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. ^{1}H- and ^{13}C-NMR: Bruker DPX-300 spectrometer; all ^{1}H 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]

^{1}H 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 $C_7H_4{}^{79}BrNO_3$ [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]

^{1}H NMR (300 MHz, $(CD_3)_2SO$): 8.49 (s, 1H), 8.62 (s, 1H), 8.71 (s, 1H). ^{13}C NMR (75 MHz, $(CD_3)_2SO$): 122.3, 122.7, 129.8, 134.1, 137.5, 148.5, 164.2.

MS: m/z calculated for $C_7H_4{}^{79}BrNO_4$ [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]

^{1}H 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]

^{1}H NMR (300 MHz, $(CD_3)_2SO$): 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, $(CD_3)_2SO$): 121.4, 122.0, 128.4, 136.2, 137.2, 148.5, 164.2. MS: m/z calculated for $C_7H_5{}^{79}BrN_2O_3$ [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]. ^{1}H NMR (300 MHz, $(CD_3)_2SO$): 8.33 (s, 2H), 8.62 (s, 1H). ^{13}C NMR (75 MHz, $(CD_3)_2SO$): 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]
^{1}H 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 $C_6H_2{}^{79}BrClN_2O_4$ [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]
^{1}H 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. ^{1}H 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 $C_{13}H_6{}^{79}Br_2N_2O_5$ [M+] 428 found 428. IR in KBr (cm^{-1}): 1676.06, 1535.26, 1345.96.

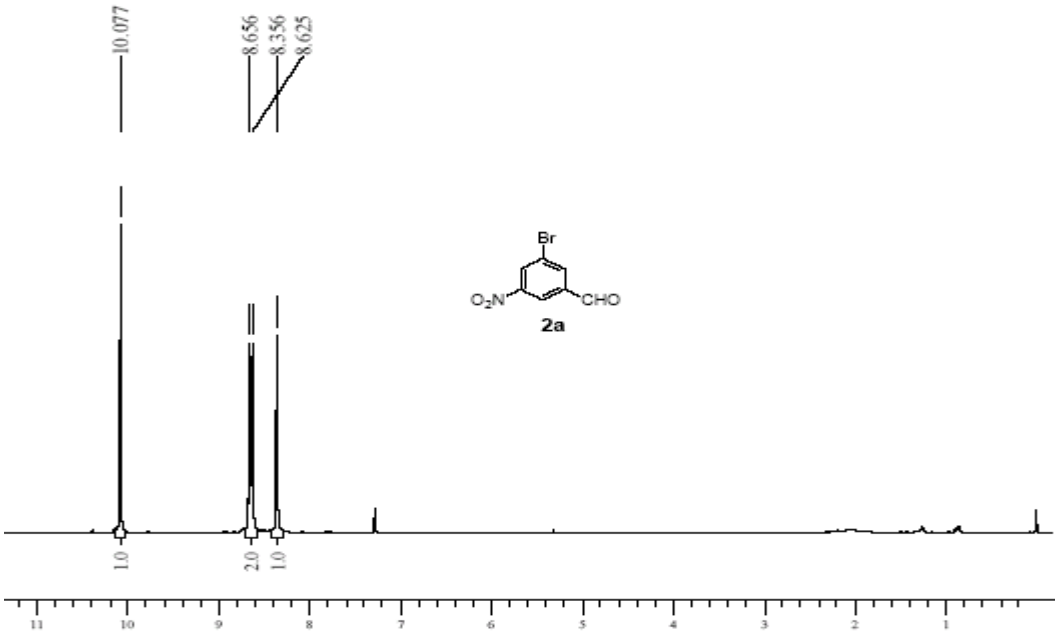
Synthesis of 4-bromo-2-nitrobenzaldehyde (10):

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

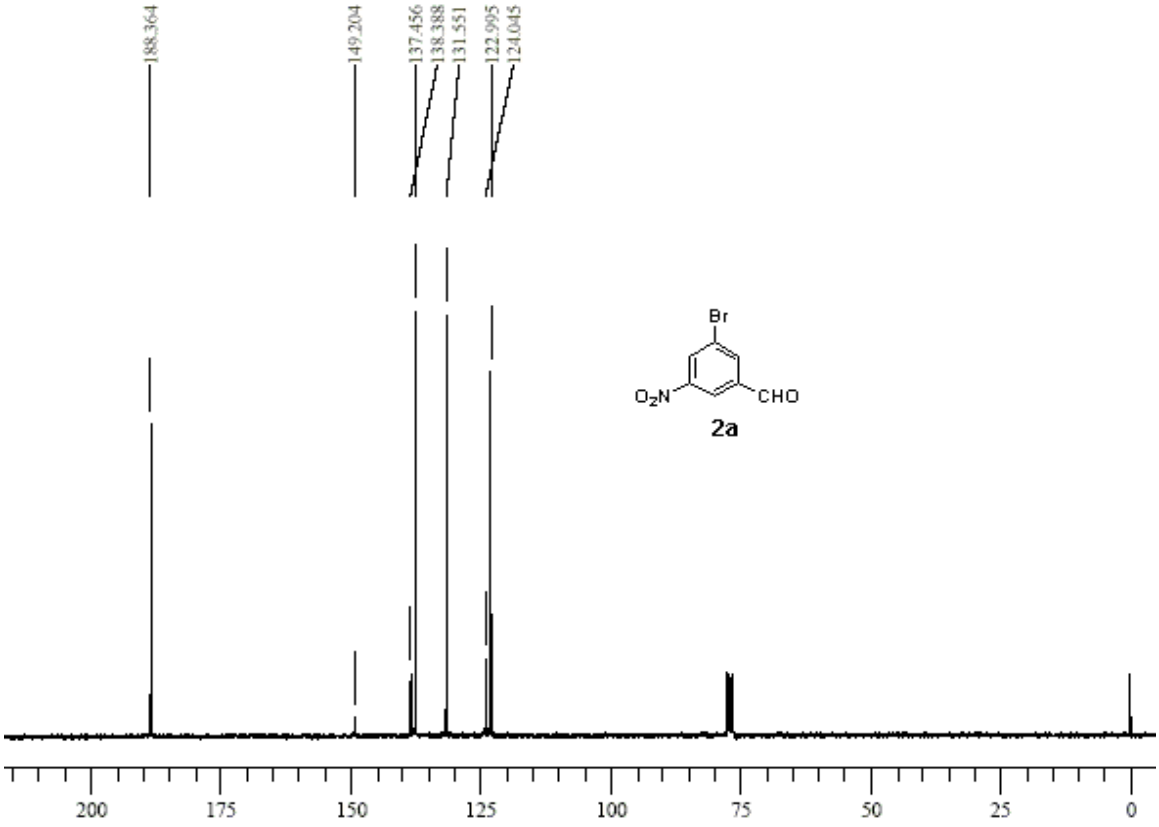
Yield: 60 %; mp 95 - 96 °C (lit. 97 - 98).[7] ^{1}H NMR (300 MHz, $CDCl_3$): 7.84 (d, 1H, J = 8.29), 7.90 (m, 1H, J = 1.4, 1.7, 4.9), 8.27 (d, 1H, J = 1.7), 10.39 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 127.6, 130.9, 137.2, 187.0.

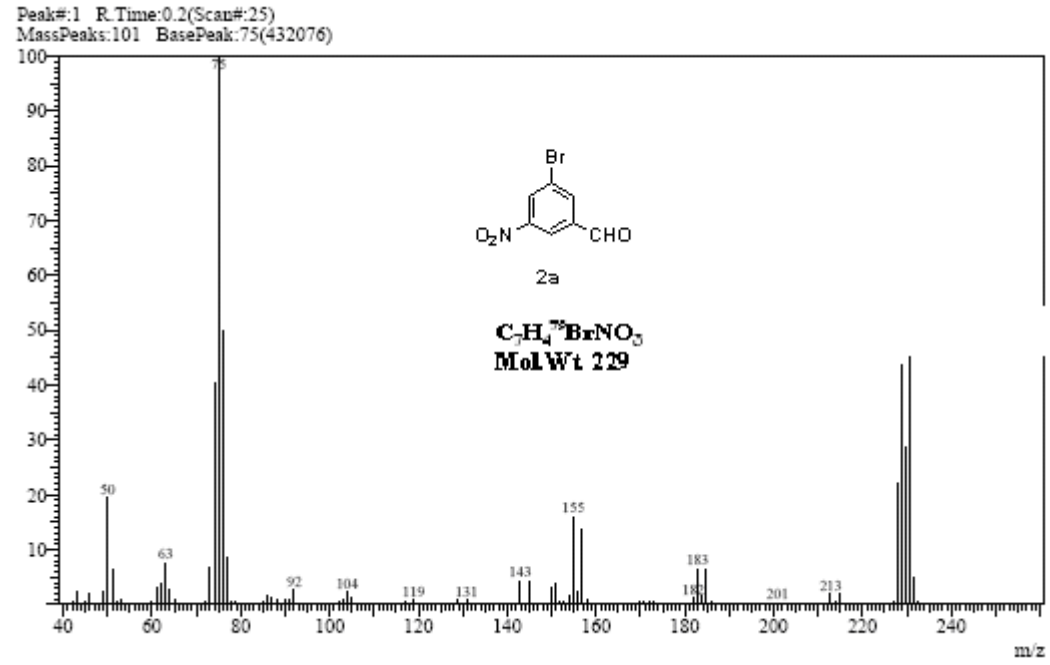
^{1}H NMR spectrum of 2a



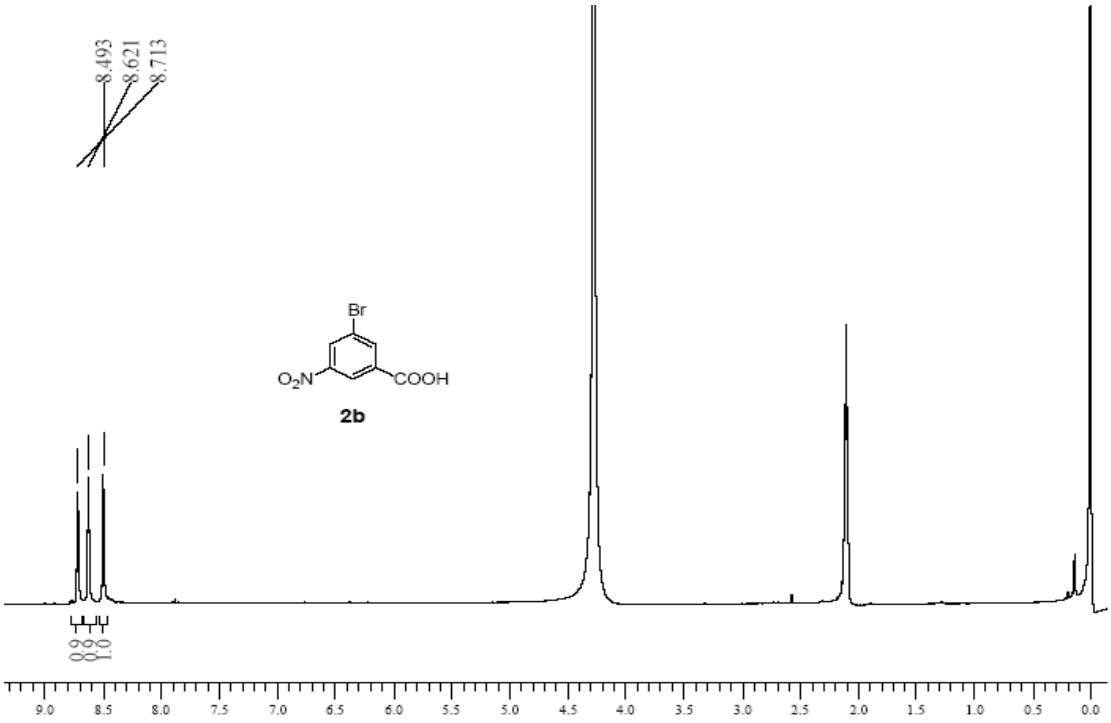
^{13}C NMR spectrum of 2a:



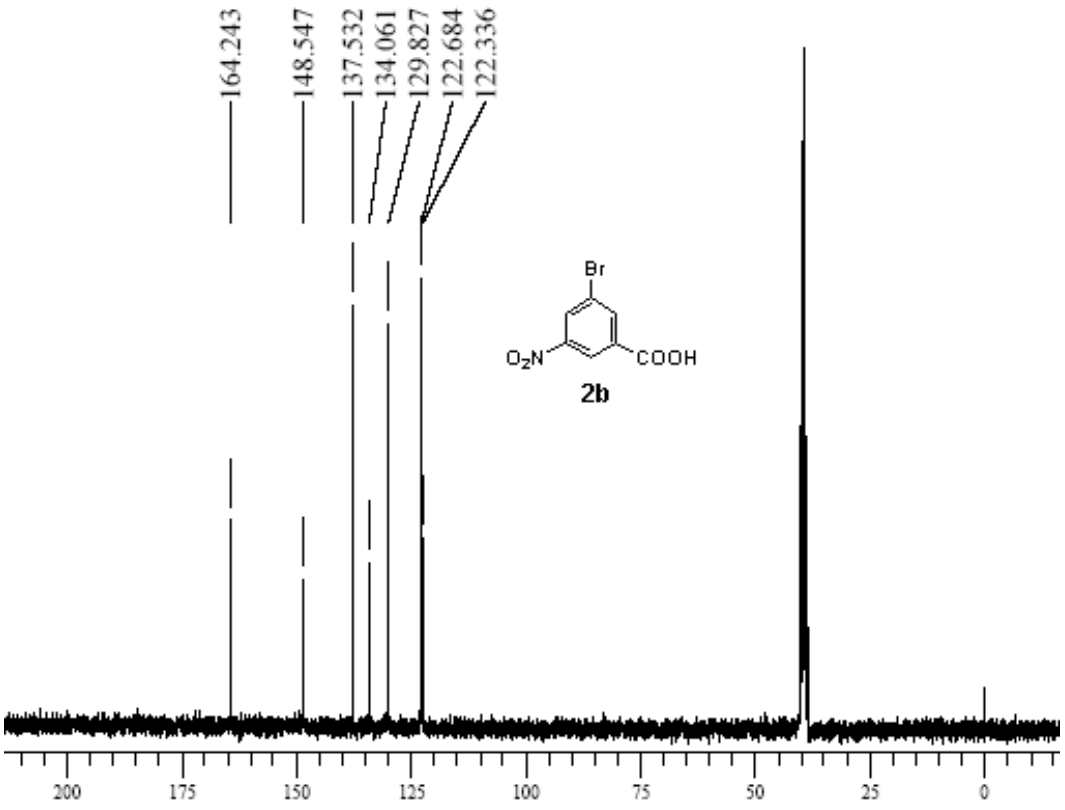
Mass spectrum of 2a



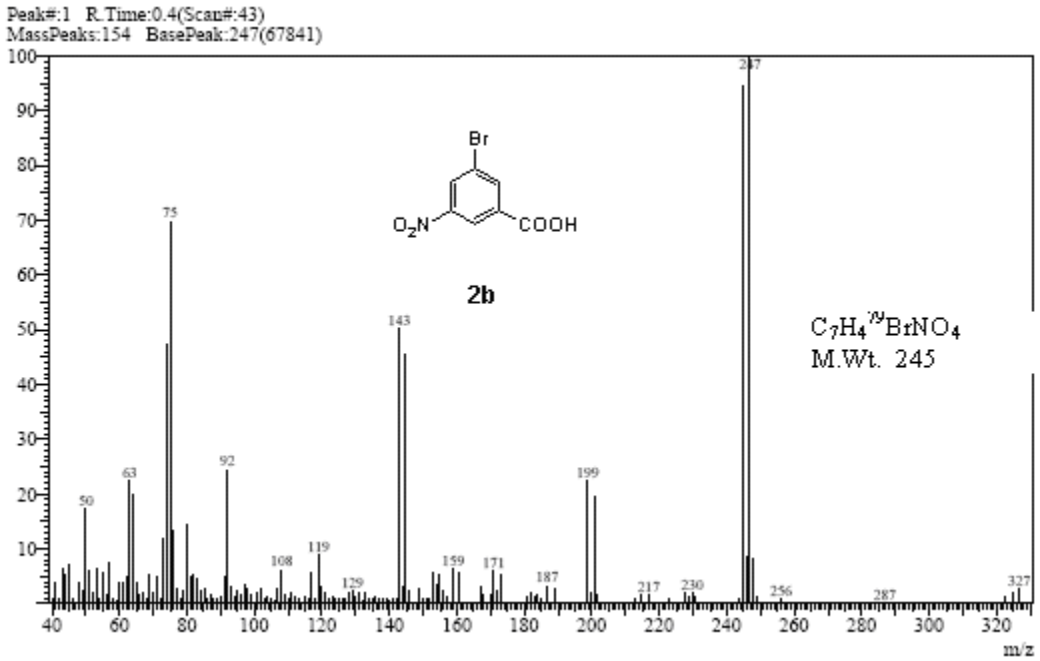
[1]H NMR spectrum of 2b



[13]C NMR spectrum of 2b



Mass spectrum of 2b



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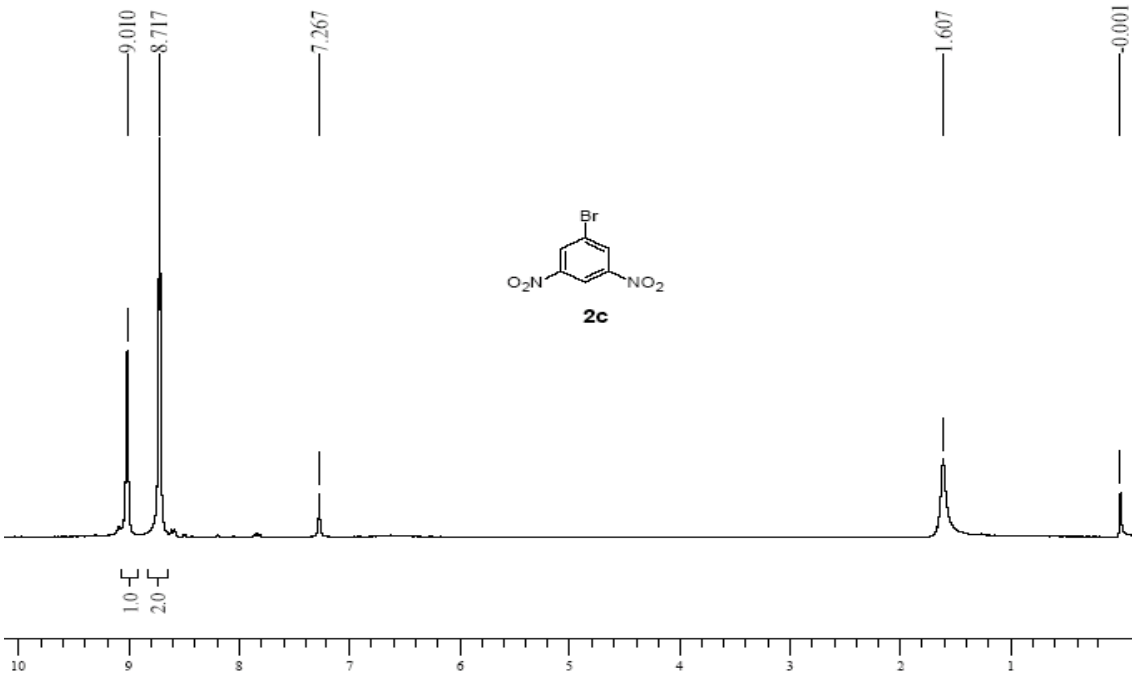
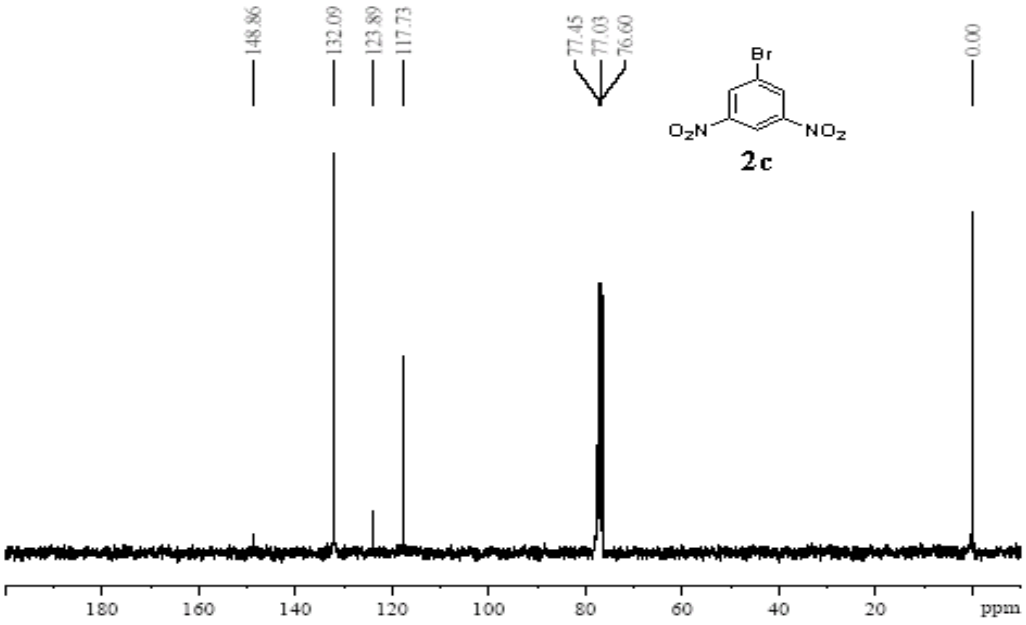
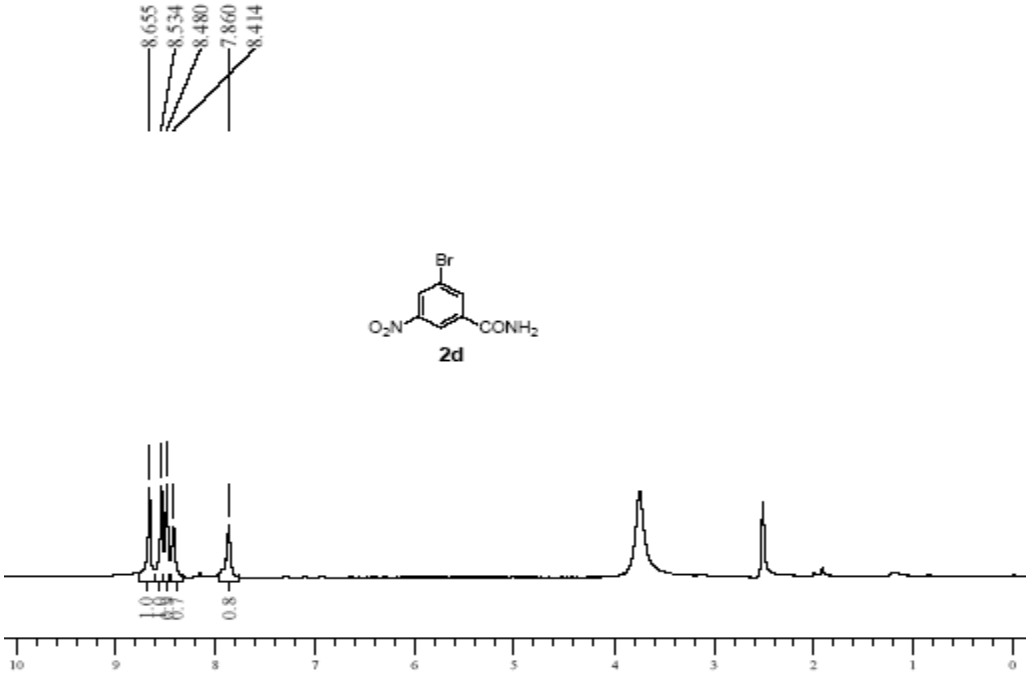
^{1}H NMR spectrum of 2c



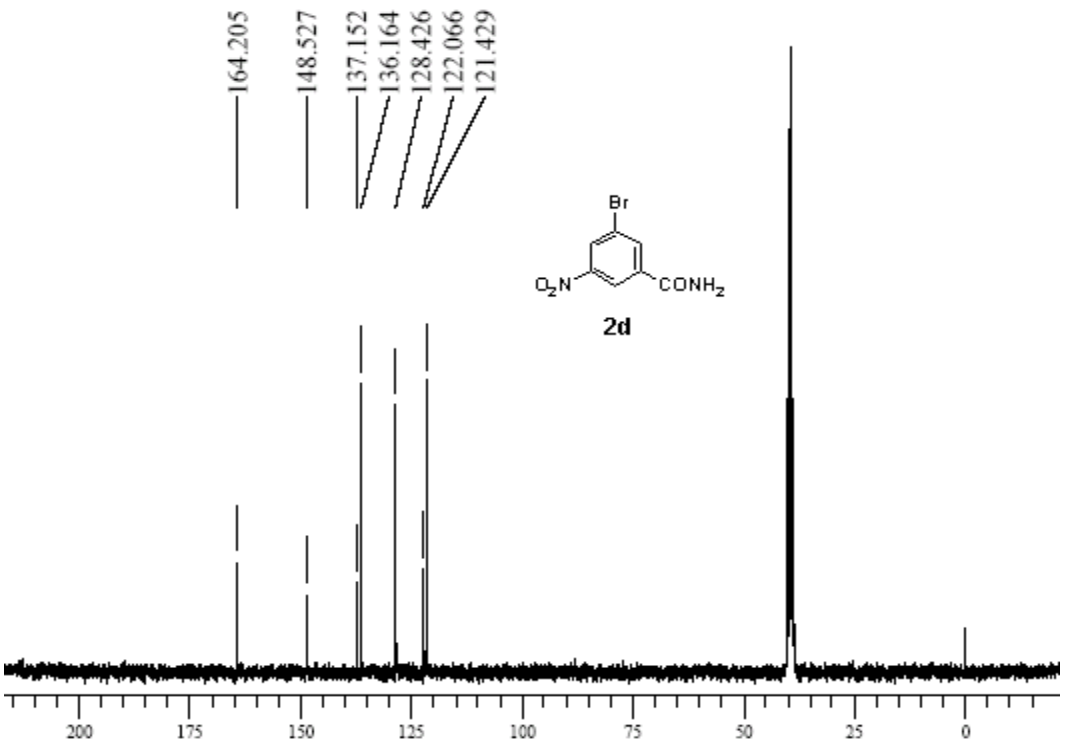
^{13}C NMR spectrum of 2c



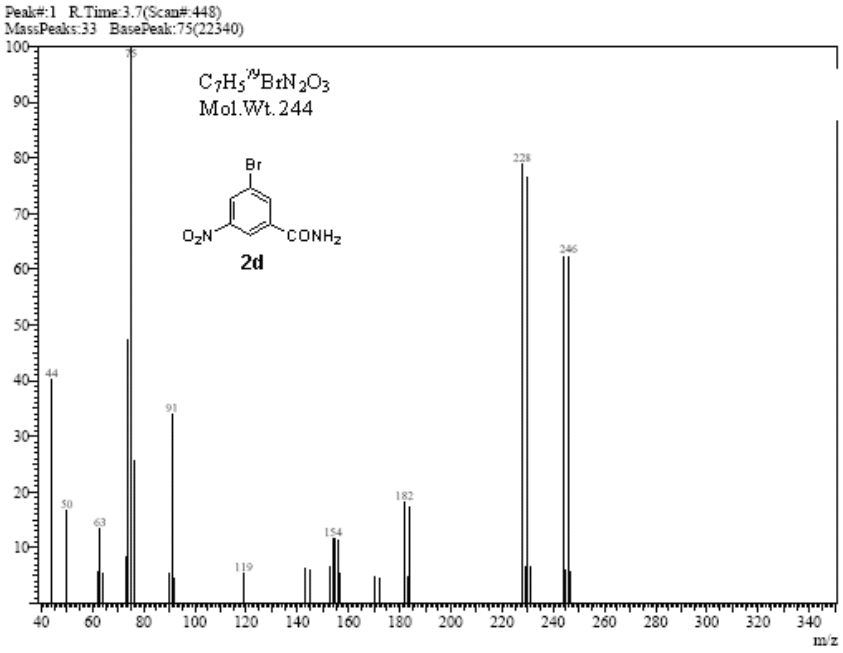
^{1}H NMR spectrum of 2d



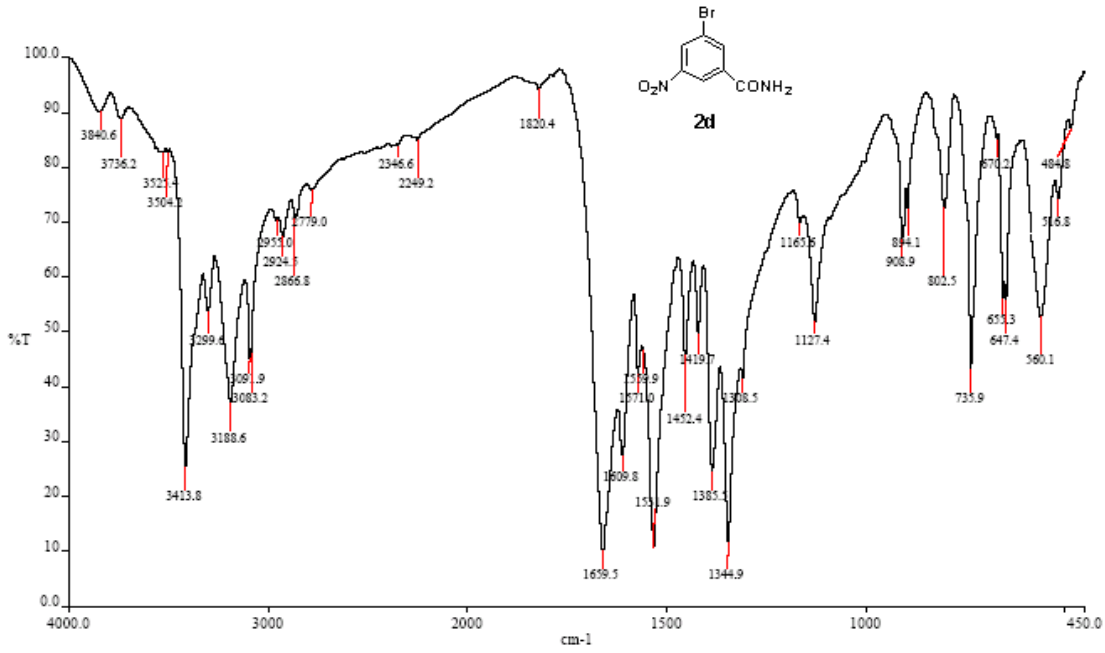
^{13}C NMR spectrum of 2d



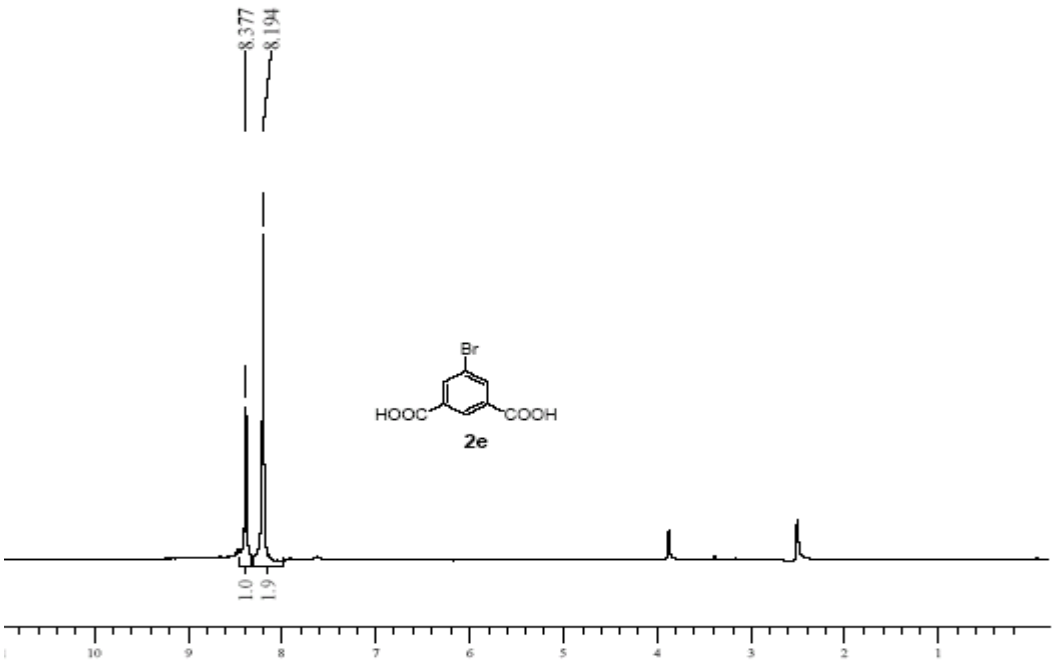
Mass spectrum of 2d



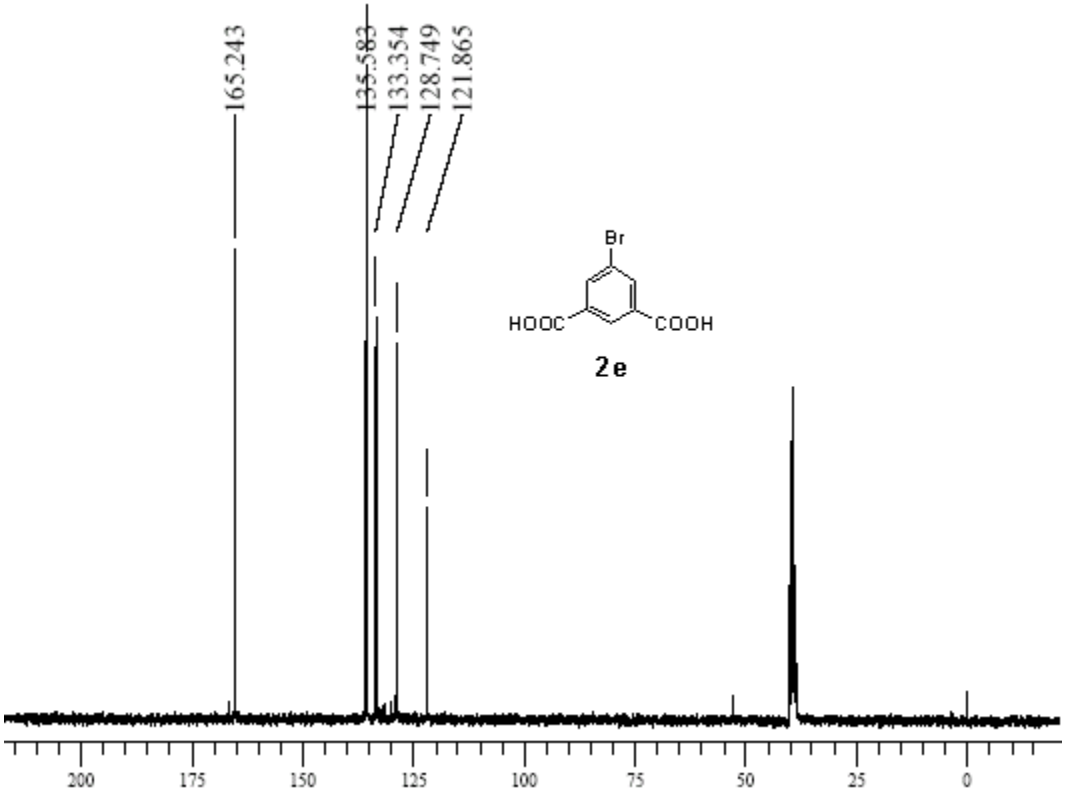
IR NMR spectrum of 2d



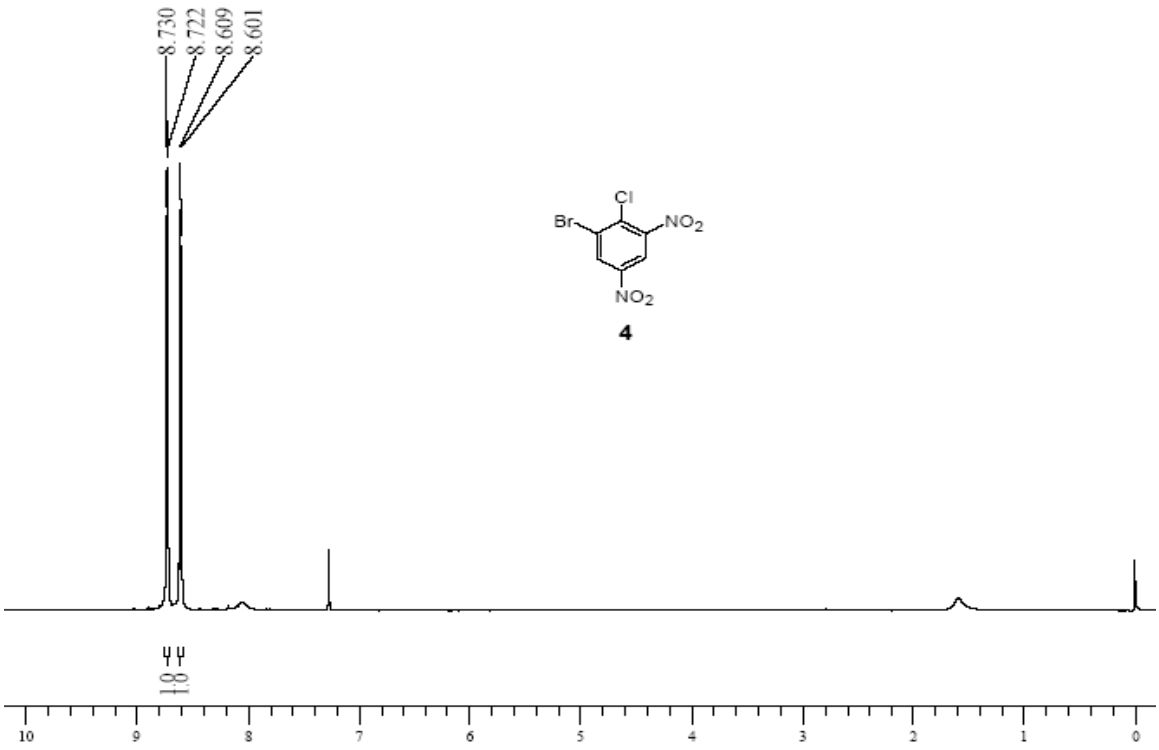
^{1}H NMR spectrum of 2e



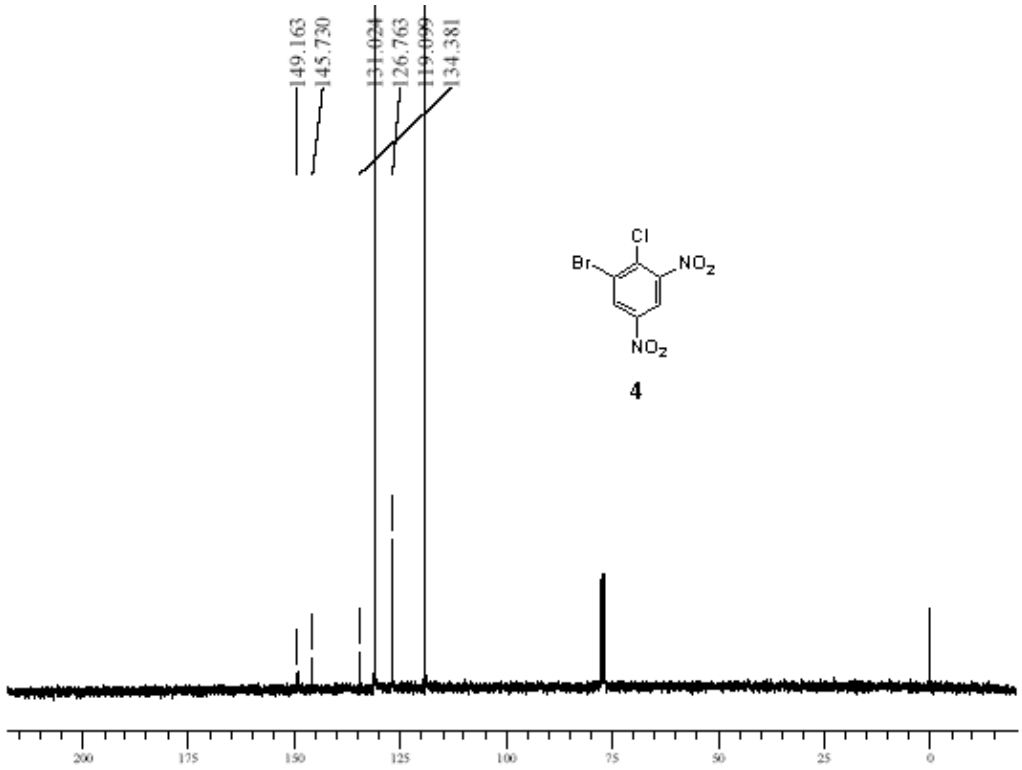
^{13}C NMR spectrum of 2e



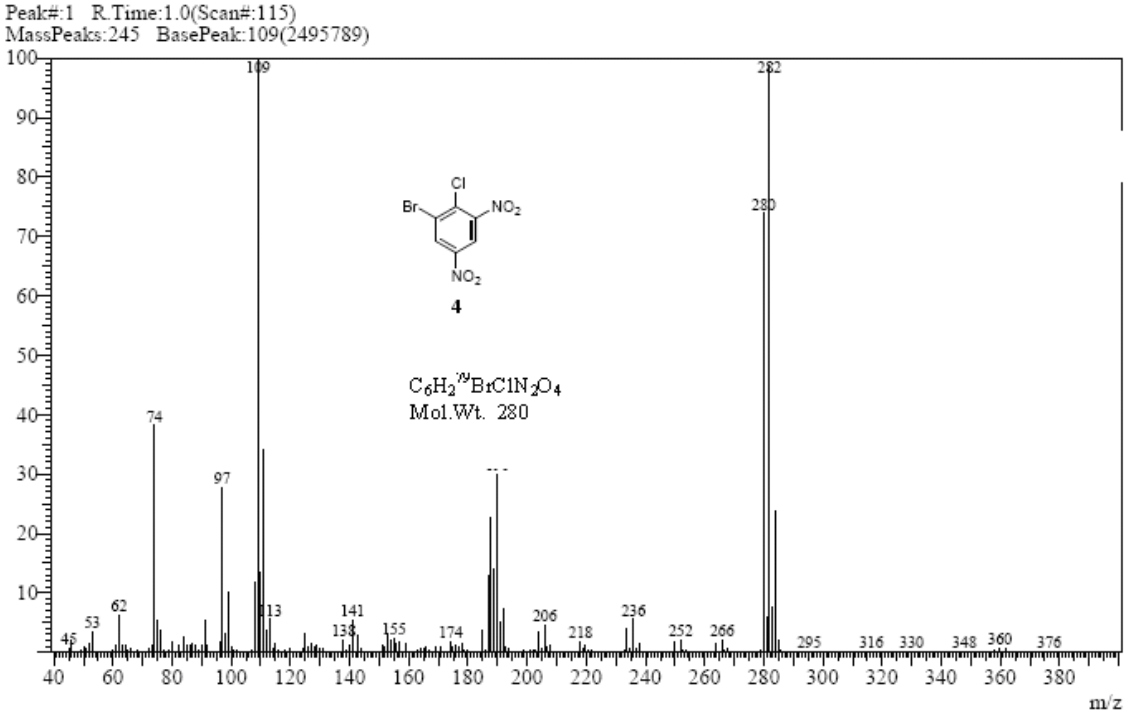
^{1}H NMR spectrum of 4



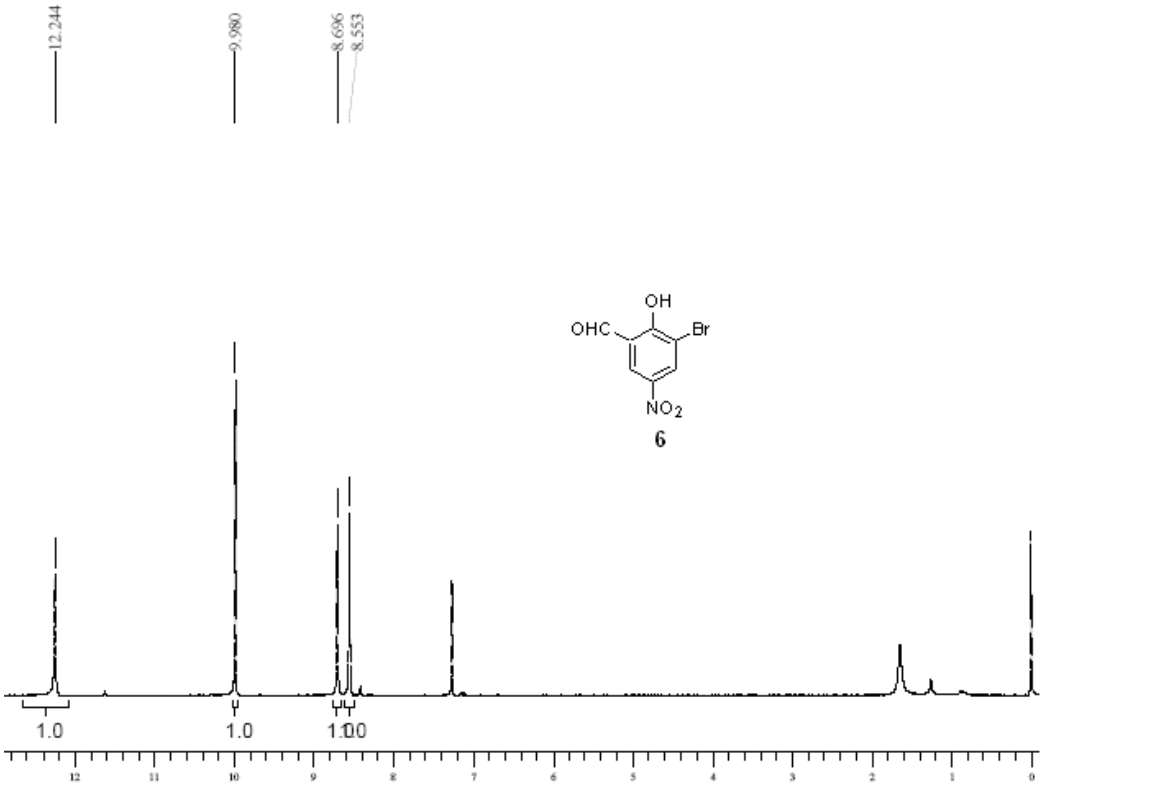
^{13}C NMR spectrum of 4



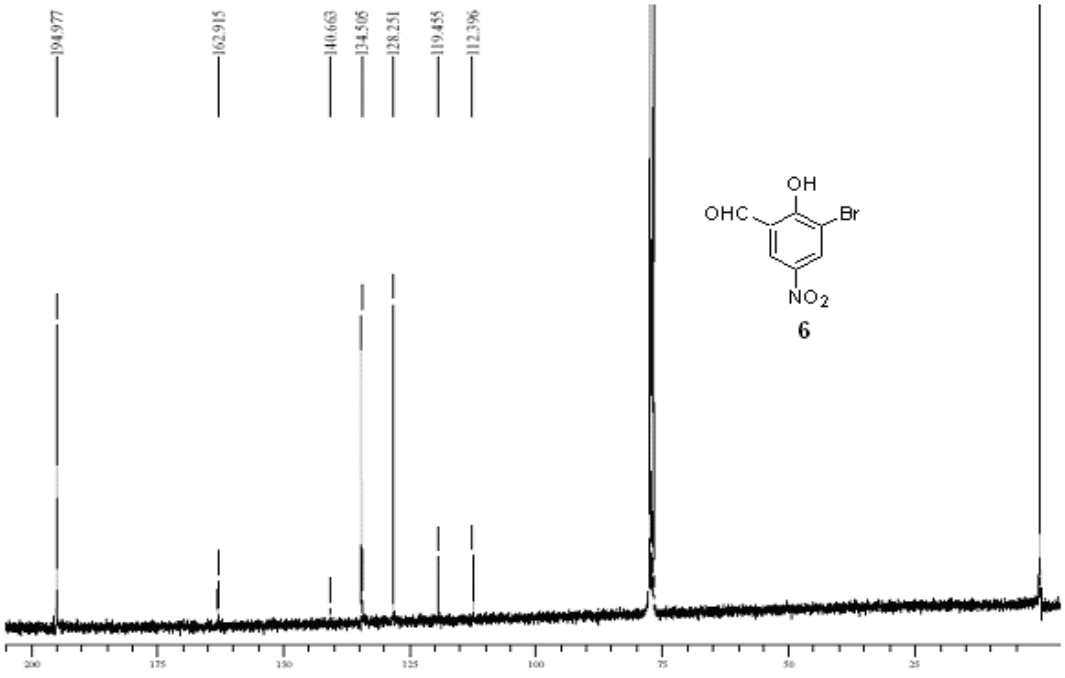
Mass spectrum of 4



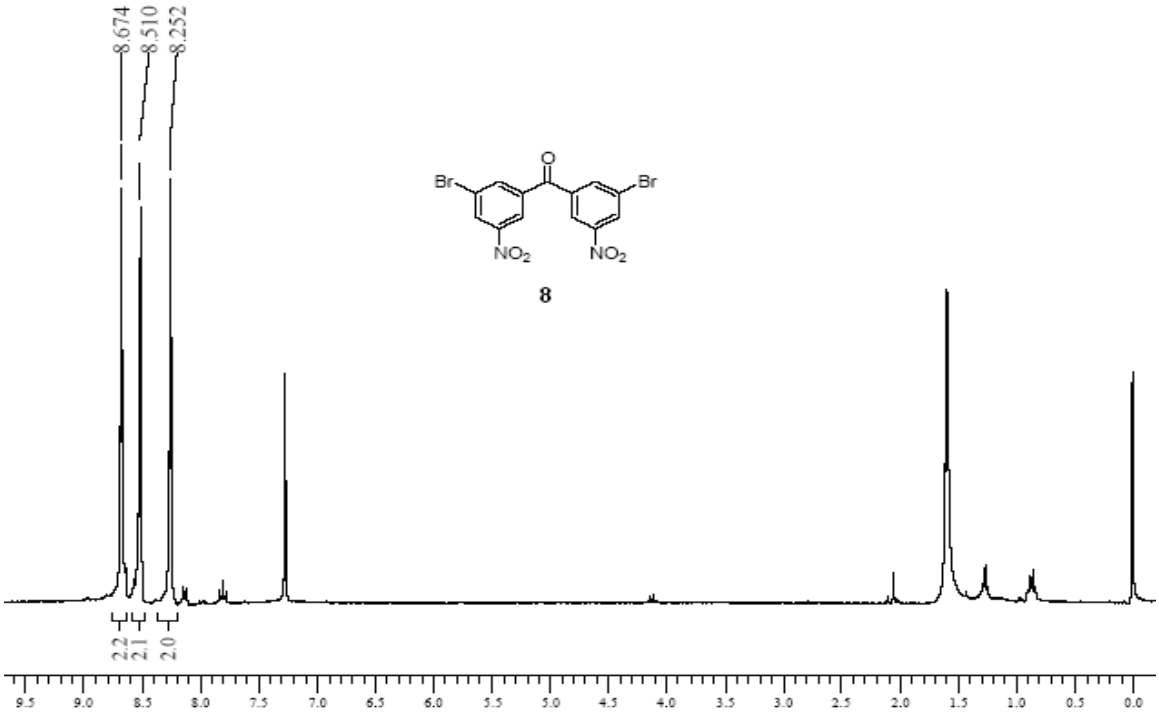
^{1}H NMR spectrum of 6



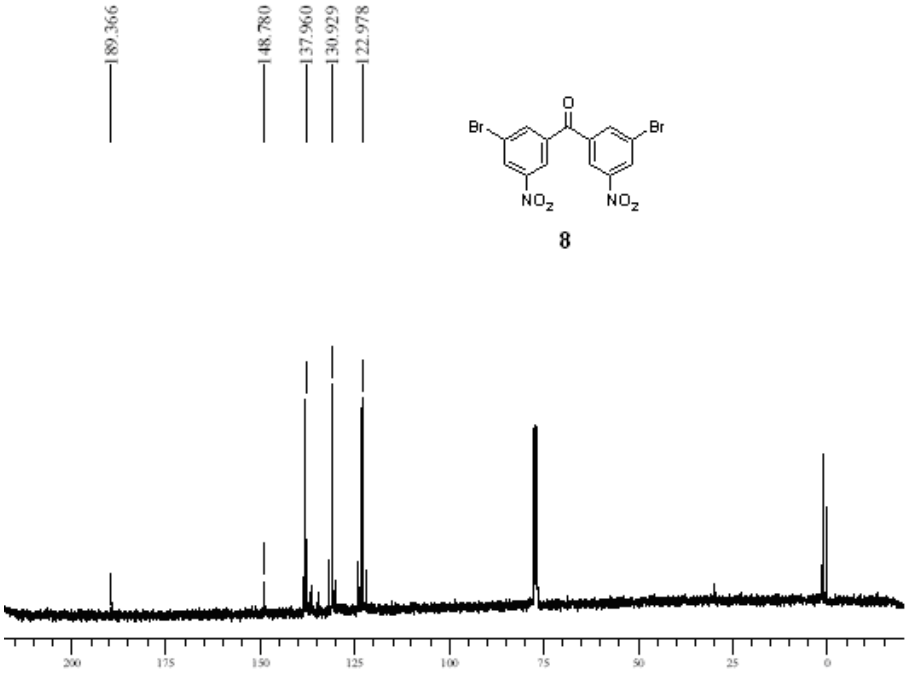
^{13}C NMR spectrum of 6



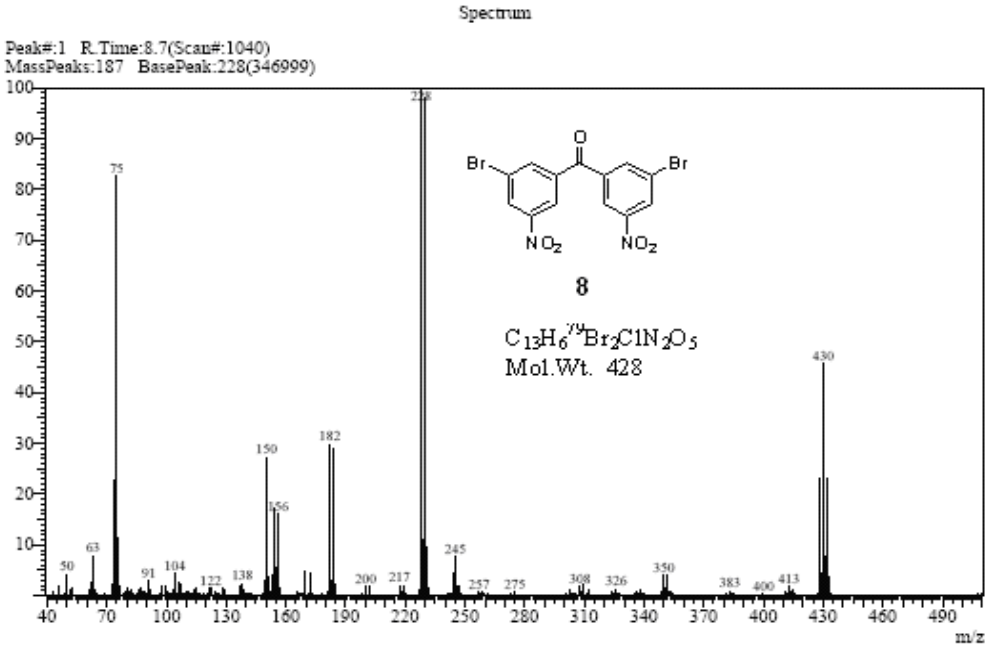
^{1}H NMR spectrum of 8



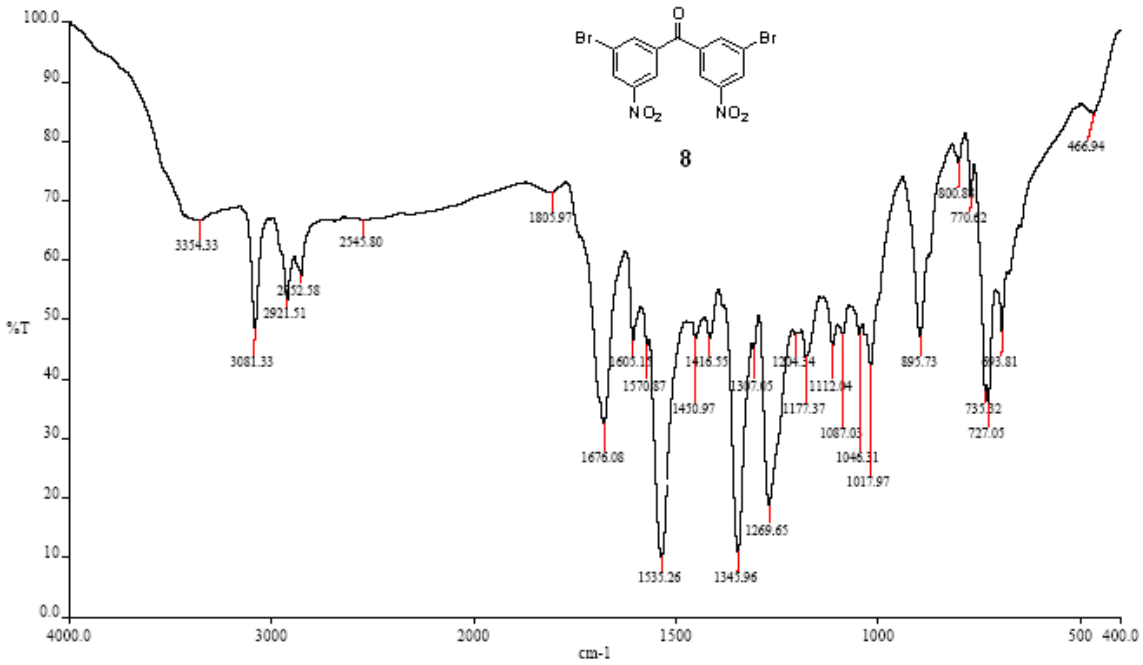
^{13}C NMR spectrum of 8



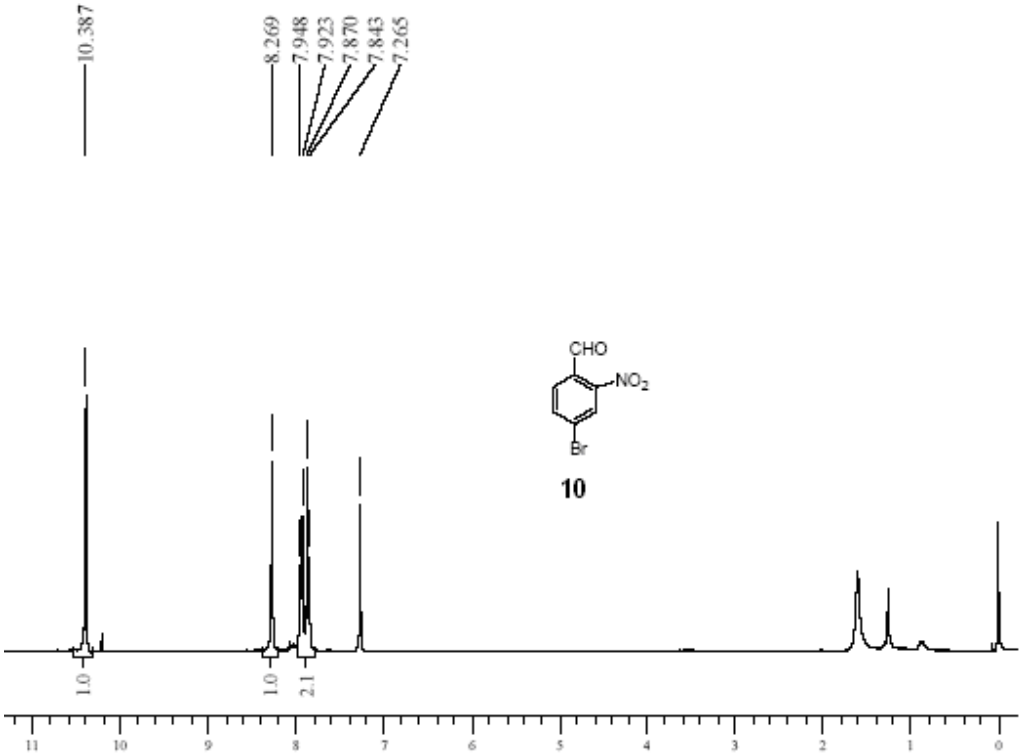
Mass spectrum of 8



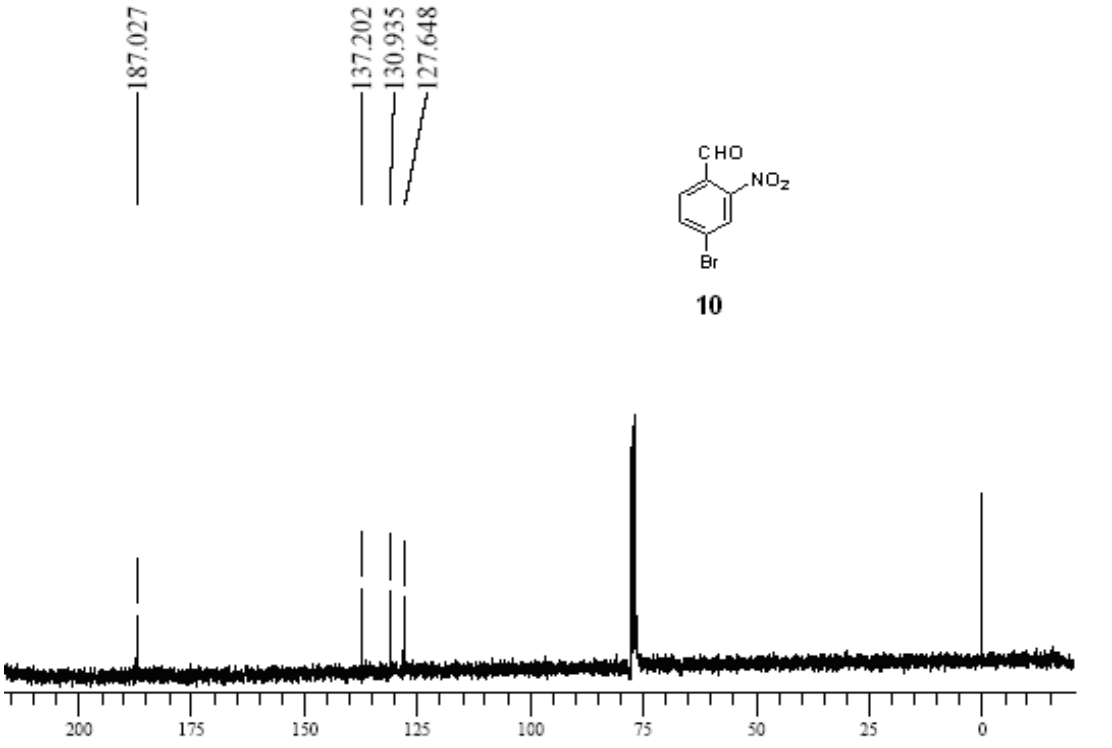
IR spectrum of 8



^{1}H NMR spectrum of 10



^{13}C NMR spectrum of 10



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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)

References

1) *Chem. Abstr*. **1913**, *7*, 769.

2) Huthmacher, K.; Effenberger, F. *Synthesis* **1978**, 693.

3) Material Safety Data sheet, Catalog Number: CA-4348, Combi-Blocks, Inc.

4) Gumbley, S. J.; Stewart, R. *J. Chem. Soc. Perkin Trans. II,* **1984**, 529.

5) Sane, S. M.; Joshi, S. S. *J. Chem. Soc*. **1924**, *125*, 2481.

6) Clinton, R. O.; Laskowski, S. C. J. Am. Chem. Soc. **1949**, *71*, 3602.

7) *Chem. Abstr*. **1968**, *69*, 106403y.