Supplementary Material (ESI) for Chemical Communications
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A highly efficient TBAF-promoted intramolecular cyclization of *gem*-dibromoolefins for the synthesis of 2-bromobenzofurans(thiophenes)

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Table of Contents for Supporting Information

1. Physical measurements and materials

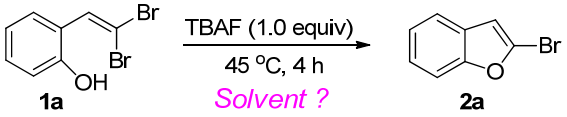
All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument. Products were purified by flash chromatography on 100–200 mesh silica gels, SiO_2. Unless otherwise noted, the chemicals and solvents were purchased from commercial suppliers either from Aldrich, USA or Shanghai Chemical Company, China and were used without purification prior to use.

2. Typical procedure for the intramolecular cyclization

A Schlenk tube with a magnetic stirring bar was charged with 2-(*gem*-dibromovinyl)phenol (**1a**), TBAF (1.0 M solution in THF, 1.0 mL, 1.0 mmol), and THF (1.0 mL). The reaction mixture was stirred for 10 min at room temperature, and then heated at 45 °C for 4 h. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: hexane/ethyl acetate) to give the intramolecular cyclization product, 2-bromobenzofuran (**2a**, 195 mg, 99% yield).

3. Optimization of partial reaction conditions

Table The effect of solvent on the intramolecular cyclization of 2-(*gem*-dibromovinyl)phenol (**1a**)[a]

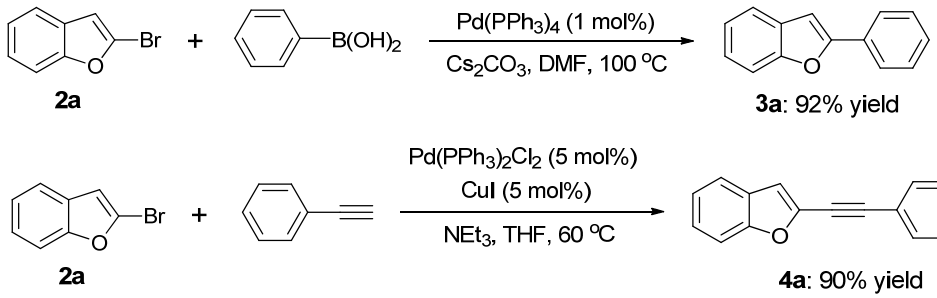


Entry	Solvent	Yield (%)[b]
1	THF	99
2	CH_3CN	98
3	DMF	99
4	DMSO	97
5	1,4-Dioxane	96
6	Toluene	81
7	H_2O	NR
8	CH_3CH_2OH	NR
9	$CH_3CH_2CH_2CH_2OH$	NR

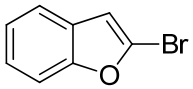
[a] Reaction conditions: 2-(*gem*-dibromovinyl)phenol (**1a**, 1.0 mmol), TBAF (1.0 mmol), solvent (2.0 mL) at 45 °C for 4 h. [b] Isolated yield.

4. Further transformation of 2-bromobenzofuran

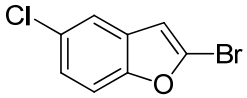
When the prepared 2-bromobenzofuran **(2a)** reacted with phenylboronic acid and phenylacetylene under the classic Suzuki reaction conditions (See: S. Thielges, E. Meddah, P. Bisseret, J. Eustache, *Tetrahedron Lett.* **2004**, *45*, 907–910) and Sonogashira reaction conditions (See: M. Nagamochi, Y.-Q. Fang, M. Lautens, *Org. Lett.* **2007**, *9*, 2955–2958), the corresponding cross-coupling product **3a** and **4a** were isolated in 90%, and 92% yields, respectively.



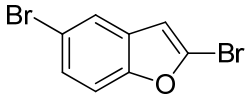
5. Characterization data for the intramolecular cyclization products



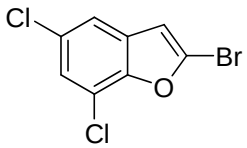
2a (Colorless oil):[1] ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.43–7.50 (m, 2H), 7.19–7.26 (m, 2H), 6.71 (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 155.7, 128.7, 128.2, 124.2, 123.3, 120.1, 110.9, 108.2.



2b (White solid, m.p. 41–43 °C):[1] ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.48 (d, J = 1.2 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.23 (dd, J_1 = 8.8 Hz, J_2 = 1.2 Hz, 1H), 6.69 (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 154.1, 129.9, 129.8, 129.1, 124.4, 119.6, 111.8, 108.0.

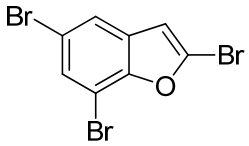


2c (Yellow solid, m.p. 55–58 °C):[1] ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.64 (d, J = 0.8 Hz, 1H), 7.31–7.38 (m, 2H), 6.69 (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 154.4, 130.5, 129.7, 127.1, 122.7, 116.6, 112.3, 107.8.

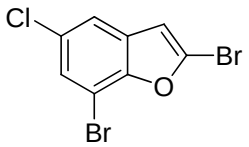


2d (White solid, m.p. 70–72 °C): ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.37 (d, J = 1.6 Hz,

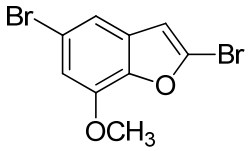
1H), 7.26 (d, J = 1.2 Hz, 1H), 6.72 (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 150.2, 130.8, 130.8, 129.4, 124.5, 118.3, 116.9, 108.7. HRMS (EI): calcd for $C_8H_3BrCl_2O$, 263.8742; found, 263.8744.



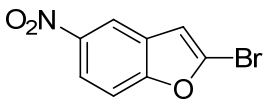
2e (Yellow solid, m.p. 87–89 °C): ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.59 (d, J = 1.6 Hz, 1H), 7.57 (d, J = 1.2 Hz, 1H), 6.76 (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 152.0, 131.1, 130.7, 129.7, 121.9, 116.8, 108.7, 104.2. HRMS (EI): calcd for $C_8H_3Br_3O$, 351.7730; found, 351.7734.



2f (Yellow solid, m.p. 80–82 °C): ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.44–7.42 (m, 2H), 6.76 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$): δ = 151.7, 130.8, 130.4, 129.7, 127.2, 118.9, 108.9, 103.8. HRMS (EI): calcd for $C_8H_3Br_2ClO$, 307.8237; found, 307.8239.

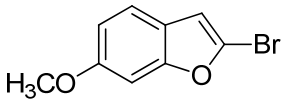


2g (White solid, m.p. 76–78 °C): ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.25 (d, J = 1.6 Hz, 1H), 6.90 (d, J = 1.2 Hz, 1H), 6.66 (s, 1H), 3.99 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 145.0, 144.1, 131.4, 129.3, 116.7, 115.0, 110.2, 108.1, 56.4. HRMS (EI): calcd for $C_9H_6Br_2O_2$, 303.8734; found, 303.8735.

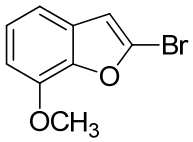


2h (Yellow solid, m.p. 94–96 °C): ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.46 (d, J = 2.0 Hz, 1H), 8.22 (dd, J_1 = 9.2 Hz, J_2 = 2.0 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 6.91 (s, 1H); ^{13}C

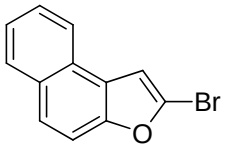
NMR (100 Hz, $CDCl_3$): δ = 158.3, 144.6, 131.9, 129.0, 120.1, 116.5, 111.3, 109.2. HRMS (EI): calcd for $C_8H_3BrNO_3$, 240.9372; found, 240.9375.



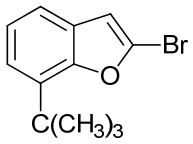
2i (Colorless oil):[1] ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.37 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 1.2 Hz, 1H), 6.88 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 6.65 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 157.8, 156.6, 126.0, 122.0, 120.1, 112.2, 108.0, 95.7, 55.7.



2j (Colorless oil):[1] ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.16 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.72 (s, 1H), 4.01 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 145.1, 144.7, 130.3, 128.1, 124.1, 112.3, 108.6, 106.5, 56.1.

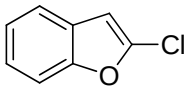


2k (Colorless oil):[1] ^{1}H NMR (400 Hz, $CDCl_3$): δ = 8.01 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.54–7.58 (m, 2H), 7.46–7.50 (t, *J* = 7. 6 Hz, 1H), 7.16 (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 153.4, 130.3, 128.7, 126.6, 126.6, 126.3, 125.1, 124.9, 124.1, 123.3, 111.7, 107.4.

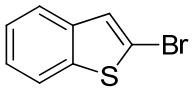


2l (Colorless oil): ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.38–7.36 (m, 1H), 7.18–7.17 (m, 2H), 6.72 (s, 1H), 1.52 (s, 9H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 154.2, 134.6, 129.3, 127.1, 123.3, 121.0, 118.0, 108.1, 34.3, 29.8. HRMS (EI): calcd for $C_{12}H_{13}BrO$,

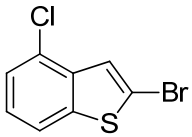
252.0151; found, 252.0150.



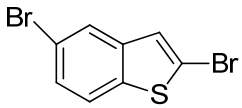
2m (Colorless oil): ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.52–7.44 (m, 2H), 7.31–7.24 (m, 2H), 6.60 (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 154.1, 141.4, 128.3, 124.2, 123.4, 120.2, 110.9, 103.1. HRMS (EI): calcd for C_8H_5ClO, 152.0028; found, 152.0029.



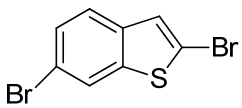
2n (Colorless oil):[1] ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.75–7.69 (m, 2H), 7.36–7.30 (m, 3H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 141.0, 139.5, 126.6, 124.7, 124.5, 122.7, 121.6, 115.4.



2o (White solid, m.p. 35–37 °C):[1] ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.60 (d, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 141.9, 137.9, 127.7, 125.1, 125.0, 124.7, 120.0, 116.6.



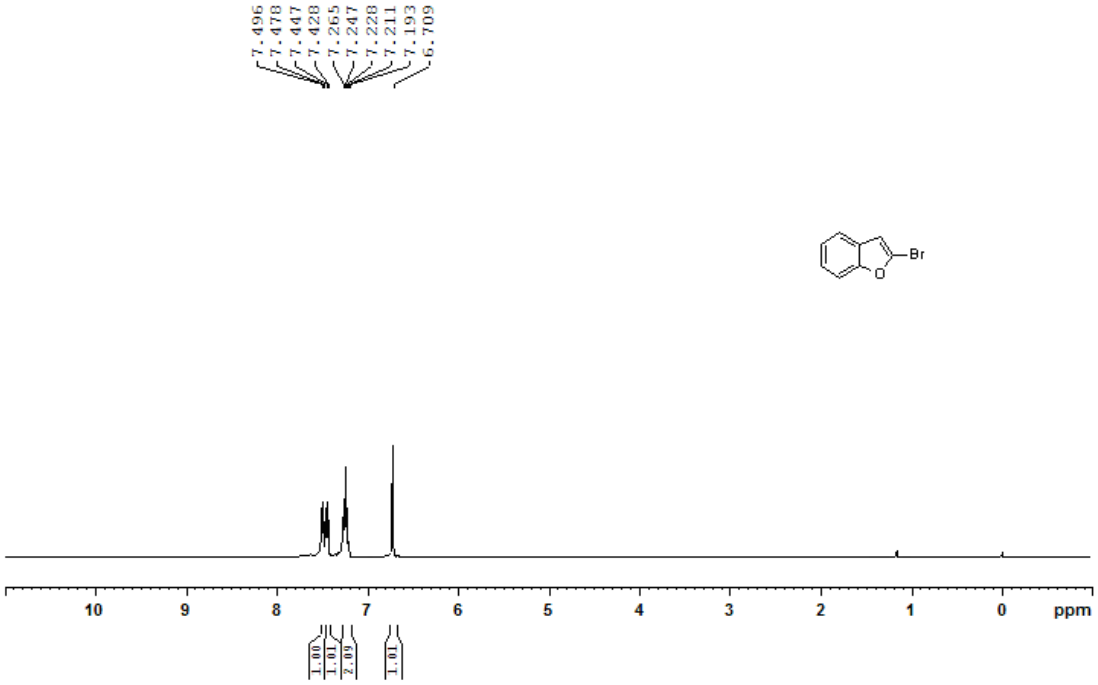
2p (White solid, m.p. 55–57 °C):[1] ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.80 (d, J = 2.0 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.41 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.23 (s, 1H); ^{13}C NMR (100 Hz, $CDCl_3$): δ = 140.9, 139.4, 127.4, 125.7, 125.2, 122.7, 118.8, 117.2.

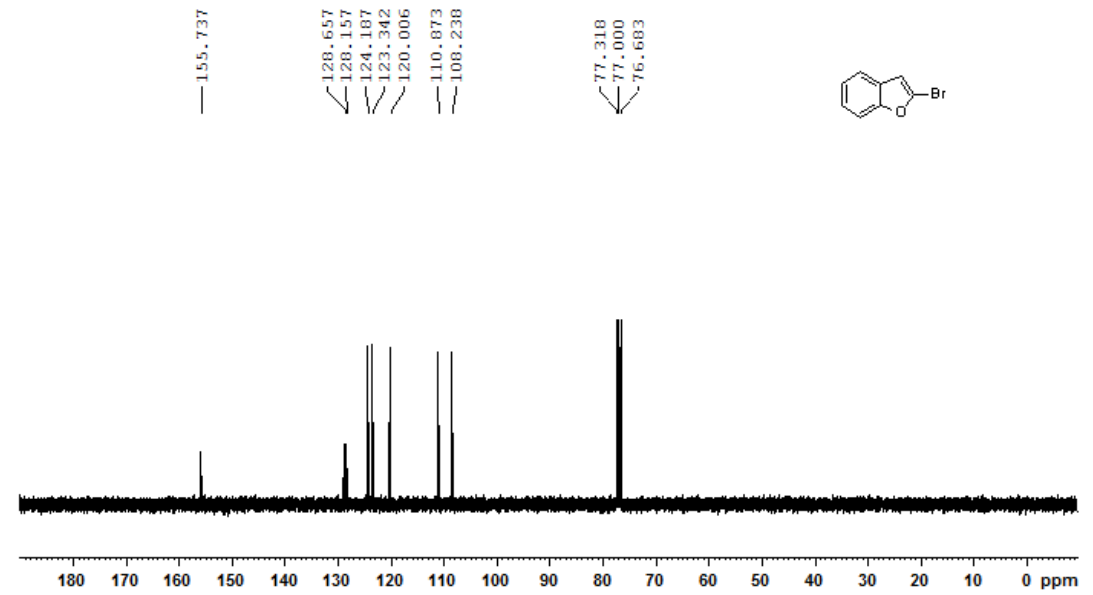


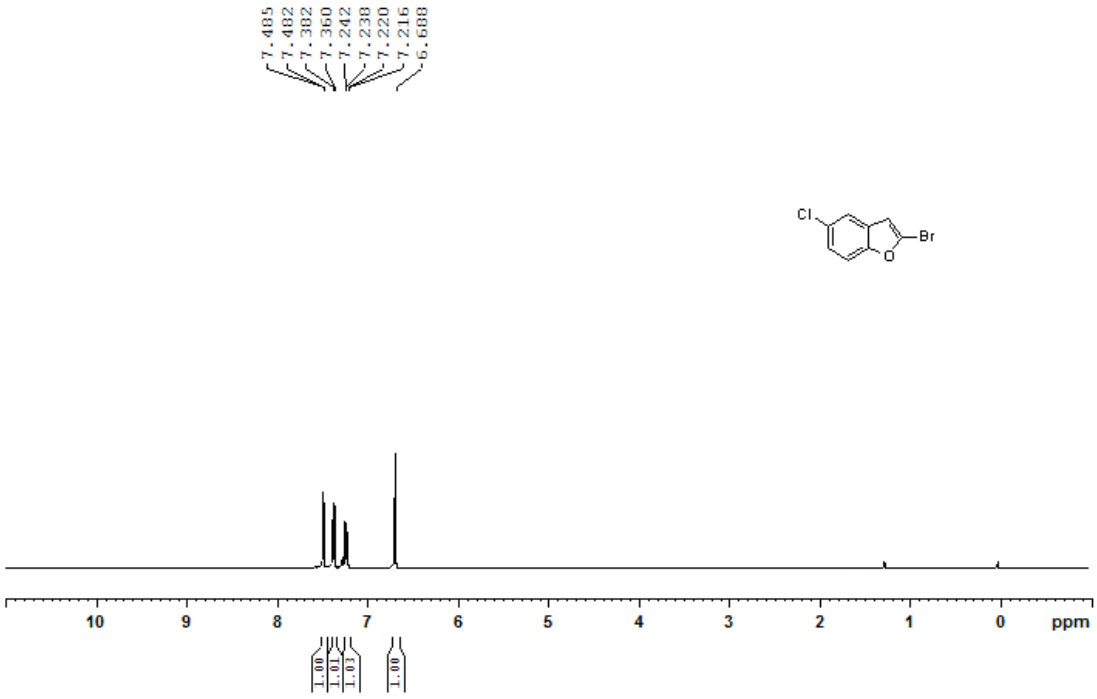
2q (White solid, m.p. 48–50 °C):[1] ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.84 (s, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.42 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.26 (s, 1H); ^{13}C NMR (100

Hz, $CDCl_3$): δ = 142.2, 138.2, 128.2, 126.2, 124.0, 123.7, 118.4, 115.9.

6. ^{1}H NMR, ^{13}C NMR spectra and HRMS data




155.737
128.657
128.157
124.187
123.342
120.006
110.873
108.238
77.318
77.000
76.683
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.485
7.482
7.382
7.360
7.242
7.238
7.220
7.216
6.688
Cl
Br
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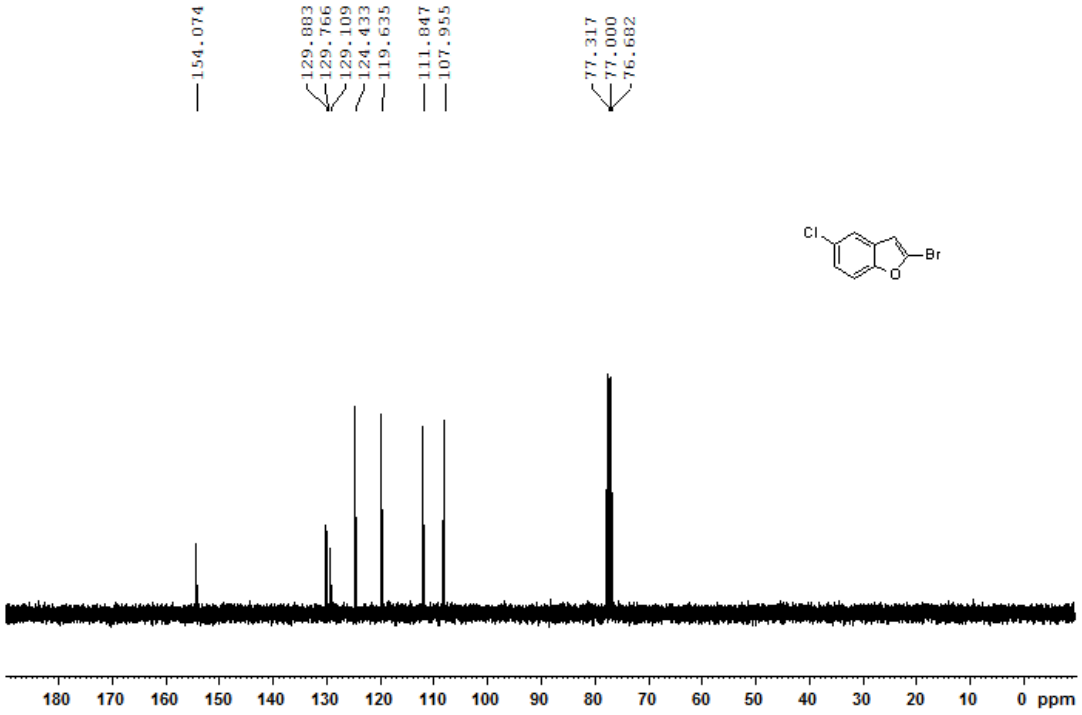
1.00
1.01
1.01
1.00


154.074
129.883
129.766
129.109
124.433
119.635
111.847
107.955
77.317
77.000
76.682
Cl
Br
O
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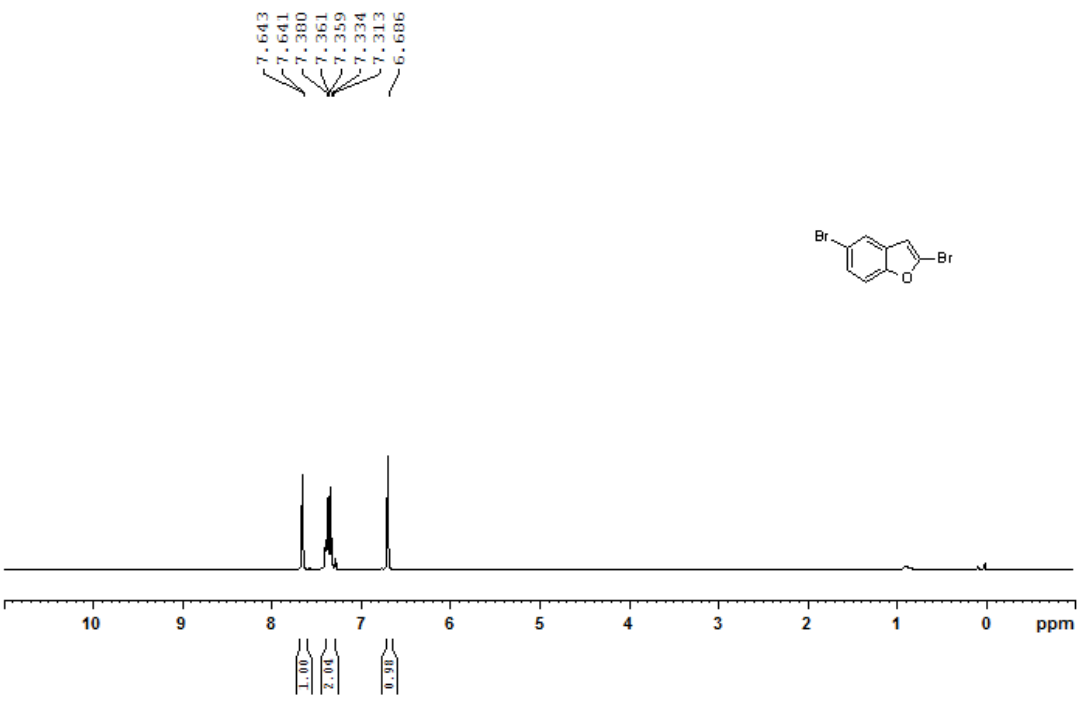
7.643
7.641
7.380
7.361
7.359
7.334
7.313
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Br
O
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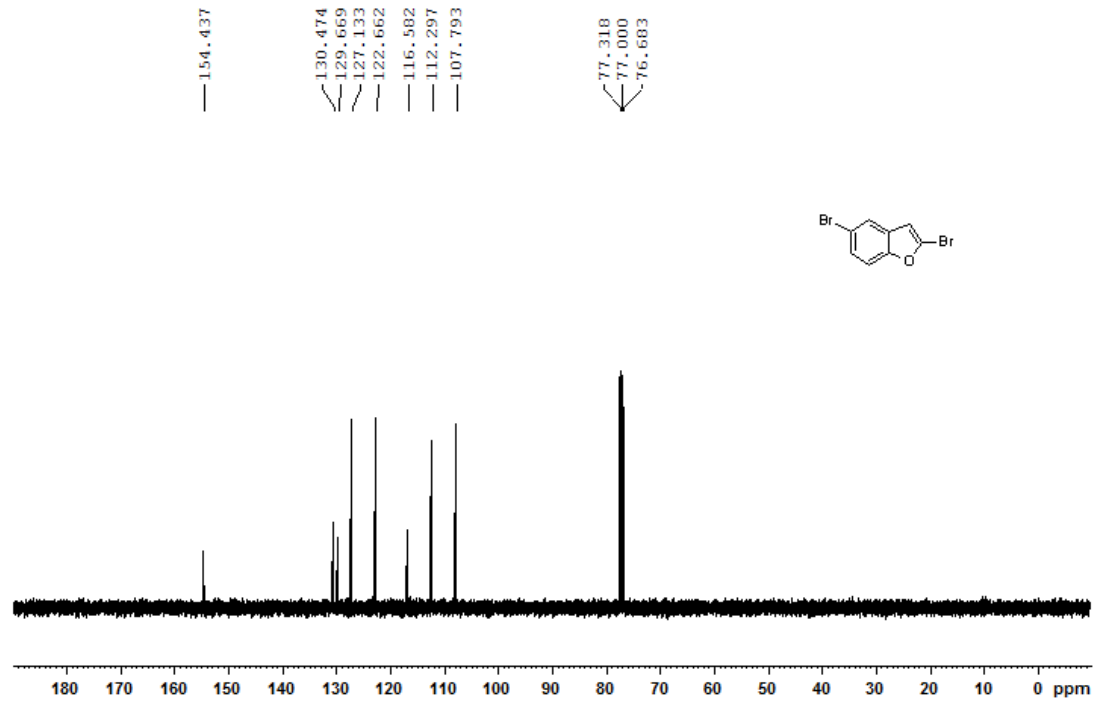
1.00
2.04
0.98


154.437
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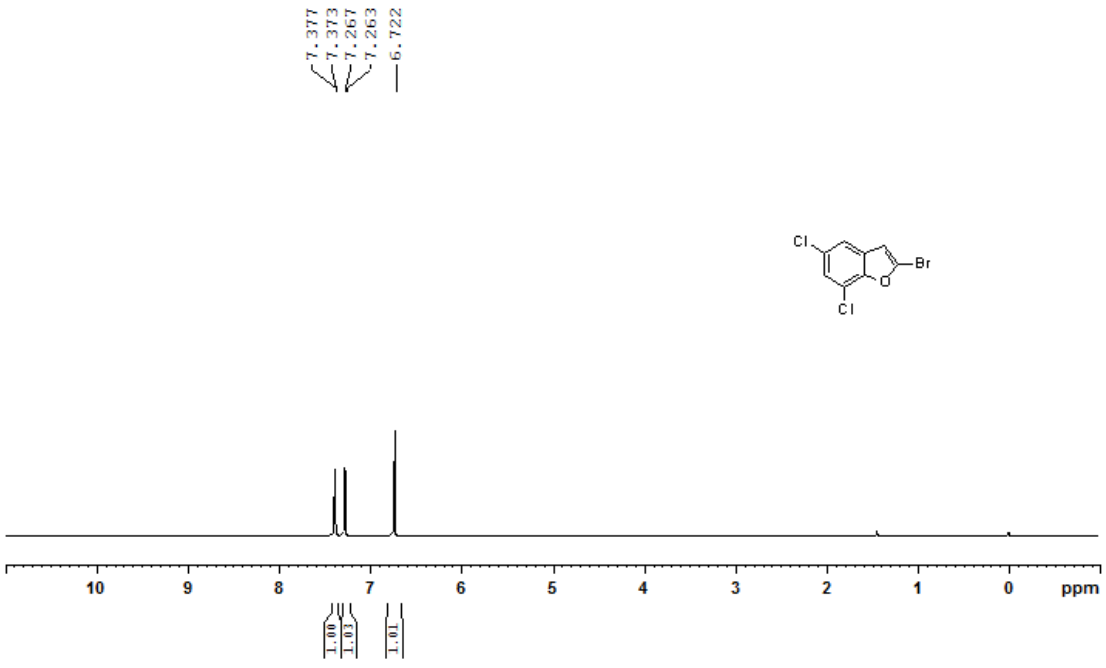
129.669
127.133
122.662
116.582
112.297
107.793
77.318
77.000
76.683
Br
Br
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.267
7.263
6.722
Cl
Br
Cl
O
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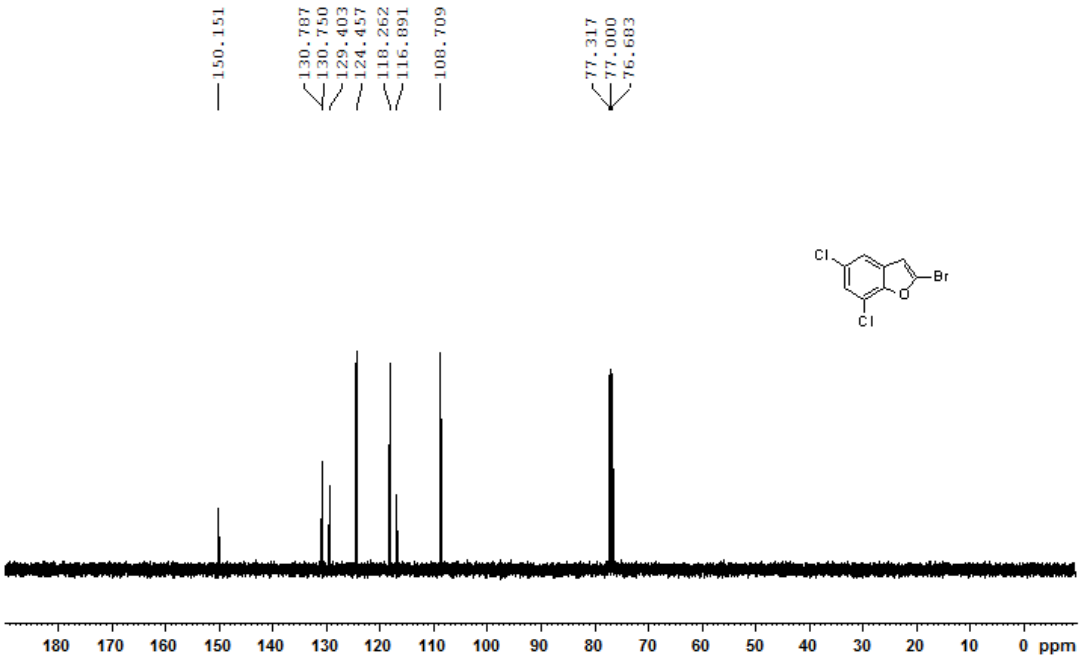
1.00
1.03
1.01


150.151
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130.750
129.403
124.457
118.262
116.891
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77.317
77.000
76.683
Cl
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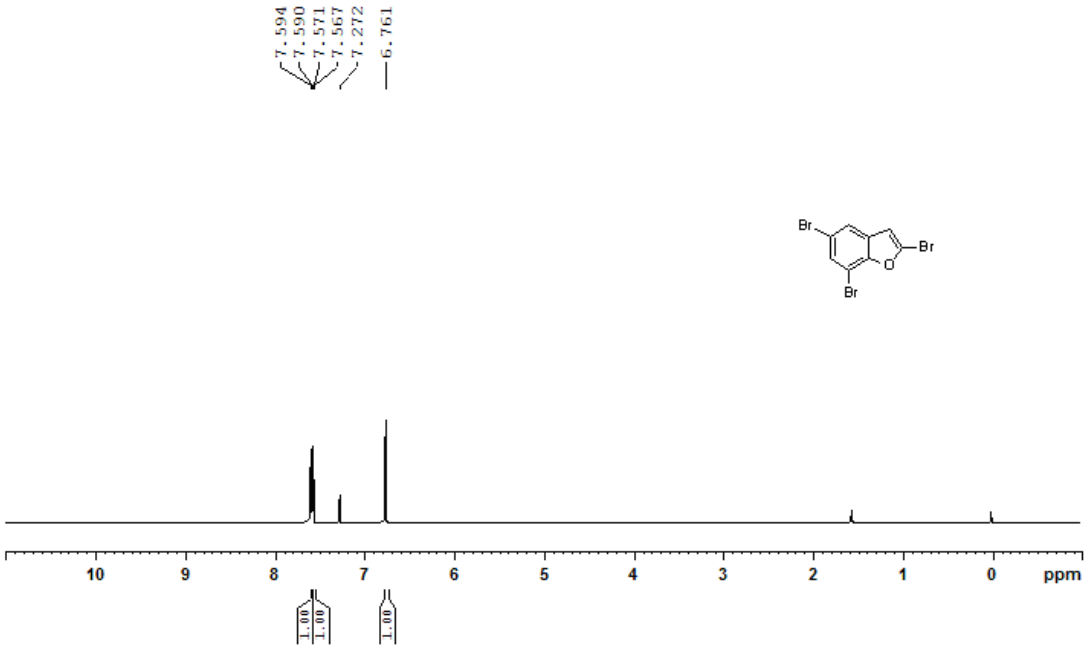
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.594
7.590
7.571
7.567
7.272
6.761
Br
Br
Br
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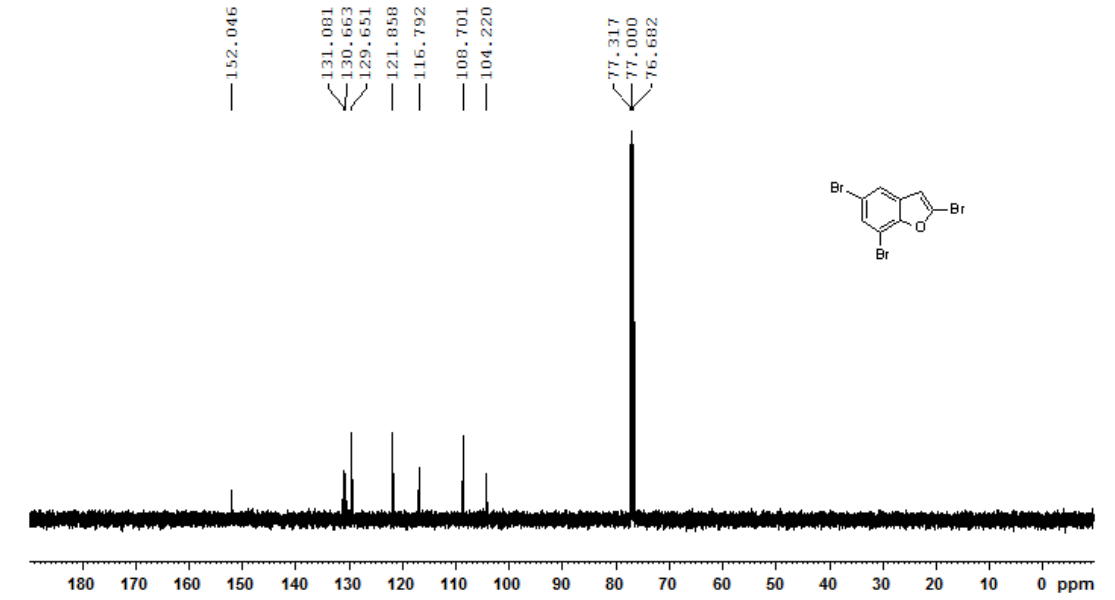
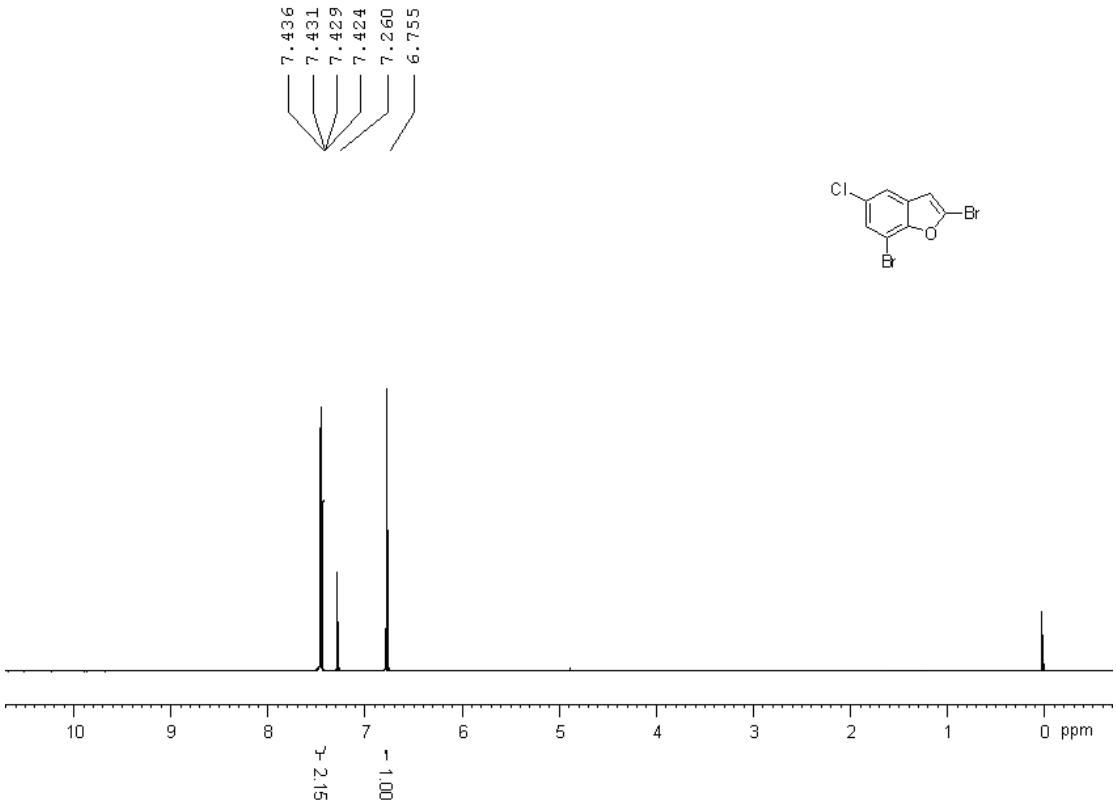
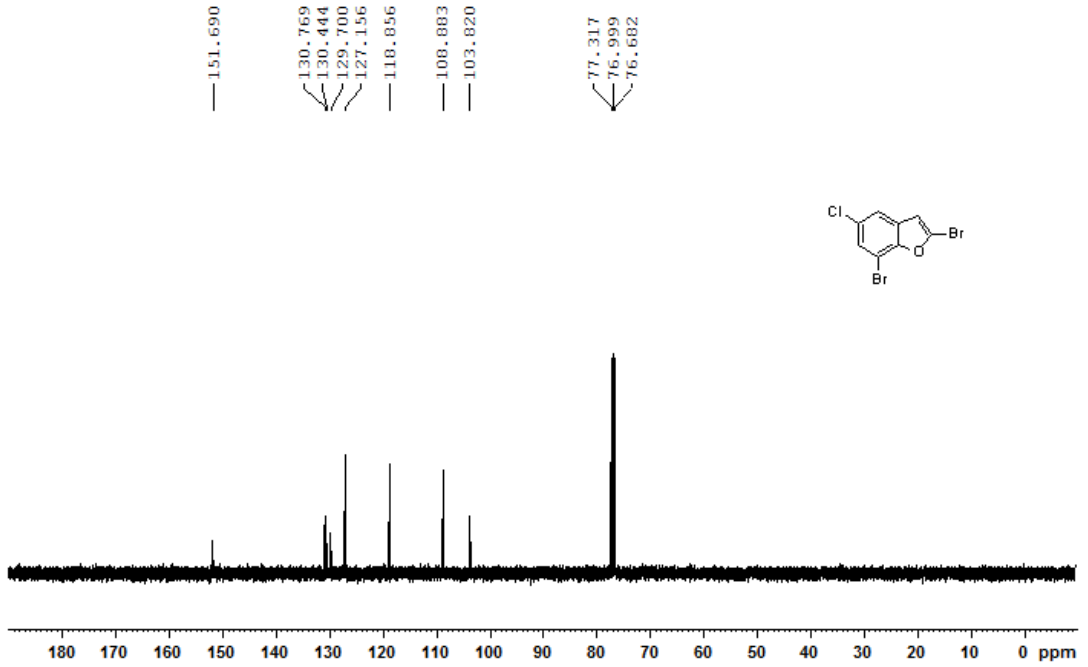
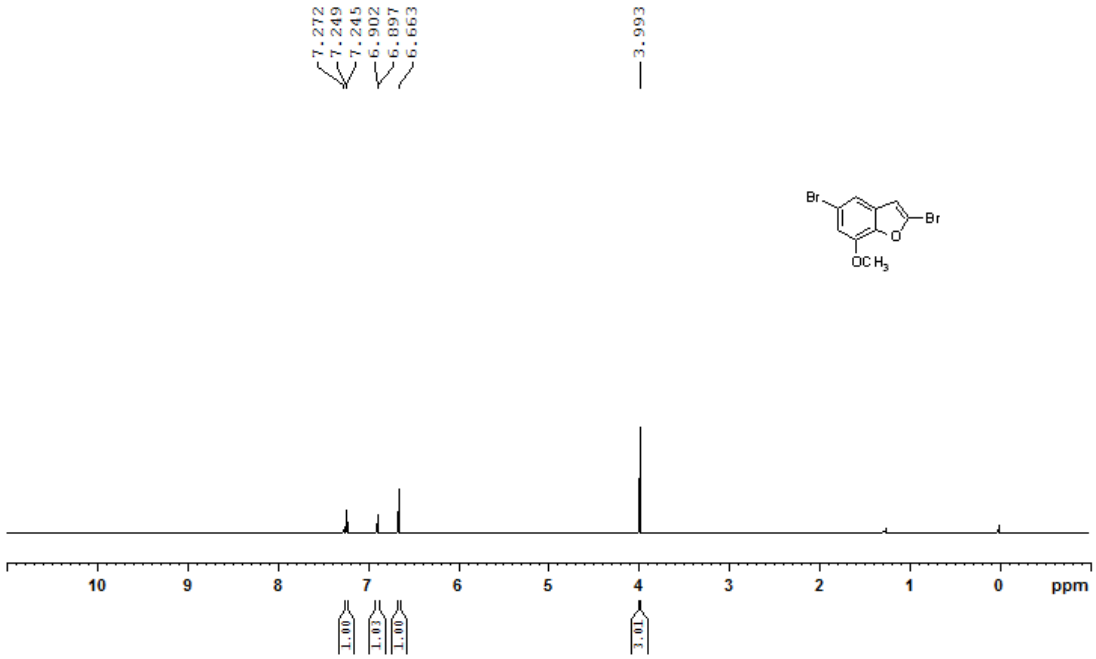
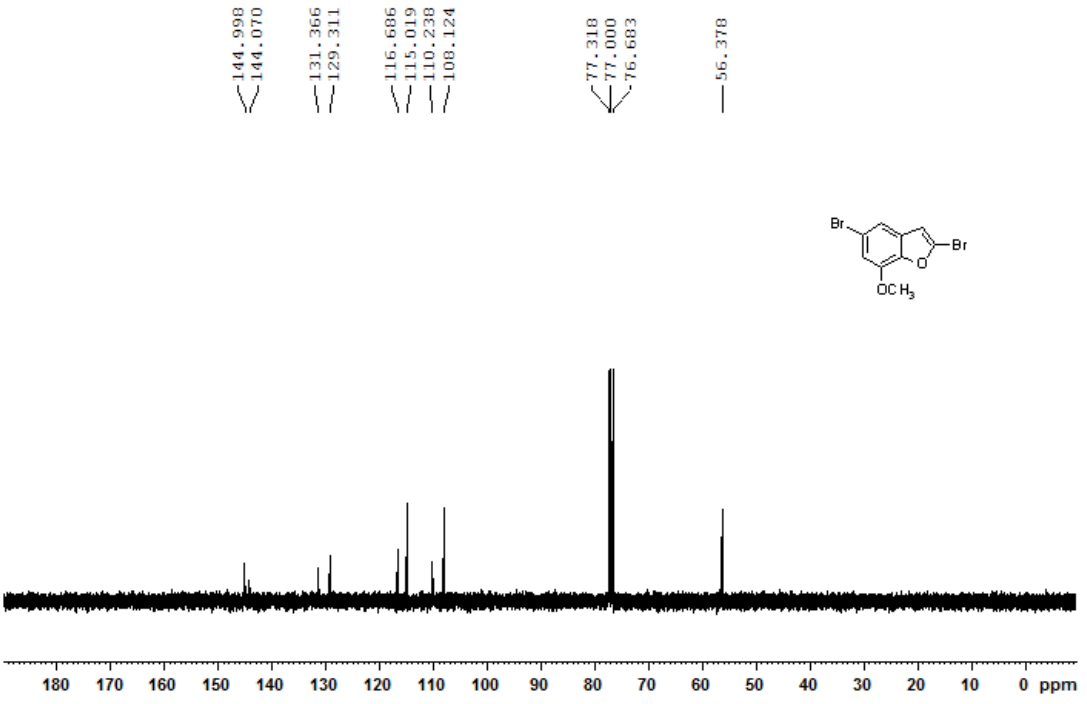
1.00
1.00
1.00

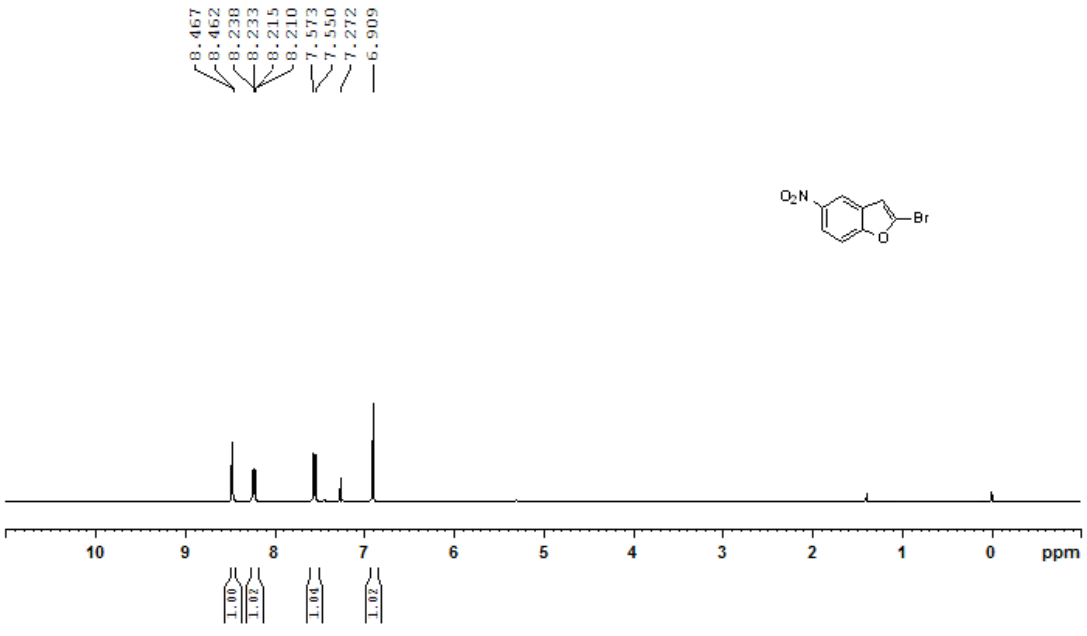

152.046
131.081
130.663
129.651
121.858
116.792
108.701
104.220
77.317
77.000
76.682
Br
Br
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

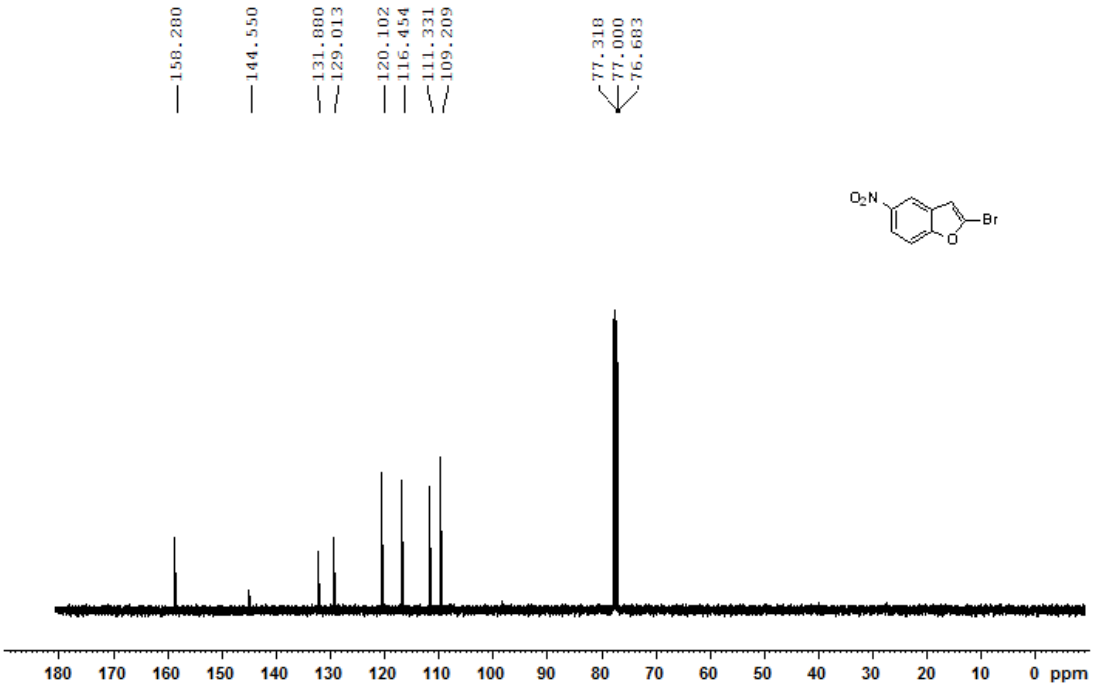

7.436
7.431
7.429
7.424
7.260
6.755
Cl
Br
Br
10 9 8 7 6 5 4 3 2 1 0 ppm
2.15
1.00

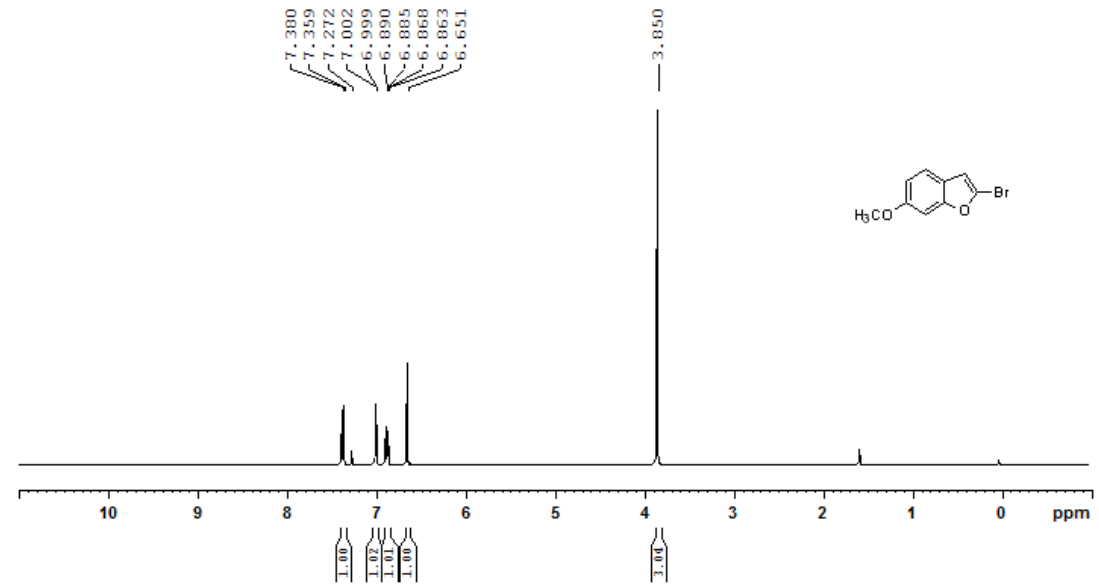

151.690
130.769
130.444
129.700
127.156
118.856
108.883
103.820
77.317
76.999
76.682
Cl
Br
O
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

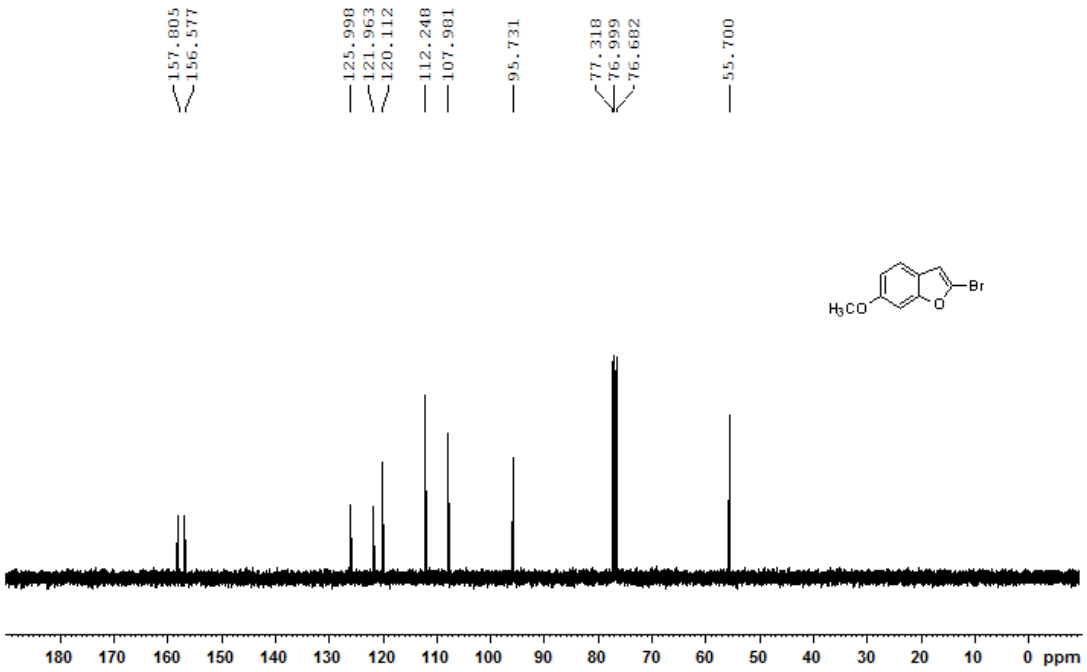

7.272
7.249
7.245
6.902
6.897
6.663
3.993
Br
Br
O
OCH3
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.03
1.00
3.01

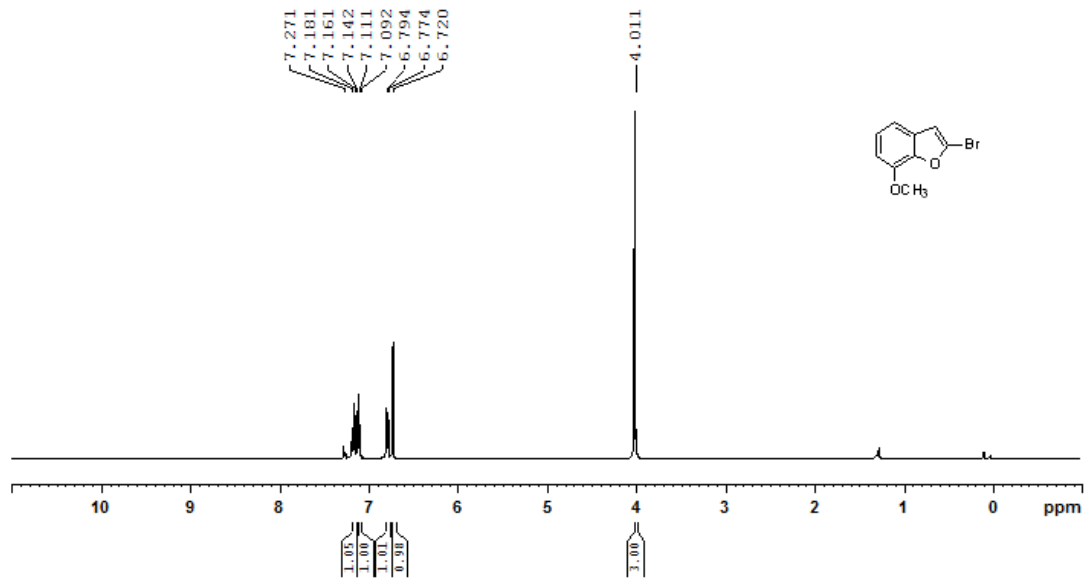

144.998
144.070
131.366
129.311
116.686
115.019
110.238
108.124
77.318
77.000
76.683
56.378
Br
Br
O
OCH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

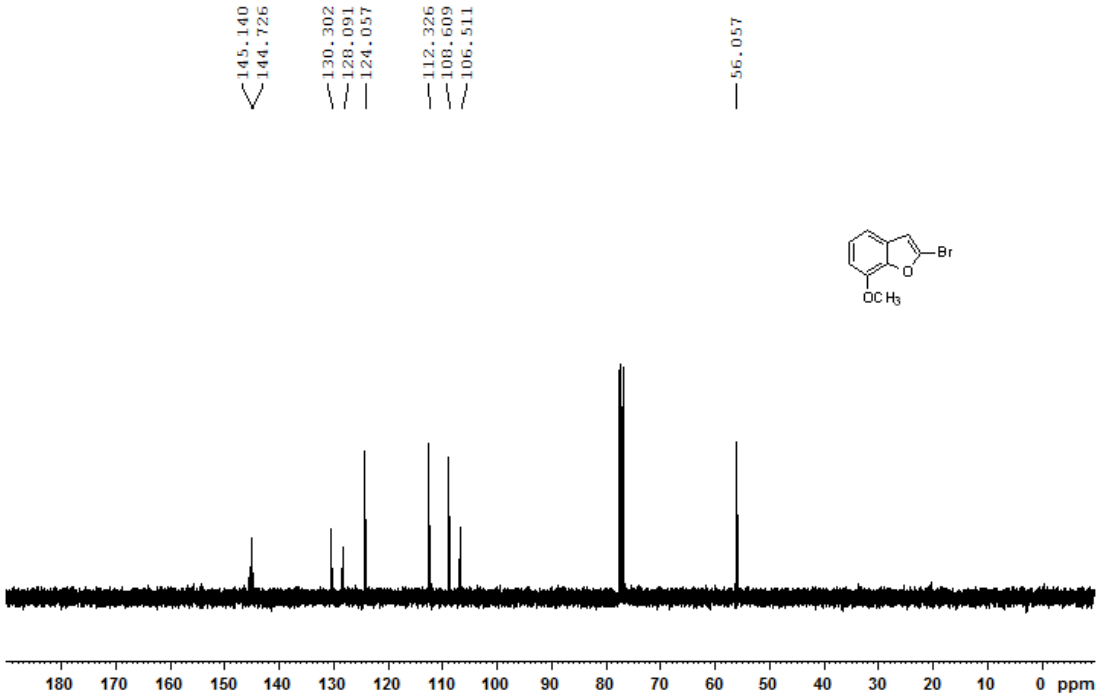

8.467
8.462
8.238
8.233
8.215
8.210
7.573
7.550
7.272
6.909
O2N
Br
O
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.02
1.04
1.02

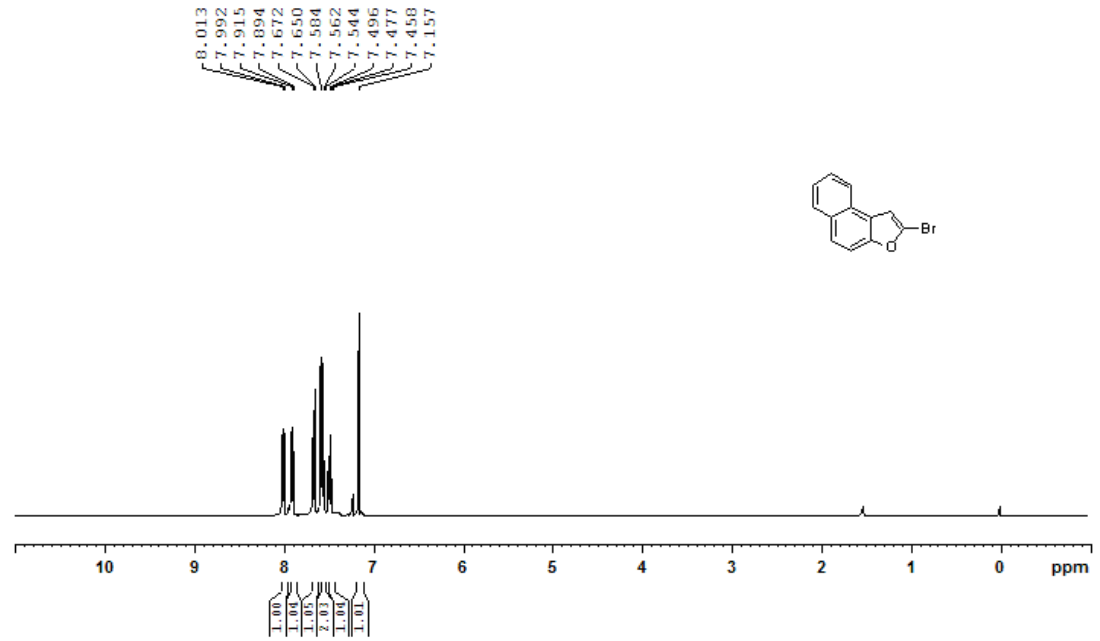

158.280
144.550
131.880
129.013
120.102
116.454
111.331
109.209
77.318
77.000
76.683
O2N
Br
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

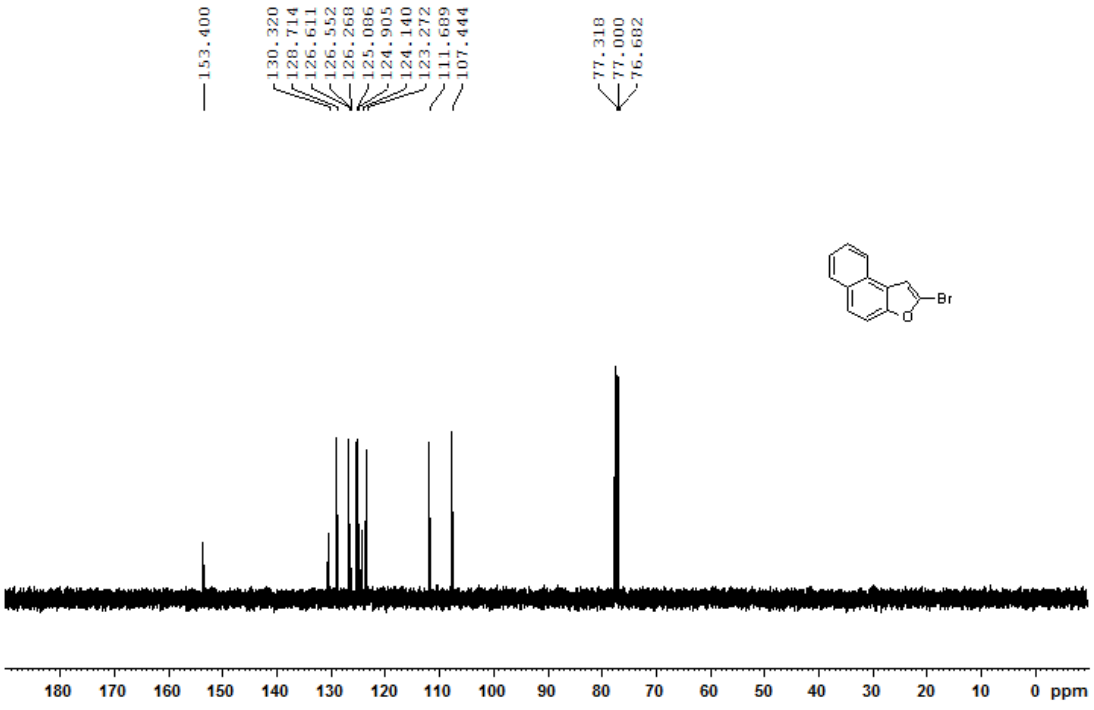

7.380
7.359
7.272
7.002
6.999
6.890
6.885
6.868
6.863
6.651
3.850
Br
H3CO
O
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.02
1.01
1.00
3.04

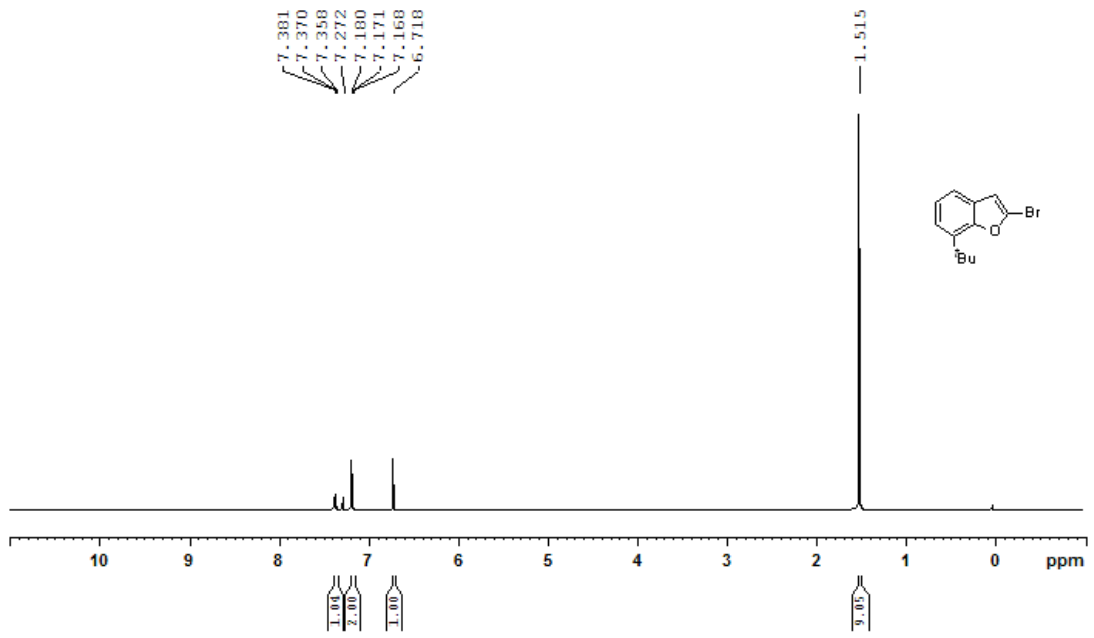

157.805
156.577
125.998
121.963
120.112
112.248
107.981
95.731
77.318
76.999
76.682
55.700
H3CO
Br
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

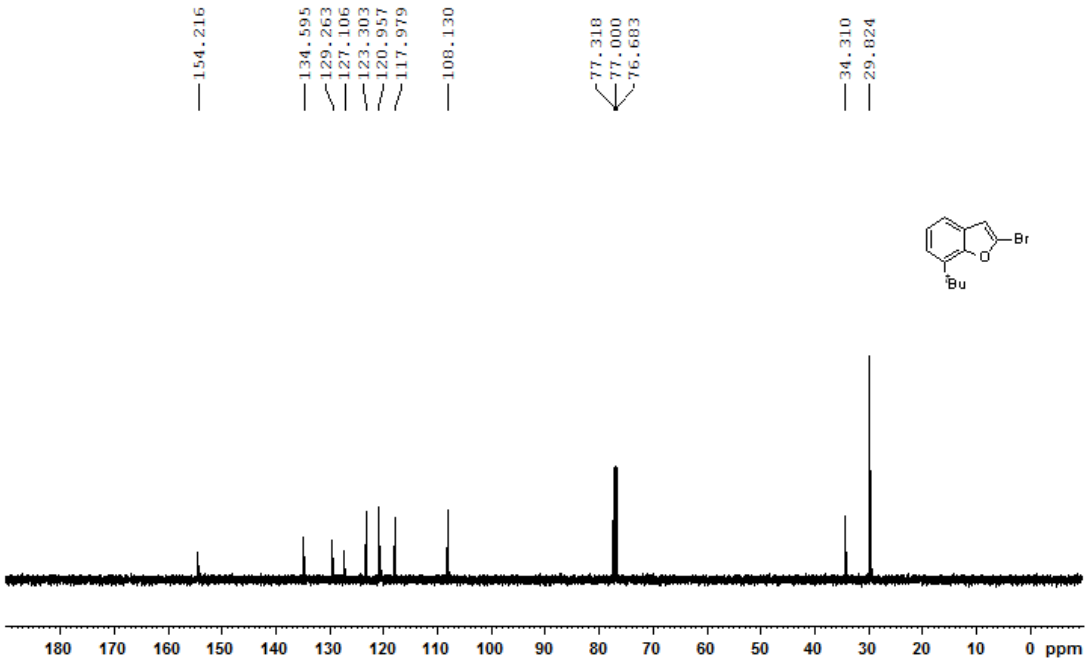

7.271
7.181
7.161
7.142
7.111
7.092
6.794
6.774
6.720
4.011
Br
O
OCH3
10 9 8 7 6 5 4 3 2 1 0 ppm
1.05
1.00
1.01
0.98
3.00

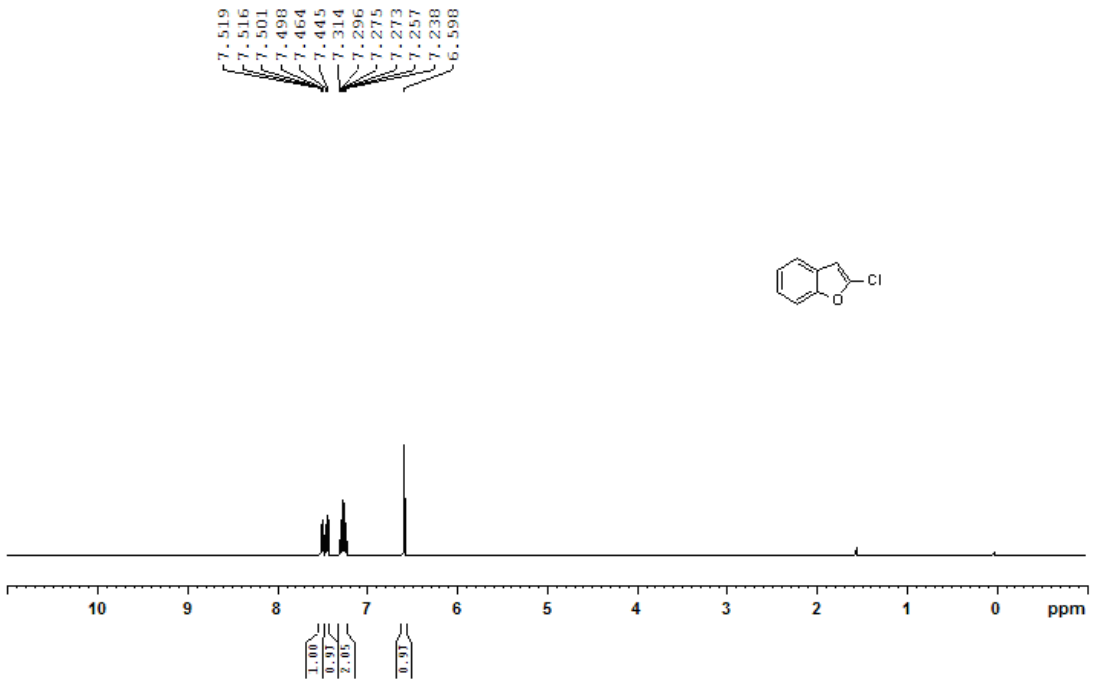

145.140
144.726
130.302
128.091
124.057
112.326
108.609
106.511
56.057
Br
O
OCH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

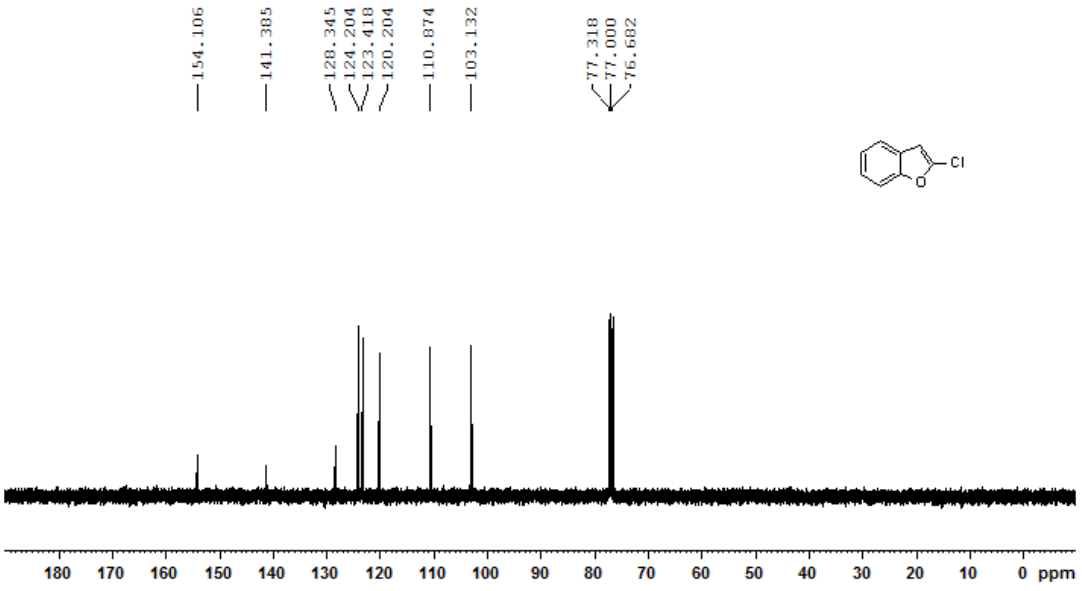

8.013
7.992
7.915
7.894
7.672
7.650
7.584
7.562
7.544
7.496
7.477
7.458
7.157
Br
O
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.04
1.05
2.03
1.04
1.01

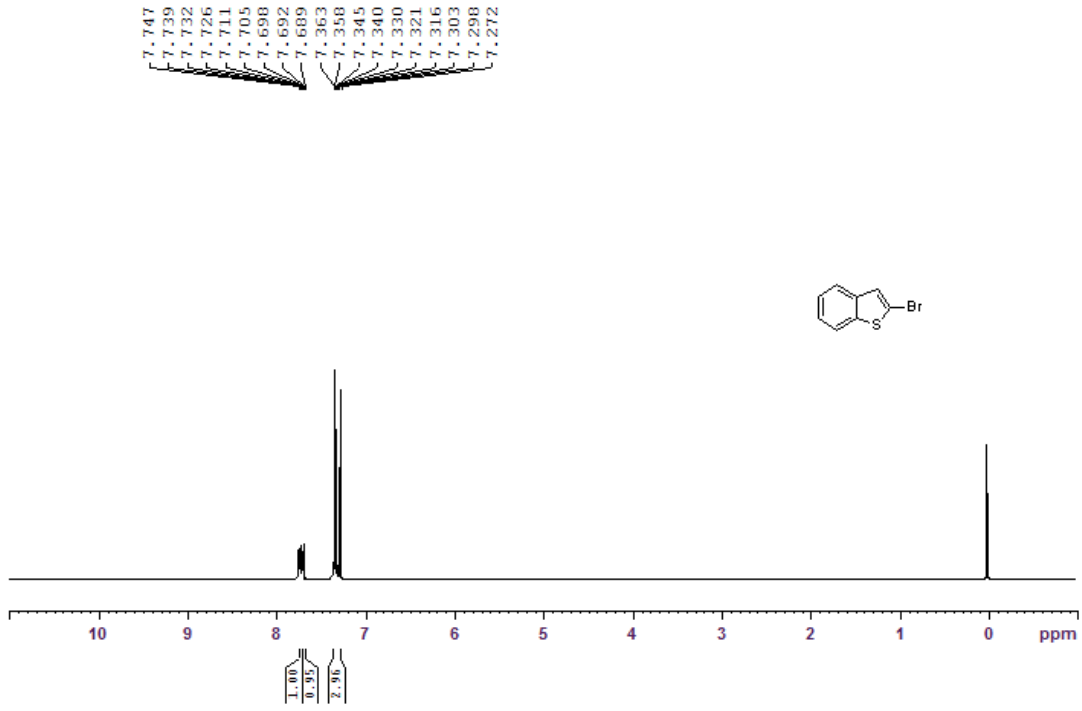

153.400
130.320
128.714
126.611
126.552
126.268
125.086
124.905
124.140
123.272
111.689
107.444
77.318
77.000
76.682
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

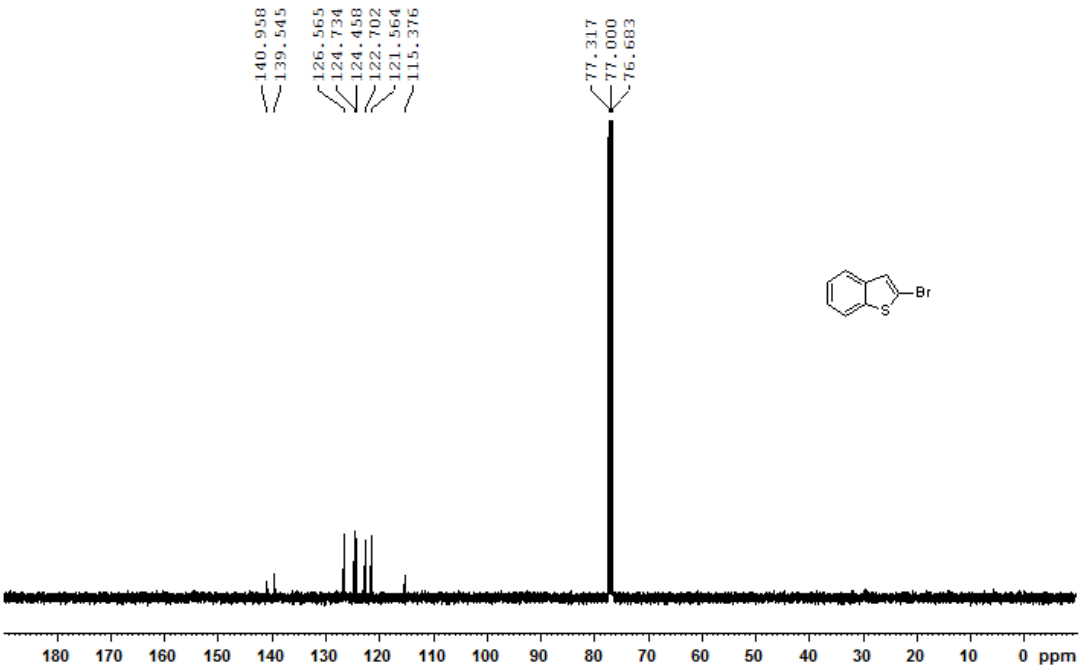

7.381
7.370
7.358
7.272
7.180
7.171
7.168
6.718
1.515
Br
tBu
10 9 8 7 6 5 4 3 2 1 0 ppm
1.04
2.00
1.00
9.06

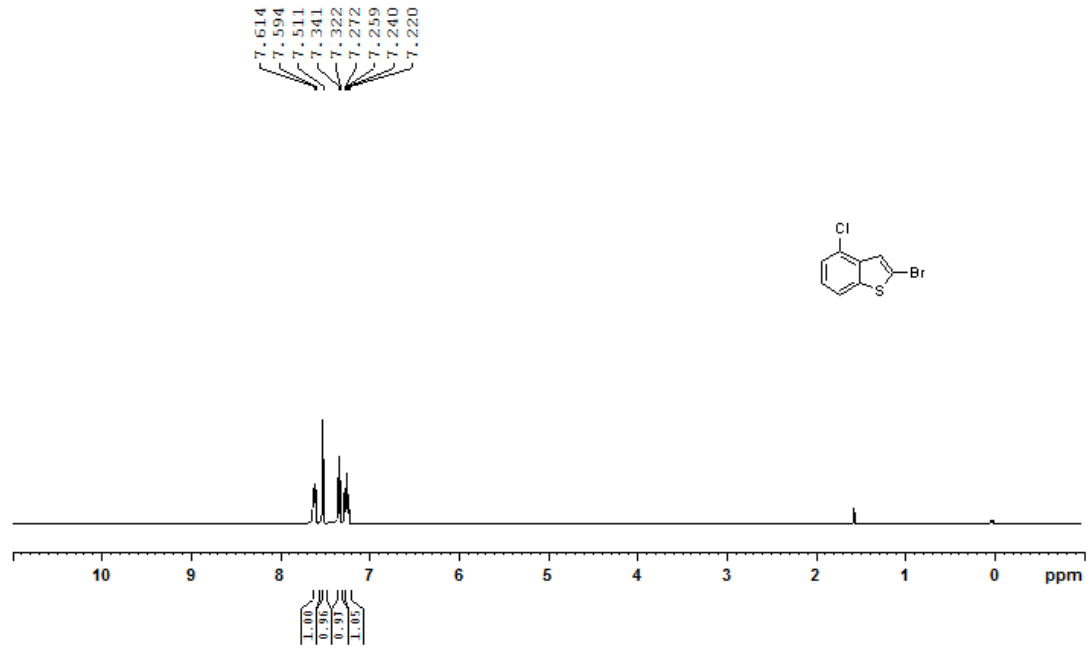

154.216
134.595
129.263
127.106
123.303
120.957
117.979
108.130
77.318
77.000
76.683
34.310
29.824
Br
tBu
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

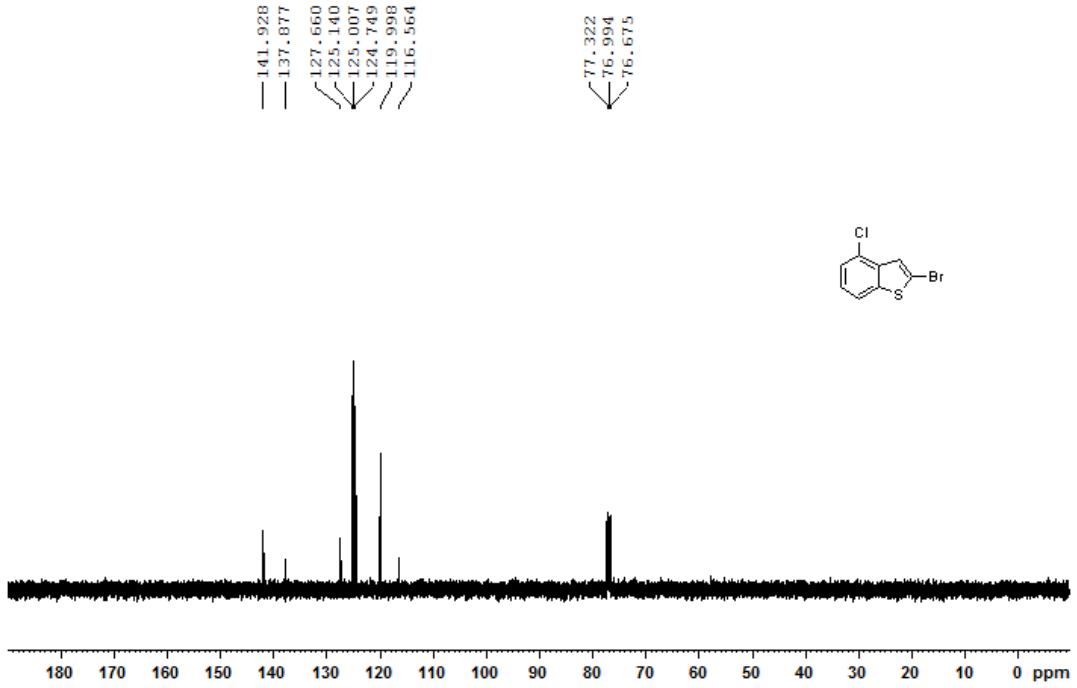

7.519
7.516
7.501
7.498
7.464
7.445
7.314
7.296
7.275
7.273
7.257
7.238
6.598
Cl
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.91
2.05
0.91

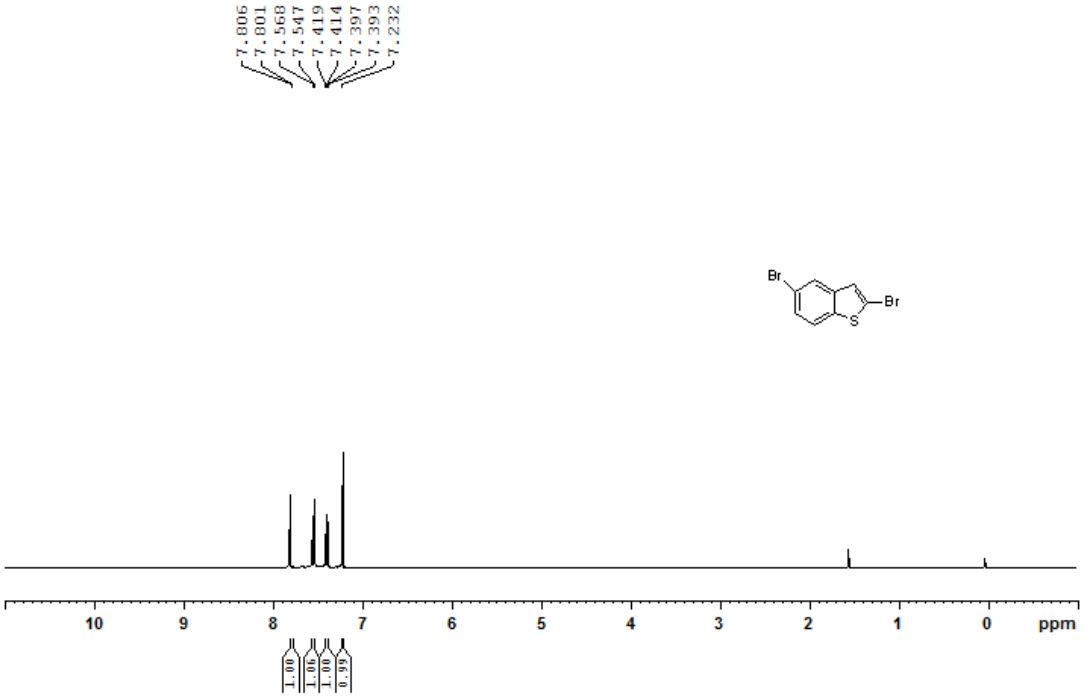

154.106
141.385
128.345
124.204
123.418
120.204
110.874
103.132
77.318
77.000
76.682
Cl
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

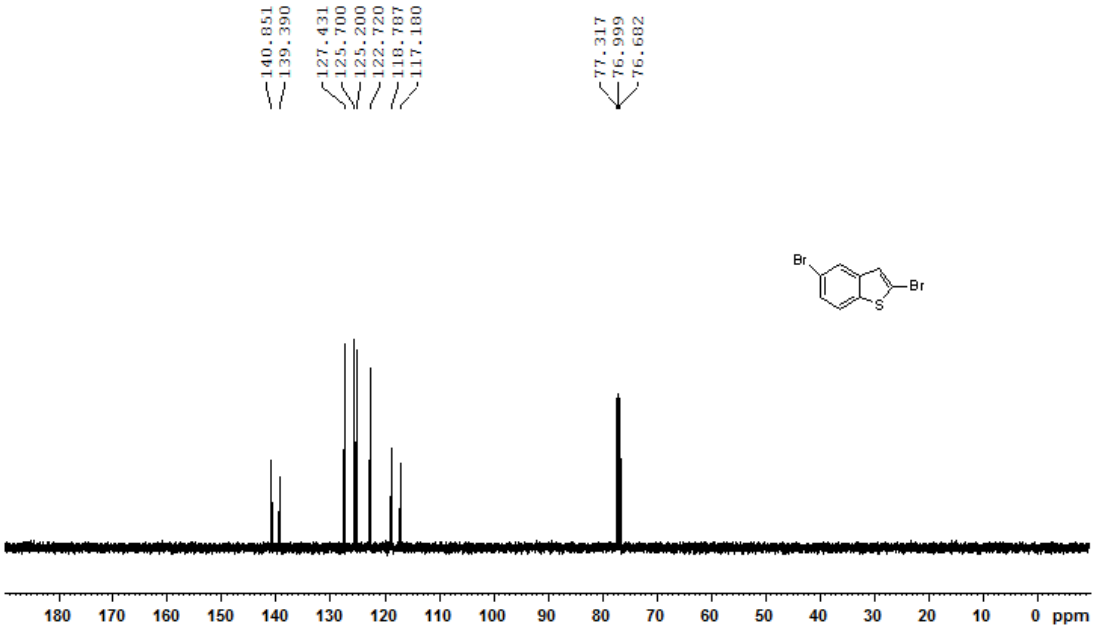

7.747
7.739
7.732
7.726
7.711
7.705
7.698
7.692
7.689
7.363
7.358
7.345
7.340
7.330
7.321
7.316
7.303
7.298
7.272
Br
S
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.95
2.96

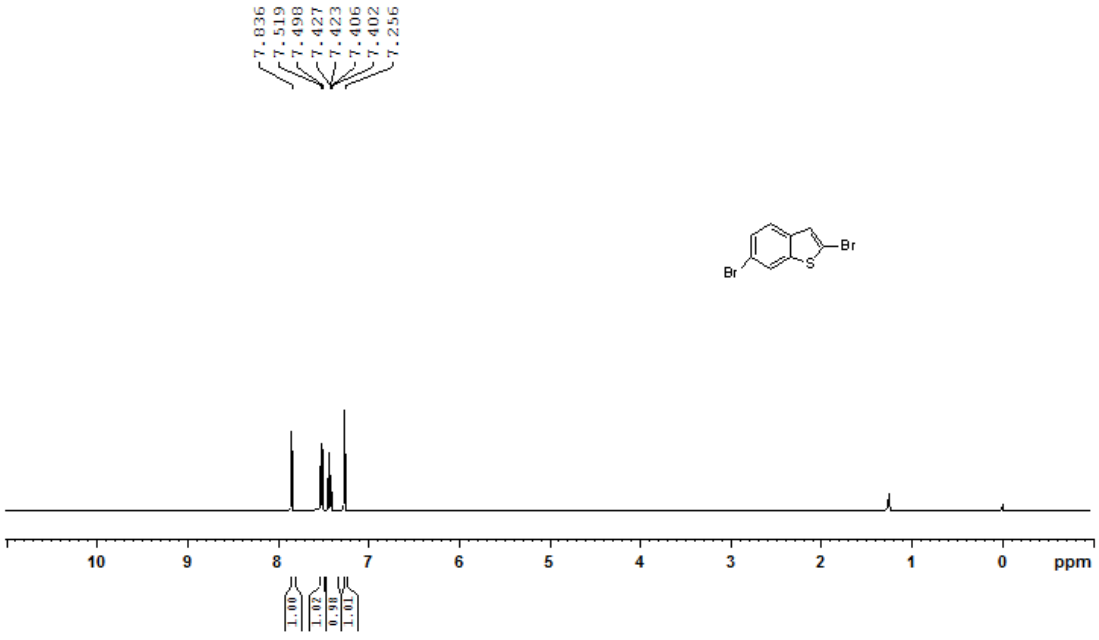

140.958
139.545
126.565
124.734
124.458
122.702
121.564
115.376
77.317
77.000
76.683
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

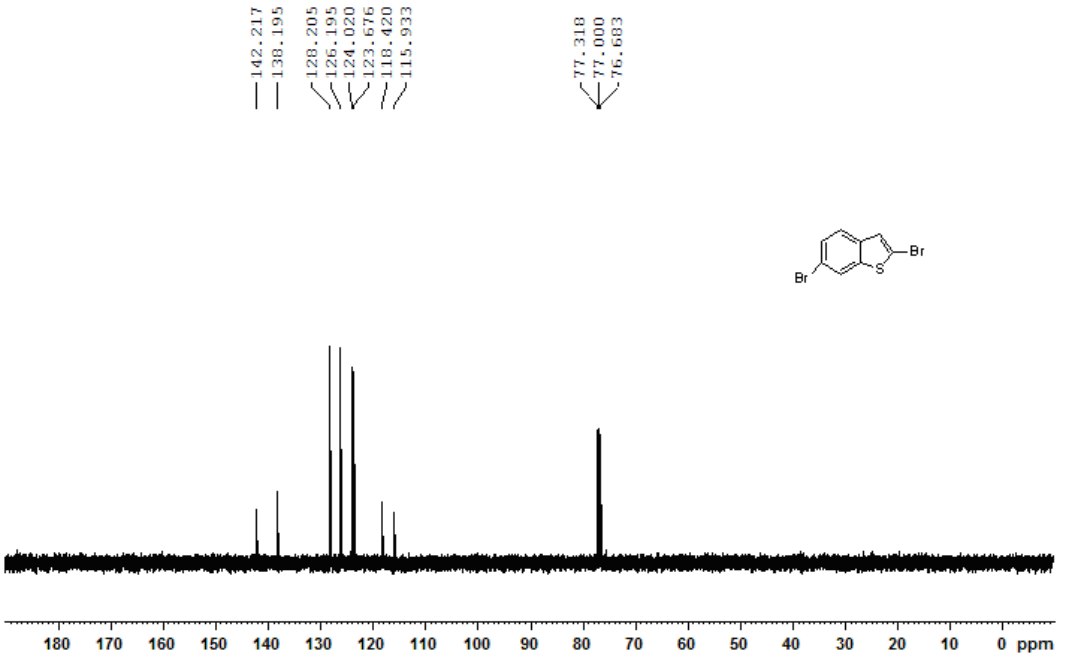

7.614
7.594
7.511
7.341
7.322
7.272
7.259
7.240
7.220
Cl
Br
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
0.96
0.93
1.05


141.928
137.877
127.660
125.140
125.007
124.749
119.998
116.564
77.322
76.994
76.675
Cl
Br
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.806
7.801
7.568
7.547
7.419
7.414
7.397
7.393
7.232
Br
Br
S
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.06
1.00
0.99


140.851
139.390
127.431
125.700
125.200
122.720
118.787
117.180
77.317
76.999
76.682
Br
Br
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.836
7.519
7.498
7.427
7.423
7.406
7.402
7.256
Br
Br
S
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.02
0.98
1.01



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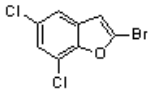
High Resolution MS Data Report

Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV




```
Card Serial Number:   GCT-P-T11-05-OS0407
Sample Serial Number:   HBSF-L05-6
Operator:  Li
Date: 2011/05/16
Elemental Composition Report
Single Mass Analysis
Tolerance = 5.0 PPM   /   DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Odd and Even Electron Ions
936 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60   H: 0-80   N: 0-4   O: 0-6   F: 0-1   Cl: 0-2   Br: 0-1
Minimum:                                  -1.5
Maximum:                    1.5       5.0       50.0
Mass       Calc. Mass       mDa       PPM       DBE        i-FIT     Formula
263.8742      263.8742       0.0       0.0       2.5        233.0     C3  H2  N3  O  F  Cl2  Br
              263.8744      -0.2      -0.8       6.0         14.0     C8  H3  O  Cl2  Br
              263.8731       1.1       4.2       6.5         50.9     C6  H  N3  Cl2  Br
```

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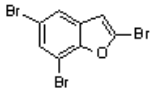
Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV




```
Card Serial Number:   GCT-P-T11-05-OS0408
Sample Serial Number:    HBSF-L05-7
Operator:  Li
Date: 2011/05/16
Elemental Composition Report
Single Mass Analysis
Tolerance = 5.0 PPM   /   DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Odd and Even Electron Ions
1891 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60   H: 0-80   N: 0-4   O: 0-6   F: 0-1   Cl: 0-2   Br: 0-3
Minimum:                                        -1.5
Maximum:                    1.5       5.0       50.0
Mass       Calc. Mass       mDa       PPM       DBE       i-FIT      Formula
351.7730      351.7732      -0.2      -0.6       2.5       116.2      C3  H2  N3  O  F  Br3
              351.7734      -0.4      -1.1       6.0         1.7      C8  H3  O  Br3
              351.7738      -0.8      -2.3      -0.5       350.3      H2  N3  O5  Cl2  Br2
              351.7739      -0.9      -2.6       1.5       107.5      C5  H6  N  Cl  Br3
              351.7721       0.9       2.6       6.5        15.8      C6  H  N3  Br3
              351.7745      -1.5      -4.3       2.0        68.1      C5  H4  O2  F  Br3
```

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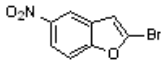
High Resolution MS Data Report

Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV




```
Card Serial Number:   GCT-P-T11-05-OS0409
Sample Serial Number:    HBSF-L05-8
Operator:  Li
Date: 2011/05/16
Elemental Composition Report
Single Mass Analysis
Tolerance = 5.0 PPM   /   DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Odd and Even Electron Ions
870 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60   H: 0-80   N: 0-4   O: 0-6   F: 0-1   Cl: 0-2   Br: 0-3
Minimum:                                        -1.5
Maximum:                    1.5       5.0       50.0
Mass       Calc. Mass       mDa       PPM       DBE       i-FIT      Formula
240.9372      240.9372       0.0       0.0       9.5        77.9      C9  N2  O  F  Cl2
              240.9373      -0.1      -0.4       3.5         0.3      C3  H3  N4  O3  F  Br
              240.9375      -0.3      -1.2       7.0        19.1      C8  H4  N  O3  Br
              240.9379      -0.7      -2.9       2.5        20.5      C5  H7  N2  O2  Cl  Br
              240.9361       1.1       4.6       7.5        11.4      C6  H2  N4  O2  Br
```

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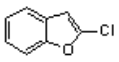
High Resolution MS Data Report

Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV




```
Card Serial Number:   GCT-P-T11-05-OS0500
Sample Serial Number:    HBSF-CW4-S3
Operator: Li
Date: 2011/06/23
Elemental Composition Report
Single Mass Analysis
Tolerance = 5.0 PPM   /   DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Odd and Even Electron Ions
160 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60   H: 0-80   N: 0-4   O: 0-6   Cl: 0-3
Minimum:                                    -1.5
Maximum:                    1.5      5.0    50.0
Mass       Calc. Mass       mDa      PPM     DBE      i-FIT      Formula
152.0028      152.0029      -0.1     -0.7     6.0      3.9       C8  H5  O  Cl
          152.0034      -0.6      -3.9      1.5      169.9      C5  H8  N  Cl2
```

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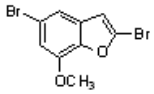
Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences
High Resolution MS Data Report

Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV




```
Card Serial Number:   GCT-P-T11-05-OS0450
Sample Serial Number:    HBSF-J08-Sample1
Operator: Li
Date: 2011/06/03
Elemental Composition Report
Single Mass Analysis
Tolerance = 1.5 mDa   /   DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Odd and Even Electron Ions
777 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60   H: 0-80   N: 0-4   O: 0-6   S: 0-1   Br: 0-2   I: 0-2
Minimum:                                    -1.5
Maximum:                    1.5      5.0    50.0
Mass       Calc. Mass       mDa      PPM     DBE      i-FIT      Formula
303.8734      303.8735      -0.1     -0.3     6.0      0.6       C9  H6  O2  Br2
          303.8721      1.3       4.3       6.5      3.2       C7  H4  N3  O  Br2
```

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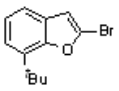
Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences

High Resolution MS Data Report

Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV




```
Card Serial Number:   GCT-P-T11-05-OS0452
Sample Serial Number:   HBSF-J08-Sample3
Operator: Li
Date: 2011/06/03
Elemental Composition Report
Single Mass Analysis
Tolerance = 5.0 PPM  /  DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Odd and Even Electron Ions
491 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60   H: 0-80   N: 0-4   O: 0-6   Cl: 0-1   Br: 0-2   I: 0-2
Minimum:                                    -1.5
Maximum:                  1.5       5.0     50.0
Mass      Calc. Mass      mDa       PPM     DBE       i-FIT     Formula
252.0151     252.0150     0.1       0.4     6.0       1.0       C12 H13 O Br
          252.0149     0.2       0.8     4.0       372.4     C7 H9 N2 O6 Cl
          252.0155     -0.4      -1.6    1.5       65.3      C9 H16 N Cl Br
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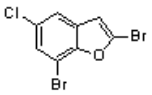
Shanghai Mass Spectrometry Center

Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences

High Resolution MS Data Report

Instrument: Waters Micromass GCT Premier Ionisation Mode: EI+ Electron Energy: 70eV




```
Card Serial Number:   GCT-P-T11-05-OS0451
Sample Serial Number:   HBSF-J08-Sample2
Operator: Li
Date: 2011/06/03
Elemental Composition Report
Single Mass Analysis
Tolerance = 1.5 mDa  /  DBE: min = -1.5, max = 50.0
Element prediction: Off
Monoisotopic Mass, Odd and Even Electron Ions
777 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60   H: 0-80   N: 0-4   O: 0-6   Cl: 0-1   Br: 0-2   I: 0-2
Minimum:                                    -1.5
Maximum:                  1.5       5.0     50.0
Mass      Calc. Mass      mDa       PPM     DBE       i-FIT     Formula
307.8237     307.8239     -0.2      -0.6    6.0       0.6       C8 H3 O Cl Br2
          307.8226     1.1       3.6     6.5       4.0       C6 H N3 Cl Br2
```

7. References

[1] S. G. Newman, V. Aureggi, C. S. Bryan, M. Lautens, *Chem. Commun.* **2009**, 5236–5238.