

The First Report on the Transition Metal-Free Homocoupling of Aryl Halides in the presence of L-Cysteine

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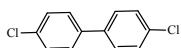
Experimental

Materials

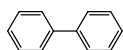
Chemicals and solvents used in this work were obtained from Sigma-Aldrich, Fluka or Merck chemical companies and used without further purification. ^1H and ^{13}C NMR data were recorded in CDCl_3 solutions with a Bruker DRX-400 spectrometer at 400 MHz. Melting points were measured with an Electrothermal 9100 apparatus. MS Model: 5975C VL MSD with Tripe-Axis Detector. IR spectra were recorded as KBr pellets on a VRTEX 70 model BRUKER FT-IR spectrophotometer. ICP-OES simultaneous, Model: Arcos EOP, Company: Spectro, Country: Germany, Torch type: quartz - axial, Detector type: 32 Linear CCD, Spray chamber: Cyclonic

Typical experimental procedure for homocoupling of aryl halides

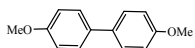
A mixture of aryl halide (1 mmol), L-cysteine (0.8 mmol), KOH (0.4gr), H_2O (0.1 mL), and DMSO (2mL) was stirred at 100°C until complete consumption of starting material as judged by TLC. After completion of the reaction, the reaction mixture was quenched and extracted with ethyl acetate. The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The crude products were purified by silica gel chromatograph to yield the desired product.



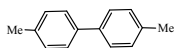
4, 4'-Dichlorobiphenyl [1] MP($^\circ\text{C}$): 144-148. ^1H NMR (400 MHz, CDCl_3): δ = 6.96(J = 8.0 Hz, 2H), 7.6(d, J = 7.6 Hz, 2H) . MS (m/z, %): 222



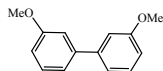
Biphenyl [2] MP($^\circ\text{C}$): 68-70. ^1H NMR (400 MHz, CDCl_3) δ = 7.4 (d, J = 7.6 Hz, 1H), 7.58-7.54 (m, 2H), 7.73 (d, J = 7.6 Hz, 2H), ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 127.4, 127.5, 128.6, 128.9, 129.2, 141.3.



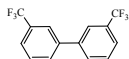
4, 4'-Methoxybiphenyl [3] MP($^\circ\text{C}$): 170-174. ^1H NMR (400 MHz, CDCl_3): δ = 3.83(s, 3H), 6.94(d, J = 10.4 Hz, 2H), 7.48(d, J = 10 Hz, 2H). MS (m/z, %): 214



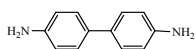
4, 4'- Methylbiphenyl [4] MP(°C): 122-123. ¹H NMR (400 MHz, CDCl₃): δ = 2.34(s, 3H), 7.28(d, J = 8 Hz, 2H), 7.53(d, J = 8 Hz, 2H). MS (m/z, %): 183.



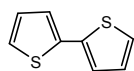
3, 3'-Methoxybiphenyl [1] MP(°C): oil. ¹H NMR (400 MHz, CDCl₃): δ = 3.90(s, 3H), 7.14(d, J = 6.4 Hz, 1H), 7.41(d, J = 6.4 Hz, 1H), 7.58-7.54(m, 1H), 7.76-7.73(m, 1H). MS (m/z, %): 214



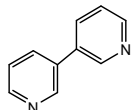
3,3'-bis(trifluoromethyl)biphenyl [5] MP(°C): oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.44-7.40(m, 1H), 7.56-7.50(m, 1H), 7.65(m, 1H). MS (m/z, %): 290



4,4'-Diaminobiphenyl [6] MP(°C): 125-128. ¹H NMR (400 MHz, CDCl₃): δ = 4.46(s, 2H), 6.67(d, J = 9.2, 2H), 8.11(d, J = 9.2, 2H), 7.65(m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 115.7, 129.3, 141.1, 161.3. FT-IR (KBr) ν_{max}/cm⁻¹: 470, 511, 676, 735, 1078, 1174, 1499, 1582, 1618, 2858, 3057, 3377, 3462.



2,2'-Bithiophene [7] MP(°C): 31-33. ¹H NMR (400 MHz, CDCl₃): δ = 7.13-7.08 (m, 1H), 7.33-7.31(m, 2H).



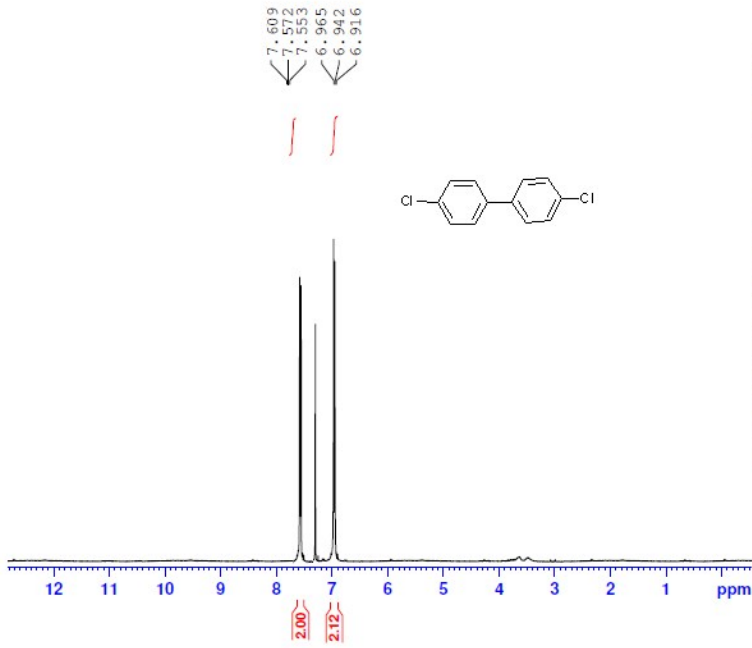
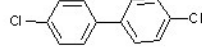
3,3'-Bipyridine [8] MP(°C): 64-68. ¹H NMR (400 MHz, CDCl₃): δ = 7.36-7.32 (m, 1H), 7.74-7.72 (m, 1H), 8.58(d, J = 4, 1H), 8.63(s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 124.4, 132.0, 139.2, 148.2, 151.3.

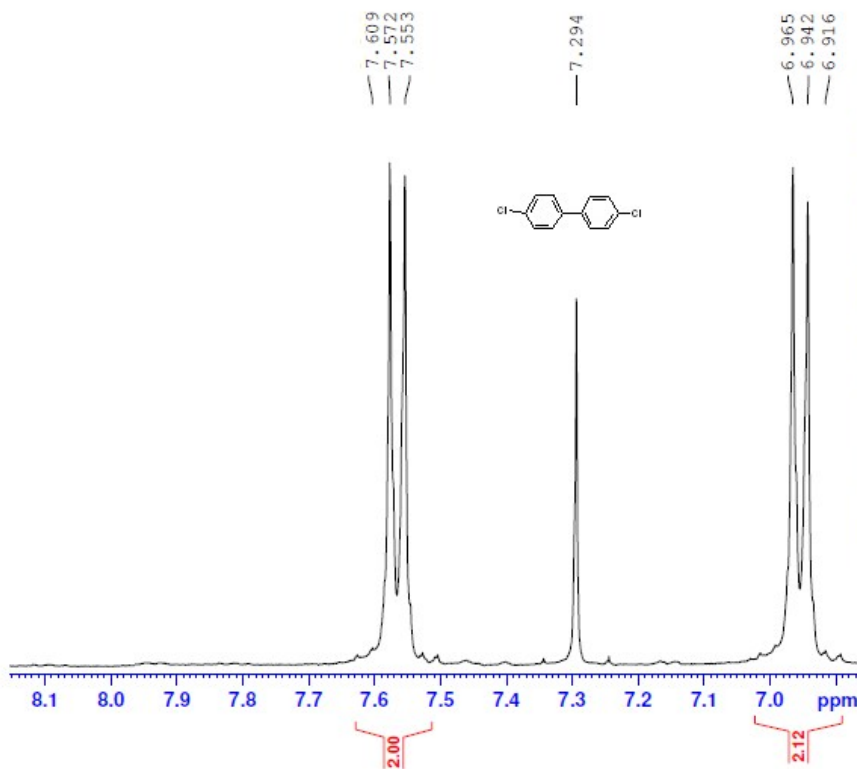
1. X. Li, D. Li, Y. Bai, C. Zhang, H. Chang, W. Gao, W. Wei, *Tetrahedron.*, 2016, 77, 6996.
2. W. Han, C. Liu, Z.-L. Jin, *Org. Lett.*, 2007, 9, 4005.
3. J. Bergman, R. Carlsson, B. Sjöberg, *Org. Synth.* 1977, 57, 18.
4. L.F. Elsom, A. Mckillop, C. Taylor, *Org. Synth.*, 1976, 55, 48.
5. M.R. Pettit, J.C. Tatlow, *J. Chem. Soc.* 1954, 1071.
6. J. Cheng, G. Zhang, J. Du, L. Tang, J. Xu, J. Li, *J. Mater. Chem. A.*, 2011, 21, 3485.
7. S. Dwivedi, S. Bardhan, P. Ghosh, S. Das, *RSC Adv.* 2014, 4, 41045-41050.
8. Y.Y. Zhang, J.D. Lin, X.L. Xu, J.H. Li, *Synth. Commun.*, 2010, 40, 2556



NAME ilam UN
EXPNO 1432
PROCNO 1
Date_ 20171212
Time 8.43
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 256
DW 62.400 usec
DE 6.50 usec
TE 293.6 K
D1 4.00000000 sec
TDO 1

==== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDM EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



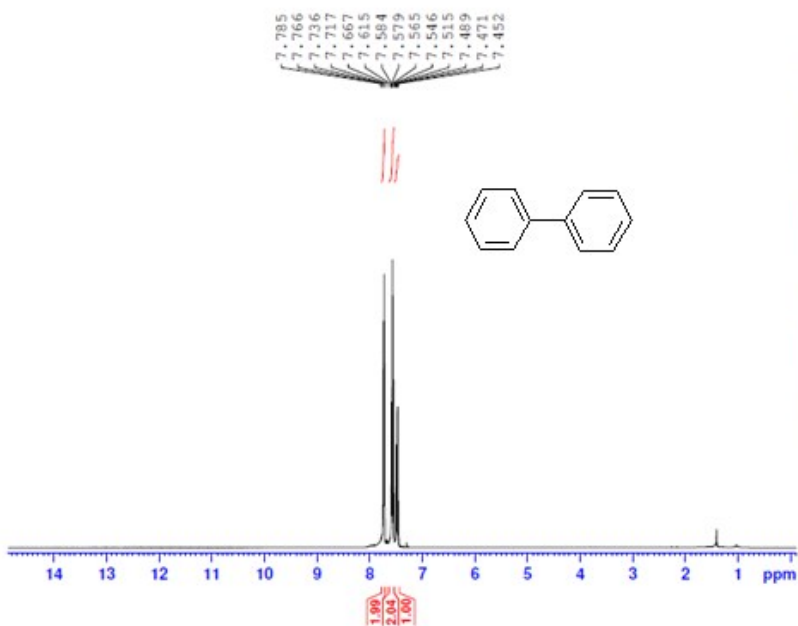


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NAME      ilam UN
EXPNO     1432
PROCNO    1
Date_     20171212
Time      8.43
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PULPROG   zg30
TD        65536
SOLVENT   CDCl3
NS        20
DS        0
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FIDRES    0.122266 Hz
AQ        4.0894966 sec
RG        256
DW        62.400 usec
DE        6.50 usec
TE        293.6 K
D1        4.0000000 sec
TDO       1
  
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===== CHANNEL f1 =====
NUC1      1H
P1        14.00 usec
PL1       -2.00 dB
PL1W      11.86359406 W
SFO1      400.2236020 MHz
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WDW       EM
SSB       0
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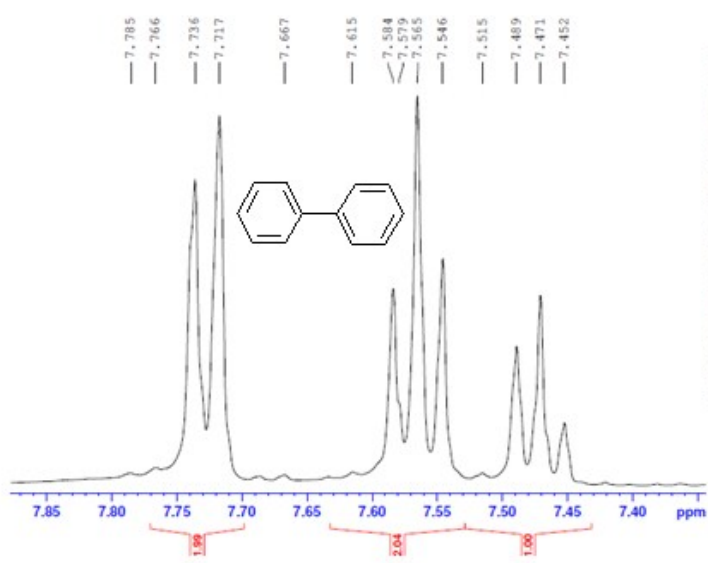


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PROCNO    1
Date_     20171211
Time      18.34
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NS        20
DS        0
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FIDRES    0.122266 Hz
AQ        4.0894966 sec
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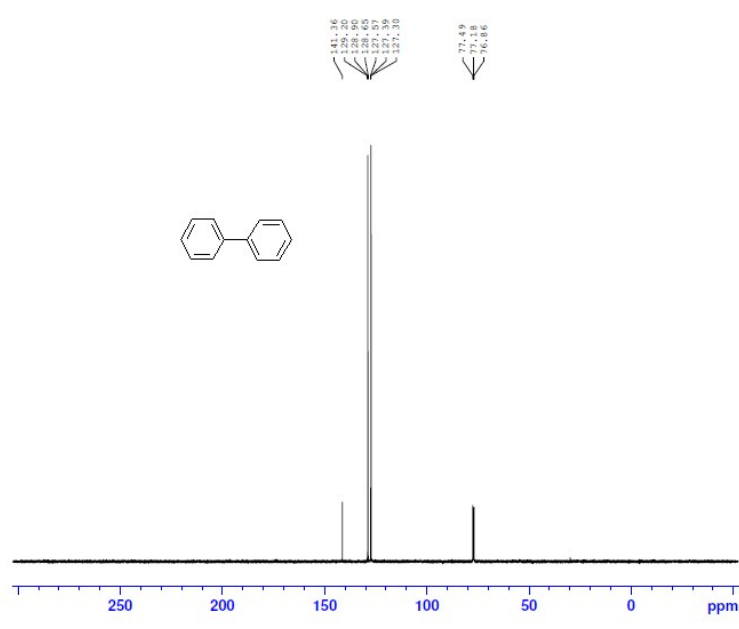
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SI        32768
SF        400.2200000 MHz
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NAME      13mm UN
EXPNO     1427
PROCNO    1
Date_     20171211
Time      18.34
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         20
DS         0
SWH        8012.820 Hz
FIDRES     0.122264 Hz
AQ         4.0894964 sec
RG         34
DW         62.600 usec
DE         6.50 usec
TE         293.2 K
D1         4.0000000 sec
D11        1
TDO        1

===== CHANNEL f1 =====
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P1        14.00 usec
PL1       -2.00 dB
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SFO1      400.2236020 MHz
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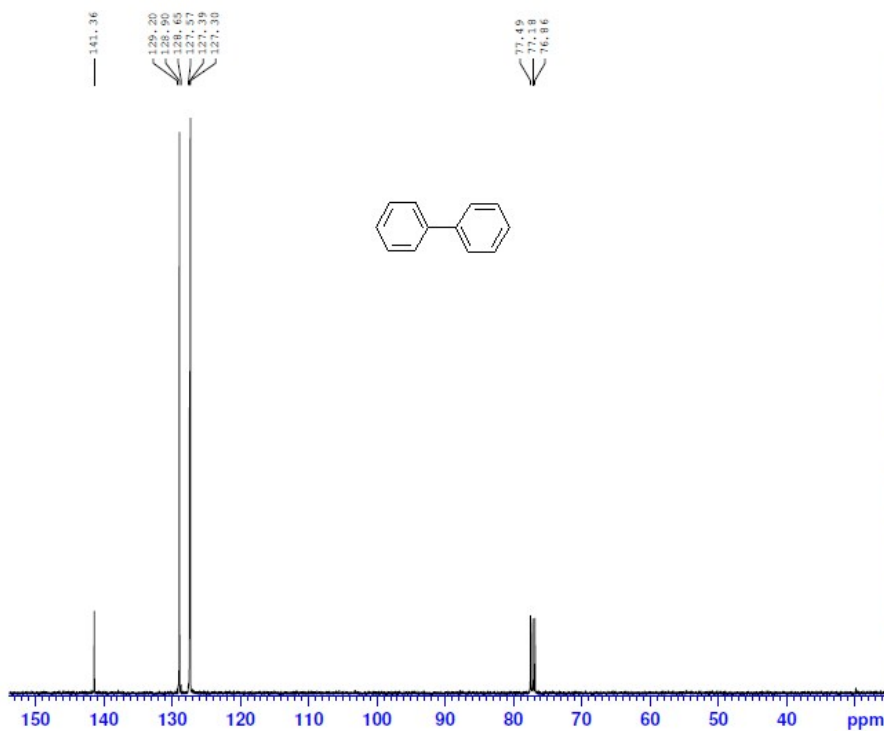


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DS         0
SWH        35714.285 Hz
FIDRES     0.544957 Hz
AQ         0.9175540 sec
RG         2050
DW         14.000 usec
DE         6.50 usec
TE         293.2 K
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D11        0.0300000 sec
TDO        1

===== CHANNEL f1 =====
NUC1      13C
P1        9.00 usec
PL1       -0.90 dB
PL1W      42.02801895 W
SFO1      100.6479784 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     90.00 usec
PL2       -2.00 dB
PL12      14.48 dB
PL13      17.90 dB
PL2W      11.86359406 W
PL12W     0.26681873 W
PL13W     0.12139934 W
SFO2      400.2216009 MHz
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PC        1.40
  
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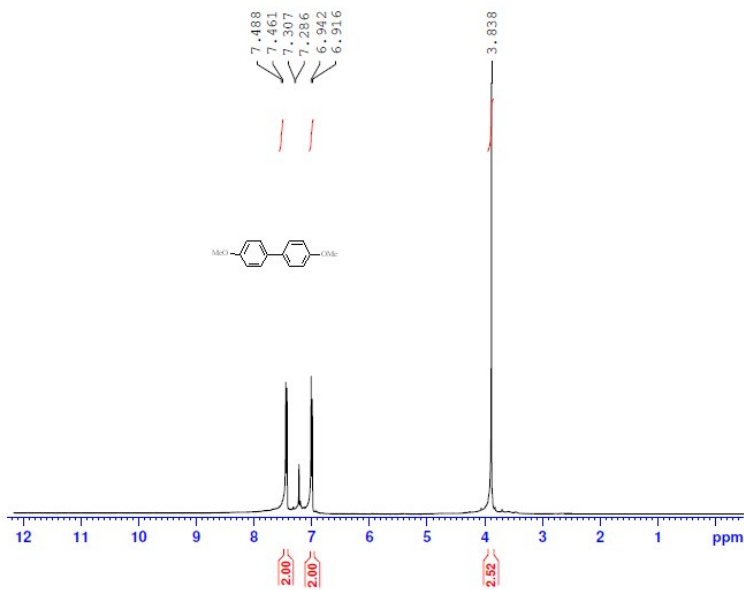
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Time      18.37
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TD         65536
SOLVENT   CDCl3
NS         176
DS         0
SWH        35714.285 Hz
FIDRES    0.544957 Hz
AQ         0.9175540 sec
RG         2050
DW         14.000 usec
DE         6.50 usec
TE         293.8 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0        1
  
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```

===== CHANNEL f1 =====
NUC1      13C
P1         9.00 usec
PL1        -0.90 dB
PL1W       42.02801895 W
SFO1      100.6479784 Mhz
  
```

```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     90.00 usec
PL2        -2.00 dB
PL12       14.48 dB
PL13       17.90 dB
PL2W       11.86359406 W
PL12W      0.26681873 W
PL13W      0.12139934 W
SFO2      400.2216009 Mhz
SI         32768
SF         100.6353990 Mhz
WDW        EM
SSB         0
LB          1.00 Hz
GB          0
PC          1.40
  
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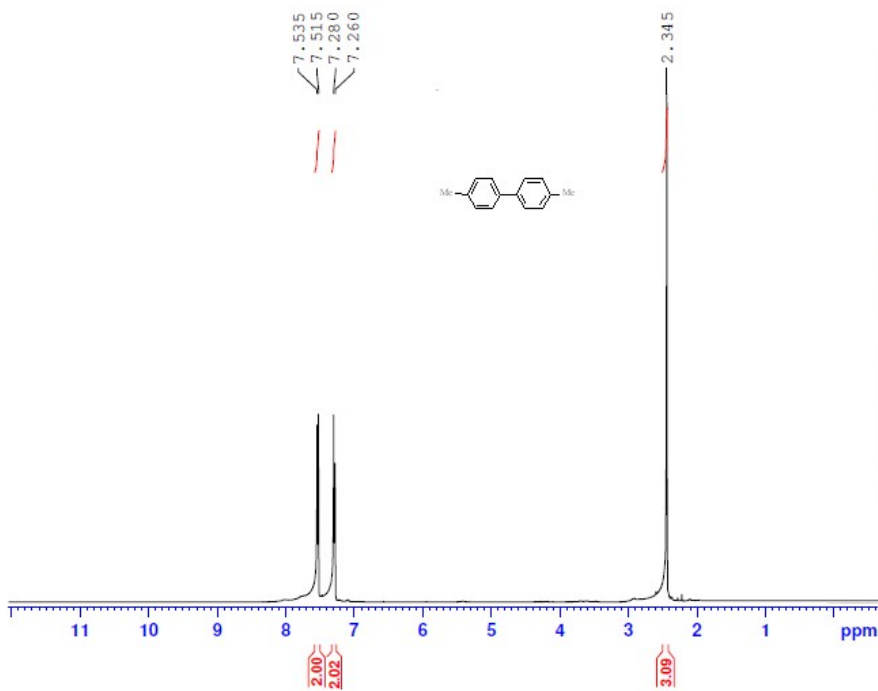


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NAME      ilam UN
EXPNO     1428
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Date_     20171212
Time      8.10
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PULPROG   zg30
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SOLVENT   CDCl3
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DS         0
SWH        8012.820 Hz
FIDRES    0.122266 Hz
AQ         4.089496 sec
RG         256
DW         62.400 usec
DE         6.50 usec
TE         293.5 K
D1         4.00000000 sec
TD0        1
  
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```

===== CHANNEL f1 =====
NUC1      1H
P1         14.00 usec
PL1        -2.00 dB
PL1W       11.86359406 W
SFO1      400.2236020 Mhz
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SF         400.2200000 Mhz
WDW        EM
SSB         0
LB          0.30 Hz
GB          0
PC          1.00
  
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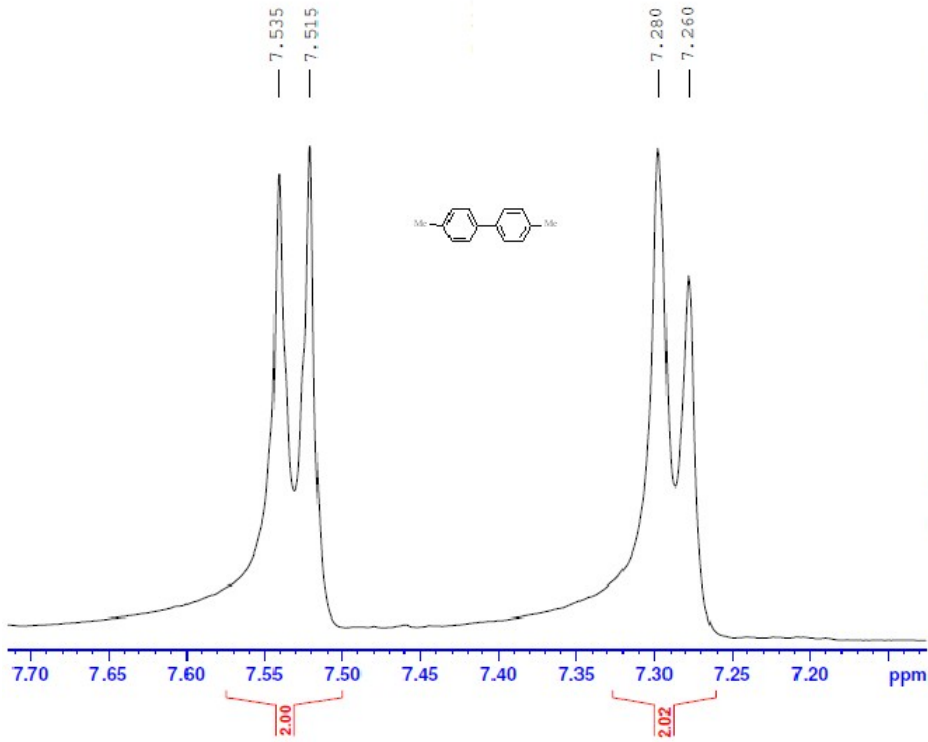
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TE 294.4 K
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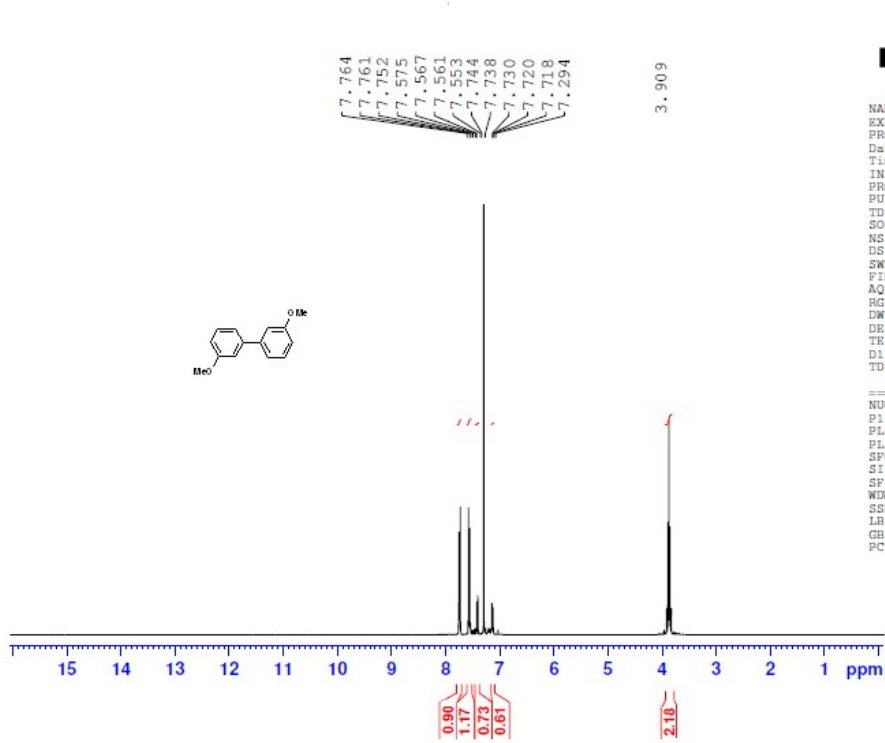
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SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME ilam UN
EXPNO 1405
PROCNO 1
Date_ 20171211
Time 8.39
INSTRUM spect
PROBHD 5 mm PABBO B8
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 20
DS 0
SWH 8012.820 Hz
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AQ 4.0894966 sec
RG 114
DW 62.400 usec
DE 6.50 usec
TE 294.4 K
D1 4.0000000 sec
TD0 1

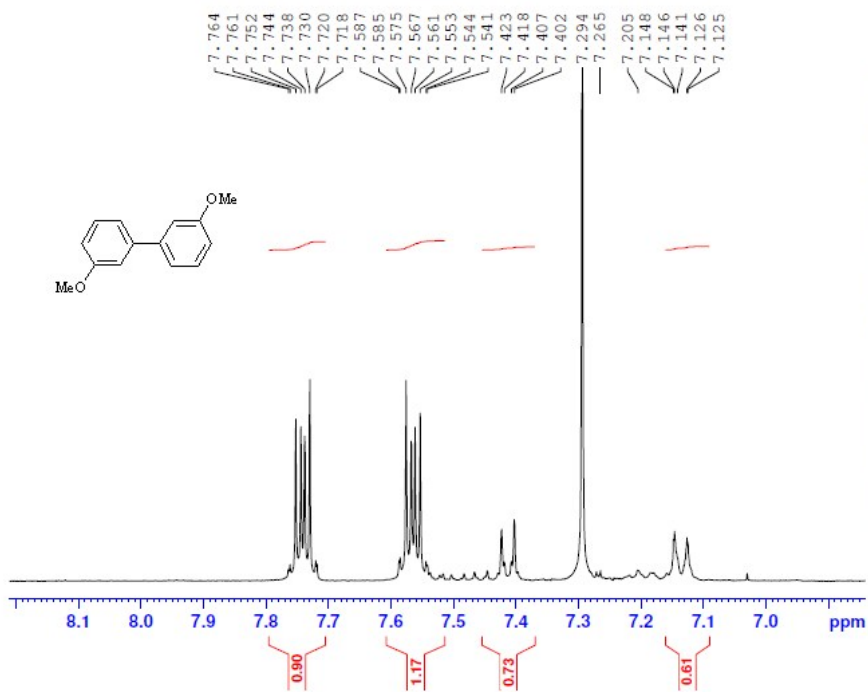
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WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





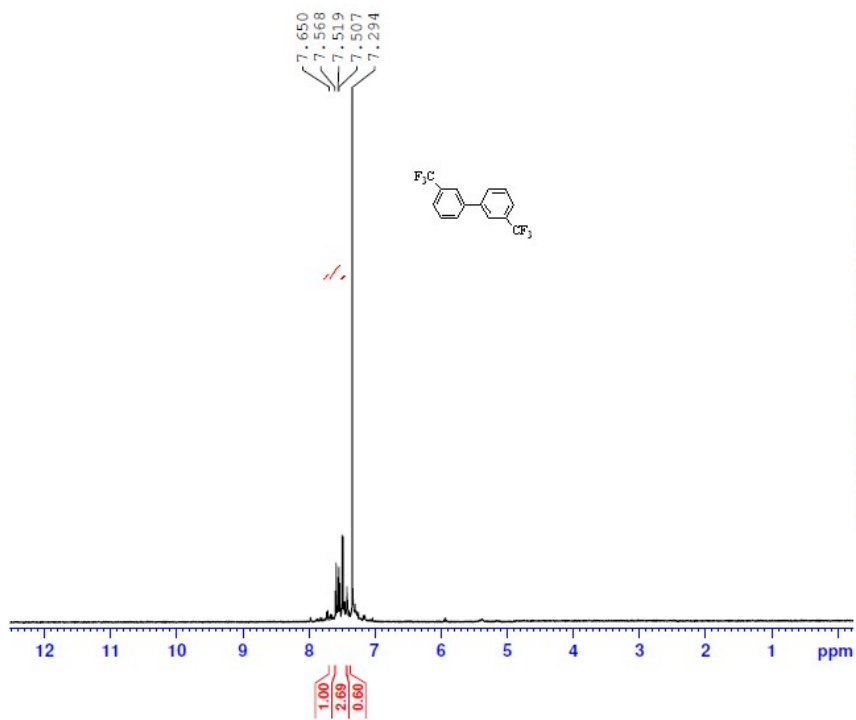
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 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 20
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 256
 DW 62.400 usec
 DE 6.50 usec
 TE 293.6 K
 D1 4.00000000 sec
 TDO 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 -2.00 dB
 PL1W 11.86359406 W
 SFO1 400.2236020 MHz
 SI 32768
 SF 400.2200000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NAME ilam UN
 EXPNO 1430
 PROCNO 1
 Date_ 20171212
 Time 8.29
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 20
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 256
 DW 62.400 usec
 DE 6.50 usec
 TE 293.6 K
 D1 4.00000000 sec
 TDO 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 -2.00 dB
 PL1W 11.86359406 W
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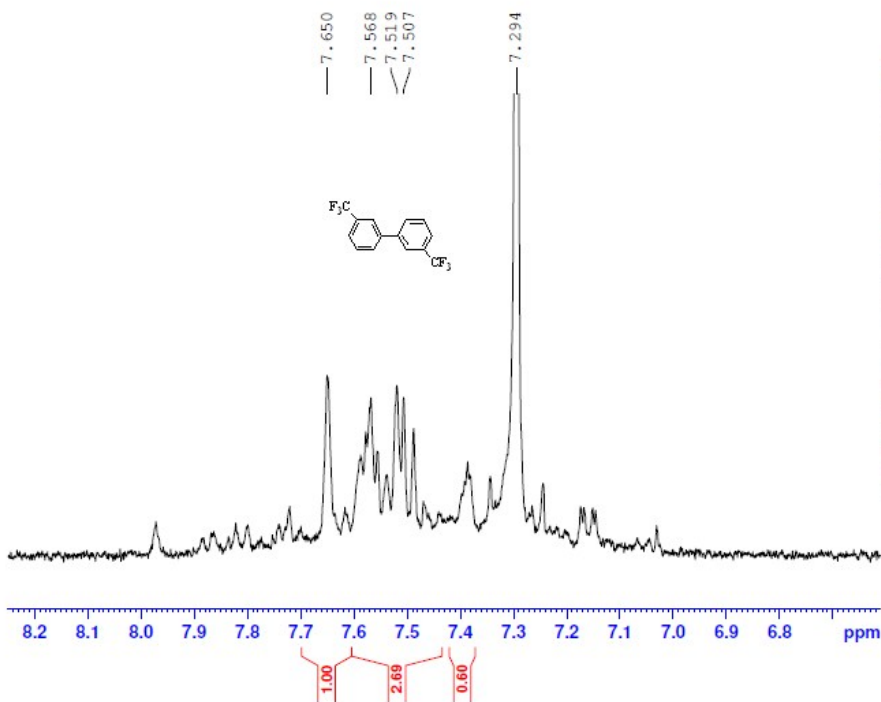


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PROCNO    1
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TD         65536
SOLVENT   CDCl3
NS         20
DS         0
SWH        8012.820 Hz
FIDRES     0.122266 Hz
AQ         4.0894966 sec
RG         228
DW         62.400 usec
DE         6.50 usec
TE         293.8 K
D1         4.0000000 sec
TDO        1
  
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```

===== CHANNEL f1 =====
NUC1      1H
P1        14.00 usec
PL1       -2.00 dB
PL1W      11.86359406 W
SFO1      400.2236020 MHz
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SF        400.2200000 MHz
WDW       EM
SSB       0
LB        0.30 Hz
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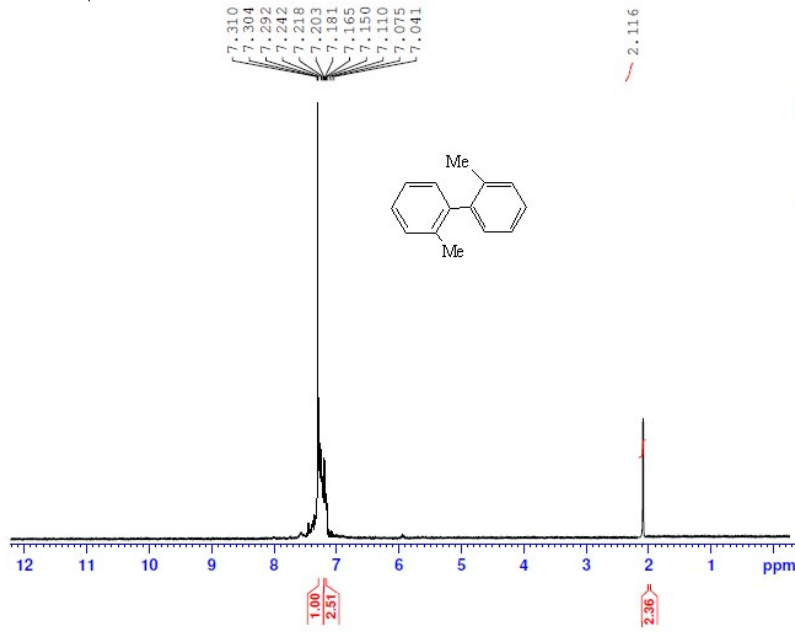


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NAME      ilam UN
EXPNO     1426
PROCNO    1
Date_     20171211
Time      18.24
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PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         20
DS         0
SWH        8012.820 Hz
FIDRES     0.122266 Hz
AQ         4.0894966 sec
RG         228
DW         62.400 usec
DE         6.50 usec
TE         293.8 K
D1         4.0000000 sec
TDO        1
  
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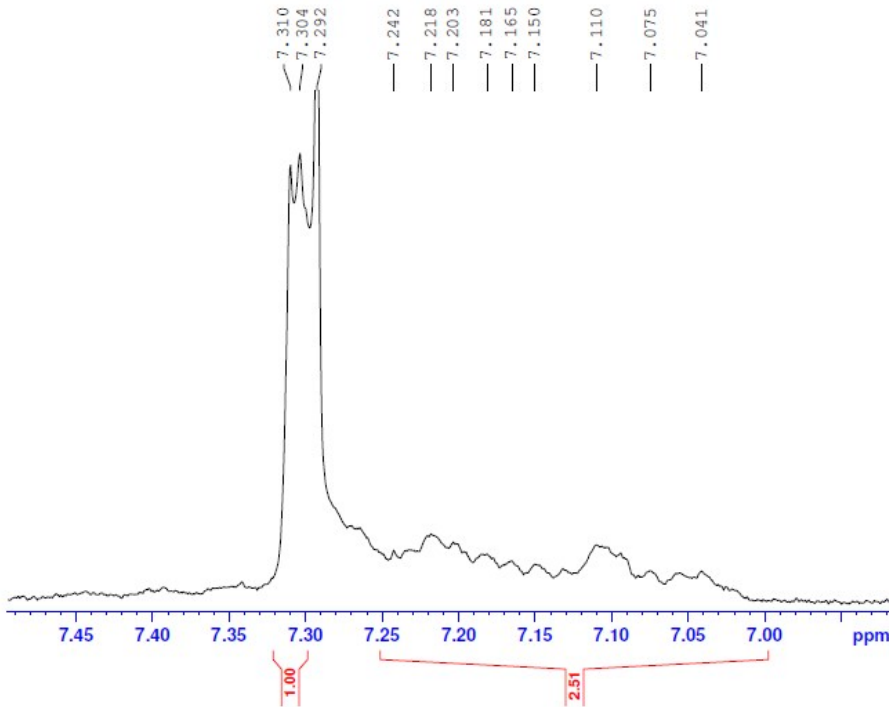
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SFO1      400.2236020 MHz
SI        32768
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WDW       EM
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PC        1.00
  
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```

NAME      ilam UN
EXPNO     1431
PROCNO    1
Date_     20171212
Time      8.36
INSTRUM   spect
PROBRD    5 mm PABBO BH-
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TD         65536
SOLVENT   CDCl3
NS         20
DS         0
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FIDRES     0.122266 Hz
AQ         4.0894966 sec
RG         256
DW         62.400 usec
DE         6.50 usec
TE         293.6 K
D1         4.0000000 sec
TDO        1

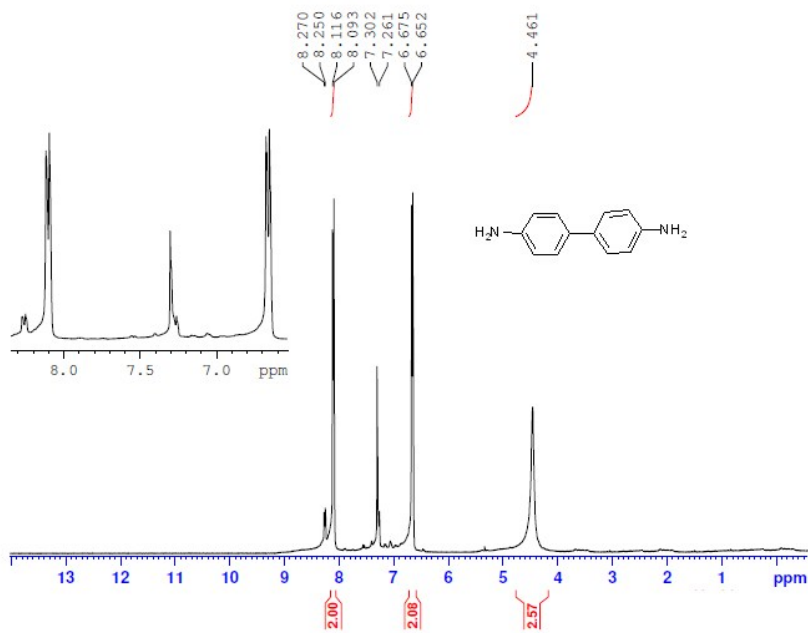
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PL1        -2.00 dB
PL1W       11.86359406 W
SFO1       400.2236020 MHz
SI         32768
SF         400.2200000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```



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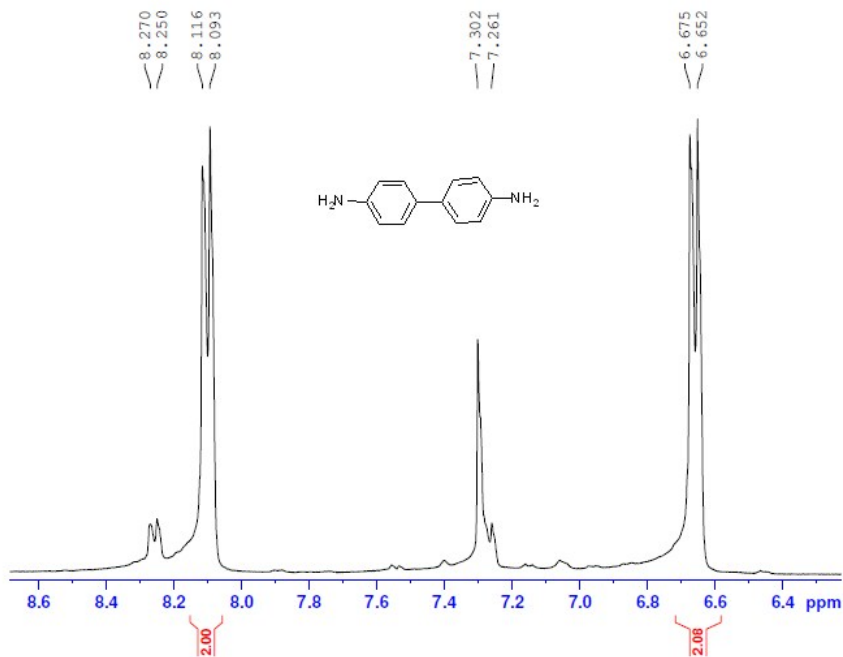
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PROCNO    1
Date_     20171212
Time      8.36
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PROBRD    5 mm PABBO BH-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         20
DS         0
SWH        8012.820 Hz
FIDRES     0.122266 Hz
AQ         4.0894966 sec
RG         256
DW         62.400 usec
DE         6.50 usec
TE         293.6 K
D1         4.0000000 sec
TDO        1

===== CHANNEL f1 =====
NUC1       1H
P1         14.00 usec
PL1        -2.00 dB
PL1W       11.86359406 W
SFO1       400.2236020 MHz
SI         32768
SF         400.2200000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```



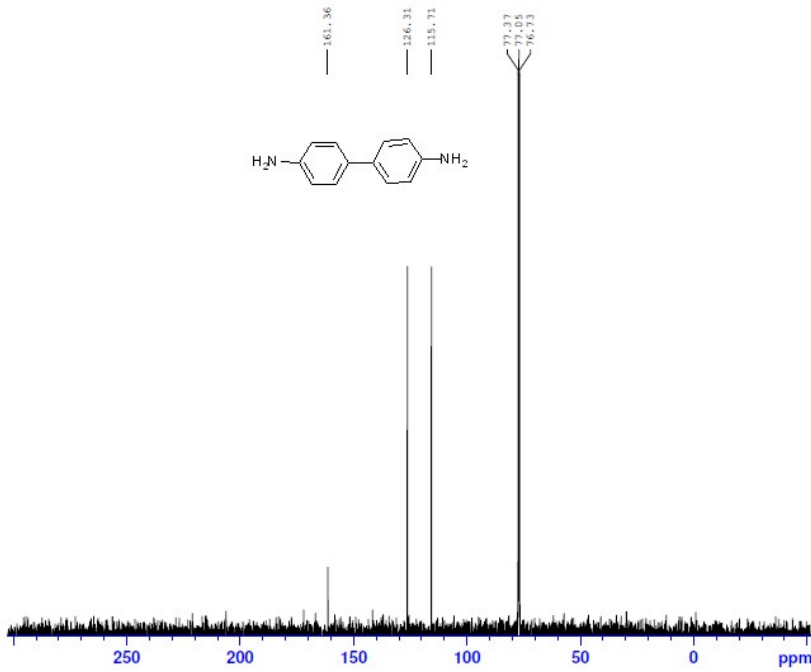
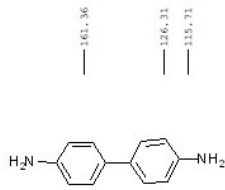
NAME ilam UN
 EXPNO 1381
 PROCNO 1
 Date_ 20171212
 Time 7.33
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 20
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 161
 DW 62.400 usec
 DE 6.50 usec
 TE 293.8 K
 D1 4.0000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 -2.00 dB
 PL1W 11.86359406 W
 SFO1 400.2236020 MHz
 SI 32768
 SF 400.2200000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



NAME ilam UN
 EXPNO 1381
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 Date_ 20171212
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 TDO 1

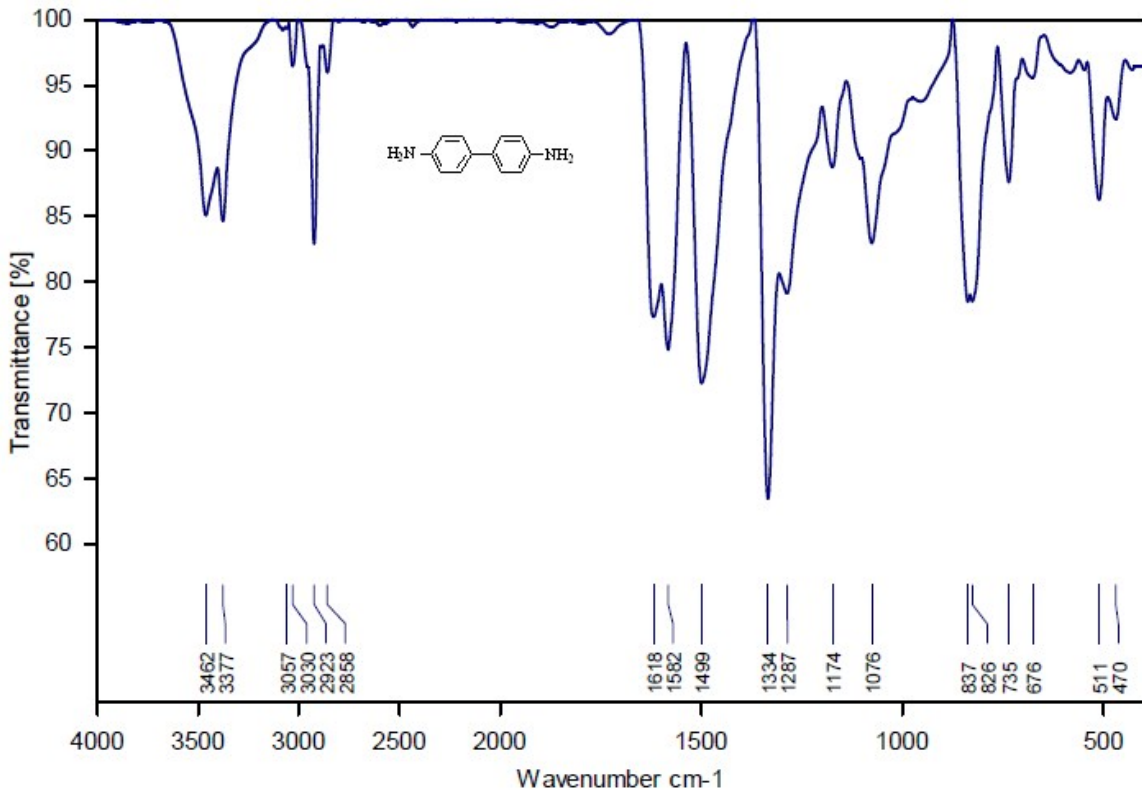
===== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 -2.00 dB
 PL1W 11.86359406 W
 SFO1 400.2236020 MHz
 SI 32768
 SF 400.2200000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

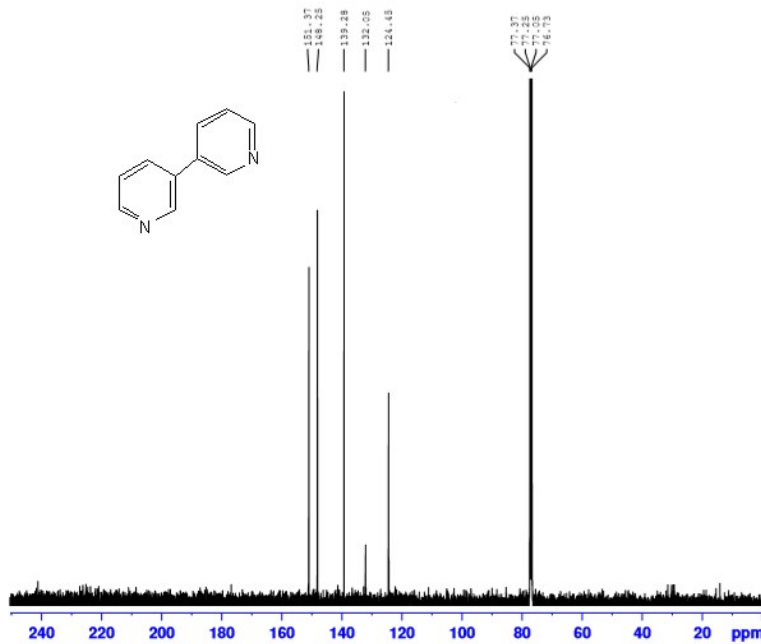


```
NAME      ilam UN
EXPNO     1433
PROCNO    1
Date_     20171212
Time      8.50
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         750
DS         0
SWH       35714.285 Hz
FIDRES    0.544957 Hz
AQ         0.9175540 sec
RG         2050
DW         14.000 usec
DE         6.50 usec
TE         293.8 K
D1         1.0000000 sec
D11        0.0300000 sec
TDO       1

===== CHANNEL f1 =====
NUC1       13C
P1         9.00 usec
PL1        -0.90 dB
PL1W       42.02801895 W
SFO1       100.6479784 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     90.00 usec
PL2        -2.00 dB
PL12       14.48 dB
PL13       17.90 dB
PL2W       11.06359406 W
PL12W      0.26681873 W
PL13W      0.12139934 W
SFO2       400.2216009 MHz
SI         32768
SP         100.6353990 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
```





```

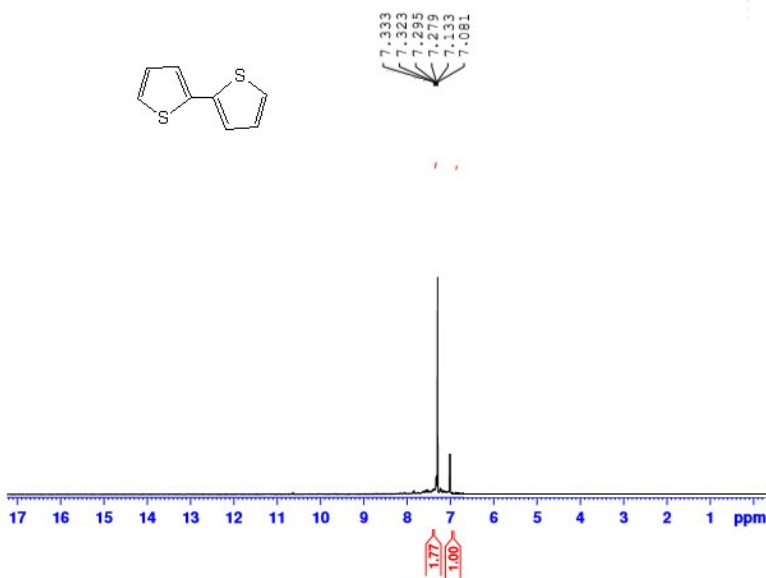
NAME      11am UN
EXPNO     936
PROCNO    1
Date_     20180516
Time      1.44
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         1020
DS         0
SWH        25252.525 Hz
FIDRES     0.385323 Hz
AQ         1.2976629 sec
RG         2050
DW         19.800 usec
DE         6.50 usec
TE         296.0 K
D1         1.00000000 sec
D11        0.03000000 sec
TDO        1
  
```

```

===== CHANNEL f1 =====
NUC1       13C
P1         9.00 usec
PL1        -0.90 dB
PL1W       42.02801895 W
SFO1       100.6479784 MHz
  
```

```

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2        1H
PCPD2       90.00 usec
PL2         -2.00 dB
PL12        14.16 dB
PL13        17.90 dB
PL2W        11.86359406 W
PL12W       0.28722104 W
PL13W       0.12139934 W
SFO2        400.2216009 MHz
SI          32768
SF          100.6353990 MHz
W0W         EM
S0B         0
LB          1.00 Hz
GB          0
PC          1.40
  
```



```

NAME      11am UN
EXPNO     1481
PROCNO    1
Date_     20180516
Time      8.39
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         20
DS         0
SWH        8012.820 Hz
FIDRES     0.122266 Hz
AQ         4.8894966 sec
RG         256
DW         62.400 usec
DE         6.50 usec
TE         293.9 K
D1         4.00000000 sec
TDO        1
  
```

```

===== CHANNEL f1 =====
NUC1       1H
P1         14.00 usec
PL1        -2.00 dB
PL1W       11.86359406 W
SFO1       400.2236020 MHz
SI          32768
SF          400.2200000 MHz
W0W         EM
S0B         0
LB          0.30 Hz
GB          0
PC          1.00
  
```