Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Elemental sulfur mediated synthesis of benzoxazoles, benzothiazoles and quinoxalines via decarboxylative coupling of 2-hydroxy/mercapto/amino-anilines with cinnamic acids

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TABLE OF CONTENTS

1. General information

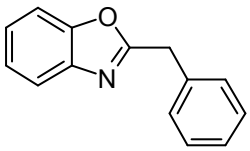
All the reagents were purchased from Sigma-Aldrich, Alfa Aesar, and E. Merck, and were used as received. The reactions were monitored by thin layer chromatography (TLC) using Merck Kieselgel 60 GF 254 plates (thickness 0.25 mm). Visualization of TLC was performed using UV light; products purification was done using Merck silica gel (100-200 mess) column chromatography. NMR spectra were recorded with a 300 or 500 MHz spectrometer for ^{1}H NMR, and 75 or 125 MHz for ^{13}C NMR spectroscopy using $CDCl_3$ solution. HRMS was recorded by using Q-TOF mass spectrometer. Chemical shifts are given in δ ppm and are measured relative to tetramethylsilane (TMS) as internal standard.

2. General procedure for the synthesis of benzoxazoles, benzothiazoles and quinoxalines

2-Hydroxy/mercapto/amino-aniline (1.0 mmol), cinnamic acid/phenylpropiolic acid (1.0 mmol), elemental sulfur (3.0 mmol, 96 mg) and *N*-methylmorpholine (3.0 mmol) were placed in a vial (10 mL) containing a magnetic stirring bar. The vial was capped and the mixture was stirred at 130 °C for 15 h. After the reaction was completed (TLC), the mixture was cooled to room temperature. To it was added ethyl acetate followed by washing with $NaHCO_3$ aq. solution. The organic phase was dried over anhyd Na_2SO_4, filtered, evaporated under reduced pressure and purified by column chromatography using n-hexane and ethyl acetate as eluent.

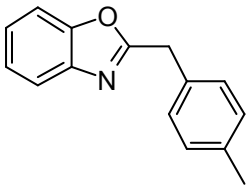
3. Characterization Data of the Products

2-Benzylbenzo[d]oxazole (4a)[1]:



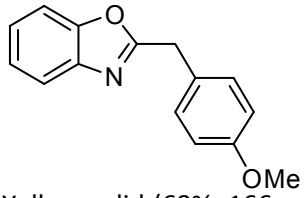
Light yellow solid (72%, 150 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.68-7.65 (m, 1H), 7.39-7.22 (m, 8H), 4.22 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 165.0, 150.9, 141.2, 134.6, 128.8, 128.6, 127.1, 124.5, 124.0, 119.6, 110.3, 35.1.

2-(4-Methylbenzyl)benzo[d]oxazole (4b)[1]:



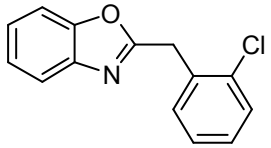
Yellow solid (70%, 156 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.68 (t, J = 4.0 Hz, 1H), 7.45-7.43 (m, 1H), 7.28-7.26 (m, 4H), 7.15 (d, J = 8.5 Hz, 2H), 4.22 (s, 2H), 2.32 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 165.6, 151.2, 141.5, 137.1, 131.8, 129.6, 129.0, 124.7, 124.2, 119.9, 110.5, 35.0, 21.2

2-(4-Methoxybenzyl)benzo[d]oxazole (4c)[1]:



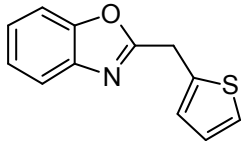
Yellow solid (68%, 166 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.68-7.66 (m, 1H), 7.45-7.30 (m, 1H), 7.28-7.26 (m, 4H), 6.88-6.85 (m, 2H), 4.20 (s, 2H), 3.77 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 165.7, 159.0, 151.1, 141.5, 130.2, 126.9, 124.7, 124.3, 119.9, 114.3, 110.5, 55.4, 34.5.

2-(2-Chlorobenzyl)benzo[d]oxazole (4d)[1]:



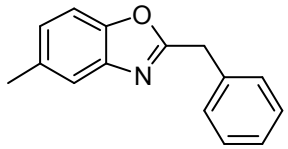
Light yellow solid (65%, 155 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.67 (t, J = 3.9 Hz, 1H), 7.46-7.21 (m, 7H), 4.40 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 165.1, 150.8, 141.2, 134.2, 132.7, 131.0, 129.7, 128.8, 127.1, 124.7, 124.1, 119.8, 110.4, 32.8.

2-(Thiophen-2-ylmethyl)benzo[d]oxazole (4e)[2]:



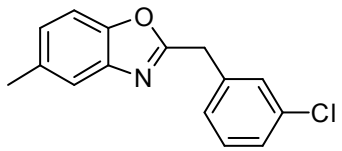
Brown solid (59%, 118 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.62-7.60 (m, 1H), 7.40-7.37 (m, 1H), 7.22-7.12 (m, 3H), 6.95-6.87 (m, 2H), 4.38 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 164.0, 151.0, 141.2, 135.9, 127.1, 126.8, 125.1, 124.8, 124.2, 119.9, 110.5, 32.8.

2-Benzyl-5-methylbenzo[d]oxazole (4f)[1]:



Brown solid (75%, 166 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.45 (s, 1H), 7.35-7.21 (m, 6H), 7.06 (d, J = 8.1, 1H), 4.21 (s, 2H), 2.41 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 165.1, 149.2, 141.4, 134.8, 133.8, 128.9, 128.7, 127.1, 125.6, 119.6, 109.7, 35.2, 21.3.

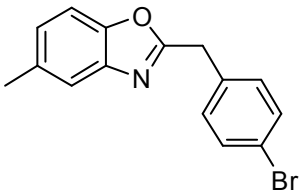
2-(3-Chlorobenzyl)-5-methylbenzo[d]oxazole (4g):



Yellow solid (73%, 162 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.47 (s, 1H), 7.36-7.25 (m, 5H), 7.12 (d, *J* = 8.4, 1H), 4.21 (s, 2H), 2.44 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 164.4, 149.2, 141.4, 136.7, 134.5, 134.1, 130.0, 129.1, 127.6, 127.1, 125.9, 119.8, 109.8, 34.8, 21.4.

HRMS (ESI +): $(M+H)^+$ calcd. For $C_{15}H_{13}ClNO$: 257.0607; Found: 257.0612.

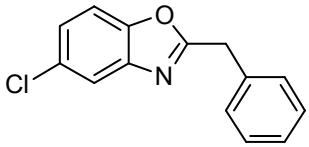
2-(4-Bromobenzyl)-5-methylbenzo[d]oxazole (4h):



Light yellow solid (72%, 216 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.42 (t, *J* = 8.7 Hz, 3H), 7.30-7.18 (m, 3H), 7.06 (d, *J* = 8.1, 1H), 4.14 (s, 2H), 2.40 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 164.3, 149.1, 141.3, 133.9, 133.6, 131.7, 130.5, 125.7, 121.1, 119.6, 109.6, 34.4, 21.1.

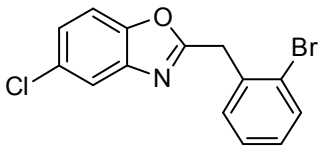
HRMS (ESI +): $(M+H)^+$ calcd. For $C_{15}H_{13}BrNO$: 302.0175; Found: 302.0176.

2-Benzyl-5-chlorobenzo[d]oxazole (4i)[1]:



Light yellow solid (66%, 166 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.65 (s, 1H), 7.33 (bs, 7H), 4.23 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 166.6, 149.5, 142.4, 134.3, 129.6, 128.8, 127.4, 124.9, 124.1, 119.7, 111.1, 35.1.

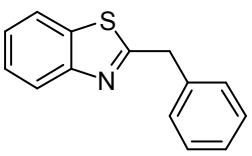
2-(2-Bromobenzyl)-5-chlorobenzo[d]oxazole (4j):



Light yellow solid (61%, 160 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.90-7.46 (m, 2H), 7.40-7.17 (m, 5H), 4.43 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 165.6, 149.5, 133.2, 133.1, 129.3, 129.1, 127.8, 125.1, 124.7, 124.2, 119.9, 111.2, 110.1, 35.5.

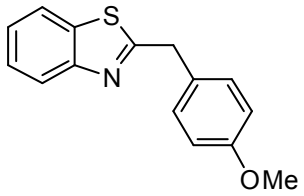
HRMS (ESI +): $(M+H)^+$ calcd. For $C_{14}H_{10}BrClNO$: 321.9629; Found: 321.9731.

2-Benzylbenzo[d]thiazole (5a)[3]:



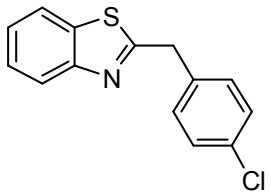
Yellow solid (71%, 159 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.8, 1H), 7.46-7.24 (m, 7H), 4.43 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.2, 153.2, 137.1, 135.6, 129.1, 128.8, 127.3, 125.9, 124.8, 122.6, 121.2, 40.6.

2-(4-Methoxybenzyl)benzo[d]thiazole (5b)[3]:



Light yellow solid (69%, 175mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.1, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.45-7.24 (m, 5H), 6.89 (d, *J* = 8.4, 2H), 4.36 (s, 2H), 3.78 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 172.0, 158.8, 153.3, 135.6, 130.2, 129.2, 125.9, 124.7, 122.7, 121.5, 114.2, 55.2, 39.7.

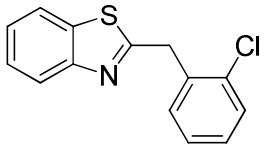
2-(4-Chlorobenzyl)benzo[d]thiazole (5c):



Yellow solid (70%, 181 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 7.8, 1H), 7.48-7.25 (m, 6H), 4.40 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 170.3, 153.2, 146.2, 135.6, 133.3, 130.4, 129.0, 126.1, 125.0, 122.8, 121.5, 39.8.

HRMS (ESI +): $(M+H)^+$ calcd. For $C_{14}H_{11}ClNS$: 260.0295; Found: 260.0289.

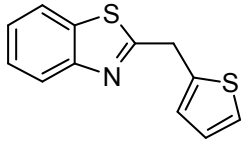
2-(2-Chlorobenzyl)benzo[d]thiazole (5d):



Yellow solid (66%, 170 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.5, 1H), 7.43-7.20 (m, 6H), 4.54 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 169.4, 153.0, 135.4, 134.9, 134.1, 131.2, 129.7, 128.8, 127.1, 125.8, 124.7, 122.6, 121.3, 37.9.

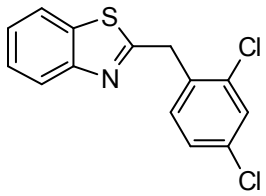
HRMS (ESI +): $(M+H)^+$ calcd. For $C_{14}H_{11}ClNS$: 260.0295; Found: 260.0289.

2-(Thiophen-2-ylmethyl)benzo[d]thiazole (5e)[4]:



Yellow solid (51%, 110 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.8, 1H), 7.50-7.17 (m, 4H), 6.97-6.91 (m, 1H), 4.57 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 170.3, 153.2, 138.6, 127.2, 127.0, 126.8, 126.0, 125.3, 125.0, 122.9, 121.6, 34.6.

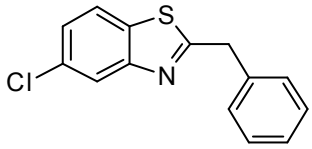
2-(2,4-Dichlorobenzyl)benzo[d]thiazole (5f):



Yellow solid (55%, 160 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 8.1, 1H), 7.80 (d, *J* = 8.1, 1H), 7.47-7.21 (m, 5H), 4.52 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 168.7, 153.1, 135.4, 134.9, 134.0, 133.6, 132.0, 129.5, 127.5, 126.0, 125.0, 122.8, 121.5, 37.4.

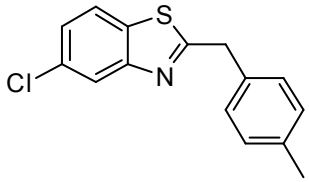
HRMS (ESI +): $(M+H)^+$ calcd. For $C_{14}H_{10}Cl_2NS$: 293.9906; Found: 293.9898.

2-Benzyl-5-chlorobenzo[d]thiazole (5g)[4]:



Yellow solid (67%, 173 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.95 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.34-7.28 (m, 6H), 4.39 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 173.2, 154.1, 136.7, 133.8, 131.9, 129.1, 128.8, 127.4, 125.2, 122.6, 122.1, 40.6.

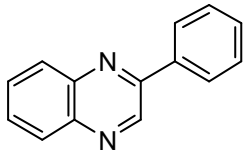
5-Chloro-2-(4-methylbenzyl)benzo[d]thiazole (5h):



Yellow solid (64%, 174 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.93 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.23-7.10 (m, 5H), 4.33 (s, 2H), 2.30 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 173.5, 154.0, 137.0, 133.8, 133.7, 131.7, 129.4, 128.9, 125.0, 122.5, 122.0, 40.1, 21.0.

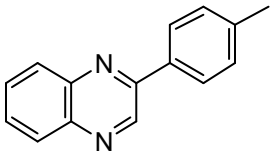
HRMS (ESI +): $(M+H)^+$ calcd. For $C_{15}H_{13}ClNS$: 274.0452; Found: 274.0463.

2-Phenylquinoxaline (7a)[5]:



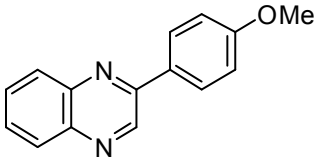
Light yellow solid (67%, 138 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 9.31 (s, 1H), 8.19-8.09 (m, 4H), 7.77-7.72 (m, 2H), 7.56-7.50 (m, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 151.8, 143.3, 143.2, 142.2, 141.5, 136.7, 130.2, 130.1, 129.6, 129.5, 129.1, 127.5.

2-(p-Tolyl)quinoxaline (7b)[5]:



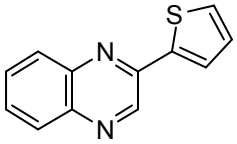
Yellow solid (65%, 143 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.31 (s, 1H), 8.15-8.09 (m, 3H), 7.92-7.90 (m, 1H), 7.77-7.72 (m, 2H), 7.37-7.36 (m, 2H), 2.45 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 151.9, 143.4, 142.4, 141.5, 140.6, 134.1, 130.3, 130.0, 129.6, 129.4, 129.2, 127.5, 21.5.

2-(4-Methoxyphenyl)quinoxaline (7c)[5]:



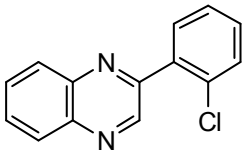
Yellow solid (61%, 144 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.29 (s, 1H), 8.18-8.16 (m, 2H), 8.12-8.08 (m, 2H), 7.76-7.71 (m, 2H), 7.09-7.07 (m, 2H), 3.90 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 161.6, 151.5, 143.2, 142.2, 141.3, 130.3, 129.5, 129.4, 129.2, 129.1, 129.1, 114.7, 55.5.

2-(Thiophen-2-yl)quinoxaline (7d)[5]:



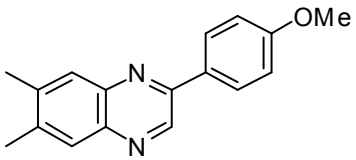
Light yellow solid (55%, 116 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.24 (s, 1H), 8.08-8.07 (m, 2H), 7.87-7.86 (m, 1H), 7.75-7.70 (m, 2H), 7.56-7.55 (m, 1H), 7.22-7.20 (m, 1H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 147.5, 142.5, 142.2, 142.2, 141.4, 130.5, 130.2, 129.9, 129.3, 129.2, 128.6, 127.1.

2-(2-Chlorophenyl)quinoxaline (7e)[5]:



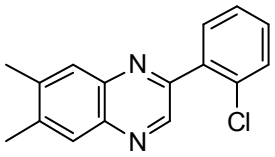
Light yellow solid (58%, 139 mg); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.15 (s, 1H), 8.12-8.10 (m, 2H), 7.76-7.74 (m, 2H), 7.68-7.66 (m, 1H), 7.50-7.48 (m, 1H), 7.41-7.39 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 152.5, 146.3, 142.4, 141.5, 136.6, 132.7, 132.1, 131.5, 130.9, 130.4, 130.3, 129.7, 129.3 127.6.

2-(4-Methoxyphenyl)-6,7-dimethylquinoxaline (7f)[6]:



Yellow solid (56%, 147 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 9.09 (s, 1H), 8.07-8.04 (m, 2H), 7.78-7.74 (m, 2H), 7.00-6.97 (m, 2H), 3.81 (s, 3H), 2.44 (s, 6H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 161.2, 150.6, 142.1, 141.2, 140.6, 142.2, 139.5, 129.7, 128.7, 128.5, 128.1, 114.5, 55.4, 20.3.

2-(2-Chlorophenyl)-6,7-dimethylquinoxaline (7g)[7]:

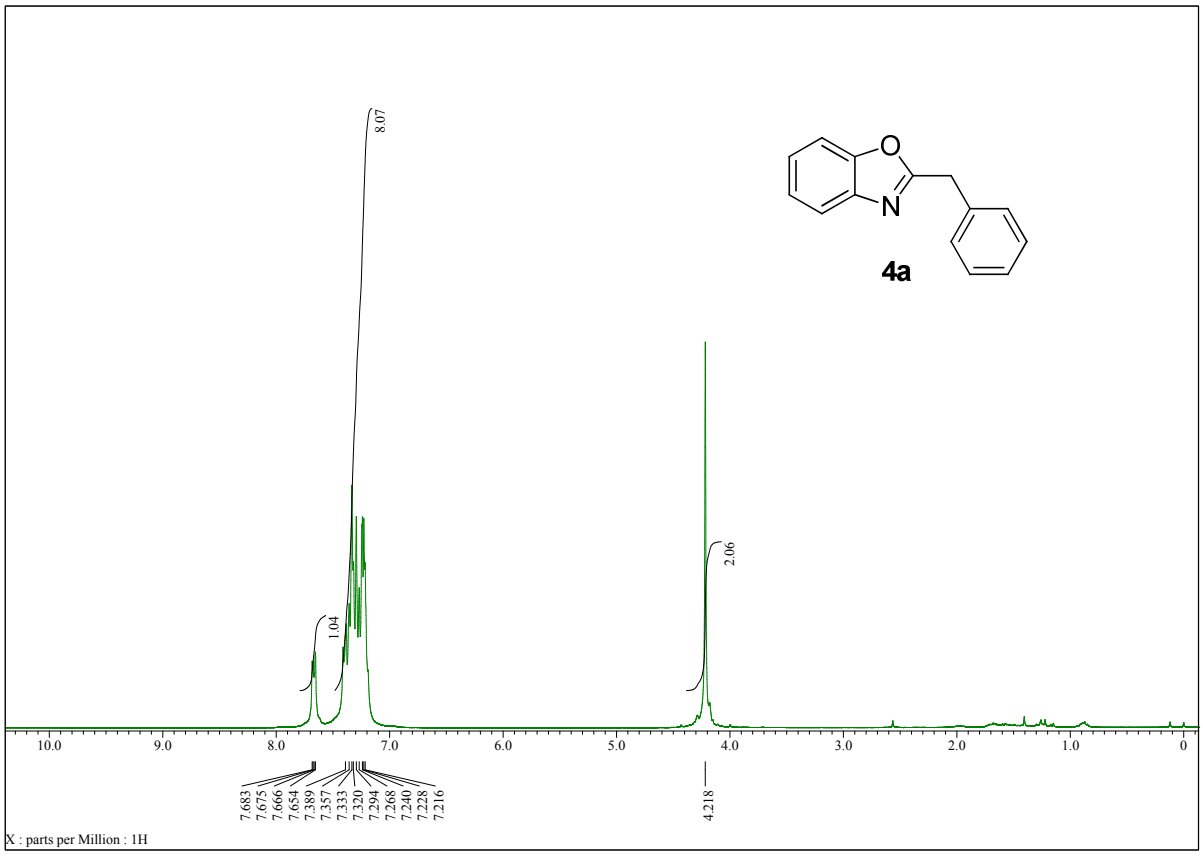


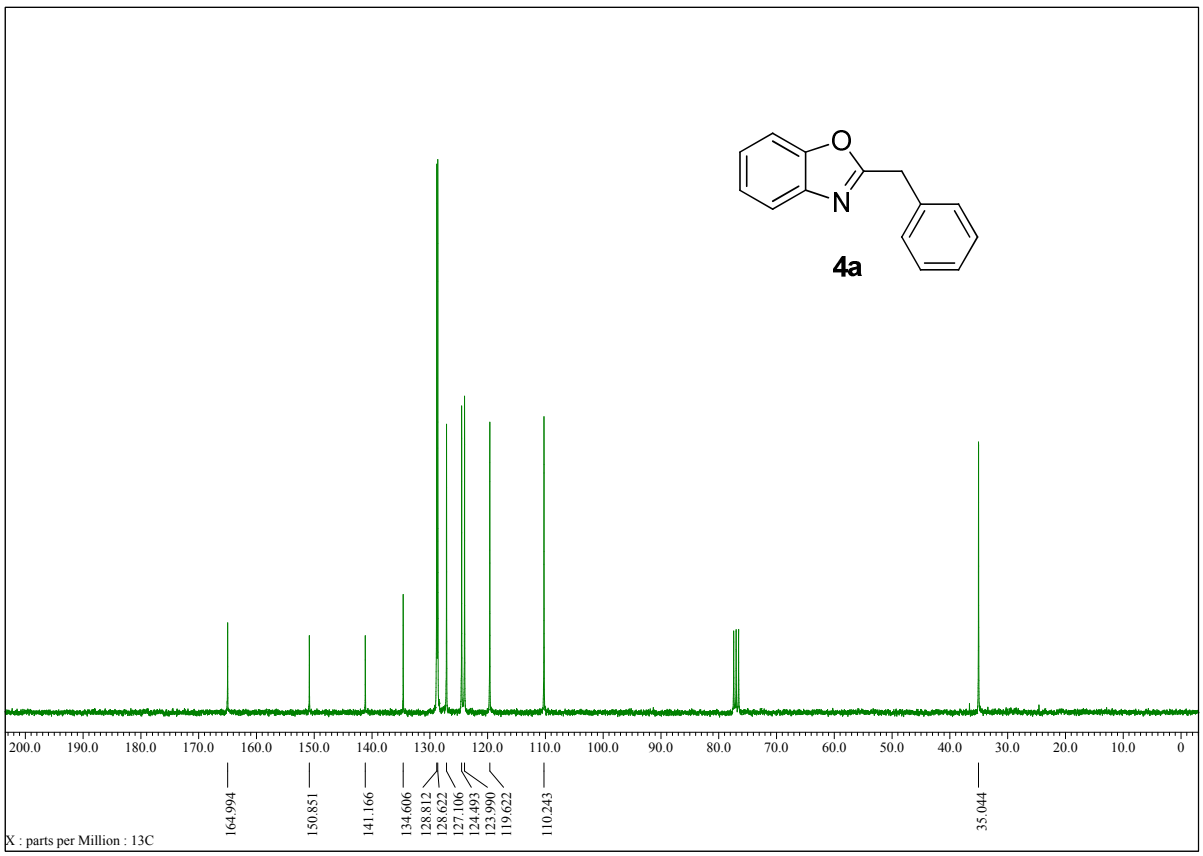
Light yellow solid (54%, 144 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 9.02 (s, 1H), 7.84-7.83 (m, 2H), 7.65-7.62 (m, 1H), 7.48-7.35 (m, 3H), 2.46 (s, 6H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 162.2, 151.4, 141.2, 140.8, 140.8, 136.9, 131.9, 130.5, 130.2, 128.7, 128.6, 128.3, 128.2, 127.4, 20.4.

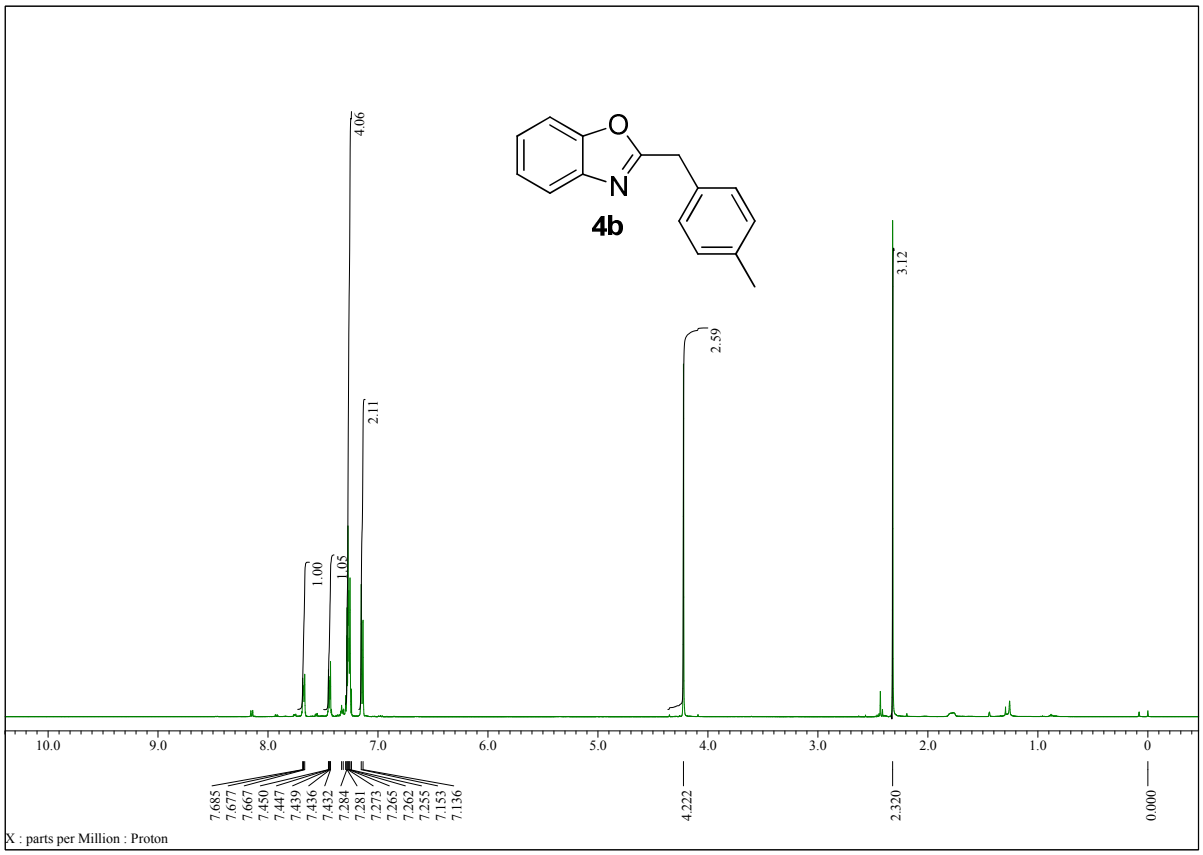
4. References:

1. T. Mukai, K. Hirano, T. Satoh and M. Miura, *Org. Lett*., 2010, **12**, 1360.
2. G. Li, M. Arisawa and M. Yamaguchi, *Chem. Commun*., 2014, **50**, 4328.
3. R. Shang, Z.-W.Yang, Y. Wang, S.-L. Zhang and L. Liu, *J. Am.Chem. Soc*., 2010, **132**, 14391.
4. A. Dos Santos,; L. El Kaim and L. Grimaud, *Org. Biomol. Chem*., 2013, **11**, 3282.
5. T. Chen, Xun. Chen, J. Wei, D. Lin, Y. Xie and Wei. Zeng, *Org. Lett*., 2016, **18**, 2078.
6. M. Lian, Q. Li, Y. Zhu, G. Yin and A. Wu, *Tetrahedron,* 2012, **68**, 9598.
7. T. Huang, Q. Zhang, J. Chen, W. Gao, J. Ding and H. Wu, *J. Chem. Res*. 2009, 761.

5. COPIES OF ^{1}H- & ^{13}C-NMR SPECTRA OF THE PRODUCTS:



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1.00
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10.0
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8.0
7.0
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5.0
4.0
3.0
2.0
1.0
0
7.685
7.677
7.667
7.450
7.447
7.439
7.436
7.432
7.284
7.281
7.273
7.265
7.262
7.255
7.153
7.136
4.222
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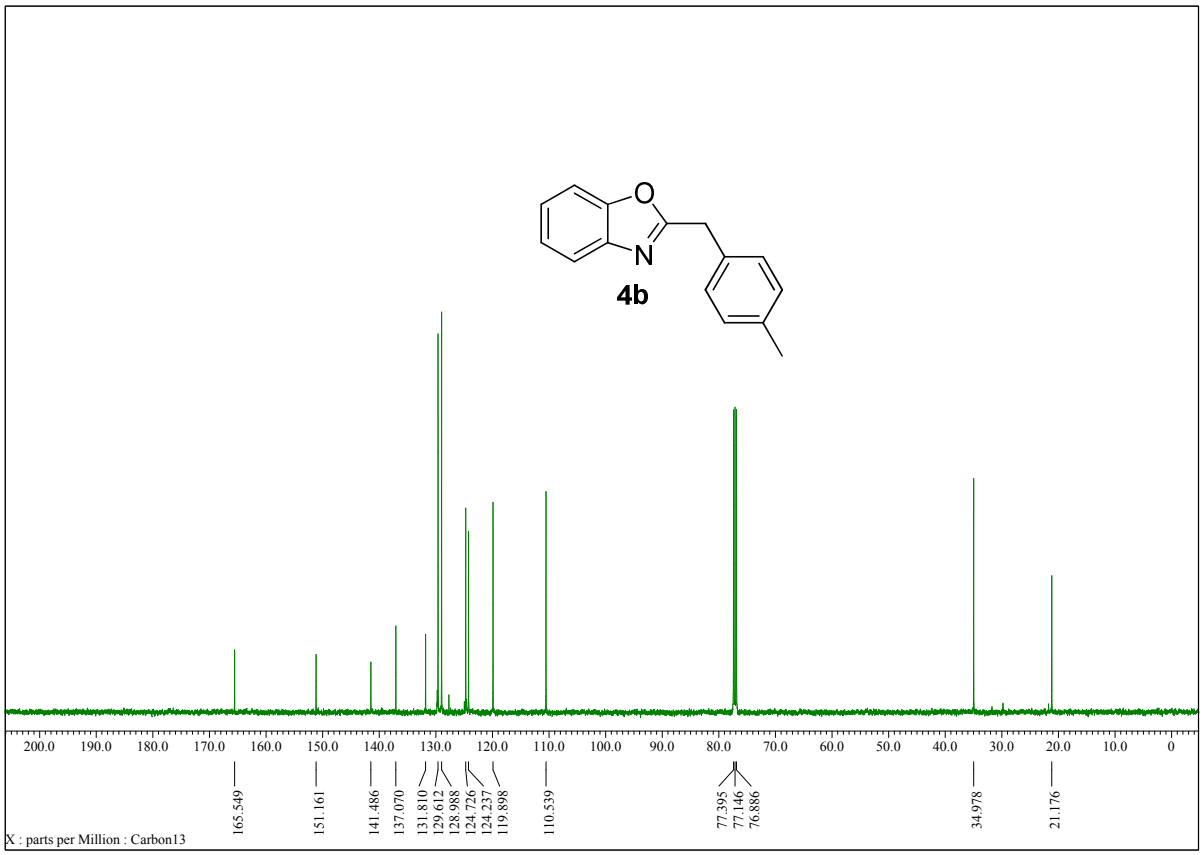
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150.0
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120.0
110.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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151.161
141.486
137.070
131.810
129.612
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124.237
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76.886
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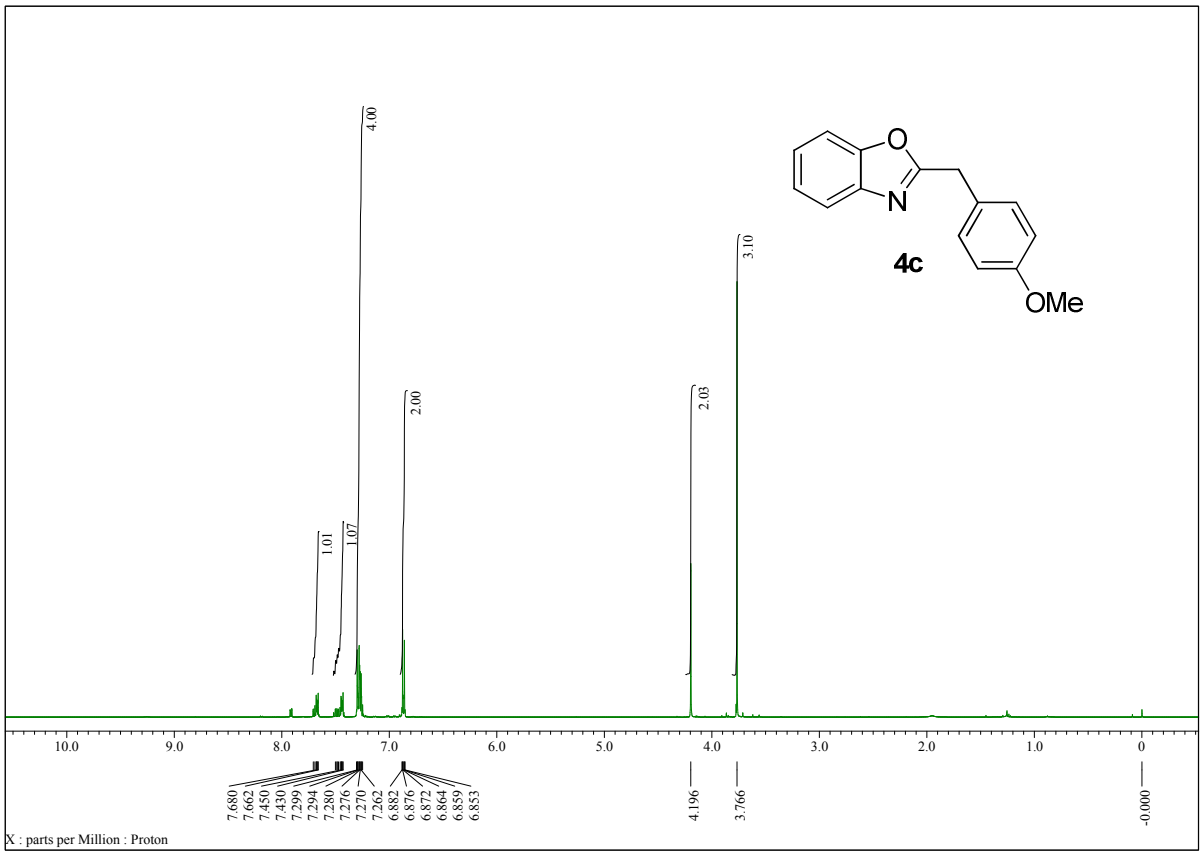
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3.10
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2.03
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1.07
4c
OMe
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.662
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7.430
7.299
7.294
7.280
7.276
7.270
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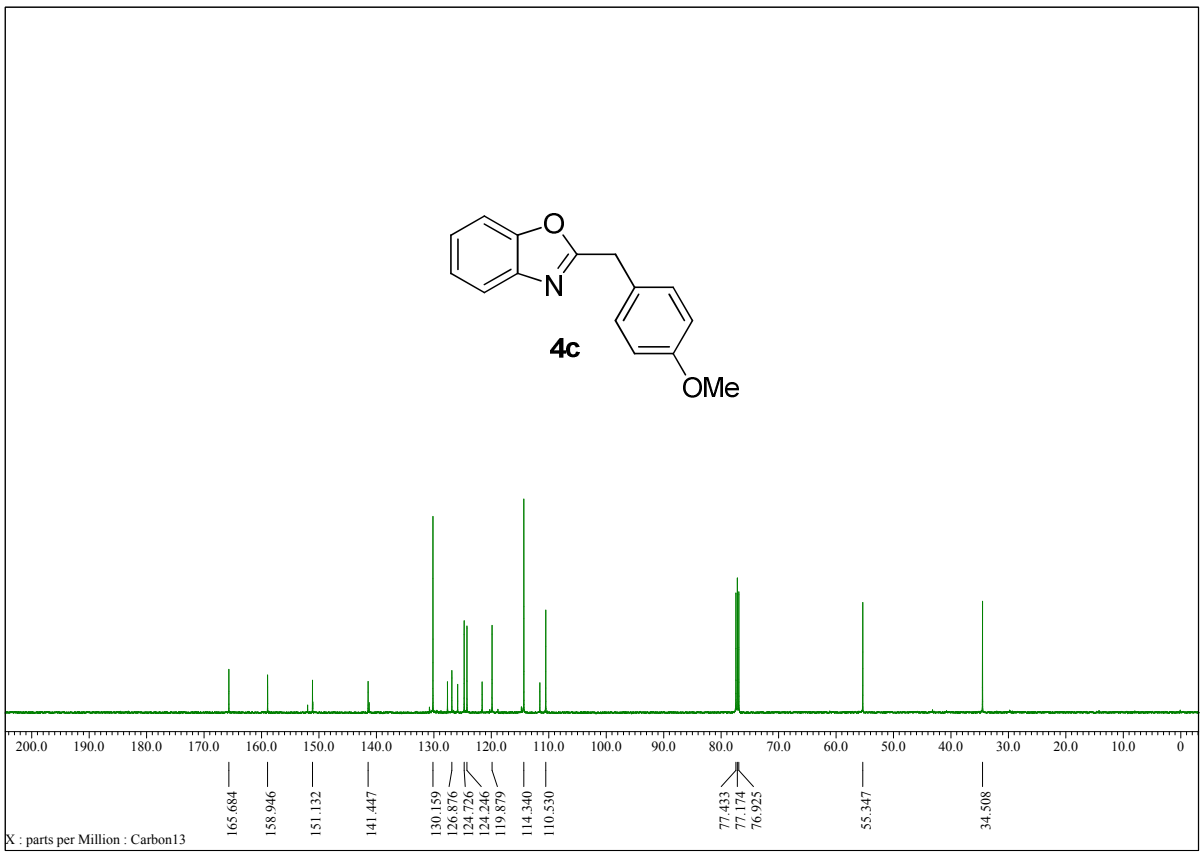
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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158.946
151.132
141.447
130.159
126.876
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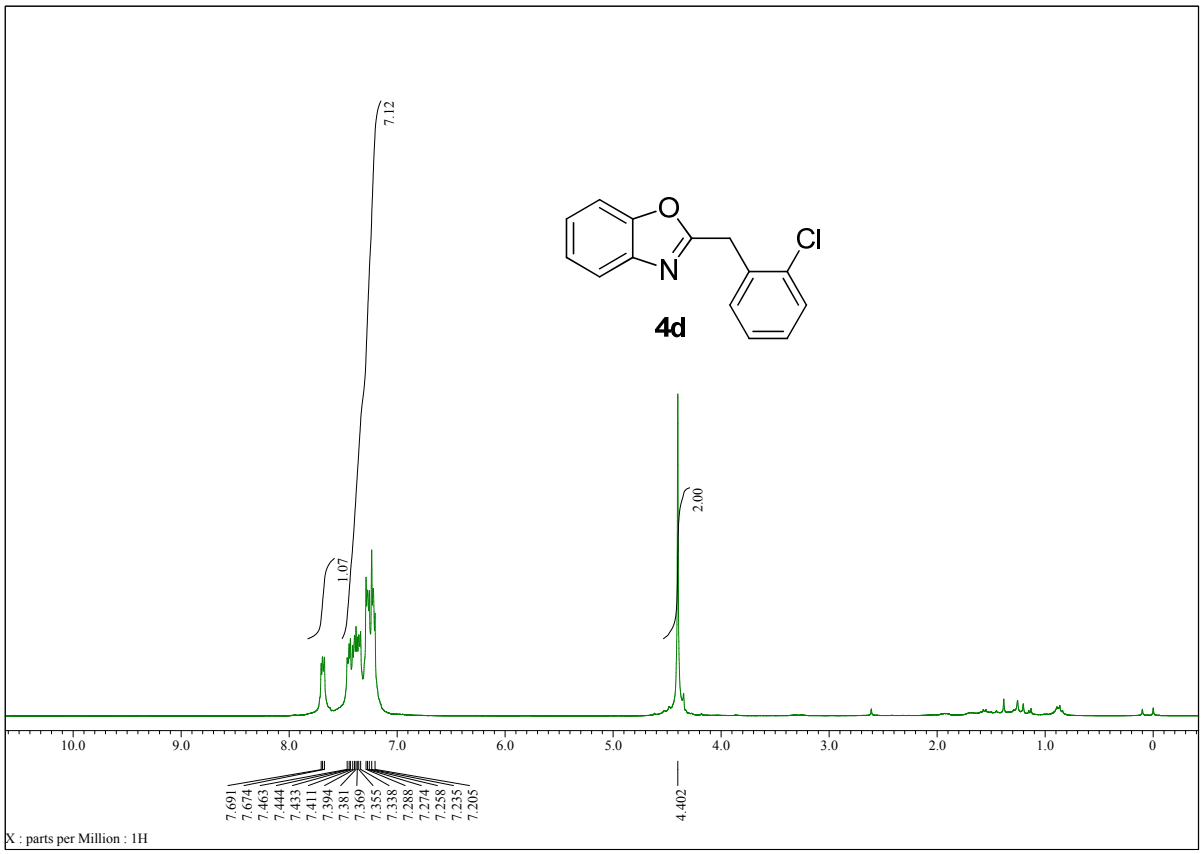
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3.0
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1.0
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7.394
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7.235
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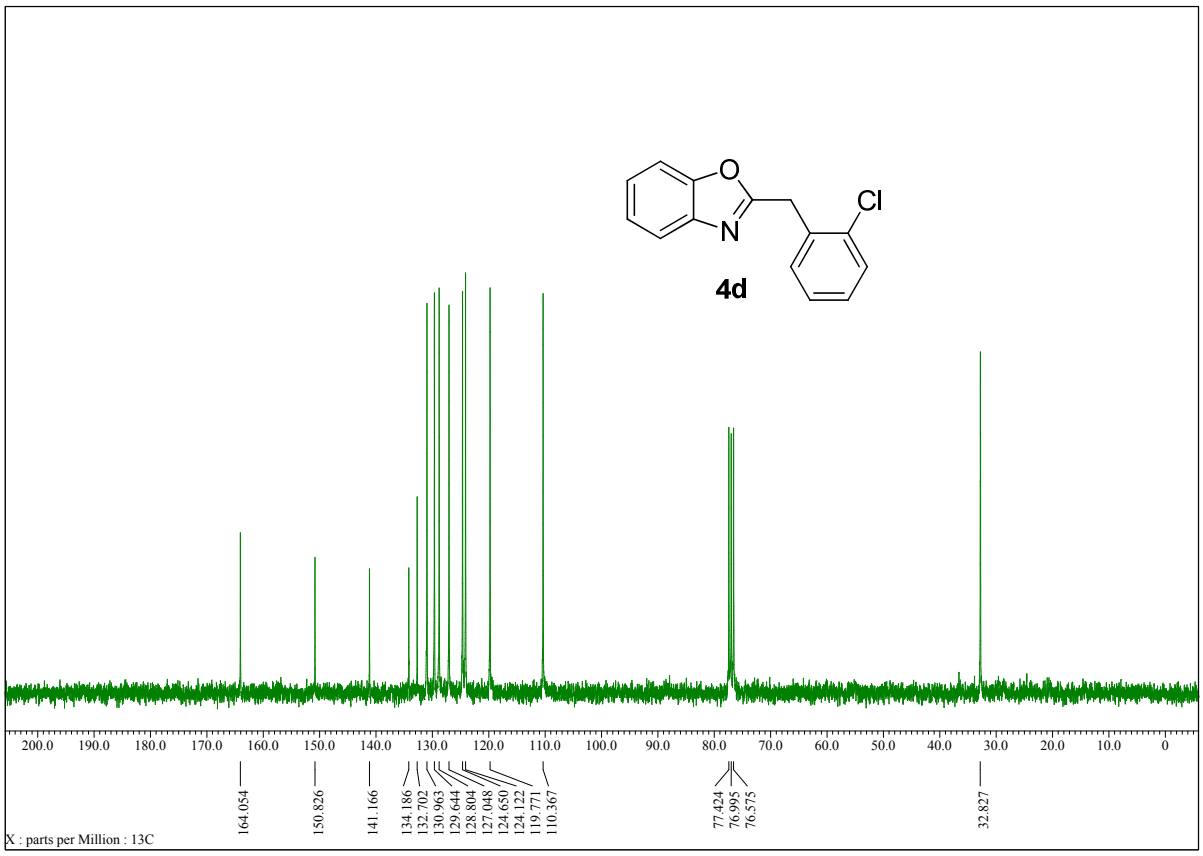
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Cl
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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150.826
141.166
134.186
132.702
130.963
129.644
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76.575
32.827
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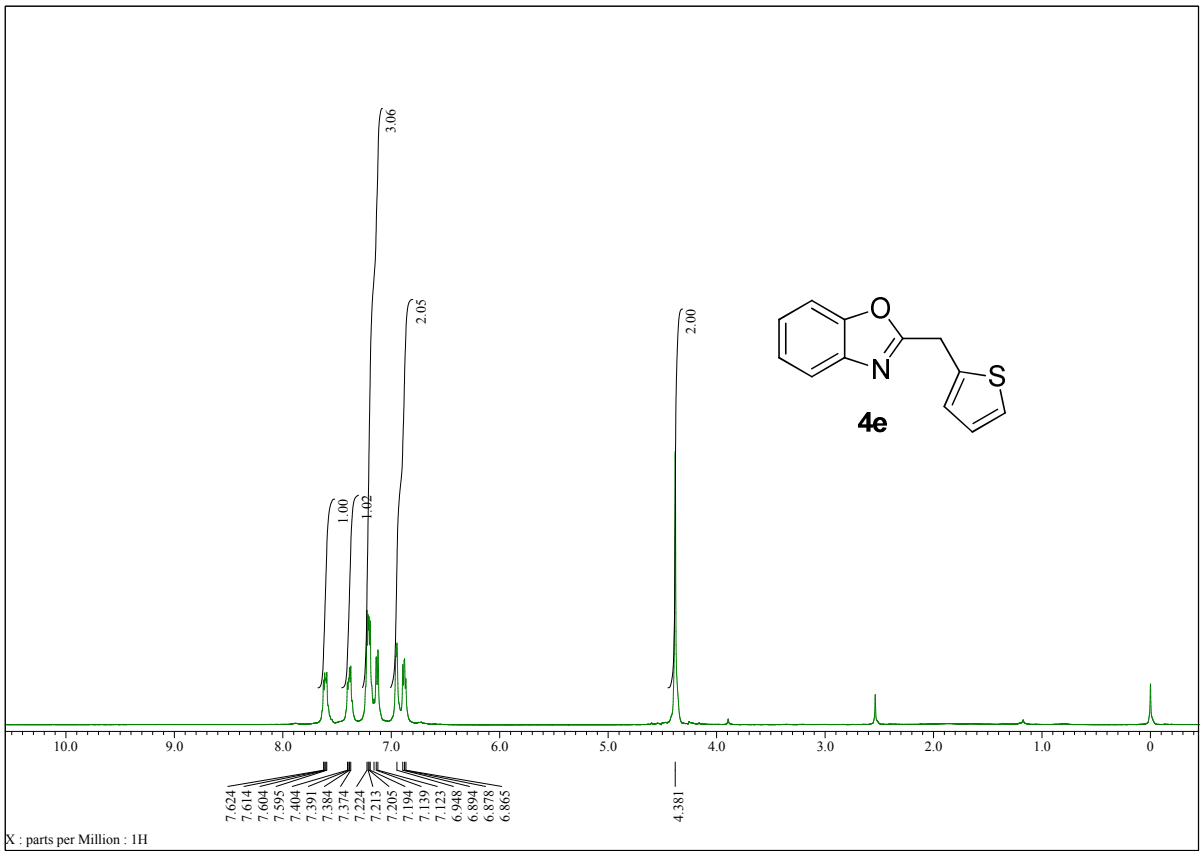
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6.0
5.0
4.0
3.0
2.0
1.0
0
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7.604
7.595
7.404
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7.384
7.374
7.224
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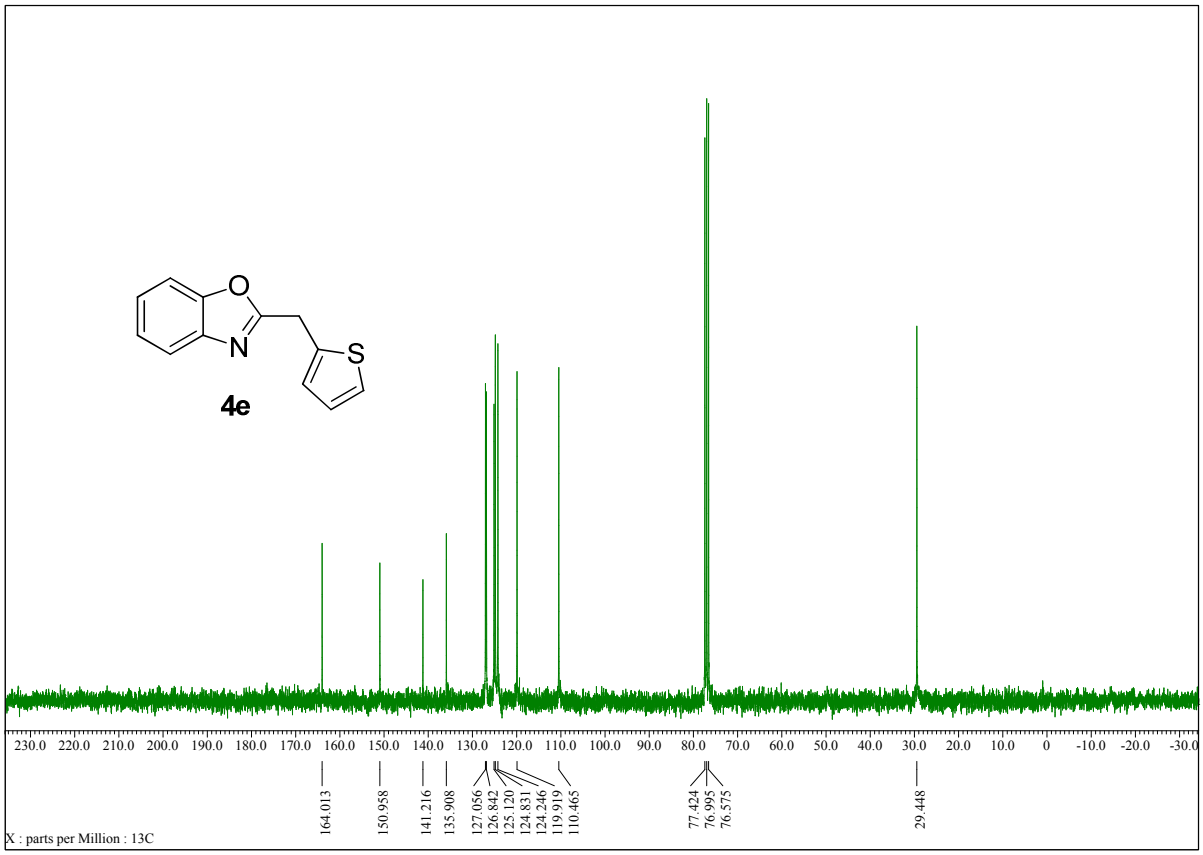
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10.0
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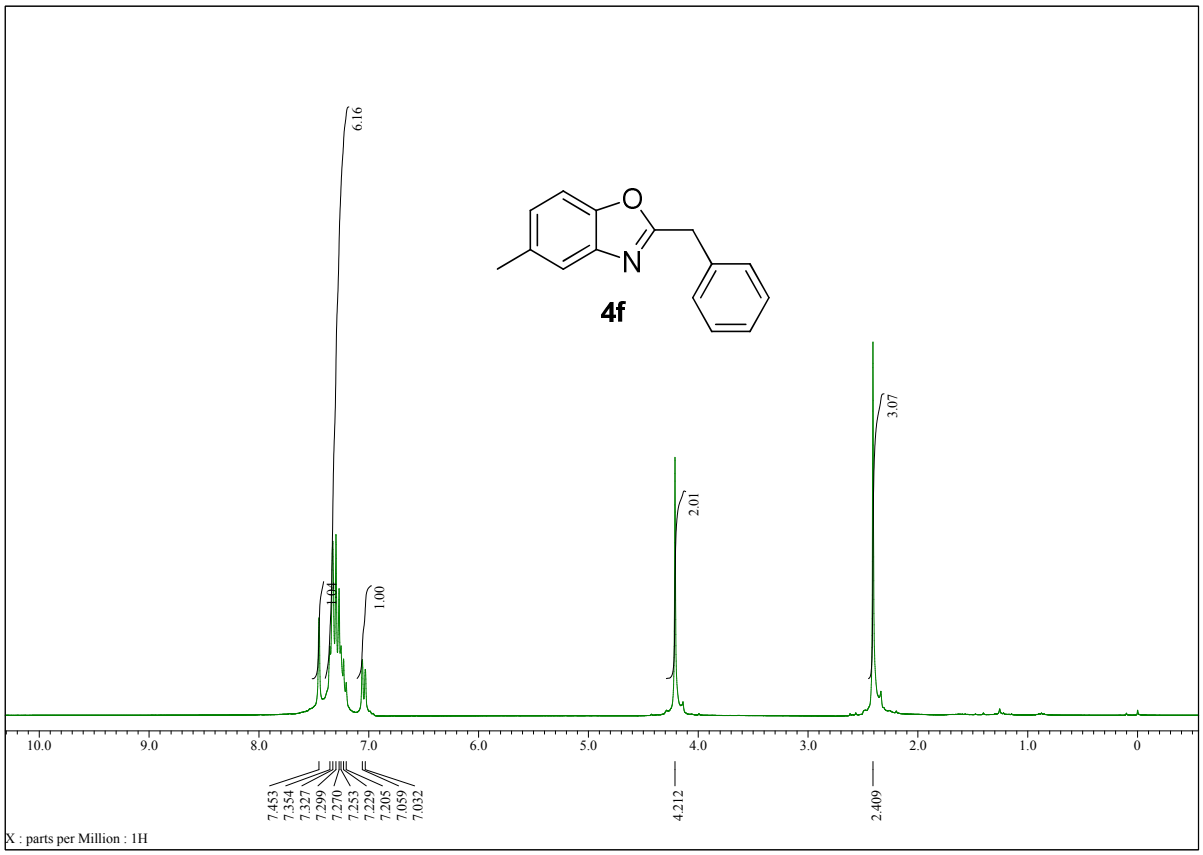
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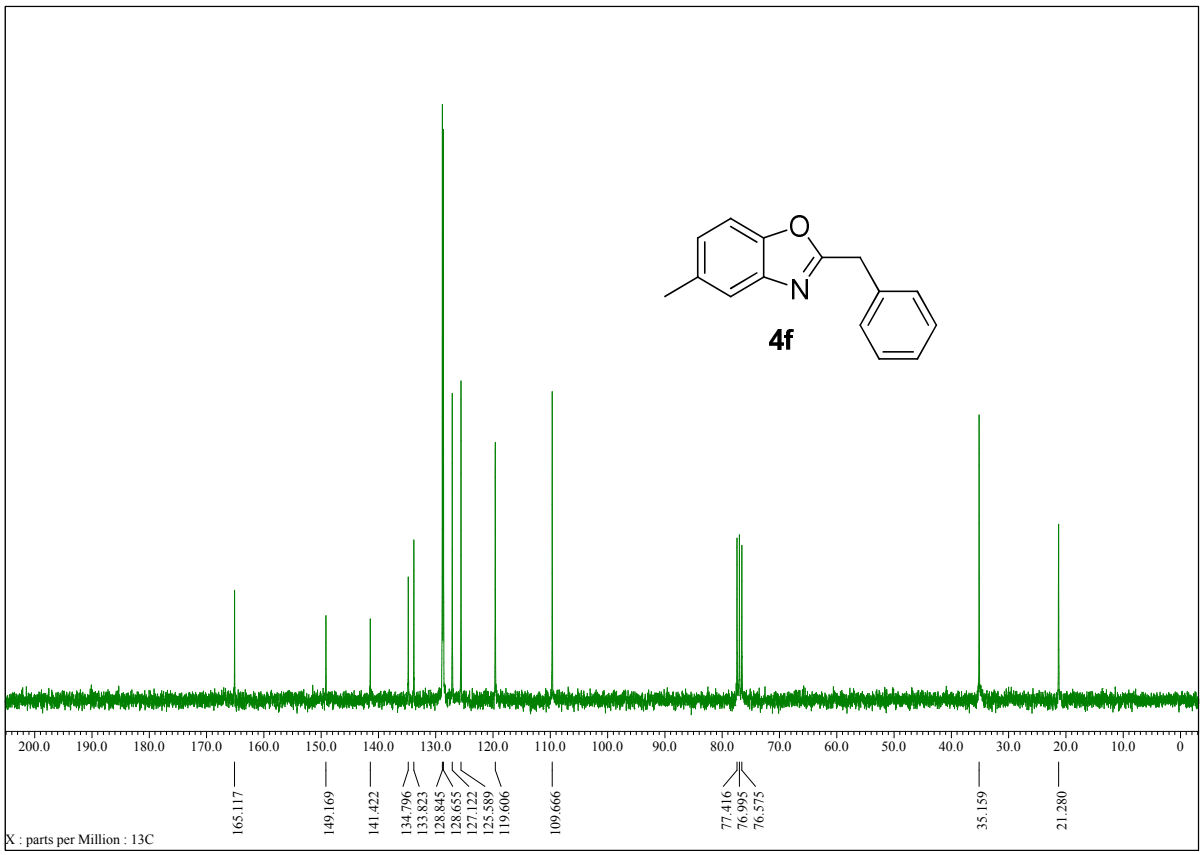
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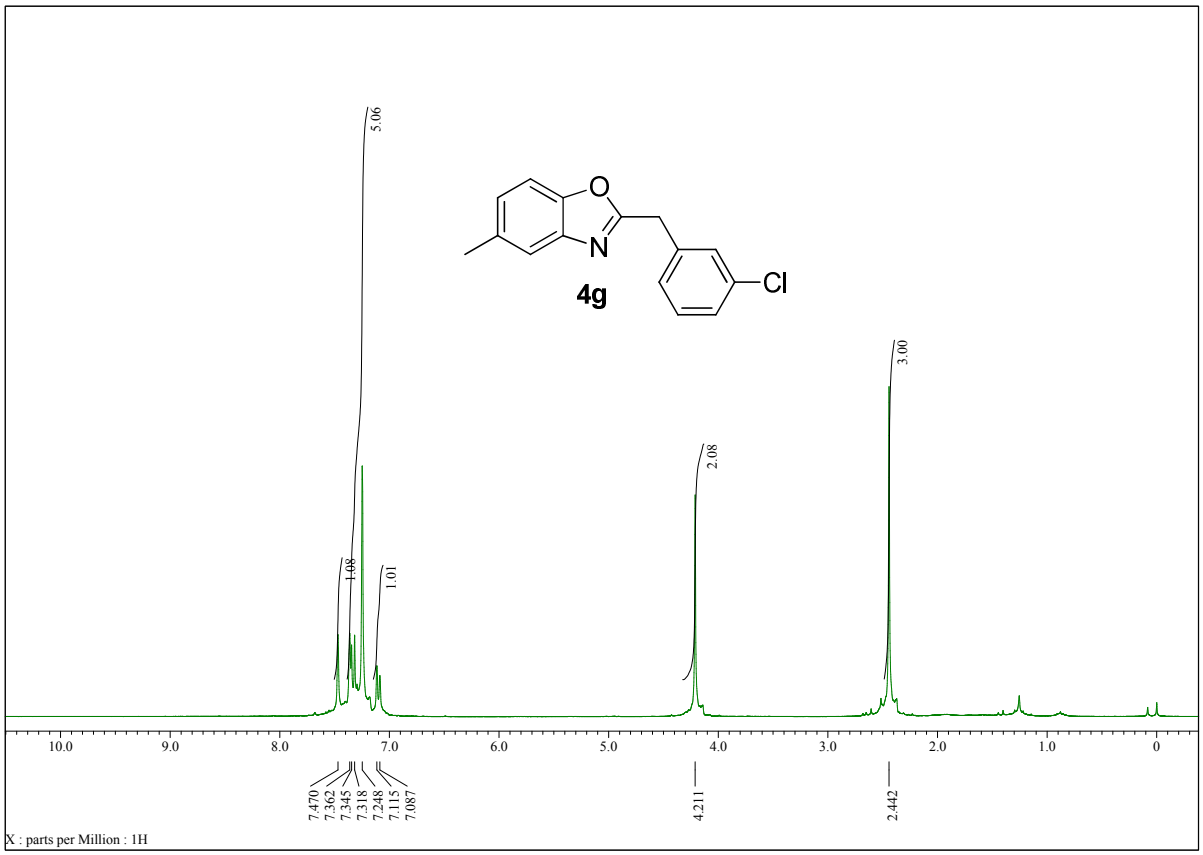
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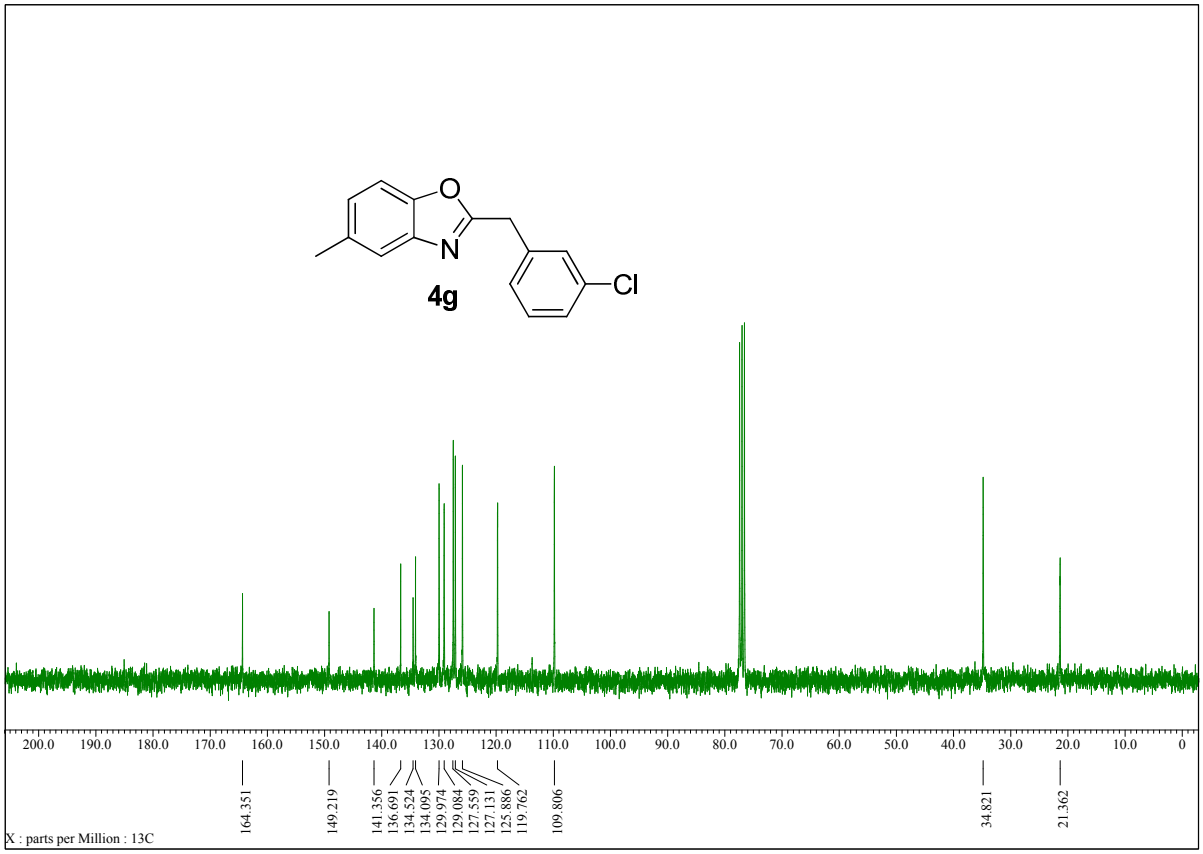
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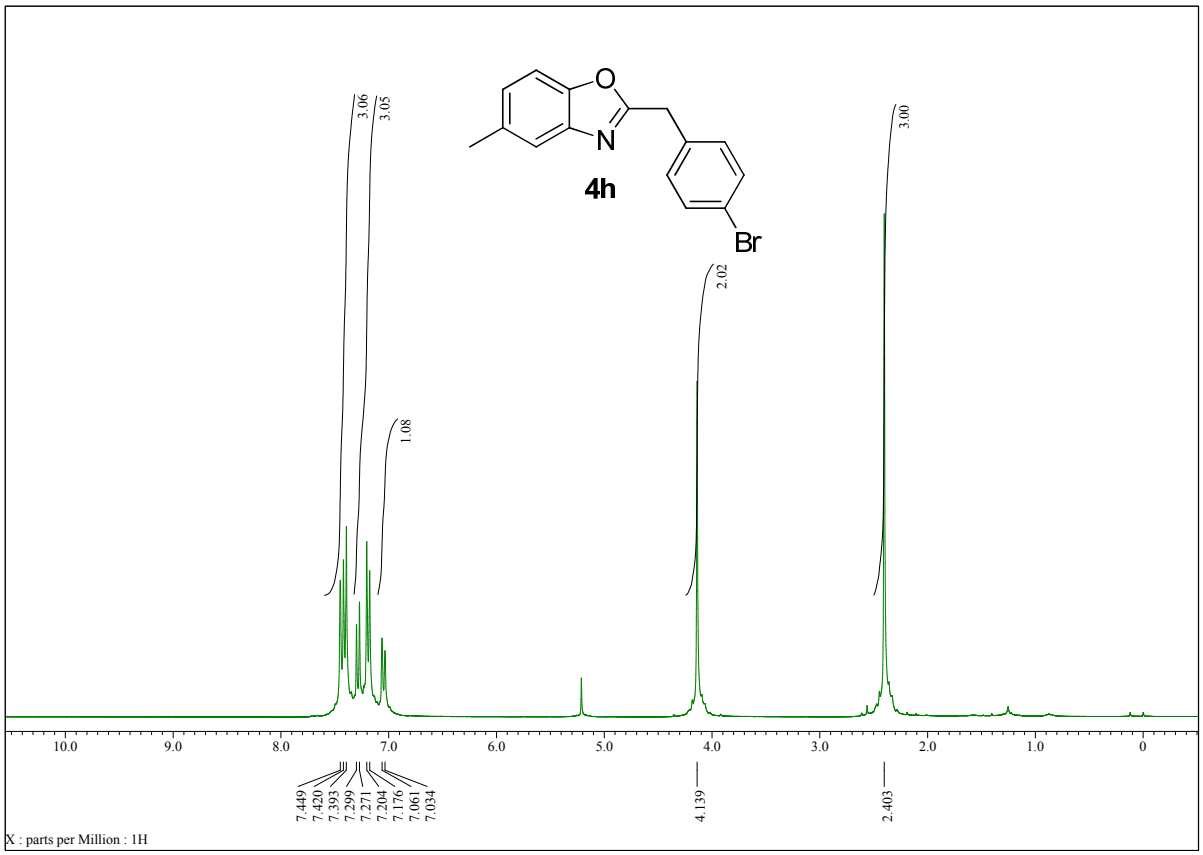
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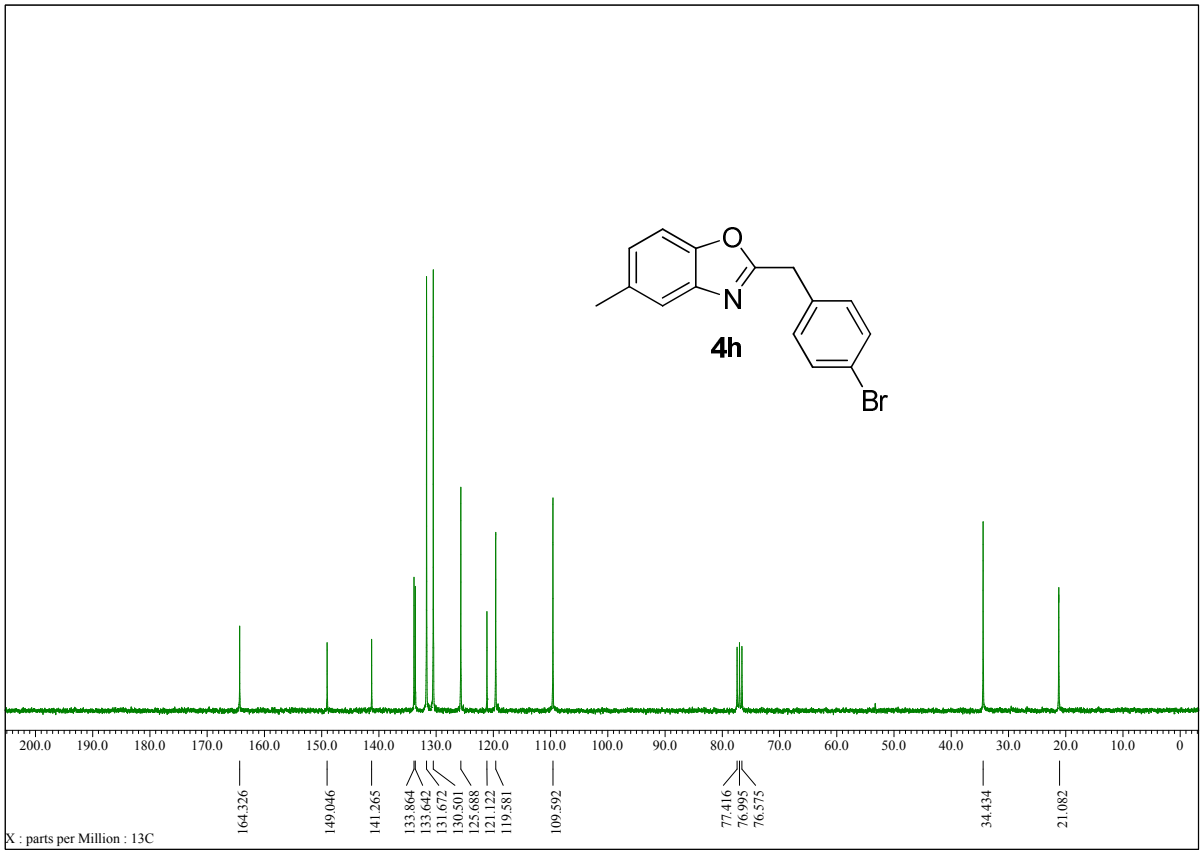
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70.0
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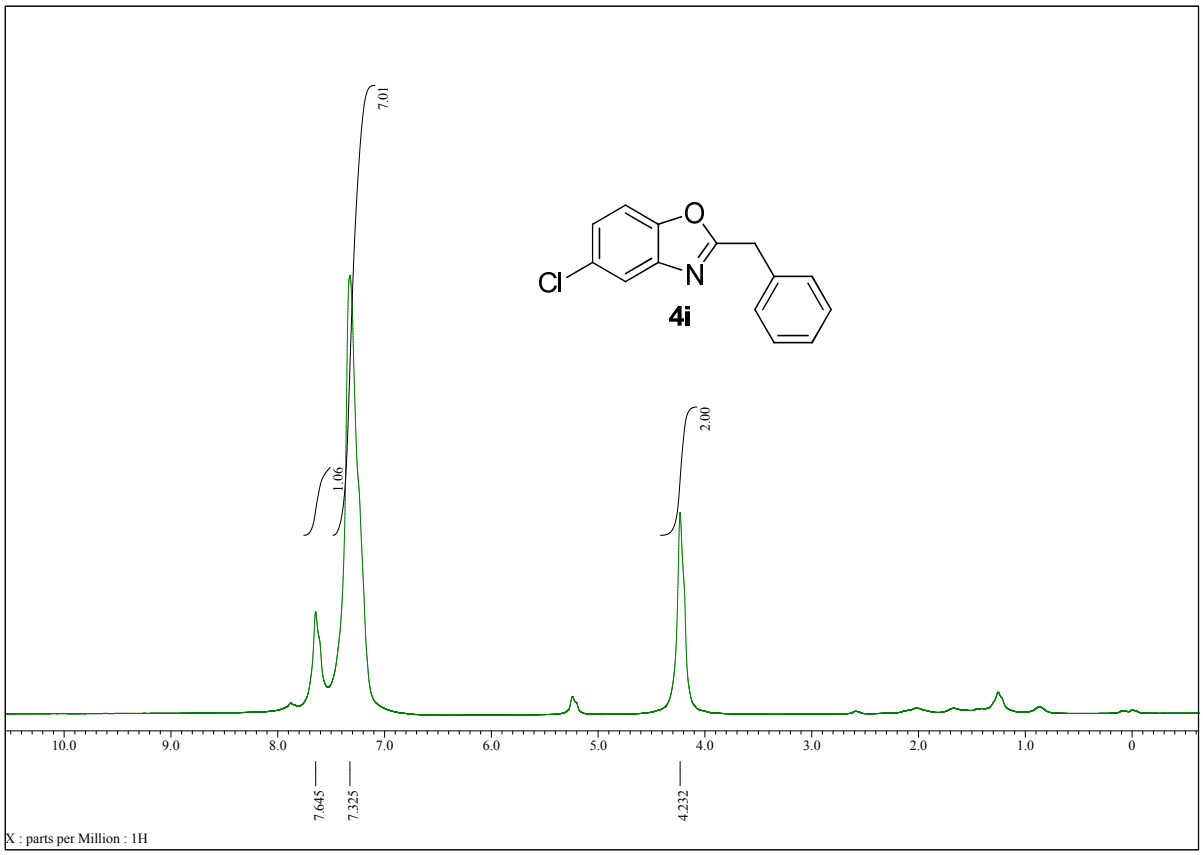
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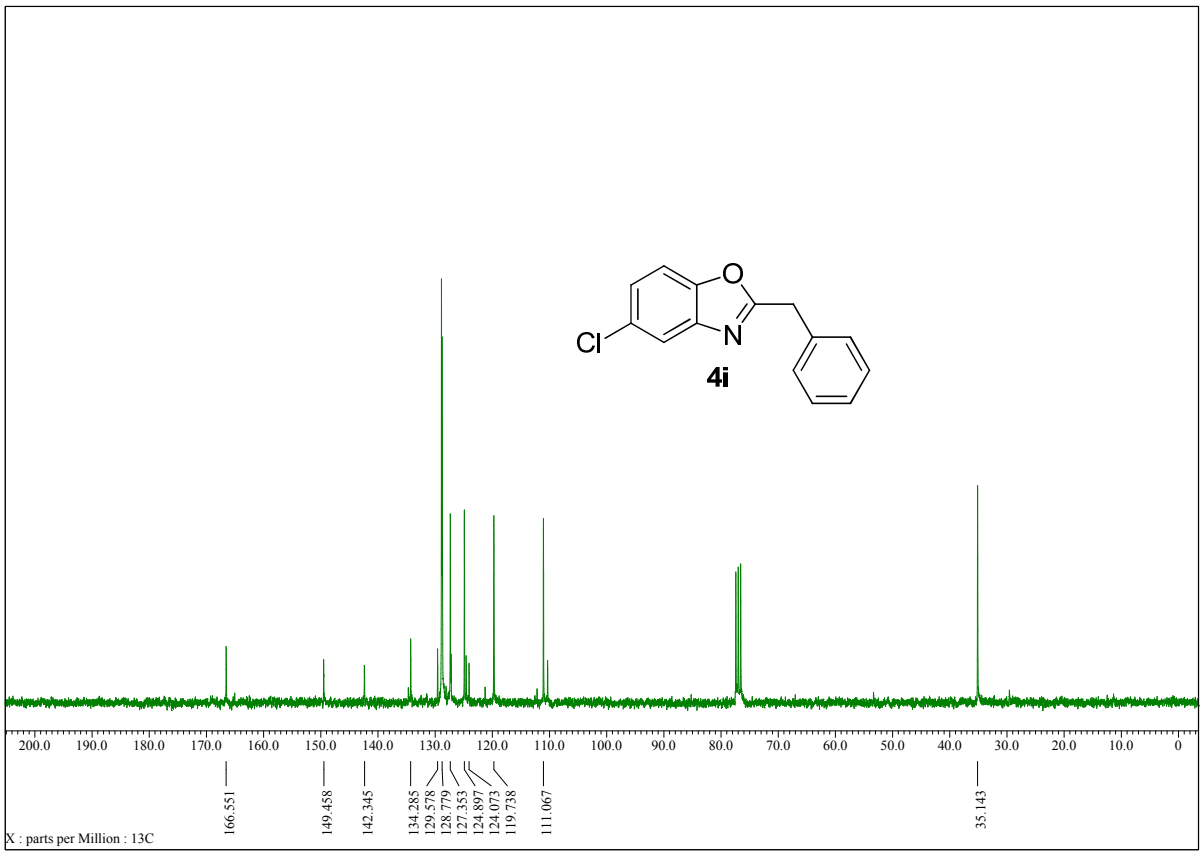
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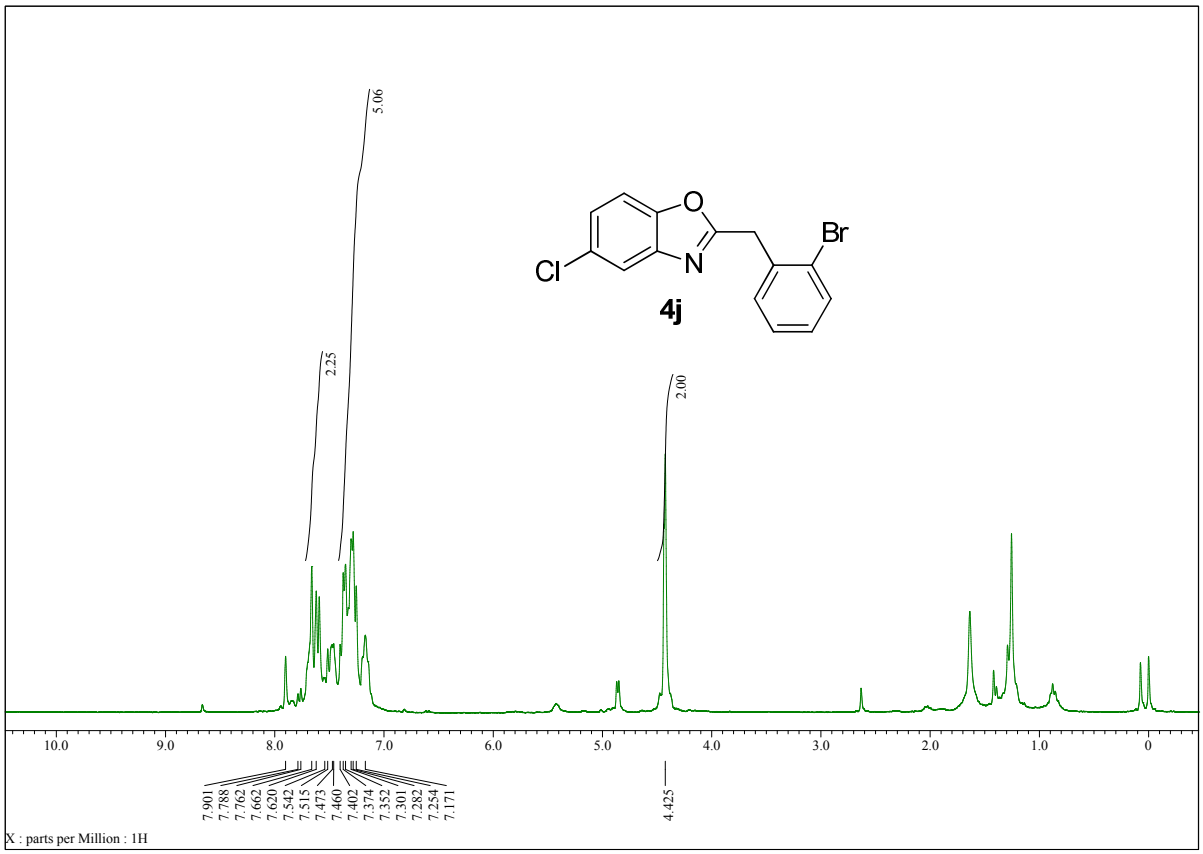
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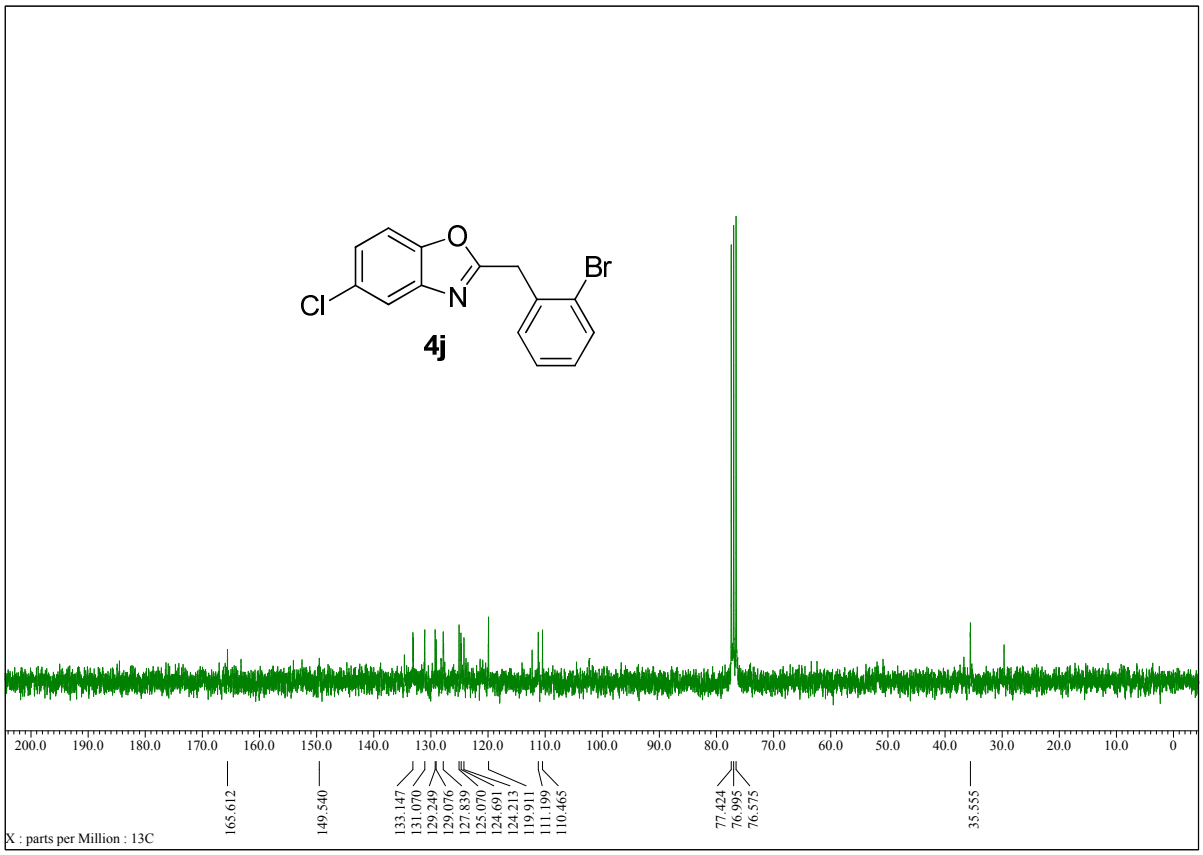
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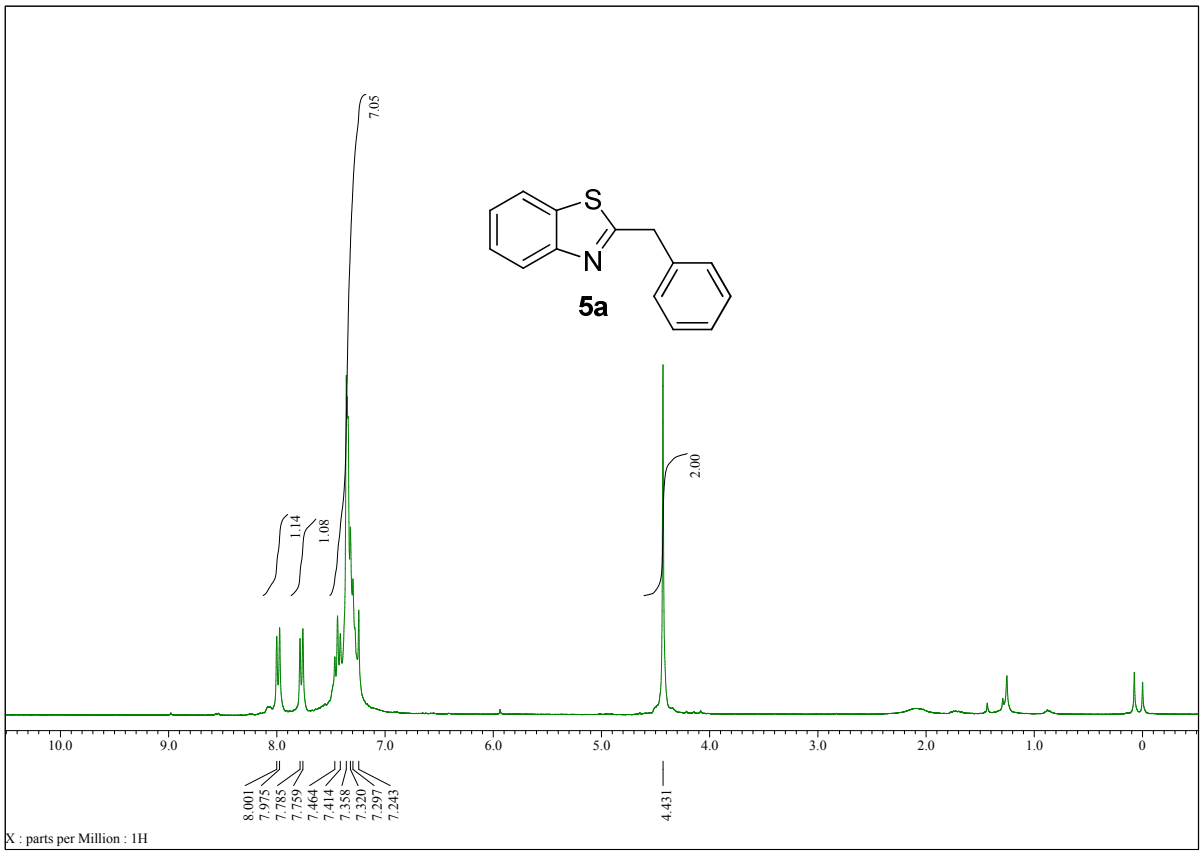
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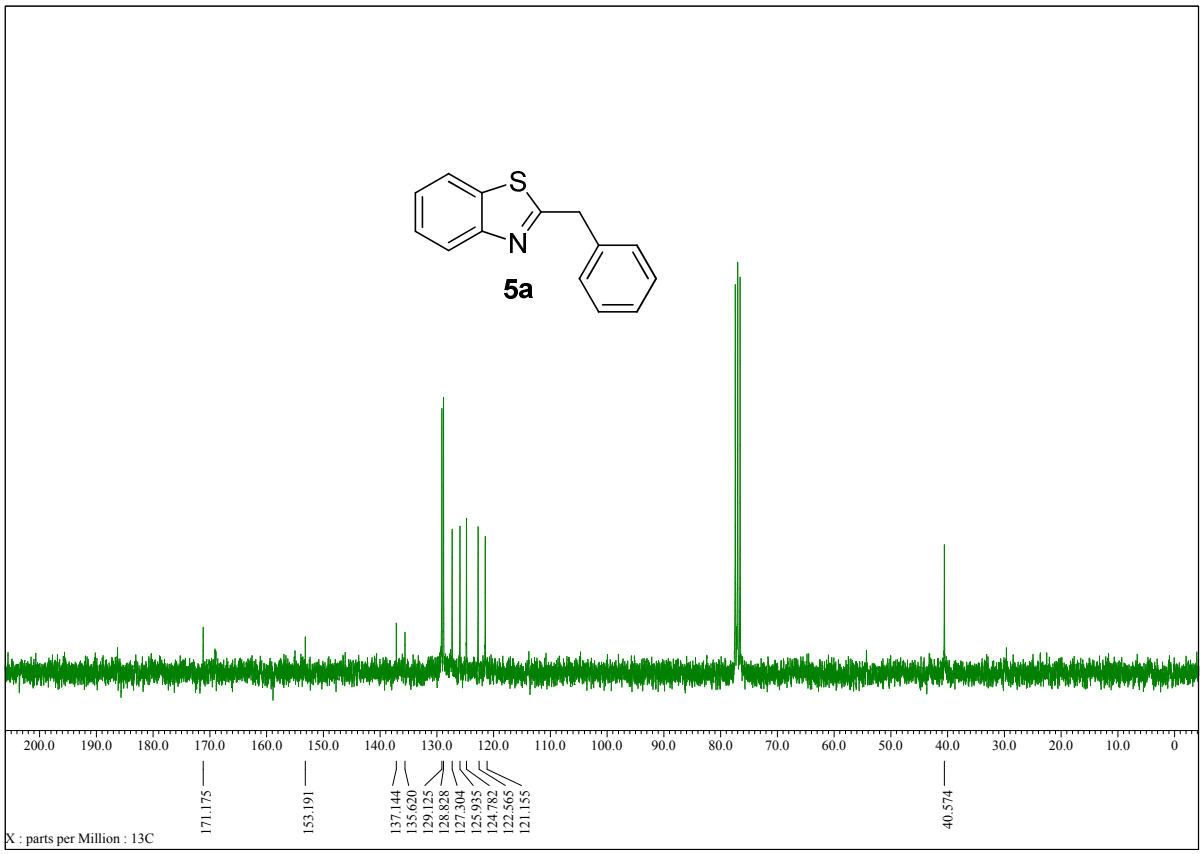
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90.0
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70.0
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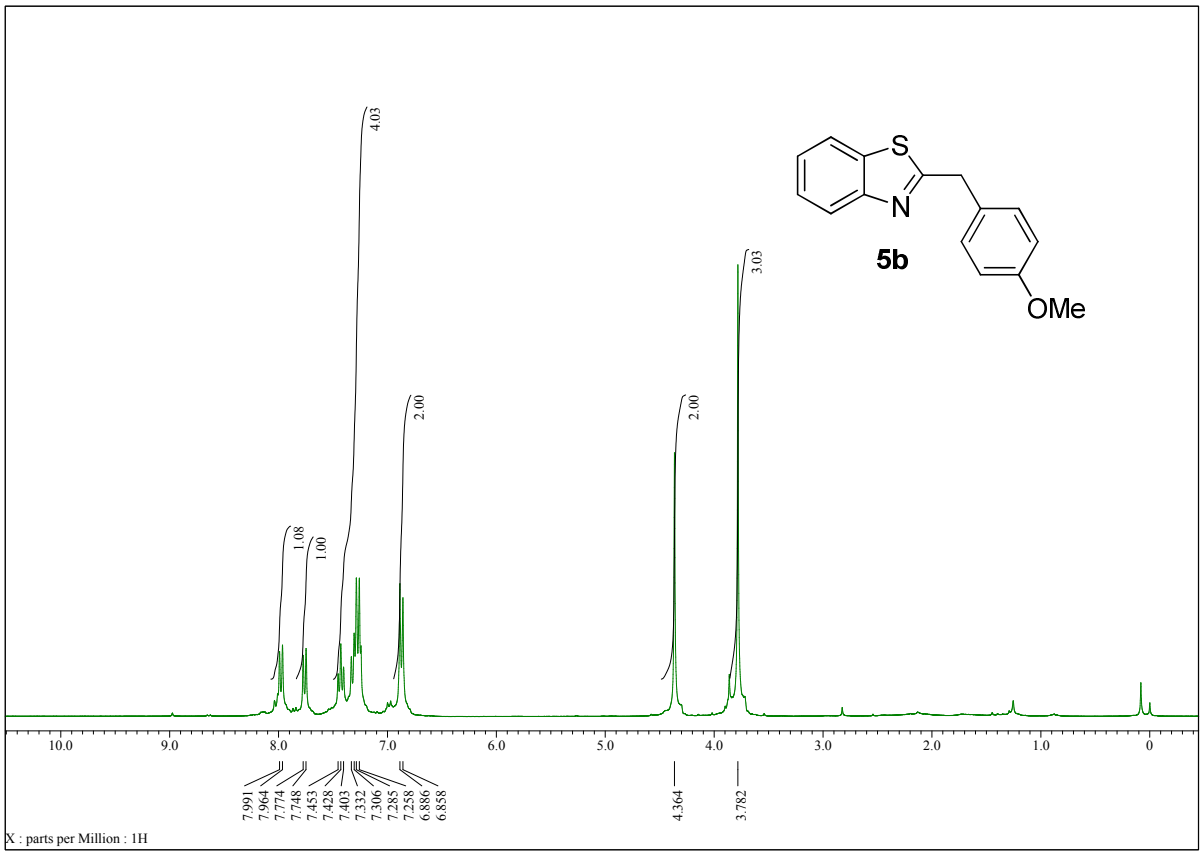
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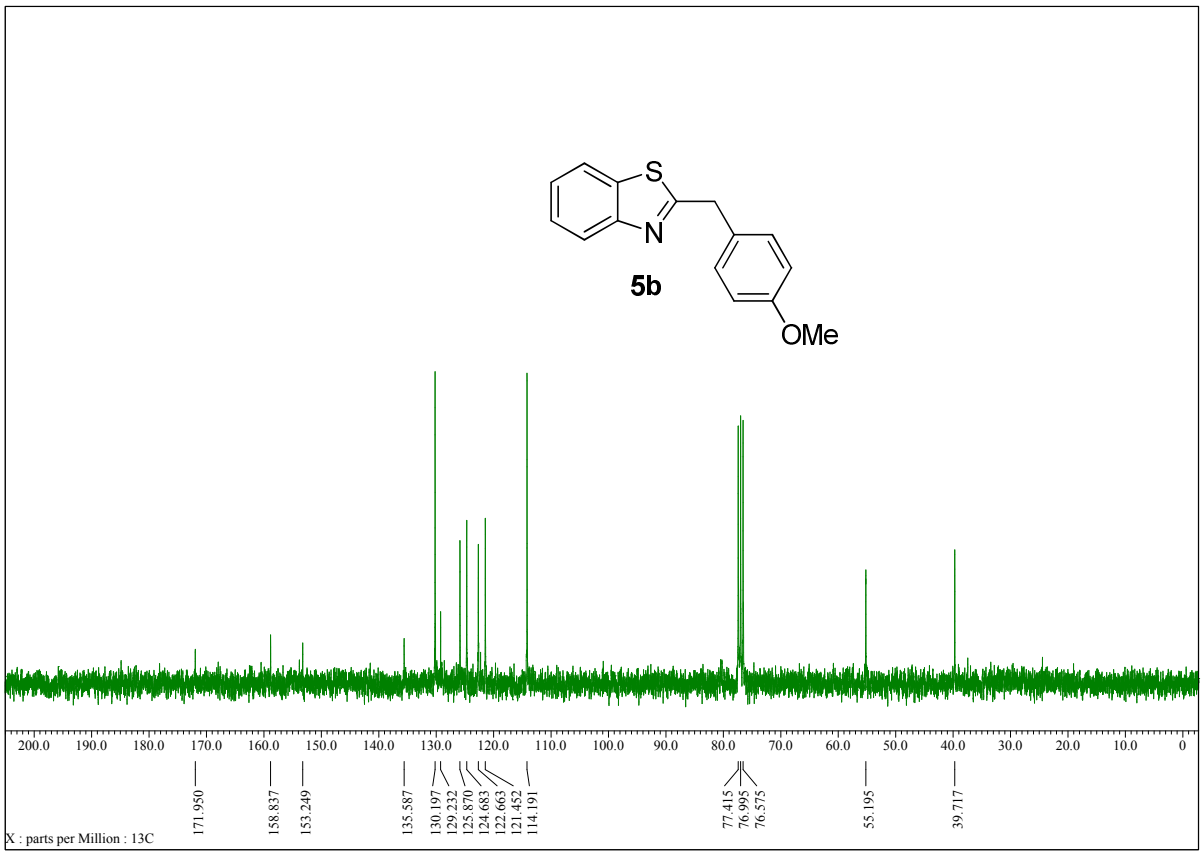
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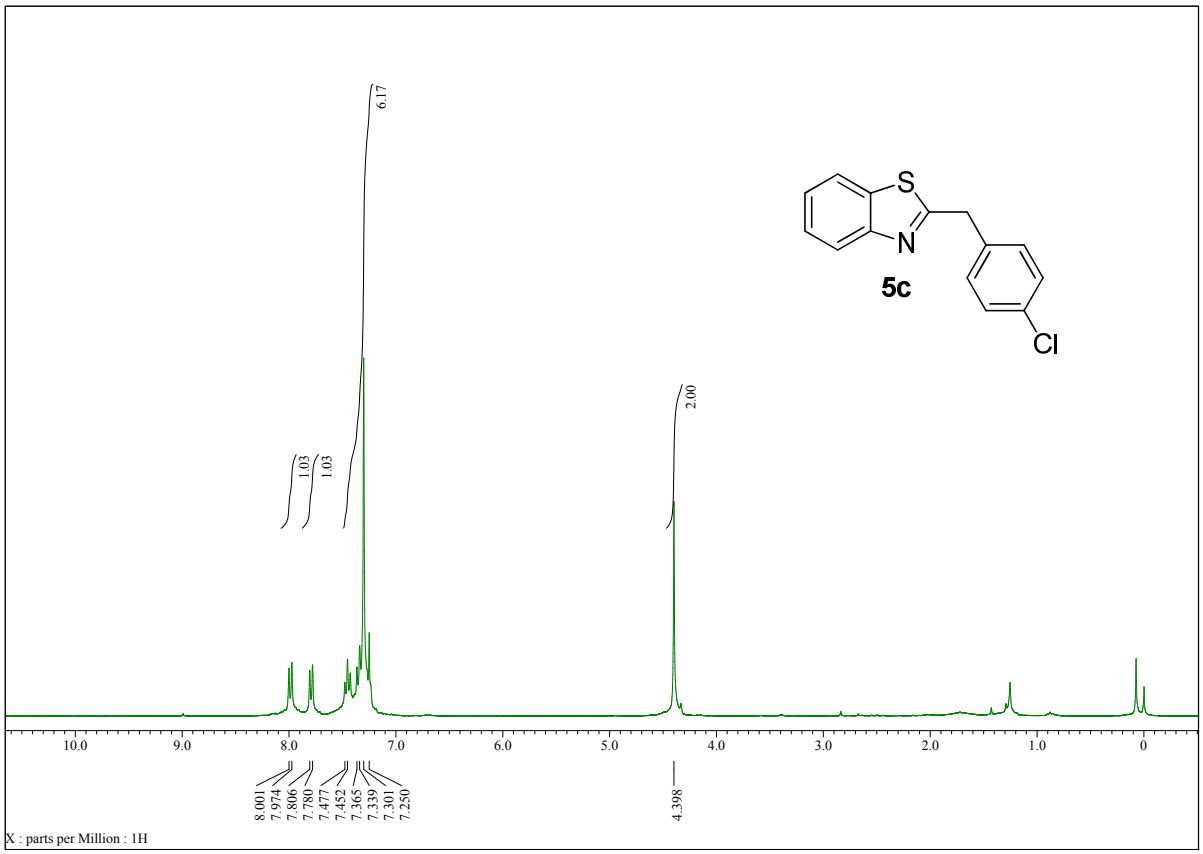
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7.452
7.365
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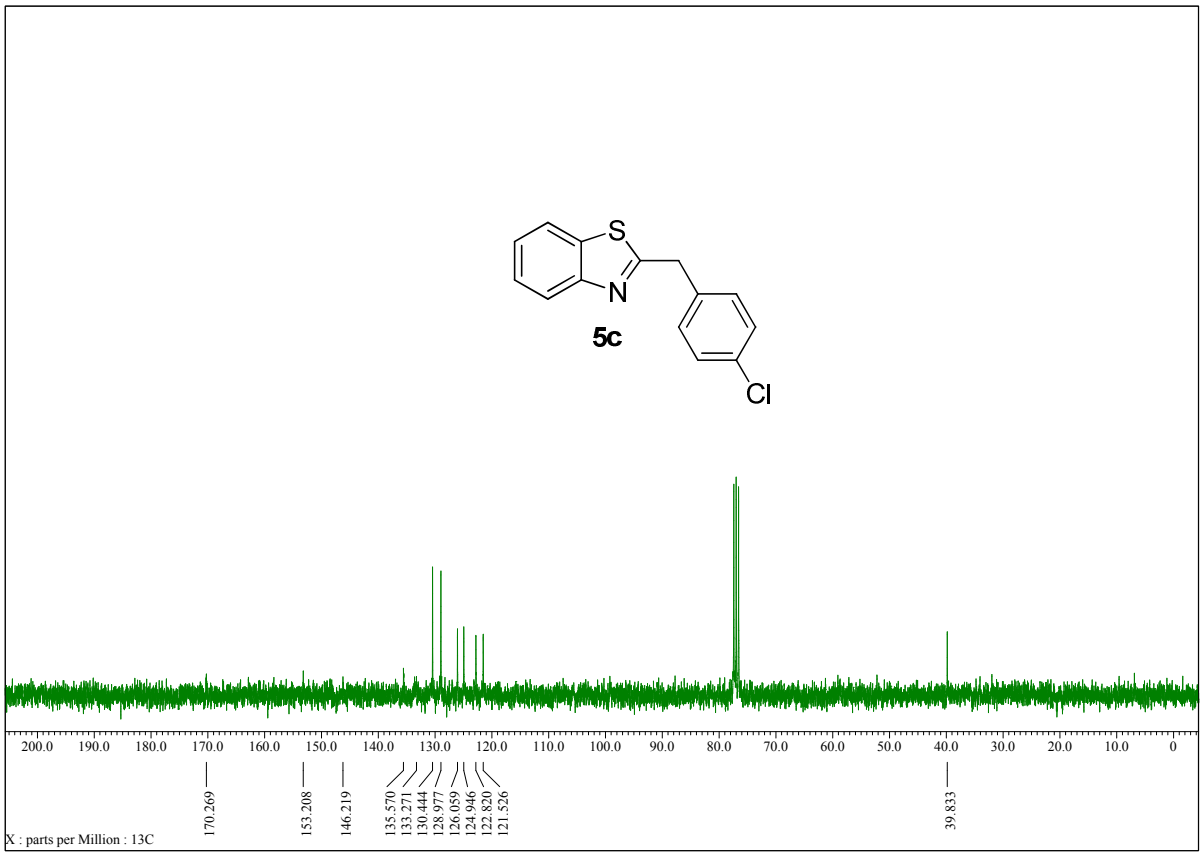
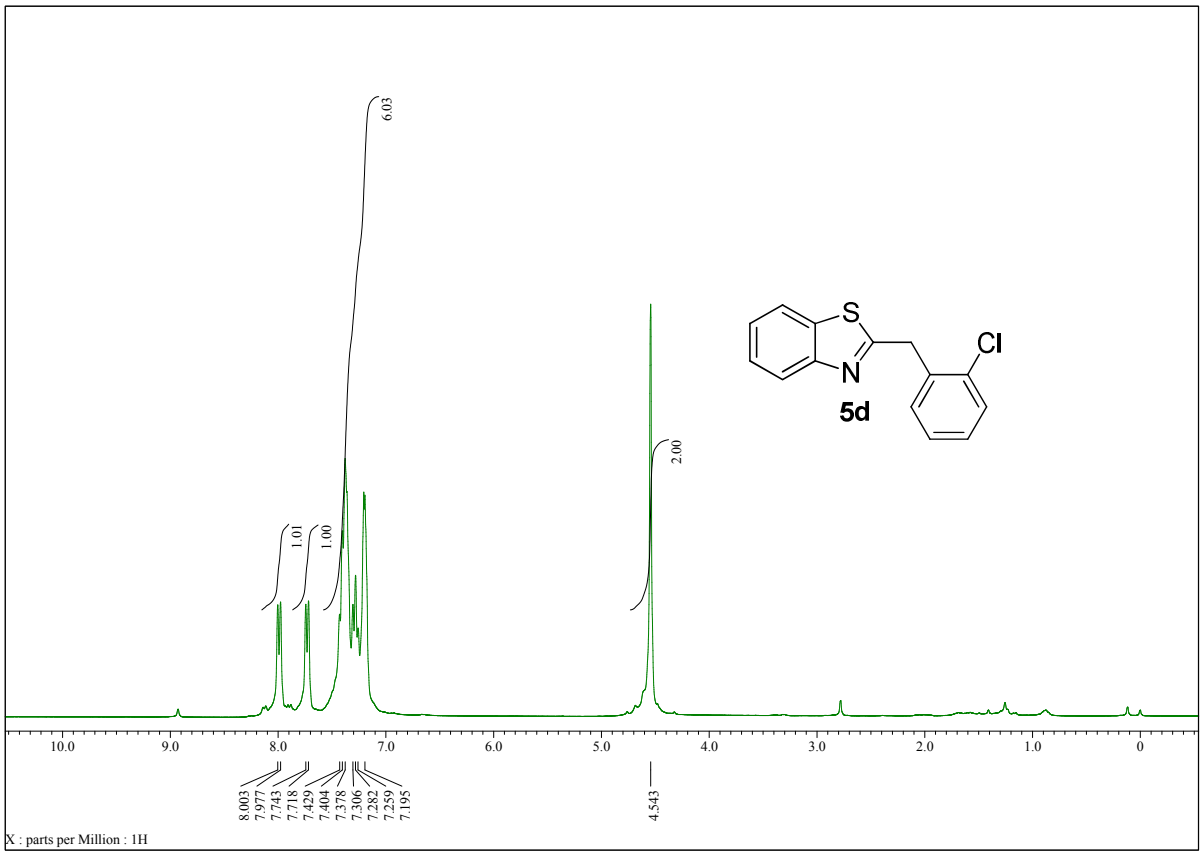
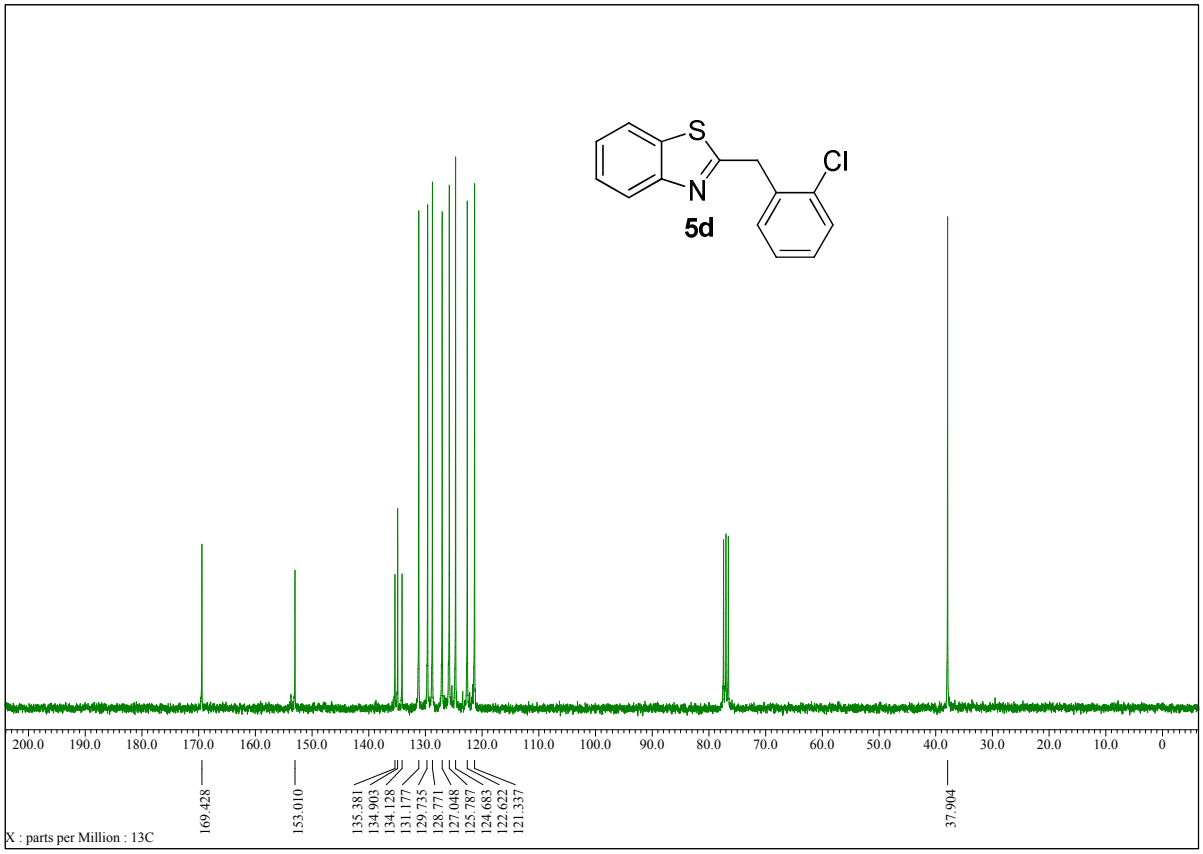
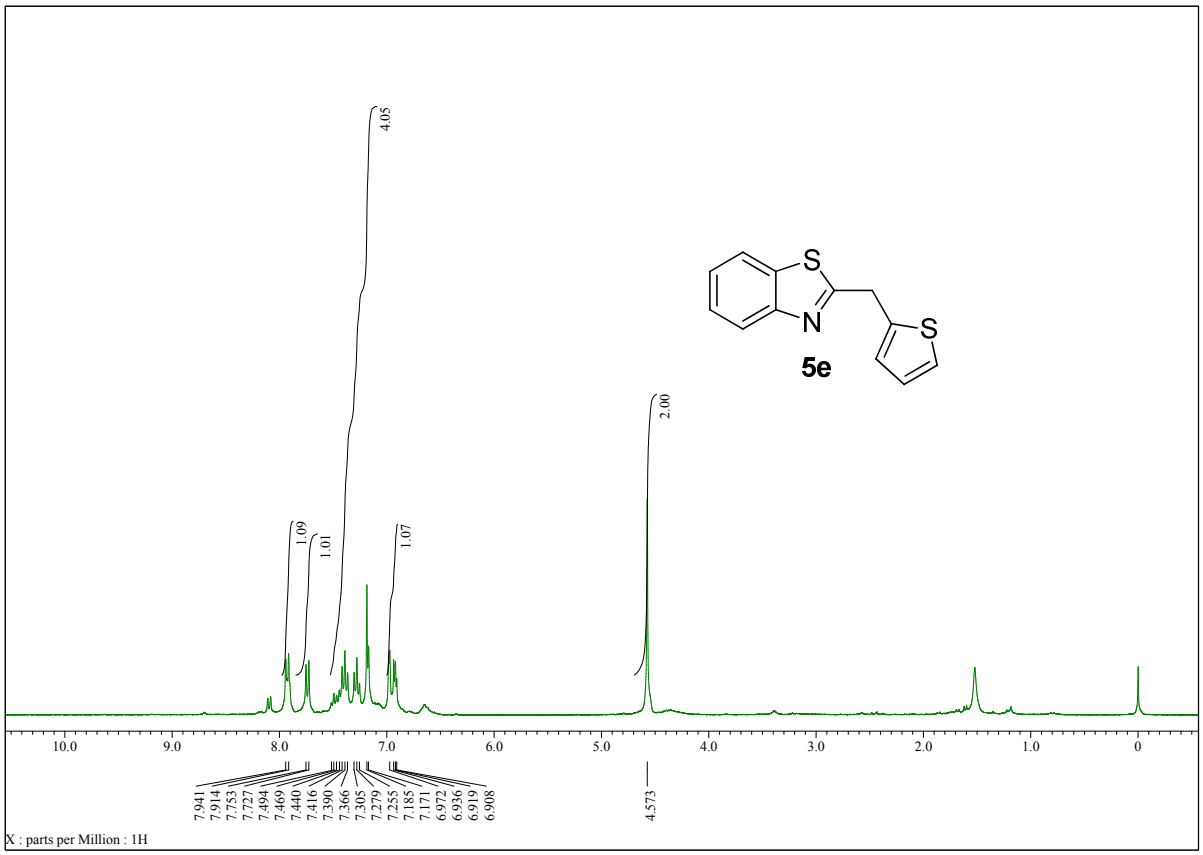
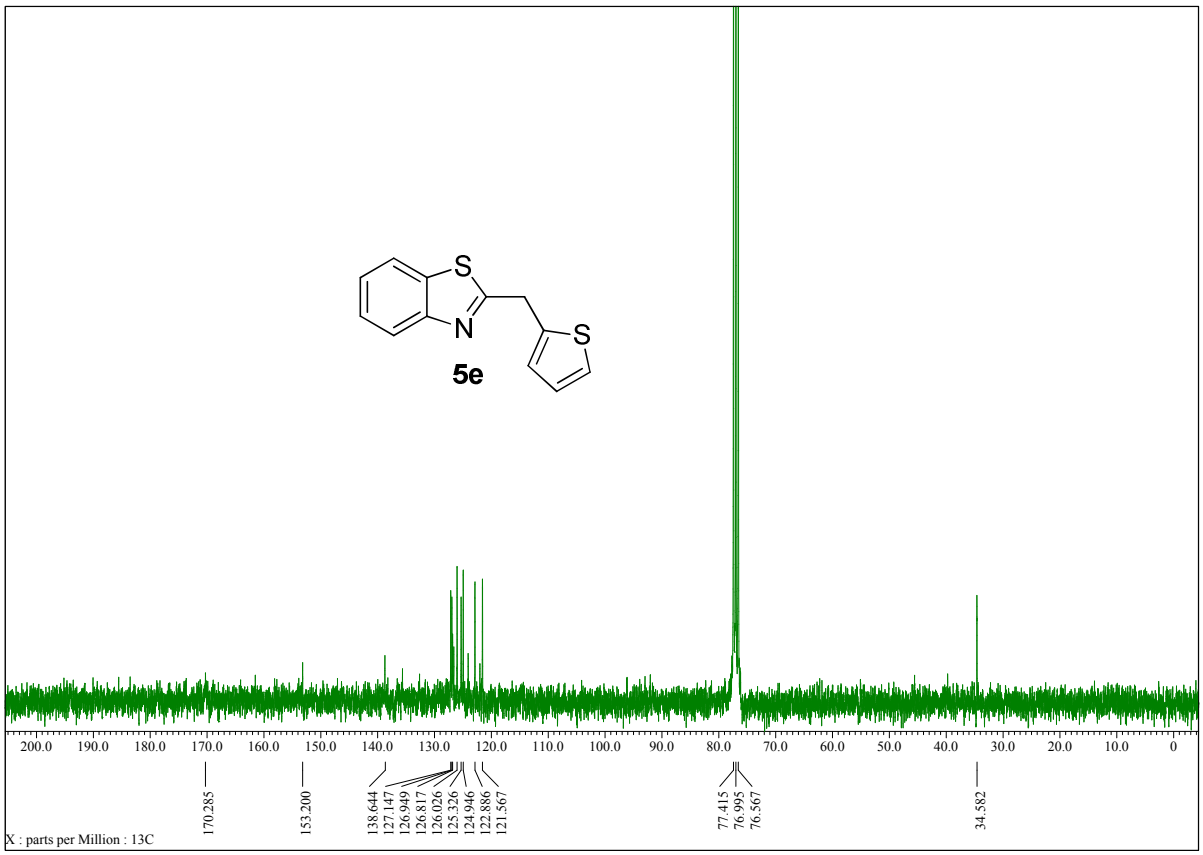
4.398
X : parts per Million : 1H

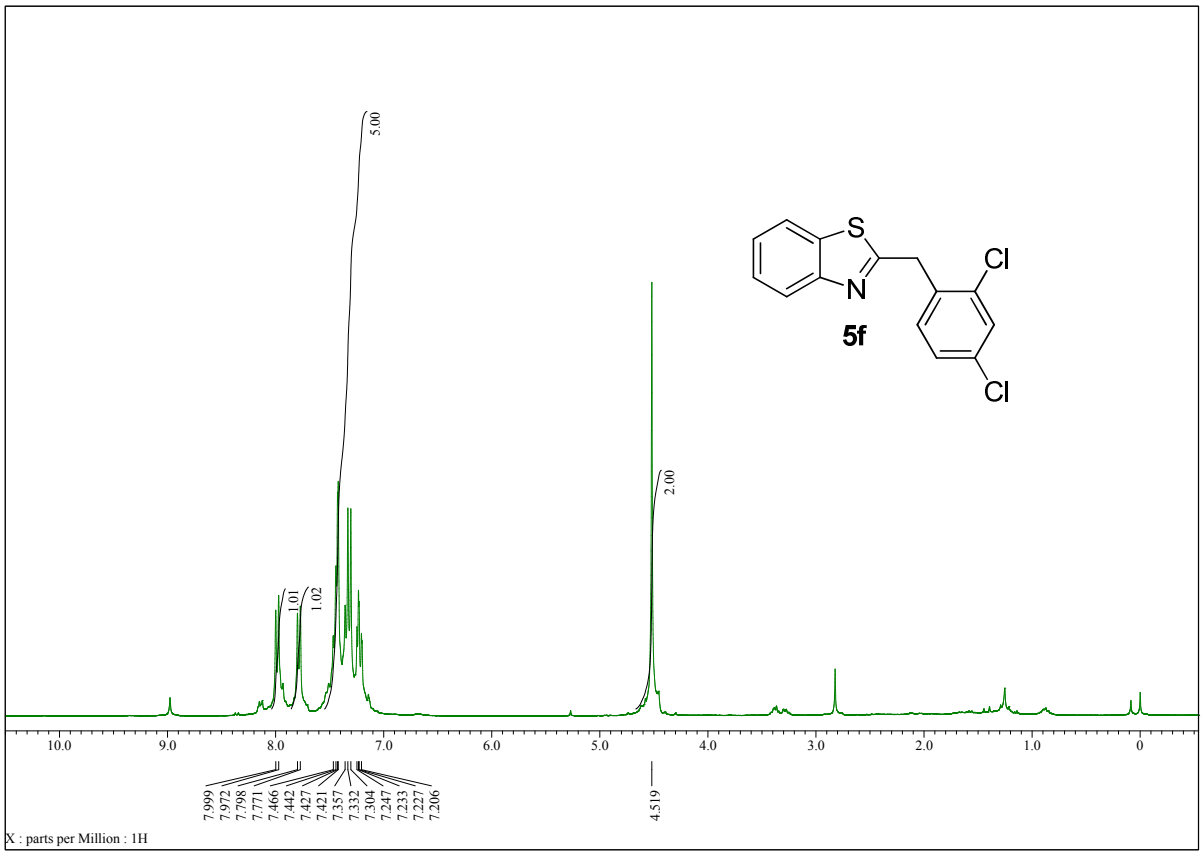

S
N
5c
Cl
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.269
153.208
146.219
135.570
133.271
130.444
128.977
126.059
124.946
122.820
121.526
39.833
X : parts per Million : 13C

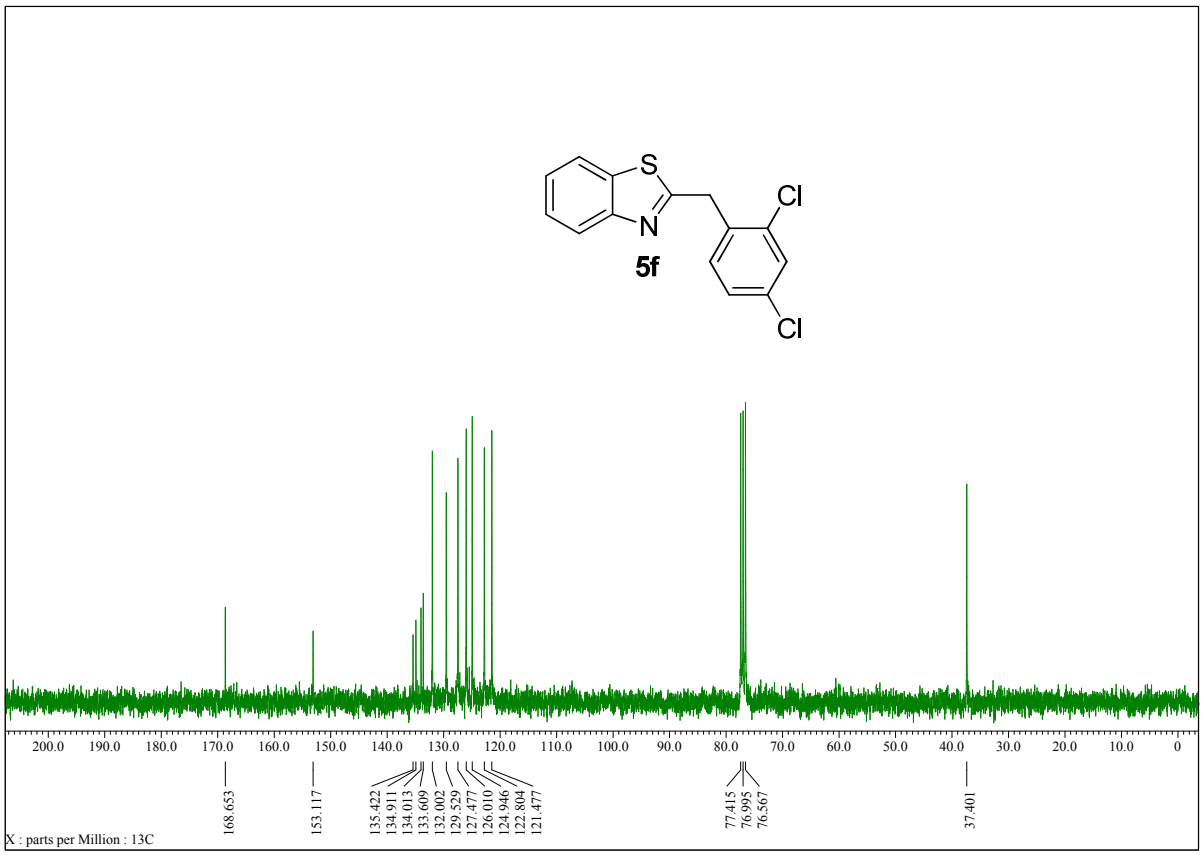

6.03
2.00
1.01
1.00
S
N
Cl
5d
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.003
7.977
7.743
7.718
7.429
7.404
7.378
7.306
7.282
7.259
7.195
4.543
X : parts per Million : 1H

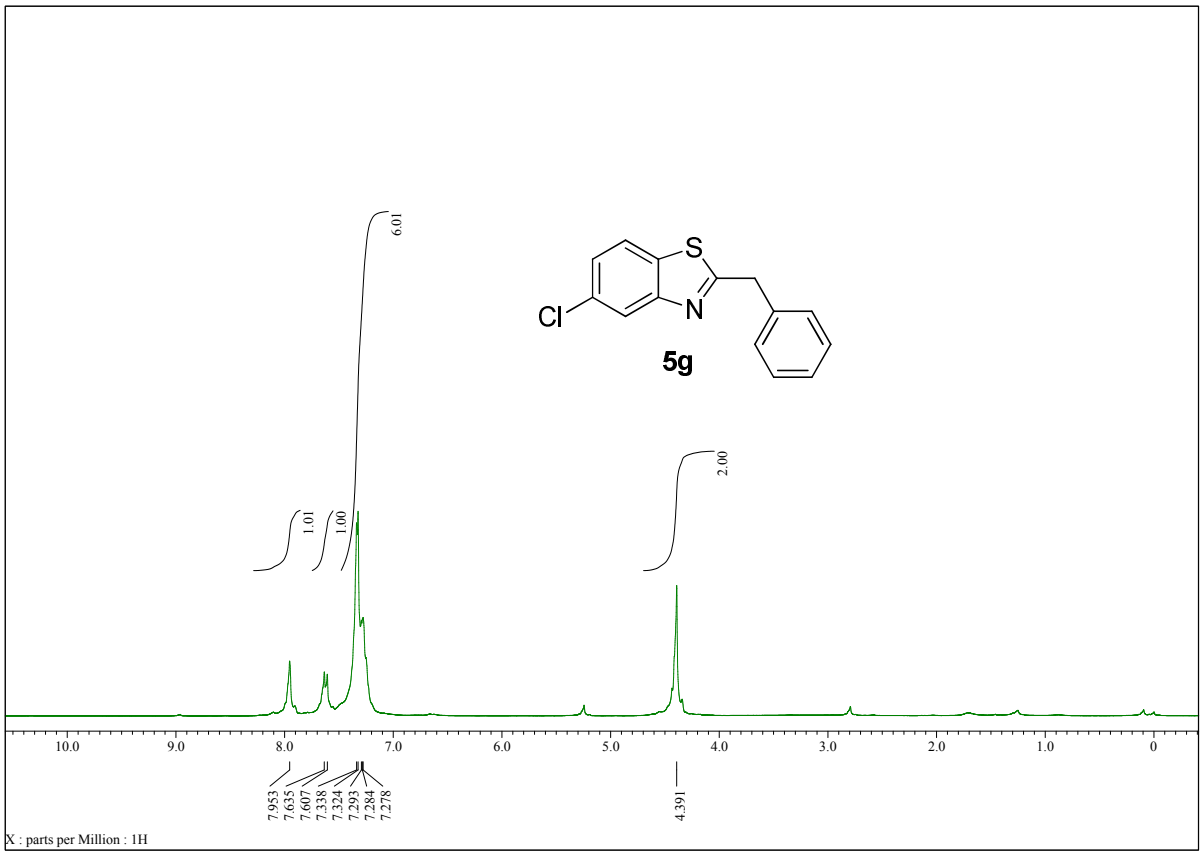

S
N
Cl
5d
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.428
153.010
135.381
134.903
134.128
131.177
129.735
128.771
127.048
125.787
124.683
122.622
121.337
37.904
X : parts per Million : 13C

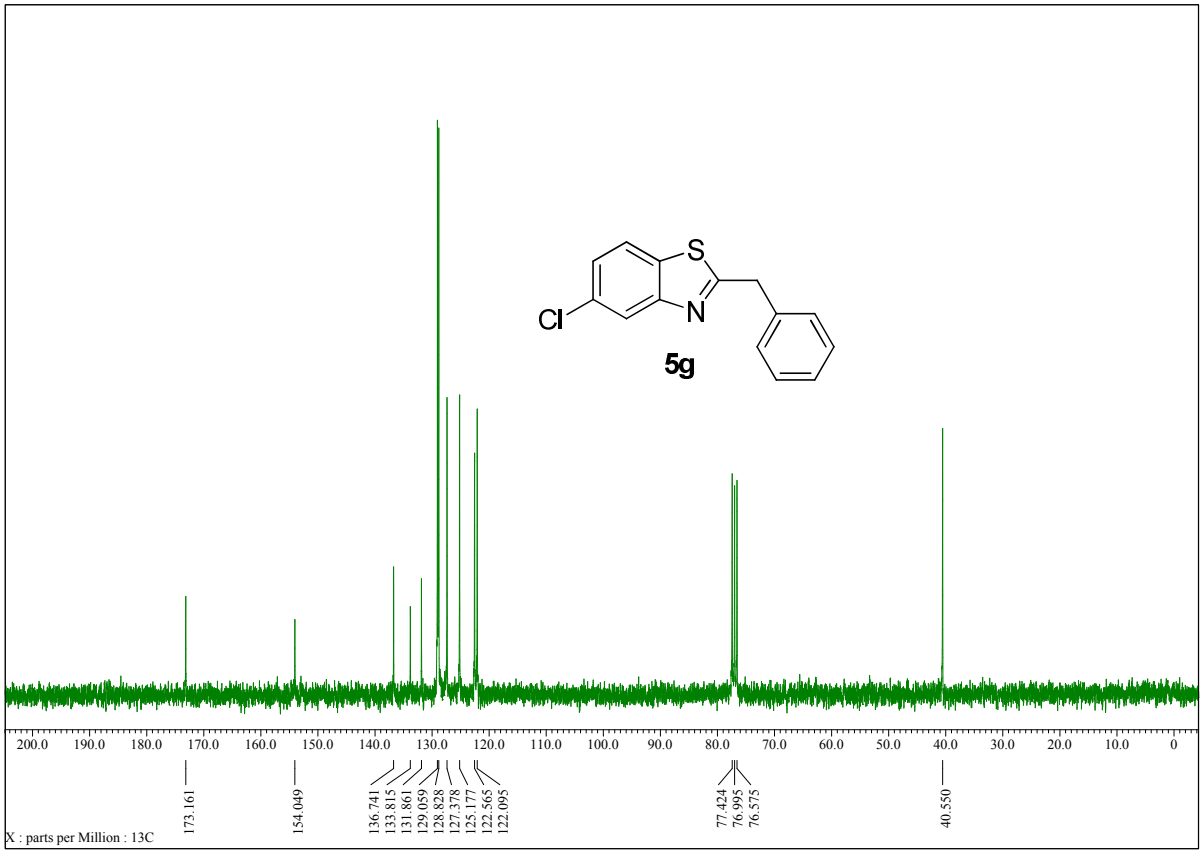

4.05
2.00
1.09
1.01
1.07
5e
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.941
7.914
7.753
7.727
7.494
7.469
7.440
7.416
7.390
7.366
7.305
7.279
7.255
7.185
7.171
6.972
6.936
6.919
6.908
4.573
X : parts per Million : 1H

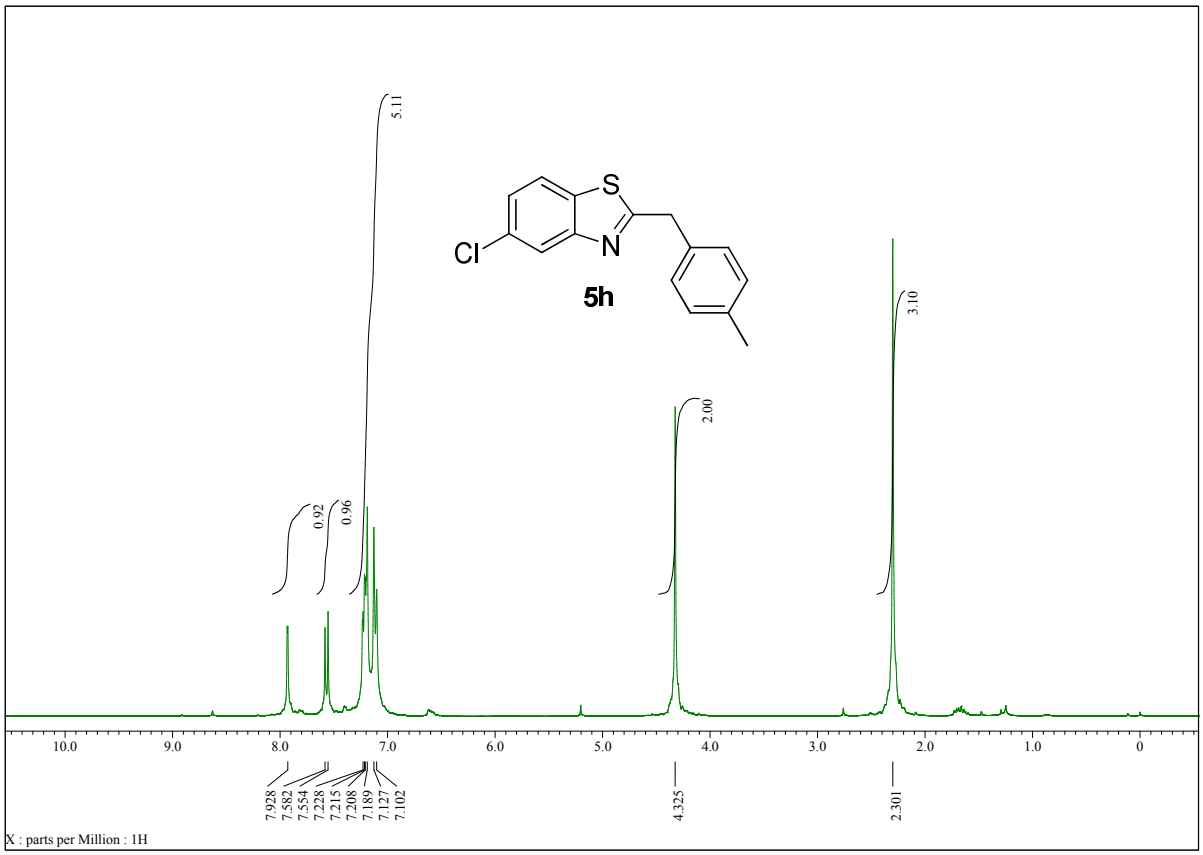

5e
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.285
153.200
138.644
127.147
126.949
126.817
126.026
125.326
124.946
122.886
121.567
77.415
76.995
76.567
34.582
X : parts per Million : 13C

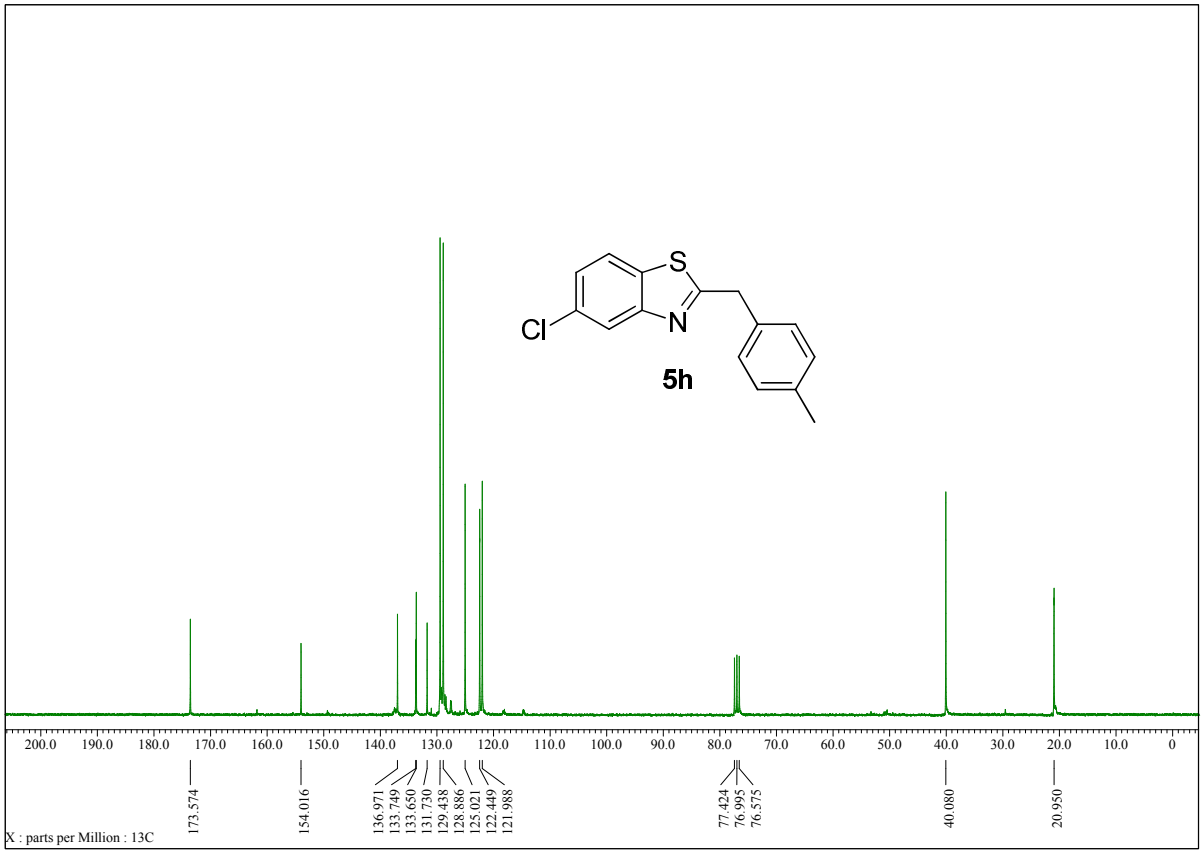

5.00
1.01
1.02
2.00
S
N
Cl
Cl
5f
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.999
7.972
7.798
7.771
7.466
7.442
7.427
7.421
7.357
7.332
7.304
7.247
7.233
7.227
7.206
4.519
X : parts per Million : 1H

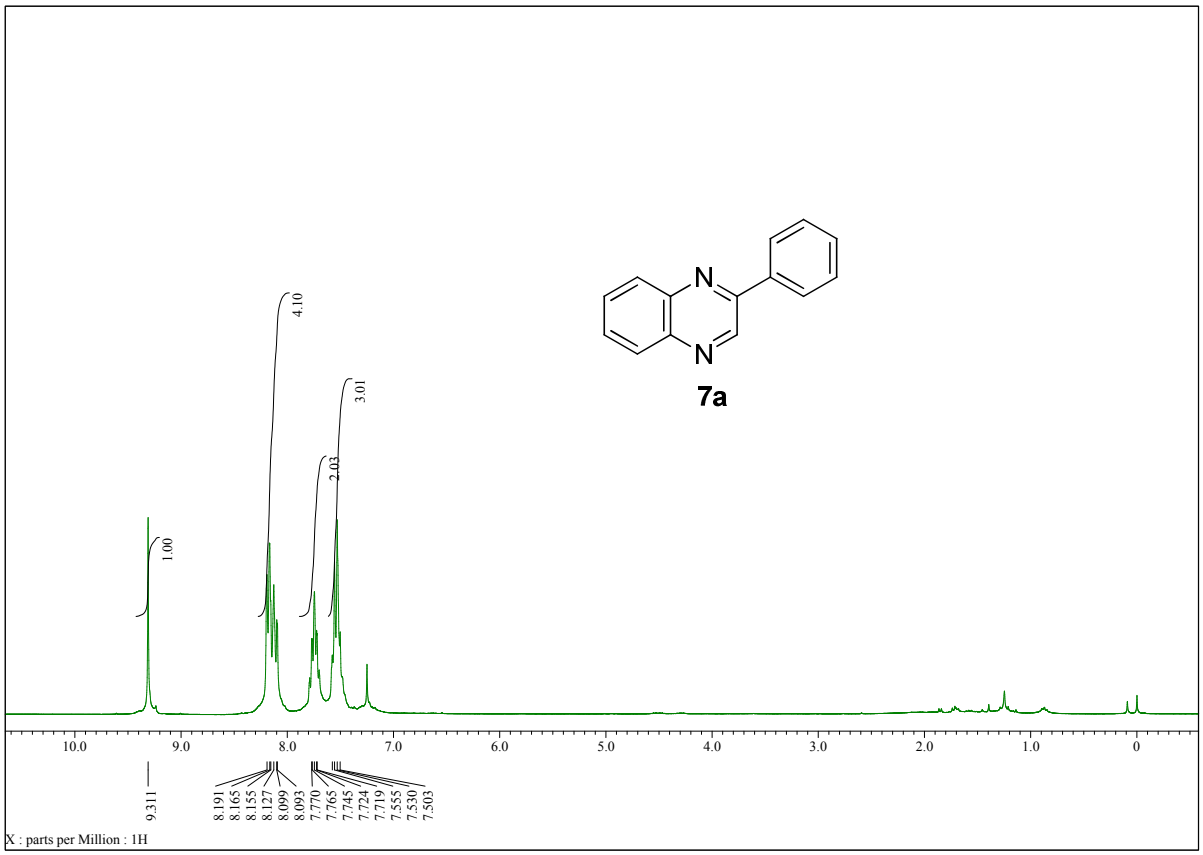

S
N
Cl
Cl
5f
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.653
153.117
135.422
134.911
134.013
133.609
132.002
129.529
127.477
126.010
124.946
122.804
121.477
77.415
76.995
76.567
37.401
X : parts per Million : 13C

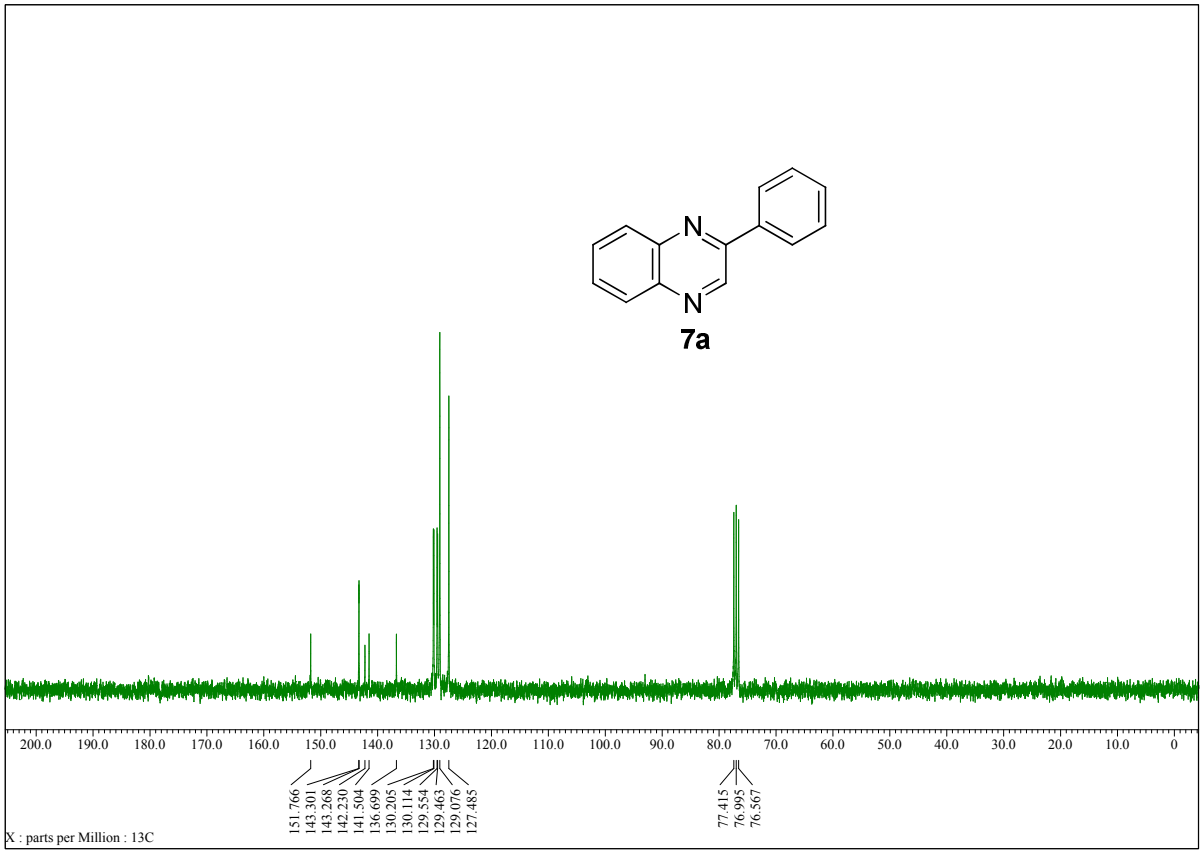

6.01
2.00
1.01
1.00
S
N
Cl
5g
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.953
7.635
7.607
7.338
7.324
7.293
7.284
7.278
4.391
X : parts per Million : 1H

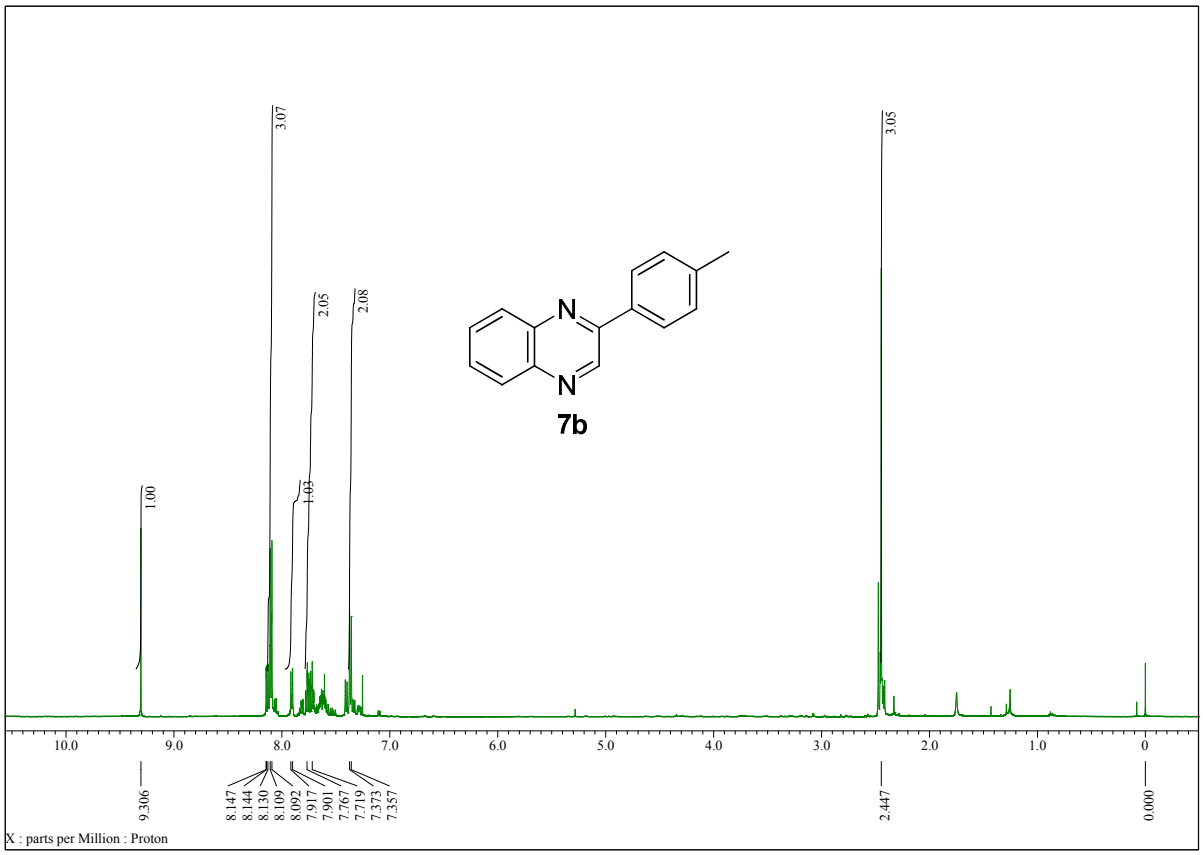

S
N
Cl
5g
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.161
154.049
136.741
133.815
131.861
129.059
128.828
127.378
125.177
122.565
122.095
77.424
76.995
76.575
40.550
X : parts per Million : 13C

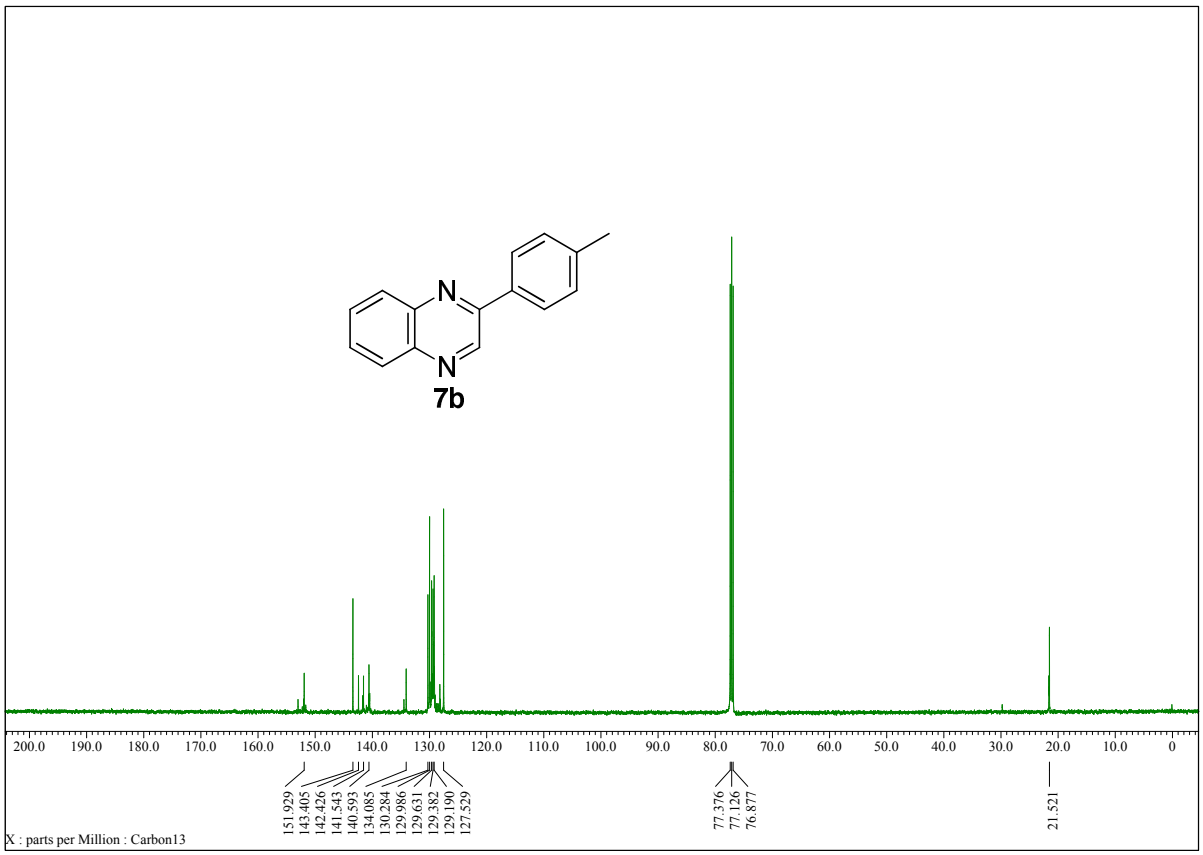

5.11
3.10
2.00
0.92
0.96
S
N
Cl
5h
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.928
7.582
7.554
7.228
7.215
7.208
7.189
7.127
7.102
4.325
2.301
X : parts per Million : 1H

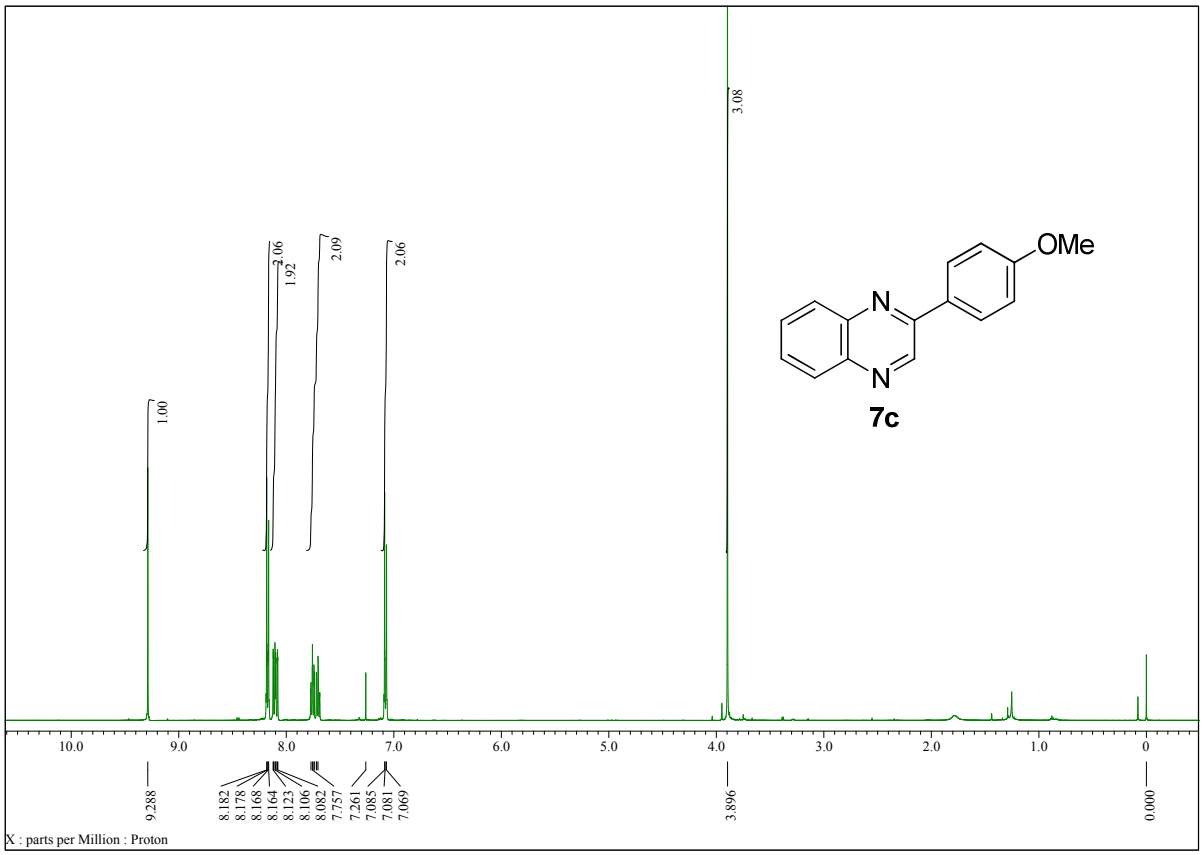

S
N
Cl
5h
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.574
154.016
136.971
133.749
133.650
131.730
129.438
128.886
125.021
122.449
121.988
77.424
76.995
76.575
40.080
20.950
X : parts per Million : 13C

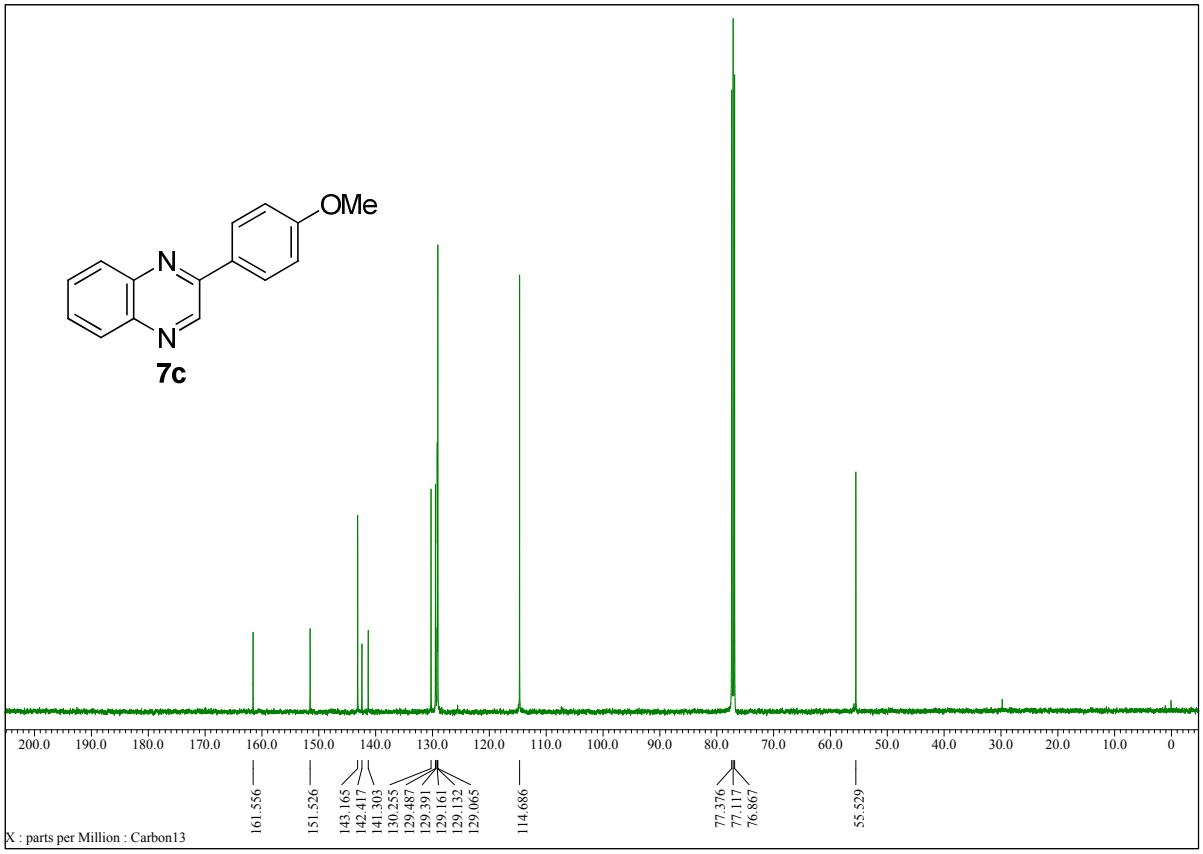

7a
4.10
3.01
2.03
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.311
8.191
8.165
8.155
8.127
8.099
8.093
7.770
7.765
7.745
7.724
7.719
7.555
7.530
7.503
X : parts per Million : 1H

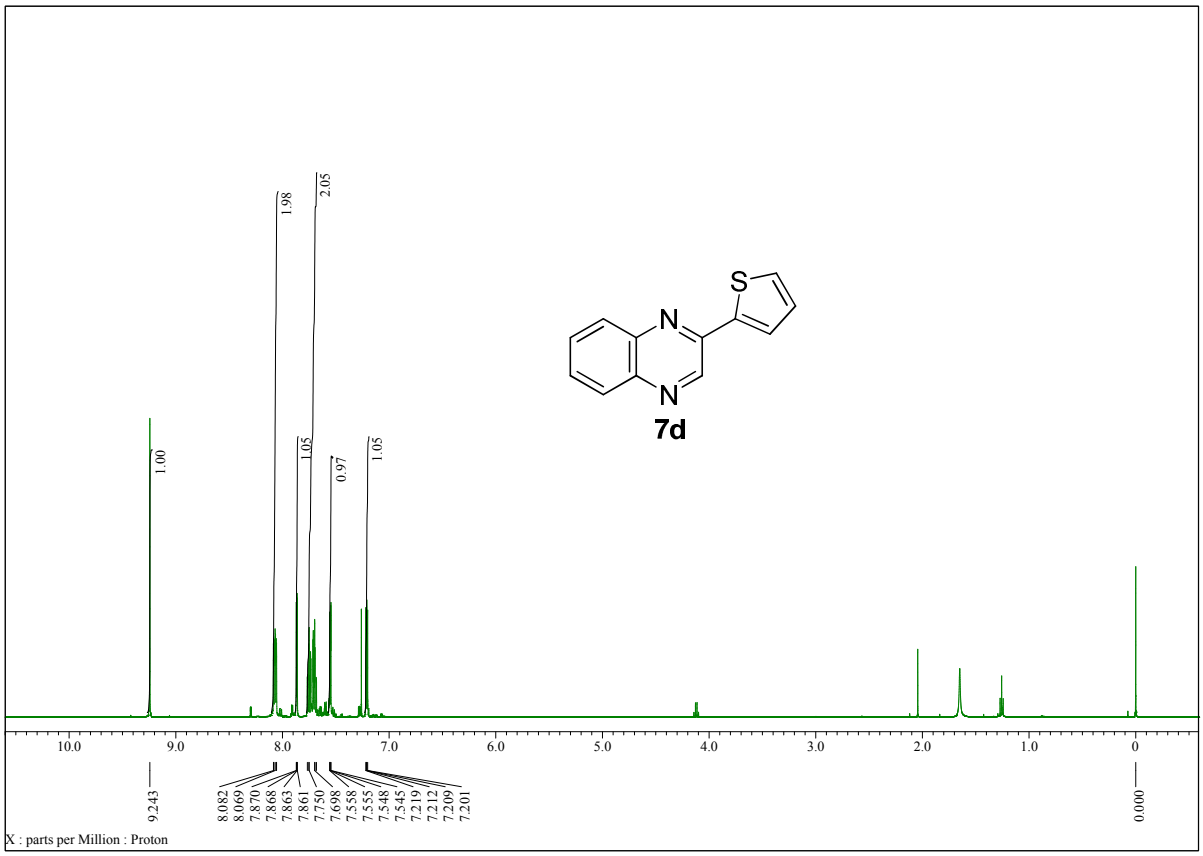

7a
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
151.766
143.301
143.268
142.230
141.504
136.699
130.205
130.114
129.554
129.463
129.076
127.485
77.415
76.995
76.567
X : parts per Million : 13C

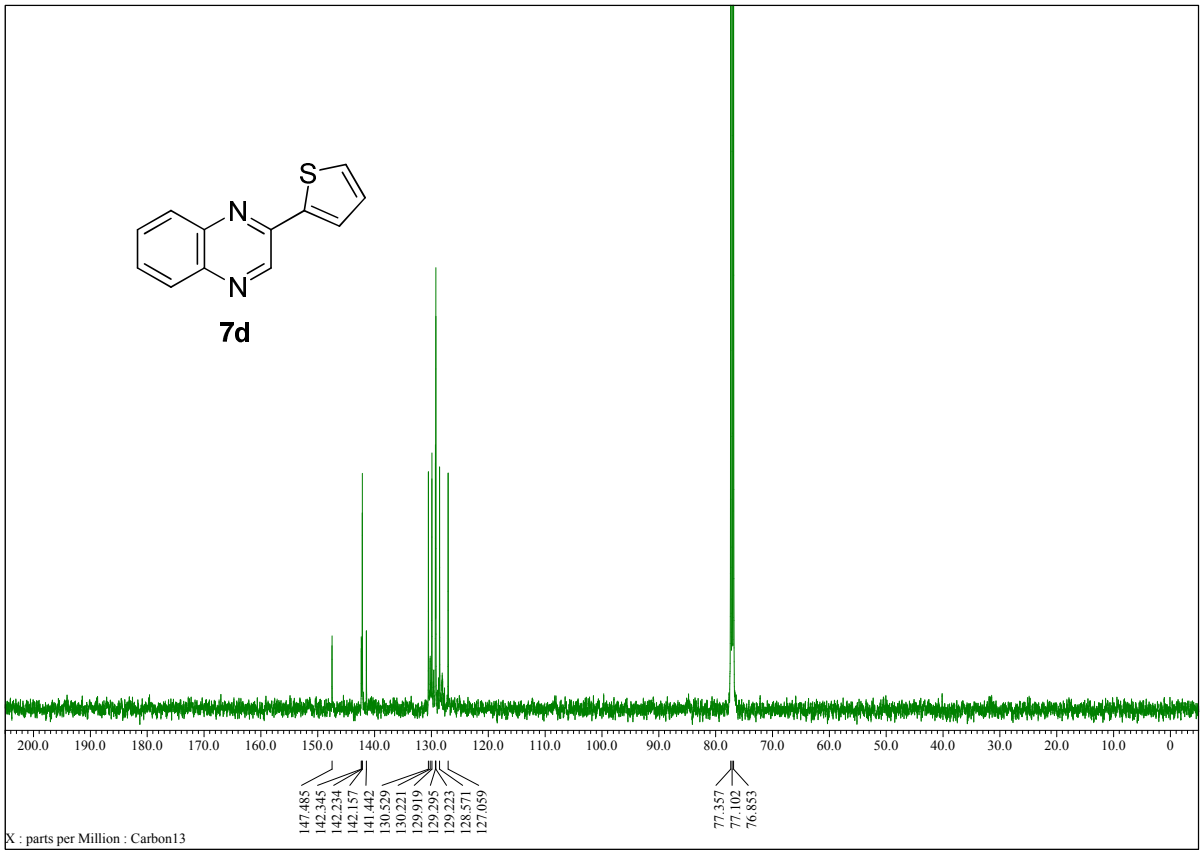

3.07
3.05
2.05
2.08
1.00
1.03
N
N
7b
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.306
8.147
8.144
8.130
8.109
8.092
7.917
7.901
7.767
7.719
7.373
7.357
2.447
0.000
X : parts per Million : Proton

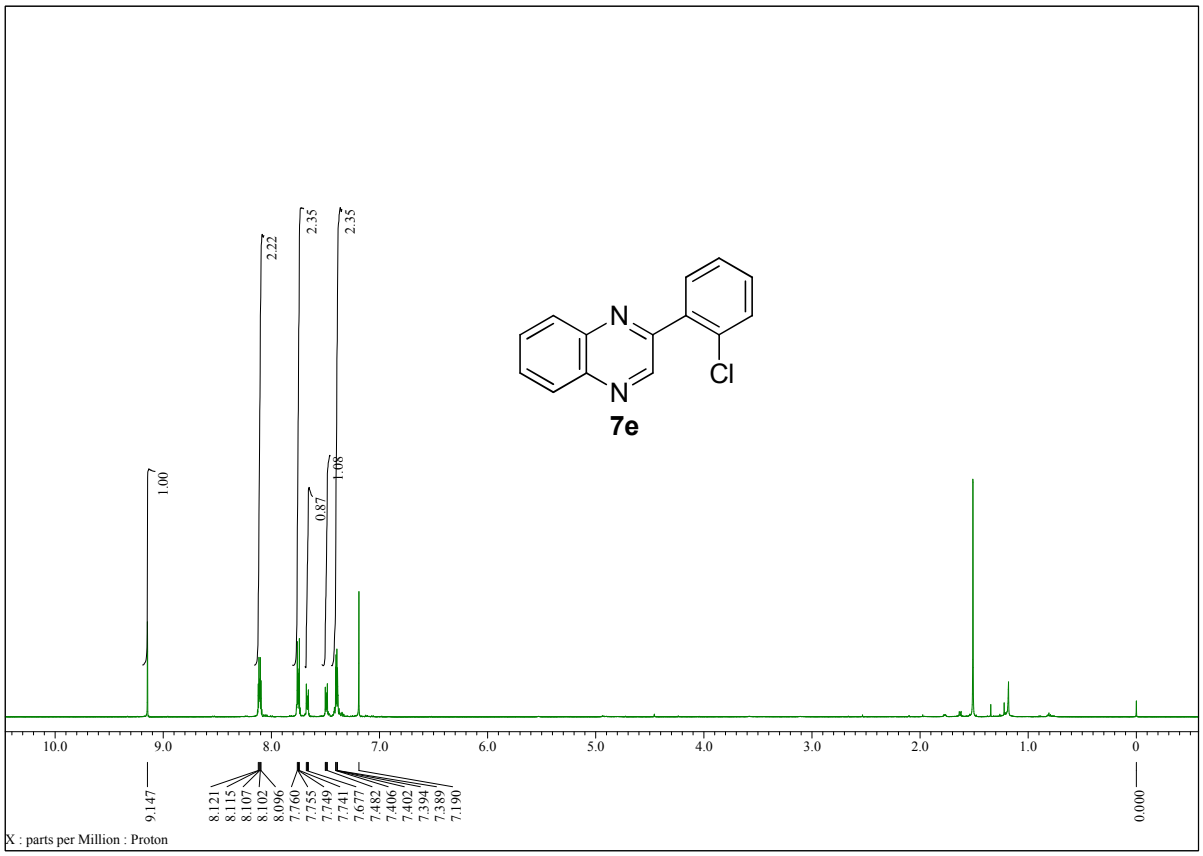

N
N
7b
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
151.929
143.405
142.426
141.543
140.593
134.085
130.284
129.986
129.631
129.382
129.190
127.529
77.376
77.126
76.877
21.521
X : parts per Million : Carbon13

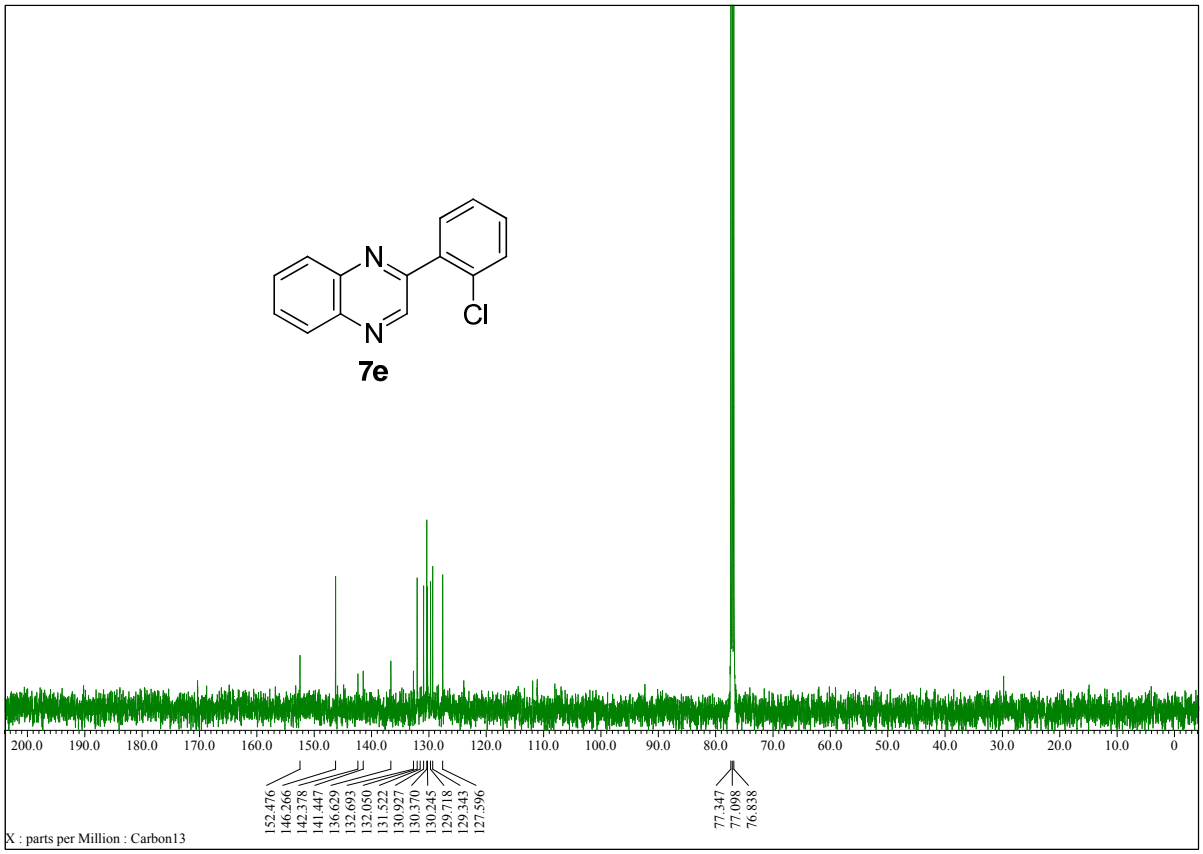

3.08
2.06
1.92
2.09
2.06
1.00
OMe
N
N
7c
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.288
8.182
8.178
8.168
8.164
8.123
8.106
8.082
7.757
7.261
7.085
7.081
7.069
3.896
0.000
X : parts per Million : Proton

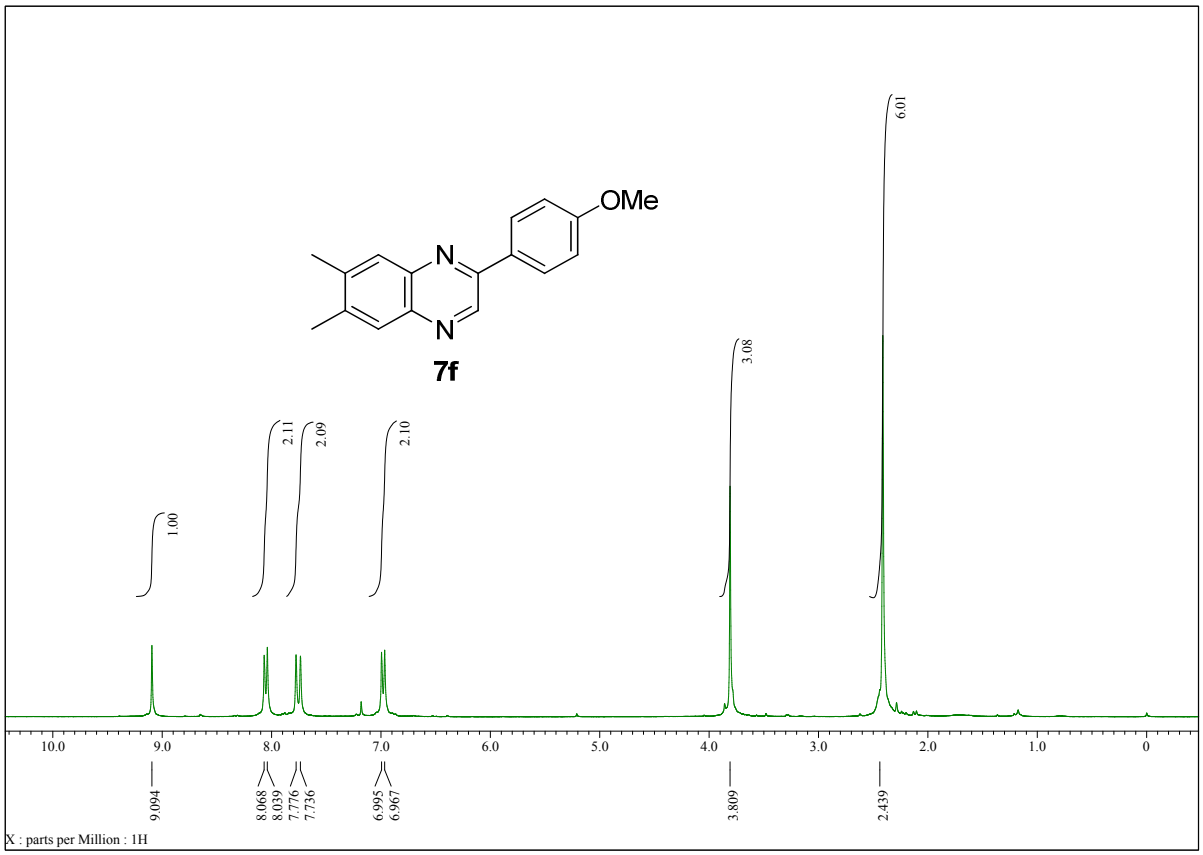

OMe
N
N
7c
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
161.556
151.526
143.165
142.417
141.303
130.255
129.487
129.391
129.161
129.132
129.065
114.686
77.376
77.117
76.867
55.529
X : parts per Million : Carbon13

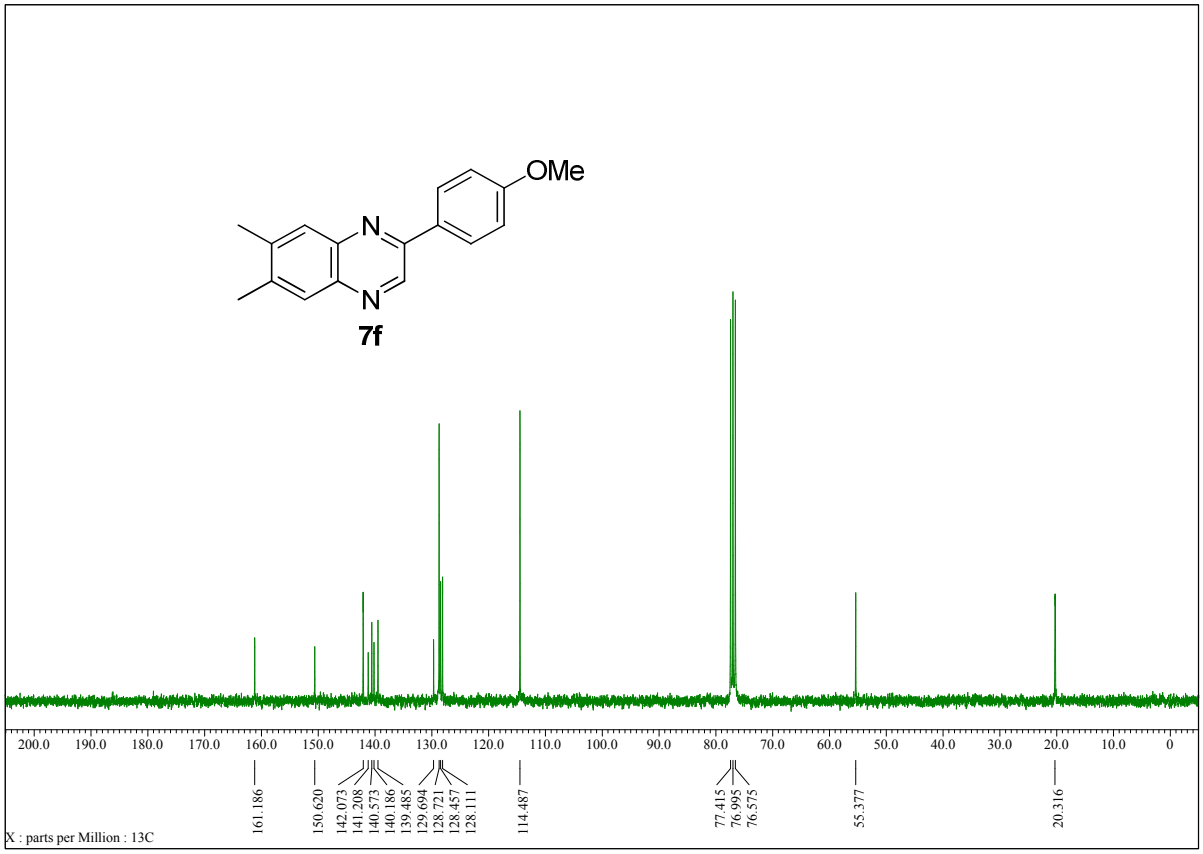

1.98
2.05
1.00
1.05
0.97
1.05
S
N
N
7d
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.243
8.082
8.069
7.870
7.868
7.863
7.861
7.750
7.698
7.558
7.555
7.548
7.545
7.219
7.212
7.209
7.201
0.000
X : parts per Million : Proton

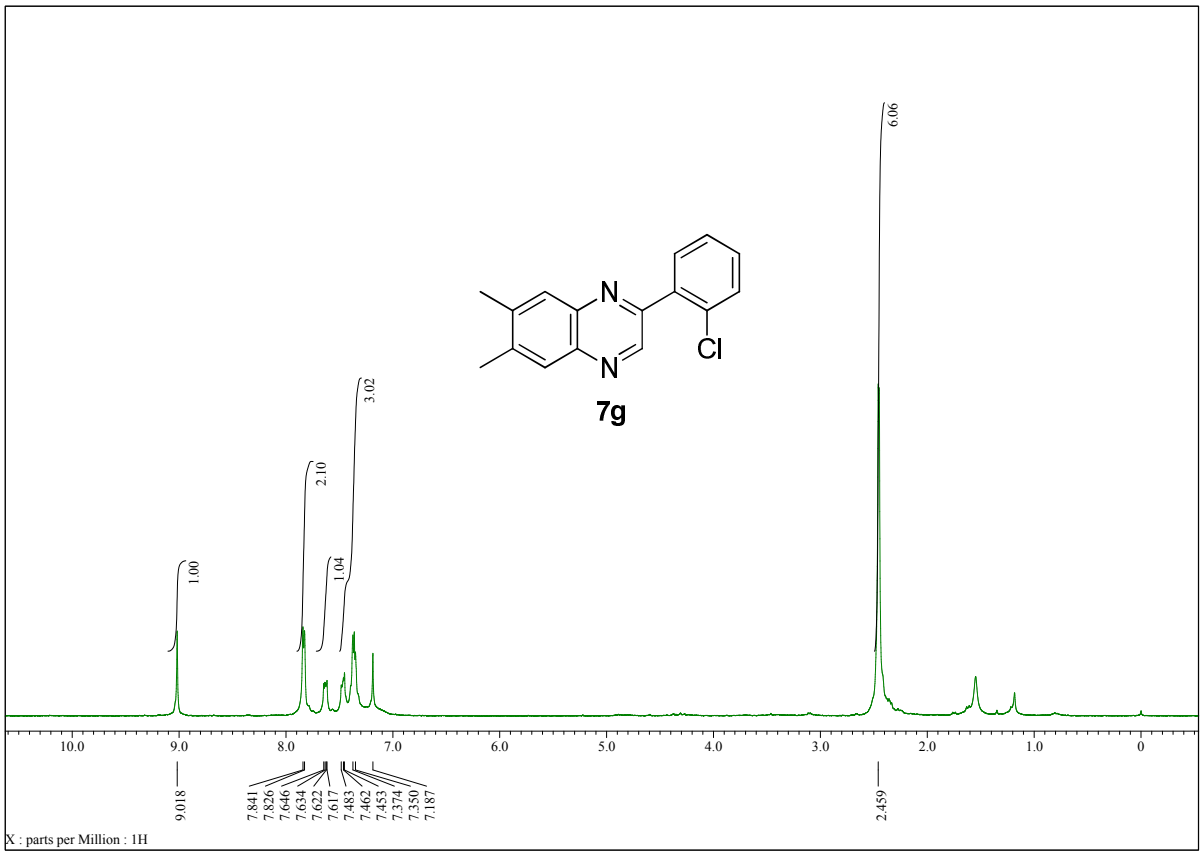

S
N
N
7d
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
147.485
142.345
142.234
142.157
141.442
130.529
130.221
129.919
129.295
129.223
128.571
127.059
77.357
77.102
76.853
X : parts per Million : Carbon13

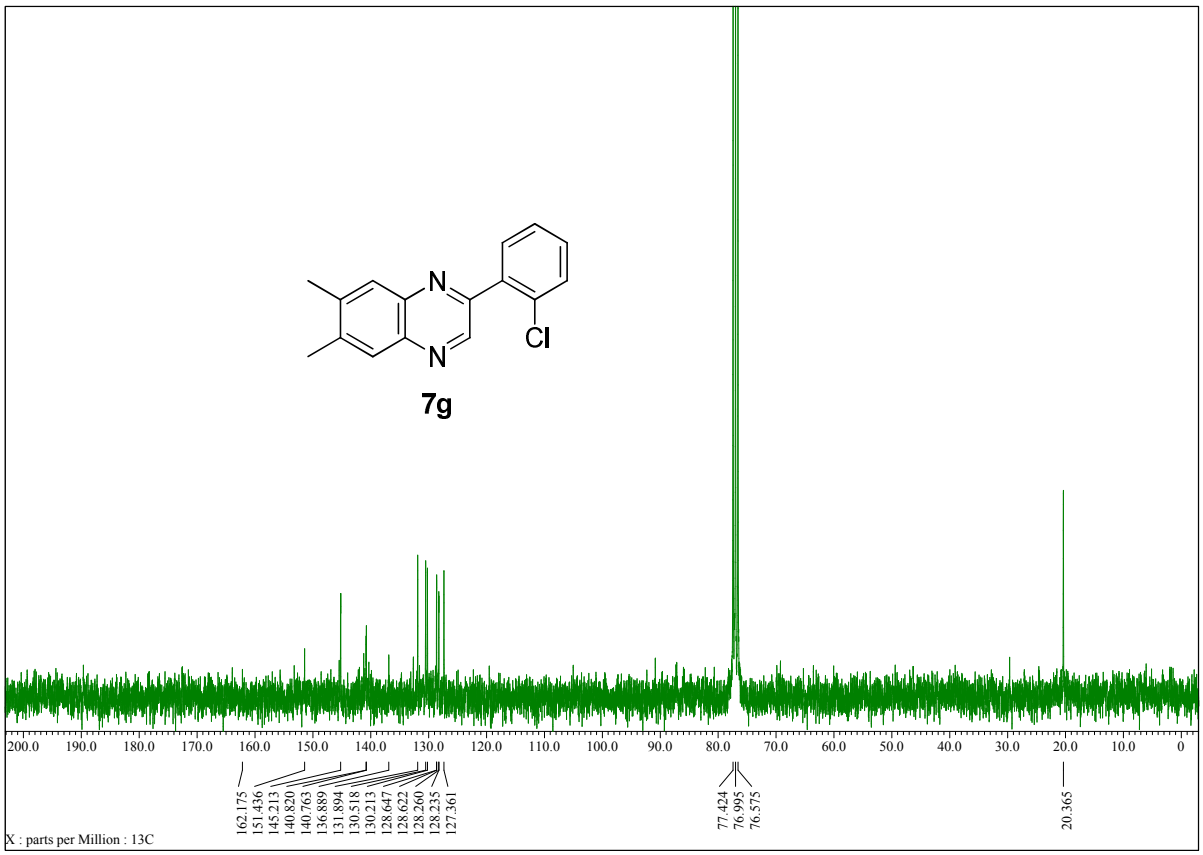

N
N
Cl
7e
2.22
2.35
2.35
1.00
0.87
1.08
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.147
8.121
8.115
8.107
8.102
8.096
7.760
7.755
7.749
7.741
7.677
7.482
7.406
7.402
7.394
7.389
7.190
0.000
X : parts per Million : Proton


N
N
Cl
7e
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
152.476
146.266
142.378
141.447
136.629
132.693
132.050
131.522
130.927
130.370
130.245
129.718
129.343
127.596
77.347
77.098
76.838
X : parts per Million : Carbon13


OMe
N
N
7f
6.01
3.08
2.11
2.09
2.10
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.094
8.068
8.039
7.776
7.736
6.995
6.967
3.809
2.439
X : parts per Million : 1H


OMe
N
N
7f
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
161.186
150.620
142.073
141.208
140.573
140.186
139.485
129.694
128.721
128.457
128.111
114.487
77.415
76.995
76.575
55.377
20.316
X : parts per Million : 13C


N
N
Cl
7g
6.06
3.02
2.10
1.04
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.018
7.841
7.826
7.646
7.634
7.622
7.617
7.483
7.462
7.453
7.374
7.350
7.187
2.459
X : parts per Million : 1H


N
N
Cl
7g
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.175
151.436
145.213
140.820
140.763
136.889
131.894
130.518
130.213
128.647
128.622
128.260
128.235
127.361
77.424
76.995
76.575
20.365
X : parts per Million : 13C