Supporting Information

Bromination of Deactivated Aromatics – A Simple and Efficient Method

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1. General. Reagents and solvents were purchased from commercial suppliers and used without further purification. ^1H - and ^{13}C -NMR: Bruker DPX-300 spectrometer; all ^1H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz in CDCl_3 or DMSO-d_6 . Melting points were recorded on Veego Model no. VMP-PM melting point apparatus. Mass spectra were recorded on Shimadzu QP 2010, and IR spectra recorded on Perkin Elmer FT-IR.

2. Spectroscopic data of compounds 2a, 2b, 2c, 2d, 2e, 4, 6, 8 & 10

Synthesis of 3-bromo-5-nitrobenzaldehyde (2a):

Reaction temperature: 60 °C; Reaction time: 1.5 h; Recrystallization from n-hexane yielded **2a** as off white crystalline solid. Yield: 92 %; mp 97 – 99 °C (lit. 100 °C).¹

^1H NMR (300 MHz, CDCl_3): 8.36 (s, 1H), 8.63 (s, 1H), 8.66 (s, 1H), 10.08 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3): 123.0, 124.1, 131.6, 137.5, 138.4, 149.2, 188.4.

MS: m/z calculated for $\text{C}_7\text{H}_4^{79}\text{BrNO}_3$ [M+] 229 found 229.

Synthesis of 3-bromo-5-nitrobenzoicacid (2b):

Reaction temperature: 60 °C; Reaction time: 1.5 h; Recrystallization from petroleum ether yielded **2b** as pale brown solid. Yield: 83 %; mp 161-162 °C (lit. 161 °C).¹

^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$): 8.49 (s, 1H), 8.62 (s, 1H), 8.71 (s, 1H). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{SO}$): 122.3, 122.7, 129.8, 134.1, 137.5, 148.5, 164.2.

MS: m/z calculated for $\text{C}_7\text{H}_4^{79}\text{BrNO}_4$ [M+] 245 found 245.

Synthesis of 1-bromo-3,5-dinitrobenzene (2c):

Reaction temperature: 60 °C; Reaction time: 2.5 h; Recrystallization from petroleum ether yielded **2c** as pale brown solid. Yield: 87 %; mp 75 - 76 °C (lit. 75-76 °C).²

^1H NMR (300 MHz, CDCl_3): 8.7 (s, 2H), 9.01 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3): 117.7, 123.9, 132.1, 148.9.

Synthesis of 3-bromo-5-nitrobenzamide (2d):

Reaction temperature: 60 °C; Reaction time: 1.5 h; Recrystallization from methanol yielded **2d** as off white solid. Yield: 86 %; mp 189-191 °C (lit. 187- 192).³

^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$): 7.86 (s, 1H), 8.41 (s, 1H), 8.48 (s, 1H), 8.53 (s, 1H), 8.66 (s, 1H). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{SO}$): 121.4, 122.0, 128.4, 136.2, 137.2, 148.5, 164.2. MS: m/z calculated for $\text{C}_7\text{H}_5^{79}\text{BrN}_2\text{O}_3$ [M+] 244 found 244. IR in KBr (cm^{-1}): 3413.8, 1659.5, 1551.9, 1344.9.

Synthesis of 5-bromoisophthalic acid (2e):

Reaction temperature: 60 °C; Reaction time: 1.5 h; Recrystallization from ethyl acetate yielded **2e** as off white solid. Yield: 86 %; mp 275-277 °C. (lit. 281-283)⁴. ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$): 8.33 (s, 2H), 8.62 (s, 1H). ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{SO}$): 121.9, 128.7, 133.4, 135.6, 165.2.

Synthesis of 1-bromo-2-chloro-3,5-dinitrobenzene (4):

Reaction temperature: 60 °C; Reaction time: 2 h; Recrystallization from petroleum ether yielded **4** as pale yellow solid. Yield: 84 %; mp 61-62 °C (lit. 63 °C).⁵

^1H NMR (300 MHz, CDCl_3): 8.6 (d, 1H, $J = 2.45$), 8.72 (d, 1H, $J = 2.45$). ^{13}C NMR (75 MHz, CDCl_3): 119.1, 126.8, 131.0, 134.4, 145.7, 149.2.

MS: m/z calculated for $\text{C}_6\text{H}_2^{79}\text{BrClN}_2\text{O}_4$ [M+] 280 found 280.

Synthesis of 3-bromo-5-nitrosalicylaldehyde (6):

Reaction temperature: 60 °C; Reaction time: 2 h; Recrystallization from Hexane yielded **6** as pale yellow crystals. Yield: 84 %; mp 148 - 149 °C (lit. 149-150 °C).⁶

^1H NMR (300 MHz, CDCl_3): 8.6 (s, 1H), 8.7 (s, 1H), 9.98 (s, 1H), 12.25 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3): 112.4, 119.5, 128.3, 134.5, 140.7, 162.9, 195.0.

Synthesis of Bis-(3-bromo-5-nitrophenyl)methanone (8):

Reaction temperature: 60 °C; Reaction time: 2 h; Recrystallization from hexane yielded **4** as off white solid. Yield: 81 %; mp 110 - 112 °C. ^1H NMR (300 MHz, CDCl_3): 8.25 (s, 2H), 8.5 (s, 2H), 8.67 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): 123.0, 130.9, 138.0, 148.8, 189.4. MS: m/z calculated for $\text{C}_{13}\text{H}_6^{79}\text{Br}_2\text{N}_2\text{O}_5$ [M+] 428 found 428. IR in KBr (cm^{-1}): 1676.06, 1535.26, 1345.96.

Synthesis of 4-bromo-2-nitrobenzaldehyde (**10**):

Reaction temperature: 25 °C; Reaction time: 3 h; **4** obtained as off white solid.

Yield: 60 %; mp 95 - 96 °C (lit. 97 - 98).⁷ ¹H NMR (300 MHz, CDCl₃): 7.84 (d, 1H, J = 8.29), 7.90 (m, 1H, J = 1.4, 1.7, 4.9), 8.27 (d, 1H, J = 1.7), 10.39 (s, 1H).

¹³C NMR (75 MHz, CDCl₃): 127.6, 130.9, 137.2, 187.0.

¹H NMR spectrum of **2a**

¹³C NMR spectrum of 2a:

Mass spectrum of 2a

Peak#:1 R.Time:0.2(Scan#:25)
MassPeaks:101 BasePeak:75(432076)

^1H NMR spectrum of 2b

^{13}C NMR spectrum of 2b

Mass spectrum of 2b

1H NMR spectrum of 2c

¹³C NMR spectrum of 2c

¹H NMR spectrum of 2d

¹³C NMR spectrum of 2d

Mass spectrum of 2d

IR NMR spectrum of 2d

¹H NMR spectrum of 2e

^{13}C NMR spectrum of 2e

^1H NMR spectrum of 4

¹³C NMR spectrum of 4

Mass spectrum of 4

Peak#:1 R.Time:1.0(Scan#:115)
MassPeaks:245 BasePeak:109(2495789)

^1H NMR spectrum of 6

¹³C NMR spectrum of 6

¹H NMR spectrum of 8

¹³C NMR spectrum of 8

Mass spectrum of 8

IR spectrum of 8

¹H NMR spectrum of 10

¹³C NMR spectrum of 10

4. Chemical Abstracts Nomenclature (Registry Number)

2a : 3-bromo-5-nitrobenzaldehyde (355134-13-3)

2b : 3-bromo-5-nitrobenzoic acid (6307-83-1)

2c : 1-bromo-3,5-dinitrobenzene (18242-39-2)

2d : 3-bromo-5-nitrobenzamide (54321-80-1)

2e : 5-bromo-isophthalic acid (23351-91-9)

4 : 1-bromo-2-chloro-3,5-dinitrobenzene (51796-81-7)

6 : 3-bromo-5-nitrosalicylaldehyde (16789-84-7)

8 : bis-(3-bromo-5-nitrophenyl)methanone

10 : 4-bromo-2-nitrobenzaldehyde (5551-12-2)

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