Electronic Supplementary Material (ESI) for Dalton Trans
This journal is © The Royal Society of Chemistry 2014

Supporting Information

New Library of Arsine, Stibine-Stablied *N*-heterocyclic Carbene Palladium Complexes: Synthesis, Structures and Activities in C–C and C–N Coupling Reactions

Jin Yang,[a] Pinhua Li,[a] Yicheng Zhang,[a] and Lei Wang[a,b,*]

[a] *Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P R China*
Tel: + 86-561-3802-069 Fax: + 86-561-3090-518 E-mail: leiwang@chnu.edu.cn

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P R China*

Table of Contents for Supporting Information

Table S1 Crystallographic data for complexes **1a**−**1d** and **2a**−**2d**

Compound	**1a**	**1b**•CH_2Cl_2	(**1c**)$_4$•CH_2Cl_2	(**1d**)$_2$•CH_2Cl_2
formula	$C_{39}H_{39}AsCl_2N_2Pd$	$C_{40}H_{41}Cl_4N_2PdSb$	$C_{181}H_{206}As_4Cl_{10}N_8Pd_4$	$C_{91}H_{104}Cl_6N_4Pd_2Sb_2$
fw	787.94	919.70	3573.32	1922.78
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*	*C*2/*c*
a /Å	17.556(7)	19.8365(19)	24.870(6)	31.143(6)
b /Å	13.840(6)	13.9429(13)	19.199(5)	13.853(3)
c /Å	15.138(6)	14.4872(14)	18.773(4)	23.658(5)
□ α /deg	90.00	90.00	90.00	90.00
□ β /deg	92.799(7)	91.9250(10)	101.939(5)	114.411(3)
□ γ /deg	90.00	90.00	90.00	90.00
V /Å^3	3674(3)	4004.6(7)	8770(3)	9294(3)
Z	4	4	2	4
D_{calc}/g cm^{-3}	1.425	1.525	1.353	1.374
F(000)	1600	1840	3668	3896
μ /mm^{-1}	1.573	1.420	1.356	1.171
GOF	1.049	1.030	0.997	1.016
reflections collected	17968	19934	44371	23266
independent reflections (R_{int})	6452 (0.0551)	7054 (0.0210)	15414 (0.0967)	8158 (0.0248)
observed reflections [$I > 2\sigma(I)$]	4825	6085	7894	6540
refined parameters	412	449	872	495
$R1$ [$I > 2\sigma(I)$]	0.0495	0.0277	0.0525	0.0308
$wR2$ (all data)	0.1522	0.0687	0.1352	0.0765

Compound	**2a**	**(2b)**•CH_2Cl_2	**2c**•0.5CH_2Cl_2	**2d**
formula	$C_{39}H_{41}AsCl_2N_2Pd$	$C_{40}H_{43}Cl_4N_2PdSb$	$C_{45.5}H_{54}AsCl_3N_2Pd$	$C_{45}H_{53}Cl_2N_2PdSb$
fw	789.96	921.71	916.58	920.94
crystal system	monoclinic	monoclinic	monoclinic	hexagonal
space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*n*	$P\bar{6}5$
a /Å	17.317(6)	19.780(3)	10.684(4)	25.982(5)
b /Å	13.876(5)	13.9846(17)	12.179(5)	25.982(5)
c /Å	15.020(5)	14.4282(18)	35.633(13)	12.486(2)
□ α /deg	90.00	90.00	90.00	90.00
□ β /deg	92.337(5)	92.037(2)	93.220(6)	90.00
□ γ /deg	90.00	90.00	90.00	120.00
V /Å^3	3606(2)	3988.5(9)	4629(3)	7299(2)
Z	4	4	4	6
D_{calc}/g cm^{-3}	1.455	1.535	1.315	1.257
F(000)	1608	1848	1884	2808
μ /mm^{-1}	1.603	1.426	1.314	1.062
GOF	1.043	1.011	1.082	1.111
reflections collected	18014	19915	22942	36826
independent reflections (R_{int})	6327 (0.0262)	7009 (0.0196)	8110 (0.0300)	8505 (0.0312)
observed reflections [$I > 2\sigma(I)$]	6327	6052	7035	7827
refined parameters	400	449	468	457
$R1$ [$I > 2\sigma(I)$]	0.0297	0.0266	0.0348	0.0397
$wR2$ (all data)	0.0797	0.0730	0.0751	0.1028

Characterization data for the products

4-Methoxybiphenyl[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.51 (m, 4H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.87 (3H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

3-Methoxybiphenyl[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.32–7.29 (3H, m), 7.02 (d, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 8.4 Hz, 1H), 3.78 (3H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 138.5, 130.8, 130.6, 129.5, 128.6, 127.9, 126.9, 120.8, 111.1, 55.5.

2-Methoxybiphenyl[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.56 (m, 2H), 7.43–7.39 (m, 2H), 7.35–7.31 (m, 2H), 7.17–7.12 (m, 2H), 6.89–6.86 (m, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 142.7, 141.0, 129.7, 128.7, 127.4, 127.1, 119.6, 112.8, 112.6, 55.2.

2-Phenylpyridine[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60−8.58 (m, 1H), 7.90 (d, *J* = 7.2 Hz, 2H), 7.59−7.58 (2H, m), 7.39–7.35 (m, 2H), 7.32–7.28 (m, 1H), 7.10–7.07 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 149.5, 139.2, 136.6, 128.8, 128.6, 126.8, 121.9, 120.4.

3-Phenylpyridine[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (s, 1H,), 8.50−8.49 (m, 1H,), 7.78–7.76 (m, 1H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.40−7.36 (t, *J* = 7.2 Hz, 2H), 7.32–7.27 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 148.3, 137.8, 136.6, 134.3, 129.0, 128.1, 127.1, 123.5.

4-Methyl-*N*-phenylaniline[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (t, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.06–7.04 (m, 4H), 6.92 (t, *J* = 7.2 Hz, 1H), 5.64 (s, 1H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 140.2, 130.8, 129.8, 129.2, 120.2, 118.8, 116.7, 20.6.

4-Methoxy-*N*-phenylaniline[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (t, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.94–6.84 (m, 5H), 5.52 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1, 145.0, 135.6, 129.2, 122.1, 119.4, 115.5, 114.5, 55.5.

***N*-(4-Methylphenyl)-2,6-dimethylaniline**[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 6.8 Hz, 2H), 7.11 (d, *J* = 6.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.13 (s, 1H), 2.29 (s, 3H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 138.6, 135.4, 129.6, 128.4, 127.4, 125.3, 113.7, 20.4, 18.3.

***N*-(4-Methoxyphenyl)-2,6-dimethylaniline[2]**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 6.8 Hz, 2H), 7.11 (d, *J* = 6.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 8.0 Hz, 2H), 5.13 (s, 1H), 2.29 (s, 3H), 2.25 (s, 6H).

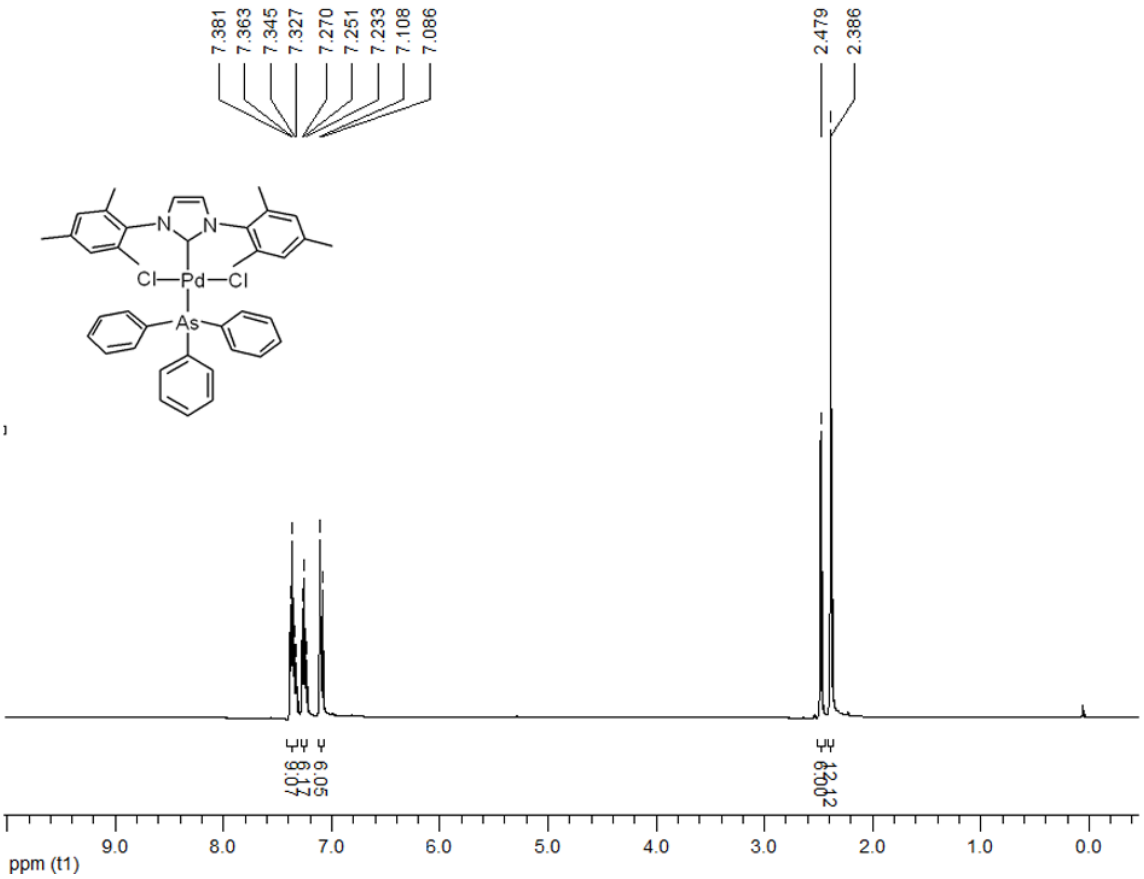
^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 140.1, 139.2, 134.9, 128.6, 125.0, 115.2, 114.7, 55.6, 18.3.

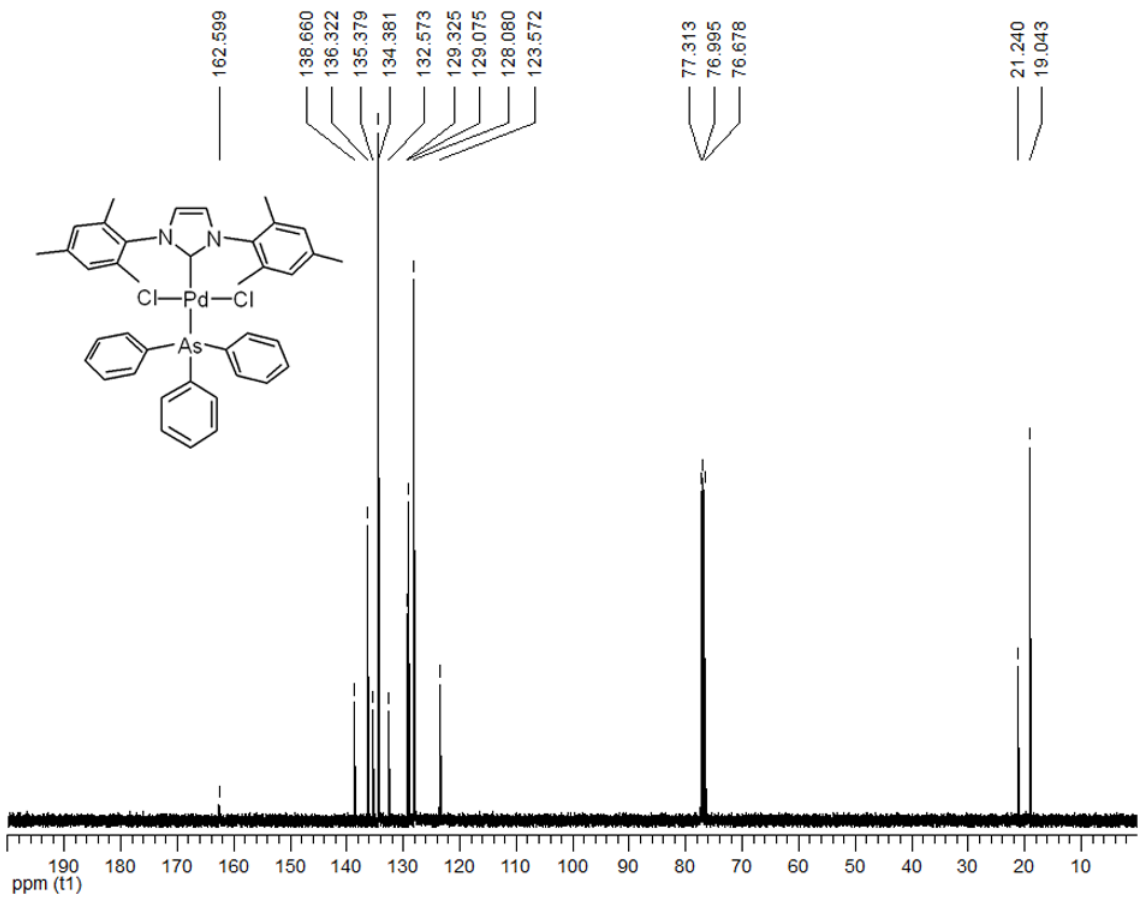
***N*-(2,6-Dimethylphenyl)naphthalen-2-amine[3]**

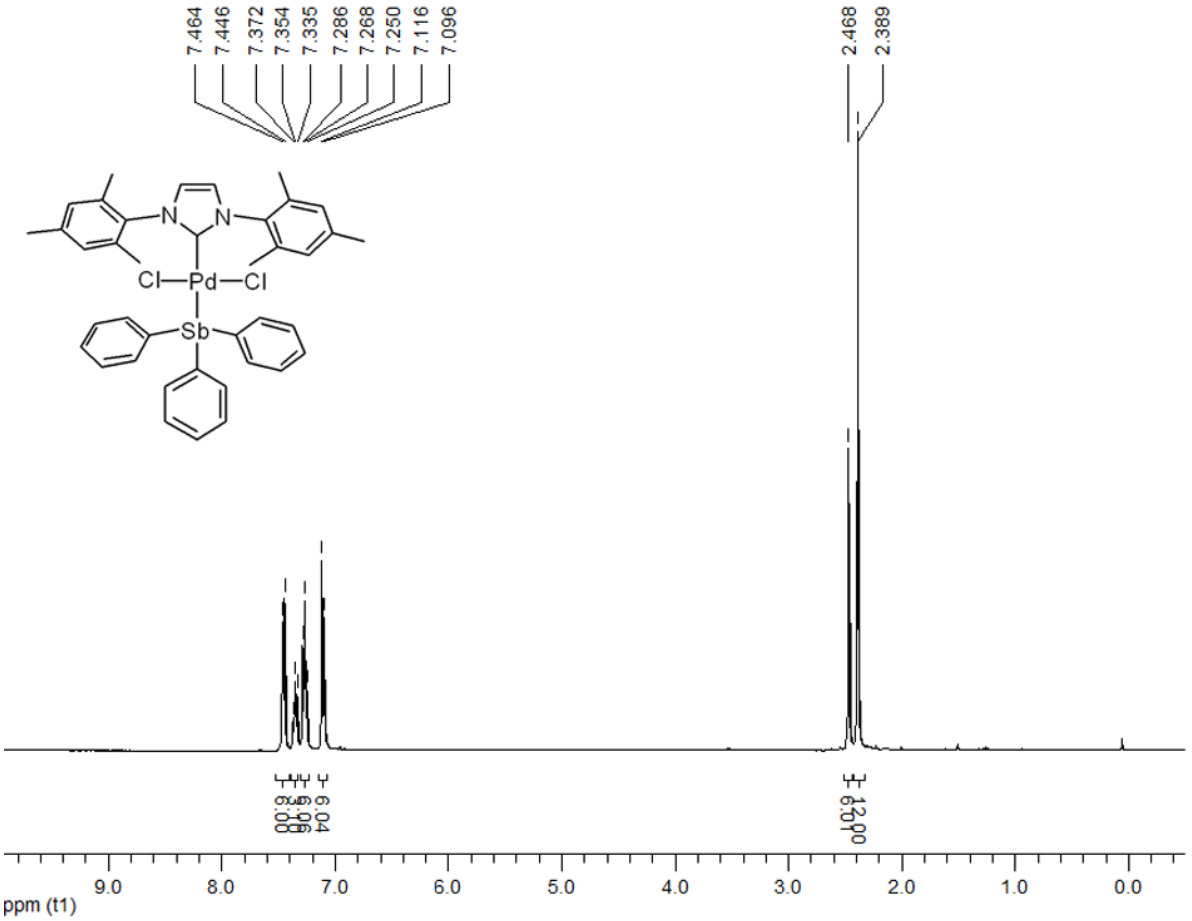
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.72 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.28–7.20 (m, 4H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.65 (s, 1H), 2.31 (s, 6H).

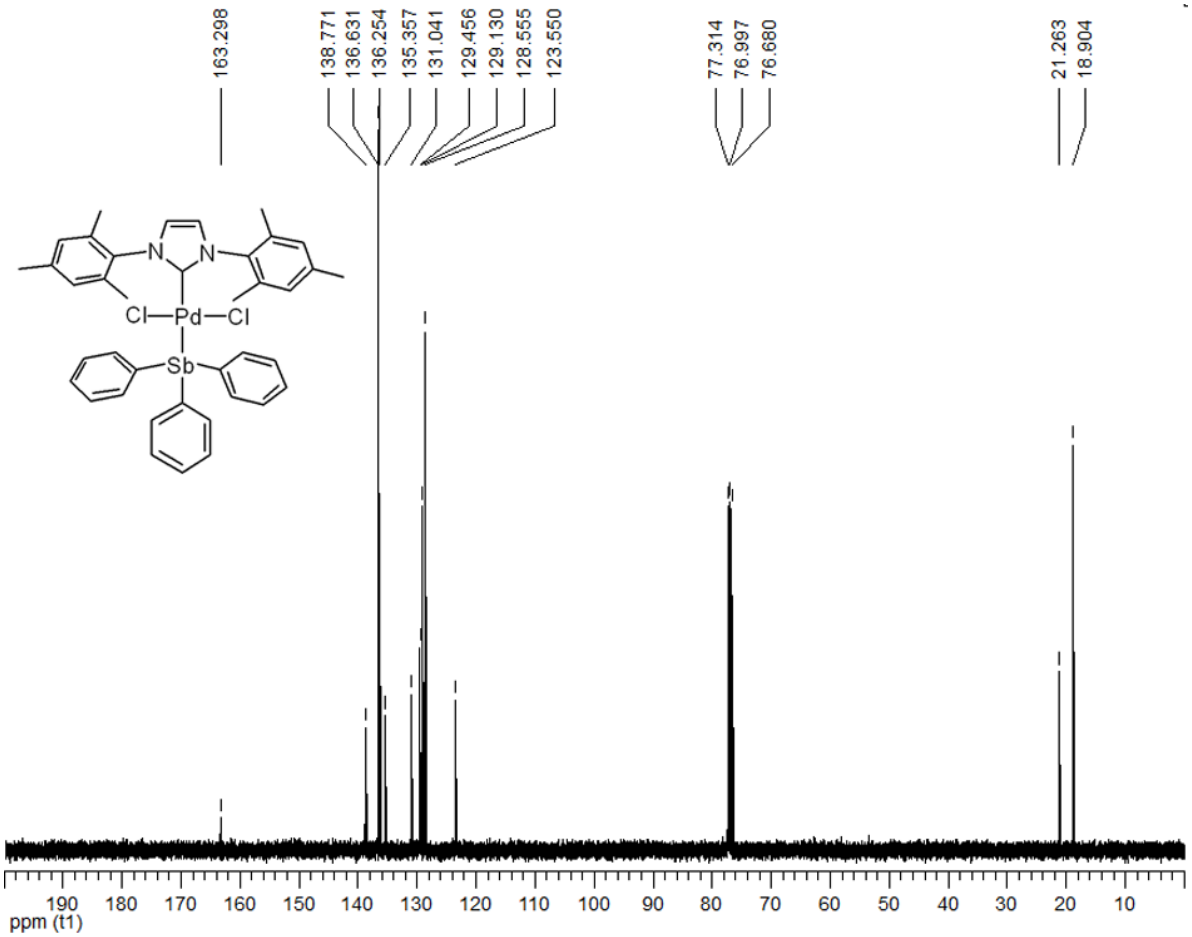
^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 137.8, 136.0, 134.9, 129.1, 128.6, 127.6, 126.3, 126.0, 126.0, 122.3, 117.6, 106.5, 18.3.

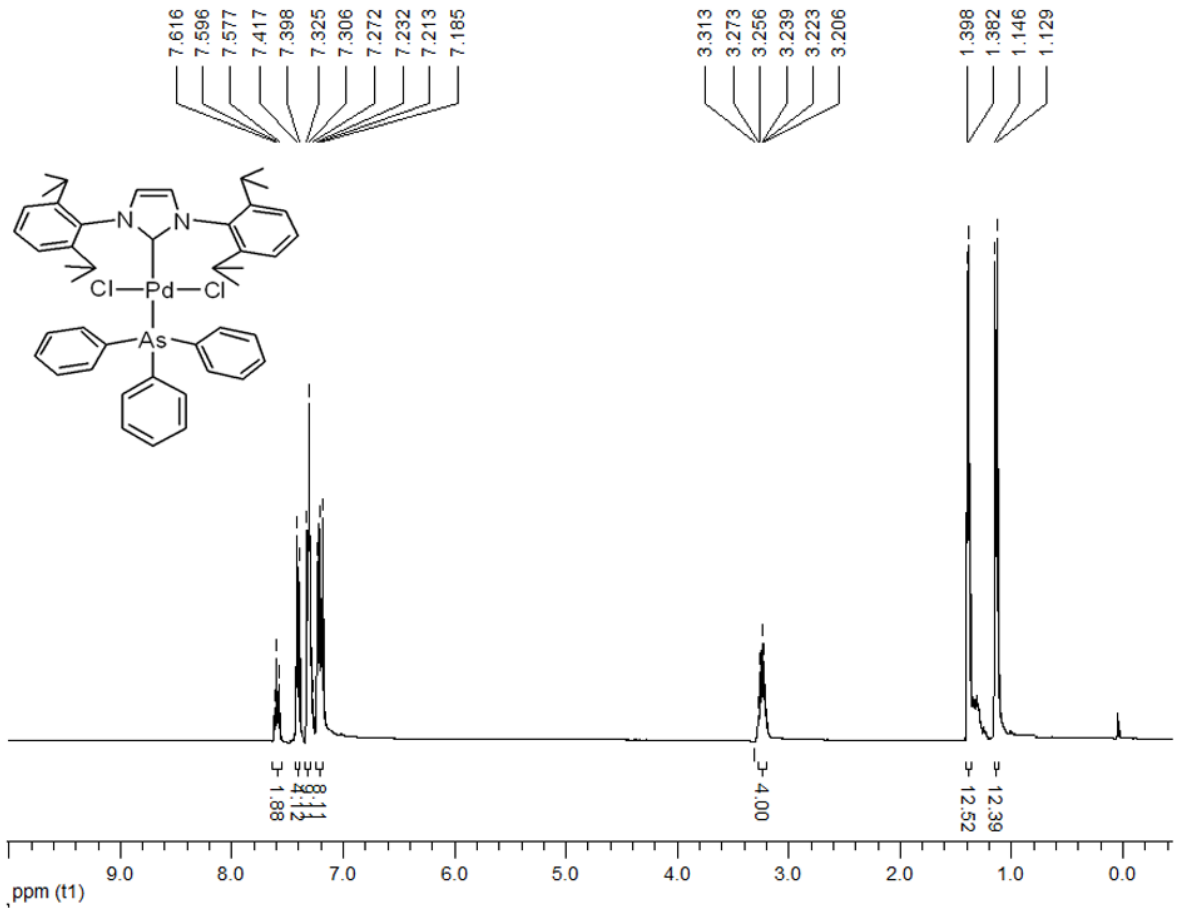
^{1}H NMR and ^{13}C NMR spectra

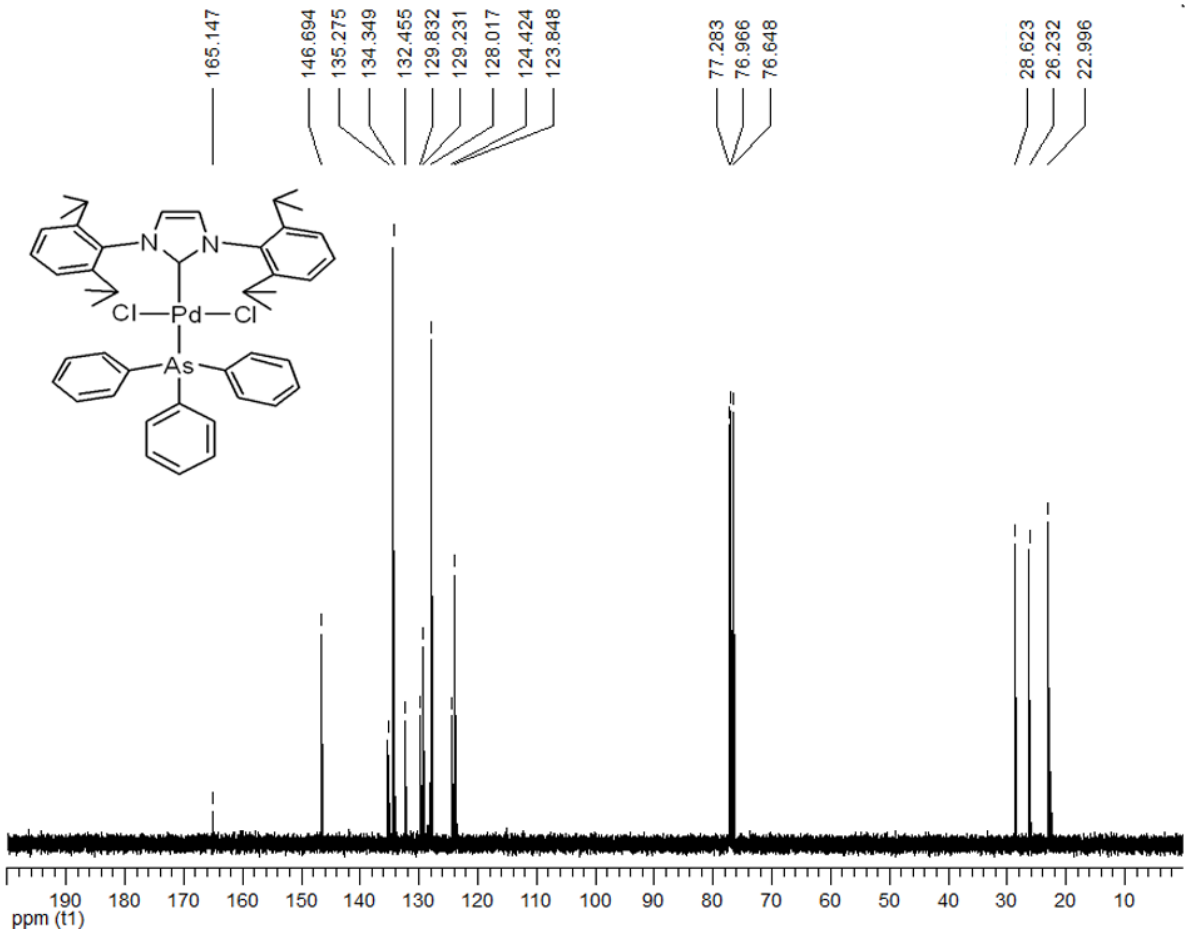


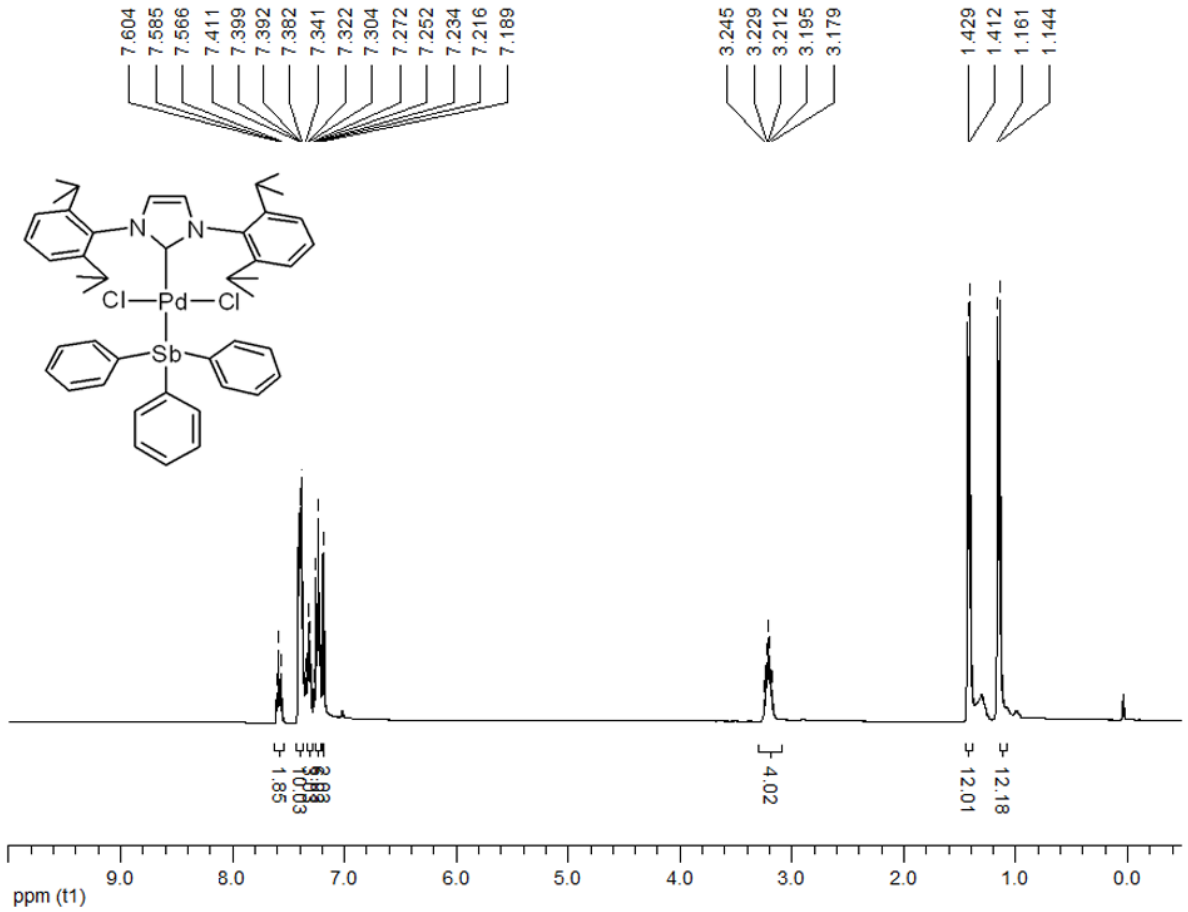


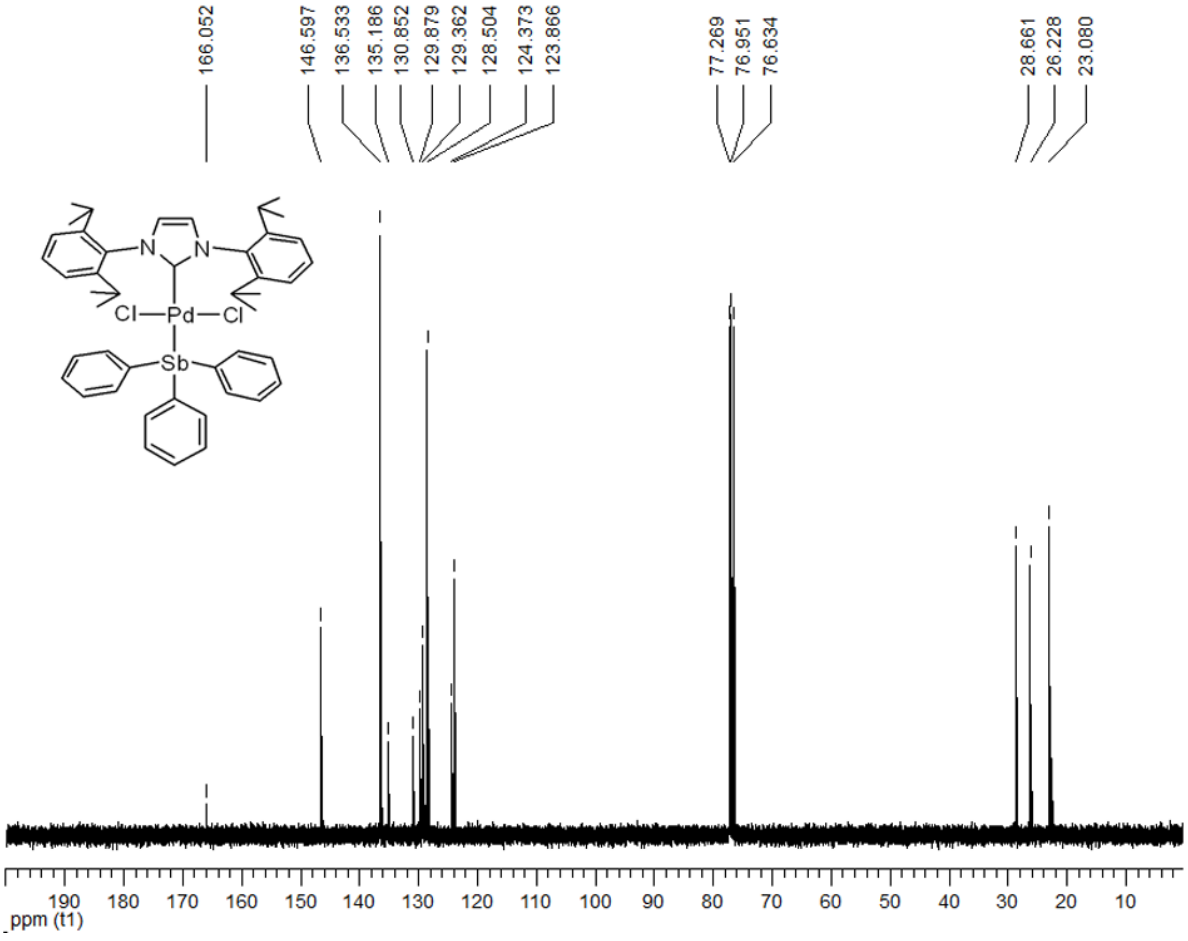

7.464
7.446
7.372
7.354
7.335
7.286
7.268
7.250
7.116
7.096
2.468
2.389
Cl—Pd—Cl
Sb
6.00
6.04
6.00
12.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

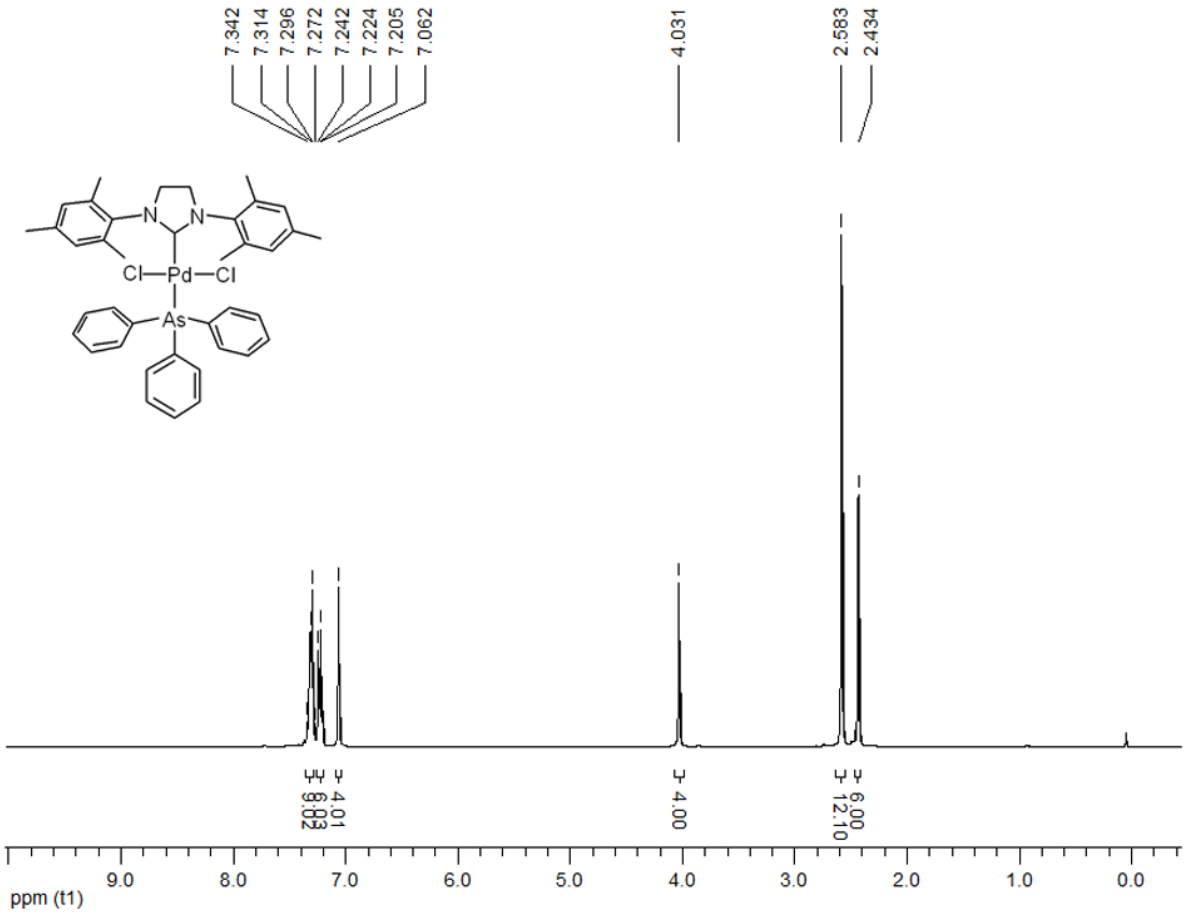

163.298
138.771
136.631
136.254
135.357
131.041
129.456
129.130
128.555
123.550
77.314
76.997
76.680
21.263
18.904
Cl—Pd—Cl
Sb
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

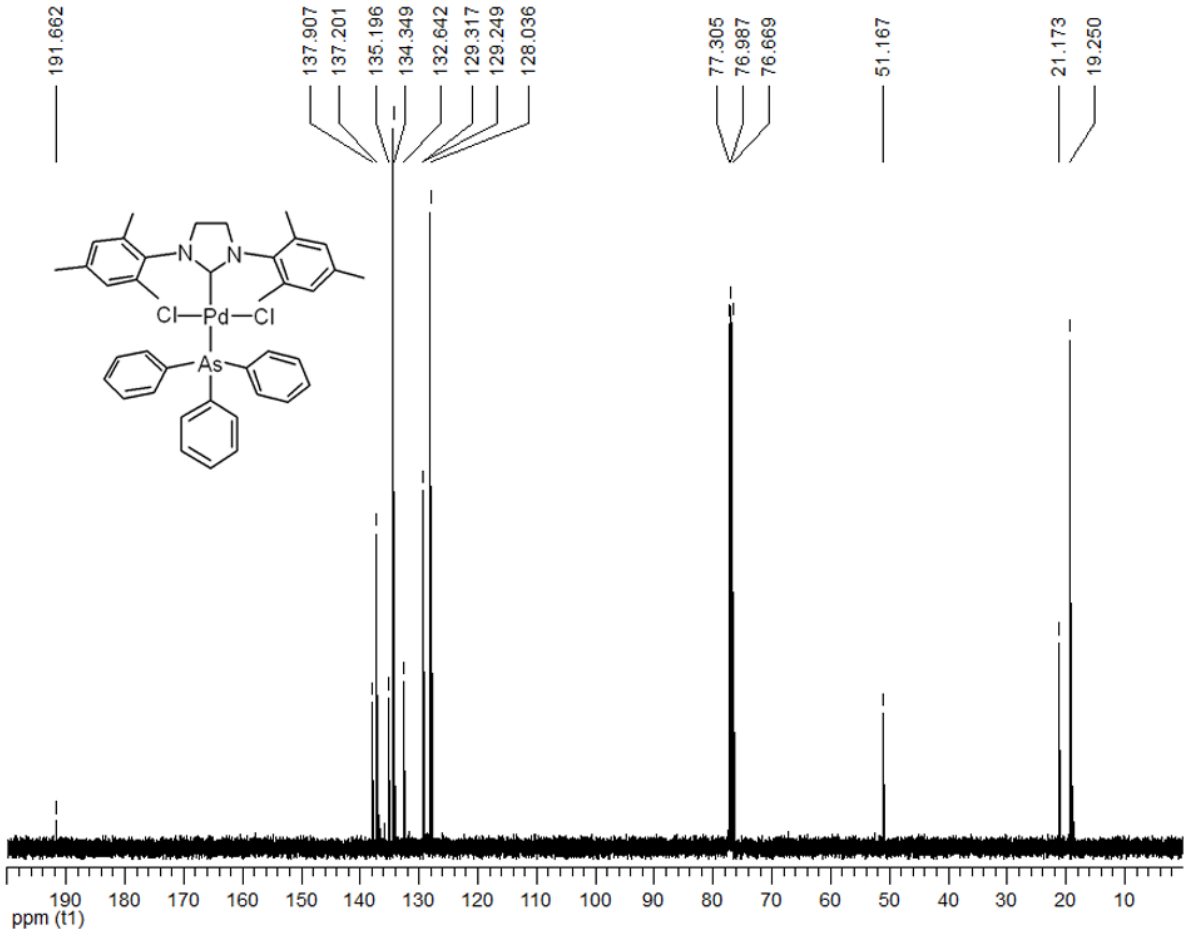

7.616
7.596
7.577
7.417
7.398
7.325
7.306
7.272
7.232
7.213
7.185
3.313
3.273
3.256
3.239
3.223
3.206
1.398
1.382
1.146
1.129
Cl—Pd—Cl
As
1.88
4.32
8.11
4.00
12.52
12.39
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

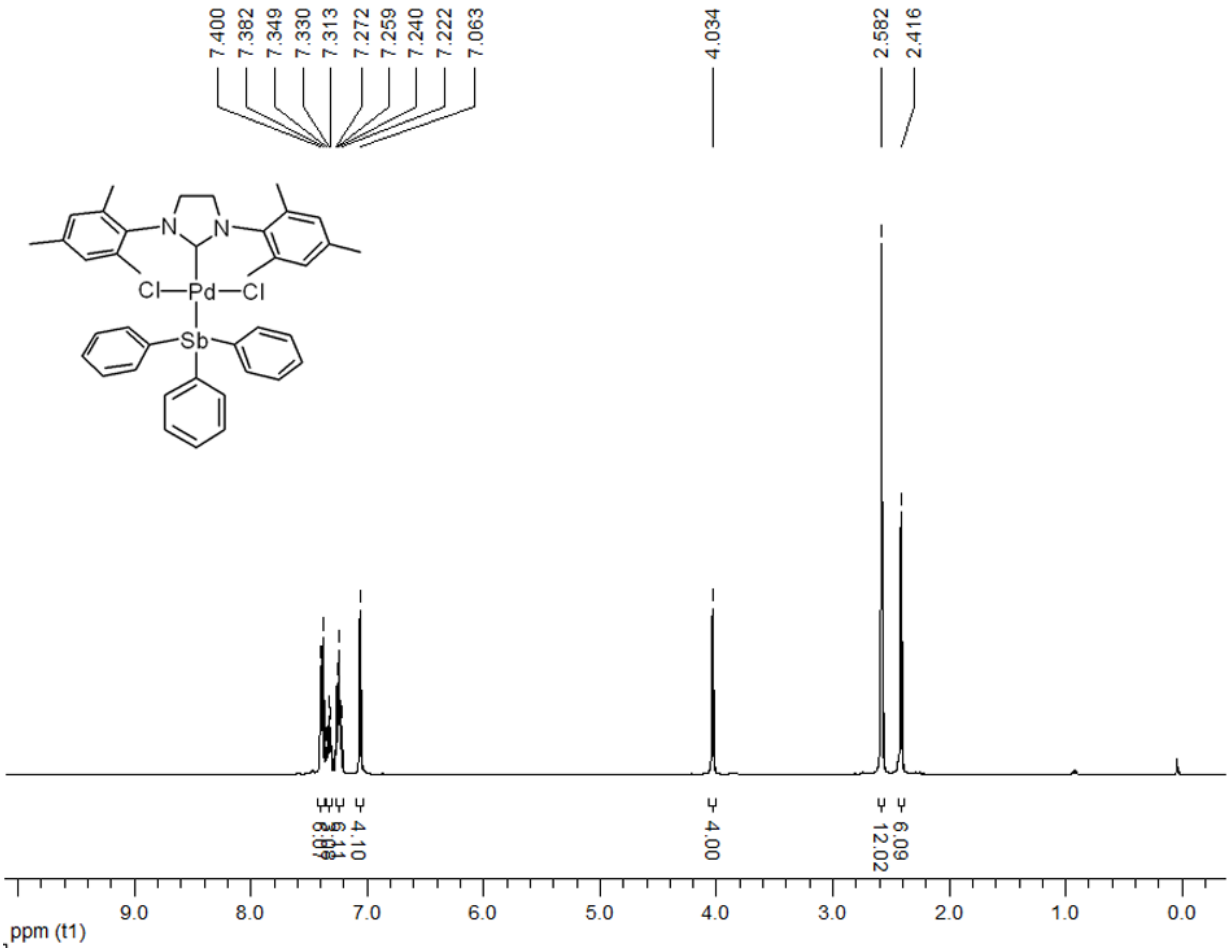

165.147
146.694
135.275
134.349
132.455
129.832
129.231
128.017
124.424
123.848
77.283
76.966
76.648
28.623
26.232
22.996
Cl—Pd—Cl
As
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

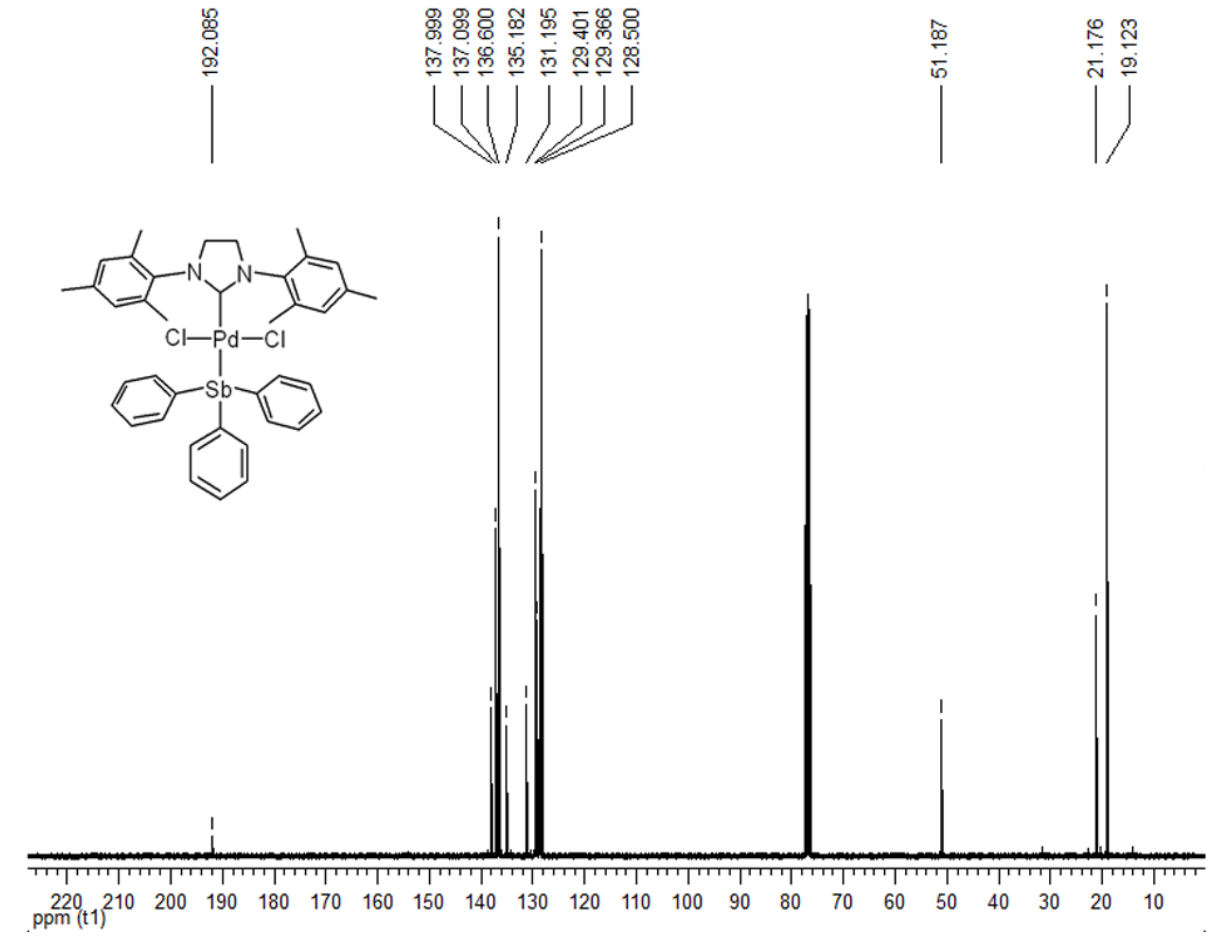

7.604
7.585
7.566
7.411
7.399
7.392
7.382
7.341
7.322
7.304
7.272
7.252
7.234
7.216
7.189
3.245
3.229
3.212
3.195
3.179
1.429
1.412
1.161
1.144
Cl—Pd—Cl
Sb
4.02
12.01
12.18
ppm (t1)

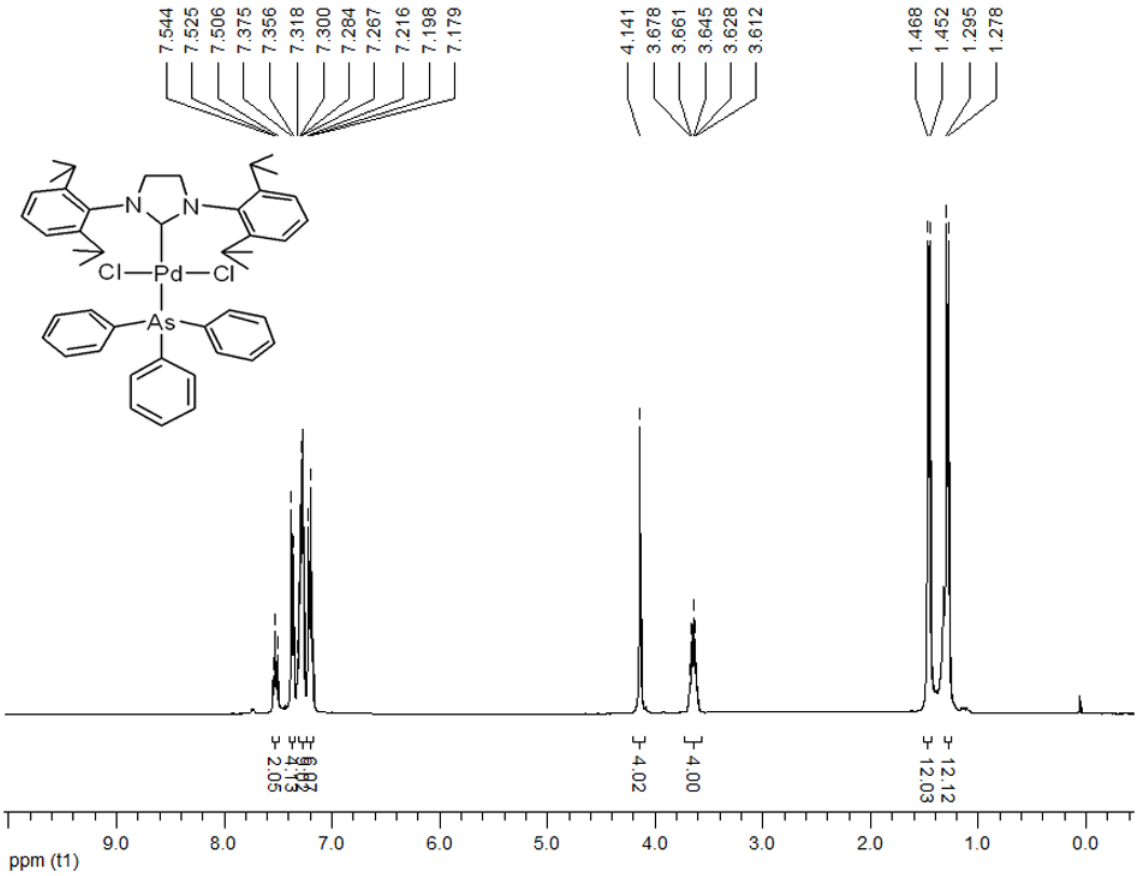

166.052
146.597
136.533
135.186
130.852
129.879
129.362
128.504
124.373
123.866
77.269
76.951
76.634
28.661
26.228
23.080
Cl—Pd—Cl
Sb
ppm (t1)

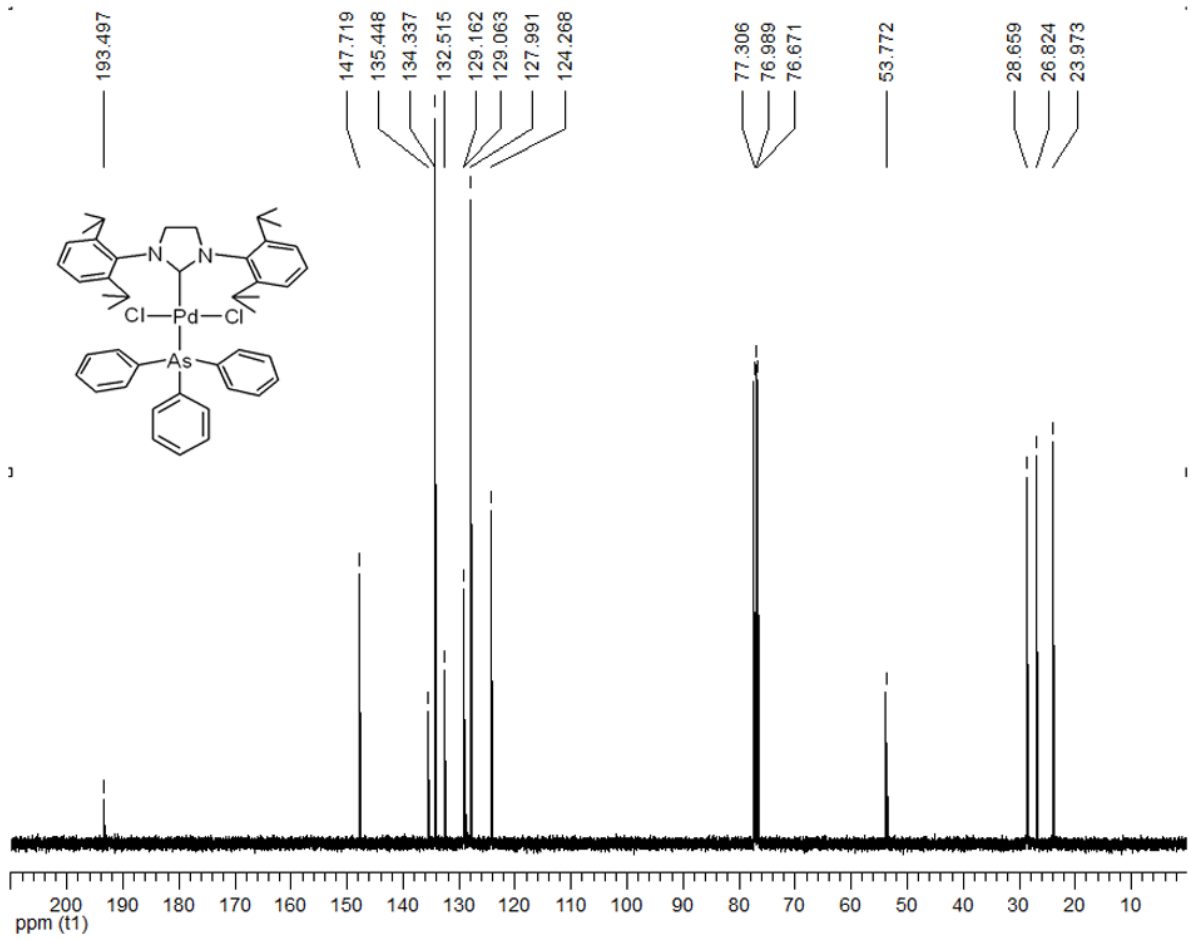

7.342
7.314
7.296
7.272
7.242
7.224
7.205
7.062
4.031
2.583
2.434
Cl—Pd—Cl
As
5.03
4.01
4.00
12.10
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

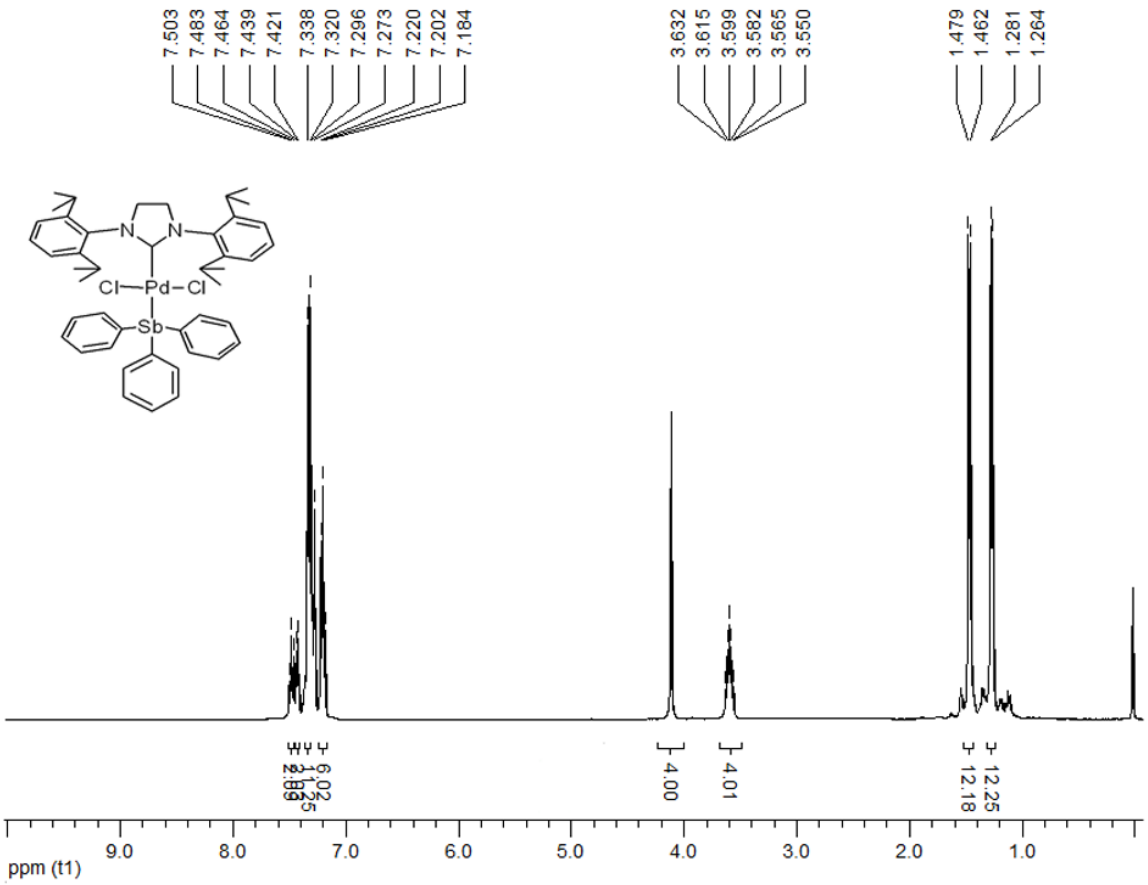

191.662
137.907
137.201
135.196
134.349
132.642
129.317
129.249
128.036
77.305
76.987
76.669
51.167
21.173
19.250
Cl—Pd—Cl
As
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

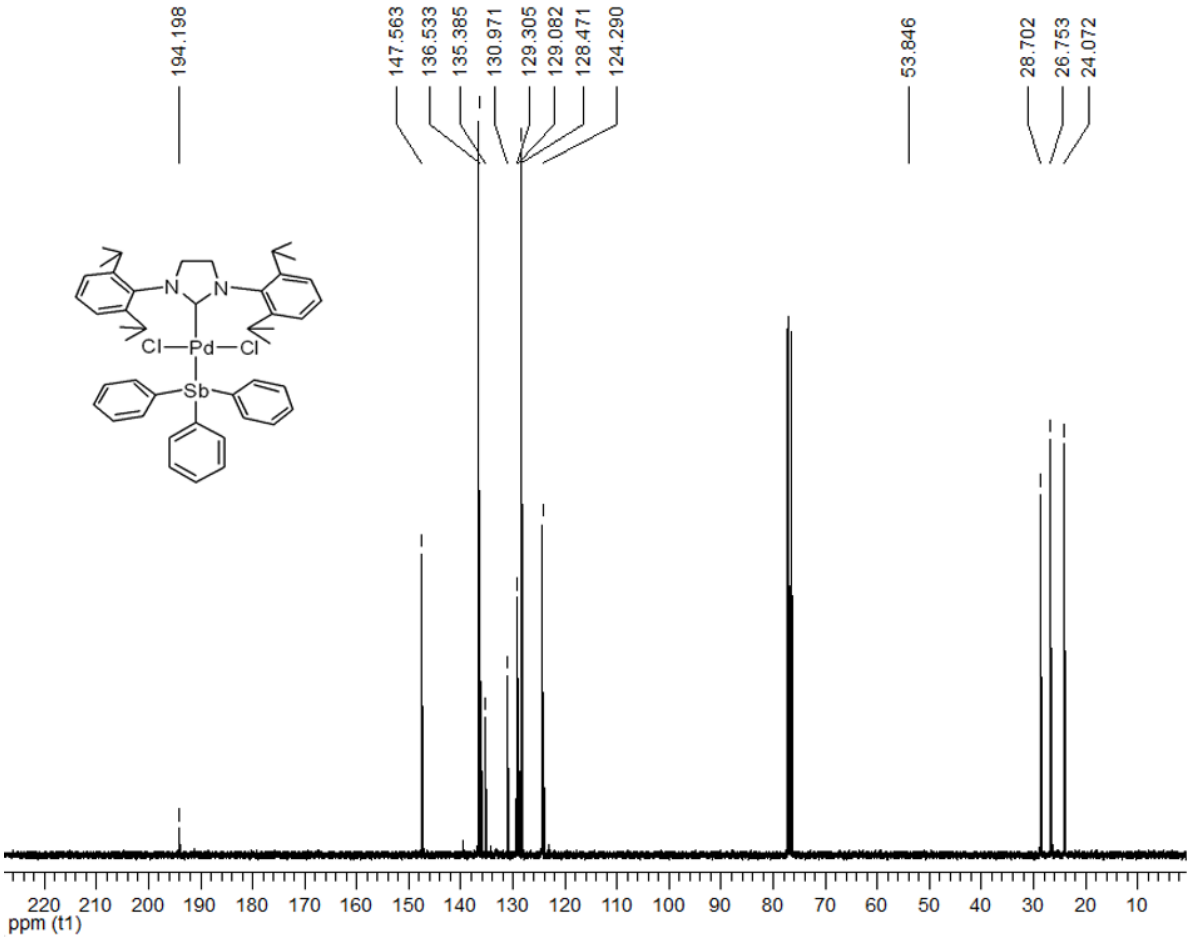

7.400
7.382
7.349
7.330
7.313
7.272
7.259
7.240
7.222
7.063
4.034
2.582
2.416
Cl—Pd—Cl
Sb
4.10
4.00
12.02
6.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

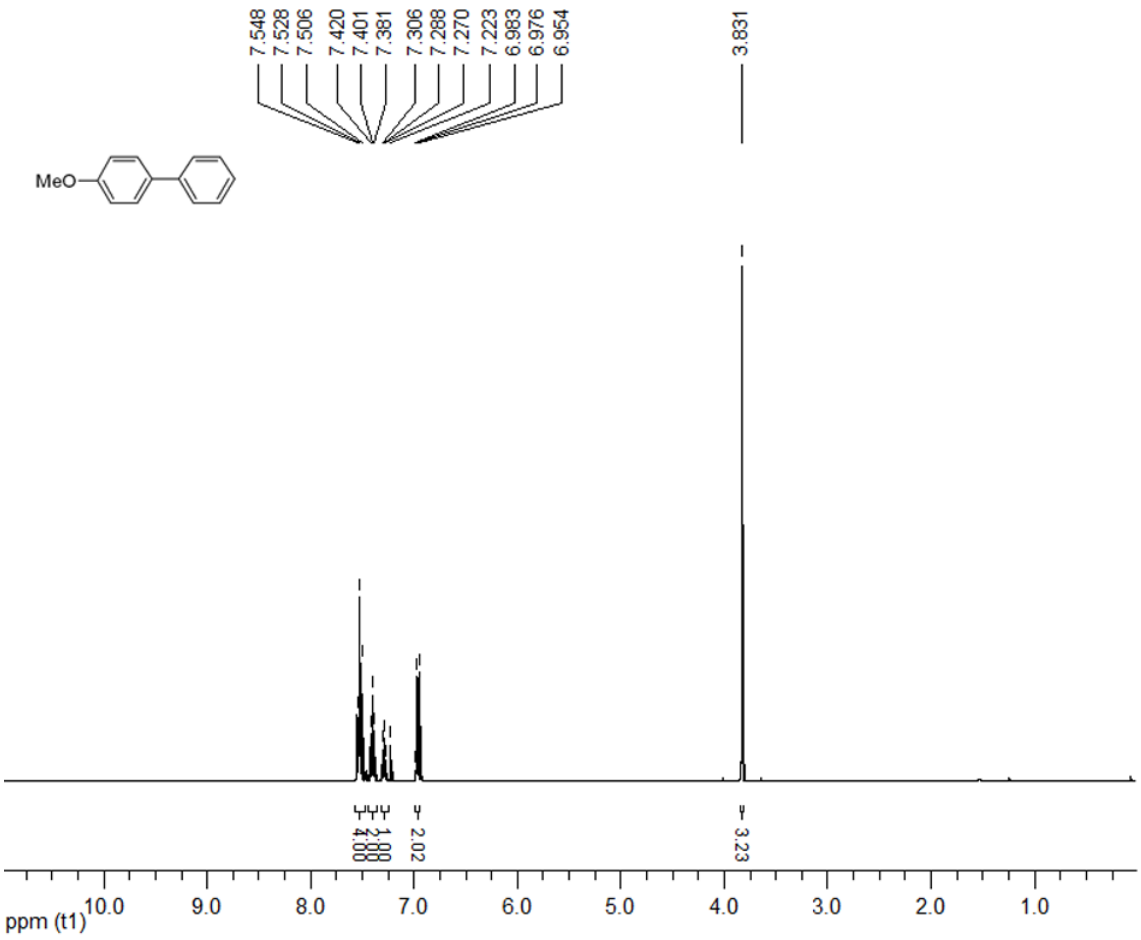

192.085
137.999
137.099
136.600
135.182
131.195
129.401
129.366
128.500
51.187
21.176
19.123
Cl—Pd—Cl
Sb
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

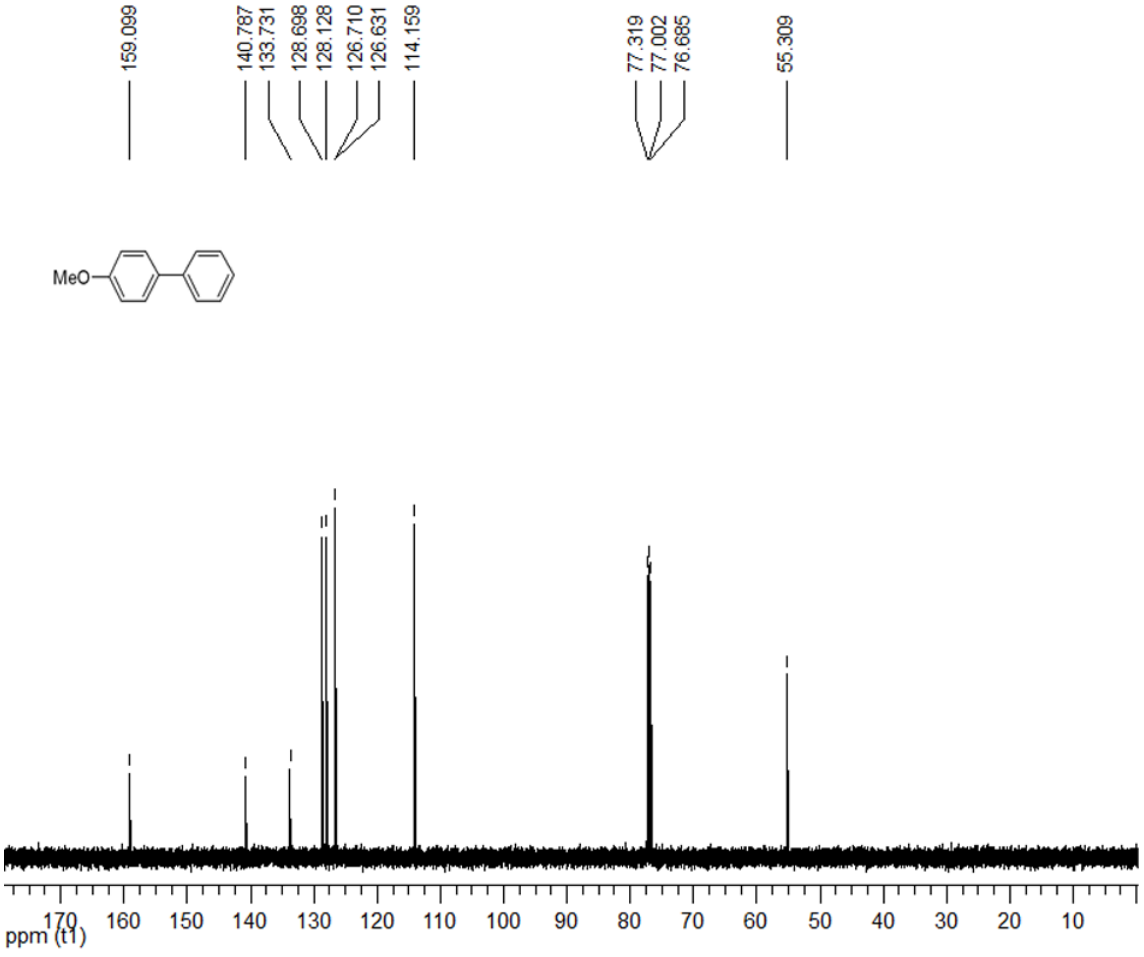

7.544
7.525
7.506
7.375
7.356
7.318
7.300
7.284
7.267
7.216
7.198
7.179
4.141
3.678
3.661
3.645
3.628
3.612
1.468
1.452
1.295
1.278
Cl—Pd—Cl
As
2.05
4.02
4.00
12.03
12.12
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

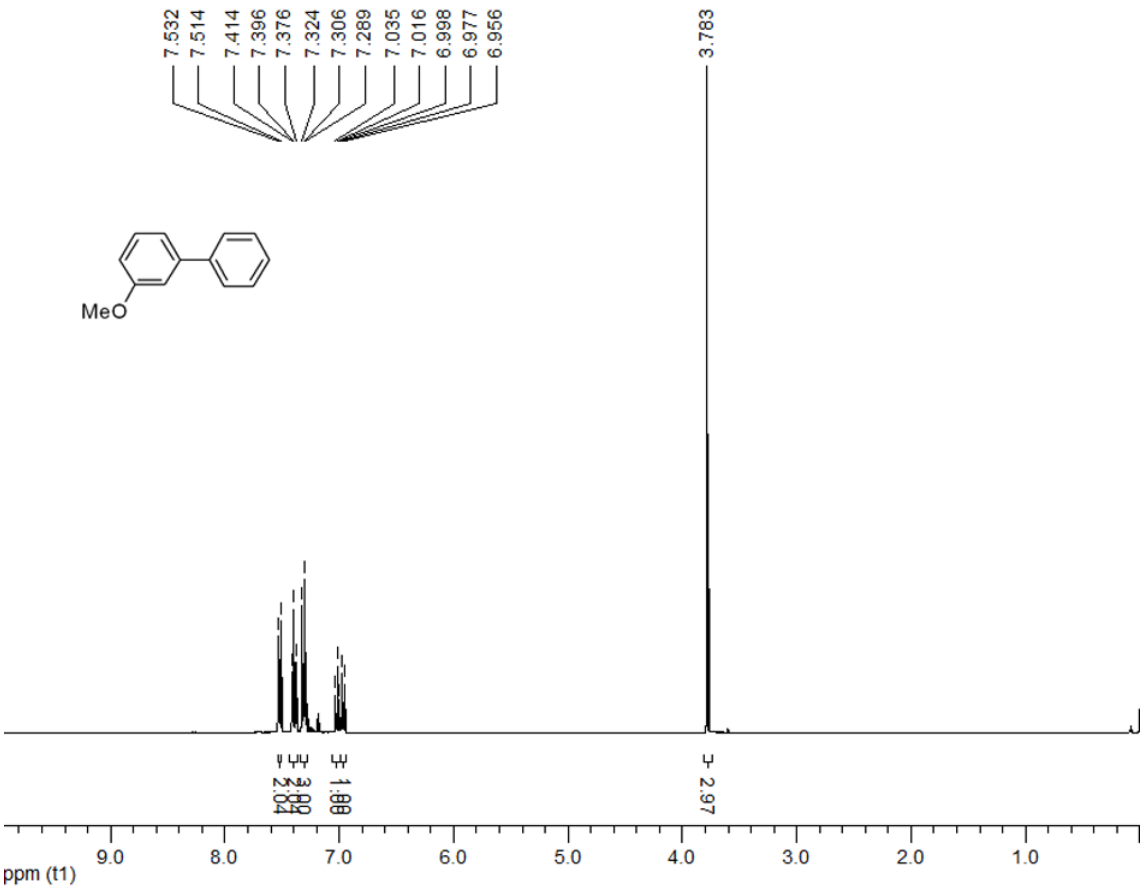

193.497
147.719
135.448
134.337
132.515
129.162
129.063
127.991
124.268
77.306
76.989
76.671
53.772
28.659
26.824
23.973
Cl—Pd—Cl
As
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

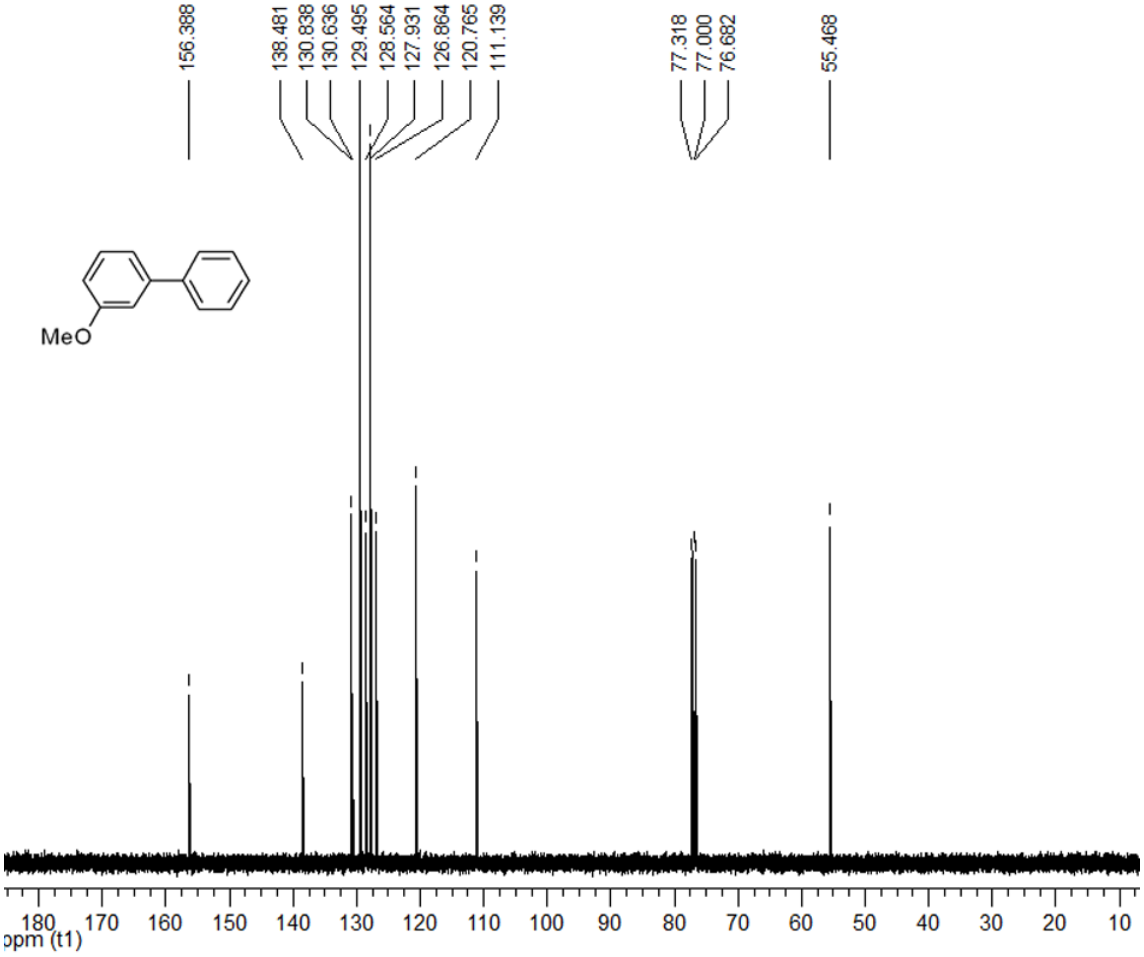

7.503
7.483
7.464
7.439
7.421
7.338
7.320
7.296
7.273
7.220
7.202
7.184
3.632
3.615
3.599
3.582
3.565
3.550
1.479
1.462
1.281
1.264
Cl—Pd—Cl
Sb
4.00
4.01
12.18
12.25
ppm (t1)

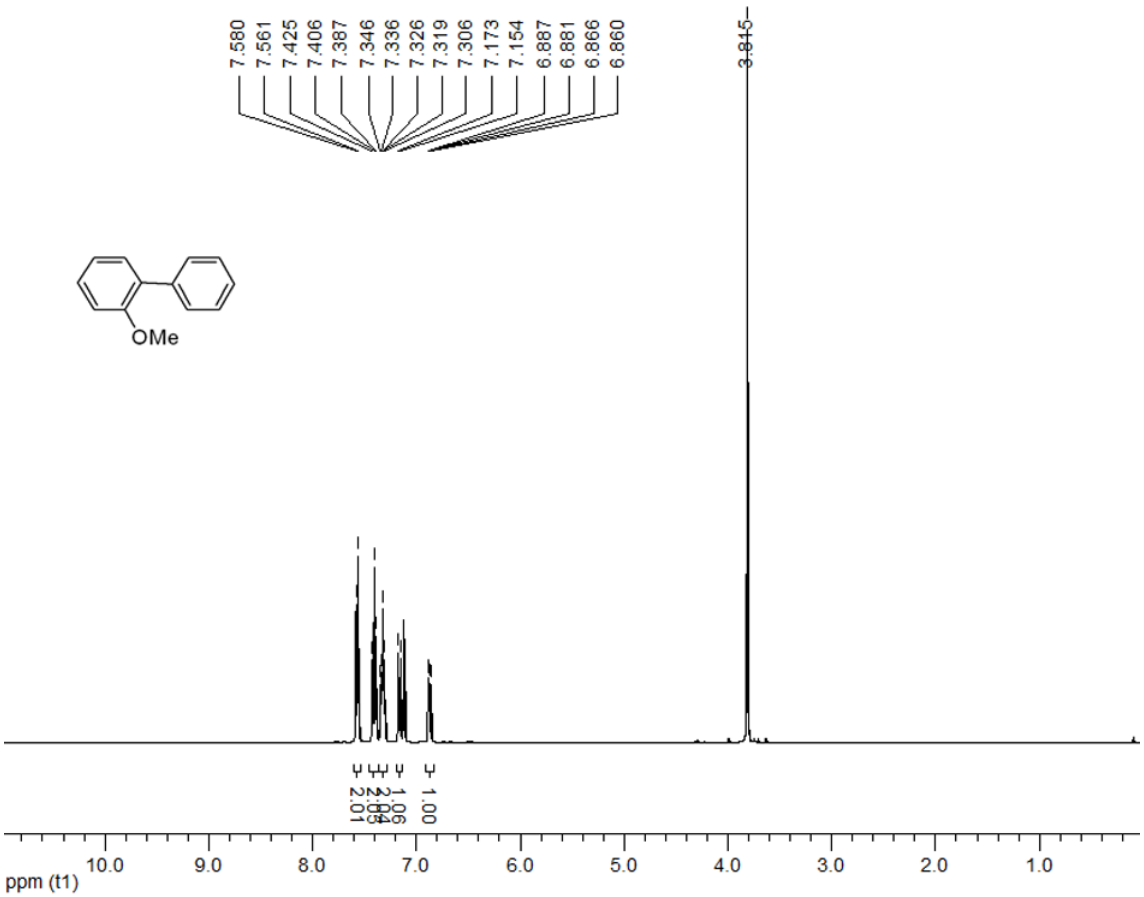

194.198
147.563
136.533
135.385
130.971
129.305
129.082
128.471
124.290
53.846
28.702
26.753
24.072
Cl—Pd—Cl
Sb
ppm (t1)

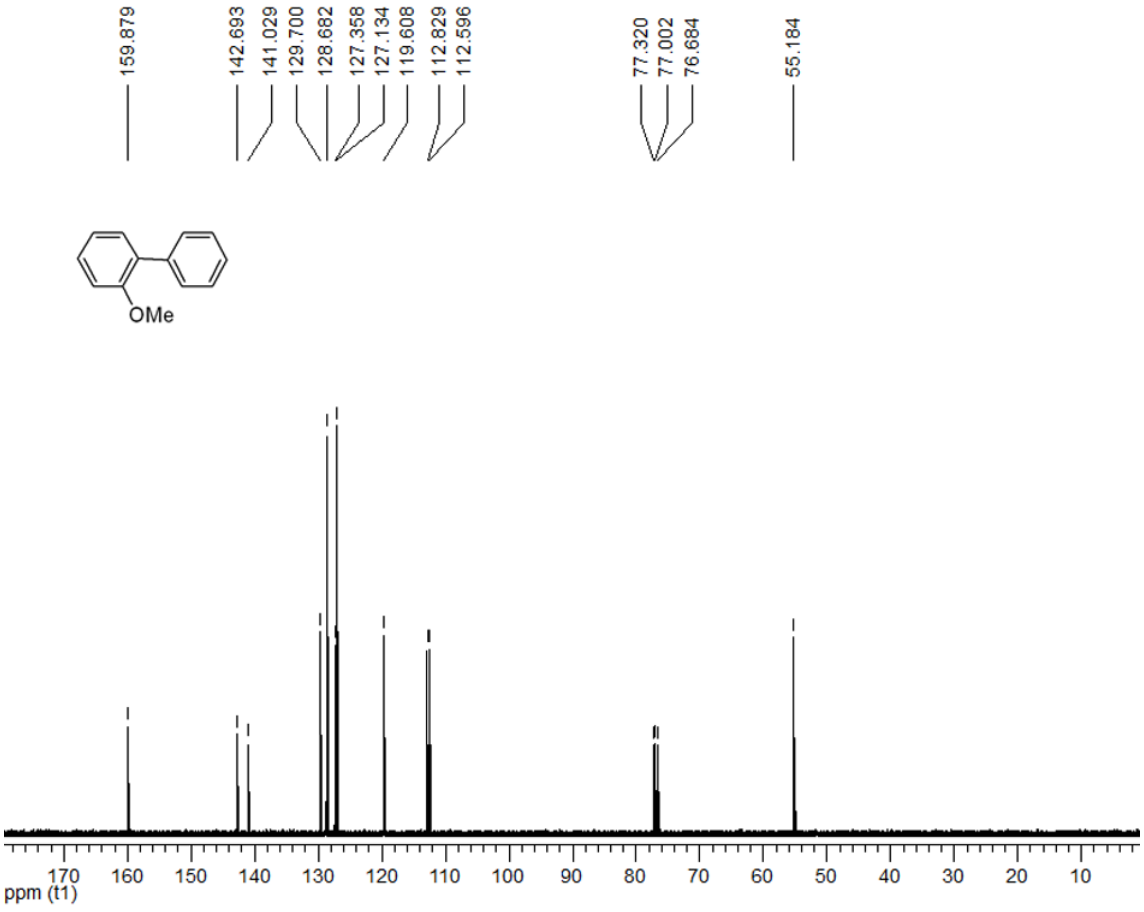

7.548
7.528
7.506
7.420
7.401
7.381
7.306
7.288
7.270
7.223
6.983
6.976
6.954
3.831
MeO
4.00
2.00
2.02
3.23
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

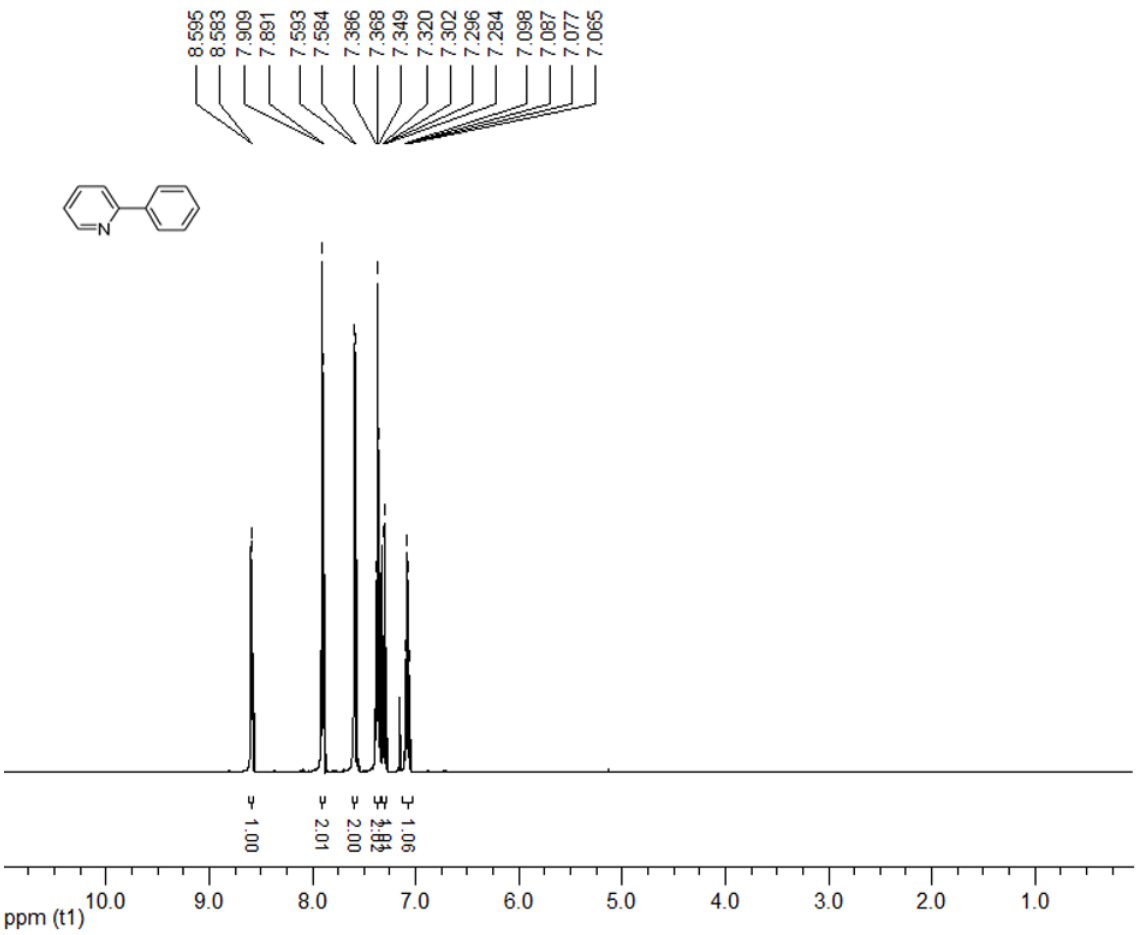

159.099
140.787
133.731
128.698
128.128
126.710
126.631
114.159
77.319
77.002
76.685
55.309
MeO
ppm (t1)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

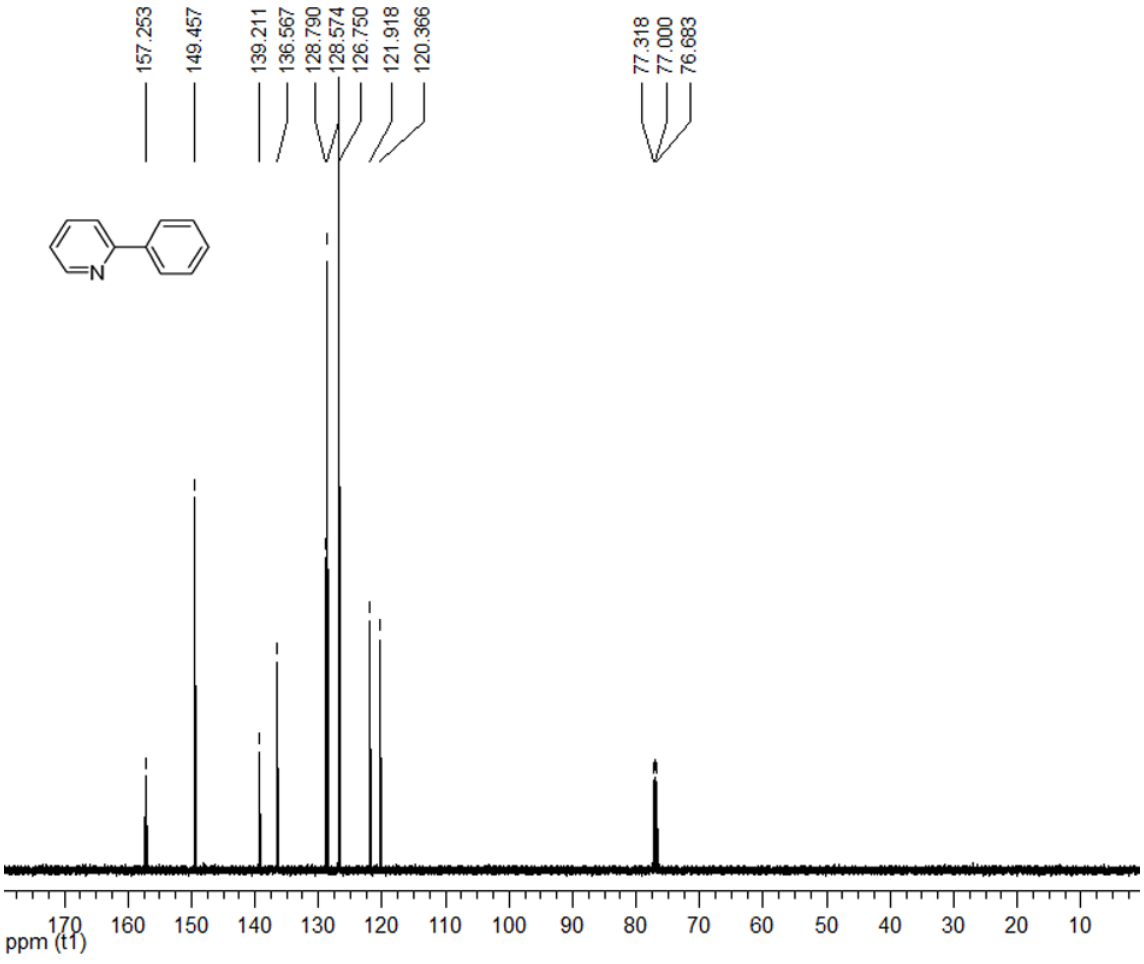

7.532
7.514
7.414
7.396
7.376
7.324
7.306
7.289
7.035
7.016
6.998
6.977
6.956
3.783
MeO
2.04
3.00
2.14
1.00
2.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

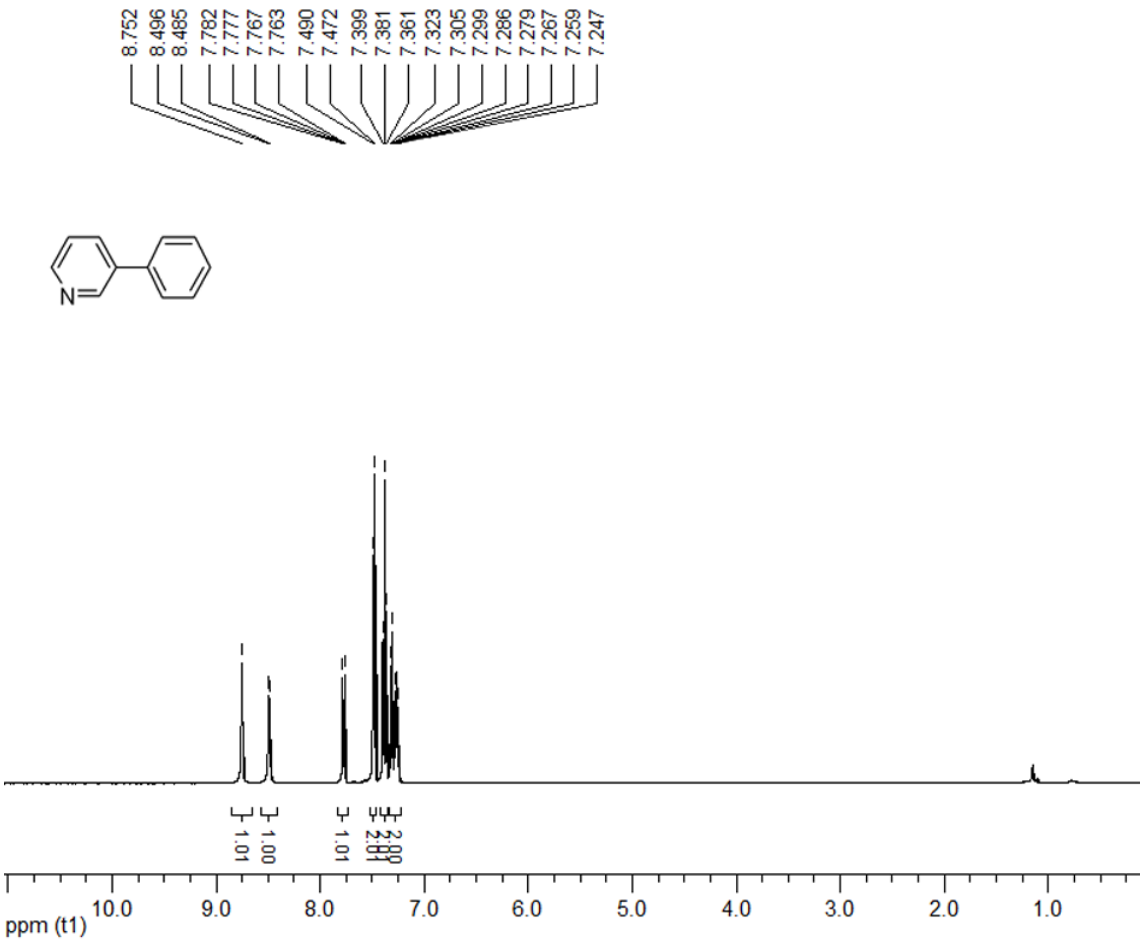

156.388
138.481
130.838
130.636
129.495
128.564
127.931
126.864
120.765
111.139
77.318
77.000
76.682
55.468
MeO
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

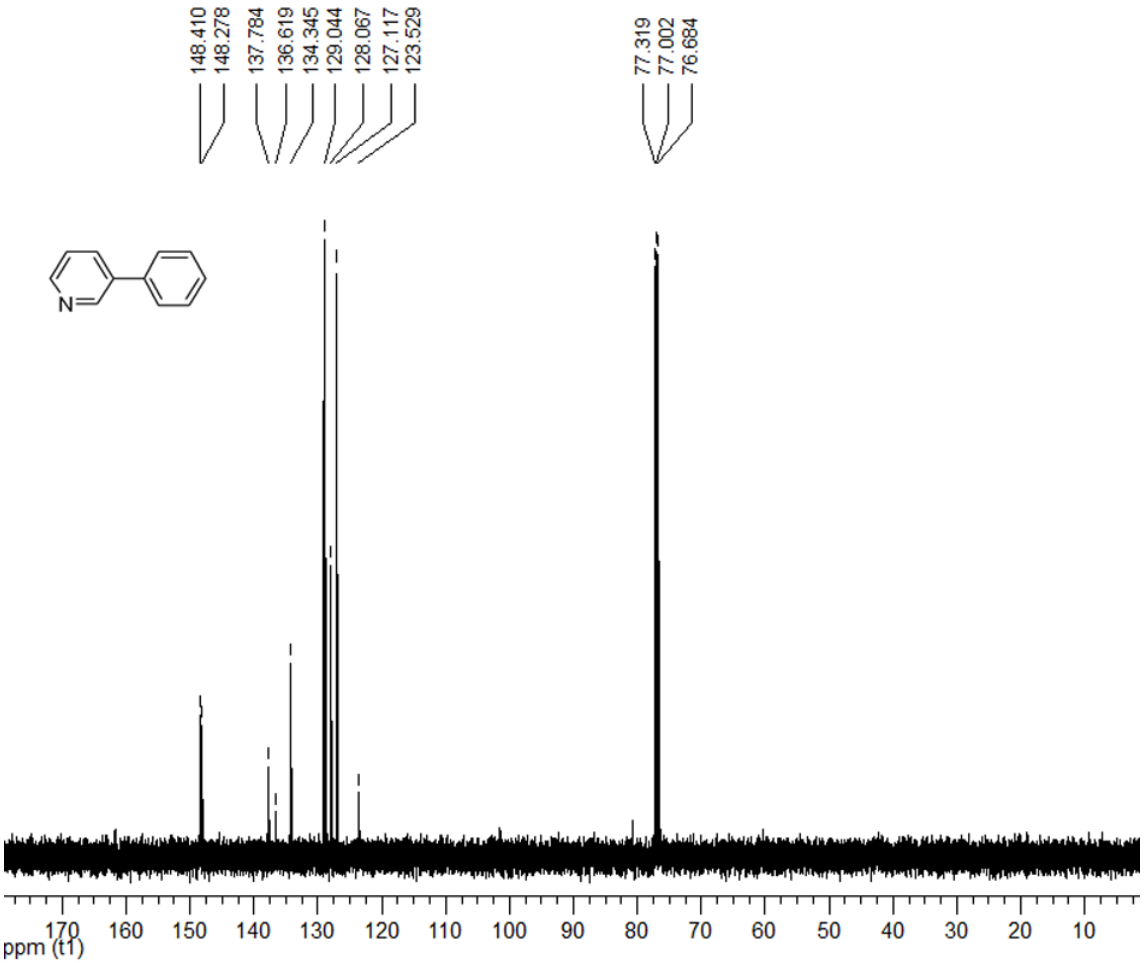

7.580
7.561
7.425
7.406
7.387
7.346
7.336
7.326
7.319
7.306
7.173
7.154
6.887
6.881
6.866
6.860
3.815
OMe
2.01
2.14
2.05
1.06
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

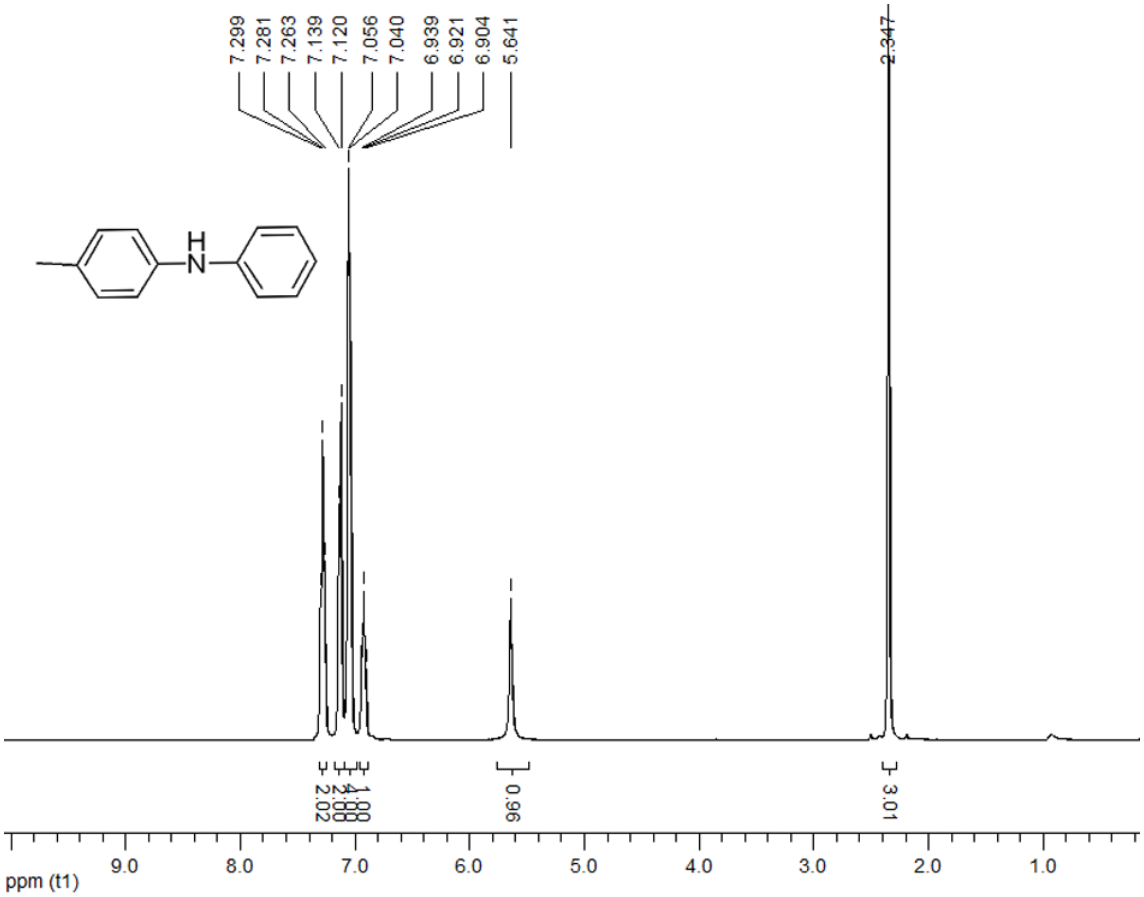

159.879
142.693
141.029
129.700
128.682
127.358
127.134
119.608
112.829
112.596
77.320
77.002
76.684
55.184
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

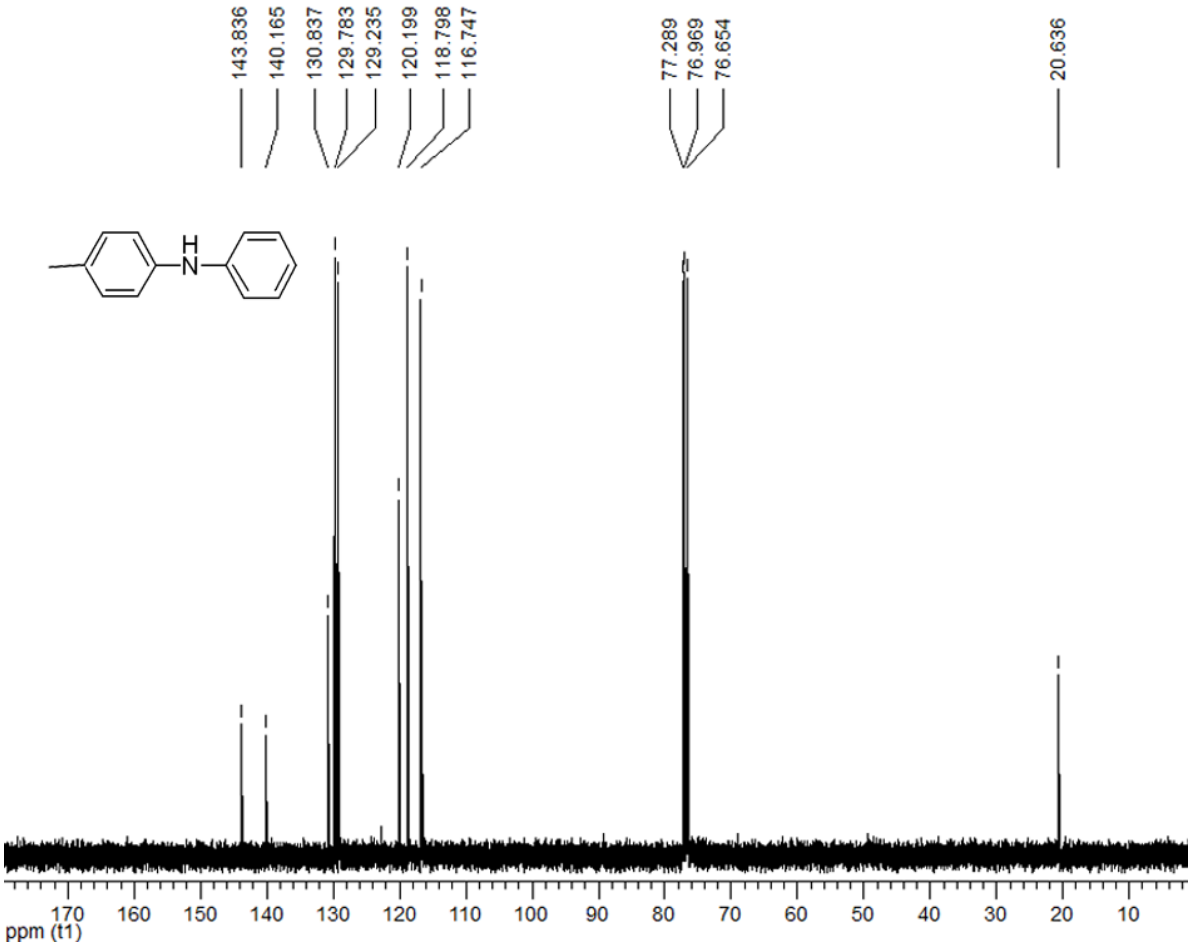

8.595
8.583
7.909
7.891
7.593
7.584
7.386
7.368
7.349
7.320
7.302
7.296
7.284
7.098
7.087
7.077
7.065
1.00
2.01
2.00
2.82
1.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

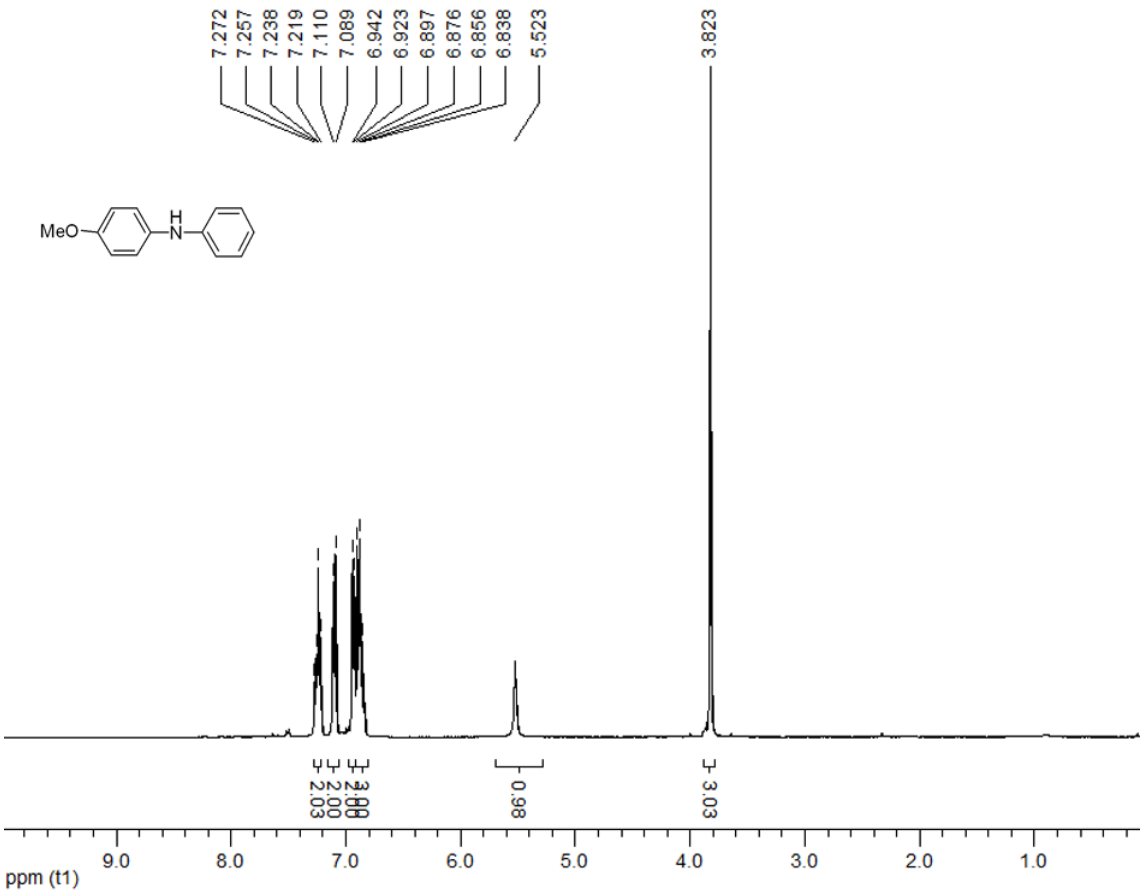

157.253
149.457
139.211
136.567
128.790
128.574
126.750
121.918
120.366
77.318
77.000
76.683
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

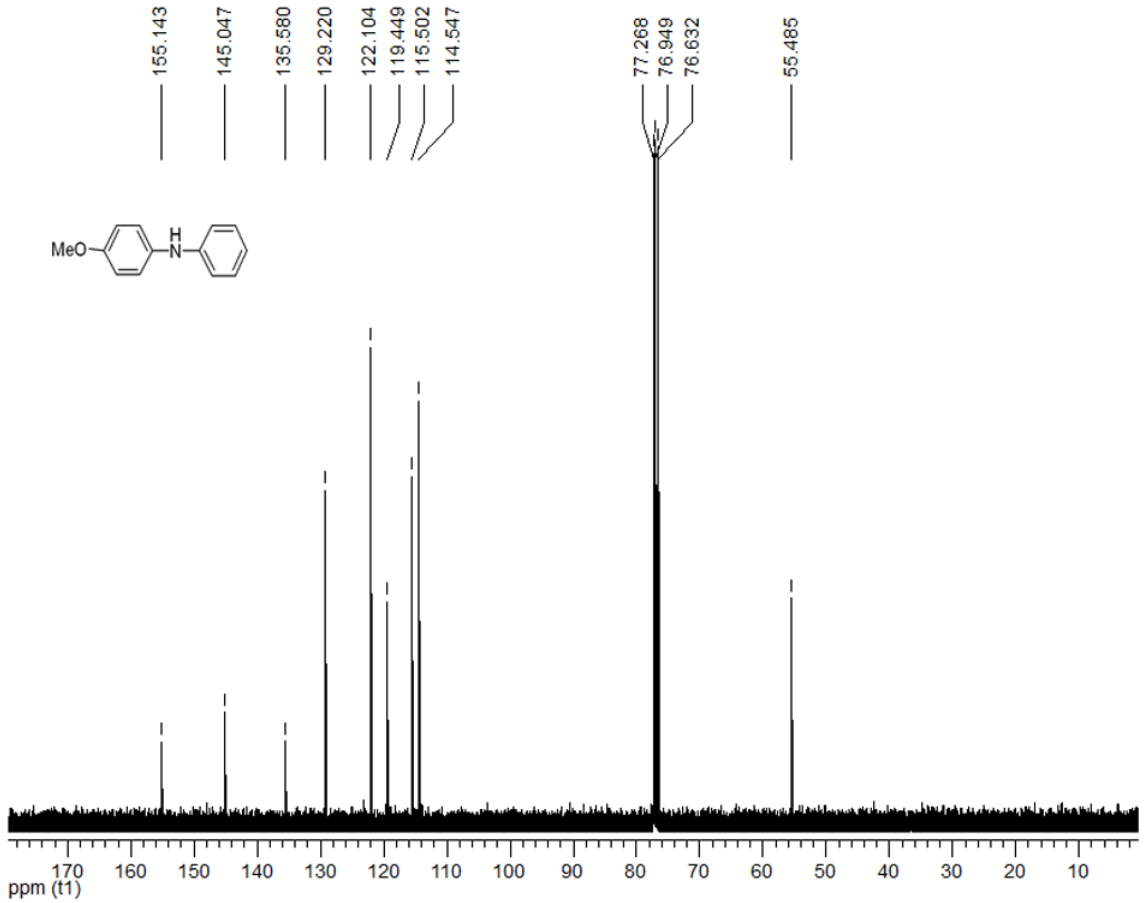

8.752
8.496
8.485
7.782
7.777
7.767
7.763
7.490
7.472
7.399
7.381
7.361
7.323
7.305
7.299
7.286
7.279
7.267
7.259
7.247
N
1.01
1.00
1.01
2.81
2.00
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

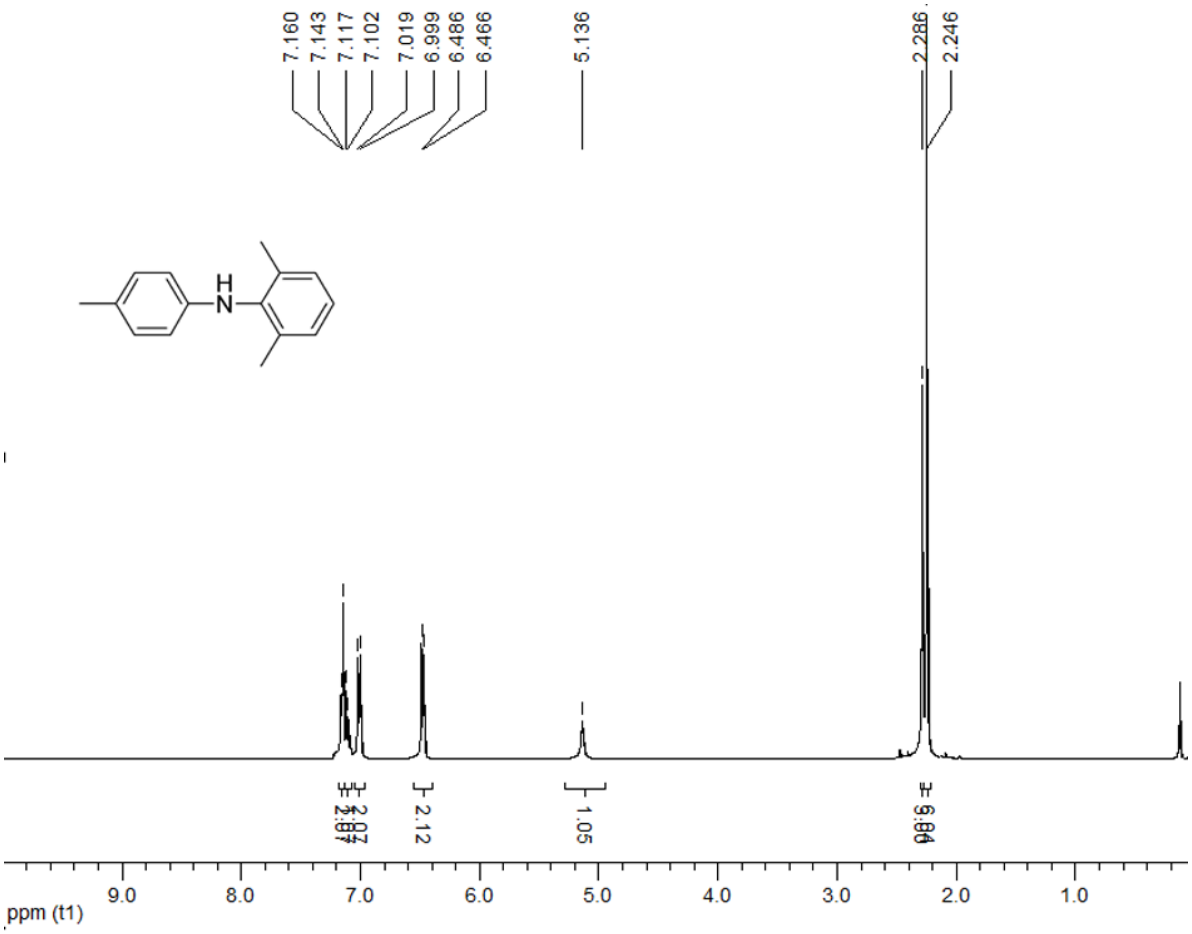

148.410
148.278
137.784
136.619
134.345
129.044
128.067
127.117
123.529
77.319
77.002
76.684
N
ppm (t1)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

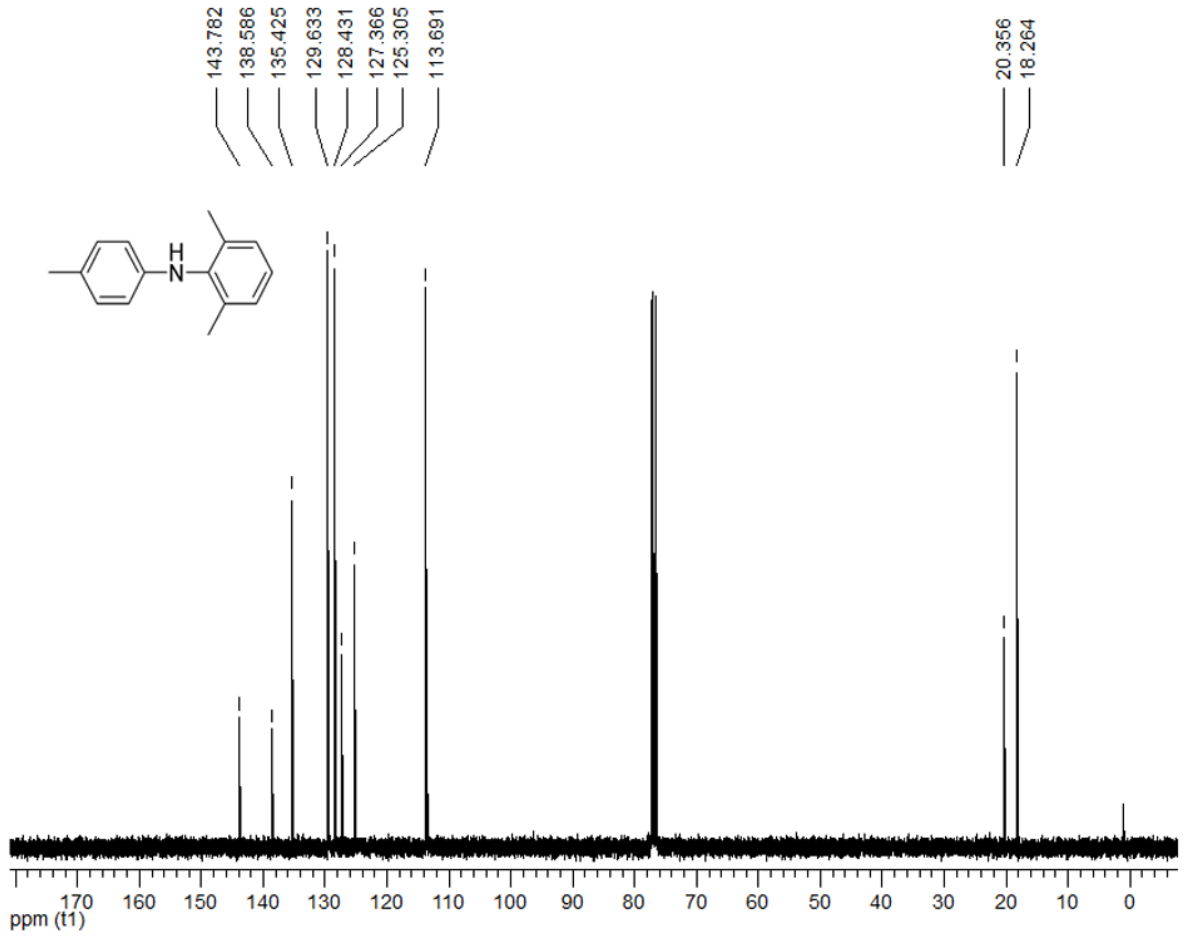

7.299
7.281
7.263
7.139
7.120
7.056
7.040
6.939
6.921
6.904
5.641
2.347
2.02
2.00
2.00
2.00
2.00
0.96
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

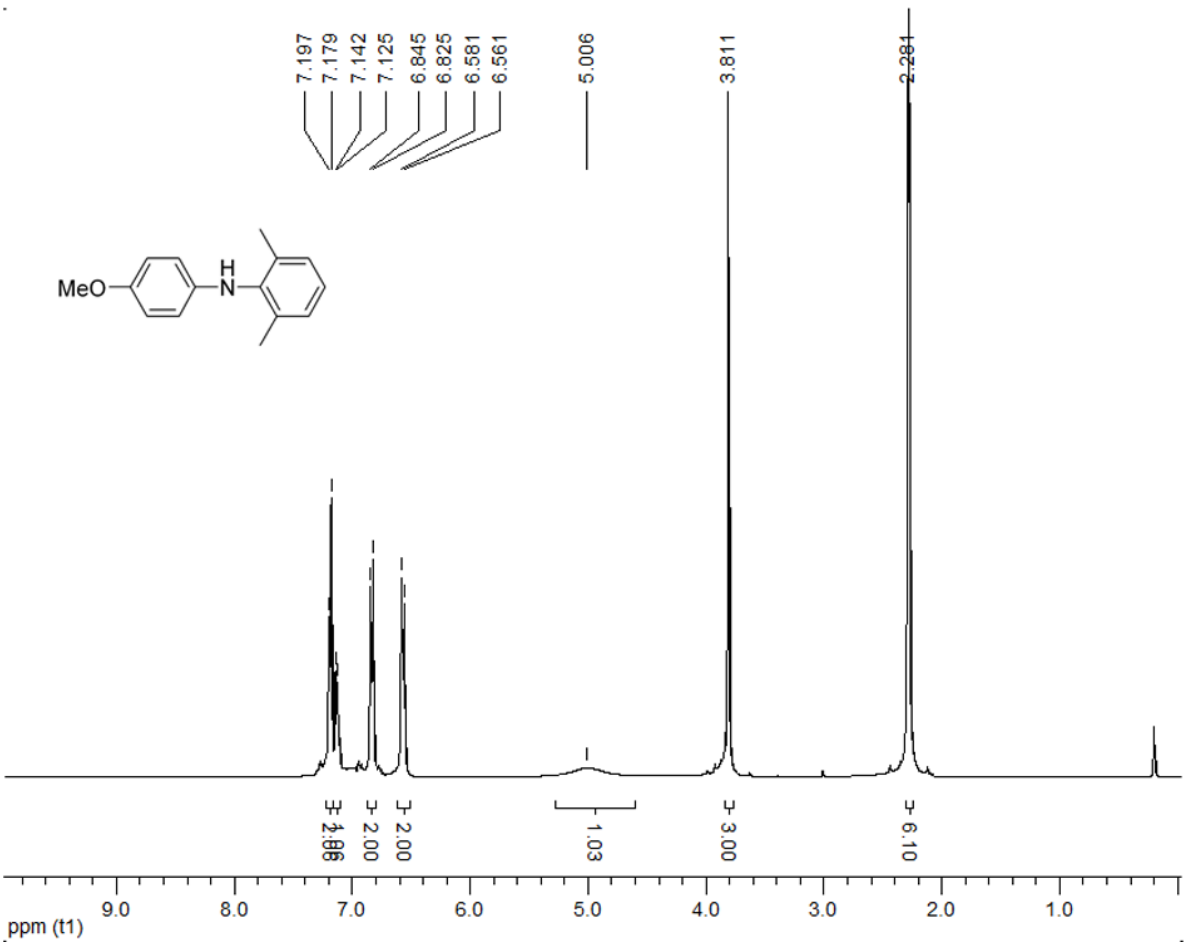

143.836
140.165
130.837
129.783
129.235
120.199
118.798
116.747
77.289
76.969
76.654
20.636
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

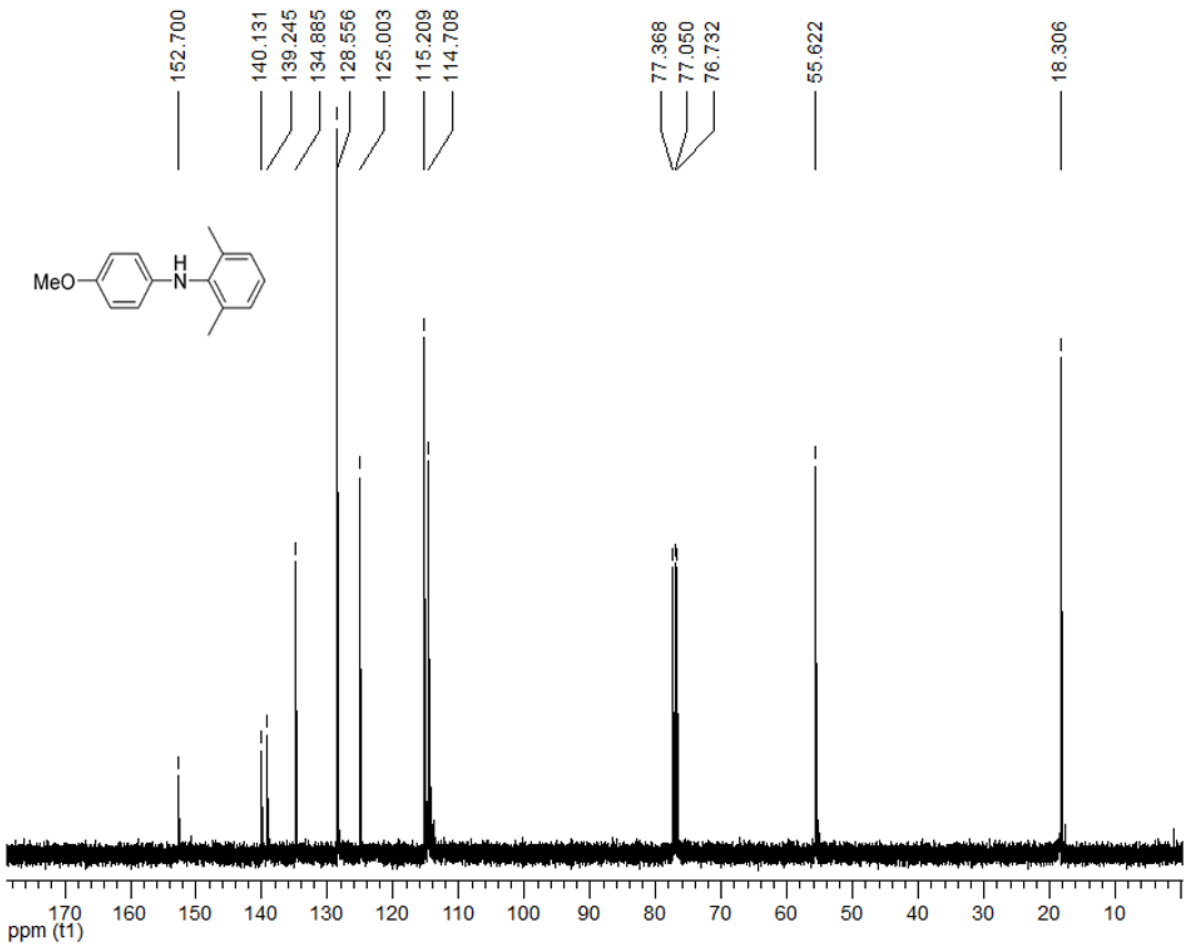

7.272
7.257
7.238
7.219
7.110
7.089
6.942
6.923
6.897
6.876
6.856
6.838
5.523
3.823
MeO
2.03
2.00
2.00
0.98
3.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

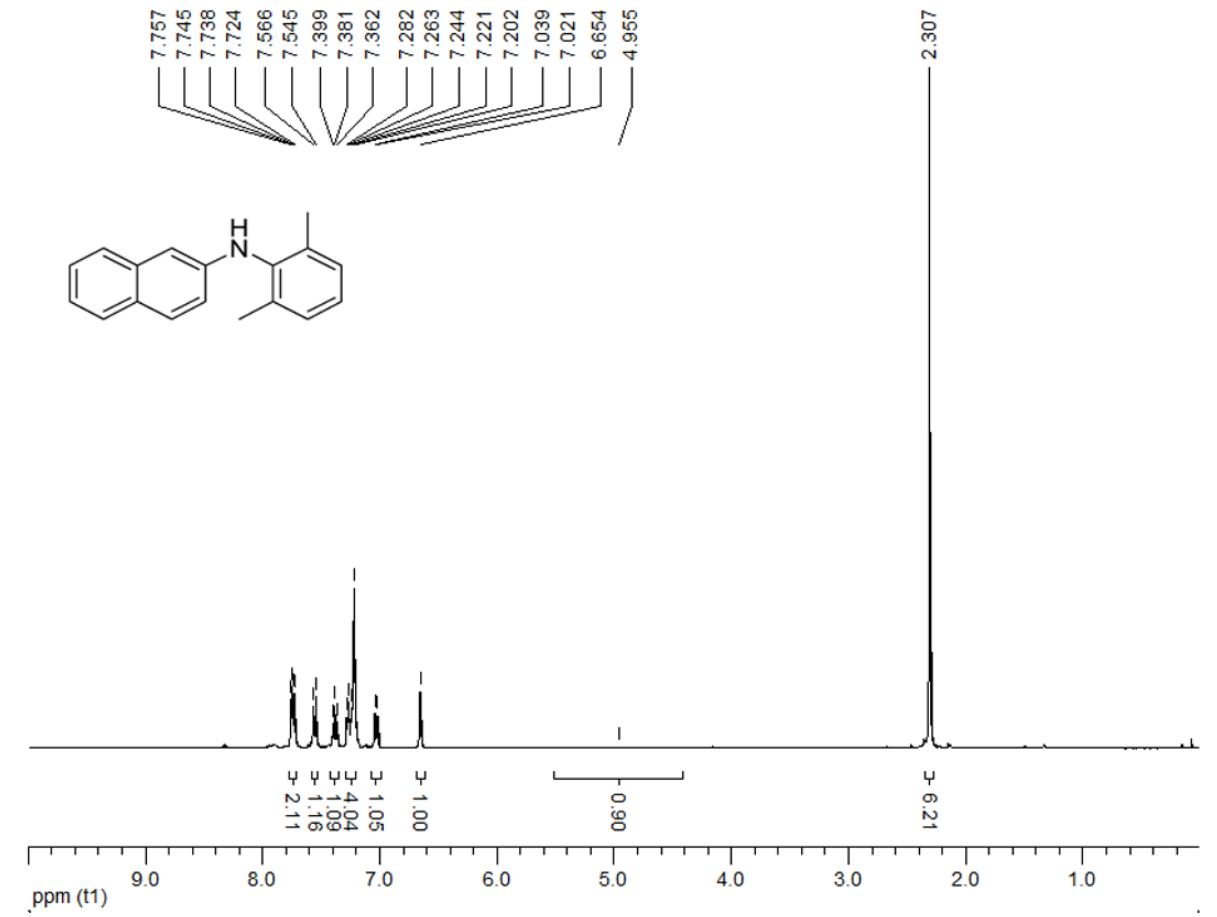

155.143
145.047
135.580
129.220
122.104
119.449
115.502
114.547
77.268
76.949
76.632
55.485
MeO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

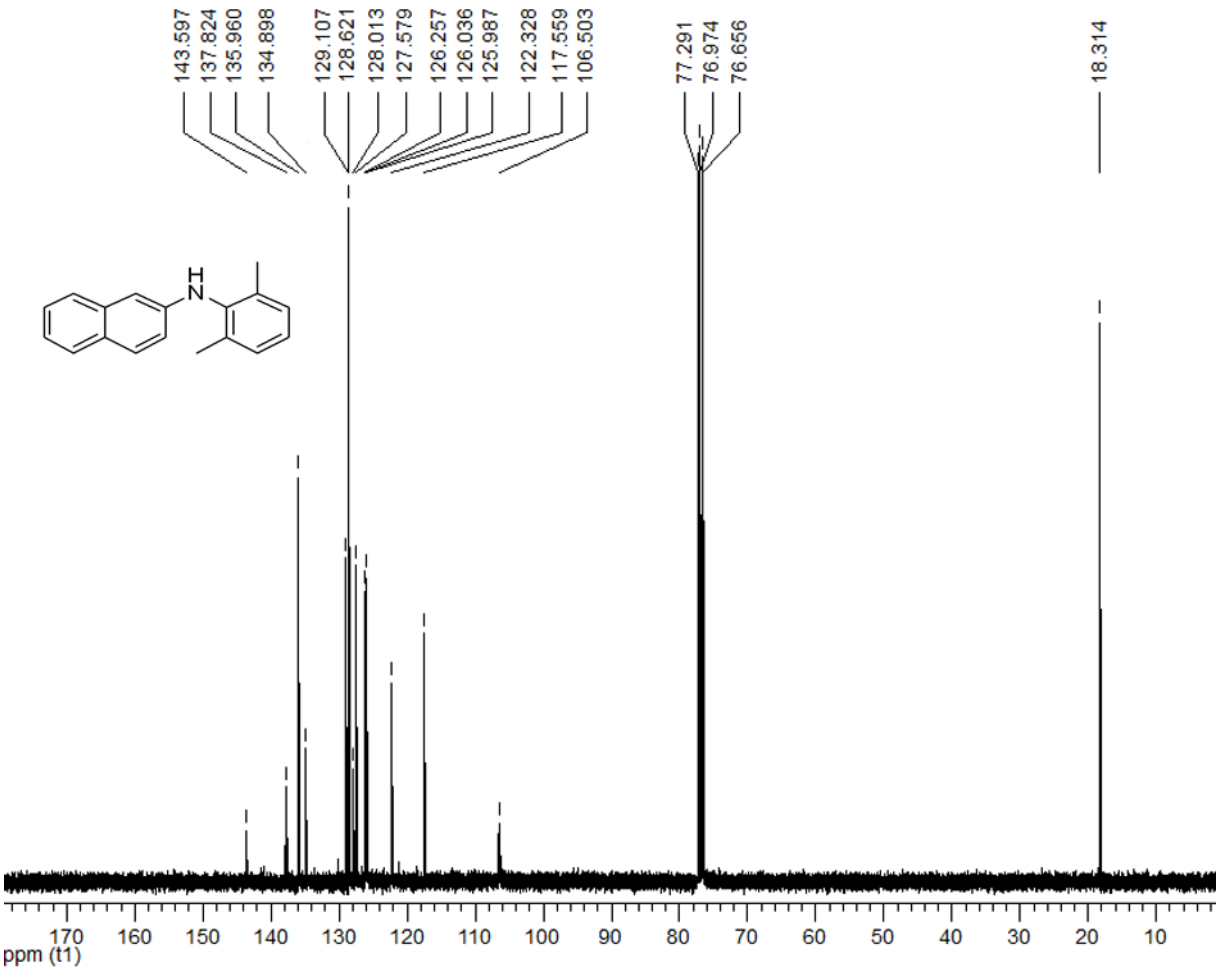

7.160
7.143
7.117
7.102
7.019
6.999
6.486
6.466
5.136
2.286
2.246
2.07
2.12
1.05
9.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


143.782
138.586
135.425
129.633
128.431
127.366
125.305
113.691
20.356
18.264
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)


7.197
7.179
7.142
7.125
6.845
6.825
6.581
6.561
5.006
3.811
2.281
MeO
H
N
2.00
2.00
1.03
3.00
6.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


152.700
140.131
139.245
134.885
128.556
125.003
115.209
114.708
77.368
77.050
76.732
55.622
18.306
MeO
H
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)


7.757
7.745
7.738
7.724
7.566
7.545
7.399
7.381
7.362
7.282
7.263
7.244
7.221
7.202
7.039
7.021
6.654
4.955
2.307
2.11
1.16
1.09
4.04
1.05
1.00
0.90
6.21
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


143.597
137.824
135.960
134.898
129.107
128.621
128.013
127.579
126.257
126.036
125.987
122.328
117.559
106.503
77.291
76.974
76.656
18.314
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

References

(1) T. E. Schmid, D. C. Jones, O. Songis, O. Diebolt, M. R. L. Furst, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans.*, 2013, **42**, 7345.

(2) C. Desmarets, R. Schneider and Y. Fort, *J. Org. Chem*., 2002, **67**, 3029.

(3) C.-Y. Gao and L.-M. Yang, *J. Org. Chem.*, 2008, **73**, 1624.