

*This version of the ESI published on 21/11/2022 replaces the original version published on 31/10/2022. In the original ESI, the turnover numbers (TONs) were incorrectly given as  $10^3$ , rather than  $10^4$*

## Electronic Supplementary Information (ESI)

### Palladium nanoparticles immobilized on polyethylenimine-derivatized gold surfaces for catalysis of Suzuki reactions: development and application in a lab-on-a-chip context

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## 1. Materials and methods

### 1.1. Chemicals

Palladium acetate, 11-mercaptoundecanoic acid (MuDA), *N*-hydroxy succinamide (NHS), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC.HCl), polyethylene imine (PEI), phosphate buffer saline (PBS) tablet, potassium carbonate, 2-tolylboronic acid, bromobenzene, 2-cyanophenylboronic acid, 4-cyanophenylboronic acid, 3-methoxyphenylboronic acid were purchased from Sigma Aldrich (Steinheim, Germany) and used without any purification process. Glacial acetic acid purchased from Merck (Germany), iodobenzene purchased from Riedel-De Haen AG Seelze (Hannover, Germany), phenylboronic acid purchased from AK Scientific, (USA). Ethanol (99.7%) purchased from Solveko, Sweden, ethyl acetate, and petroleum ether used without further distillation. Water was purified (resistance value < 18.2 M $\Omega$ ) using a Milli-Q gradient water filtration system (Millipore, MA, USA) and was used for solution preparation, Suzuki reaction and rinsing of substrates

### 1.2. Instrumentation

#### 1.2.1. Quartz crystal microbalance (QCM) studies

Piezoelectric microgravimetric analysis were performed using quartz crystal microbalance (Attana, NC100, Attana AB, Stockholm, Sweden). QCM was constituted to control Attester software (Attana, NC100, Attana AB, Stockholm, Sweden). Dimensions used for the system was 10 MHz AT-cut quartz resonators (Attana AB, Stockholm, Sweden, 8 mm diameter, sputter-coated on both the sides with 45 mm diameter and 140 nm thick gold over a 10 nm Ti or Cr underlying layer). This was used not only as substrate but also as working electrode for the immobilization of PEI. Piranha solution (H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>, 1:3, v/v) (*Caution: 'Piranha' solution should be handled with extreme care as it reacts violently with most organic materials and is dangerous when in contact with eye and skin*) was used for cleaning the substrates followed by copious amount of ultrapure water. Later it was dried under nitrogen gas and stored under vacuum until further use.

#### 1.2.2. IR spectroscopy

Bruker Hyperion 3000 IR microscope coupled to a Tensor 27 IR spectrometer was used to record refractive angle of the polymer film coated gold quartz surfaces and computerized sample stage. It is recommended to have grazing angle objective to avoid damage to the sample surface due to double surface reflections. The spectra used to acquire resolution of 4 cm<sup>-1</sup> was collected by single element mercury-cadmium-telluride (MCT) detector. Nitrogen atmosphere was maintained in the sample chamber throughout the measurement. Before Fourier transformation, a three-term Blackmann-Harris apodization function was applied to the interferograms. An unmodified gold resonator was used to acquire background spectrum.

#### 1.2.3. Scanning electron microscopy (SEM)

Leo 1550 Gemini instrument used to image electron micrograph of immobilized palladium particles that furnishes in high vacuum mode with a field emission electron gun. Resonators were kept on a black carbon tape attached to alumina stubs and coated with a thin layer of platinum sputtering unit (LEICA EM SCD 500) and after that they inserted in the SEM instrument.  $2 \times 10^{-5}$  mbar pressure of measurement was maintained. To scan the sample surface, a 3 kV potential was applied to the electron gun to generate electron beam. EDX analysis was performed at an accelerating voltage of 20 kV.

#### 1.2.4. X-ray photoelectron spectroscopy (XPS)

Physical electronics Quantum 2000 scanning ESCA Microprobe equipped with a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV) was used to record all XPS measurements. For the survey

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spectra the pass energy was 50.0 eV which were collected in the range between 0 to 1350 eV. Using 200.0 eV pass energy and 0.1 eV increment, the Au4f and N1s core level spectra were recorded. During this process pressure of the sample chamber was maintained at  $5 \times 10^{-9}$  mbar and spot size is 400  $\mu\text{m}$  and number of scans 20. Shirley method used to correct the spectral background for data processing and for different nitrogen atoms the spectral bands were deconvoluted.

### 1.2.5. High Performance Liquid Chromatography (HPLC)

HPLC was performed on Merck-Hitachi D-7000 HSM program that analyzes two-dimensional and three-dimensional data acquired from High-Performance Liquid Chromatography (HPLC) system. The HPLC System Manager (HSM) program is linked through a D-7000 Interface Module (IFM) to control Hitachi L-7000 series pumps, autosamplers, ovens and detector using Hitachi's D-Line (Digital-Line) interface. The Silica column used contains Material: Ultrasphere 5 S, Batch: S806073, Dimensions: 250 X 4.6mm, Part No: 235341, Serial No: H80153

### 1.2.6. Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance spectroscopy was performed at 400 MHz ( $^1\text{H}$  NMR), 101 MHz ( $^{13}\text{C}$  NMR) on Bruker Ascend instrument. Chemical shifts ( $\delta$ ) are provided in ppm and spectra referred to non-deuterated solvent signal.

### 1.2.7. High resolution mass spectrometry (HRMS)

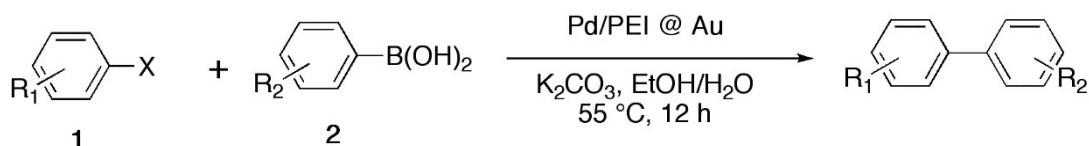
Mass spectra (HRMS) were obtained from Lund University Kemi Centrum Mass Spectrometry facility. Instrument: Waters XEVO-G2 QTOF. ESI+: Capillary voltage 3 kV, Cone voltage 35V, Ext 4, Source Temp 120, Des Temp 300, Cone gas 50, Des gas 400. Continuum resolution mode, m/z 100–1200, manual lock mass correction by Leucine Enkephalin

## 1.3. Preparation of the catalytic surface

Gold coated quartz resonators were cleaned with ethanol for 15 mins, dried under nitrogen and immersed in 5  $\mu\text{M}$  MuDA solution for 24 h. The modified gold surfaces were rinsed in EtOH, 10 % AcOH and water for 15 mins in each solution, dried under  $\text{N}_2$  and immersed in mixture of 15 mM NHS and 45 mM of EDC.HCl in water for 1 h to activate the -COOH group. The substrates were dried under  $\text{N}_2$  and subsequently incubated in PEI (5 %, w/v) in PBS (10 mM, pH 8.2) for 2 days. After rinsing with excess of water, the substrates were dried under nitrogen and frequency of the resonators were recorded in QCM.

## 1.4. Suzuki reaction

### 1.4.1 General procedure for Suzuki coupling



A reaction tube charged with 1 mmol of **1** in ethanol, 1.2 mmol of **2** followed by 2.0 mmol of  $\text{K}_2\text{CO}_3$  in water and the resulting mixture was purged with nitrogen for 5 min. Palladium nanoparticle immobilized gold resonator was immersed in the reaction tube and reaction mixture was kept in a waterbath at  $55\text{ }^\circ\text{C}$  @ 100 RPM for 12 h. After that, gold quartz resonator was removed, rinsed with EtOH, dried under nitrogen and frequency was recorded. Reaction mixture was concentrated under vacuum and crude product was diluted with water and extracted with ethyl acetate (2 – 3 times). The resulting organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered, concentrated under vacuum and the

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crude product was purified by preparative TLC (9:1 petroleum ether: acetone) as the eluent. the product was confirmed by  $^1\text{H}$  NMR.

#### ***1.4.2 $\text{PPh}_3$ poisoning test***

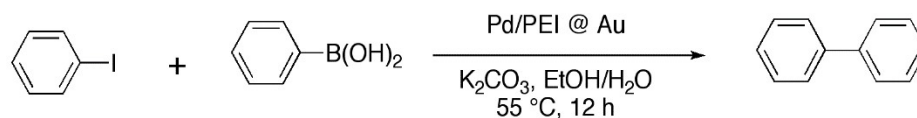
$\text{PPh}_3$  poisoning test was performed using 5 equivalents of  $\text{PPh}_3$  combined with 1 equivalent of the catalyst and stirred for 15 minutes before the addition of iodobenzene (0.098 mmol, 20 mg) and phenylboronic acid (0.11 mmol, 14.3 mg). After 12 hours, the biphenyl product was obtained in 93% yield.

#### ***1.4.3 Suzuki coupling reaction on PEI/Pd surface in Lab-on-a-chip format.***

The catalytic performance of the palladium immobilized PEI coated Au/quartz catalyst substrates was evaluated under FIA (dynamic) conditions. The substrates were mounted in the flow cell holders provided by the manufacturer (Attana AB). A step-up motor (hydraulic pump, VICI), equipped within the QCM instrument, was used to pump the reaction mixture containing 1.0 mmol of iodobenzene, 1.2 mmol of phenylboronic acid, 2.0 mmol of  $\text{K}_2\text{CO}_3$ , in  $\text{H}_2\text{O}/\text{EtOH}$  over the Pd immobilized PEI substrates at  $10\ \mu\text{L}/\text{min}$  flow rate. The reaction mixture from the vent tube was collected, concentrated under vacuum and crude product was diluted with water, extracted with ethyl acetate and analyzed with HPLC.

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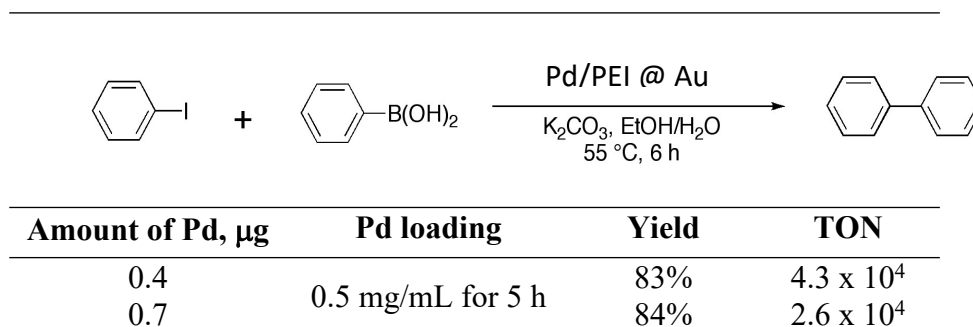
Table 1-SI Suzuki cross-coupling reactions of iodobenzene and phenylboronic acid in the presence of catalytic Pd immobilized PEI coated Au/quartz surface.



Amount of Pd, $\mu\text{g}$	Amount of Pd, $/\text{cm}^2$	Pd loading	Yield	TON
1.6	3.13		67%	$8.7 \times 10^4$
2.5	4.90	1 mg/mL for 2 h	80%	$6.9 \times 10^4$
2.5	4.90		74%	$6.7 \times 10^4$
7.8	15.29		74%	$2.0 \times 10^4$
6.1	11.96	1 mg/mL for 5 h	80%	$2.8 \times 10^4$
5.5	10.78		80%	$3.1 \times 10^4$
0.4	0.78	0.5 mg/mL for 30 min	60%	$2.9 \times 10^4$
1.1	2.15		70%	$1.2 \times 10^4$
0.74	1.45		54%	$1.5 \times 10^4$
0.45	0.88	0.5 mg/mL for 1 h	54%	$2.5 \times 10^4$
1.31	2.56		54%	$0.8 \times 10^4$
0.54	1.05	0.5 mg/mL for 2 h	74%	$2.9 \times 10^4$
0.62	1.21		67%	$2.3 \times 10^4$
2.2	4.31		93%	$0.8 \times 10^4$
1.8	3.52	0.5 mg/mL for 5 h	90%	$1.0 \times 10^4$
2.0	3.92		90%	$2.2 \times 10^4$

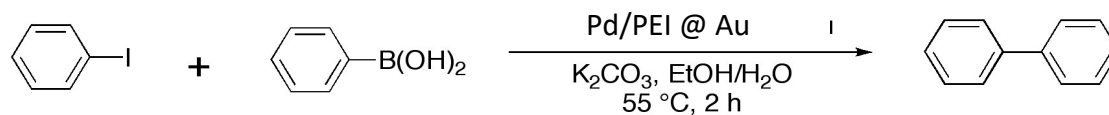
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Table 2-SI. Suzuki cross-coupling reactions of iodobenzene and phenylboronic acid in the presence of catalytic Pd immobilized PEI coated Au/quartz surface for 6 h.



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Table 3-SI Suzuki cross-coupling reactions of iodobenzene and phenylboronic acid in the presence of catalytic Pd immobilized PEI coated Au/quartz surface for 2 h.



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Amount of Pd, $\mu\text{g}$	Pd loading	Yield	TON
0.65	0.5 mg/mL for 5 h	78%	$2.5 \times 10^3$

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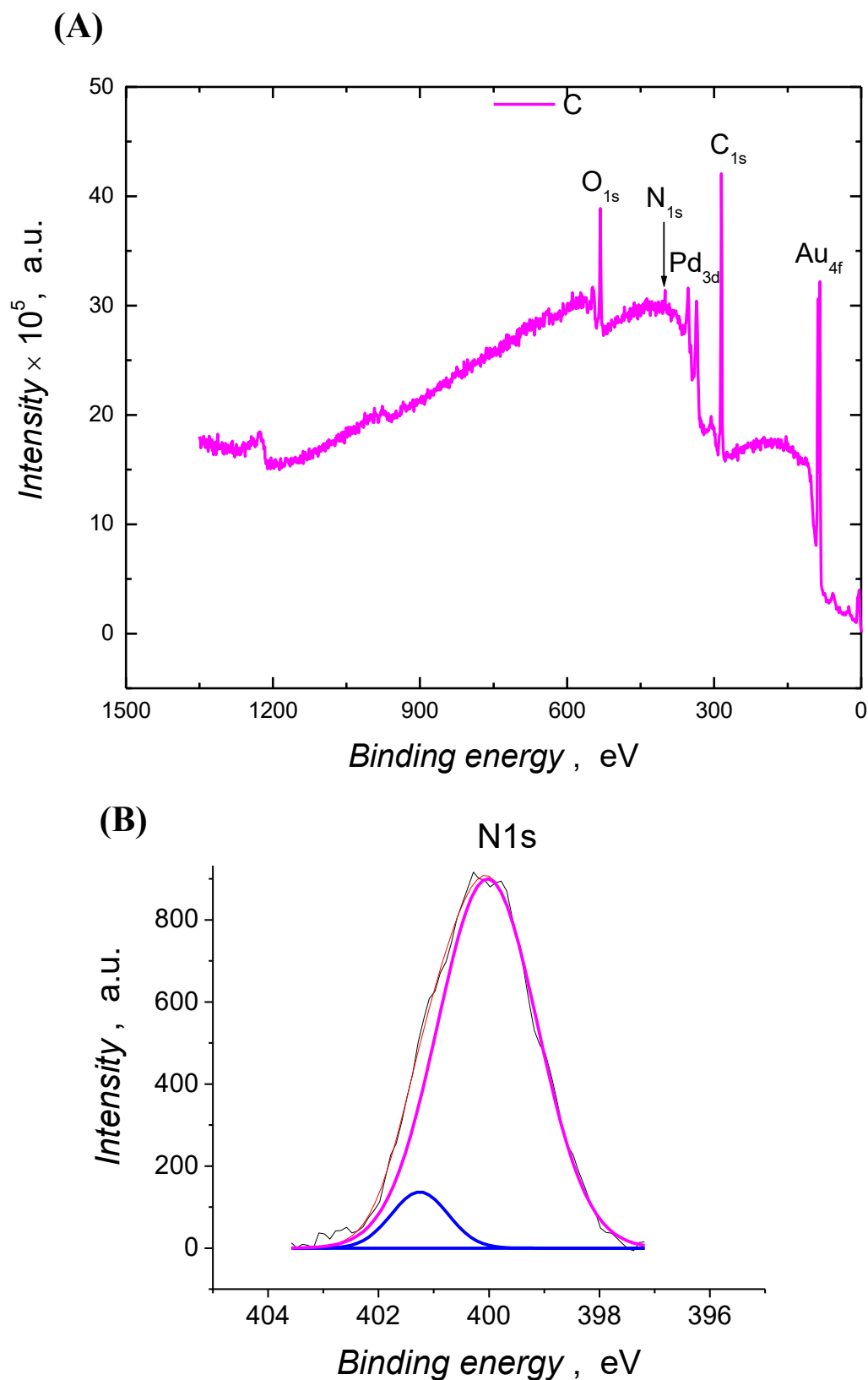
Table 4-SI: Comparison of other reported catalytic systems on Suzuki reaction of halobenzenes with phenylboronic acid

Entry	Catalysts <sup>a</sup>	Size (nm)	(%)	Time (h) <sup>b</sup>	Temp (°C) <sup>c</sup>	Solvent <sup>d</sup>	Yield (%)
1	Au-G <sup>1</sup>	2-3	1.0 mol	4	100	H <sub>2</sub> O	85
2	Fe <sub>3</sub> O <sub>4</sub> -Bpy-Pd(OAc) <sub>2</sub> <sup>2</sup>	6-20	15 mg	6	80	Toluene	>99
3	Pd/NiFe <sub>2</sub> O <sub>4</sub> <sup>3</sup>	100-300	0.1 mol	5	90	DMF:H <sub>2</sub> O (5:2)	97
4	Pd/NiFe <sub>2</sub> O <sub>4</sub> <sup>4</sup>	10-12	50 mg	30	110	DMF	97
5	Pd/NiFe <sub>2</sub> O <sub>4</sub> <sup>5</sup>	>50	0.08 mol	4	80	NMP:H <sub>2</sub> O (3:1)	97
6	Pd/Fe <sub>3</sub> O <sub>4</sub> nanocrystals <sup>6</sup>	36	1.0 mol	24	>80	DME:H <sub>2</sub> O (3:1)	99
7	Pd/G <sup>7</sup>	7-9	0.3 mol	10	~80	H <sub>2</sub> O:EtOH (1:1)	>99
8	Pd/GO <sup>7</sup>	12-18	0.3 mol	10	~80	H <sub>2</sub> O:EtOH (1:1)	>99
9	Pd-SBA-15 <sup>8</sup>	1.5	0.5 mol	30 min	100	H <sub>2</sub> O:EtOH (3:2)	21
10	Pd-SBA-16 <sup>9</sup>	10-25	0.01 mol	5	50	EtOH	99
11	Fe <sub>3</sub> O <sub>4</sub> -Pd <sup>(0)</sup> <sup>10</sup>	8-10	5.0 mol	24	50	DMF	54
12	Ru/Al <sub>2</sub> O <sub>3</sub> <sup>11</sup>	2-3	5.0 mol	12	60	DME:H <sub>2</sub> O (1:1)	96
13	LDH-Pd <sup>(0)</sup> <sup>12</sup>	4-6	1.0 mol	10	100	1,4-dioxane:H <sub>2</sub> O (5:1)	93
14	Diatomite-Pd <sup>(0)</sup> <sup>13</sup>	20-100	0.1 mol	20 min	110	DME:H <sub>2</sub> O (1:1)	95
15	Polyoxometalate-Pd <sup>(0)</sup> <sup>14</sup>	15-20	0.01 mol	12	80-85	H <sub>2</sub> O:EtOH (1:4)	92
16	MES-IMes (20%)-Pd <sup>15</sup>	>20	0.5 mol	24	80	Isopropyl alcohol	78
17	Organostannoxane-Pd <sup>(0)</sup> <sup>16</sup>	4.3	5.0 mg	4	110	Toluene	95
18	Pd/SiO <sub>2</sub> <sup>17</sup>	>100	100 mg	12	100	CH <sub>3</sub> CN:H <sub>2</sub> O (3:1)	>90
19	SiO <sub>2</sub>	>100	0.05 mol	12	60-70	H <sub>2</sub> O	Trace <sup>b</sup>
20	NH <sub>2</sub> -SiO <sub>2</sub>	>100	0.05 mol	12	60-70	H <sub>2</sub> O	Trace <sup>c</sup>
21	Pd/NH <sub>2</sub> -SiO <sub>2</sub> <sup>18</sup>	5-6	0.05 mol	1	60-70	H <sub>2</sub> O	96 <sup>d</sup>
<b>22</b>	<b>PEI/Pd</b>	<b>20-100</b>	<b>&lt;0.001 mol</b>	<b>12</b>	<b>55</b>	<b>H<sub>2</sub>O:EtOH (1:1)</b>	<b>95</b>

<sup>a</sup> References.

<sup>b-d</sup> Reaction conditions as exemplified in the experimental procedure, where G, graphene; GO, graphene oxide; DMF, dimethylformamide; DME, dimethyl ether; NMP, N-methyl-2-pyrrolidone; CH<sub>3</sub>CN, acetonitrile respectively.





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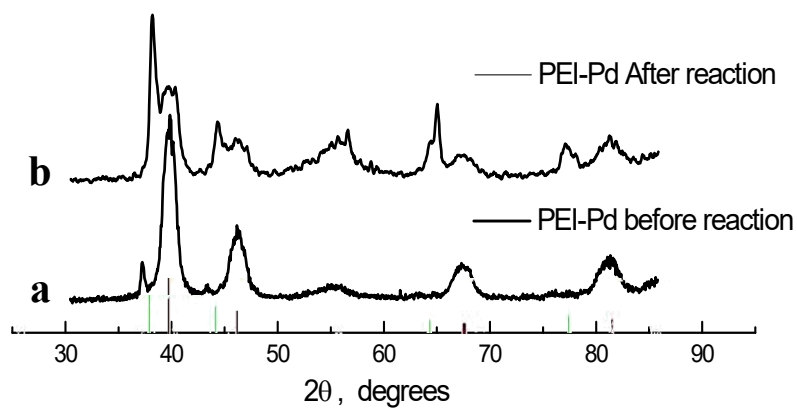


Figure 2-SI. Powder X-ray diffraction pattern of Pd immobilized PEI coated Au/quartz surfaces before (Curve *a*) and after (Curve *b*) catalyzing Suzuki reaction.

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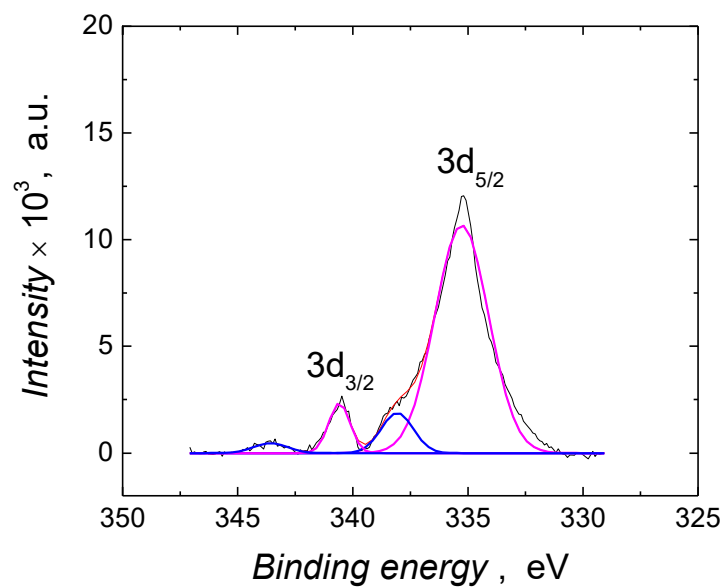


Figure 3-SI. Deconvoluted XPS bands of Pd<sub>3d</sub> for the palladium nanoparticle immobilized PEI coated Au/quartz surface, measured after catalyzing the Suzuki reaction.

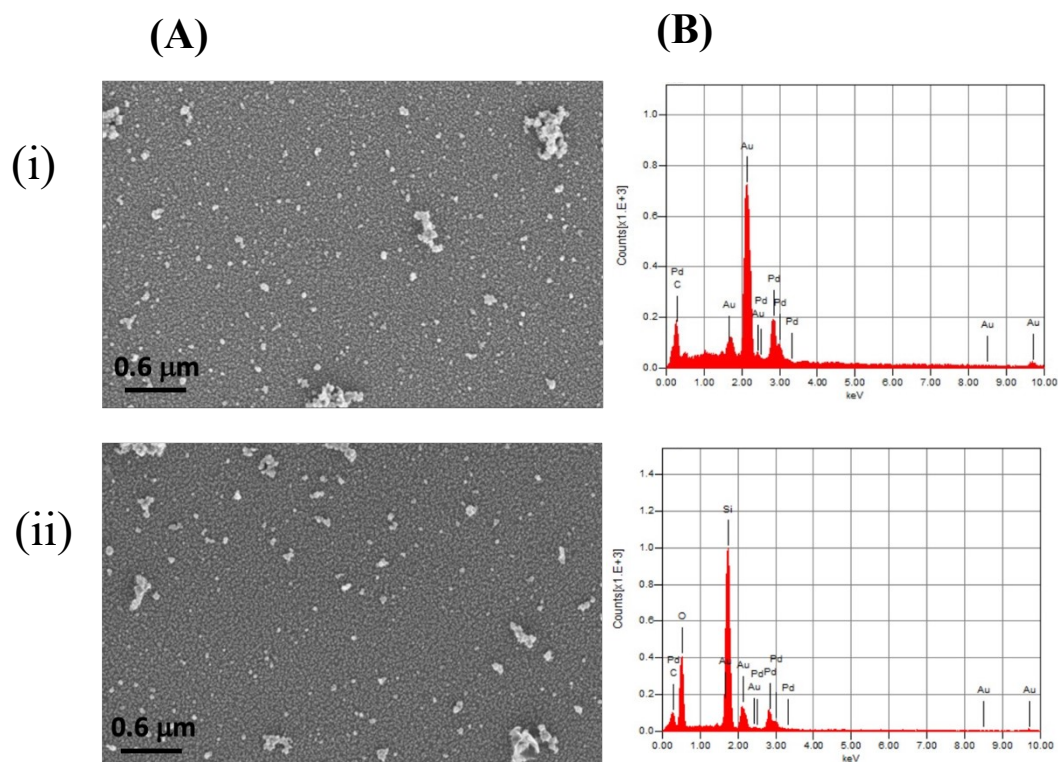


Figure 4-SI. (A) Scanning electron microscopy (SEM) image and (B) energy dispersive X-ray spectrum (EDX) of palladium nanoparticle immobilized PEI coated Au/quartz surface, measured (i) before and (ii) after being used to catalyse Suzuki coupling reaction. Palladium was immobilized on PEI film as shown in Scheme 1 from 0.5 mg/mL of palladium acetate for 5 h.

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HPLC of Biphenyl:

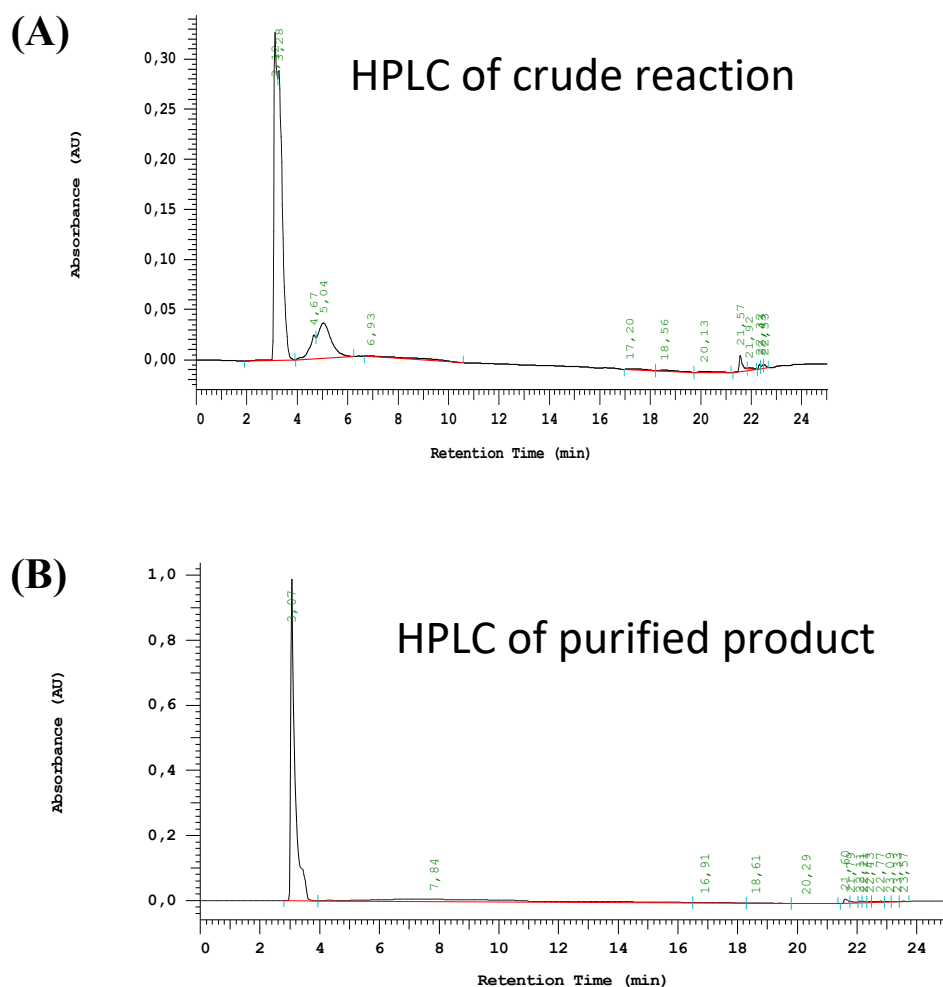
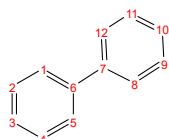


Figure 5-SI. (A) HPLC of collected reaction mixture after allowing to flow through the QCM microreactor. (B) is the HPLC of the purified biphenyl product.

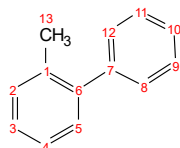
### NMR data



$^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ )  $\delta$  7.76 (d,  $J$  = 7.3 Hz, 1H), 7.64 – 7.57 (m, 3H), 7.47 – 7.40 (m, 2H), 7.40 – 7.30 (m, 4H).

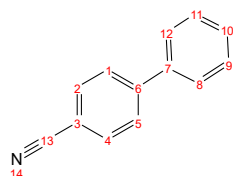
$^{13}\text{C}$  NMR (101 MHz, Methanol- $d_4$ )  $\delta$  141.1, 133.4, 133.0, 129.8, 129.2, 128.4, 127.2, 127.0, 126.9, 126.5.

HRMS: calculated: 154.0783, found: 154.0777



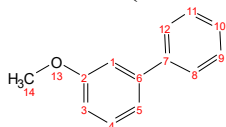
$^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ )  $\delta$  7.46 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 7.32 – 7.28 (m, 2H), 7.28 – 7.21 (m, 3H), 7.20 – 7.16 (m, 1H), 2.25 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, Methanol- $d_4$ )  $\delta$  142.0, 134.8, 129.8, 129.2, 128.7, 127.7, 126.9, 126.4, 125.4, 19.1



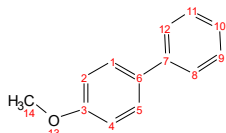
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.79 – 7.73 (m, 2H), 7.73 – 7.68 (m, 2H), 7.63 (d,  $J$  = 1.6 Hz, 1H), 7.61 (t,  $J$  = 1.4 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.48 – 7.42 (m, 1H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  145.7, 139.2, 132.6, 129.1, 128.6, 127.7, 127.2, 118.9, 110.9.



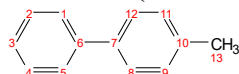
$^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ )  $\delta$  7.62 (d,  $J$  = 1.4 Hz, 1H), 7.60 (d,  $J$  = 1.1 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.39 – 7.35 (m, 1H), 7.35 – 7.31 (m, 1H), 7.19 (ddd,  $J$  = 7.7, 1.7, 1.0 Hz, 1H), 7.15 (dd,  $J$  = 2.6, 1.7 Hz, 1H), 6.92 (ddd,  $J$  = 8.2, 2.6, 0.9 Hz, 1H), 3.86 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, Methanol- $d_4$ )  $\delta$  160.1, 142.6, 141.0, 129.4, 128.3, 127.0, 126.6, 119.0, 112.2, 54.3.



$^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ )  $\delta$  7.65 – 7.50 (m, 4H), 7.45 – 7.35 (m, 2H), 7.34 – 7.24 (m, 1H), 7.05 – 6.97 (m, 2H), 3.84 (s, 3H).

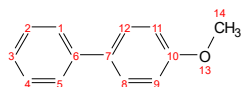
$^{13}\text{C}$  NMR (101 MHz, Methanol- $d_4$ )  $\delta$  159.3, 140.7, 133.5, 128.3, 127.5, 126.2, 126.1, 113.8, 54.3.



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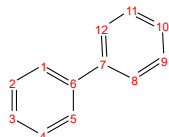
$^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ )  $\delta$  7.61 – 7.56 (m, 2H), 7.52 – 7.48 (m, 2H), 7.45 – 7.38 (m, 2H), 7.35 – 7.28 (m, 1H), 7.28 – 7.23 (m, 2H), 2.38 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, Methanol- $d_4$ )  $\delta$  141.0, 138.2, 136.7, 129.0, 128.3, 126.5, 126.4, 126.3, 19.7.



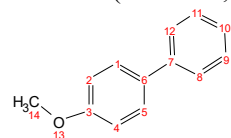
$^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ )  $\delta$  7.64 – 7.49 (m, 4H), 7.45 – 7.35 (m, 2H), 7.32 – 7.23 (m, 1H), 7.03 – 6.95 (m, 2H), 3.84 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz, Methanol- $d_4$ )  $\delta$  159.3, 140.7, 133.5, 128.3, 127.5, 126.2, 126.1, 113.8, 54.3.



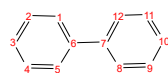
$^1\text{H}$  NMR (400 MHz, Methanol- $d_4$ )  $\delta$  7.67 – 7.58 (m, 4H), 7.50 – 7.39 (m, 4H), 7.38 – 7.29 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz, Methanol- $d_4$ )  $\delta$  141.1, 128.4, 126.8, 126.5.



$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.63 – 7.52 (m, 4H), 7.50 – 7.41 (m, 2H), 7.37 – 7.29 (m, 1H), 7.04 – 6.98 (m, 2H), 3.89 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

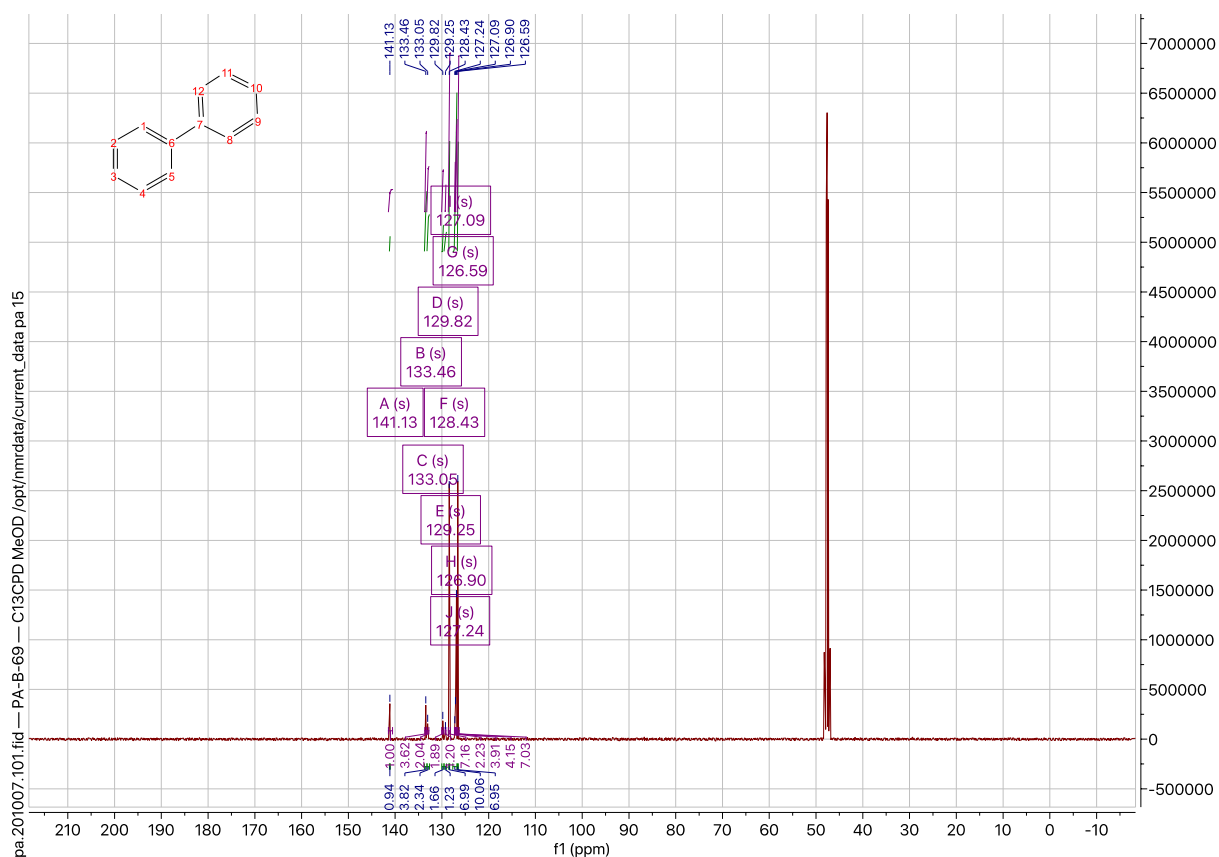
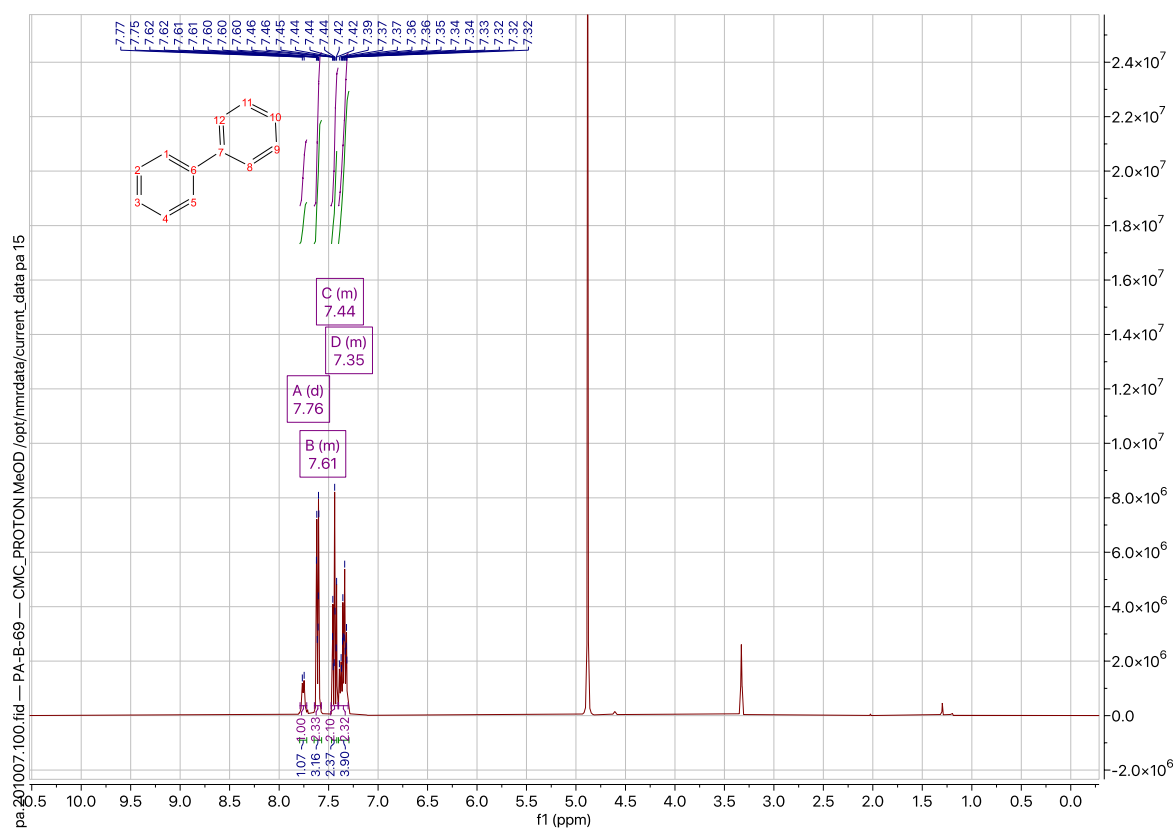


$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.68 – 7.58 (m, 4H), 7.54 – 7.42 (m, 4H), 7.43 – 7.34 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  141.2, 128.7, 127.2, 127.1.

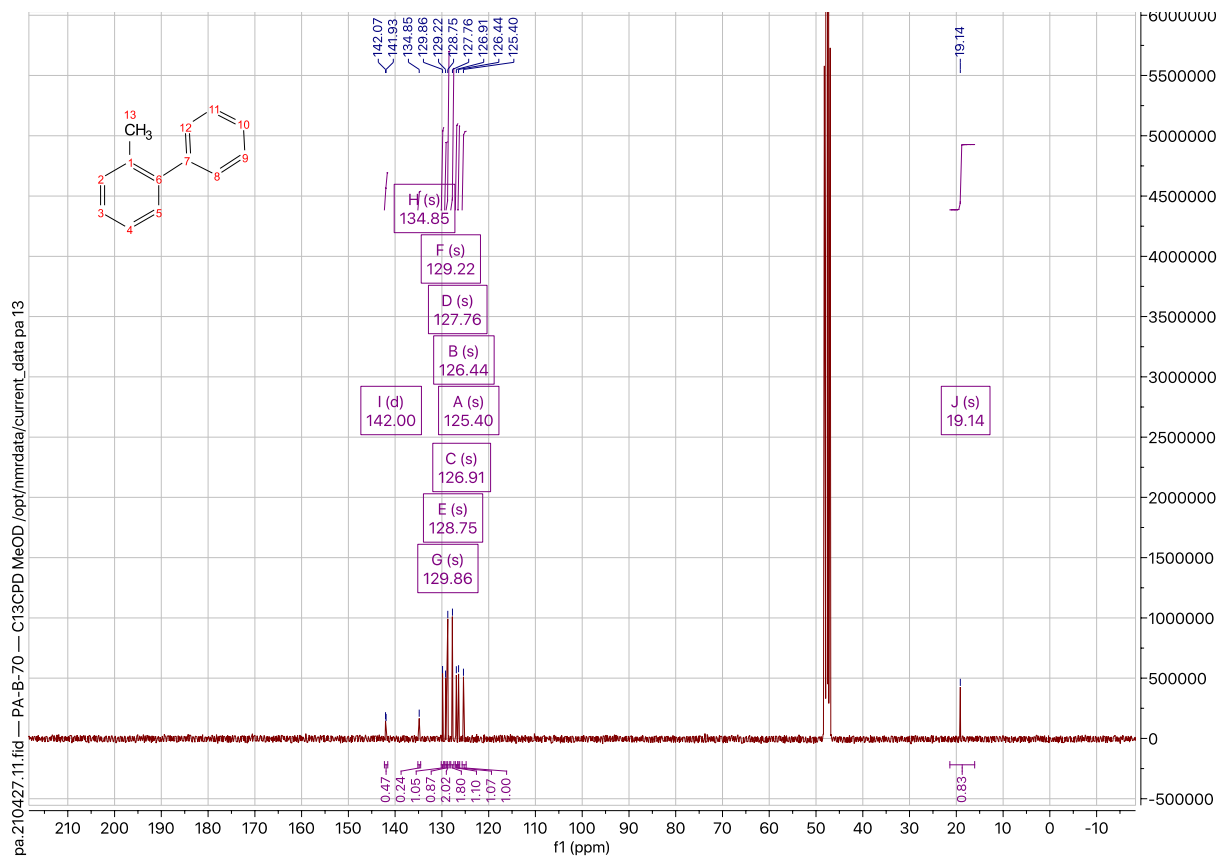
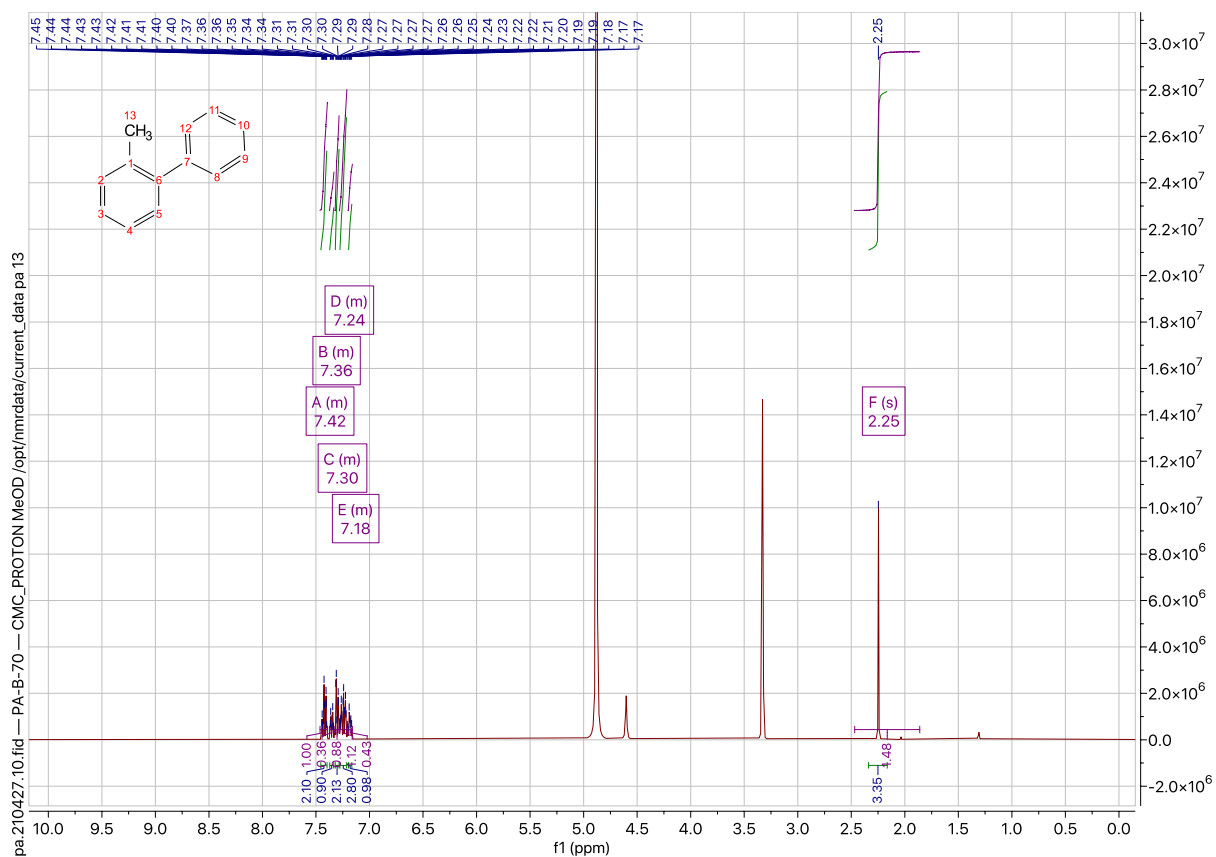
## Spectral data

This version of the ESI published on 21/11/2022 replaces the original version published on 31/10/2022. In the original ESI, the turnover numbers (TONs) were incorrectly given as  $10^3$ , rather than  $10^4$

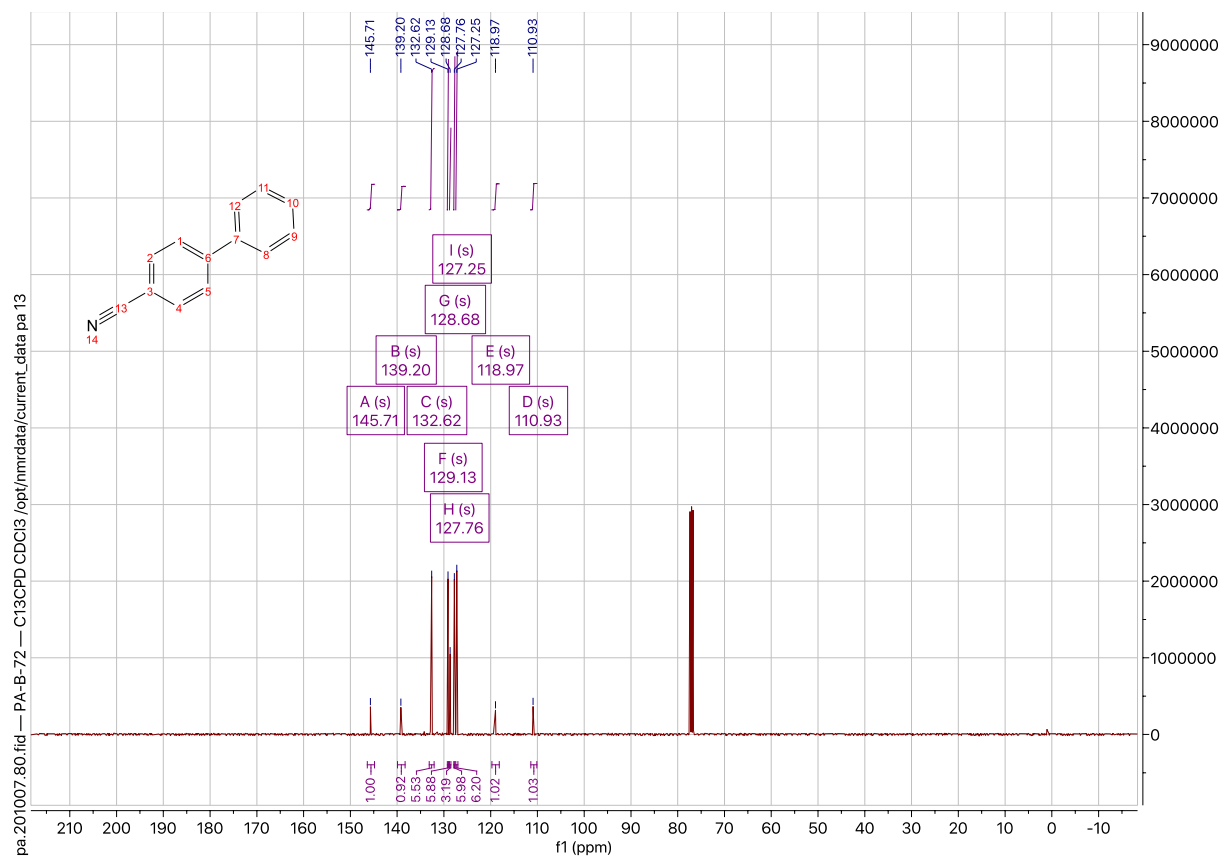
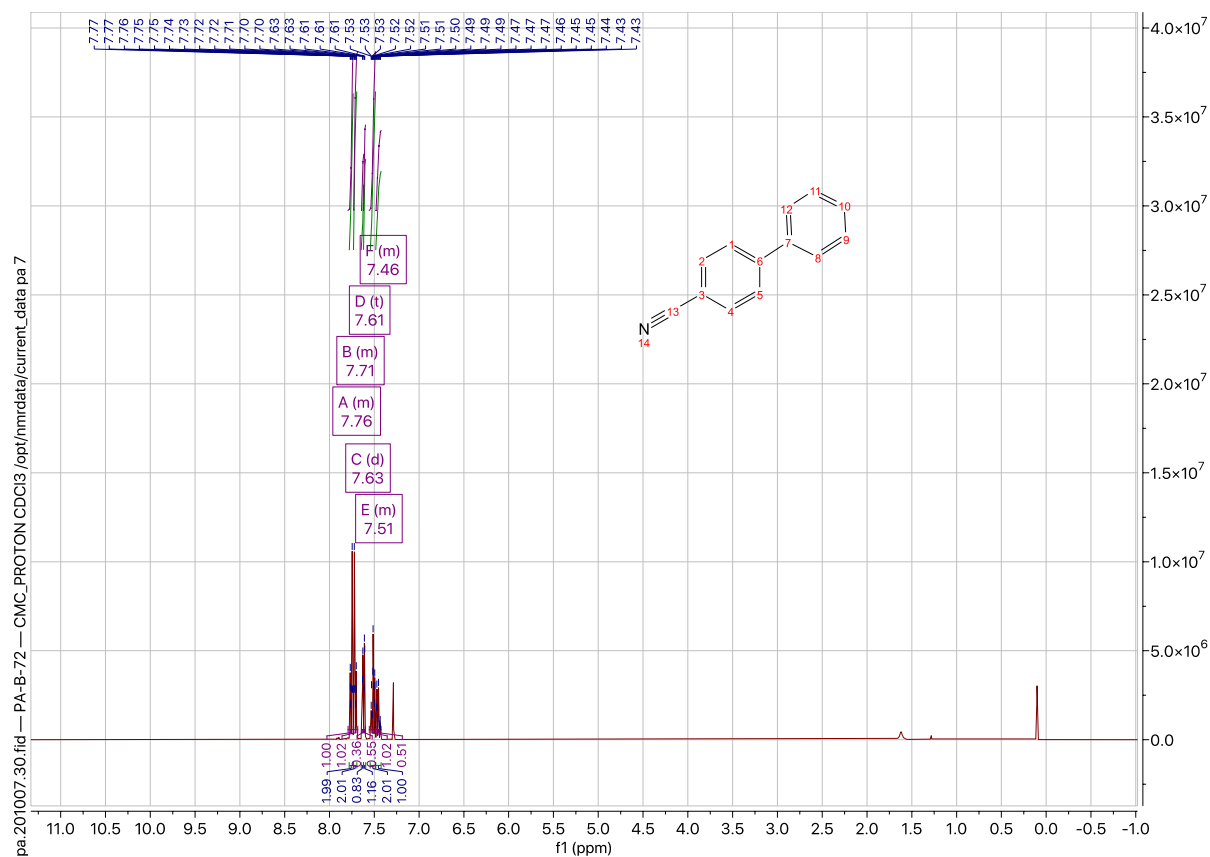




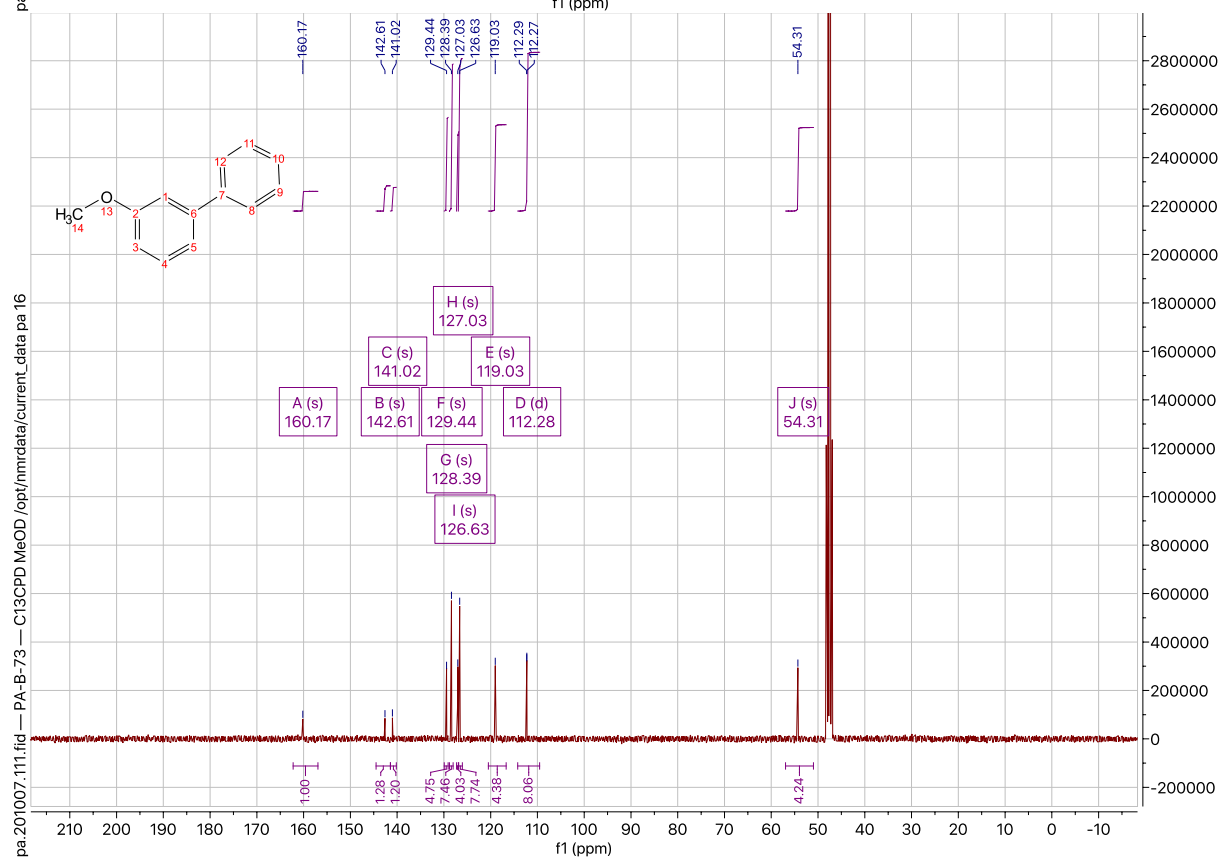
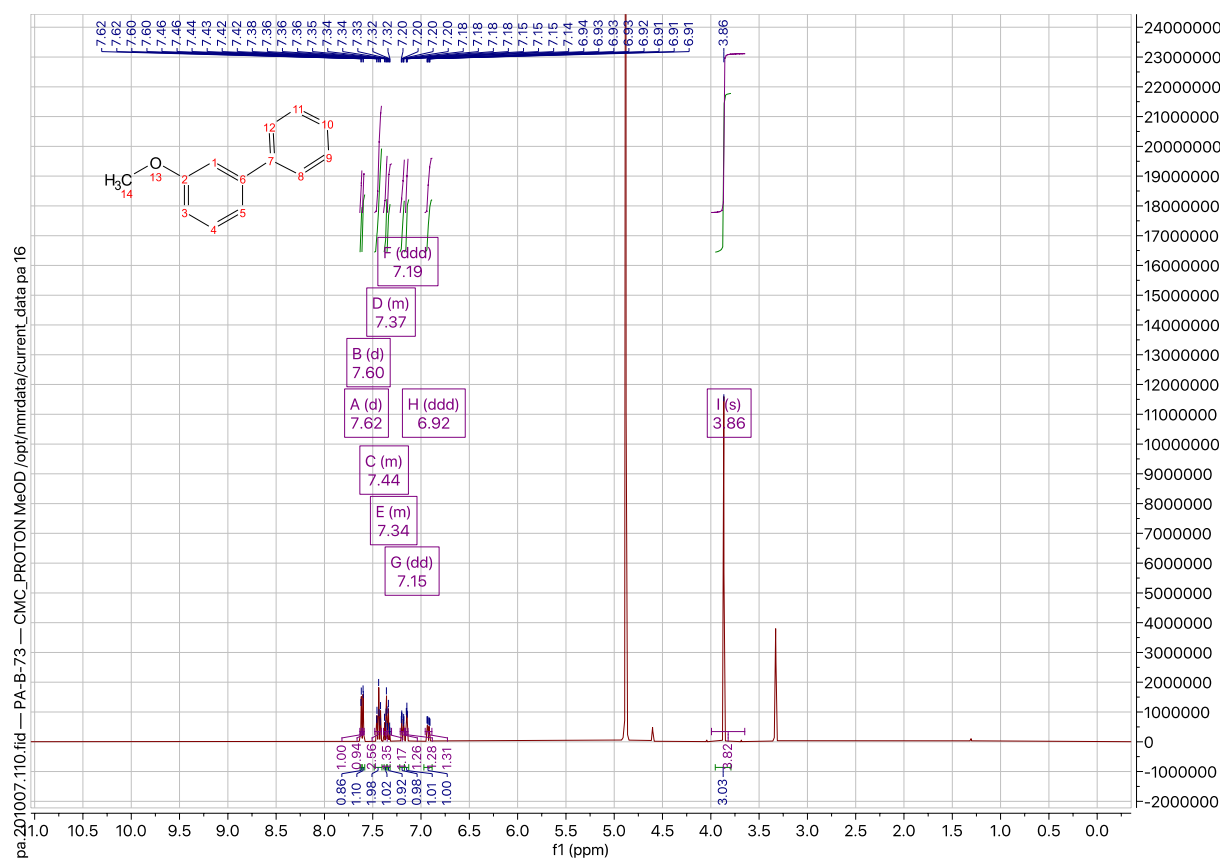
This version of the ESI published on 21/11/2022 replaces the original version published on 31/10/2022. In the original ESI, the turnover numbers (TONs) were incorrectly given as  $10^3$ , rather than  $10^4$



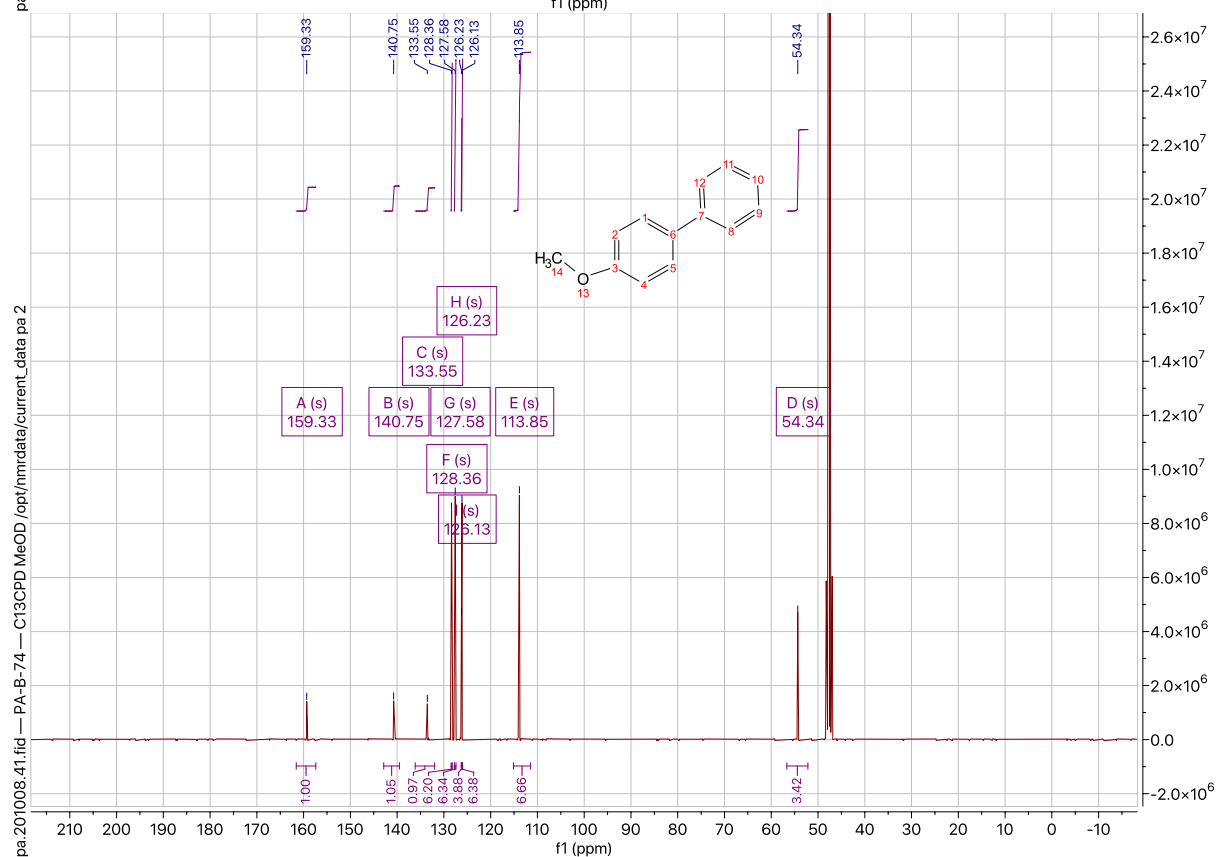
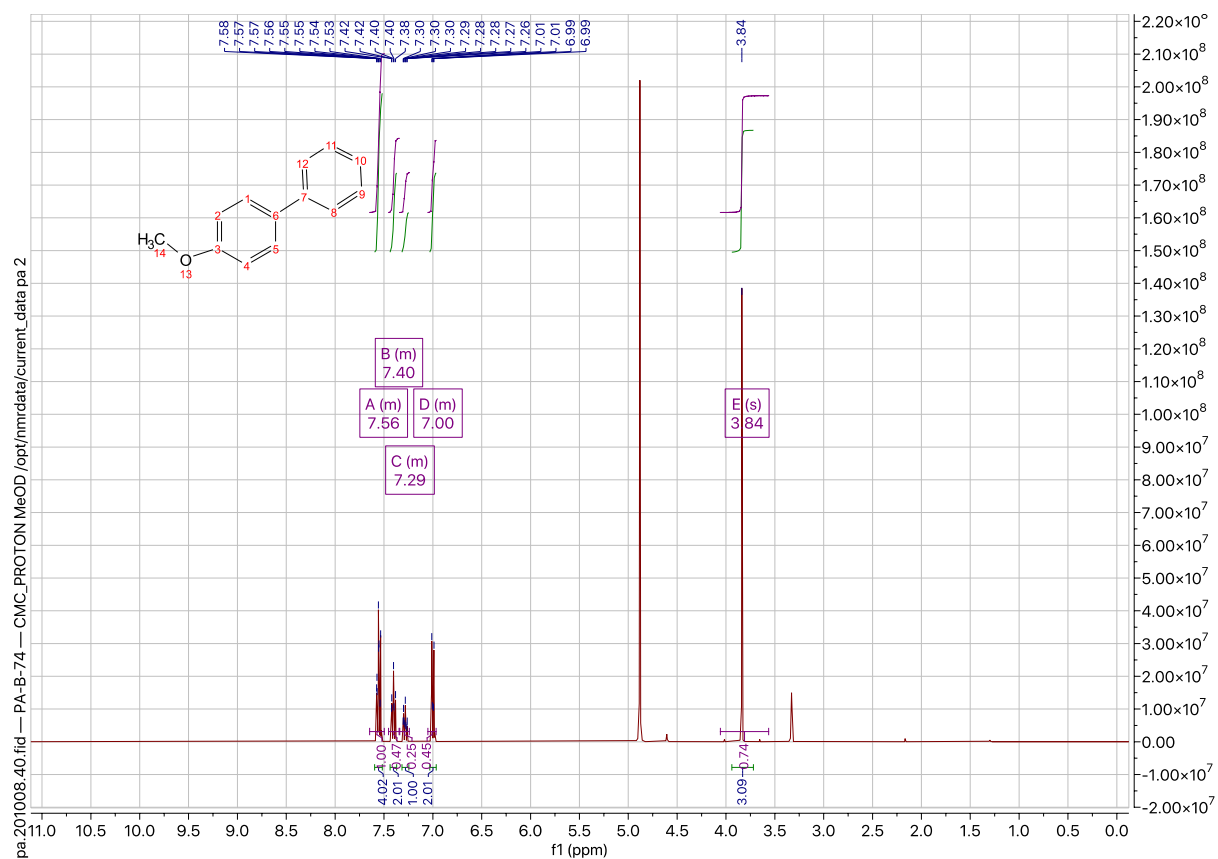
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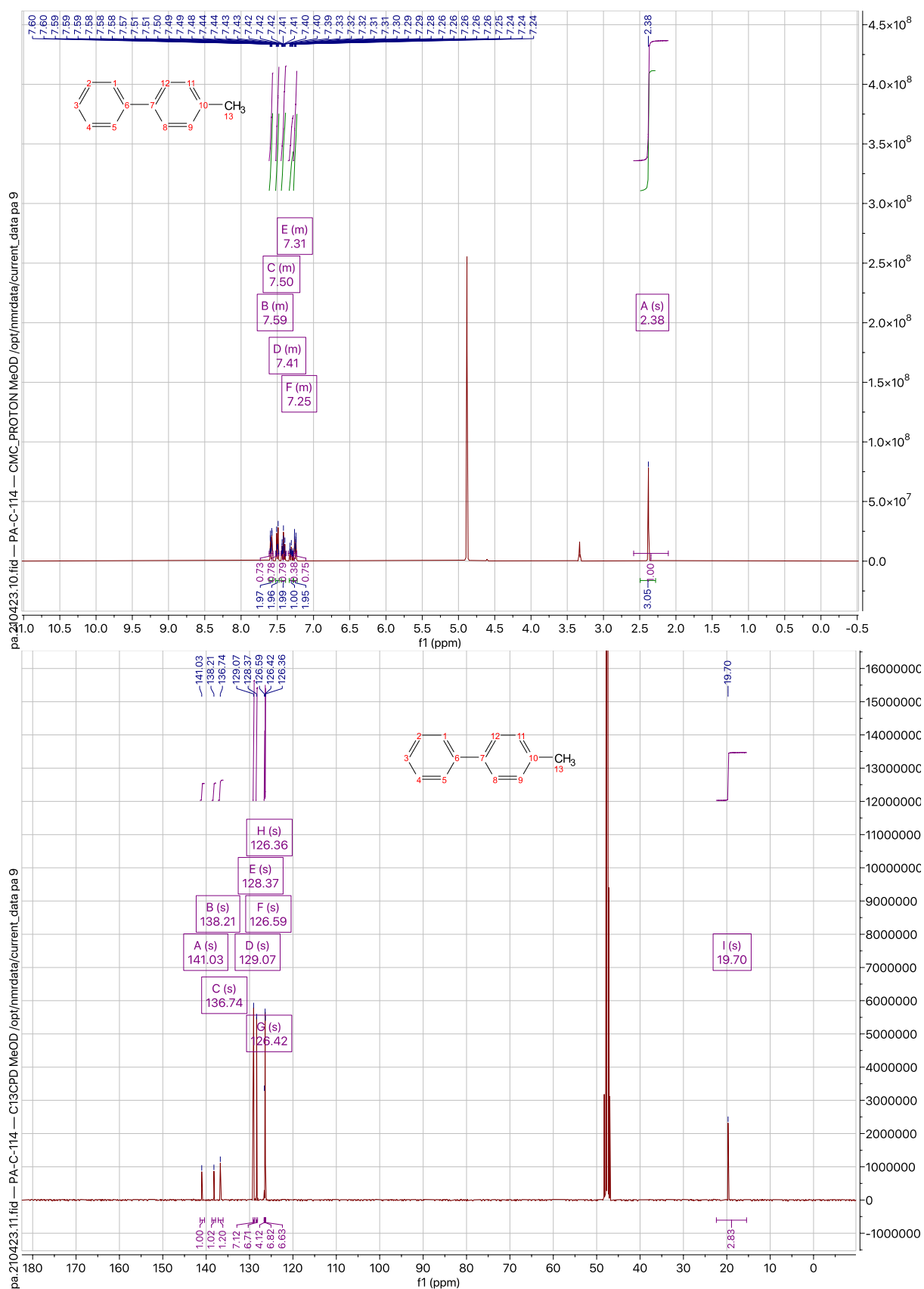
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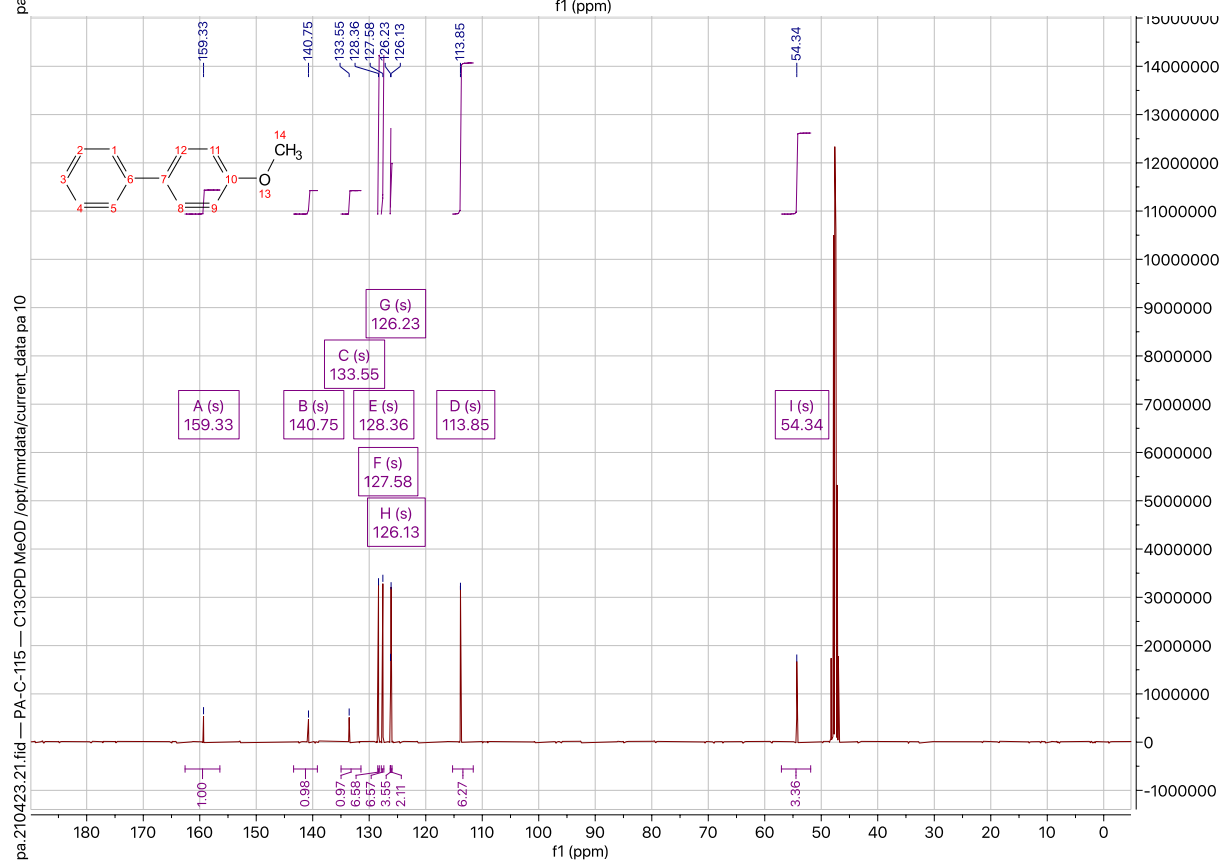
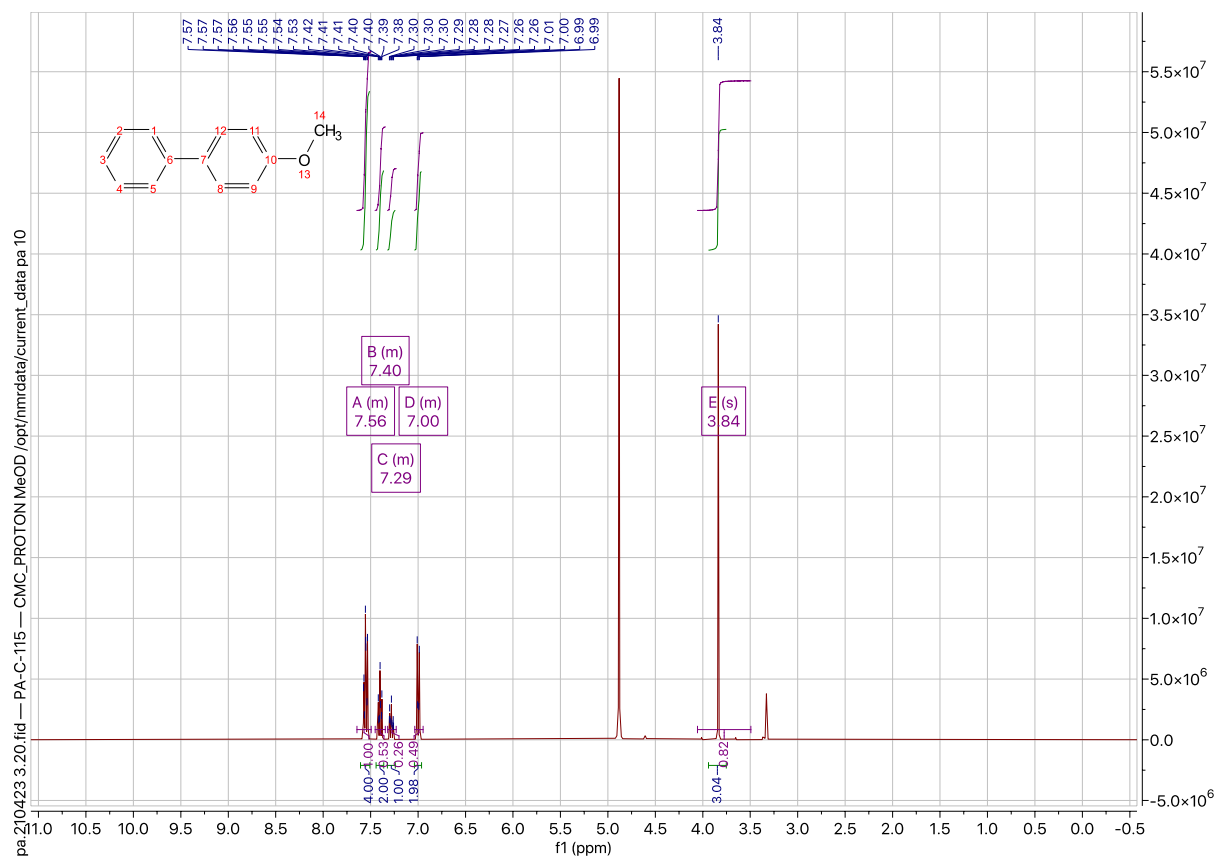
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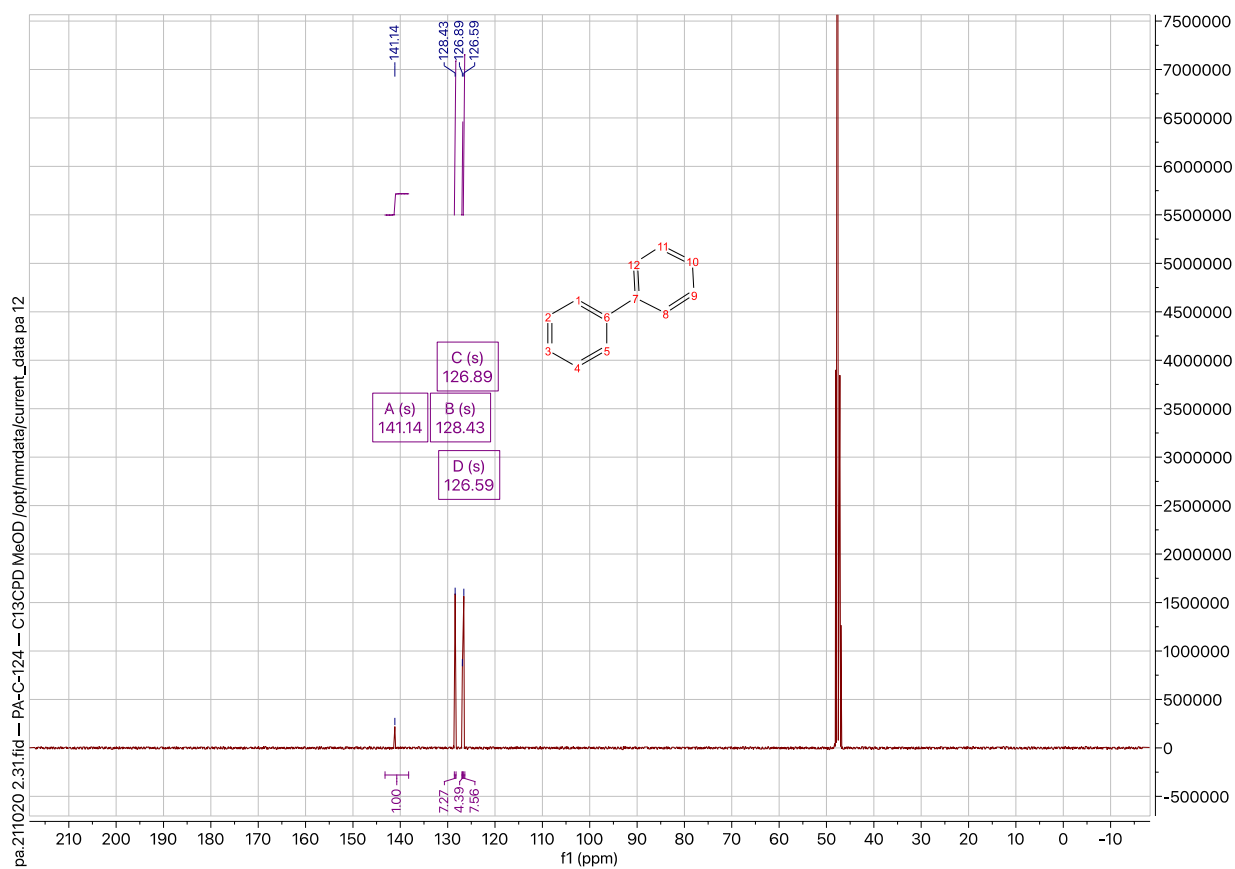
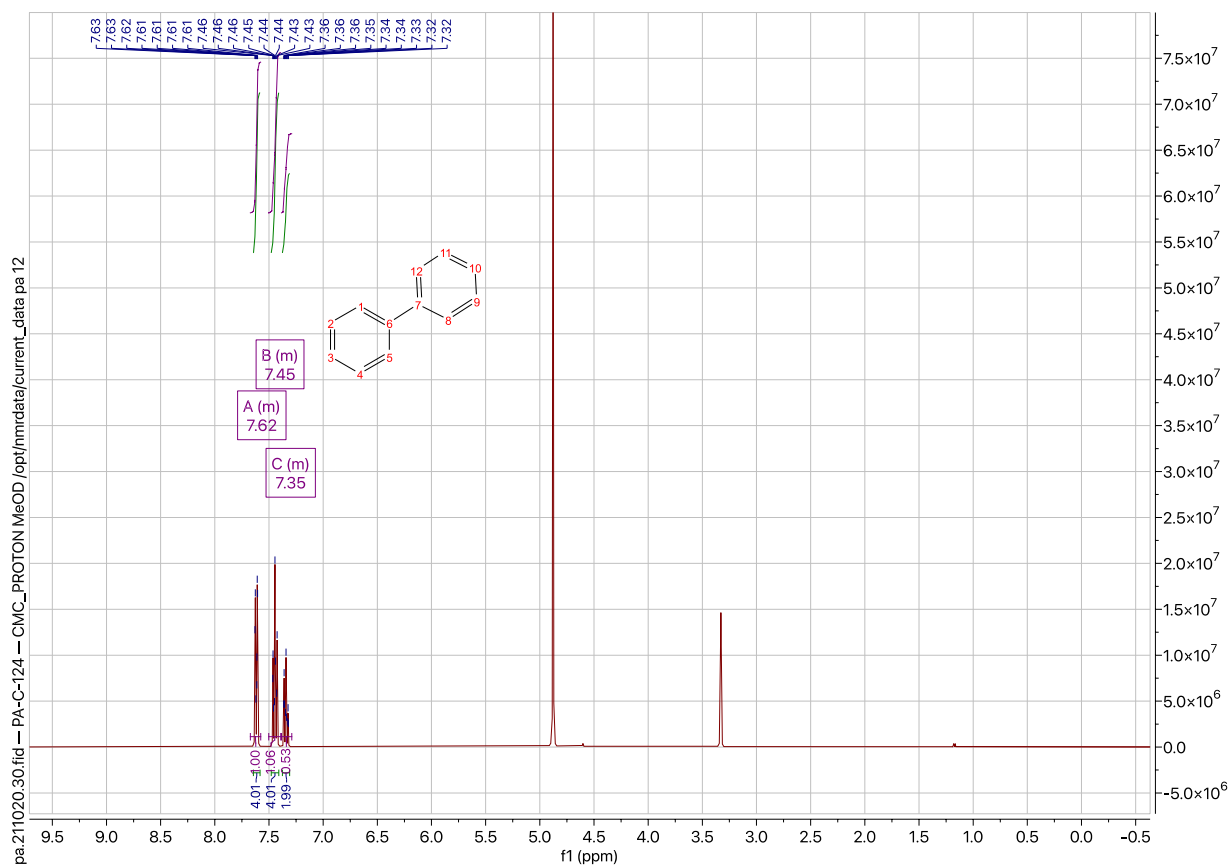
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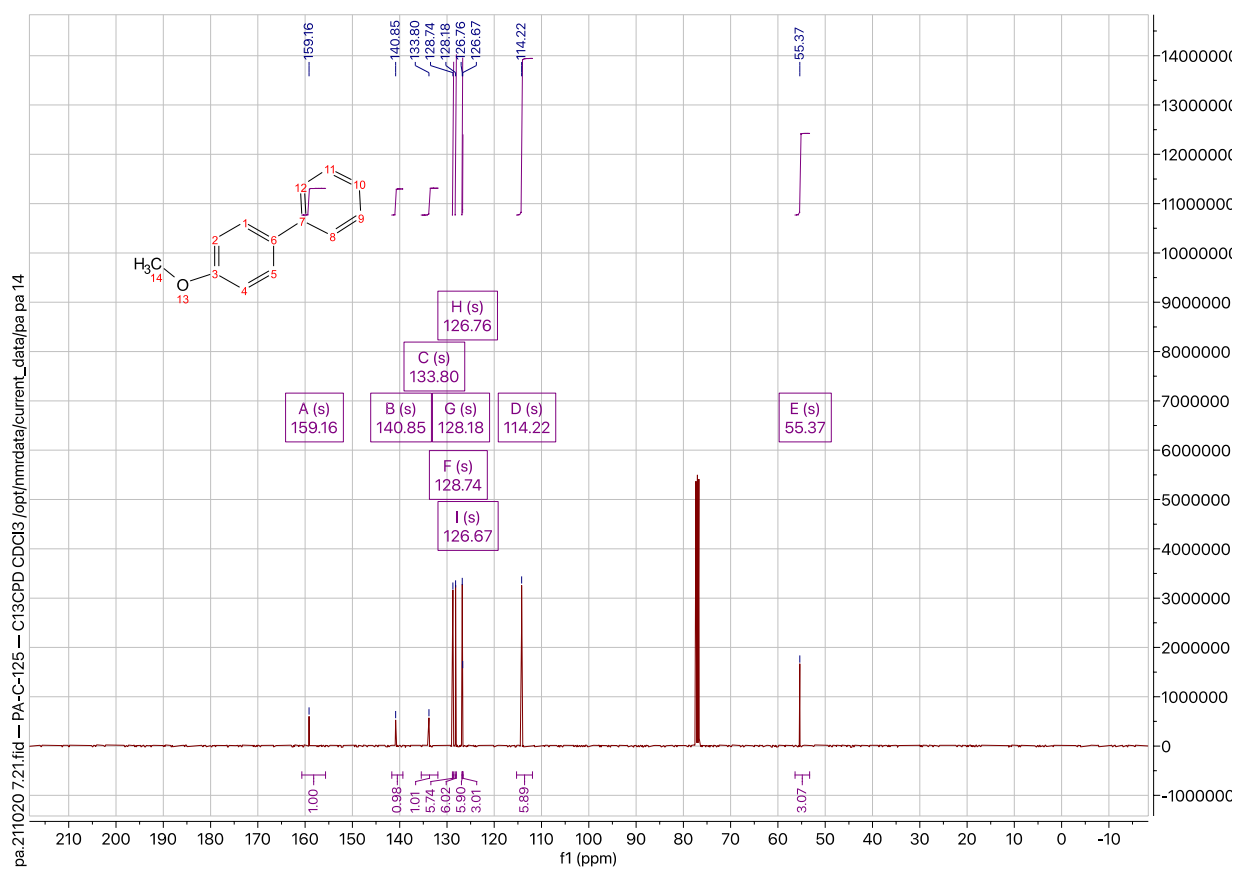
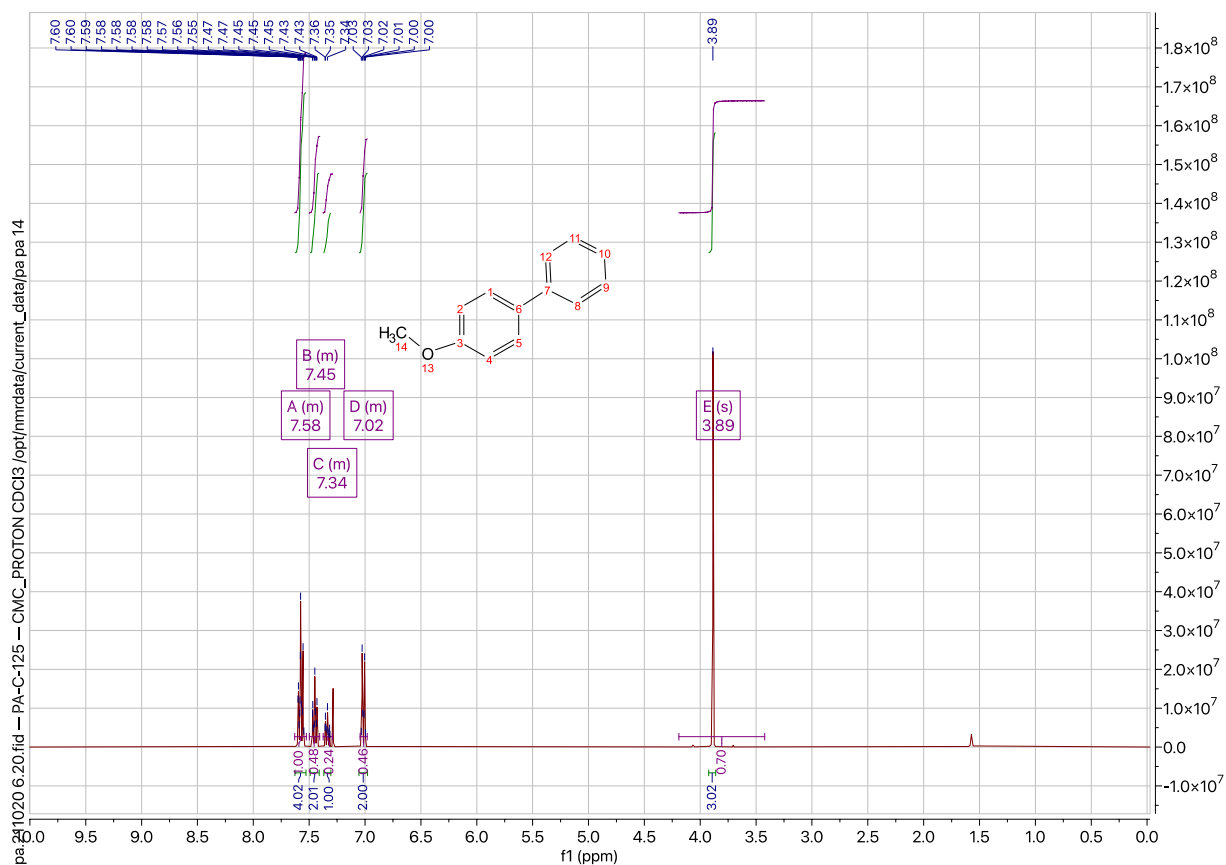
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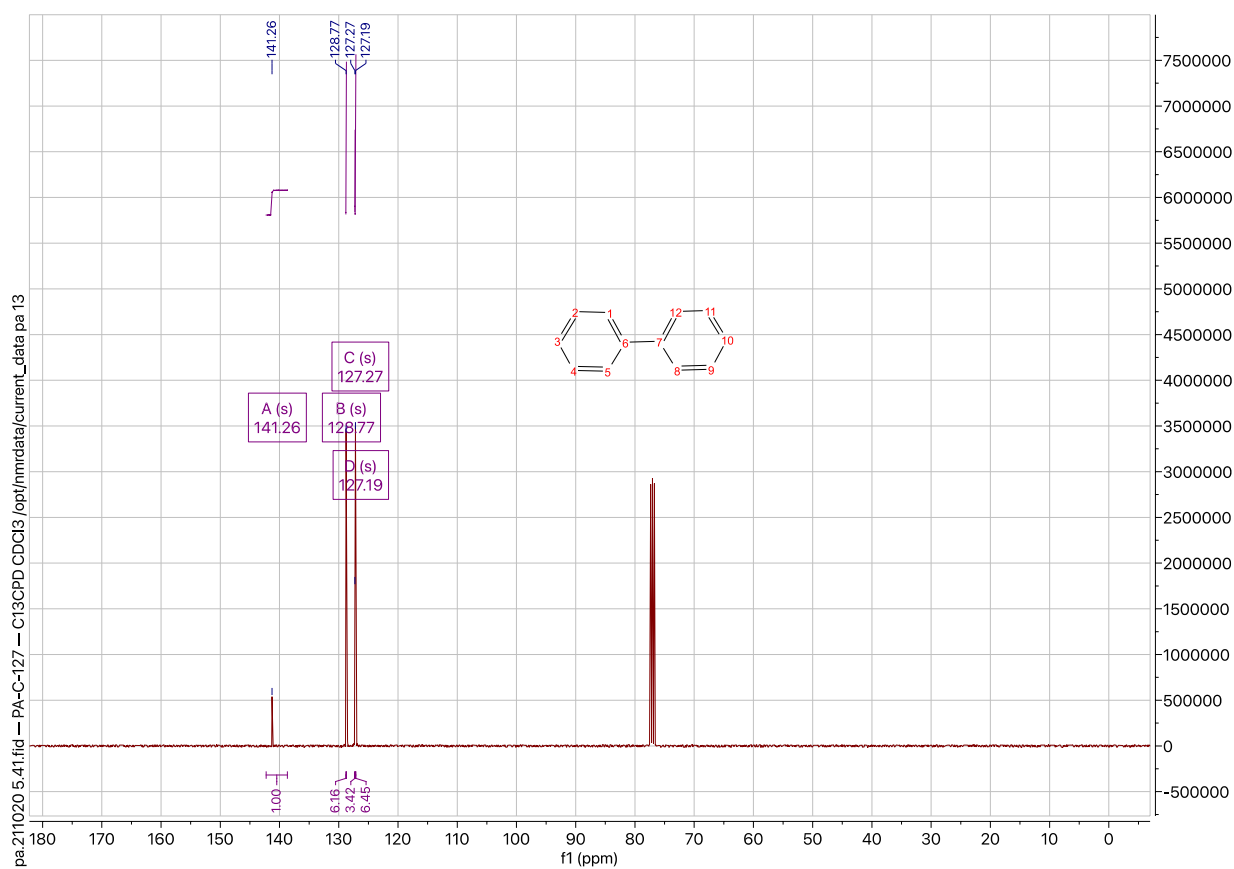
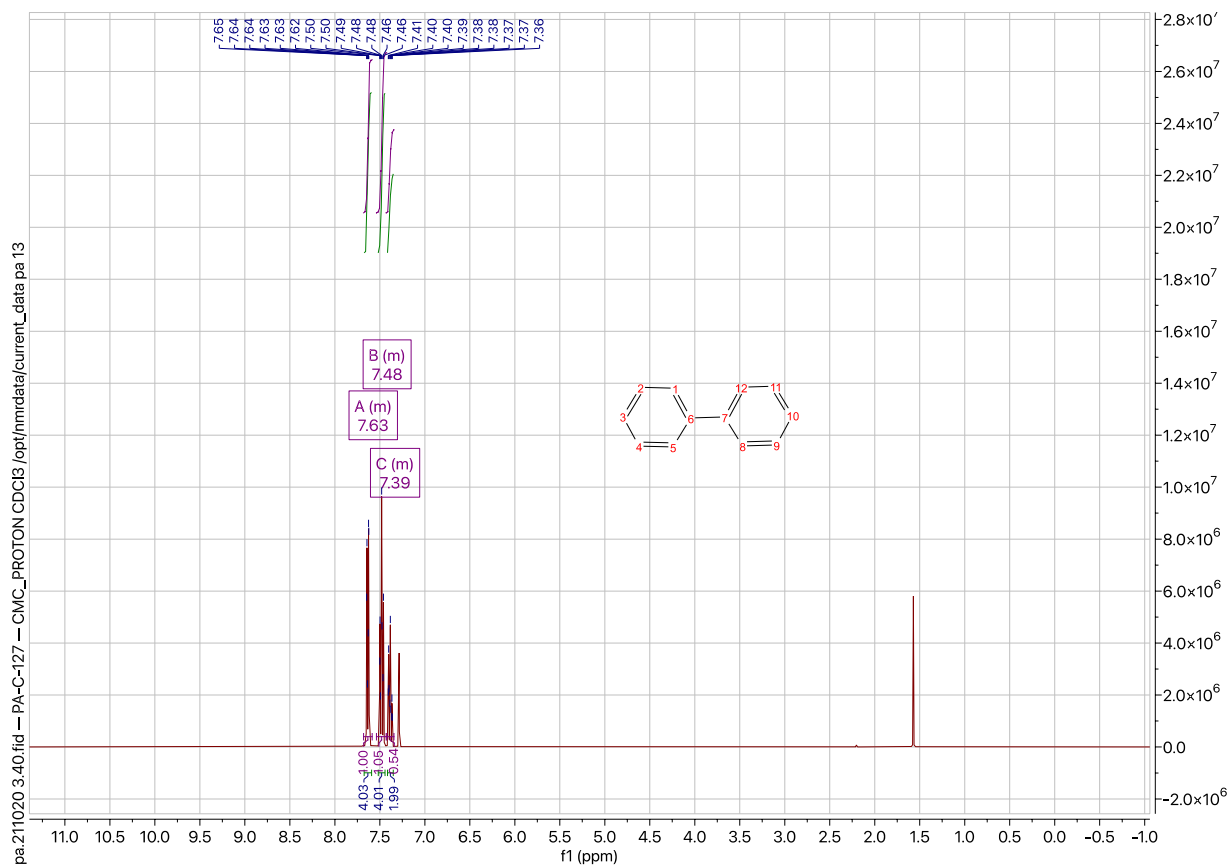


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