

Electronic Supplementary Material (ESI) for Green Chemistry.
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Supporting Information

Ligand-free palladium catalyzed ullmann biaryl synthesis:

‘household’ reagents and mild reaction conditions

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List of contents

1.General Information	2
2.General procedure for synthesis of 2a-2p’ and 4ah-4fi	2
3.Compound characterizations.....	3-6
4.General procedure for synthesis of PdNPs	7
5.References.....	7
6.Spectroscopic Data for Products.....	8-27

1. General Information

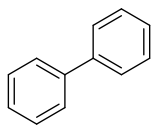
Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^1H (400MHz) and ^{13}C NMR (100MHz) data were recorded on Bruker AVANCEII400MHz spectrometer using CDCl_3 as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. ^1H NMR spectra was recorded with tetramethylsilane ($\delta = 0.00$ ppm) as internal reference; ^{13}C NMR spectra was recorded with CDCl_3 ($\delta = 77.00$ ppm) as internal reference.

Microstructure of palladium nanoparticles (PdNPs) can be observed by Field Emission. Scanning Electron Microscope JSM-7800F.

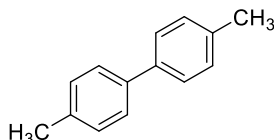
2. General procedures for synthesis of 2a-2k and 4ah-4fi

An oven-dried flask tube was charged with aryl iodide (1mmol), catalyst $\text{Pd}(\text{OAc})_2$ (0.01mmol), base K_3PO_4 (1mmol), DMSO (10mmol) and DMF (0.75mL), finally, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (4mmol) was added in the solution. The reaction mixture was stirred at room temperature under air atmosphere for 8h. The reaction was monitored by thin layer chromatography (TLC). When the reaction was completed, it was diluted with water and extracted with ethyl acetate 3 times. The organic phase was concentrated using the rotary evaporator. Removal of solvent followed by column chromatography afforded desired products.

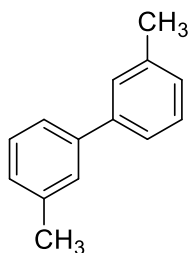
3. Compound characterizations



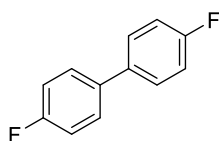
Diphenyl (2a)^{[1][2]}. Petroleum ether, white solid. ¹H NMR(400 MHz, CDCl₃, TMS) δ(ppm)7.67-7.65(m, 4H), 7.44-7.40(m, 4H), 7.35-7.31(m, 2H); ¹³C NMR(100 MHz, CDCl₃, TMS) (ppm) 141.3, 128.8, 127.3, 127.2.



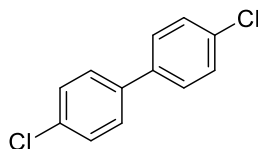
4, 4'-Dimethyldiphenyl (2b)^{[1][2]}. Pure petroleum ether, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 7.48-7.46 (d, *J*=8.0 Hz, 4H), 7.23-7.21 (d, *J*=8.0Hz, 4H), 2.38(s, 6H); ¹³C NMR (100 MHz, CDCl₃, TMS) (ppm) 138.3, 136.7, 129.5, 126.9, 21.2.



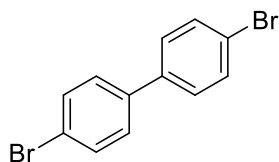
3, 3'-Dimethylbiphenyl (2c)^[7]. Pure petroleum ether, colorless oil. ¹H NMR(400 MHz, CDCl₃, TMS) δ (ppm) 7.54-7.51(m, 4H), 7.45(t, *J*=8.0Hz, 2H), 7.28(d, *J*=7.1Hz, 2H), 2.55(s, 6H); ¹³C NMR(100 MHz, CDCl₃, TMS) δ(ppm) 141.7, 138.4, 128.7, 128.1, 128.0, 124.4, 21.7.



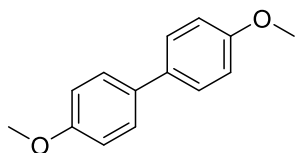
4, 4'-Difluorodiphenyl (2e)^{[1][2]}. Pure petroleum ether, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 7.51-7.48 (m, 4H), 7.13 (t, *J*=8.6Hz, 4H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm) 162.4 (d, *J*=237.2Hz), 136.4 (d, *J*=3.2Hz), 128.6 (d, *J*=7.8Hz), 115.7(d, *J*=21.3Hz).



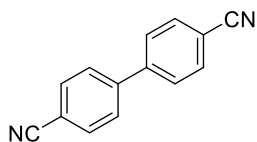
4, 4'-Dichlorobiphenyl (2f)^[2]. Pure petroleum ether, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 7.46-7.49(m, 4H), 7.40-7.42 (m, 4H); ¹³C NMR (100 MHz, CDCl₃, TMS)δ (ppm) 138.4, 133.8, 129.1, 128.2.



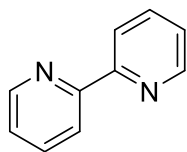
4, 4'-Dibromobiphenyl (2g)^[1]. Pure petroleum ether, white solid. ¹H NMR(400 MHz, CDCl₃, TMS) δ(ppm) 7.56(m, 4H), 7.42(m, 4H); ¹³C NMR(100 MHz, CDCl₃, TMS) δ (ppm) 138.9, 132.0, 128.5, 121.8.



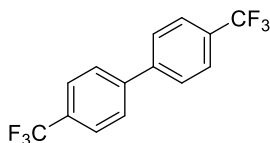
4, 4'-Dimethoxybiphenyl (2h)^{[1][2]}. Pure petroleum ether, white solid. ¹H NMR(400 MHz, CDCl₃, TMS) δ(ppm) 7.49(d, *J*=8.6Hz, 4H), 6.97(d, *J*=8.6Hz, 4H), 3.86(s, 6H); ¹³C NMR(100 MHz, CDCl₃, TMS) δ(ppm) 158.7, 133.5, 127.8, 114.2, 55.4.



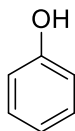
4, 4'-Biphenyldicarbonitrile (2i)^[2]. Petroleum ether/Ethyl acetate=50:1, white solid. ¹H NMR(400 MHz, CDCl₃, TMS) δ(ppm) 7.74(q, *J*₁=8.2Hz, *J*₂=33.2Hz, 8H); ¹³C NMR(100 MHz, CDCl₃, TMS) δ(ppm) 143.5, 132.9, 127.9, 118.4, 112.4.



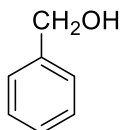
2, 2'-bipyridines (2j)^[6]. Petroleum ether/Ethyl acetate=10:1, yellow solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm)8.67-8.68(m, 2H), 8.38-8.40(m, 2H), 7.79-7.83(m, 2H), 7.28-7.32(m, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm)156.2, 149.2, 137.0, 123.7, 121.1.



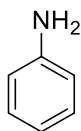
4, 4'-Bis(trifluoromethyl)biphenyl (2k)^{[1][2]}. Petroleum ether, white solid. ¹H NMR(400 MHz, CDCl₃, TMS) δ(ppm)7.76-7.70(m, 8H); ¹³C NMR(100 MHz, CDCl₃, TMS) δ(ppm) 143.2, 130.5(d, *J*=33.5Hz), 127.6, 125.9(q, *J*=4.1Hz), 124.1(d, *J*=272.9Hz).



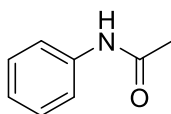
Benzenol (2l')^[12]. Petroleum ether/Ethyl acetate=50:1, white solid. ¹H NMR(400 MHz, CDCl₃, TMS) δ(ppm) 7.30-7.26(m, 2H), 6.98(t, *J*=7.3Hz, 1H), 6.90-6.87(m, 2H); ¹³C NMR(100 MHz, CDCl₃, TMS) δ (ppm) 155.1, 129.7, 120.9, 115.3.



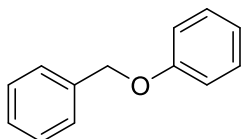
Benzenemethanol (2m')^[13]. Petroleum ether/Ethyl acetate=50:1, colorless oil. ¹H NMR(400 MHz, CDCl₃, TMS) δ(ppm) 7.42-7.32(m, 5H), 4.59(s, 2H), 3.88(s, 1H); ¹³C NMR(100 MHz, CDCl₃, TMS) δ (ppm) 140.7, 128.2, 127.2, 126.7, 64.4.



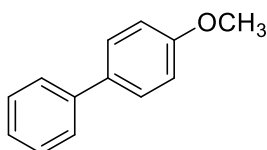
Benzenamine (2n')^[12]. Petroleum ether/Ethyl acetate=50:1, colorless oil. ¹H NMR(400 MHz, CDCl₃, TMS) δ(ppm) 7.21-7.18(m, 2H), 6.80(t, *J*=7.5Hz, 1H), 6.72-6.70(m, 2H); ¹³C NMR(100 MHz, CDCl₃, TMS) δ (ppm) 146.3, 129.2, 118.5, 115.0.



N-Phenylacetamide (2o')^[14]. Petroleum ether/Ethyl acetate=5:1, white solid. ¹H NMR(400 MHz, CDCl₃, TMS) δ(ppm) 8.28(s, 1H), 7.54(d, *J*=7.8Hz, 2H), 7.30(t, *J*=7.8Hz, 2H), 7.10(t, *J*=7.3Hz, 1H), 2.16(s, 3H); ¹³C NMR(100 MHz, CDCl₃, TMS) δ (ppm) 169.0, 138.0, 128.8, 124.2, 120.1, 24.3.

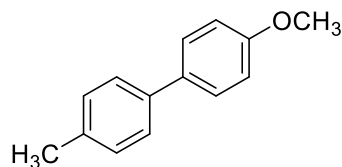


Benzyloxybenzene (2p')^[15]. Petroleum ether, white solid. ¹H NMR(400 MHz, CDCl₃, TMS) δ(ppm) 7.48(d, *J*=7.5Hz, 2H), 7.42(t, *J*=7.0Hz, 2H), 7.38-7.31(m, 3H), 7.03-6.98(m, 3H), 5.10(s, 2H); ¹³C NMR(100 MHz, CDCl₃, TMS) δ (ppm) 158.77, 137.06, 129.45, 128.54, 127.90, 127.44, 120.91, 114.83, 69.88.

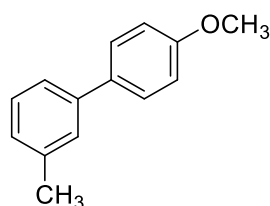


4-Methoxy-biphenyl (4ah)^{[4][7]}. Pure petroleum ether, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 7.58- 7.53(m, 4H), 7.43(t, *J*=7.9Hz, 2H), 7.33-7.31(m,

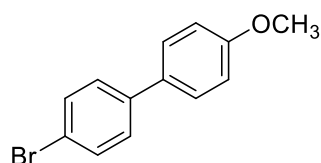
1H), 7.00(m, 2H), 3.86(s, 3H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm)159.16, 140.85, 133.80, 128.74, 128.17, 126.76, 126.67, 114.22, 55.36.



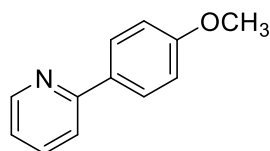
4-Methoxy-4'-methyl-biphenyl (4bh)^[7]. Pure petroleum ether, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm)7.51(d, *J*=8.8Hz, 2H), 7.45(d, *J*=8.4Hz, 2H), 7.23(d, *J*=8.9Hz, 2H), 6.97(d, *J*=8.8Hz, 2H), 3.85(s, 3H), 2.39(s, 3H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm)158.95, 137.98, 136.35, 133.77, 129.43, 127.95, 126.59, 114.17, 55.35, 21.04.



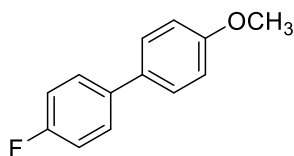
4-Methoxy-3'-methyl-biphenyl (4ch)^[8]. Pure petroleum ether, Colorless oil. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm)7.54(d, *J*=7.8Hz, 2H), 7.39-7.31(m, 3H), 7.14(d, *J*=6.9Hz, 1H), 6.99(d, *J*=8.7Hz, 2H), 3.86(s, 3H), 2.43(s, 3H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm)159.09, 140.84, 138.30, 133.92, 128.66, 128.19, 127.59, 127.44, 123.88, 114.16, 55.36, 21.59.



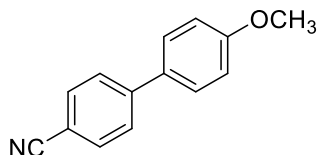
4-Bromo-4'-methoxy-biphenyl (4gh)^[4]. Pure petroleum ether, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 7.54-7.48(dd, *J*=8.1Hz, 4H), 7.41(d, *J*=8.7Hz, 2H), 6.98(d, *J*=8.2Hz, 2H), 3.85(s, 3H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm) 159.4, 139.8, 132.5, 131.8, 128.3, 128.0, 120.8, 114.4, 55.4.



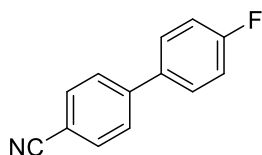
2-(4'-Methoxyphenyl) pyridine (2jh)^[9]. Petroleum ether/Ethyl acetate=20:1, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 8.65(d, *J*=5.6Hz, 1H), 7.95(d, *J*=6.9Hz, 2H), 7.67-7.71(m, 2H), 7.15-7.18(m, 1H), 7.01(d, *J*=9.0Hz, 2H), 3.86(s, 3H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm) 160.46, 157.14, 149.55, 136.67, 132.05, 128.17, 121.42, 119.82, 114.13, 55.36.



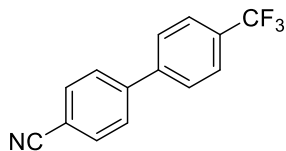
4-Fluoro-4'-methoxybiphenyl (4eh)^[10]. Pure petroleum ether, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 7.52-7.46(m, 4H), 7.10(t, *J*=8.7Hz, 2H), 6.98(d, *J*=8.6Hz, 2H), 3.85(s, 3H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm) 163.3(d, *J*=245.9Hz), 159.1, 137.0(d, *J*=2.9Hz), 132.9, 128.0, 115.6(d, *J*=21.5Hz), 114.3, 55.4.



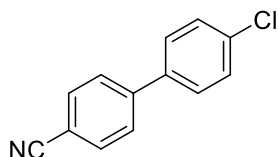
4'-Methoxy-biphenyl-4-carbonitrile (4hi)^[3]. Petroleum ether/Ethyl acetate=30:1, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 7.67(q, *J*₁=7.9Hz, *J*₂=21.3Hz, 4H), 7.54(d, *J*=8.8Hz, 2H), 7.01(d, *J*=8.8Hz, 2H), 3.86(s, 6H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm) 160.2, 145.2, 132.6, 131.5, 128.4, 127.1, 119.1, 114.6, 110.1, 55.4.



4'-Fluoro-biphenyl-4-carbonitrile (4ei)^[3]. Petroleum ether/Ethyl acetate=50:1, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 7.71-7.65(m, 4H), 7.58-7.53(m, 2H), 7.17(t, *J*=8.6Hz, 2H), ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm) 164.5, 162.0, 144.6, 135.3, 132.7, 128.9(d, *J*=8.1Hz), 127.6, 118.8, 116.0(d, *J*=21.6Hz), 111.0.



4'-Trifluoromethyl-biphenyl-4-carbonitrile (4ki)^[11]. Petroleum ether/Ethyl acetate=50:1, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 7.69- 7.78(m, 8H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm) 144.1, 142.7, 132.8, 130.9(d, *J*=33.1Hz), 128.0, 127.6, 126.1(q, *J*₁=3.8Hz, *J*₂=7.8Hz), 125.4(d, *J*=253.6Hz), 118.6, 112.0.



4'-Chloro-biphenyl-4-ylcarbonitrile (4fi)^[5]. Petroleum ether/Ethyl acetate=50:1, white solid. ¹H NMR (400 MHz, CDCl₃, TMS) δ(ppm) 7.69(q, *J*₁=8.5Hz, *J*₂=32.9Hz, 4H), 7.49(q, *J*₁=8.5Hz, *J*₂=27.1Hz, 4H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ(ppm) 144.4, 137.6, 135.0, 132.7, 129.3, 128.5, 127.6, 118.8, 111.3.

4. General procedure for synthesis of PdNPs

To a 10 mL reaction tube was added 30 mg of palladium acetate, and then 1 mL of a solvent (DMF:DMSO=3:1) was added, and 0.2 mL of hydrazine hydrate was added dropwise to the reaction system while stirring. After sonication for 20 min, filter, it was washed for several times with water and acetone, and dried to give a dark grey powder 10mg, yield 71% (Figure 1) .

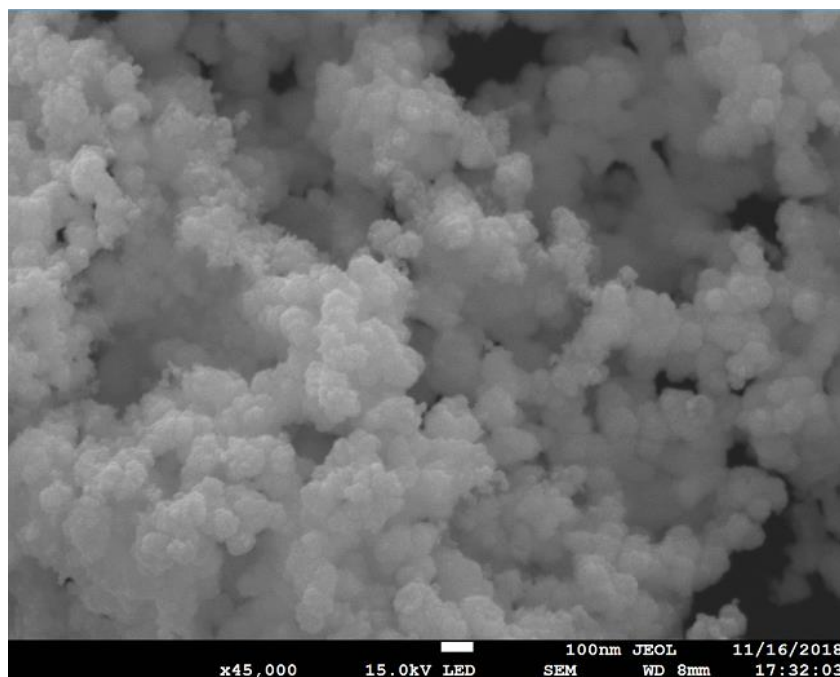
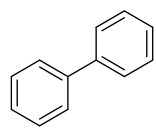


Figure 1

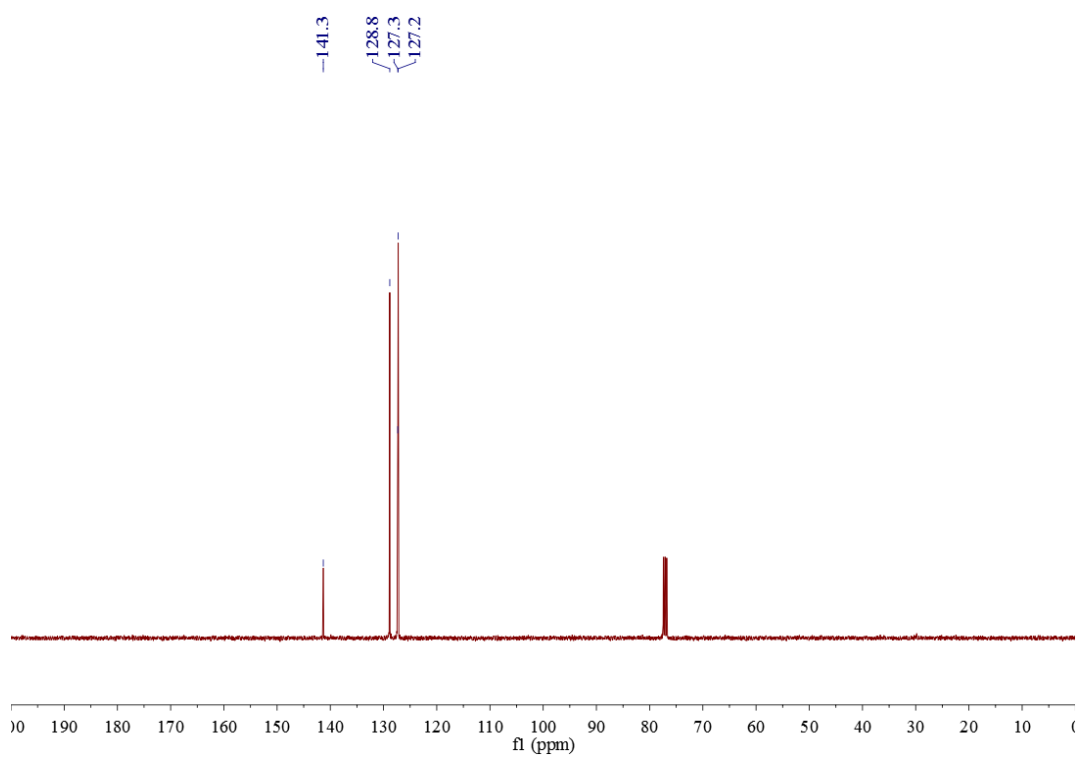
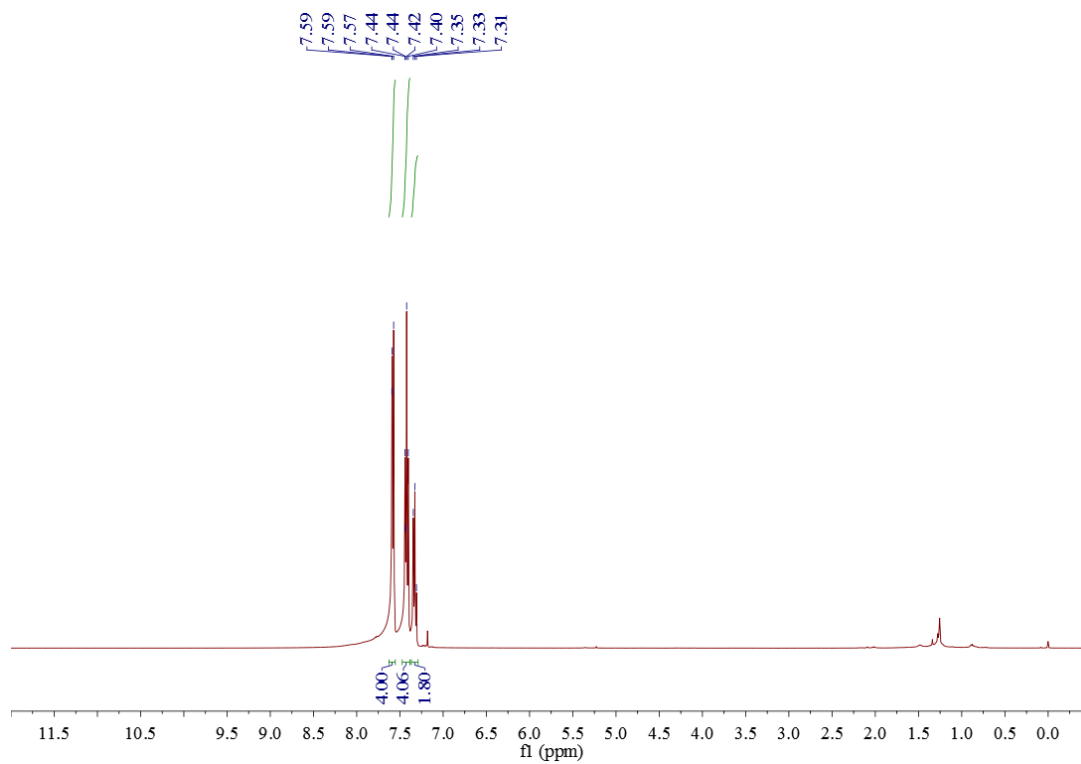
5. References

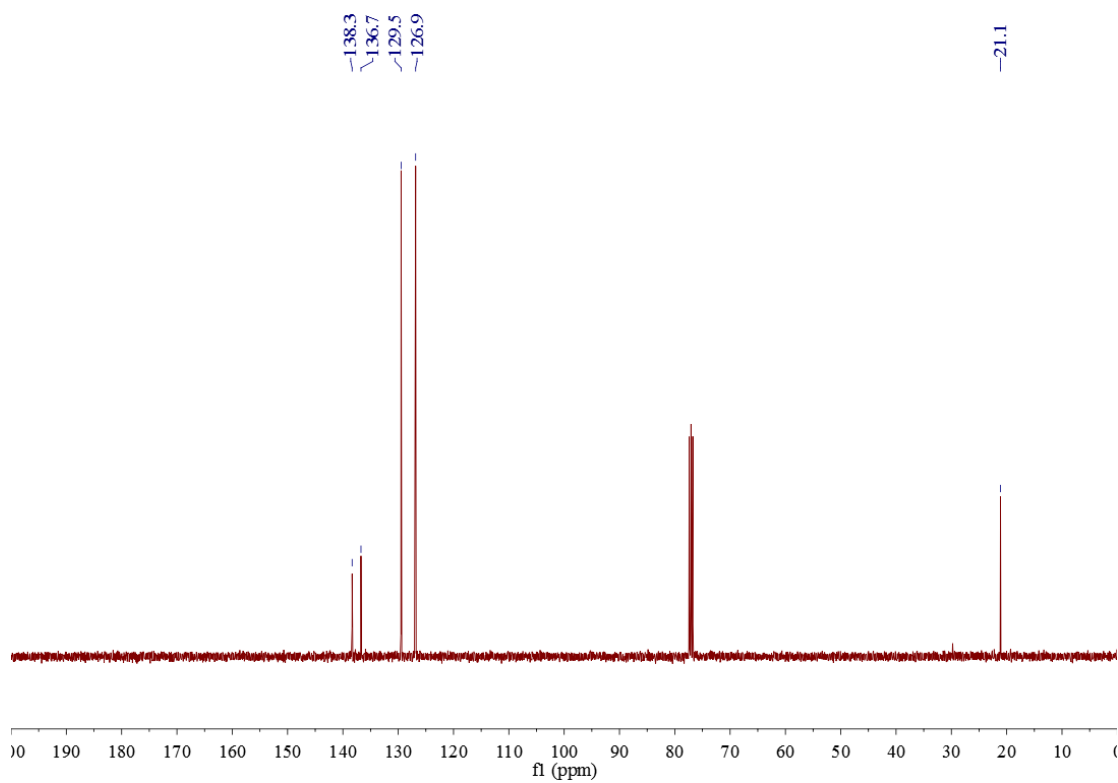
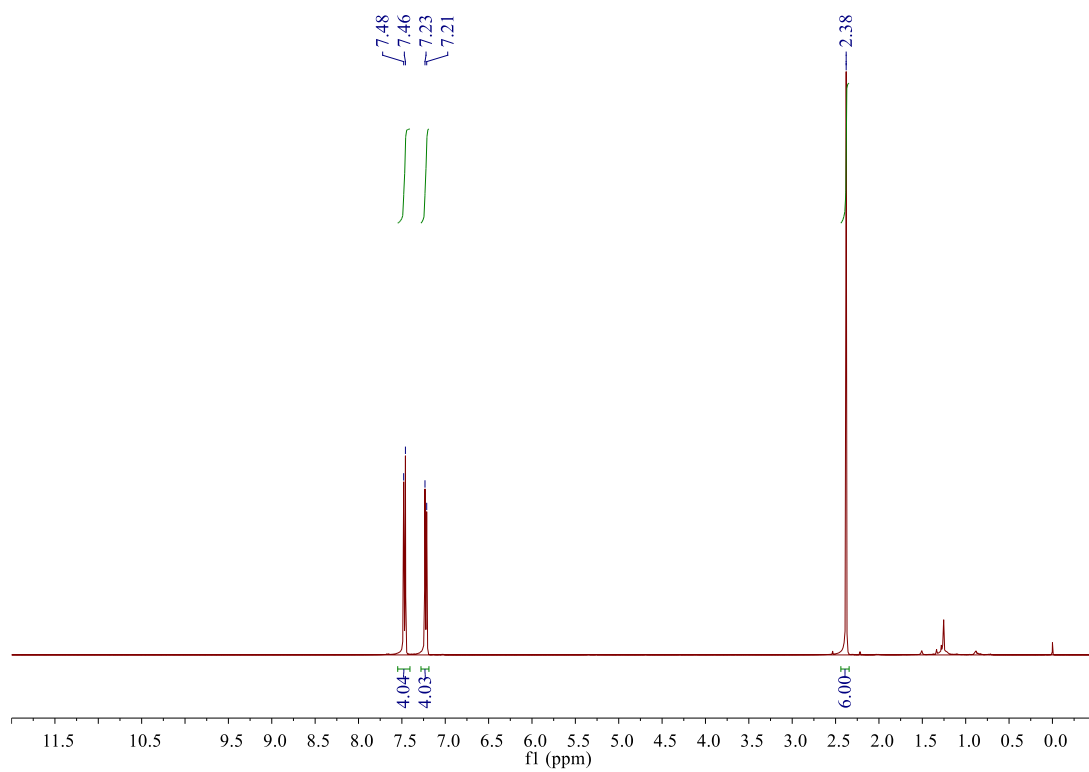
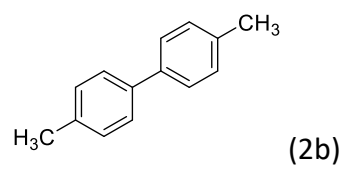
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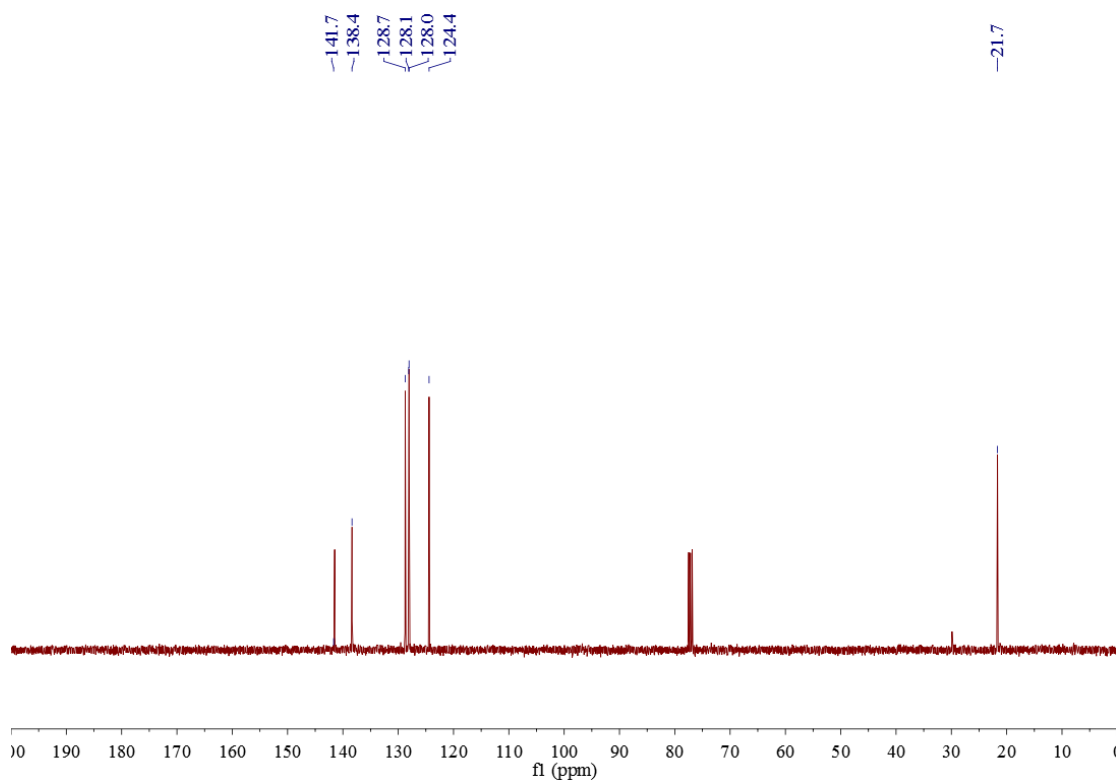
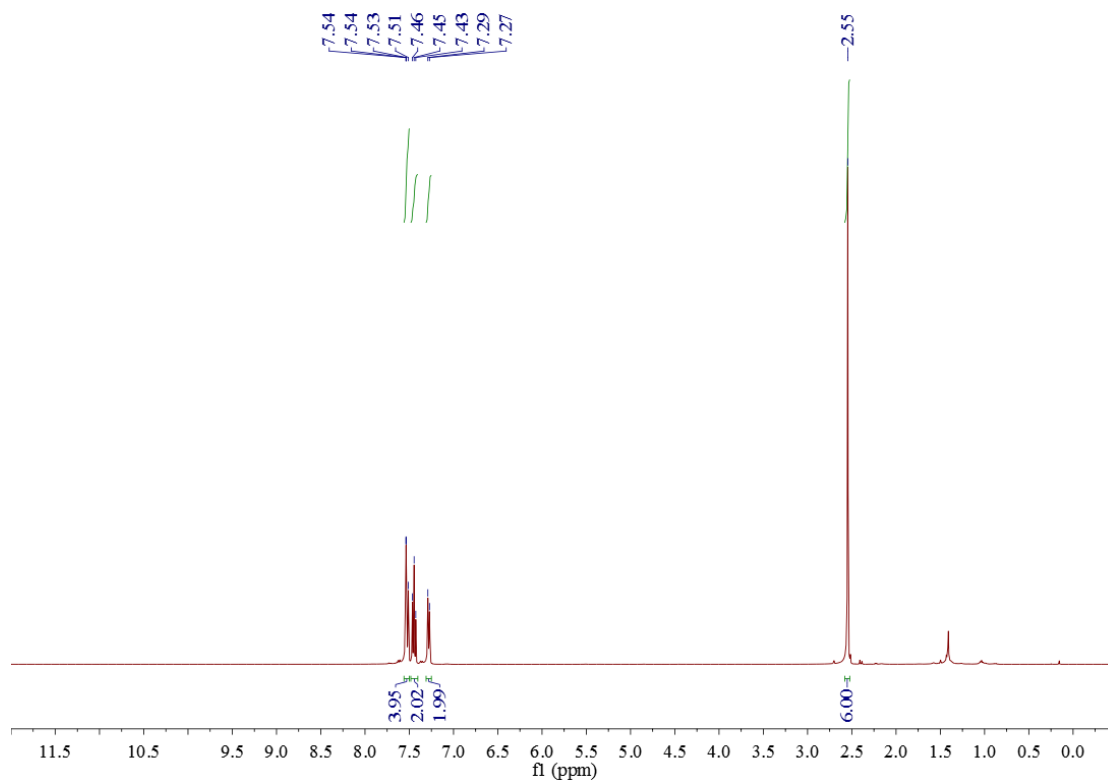
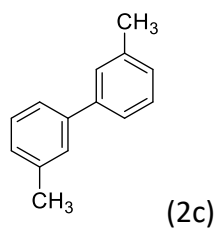
5. Spectroscopic Data for Products

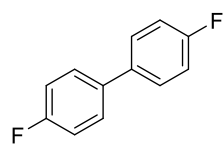


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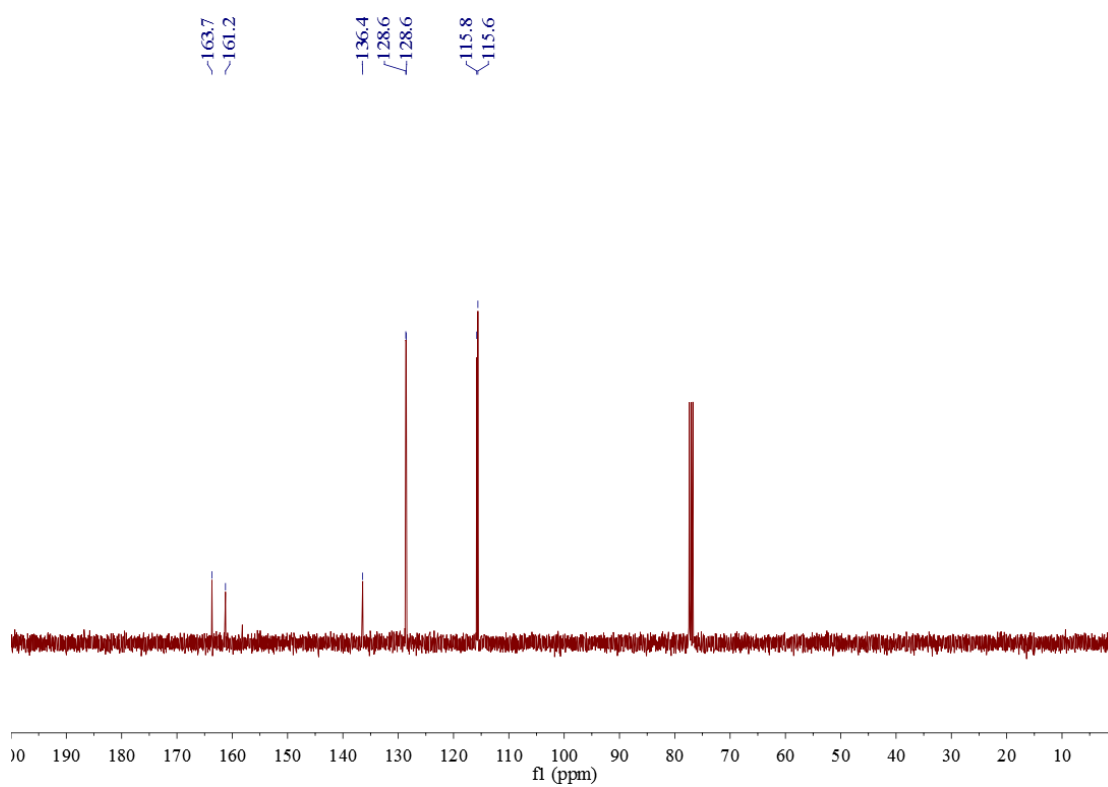
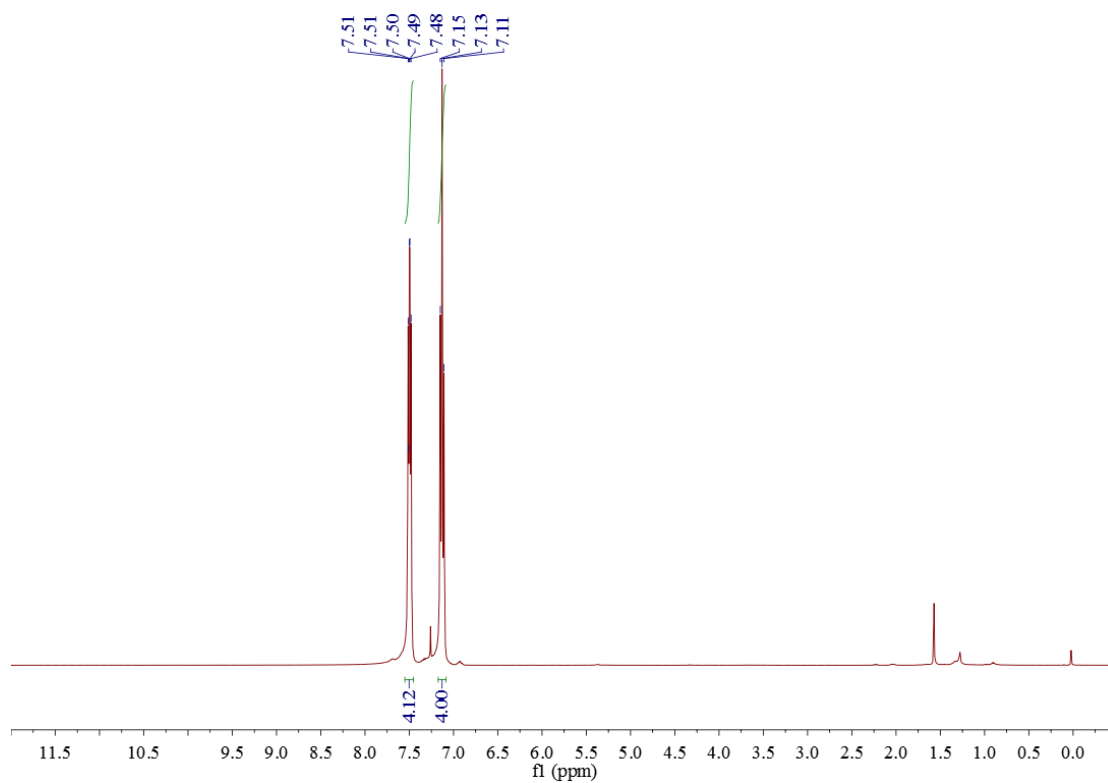


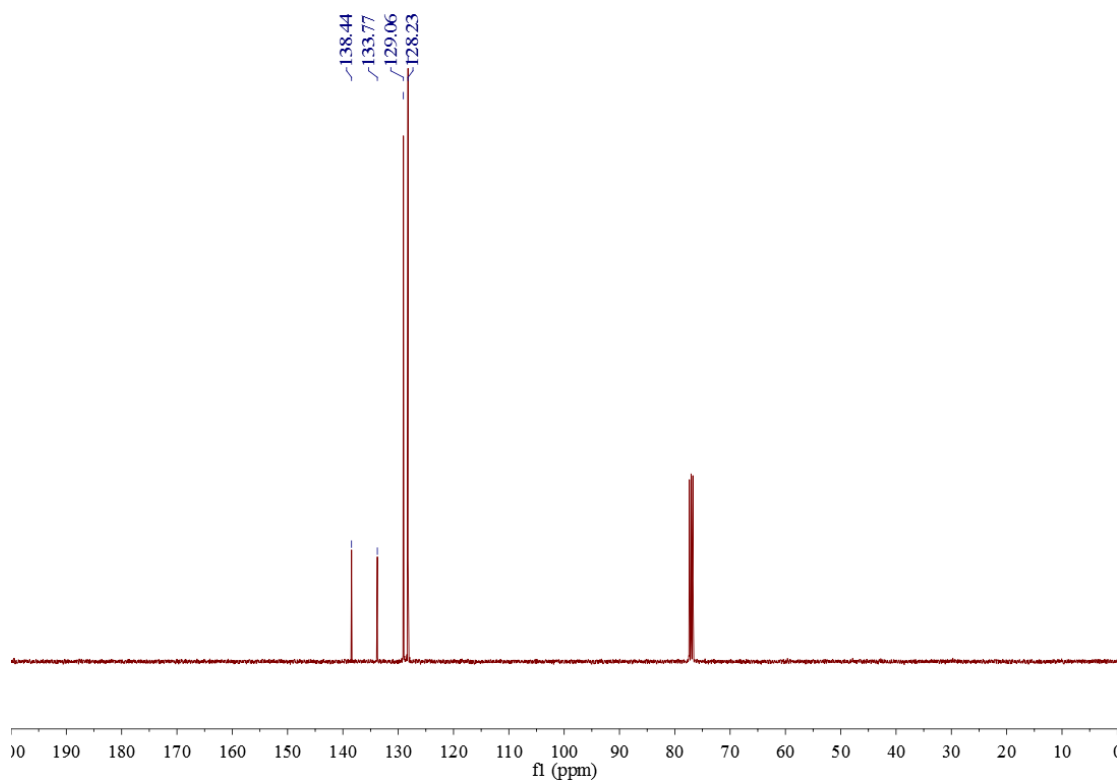
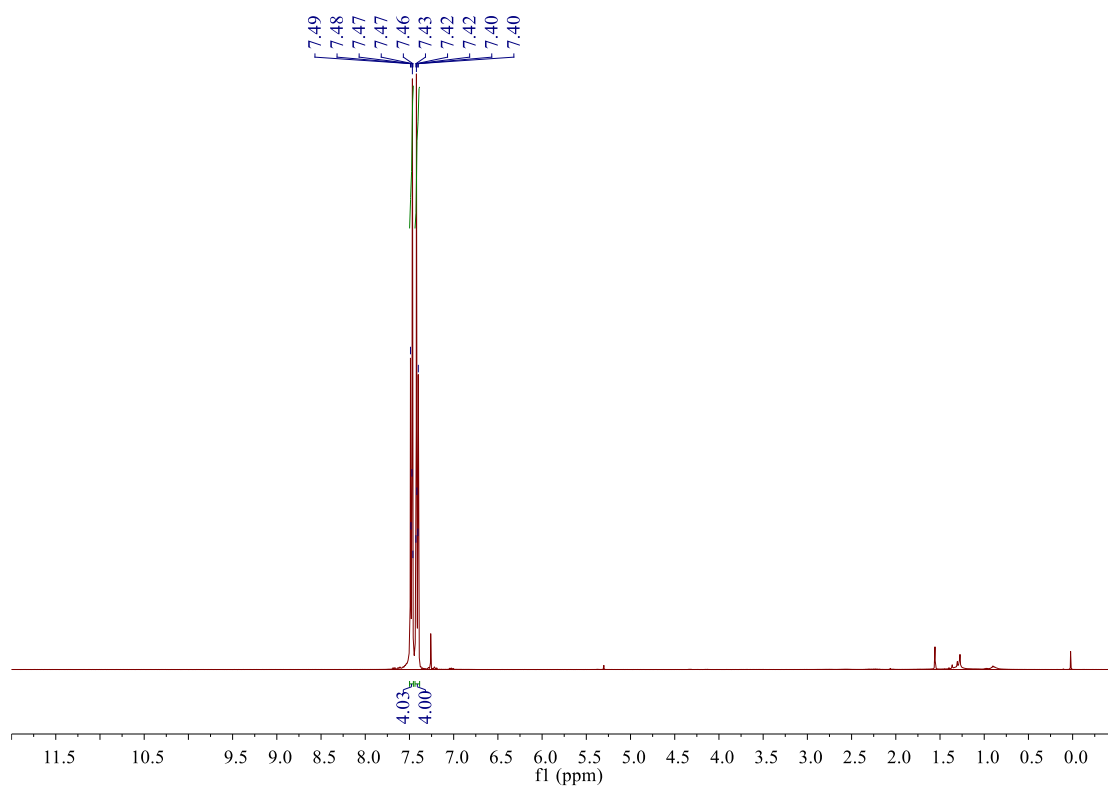
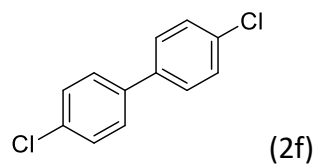


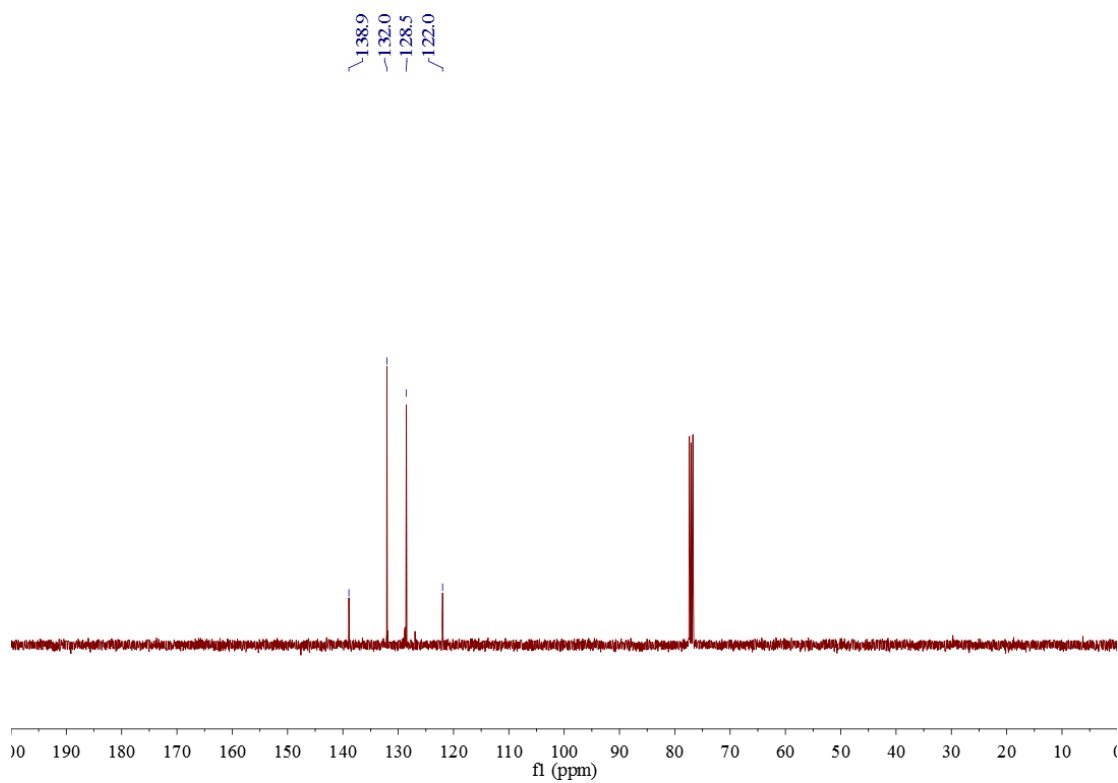
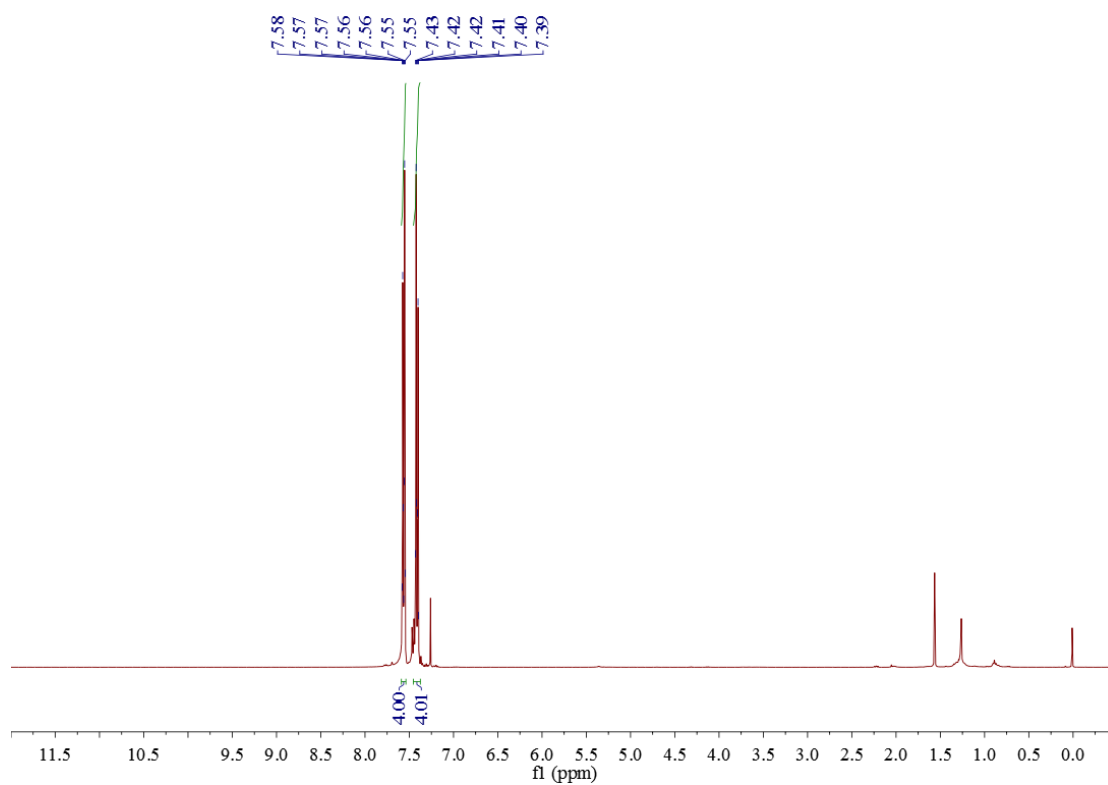
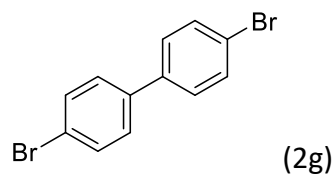


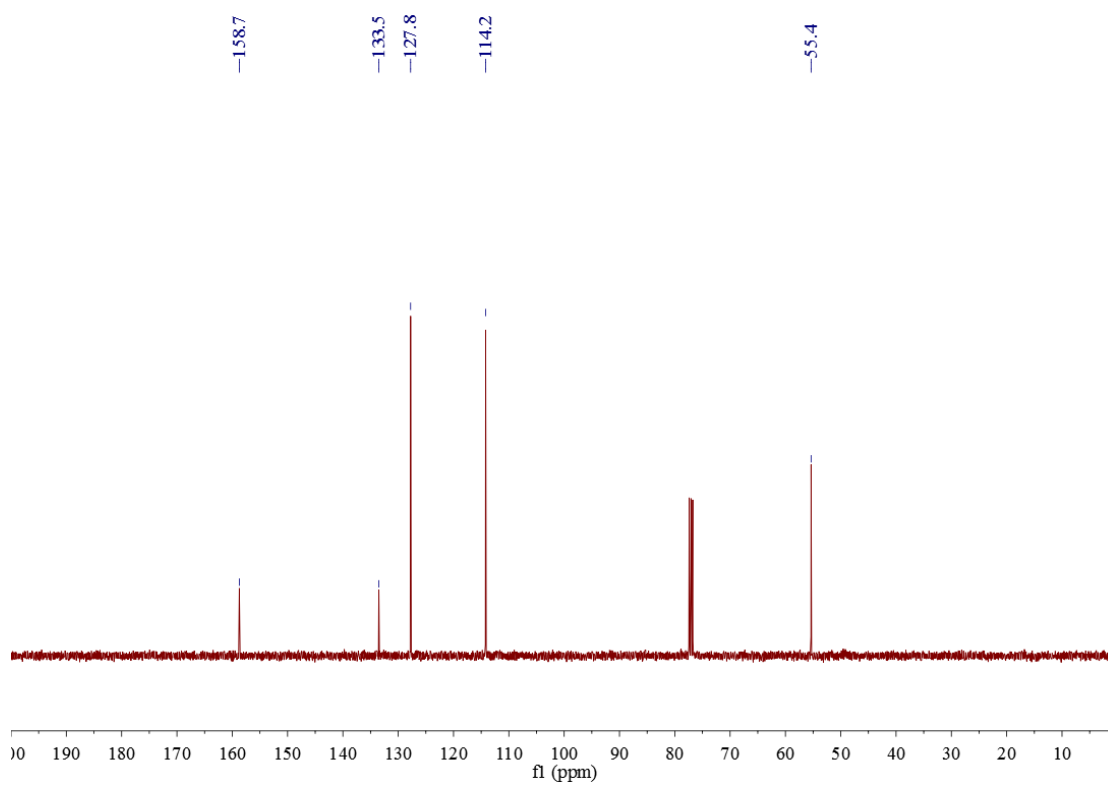
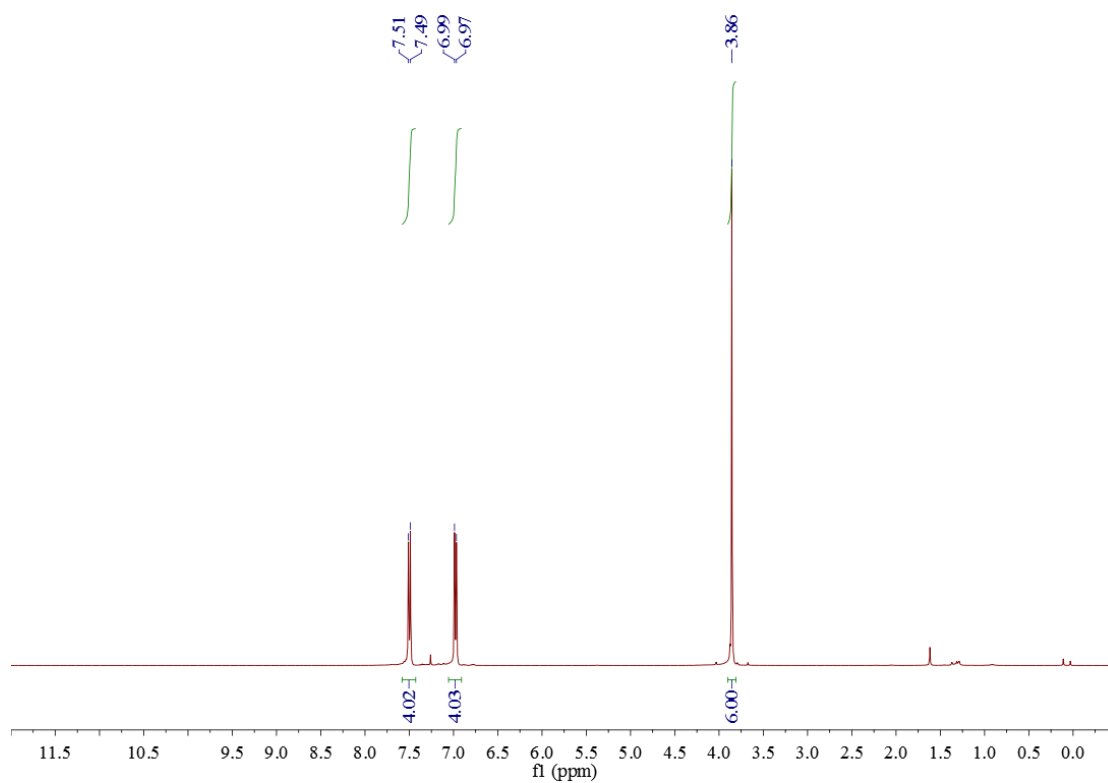
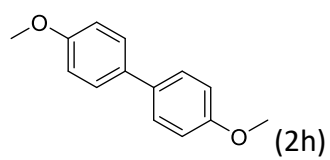


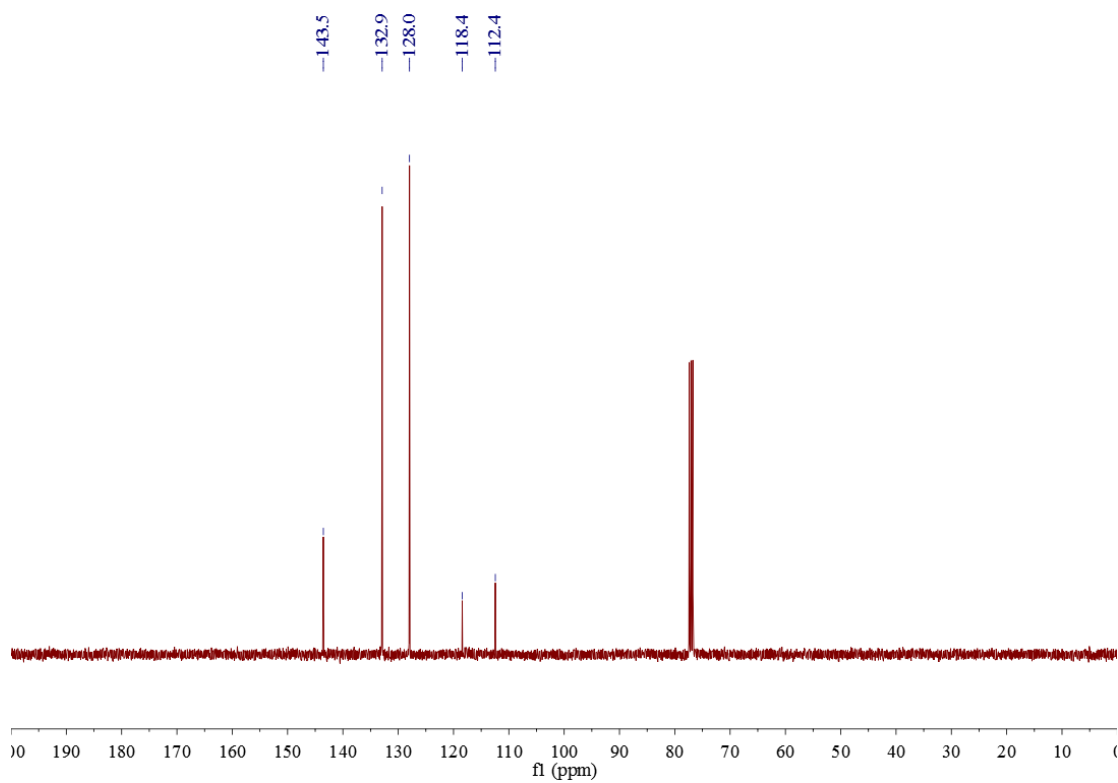
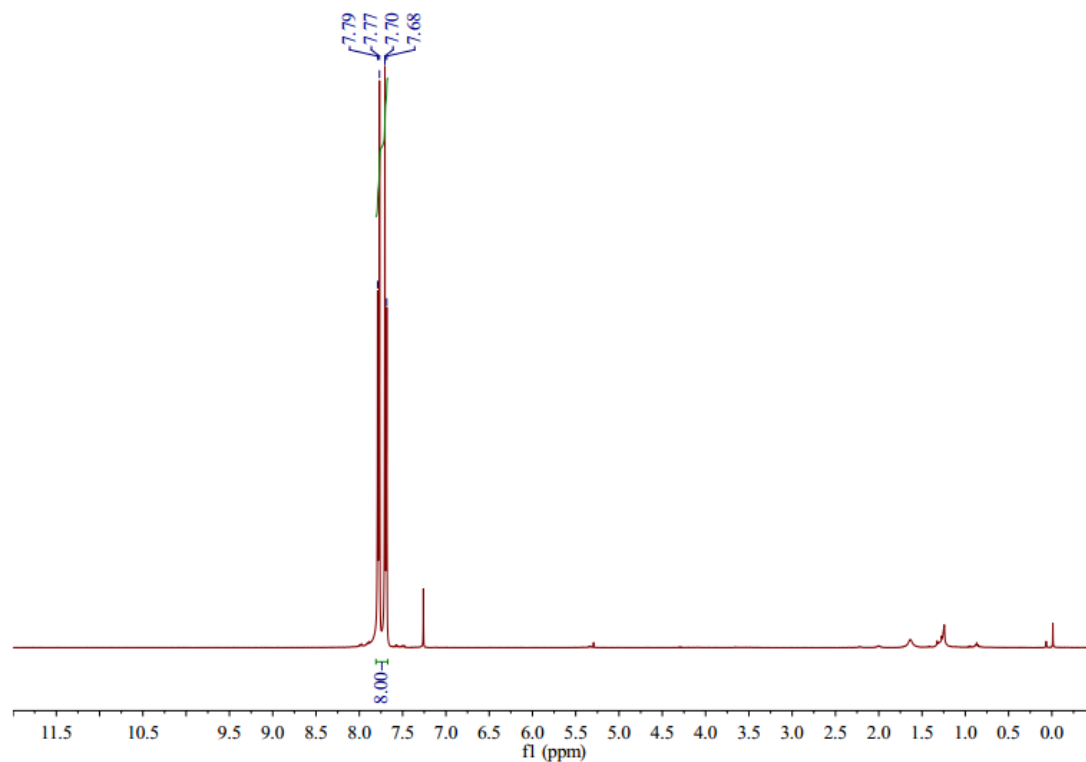
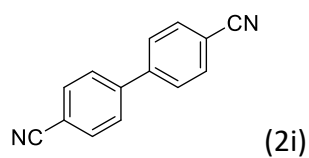
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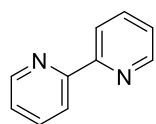




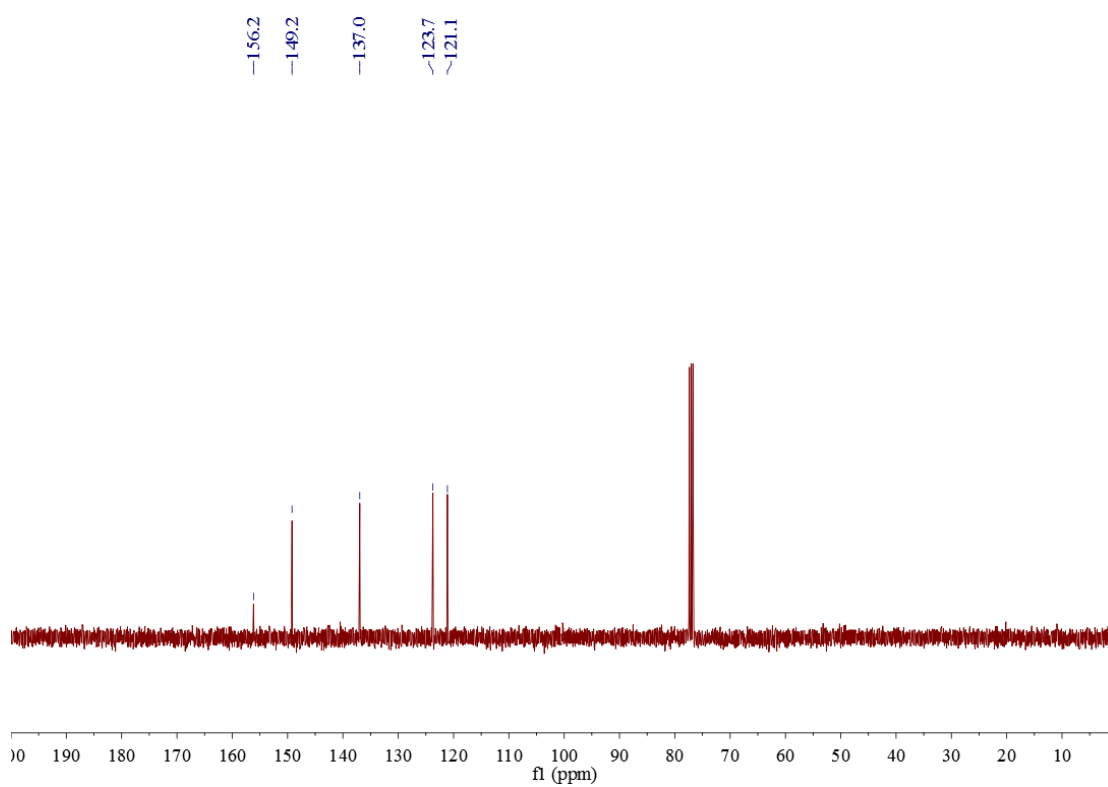
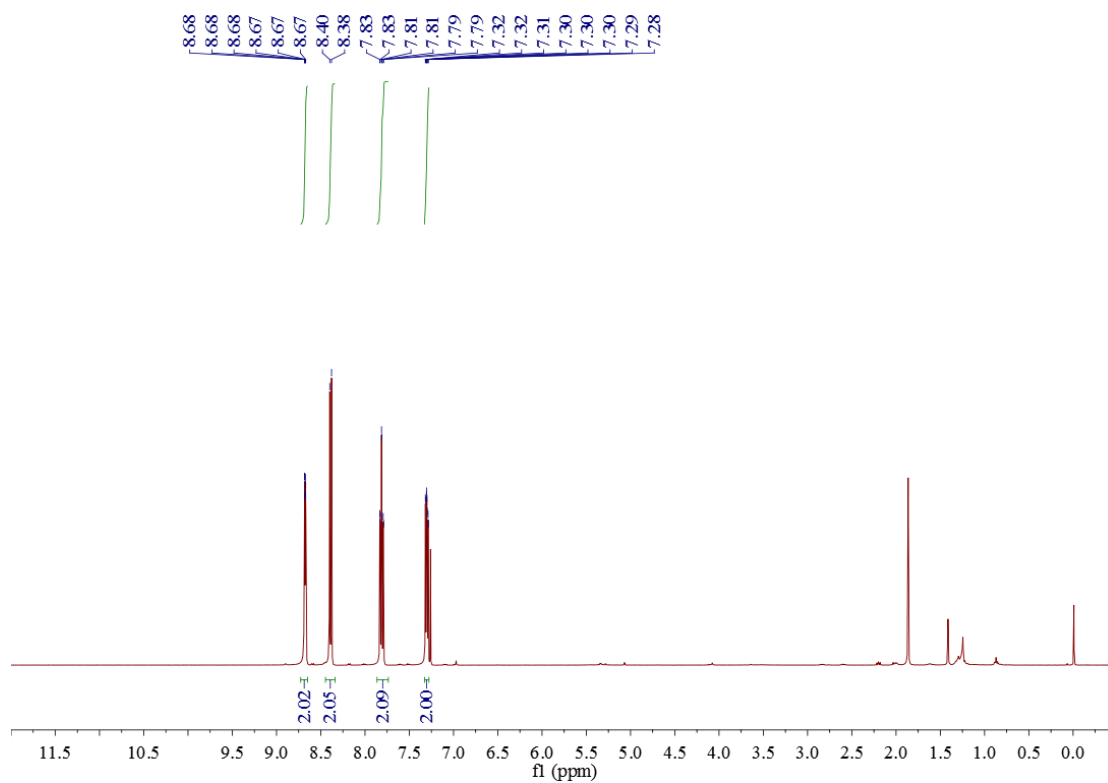


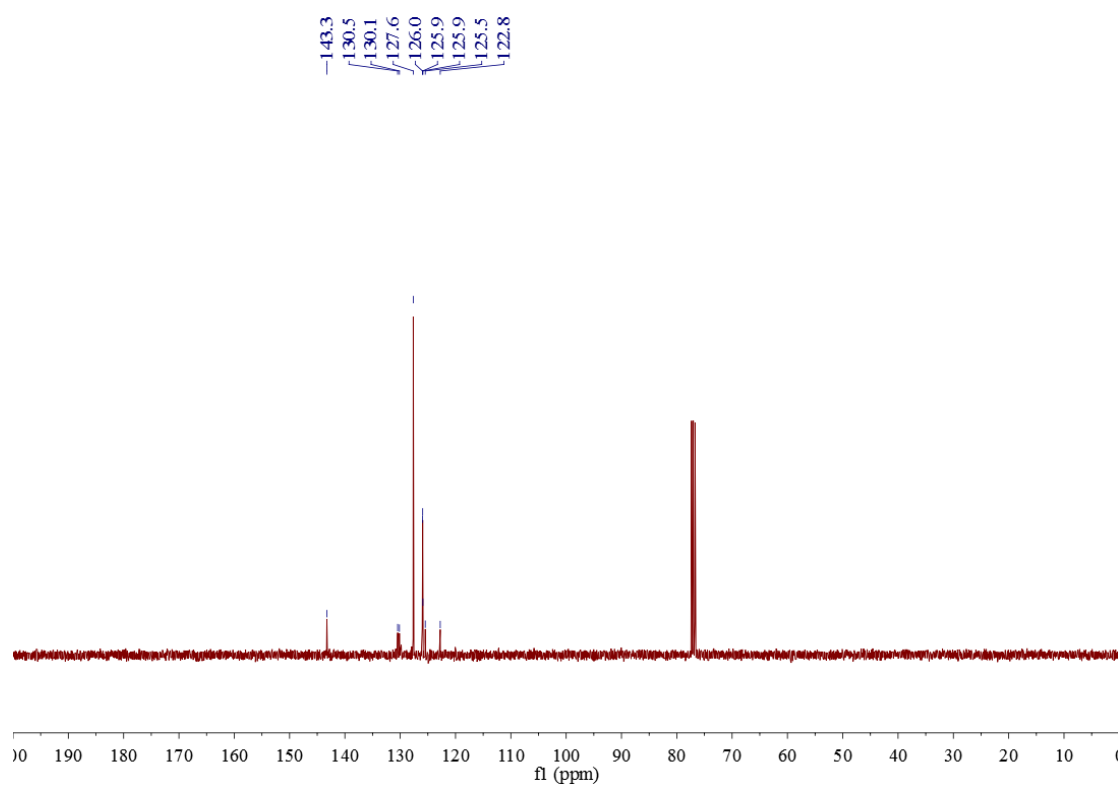
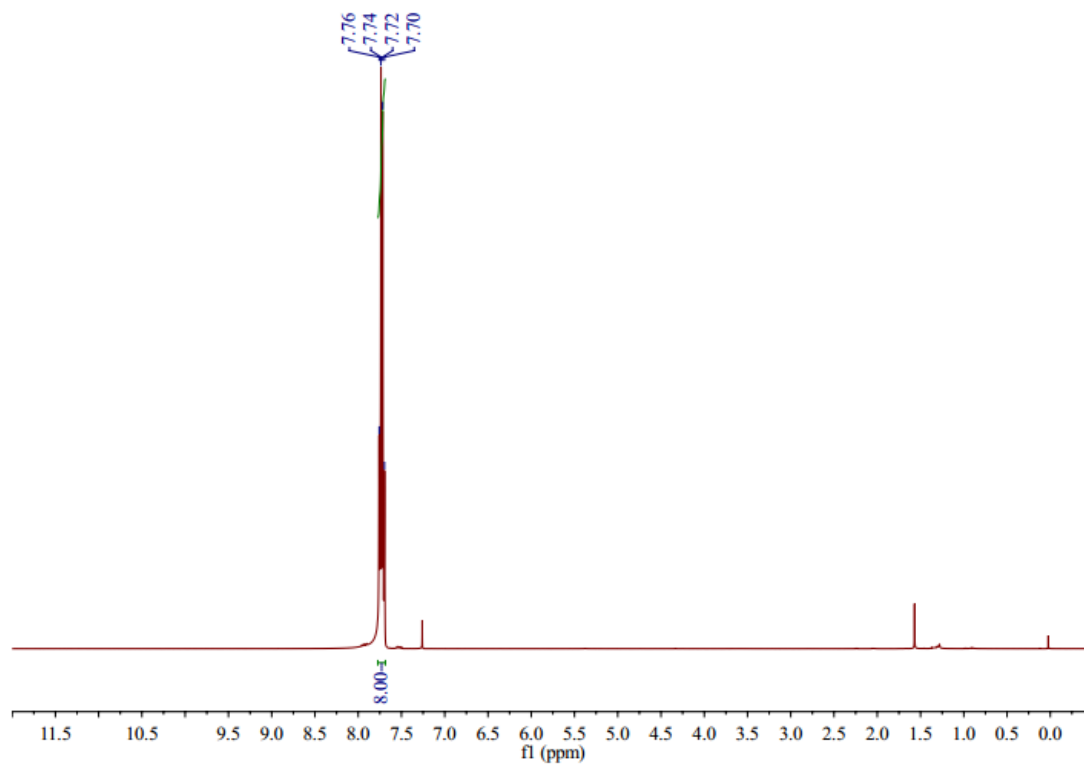
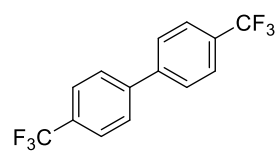


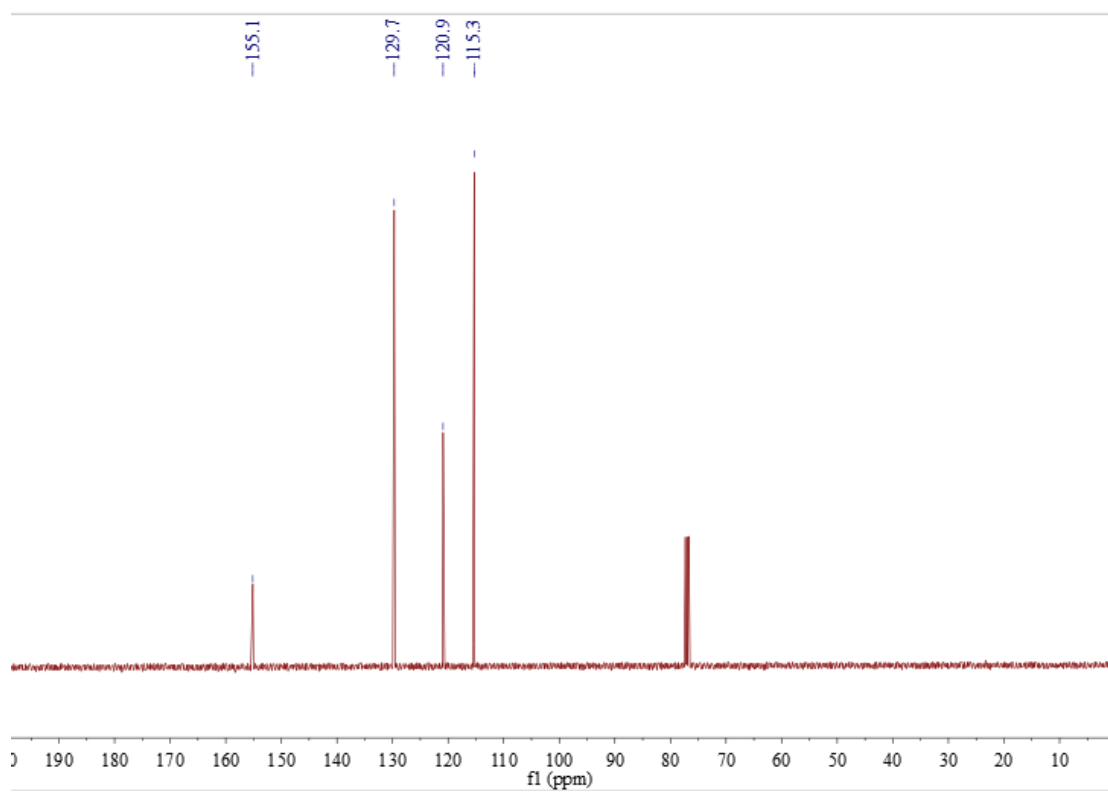
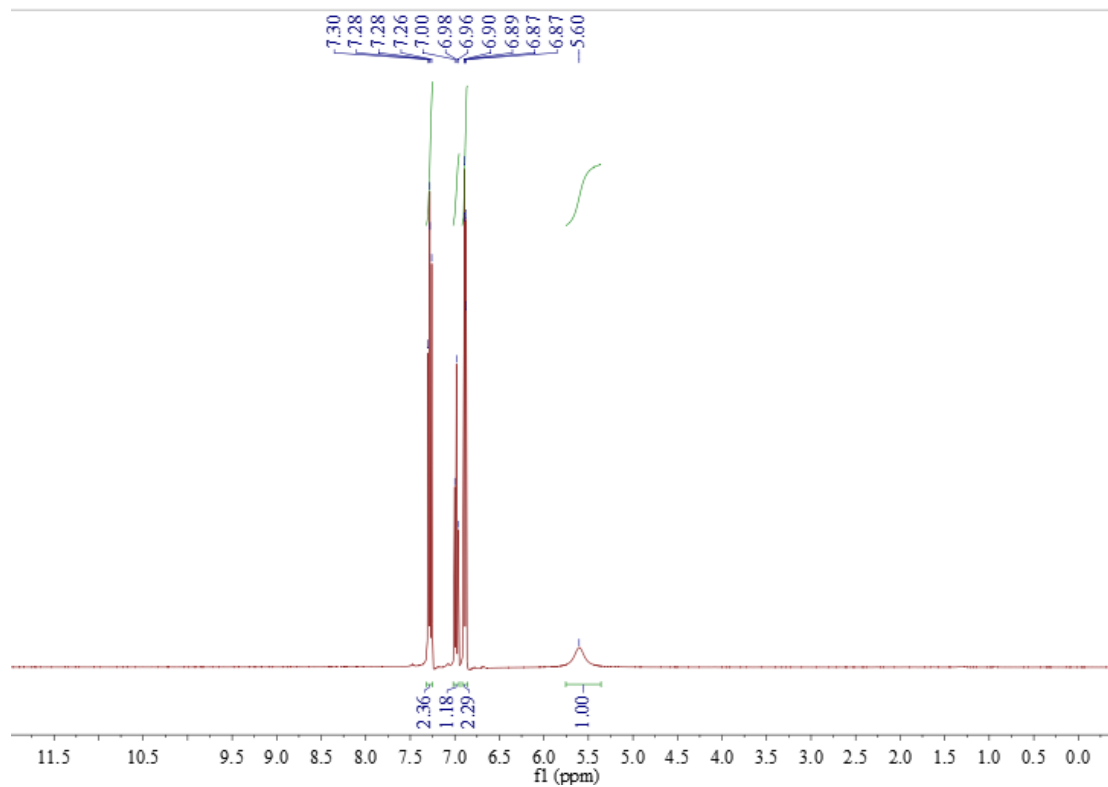
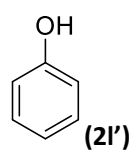


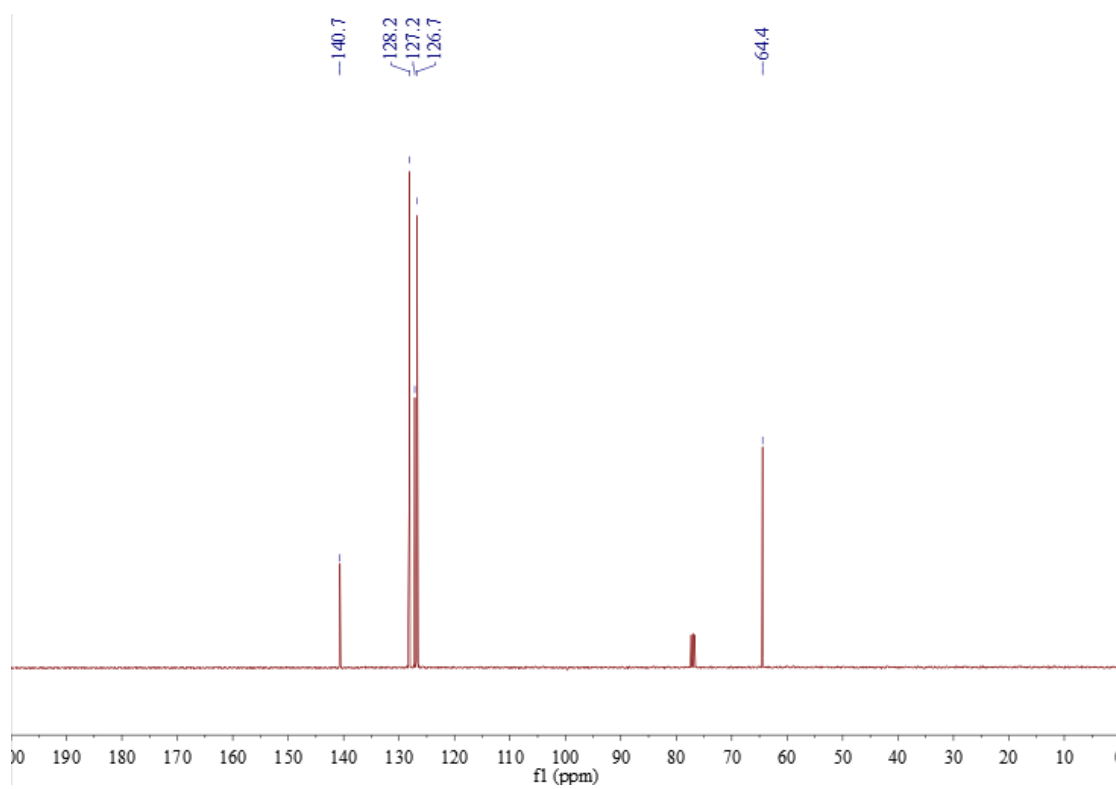
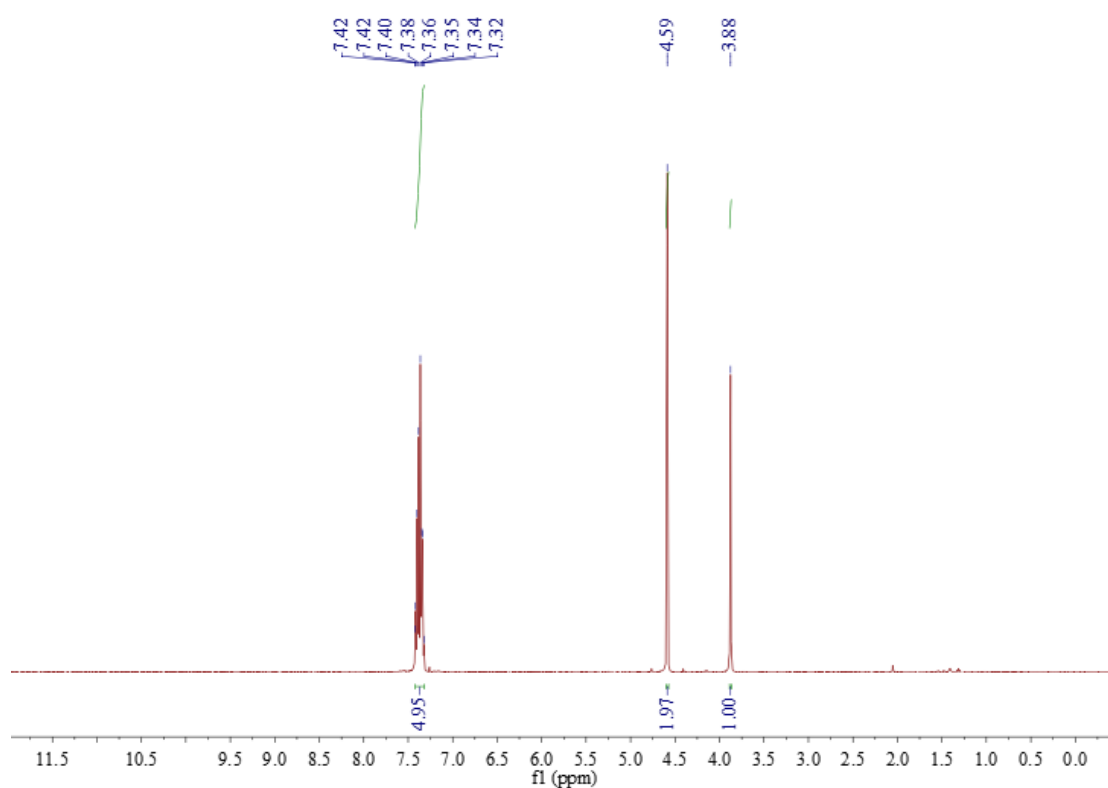
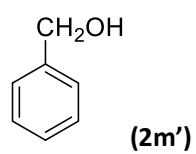


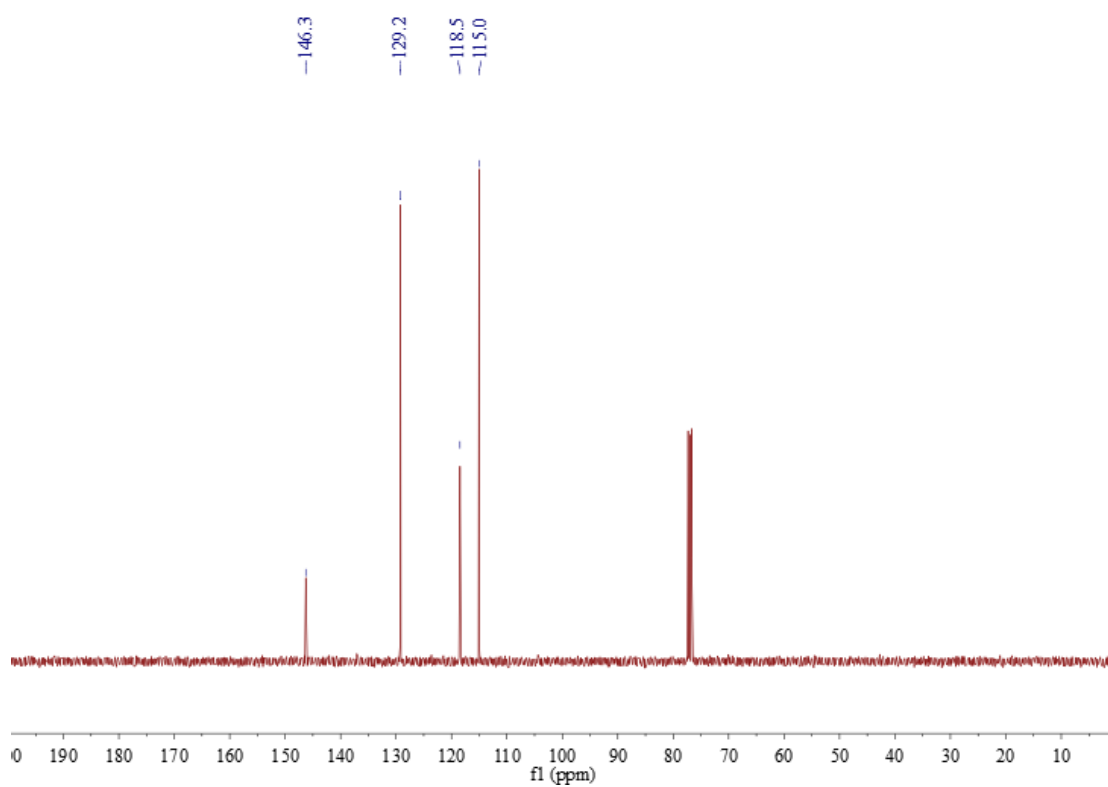
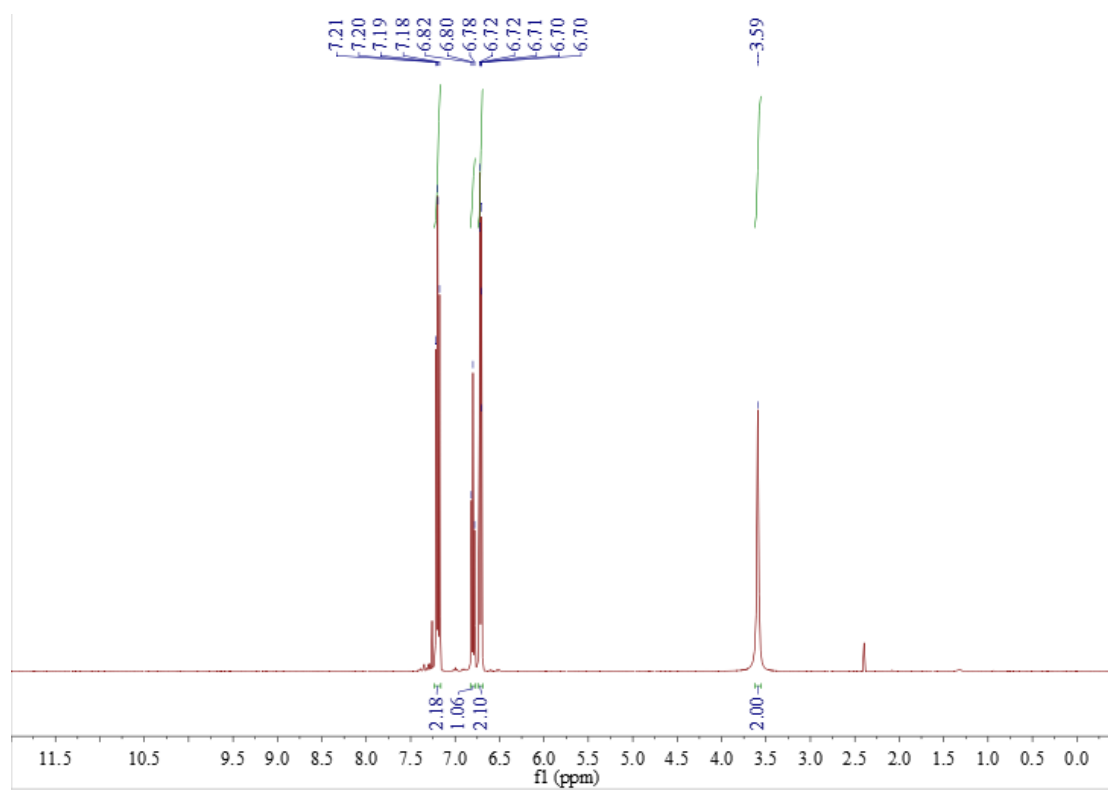
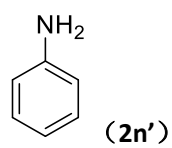
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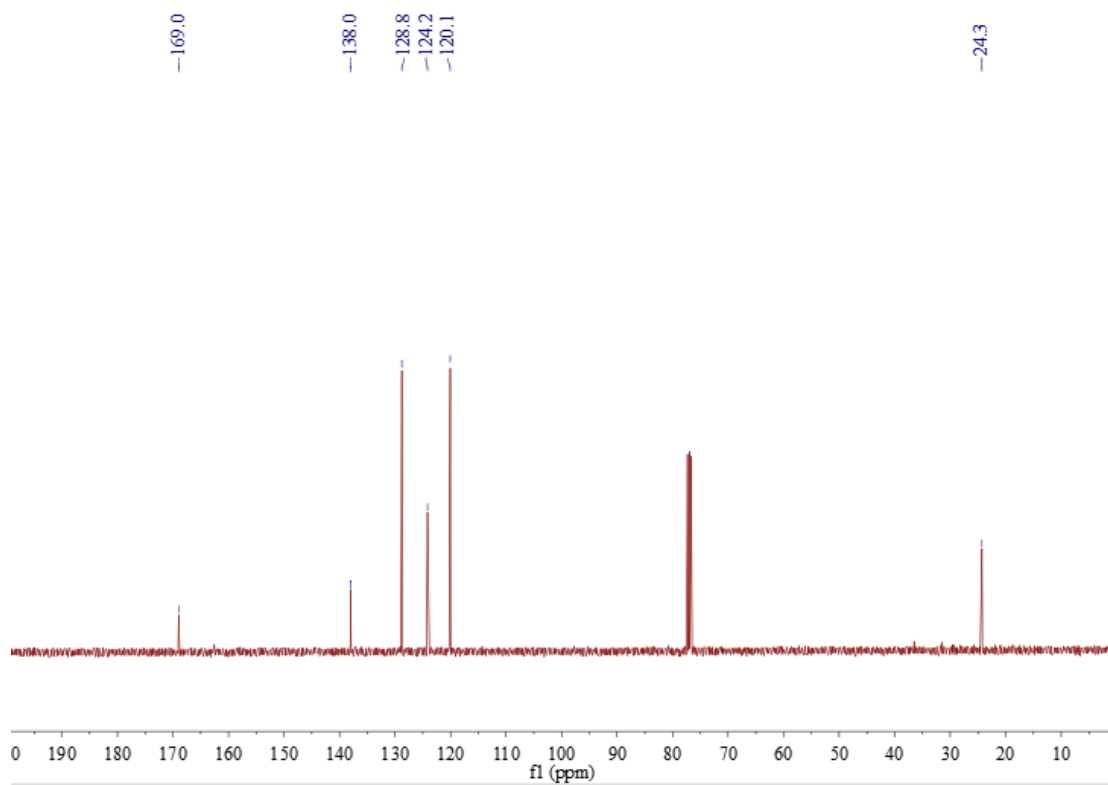
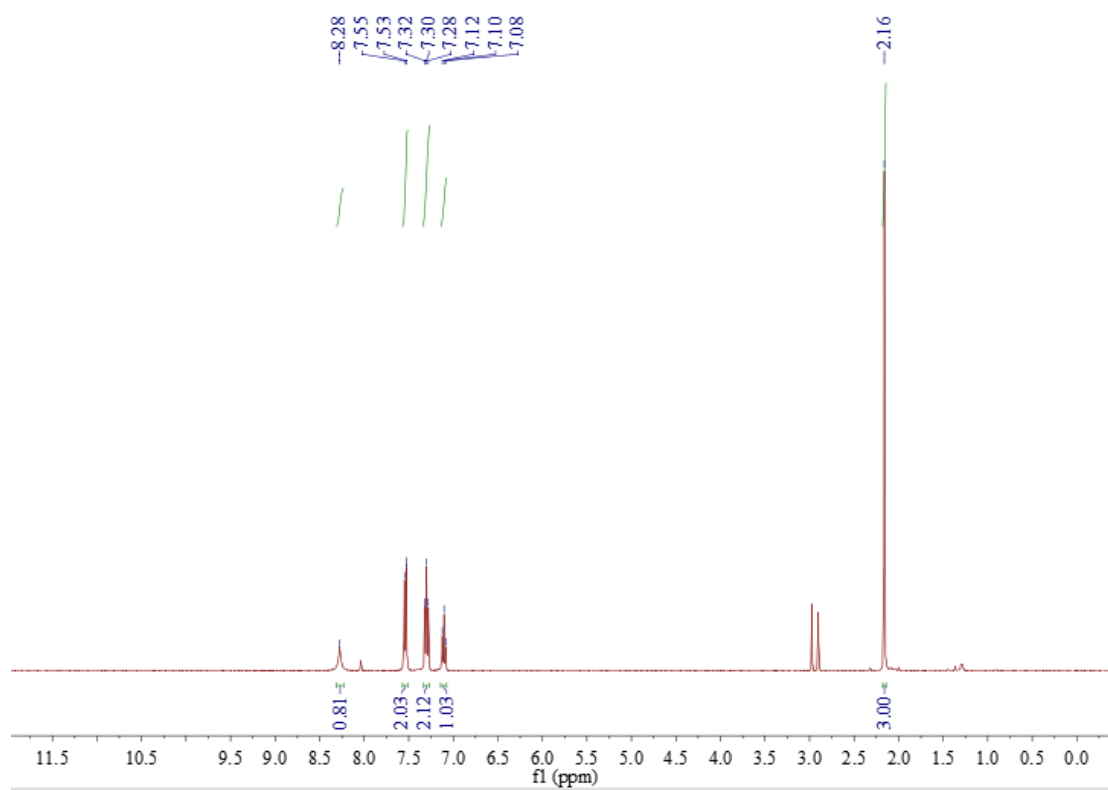
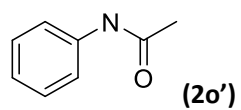


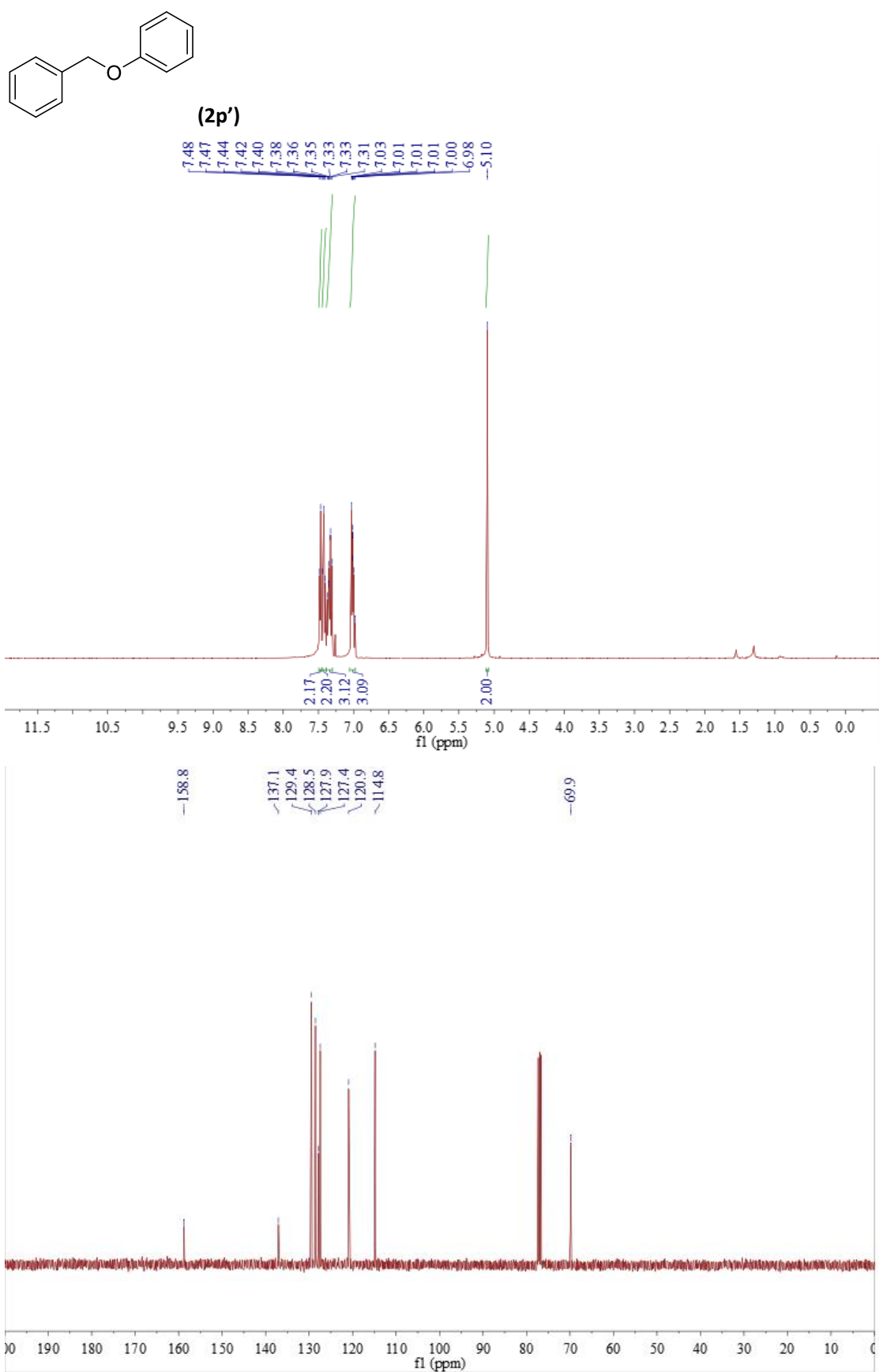


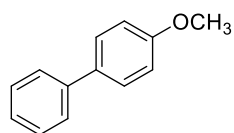




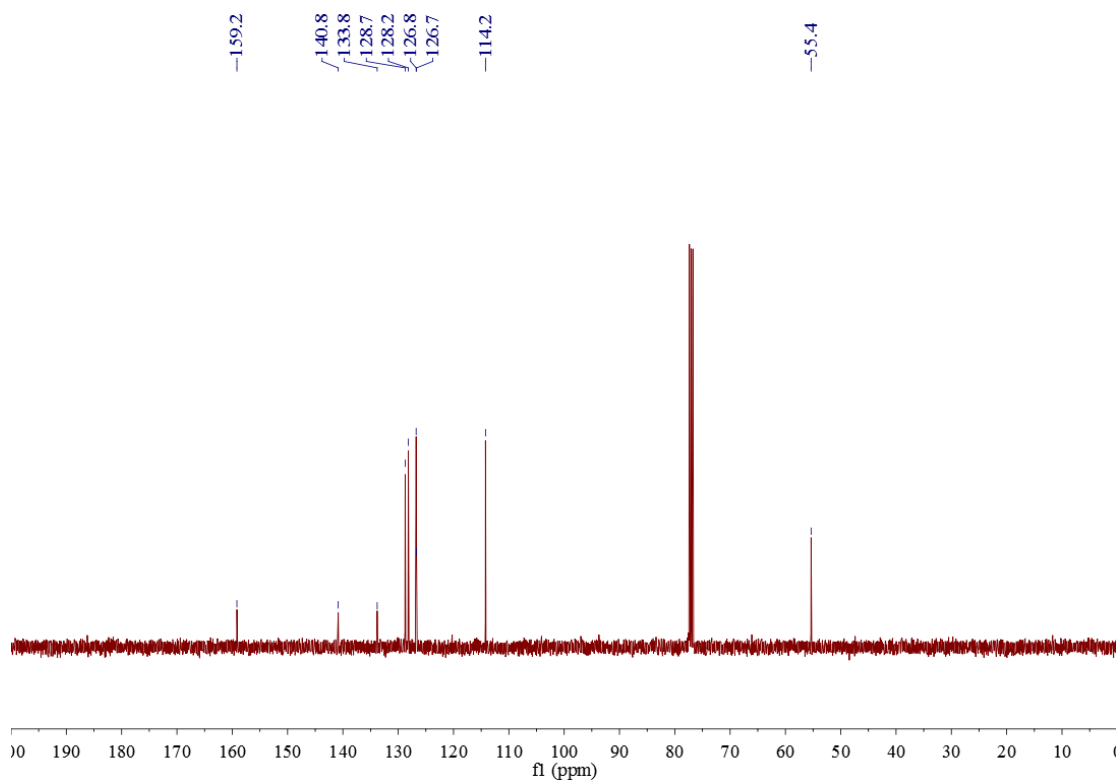
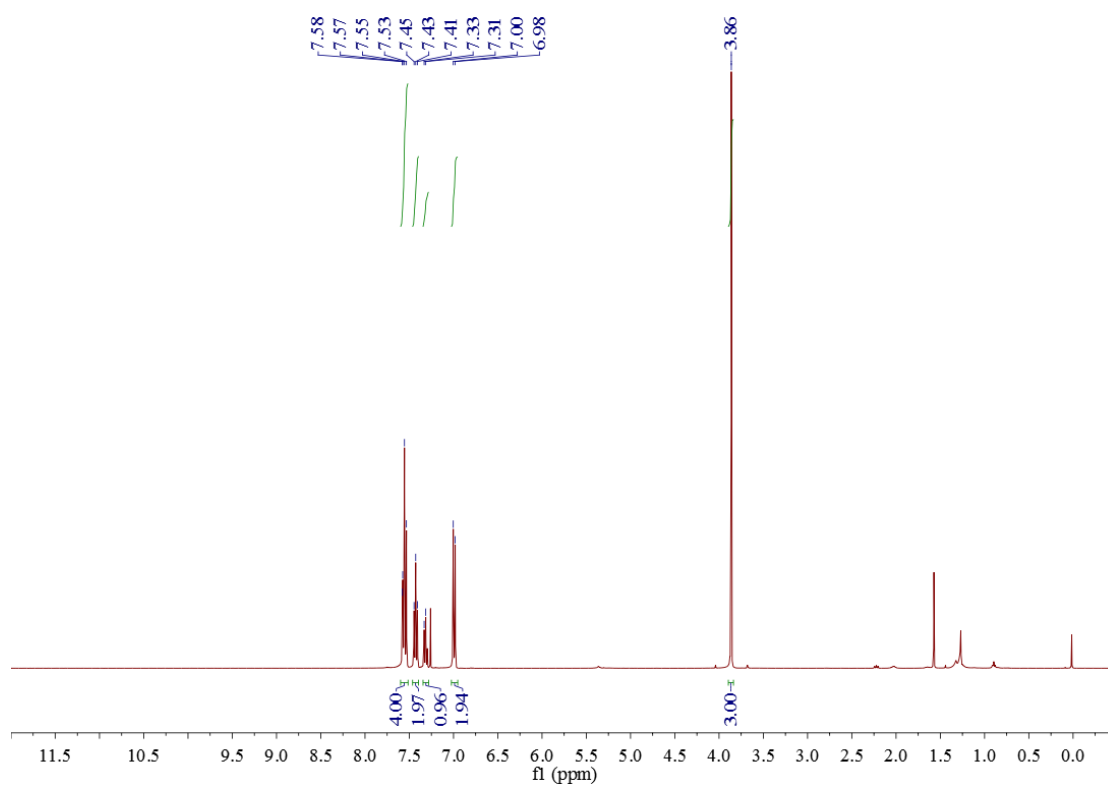


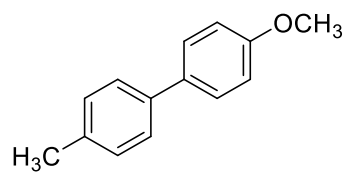




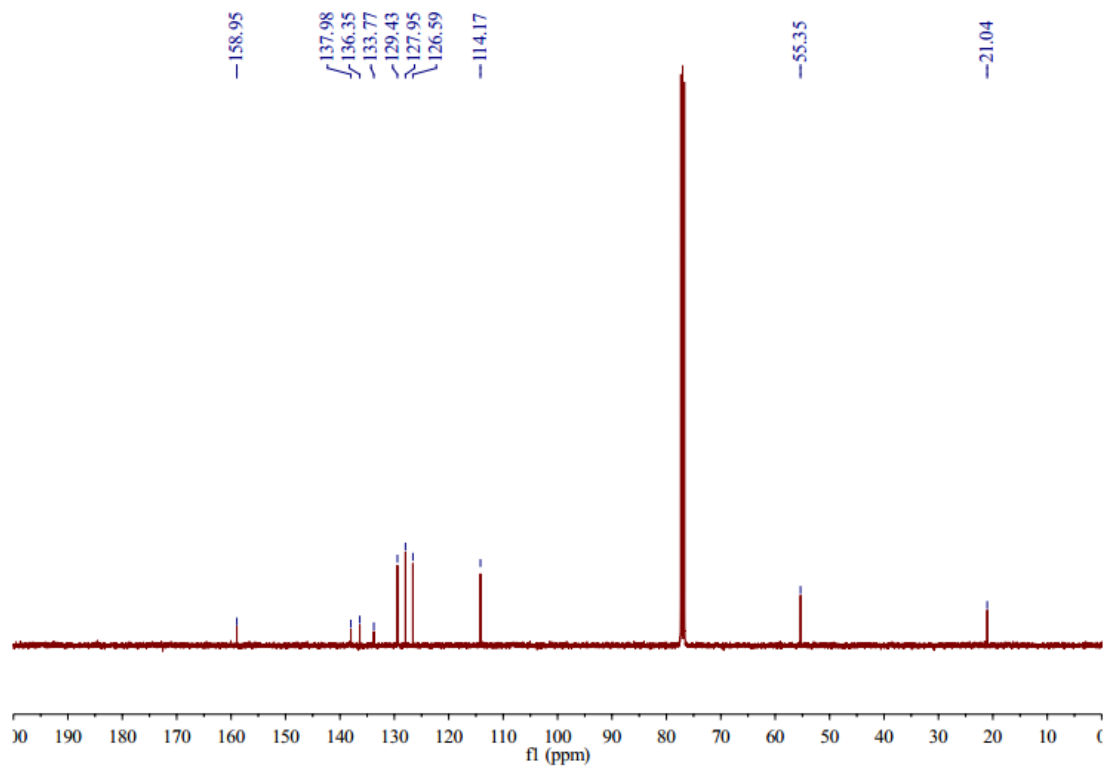
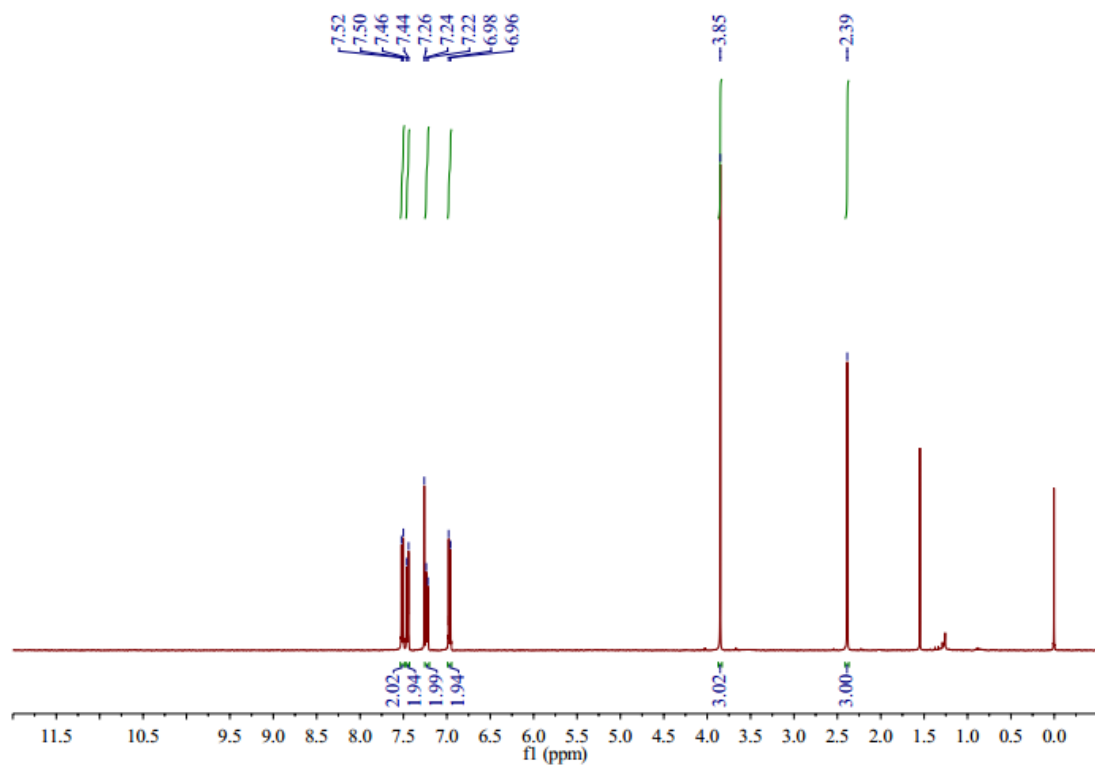


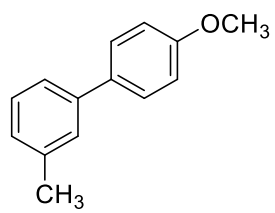
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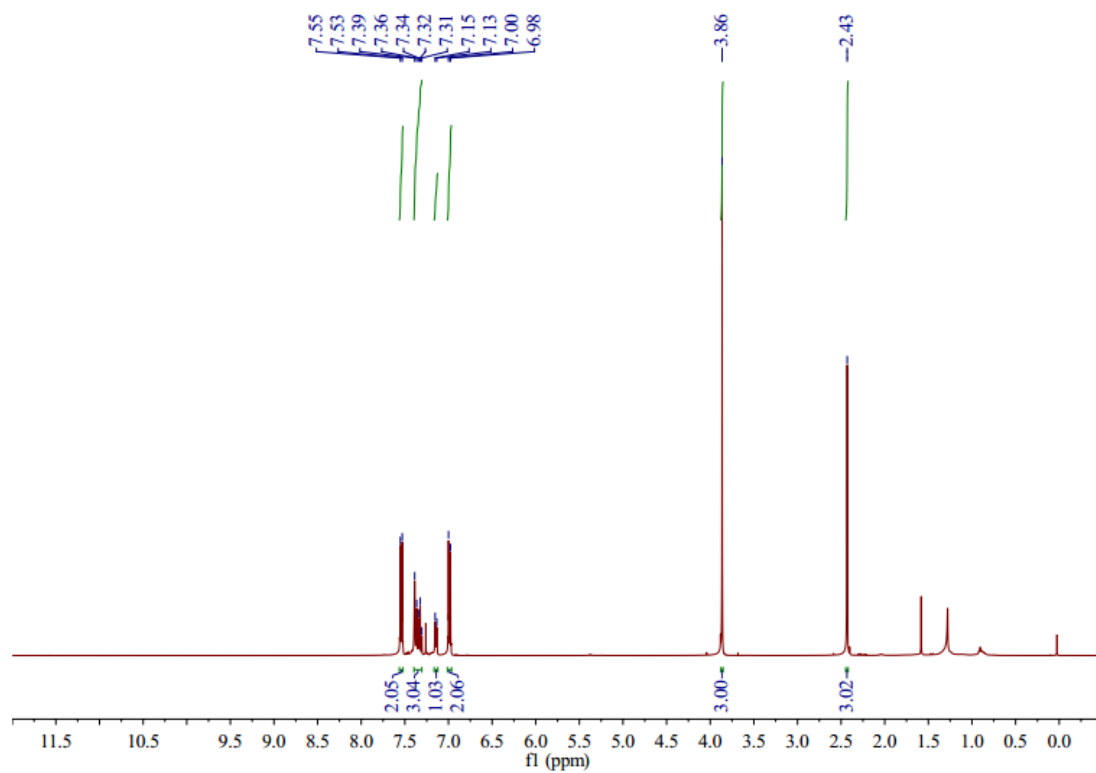


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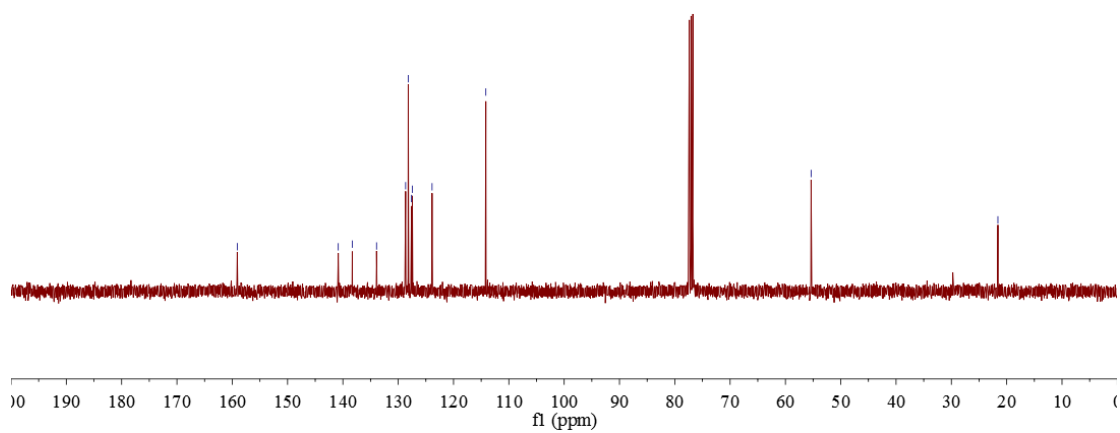


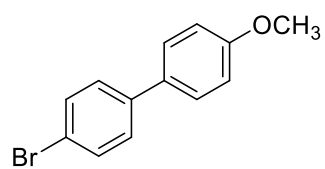


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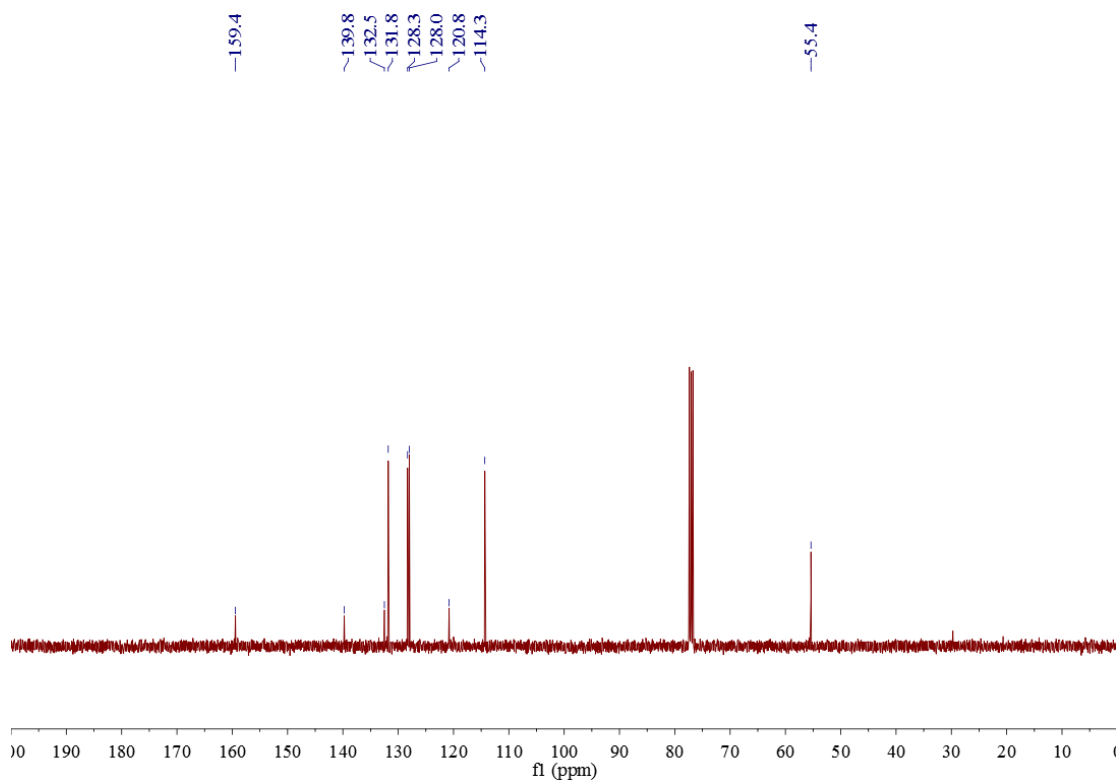
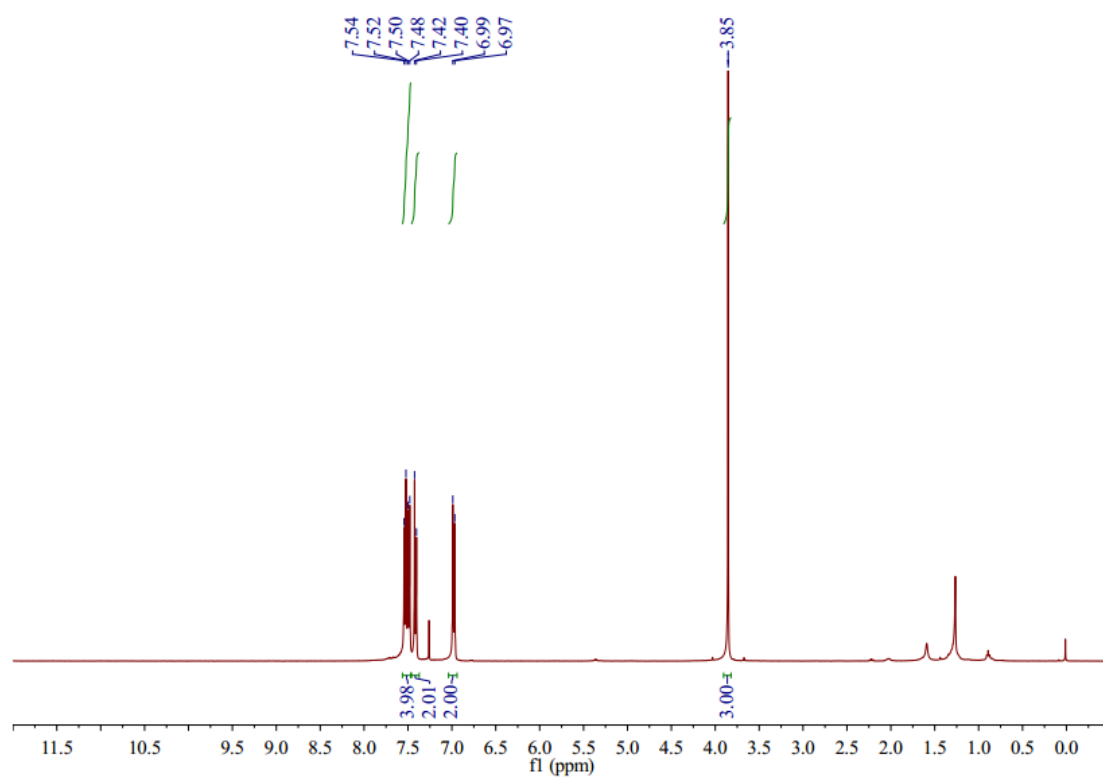


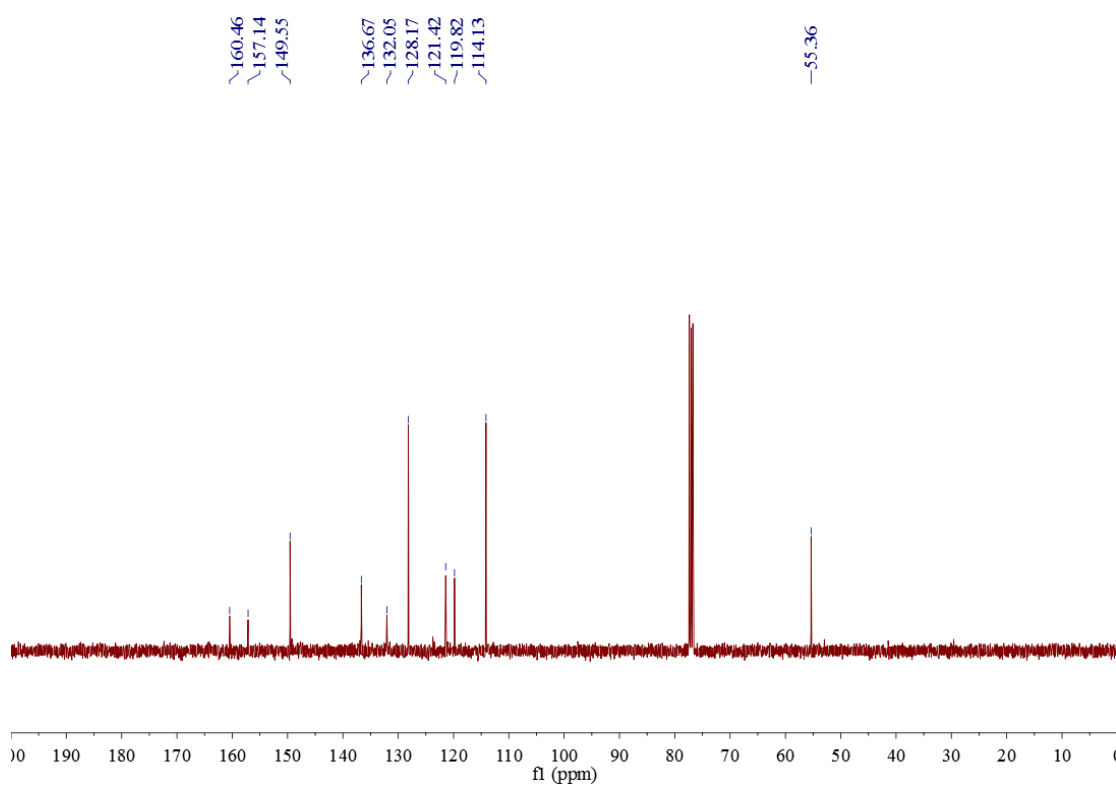
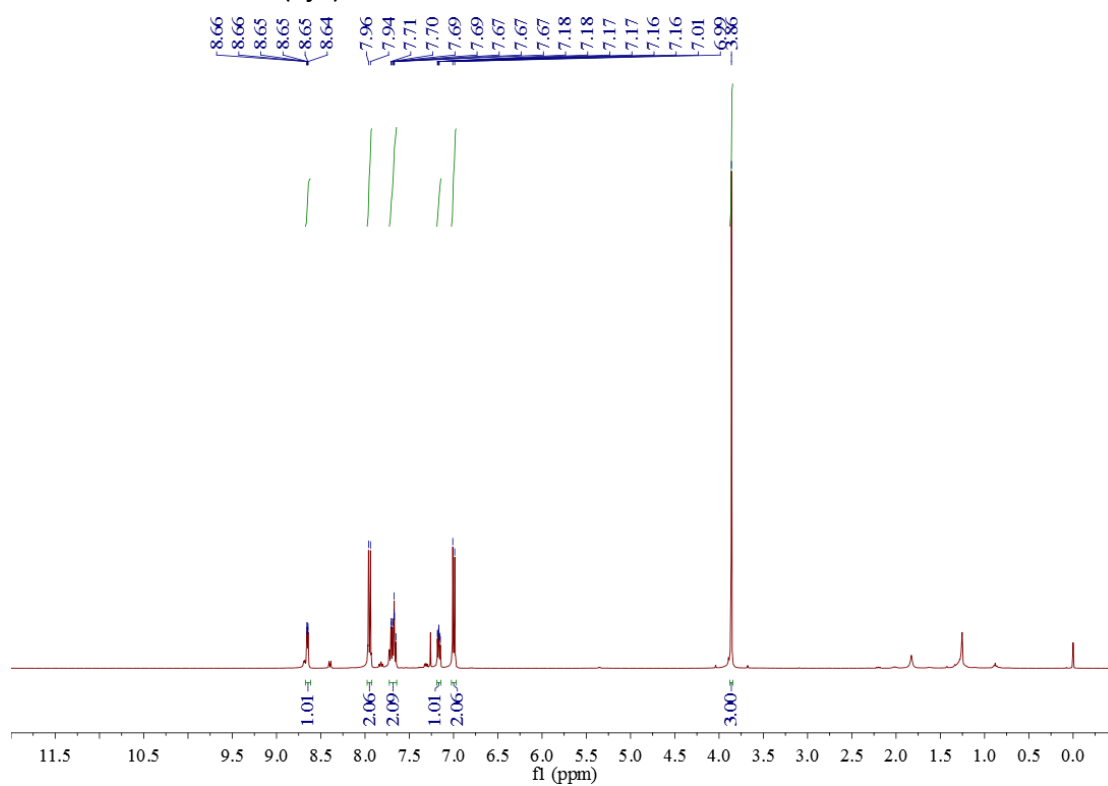
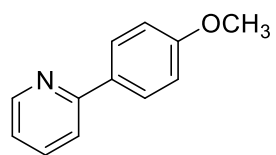
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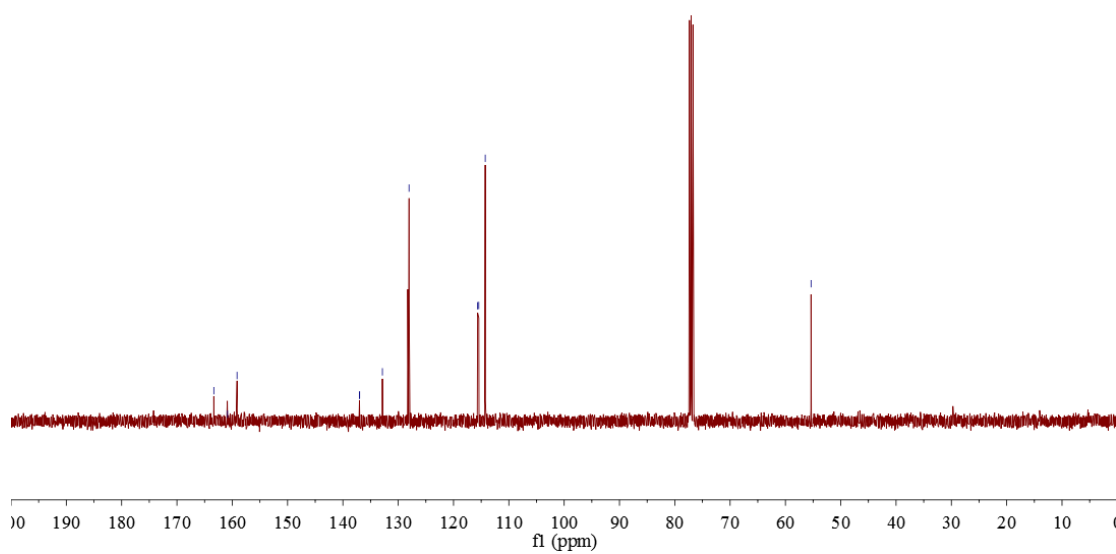
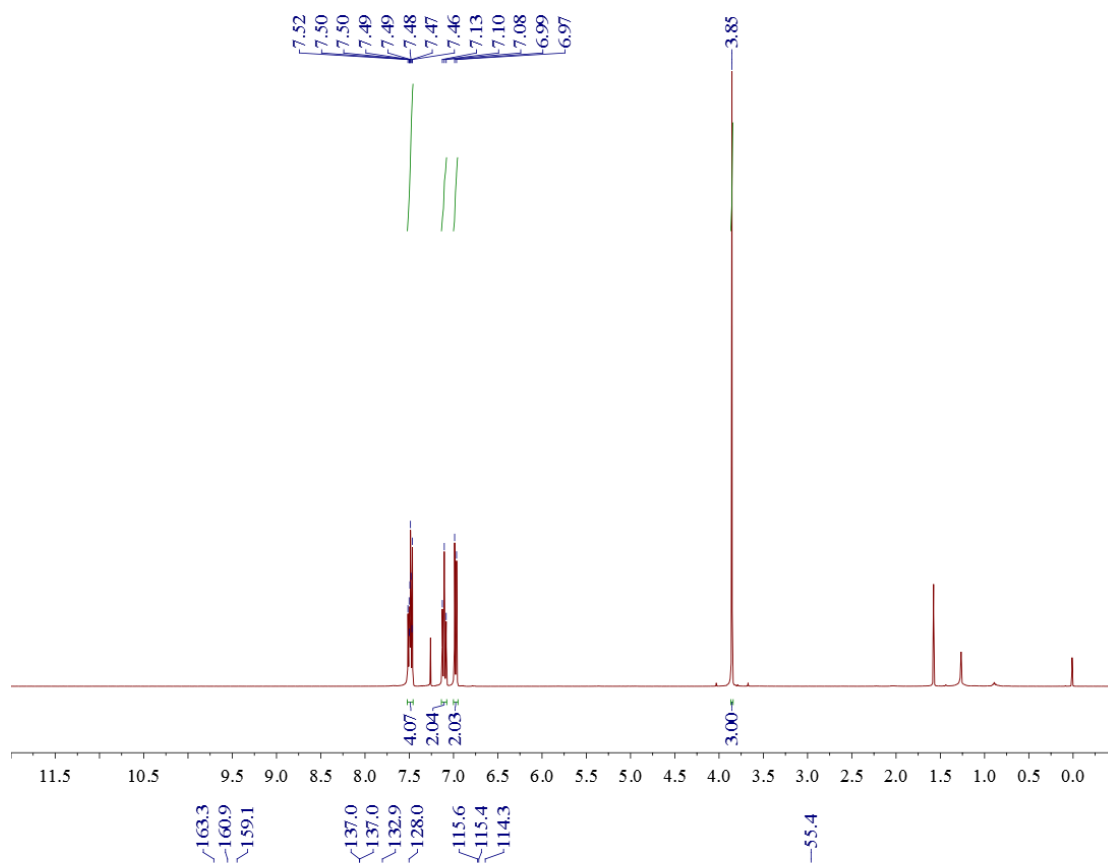
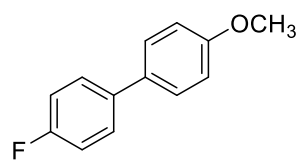


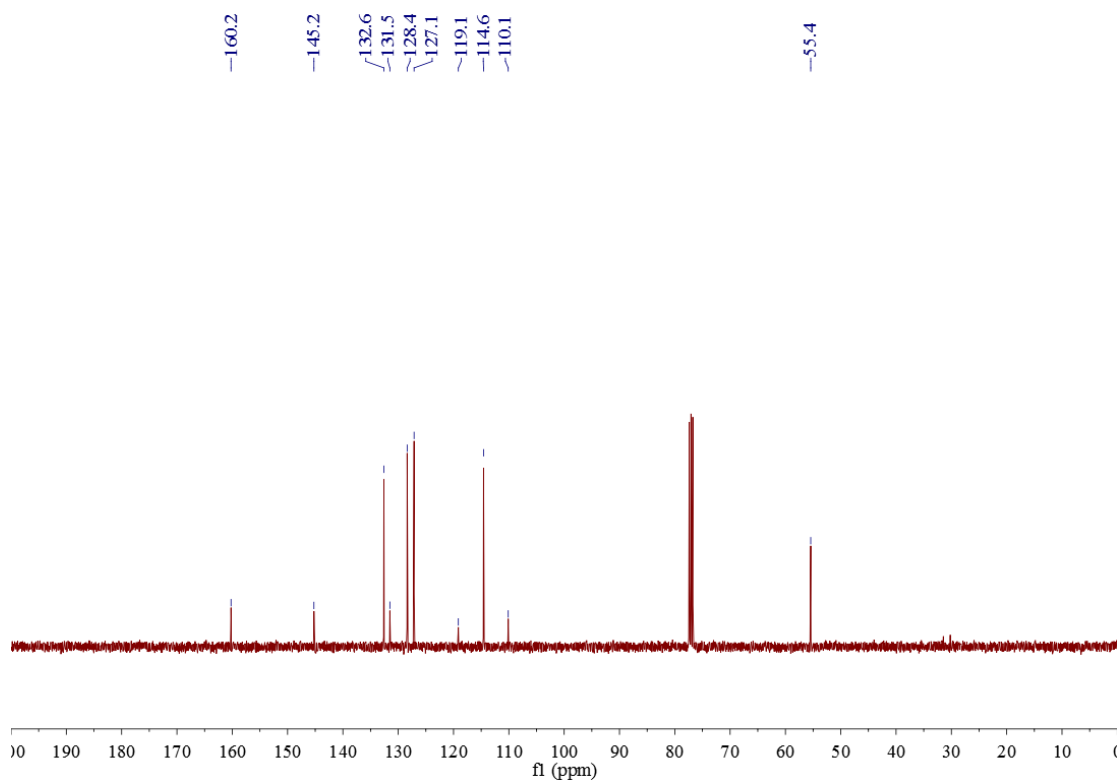
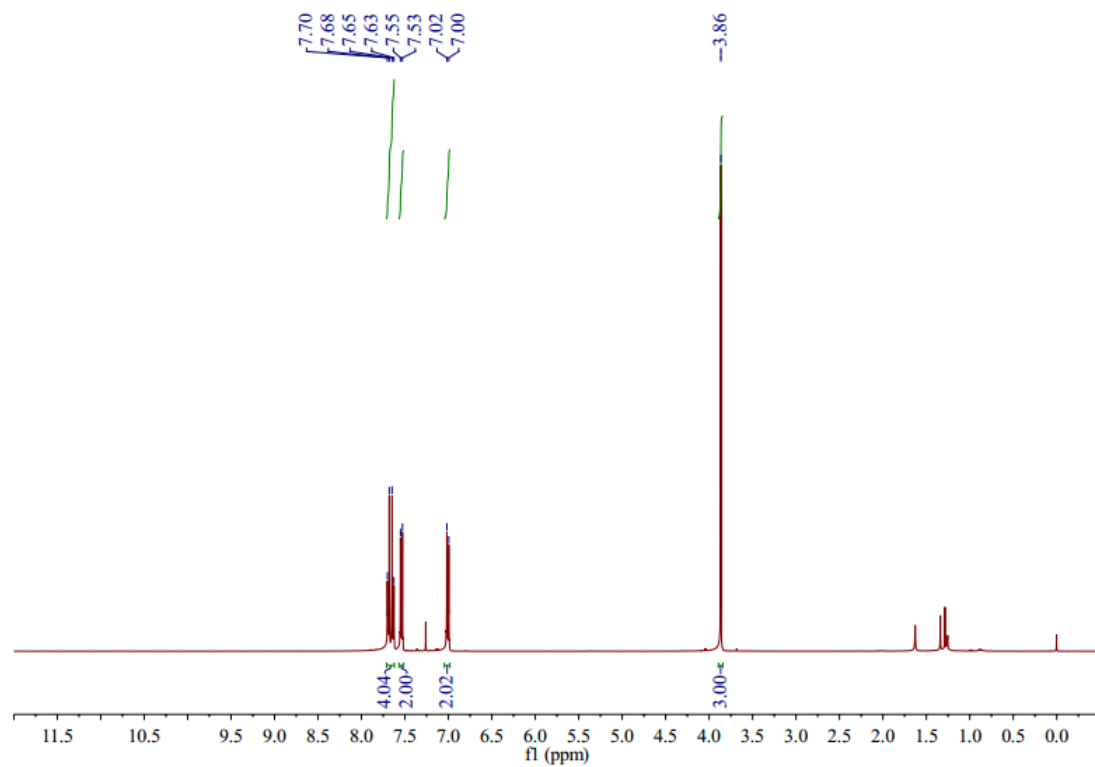
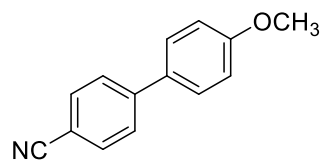


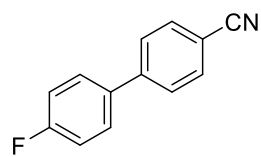
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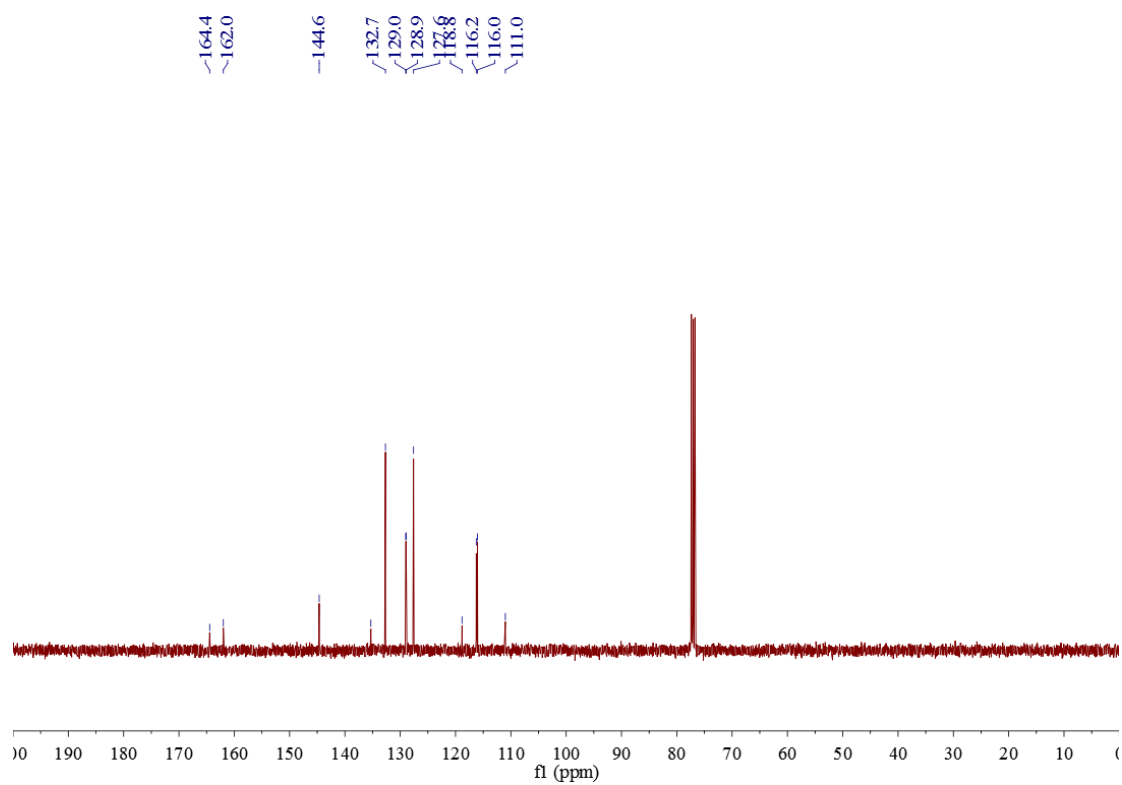
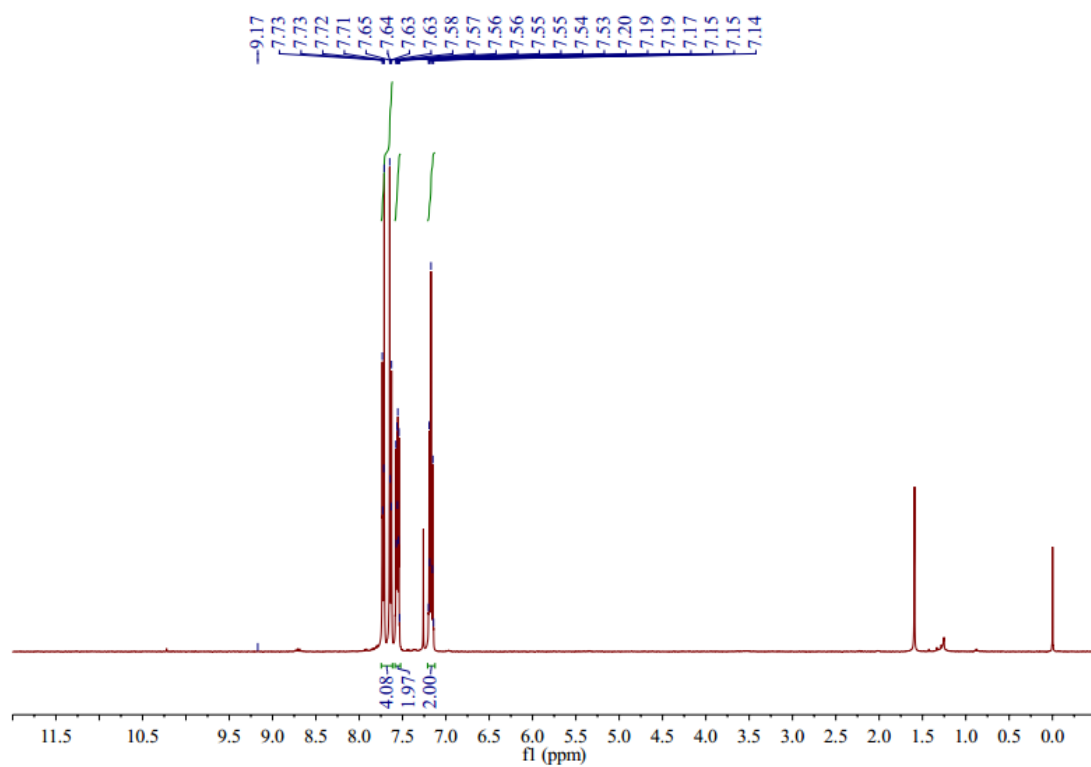


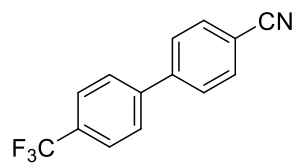






(4ei)





(4ki)

