

Supporting Information

Convenient and Mild Synthesis of Nitroarenes by Metal-Free Nitration of Arylboronic Acids

Xiao-Feng Wu,* Johannes Schranck, Helfried Neumann, and Matthias Beller*

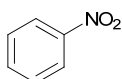
Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

General comments: All reactions were carried out under air atmosphere. Dioxane was distilled from sodium ketyl and stored in ©Aldrich Sure/Store flasks under argon. Arylboronic acids, boric acid and *tert*-butyl nitrite were purchased from Aldrich or ABCR and used as received. Column chromatography was performed using Merck Silicagel 60 (0.043-0.06 mm). NMR data were recorded on a Bruker ARX 300 and Bruker ARX 400 spectrometers. ¹³C and ¹H NMR spectra were referenced to signals of deuterio solvents and residual protiated solvents, respectively. Gas chromatography analysis was performed on an Agilent HP-5890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 µm film thickness) using argon as carrier gas. ESI measurements were performed on an Agilent 1969A TOF mass-spectrometer.

General procedure for the nitration of arylboronic acids: An 8 mL glass vial equipped with a stirring bar was charged with the corresponding arylboronic acid (1 mmol), dioxane (2 mL), and *tert*-butyl nitrite (10 mmol). Then, it was closed with a septum. The vial was placed in an alloy plate, and the reaction was performed for 16 hours at 80 °C. Afterwards, the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The product was purified by silica gel chromatography using *n*-heptane-AcOEt (4:1) as an eluent.

Nitrobenzene

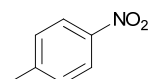


¹H NMR (300 MHz, CDCl₃): δ 8.17-8.26 (m, 2H), 7.35-7.42 (m, 2H), 7.47 (t, 1H, *J* = 7.47 Hz), 7.50-7.62 (m, 2H).

¹³C NMR (75 MHz, CDCl₃): δ 147.9, 134.5, 129.1, 123.2.

GC-MS (EI, 70eV): *m/z*(%) = 123 (M⁺, 80), 93 (15), 77 (100), 65 (10), 51 (30).

1-Methyl-4-nitrobenzene

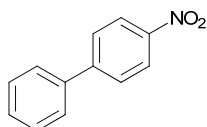


¹H NMR (300 MHz, CDCl₃): δ 8.07 (d, 2H, *J* = 8.73 Hz), 7.31 (d, 2H, *J* = 8.34 Hz), 2.45 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 145.9, 129.6, 123.2, 21.3.

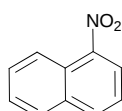
GC-MS (EI, 70eV): *m/z*(%) = 137 (M⁺, 100), 107 (25), 91 (90), 77 (15), 65 (55).

4-Nitrobiphenyl



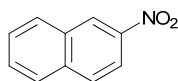
¹H NMR (300 MHz, CDCl₃): δ 8.18-8.26 (m, 2H), 7.61-7.71 (m, 2H), 7.50-7.57 (m, 2H), 7.33-7.46 (m, 3H).
¹³C NMR (75 MHz, CDCl₃): δ 147.7, 147.1, 138.8, 129.2, 128.9, 127.8, 127.4, 124.2.
GC-MS (EI, 70eV): m/z(%) = 199 (M⁺, 100), 169 (55), 152 (85), 141 (20), 115 (10).

1-Nitronaphthalene



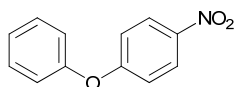
¹H NMR (300 MHz, CDCl₃): δ 8.43 (dd, 1H, $J^1 = 0.96$ Hz, $J^2 = 8.64$ Hz), 8.10 (dd, 1H, $J^1 = 1.21$ Hz, $J^2 = 7.62$ Hz), 7.99 (d, 1H, $J = 8.21$ Hz), 7.83 (bd, 1H, $J = 8.39$ Hz), 7.55-7.63 (m, 1H), 7.46-7.54 (m, 1H), 7.41 (t, 1H, $J = 7.94$ Hz).
¹³C NMR (75 MHz, CDCl₃): δ 146.4, 134.6, 134.2, 129.4, 128.5, 127.2, 124.9, 124.0, 123.9, 122.9.
GC-MS (EI, 70eV): m/z(%) = 173 (M⁺, 80), 143 (40), 127 (100), 115 (90), 101 (10), 77 (15).

2-Nitronaphthalene

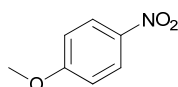


¹H NMR (300 MHz, CDCl₃): δ 8.66 (d, 1H, $J = 2.21$ Hz), 8.11 (dd, 1H, $J^1 = 2.45$ Hz, $J^2 = 9.01$ Hz), 7.90 (d, 1H, $J = 8.17$ Hz), 7.83 (bs, 2H, $J = 9.13$ Hz), 7.49-7.62 (m, 2H).
¹³C NMR (75 MHz, CDCl₃): δ 145.4, 135.7, 131.8, 129.9, 129.7, 129.4, 127.9, 127.8, 124.5, 119.1.
GC-MS (EI, 70eV): m/z(%) = 173 (M⁺, 80), 143 (20), 127 (100), 115 (30), 101 (10), 77 (10).

1-Nitro-4-phenoxybenzene



¹H NMR (300 MHz, CDCl₃): δ 8.04-8.14 (m, 2H), 7.29-7.39 (m, 2H), 7.12-7.24 (m, 1H), 6.97-7.04 (m, 2H), 6.87-6.95 (m, 2H).
¹³C NMR (75 MHz, CDCl₃): δ 163.4, 155.1, 142.6, 130.4, 125.9, 125.5, 120.6, 117.2.
GC-MS (EI, 70eV): m/z(%) = 215 (M⁺, 100), 185 (20), 141 (15), 115 (20), 77 (35).
1-Methoxy-4-nitrobenzene

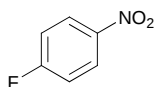


¹H NMR (300 MHz, CDCl₃): δ 8.13 (d, 2H, *J* = 9.24 Hz), 6.89 (d, 2H, *J* = 9.23 Hz), 3.84 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 164.6, 141.6, 125.9, 114.0, 56.0.

GC-MS (EI, 70eV): *m/z*(%) = 153 (*M*⁺, 100), 123 (50), 92 (40), 77 (35), 64 (20).

5 **1-Fluoro-4-nitrobenzene**

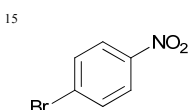


¹H NMR (300 MHz, CDCl₃): δ 8.27-8.35 (m, 2H), 7.21-7.29 (m, 2H).

10 **¹³C NMR (75 MHz, CDCl₃):** δ 166.2 (d, *J* = 257.71 Hz), 144.3, 126.2 (d, *J* = 9.70 Hz), 116.3 (d, *J* = 23.82 Hz).

GC-MS (EI, 70eV): *m/z*(%) = 141 (*M*⁺, 100), 111 (40), 95 (95), 83 (30), 75 (60).

1-Bromo-4-nitrobenzene

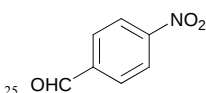


¹H NMR (300 MHz, CDCl₃): δ 8.10-8.18 (m, 2H), 7.68-7.77 (m, 2H).

¹³C NMR (75 MHz, CDCl₃): δ 146.9, 132.6, 129.9, 124.9.

20 **GC-MS (EI, 70eV):** *m/z*(%) = 203 (*M*⁺, 100), 201 (*M*⁺, 100), 173 (70), 171 (70), 157 (80), 155 (80), 145 (35), 143 (35), 76 (40), 75 (45), 50 (25).

4-Nitrobenzaldehyde



¹H NMR (300 MHz, DMSO-*d*₆): δ 10.14 (s, 1H), 8.37 (d, 2H, *J* = 8.73 Hz), 8.13 (d, 2H, *J* = 8.54 Hz).

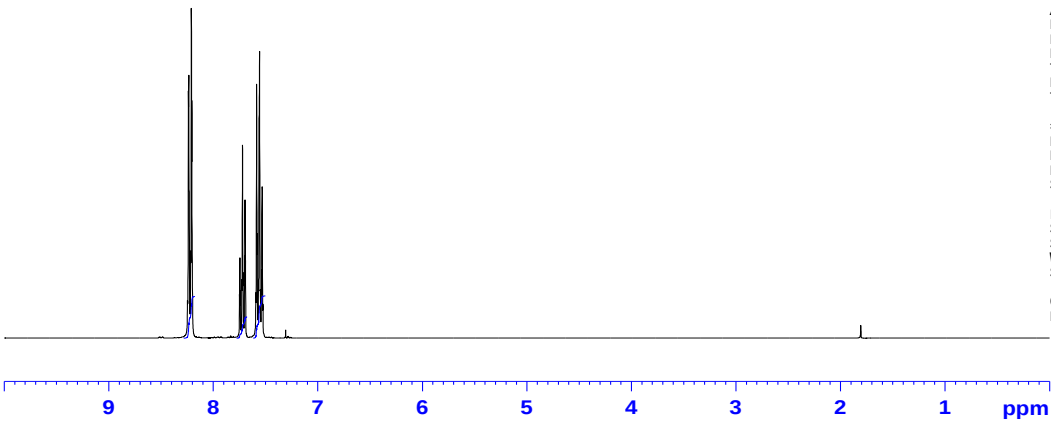
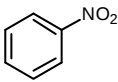
¹³C NMR (75 MHz, DMSO-*d*₆): δ 192.2, 150.5, 139.9, 130.5, 124.1.

GC-MS (EI, 70eV): *m/z*(%) = 151 (*M*⁺, 100), 150 (98), 105 (15), 104 (15), 92 (10), 77 (40), 51 (30).

¹H NMR (300 MHz, CDCl₃, 24 °C):

XW3041

Au1H CDCl3 /opt/topspin 1011 44



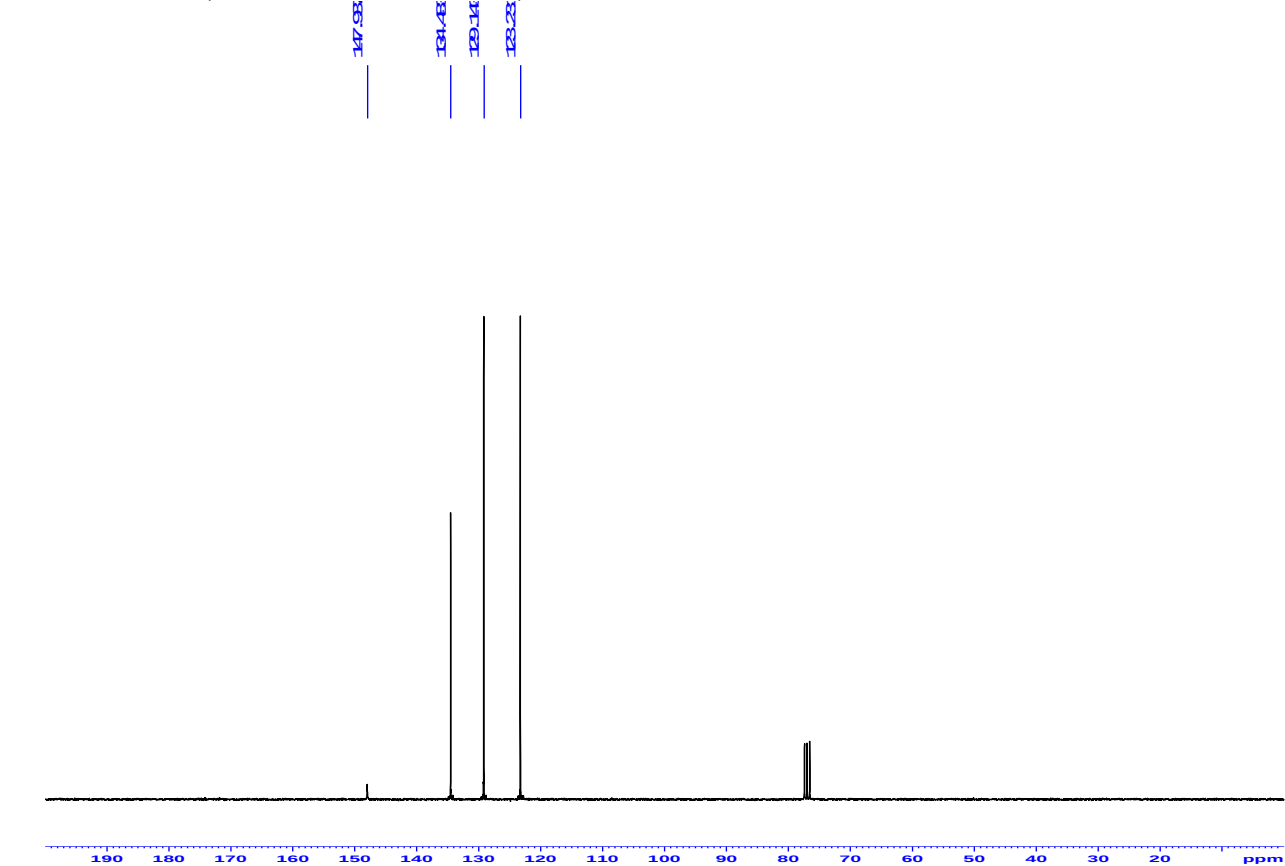
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PROCNO 1

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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 64
DW 81.000 usec
DE 6.00 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1

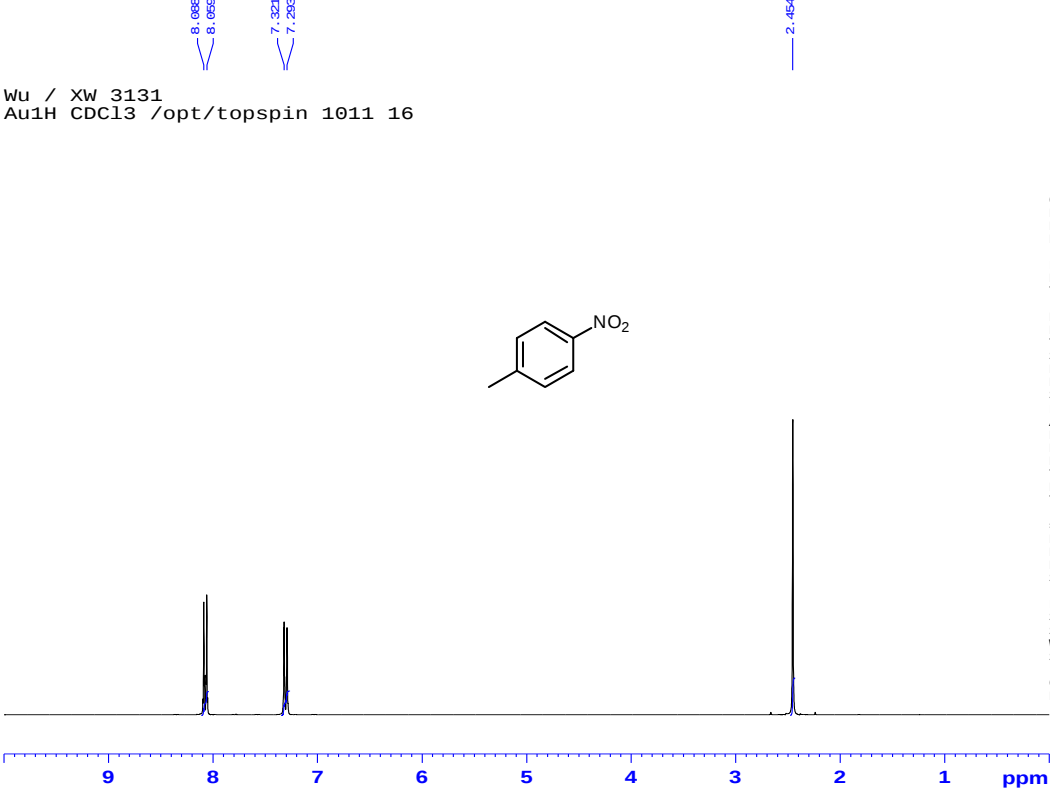
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F2 - Processing parameters
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SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

¹³C{¹H} NMR (75 MHz, CDCl₃, 24 °C):



¹H NMR (300 MHz, CDCl₃, 24 °C):



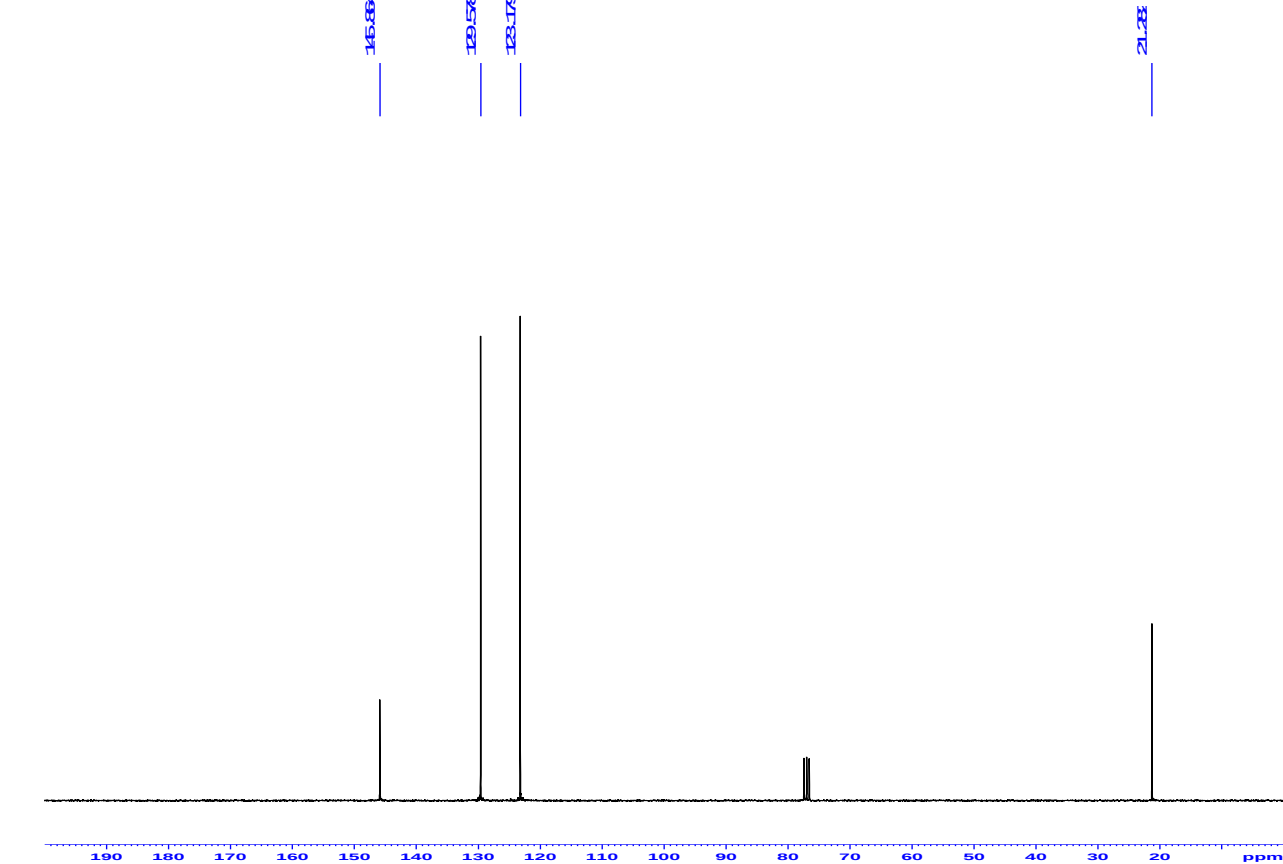
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EXPNO 10
PROCNO 1

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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 45.3
DW 81.000 usec
DE 6.00 usec
TE 294.9 K
D1 1.00000000 sec
TD0 1

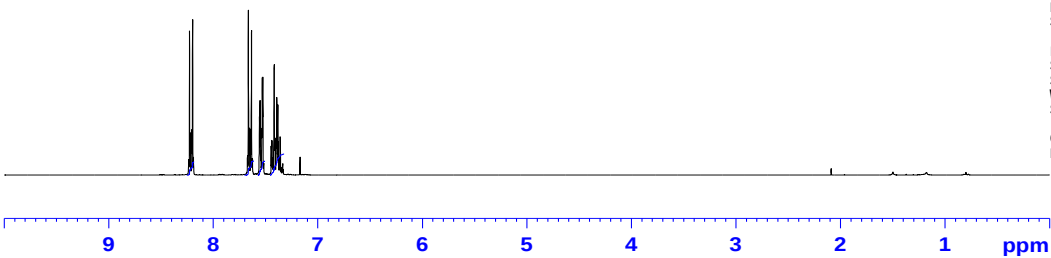
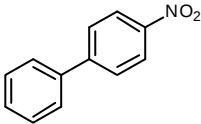
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F2 - Processing parameters
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WDW EH
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

¹³C{¹H} NMR (75 MHz, CDCl₃, 24 °C):



¹H NMR (300 MHz, CDCl₃, 24 °C):
WU XW 3107
Au1H CDCl3 /opt/topspin 1011 34



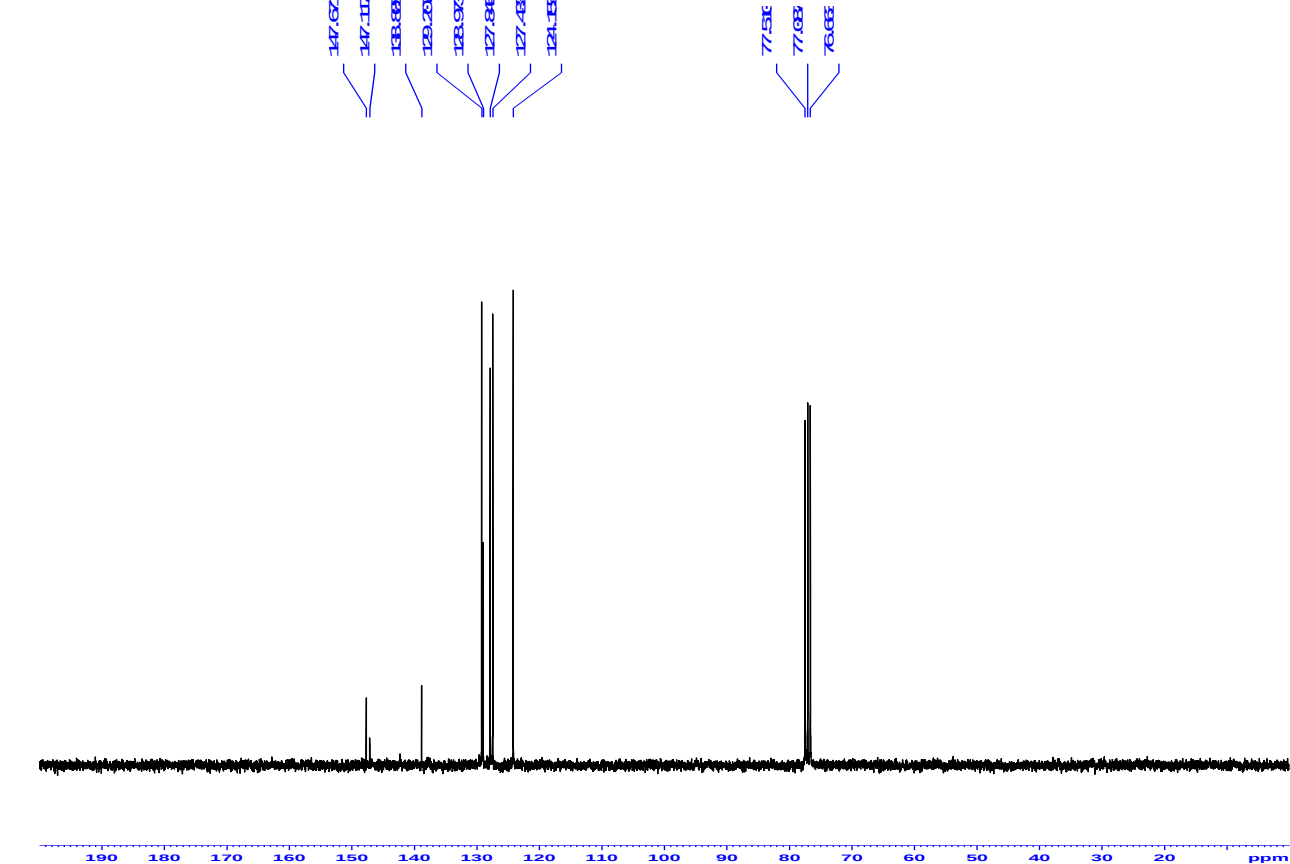
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 181
DW 81.000 usec
DE 6.00 usec
TE 295.0 K
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 11.00 usec
PL1 0.00 dB
SF01 300.1318534 MHz

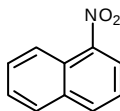
F2 - Processing parameters
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WDW EM
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LB 0.10 Hz
GB 0
PC 1.00

¹³C{¹H} NMR (75 MHz, CDCl₃, 24 °C):



¹H NMR (300 MHz, CDCl₃, 24 °C):

WU XW 3105
Au1H CDC13 /opt/topspin 1011 23

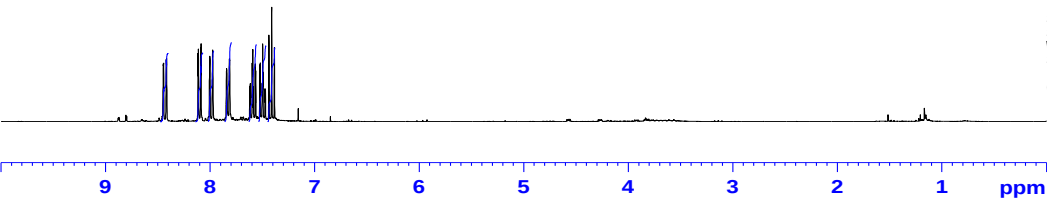


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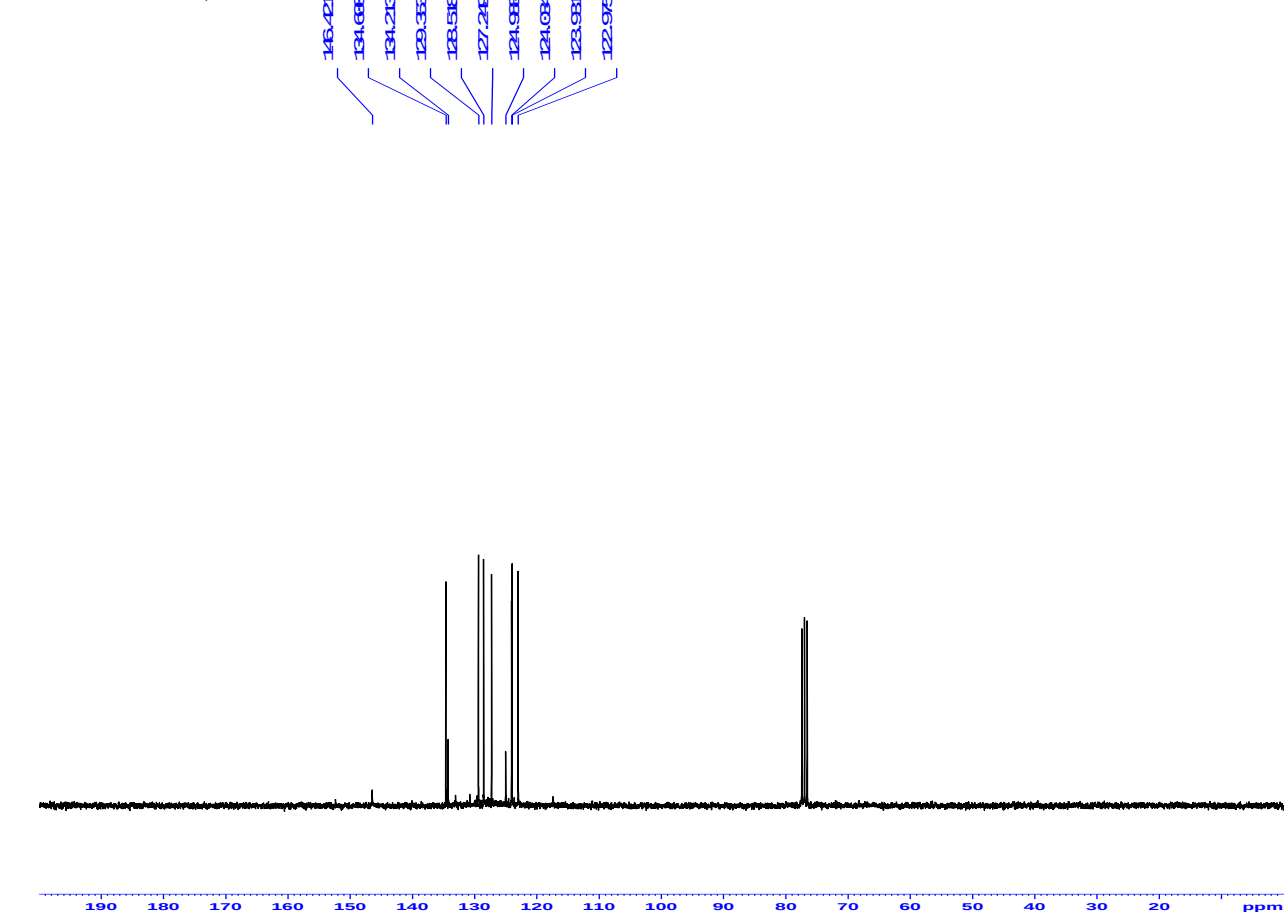
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PULPROG zg30
TD 32768
SOLVENT CDC13
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 114
DW 81.000 usec
DE 6.00 usec
TE 294.7 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
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PL1 0.00 dB
SF01 300.1318534 MHz

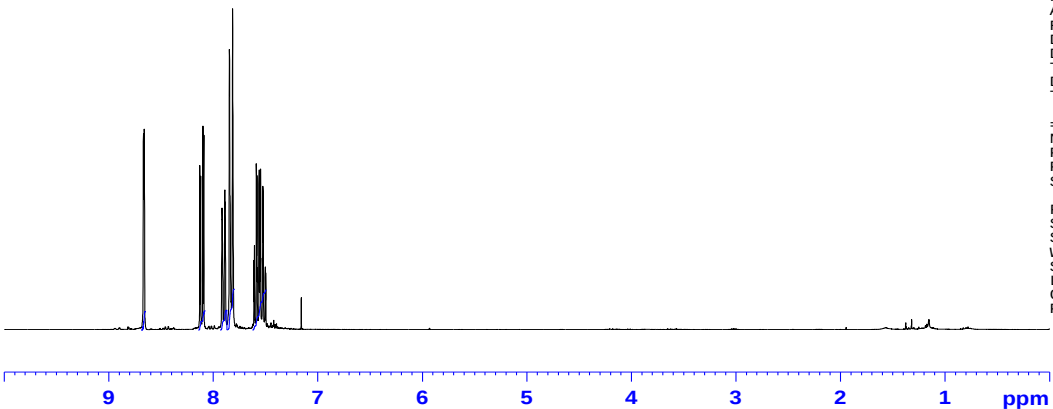
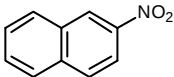
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SSB 0
LB 0.10 Hz
GB 0
PC 1.00



¹³C{¹H} NMR (75 MHz, CDCl₃, 24 °C):



¹H NMR (300 MHz, CDCl₃, 24 °C):
WU XW 3106
Au1H CDCl3 /opt/topspin 1011 22



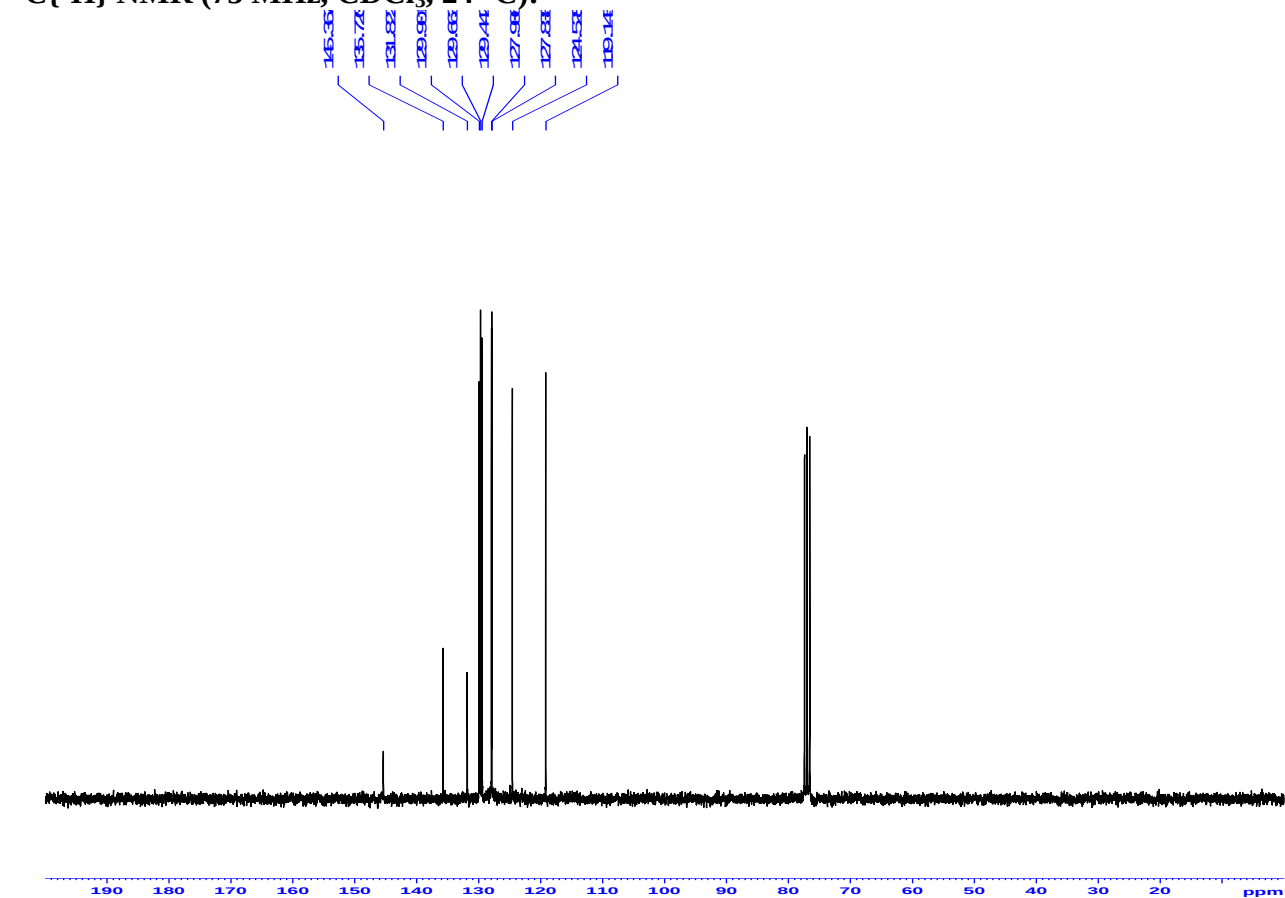
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PROCNO 1

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SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 128
DW 81.000 usec
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TE 294.7 K
D1 1.00000000 sec
TD0 1

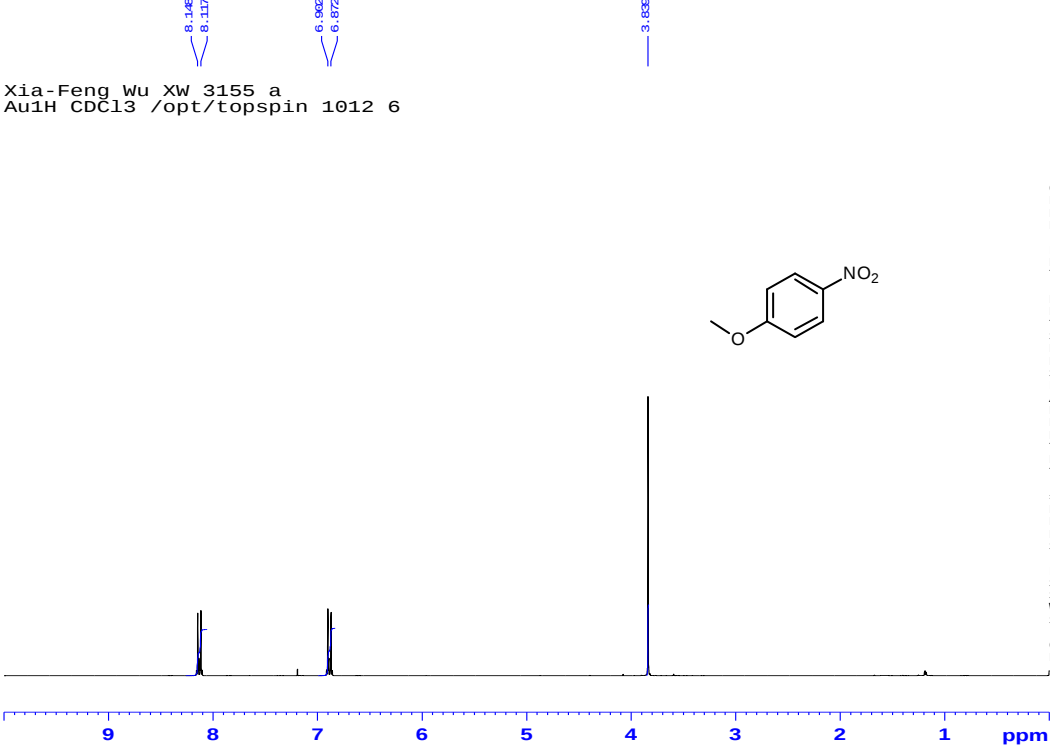
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LB 0.10 Hz
GB 0
PC 1.00

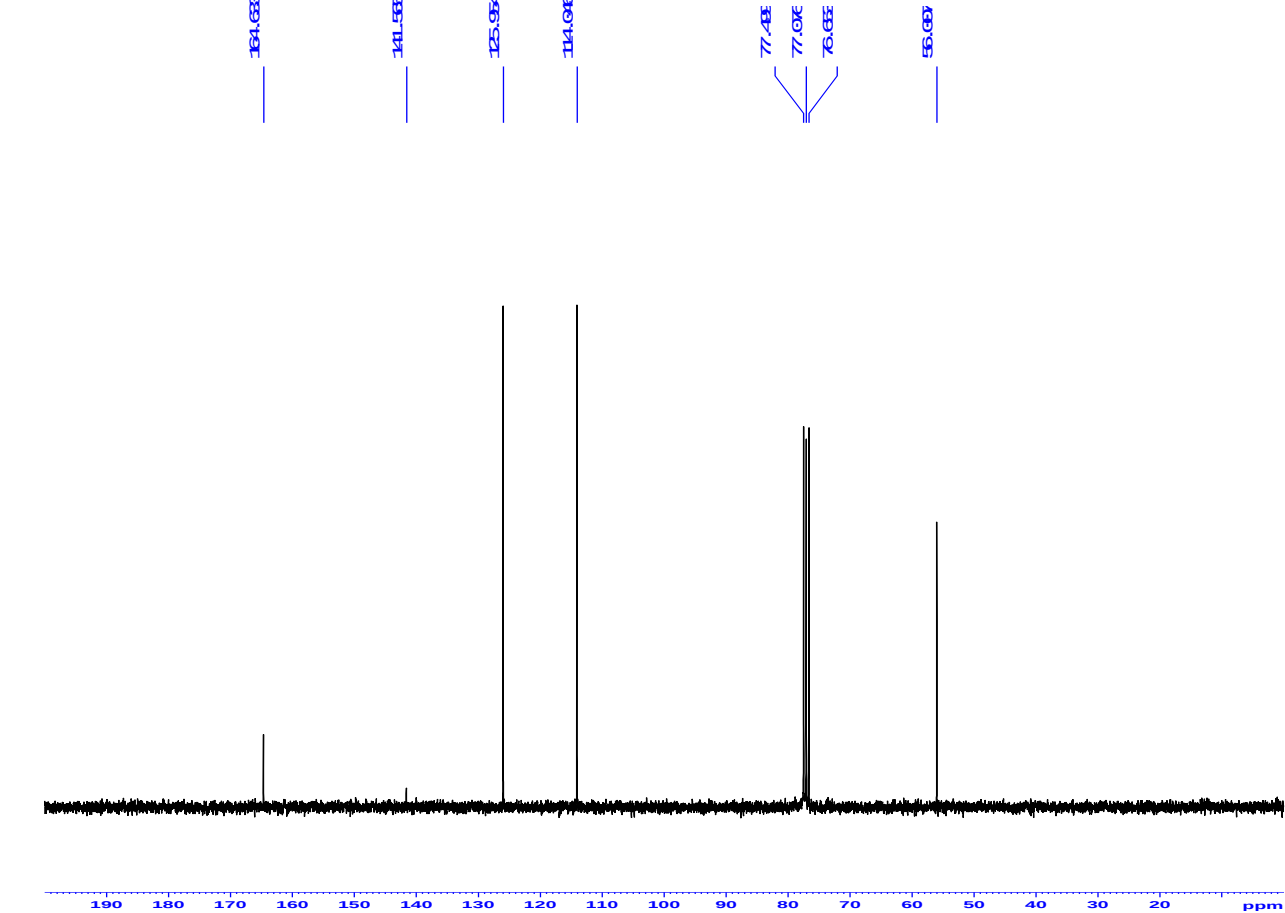
¹³C{¹H} NMR (75 MHz, CDCl₃, 24 °C):



¹H NMR (300 MHz, CDCl₃, 24 °C):

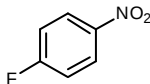


¹³C{¹H} NMR (75 MHz, CDCl₃, 24 °C):



¹H NMR (300 MHz, CDCl₃, 24 °C):

WU XW 3135
Au1H CDCl3 /opt/topspin 1011 19

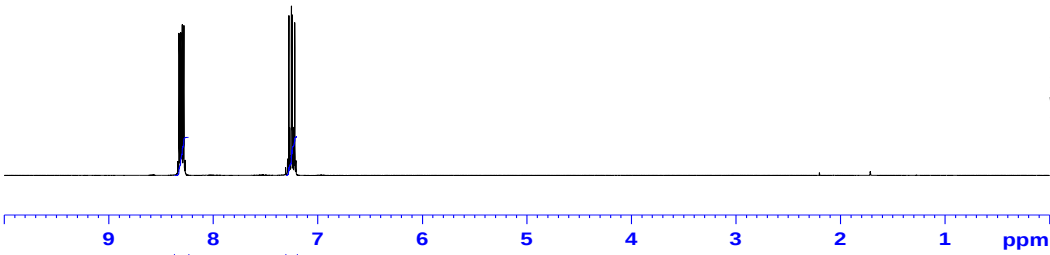


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PROCNO 1

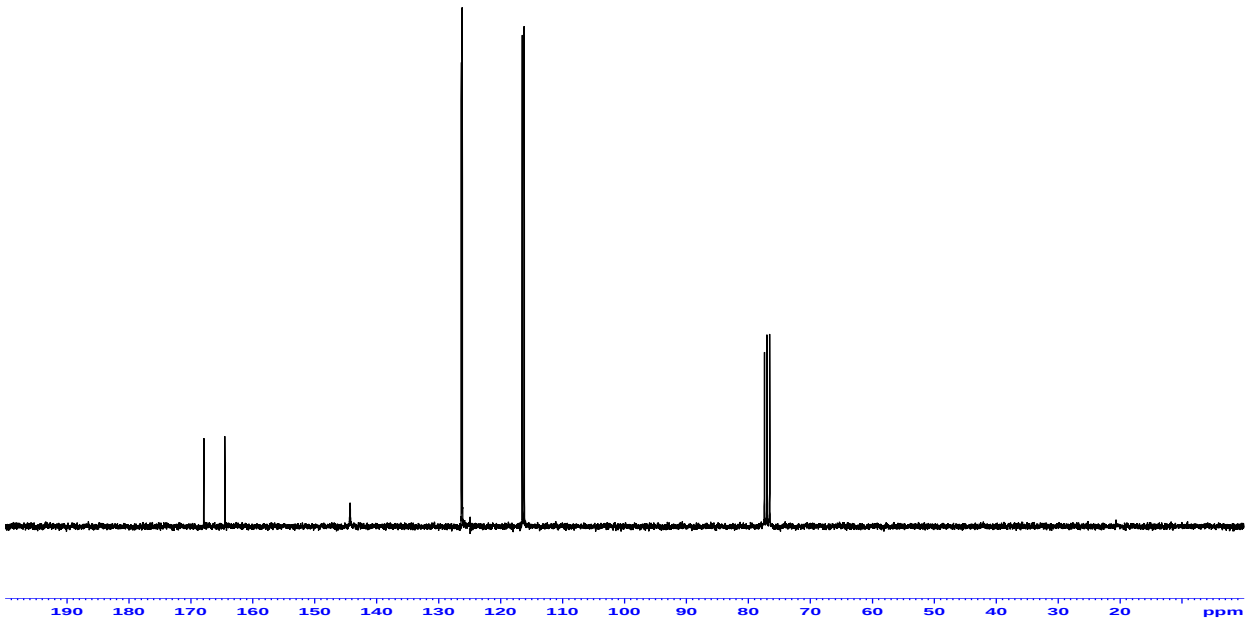
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 114
DW 81.000 usec
DE 6.00 usec
TE 294.8 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 11.00 usec
PL1 0.00 dB
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F2 - Processing parameters
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WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

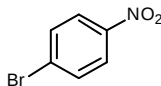


¹³C{¹H} NMR (75 MHz, CDCl₃, 24 °C):



¹H NMR (300 MHz, CDCl₃, 24 °C):

WU XW 3133
Au1H CDC13 /opt/topspin 1011 20

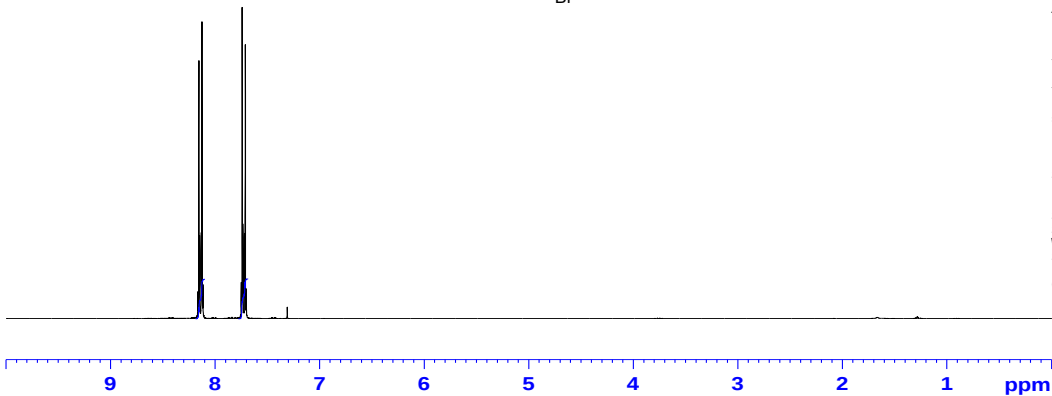


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PROCNO 1

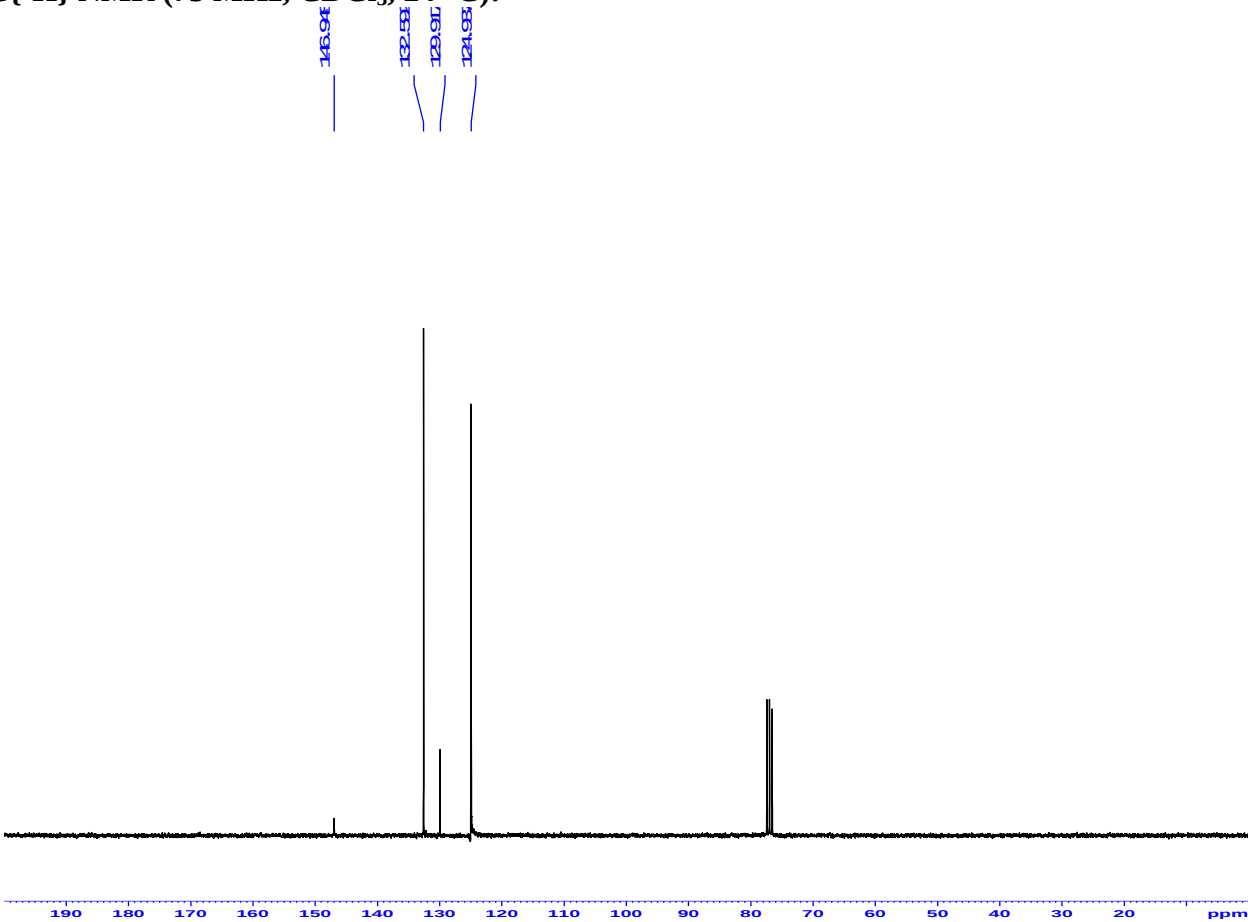
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TD 32768
SOLVENT CDC13
NS 32
DS 4
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 161.3
DW 81.000 usec
DE 6.00 usec
TE 294.8 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 11.00 usec
PL1 0.00 dB
SF01 300.1318534 MHz

F2 - Processing parameters
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WDW EM
SSB 0
LB 0.10 Hz
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PC 1.00



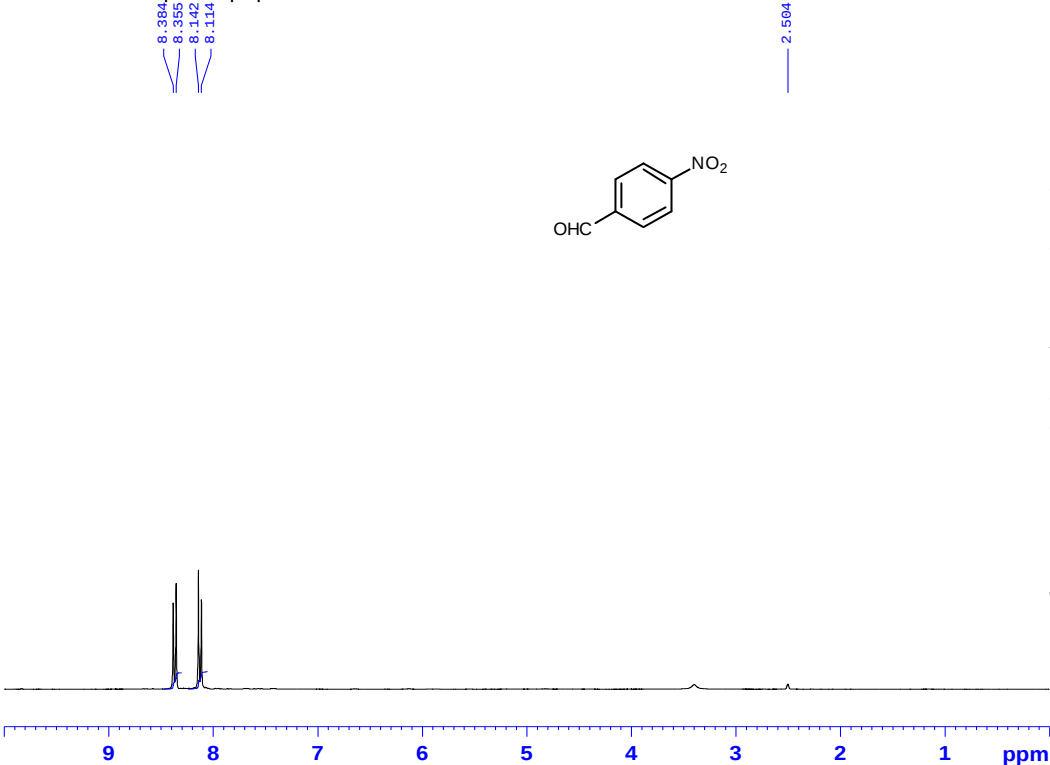
¹³C{¹H} NMR (75 MHz, CDCl₃, 24 °C):



¹H NMR (300 MHz, DMSO^{d6}, 24 °C):

WU XW 3132

Au1H DMSO /opt/topspin 1011 21



Current Data Parameters
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EXPNO 10
PROCNO 1

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PULPROG zg30
TD 32768
SOLVENT DMSO
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SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 101.6
DW 81.000 usec
DE 6.00 usec
TE 294.6 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 11.00 usec
PL1 0.00 dB
SF01 300.1318534 MHz

F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

¹³C{¹H} NMR (75 MHz, DMSO^{d6}, 24 °C):

