Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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A tandem elimination–cyclization–desulfitative arylation reaction of 2-(*gem*-dibromovinyl)phenols(thiophnols) with sodium arylsulfinates

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Table of Contents for Supporting Information

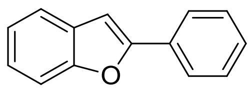
1. General considerations

All the tandem reactions of 2-(*gem*-dibromovinyl)phenols(thiophnols) with sodium arylsulfinates were carried out under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 400 MHz NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument. The solvents and general chemicals were purchased from commercial suppliers and used without further purification. All the *gem*-dibromovinyl substrates were synthesized according to the reported procedures in the literature (Newman, S. G.; Aureggi, V.; Bryan, C. S.; Lautens, M. *Chem. Commun.* **2009**, 5236–5238).

2. Typical procedure for the tandem elimination–cyclization –desulfitative arylation reaction

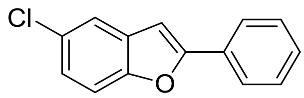
A sealable reaction tube equipped with a magnetic stirrer bar was charged with *gem*-dibromovinyl substrate (0. 50 mmol), TBAF (1.0 mmol) and DMF (3.0 mL). The reaction mixture was stirred for 4 h at room temperature, than sodium arylsulfinate (1.0 mmol), $PdCl_2$ (0. 050 mmol), $Cu(OAc)_2$ (1.0 mmol), NEt_3 (1.0 mmol) were added to the reaction system. The rubber septum was then replaced by a Teflon-coated screw cap, and the reaction vessel placed in an oil bath at 110 °C. After stirring the mixture at this temperature for 12 h, it was cooled to room temperature and diluted with ethyl acetate, washed with water and brine, dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (eluant: petroleum ether) to afford the corresponding product.

3. Characterization data for all products



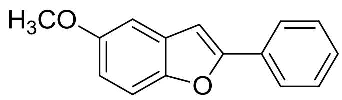
3a:[1] mp 120–121 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.49–7.46 (m, 2H), 7.40–7.36 (m, 1H), 7.33–7.24 (m, 2H), 7.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 154.9, 130.5, 129.2, 128.8, 128.5, 124.9, 124.2, 122.9, 120.9, 111.2, 101.3.



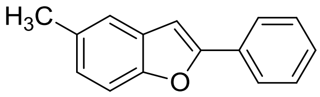
3b:[1] mp 155–156 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.81 (m, 2H), 7.51–7.50 (m, 1H), 7.45–7.33 (m, 4H), 7.22–7.19 (m, 1H), 6.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 153.2, 130.6, 129.9, 129.0, 128.8, 128.5, 125.0, 124.4, 120.4, 112.1, 100.8.



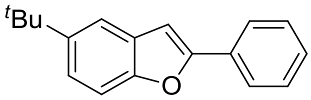
3c:[1] mp 131–132 °C.

^{1}H NMR (400MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.0 Hz, 2H), 7.48–7.42 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 2.8 Hz, 1H), 6.98 (s, 1H), 6.92 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 156.1, 150.0, 130.6, 129.8, 128.8, 128.5, 124.9, 113.0, 111.6, 103.3, 101.5, 55.9.



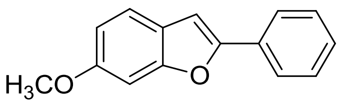
3d:[1] mp 129–130 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.0 Hz, 2H), 7.48–7.34 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.97 (s, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 153.3, 132.3, 130.6, 129.3, 128.8, 128.4, 125.5, 124.9, 120.7, 110.7, 101.1, 21.4.



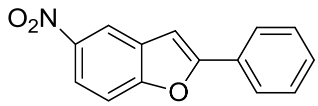
3e:[1] mp 103–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.91 (m, 2H), 7.65 (s, 1H), 7.52–7.48 (m, 3H), 7.43–7.39 (m, 2H), 7.05 (s, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 153.2, 146.0, 130.7, 128.9, 128.7, 128.3, 124.8, 122.2, 117.1, 110.4, 101.5, 34.7, 31.8.



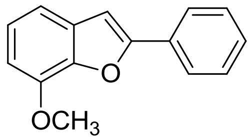
3f:[1] mp 78–79 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 2H), 7.47–7.43 (m, 3H), 7.36–7.32 (m, 1H), 7.00 (d, *J* = 1.6 Hz, 1H), 6.97 (s, 1H), 6.90 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 155.9, 155.1, 130.7, 128.7, 128.0, 124.4, 122.6, 121.0, 112.0, 101.1, 95.9, 55.7.



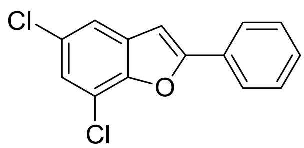
3g:[1] mp 151–152 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 2.4 Hz, 1H), 8.22 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.90–7.88 (m, 2H), 7.60 (d, *J* = 9.2 Hz, 1H), 7.52–7.48 (m, 2H), 7.46–7.42 (m, 1H), 7.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 157.6, 144.3, 129.7, 129.6, 129.2, 129.0, 125.3, 120.1, 117.2, 111.4, 101.6.



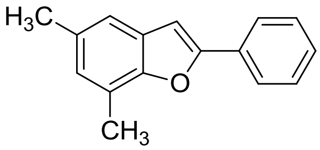
3h:[1] mp 78–79 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.92 (m, 2H), 7.49–7.45 (m, 2H), 7.39–7.36 (m, 1H), 7.23–7.16 (m, 2H), 7.04 (s, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1, 145.4, 144.2, 131.0, 130.4, 128.7, 128.6, 125.1, 123.6, 113.4, 106.7, 101.7, 56.2.



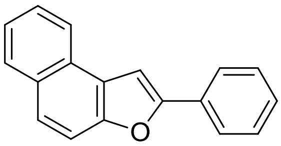
3i:[2] mp 128–129 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.0 Hz, 2H), 7.50–7.40 (m, 4H), 7.28 (d, *J* = 1.6 Hz, 1H), 6.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 149.2, 131.5, 129.4, 129.3, 128.9, 128.7, 125.2, 124.3, 119.0, 117.1, 101.2.



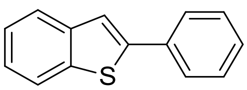
3j:[1] mp 60–61 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.83 (m, 2H), 7.43–7.39 (m, 2H), 7.33–7.29 (m, 1H), 7.16 (s, 1H), 6.90–6.88 (m, 2H), 2.52 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.6, 152.4, 132.3, 130.8, 128.8, 128.7, 128.2, 126.6, 124.8, 120.8, 118.1, 101.3, 21.3, 15.0.



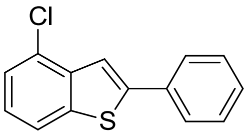
3k:[1] mp 142–143 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.0 Hz, 1H), 7.98–7.94 (m, 3H), 7.76–7.70 (m, 2H), 7.64–7.60 (m, 1H), 7.55 (s, 1H), 7.53–7.48 (m, 3H), 7.39–7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 152.4, 130.7, 130.4, 128.9, 128.8, 128.3, 127.6, 126.3, 125.2, 124.7, 124.6, 124.5, 123.5, 112.3, 100.5.



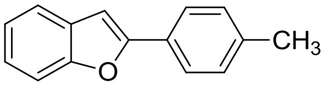
3l:[1] mp 174–176 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.85 (m, 1H), 7.81–7.79 (m, 1H), 7.76–7.74 (m, 2H), 7.58 (s, 1H), 7.47–7.44 (m, 2H), 7.40–7.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 140.7, 139.5, 134.3, 128.9, 128.2, 126.5, 124.5, 124.3, 123.5, 122.2, 119.4.



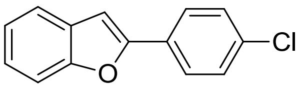
3m:[1] mp 111–112 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.71 (m, 4H), 7.48–7.45 (m, 2H), 7.41–7.37 (m, 2H), 7.27–7.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 140.4, 138.9, 133.7, 129.0, 128.6, 128.4, 126.5, 124.8, 124.4, 120.7, 117.6.



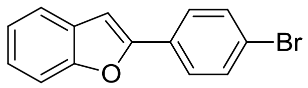
4a:[3] mp 126–127 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 2H), 7.61–7.53 (m, 2H), 7.32–7.23 (m, 4H), 6.99 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 154.8, 138.6, 129.5, 129.4, 127.8, 124.9, 124.0, 122.9, 120.7, 111.1, 100.6, 21.4.



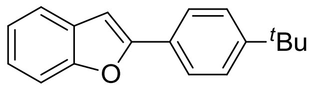
4b:[4] mp 148–149 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.35–7.25 (m, 2H), 7.01 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 154.8, 134.3, 129.1, 129.0, 129.0, 126.1, 124.6, 123.1, 121.0, 111.2, 101.8.



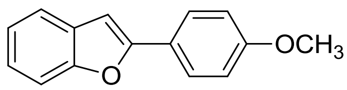
4c:[5] mp 148–149 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.0 Hz, 2H), 7.61–7.53 (m, 4H), 7.34–7.24 (m, 2H), 7.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 154.7, 131.9, 129.4, 129.0, 126.3, 124.6, 123.1, 122.5, 121.0, 111.2, 101.8.



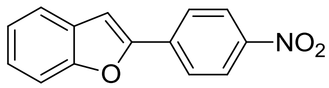
4d:[6] mp 128–129 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.34–7.25 (m, 2H), 7.02 (s, 1H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 154.9, 151.8, 129.4, 127.8, 125.8, 124.8, 124.0, 122.9, 120.8, 111.2, 100.7, 34.8, 31.3.



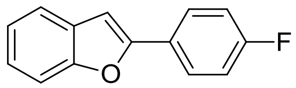
4e:[3] mp 149–150 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.8 Hz, 2H), 7.58–7.57 (m, 1H), 7.53–7.51 (m, 1H), 7.29–7.22 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.91 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 156.1, 154.7, 129.5, 126.4, 123.7, 123.4, 122.8, 120.6, 114.3, 111.0, 99.7, 55.4.



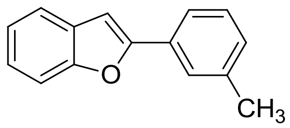
4f:[7] mp 183–184 °C.

[1]H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.66–7.64 (m, 1H), 7.58–7.56 (m, 1H), 7.40–7.36 (m, 1H), 7.31–7.27 (m, 1H), 7.24 (s, 1H); [13]C NMR (100 MHz, $CDCl_3$): δ = 155.4, 153.2, 147.2, 136.3, 128.6, 125.8, 125.2, 124.3, 123.5, 121.6, 111.5, 105.1.



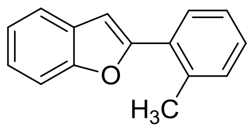
4g:[3] mp 119–120 °C.

[1]H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.84 (m, 2H), 7.61–7.60 (m, 1H), 7.56–7.54 (m, 1H), 7.34–7.27 (m, 2H), 7.19–7.14 (m, 2H), 6.97 (s, 1H); [13]C NMR (100 MHz, $CDCl_3$): δ = 162.8 (d, *J* = 247.2 Hz), 155.0, 154.8, 129.1, 126.7 (d, *J* = 8.1 Hz), 124.3, 123.0, 120.9, 115.8 (d, *J* = 21.8 Hz), 111.1, 101.0, 100.9.



4h:[8] mp 77–78 °C.

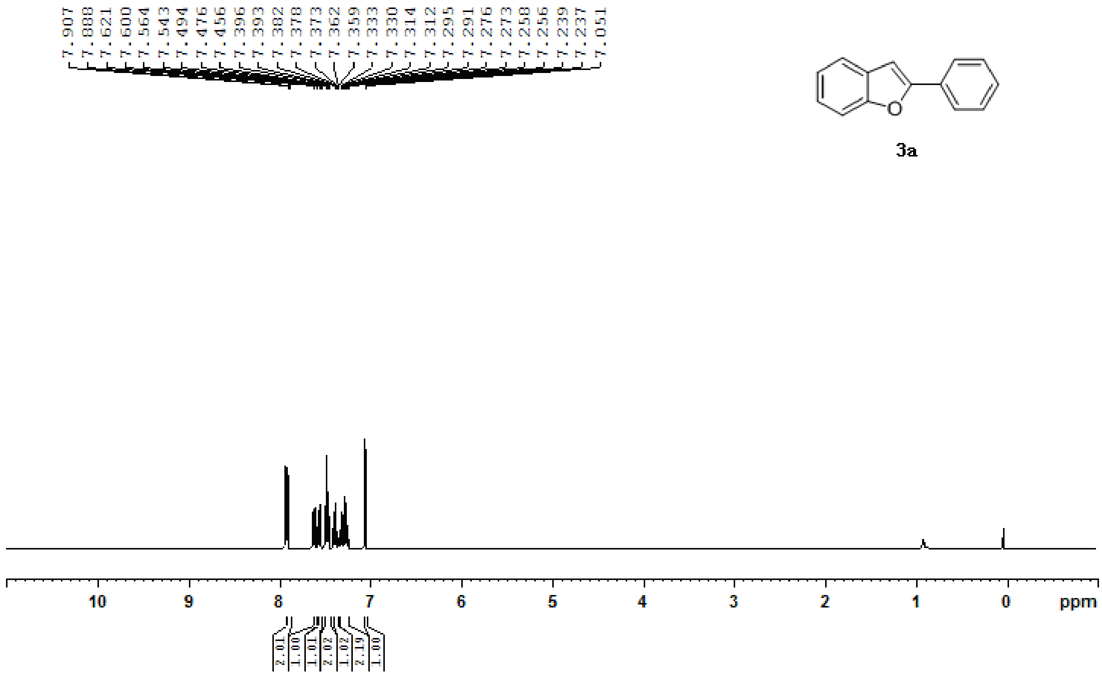
[1]H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.70 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.39–7.24 (m, 3H), 7.21–7.19 (m, 1H), 7.04 (s, 1H), 2.46 (s, 3H); [13]C NMR (100 MHz, $CDCl_3$): δ = 156.1, 154.9, 138.4, 130.4, 129.4, 129.3, 128.7, 125.5, 124.2, 122.9, 122.1, 120.8, 111.1, 101.2, 21.5.

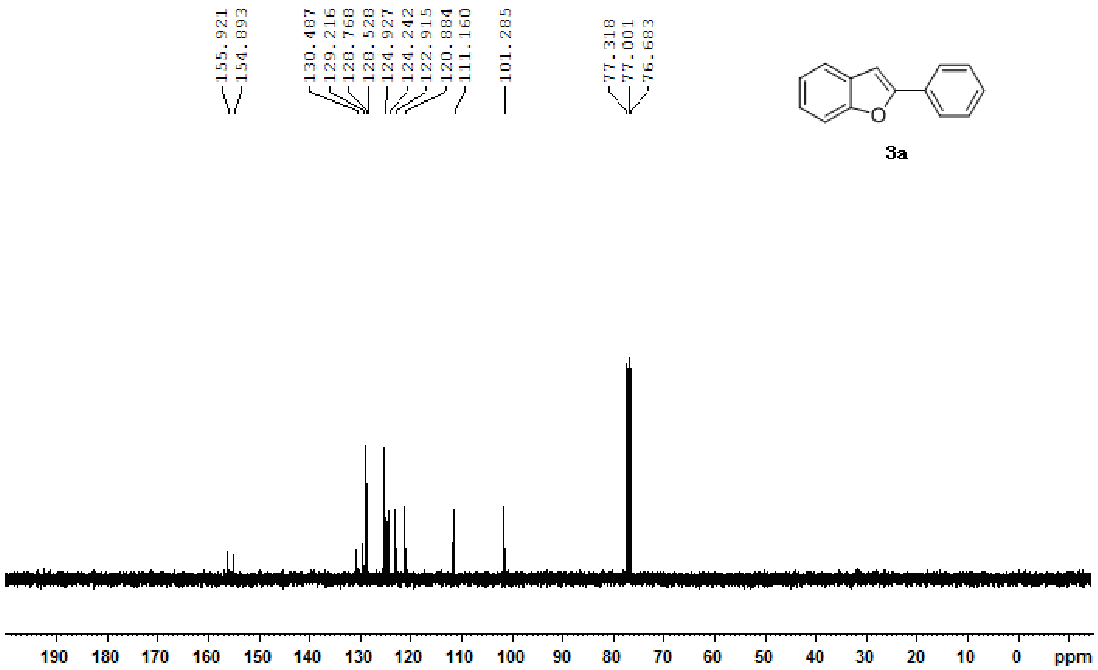


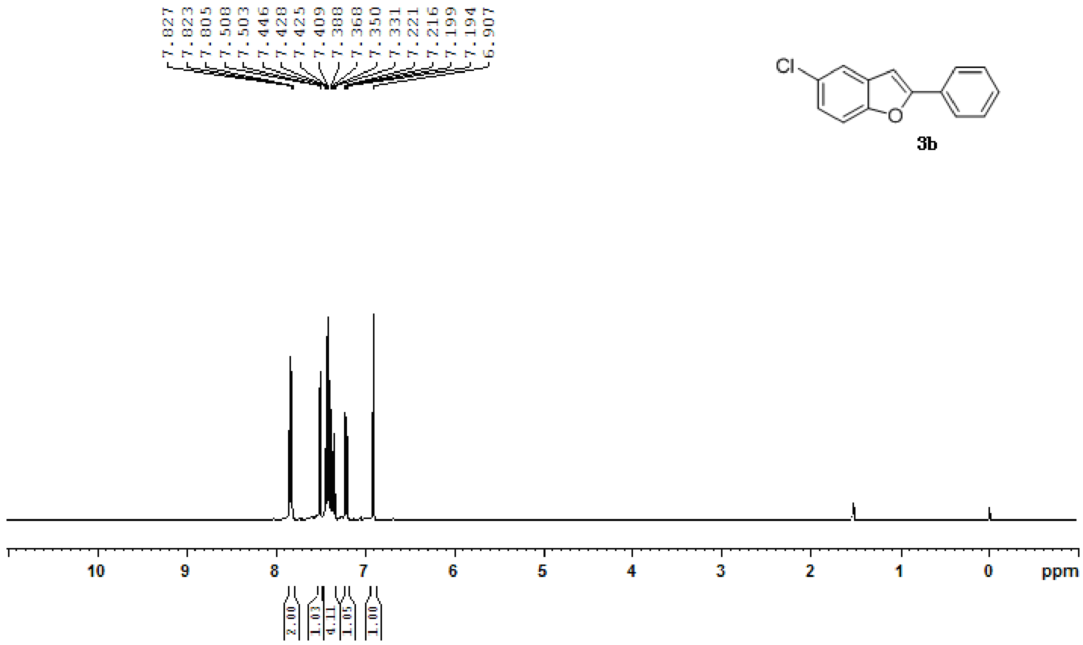
4i:[7] mp 98–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.84 (m, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.32–7.28 (m, 4H), 7.26–7.24 (m, 1H), 6.90 (s, 1H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.7, 154.4, 135.9, 131.2, 130.0, 129.2, 128.5, 128.2, 126.1, 124.2, 122.8, 120.9, 111.1, 105.1, 21.9.

4. ^{1}H and ^{13}C NMR spectra of the products



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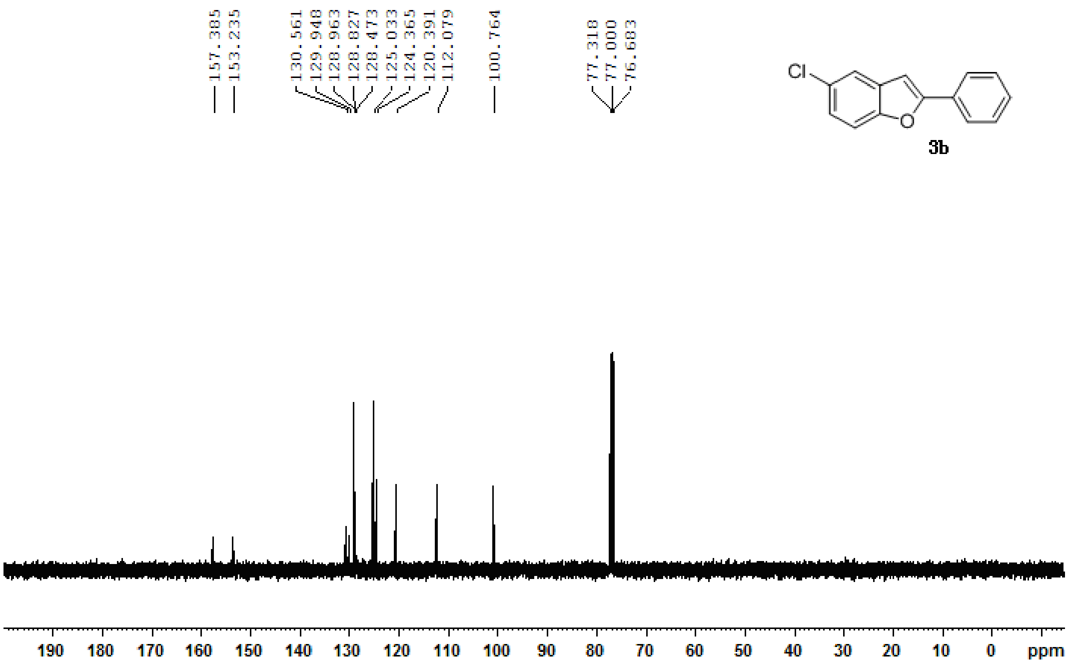
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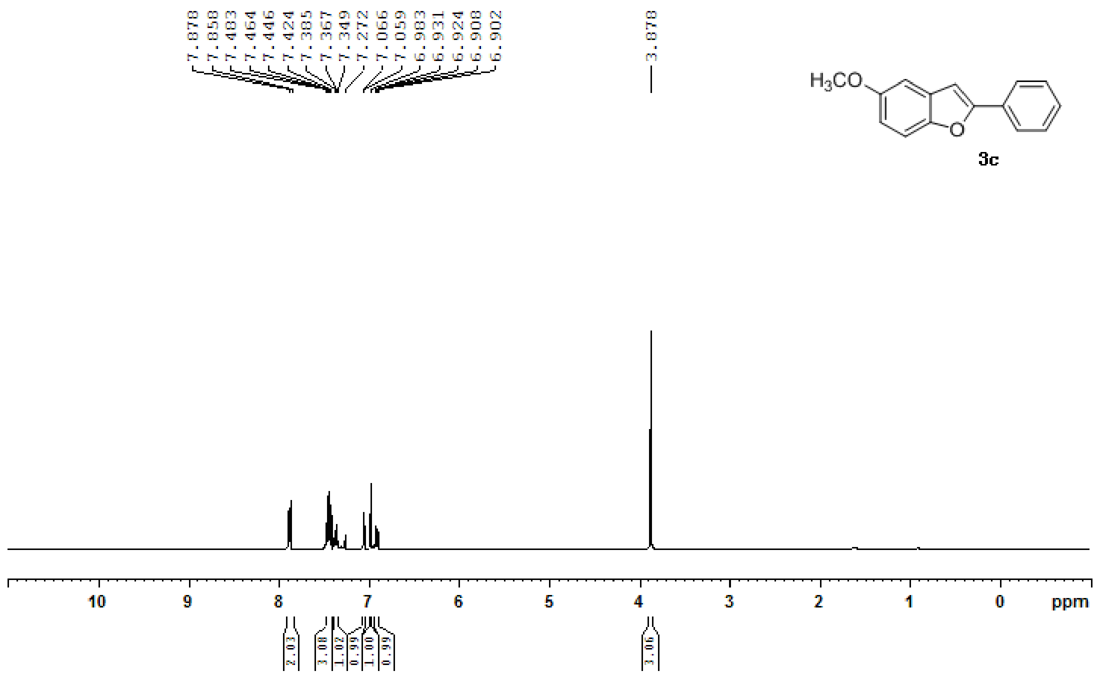
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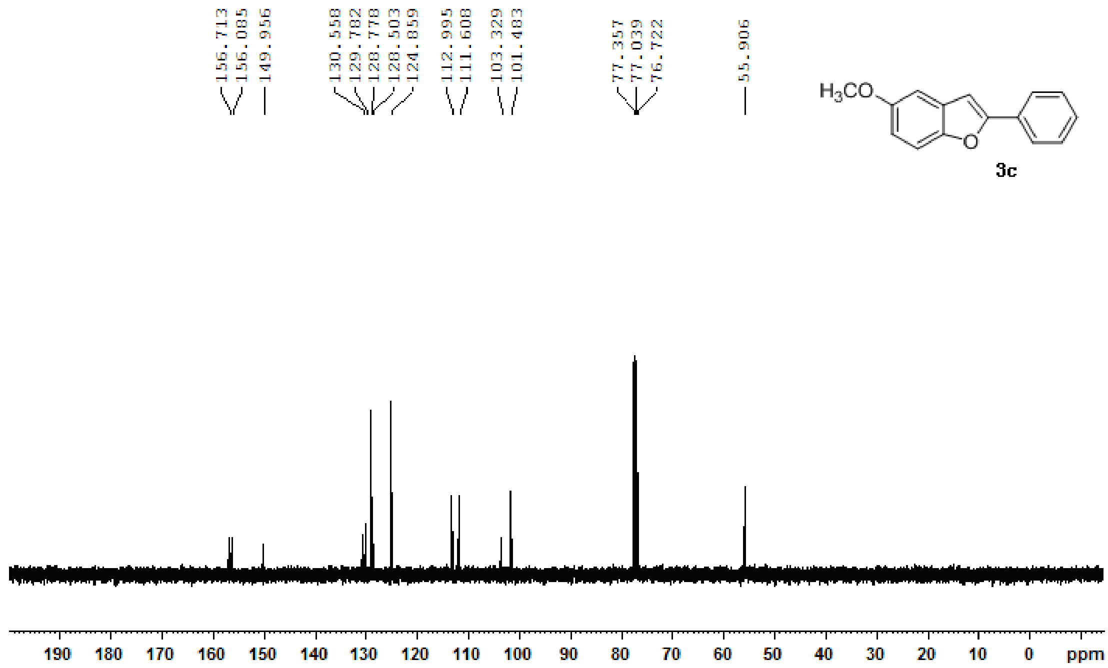
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77.357
77.039
76.722
55.906
H3CO
O
3c
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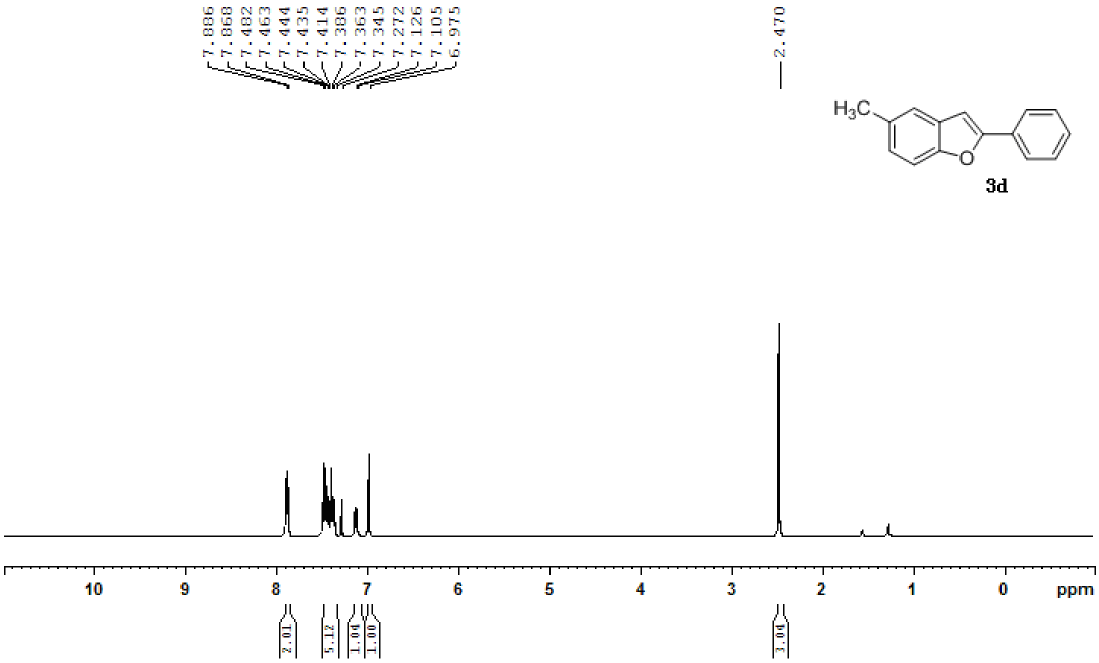
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7.105
6.975
2.470
H3C
O
3d
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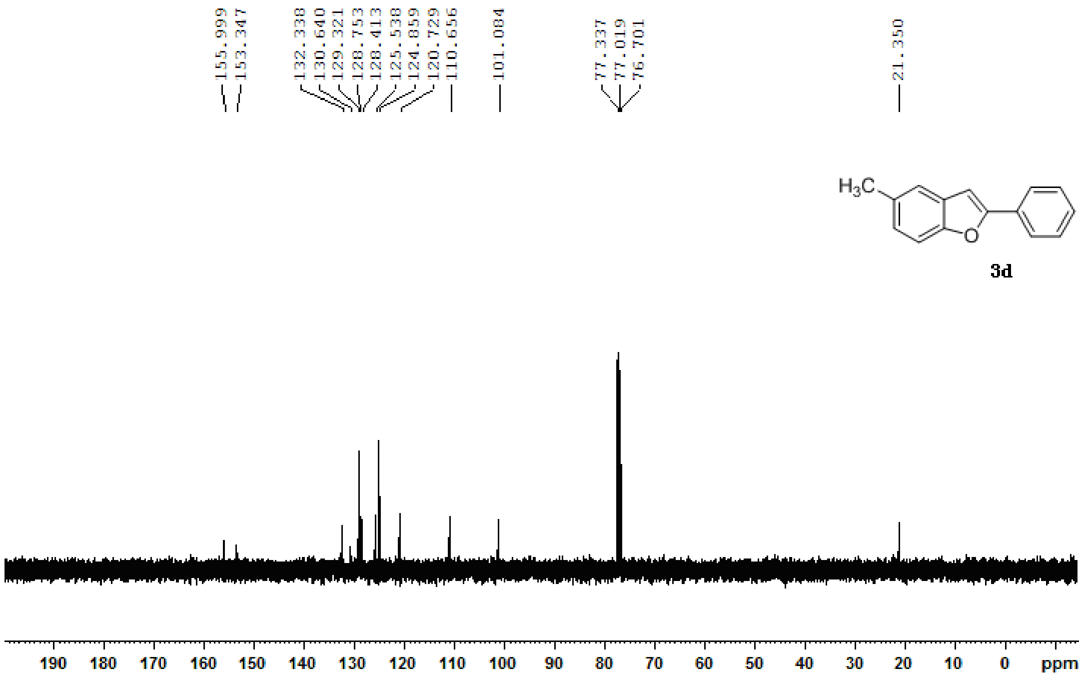
3.04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77.019
76.701
21.350
H3C
O
3d
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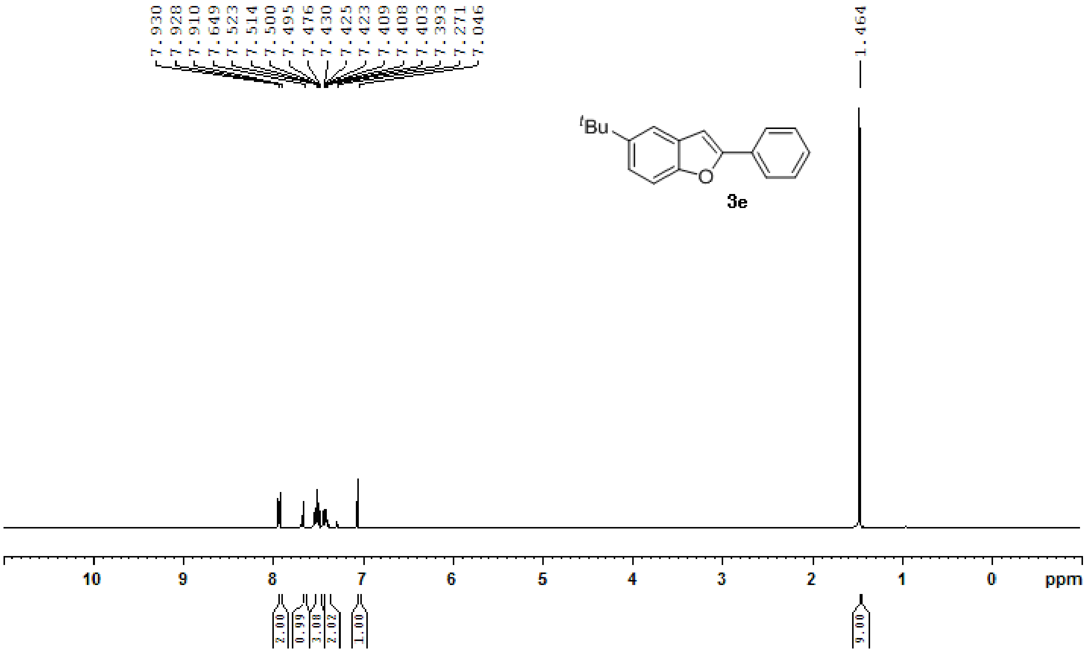
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7.495
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7.425
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7.409
7.408
7.403
7.393
7.271
7.046
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3e
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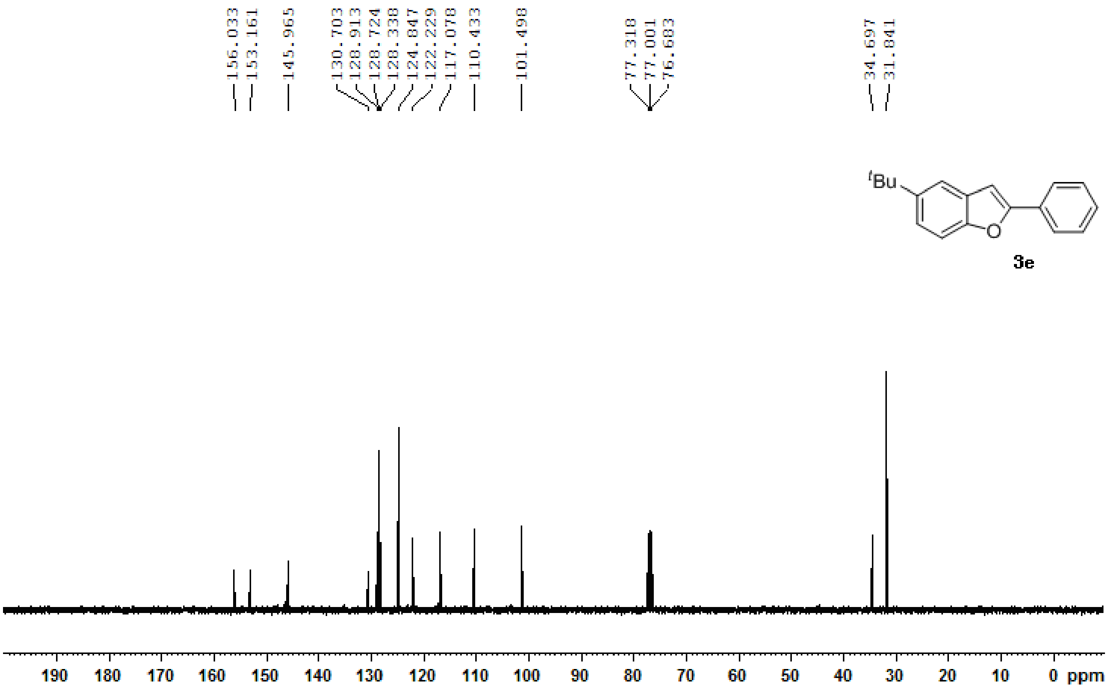
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101.498
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76.683
34.697
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tBu
O
3e
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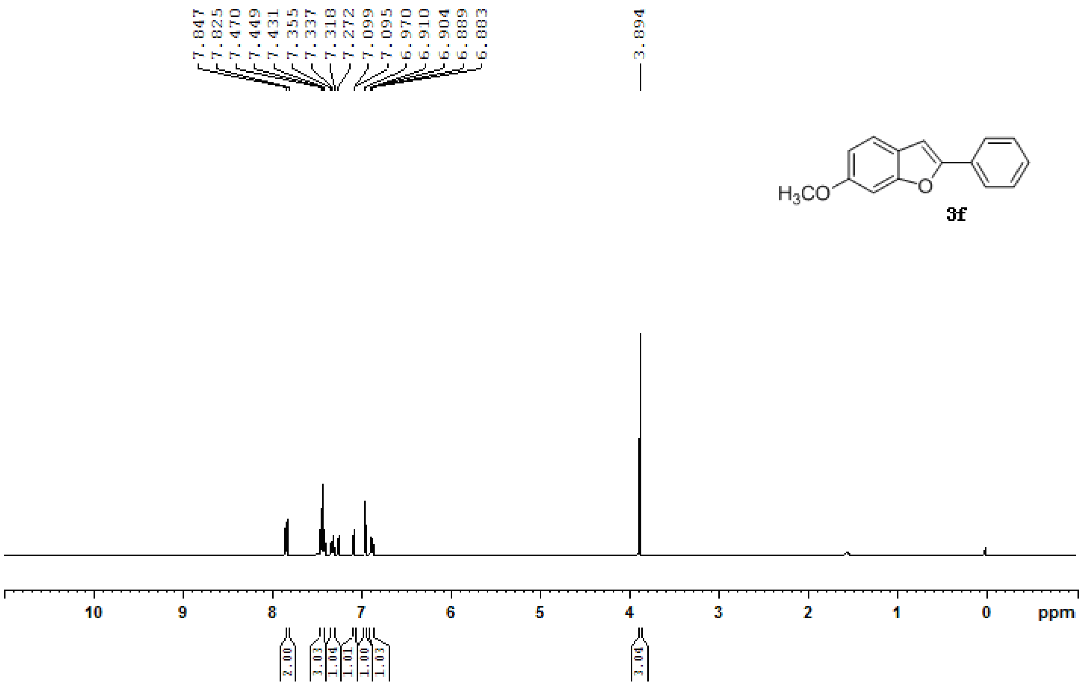
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6.904
6.889
6.883
3.894
H3CO
O
3f
10
9
8
7
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2
1
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1.04
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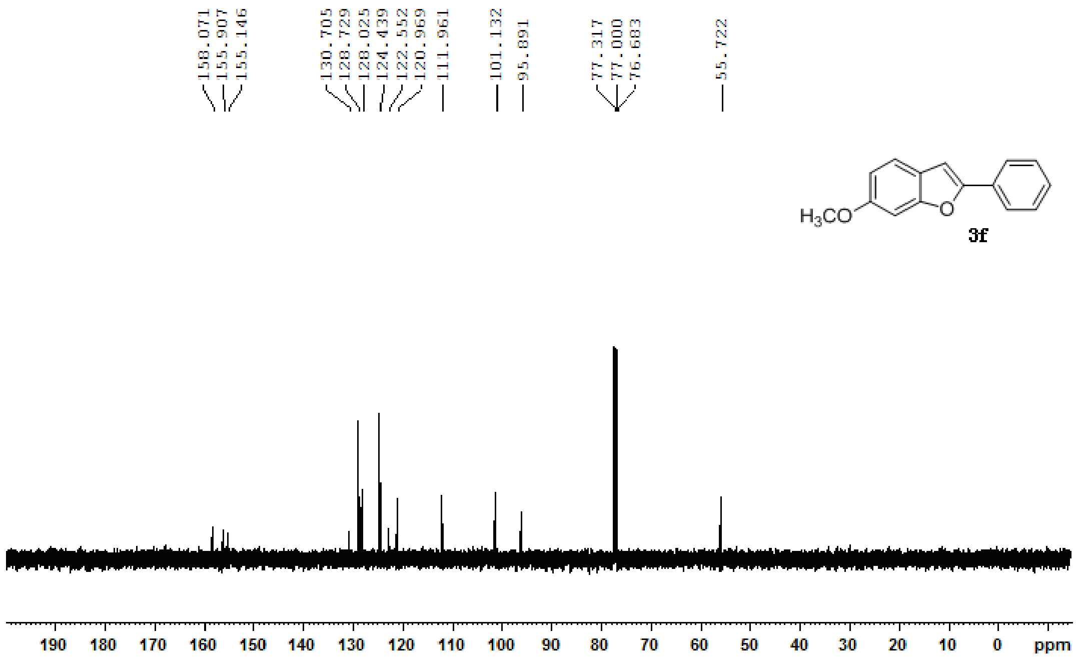
1.03
3.04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77.317
77.000
76.683
55.722
H3CO
O
3f
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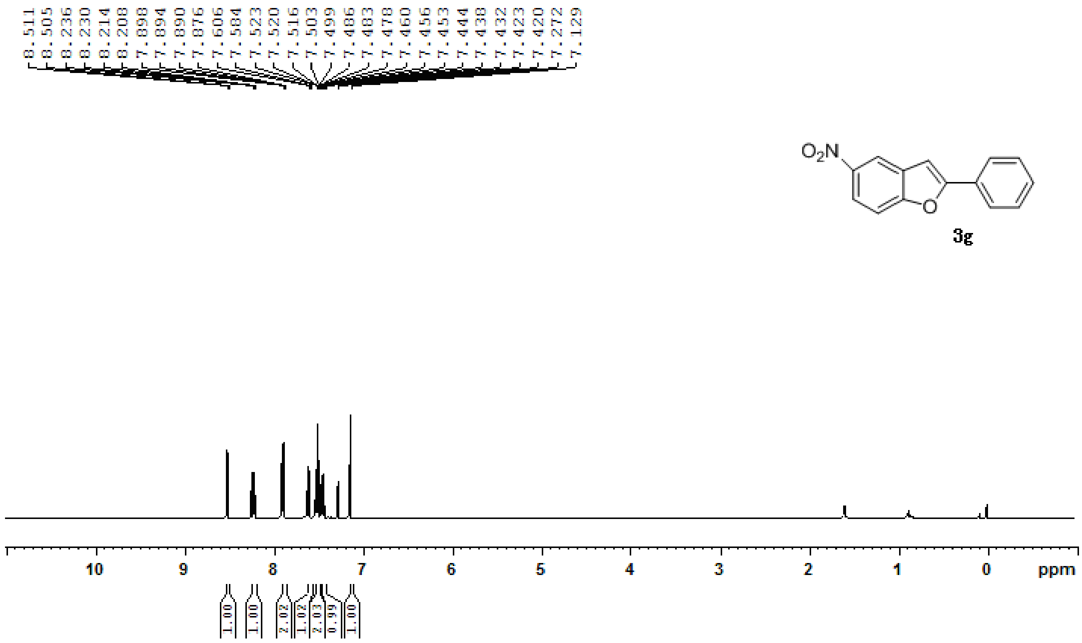
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7.520
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7.503
7.499
7.486
7.483
7.478
7.460
7.456
7.453
7.444
7.438
7.432
7.423
7.420
7.272
7.129
O_2N
O
3g
10
9
8
7
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3
2
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ppm
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1.00
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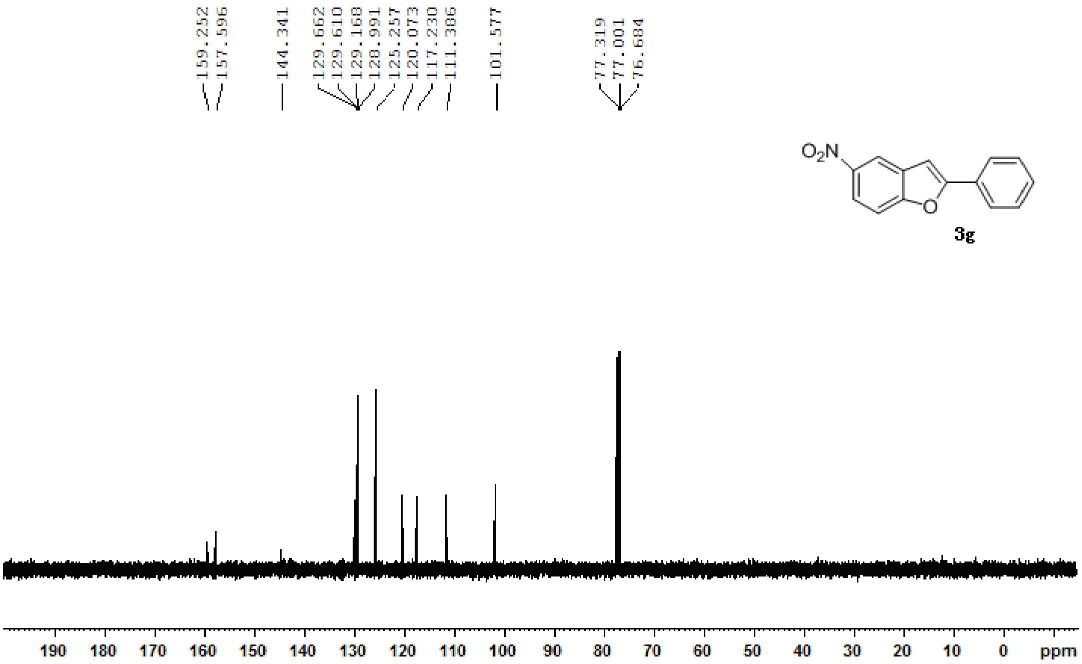
1.00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128.991
125.257
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111.386
101.577
77.319
77.001
76.684
O_2N
O
3g
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180
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80
70
60
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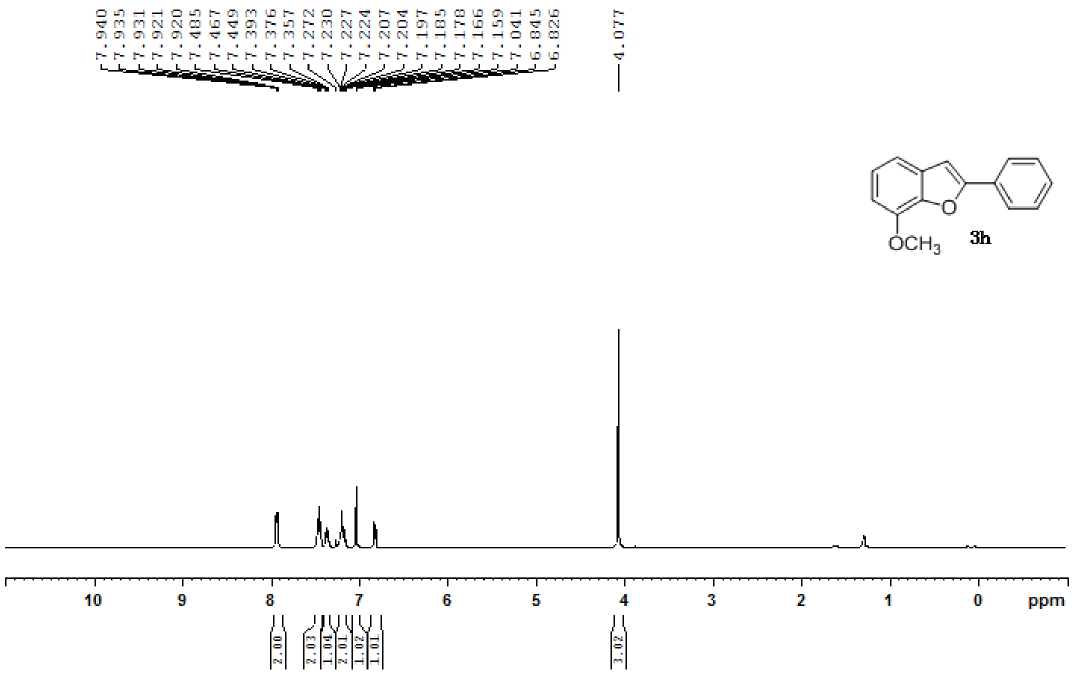
ppm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7.393
7.376
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7.272
7.230
7.227
7.224
7.207
7.204
7.197
7.185
7.178
7.166
7.159
7.041
6.845
6.826
4.077
OCH3
3h
10
9
8
7
6
5
4
3
2
1
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ppm
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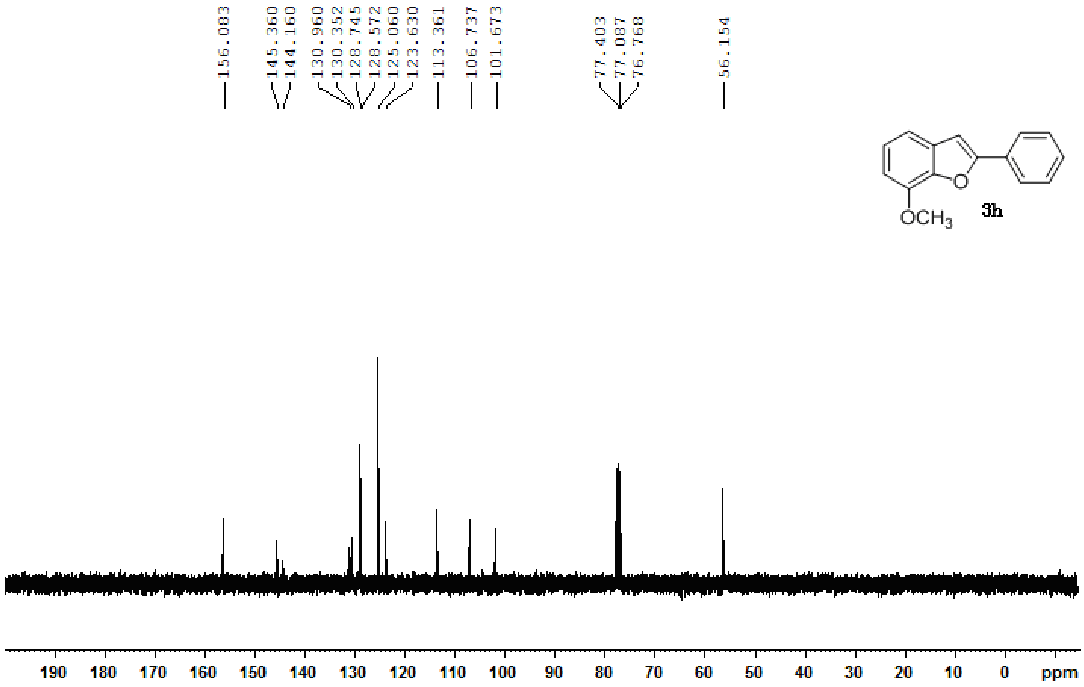
1.02
1.01
3.02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77.087
76.768
56.154
OCH3
3h
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160
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130
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80
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20
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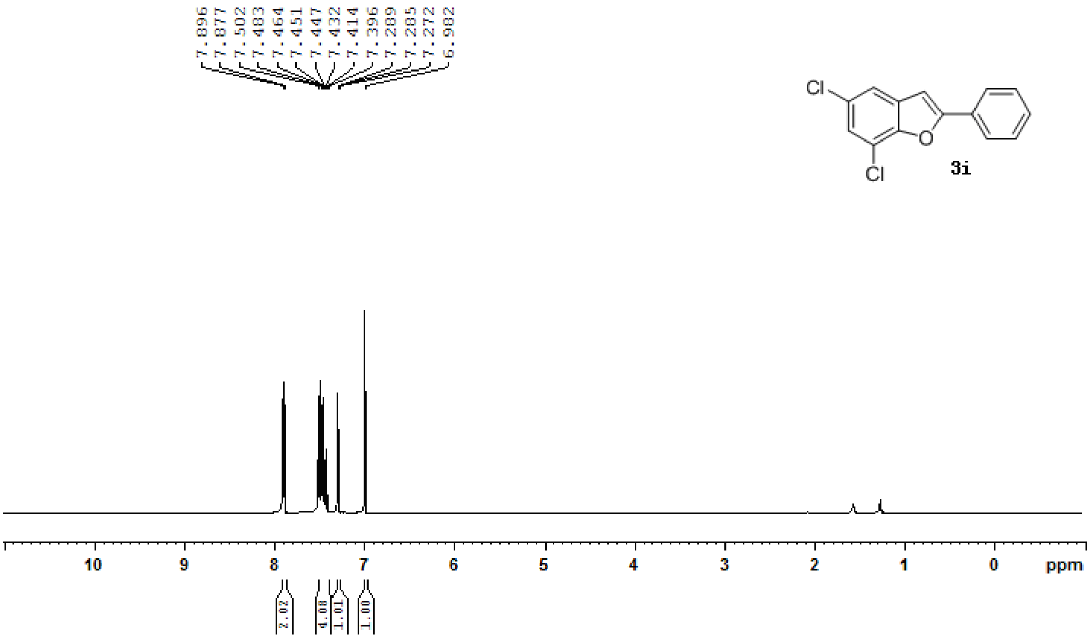
0
ppm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7.432
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7.285
7.272
6.982
Cl
O
Cl
3i
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7
6
5
4
3
2
1
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ppm
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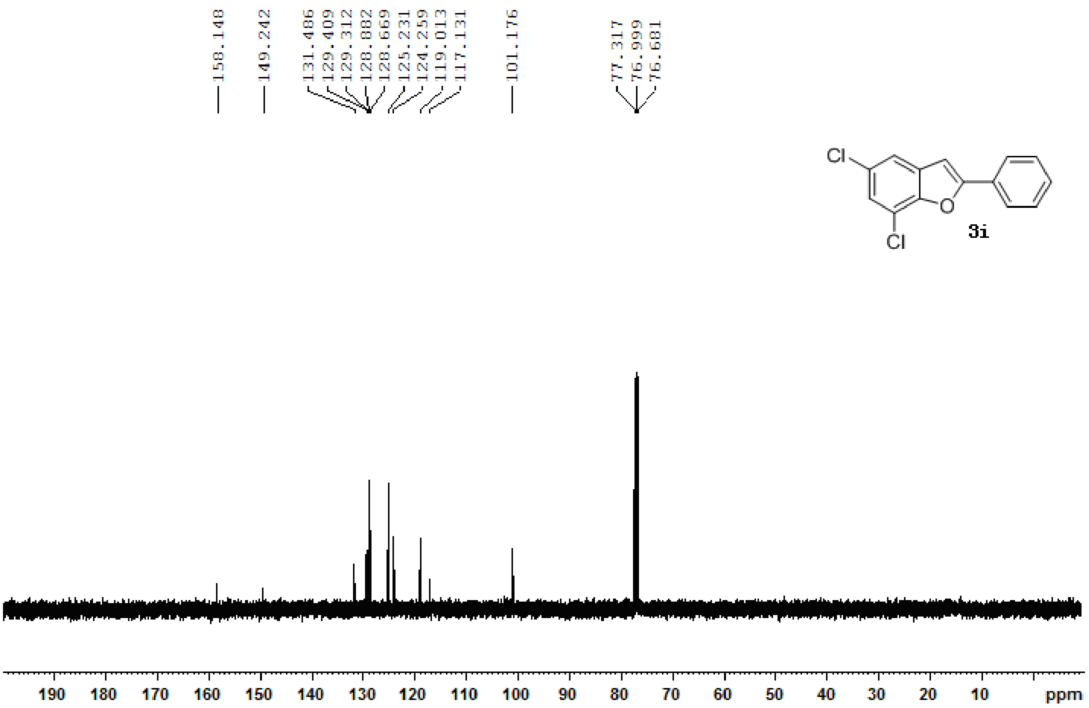
4.08
1.01
1.00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76.999
76.681
Cl
O
Cl
3i
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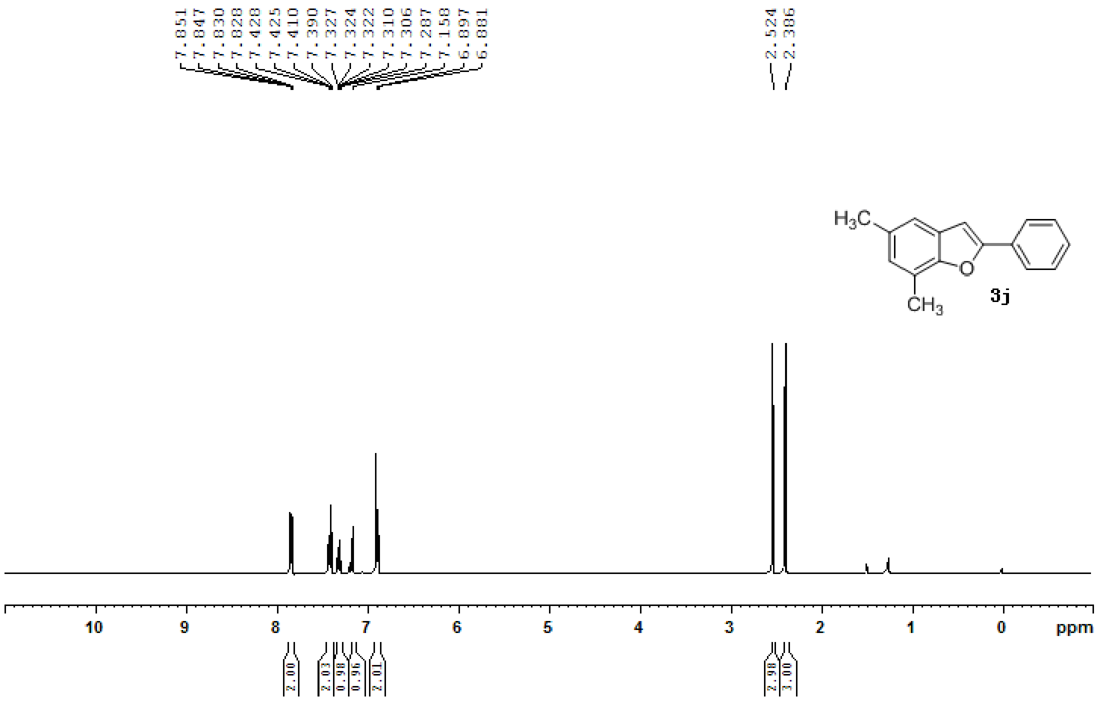
10
ppm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7.306
7.287
7.158
6.897
6.881
2.524
2.386
H3C
O
CH3
3j
10
9
8
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2
1
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ppm
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2.98
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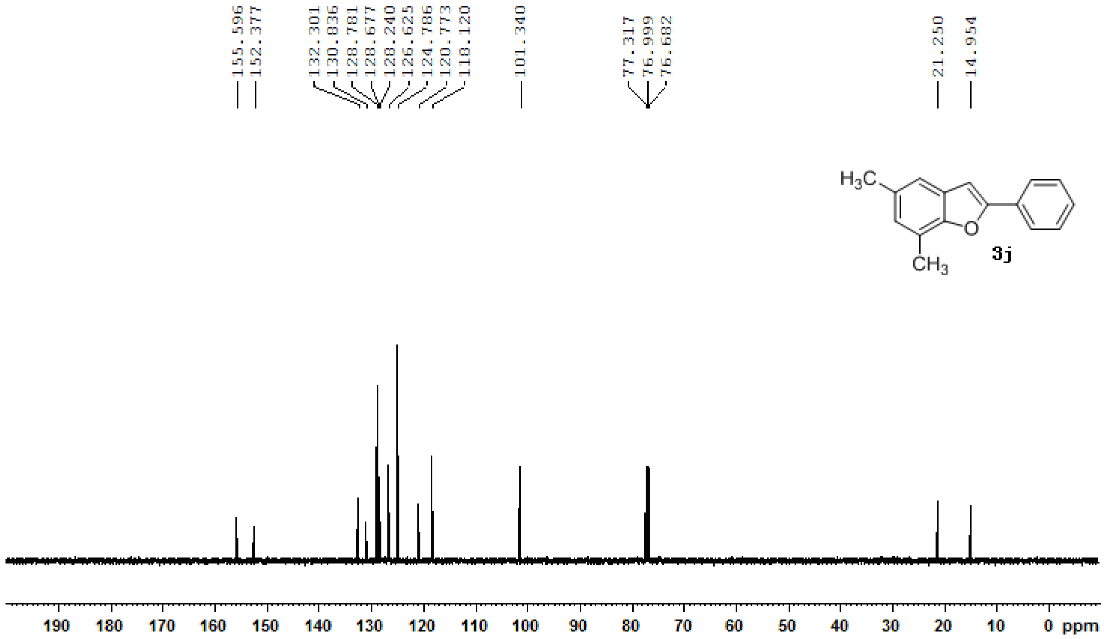
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76.999
76.682
21.250
14.954
H3C
O
CH3
3j
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80
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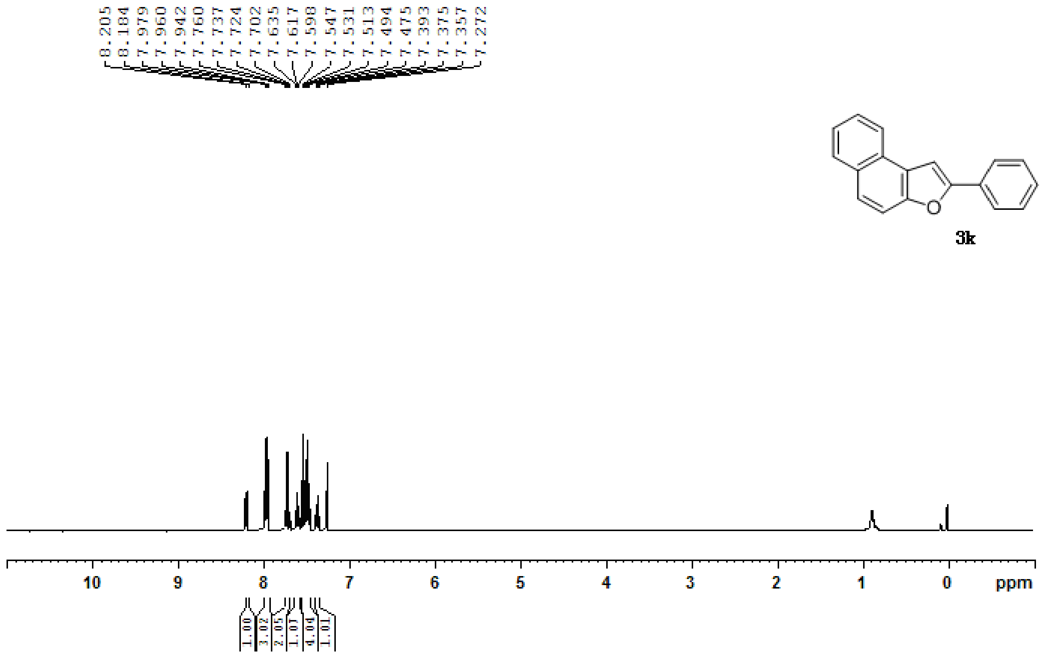
20
10
0
ppm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7.598
7.547
7.531
7.513
7.494
7.475
7.393
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3k
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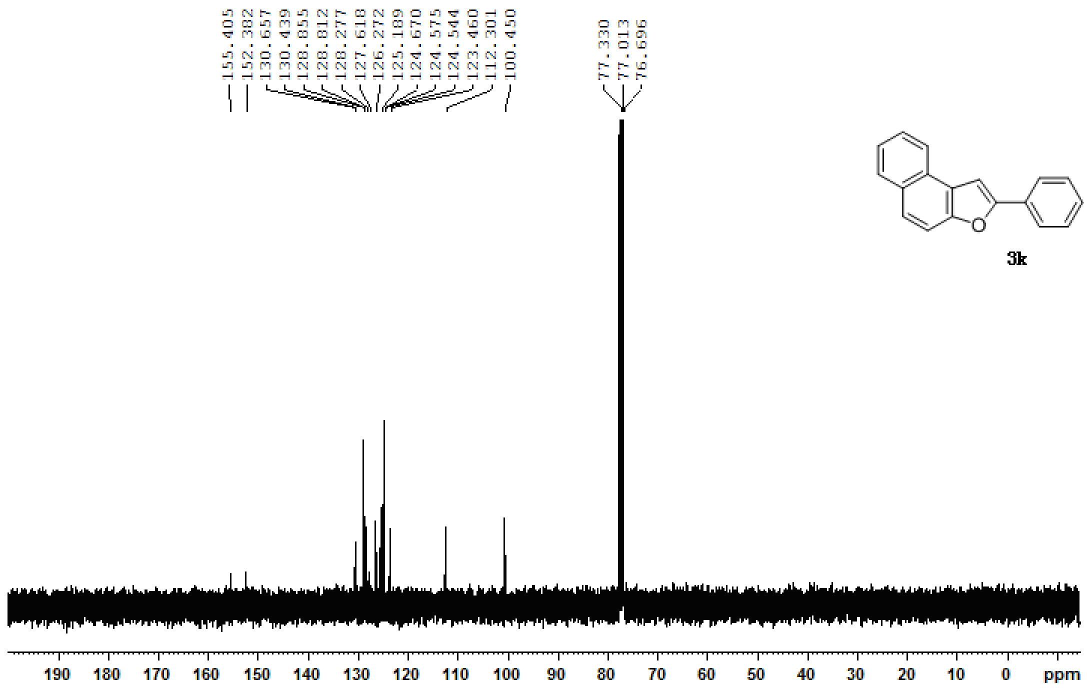
2.05
1.07
4.04
1.01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124.575
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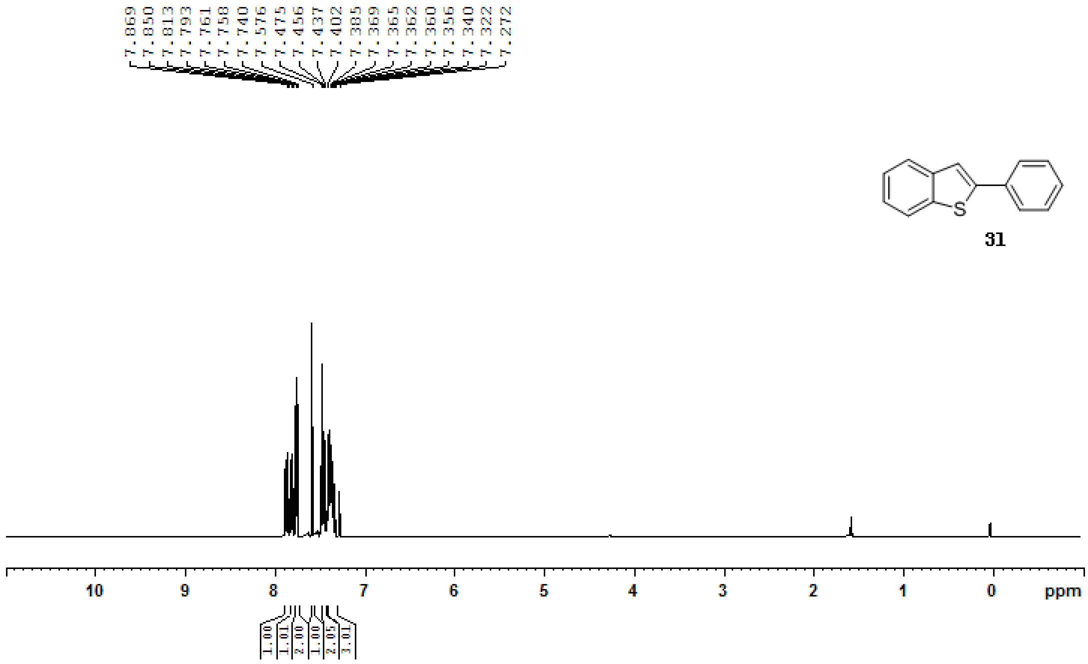
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7.369
7.365
7.362
7.360
7.356
7.340
7.322
7.272
S
31
10
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2.00
1.00
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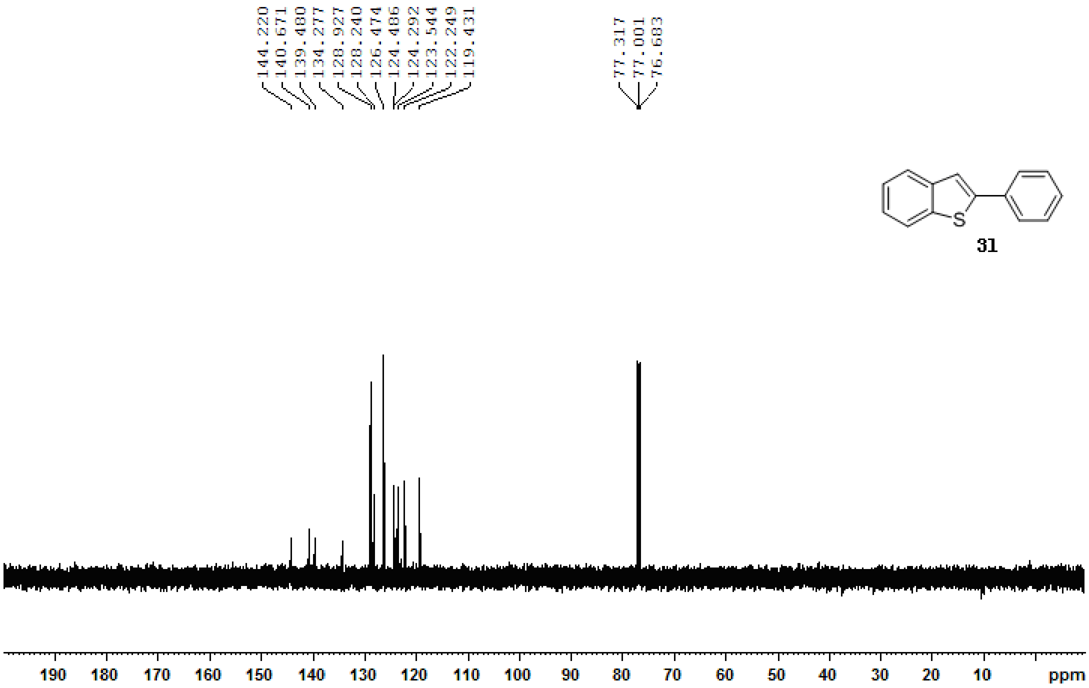
3.01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77.317
77.001
76.683
S
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30
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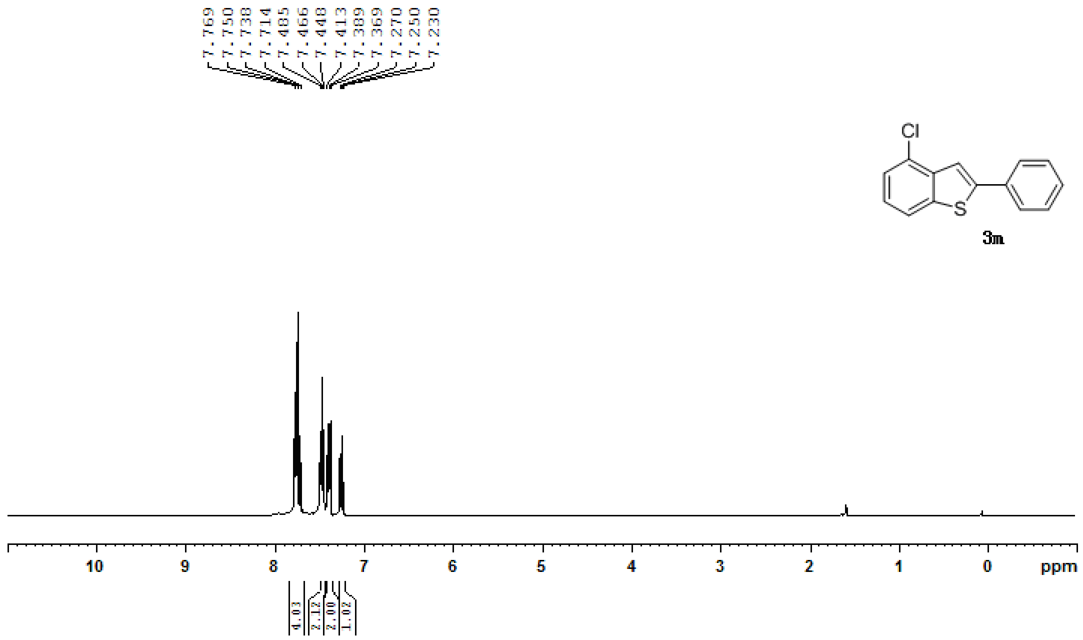
ppm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7.230
Cl
S
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ppm
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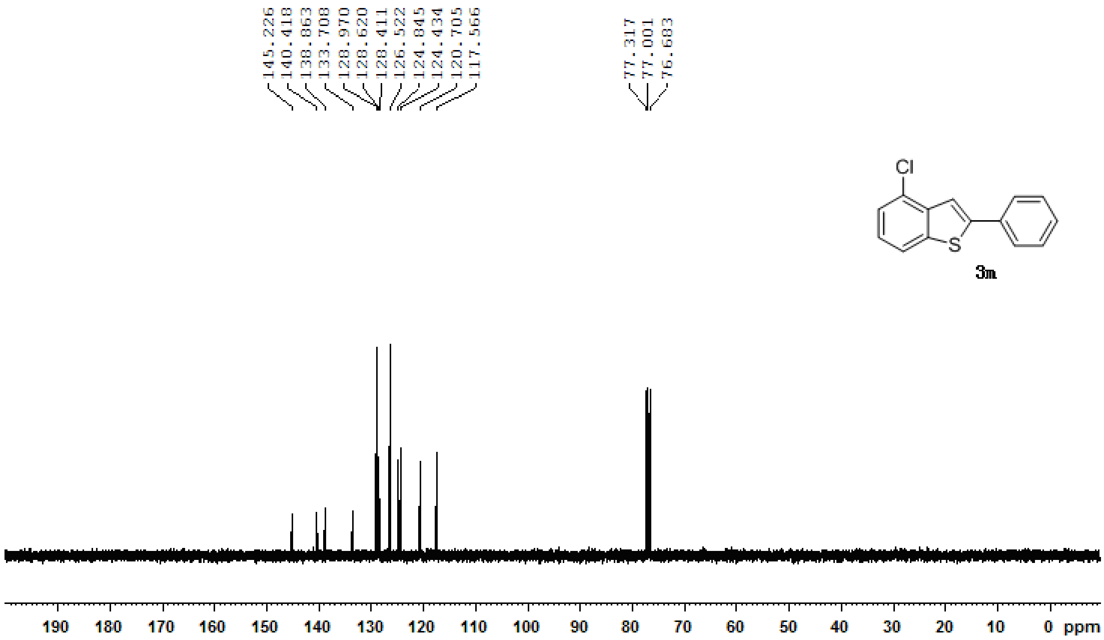
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77.317
77.001
76.683
Cl
S
3m
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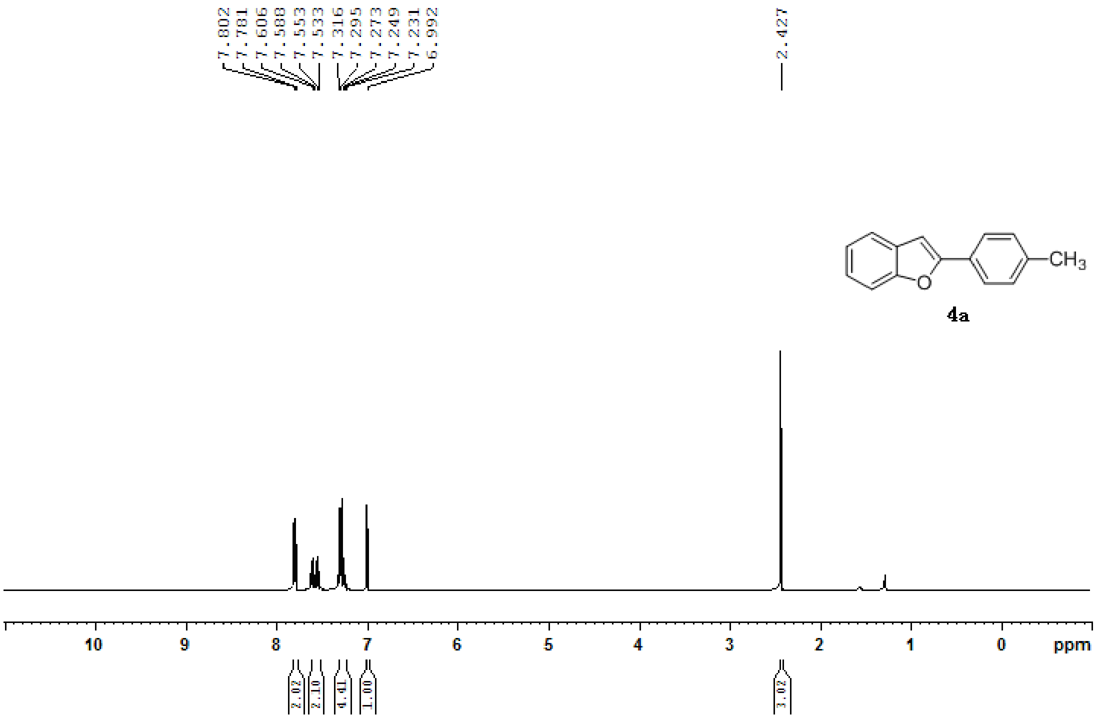
ppm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2.427
CH3
O
4a
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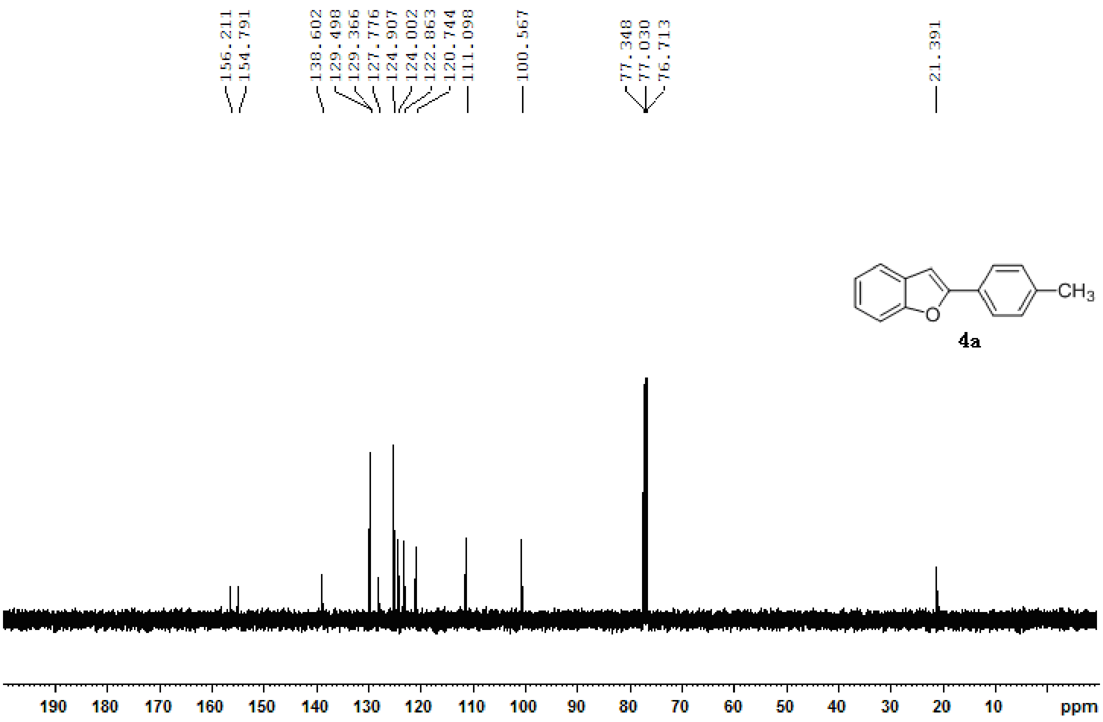
3.02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77.030
76.713
21.391
CH3
O
4a
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20
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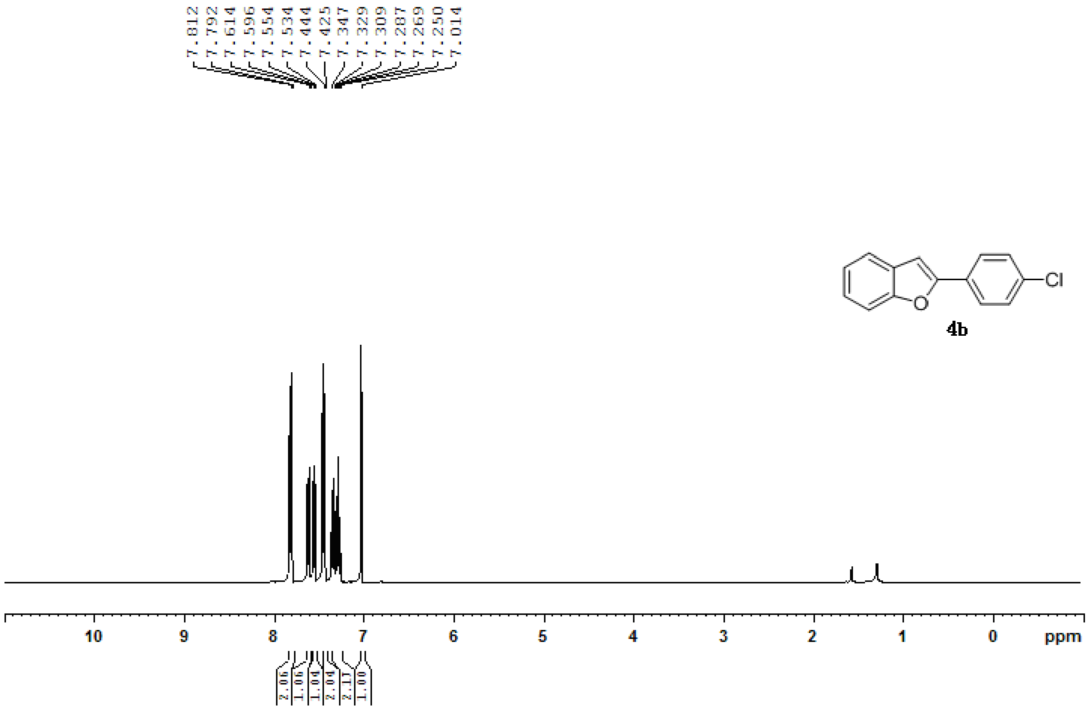
ppm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7.287
7.269
7.250
7.014
Cl
O
4b
10
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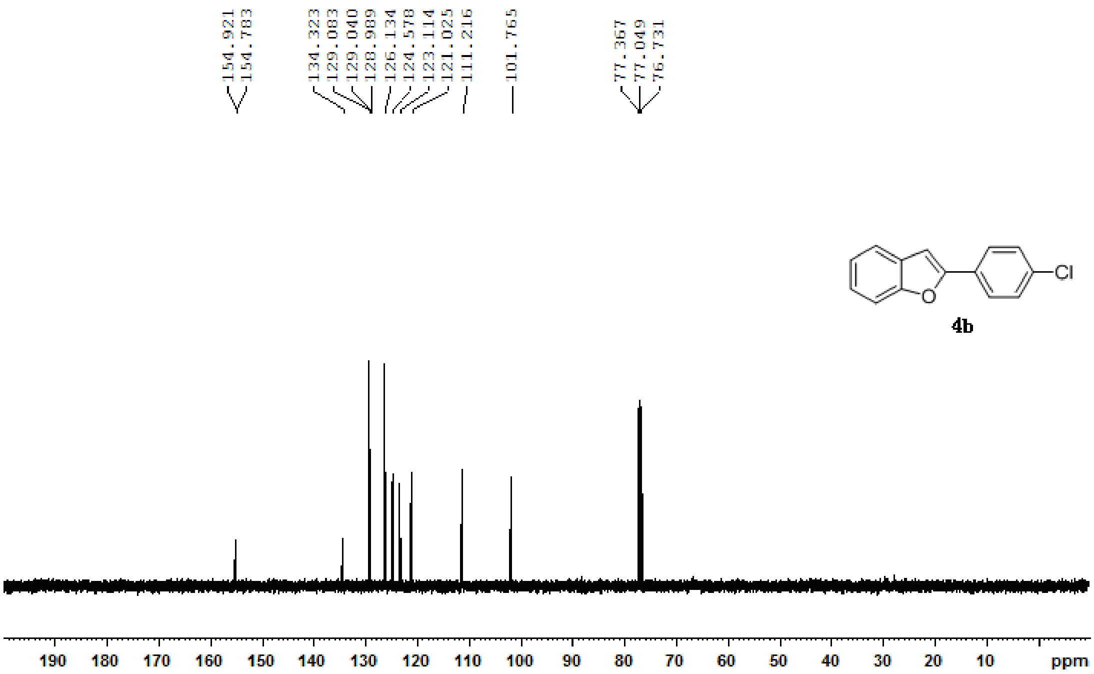
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77.367
77.049
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Cl
O
4b
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20
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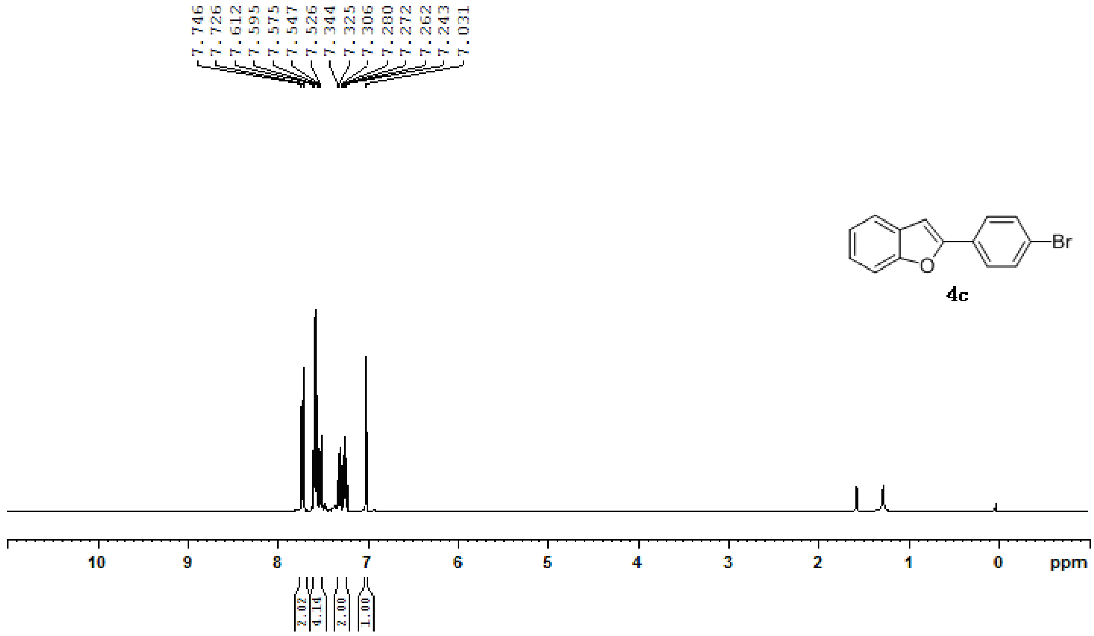
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7.262
7.243
7.031
Br
O
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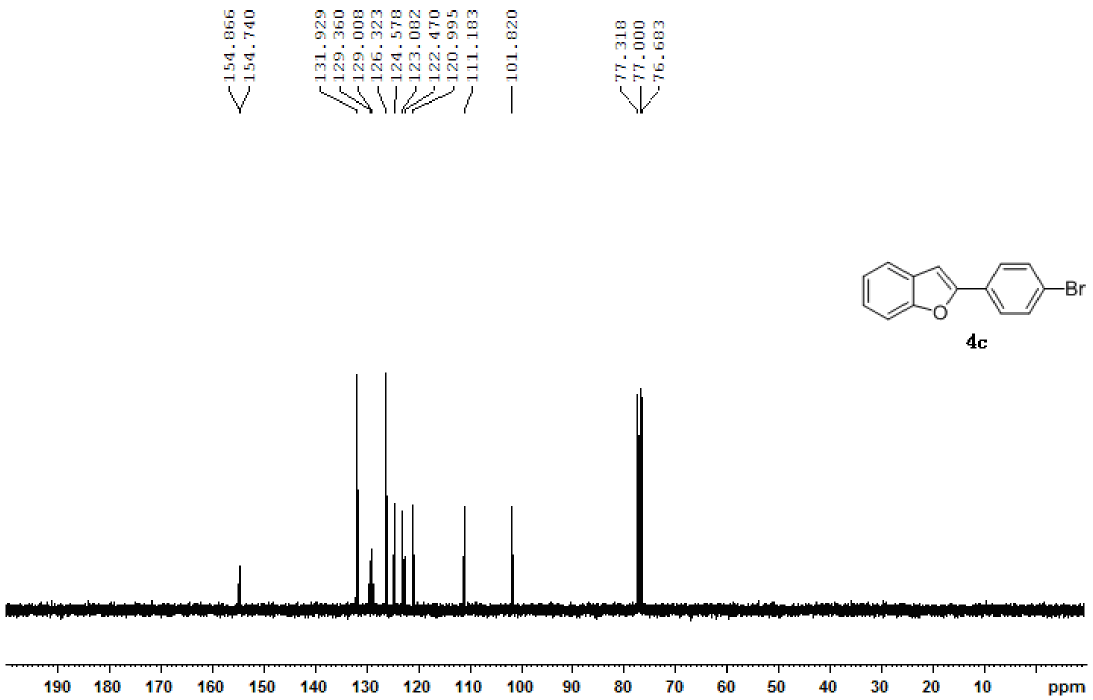
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77.000
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Br
O
4c
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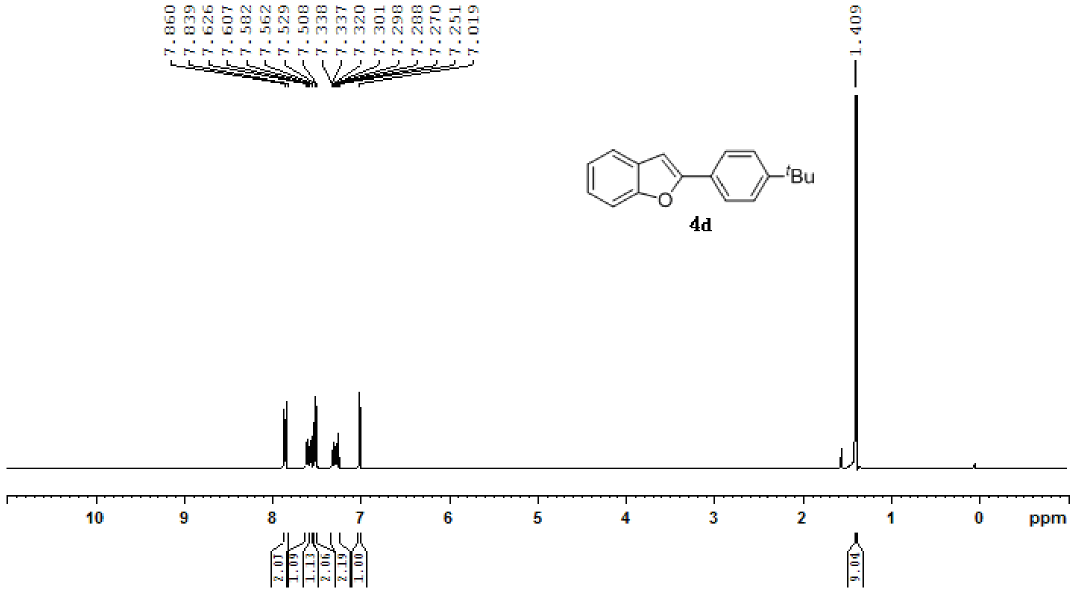
ppm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7.337
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7.301
7.298
7.288
7.270
7.251
7.019
1.409
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O
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10 9 8 7 6 5 4 3 2 1 0 ppm
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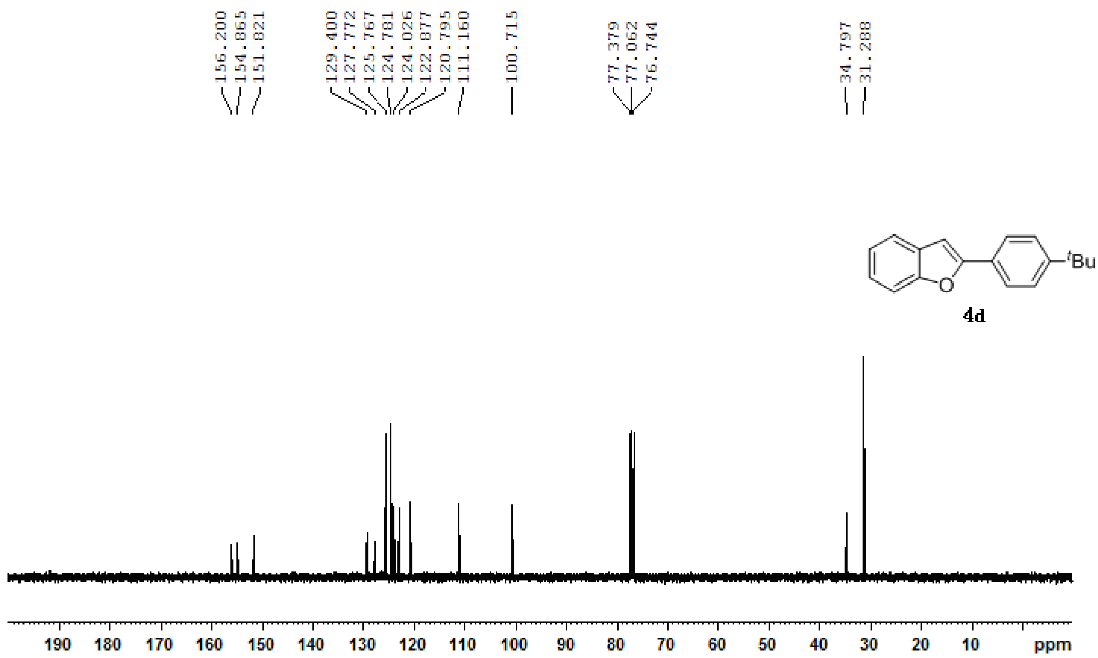
1.09
1.13
2.06
2.10
1.00
9.04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124.026
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111.160
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4d
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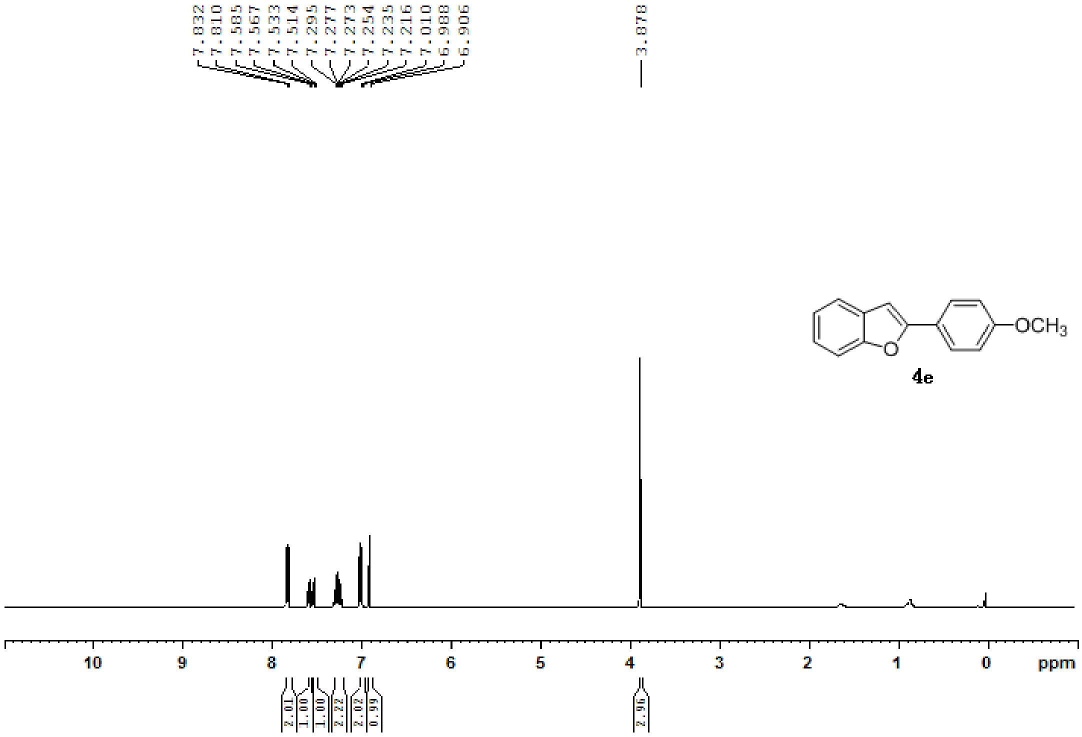
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7.254
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7.216
7.010
6.988
6.906
3.878
OCH3
4e
10
9
8
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1.00
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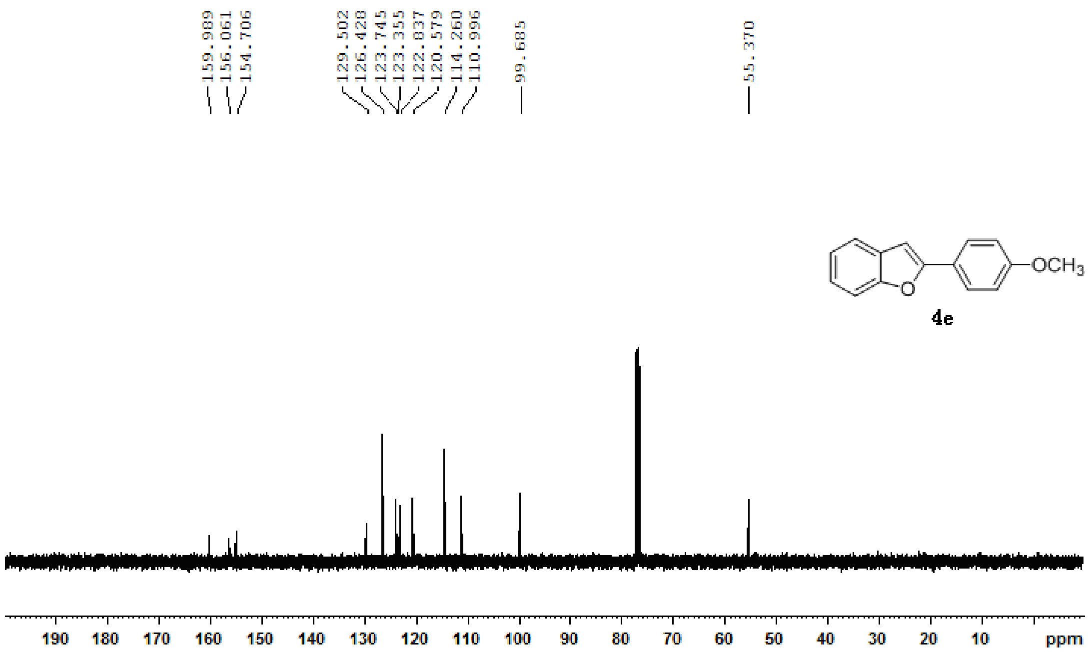
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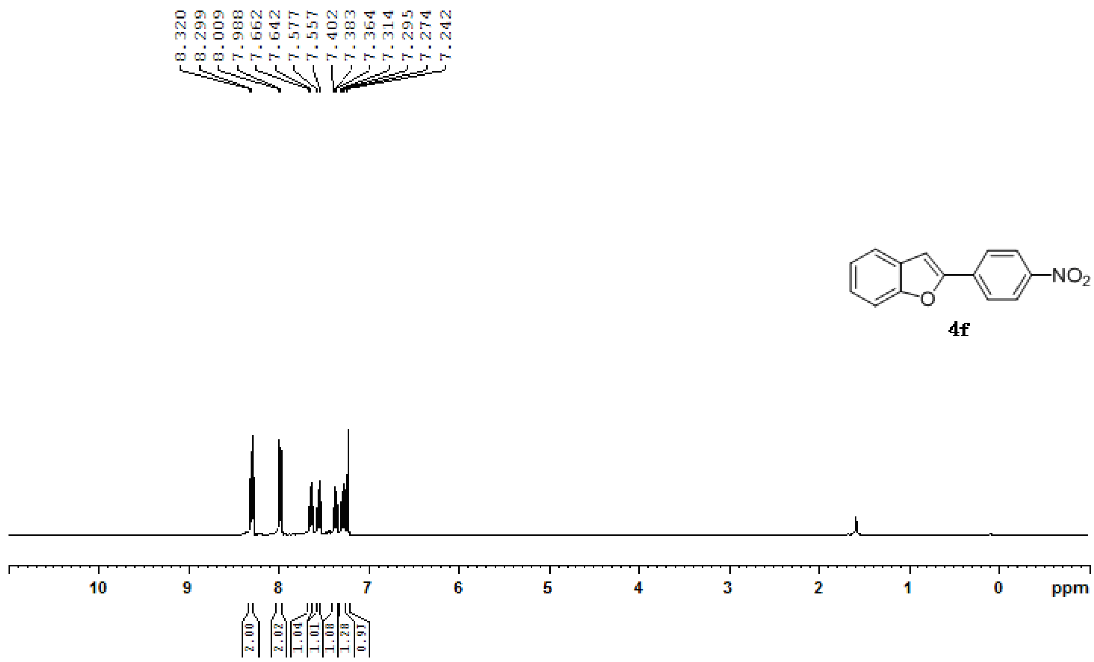
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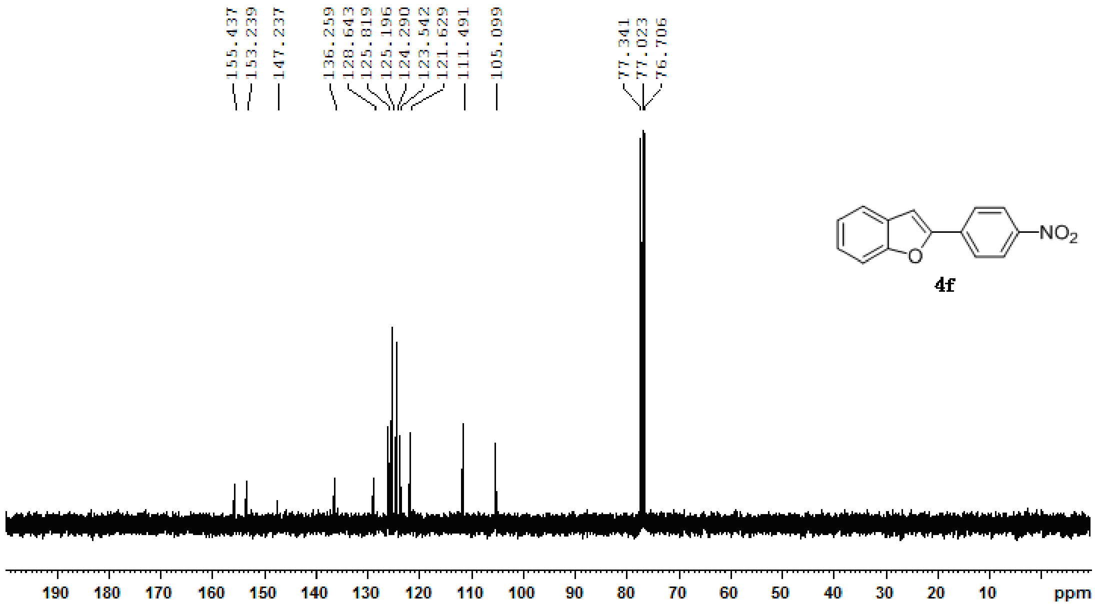
7.364
7.314
7.295
7.274
7.242
NO2
4f
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
1.04
1.01
1.00
1.28
0.91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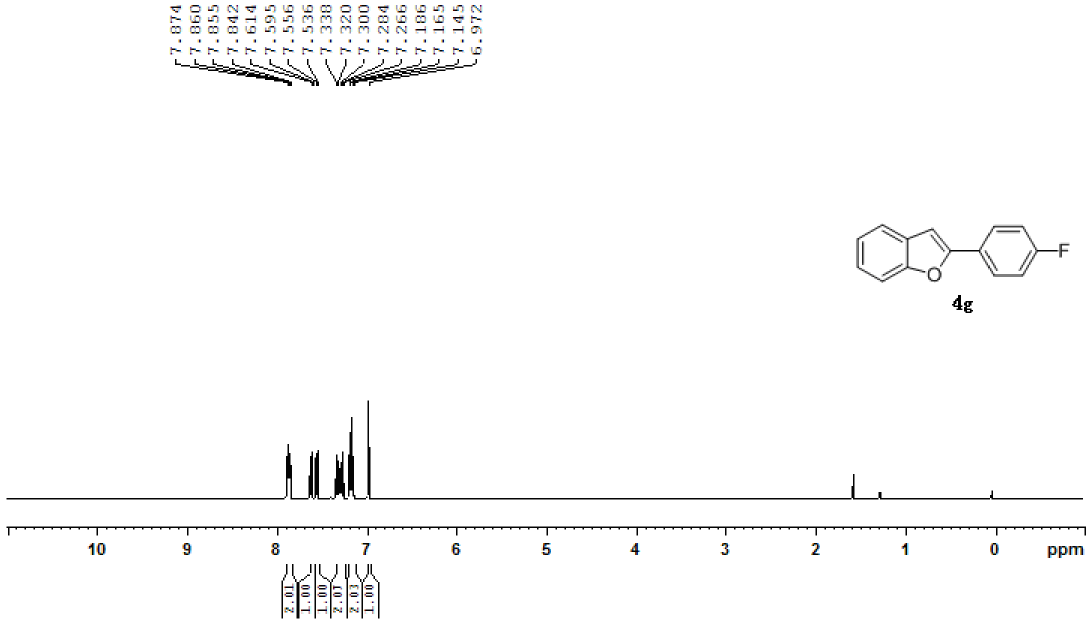
153.239
147.237
136.259
128.643
125.819
125.196
124.290
123.542
121.629
111.491
105.099
77.341
77.023
76.706
NO2
4f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.860
7.855
7.842
7.614
7.595
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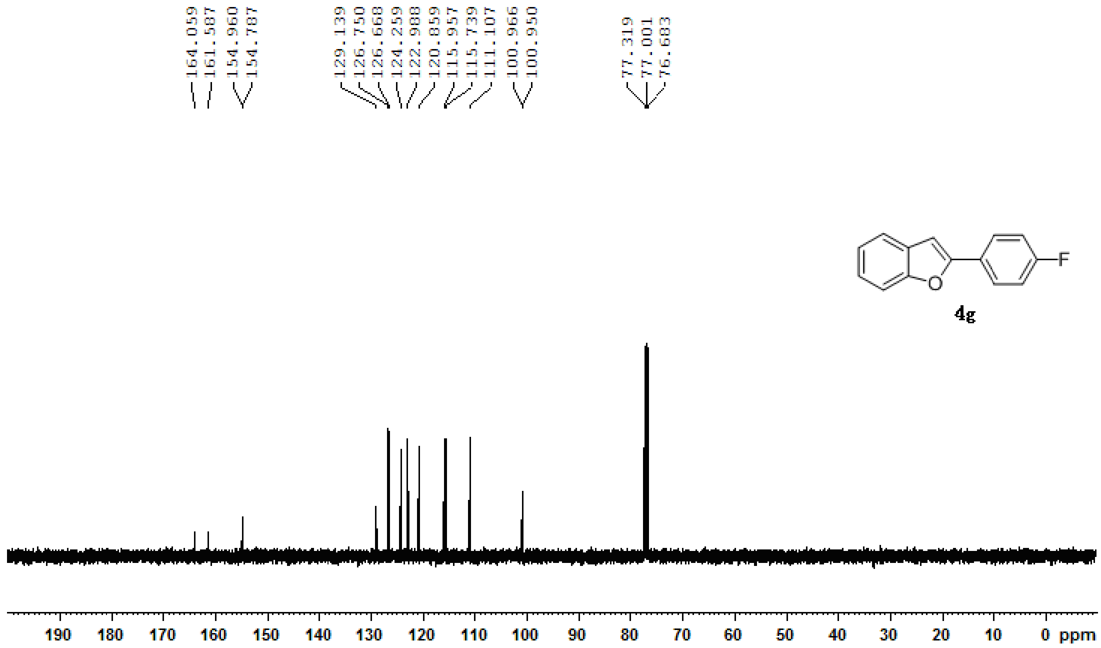
7.300
7.284
7.266
7.186
7.165
7.145
6.972
F
O
4g
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.00
1.00
2.07
2.03
1.00


164.059
161.587
154.960
154.787
129.139
126.750
126.668
124.259
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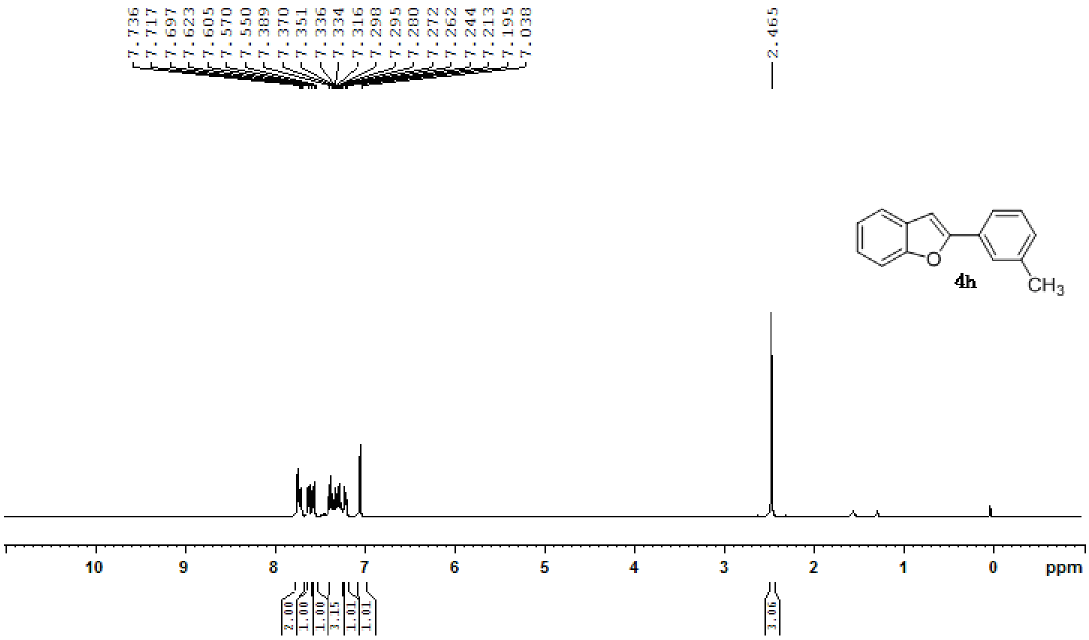
120.859
115.957
115.739
111.107
100.966
100.950
77.319
77.001
76.683
F
O
4g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.717
7.697
7.623
7.605
7.570
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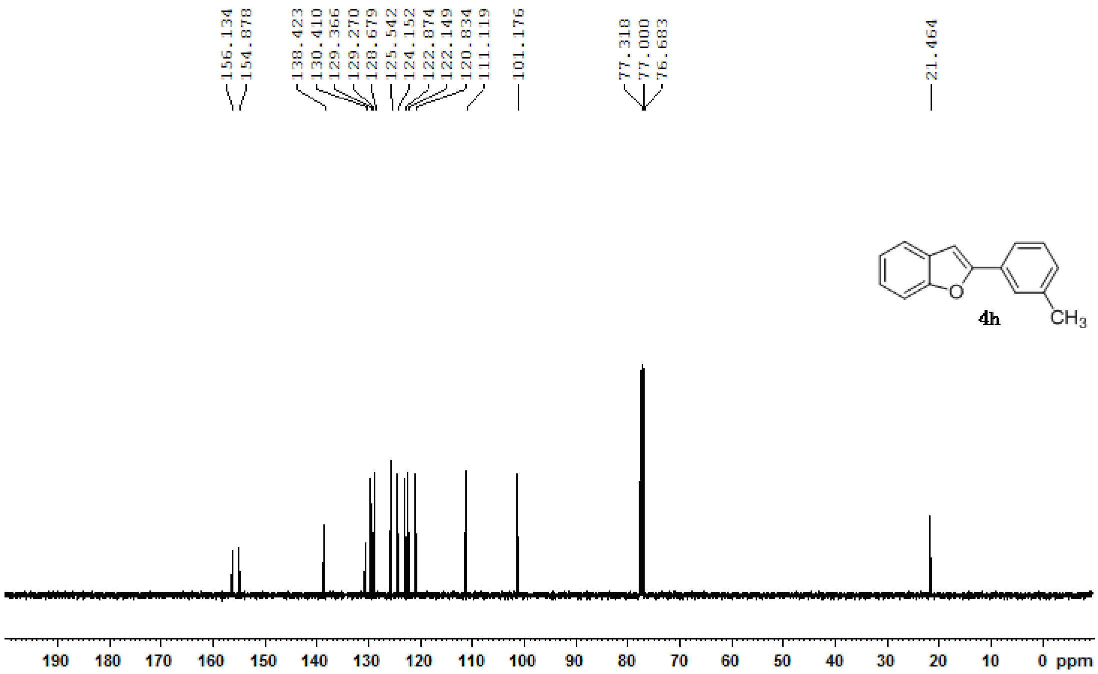
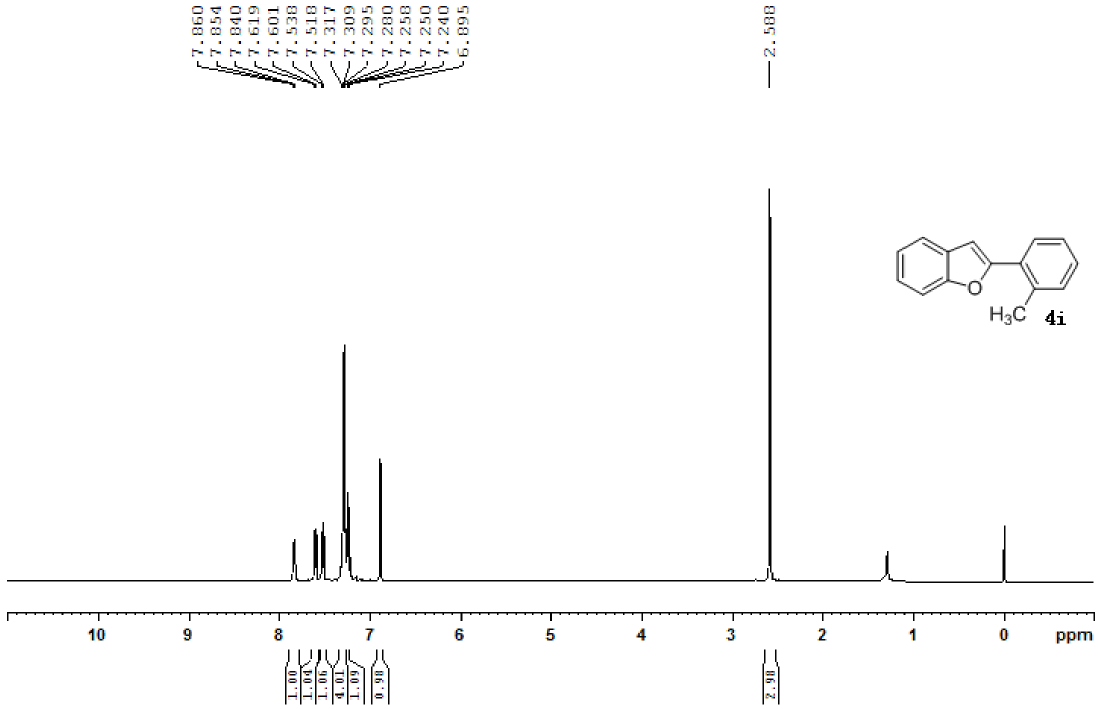
7.389
7.370
7.351
7.336
7.334
7.316
7.298
7.295
7.280
7.272
7.262
7.244
7.213
7.195
7.038
2.465
O
4h
CH3
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.00
1.00
3.15
1.01
1.01
3.06


156.134
154.878
138.423
130.410
129.366
129.270
128.679
125.542
124.152
122.874
122.149
120.834
111.119
101.176
77.318
77.000
76.683
21.464
O
4h
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.538
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7.317
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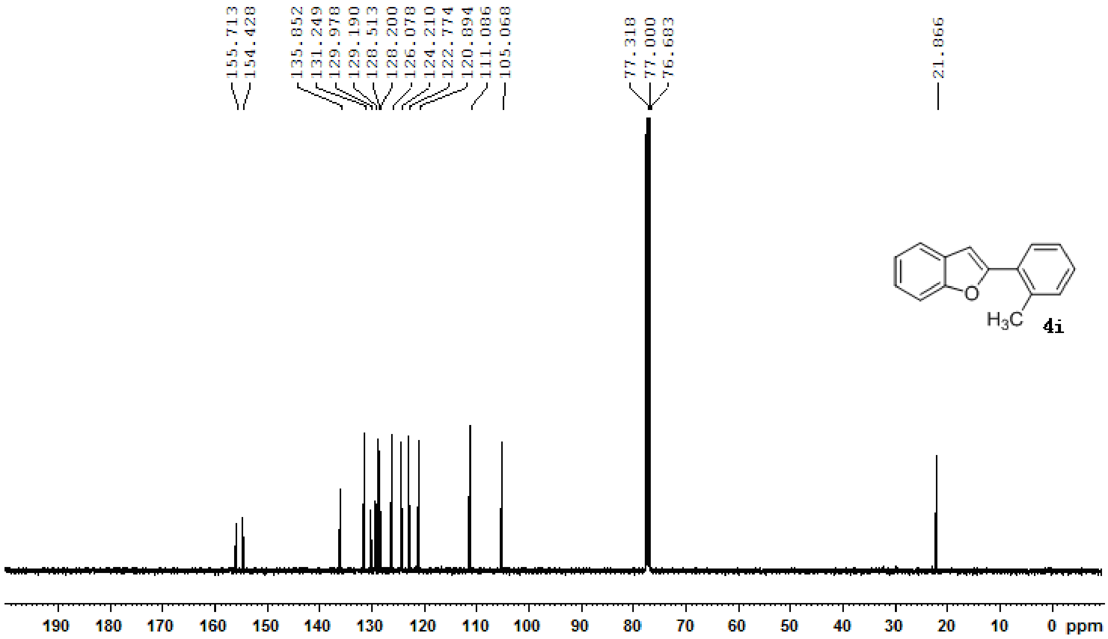
7.295
7.280
7.258
7.250
7.240
6.895
2.588
H3C
4i
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.06
4.01
1.09
0.98
2.98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124.210
122.774
120.894
111.086
105.068
77.318
77.000
76.683
21.866
H3C
4i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

5. References

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