Supporting Information:

The Impact of the Physical State and the Reaction Phase in the Direct Mechanocatalytic Suzuki-Miyaura Coupling Reaction

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I. Quantum Chemical Calculations (DFT)

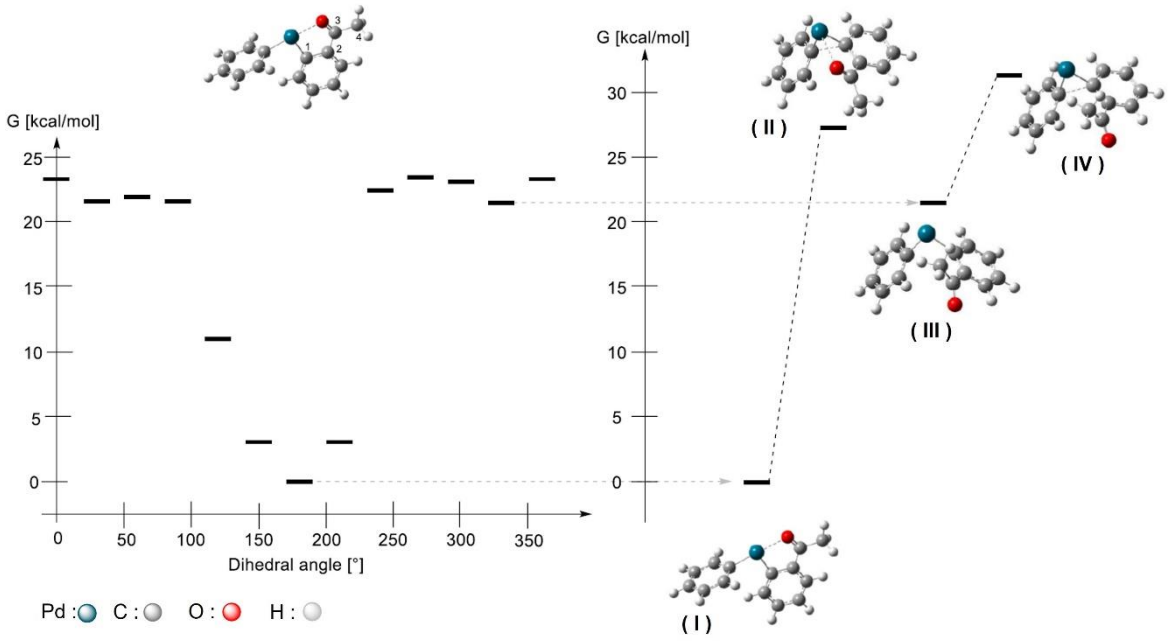
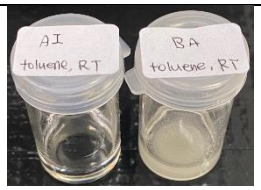


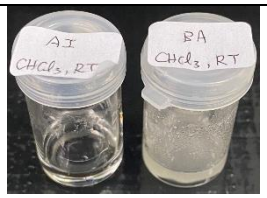
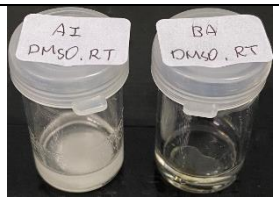
Figure S1. ΔG value as a function of the dihedral angle (left) and transition states (right) calculated by means of wB97XD in combination with the 6-31* and def2TZVP basis sets.

To determine the most stable starting conformation of the elimination step we varied the dihedral angle between C1, C2, C3 and C4 and calculated the thermodynamical parameters by DFT calculations. Figure S1 (left side) shows the ΔG value as a function of the dihedral angle. Two obvious minima were found for dihedral angles of 180° and 320°. It turned out that a dihedral angle of 180° results in a strong interaction between the Palladium and oxygen atom and thus this conformation (I) is the most stable one. The barrier to reach the transition state (II) of the reductive elimination from this conformation (I) amounts to 27.18 kcal/mol (see right side of Figure S1). The conformation with a dihedral angle of 320° (III) is less stable than (I) by 21.51 kcal/mol but the barrier for the transition state for the reductive elimination of this conformation only amounts to 9.92 kcal/mol. However, the stability of conformation (I) prevents the formation of transition state (II) and the formation of the conformation (III) and thus no product is formed.

II. Solubility test of 4-iodobiphenyl and phenylboronic acid

Table S2. Solubility test of 4-iodobiphenyl and phenylboronic acid in different LAG solvents.[a]

Entry	Solvent	Solubility		
		4-Iodobphenyl	Phenylboronic acid	
1	Toluene	Completely dissolved	Partially dissolved	
2[b]	Toluene	Completely dissolved	Completely dissolved	

3	Hexane	Slightly dissolved	Slightly dissolved	
4	CH_2Cl_2	Completely dissolved	Partially dissolved	
5	$CHCl_3$	Completely dissolved	Partially dissolved	
6	MeCN	Partially dissolved	slightly dissolved	
7	DMSO	Partially dissolved	Completely dissolved	
8	H_2O	Insoluble	Partially dissolved	
9	EtOH	Partially dissolved	Completely dissolved	

[a] All measurements were confirmed after sonication (1 min). The concentration was set at 1 mM. [b] After shaking (1 min) in an oil bath at 80 °C.

III. Characterization of mono- and diethyl phenylboronate using NMR and IR

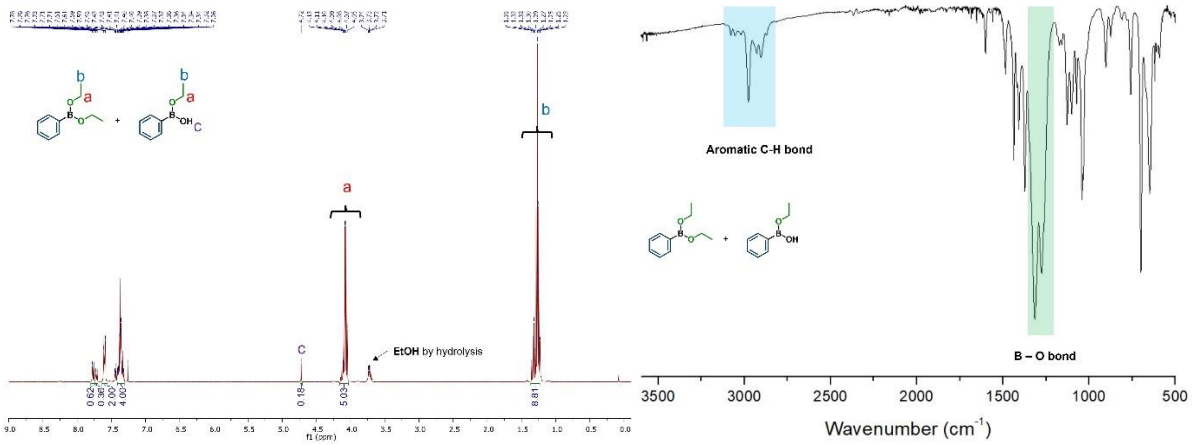
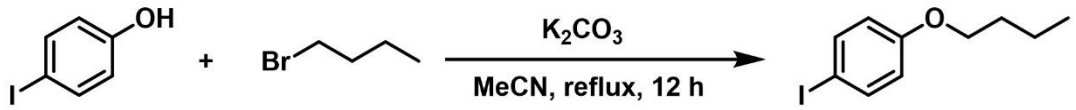


Figure S2. ^{1}H NMR (left) and IR spectroscopy(right) data of mono- and diethyl phenylboronate mixture.

IV. Preparation and characterization of starting materials[1–4]

1. Synthesis of 1-butoxy-4-iodobenzene



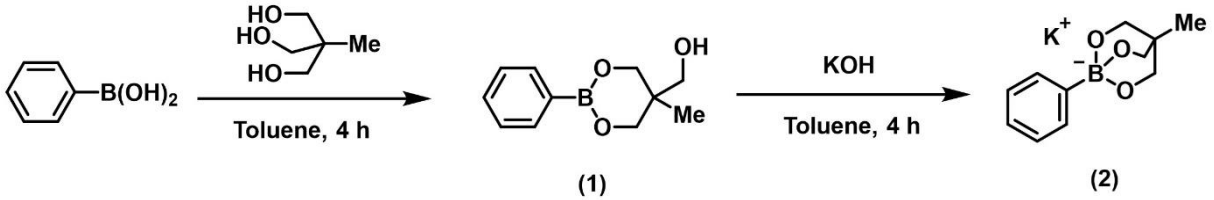
Scheme S1. Synthesis of 1-butoxy-4-iodobenzene.

To a solution of 4-iodophenol (1.1 g, 5 mmol), 1-bromobutane (2.1 g, 15 mmol) and potassium carbonate (2.1 g, 15 mmol) in acetonitrile (20 mL) was refluxed for 12 h. After the reaction, the solvent was removed under reduced pressure and water was added. The reaction mixture was extracted with ether three times. The combined organic layers were dried over MgSO4, filtered and concentrated under reduced pressure. The residue was purified by chromatography in silica gel (n-hexane/EtOAc) to give the desired products (1.2 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 1.81 – 1.69 (m, 2H), 1.48 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 138.1, 116.9, 82.4, 67.8, 31.2, 19.2, 13.8.

2. Synthesis of aryl boron reagents

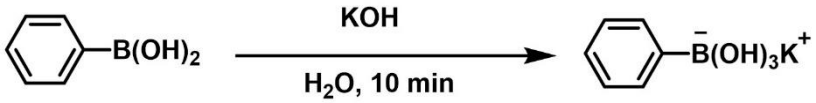
Scheme S2. Synthesis of 2-phenylbenzo[*d*][1,3,2]dioxaborole

A catechol (1.7 g, 15 mmol) was added into a suspension of phenylboronic acid (1.8 g, 15 mmol) in DCM (0.3 mM). Ethyl acetate was added until a homogenous solution was obtained. The reaction mixture was stirred at room temperature for 12 h. After the reaction, a solution was dried over MgSO4, filtered and evaporated solvent. The crude mixture was purified by recrystallization in n-hexane at 0 °C for 24 h (1.8 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.18 – 7.09 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 135.0, 132.4, 128.2, 122.8, 112.6.



Scheme S3. Synthesis of potassium cyclic triolborate (2).

To a solution of phenylboronic acid(2.4 g, 20 mmol) and 1,1,1-tris(hydroxymethyl)ethane (2.4 g, 20 mmol) were dissolved in toluene (50 mL) and refluxed for 4 h. Water was removed by distillation using Dean-Stark apparatus. After the reaction, solvents were removed to give crude (1). The crude product was used next step without any further purification. The crude product (1) and KOH (1 g, 18 mmol) were dissolved in toluene and refluxed for 4 h using Dean-Stark method. The potassium cyclic triolborate that precipitated was collected by filtration, washed with acetone, and dried under reduced pressure to give the desired product (4.4 g, 91%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31 (d, J = 6.6 Hz, 2H), 6.97 (t, J = 7.1 Hz, 2H), 6.90 (dd, J = 8.4, 5.9 Hz, 1H), 3.57 (s, 6H), 0.48 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 132.1, 125.4, 123.9, 73.6, 16.2.

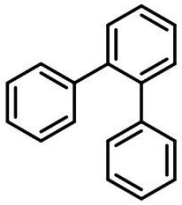


Scheme S4. Synthesis of potassium trihydroxy(phenyl)borate.

A mixture of phenylboronic acid (2.4 g, 20 mmol) and KOH (1.1 g, 20 mmol) were placed in a round bottom flask. Water (3 mL) was added and the mixture was heated to 100 °C until all solids were dissolved. Then, Isopropanol (400 mL) was added, and the reaction mixture was allowed to cool to room temperature. After cooling, the reaction mixture was cooled to 4 °C and a colorless crystalline solid was formed after 24 h. the crystalline solid was filtered and washed with Isopropanol (30 mL) and diethyl ether(50 mL) and dried under reduced pressure to give the desired product (1.5 g, 41%). ^{1}H NMR (400 MHz, MeOD) δ 7.50 (d, J = 6.7 Hz, 2H), 7.18 – 7.08 (m, 2H), 7.06 – 6.97 (m, 1H). ^{13}C NMR (75 MHz, MeOD) δ 134.1, 127.3, 125.8.

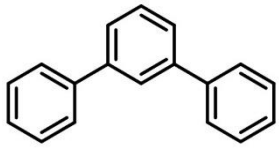
V. ^{1}H NMR and ^{13}C NMR data of poducts[5–8]

***o*-Terphenyl**



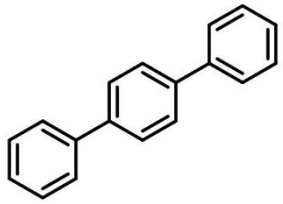
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.16 – 7.10 (m, 6H), 7.10 – 7.02 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 140.6, 130.6, 129.9, 127.8, 127.4, 126.4.

***m*-Terphenyl**



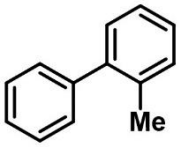
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, J = 1.5 Hz, 1H), 7.67 (dd, J = 8.0, 0.9 Hz, 4H), 7.62 – 7.57 (m, 2H), 7.56 – 7.44 (m, 5H), 7.39 (t, J = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 141.2, 129.2, 128.8, 127.4, 127.3, 126.2, 126.1.

***p*-Terphenyl**



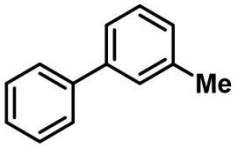
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 4H), 7.59 – 7.55 (m, 4H), 7.39 (t, *J* = 7.6 Hz, 4H), 7.29 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 140.1, 128.8, 127.5, 127.3, 127.0.

2-Methyl-1,1'-biphenyl



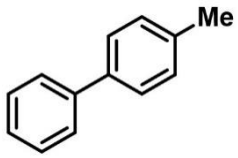
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.2 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.29 – 7.22 (m, 4H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 141.9, 135.3, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, 20.4.

3-Methyl-1,1'-biphenyl



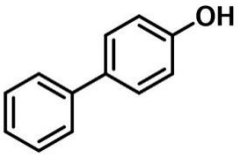
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 2H), 7.48 – 7.39 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 141.2, 138.3, 128.7, 128.6, 128.0, 128.0, 127.2, 127.1, 124.3, 21.5.

4-Methyl-1,1'-biphenyl



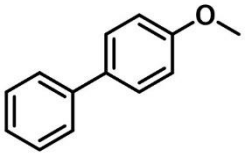
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.23 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 138.4, 137.0, 129.5, 128.7, 127.0, 127.0, 21.1.

[1,1'-Biphenyl]-4-ol



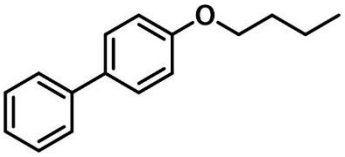
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.81 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 140.78, 134.1, 128.7, 128.4, 126.7, 117.8, 115.6.

4-Methoxy-1,1'-biphenyl



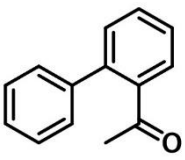
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 4H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.02 – 6.95 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

4-Butoxy-1,1'-biphenyl



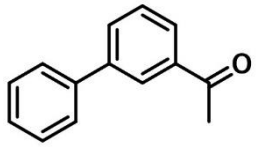
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 4H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.02 – 6.94 (m, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 1.80 (dt, *J* = 14.5, 6.6 Hz, 2H), 1.57 – 1.47 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 140.9, 133.6, 128.7, 128.1, 126.7, 126.6, 114.8, 67.8, 31.4, 19.3, 13.8.

1-([1,1'-Biphenyl]-2-yl)ethan-1-one



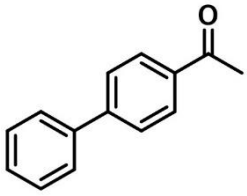
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H), 7.47 – 7.37 (m, 5H), 7.37 – 7.32 (m, 2H), 2.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 140.9, 140.7, 140.5, 130.7, 130.2, 128.8, 128.6, 127.8, 127.8, 127.4, 30.4.

1-([1,1'-Biphenyl]-3-yl)ethan-1-one



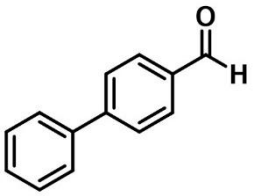
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (t, *J* = 1.7 Hz, 1H), 7.96 – 7.91 (m, 1H), 7.80 (ddd, *J* = 7.7, 1.7, 1.1 Hz, 1H), 7.63 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.48 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.42 – 7.36 (m, 1H), 2.66 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 141.7, 140.1, 137.6, 131.7, 129.0, 128.9, 127.8, 127.1, 126.9, 26.7.

1-([1,1'-Biphenyl]-4-yl)ethan-1-one



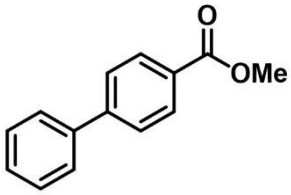
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.72 – 7.67 (m, 2H), 7.66 – 7.61 (m, 2H), 7.48 (dd, *J* = 10.2, 4.8 Hz, 2H), 7.43 – 7.38 (m, 1H), 2.65 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 145.8, 139.9, 135.9, 128.9, 128.9, 128.2, 127.3, 127.2, 26.6.

[1,1'-Biphenyl]-4-carbaldehyde



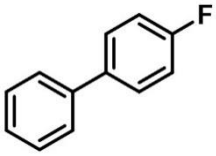
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.69 – 7.62 (m, 2H), 7.49 (dd, *J* = 10.0, 4.7 Hz, 2H), 7.45 – 7.39 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.8, 147.1, 139.7, 135.2, 130.2, 129.0, 128.4, 127.6, 127.3.

Methyl [1,1'-biphenyl]-4-carboxylate



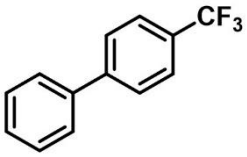
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.70 – 7.60 (m, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 145.59, 139.99, 130.09, 128.89, 128.1, 127.2, 126.9, 52.0.

4-Fluoro-1,1'-biphenyl



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 4H), 7.44 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.35 (ddd, *J* = 7.3, 3.8, 1.2 Hz, 1H), 7.18 – 7.09 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 160.8, 140.3, 137.4, 137.3, 128.8, 128.7, 128.6, 127.2, 127.0, 115.7, 115.4.

4-(Trifluoromethyl)-1,1'-biphenyl



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 4H), 7.63 – 7.57 (m, 2H), 7.48 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.44 – 7.37 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 139.8, 129.6, 129.2, 129.0, 128.2, 127.4. 127.3, 126.1, 125.8, 125.7, 125.7, 125.6, 122.5.

VI. References

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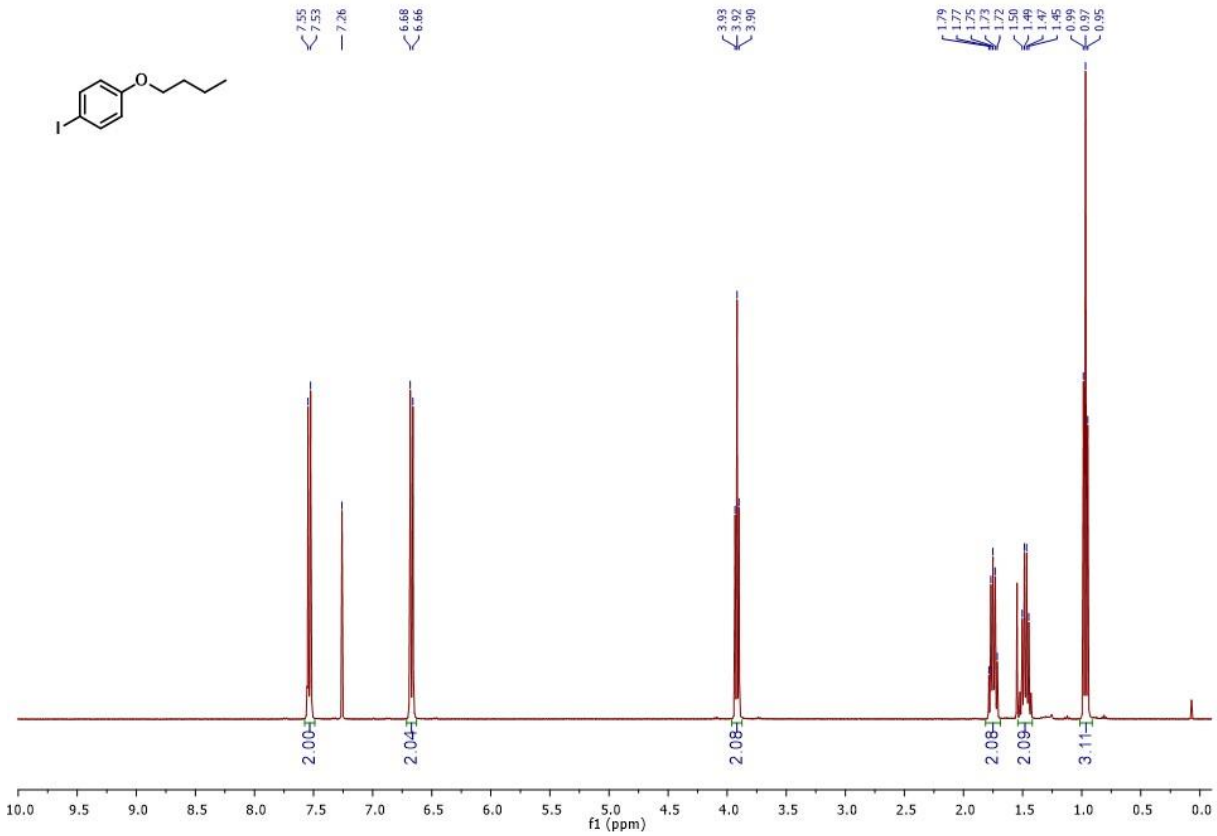
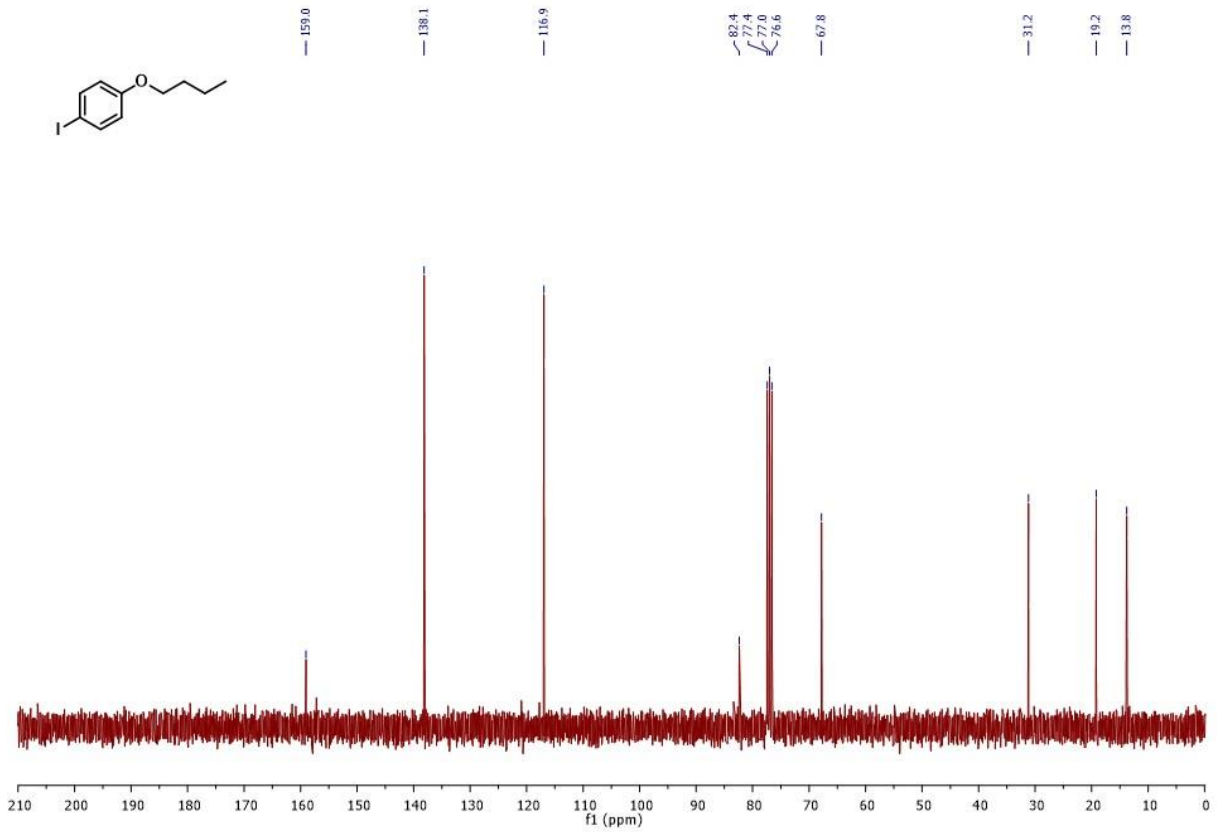
Appendix I

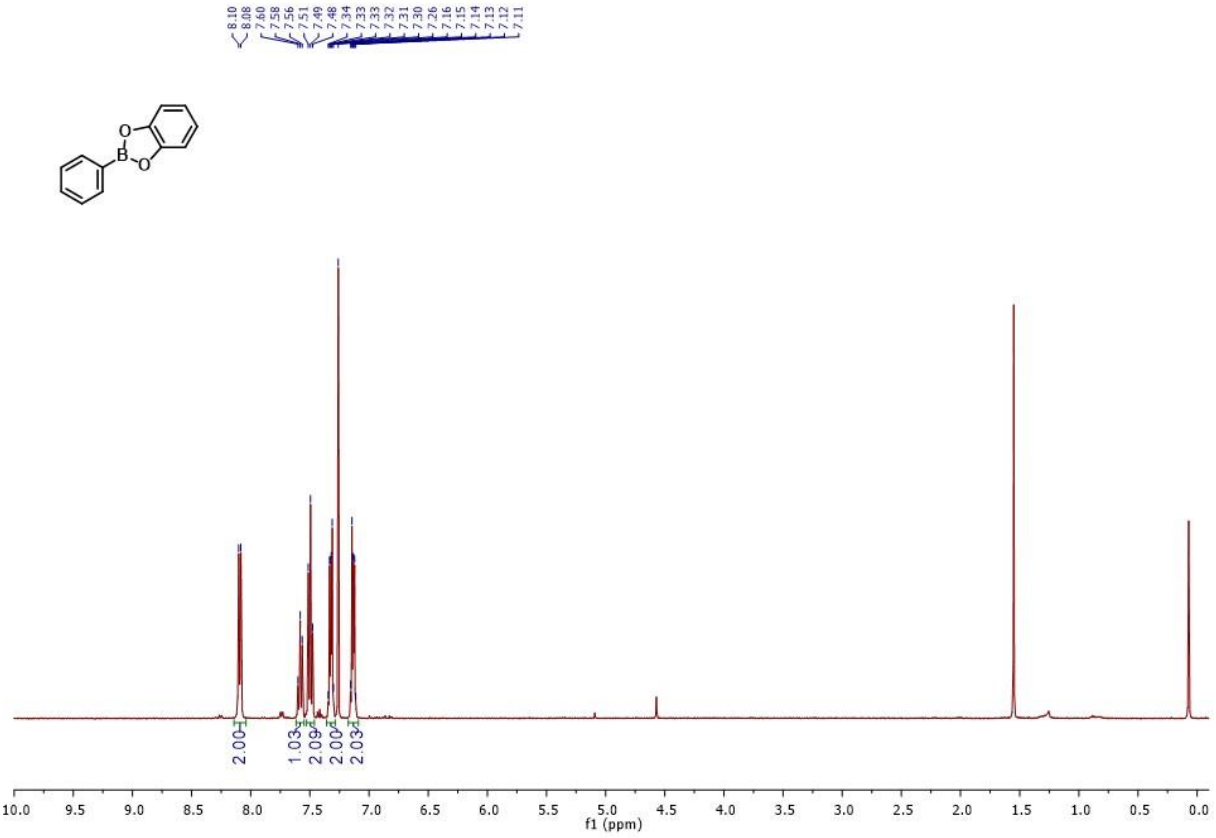
Spectral Copies of ^{1}H and ^{13}C-NMR of Compounds Obtained in this Study

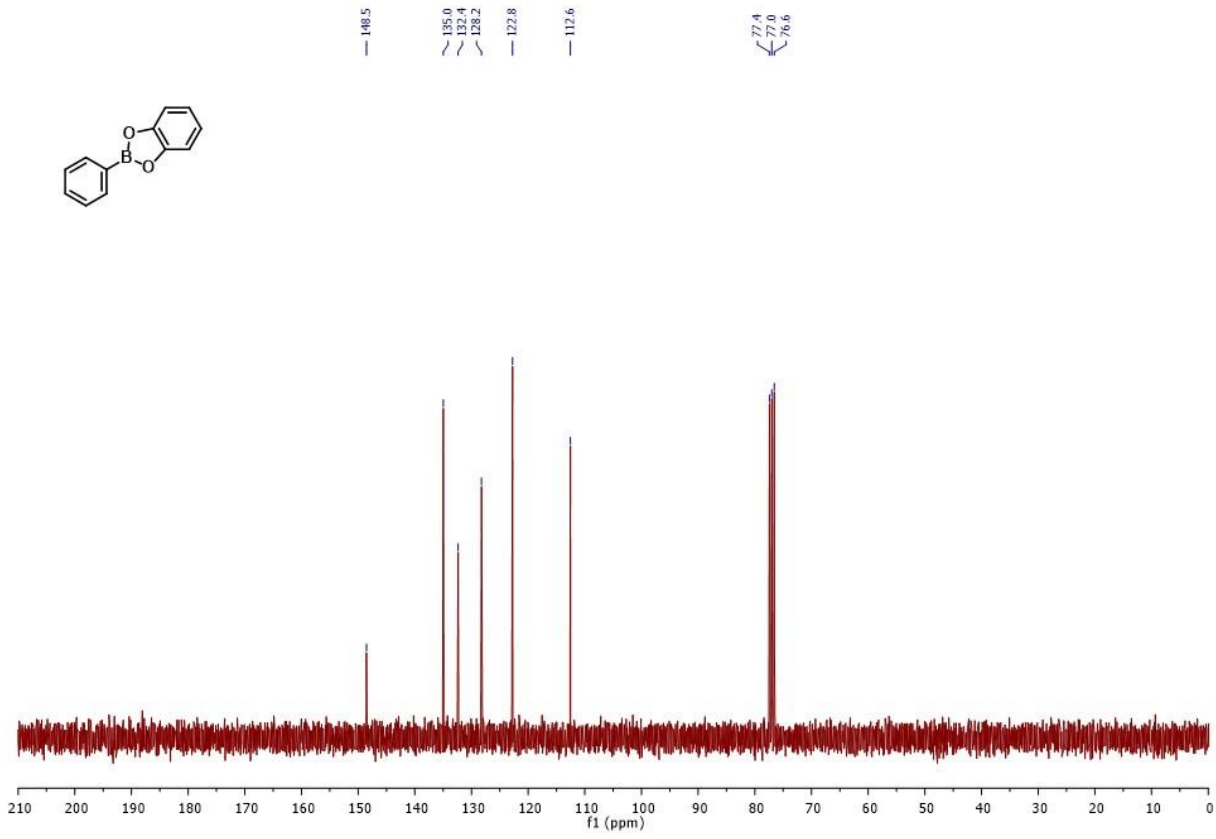
1-Butoxy-4-iodobenzene



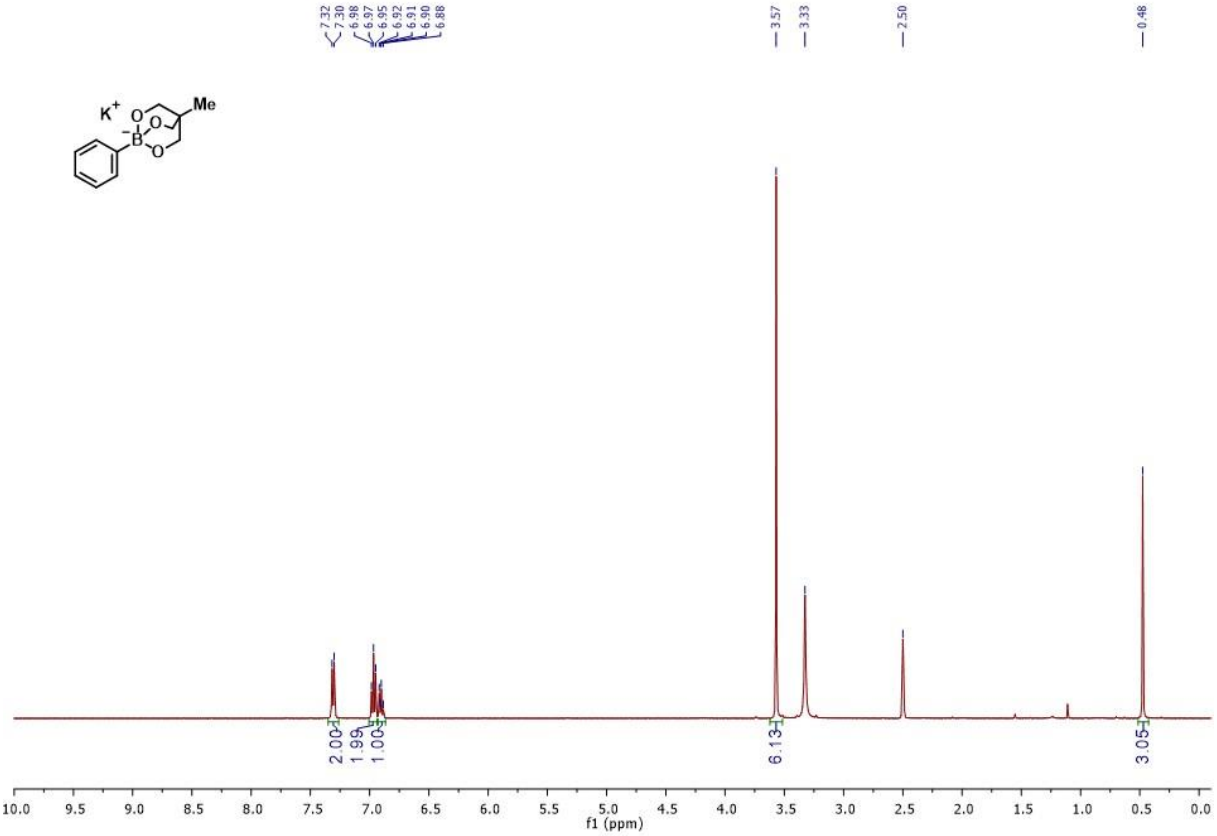


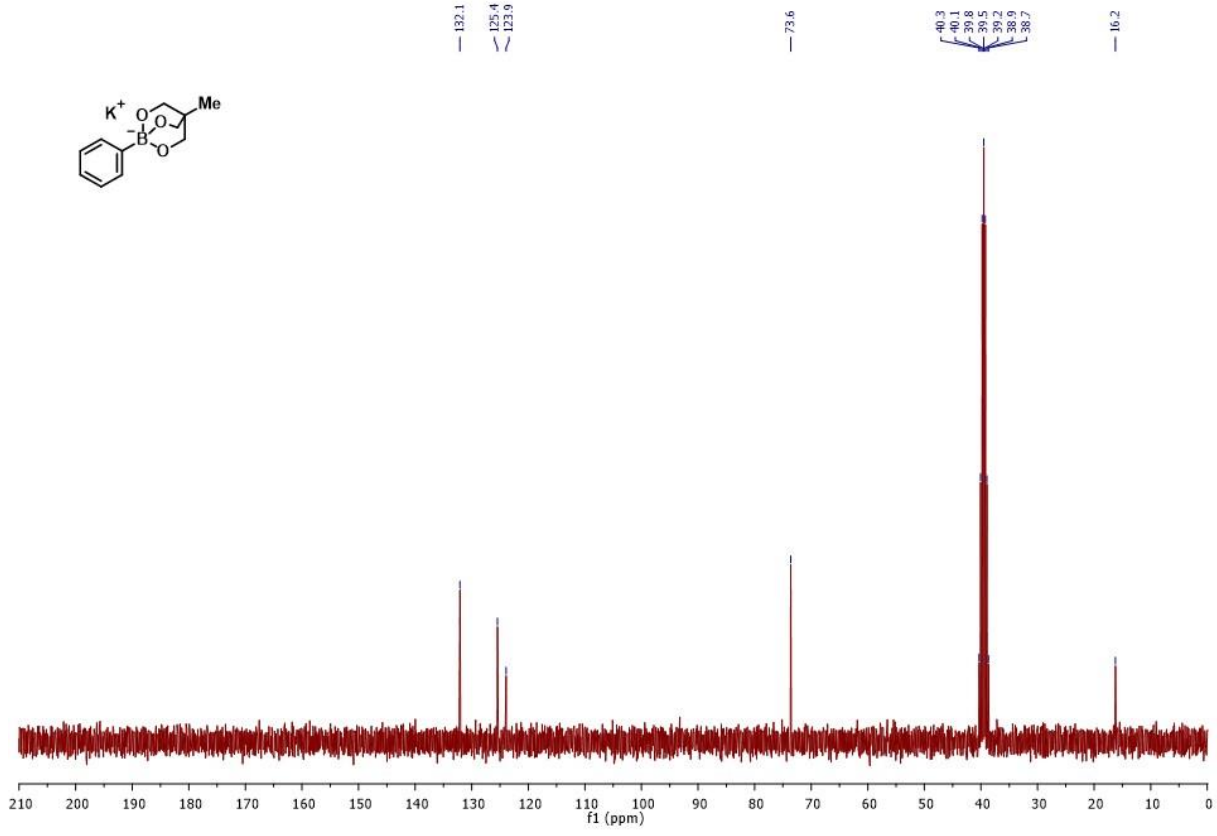
2-Phenylbenzo[*d*][1,3,2]dioxaborole



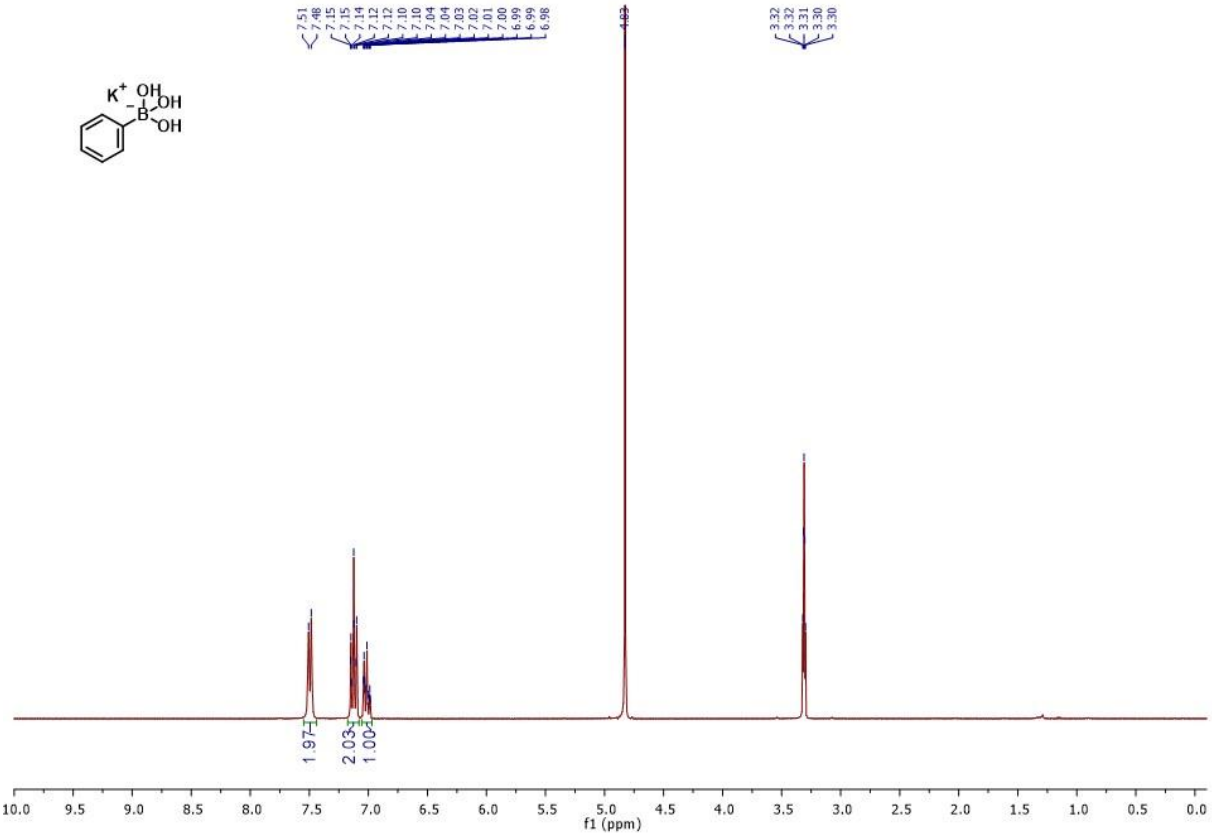


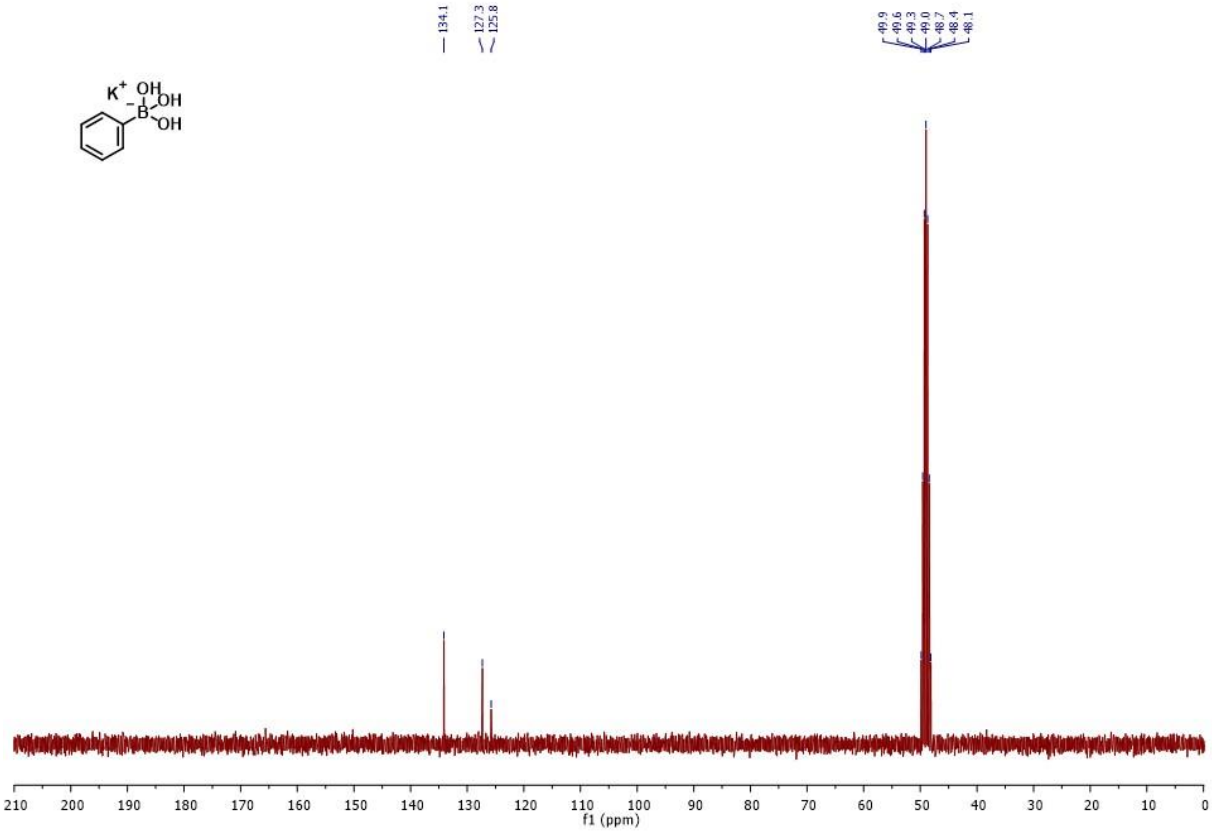
Potassium cyclic triolborate



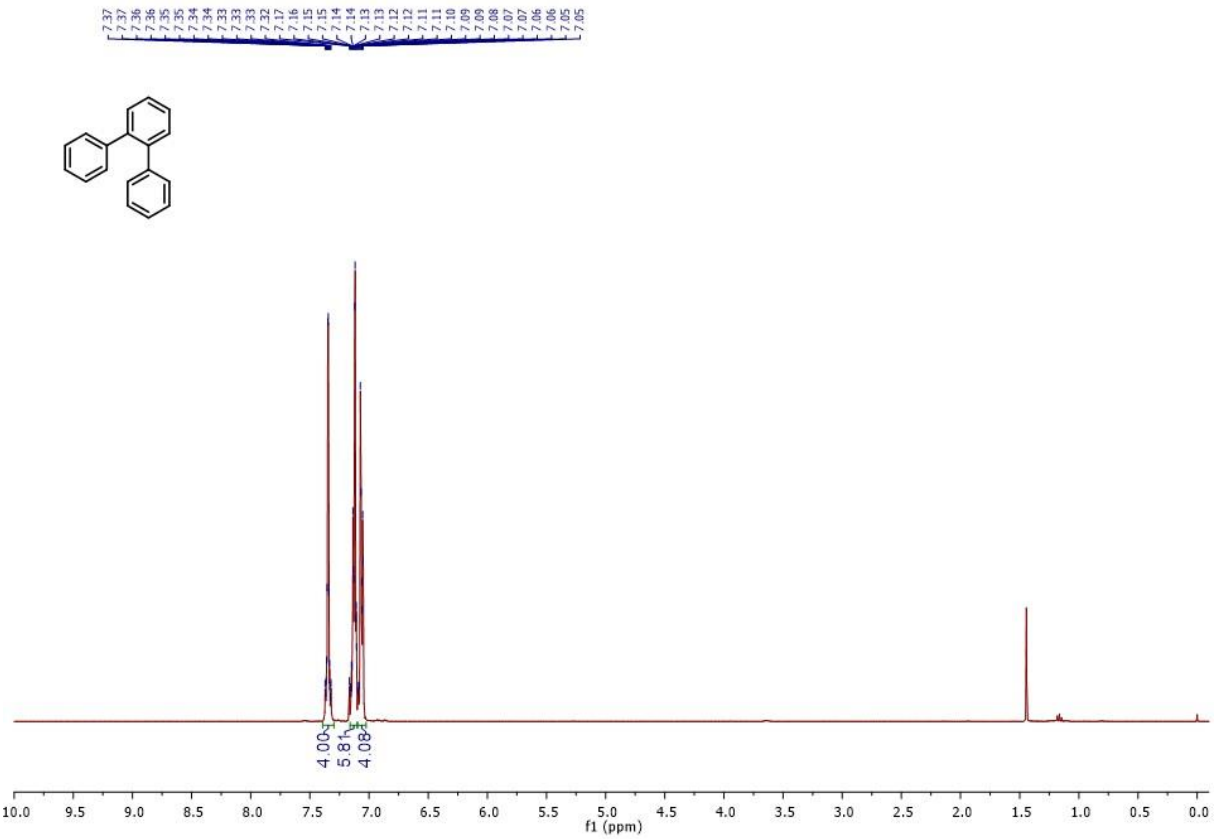


Potassium trihydroxy(phenyl)borate





***o*-Terphenyl**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7.37
7.36
7.36
7.35
7.35
7.34
7.34
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7.33
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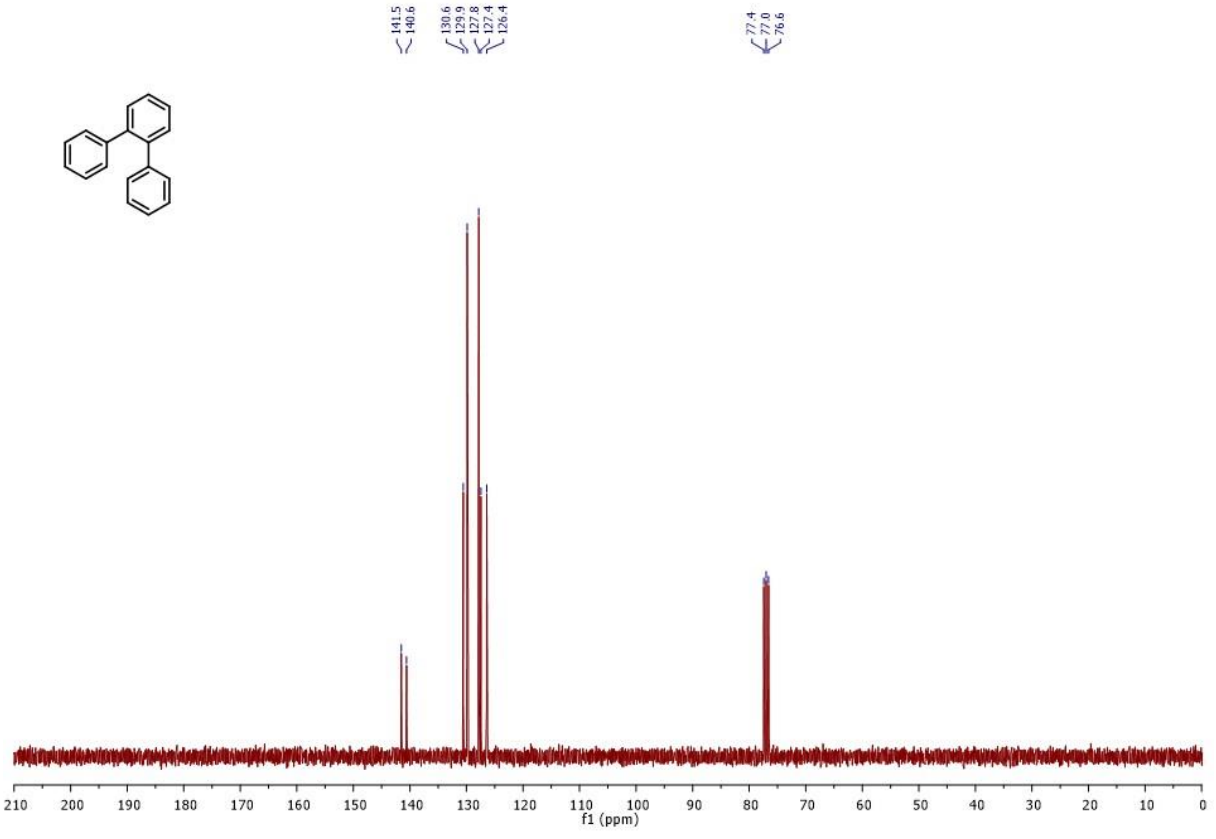
7.32
7.17
7.16
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.09
7.09
7.08
7.07
7.07
7.06
7.06
7.05
7.05
4.00
5.81
4.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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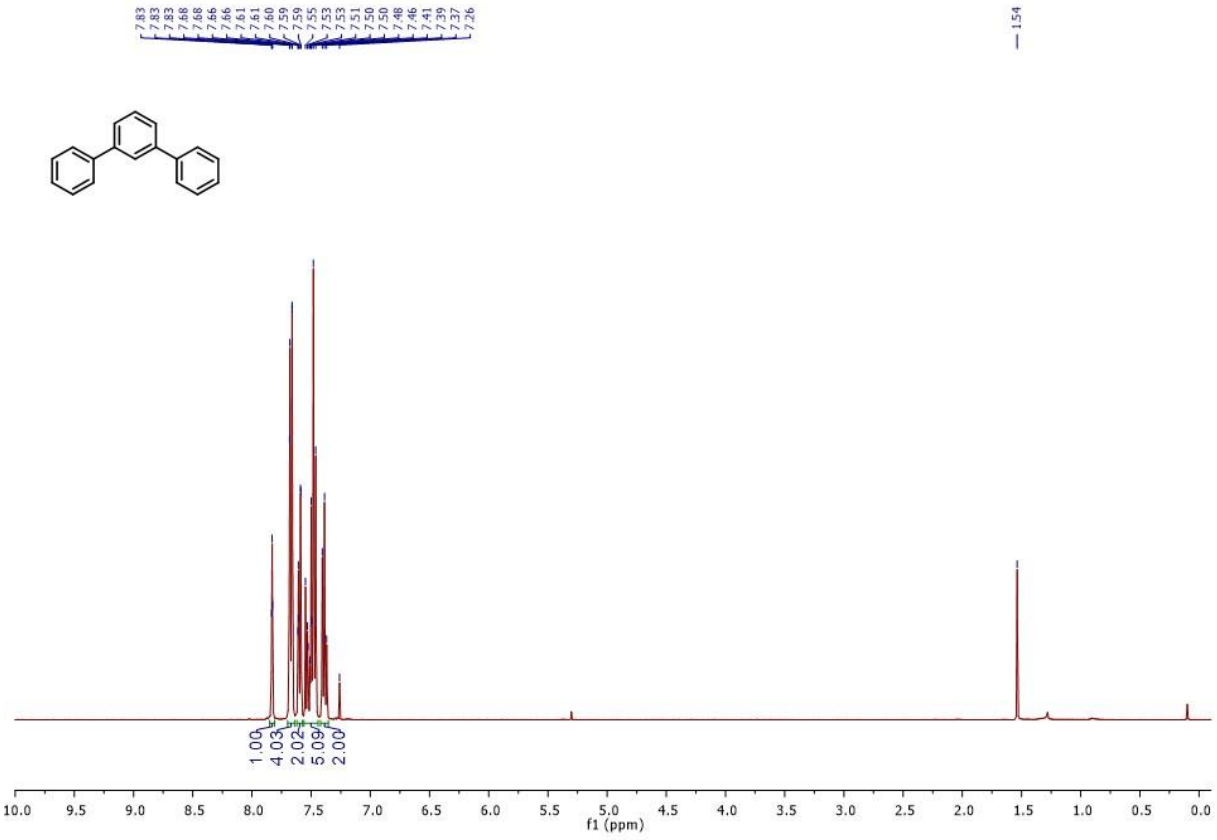
140.6
130.6
129.9
127.8
127.4
126.4
77.4
77.0
76.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

***m*-Terphenyl**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7.83
7.83
7.68
7.68
7.66
7.66
7.61
7.61
7.60
7.59
7.59
7.55
7.53
7.53
7.51
7.50
7.50
7.48
7.46
7.41
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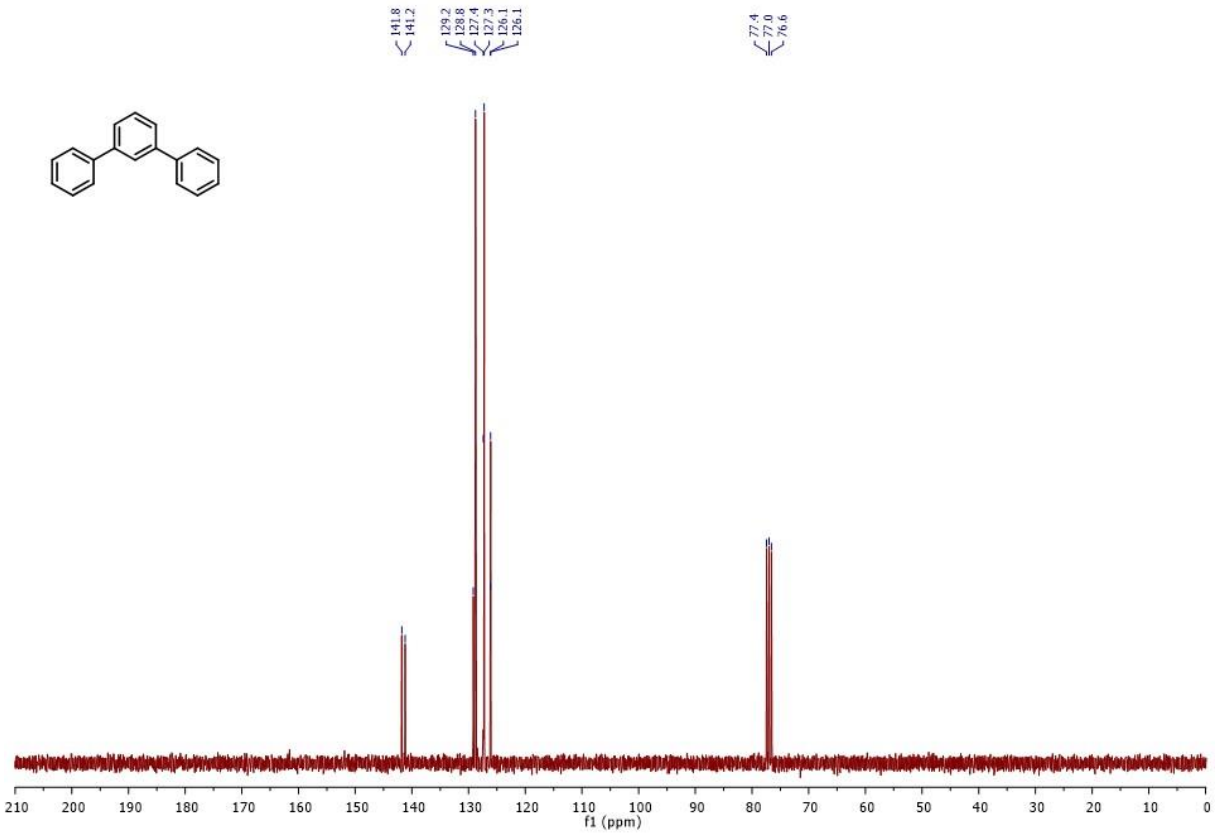
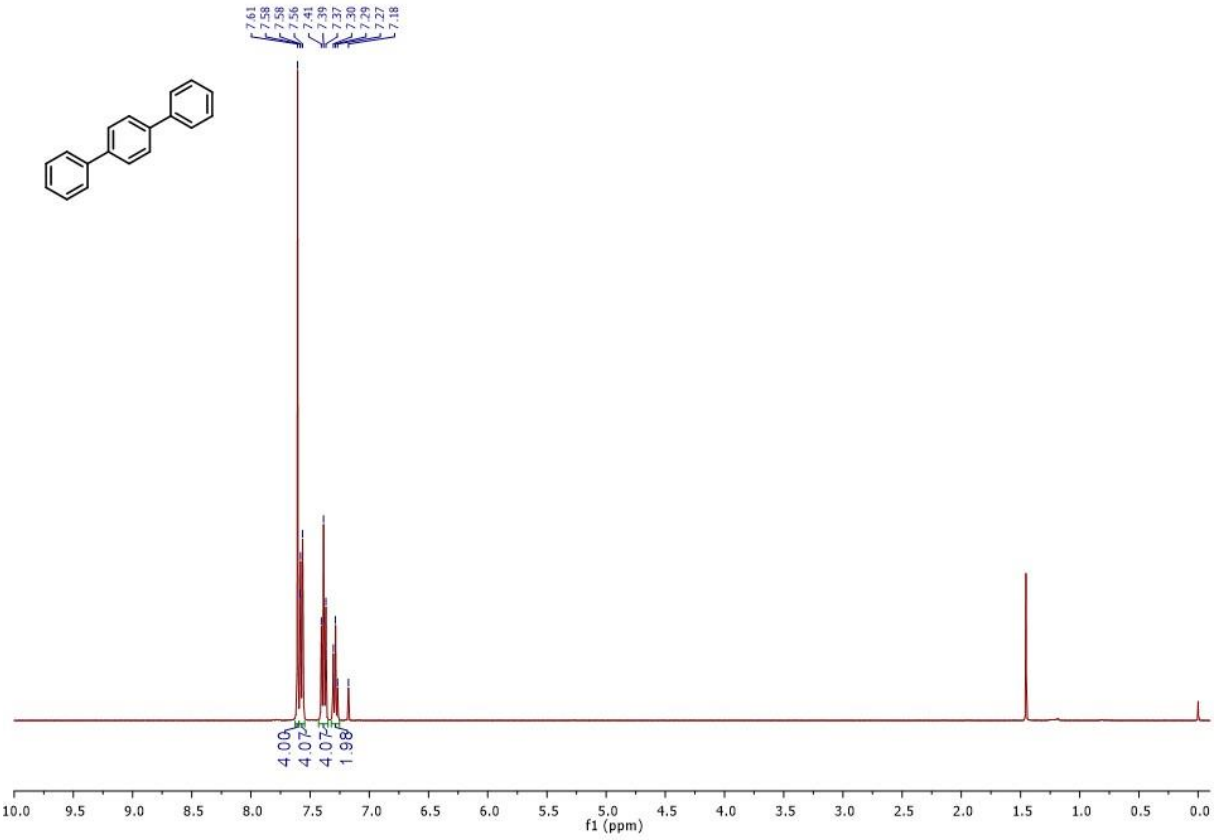
7.37
7.26
1.54
1.00
4.03
2.02
5.09
2.00
f1 (ppm)


141.8
141.2
129.2
128.8
127.4
127.3
126.1
126.1
77.4
77.0
76.6
f1 (ppm)

***p*-Terphenyl**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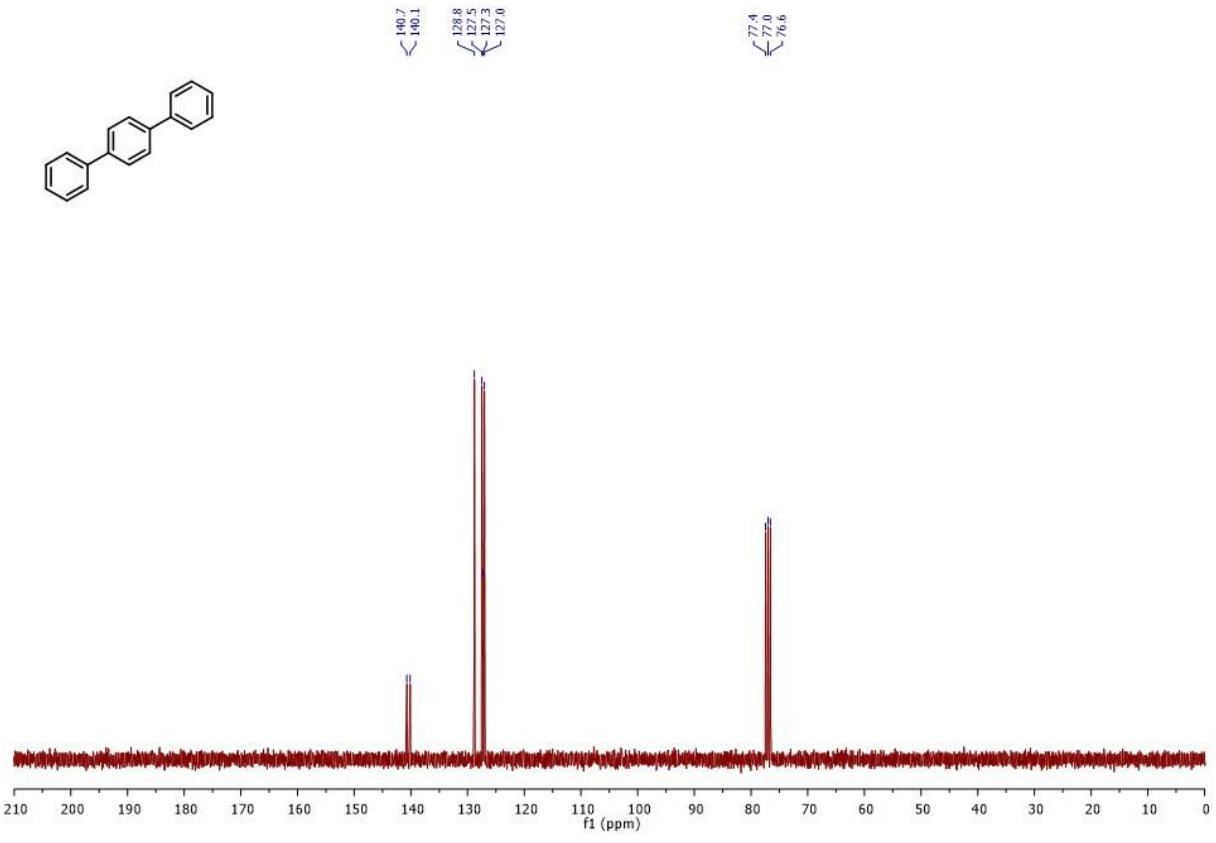
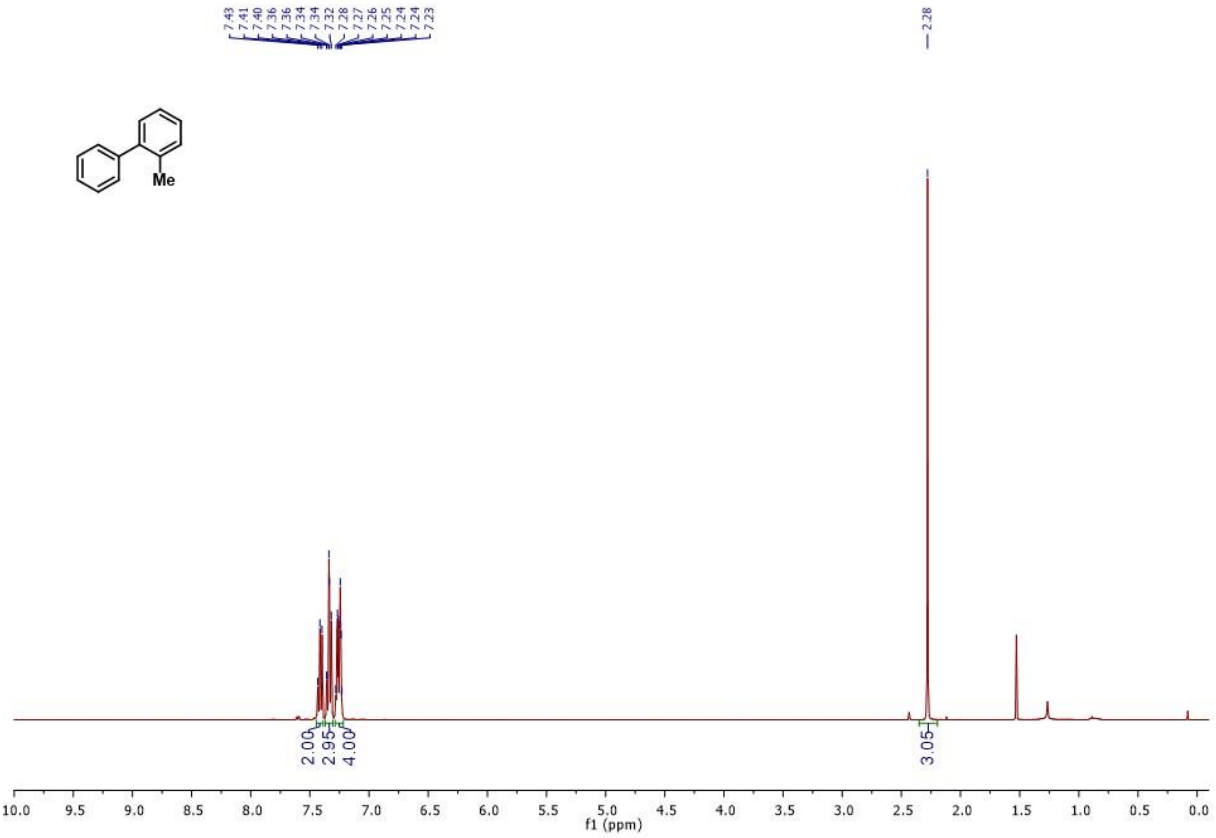
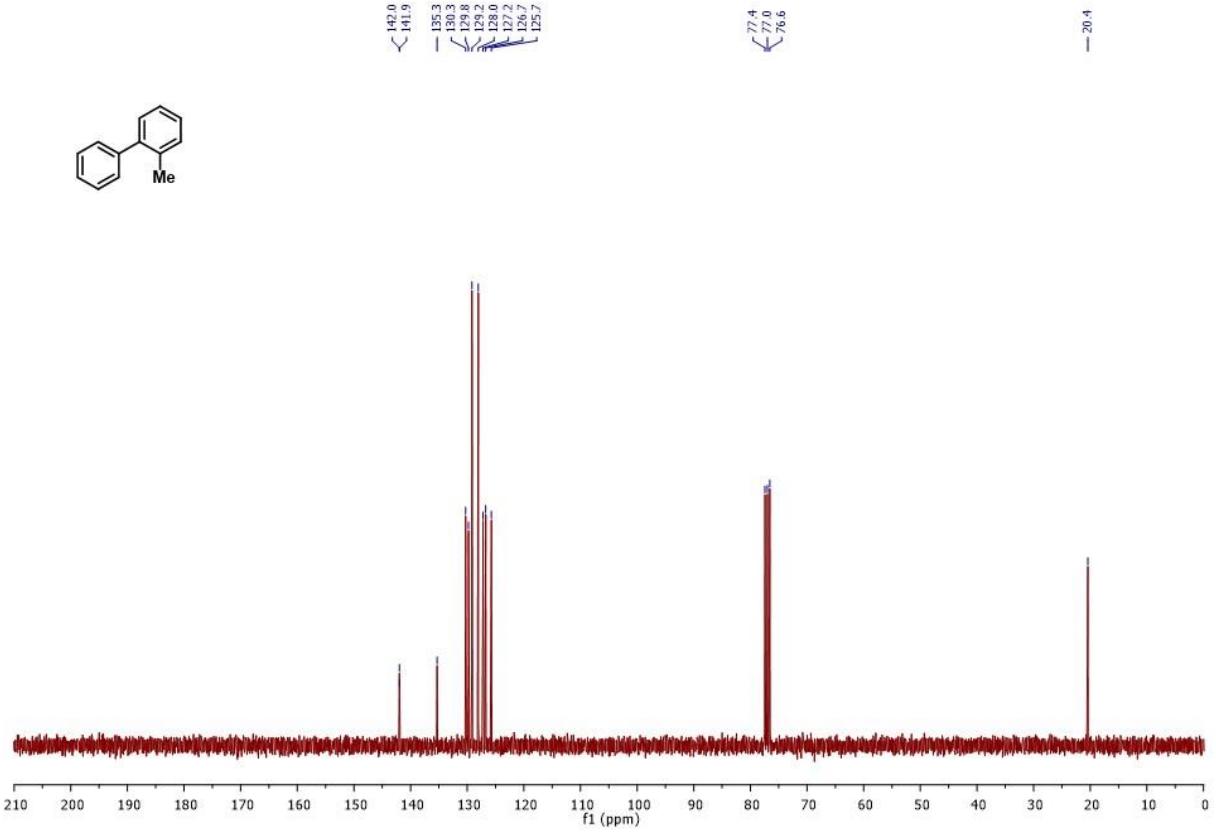
7.58
7.58
7.56
7.41
7.39
7.37
7.30
7.29
7.27
7.18
4.00
4.07
4.07
1.98
f1 (ppm)


140.7
140.1
128.8
127.5
127.3
127.0
77.4
77.0
76.6
f1 (ppm)

2-Methyl-1,1'-biphenyl





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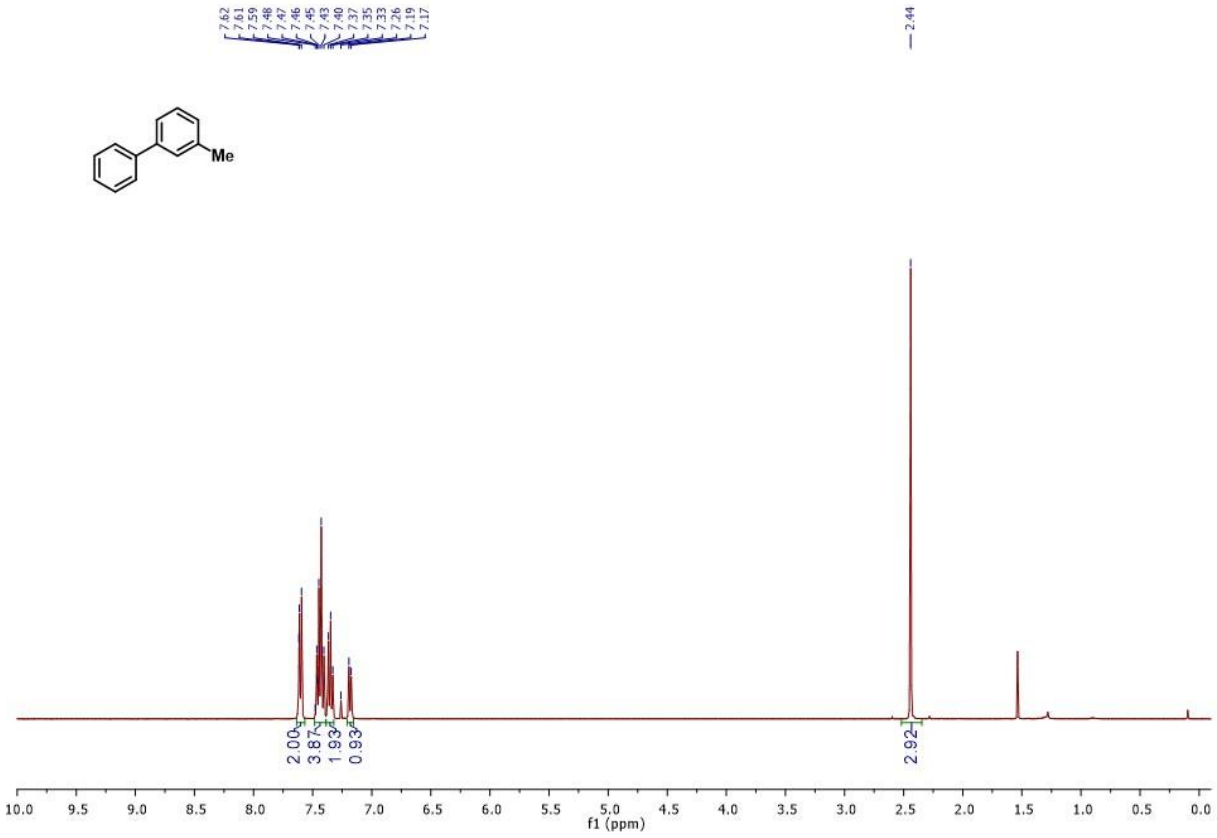
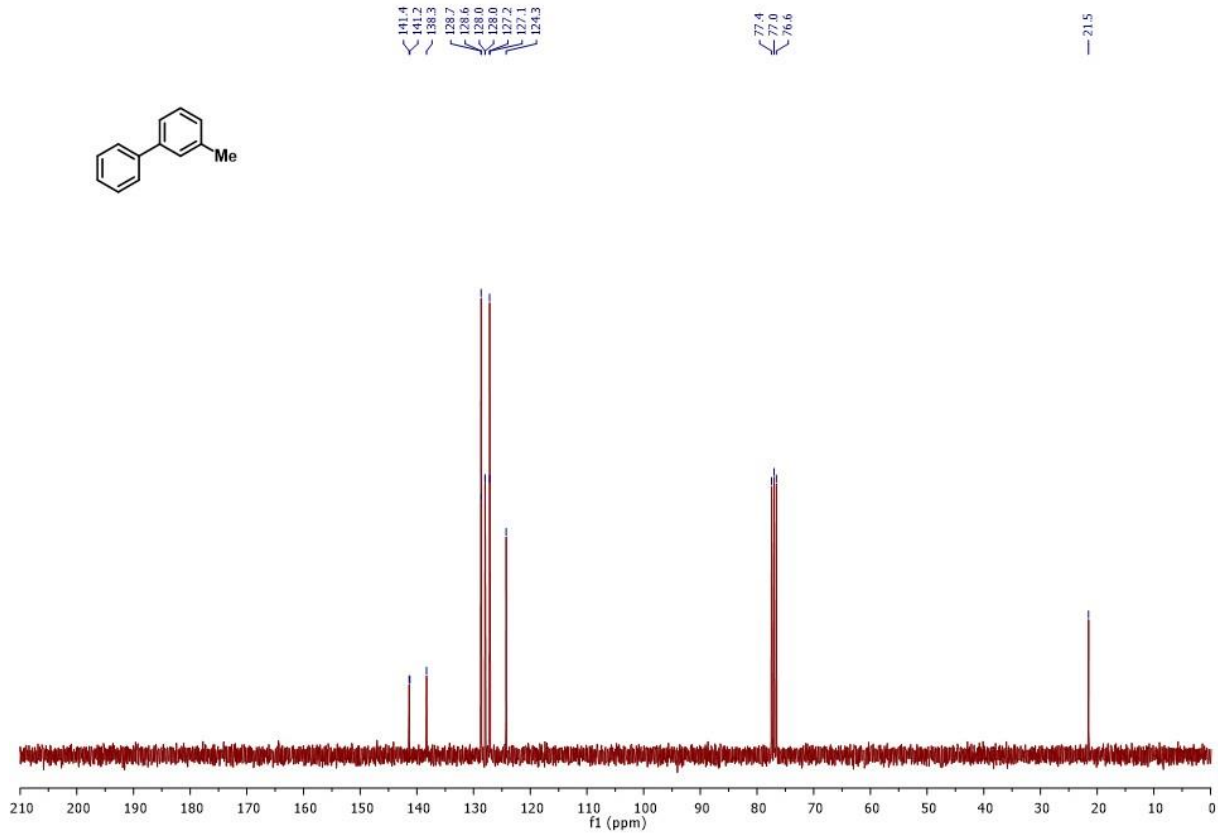
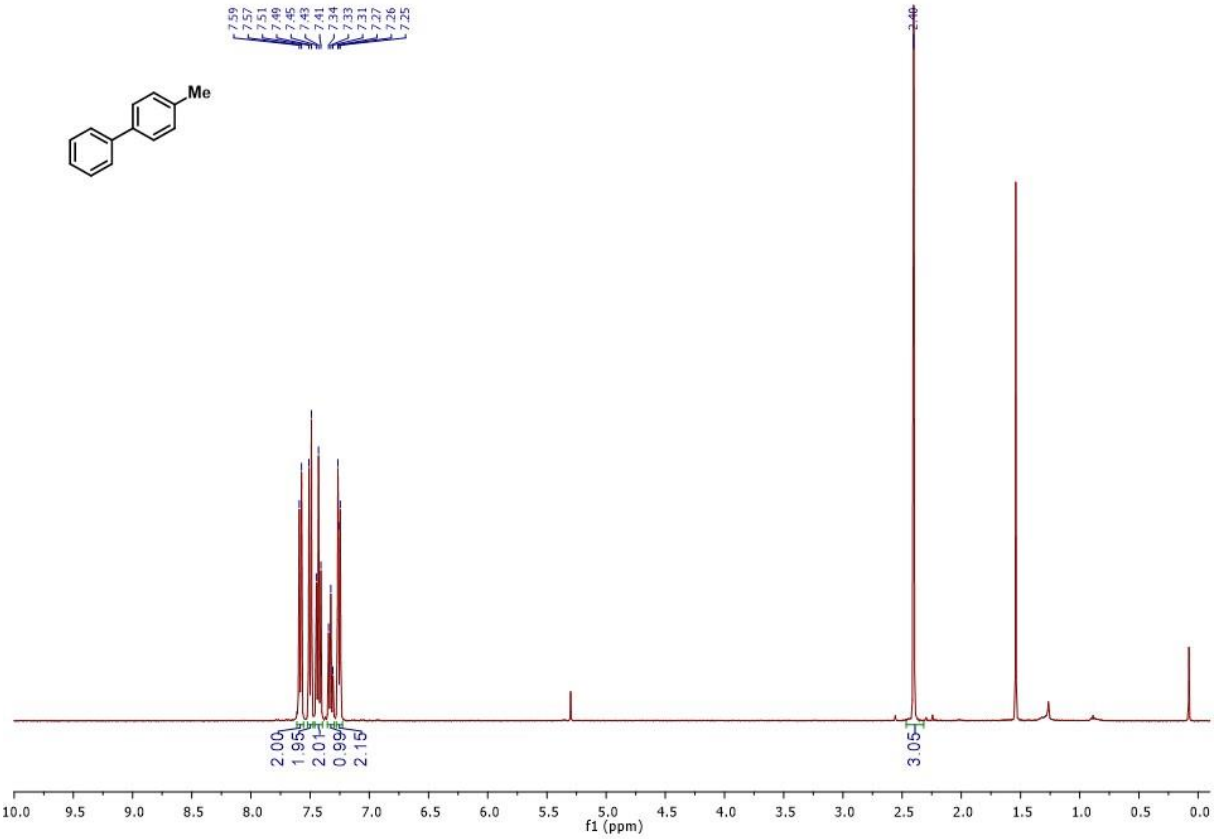
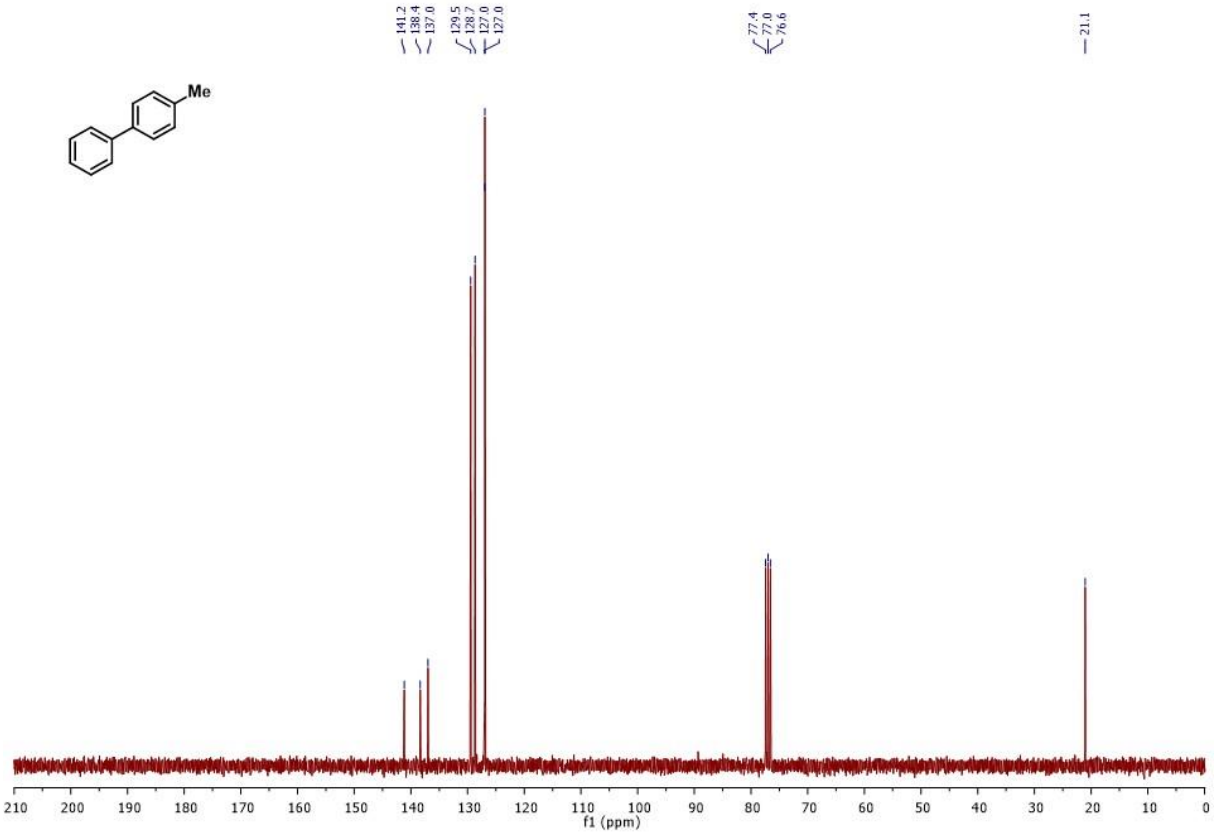


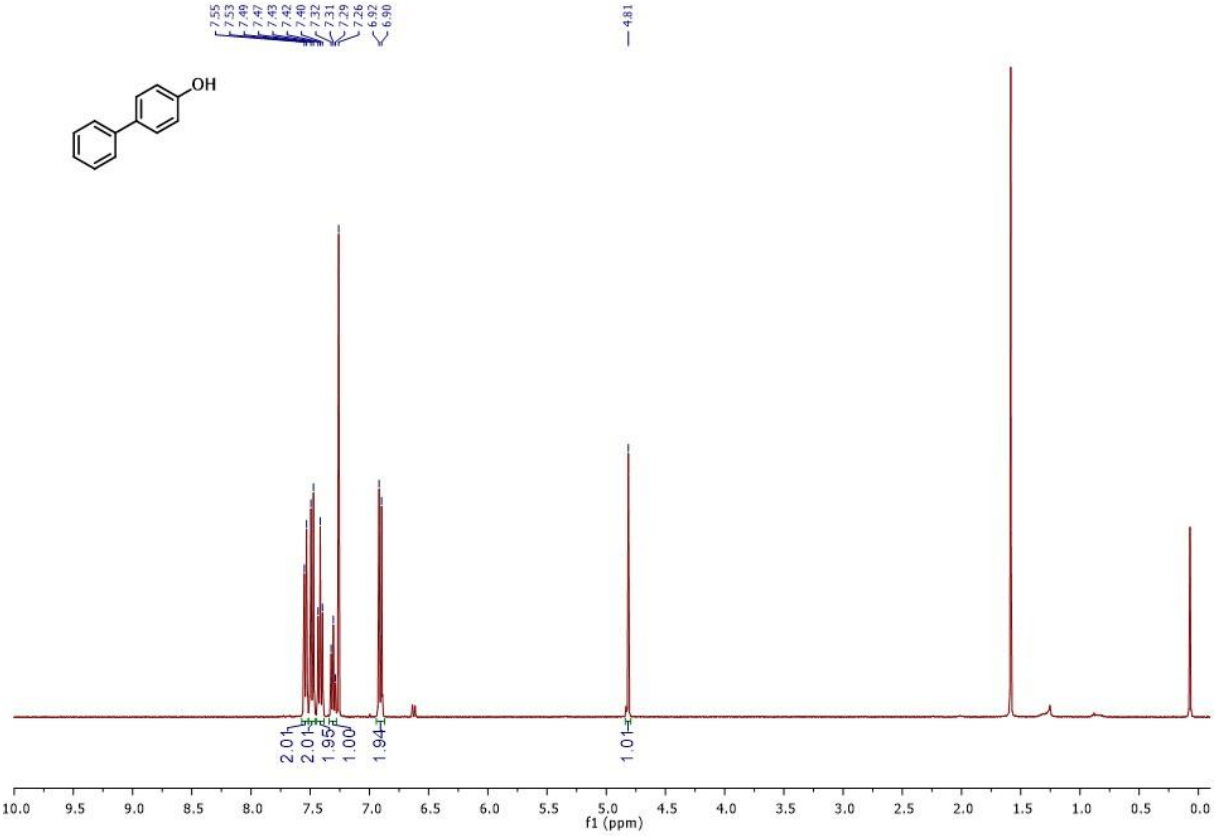


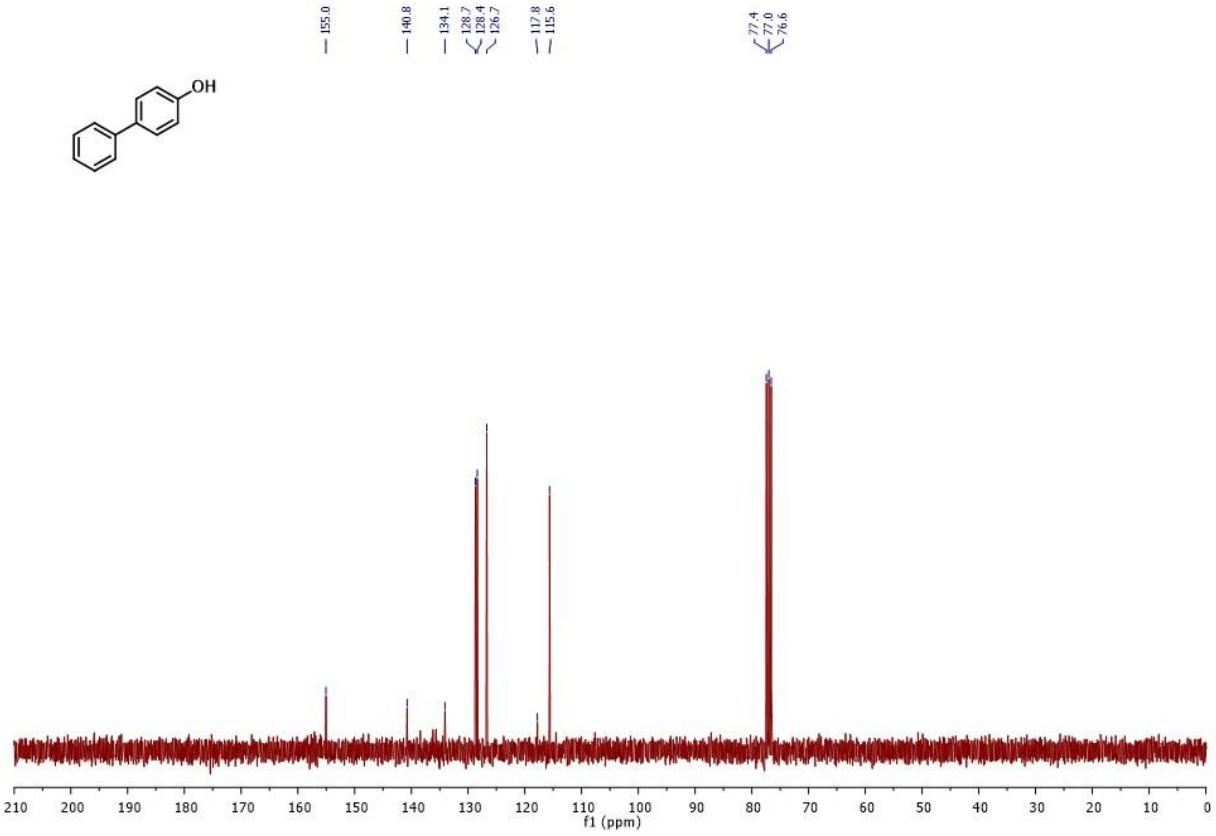
4-Methyl-1,1'-biphenyl



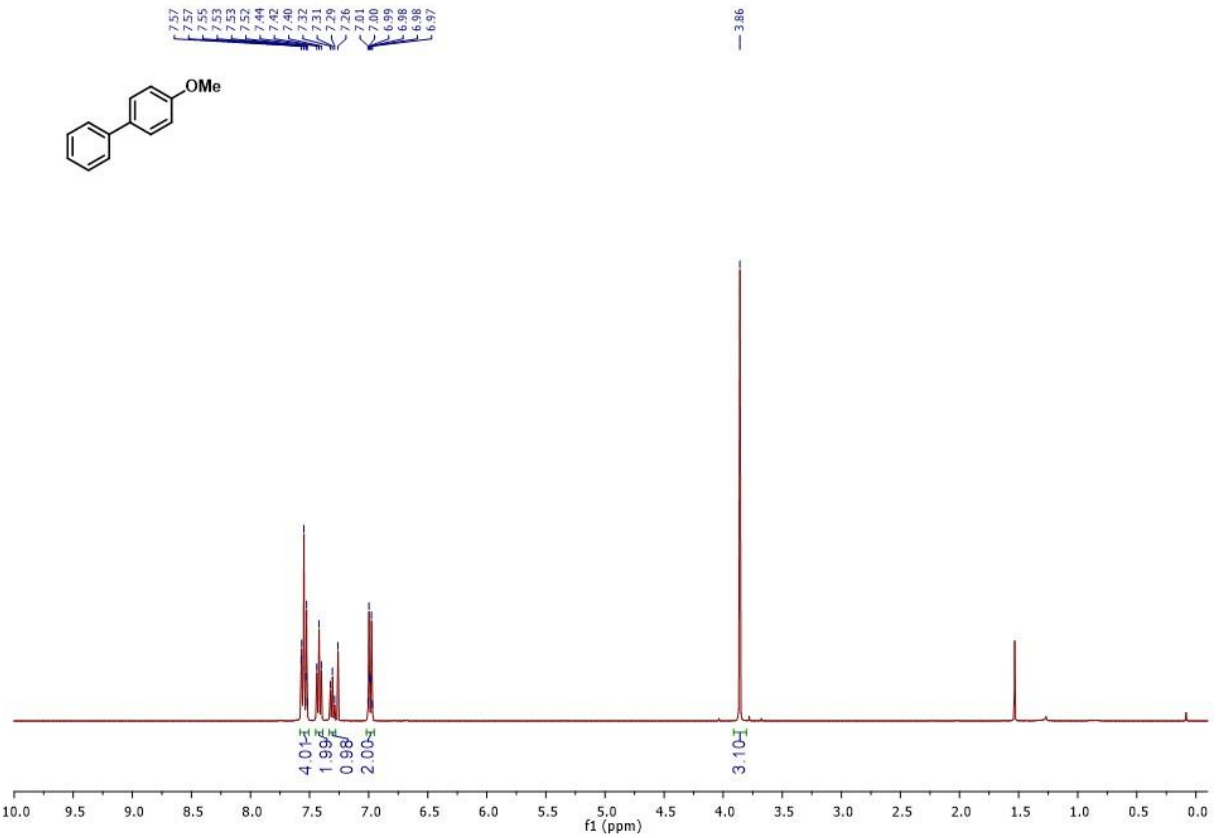


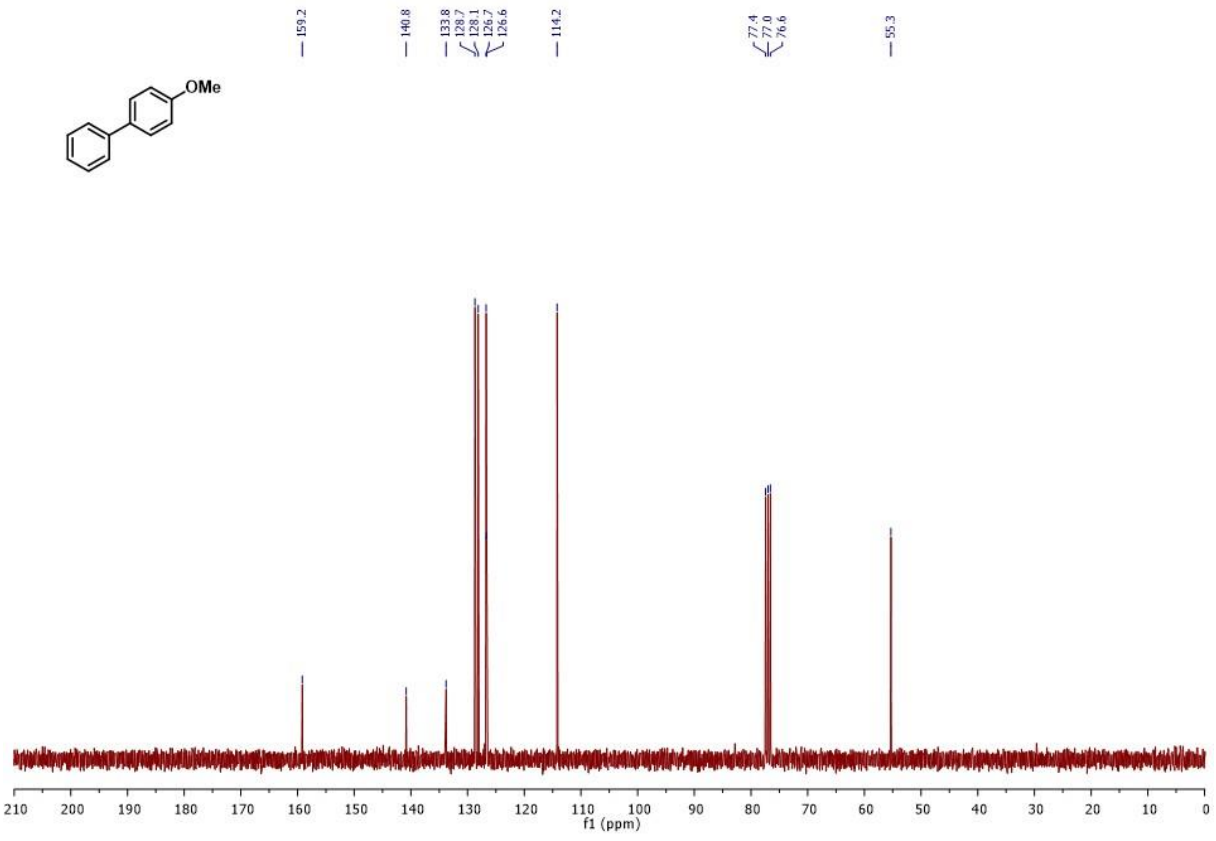
[1,1'-Biphenyl]-4-ol



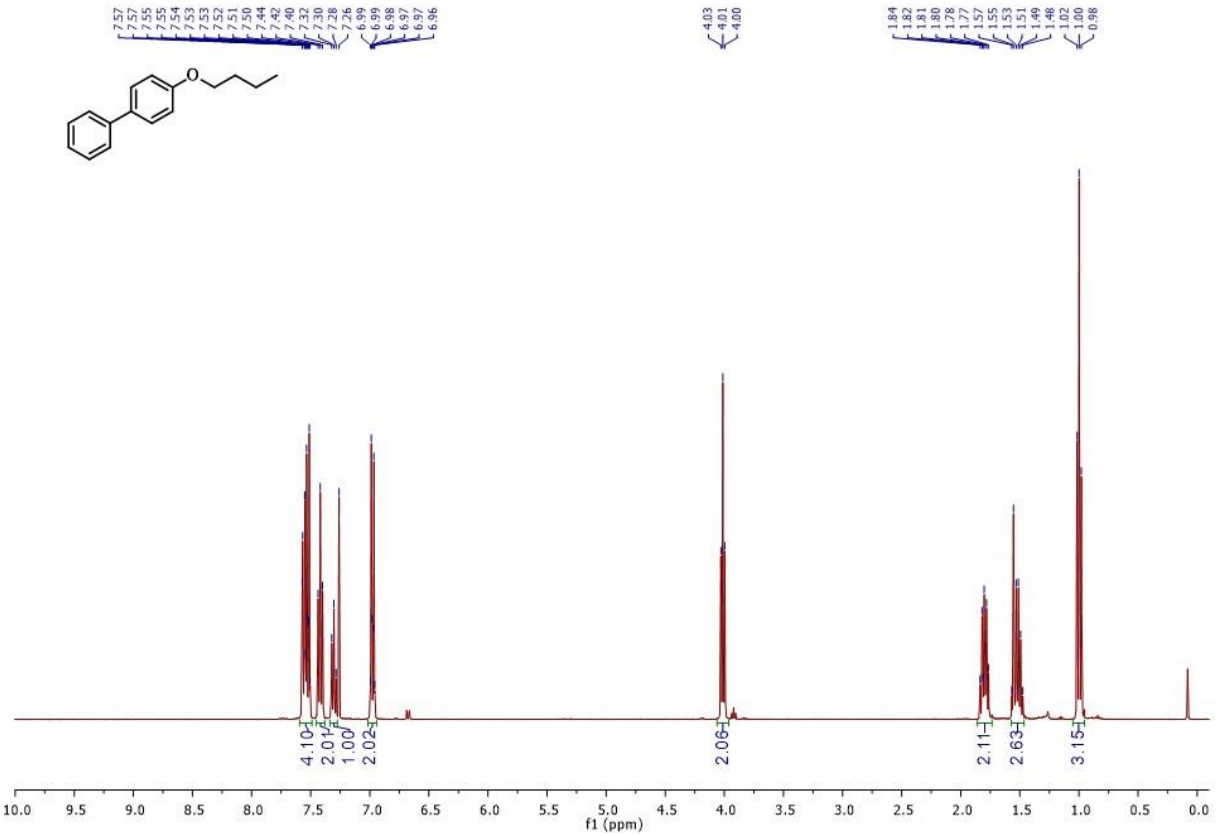


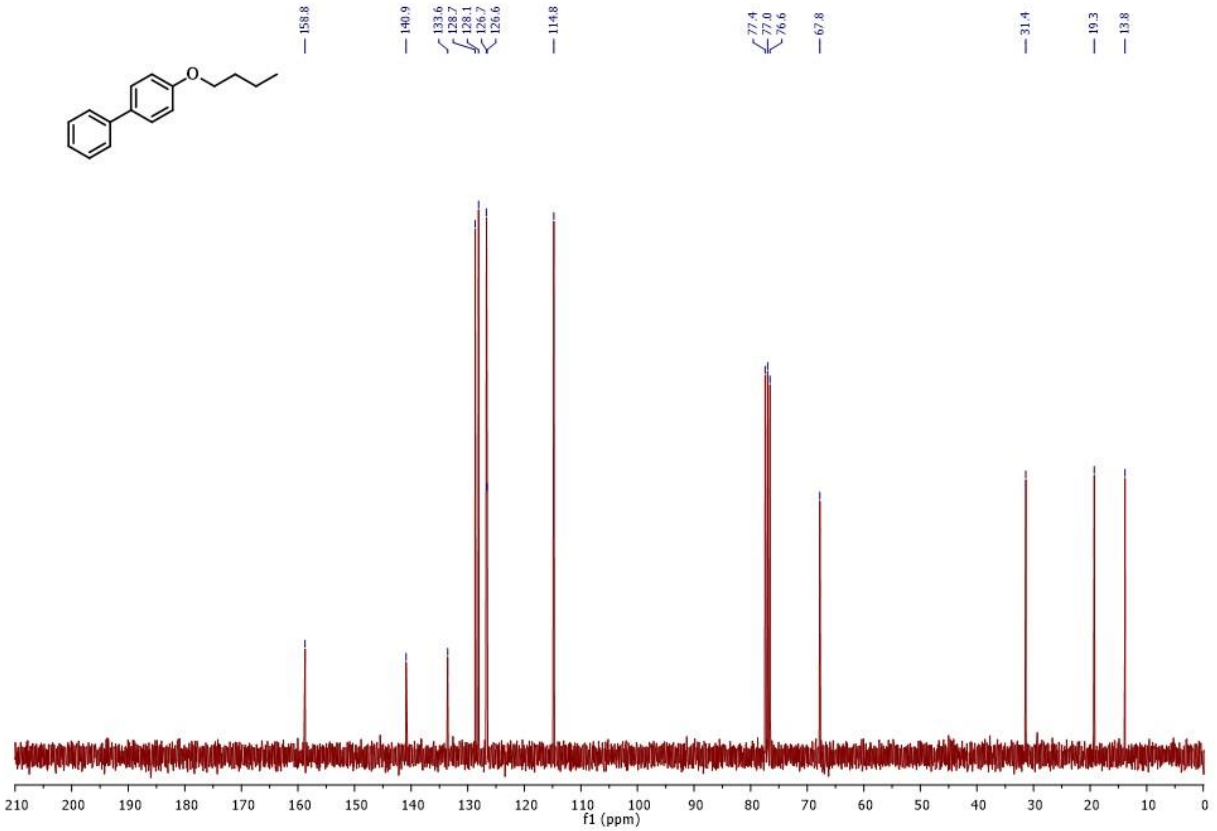
4-Methoxy-1,1'-biphenyl



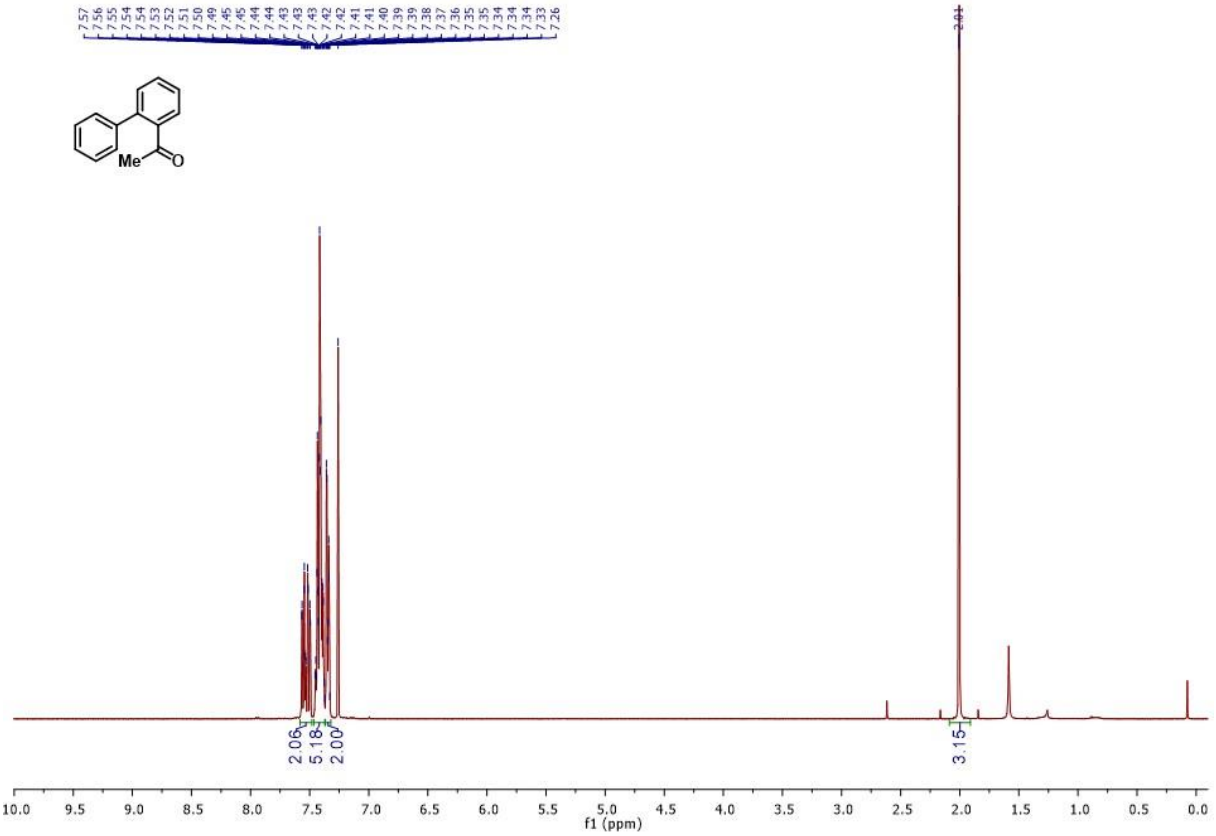


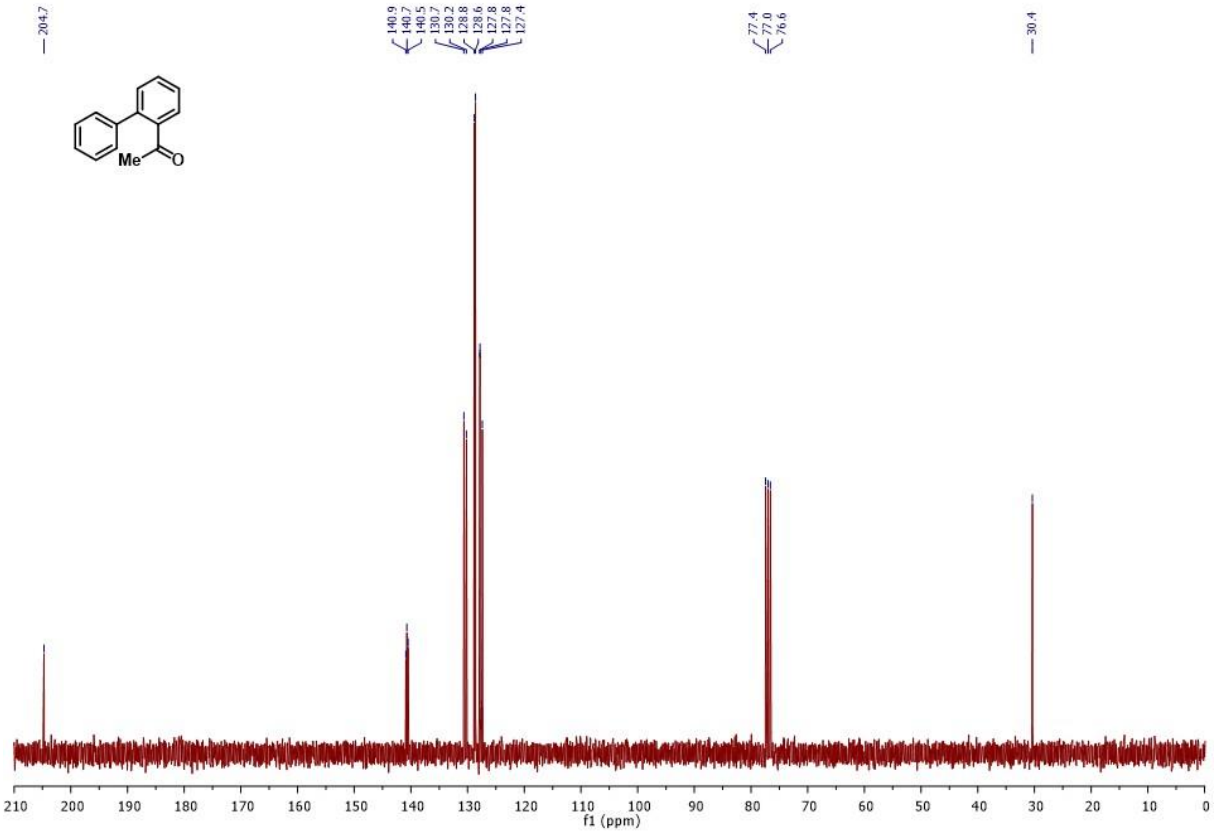
4-Butoxy-1,1'-biphenyl





1-([1,1'-Biphenyl]-2-yl)ethan-1-one





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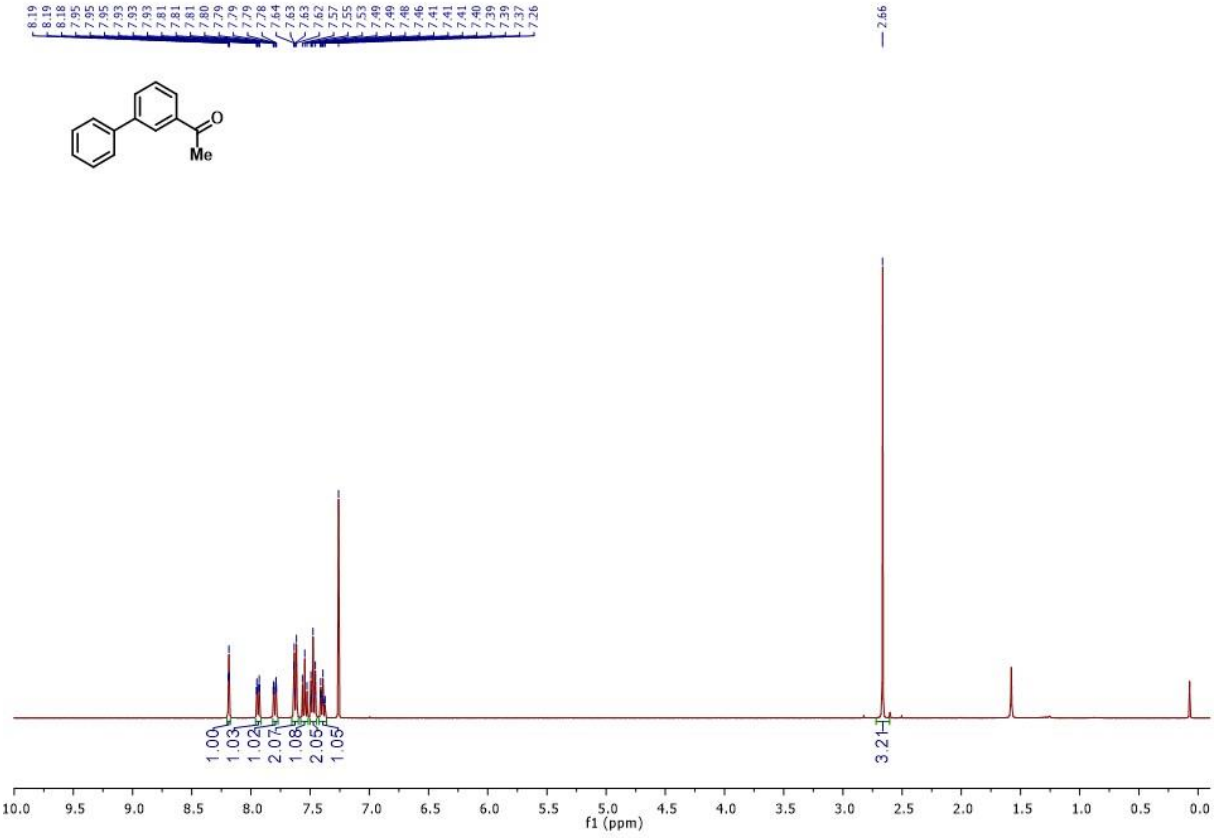
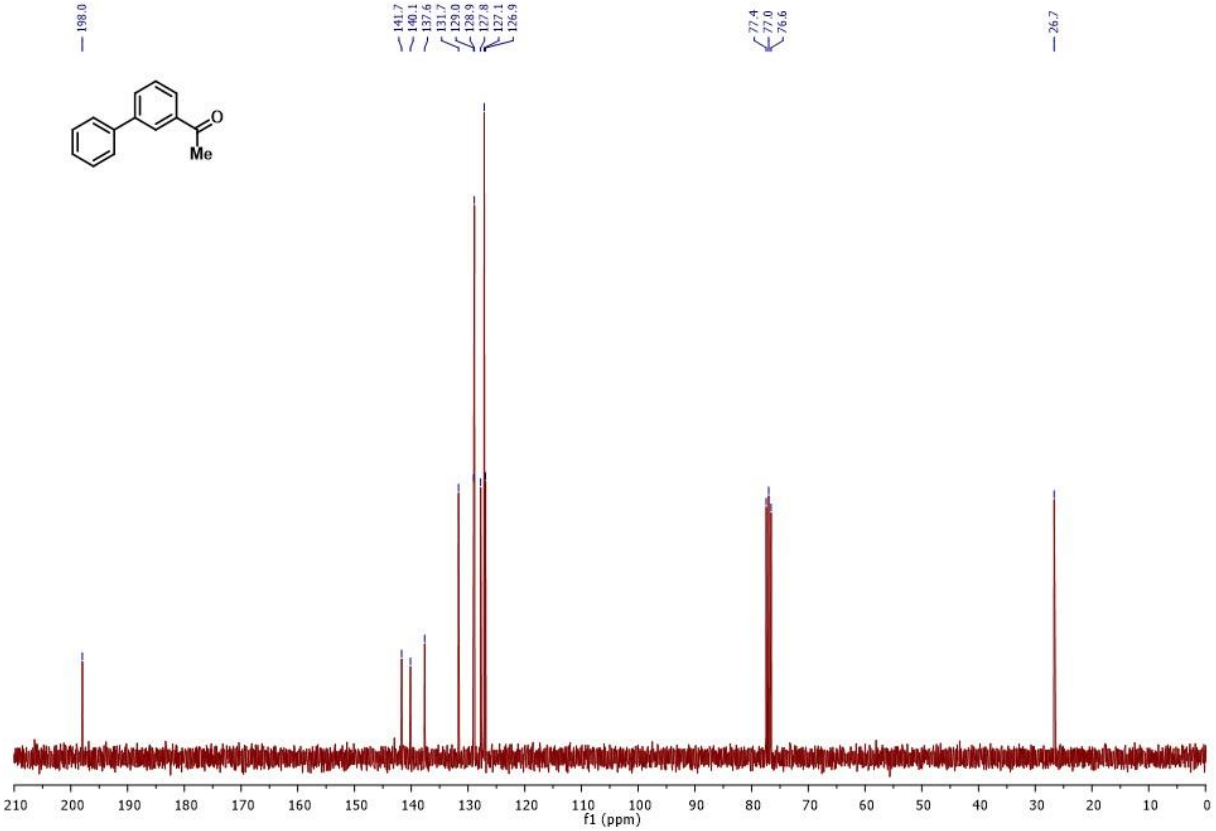
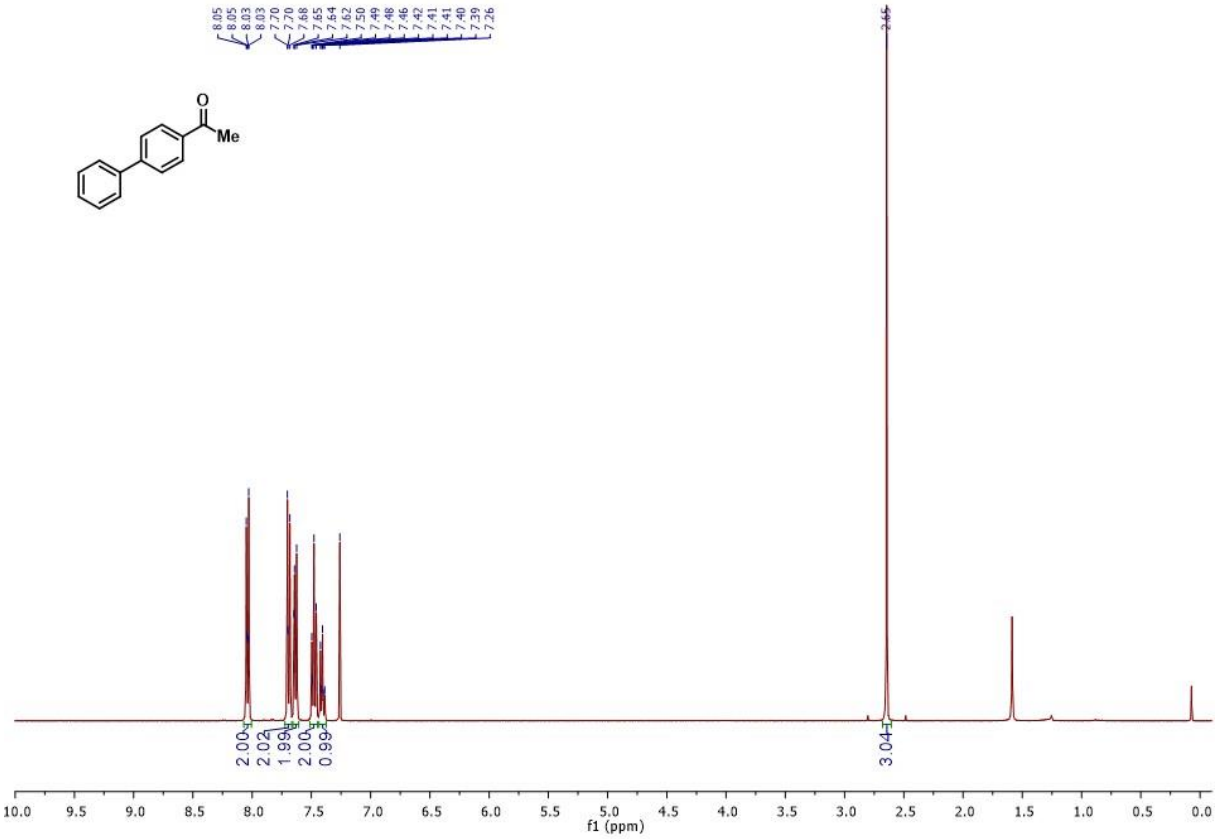
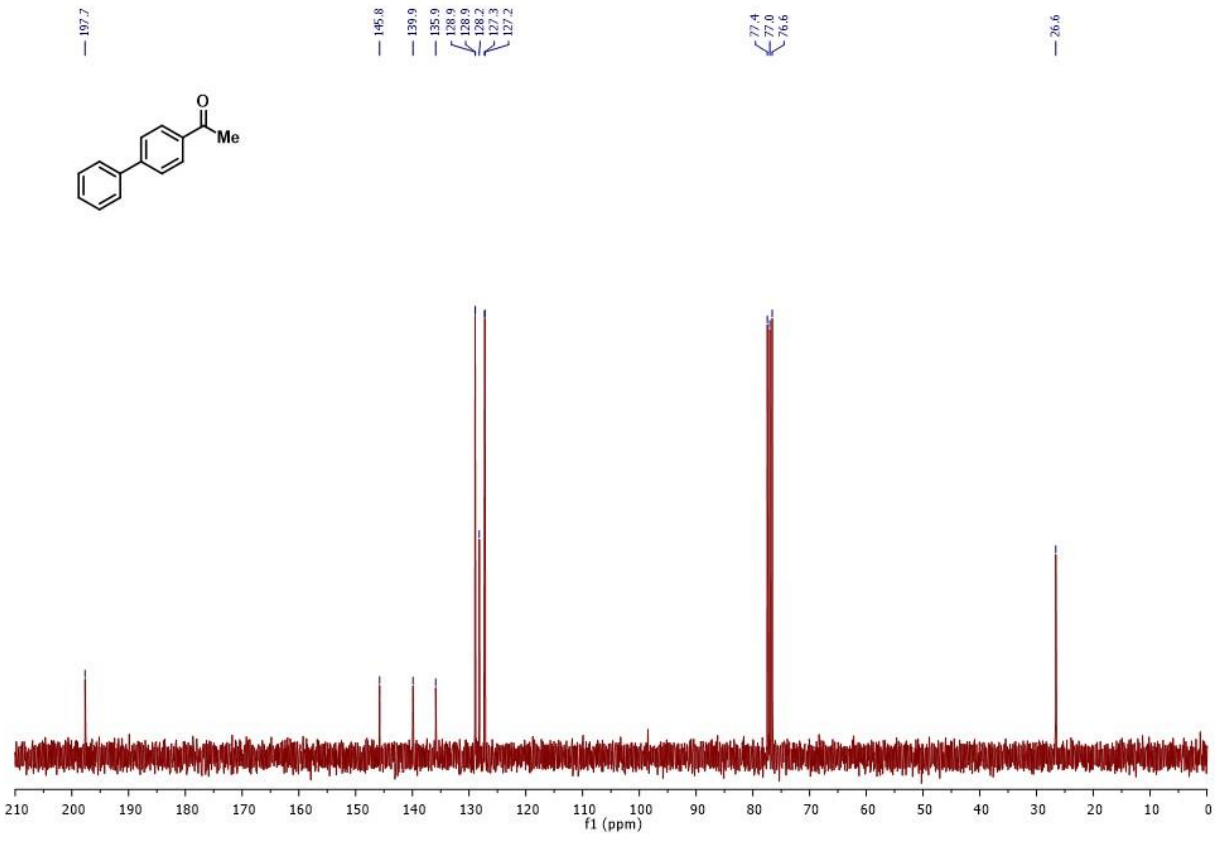


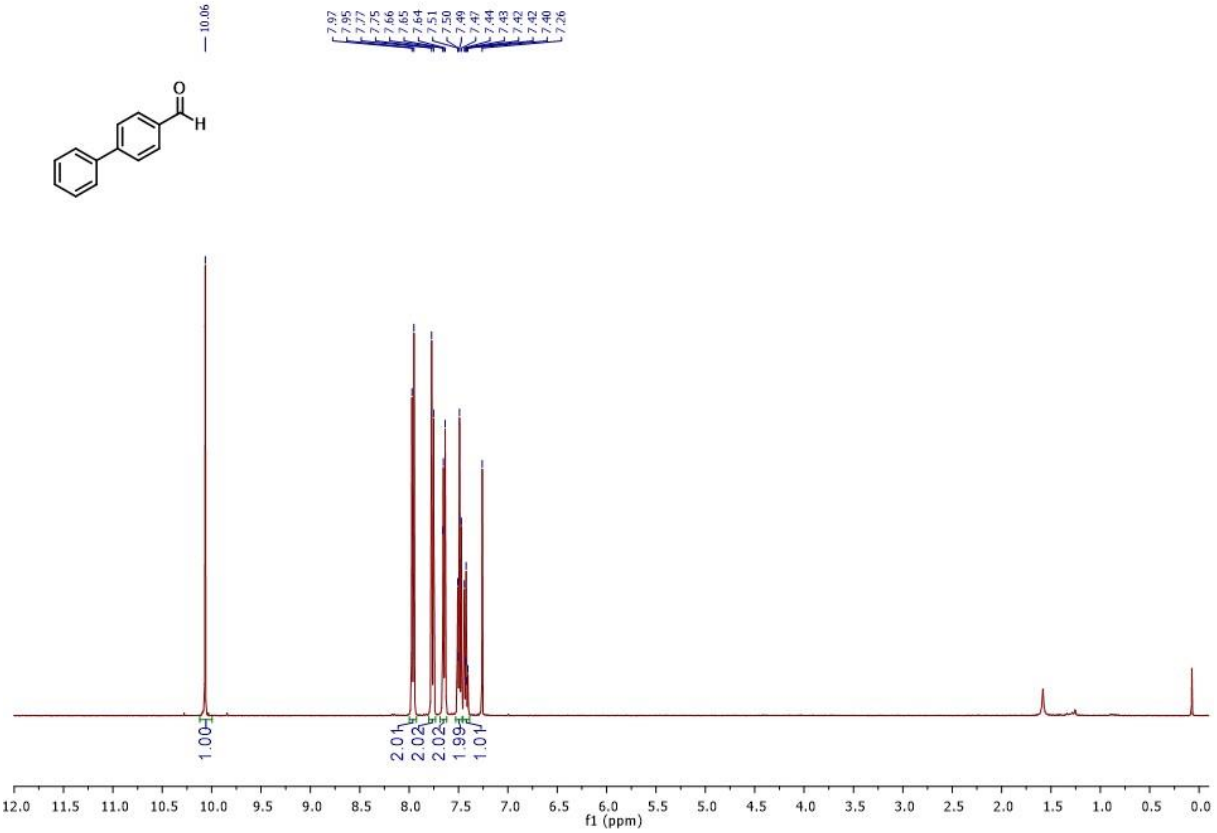


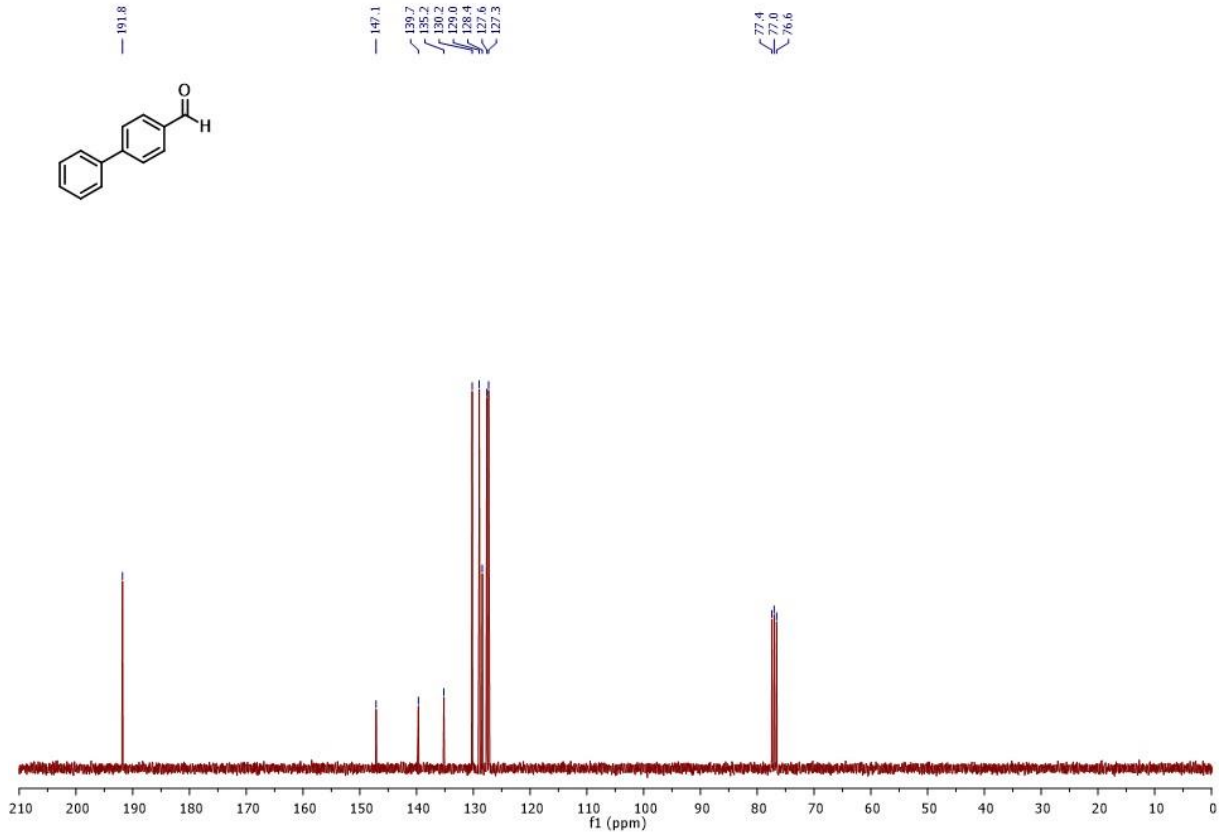
1-([1,1'-Biphenyl]-4-yl)ethan-1-one



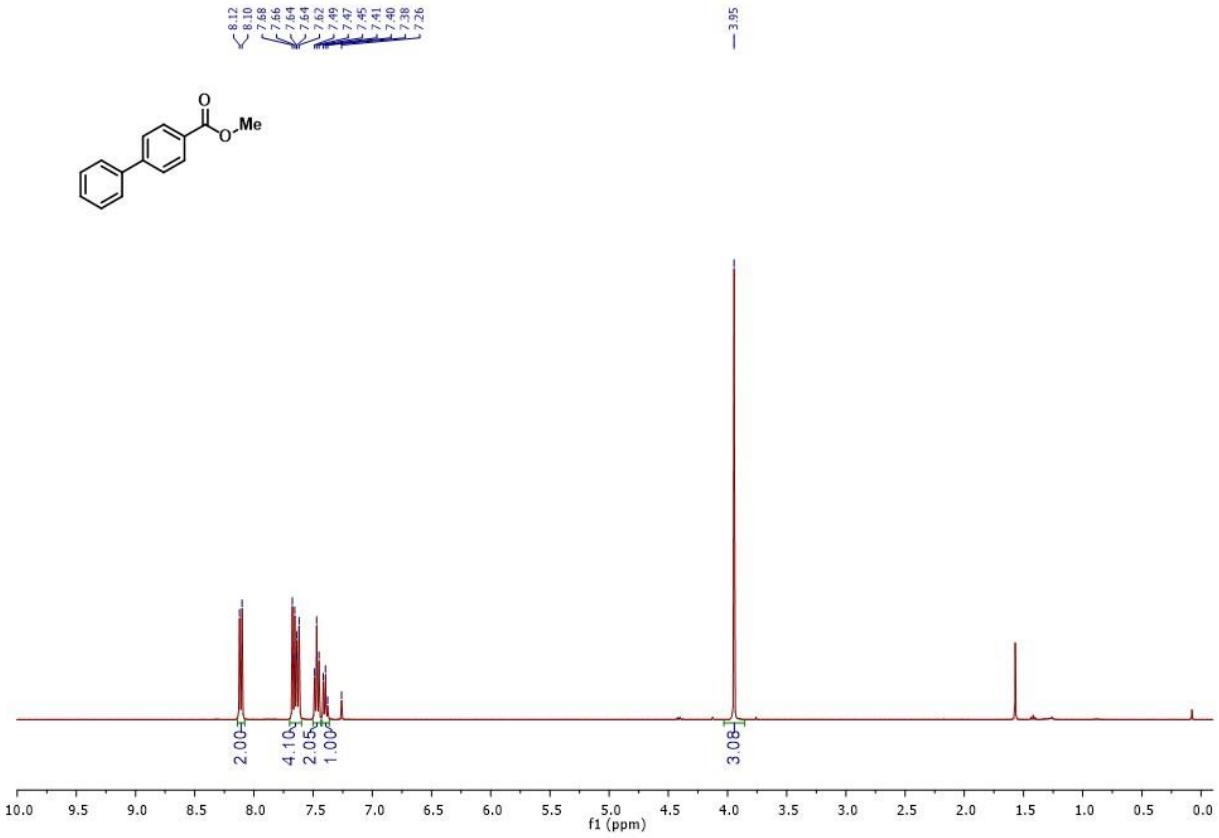


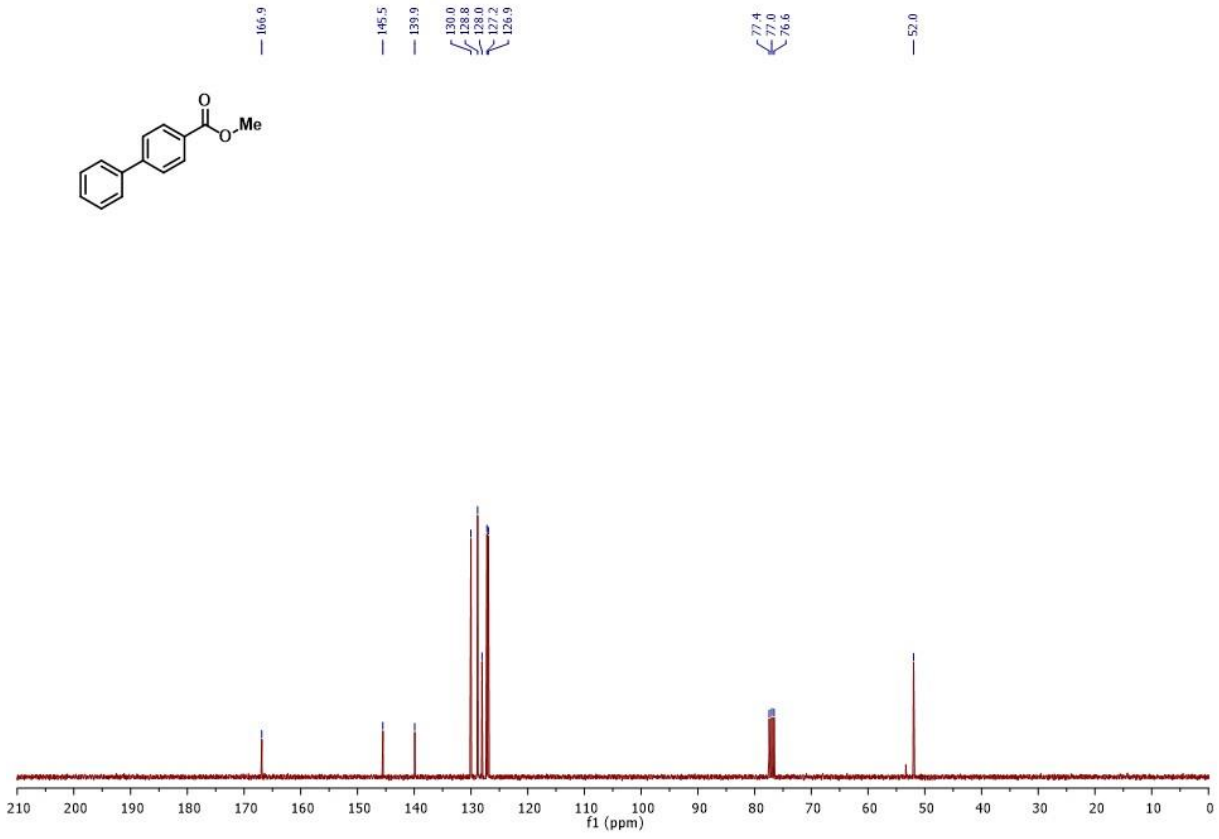
[1,1'-Biphenyl]-4-carbaldehyde



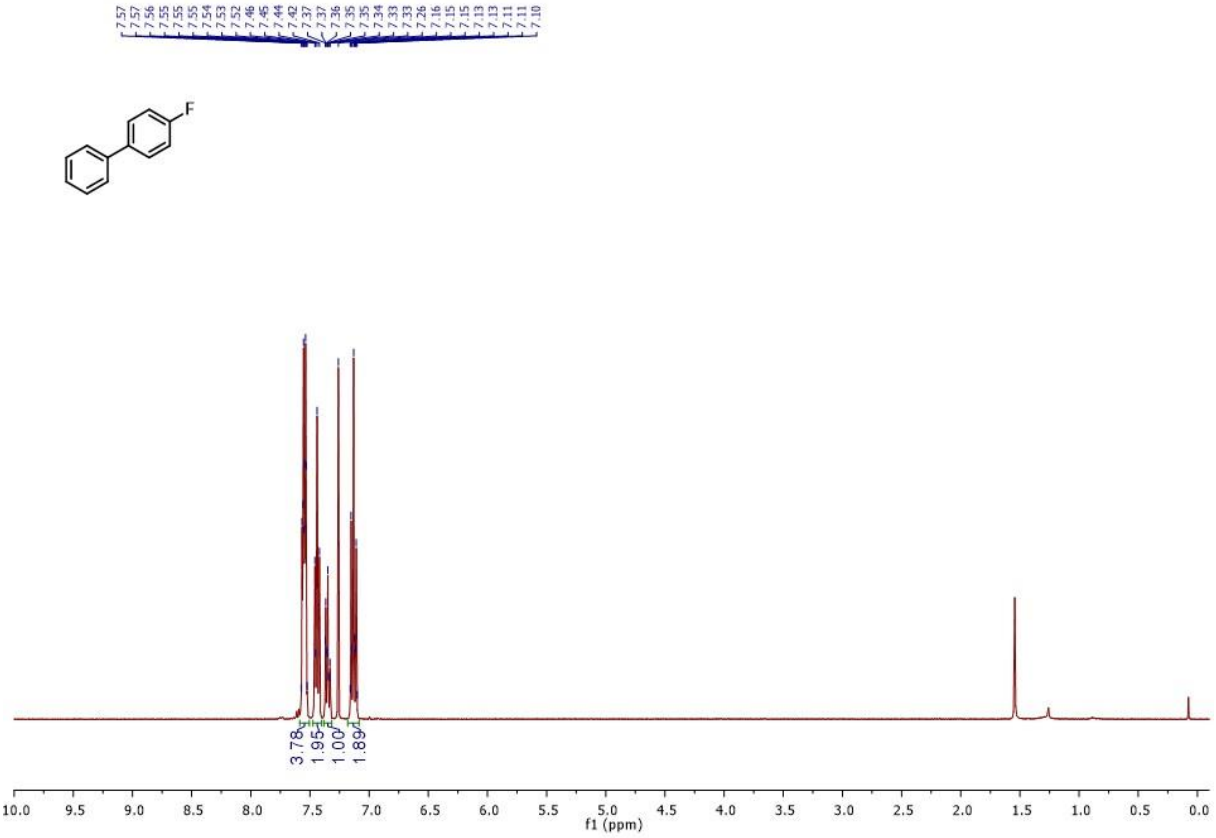


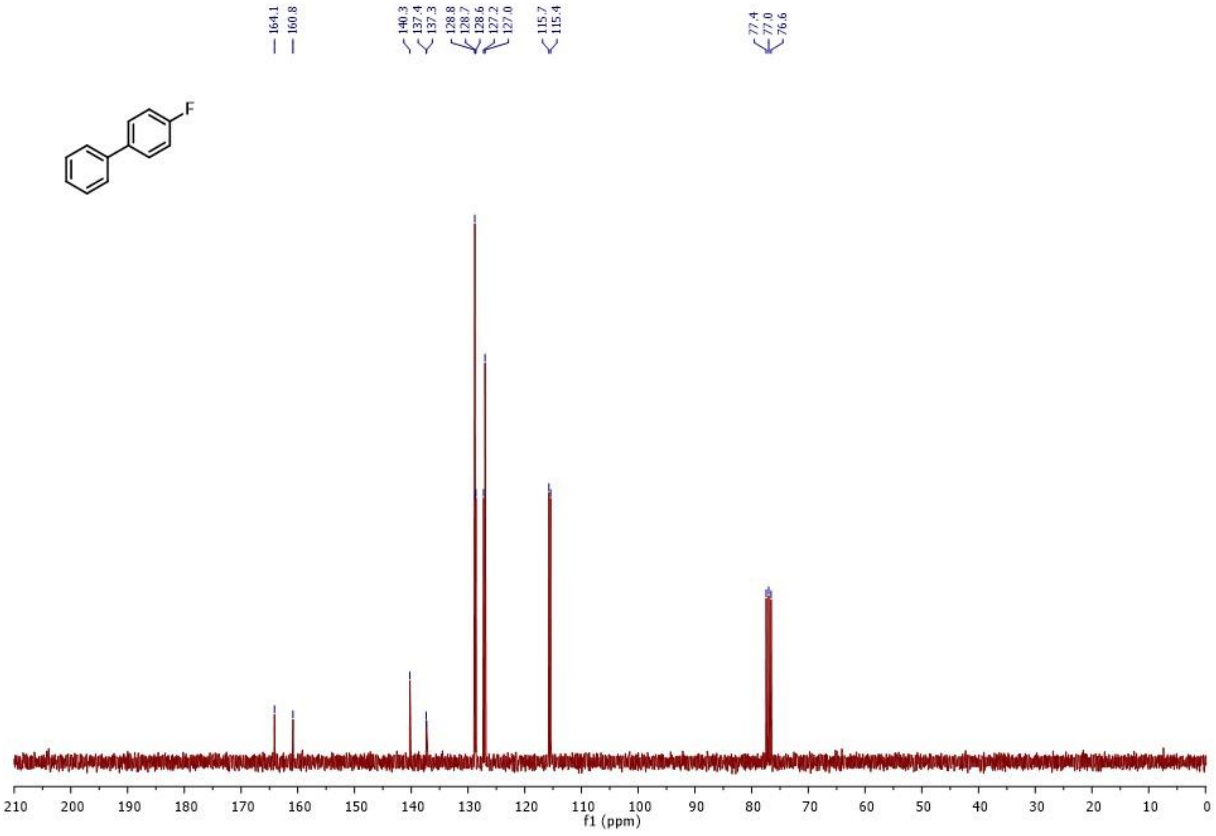
Methyl [1,1'-biphenyl]-4-carboxylate





4-Fluoro-1,1'-biphenyl





4-(Trifluoromethyl)-1,1'-biphenyl