Progressive release of a palladium-pyridyl complex from a Layer-by-layer multilayer and illustrative application to catalytic Suzuki coupling

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Materials

Poly(ethylenimine) (PEI, MW = 6,0000, 50 wt% aqueous solution), 4,4'-azopyridine (azpy), 4-bipyridine (bpy), 1, 2-bis(4-pyridyl)ethane) (bpe) and 1, 3-di(4-pyridyl)propane) (dpp) were purchased from Aldrich Chemical Co. All reagents were used as received, and solutions were prepared with deionized water (Milli-Q, 18.2 MΩ cm).

Instruments and characterization

UV-vis absorption spectra were recorded on a quartz slide with a Lambda35 spectrophotometer (Perkin-Elmer, USA). High-resolution X-ray photoelectron spectra (XPS) were collected at a takeoff angle of 45° using PHI Quantum 2000 scanning ESCA microprobe (Physical Electronics, USA) with an Alα X-ray line (1486.6 eV). All AFM images were taken on a single-crystal silicon slide using a Veeco Multimode NS3A-02NanoscopeⅢ atomic force microscope with silicon tips. Height images of the films were recorded using tapping-mode AFM. Gas chromatography-mass spectrometry (GC-MS) was performed on 430 GC (Varian, USA). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker AVANCE 400 spectrometer. Analysis of Pd content was measured by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) using Ultima.

Layer-by-layer assembly PEI-(Pd/Azpy)$_n$ multilayer films

The quartz slides (size 25 mm × 12 mm × 1 mm) (or single-crystal silicon slides) were cleaned with a "piranha solution" at 80 ℃ for 40 min, and thoroughtly rinsed with distilled water. Further purification was carried out by immersion in a $H_2O/H_2O_2/NH_3OH$ (5:1:1) (V/V/V) bath for 30 min at 70 ℃. The clean slides were first immersed in PEI solution for 20 min. The slides pre-coated with PEI were alternately immersed in $PdCl_2$ (or K_2PdCl_4 or $Pd(OAc)_2$) aqueous solution (5 mM, 10 ml) and Azpy (2 mM, 10 ml) solution for 30 min. Between each immersion step, the substrates were washed with water and dried with nitrogen stream. By repeating the two steps, PEI-$(PdCl_2/Azpy)_n$, PEI-$(K_2PdCl_4/Azpy)_n$ and PEI-$(Pd(OAc)_2/Azpy)_n$ multilayer films were prepared, respectively.

Layer-by-layer assembly PEI-$(PdCl_2$/pyridyl ligand$)_n$ multilayer films

The quartz slides (size 25 mm × 12 mm × 1 mm) were cleaned with a "piranha solution" at 80 ℃ for 40 min, and thoroughtly rinsed with distilled water. Further purification was carried out by immersion in a $H_2O/H_2O_2/NH_3OH$ (5:1:1) (V/V/V) bath for 30 min at 70 ℃. The clean slides were first immersed in PEI solution for 20 min. The slides pre-coated with PEI were alternately immersed in $PdCl_2$ aqueous solution (5 mM, 10 ml) and bpy (or bpe or dpp) (2 mM, 10 ml) ethanol solution for 30 min. Between each immersion step, the substrates were washed with water and dried with nitrogen stream. By repeating the two steps, PEI-$(PdCl_2/bpy)_n$, PEI-$(PdCl_2/bpe)_n$ and PEI-$(PdCl_2/dpp)_n$ multilayer films were prepared, respectively.

General procedure for the Suzuki coupling reactions (Table 1)

General procedure for the coupling reactions of aryl halides with arylboronic acid is as follows: Aryl halide (1.0 mmol), arylboronic acid (1.05 mmol), K_2CO_3 (3.0 mmol), the quartz slide with $(PdCl_2/Azpy)_8$ film (size 25 mm × 12 mm × 1 mm), EtOH (3 ml) and H_2O (4 ml) were introduced to a flask under ambient atmosphere. After the mixture was stirred under certain temperature for a certain time, the resultant mixture was extracted three times with ethyl acetate (10 ml). The organic phase was combined together and washed with brine. The organic layer was dried over Na_2SO_4, filtered, and the organic

solvent was removed under reduced pressure. The biaryl product was characterized by gas chromatography-mass spectrometry (GC-MS). The final products were purified by column chromatography on silica gel (hexane or ethyl acetate/hexane 1:8) to afford the desired products. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ solutions. For 4-Biphenylcarboxylic acid, the final product was recrystallized from ethanol-water. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of 4-Biphenylcarboxylic acid were recorded using DMSO-d_6 as solvent.

The release property of $(PdCl_2/Azpy)_n$ multilayer films

The quartz slide coated with $(PdCl_2/Azpy)_8$ was immersed into a K_2CO_3 (3 mmol), EtOH (3 ml) and H_2O (4 ml) mixed solution for 30 min, 60 min, 90 min, 120 min and 150 min, respectively. After immersing, the coated quartz slide was used for UV-vis determination to monitor the change of films.

Preparation of Pd-Azpy precipitates

$PdCl_2$ (5mM) aqueous solution was mixed with Azpy (2mM) aqueous solution and Pd-Azpy precipitates were obtained. Pd-Azpy precipitates were collected by centrifugal separation, washed with H_2O and EtOH, and dried at 50 ℃ for 6 h.

The release property of Pd-Azpy precipitates

Pd-Azpy precipitates (3 mg) were immersed into a K_2CO_3 (3 mmol), EtOH (3 ml) and H_2O (4 ml) mixed solution for 60 min. Pd-Azpy precipitates were collected by centrifugal separation. The mixed solution was used for Pd determination.

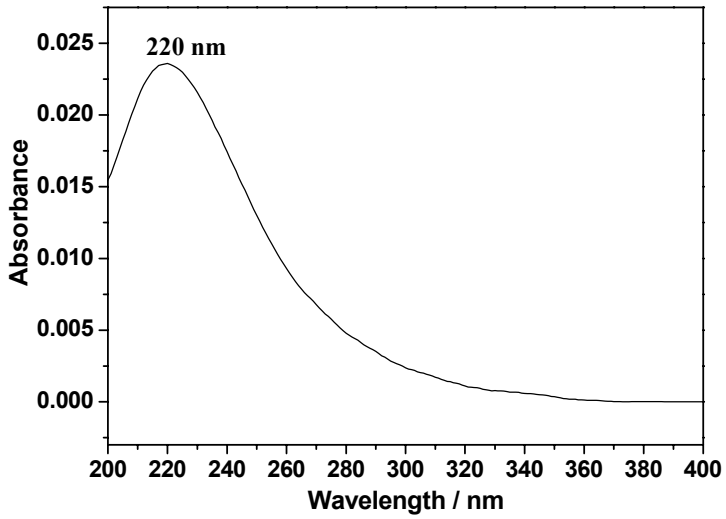


Fig.S1 UV-vis spectrum of the PEI/Pd（Ⅱ）film.

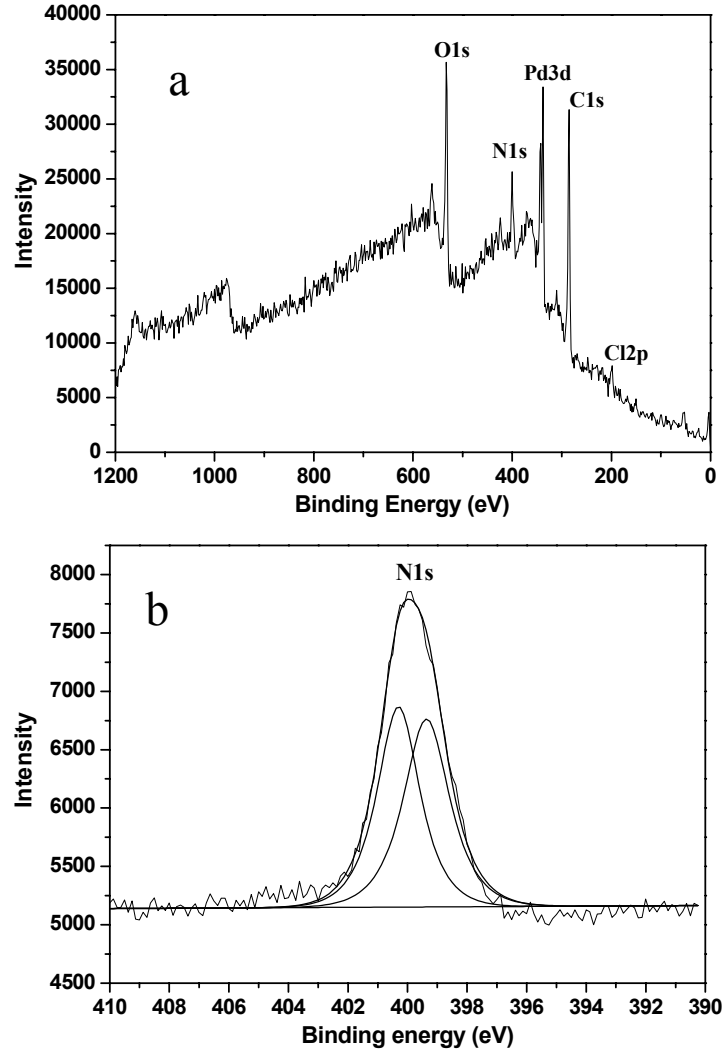


Fig.S2 XPS spectrum of a $(PdCl_2/Azpy)_5$ film deposited on the single-crystal silicon substrate (a) survey, (b) N_{1s}

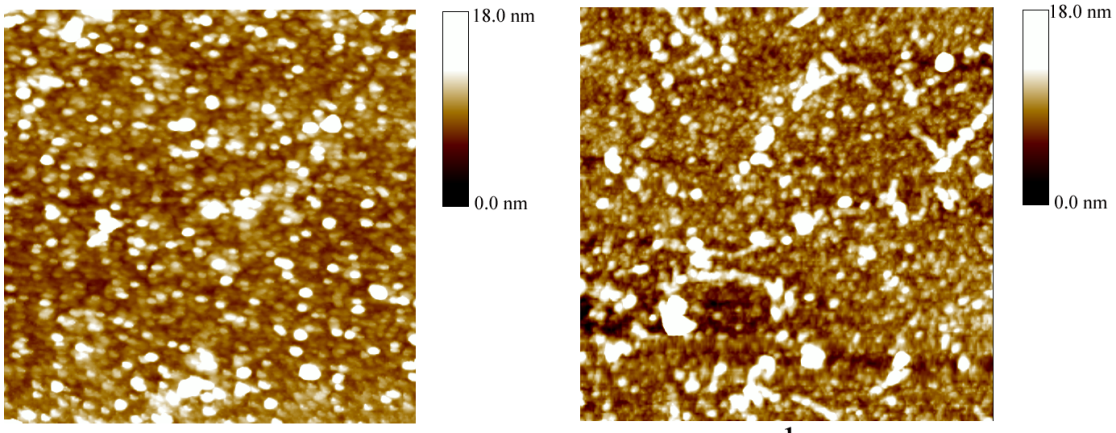
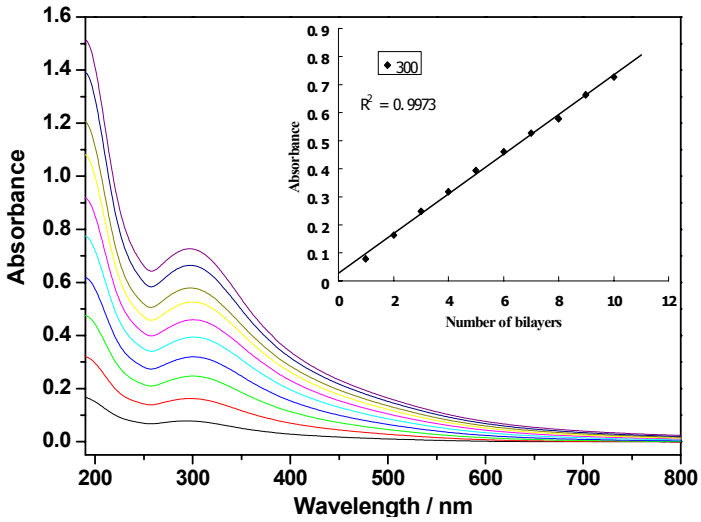
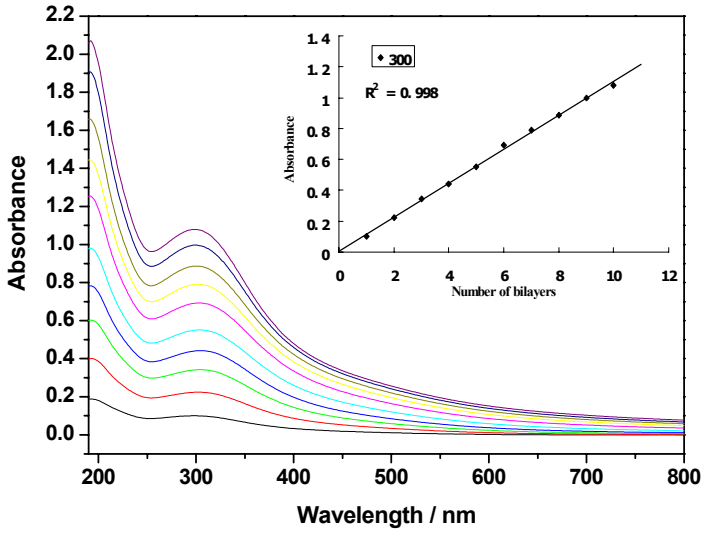


Fig. S3 Typical height images of the films (scan area is 1.0 × 1.0 μm^2). a: PEI-$(PdCl_2/Azpy)_5$, b: PEI-$(PdCl_2/Azpy)_{10}$

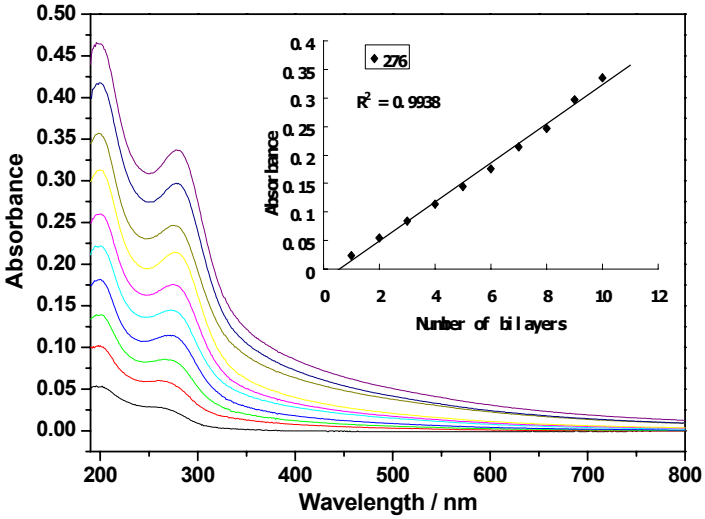


(a)

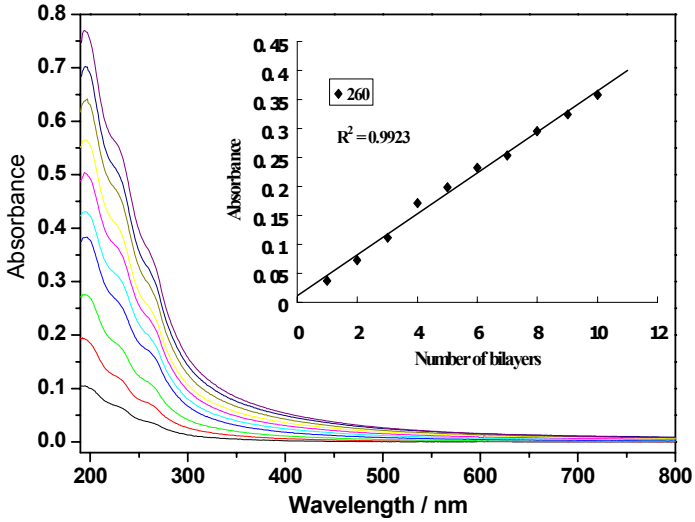


(b)

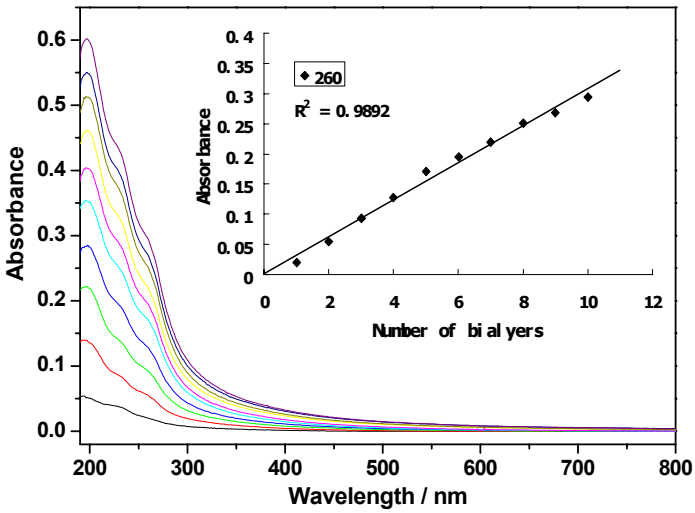
Fig.S4 UV-vis spectra of the (Pd/Azpy)n films. (a) K_2PdCl_4; (b) $Pd(OAc)_2$. Inset: increase in the absorbance at 300 nm as a function of the number of layers of Pd/Azpy



(a) PEI-$(PdCl_2/bpy)_n$



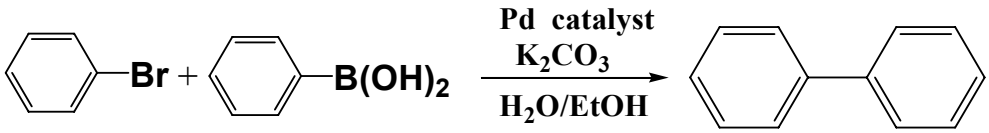
(b) PEI-$(PdCl_2/bpe)_n$



(c) PEI-$(PdCl_2/dpp)_n$

Fig. S5 UV-vis spectra of films. Inset: increase in the absorbance as a function of the number of layers of $PdCl_2$/pyridyl ligand

Table S1 Suzuki cross-coupling of aryl bromide with phenylboronic acid using Pd-azpy complex catalyst-loaded quartz slide



Entry	Catalyst	Time (h)	Yield (%)[a]
1	$(PdCl_2/Azpy)_{10}$	1	96
2	$(Pd(OAc)_2/Azpy)_{10}$	1	96
3	$(K_2PdCl_4/Azpy)_{10}$	1	80

General procedure: 1 mmol of aryl bromide, 1.05 mmol of $PhB(OH)_2$, 3 mmol of K_2CO_3, in H_2O /EtOH (4:3) at 50 ℃ under ambient atmosphere, [a] Determined by GC.

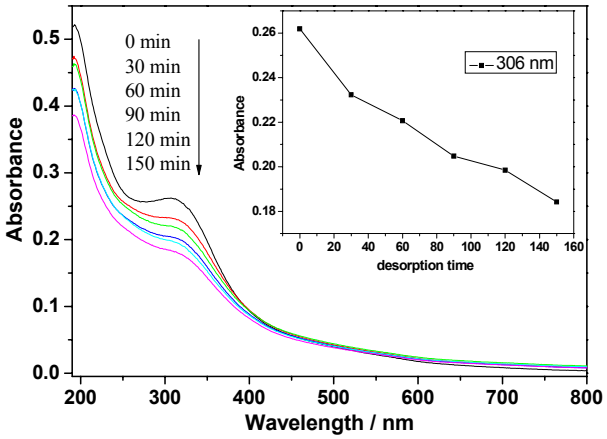
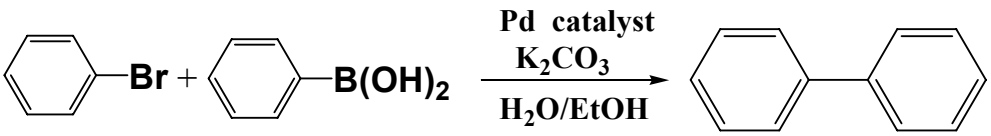


Fig. S6 UV-vis spectra of $(PdCl_2/Azpy)_8$ multilayer at different desorption time. Inset: decrease in the absorbance at 306 nm as a function of the desorption time

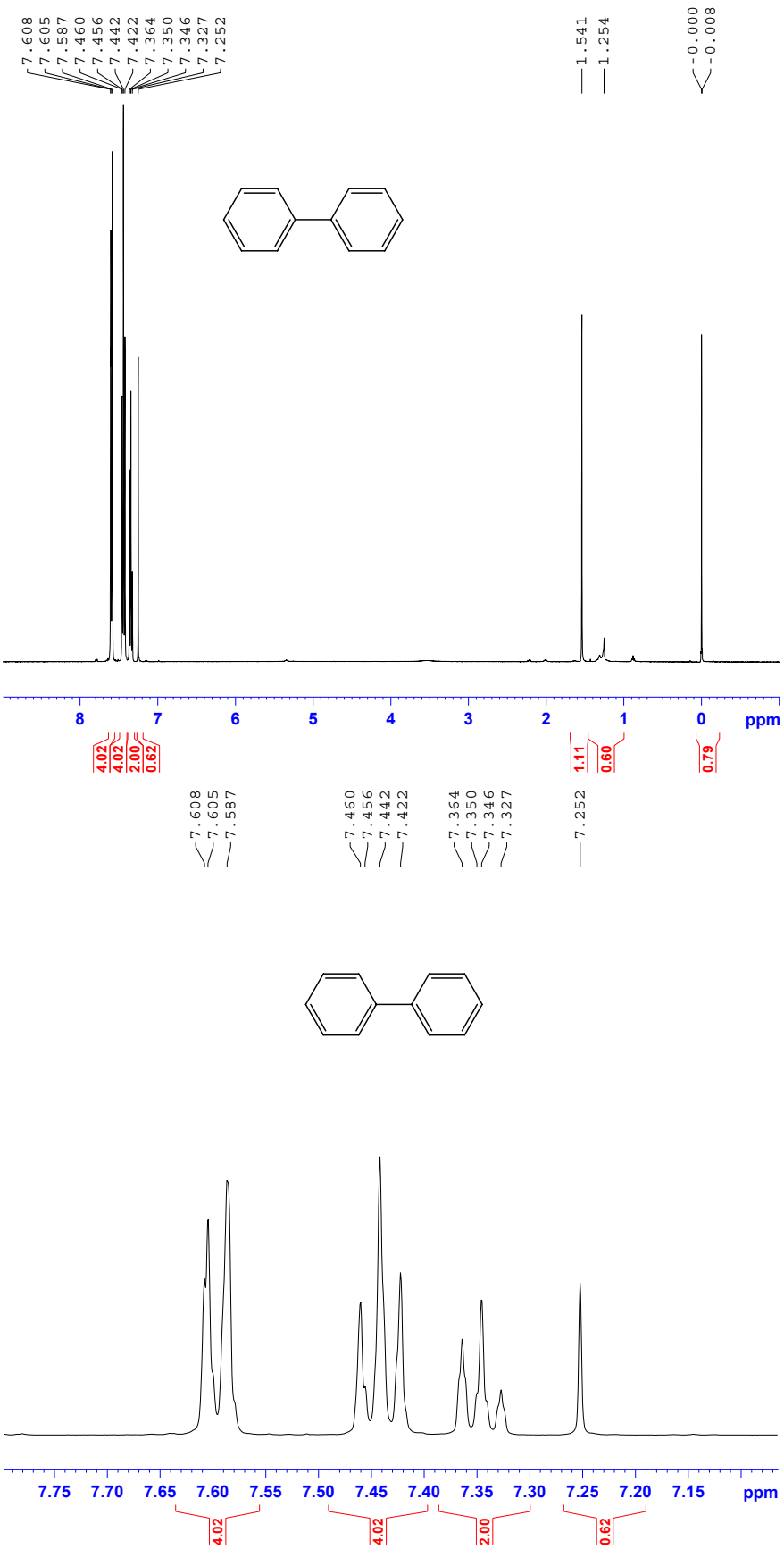
Table S2 Suzuki cross-coupling of aryl bromide with phenylboronic acid using Pd-azpy complex catalyst released from $(Pd/Azpy)_8$ films

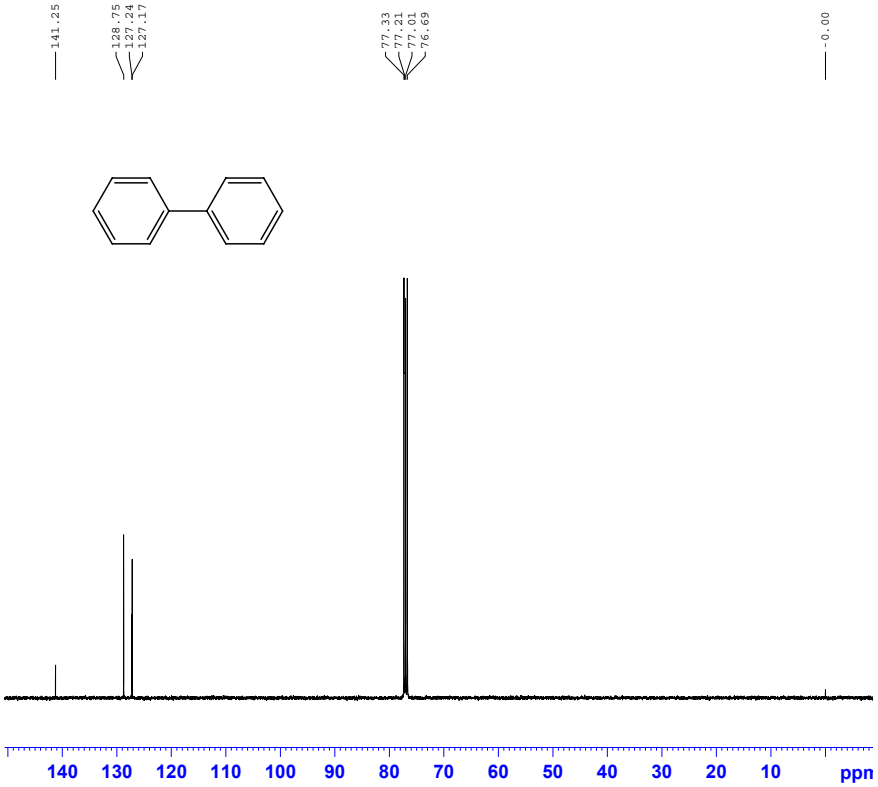


Entry	Run	Yield [a] (%)
1	1st	100%
2	2nd	99%
3	3rd	100%
4	4th	100%
5	5th	100%

General procedure: 1 mmol of aryl bromide, 1.05 mmol of $PhB(OH)_2$, 3 mmol of K_2CO_3, in H_2O /EtOH (4:3) at 50 ℃ under ambient atmosphere for 20 h, [a] Determined by GC.

^{1}H NMR and ^{13}C NMR Spectra of the products

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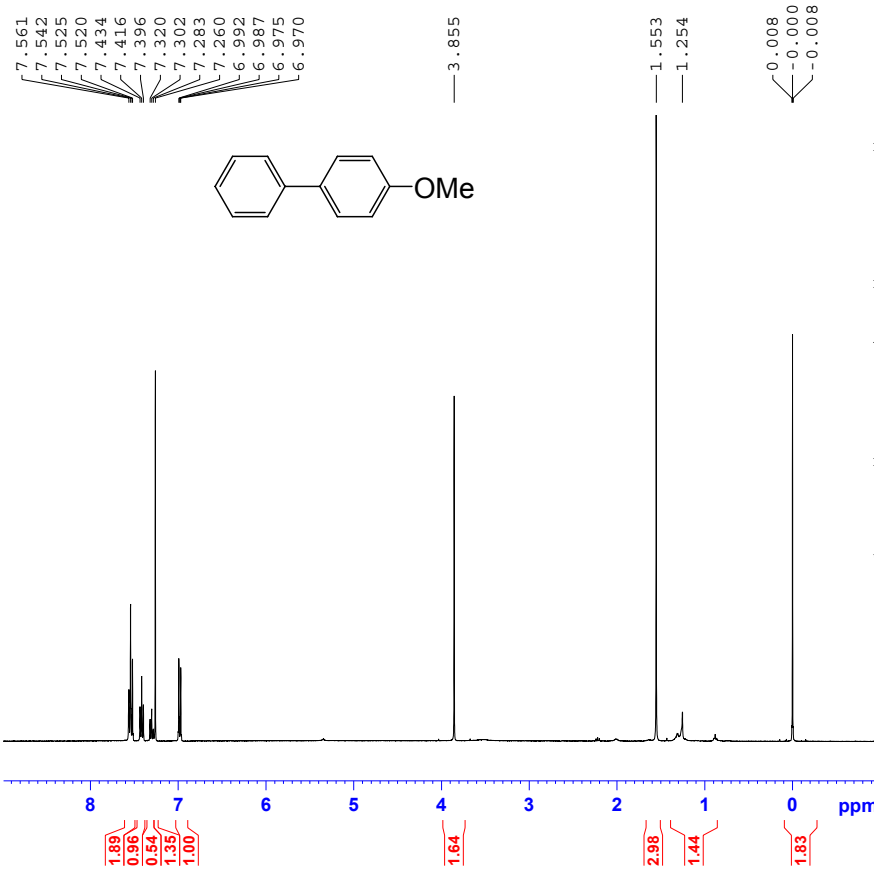
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6.975
6.970
3.855
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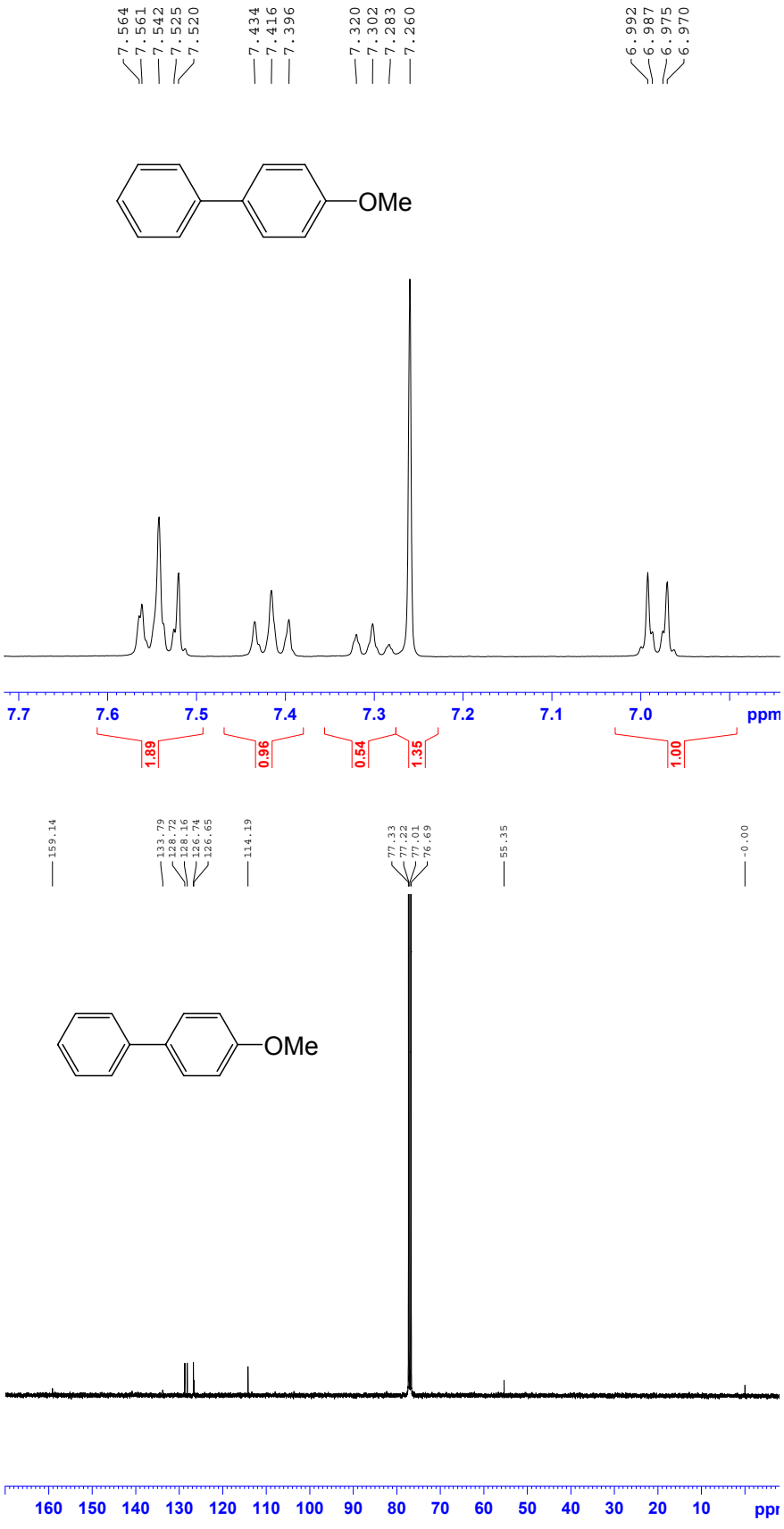
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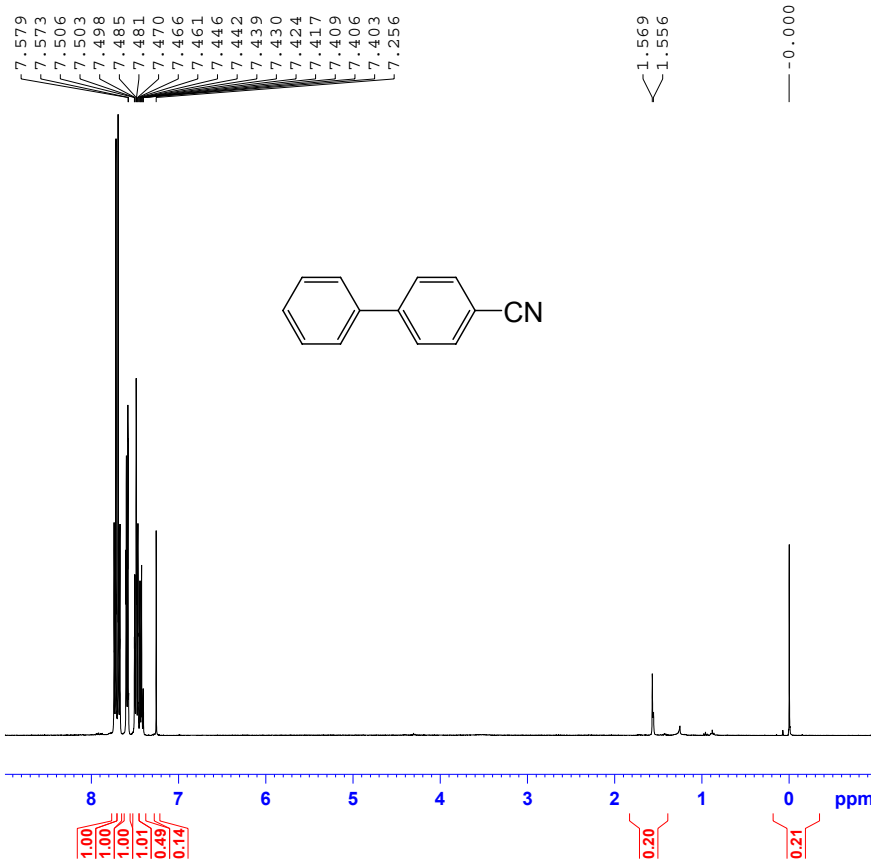
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7.430
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7.417
7.409
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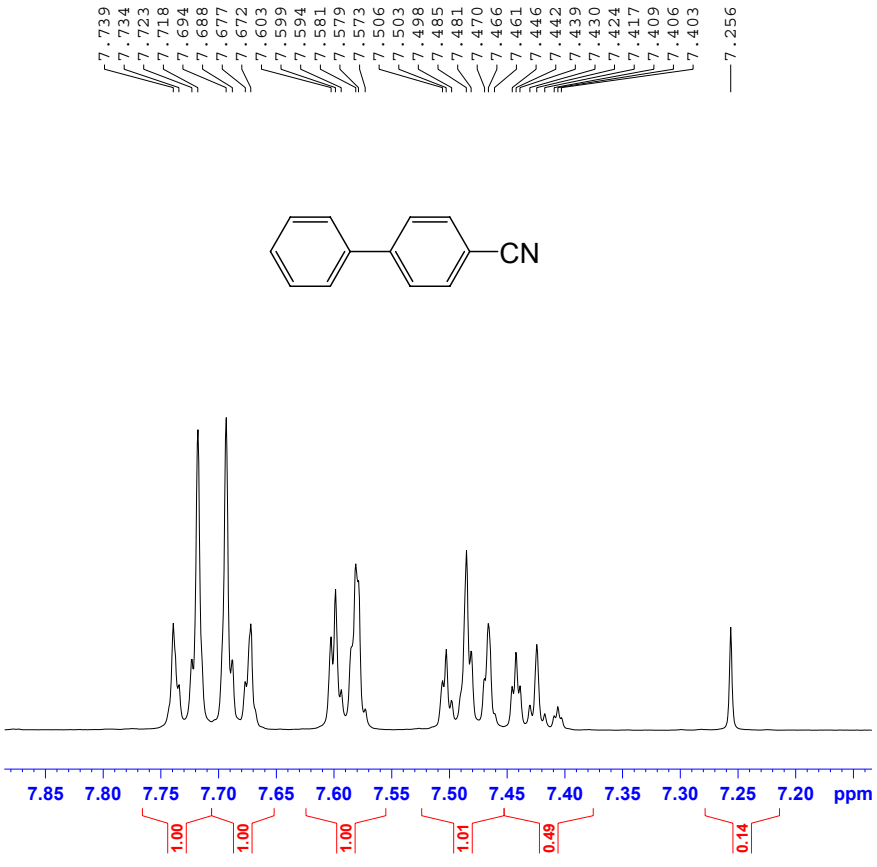
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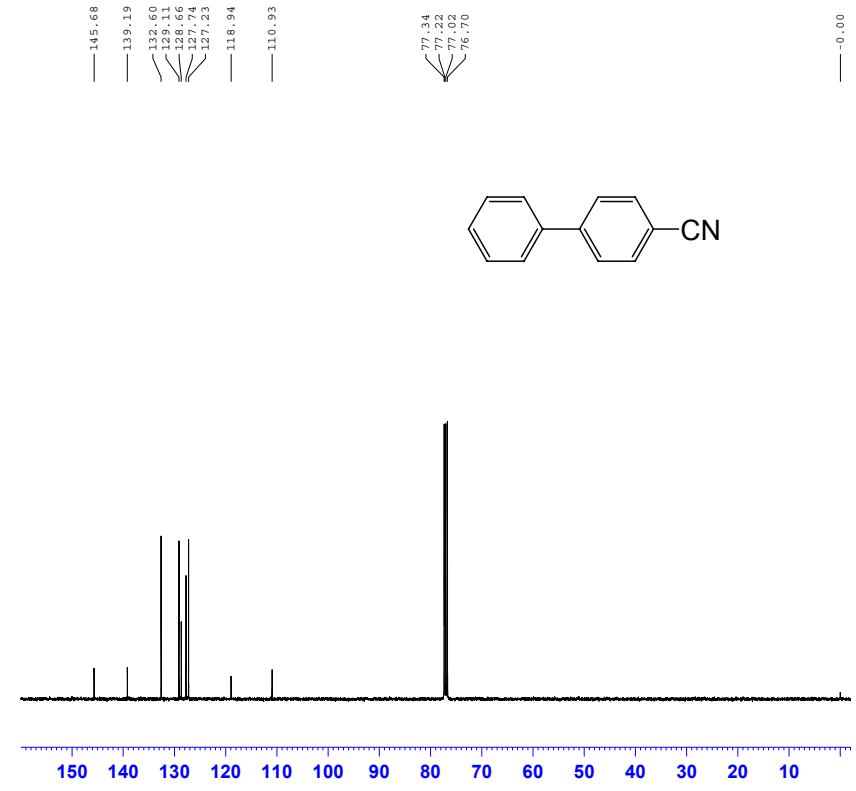
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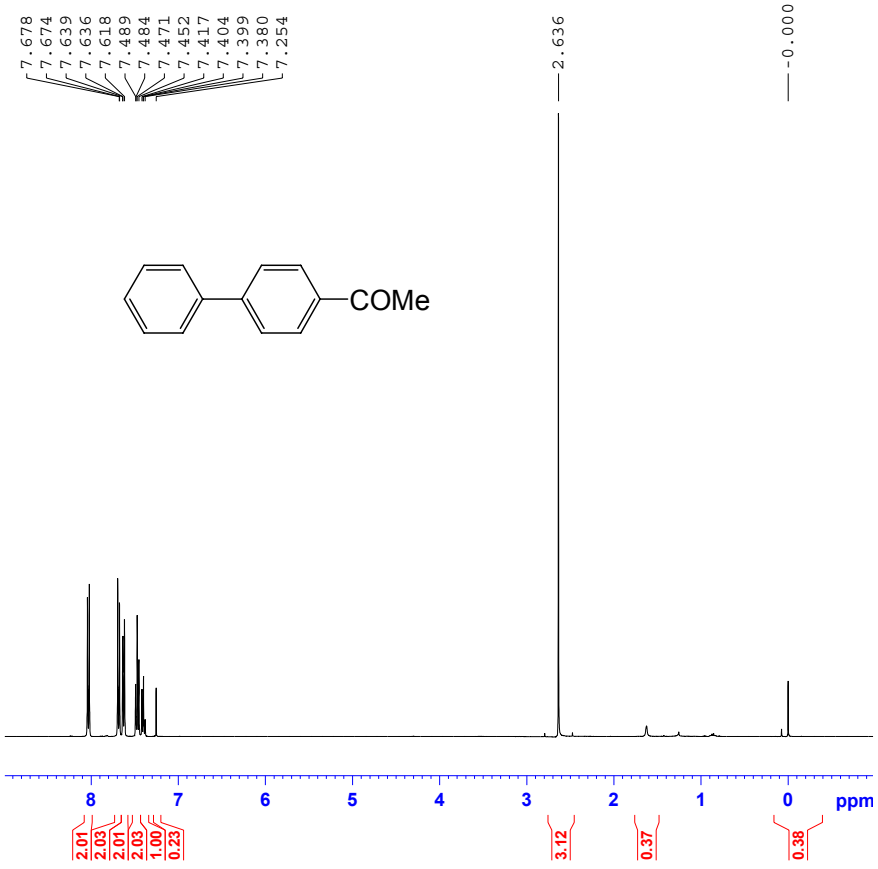
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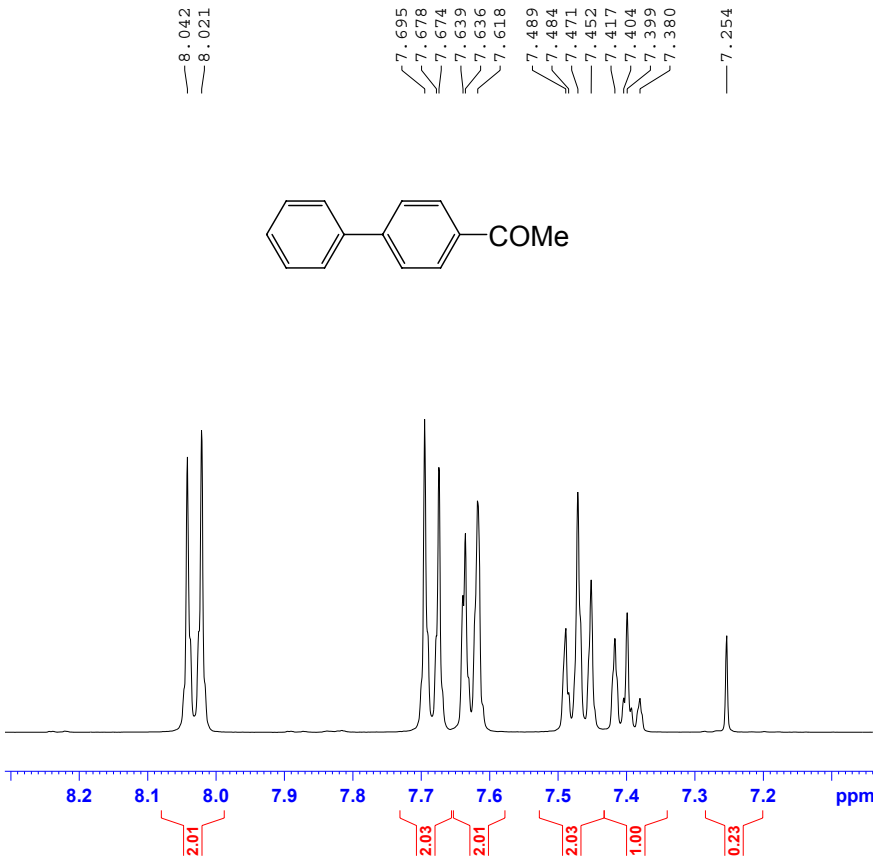
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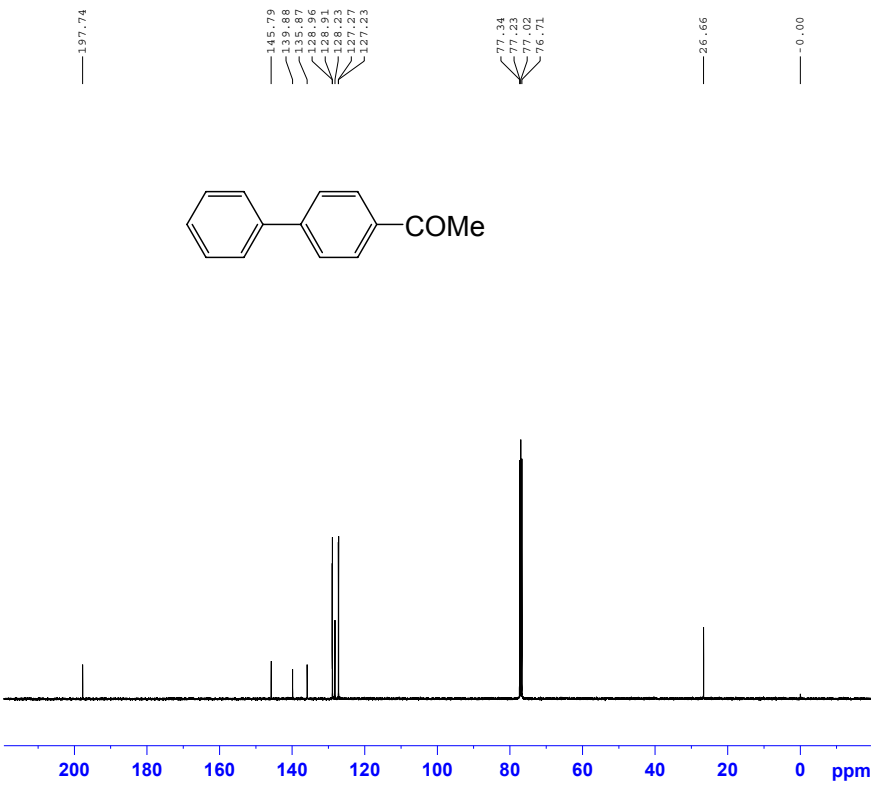
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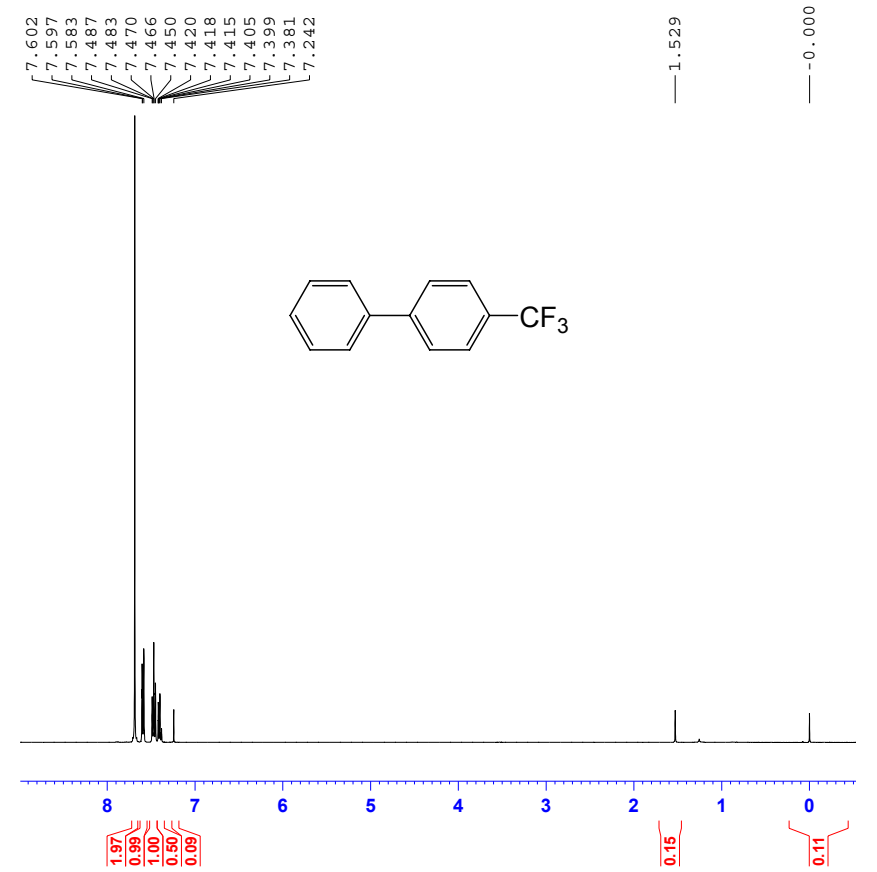
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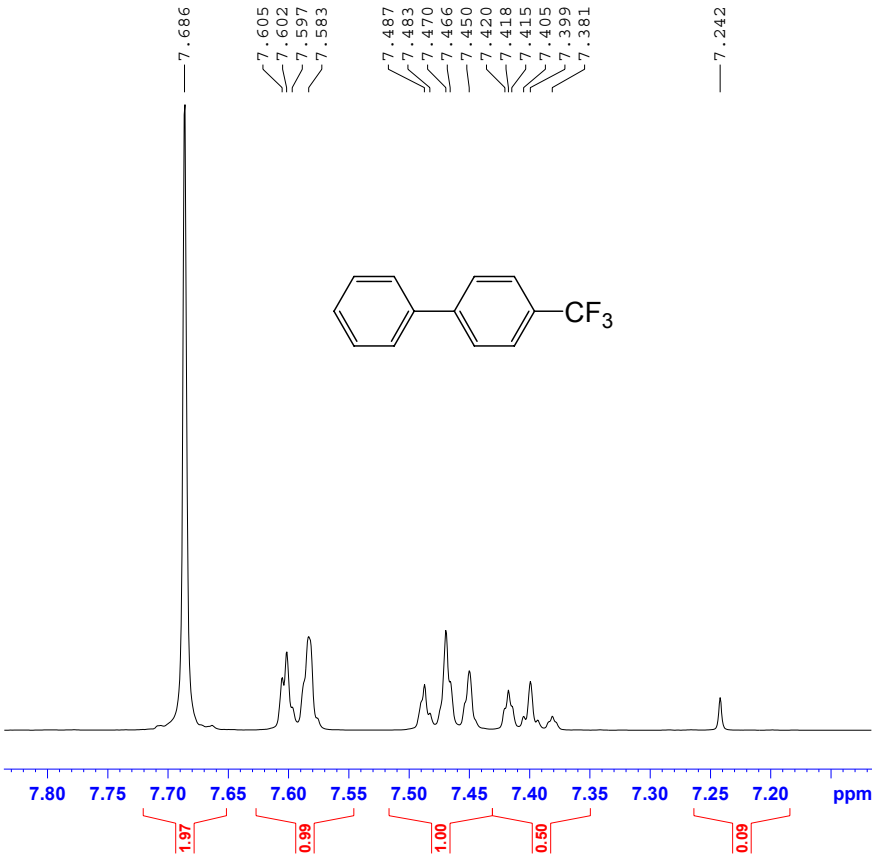
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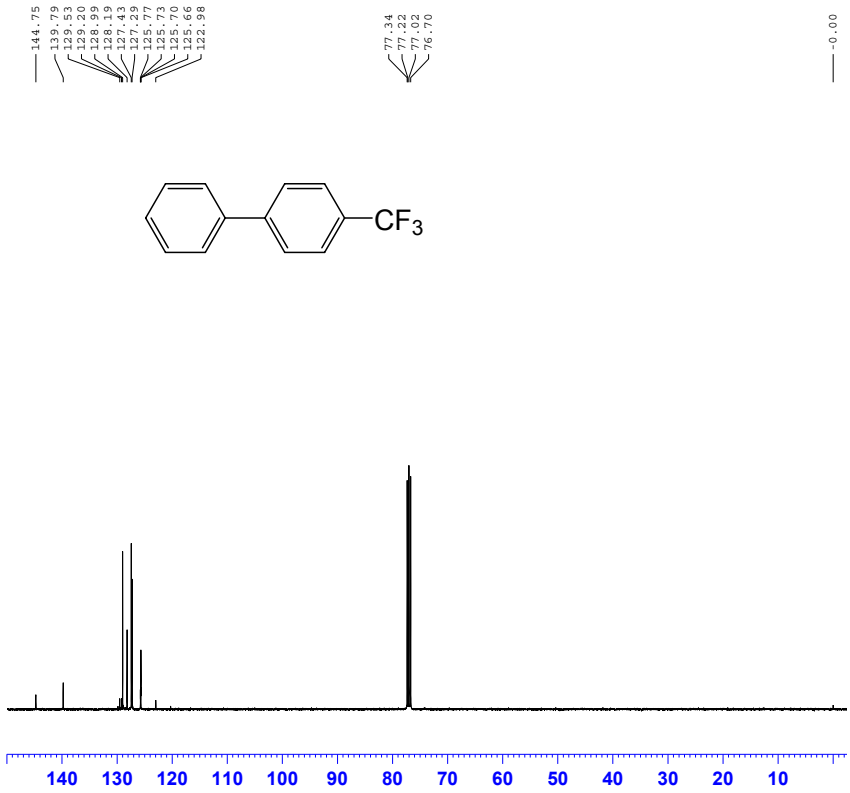
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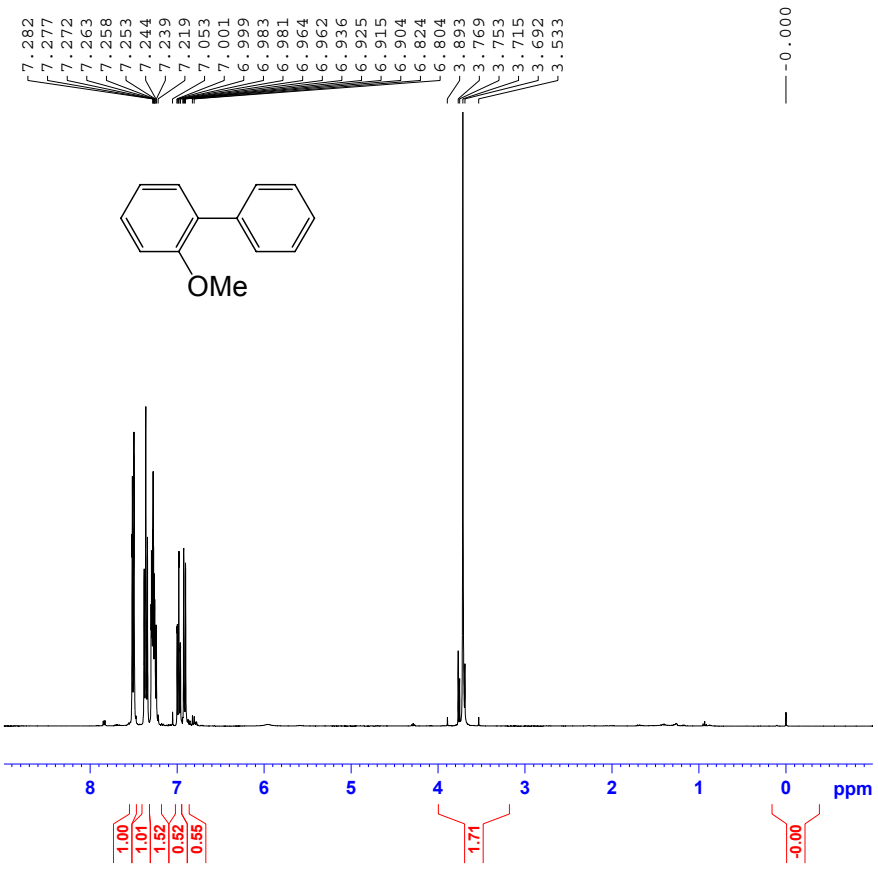
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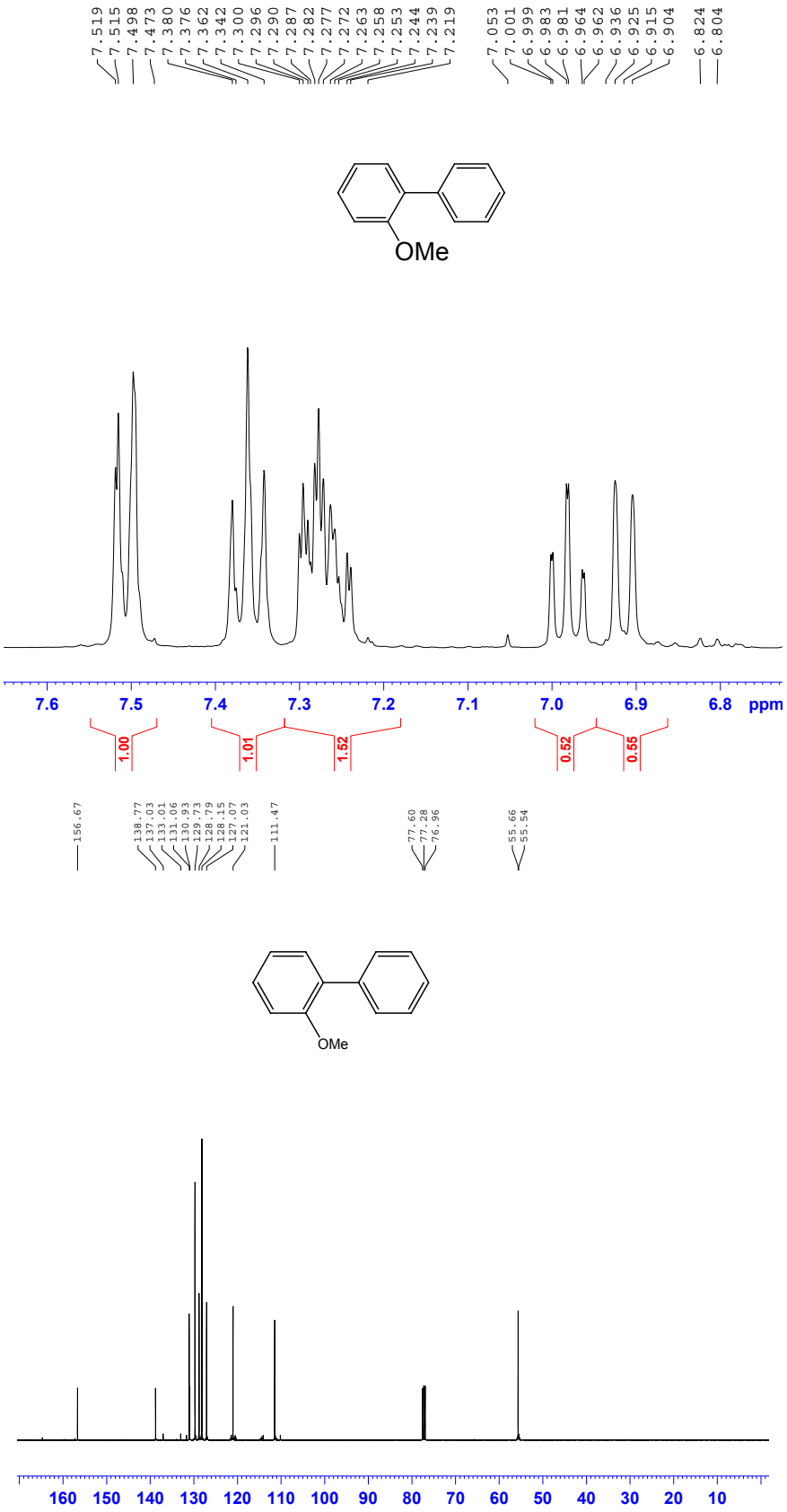
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6.8
ppm
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1.01
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156.67
138.77
137.03
133.01
131.06
130.93
129.73
128.79
128.15
127.07
121.03
111.47
77.60
77.28
76.96
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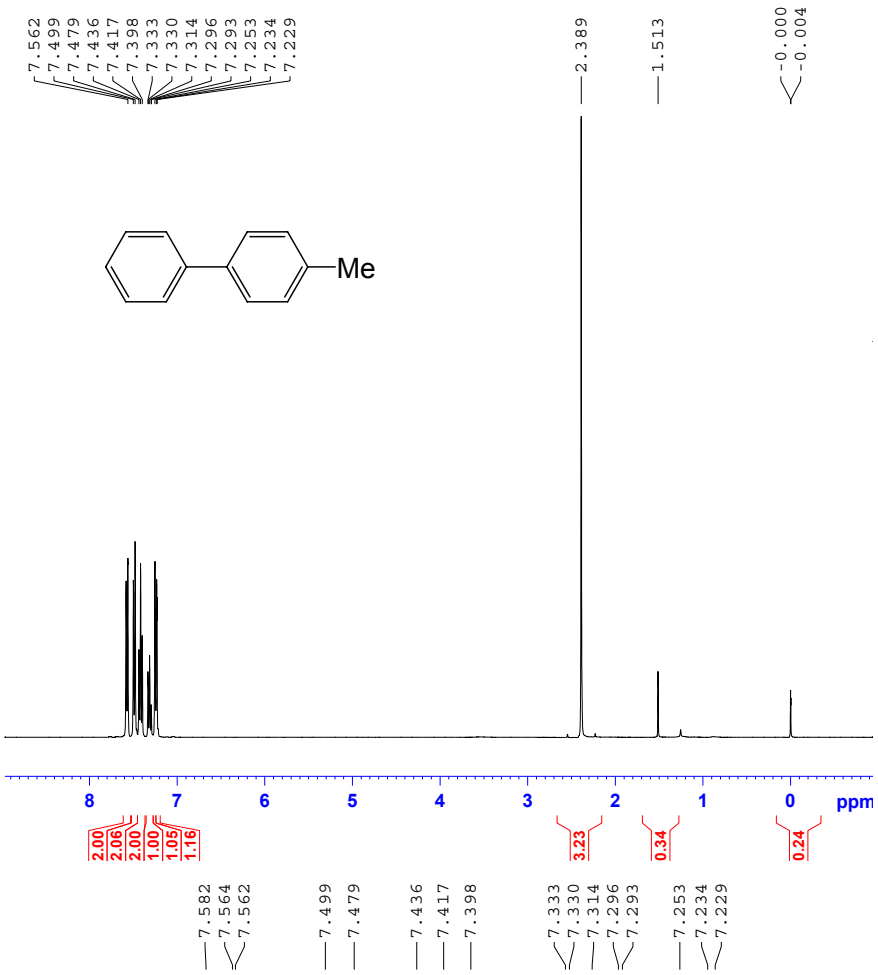
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7.229
2.389
1.513
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Me
8
7
6
5
4
3
2
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2.06
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3.23
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7.562
7.499
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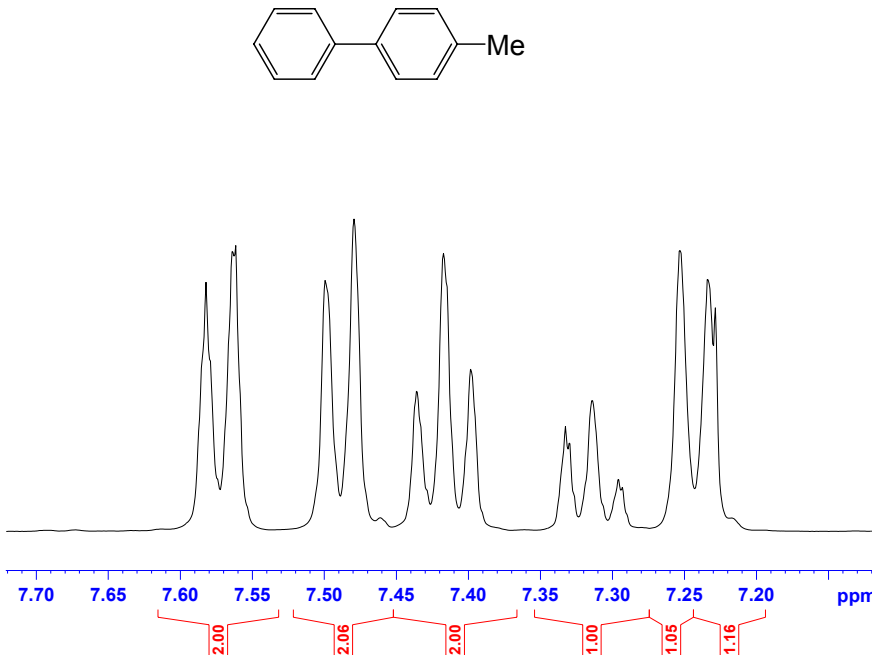
Me
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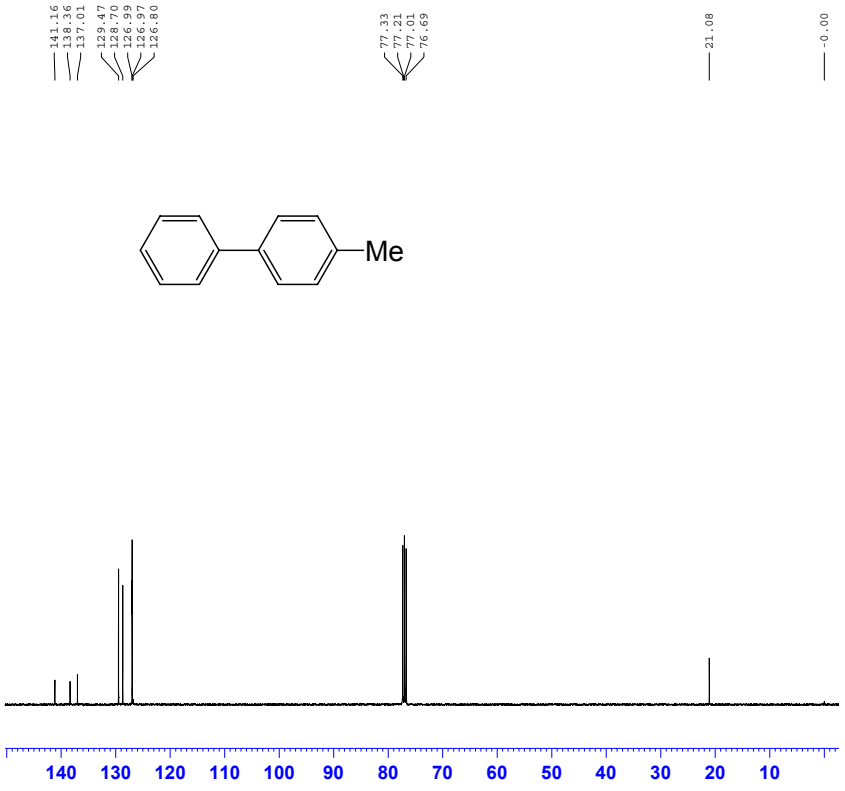
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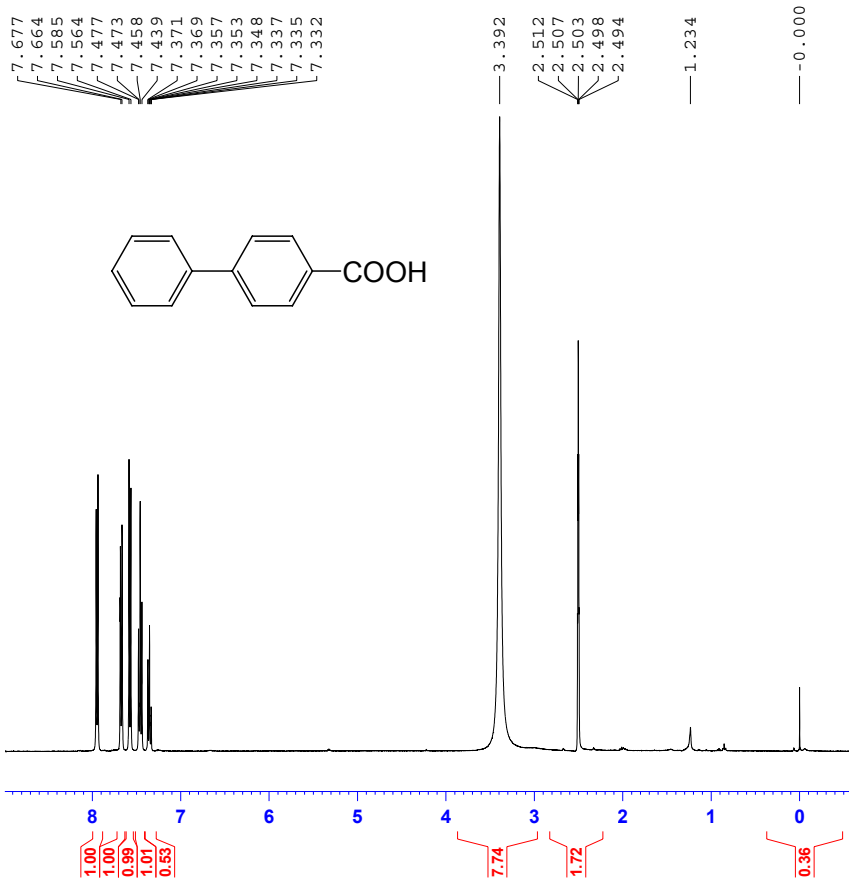
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7.439
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7.353
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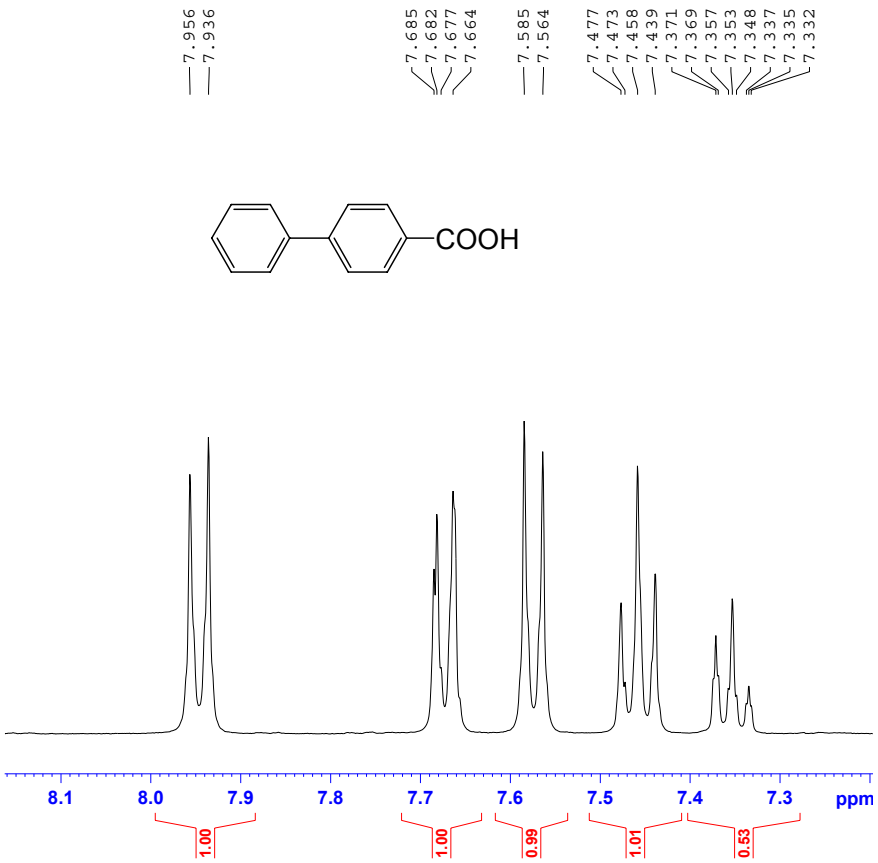
7.337
7.335
7.332
3.392
2.512
2.507
2.503
2.498
2.494
1.234
-0.000
COOH
8
7
6
5
4
3
2
1
0
1.00
1.00
0.99
1.01
0.53
7.74
1.72
0.36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7.664
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7.564
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7.473
7.458
7.439
7.371
7.369
7.357
7.353
7.348
7.337
7.335
7.332
COOH
8.1
8.0
7.9
7.8
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7.6
7.5
7.4
7.3
ppm
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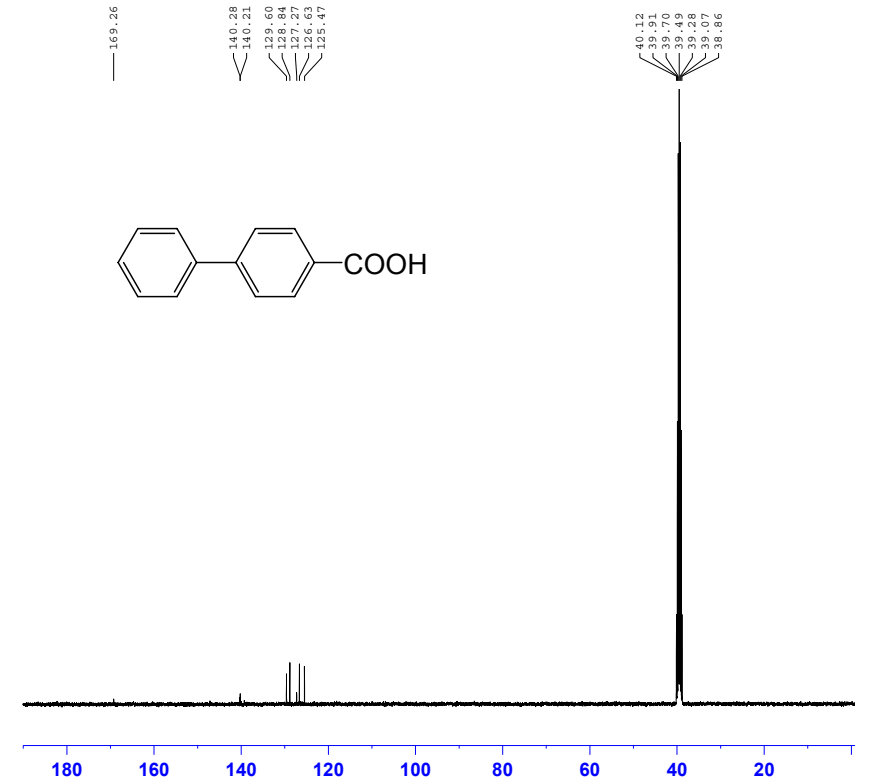
1.00
0.99
1.01
0.53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39.28
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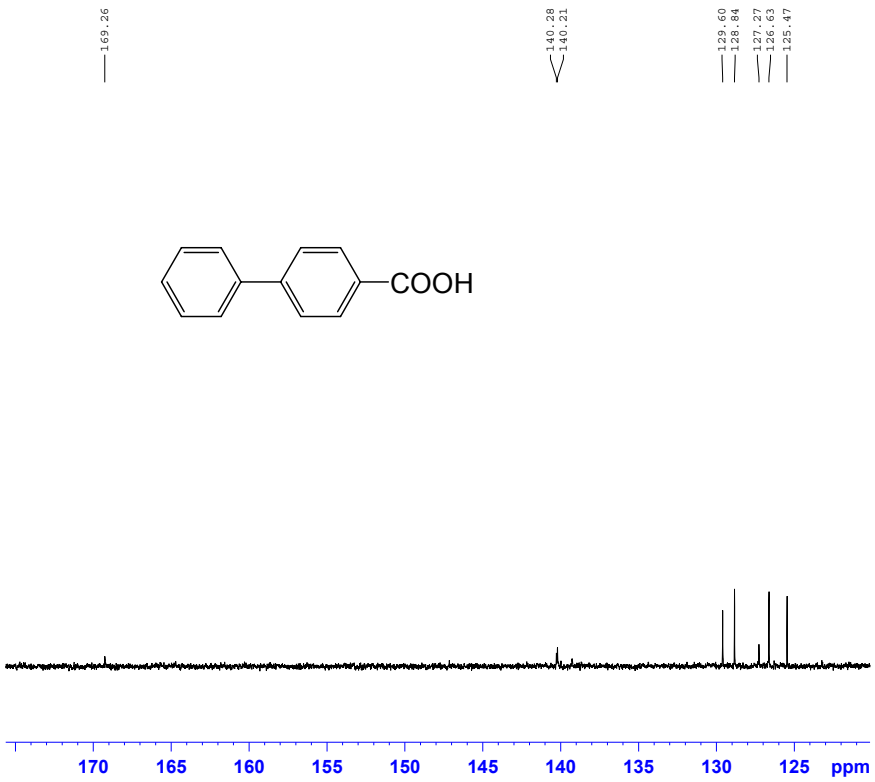
38.86
COOH
180
160
140
120
100
80
60
40
20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140.28
140.21
129.60
128.84
127.27
126.63
125.47
COOH
170
165
160
155
150
145
140
135
130
125
ppm