A biomimetic magnetically recoverable Palladium nanocatalyst for Suzuki cross-coupling reaction

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Materials and Methods:

All reagents and starting materials were obtained commercially sources and were used without additional purification. Thin Layer Chromatography (TLC) was performed on silica (Silica Gel 60 F254) pre-coated aluminium plates and the products were visualized by UV lamp (PHILIPS TUV 8W lamp) and I_2 stain. X-ray powder diffraction (XRD) patterns were recorded on a (Shimadzu XRD-6100 using CuK radiations = 1.5405 Å) powder diffractometer instrument. Transmission Electron Microscopy studies were performed using a PHILIPS CM200 Transmission Electron Microscope (TEM) at 100 kV. ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometer) were performed using ARCOS model instrument from M/s Spectro, Germany. The ^{1}H and ^{13}C NMR was recorded in $CDCl_3$ using residual solvent peak as a reference on an Avance III and Bruker NMR spectrophotometer at 400 MHz and 100 MHz respectively.

Preparation of Fe_3O_4@Polydopamine (PDA) Core-Shell:

Fe_3O_4 nanoparticles (1 gram) were dispersed (pre-sonicated for 30 minutes) in 300 ml of de-ionized water and the pH was maintained at 8.5 by adding 10 mM Tris-HCl buffer. To this dopamine (1 gram) pre-dissolved in 200 mL of deionized water was added all at once. The solution is stirred by using a mechanical overhead stirrer fitted with a rod at room temperature for 24 hr. The polydopamine capped Fe_3O_4 nanoparticles were collected by using laboratory permanent magnet and washed 3 times with water, ethanol and acetone. The as prepared polydopamine capped Fe_3O_4 nanoparticles are dried overnight at room temperature in a desiccator.

Preparation of Pd/Fe_3O_4@PDA:

1 gram of Polydopamine capped Fe_3O_4 nanoparticles (Fe_3O_4@PDA) which were prepared by the above mentioned procedure was dispersed in 500 ml of de-ionized water by sonication for 30 min using an ultrasonication bath. To this, Na_2PdCl_4 solution [prepared by dissolving 90 mg (0.51mmol) of $PdCl_2$ and 60 mg (1 .03 mmol) of NaCl in 15mL of water] was added. After stirring for 30 minutes, $NaBH_4$ solution [30 mg (0.79mmol) dissolved in 10

mL of deionized water] was slowly added dropwise and this mixture was stirred overnight at room temperature with the help of a mechanical overhead stirrer. The Pd immobilized Fe_3O_4@PDA nanoparticles were collected magnetically by using laboratory permanent magnet. The particles were washed thrice with water, ethanol and acetone. The as prepared Pd/Fe_3O_4@PDA catalyst was dried overnight at room temperature in a desiccator and later completely characterized by spectroscopic and analytical techniques. The loading of Palladium was found to be 3.88wt% as revealed by ICP-AES analysis.

General experimental procedure for Suzuki reaction:

To a 25mL round bottomed flask (backfilled with nitrogen) equipped with a Teflon coated magnetic bar, aryl halide (0.5 mmol) and arylboronic acid (0.55 mmol) were added. To this, K_2CO_3 (1 mmol, 138mg) and Pd/Fe_3O_4@PDA (0.46 mol % of Pd) were added followed by 4mL of H_2O: EtOH (1:1). The reaction mixture was stirred for the indicated time at 80 ^oC for aryl iodides and 100^oC for aryl bromides till the time taken for complete consumption of the reactants as confirmed by TLC, the solution was extracted four times with ethyl acetate (4 × 10 mL). The organic solvents were removed under pressure and the residue was column chromatographed using silica gel with petroleum ether/ethyl acetate as eluents to get the desired coupling product (most cases it was only filter column).

Catalyst recyclability study:

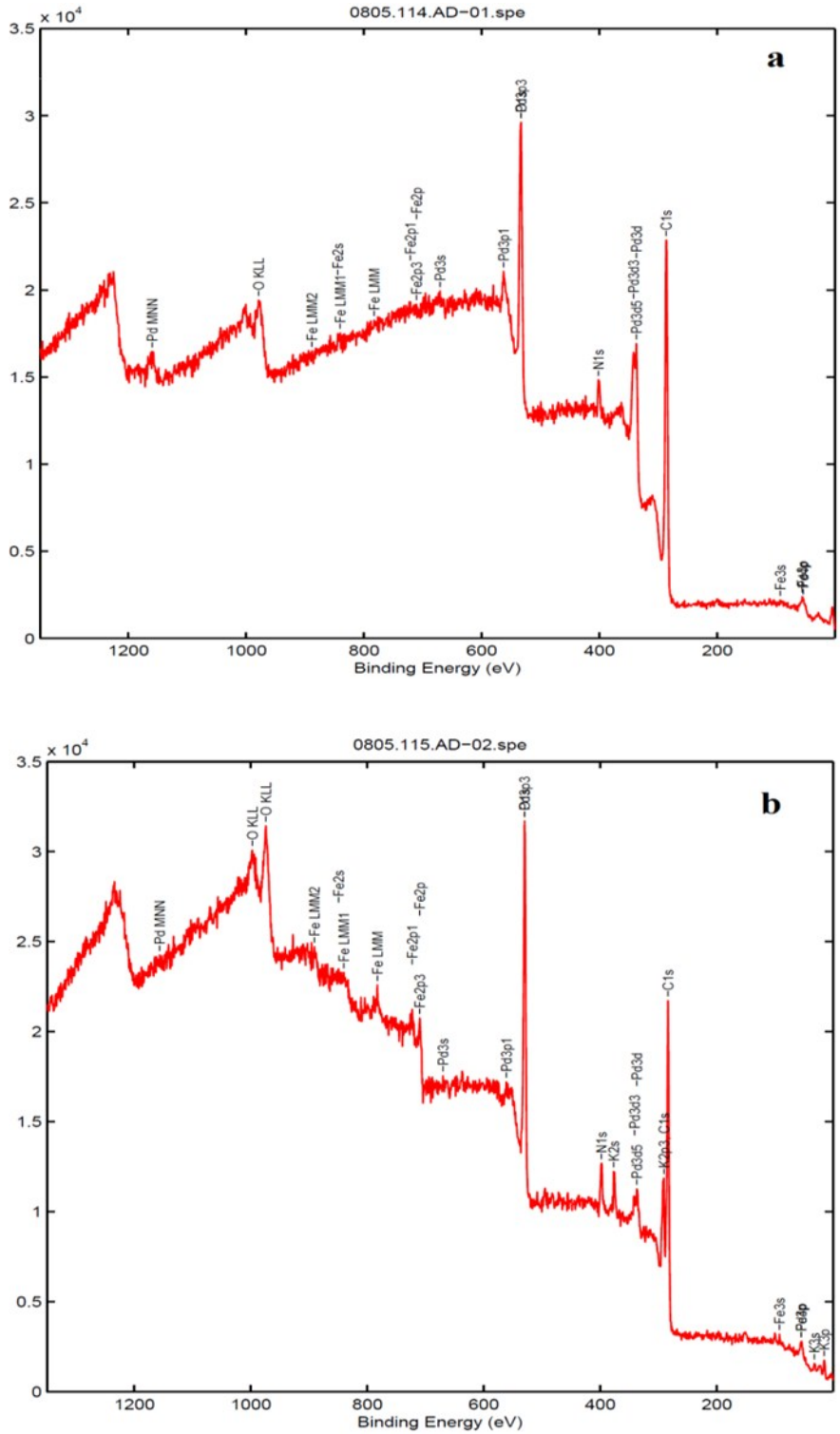
To a 25mL round bottomed flask (backfilled with nitrogen) equipped with a Teflon coated magnetic bar, aryl halide (0.5 mmol) and arylboronic acid (0.55 mmol) were added. To this, K_2CO_3 (1 mmol, 138mg) and Pd/Fe_3O_4@PDA (0.46 mol % of Pd) were added followed by 4mL of H_2O: EtOH (1:1). The reaction mixture was stirred for the indicated time at 80^oC. After consumption of the reactants as confirmed by TLC, the solution was extracted four times with ethyl acetate (4 × 10 mL). The organic solvents were removed under pressure and the residue was column chromatographed using silica gel with petroleum ether/ethyl acetate as eluents to get the desired coupling products (most cases it was only filter column). The magnetically recovered catalyst was washed with water and acetone, dried in a desiccator overnight and subsequently used for the next cycle. As such the catalyst was reused for five more cycles.

Hot Test Experiment conditions under centrifugation conditions:

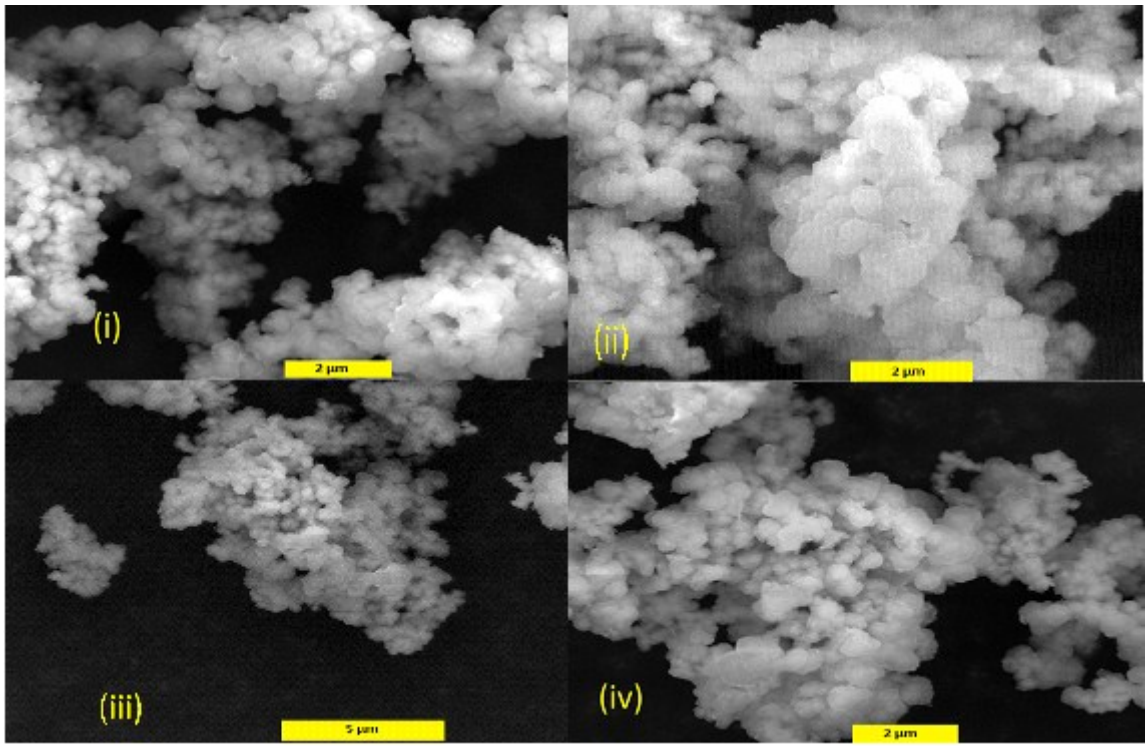
To a 25mL round bottomed flask (backfilled with nitrogen) equipped with a Teflon coated magnetic bar, aryl halide (0.5 mmol) and arylboronic acid (0.55 mmol) were added. To this, K_2CO_3 (1 mmol, 138mg) and Pd/Fe_3O_4@PDA (0.46 mol % of Pd) were added followed by 4mL of H_2O: EtOH (1:1).The reaction was stirred for 2 hours at 80 ^oC. The reaction mixture was centrifuged at 3000 rpm on an ultracentrifuge machine for 30 minutes and the solution was filtered with 0.44 μm, PTFE syringe filter and the afforded solution was transferred to another flask and reaction was allowed to stir at 80 ^oC for 24 hours.

Hot Test Experiment conditions under non-centrifugation conditions:

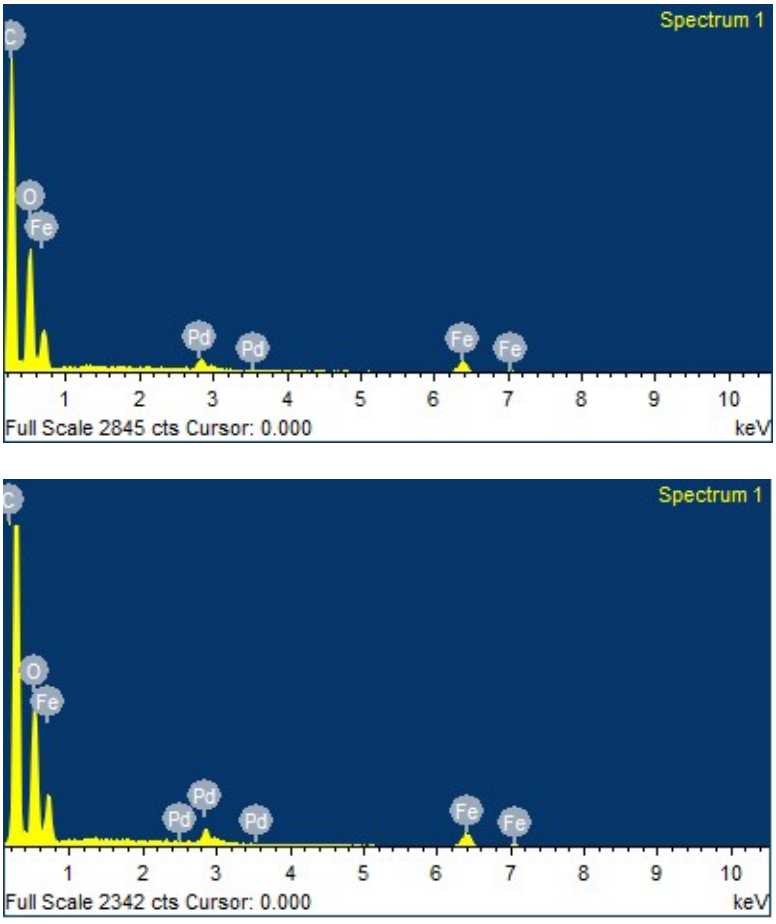
To a 25mL round bottomed flask (backfilled with nitrogen) equipped with a Teflon coated magnetic bar, aryl halide (0.5 mmol) and arylboronic acid (0.55 mmol) were added. To this, K_2CO_3 (1 mmol, 138mg) and Pd/Fe_3O_4@PDA (0.46 mol % of Pd) were added followed by 4mL of H_2O: EtOH (1:1).The reaction was stirred for 2 hours at 80 ^oC. The reaction mixture was filtered with 0.44 μm, PTFE syringe filter and the afforded solution was transferred to another flask and reaction was allowed to stir at 80 ^oC for 24 hours.



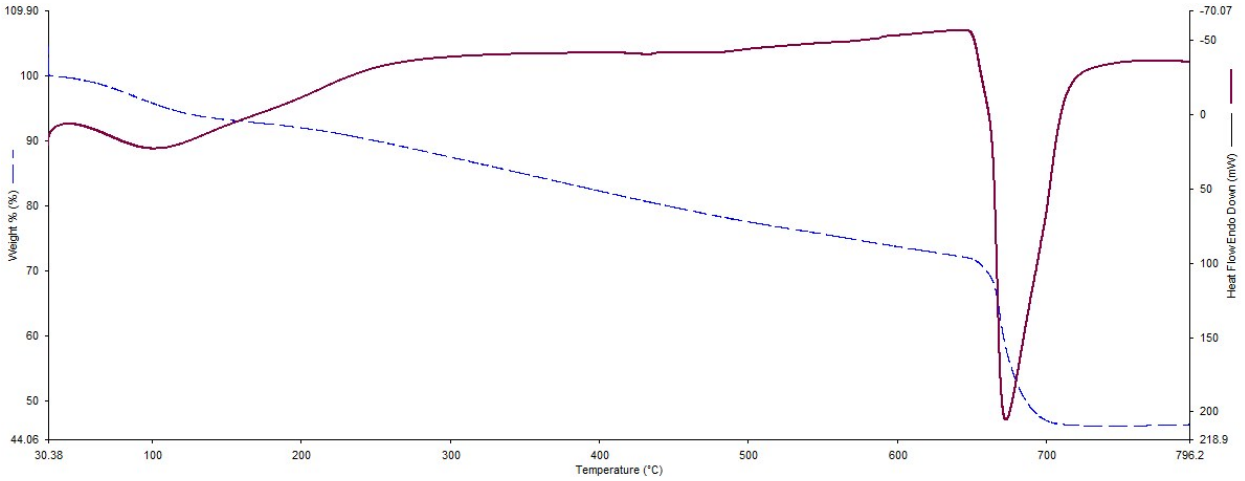
XPS of Pd/Fe3O4@PDA nanoparticles (a) native (b) after five cycles[1]



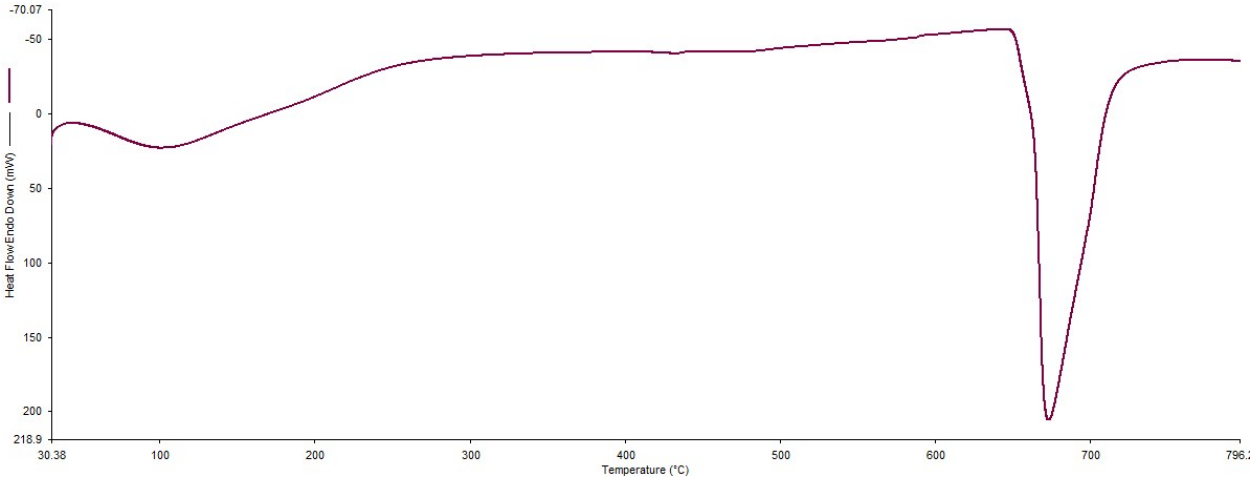
SEM images of Pd/PDA@Fe_3O_4: (i-ii) native (iii-iv) after five cycles.



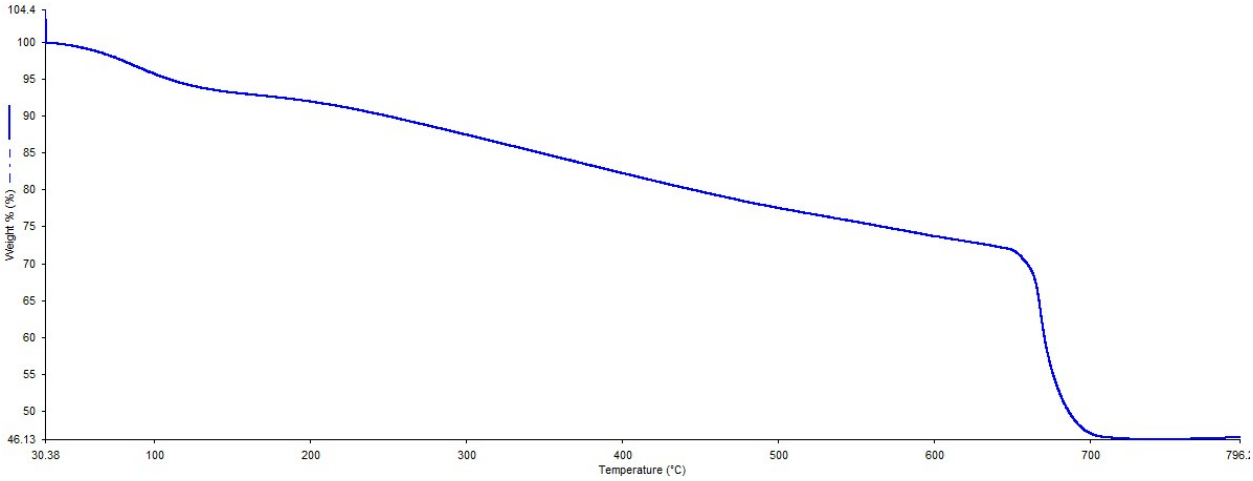
EDAX Spectra of native and recycled Pd/ Fe_3O_4@PDA



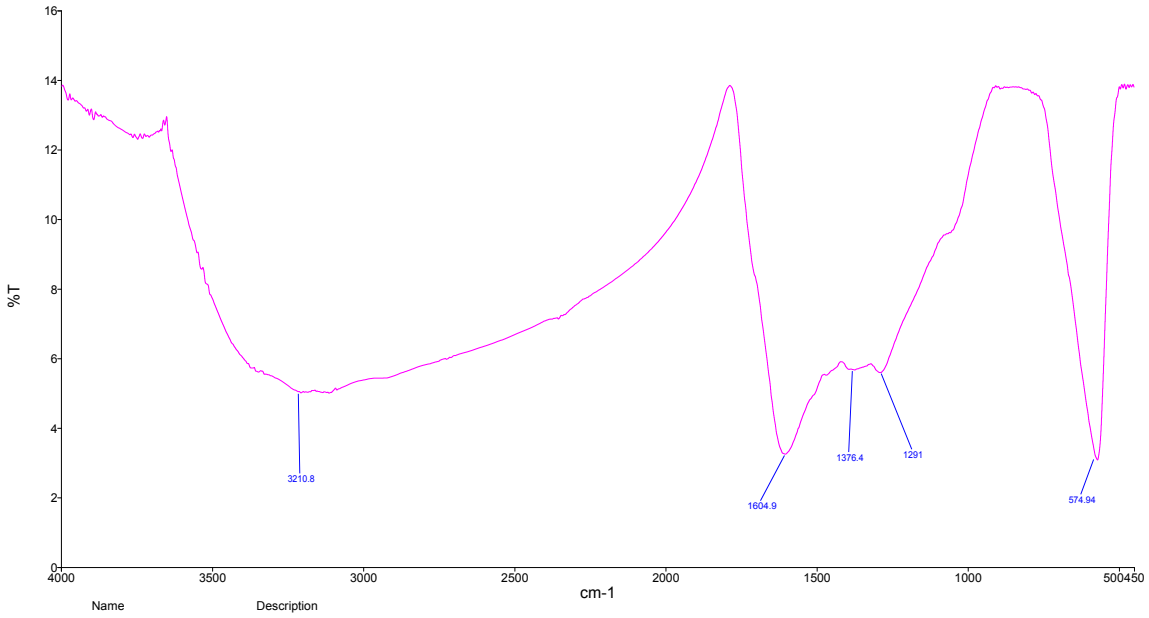
DSC TGA of Pd/Fe_3O_4@PDA native catalyst



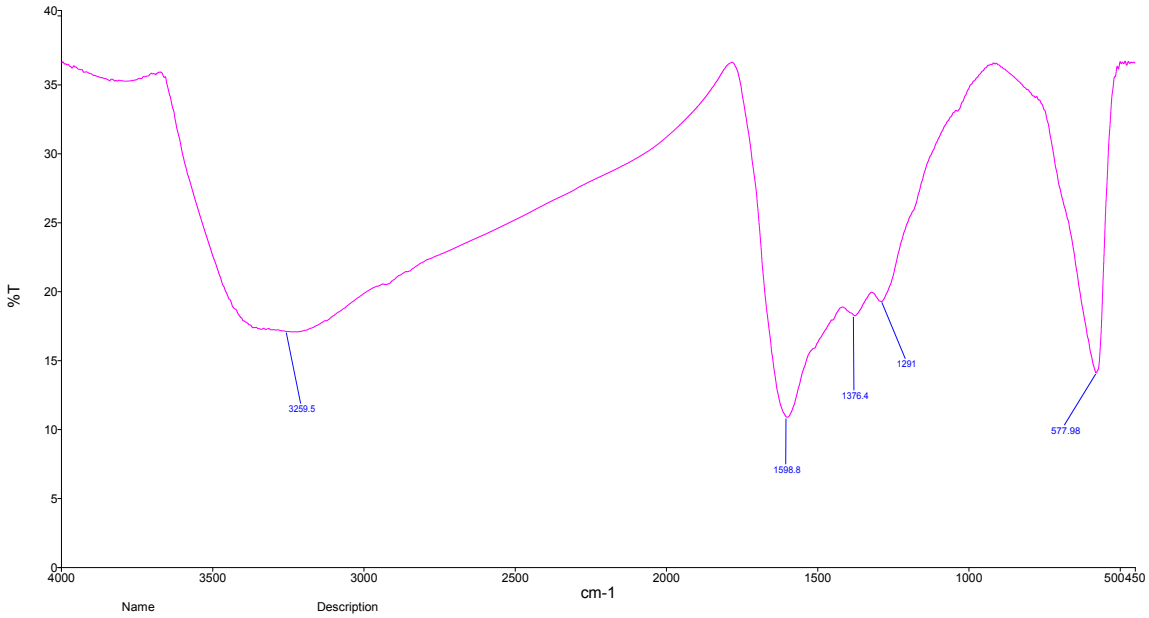
DSC of Pd/Fe_3O_4@PDA native catalyst



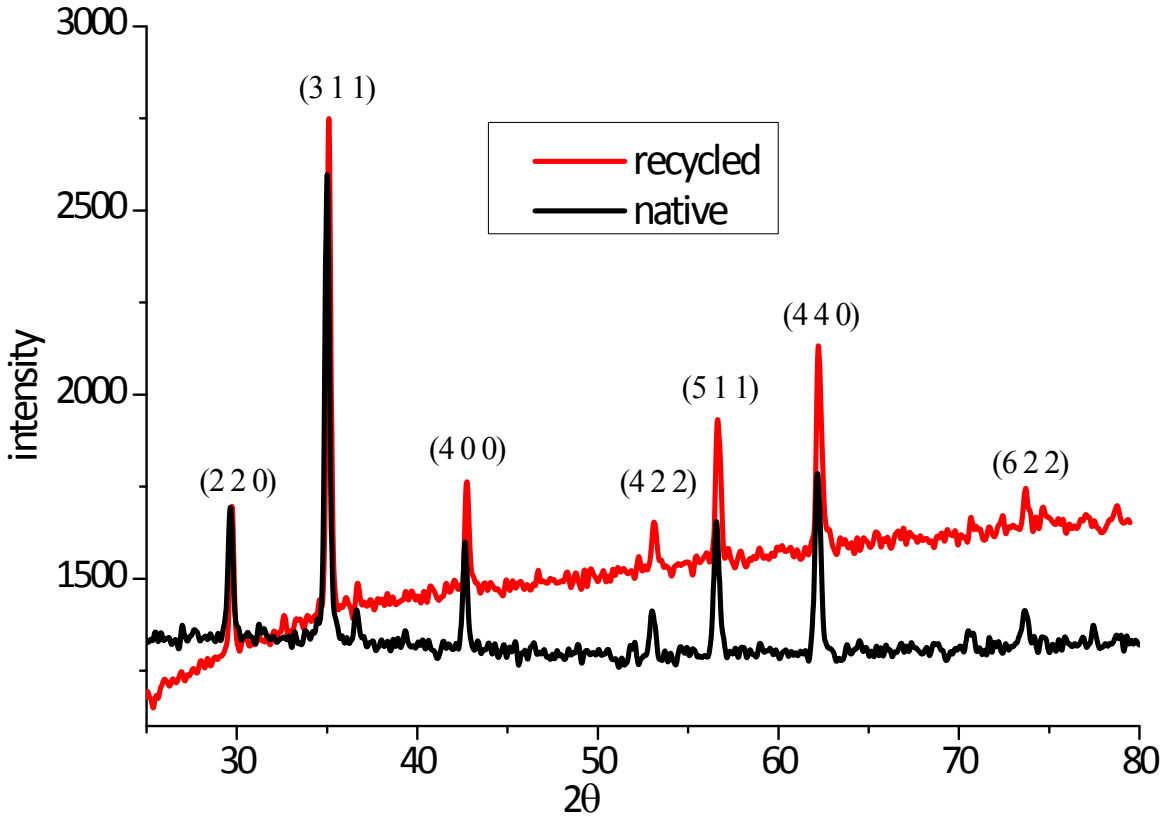
TGA of Pd/Fe_3O_4@PDA native catalyst



FT-IR of native Pd/Fe_3O_4@PDA catalyst



FT-IR of recycled Pd/Fe_3O_4@PDA catalyst

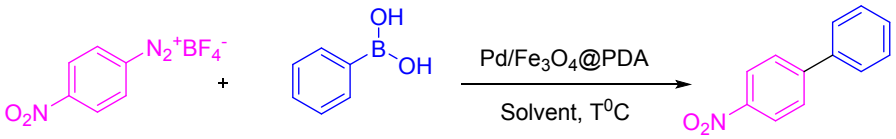


X-ray powder diffractogram of the fresh and reused Pd/Fe_3O_4@PDA nanoparticles

General experimental procedure for Suzuki reaction: (with aryldiazonium tetrafluoroborate salts)

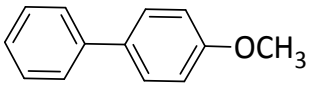
To a 25mL round bottomed flask Teflon coated magnetic bar, aryl diazoniumtetrafluoroborate (0.5 mmol) and arylboronic acid (0.55 mmol) were added. To this 0.27 mol % of Pd were added followed by 4mL of Methanol. The reaction mixture was stirred for the indicated time at room temperature in air till the complete consumption of the reactants as confirmed by TLC. After completion of reaction 2ml of water added and solution was extracted four times with ethyl acetate (4 × 10 mL). The organic solvents were removed under pressure and the residue was column chromatographed using silica gel with petroleum ether/ethyl acetate as eluents to get the desired coupling product (most cases it was only filter column).

Table Optimization of reaction conditions of Suzuki cross-coupling of aryldiazonium salts with arylboronic acids by Pd/Fe_3O_4@PDA nanocatalyst[a]



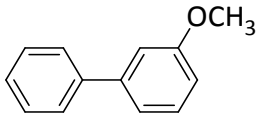
Entry	Solvent	Time (h)	Yield[b] (%)
1	CH_3CN	24	33
2	DMSO	24	51
3	DMF	24	46
4	CH_2Cl_2	24	28
5	$CHCl_3$	24	32
6	NMP	24	38
7	THF	24	24
8	1,4-dioxane	24	21
9	H_2O	24	10
10	H_2O	24	10[c]
11	EtOH:H_2O(1:1)	24	26
12	EtOH	3	15
13	EtOH	24	63
14	**MeOH**	**3**	**85**
15	MeOH	24	85
16	MeOH	24	60[d]
17	MeOH	24	0[e]

[a]Reaction conditions: phenylboronic acid (0.55 mmol), arenediazonium salts (0.5 mmol), Pd/Fe_3O_4@PDA (0.27 mol % of Pd).
[b]isolated yield.
[c]reaction temperature 60 °C
[d]Pd/Fe_3O_4@PDA (0.18 mol % of Pd)
[e]without catalyst



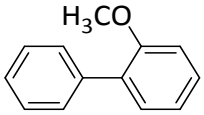
4-Methoxy-1,1'-biphenyl (1a) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 4H), 7.50 – 7.44 (m, 2H), 7.39 – 7.33 (m, 1H), 7.06 – 7.01 (m, 2H), 3.90 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.19, 140.87, 133.82, 128.77, 128.20, 126.78, 126.71, 114.25, 55.37.



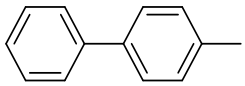
3-Methoxy-1,1'-biphenyl (1b) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 2H), 7.54 – 7.37 (m, 4H), 7.25 (m, J = 17.0, 12.6, 11.9 Hz, 2H), 6.97 (dd, J = 8.2, 2.6 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.01, 142.83, 141.17, 129.80, 128.78, 127.46, 127.25, 119.74, 112.97, 112.74, 55.33.



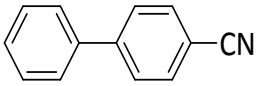
2-Methoxy-1,1'-biphenyl (1c) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (m, J = 7.0, 4.4, 2.5 Hz, 3H), 7.12 – 7.01 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.48, 138.56, 130.89, 130.75, 129.55, 128.61, 127.97, 126.91, 120.84, 111.27, 55.56.



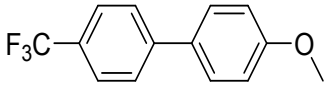
4-Methyl-1,1'-biphenyl (1d) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 2H), 7.57 (t, J = 7.4 Hz, 2H), 7.78 – 7.23 (m, 2H), 7.54 – 7.47 (m, 1H), 7.44 – 7.37 (m, 2H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.24, 138.43, 137.07, 129.55, 128.78, 127.06, 21.16.



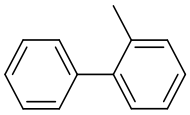
[1,1'-Biphenyl]-4-carbonitrile (1e) [3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (m, J = 8.5, 4.2 Hz, 4H), 7.62 (dd, J = 5.2, 3.3 Hz, 2H), 7.55 – 7.38 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.70, 139.20, 132.61, 129.13, 128.68, 127.75, 127.24, 118.95, 110.95.



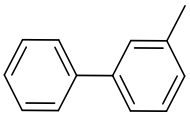
4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (1f) [4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (m, 4H), 7.53 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.81, 144.24, 132.14, 128.30, 126.82, 125.68, 125.64, 125.60, 114.39, 55.34.



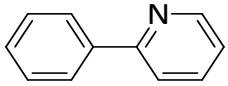
2-Methyl-1,1'-biphenyl (1g) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.25 (m, 9H), 2.33 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.00, 141.97, 135.37, 130.33, 129.82, 129.22, 128.78, 128.09, 127.27, 127.20, 126.78, 125.78, 20.49.



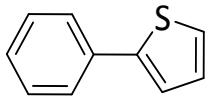
3-Methyl-1,1'-biphenyl (1h) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.42 (m, J = 10.6, 7.4, 1.5 Hz, 6H), 7.21 (d, J = 7.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.37, 141.25, 138.32, 128.69, 128.66, 127.99, 127.18, 124.27, 21.55.



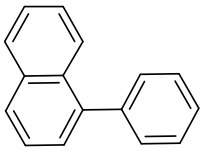
2-Phenylpyridine (1i) [5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 – 8.67 (m, 1H), 8.02 – 7.96 (m, 2H), 7.79 – 7.69 (m, 2H), 7.51 – 7.38 (m, 3H), 7.27 – 7.18 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.49, 149.69, 139.43, 136.76, 128.97, 128.77, 126.94, 122.12, 120.60.



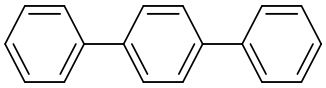
2-Phenylthiophene (1j) [6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.46 – 7.27 (m, 5H), 7.12 (dd, J = 5.0, 3.6 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 144.47, 134.44, 128.91, 128.14, 127.48, 125.88, 124.82, 123.10.



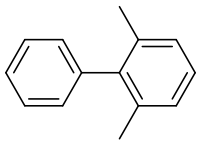
1-Phenylnaphthalene (1k) [6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.86 (m, 3H), 7.61 – 7.44 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.79, 140.29, 133.82, 131.65, 130.10, 128.28, 127.65, 127.26, 126.95, 126.04, 125.78, 125.40.



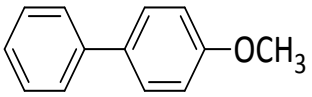
1,1':4',1''-Terphenyl (1l) [7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 8H), 7.49 – 7.43 (m, 4H), 7.39 – 7.34 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 140.73, 140.15, 128.84, 127.53, 127.37, 127.08.



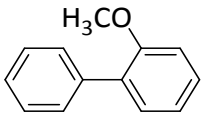
2,6-dimethyl-1,1'-biphenyl (1m) [11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, J = 45.4, 27.3, 7.7 Hz, 6H), 6.98 (d, J = 8.8 Hz, 2H), 3.84 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.10, 140.79, 133.74, 128.70, 128.13, 126.71, 126.63, 114.17, 55.32.



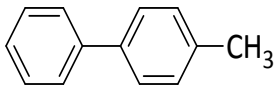
4-Methoxy-1,1'-biphenyl (1n) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 4H), 7.47 (m, J = 7.6, 3.5 Hz, 2H), 7.36 (m, J = 10.9, 5.6, 2.6 Hz, 1H), 7.03 (dd, J = 8.7, 3.2 Hz, 2H), 3.90 (s, J = 1.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.20, 140.87, 133.82, 128.77, 128.19, 126.78, 126.70, 114.26, 55.37.



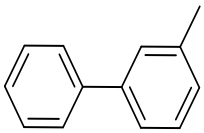
2-Methoxy-1,1'-biphenyl (1o) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.47 (dd, J = 10.3, 4.7 Hz, 2H), 7.38 (m, J = 7.6, 4.2, 1.1 Hz, 3H), 7.14 – 7.01 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.47, 138.54, 130.88, 130.74, 129.53, 128.59, 127.96, 126.89, 120.82, 111.25, 55.55.



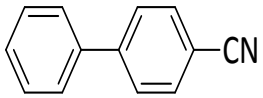
4-Methyl-1,1'-biphenyl (1p) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.25 (m, 9H), 2.45 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.16, 138.36, 137.03, 129.50, 128.73, 126.99, 21.13.



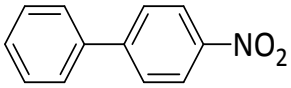
3-Methyl-1,1'-biphenyl (1q) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 2H), 7.42 (m, J = 29.7, 11.1, 4.6 Hz, 6H), 7.20 (d, J = 7.3 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.39, 141.27, 138.34, 128.71, 128.68, 128.00, 127.18, 124.30, 21.57.



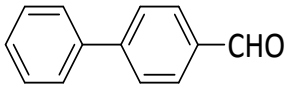
[1,1'-Biphenyl]-4-carbonitrile (1r) [3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 4H), 7.66 – 7.57 (m, 2H), 7.56 – 7.42 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.70, 139.20, 132.61, 129.13, 128.68, 127.75, 127.25, 118.96, 110.94.



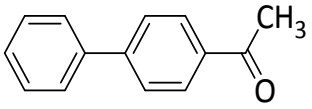
4-Nitro-1,1'-biphenyl (1s) [3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 7.0 Hz, 2H), 7.76 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 9.7 Hz, 2H), 7.57 – 7.43 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.64, 147.11, 138.78, 129.18, 128.95, 127.81, 127.40, 124.12.



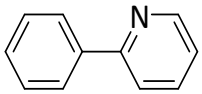
[1,1'-Biphenyl]-4-carbaldehyde (1t) [5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.67 (dd, J = 5.3, 3.4 Hz, 2H), 7.55 – 7.41 (m, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 191.89, 147.19, 139.71, 135.21, 130.25, 129.01, 128.46, 127.68, 127.36.



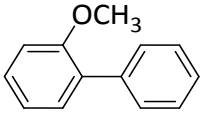
1-([1,1'-Biphenyl]-4-yl)ethanone (1u) [8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 2H), 7.76 – 7.62 (m, 4H), 7.54 – 7.39 (m, 3H), 2.67 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.76, 145.80, 139.90, 135.88, 128.97, 128.93, 128.25, 127.29, 127.24, 26.67.



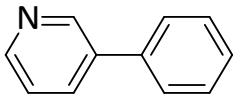
2-Phenylpyridine (1v) [5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 4.8 Hz, 1H), 8.03 (d, J = 7.2 Hz, 2H), 7.82 – 7.72 (m, 2H), 7.58 – 7.39 (m, 3H), 7.25 (m, J = 8.2, 7.4, 5.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.51, 149.81, 149.59, 139.45, 136.87, 136.60, 128.86, 128.66, 127.08, 126.79, 122.11, 121.75, 120.72, 120.58, 120.44.



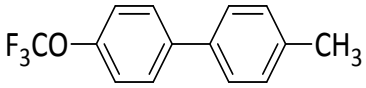
2-Methoxy-1,1'-biphenyl (1w) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.11 – 6.99 (m, 2H), 3.85 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 156.47, 138.55, 130.89, 130.74, 129.54, 128.60, 127.96, 126.90, 120.83, 111.25, 55.56.



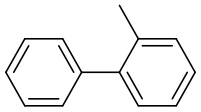
3-Phenylpyridine (1x) [9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.62 (d, J = 3.7 Hz, 1H), 7.94 – 7.86 (m, 1H), 7.66 – 7.35 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.54, 148.39, 148.30, 148.21, 137.85, 136.71, 134.56, 134.28, 129.20, 128.11, 127.28, 127.05, 123.60.



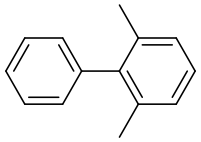
4-Methyl-4'-(trifluoromethoxy)-1,1'-biphenyl (1y) [10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.30 (dd, J = 8.0, 3.9 Hz, 4H), 2.44 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.48, 139.95, 137.55, 137.00, 129.63, 128.24, 126.96, 121.22, 21.10.



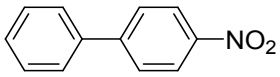
2-methyl-1,1'-biphenyl (1z) [2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.23 (m, 9H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.95, 141.92, 135.33, 130.30, 129.79, 129.19, 128.06, 127.24, 126.75, 125.75, 20.48.



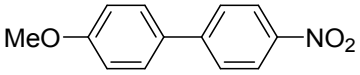
2,6-dimethyl-1,1'-biphenyl (1aa)[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.19 (m, 6H), 6.65 (d, J = 8.4 Hz, 2H), 3.72 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.63, 134.09, 130.86, 128.61, 127.64, 126.74, 104.16, 55.89.



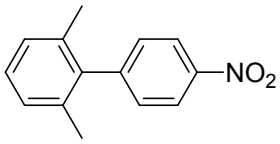
4-nitro-1,1'-biphenyl (1ab) [12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.6 Hz, 2H), 7.78 – 7.37 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.59, 147.03, 138.72, 129.12, 128.89, 127.76, 127.35, 124.07.



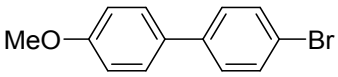
4-methoxy-4'-nitro-1,1'-biphenyl (1ac)[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.3 Hz, 2H), 7.61 (dd, J = 43.6, 8.2 Hz, 4H), 7.00 (d, J = 8.2 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.39, 147.17, 146.49, 131.03, 128.53, 127.03, 124.11, 114.56, 55.40.



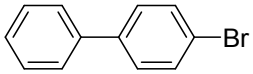
2,6-dimethyl-4'-nitro-1,1'-biphenyl (1ad)[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 9.0 Hz, 2H), 7.85 (dd, J = 55.9, 9.0 Hz, 3H), 6.56 (dd, J = 11.7, 5.5 Hz, 2H), 4.01 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.89, 145.67, 139.26, 136.83, 130.90, 128.80, 127.44, 123.06, 20.51.



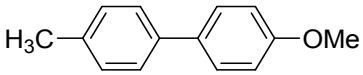
4-bromo-4'-methoxy-1,1'-biphenyl (1ae)[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.35 (m, 6H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.35, 139.69, 132.44, 131.75, 128.26, 127.95, 120.75, 114.29, 55.34.



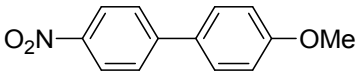
4-bromo-1, 1'-biphenyl (1af)[14]

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.63 – 7.30 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 139.95, 139.63, 133.34, 128.88, 128.85, 128.36, 127.56, 126.96.



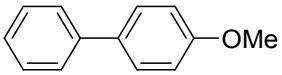
4-methoxy-4'-methyl-1'-biphenyl (1ag)[15]

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.58 – 7.42 (m, 4H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.02 – 6.91 (m, 2H), 3.84 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 158.91, 137.94, 136.33, 133.72, 129.42, 127.93, 126.56, 114.14, 55.31, 21.04.



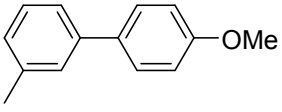
4-methoxy-4'-nitro-1,1'-biphenyl (1ah)[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.61 (dd, *J* = 43.2, 8.5 Hz, 4H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 160.39, 147.16, 146.48, 131.01, 128.53, 127.02, 124.11, 114.56, 55.40.



4-methoxy-1, 1'-biphenyl (1ai)[12]

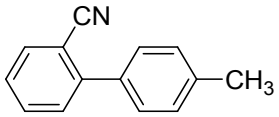
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43 (m, *J* = 45.4, 27.3, 7.7 Hz, 7H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.10, 140.79, 133.74, 128.70, 128.13, 126.71, 126.63, 114.17, 55.32.



4'-methoxy-3-methyl-1,1'-biphenyl (1aj)[16]

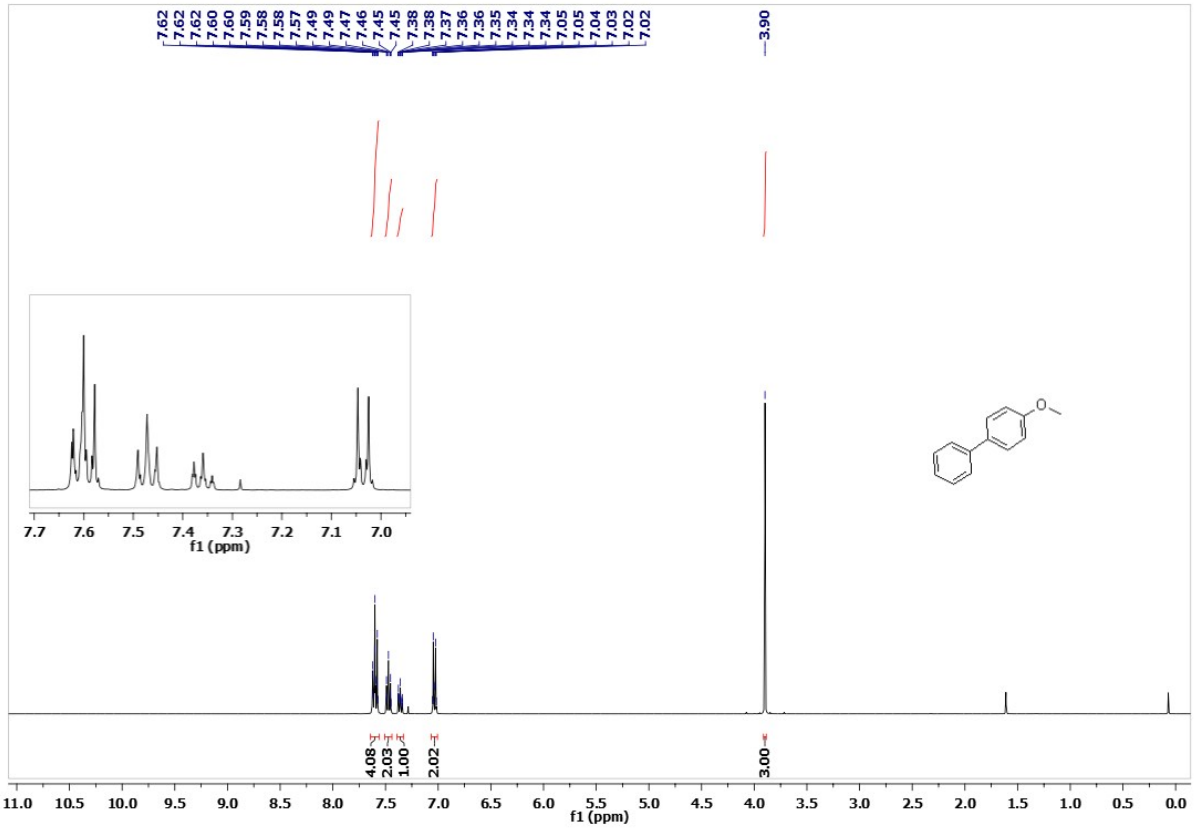
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.52 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.27 (m, 3H), 7.12 (d, *J* = 7.0 Hz, 1H),

6.96 (d, J = 8.5 Hz, 2H), 3.84 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.03, 140.78, 138.24, 133.86, 128.60, 128.13, 127.53, 127.39, 123.82, 114.10, 55.31, 21.54.



4'-Methyl-[1, 1'-biphenyl]-2-carbonitrile (1ak) [10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.7 Hz, 1H), 7.61 (dd, J = 12.1, 4.5 Hz, 1H), 7.53 – 7.37 (m, 4H), 7.33 – 7.23 (m, 3H), 2.41 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 145.53, 138.68, 135.27, 133.70, 132.73, 129.96, 129.43, 128.60, 127.25, 118.84, 111.21, 21.24.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7.03
7.02
7.02
3.90
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
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1.00
2.02
3.00
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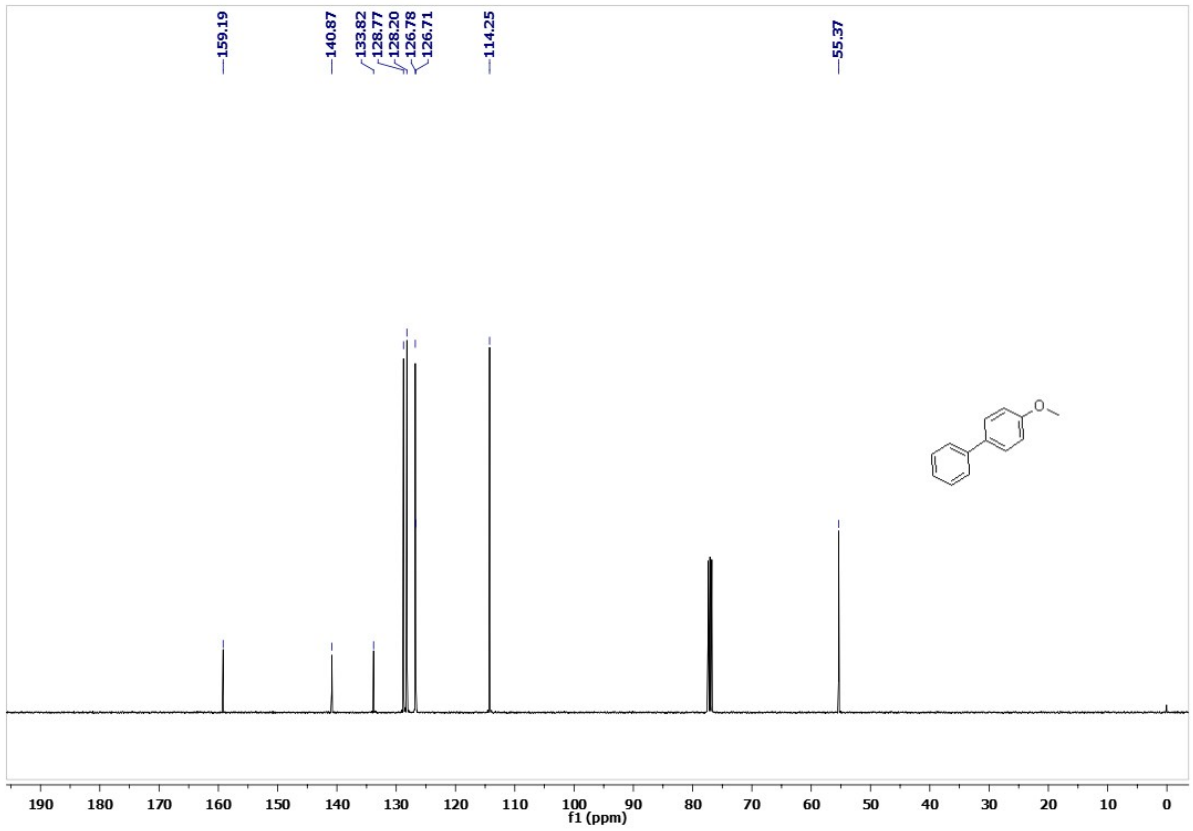
f1 (ppm)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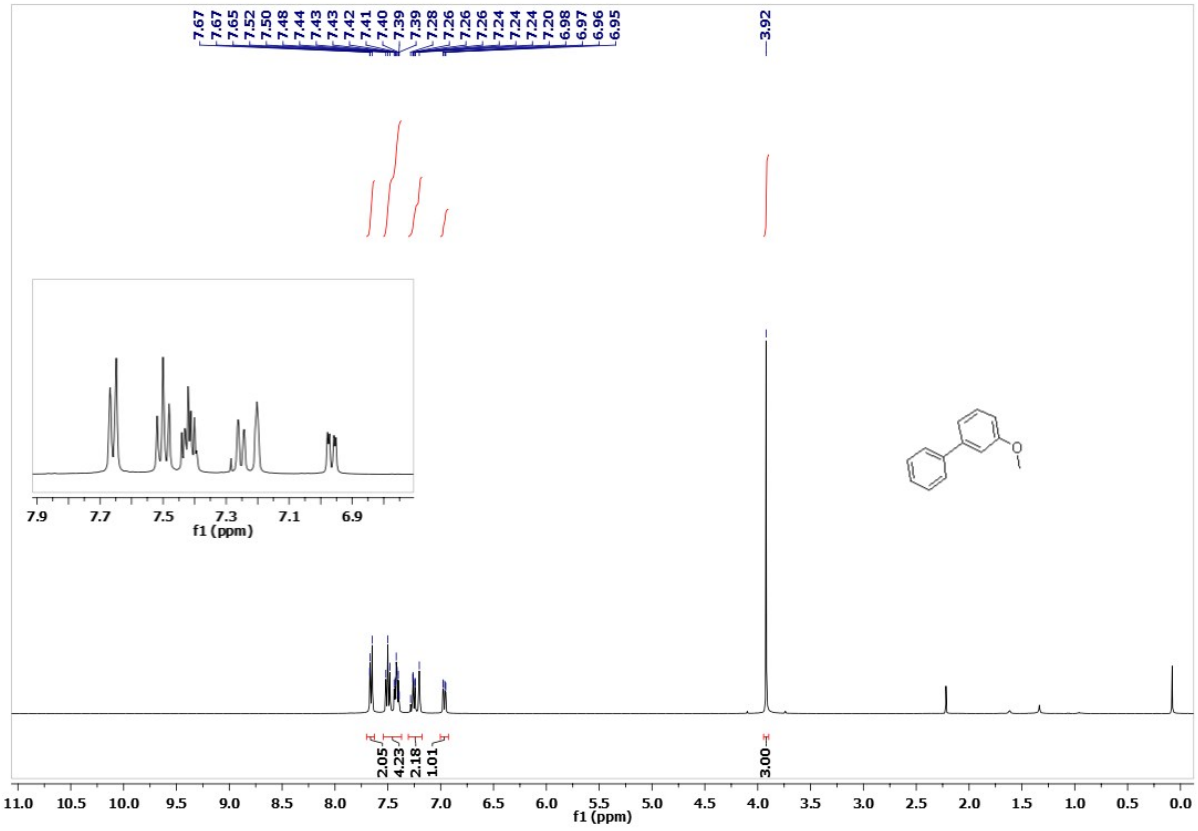
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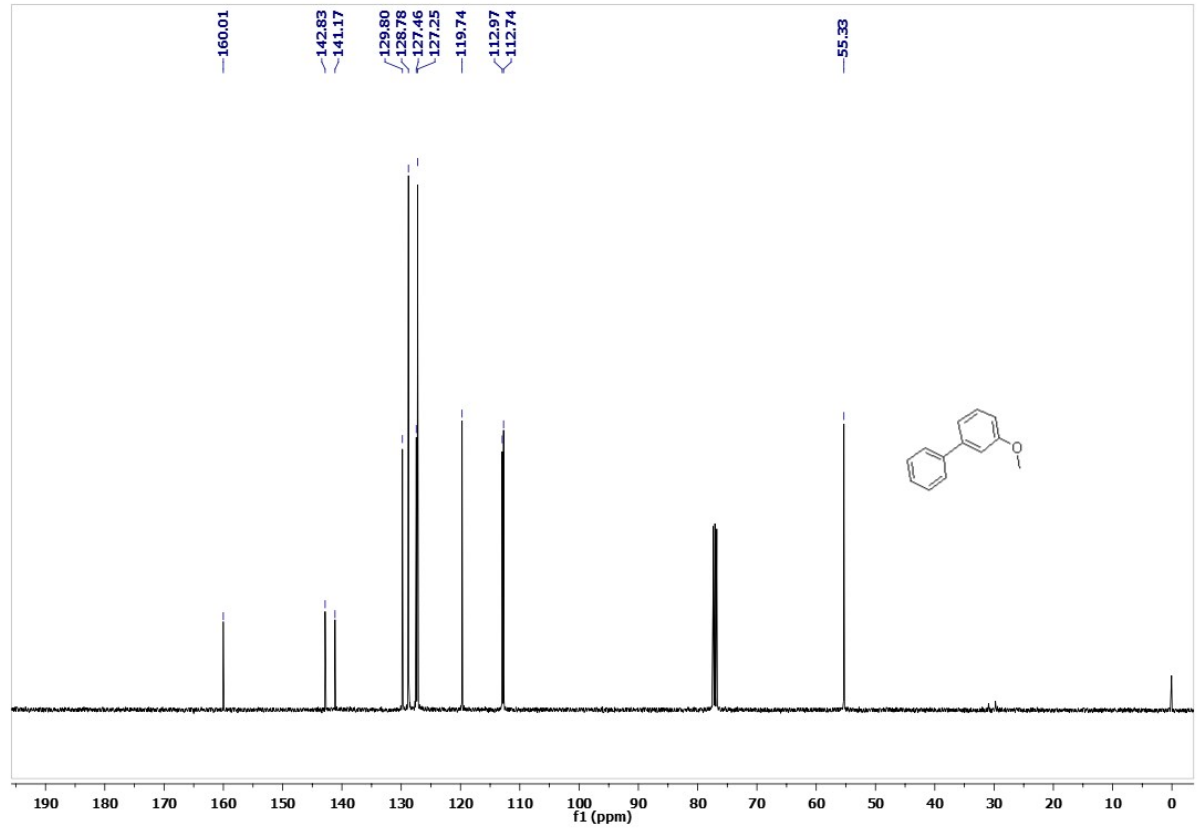
f1 (ppm)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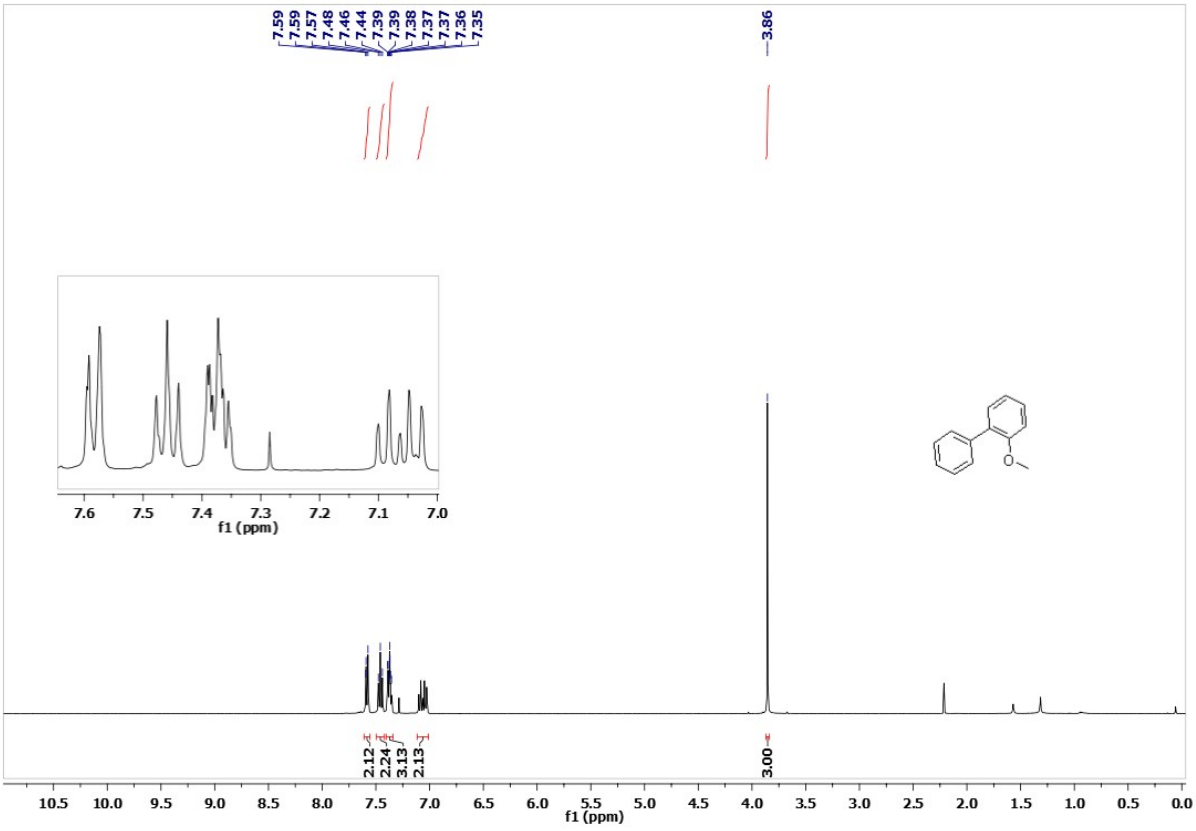
70
60
50
40
30
20
10
0
f1 (ppm)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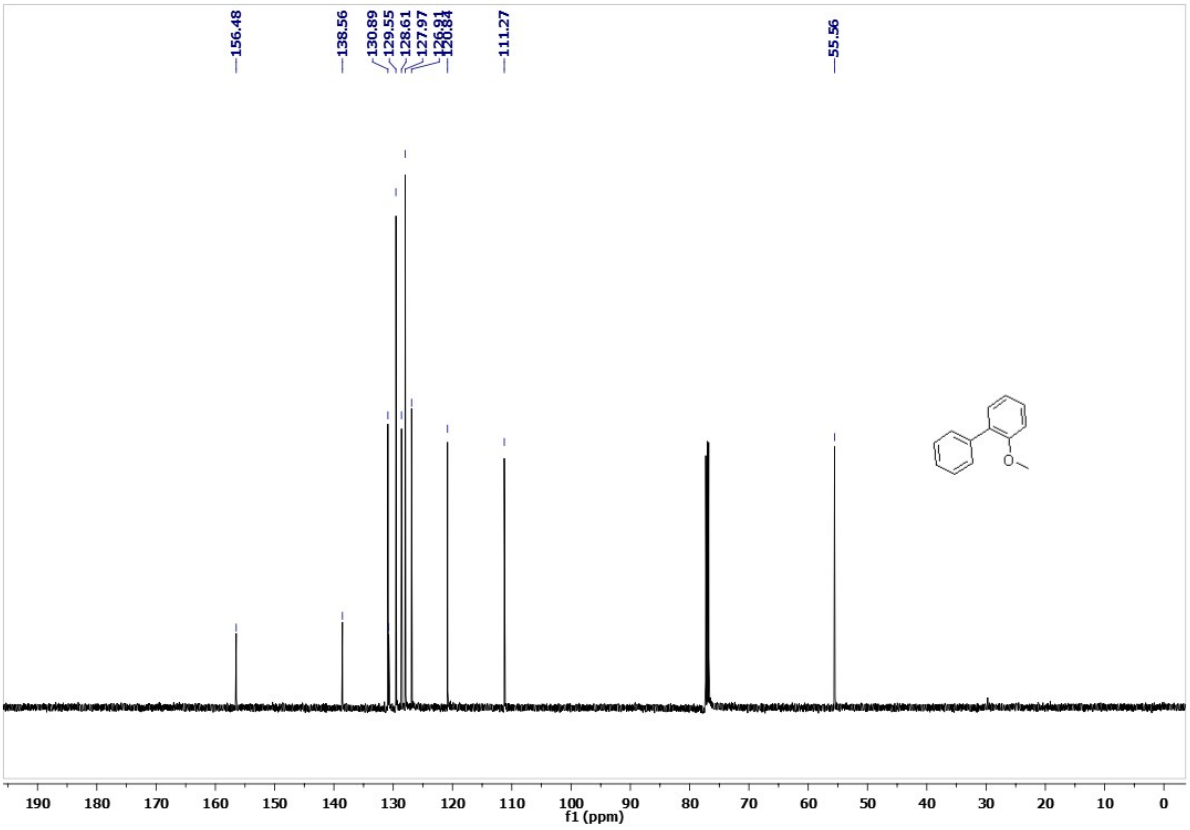
7.37
7.36
7.35
3.86
7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
2.12
2.24
3.13
2.13
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.55
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126.91
120.84
111.27
55.56
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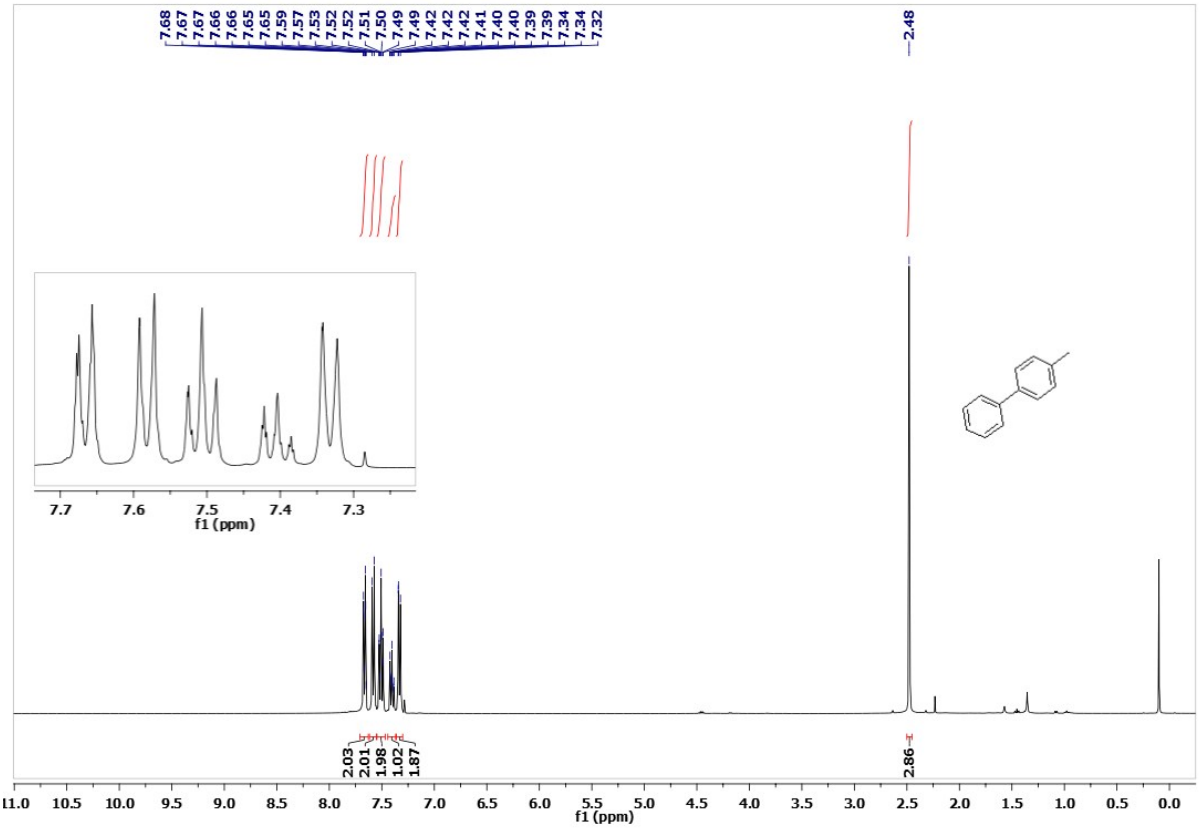
f1 (ppm)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7.49
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7.42
7.41
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7.39
7.39
7.34
7.34
7.32
2.48
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
2.03
2.01
1.98
1.02
1.87
2.86
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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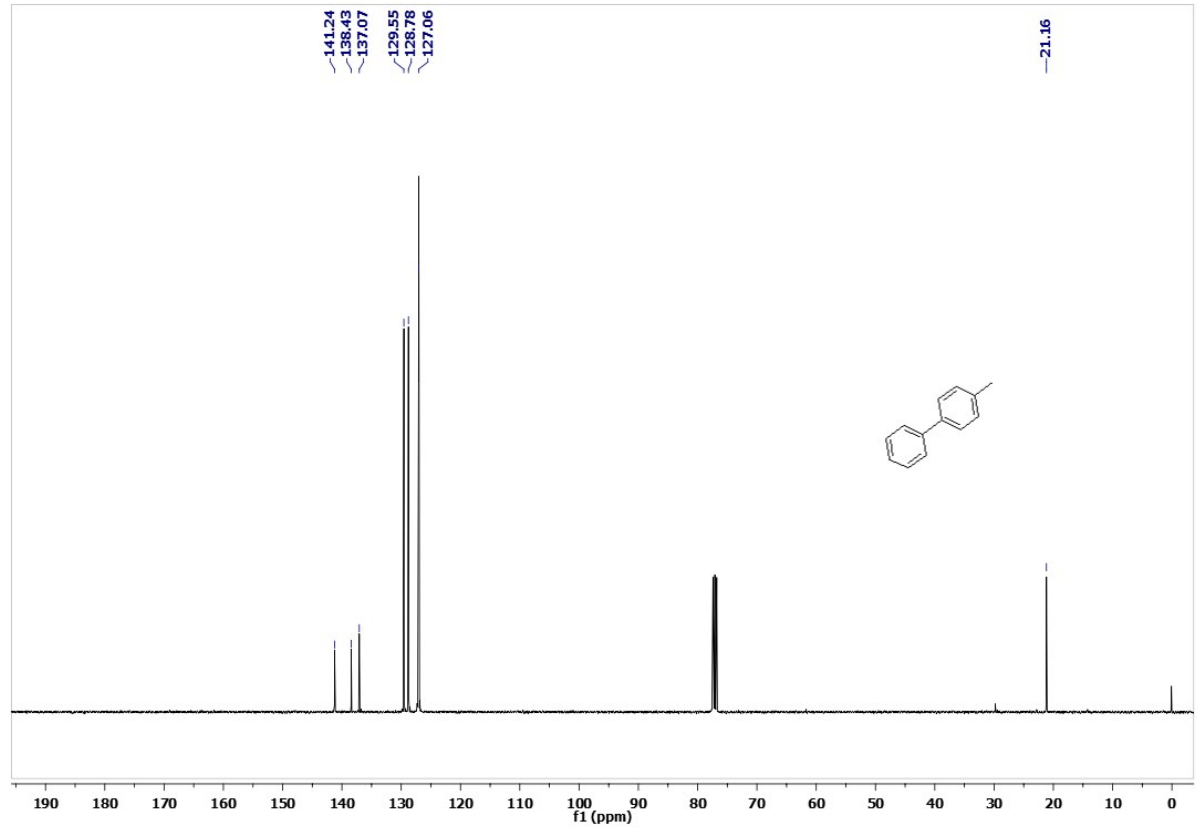
0.0
f1 (ppm)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190
180
170
160
150
140
130
120
110
100
90
80
70
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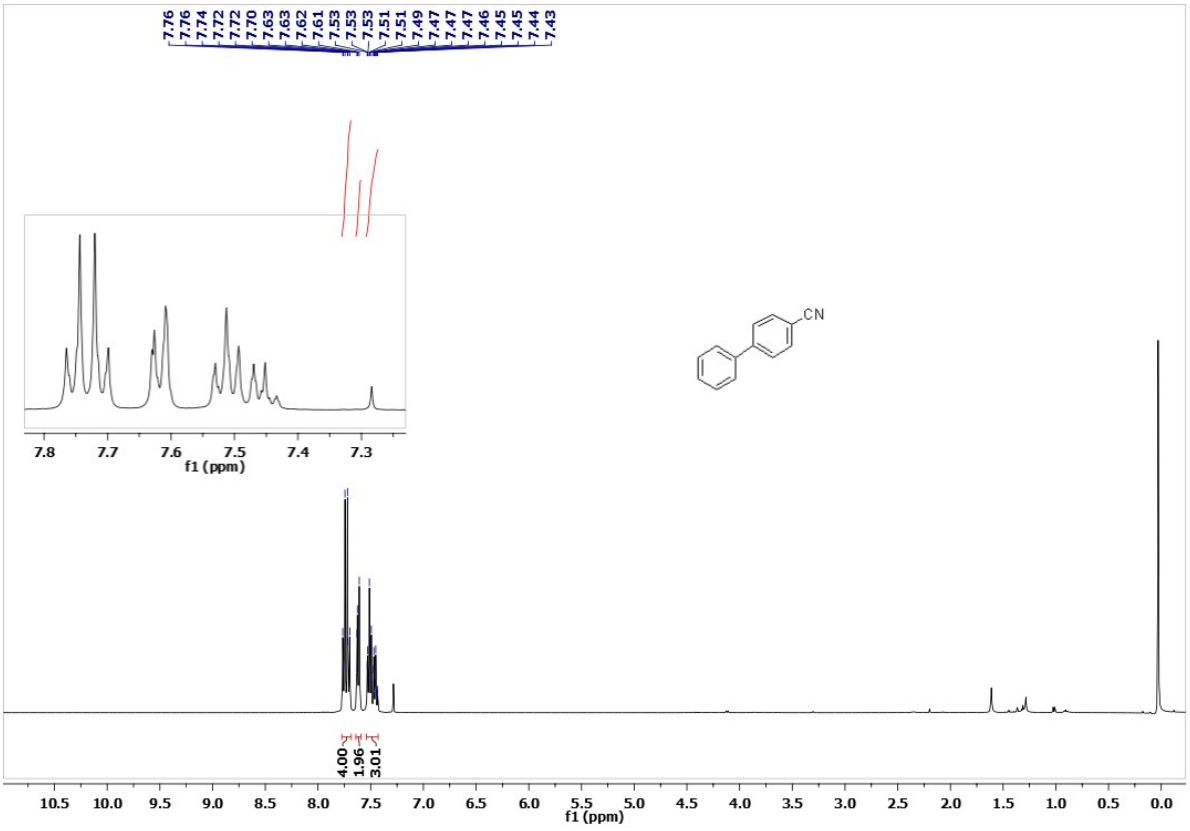
50
40
30
20
10
0
f1 (ppm)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7.62
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7.53
7.53
7.51
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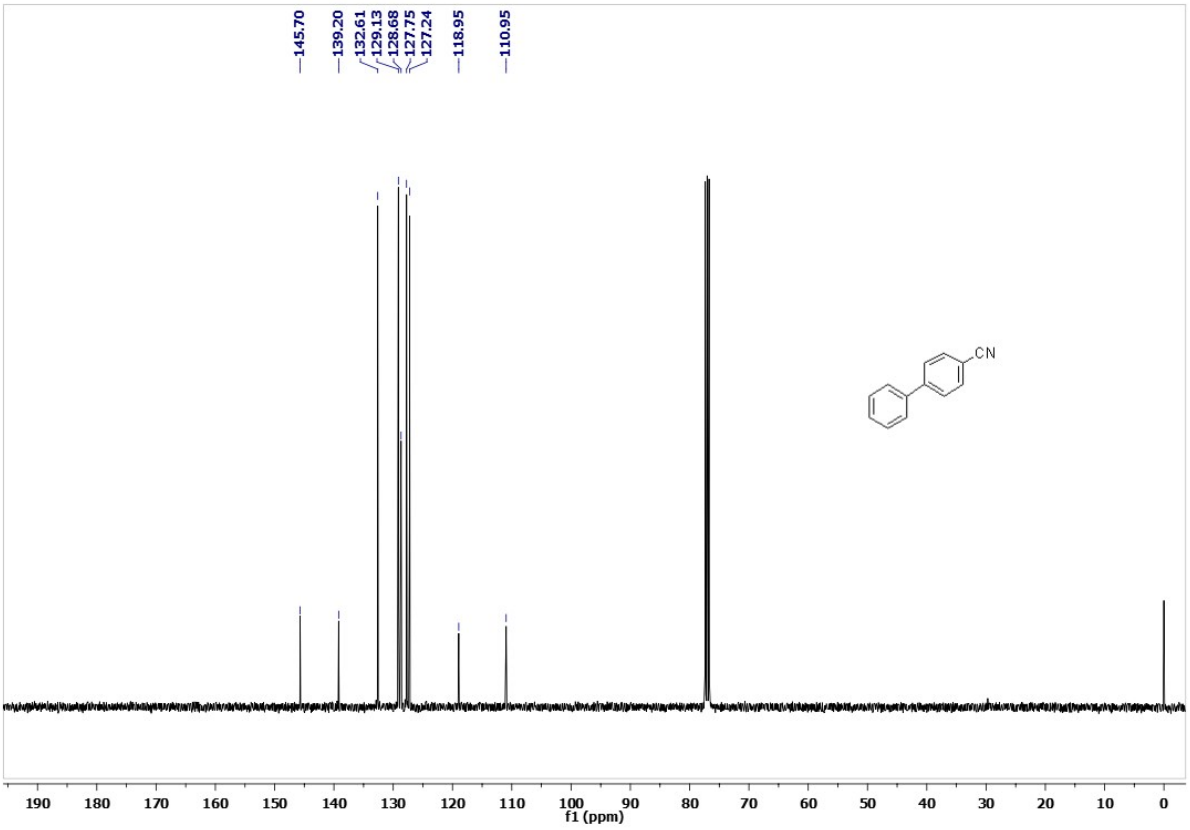
7.43
CN
4.00
1.96
3.01
f1 (ppm)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132.61
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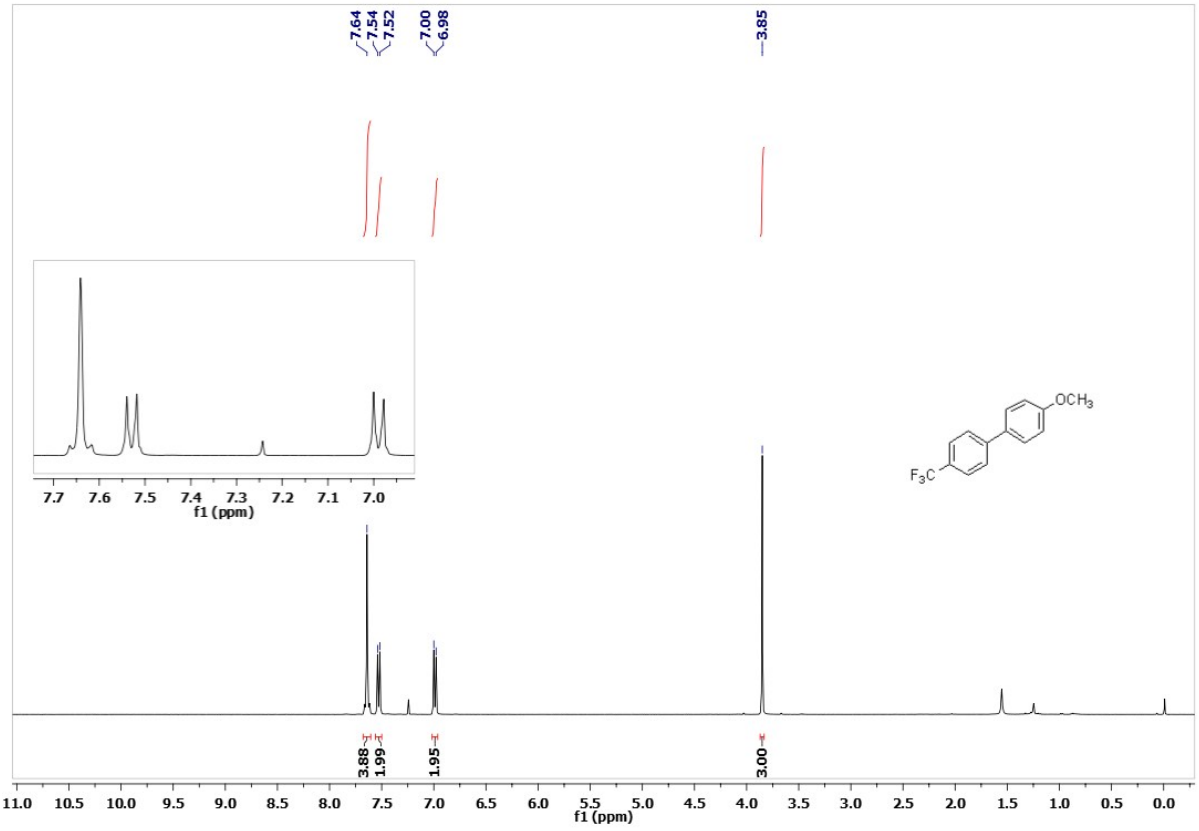
127.75
127.24
118.95
110.95
CN
f1 (ppm)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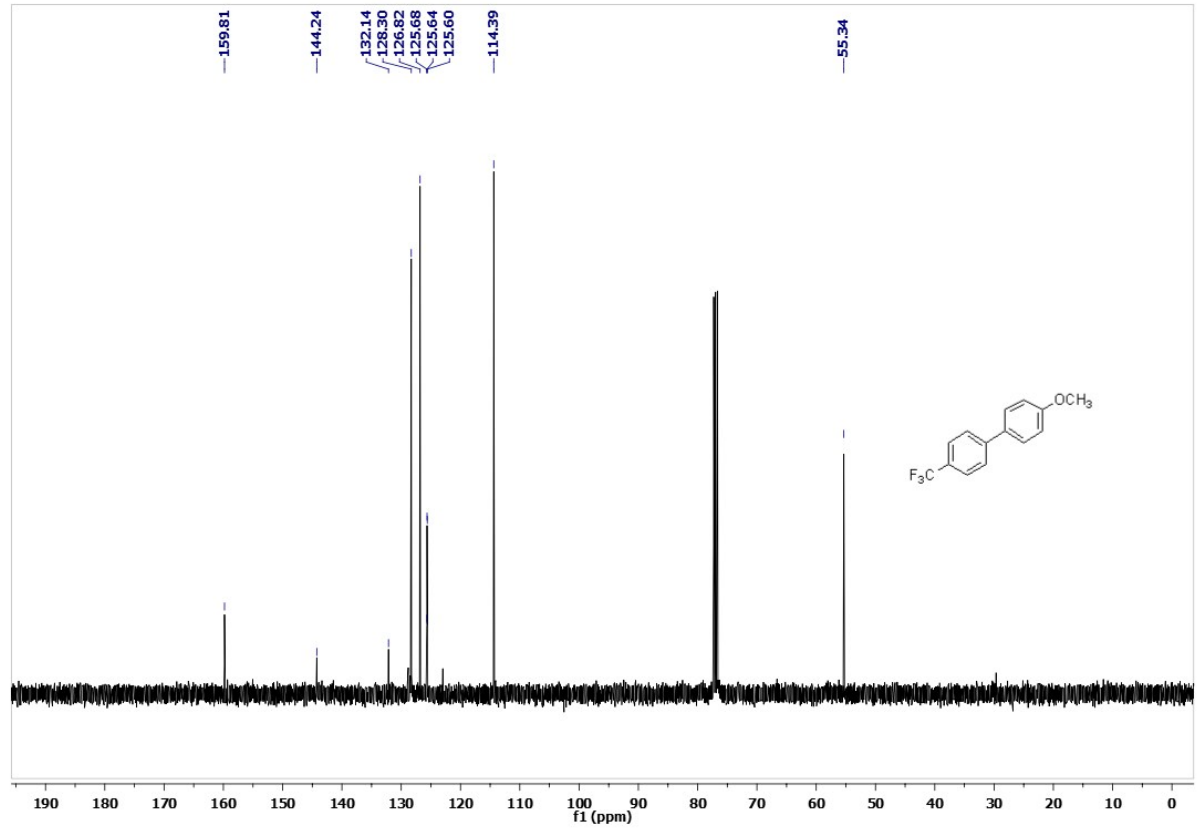
6.98
3.85
OCH3
F3C
f1 (ppm)
3.88
1.99
1.95
3.00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144.24
132.14
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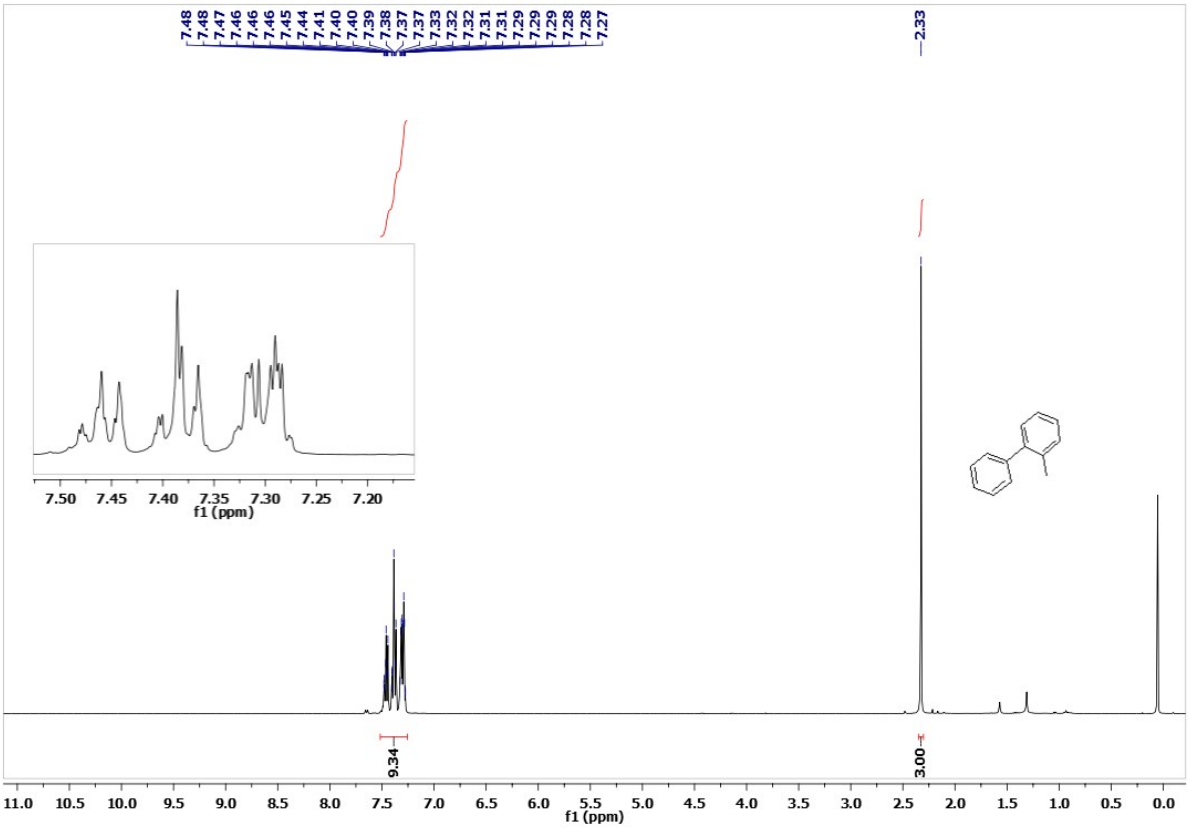
125.68
125.64
125.60
114.39
55.34
OCH3
F3C
f1 (ppm)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7.39
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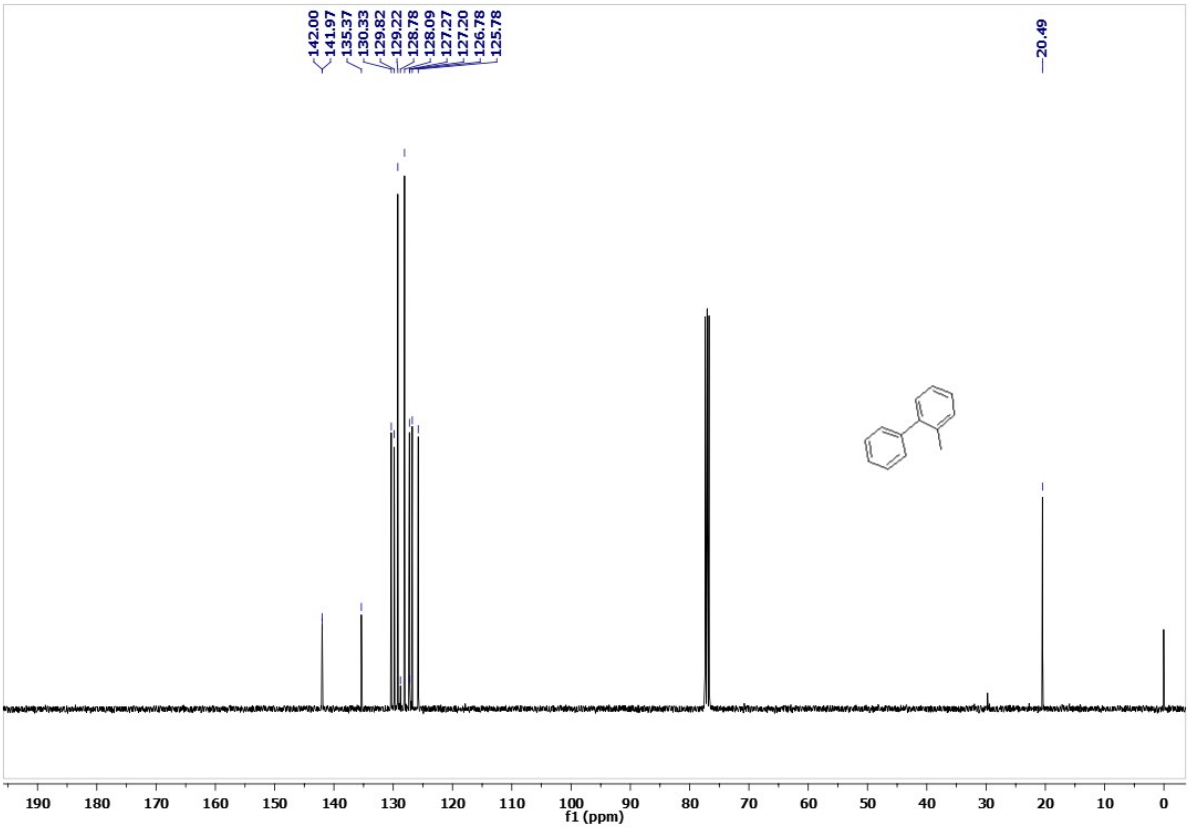
7.37
7.37
7.33
7.32
7.32
7.31
7.29
7.29
7.29
7.28
7.28
7.27
2.33
7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
9.34
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.78
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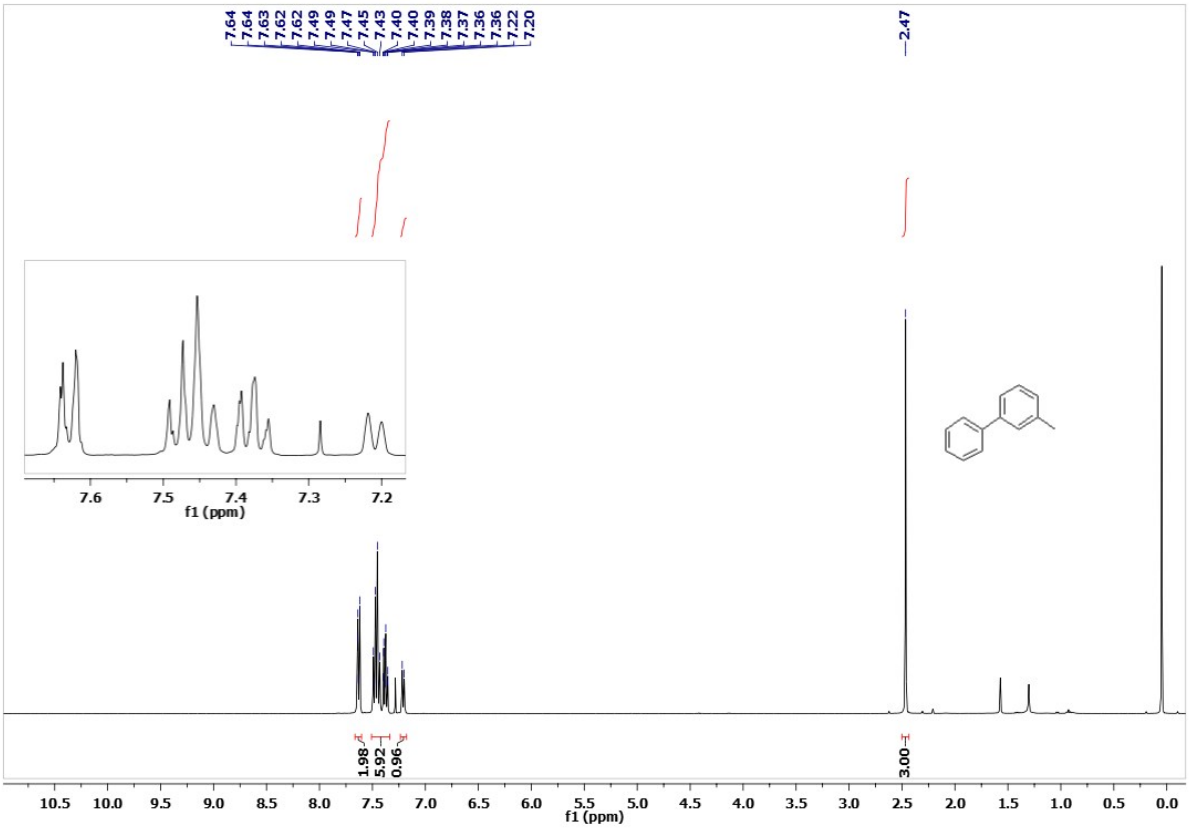
127.20
126.78
125.78
20.49
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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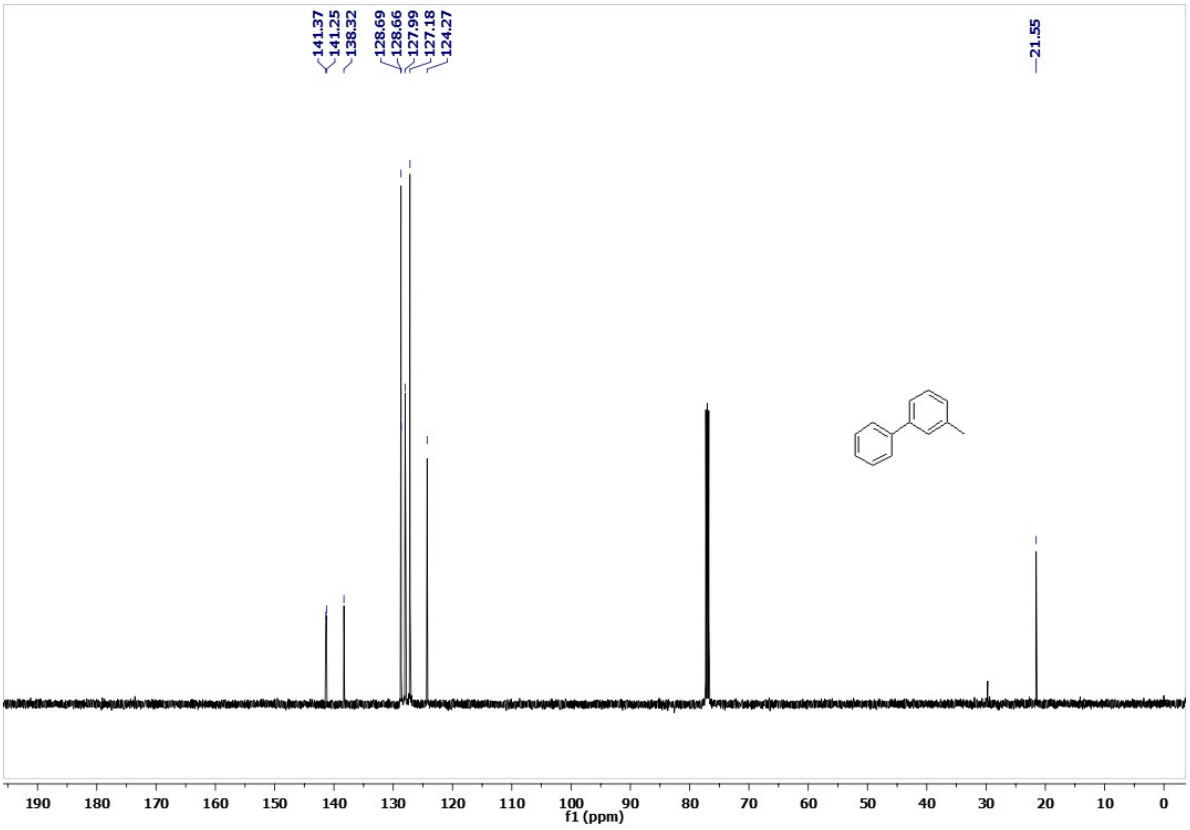
7.47
7.45
7.43
7.40
7.40
7.39
7.38
7.37
7.36
7.36
7.22
7.20
2.47
1.98
5.92
0.96
3.00
f1 (ppm)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141.25
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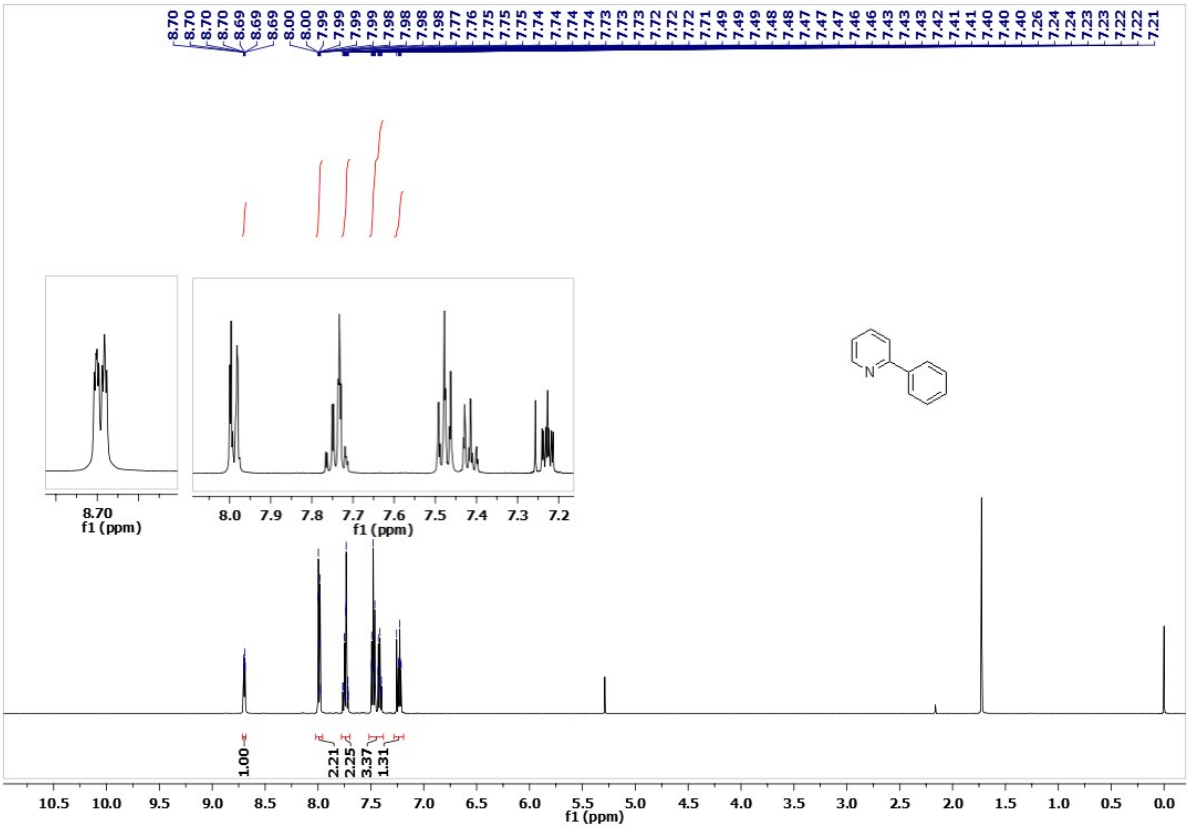
127.99
127.18
124.27
21.55
f1 (ppm)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8.70
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8.69
8.69
8.00
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7.98
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7.43
7.42
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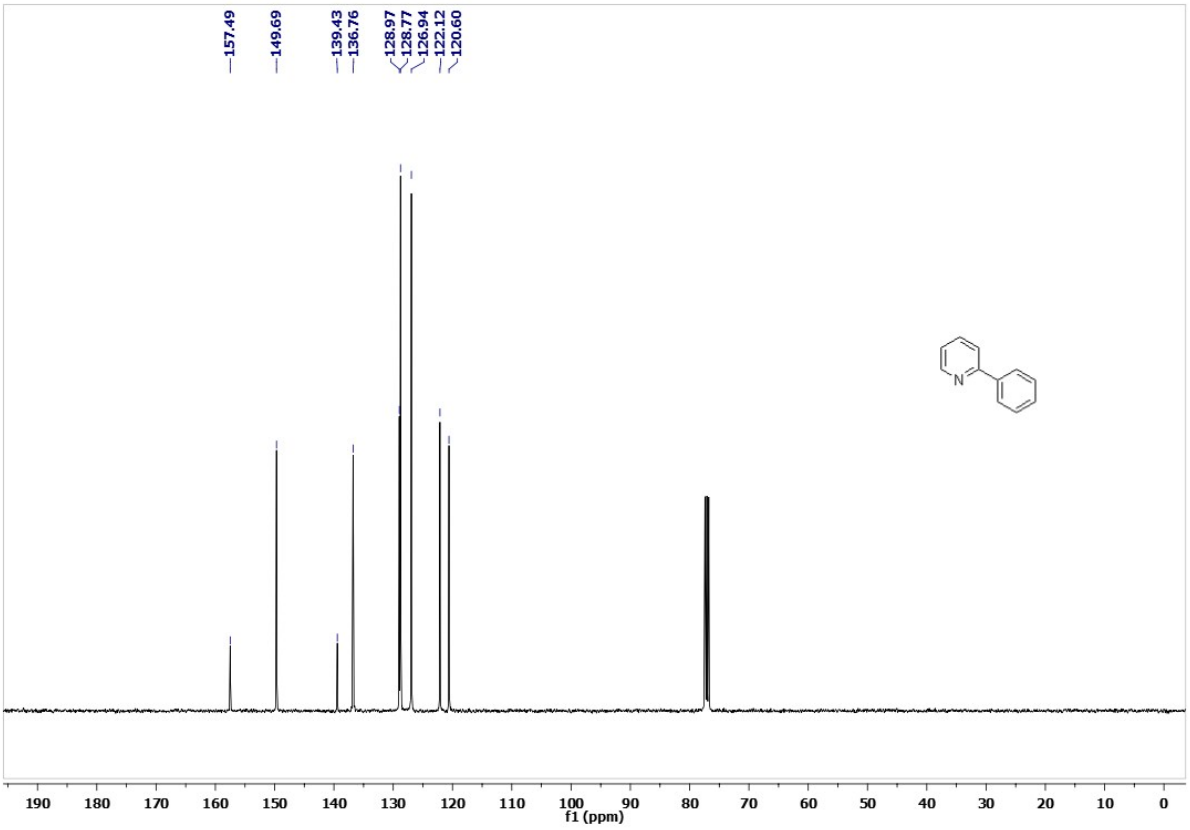
7.40
7.40
7.26
7.24
7.24
7.23
7.23
7.22
7.22
7.21
8.70
f1 (ppm)
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
N
1.00
2.21
2.25
3.37
1.31
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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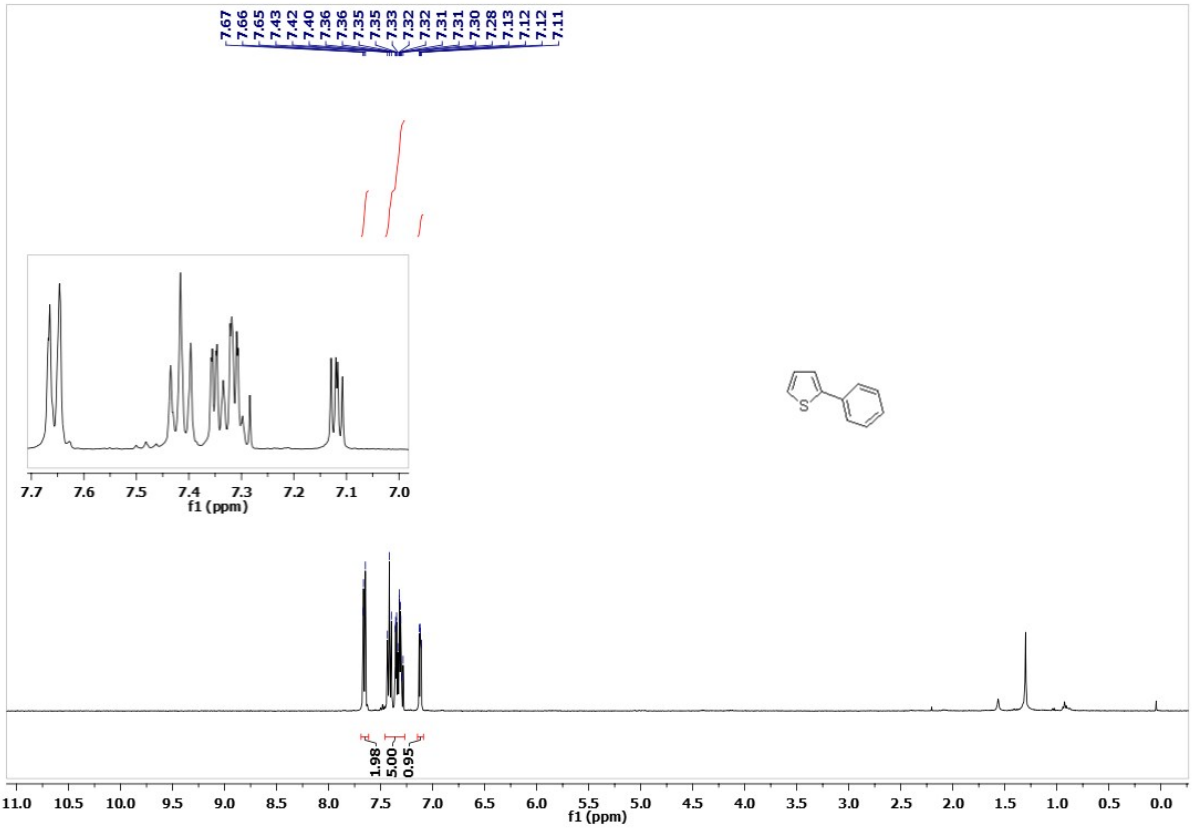
139.43
136.76
128.97
128.77
126.94
122.12
120.60
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.35
7.35
7.33
7.32
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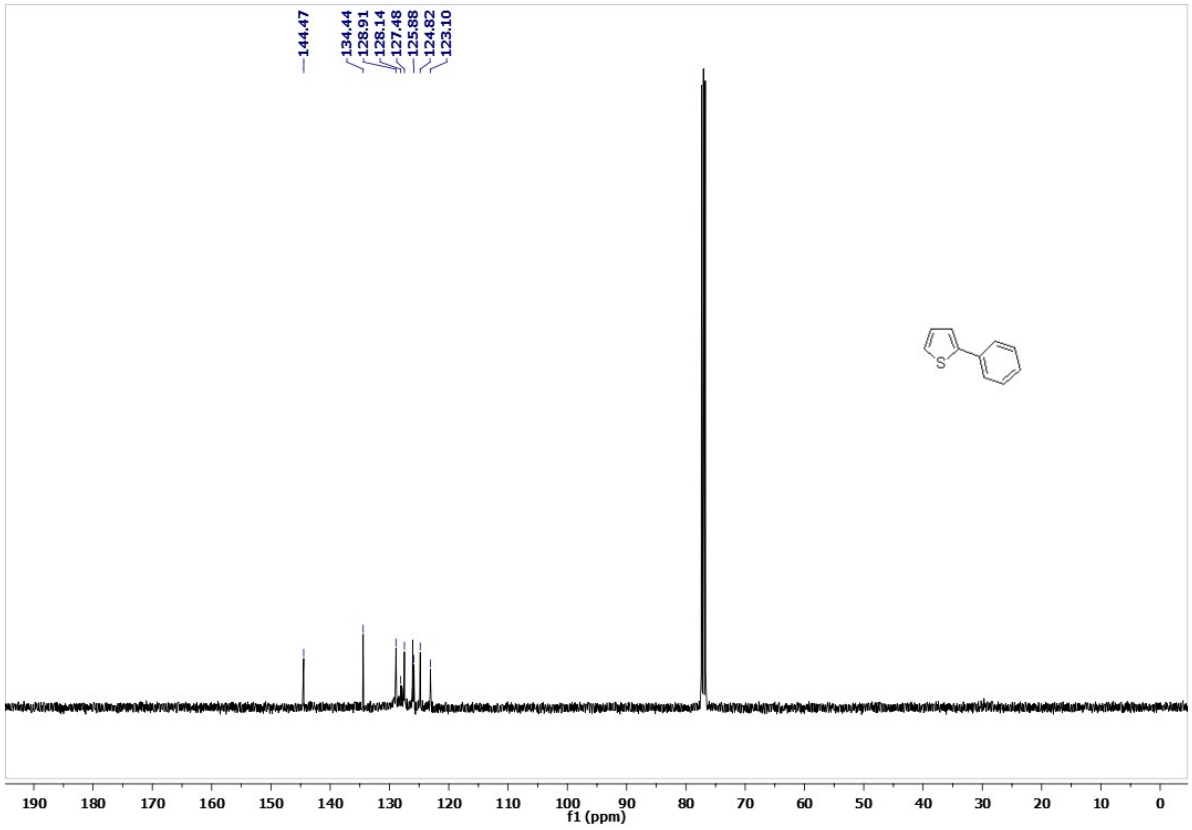
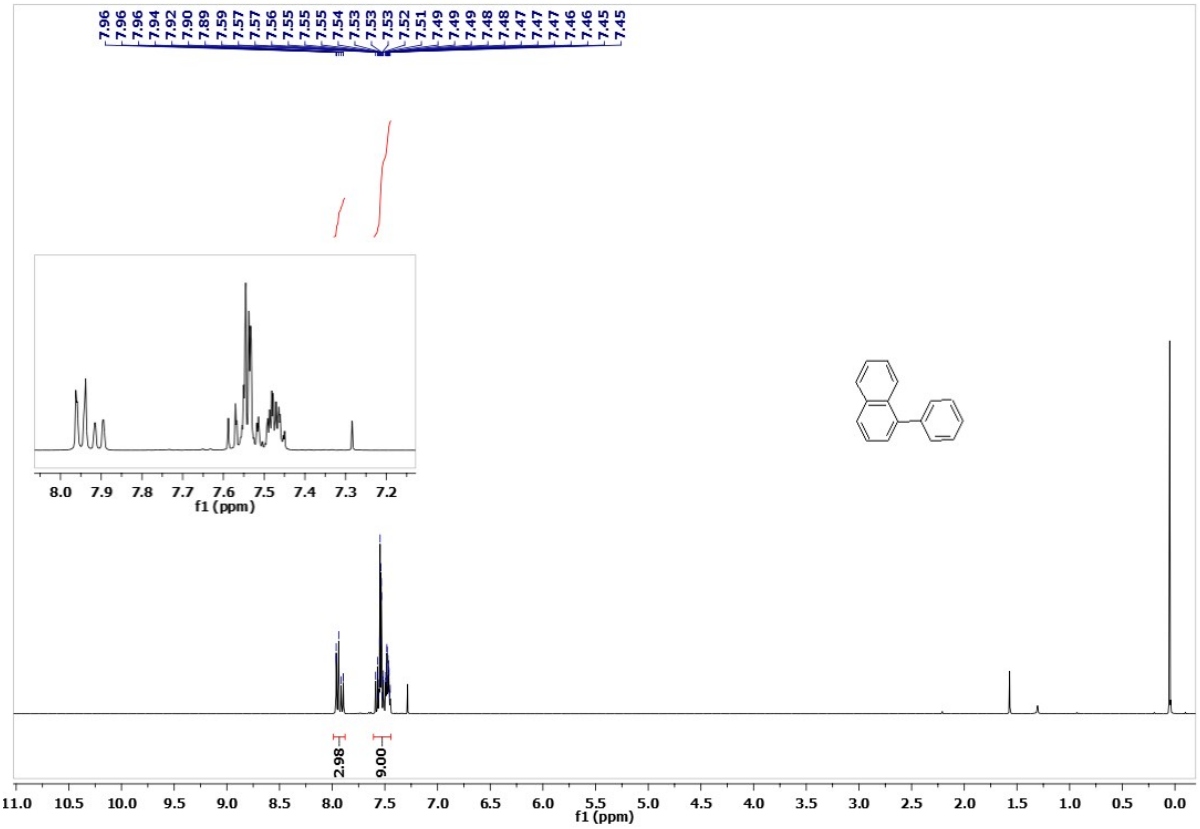
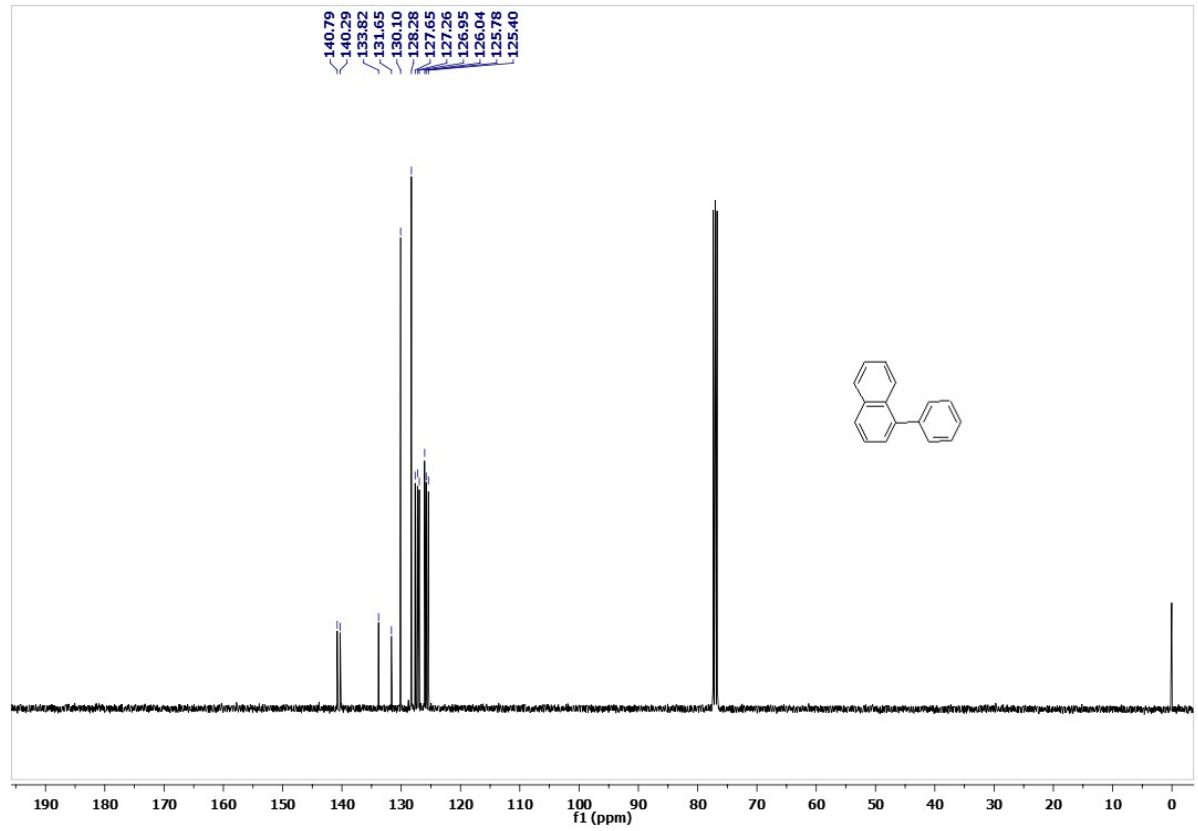
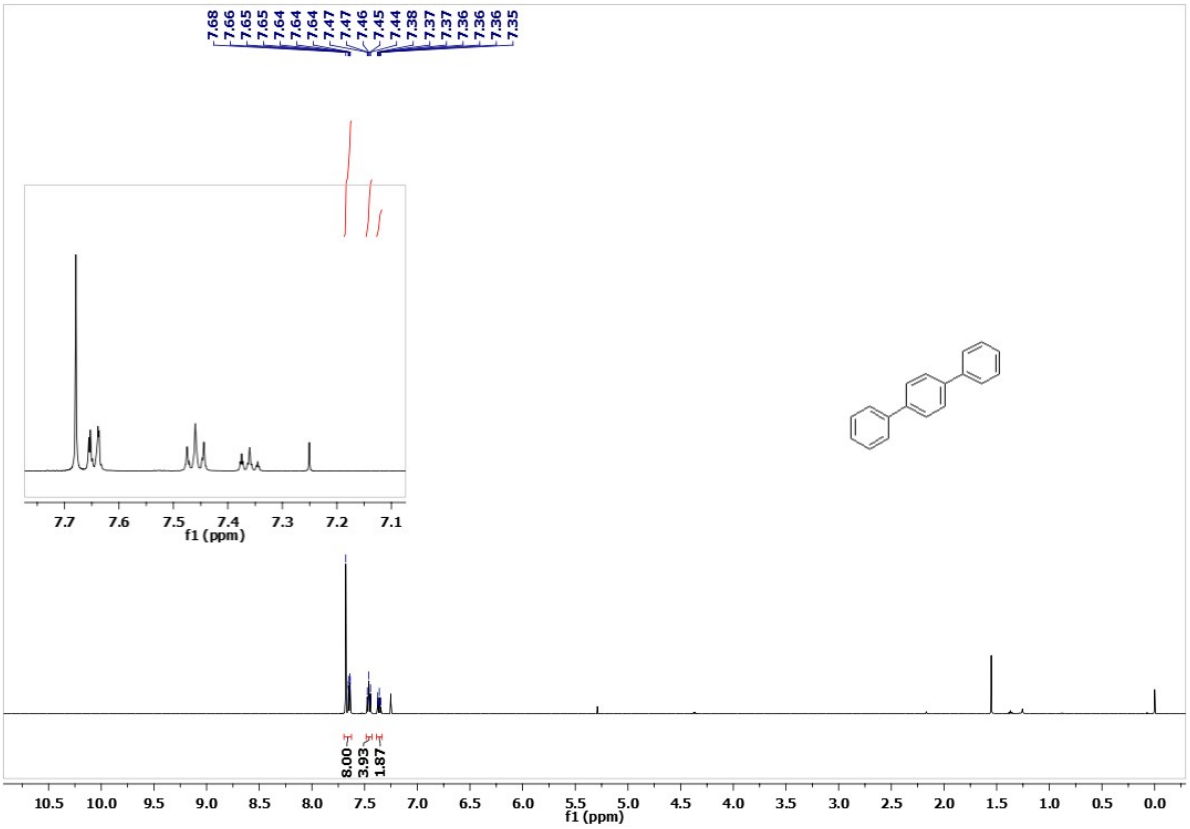
7.31
7.31
7.30
7.28
7.13
7.12
7.12
7.11
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.98
5.00
0.95
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.47
134.44
128.91
128.14
127.48
125.88
124.82
123.10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.96 7.96 7.96 7.94 7.92 7.90 7.89 7.59 7.57 7.57 7.56 7.55 7.55 7.55 7.54 7.53 7.53 7.53 7.52 7.51 7.49 7.49 7.49 7.48 7.48 7.47 7.47 7.47 7.46 7.45 7.45
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
2.98
9.00
11.0 10.5 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)


140.79 140.29 133.82 131.65 130.10 128.28 127.65 127.26 126.95 126.04 125.78 125.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.64
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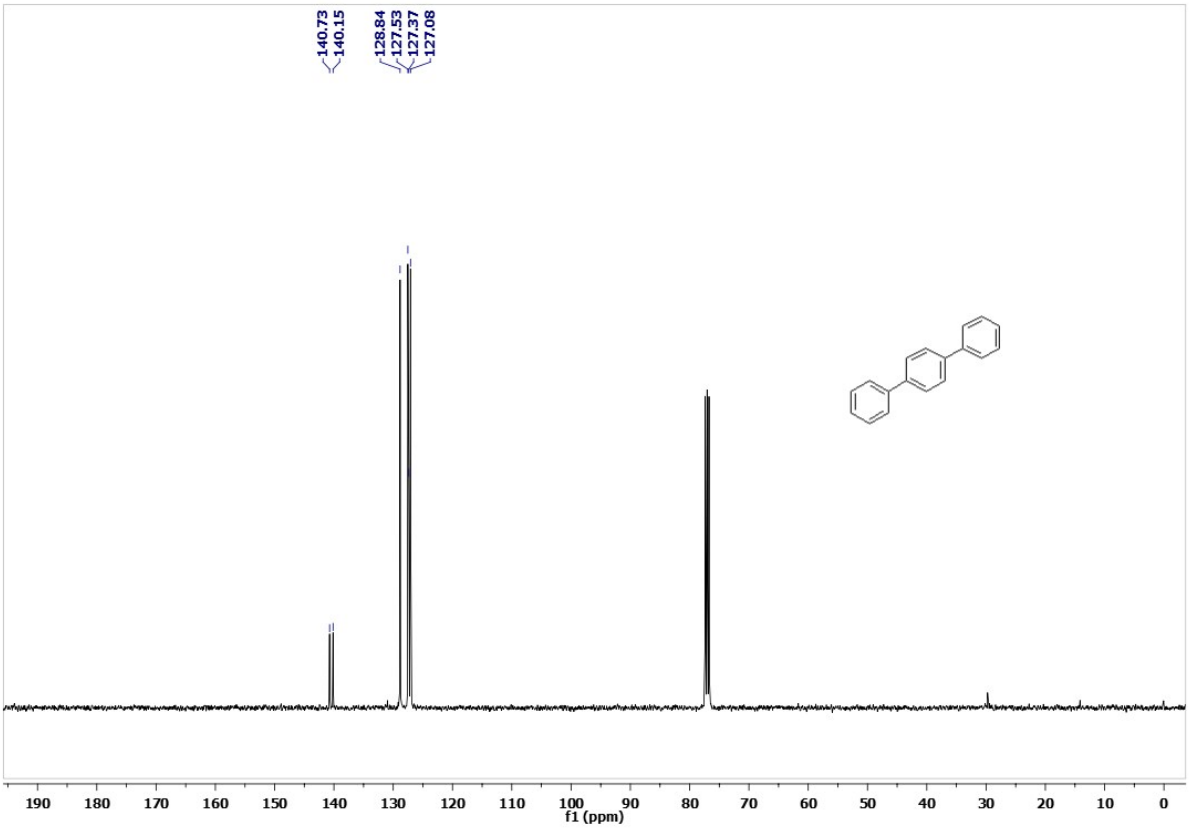
7.46
7.45
7.44
7.38
7.37
7.37
7.36
7.36
7.35
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
8.00
3.93
1.87
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.53
127.37
127.08
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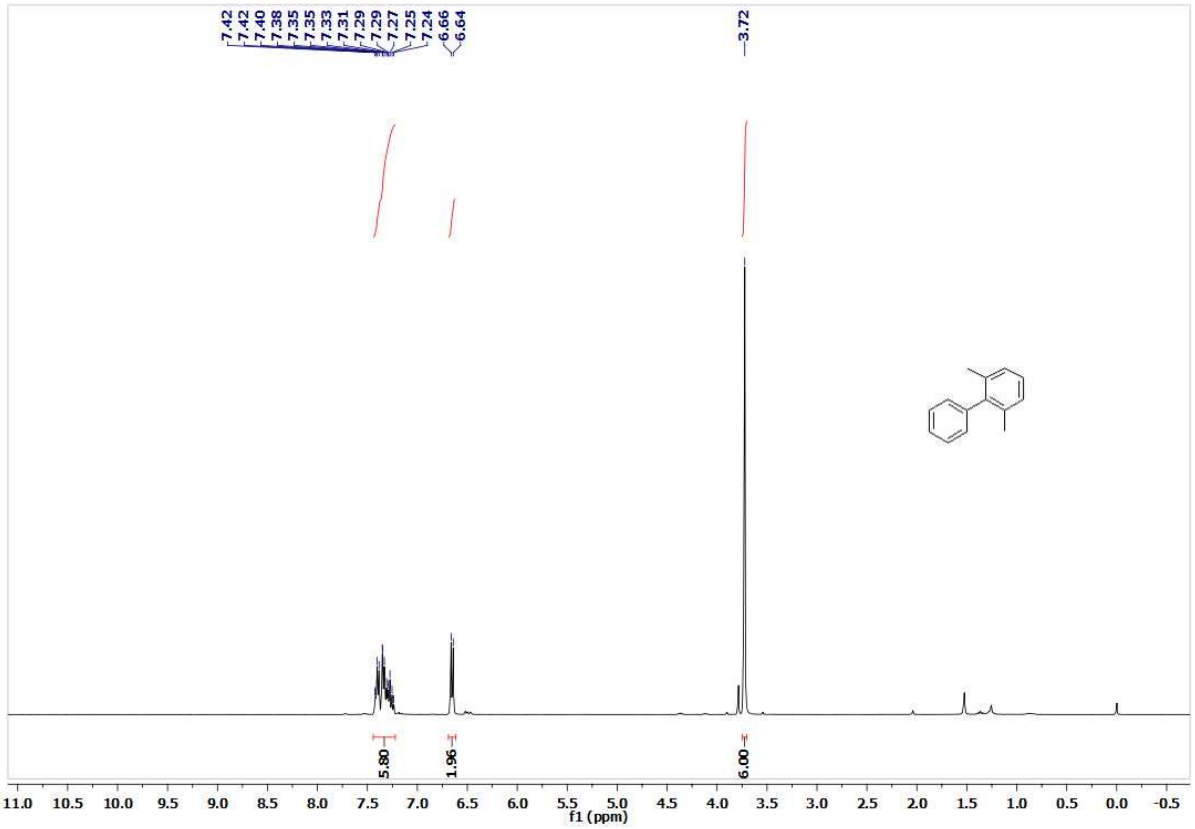
f1 (ppm)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7.31
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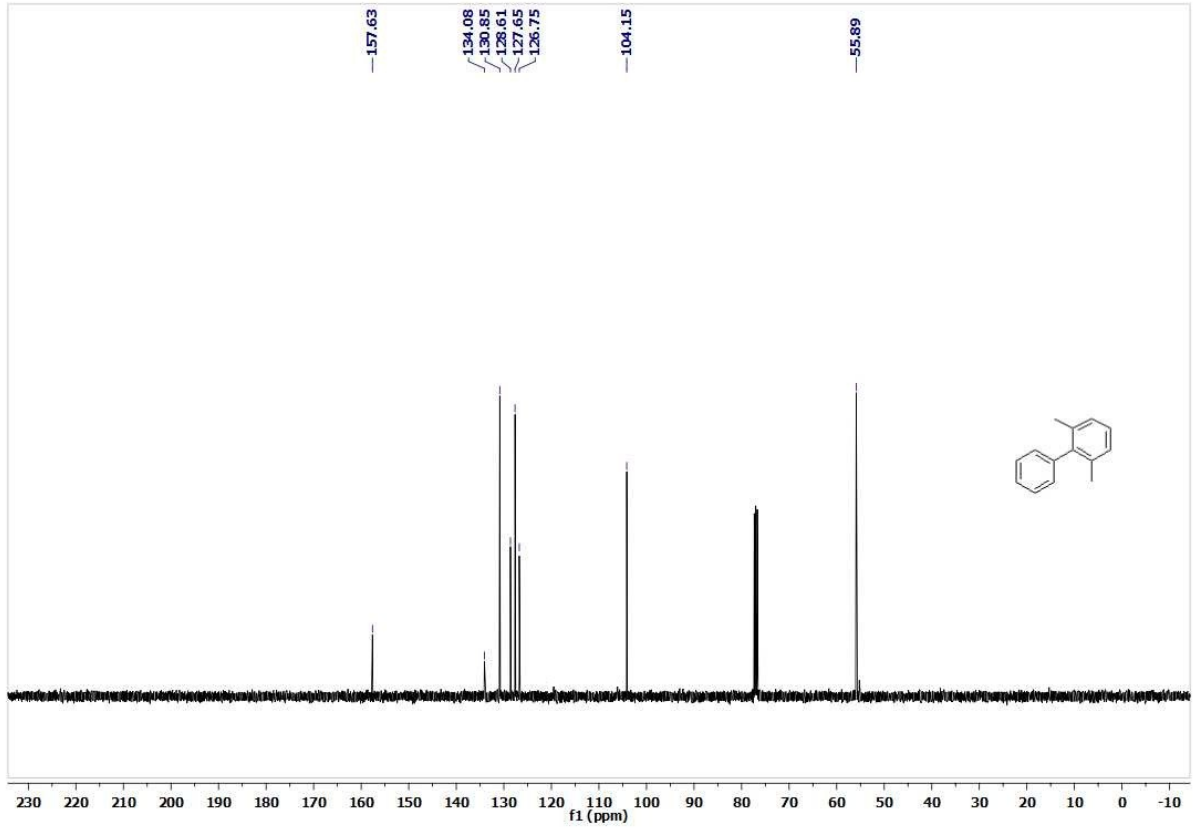
7.25
7.24
6.66
6.64
3.72
5.80
1.96
6.00
f1 (ppm)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126.75
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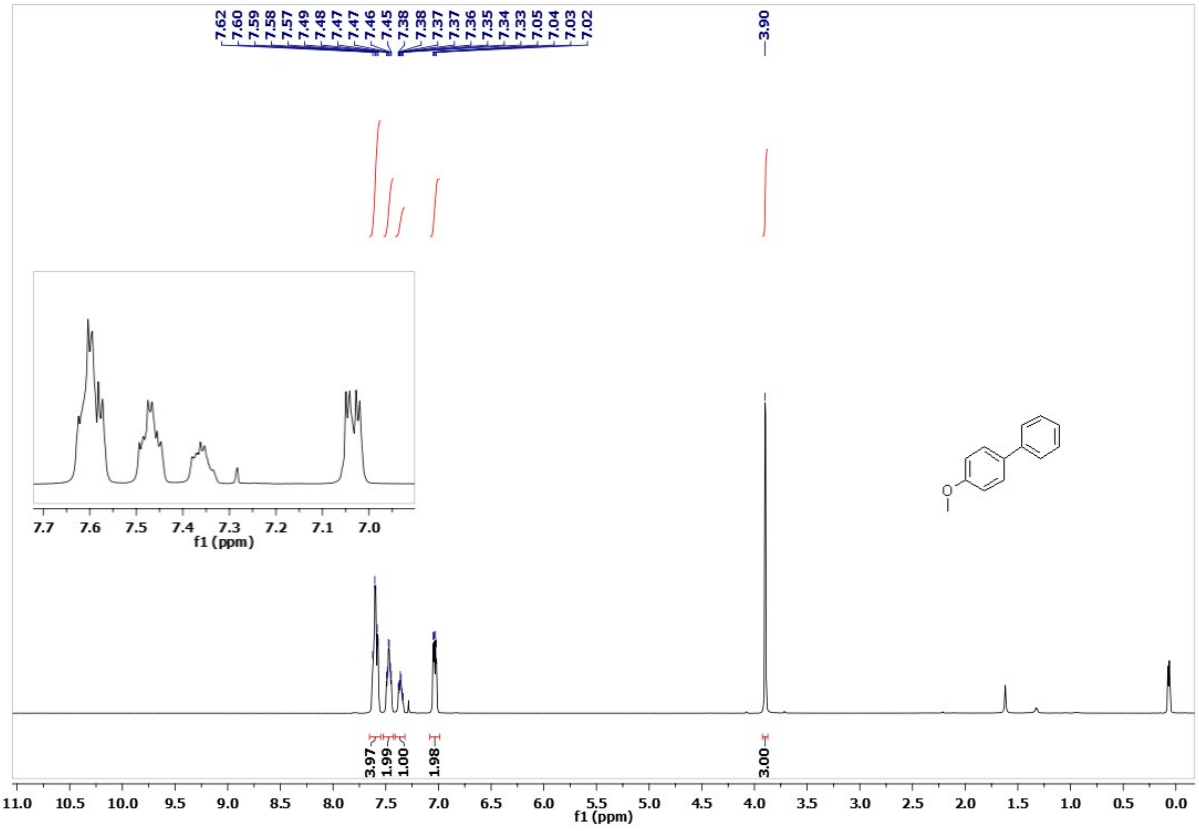
55.89
f1 (ppm)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7.38
7.37
7.37
7.36
7.35
7.34
7.33
7.05
7.04
7.03
7.02
3.90
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
3.97
1.99
1.00
1.98
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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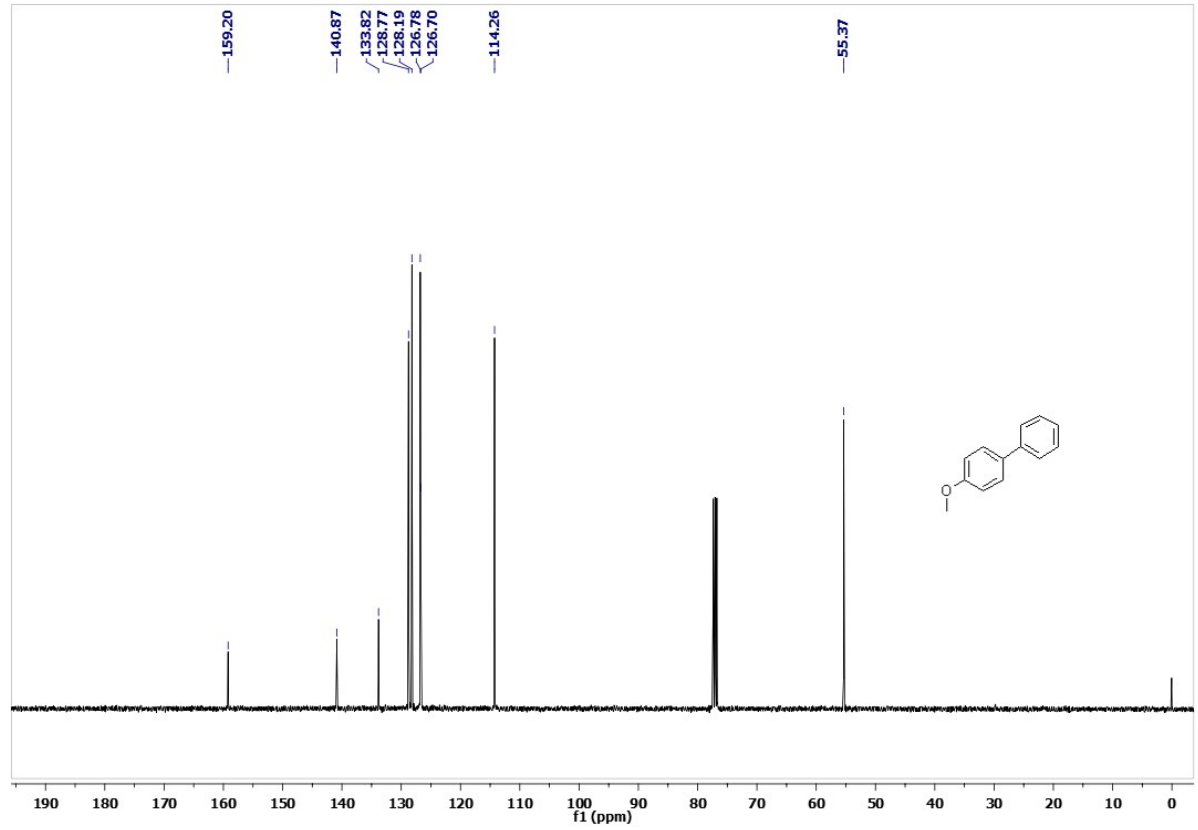
0.0
f1 (ppm)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180
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50
40
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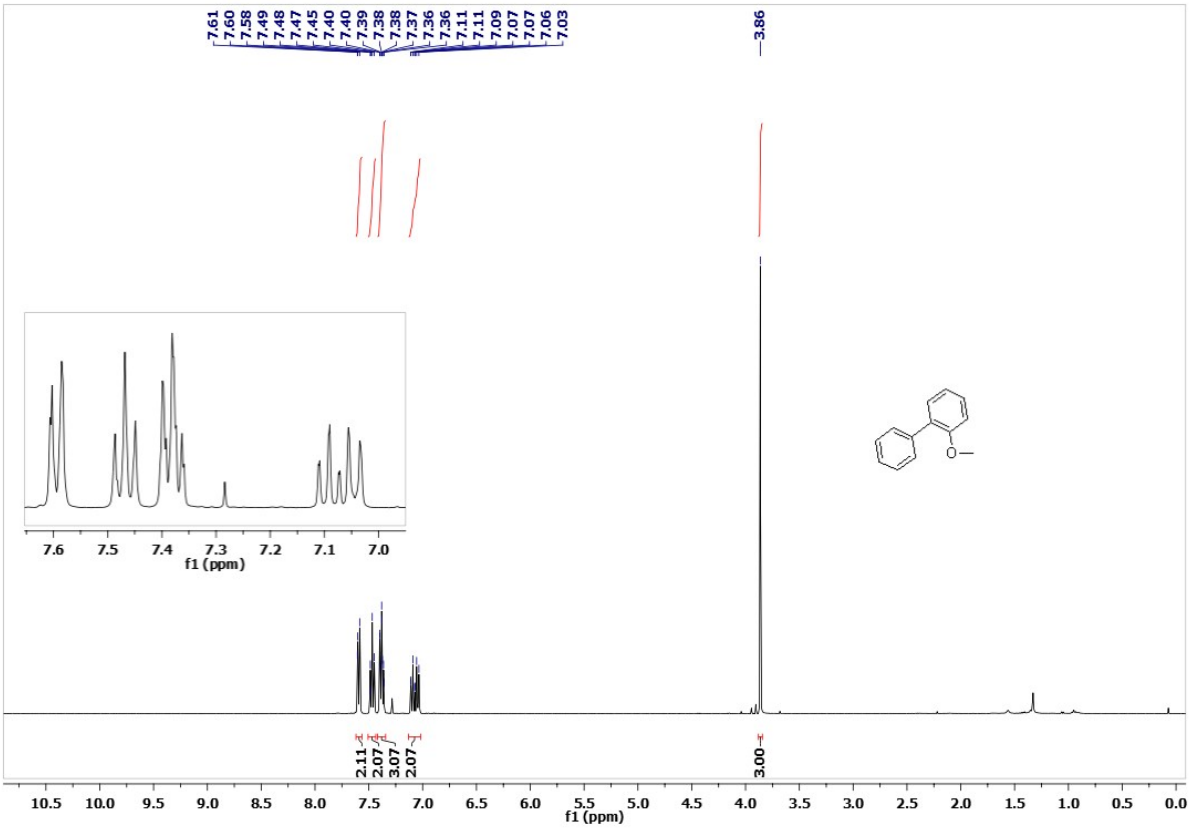
20
10
0
f1 (ppm)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7.37
7.36
7.36
7.11
7.11
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7.07
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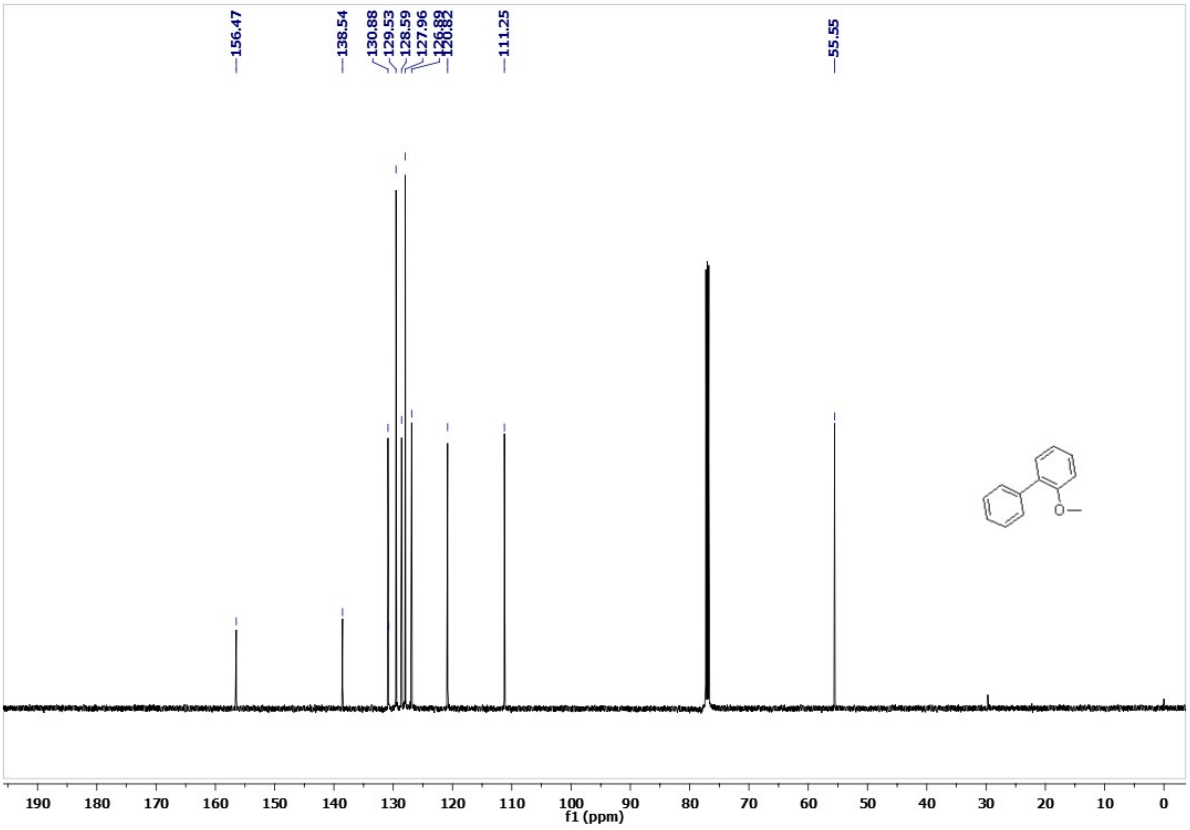
7.06
7.03
3.86
2.11
2.07
3.07
2.07
3.00
f1 (ppm)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138.54
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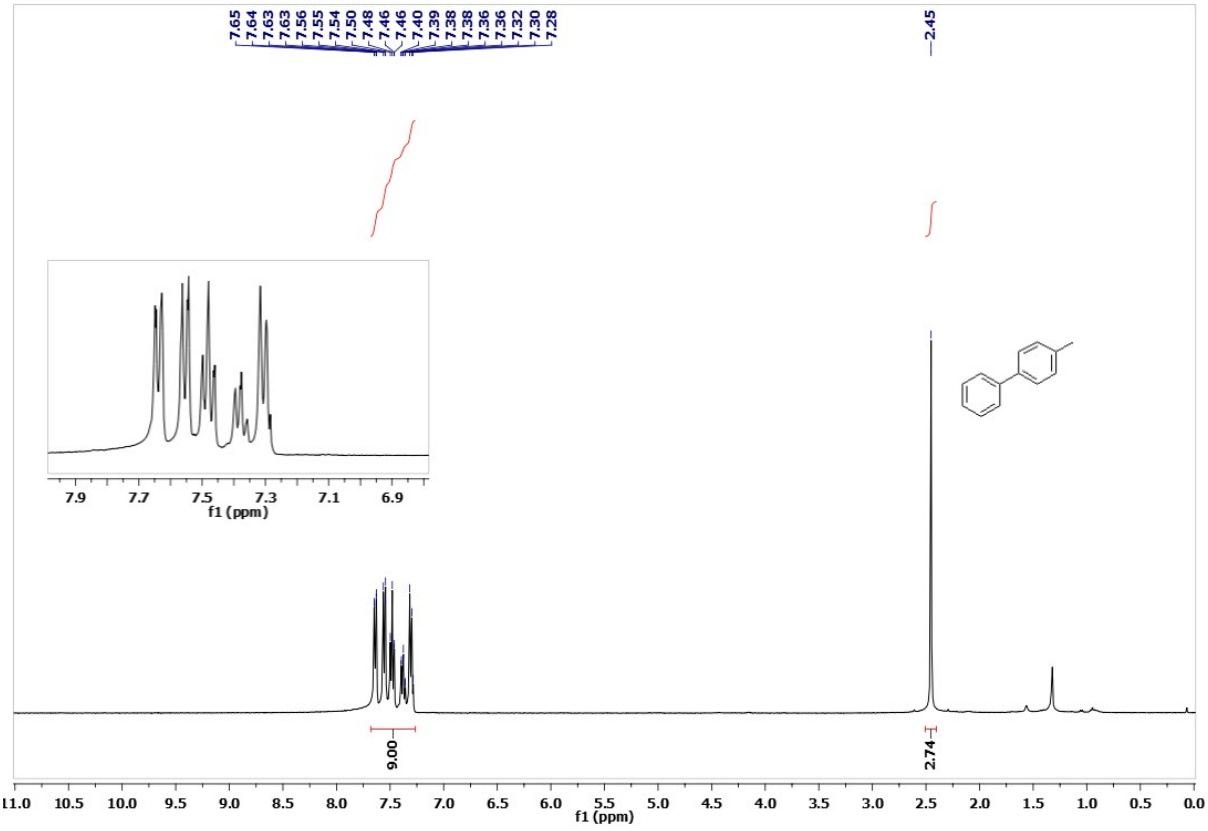
129.53
128.59
127.96
126.89
126.82
111.25
55.55
f1 (ppm)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7.46
7.46
7.40
7.39
7.38
7.38
7.36
7.36
7.32
7.30
7.28
2.45
7.9
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
9.00
2.74
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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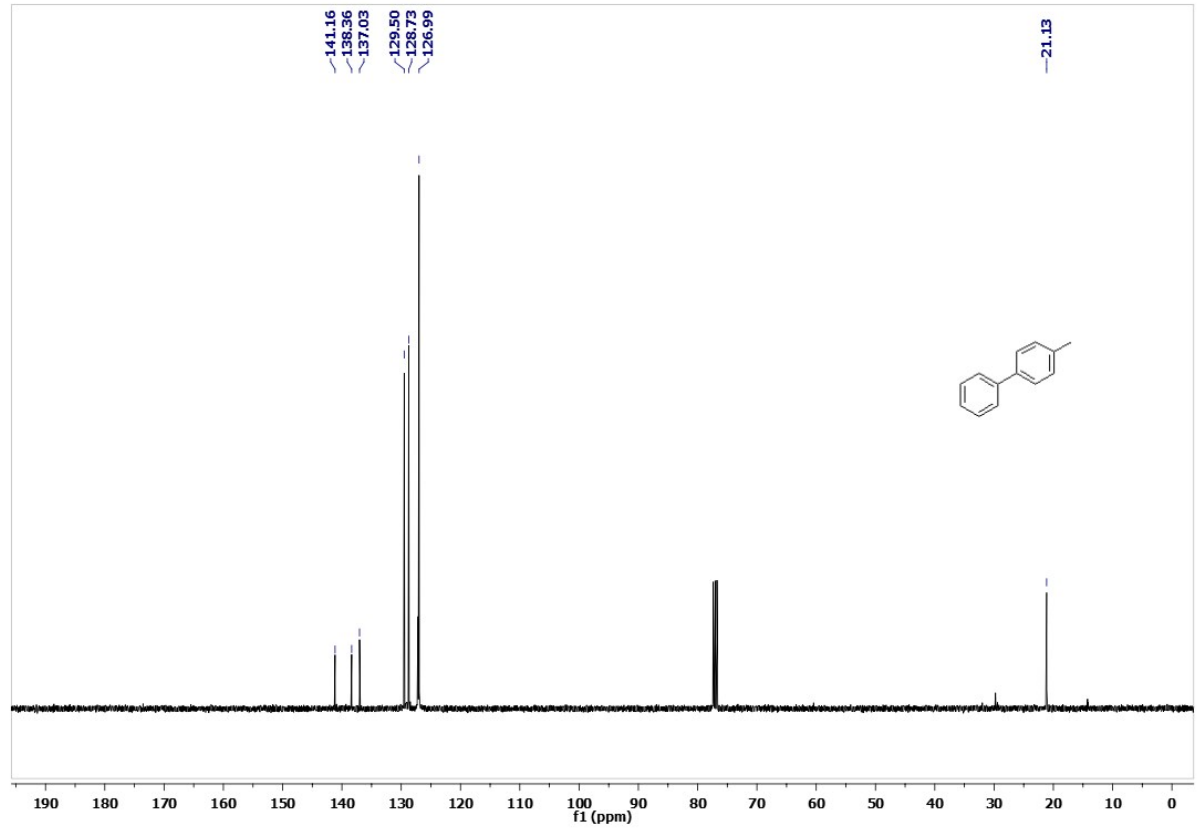
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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180
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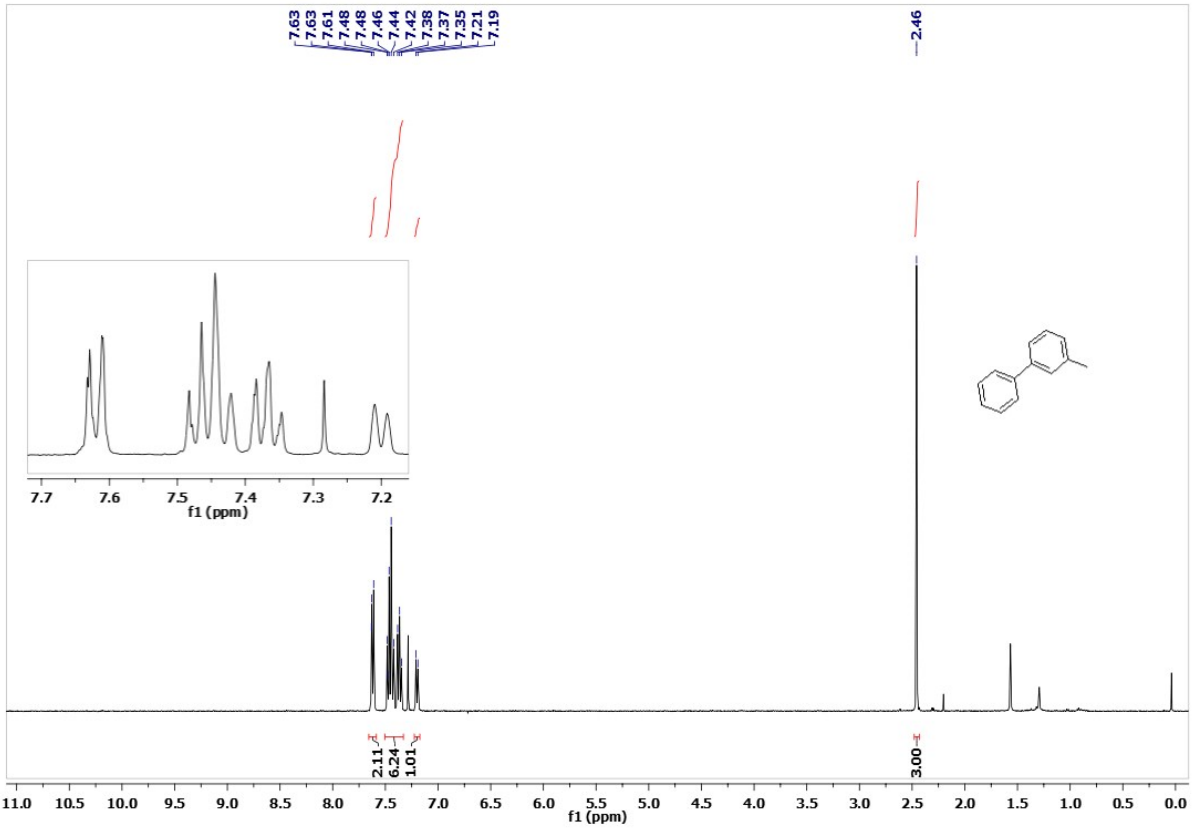
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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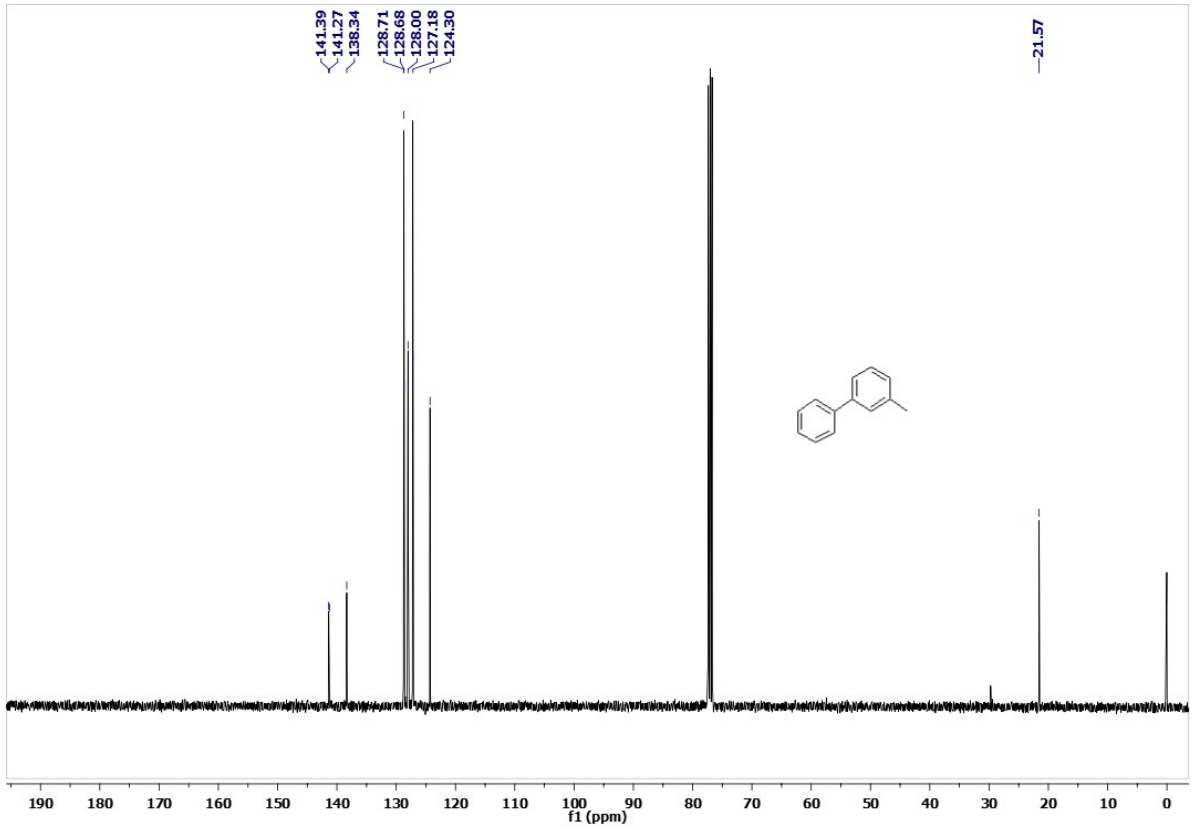
7.63
7.61
7.48
7.48
7.46
7.44
7.42
7.38
7.37
7.35
7.21
7.19
2.46
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
2.11
6.24
1.01
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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138.34
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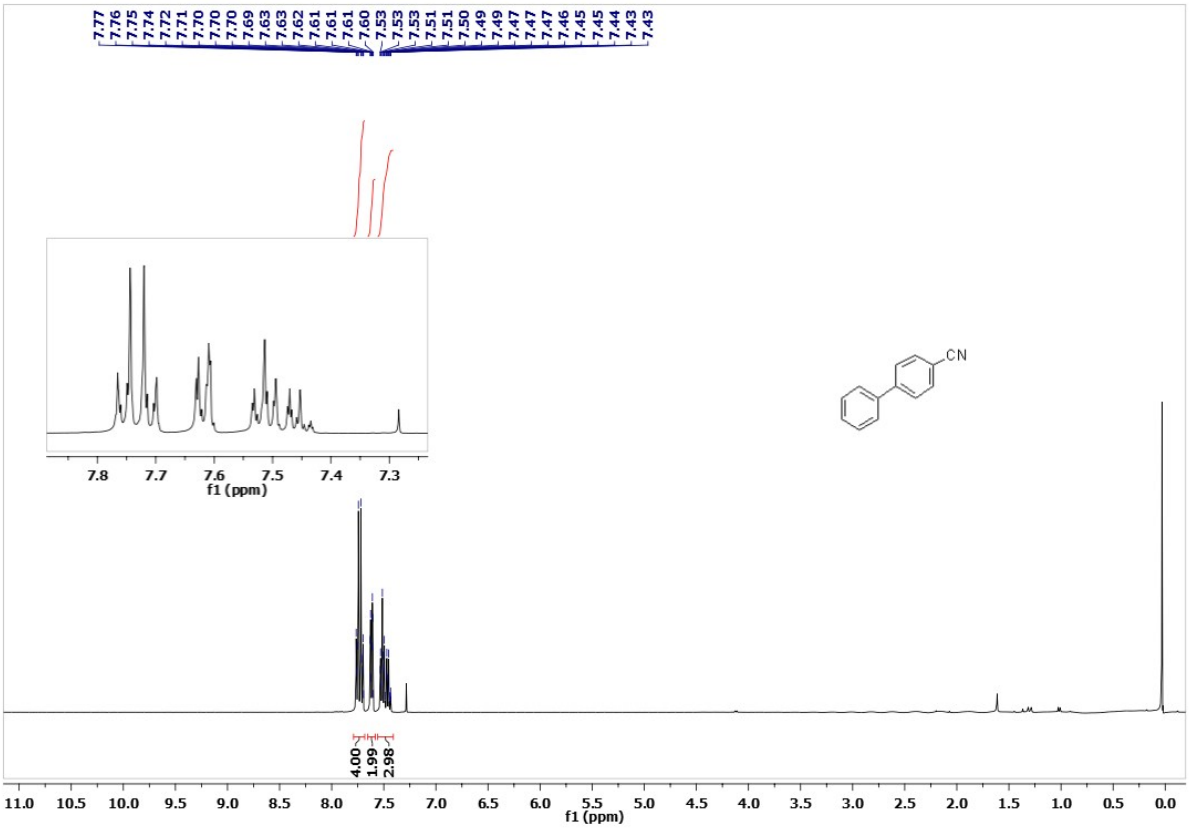
128.68
128.00
127.18
124.30
21.57
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.76
7.75
7.74
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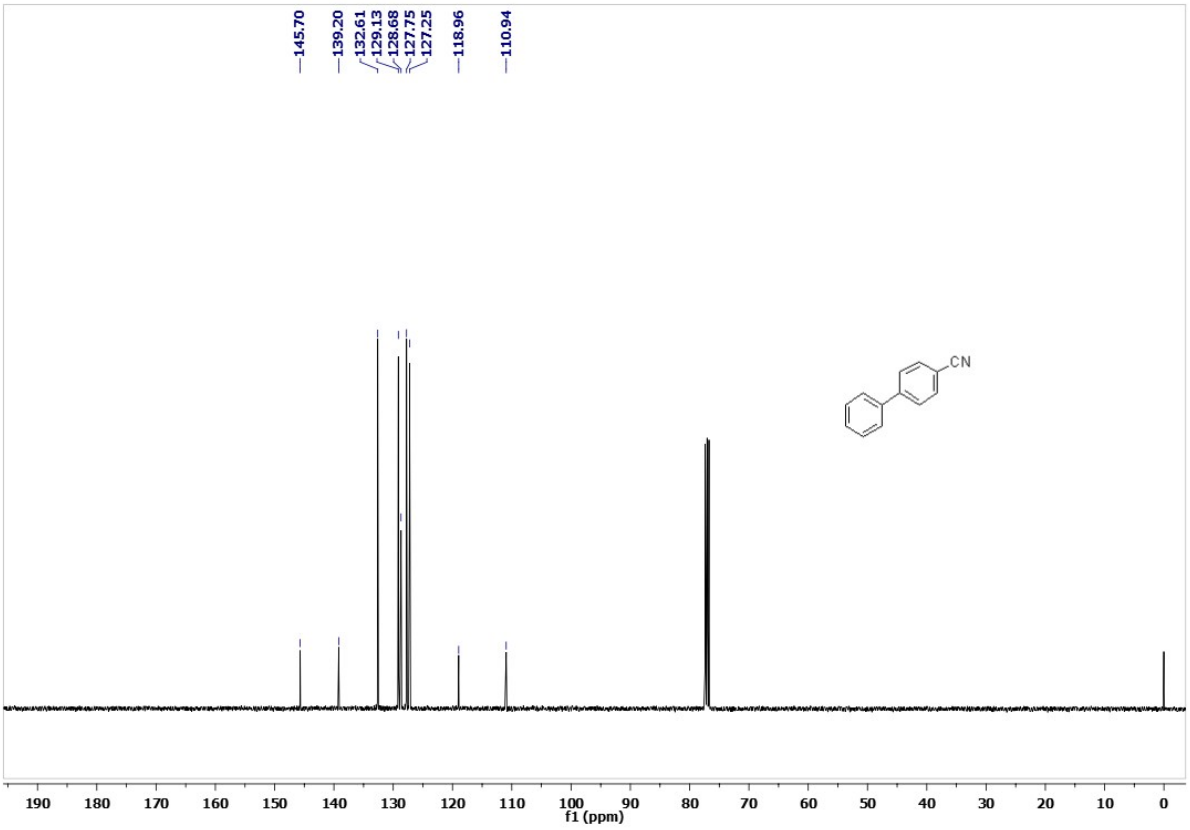
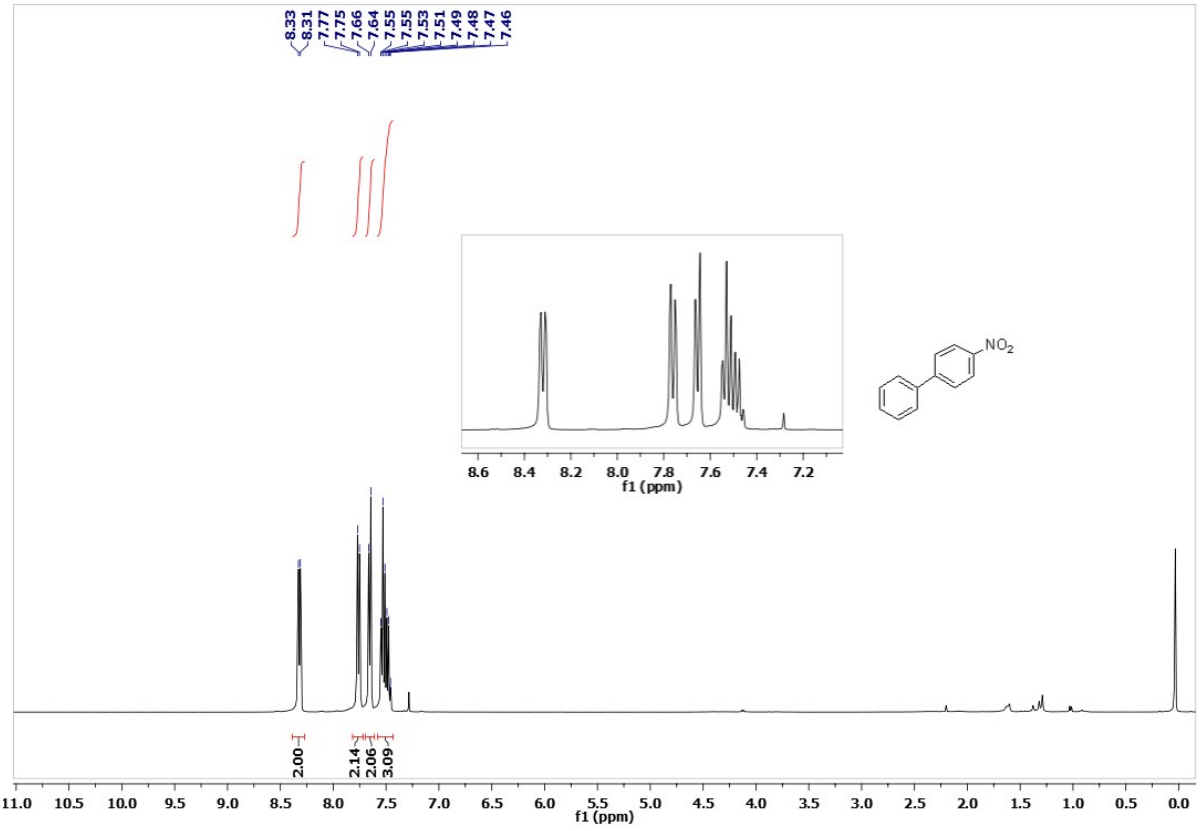
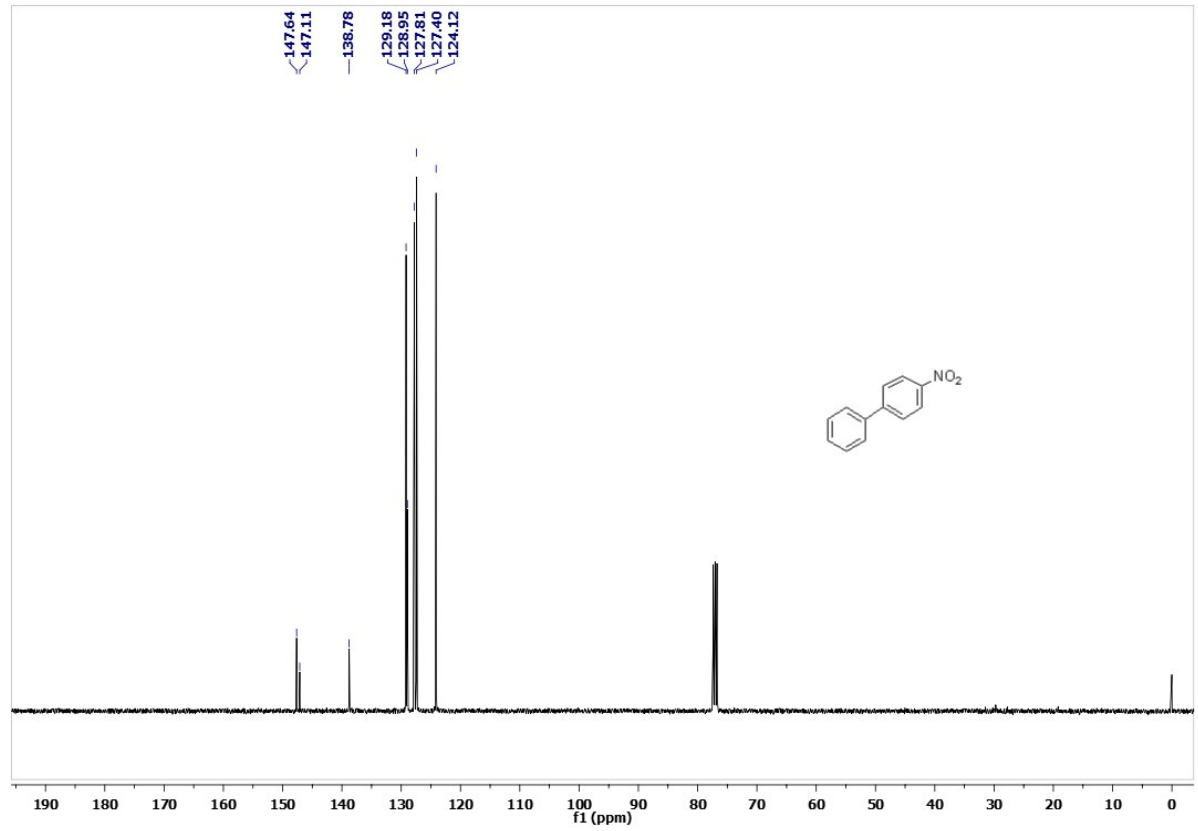
7.70
7.70
7.70
7.69
7.63
7.63
7.62
7.61
7.61
7.61
7.60
7.53
7.53
7.51
7.51
7.50
7.49
7.49
7.47
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.43
CN
4.00
1.99
2.98
f1 (ppm)


145.70
139.20
132.61
129.13
128.68
127.75
127.25
118.96
110.94
CN
f1 (ppm)


8.33
8.31
7.77
7.75
7.66
7.64
7.55
7.55
7.53
7.51
7.49
7.48
7.47
7.46
NO2
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2
f1 (ppm)
2.00
2.14
2.06
3.09
11.0 10.5 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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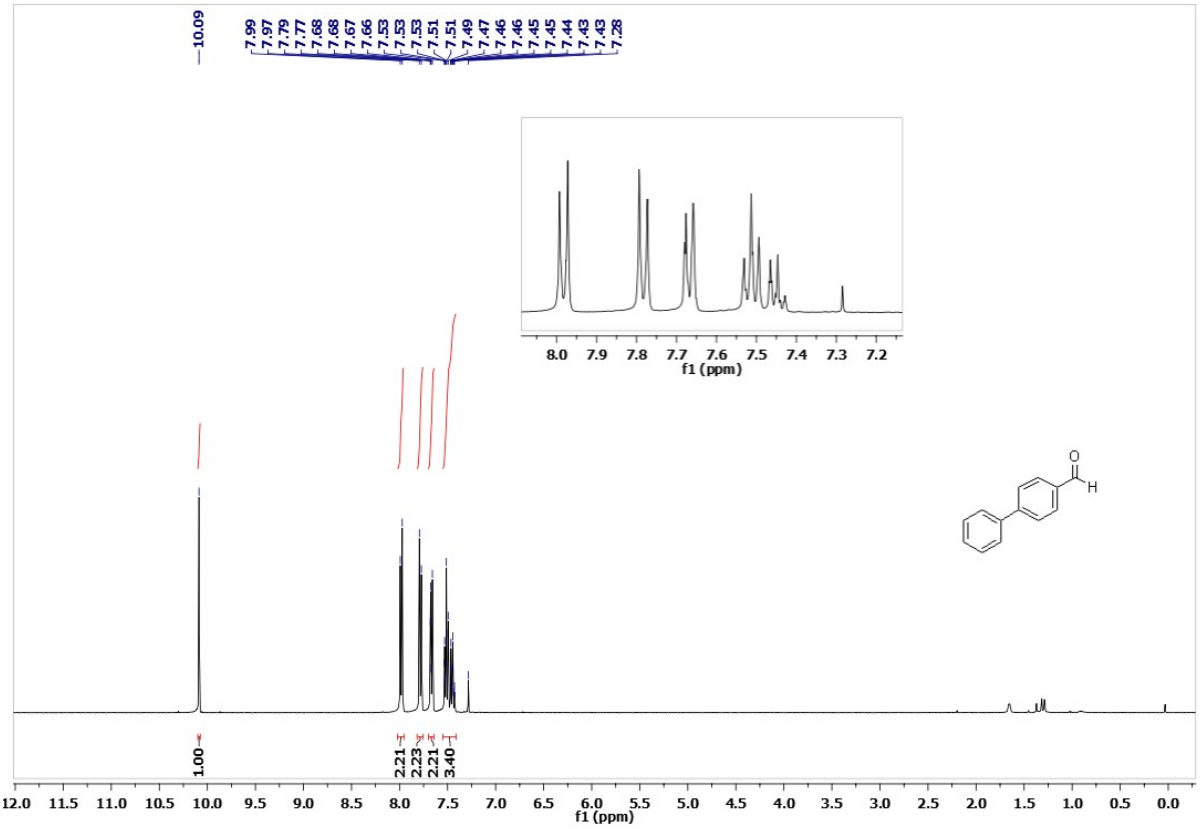
147.11
138.78
129.18
128.95
127.81
127.40
124.12
NO2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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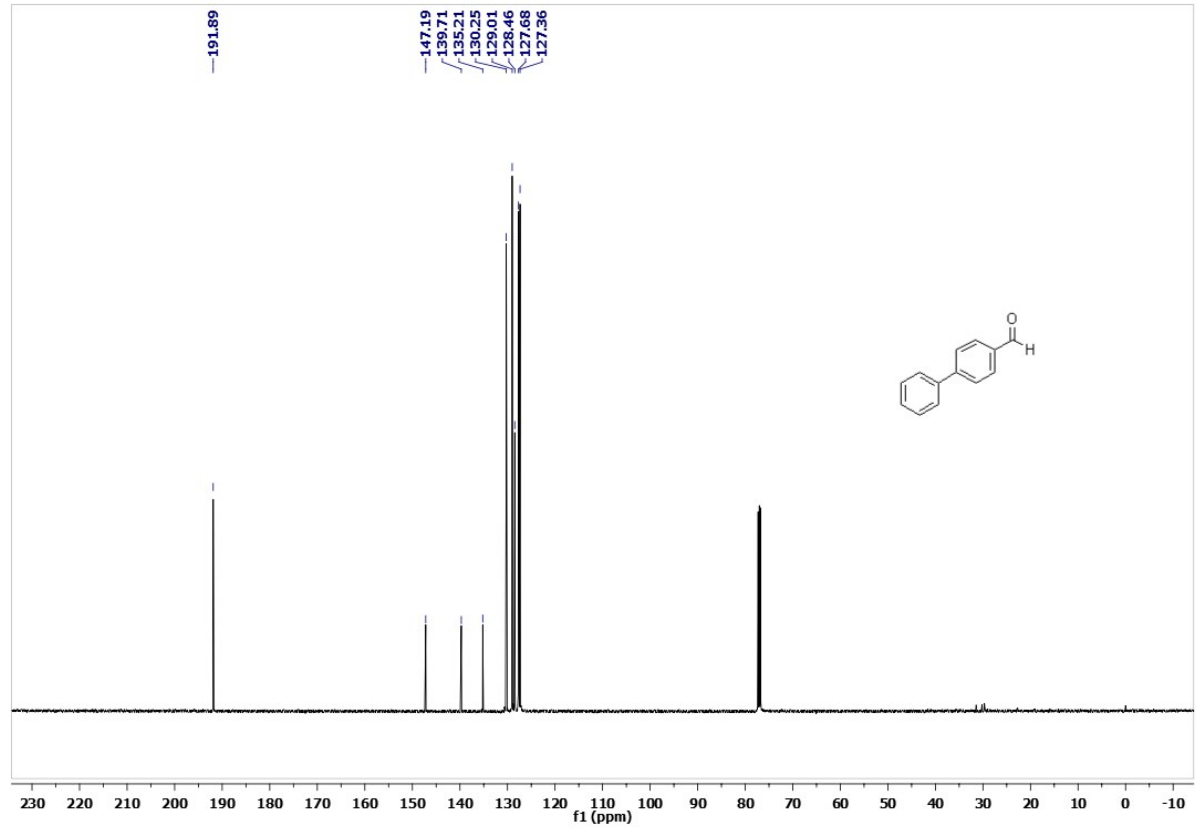
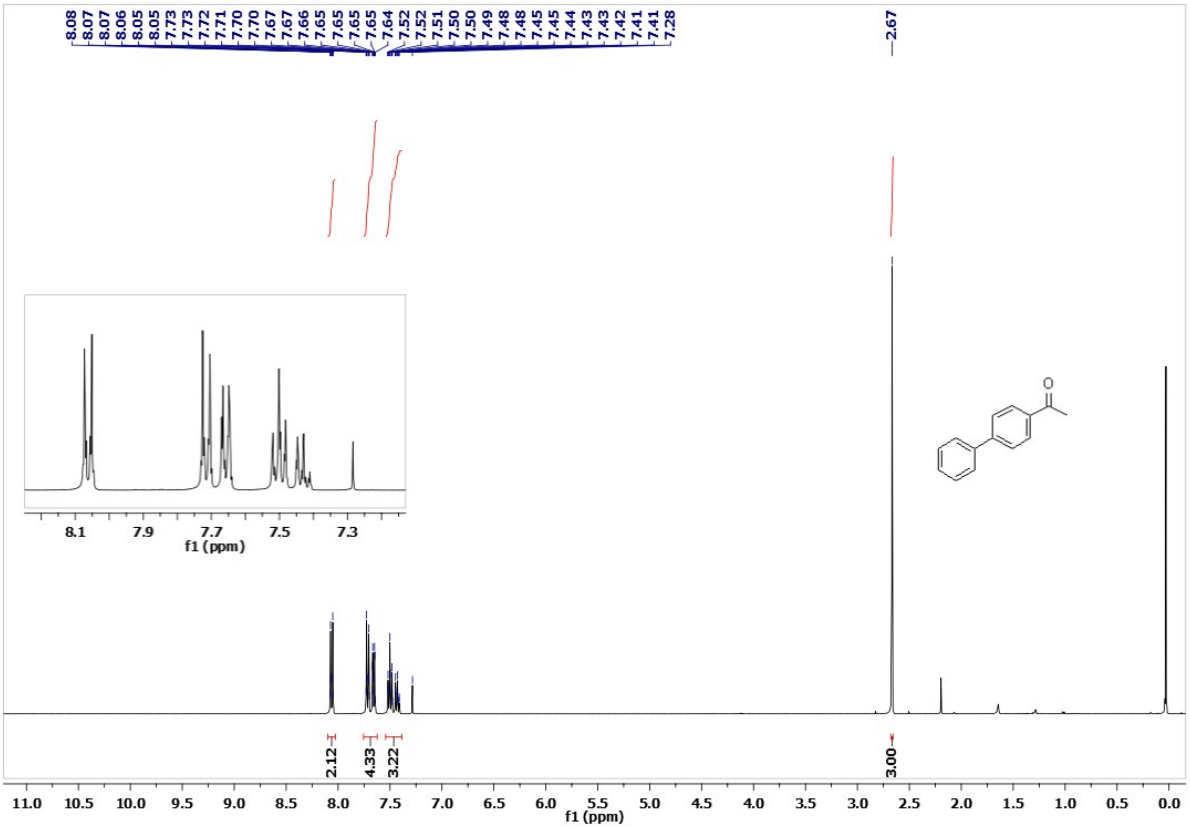
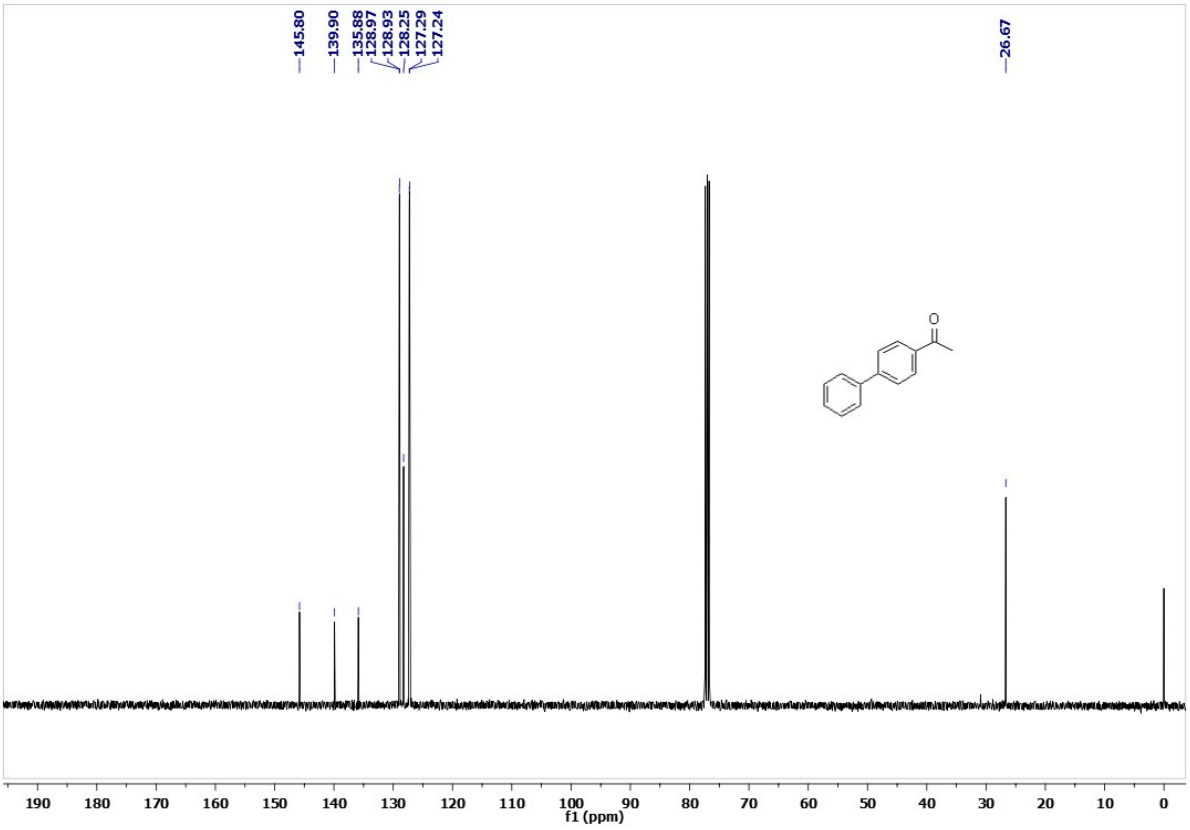
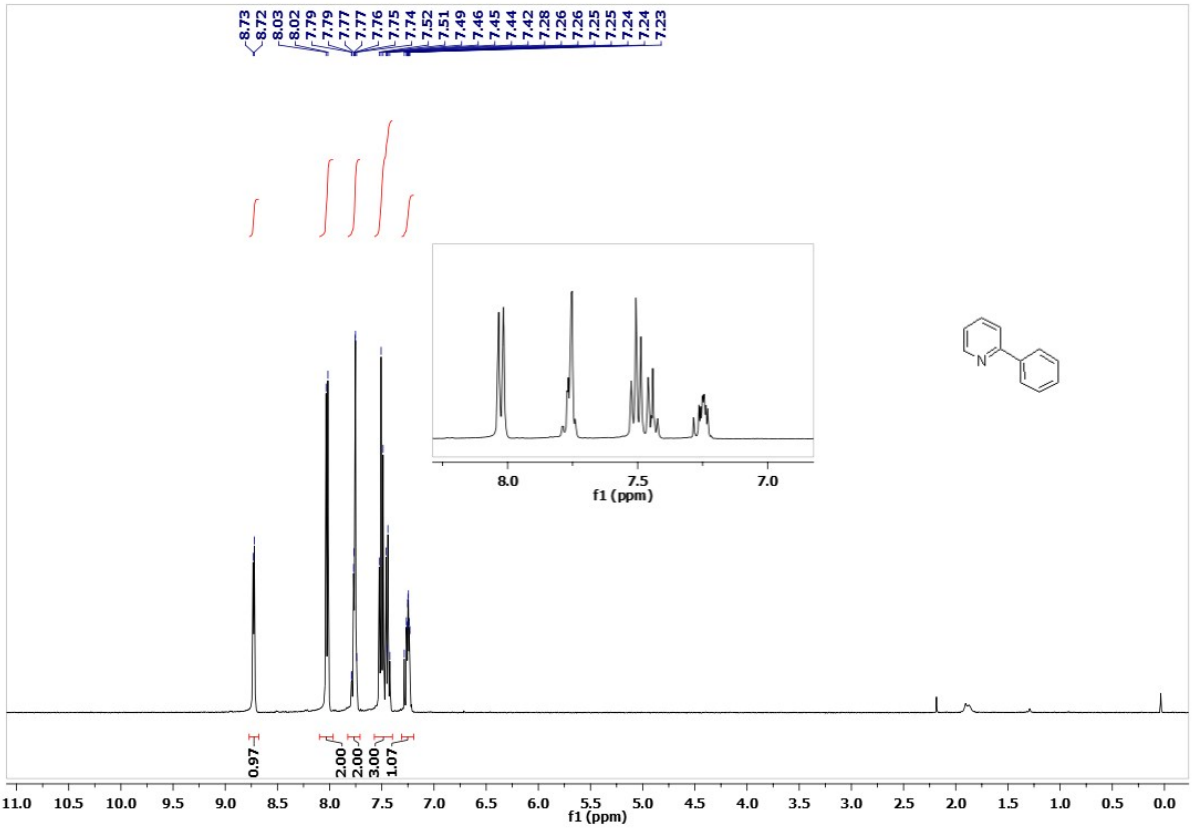
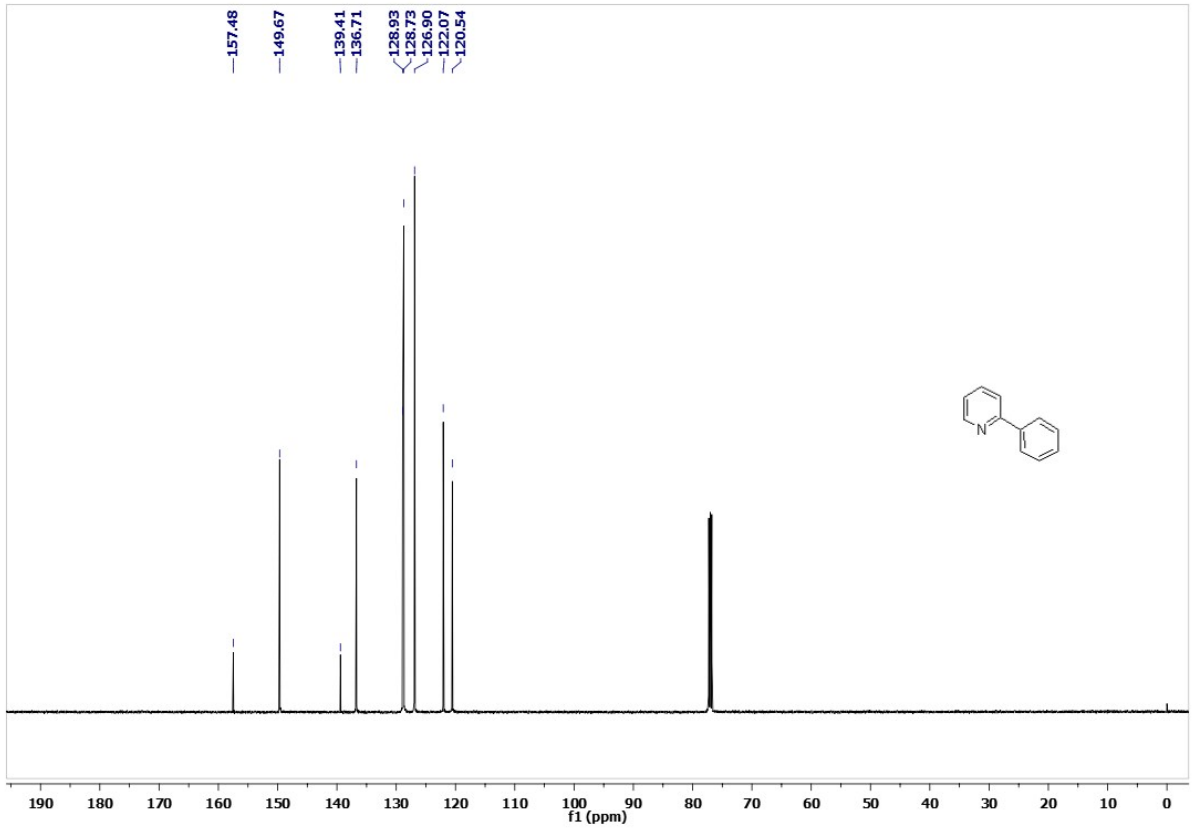
7.99
7.97
7.79
7.77
7.68
7.68
7.67
7.66
7.53
7.53
7.53
7.51
7.51
7.49
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.28
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
O
H
1.00
2.21
2.23
2.21
3.40
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

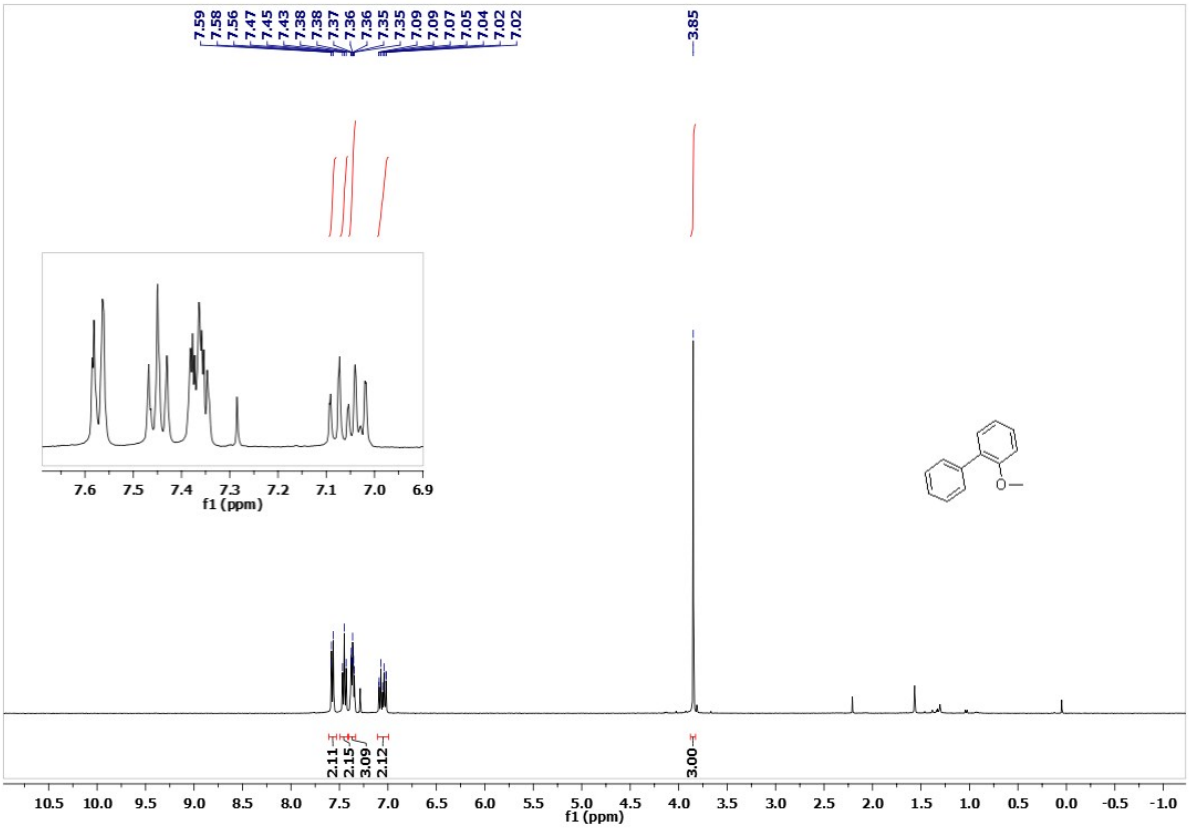

191.89
147.19
139.71
135.21
130.25
129.01
128.46
127.68
127.36
O
H
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

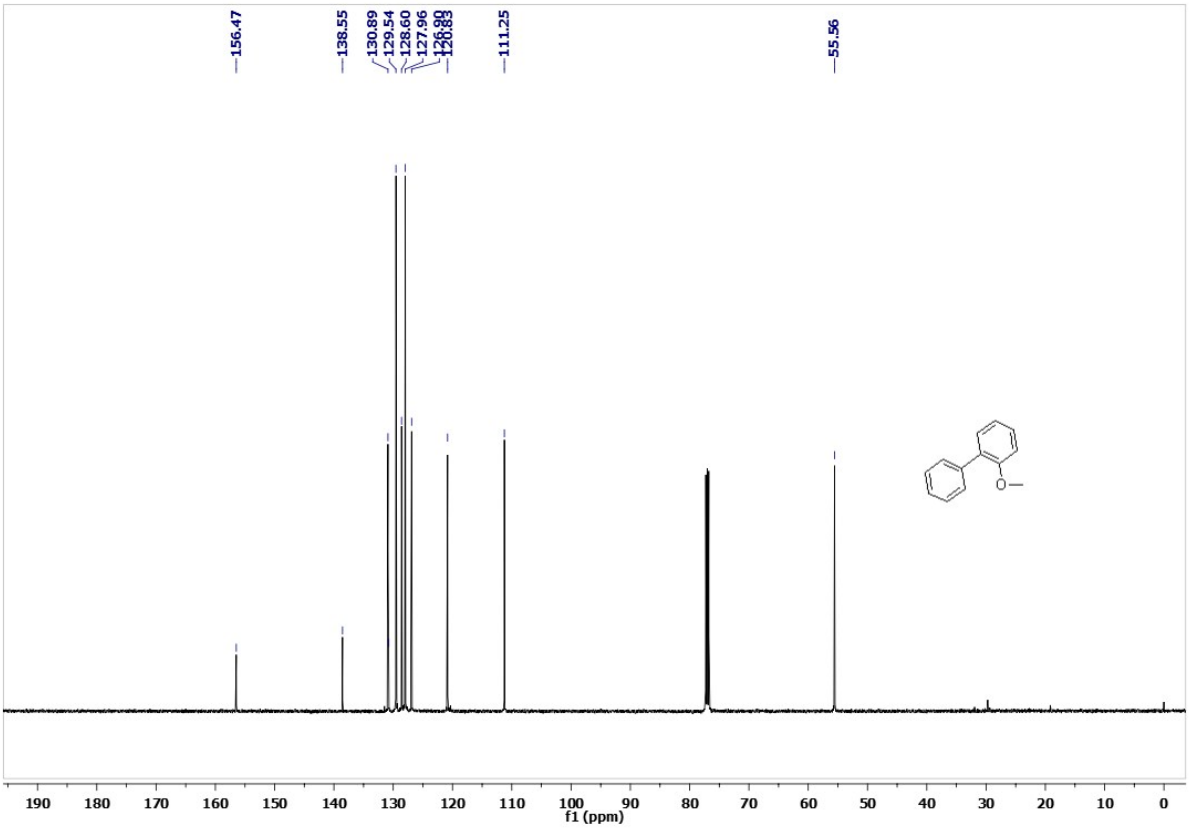

8.08
8.07
8.07
8.06
8.05
8.05
7.73
7.73
7.72
7.71
7.70
7.70
7.67
7.67
7.66
7.65
7.65
7.65
7.64
7.52
7.51
7.50
7.49
7.48
7.48
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.28
2.67
8.1
7.9
7.7
7.5
7.3
f1 (ppm)
2.12
4.33
3.22
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O

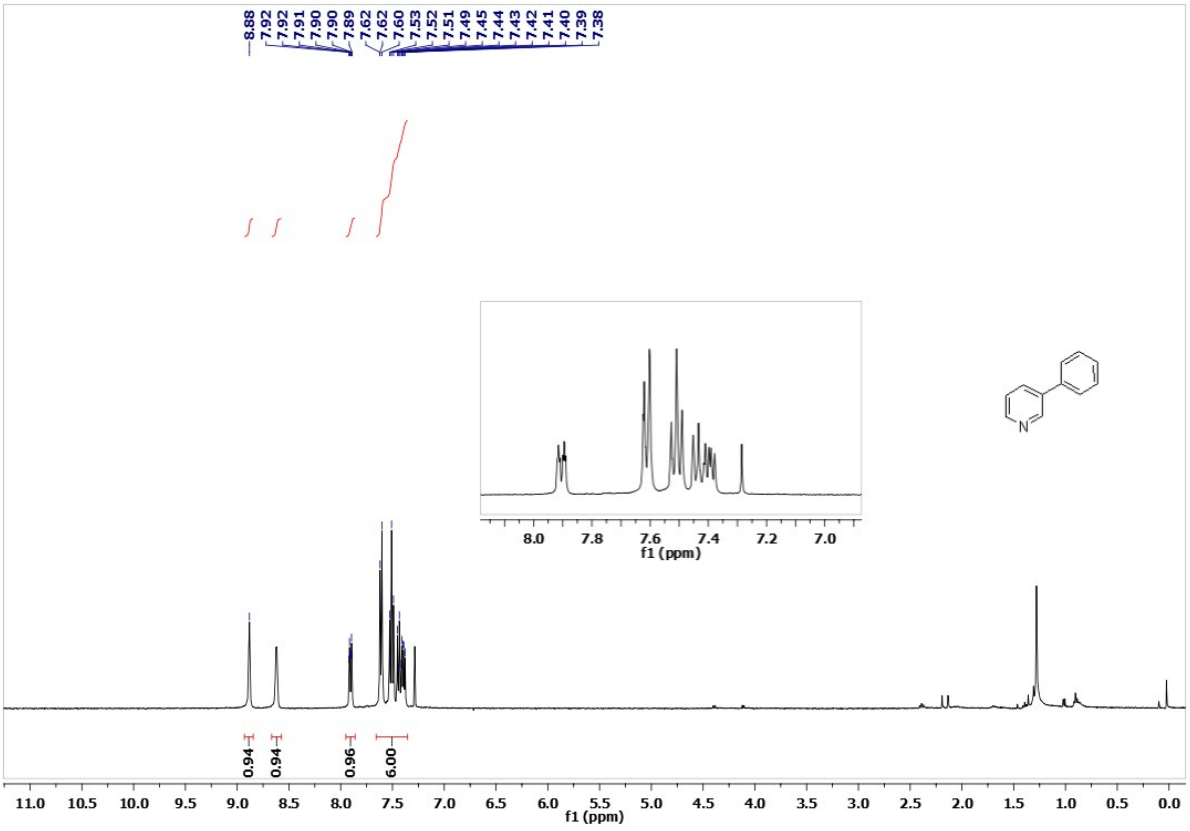

145.80
139.90
135.88
128.97
128.93
128.25
127.29
127.24
26.67
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O


8.73
8.72
8.03
8.02
7.79
7.79
7.77
7.77
7.77
7.76
7.75
7.74
7.52
7.51
7.49
7.46
7.45
7.44
7.42
7.28
7.26
7.26
7.25
7.25
7.24
7.24
7.23
8.0
7.5
7.0
f1 (ppm)
0.97
2.00
2.00
3.00
1.07
11.0 10.5 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)


157.48
149.67
139.41
136.71
128.93
128.73
126.90
122.07
120.54
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.59
7.58
7.56
7.47
7.45
7.43
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.09
7.09
7.07
7.05
7.04
7.02
7.02
3.85
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
2.11
2.15
3.09
2.12
3.00
10.5 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 -0.5 -1.0
f1 (ppm)


156.47
138.55
130.89
129.54
128.60
127.96
126.90
126.83
111.25
55.56
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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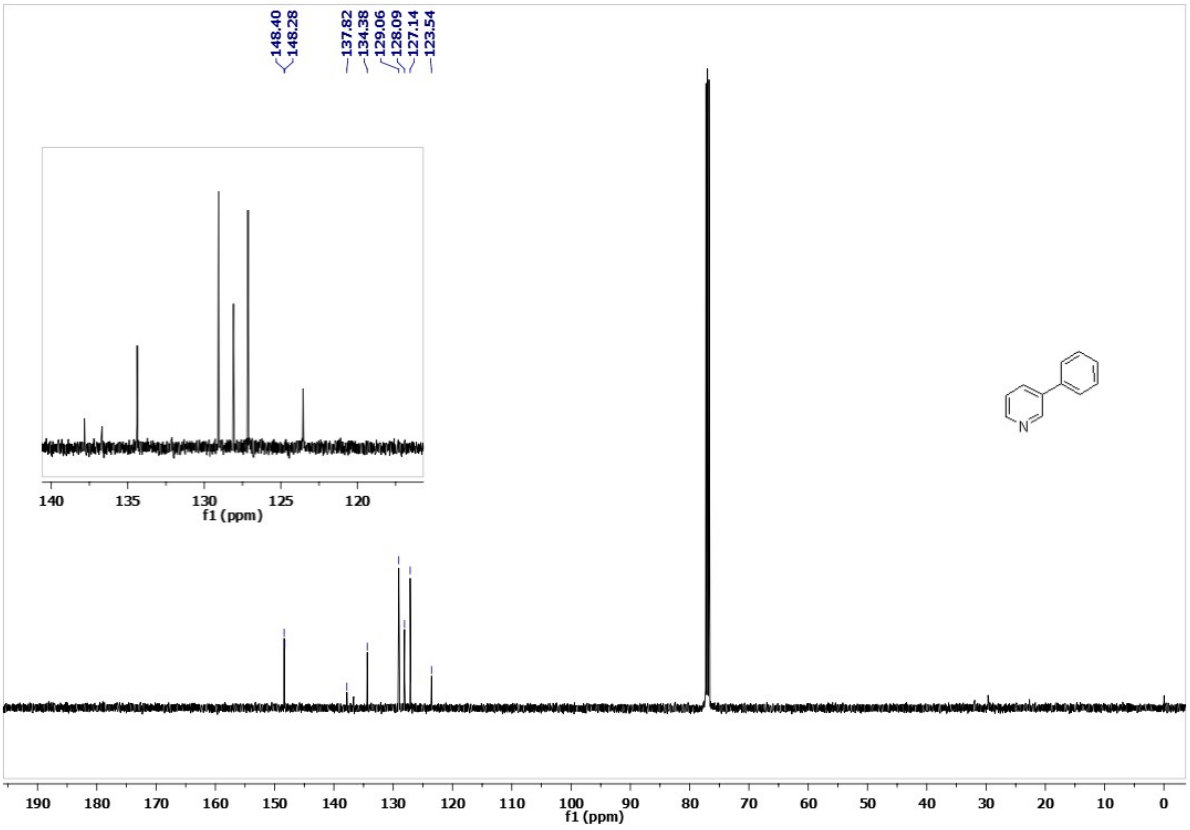
7.92
7.92
7.91
7.90
7.90
7.89
7.62
7.62
7.60
7.53
7.52
7.51
7.49
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.38
0.94
0.94
0.96
6.00
f1 (ppm)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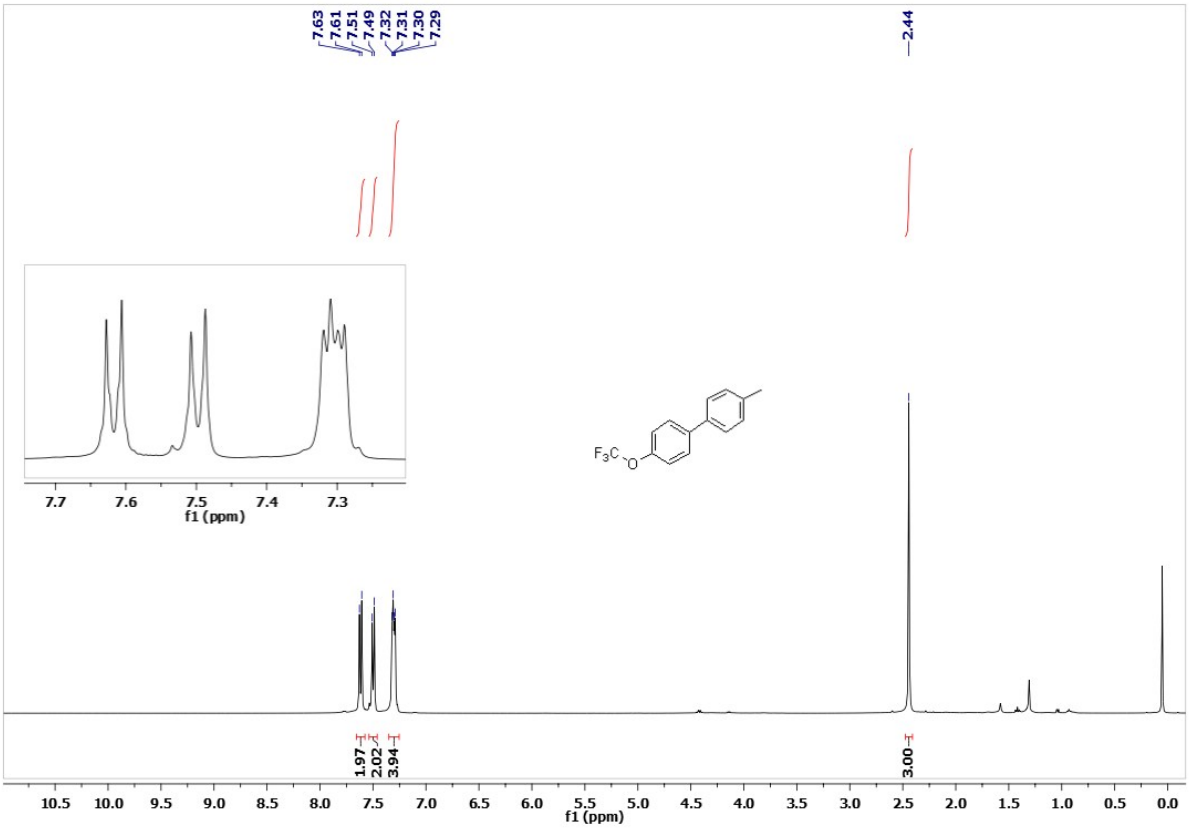
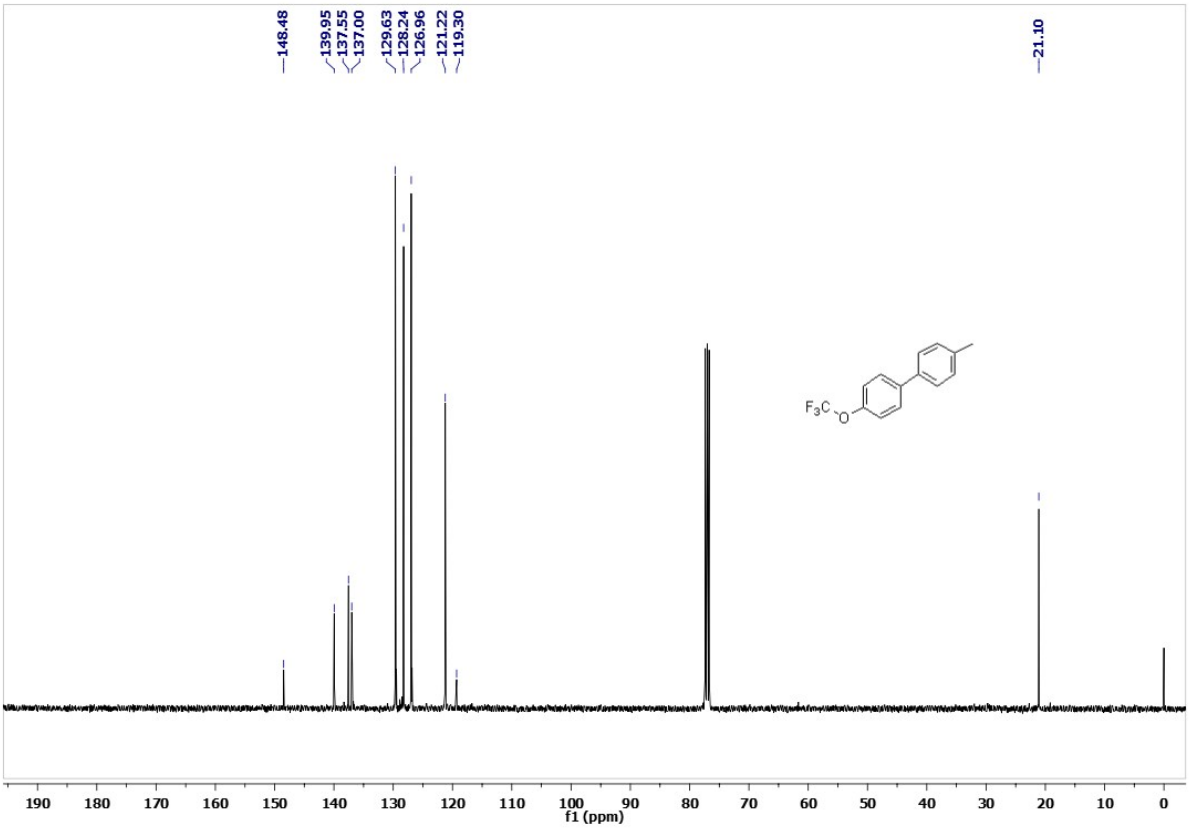
148.28
137.82
134.38
129.06
128.09
127.14
123.54
f1 (ppm)


7.63
7.61
7.51
7.49
7.32
7.31
7.30
7.29
2.44
F3C
O
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
1.97
2.02
3.94
3.00
10.5 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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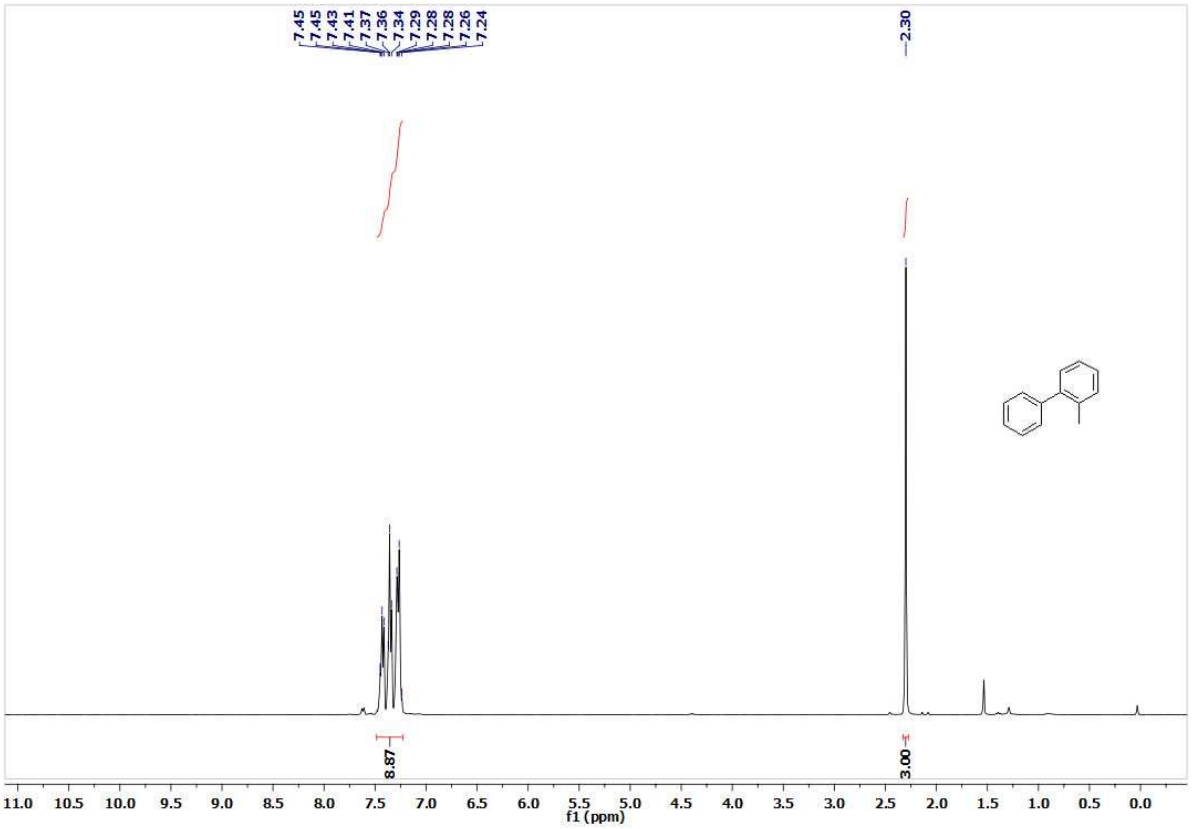
137.55
137.00
129.63
128.24
126.96
121.22
119.30
21.10
F3C
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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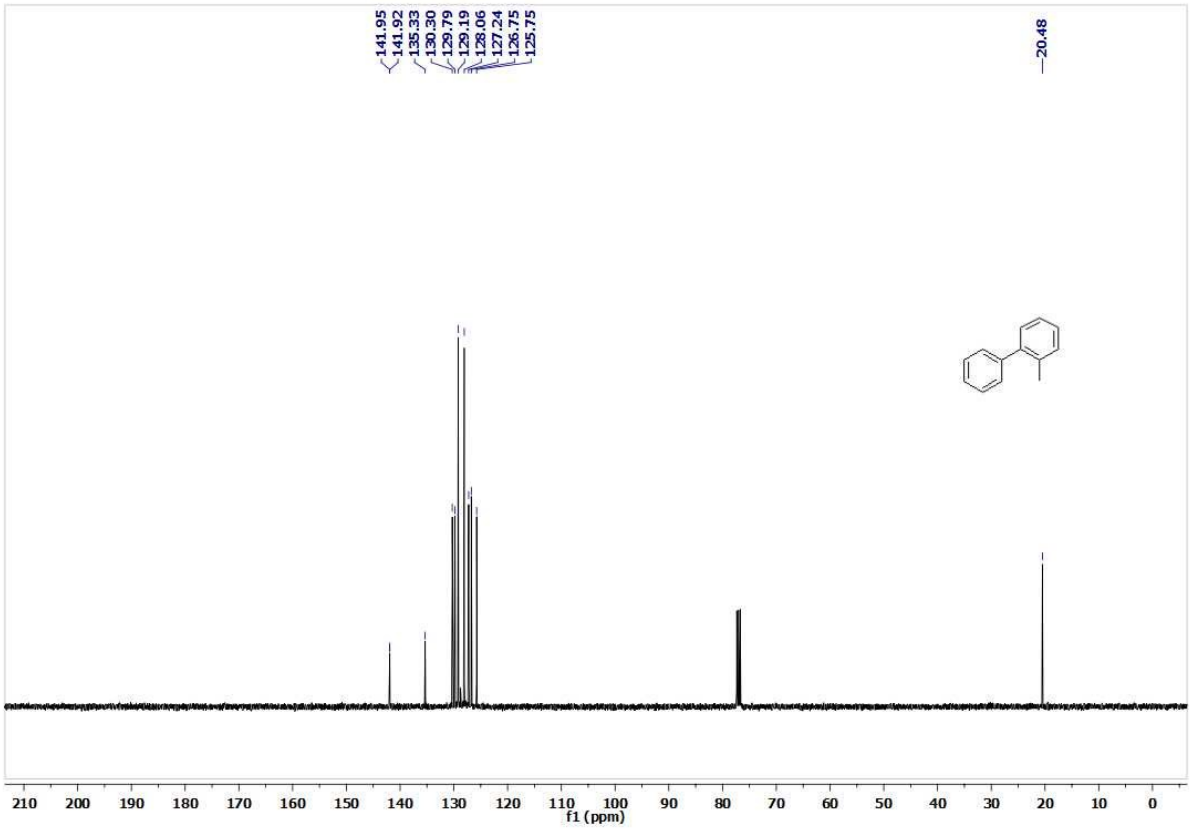
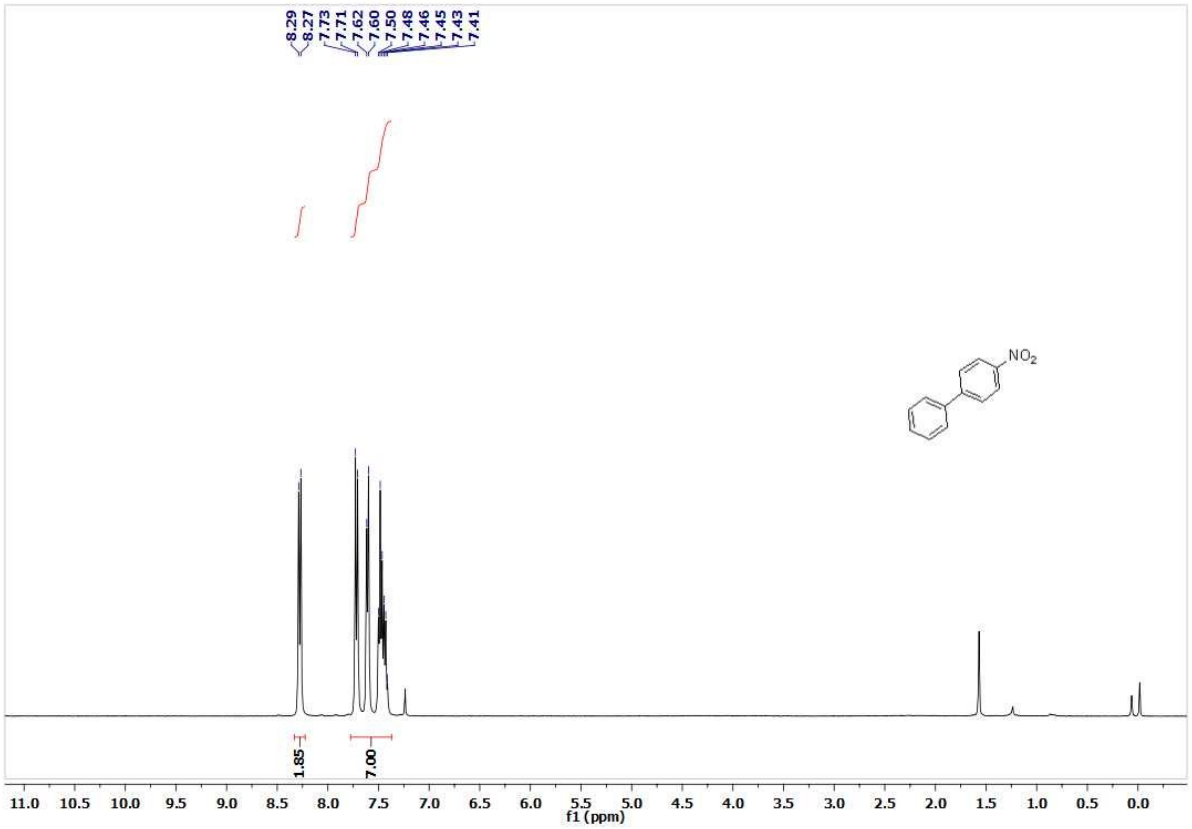
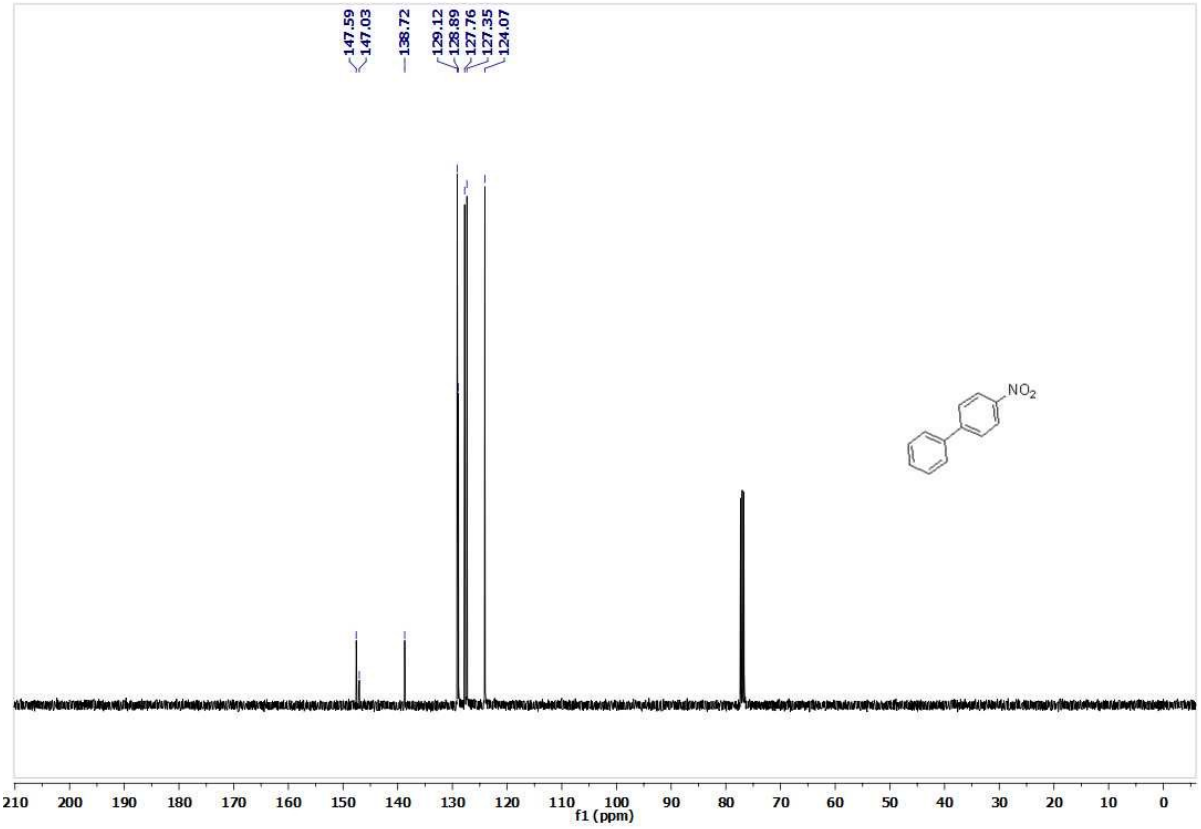
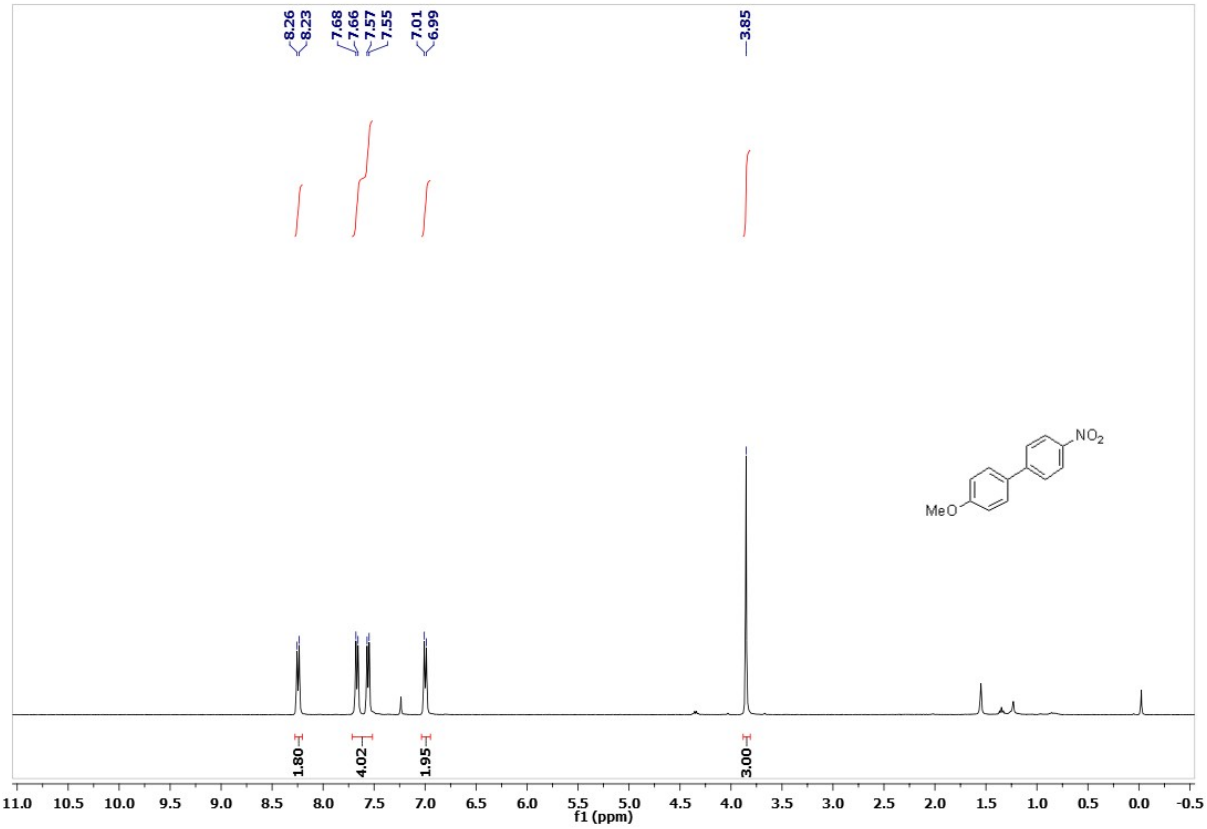
7.45
7.43
7.41
7.37
7.36
7.34
7.29
7.28
7.28
7.26
7.24
2.30
8.87
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


141.95
141.92
135.33
130.30
129.79
129.19
128.06
127.24
126.75
125.75
20.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.29
8.27
7.73
7.71
7.62
7.60
7.50
7.48
7.46
7.45
7.43
7.41
NO2
1.85
7.00
11.0 10.5 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)


147.59
147.03
138.72
129.12
128.89
127.76
127.35
124.07
NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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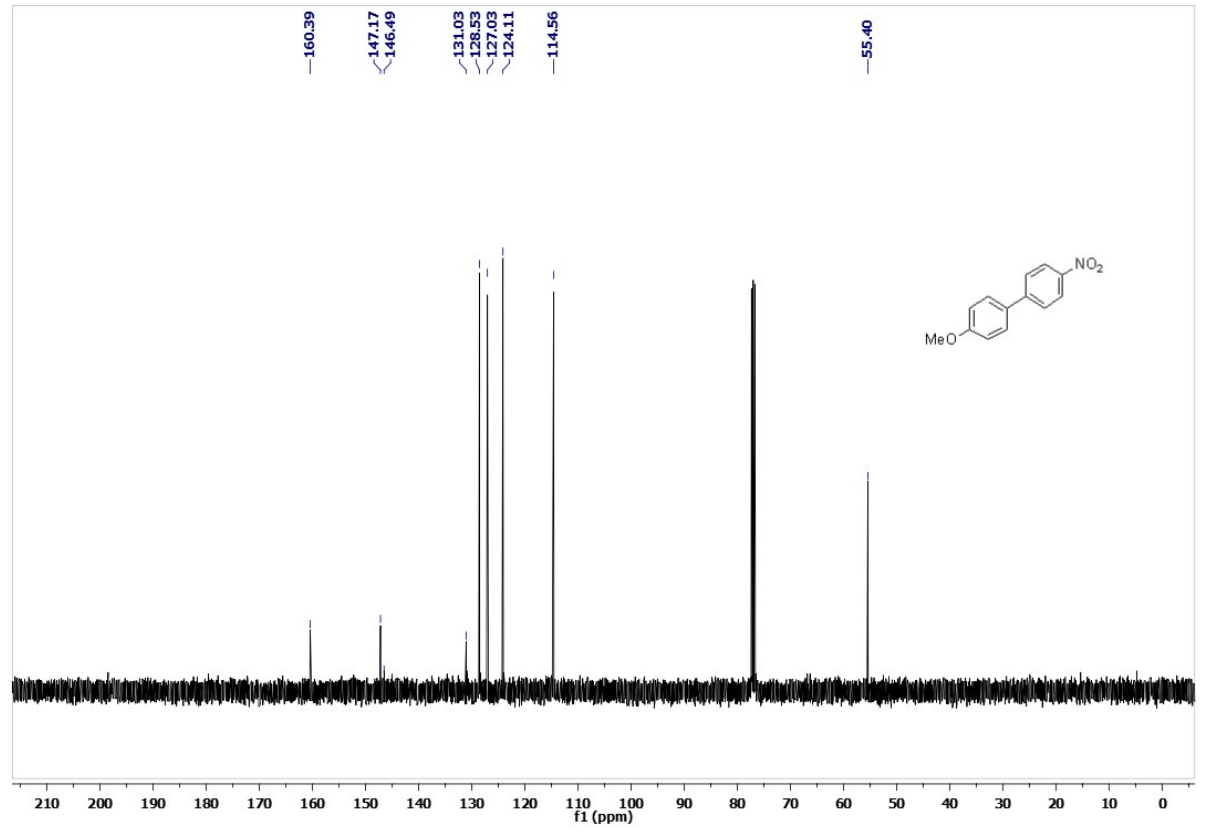
8.23
7.68
7.66
7.57
7.55
7.01
6.99
3.85
NO2
MeO
1.80
4.02
1.95
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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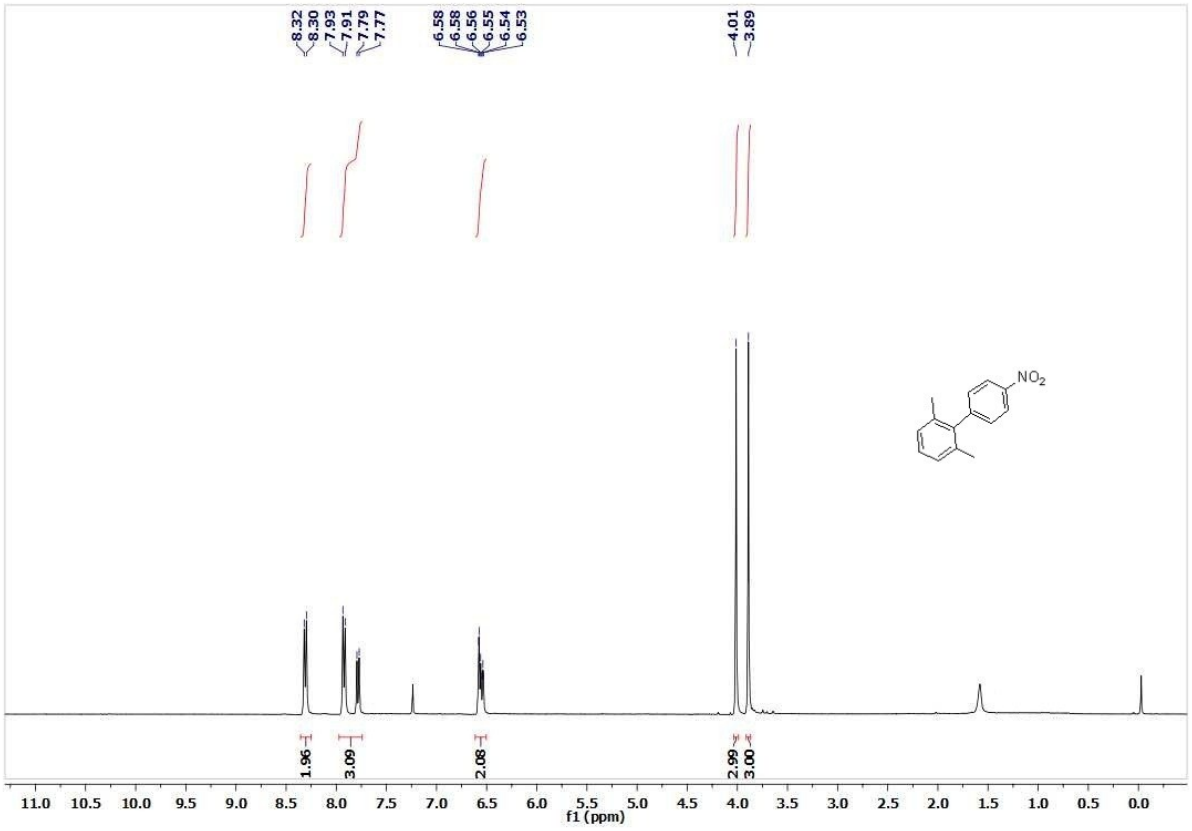
147.17
146.49
131.03
128.53
127.03
124.11
114.56
55.40
NO2
MeO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.32
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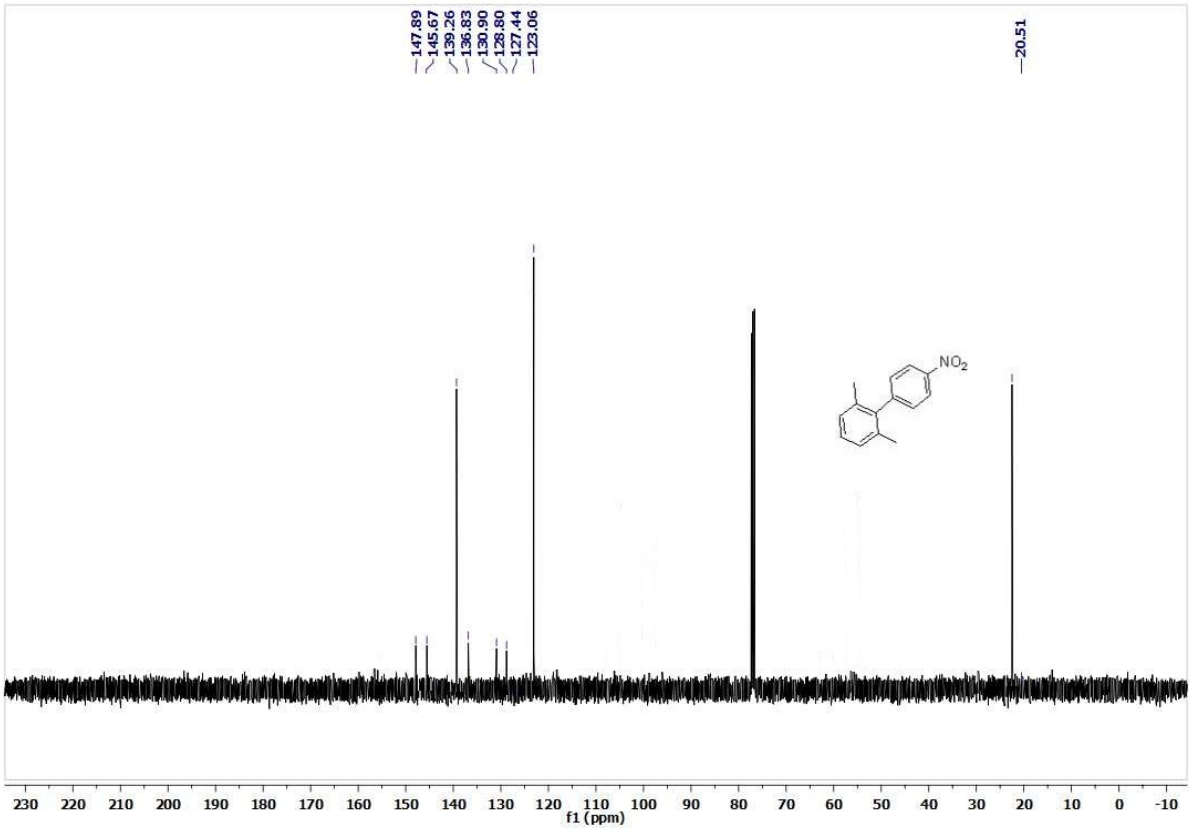
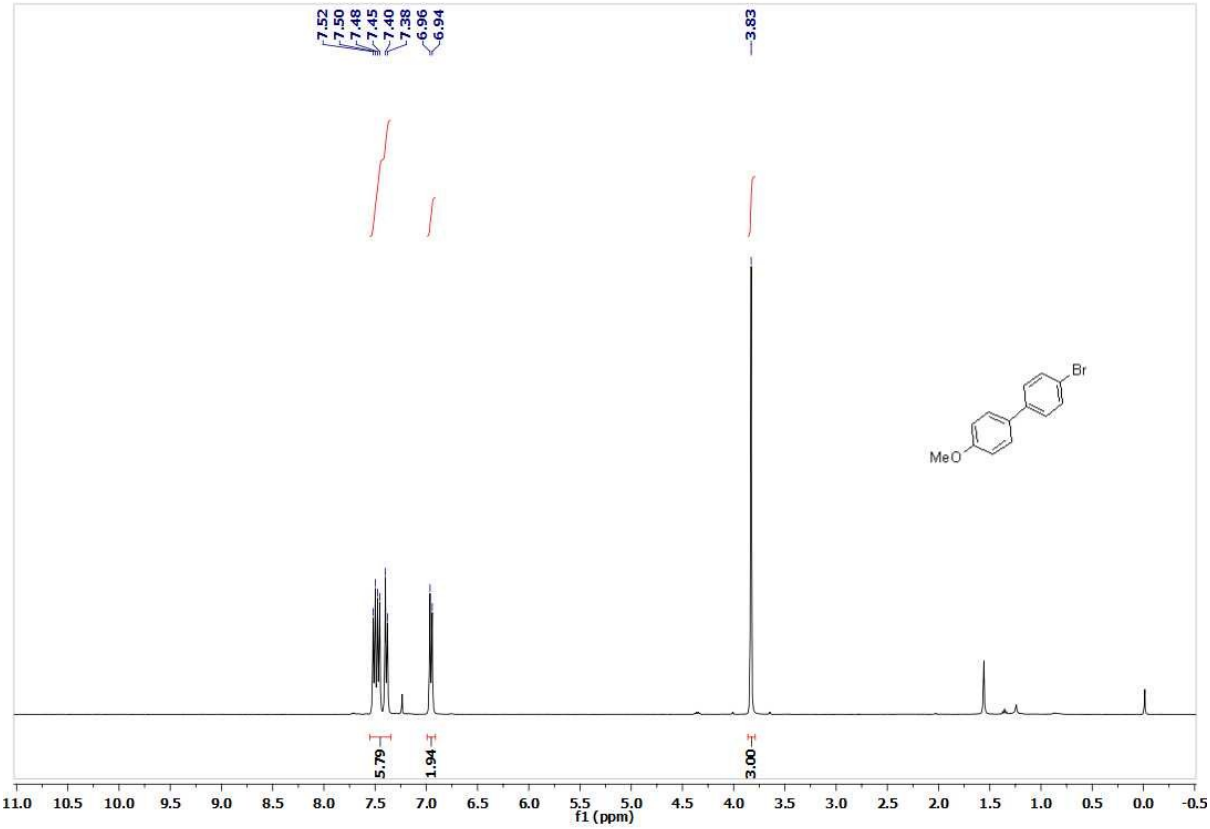
7.77
6.58
6.58
6.56
6.55
6.54
6.53
4.01
3.89
NO2
1.96
3.09
2.08
2.99
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.89
145.67
139.26
136.83
130.90
128.80
127.44
123.06
20.51
NO2
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.52
7.50
7.48
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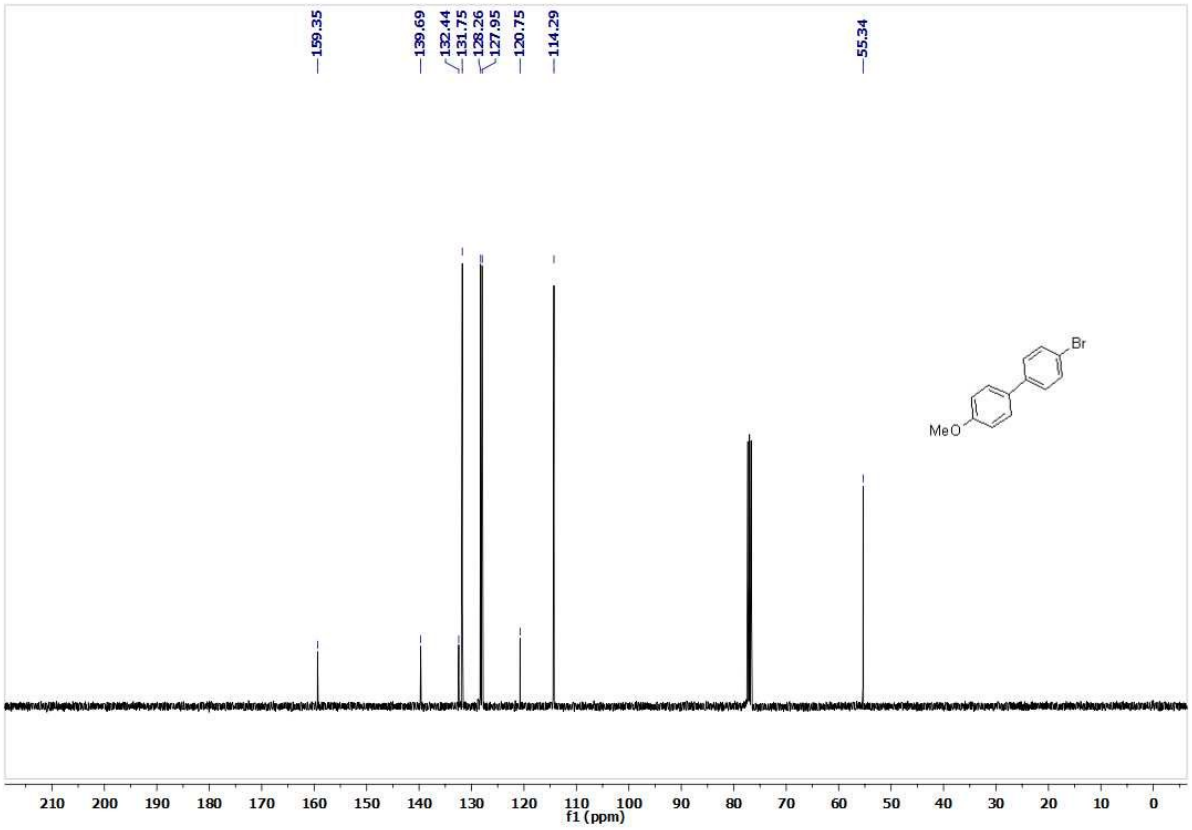
7.40
7.38
6.96
6.94
3.83
Br
MeO
5.79
1.94
3.00
f1 (ppm)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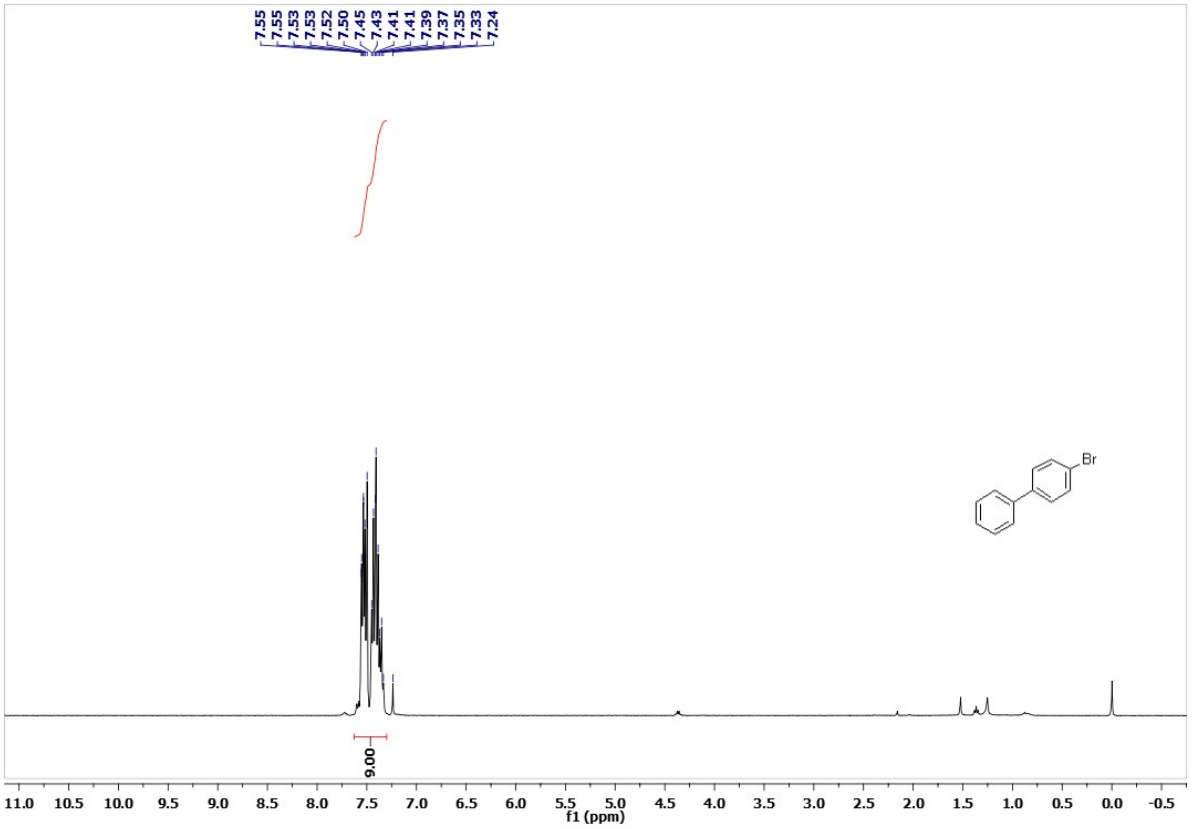
128.26
127.95
120.75
114.29
55.34
Br
MeO
f1 (ppm)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7.53
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7.52
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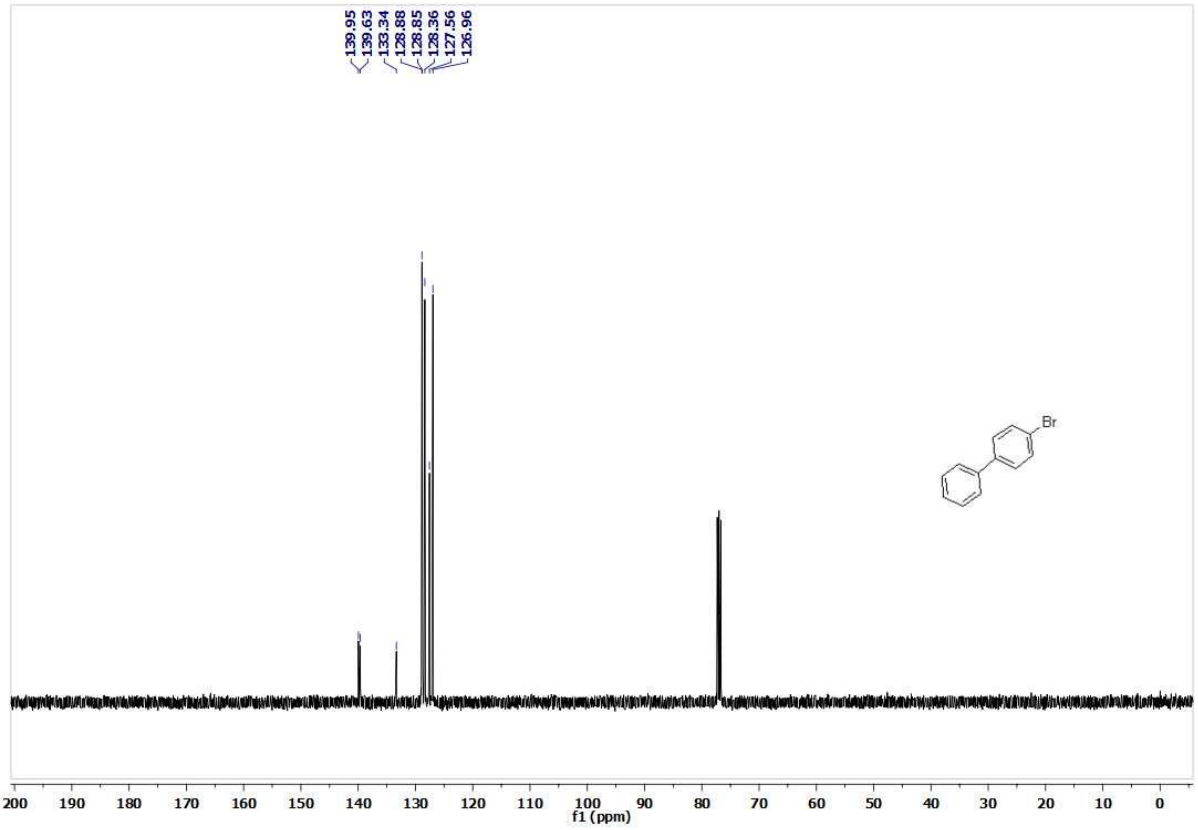
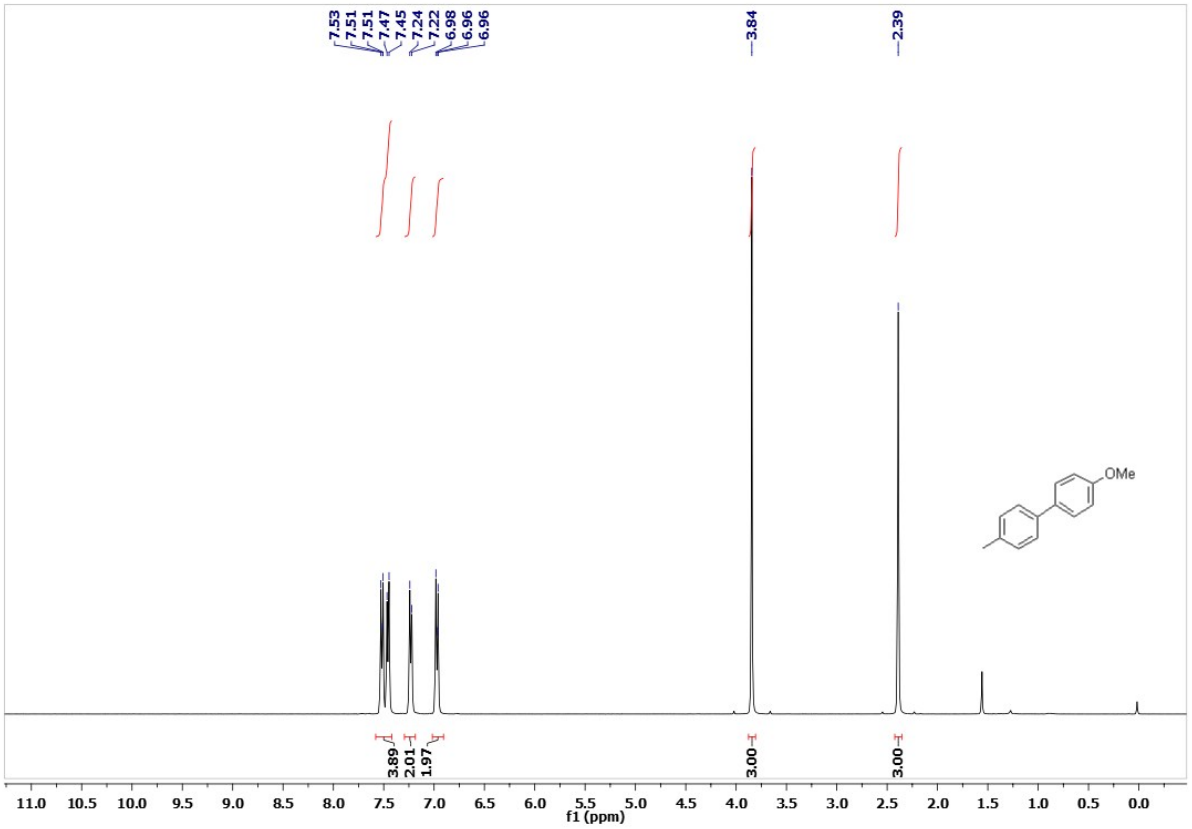
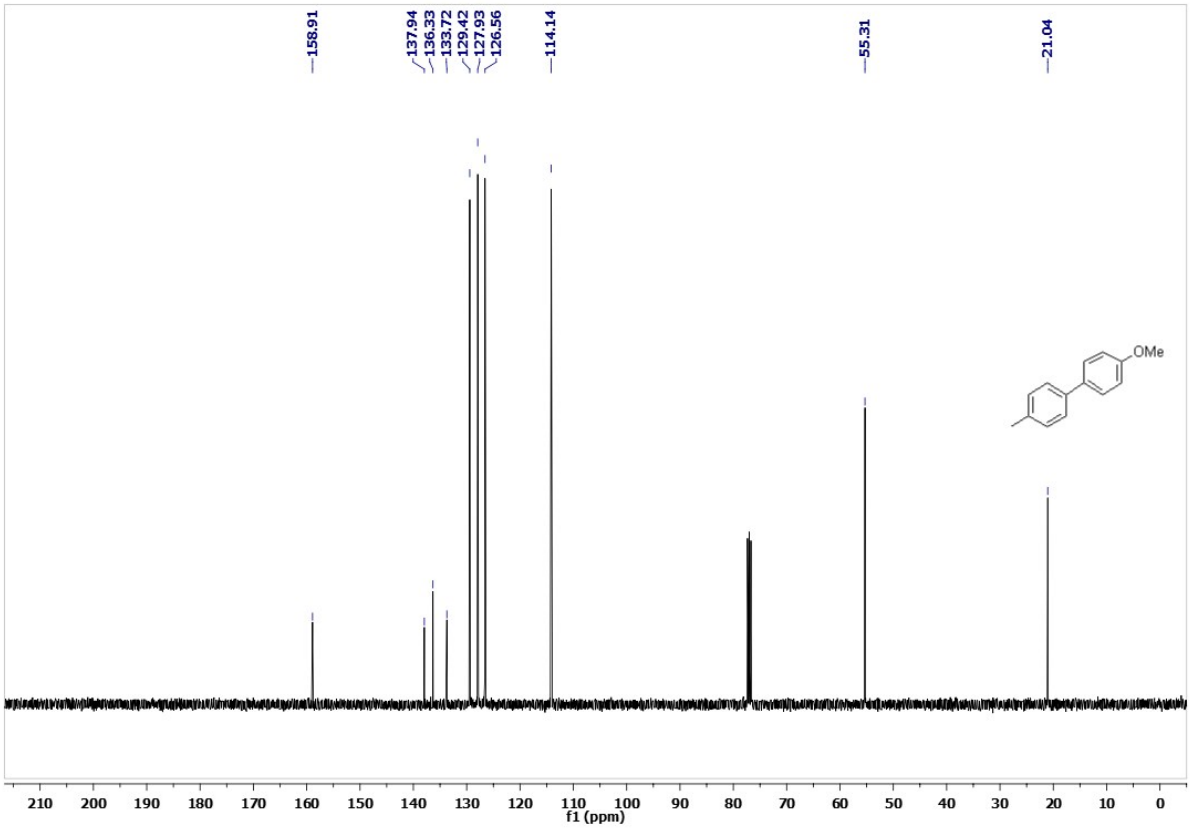
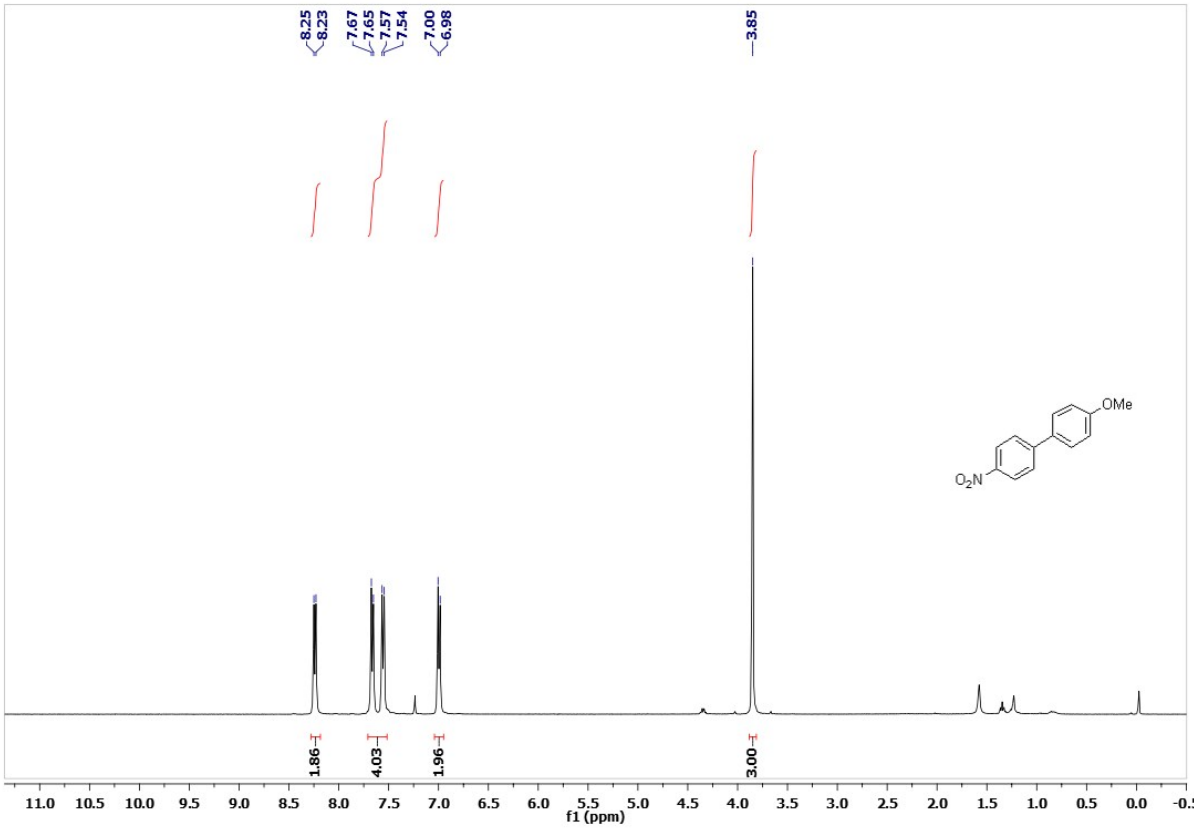
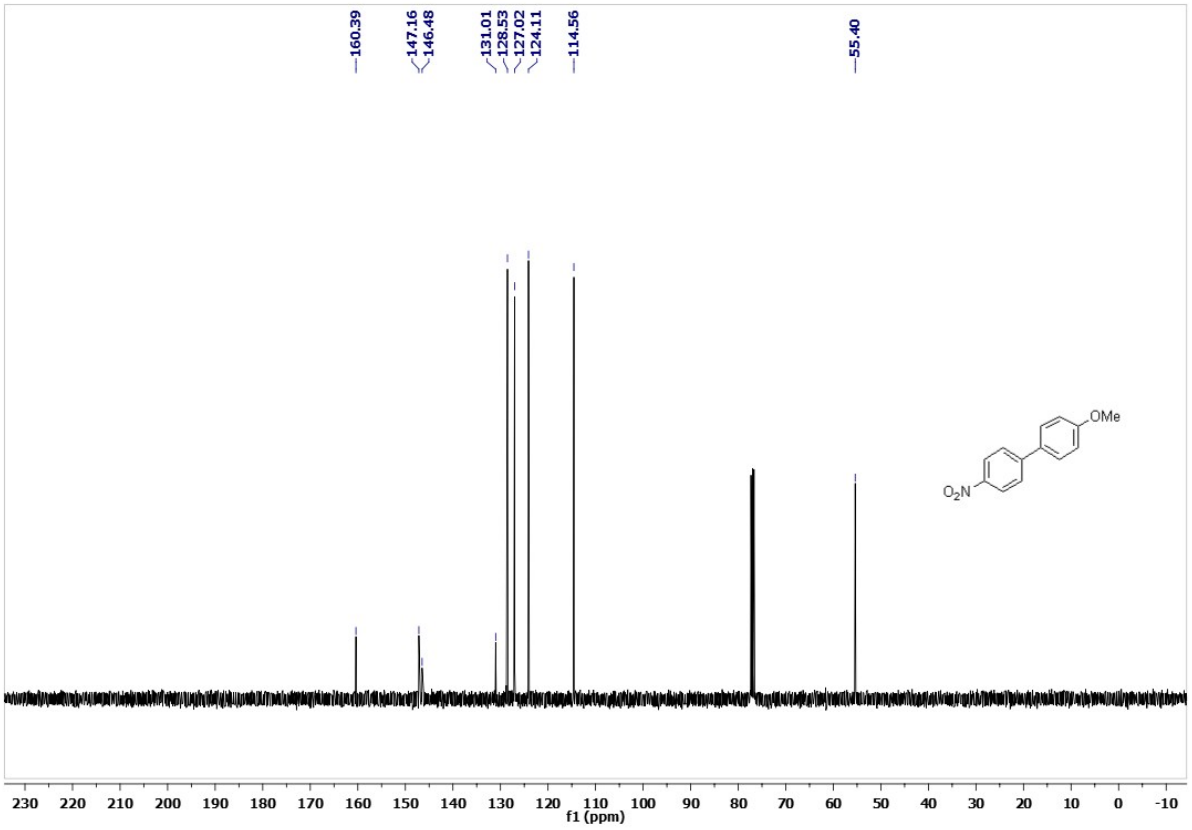
7.45
7.43
7.41
7.41
7.39
7.37
7.35
7.33
7.24
Br
9.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

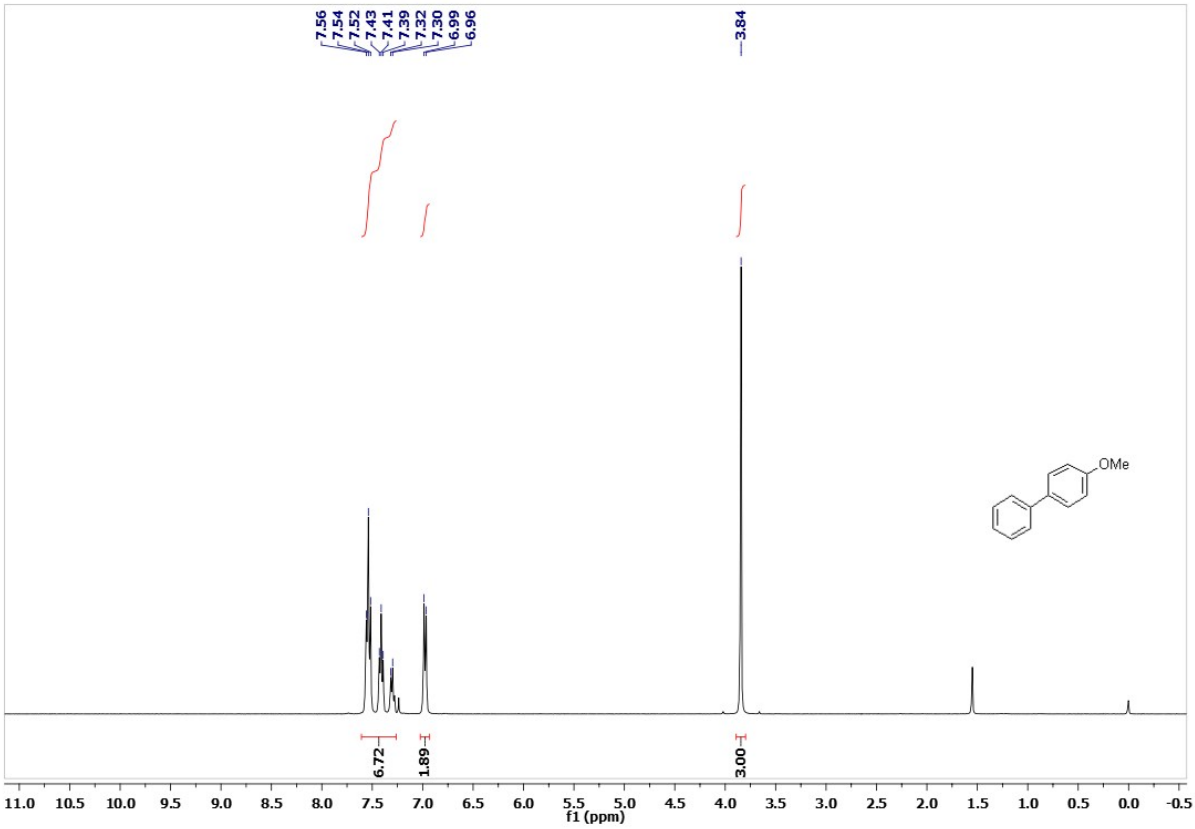

139.95
139.63
133.34
128.88
128.85
128.36
127.56
126.96
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

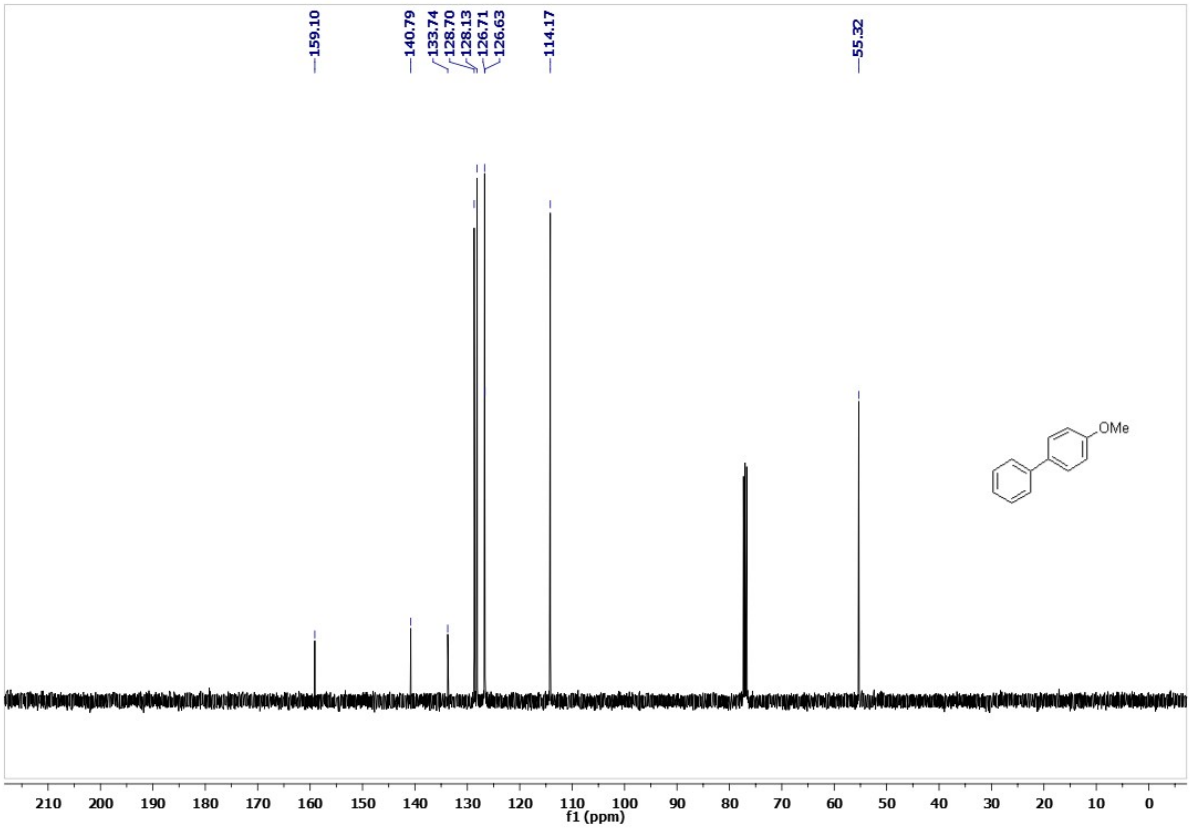

7.53
7.51
7.51
7.47
7.45
7.24
7.22
6.98
6.96
6.96
3.84
2.39
OMe
3.89
2.01
1.97
3.00
3.00
f1 (ppm)

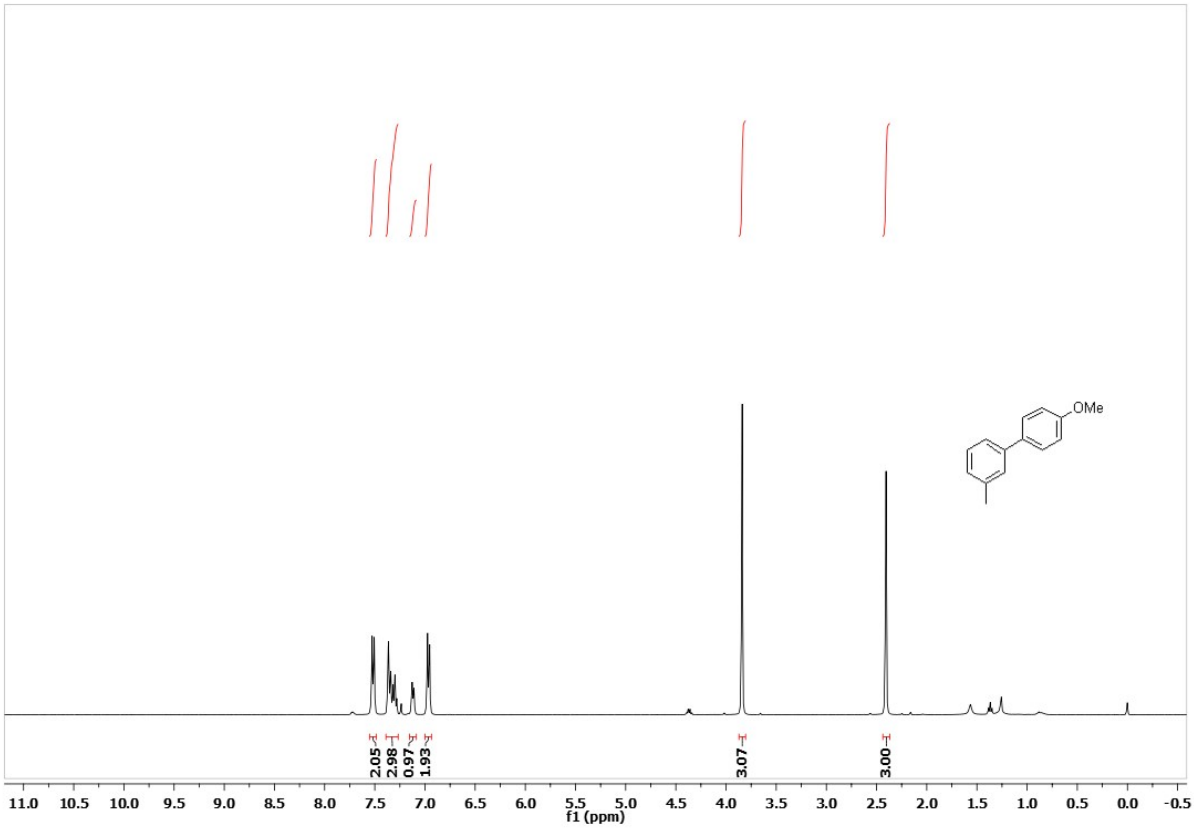

158.91
137.94
136.33
133.72
129.42
127.93
126.56
114.14
55.31
21.04
OMe
f1 (ppm)

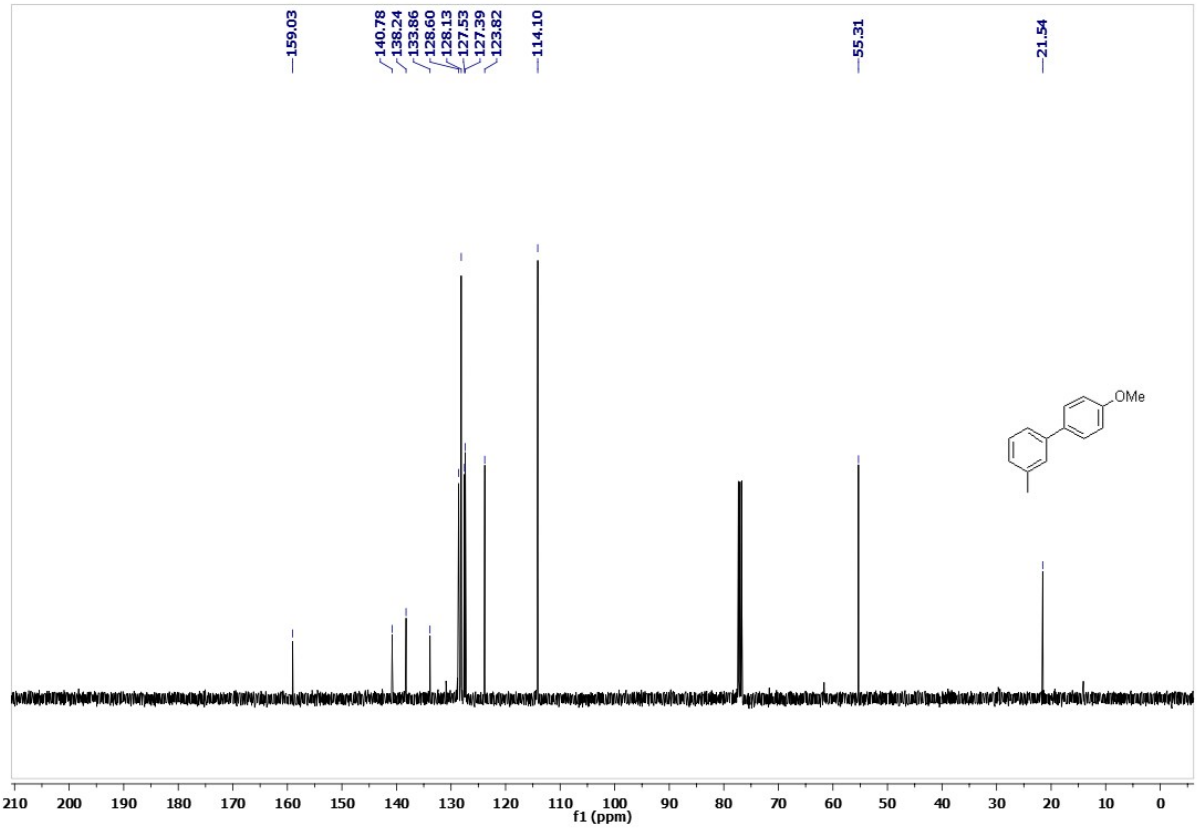

8.25
8.23
7.67
7.65
7.57
7.54
7.00
6.98
3.85
OMe
O_2N
1.86
4.03
1.96
3.00
f1 (ppm)

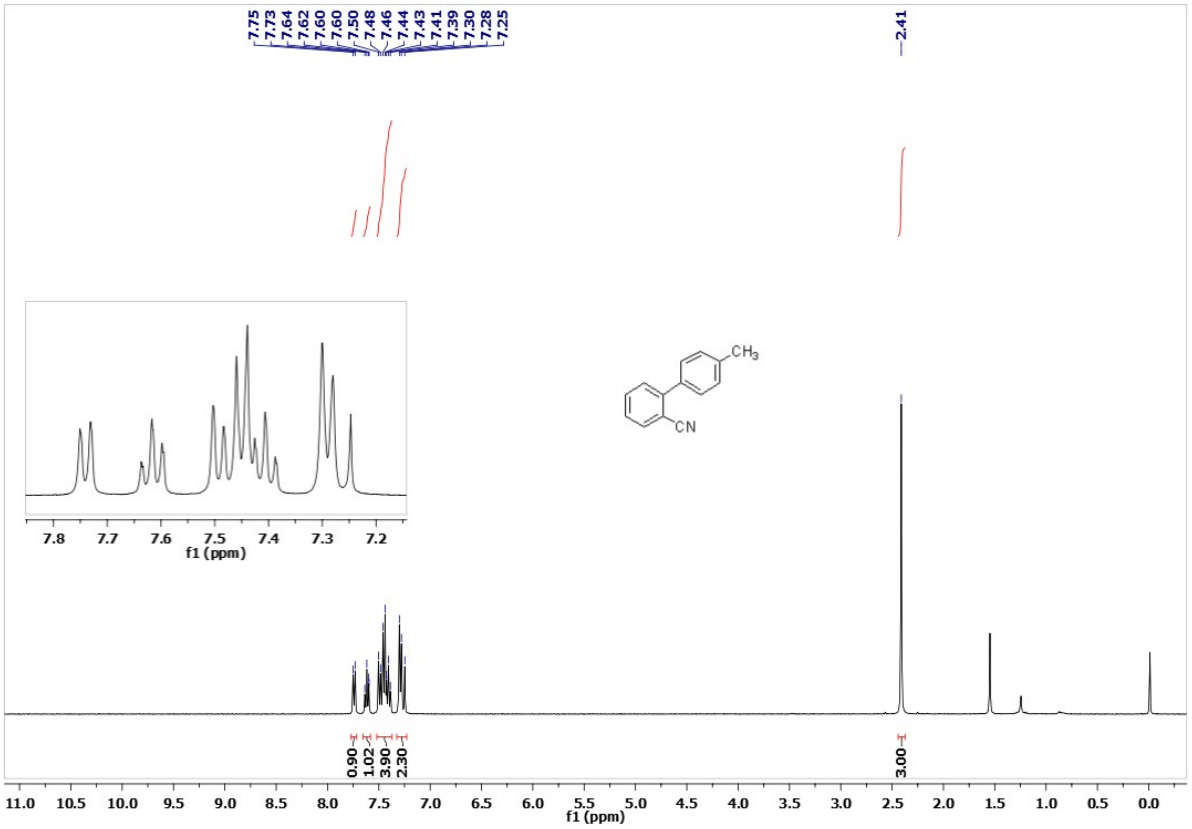

160.39
147.16
146.48
131.01
128.53
127.02
124.11
114.56
55.40
OMe
O_2N
f1 (ppm)

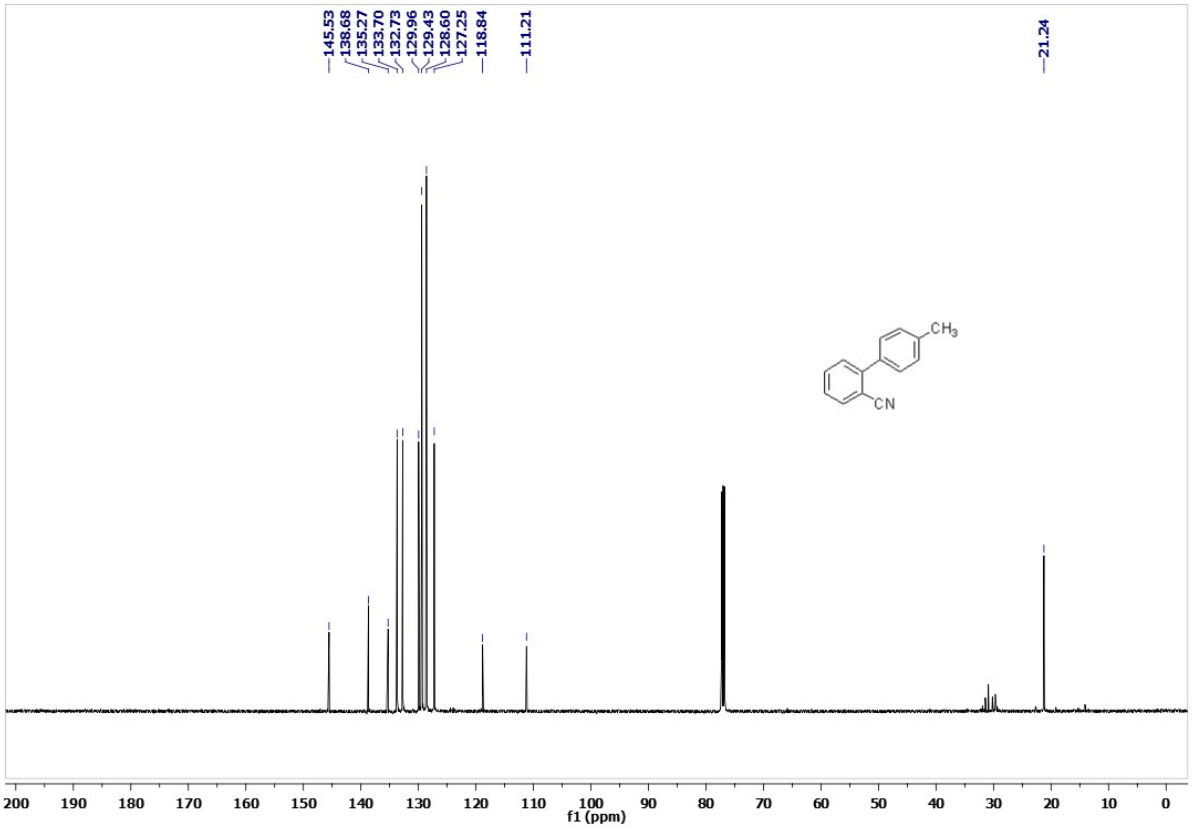

7.56
7.54
7.52
7.43
7.41
7.39
7.32
7.30
6.99
6.96
3.84
OMe
6.72
1.89
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


159.10
140.79
133.74
128.70
128.13
126.71
126.63
114.17
55.32
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe
2.05
2.98
0.97
1.93
3.07
3.00
11.0 10.5 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 -0.5
f1 (ppm)


159.03
140.78
138.24
133.86
128.60
128.13
127.53
127.39
123.82
114.10
55.31
21.54
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.75
7.73
7.64
7.62
7.60
7.60
7.50
7.48
7.46
7.44
7.43
7.41
7.39
7.30
7.28
7.25
2.41
CH3
CN
0.90
1.02
3.90
2.30
3.00
f1 (ppm)


145.53
138.68
135.27
133.70
132.73
129.96
129.43
128.60
127.25
118.84
111.21
21.24
CH3
CN
f1 (ppm)

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