Supplementary Materials: Synthesis, Spectral Characterization of Several Novel Pyrene-Derived Aminophosphonates and Their Ecotoxicological Evaluation Using *Heterocypris incongruens* and *Vibrio fisheri* Tests

Jarosław Lewkowski, Maria Rodriguez Moya, Marta Chmielak, Diana Rogacz, Kamila Lewicka, and Piotr Rychter

Figures 1–7—Spectra of compounds **3a–d**, **4** and **5**.

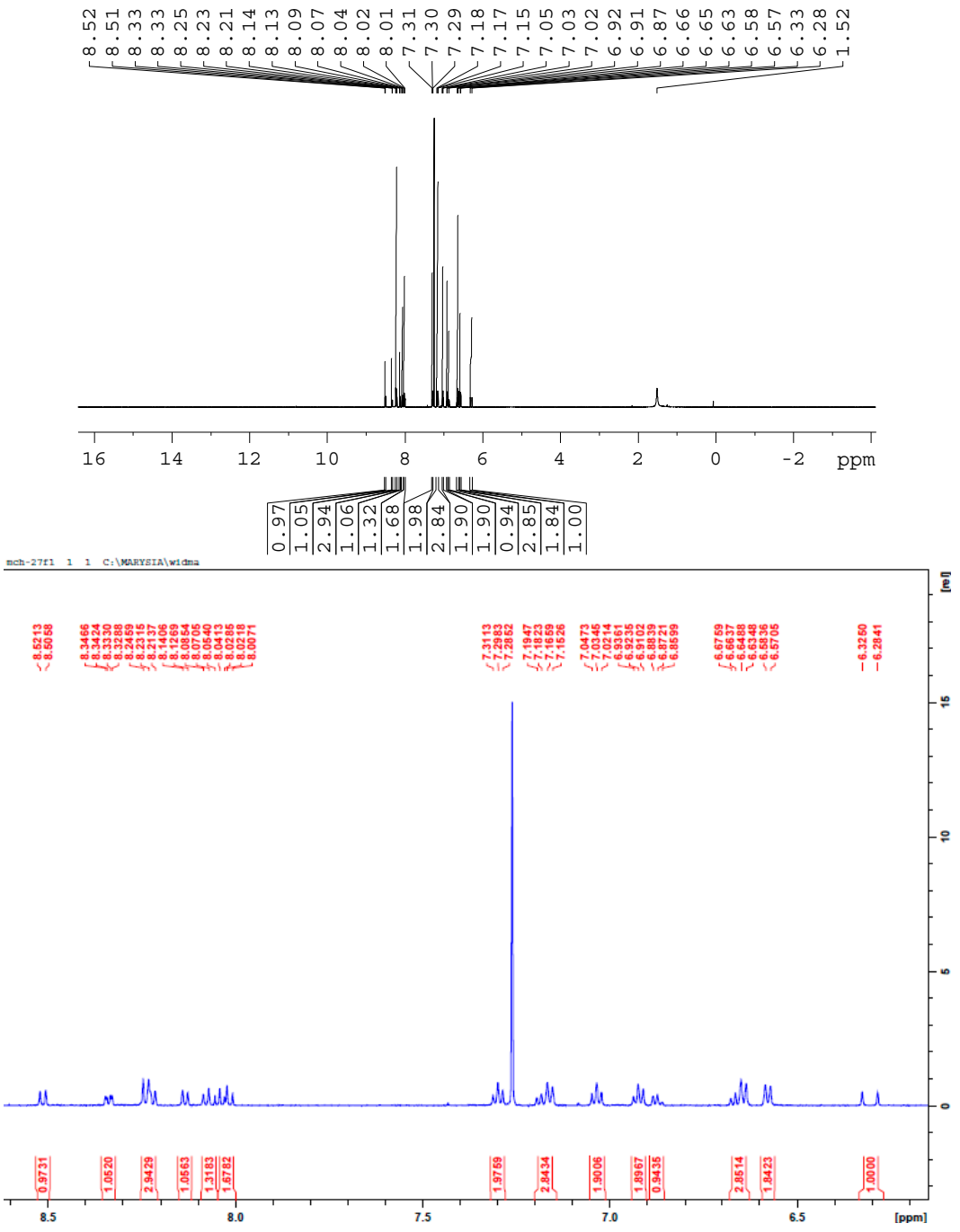


Figure S1. (**a**) Diphenyl *N*-phenylamino(pyren-1-yl)methylphosphonate (**3a**). ^{1}H-NMR—followed by enlarged fragments.

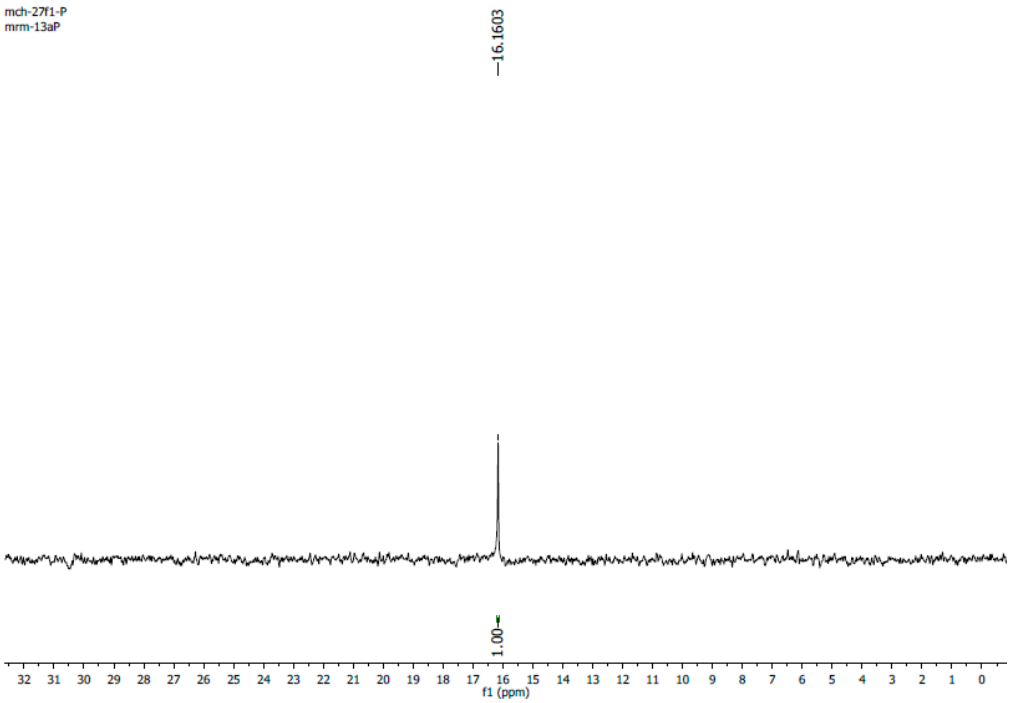
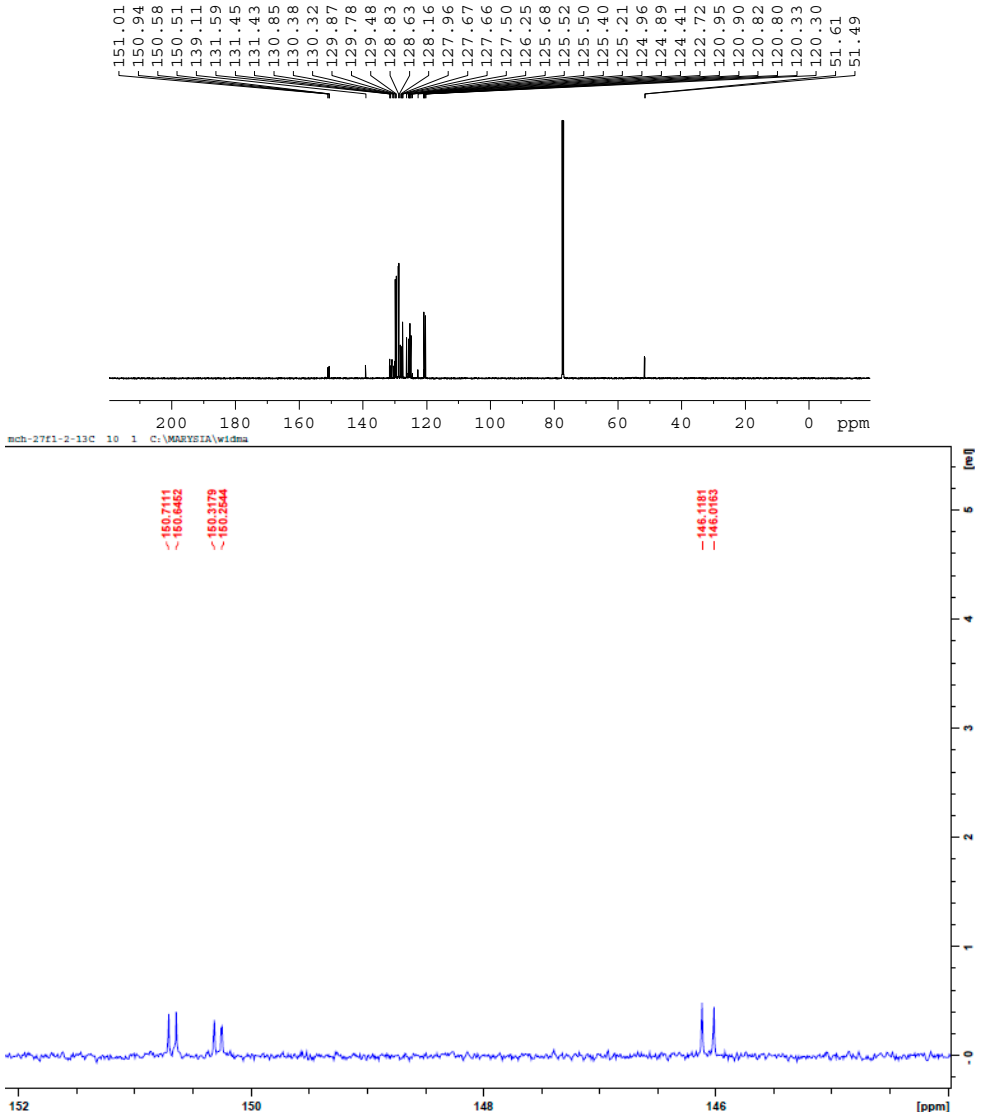
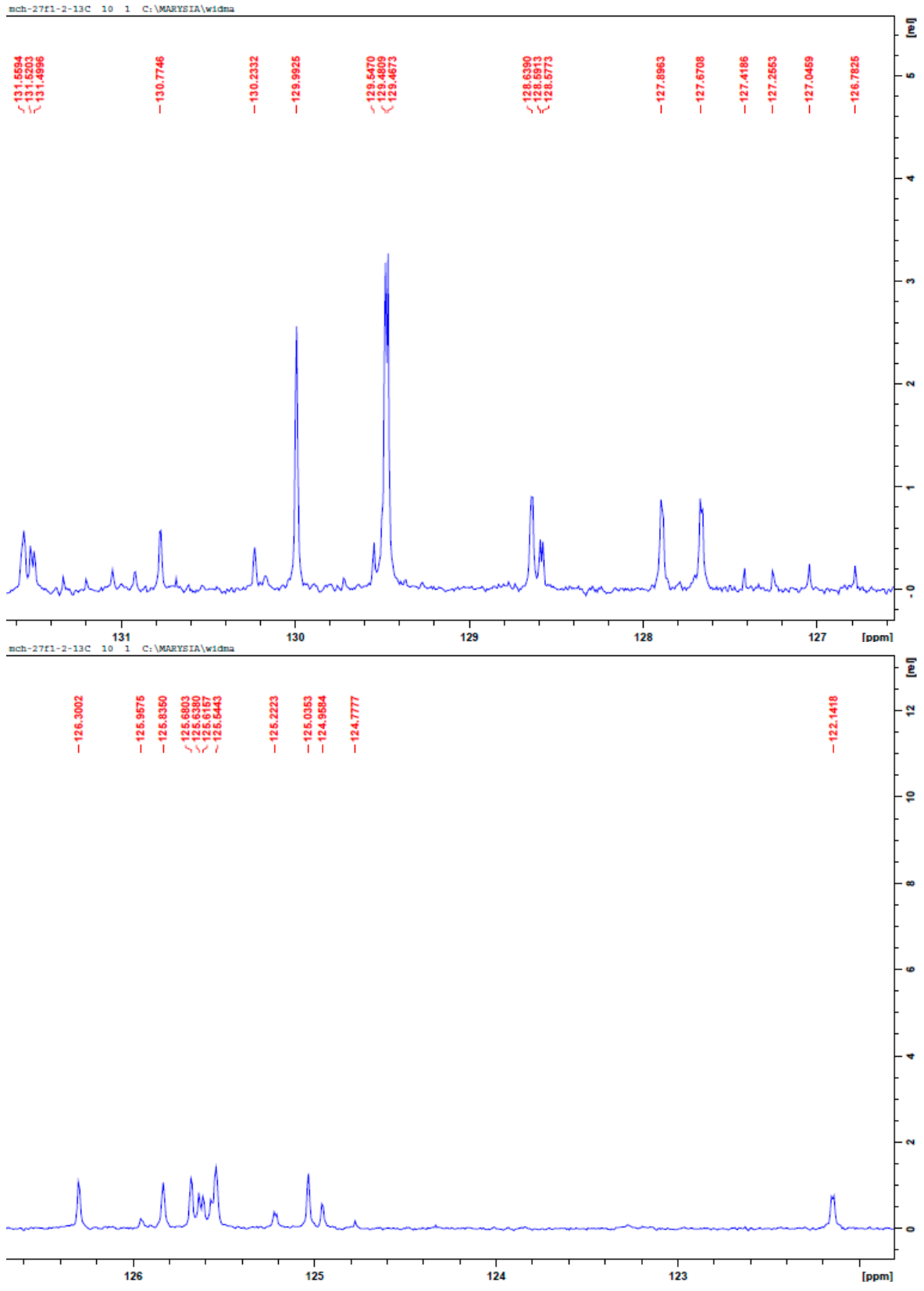


Figure S1. (**b**) Diphenyl *N*-phenylamino(pyren-1-yl)methylphosphonate (**3c**). ^{31}P-NMR.

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129.9925
129.5470
129.4809
129.4673
128.6390
128.5913
128.5773
127.8963
127.6708
127.4186
127.2553
127.0459
126.7825
[rel]
131
130
129
128
127
[ppm]
mch-27f1-2-13C 10 1 C:\MARYSIA\widma
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126.9575
126.8350
125.6803
125.6380
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124.7777
122.1418
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126
125
124
123
[ppm]

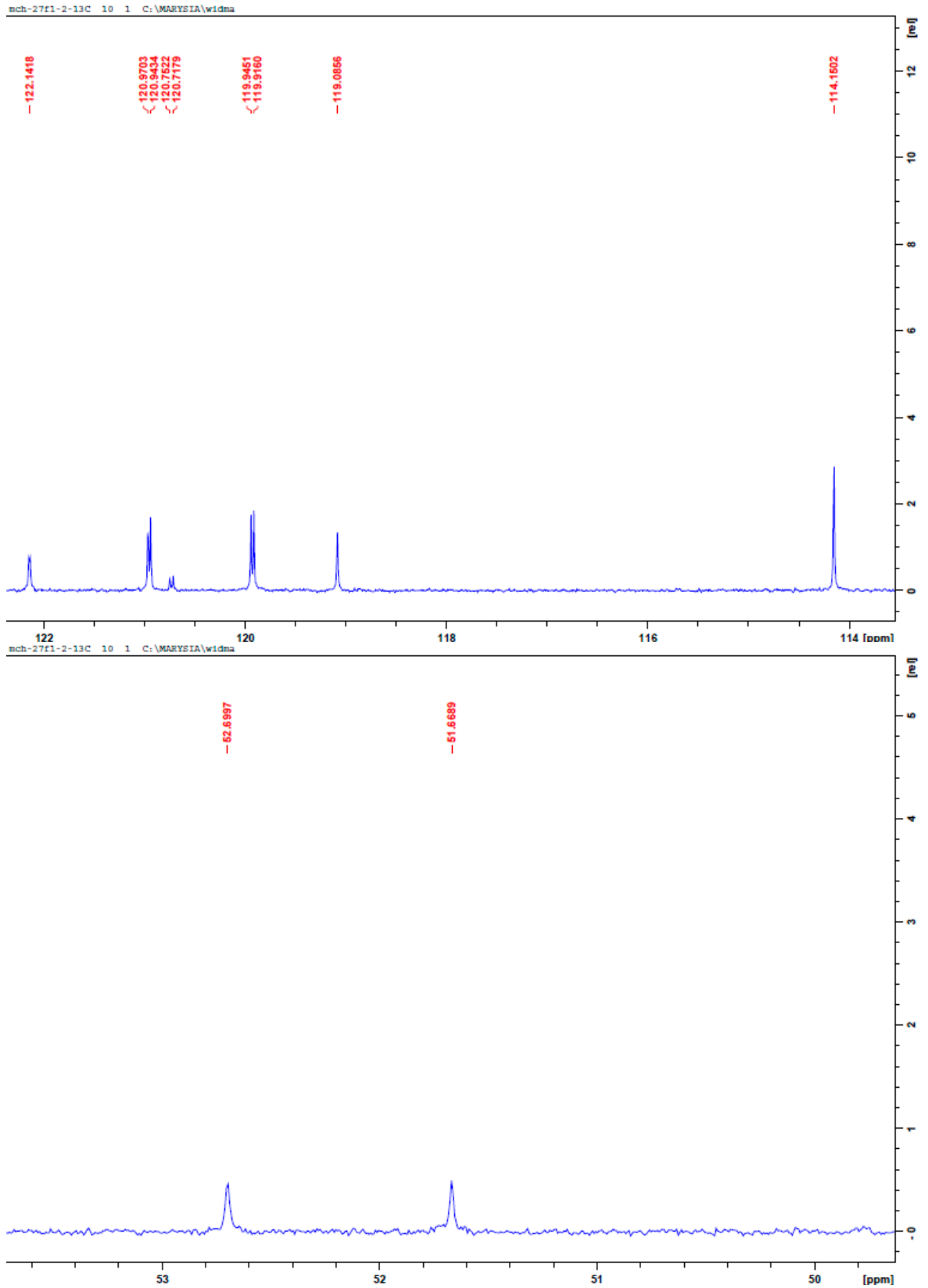
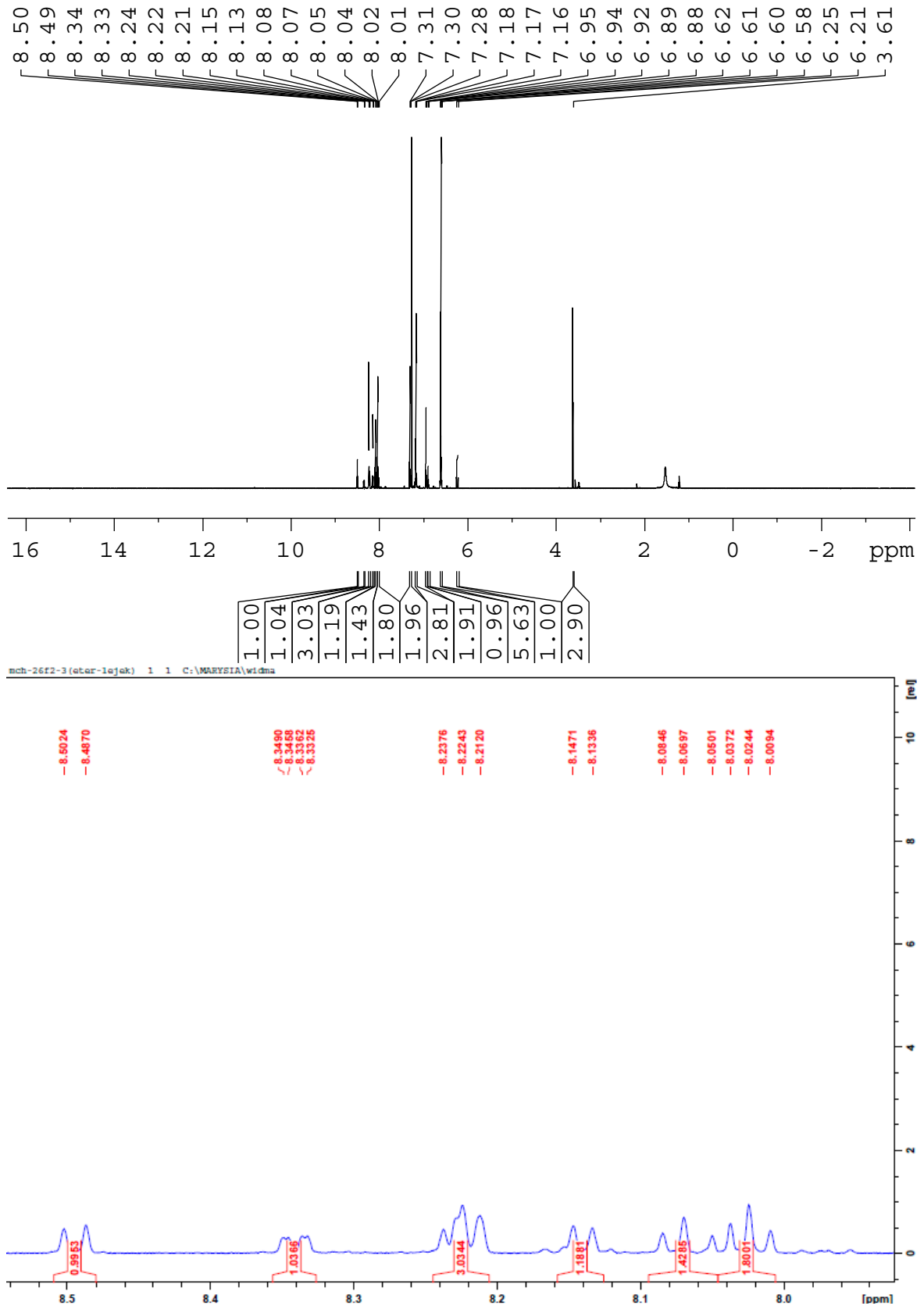


Figure S1. (**c**) Diphenyl *N*-phenylamino(pyren-1-yl)methylphosphonate (**3a**). ^{13}C-NMR—followed by enlarged fragments.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8.33
8.24
8.22
8.21
8.15
8.13
8.08
8.07
8.05
8.04
8.02
8.01
7.31
7.30
7.28
7.18
7.17
7.16
6.95
6.94
6.92
6.89
6.88
6.62
6.61
6.60
6.58
6.25
6.21
3.61
16
14
12
10
8
6
4
2
0
-2
ppm
1.00
1.04
3.03
1.19
1.43
1.80
1.96
2.81
1.91
0.96
5.63
1.00
2.90
mch-26f2-3(eter-1ejek) 1 1 C:\MARYSIA\widma
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8.4870
8.3490
8.3458
8.3362
8.3325
8.2376
8.2243
8.2120
8.1471
8.1336
8.0846
8.0697
8.0501
8.0372
8.0244
8.0094
[rel]
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1.0366
3.0344
1.1881
1.4285
1.8001
8.5
8.4
8.3
8.2
8.1
8.0
[ppm]

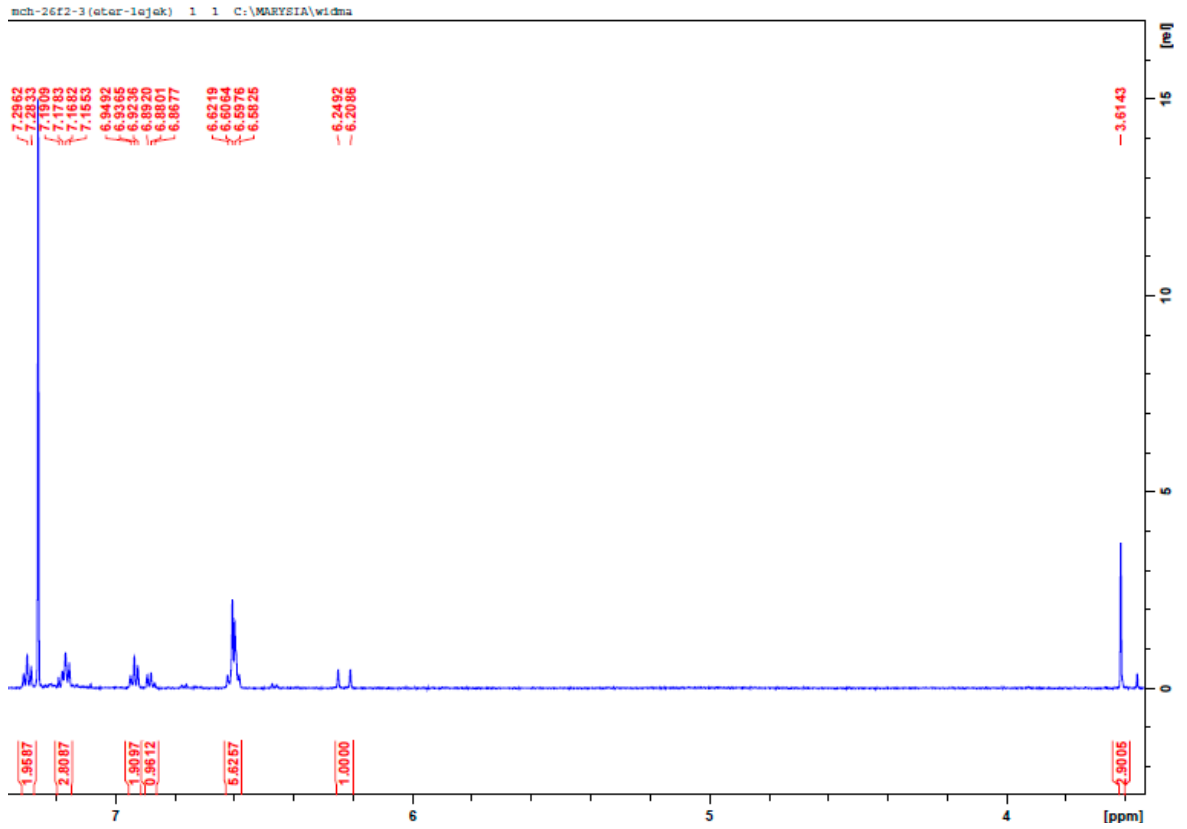
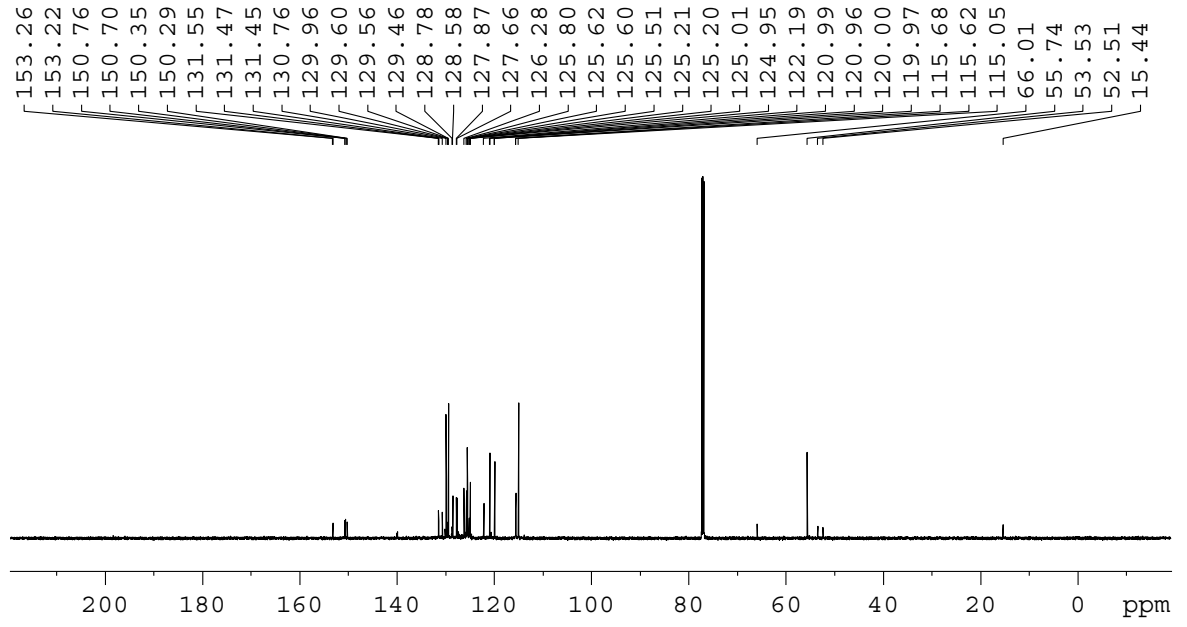
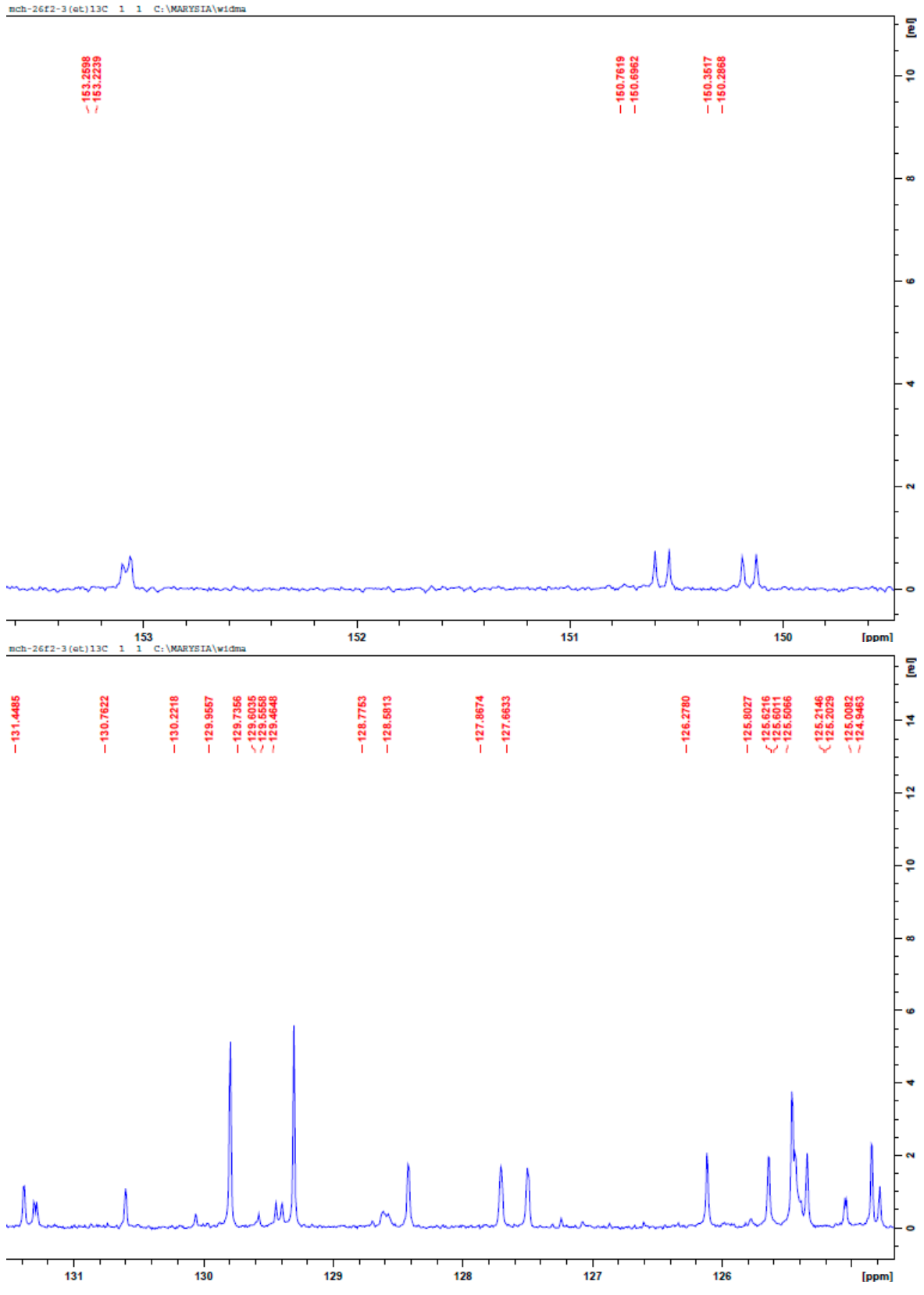


Figure S2. (**a**) Diphenyl *N*-(4-methoxyphenyl)amino(pyren-1-yl)methylphosphonate (**3b**). ^{1}H-NMR— followed by enlarged fragments.

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150.6962
150.3517
150.2868
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[ppm]
mch-26f2-3(qt)13C 1 1 C:\MARYSIA\widma
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130.7622
130.2218
129.9557
129.7356
129.6035
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127.8674
127.6633
126.2780
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125.0082
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[rel]
[ppm]

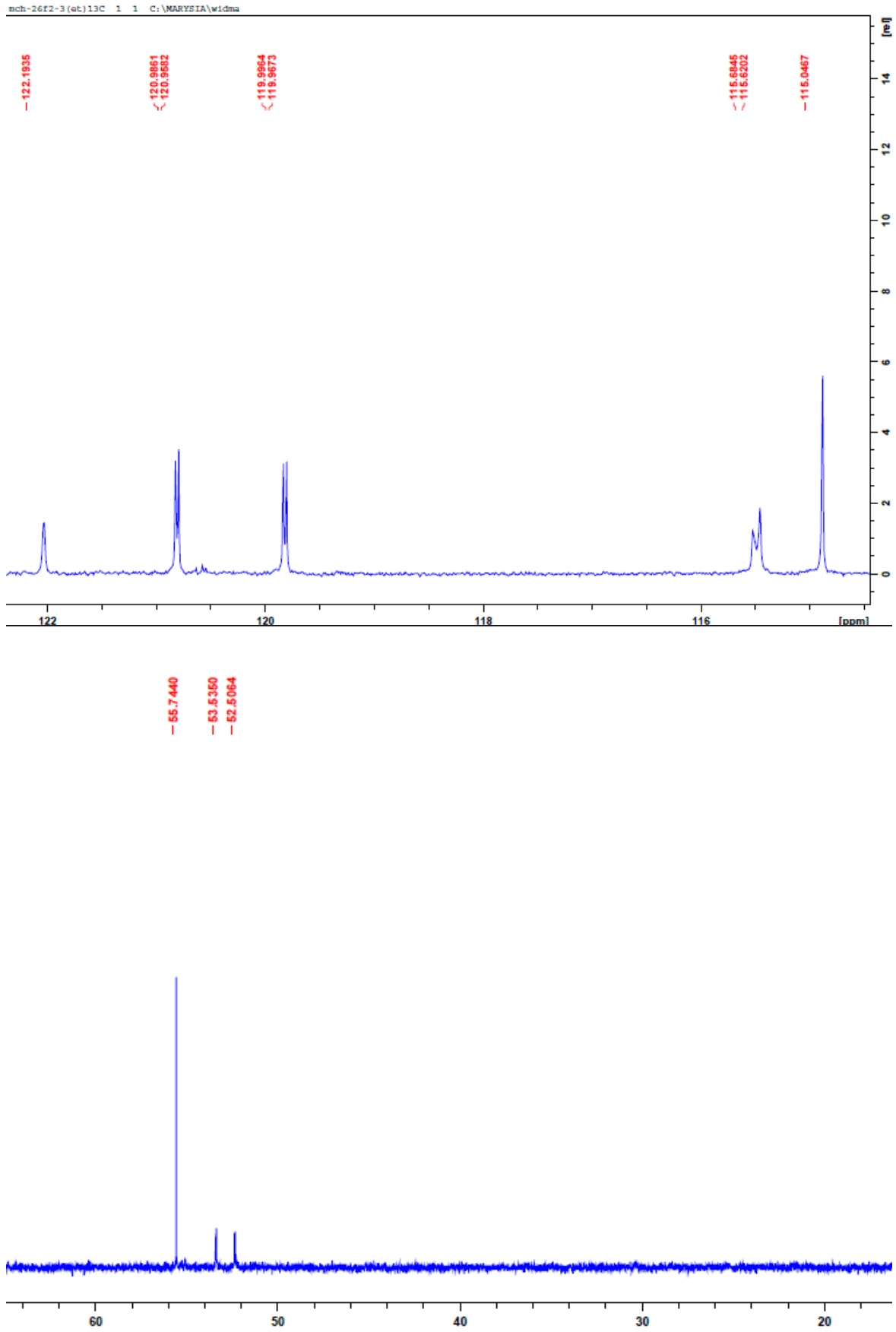


Figure S2. (**b**) Diphenyl *N*-(4-methoxyphenyl)amino(pyren-1-yl)methylphosphonate (**3b**). ^{13}C-NMR—followed by enlarged fragments.

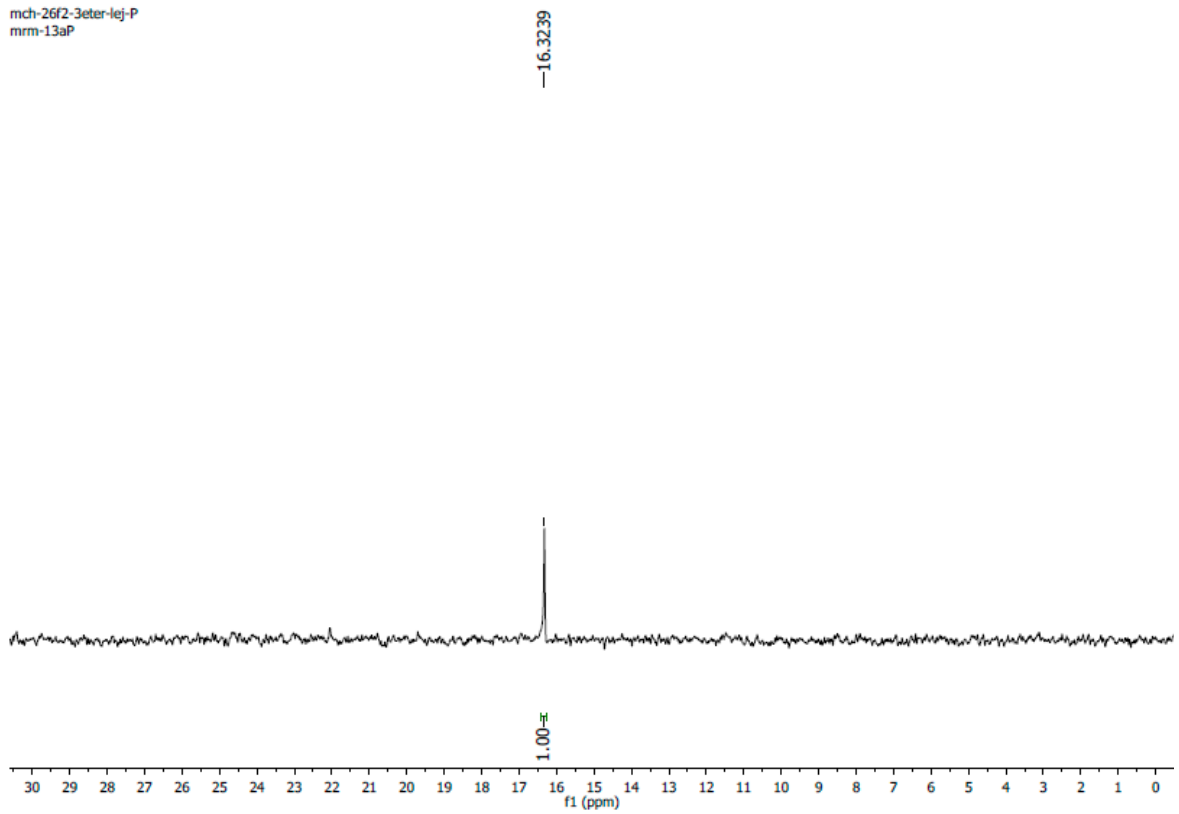
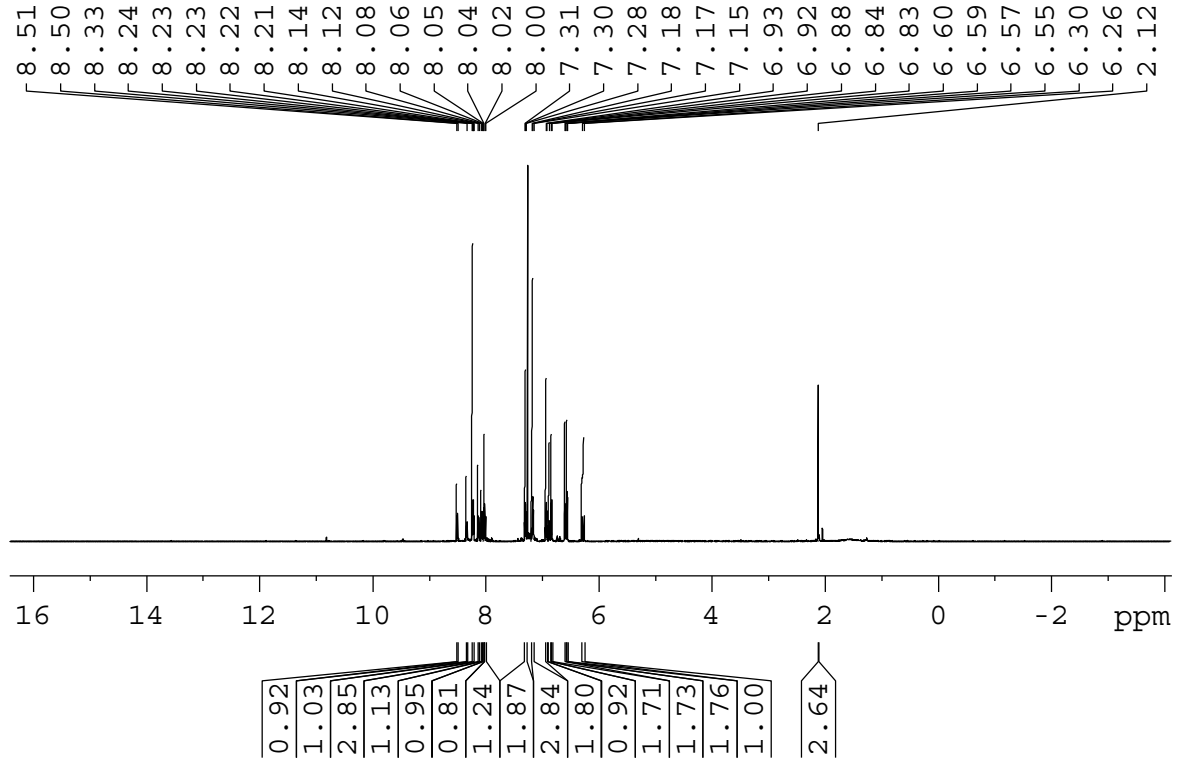
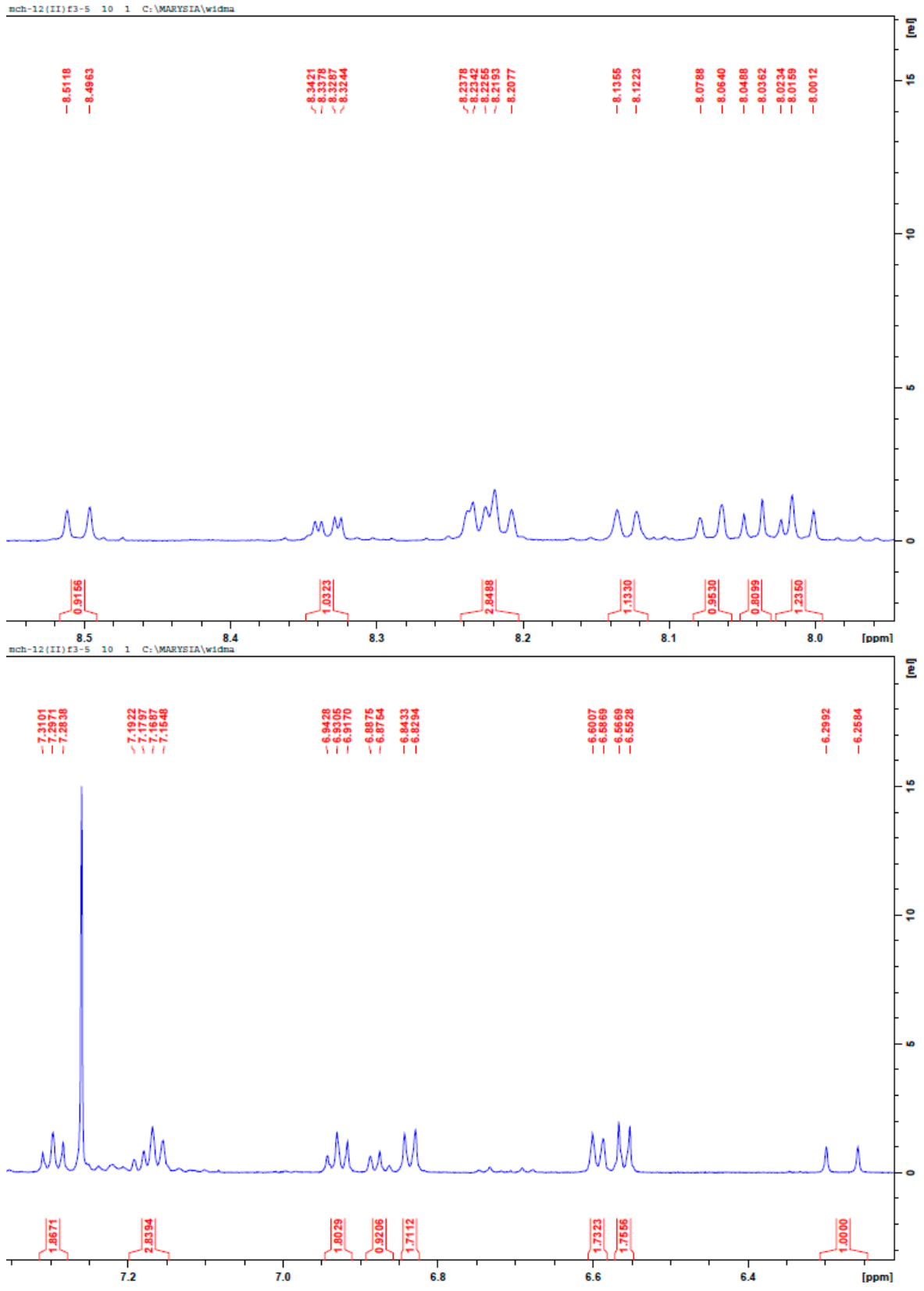


Figure S2. (**c**) Diphenyl *N*-(4-methoxyphenyl)amino(pyren-1-yl)methylphosphonate (**3b**). ^{31}P-NMR.

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8.3421
8.3378
8.3287
8.3244
8.2378
8.2342
8.2255
8.2193
8.2077
8.1355
8.1223
8.0788
8.0640
8.0488
8.0362
8.0234
8.0159
8.0012
0.9156
1.0323
2.8488
1.1330
0.9530
0.8099
1.2350
8.5
8.4
8.3
8.2
8.1
8.0
[ppm]
[mI]
mch-12(II)f3-5 10 1 C:\MARYSIA\widma
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6.9170
6.8875
6.8754
6.8433
6.8294
6.6007
6.5869
6.5669
6.5528
6.2992
6.2584
1.8671
2.8394
1.8029
0.9206
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1.7566
1.0000
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7.0
6.8
6.6
6.4
[ppm]
[mI]

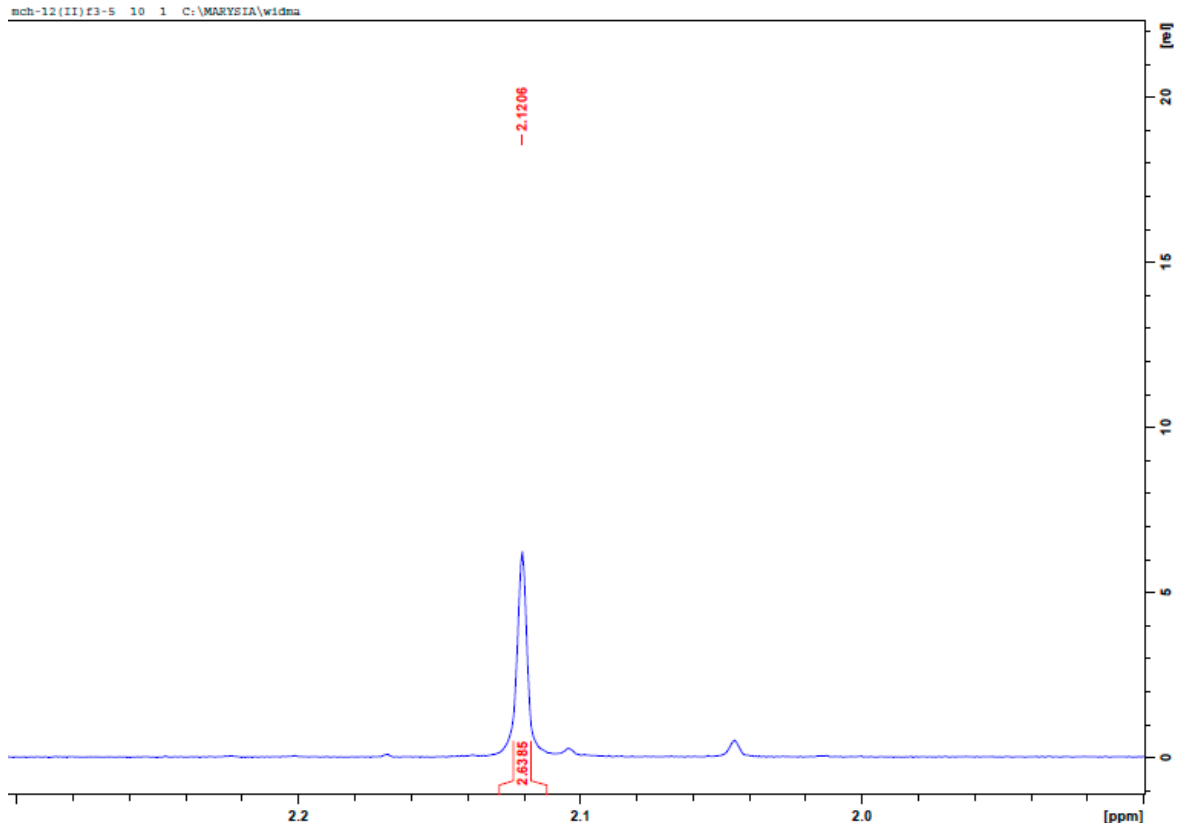


Figure S3. (**a**) Diphenyl *N*-(4-methylphenyl)amino(pyren-1-yl)methylphosphonate (**3c**). ^{1}H-NMR—followed by enlarged fragments.

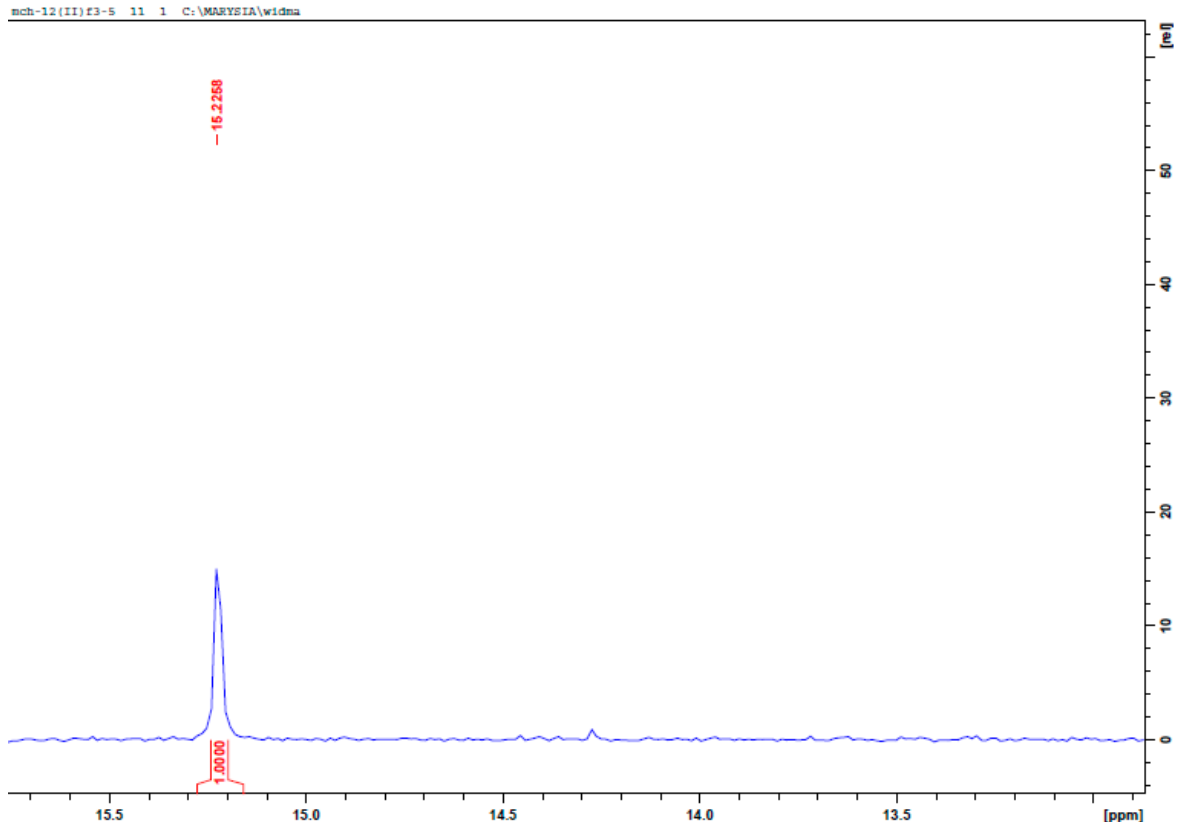
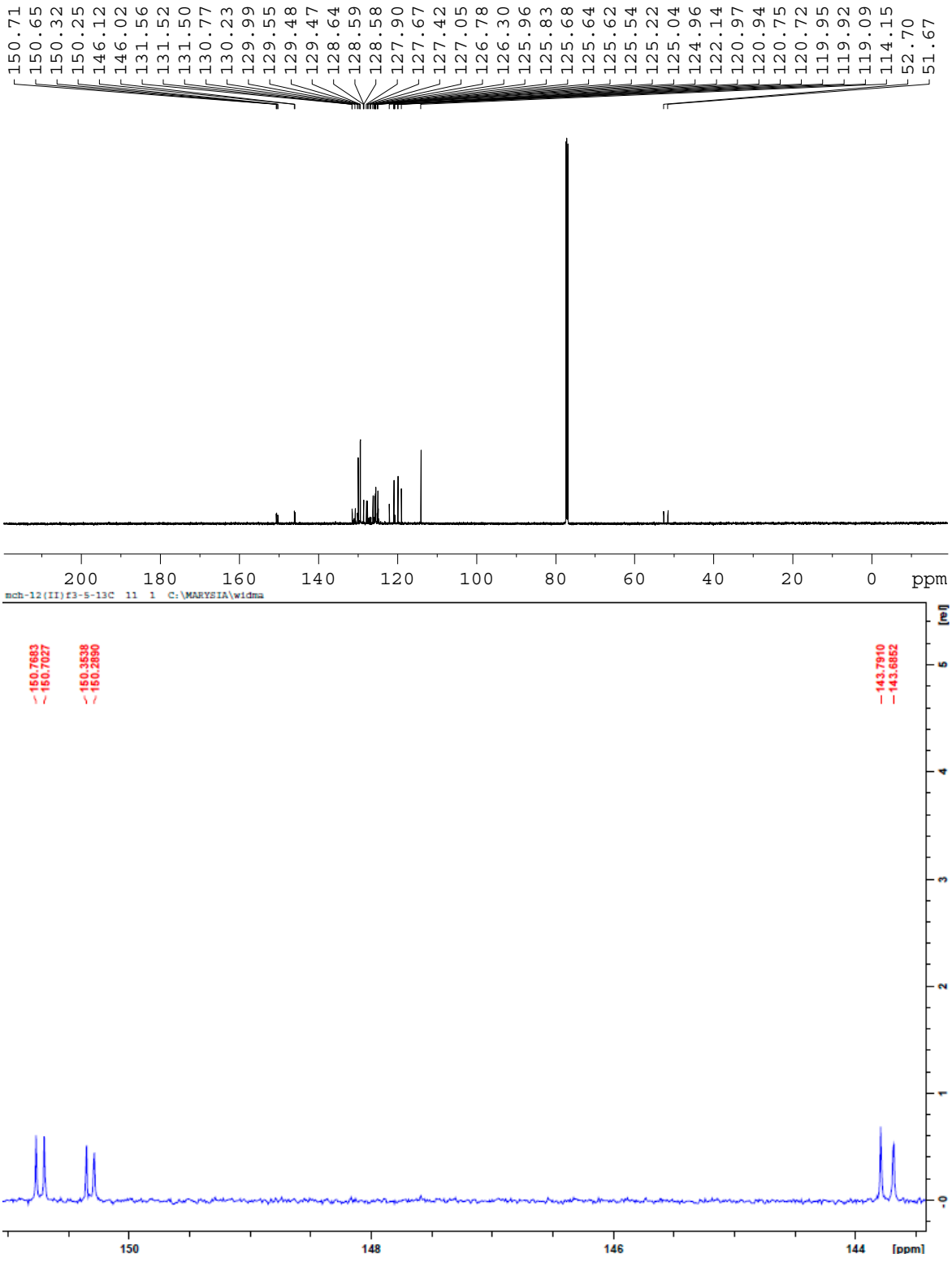


Figure S3. (**b**) Diphenyl *N*-(4-methylphenyl)amino(pyren-1-yl)methylphosphonate (**3c**). ^{31}P-NMR.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146.02
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131.52
131.50
130.77
130.23
129.99
129.55
129.48
129.47
128.64
128.59
128.58
127.90
127.67
127.42
127.05
126.78
126.30
125.96
125.83
125.68
125.64
125.62
125.54
125.22
125.04
124.96
122.14
120.97
120.94
120.75
120.72
119.95
119.92
119.09
114.15
52.70
51.67
200
180
160
140
120
100
80
60
40
20
0
ppm
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143.6852
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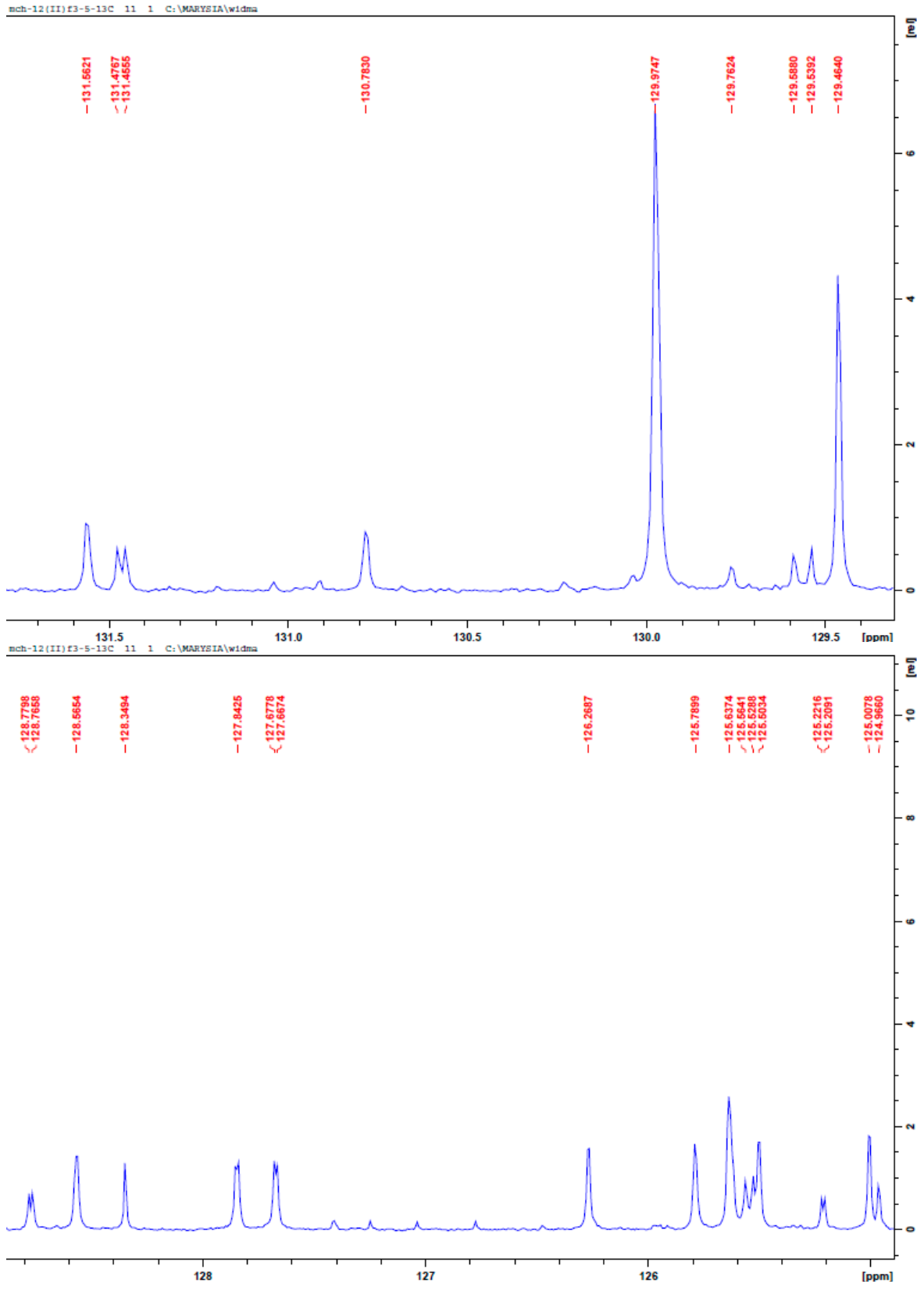
146
144
[ppm]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131.5
131.0
130.5
130.0
129.5
[ppm]
[rel]
mch-12(II)f3-5-13C 11 1 C:\MARYSIA\widma
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128.5654
128.3494
127.8425
127.6778
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126
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[rel]

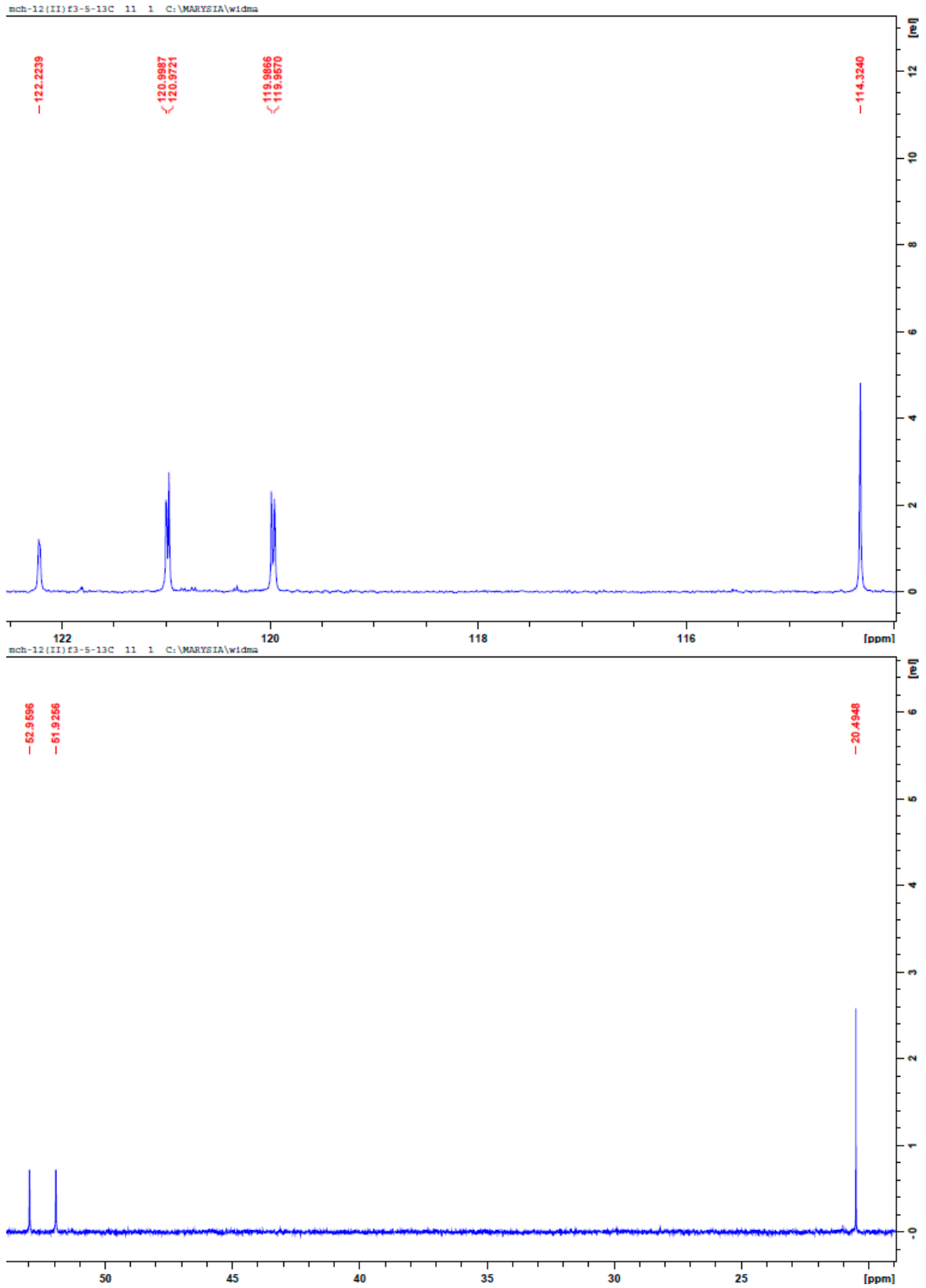
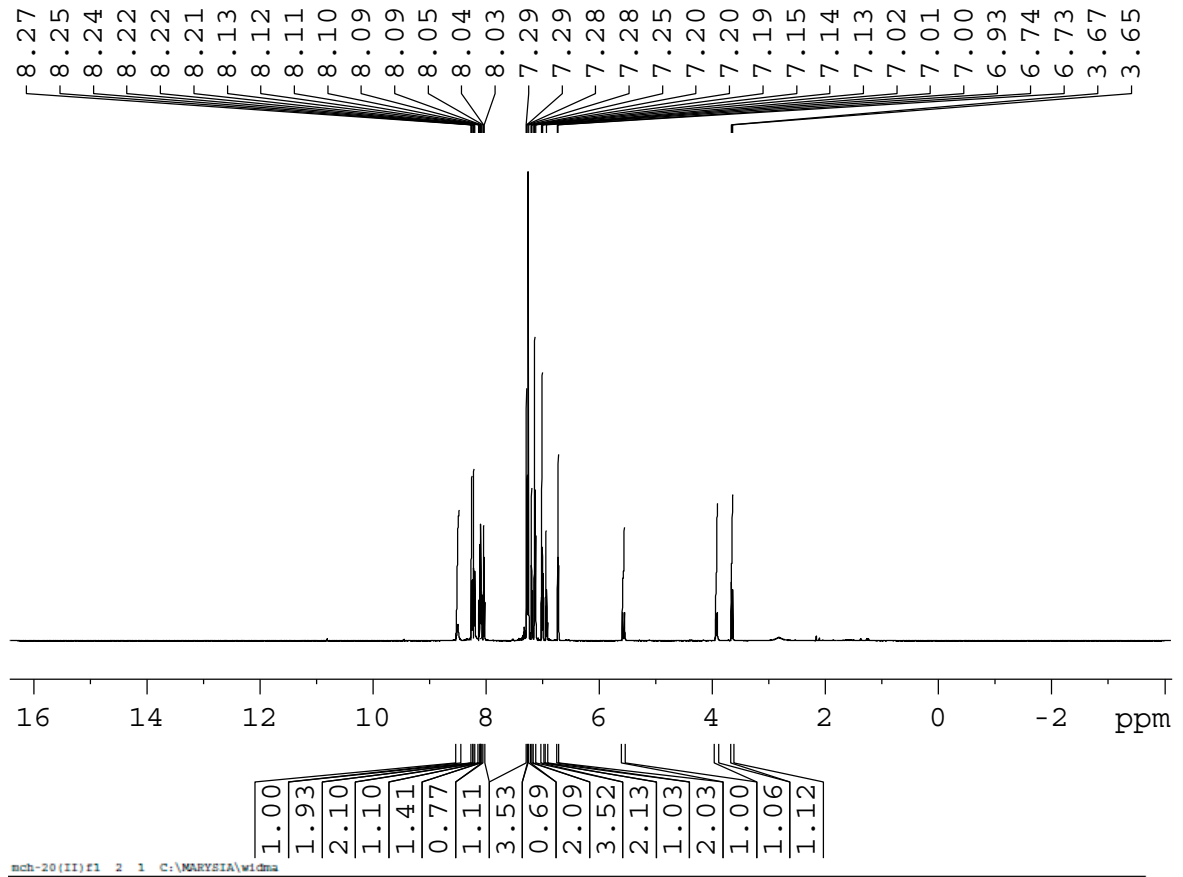


Figure S3. (**c**) Diphenyl *N*-(4-methylphenyl)amino(pyren-1-yl)methylphosphonate (**3c**). ^{13}C-NMR—followed by enlarged fragments.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16 14 12 10 8 6 4 2 0 -2 ppm
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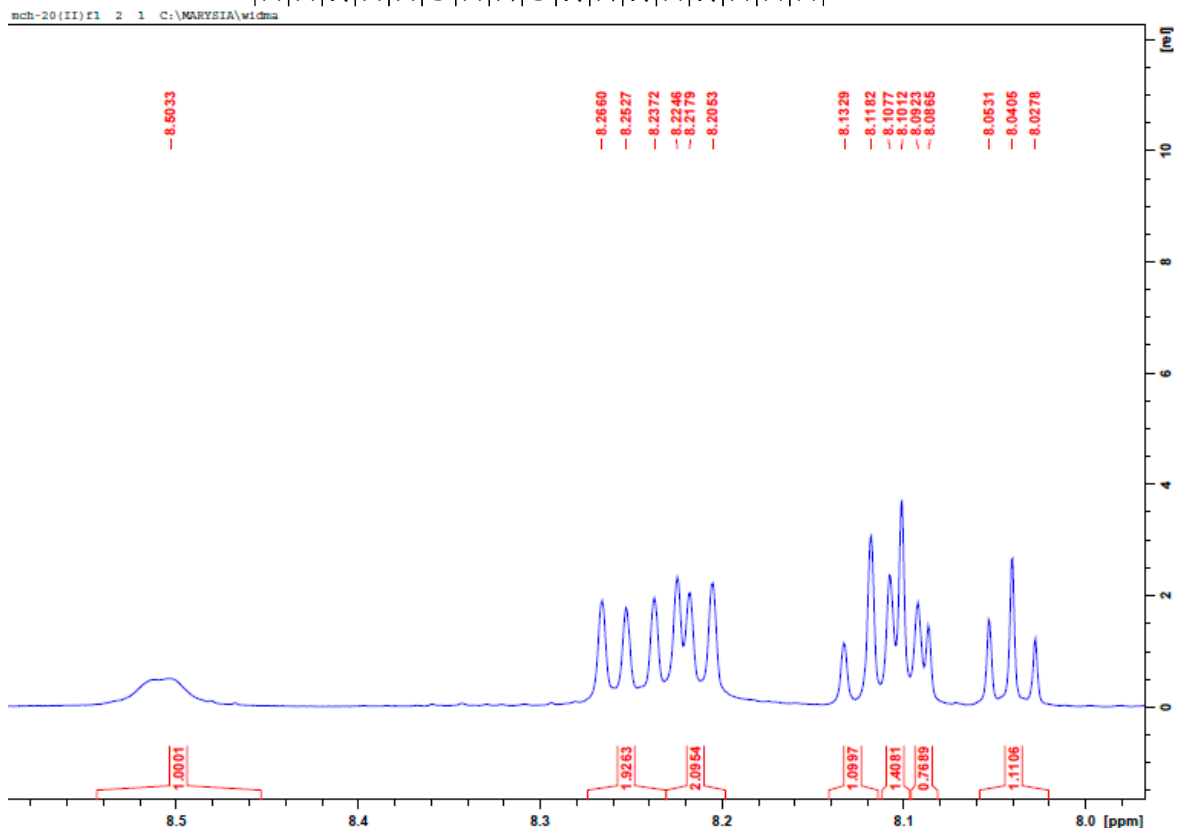
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8.2660 8.2527 8.2372 8.2246 8.2179 8.2053
8.1329 8.1182 8.1077 8.1012 8.0923 8.0865
8.0531 8.0405 8.0278
[rel]
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8.5 8.4 8.3 8.2 8.1 8.0 [ppm]

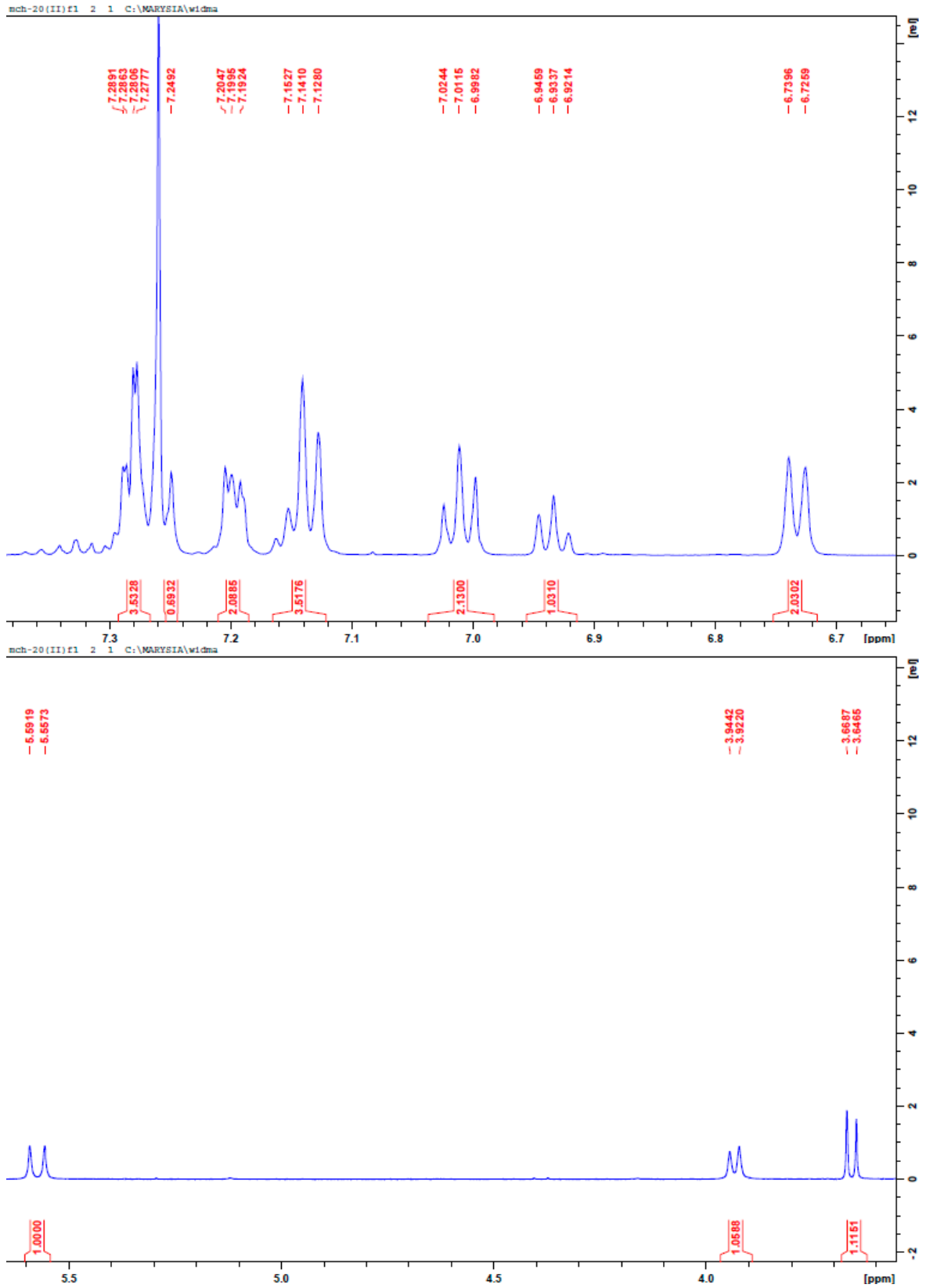


Figure S4. (**a**)Diphenyl *N*-benzylamino(pyren-1-yl)methylphosphonate (**3d**). ^{1}H-NMR—followed by enlarged fragments.

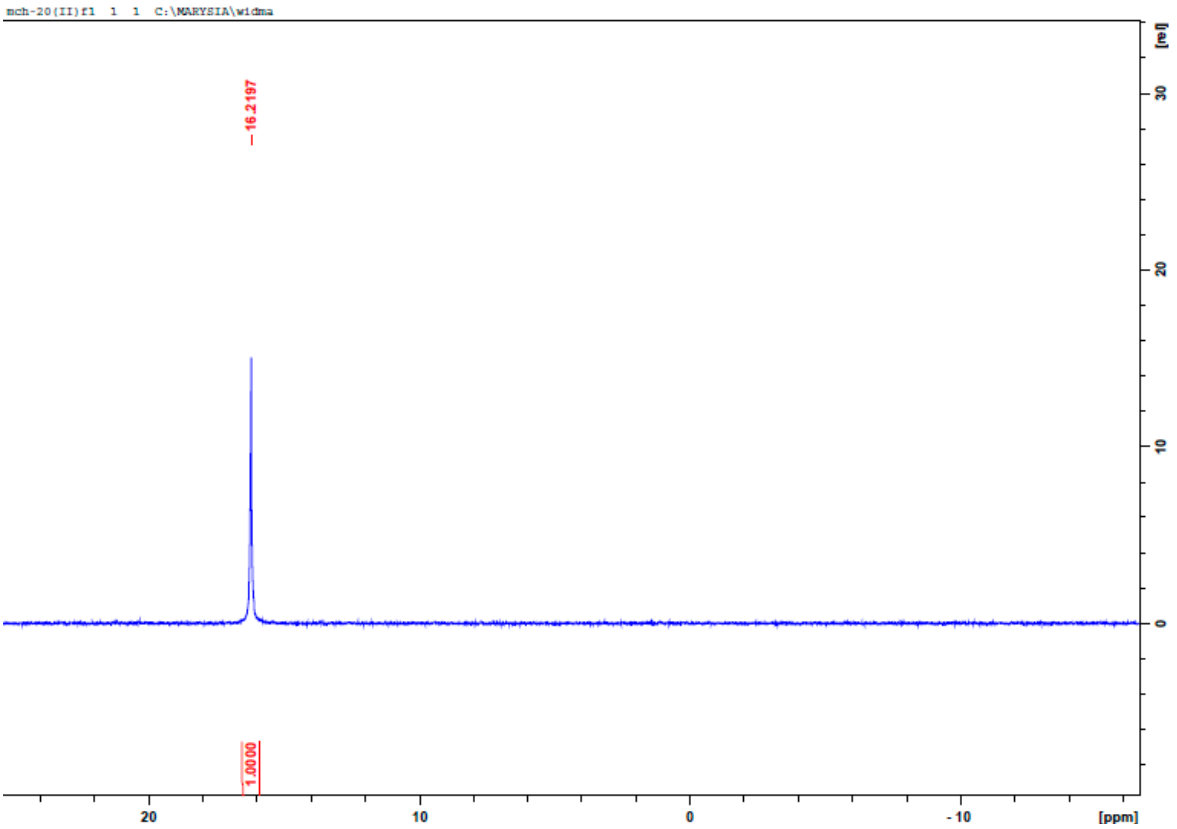
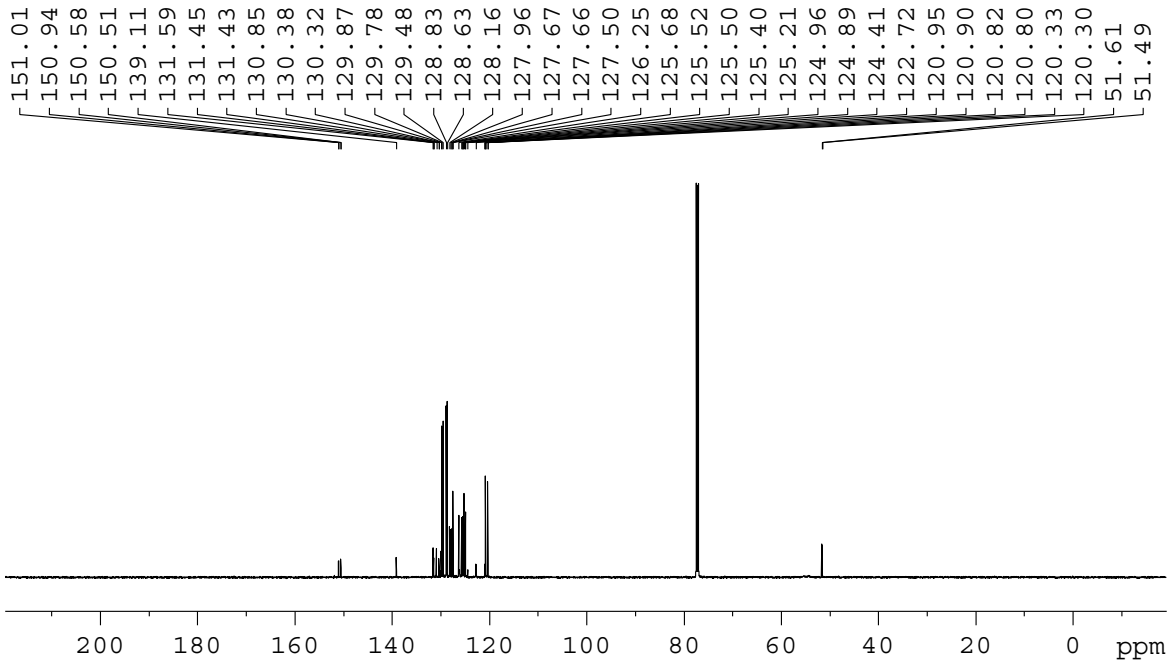
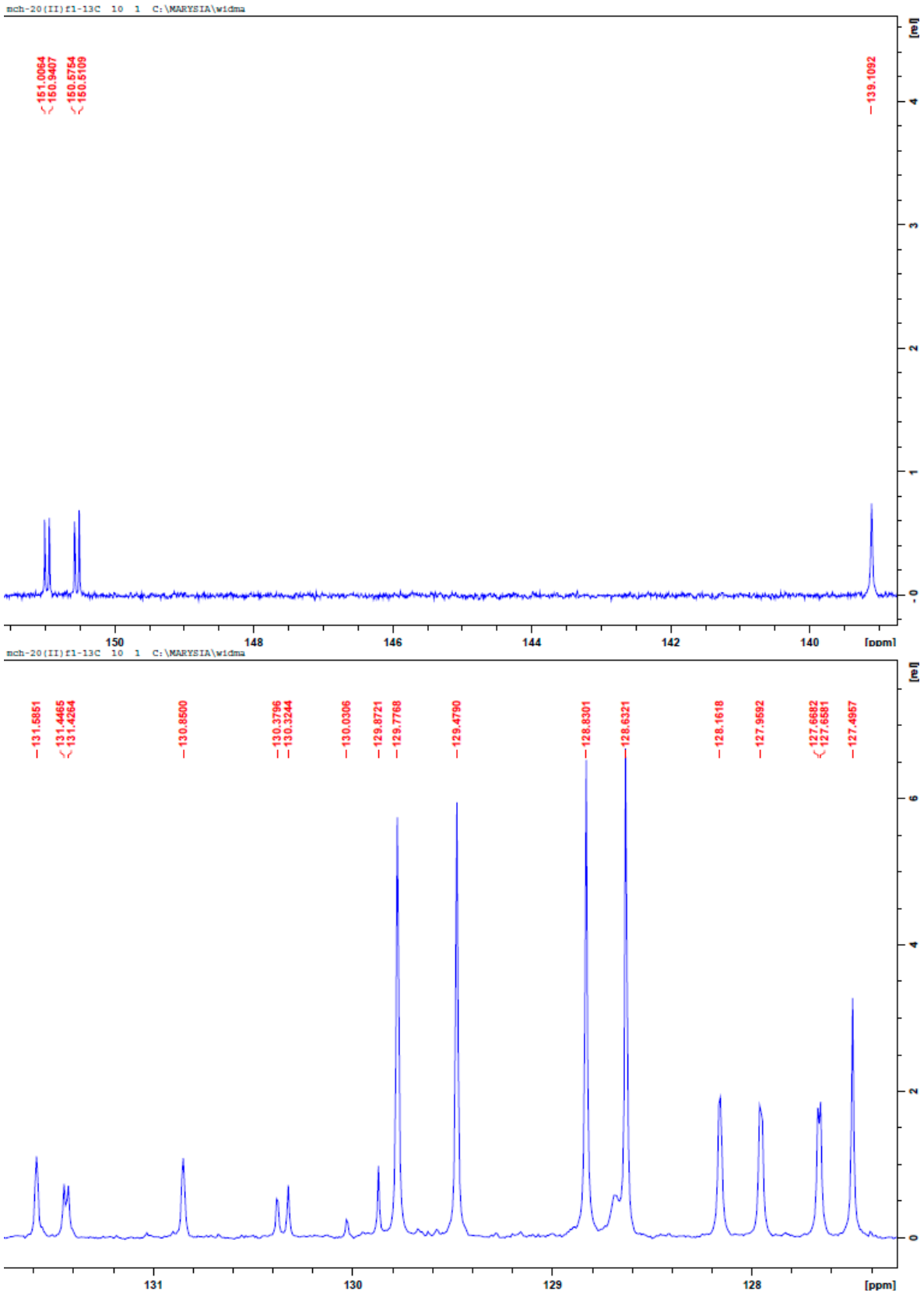


Figure S4. (**b**) Diphenyl *N*-benzylamino(pyren-1-yl)methylphosphonate (**3d**). ^{31}P-NMR.

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150.5754
150.5109
139.1092
[rel]
150
148
146
144
142
140
[ppm]
mch-20(II)f1-13C 10 1 C:\MARYSIA\widma
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131.4465
131.4264
130.8500
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130.3244
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129.4790
128.8301
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127.4957
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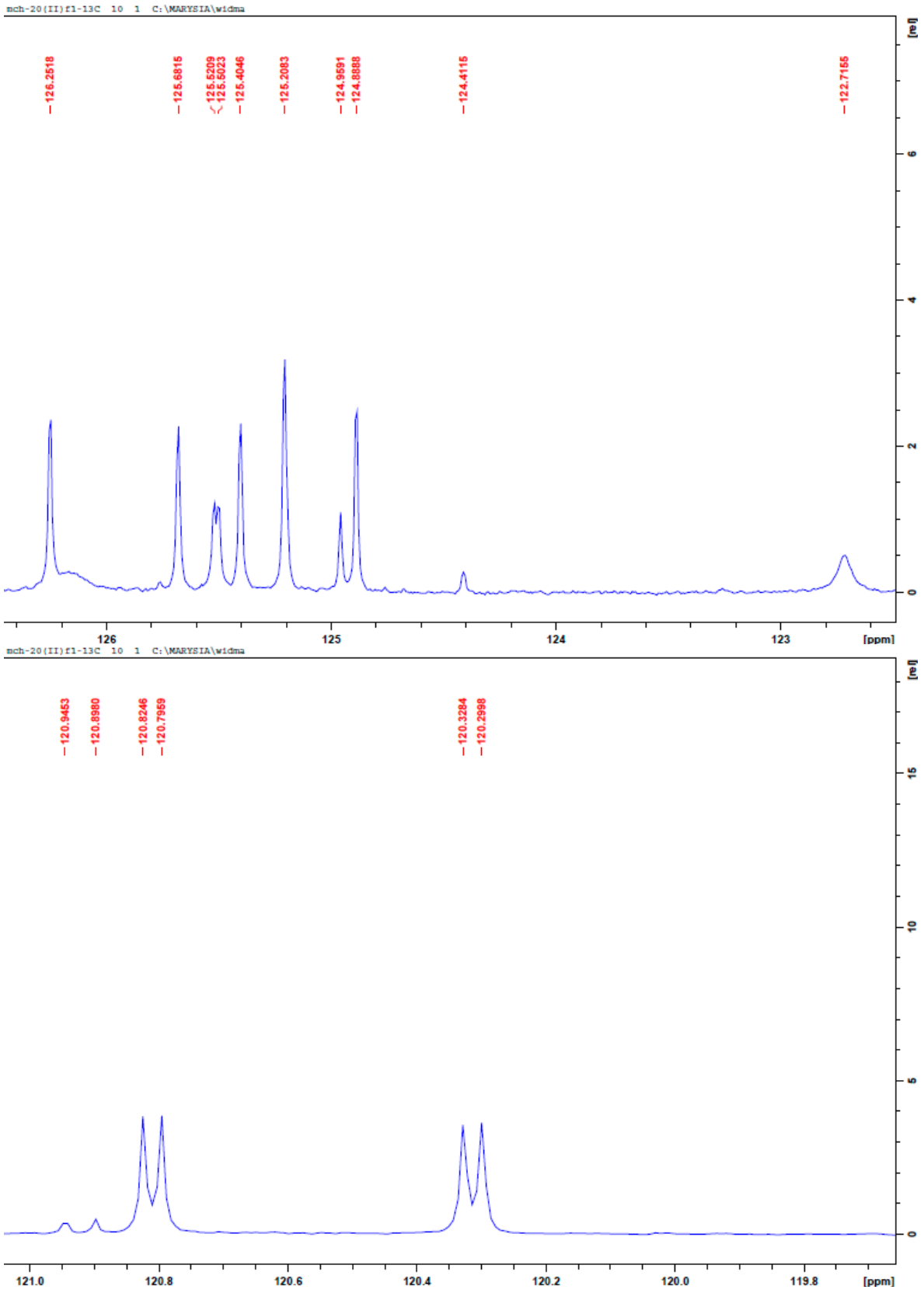
129
128
[ppm]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126.5209
126.5023
125.4046
125.2083
124.9591
124.8888
124.4115
122.7155
[rel]
126
125
124
123
[ppm]
mch-20(II)f1-13C 10 1 C:\MARYSIA\widma
120.9453
120.8980
120.8246
120.7959
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120.4
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120.0
119.8
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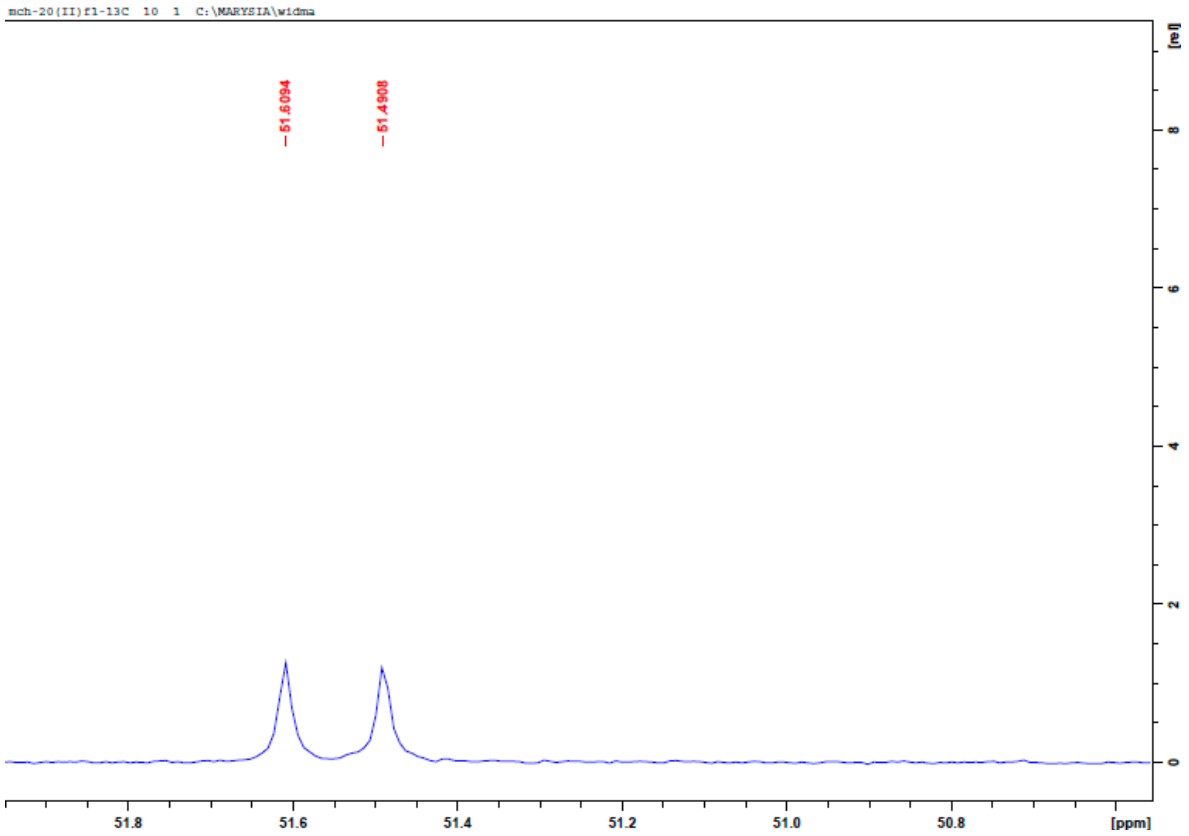
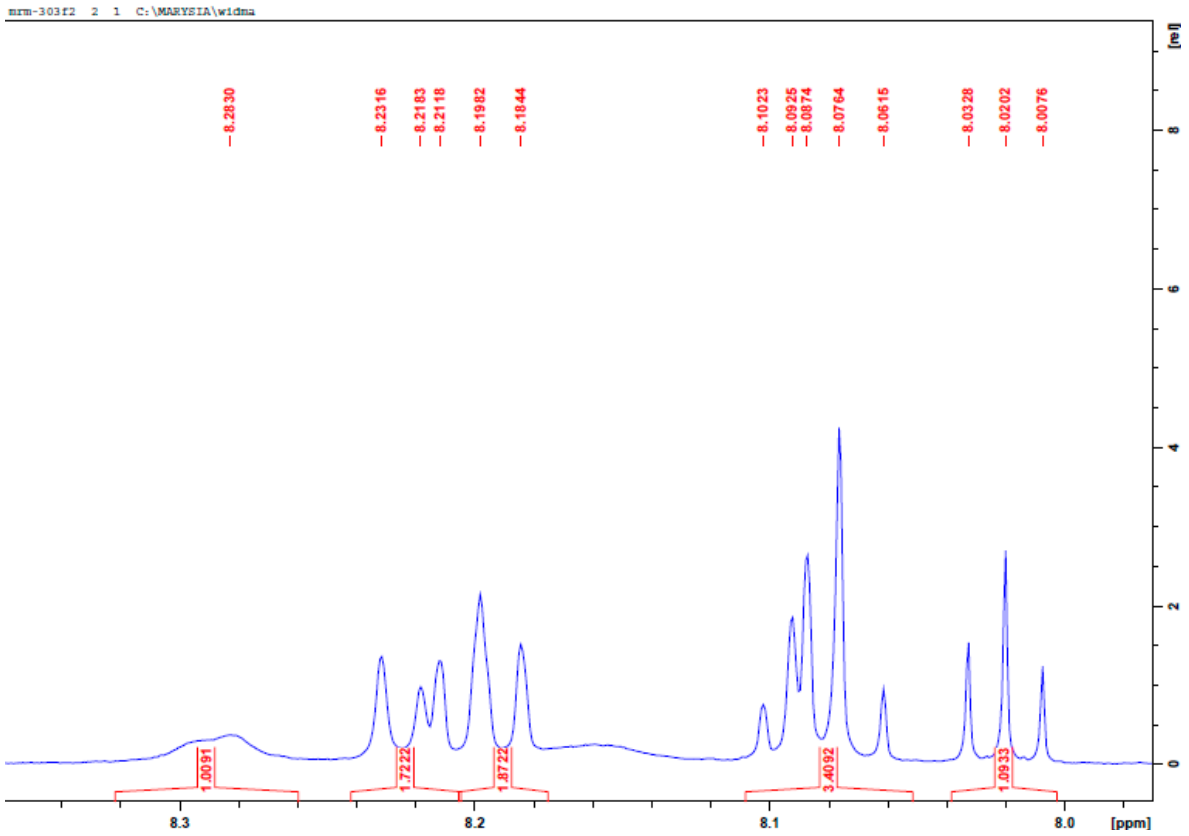
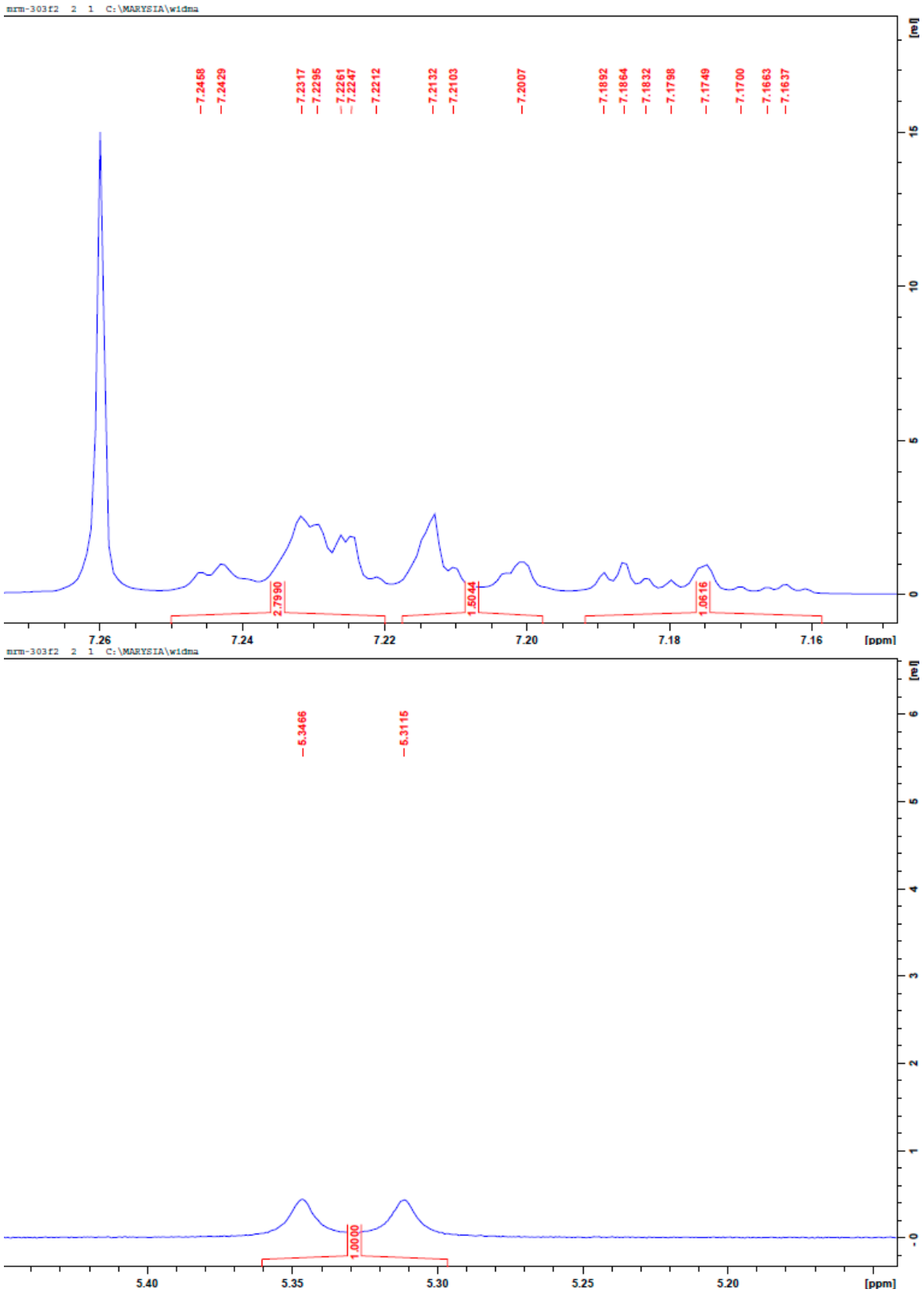


Figure S4. (**c**) Diphenyl *N*-benzylamino(pyren-1-yl)methylphosphonate (**3d**). ^{13}C-NMR—followed by enlarged fragments.

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7.2429
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7.2295
7.2261
7.2247
7.2212
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7.2103
7.2007
7.1892
7.1864
7.1832
7.1798
7.1749
7.1700
7.1663
7.1637
2.7990
1.5044
1.0616
7.26
7.24
7.22
7.20
7.18
7.16
[ppm]
[rel]
mrm-303f2 2 1 C:\MARYSIA\widma
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5.40
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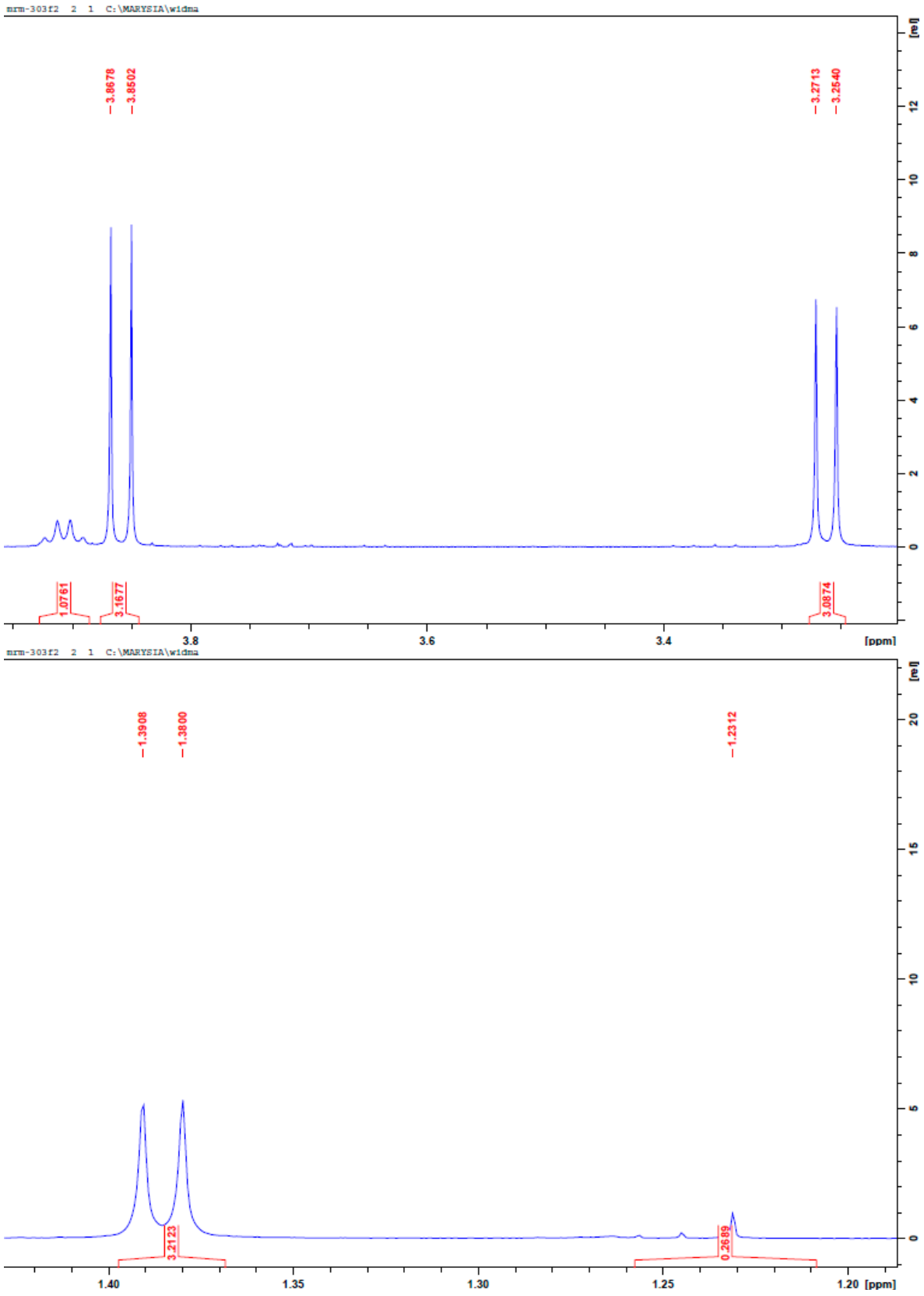


Figure S5. (**a**) Dimethyl *N*-(*R*)-*α*-methylbenzylamino(pyren-1-yl)methylphosphonate (**4**). Isolated predominant diastereoisomer ^{1}H-NMR—followed by enlarged fragments.

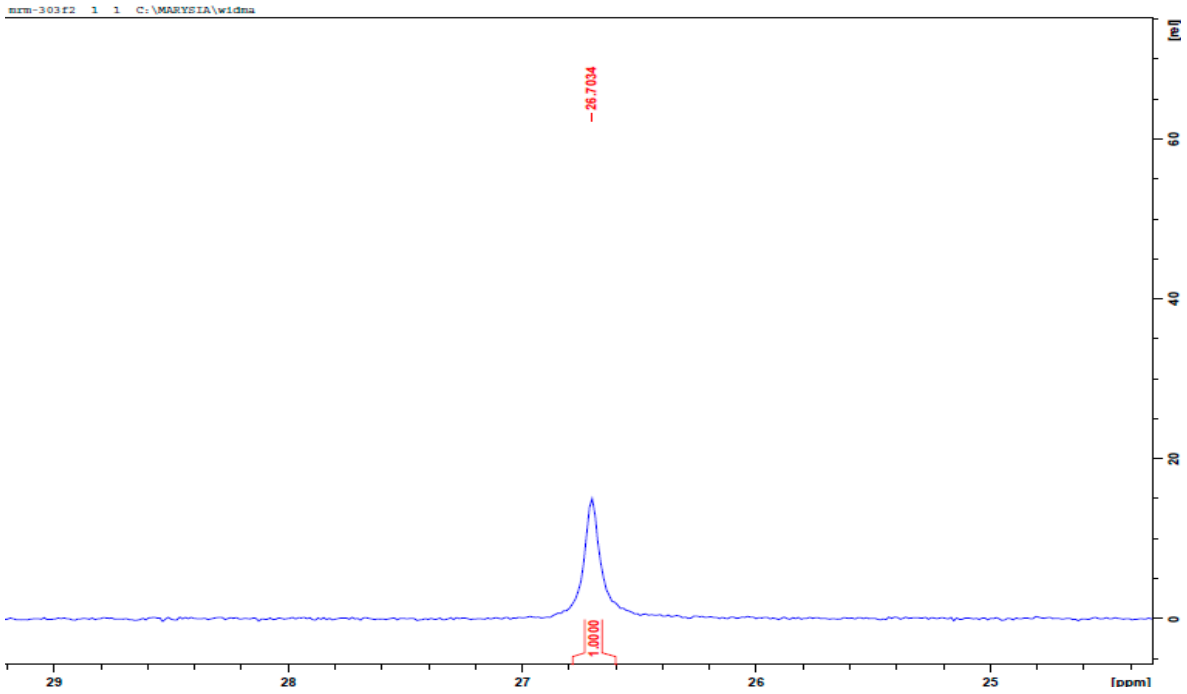
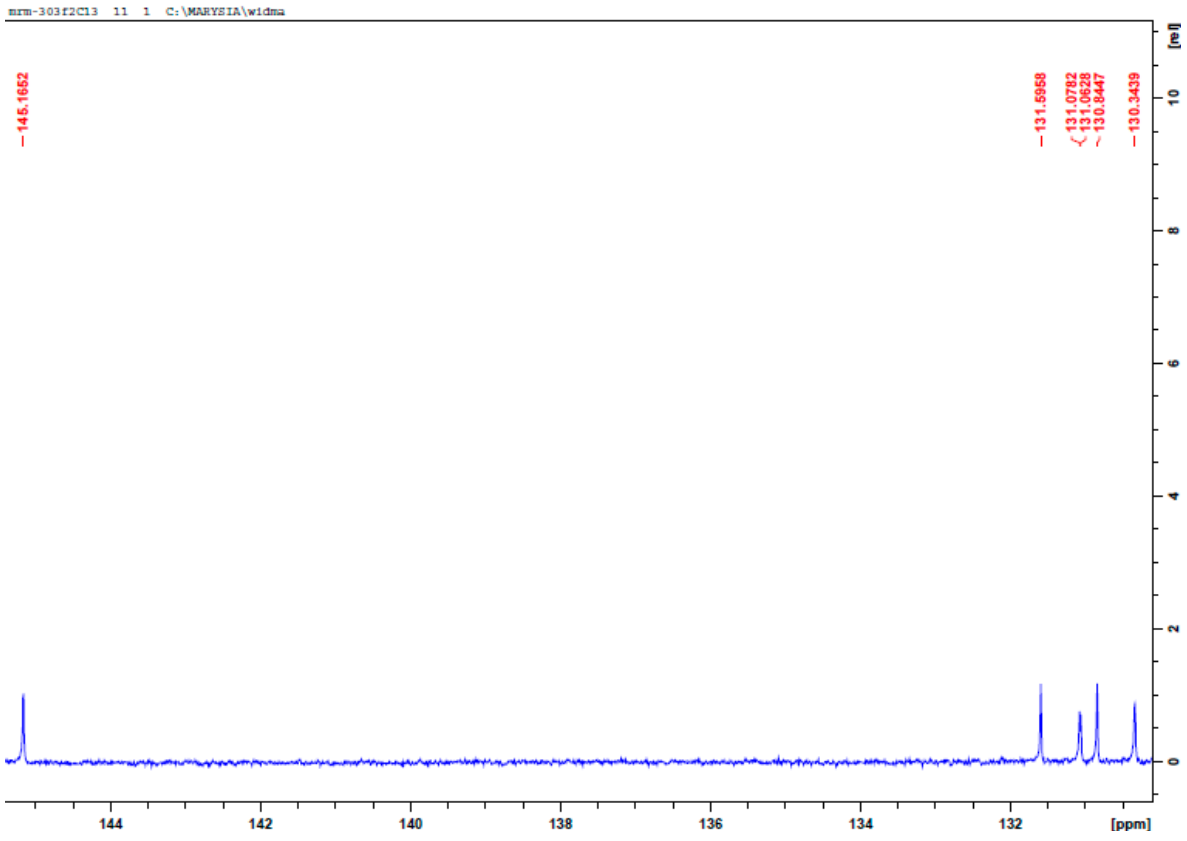
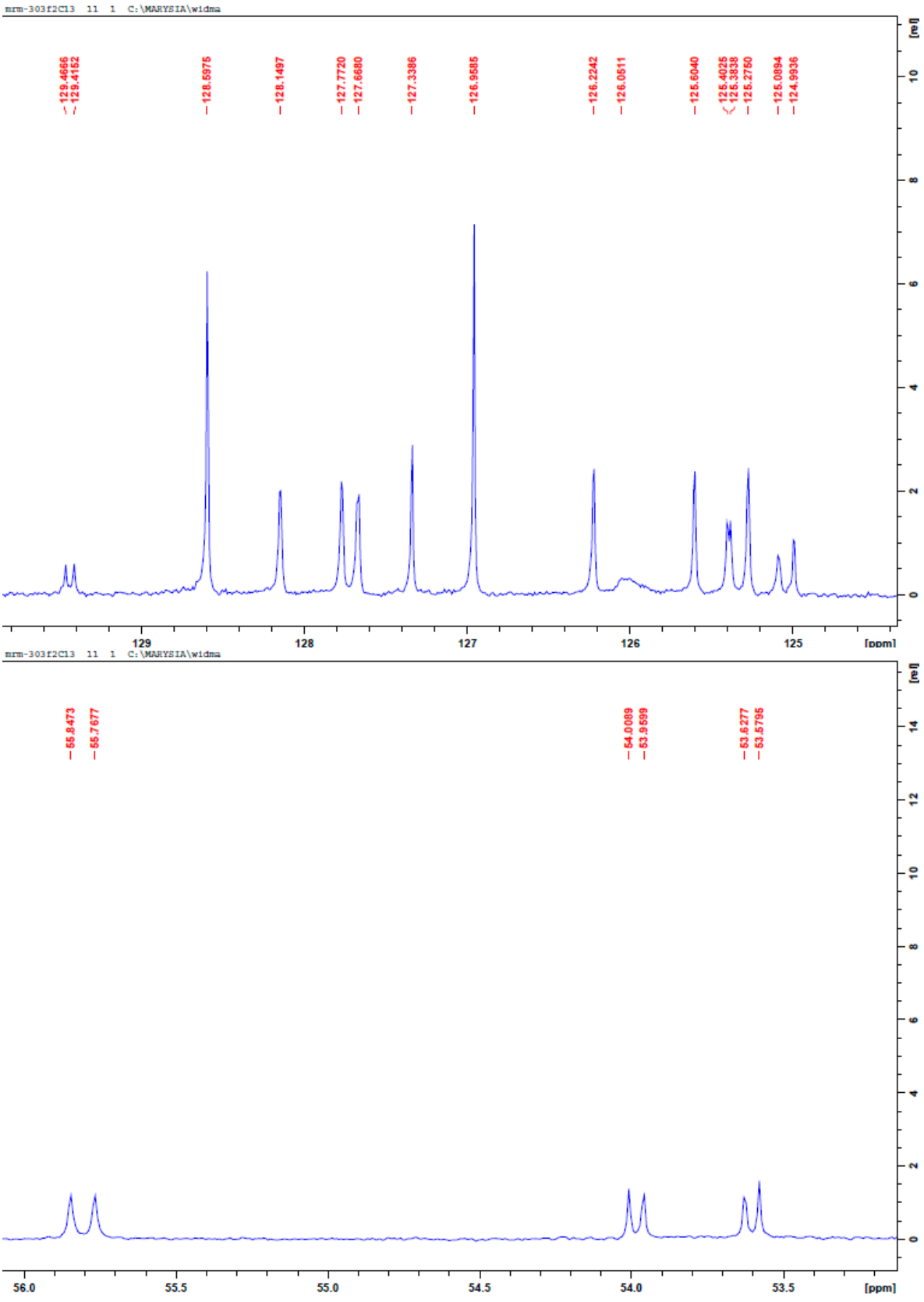


Figure S5. (**b**) Dimethyl *N*-(*R*)-*α*-methylbenzylamino(pyren-1-yl)methylphosphonate (**4**). Isolated predominant diastereoisomer ^{31}P-NMR.

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125.4025
125.3838
125.2750
125.0894
124.9936
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129
128
127
126
125
[ppm]
mrm-303f2C13 11 1 C:\MARYSIA\widma
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55.7677
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53.9599
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55.5
55.0
54.5
54.0
53.5
[ppm]

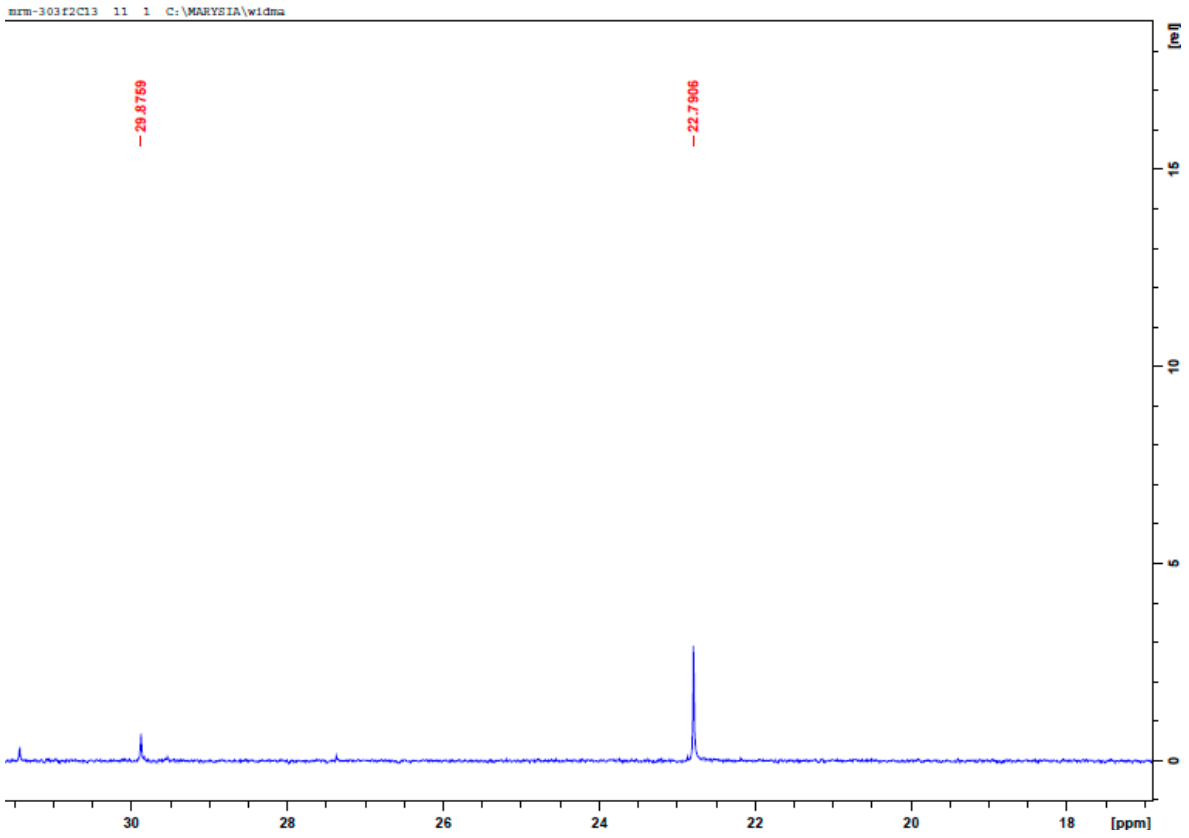
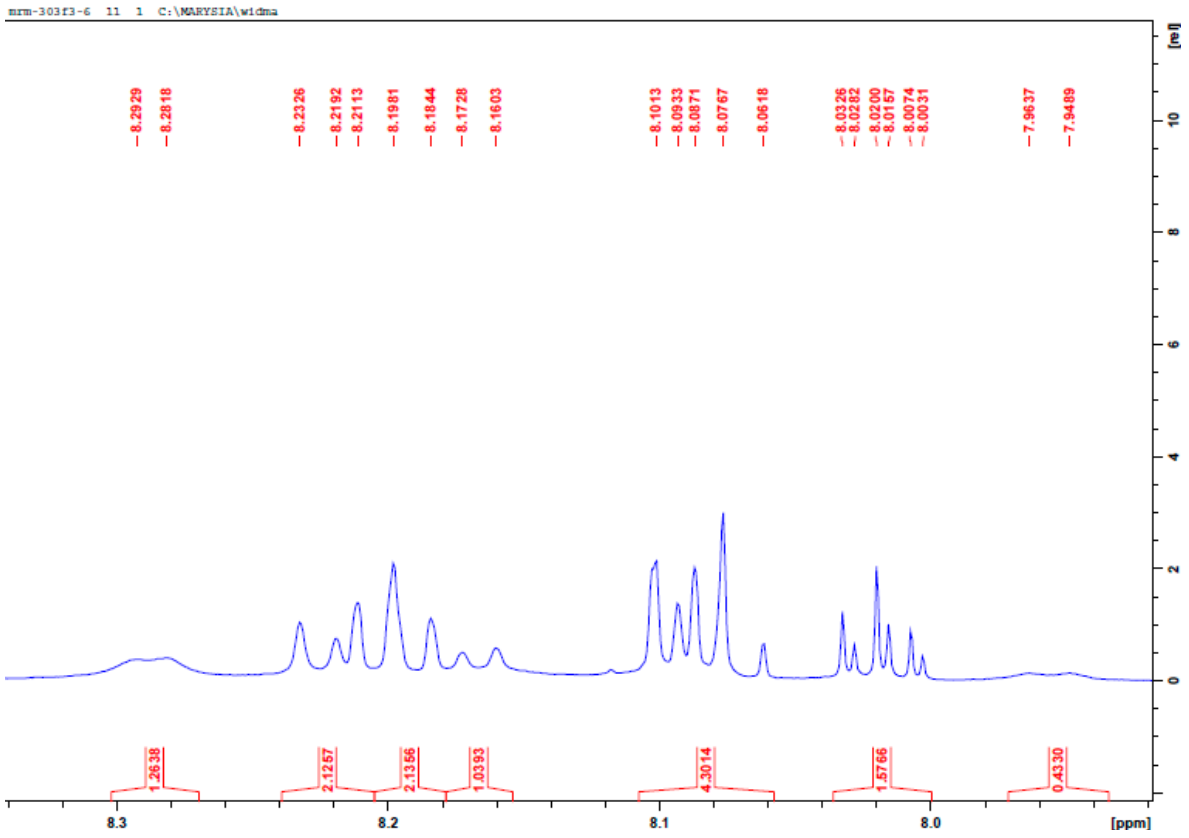
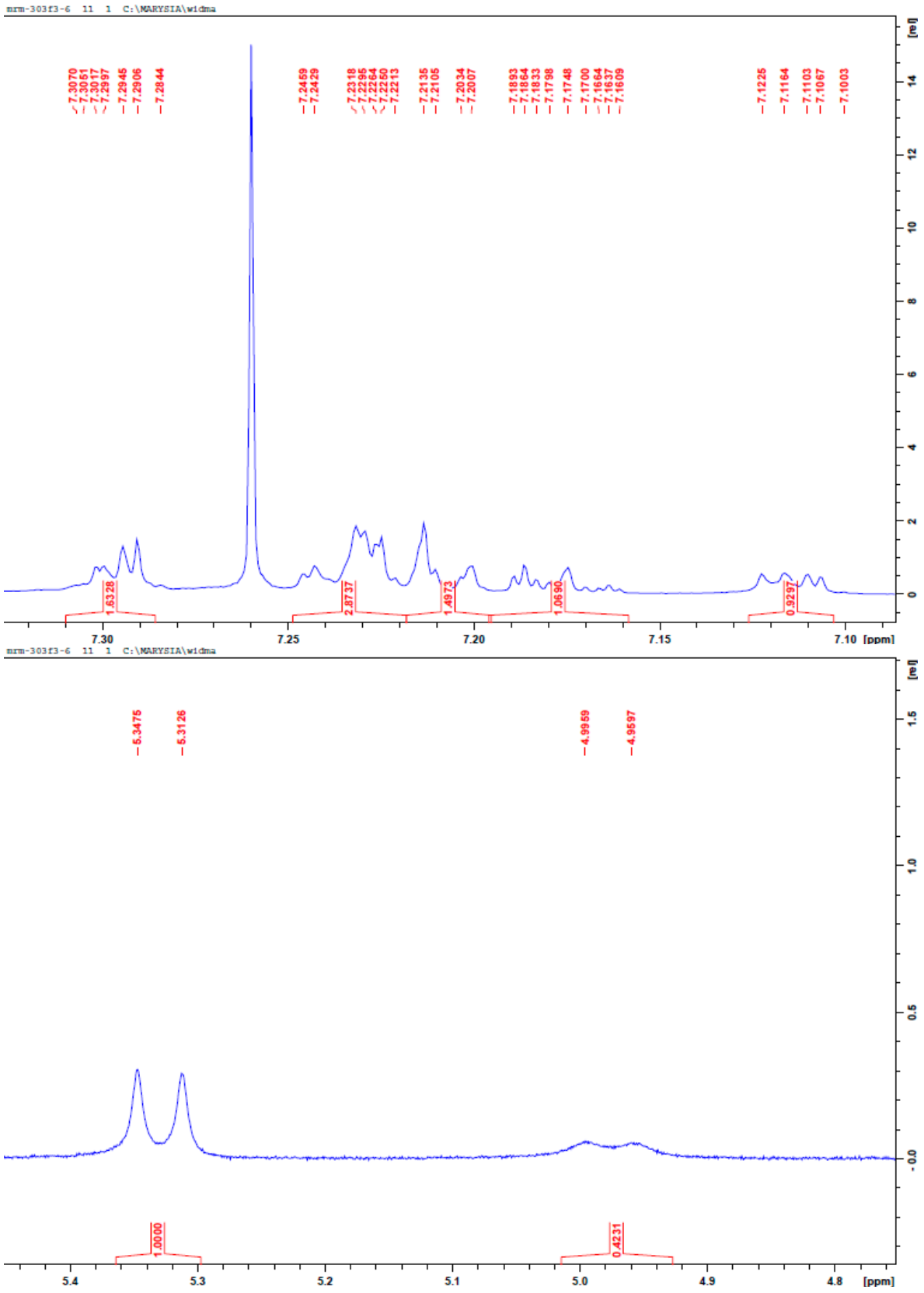


Figure S5. (**c**) Dimethyl *N*-(*R*)-*α*-methylbenzylamino(pyren-1-yl)methylphosphonate (**4**). Isolated predominant diastereoisomer ^{13}C-NMR—followed by enlarged fragments.

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7.3051
7.3017
7.2997
7.2945
7.2906
7.2844
7.2459
7.2429
7.2318
7.2295
7.2264
7.2250
7.2213
7.2135
7.2105
7.2034
7.2007
7.1893
7.1864
7.1833
7.1798
7.1748
7.1700
7.1664
7.1637
7.1609
7.1225
7.1164
7.1103
7.1067
7.1003
1.6328
2.8737
1.4973
1.0690
0.9297
7.30
7.25
7.20
7.15
7.10 [ppm]
[rel]
mrm-303f3-6 11 1 C:\MARYSIA\widma
5.3475
5.3126
4.9959
4.9597
1.0000
0.4231
5.4
5.3
5.2
5.1
5.0
4.9
4.8 [ppm]
[rel]

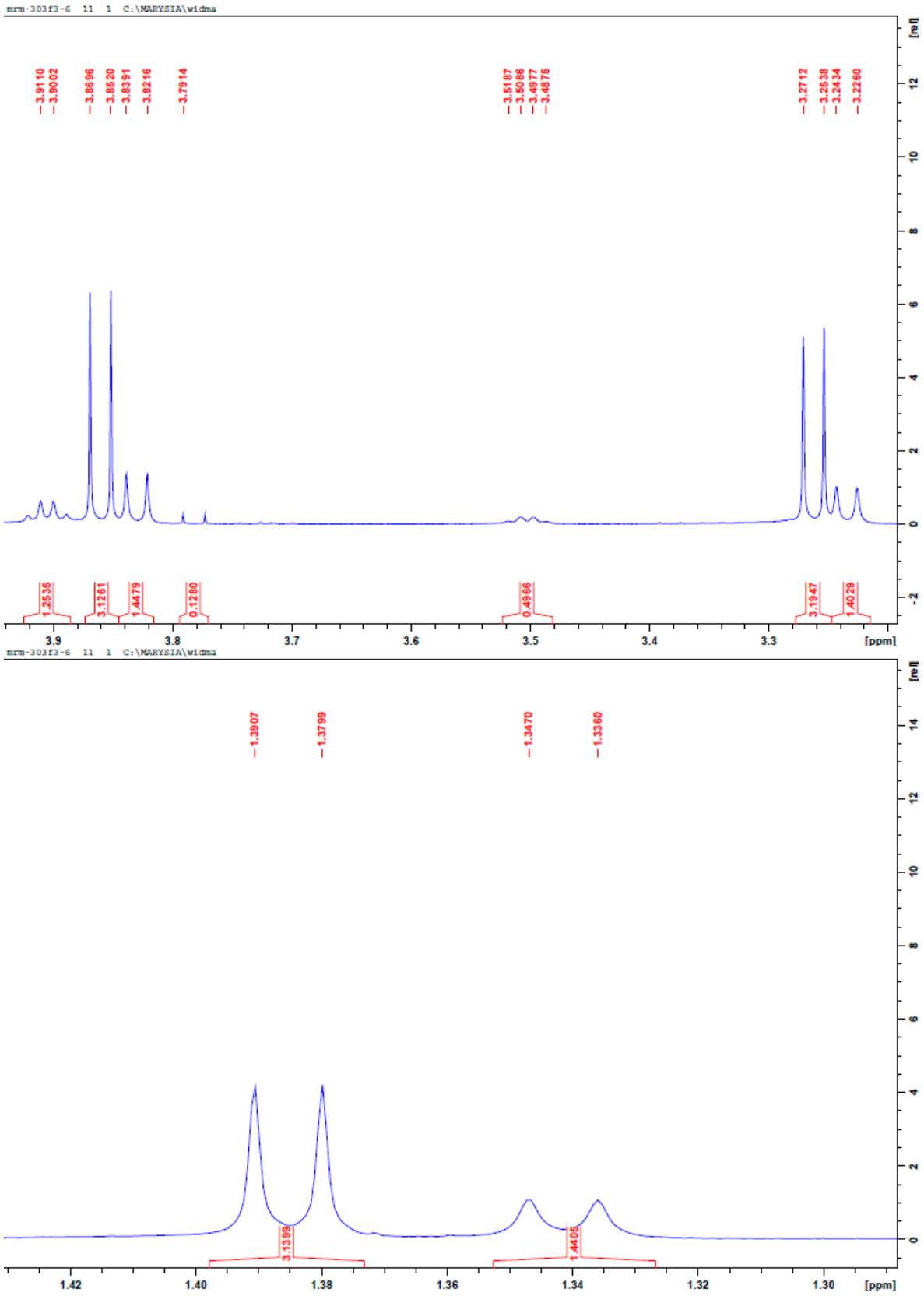


Figure S6. (**a**) Dimethyl *N*-(*R*)-*α*-methylbenzylamino(pyren-1-yl)methylphosphonate (**4**). Mixture of diastereoisomers ^{1}H-NMR—followed by enlarged fragments.

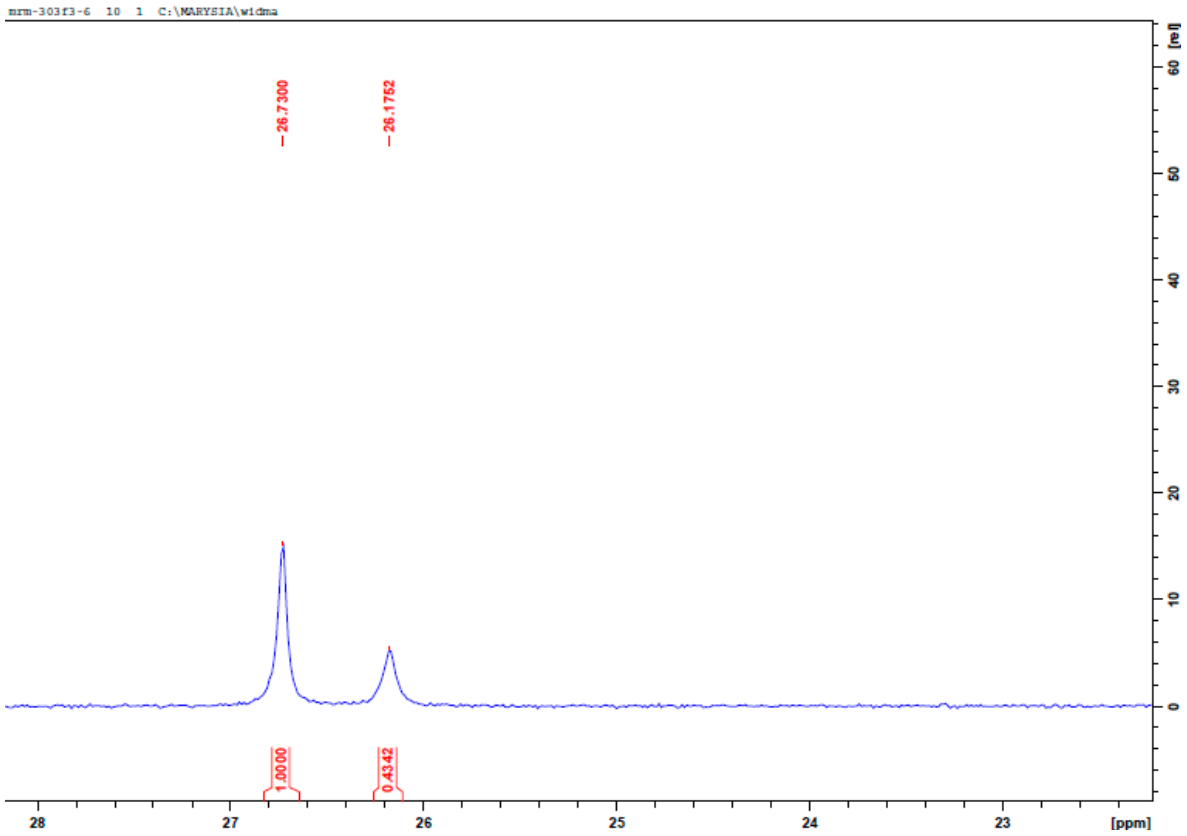
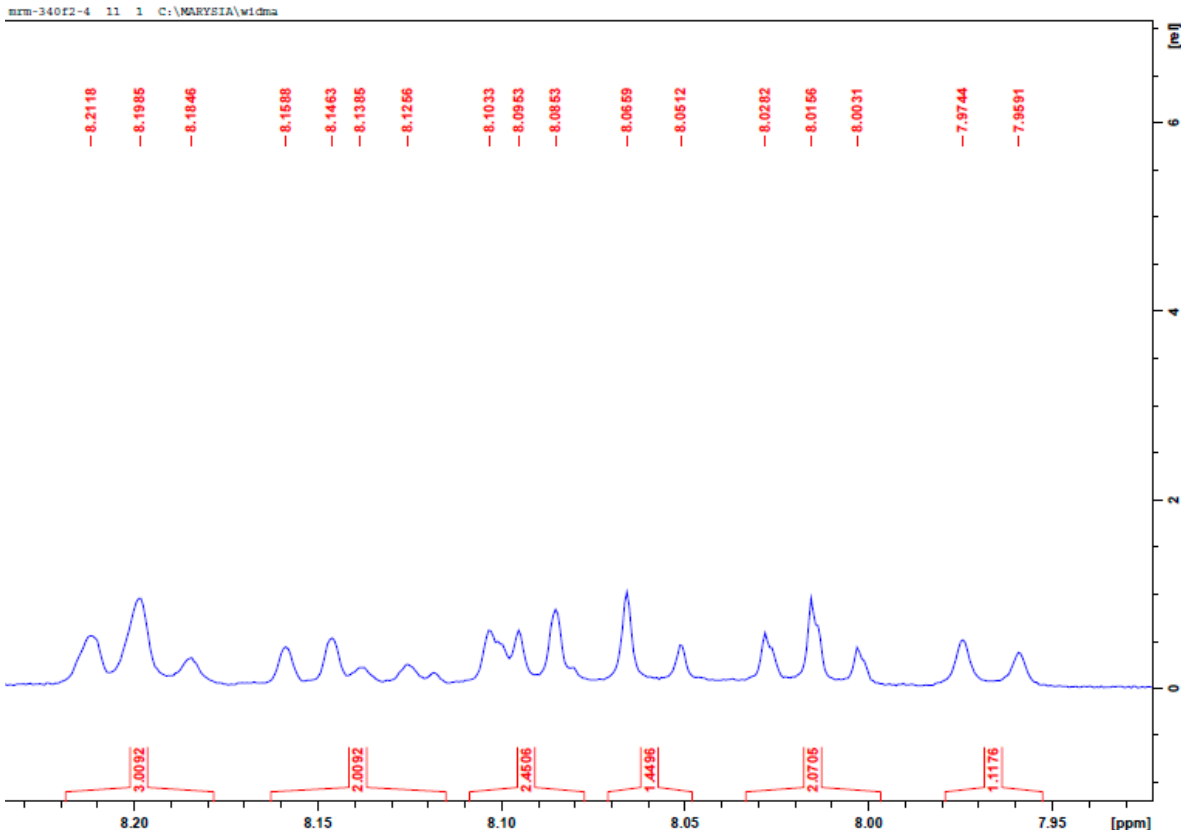
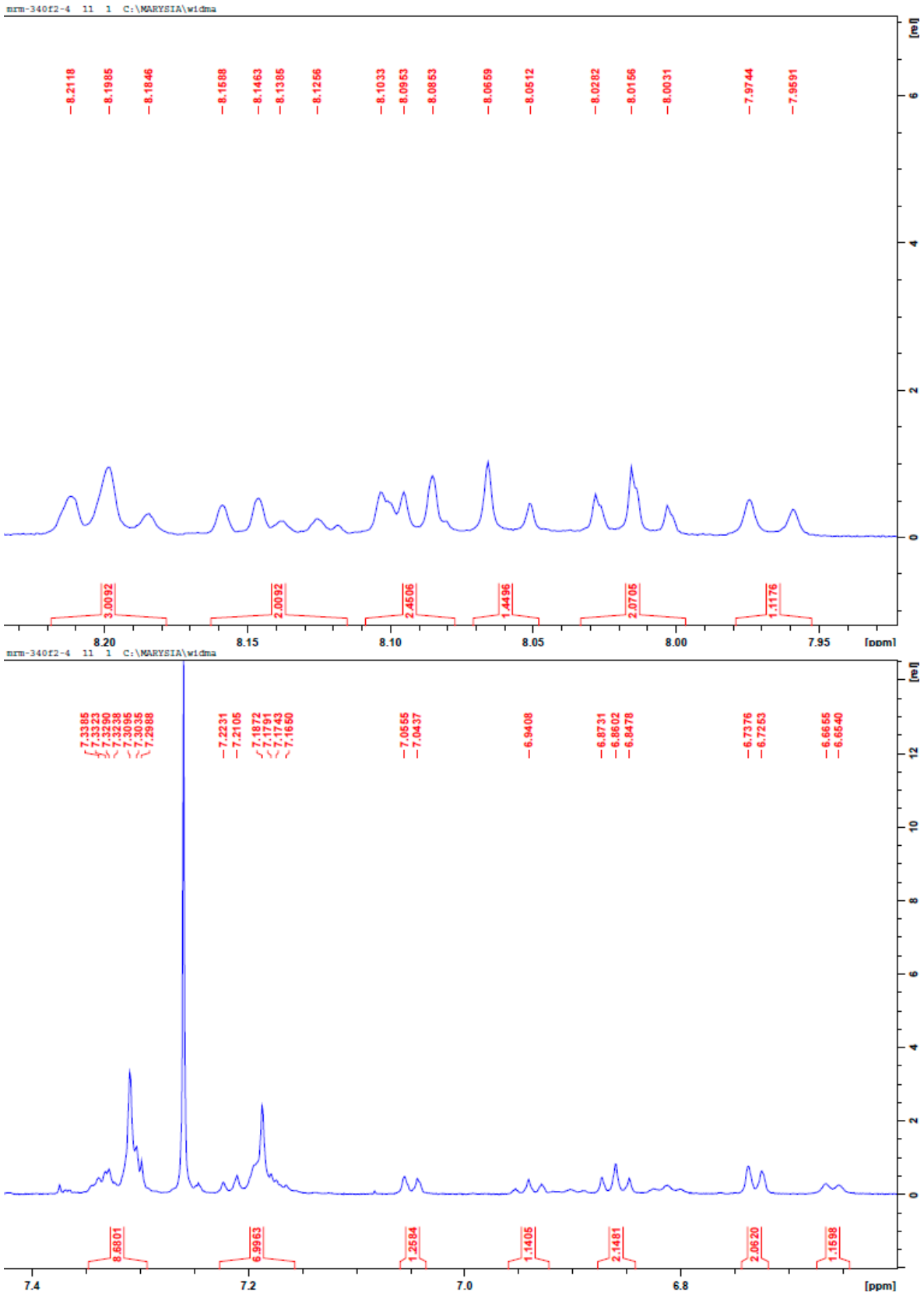


Figure S6. (**b**) Dimethyl *N*-(*R*)-*α*-methylbenzylamino(pyren-1-yl)methylphosphonate (**4**). Mixture of diastereoisomers ^{31}P-NMR.

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8.1846
8.1588
8.1463
8.1385
8.1256
8.1033
8.0953
8.0853
8.0659
8.0512
8.0282
8.0166
8.0031
7.9744
7.9591
3.0092
2.0092
2.4506
1.4496
2.0705
1.1176
8.20
8.15
8.10
8.05
8.00
7.95
[ppm]
[rel]
mrm-340f2-4 11 1 C:\MARYSIA\widma
7.3385
7.3323
7.3290
7.3238
7.3096
7.3035
7.2988
7.2231
7.2105
7.1872
7.1791
7.1743
7.1650
7.0555
7.0437
6.9408
6.8731
6.8602
6.8478
6.7376
6.7263
6.6655
6.6540
8.6801
6.9963
1.2584
1.1405
2.1481
2.0620
1.1598
7.4
7.2
7.0
6.8
[ppm]
[rel]

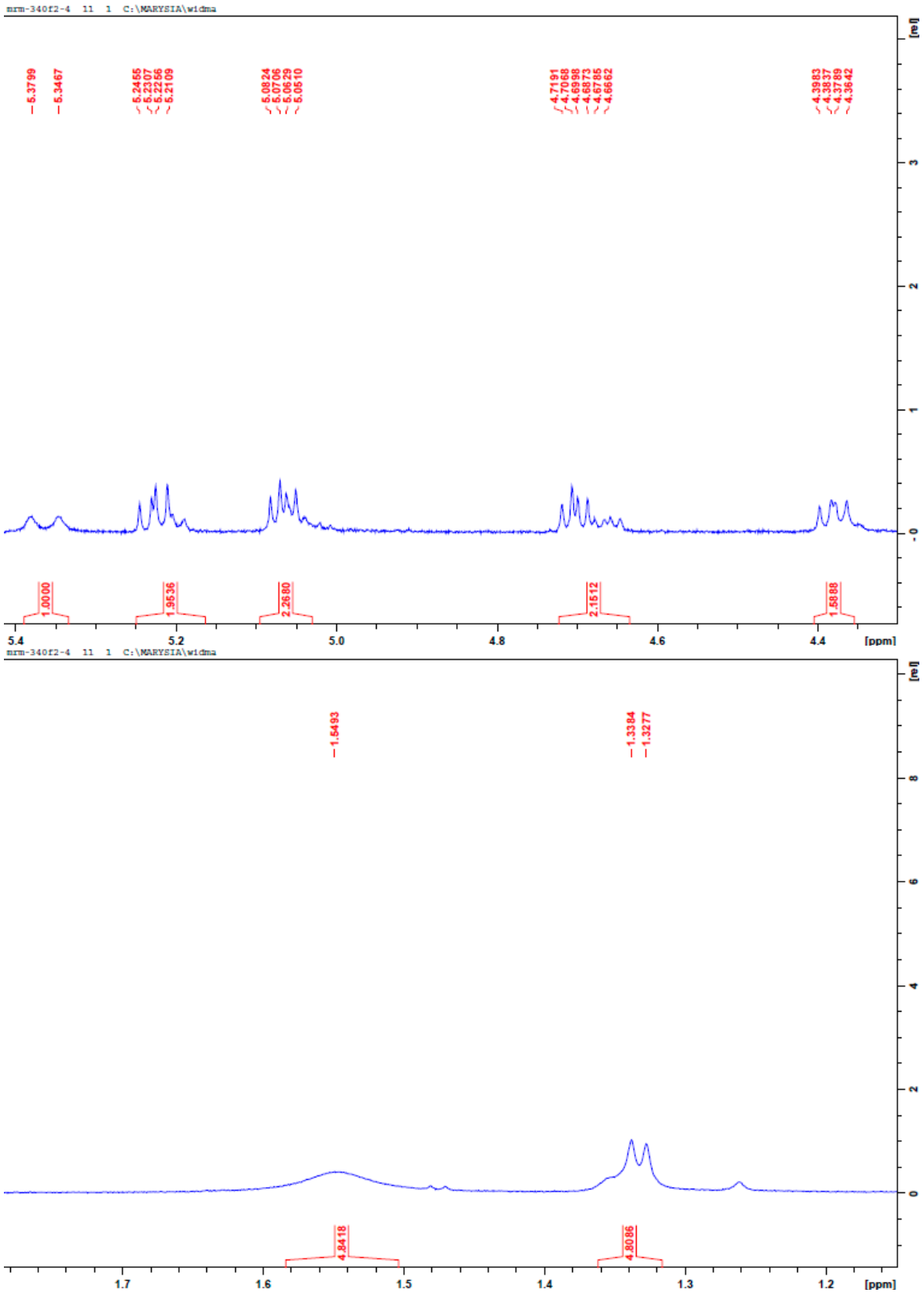


Figure S7. (**a**) Dibenzyl *N*-(*R*)-*α*-methylbenzylamino(pyren-1-yl)methylphosphonate (**5**). Mixture of diastereoisomers ^{1}H-NMR—followed by enlarged fragments.

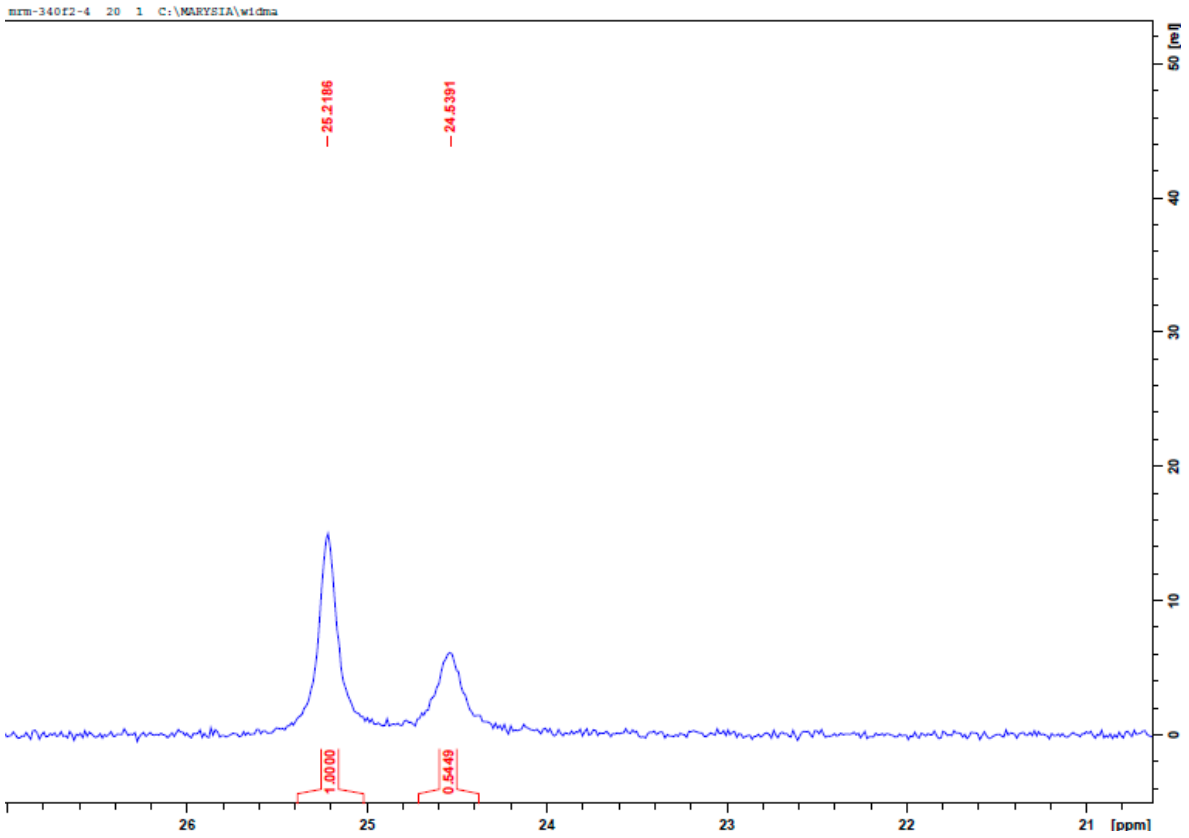
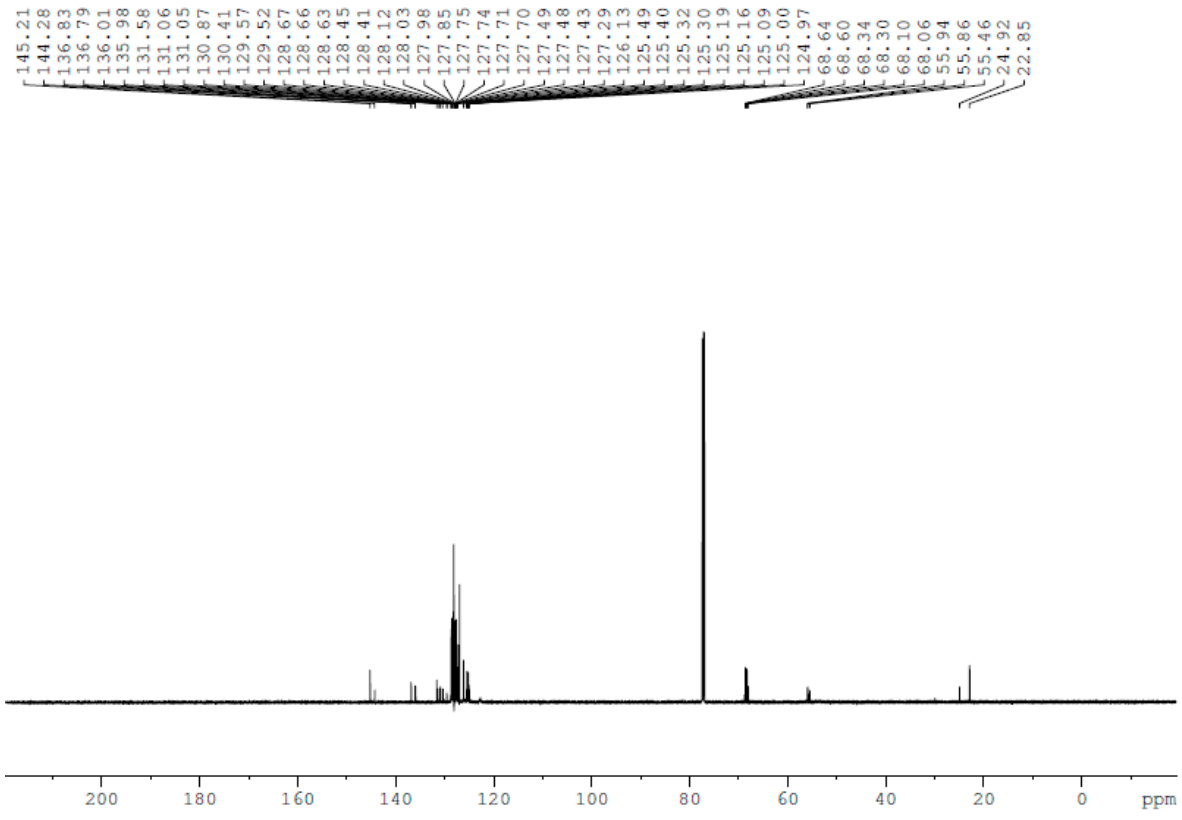
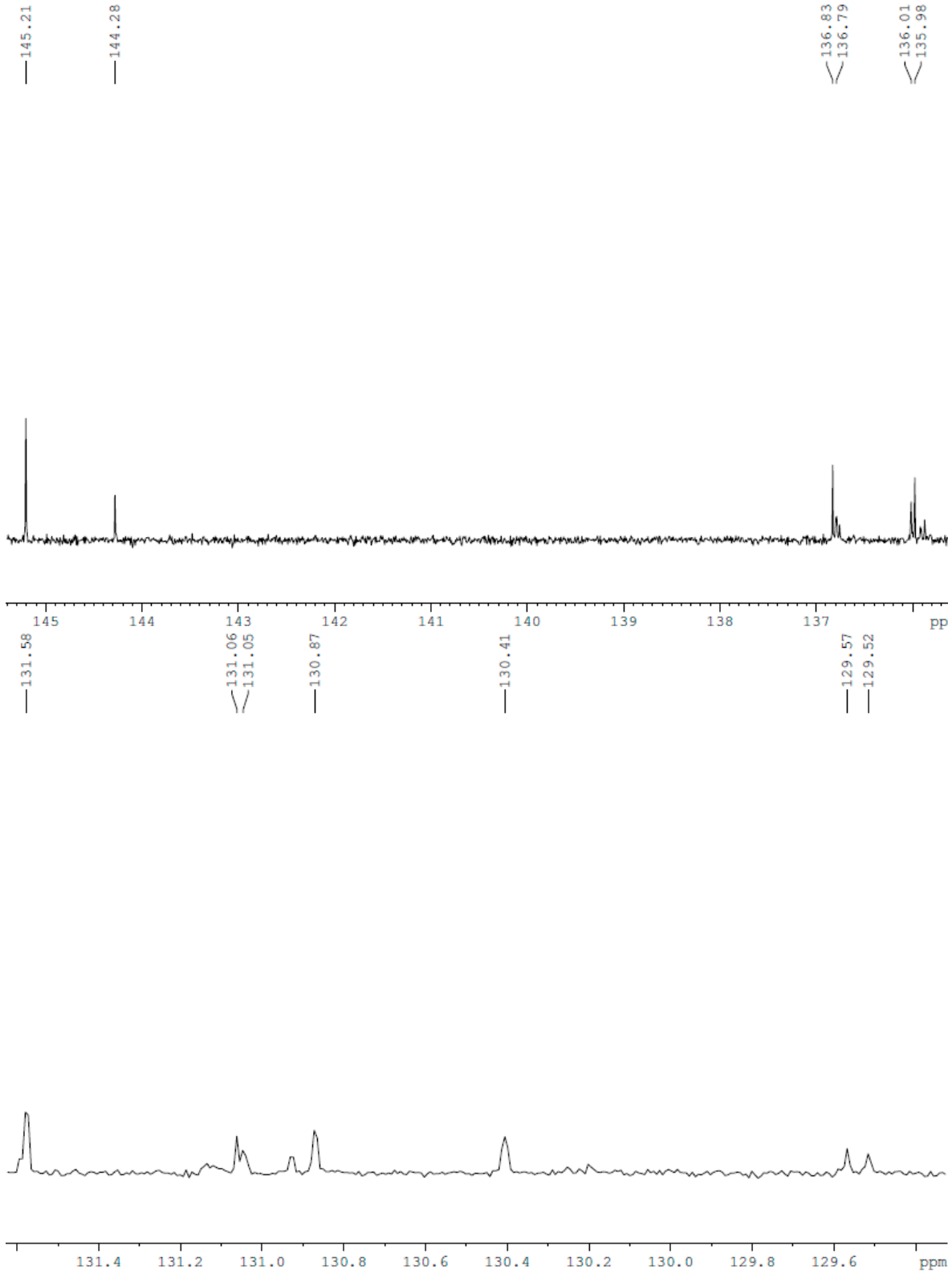


Figure S7. (**b**) Dibenzyl *N*-(*R*)-*α*-methylbenzylamino(pyren-1-yl)methylphosphonate (**5**). Mixture of diastereoisomers ^{31}P-NMR.

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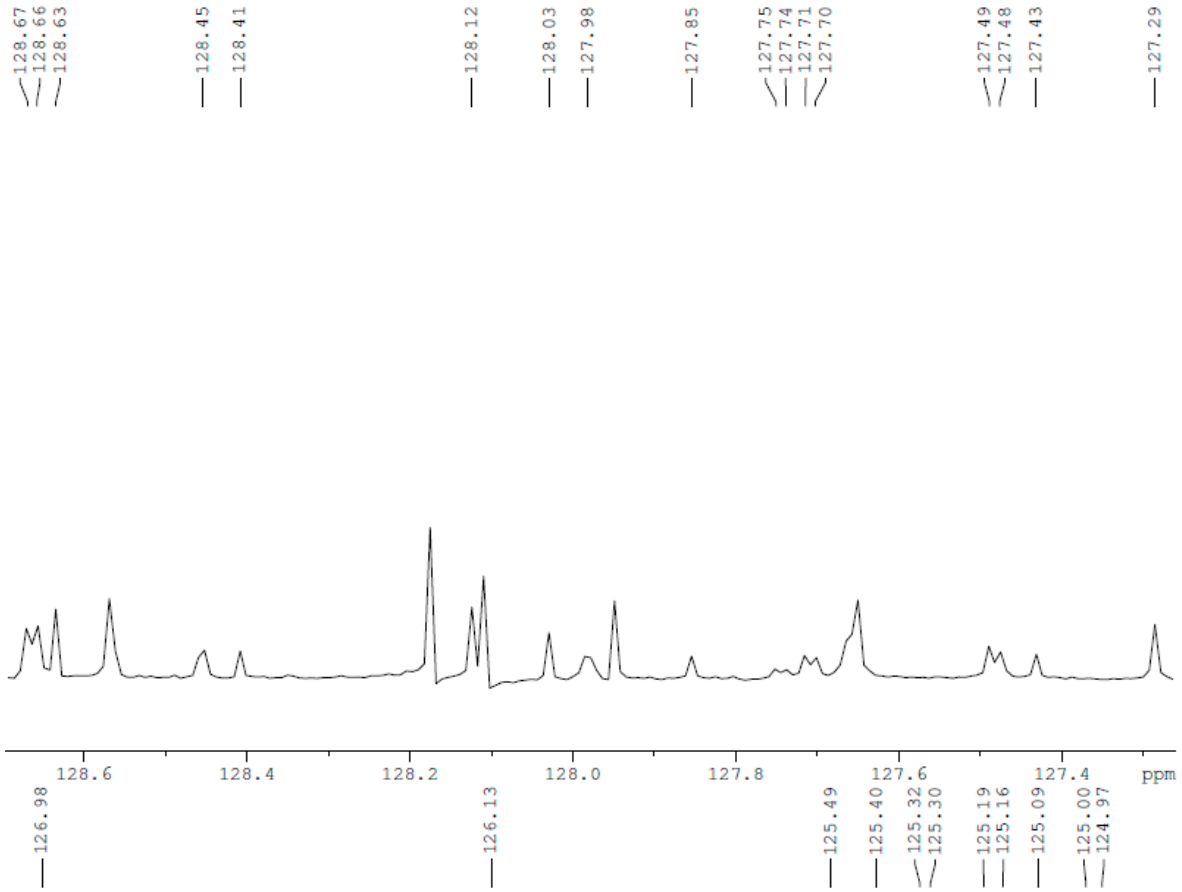
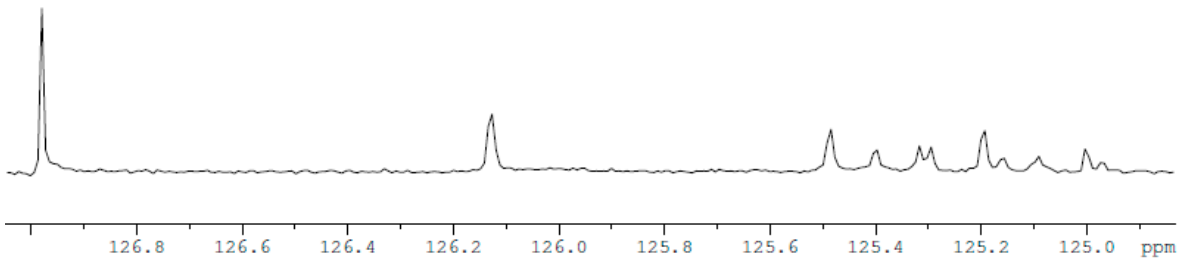
144.28
136.83
136.79
136.01
135.98
145
144
143
142
141
140
139
138
137
pp
131.58
131.06
131.05
130.87
130.41
129.57
129.52
131.4
131.2
131.0
130.8
130.6
130.4
130.2
130.0
129.8
129.6
ppm


128.67
128.66
128.63
128.45
128.41
128.12
128.03
127.98
127.85
127.75
127.74
127.71
127.70
127.49
127.48
127.43
127.29
128.6
128.4
128.2
128.0
127.8
127.6
127.4
ppm
126.98
126.13
125.49
125.40
125.32
125.30
125.19
125.16
125.09
125.00
124.97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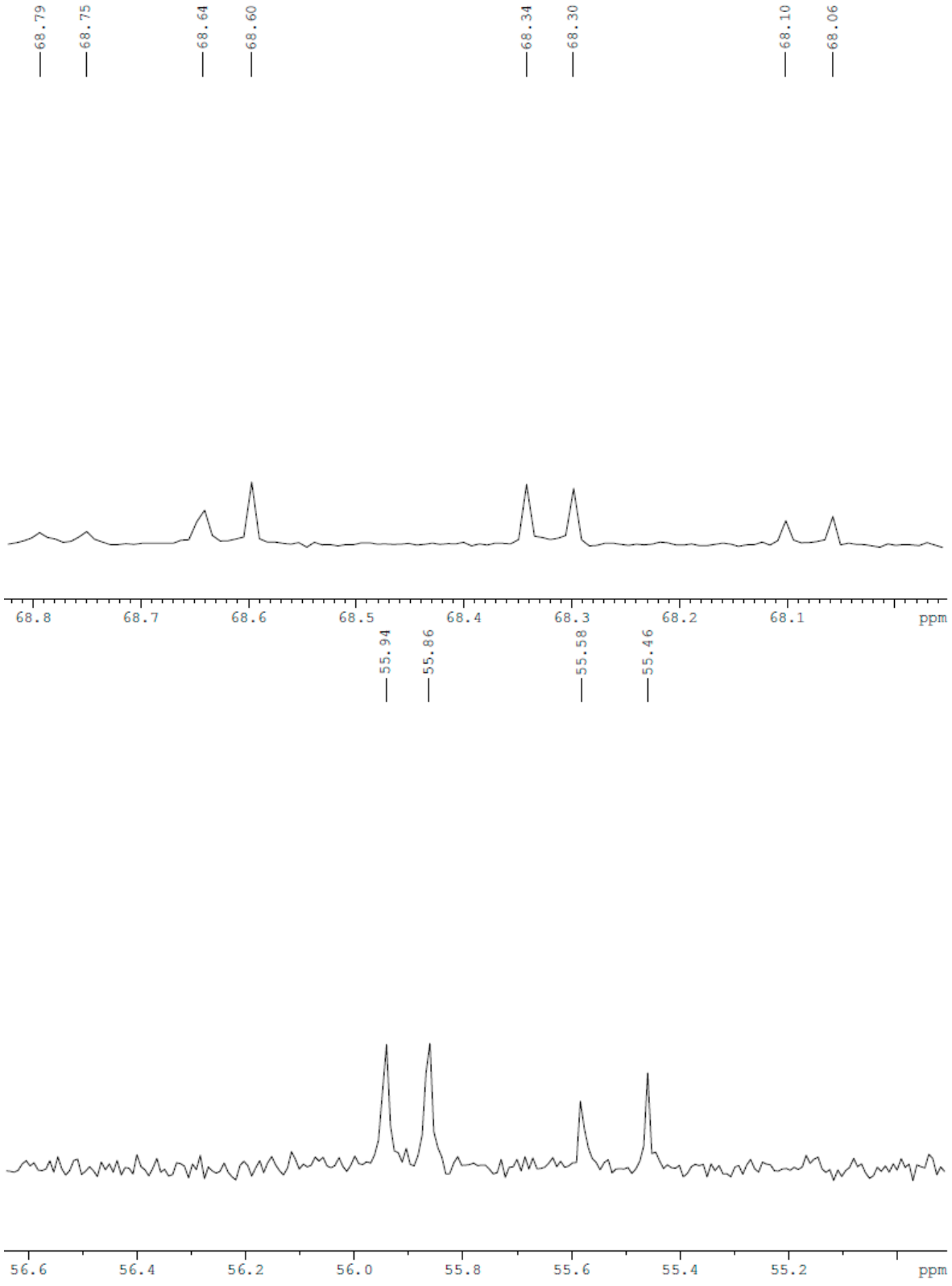
126.6
126.4
126.2
126.0
125.8
125.6
125.4
125.2
125.0
ppm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68.64
68.60
68.34
68.30
68.10
68.06
68.8
68.7
68.6
68.5
68.4
68.3
68.2
68.1
ppm
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56.0
55.8
55.6
55.4
55.2
ppm

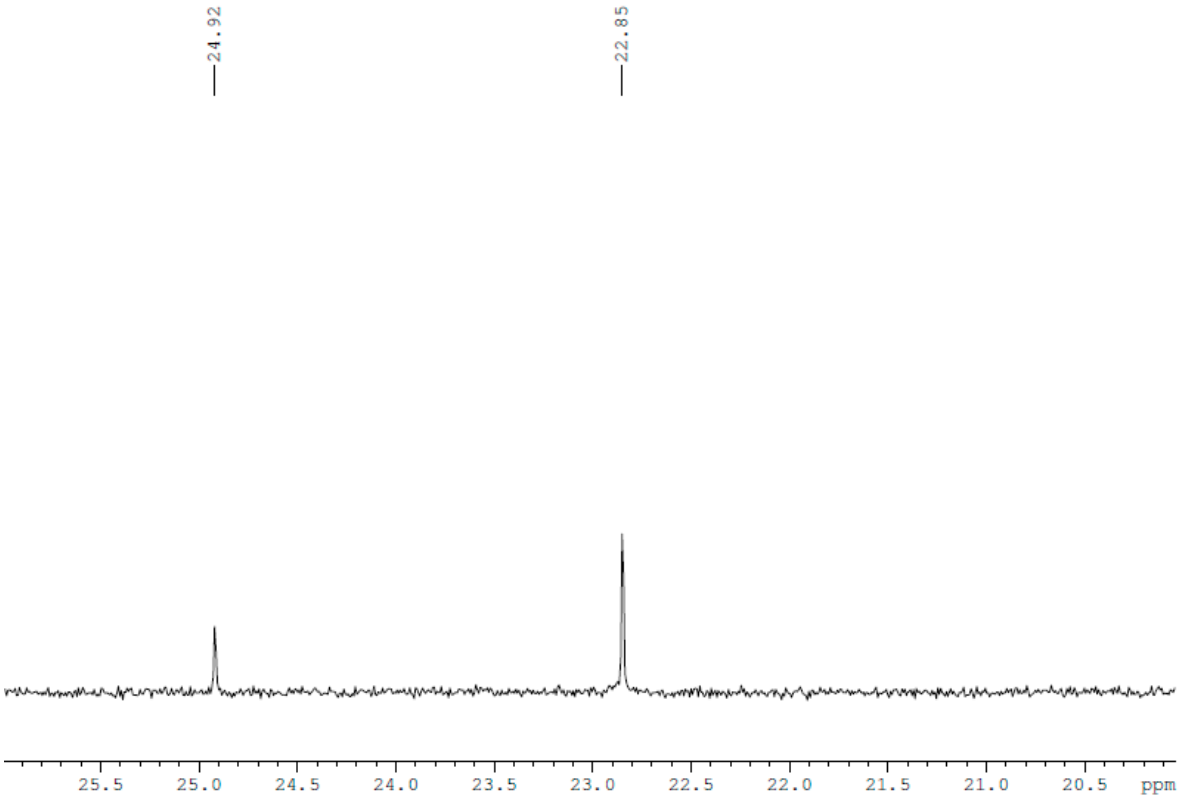

Figure S7. (**c**) Dibenzyl *N*-(*R*)-*α*-methylbenzylamino(pyren-1-yl)methylphosphonate (**5**). Mixture of diastereoisomers ^{13}C-NMR—followed by enlarged fragments.