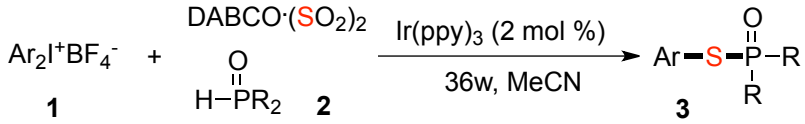
Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

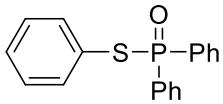
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

*General experimental procedure for the photoinduced three-components reaction of diaryliodonium tetrafluoroborates **1**, DABCO·$(SO_2)_2$ and diarylphosphine oxides **2**.*



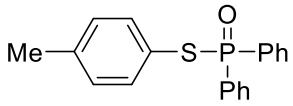
Acetonitrile (2.0 mL) was added to a mixture of diaryliodonium tetrafluoroborate **1** (0.20 mmol), DABCO·$(SO_2)_2$ (0.25 mmol), $Ir(ppy)_3$ (2.0 mol %) and diarylphosphine oxide **2** (0.60 mmol) at N_2 atmosphere. The mixture was stirred under 36w at room temperature. After 12 hours, the solvent was evaporated under reduced pressure. The residue was purified directly by flash column chromatography (*n*-hexane/ethyl acetate = 4:1) to give the corresponding product **3**.



S-phenyl diphenylphosphinothioate (**3a**).

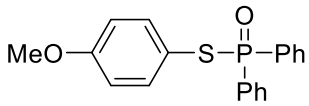
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 12.7, 7.7 Hz, 4H), 7.55 – 7.38 (m, 8H), 7.29 – 7.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4, 135.3, 133.0, 132.3, 132.3, 132.0, 131.7, 131.6, 129.1, 129.1, 128.9, 128.9, 128.6, 128.4, 126.2, 126.1. HRMS (ESI) calcd for

$C_{18}H_{16}OPS^+$: 333.0473 ($M+Na^+$), found: 333.0460.



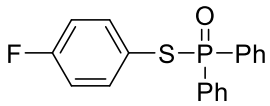
S-(*p*-tolyl) diphenylphosphinothioate (**3b**).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 12.6, 7.7 Hz, 4H), 7.52 – 7.37 (m, 6H), 7.32 (d, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 7.7 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 139.1, 135.4, 135.3, 133.2, 132.3, 132.2, 132.1, 131.7, 131.6, 123.0, 123.0, 128.6, 128.4, 122.3, 122.2, 21.1. HRMS (ESI) calcd for $C_{19}H_{18}OPS^+$: 325.0810 ($M+H^+$), found: 325.0808.



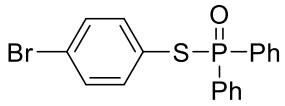
S-(4-methoxyphenyl) diphenylphosphinothioate (**3c**).

^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (dd, *J* = 12.6, 7.7 Hz, 4H), 7.54 – 7.40 (m, 6H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.3 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 137.1, 137.0, 133.1, 132.2, 132.2, 132.1, 131.7, 131.6, 128.6, 128.4, 113.0, 115.9, 114.8, 114.8, 55.2. HRMS (ESI) calcd for $C_{19}H_{18}O_2PS^+$: 341.0760 ($M+H^+$), found: 341.0768.



S-(4-fluorophenyl) diphenylphosphinothioate (**3d**).

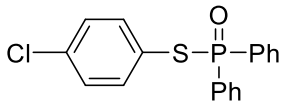
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 12.8, 7.7 Hz, 4H), 7.57 – 7.37 (m, 8H), 6.89 (t, J = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4 (dd, *J* = 249.7, 2.4 Hz), 137.5, 137.4, 137.4, 137.3, 132.8, 132.4, 132.4, 131.7, 131.6, 131.5, 128.6, 128.5, 121.2, 116.3 (dd, *J* = 22.1, 1.7 Hz). HRMS (ESI) calcd for $C_{18}H_{15}FOPS^+$: 329.0560 ($M+H^+$), found: 329.0556.



S-(4-bromophenyl) diphenylphosphinothioate (**3e**).

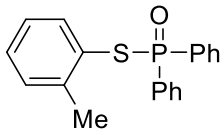
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.77 (m, 4H), 7.56 – 7.49 (m, 2H), 7.48 – 7.42 (m, 4H), 7.40 – 7.34 (m, 2H), 7.17 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 136.5,

135.5, 135.5, 132.7, 132.5, 132.5, 131.7, 131.6, 131.5, 129.3, 129.3, 128.7, 128.5, 124.7, 124.7. HRMS (ESI) calcd for $C_{18}H_{15}BrOPS^+$: 388.9759 ($M+H^+$), found: 388.9761.



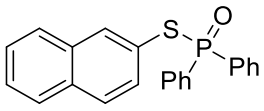
S-(4-chlorophenyl) diphenylphosphinothioate (**3f**).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.78 (m, 4H), 7.58 – 7.49 (m, 2H), 7.48 – 7.41 (m, 4H), 7.32 (s, 4H).^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 136.7, 132.7, 132.5, 132.5, 132.3, 132.2, 131.6, 131.5, 128.7, 128.6, 125.4, 125.4, 123.8, 123.7. HRMS (ESI) calcd for $C_{18}H_{15}ClOPS^+$: 345.0264 ($M+H^+$), found: 345.0279.



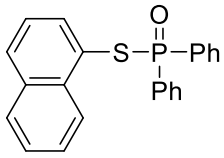
S-(*o*-tolyl) diphenylphosphinothioate (**3g**).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 12.5, 7.7 Hz, 4H), 7.56 – 7.39 (m, 7H), 7.14 (t, *J* = 8.7 Hz, 2H), 7.00 (t, *J* = 7.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 142.9, 142.8, 136.8, 136.7, 133.3, 132.3, 132.3, 131.5, 131.4, 130.7, 130.7, 129.3, 129.3, 128.5, 128.4, 126.5, 126.4, 125.4, 125.3. HRMS (ESI) calcd for $C_{19}H_{18}OPS^+$: 325.0810 ($M+H^+$), found: 325.0801.



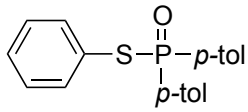
S-(naphthalen-2-yl) diphenylphosphinothioate (**3h**).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.87 (dd, *J* = 12.8, 7.8 Hz, 4H), 7.69 (ddd, *J* = 19.8, 12.6, 5.6 Hz, 3H), 7.45 (dd, *J* = 20.2, 5.9 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4, 135.3, 133.5, 133.1, 133.0, 132.3, 132.3, 132.0, 131.7, 131.6, 131.5, 131.5, 128.7, 128.6, 128.5, 127.8, 127.6, 126.9, 126.4, 123.5, 123.5. HRMS (ESI) calcd for $C_{22}H_{18}OPS^+$: 361.0810 ($M+H^+$), found: 361.0819.



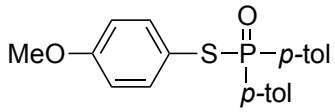
S-(naphthalen-1-yl) diphenylphosphinothioate (**3i**).

^{1}H NMR (400 MHz, $CDCl_3$): 8.39 (d, *J* = 8.1 Hz, 1H), 7.86 – 7.70 (m, 7H), 7.50 – 7.39 (m, 4H), 7.38 – 7.26 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 135.5, 135.0, 134.1, 133.0, 132.3, 132.2, 131.9, 131.6, 131.4, 123.0, 123.0, 128.5, 128.3, 128.3, 126.7, 126.2, 126.0, 125.5, 125.5, 123.5. HRMS (ESI) calcd for $C_{22}H_{18}OPS^+$: 361.0810 ($M+H^+$), found: 361.0819.



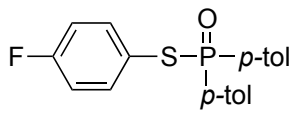
S-phenyl di-*p*-tolylphosphinothioate (**3j**).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, *J* = 12.6, 7.8 Hz, 4H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.29 – 6.98 (m, 7H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 142.8, 135.2, 135.2, 131.7, 131.6, 130.0, 129.3, 129.2, 129.0, 129.0, 128.9, 128.7, 128.7, 126.7, 126.6, 21.6, 21.6. HRMS (ESI) calcd for $C_{20}H_{20}OPS^+$: 339.0967 ($M+H^+$), found: 339.0955.



S-(4-methoxyphenyl) di-*p*-tolylphosphinothioate (**3k**).

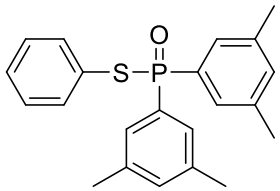
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 12.6, 8.0 Hz, 4H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.28 – 7.15 (m, 4H), 6.73 (d, *J* = 8.7 Hz, 2H), 3.73 (s, 3H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 142.7, 136.9, 136.9, 131.7, 131.5, 130.1, 129.3, 129.1, 123.0, 116.5, 114.7, 77.3, 77.0, 76.7, 55.2, 29.7, 21.6. HRMS (ESI) calcd for $C_{21}H_{22}O_2PS^+$: 369.1073 ($M+H^+$), found: 369.1081.



S-(4-fluorophenyl) di-*p*-tolylphosphinothioate (**3l**).

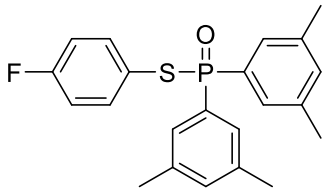
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 12.6, 8.0 Hz, 4H), 7.48 – 7.32 (m, 2H), 7.24 (d, *J*

= 4.8 Hz, 4H), 6.89 (t, *J* = 8.5 Hz, 2H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3 (d, *J* = 250.7 Hz), 143.0, 137.3, 137.3, 137.2, 131.6, 131.5, 129.7, 129.4, 129.2, 128.6, 121.6, 116.2 (d, *J* = 22.0 Hz), 21.6. HRMS (ESI) calcd for $C_{20}H_{19}FOPS^+$: 357.0873 ($M+H^+$), found: 357.0863.



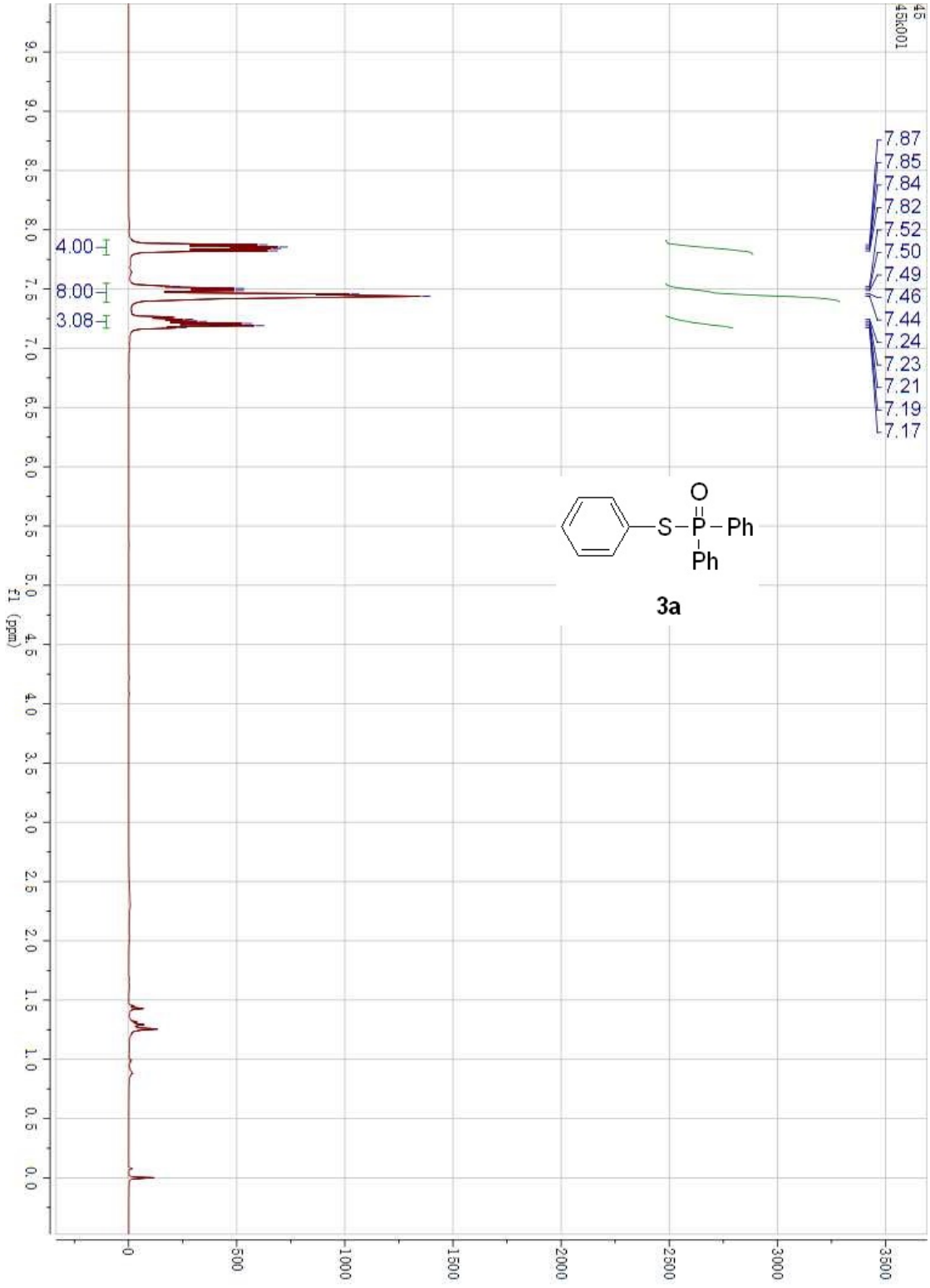
S-phenyl bis(3,5-dimethylphenyl)phosphinothioate (**3m**).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 13.3 Hz, 6H), 7.22 (dt, *J* = 14.0, 7.1 Hz, 3H), 7.11 (s, 2H), 2.31 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 138.1, 135.4, 135.3, 134.0, 134.0, 132.8, 131.8, 129.2, 129.1, 129.0, 129.0, 128.8, 128.7, 126.7, 126.6, 21.3. HRMS (ESI) calcd for $C_{22}H_{24}OPS^+$: 367.1280 ($M+H^+$), found: 367.1266.



S-(4-fluorophenyl) bis(3,5-dimethylphenyl)phosphinothioate (**3n**).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (t, *J* = 9.9 Hz, 6H), 7.10 (s, 2H), 6.88 (t, *J* = 8.4 Hz, 2H), 2.29 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3 (d, *J* = 249.4 Hz), 138.4, 138.2, 137.4, 137.4, 137.3, 137.3, 135.0, 134.1, 134.1, 132.6, 131.5, 129.1, 129.0, 128.8, 121.7, 116.2 (dd, *J* = 22.0, 1.4 Hz), 21.2. HRMS (ESI) calcd for $C_{22}H_{23}FOPS^+$: 385.1186 ($M+H^+$), found: 385.1191.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8.00
3.08
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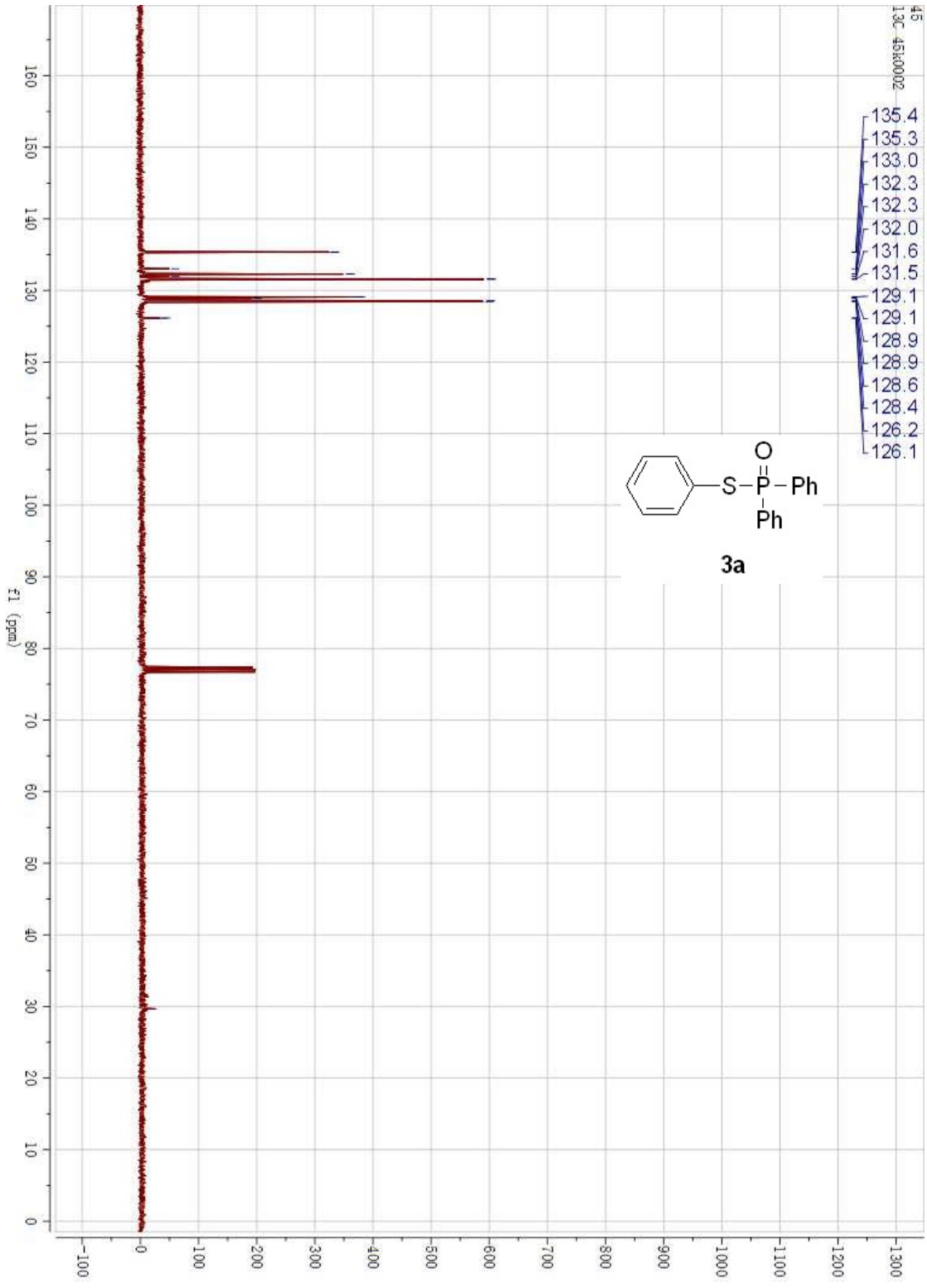
S
P
Ph
Ph
3a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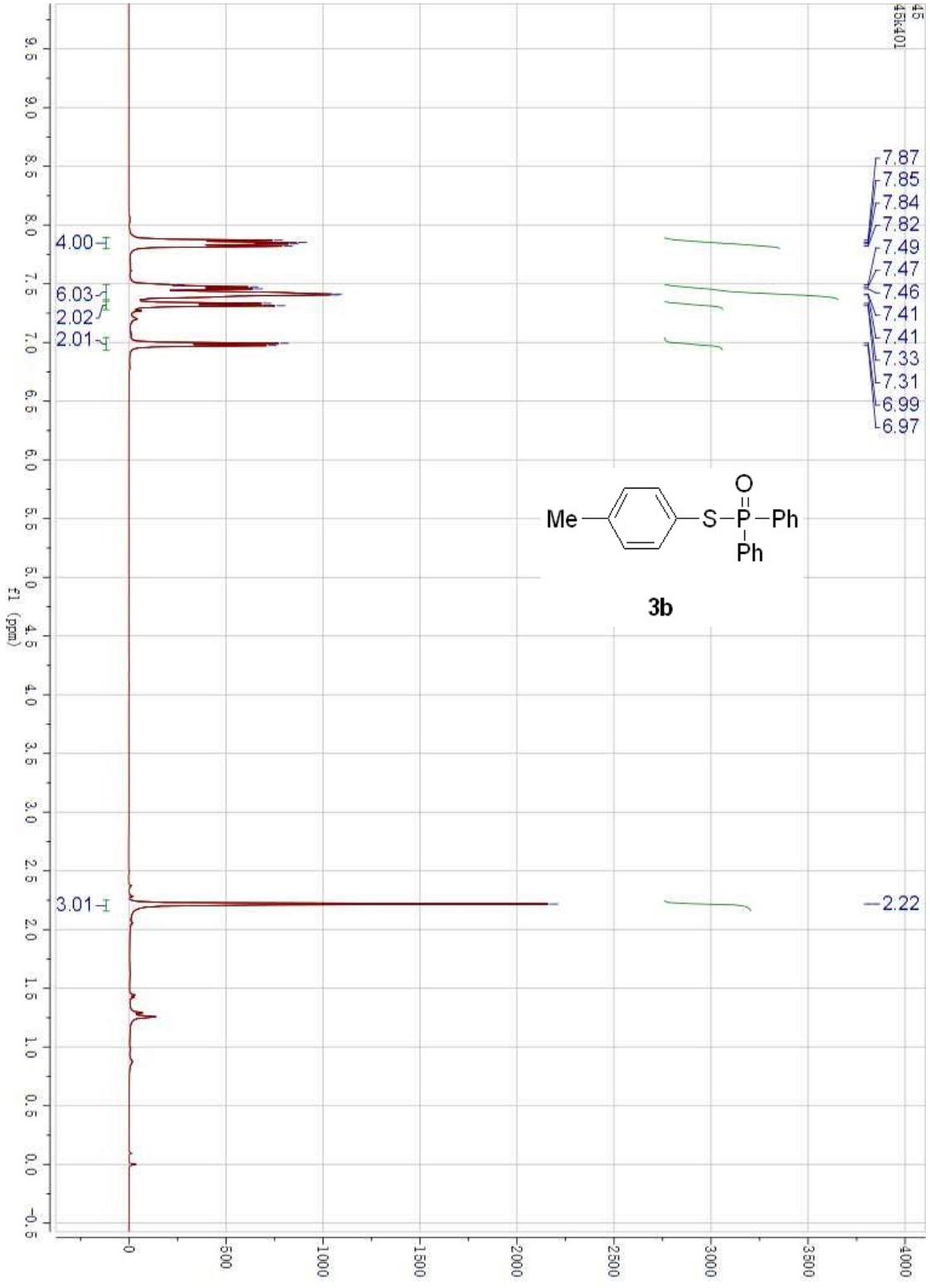
O
S–P–Ph
Ph
3a
f1 (ppm)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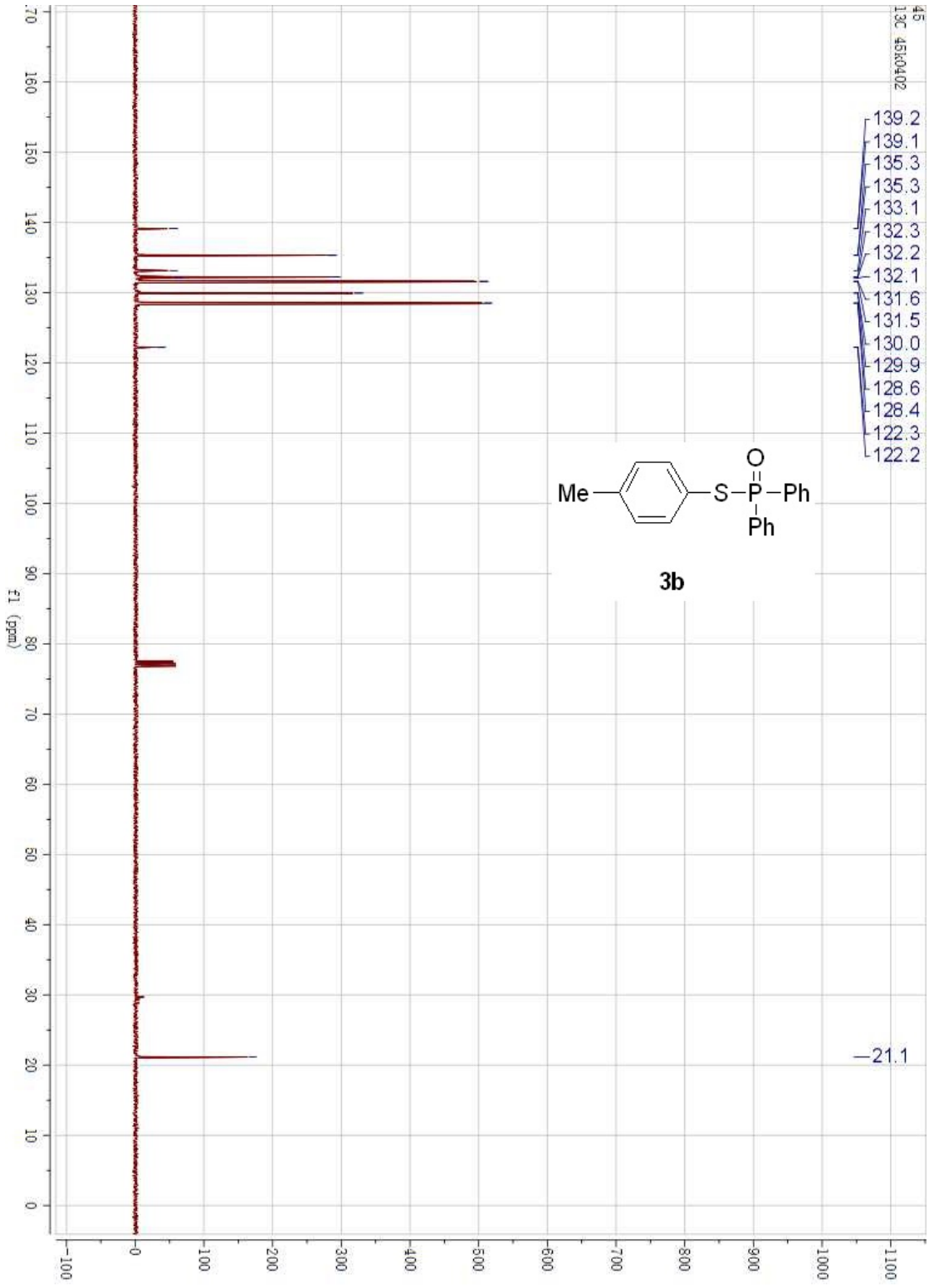
3b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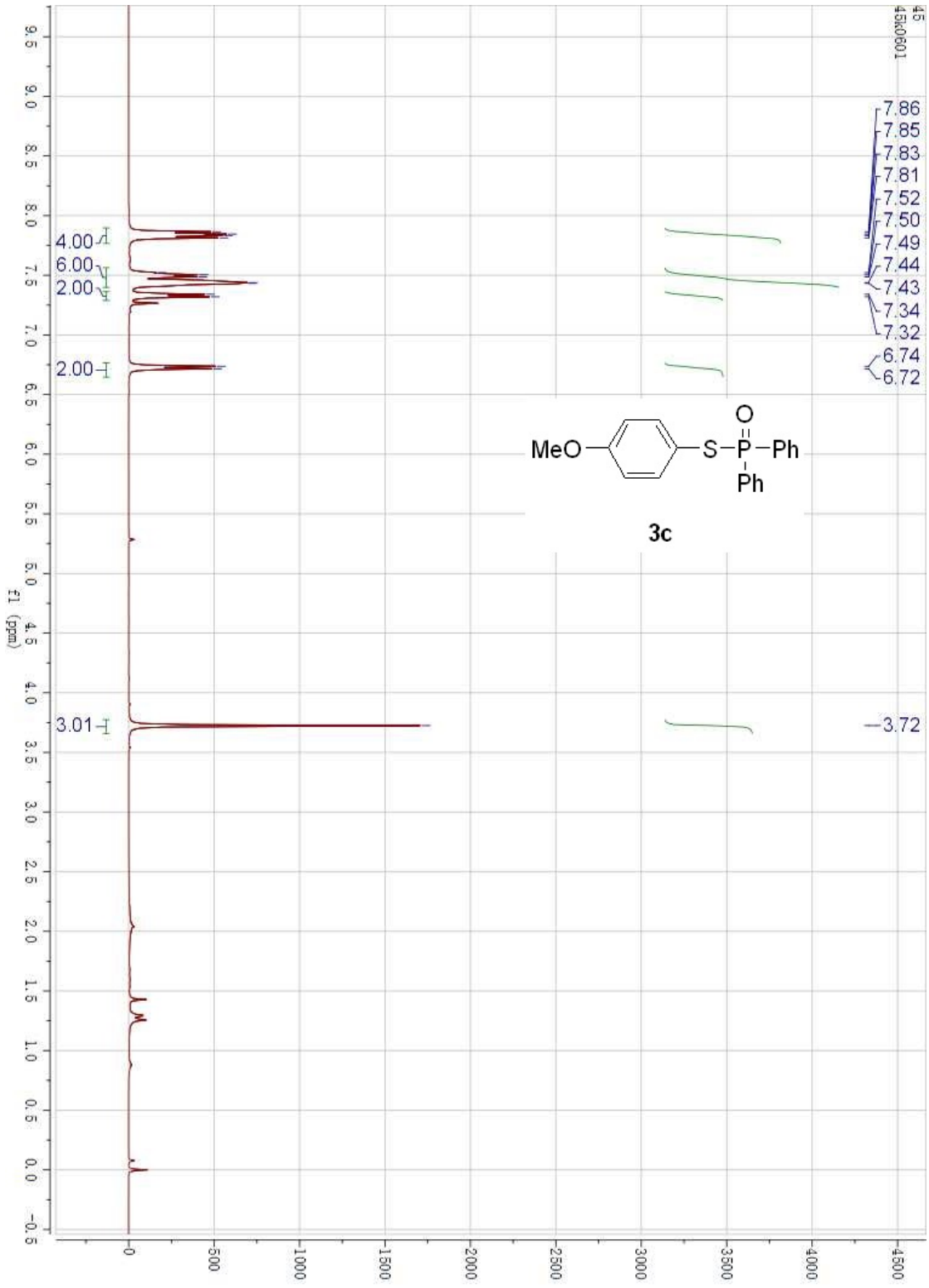
S
P
O
Ph
Ph
3b
f1 (ppm)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Ph
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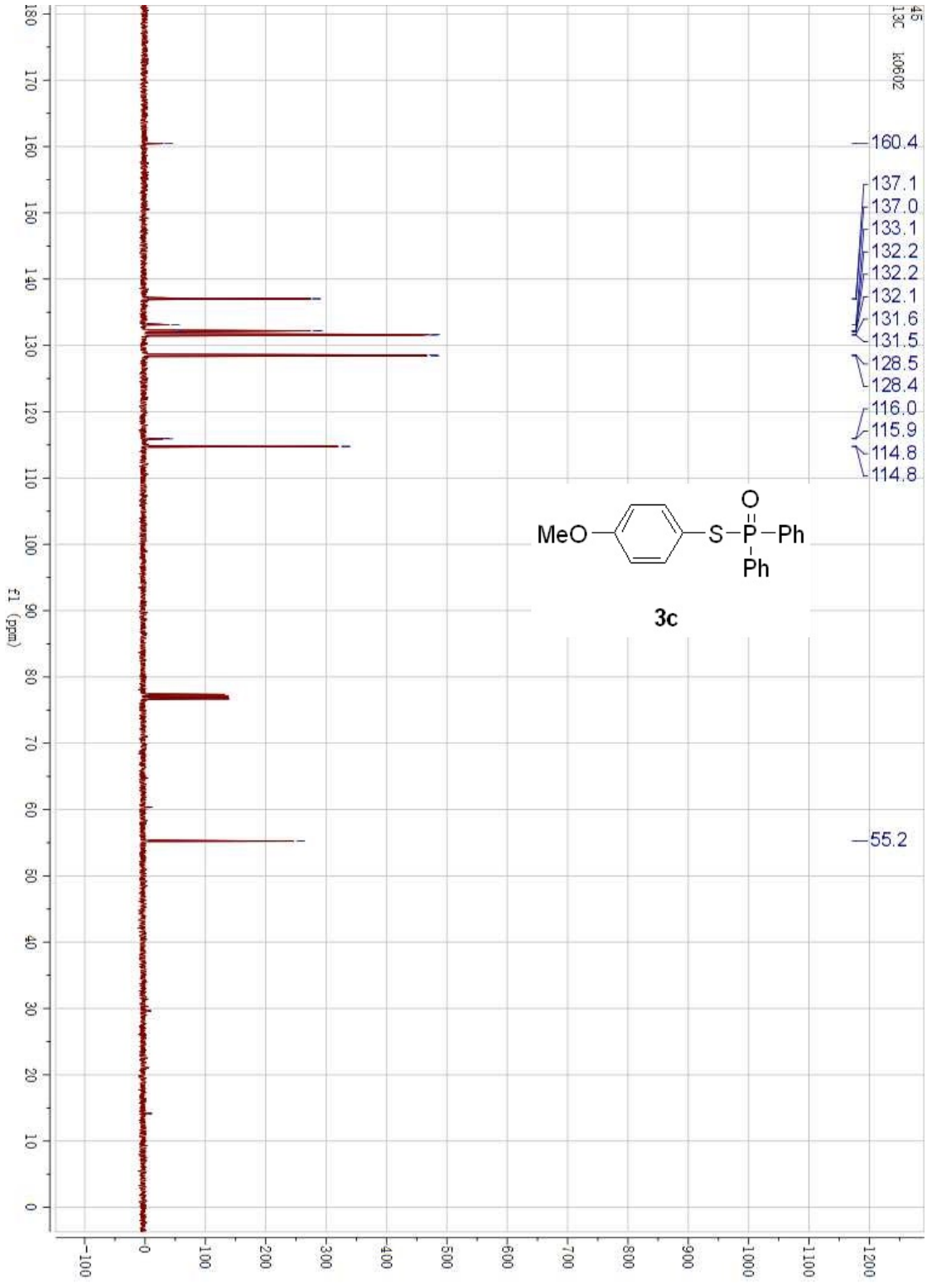
f1 (ppm)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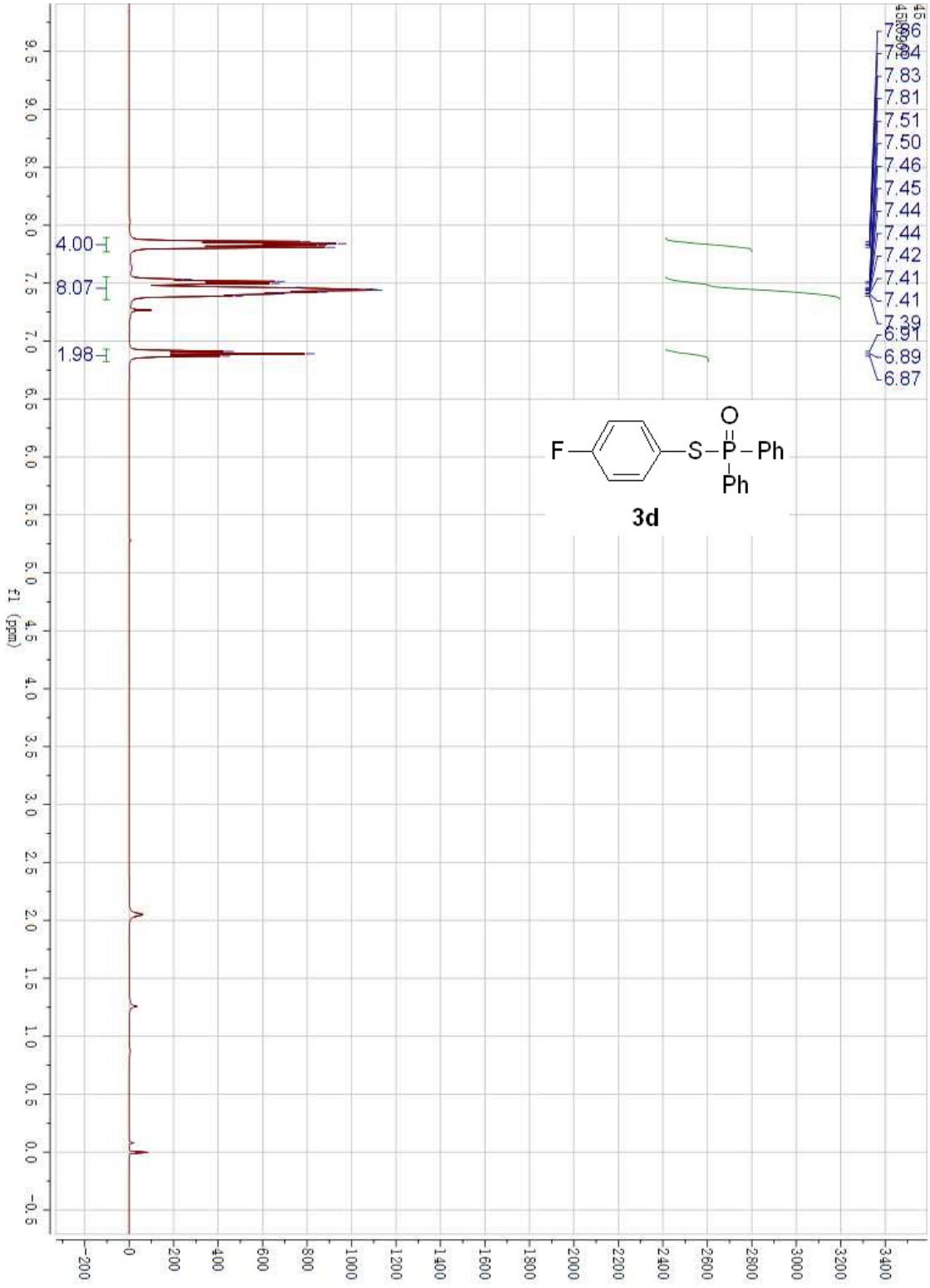
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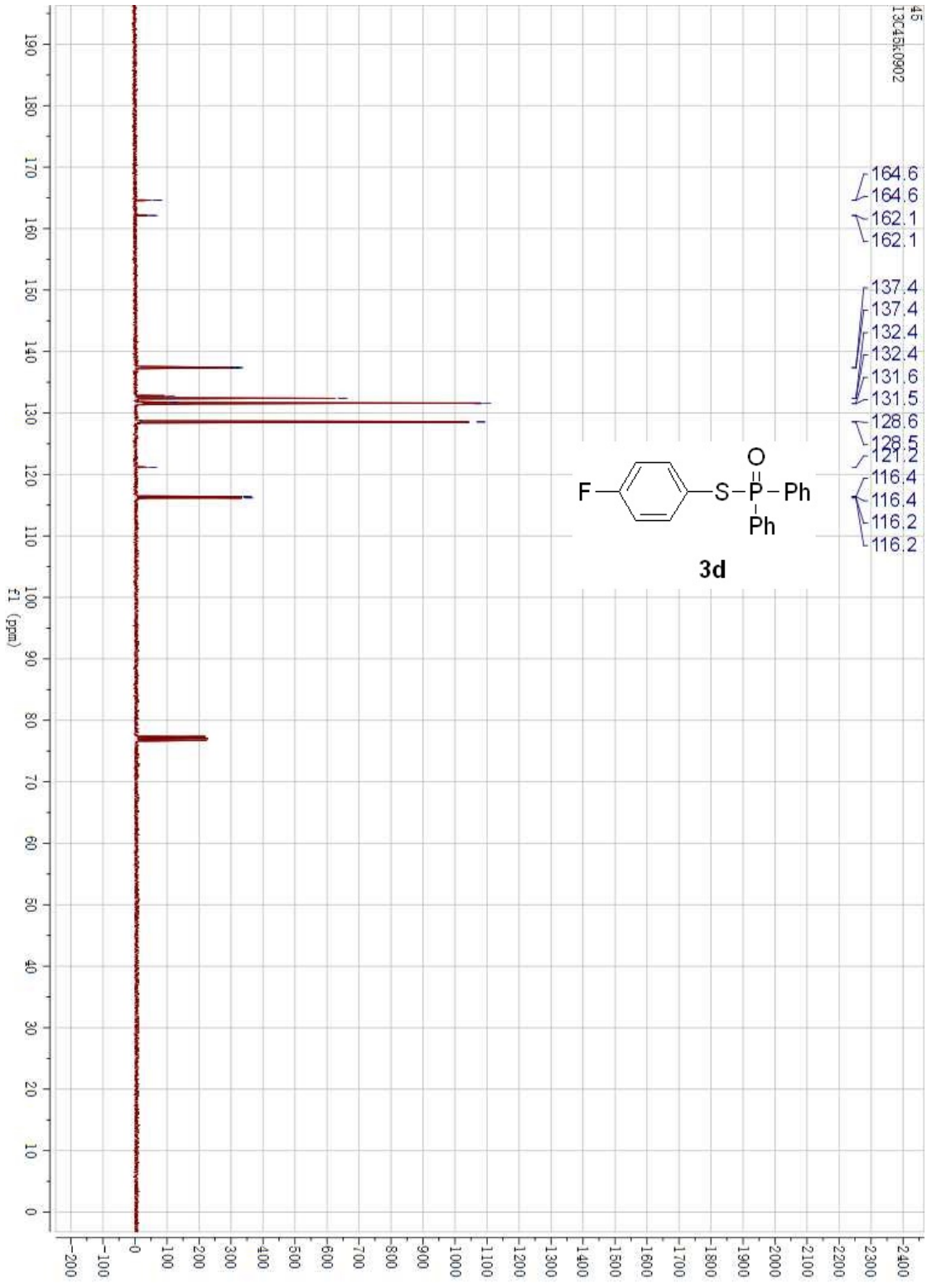
F
S
P
O
Ph
Ph
3d
f1 (ppm)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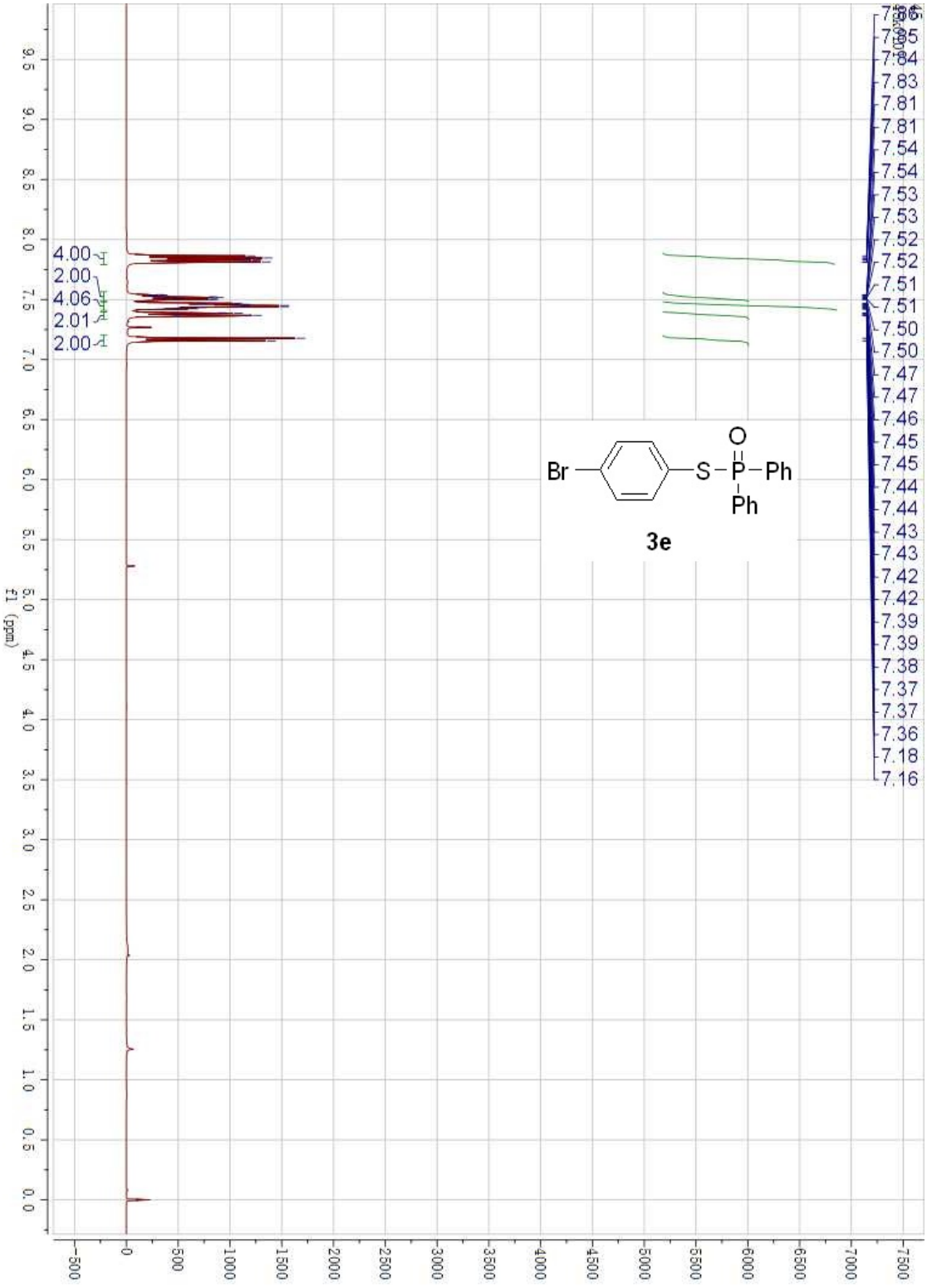
F
S
P
O
Ph
Ph
3d
f1 (ppm)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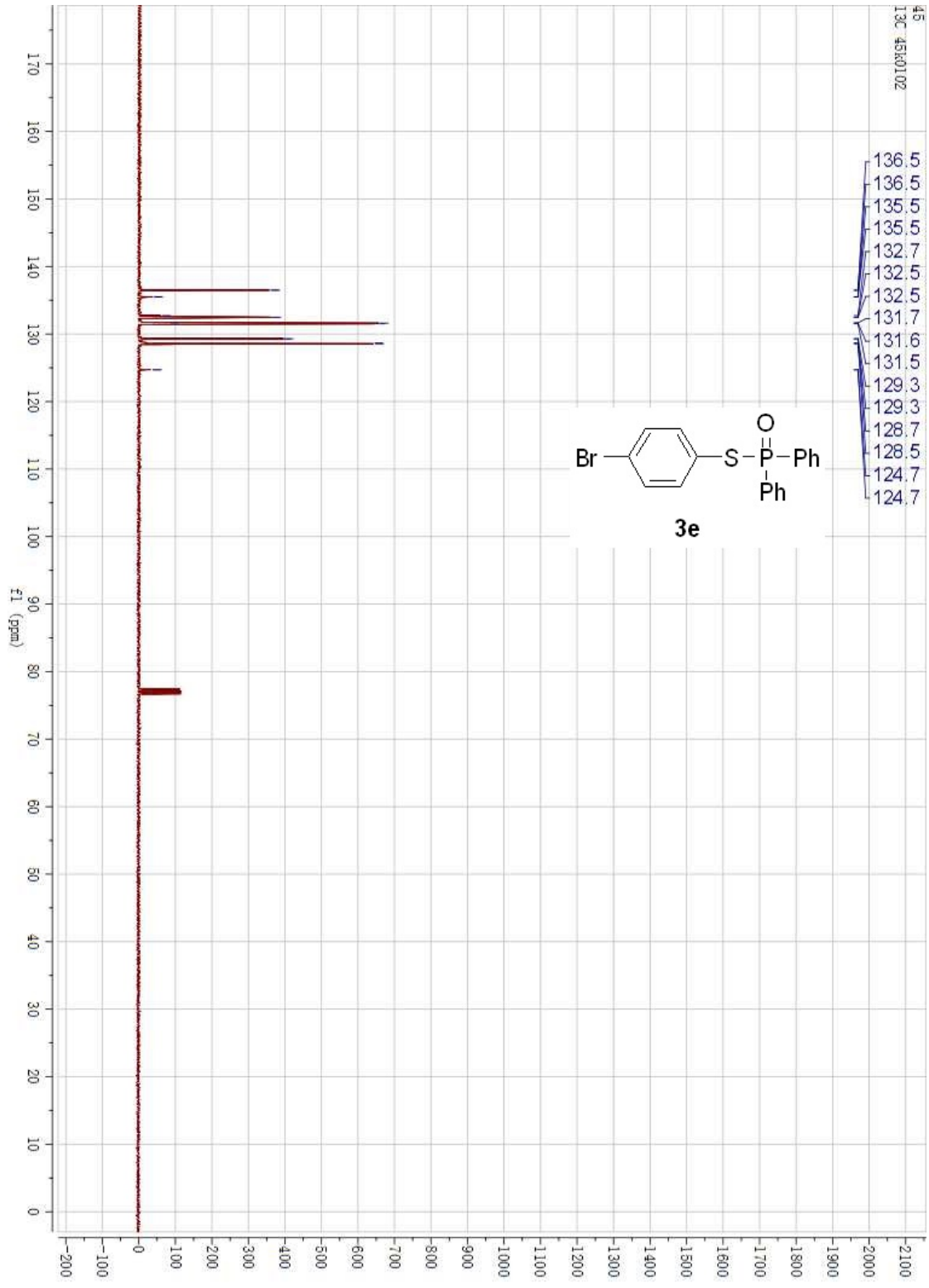
f1 (ppm)
Br
S
P
O
Ph
Ph

3e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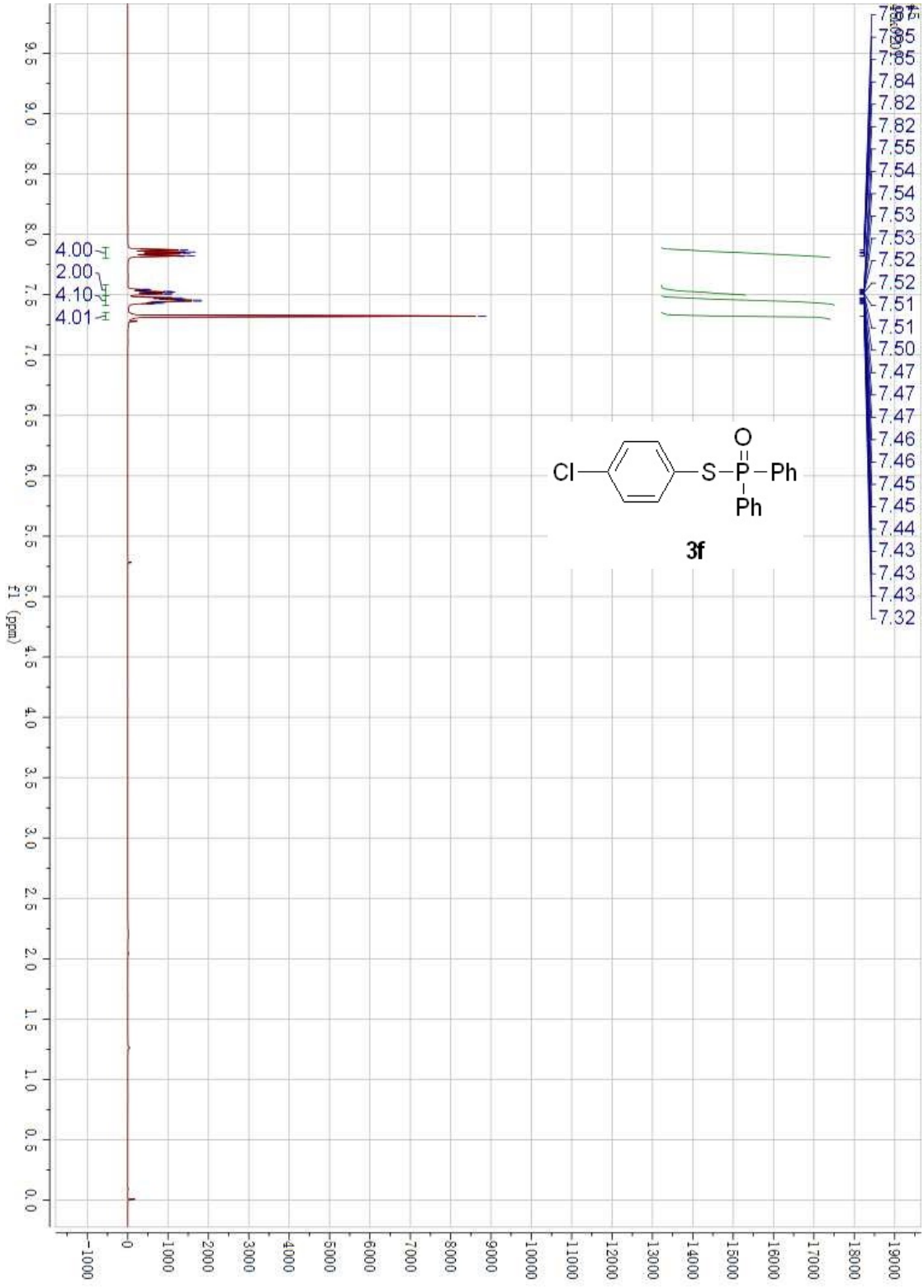
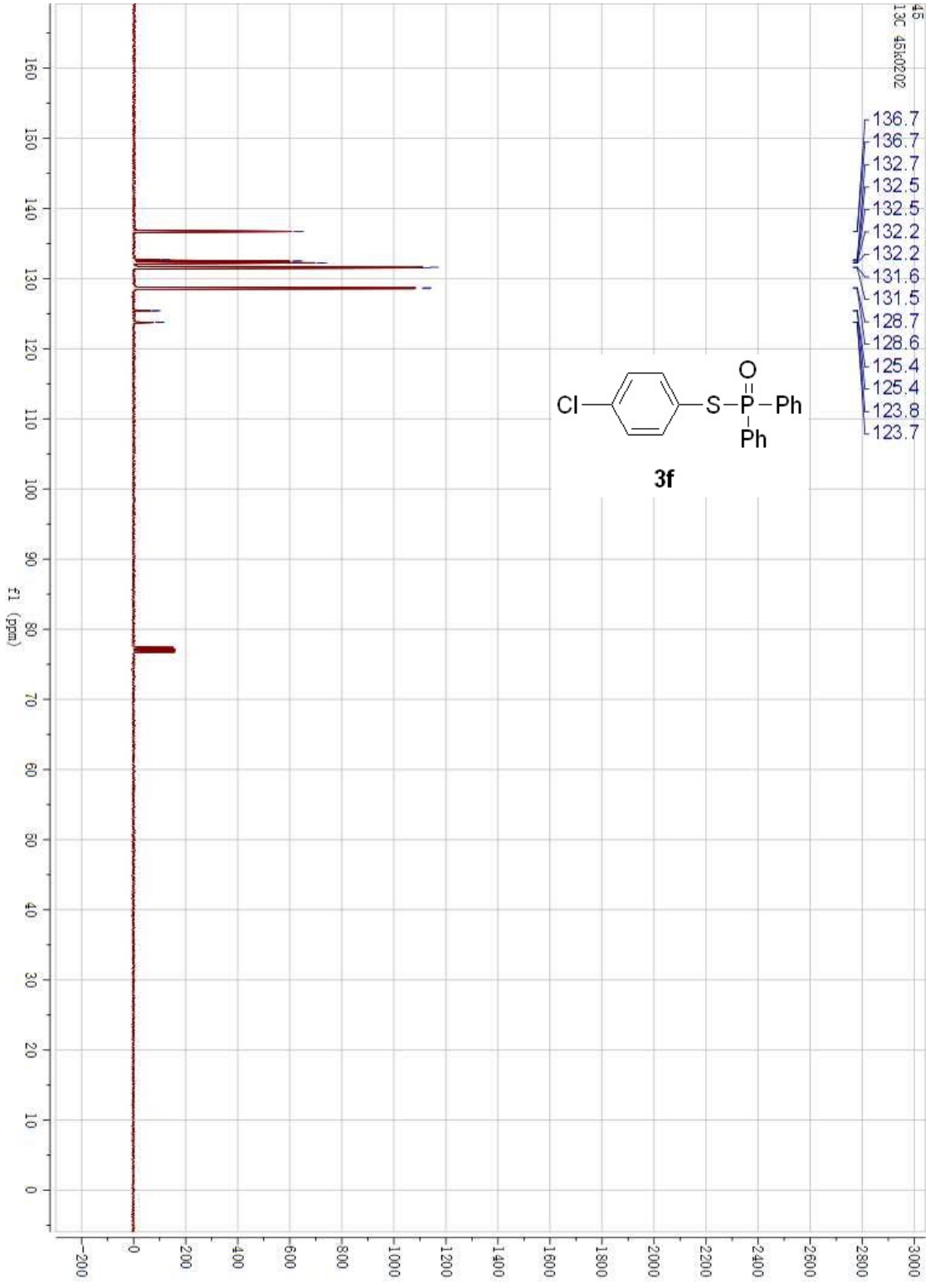
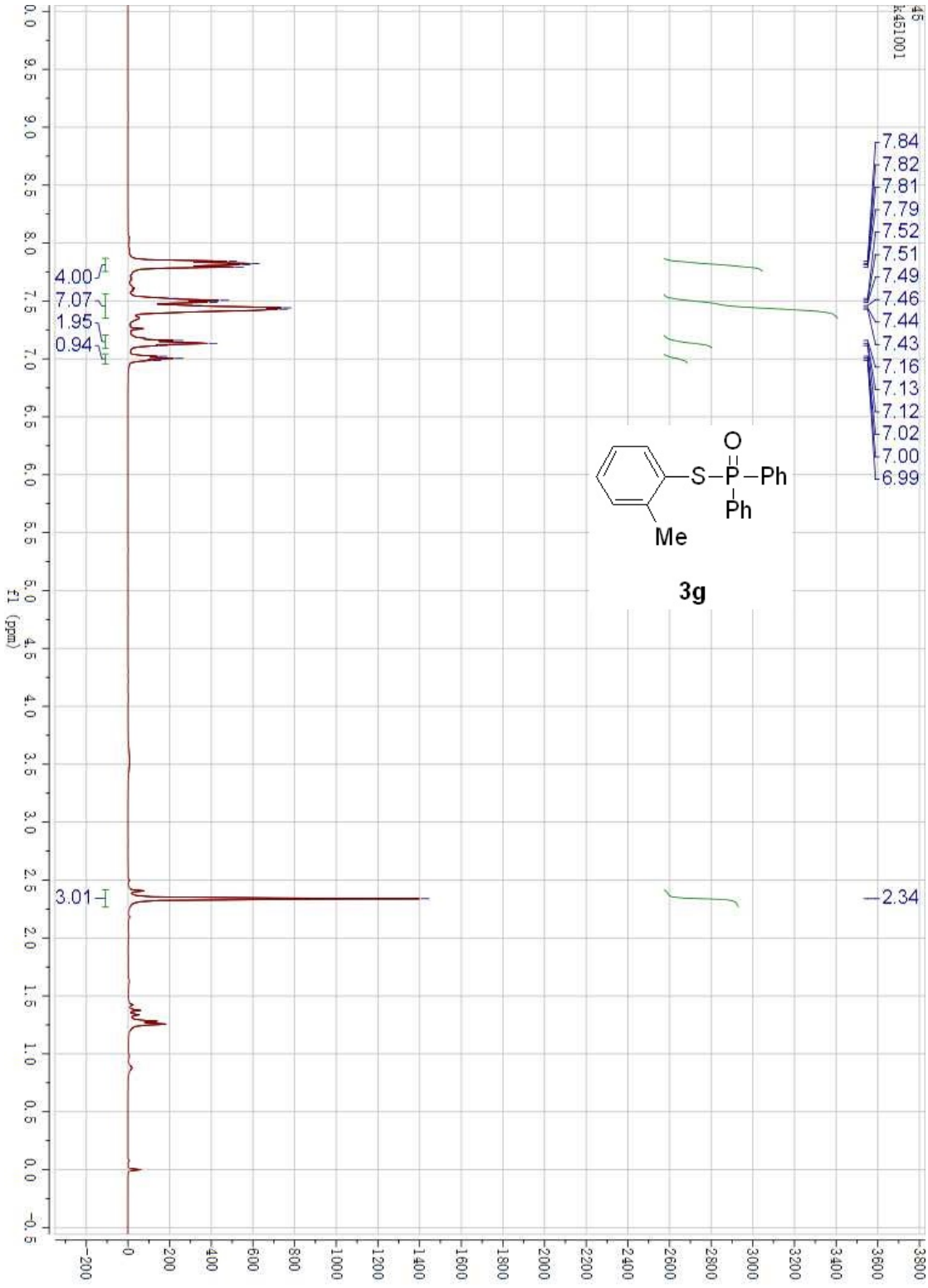
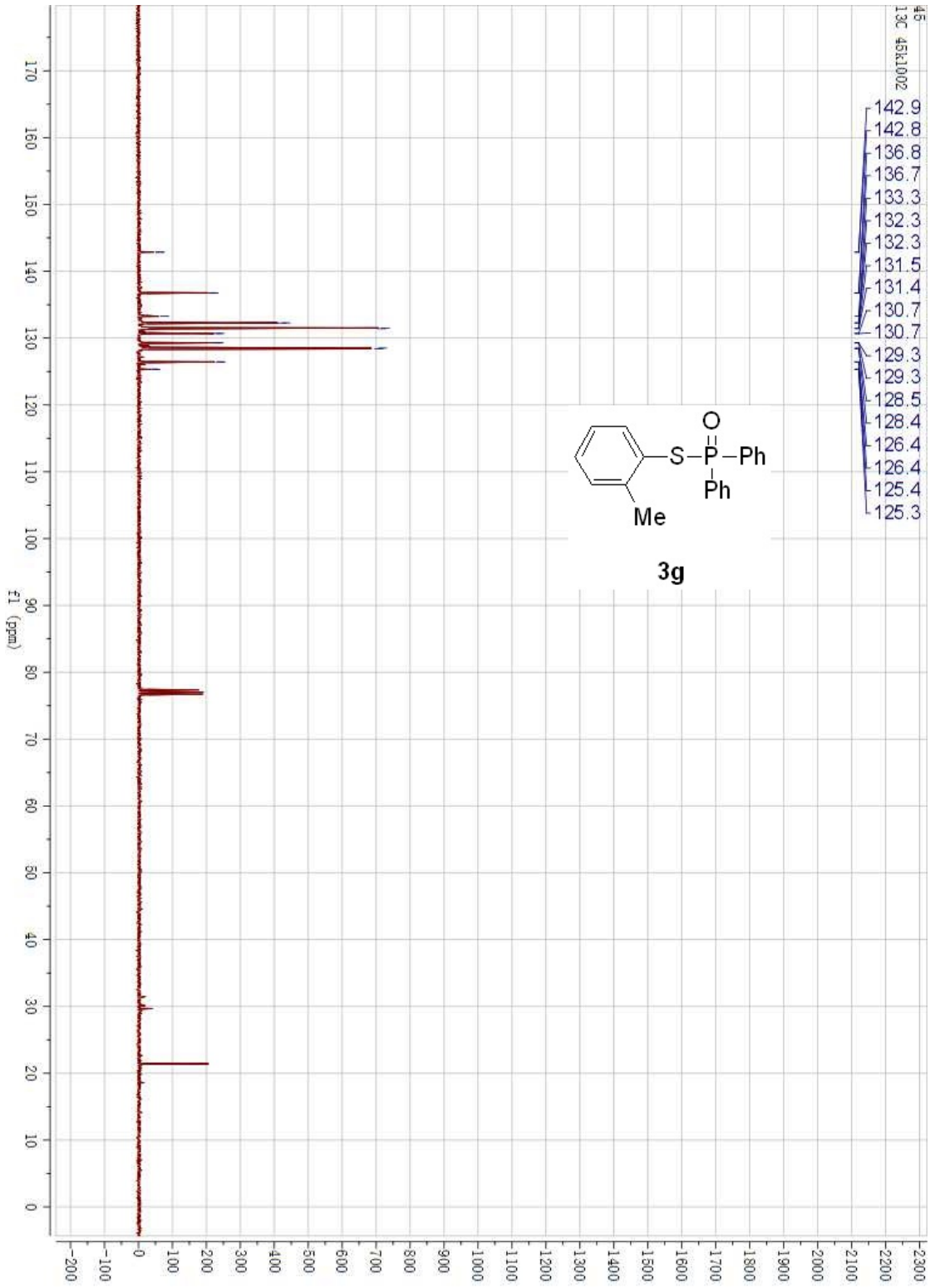
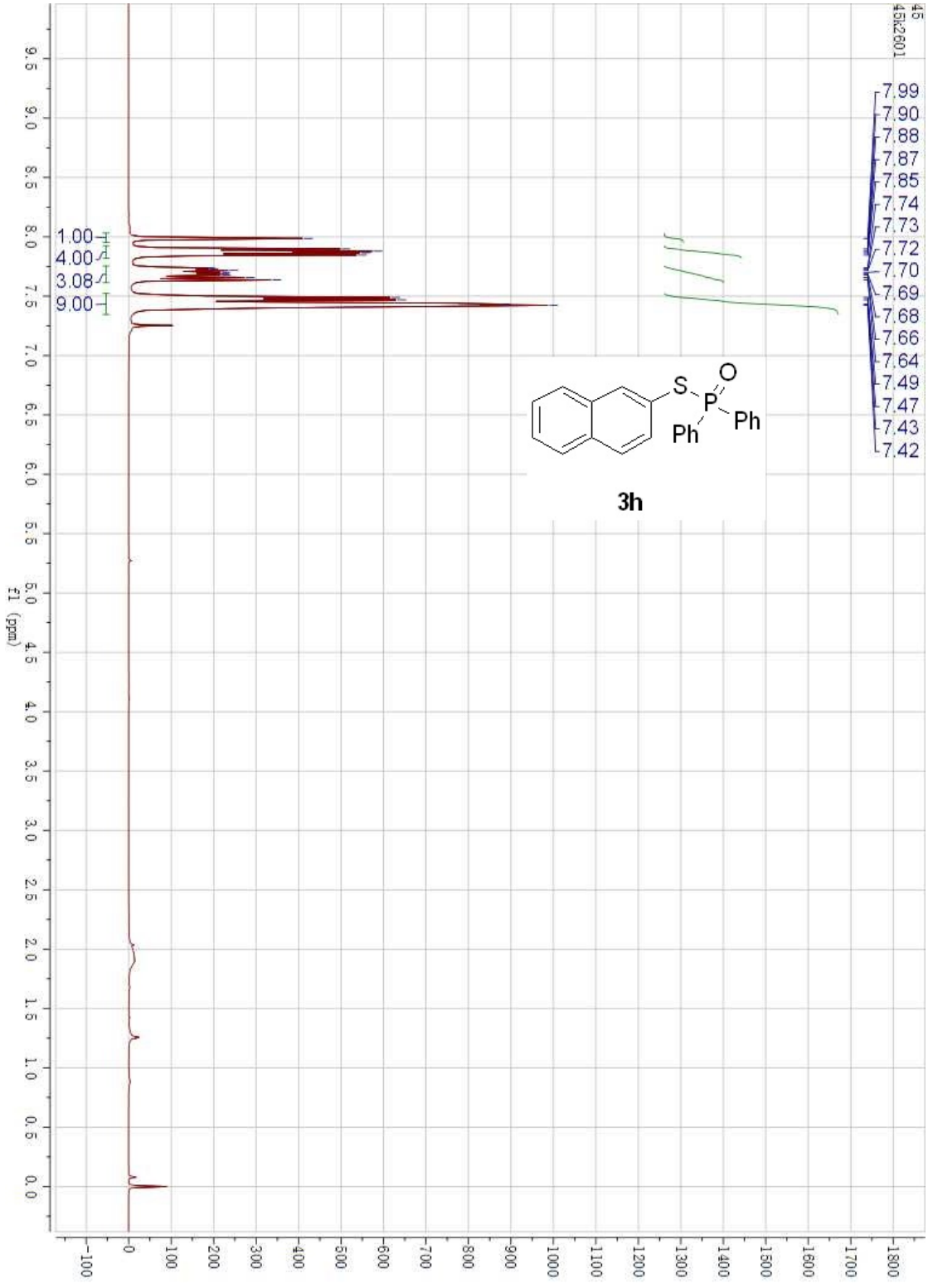
129.3
128.7
128.5
124.7
124.7
Br
S
P
O
Ph
Ph
3e
f1 (ppm)


4.00
2.00
4.10
4.01
7.85
7.84
7.82
7.82
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.43
7.32
Cl
S
O
P
Ph
Ph
3f
f1 (ppm)

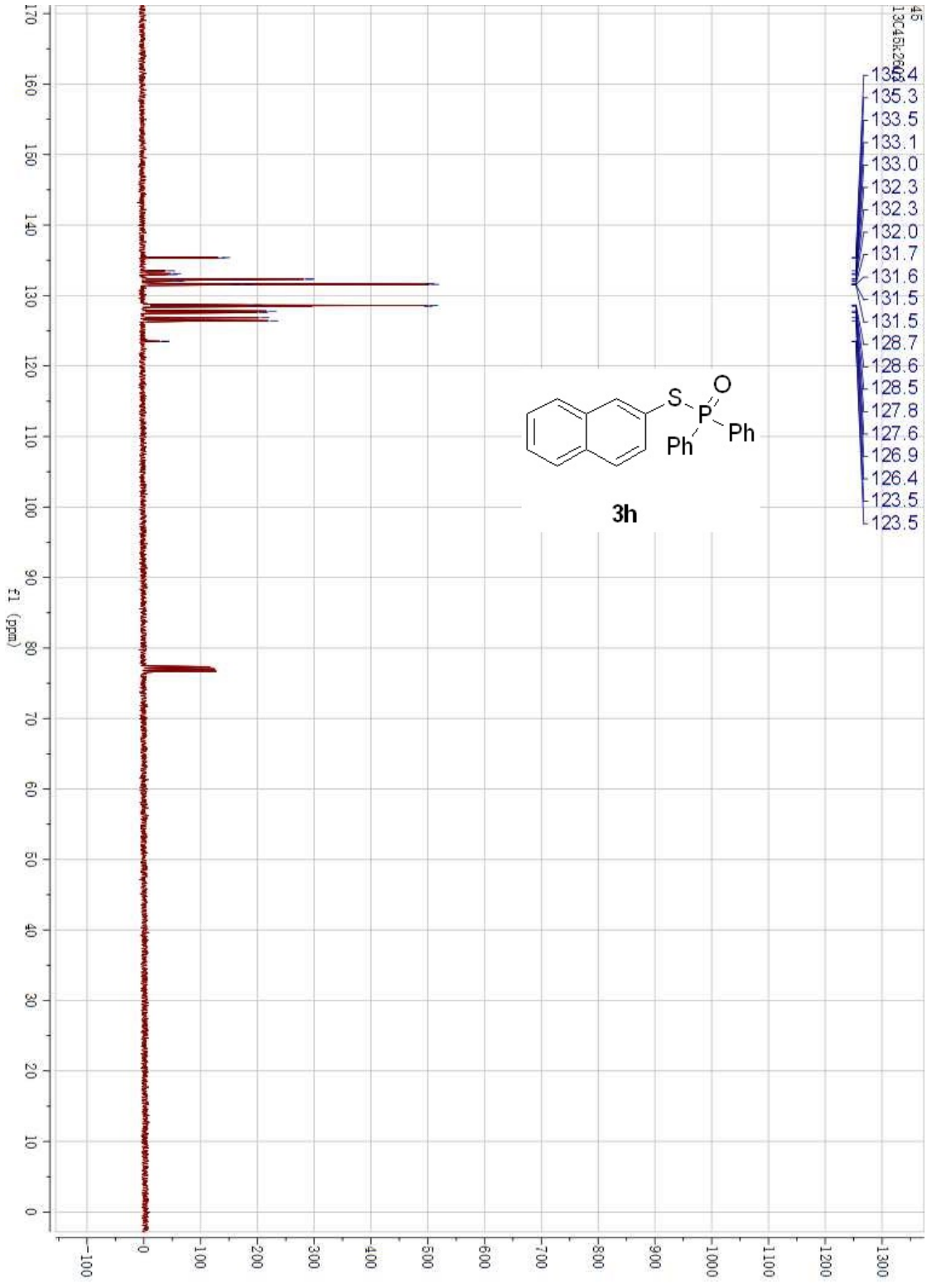

45
13C 45k0202
136.7
136.7
132.7
132.5
132.5
132.2
132.2
131.6
131.5
128.7
128.6
125.4
125.4
123.8
123.7
Cl
S
P
O
Ph
Ph
3f
f1 (ppm)

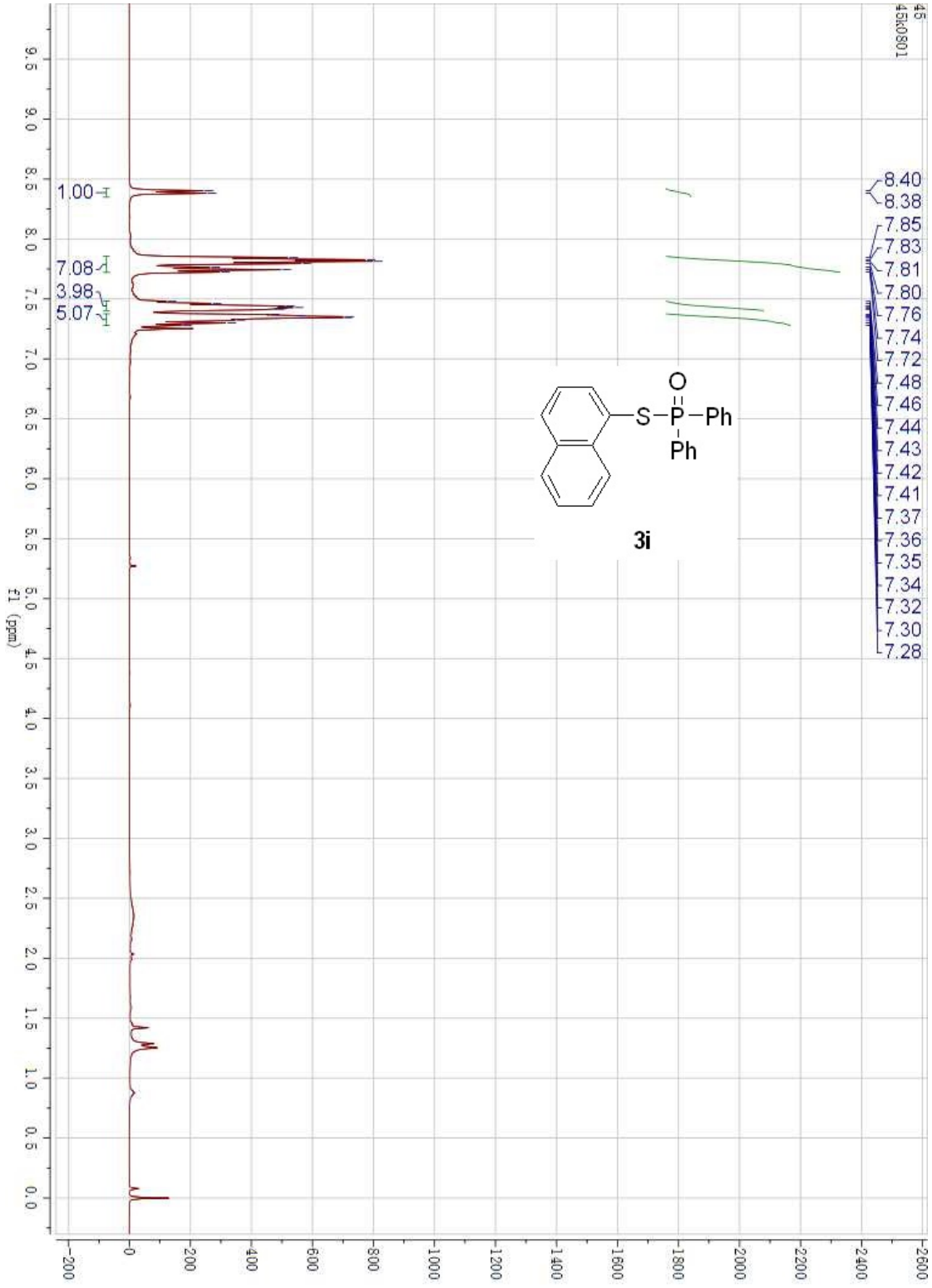

7.84
7.82
7.81
7.79
7.52
7.51
7.49
7.46
7.44
7.43
7.16
7.13
7.12
7.02
7.00
6.99
4.00
7.07
1.95
0.94
3.01
2.34
O
S–P–Ph
Ph
Me
3g
f1 (ppm)

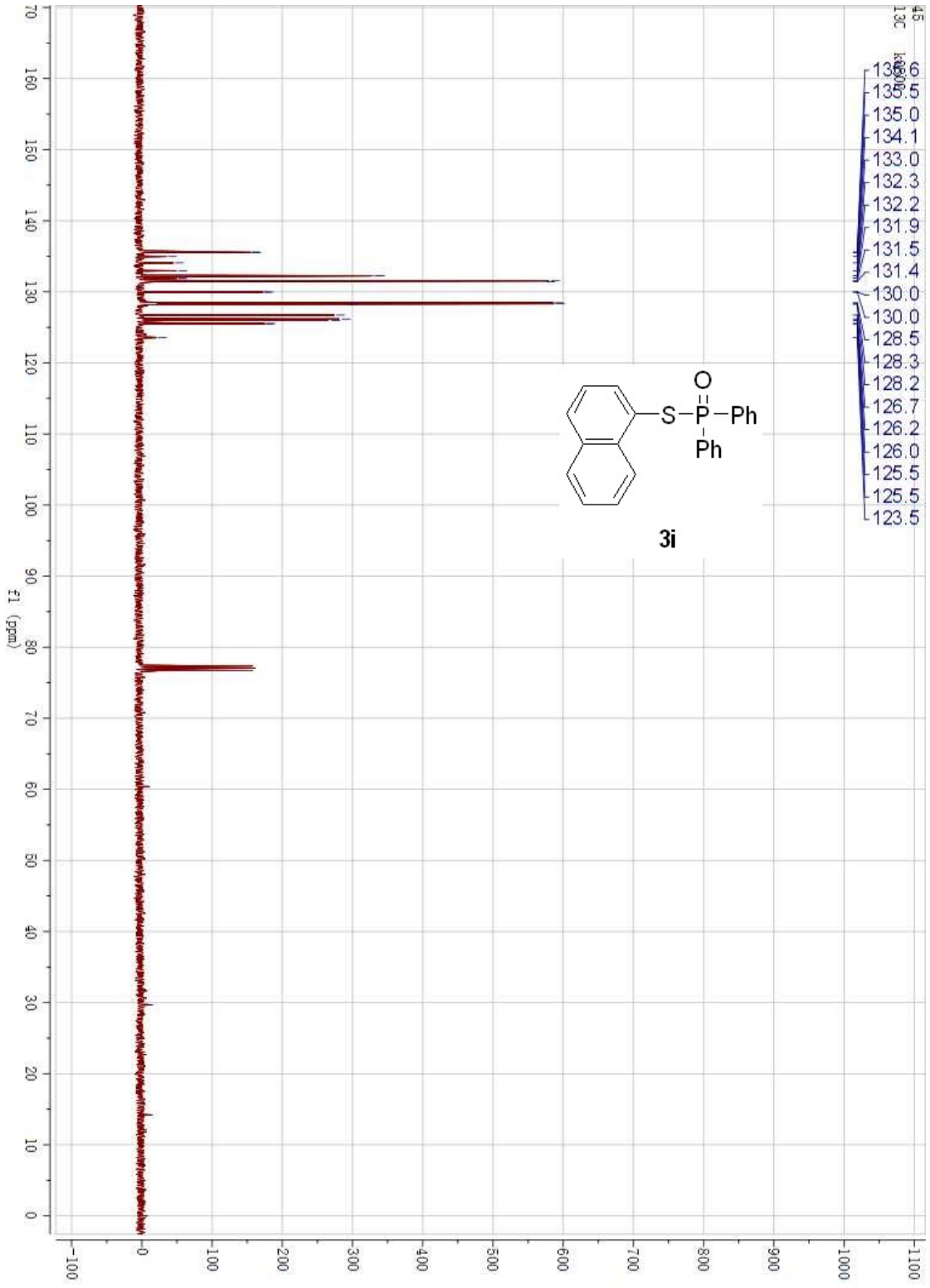

45
13C 45k1002
142.9
142.8
136.8
136.7
133.3
132.3
132.3
131.5
131.4
130.7
130.7
129.3
129.3
128.5
128.4
126.4
126.4
125.4
125.3
O
S
P
Ph
Ph
Me
3g
f1 (ppm)

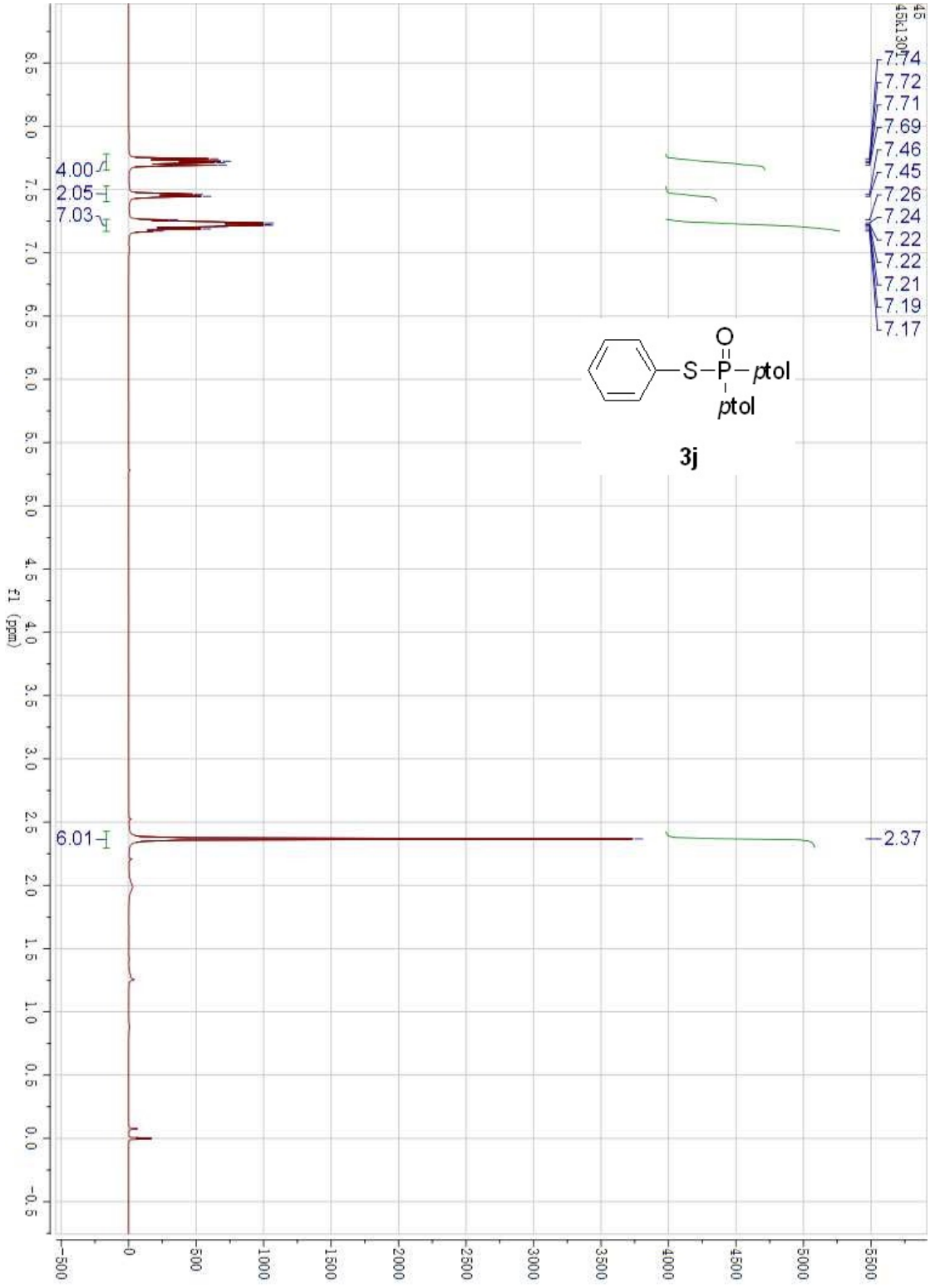

45
45k2601
7.99
7.90
7.88
7.87
7.85
7.74
7.73
7.72
7.70
7.69
7.68
7.66
7.64
7.49
7.47
7.43
7.42
1.00
4.00
3.08
9.00
S
O
P
Ph
Ph
f1 (ppm)

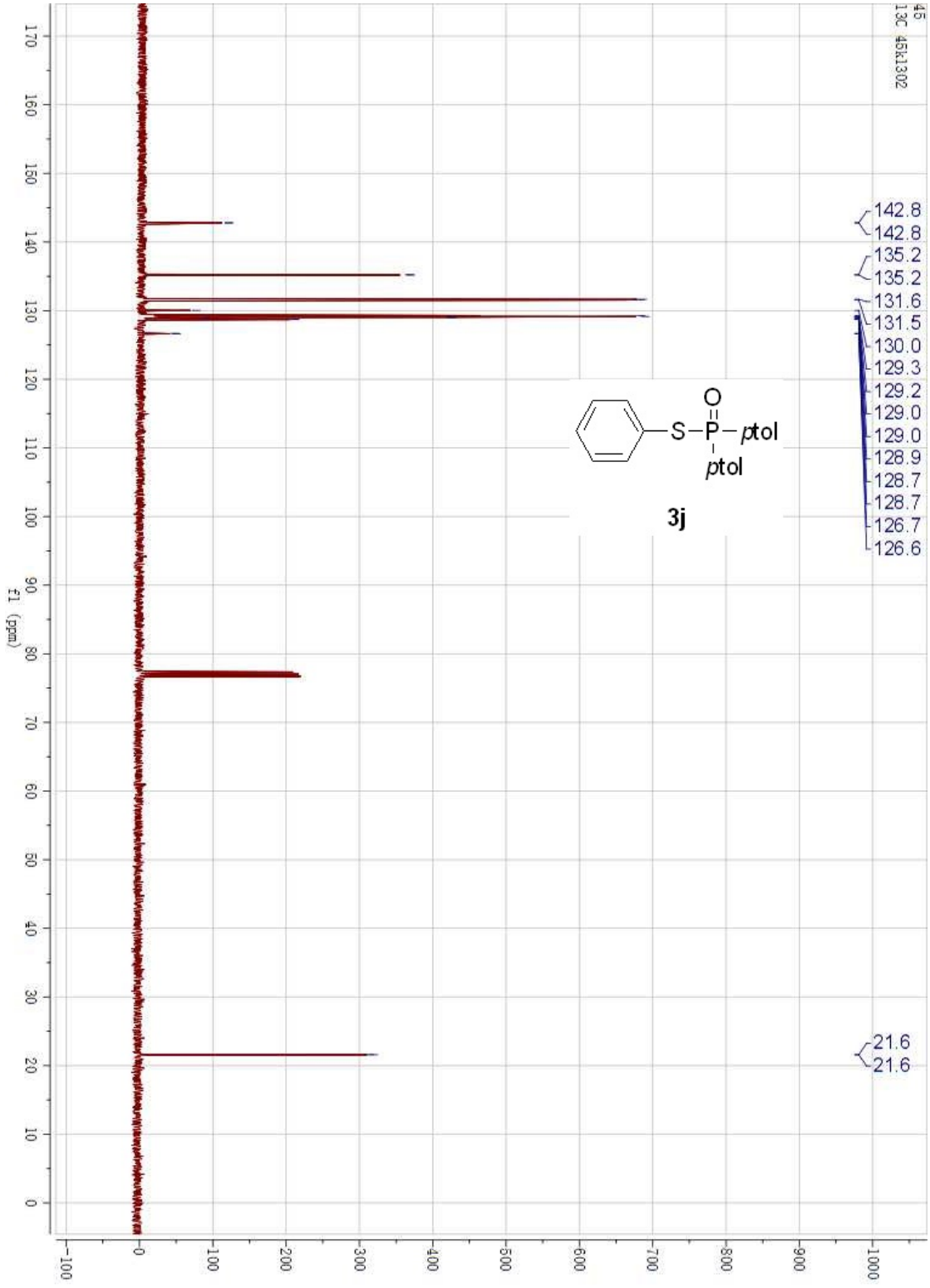
3h

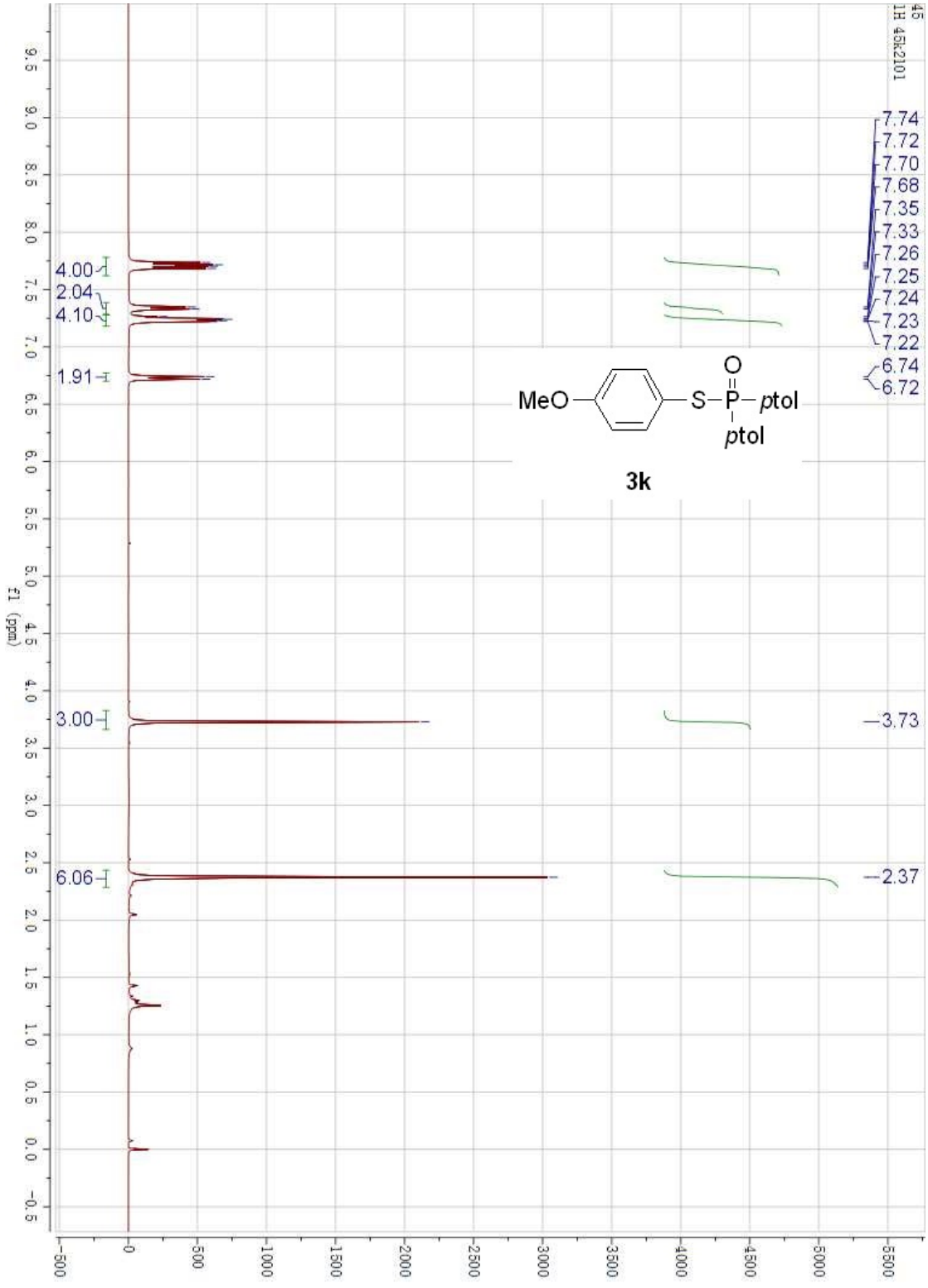

135.4
135.3
133.5
133.1
133.0
132.3
132.3
132.0
131.7
131.6
131.5
131.5
128.7
128.6
128.5
127.8
127.6
126.9
126.4
123.5
123.5
S
O
P
Ph
Ph
3h
f1 (ppm)


45
45k0801
1.00
7.08
3.98
5.07
8.40
8.38
7.85
7.83
7.81
7.80
7.76
7.74
7.72
7.48
7.46
7.44
7.43
7.42
7.41
7.37
7.36
7.35
7.34
7.32
7.30
7.28
O
S
P
Ph
Ph
3i
f1 (ppm)

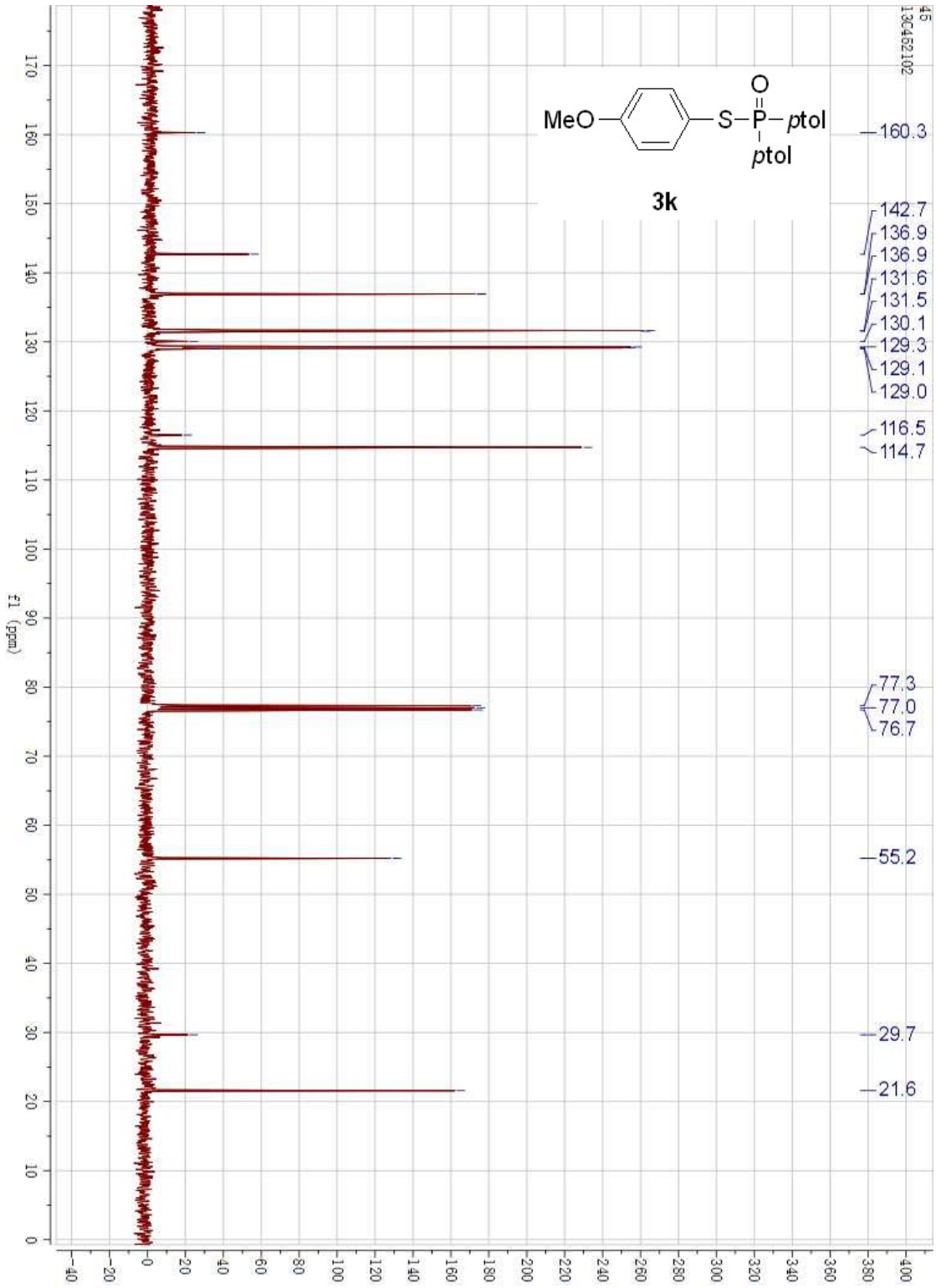

135.6
135.5
135.0
134.1
133.0
132.3
132.2
131.9
131.5
131.4
130.0
130.0
128.5
128.3
128.2
126.7
126.2
126.0
125.5
125.5
123.5
O
S
P
Ph
Ph
3i
f1 (ppm)

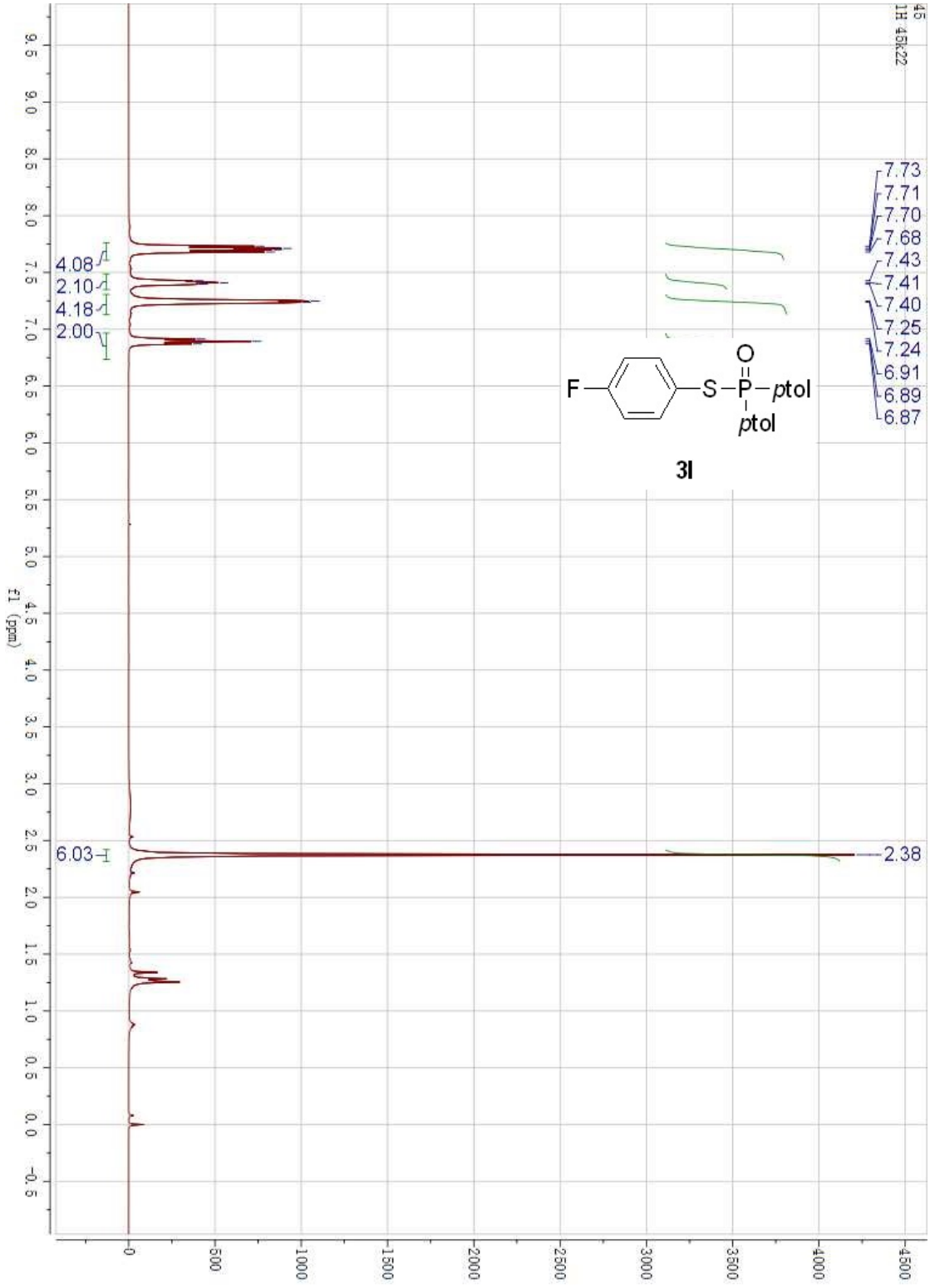

45
45k130
7.74
7.72
7.71
7.69
7.46
7.45
7.26
7.24
7.22
7.22
7.21
7.19
7.17
4.00
2.05
7.03
6.01
2.37
O
S–P–ptol
ptol
3j
f1 (ppm)

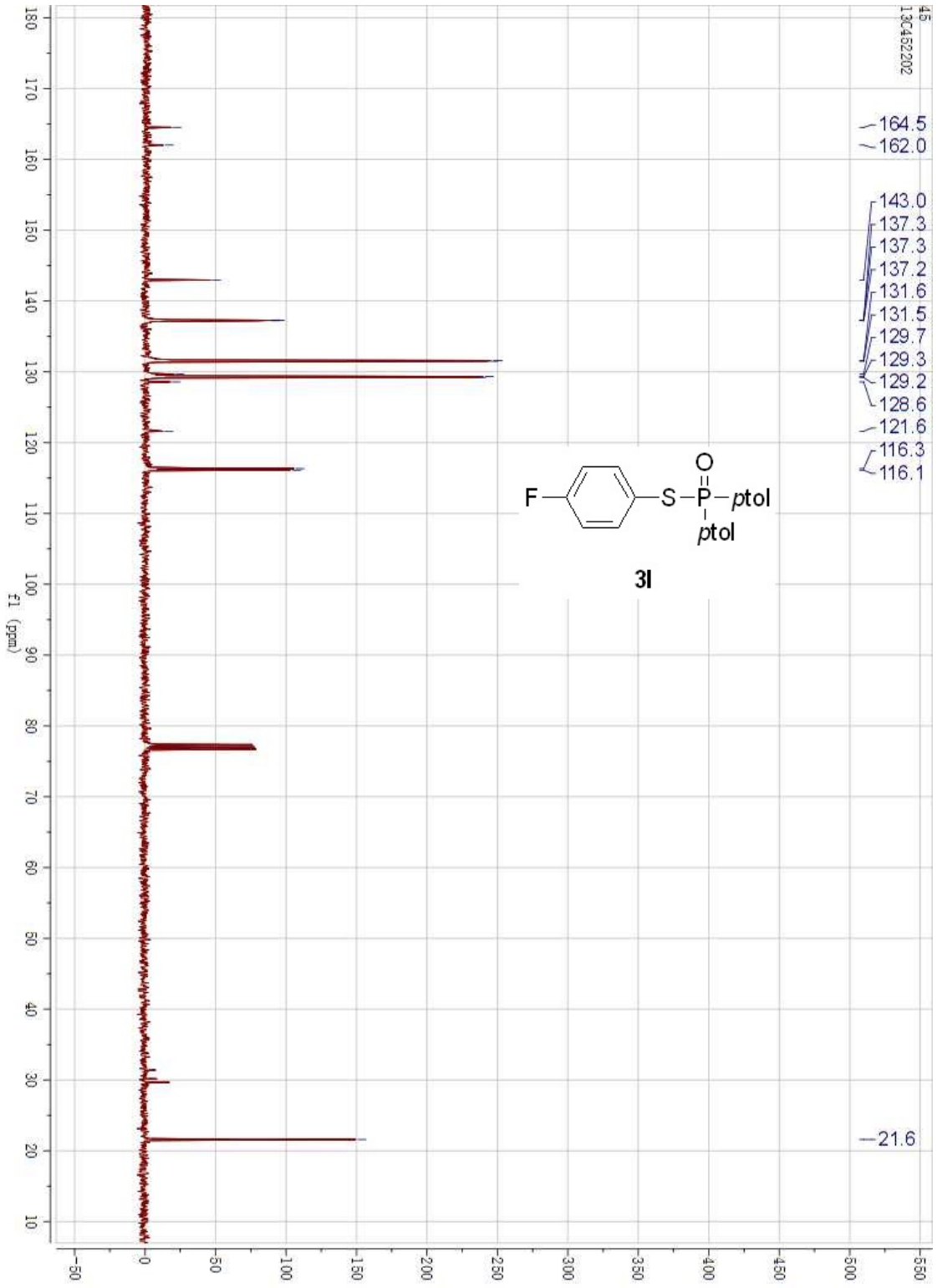

45
13C 45k1302
142.8
142.8
135.2
135.2
131.6
131.5
130.0
129.3
129.2
129.0
129.0
128.9
128.7
128.7
126.7
126.6
21.6
21.6
O
S–P–ptol
ptol
3j
f1 (ppm)

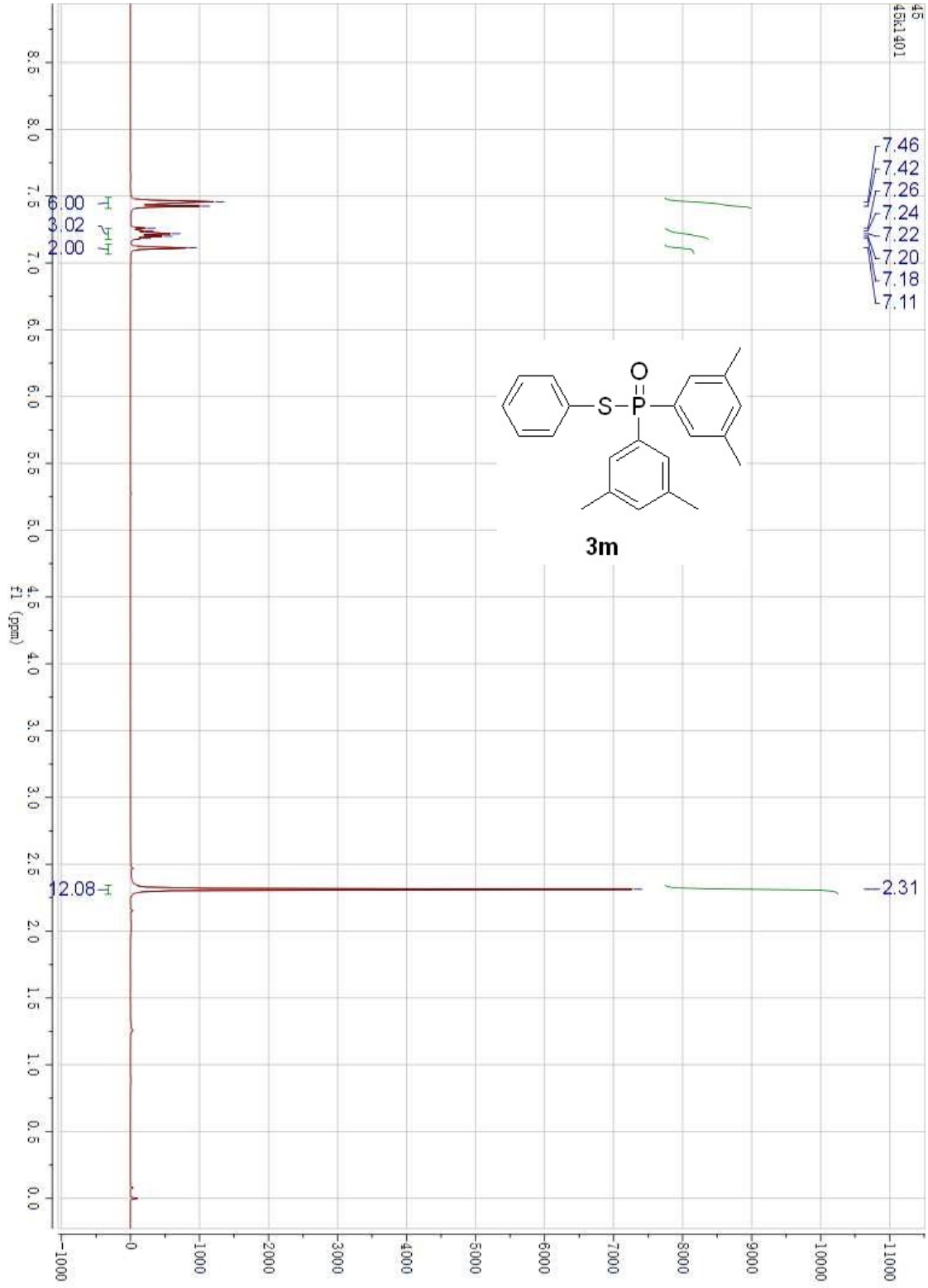

46
1H 45k2101
7.74
7.72
7.70
7.68
7.35
7.33
7.26
7.25
7.24
7.23
7.22
6.74
6.72
4.00
2.04
4.10
1.91
3.00
6.06
3.73
2.37
MeO
S
P
O
ptol
ptol
f1 (ppm)

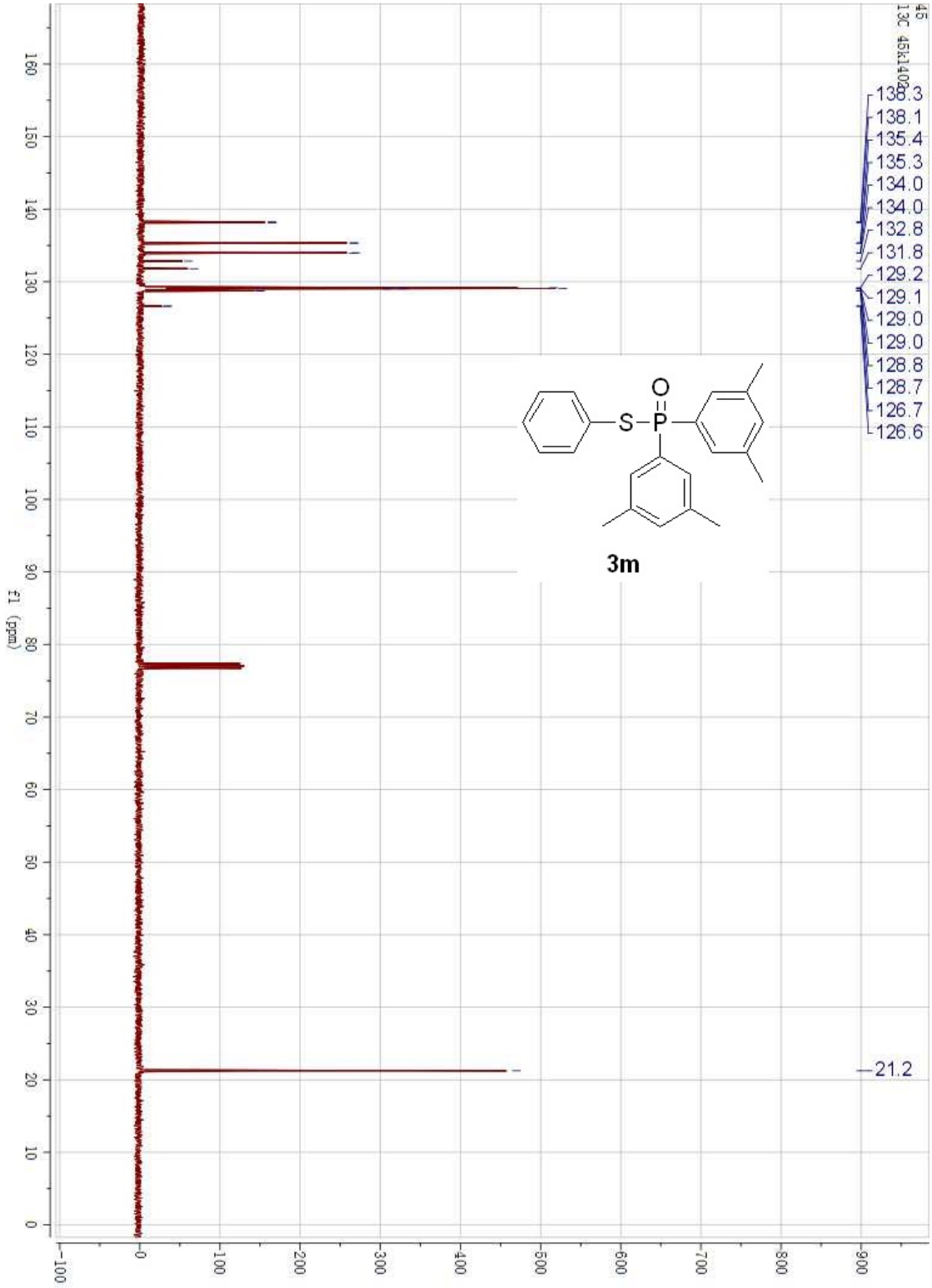
3k

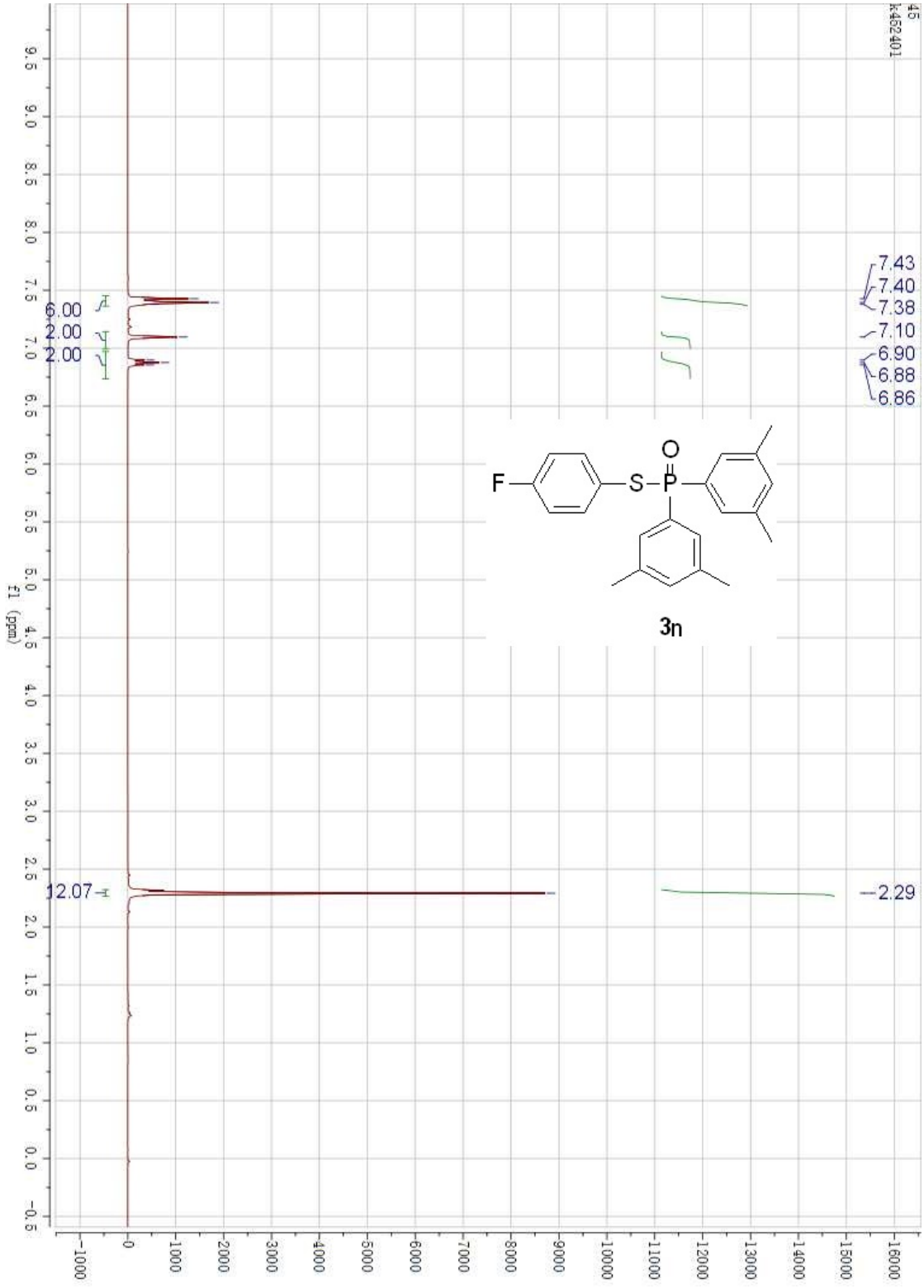

MeO
S
P
O
ptol
ptol
3k
160.3
142.7
136.9
136.9
131.6
131.5
130.1
129.3
129.1
129.0
116.5
114.7
77.3
77.0
76.7
55.2
29.7
21.6
f1 (ppm)

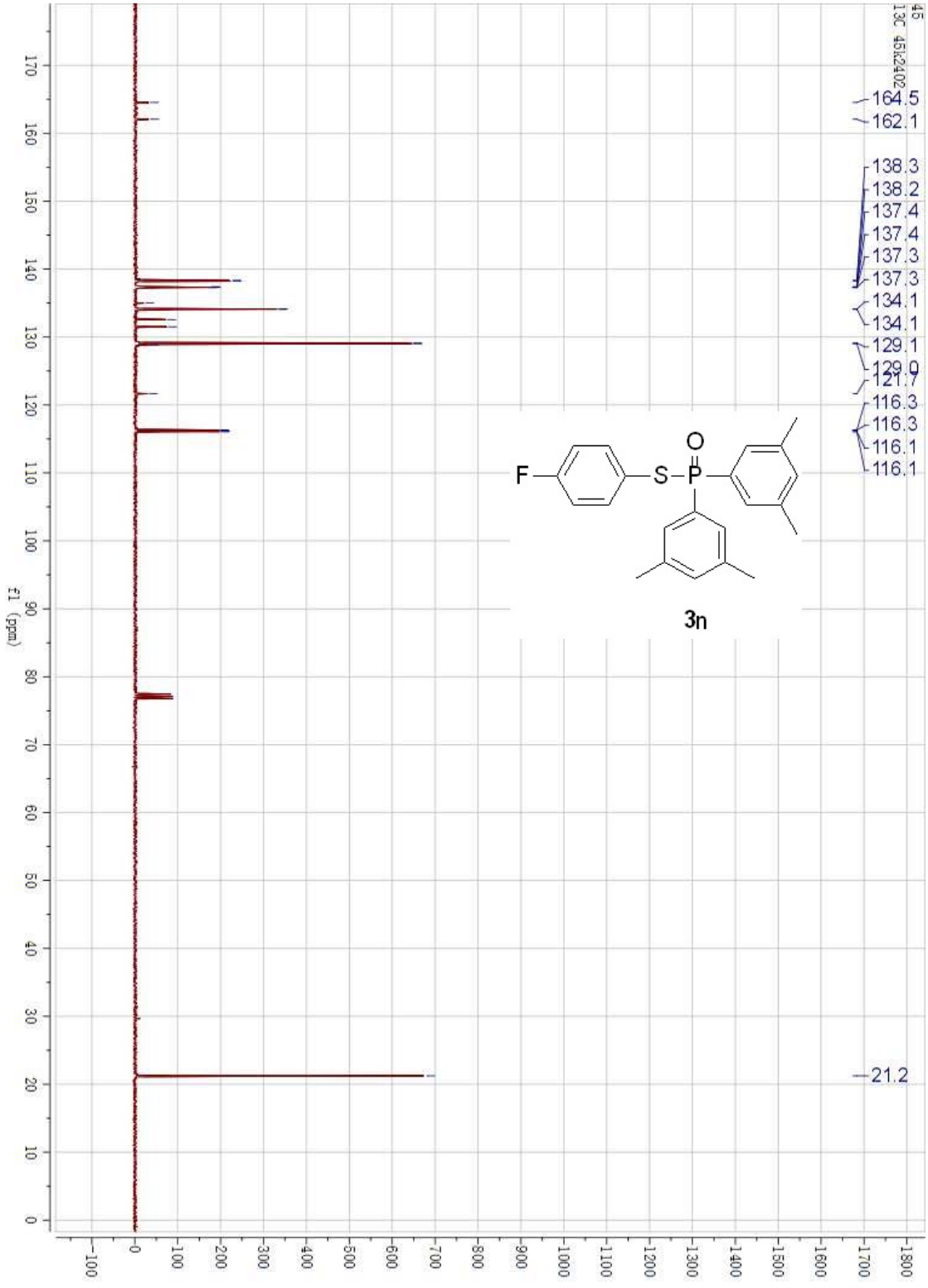

46
1H 45k22
7.73
7.71
7.70
7.68
7.43
7.41
7.40
7.25
7.24
6.91
6.89
6.87
4.08
2.10
4.18
2.00
6.03
2.38
F
S
P
O
ptol
ptol
3l
f1 (ppm)


46
130452202
164.5
162.0
143.0
137.3
137.3
137.2
131.6
131.5
129.7
129.3
129.2
128.6
121.6
116.3
116.1
21.6
F
S
P
O
ptol
ptol
3l
f1 (ppm)


45
45k1401
7.46
7.42
7.26
7.24
7.22
7.20
7.18
7.11
6.00
3.02
2.00
12.08
2.31
O
S
P
3m
f1 (ppm)


138.3
138.1
135.4
135.3
134.0
134.0
132.8
131.8
129.2
129.1
129.0
129.0
128.8
128.7
126.7
126.6
21.2
O
S
P
3m
f1 (ppm)


7.43
7.40
7.38
7.10
6.90
6.88
6.86
6.00
2.00
2.00
12.07
-2.29
F
S
P
O
3n
f1 (ppm)


45
13C 451-2402
164.5
162.1
138.3
138.2
137.4
137.4
137.3
137.3
134.1
134.1
129.1
129.0
121.7
116.3
116.3
116.1
116.1
21.2
F
S
P
O
f1 (ppm)

3n