

**Palladium Supported on Phosphinite Functionalized  $\text{Fe}_3\text{O}_4$  Nanoparticles as a  
New Magnetically Separable Catalyst for Suzuki-Miyaura Coupling Reaction  
in Aqueous Media**

Mohammad Gholinejad,<sup>\*a</sup> Mehran Razeghi,<sup>a</sup> and Arash Ghaderi<sup>\*b</sup> Pullithadathil  
Biji<sup>c</sup>

*Department of Chemistry, Institute for Advanced Studies in Basic Sciences  
(IASBS), P. O. Box 45195-1159, Gavazang, Zanjan 45137-6731, Iran. Email:  
[gholinejad@iasbs.ac.ir](mailto:gholinejad@iasbs.ac.ir)*

*<sup>b</sup> Department of Chemistry, College of Sciences, Hormozgan University, Bandar  
Abbas, 71961, Iran. Fax: +98-761-766-0032; Tel: +98-761-766-0042; Email:  
[aghaderi@hormozgan.ac.ir](mailto:aghaderi@hormozgan.ac.ir)*

<sup>c</sup> Nanotech Research, Innovation and Incubation Center, PSG Institute of  
Advanced Studies, Coimbatore-641 004, India.

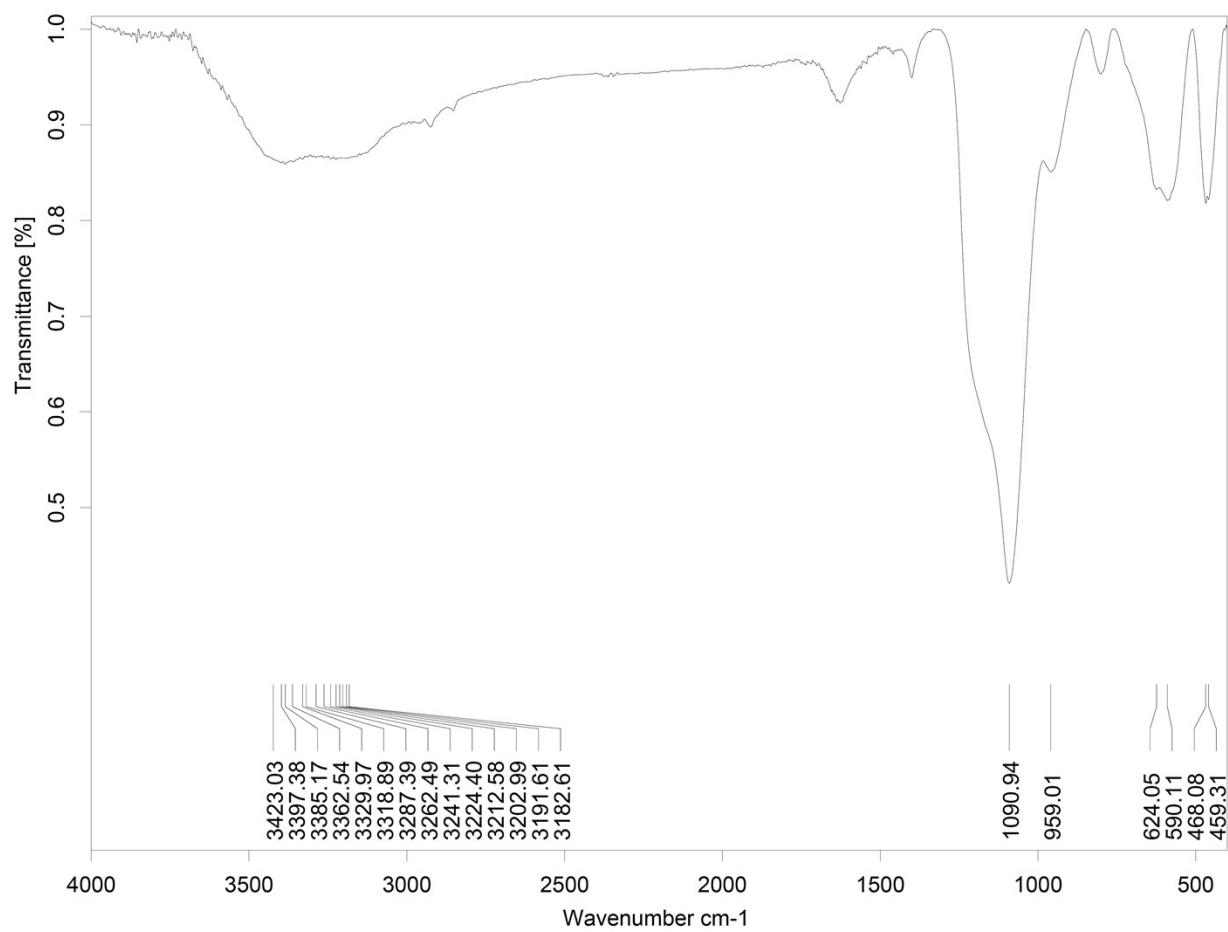


Figure 1. FT-IR of  $\text{SiO}_2@\text{Fe}_3\text{O}_4$

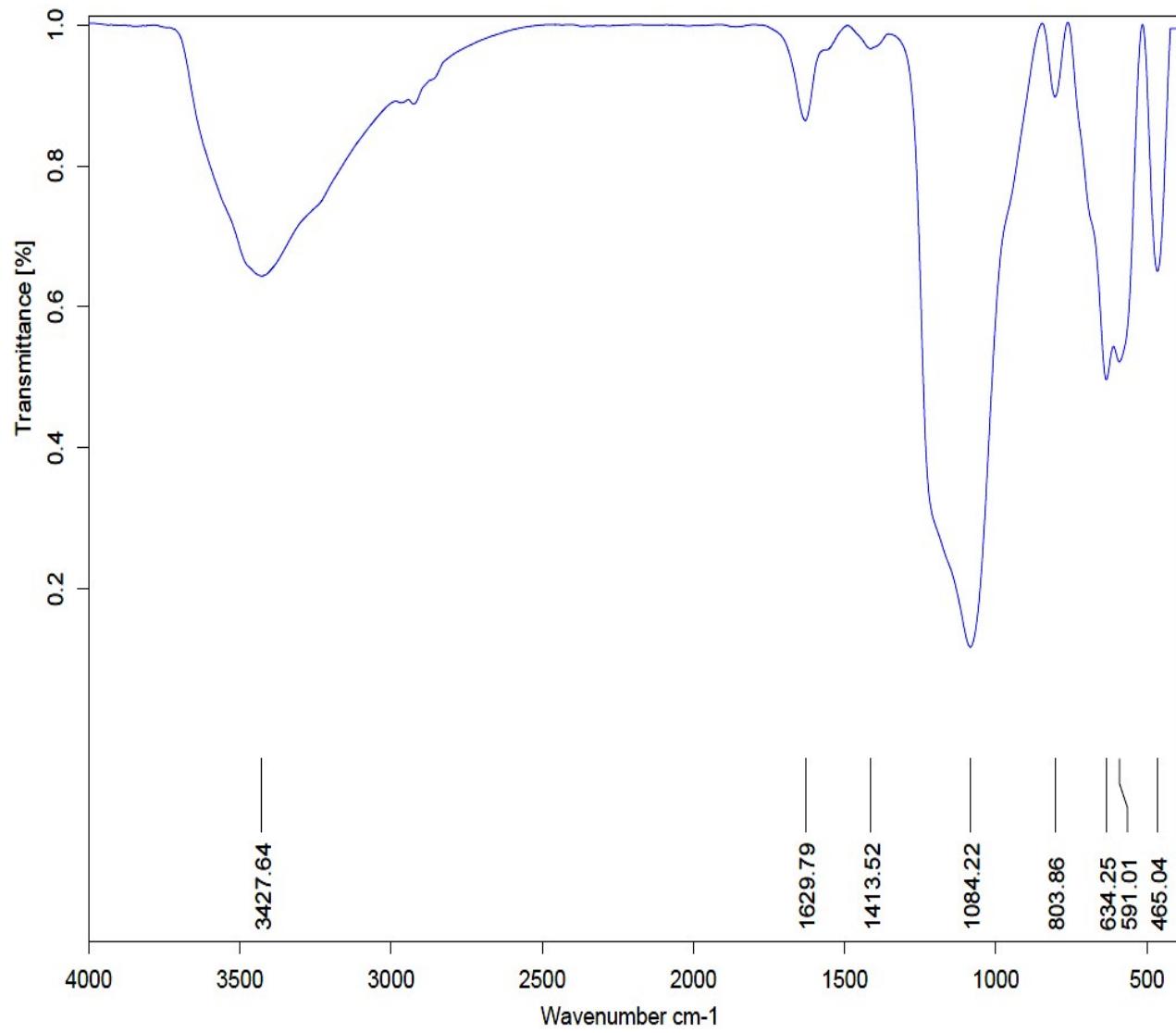
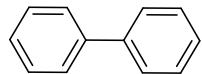


Figure 2. FT-IR of catalyst after 3<sup>rd</sup> run

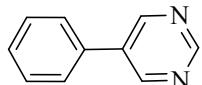
## Characterizations of products:

### 1'-biphenyl <sup>1</sup>:



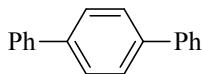
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.63 (d, 2H, *J*=7.6), 7.50-7.46 (t, 2H), 7.40-7.37 (t, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 141.26, 128.79, 127.79, 127.20 .

### 5-phenylpyrimidine <sup>1</sup>:



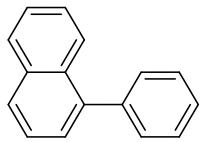
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 9.26 (s, 1H), 9.01 (s, 2H), 7.63-7.49 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 157.17, 154.89, 134.48, 134.12, 129.51, 129.15, 127.84, 127.04 .

### 1,1':4',1''-terphenyl <sup>2</sup>:



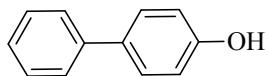
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.72-7.67 (t, 3H), 7.52-7.48 (t, 2H), 7.42-7.38 (t, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 140.73, 140.14, 128.84, 127.53, 127.37, 127.08.

**1-phenylnaphthalene <sup>3</sup>:**



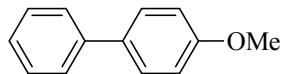
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.96, 7.89 (m, 3H), 7.59-7.45 (m, 8H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 140.79, 140.29, 133.82, 131.64, 130.11, 128.29, 127.66, 127.26, 126.95, 126.05, 125.79, 124.41.

**[1,1'-biphenyl]-4-ol <sup>1</sup>:**



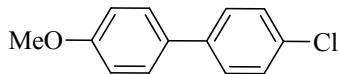
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.77-7.71 (m, 3H), 7.64-7.61 (t, 2H), 7.54-7.50 (t, 2H), 7.47-7.44 (m, 1H), 1.67 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 145.71, 139.21, 132.63, 129.14, 128.69, 127.77, 127.26, 118.98, 110.94 .

**4-methoxy-1,1'-biphenyl <sup>1</sup>:**



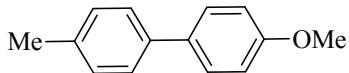
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.60 -7.55 (m, 4H), 7.47-7.43 (m, 2H), 7.35-7.32 (t, 1H), 7.03-7.00 (m, 2H), 3.89 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 159.17, 140.87, 133.81, 128.74, 128.18, 126.76, 126.68, 114.21, 55.37 .

**4-chloro-4'-methoxy-1,1'-biphenyl <sup>4</sup>:**



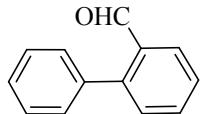
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.54-7.49 (m, 4H), 7.42-7.40 (m, 2H), 7.03-6.99 (m, 2H), 3.88 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 159.38, 139.29, 132.69, 132.52, 128.86, 128.04, 127.96, 114.33, 55.39 .

#### 4-methoxy-4'-methyl-1,1'-biphenyl <sup>1</sup>:



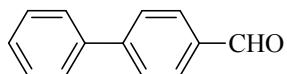
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.56-7.53 (t, 2H), 7.49 (d, 2H, *J*=8.4), 7.27 (d, 2H, *J*=8), 7.01 (d, 2H, *J*=8.4), 3.88 (s, 3H), 2.42 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 158.95, 137.99, 136.39, 133.77, 129.47, 127.99, 126.61, 114.18, 55.37, 21.09 .

#### [1,1'-biphenyl]-2-carbaldehyde <sup>1</sup>:



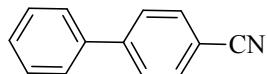
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.02 (s, 1H), 8.08-8.06 (m, 1H), 7.70-7.66 (m, 1H), 7.55-7.41 (m, 7H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 192.53, 146.01, 137.76, 133.72, 133.61, 130.81, 130.14, 128.47, 128.16, 127.81, 127.59 .

#### [1,1'-biphenyl]-4-carbaldehyde <sup>1</sup>:



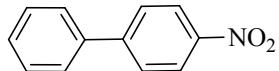
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.09 (s, 1H), 7.99 (d, 2H, *J*=8.4), 7.80-7.75 (t, 2H), 7.68-7.66 (t, 2H), 7.54-7.45 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 192.02, 147.25, 139.75, 135.20, 130.32, 129.05, 128.51, 127.73, 127.40 .

**[1,1'-biphenyl]-4-carbonitrile <sup>1</sup>:**



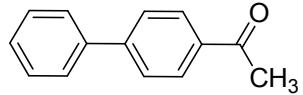
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.77-7.70 (q, 4H), 7.64-7.62 (t, 2H), 7.54-7.50 (t, 2H), 7.48-7.44 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 145.69, 139.19, 132.64, 129.16, 128.72, 127.77, 127.27, 119.01, 110.92 .

**4-nitro-1,1'-biphenyl <sup>1</sup>:**



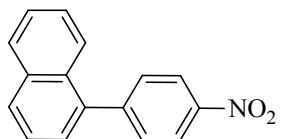
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.32 (d, 2H, *J*=8.8), 7.76 (d, 2H, *J*=2H), 7.67-7.65 (t, 2H), 7.55-7.46 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 147.64, 147.08, 138.76, 129.21, 128.98, 127.83, 127.42, 124.14 .

**1-([1,1'-biphenyl]-4-yl)ethanone <sup>4</sup>:**



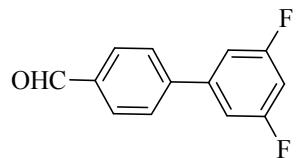
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.07 (d, 2H, *J*= 8.4), 7.72(d, 2H, *J*=8.8), 7.68-7.65(t, 2H), 7.53-7.43 (m, 3H), 2.67 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 145.82, 139.90, 135.86, 128.99, 128.95, 128.26, 127.31, 127.26, 26.72 .

**1-(4-nitrophenyl)naphthalene <sup>5</sup>:**



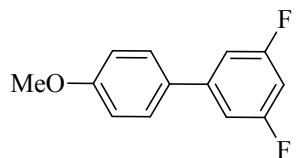
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.40(d, 2H, *J*=8.8), 7.99-7.96(m, 2H), 7.82(d, 1H, *J*=8.4), 7.71(d, 2H, *J*=8.8), 7.61-7.46 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 147.71, 147.21, 137.81, 133.82, 130.95, 129.00, 128.61, 127.13, 126.77, 126.26, 125.35, 125.17, 123.63 .

**3',5'-difluoro-[1,1'-biphenyl]-4-carbaldehyde <sup>6</sup>:**



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.11 (s, 1H), 8.01 (d, 2H, *J*=8), 7.75 (d, 2H, *J*=8), 7.21-7.16 (m, 2H), 6.92-6.87 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 191.66, 144.64, 143.02, 136.08, 130.41, 127.71, 110.49, 110.42, 110.31, 110.31, 110.23, 103.98, 103.78, 103.48 . <sup>19</sup>F NMR(CDCl<sub>3</sub>, 376 MHz): δ – 108.78 .

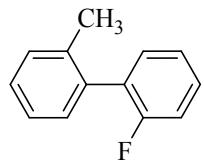
**3,5-difluoro-4'-methoxy-1,1'-biphenyl :**



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.52(d, 2H, *J*= 8.8), 7.11-7.06 (m, 2H), 7.01(d, 2H, *J*=8.8), 7.79-7.74 (m, 1H), 3.89 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 164.64, 164.51, 162.18, 162.05, 159.98, 144.24, 144.15, 144.05, 131.37, 131.35, 131.32,

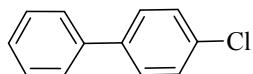
128.11, 114.41, 109.50, 109.44, 109.32, 109.25, 102.08, 101.82, 101.57, 55.40 .  $^{19}\text{F}$  NMR( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -110.03 .

**2-fluoro-2'-methyl-1,1'-biphenyl :**



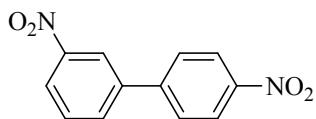
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.41- 7.15 (m, 7H), 2.25 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  160.89, 136.69, 135.78, 131.61, 131.57, 130.10, 129.98, 129.35, 129.18, 129.11, 129.03, 128.00, 1225.66, 124.02, 123.98, 115.65, 115.43, 19.98, 19.95 .  $^{19}\text{F}$  NMR( $\text{CDCl}_3$ , 376 MHz):  $\delta$  -114.8 .

**4-chloro-1,1'-biphenyl<sup>4</sup>:**



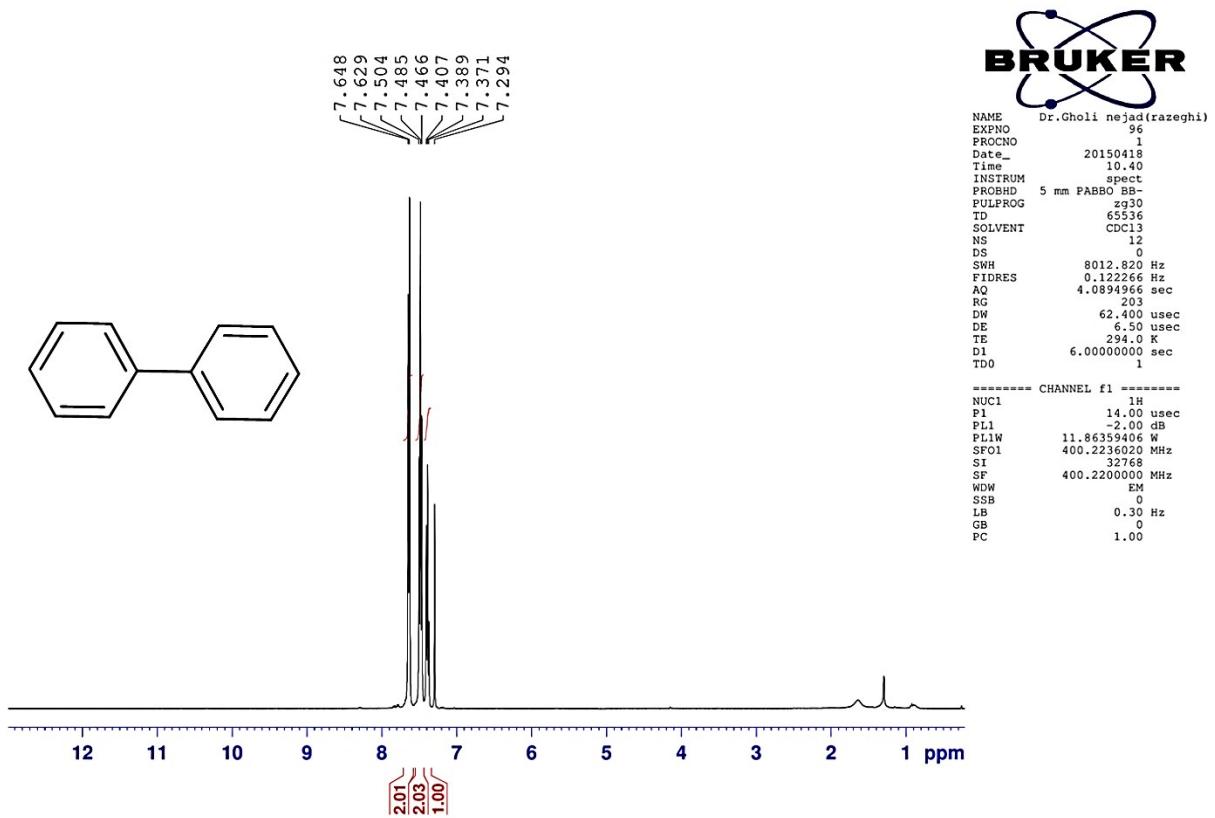
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.63-7.56 (m, 4H), 7.53-7.41 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  140.04, 139.71, 133.44, 128.98, 128.96, 128.46, 127.66, 127.06 .

**3,4'-dinitro-1,1'-biphenyl:**



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.53 (s, 1H), 8.40 (d, 1H, *J*=8.8), 8.36-8.33 (m, 1H), 8.01-7.98 (m, 1H), 7.84-7.84 (t, 1H), 7.76-7.72 (t, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 148.87, 147.93, 144.89, 140.46, 140.36, 133.24, 133.09, 130.30, 128.14, 124.49, 123.59, 123.34, 122.33, 122.15.

## Copy of Original $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of products



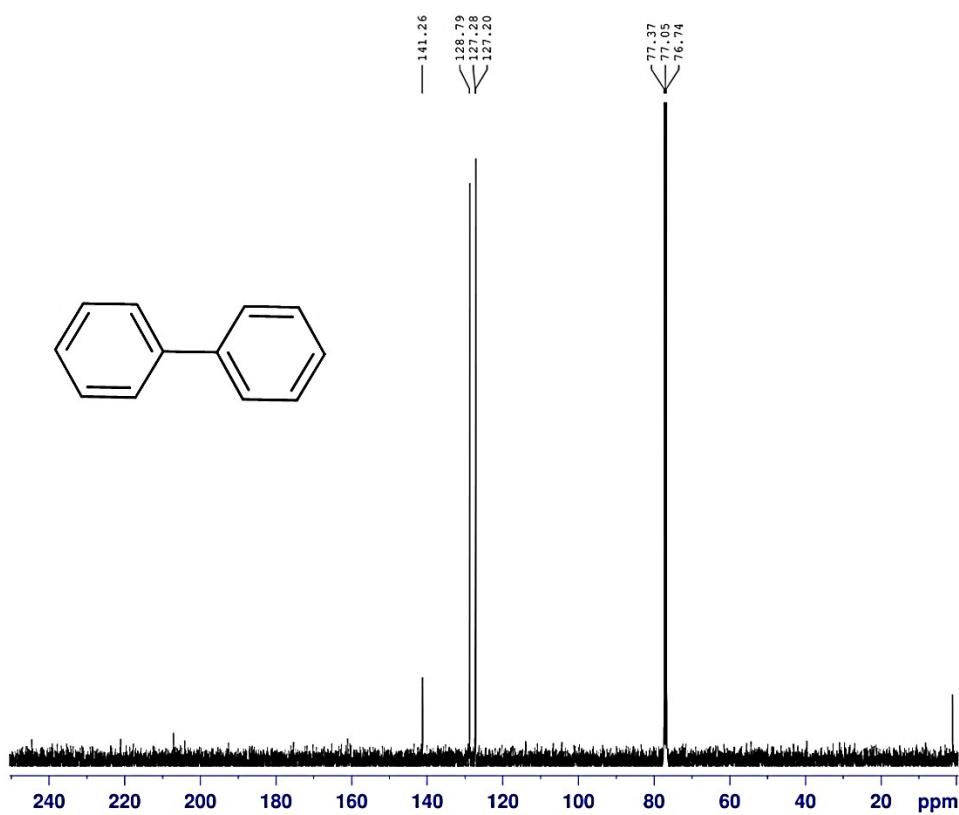
$^1\text{H}$  NMR of 1,1'-biphenyl



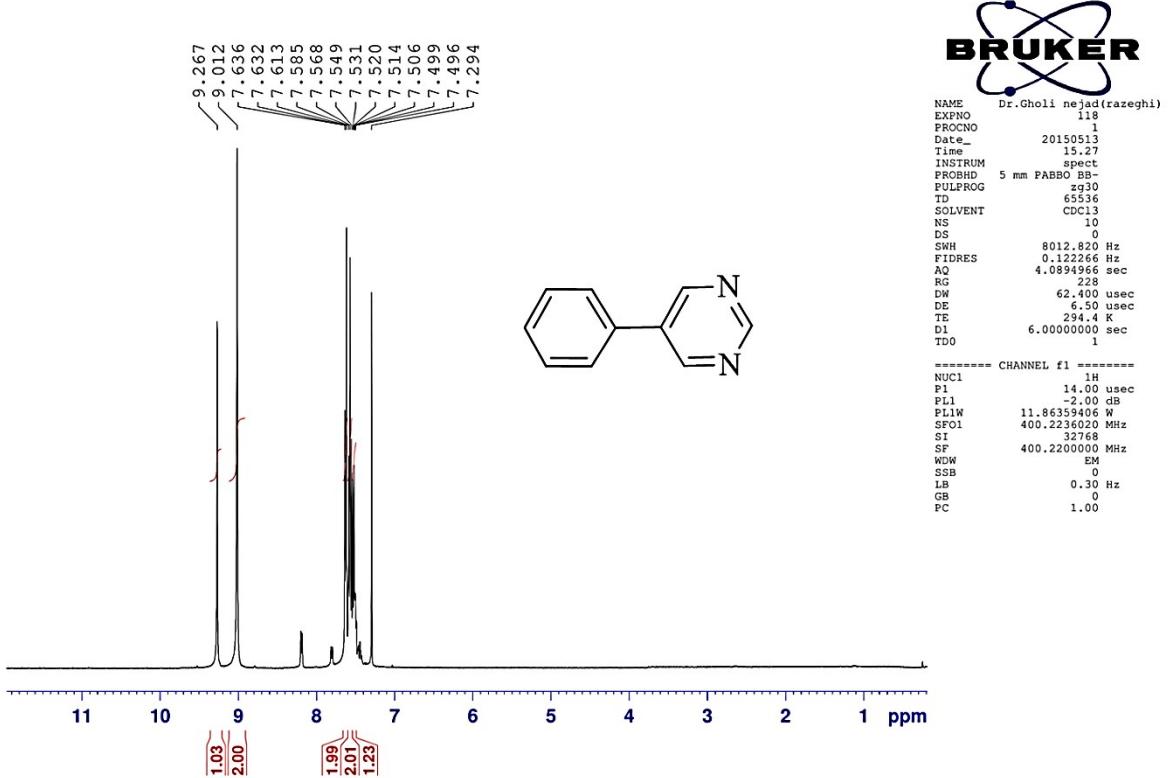
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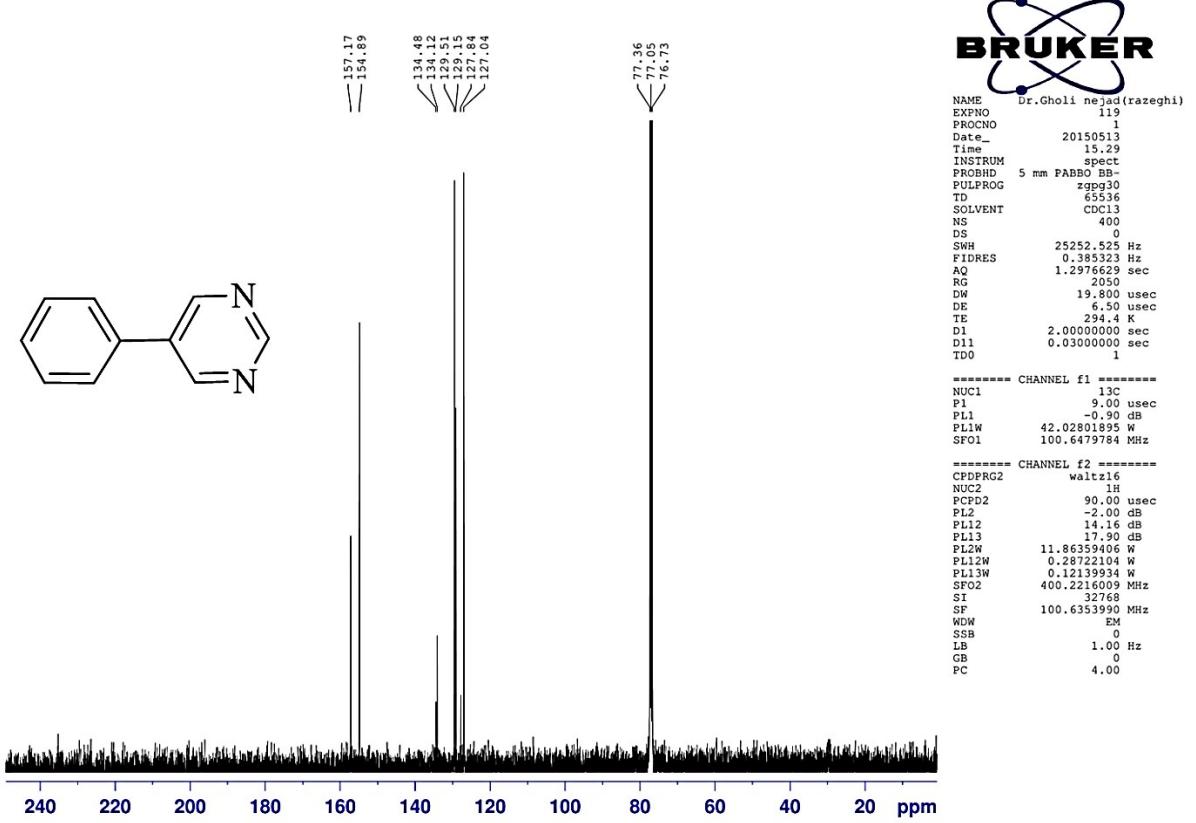
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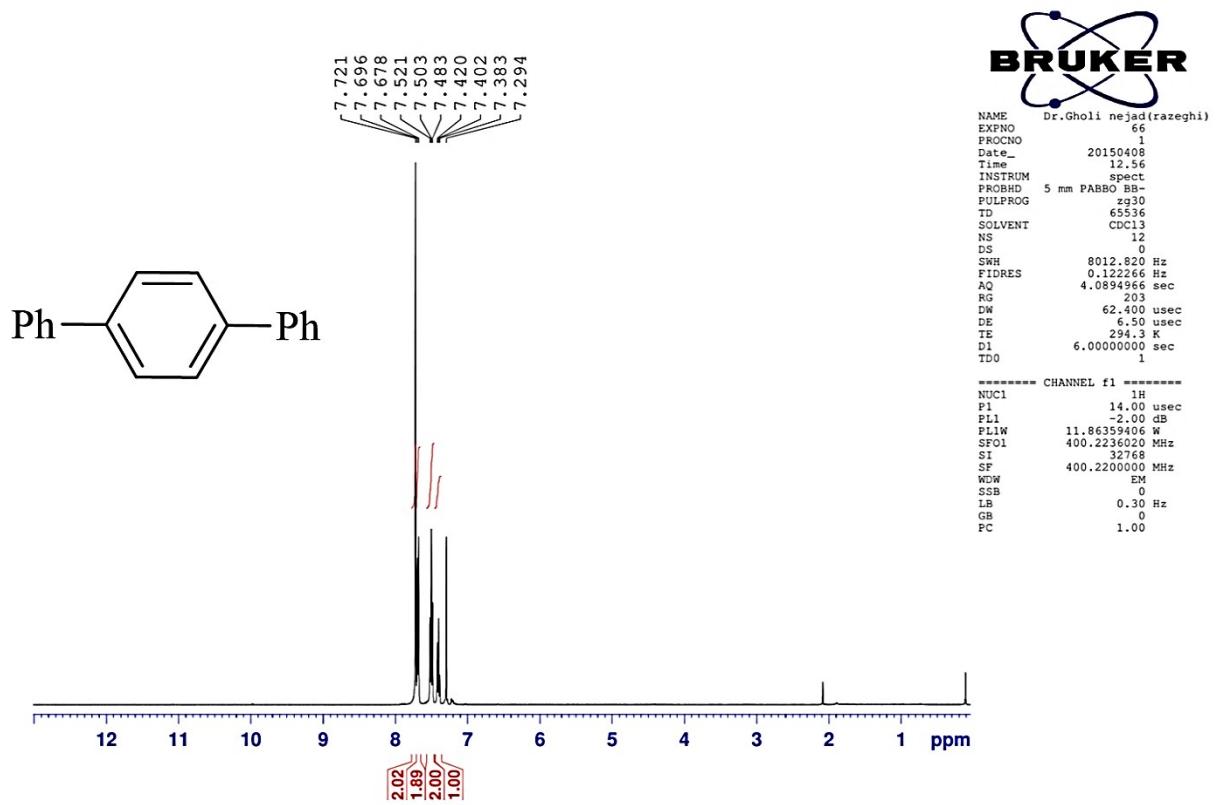
<sup>13</sup>C NMR of 1,1'-biphenyl



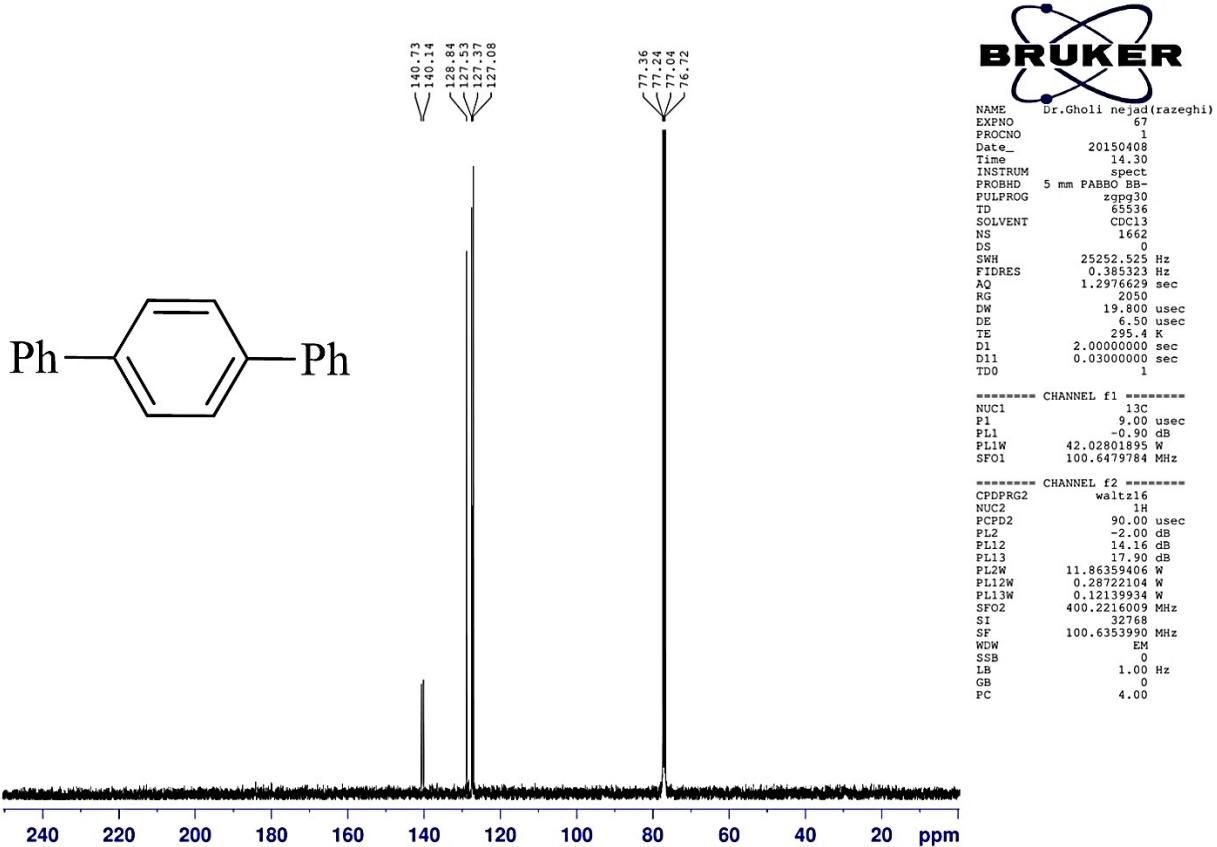
**<sup>1</sup>H NMR of 5-phenylpyrimidine**



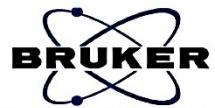
<sup>13</sup>C NMR of 5-phenylpyrimidine



<sup>1</sup>H NMR of 1,1':4',1''-terphenyl



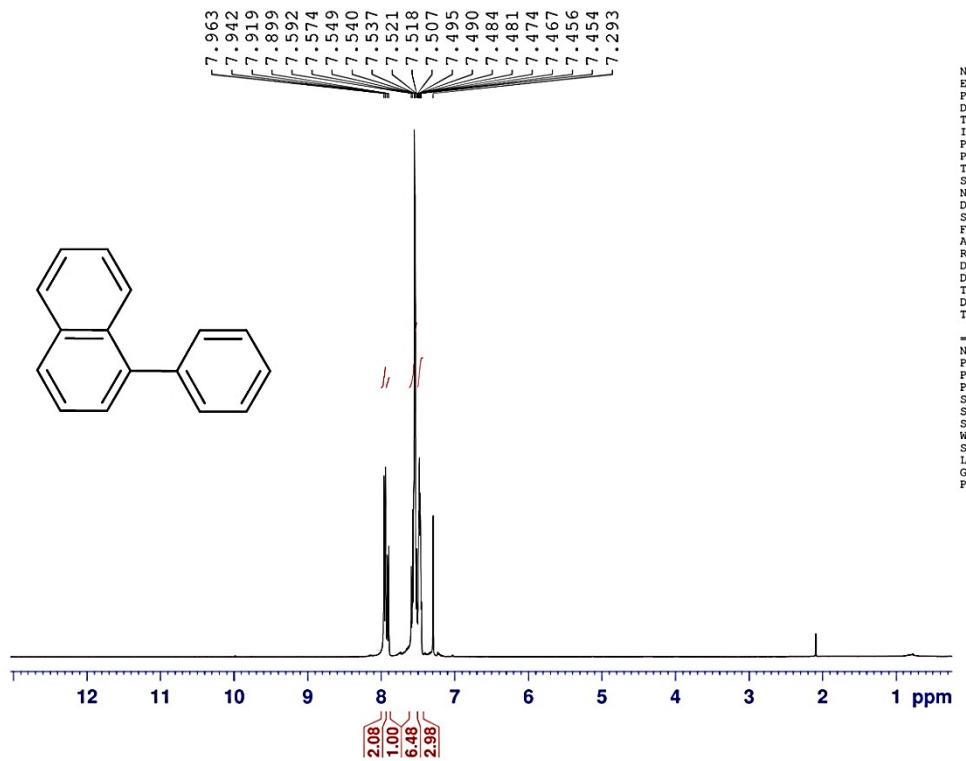
<sup>13</sup>C NMR of 1,1':4',1''-terphenyl



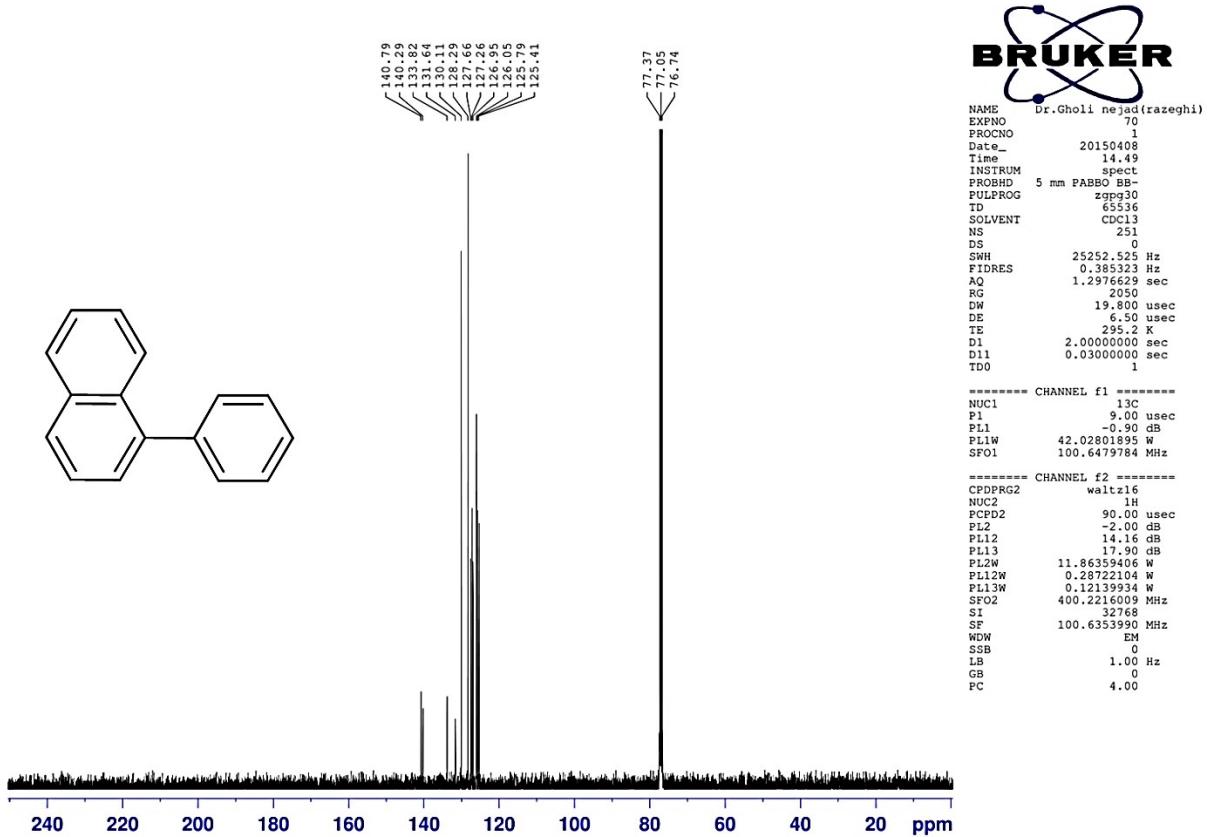
Dr.Gholi nejad(razeghi)

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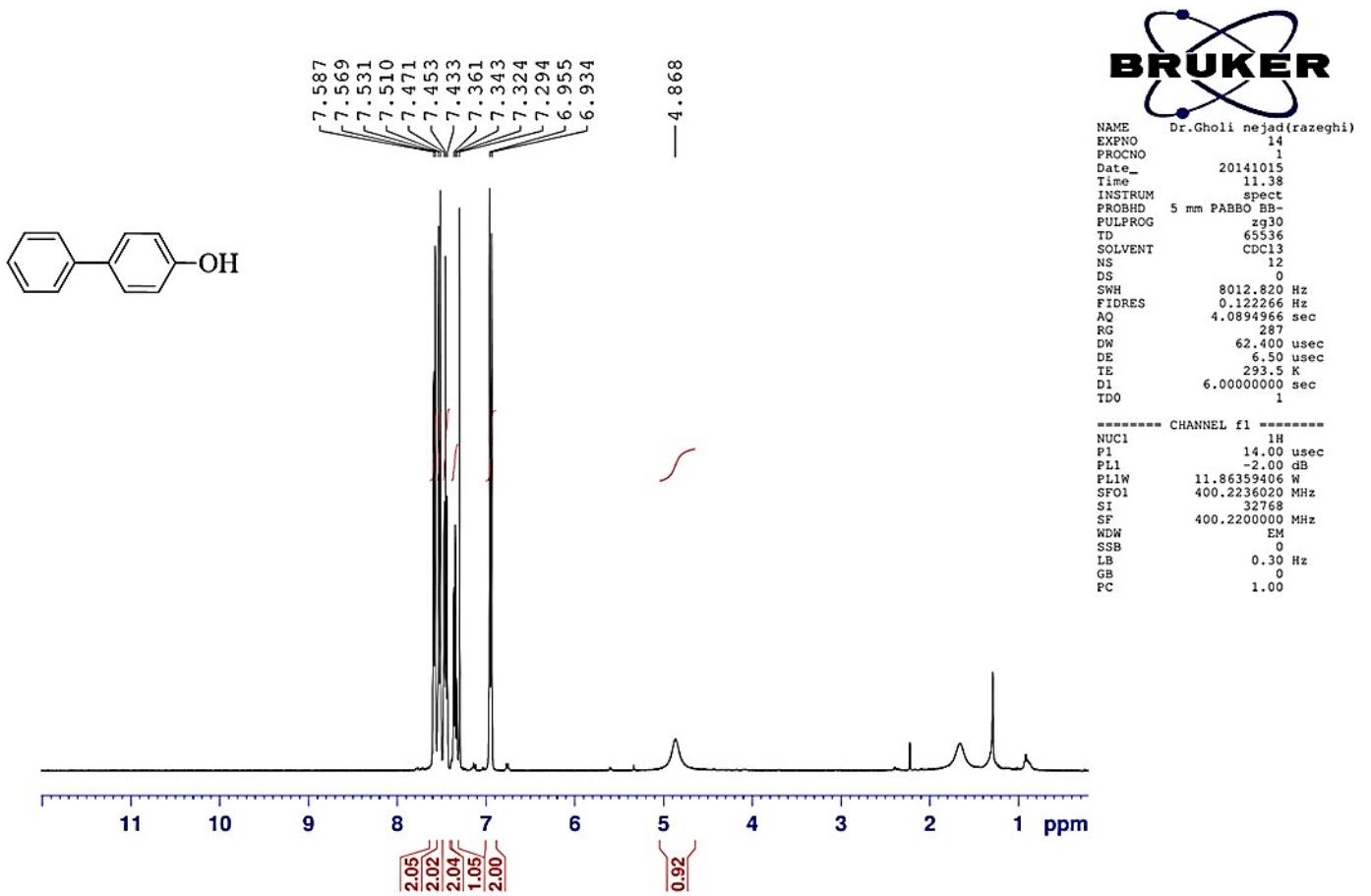
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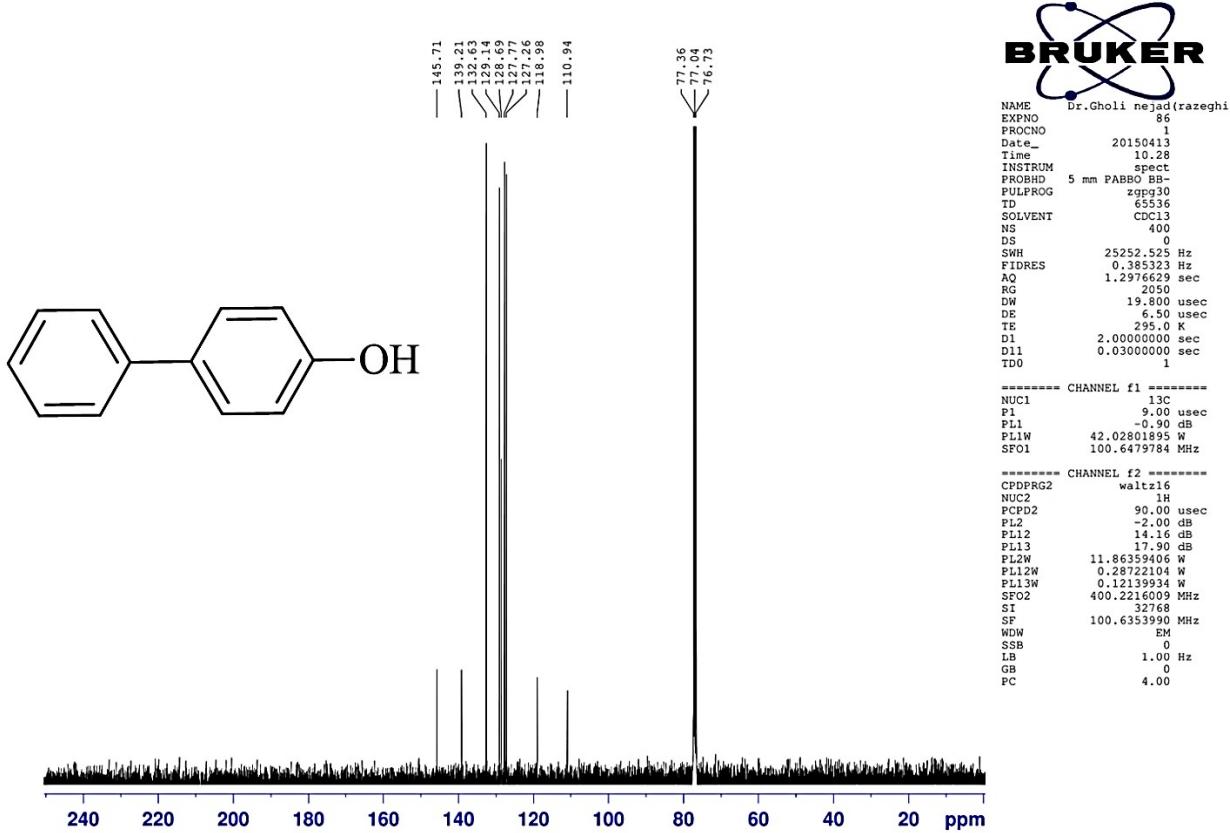
<sup>1</sup>H NMR of 1-phenylnaphthalene



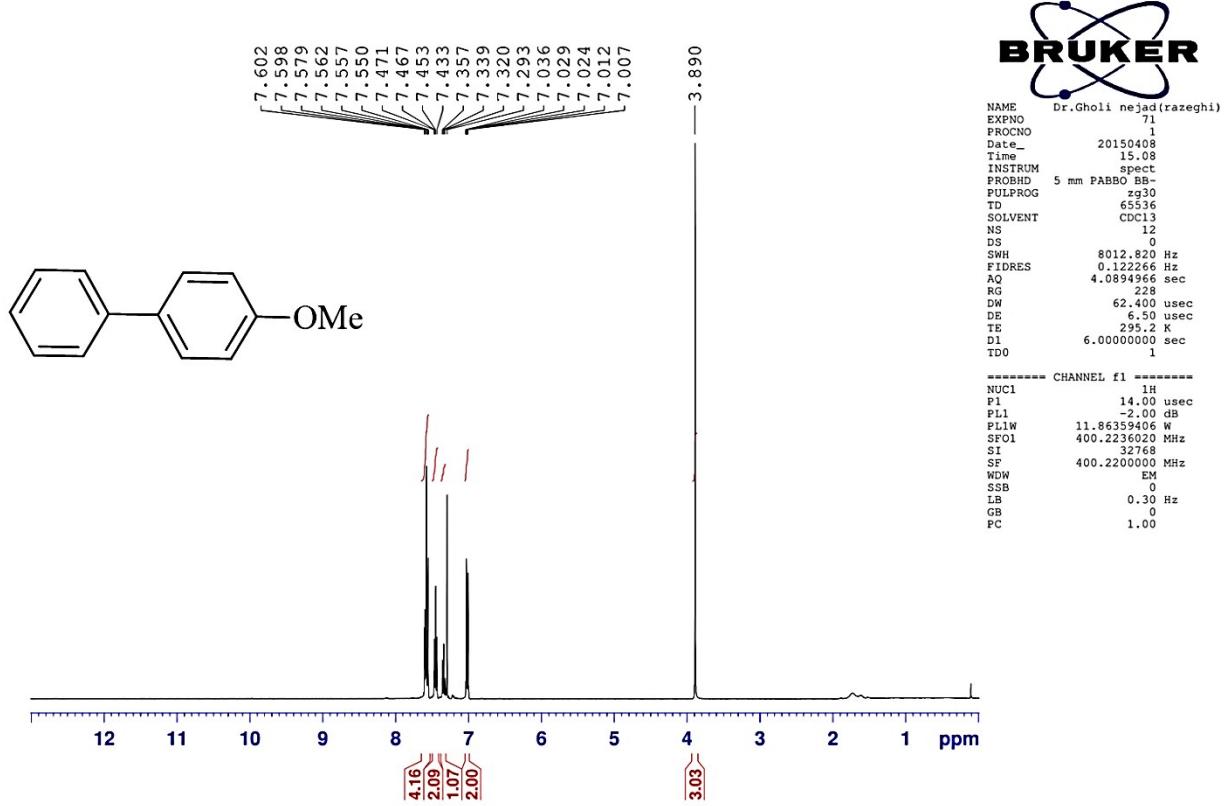
**<sup>13</sup>C NMR of 1-phenylnaphthalene**



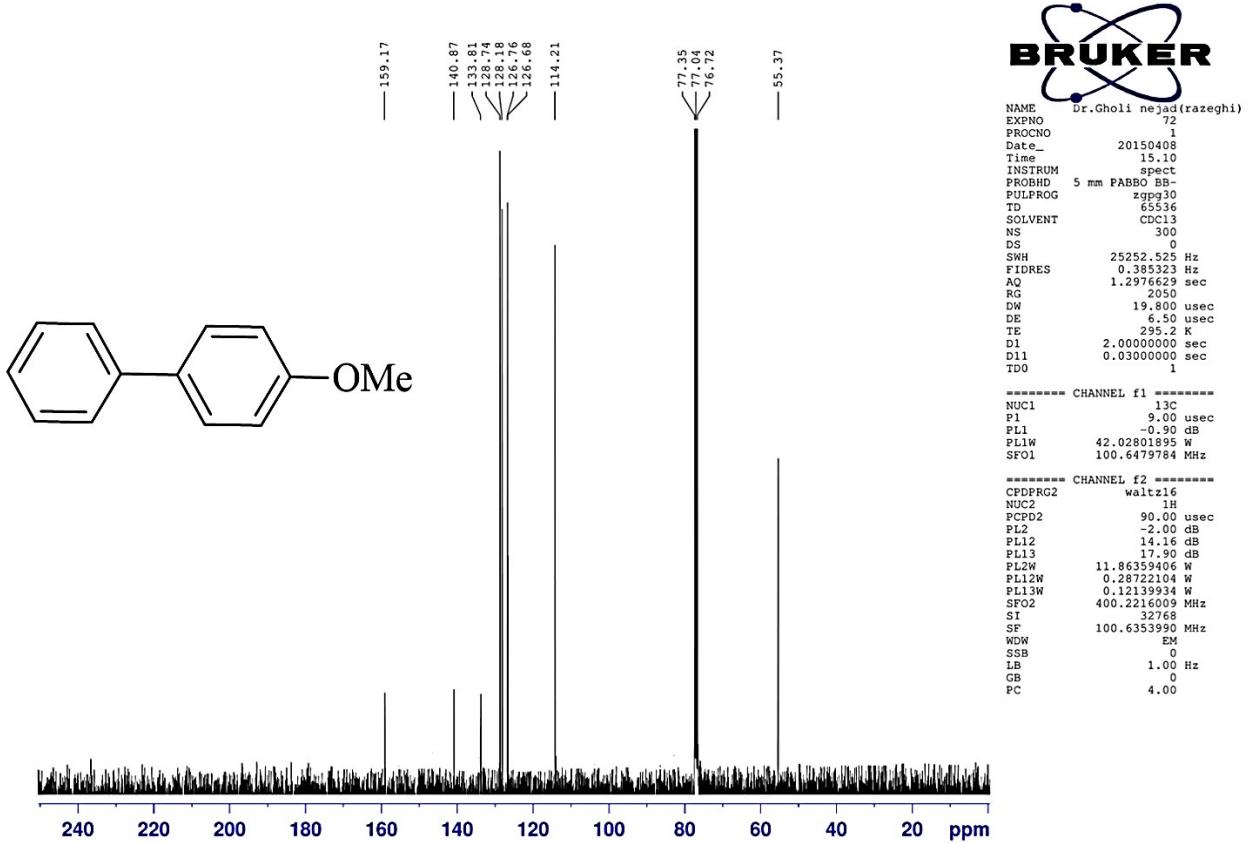
**<sup>1</sup>H NMR of [1,1'-biphenyl]-4-ol**



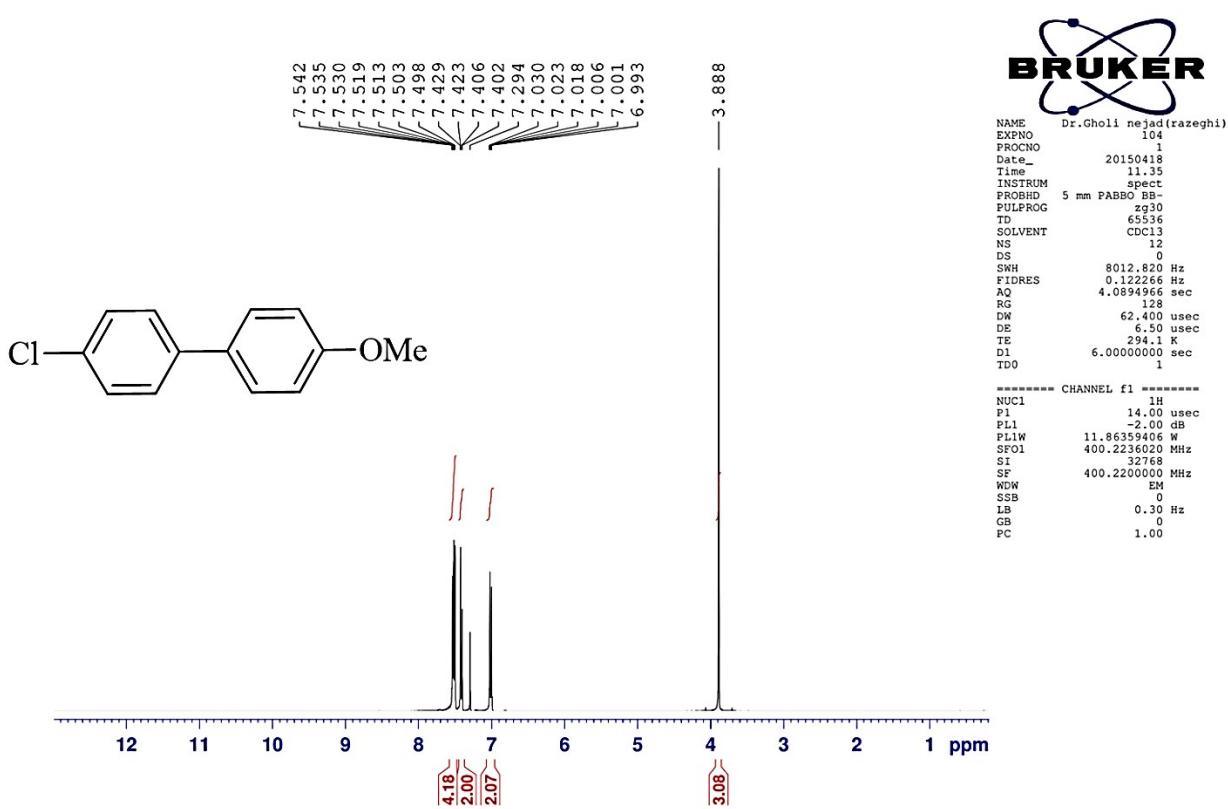
$^{13}\text{C}$  NMR of [1,1'-biphenyl]-4-ol



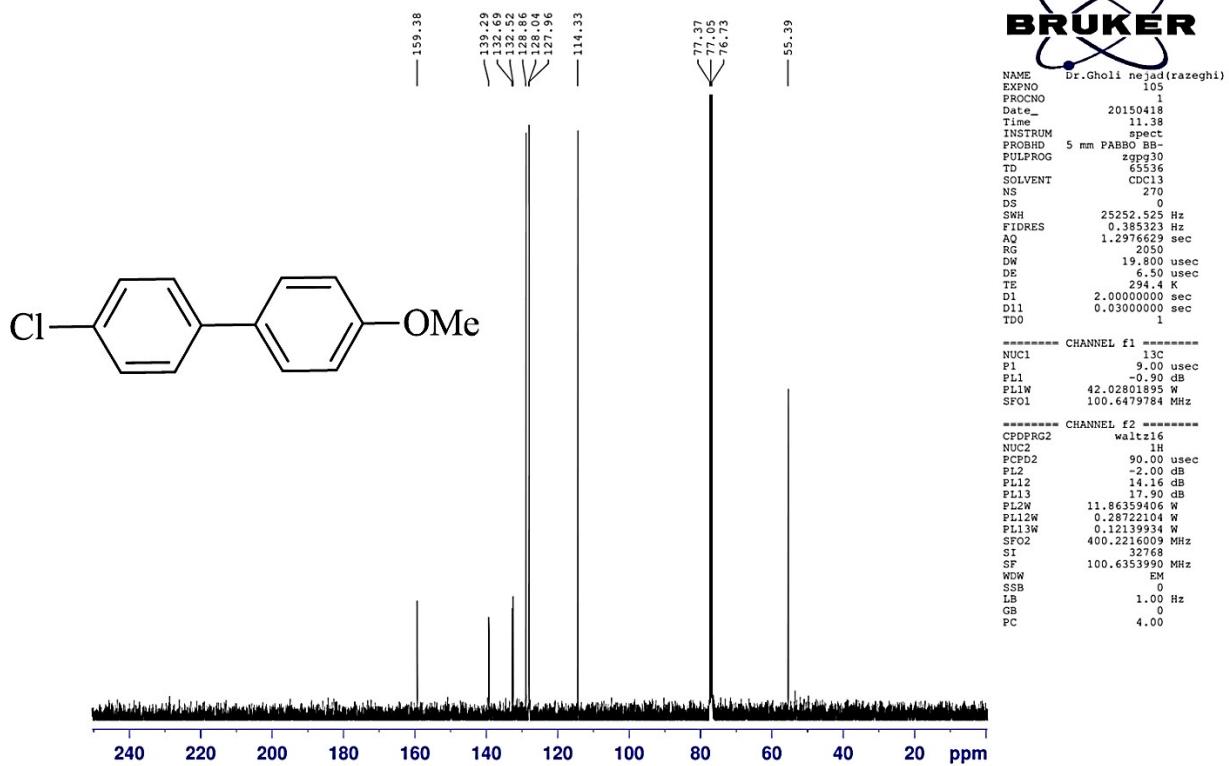
**<sup>1</sup>H NMR of 4-methoxy-1,1'-biphenyl**



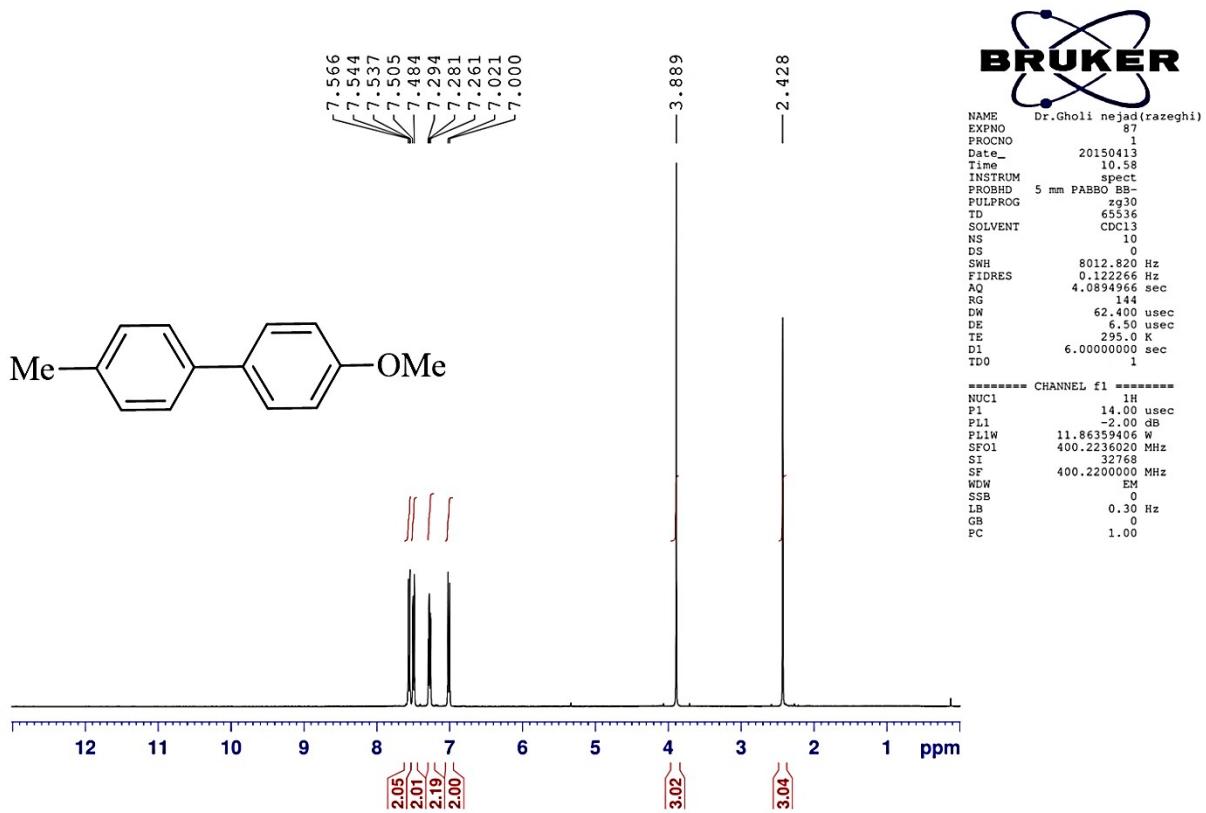
**$^{13}\text{C}$  NMR of 4-methoxy-1,1'-biphenyl**



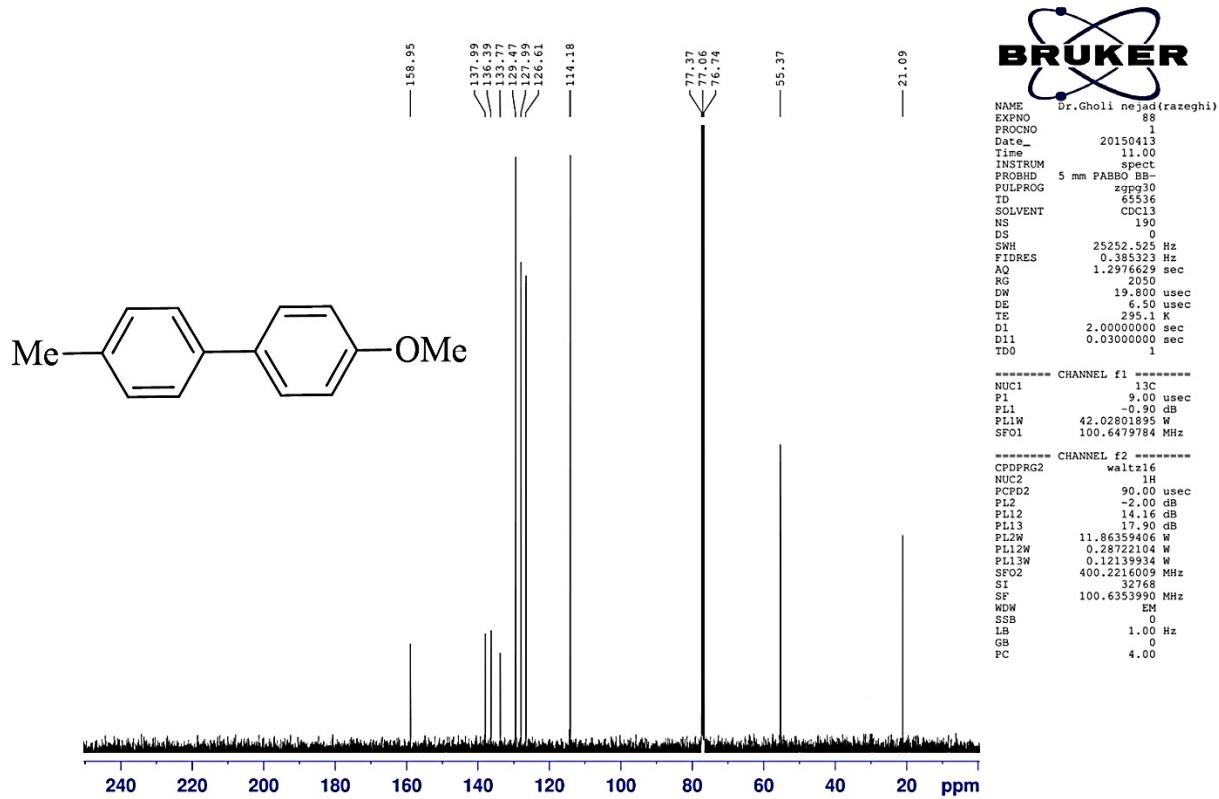
**<sup>1</sup>H NMR of 4-chloro-4'-methoxy-1,1'-biphenyl**



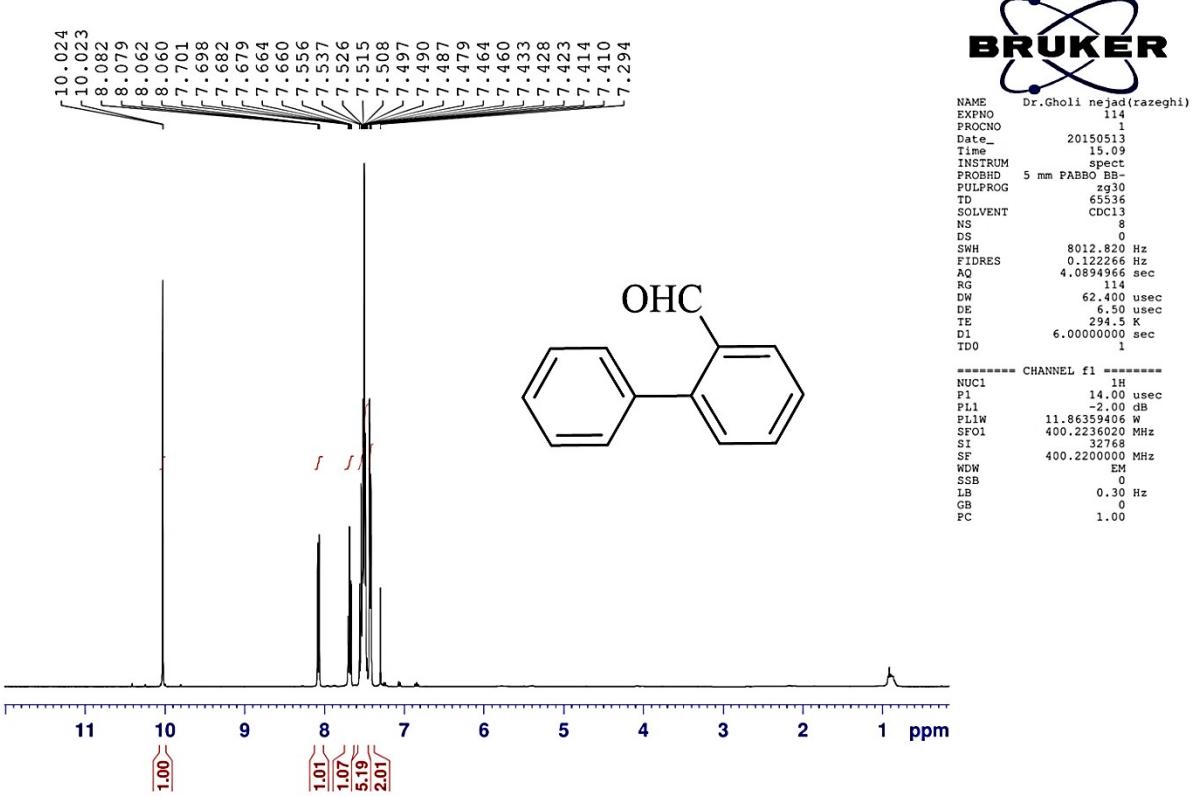
$^{13}\text{C}$  NMR of 4-chloro-4'-methoxy-1,1'-biphenyl



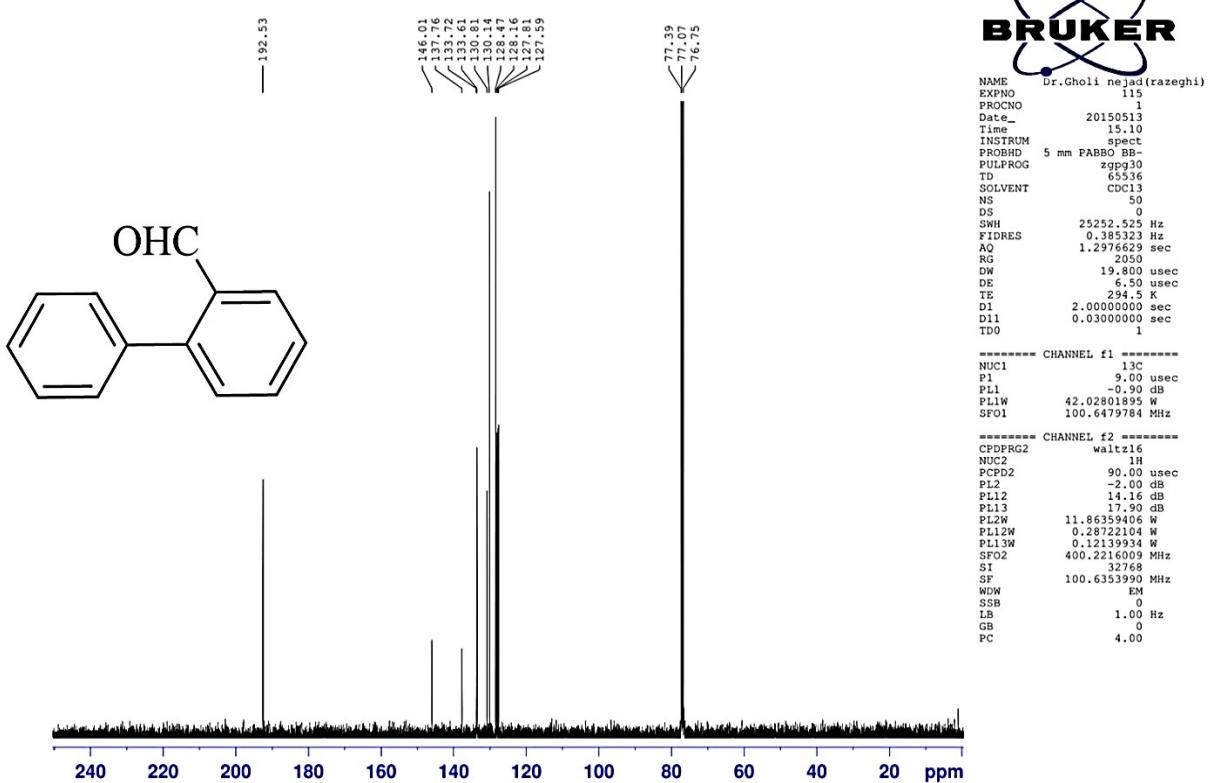
**<sup>1</sup>H NMR of 4-methoxy-4'-methyl-1,1'-biphenyl**



$^{13}\text{C}$  NMR of 4-methoxy-4'-methyl-1,1'-biphenyl



<sup>1</sup>H NMR of [1,1'-biphenyl]-2-carbaldehyde



**<sup>13</sup>C NMR of [1,1'-biphenyl]-2-carbaldehyde**



NAME Dr.Gholi nejad(razeghi)

EXPNO 65

PROCNO 1

Date 20150408

Time 12.49

INSTRUM spect

PROBHD 5 mm PABBO BB-

PULPROG zg30

TD 65536

SOLVENT CDCl3

NS 6

DS 0

SWH 8012.820 Hz

FIDRES 0.122266 Hz

AQ 4.0894966 sec

RG 128

DW 62.400 usec

DE 6.50 usec

TE 294.4 K

D1 6.0000000 sec

TD0 1

===== CHANNEL f1 =====

NUC1 1H

P1 14.00 usec

PL1 -2.00 dB

PL1W 11.86359406 W

SF01 400.223666 MHz

SI 32768

SF 400.2200000 MHz

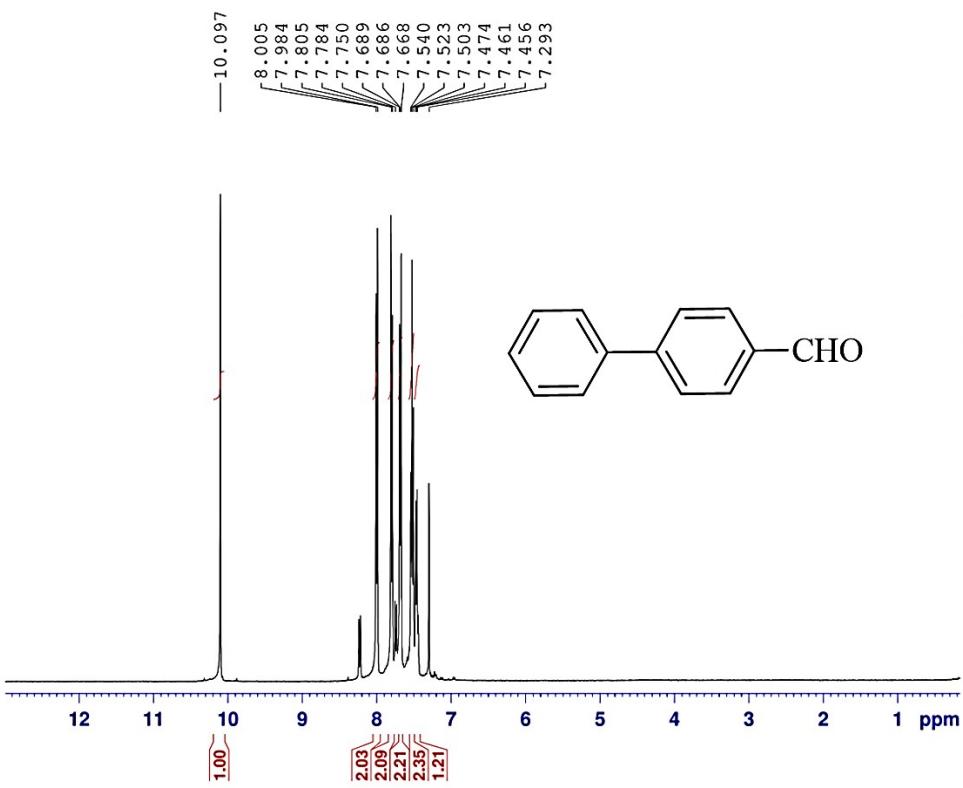
WDW EM

SSB 0

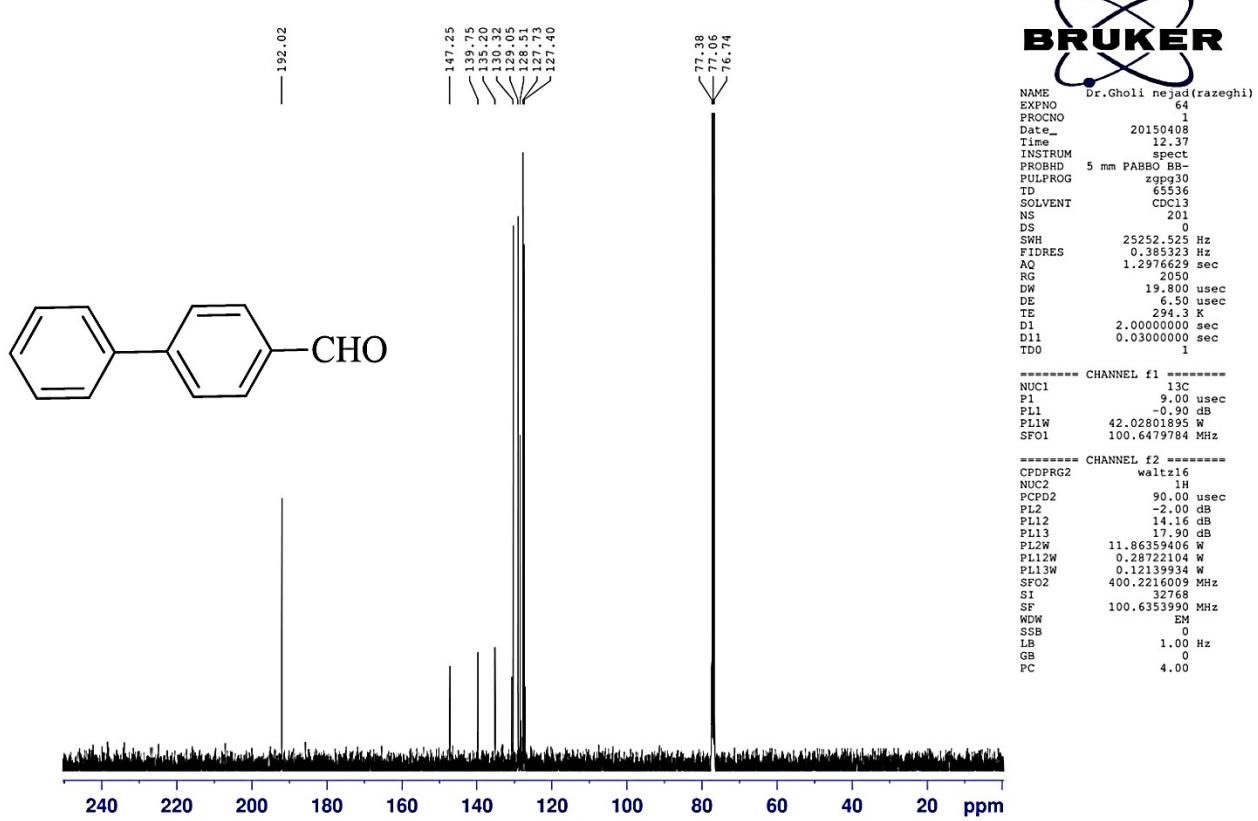
LB 0.30 Hz

GB 0

PC 1.00



<sup>1</sup>H NMR of [1,1'-biphenyl]-4-carbaldehyde



**<sup>13</sup>C NMR of [1,1'-biphenyl]-4-carbaldehyde**



NAME Dr.Gholi nejad(trazeghi)

EXPNO 110

PROCNO 1

Date\_ 20150511

Time\_ 12.32

INSTRUM spect

PROBHD 5 mm PABBO BB-

PULPROG zg30

TD 65536

SOLVENT CDCl3

NS 8

DS 0

SWH 8012.820 Hz

FIDRES 0.122264 Hz

AQ 4.0894596 sec

RG 101

DW 62.400 usec

DE 6.50 usec

TE 294.1 K

D1 6.0000000 sec

TDO 1

----- CHANNEL f1 -----

NUC1 1H

P1 14.00 usec

PL1 -2.00 dB

PL1W 11.86359406 W

SF1 400.2236020 MHz

SI 32768

SF 400.2200000 MHz

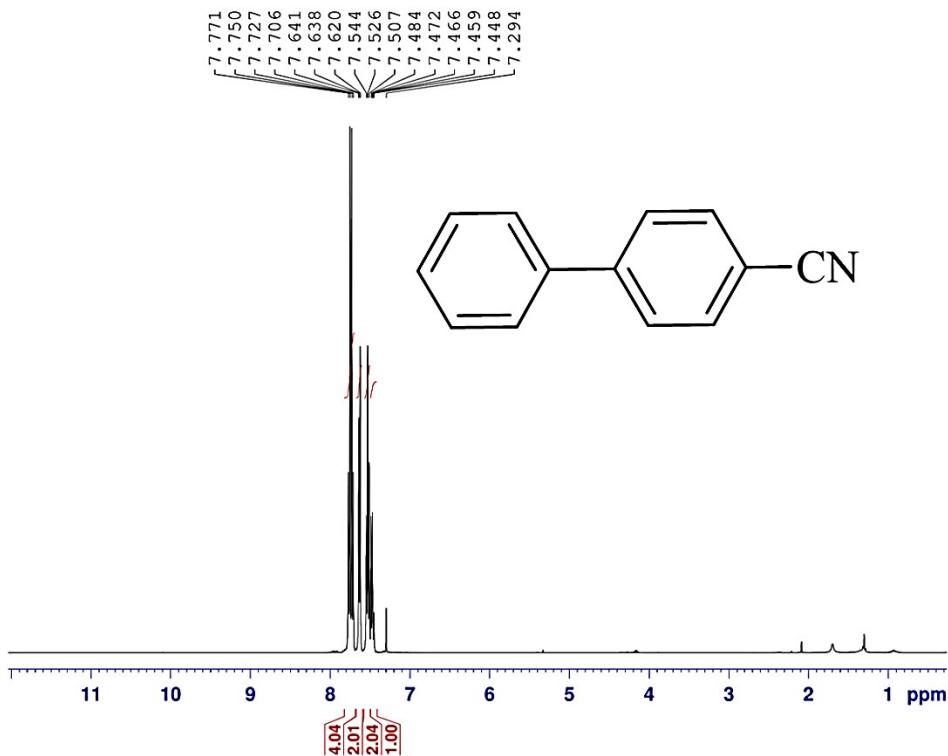
WDW EM

SSB 0

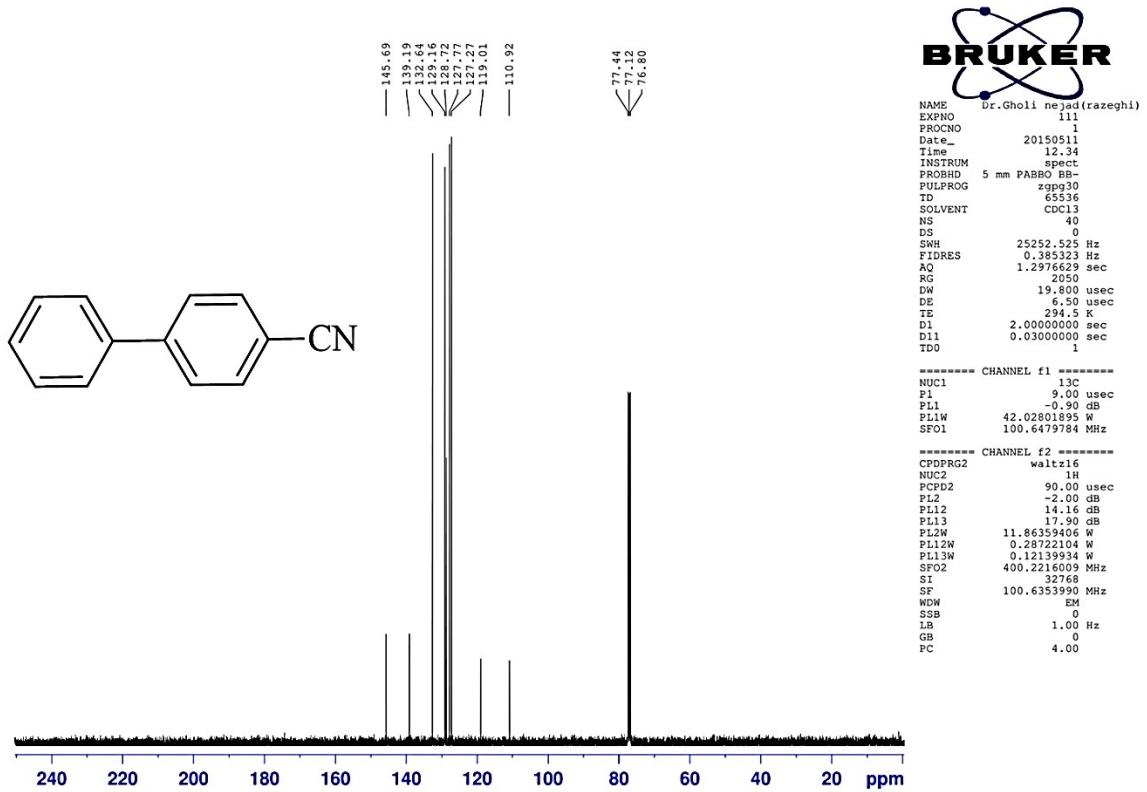
LB 0.30 Hz

GB 0

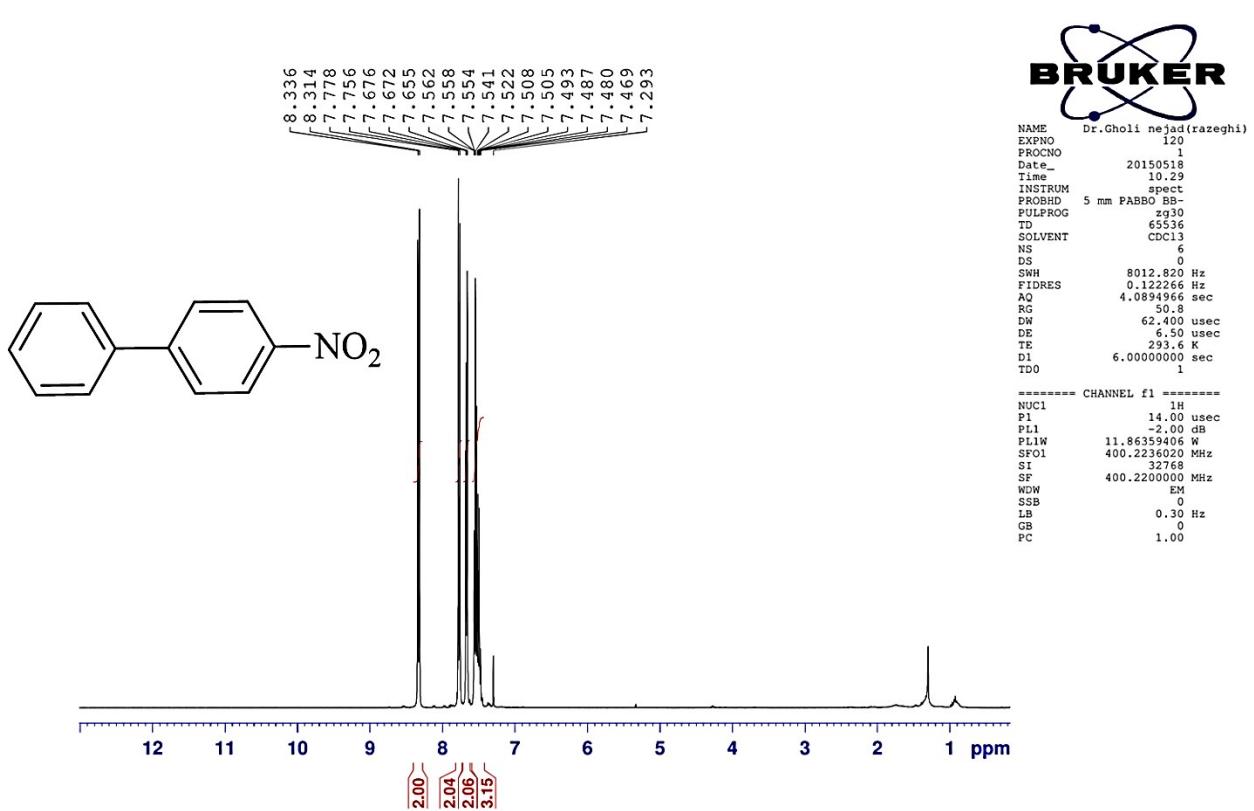
PC 1.00



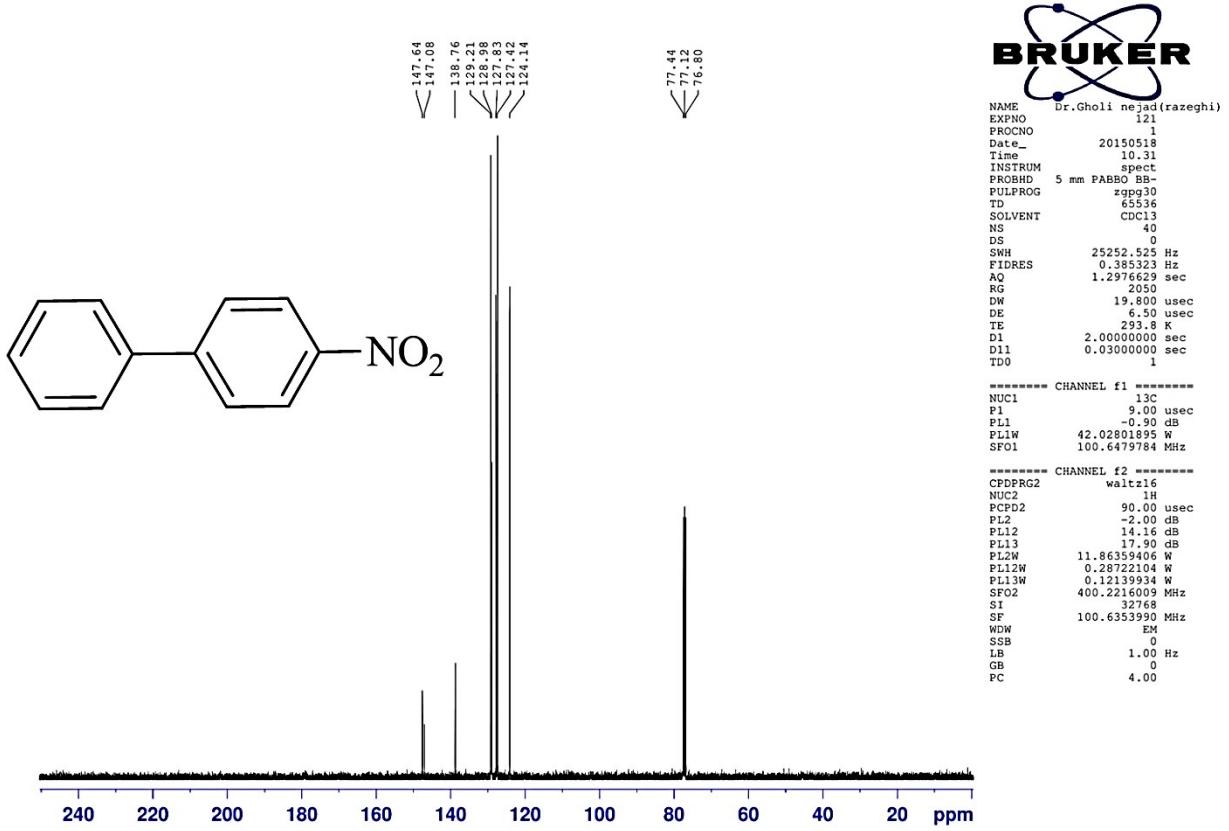
<sup>1</sup>H NMR of [1,1'-biphenyl]-4-carbonitrile



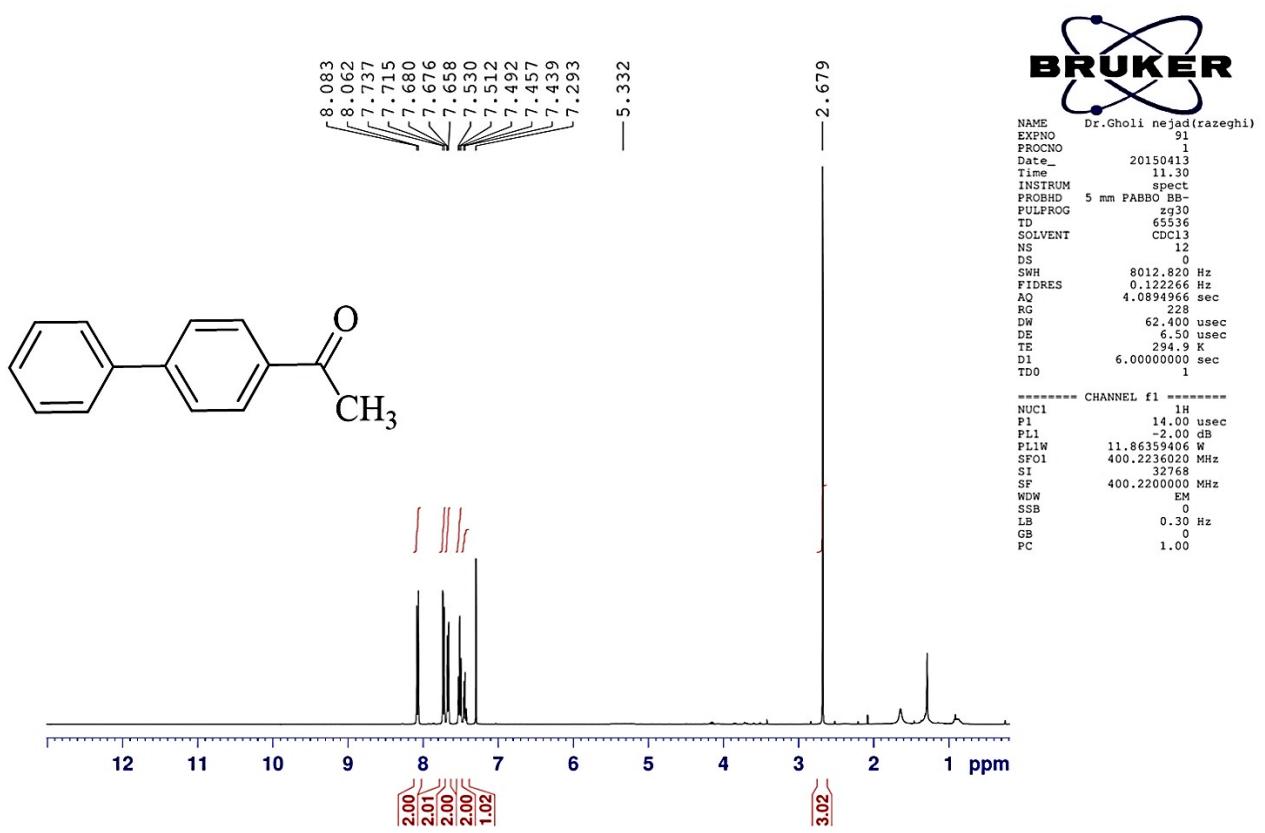
<sup>13</sup>C NMR of [1,1'-biphenyl]-4-carbonitrile



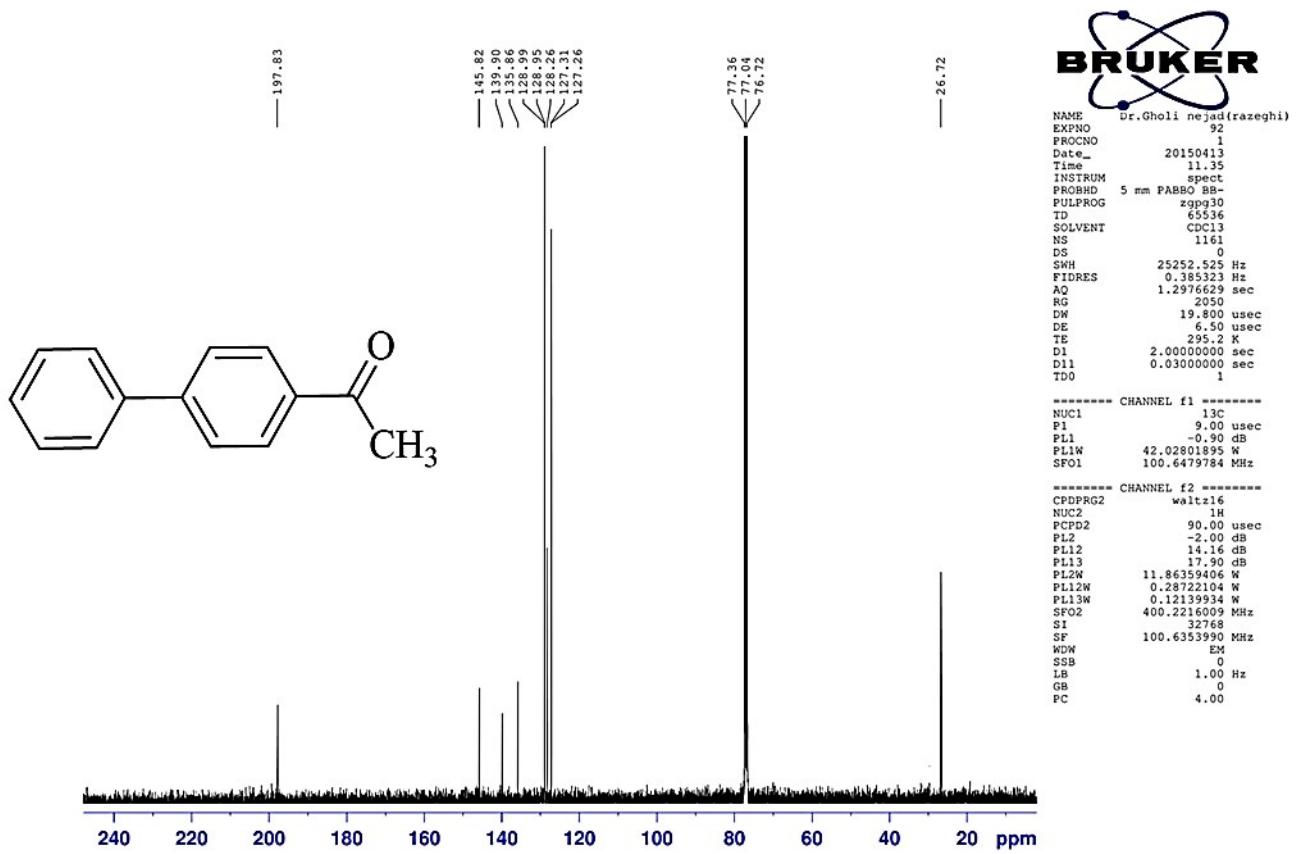
**<sup>1</sup>H NMR of 4-nitro-1,1'-biphenyl**



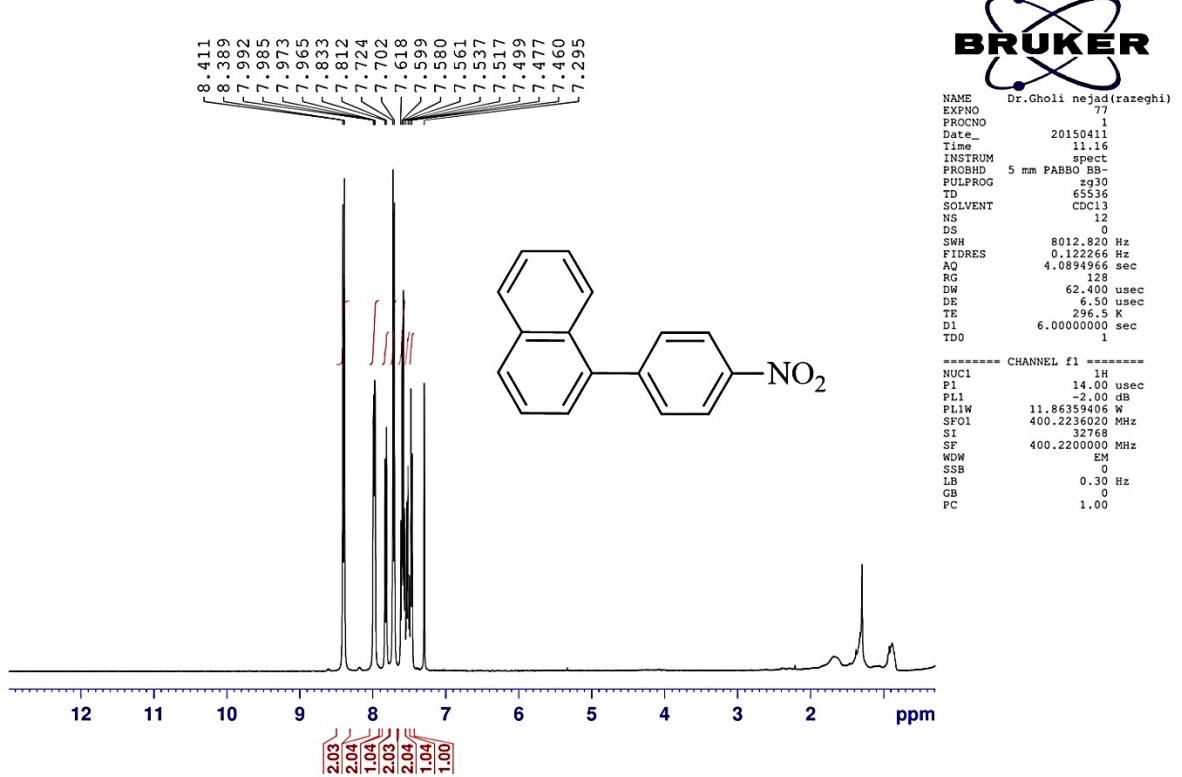
$^{13}\text{C}$  NMR of 4-nitro-1,1'-biphenyl



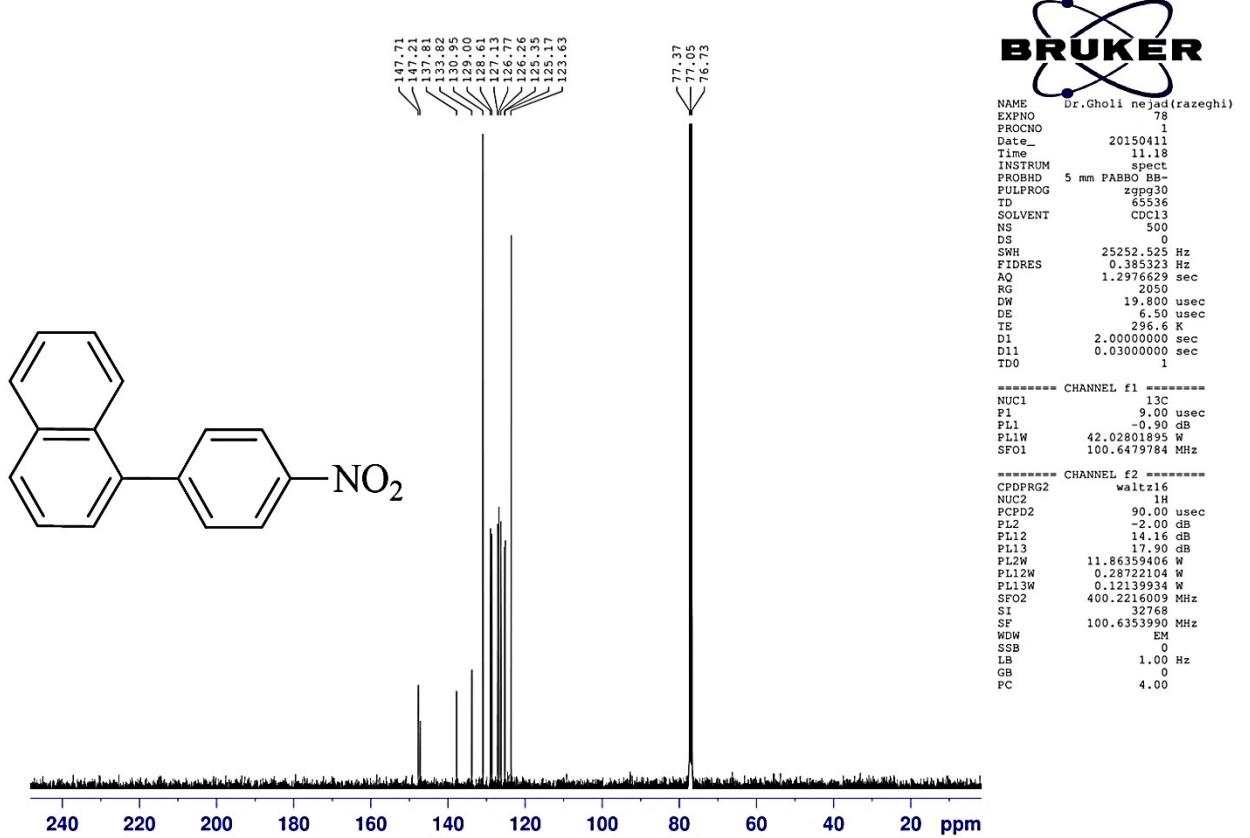
**<sup>1</sup>H NMR of 1-([1,1'-biphenyl]-4-yl)ethanone**



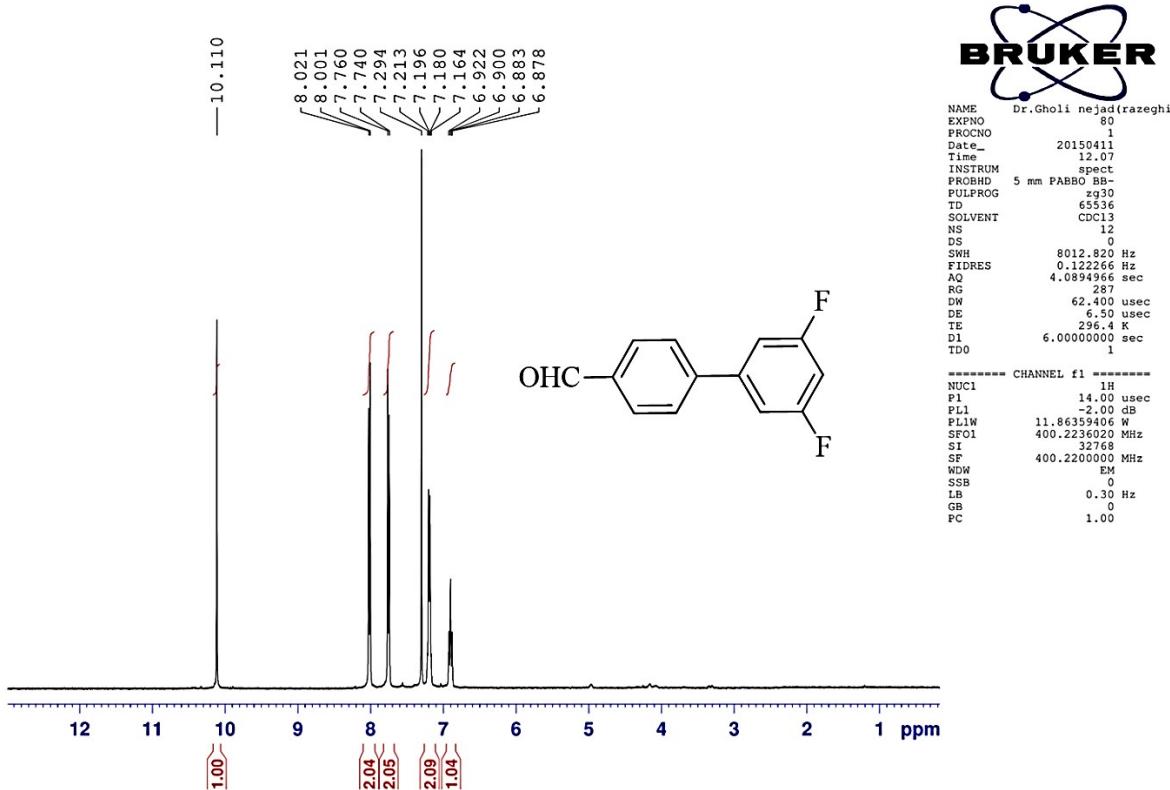
**<sup>13</sup>C NMR of 1-([1,1'-biphenyl]-4-yl)ethanone**



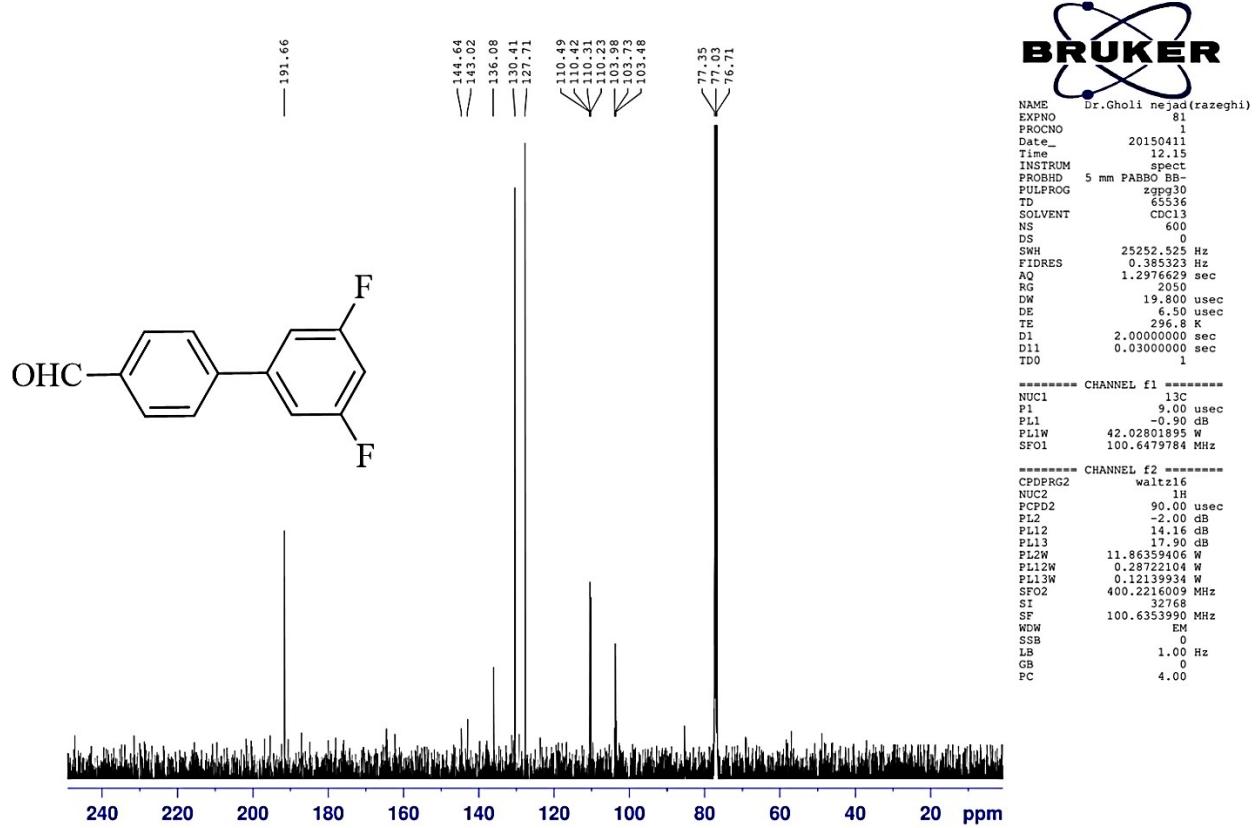
**<sup>1</sup>H NMR of 1-(4-nitrophenyl)naphthalene**



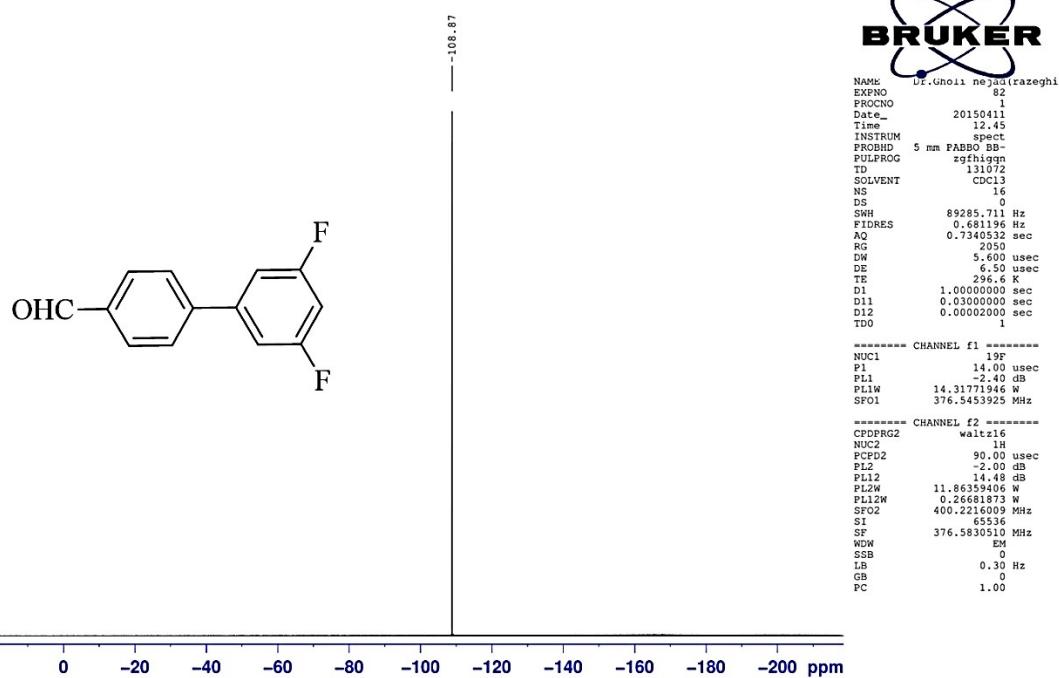
**<sup>13</sup>C NMR of 1-(4-nitrophenyl)naphthalene**



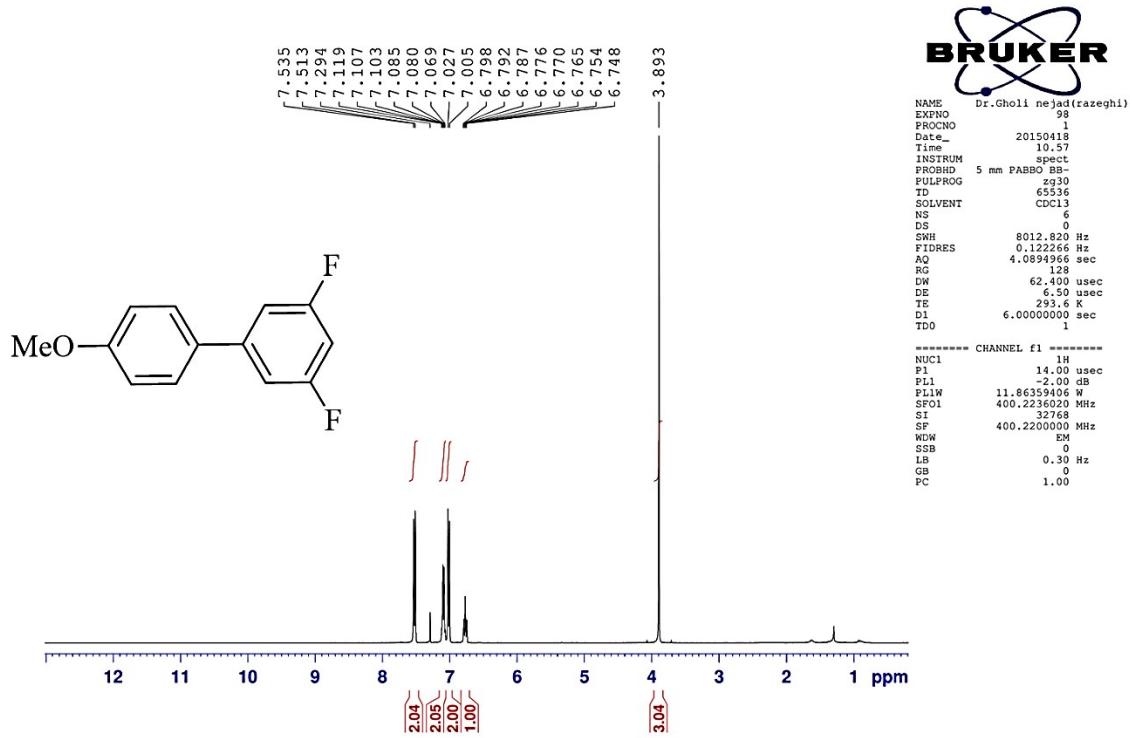
<sup>1</sup>H NMR of 3',5'-difluoro-[1,1'-biphenyl]-4-carbaldehyde



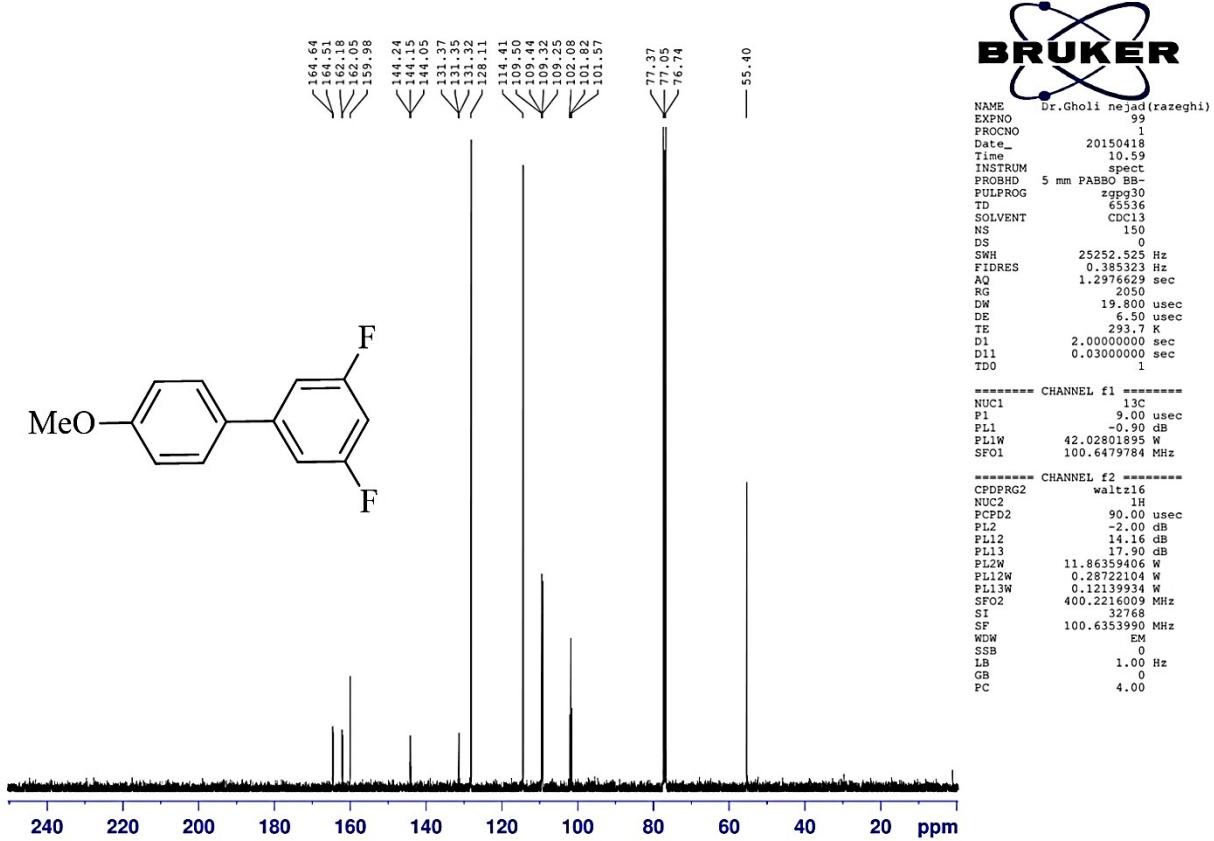
**<sup>13</sup>C NMR of 3',5'-difluoro-[1,1'-biphenyl]-4-carbaldehyde**



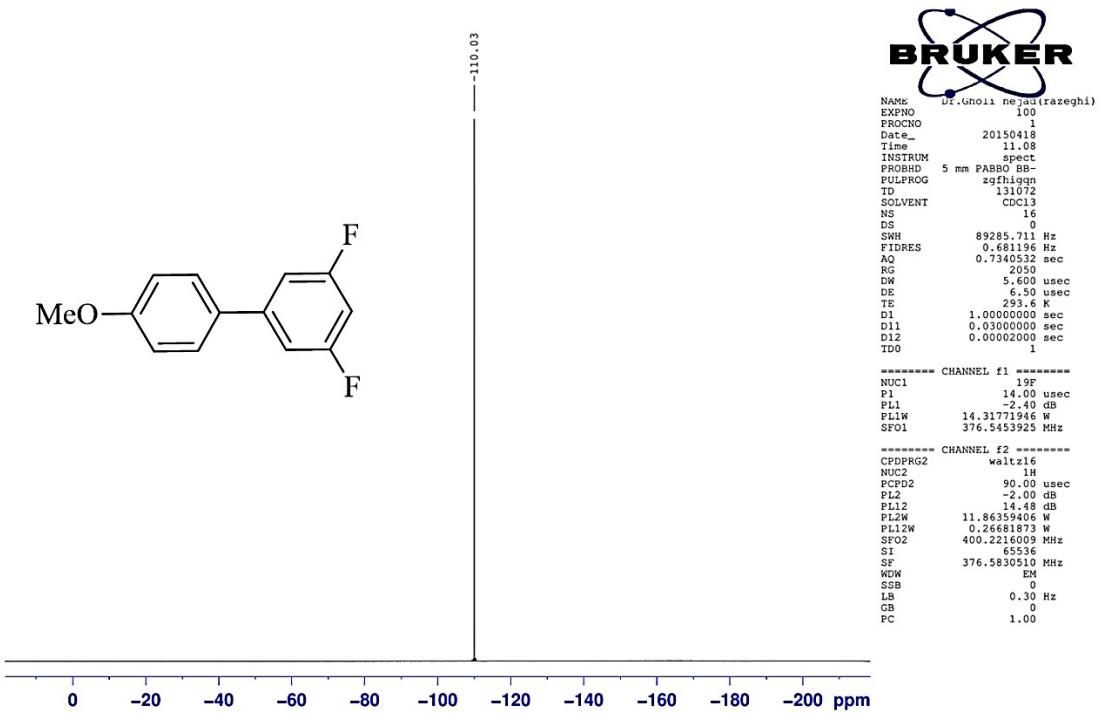
**<sup>19</sup>F NMR of 3',5'-difluoro-[1,1'-biphenyl]-4-carbaldehyde**



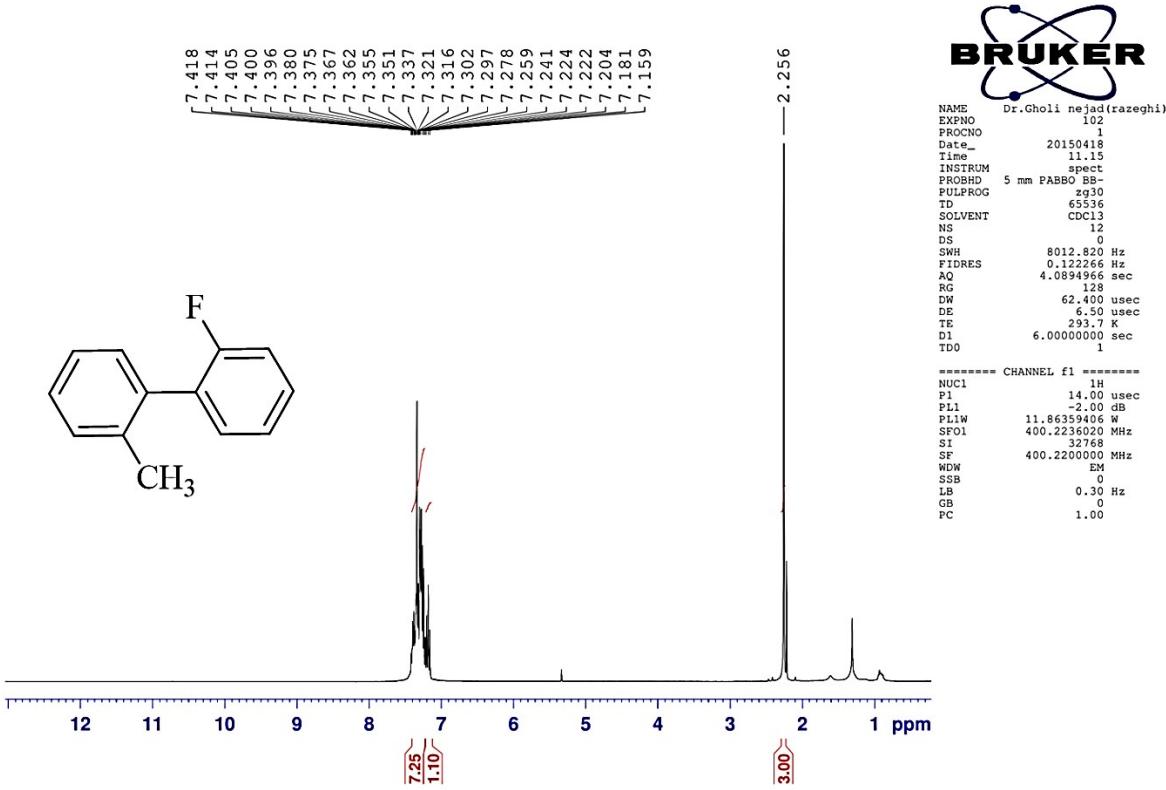
**<sup>1</sup>H NMR of 3,5-difluoro-4'-methoxy-1,1'-biphenyl**



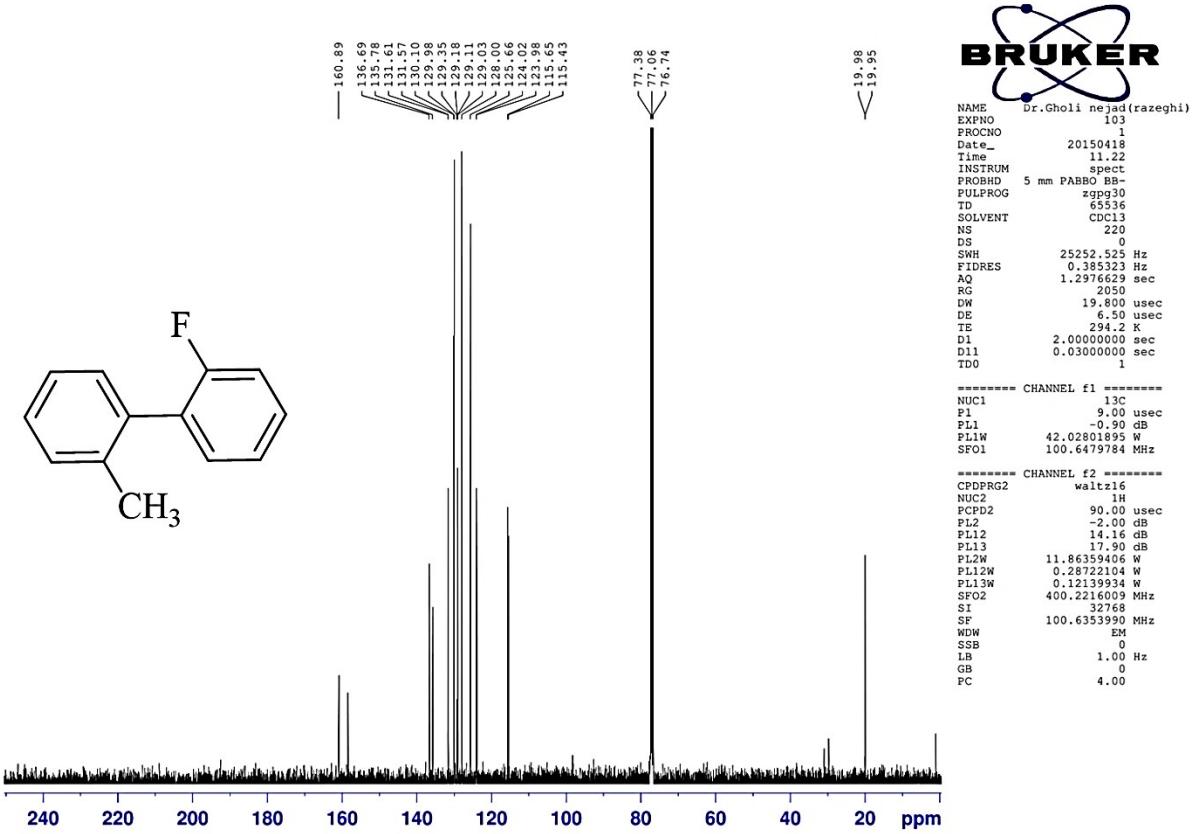
$^{13}\text{C}$  NMR of 3,5-difluoro-4'-methoxy-1,1'-biphenyl



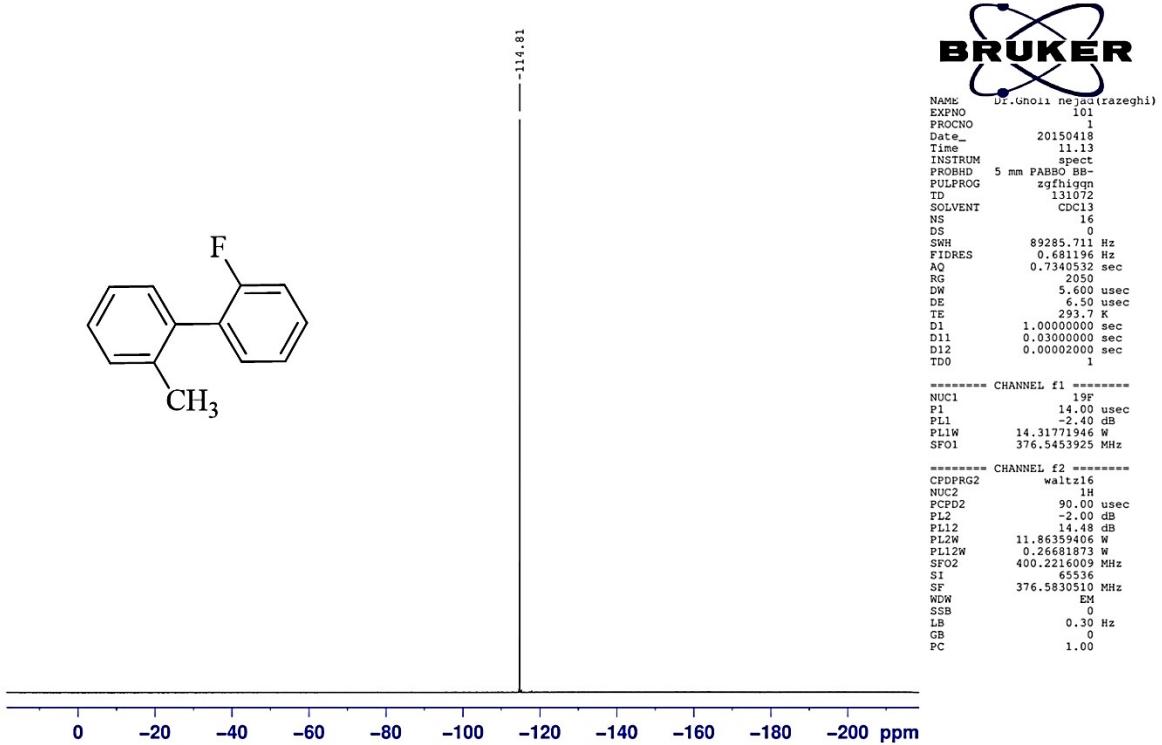
**<sup>19</sup>F NMR of 3,5-difluoro-4'-methoxy-1,1'-biphenyl**



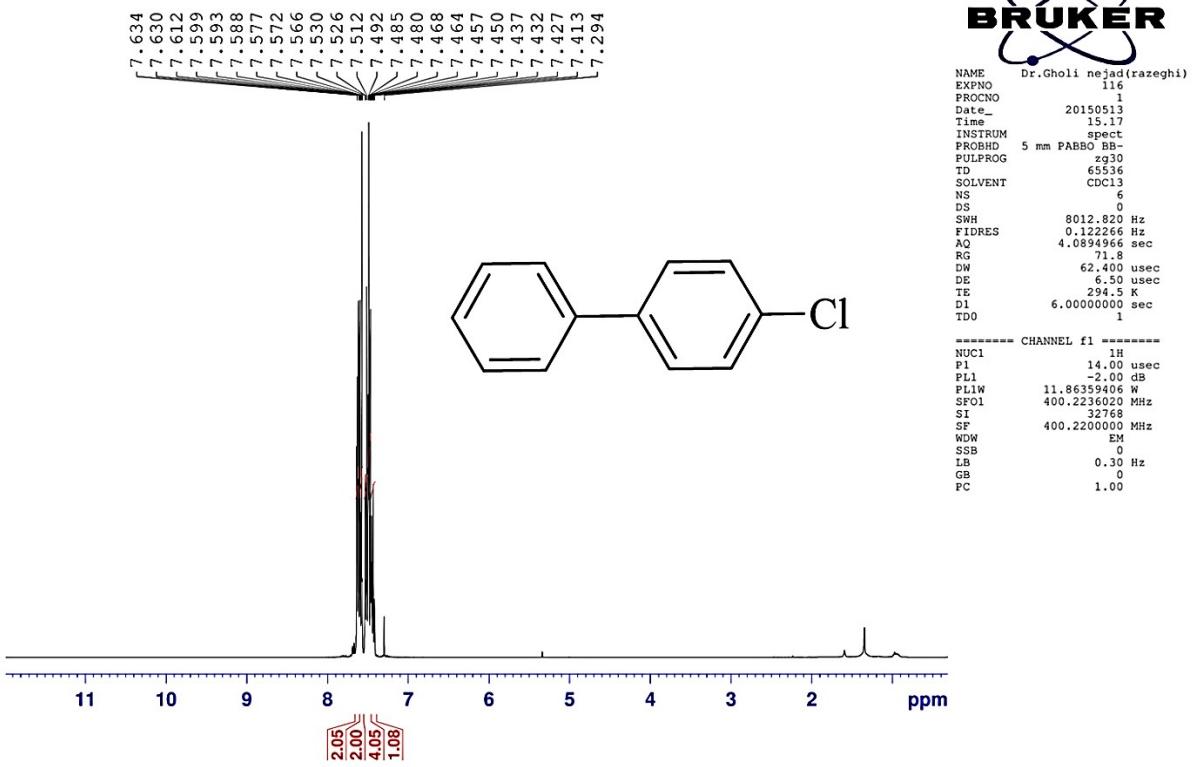
**<sup>1</sup>H NMR of 2-fluoro-2'-methyl-1,1'-biphenyl**



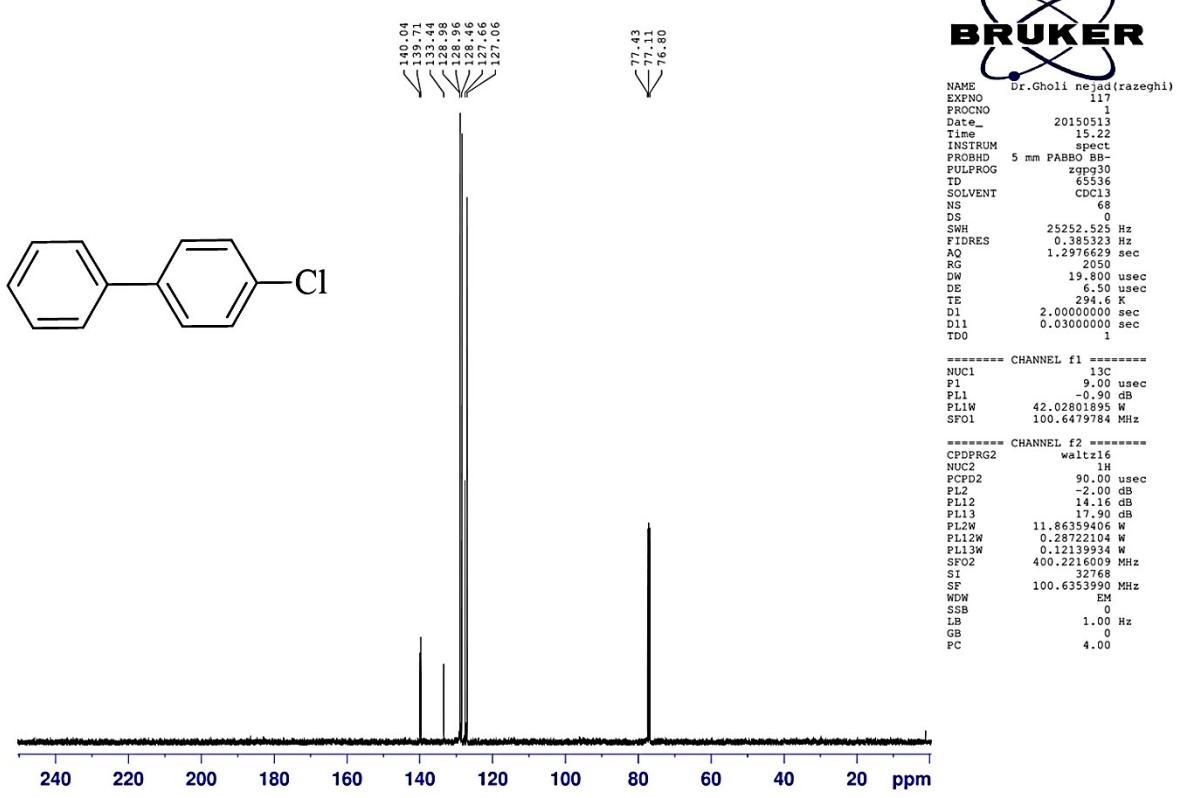
**$^{13}\text{C}$  NMR 2-fluoro-2'-methyl-1,1'-biphenyl**



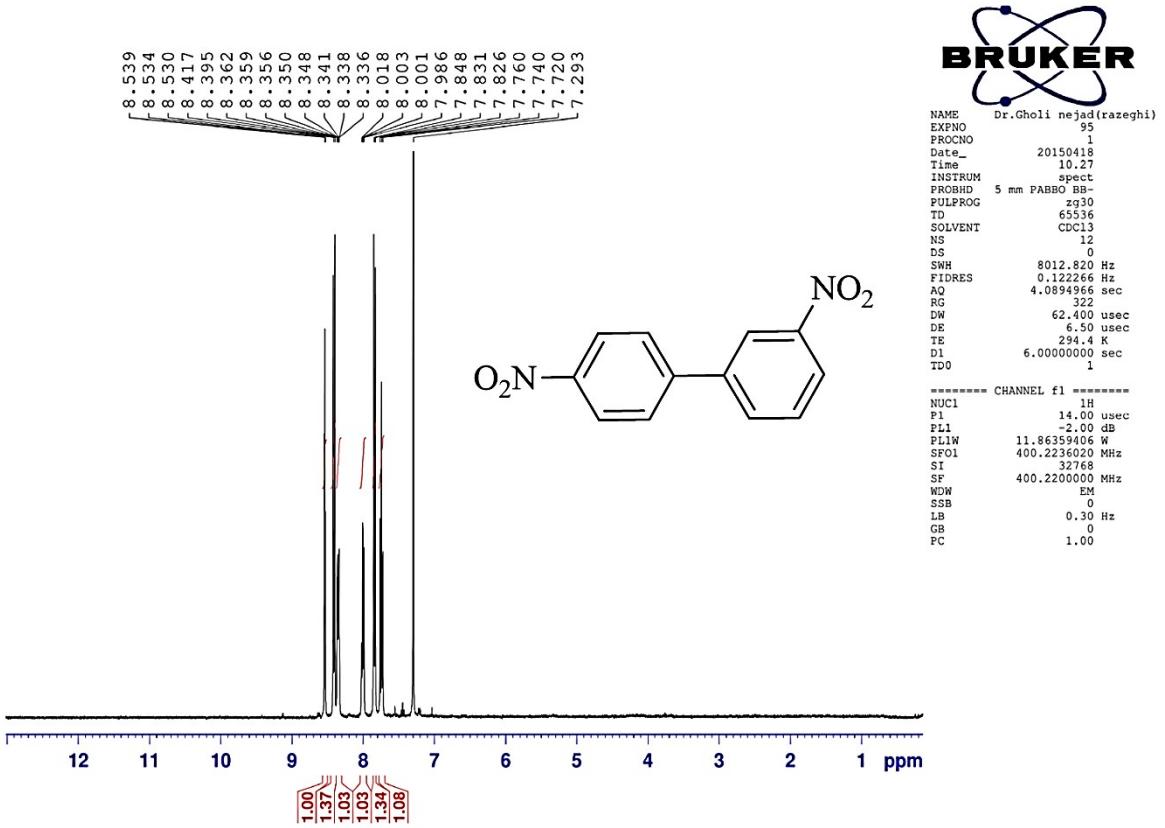
**<sup>19</sup>F NMR of 2-fluoro-2'-methyl-1,1'-biphenyl**



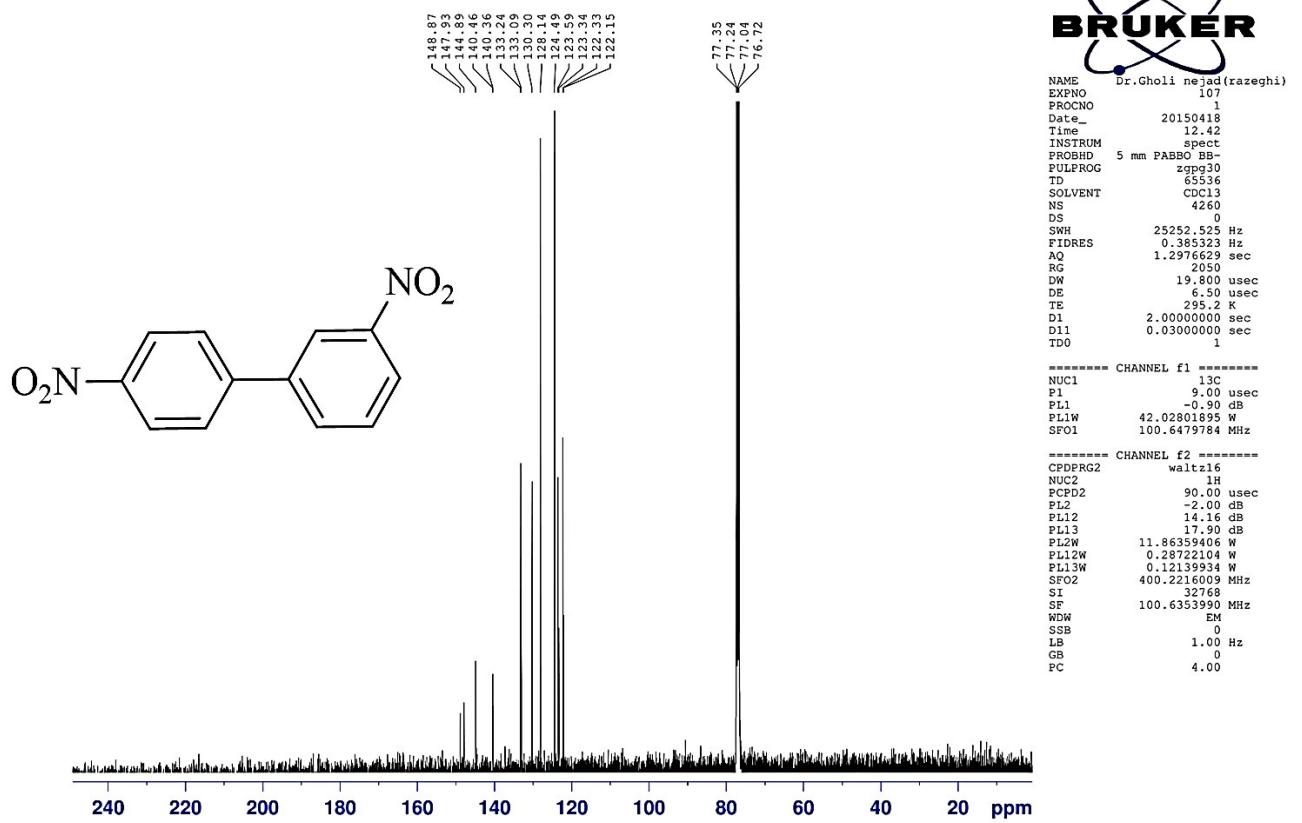
**<sup>1</sup>H NMR of 4-chloro-1,1'-biphenyl**



**<sup>13</sup>C NMR of 4-chloro-1,1'-biphenyl**



<sup>1</sup>H NMR of 3,4'-dinitro-1,1'-biphenyl



**$^{13}\text{C}$  NMR of 3,4'-dinitro-1,1'-biphenyl**

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2. C.-W. Zhao, J.-P. Ma, Q.-K. Liu, Y. Yu, P. Wang, Y.-A. Li, K. Wang and Y.-B. Dong, *Green Chem.*, 2013, **15**, 3150.
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