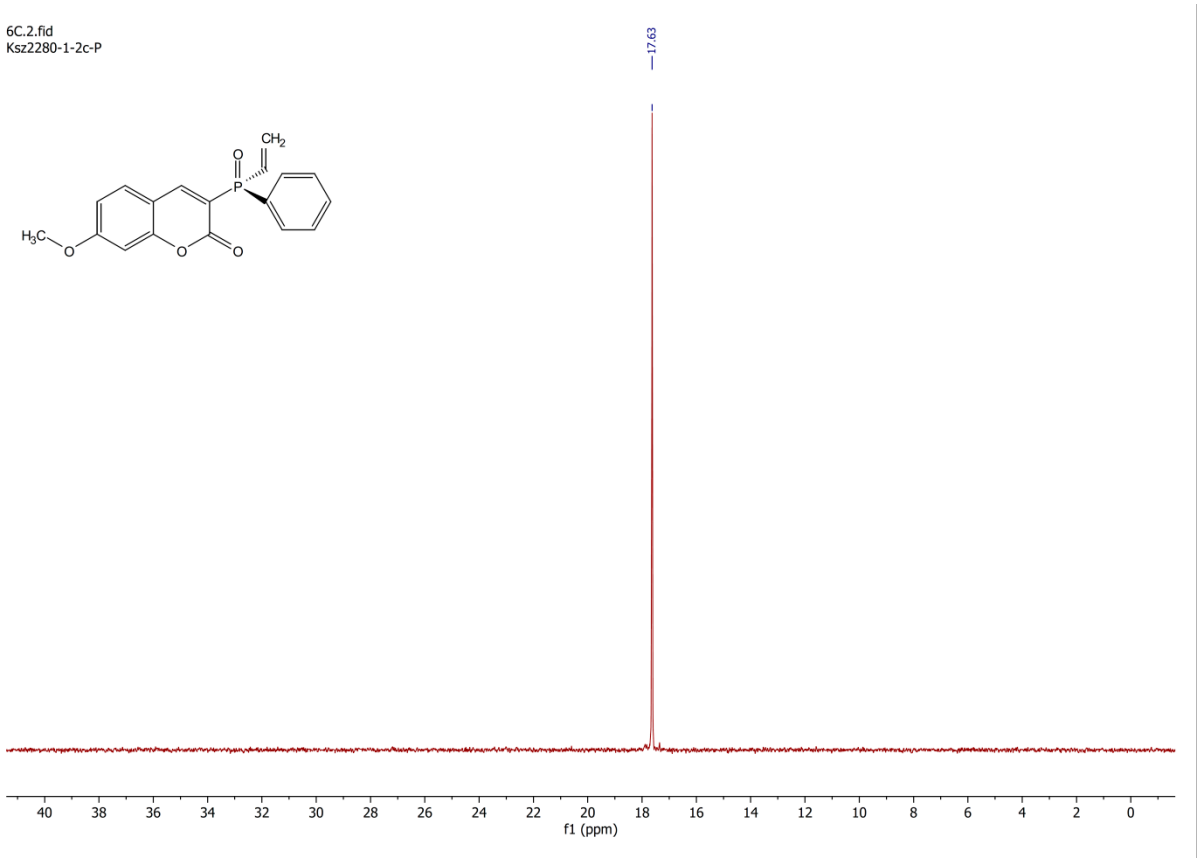
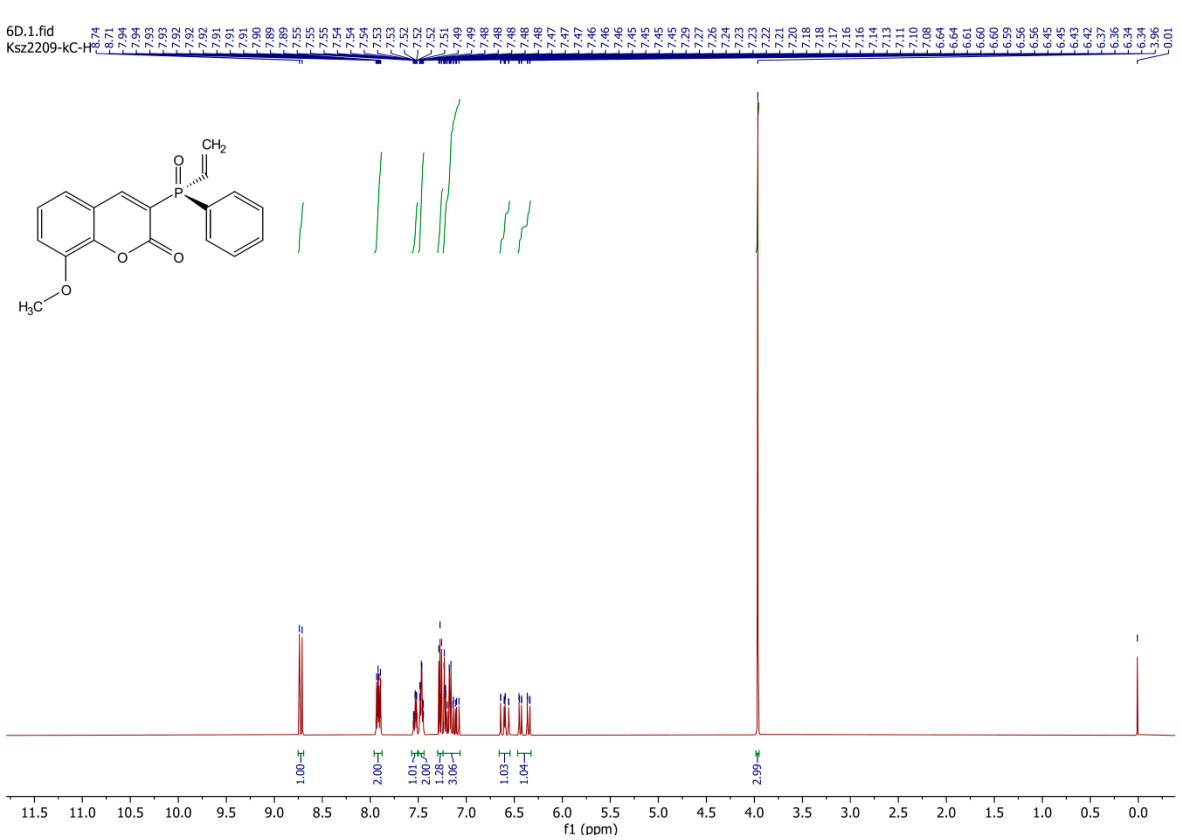
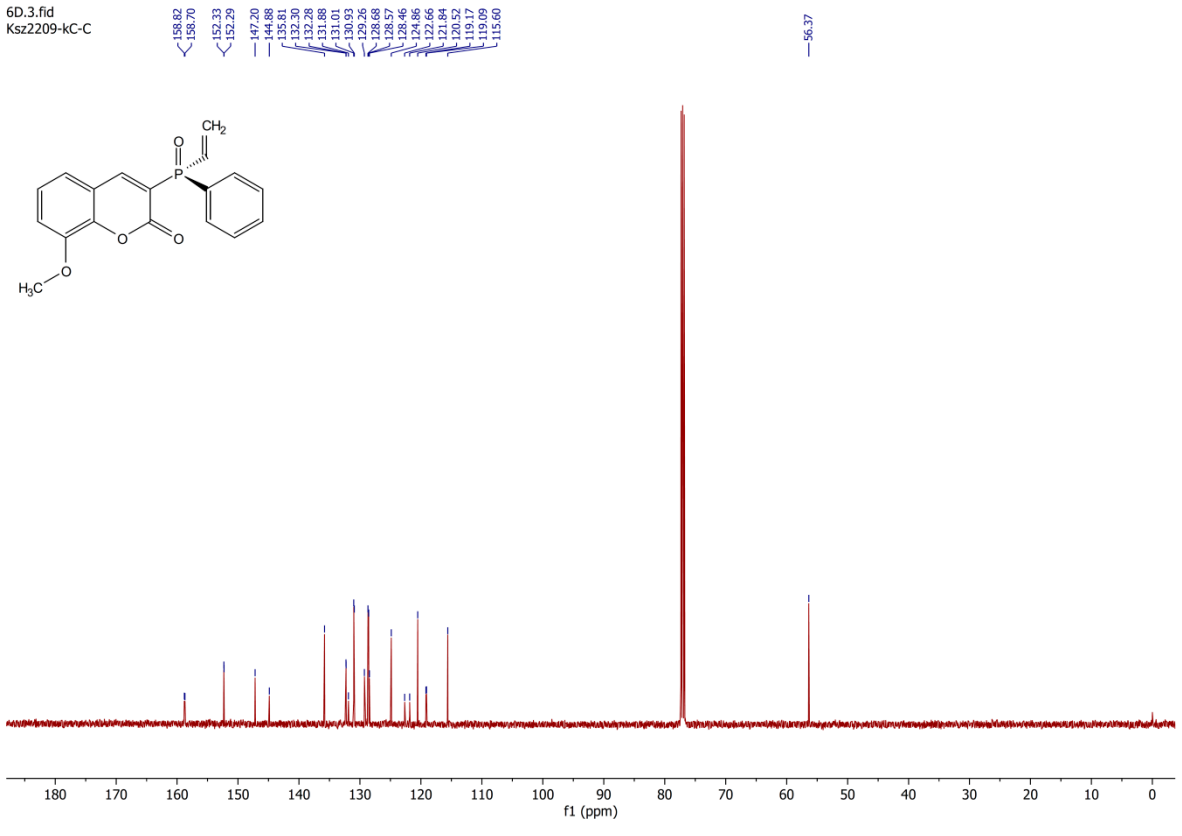


Figure S-18. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(*S*$_P$)-(Phenyl(vinyl)phosphinyl)-7-methoxy-2*H*-chromen-2-one (**6c**) in $CDCl_3$.


6D.1.fid
Ksz2209-kC-H
f1 (ppm)


6D.3.fid
Ksz2209-kC-C
f1 (ppm)

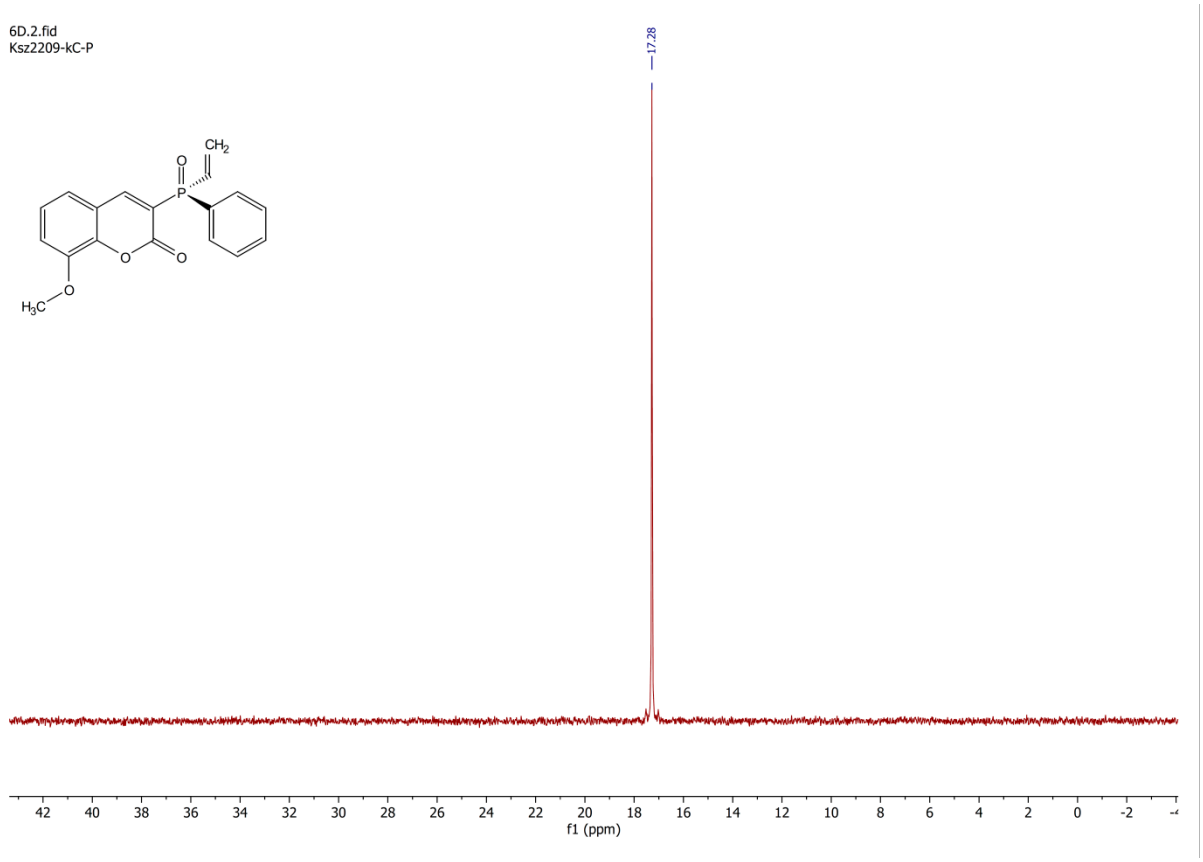
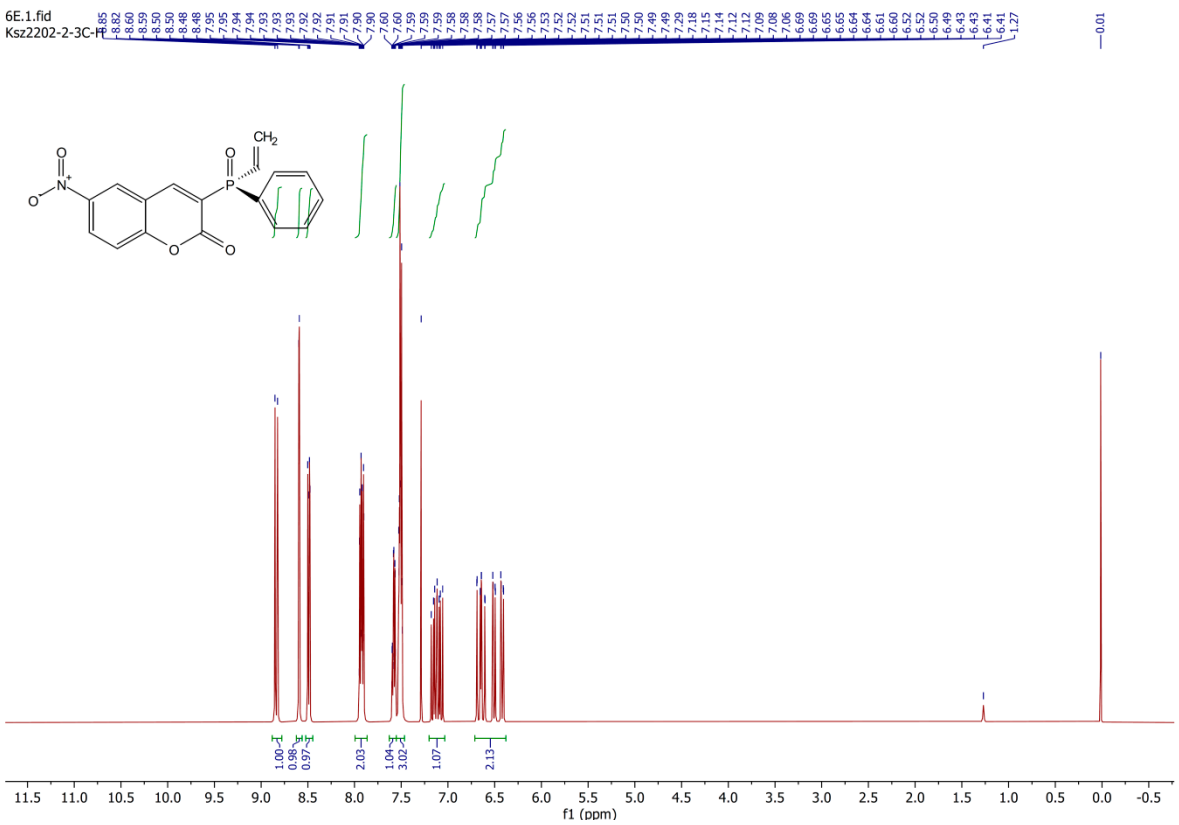
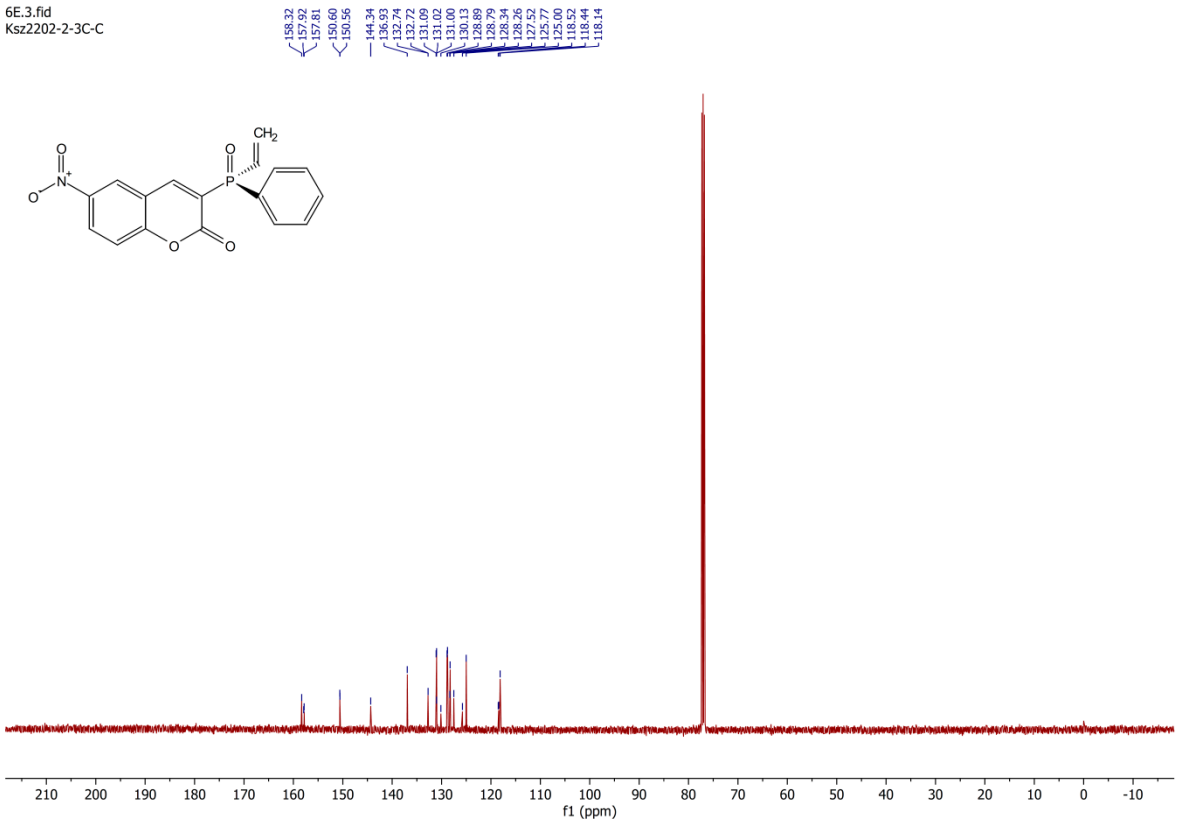


Figure S-19. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(*S*$_P$)-(Phenyl(vinyl)phosphinyl)-8-methoxy-2*H*-chromen-2-one (**6d**) in $CDCl_3$.


6E.1.fid
Ksz2202-2-3C-H
f1 (ppm)


6E.3.fid
Ksz2202-2-3C-C
f1 (ppm)

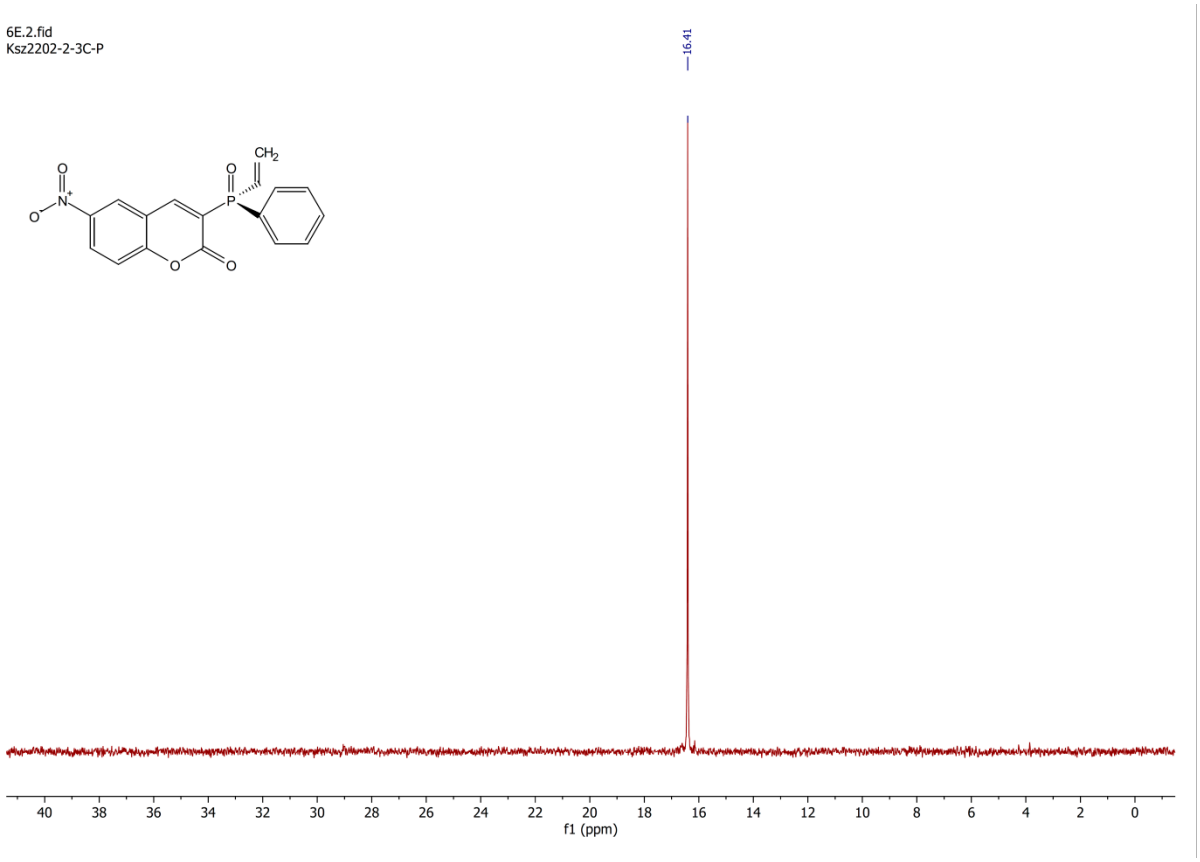
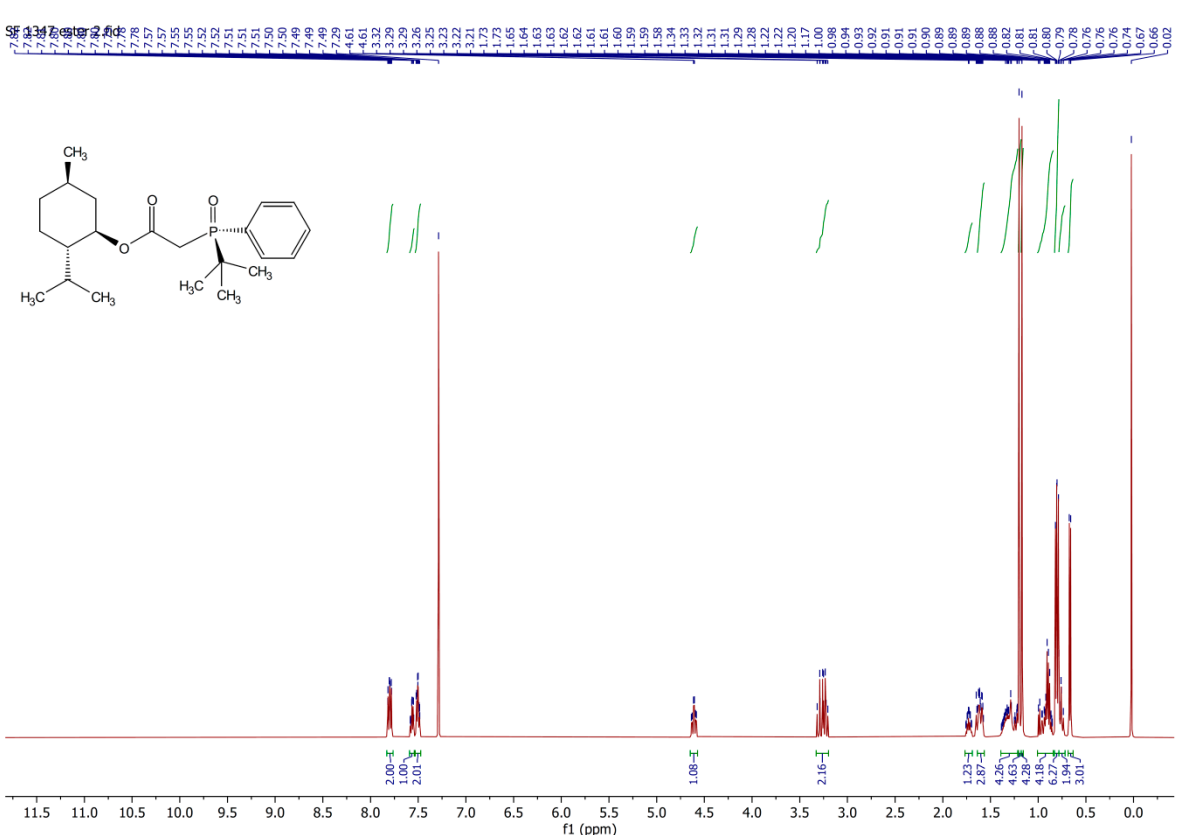
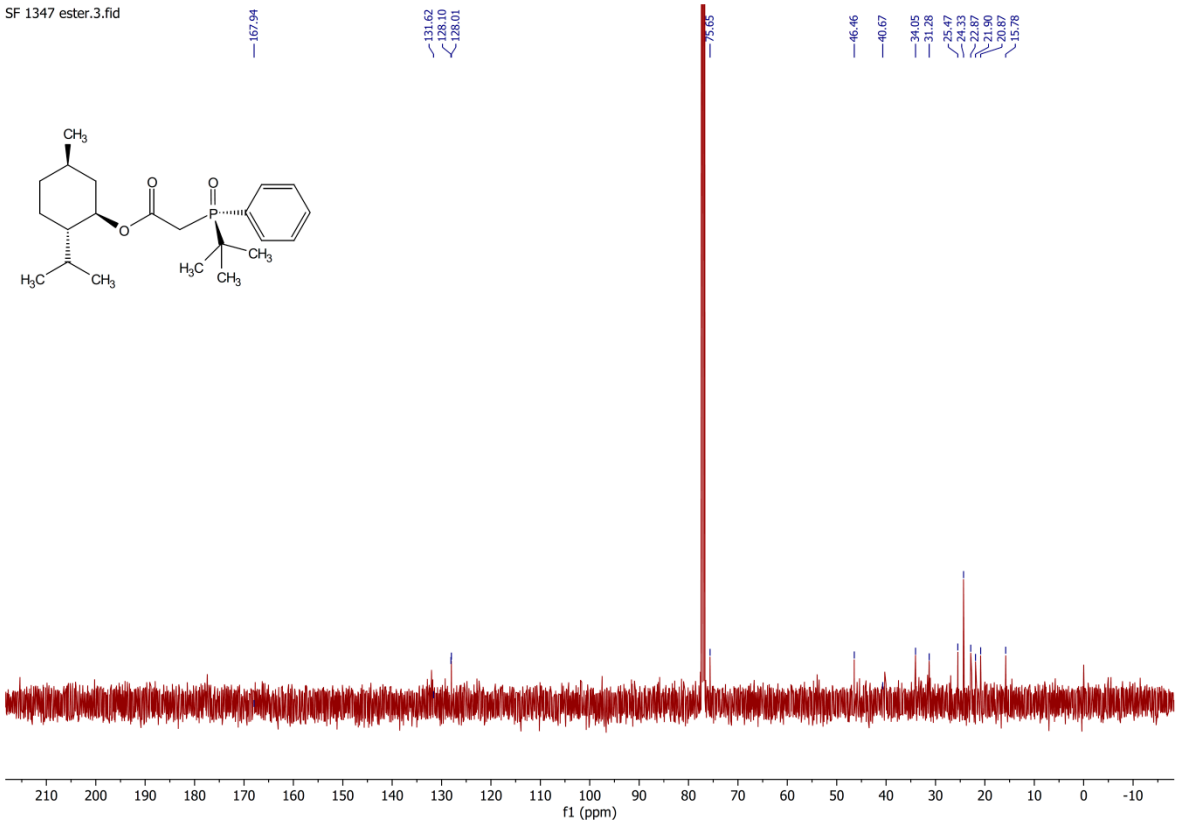


Figure S-20. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(S_P)-(Phenyl(vinyl)phosphinyl)-6-nitro-2*H*-chromen-2-one (**6e**) in $CDCl_3$.


SF 1347 ester.2.fid
CH3
O
O
P
CH3
H3C
CH3
H3C
CH3
2.00
1.00
2.01
1.08
2.16
1.23
2.87
4.26
4.63
4.28
4.18
6.27
1.94
3.01
11.5 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
f1 (ppm)


SF 1347 ester.3.fid
167.94
131.62
128.10
128.01
75.65
46.46
40.67
34.05
31.28
25.47
24.33
22.87
21.90
20.87
15.78
CH3
O
O
P
CH3
H3C
CH3
H3C
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

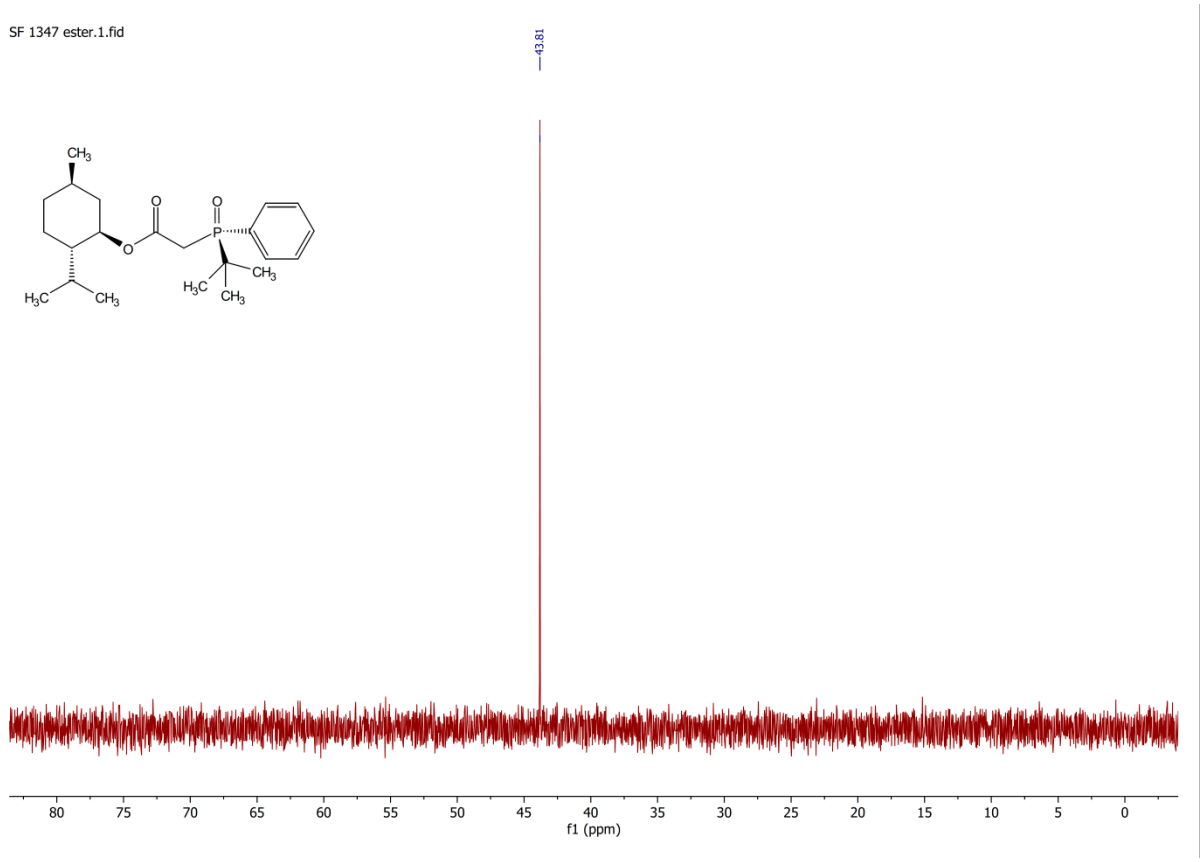
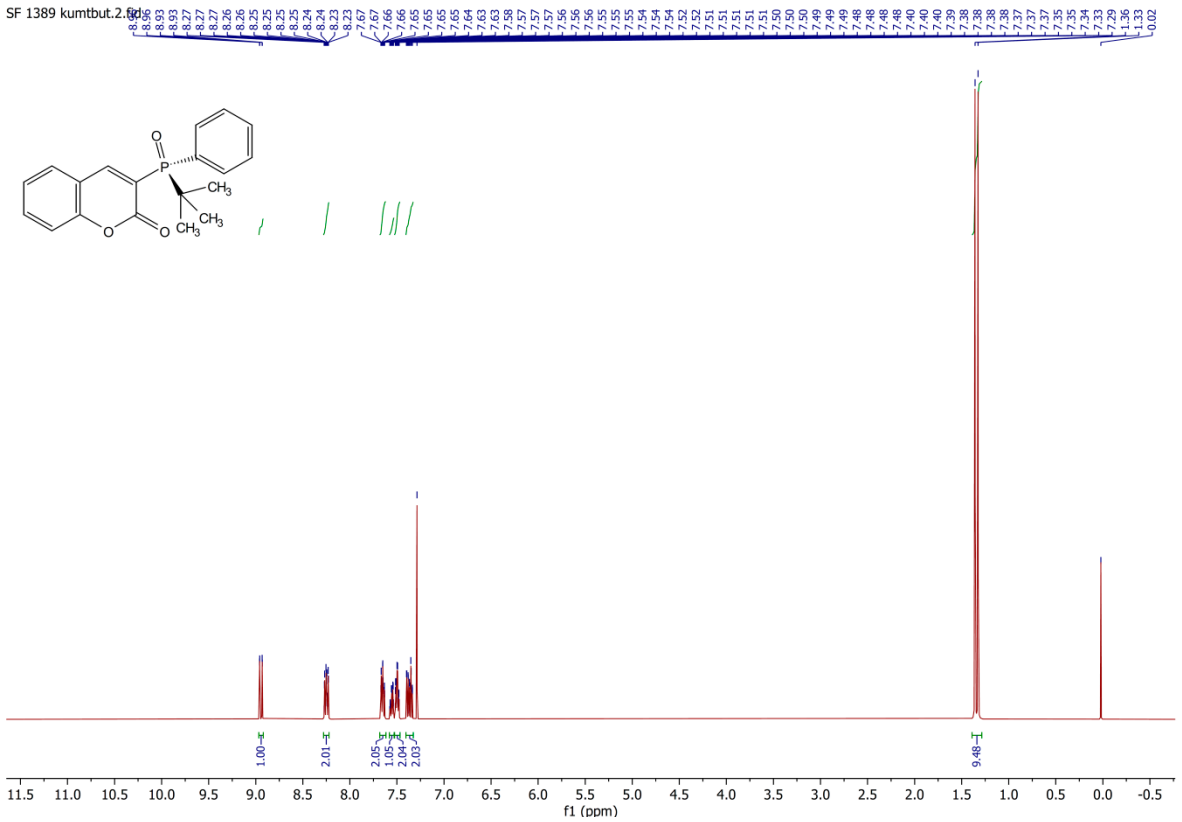
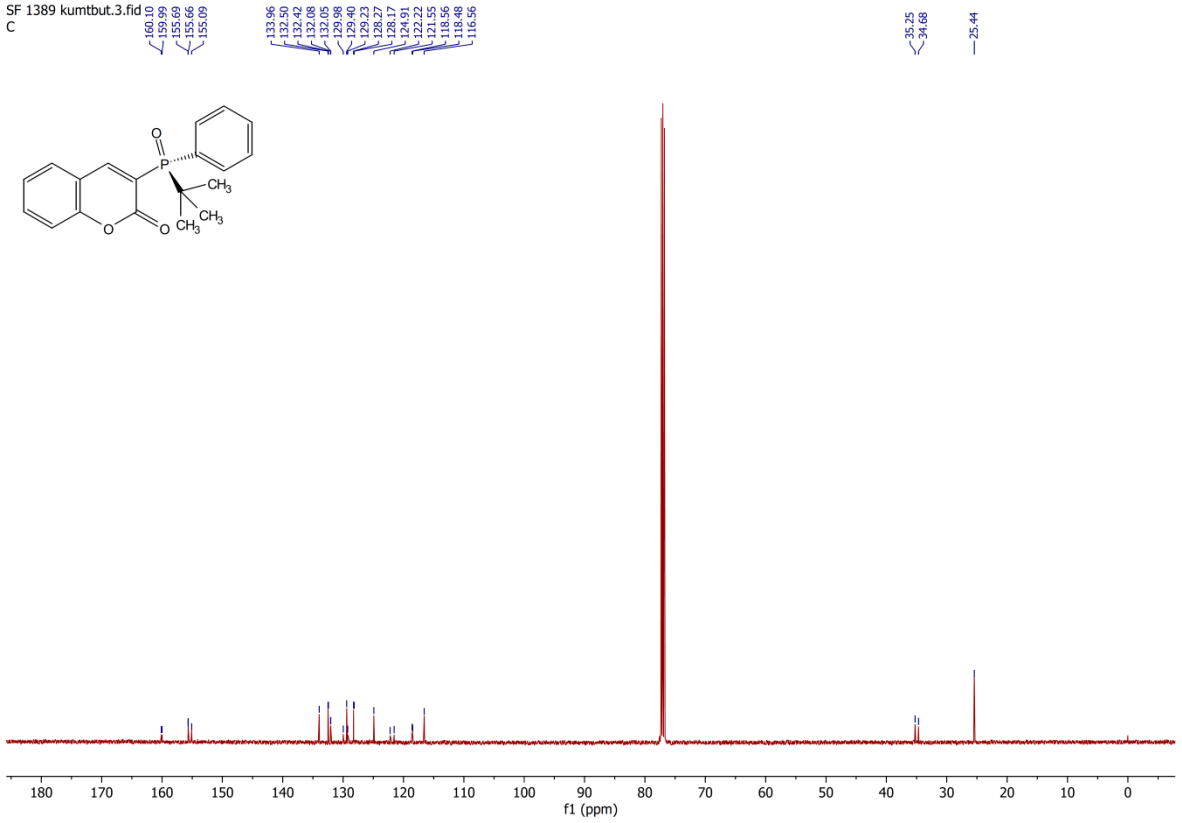


Figure S-20. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of (R_P)-*tert*-butylphenylphosphinyl acetic acid menthyl ester (**7**) in $CDCl_3$.


SF 1389 kumtbut.2.fid
1.00
2.01
2.05
1.05
2.04
2.03
9.48
f1 (ppm)


SF 1389 kumtbut.3.fid
C
160.10
159.99
155.69
155.66
155.09
133.96
132.50
132.42
132.08
132.05
129.98
129.40
129.23
128.27
128.17
124.91
122.22
121.55
118.56
118.48
116.56
35.25
34.68
25.44
f1 (ppm)

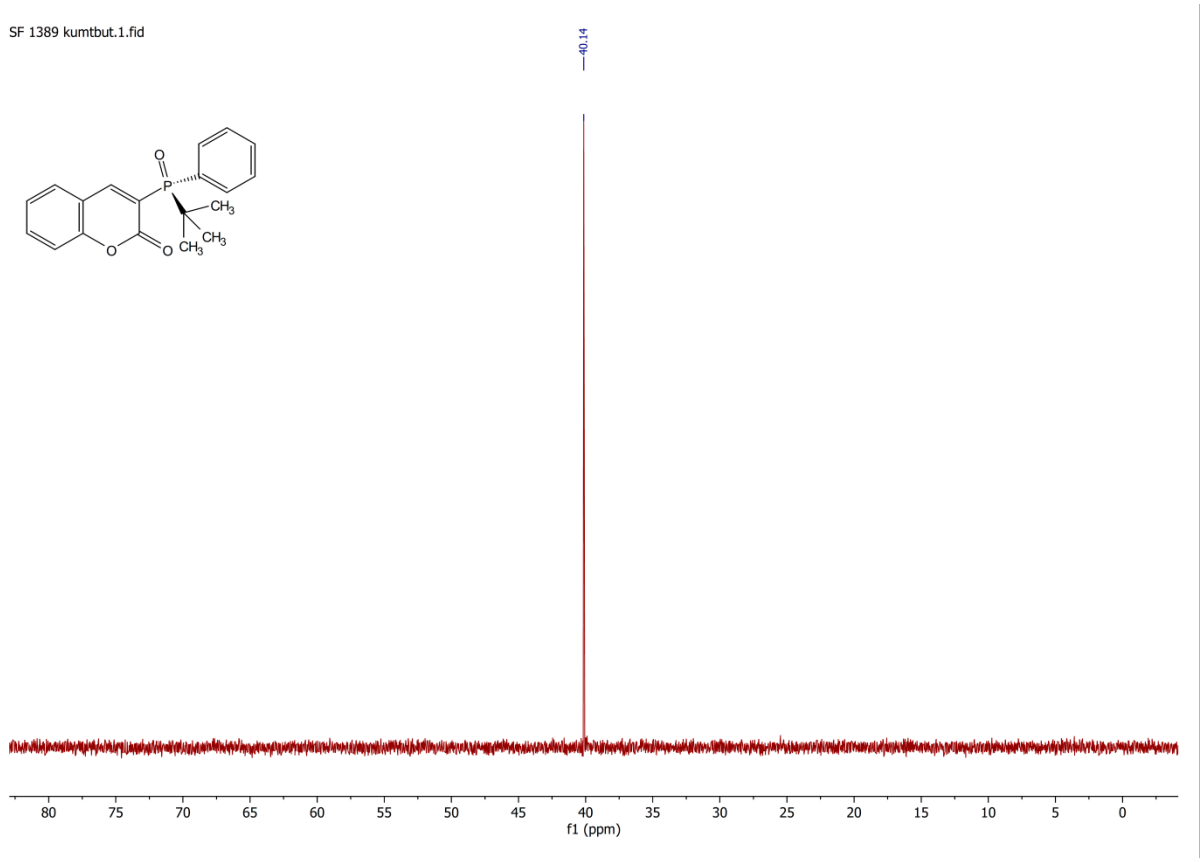
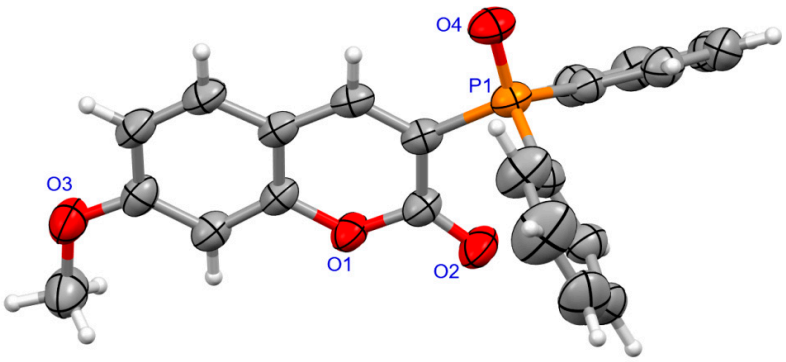
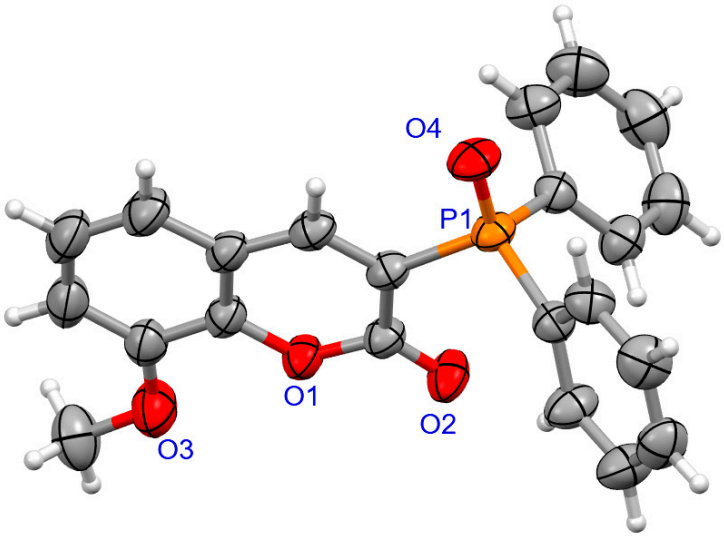
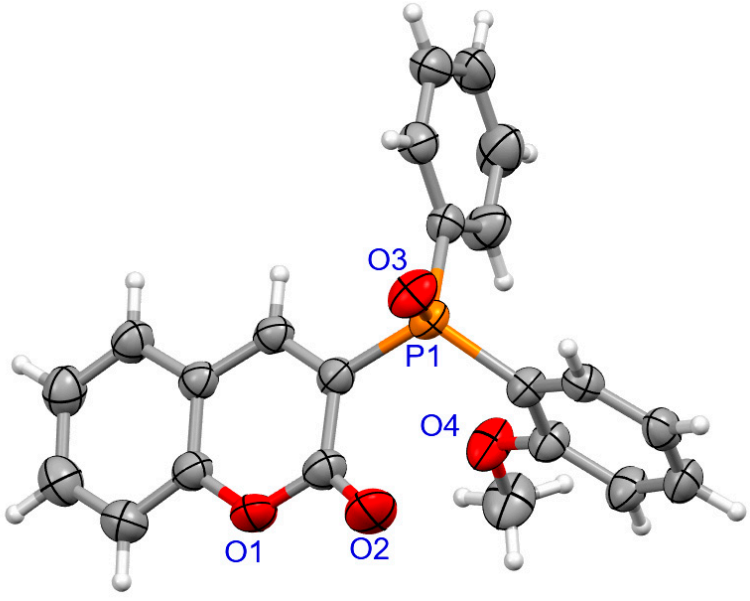
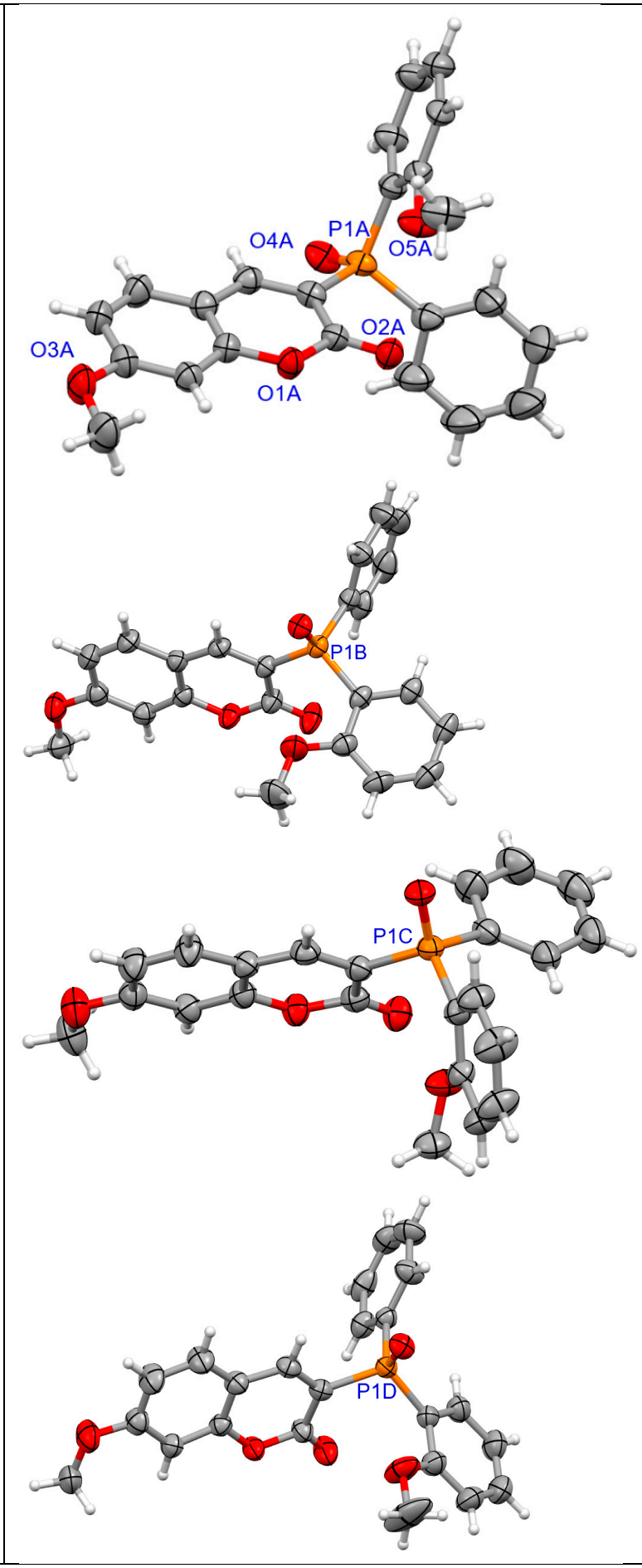


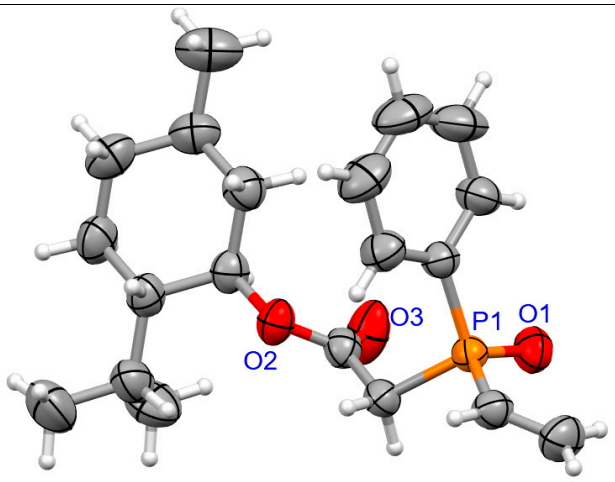
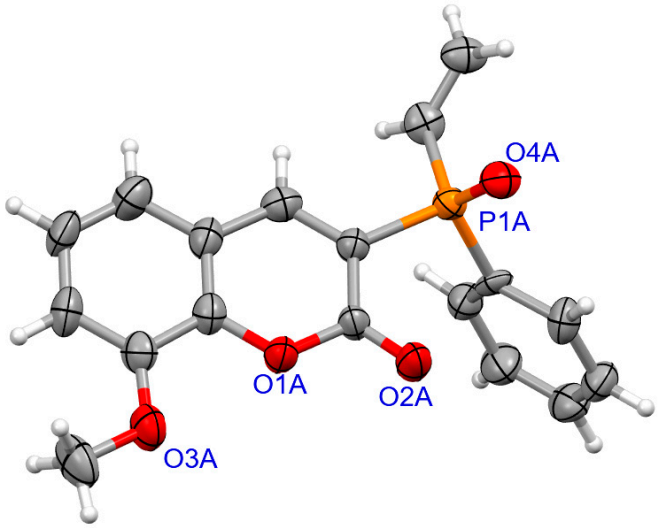
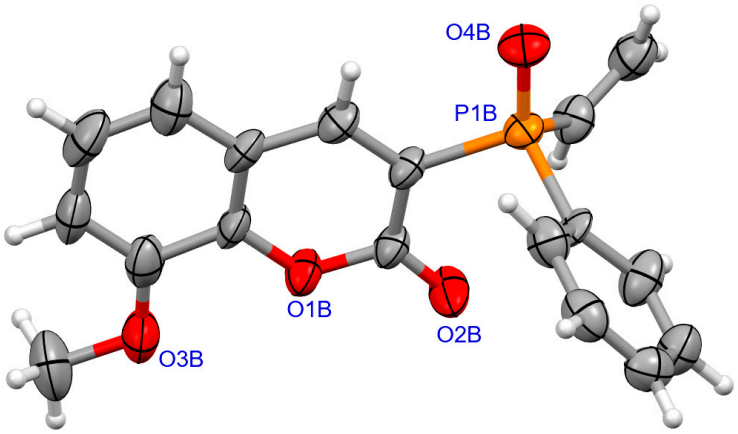
Figure S-21. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) of 3-(R_P)-(*t*-butylphenylphosphinyl)-2H-chromen-2-one (**8a**)in $CDCl_3$.

2. The single-crystal-diffraction data

Table S1 presents all molecules for which the crystal structure has been determined, viz. **2d**, **2e**, **4a**, **4d**, **5**, **6d,** and **6e**. Some compounds crystallize with more than one molecule in the symmetrically independent part. In the crystals of compounds **6d** and **6e**, the unit cells contain two conformers, while for **4d** they contain four. In this way, thanks to the possibility of rotation of the substituents around the P-C bonds, the energy minimum of the crystal lattice is achieved.

2d		3-(diphenylphosphinyl)-7-methoxy-2*H*-chromen-2-one
2e		3-(diphenylphosphinyl)-8-methoxy-2*H*-chromen-2-one
4a		3-(S_P)-(2-methoxyphenyl) phenyl-phosphinyl)-2*H*-chromen-2-one

4d **mole-cule A** **4d** **mole-cule B** **4d** **mole-cule C** **4d** **mole-cule D**		3-(S_P)-(2-methoxyphenyl) phenylphosphinyl)-7-methoxy-2*H*-chromen-2-one

5		(S_P)-L-menthyl phenylvinylphosphinylacetate
6d **molecule A**		3-(S_P)-(phenyl(vinyl)phosphinyl)-8-methoxy-2*H*-chromen-2-one
6d **molecule B**		

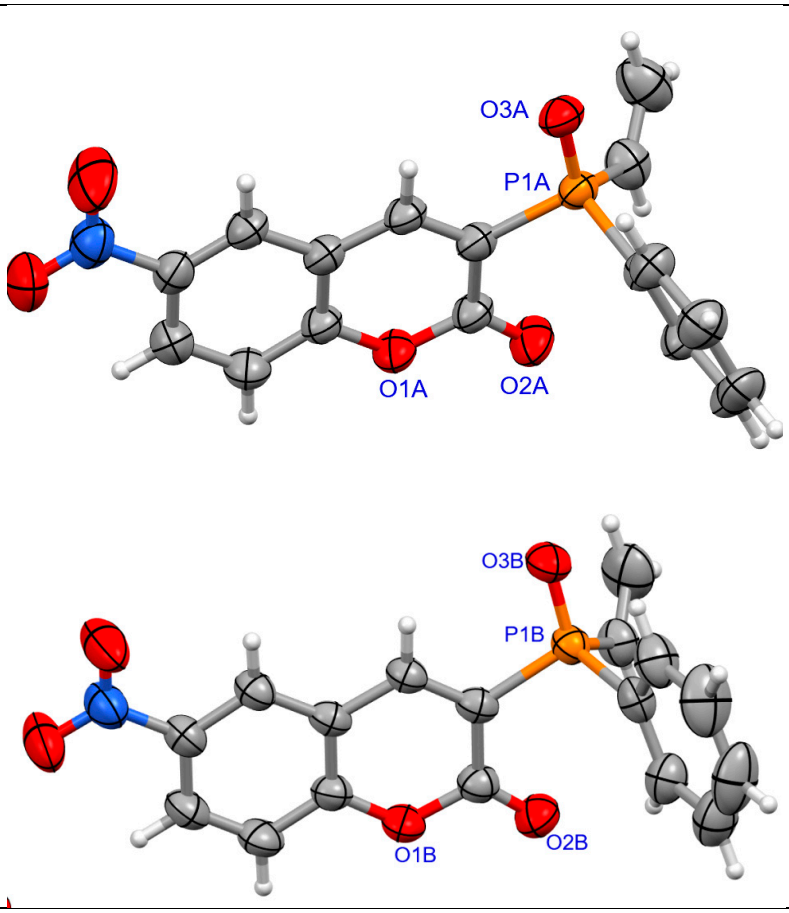
6e **mole-cule A** **6e** **mole-cule B**		3-(*S*P)-(phenyl(vinyl) phosphinyl)-6-nitro-2*H*-chromen-2-one

Table S1. Illustration of molecular conformers observed in crystals. The drawings were prepared using the ORTEP program; the thermal ellipsoids are shown with a probability of 50%.