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Supporting Information

Mono- and Dinuclear Palladium(II) Complexes Containing Both N-Heterocyclic Carbenes and Tetrazole Ligands as Catalysts for Hiyama coupling

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1. Selected bond lengths, bond lengths, dihedral angles and $\%V_{Bur}$ values for 1–6

Table S1. Selected bond lengths, dihedral angles and $\%V_{Bur}$ values for **1–6**

Complex	**1**	**2**	**3**	**4**	**5**	**6**
Pd−$C_{carbene}$ (Å)	1.961(2)	1.991(4)	1.949(3)	1.972(6)	1.994(7)	1.968(3)
			1.950(3)		1.982(7)	1.948(3)
Pd−N (Å)	2.084(2)	2.116(3)	2.088(3)	2.117(5)	2.120(6)	2.084(3)
			2.109(2)		2.076(6)	2.035(3)
Pd−Cl (Å)	2.2864(7)	2.3219(16)	2.2905(10)	2.315(2)	2.302(3)	2.2714(10)
	2.3091(6)	2.3370(16)	2.2940(9)	2.329(2)	2.342(3)	2.3053(9)
			2.2715(10)		2.289(3)	2.2676(10)
			2.2813(10)		2.400(3)	2.3762(9)
C–Pd–Cl	87.18(6)	86.58(10)	89.23(8)	89.32(18)	90.3(2)	90.01(10)
	93.33(6)	94.44(10)	91.31(8)	90.94(18)	89.4(2)	90.04(10)
			90.48(8)		89.7(2)	90.34(10)
			89.54(8)		178.1(2)	178.03(10)
N–Pd–Cl	87.93(6)	87.66(10)	91.59(9)	90.80(16)	90.5(2)	91.02(8)
	91.64(6)	91.45(10)	87.99(9)	88.94(16)	89.8(2)	88.92(8)
			91.88(8)		88.96(16)	88.99(8)
			88.44(8)		174.95(15)	173.56(9)
$PdCNCl_2$/carbene	72.97	75.13	67.24	69.58	65.59	64.55
dihedral angle (°)			65.81		73.84	74.15
$PdCPCl_2$/Tetrazole	34.99	35.50	37.79	15.64	22.04	22.05
dihedral angle (°)			15.82		15.87	18.00
Carbene/Tetrazole	38.48	40.34	75.24	84.16	44.08	42.52
dihedral angle (°)			53.65		81.19	83.82
NHC $\%V_{Bur}$[a]	37.5	37.9	38.9	38.2	37.6	39.7
					36.2	37.7

[a] $\%V_{bur}$ calculated for Bondi radii scaled by 1.17, sphere radius R = 3.5 Å and Pd–C distance d = 2.00 Å.

2. Crystallographic data for 1–6

Table S2 Crystallographic data for compounds **1**−**6**

Compound	**1**	**2**	(**3**)$_2$•0.5CH_2Cl_2	**4**•CH_2Cl_2	**5**	**6**•1.5CH_2Cl_2
formula	$C_{28}H_{38}Cl_2N_6Pd$	$C_{28}H_{40}Cl_2N_6Pd$	$C_{137}H_{170}Cl_{10}N_{24}Pd_4$	$C_{35}H_{46}Cl_4N_6Pd$	$C_{61}H_{77}Cl_3N_8Pd$	$C_{125}H_{168}Cl_{12}N_{16}Pd_4$
fw	635.94	637.96	2933.07	798.98	1241.46	2745.75
crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*$\bar{1}$	*P*2(1)/*c*	*P*$\bar{1}$	*P*$\bar{1}$
a /Å	15.3005(15)	15.464(11)	14.712(4)	12.022(9)	12.632(16)	12.7041(18)
b /Å	16.0897(6)	16.201(12)	15.207(4)	20.900(16)	15.50(2)	15.216(2)
c /Å	12.2535(4)	12.484(9)	20.231(5)	16.374(12)	19.61(3)	19.059(3)
α /deg	90.00	90.00	68.845(4)	90.00	79.27(2)	80.336(2)
β /deg	93.0270(10)	92.812(13)	72.185(4)	103.443(11)	85.87(2)	84.728(2)
γ /deg	90.00	90.00	63.367(3)	90.00	81.40(2)	81.324(2)
V /Å^3	3012.36(18)	3124(4)	3716.3(16)	4001(5)	3725(8)	3582.2(9)
Z	4	4	1	4	2	1
D_{calc} /g cm^{-3}	1.402	1.356	1.311	1.326	1.107	1.273
F(000)	1312	1320	1514	1648	1284	1418
μ /mm^{-1}	0.821	0.791	0.710	0.762	0.626	0.766
GOF	0.960	1.060	1.044	1.052	1.021	1.036
reflections collected	43968	15061	19021	16825	17714	18305
independent reflections (R_{int})	5250 (0.0264)	5431 (0.0268)	12946 (0.0169)	6887 (0.0639)	12702 (0.0604)	12472 (0.0141)
observed reflections [$I > 2\sigma(I)$]	4753	4611	10691	4078	5814	10406
refined parameters	342	342	819	423	672	765
*R*1 [$I > 2\sigma(I)$]	0.0267	0.0350	0.0317	0.0571	0.0734	0.0365
*wR*2 (all data)	0.0761	0.1316	0.0886	0.2103	0.1359	0.1062

3. Characterization data for the products

4-Nitrobiphenyl[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.31–8.29 (m, 2H), 7.74 (dt, J = 8.8 Hz and 2.4 Hz, 2H), 7.63 (dt, J = 8.4 Hz and 2.0 Hz, 2H), 7.52–7.49 (m, 2H), 7.47–7.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 147.6, 147.0, 138.7, 129.1, 128.9, 127.8, 127.4, 124.1.

4-Methylbiphenyl[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.66–7.64 (m, 2H), 7.57–7.55 (m, 2H), 7.51–7.47 (m, 2H), 7.40–7.37 (m, 1H), 7.32–7.30 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 141.1, 138.3, 137.0, 129.5, 128.7, 127.0, 126.9, 21.1.

Biphenyl[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.61 (m, 4H), 7.47 (dt, J = 7.2 Hz and 1.6 Hz, 4H), 7.37 (tt, J = 7.2 Hz and 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 128.7, 127.2, 127.2.

4-Fluorobiphenyl[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.59 (m, 4H), 7.53–7.49 (m, 2H), 7.44–7.40 (m, 1H), 7.22–7.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (d, J = 244.8 Hz), 140.2, 137.3 (d, J = 3.2 Hz), 128.8, 128.6 (d, J = 8.0 Hz), 127.2, 127.0, 115.6 (d, J = 21.3 Hz).

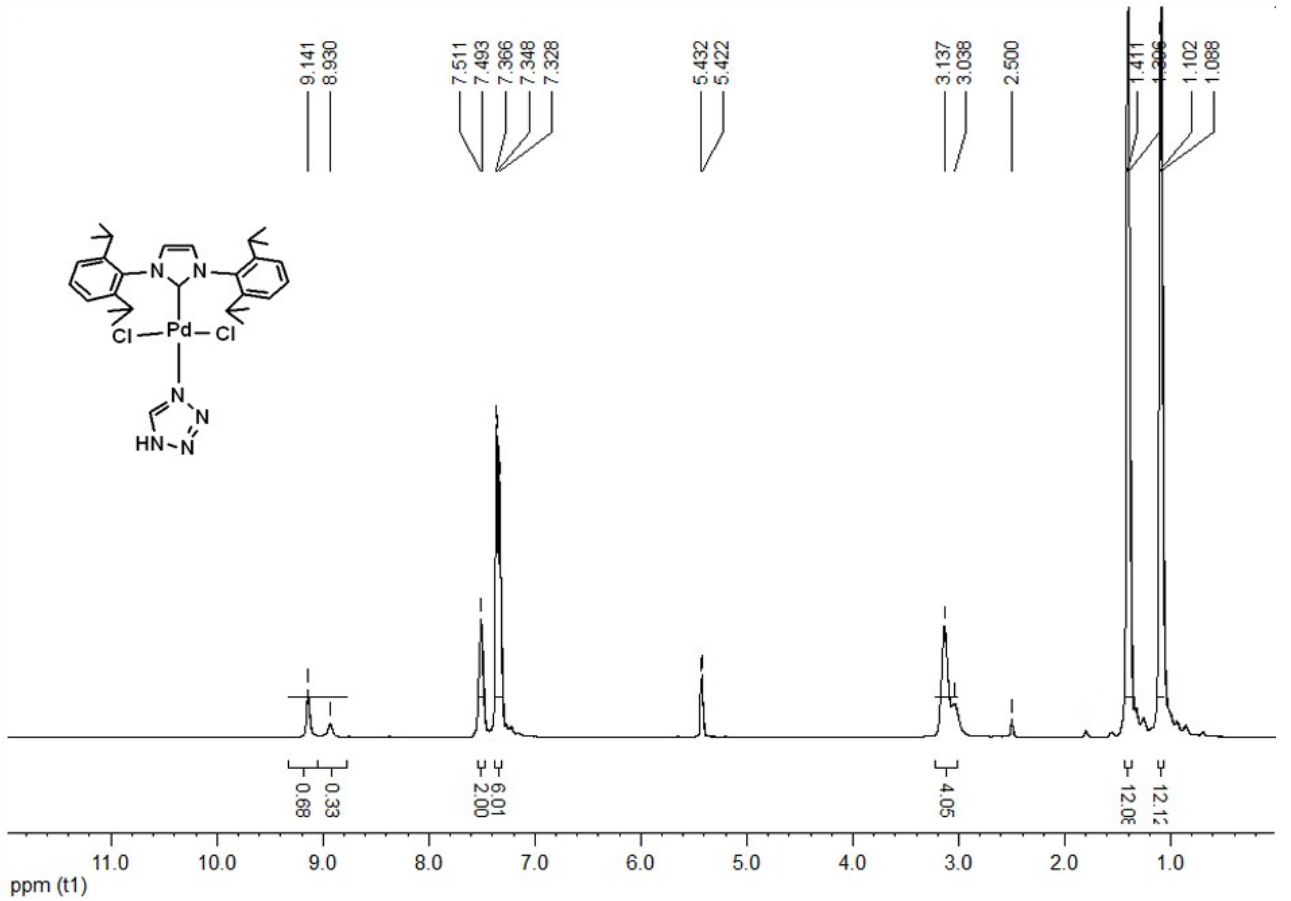
3-Fluorobiphenyl[3]

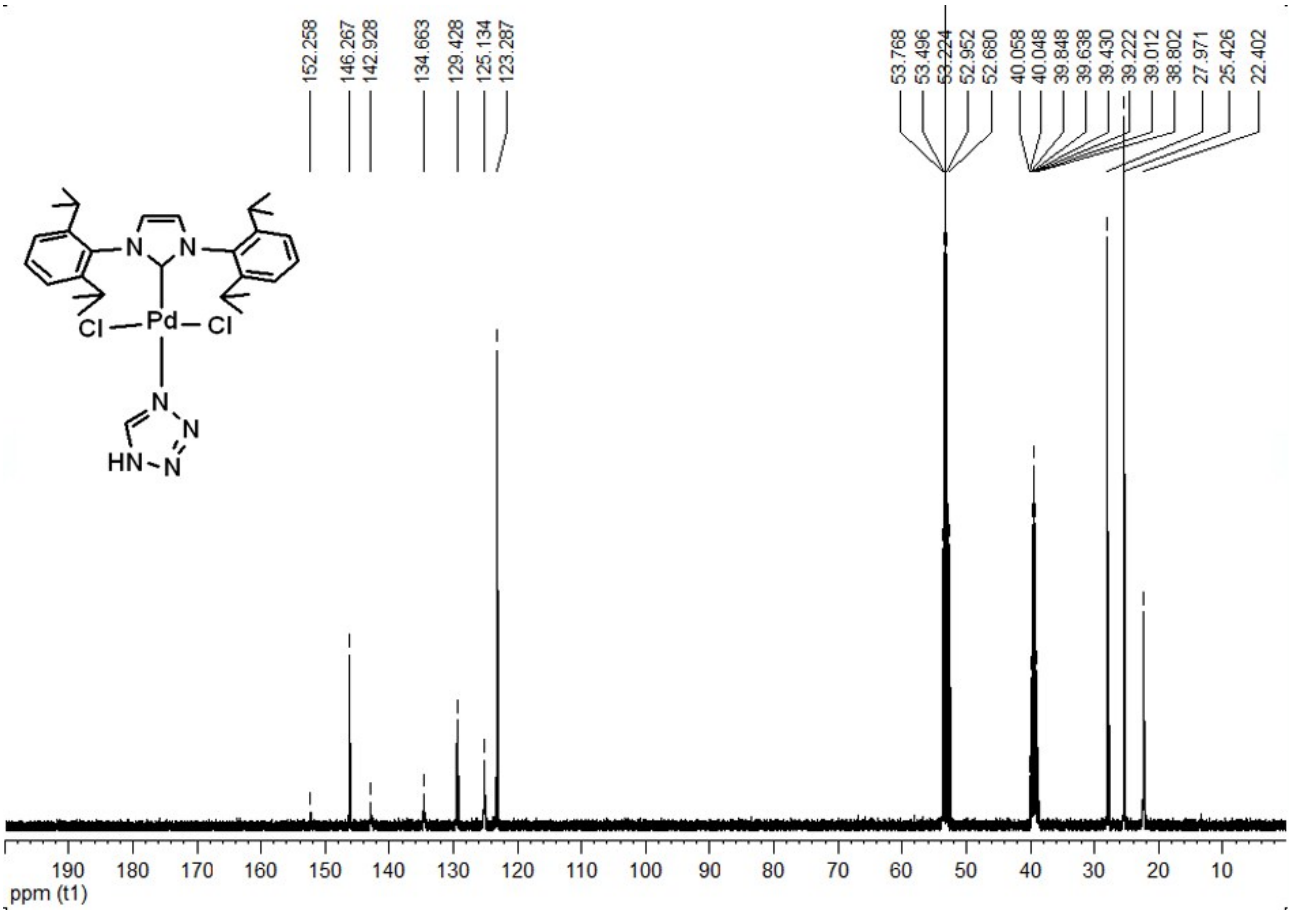
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.66 (m, 2H), 7.56–7.52 (m, 2H), 7.49–7.47 (m, 3H), 7.42–7.40 (m, 1H), 7.16–7.14 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2 (d, J = 244.0 Hz), 143.5 (d, J = 7.7 Hz), 139.9 (d, J = 2.2 Hz), 130.1 (d, J = 8.3 Hz), 128.8, 127.9, 127.0, 122.7 (d, J = 2.8 Hz), 114.1, 113.9 (d, J = 1.5 Hz).

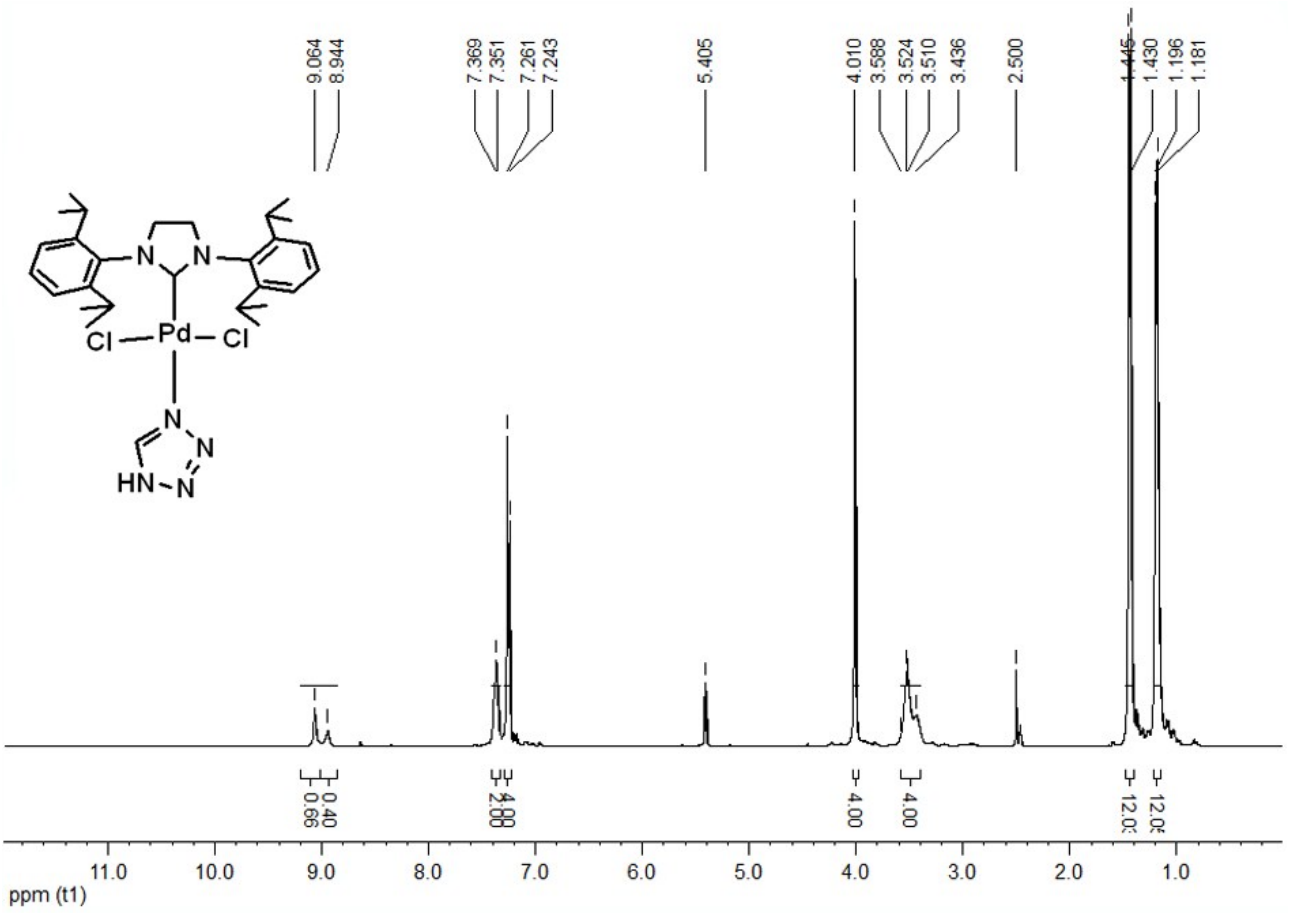
2-Fluorobiphenyl[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, J = 7.6 Hz, 2H), 7.53–7.51 (m, 3H), 7.47–7.44 (m, 1H), 7.41–7.36 (m, 1H), 7.30–7.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.8 (d, J = 246.3 Hz), 135.8 (d, J = 1.0 Hz), 130.8 (d, J = 3.4 Hz), 129.0 (d, J = 2.9 Hz), 128.9 (d, J = 43.5 Hz), 128.9 (d, J = 8.2 Hz), 128.4, 127.6, 124.3 (d, J = 3.7 Hz), 116.1 (d, J = 22.6 Hz).

4. ^{1}H and ^{13}C NMR spectra of 1–6



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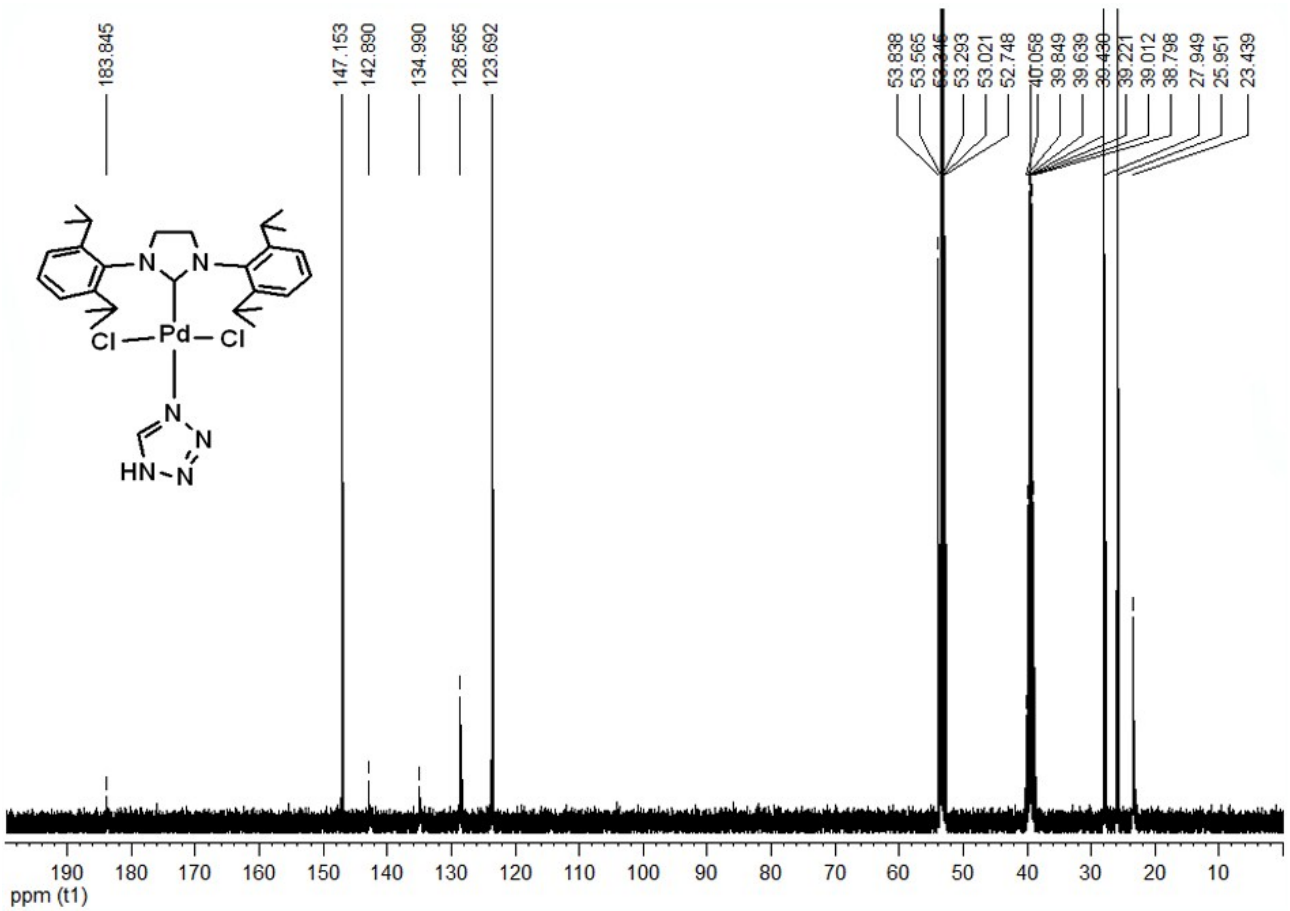
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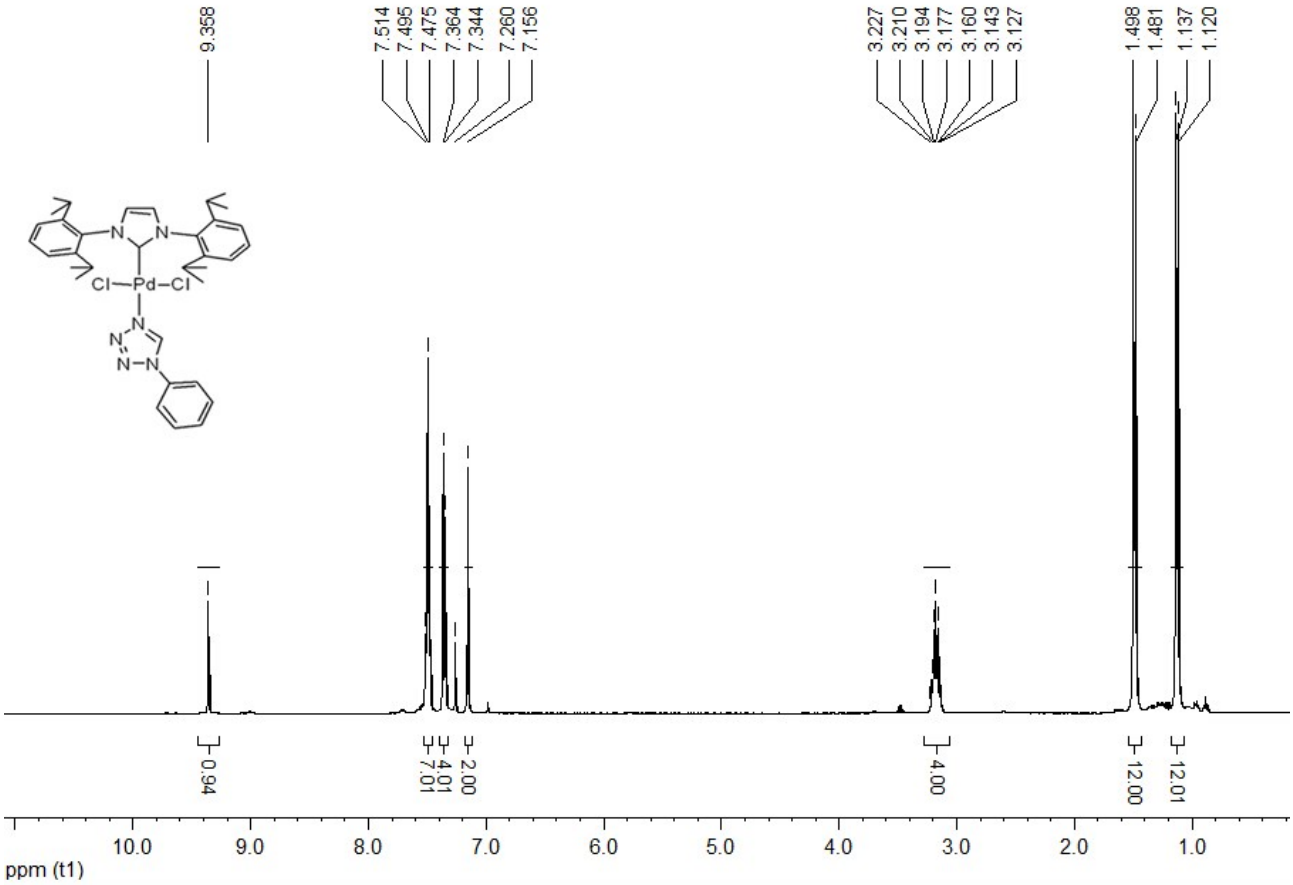
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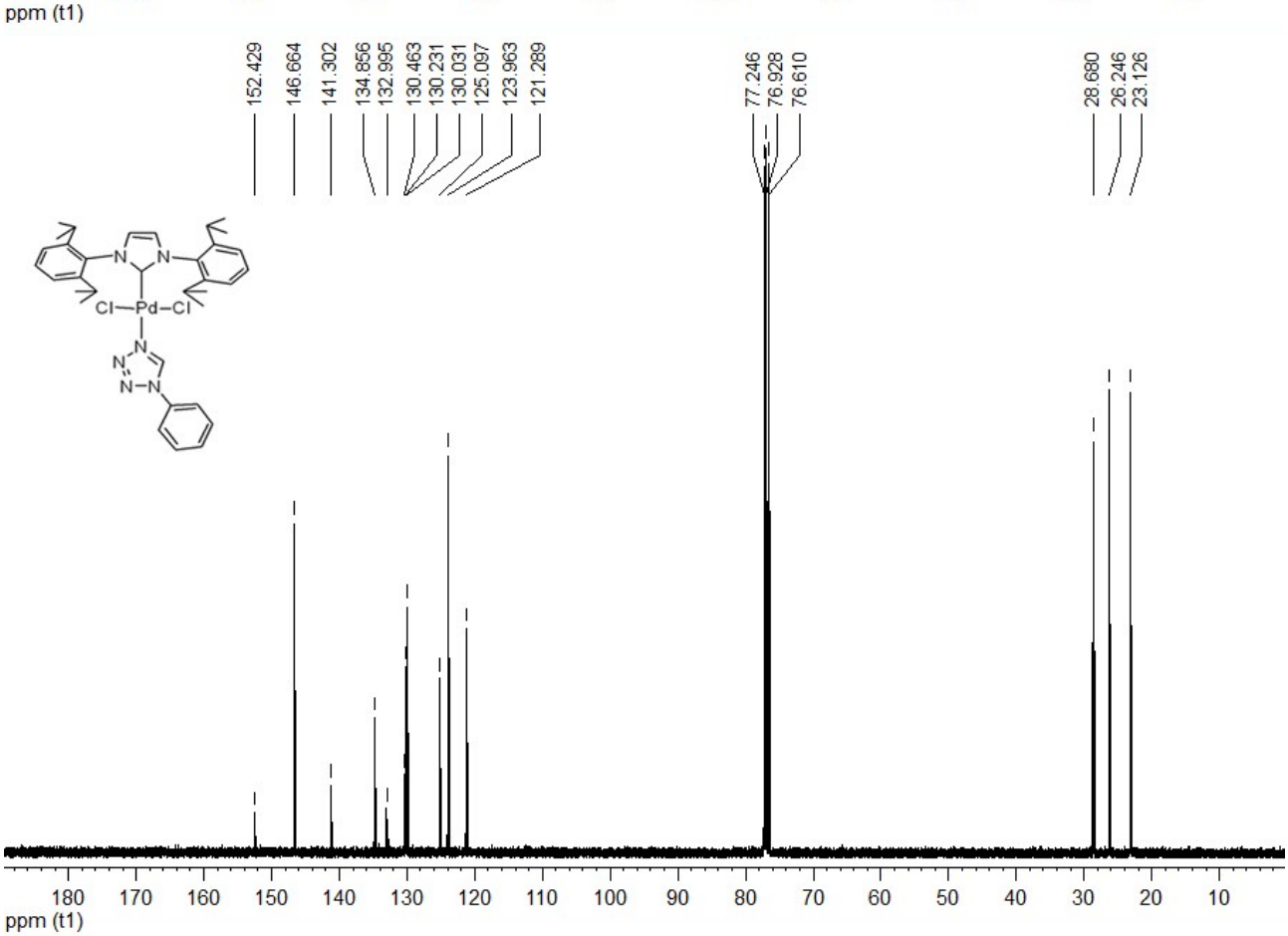
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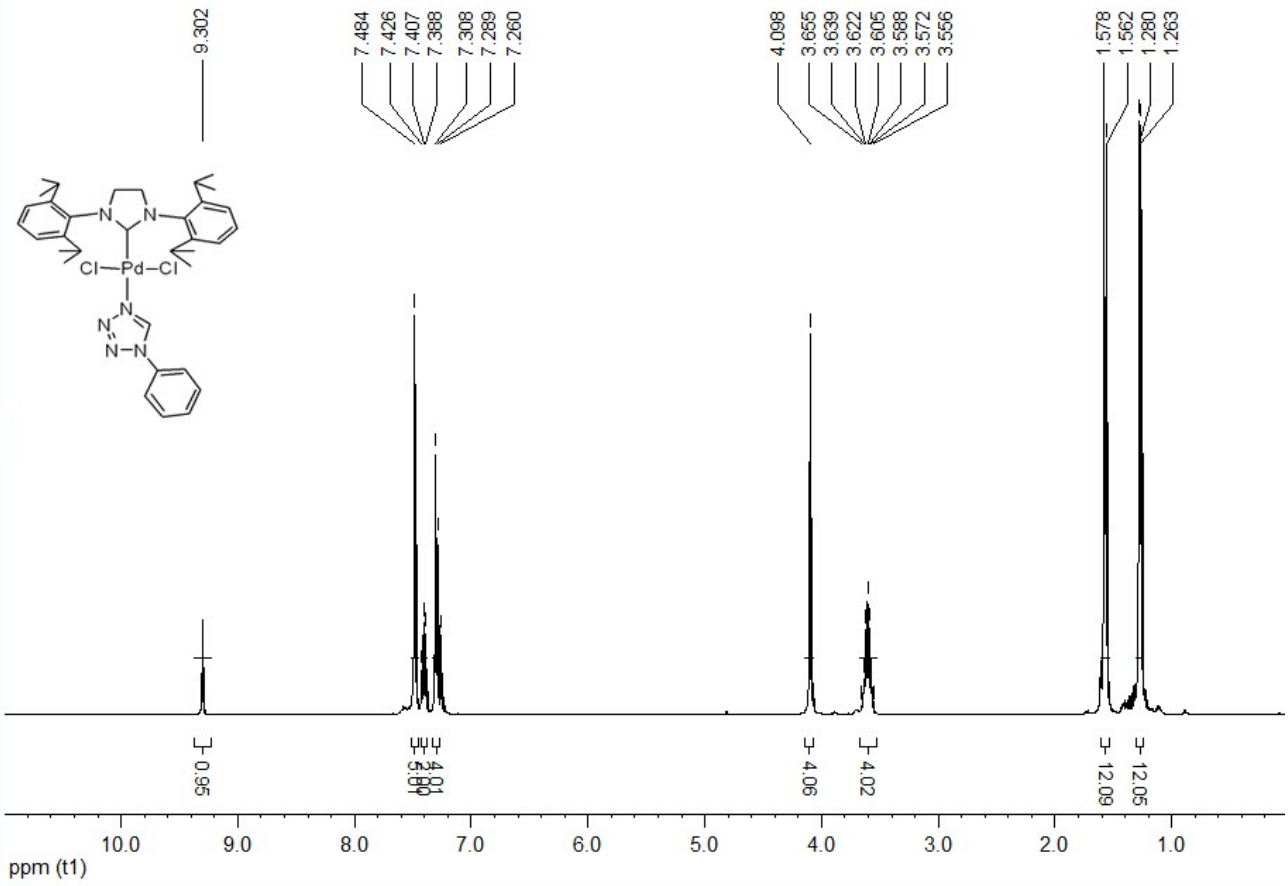
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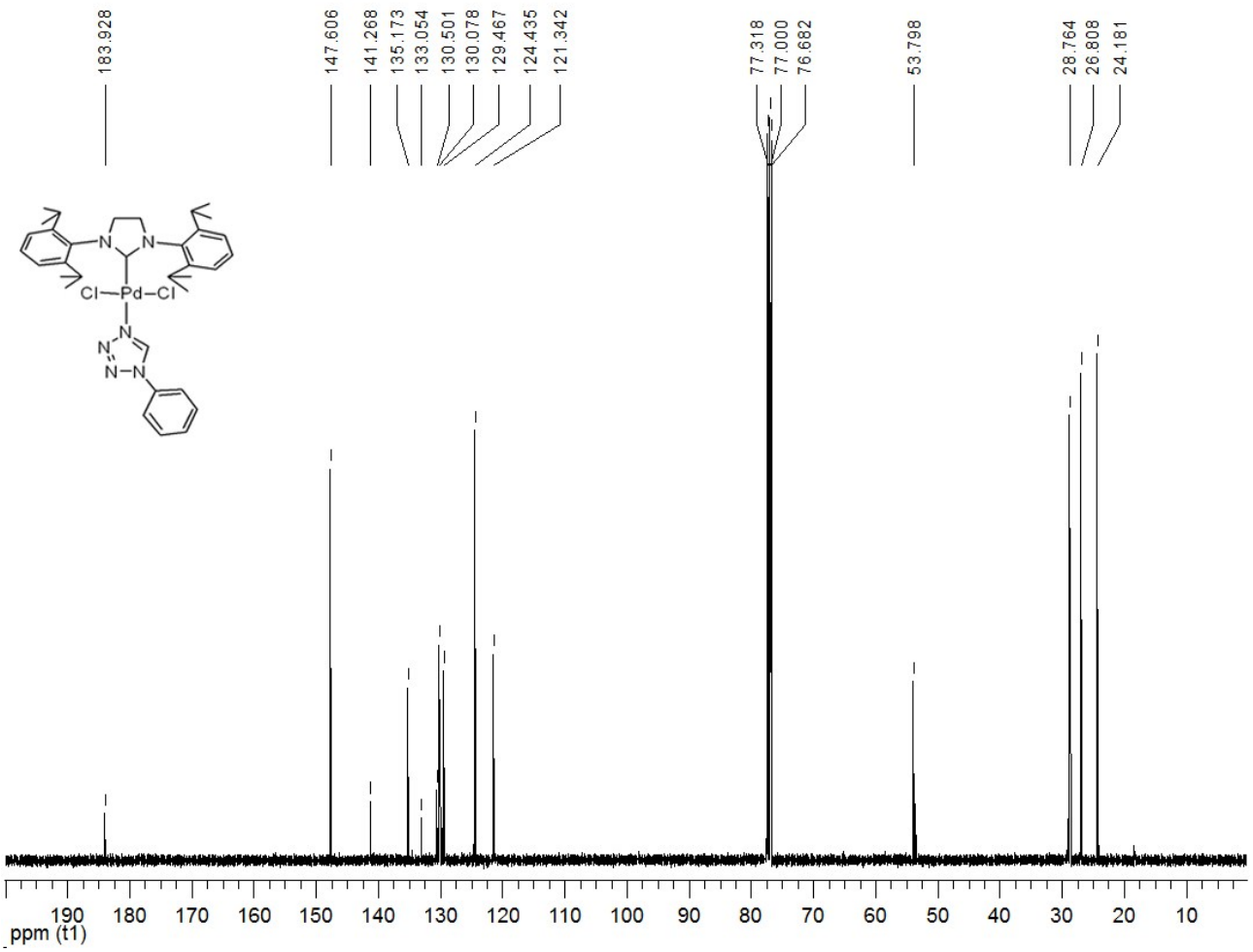
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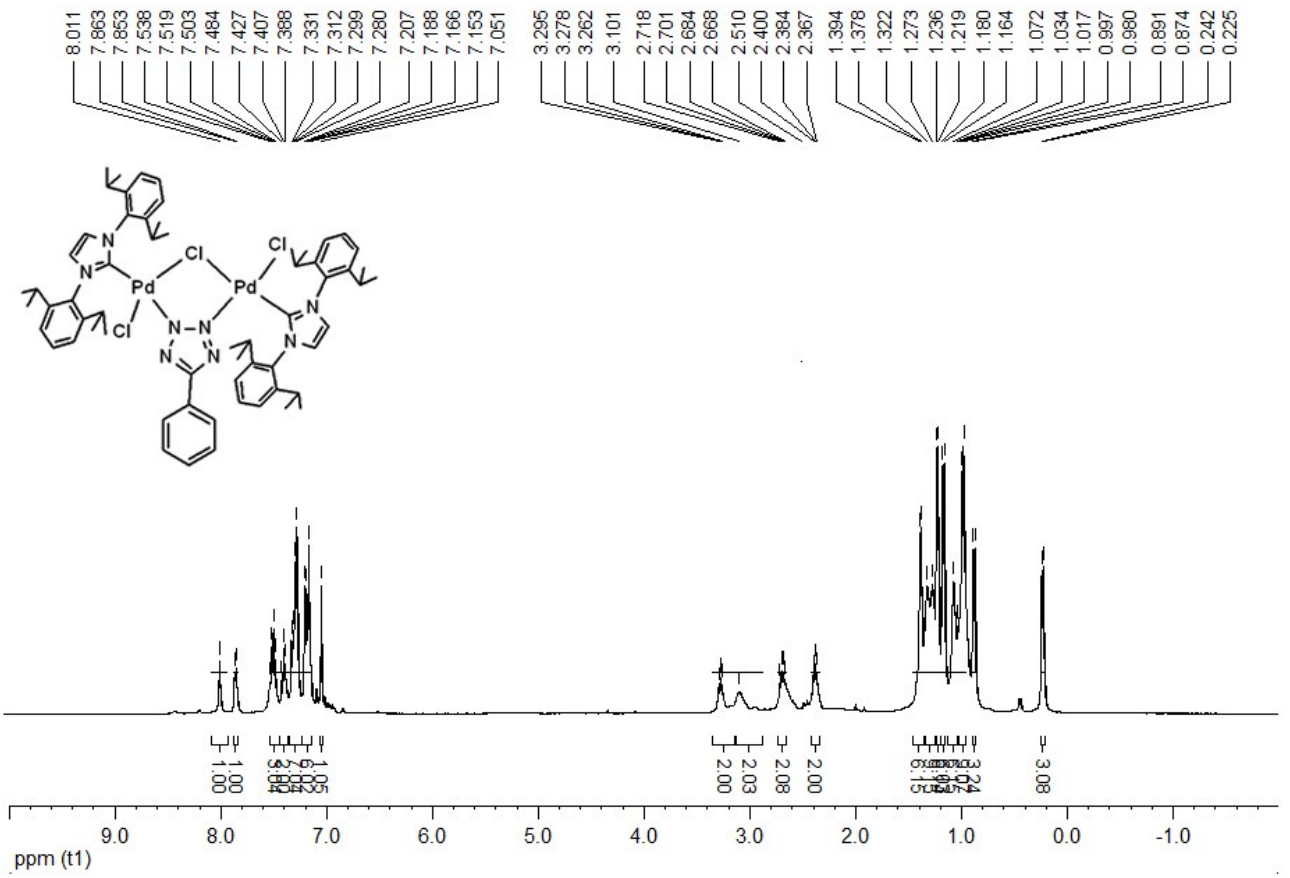
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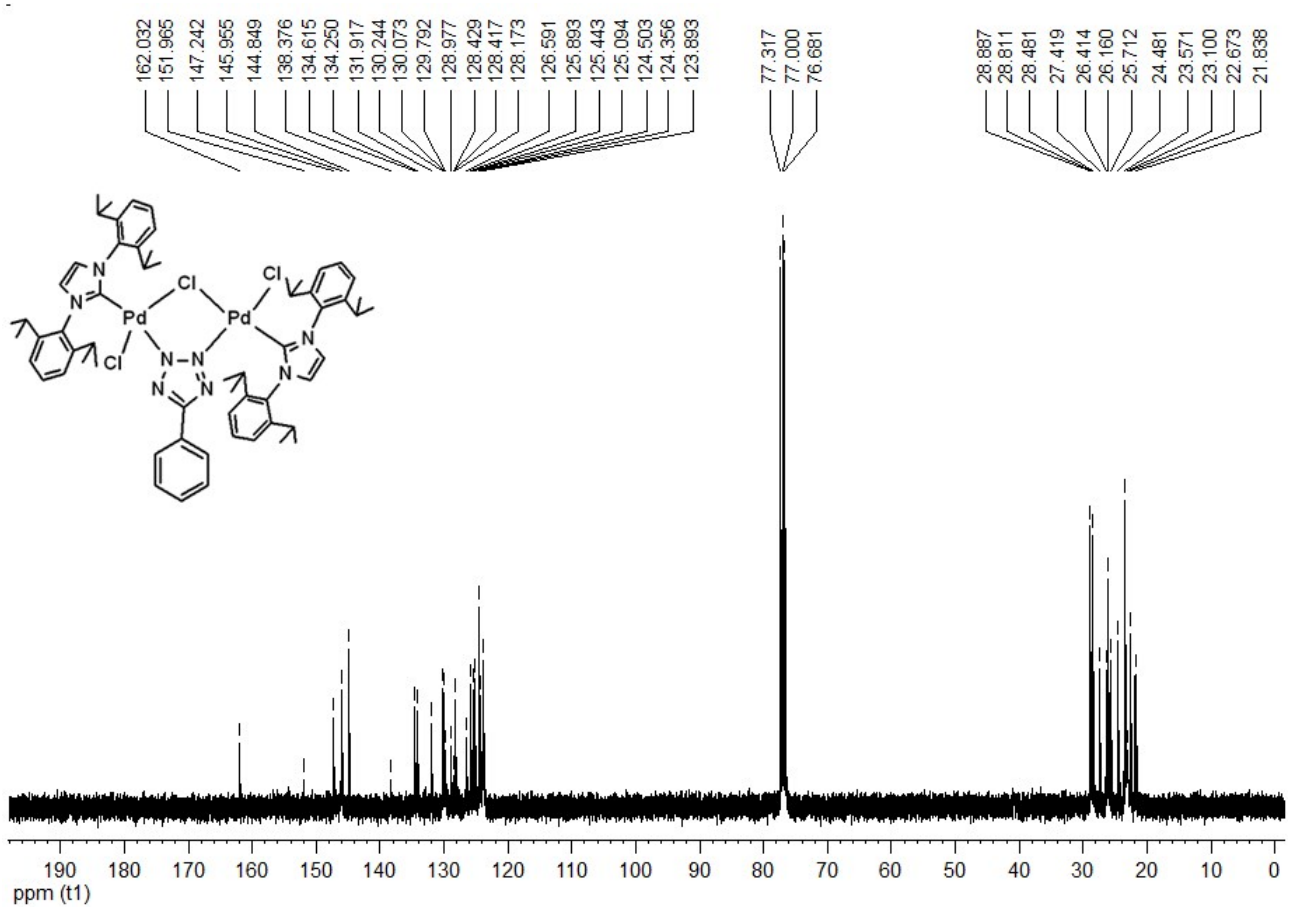
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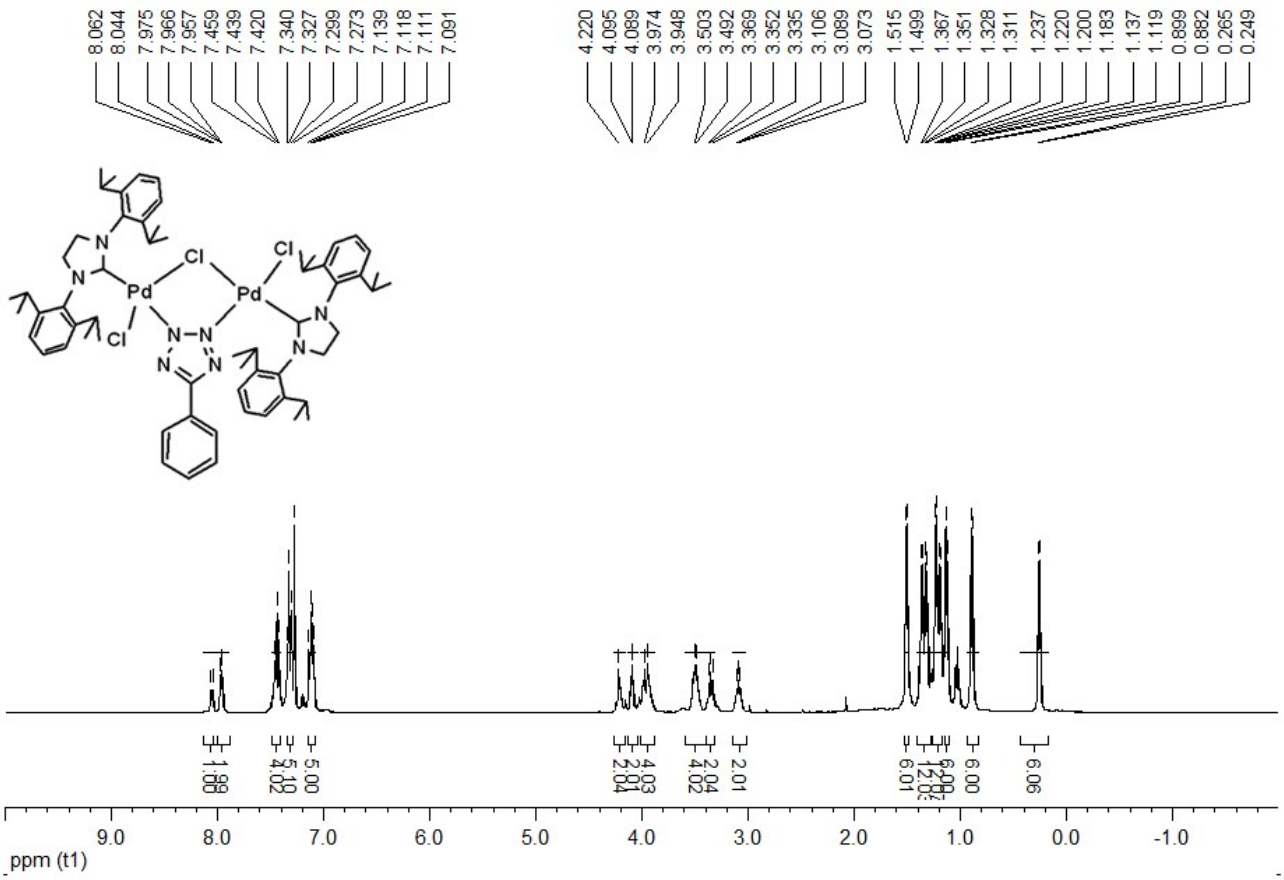
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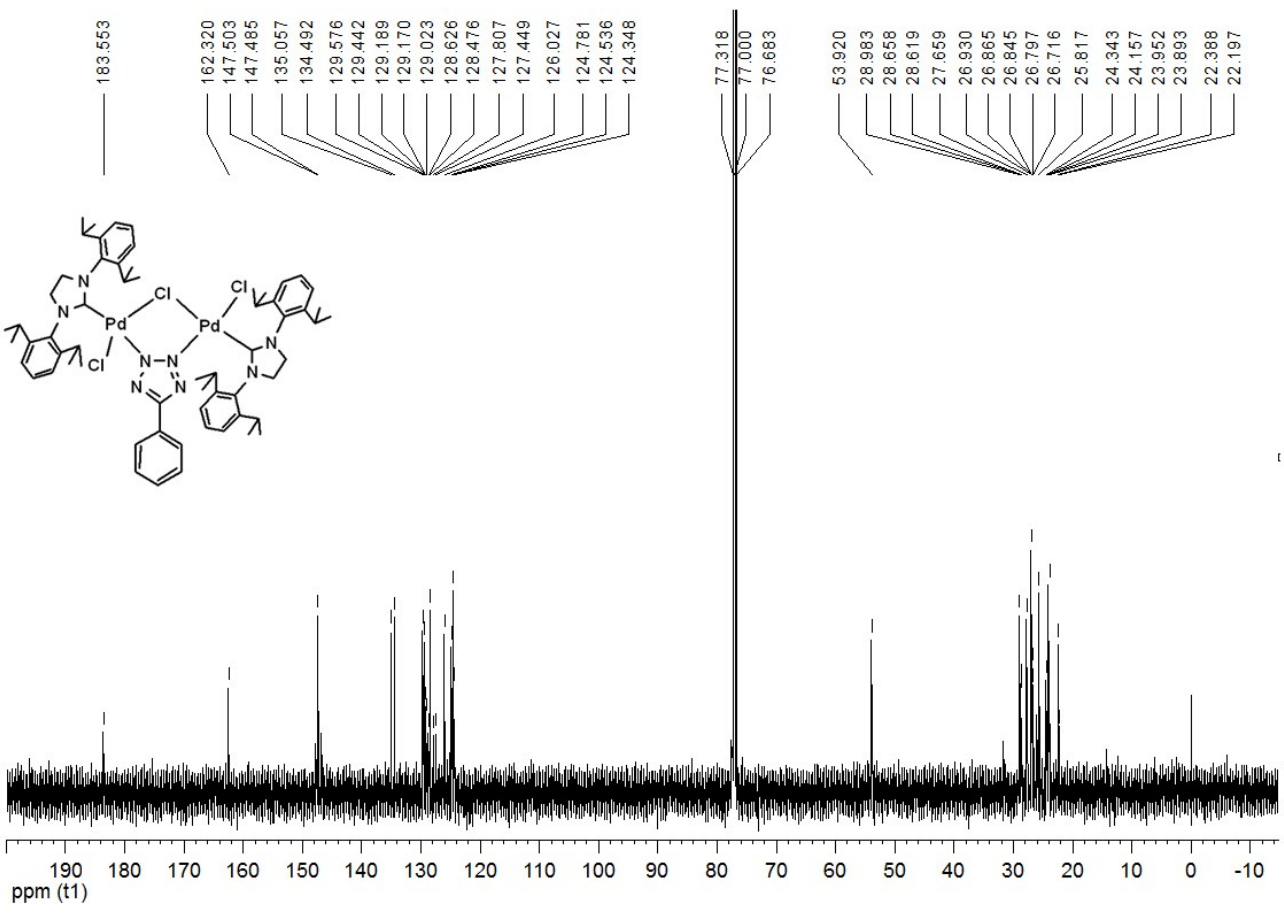
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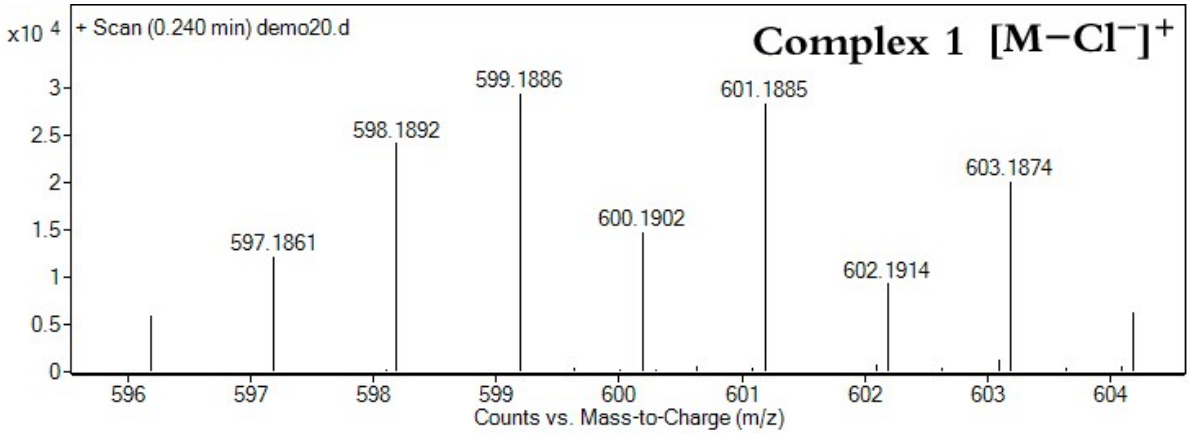
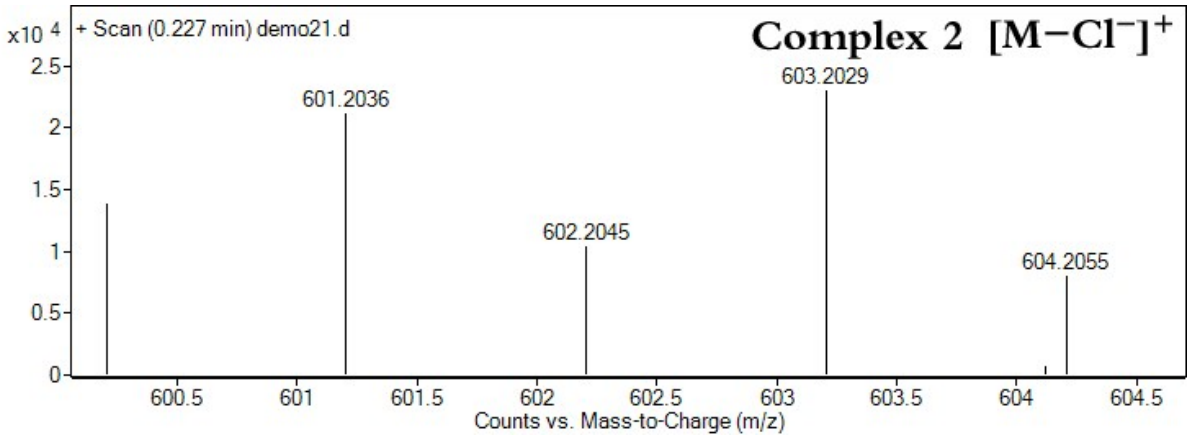
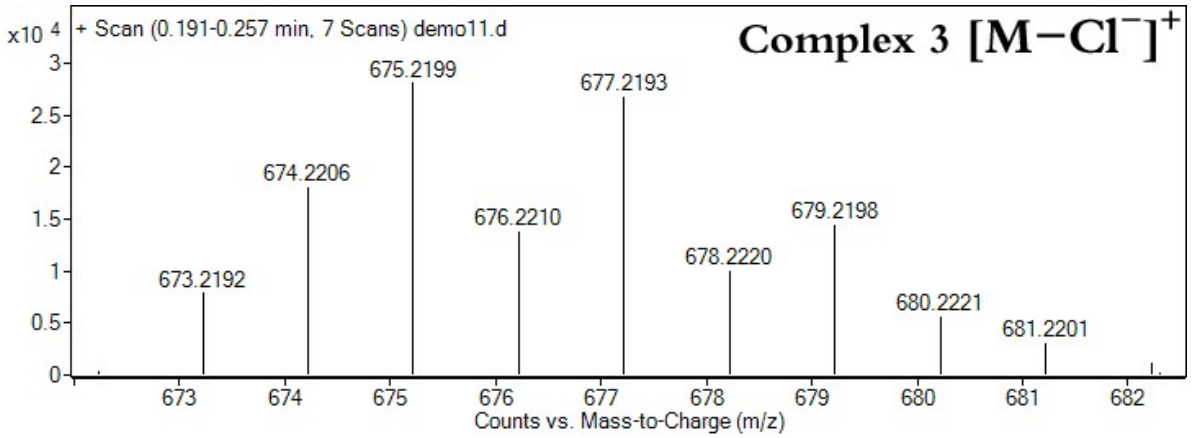
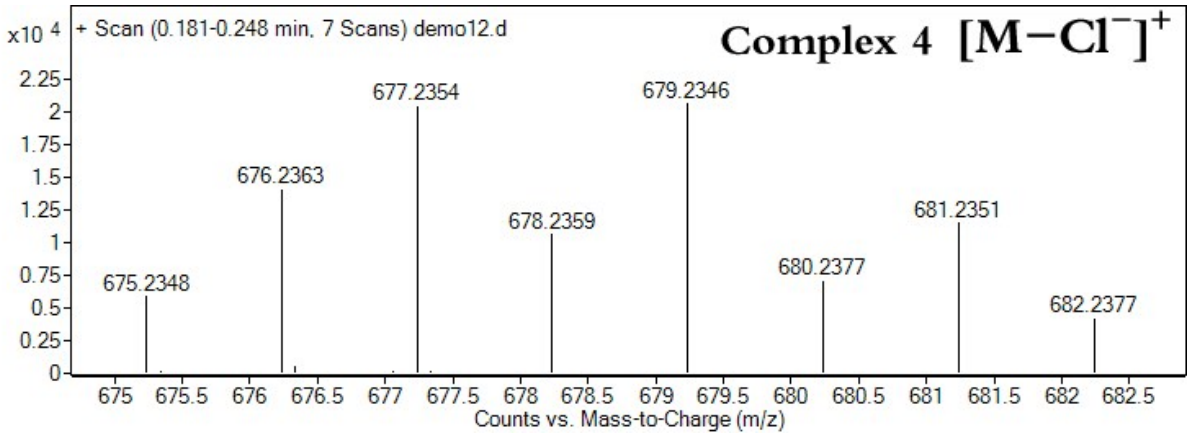
5. High-resolution mass spectrometry of 1–6





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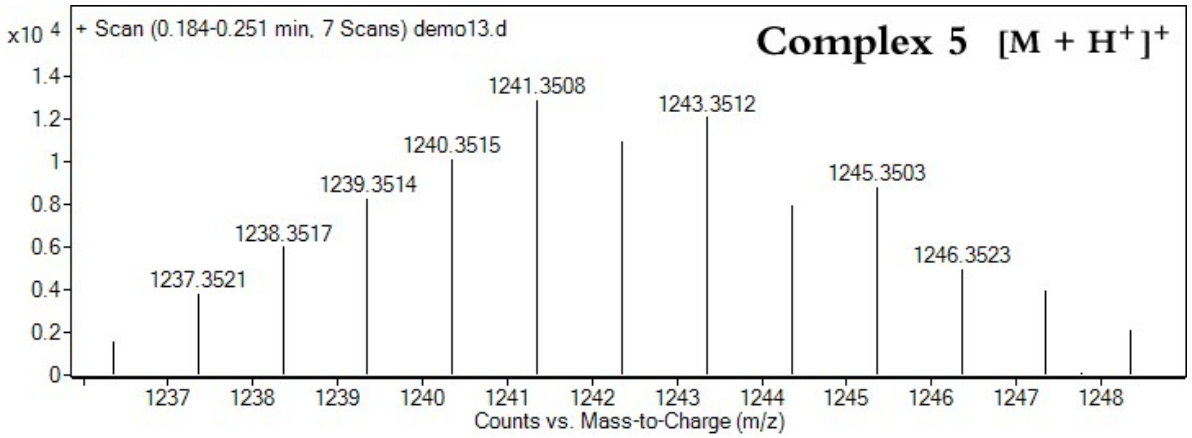
Counts vs. Mass-to-Charge (m/z)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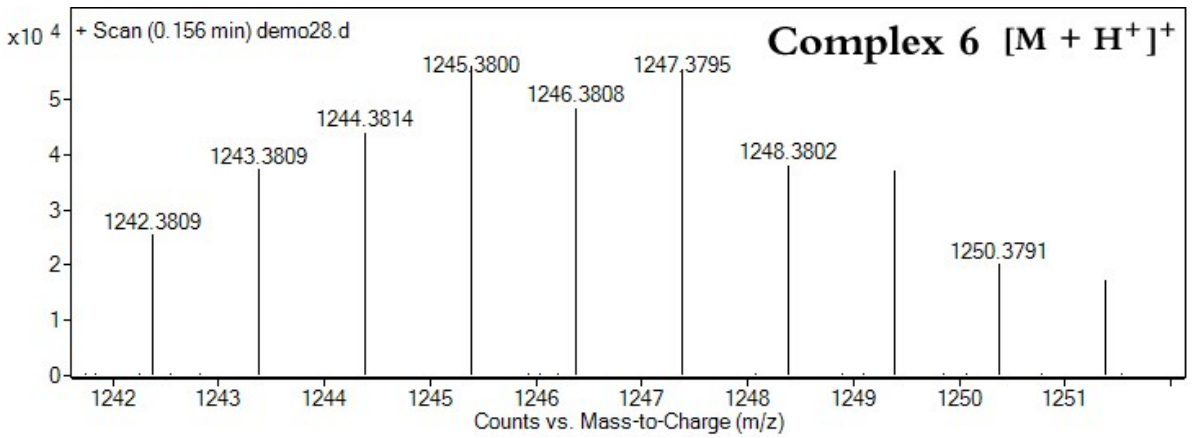
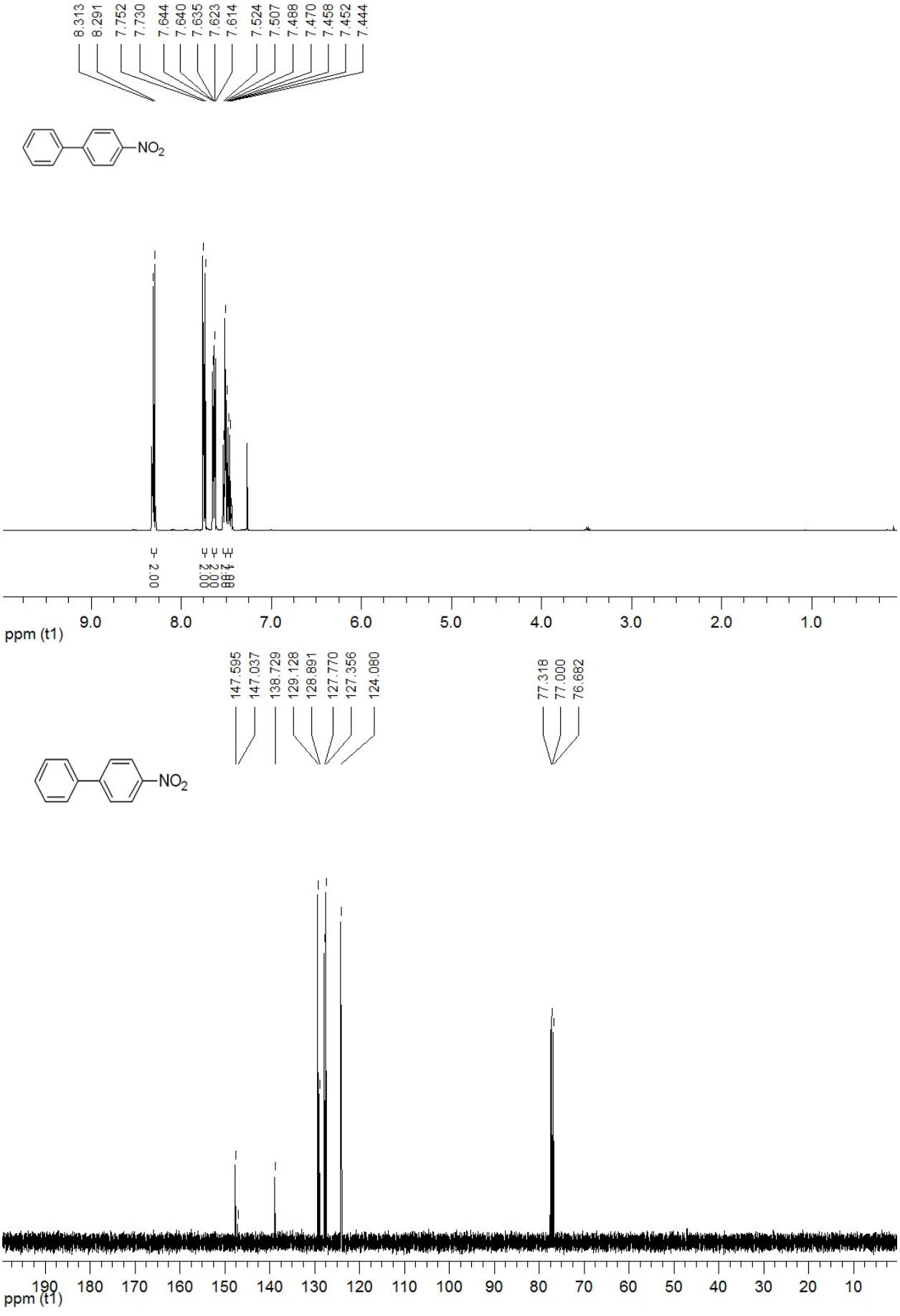
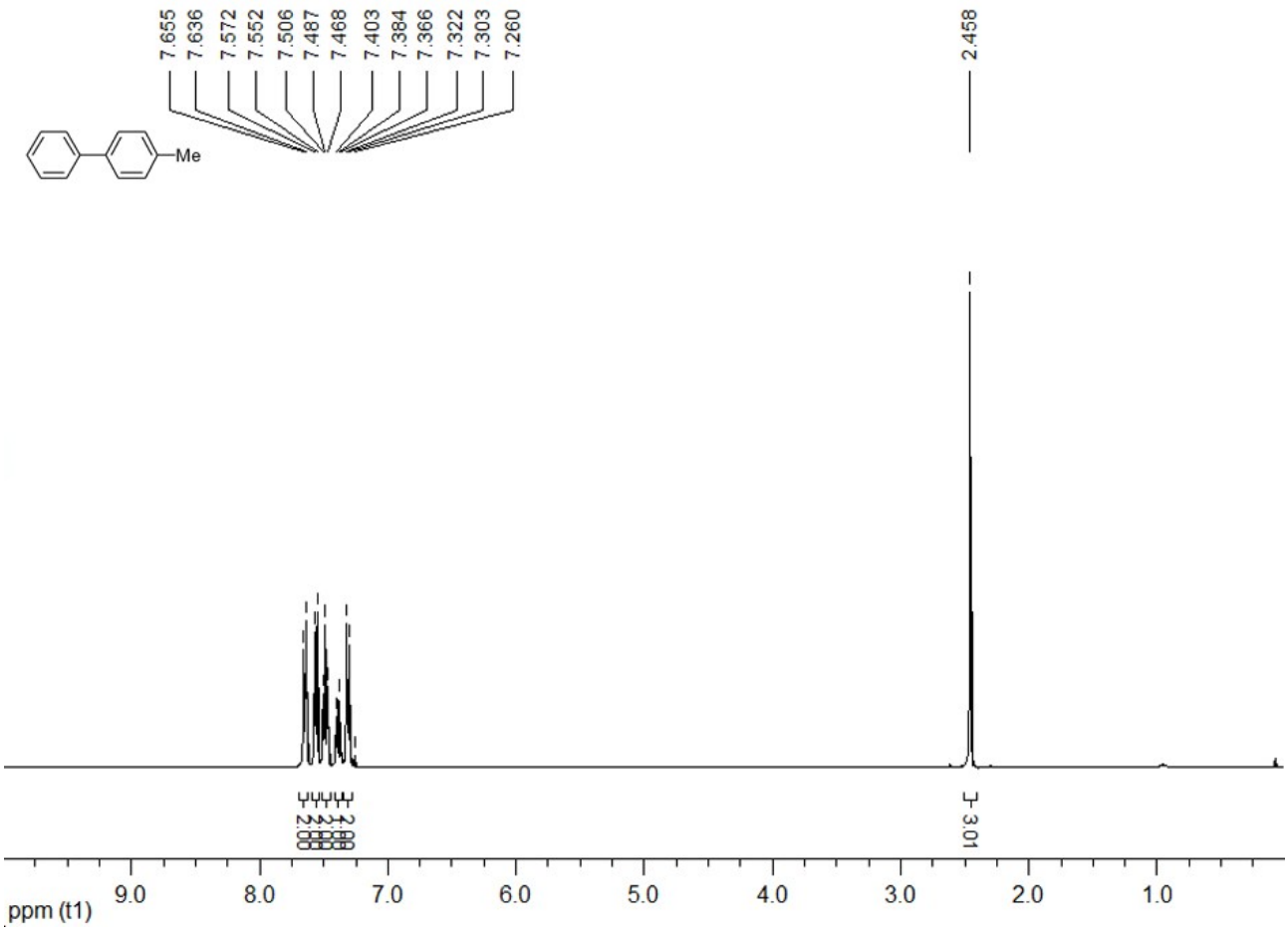
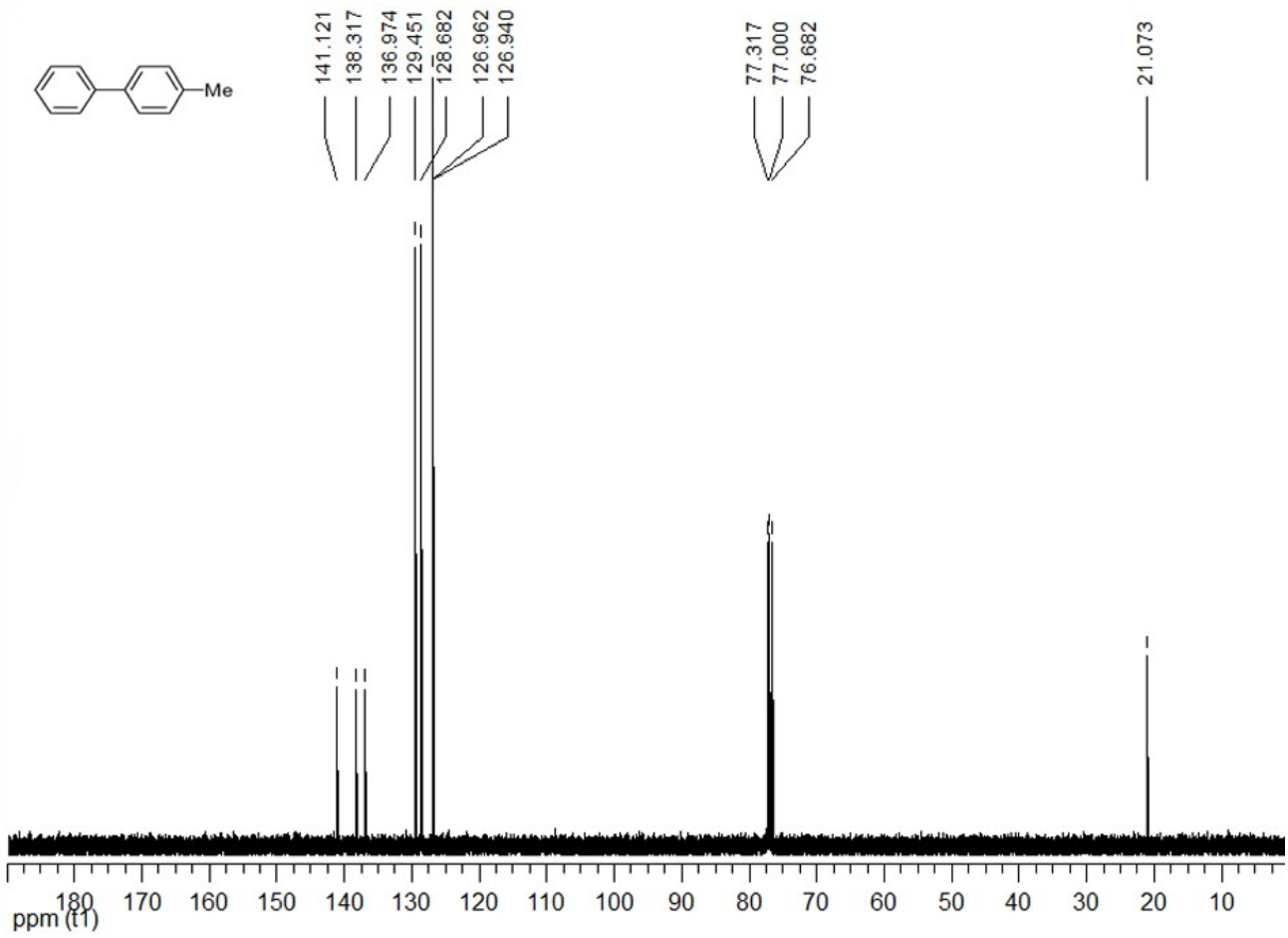
1246.3523
Counts vs. Mass-to-Charge (m/z)

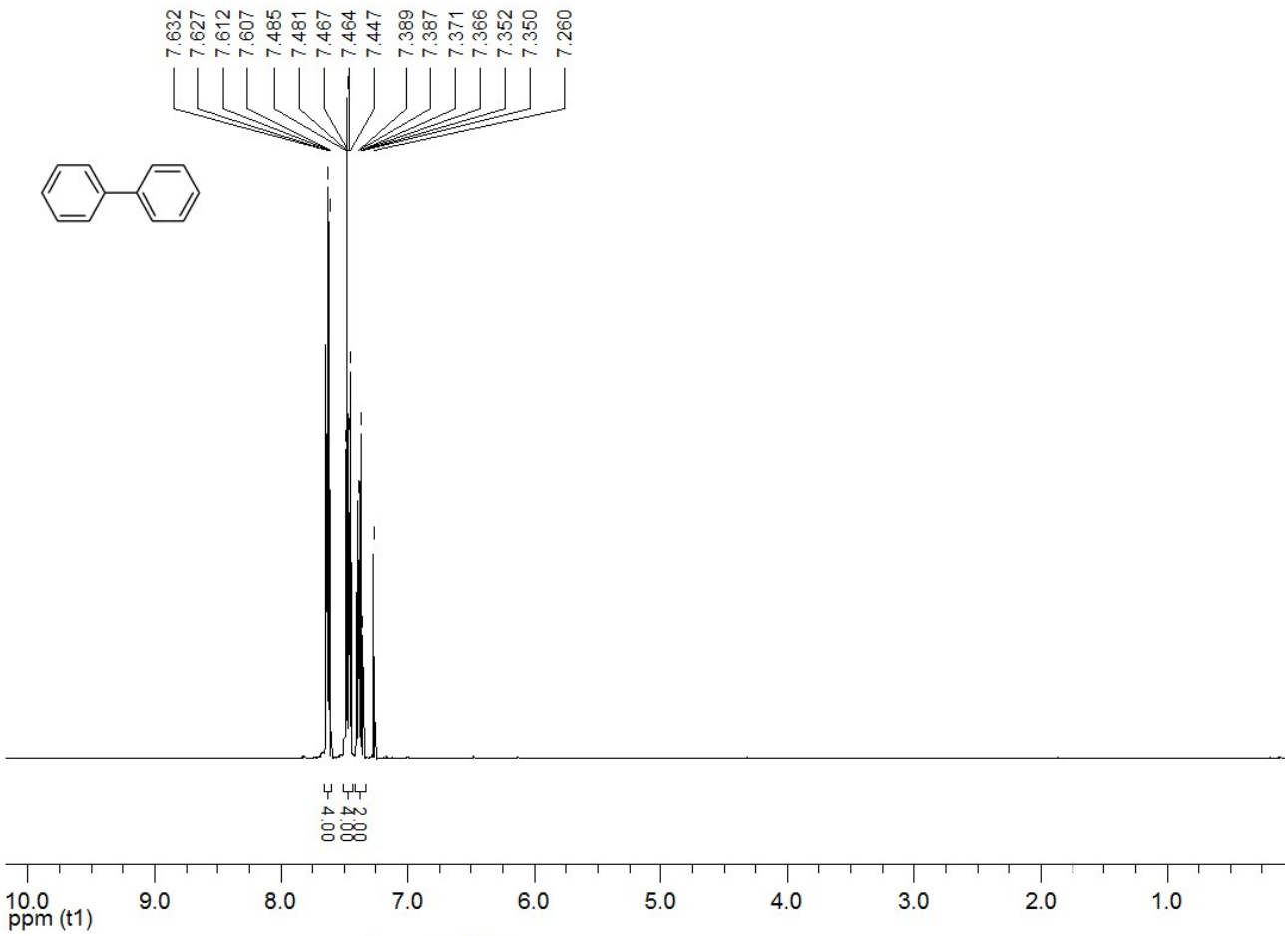

x10 4
+ Scan (0.156 min) demo28.d
Complex 6 [M + H⁺]⁺
1242.3809
1243.3809
1244.3814
1245.3800
1246.3808
1247.3795
1248.3802
1250.3791
Counts vs. Mass-to-Charge (m/z)

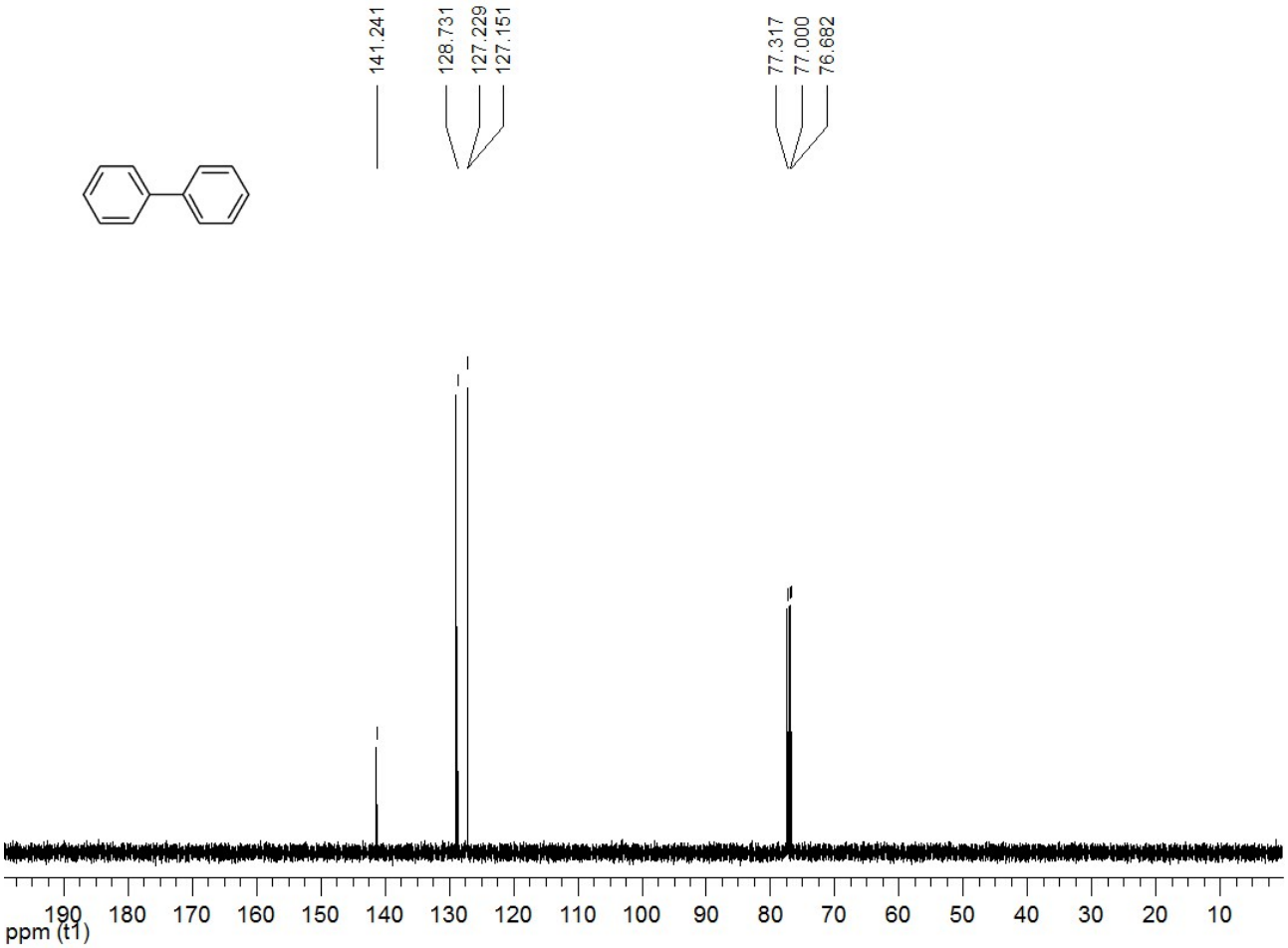
6. ^{1}H and ^{13}C NMR spectra of the pruducts

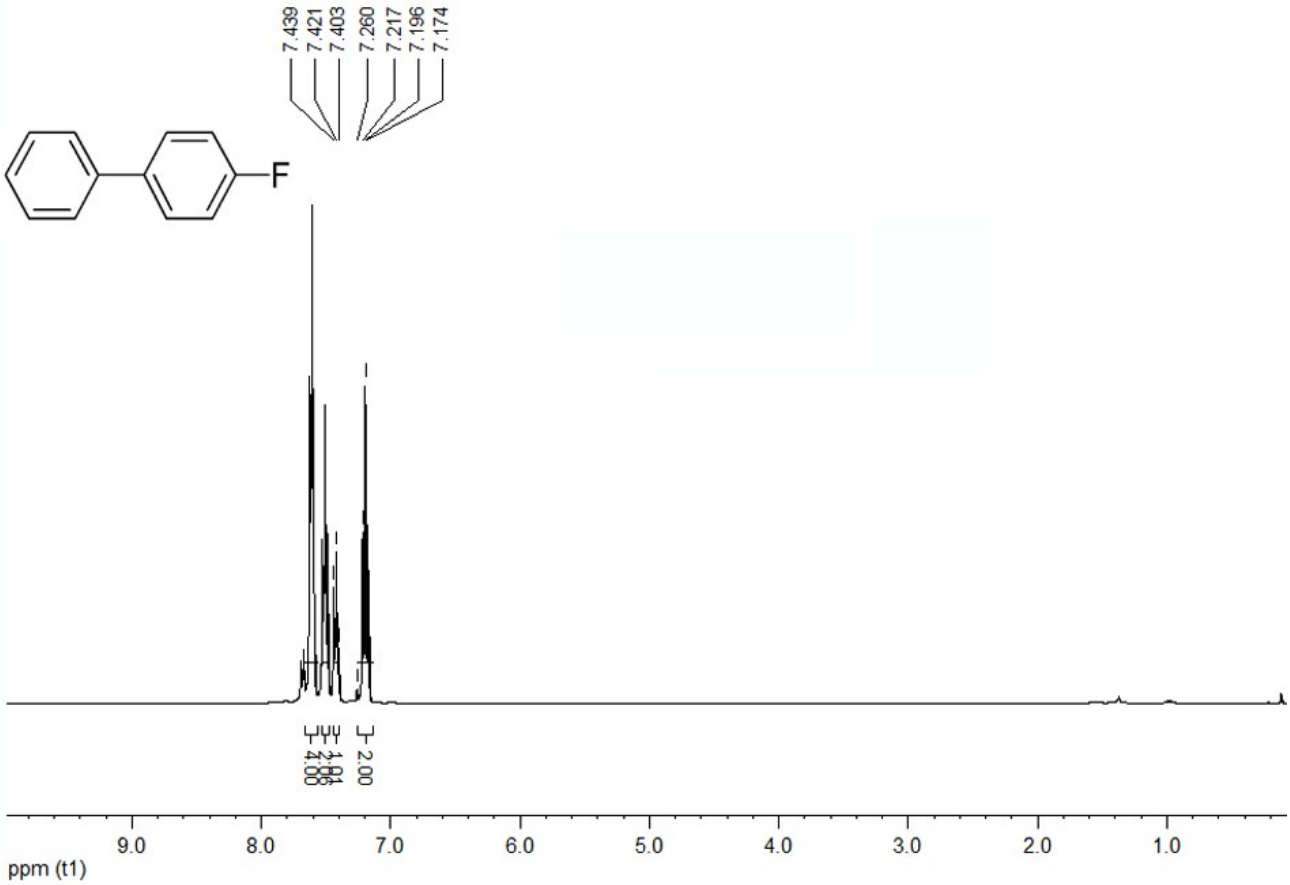


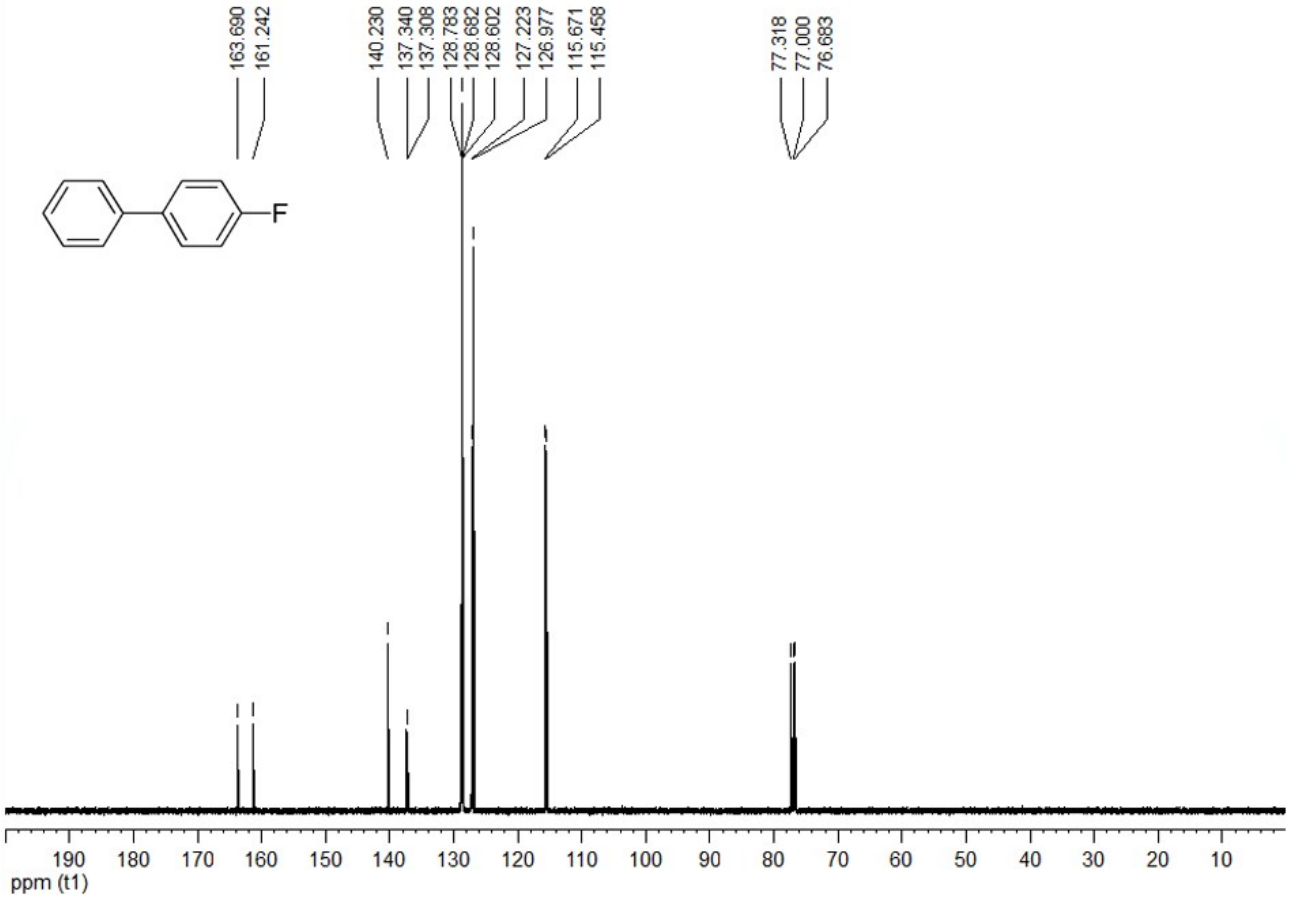

7.655
7.636
7.572
7.552
7.506
7.487
7.468
7.403
7.384
7.366
7.322
7.303
7.260
2.458
Me
3.01
ppm (t1)

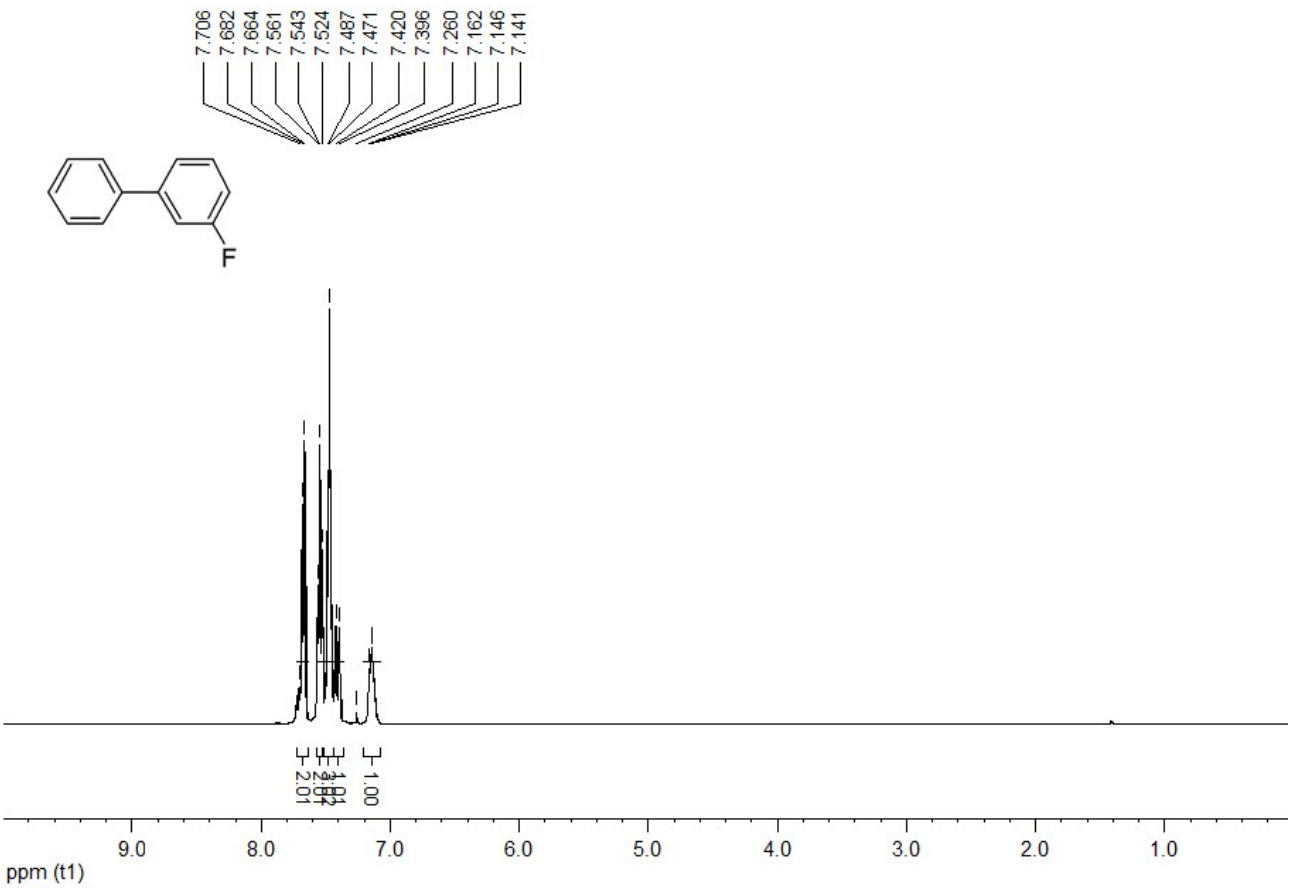

141.121
138.317
136.974
129.451
128.682
126.962
126.940
77.317
77.000
76.682
21.073
Me
ppm (t1)

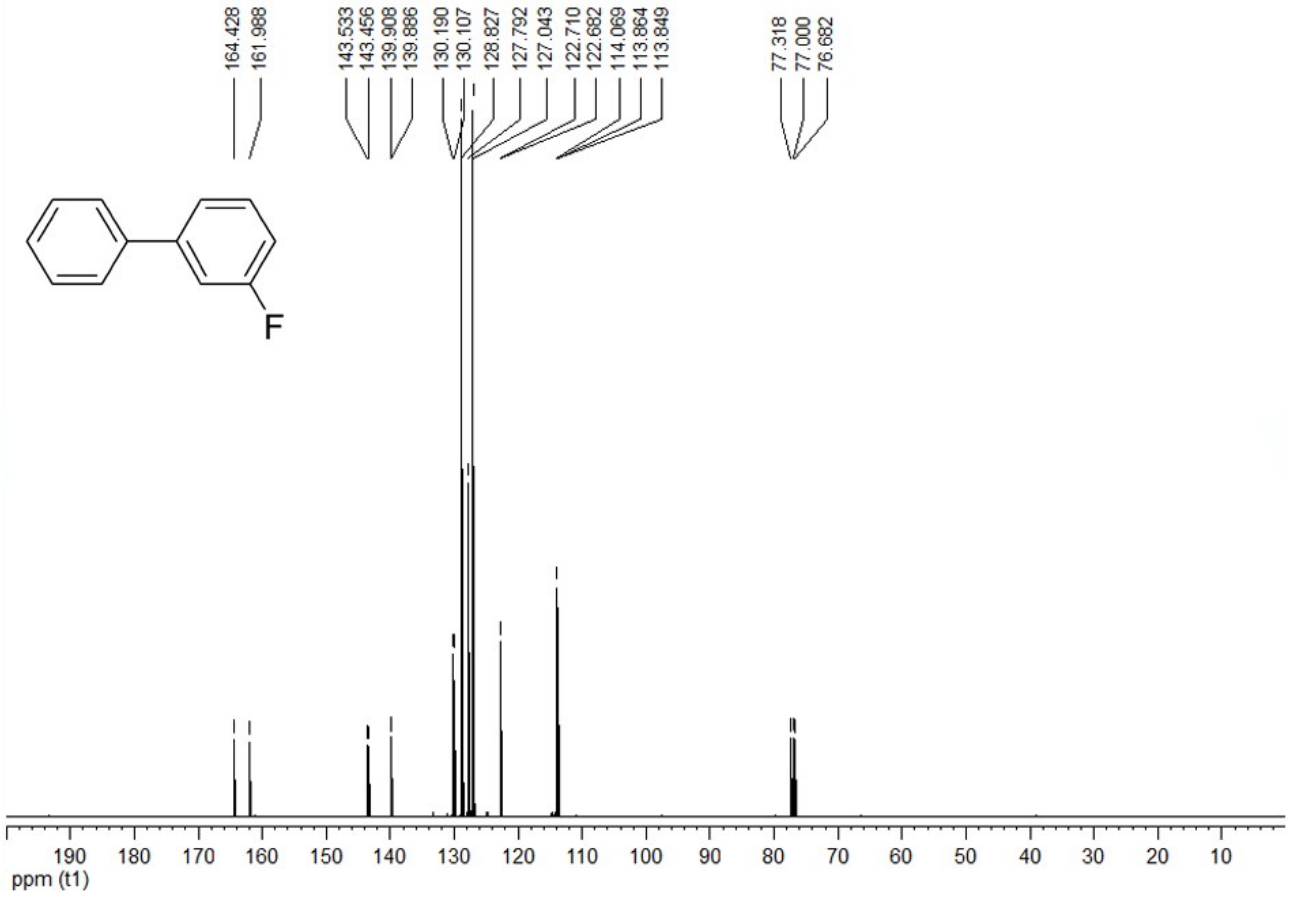

7.632
7.627
7.612
7.607
7.485
7.481
7.467
7.464
7.447
7.389
7.387
7.371
7.366
7.352
7.350
7.260
4.00
2.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

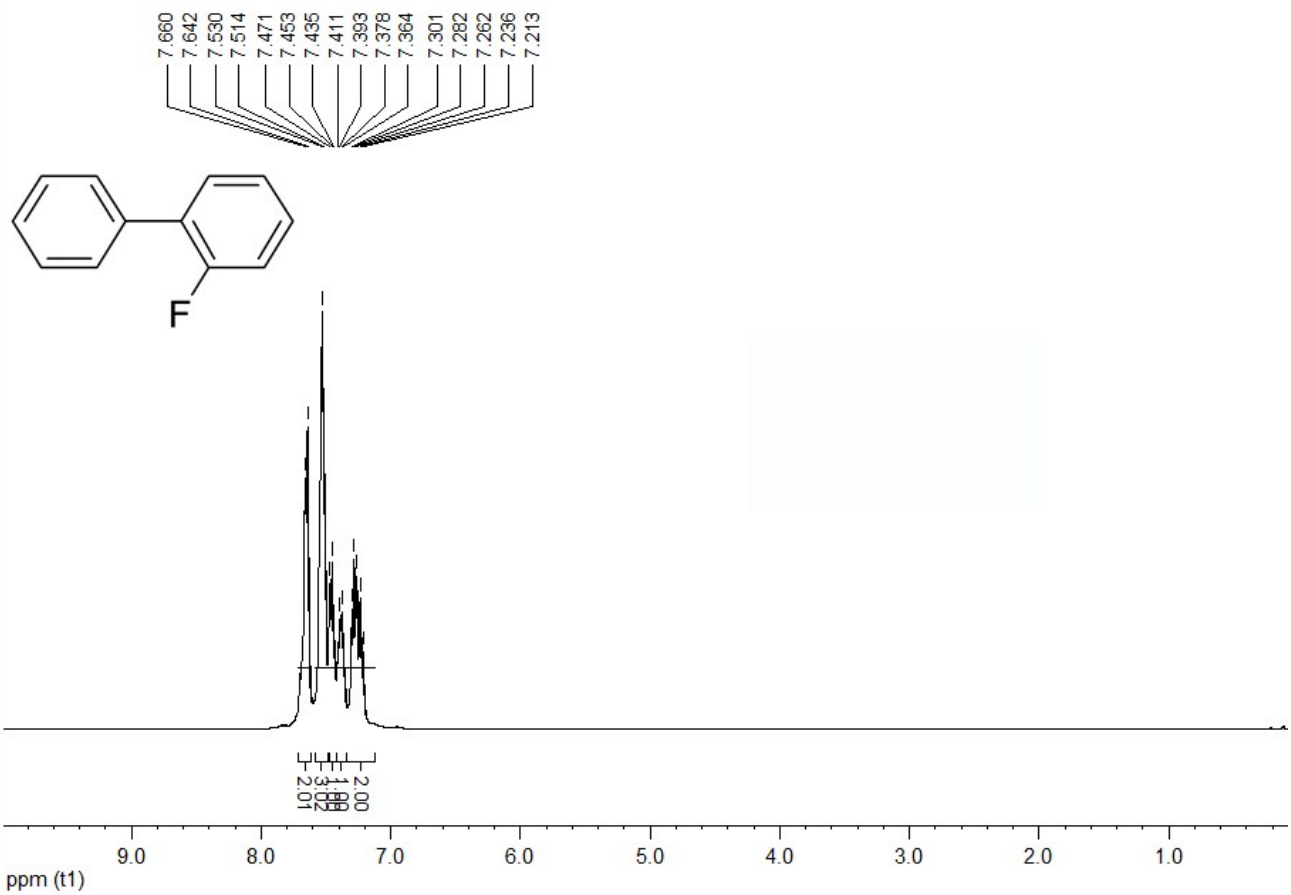

141.241
128.731
127.229
127.151
77.317
77.000
76.682
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

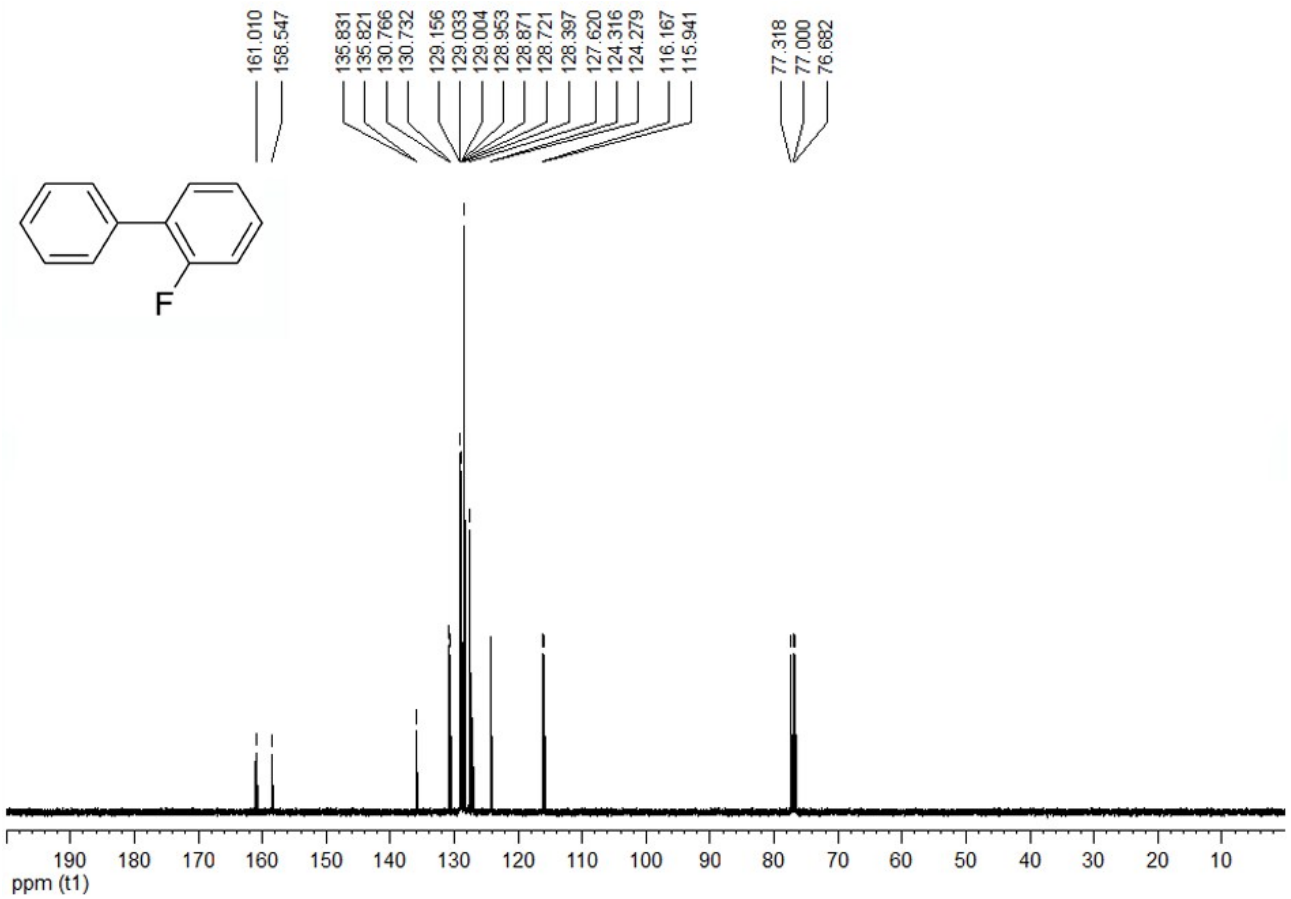

7.439
7.421
7.403
7.260
7.217
7.196
7.174
F
4.00
4.08
3.91
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


163.690
161.242
140.230
137.340
137.308
128.783
128.682
128.602
127.223
126.977
115.671
115.458
77.318
77.000
76.683
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)


7.706
7.682
7.664
7.561
7.543
7.524
7.487
7.471
7.420
7.396
7.260
7.162
7.146
7.141
F
2.01
3.13
2.04
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


164.428
161.968
143.533
143.456
139.908
139.886
130.190
130.107
128.827
127.792
127.043
122.710
122.682
114.069
113.864
113.849
77.318
77.000
76.682
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)


7.660
7.642
7.530
7.514
7.471
7.453
7.435
7.411
7.393
7.378
7.364
7.301
7.282
7.262
7.236
7.213
F
2.01
2.03
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


161.010
158.547
135.831
135.821
130.766
130.732
129.156
129.033
129.004
128.953
128.871
128.721
128.397
127.620
124.316
124.279
116.167
115.941
77.318
77.000
76.682
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)

7. References

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2. M. E. Budén, J. F. Guastavino and R. A. Rossi, *Org. Lett.*, 2013, **15**, 1174.

3. J. Yu, J. Liu, G. Shi, C. Shao and Y. Zhang, *Angew. Chem. Int. Ed.*, 2015, **54**, 4079.