

Fe₃O₄@SiO₂@PolyIonene/Br₃⁻ core-shell-shell magnetic nanoparticles: a novel catalyst for the synthesis of imidazole derivatives in solvent-free conditions

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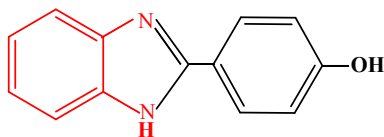
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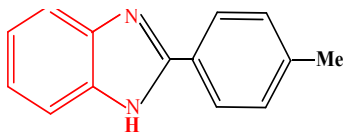
Spectroscopic data:

2-(4-Hydroxyphenyl)-1H-benzimidazole (Table 3, Entry 3):



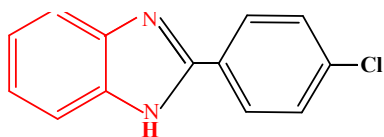
^1H NMR (200 MHz, $\text{DMSO-}d_6$): δ 5.04 (br, 1H, OH), 6.91 (d, $J = 8.7$ Hz, 2H), 7.12-7.21 (m, 2H), 7.48-7.57 (m, 2H), 7.97 (d, $J = 8.7$ Hz, 2H), 10.02 (br, 1H, NH). ^{13}C NMR (50 MHz, $\text{DMSO-}d_6$): δ 120.1, 121.4, 125.9, 127.6, 133.9, 144.2, 157.1, 165.0.

2-(p-Tolyl)-1H-benzimidazole (Table 3, Entry 4):



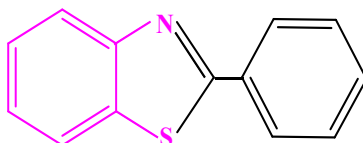
^1H NMR (200 MHz, $\text{DMSO-}d_6$): δ (ppm): 2.57 (s, 3H), 7.14-7.20 (m, 2H), 7.34 (t, $J = 8.0$ Hz, 2H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.62 (t, $J = 8.0$ Hz, 1H), 8.03-8.07 (m, 2H), 12.92 (br, 1H, NH). ^{13}C NMR (50 MHz, $\text{DMSO-}d_6$): δ (ppm): 21.3, 111.5, 119.1, 122.3, 127.3, 129.9, 135.3, 144.2, 151.7.

2-(4-Chlorophenyl)-1H-benzimidazole (Table 3, Entry 6):



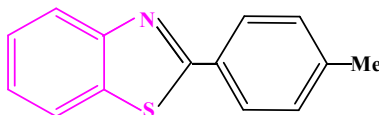
^1H NMR (200 MHz, $\text{DMSO-}d_6$): δ (ppm): 7.35-7.41 (m, 2H), 7.76-7.83 (m, 4H), 8.32-8.39 (m, 2H), 13.17 (br, 1H, NH). ^{13}C NMR (50 MHz, $\text{DMSO-}d_6$): δ (ppm): 111.9, 119.4, 122.3, 123.2, 128.6, 129.5, 135.2, 150.6.

2-Phenylbenzothiazole (Table 4, Entry 1):



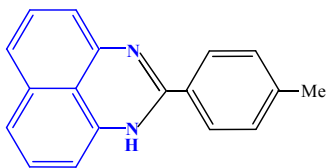
^1H NMR (200 MHz, $\text{DMSO-}d_6$): δ (ppm): 7.54–7.59 (m, 5H), 8.07-8.13 (m, 4H). ^{13}C NMR (50 MHz, $\text{DMSO-}d_6$): δ (ppm): 123.3, 123.8, 126.5, 127.6, 128.1, 130.3, 132.3, 133.7, 135.3, 154.4, 168.2.

2-(p-Tolyl)benzothiazole (Table 4, Entry 4) :



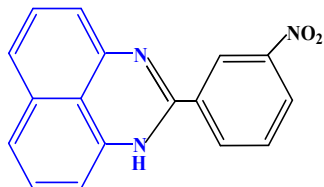
^1H NMR (200 MHz, CDCl_3), δ (ppm): 2.40 (s, 3 H), 7.24-7.48 (m, 4 H), 7.85-8.03 (m, 4 H). ^{13}C NMR (50 MHz, CDCl_3), δ (ppm): 22.0, 122.0, 123.5, 125.4, 126.7, 127.9, 130.2, 131.3, 135.4, 141.9, 154.6, 168.7.

2-(p-Tolyl)-2,3-dihydro-1H-perimidine (Table 5, Entry 3):



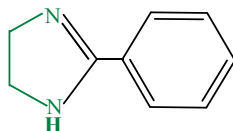
IR (KBr): $\nu = 3365, 3039, 2922, 1601, 1485, 1417$. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ (ppm): 2.35 (s, 3H, CH_3), 5.34 (s, 1H, CH), 6.49-7.51 (m, 12H, CH_{arom} , 2NH). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$): δ (ppm): 20.8, 66.6, 104.2, 112.4, 115.1, 126.8, 127.8, 128.7, 134.3, 137.7, 138.8, 143.1.

2-(3-Nitrophenyl)-2,3-dihydro-1H-perimidine (Table 5, Entry 5):



IR (KBr): $\nu = 3344, 3226, 2821, 1606, 1529, 1415, 1333$. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ (ppm): 5.56 (s, 1H, CH), 6.52-8.45 (m, 12H, CH_{arom} , 2 NH). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$): δ (ppm): 64.8, 104.6, 112.4, 115.6, 122.6, 123.2, 126.9, 129.9, 134.2, 134.6, 142.2, 144.5, 147.6.

2-Phenyl-1H-imidazole (Table 6, Entry 1):



$^1\text{H NMR}$ (200 MHz, $\text{DMSO-}d_6$): δ 7.19-7.23 (m, 2H), 7.51-7.61 (m, 5H), 8.16-8.21 (m, 2H), 12.91 (br, 1H, NH). $^{13}\text{C NMR}$ (50 MHz, $\text{DMSO-}d_6$): δ 120.1, 123.2, 127.0, 127.3, 129.7, 130.7, 131.0, 152.1.

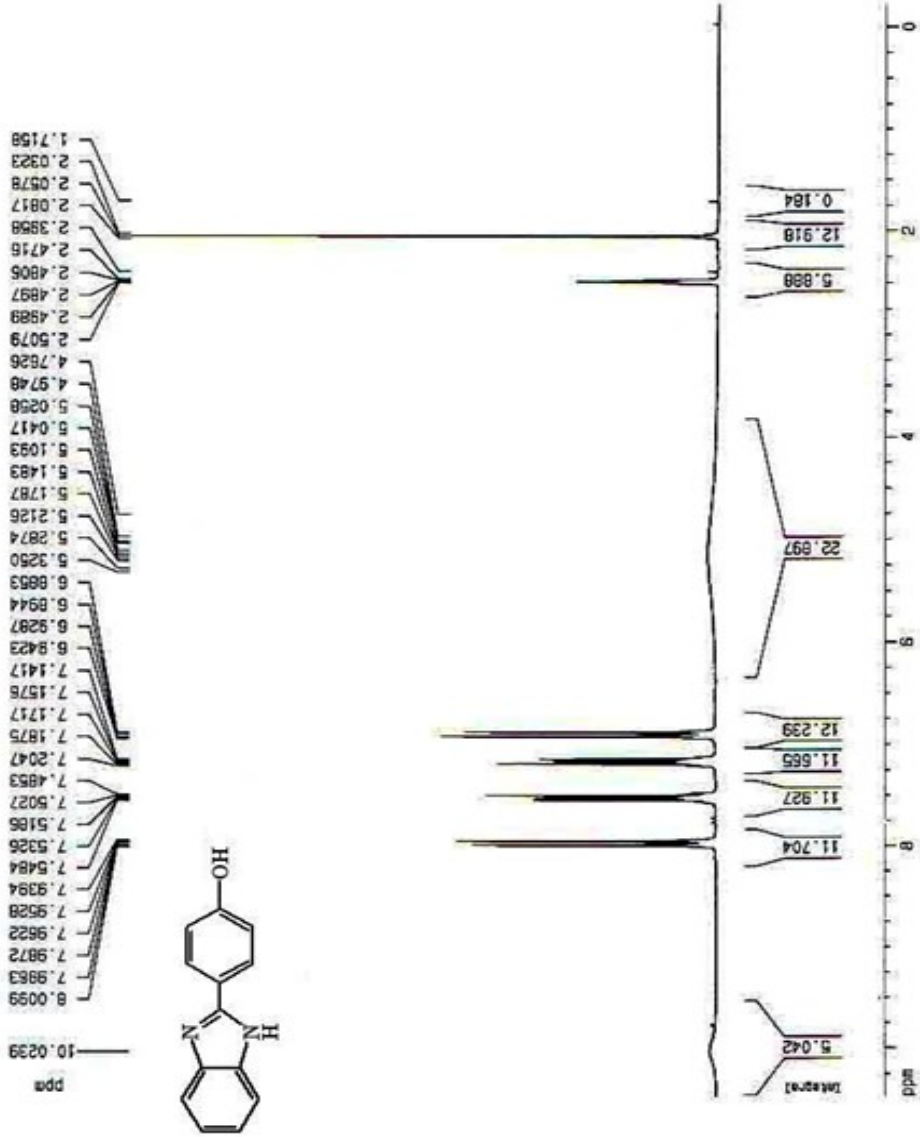
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PRONO 1

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TD 65536
SOLVENT DMSO
NS 12
DS 0
SWH 5995.204 Hz
FIDRES 0.091400 Hz
AQ 5.460700 sec
RG 382
DM 83.400 usec
DE 7.50 usec
TE 300.0 K
D1 1.00000000 sec

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NUC1 1H
P1 19.70 usec
PL1 -2.00 dB
SFO1 200.1312453 MHz

F2 - Processing parameters
SI 32768
SF 200.1300071 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CK 20.00 cm
F1P 10.475 ppm
F1 2000.37 Hz
F2P -0.217 ppm
F2 -0.33 Hz
PPhM -0.33453 ppm/cm
HCOH 505.96505 Hz/cm



¹H NMR spectra of 2-(4-Hydroxyphenyl)-1H-benzimidazole

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Current Data Parameters
NAME: 13C
EXPNO: 25
PROCNO: 1

F2 - Acquisition Parameters
Date_ 20130801
Time 15.13
INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT DMSO-D6
NS 4
DS 4
SWH 15662.814 Hz
FIDRES 0.191680 Hz
AQ 2.0082827 sec
RG 32768
DE 39.880 usec
TE 300.0 K
TD 2.00000000 sec
D1 0.03000000 sec
D12 0.00000000 sec

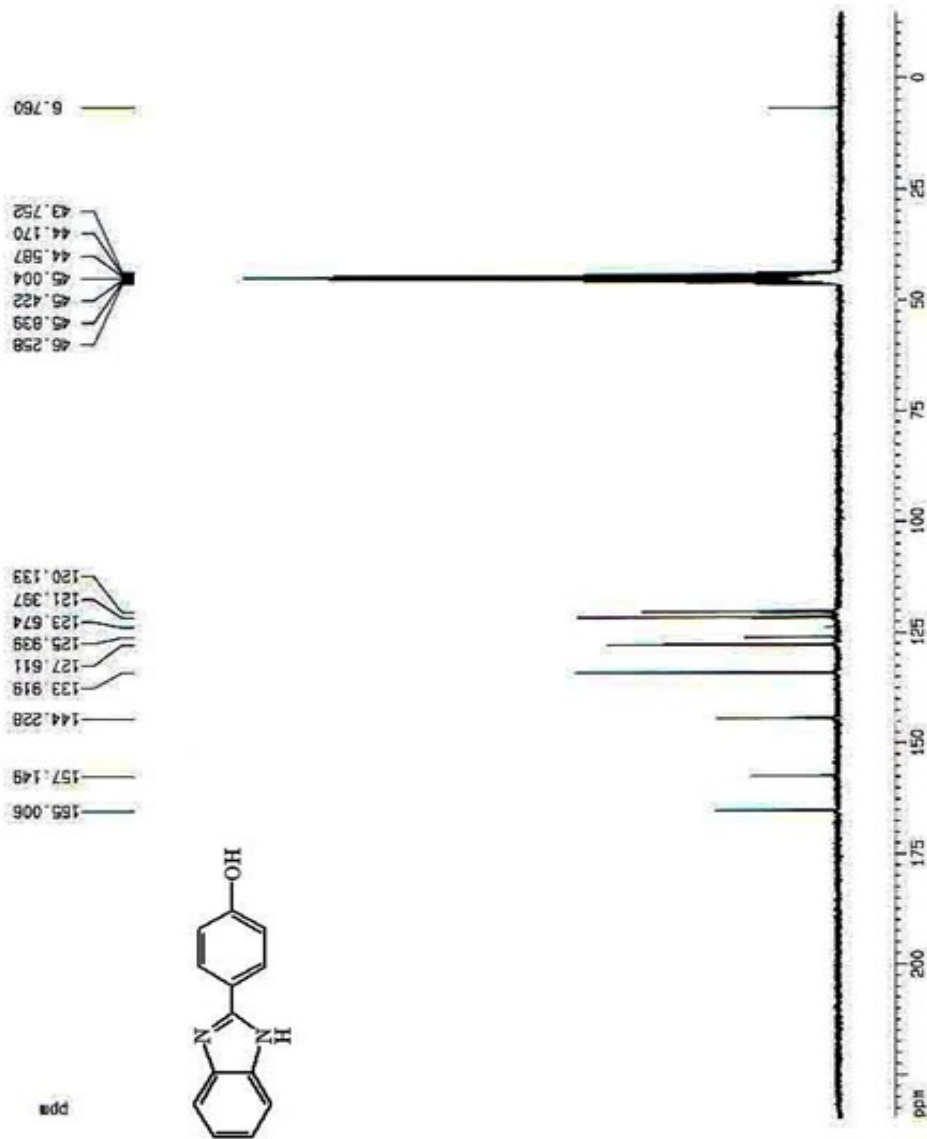
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P1 10.00 usec
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SFO1 80.302440 MHz

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NUC2 1H
P2 80.00 usec
PL2 190.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 200.136025 MHz

F2 - Processing parameters
SI 32768
SF 50.302440 MHz
AQ 2.0082827 sec
RG 32768
DE 39.880 usec
TE 300.0 K
TD 2.00000000 sec
D1 0.03000000 sec
D12 0.00000000 sec

1D NMR plot parameters
CX 20.00 cm
F1p 254.813 ppm
F1 1816.42 Hz
F2p -14.832 ppm
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PPHON 32.48225 ppm/cm
LOCK 880.14060 Hz/CW

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¹³CNMR spectra of 2-(4-Hydroxyphenyl)-1H-benzimidazole

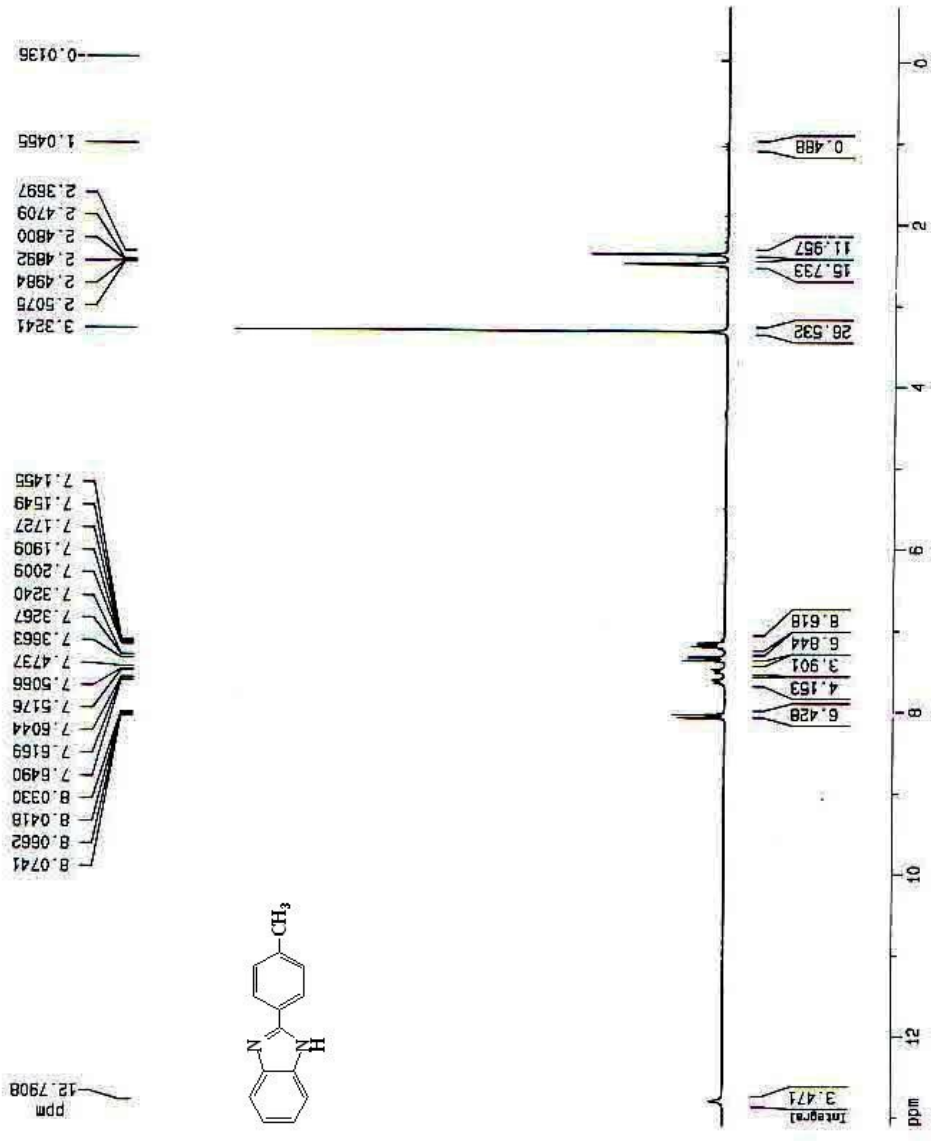
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 NAME HI
 EXPNO 32
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20130801
 Time_ 12.53
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 PROBHD 5 mm Nujolnu
 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 12
 DS 0
 SWH 4139.073 Hz
 FIDRES 0.063157 Hz
 AQ 7.918796 sec
 RG 812.7
 DM 120.800 usec
 DE 7.50 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.70 usec
 PL1 -2.00 dB
 SFO1 200.131259 MHz

F2 - Processing parameters
 SI 32768
 SF 200.1300072 MHz
 MDN 0
 SSB 0
 LB 0.00 Hz
 BB 0
 PC 1.00

-----f1 NMR plot parameters-----
 CX 20.00 cm
 F1P 13.086 ppm
 F1 2620.51 Hz
 F2P -0.675 ppm
 F2 -135.34 Hz
 PPMCM 0.68861 ppm/cm
 HZCM 137.61232 Hz/cm



¹H NMR spectra of 2-(p-Tolyl)-1H-benzimidazole

Current Data Parameters
 NAME 13C
 EXPNO 40
 PROCNO 1

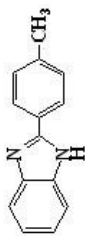
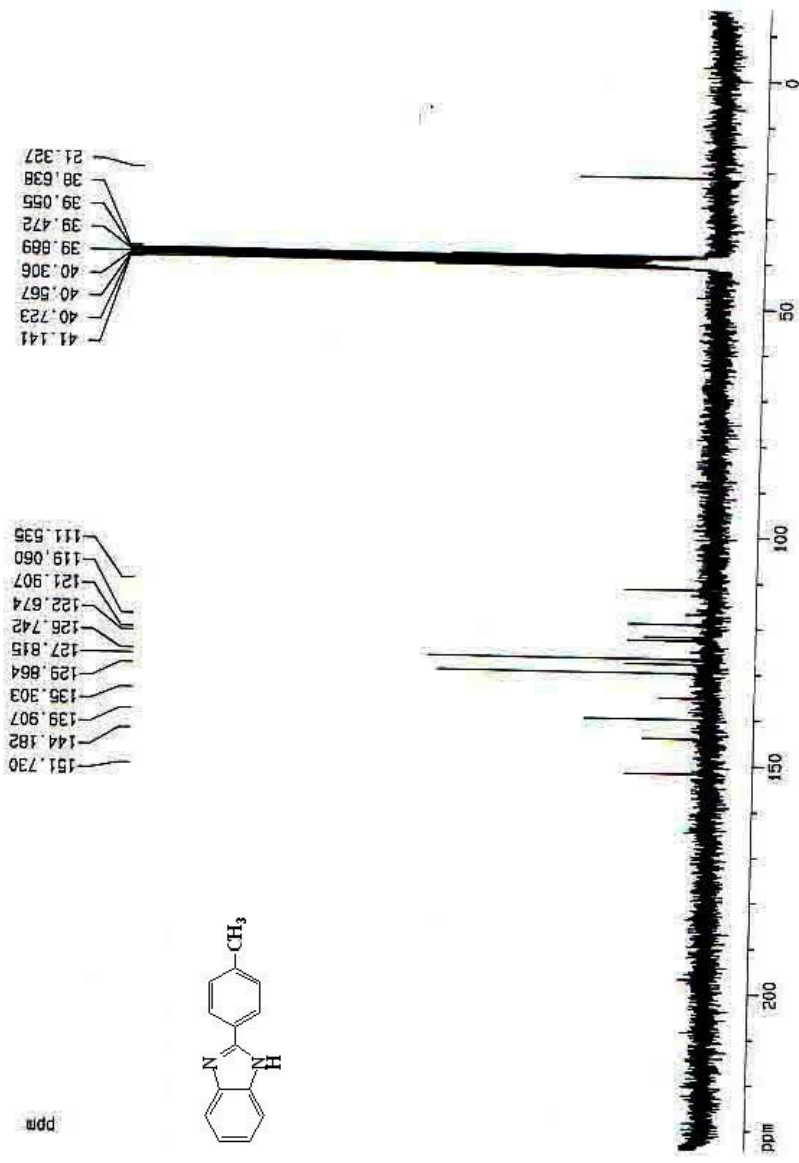
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 TD 65536
 SOLVENT DMSO
 NS 1071
 DS 4
 SMH 12562.814 Hz
 FIDRES 0.191893 Hz
 AQ 2.609827 sec
 RG 4096
 DW 39.800 usec
 DE 7.50 usec
 TE 300.0 K
 D1 2.0000000 sec
 D11 0.0500000 sec
 D12 0.0000200 sec

CHANNEL F1
 NUC1 13C
 P1 10.00 usec
 PL1 -5.00 dB
 SF01 50.3282445 MHz

CHANNEL F2
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 120.00 dB
 PL12 20.00 dB
 PL13 20.00 dB
 SF02 200.1308005 MHz

F2 - Processing parameters
 SI 32768
 SF 50.3227353 MHz
 EQ 0
 NSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

3D NMR plot parameters
 CX 20.00 cm
 F1P 254.300 ppm
 F1 13780.64 Hz
 F2P -45.344 ppm
 F2 -772.18 Hz
 FREQH 12.4624 ppm/cm
 HZCH 626.14069 Hz/cm



¹³CNMR spectra of 2-(p-Tolyl)-1H-benzimidazole

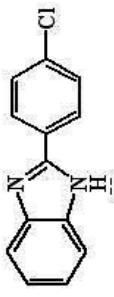
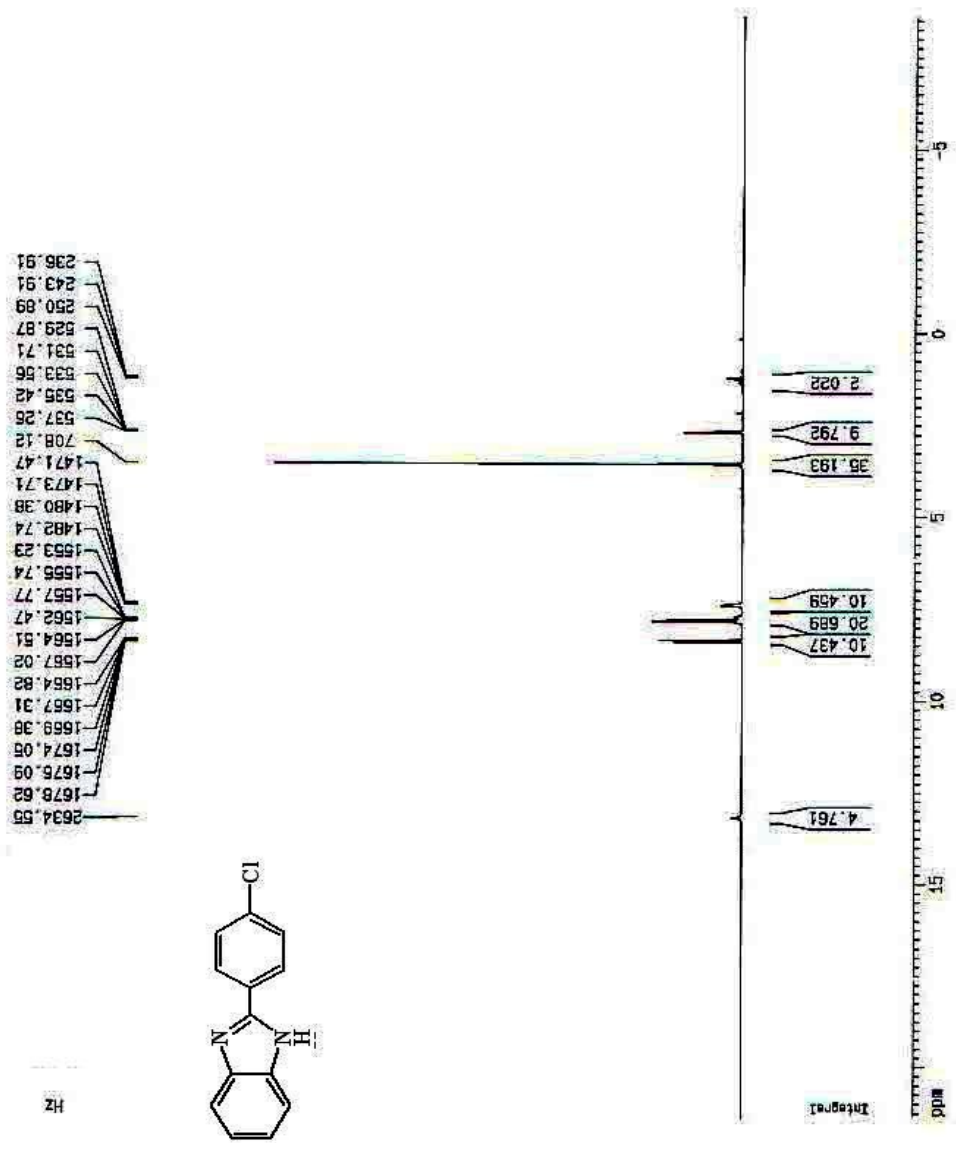
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 NAME proton
 EXPNO 96
 PROCNO 1

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 Time 14.08
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 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 12
 DS 0
 SWH 5885.204 Hz
 FIDRES 0.091486 Hz
 AQ 5.4657266 sec
 RG 574.7
 DK 83.400 usec
 DE 7.50 usec
 TE 300.0 K
 D1 1.0000000 sec

CHANNEL f1
 NUC1 1H
 P1 10.70 usec
 PL1 -2.00 dB
 SFO1 200.1312465 MHz

F2 - Processing parameters
 SI 32768
 SF 200.1299719 MHz
 NQW 0
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 FXP 21.344 ppa
 F1 -4271.00 Hz
 F2 -8.615 ppa
 F2 -1724.21 Hz
 PPMCM 1.49783 ppa/cm
 RCM 299.76019 Hz/cm



¹H NMR spectra of 2-(4-Chlorophenyl)-1H-benzimidazole

Current Data Parameters
 NAME C13
 EXPNO 24
 PROCNO 1

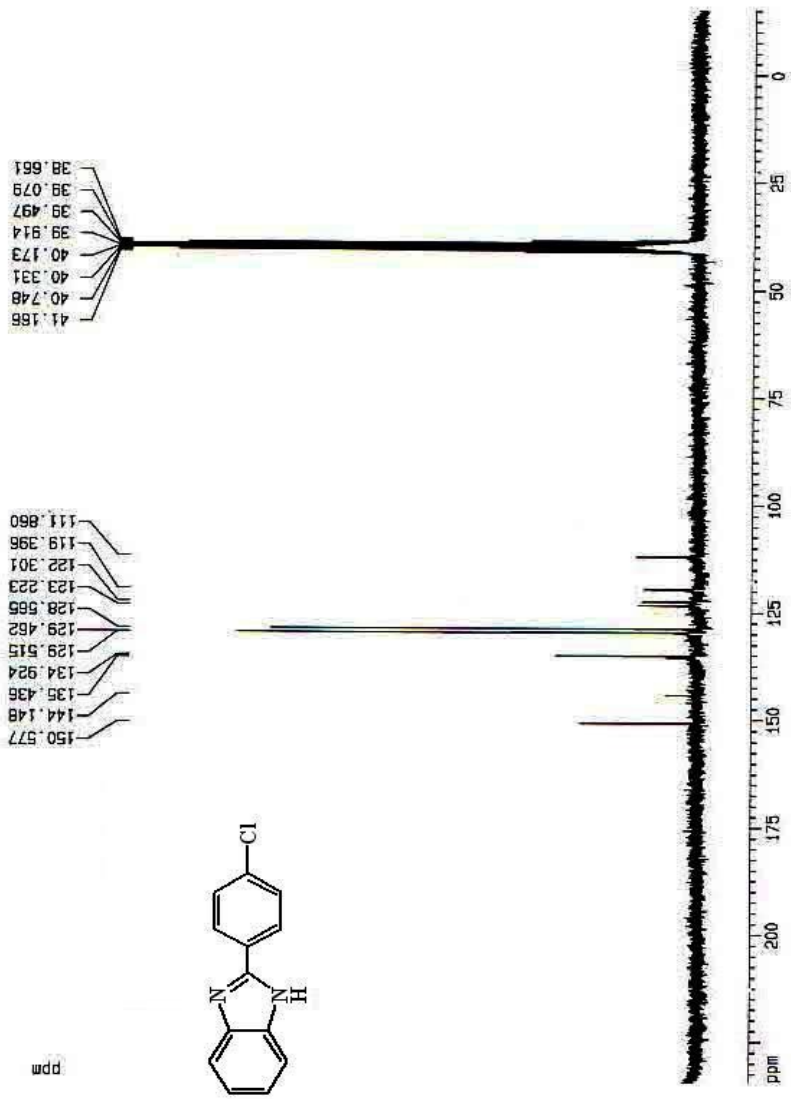
F2 - Acquisition Parameters
 Date_ 20130801
 Time 15.05
 INSTRUM spect
 PROBHD 5 mm NUC1216
 PULPROG zgpg30
 ID 65586
 SOLVENT DMSO
 NS 1567
 DS 1
 SWH 12582.814 Hz
 FIDRES 0.191693 Hz
 AQ 2.6189367 sec
 RG 4096
 DW 39.800 usec
 DE 7.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 D12 0.00002000 sec

CHANNEL F1
 NUC1 13C
 P1 10.00 usec
 PL1 -8.00 dB
 SFO1 50.3282445 MHz

CHANNEL F2
 CPDPRG2 waltz16
 NUC2 1H
 P2 90.00 usec
 PL2 120.00 dB
 PL12 20.00 dB
 PL13 20.00 dB
 SFO2 200.1300905 MHz

F2 - Processing parameters
 SI 32768
 SF 50.3282314 MHz
 MDN 0
 EHQ 0
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 F1P 234.377 ppm
 F1 11784.47 Hz
 F2P -15.268 ppm
 F2 -768.34 Hz
 PRCHN 12.46265 ppm/cm
 HZCM 628.14068 Hz/cm



¹³C NMR spectra of 2-(4-Chlorophenyl)-1H-benzimidazole

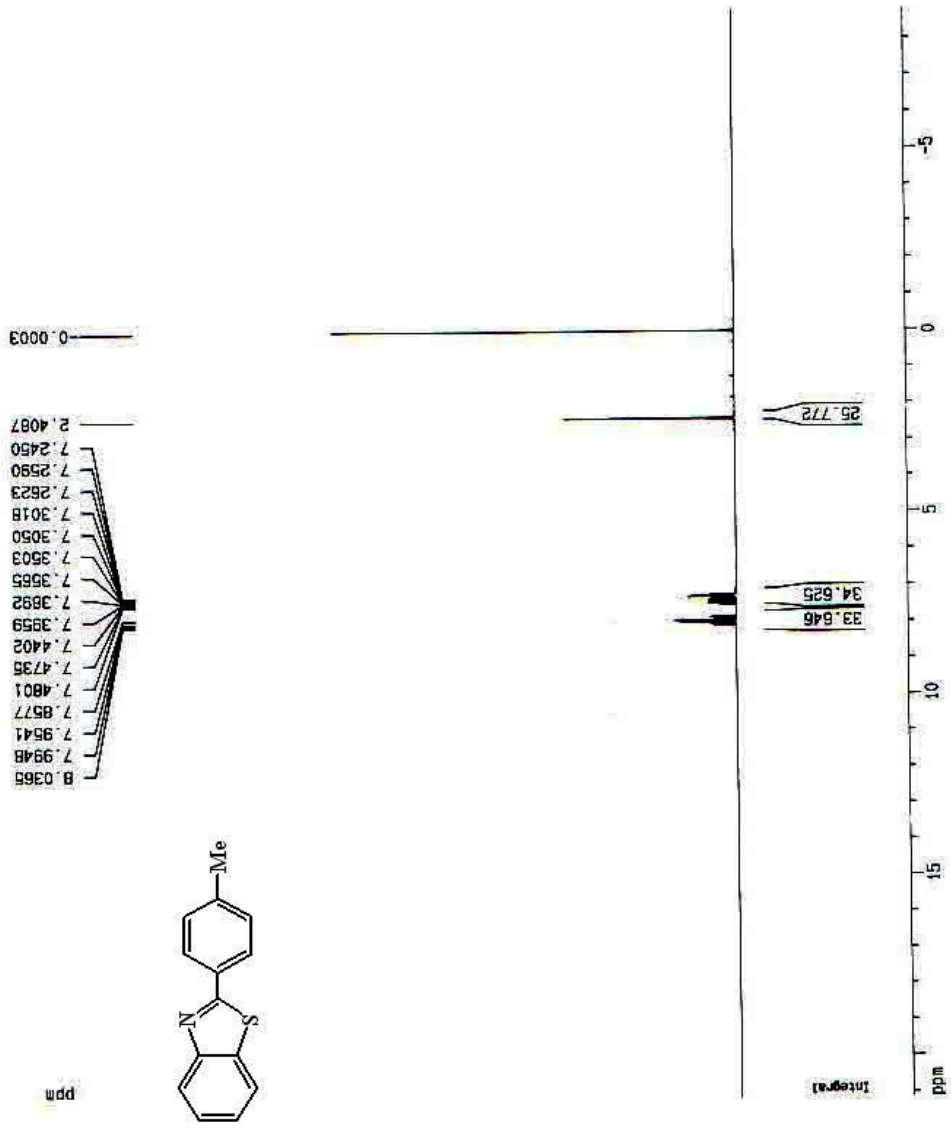
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 EXPNO 21
 PROCNO 1

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 Date_ 20130801
 Time 8.27
 INSTRUM spect
 PROBHD 5 mm Multinu
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 12
 DS 0
 SH 5995.204 Hz
 FIDRES 0.091460 Hz
 AQ 5.4697926 sec
 RG 256
 DW 93.400 usec
 DE 7.50 usec
 TE 300.0 K
 D1 1.00000000 sec

CHANNEL f1
 NUC1 1H
 PL 10.70 usec
 PL1 -2.00 dB
 SFO1 200.1312463 Mhz

F2 - Processing parameters
 SI 32768
 SF 200.1300116 Mhz
 MVM EM
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

ID NMR plot parameters
 CX 20.00 cm
 FIP 21.143 ppm
 F1 4231.30 Hz
 F2 -8.814 ppm
 PPMCH 1.48753 ppm/cm
 HCM 298.76019 Hz/cm



¹H NMR spectra of 2-(p-Tolyl)benzothiazole

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Current Data Parameters
NAME      C13
EXPNO    20
PROCNO   1

F2 - Acquisition Parameters
Date_    20130801
Time     5.44
INSTRUM spect
PROBHD   5 mm NUK11HN
PULPROG zgpg30
TD        65536
SOLVENT  CDCl3
NS        321
DS        4
SWH       12562.814 Hz
FIDRES    0.191693 Hz
AQ        2.5695927 sec
RG        32768
DN        38.800 uSec
DE        7.50 uSec
TE        300.0 K
D1        2.00000000 sec
D11       0.03000000 sec
D12       0.00002000 sec

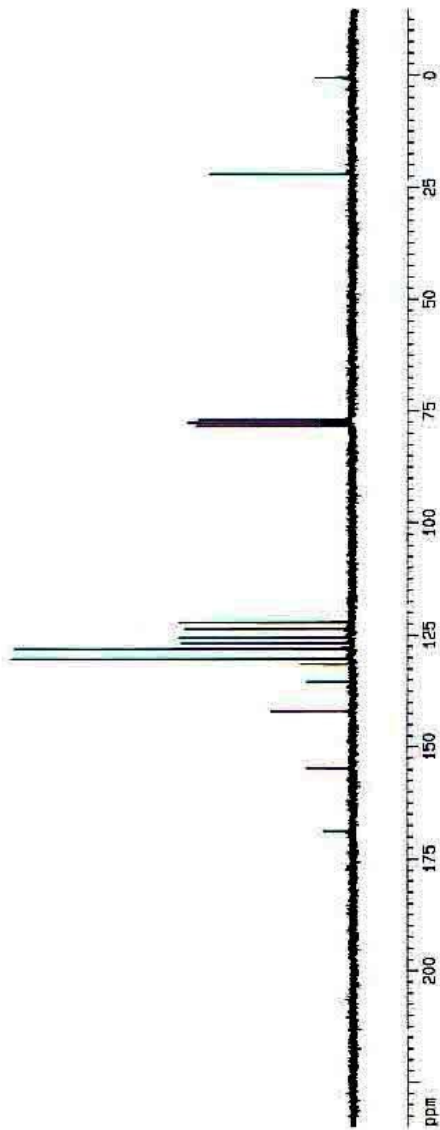
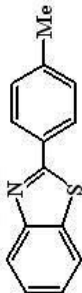
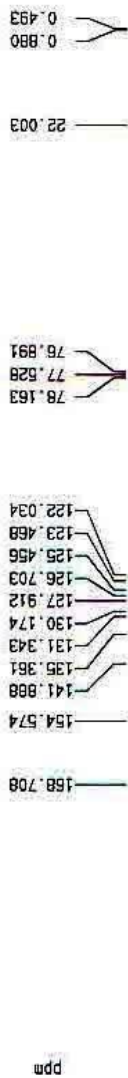
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NUC2      1H
P2        80.00 uSec
PL2       120.00 dB
PL12      20.00 dB
PL13      20.00 dB
SFO2      200.1306805 MHz

F2 - Processing parameters
SI        32768
SF        50.327090 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40

3D NMR plot parameters
CX        20.00 cm
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F1        11915.42 Hz
F2P       -14.852 ppm
F2        -76.40 Hz
PPHOCM    12.46225 ppm/cm
HCOH      628.14055 Hz/cm

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¹³C NMR spectra of 2-(p-Tolyl)benzothiazole

NAME FENG2004-71.78

EXPNO 40

PROCNO 1

Date_ 20130901

Time 1.09

INSTRUM spect

PROBHD 5 mm PABBO BB-

PULPROG zg

TD 32768

SOLVENT DMSO

NS 32

DS 2

SF 8417.508 Hz

FIDRES 0.256982 Hz

AQ 1.9464682 sec

RG 101

DW 68.400 usec

DE 6.50 usec

TE 295.7 K

D1 1.0000000 sec

TD0 1

CHANNEL1

NUC1 1H

P1 11.00 usec

PL1 -2.00 dB

PL1W 17.51671600 W

SFO1 400.1326008 MHz

SI 32768

SF 400.1300000 MHz

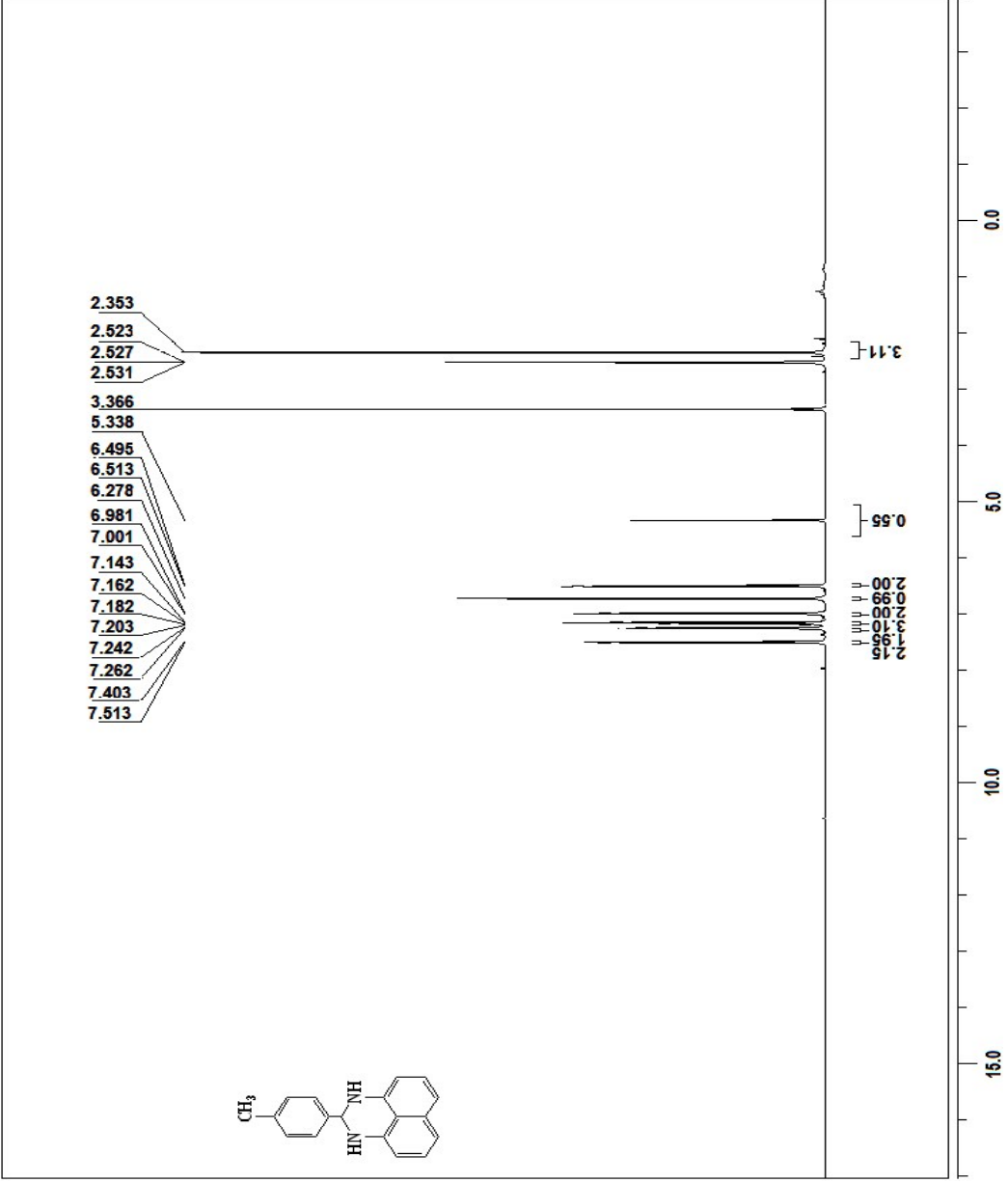
WDW EM

SSB 0

LB 0.30 Hz

GB 0

PC 1.00

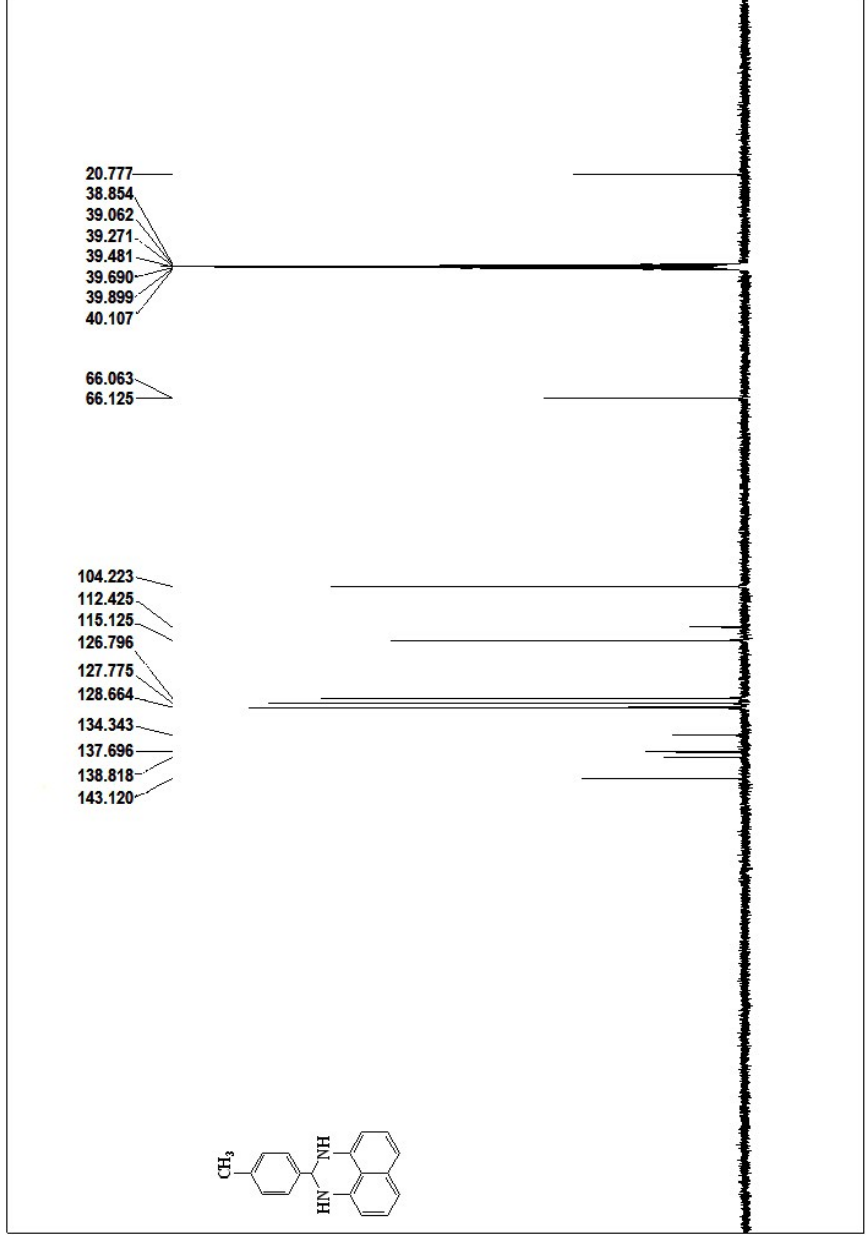


¹H NMR spectra of 2-(p-Tolyl)-2,3-dihydro-1H-perimidine

NAME F-EN20094-71_78
 EXPNO 41
 PROCNO 1
 Date_ 20130901
 Time 1.53
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 32768
 SOLVENT DMSO
 NS 1600
 DS 2
 SWH 25252.525 Hz
 FIDRES 0.770646 Hz
 AQ 0.6488564 sec
 RG 2050
 DW 19.900 usec
 DE 6.50 usec
 TE 296.2 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TDD 1

CHANNEL 11
 NUC1 13C
 P1 8.70 usec
 PL1 -1.00 dB
 PL1W 42.68075012 W
 SFO1 100.6233654 MHz

CHANNEL 12
 CPDPRG2 waltz16
 NUC2 1H
 PCPDZ 80.00 usec
 PL2 0.00 dB
 PL12 15.26 dB
 PL13 18.26 dB
 PL2W 11.05230045 W
 PL12W 0.32919458 W
 PL13W 0.16489812 W
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 SF 100.6128163 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

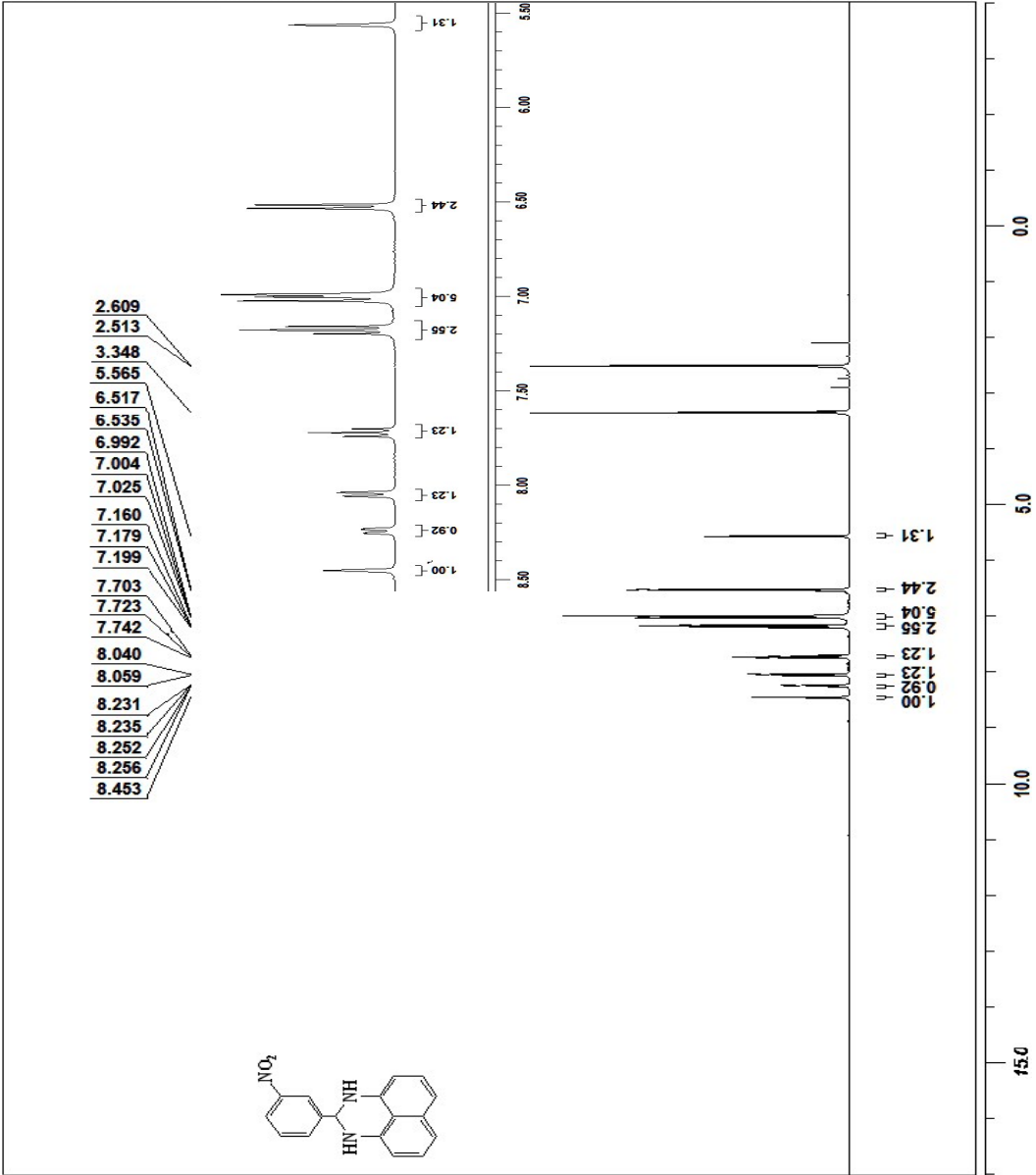


¹³CNMR spectra of 2-(p-Tolyl)-2,3-dihydro-1H-perimidine

NAME F:ENZ0004-71_78
 EXPNO 30
 PROCNO 1
 Date_ 20130801
 Time 0.21
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg

TD 32768
 SOLVENT DMSO
 NS 32
 DS 2
 SWH 8417.508 Hz
 FIDRES 0.256882 Hz
 AQC 1.9464832 sec
 RG 101
 DW 58.400 usec
 DE 6.50 usec
 TE 295.7 K
 D1 1.00000000 sec
 TD0 1

CHANNEL f1
 NUC1 1H
 P1 11.00 usec
 PL1 -2.00 dB
 PL1W 17.51671600 W
 SFO1 400.1326008 MHz
 SI 32768
 SF 400.130000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



¹H NMR spectra of 2-(3-Nitrophenyl)-2,3-dihydro-1H-perimidine

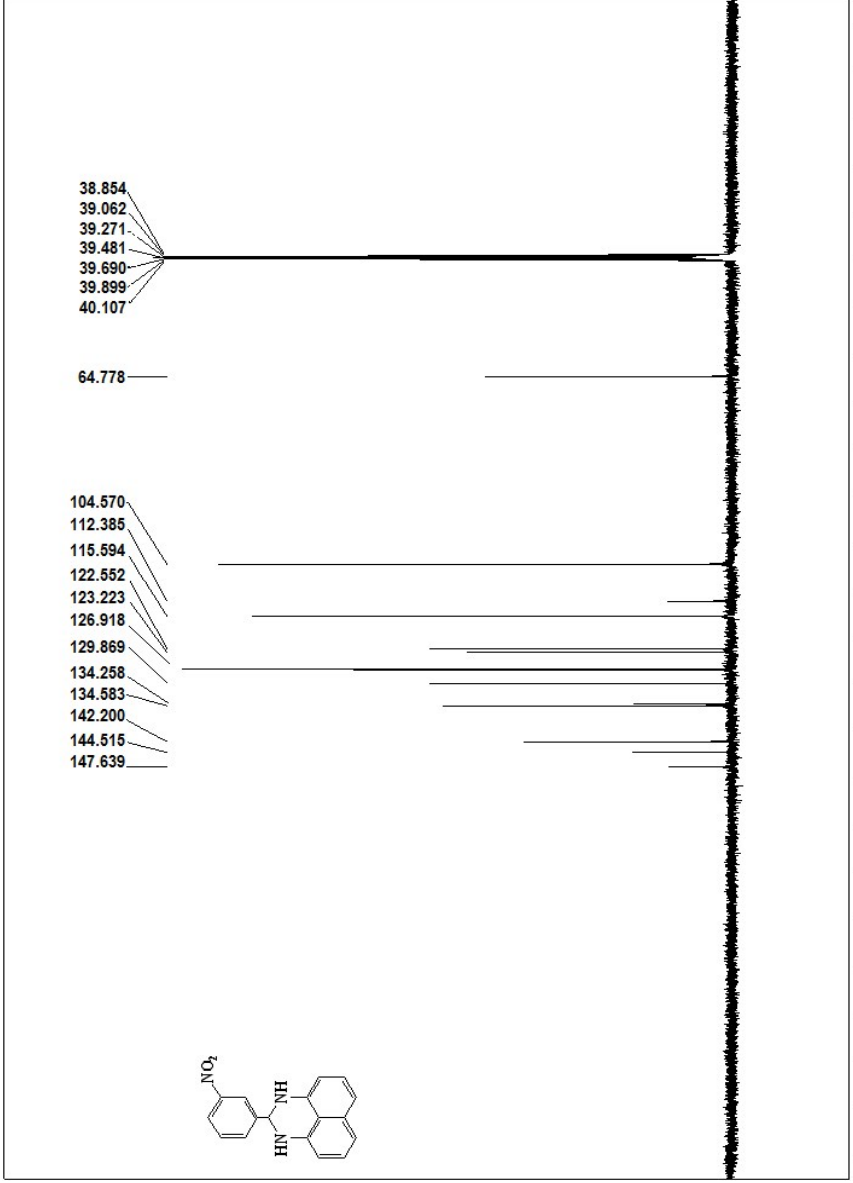


¹HNMR spectra of 2-(3-Nitrophenyl)-2,3-dihydro-1H-perimidine

NAME F-ENG20004-71..78
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 PROCNO 1
 Date_ 20130901
 Time 1.05
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 PULPROG zgpg30
 TD 32768
 SOLVENT DMSO
 NS 1600
 DS 2
 SWH 25252.525 Hz
 FWHM 0.770646 Hz
 AQ 0.6488564 sec
 RG 2050
 DW 18.800 usec
 DE 6.50 usec
 TE 296.3 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1

CHANNEL F1
 NUC1 13C
 P1 8.70 usec
 PL1 -1.00 dB
 PL1W 42.68075012 W
 SFO1 100.628364 MHz

CHANNEL F2
 CPDPRG2 waltz16
 NUC2 1H
 PCPDZ 80.00 usec
 PL2 0.00 dB
 PL12 15.26 dB
 PL13 18.26 dB
 PL2W 11.05230045 W
 PL12W 0.32819458 W
 PL13W 0.16498812 W
 SFO2 400.1316005 MHz
 SI 32768
 SF 100.6128183 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



¹³CNMR spectra of 2-(3-Nitrophenyl)-2,3-dihydro-1H-perimidine