Supporting information

Exceptional Effect of Nitro Substituent on the Phosphonation of Imines: The First Report on Phosphonation of Imines to α-Iminophosphonates and α-(N-phosphorylamino)phosphonates

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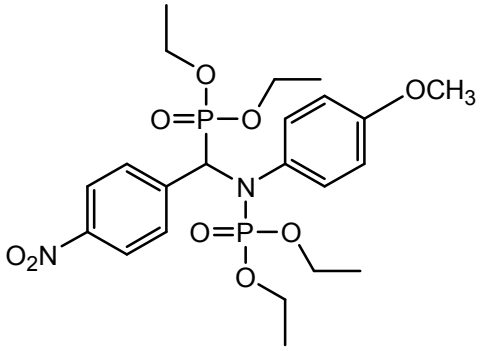
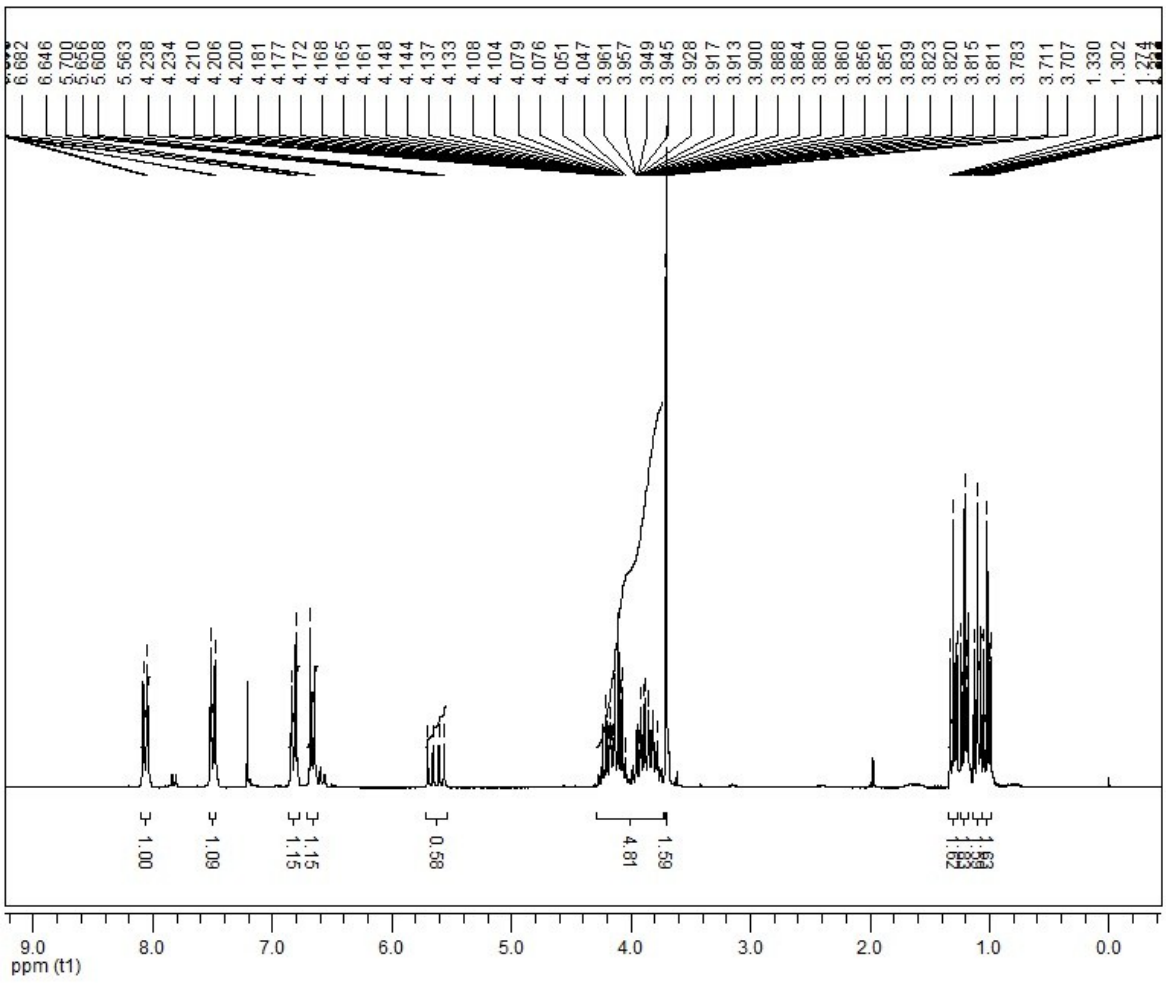
Spectral data:

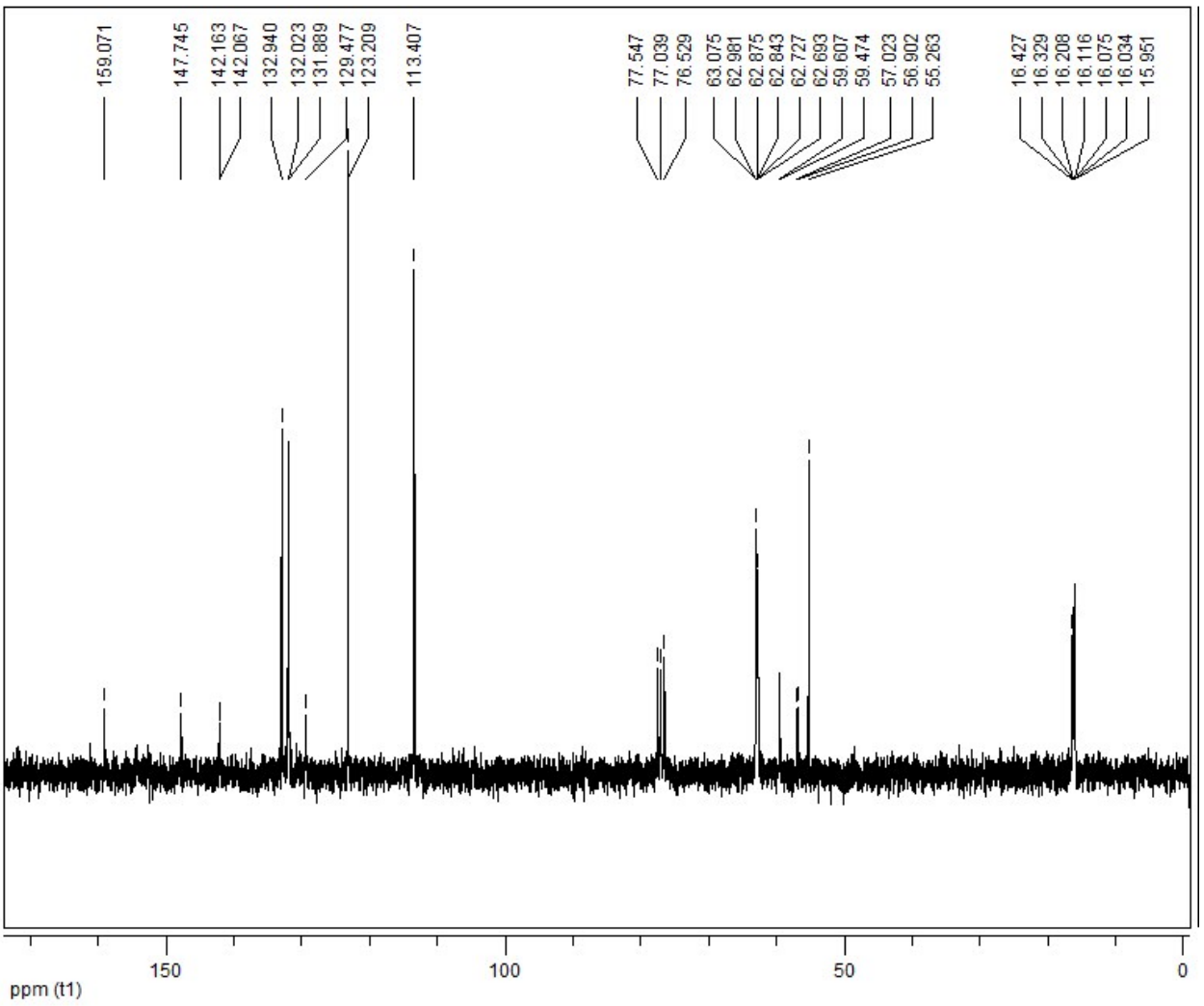
(2a):



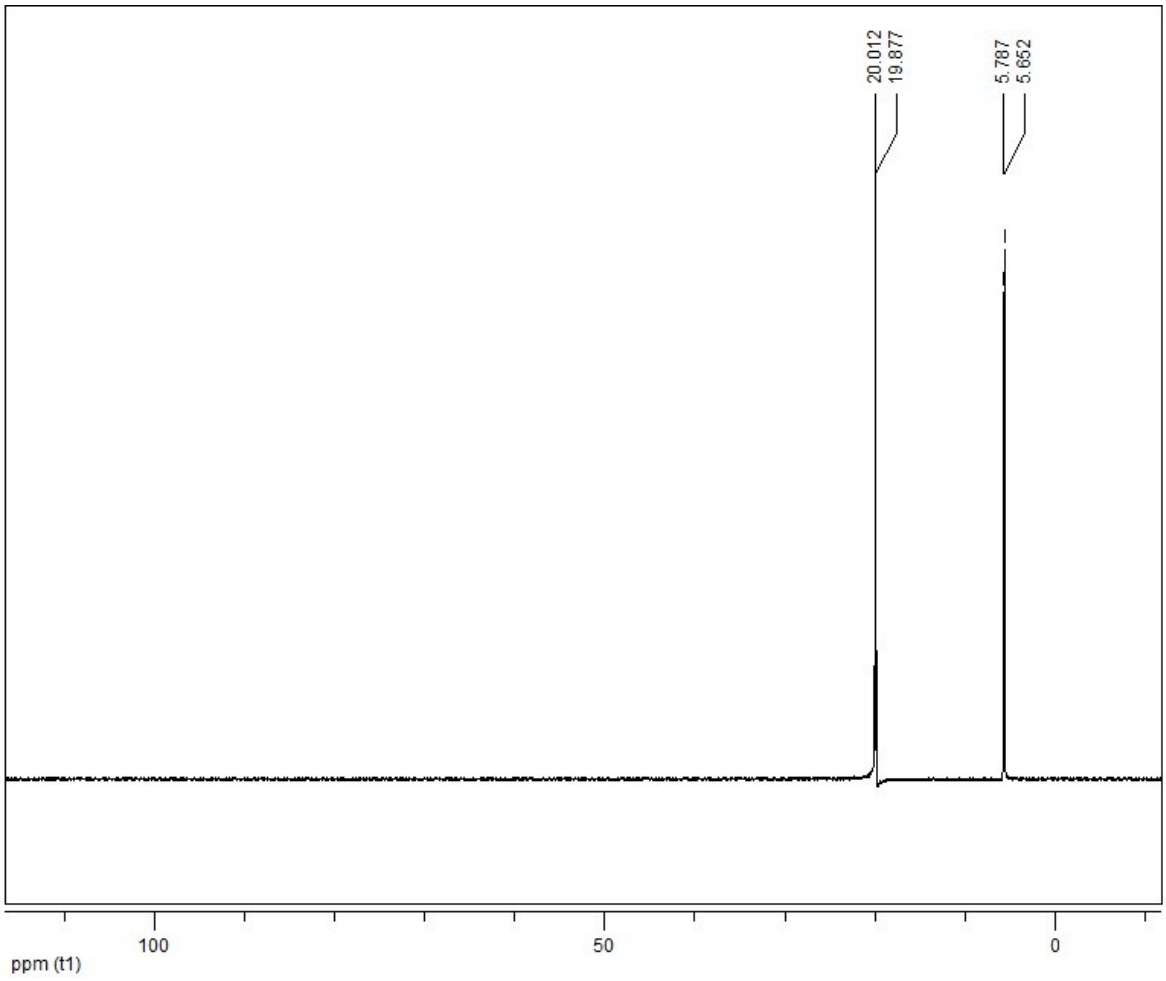
Yellow oil; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm):8.06 (d, 2H, J=9Hz), 7.49 (d, 2H, J= 9Hz), 6.82 (d, 2H, J= 9Hz), 6.66 (d, 2H, J= 9Hz), 5.63 (dd, 1H, ^{2}J (H-P)= 23.1Hz, ^{3}J (H-P)= 11Hz),4.23-3.78 (m, 8H),3.70 (d, 3H, J= 1Hz),1.30 (t, 3H, J= 7Hz), 1.20 (mt, 3H,), 1.10 (mt, 3H), 1.02 (t, 3H, J= 7Hz); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 159.0, 147.7 , 142.1 (d, ^{2}J(C-P)= 6.0Hz), 132.9, 131.9 (d, ^{2}J(C-P)= 8.4Hz), 129.4, 123.2, 113.4, 62.6- 63.0 (m, 4C, -CH_2-,), 58.5 (dd, -CH-, ^{2}J (C-P)= 8.3Hz, ^{1}J (C-P)= 162.1Hz), 55.2 (1C, -OCH_3), 15.9-16.4 (m, 4C, -CH_3); ^{31}P-NMR ($CDCl_3$, 162 MHz)δ (ppm): 19.94 (d, ^{3}J(P-P)= 21.8 Hz), 5.71(d, ^{3}J (P-P)= 21.8 Hz); IR (KBr): ν [cm^{-1}] 2985.6, 2931.6, 2869.9, 1604.7, 1519.8, 1350.1, 1249.8, 1026.1, 964.3, 864.1; Anal. Calcd for $C_{22}H_{32}N_2O_9P_2$: C, 49.81; H, 6.08; N, 5.28. Found: C, 49.42; H, 5.83; N, 4.98.


6.682
6.646
5.700
5.656
5.608
5.563
4.238
4.234
4.210
4.206
4.200
4.181
4.177
4.172
4.168
4.165
4.161
4.148
4.144
4.137
4.133
4.108
4.104
4.079
4.076
4.051
4.047
3.961
3.957
3.949
3.945
3.928
3.917
3.913
3.900
3.888
3.884
3.880
3.860
3.856
3.851
3.839
3.823
3.820
3.815
3.811
3.783
3.711
3.707
1.330
1.302
1.00
1.09
1.15
1.15
0.58
4.81
1.59
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

^{1}H NMR

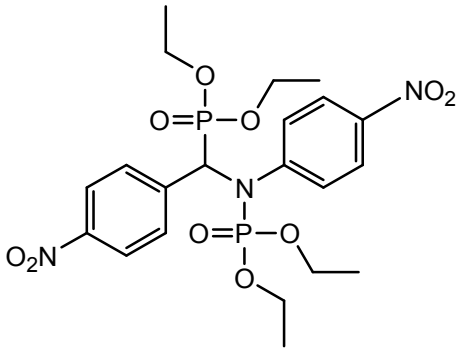

159.071
147.745
142.163
142.067
132.940
132.023
131.889
129.477
123.209
113.407
77.547
77.039
76.529
63.075
62.981
62.875
62.843
62.727
62.693
59.607
59.474
57.023
56.902
55.263
16.427
16.329
16.208
16.116
16.075
16.034
15.951
150
100
50
0
ppm (t1)

^{13}C NMR



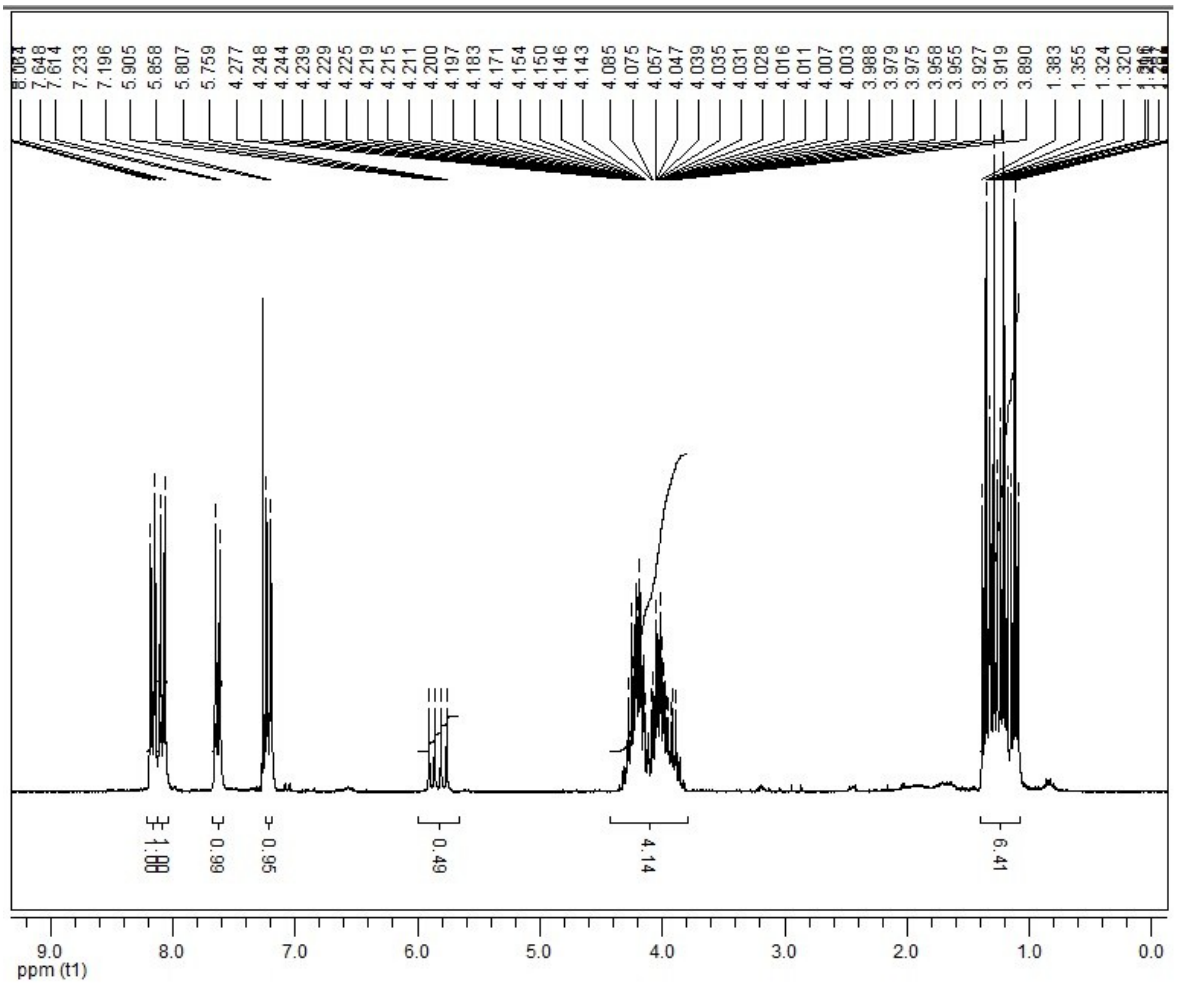
^{13}P NMR

(2b):

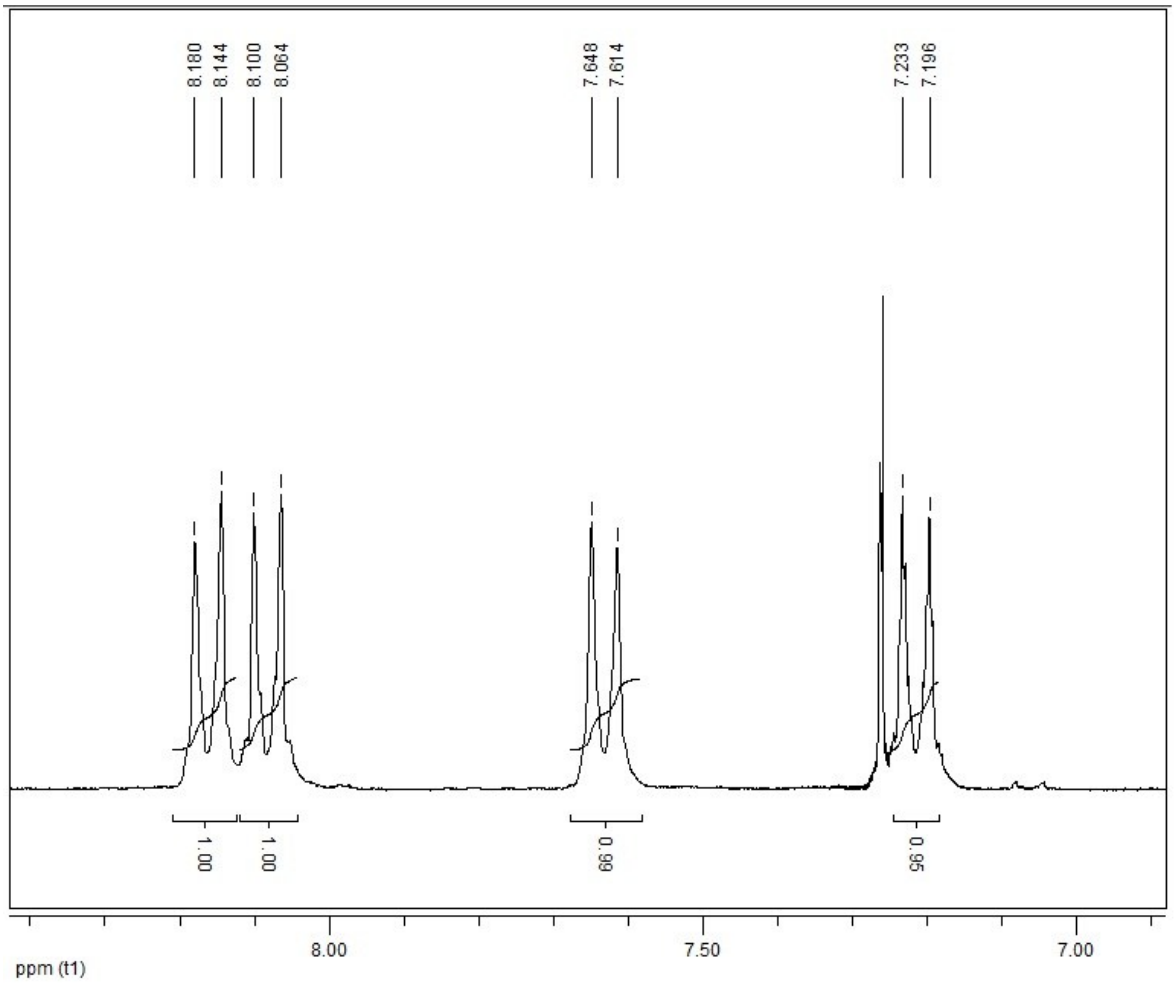


Pale yellow solid (mp: 87-88 ºC); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.16 (d, 2H, J= 9Hz), 8.08 (d, 2H, J= 9Hz), 7.63 (d, 2H, J= 9Hz), 7.21 (d, 2H, J= 9Hz), 5.83 (dd, 1H, ^{2}J(H-P)= 24.6Hz, ^{3}J(H-P)=11.8Hz),4.31-3.85 (m, 8H),1.35 (t, 3H, J= 7Hz), 1.29 (mt, 3H), 1.20 (t, 3H), 1.12 (t, 3H, J= 7Hz); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 147.8, 146.2, 144.5, 141.5 (d, ^{3}J(C-P)= 3.5Hz), 131.1 (d, ^{2}J(C-P)=7.9Hz), 130.4, 123.6 (d, ^{2}J(C-P)= 7.9Hz), 63.0-63.7 (m, 4C, -CH_2-), 58.4 (dd, -

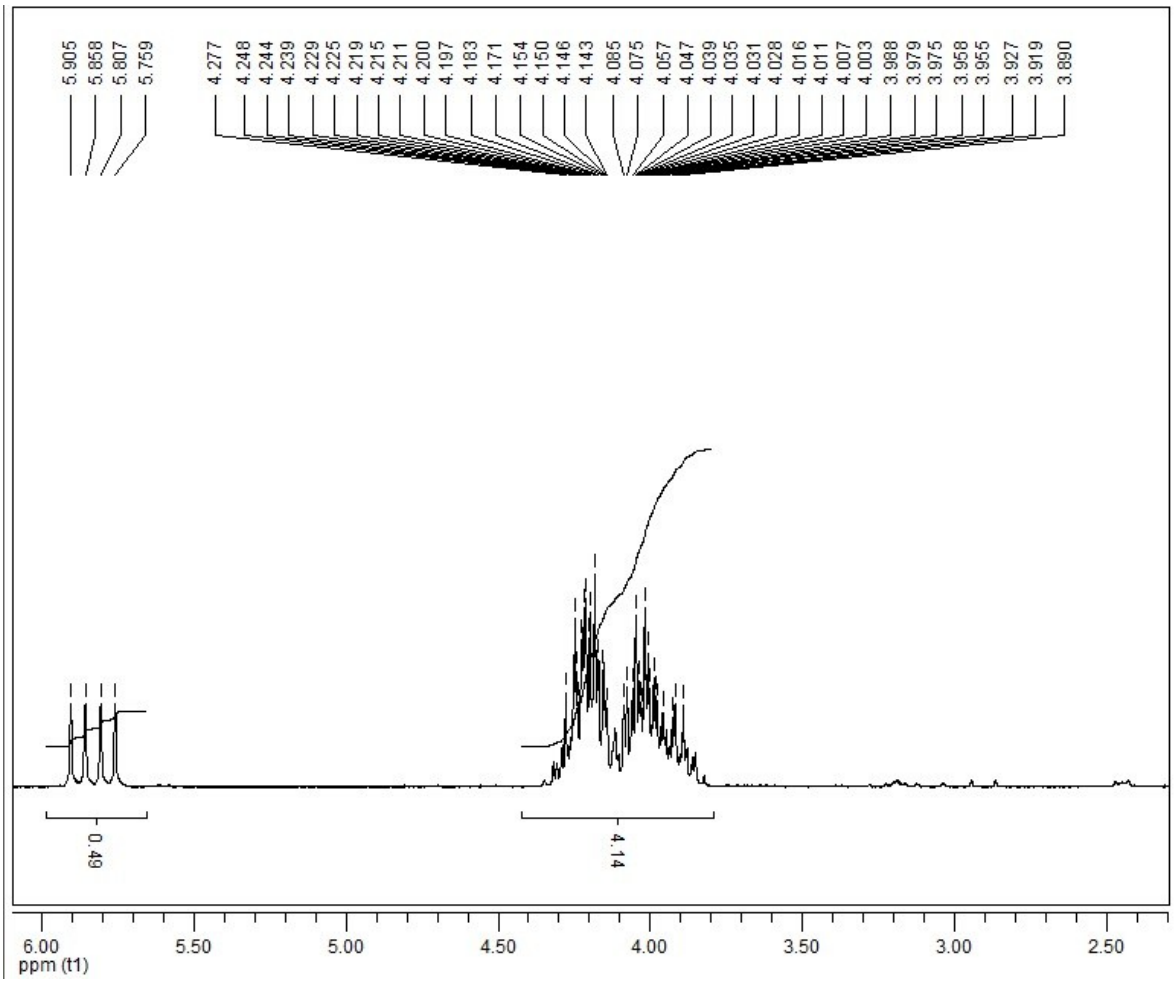
CH-, ^{2}J (C-P)= 5.5Hz, ^{1}J (C-P)= 161.0Hz), 15.9-16.4 (m, 4C, -CH_3); ^{31}P-NMR ($CDCl_3$, 162 MHz)δ (ppm): 19.28 (d, ^{3}J(P-P)= 20.5 Hz), 4.51 (d, ^{3}J(P-P)= 20.5 Hz); IR (KBr): ν [cm^{-1}]2977.9, 2916.2, 1595.9, 1519.8, 1350.1, 1249.8, 1026.1, 972.1;MS (70 eV, EI): m/z (%):545, M^+ (0.4), 408 (100.0);Anal. Calcd for $C_{21}H_{29}N_3O_{10}P_2$: C, 46.24; H, 5.36; N, 7.70. Found: C, 46.25; H, 5.75; N, 8.00.



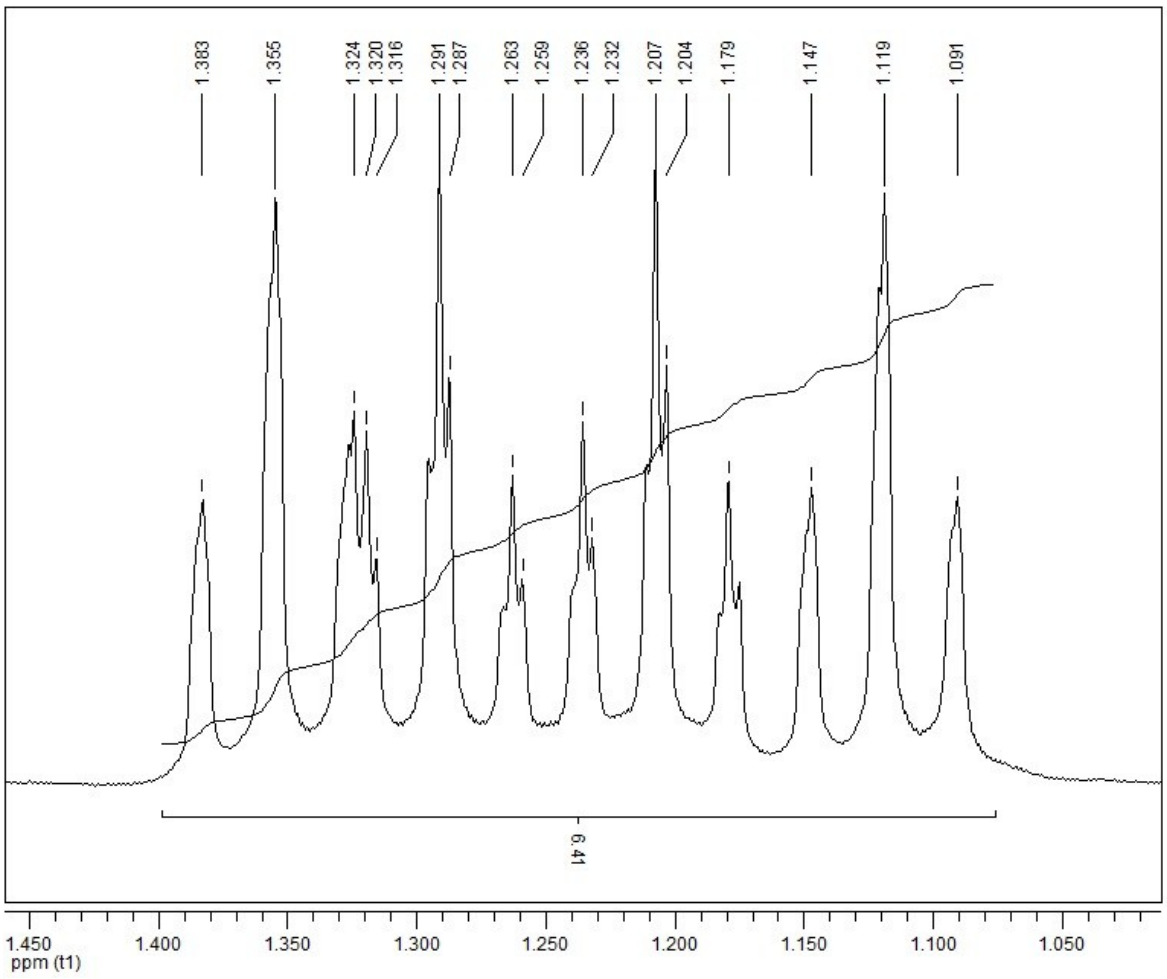
^{1}H NMR



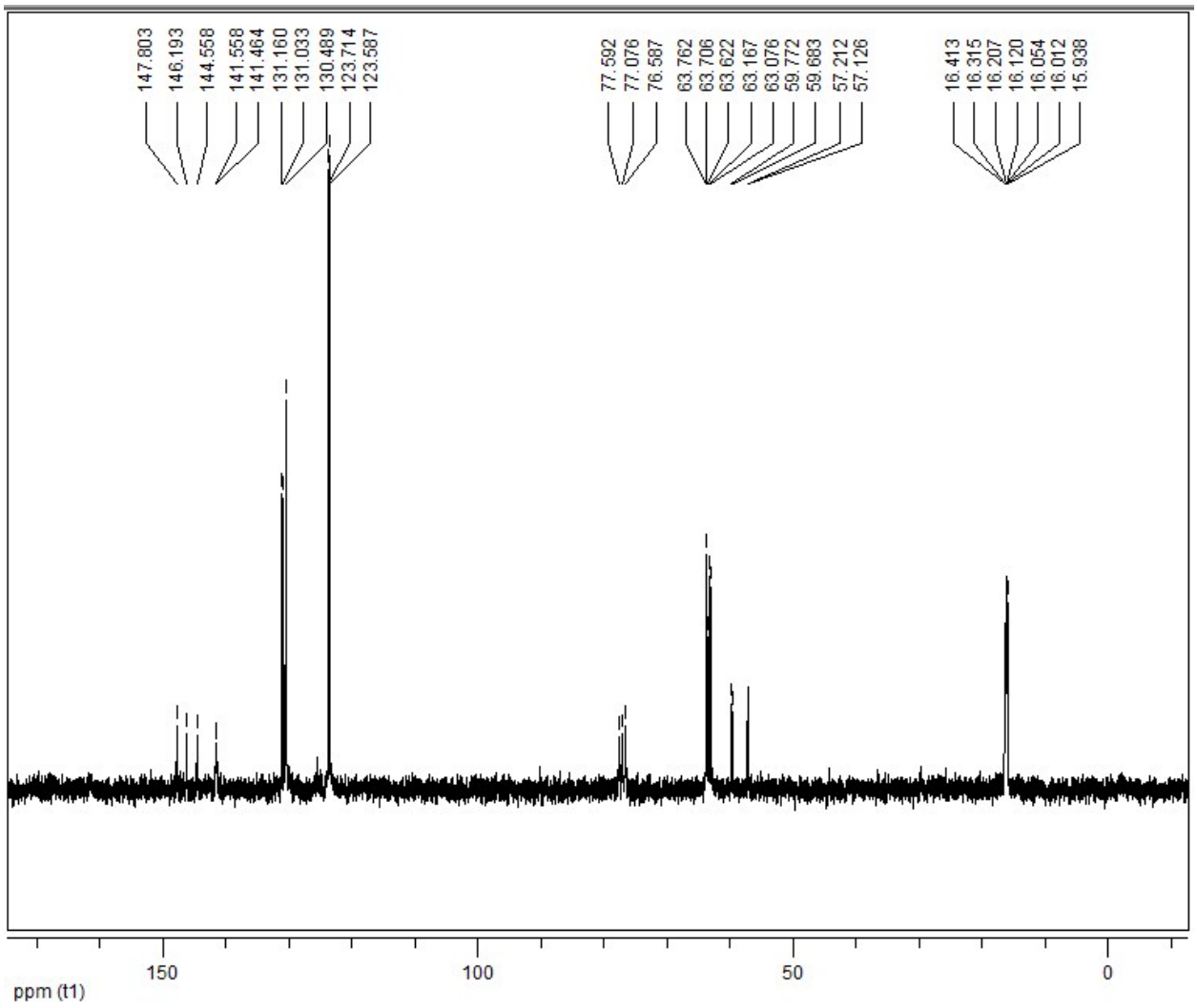
Expanded ^{1}H NMR of aromatic area



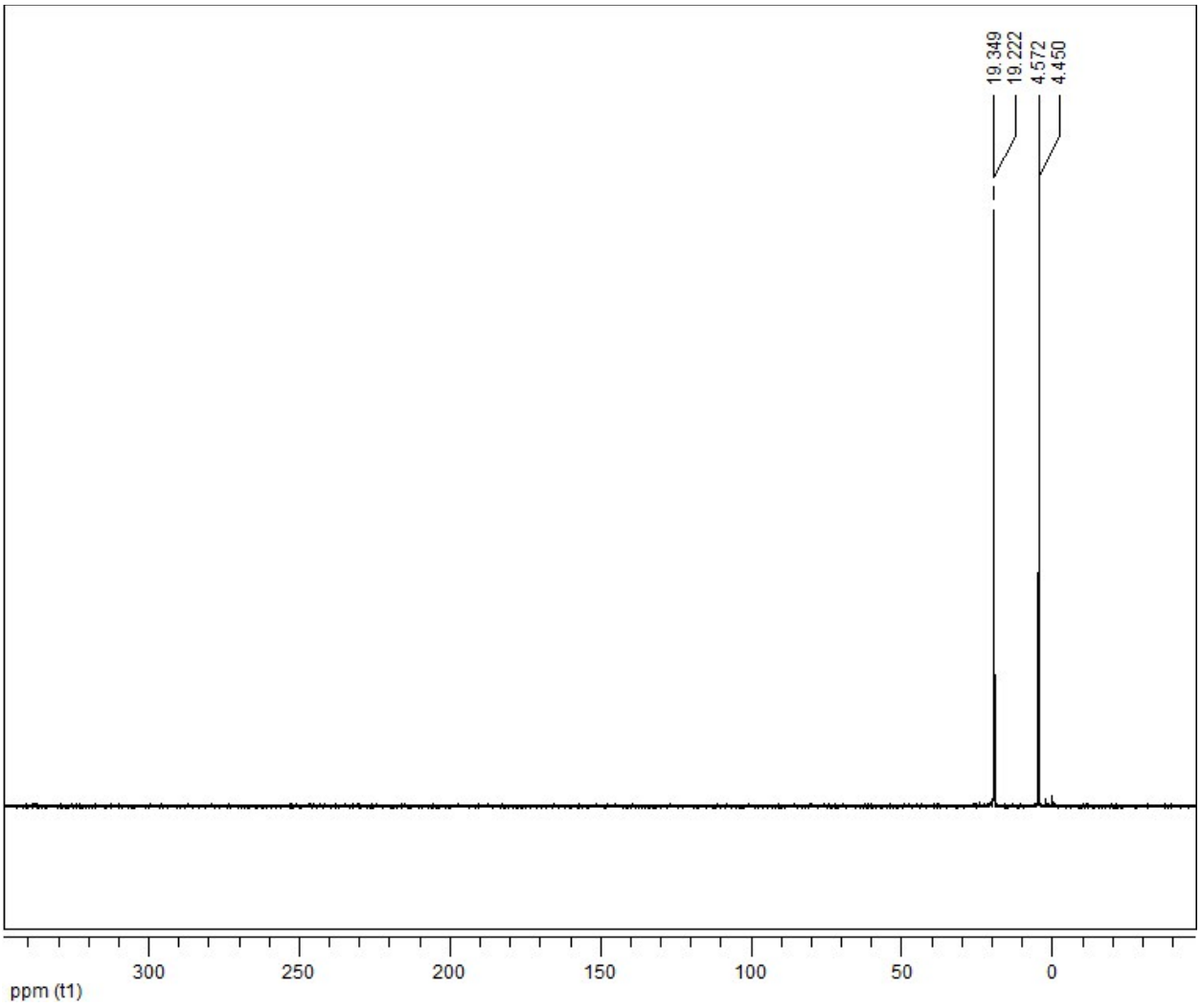
Expanded ^{1}H NMR of –CH, -CH_2



Expanded ^{1}H NMR of -CH_3

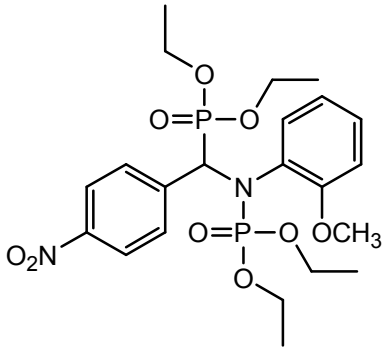

147.803
146.193
144.558
141.558
141.464
131.160
131.033
130.489
123.714
123.587
77.592
77.076
76.587
63.762
63.706
63.622
63.167
63.076
59.772
59.683
57.212
57.126
16.413
16.315
16.207
16.120
16.054
16.012
15.938
150
100
50
0
ppm (t1)

^{13}C NMR

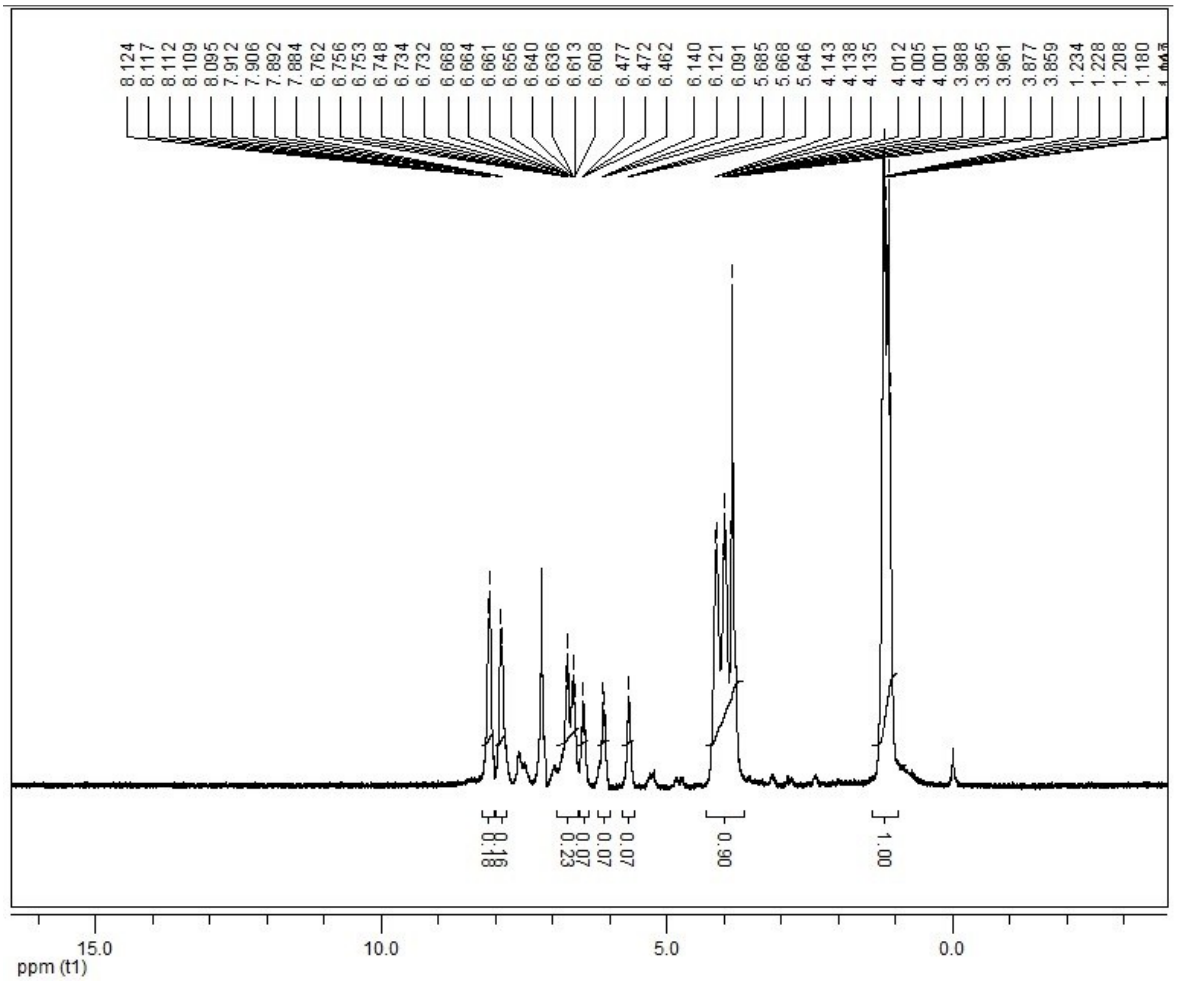

19.349
19.222
4.572
4.450
300
250
200
150
100
50
0
ppm (t1)

^{31}P NMR

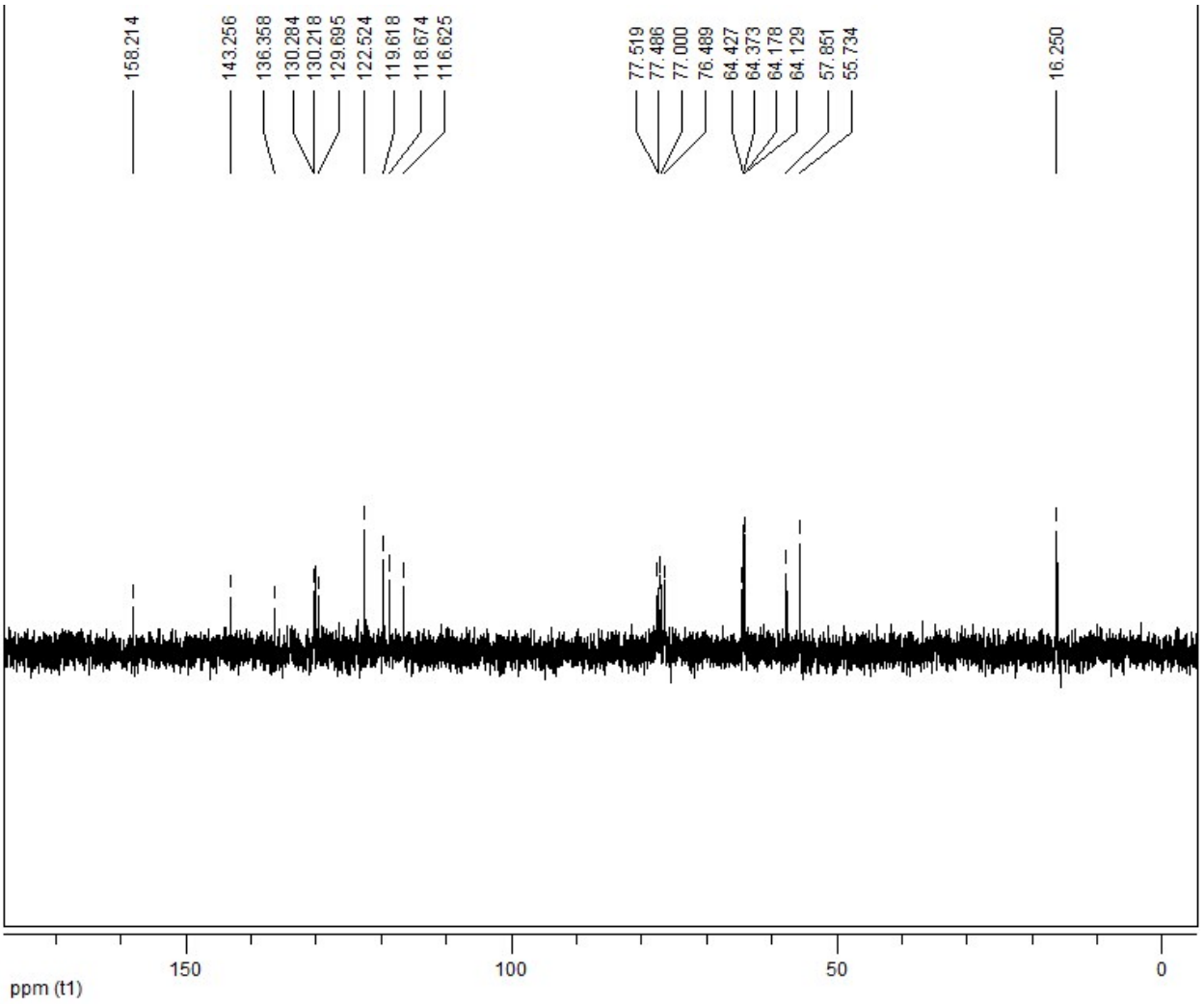
(2c):


O
O=P–O
N
O=P–O
OCH3
O
O2N

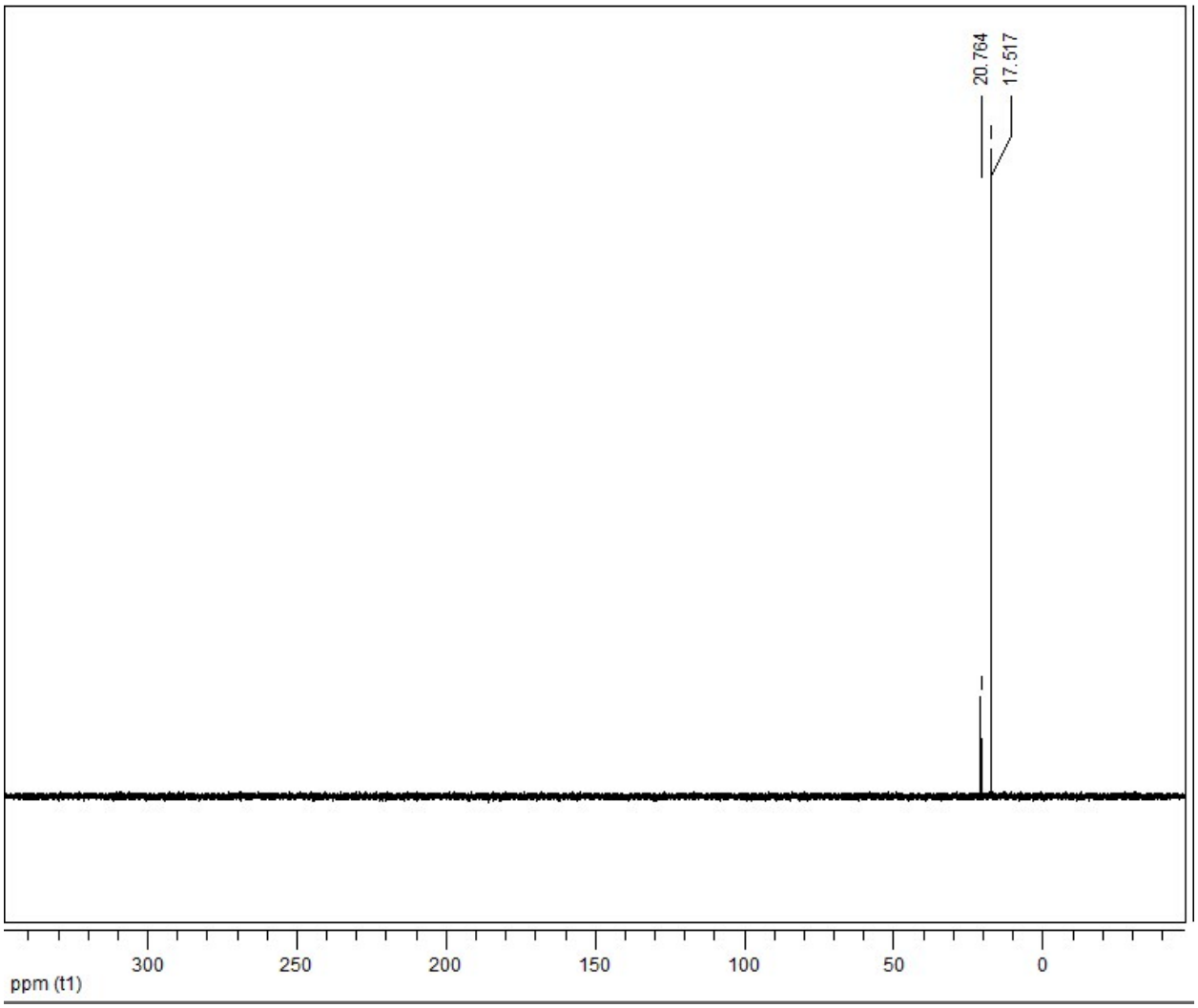
Pale yellow solid (mp: 115-115.5 ºC); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.12-8.09 (m, 2H), 7.91-7.88 (m, 2H), 6.76-6.60 (m, 2H), 6.49- 6.41 (m, 1H), 6.10 (d, 1H, J= 7.5Hz), 5.68-5.64 (m, 1H), 4.21-3.96 (m, 11H), 1.23-1.09 (m, 12H); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 158.2, 143.2, 136.3, 130.2 (d, ^{2}J(C-P)= 4.1Hz), 129.6, 122.5, 119.6, 118.6, 116.6, 64.1-64.4 (m, 4C, -CH_2-), 57.8 (broad s, 1C, -CH-), 55.7 (1C, -OCH_3), 16.2 (broad s, 4C, -CH_3); ^{31}P-NMR ($CDCl_3$, 162 MHz)δ (ppm): 20.76, 17.51; IR (KBr): ν [cm^{-1}] 2985.6, 2931.6, 1596.9, 1519.8, 1458.1, 1342.4, 1249.8, 1164.9, 1118.6, 1026.1, 972.1, 856.3, 740.6; MS (70 eV, EI): m/z (%): 530, M^+ (5.7), 255 (100.0);Anal. Calcd for $C_{22}H_{33}N_2O_9P_2$: C, 49.81; H, 6.08; N, 5.28. Found: C, 49.50; H, 5.78; N, 5.08.



^{1}H NMR

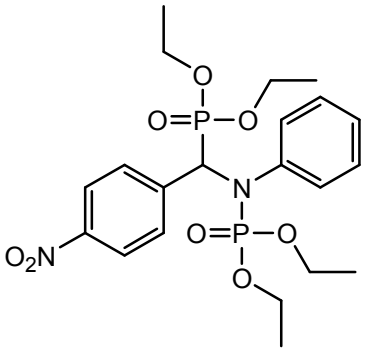

158.214
143.256
136.358
130.284
130.218
129.695
122.524
119.618
118.674
116.625
77.519
77.486
77.000
76.489
64.427
64.373
64.178
64.129
57.851
55.734
16.250
150
100
50
0
ppm (t1)

^{13}C NMR

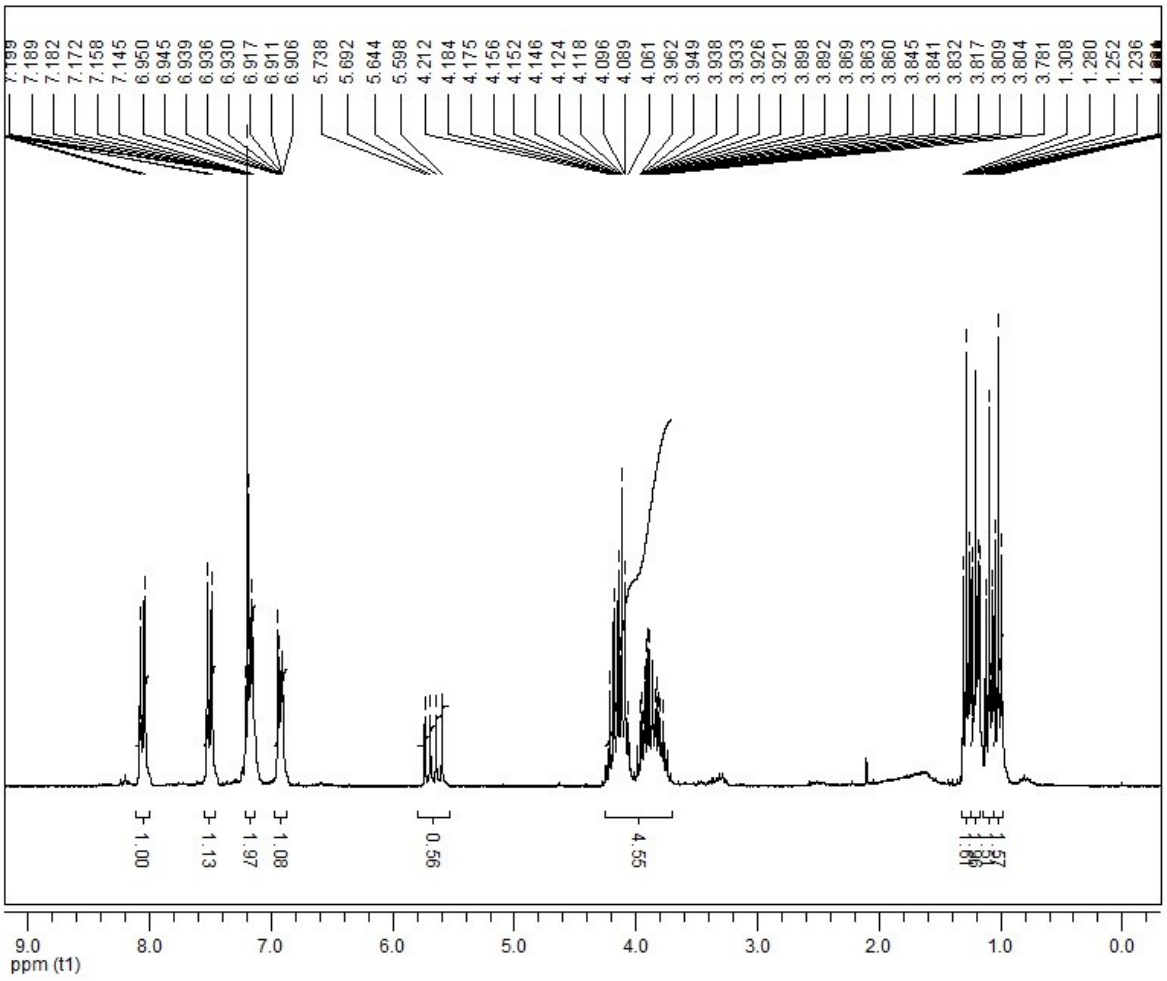


^{31} P NMR

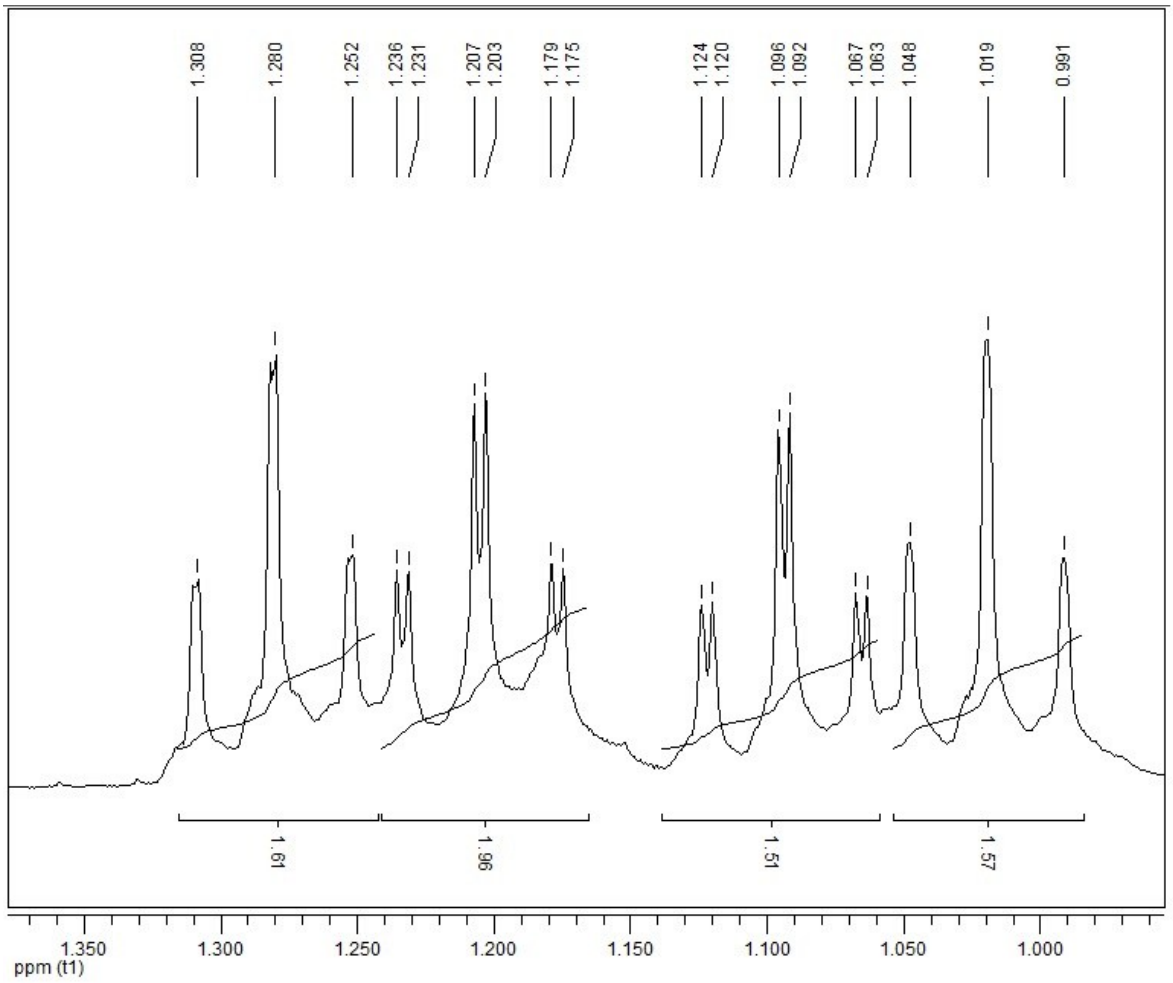
(2d):



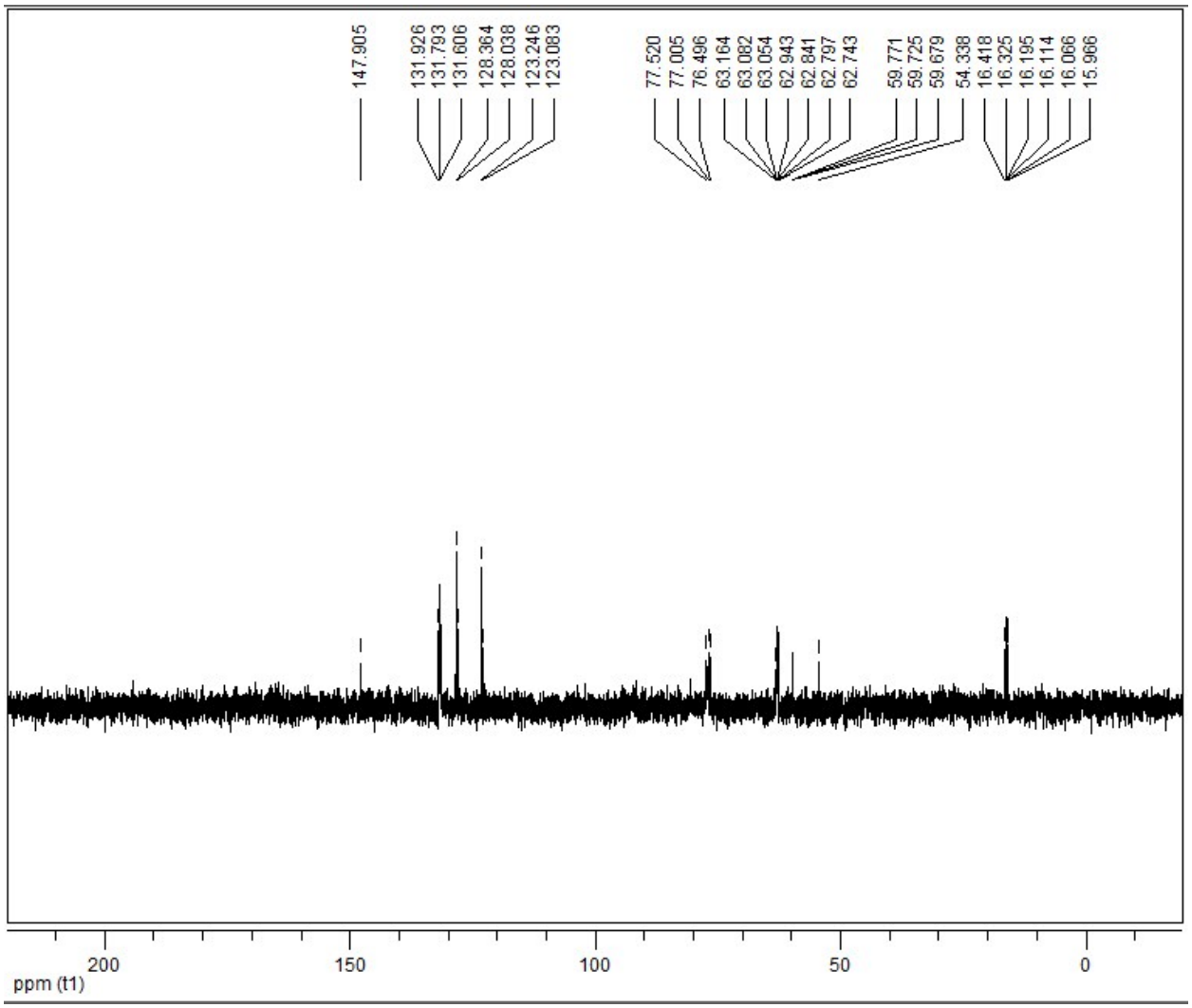
Yellow oil; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm):8.06 (d, 2H, J= 8.2Hz),7.51 (d, 2H, J= 8.7Hz), 7.20-7.14 (m, 3H), 6.95-6.90 (m, 2H), 5.66 (dd, 1H, ^{2}J (H-P)= 23.5Hz, ^{3}J (H-P)= 11.5Hz), 4.25-3.74 (m, 8H), 1.28 (t, 3H, J= 7Hz), 1.21 (mt, 3H),1.09 (mt, 3H), 1.02 (t, 3H, J= 7Hz); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 147.9, 131.8 (d, ^{2}J(C-P)= 8.4Hz, two peaks), 131.6, 128.3, 128.0, 123.2, 123.0, 62.6-63.1 (m, 4C, -CH_2-), 59.6-59.7 (m, 1C, -CH-), 54.3 (broad s, 1C, -CH-), 15.9-16.4 (m, 4C, -CH_3); ^{31}P-NMR ($CDCl_3$, 162 MHz)δ (ppm): 19.60, 3.08; IR (KBr): ν [cm^{-1}] 2985.6, 2931.6, 1596.9, 1527.5, 1490.1, 1442.7, 1350.1, 1257.5, 1164.9, 1026.1, 972.1, 864.1, 794.6;MS (70 eV, EI): m/z (%): 500, M^{+} (1.0), 363 (100.0); Anal. Calcd for $C_{21}H_{31}N_2O_8P_2$: C, 50.40; H, 6.04; N, 5.60. Found: C, 50.12; H, 5.72; N, 5.30.



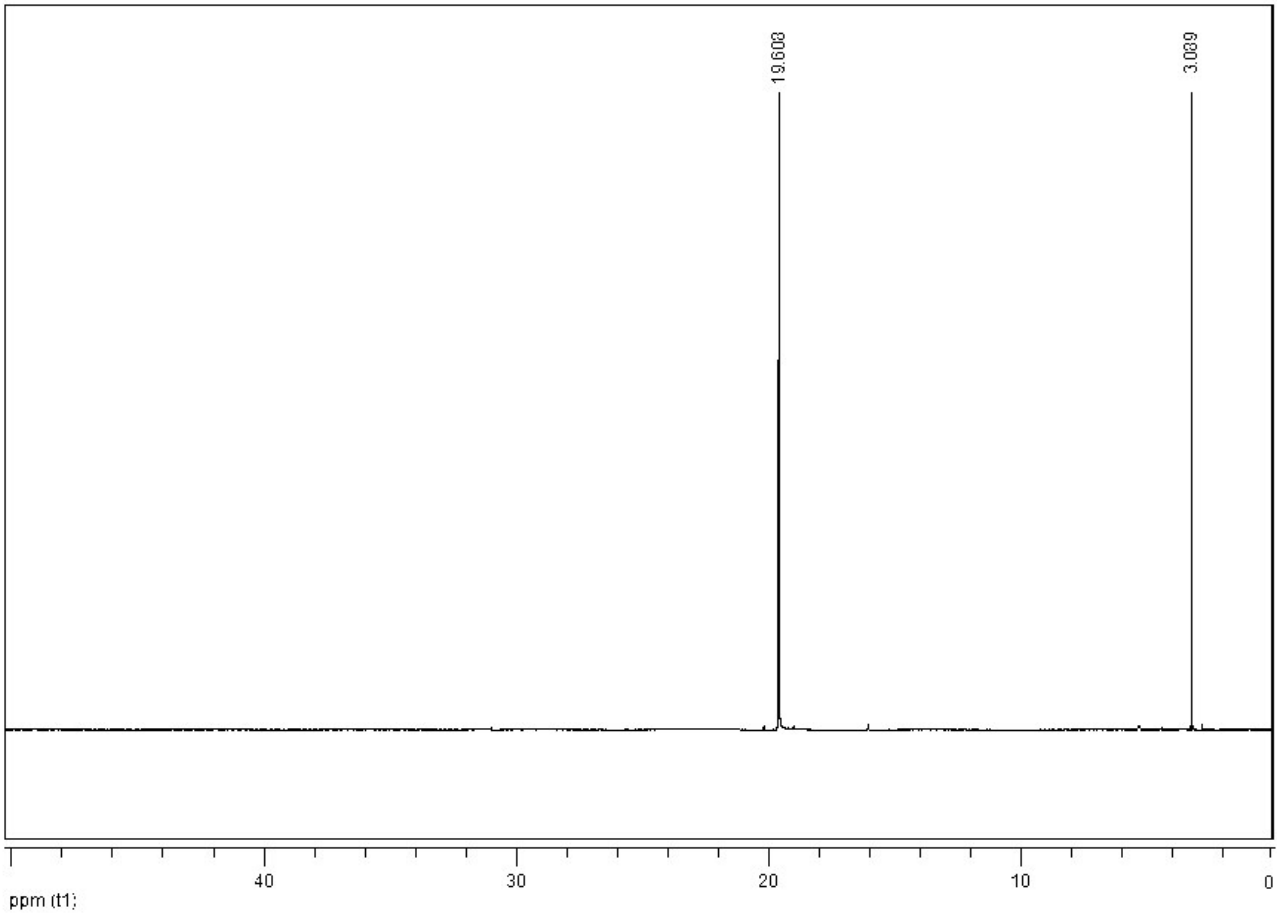
^{1}H NMR



Expanded ^{1}H NMR of –CH_3

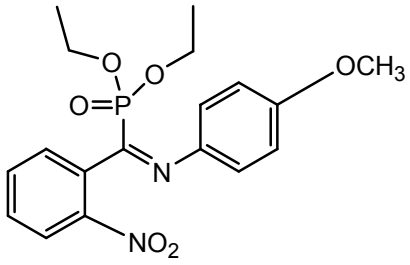

147.905
131.926
131.793
131.606
128.364
128.038
123.246
123.083
77.520
77.005
76.496
63.164
63.082
63.054
62.943
62.841
62.797
62.743
59.771
59.725
59.679
54.338
16.418
16.325
16.195
16.114
16.066
15.966
200
150
100
50
0
ppm (t1)

^{13}C NMR

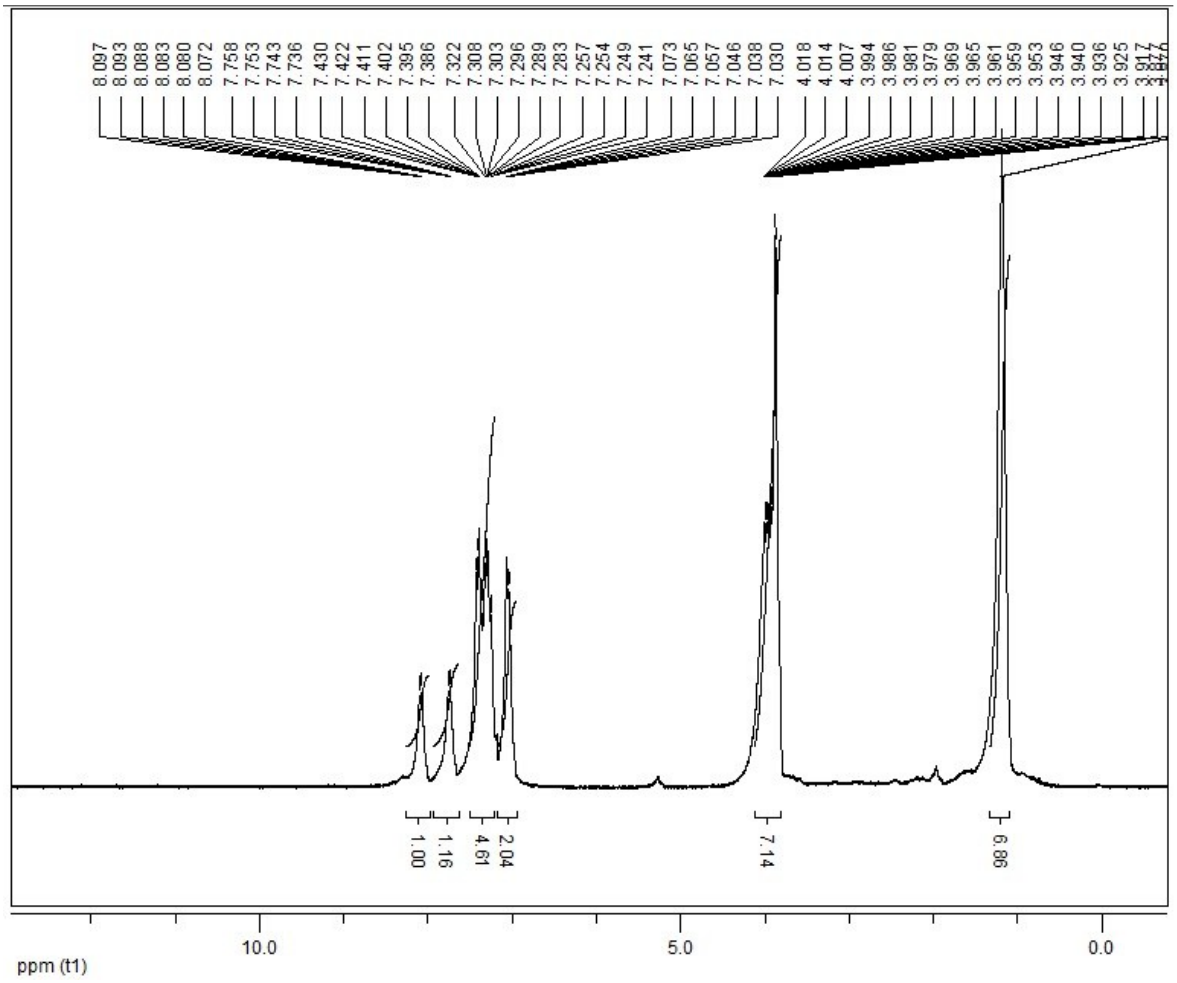


^{31}P NMR

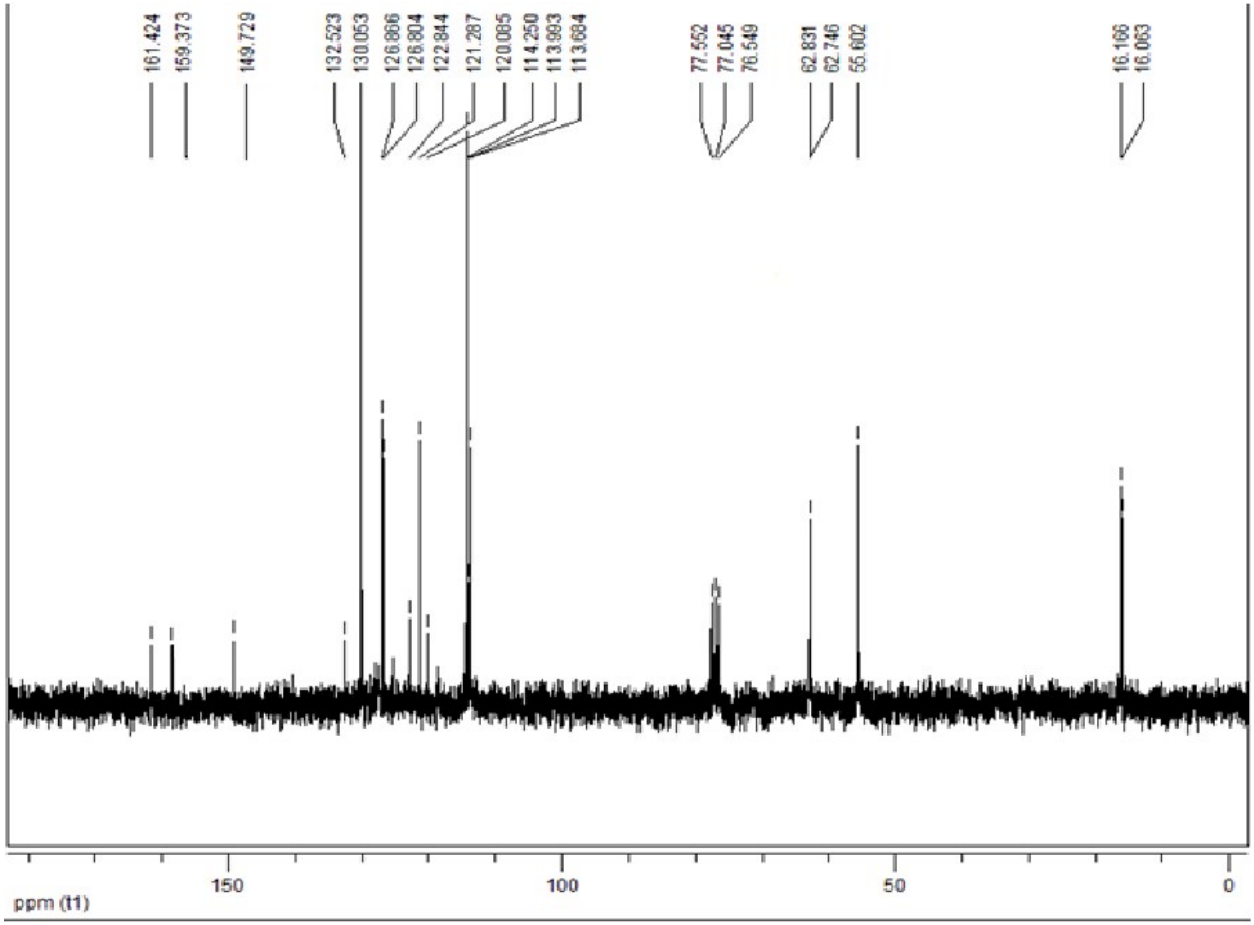
(2e):



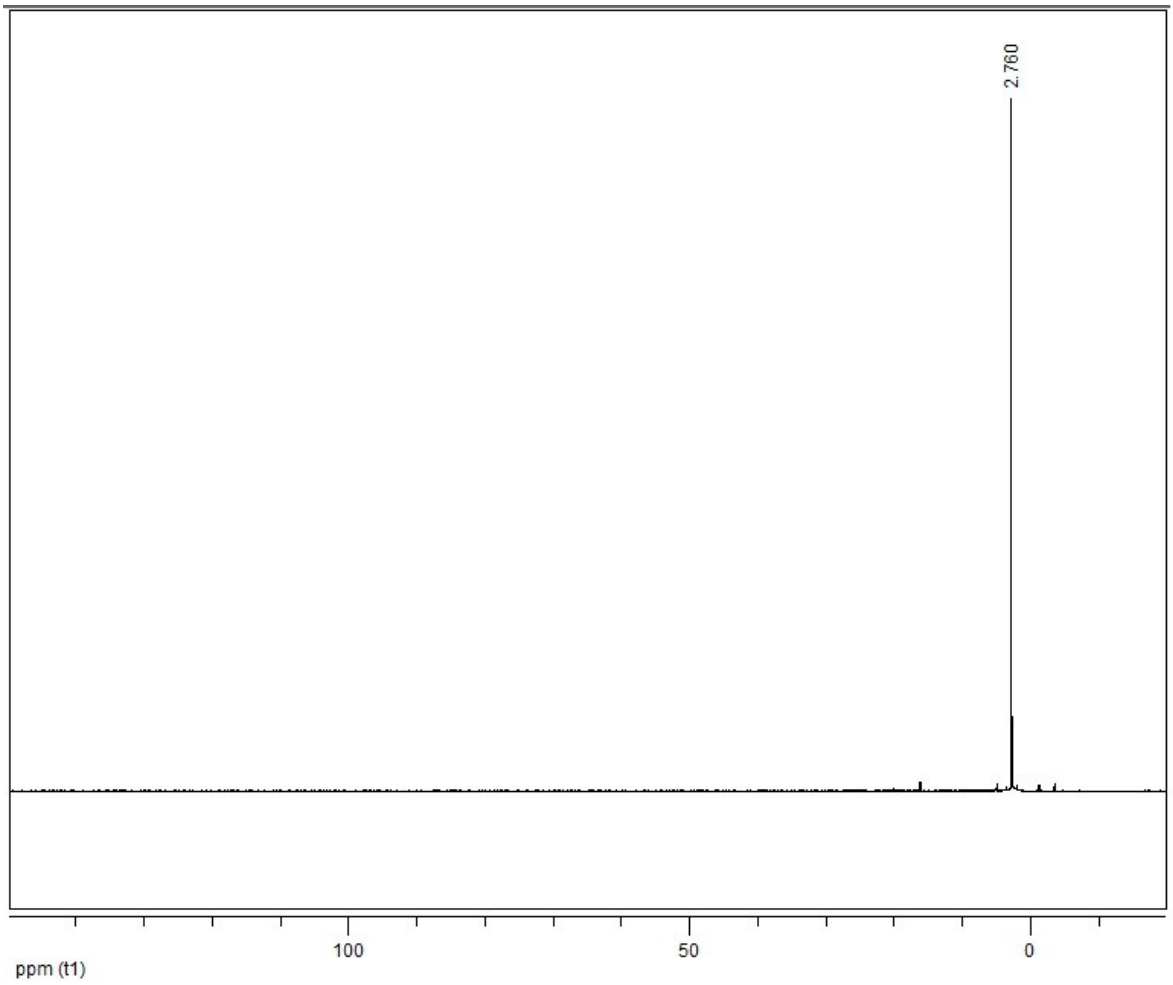
Pale yellow solid (mp: 77-78 ºC); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.09-8.07 (m, 1H), 7.75-7.73 (m, 1H), 7.43-7.24 (m, 4H), 7.07-7.03(m, 2H),4.01-3.87 (m, 7H), 1.21-1.18 (m, 6H); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 161.4, 159.3, 149.7, 132.5, 130.0, 126.8 (d, ^{4}J(C-P)= 4.0Hz), 122.8, 121.2, 120.0, 114.2, 113.6, 62.7 (d, $2CH_2$, ^{2}J(C-P)= 5.3Hz), 55.6 (OCH_3), 16.0 (d, $2CH_3$, ^{3}J(C-P)= 6.4Hz); ^{31}P-NMR ($CDCl_3$, 162 MHz)δ (ppm): 2.76; IR (KBr): ν [cm^{-1}] 2985.6, 2931.6, 2839.0, 1643.2, 1604.7, 1512.1, 1450.4, 1388.7, 1296.1, 1249.8, 1172.6, 1026.1, 972.1, 833.2, 756.0; Anal. Calcd for $C_{18}H_{21}N_2O_6P$: C, 55.10; H, 5.39; N, 7.14. Found: C, 54.85; H, 5.04; N, 6.84.


8.097
8.093
8.088
8.083
8.080
8.072
7.758
7.753
7.743
7.736
7.430
7.422
7.411
7.402
7.395
7.386
7.322
7.308
7.303
7.296
7.289
7.283
7.257
7.254
7.249
7.241
7.073
7.065
7.057
7.046
7.038
7.030
4.018
4.014
4.007
3.994
3.986
3.981
3.979
3.969
3.965
3.961
3.959
3.953
3.946
3.940
3.936
3.925
1.00
1.16
4.61
2.04
7.14
6.86
10.0
5.0
0.0
ppm (t1)

^{1}H NMR

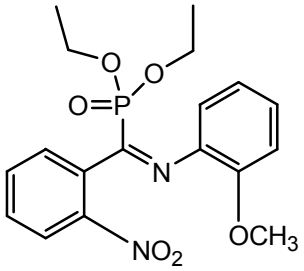

161.424
159.373
149.729
132.523
130.053
126.866
126.804
122.844
121.287
120.085
114.250
113.993
113.684
77.552
77.045
76.549
62.831
62.746
55.602
16.166
16.063
150
100
50
0
ppm (f1)

^{13}C NMR



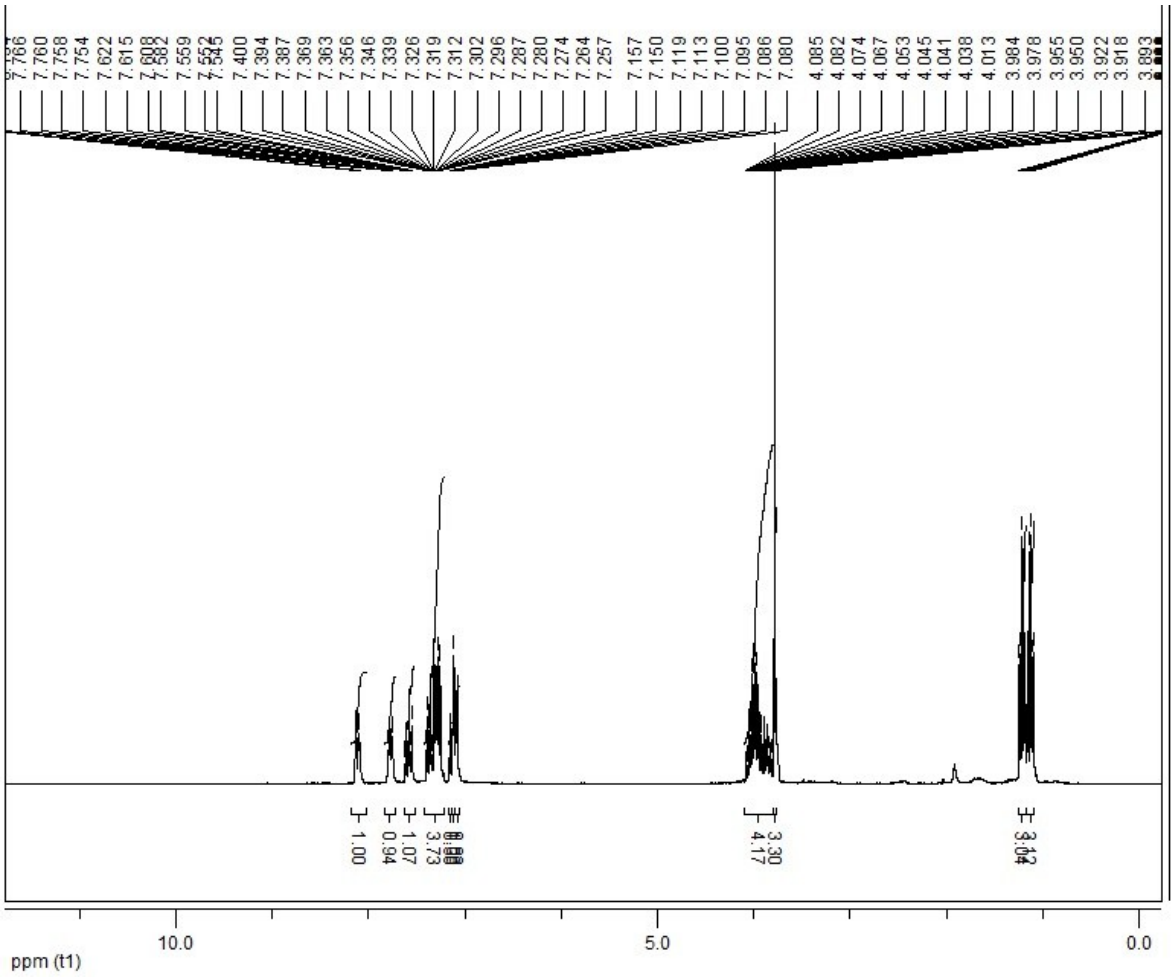
^{31}P NMR

(2f):

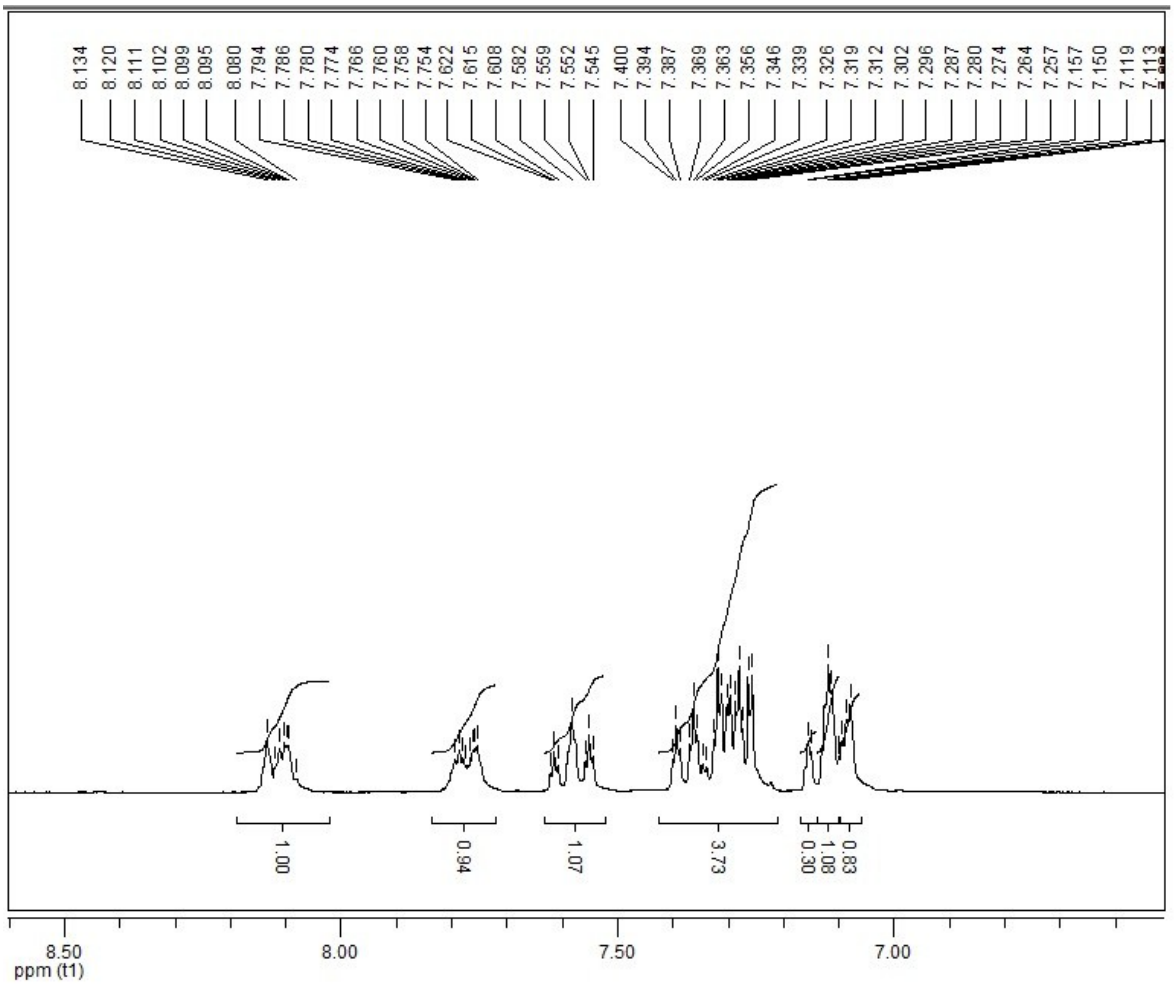


Pale yellow solid (mp: 147-148 ºC);^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.13-8.08 (m, 1H), 7.79-7.75 (m, 1H), 7.62-7.54 (m, 1H), 7.40-7.25 (m, 4H),7.12-7.11 (m, 1H), 7.10-7.08 (m, 1H), 4.08-3.81 (m, 4H), 3.78 (d, 3H, J= 1.8 Hz),1.22 (mt, 3H), 1.13 (mt, 3H); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm):157.6, 156.2, 147.9, 133.0, 132.3, 130.6, 128.6, 126.6, 126.4, 121.3, 120.4, 113.8, 111.9, 62.6 (d, $2CH_2$, ^{2}J(C-P)= 4.8Hz), 55.8 (OCH_3), 15.9-16.1 (m, $2CH_3$); ^{31}P-NMR ($CDCl_3$, 162 MHz) δ (ppm): 2.50; IR(KBr): ν [cm^{-1}]2977.9, 2893.0, 1604.7, 1504.4, 1473.3, 1300.1,

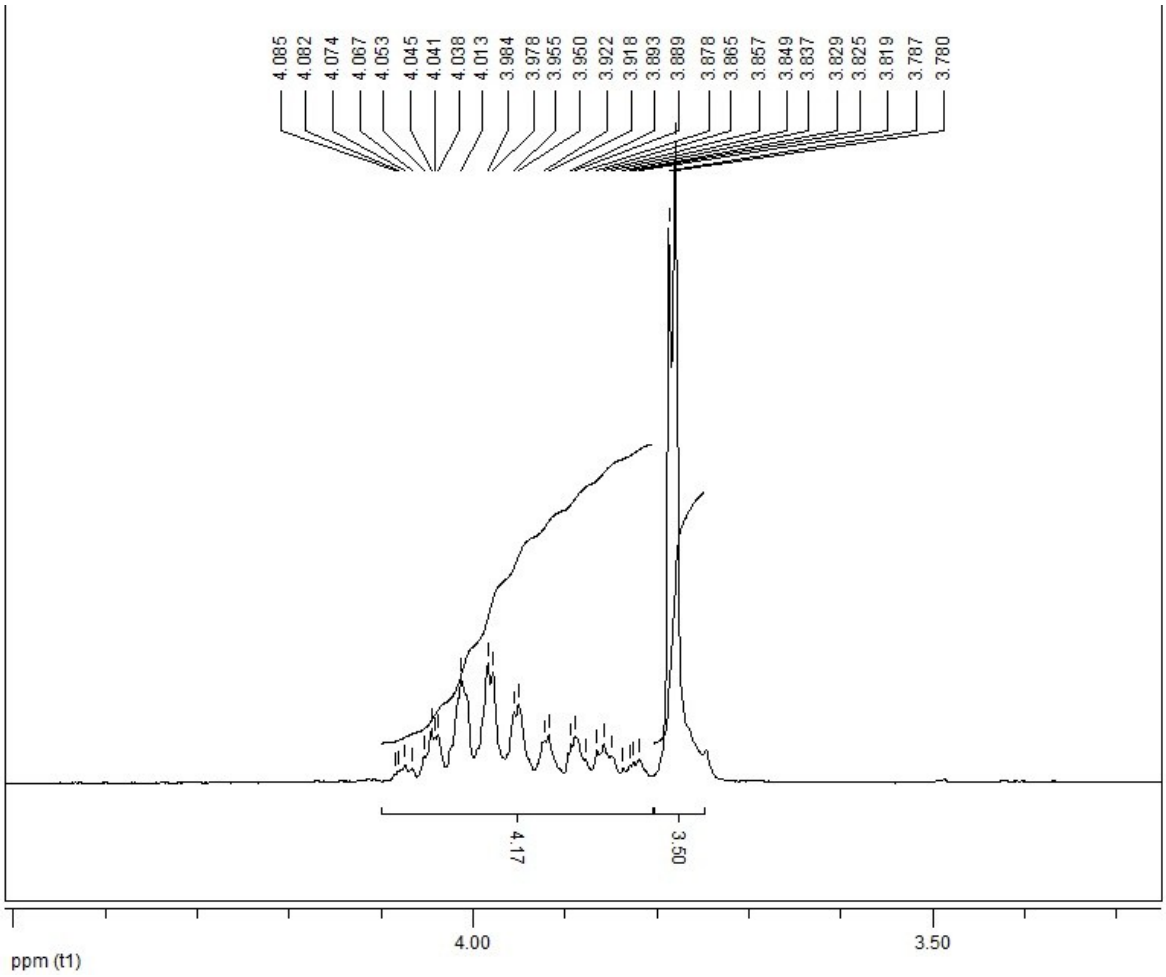
1280.6, 1249.8, 1164.9, 1010.6, 979.8,840.9, 763.8; MS (70 eV, EI): m/z (%): 392, M^+(1.1), 223 (100.0);Anal. Calcd for $C_{18}H_{21}N_2O_6P$: C, 55.10; H, 5.39; N, 7.14. Found: C, 55.38; H, 5.74; N, 7.46.



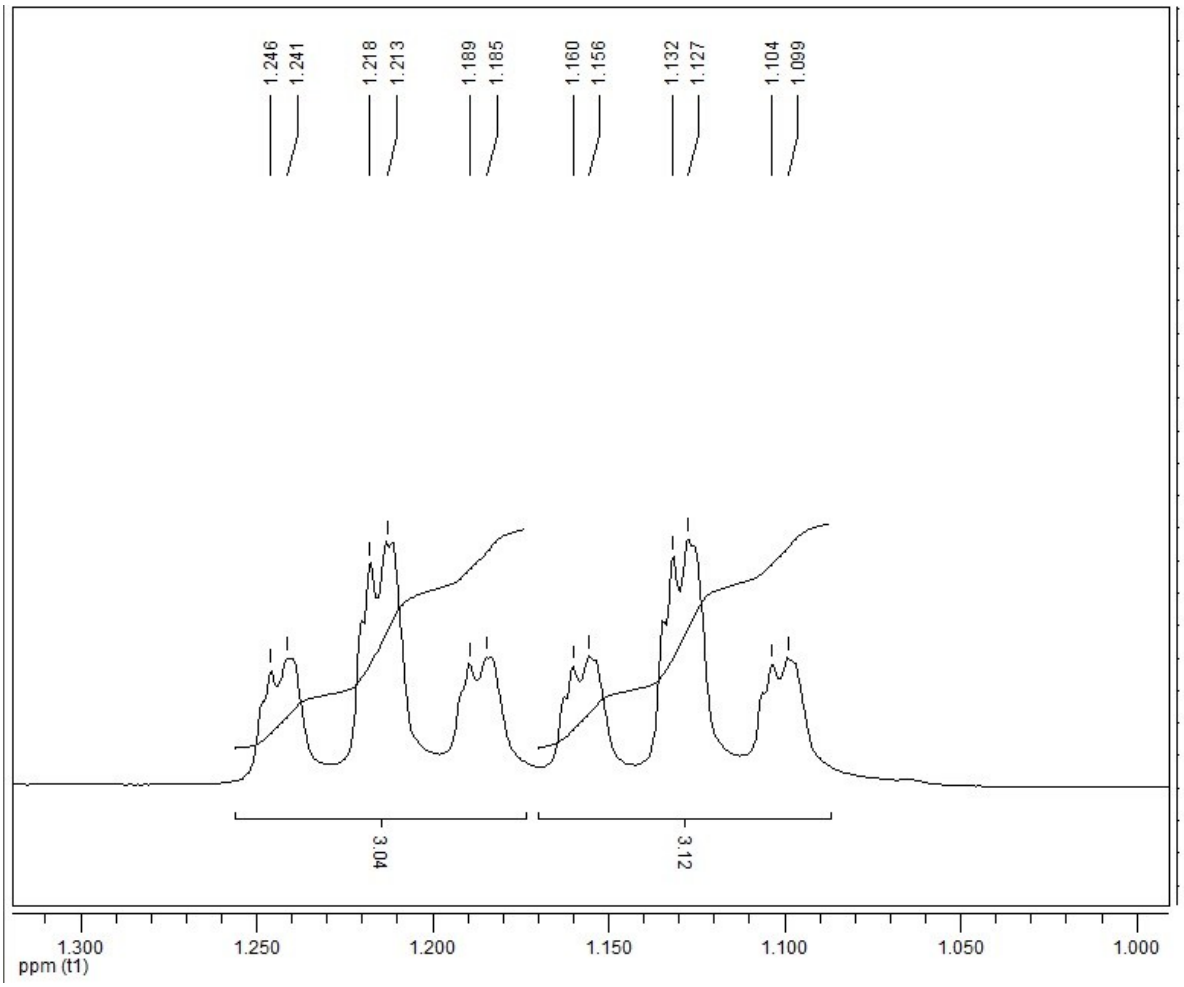
^{1}H NMR



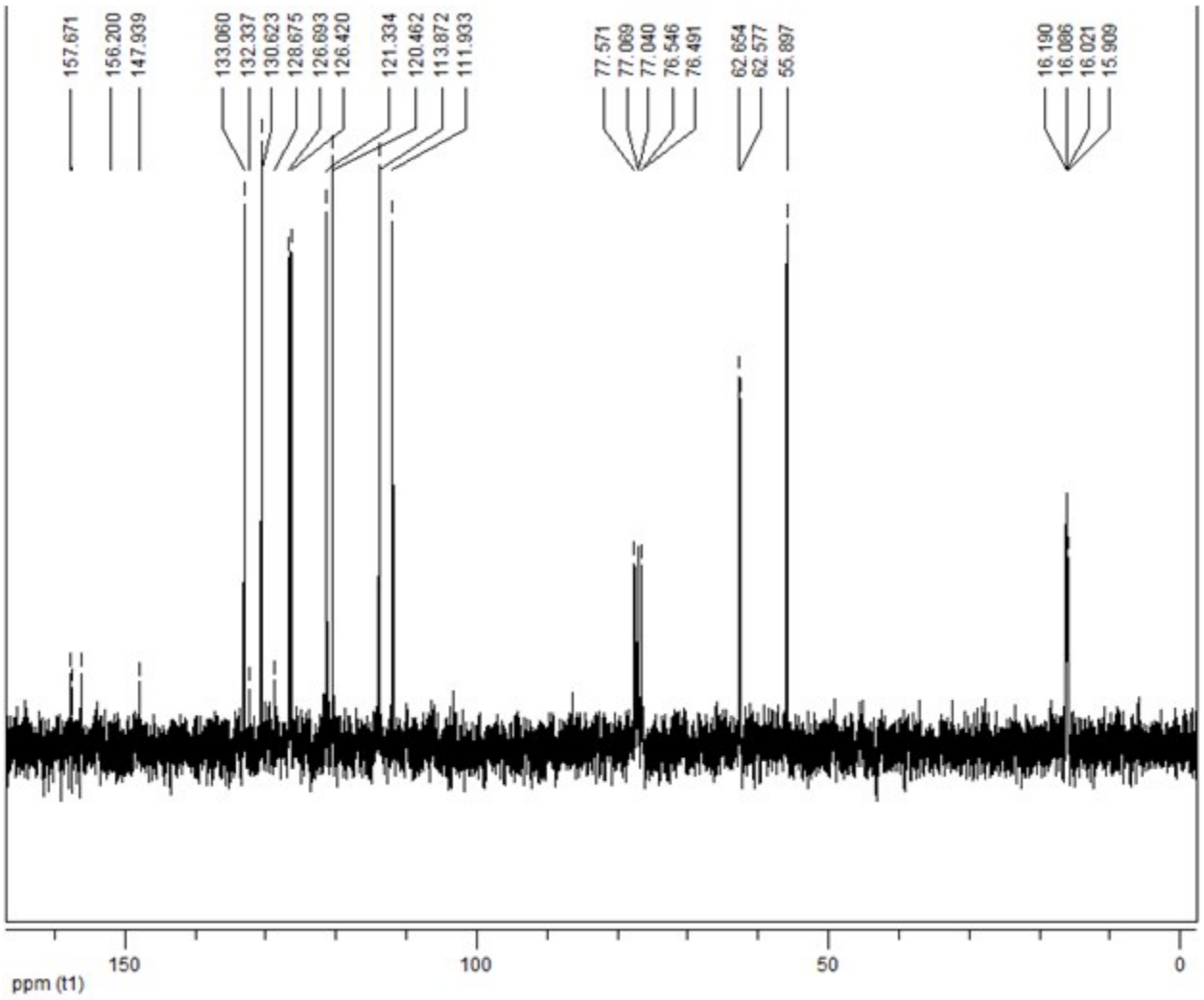
Expanded ^{1}H NMR of aromatic area



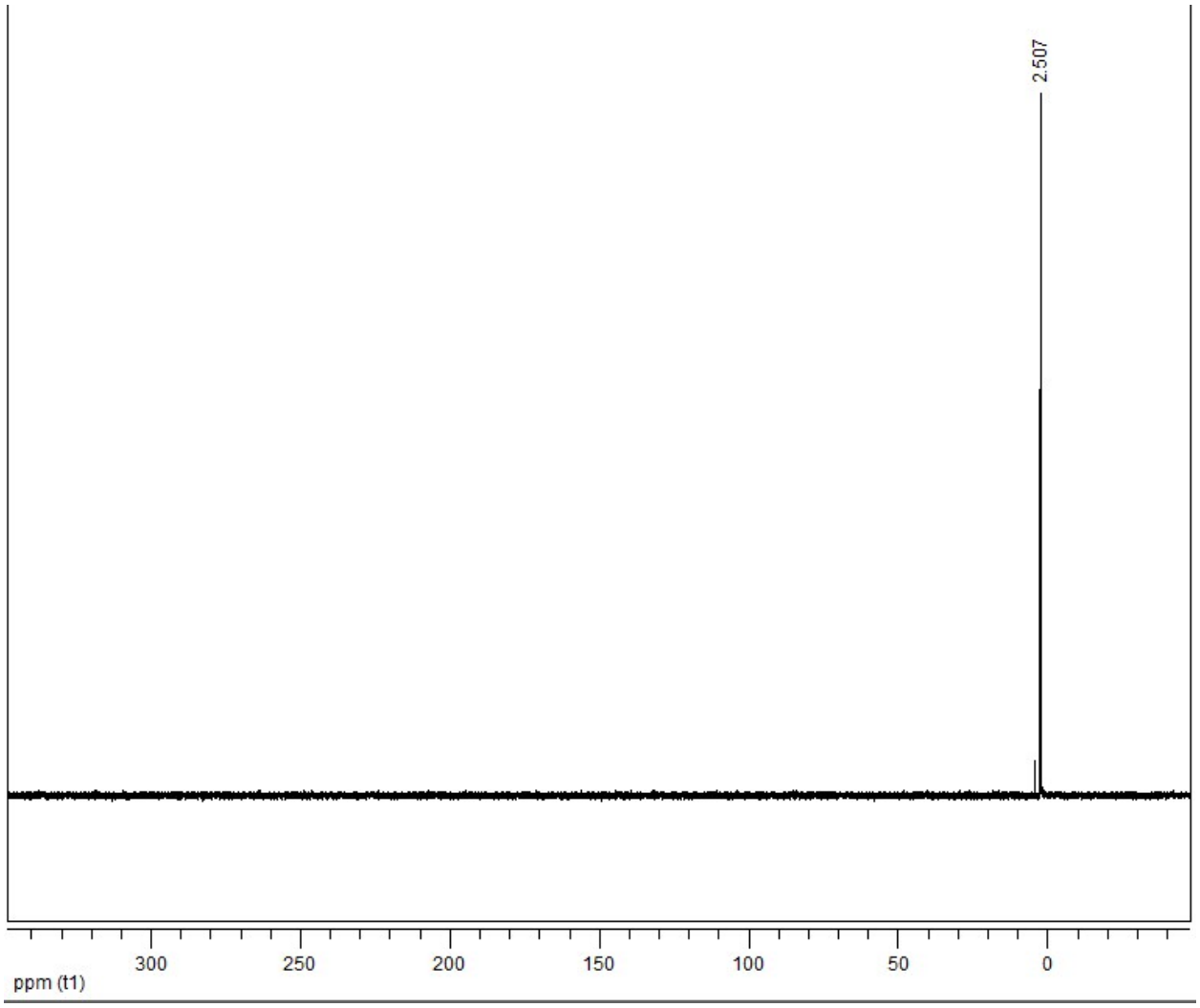
Expanded ^{1}H NMR of $–CH_2$ and $-OCH_3$



Expanded ^{1}H NMR of $-CH_3$

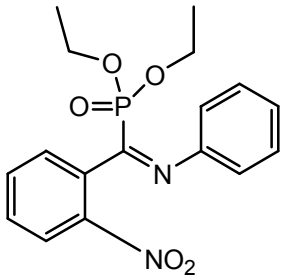

157.671
156.200
147.939
133.060
132.337
130.623
128.675
126.693
126.420
121.334
120.462
113.872
111.933
77.571
77.069
77.040
76.546
76.491
62.654
62.577
55.897
16.190
16.086
16.021
15.909
150
100
50
0
ppm (t1)

^{13}C NMR



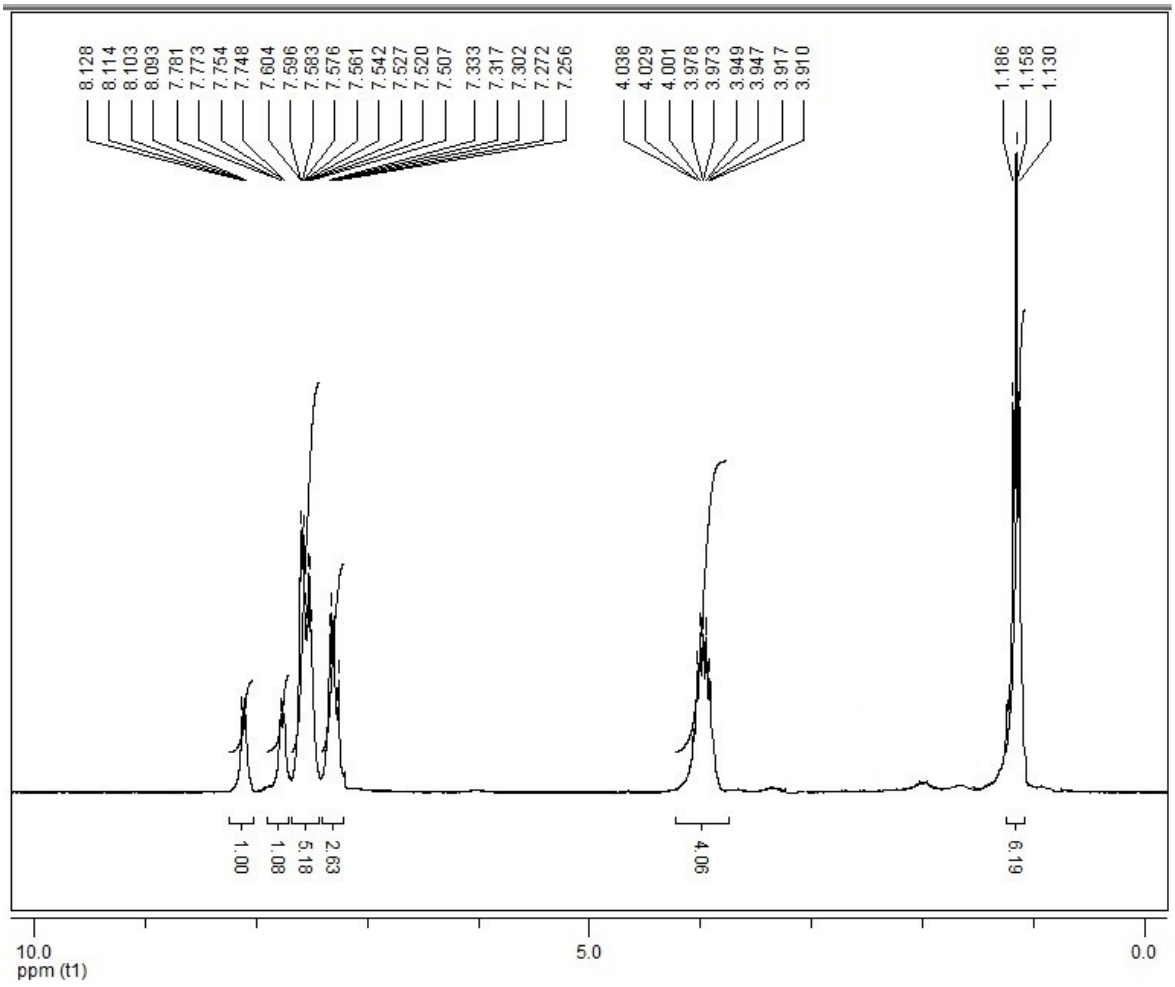
^{31}P NMR

(2g):

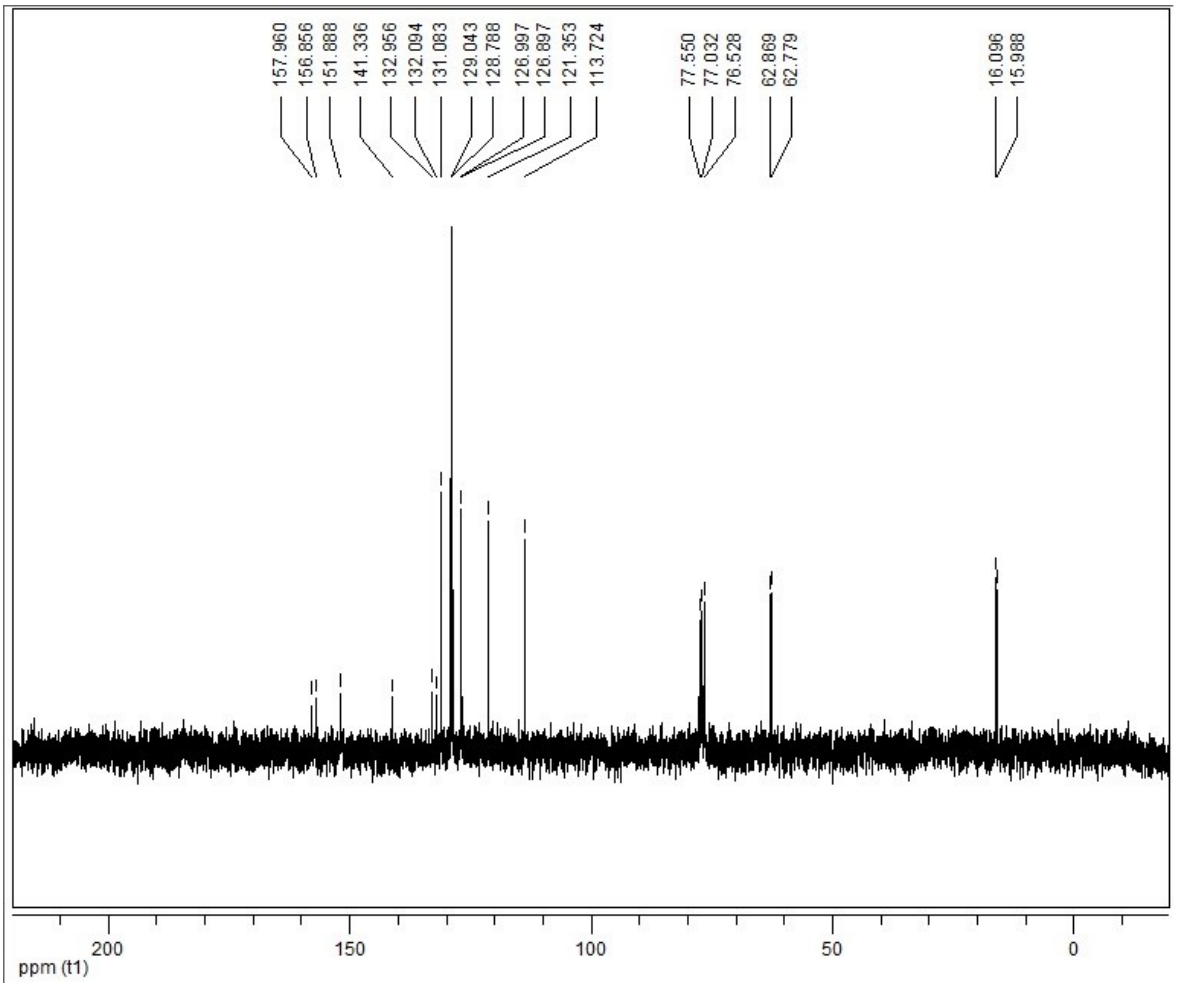


Yellow oil,^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.12-8.09 (m, 1H), 7.78-7.74 (m, 1H), 7.60-7.50 (m, 5H), 7.33-7.30 (m, 2H), 4.03-3.91(m, 4H), 1.16 (t, 6H, J= 7Hz); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 157.9, 156.8, 151.8, 141.3, 132.9, 131.0, 129.0, 128.7, 126.9 (d, ^{3}J(C-P)= 6.3Hz),

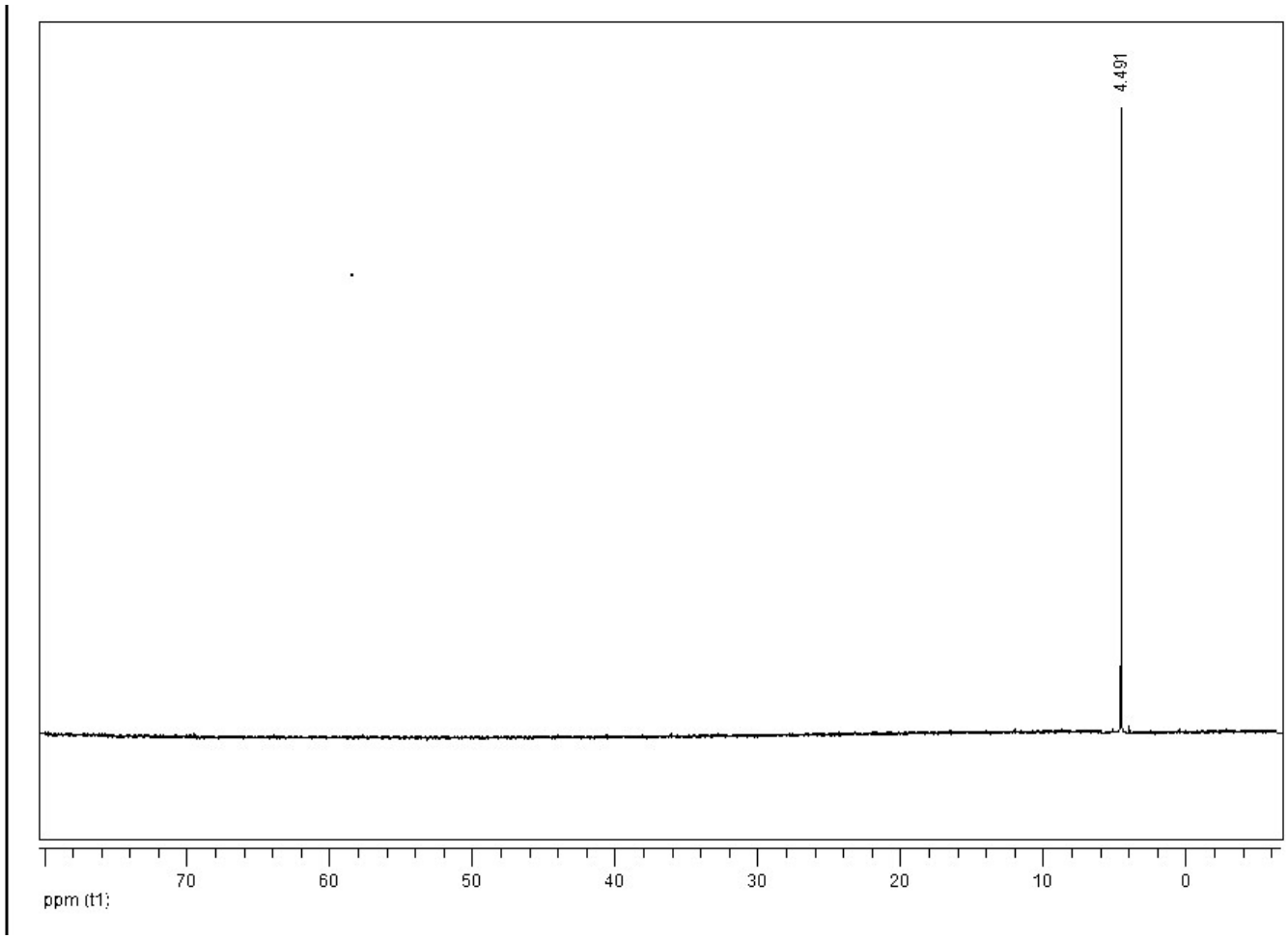
121.3, 113.7, 62.8 (d, $2CH_2$, ^2J(C-P)= 5.6Hz), 16.0 (d, $2CH_3$, ^3J(C-P)= 6.7Hz); ^{31}P-NMR ($CDCl_3$, 162 MHz) δ (ppm): 4.49; IR (KBr): ν [cm^{-1}]2985.6, 2931.6,1658.7,1596.9, 1504.4, 1473.5, 1388.7, 1257.5, 1164.9, 1110.9, 1049.2, 1010.6, 979.8, 840.9, 748.3;MS (70 eV, EI): m/z (%): 362, M^+(0.4), 179 (100.0);Anal. Calcd for $C_{17}H_{19}N_2O_5P$: C, 56.35; H, 5.29; N, 7.73. Found: C, 56.05; H, 5.01; N, 7.50.



^{1}H NMR

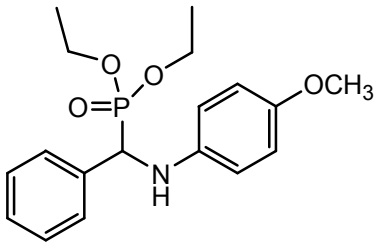

157.960
156.856
151.888
141.336
132.956
132.094
131.083
129.043
128.788
126.997
126.897
121.353
113.724
77.550
77.032
76.528
62.869
62.779
16.096
15.988
200
150
100
50
0
ppm (t1)

^{13}C NMR

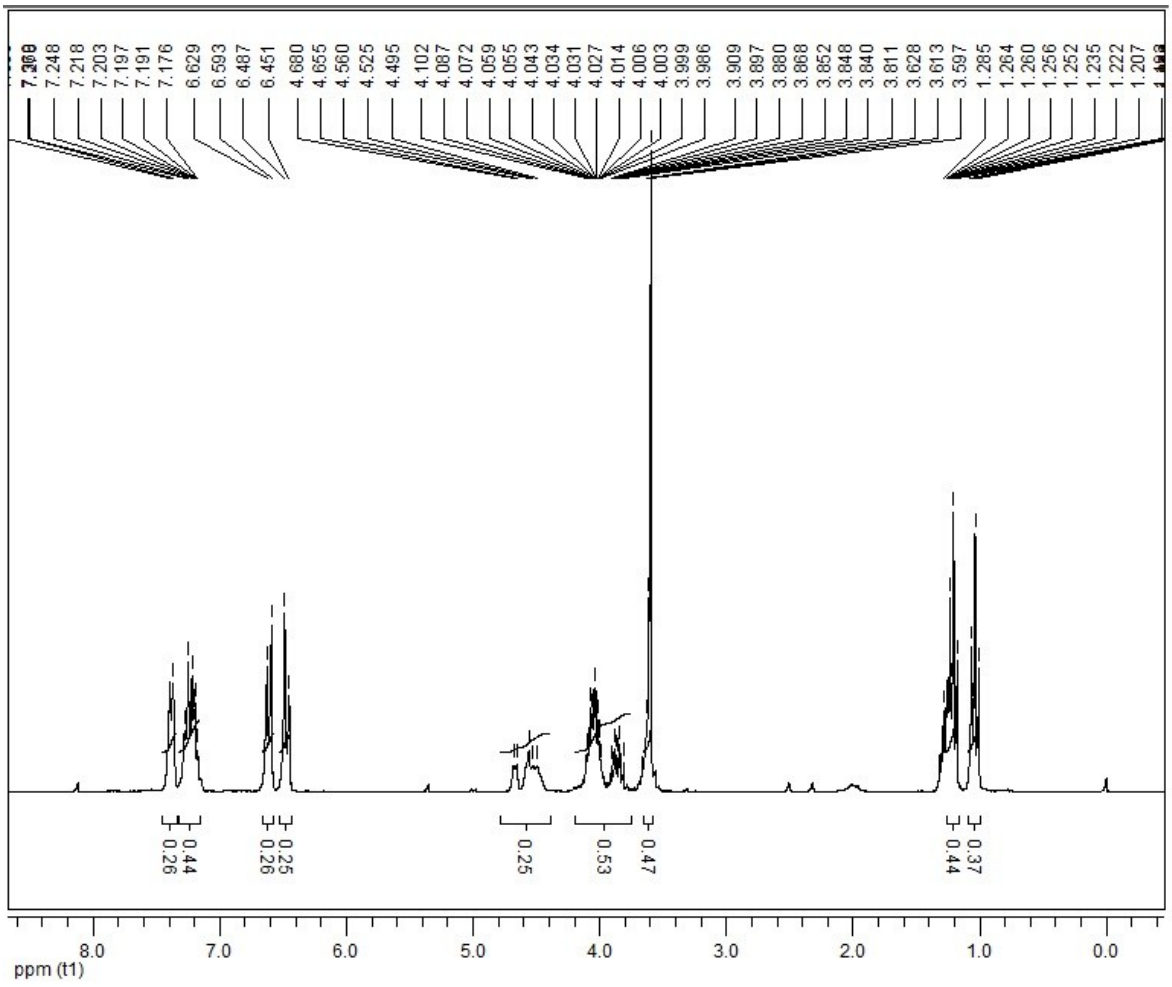


^{31}P NMR

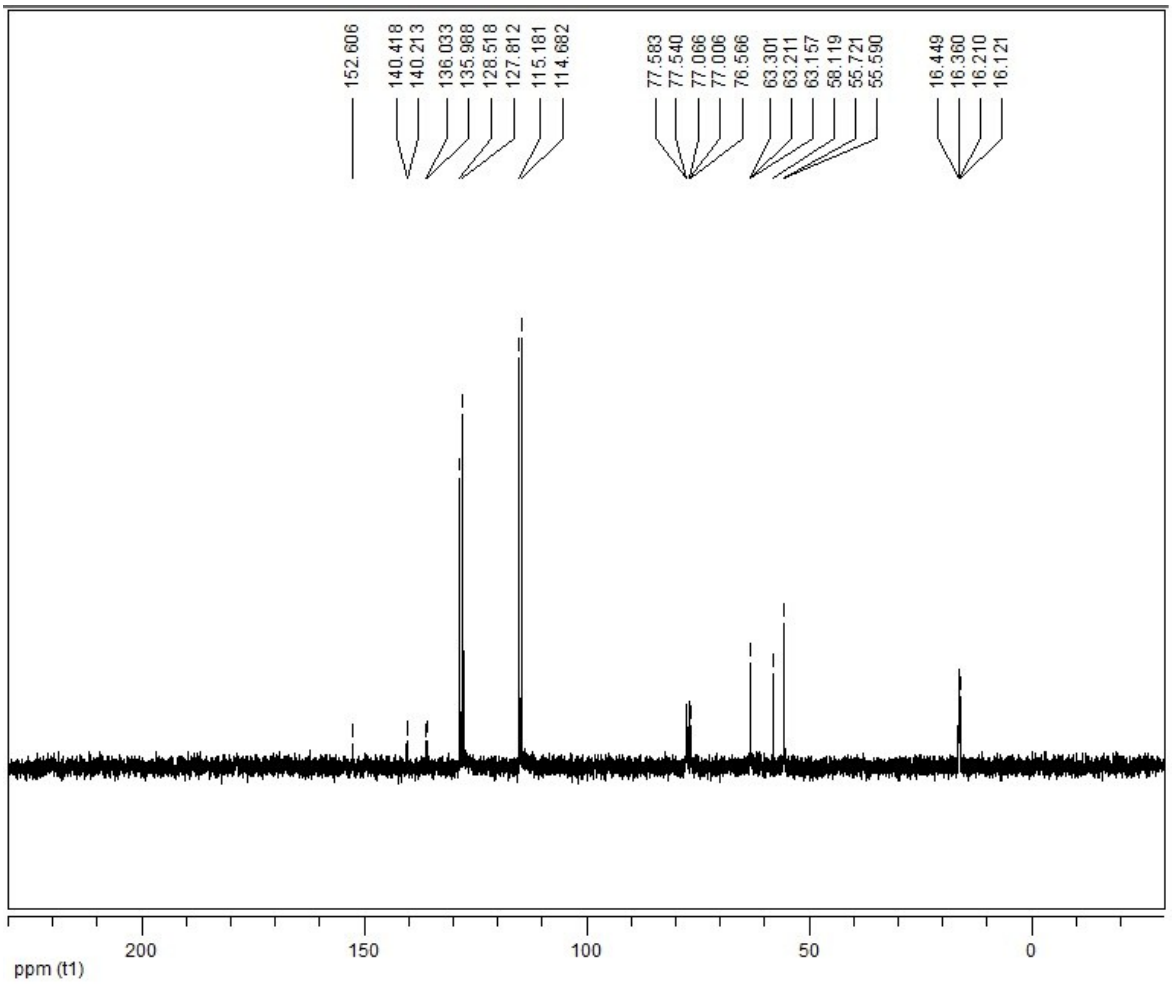
(2h):



Pale yellow solid (mp: 67-70 ºC, Lit. 70-73ºC);[121]H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.39-7.36 (m, 2H), 7.27-7.17 (m, 3H), 6.61 (d, 2H, J= 9 Hz), 6.46 (d, 2H, J= 9 Hz), 4.68-4.49 (m, 2H), 4.10-3.81 (m, 4H),3.60 (d, 3H, J= 4Hz),1.20 (t, 3H, J= 7Hz), 1.03 (t, 3H, J= 7Hz); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 152.6, 140.4, 140.2, 136.0 (d, ^{2}J(C-P)= 2.8Hz), 128.5, 127.8, 115.1, 114.6, 63.1-63.2 (m, 2C, -CH_2-), 58.1 (1C, -OCH_3), 55.6 (d, -CH-, ^{1}J(C-P)= 8.2Hz), 16.1-16.4 (m, 2C, -CH_3); IR(KBr): ν [cm^{-1}]3301.9, 2990.0, 2895.5, 2820.9, 1512.1, 1450.6, 1380.1, 1234.4, 1026.1, 964.3, 800.1, 750.9, 686.6.

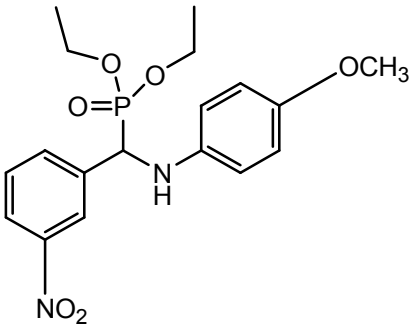

7.248
7.218
7.203
7.197
7.191
7.176
6.629
6.593
6.487
6.451
4.680
4.655
4.560
4.525
4.495
4.102
4.087
4.072
4.059
4.055
4.043
4.034
4.031
4.027
4.014
4.006
4.003
3.999
3.986
3.909
3.897
3.880
3.868
3.852
3.848
3.840
3.811
3.628
3.613
3.597
1.285
1.264
1.260
1.256
1.252
1.235
1.222
1.207
0.26
0.44
0.26
0.25
0.26
0.25
0.53
0.47
0.44
0.37
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

^{1}H NMR



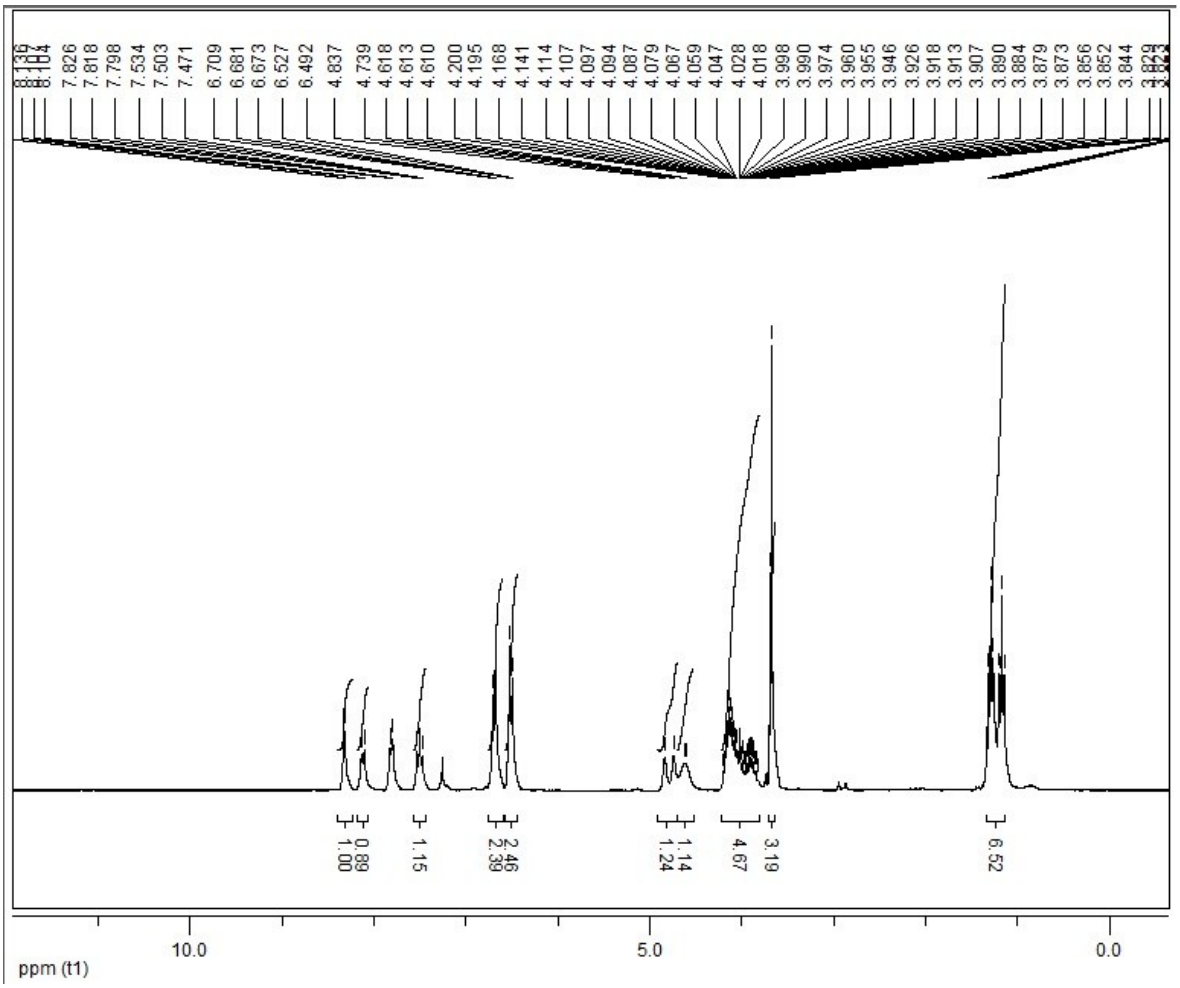
^{13}C NMR

(2k):

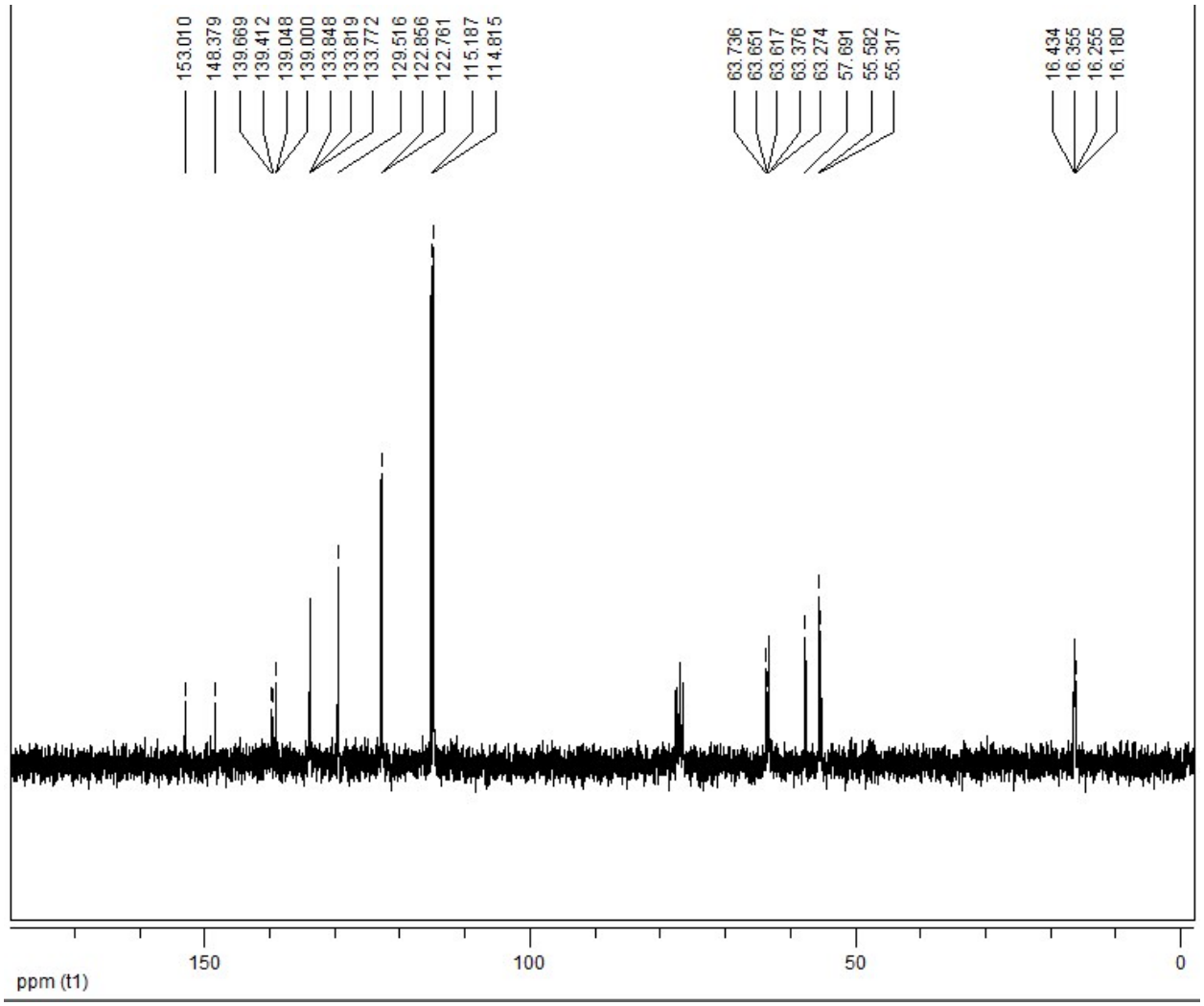


Pale yellow solid (mp: 99.7-100.5 ºC);[23] ^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.32-8.31 (m, 1H), 8.12 (d, 1H, J= 8Hz),7.81 (d, 1H, J= 7Hz), 7.50 (t, 1H, J= 8Hz), 6.69 (d, 2H, J= 9Hz), 6.51 (d, 2H, J=9Hz), 4.78 (d, 1H, 24.5Hz), 4.62-4.61 (m, 1H), 4.20-3.82 (m, 4H), 3.68 (d, 3H, J= 2.0

Hz), 1.29 (t, 3H, J= 7Hz), 1.17 (t, 3H, J= 7Hz); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 153.0, 148.3, 139.6, 139.4, 139.0, 133.8 (d, ^{4}J(C-P)= 4.8Hz), 129.5, 122.8 (d, ^{5}J(C-P)= 6.0Hz), 115.1, 114.8, 63.2- 63.7 (m, 2C, -CH_2-), 57.6 (1C, -OCH_3), 55.4 (d, -CH-, ^{1}J(C-P)= 16.6Hz), 16.1-16.4 (m, 2C, -CH_3); IR (KBr): ν [cm^{-1}] 3294.2, 2985.6, 2931.6, 2831.3, 1512.1, 1447.7, 1350.1, 1234.4, 1026.1, 972.1, 817.8, 686.6; MS (70 eV, EI): m/z (%):394, M^+ (9.1), 257 (100.0).

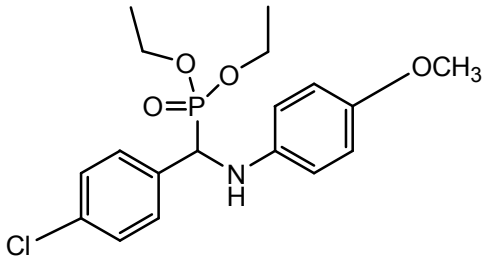


^{1}H NMR



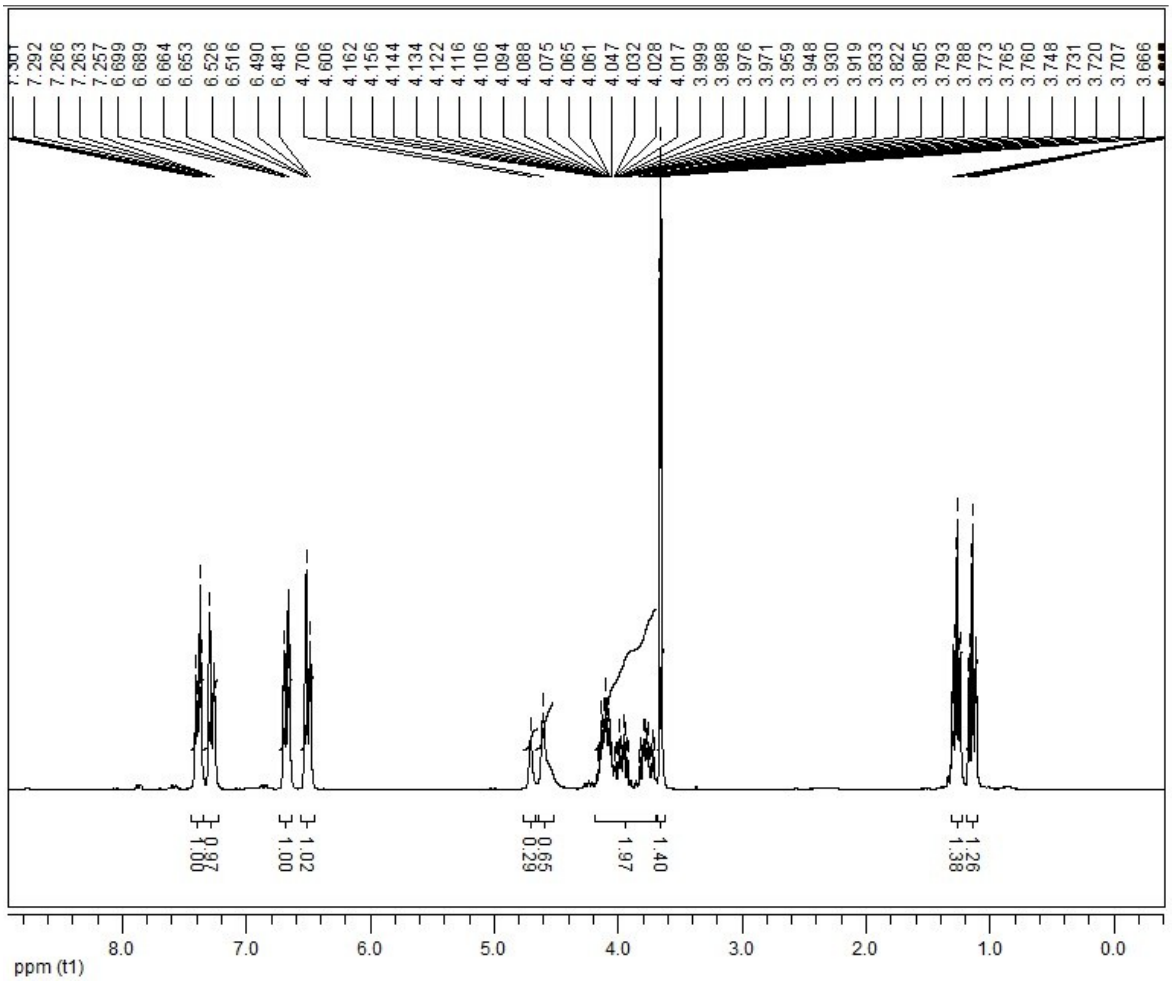
^{13}C NMR

(2l):

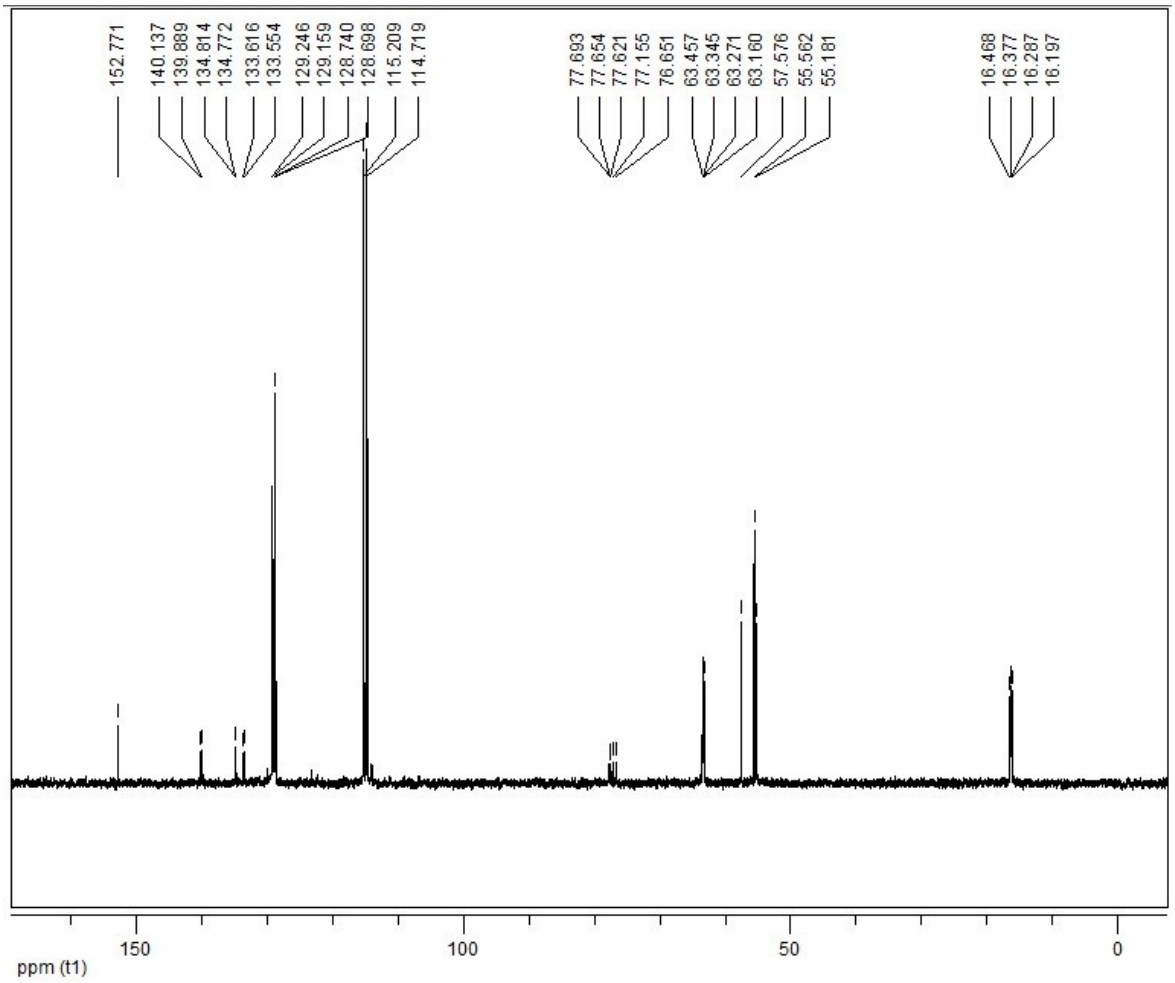


Yellow solid (mp: 99.5-100 ºC);[24] ^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm):7.40-7.36 (m, 2H), 7.30-7.25(m, 2H), 6.67 (dd, 2H, J= 9.7Hz, J´= 2.7Hz), 6.50 (dd, 2H, J= 8.8Hz, J´= 2.2Hz),4.70 (broad s, 1H), 4.60 (broad s, 1H), 4.14-3.70 (m, 4H), 3.65 (d, 3H, J= 3.2Hz),1.27 (mt, 3H),1.14 (mt, 3H);^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 152.7, 140.0 (d, ^{3}J(C-P)= 15.5Hz), 134.8 (d, ^{5}J(C-P)= 2.6Hz), 133.5 (d, ^{2}J(C-P)= 4.0Hz), 129.2 (d, ^{3}J(C-P)= 5.5Hz), 128.6 (d, ^{4}J(C-P)= 2.7Hz),

115.2, 114.7, 63.1-63.4 (m, 2C, -CH_3), 56.3 (d, -CH-, ^{1}J(C-P)= 150.6Hz), 55.5 (OCH_3), 16.1-16.4 (m, 2C, -CH_3); IR (KBr): ν [cm^{-1}] 3309.6, 2993.9, 1512.1, 1396.4, 1242.1, 1164.9, 1018.3, 964.3, 825.5.

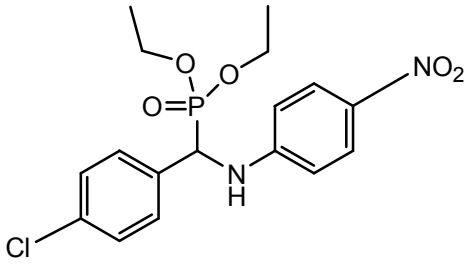


^{1}H NMR



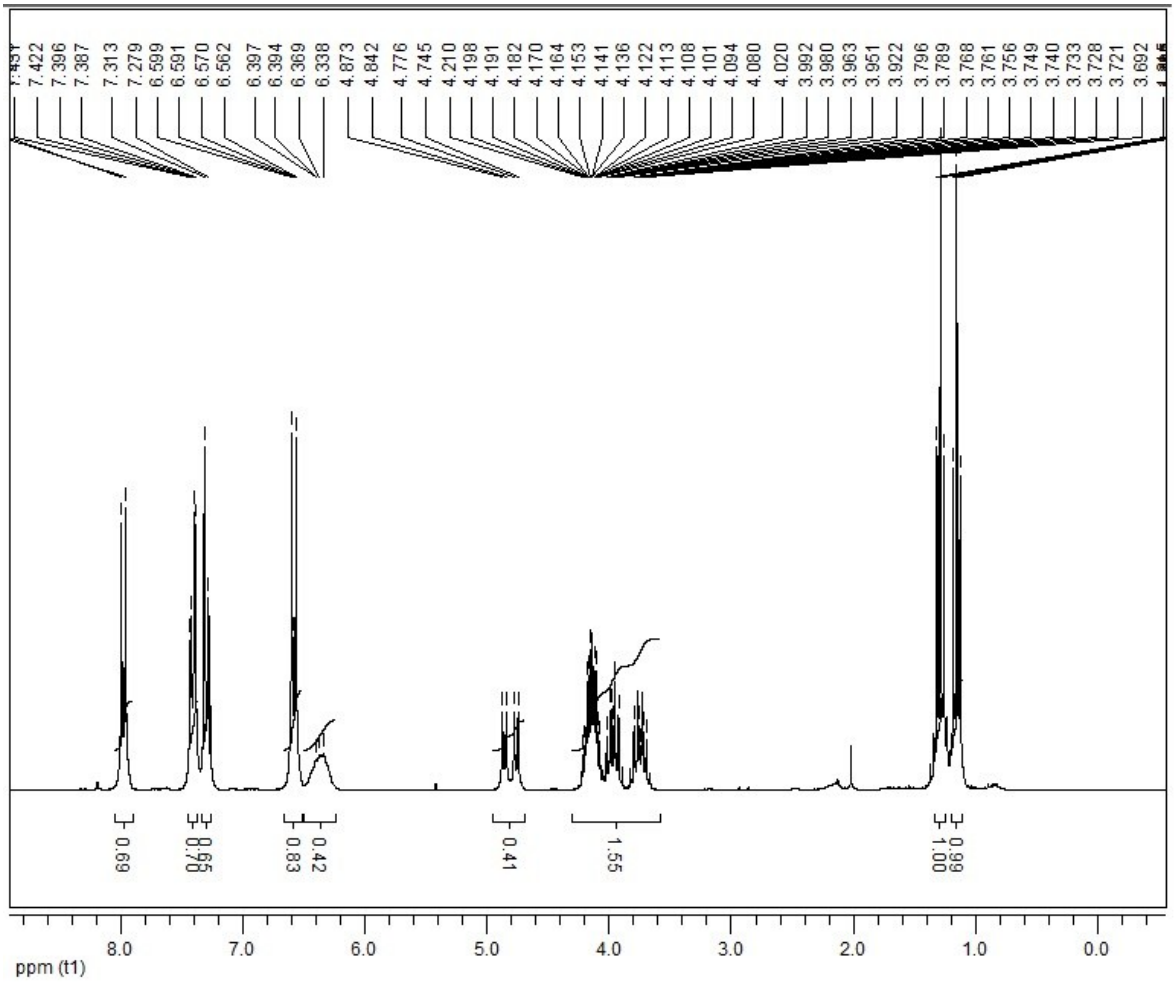
^{13}C NMR

(2m):

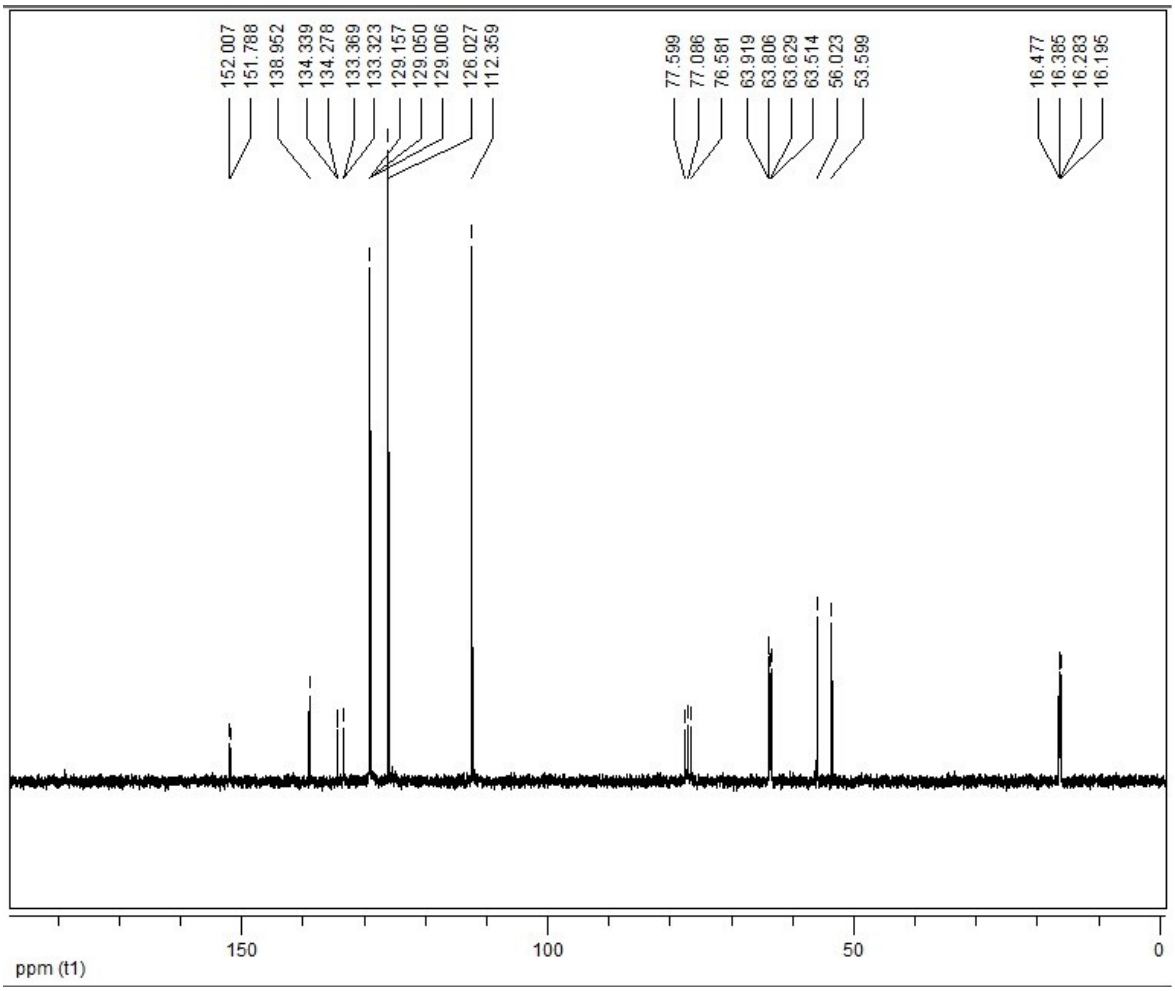


Pale yellow solid (mp: 135-136 ºC, Lit. 131-132 °C);[25] ^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.97 (d, 2H, J= 9Hz), 7.40 (dd, 2H, J= 8.7Hz, J´= 2.2Hz),7.29 (d, 2H, J= 8.5 Hz), 6.58 (d, 2H, J= 9.2Hz), 6.39-6.33 (m, 1H), 4.89 (dd, 1H, J= 24.2Hz, J´= 7.7Hz),4.21-3.92 (m, 4H),1.28 (t, 3H, J= 7Hz), 1.15 (t, 3H, 7Hz);^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 152.0 (d, ^{3}J(C-P)= 13.7Hz), 138.9, 134.3 (d, ^{2}J(C-P)= 3.8Hz), 133.3 (d, ^{5}J(C-P)= 3.0Hz), 129.1, 129.0 (d, ^{3}J(C-P)= 2.7Hz), 126.0, 112.3, 63.5-63.9 (m, 2C, -CH_3), 54.8 (d, -CH-, ^{1}J(C-P)= 152.4Hz), 16.1-16.4 (m, 2C, -

CH_2-); IR (KBr): ν [cm^{-1}] 3271.0, 3078.2, 2977.9, 2916.2, 1596.9, 1488.9, 1319.2, 1234.3, 1103.2, 1033.8, 964.3, 840.9, 740.6.

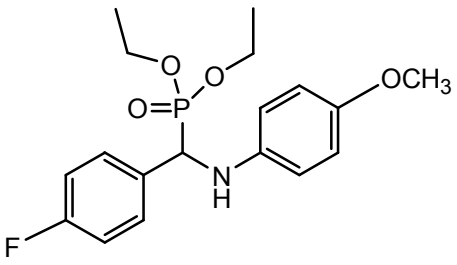


^{1}H NMR

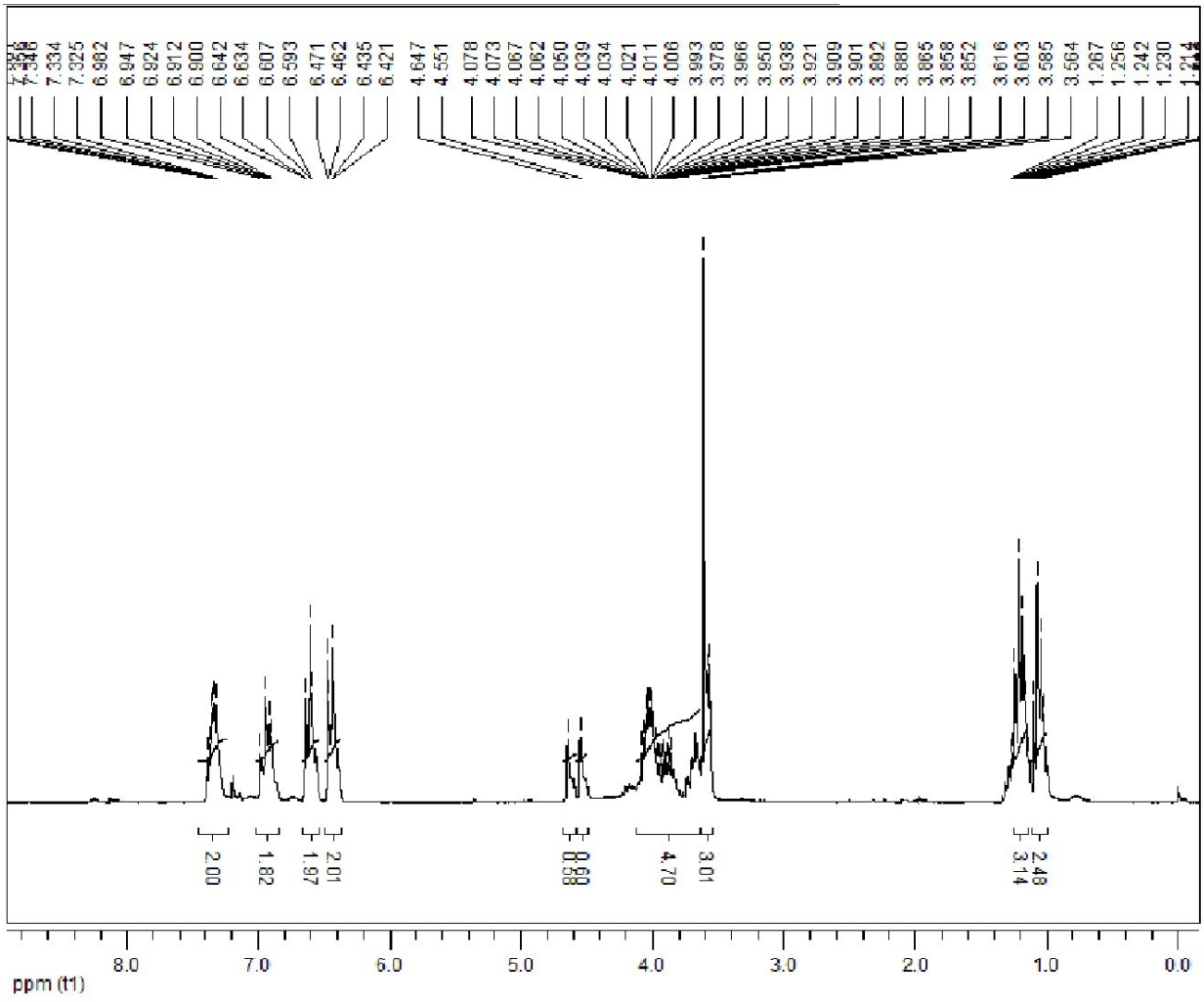

152.007
151.788
138.952
134.339
134.278
133.369
133.323
129.157
129.050
129.006
126.027
112.359
77.599
77.086
76.581
63.919
63.806
63.629
63.514
56.023
53.599
16.477
16.385
16.283
16.195
150
100
50
0
ppm (t1)

^{13}C NMR

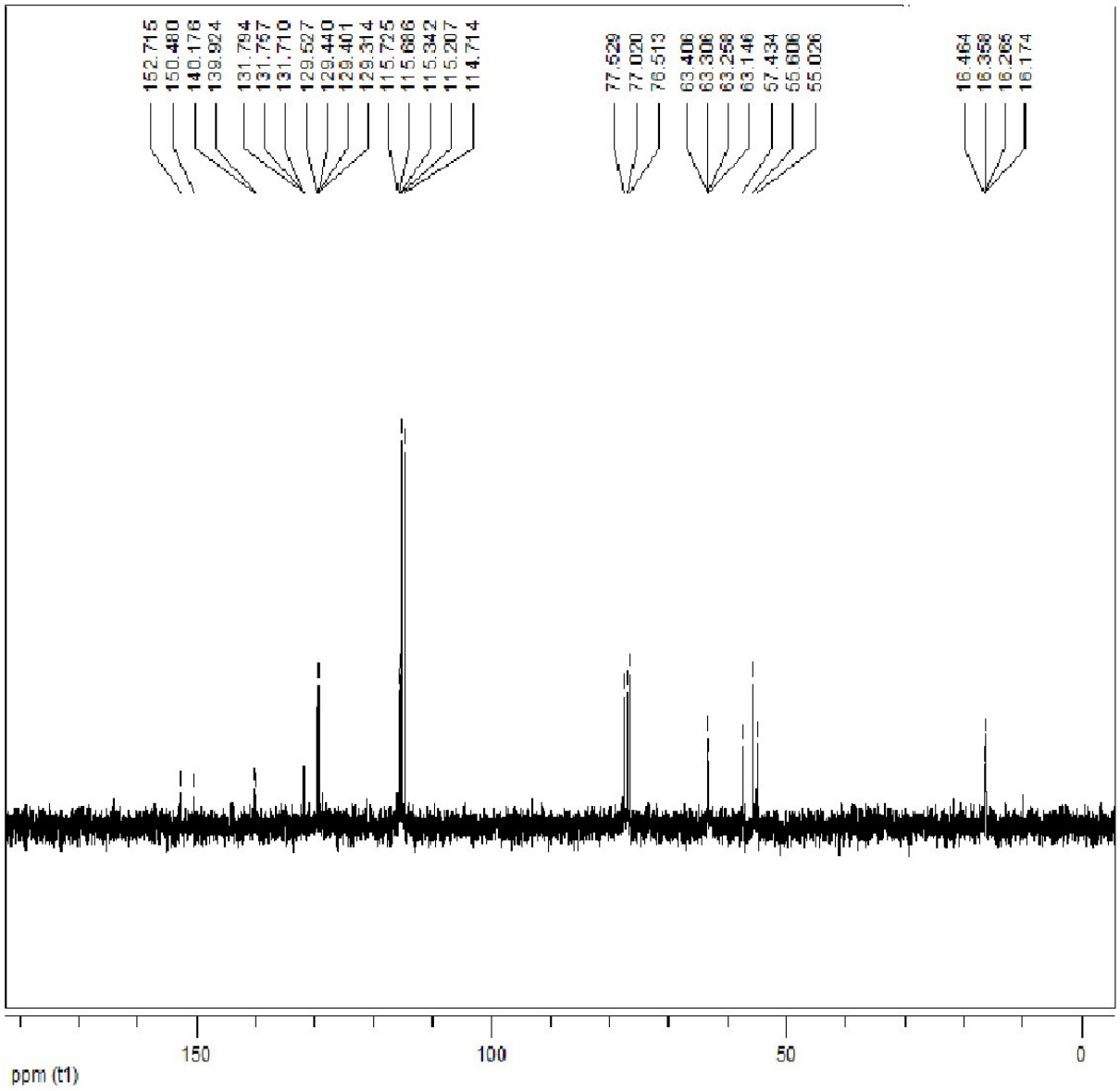
(2n):


O
O
O=P
OCH3
N
H
F

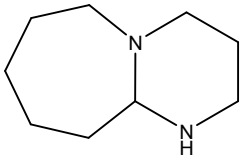
White solid (mp: 50-54 ºC, Lit.45-48ºC);[12] ^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 7.37-7.35 (m, 2H), 6.98-6.90 (m, 2H), 6.62 (d, 2H, J= 9Hz), 6.45 (d, 2H, J= 9Hz), 4.64-4.59 (m, 1H), 4.55-4.50 (m, 1H), 4.10-3.64 (m, 4H), 3.61-3.56 (m, 3H), 1.21 (mt, 3H), 1.07 (mt, 3H); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 152.7, 150.4, 140.0 (d, ^{3}J(C-P)= 15.8Hz), 131.7 (d, ^{2}J(C-P)= 5.3Hz), 129.5 (dd, ^{3}J(C-F)= 8.0Hz, ^{3}J(C-P)= 5.5Hz), 115.5 (d, ^{2}J(C-F)= 22.8Hz), 115.2, 114.7, 63.1-63.4 (m, 2C, -CH_2-), 56.2(d, -CH-, ^{1}J(C-P)= 151.4Hz), 55.6 (-OCH_3), 16.1-16.4 (m, 2C, -CH_3); IR (KBr): ν [cm^{-1}] 3320, 2930, 2880, 2800, 1640, 1560, 1250, 1020, 996.0.



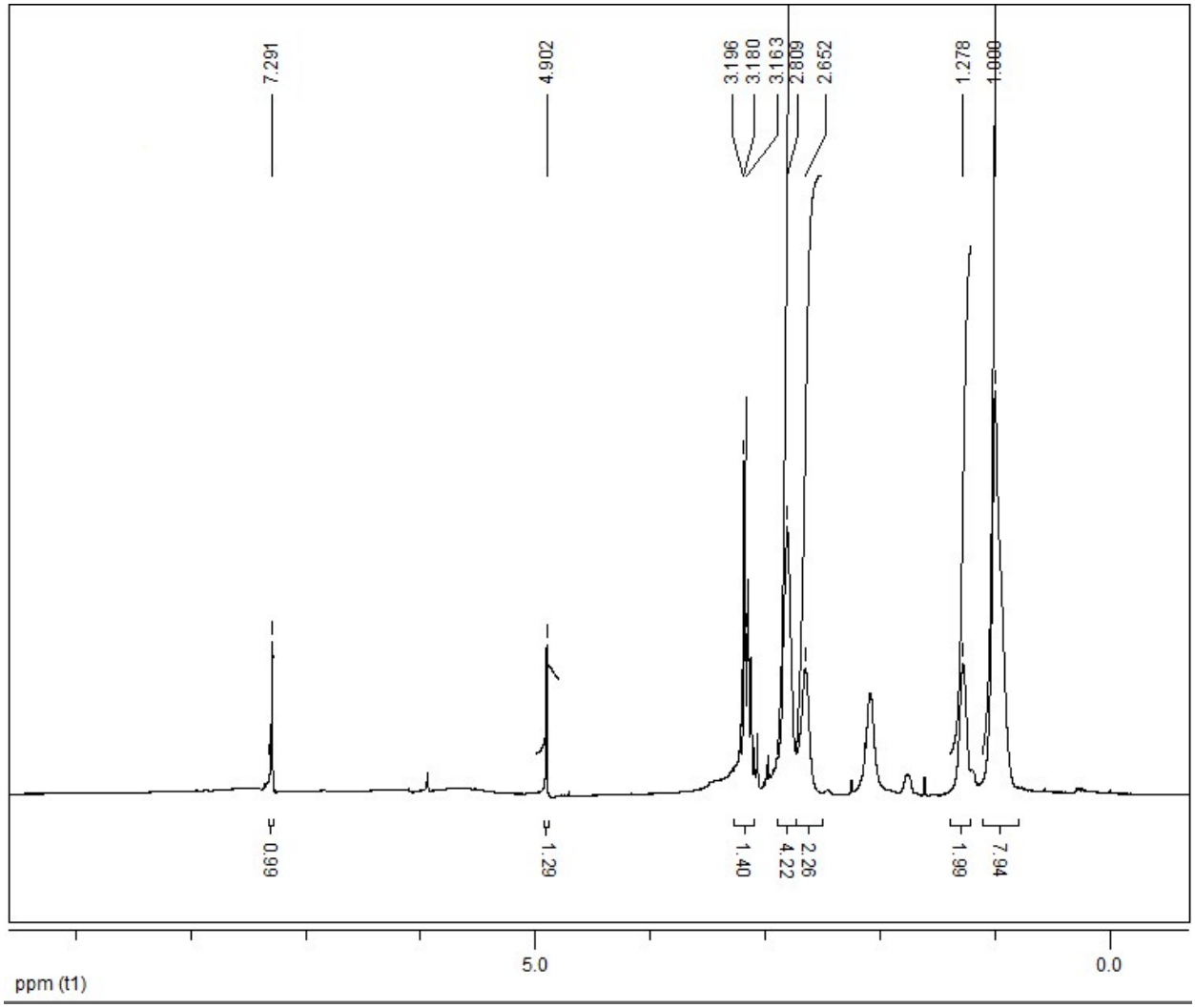
^{1}H NMR


152.715
150.480
140.176
139.924
131.794
131.757
131.710
129.527
129.440
129.401
129.314
115.725
115.686
115.342
115.207
114.714
77.529
77.020
76.513
63.406
63.306
63.258
63.146
57.434
55.606
55.026
16.464
16.358
16.266
16.174
150
100
50
0
ppm (t1)

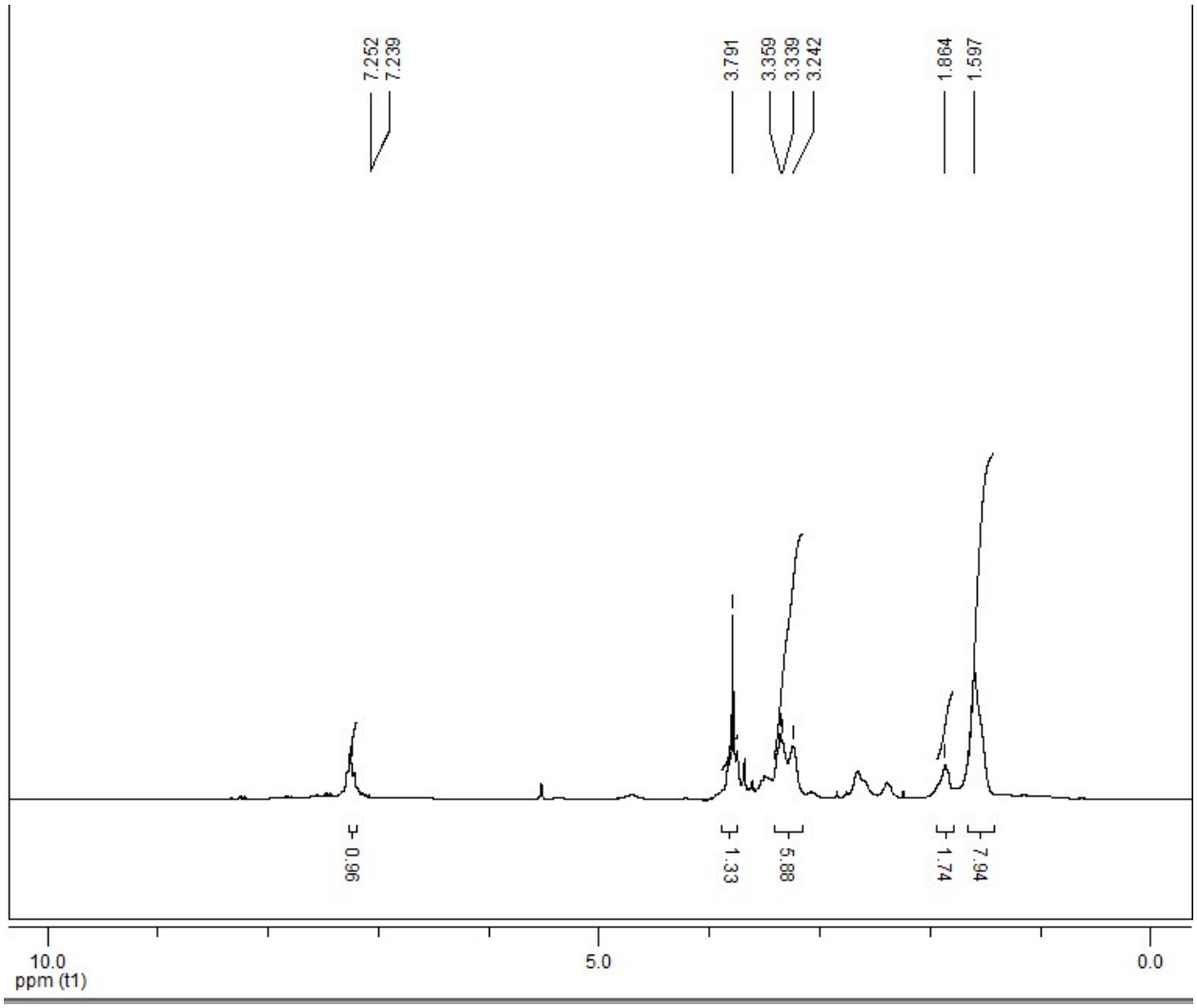
^{13}C NMR



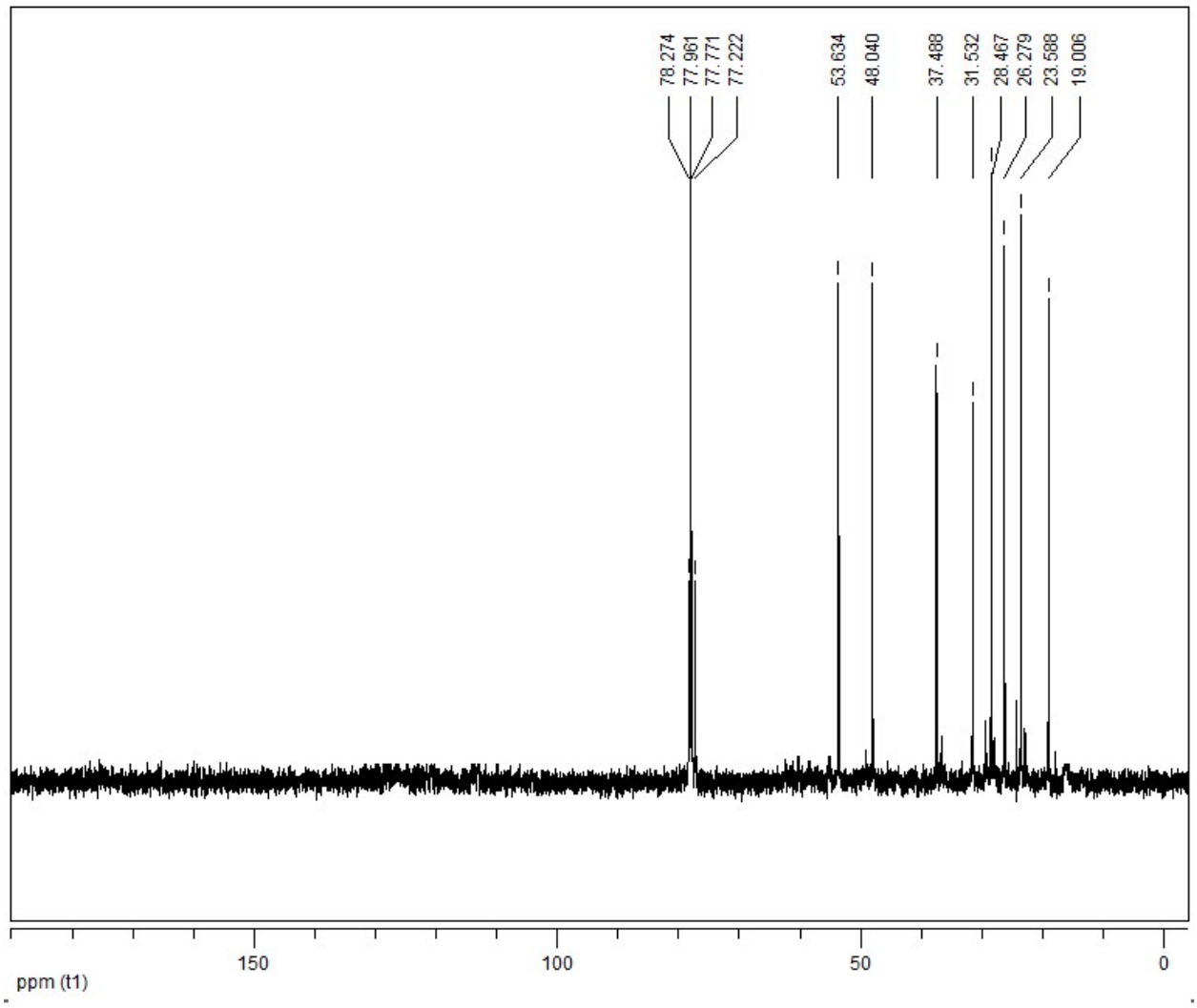
^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 4.9 (s, 1H), 3.18 (t, 1H, J= 4.0Hz), 2.80 (broad s, 4H), 2.65 (broad s, 2H), 1.27 (broad s, 2H), 1.00 (broad s, 8H); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 77.2 (-CH-), 53.6, 48.0, 37.4, 31.5, 28.4, 26.2, 23.5, 19.0.



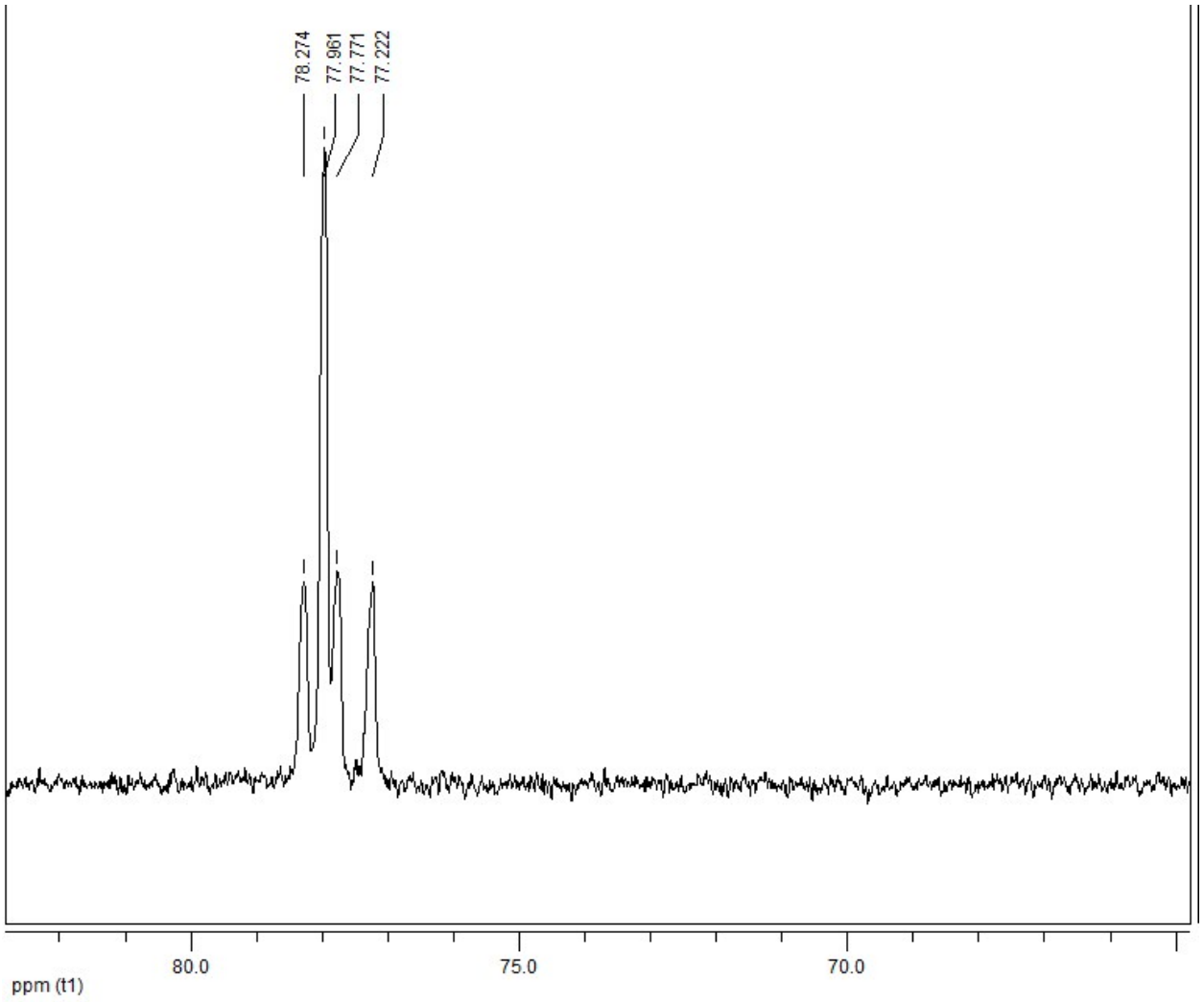
^{1}H NMR of the reaction mixture after removing the main product (Reduced form of DBU)



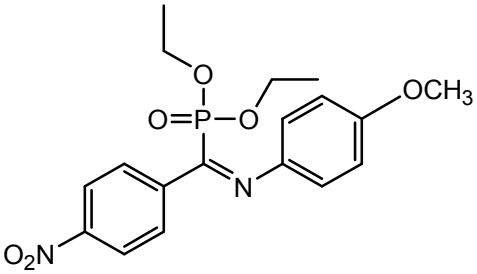
^{1}H NMR of reduced form of DBU & D_2O


78.274
77.961
77.771
77.222
53.634
48.040
37.488
31.532
28.467
26.279
23.588
19.006
150
100
50
0
ppm (t1)

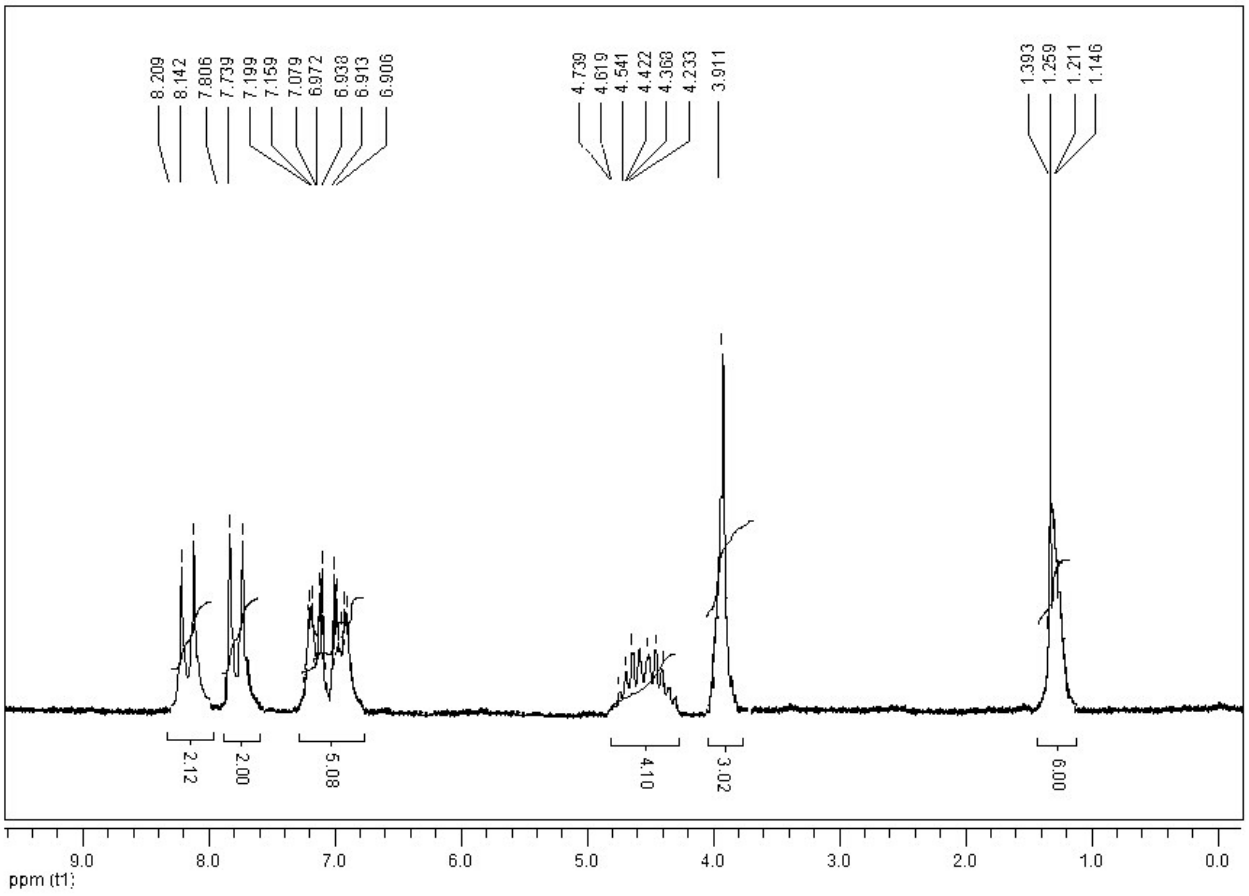
^{13}C NMR



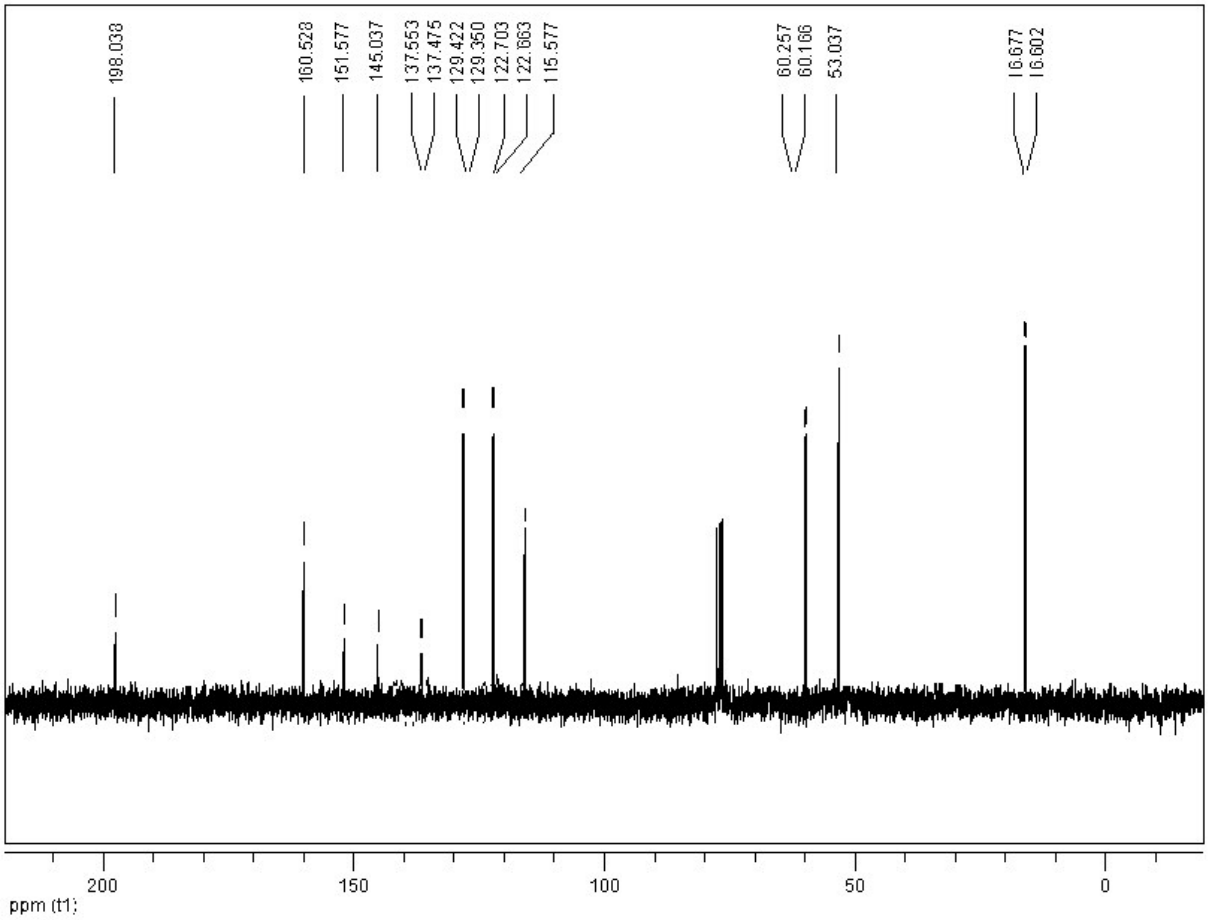
Expanded ^{13}C NMR of $CDCl_3$ and –CH-



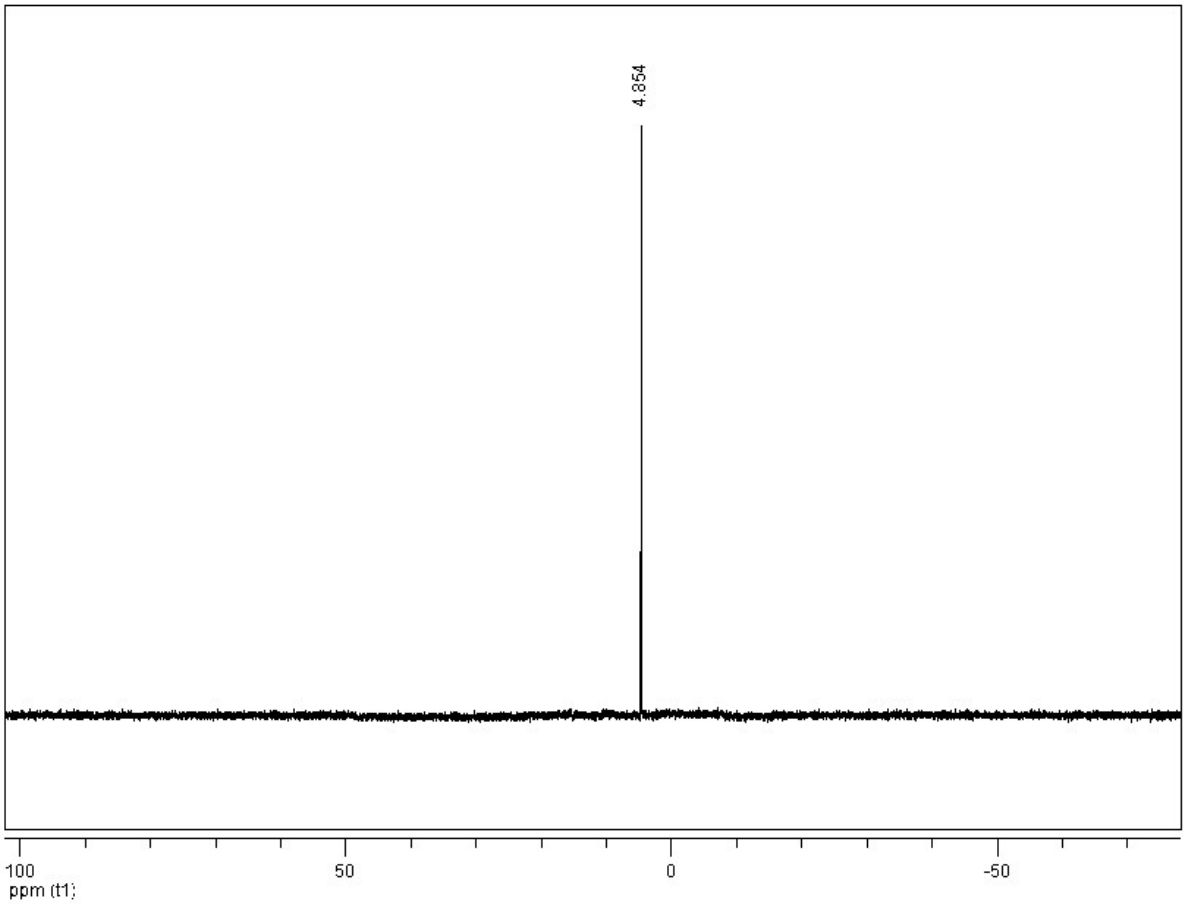
Yellow oil; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ (ppm): 8.17 (d, 2H, J= 16.7Hz), 7.77 (d, 2H, J= 16.7Hz), 7.19-6.90 (m, 4H), 4.73-4.23 (m, 4H), 3.91 (s, 3H), 1.39-1.14 (m, 6H); ^{13}C-NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 198.7, 160.5, 151.5, 145.0 , 137.5 (d, ^{2}J(C-P)= 4.9Hz), 129.3 (d, ^{2}J(C-P)= 4.5Hz), 122.7, 122.6, 115.5, 60.2 (d, -CH_2-,^{2}J (C-P)= 5.7Hz), 53.0 (1C, -OCH_3), 16.6 (d, -CH_3, ^{3}J (C-P)= 4.7Hz); ^{31}P-NMR ($CDCl_3$, 162 MHz)δ (ppm): 4.85.


8.209
8.142
7.806
7.739
7.199
7.159
7.079
6.972
6.938
6.913
6.906
4.739
4.619
4.541
4.422
4.368
4.233
3.911
1.393
1.259
1.211
1.146
2.12
2.00
5.08
4.10
3.02
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

^{1}H NMR


198.038
160.528
151.577
145.037
137.553
137.475
129.422
129.350
122.703
122.663
115.577
60.257
60.166
53.037
16.677
16.602
200
150
100
50
0
ppm (t1)

^{13}C NMR



^{31}P NMR