Supporting Information

Iodine-Mediated Arylation of Benzoxazoles with Aldehydes

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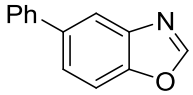
General procedures and methods

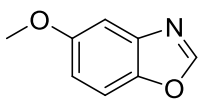
^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm). The residual solvent peak or tetramethylsilane was used as an internal reference. GC-MS analyses were performed on a Shimadzu GCMS QP2010 system and high resolution mass spectrum was obtained on a Finnigan/MAT 95XL-T spectrometer. Reaction temperatures refer to the temperatures of the heating blocks. Purification of reaction mixtures were performed with column chromatography or preparative thin layer chromatography methods. Reagents and solvents were commercial grade and were used as supplied without further purification, unless otherwise stated.

General procedure for the synthesis of substituted benzoxazoles

According to a procedure described by *Chang et al.*,[1] the corresponding 2-aminophenol (5 mmol) and triethyl orthoformate (15 mL) was refluxed for 4 h. After cooling to room temperature, the remaining triethyl orthoformate was removed under reduced pressure and the residue was purified by column chromatography to yield the desired substituted benzoxazole.

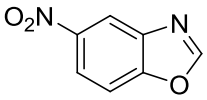


5-Phenylbenzoxazole: beige solid (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.00 (t, J = 1.2 Hz, 1H), 7.66 – 7.59 (m, 4H), 7.51 – 7.44 (m, 2H), 7.39 (dt, J = 9.3, 4.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.01, 149.40, 140.76, 140.58, 138.47, 128.81, 127.41, 127.27, 125.18, 118.97, 110.90.

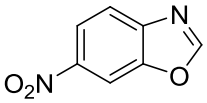


5-Methoxybenzoxazole: yellow solid (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.50 – 7.42 (m, 1H), 7.28-7.26 (m, 1H), 7.07 – 6.90 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.36, 153.23,

144.58, 140.84, 114.51, 111.10, 103.10, 55.94.

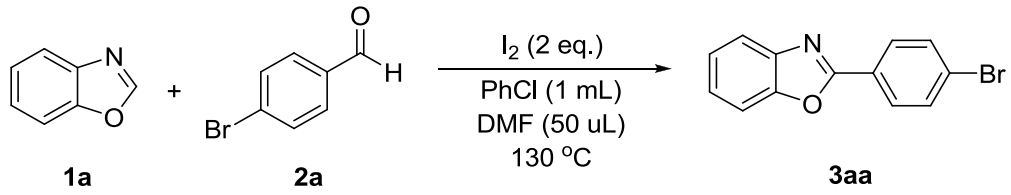


5-Nitrobenzoxazole: yellow solid (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 2.3 Hz, 1H), 8.37 (dd, *J* = 9.0, 2.3 Hz, 1H), 8.28 (s, 1H), 7.72 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.14, 153.38, 145.45, 140.43, 121.73, 117.17, 111.37.



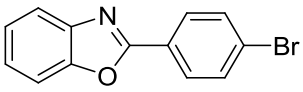
4-Nitrobenzoxazole: yellow solid (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 2.1 Hz, 1H), 8.35 (s, 1H), 8.32 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.50, 149.10, 145.74, 145.01, 120.74, 120.58, 107.72.

Representative procedure for the I_2-mediated arylation of benzoxazoles with 4-bromobenzaldehyde

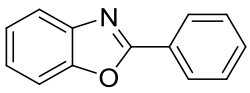


1a **2a** **3aa**

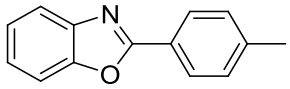
Iodine (254 mg, 1.00 mmol, 2 equiv) and DMF (50 μL) were added to 4-bromobenzaldehyde **1a** (92.5 mg, 0.50 mmol, 1.0 equiv) and benzoxazole **2a** (119 mg, 1.00 mmol, 2.0 equiv) in 1.0 mL PhCl. The resulting solution was stirred at 130 °C and the reaction monitored by TLC. Upon reaction completion, the reaction was allowed to cool to room temperature before the addition of a saturated solution of $Na_2S_2O_3$ (10 mL). The mixture was then extracted 3 times with 15 mL ethyl acetate. The combined organic phases were dried with Na_2SO_4 and evaporated under vacuum. The residue was purified using flash chromatography using hexane/ethyl acetate (10:1) as eluent to afford the pure arylated product.



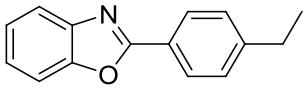
2-(4-bromophenyl)benzoxazole (3aa).[2] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 2H), 7.78 – 7.72 (m, 1H), 7.66 – 7.60 (m, 2H), 7.58 – 7.52 (m, 1H), 7.37 – 7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.01, 150.62, 141.88, 132.13, 128.89, 126.15, 125.96, 125.31, 124.68, 120.01, 110.56. GC-MS: 275.



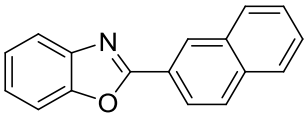
2-phenylbenzoxazole (3ab).[3] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (m, 2H), 7.81 – 7.74 (m, 1H), 7.61 – 7.55 (m, 1H), 7.53-7.51 (m, 3H), 7.37 – 7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.95, 150.65, 141.99, 131.45, 128.83, 127.53, 127.05, 125.04, 124.51, 119.93, 110.52. GC-MS: 195



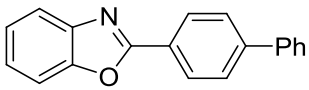
2-p-tolylbenzoxazole (3ac).[3] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 2H), 7.82 – 7.71 (m, 1H), 7.61 – 7.51 (m, 1H), 7.37 – 7.27 (m, 4H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.23, 150.59, 142.06, 142.01, 129.59, 127.52, 124.81, 124.43, 124.29, 119.76, 110.44, 21.60. GC-MS: 209



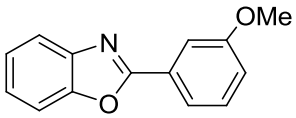
2-(4-ethylphenyl)benzoxazole (3ad).[2] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 2H), 7.81 – 7.72 (m, 1H), 7.60 – 7.51 (m, 1H), 7.39 – 7.28 (m, 4H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.19, 150.58, 148.17, 142.05, 128.35, 127.61, 124.76, 124.47, 124.38, 119.74, 110.39, 28.85, 15.13. GC-MS: 223



2-(naphthalen-3-yl)benzoxazole (3ae).[2] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 0.6 Hz, 1H), 8.30 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.95 (m, 2H), 7.89 – 7.77 (m, 2H), 7.64 – 7.56 (m, 1H), 7.54 (m, 2H), 7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.06, 150.73, 142.12, 134.62, 132.84, 128.83, 128.64, 128.02, 127.78, 127.66, 126.77, 125.06, 124.52, 124.25, 123.83, 119.92, 110.48. GC-MS: 245

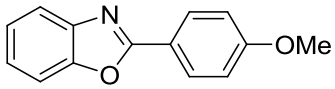


2-(biphenyl-4-yl)benzoxazole (3af).[3] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.27 (m, 2H), 7.85 – 7.78 (m, 1H), 7.77 – 7.71 (m, 2H), 7.66 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.47 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.44 – 7.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.76, 150.64, 144.01, 142.08, 139.80, 128.81, 127.94, 127.93, 127.37, 127.01, 125.79, 124.96, 124.47, 119.86, 110.46. GC-MS: 271

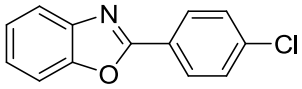


2-(3-methoxyphenyl)benzoxazole (3ag).[4] White solid ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 1H), 7.80 – 7.74 (m, 2H), 7.60 – 7.53 (m, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.07 (ddd, *J*

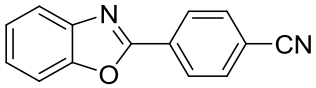
= 8.3, 2.6, 0.9 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.87, 159.84, 150.64, 141.93, 129.94, 128.22, 125.11, 124.54, 120.03, 119.92, 118.27, 111.78, 110.54, 55.44. GC-MS: 225



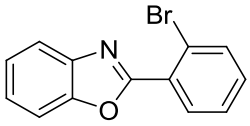
2-(4-methoxyphenyl)benzoxazole (3ah).[3] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.12 (m, 2H), 7.77 – 7.69 (m, 1H), 7.57 – 7.50 (m, 1H), 7.36 – 7.27 (m, 2H), 7.05 – 6.97 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.10, 162.24, 150.58, 142.18, 129.31, 124.54, 124.36, 119.59, 119.54, 114.28, 110.33, 55.38. GC-MS: 225



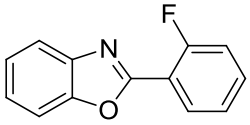
2-(4-chlorophenyl)benzo[d]oxazole (3ai).[3] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.09 (m, 2H), 7.79 – 7.69 (m, 1H), 7.59 – 7.49 (m, 1H), 7.49 – 7.41 (m, 2H), 7.33 (dd, *J* = 5.9, 3.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.96, 150.64, 141.90, 137.67, 129.19, 128.75, 125.54, 125.28, 124.67, 120.01, 110.56. GC-MS: 229



4-(benzo[d]oxazol-2-yl)benzonitrile (3aj).[5] White solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.29 (m, 2H), 7.81 (dd, *J* = 8.6, 1.7 Hz, 3H), 7.61 (ddd, *J* = 3.8, 2.1, 0.6 Hz, 1H), 7.46 – 7.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.88, 150.85, 141.80, 132.65, 131.07, 127.92, 126.14, 125.10, 120.53, 118.13, 114.70, 110.84. GC-MS: 220

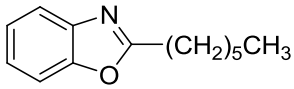


2-(2-bromophenyl)benzoxazole (3ak).[6] White solid^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.90 – 7.79 (m, 1H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.45 (td, *J* = 7.6, 1.2 Hz, 1H), 7.40 – 7.31 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.44, 150.55, 141.53, 134.60, 132.07, 131.92, 128.28, 127.37, 125.50, 124.58, 121.82, 120.45, 110.70. GC-MS: 275

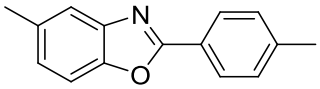


2-(2-fluorophenyl)benzoxazole (3al).[7] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (td, *J* = 7.5, 1.8 Hz, 1H), 7.83 (ddd, *J* = 5.1, 2.9, 0.6 Hz, 1H), 7.60 (ddd, *J* = 4.8, 2.8, 0.6 Hz, 1H), 7.55 – 7.45 (m, 1H), 7.42 – 7.32 (m, 2H), 7.33 – 7.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.75 (d, *J* = 257 Hz), δ 159.37 (d, *J* = 5.0 Hz), 150.40 (d, *J* = 1.0 Hz), 141.69, 133.00 (d, *J* = 8.0 Hz), 130.46 (d, *J* = 1.0 Hz),

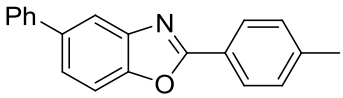
125.42, 124.63, 124.43 (d, *J* = 3.0 Hz), 120.30, 117.02 (d, *J* = 21 Hz), 115.43 (d, *J* = 10 Hz), 110.63. GC-MS: 213



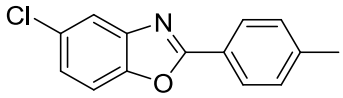
2-hexylbenzoxazole (3am).[8] Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 1H), 7.49-7.47 (m, 1H), 7.32 – 7.27 (m, 2H), 2.92 (t, *J* = 7.9 Hz, 2H), 2.00 – 1.79 (m, 2H), 1.51 – 1.37 (m, 1H), 1.37 – 1.26 (m, 2H), 0.88 (t, *J* = 7.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.36, 150.72, 141.32, 124.34, 123.98, 119.46, 110.21, 31.38, 28.82, 28.62, 26.71, 22.45, 14.00. GC-MS: 201



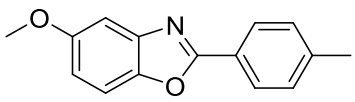
5-methyl-2-p-tolylbenzoxazole (3bc).[9] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.04 (m, 2H), 7.54 – 7.48 (m, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.26 (m, 2H), 7.09 (m, 1H), 2.44 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.21, 148.78, 142.23, 141.70, 134.10, 129.45, 127.37, 125.82, 124.41, 119.62, 109.69, 21.48, 21.39. GC-MS: 223



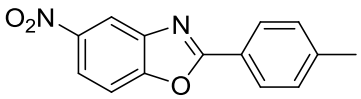
5-phenyl-2-p-tolylbenzoxazole (3cc).[10] White solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.13 (m, 2H), 7.97 (m, 1H), 7.68 – 7.53 (m, 4H), 7.52 – 7.43 (m, 2H), 7.41 – 7.31 (m, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.81, 150.16, 142.72, 142.09, 141.02, 138.25, 129.60, 128.80, 127.54, 127.37, 127.15, 124.41, 124.23, 118.18, 110.41, 21.61. GC-MS: 285



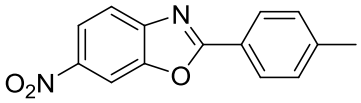
5-chloro-2-p-tolylbenzoxazole (3dc).[9] White solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.03 (m, 2H), 7.72 – 7.66 (m, 1H), 7.48 – 7.40 (m, 1H), 7.28 (m, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.55, 149.17, 143.21, 142.51, 129.87, 129.64, 127.64, 125.03, 123.79, 119.68, 111.11, 21.62. GC-MS: 243



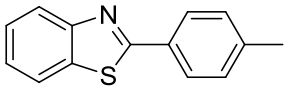
5-methoxy-2-p-tolylbenzoxazole (3ec).[11] White solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 2.5 Hz, 1H), 6.93 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.86 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.04, 157.30, 145.31, 142.96, 141.90, 129.60, 127.42, 124.47, 113.34, 110.56, 102.79, 55.91, 21.61. GC-MS: 239



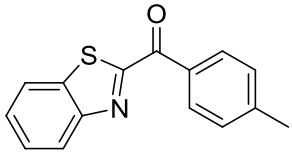
5-nitro-2-p-tolylbenzoxazole (3fc).[12] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.2 Hz, 1H), 8.26 (dd, *J* = 8.9, 2.2 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.12, 154.13, 145.25, 143.38, 142.55, 129.79, 127.91, 123.04, 120.81, 115.92, 110.49, 21.68. GC-MS: 254



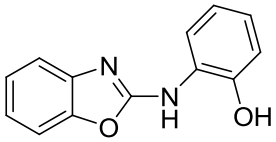
6-nitro-2-p-tolylbenzoxazole (3gc).[13] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.34 (m, 1H), 8.24 (dd, *J* = 8.8, 2.2 Hz, 1H), 8.13 – 8.04 (m, 2H), 7.79 – 7.70 (m, 1H), 7.31 (dd, *J* = 8.5, 0.6 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.46, 149.56, 147.36, 144.70, 143.66, 129.75, 128.01, 122.89, 120.61, 119.33, 106.90, 21.66. GC-MS: 254



2-p-tolylbenzothiazole (4a).[14] Colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (ddd, *J* = 8.2, 1.1, 0.6 Hz, 1H), 8.02 – 7.95 (m, 2H), 7.89 (ddd, *J* = 8.0, 1.2, 0.6 Hz, 1H), 7.48 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.37 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.30 (dd, *J* = 8.5, 0.6 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.20, 154.09, 141.38, 134.88, 130.88, 129.67, 127.42, 126.20, 124.95, 122.98, 121.52, 21.49. GC-MS: 225



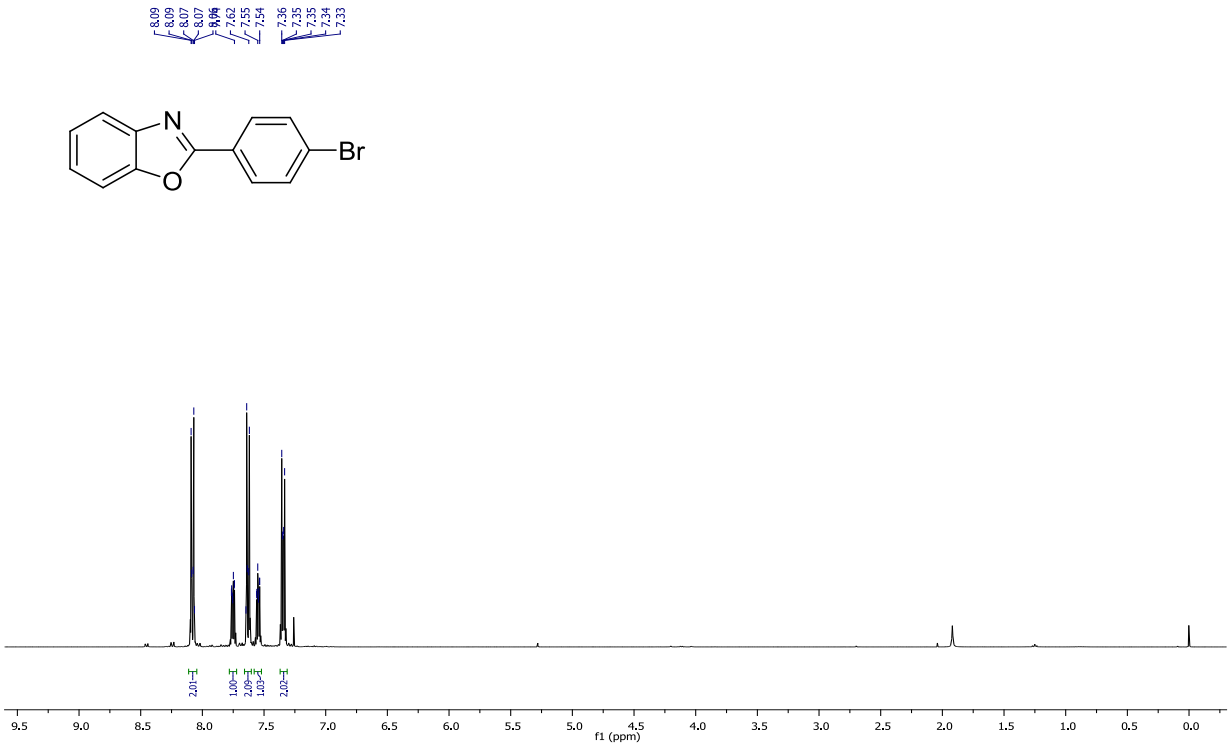
(benzothiazol-2-yl)(p-tolyl)methanone (4b).[15] Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.44 (m, 2H), 8.29 – 8.20 (m, 1H), 8.05 – 8.00 (m, 1H), 7.63 – 7.51 (m, 2H), 7.36 (dd, *J* = 8.6, 0.6 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.93, 167.42, 153.85, 145.01, 136.93, 132.36, 131.39, 129.25, 127.48, 126.83, 125.65, 122.13, 21.86. GC-MS: 253

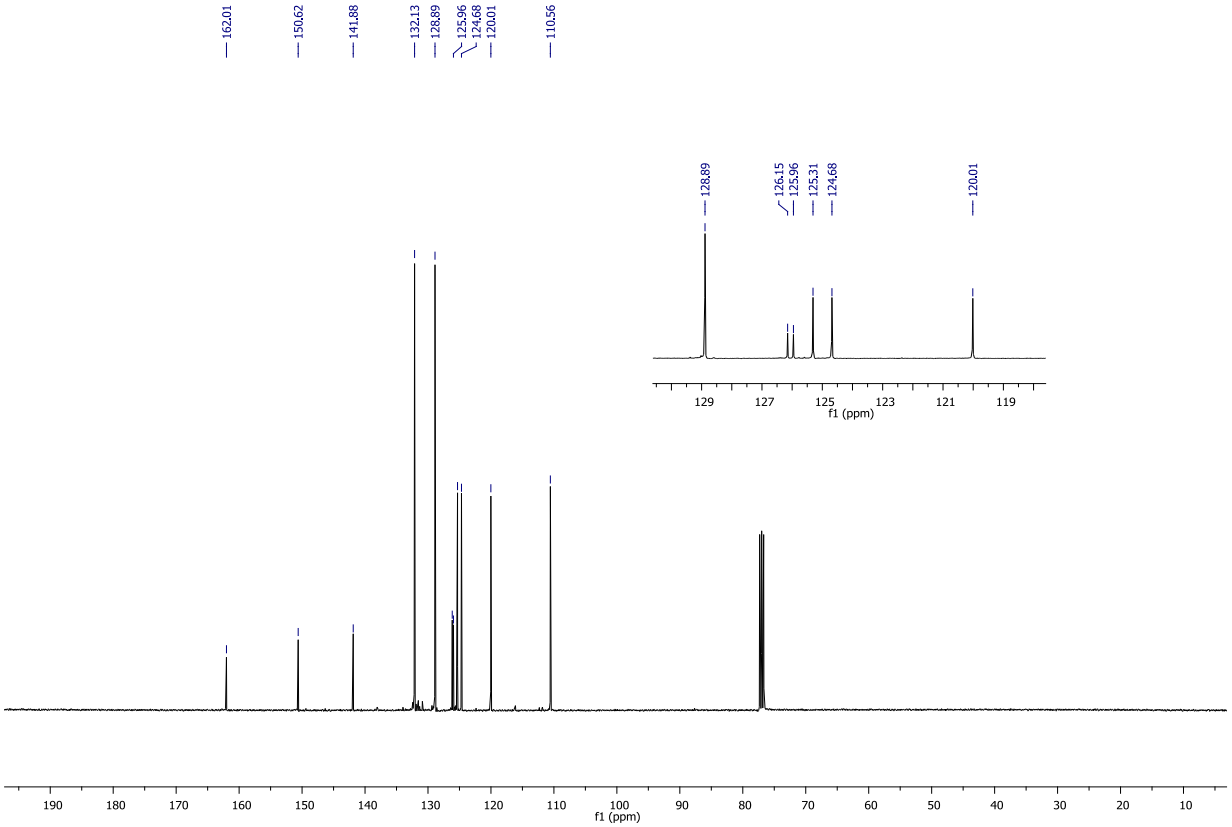


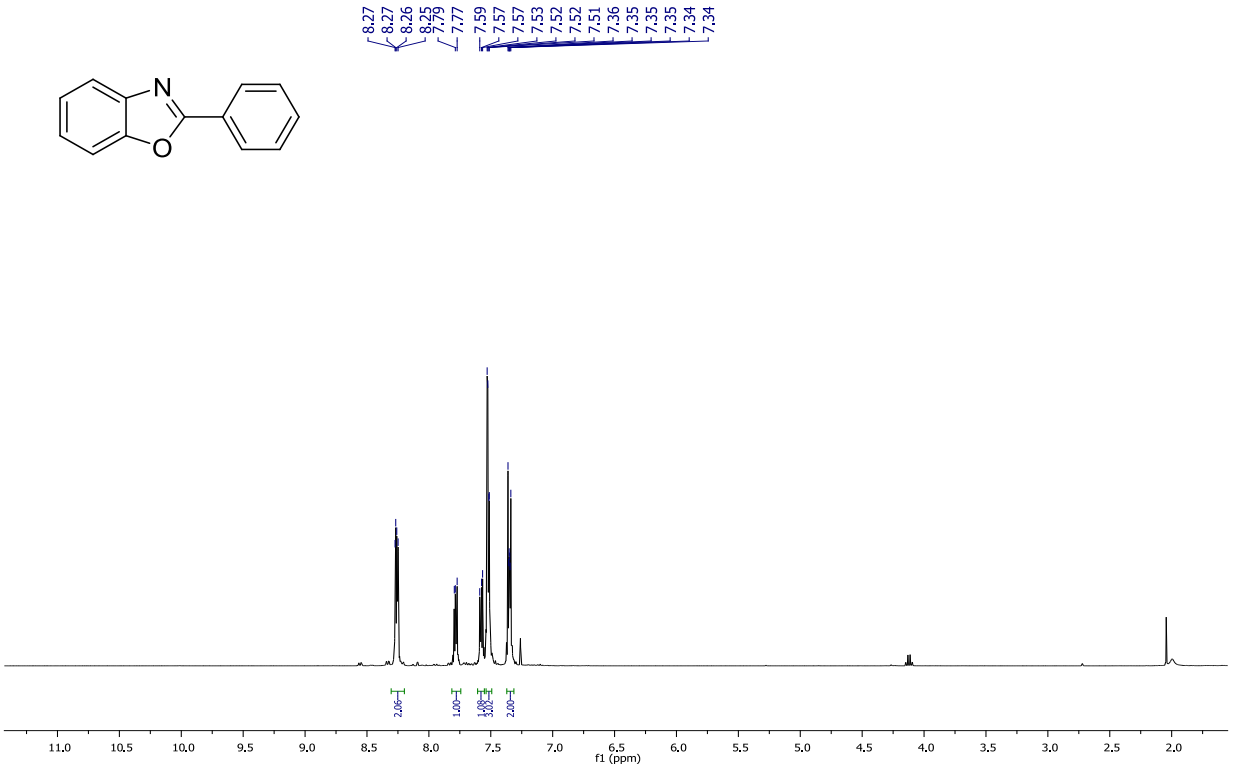
2-(benzoxazol-2-ylamino)phenol (1aa). Pale yellow solid. ^{1}H NMR (400 MHz, DMSO) δ 9.99 (s, 1H), 9.48 (s, 1H), 8.04 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55 – 7.37 (m, 2H), 7.23 (td, *J* = 7.7, 1.1 Hz, 1H), 7.13 (td, *J*

= 7.8, 1.2 Hz, 1H), 6.93 (m, 3H). ^{13}C NMR (100 MHz, DMSO) δ159.32, 148.11, 147.67, 142.85, 126.41, 124.28, 124.21, 121.64, 121.31, 119.46, 116.64, 115.62, 109.19. LRMS (ESI) m/z 227.0 ($M + H^+$), HRMS (ESI) m/z 227.0816 (227.0815 calcd for $C_{13}H_{11}N_2O_2^+$ $[M+H]^+$)

NMR Spectra



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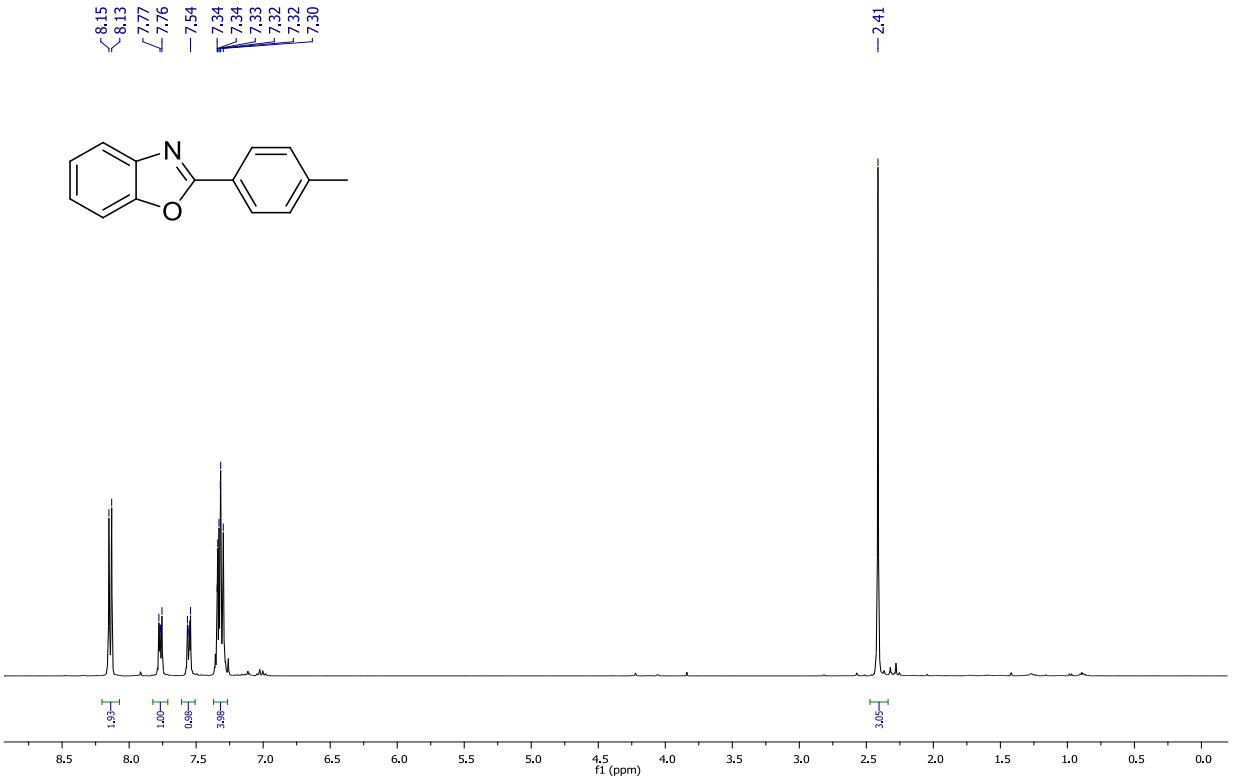
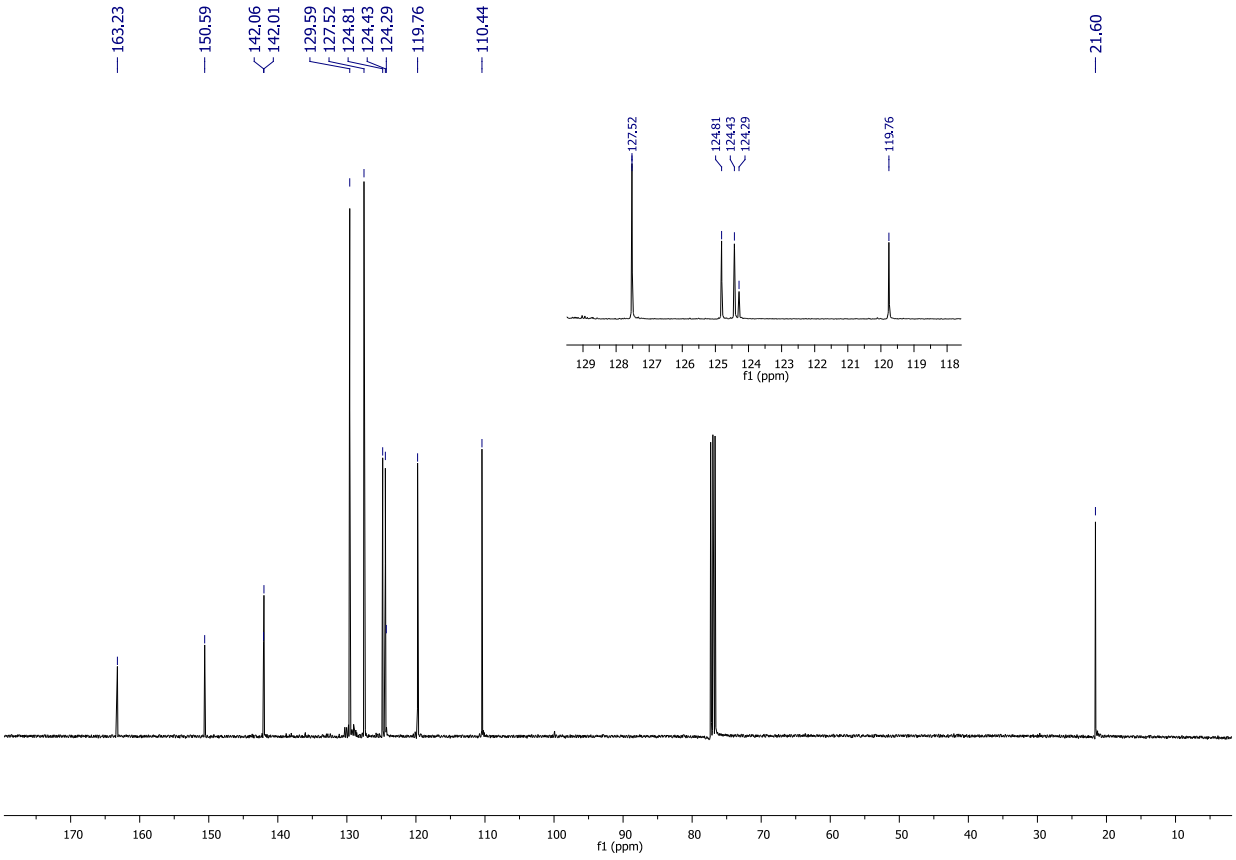
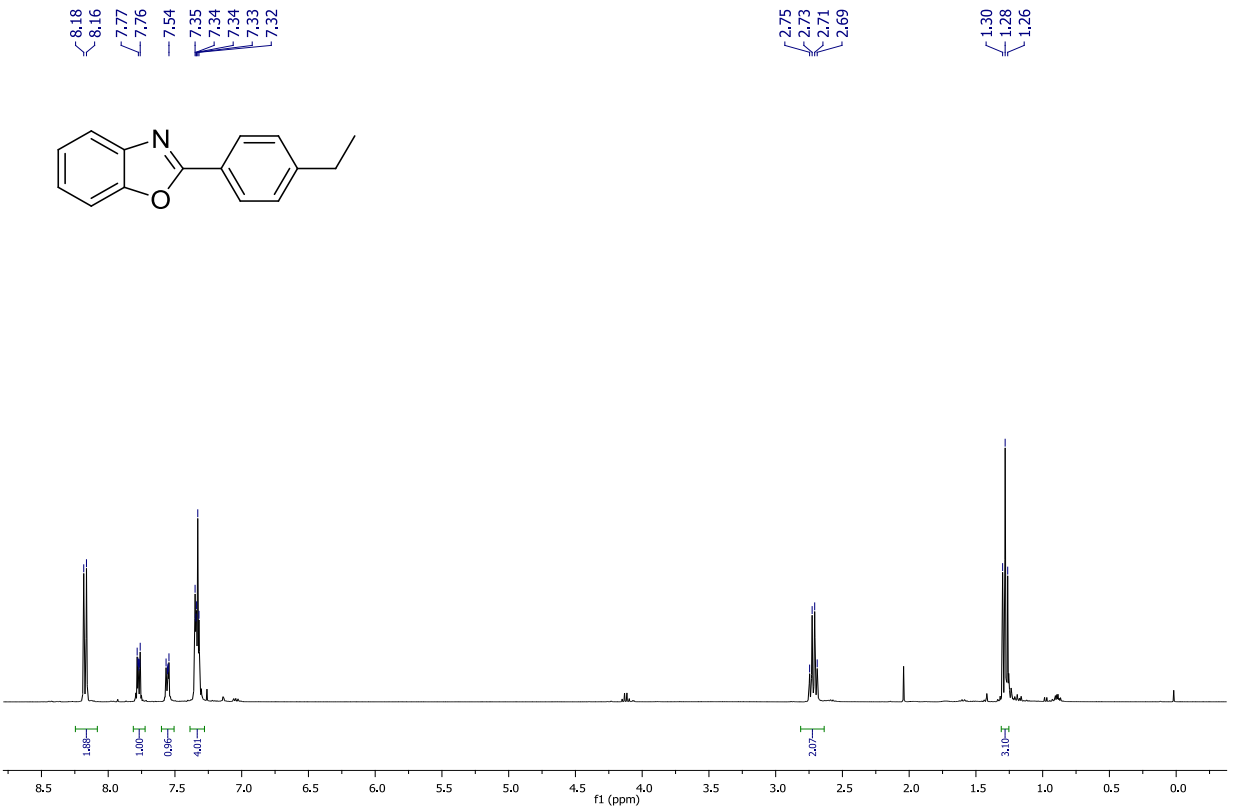
f1 (ppm)
f1 (ppm)



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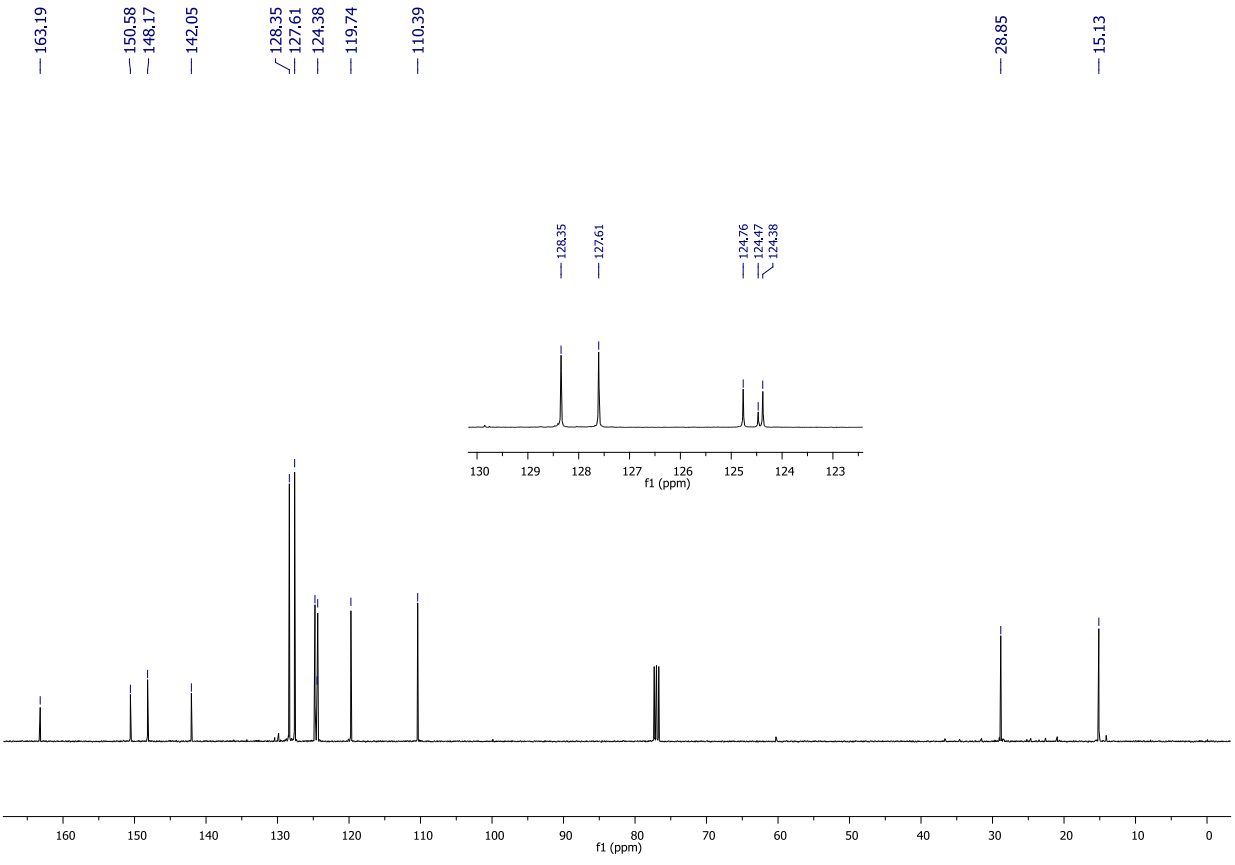
f1 (ppm)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124.76
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124.38
f1 (ppm)
f1 (ppm)


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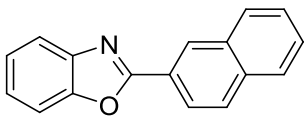
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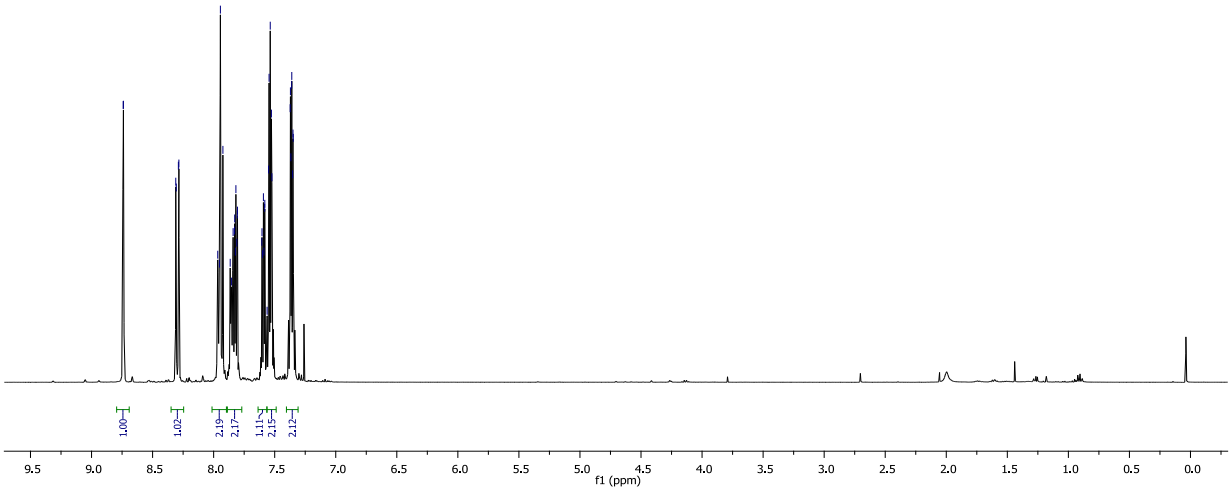
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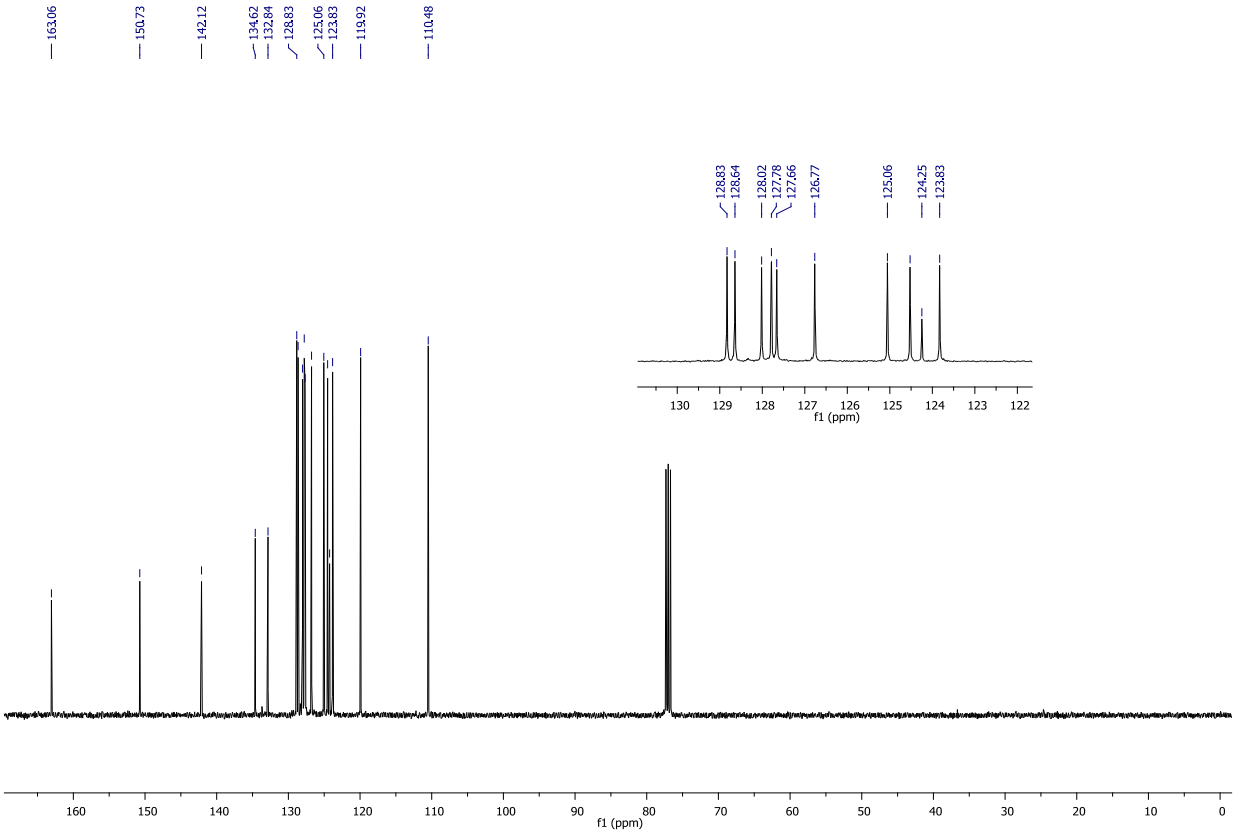
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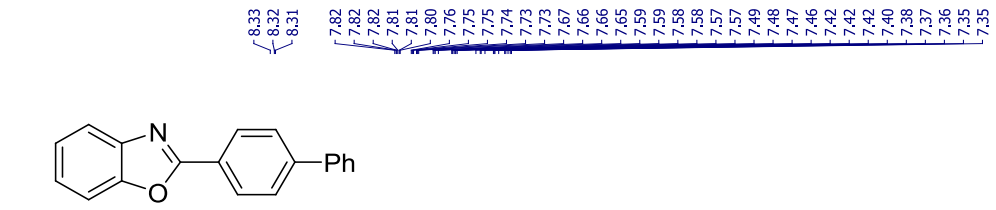
f1 (ppm)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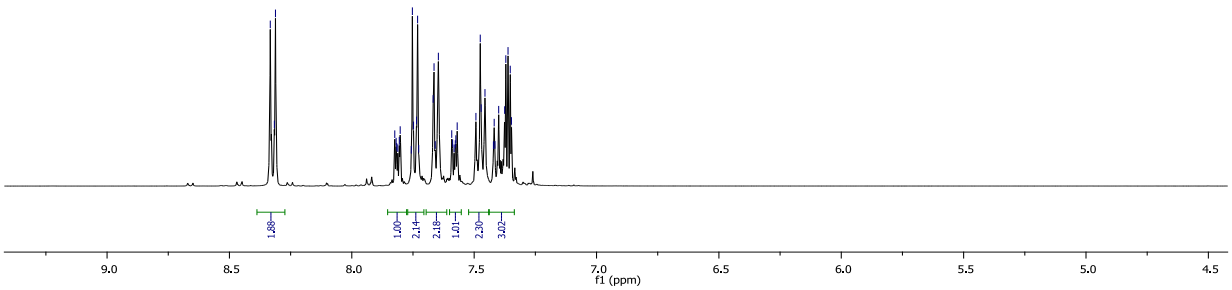
O
Ph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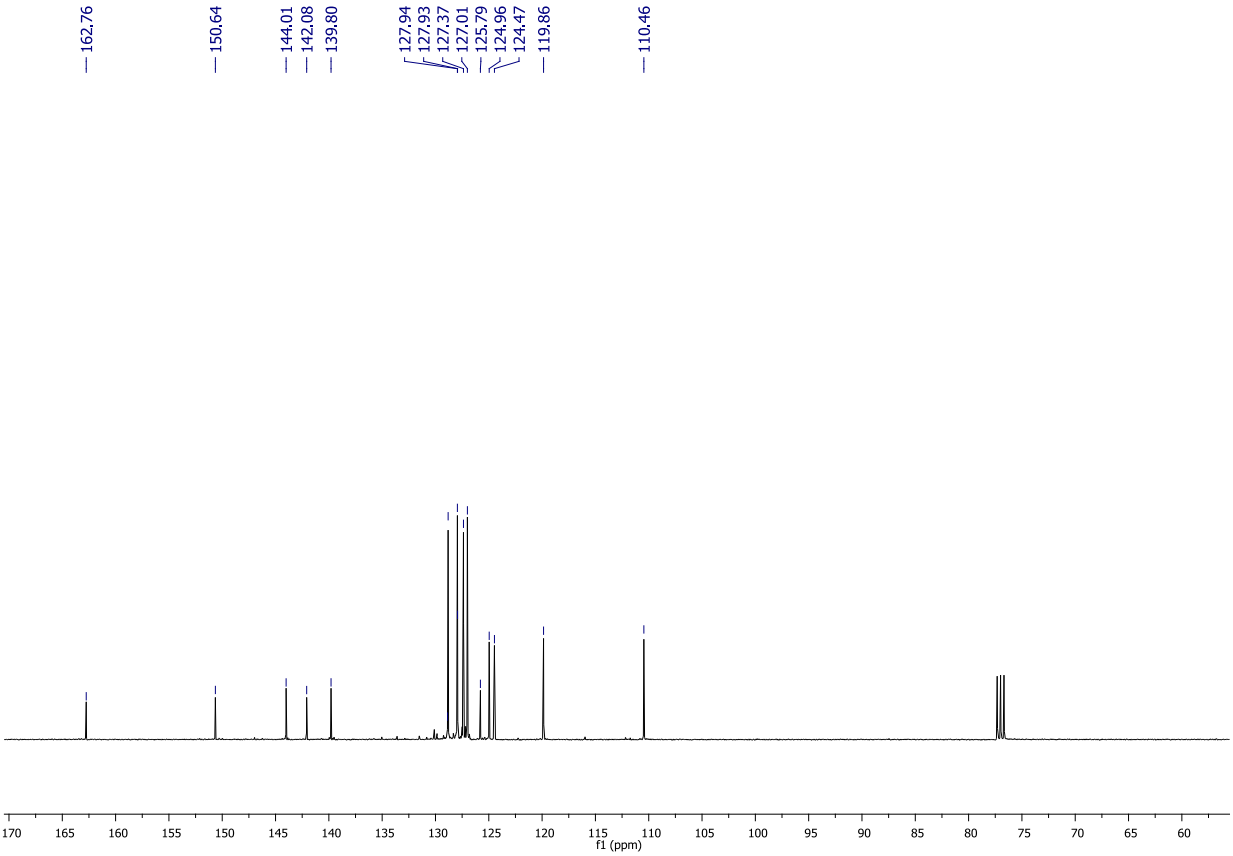
f1 (ppm)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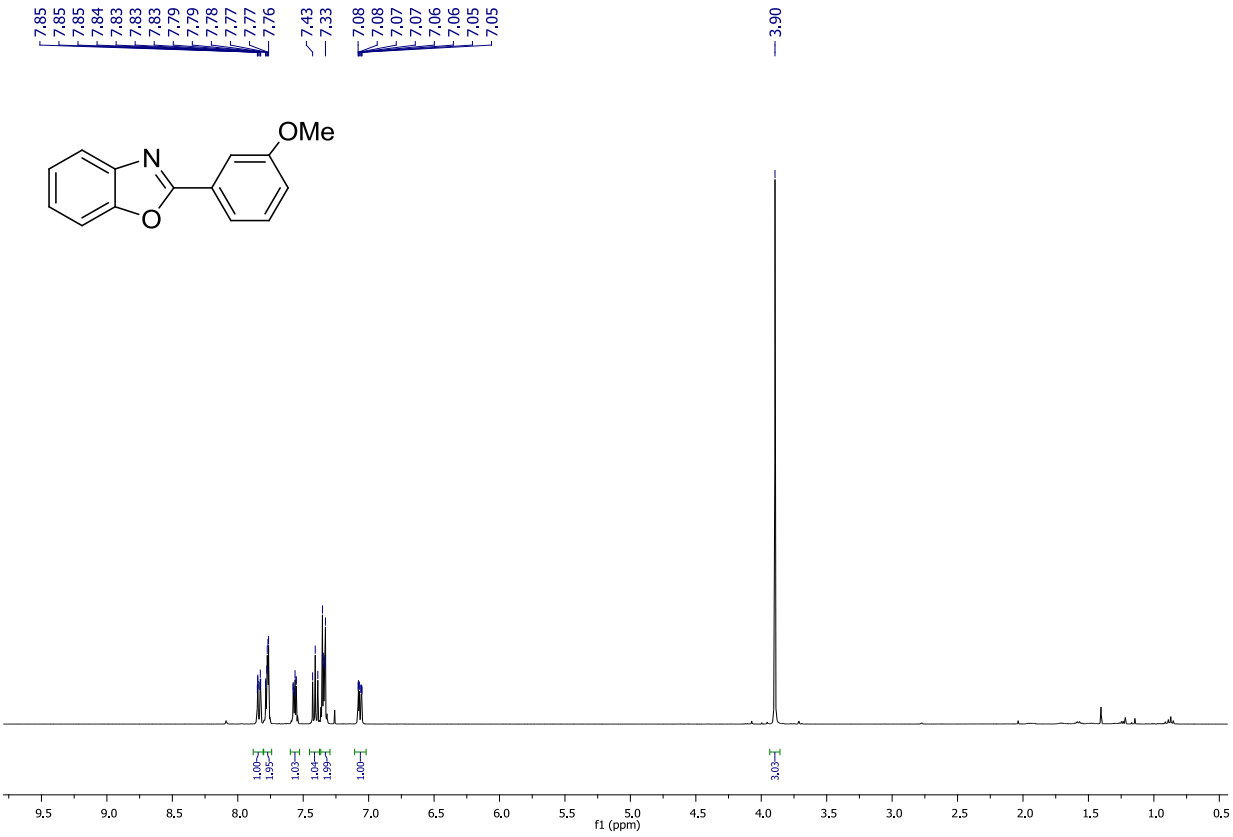
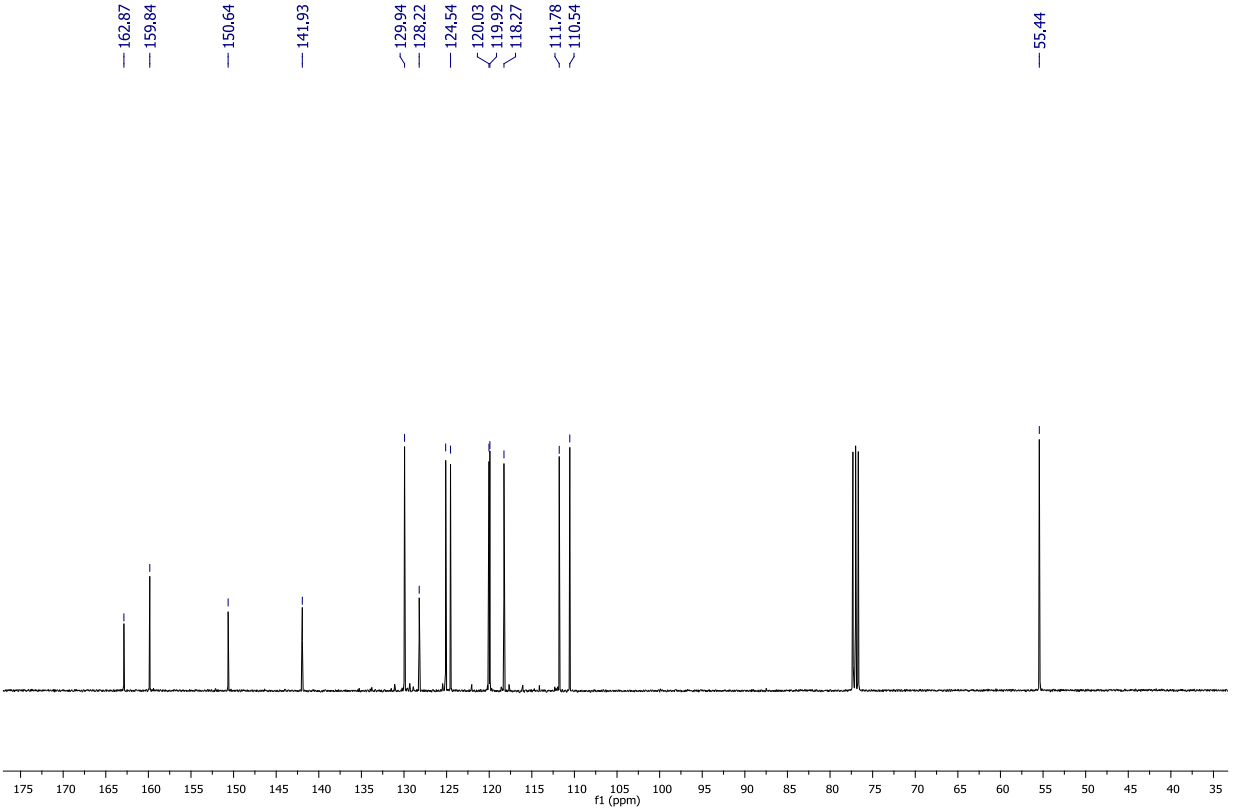
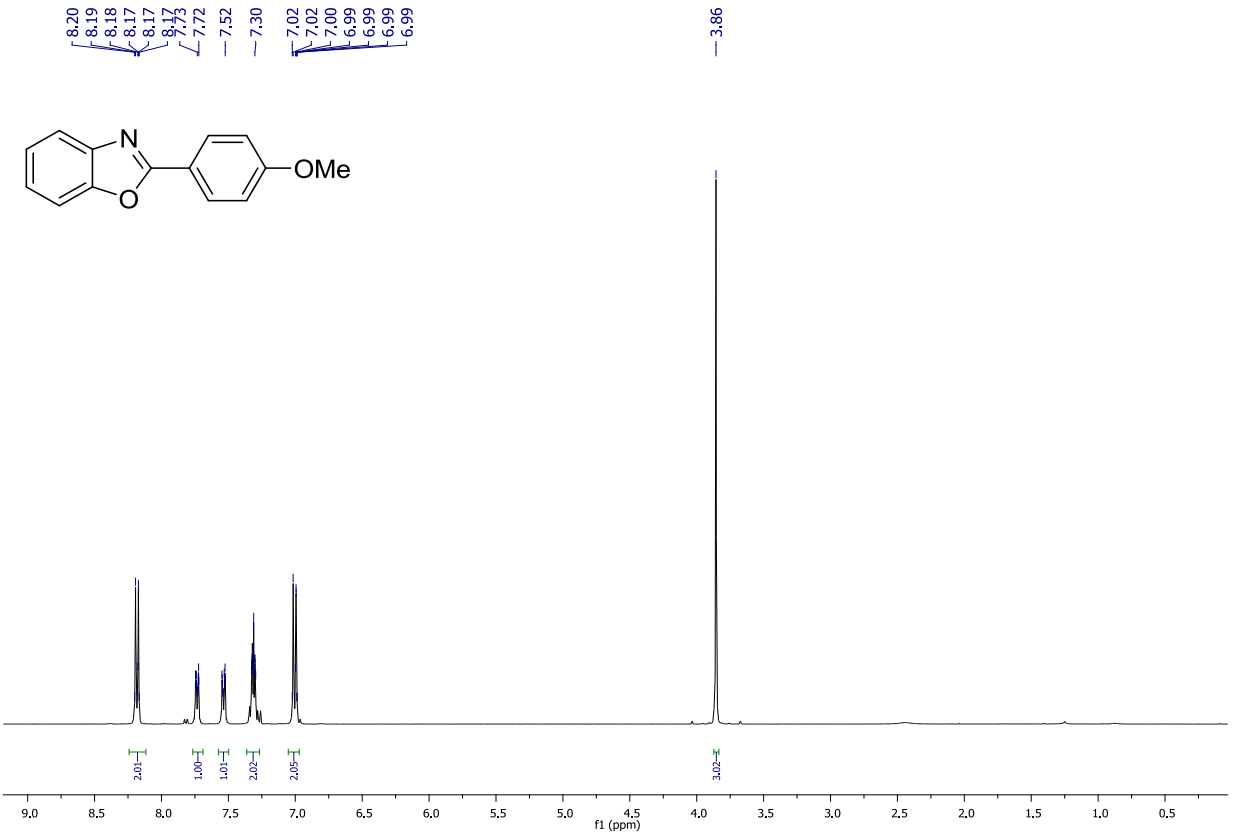
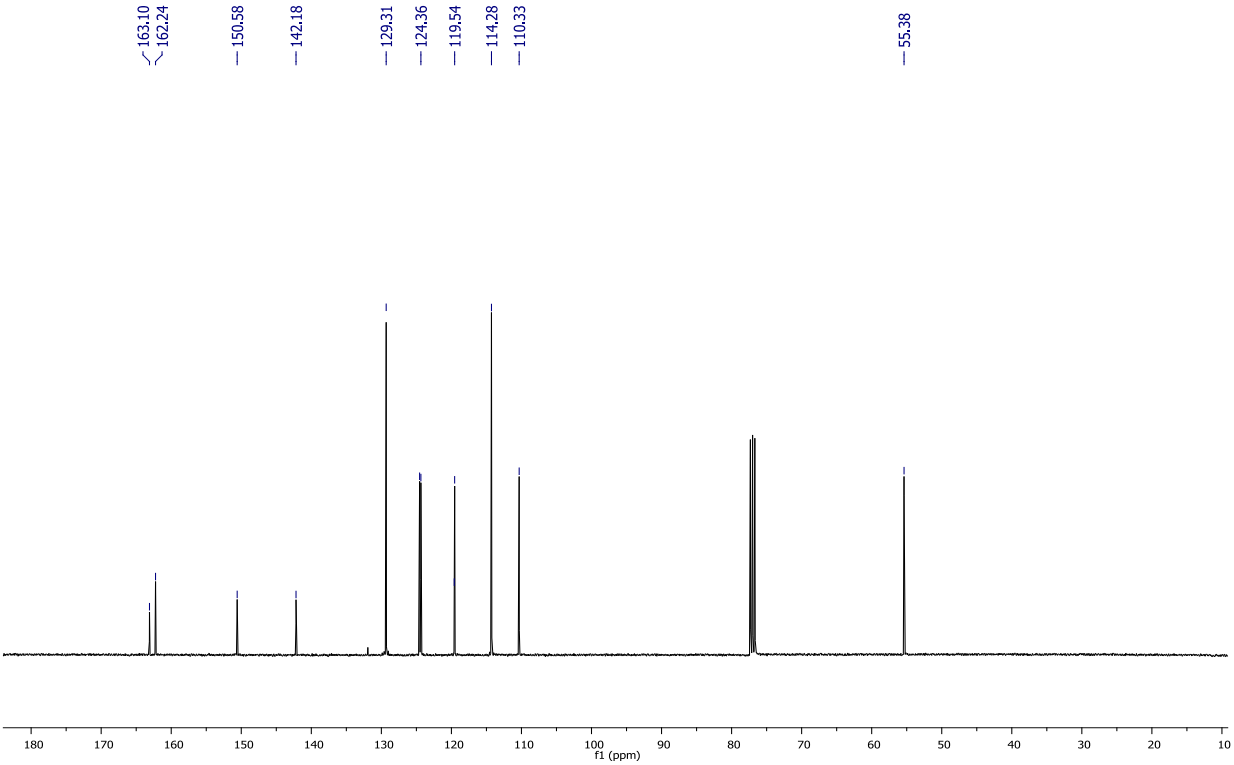
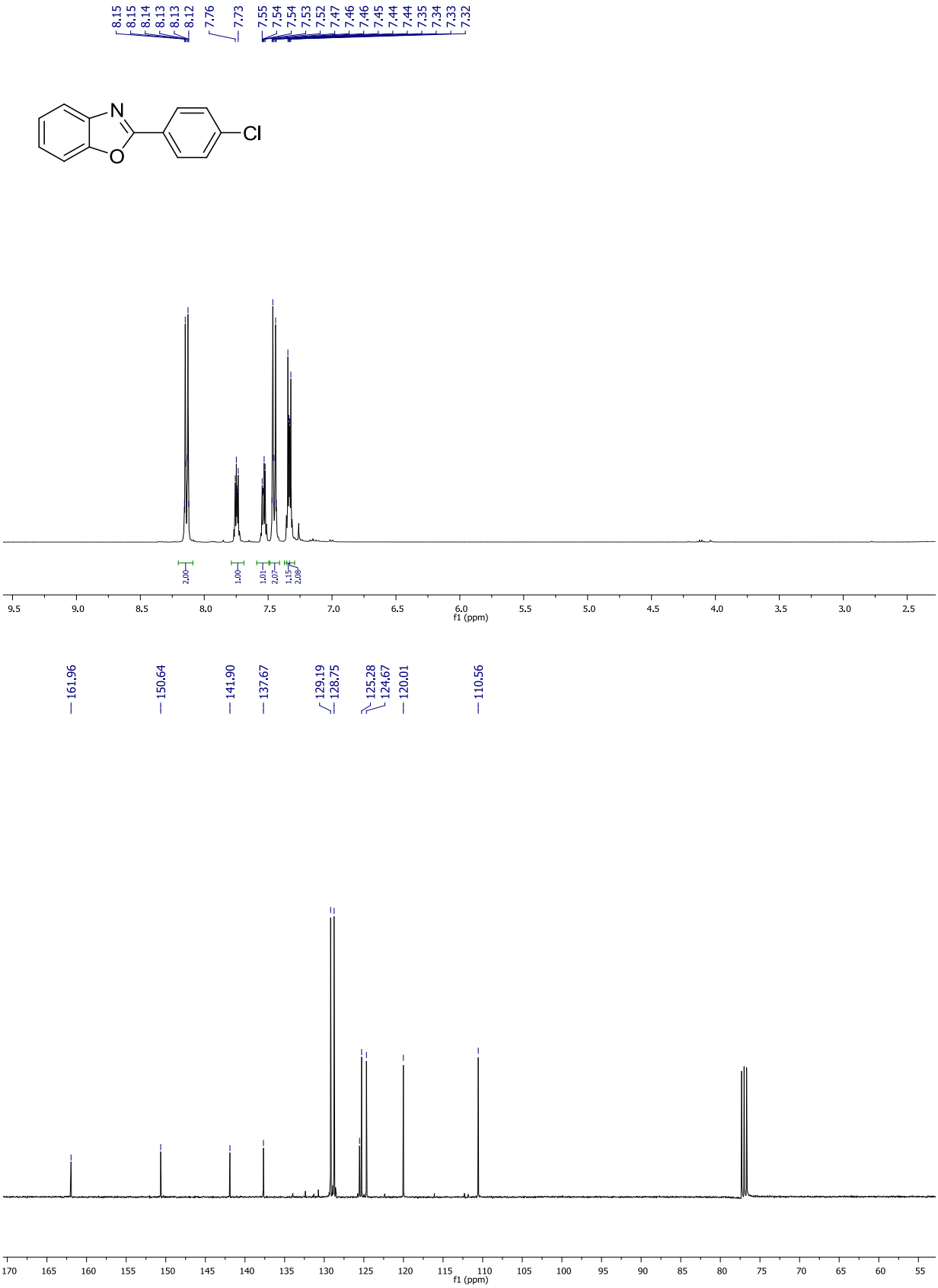
f1 (ppm)







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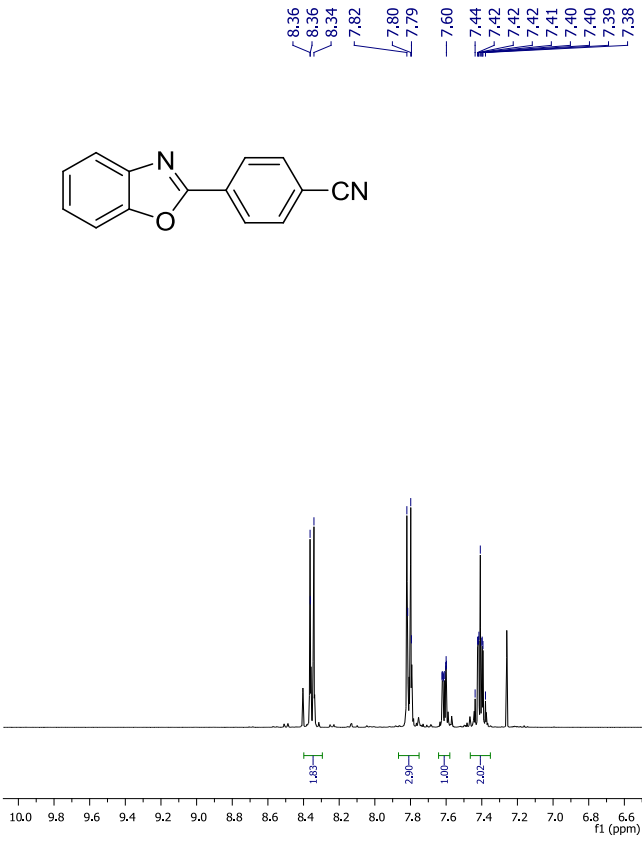
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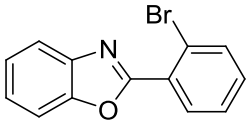

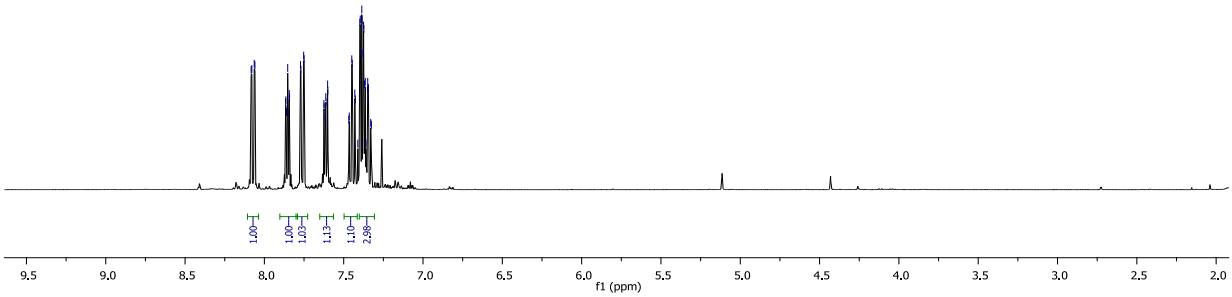

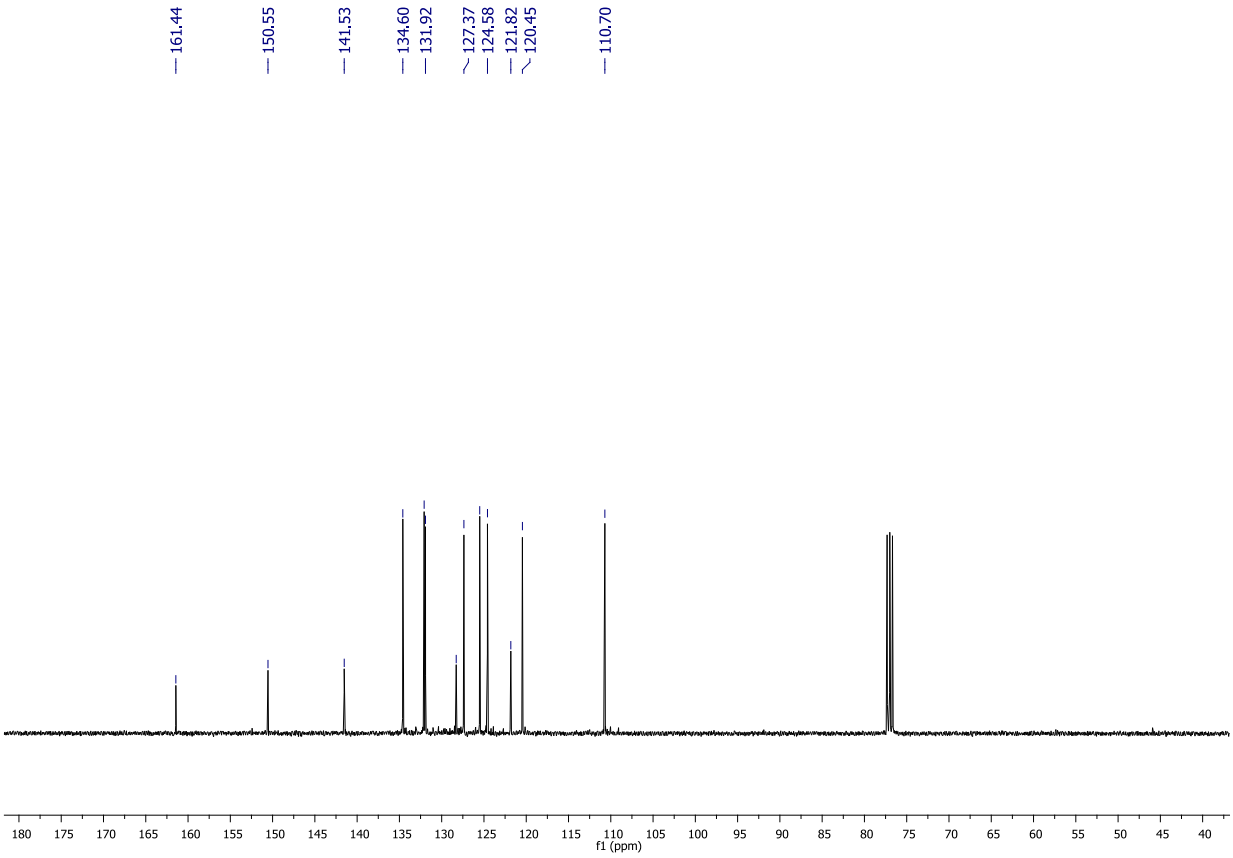


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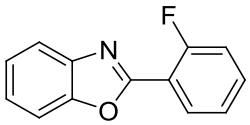
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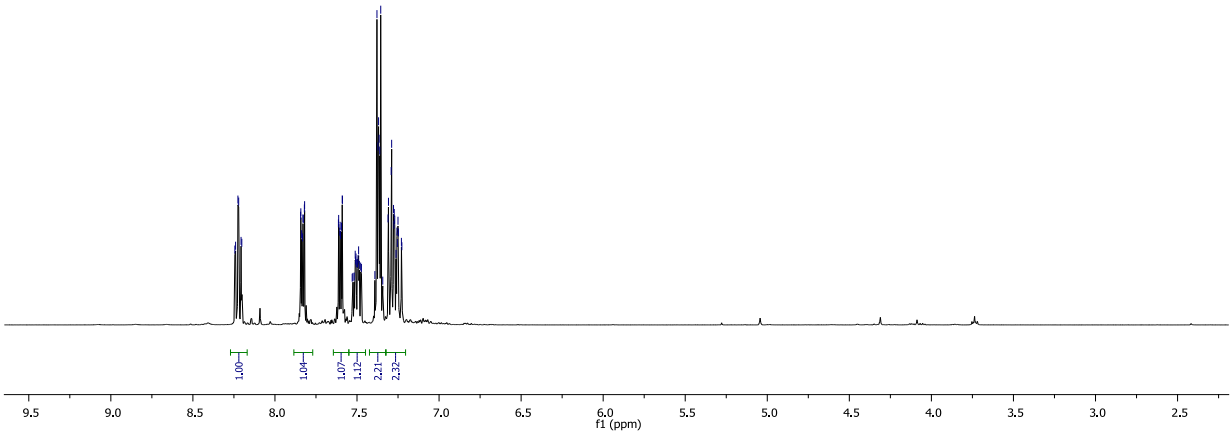
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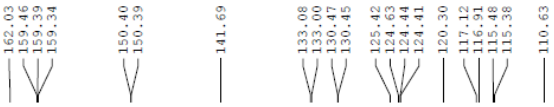
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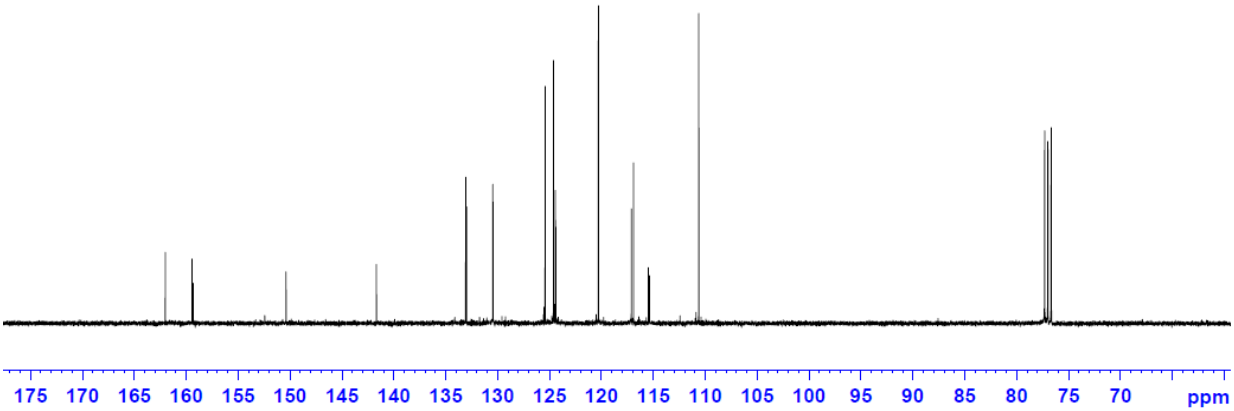
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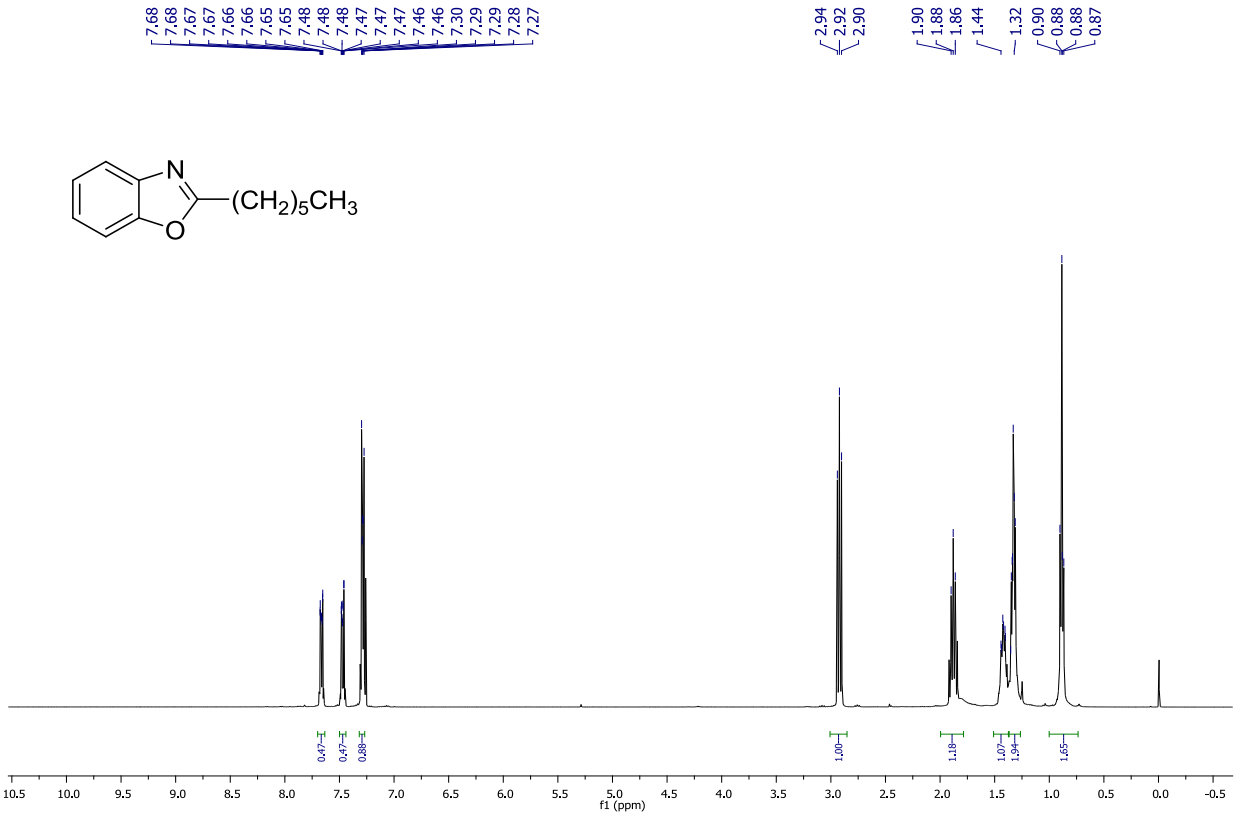
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0.47
0.88
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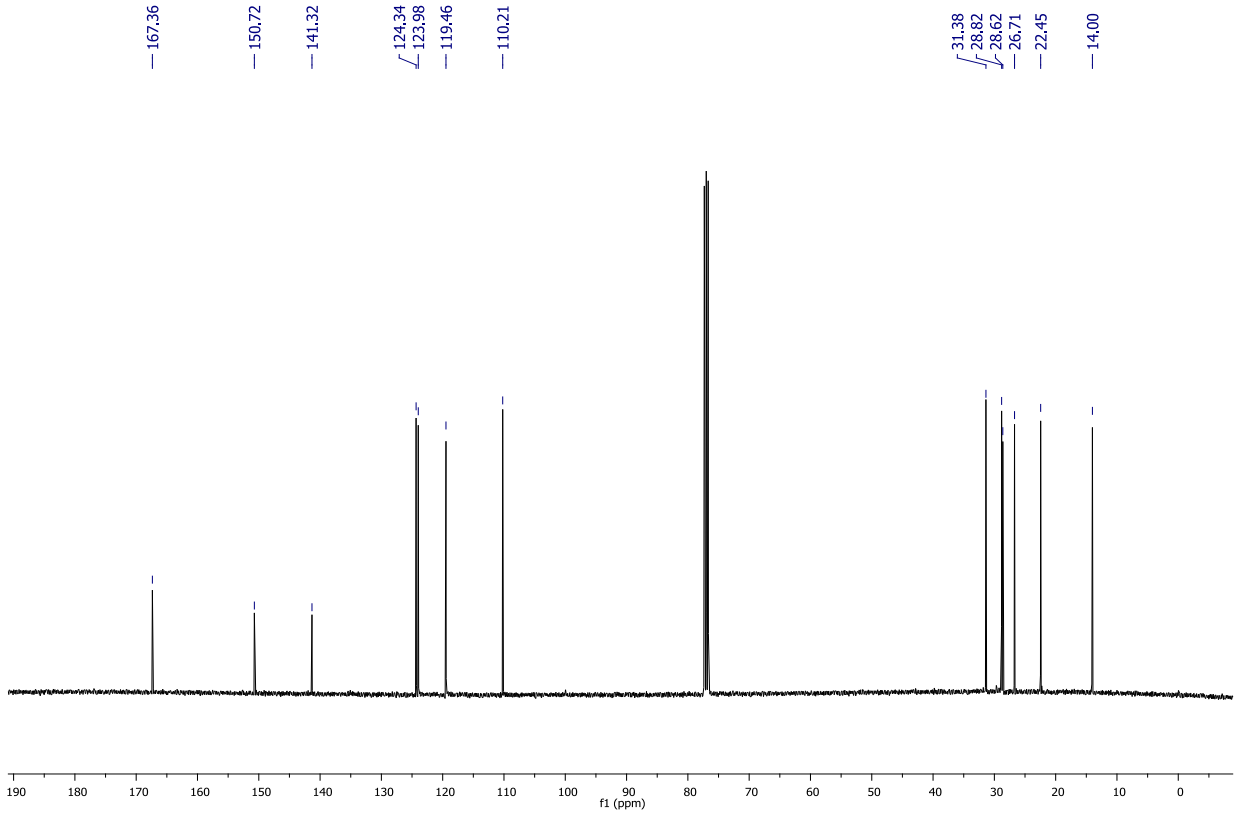
1.65
f1 (ppm)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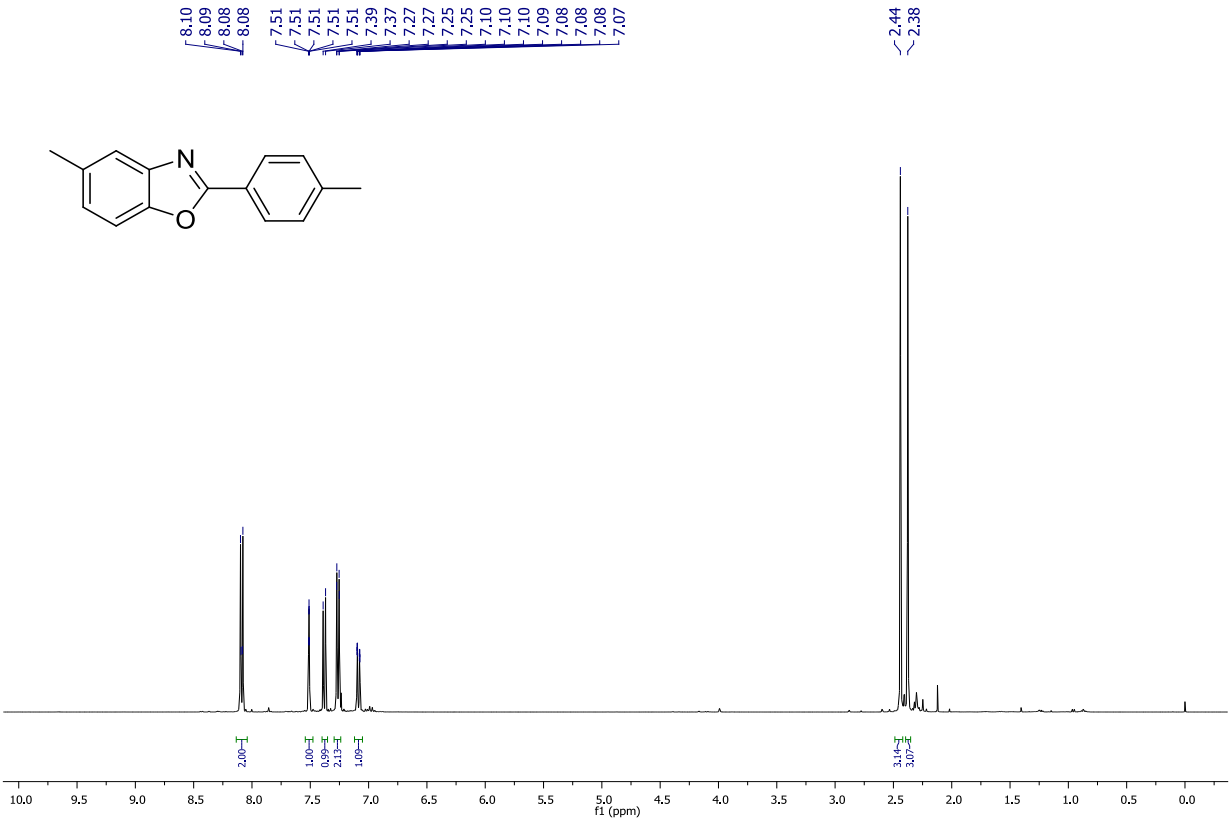
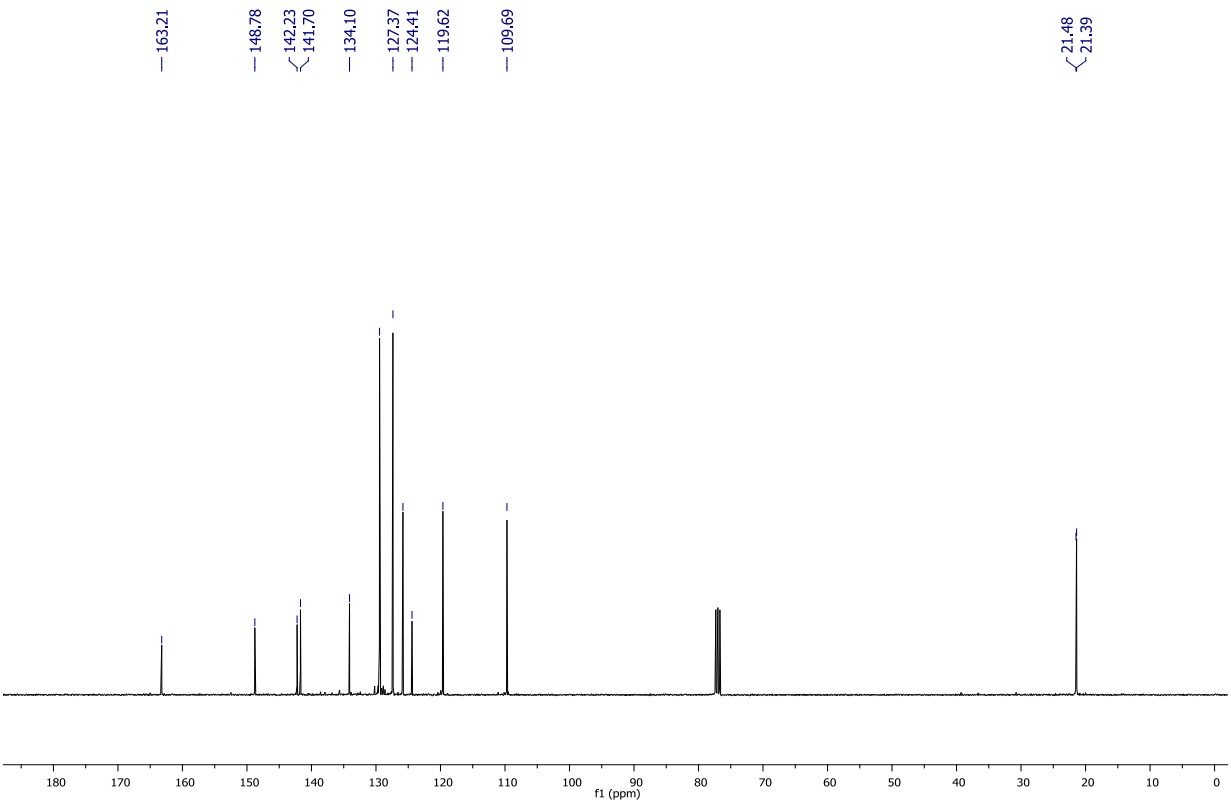
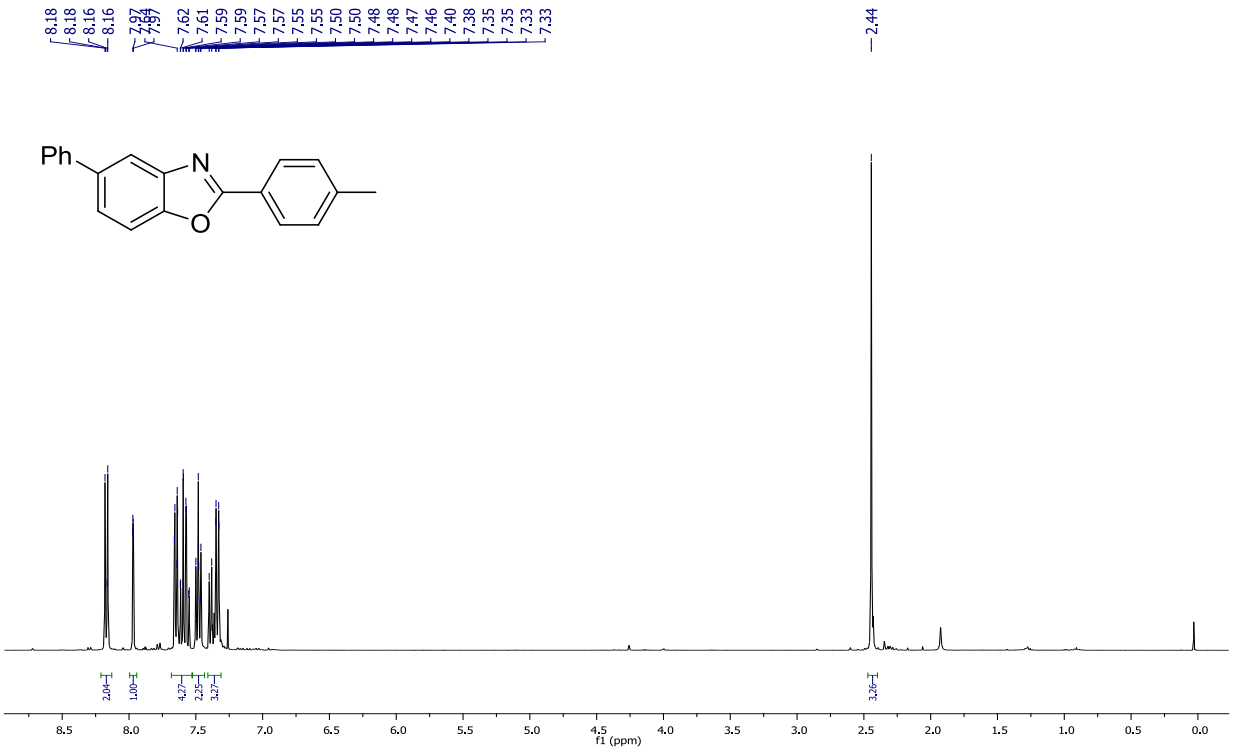
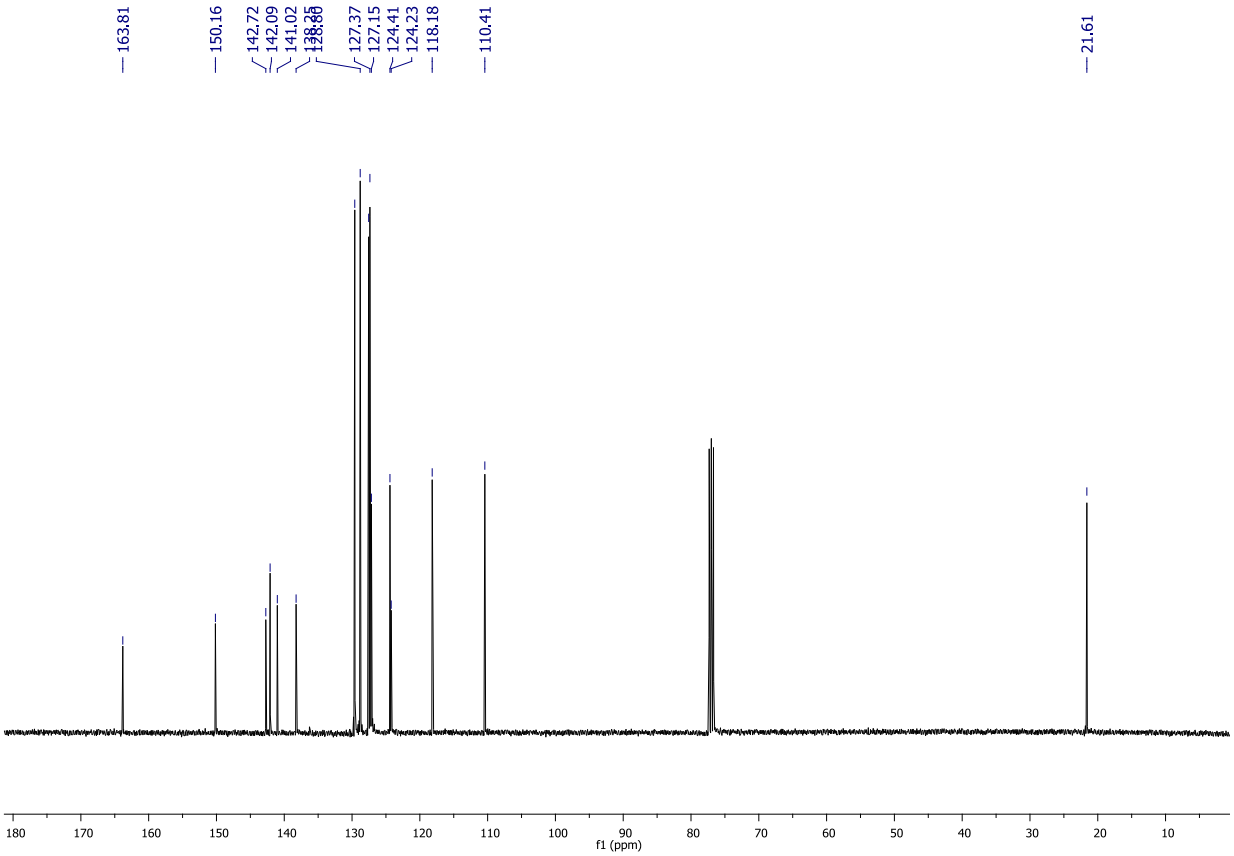
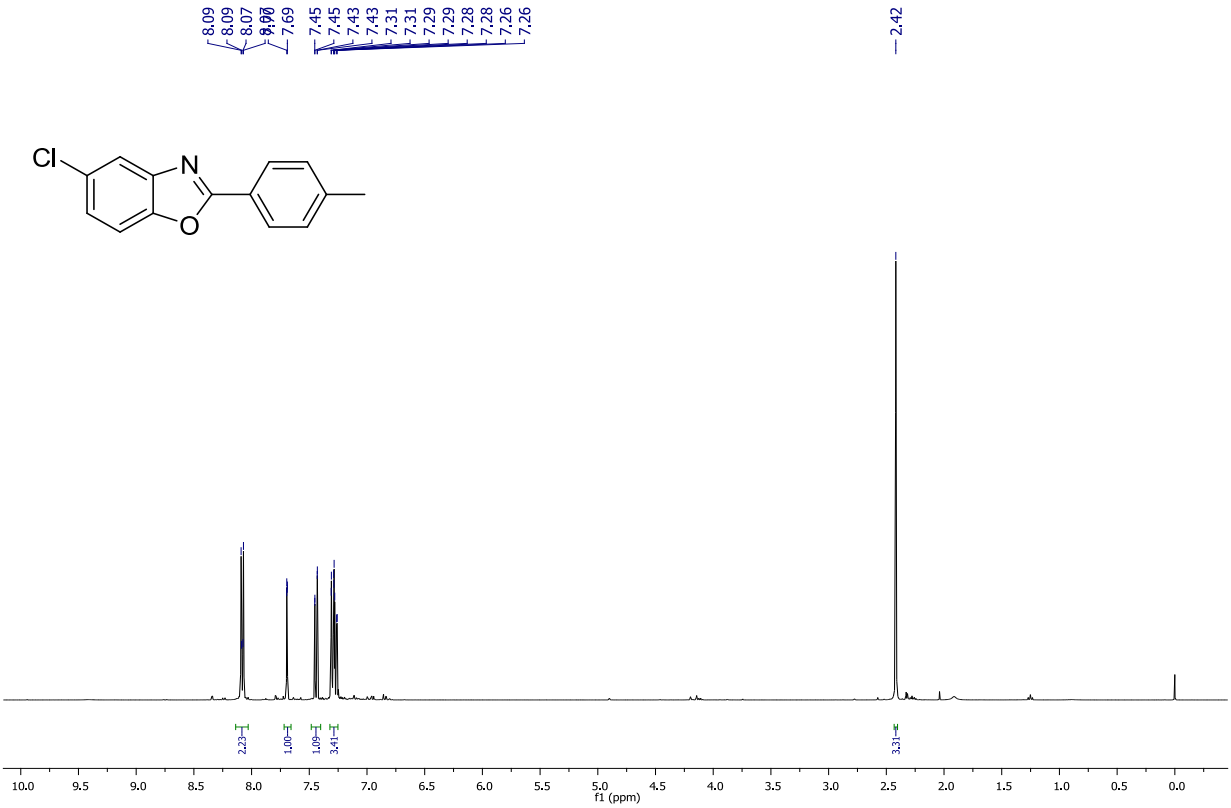
f1 (ppm)







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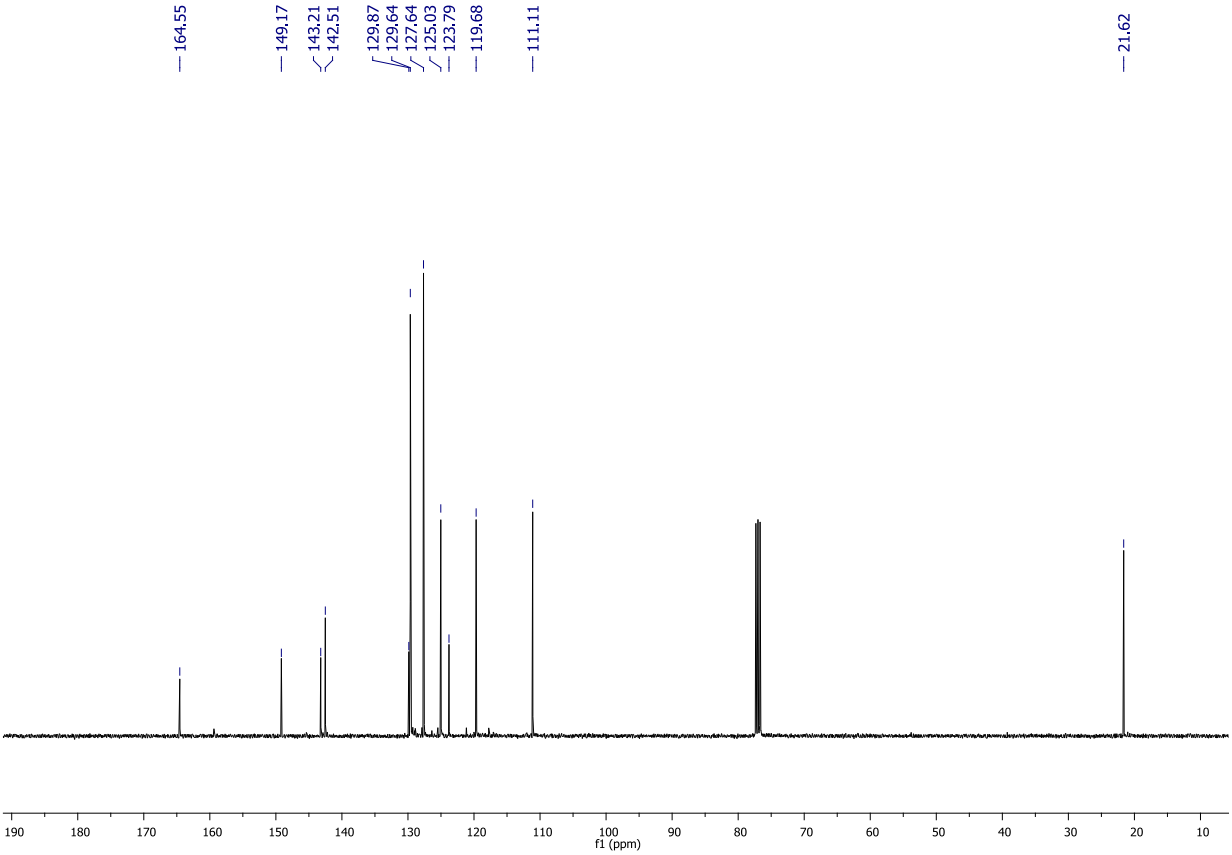
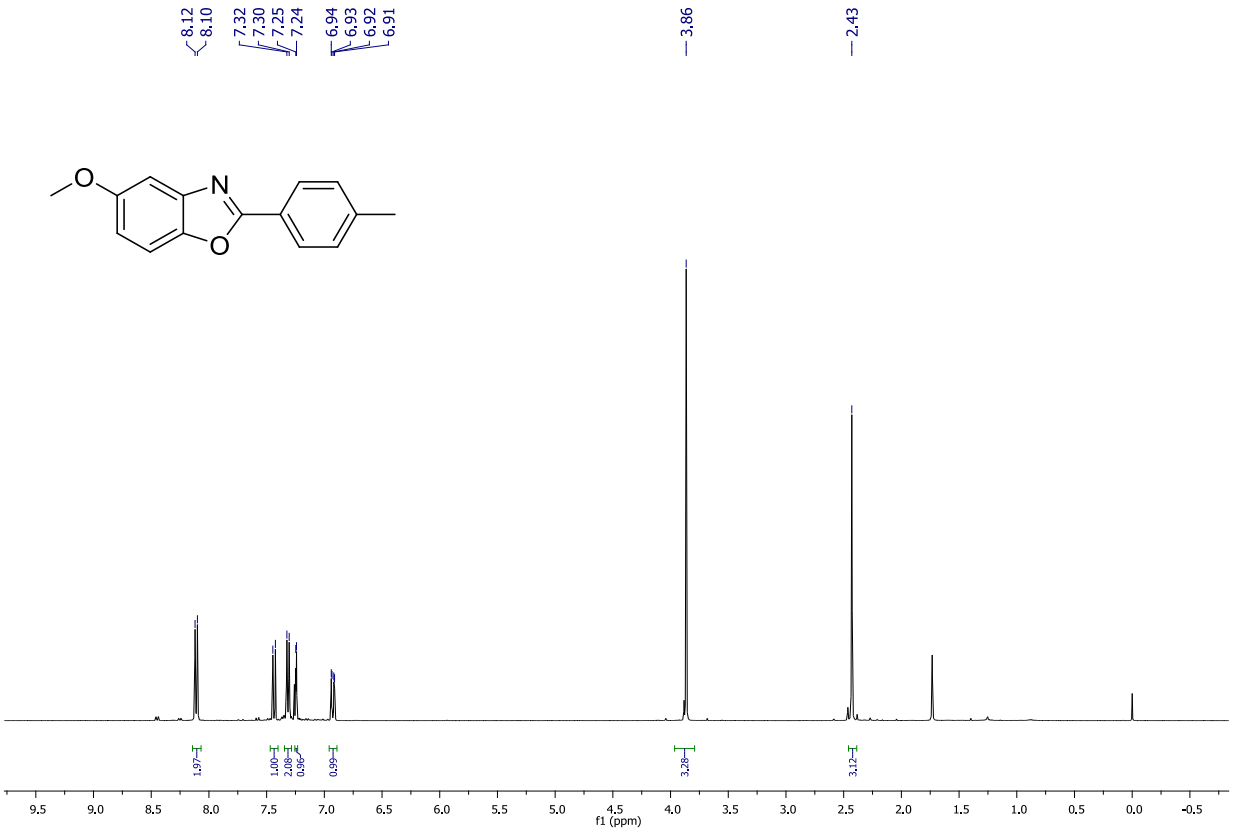
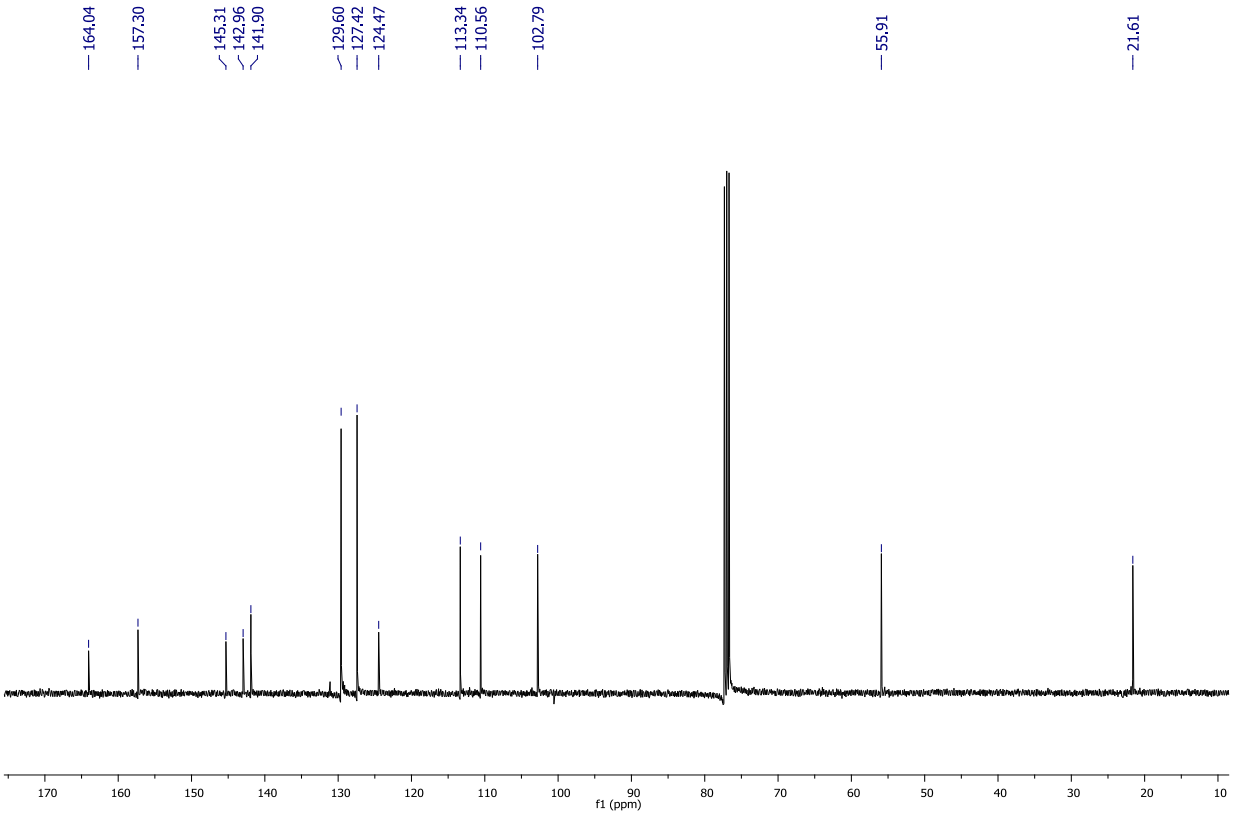
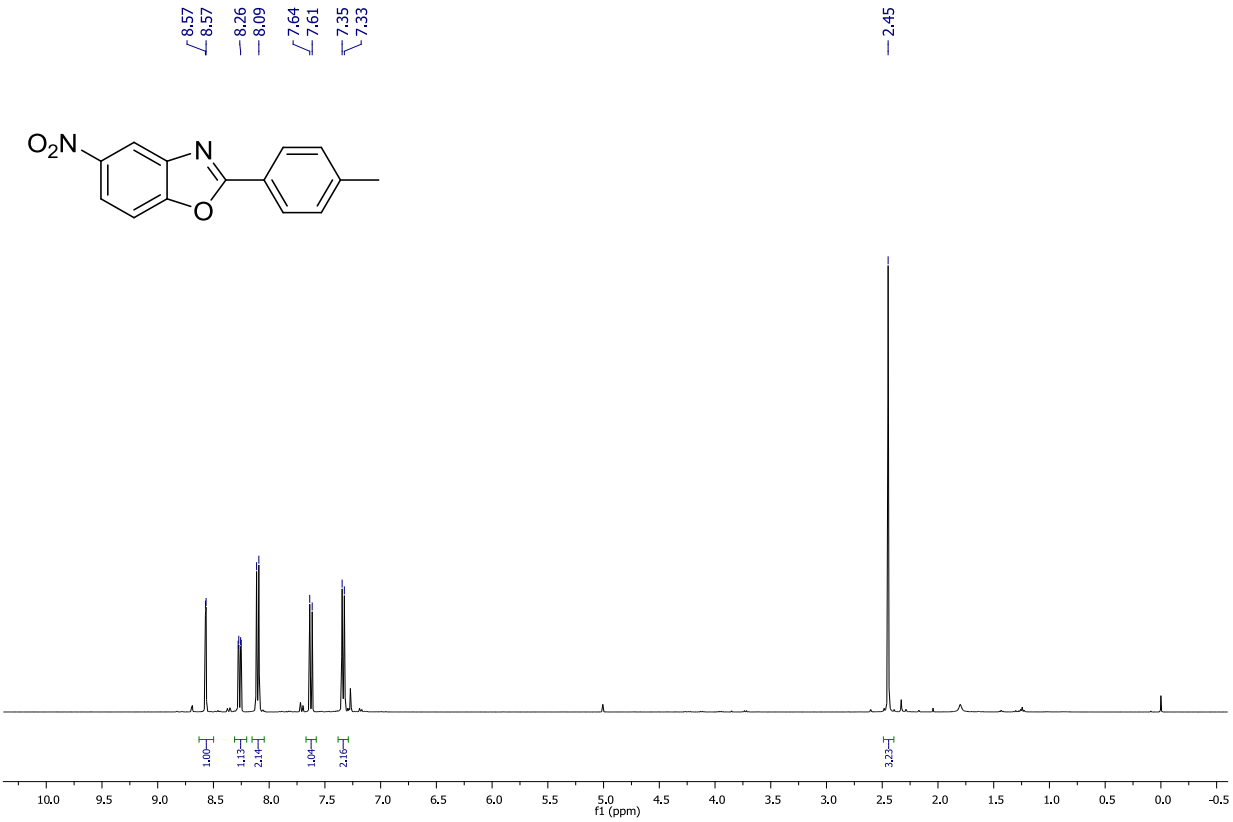
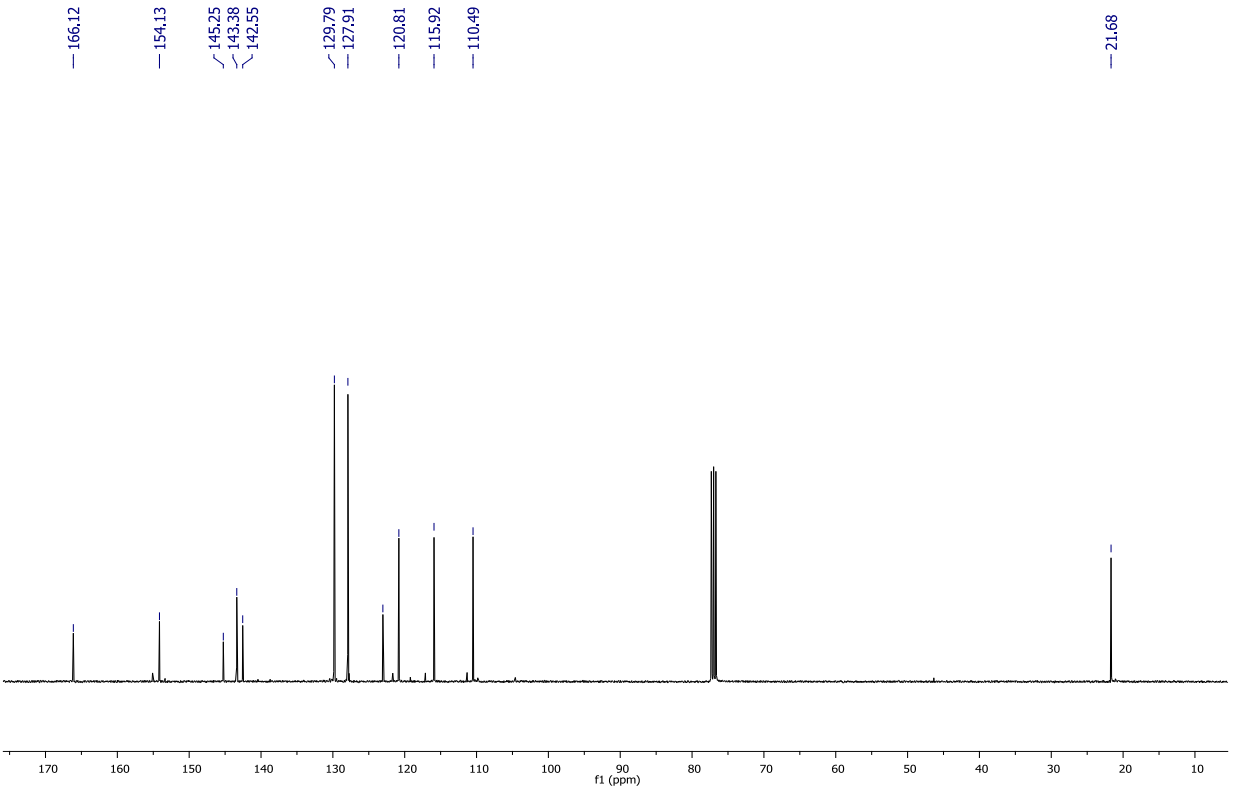
7.26
2.42
Cl
N
O
2.23
1.00
1.09
3.41
3.31
f1 (ppm)

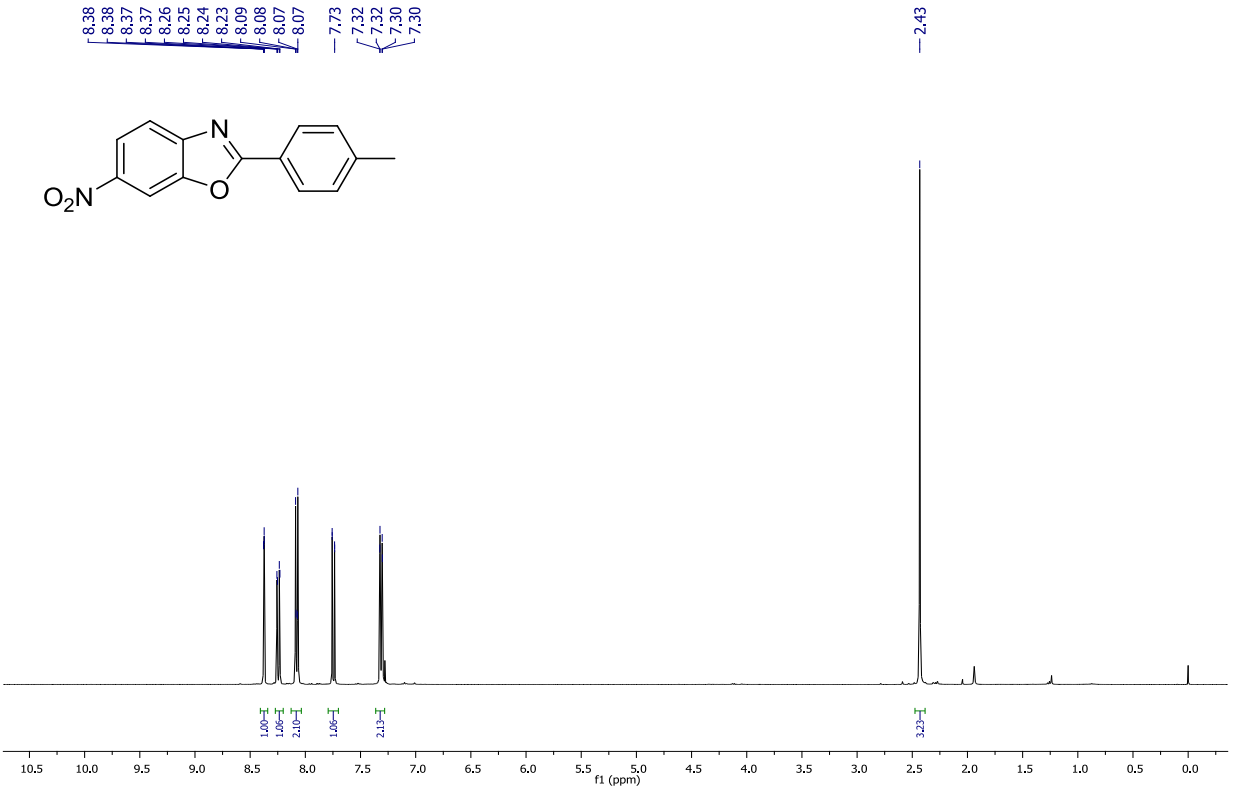

164.55
149.17
143.21
142.51
129.87
129.64
127.64
125.03
123.79
119.68
111.11
21.62
f1 (ppm)

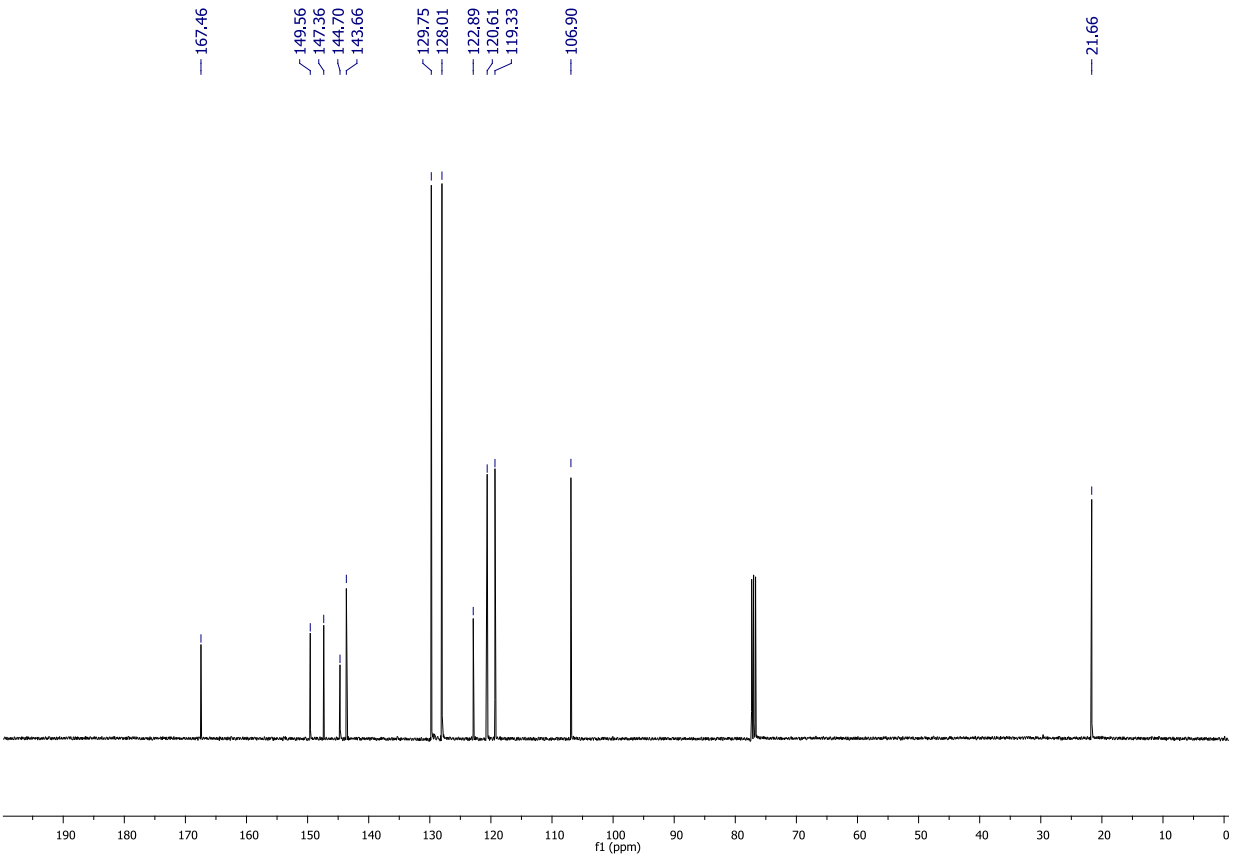


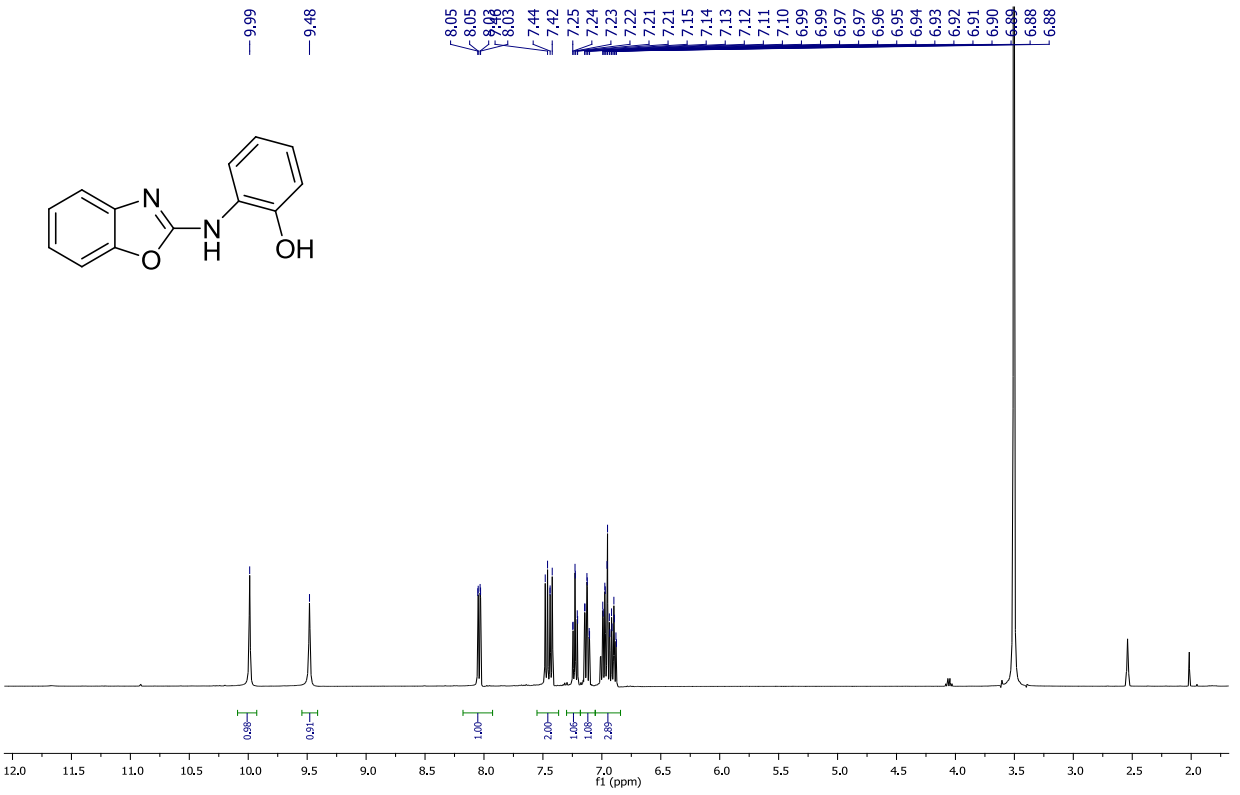


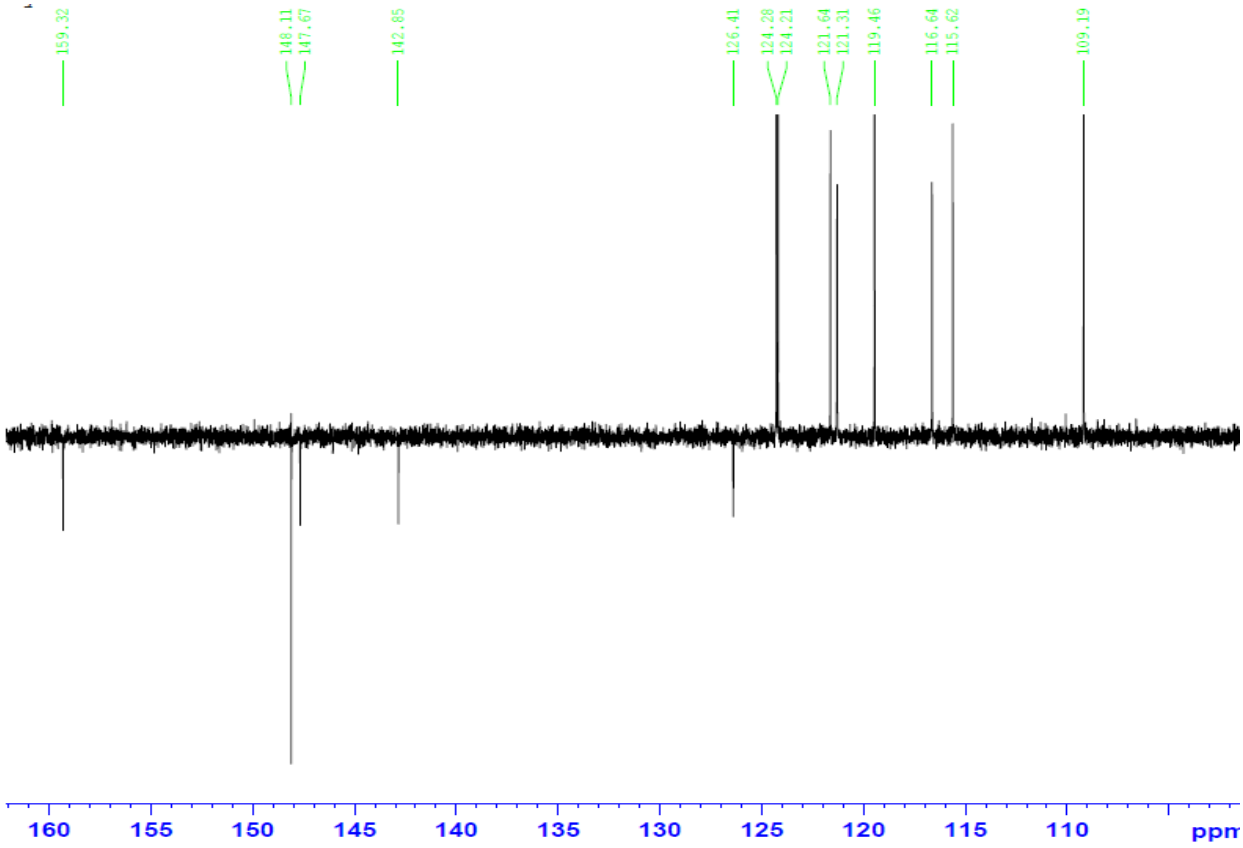












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