Supporting Information

6-Methoxy-5-phosphaphenanthrene: A molecule with an unreactive P=C double bond

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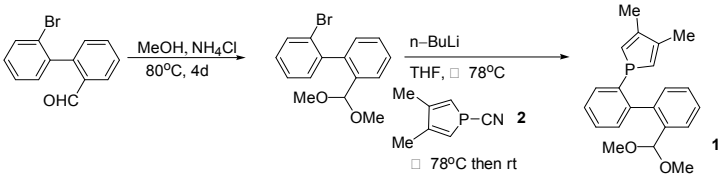
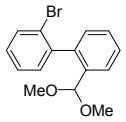
General information and materials

All reactions were routinely performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. Dry THF was obtained by distillation from Na/benzophenone. Dry toluene was obtained by distillation from P_4O_{10}. Dry acetonitrile was obtained by distillation from CaH. Dry $(COCl)_2$ was redistilled before using. *n*-butyl lithium (1.6 M in hexane) were purchased from J&K Scientific Ltd. And silica gel (200-300 mesh) purchased from Qingdao Hai Yang Chemical Industry Co. Ltd. was used for chromatographic separations. Nuclear magnetic resonance spectra were recorded on a Bruker 300 MHz spectrometer operating at 300.13 MHz for ^{1}H, 75.468 MHz for ^{13}C, 121.495 MHz for ^{31}P. Chemical shifts are expressed from internal TMS (^{1}H and ^{13}C). All coupling constants (*J* values) are reported in hertz (Hz). HRMS were obtained on an Agilent 1290-6540 Q-Tof spectrometer by electrospray ionization (ESI). Element analytic data were obtained on a Thermo Electron Corporation flash EA 1112 element spectrometer. 1-Phenyl-3, 4-dimethylphosphole[1], 1-cyano-3, 4-dimethylphosphole[2] , 2-bromobiphenyl-2'-carbaldehyde[3] were prepared according to published procedures.

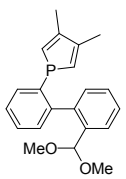
Procedure for the synthesis of 1, 3, 5, 6, 7 and their Characterization





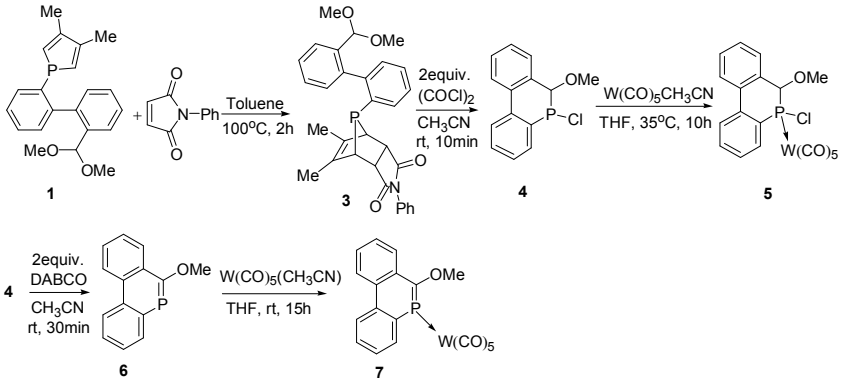
Procedure for

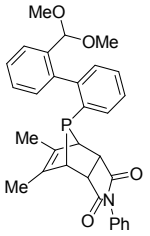
A solution of 2-bromobiphenyl-2'-carbaldehyde (5.98 g, 23 mmol), NH_4Cl (0.7g, 13 mmol), in methanol (100mL) was refluxed at 80°C for 4 days until total consumption of the starting aldehyde as monitored by GC. After removal of methanol, the reaction mixture was extracted with diethyl ether and the organic layer was dried with $MgSO_4$. After evaporation of the solvent, the crude product was chromatographed on silica gel. Elution with a mixture of hexane and CH_2Cl_2 (3:1) afforded the pure faint yellow oil (6.15 g, yield: 87 %). ^{1}H NMR($CDCl_3$): δ 3.21(s, 3H, OCH_3), 3.31(s, 3H, OCH_3), 5.04(s, 1H, CH), 7.18～7.50, 7.68~7.75(m, 8H, CH-Ph); ^{13}C NMR($CDCl_3$): δ 53.54(s, OCH_3), 54.21(s, OCH_3), 102.00(s, CH), 123.52(s, C-Ph), 126.10(s, CH-Ph), 126.86(s, CH-Ph), 127.96(s, CH-Ph), 128.23(s, CH-Ph), 129.07(s, CH-Ph), 129.88(s, CH-Ph), 131.55(s, CH-Ph), 132.48(s, CH-Ph), 135.92(s, C-Br), 140.34 (s, C-Ph), 141.06(s, C-Ph).



Procedure for **1**

To a THF (50 mL) solution of 2-Bromo-2'-dimethoxymethyl-biphenyl (3.06 g, 10 mmol), n-BuLi (6.6mL, 1.6 M, 10.5 mmol) was added at –78 °C. The reaction mixture was stirred at –78 °C for 30 min and then a THF (5 mL) solution of 1-cyano-3, 4-dimethylphosphole (1.44 g, 10.5 mmol) was added. The mixture was warmed to room temperature and stirred for 2 h. After removal of the solvent, the residue was quickly eluted with CH_2Cl_2. After evaporation of the solvent, Purification was performed via column chromatography on silica gel using CH_2Cl_2/Petroleum ether (1:1) as eluent and **1** was obtained as a faint yellow viscous oil (2.47 g, yield: 73 %). ^{31}P NMR($CDCl_3$): δ −5.1; ^{1}H NMR($CDCl_3$): δ 2.11(d, $^{4}J_{H\text{-}P}$=3.6Hz, 6H, CH_3), 3.31(s, 3H, OCH_3), 3.39(s, 3H, OCH_3), 5.17(s, 1H, CH), 6.34 (d, $^{2}J_{H\text{-}P}$=37.2Hz, 2H, P-CH), 7.27~7.55, 7.82~7.85(m, 8H, CH-Ph); ^{13}C NMR($CDCl_3$): δ 17.78(d, $^{3}J_{C\text{-}P}$=3.6Hz, 2CH_3), 53.39 (s, OCH_3), 54.38 (d, OCH_3), 102.10(d, CH_{sp3}), 126.25(s, CH), 127.52(d, $J_{C\text{-}P}$=2.2Hz, CH), 127.88(s, CH), 127.93(s, CH), 130.51(d, $J_{C\text{-}P}$=5.0Hz, CH), 130.61(d, $J_{C\text{-}P}$=2.0Hz, CH), 132.22 (d, $J_{C\text{-}P}$=3.3Hz, CH), 132.97(d, $J_{C\text{-}P}$=11.6Hz, C), 136.13(s, C), 141.19(d, $J_{C\text{-}P}$=5.1Hz, C), 144.51(d, $^{1}J_{C\text{-}P}$=24.0Hz, P-C-Ph). HRMS Calcd. For $C_{21}H_{23}O_2PNa$: $[M+Na]^+$, 361.1328. Found: 361.1330.

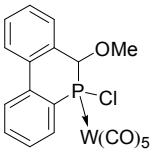




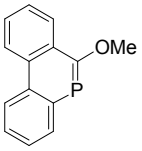
Procedure for **3**

A solution of **1**(1.35 g, 4 mmol) and N-phenylmaleimide (0.7 g, 4 mmol) in toluene was stirred at 100 °C for 2h (^{31}P NMR: δ= 49.0). After evaporation of the solvent, the crude product was chromatographed on silica gel using a mixture of ethyl acetate and Petroleum ether (1:4) as eluent and **3** was obtained as a white solid(1.69 g, yield: 82 %). ^{31}P NMR($CDCl_3$): δ 49.9; ^{1}H NMR($CDCl_3$): δ 1.67(s, 3H, CH_3), 1.68(s, 3H, CH_3), 2.76(d, *J*=12.3Hz, 2H, -CH), 3.20(s, 3H, OCH_3), 3.42(s, 3H, OCH_3), 3.56(ddd, *J* =3.6Hz, *J*=9.3Hz, *J*=14.4Hz, 2H, -CH), 5.30(s, 1H, -CH), 7.00～7.03 (m, 2H, CH-Ph), 7.27～7.54(m, 10H, CH-Ph), 7.80～7.83(m, 1H, CH-Ph); ^{13}C NMR($CDCl_3$): δ 15.30(s, CH_3), 15.32(s, CH_3), 48.64(d, $^{2}J_{C\text{-}P}$=3.1Hz, -CHCO), 48.73(d, $^{2}J_{C\text{-}P}$=3.3Hz, -CHCO), 48.76(d, $^{1}J_{C\text{-}P}$=14.3Hz, P-CH), 49.21(d, $^{1}J_{C\text{-}P}$=15.2Hz, P-CH), 52.78(s,

OMe), 54.73(s, OCH_3), 101.63(d, $J_{C\text{-}P}$=4.7Hz, CH_{sp3}), 126.50(s, 2CH-Ph), 127.15(s, CH-Ph), 128.02(s, CH-Ph), 128.14(s, CH-Ph), 128.26(s, CH-Ph), 128.55(s, CH-Ph), 128.70(s, CH-Ph), 129.18(s, 2CH-Ph), 129.76(d, $J_{C\text{-}P}$=9.0Hz, CH-Ph), 129.90(d, $J_{C\text{-}P}$=4.3Hz, CH-Ph), 131.08(s, CH-Ph), 131.93(s, C), 133.76(d, $J_{C\text{-}P}$=19.9Hz, C), 133.90(d, $J_{C\text{-}P}$=19.8Hz, C), 135.73(s, C), 139.12(s, C), 139.19(d, $^1J_{C\text{-}P}$=43.3Hz, P-C), 142.07(d, $J_{C\text{-}P}$=10.0Hz, C), 176.48(s, CO), 176.51(s, CO). HRMS (ESI) Calcd. For $C_{31}H_{30}NO_4PNa$: $[M + Na]^+$, 534.1805. Found: m/z 534.1808.

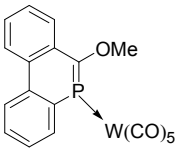
Procedure for **5** 

To a CH_3CN (7 mL) solution of **3** (0.51 g, 1 mmol), dry $(COCl)_2$ (0.17 mL, 2 mmol) was added at room temperature. The reaction mixture was stirred for 10 min (^{31}P NMR: δ= 67.0), then the solvent and unconsumed $(COCl)_2$ was evaporated under reduced pressure, then a freshly prepared THF (7 mL) solution of $W(CO)_5(CH_3CN)$ (1.2 mmol) was added. The reaction mixture was stirred at 35°C for 10 h. After evaporation of the solvent, the residue was chromatographed on silica gel with petroleum ether/CH_2Cl_2 (5:1) as eluent under N_2 atmosphere and －10 °C, to give pure **5** as a white solid. (0.27 g, yield: 46 %). ^{31}P NMR($CDCl_3$): δ 89.3($J_{P\text{-}W}$=277Hz); ^1H NMR($CDCl_3$): δ 3.81(s, 3H, OCH_3), 5.36 (d, 1H, $^1J_{H\text{-}P}$=8.7Hz), 7.45～7.62, 7.69～7.80, 7.88～7.95(m, 8H, CH-Ph); ^{13}C NMR($CDCl_3$): δ 60.98(d, $^3J_{C\text{-}P}$=6.5Hz, OCH_3), 86.78(d, $^1J_{C\text{-}P}$=34.6Hz, P-CH), 125.93(d, $J_{C\text{-}P}$=6.1Hz, CH-Ph), 127.44(d, $J_{C\text{-}P}$=3.2Hz, CH-Ph), 127.69(s, CH-Ph), 128.76(d, $J_{C\text{-}P}$=9.7Hz, CH-Ph), 129.14(s, CH-Ph), 129.73(d, $J_{C\text{-}P}$=2.6Hz, CH-Ph), 131.67(d, $J_{C\text{-}P}$=11.2Hz, CH-Ph), 131.91(d, $J_{C\text{-}P}$=6.9Hz, C-Ph), 132.60(s, CH-Ph), 133.31(d, $J_{C\text{-}P}$=5.3Hz, C-Ph), 135.82(d, $J_{C\text{-}P}$=5.6Hz, C-Ph), 194.74(d, $J_{C\text{-}P}$=7.4Hz, *cis*-CO), 198.32(d, $J_{C\text{-}P}$=33.4 Hz, *trans*-CO).

Procedure for **6** 

To a CH_3CN (7 mL) solution of **3** (0.26 g, 0.5 mmol), dry $(COCl)_2$ (0.086mL, 1mmol) was added at room temperature. The reaction mixture was stirred for 10 min (^{31}P NMR: δ=67.0), then the solvent and unconsumed $(COCl)_2$ was evaporated under reduced pressure. The residue was dissolved in CH_3CN (7mL), DABCO (112 mg, 1 mmol) was added immediately at room temperature and stirred for 30 min, a colorless salt began to precipitate. The clear yellow solvent was removed to another clean schlenk bottle via syringe. After evaporation of the solvent, the crude product was chromatographed on silica gel under N_2 atmosphere. Elution with a mixture of hexane and CH_2Cl_2 (2:1) afforded the white solid (58 mg, yield: 51 %). ^{31}P NMR($CDCl_3$): δ 96.5; ^1H NMR($CDCl_3$): δ 4.20(d, 3H, $^4J_{H\text{-}P}$ =2.7Hz, OCH_3), 7.40～7.63, 8.09～8.16, 8.34~8.37, 8.60～8.65(m, 8H, CH-Ph); ^{13}C NMR($CDCl_3$): δ 57.66(d, $^3J_{C\text{-}P}$=34.1Hz, OCH_3), 120.00(d, $J_{C\text{-}P}$=8.5Hz, CH-Ph), 123.32(s, CH-Ph), 123.35(d, $J_{C\text{-}P}$=4.1Hz, CH-

Ph), 124.63(d, $J_{C\text{-}P}$=18.9Hz, CH-Ph), 125.98(d, $J_{C\text{-}P}$=3.5Hz, CH-Ph), 126.39(d, $J_{C\text{-}P}$=3.6Hz, CH-Ph), 127.36(d, $J_{C\text{-}P}$=4.8Hz, CH-Ph), 127.73(d, $J_{C\text{-}P}$=9.1Hz, C-Ph), 130.08(d, $J_{C\text{-}P}$=8.6Hz, C-Ph), 132.35(d, $J_{C\text{-}P}$=5.0Hz, C-Ph), 133.97(d, $J_{C\text{-}P}$=46.1Hz, CH-Ph), 140.33(d, $J_{C\text{-}P}$=36.4Hz, C-Ph), 197.56(d, $J_{C\text{-}P}$=38.5Hz, C-P). HRMS Calcd. For $C_{14}H_{12}OP$: $[M+H]^+$, 227.0620. Found: 227.0616.

Procedure for **7** 

To a stirred solution of pure **6** (113 mg, 0.5 mmol) in dry THF (5 mL), a freshly prepared THF (7 mL) solution of $W(CO)_5(CH_3CN)$ (0.6 mmol) was added. The reaction mixture was stirred at room temperature for 15 h. After evaporation of the solvent, The residue was chromatographed on silica gel with petroleum ether/CH_2Cl_2 (19:1) as eluent under N_2 atmosphere and －10 °C to give pure **7** (yellow crystal, 150 mg, yield: 54 %).^{31}P NMR($CDCl_3$): δ 138.3($J_{P\text{-}W}$=267Hz); ^{1}H NMR($CDCl_3$): δ 4.17(s, 3H, OCH_3), 7.68～7.86, 8.15～8.20, 8.35~8.43, 8.77～8.87(m, 8H, CH-Ph); ^{13}C NMR($CDCl_3$): δ 66.40(d, $^3J_{C\text{-}P}$=11.1Hz, OCH_3), 120.50(d, $J_{C\text{-}P}$=12.5Hz, CH-Ph), 125.34(d, $J_{C\text{-}P}$=6.6Hz, CH-Ph), 125.38(d, $J_{C\text{-}P}$=6.4Hz, CH-Ph), 126.53(d, $J_{C\text{-}P}$=18.7Hz, CH-Ph), 128.00(d, $J_{C\text{-}P}$=4.7Hz, CH-Ph), 128.13(d, $J_{C\text{-}P}$=7.6Hz, CH-Ph), 129.80(d, $J_{C\text{-}P}$=5.3Hz, CH-Ph), 132.04(d, $J_{C\text{-}P}$=10.6Hz, C-Ph), 132.91(s, C-Ph), 133.94(d, $J_{C\text{-}P}$=7.5Hz, C-Ph), 134.11(d, $J_{C\text{-}P}$=23.6Hz, CH-Ph), 138.12(d, $J_{C\text{-}P}$=17.5Hz, C-Ph), 191.13(d, $^1J_{C\text{-}P}$=63.4Hz, C-P), 194.46(d, $J_{C\text{-}P}$=9.6Hz, *cis*-CO), 198.50(d, $J_{C\text{-}P}$=31.5Hz, *trans*-CO). Anal. Calcd. for $C_{19}H_{11}O_6PW$: C, 41.48; H, 2.02. Found: C, 41.47; H, 1.94.

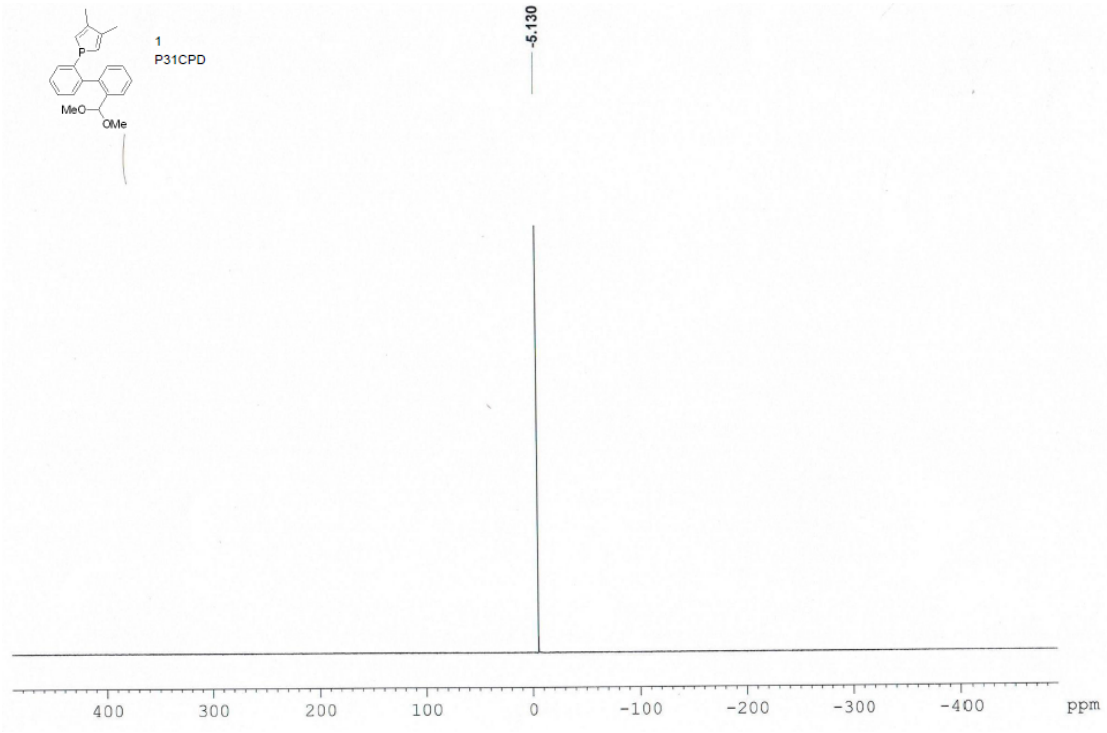
References

[1] A. Breque, F. Mathey, P. Savignac, *Synthesis* **1981**, 983.

[2] S. Holand, F. Mathey, *Organometallics* **1988**, *7*, 1796.

[3] H. Wang, W. Zhao, Y. Zhou, Z. Duan, F. Mathey, *Eur. J. Inorg. Chem.,* 2011, 4585.

NMR spectra of 1, 3, 5, 6, 7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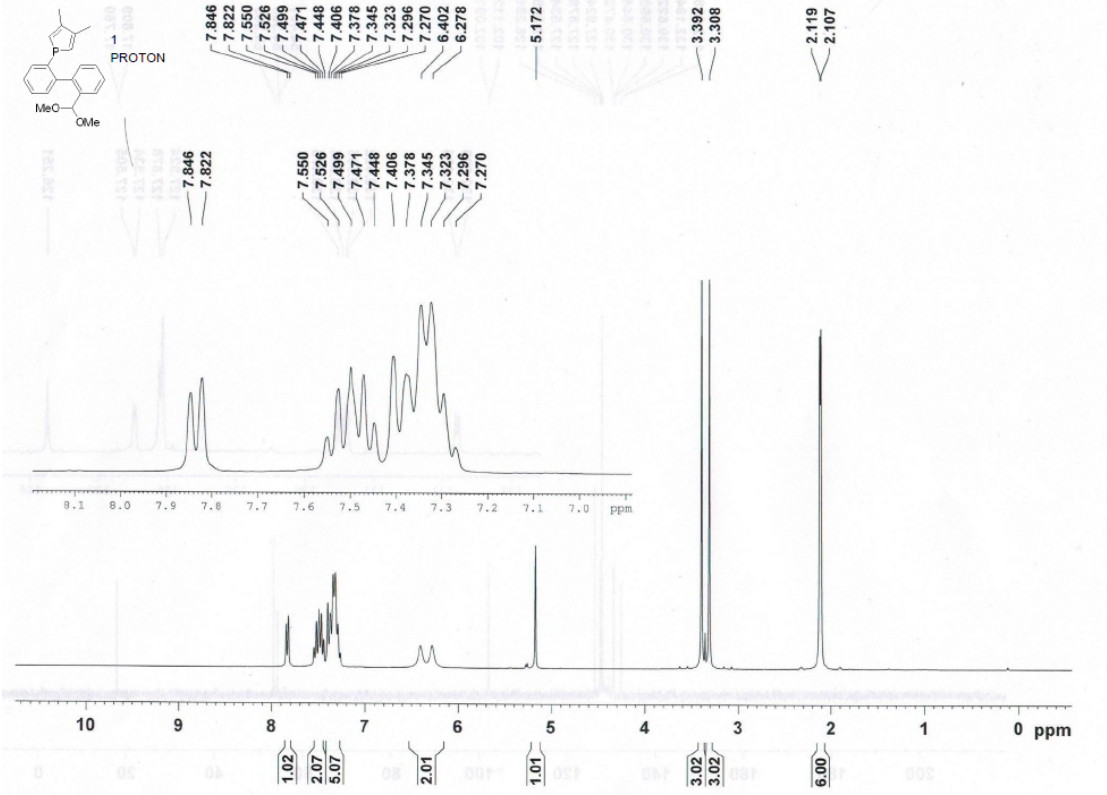
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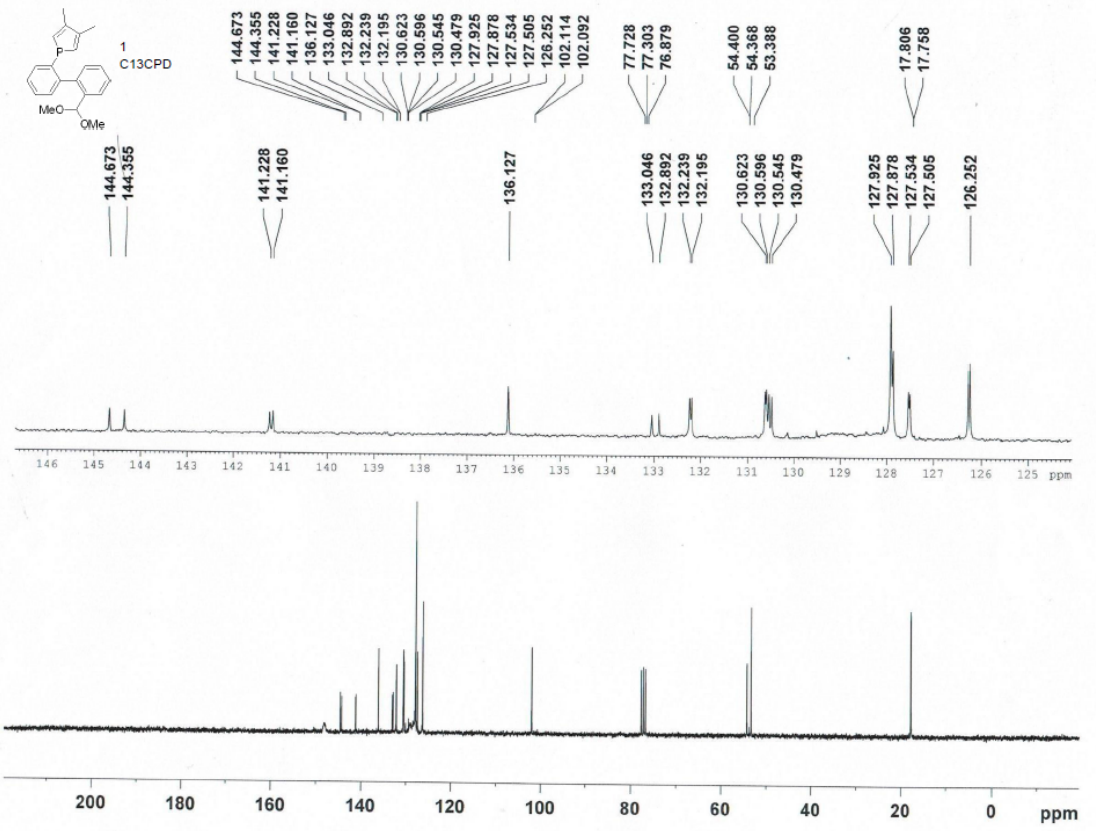
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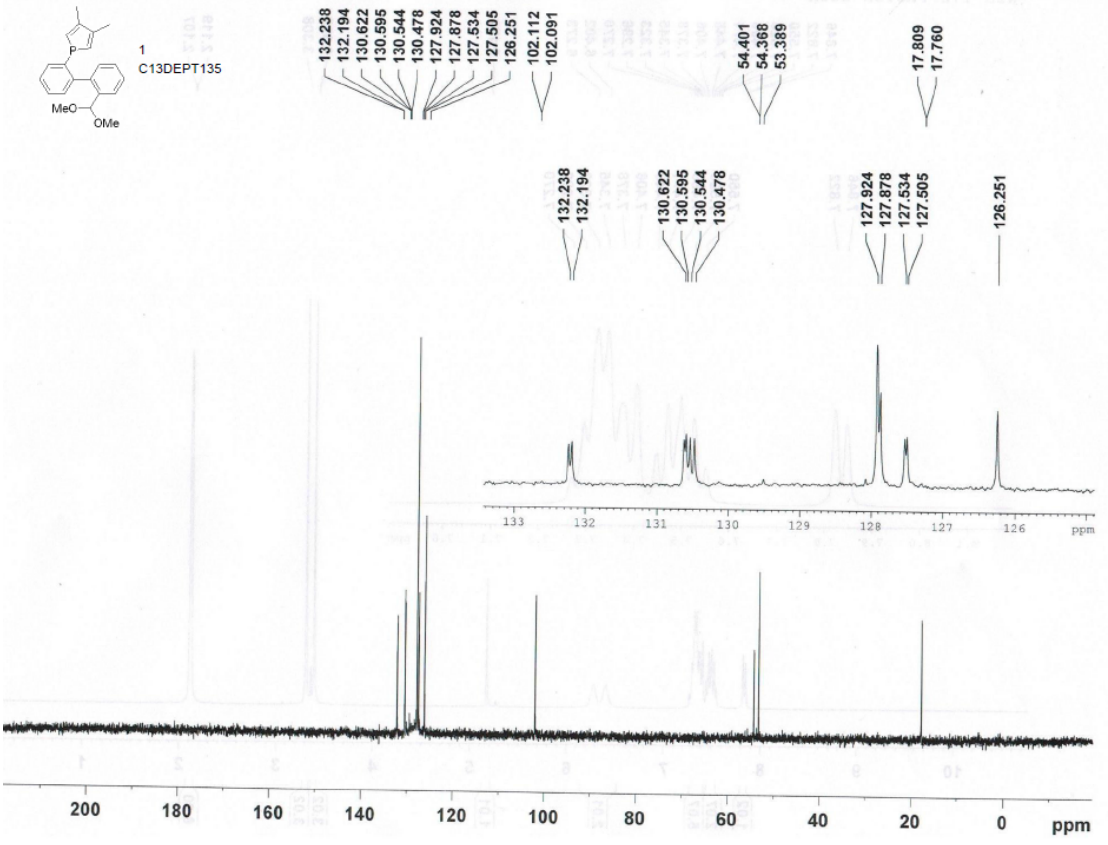
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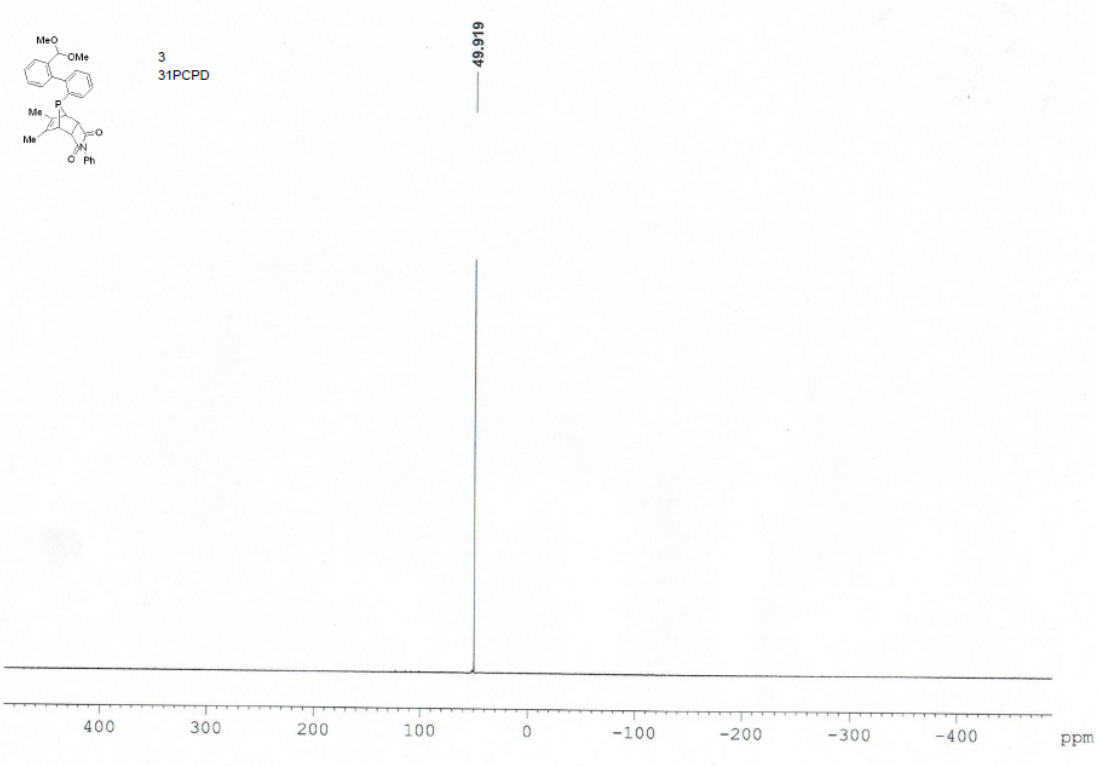
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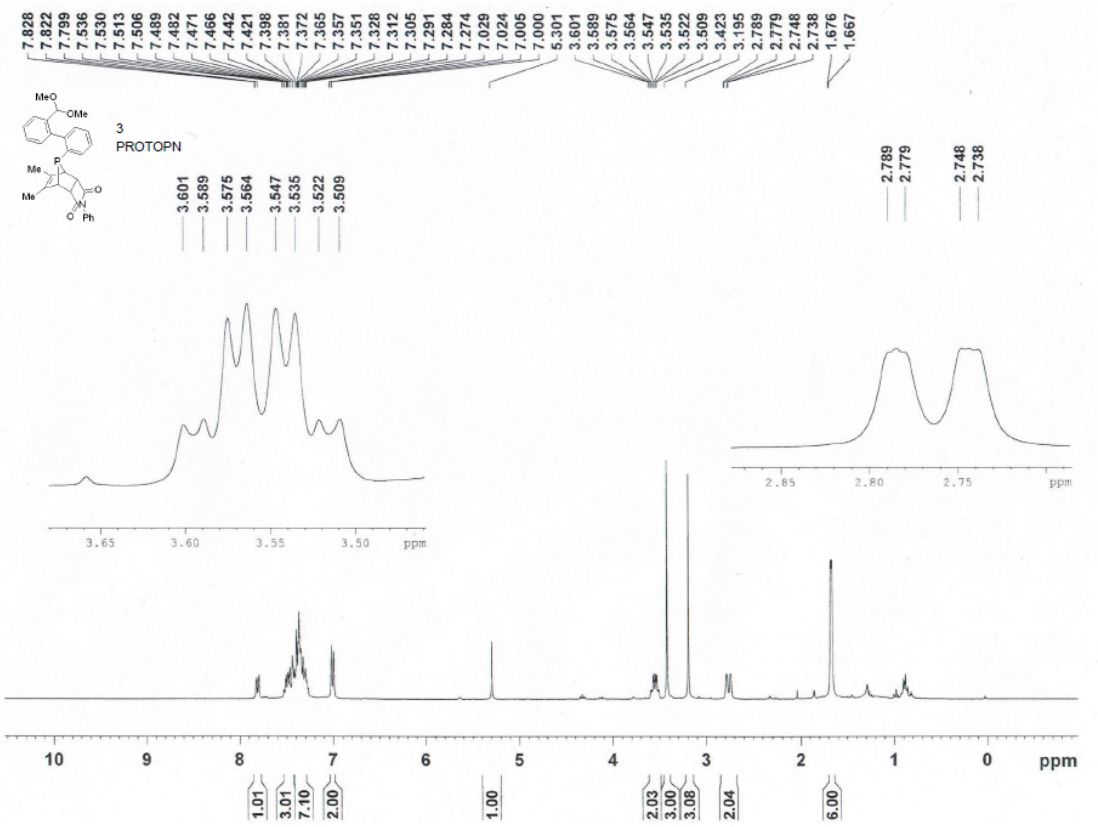
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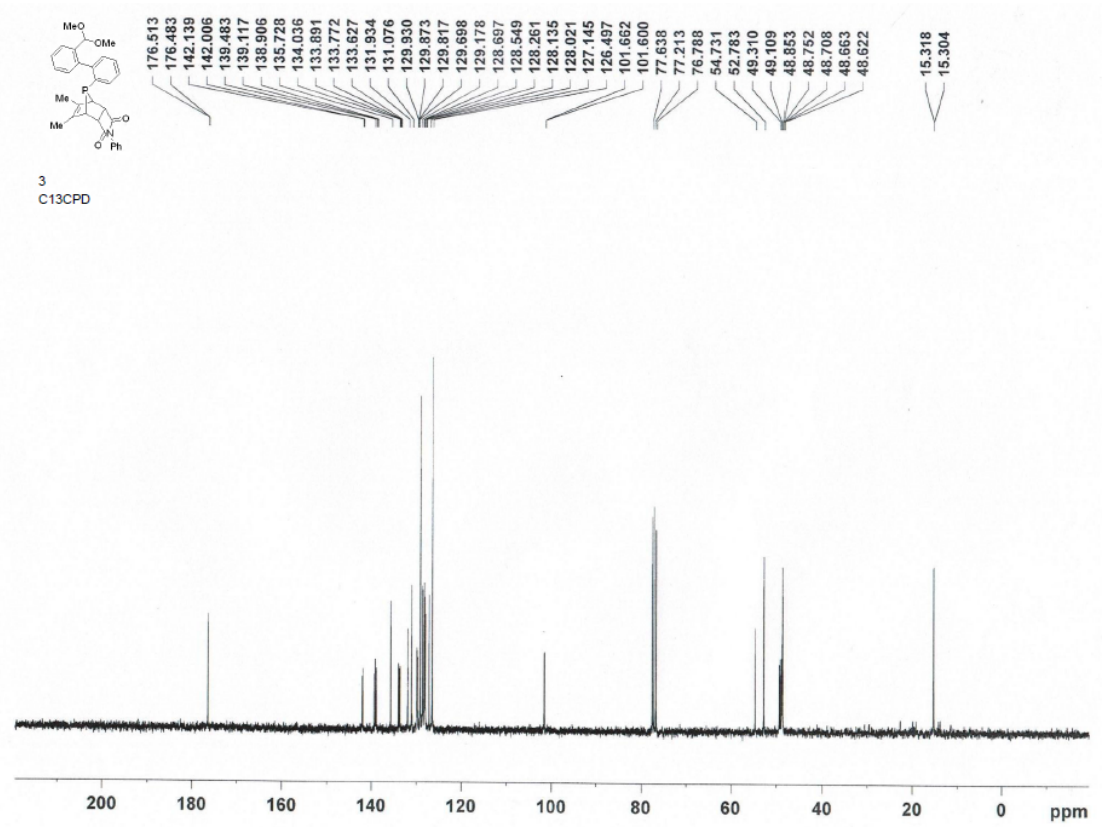
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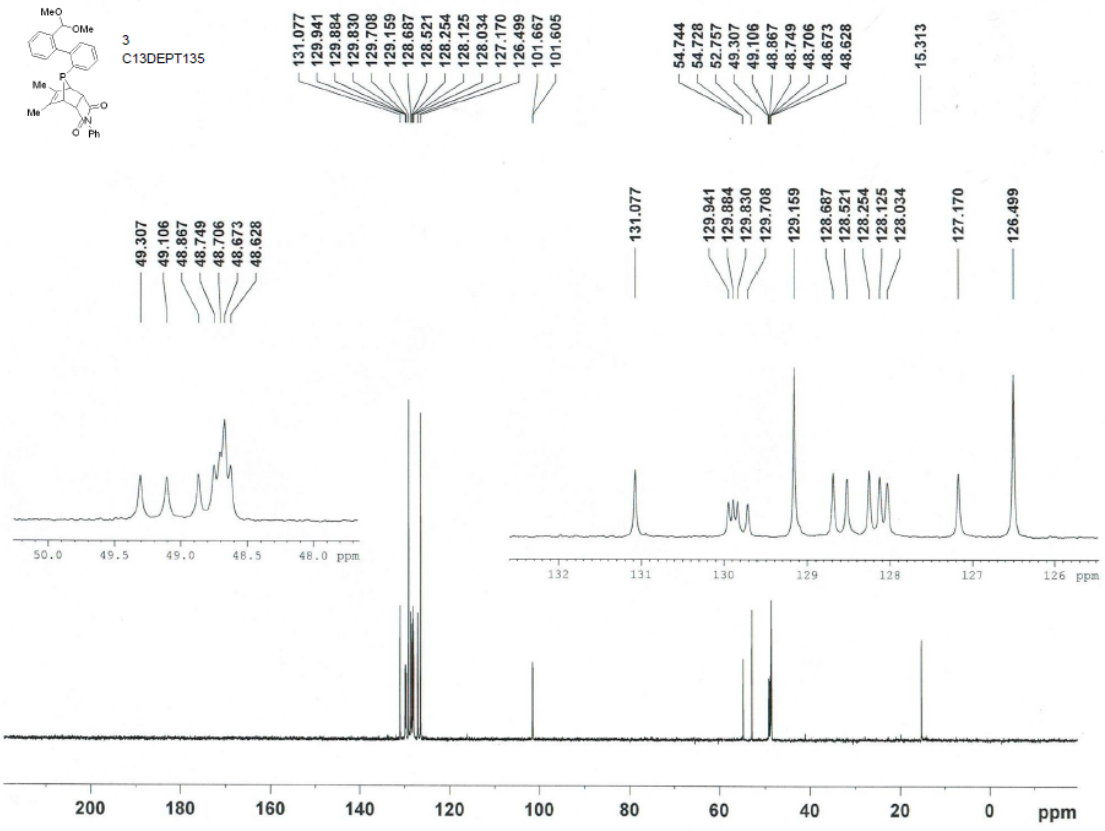
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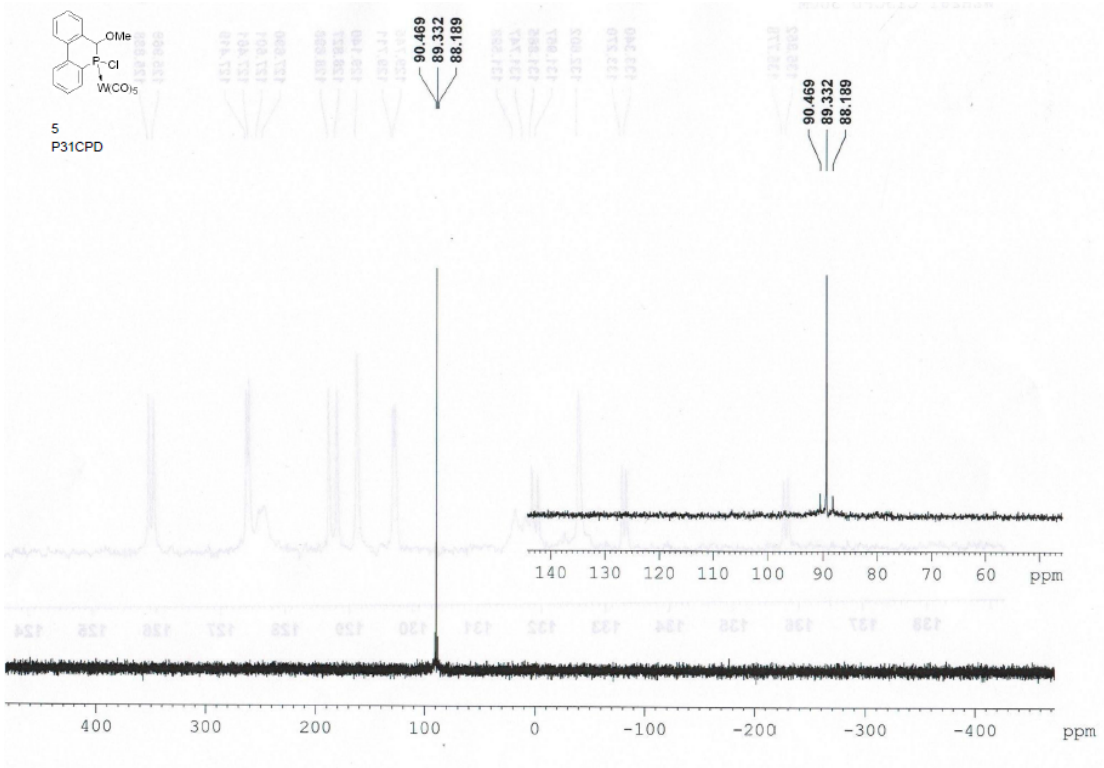
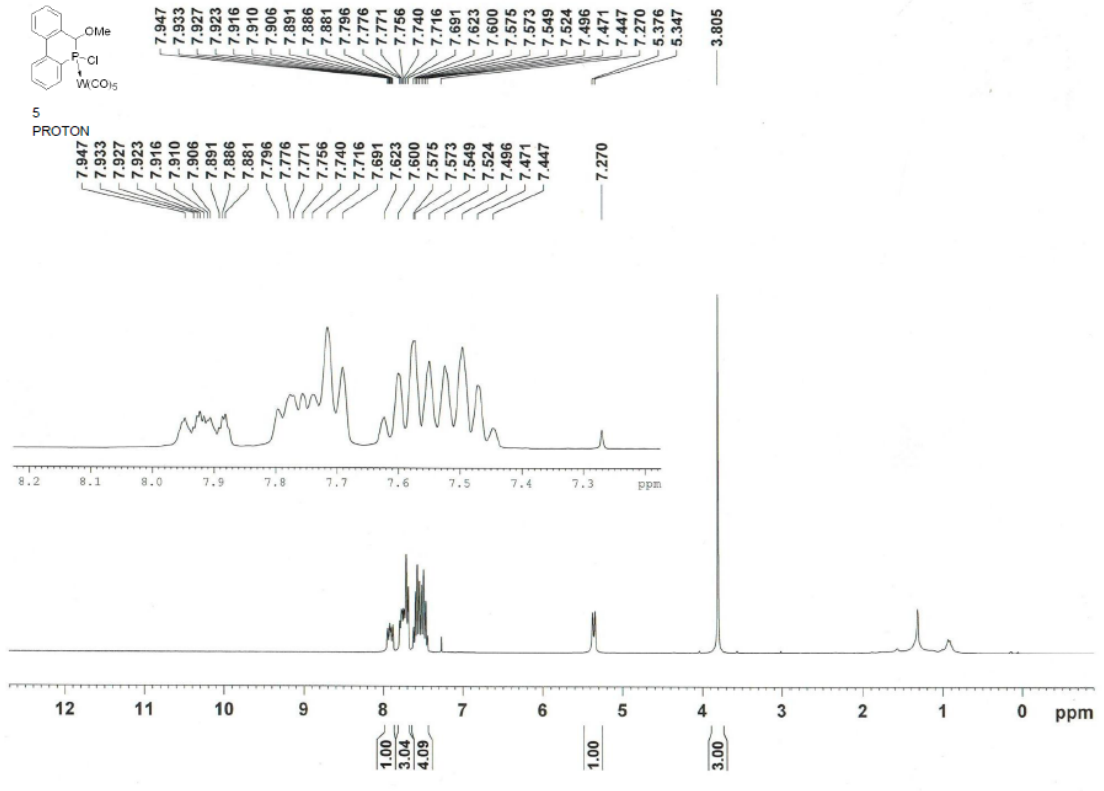
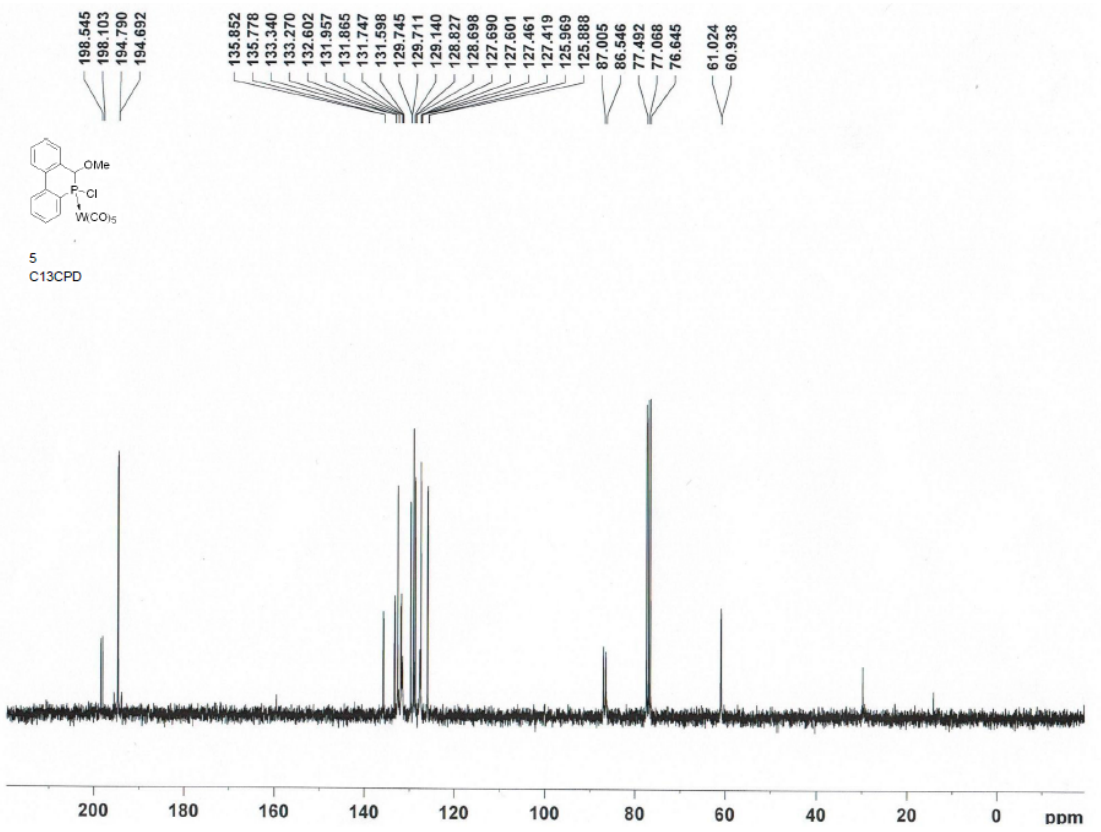
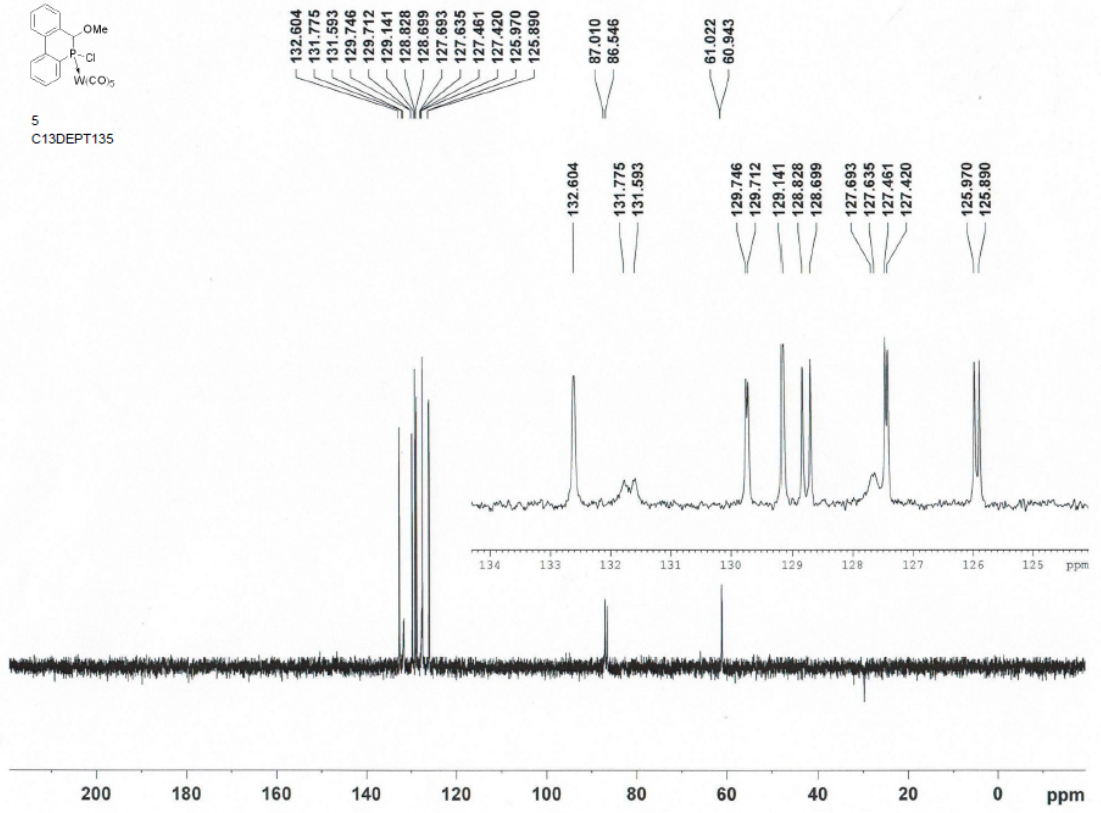
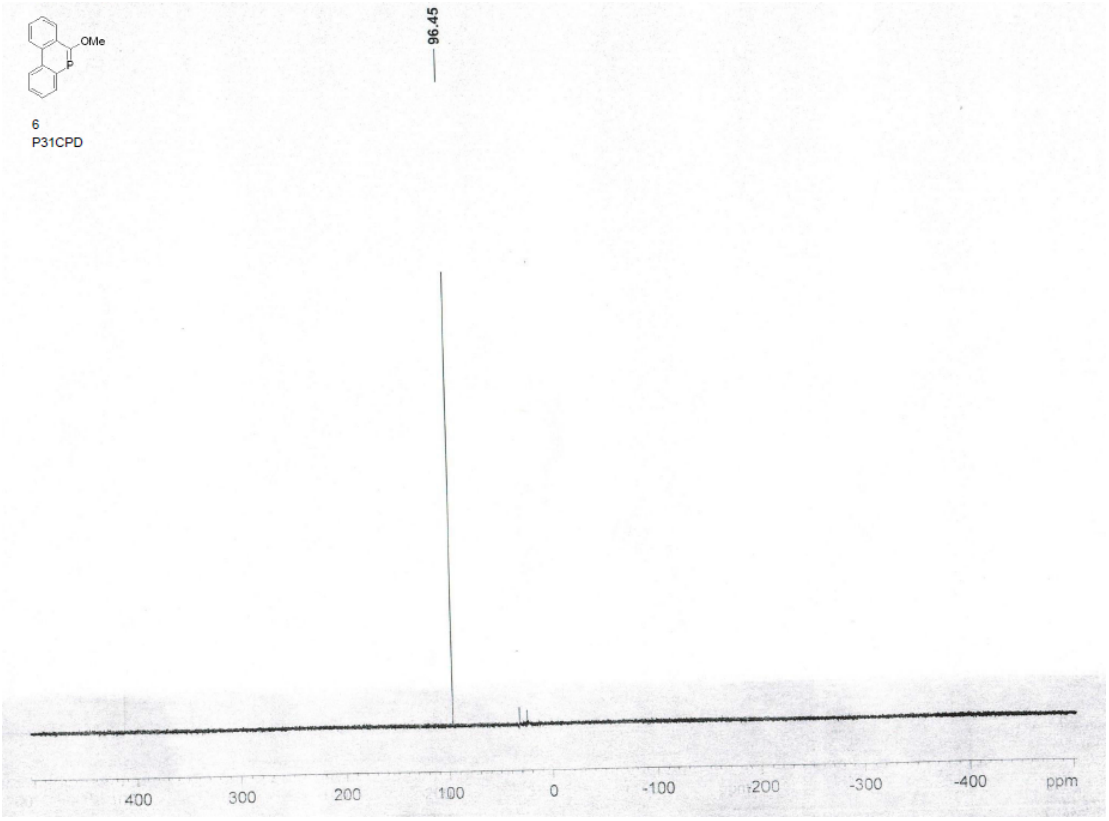
101.605
54.744
54.728
52.757
49.307
49.106
48.867
48.749
48.706
48.673
48.628
15.313
49.307
49.106
48.867
48.749
48.706
48.673
48.628
50.0
49.5
49.0
48.5
48.0 ppm
131.077
129.941
129.884
129.830
129.708
129.159
128.687
128.521
128.254
128.125
128.034
127.170
126.499
132
131
130
129
128
127
126 ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

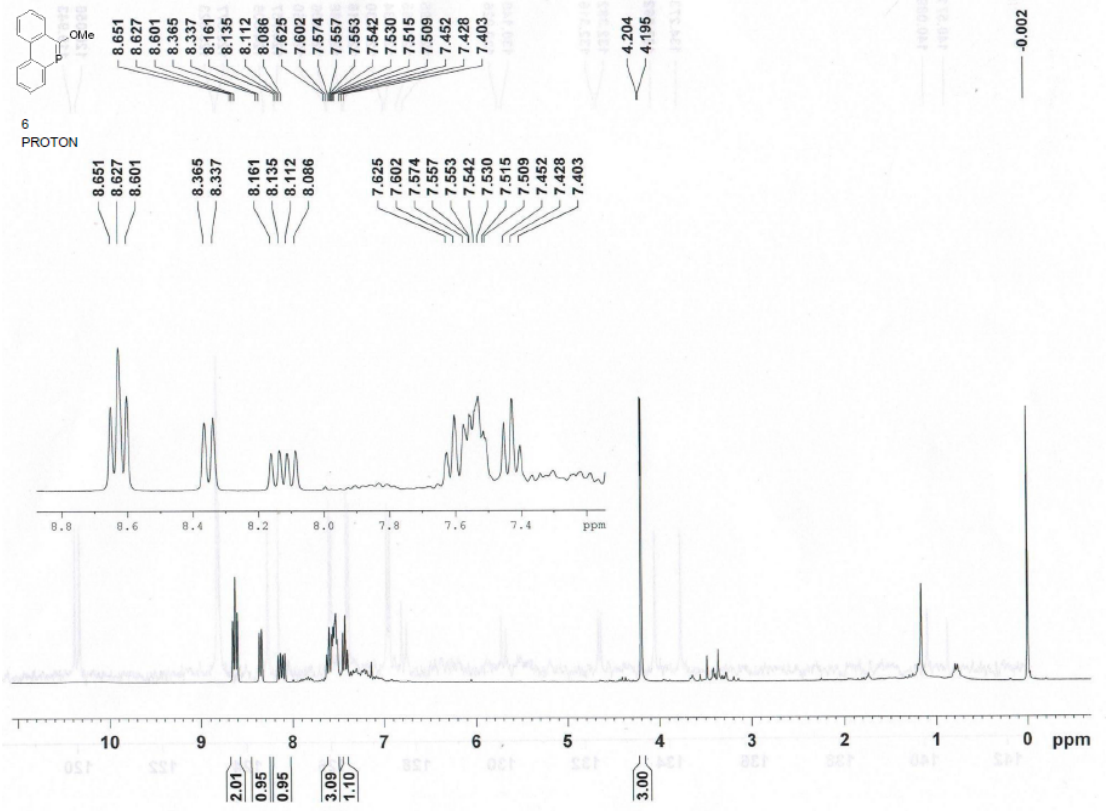

OMe
P
Cl
W(CO)5
5
P31CPD
90.469
89.332
88.189
140 130 120 110 100 90 80 70 60 ppm
400 300 200 100 0 -100 -200 -300 -400 ppm

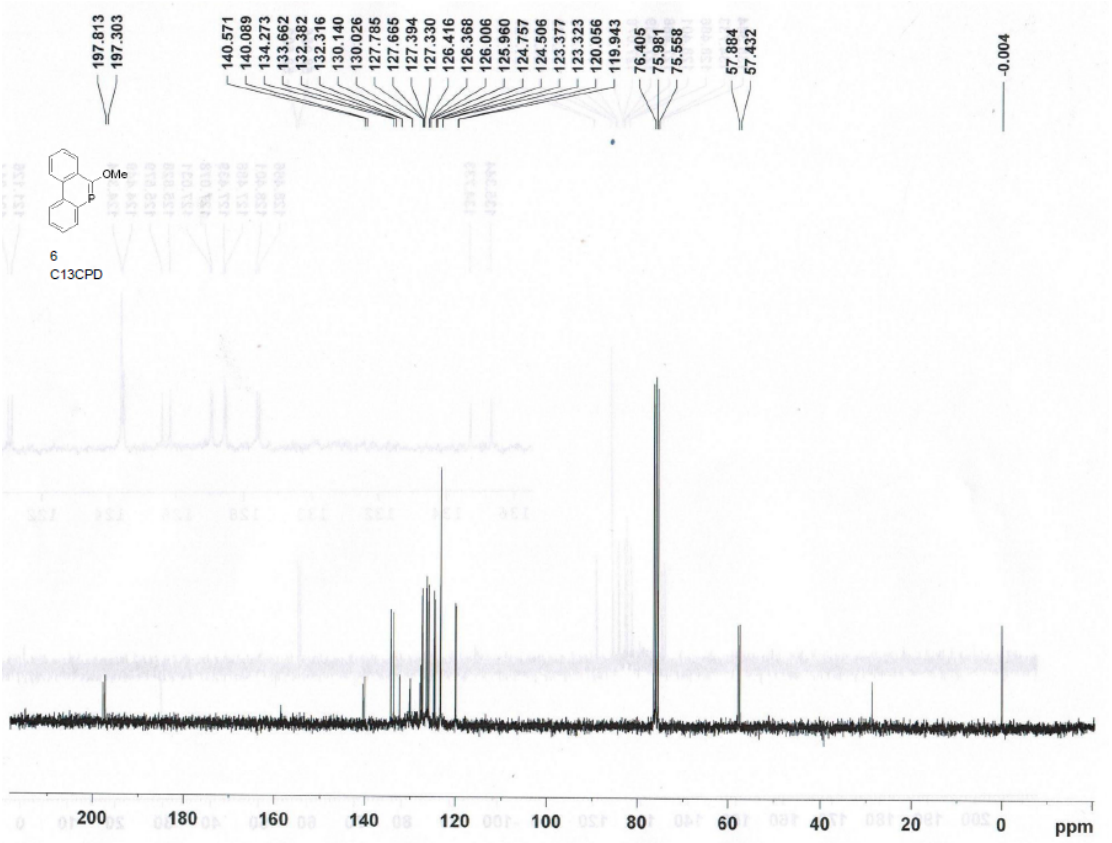

OMe
P
Cl
W(CO)5
5
PROTON
7.947
7.933
7.927
7.923
7.916
7.910
7.906
7.891
7.886
7.881
7.796
7.776
7.771
7.756
7.740
7.716
7.691
7.623
7.600
7.575
7.573
7.549
7.524
7.496
7.471
7.447
7.270
5.376
5.347
3.805
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
3.04
4.09
1.00
3.00

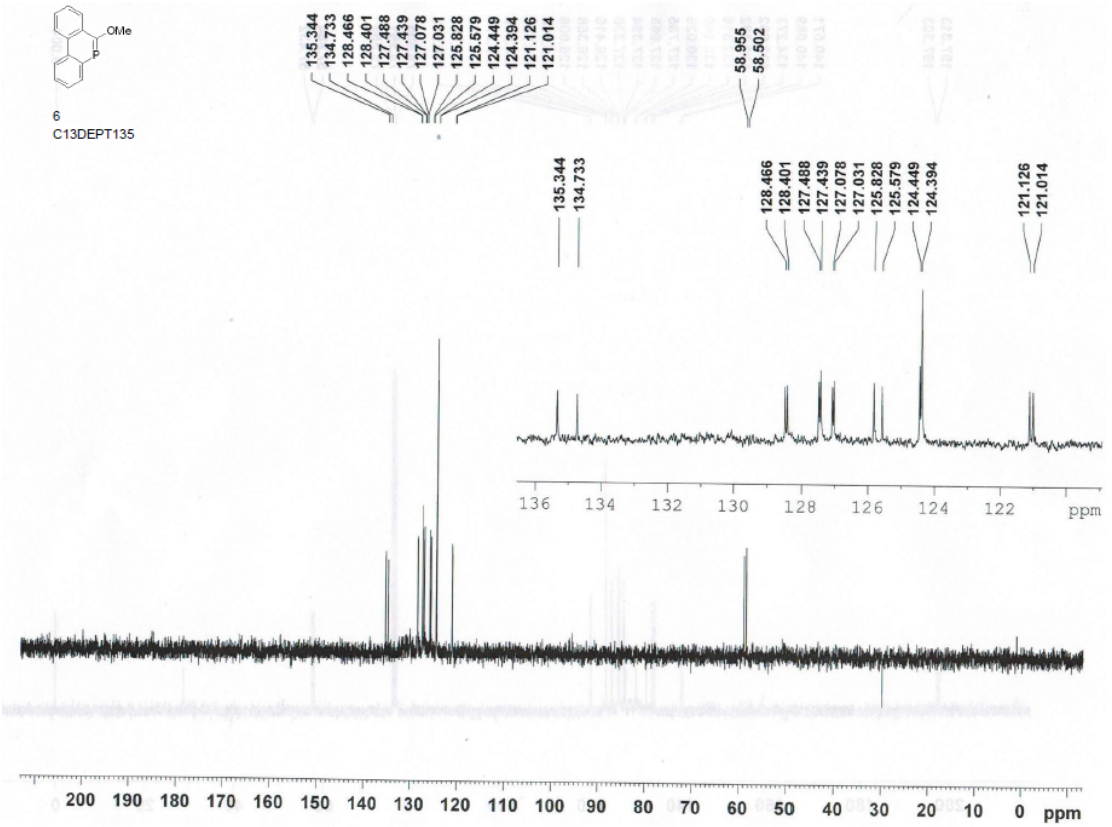

198.545
198.103
194.790
194.692
135.852
135.778
133.340
133.270
132.602
131.957
131.865
131.747
131.598
129.745
129.711
129.140
128.827
128.698
127.690
127.601
127.461
127.419
125.969
125.888
87.005
86.546
77.492
77.068
76.645
61.024
60.938
OMe
P
Cl
W(CO)5
5
C13CPD
200
180
160
140
120
100
80
60
40
20
0
ppm

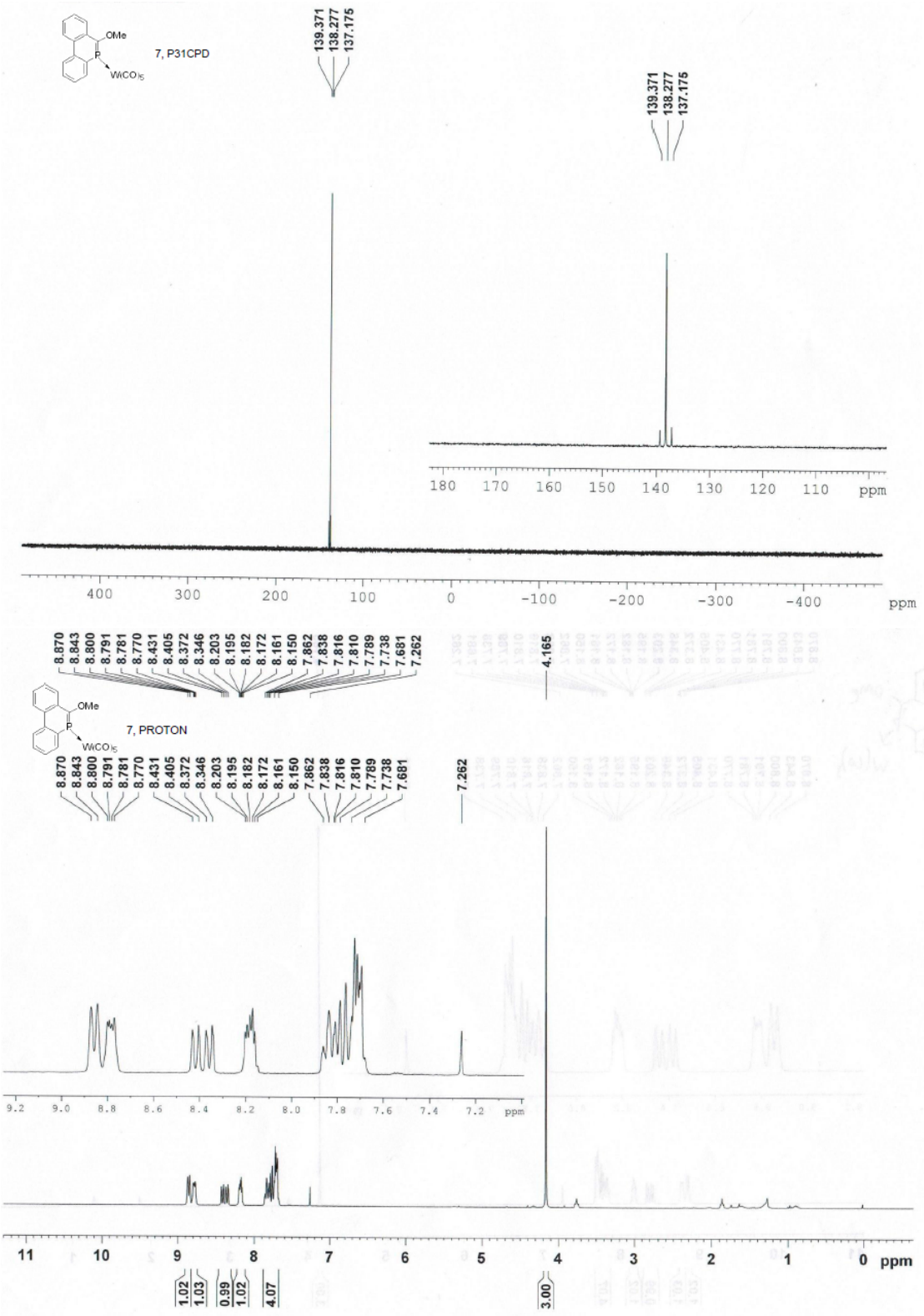

OMe
P
Cl
W(CO)5
5
C13DEPT135
132.604
131.775
131.593
129.746
129.712
129.141
128.828
128.699
127.693
127.635
127.461
127.420
125.970
125.890
87.010
86.546
61.022
60.943
134
133
132
131
130
129
128
127
126
125
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

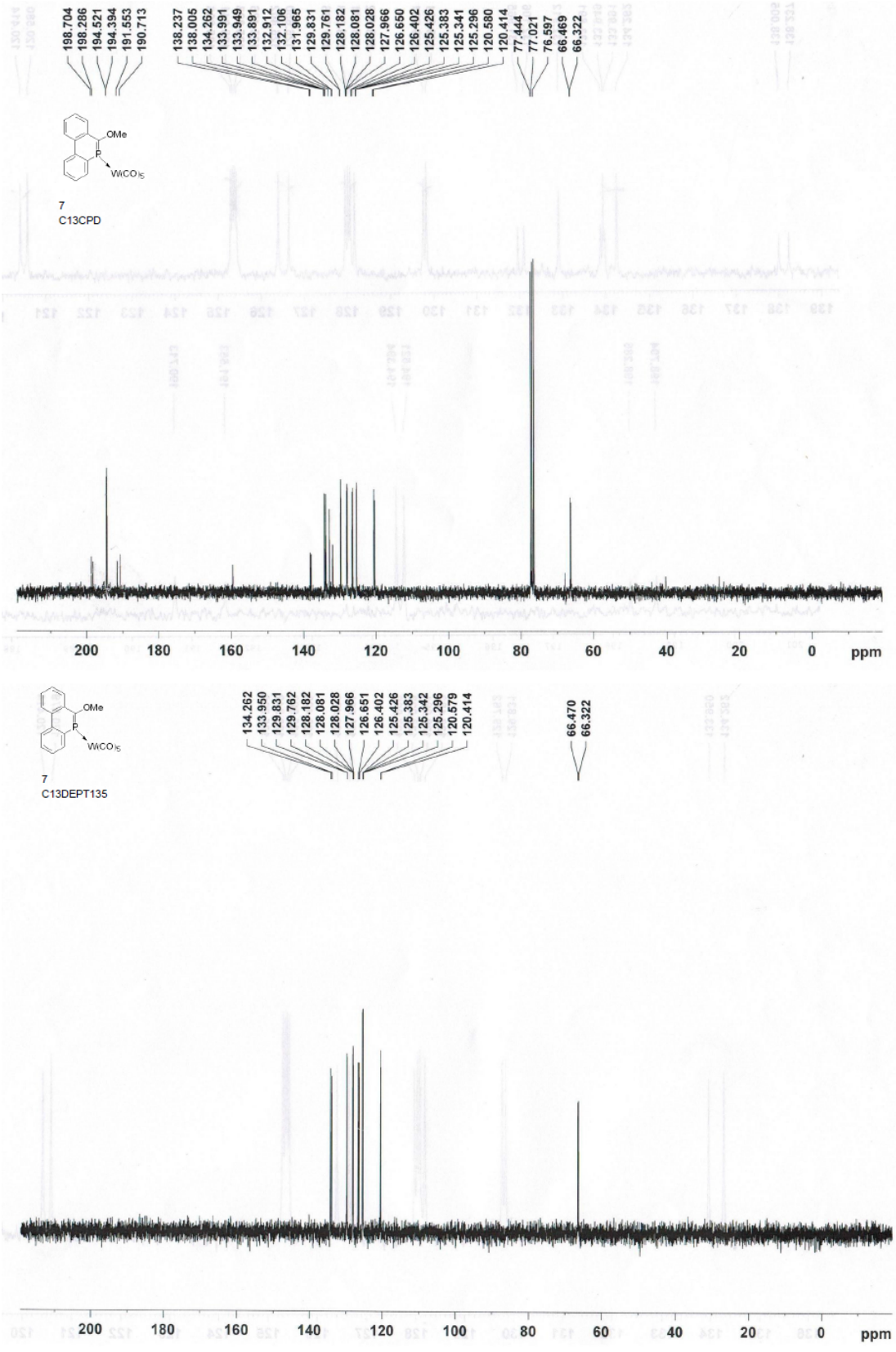

OMe
P
96.45
6
P31CPD
400
300
200
100
0
-100
-200
-300
-400
ppm


OMe
P
8.651
8.627
8.601
8.365
8.337
8.161
8.135
8.112
8.086
7.625
7.602
7.574
7.557
7.553
7.542
7.530
7.515
7.509
7.452
7.428
7.403
4.204
4.195
-0.002
6
PROTON
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
0.95
0.95
3.09
1.10
3.00


197.813
197.303
140.571
140.089
134.273
133.662
132.382
132.316
130.140
130.026
127.785
127.665
127.394
127.330
126.416
126.368
126.006
125.960
124.757
124.506
123.377
123.323
120.056
119.943
76.405
75.981
75.558
57.884
57.432
-0.004
OMe
P
6
C13CPD
200
180
160
140
120
100
80
60
40
20
0
ppm


OMe
P
6
C13DEPT135
135.344
134.733
128.466
128.401
127.488
127.439
127.078
127.031
125.828
125.579
124.449
124.394
121.126
121.014
58.955
58.502
136
134
132
130
128
126
124
122
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OMe
P
W(CO)5
7, P31CPD
139.371
138.277
137.175
180 170 160 150 140 130 120 110 ppm
400 300 200 100 0 -100 -200 -300 -400 ppm
8.870
8.843
8.800
8.791
8.781
8.770
8.431
8.405
8.372
8.346
8.203
8.195
8.182
8.172
8.161
8.150
7.862
7.838
7.816
7.810
7.789
7.738
7.681
7.262
4.165
7, PROTON
9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.02
1.03
0.99
1.02
4.07
3.00



Crystallographic Information of 5 and 7

The crystal data of 5 have been deposited in CCDC with number 1026163.

Summary of Data CCDC 1026163

Compound Name:
Formula: C19 H12 Cl1 O6 P1 W1
Unit Cell Parameters: a 12.4704(7) b 11.0754(5) c 14.5549(6) P21/n

Table 1 Crystal data and structure refinement.

Empirical formula	$C_{19}H_{12}ClO_6PW$
Formula weight	586.56
Temperature/K	291.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.4704(7)
b/Å	11.0754(5)
c/Å	14.5549(6)
α/°	90.00
β/°	90.502(5)
γ/°	90.00
Volume/Å^3	2010.16(17)
Z	4
ρ_{calc}g/cm^3	1.938
μ/mm^{-1}	5.991
F(000)	1120.0
Crystal size/mm^3	0.22 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.54 to 52.74
Index ranges	$-10 \leqslant h \leqslant 15$, $-13 \leqslant k \leqslant 13$, $-17 \leqslant l \leqslant 18$
Reflections collected	9588
Independent reflections	4099 [R_{int} = 0.0329, R_{sigma} = 0.0470]
Data/restraints/parameters	4099/0/254
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ(I)]	R_1 = 0.0332, wR_2 = 0.0616
Final R indexes [all data]	R_1 = 0.0482, wR_2 = 0.0679
Largest diff. peak/hole / e Å^{-3}	1.41/-0.76

The crystal data of 7 have been deposited in CCDC with number 1025472.
Summary of Data CCDC 1025472

Compound Name:
Formula: C19 H11 O6 P1 W1
Unit Cell Parameters: a 11.5815(7) b 13.2137(7) c 14.4201(10) P-1

Table 2 Crystal data and structure refinement.

Empirical formula	$C_{38}H_{22}O_{12}P_2W_2$
Formula weight	1100.20
Temperature/K	291.15
Crystal system	triclinic
Space group	P-1
a/Å	11.5815(7)
b/Å	13.2137(7)
c/Å	14.4201(10)
α/°	63.056(6)
β/°	74.408(5)
γ/°	84.555(5)
Volume/Å^3	1893.91(19)
Z	2
ρ_{calc}g/cm^3	1.929
μ/mm^{-1}	6.216
F(000)	1048.0
Crystal size/mm^3	0.22 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.26 to 52.74
Index ranges	$-14 \leqslant h \leqslant 14$, $-15 \leqslant k \leqslant 16$, $-16 \leqslant l \leqslant 18$
Reflections collected	15675
Independent reflections	7707 [R_{int} = 0.0419, R_{sigma} = 0.0673]
Data/restraints/parameters	7707/0/490
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ(I)]	R_1 = 0.0741, wR_2 = 0.1825
Final R indexes [all data]	R_1 = 0.1055, wR_2 = 0.2109
Largest diff. peak/hole / e Å^{-3}	5.90/-1.68