

Synthesis and Base-induced Cyclisation of 2-Benzyloxyphenylphosphonamidates giving 2,3-Dihydrobenzo[*d*][1,3]oxaphospholes

R. Alan Aitken * Khadija Ait Moulay, David B. Cordes, Ryan A. Inwood, Fraser G. Jamieson, Alexander J. B. Nelson and Aidan P. McKay
EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, UK.

Supplementary Material

Figure

¹ H NMR and DEPTQ ¹³ C NMR spectra of 13	S1, S2
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 14	S3, S4, S5
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 15	S6, S7, S8
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 16	S9, S10, S11
¹ H NMR, ¹ H{ ³¹ P} NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 17	S12, S13, S14, S15
¹ H NMR and DEPTQ ¹³ C NMR spectra of 18a	S16, S17
¹ H NMR and DEPTQ ¹³ C NMR spectra of 18b	S18, S19
¹ H NMR and DEPTQ ¹³ C NMR spectra of 18c	S20, S21
¹ H NMR and DEPTQ ¹³ C NMR spectra of 18d	S22, S23
¹ H NMR and DEPTQ ¹³ C NMR spectra of 18e	S24, S25
¹ H NMR, and DEPTQ ¹³ C NMR spectra of 18f	S26, S27
¹ H NMR, ¹⁹ F NMR and DEPTQ ¹³ C NMR spectra of 18g	S28, S29, S30
¹ H NMR, ¹⁹ F NMR and DEPTQ ¹³ C NMR spectra of 18h	S31, S32, S33
¹ H NMR and DEPTQ ¹³ C NMR spectra of 18l	S34, S35
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 19b	S36, S37, S38

¹ H NMR and ³¹ P NMR spectra of 19d	S39, S40
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 19e	S41, S42, S43
³¹ P NMR spectrum of 20	S44
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 22	S45, S46, S47
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21a	S48, S49, S50
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21b	S51, S52, S53
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21c	S54, S55, S56
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21d	S57, S58, S59
¹ H NMR and ³¹ P NMR spectra of 21e	S60, S61
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21f	S62, S63, S64
¹ H NMR, ¹⁹ F NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21g	S65, S66, S67, S68
¹ H NMR, ¹⁹ F NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21h	S69, S70, S71, S72
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21i	S73, S74, S75
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21j	S76, S77, S78
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21k	S79, S80, S81
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21l	S82, S83, S84
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 21m	S85, S86, S87
¹ H NMR, ³¹ P NMR and DEPTQ ¹³ C NMR spectra of 23c	S88, S89, S90
¹ H NMR and ³¹ P NMR spectra of 23d	S91, S92
¹ H NMR and ³¹ P NMR spectra of 23e	S93, S94
¹ H NMR and ³¹ P NMR spectra of 23g	S95, S96

^1H NMR, ^{31}P NMR and DEPTQ ^{13}C NMR spectra of **23h**

S97, S98, S99

^{31}P NMR spectrum of **23k**

S100

^1H NMR, ^{31}P NMR and DEPTQ ^{13}C NMR spectra of **23l**

S101, S102, S103

Figure S1. 300 MHz ^1H NMR spectrum of **13**

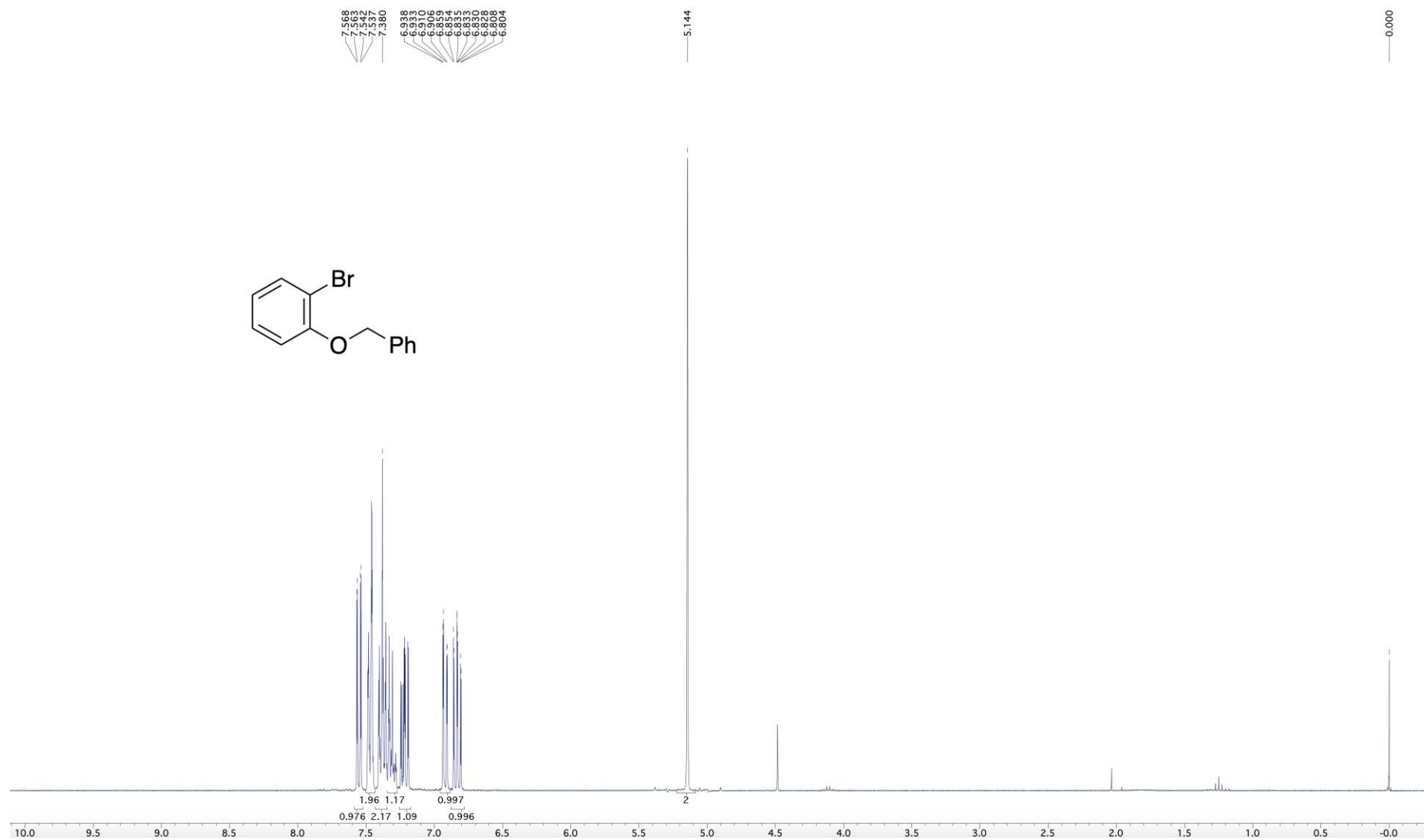


Figure S2. 100 MHz DEPTQ ^{13}C NMR spectrum of **13**

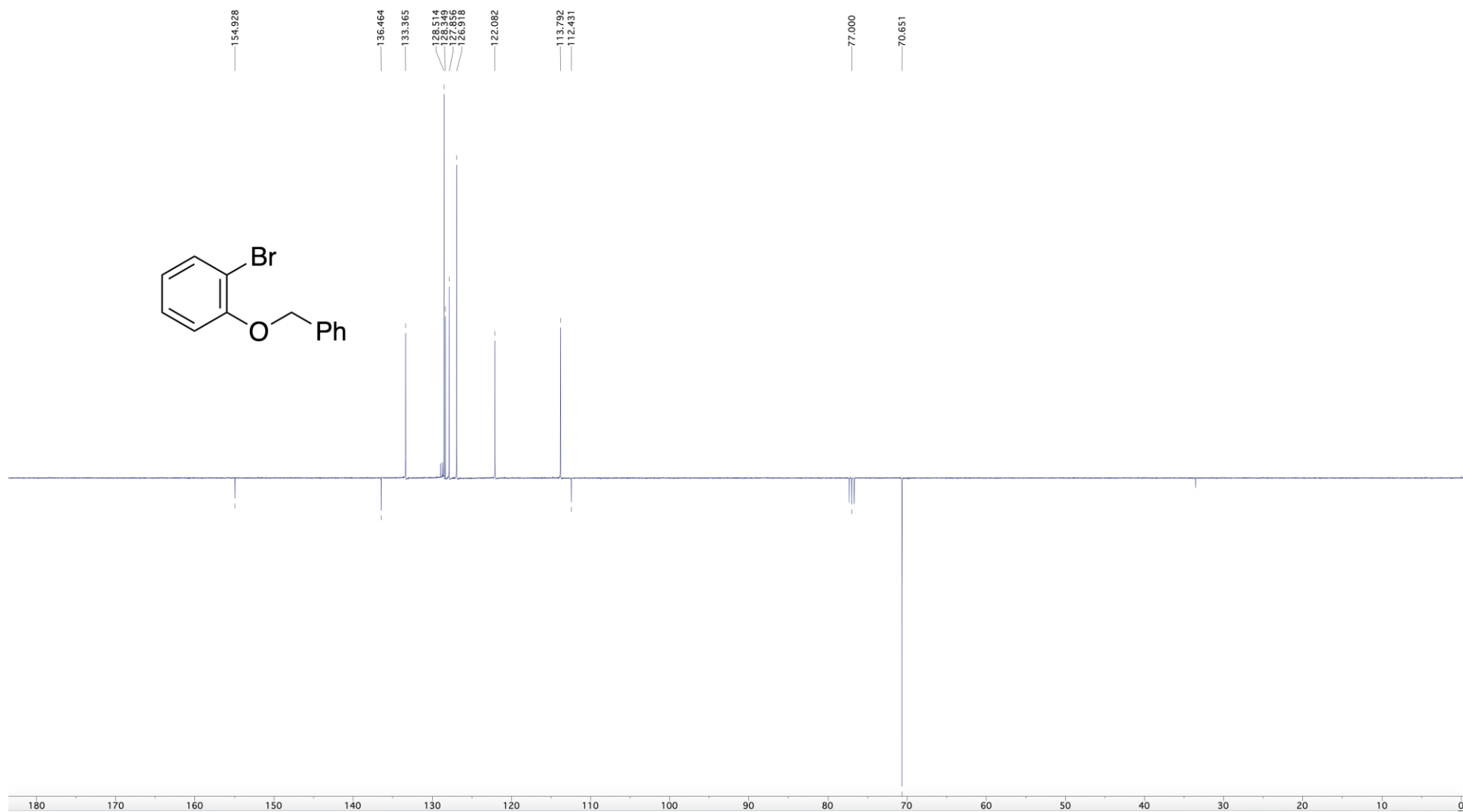


Figure S3. 400 MHz ^1H NMR spectrum of **14**

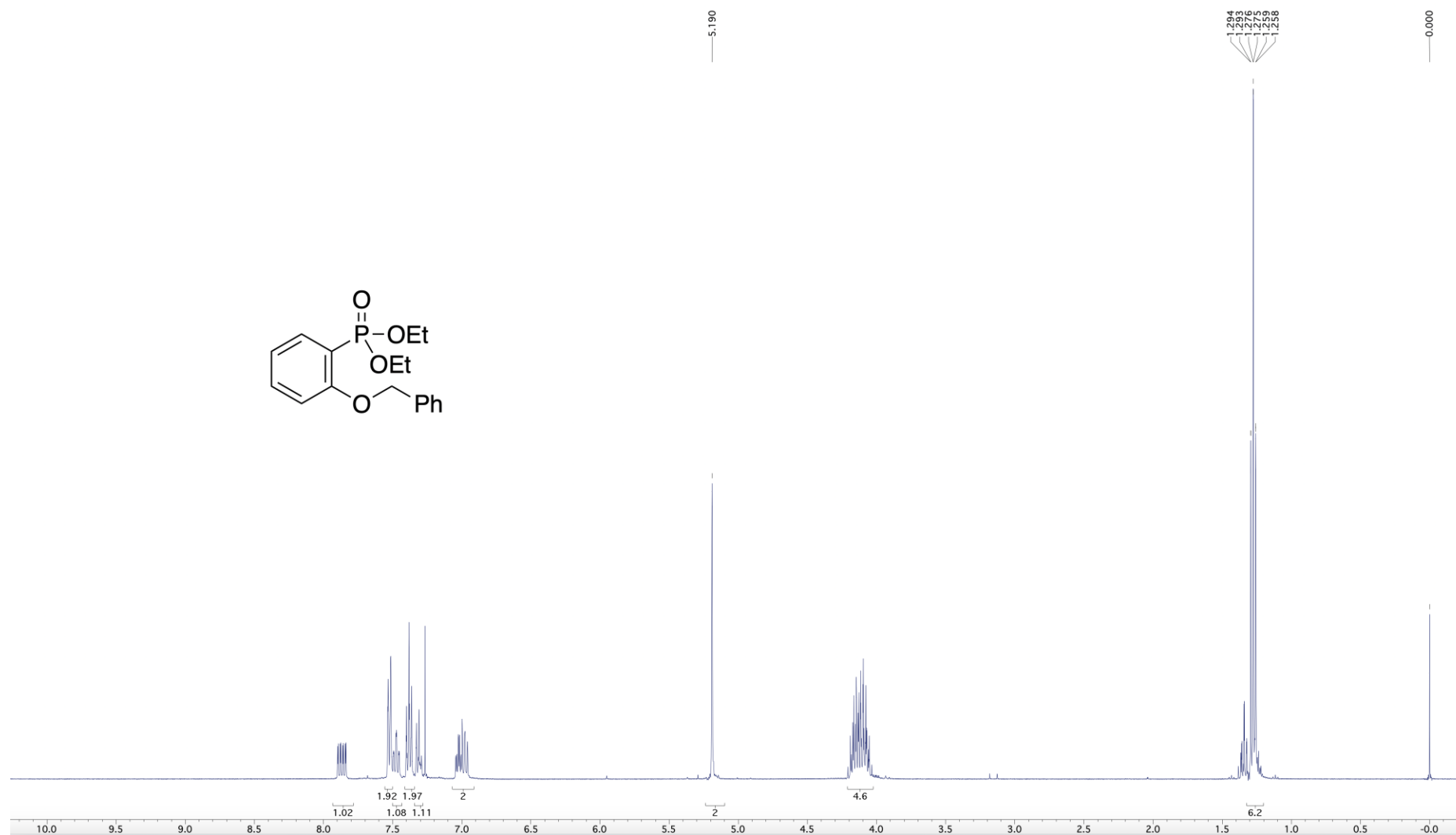


Figure S4. 162 MHz ^{31}P NMR spectrum of **14**



Figure S5. 100 MHz DEPTQ ^{13}C NMR spectrum of **14**

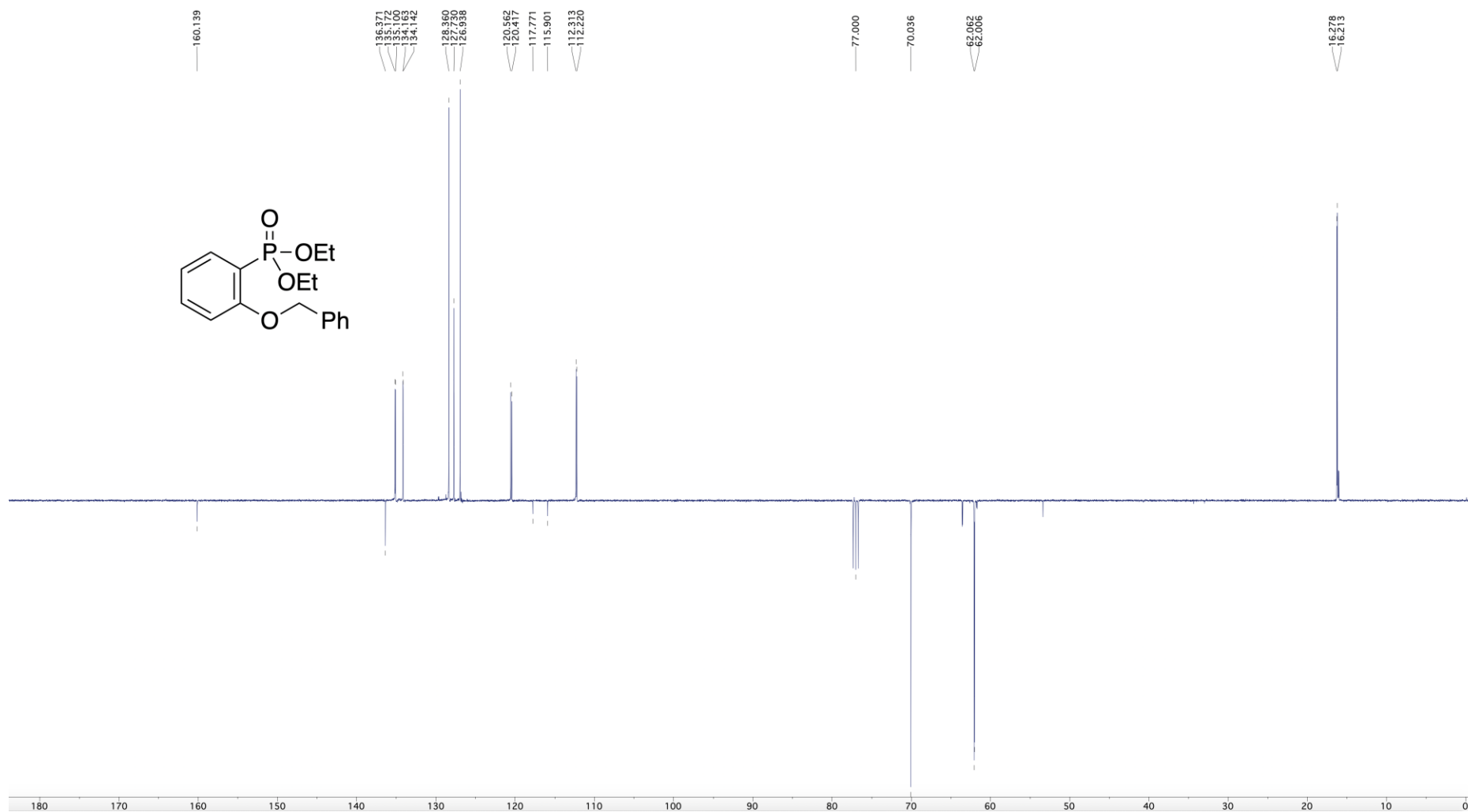


Figure S6. 400 MHz ^1H NMR spectrum of **15**

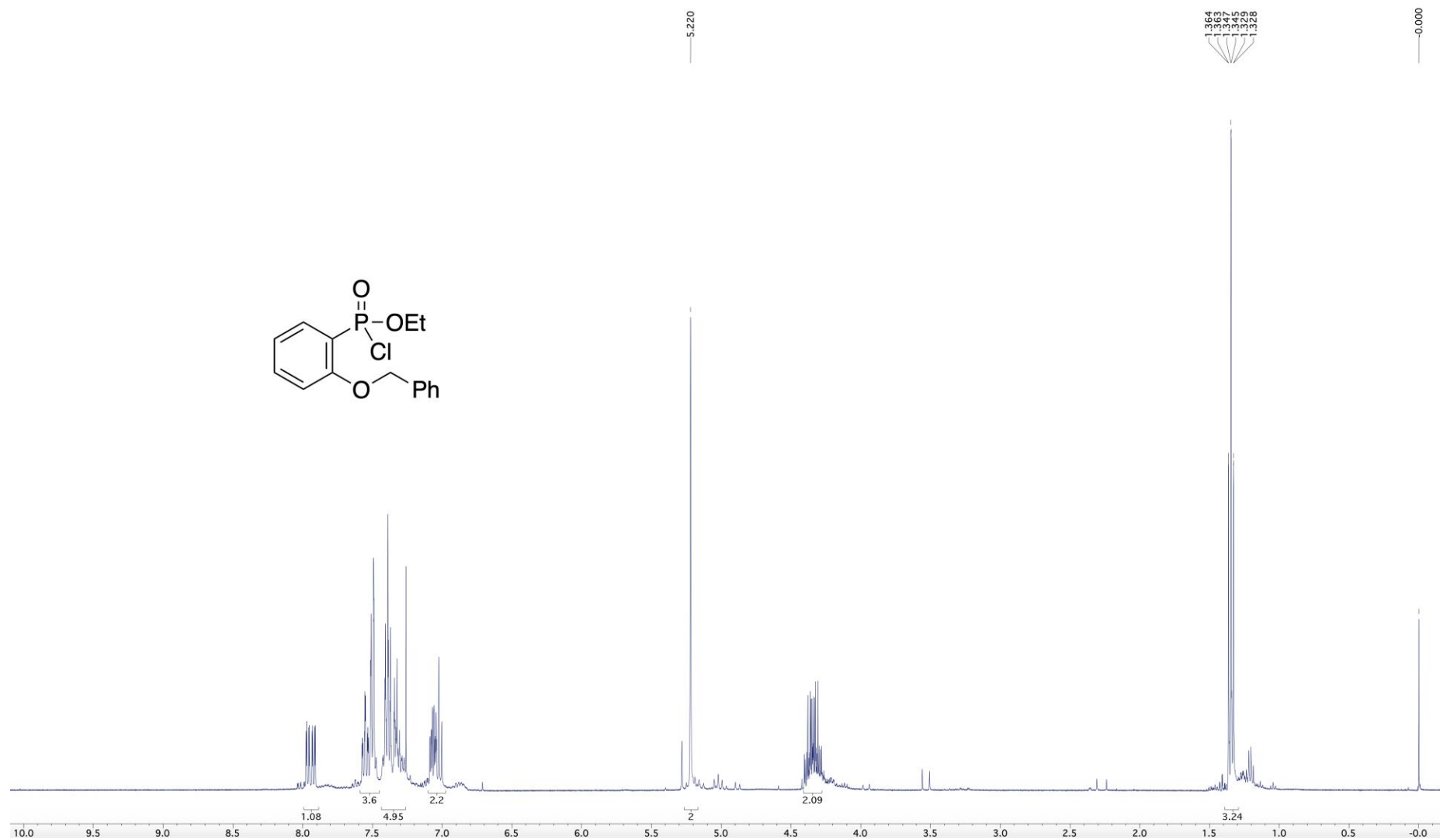


Figure S7. 162 MHz ^{31}P NMR spectrum of **15**

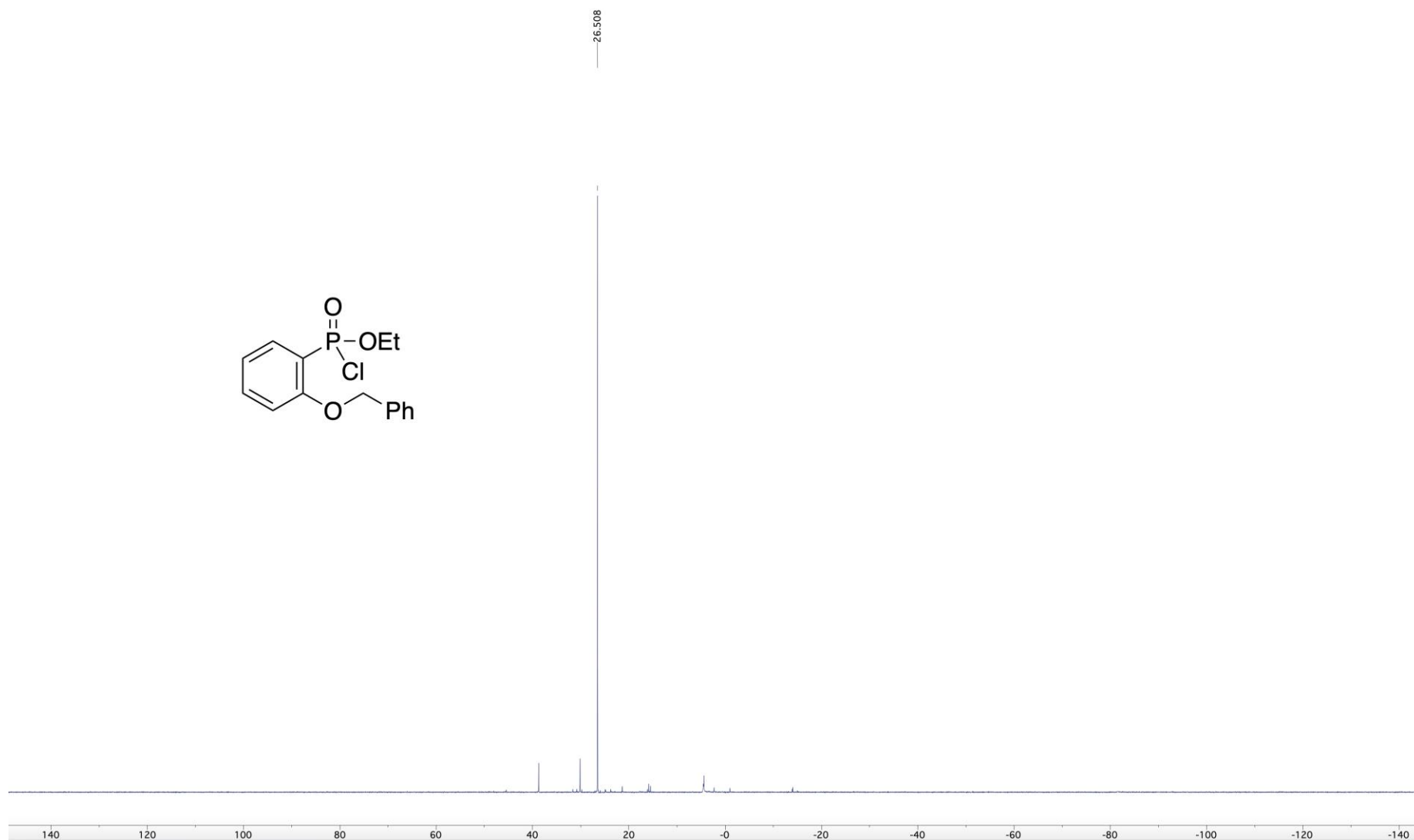


Figure S8. 125 MHz DEPTQ ^{13}C NMR spectrum of **15**

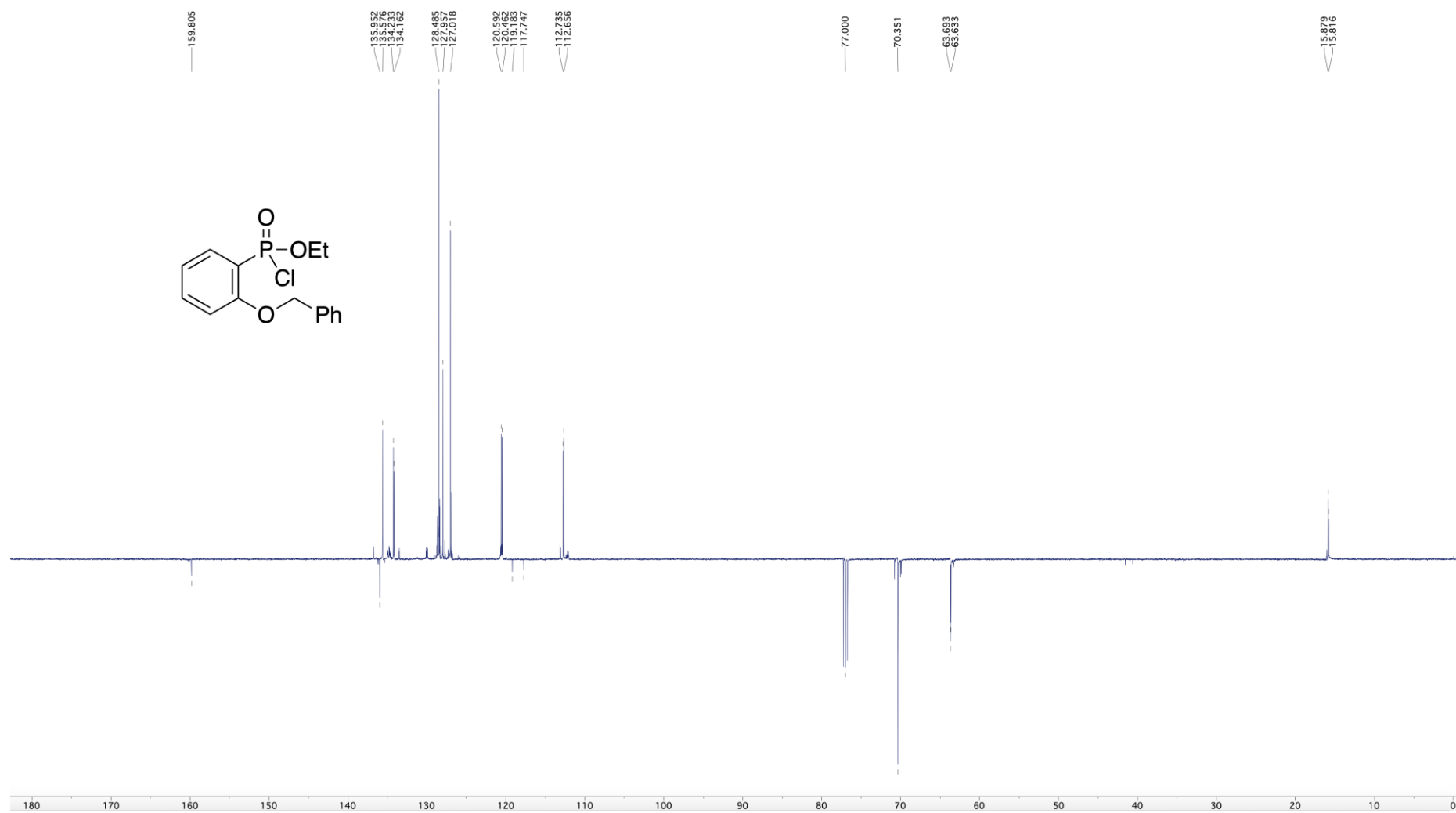


Figure S9. 400 MHz ^1H NMR spectrum of **16**

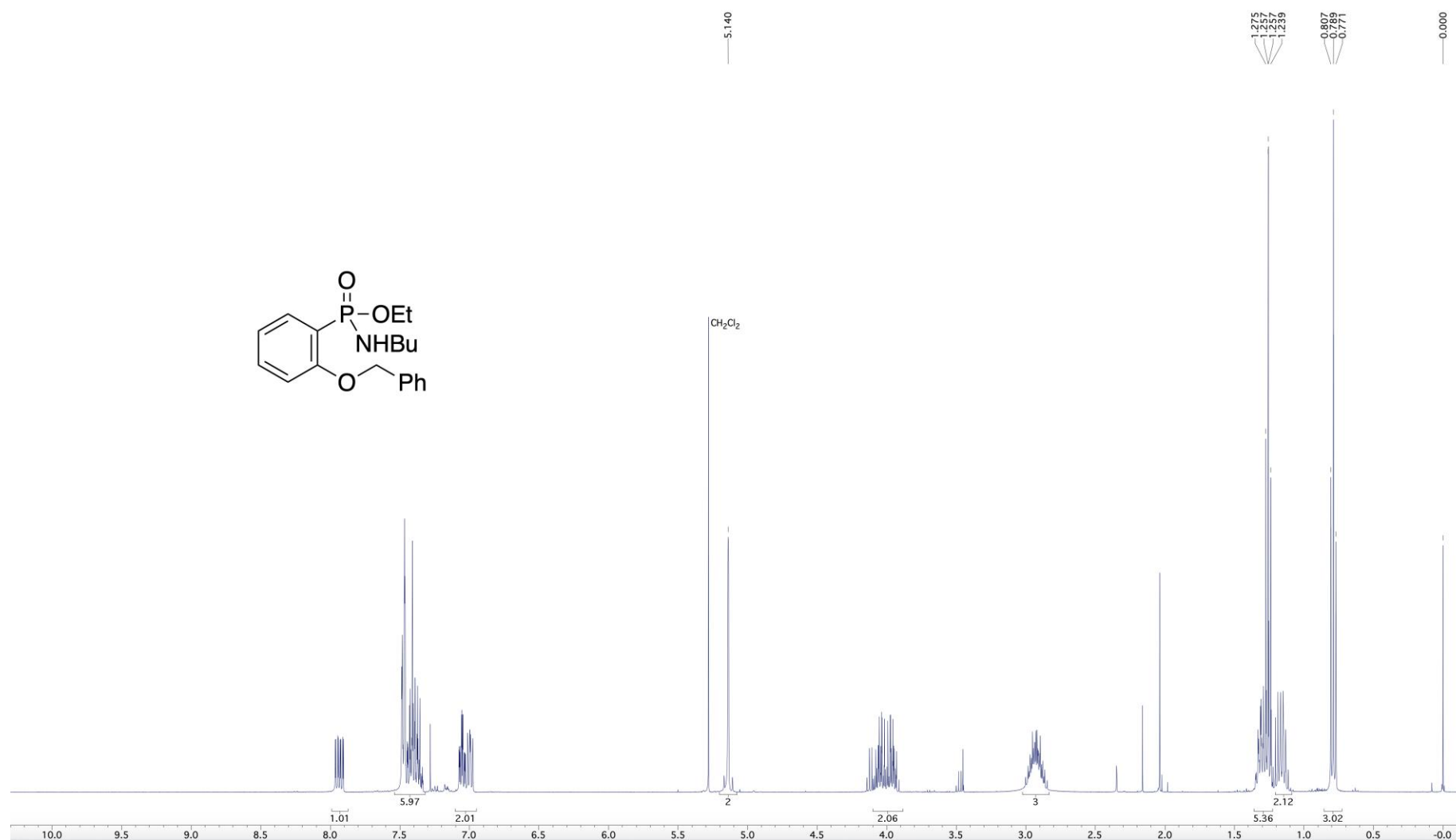


Figure S10. 162 MHz ^{31}P NMR spectrum of **16**

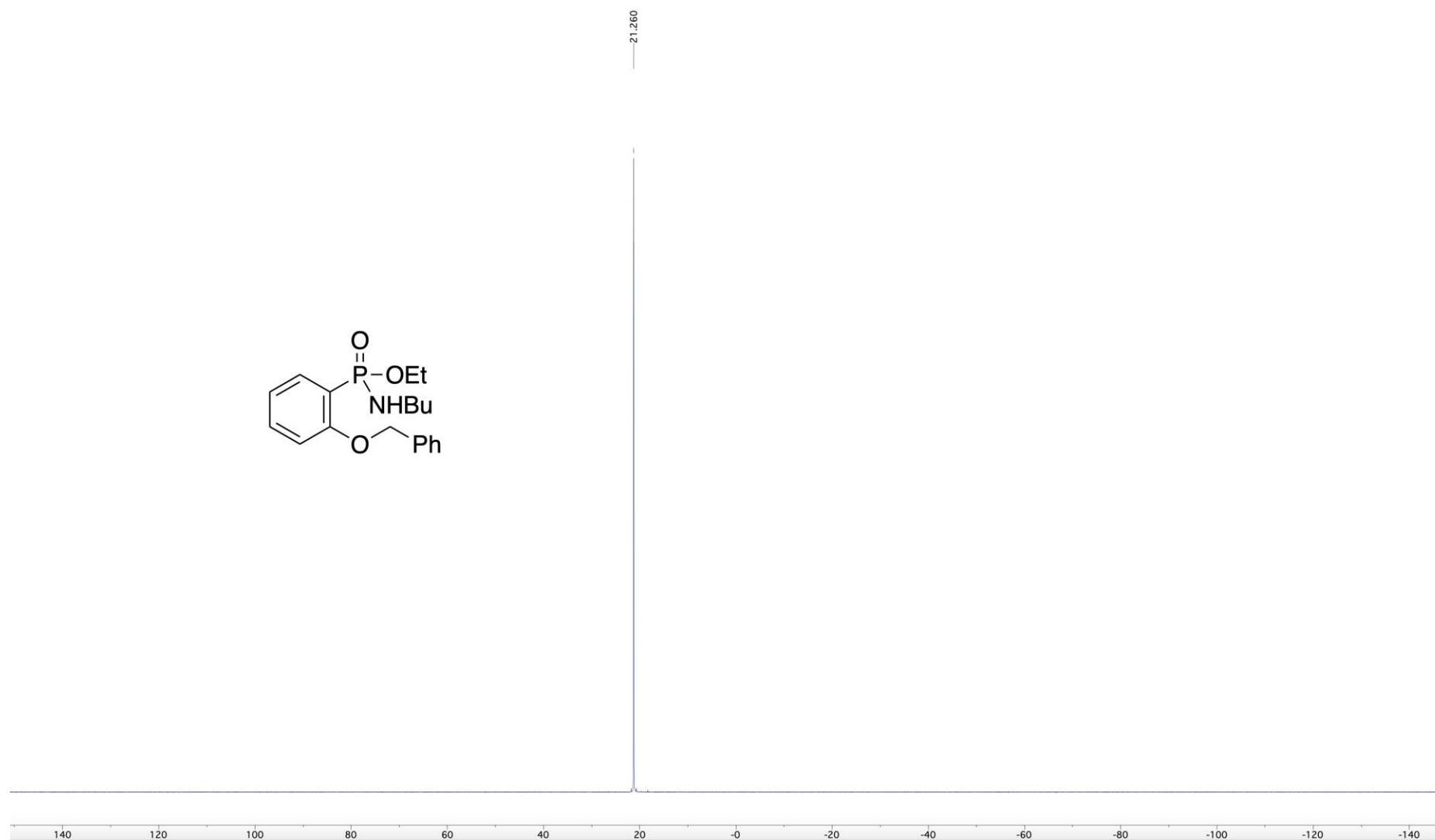


Figure S11. 125 MHz DEPTQ ^{13}C NMR spectrum of **16**

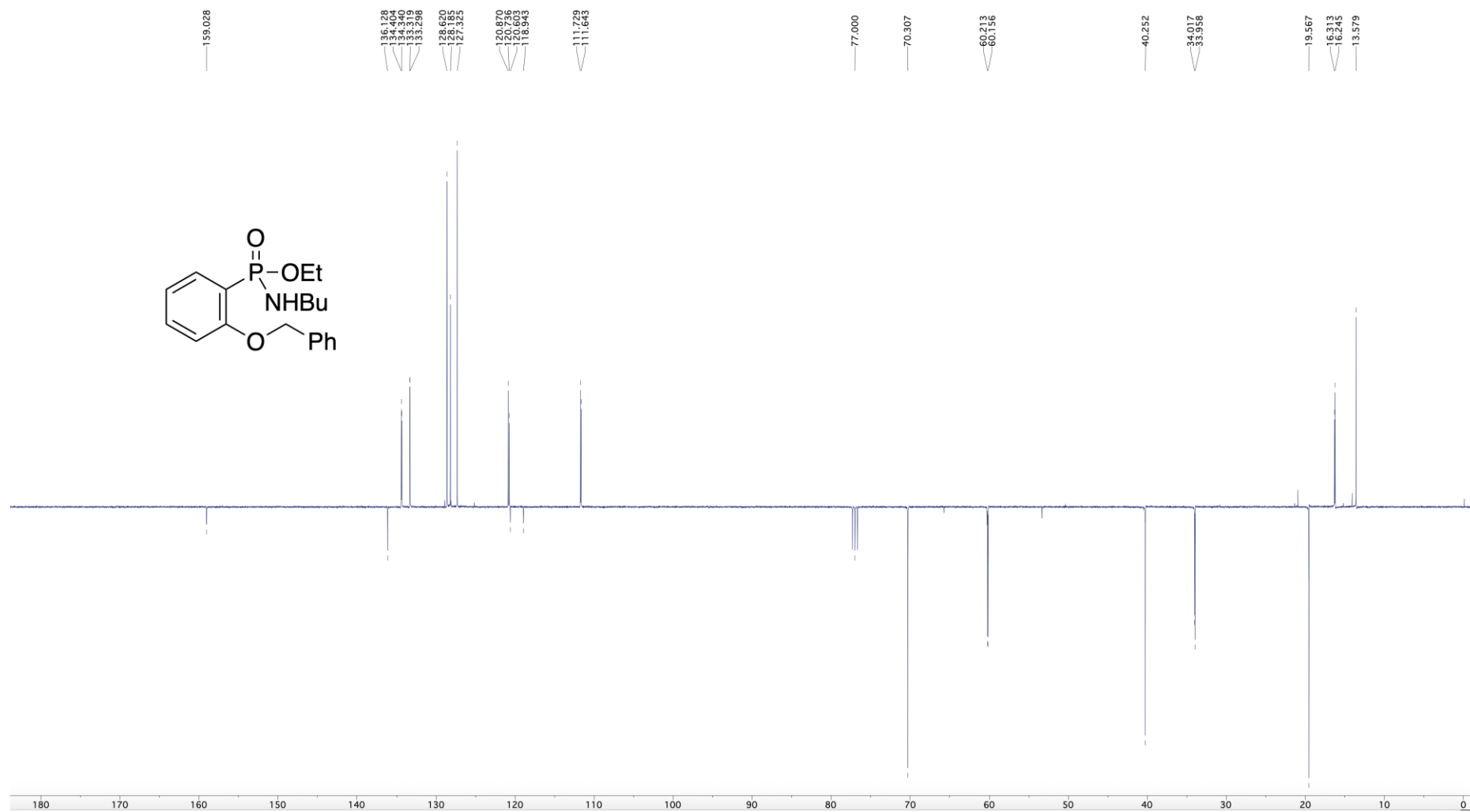


Figure S12. 400 MHz ^1H NMR spectrum of **17**

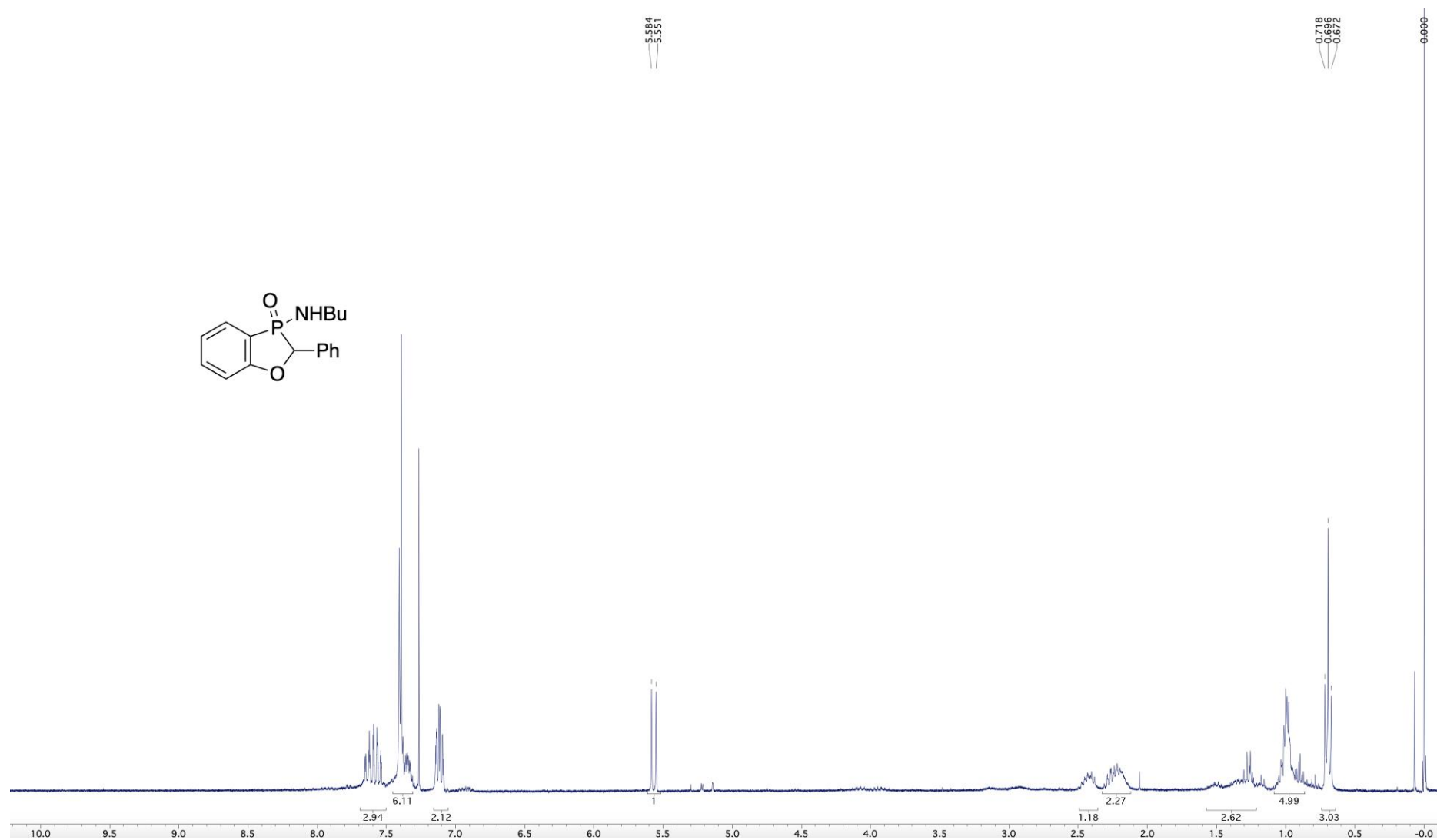


Figure S13. 400 MHz ^1H NMR spectrum of **17** (^{31}P decoupled)

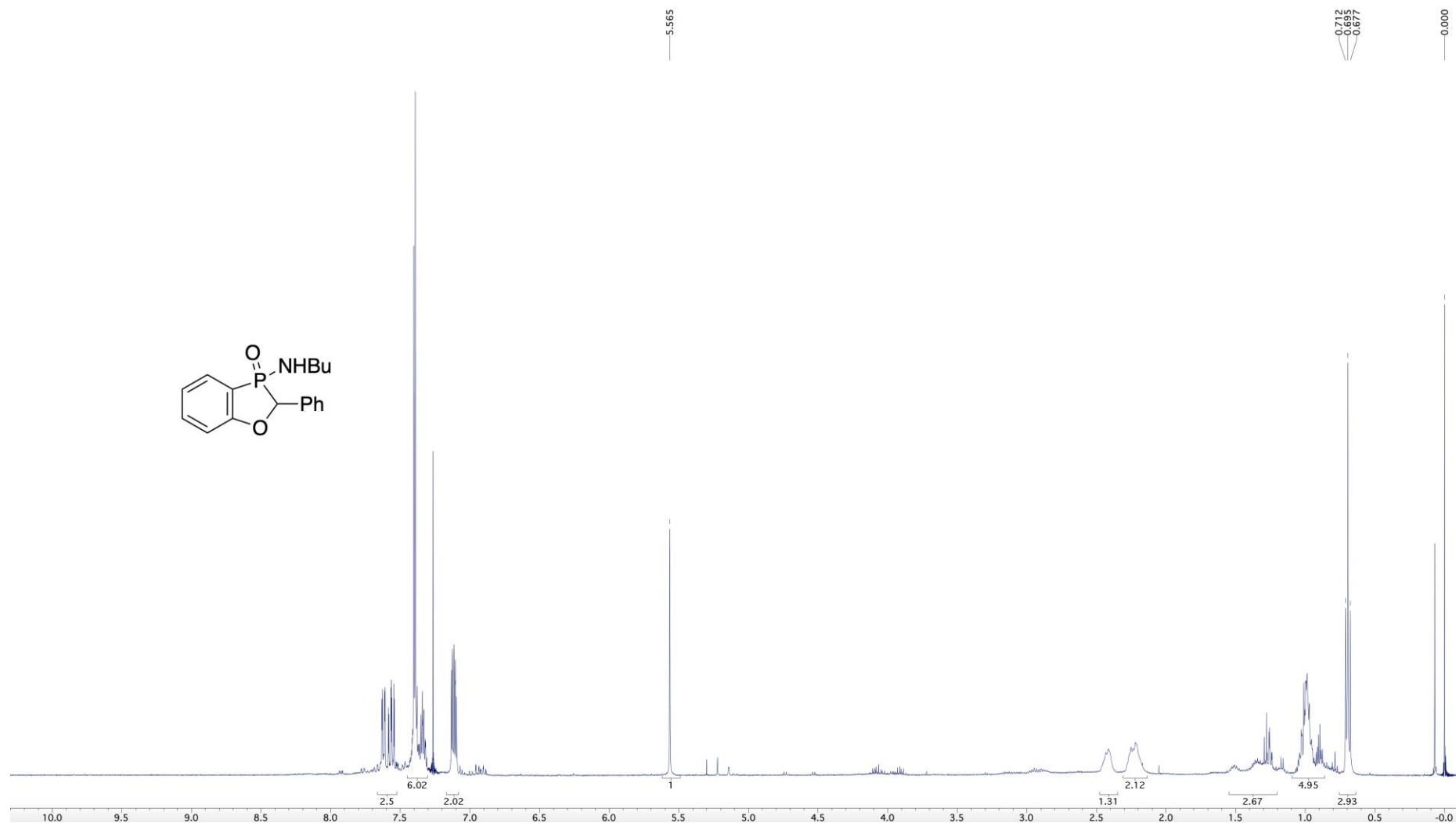


Figure S14. 202 MHz ^{31}P NMR spectrum of **17**

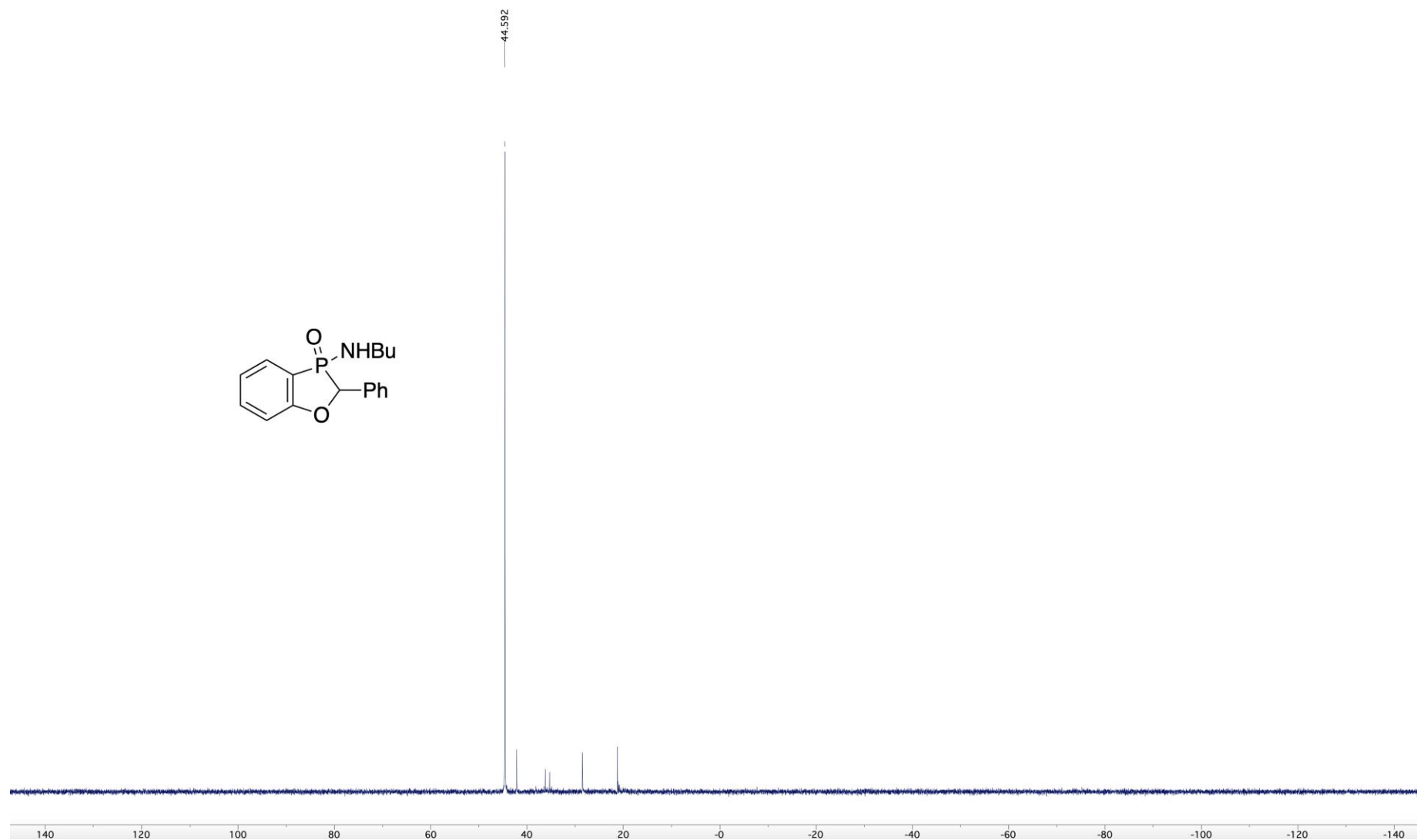


Figure S15. 100 MHz DEPTQ ^{13}C NMR spectrum of **17**

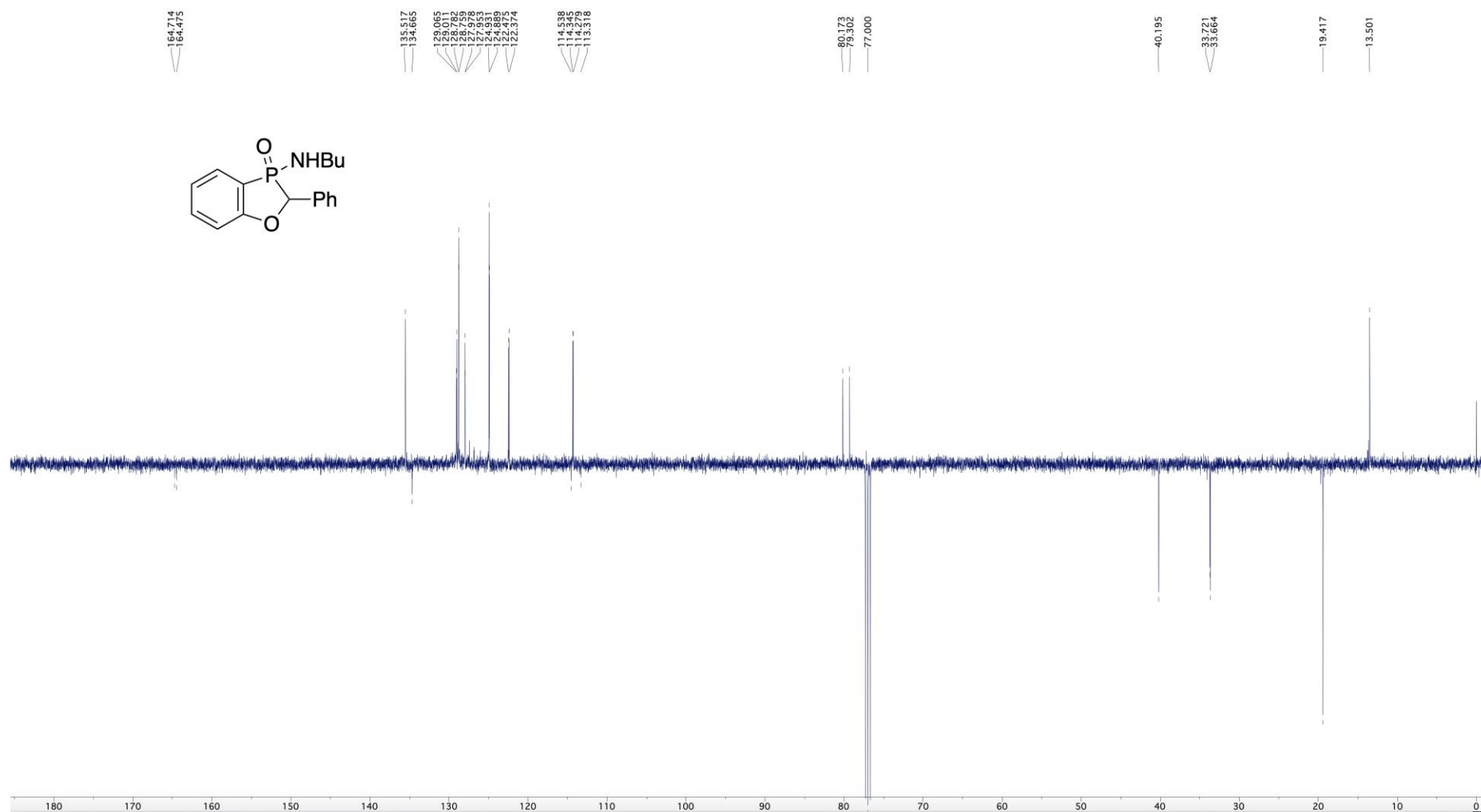


Figure S16. 300 MHz ^1H NMR spectrum of **18a**

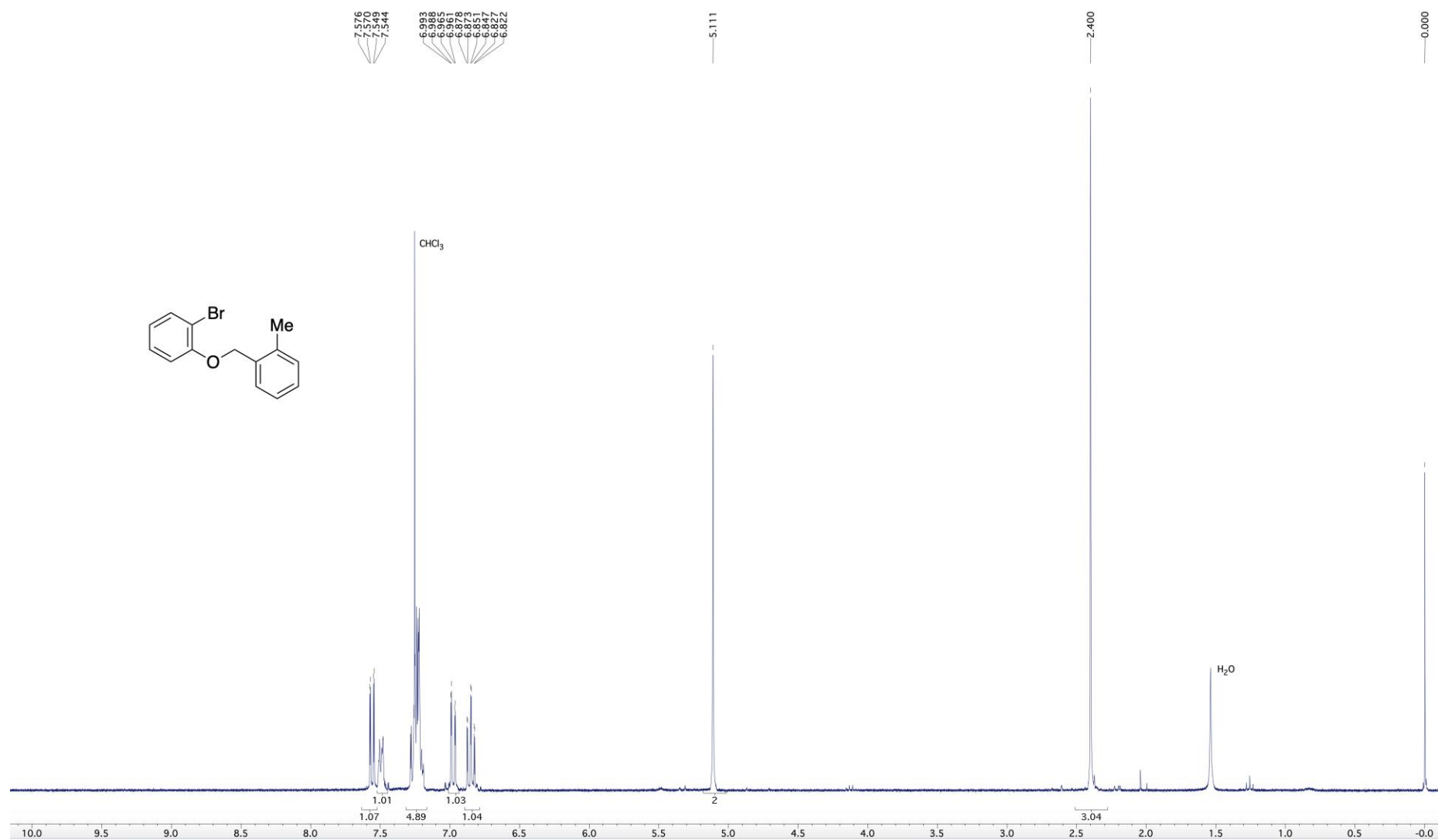


Figure S17. 75 MHz DEPTQ ^{13}C NMR spectrum of **18a**

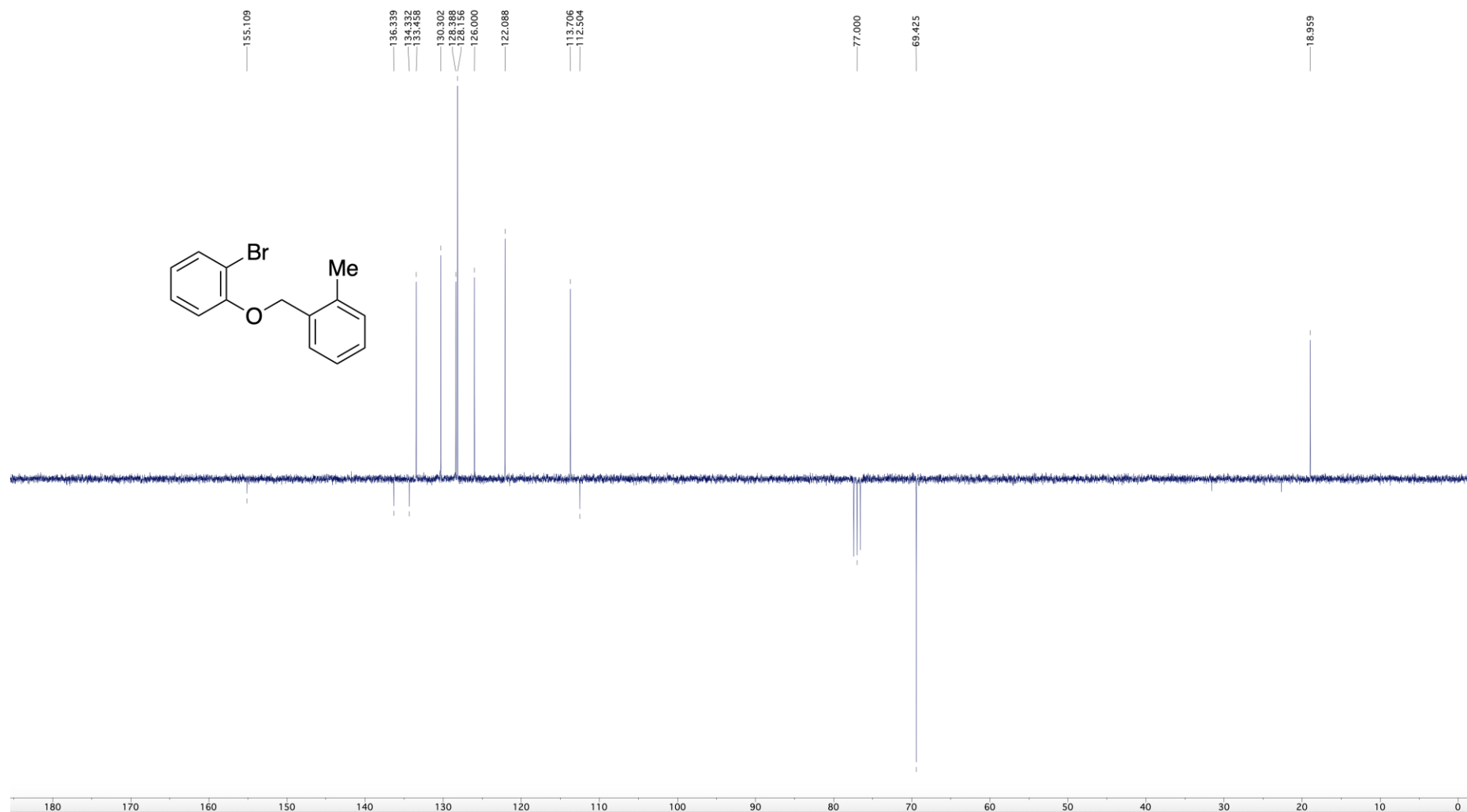


Figure S18. 300 MHz ^1H NMR spectrum of **18b**

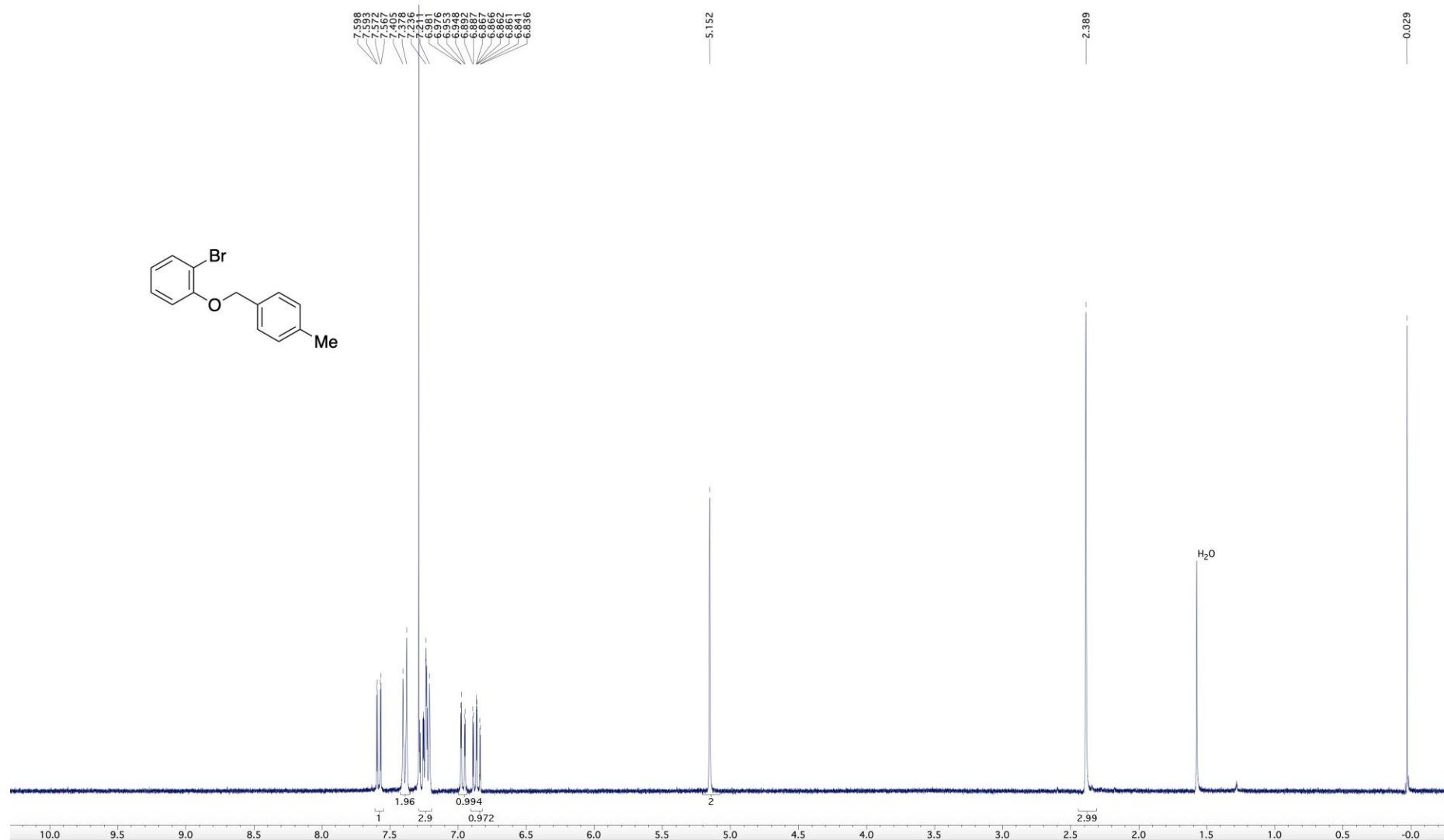


Figure S19. 125 MHz DEPTQ ^{13}C NMR spectrum of **18b**

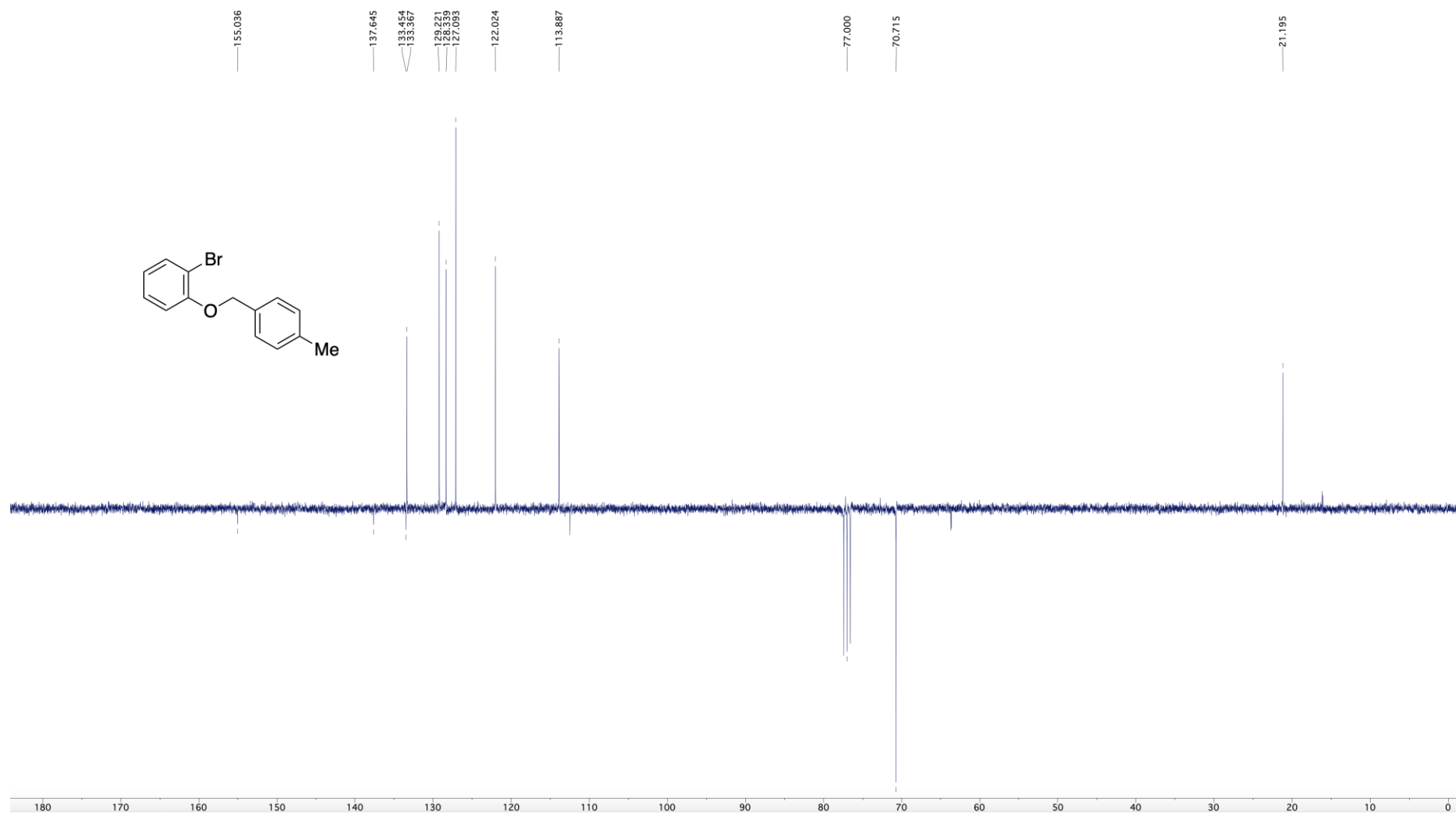


Figure S20. 300 MHz ^1H NMR spectrum of **18c**

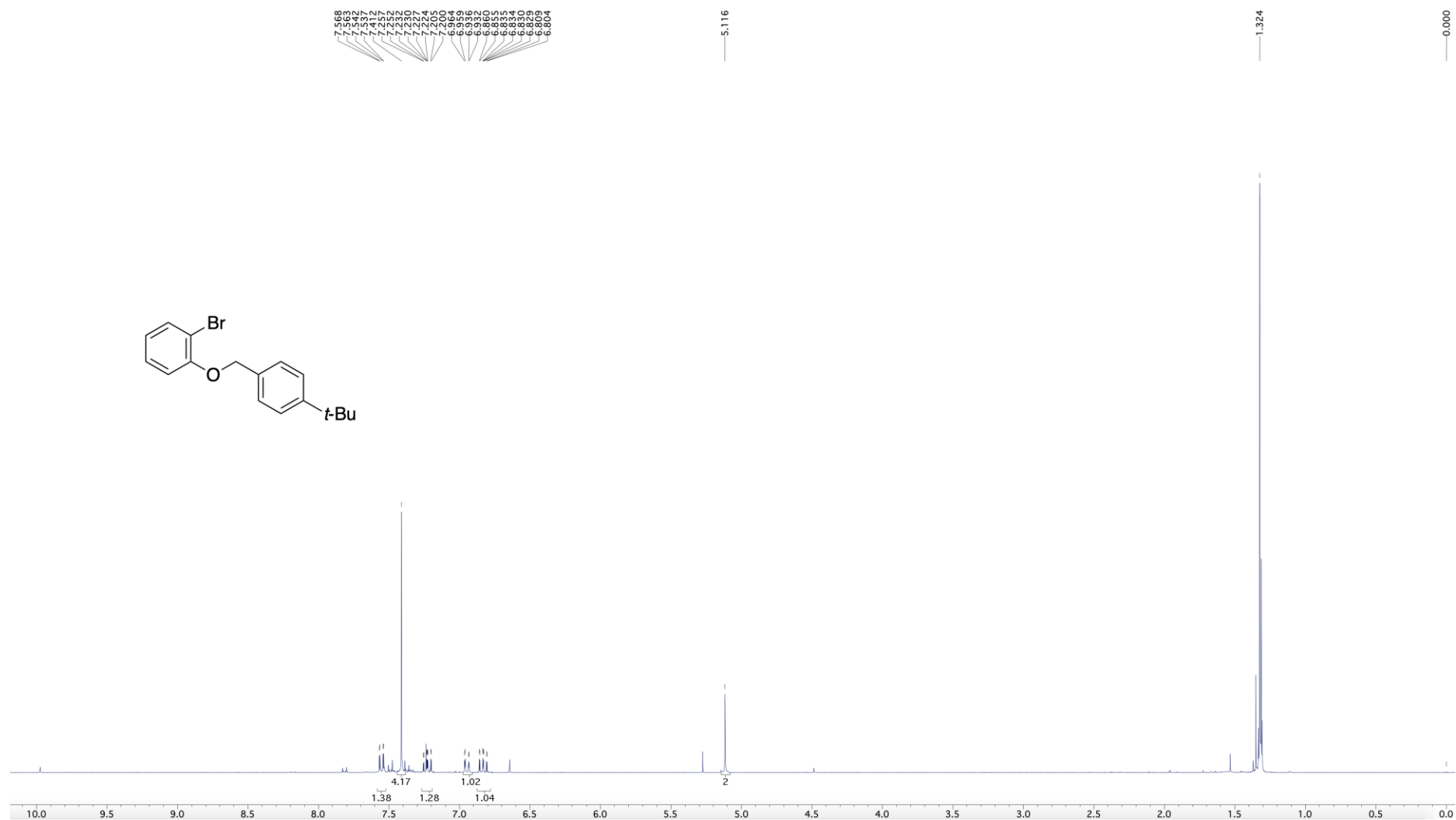


Figure S21. 125 MHz DEPTQ ^{13}C NMR spectrum of **18c**

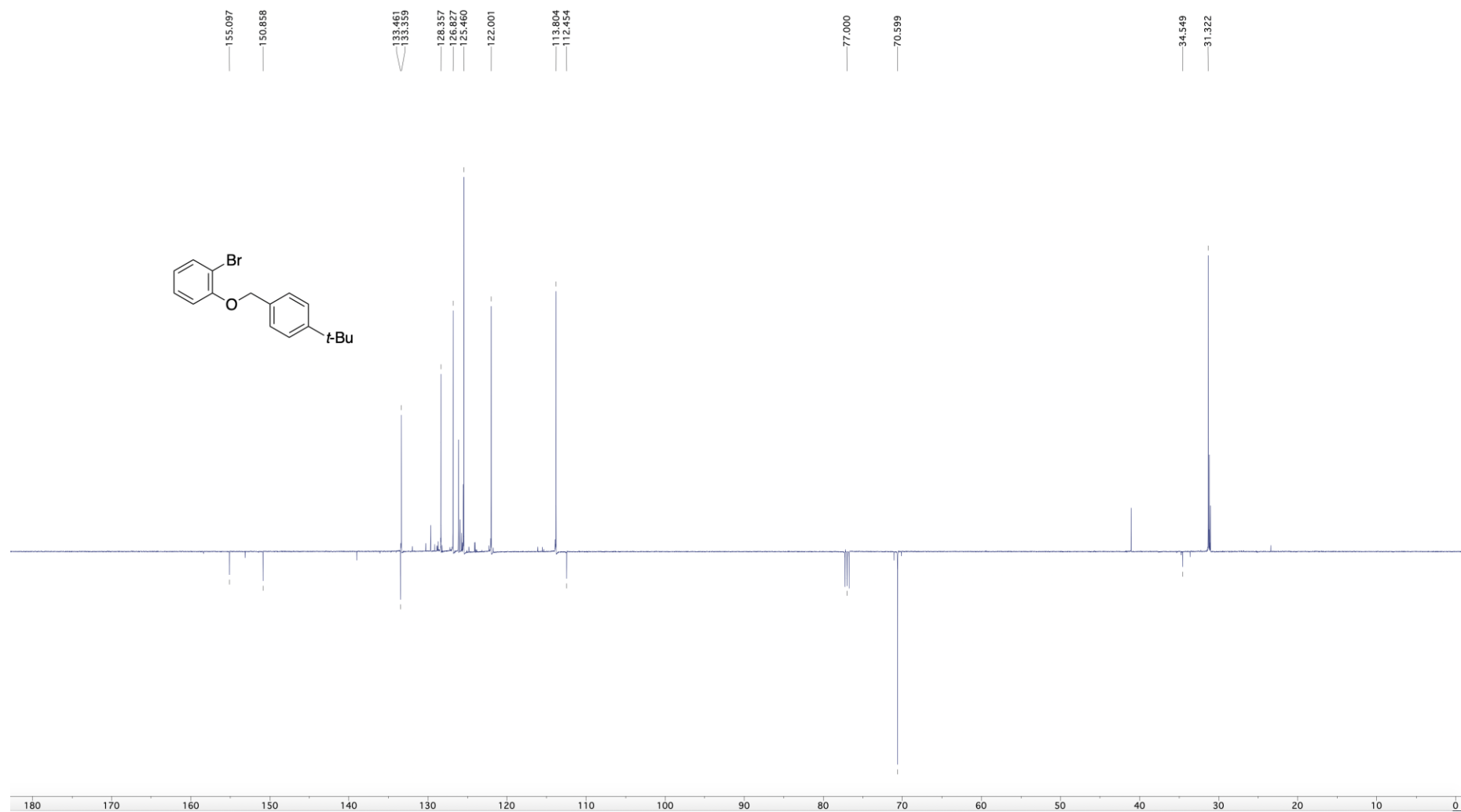


Figure S22. 300 MHz ^1H NMR spectrum of **18d**

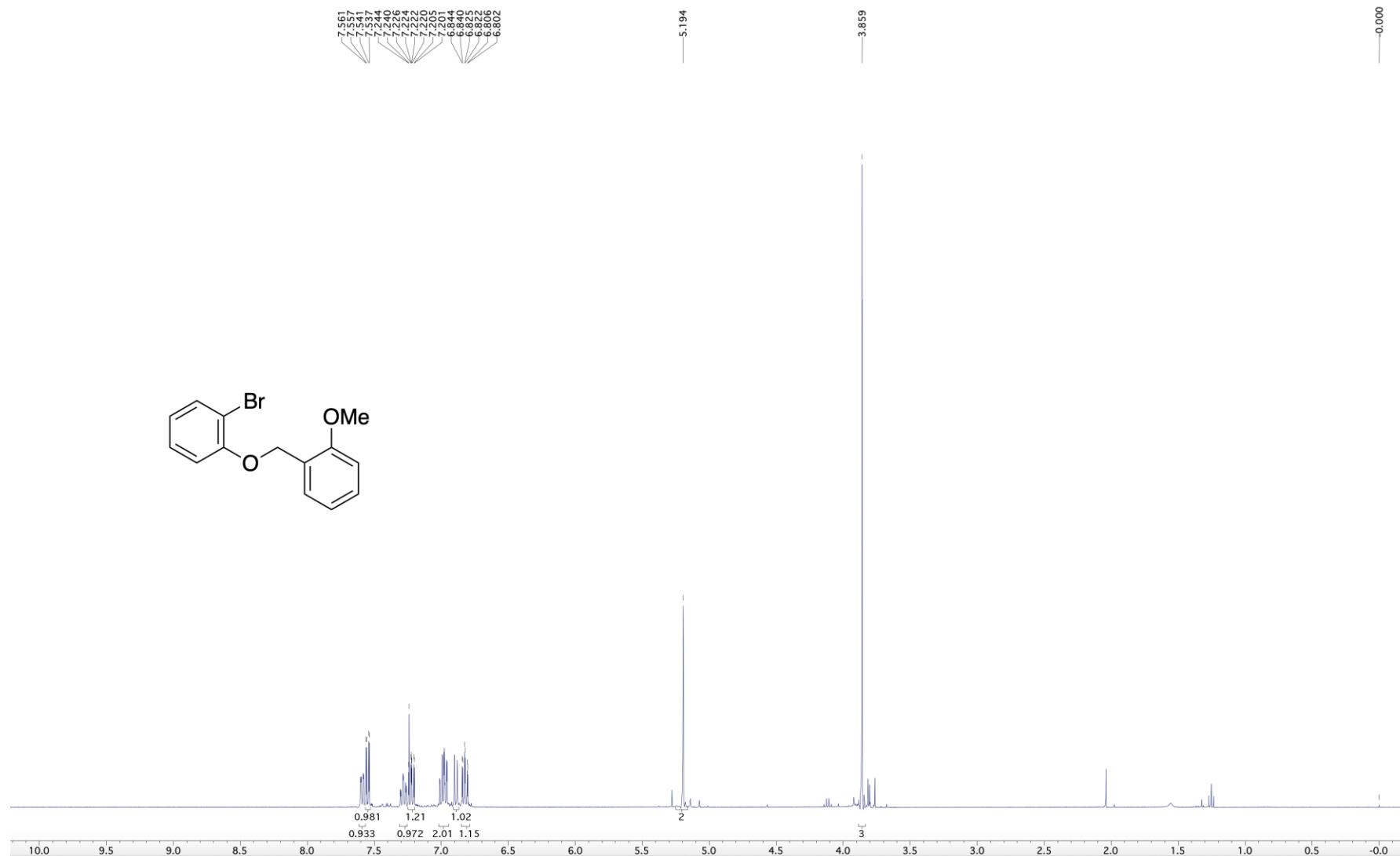


Figure S23. 75 MHz DEPTQ ^{13}C NMR spectrum of **18d**

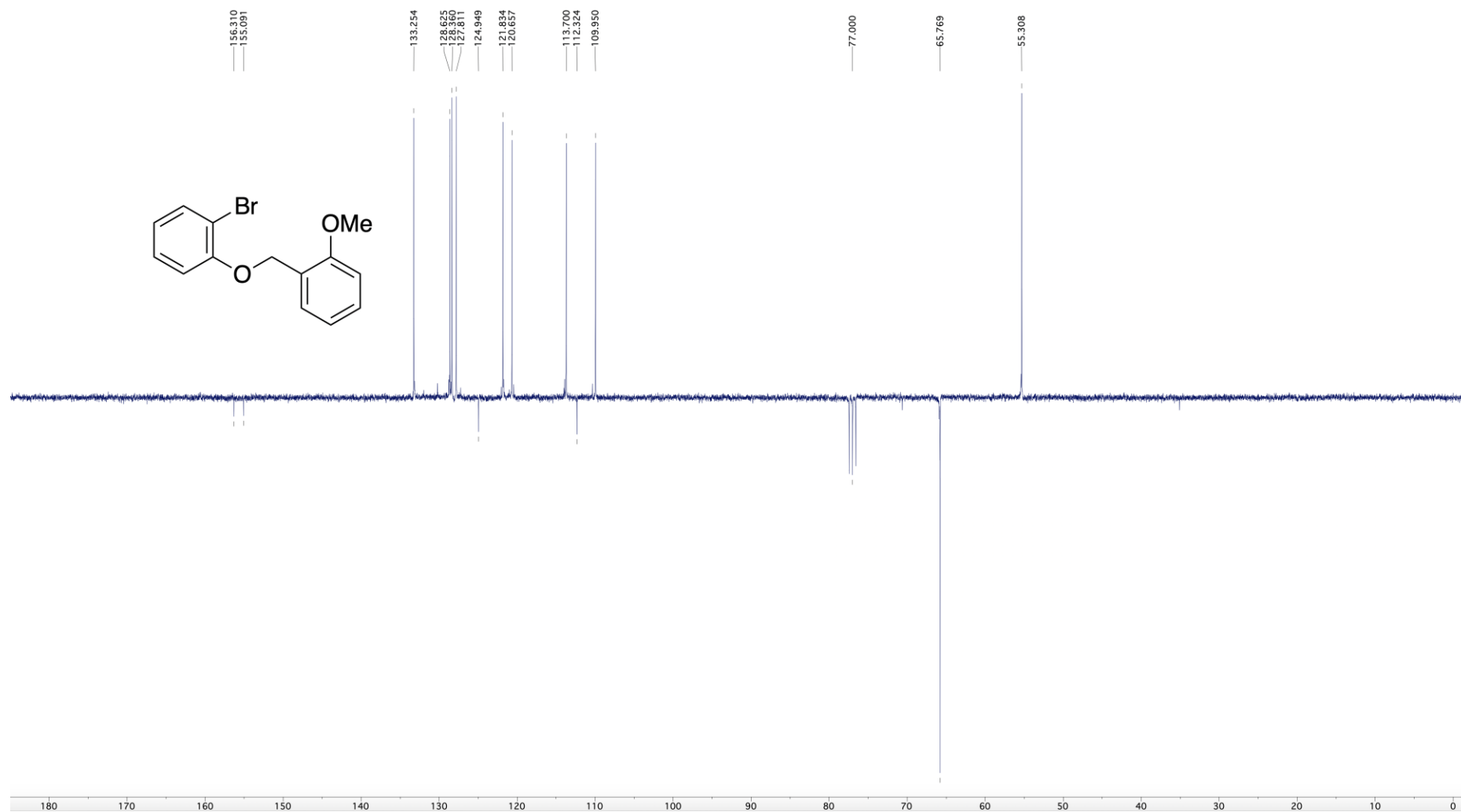


Figure S24. 300 MHz ^1H NMR spectrum of **18e**

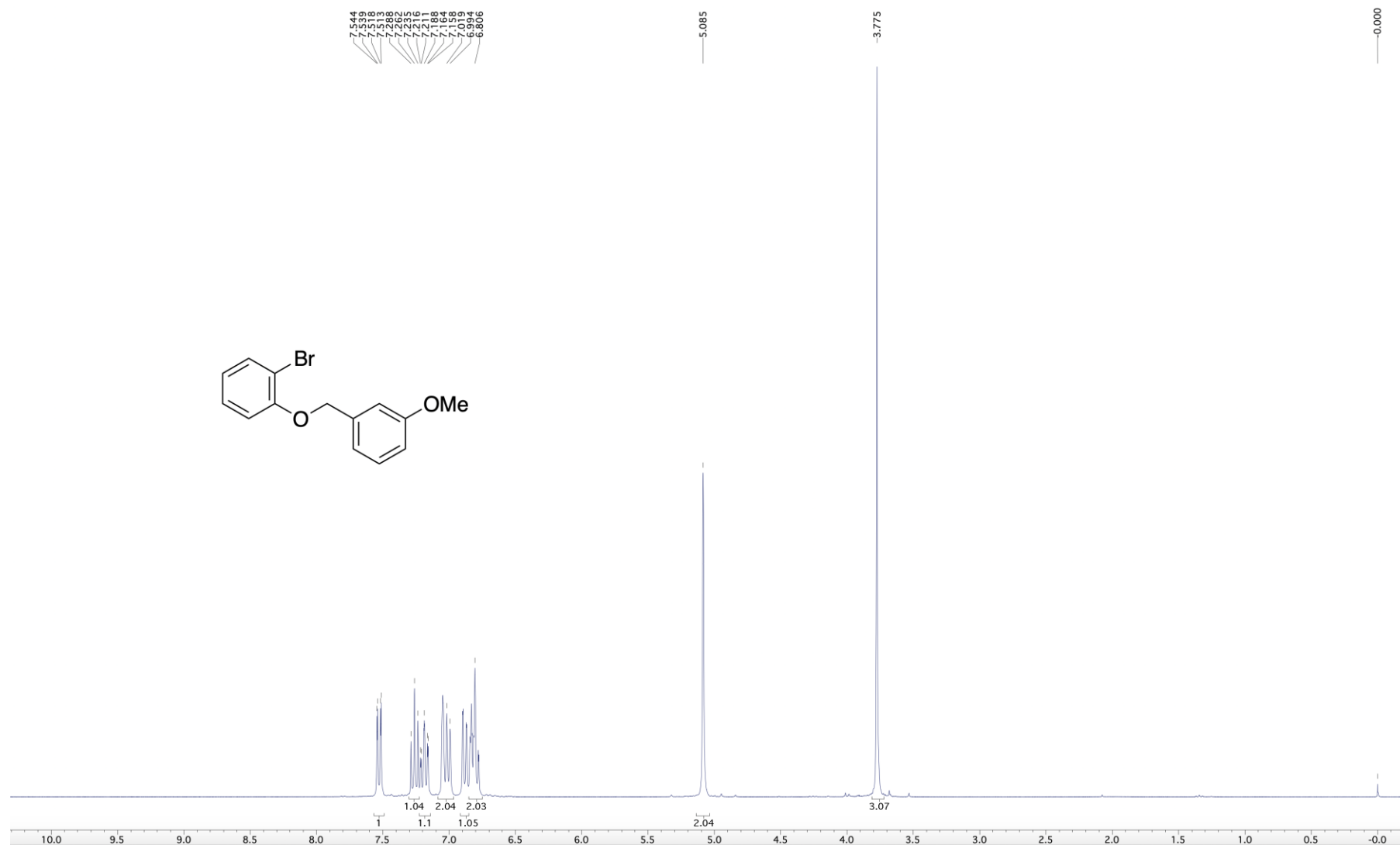


Figure S25. 75 MHz DEPTQ ^{13}C NMR spectrum of **18e**

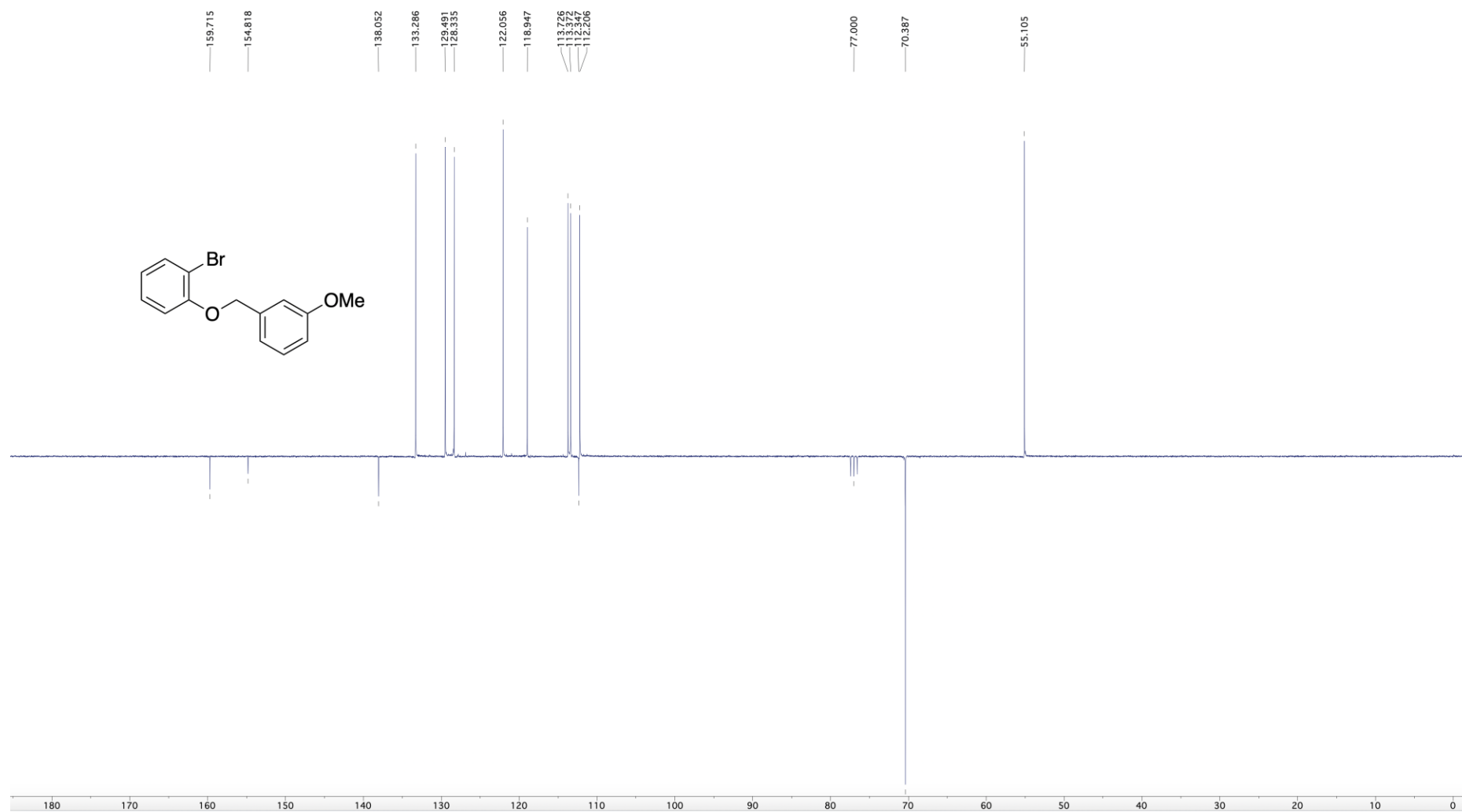


Figure S26. 300 MHz ^1H NMR spectrum of **18f**

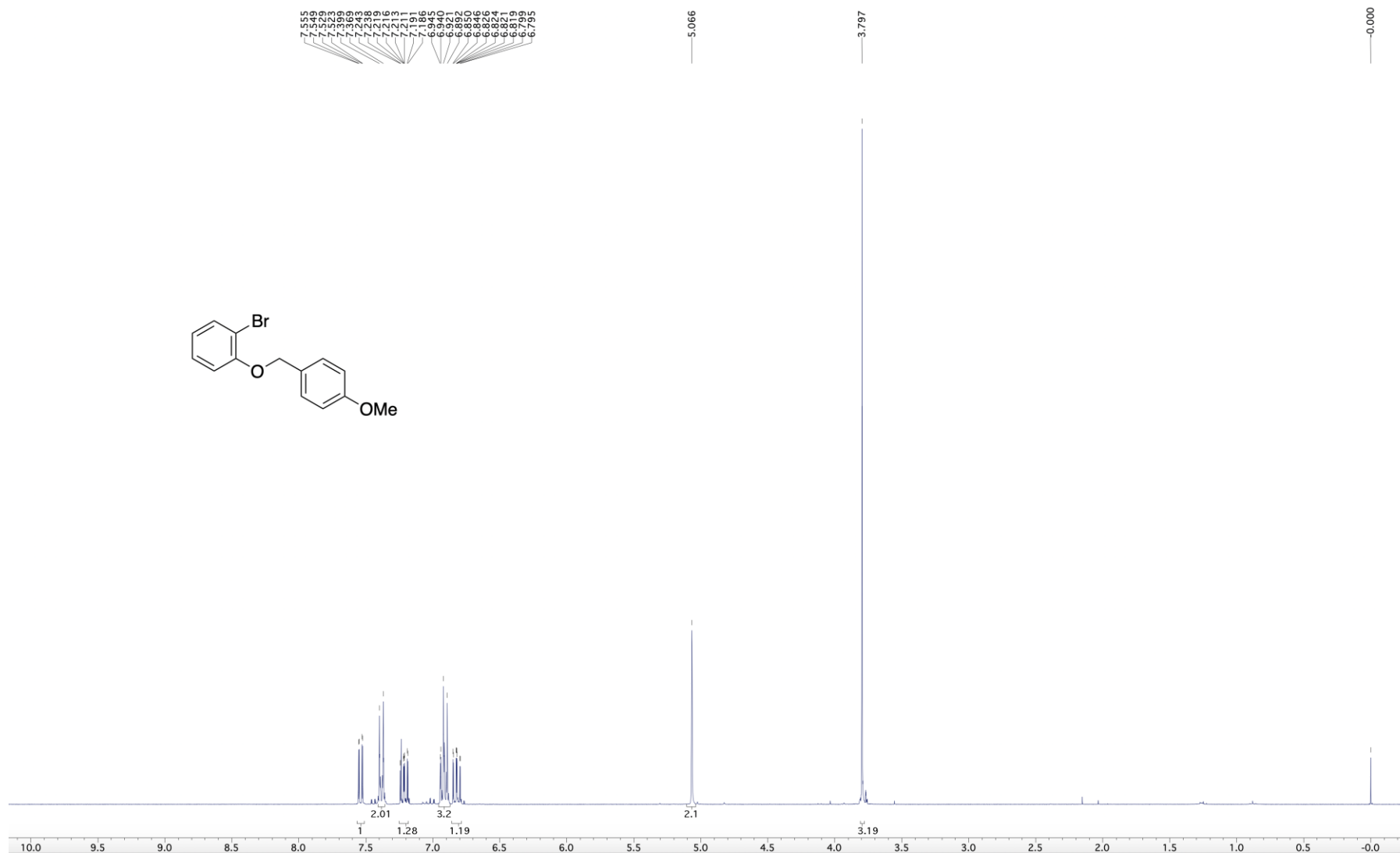


Figure S27. 750 MHz DEPTQ ^{13}C NMR spectrum of **18f**

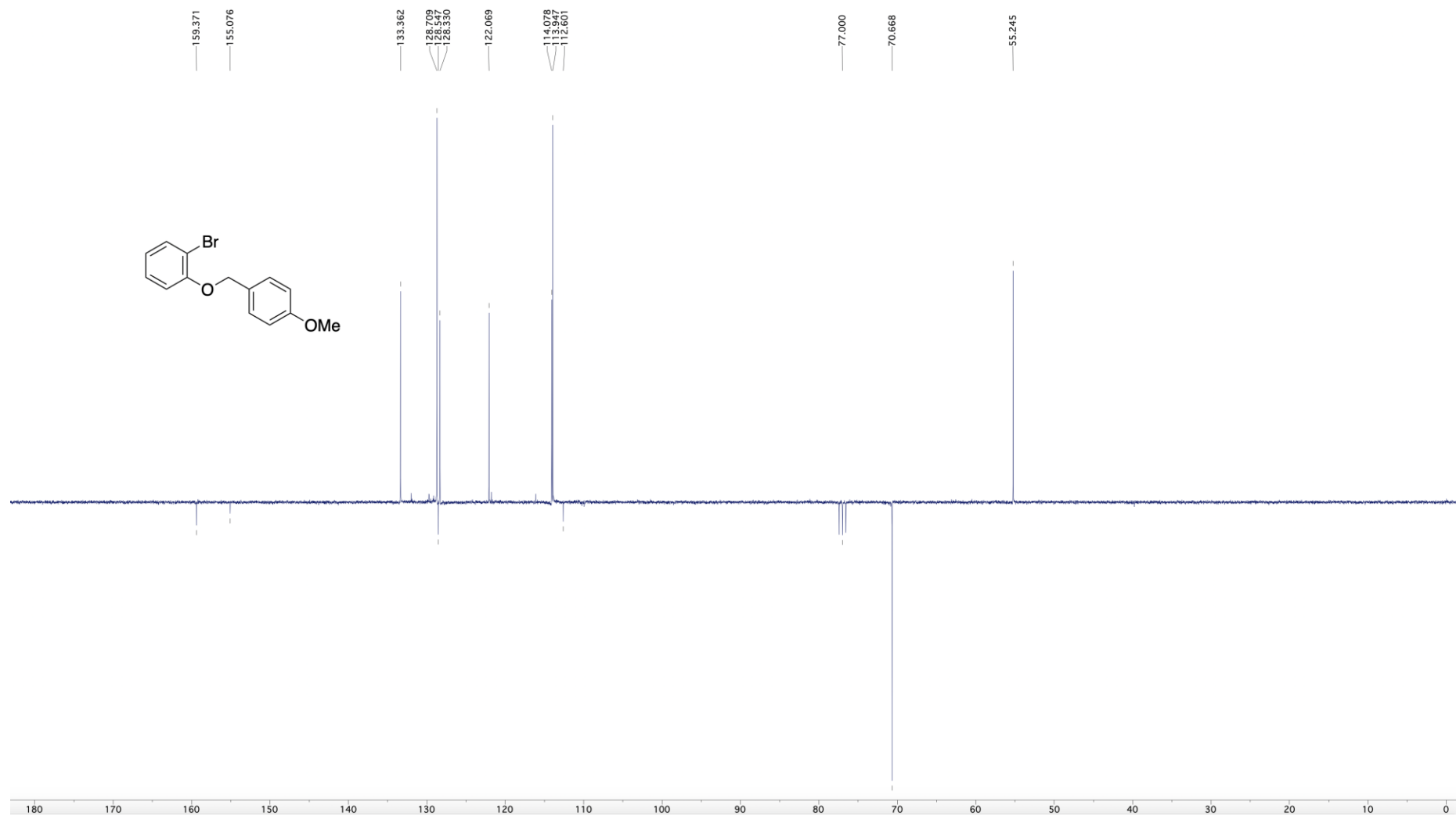


Figure S28. 300 MHz ^1H NMR spectrum of **18g**

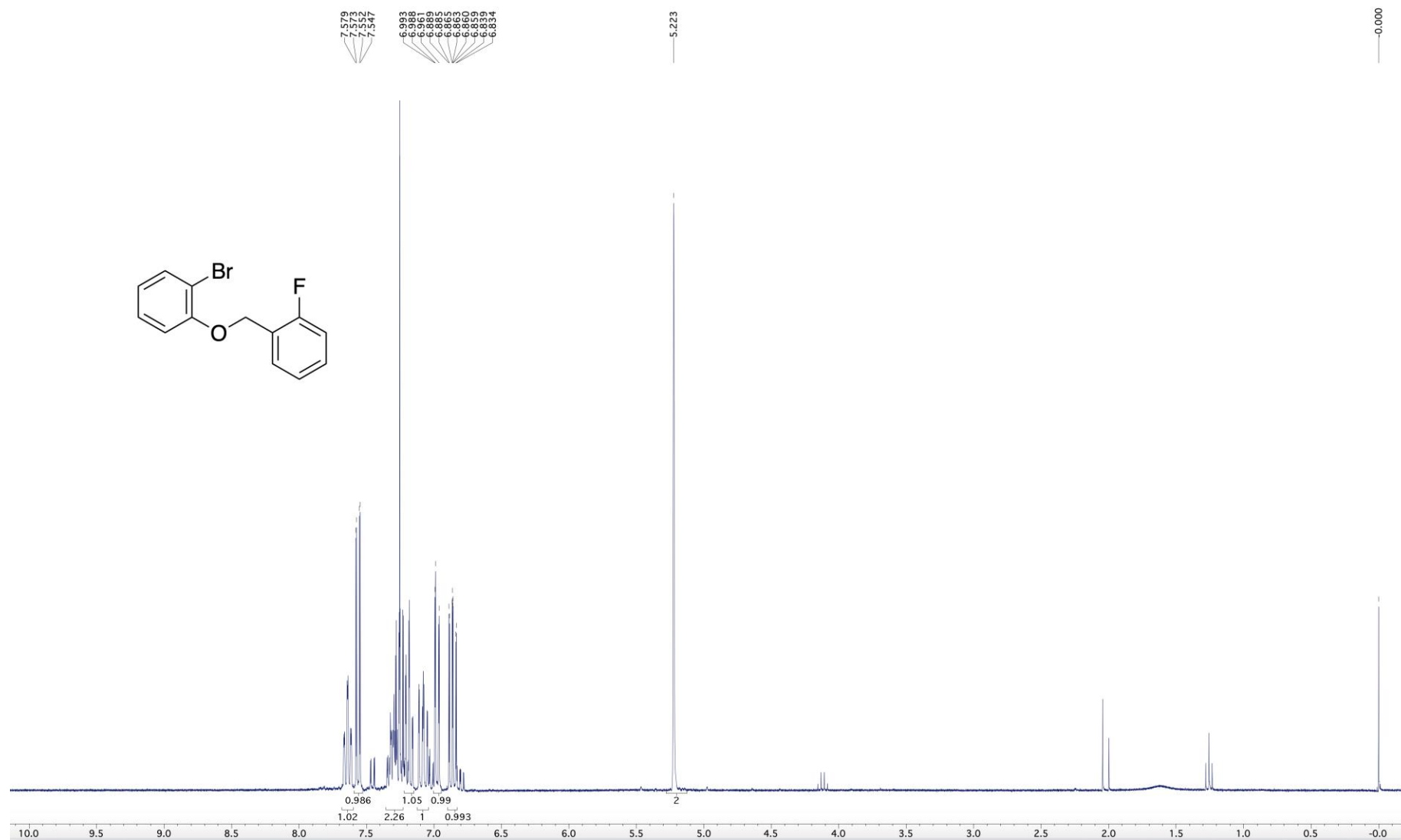


Figure S29. 376 MHz ^{19}F NMR spectrum of **18g**

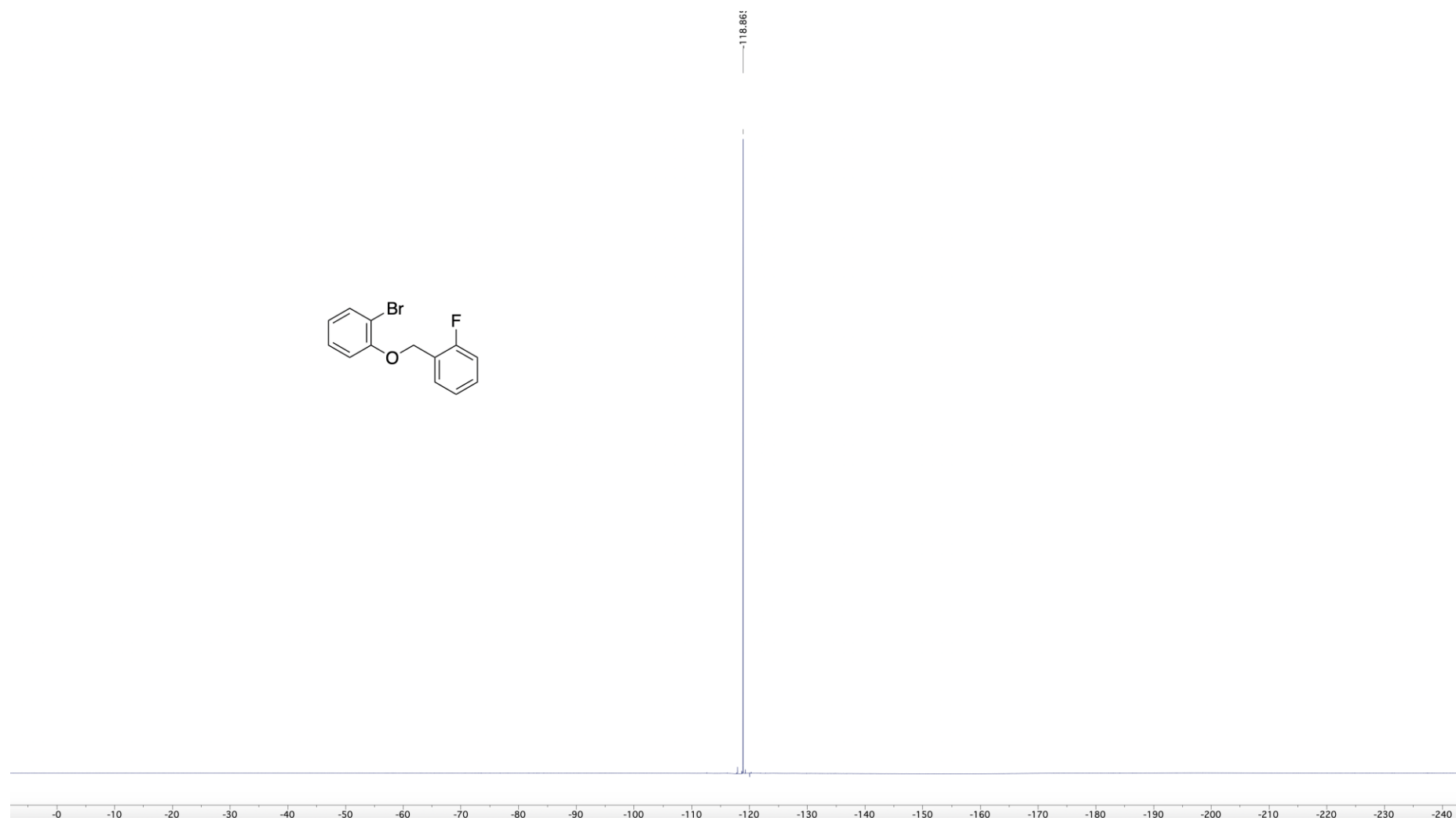


Figure S30. 100 MHz DEPTQ ^{13}C NMR spectrum of **18g**

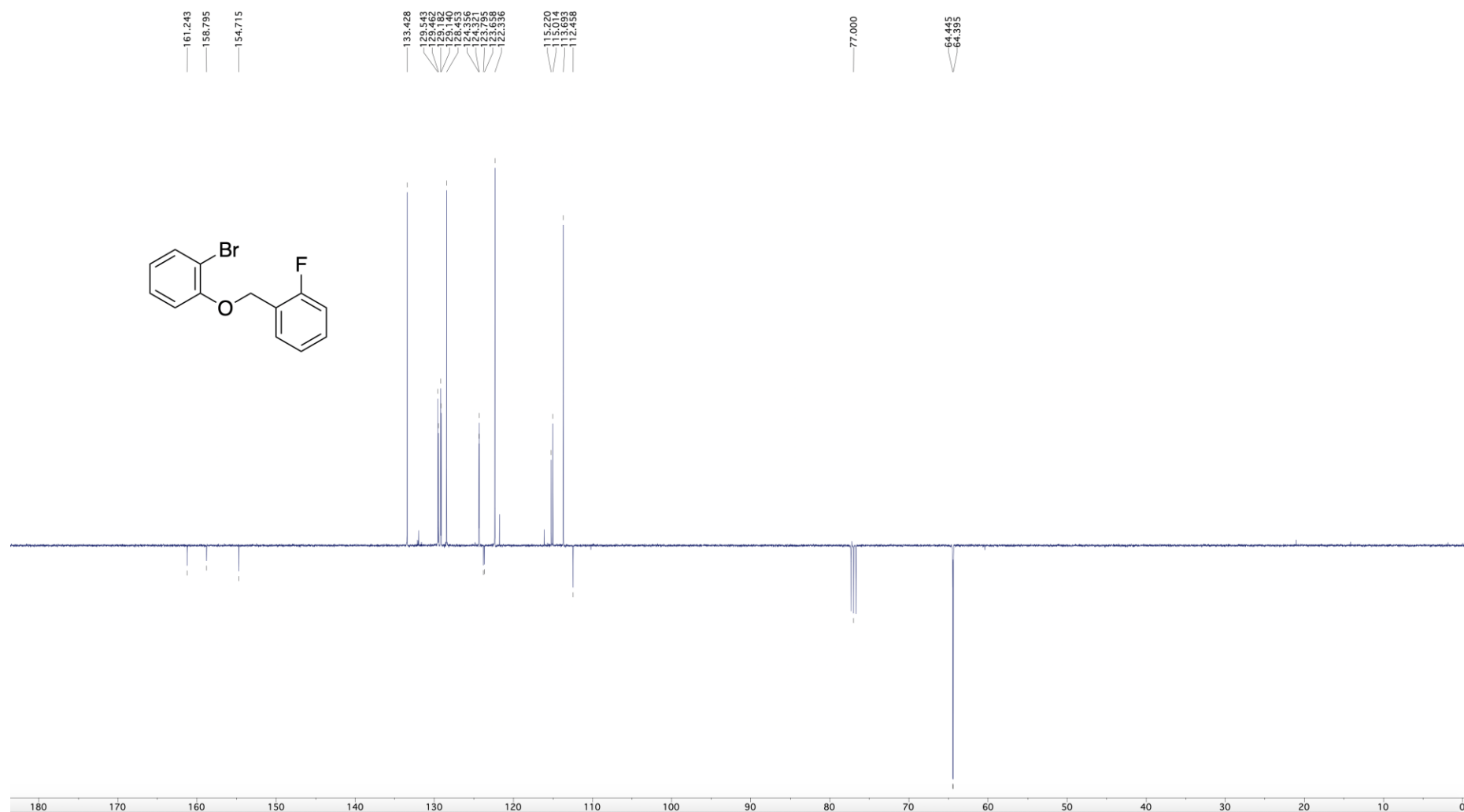


Figure S31. 300 MHz ^1H NMR spectrum of **18h**

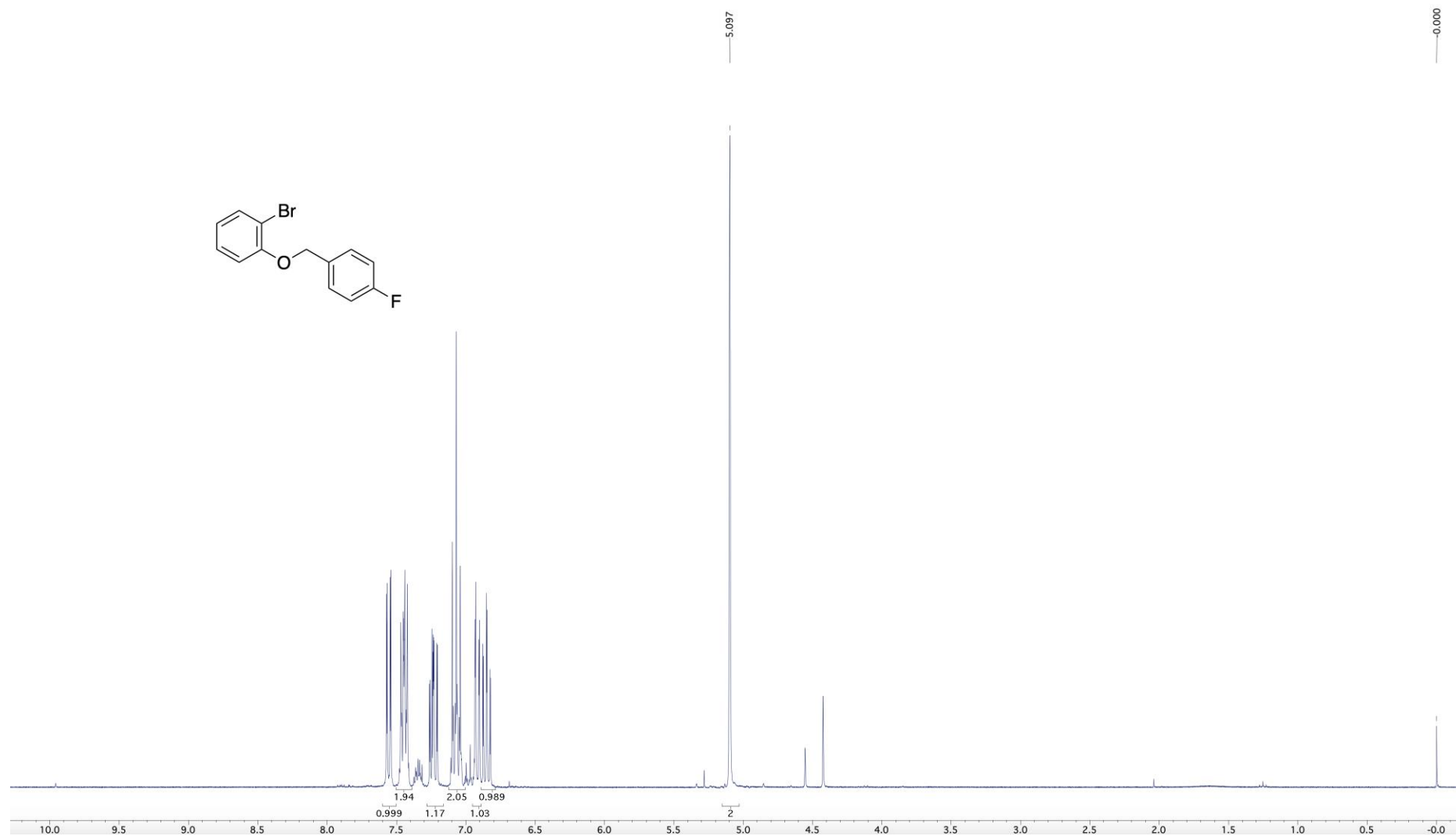


Figure S32. 376 MHz ^{19}F NMR spectrum of **18h**

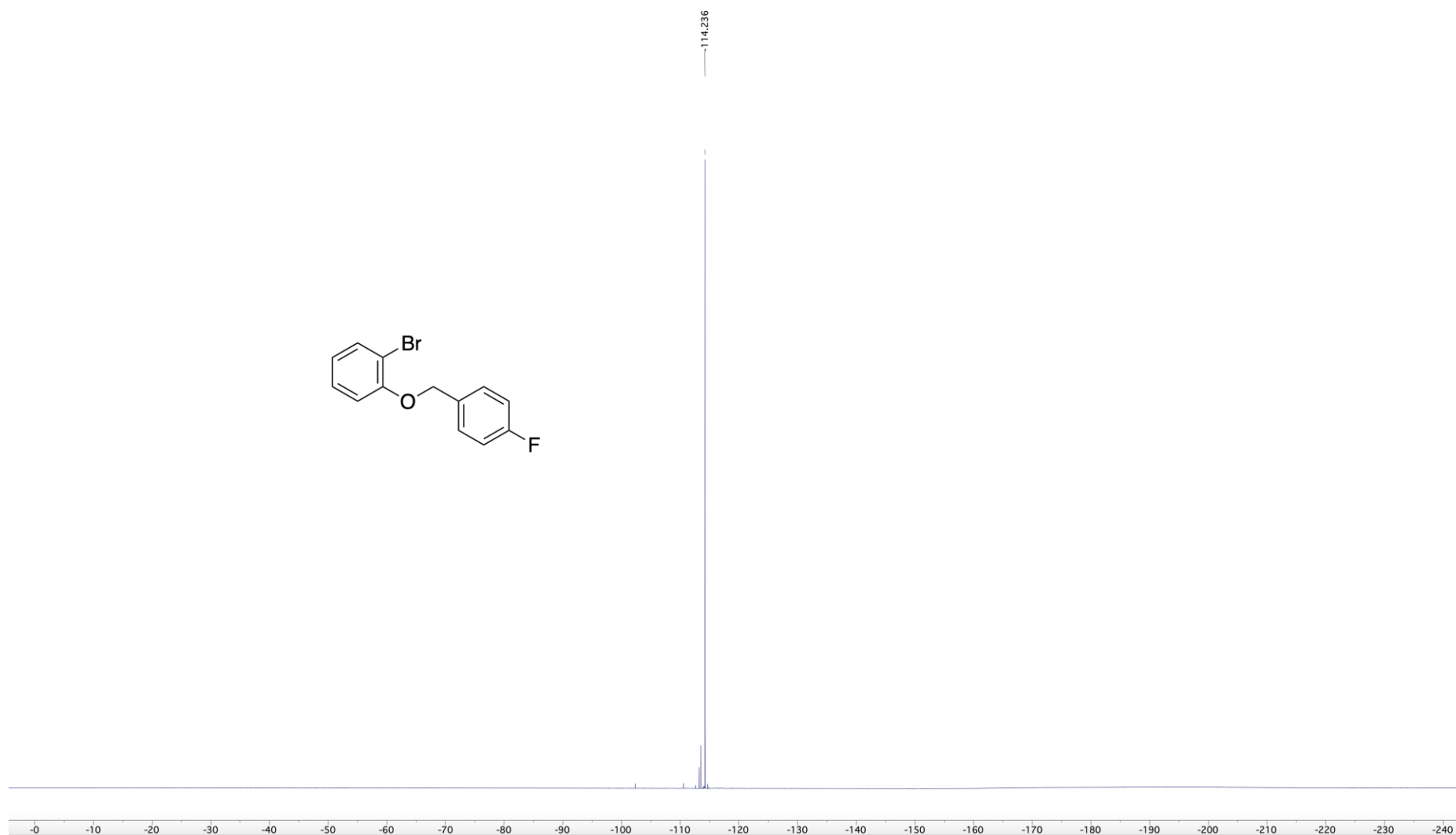


Figure S33. 75 MHz DEPTQ ^{13}C NMR spectrum of **18h**

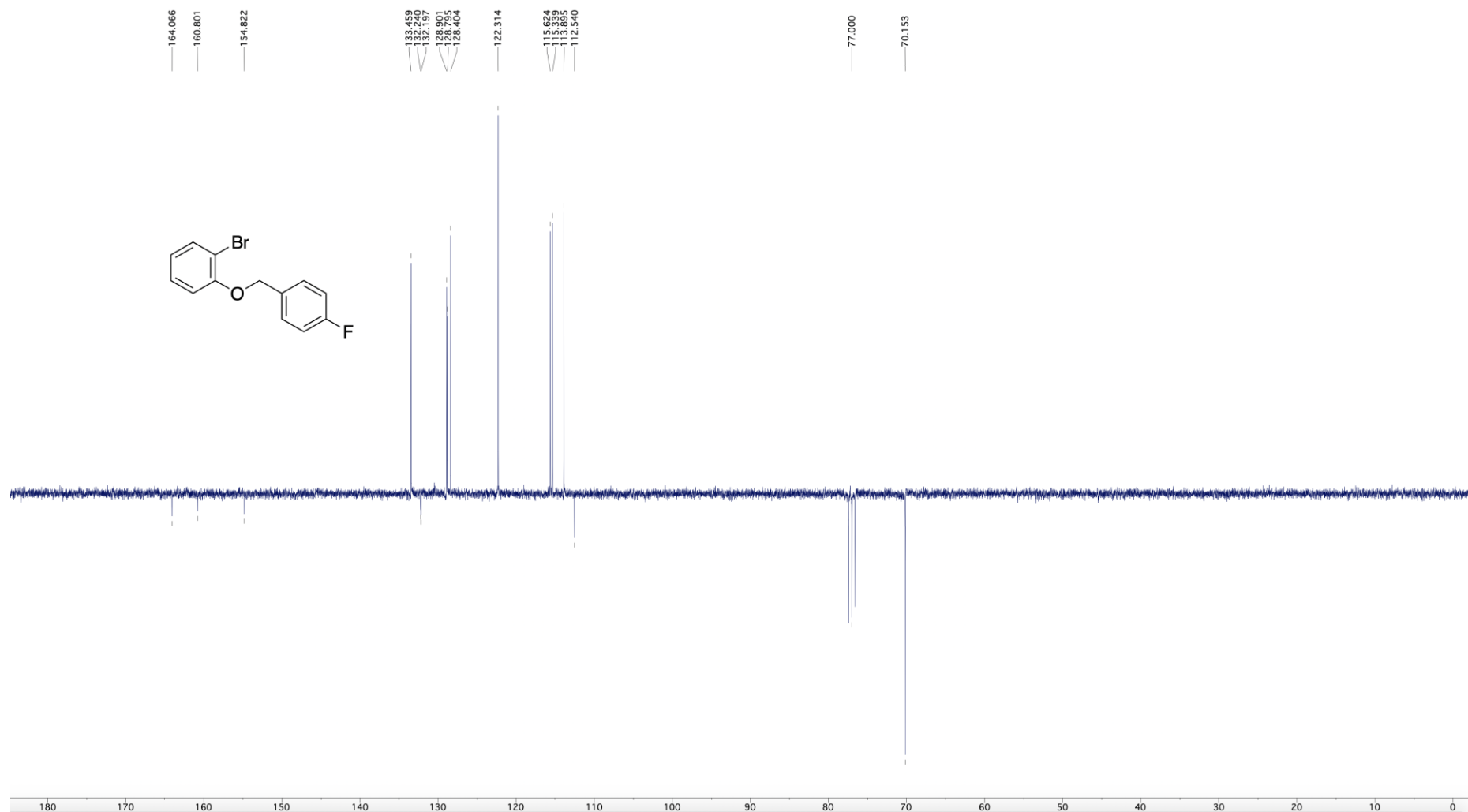


Figure S34. 300 MHz ^1H NMR spectrum of **18l**

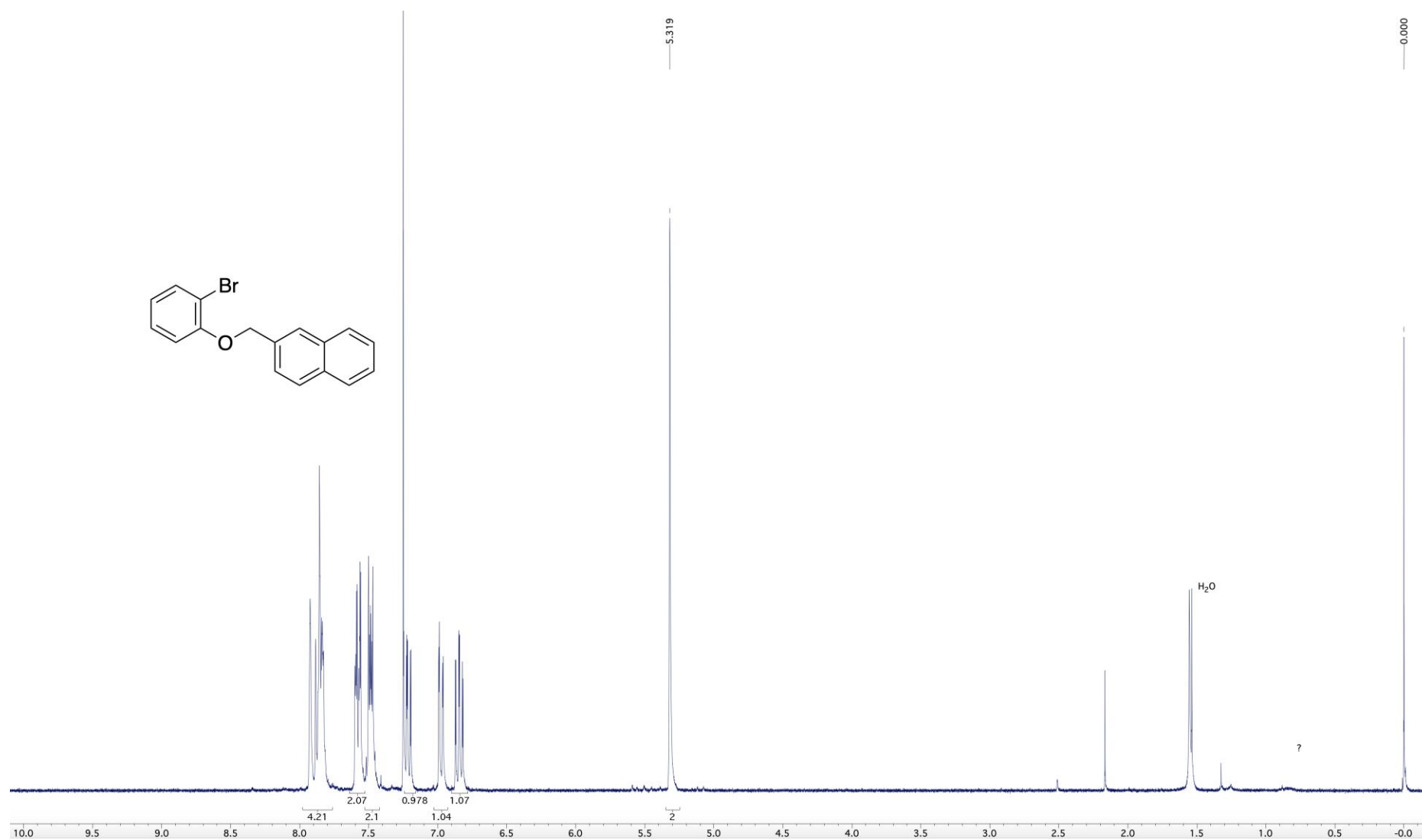


Figure S35. 75 MHz DEPTQ ^{13}C NMR spectrum of **18l**

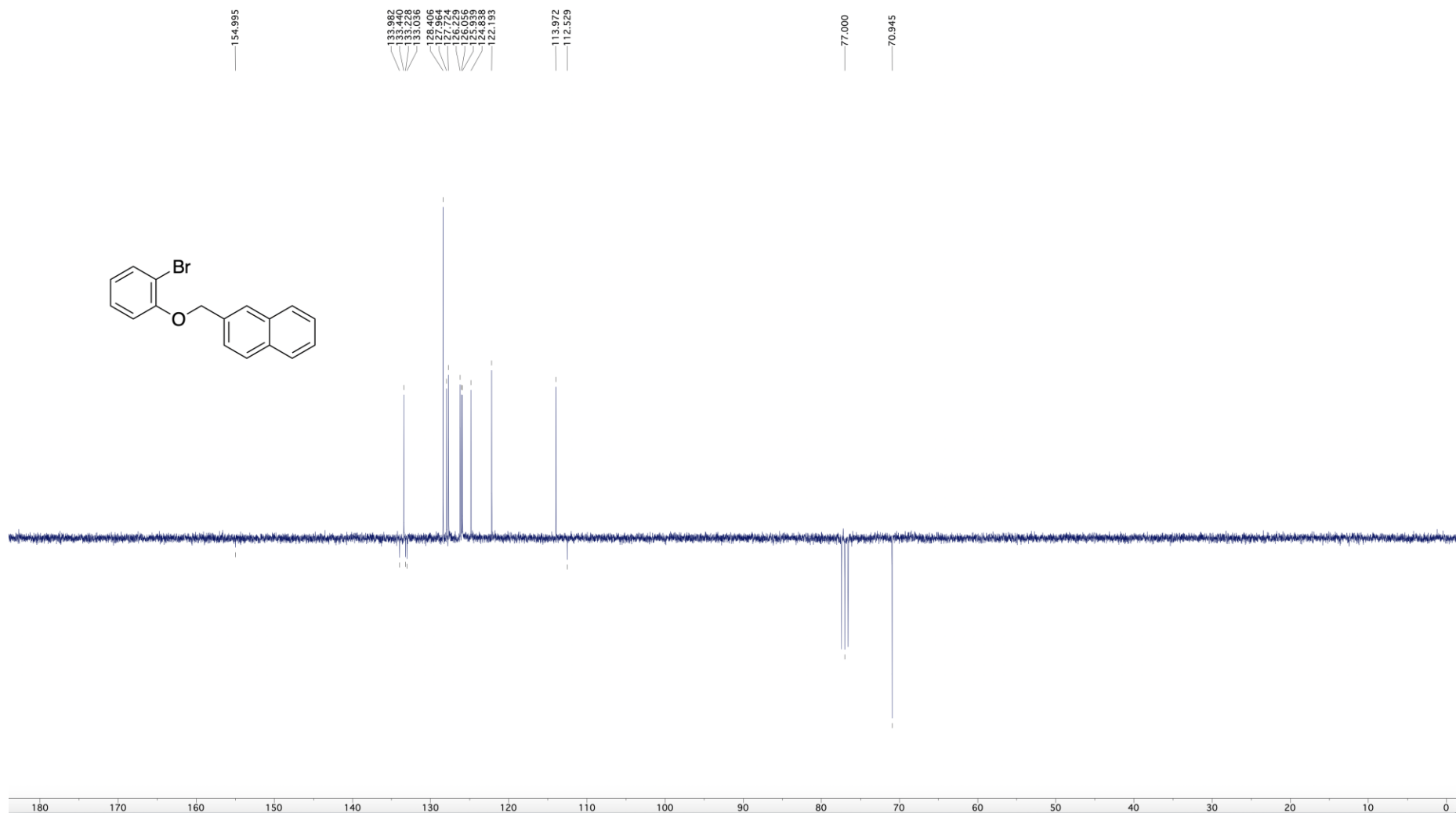


Figure S36. 300 MHz ^1H NMR spectrum of **19b**

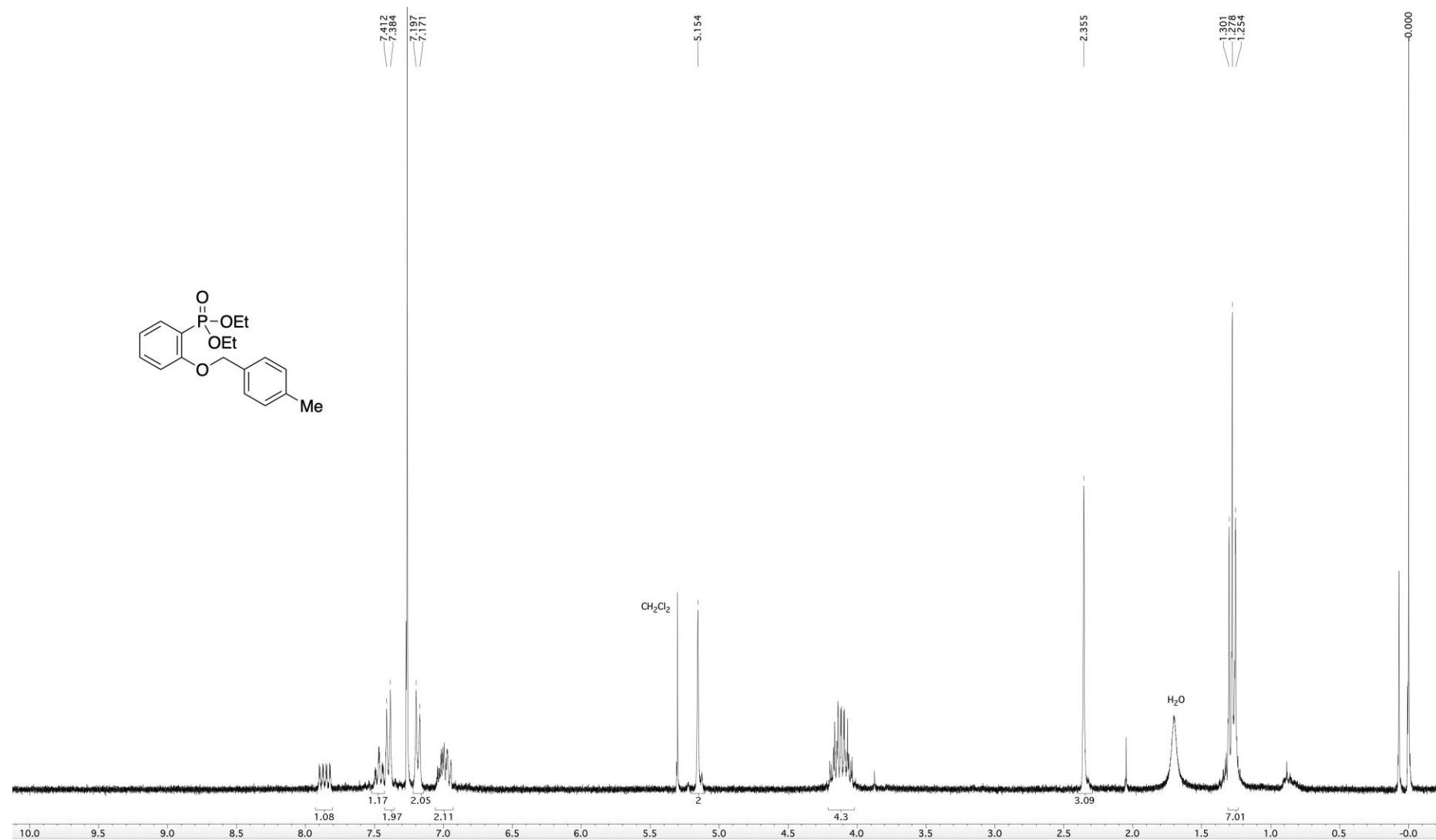


Figure S37. 162 MHz ^{31}P NMR spectrum of **19b**

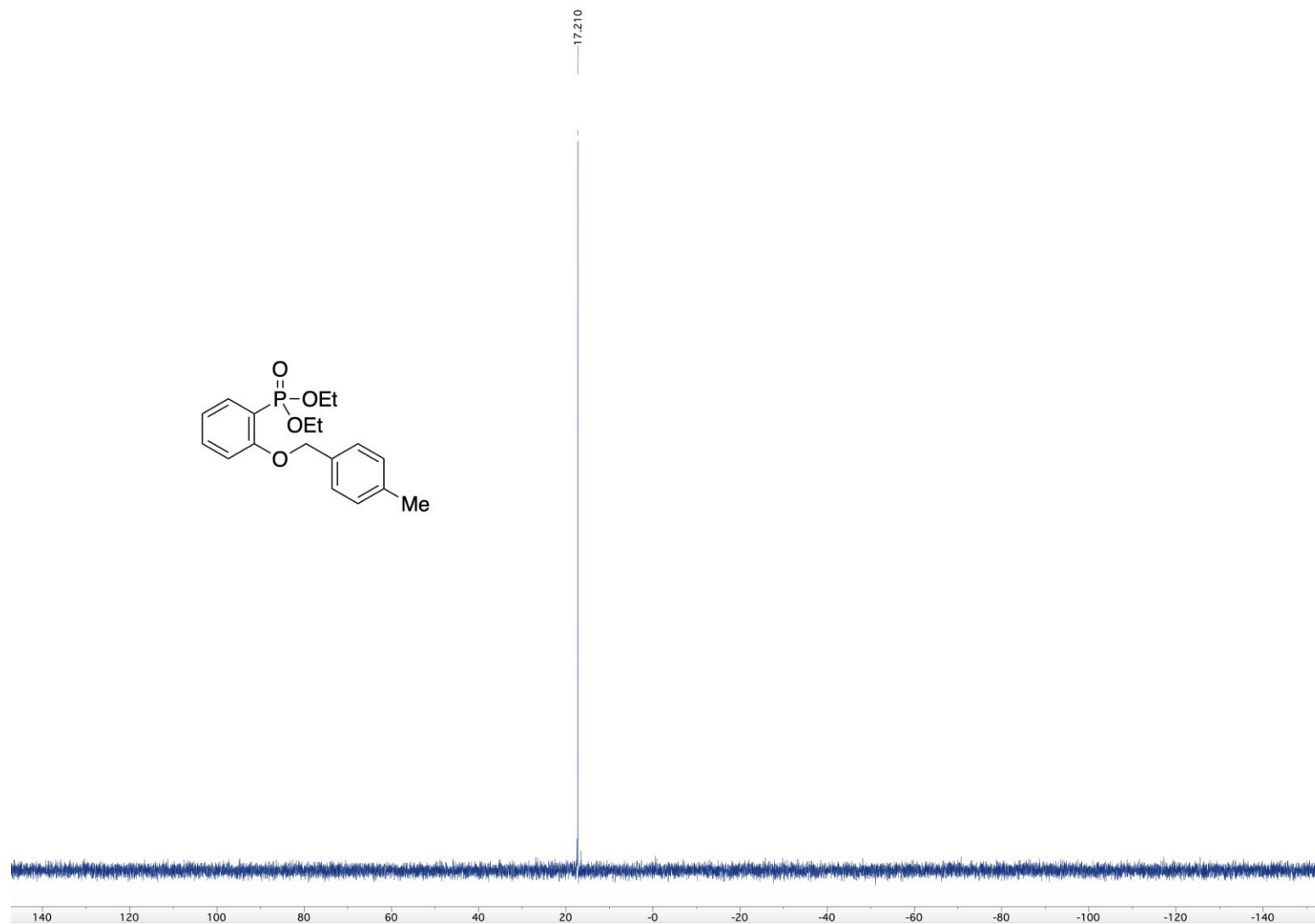


Figure S38. 125 MHz DEPTQ ^{13}C NMR spectrum of **19b**

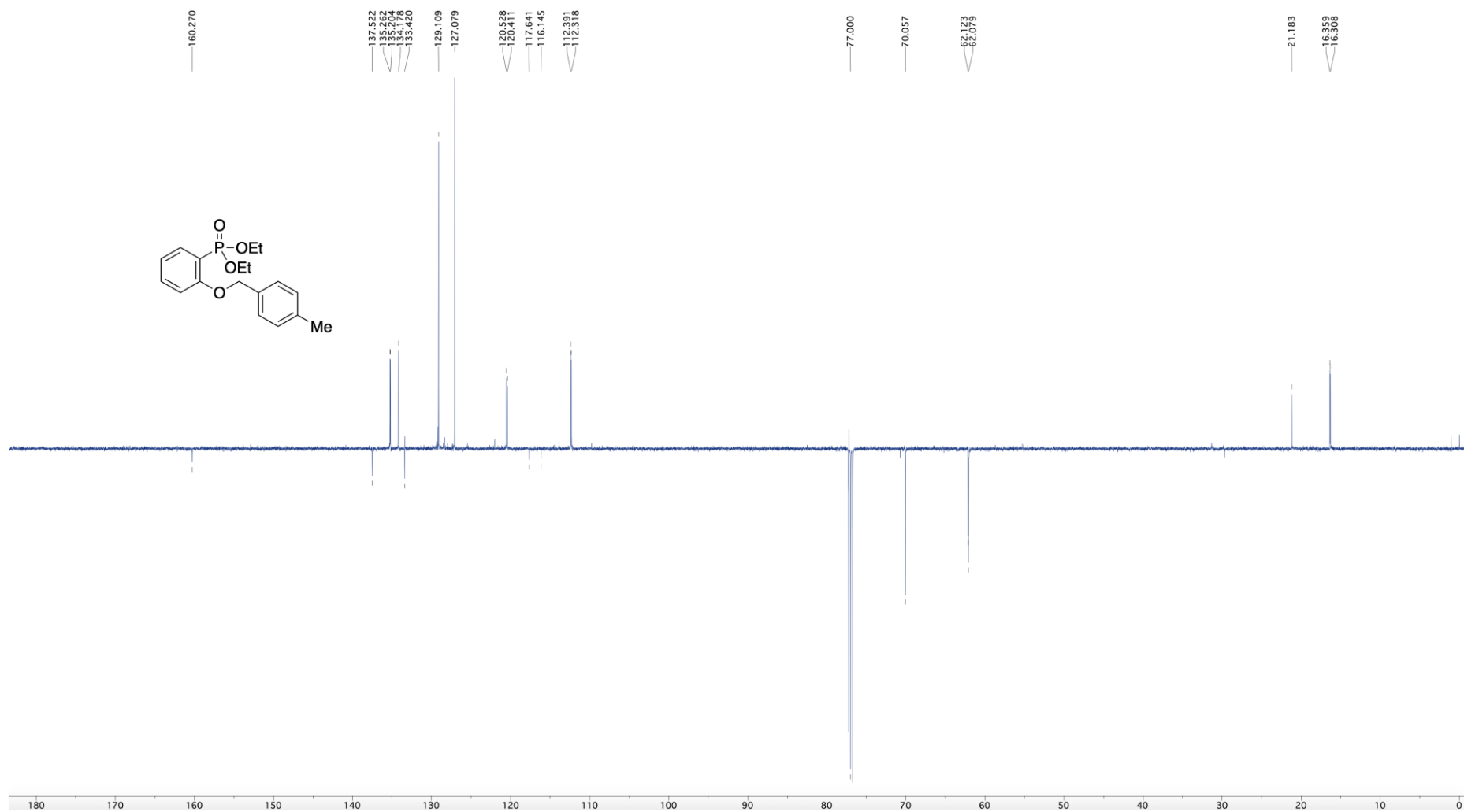


Figure S39. 300 MHz ^1H NMR spectrum of **19d**

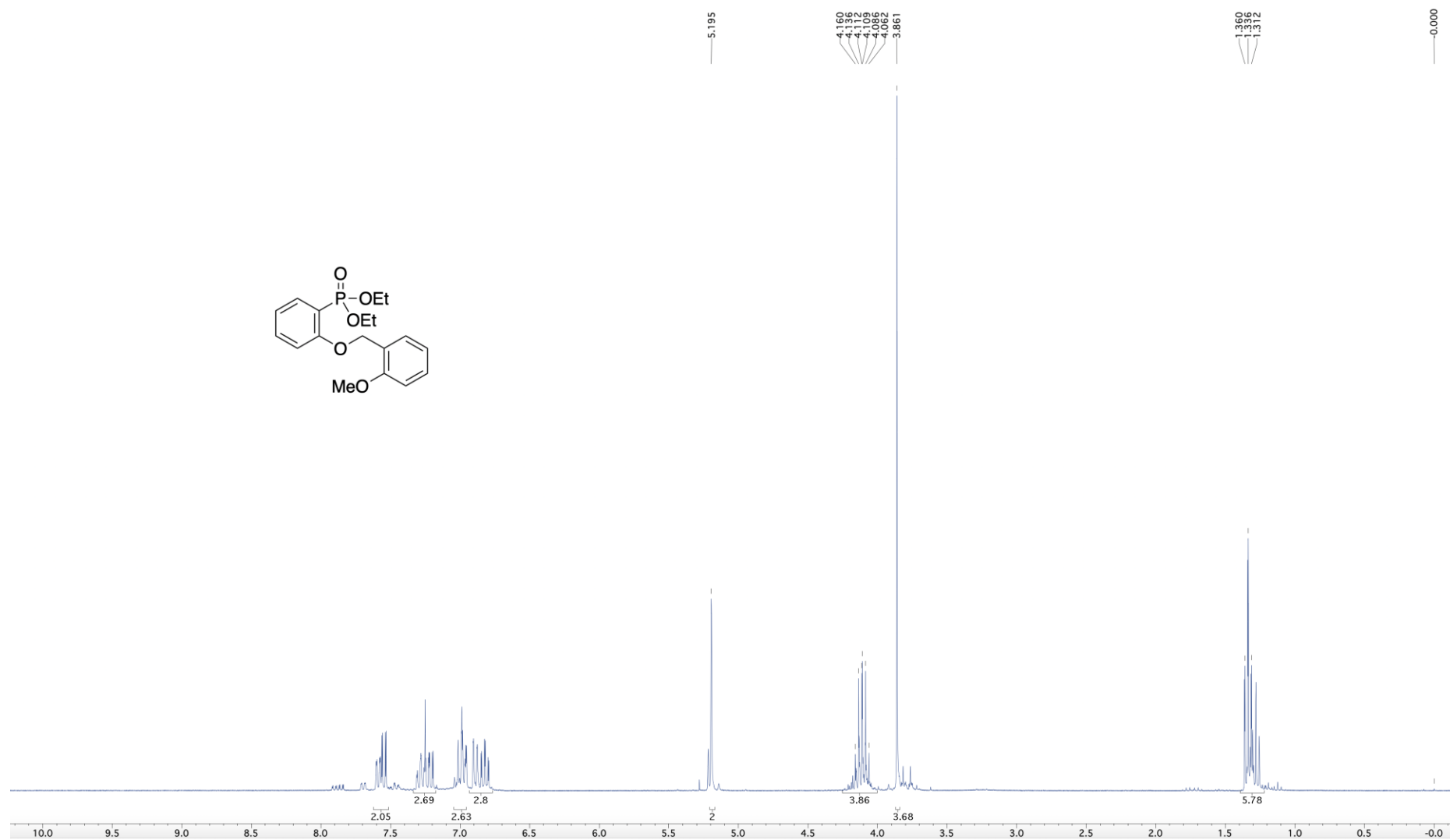


Figure S40. 121 MHz ^{31}P NMR spectrum of **19d**

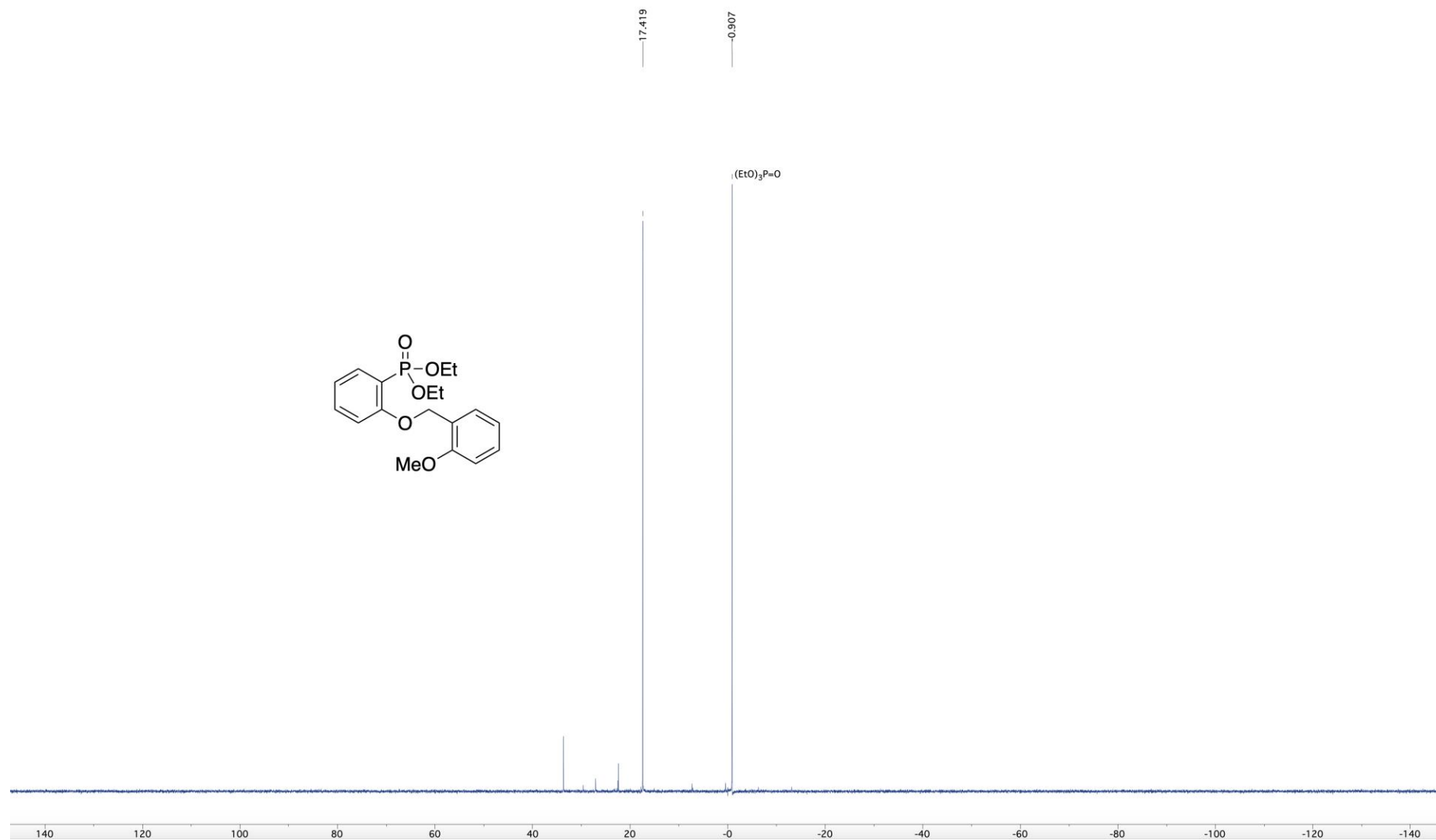


Figure S41. 300 MHz ^1H NMR spectrum of **19e**

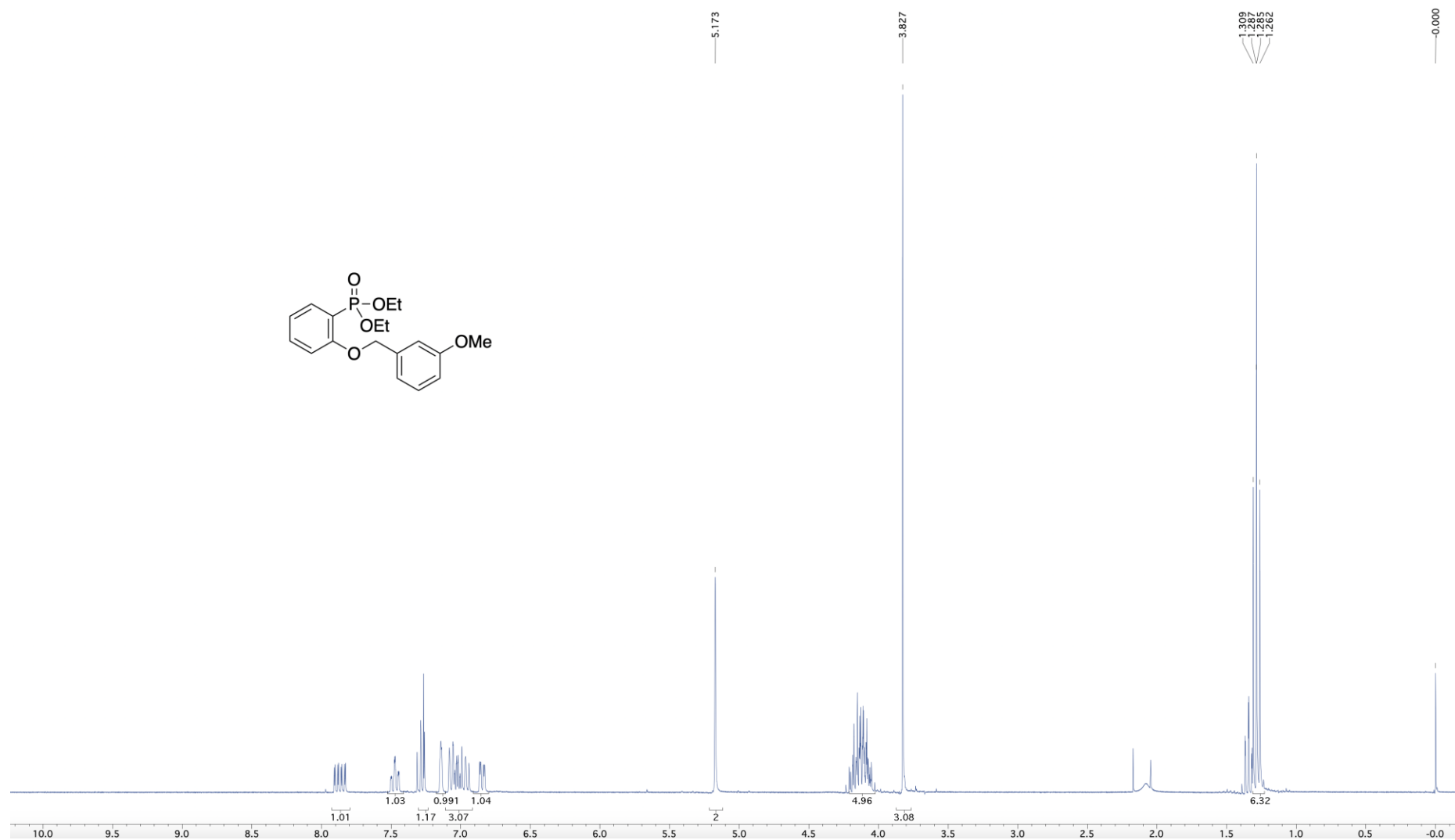


Figure S42. 202 MHz ^{31}P NMR spectrum of **19e**

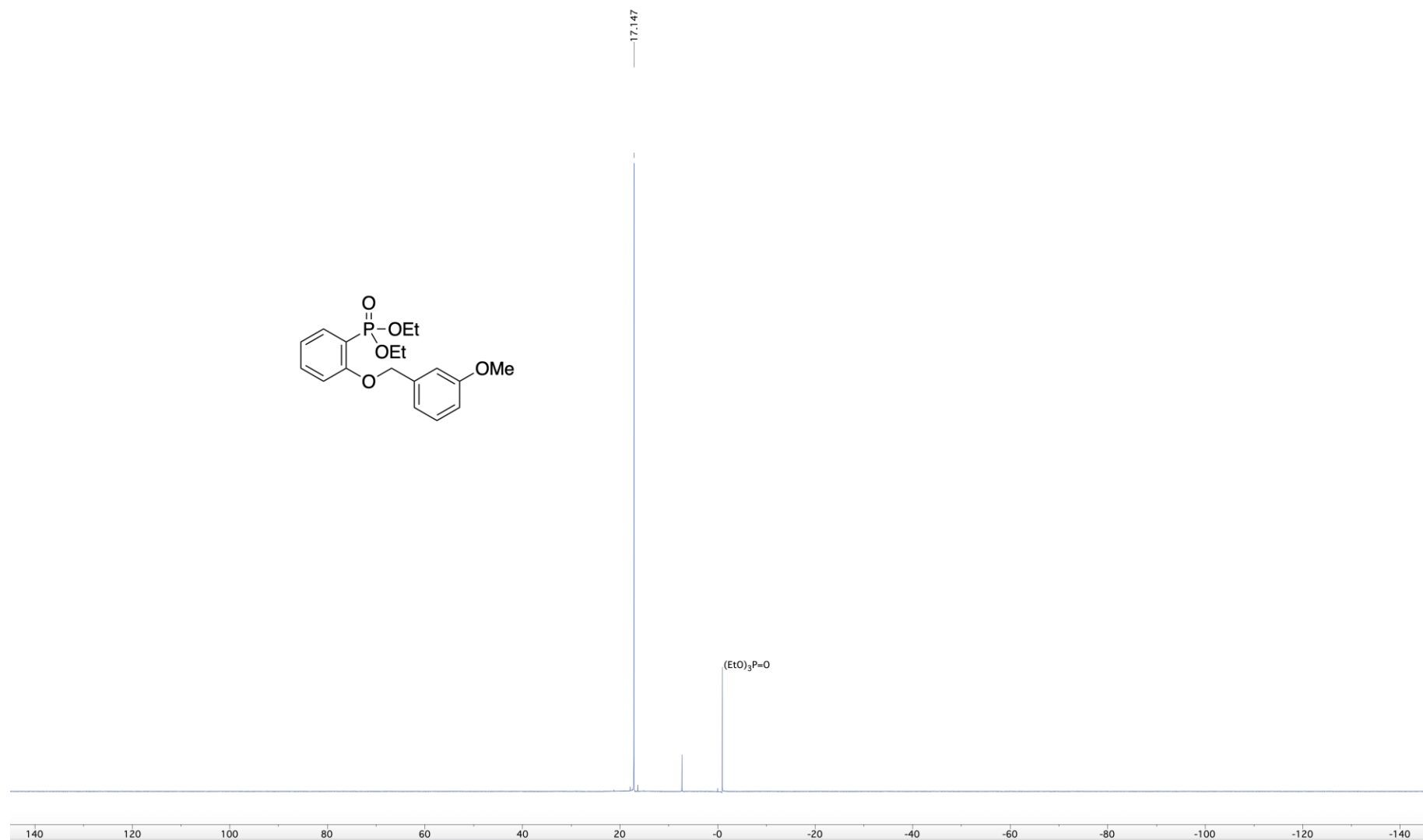


Figure S43. 75 MHz DEPTQ ^{13}C NMR spectrum of **19e**

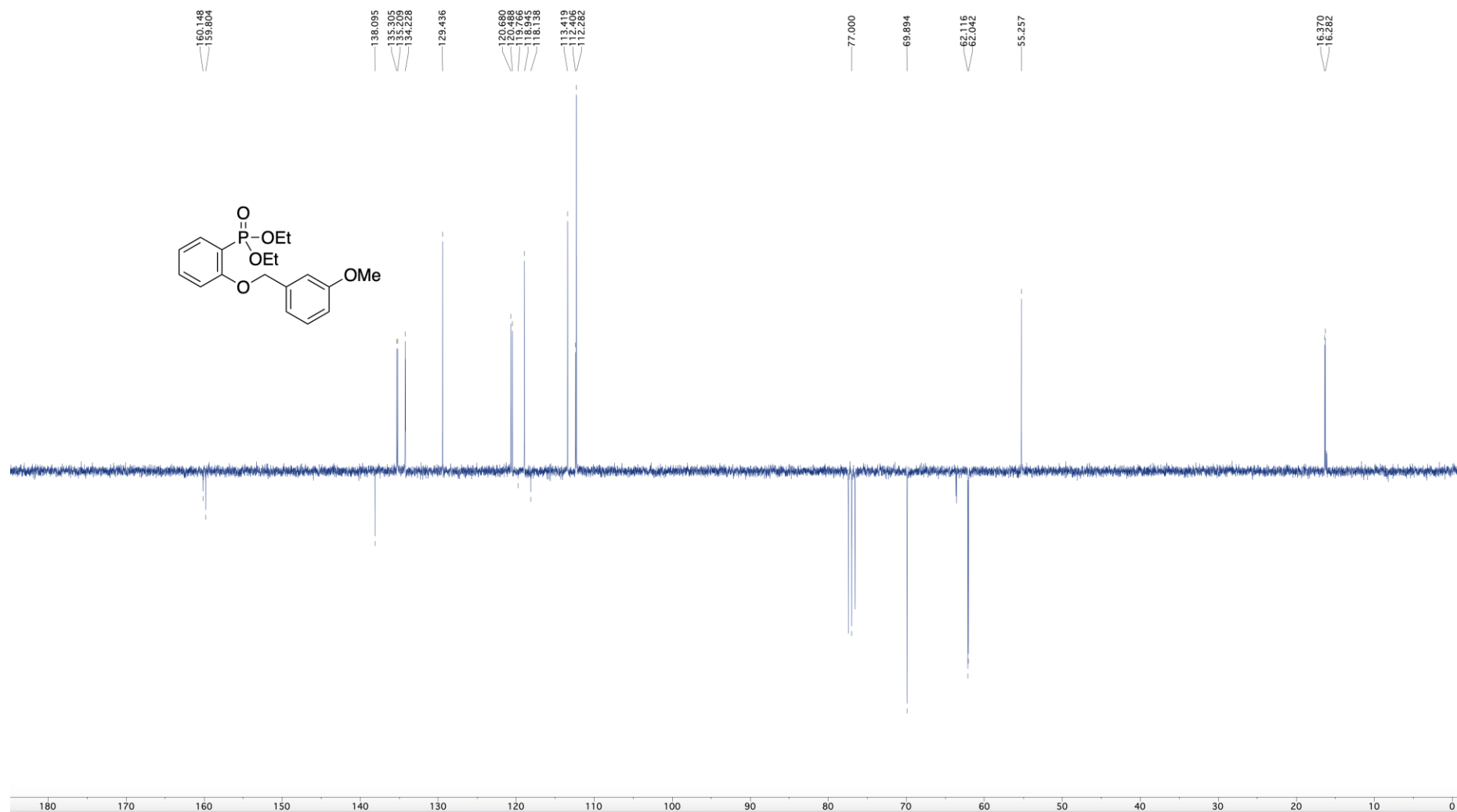


Figure S44. 121 MHz ^{31}P NMR spectrum of **20**

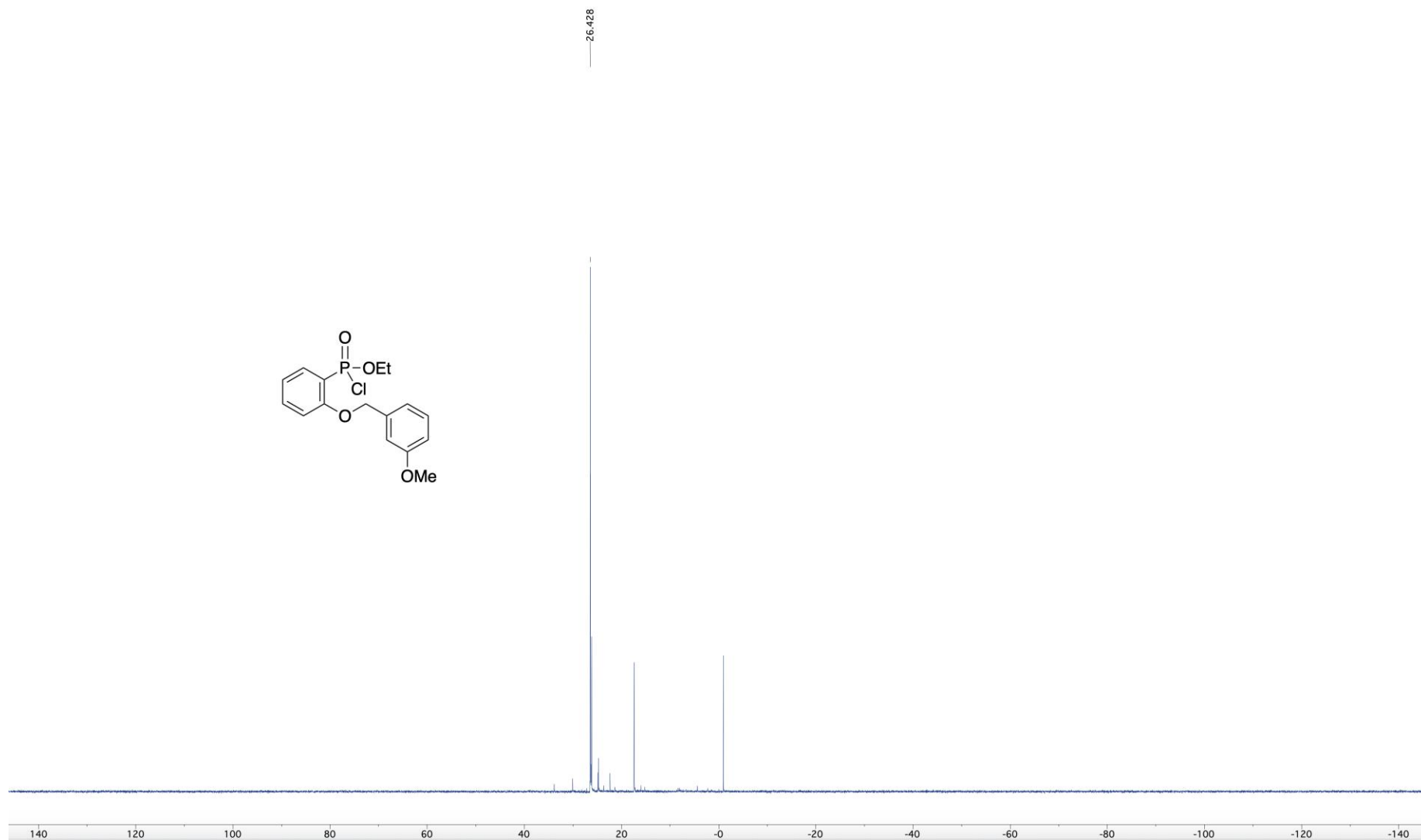


Figure S45. 300 MHz ^1H NMR spectrum of **22**

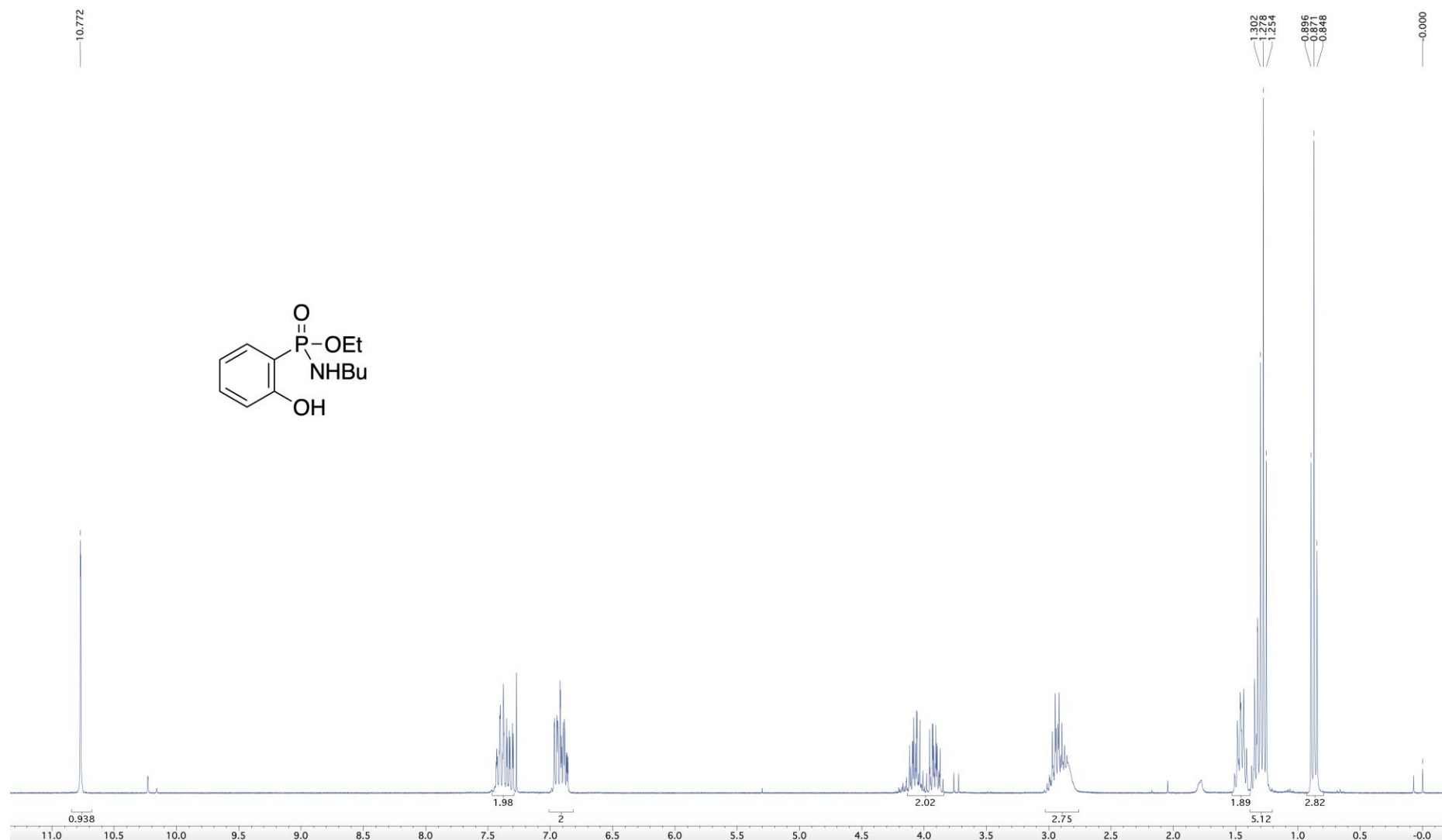


Figure S46. 121 MHz ^{31}P NMR spectrum of **22**

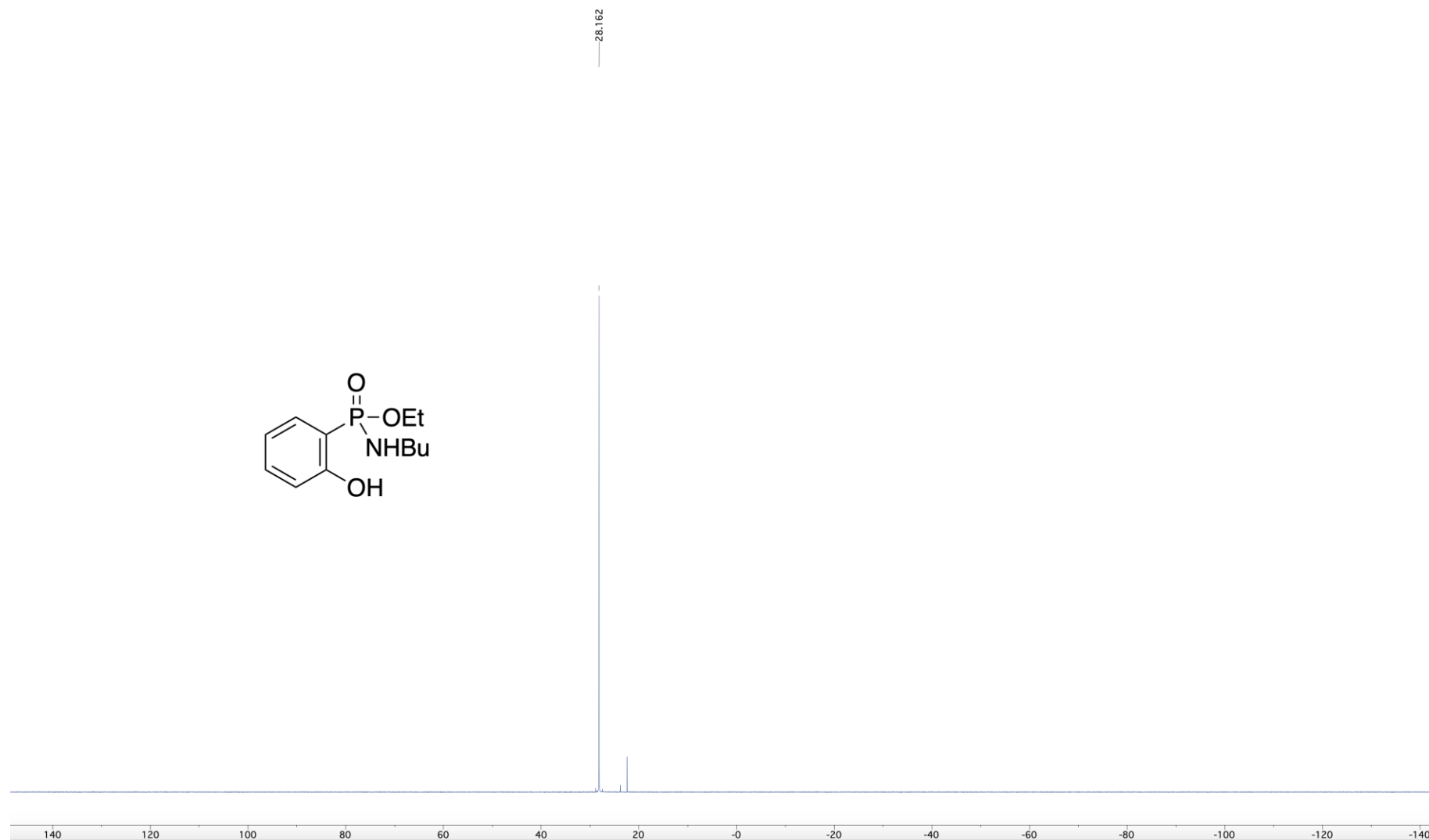


Figure S47. 75 MHz DEPTQ ^{13}C NMR spectrum of **22**

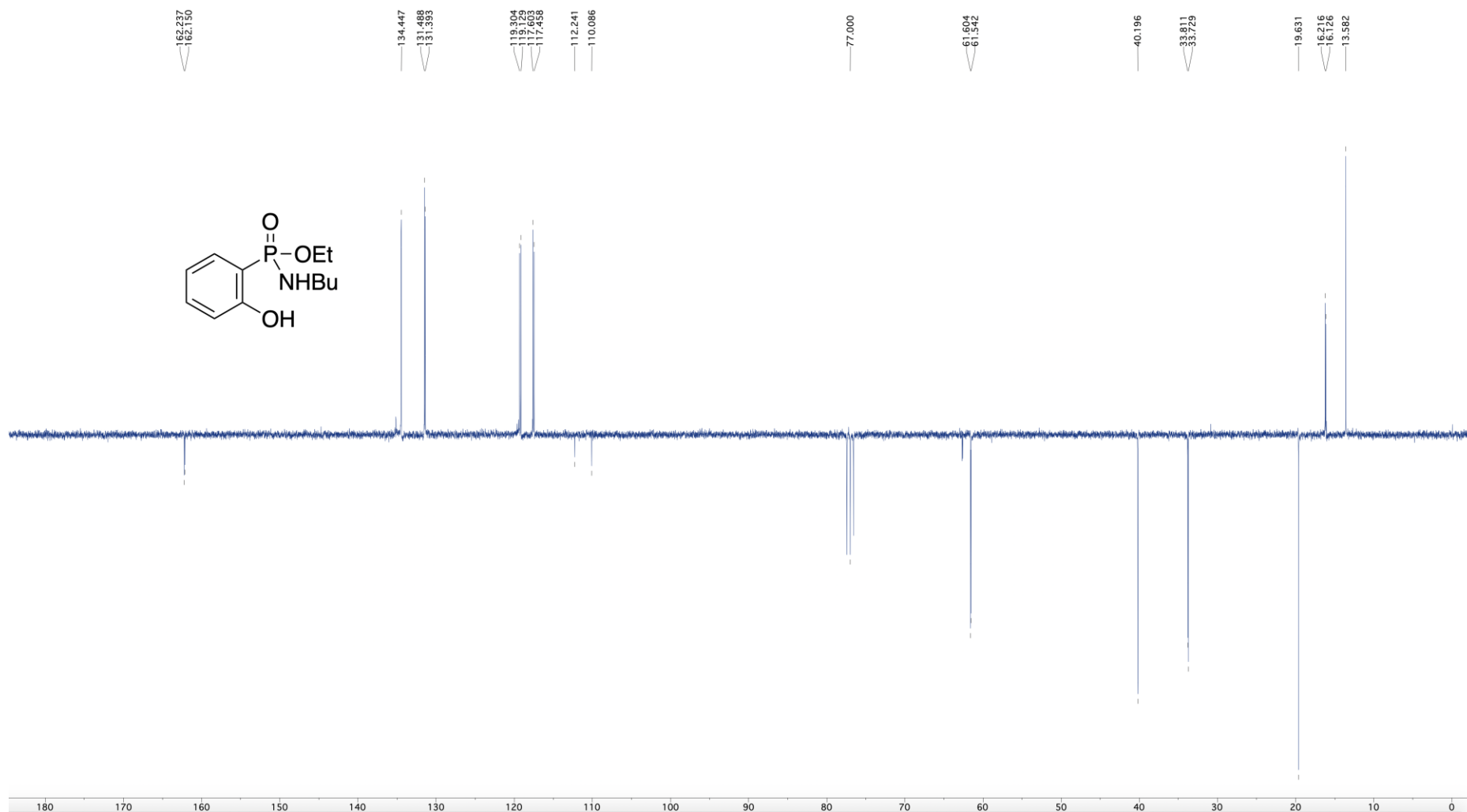


Figure S48. 300 MHz ^1H NMR spectrum of **21a**

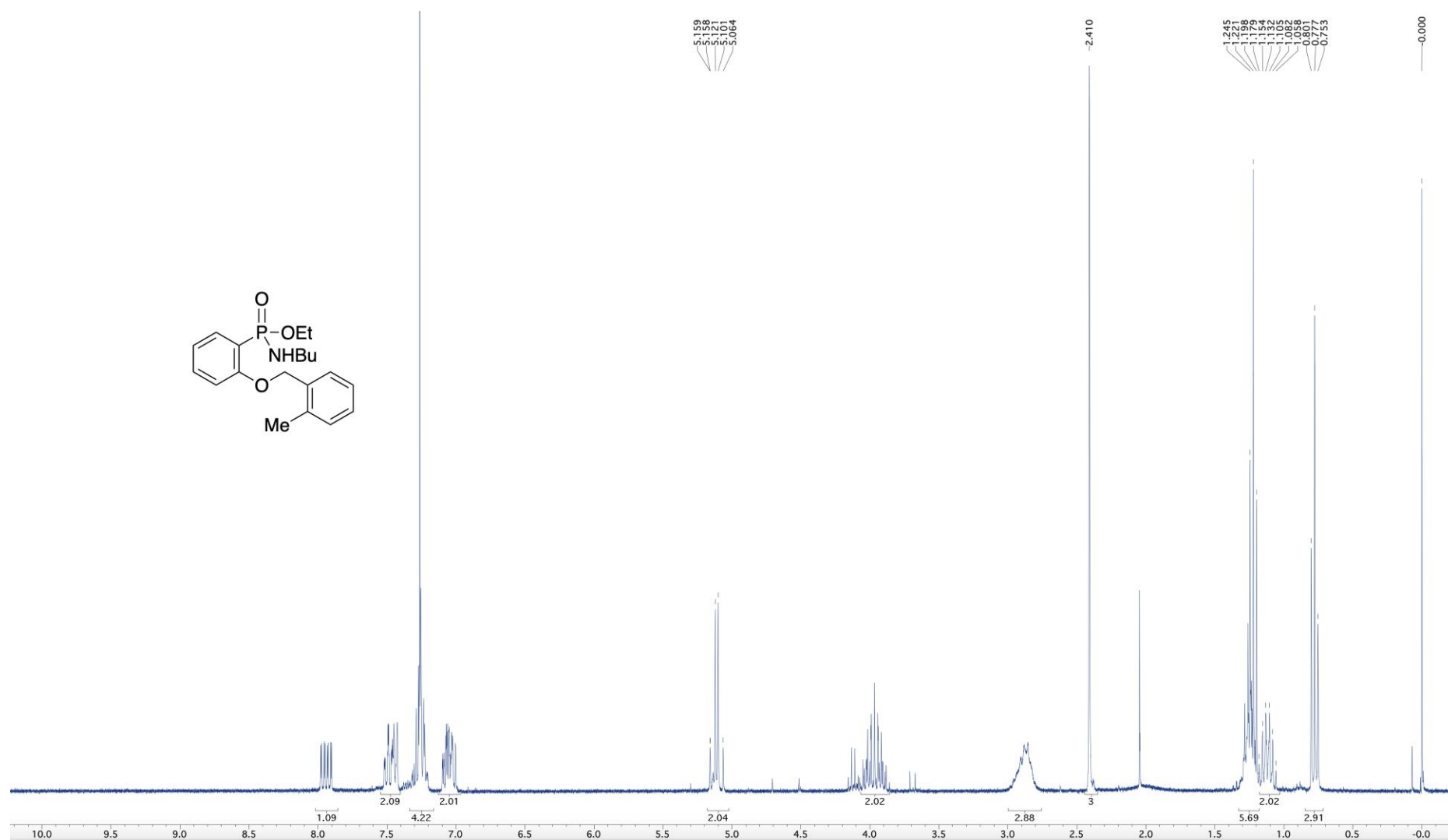


Figure S49. 121 MHz ^{31}P NMR spectrum of **21a**

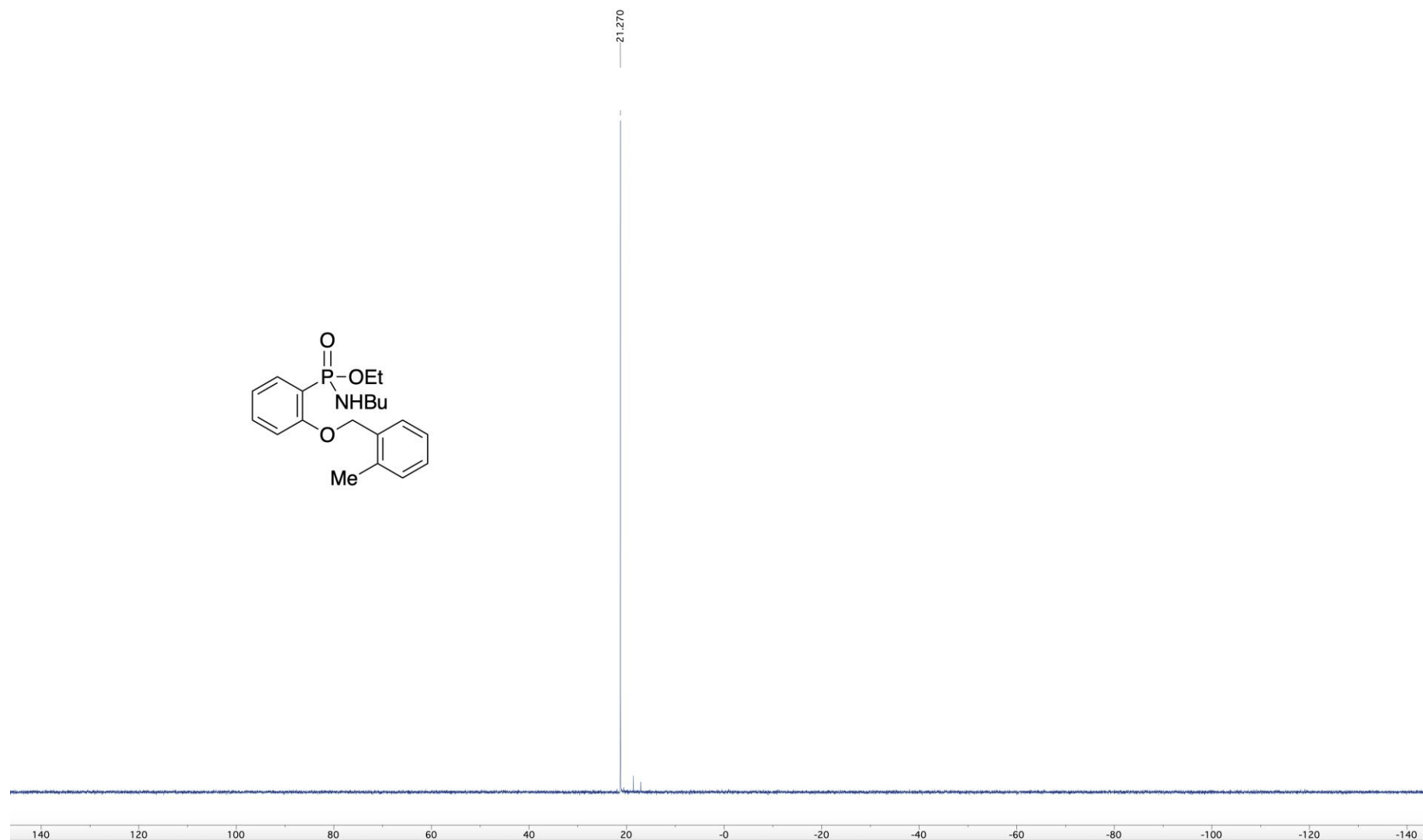


Figure S50. 75 MHz DEPTQ ^{13}C NMR spectrum of **21a**

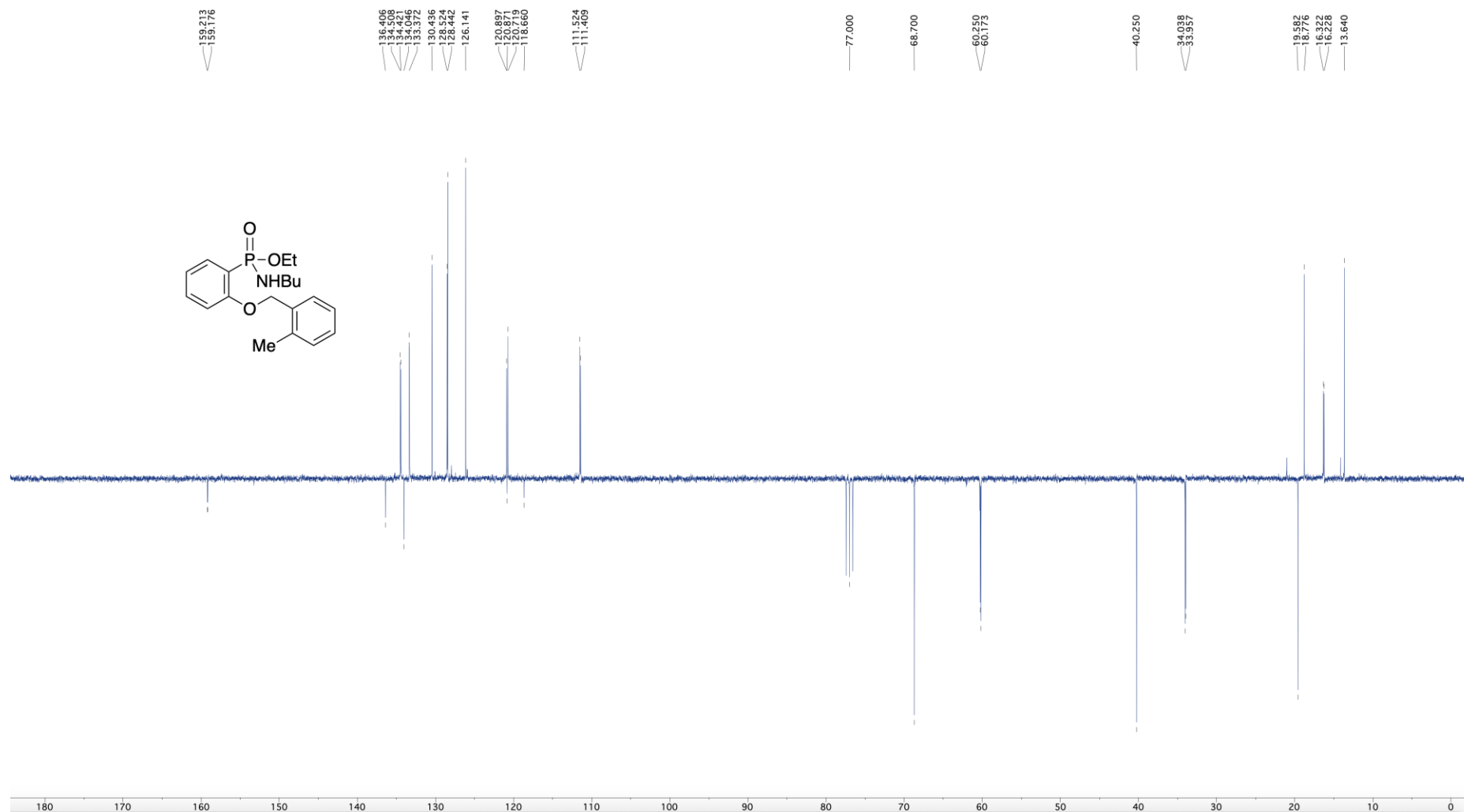


Figure S51. 400 MHz ^1H NMR spectrum of **21b**

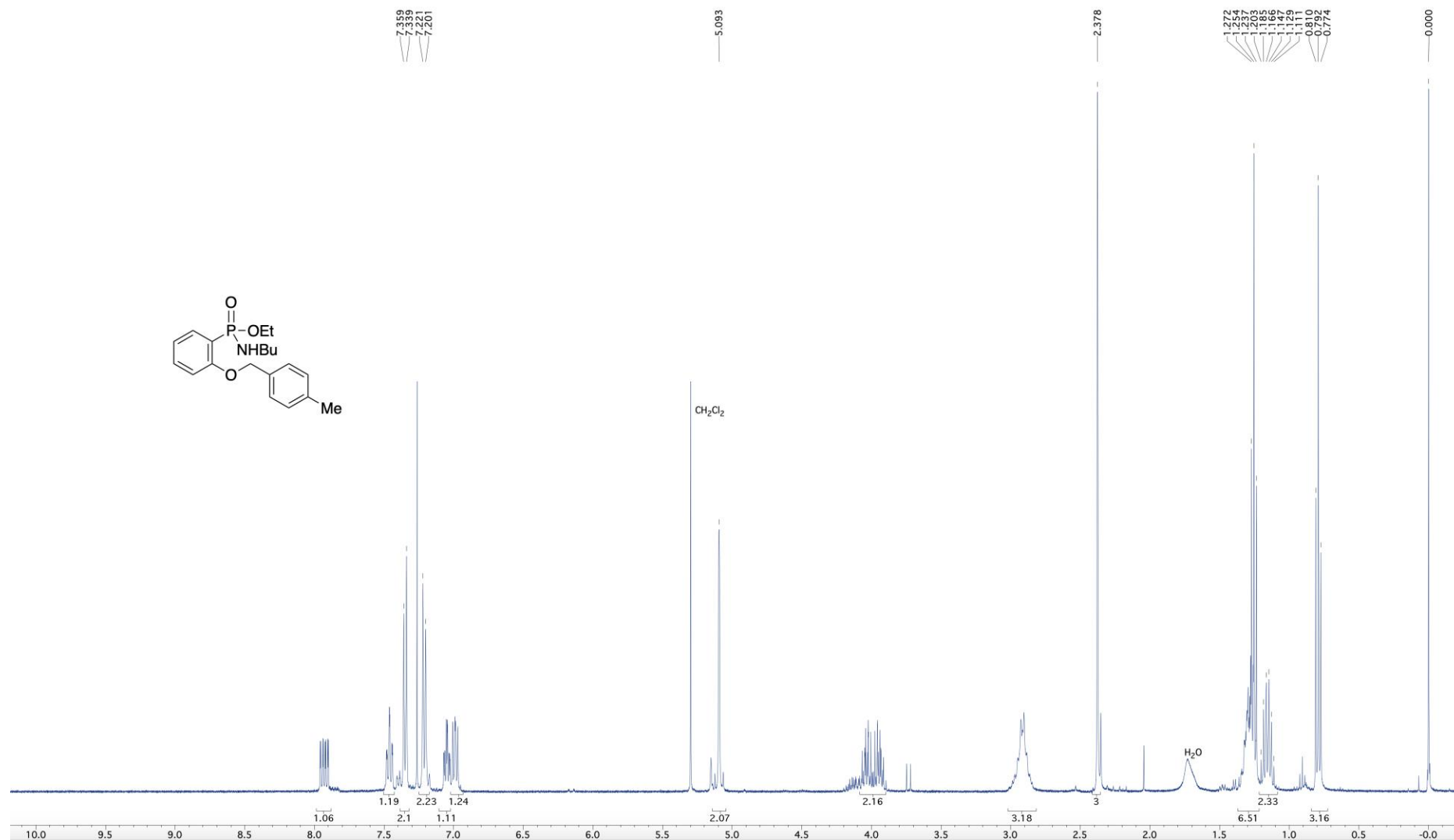


Figure S52. 162 MHz ^{31}P NMR spectrum of **21b**

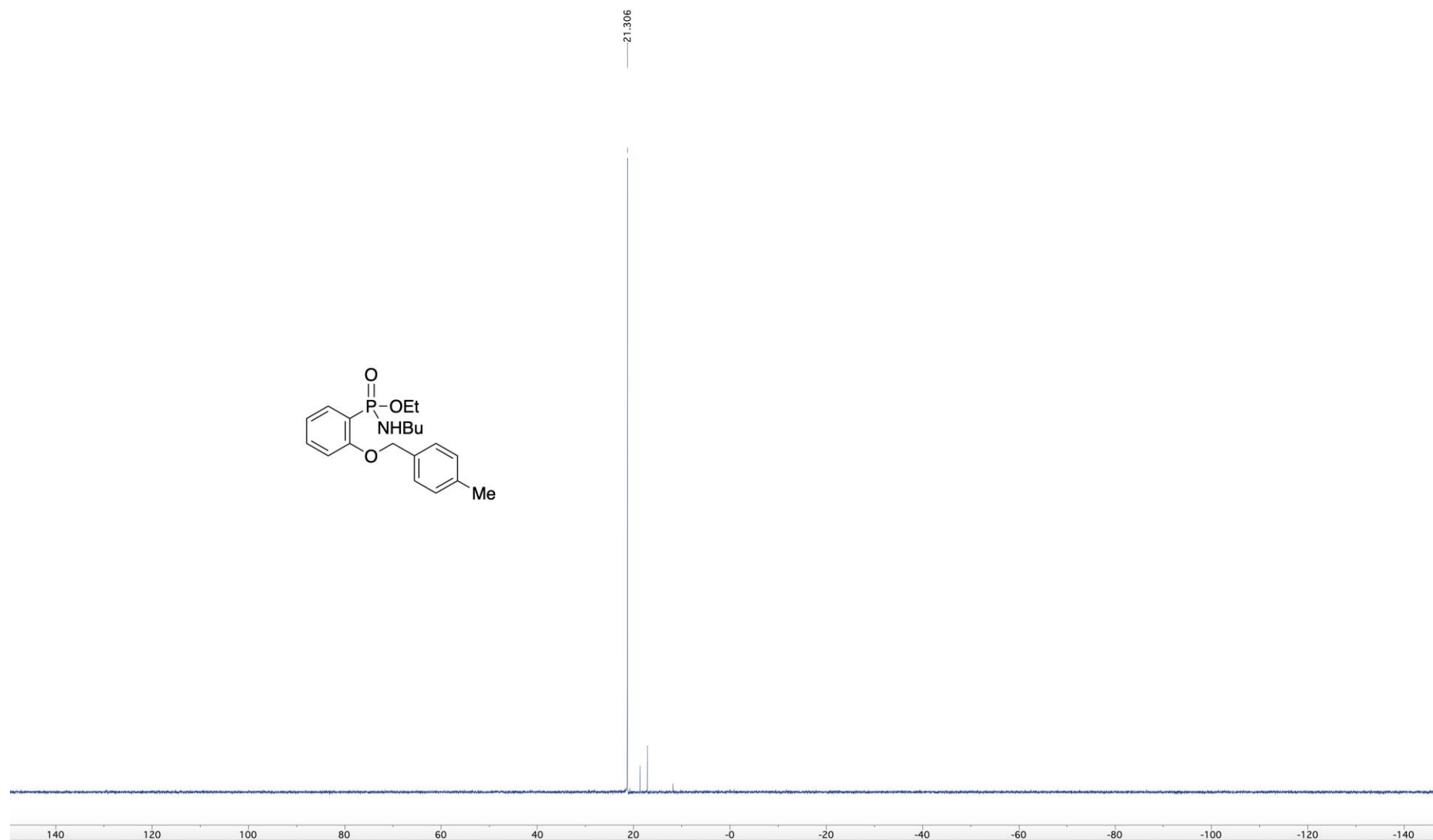


Figure S53. 100 MHz DEPTQ ^{13}C NMR spectrum of **21b**

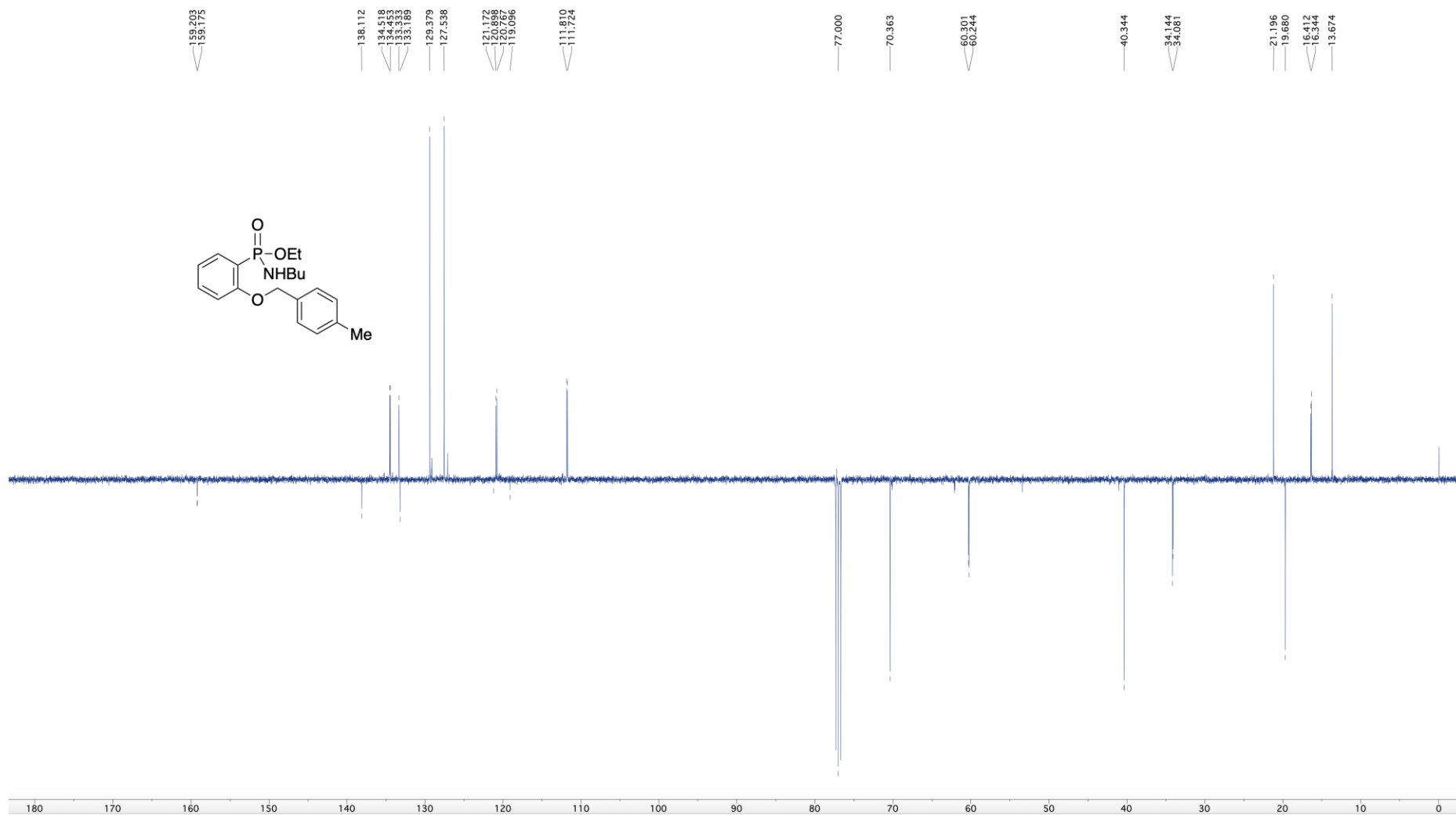


Figure S54. 400 MHz ^1H NMR spectrum of **21c**

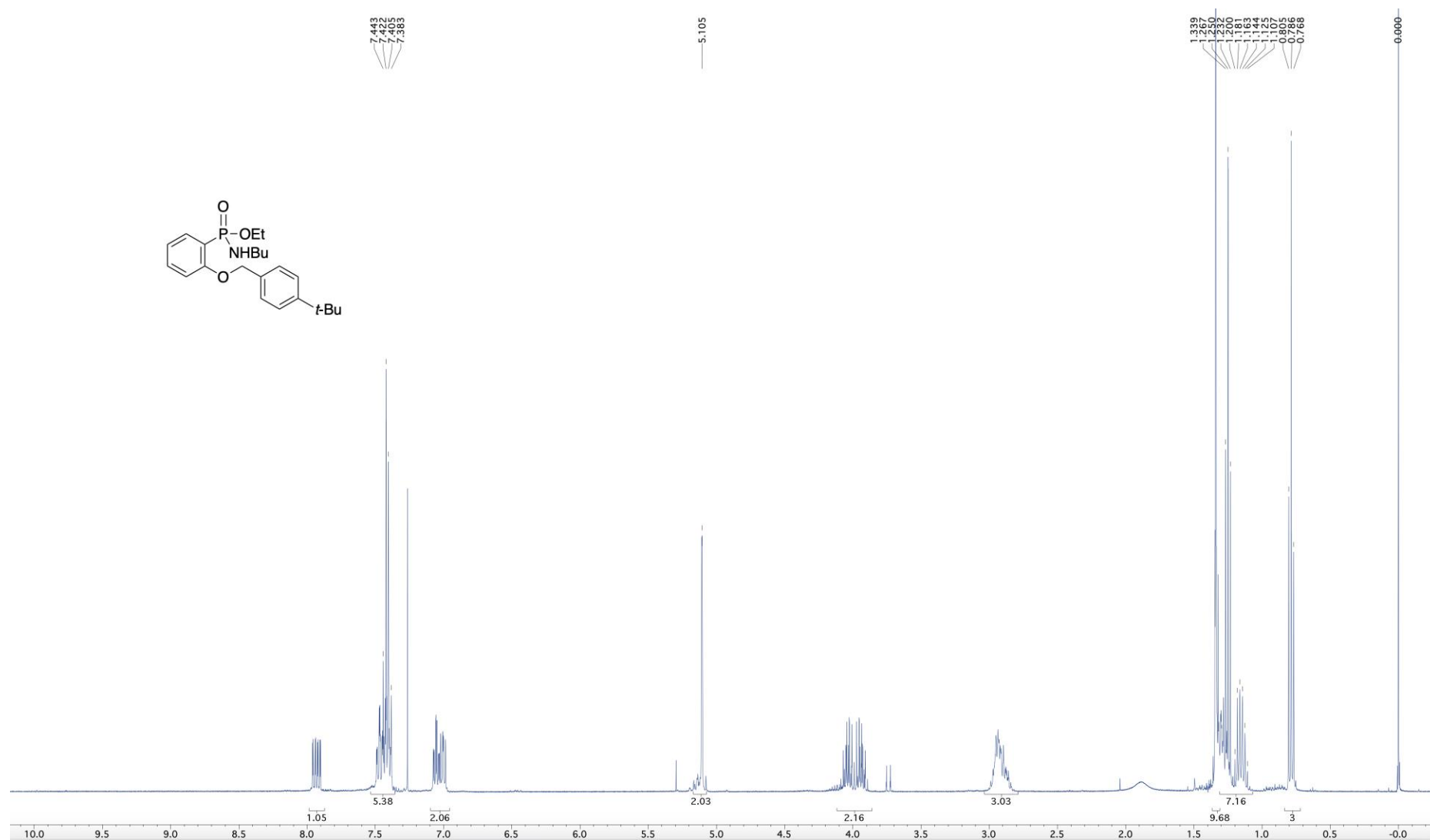


Figure S55. 162 MHz ^{31}P NMR spectrum of **21c**

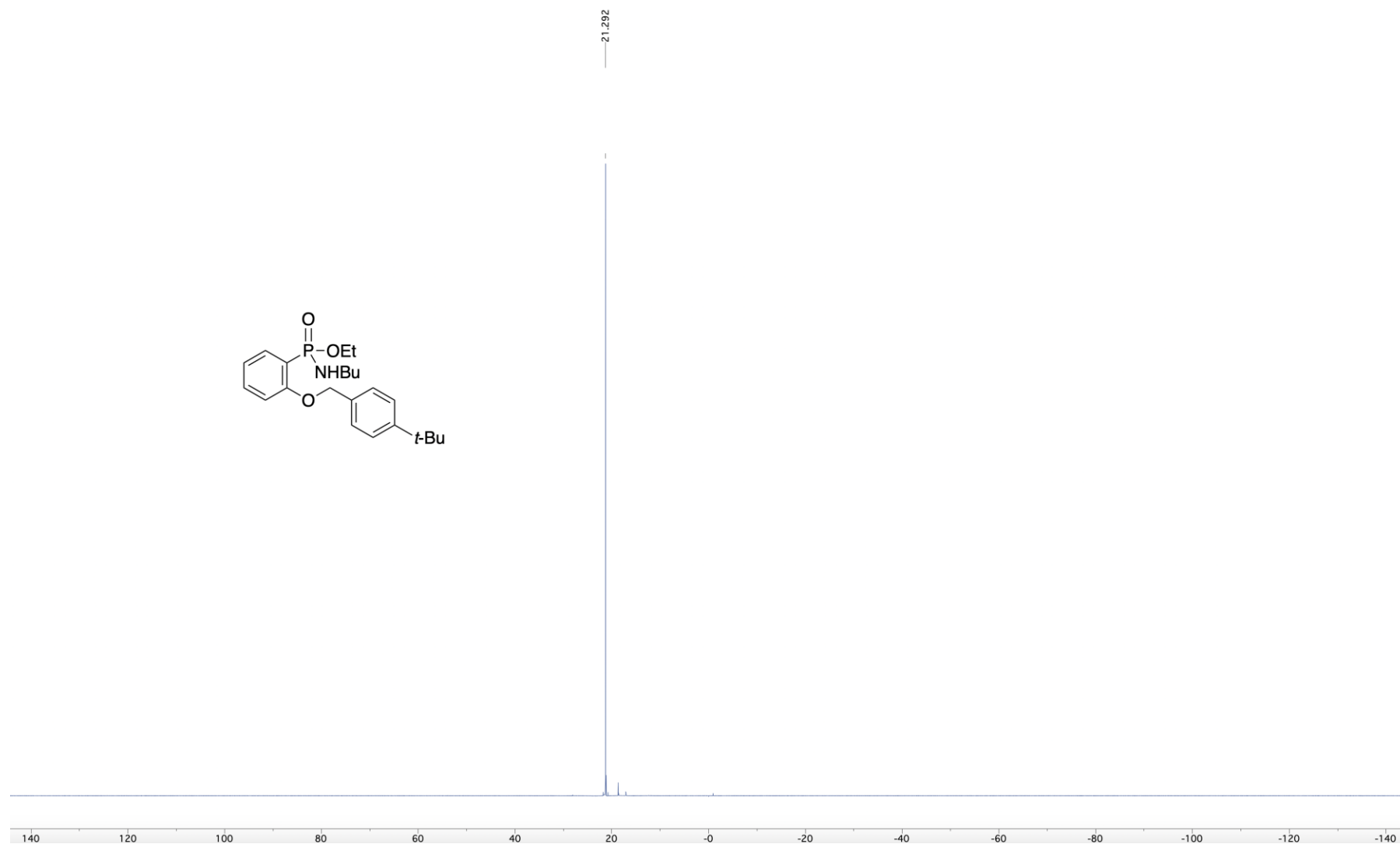


Figure S56. 100 MHz DEPTQ ^{13}C NMR spectrum of **21c**

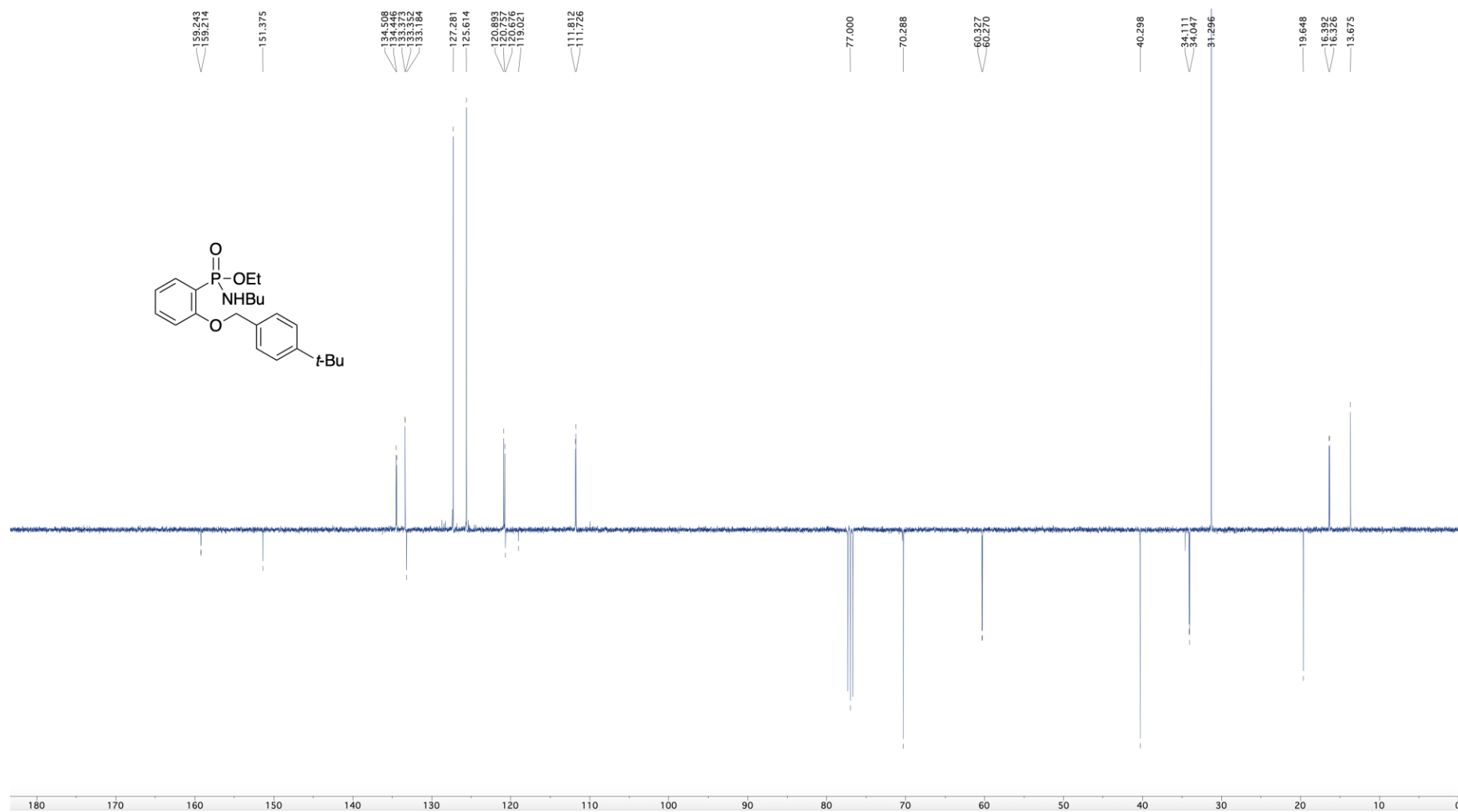


Figure S57. 400 MHz ^1H NMR spectrum of **21d**

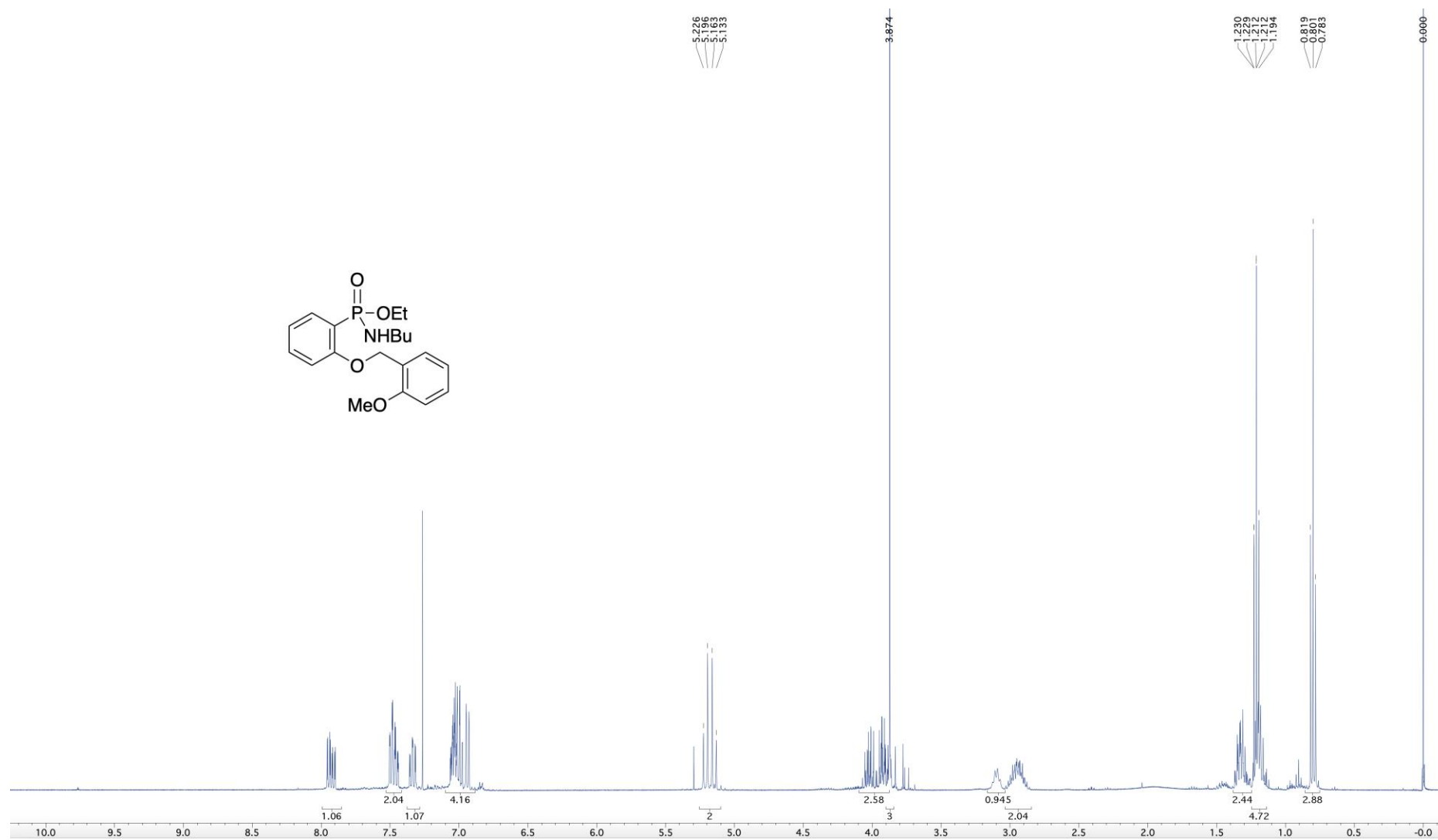


Figure S58. 162 MHz ^{31}P NMR spectrum of **21d**

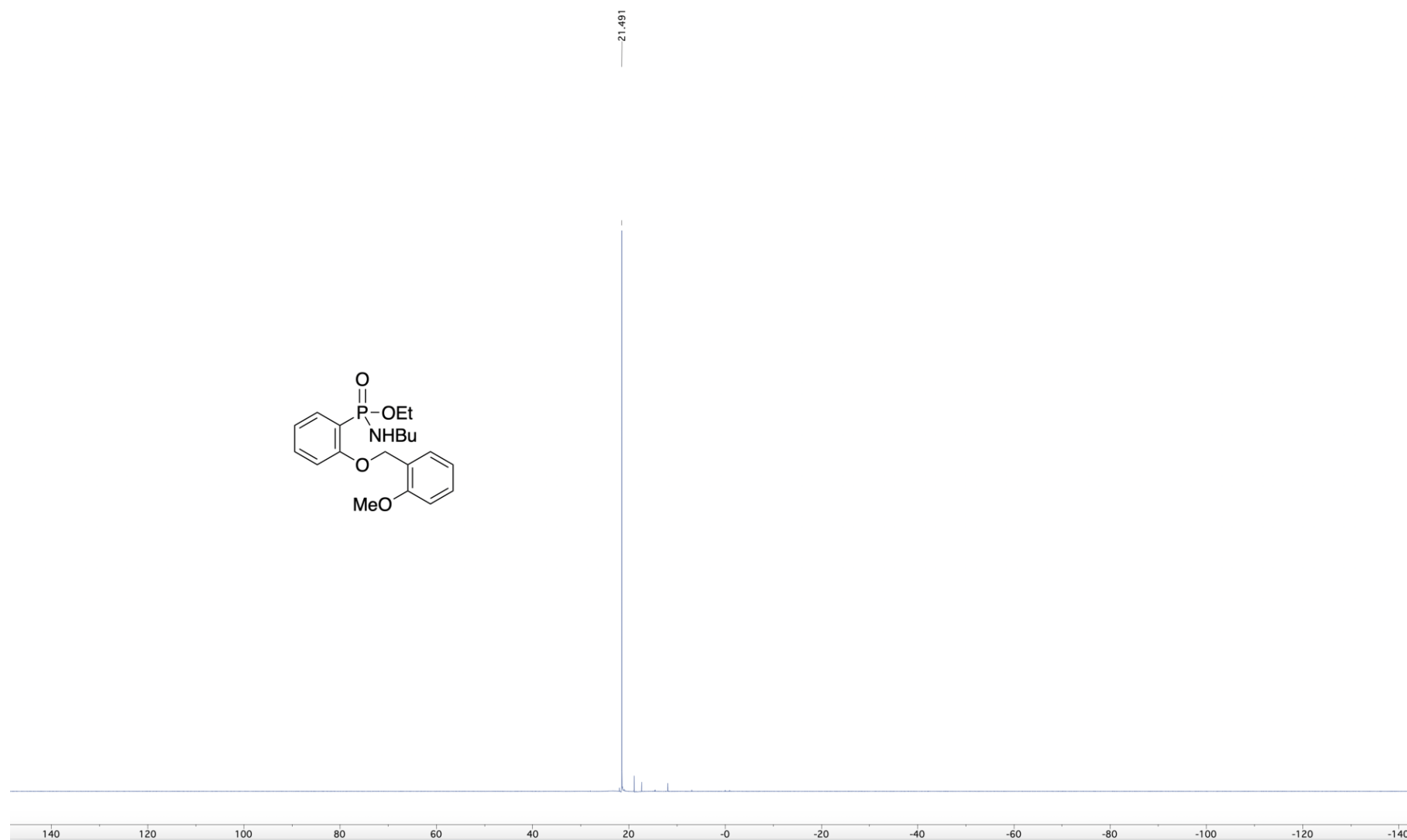


Figure S59. 100 MHz DEPTQ ^{13}C NMR spectrum of **21d**

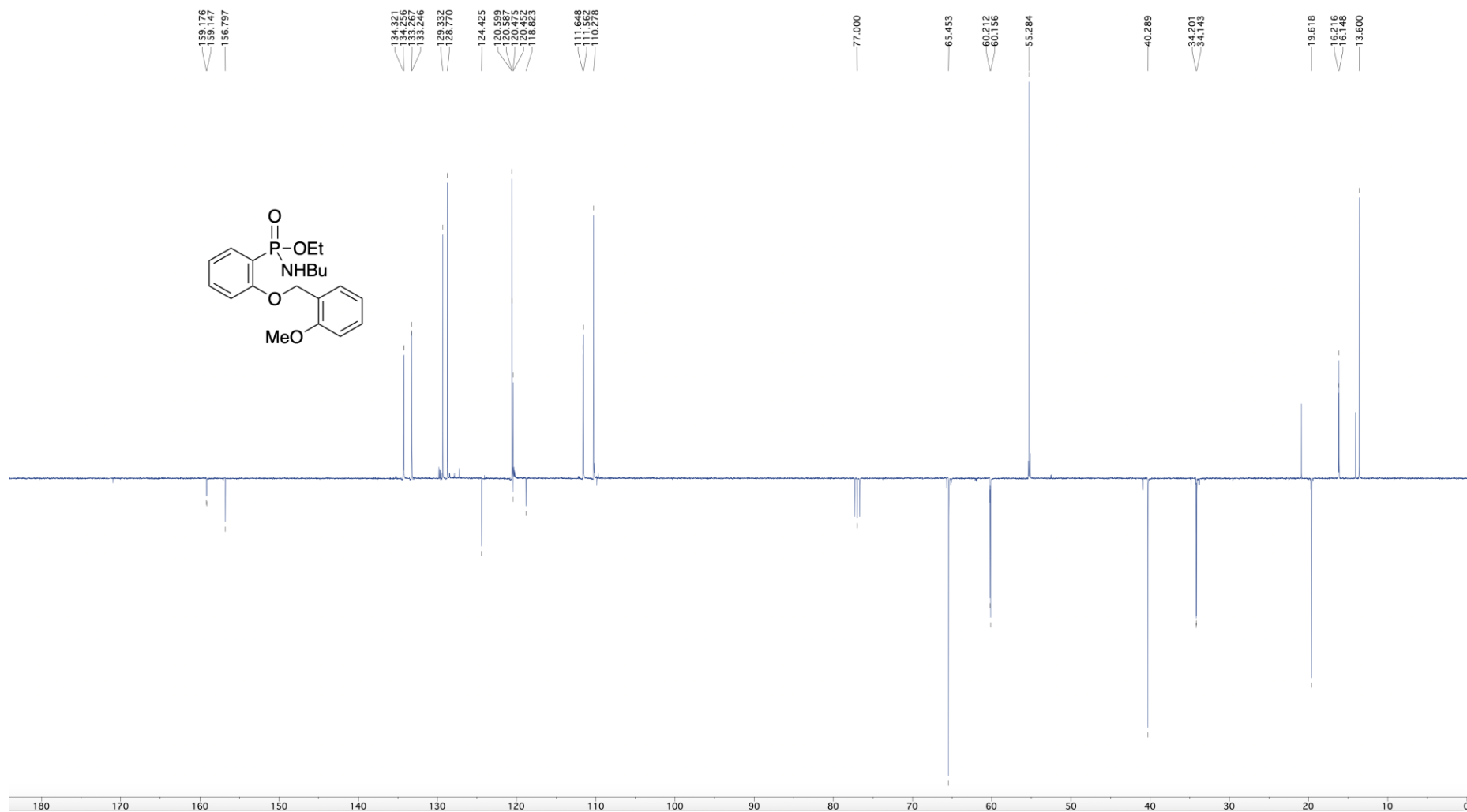


Figure S60. 400 MHz ^1H NMR spectrum of **21e**

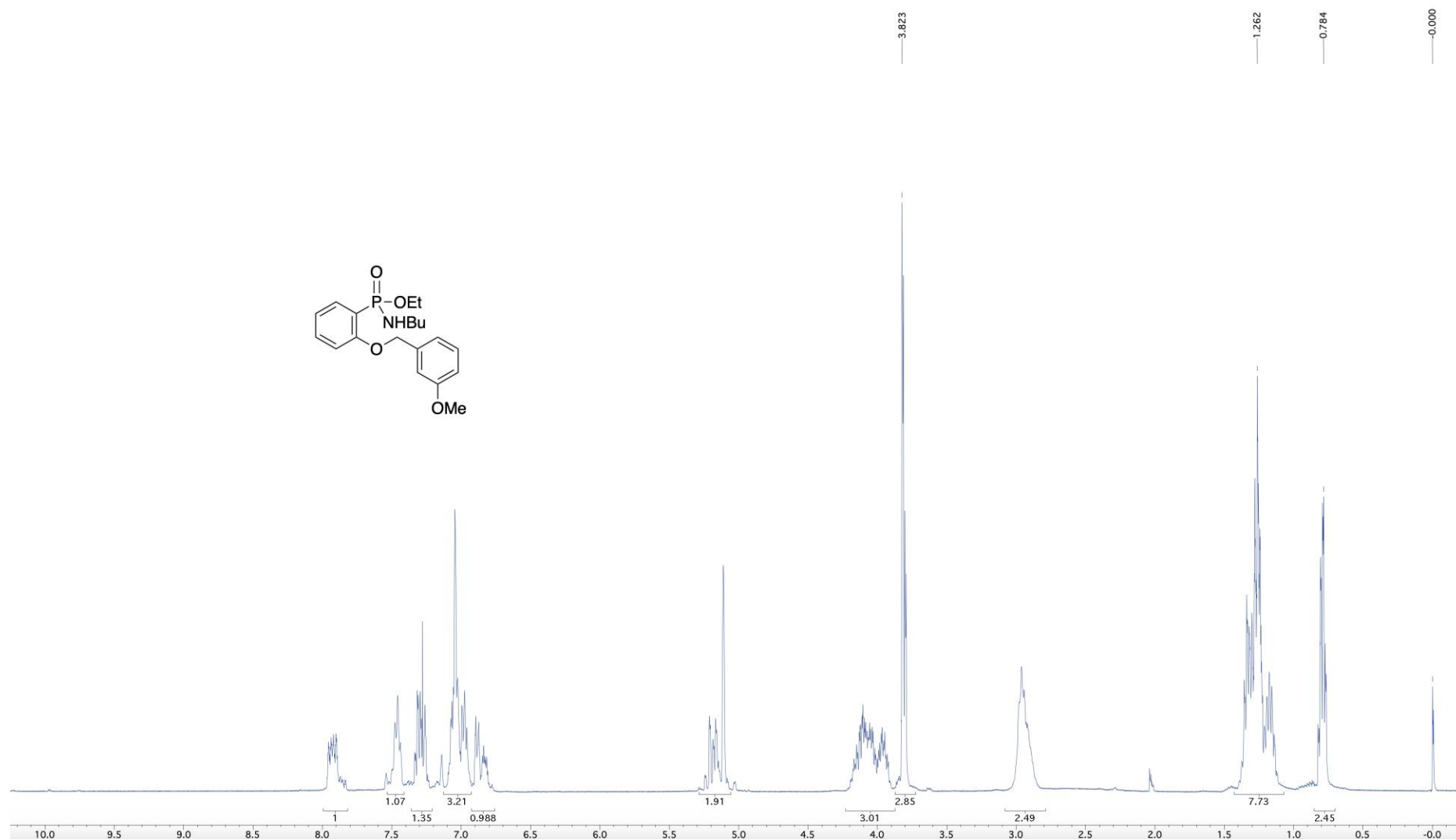


Figure S61. 121 MHz ^{31}P NMR spectrum of **21e**

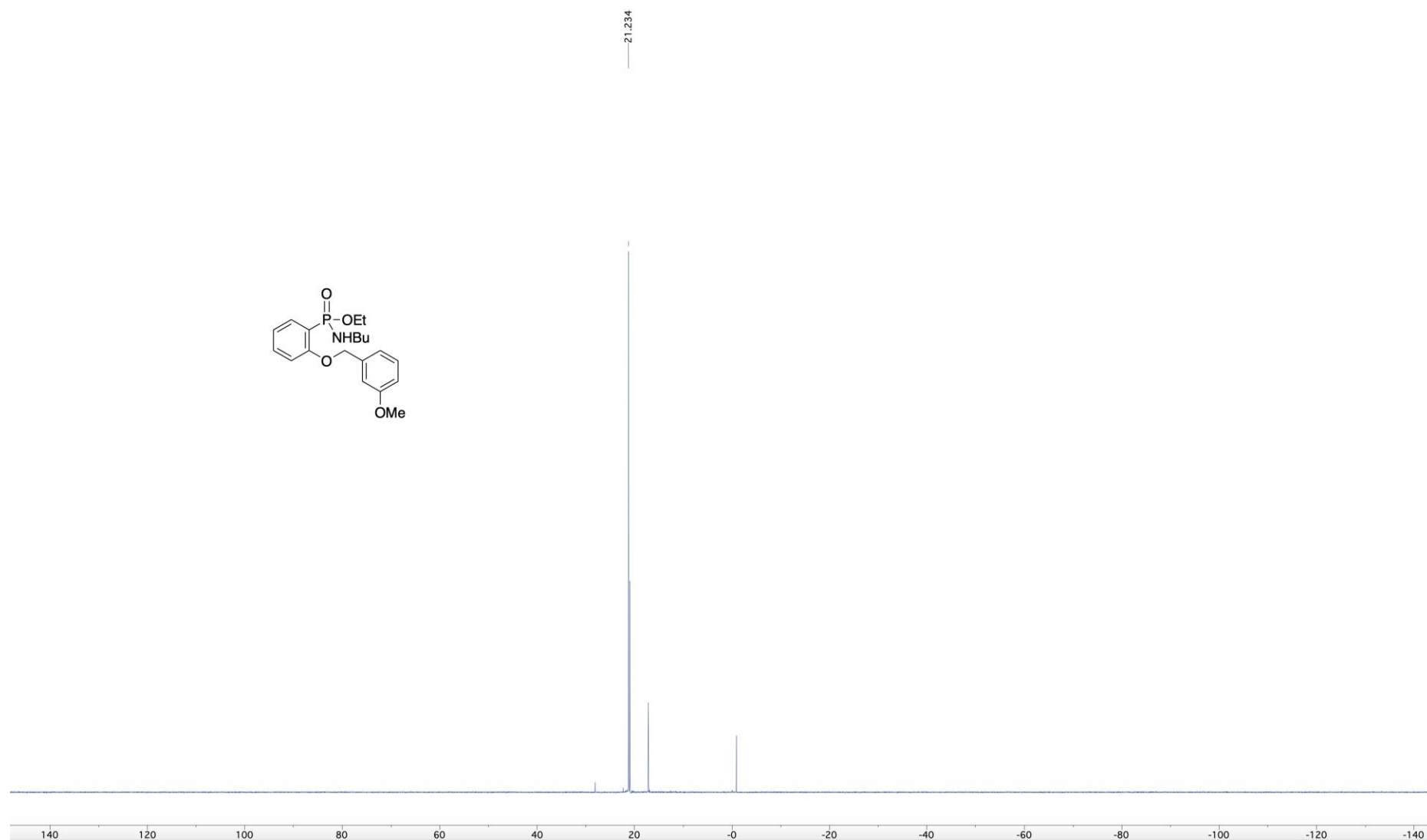


Figure S62. 400 MHz ^1H NMR spectrum of **21f**

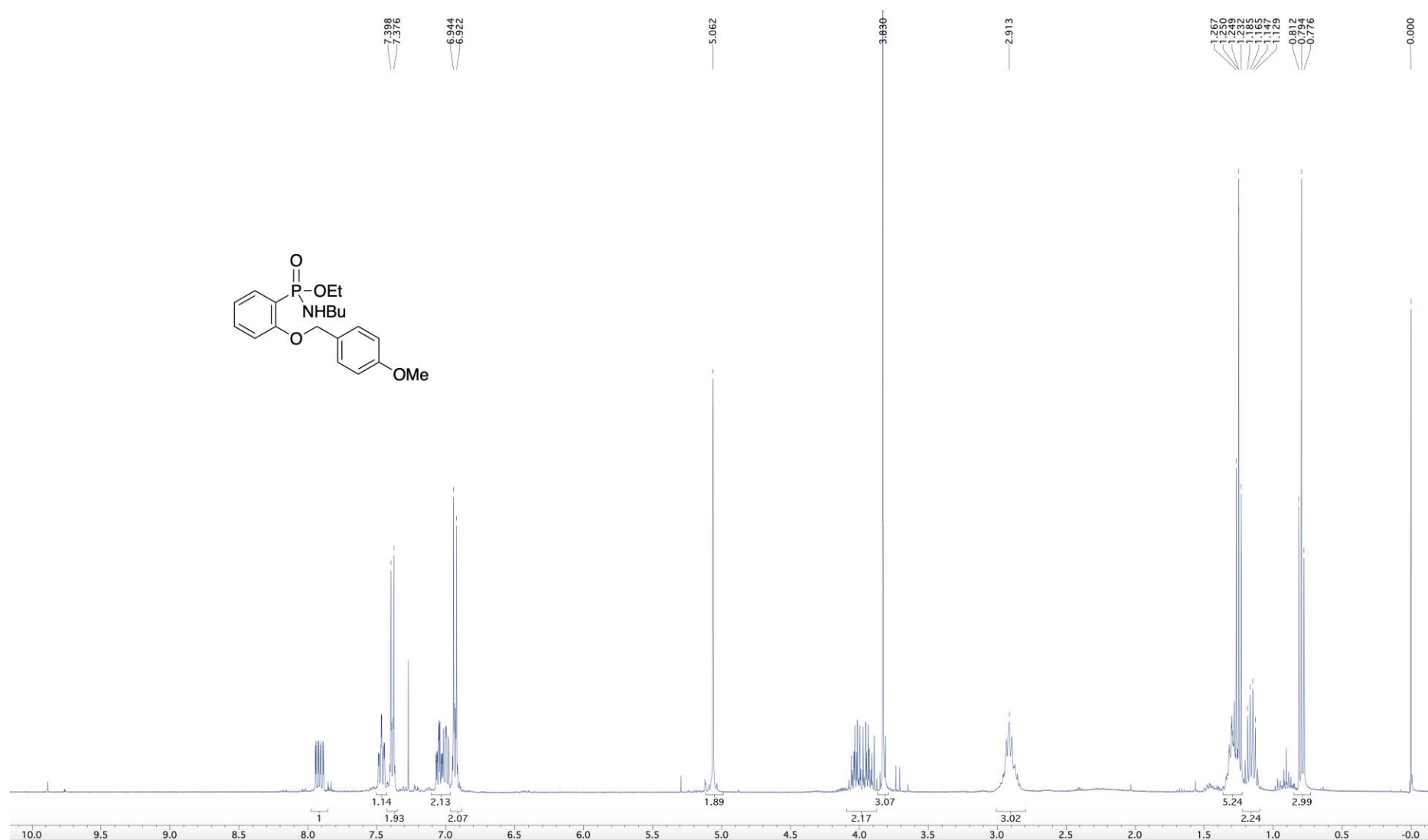


Figure S63. 162 MHz ^{31}P NMR spectrum of **21f**

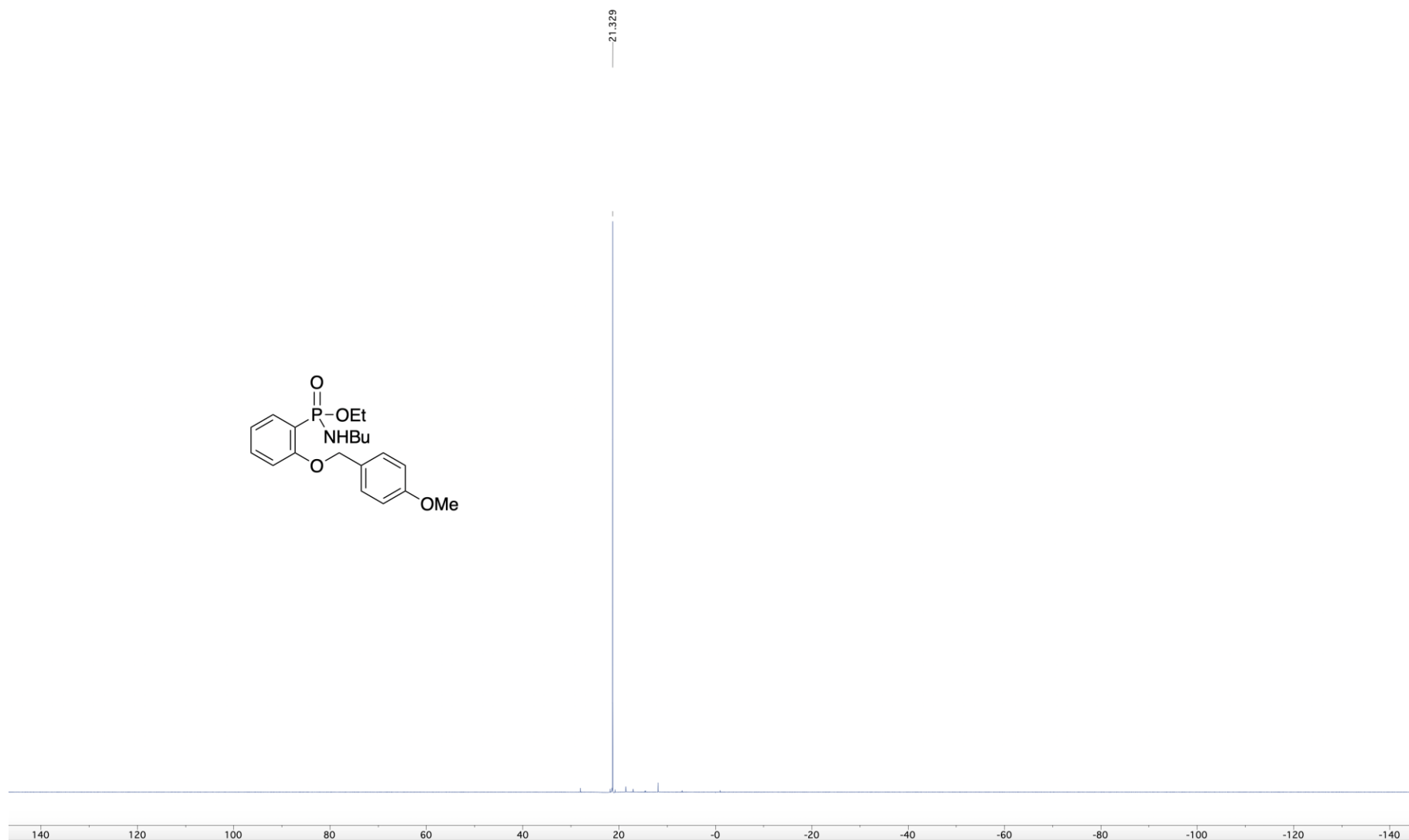


Figure S64. 100 MHz DEPTQ ^{13}C NMR spectrum of **21f**

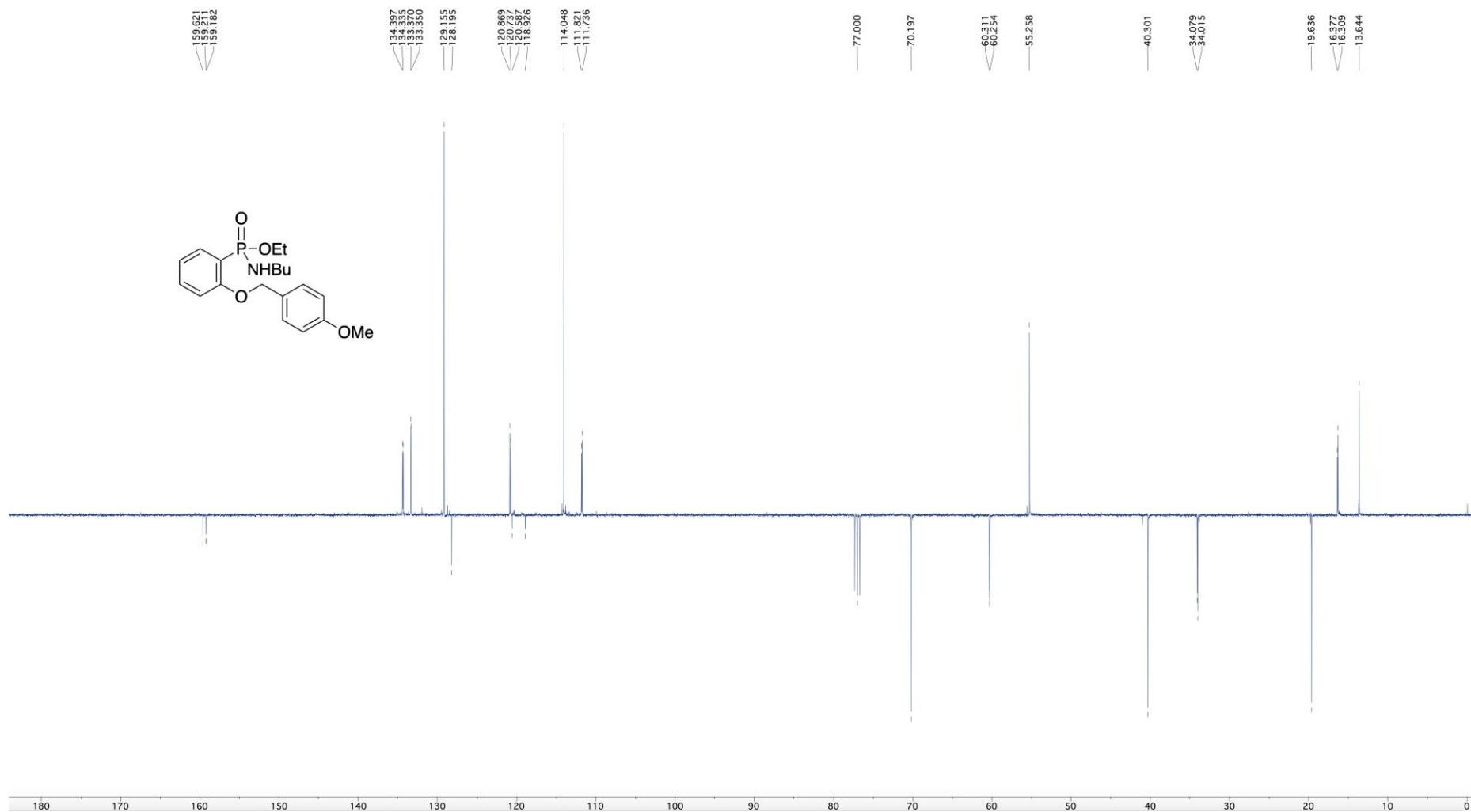


Figure S65. 400 MHz ^1H NMR spectrum of **21g**

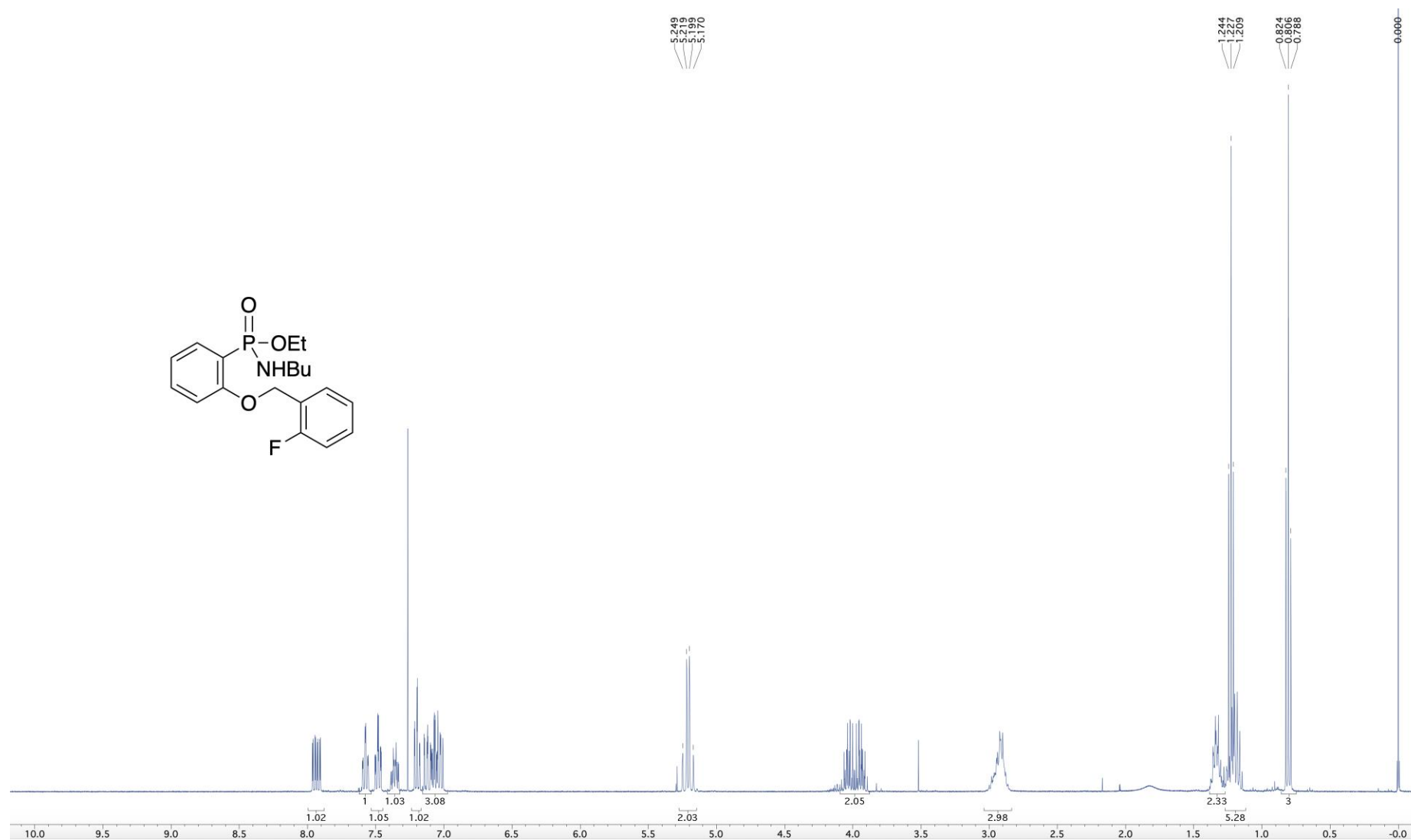


Figure S66. 376 MHz ^{19}F NMR spectrum of **21g**

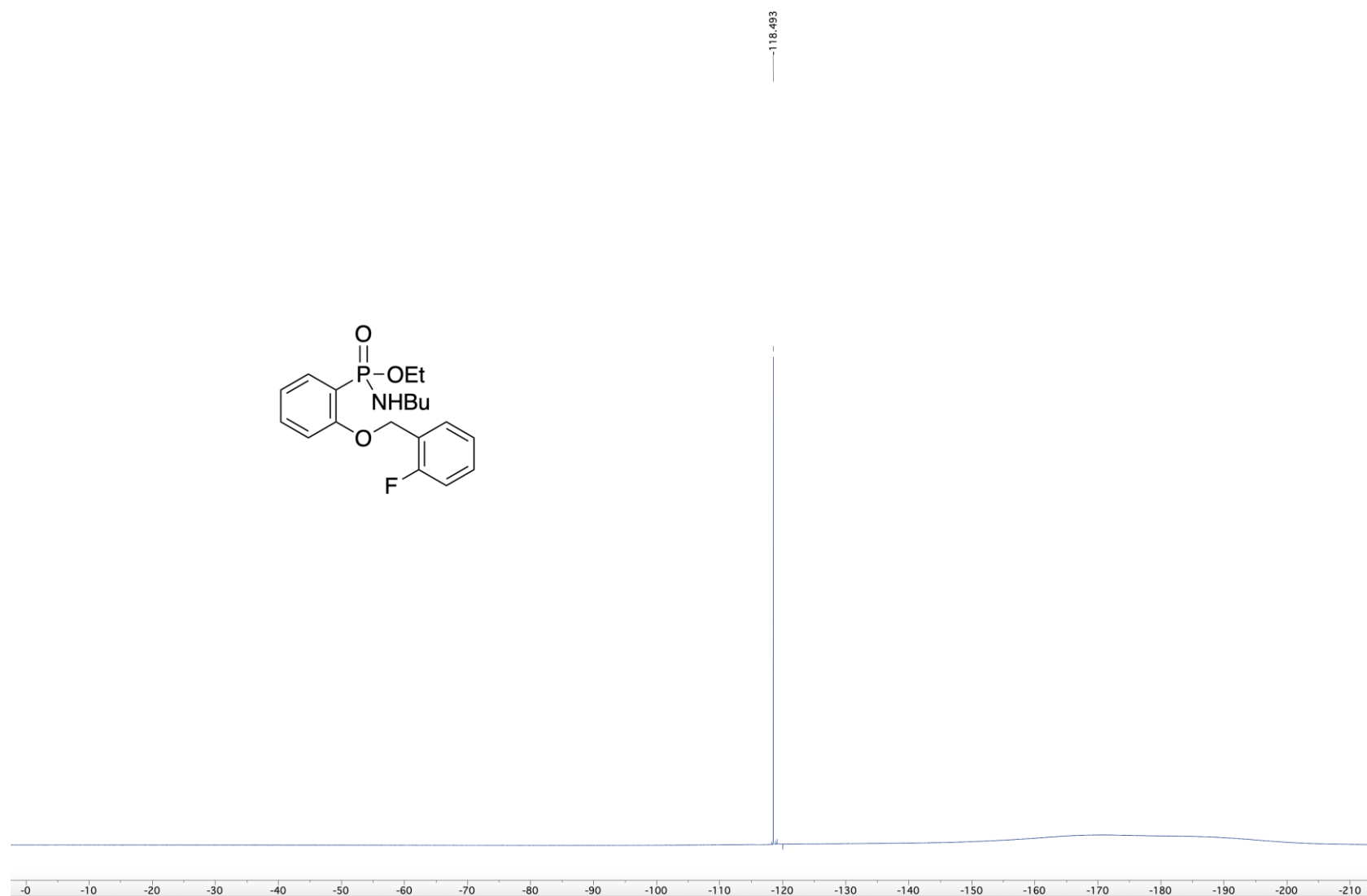


Figure S67. 162 MHz ^{31}P NMR spectrum of **21g**

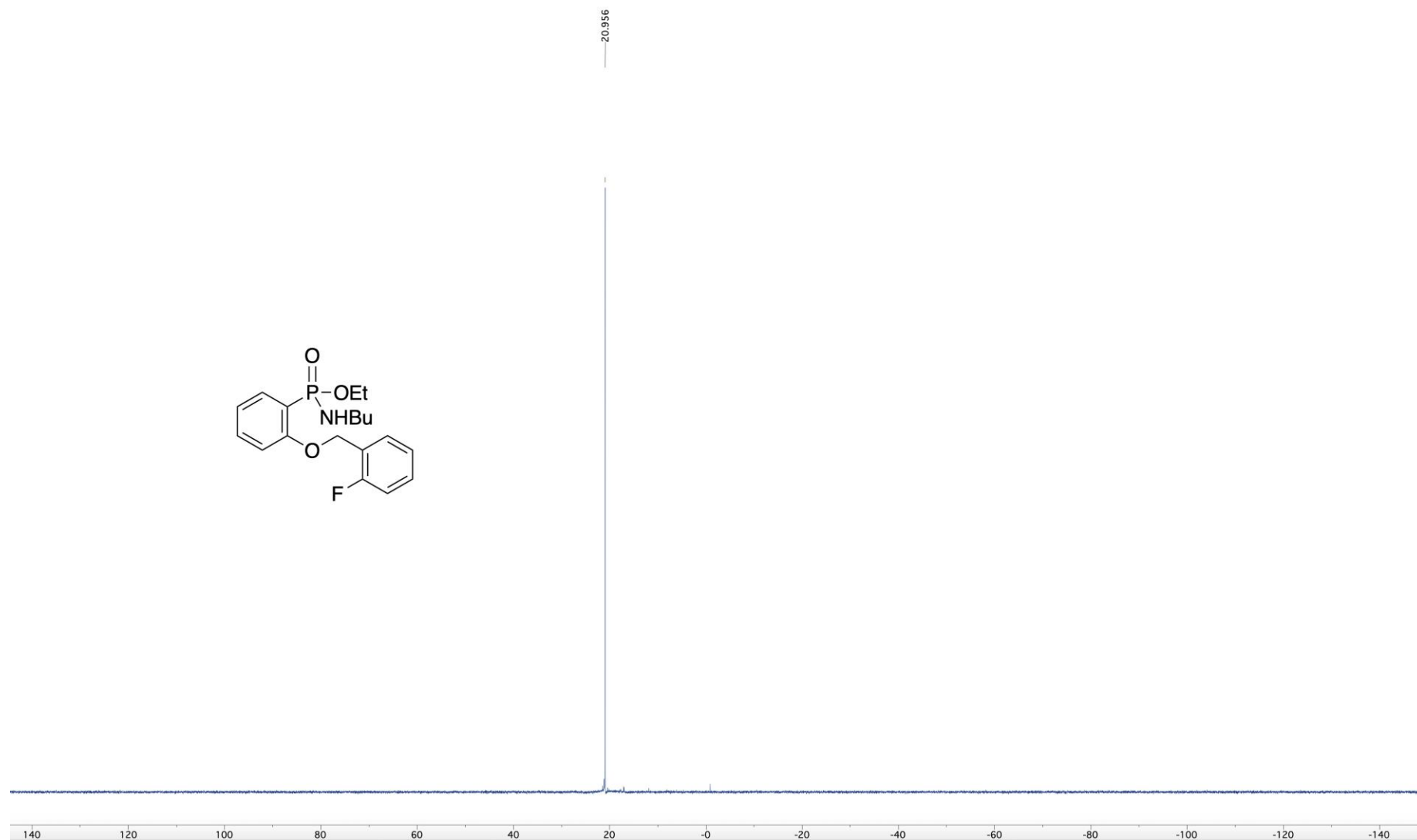


Figure S68. 100 MHz DEPTQ ^{13}C NMR spectrum of **21g**

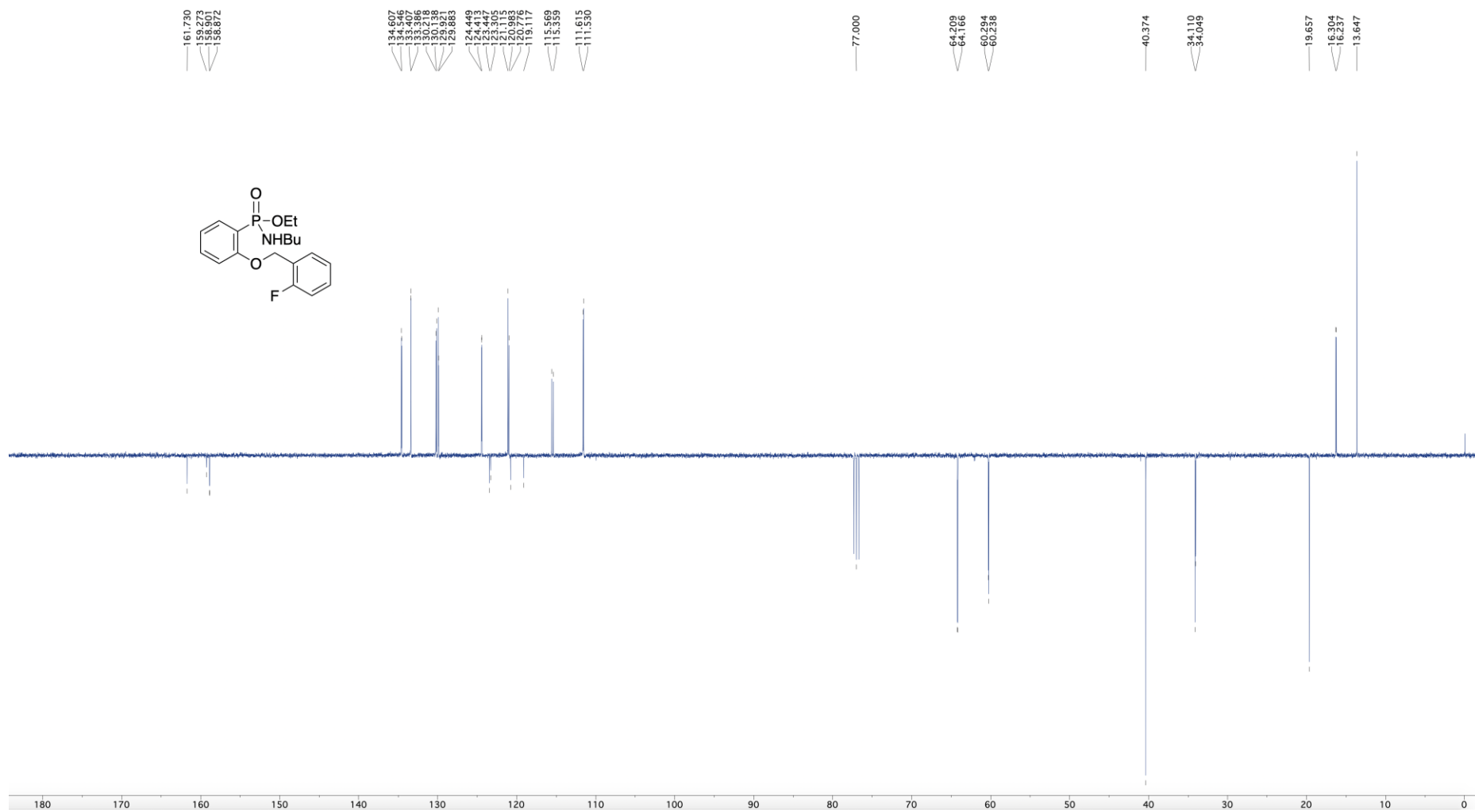


Figure S69. 400 MHz ^1H NMR spectrum of **21h**

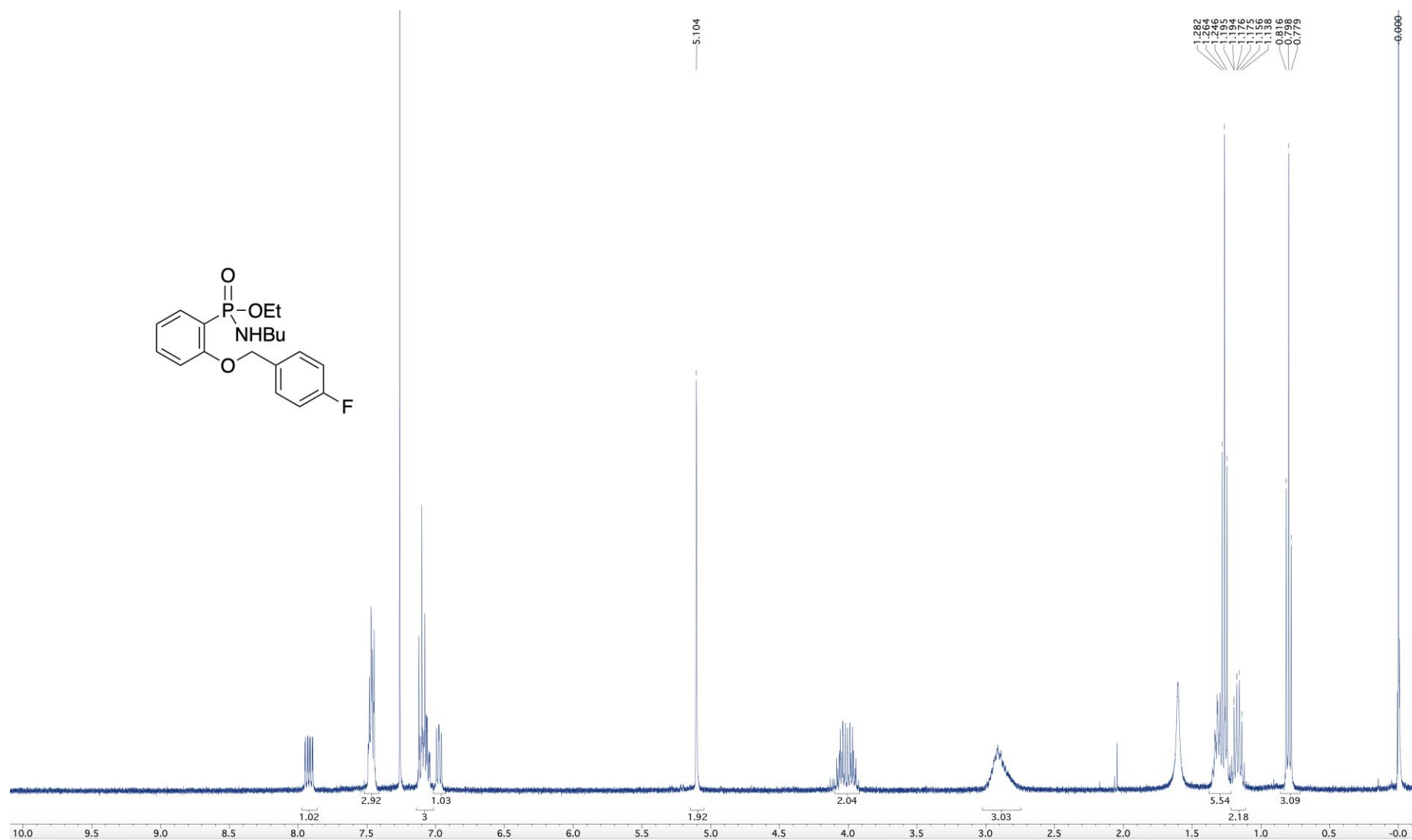


Figure S70. 376 MHz ^{19}F NMR spectrum of **21h**

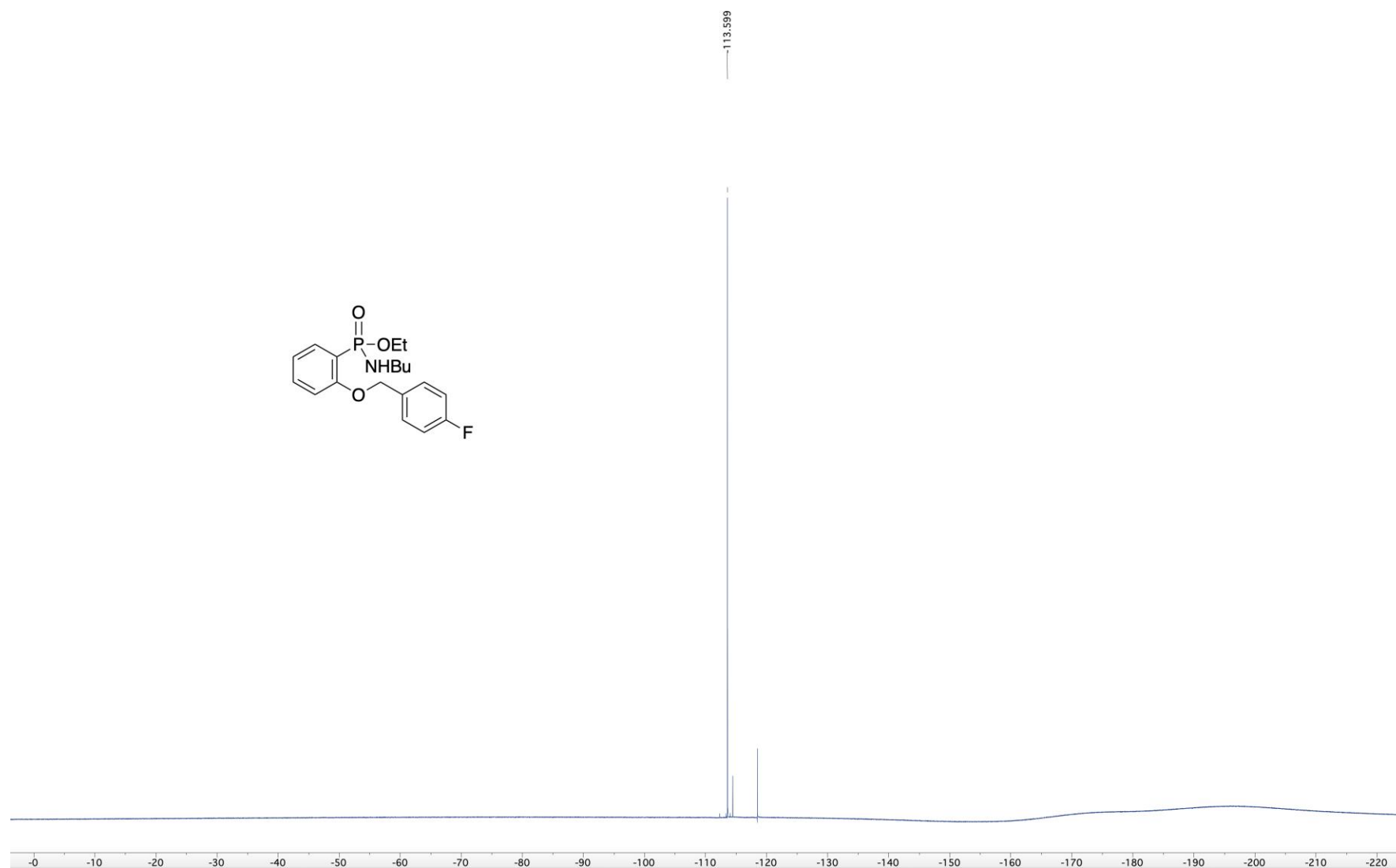


Figure S71. 162 MHz ^{31}P NMR spectrum of **21h**

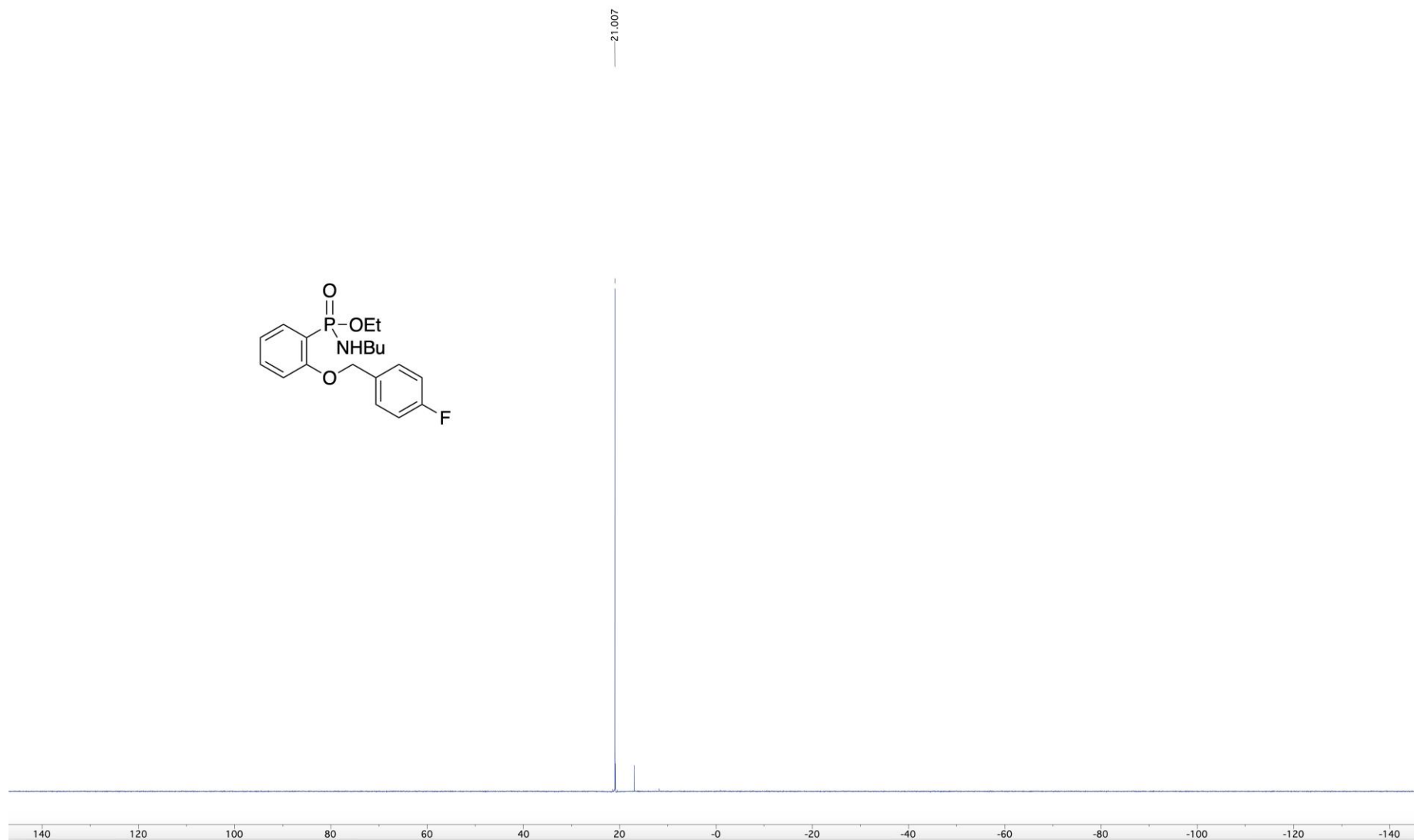


Figure S72. 100 MHz DEPTQ ^{13}C NMR spectrum of **21h**

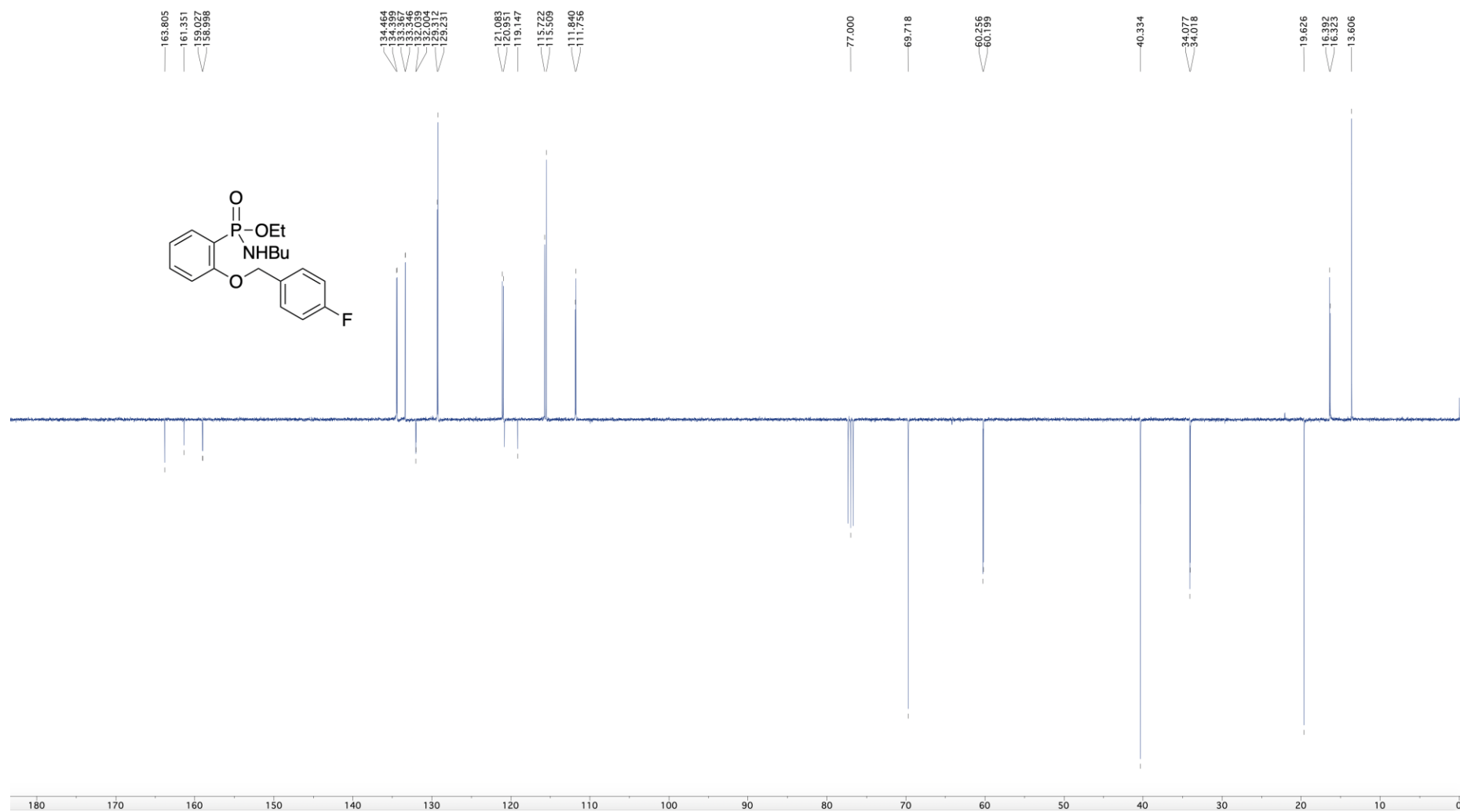


Figure S73. 400 MHz ^1H NMR spectrum of **21i**

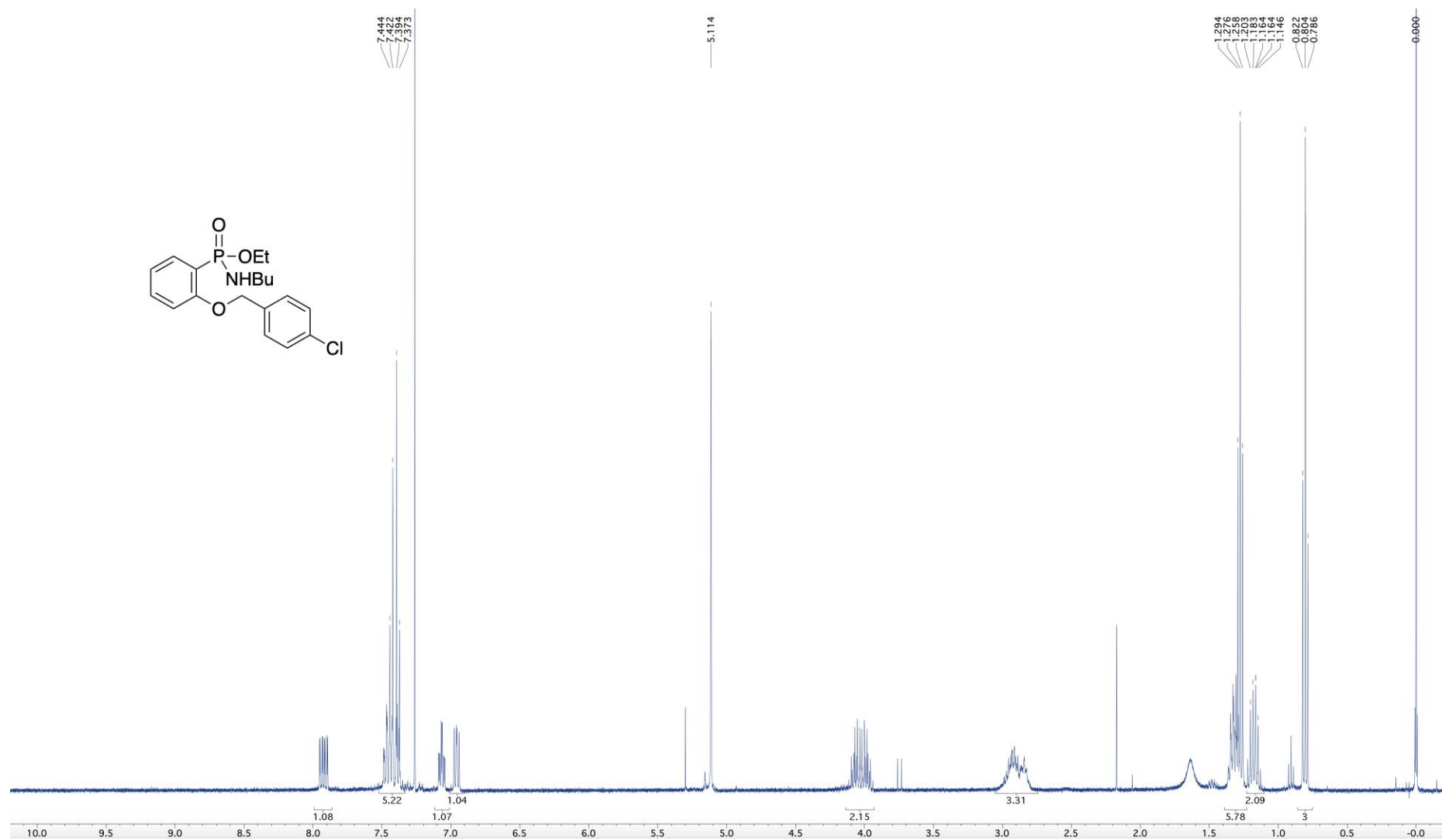


Figure S74. 162 MHz ^{31}P NMR spectrum of **21i**

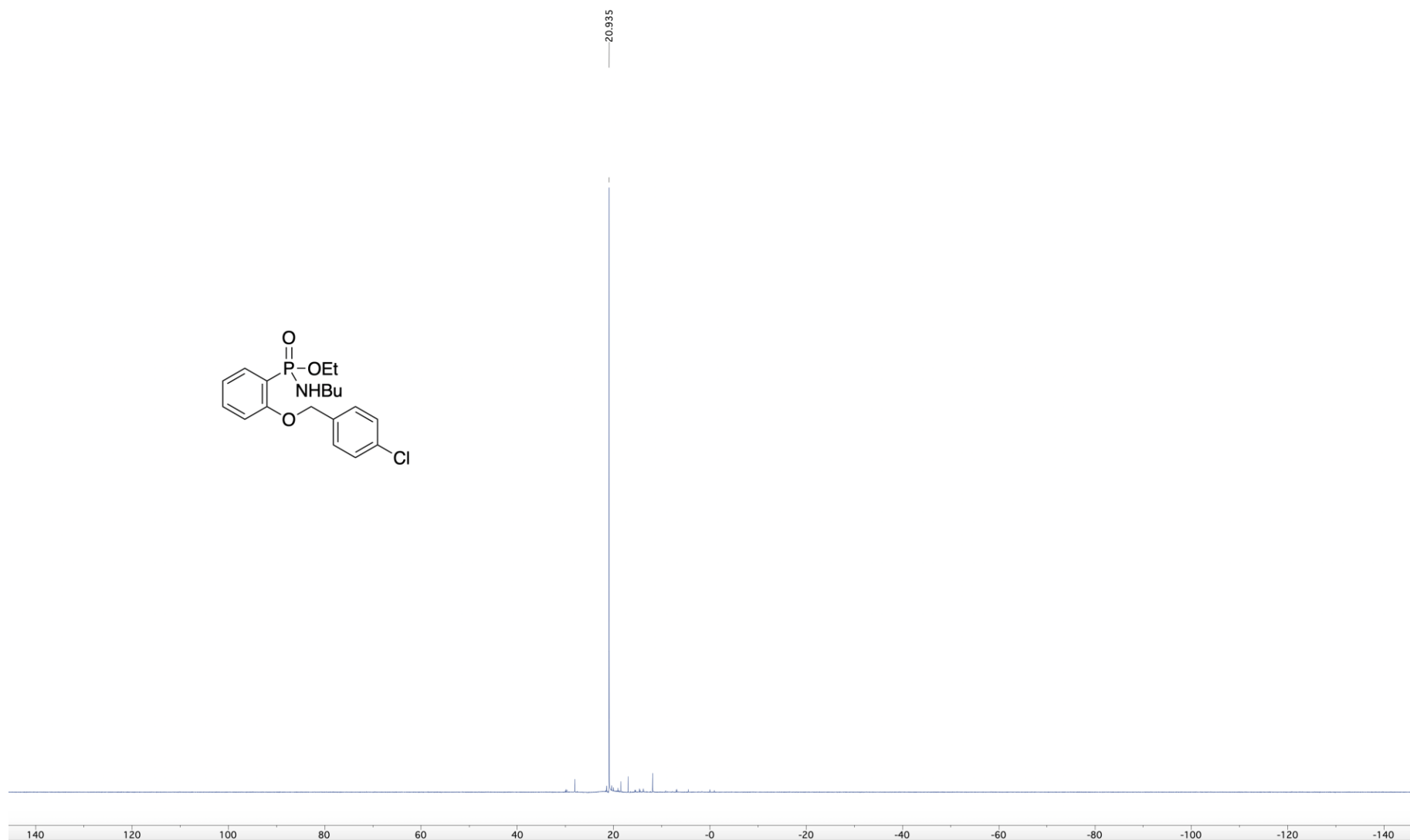


Figure S75. 100 MHz DEPTQ ^{13}C NMR spectrum of **21i**

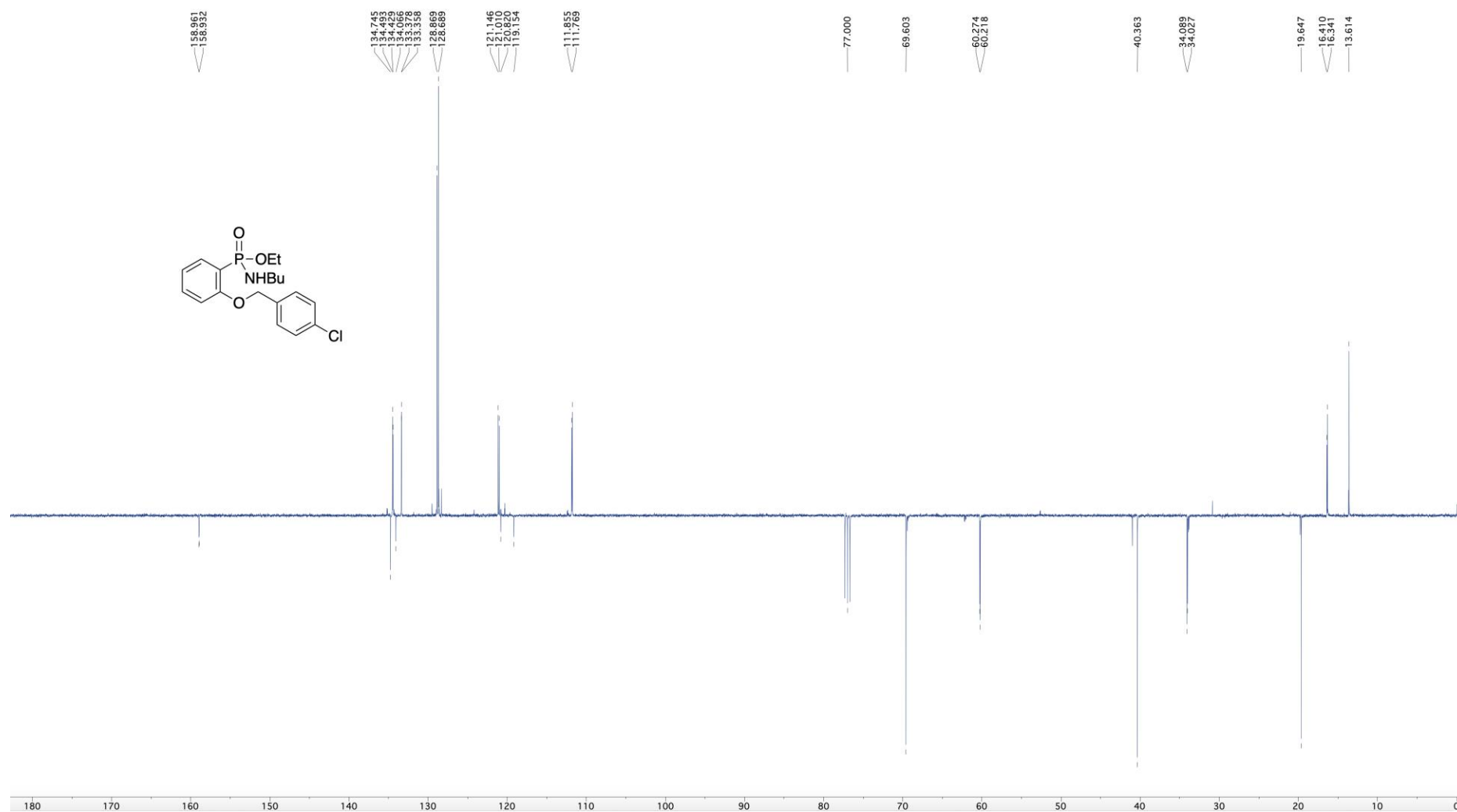


Figure S76. 400 MHz ^1H NMR spectrum of **21j**

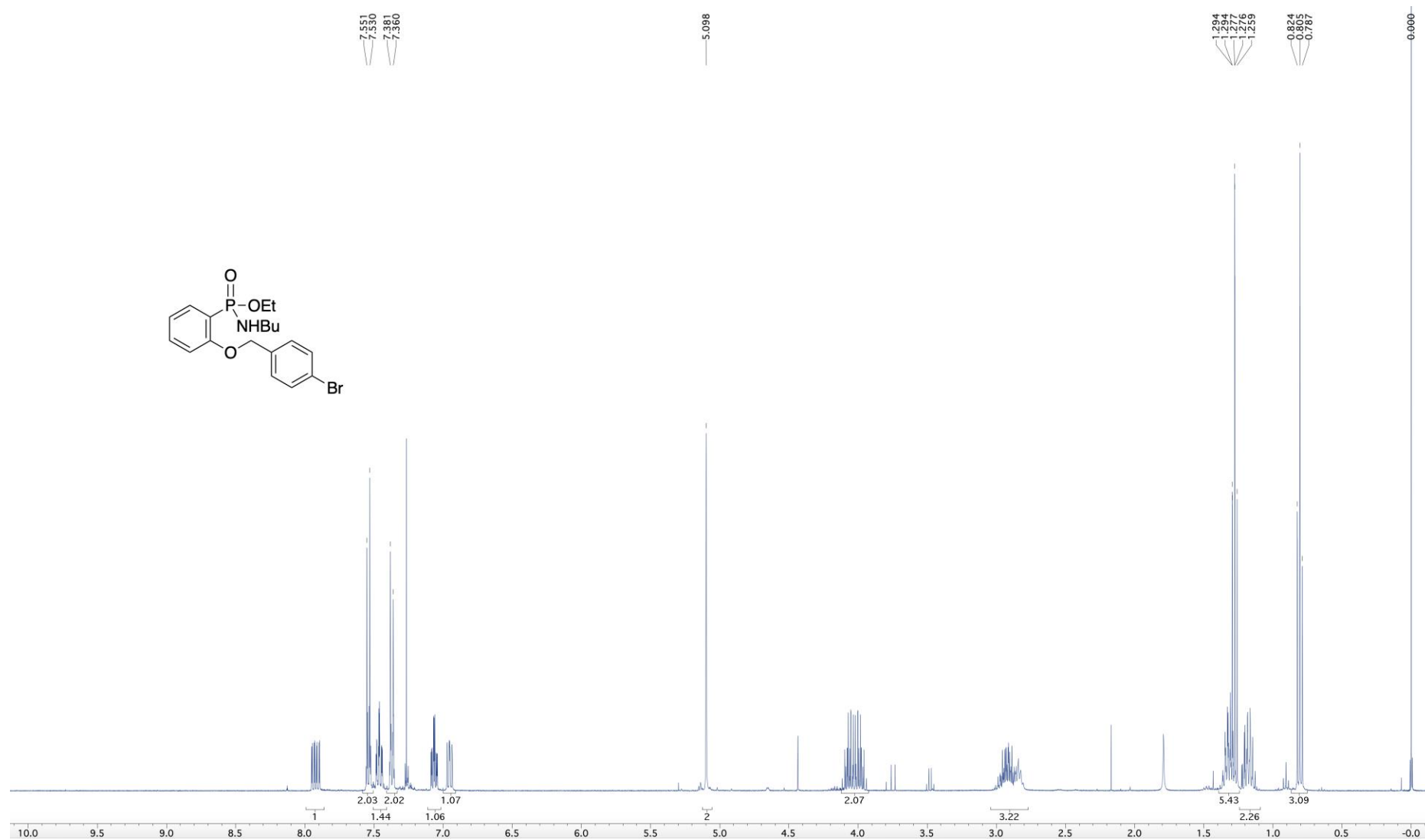


Figure S77. 162 MHz ^{31}P NMR spectrum of **21j**

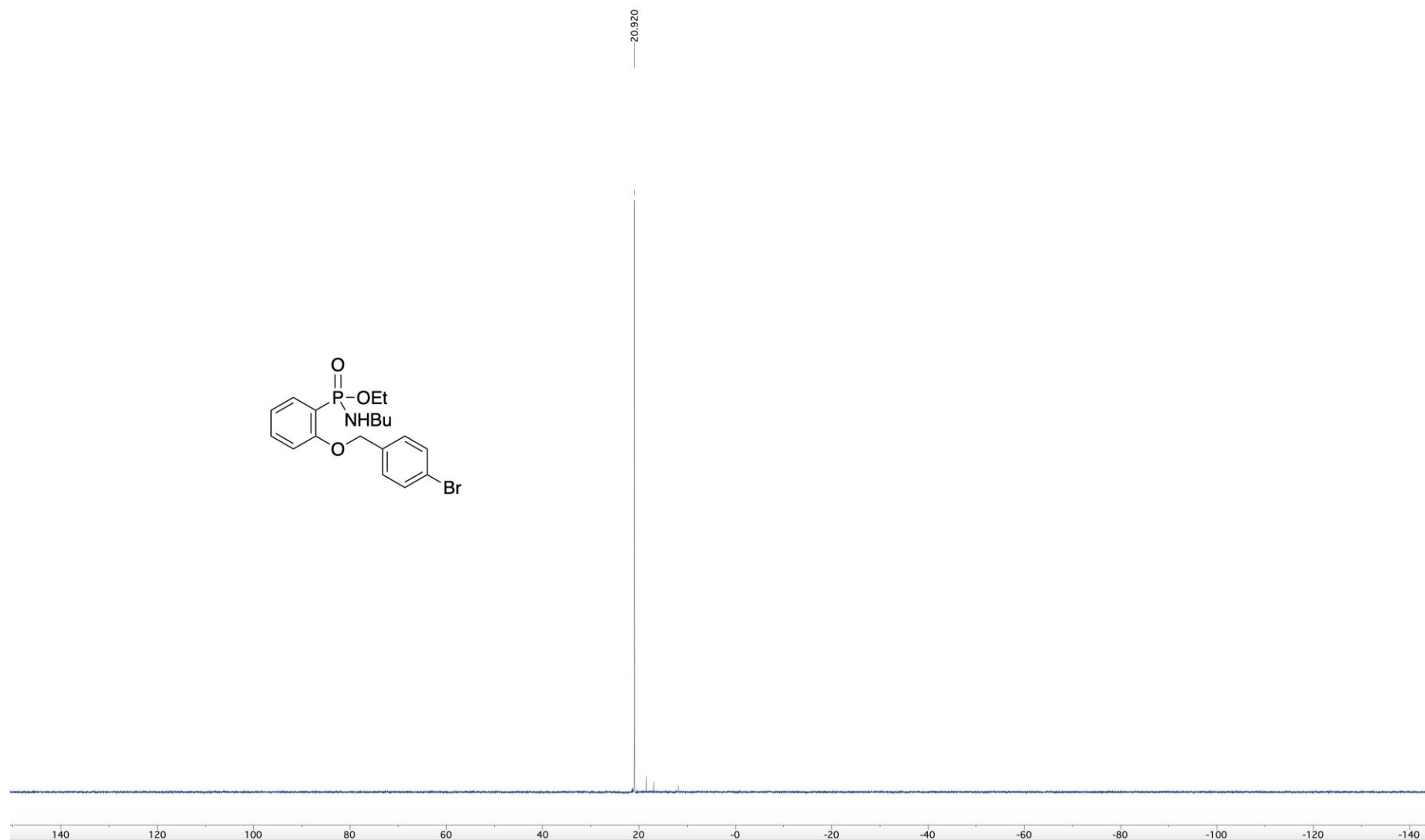


Figure S78. 100 MHz DEPTQ ^{13}C NMR spectrum of **21j**

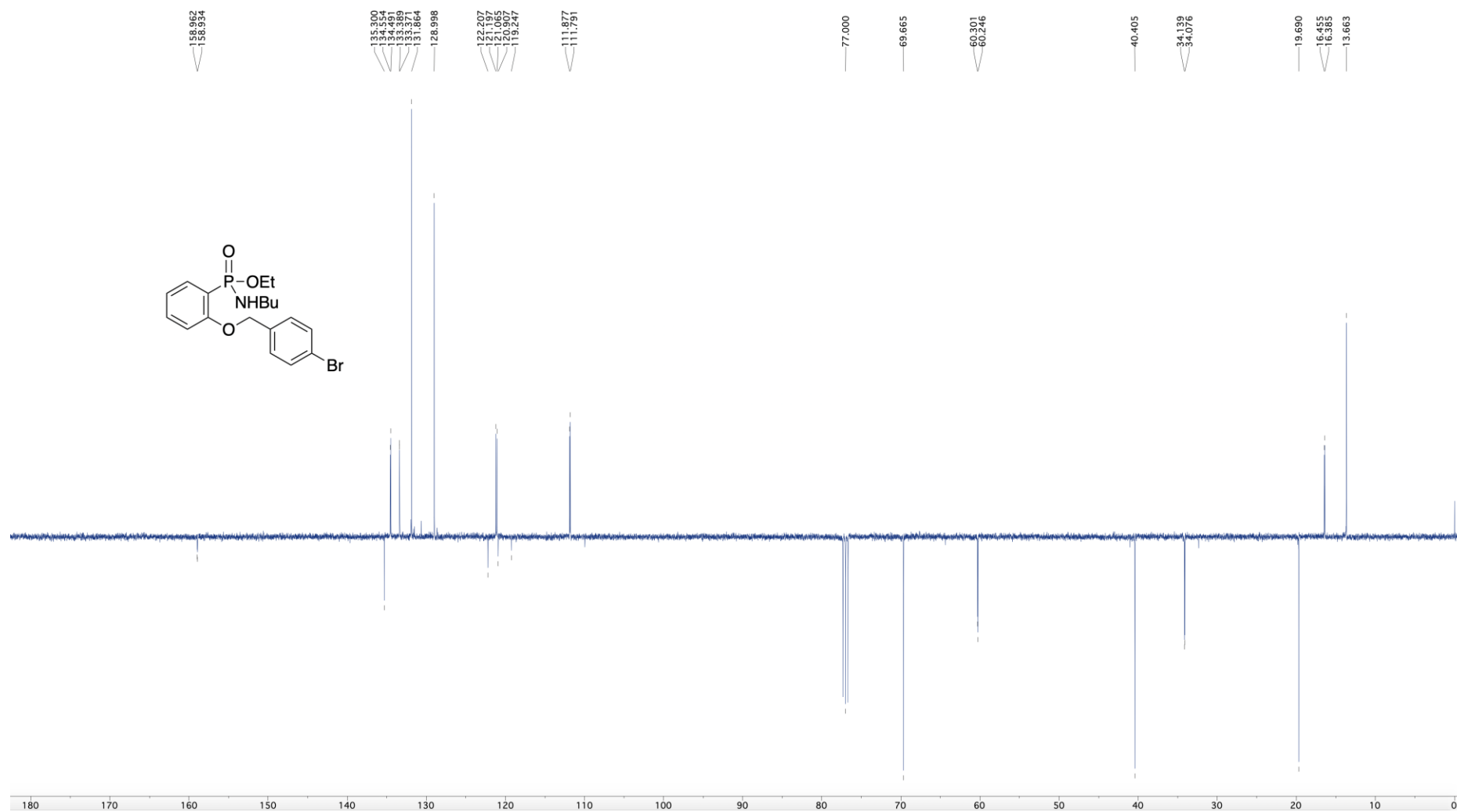


Figure S79. 400 MHz ^1H NMR spectrum of **21k**

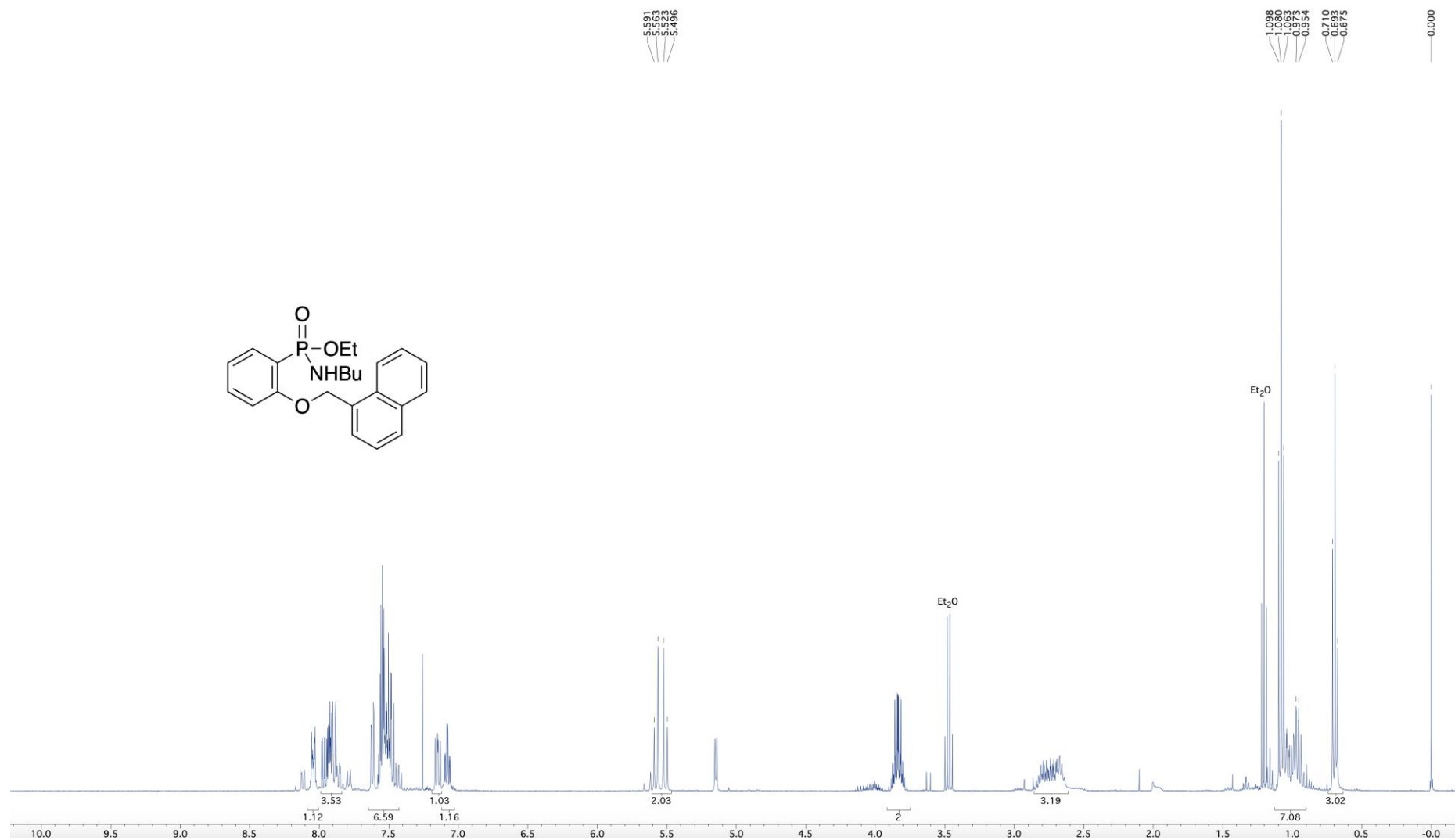
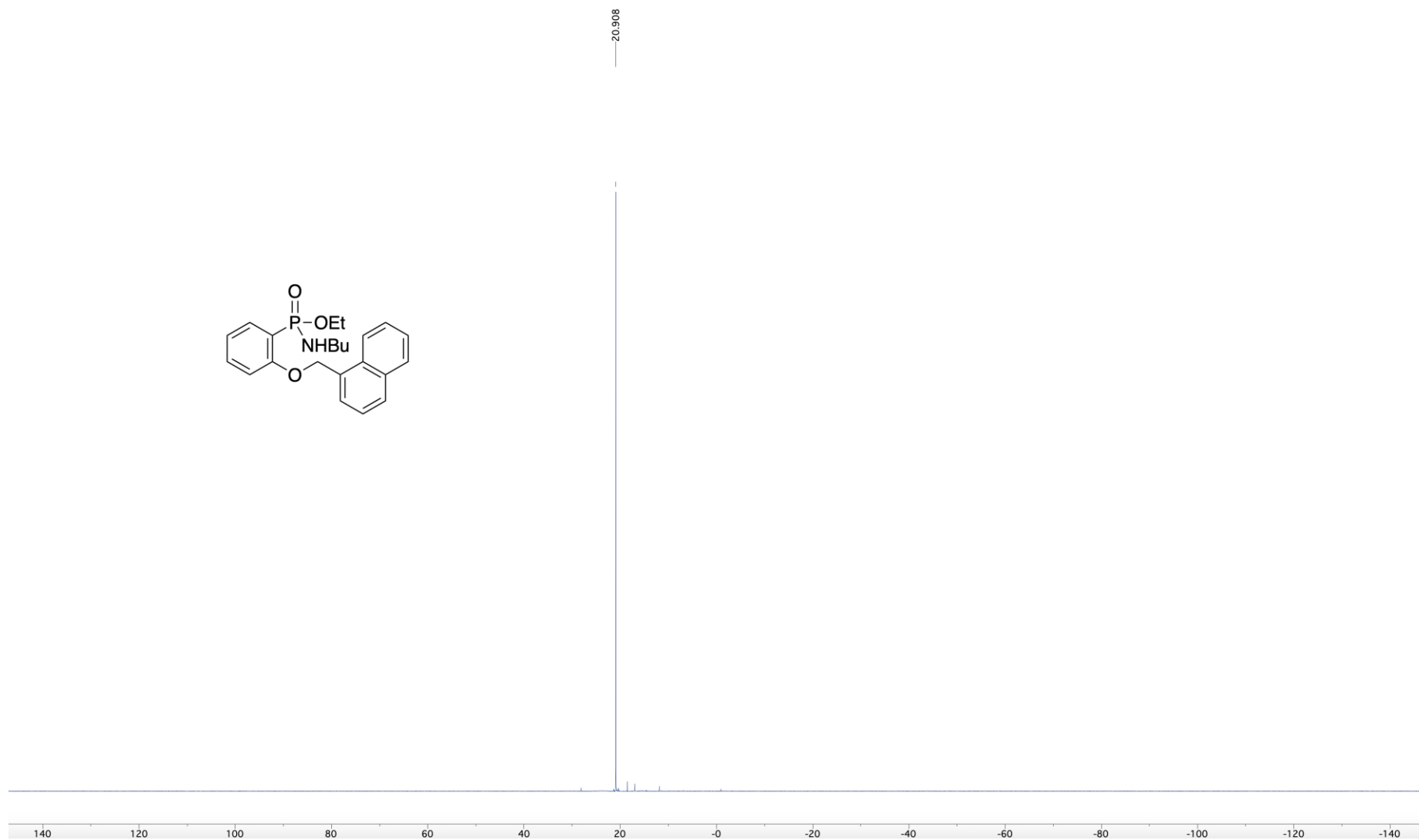


Figure S80. 162 MHz ^{31}P NMR spectrum of **21k**



CCOP(=O)(c1ccccc1)COC2=CC=CC=C2

159.128
159.099
141.94
141.29
139.29
139.25
139.15
139.12
139.06
138.96
138.50
136.94
136.54
135.98
131.004
120.872
119.152
111.455
111.372
77.000
68.781
60.161
60.103
40.197
33.970
33.911
19.506
16.212
16.148
13.605

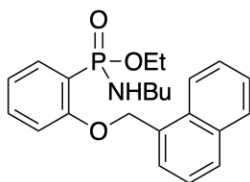


Figure S82. 400 MHz ^1H NMR spectrum of **211**

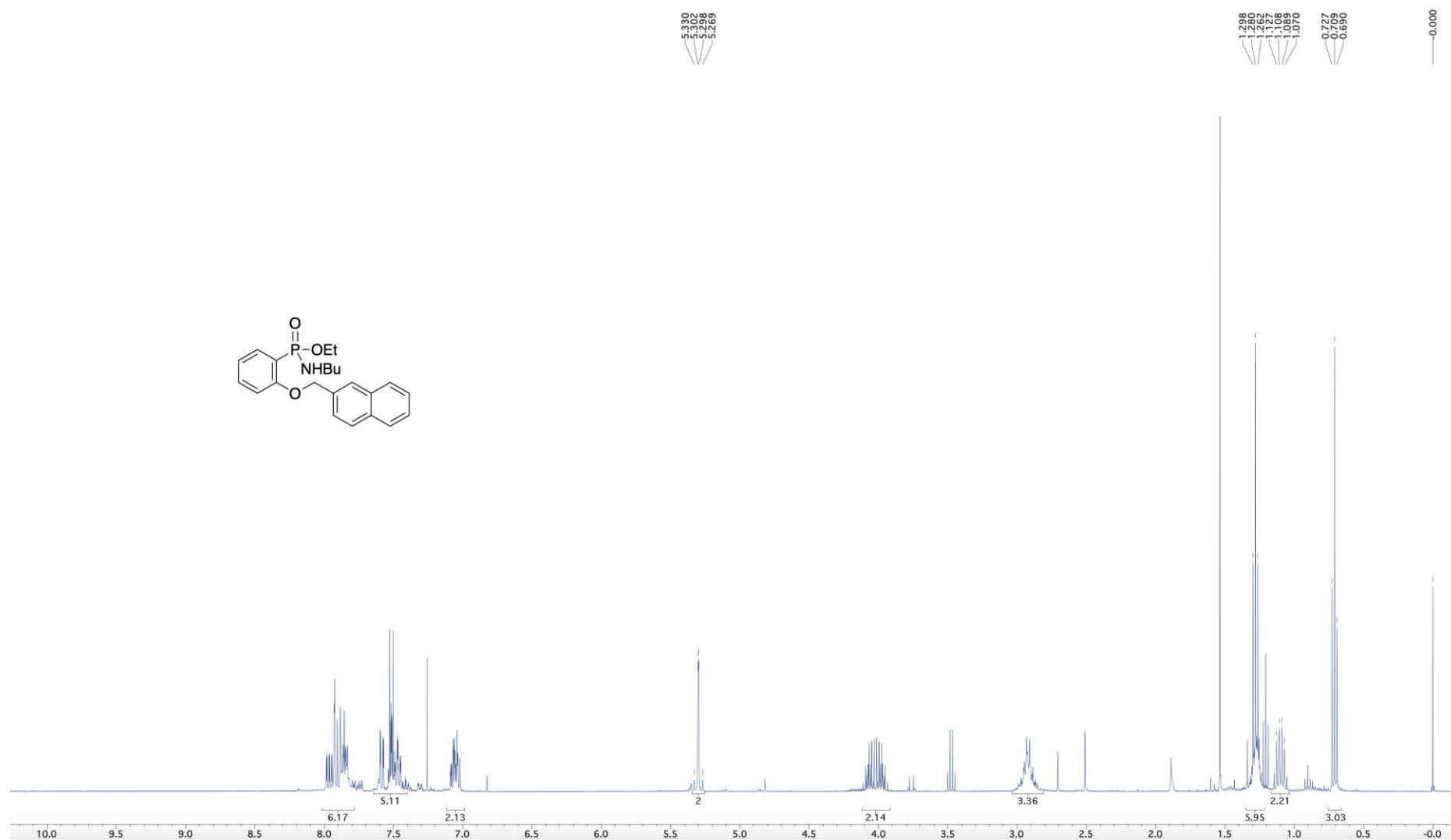
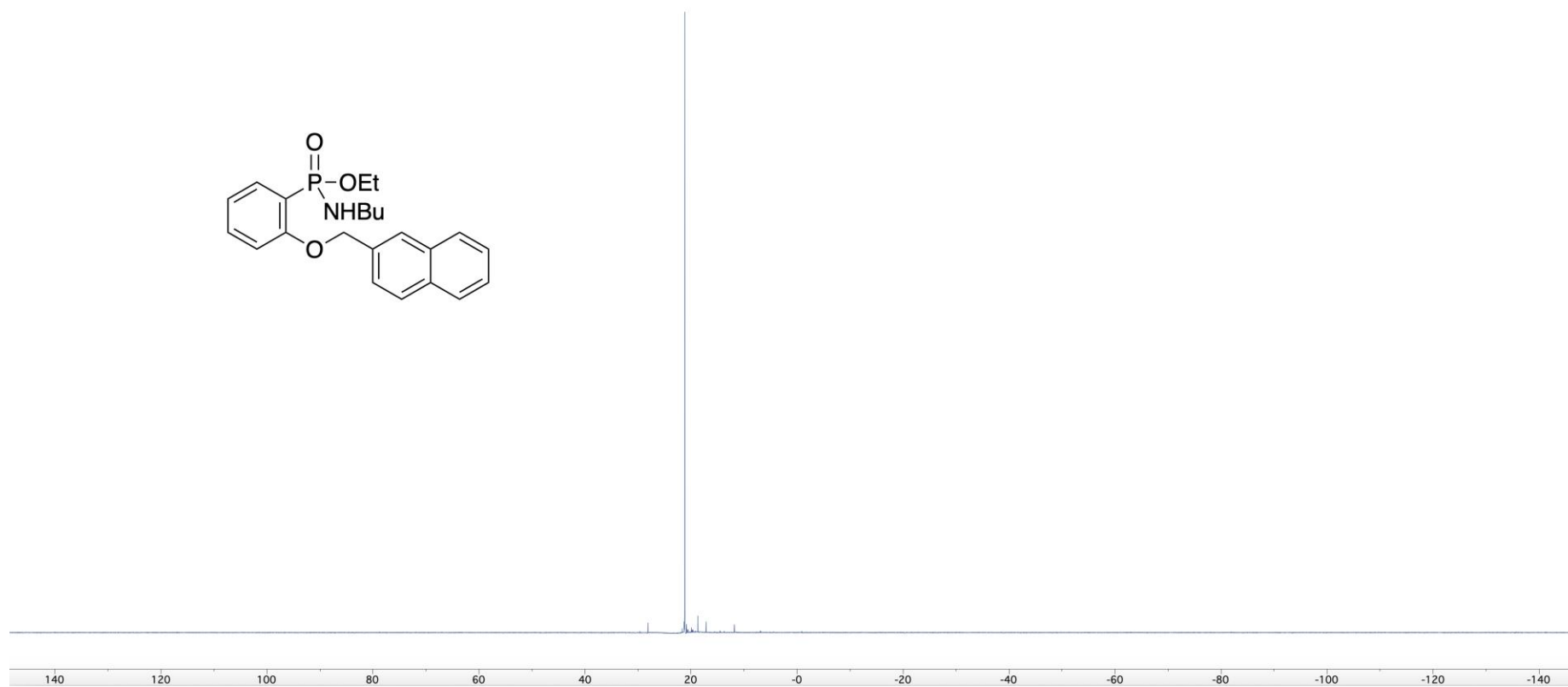


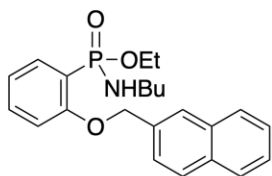
Figure S83. 162 MHz ^{31}P NMR spectrum of **211**



Chemical structure: CCOP(=O)(c1ccccc1)OCc2ccc3ccccc32

¹³C NMR spectrum (CDCl₃) showing peaks at the following chemical shifts (ppm):

Chemical Shift (ppm)
159.128
139.54
137.77
137.55
137.27
136.99
136.74
136.46
136.20
135.96
135.70
135.54
135.28
135.03
134.78
134.52
134.26
134.00
133.74
133.48
133.22
132.96
132.70
132.44
132.18
131.92
131.66
131.40
131.14
130.88
130.62
130.36
130.10
129.84
129.58
129.32
129.06
128.80
128.54
128.28
128.02
127.76
127.50
127.24
126.98
126.72
126.46
126.20
125.94
125.68
125.42
125.16
124.90
124.64
124.38
124.12
123.86
123.60
123.34
123.08
122.82
122.56
122.30
122.04
121.78
121.52
121.26
121.00
120.74
120.48
120.22
119.96
119.70
119.44
119.18
118.92
118.66
118.40
118.14
117.88
117.62
117.36
117.10
116.84
116.58
116.32
116.06
115.80
115.54
115.28
115.02
114.76
114.50
114.24
113.98
113.72
113.46
113.20
112.94
112.68
112.42
112.16
111.90
111.64
111.38
111.12
110.86
110.60
110.34
110.08
109.82
109.56
109.30
109.04
108.78
108.52
108.26
108.00
107.74
107.48
107.22
106.96
106.70
106.44
106.18
105.92
105.66
105.40
105.14
104.88
104.62
104.36
104.10
103.84
103.58
103.32
103.06
102.80
102.54
102.28
102.02
101.76
101.50
101.24
100.98
100.72
100.46
100.20
99.94
99.68
99.42
99.16
98.90
98.64
98.38
98.12
97.86
97.60
97.34
97.08
96.82
96.56
96.30
96.04
95.78
95.52
95.26
95.00
94.74
94.48
94.22
93.96
93.70
93.44
93.18
92.92
92.66
92.40
92.14
91.88
91.62
91.36
91.10
90.84
90.58
90.32
90.06
89.80
89.54
89.28
89.02
88.76
88.50
88.24
87.98
87.72
87.46
87.20
86.94
86.68
86.42
86.16
85.90
85.64
85.38
85.12
84.86
84.60
84.34
84.08
83.82
83.56
83.30
83.04
82.78
82.52
82.26
82.00
81.74
81.48
81.22
80.96
80.70
80.44
80.18
79.92
79.66
79.40
79.14
78.88
78.62
78.36
78.10
77.84
77.58
77.32
77.06
76.80
76.54
76.28
76.02
75.76
75.50
75.24
74.98
74.72
74.46
74.20
73.94
73.68
73.42
73.16
72.90
72.64
72.38
72.12
71.86
71.60
71.34
71.08
70.82
70.56
70.30
70.04
69.78
69.52
69.26
69.00
68.74
68.48



CCOP(=O)(c1ccccc1)OCc2ccsc2

Chemical structure of the compound is shown above the spectrum. The structure is a phosphonate ester derivative, specifically ethyl 2-(2-(benzyloxy)thiophen-5-yl)phosphonate, which is a derivative of the active ingredient in the pesticide mentioned in the text.

The ^1H NMR spectrum (CDCl₃) shows the following peaks and integrations:

Chemical Shift (ppm)	Integration
~8.0	1.06
~7.2	1.02
~7.0	4.32
~5.3	2.06
~4.0	2.33
~3.0	3.55
~1.3	8.27
~1.0	3.18

The spectrum displays characteristic signals for the compound, including aromatic protons (7.0-8.0 ppm), the thiophene ring protons (5.3 ppm), the benzyloxy group protons (4.0 ppm), the ethyl group protons (3.0 ppm), and the phosphonate group protons (1.0-1.3 ppm).

Figure S86. 162 MHz ^{31}P NMR spectrum of **21m**

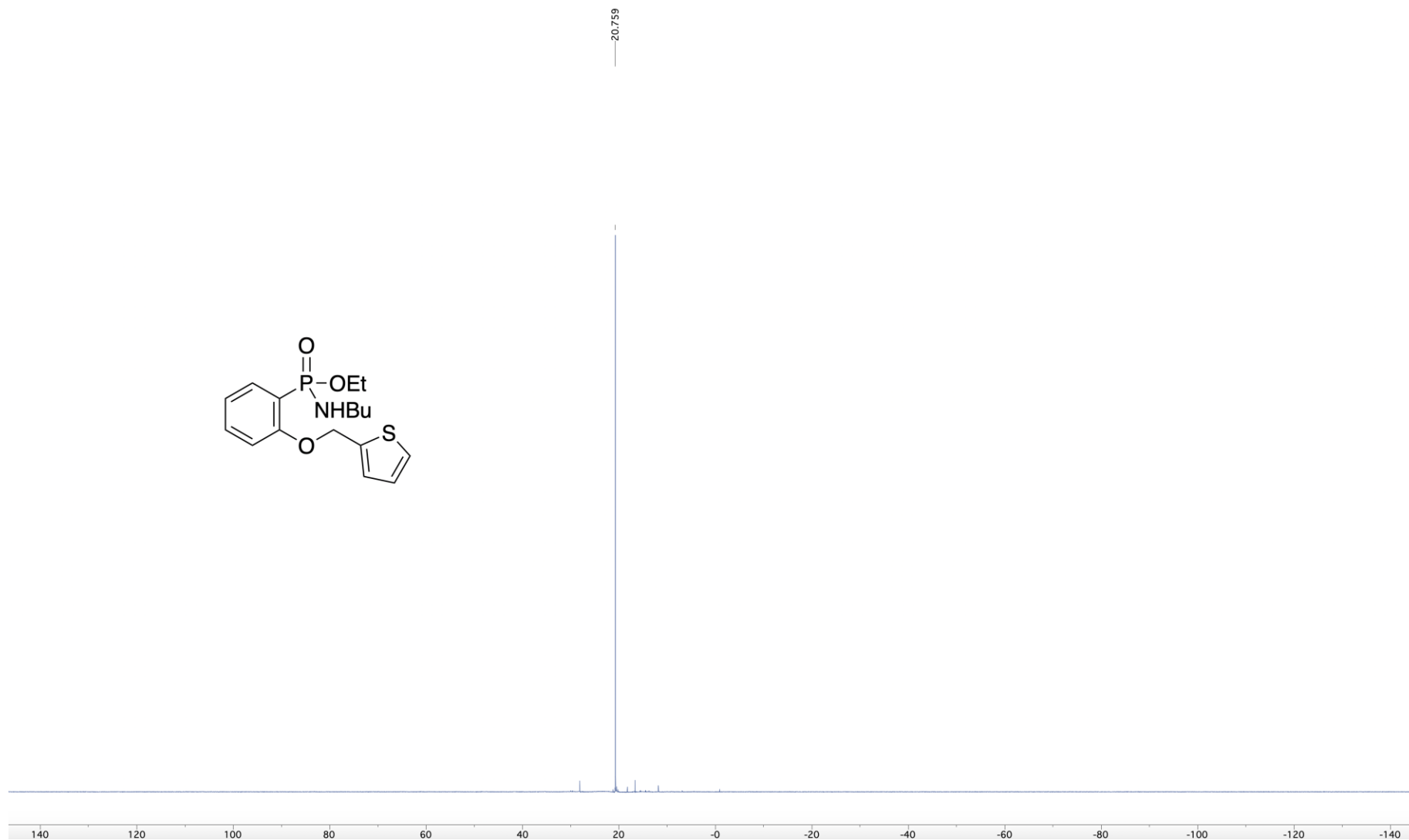


Figure S87. 100 MHz DEPTQ ^{13}C NMR spectrum of **21m**

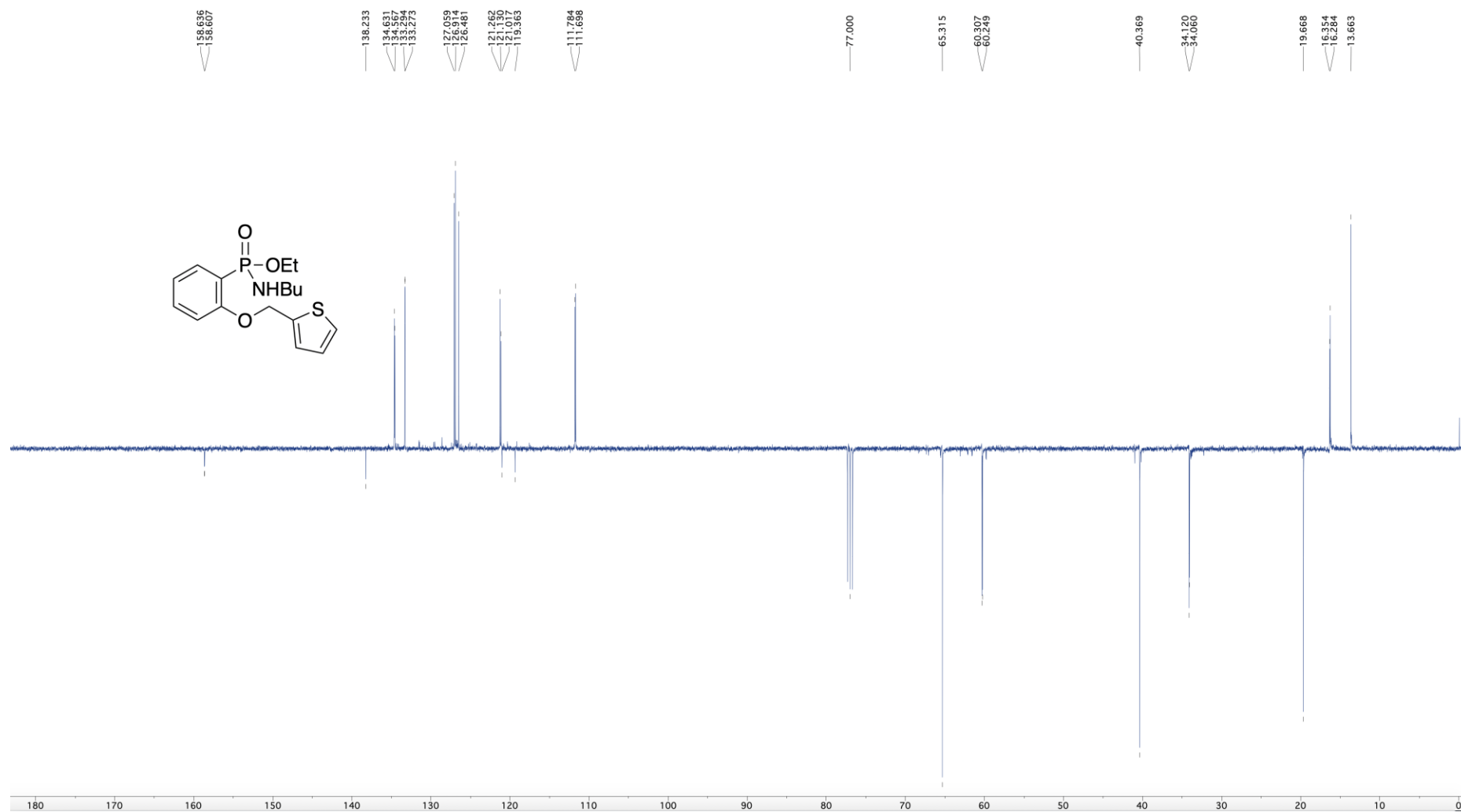


Figure S88. 400 MHz ^1H NMR spectrum of **23c**

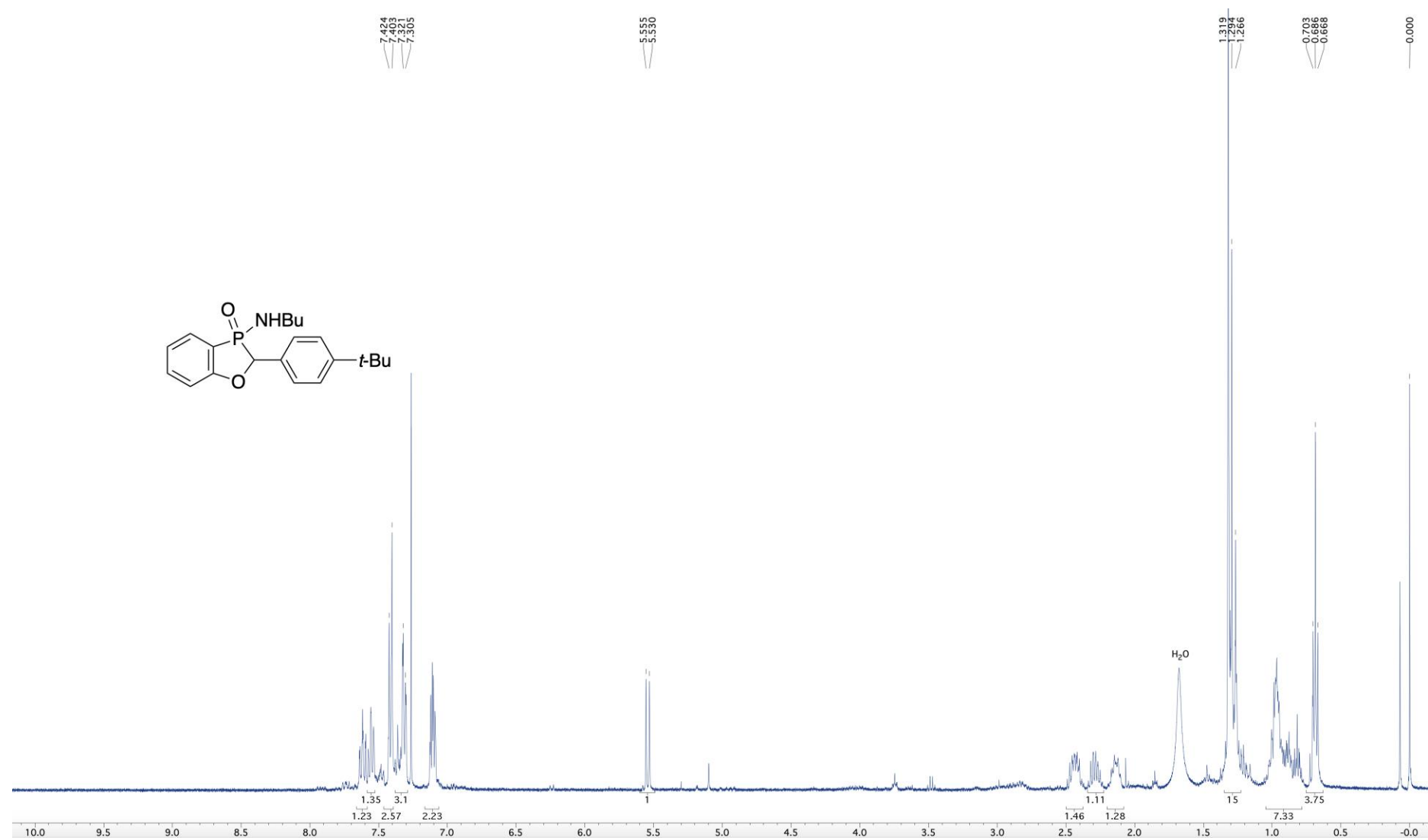


Figure S89. 162 MHz ^{31}P NMR spectrum of **23c**

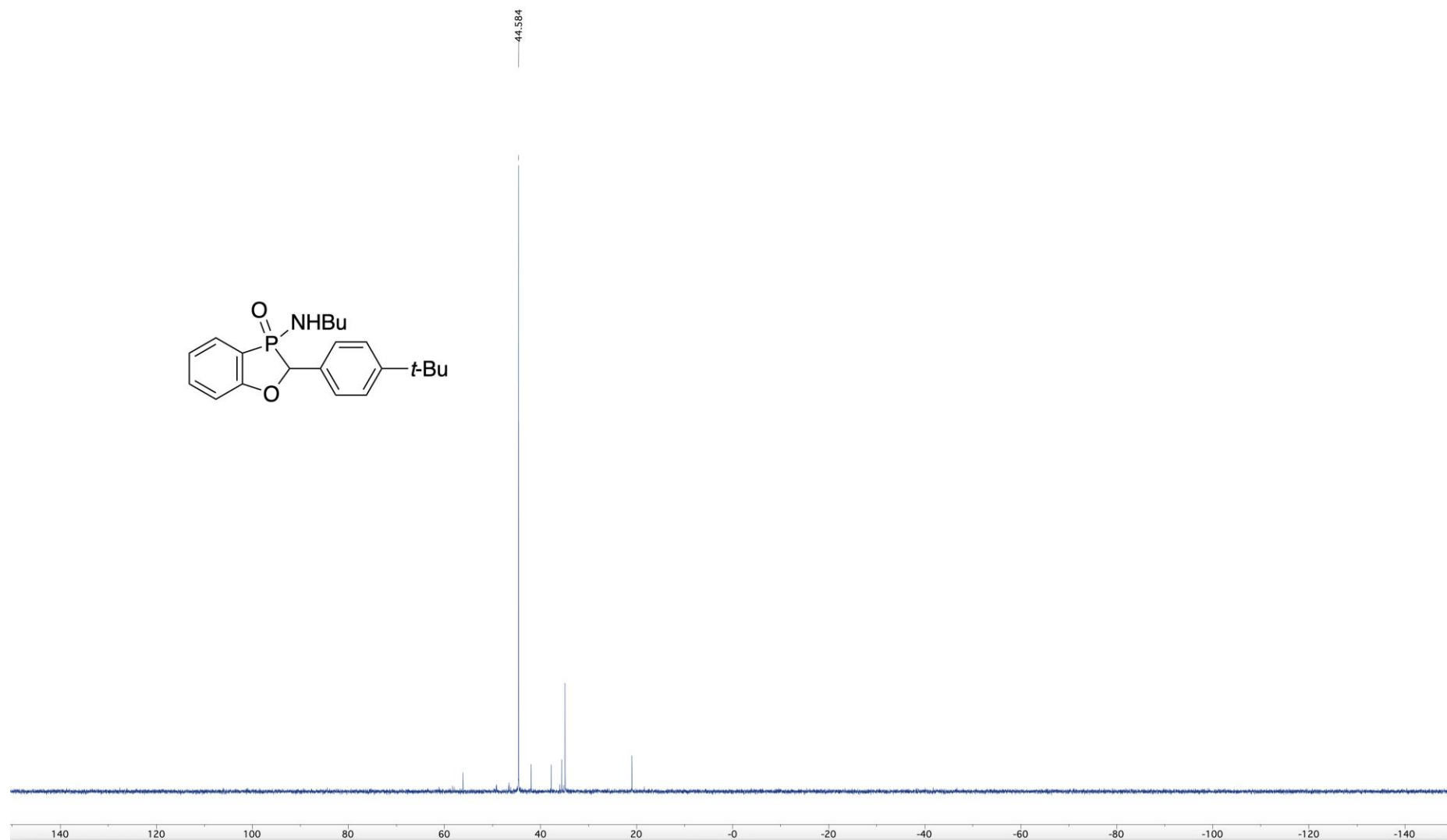


Figure S90. 176 MHz DEPTQ ^{13}C NMR spectrum of **23c**

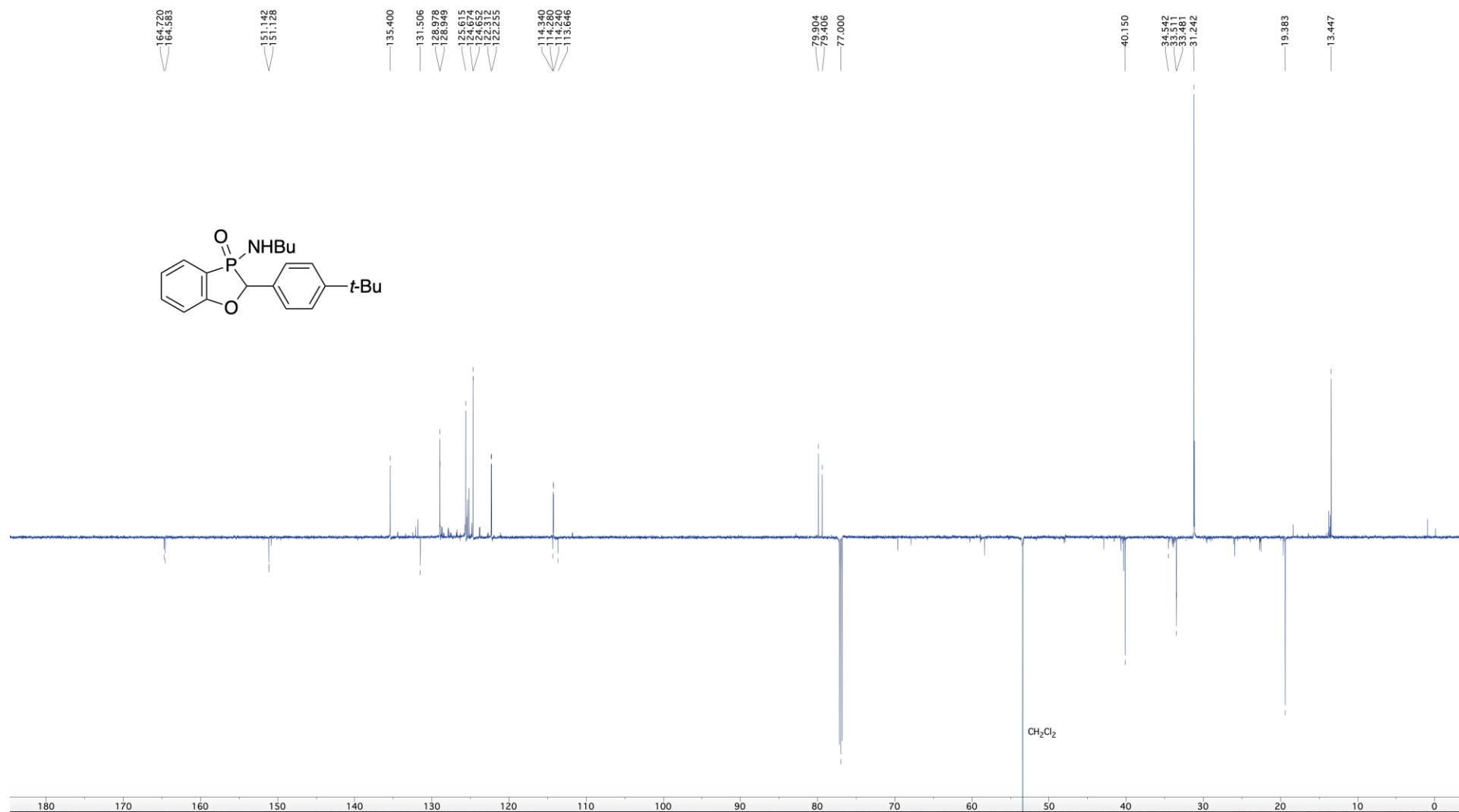


Figure S91. 400 MHz ^1H NMR spectrum of **23d**

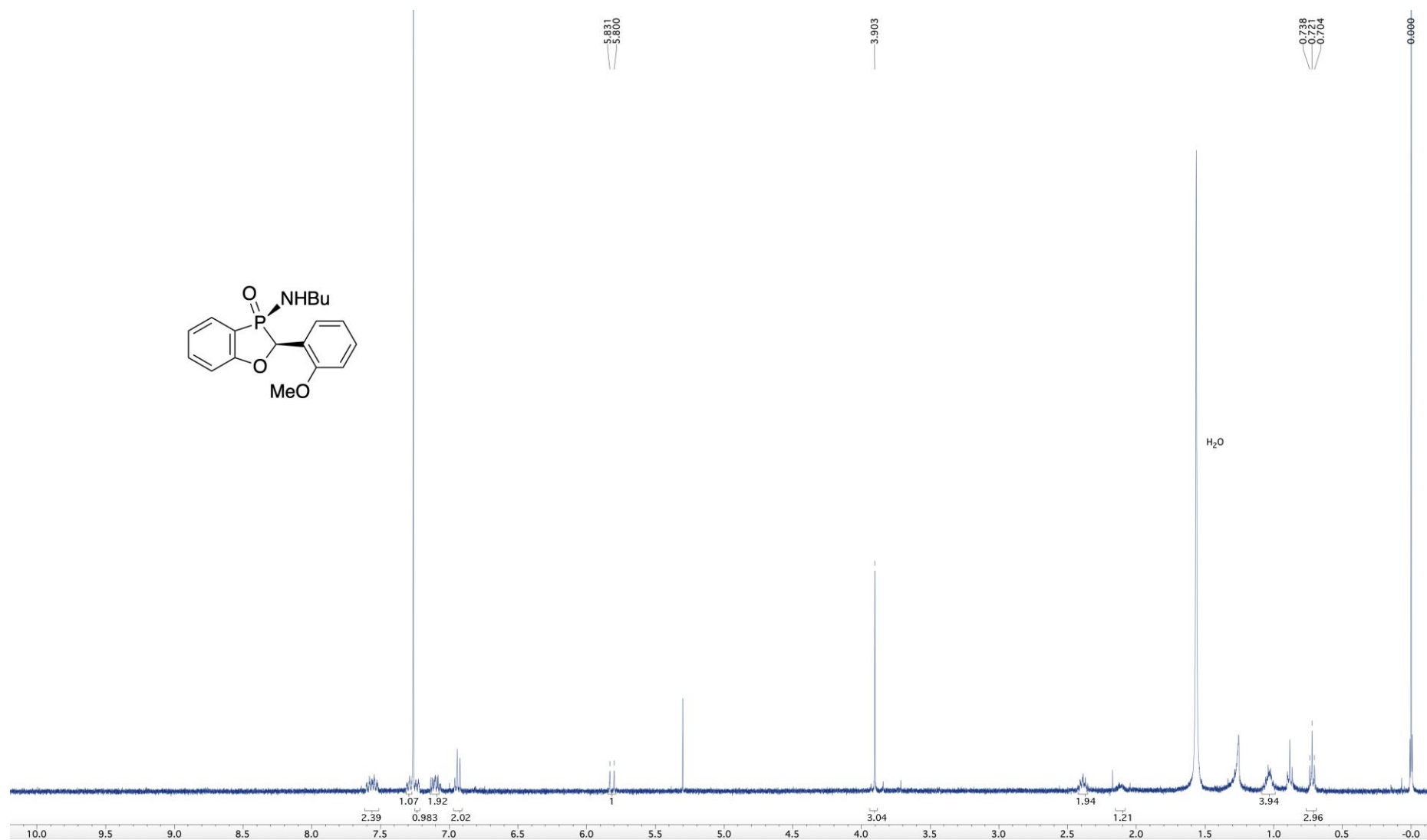


Figure S92. 162 MHz ^{31}P NMR spectrum of **23d**

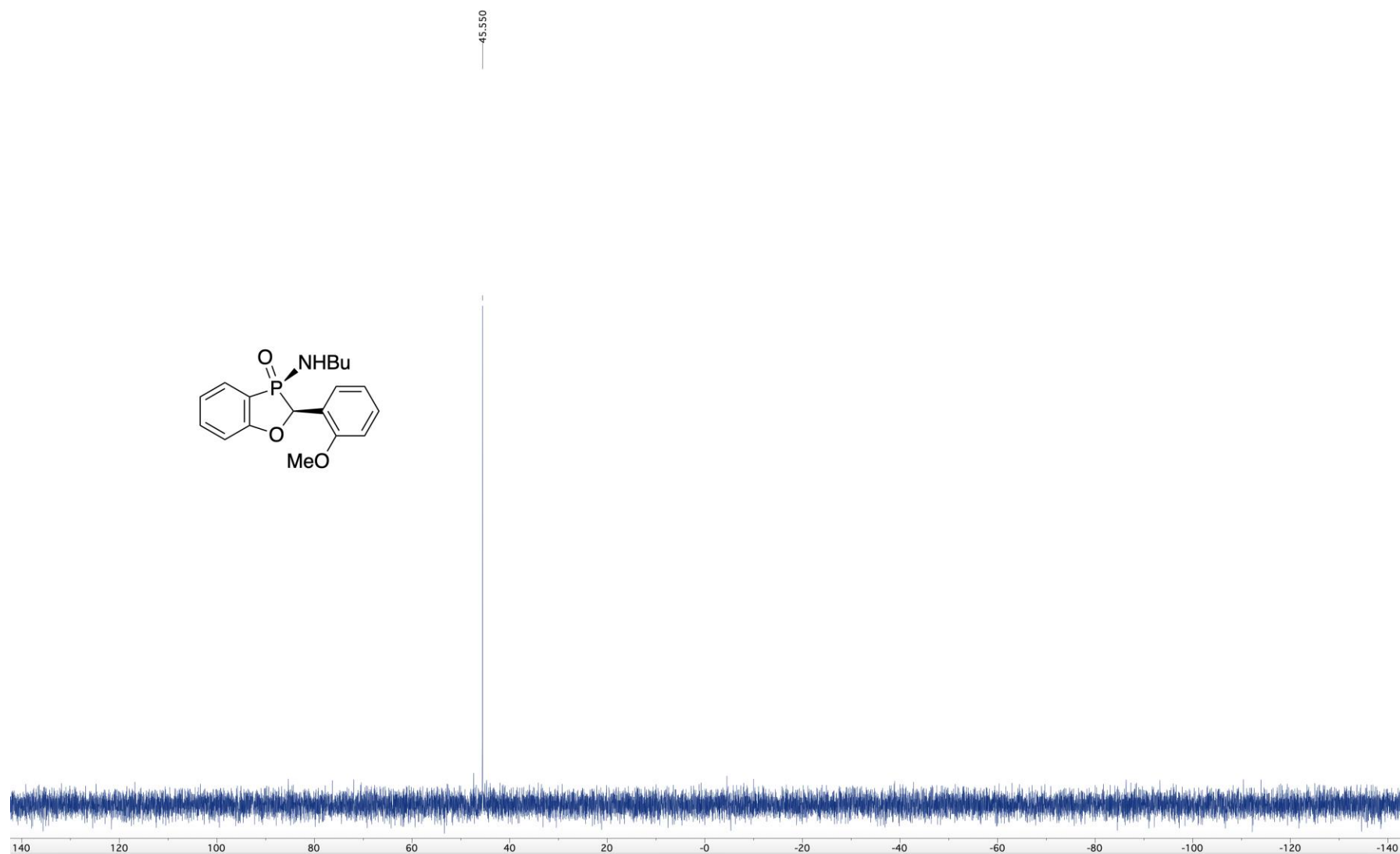


Figure S93. 400 MHz ^1H NMR spectrum of **23e**

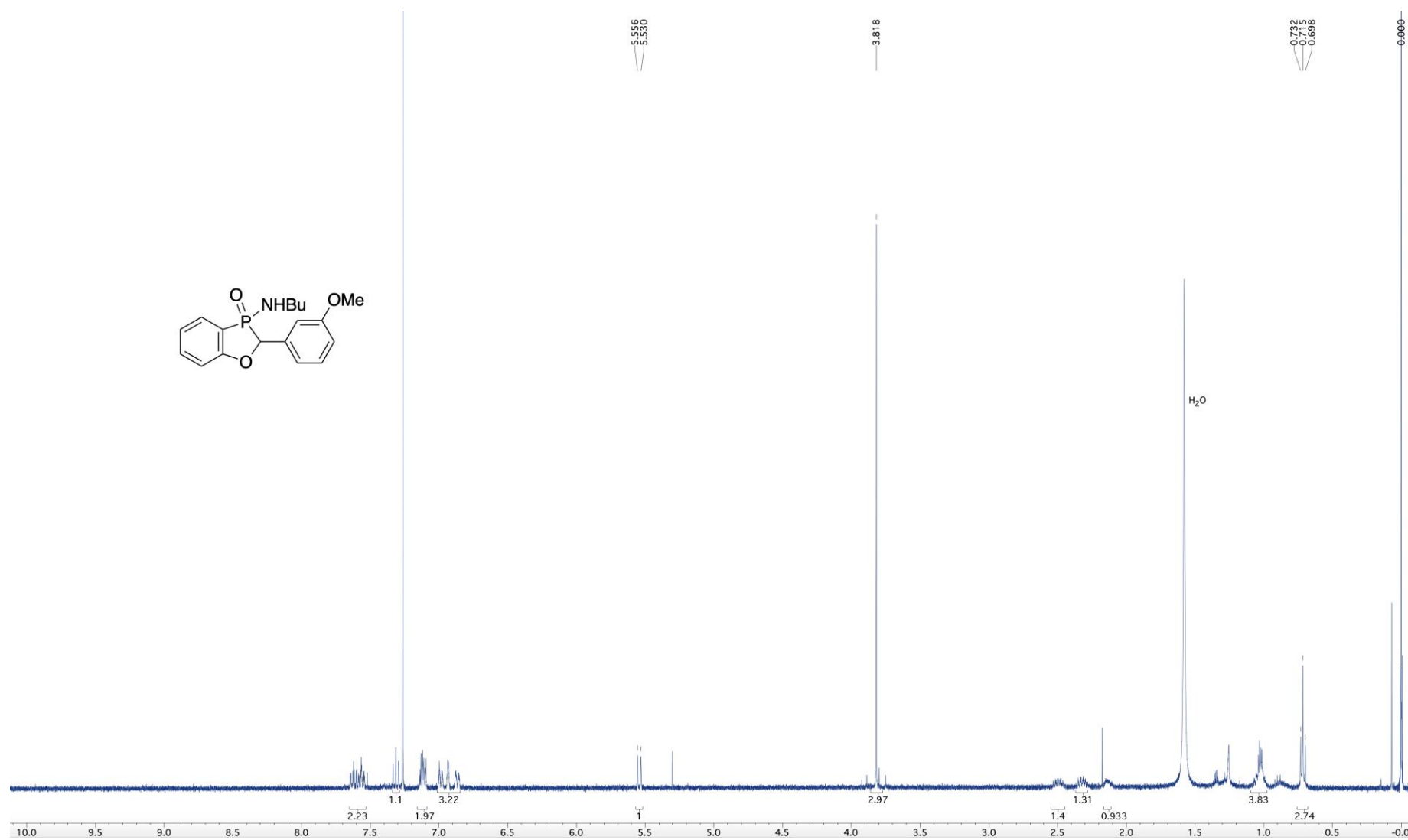


Figure S94. 162 MHz ^{31}P NMR spectrum of **23e**

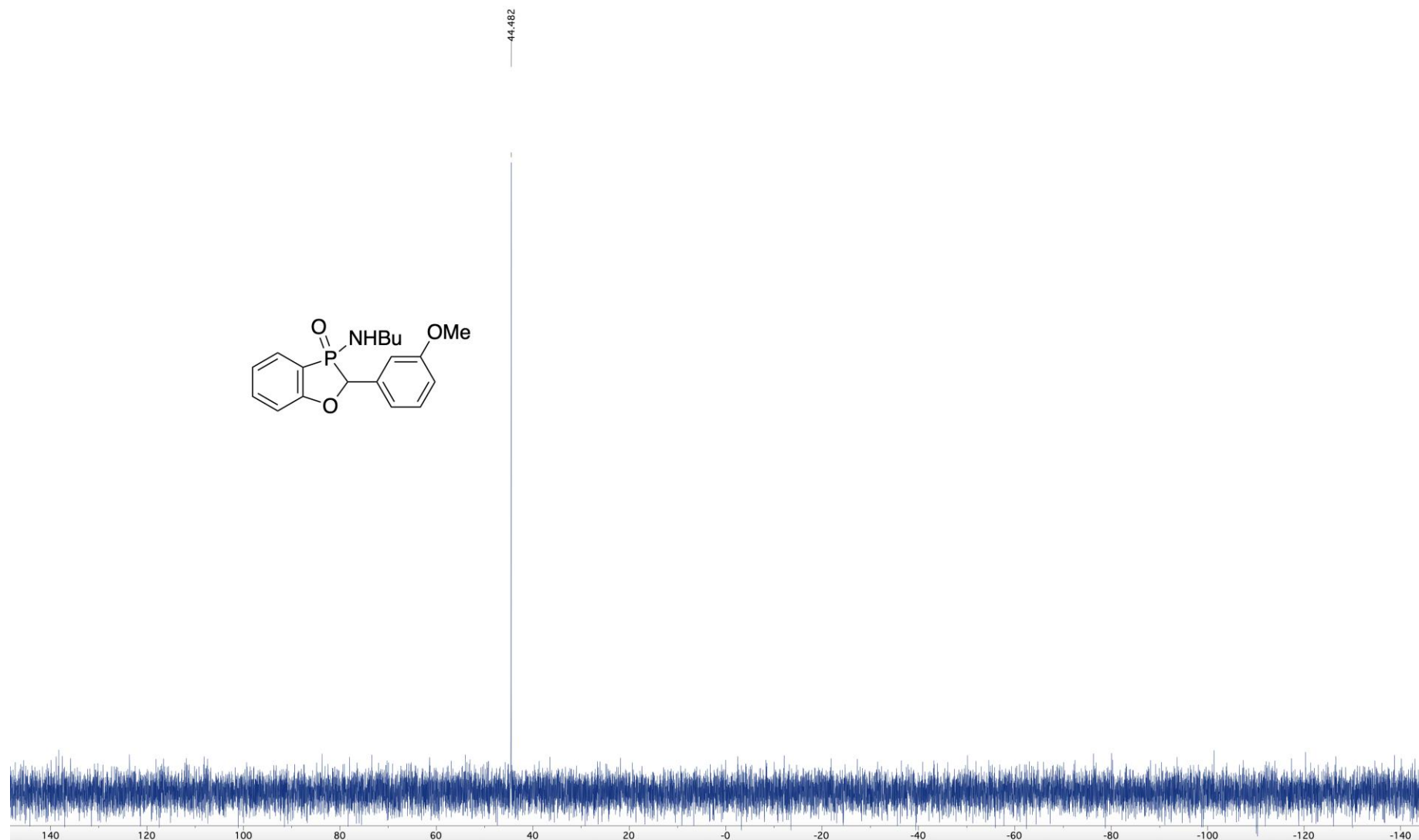


Figure S95. 400 MHz ^1H NMR spectrum of **23g**

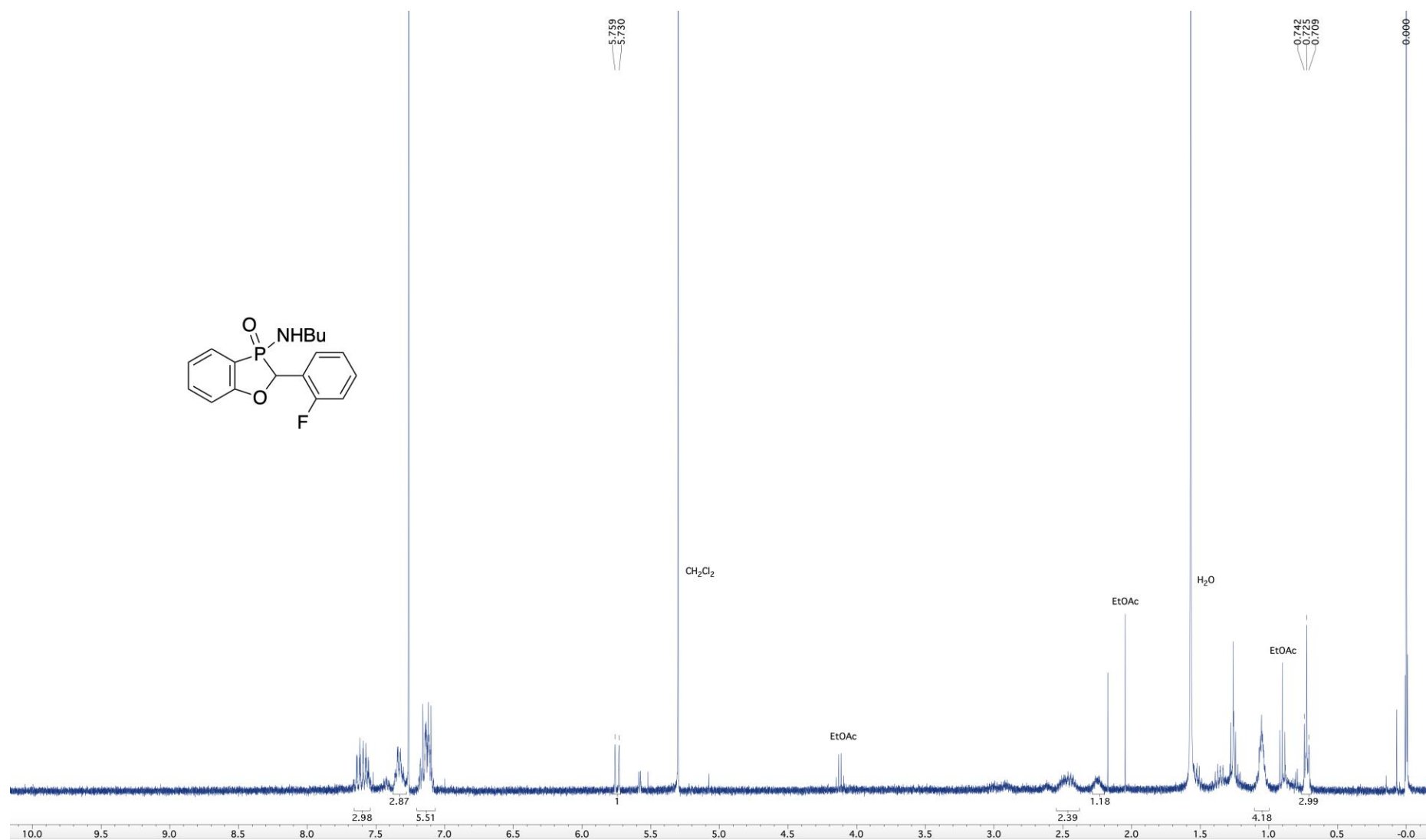


Figure S96. 162 MHz ^{31}P NMR spectrum of **23g**

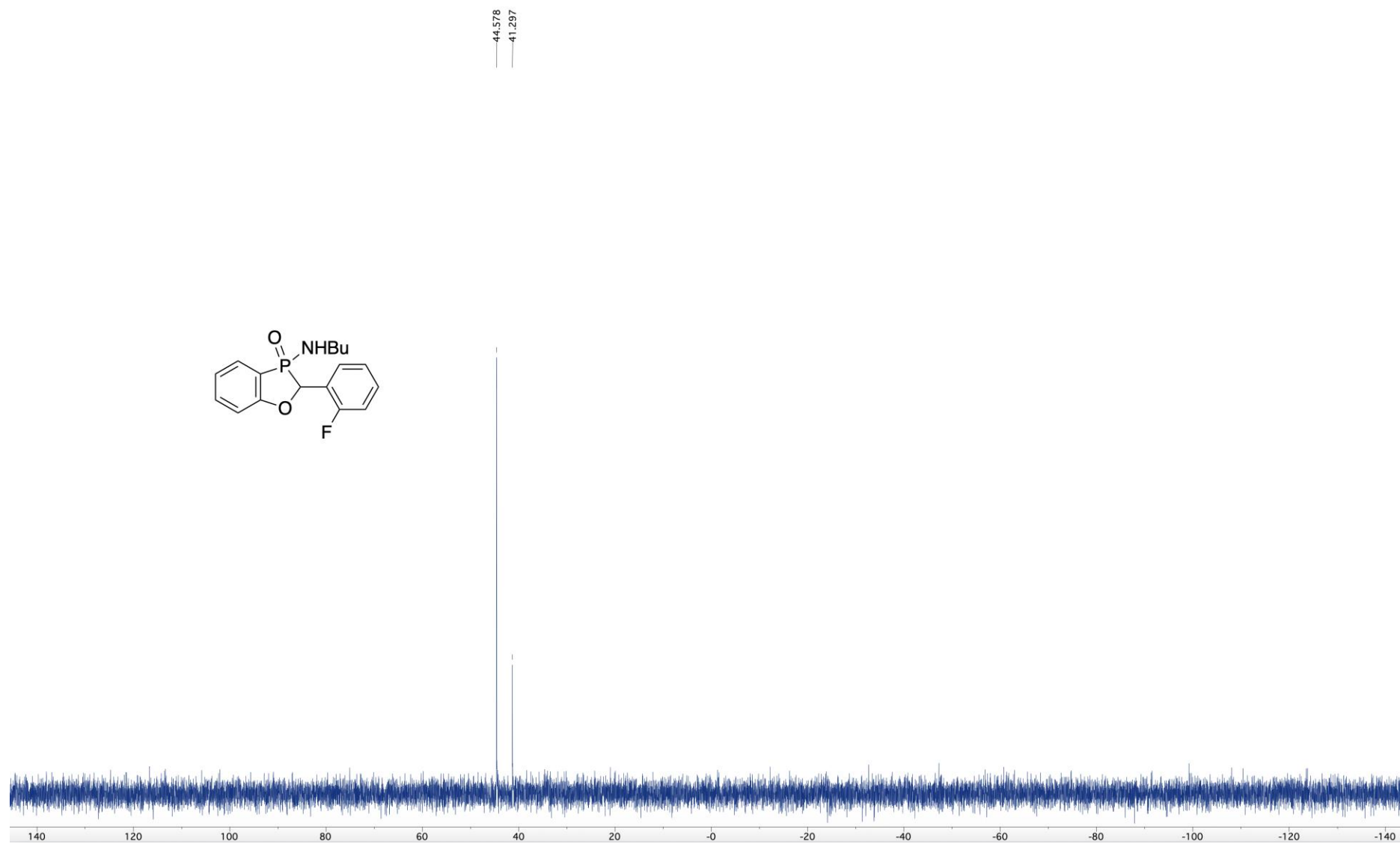


Figure S97. 400 MHz ^1H NMR spectrum of **23h**

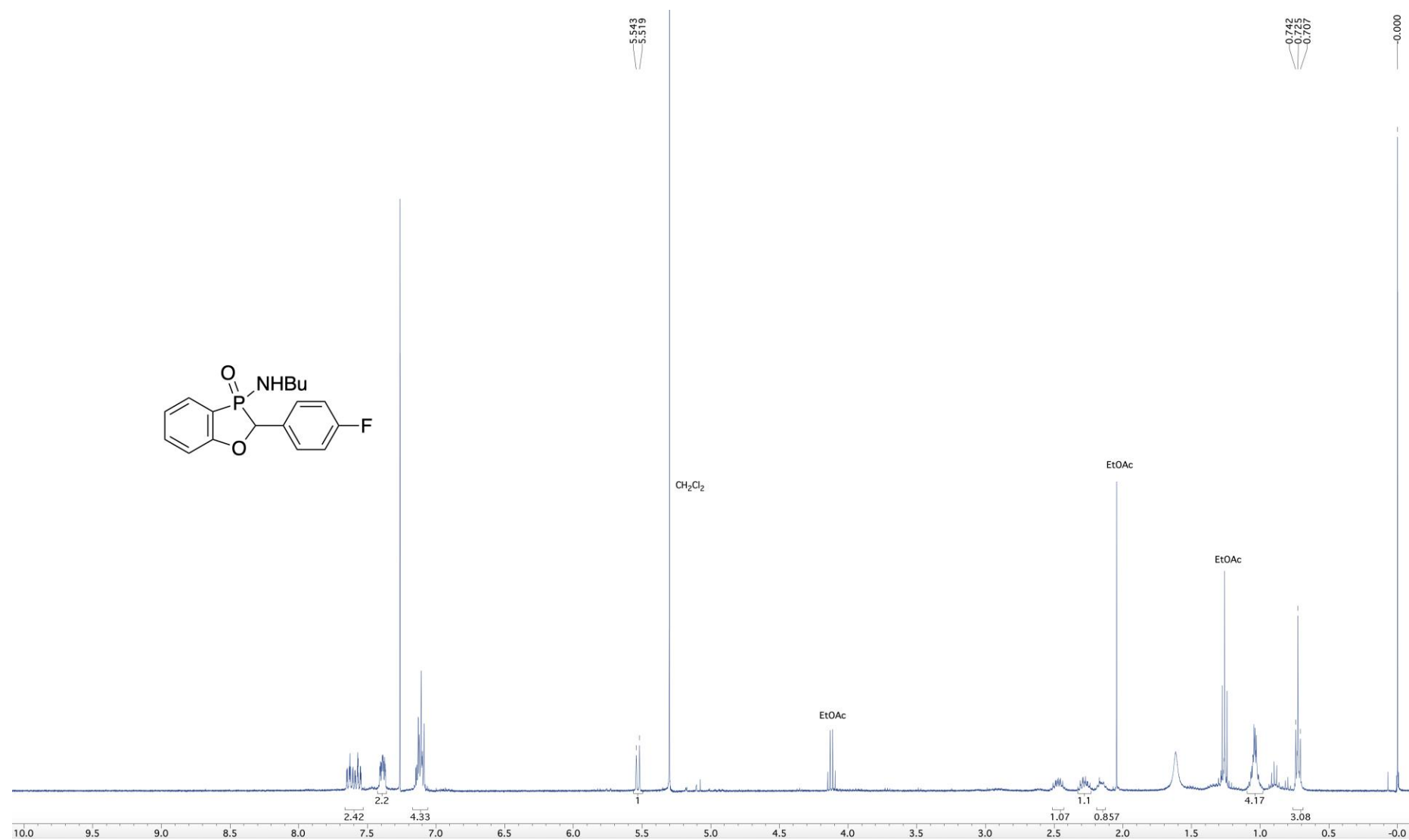


Figure S98. 162 MHz ^{31}P NMR spectrum of **23h**

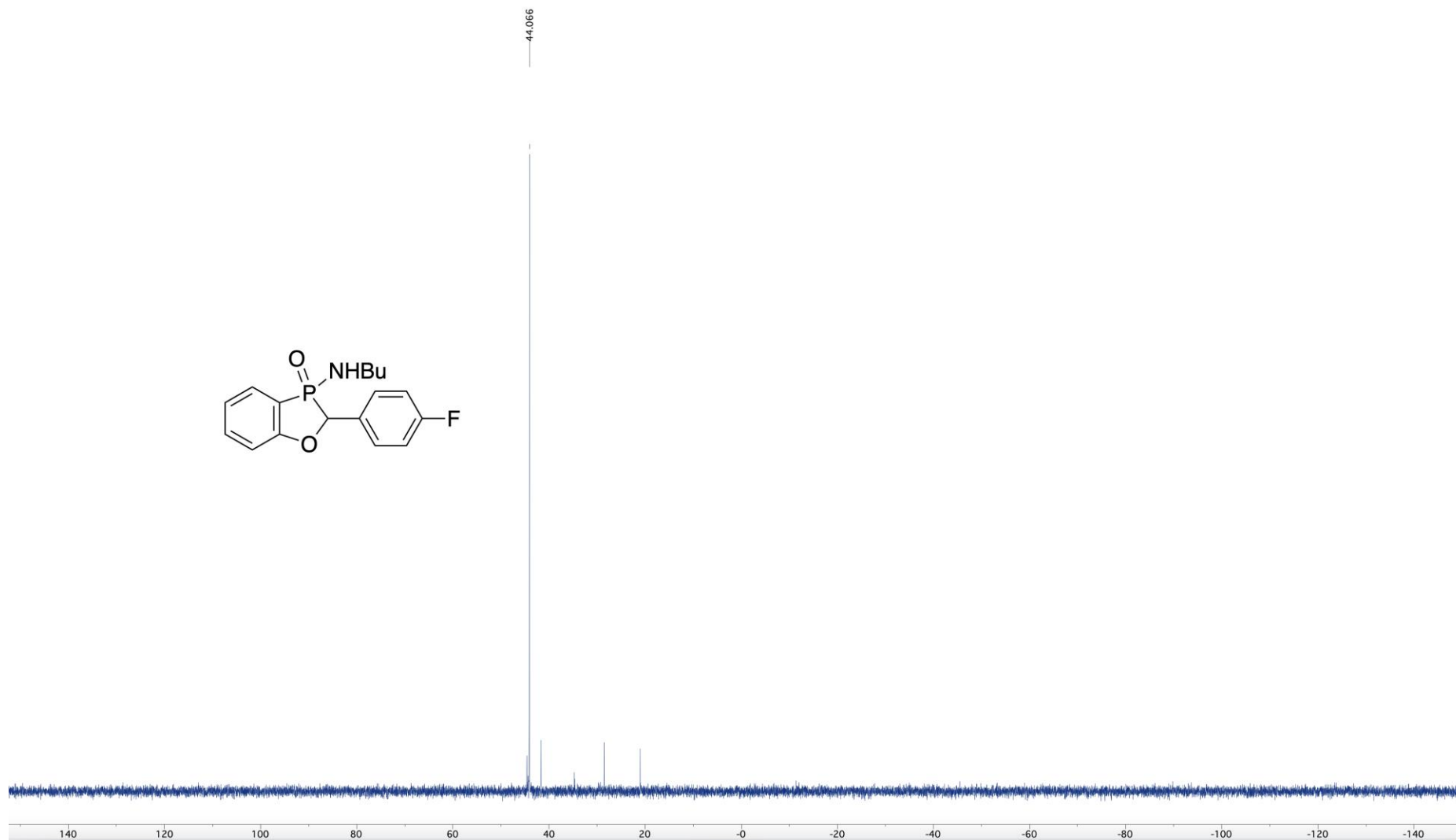


Figure S99. 100 MHz DEPTQ ^{13}C NMR spectrum of **23h**

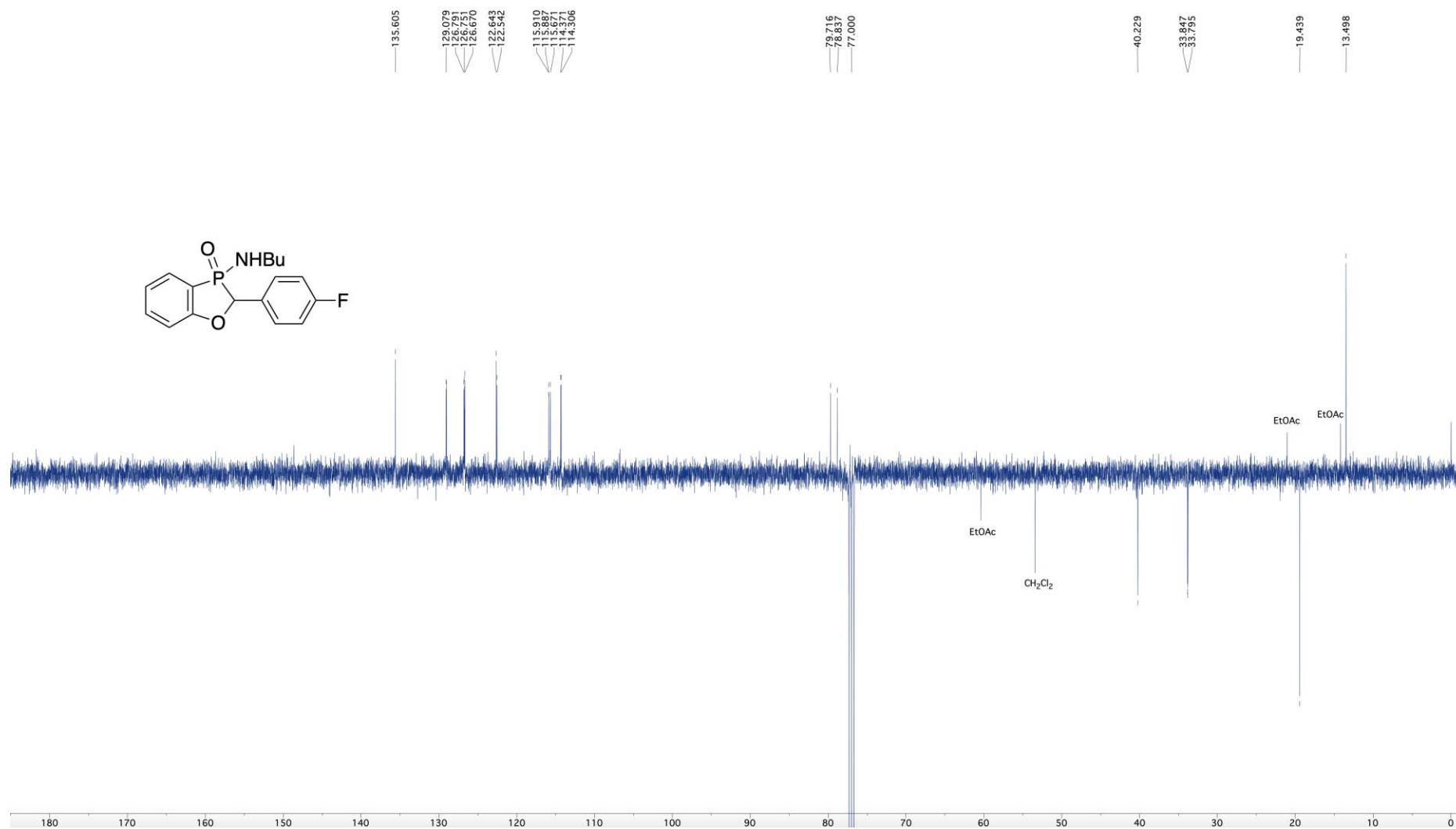


Figure S100. 162 MHz ^{31}P NMR spectrum of **23k**

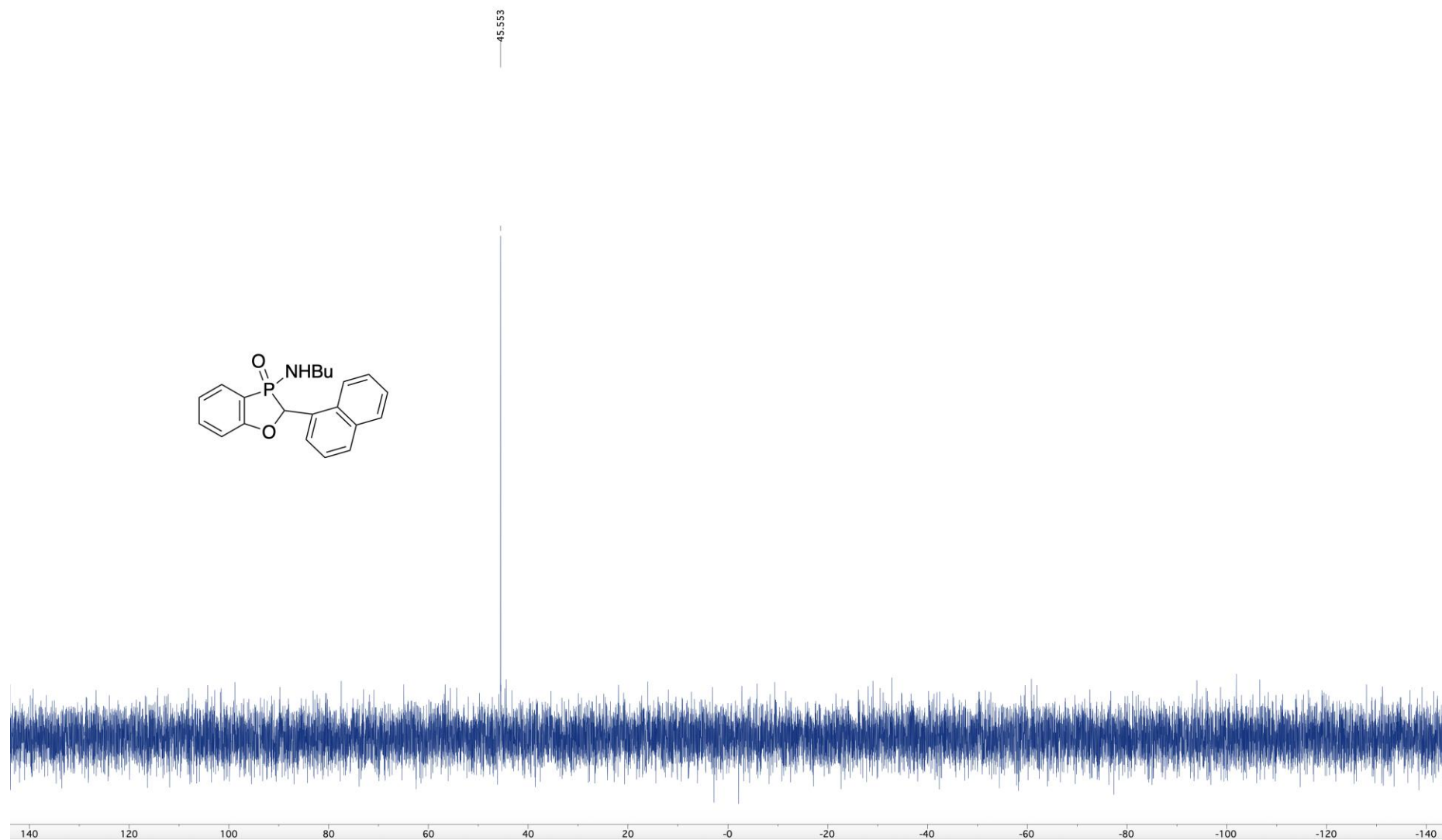


Figure S101. 400 MHz ^1H NMR spectrum of **23l**

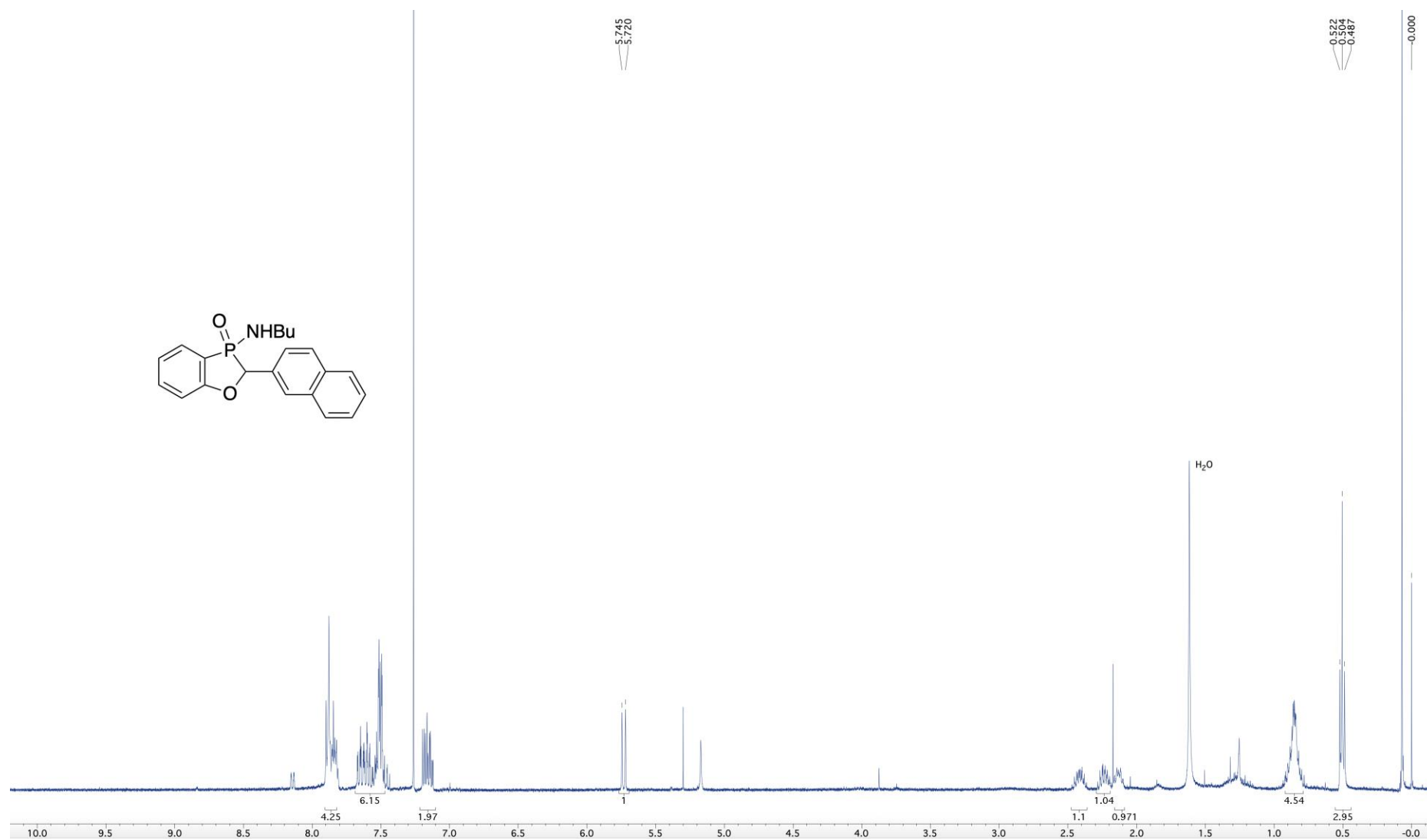
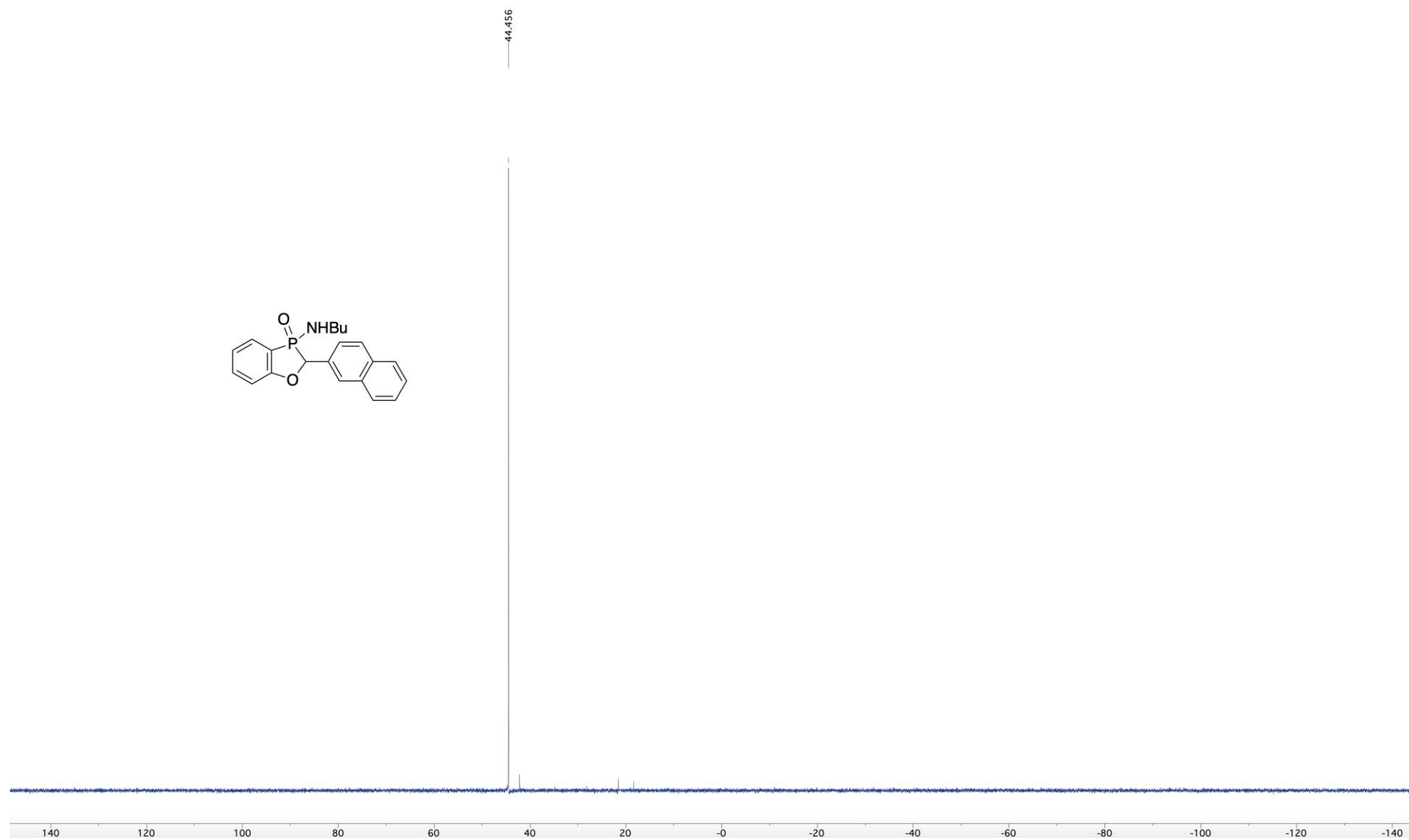


Figure S102. 162 MHz ^{31}P NMR spectrum of **231**



[illegible]