A heterogeneous catalytic strategy for facile production of benzimidazoles and quinoxalines from primary amines using Al-MCM-41 catalyst

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1. Experimental section

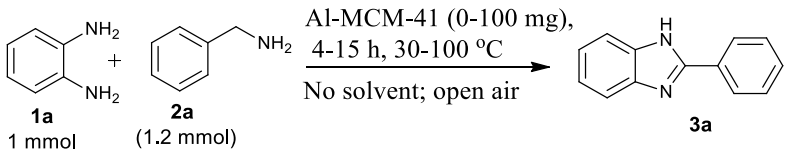
Synthesis of Al-MCM-41 catalyst

The Al-MCM-41 was synthesized using a modified procedure as described elsewhere[1]. Briefly, $Al(^{i}PrO)_3$ (0.72 g), NaOH (0.3 g) and 20 mL of deionized water were placed in a glass beaker (100 mL) and were heated at 80 ^{o}C stirring until a clear solution resulted. After cooling (0 ^{o}C), 9.4 mL of TEAOH (40 wt% solution in water) was added dropwise into this solution that was stirred for one hour (mixture A). Meanwhile, 23.86 mL of tetraethoxysilane was added to 40 mL deionized water in another glass beaker (500 mL) and stirred at RT until a uniform mixture was obtained (mixture B). The above two mixtures (mixture A & B) were combined by adding the aluminate solution (A) to a silica suspension (B) and stirred for one hour at RT. Subsequently, the cetyltrimethylammonium bromide (10.55 g) was added to the above mixture slowly and stirred for one hour at RT. Later, the resulting mixture was transferred into a Teflon-lined stainless-steel autoclave for hydrothermal treatment (48 h at 100 ℃) under steady-state. After the treatment, the product was filtered, washed, and dried. The as-synthesized (dried) sample was calcined at 550 ℃ in the air for 12 h to obtain the Al-MCM-41 catalyst.

Analytical methods

All the samples were subjected to a careful examination using several analytical and spectroscopic techniques. The mesoporous structure and crystallinity of the Al-MCM-41 catalyst were confirmed by X-ray diffraction (XRD) using a Rigaku mini flux X-ray Diffractometer. The specific surface area and porous structure of Al-MCM-41 were defined by nitrogen adsorption-desorption at -196 °C with a BET surface analyzer (ASAP 2010, Micro-metrics). The solid-state MAS-NMR (^{29}Si & ^{27}Al) analysis was carried out using an Avance-500 WB (Varian) spectrometer. The morphology of the Al-MCM-41 catalyst was identified by scanning electron microscope (SEM;

JEOL-7610F). The Si and Al contents (ratio) in the Al-MCM-41 catalyst were analyzed by X-ray fluorescence analysis (XRF; Shimadzu EDXRF-8000 model). NMR (^{1}H & ^{13}C) spectra were utilized to confirm the purified benzimidazoles and quinoxalines derivatives through an Avance spectrometer (300-500 MHz) in $CDCl_3$. The chemical shifts (δ) are stated in the ppm unit's comparative to TMS as an internal standard. Coupling constants (J) are reported in hertz (Hz), and multiplicities are indicated as follows: s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), m (multiplet). The mass spectrometric analysis was carried out using a high-resolution Q-TOF (6200 series) Mass Spectrometer (HRESI-MS). The thin-layer chromatography (TLC) monitored all the reaction performance.



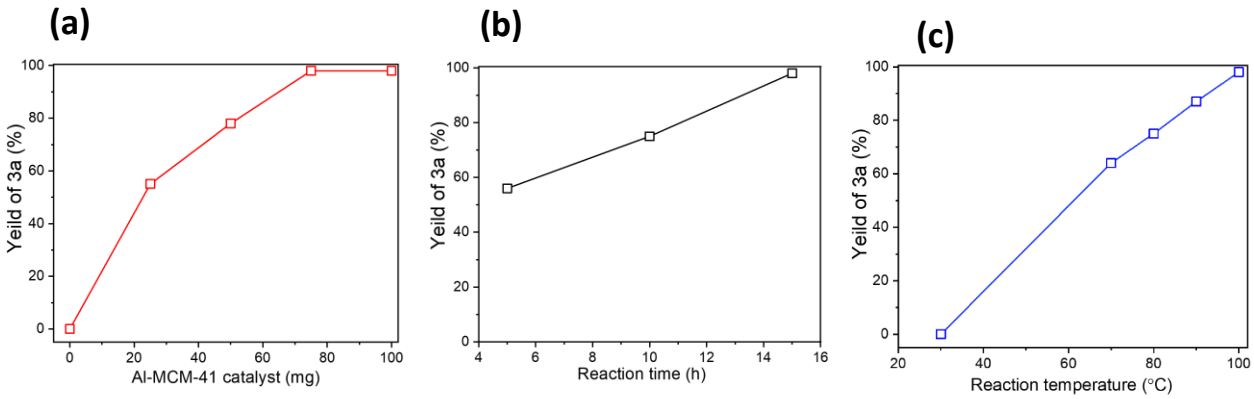


Fig. S1. Various parameters impact on the synthesis of **3a** from **1a** and **2a**. (a) Different catalyst amounts (b) Various reaction times (c) Different reaction temperatures.

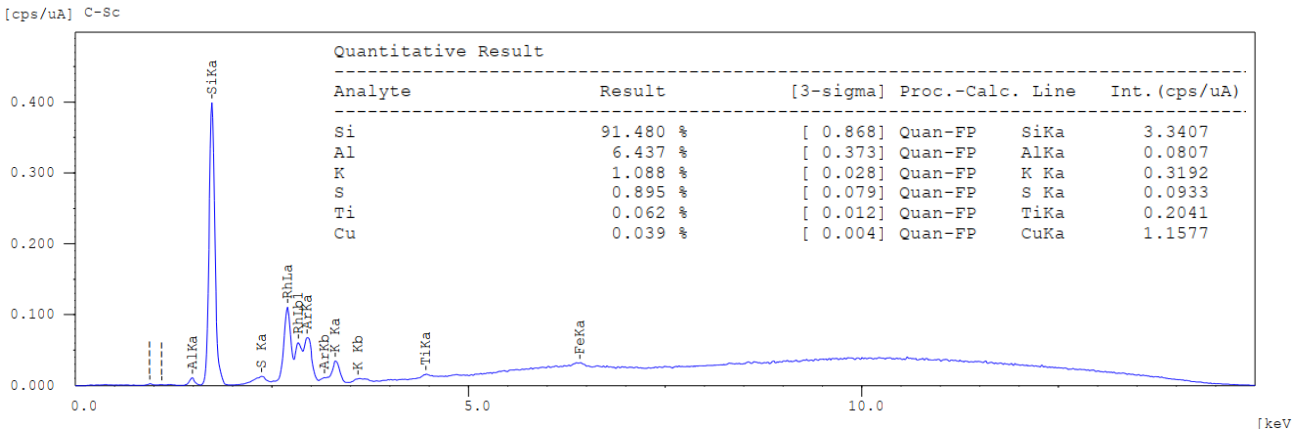


Fig. S2. XRF analysis of Al-MCM-41.

2. High Resolution ESI-MS experiments:

Electrospray ionization mass spectrometry (ESI-MS) has emerged as an important tool for analysis of high-molecular weight compounds, detection of reactive intermediates and elucidation of reaction mechanisms.[2-4] The ionization process in the ESI-MS proposed to undergo *via* acid-base reactions (protonation/deprotonation) and/or a coordination with metal cations, thus giving rise to protonated molecules ($[M+H]^+$), deprotonated molecules ($[M-H]^-$) and cationized molecules (i. e., $[M+Na]^+$). Further, the organic compounds possessing low oxidation potentials and their characteristic structural features that stabilize unpaired electrons through long conjugated π system forming radical cations (molecular ions) in positive mode of ESI analysis under suitable conditions through the loss of one or two electrons.[2]

With the demonstrated advantages of ESI-MS analysis in the detection of reactive/transient intermediates of reactions in solutions, we have attempted off-line HRESI-MS analysis to find out reaction intermediates of our reactions of **1a** with **2a** and **4a** thereby to propose suitable reaction pathways. In this connection, first, we analysed the samples of reaction of **1a** with **2a** under optimal conditions at different time intervals (30 min, 3 h, 6 h, 9 h and 15 h) after diluting in methanol. The HRESI-MS spectra of 30 min, 3 h and 9 h provided as Fig.S3-S5.

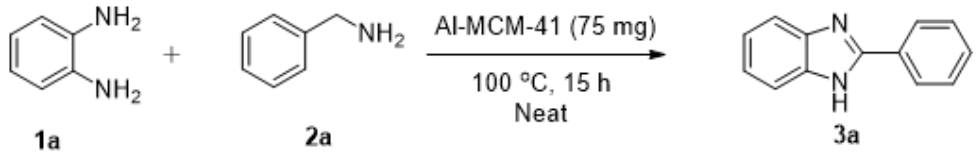
The HRESI-MS (positive mode) spectrum of 30 min sample shows more intense peak at *m/z* = 109.0757, it may be due to the protonated **1a**, i.e., $[\mathbf{1a} + H]^+$ whose theoretical elemental composition is $C_6H_9N_2$ and calculated *m/z* is 109.0766 (Fig. S3). The next abundance peak at *m/z* = 108.0803 is assigned to protonated **2a** i.e., $[\mathbf{2a} + H]^+$ whose theoretical elemental composition is $C_7H_{10}N$ and calculated *m/z* is 108.0813. Further, its fragment ion also observed at *m/z* 91.0537 as a result of loss of NH_3 from $[\mathbf{2a} + H]^+$ (Fig. S3). The low abundant peak at *m/z* = 197.1081 may be assigned as protonated **II** i.e., [**II** + H] whose theoretical elemental composition is $C_{13}H_{13}N_2$ (*m/z* = 197.1079). The next low abundant peak at *m/z* = 195.0911 may be contributed by [**3a** + H] (theoretical elemental composition is $C_{13}H_{11}N_2$ (*m/z* = 195.0922). Since, the ESI source can also generate radical cations (molecular ions) from organic molecules which possess low oxidation potentials or stabilizing lone pair of electrons through long conjugated π system during ESI process in positive ion mode under suitable conditions, the peak at *m/z* = 195.0911 may also be contributed by **II** and **III** through the loss of hydride radical from radical ion of corresponding **II** and **III** under ESI conditions (Scheme S1 and Fig. S3). As the reaction time increasing, the intensities of peaks

corresponding to **1**a and **2a** decreased and the **3a** peak intensity increased. The peak at *m/z* 197.1081 corresponding to protonated adduct of **II** was appeared as low to very low abundant and sometimes zero abundant peak in all the spectra (30 min to 15 h; 6 h and 15 h spectra are not shown). This analysis clearly indicates the presence of reaction intermediates **II** and **III**.

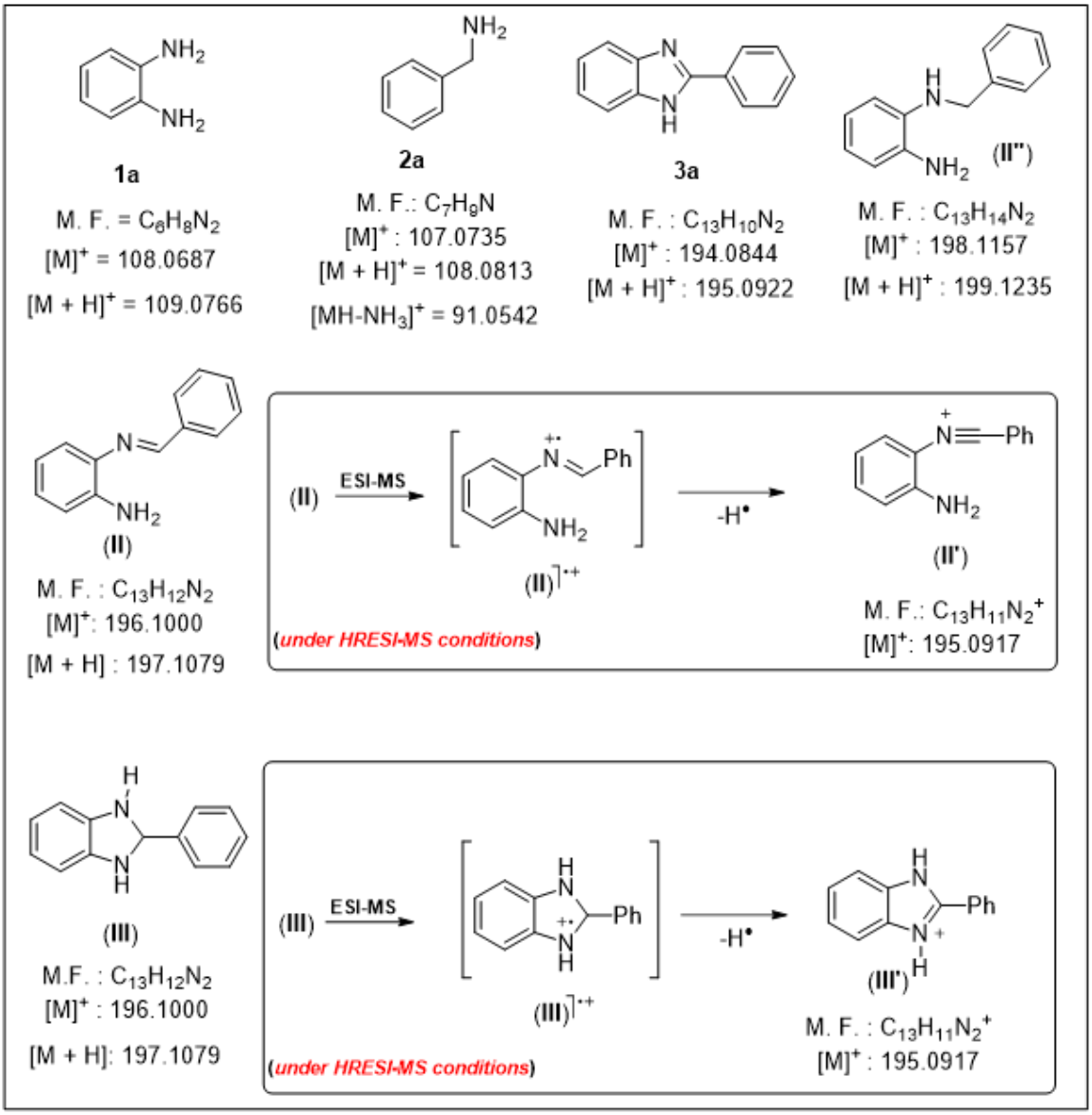
Similarly, we analysed the samples of reaction of **1a** with **4a** under optimal conditions at different time intervals (30 min, 3 h, 6 h, 10 h, 15 h, and 20 h) after diluting in methanol. The HRESI-MS spectra of 30 min, 3 h and 10 h provided as Fig.S6-S8. During this analysis, we identified the reaction intermediates **IV**, **V** and **VI** as their corresponding **IV'**, **V'** and **VI'** in spectrum (Scheme S2 and Fig. S6-S8).

For example, the HRESI-MS (positive mode) spectrum of 10 h (half of the total reaction time) sample of reaction of **1a** with **4a** under optimal conditions shows more intense peak at *m/z* = 122.0964, it may be due to the presence of [**4a** + H]$^+$ in the sample, whose theoretical elemental composition is $C_8H_{12}N$ (*m/z* = 122.0970). The peak at m/z = 109.0759 might be due to the protonated **1a**, because the theoretical elemental composition of [**1a** + H]$^+$ is $C_6H_9N_2$ and calculated *m/z* is 109.0766. The peak at *m/z* = 207.0916 may be due to the contribution of protonated **5a** ($C_{14}H_{11}N_2$; m/z = 207.0922) in the sample. As discussed earlier, the radical ions might be possible under ESI conditions, therefore, the peak at *m/z* = 209.1072 may be due to **V** and **VI** after the loss of hydride radical from their corresponding radical cationic species of **V** and **VI** (Scheme S2 and Fig. S8). Similarly, the low abundant peak at *m/z* = 223.0867 may be contributed by **VII** through the loss of hydride radical from corresponding radical cation of **VII** (Scheme S2 and Fig. S8).

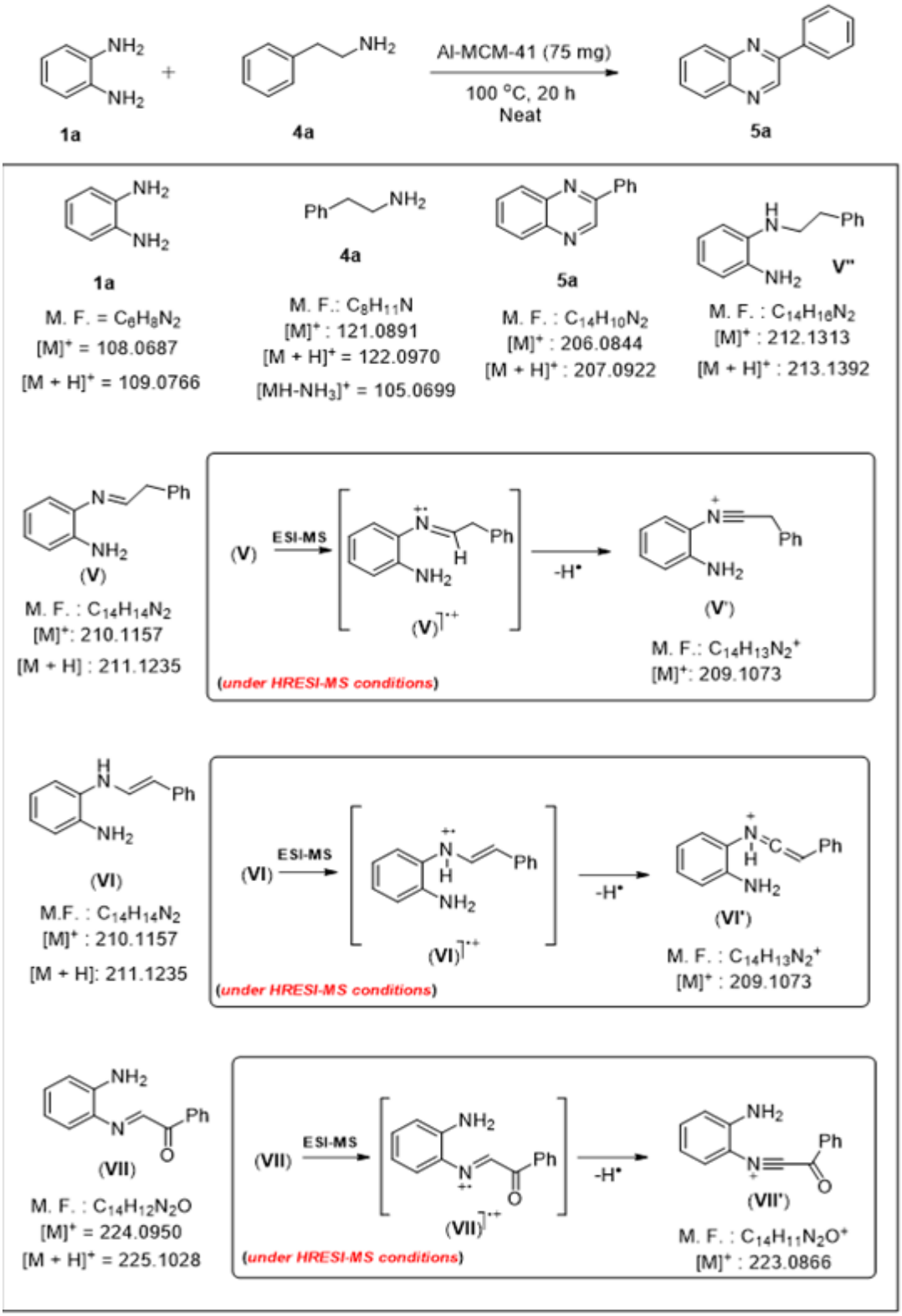
Scheme S1:



1a 2a 3a



Scheme S2:


Al-MCM-41 (75 mg)
100 °C, 20 h
Neat
1a
4a
5a
M. F. = C8H8N2
[M]+ = 108.0687
[M + H]+ = 109.0766
M. F.: C8H11N
[M]+ : 121.0891
[M + H]+ = 122.0970
[MH-NH3]+ = 105.0699
M. F. : C14H10N2
[M]+ : 206.0844
[M + H]+ : 207.0922
V''
M. F. : C14H16N2
[M]+ : 212.1313
[M + H]+ : 213.1392
(V)
M. F. : C14H14N2
[M]+: 210.1157
[M + H] : 211.1235
ESI-MS
-H•
(V)]•+
(V')
M. F.: C14H13N2+
[M]+: 209.1073
(under HRESI-MS conditions)
(VI)
M.F. : C14H14N2
[M]+ : 210.1157
[M + H]: 211.1235
(VI)]•+
(VI')
M. F. : C14H13N2+
[M]+ : 209.1073
(VII)
M. F. : C14H12N2O
[M]+ = 224.0950
[M + H]+ = 225.1028
(VII)]•+
(VII')
M. F. : C14H11N2O+
[M]+ : 223.0866

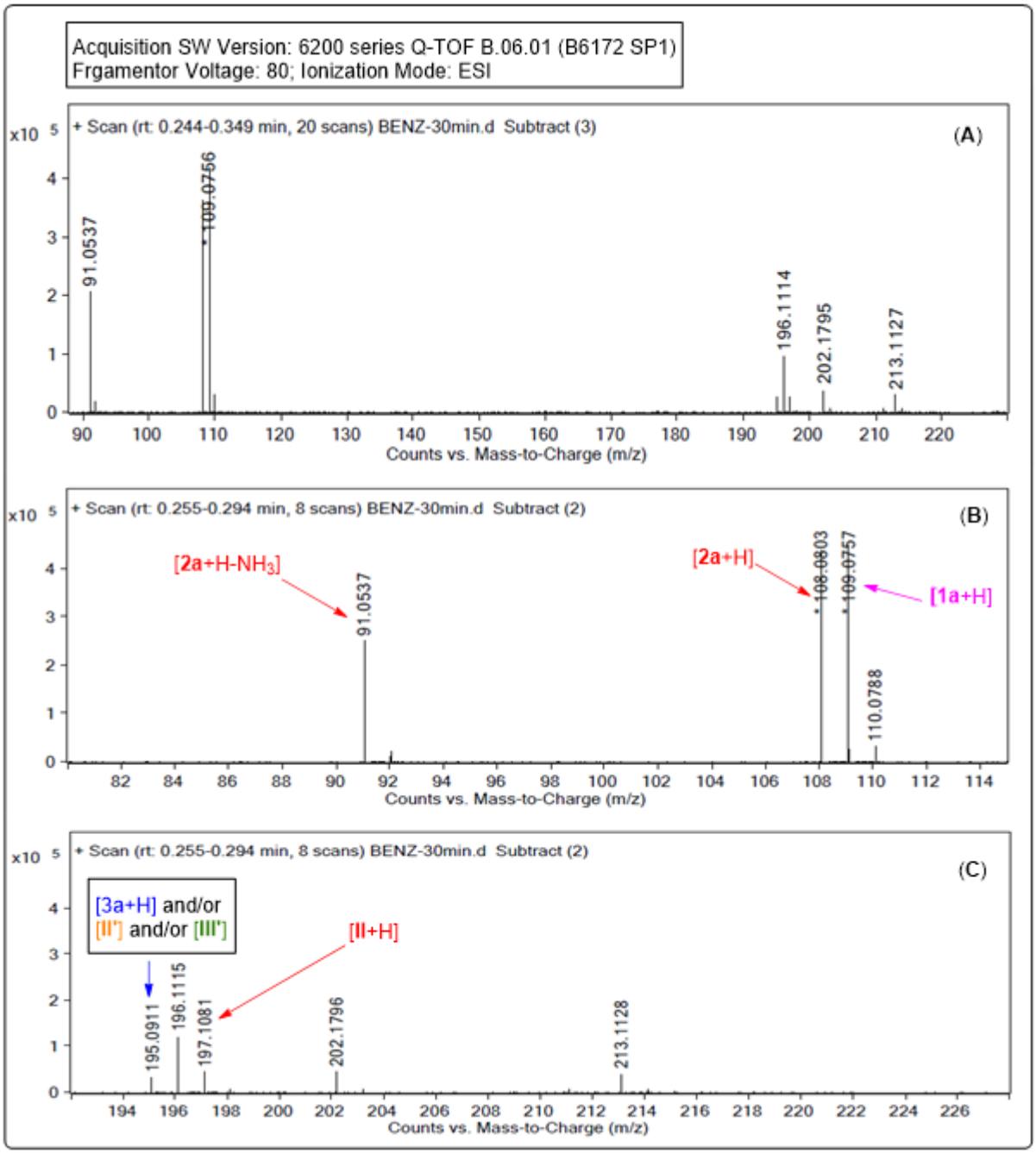


Figure S3: A) High Resolution ESI-MS (HRESI-MS) spectrum of reaction mixture of **1a** and **2a** (after 30 min of reaction time, mixture was diluted with MeOH and 10 microliters of sample was injected). B) HRESI-MS spectrum was enlarged between *m/z* = 80 and *m/z* = 115. C) HRESI-MS spectrum was enlarged between *m/z* = 192 and *m/z* = 228.

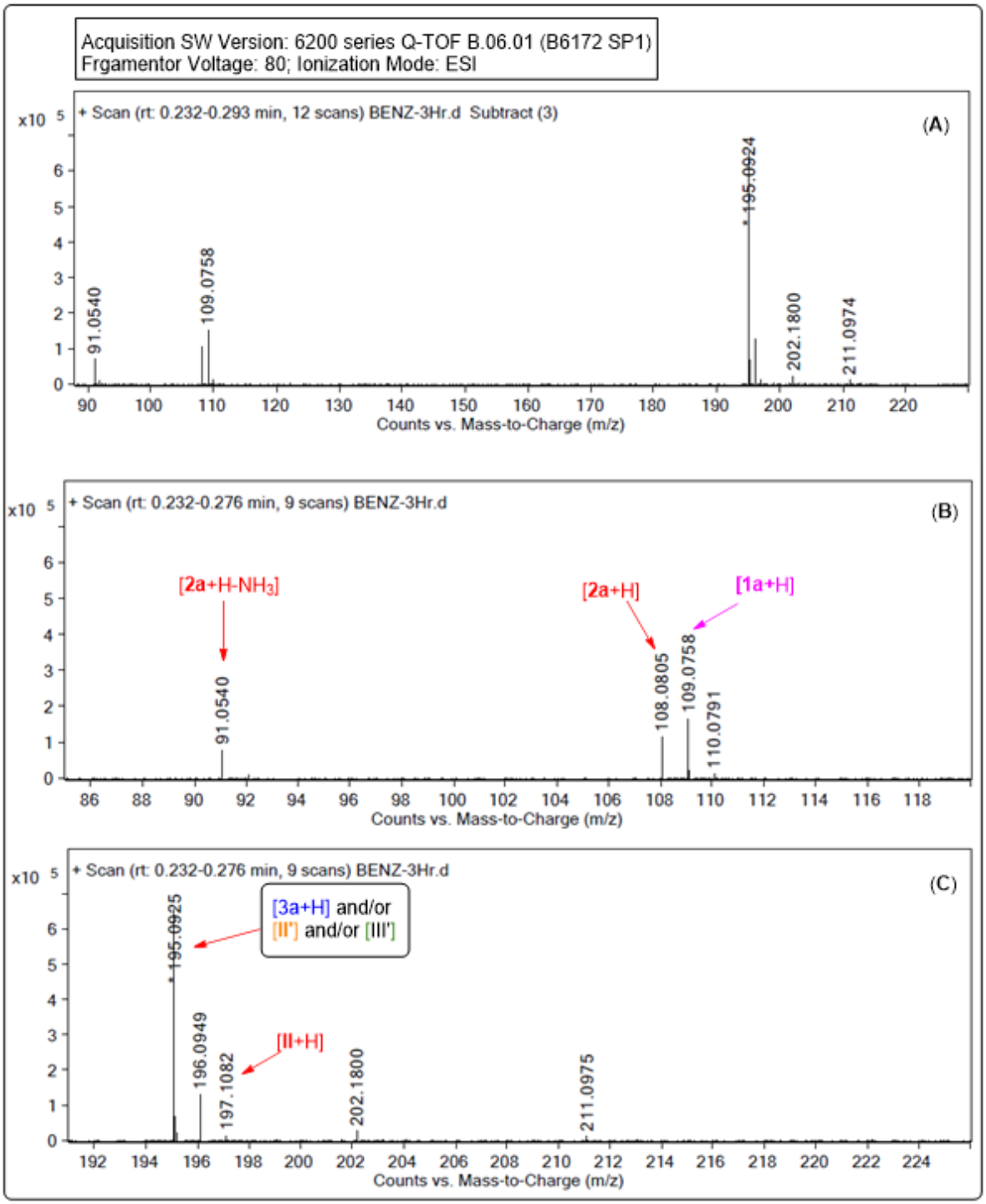


Figure S4: A) High Resolution ESI-MS (HRESI-MS) spectrum of reaction mixture of **1a** and **2a** (after 3 h of reaction time, mixture was diluted with MeOH and 10 microliters of sample was injected). B) HRESI-MS spectrum was enlarged between *m/z* = 85 and *m/z* = 120. C) HRESI-MS spectrum was enlarged between *m/z* = 191 and *m/z* = 226.

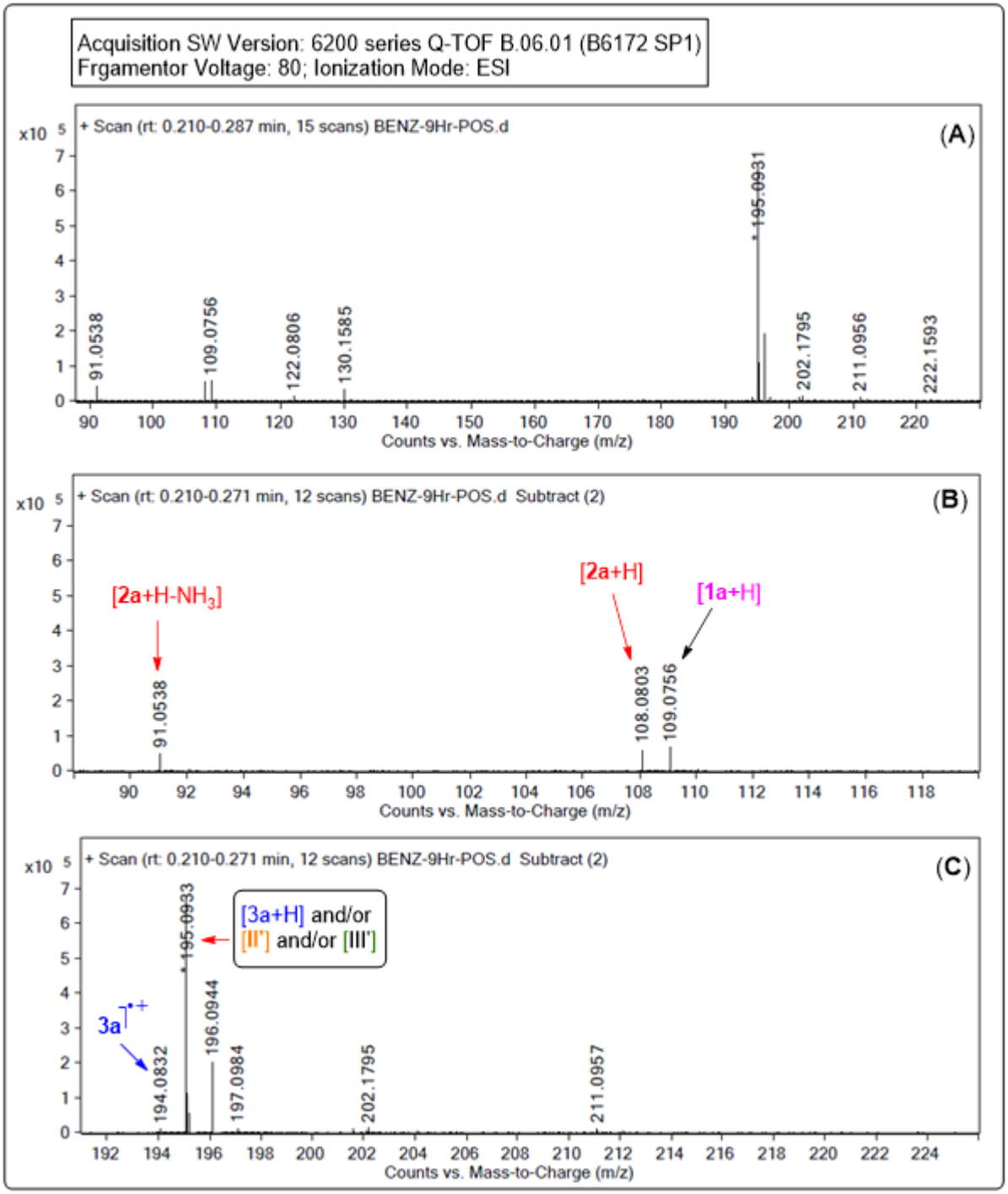


Figure S5: A) High Resolution ESI-MS (HRESI-MS) spectrum of reaction mixture of **1a** and **2a** (after 9 h of reaction time, mixture was diluted with MeOH and 10 microliters of sample was injected). B) HRESI-MS spectrum was enlarged between *m/z* = 88 and *m/z* = 120. C) HRESI-MS spectrum was enlarged between *m/z* = 191 and *m/z* = 226.

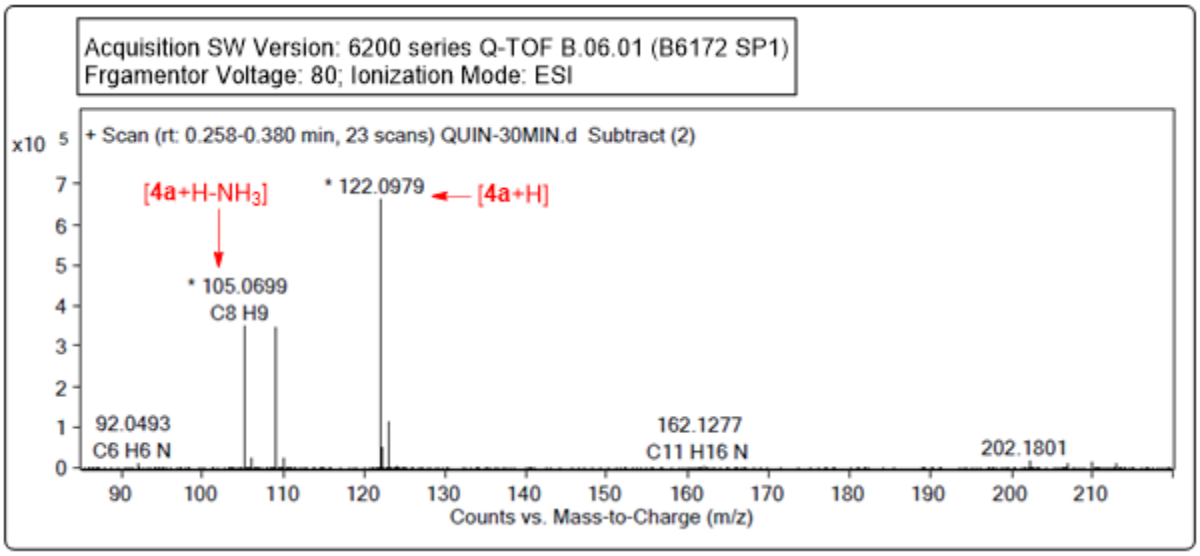


Figure S6: High Resolution ESI-MS (HRESI-MS) spectrum of reaction mixture of **1a** and 4**a** (after 30 min of reaction time, mixture was diluted with MeOH and 10 microliters of sample was injected).

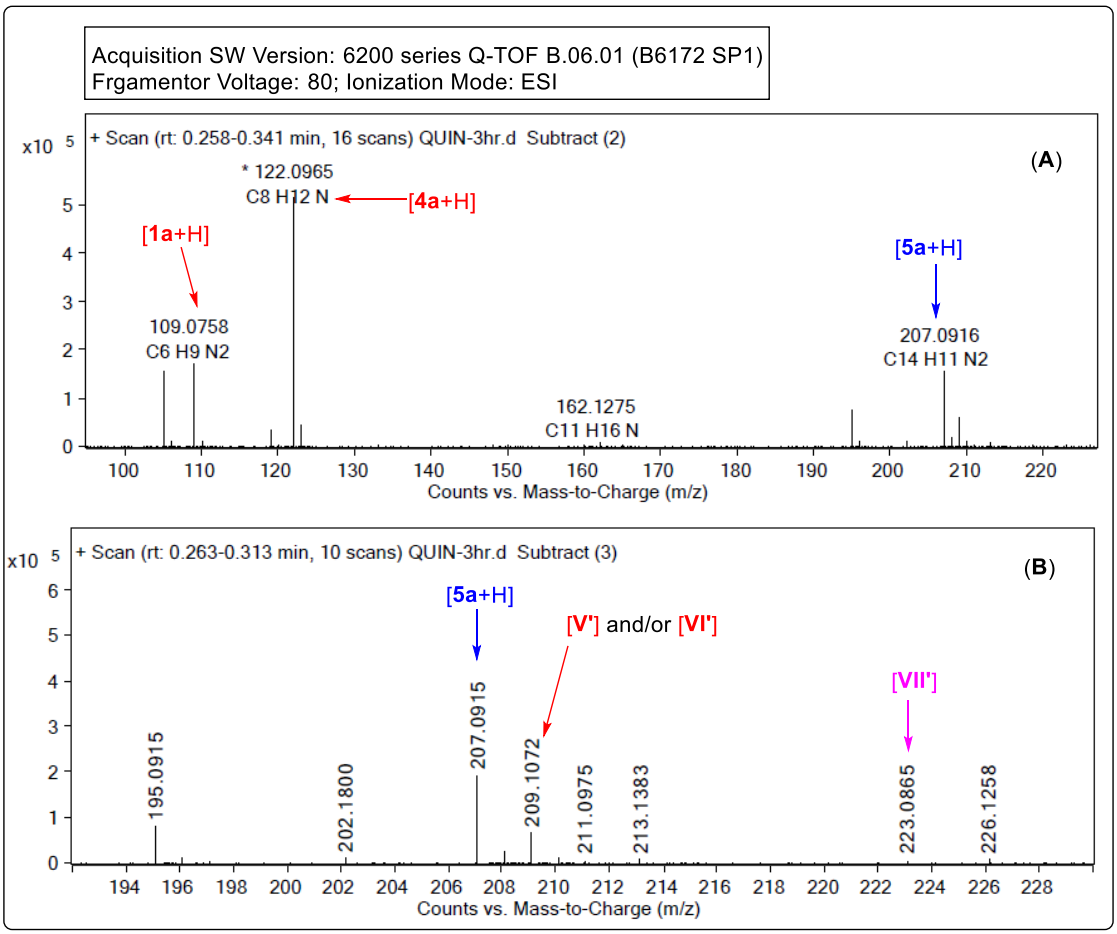


Figure S7: A) High Resolution ESI-MS (HRESI-MS) spectrum of reaction mixture of **1a** and 4**a** (after 3 h of reaction time, mixture was diluted with MeOH and 10 microliters of sample was injected). B) HRESI-MS spectrum was enlarged between *m/z* = 192 and *m/z* = 230.

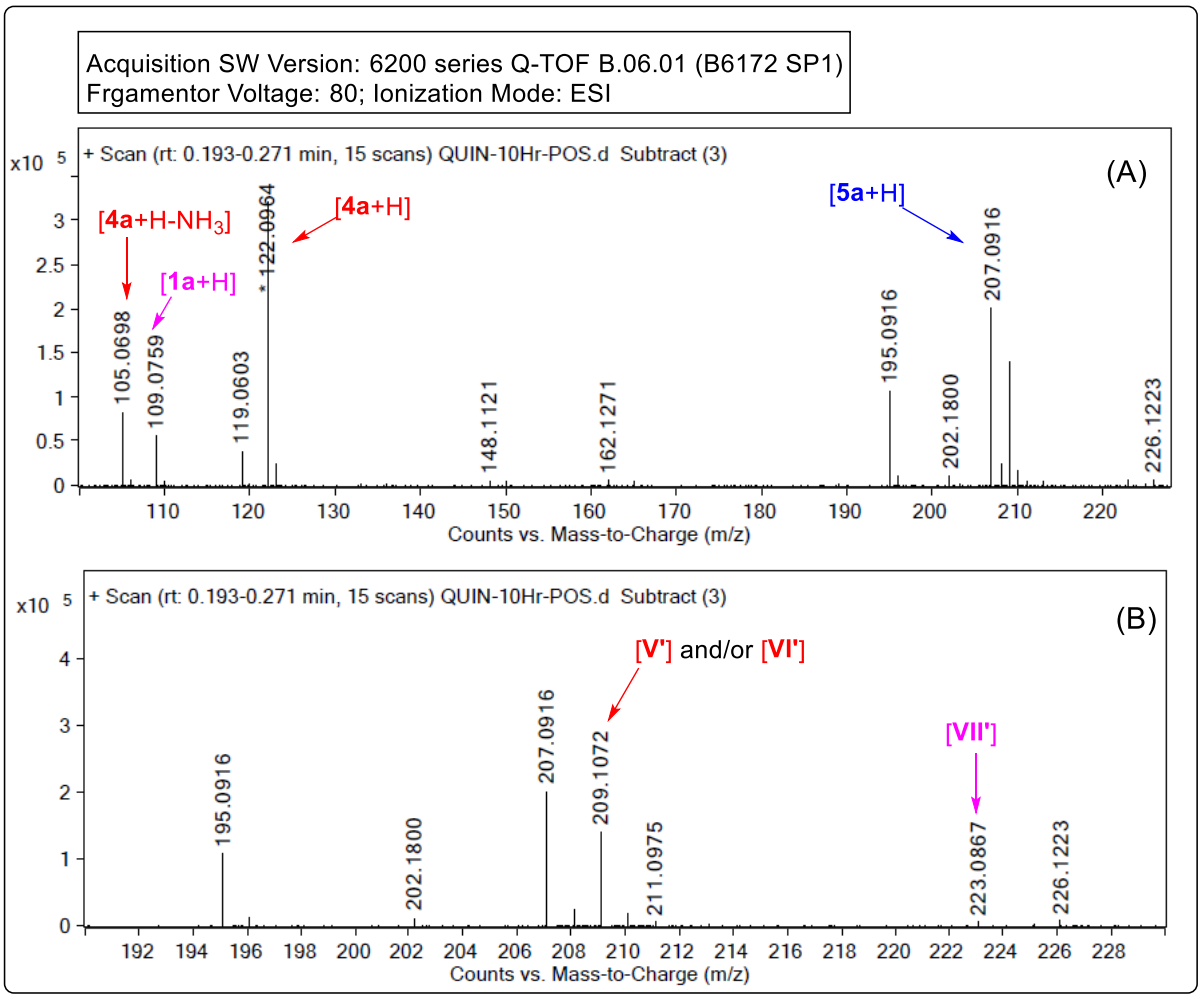
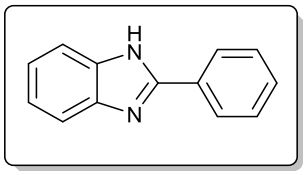


Figure S8: A) High Resolution ESI-MS (HRESI-MS) spectrum of reaction mixture of **1a** and 4**a** (after 10 h of reaction time, mixture was diluted with MeOH and 10 microliters of sample was injected). B) HRESI-MS spectrum was enlarged between *m/z* = 190 and *m/z* = 230.

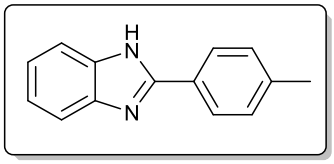
Spectroscopic Data

2-phenyl-1H-benzo[d]imidazole (Table 2, 3a)[5]



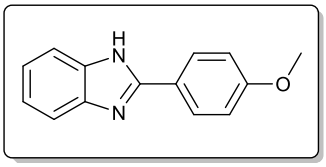
^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.92 (br s, 1H), 8.20-8.18 (m, 2H), 7.69-7.47 (m, 5H), 7.25-7.17 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 151.74, 144.28, 135.62, 130.68, 130.31, 129.43, 126.94, 122.59, 119.47, 111.92.

2-(*p*-tolyl)-1H-benzo[d]imidazole (Table 2, 3b)[5]



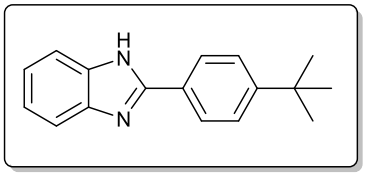
^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 12.83 (br s, 1H), 8.08 (d, *J* = 8.1 Hz, 2H), 7.64-7.53 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 4.3 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 151.38, 143.80, 139.51, 135.16, 129.47, 127.46, 126.38, 122.13, 118.69, 111.36, 21.21.

2-(4-methoxyphenyl)-1H-benzo[d]imidazole (Table 2, 3c)[5]



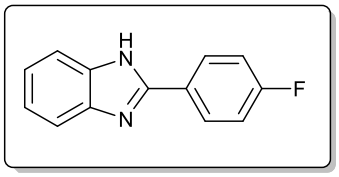
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.77 (br s, 1H), 8.15 (d, *J* = 8.8 Hz, 2H), 7.64-7.52 (m, 2H), 7.19-7.11 (m, 4H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 161.10, 151.88, 144.40, 135.44, 128.52, 123.22, 121.97, 118.99, 114.85, 111.53, 55.78.

2-(4-(tert-butyl)phenyl)-1H-benzo[d]imidazole (Table 2, 3d)[5]



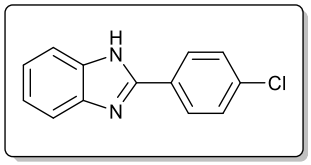
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.84 (br s, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.67-7.52 (m, 4H), 7.19 (br s, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) = 153.02, 151.80, 144.37, 135.47, 127.96, 126.74, 126.21, 122.80, 122.03, 119.23, 111.69, 35.06, 31.46.

2-(4-fluorophenyl)-1H-benzo[d]imidazole Table 2, 3e)[5]



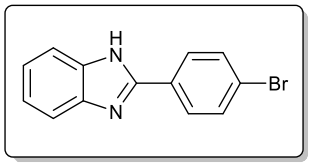
^{1}H NMR (500 MHz, DMSO) δ 12.94 (br s, 1H), 8.25 (dd, *J* = 8.9, 5.5 Hz, 2H), 7.67-7.58 (m, 2H), 7.42 (t, *J* = 8.9 Hz, 2H), 7.23 (br s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) = 163.55 (d, *J* = 245.9 Hz), 150.89, 144.27, 135.51, 129.25, 129.17, 127.31, 123.00, 122.22, 119.33, 116.58, 116.37, 111.80.

2-(4-chlorophenyl)-1H-benzo[d]imidazole (Table 2, 3f)[5]



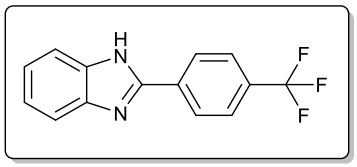
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.99 (br s, 1H), 8.20 (d, *J* = 8.7 Hz, 2H), 7.65-7.57 (m, 4H), 7.24-7.21 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 150.78, 144.33, 134.98, 129.54, 128.62, 123.07, 122.38, 119.47, 111.98.

2-(4-bromophenyl)-1H-benzo[d]imidazole (Table 2, 3g)[5]



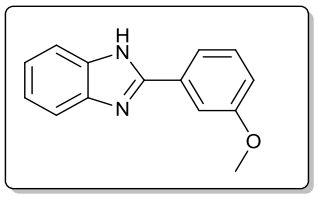
^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 13.00 (br s, 1H), 8.13 (d, *J* = 13.2 Hz, 2H), 7.78 (d, *J* = 11.0 Hz, 2H), 7.61 (br, 2H), 7.23 (br s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 150.71, 144.22, 135.50, 132.46, 129.88, 128.84, 123.74, 123.28, 122.35, 119.46, 111.91.

2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole (Table 2, 3h)[5]



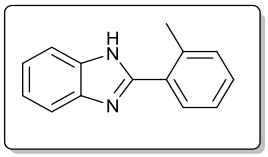
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 13.18 (s, 1H), 8.40 (d, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.66 (br s, 2H), 7.26 (dd, *J* = 6.0, 3.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 150.13, 134.44, 130.28, 129.97, 127.53, 126.41 (d, *J* = 3.4 Hz), 124.61 (d, *J* = 272.3 Hz), 119.75, 112.04.

2-(3-methoxyphenyl)-1H-benzo[d]imidazole (Table 2, 3i)[6]



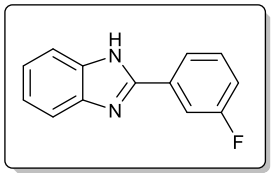
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.94 (br s, 1H), 7.77 (d, *J* = 1.6 Hz, 2H), 7.69 (d, *J* = 7.3 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 8.1 Hz, 1H), 7.25-7.19 (m, 2H), 7.09-7.06 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 160.13, 151.58, 144.22, 135.45, 131.97, 130.58, 123.08, 122.19, 119.24, 116.35, 111.88, 55.77.

2-(*o*-tolyl)-1H-benzo[d]imidazole (Table 2, 3j)[6]



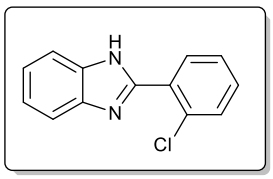
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.66 (br s, 1H), 7.76 (d, *J* = 6.9 Hz, 1H), 7.68 (br, 2H), 7.41-7.36 (m, 3H), 7.23 (br s, 2H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 152.44, 144.18, 137.51, 134.98, 131.74, 130.58, 129.93, 129.78, 126.43, 122.34, 119.31, 111.81, 21.53.

2-(3-fluorophenyl)-1H-benzo[d]imidazole (Table 2, 3k)[7]



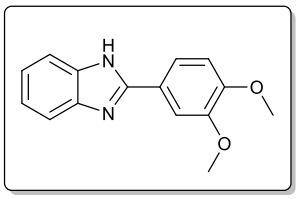
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 13.05 (br s, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 10.3 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.65-7.56 (m, 2H), 7.35 (dd, *J* = 14.3, 6.2 Hz, 1H), 7.28-7.20 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 162.95 (d, *J* = 244.13 Hz), 150.46, 144.14, 135.46, 132.99 (d, *J* = 8.4 Hz), 131.62 (d, *J* = 8.4 Hz), 123.21 (d, *J* = 41.4 Hz), 122.41, 119.57, 117.18, 116.97, 113.51 (d, *J* = 23.5 Hz), 111.98.

2-(2-chlorophenyl)-1H-benzo[d]imidazole (Table 2, 3l)[7]



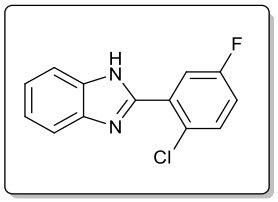
^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 12.73 (br s, 1H), 7.92 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.71-7.65 (m, 2H), 7.59-7.51 (m, 3H), 7.25 (br s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) = 149.58, 143.70, 132.57, 132.13, 131.67, 130.83, 130.47, 127.91, 123.22, 122.18, 119.58, 112.19.

2-(3,4-dimethoxyphenyl)-1H-benzo[d]imidazole (Table 2, 3m)[8]



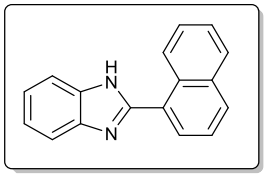
^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.78 (br s, 1H), 7.78 (d, *J* = 11.0 Hz, 2H), 7.64-7.53 (m, 2H), 7.20-7.12 (m, 3H), 3.90 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) = 151.98, 150.78, 149.41, 144.35, 135.49, 123.25, 122.60, 121.96, 119.78, 118.97, 112.31, 111.49, 110.25, 56.07.

2-(2-chloro-5-fluorophenyl)-1H-benzo[d]imidazole (Table 2, 3n)



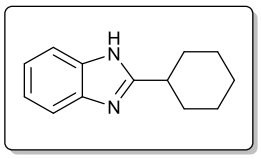
^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 12.82 (br s, 1H), 7.81-7.79 (m, 1H), 7.73-7.70 (m, 2H), 7.67 (br s, 2H), 7.47-7.43 (m, 1H), 7.27 (dd, *J* = 6.0, 3.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 161.01 (d, *J* = 245.74 Hz), 148.37, 132.83 (d, *J* = 8.5 Hz), 132.00 (d, *J* = 8.6 Hz), 127.49, 122.97, 119.14, 118. 89, 118.83, 118.60, 112.81. HRMS (ESI): m/z calcd for $C_{13}H_9N_2ClF$ $[M+H]^+$ 247.04328 found 247.04241.

2-(naphthalen-1-yl)-1H-benzo[d]imidazole (Table 2, 3o)[9]



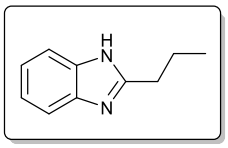
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.94 (br s, 1H), 9.13 (d, *J* = 9.7 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 8.11-8.02 (m, 2H), 7.80 (br, 1H), 7.71-7.58 (m, 4H), 7.29-7.25 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 151.34, 143.89, 133.60, 130.50, 130.11, 128.36, 127.83, 127.53, 127.03, 126.32, 125.24, 122.61, 111.33.

2-cyclohexyl-1H-benzo[d]imidazole (Table 2, 3p)[7]



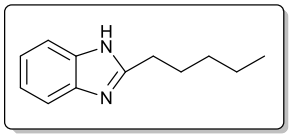
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.08 (br s, 1H), 7.45 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.12-7.07 (m, 2H), 2.87-2.79 (m, 1H), 2.01 (d, *J* = 10.2 Hz, 2H), 1.82 -1.77 (m, 2H), 1.65-1.55 (m, 3H), 1.41-1.27 (m, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 158.97, 143.06, 134.16, 121.25, 120.65, 118.15, 110.68, 37.68, 31.22, 25.49.

2-propyl-1H-benzo[d]imidazole (Table 2, 3q)[16]



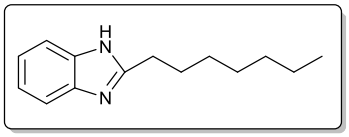
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.56-7.53 (m, 2H), 7.23-7.20 (m, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.94-1.84 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 155.29, 138.49, 122.16, 120.36, 116.82, 114.61, 31.24, 21.70, 13.88.

2-pentyl-1H-benzo[d]imidazole (Table 2, 3r)[17]



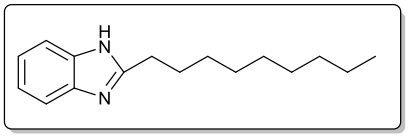
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.57-7.54 (m, 2H), 7.23-7.20 (m, 2H), 2.93 (t, *J* = 7.5 Hz, 2H), 1.90-1.82 (m, 2H), 1.35-1.29 (m, 4H), 0.84 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 155.61, 138.50, 122.12, 114.60, 31.52, 29.34, 28.10, 22.38, 13.91.

2-heptyl-1H-benzo[d]imidazole (Table 2, 3s)[18]



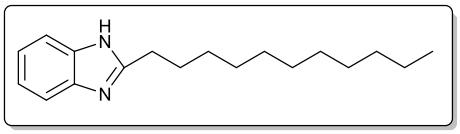
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.55-7.54 (m, 2H), 7.23-7.20 (m, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 1.88-1.82 (m, 2H), 1.36-1.22 (m, 8H), 0.83 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 155.64, 138.48, 122.12, 114.60, 31.68, 29.37, 29.01, 28.43, 22.60, 14.05.

2-nonyl-1H-benzo[d]imidazole (Table 2, 3t)[17]



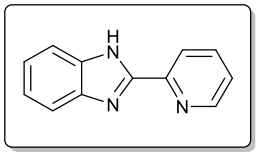
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.56-7.53 (m, 2H), 7.23-7.19 (m, 2H), 2.93 (t, *J* = 7.7 Hz, 2H), 1.89-1.81 (m, 2H), 1.36 -1.21 (m, 12H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 155.68, 138.56, 122.08, 114.60, 31.86, 29.48, 29.42, 29.38, 29.29, 28.45, 22.67, 14.12.

2-undecyl-1H-benzo[d]imidazole (Table 2, 3u)[16]



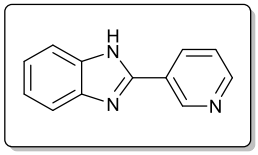
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.56-7.52 (m, 2H), 7.23-7.19 (m, 2H), 2.93 (t, *J* = 7.7 Hz, 2H), 1.89-1.81 (m, 2H), 1.38-1.21 (m, 16H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 155.59, 138.47, 122.12, 114.60, 31.94, 29.65, 29.54, 29.43, 29.39, 28.43, 22.72, 14.16.

2-(pyridin-2-yl)-1H-benzo[d]imidazole (Table 2, 3v)[10]



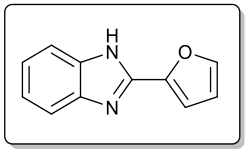
^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 13.13 (br s, 1H), 8.76-8.74 (m, 1H), 8.37 (d, *J* = 7.9 Hz, 1H), 8.03-8.00 (m, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.54-7.52 (m, 1H), 7.29-7.22 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 150.73, 149.31, 148.53, 143.87, 137.46, 134.92, 124.63, 123.08, 121.86, 121.39, 119.27, 112.05.

2-(pyridin-3-yl)-1H-benzo[d]imidazole (Table 2, 3w)[11]



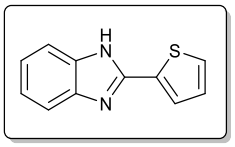
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 13.12 (br s, 1H), 9.38 (d, *J* = 2.1 Hz, 1H), 8.69 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.53-8.50 (m, 1H), 7.66-7.59 (m, 3H), 7.28-7.24 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) =150.46, 148.84, 147.50, 133.72, 126.15, 123.26, 122.57, 118.95, 111.62.

2-(furan-2-yl)-1H-benzo[d]imidazole (Table 2, 3x)[5]



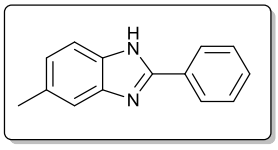
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.91 (br s, 1H), 7.95 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.63-7.50 (m, 2H), 7.20 (dd, *J* = 3.5, 0.8 Hz, 3H), 6.73 (dd, *J* = 3.4, 1.8 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 145.56, 144.57, 143.61, 134.21, 122.58, 121.76, 118.74, 112.27, 111.30, 110.42.

2-(thiophen-2-yl)-1H-benzo[d]imidazole (Table 2, 3y)[5]



^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.94 (br s, 1H), 7.84 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.73 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.56 (br s, 2H), 7.25-7.20 (m, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 147.01, 133.70, 128.69, 128.23, 126.65, 122.17, 118.33, 110.98.

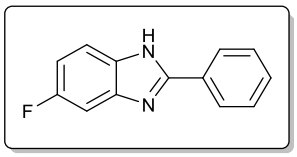
5-methyl-2-phenyl-1H-benzo[d]imidazole (Table 2, 3z)[11]



^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 12.74 (br s, 1H), 8.17 (d, *J* = 7.4 Hz, 2H), 7.56-7.32 (m, 5H), 7.06-7.01 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) = 151.21,

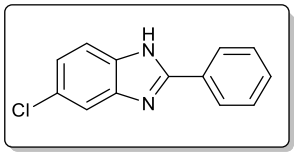
144.69, 142.45, 135.75, 132.33, 130.81, 130.09, 129.37, 126.77, 124.45, 123.72, 118.94, 111.52, 21.87.

5-fluoro-2-phenyl-1H-benzo[d]imidazole (Table 2, 3aa)[11]



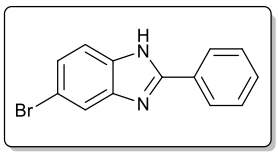
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 13.07 (br s, 1H), 8.19 (d, *J* = 7.0 Hz, 2H), 7.59-7.50 (m, 5H), 7.09 (t, *J* = 8.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) = 159.22 (d, *J* = 234.21 Hz), 153.22, 130.48, 130.38, 129.45, 126.92, 120.30, 112.25, 110.83, 105.03.

5-chloro-2-phenyl-1H-benzo[d]imidazole (Table 2, 3ab)[5]



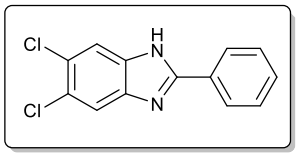
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 13.13 (br s, 1H), 8.20 (d, *J* = 7.4 Hz, 2H), 7.64-7.51 (m, 5H), 7.25 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) = 153.15, 137.16, 134.36, 130.63, 130.22, 129.44, 128.43, 127.09, 122.83, 120.94, 116.64, 115.54, 113.88.

5-bromo-2-phenyl-1H-benzo[d]imidazole (Table 2, 3ac)[5]



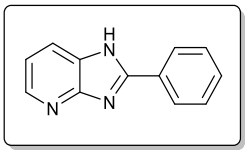
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 13.12 (s, 1H), 8.19 (d, *J* = 6.8 Hz, 2H), 7.81 (br, 1H), 7.60-7.53 (m, 4H), 7.36 (dd, *J* = 8.5, 1.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 152.97, 130.72, 130.09, 129.49, 128.59, 127.09, 125.48, 114.78.

5,6-dichloro-2-phenyl-1H-benzo[d]imidazole (Table 2, 3ad)[12]



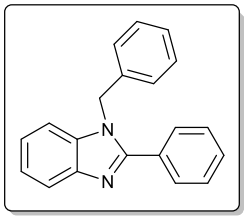
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 13.22 (br s, 1H), 8.17 (d, *J* = 6.5 Hz, 2H), 7.85 (s, 2H), 7.59-7.51 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) = 154.28, 131.00, 129.76, 129.52, 128.61, 128.54, 127.21, 124.96.

2-phenyl-1H-imidazo[4,5-b]pyridine (Table 2, 3ae)[13]



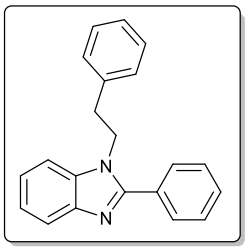
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 13.51 (br s, 1H), 8.36 (d, *J* = 3.6 Hz, 1H), 8.25 (dd, *J* = 8.1, 1.5 Hz, 2H), 8.03 (br s, 1H), 7.60-7.55 (m, 3H), 7.26 (dd, *J* = 8.0, 4.8 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 152.68, 143.79, 130.48, 129.64, 128.97, 128.29, 126.70, 118.04.

1-benzyl-2-phenyl-1H-benzo[d]imidazole (Table 2, 3af)[19]



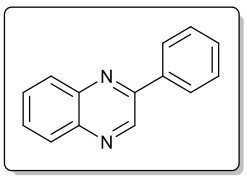
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.87 (d, *J* = 8.0 Hz, 1H), 7.70-7.67 (m, 2H), 7.47-7.42 (m, 3H), 7.34-7.28 (m, 4H), 7.25-7.19 (m, 2H), 7.09 (d, *J* = 6.5 Hz, 2H), 5.44 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 154.20, 143.22, 136.44, 136.11, 130.12, 129.96, 129.30, 129.10, 128.80, 127.82, 126.01, 123.09, 122.73, 120.03, 110.58, 48.41.

1-phenethyl-2-phenyl-1H-benzo[d]imidazole (Table 2, 3ag)



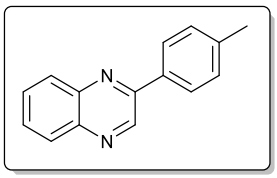
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.85-7.82 (m, 1H), 7.47-7.43 (m, 6H), 7.35-7.31 (m, 2H), 7.21-7.19 (m, 3H), 6.91-6.89 (m, 2H), 4.45 (t, *J* = 7.47 Hz, 2H), 3.07 (t, *J* = 7.62 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 153.98, 143.19, 137.39, 135.33, 130.43, 129.62, 129.28, 128.76, 128.63, 128.57, 126.95, 122.82, 122.48, 120.14, 110.08, 46.19, 35.88. HRMS (ESI): m/z calcd for $C_{21}H_{18}N_2$ $[M+H]^+$ 299.15428 found 299.15354.

2-phenylquinoxaline (Table 3, 5a)[5]



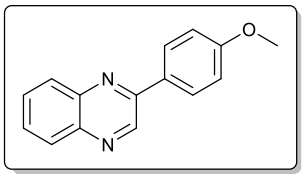
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.32 (s, 1H), 8.20-8.11 (m, 4H), 7.78-7.71 (m, 2H), 7.57-7.51 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 151.83, 143.37, 142.32, 141.60, 136.79, 130.29, 130.21, 129.66, 129.55, 129.17, 127.58.

2-(*p*-tolyl)quinoxaline (Table 3, 5b)[5]



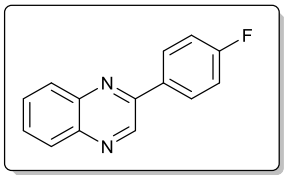
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.31 (s, 1H), 8.15-8.09 (m, 4H), 7.79-7.70 (m, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 151.88, 143.34, 142.36, 141.45, 140.54, 134.00, 130.24, 129.93, 129.56, 129.34, 129.11, 127.47, 21.47.

2-(4-methoxyphenyl)quinoxaline (Table 3, 5c)[5]



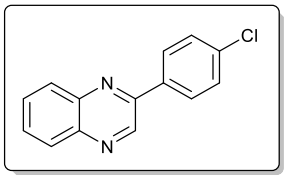
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.29 (s, 1H), 8.19-8.08 (m, 4H), 7.79-7.68 (m, 2H), 7.07 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 161.50, 151.48, 143.08, 142.34, 141.18, 130.23, 129.40, 129.29, 129.10, 129.01, 114.62, 55.47.

2-(4-fluorophenyl)quinoxaline (Table 3, 5d)[5]



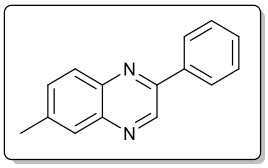
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.30 (s, 1H), 8.22-8.18 (m, 2H), 8.16-8.11 (m, 2H), 7.82 -7.74 (m, 2H), 7.28-7.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 164.28 (d, *J* = 250.88 Hz), 150.81, 142.94, 142.23, 141.46, 132.93, 130.47, 129.66, 129.59, 129.55, 129.50, 129.13, 128.75 (d, *J* = 8.3 Hz), 116.27 (d, *J* = 22.00 Hz).

2-(4-chlorophenyl)quinoxaline (Table 3, 5e)[5]



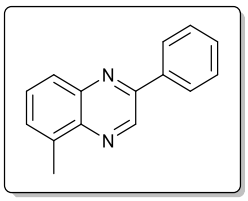
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.30 (s, 1H), 8.17-8.11 (m, 4H), 7.81 -7.74 (m, 2H), 7.54 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 150.60, 142.87, 142.22, 141.62, 136.61, 135.15, 130.53, 129.84, 129.61, 129.42, 129.16, 128.79.

6-methyl-2-phenylquinoxaline (Table 3, 5f)[5]



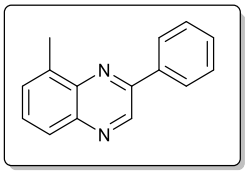
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.24 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 2H), 8.04-7.87 (m, 2H), 7.60-7.50 (m, 4H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 151.75, 151.05, 143.25, 142.46, 141.64, 140.81, 141.10, 136.96, 132.61, 131.87, 130.07, 129.97, 129.13, 128.63, 128.49, 127.99, 127.52, 127.44, 21.90.

5-methyl-2-phenylquinoxaline (Table 3, 5g)[14]



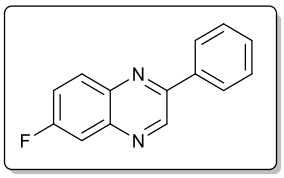
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.34 (s, 1H), 8.26 (d, *J* = 6.9 Hz, 2H), 7.97-7.94 (m, 1H), 7.65-7.52 (m, 5H), 2.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 150.22, 142.65, 141.69, 141.36, 138.03, 137.10, 130.21, 130.07, 129.33, 129.12, 127.49, 126.93, 17.15.

8-methyl-2-phenylquinoxaline (Table 3, 5g′)[14]



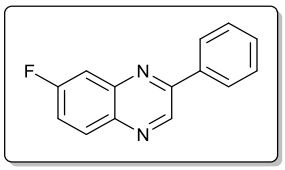
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.34 (s, 1H), 8.21-8.18 (m, 2H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.68 (t, *J* = 7.09 Hz, 1H), 7.60-7.53 (m, 4H), 2.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 151.44, 142.48, 142.04, 140.82, 137.36, 136.99, 130.08, 129.65, 129.17, 127.56, 17.35.

6-fluoro-2-phenylquinoxaline (Table 3, 5h)[15]



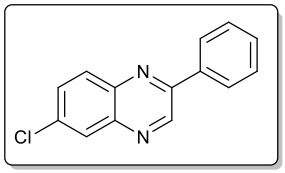
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.29 (s, 1H), 8.20-8.10 (m, 3H), 7.77 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.59-7.50 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 163.09 (d, *J* = 252.34), 152.55, 143.24 (d, *J* = 13.3 Hz), 142.68, 142.65, 138.82, 136.43, 131.20 (d, *J* = 10.2 Hz), 130.53, 129.24, 127.66, 119.91 (d, *J* = 25.6 Hz), 113.08 (d, *J* = 21.2 Hz).

7-fluoro-2-phenylquinoxaline (Table 3, 5h′)[15]



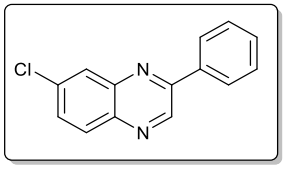
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.33 (s, 1H), 8.19-8.14 (m, 3H), 7.75 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.60-7.53 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 162.52 (d, *J* = 251.9 Hz), 151.31, 144.12, 142.25 (d, *J* = 12.9 Hz), 139.53, 136.51, 131.40 (d, *J* = 9.9 Hz), 130.30, 129.24, 127.46, 120.73 (d, *J* = 26.0 Hz), 112.74 (d, *J* = 21.6 Hz).

6-chloro-2-phenylquinoxaline (Table 3, 5i)[5]



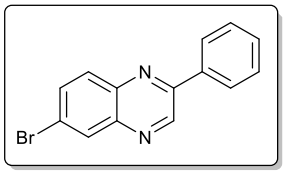
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.31 (s, 1H), 8.20-8.17 (m, 2H), 8.15 (d, *J* = 2.3 Hz, 1H), 8.05 (d, *J* = 8.9 Hz, 1H), 7.68 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.59 -7.54 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 152.59, 143.50, 142.68, 140.13, 136.34, 136.13, 130.59, 130.55, 130.38, 129.31, 128.53, 127.64.

7-chloro-2-phenylquinoxaline (Table 3, 5i′)[5]



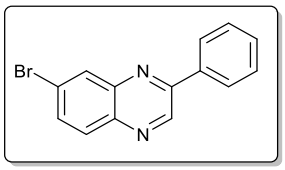
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.33 (s, 1H), 8.20-8.17 (m, 2H), 8.12-8.08 (m, 2H), 7.73 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.60 -7.54 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 151.97, 144.18, 141.84, 140.87, 136.39, 135.28, 131.36, 130.87, 130.47, 129.25, 128.11, 127.54.

6-bromo-2-phenylquinoxaline (Table 3, 5j)[5]



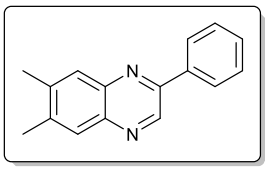
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.32 (s, 1H), 8.31 (d, *J* = 16.7 Hz, 1H), 8.18 (d, *J* = 7.4 Hz, 2H), 8.02-7.96 (m, 1H), 7.86-7.79(m, 1H), 7.60-7.53 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 152.07, 144.13, 142.14, 141.11, 136.39, 133.89, 131.49, 130.95, 130.50, 129.26, 127.56, 123.41.

7-bromo-2-phenylquinoxaline (Table 3, 5j′)[5]



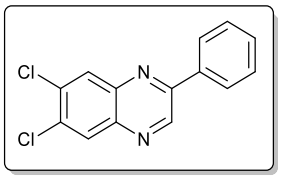
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.33 (s, 1H), 8.34 (d, *J* = 2.1 Hz, 1H), 8.20-8.17 (m, 2H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.81 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.60-7.54 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 152.51, 143.58, 142.95, 140.36, 136.31, 133.08, 131.92, 130.61, 130.47, 129.26, 127.64, 124.33.

6,7-dimethyl-2-phenylquinoxaline (Table 3, 5k)[5]



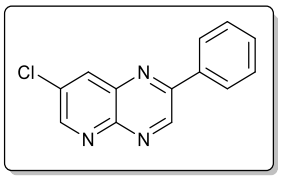
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.22 (s, 1H), 8.17 (d, *J* = 7.0 Hz, 2H), 7.91 (s, 1H), 7.85 (s, 1H), 7.57-7.48 (m, 3H), 2.51 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 151.04, 142.43, 141.26, 140.81, 140.13, 137.17, 129.84, 129.08, 128.68, 128.17, 127.40, 20.37.

6,7-dichloro-2-phenylquinoxaline (Table 3, 5l)[15]



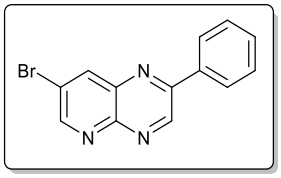
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.31 (s, 1H), 8.26-8.17 (m, 4H), 7.59-7.54 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 152.57, 144.24, 141.07, 140.25, 135.95, 134.91, 133.99, 130.78, 130.18, 129.78, 129.28, 127.57.

7-chloro-2-phenylpyrido[2,3-b]pyrazine (Table 3, 5m)



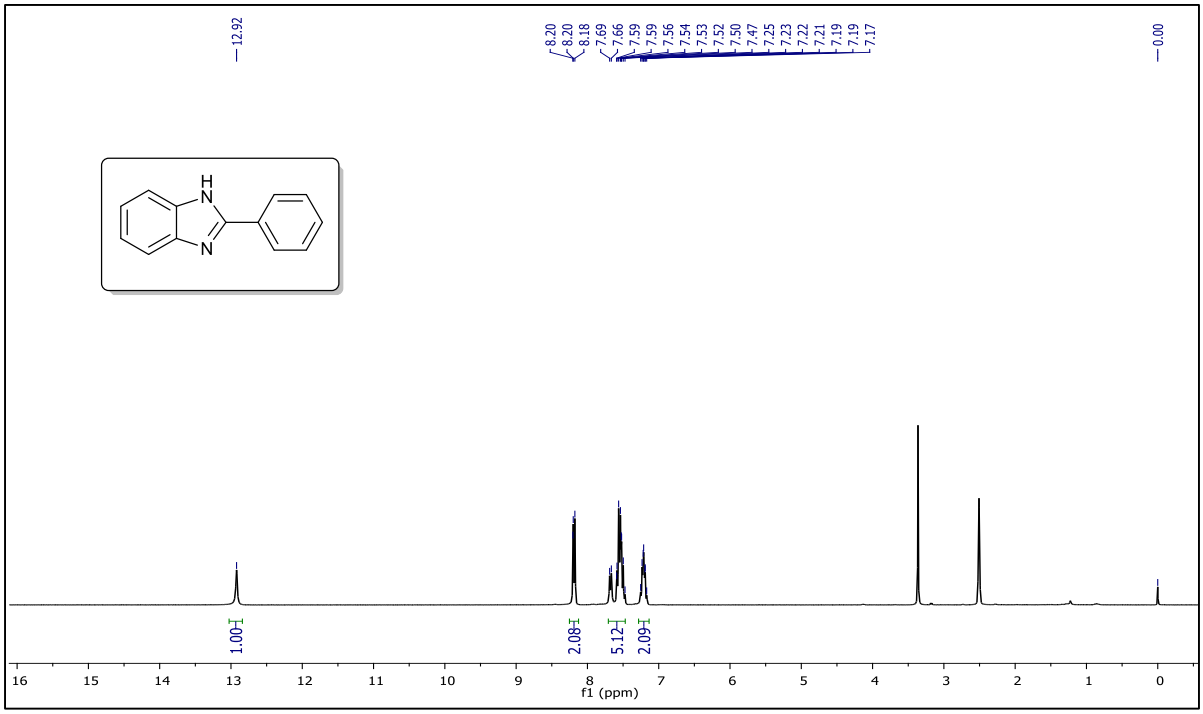
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.46 (s, 1H), 9.10 (d, *J* = 2.5 Hz, 1H), 8.46 (d, *J* = 2.5 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 2H), 7.61-7.58 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 154.69, 153.81, 149.09, 145.21, 136.53, 136.22, 135.36, 131.91, 131.31, 129.31, 128.06. HRMS (ESI): m/z calcd for $C_{13}H_9N_3Cl$ $[M+H]^+$ 242.04795 found 242.04728.

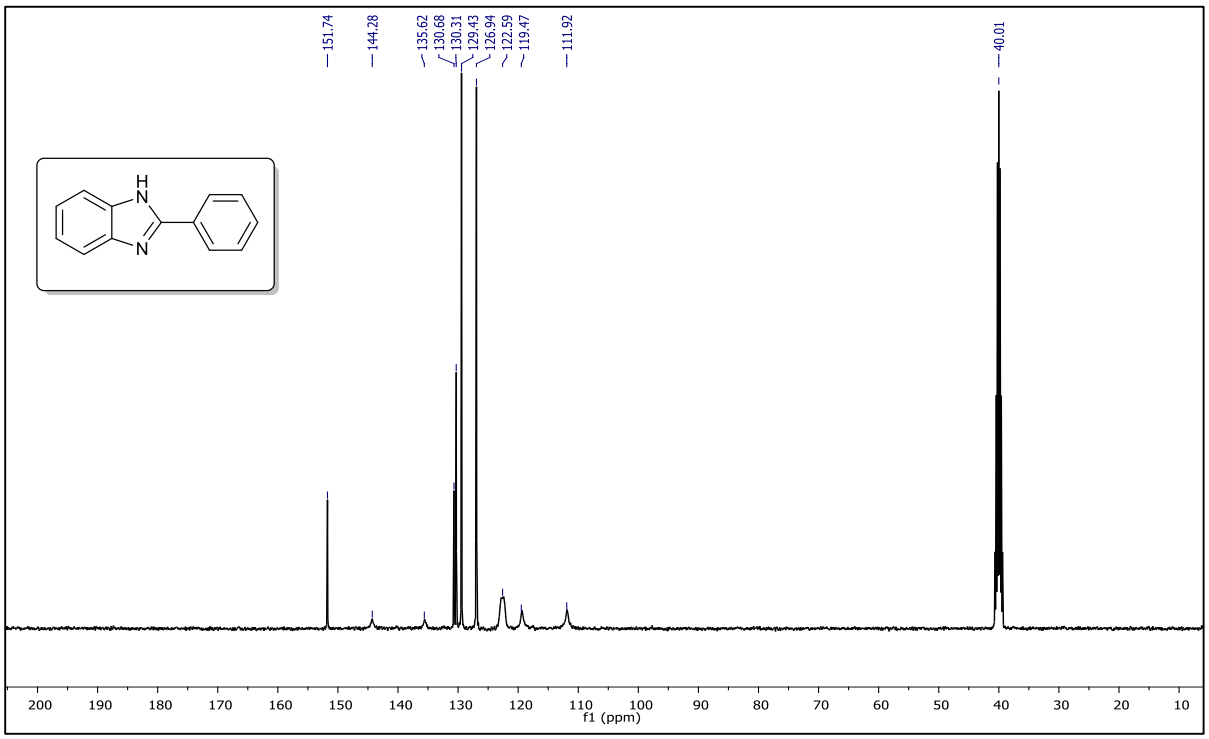
7-bromo-2-phenylpyrido[2,3-b]pyrazine (Table 3, 5n)

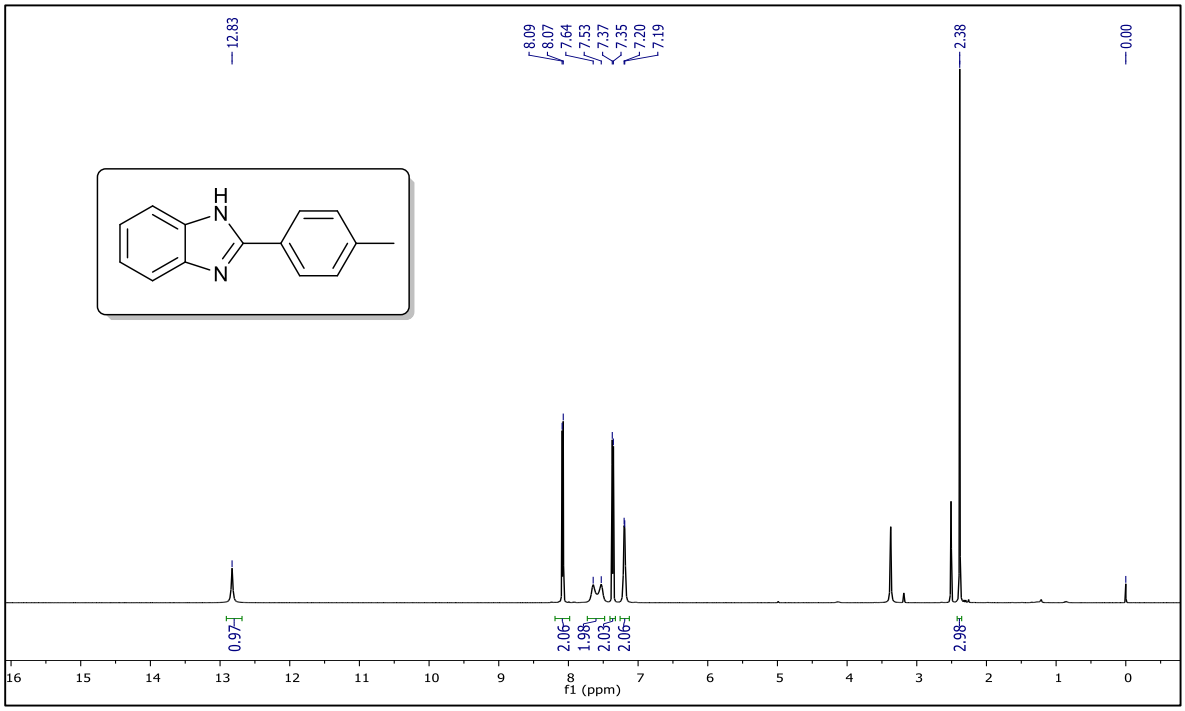


^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 9.45 (s, 1H), 9.18 (d, *J* = 2.3 Hz, 1H), 8.64 (d, *J* = 2.3 Hz, 1H), 8.34-8.32 (m, 2H), 7.61-7.58 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 155.63, 154.83, 149.31, 145.14, 139.59, 137.02, 135.39, 131.35, 129.33, 128.09, 120.52. HRMS (ESI): m/z calcd for $C_{13}H_9N_3ClBr$ $[M+H]^+$ 285.99744 found 285.99657.

Copies of ^{1}H and ^{13}C NMR spectra of products



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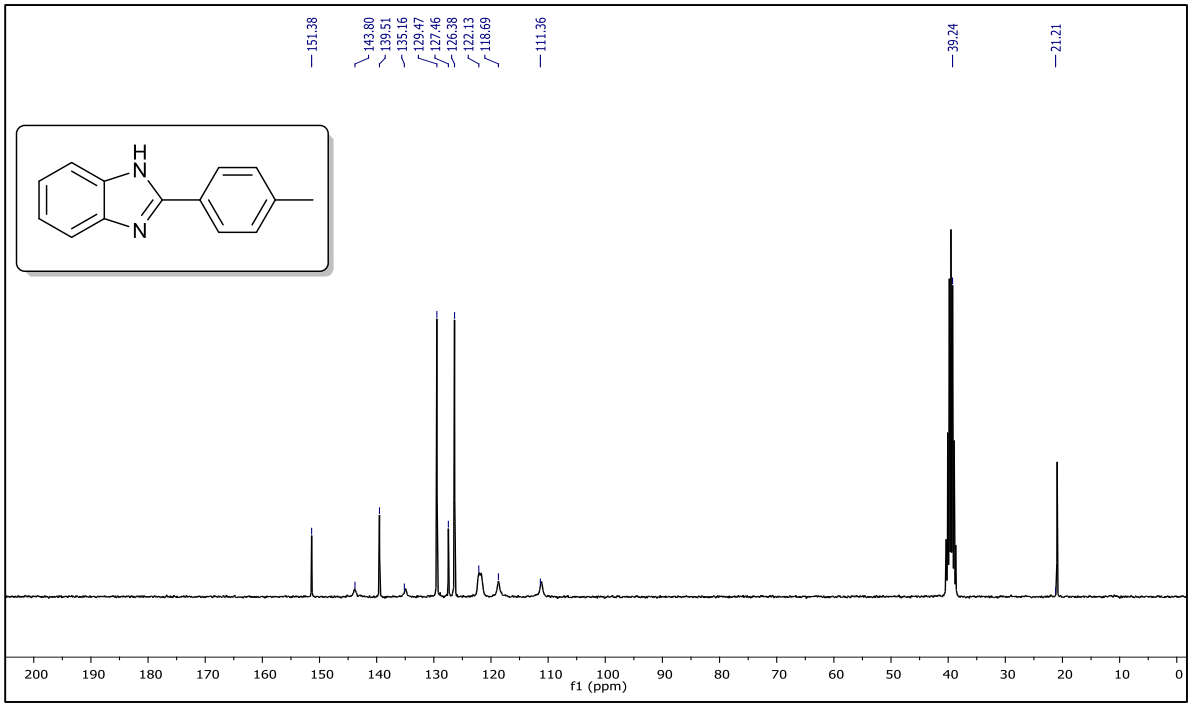
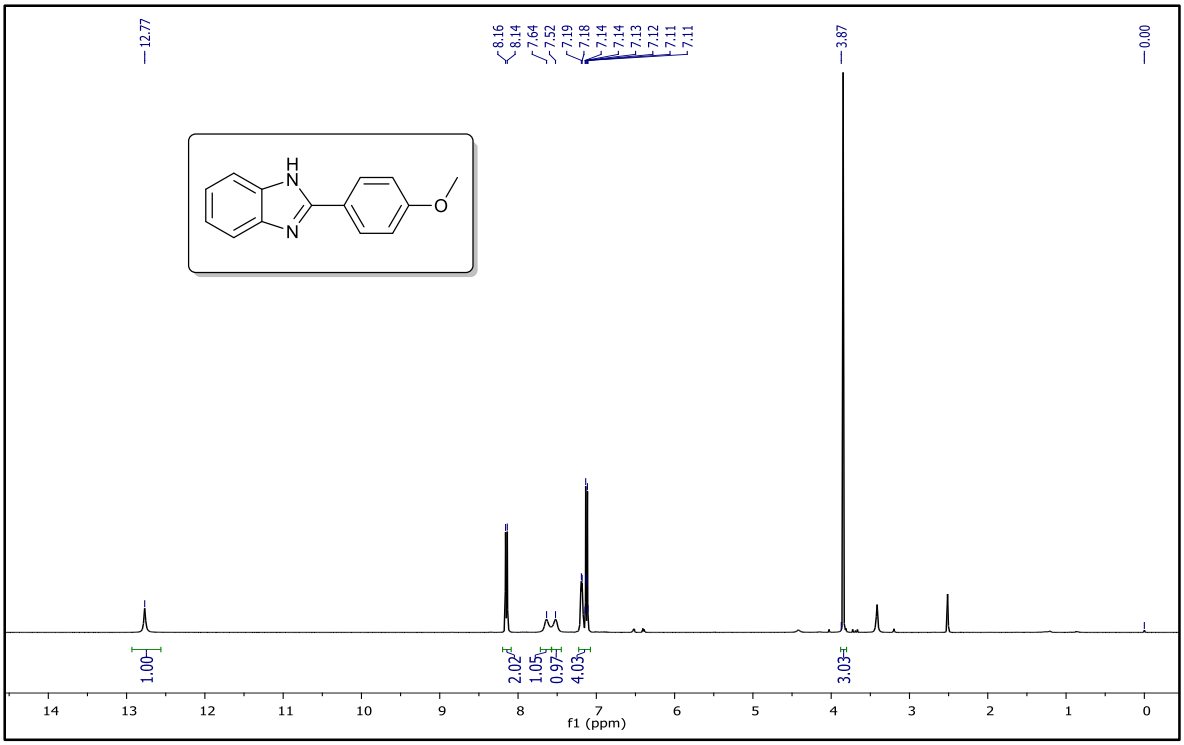
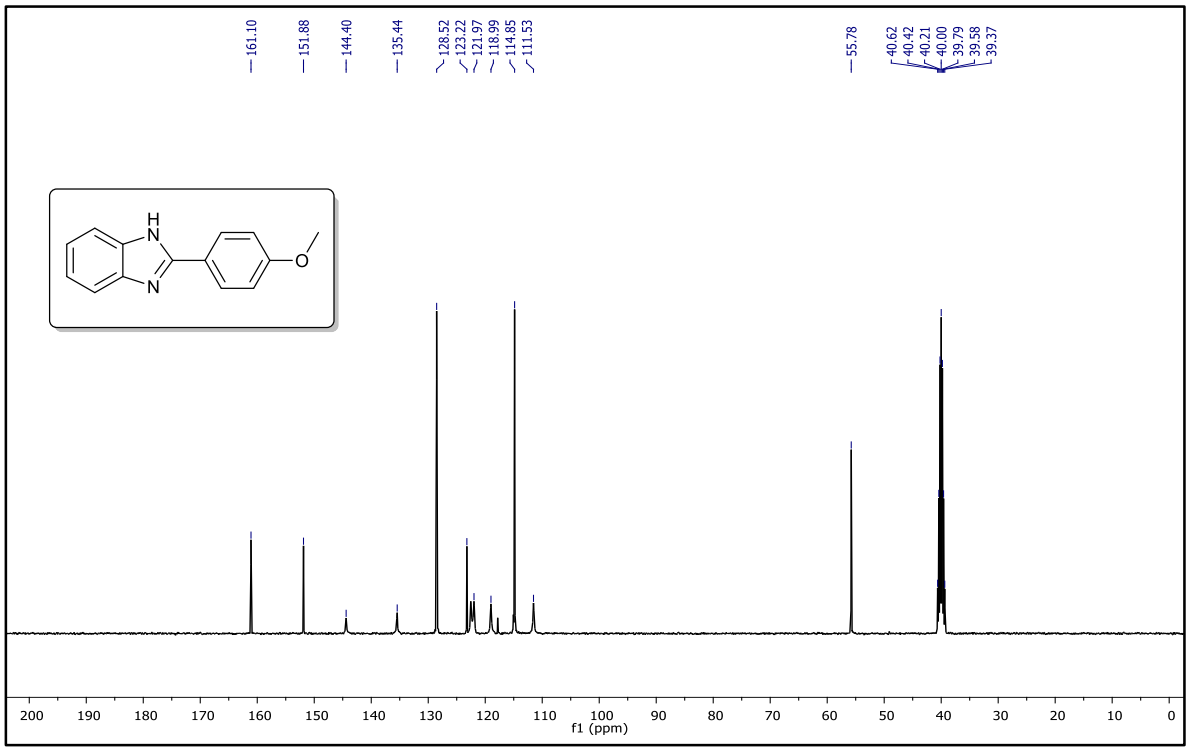
8.09
8.07
7.64
7.53
7.37
7.35
7.20
7.19
2.38
0.00
0.97
2.06
1.98
2.03
2.06
2.98
f1 (ppm)


151.38
143.80
139.51
135.16
129.47
127.46
126.38
122.13
118.69
111.36
39.24
21.21
f1 (ppm)


12.77
8.16
8.14
7.64
7.52
7.19
7.18
7.14
7.14
7.13
7.12
7.11
7.11
3.87
0.00
1.00
2.02
1.05
0.97
4.03
3.03
f1 (ppm)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128.52
123.22
121.97
118.99
114.85
111.53
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40.62
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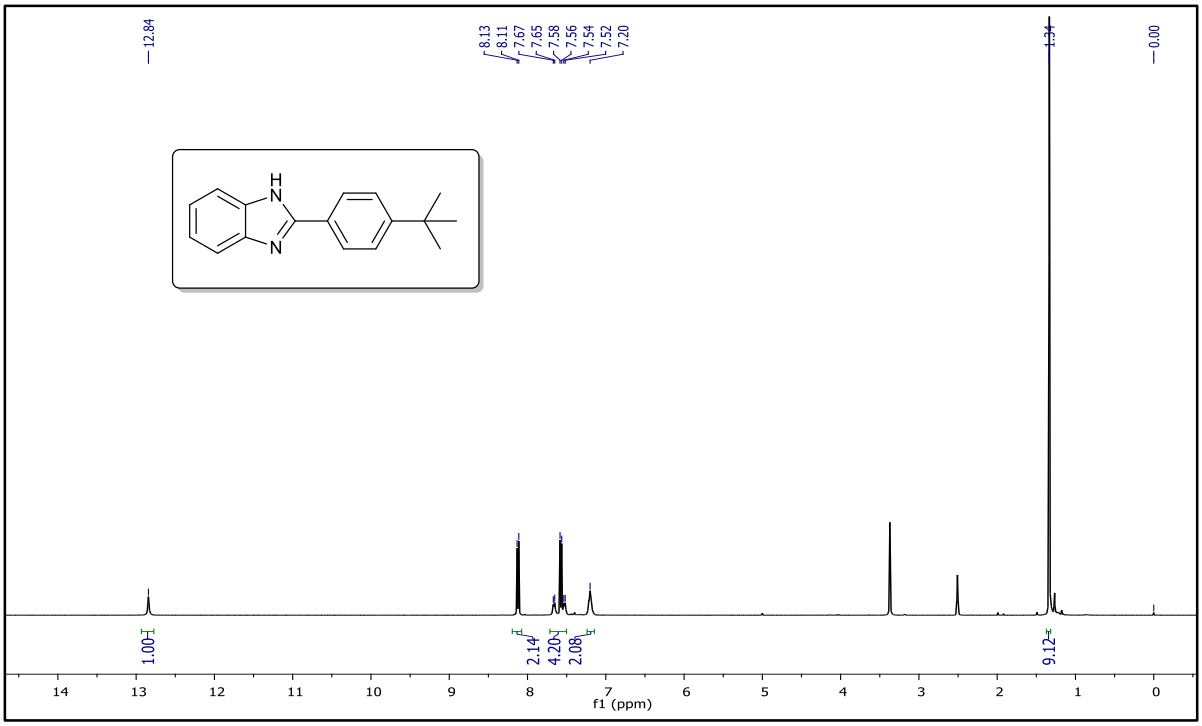
40.00
39.79
39.58
39.37
f1 (ppm)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7.54
7.52
7.20
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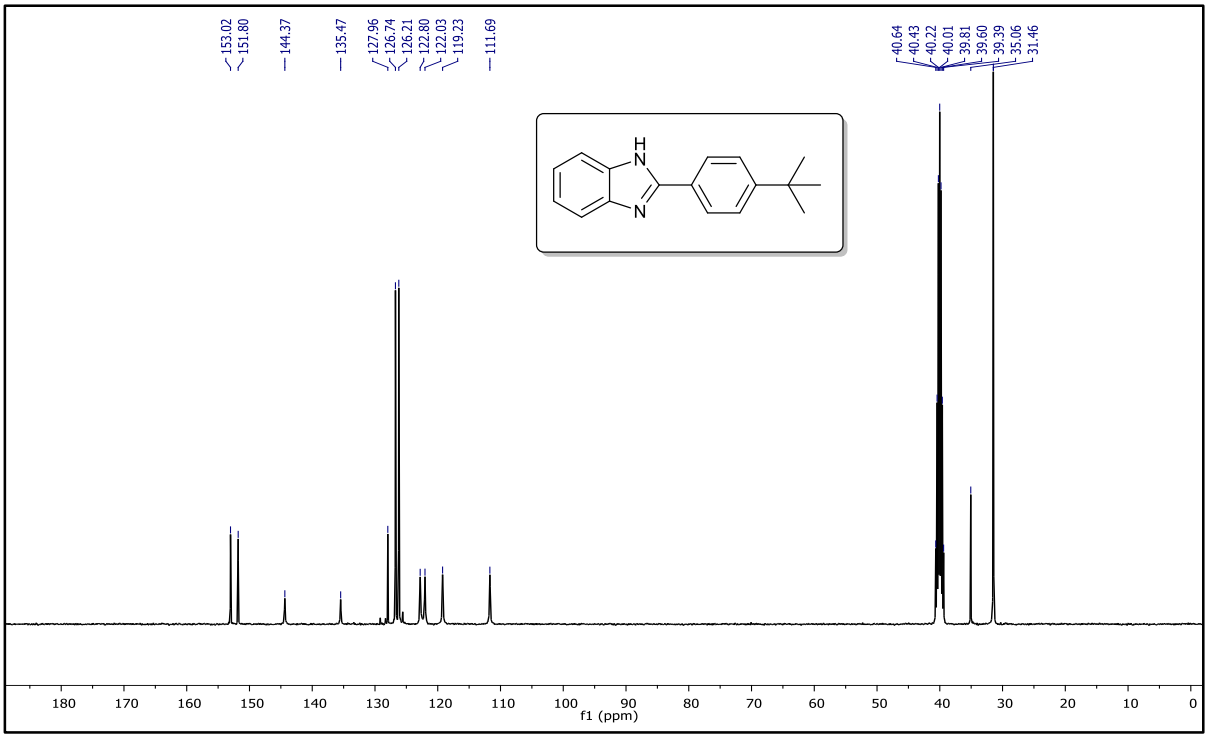
0.00
1.00
2.14
4.20
2.08
9.12
f1 (ppm)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144.37
135.47
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126.74
126.21
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111.69
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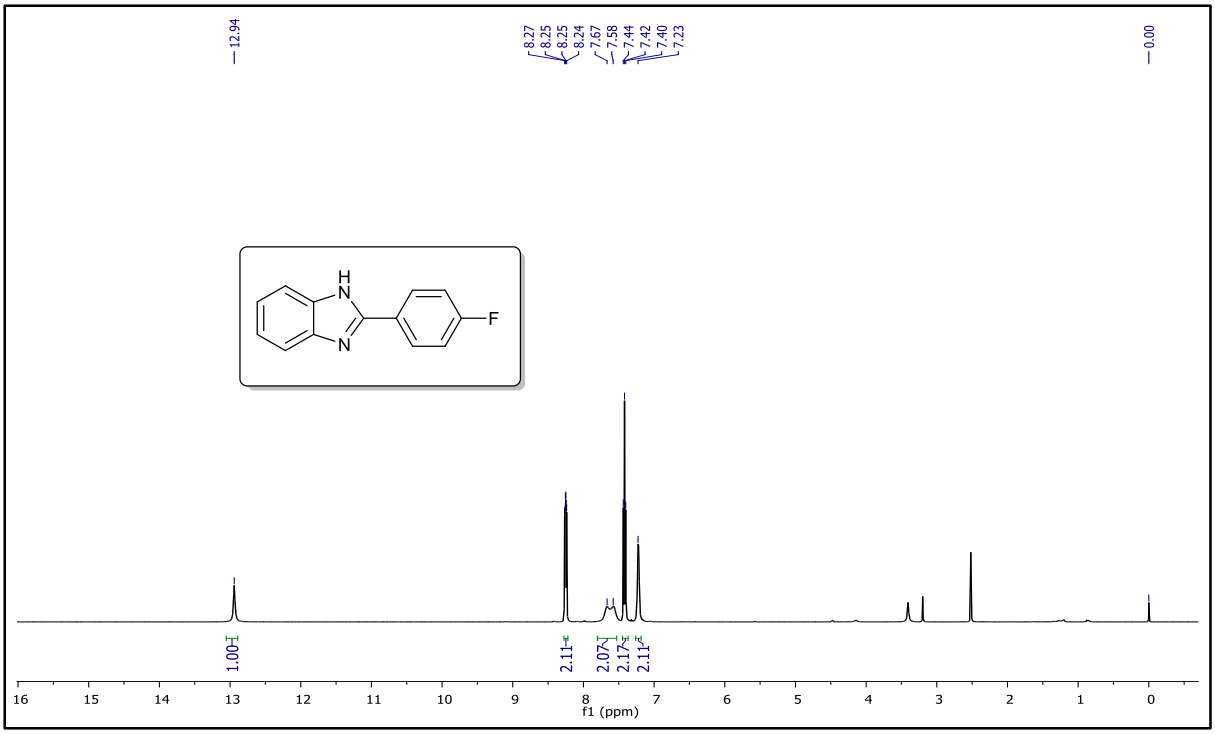
39.60
39.39
35.06
31.46
f1 (ppm)


12.94
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8.24
7.67
7.58
7.44
7.42
7.40
7.23
0.00
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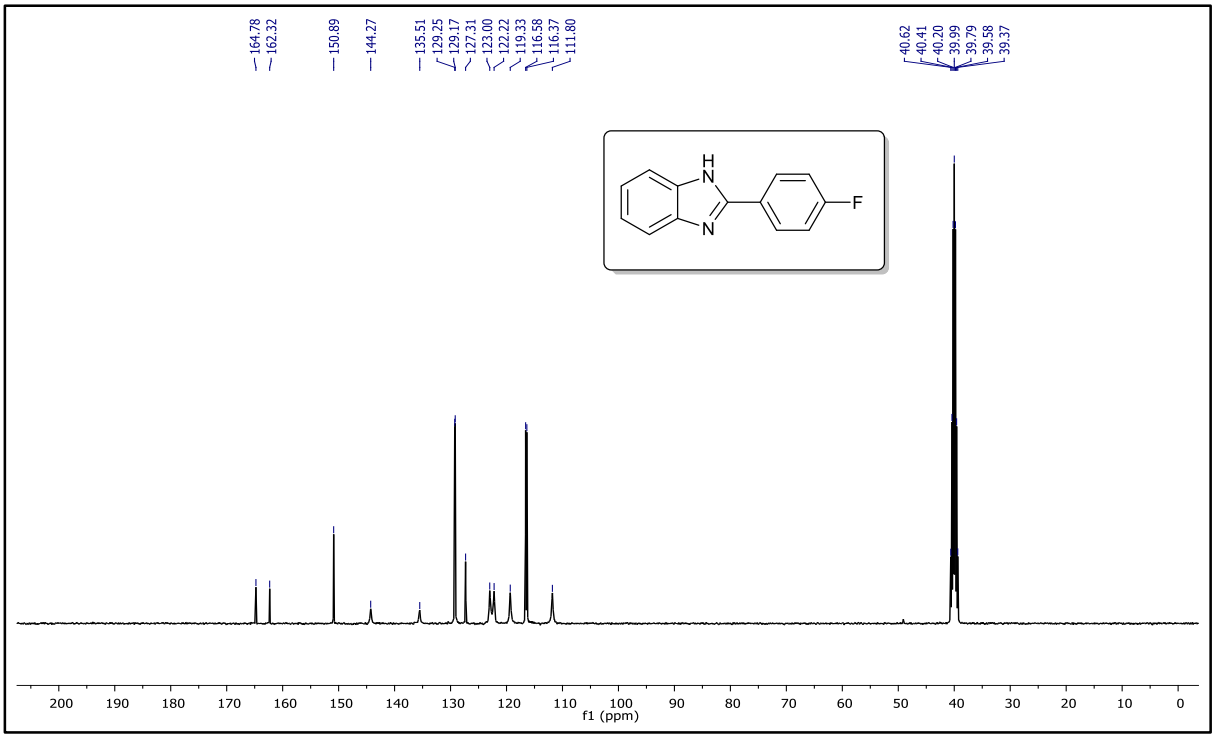
2.11
2.07
2.17
2.11
f1 (ppm)


164.78
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144.27
135.51
129.25
129.17
127.31
123.00
122.22
119.33
116.58
116.37
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40.41
40.20
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39.37
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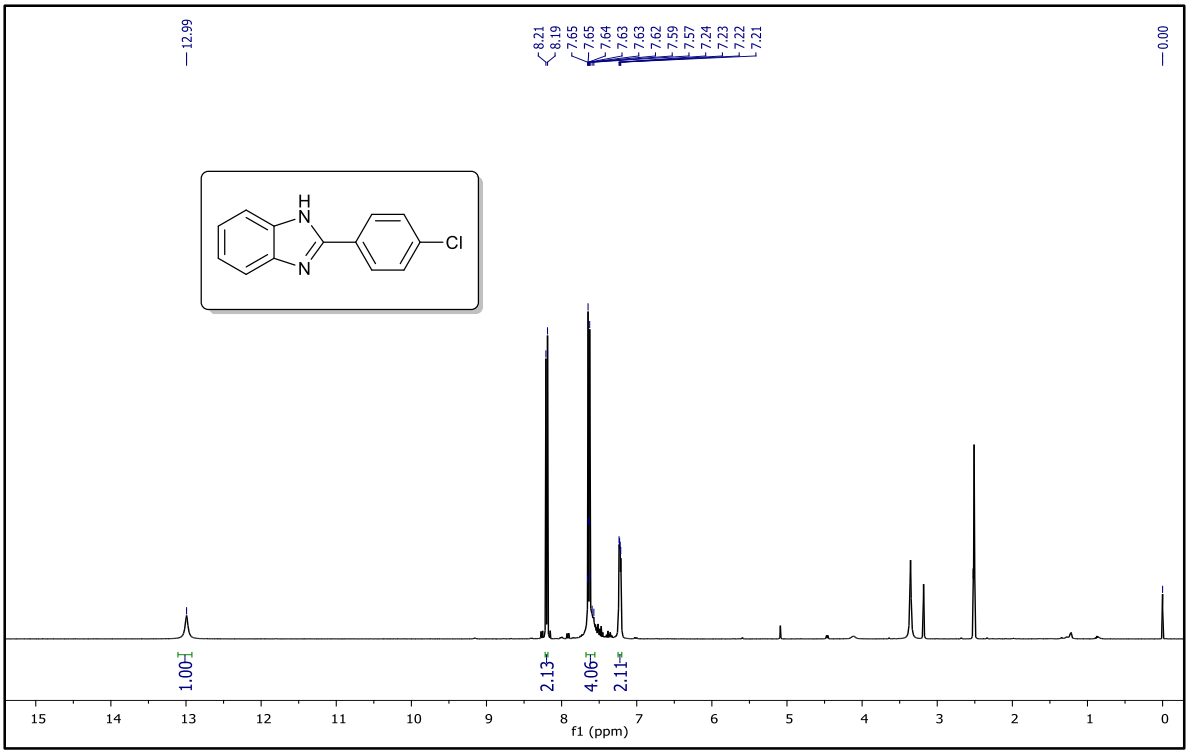
N
F
f1 (ppm)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7.64
7.63
7.63
7.62
7.59
7.57
7.24
7.23
7.22
7.21
0.00
H
N
N
Cl
1.00
2.13
4.06
2.11
15
14
13
12
11
10
9
8
7
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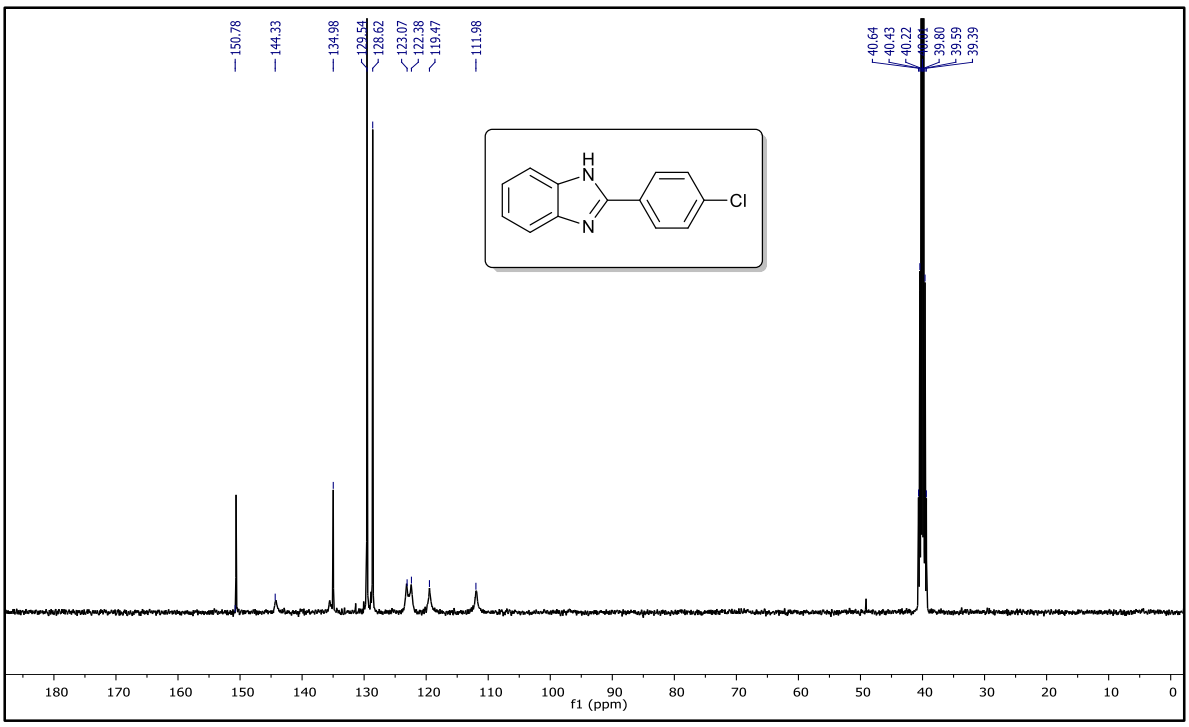
5
4
3
2
1
0
f1 (ppm)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123.07
122.38
119.47
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40.64
40.43
40.22
39.80
39.59
39.39
H
N
N
Cl
180
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110
100
90
80
70
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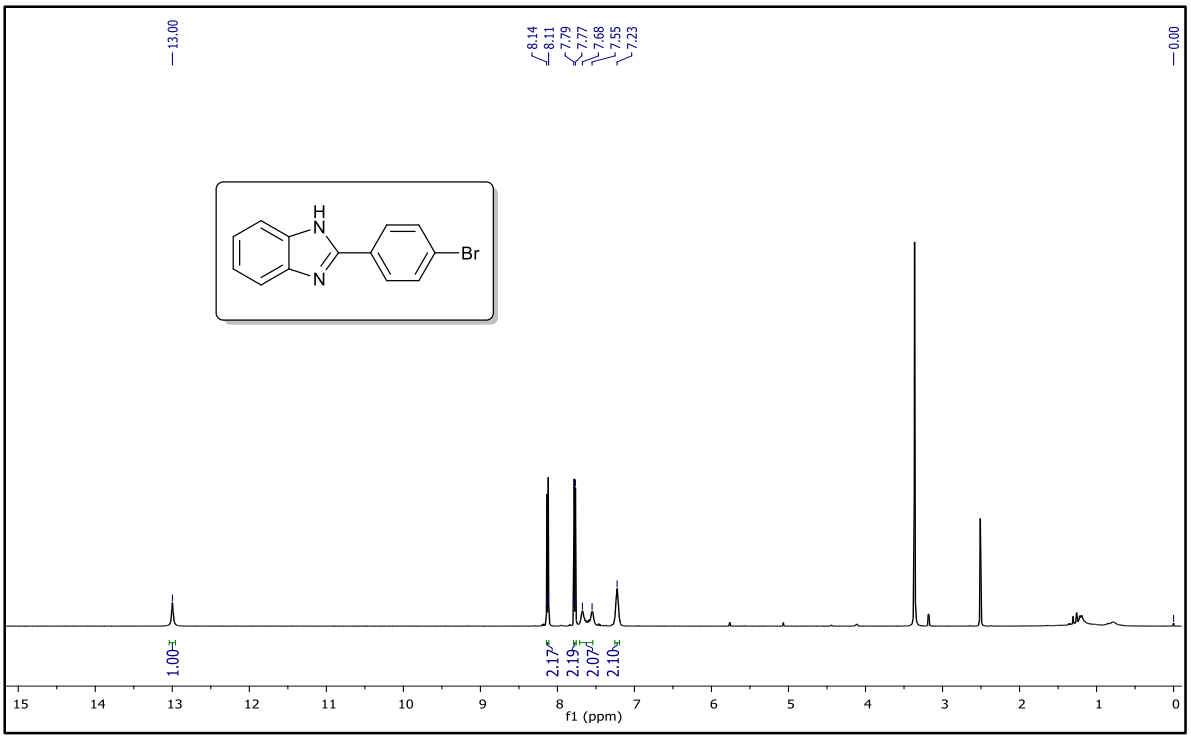
50
40
30
20
10
0
f1 (ppm)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7.68
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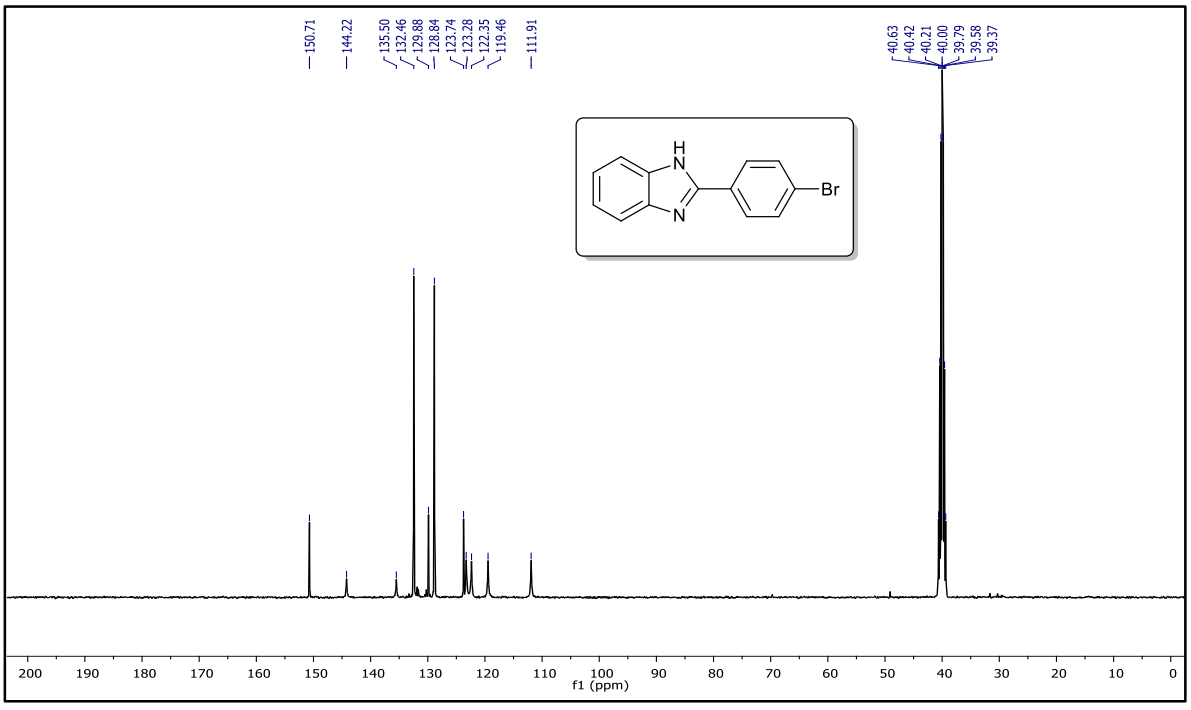
N
N
Br
1.00
2.17
2.19
2.07
2.10
f1 (ppm)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128.84
123.74
123.28
122.35
119.46
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40.21
40.00
39.79
39.58
39.37
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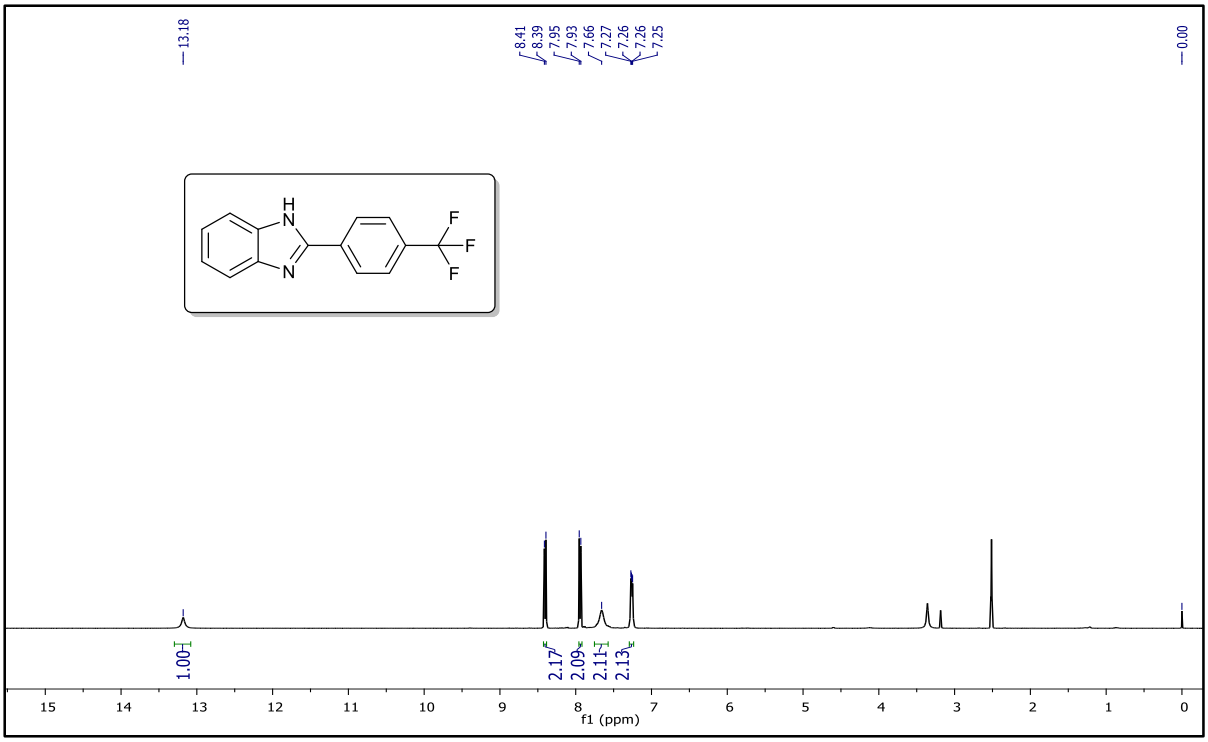
N
N
Br
f1 (ppm)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7.66
7.27
7.26
7.26
7.25
0.00
H
N
N
F
F
F
1.00
2.17
2.09
2.11
2.13
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13
12
11
10
9
8
7
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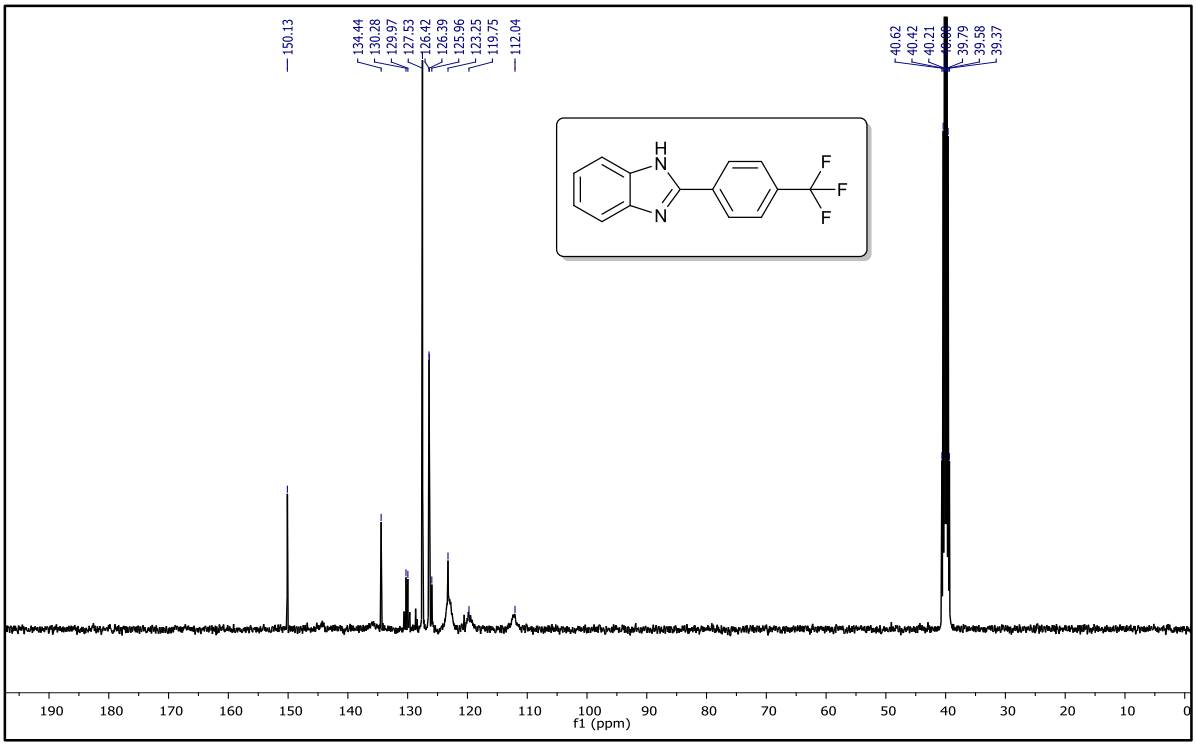
5
4
3
2
1
0
f1 (ppm)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125.96
123.25
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112.04
40.62
40.42
40.21
39.79
39.58
39.37
H
N
N
F
F
F
190
180
170
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150
140
130
120
110
100
90
80
70
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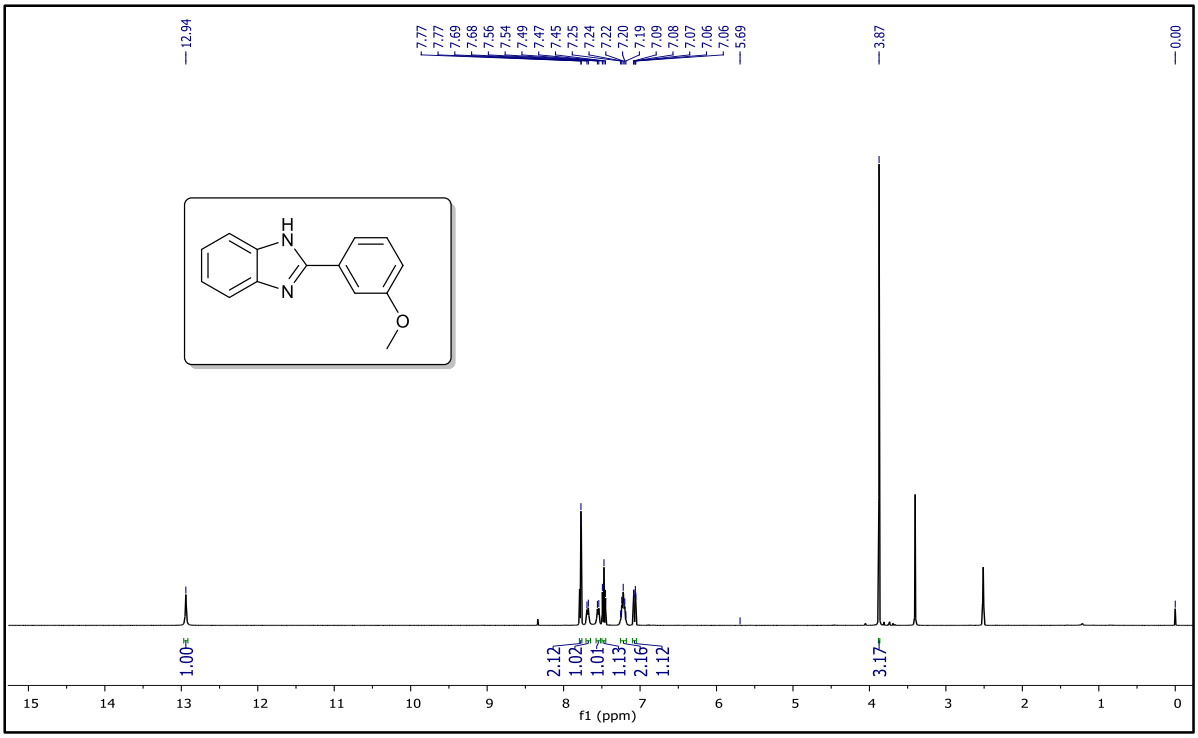
50
40
30
20
10
0
f1 (ppm)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7.56
7.54
7.49
7.47
7.45
7.25
7.24
7.22
7.20
7.19
7.09
7.08
7.07
7.06
7.06
5.69
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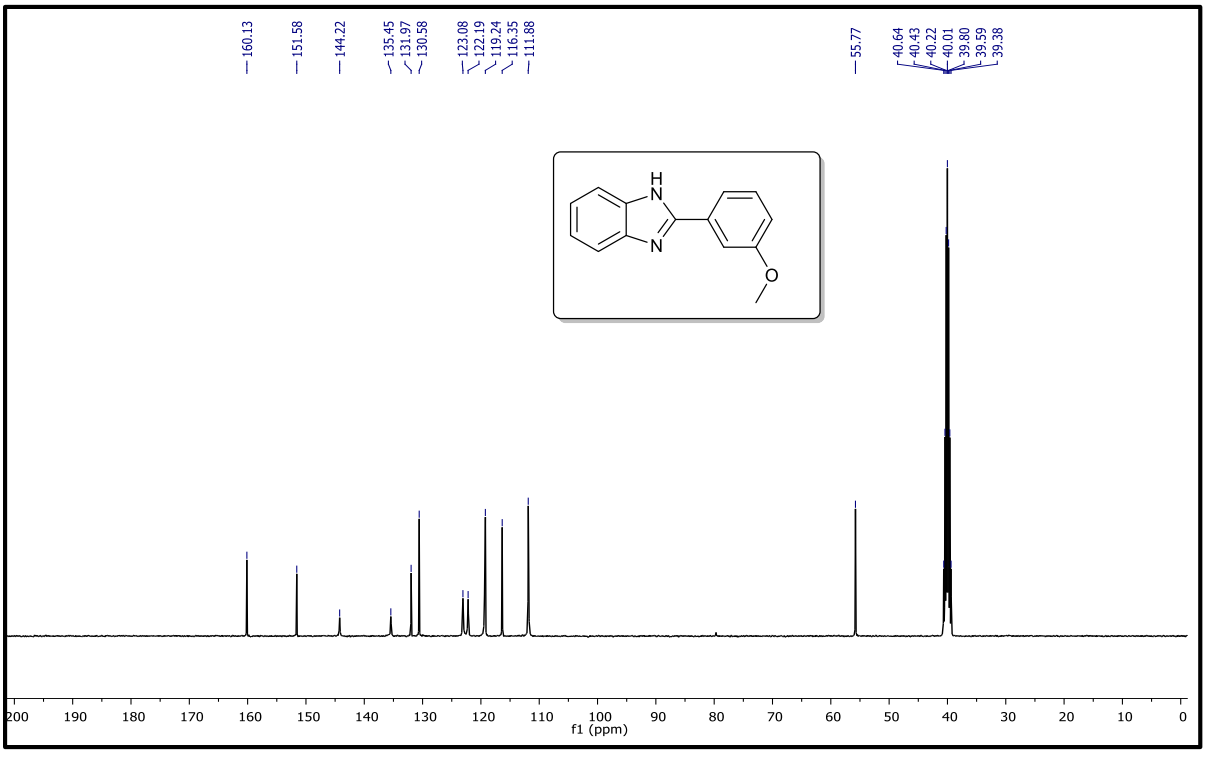
1.00
2.12
1.02
1.01
1.13
2.16
1.12
3.17
f1 (ppm)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151.58
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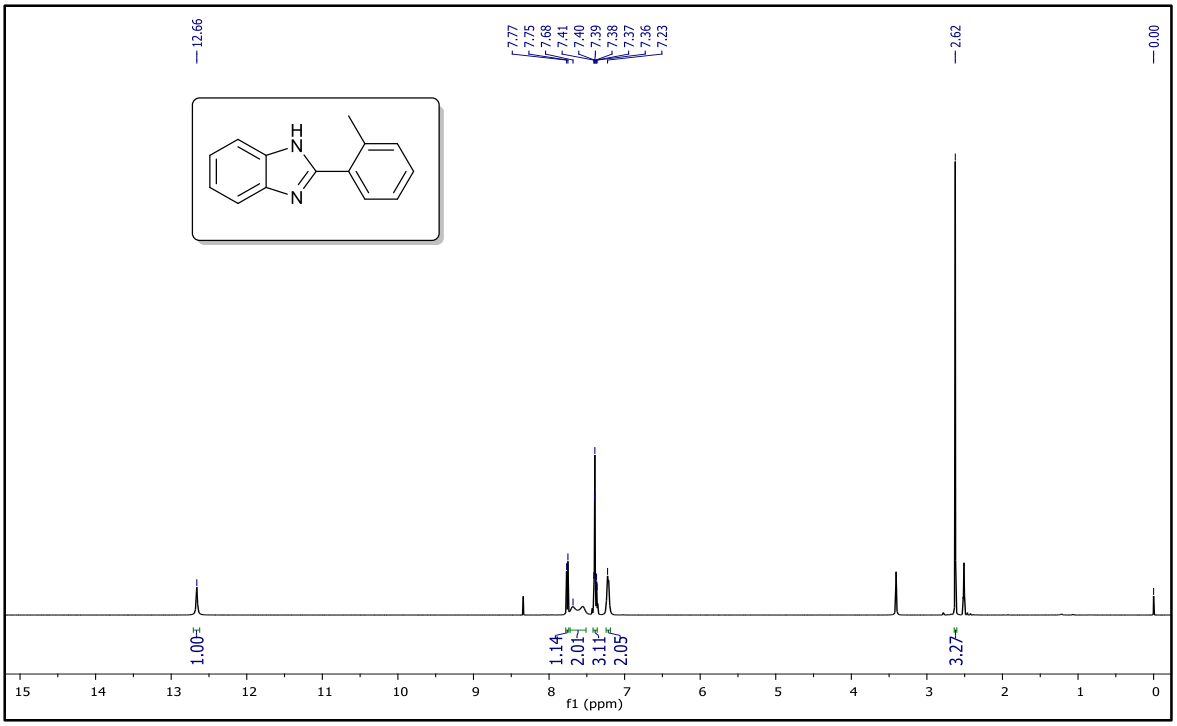
135.45
131.97
130.58
123.08
122.19
119.24
116.35
111.88
55.77
40.64
40.43
40.22
40.01
39.80
39.59
39.38
f1 (ppm)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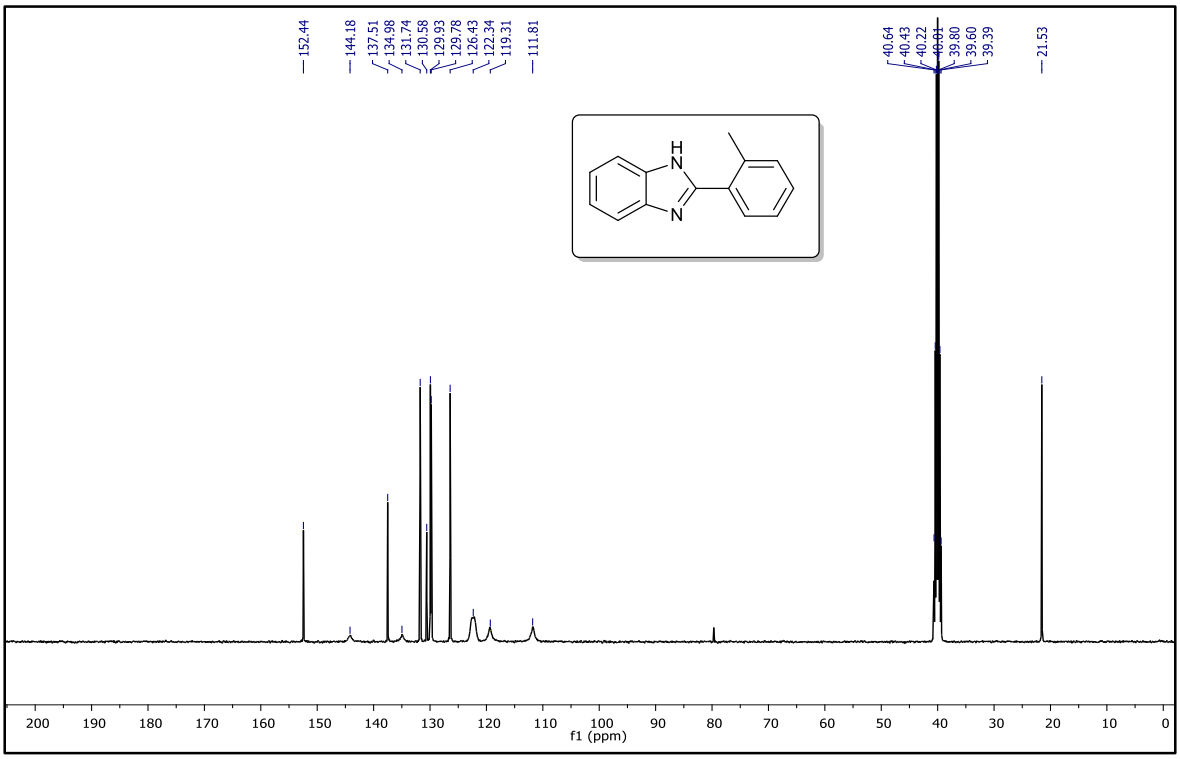
7.77
7.75
7.68
7.41
7.40
7.39
7.38
7.37
7.36
7.23
2.62
0.00
1.00
1.14
2.01
3.11
2.05
3.27
f1 (ppm)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144.18
137.51
134.98
131.74
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129.93
129.78
126.43
122.34
119.31
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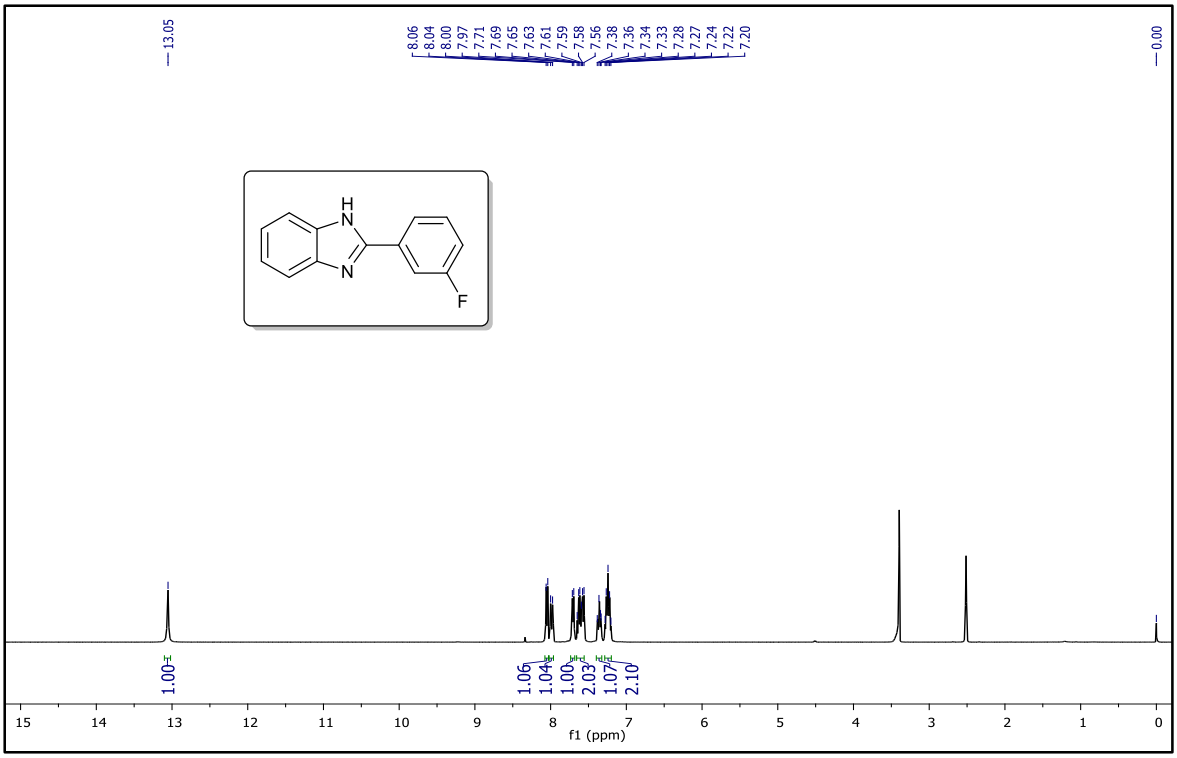
40.64
40.43
40.22
40.01
39.80
39.60
39.39
21.53
f1 (ppm)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8.06
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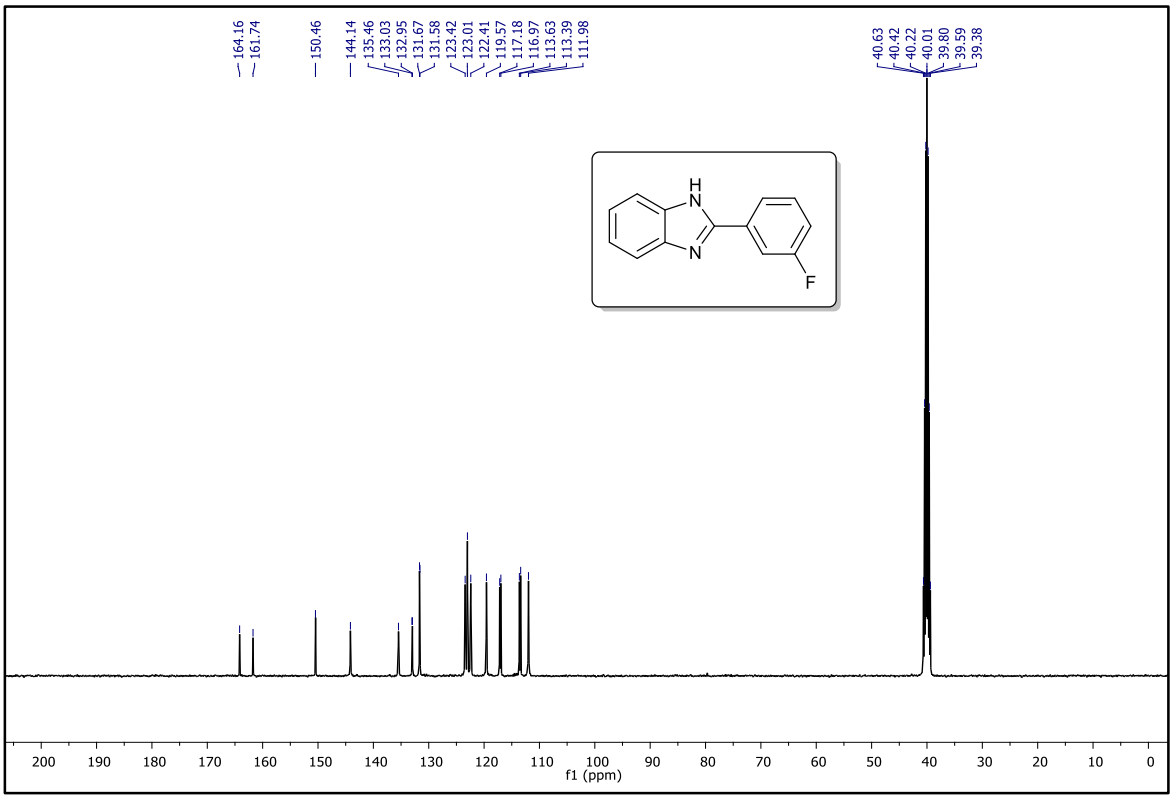
8.00
7.97
7.71
7.69
7.65
7.63
7.61
7.59
7.58
7.56
7.38
7.36
7.34
7.33
7.28
7.27
7.24
7.22
7.20
0.00
H
N
N
F
1.00
1.06
1.04
1.00
2.03
1.07
2.10
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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150.46
144.14
135.46
133.03
132.95
131.67
131.58
123.42
123.01
122.41
119.57
117.18
116.97
113.63
113.39
111.98
40.63
40.42
40.22
40.01
39.80
39.59
39.38
H
N
N
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
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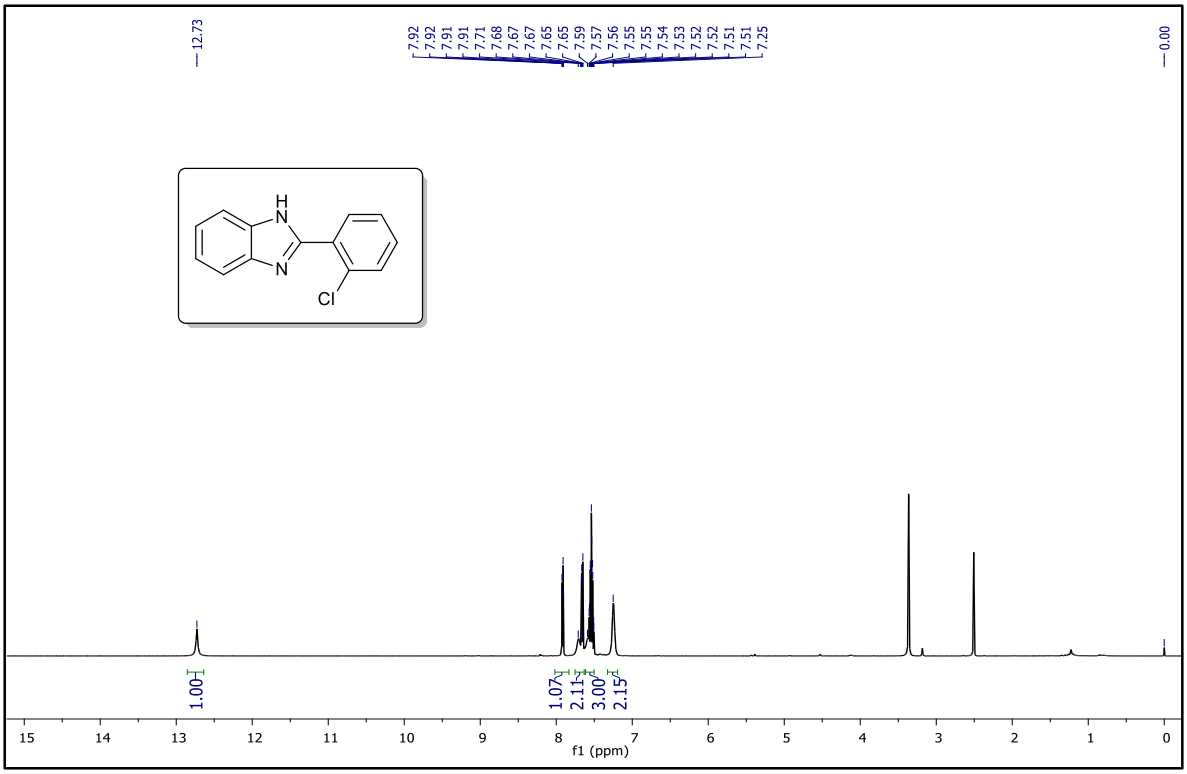
10
0
f1 (ppm)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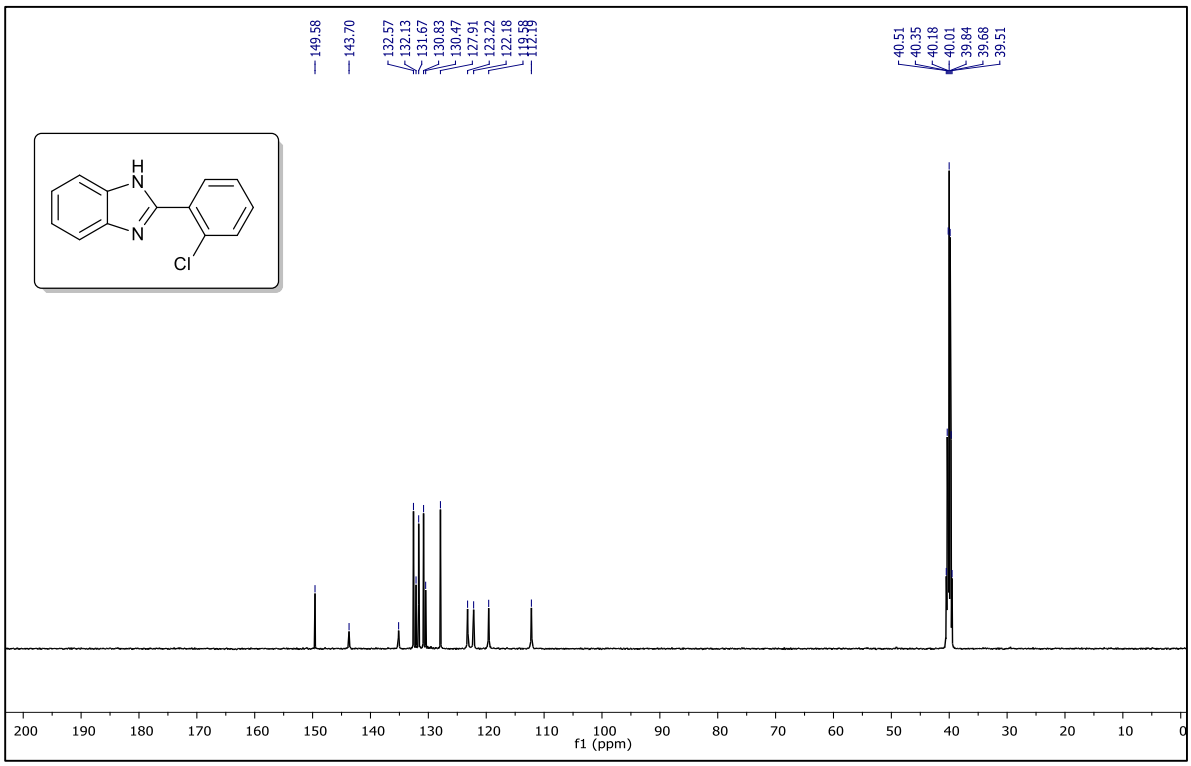
7.92
7.91
7.91
7.71
7.68
7.67
7.67
7.65
7.65
7.59
7.57
7.56
7.55
7.55
7.54
7.53
7.52
7.52
7.51
7.51
7.25
0.00
H
N
N
Cl
1.00
1.07
2.11
3.00
2.15
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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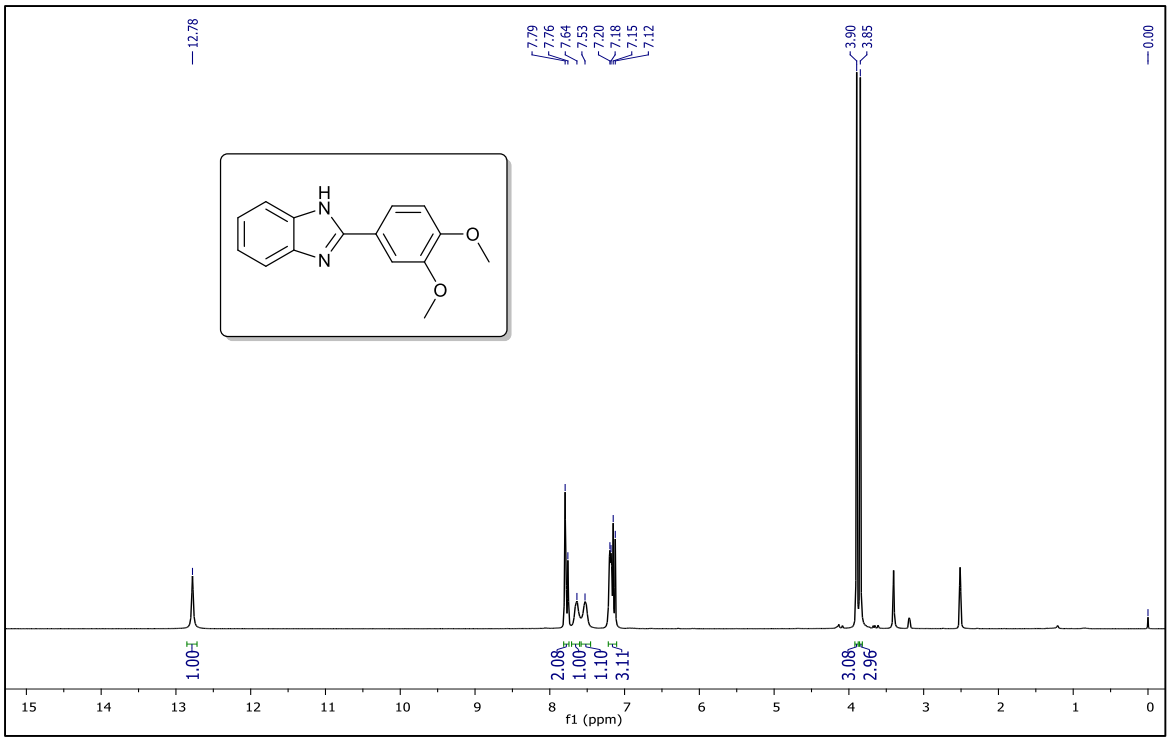
131.67
130.83
130.47
127.91
123.22
122.18
119.58
112.18
40.51
40.35
40.18
40.01
39.84
39.68
39.51
H
N
N
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.79
7.76
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7.15
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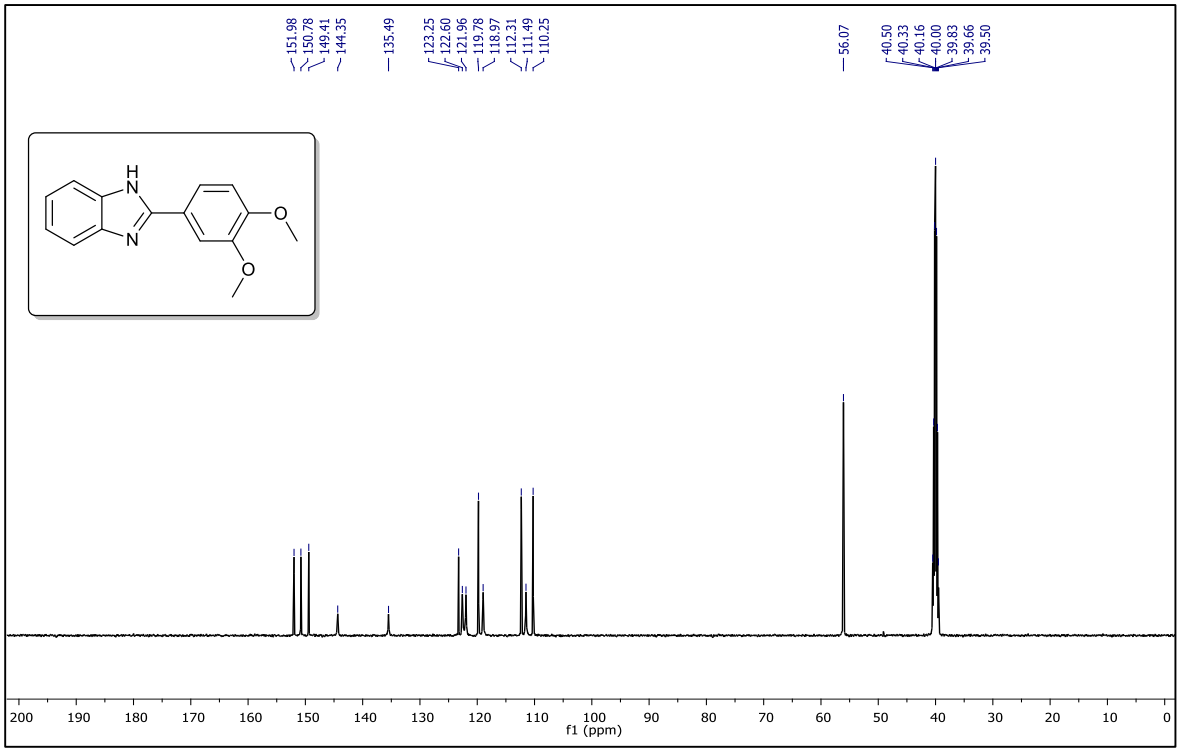
0.00
1.00
2.08
1.00
1.10
3.11
3.08
2.96
f1 (ppm)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144.35
135.49
123.25
122.60
121.96
119.78
118.97
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111.49
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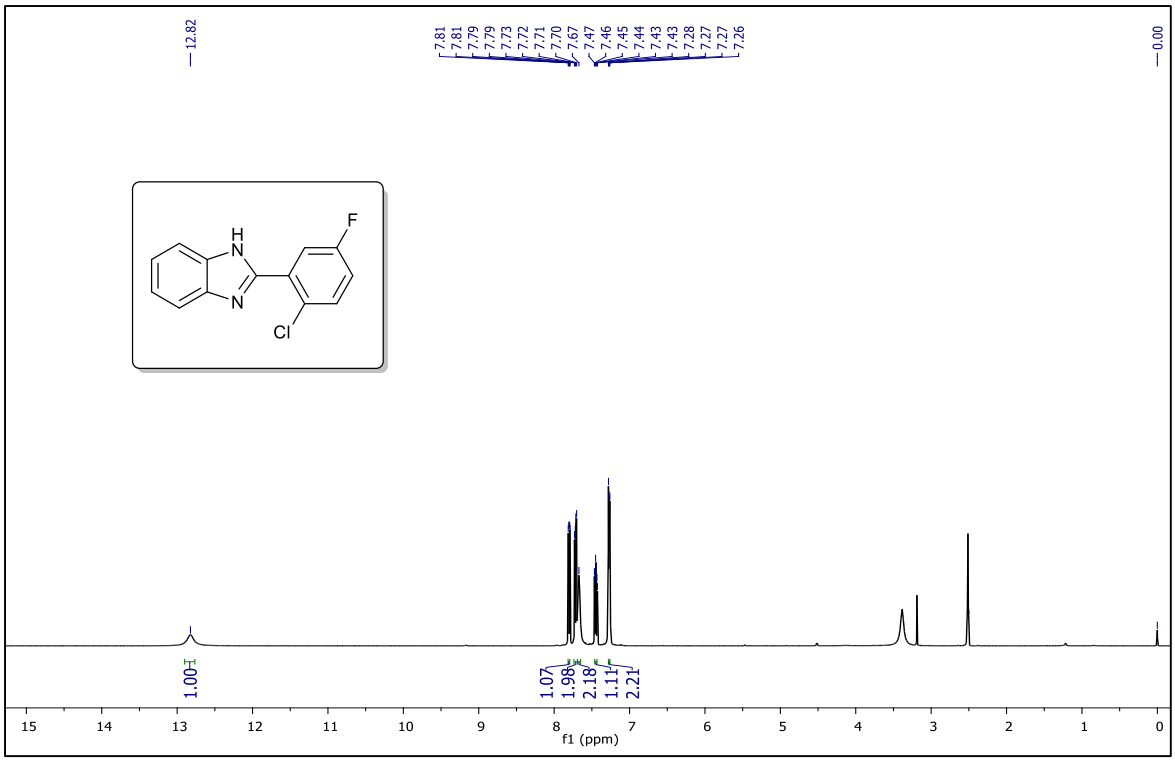
40.00
39.83
39.66
39.50
f1 (ppm)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7.79
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7.72
7.71
7.70
7.67
7.47
7.46
7.45
7.44
7.43
7.43
7.28
7.27
7.27
7.26
0.00
H
N
N
F
Cl
1.00
1.07
1.98
2.18
1.11
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12
11
10
9
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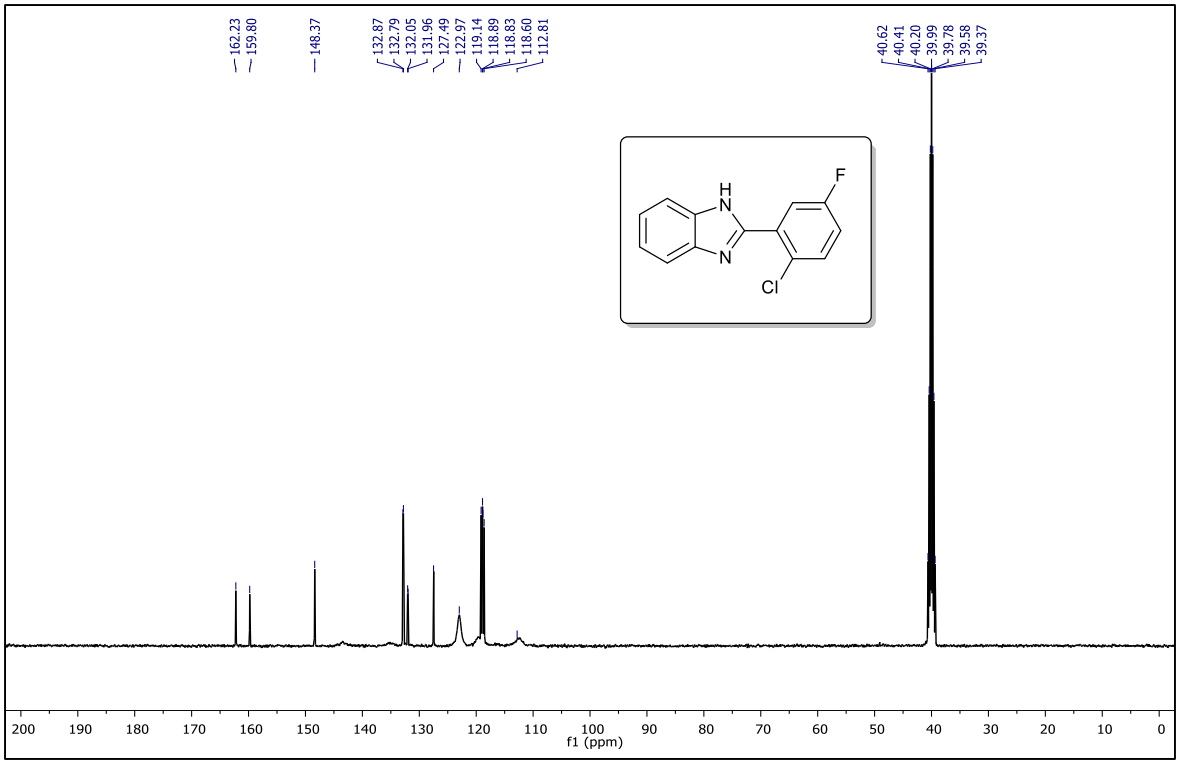
7
6
5
4
3
2
1
0
f1 (ppm)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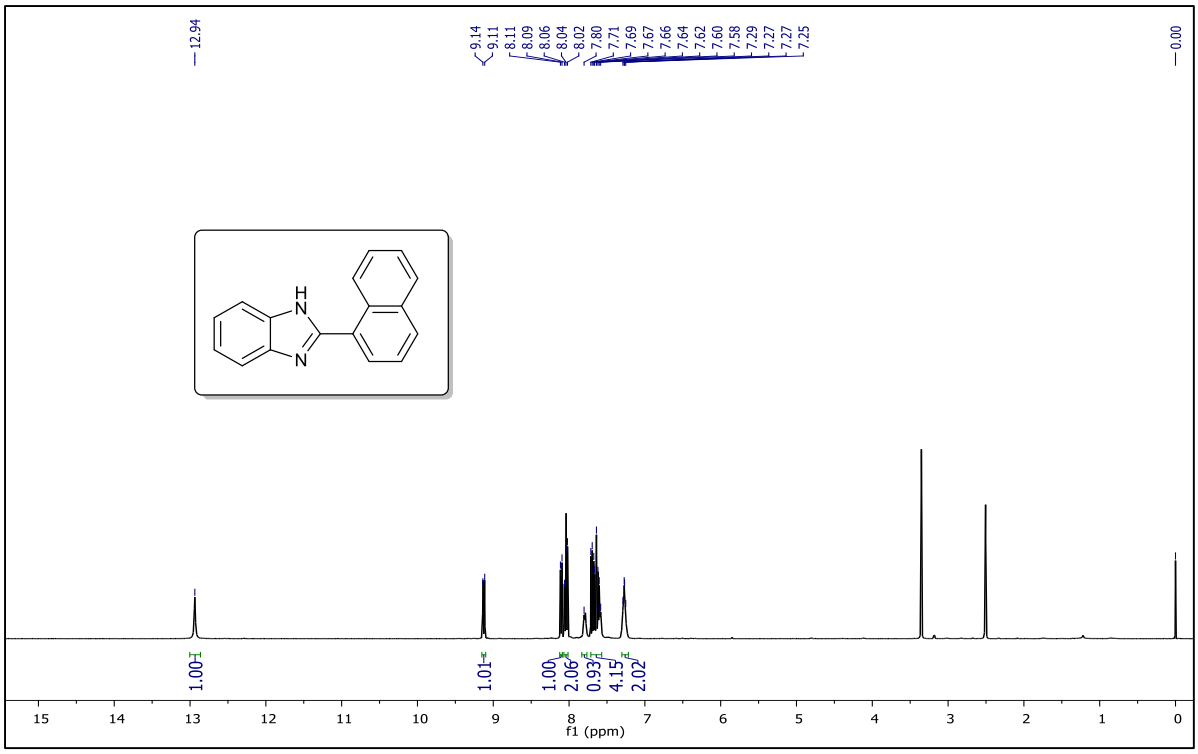
119.14
118.89
118.83
118.60
112.81
40.62
40.41
40.20
39.99
39.78
39.58
39.37
H
N
N
F
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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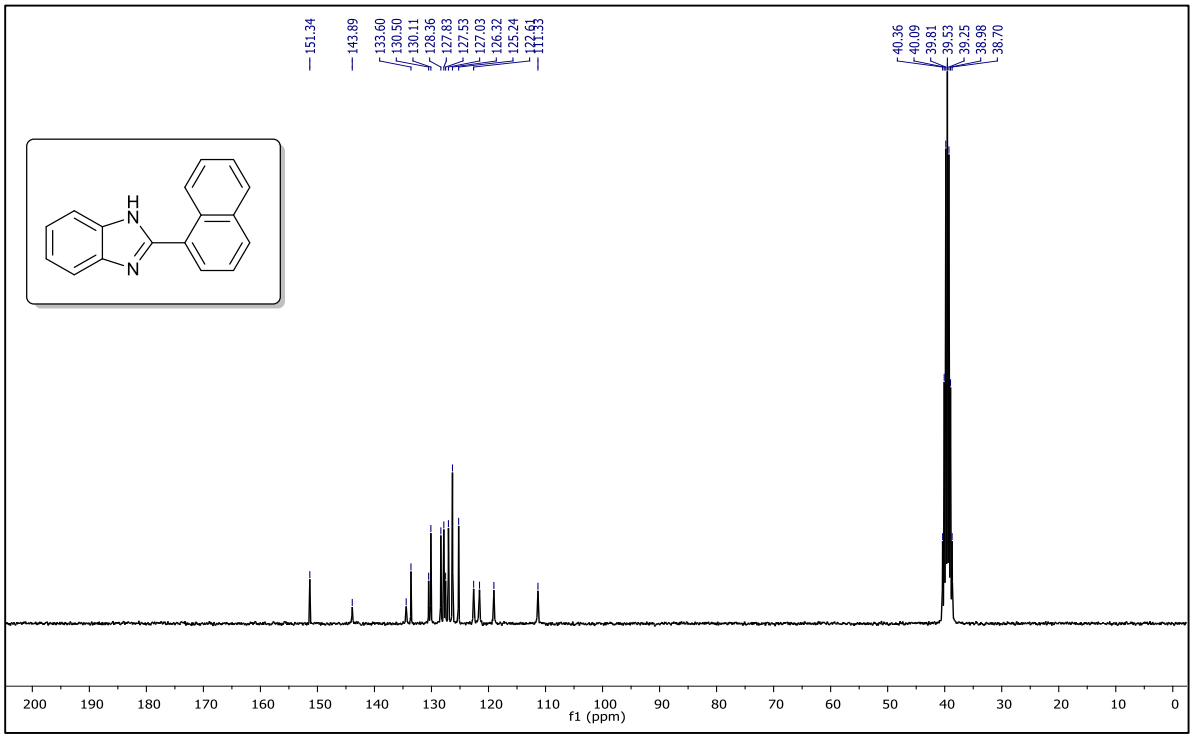
7.69
7.67
7.66
7.64
7.62
7.60
7.58
7.29
7.27
7.27
7.25
0.00
1.00
1.01
1.00
2.06
0.93
4.15
2.02
f1 (ppm)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128.36
127.83
127.53
127.03
126.32
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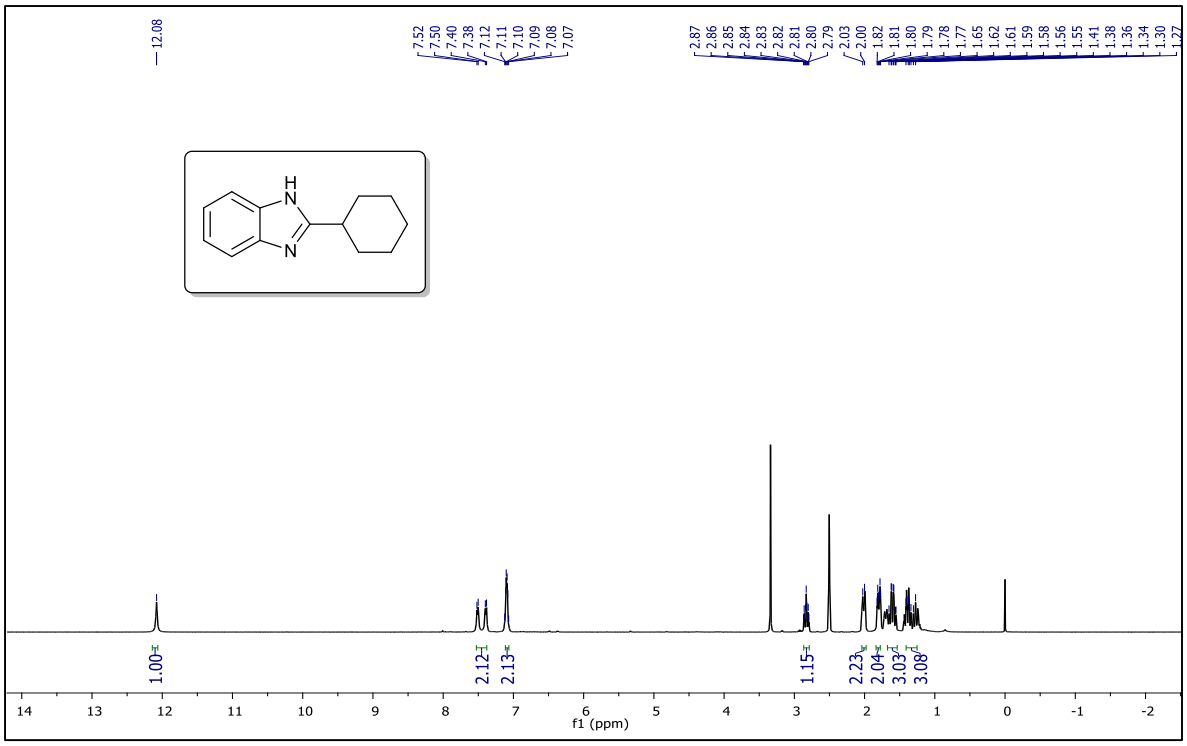
111.93
40.36
40.09
39.81
39.53
39.25
38.98
38.70
f1 (ppm)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7.11
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7.09
7.08
7.07
2.87
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2.85
2.84
2.83
2.82
2.81
2.80
2.79
2.03
2.00
1.82
1.81
1.80
1.79
1.78
1.77
1.65
1.62
1.61
1.59
1.58
1.56
1.55
1.41
1.38
1.36
1.34
1.30
1.27
H
N
N
1.00
2.12
2.13
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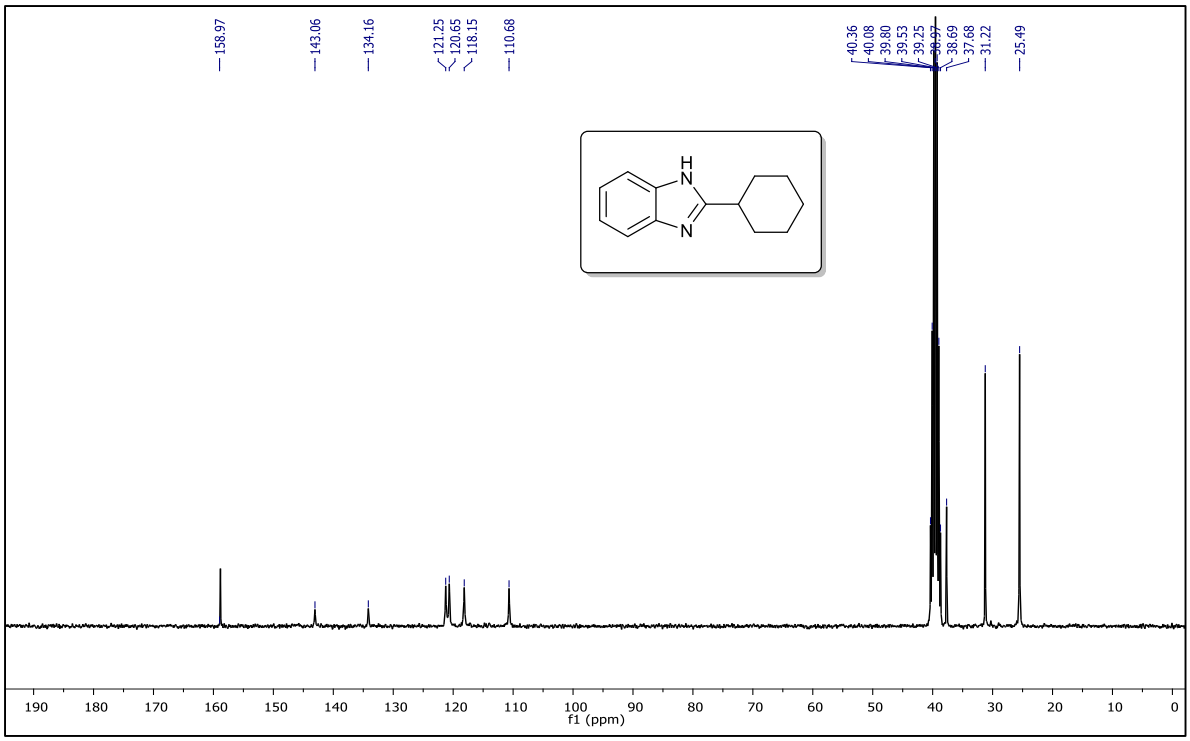
2.23
2.04
3.03
3.08
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)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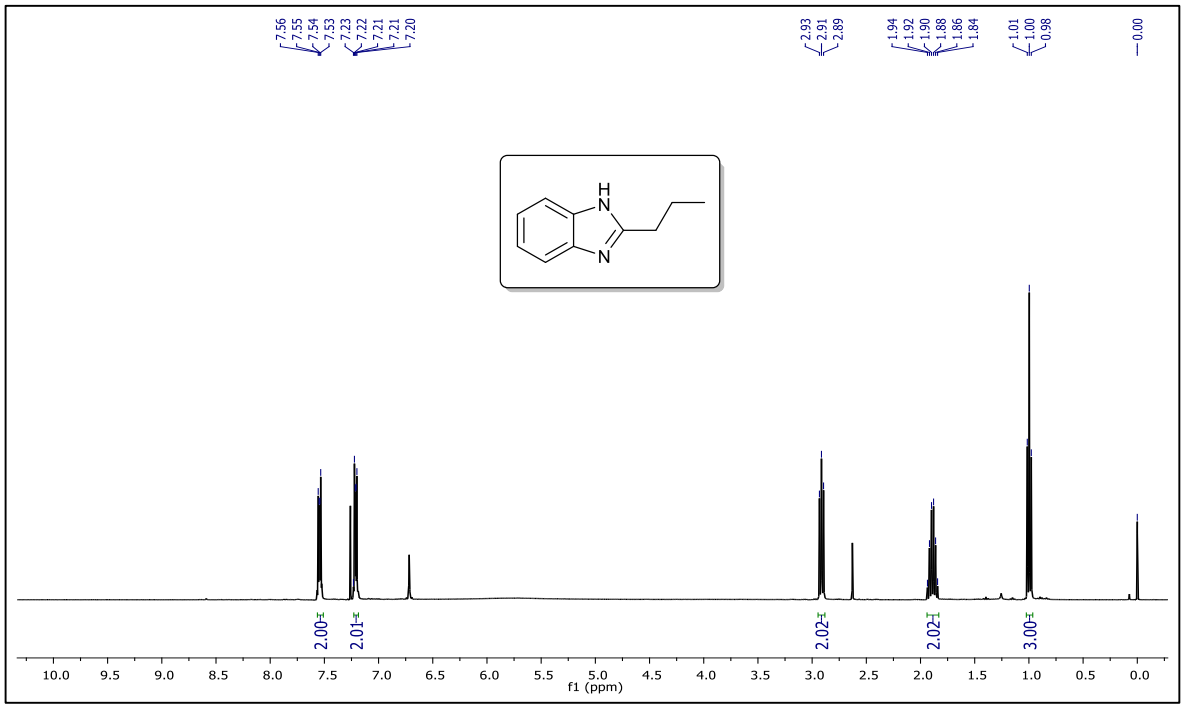
120.65
118.15
110.68
40.36
40.08
39.80
39.53
39.25
38.97
38.69
37.68
31.22
25.49
H
N
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.21
7.20
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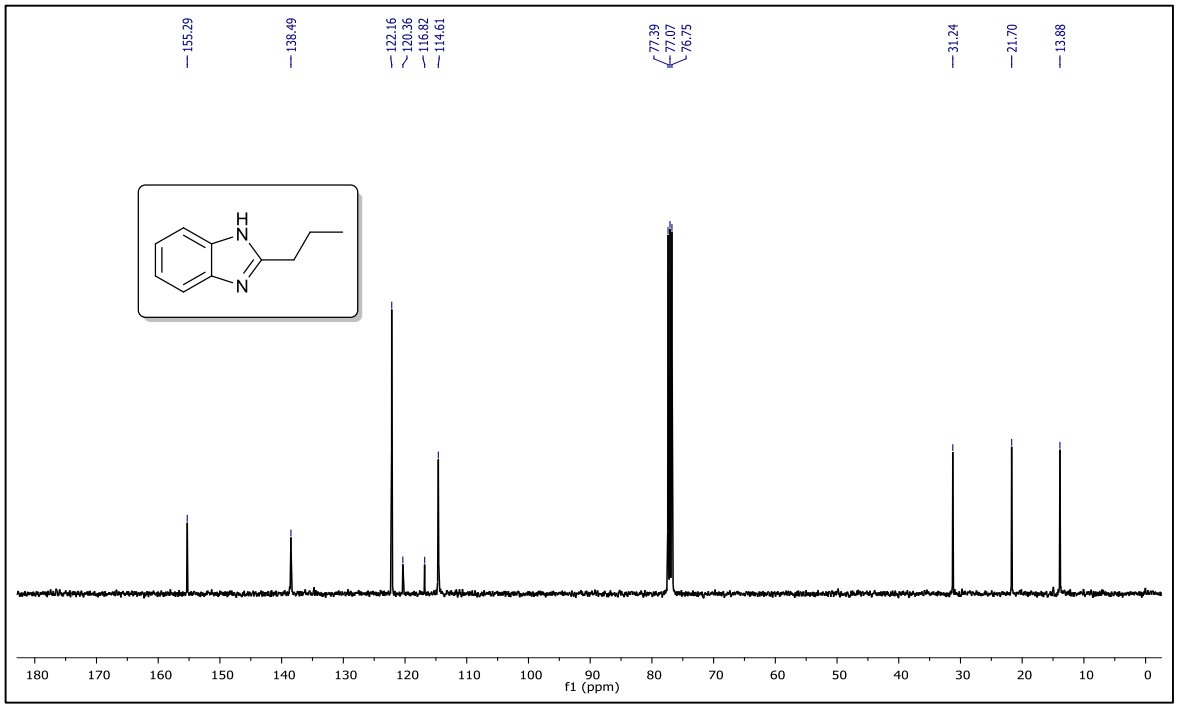
2.91
2.89
1.94
1.92
1.90
1.88
1.86
1.84
1.01
1.00
0.98
0.00
H
N
N
2.00
2.01
2.02
2.02
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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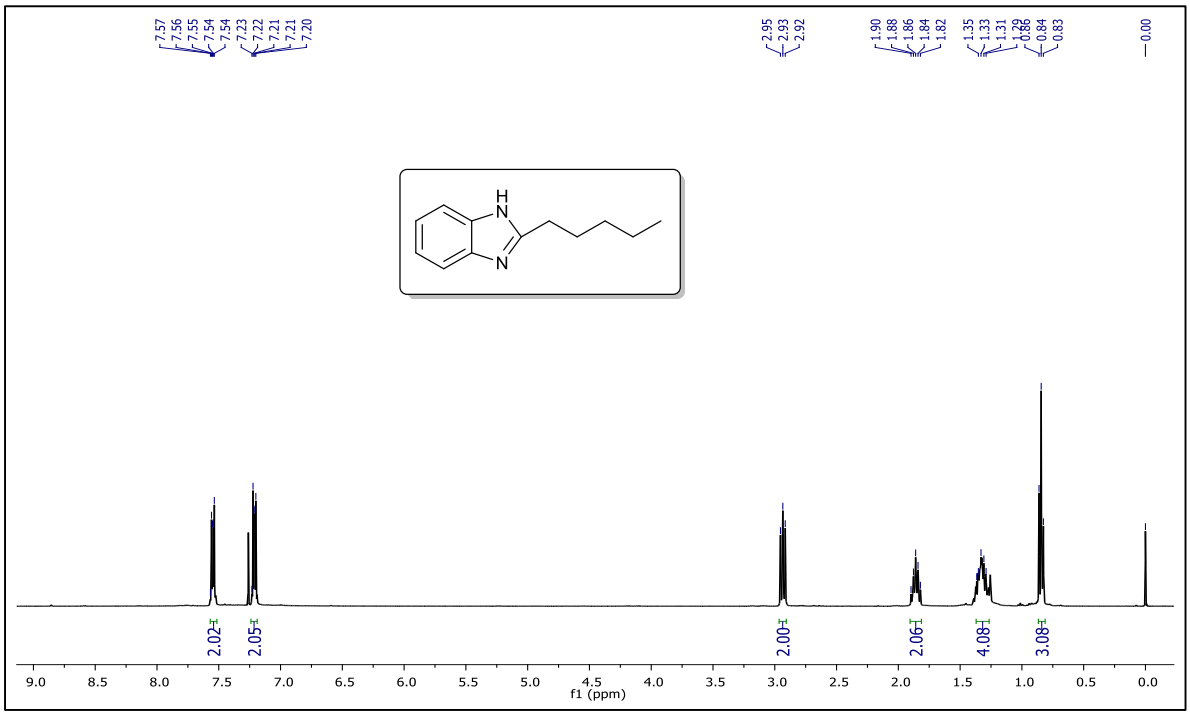
120.36
116.82
114.61
77.39
77.07
76.75
31.24
21.70
13.88
H
N
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.20
2.95
2.93
2.92
1.90
1.88
1.86
1.84
1.82
1.35
1.33
1.31
1.29
0.86
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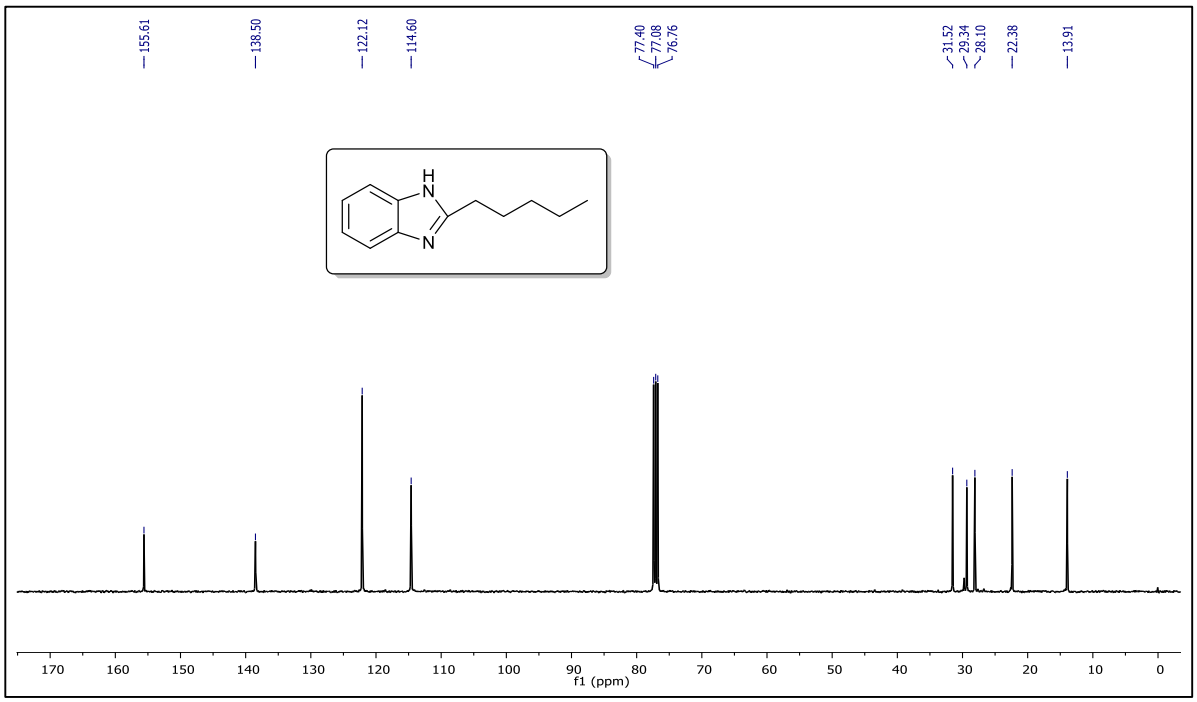
H
N
N
2.02
2.05
2.00
2.06
4.08
3.08
f1 (ppm)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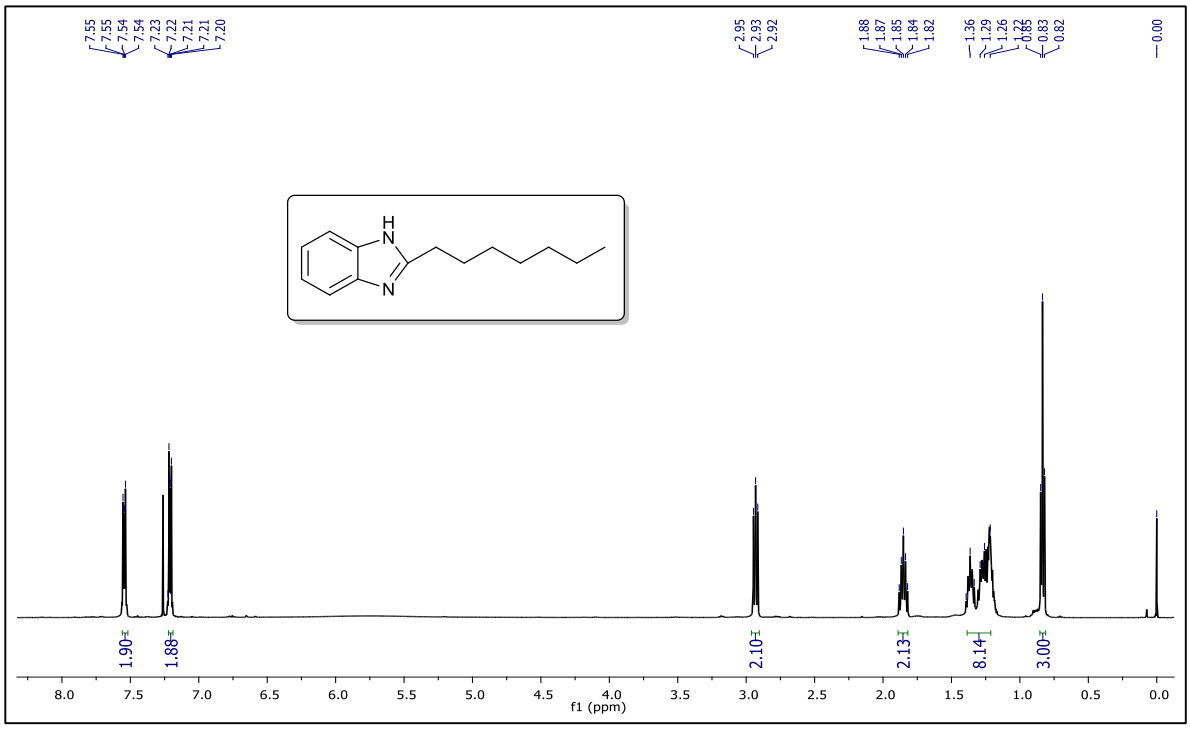
76.76
31.52
29.34
28.10
22.38
13.91
H
N
N
f1 (ppm)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7.20
2.95
2.93
2.92
1.88
1.87
1.85
1.84
1.82
1.36
1.29
1.26
1.22
0.85
0.83
0.82
0.00
1.90
1.88
2.10
2.13
8.14
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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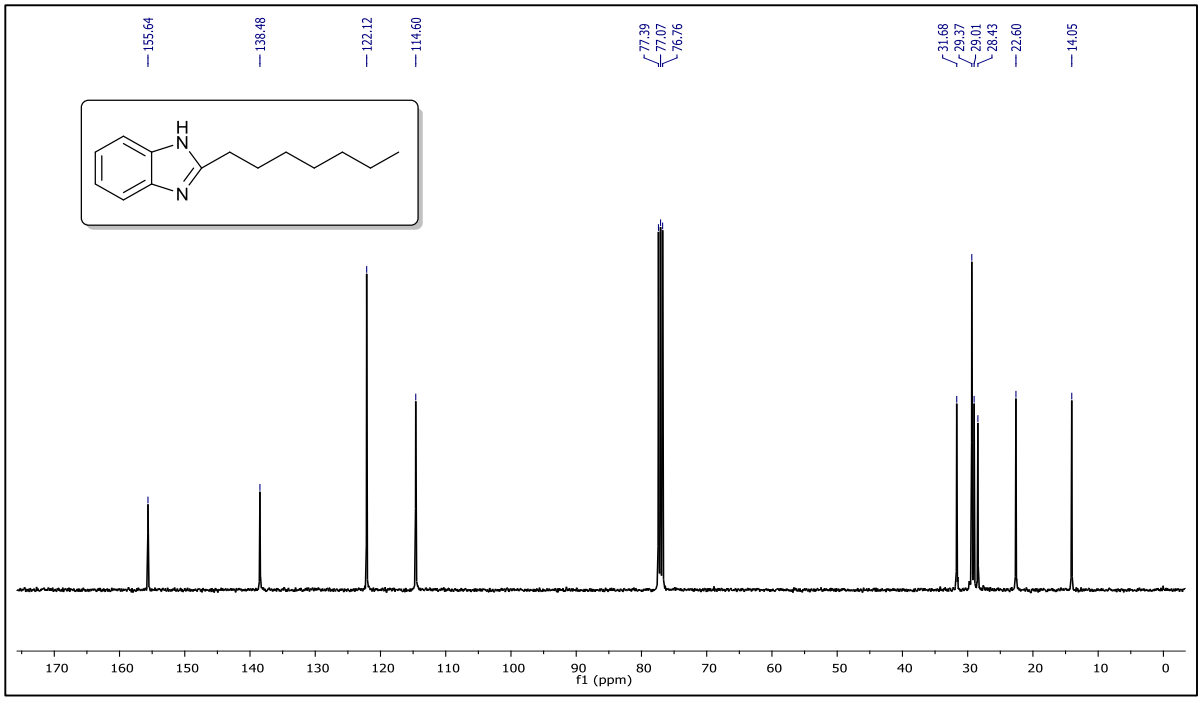
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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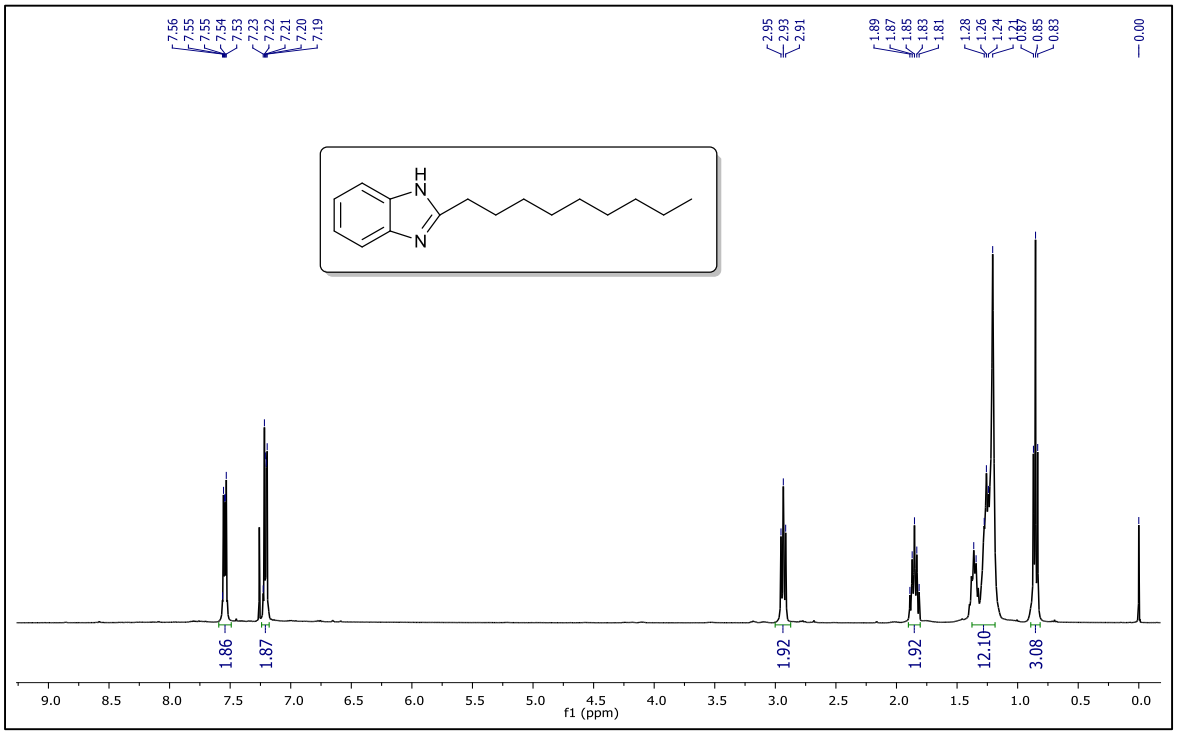
77.07
76.76
31.68
29.37
29.01
28.43
22.60
14.05
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.19
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2.91
1.89
1.87
1.85
1.83
1.81
1.28
1.26
1.24
1.21
0.87
0.85
0.83
0.00
H
N
N
1.86
1.87
1.92
1.92
12.10
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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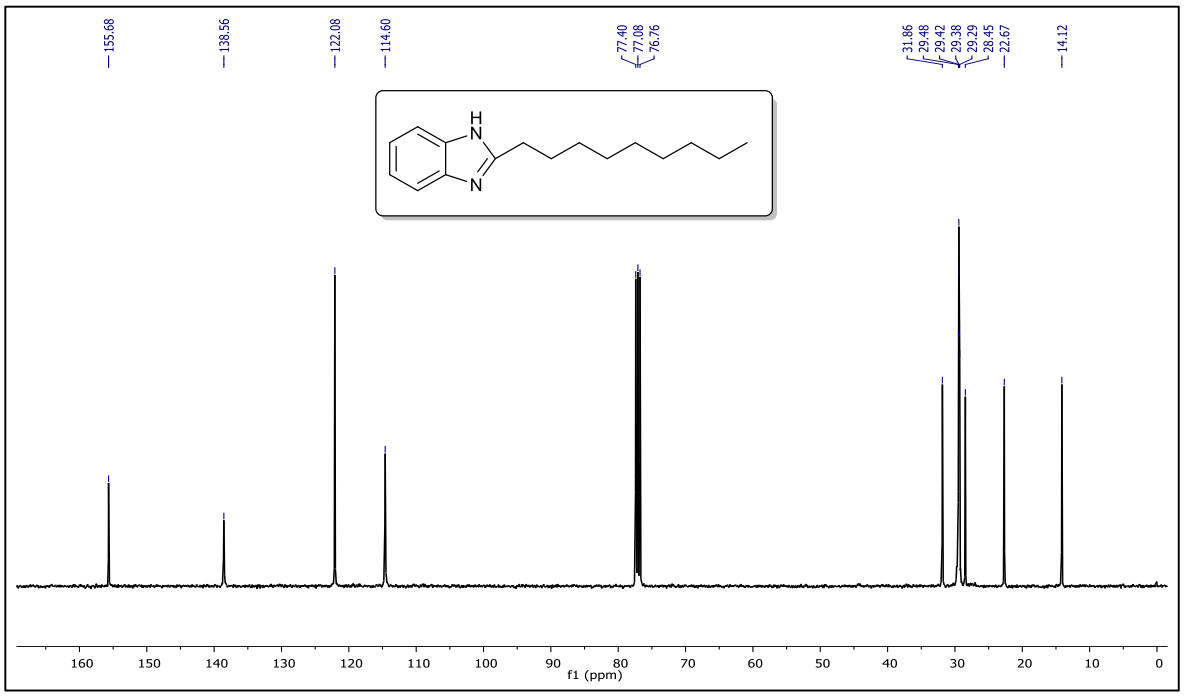
f1 (ppm)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77.08
76.76
31.86
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29.42
29.38
29.29
28.45
22.67
14.12
H
N
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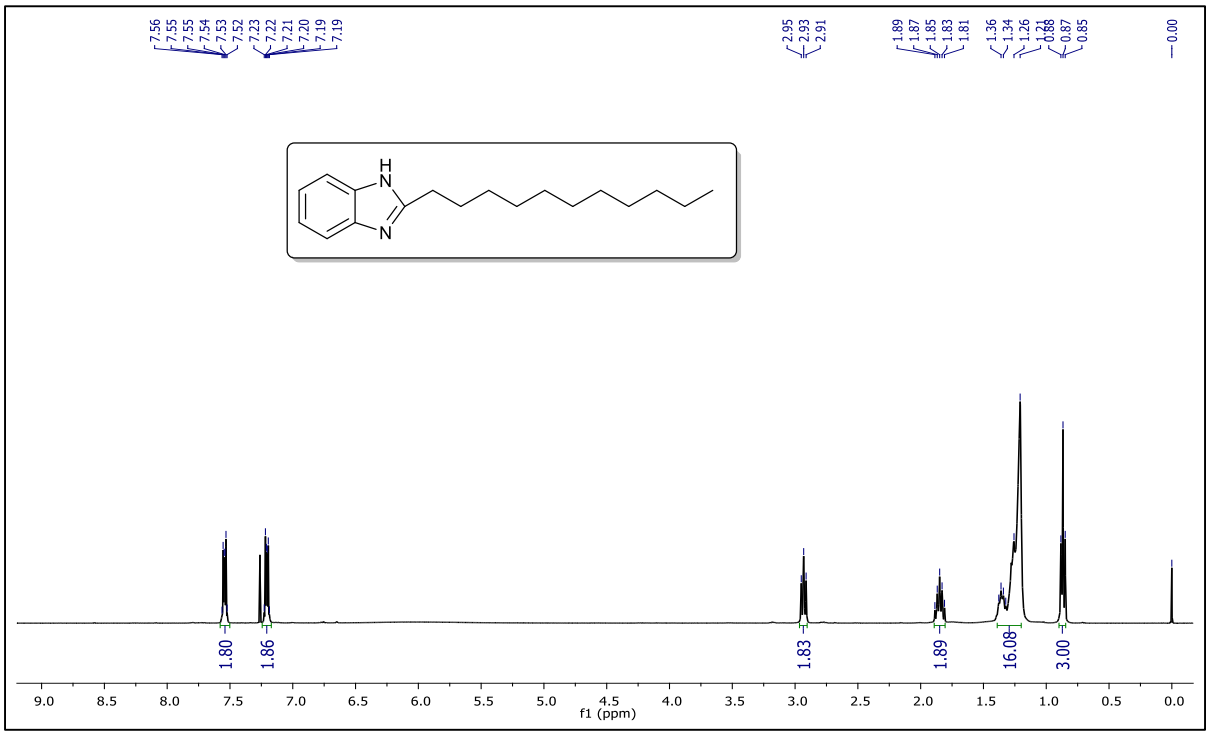
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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2.91
1.89
1.87
1.85
1.83
1.81
1.36
1.34
1.26
1.21
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0.87
0.85
0.00
H
N
N
1.80
1.86
1.83
1.89
16.08
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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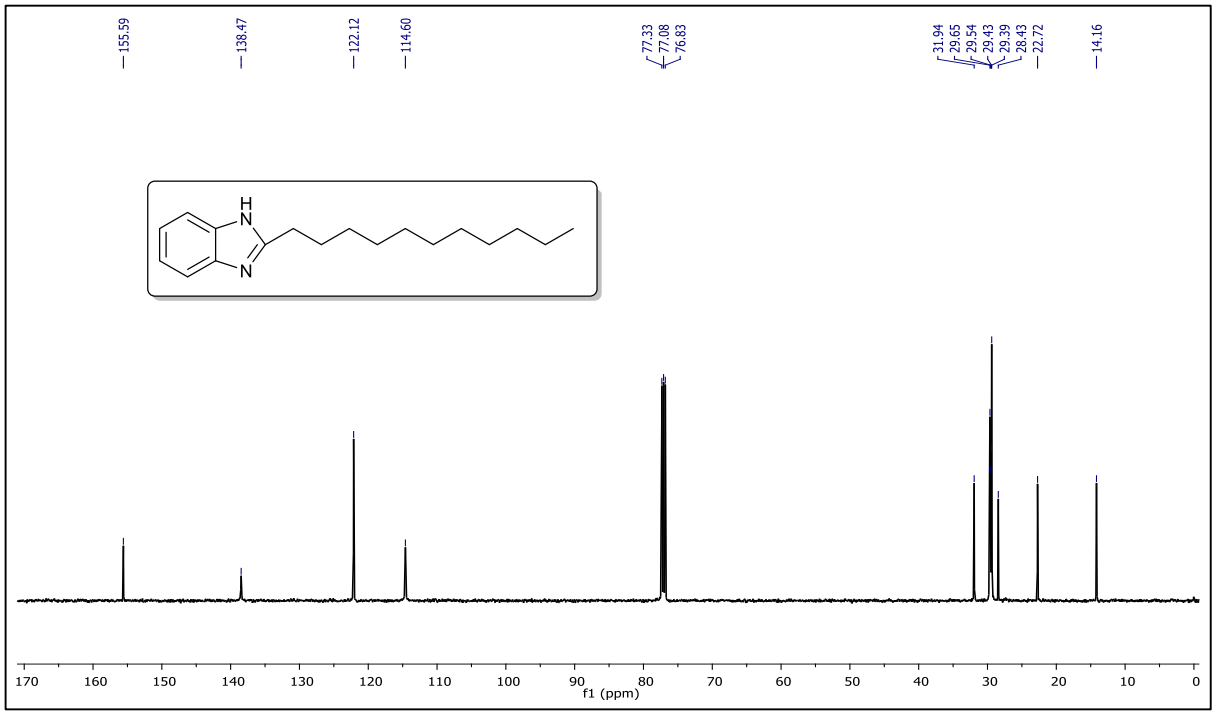
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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29.39
28.43
22.72
14.16
H
N
N
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90
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50
40
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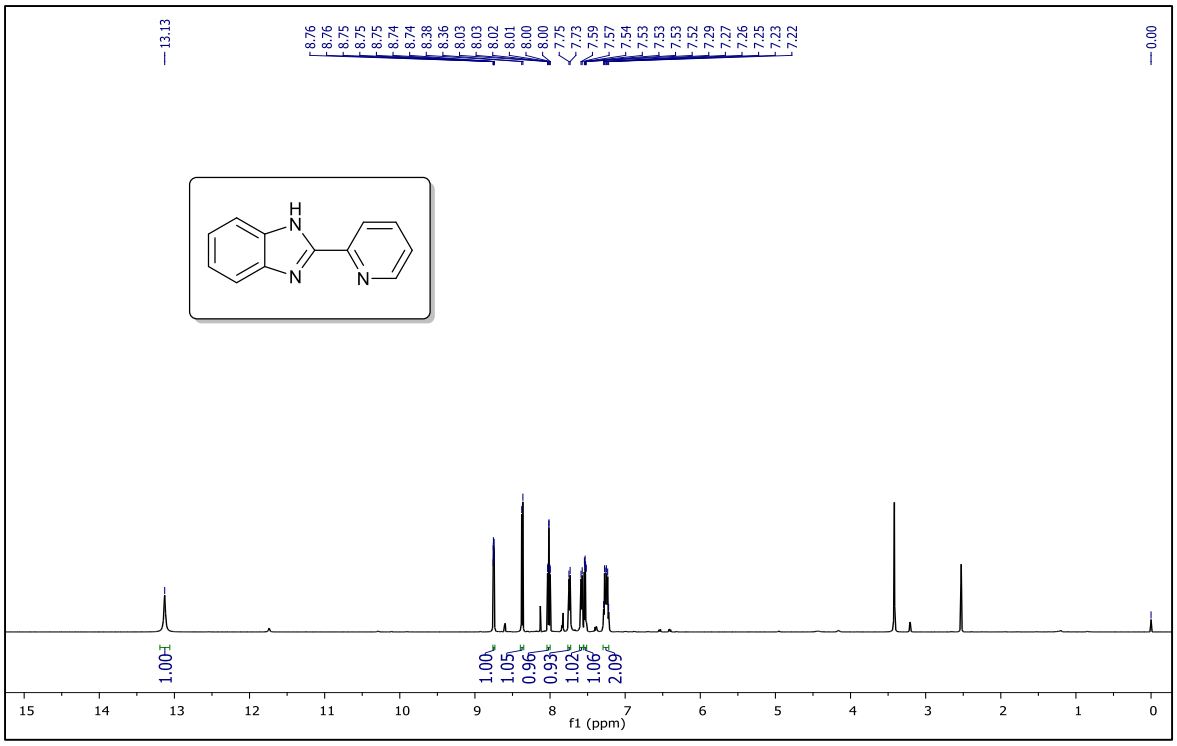
f1 (ppm)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8.76
8.75
8.75
8.75
8.74
8.74
8.38
8.36
8.03
8.03
8.02
8.01
8.00
8.00
7.75
7.73
7.59
7.57
7.54
7.53
7.53
7.53
7.52
7.29
7.27
7.26
7.25
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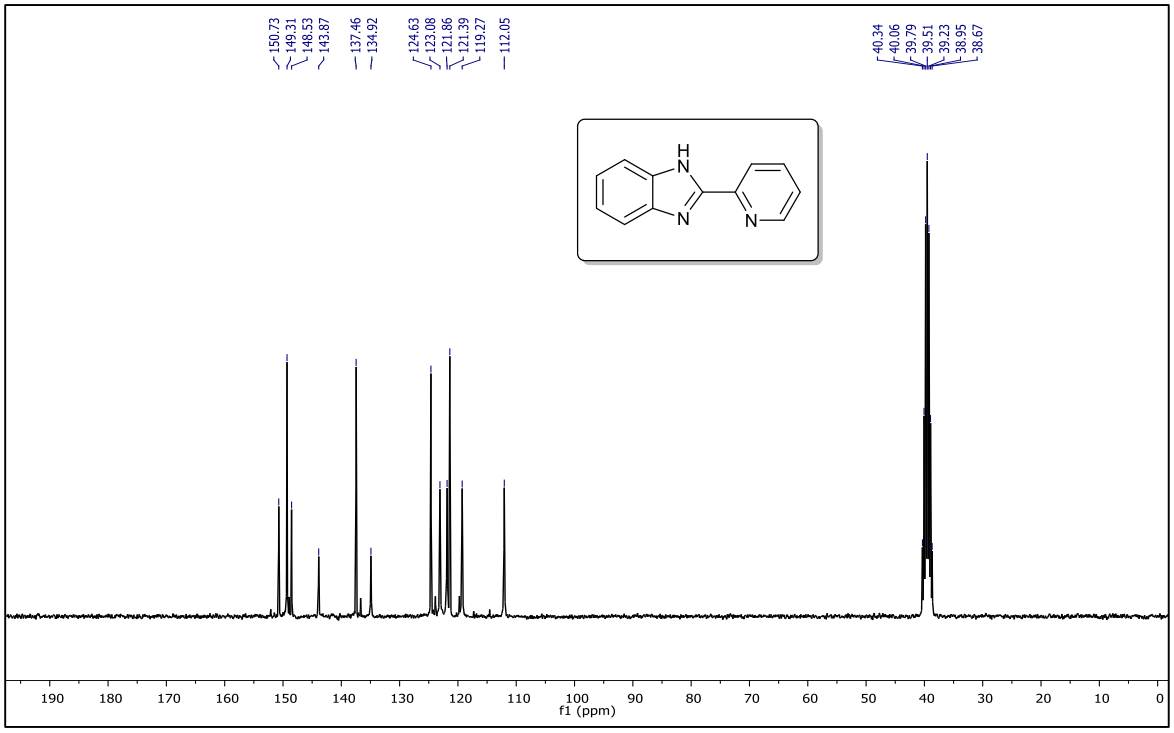
1.02
1.06
2.09
f1 (ppm)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123.08
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40.06
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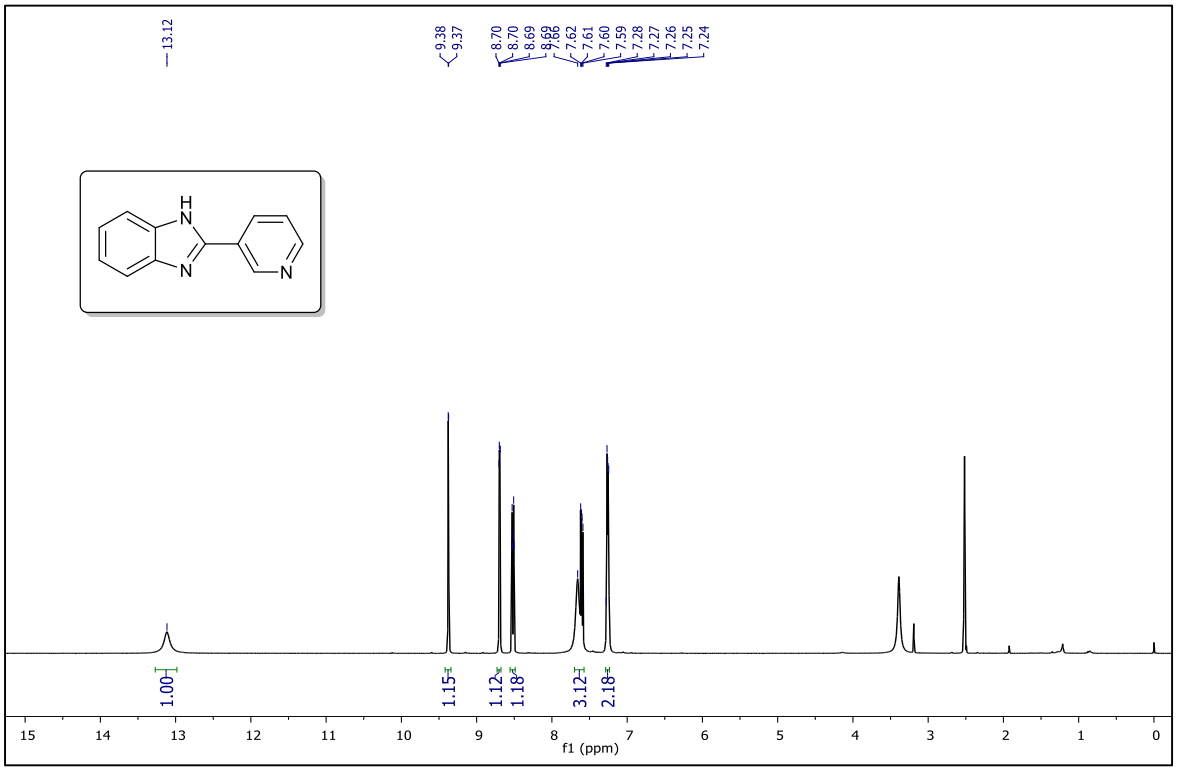
39.23
38.95
38.67
f1 (ppm)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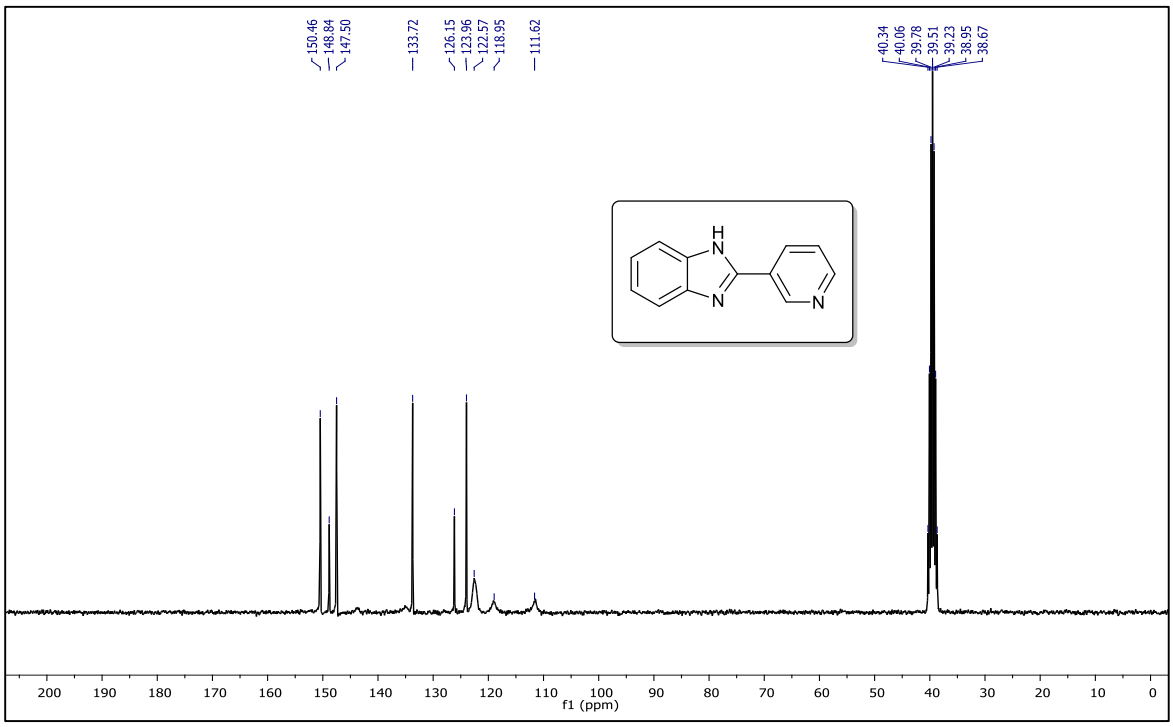
7.61
7.60
7.59
7.28
7.27
7.26
7.25
7.24
H
N
N
N
1.00
1.15
1.12
1.18
1.18
3.12
2.18
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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147.50
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126.15
123.96
122.57
118.95
111.62
40.34
40.06
39.78
39.51
39.23
38.95
38.67
H
N
N
N
200
190
180
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150
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130
120
110
100
90
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70
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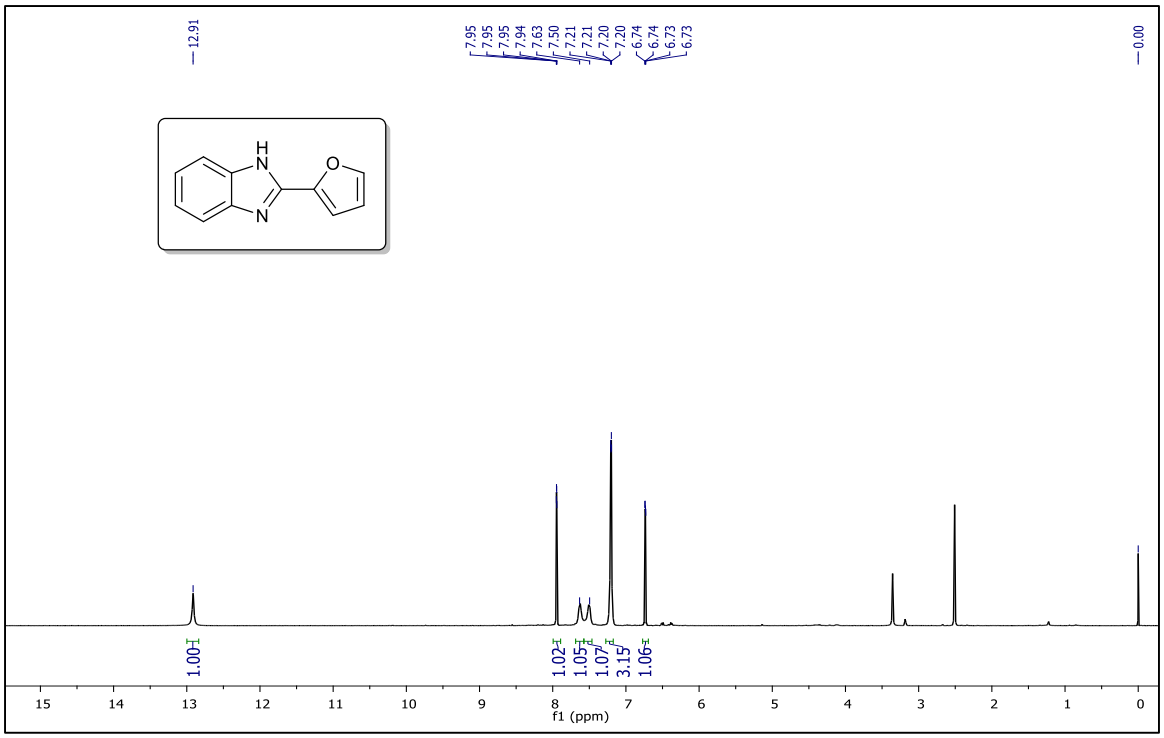
50
40
30
20
10
0
f1 (ppm)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7.94
7.63
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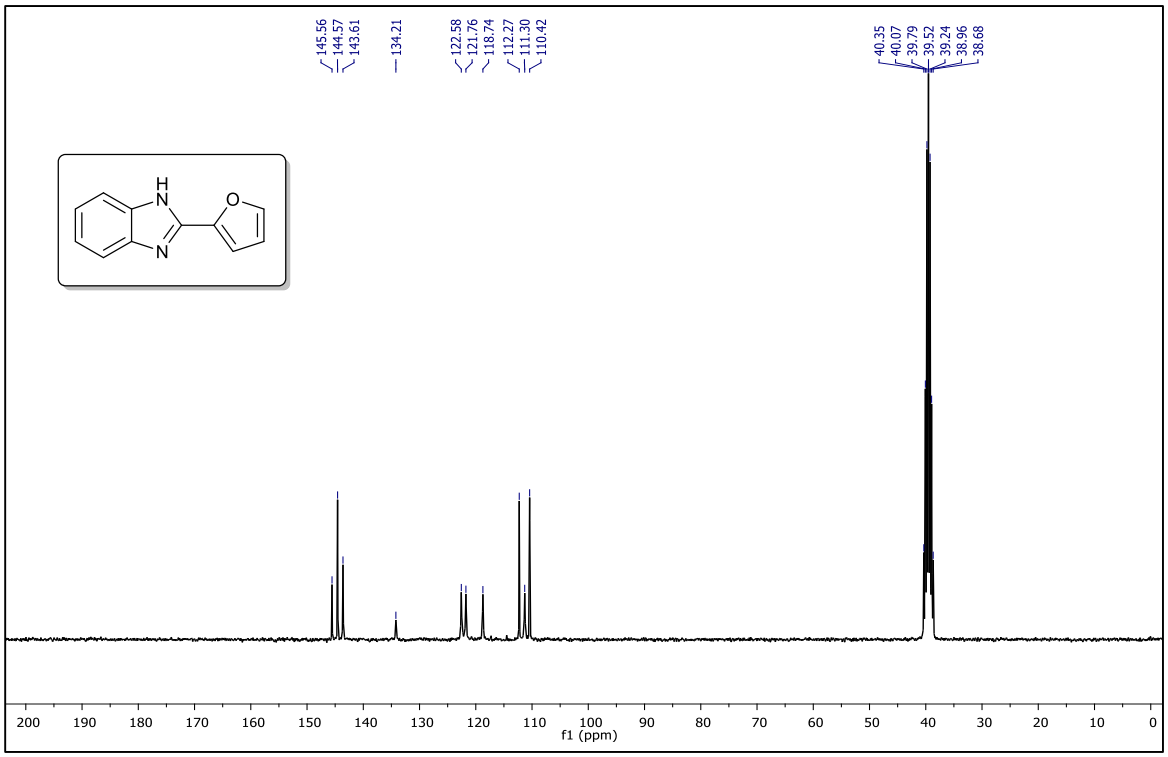
7.21
7.20
7.20
6.74
6.74
6.73
6.73
0.00
H
N
O
N
1.00
1.02
1.05
1.07
3.15
1.06
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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121.76
118.74
112.27
111.30
110.42
40.35
40.07
39.79
39.52
39.24
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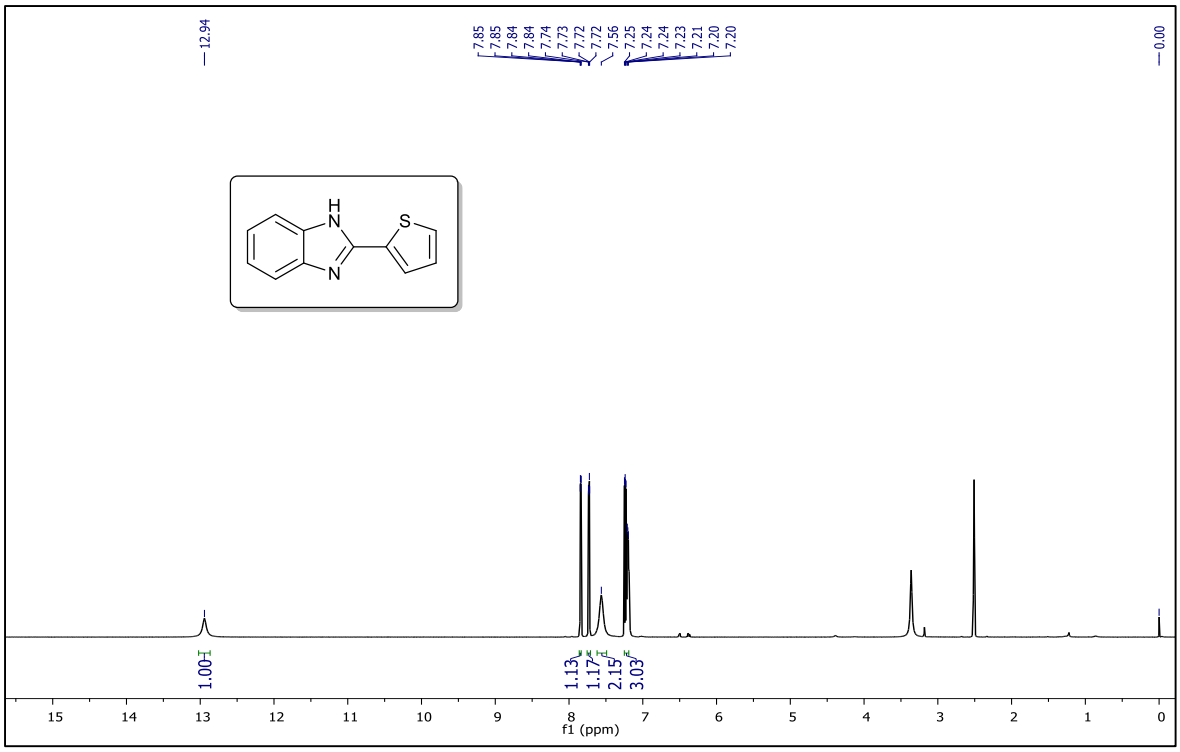
38.68
H
N
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.74
7.73
7.72
7.72
7.56
7.25
7.24
7.24
7.23
7.21
7.20
7.20
0.00
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N
N
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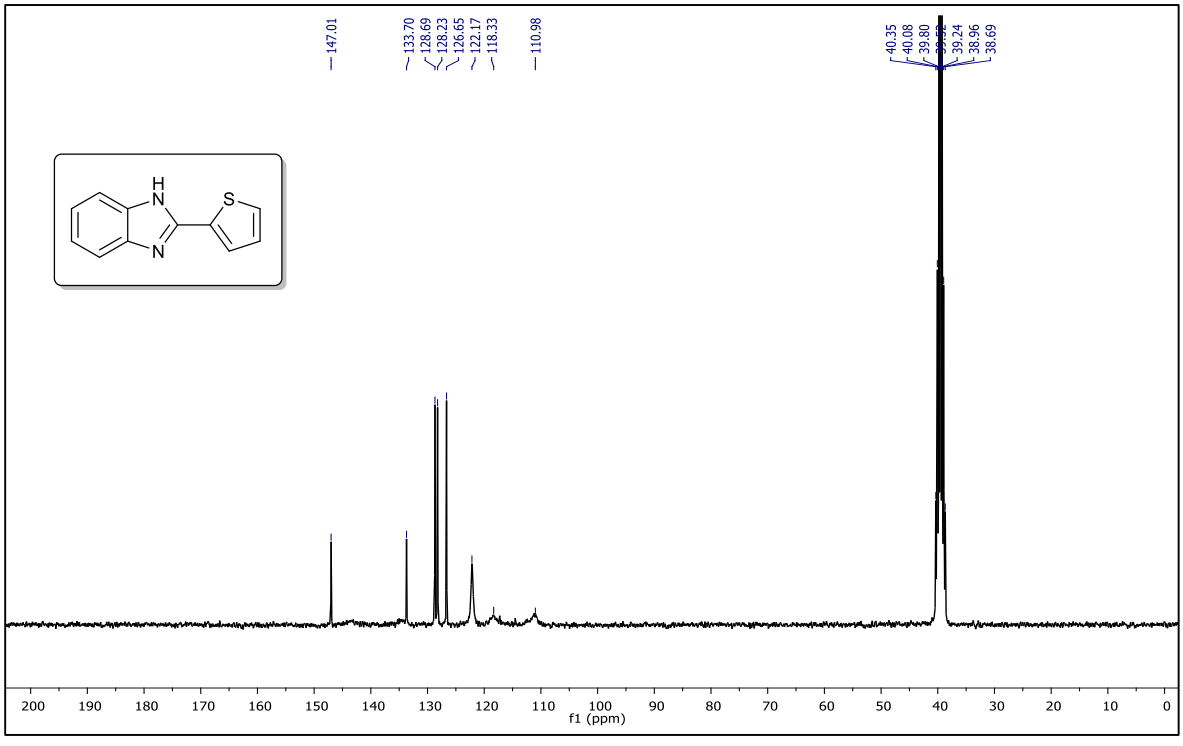
1.00
1.13
1.17
2.15
3.03
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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133.70
128.69
128.23
126.65
122.17
118.33
110.98
40.35
40.08
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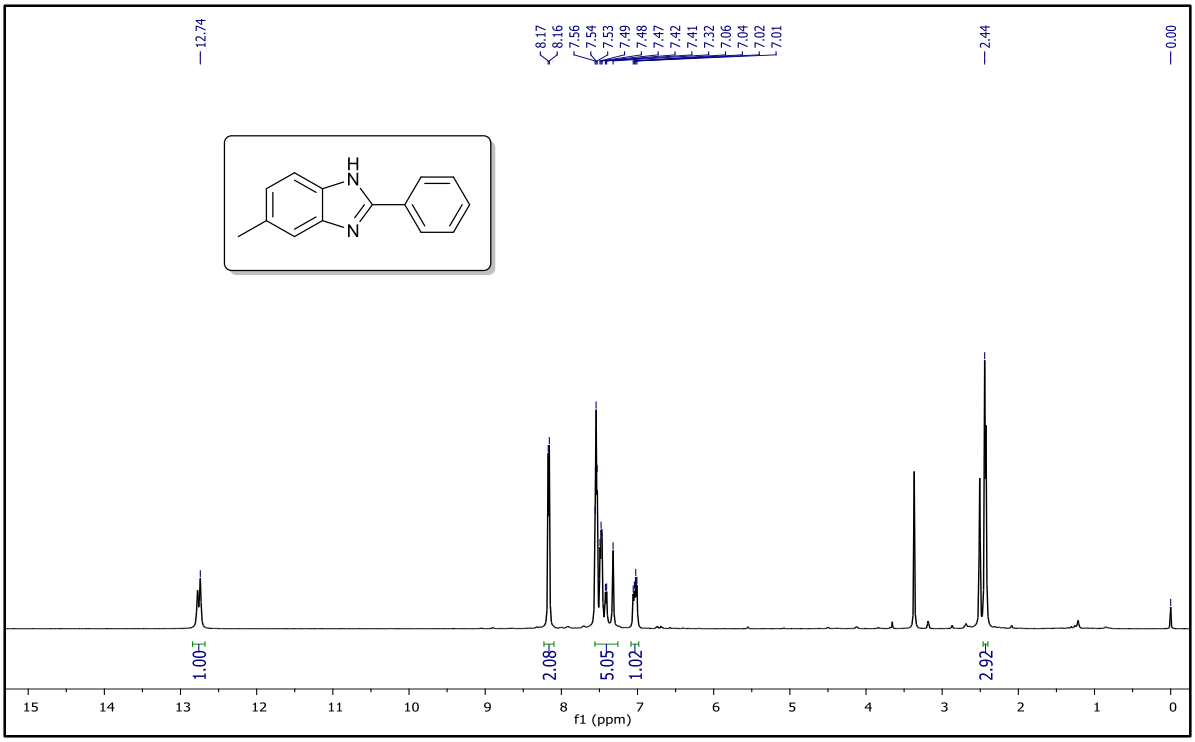
39.24
38.96
38.69
H
N
N
S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.16
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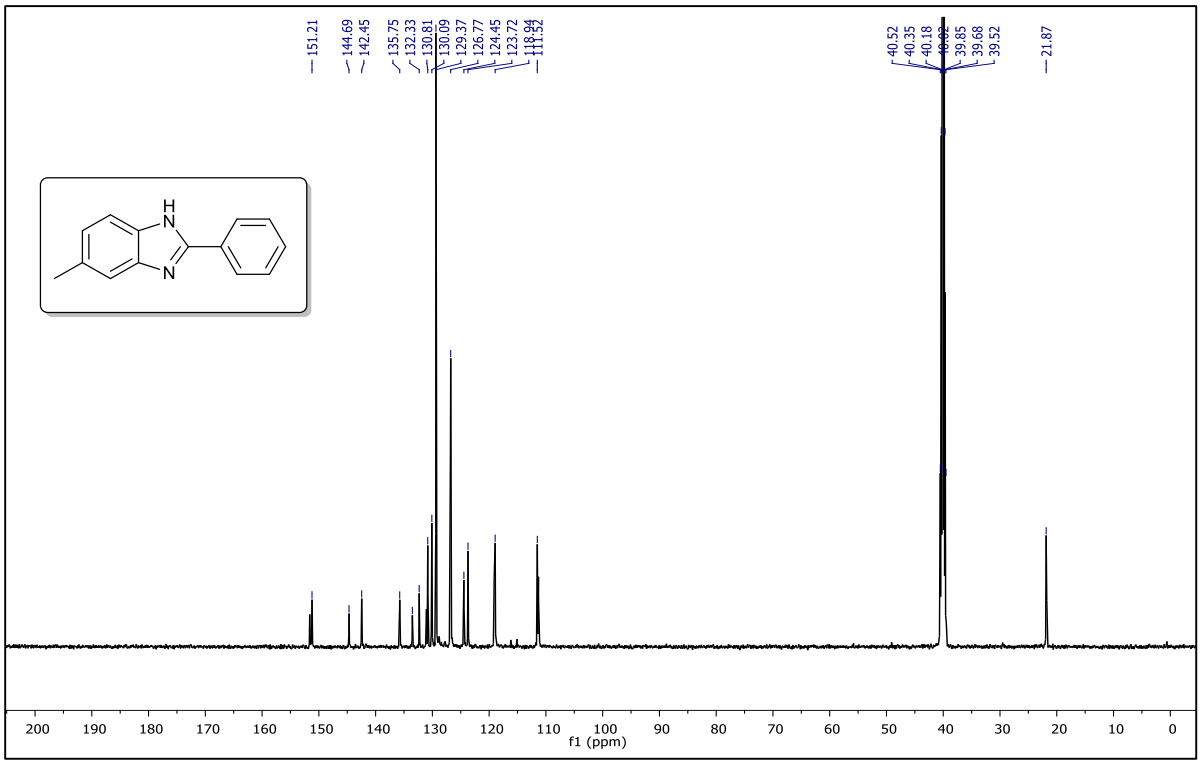
7.54
7.53
7.49
7.48
7.47
7.42
7.41
7.32
7.06
7.04
7.02
7.01
2.44
0.00
1.00
2.08
5.05
1.02
2.92
f1 (ppm)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132.33
130.81
130.09
129.37
126.77
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123.72
40.52
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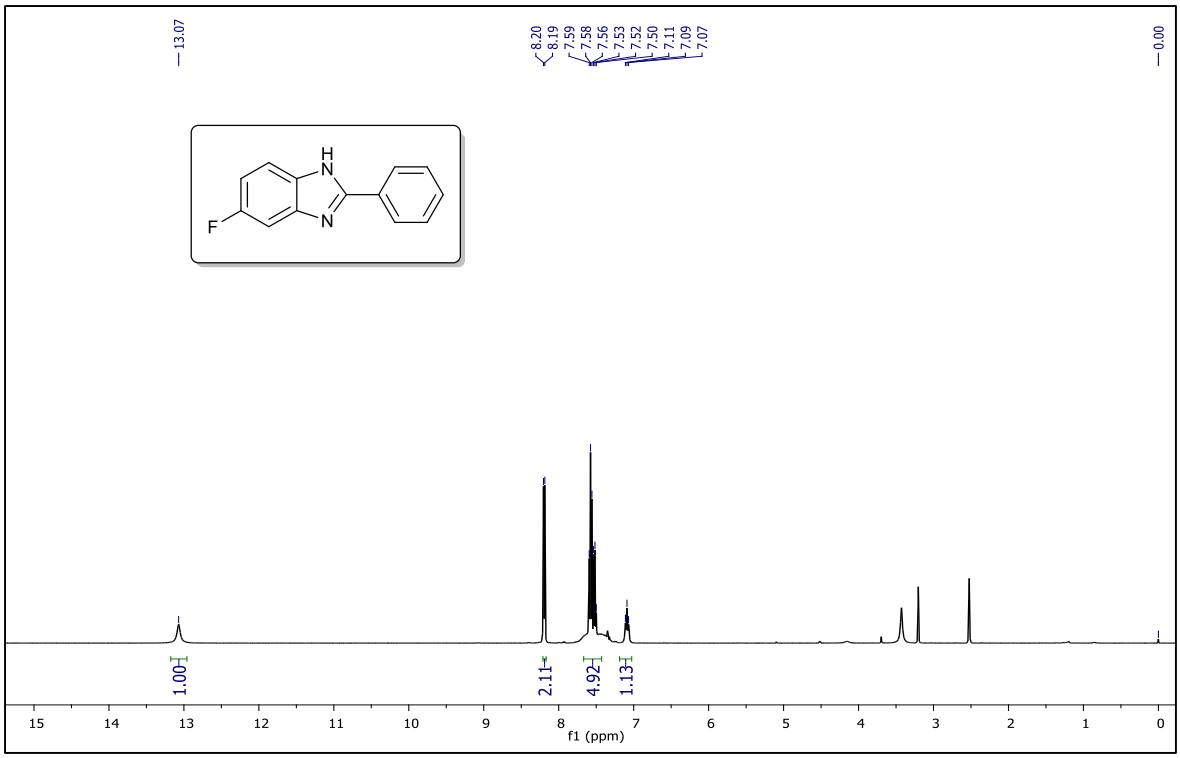
39.85
39.68
39.52
21.87
f1 (ppm)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8.20
8.19
7.59
7.58
7.56
7.53
7.52
7.50
7.11
7.09
7.07
0.00
H
N
N
F
1.00
2.11
4.92
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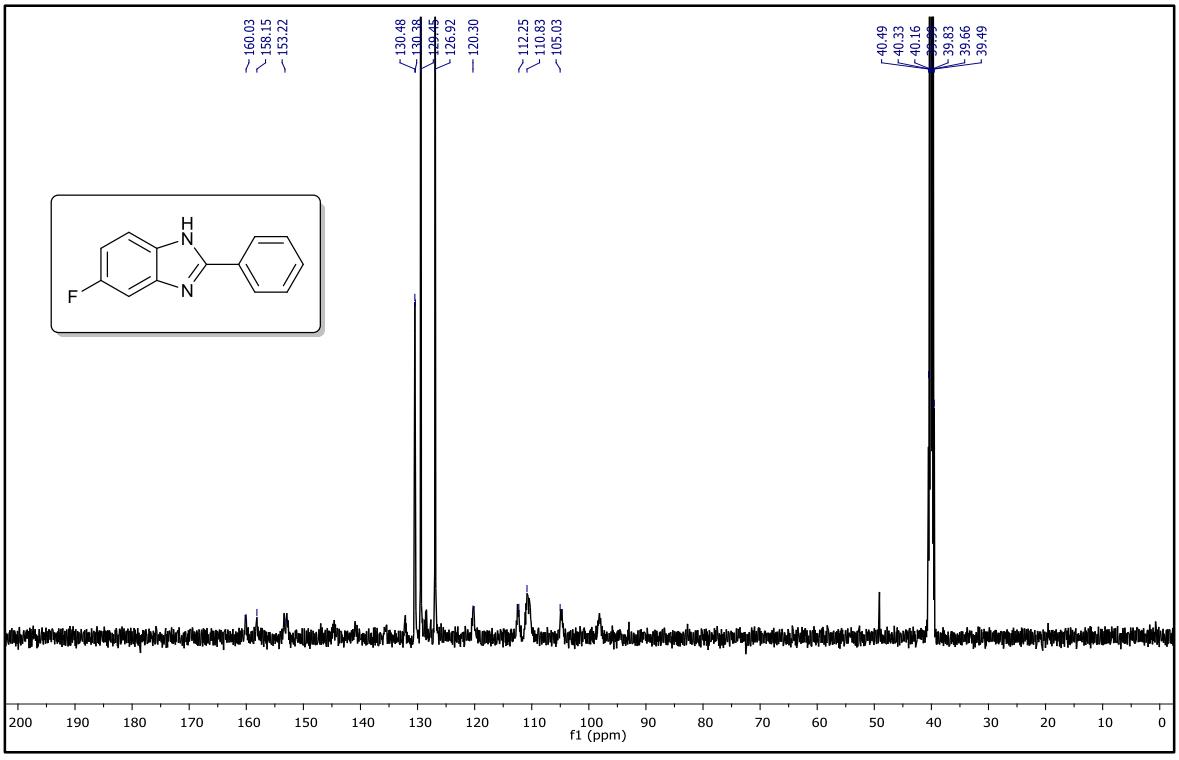
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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158.15
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130.38
129.45
126.92
120.30
112.25
110.83
105.03
40.49
40.33
40.16
39.83
39.66
39.49
H
N
N
F
200
190
180
170
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150
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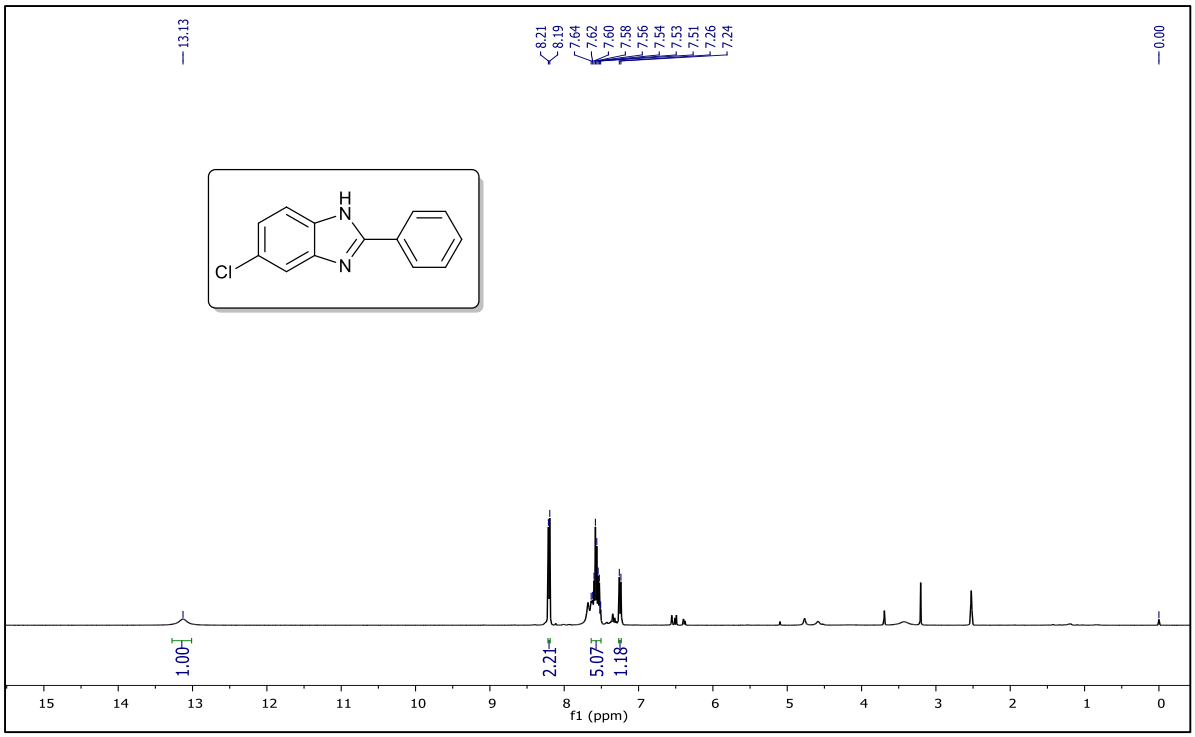
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.56
7.54
7.53
7.51
7.26
7.24
0.00
Cl
H
N
N
1.00
2.21
5.07
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15
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13
12
11
10
9
8
7
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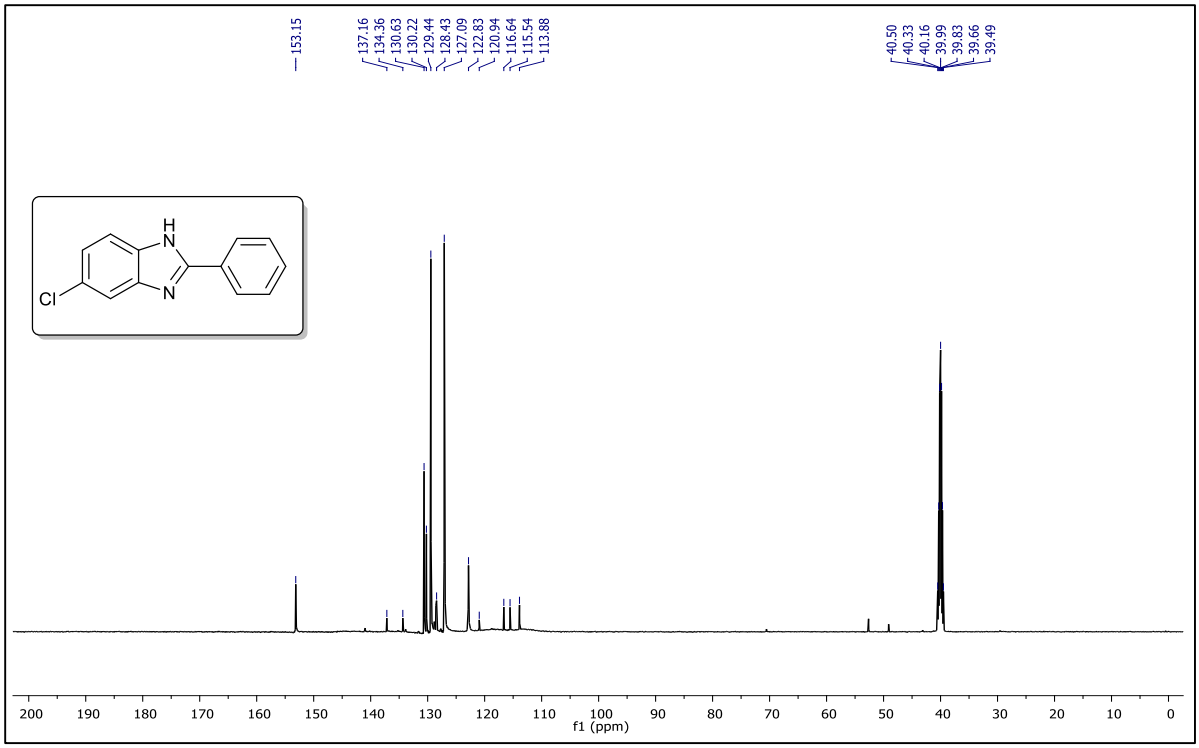
5
4
3
2
1
0
f1 (ppm)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122.83
120.94
116.64
115.54
113.88
40.50
40.33
40.16
39.99
39.83
39.66
39.49
Cl
H
N
N
200
190
180
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150
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130
120
110
100
90
80
70
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50
40
30
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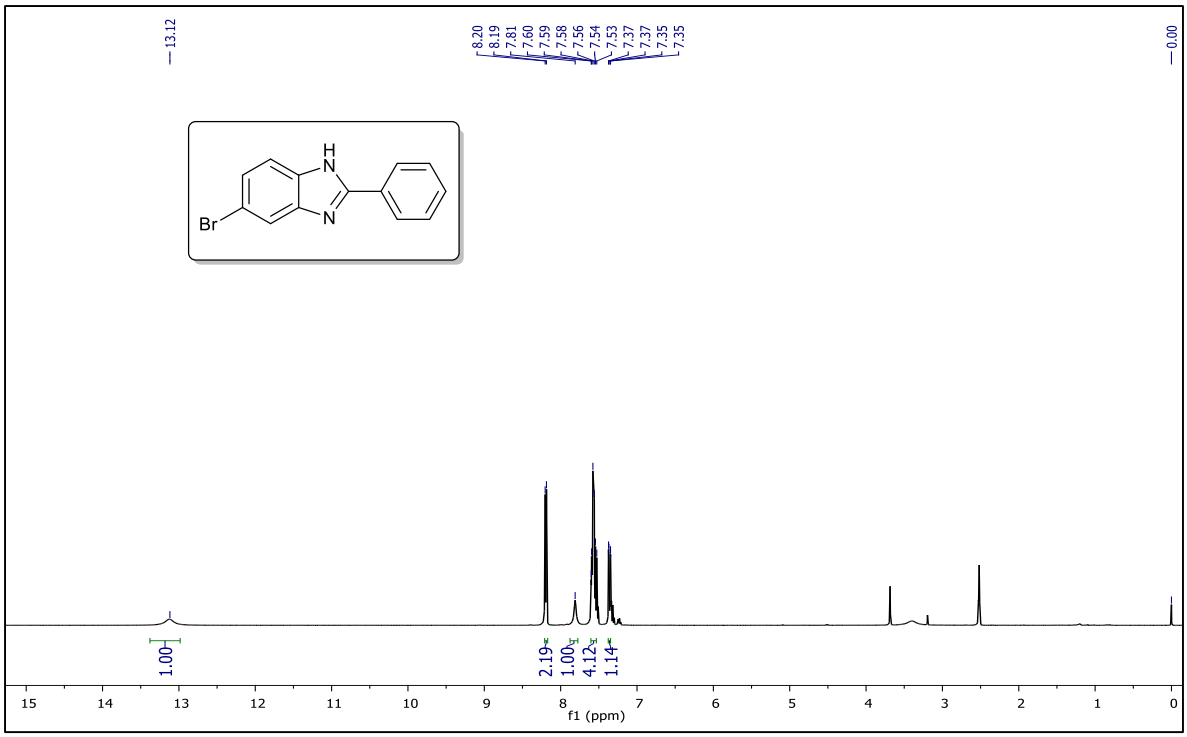
10
0
f1 (ppm)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7.54
7.53
7.37
7.37
7.35
7.35
0.00
H
N
N
Br
1.00
2.19
1.00
4.12
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15
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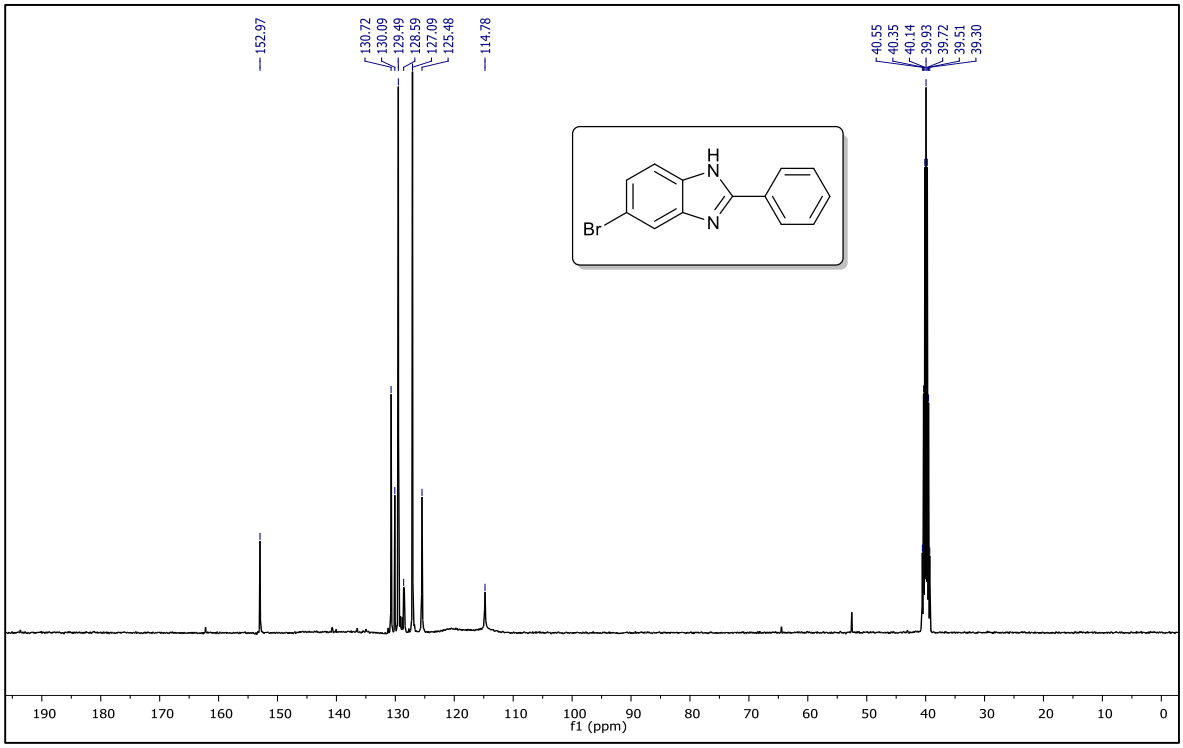
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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127.09
125.48
114.78
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40.35
40.14
39.93
39.72
39.51
39.30
H
N
N
Br
190
180
170
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150
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130
120
110
100
90
80
70
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50
40
30
20
10
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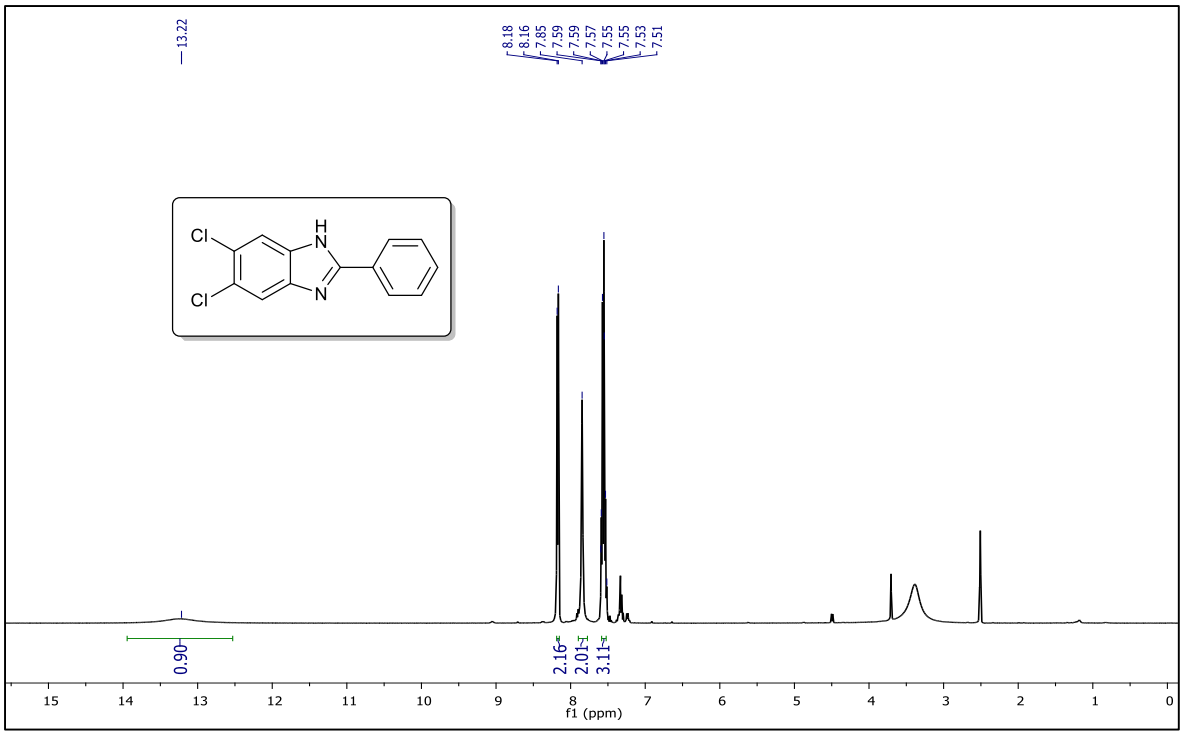
f1 (ppm)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7.59
7.57
7.55
7.55
7.53
7.51
Cl
Cl
H
N
N
0.90
2.16
2.01
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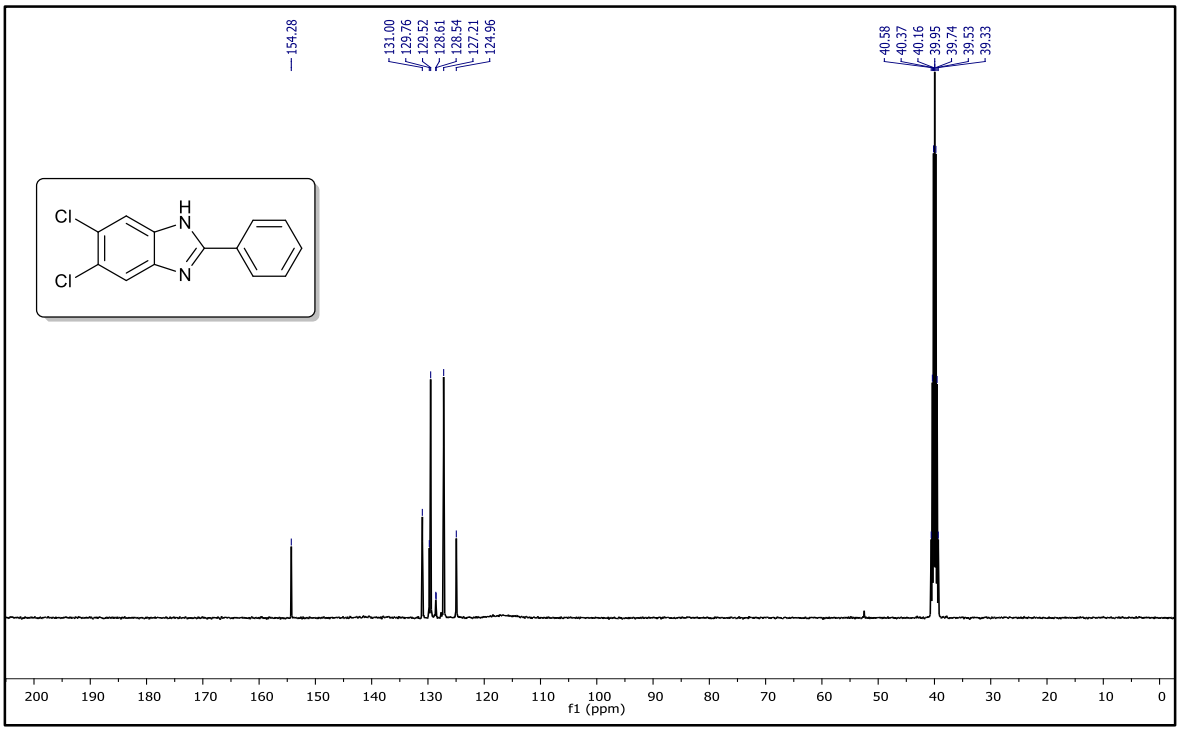
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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39.74
39.53
39.33
Cl
Cl
H
N
N
200
190
180
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150
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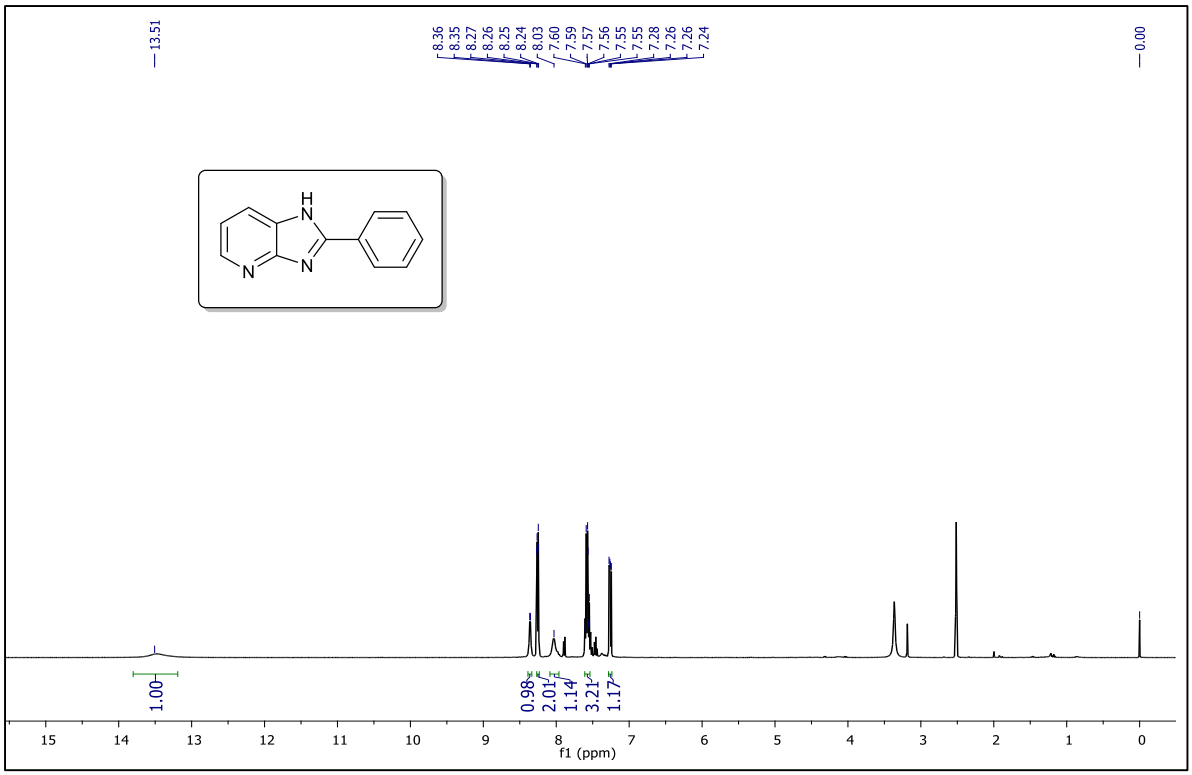
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.03
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7.59
7.57
7.56
7.55
7.55
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7.26
7.24
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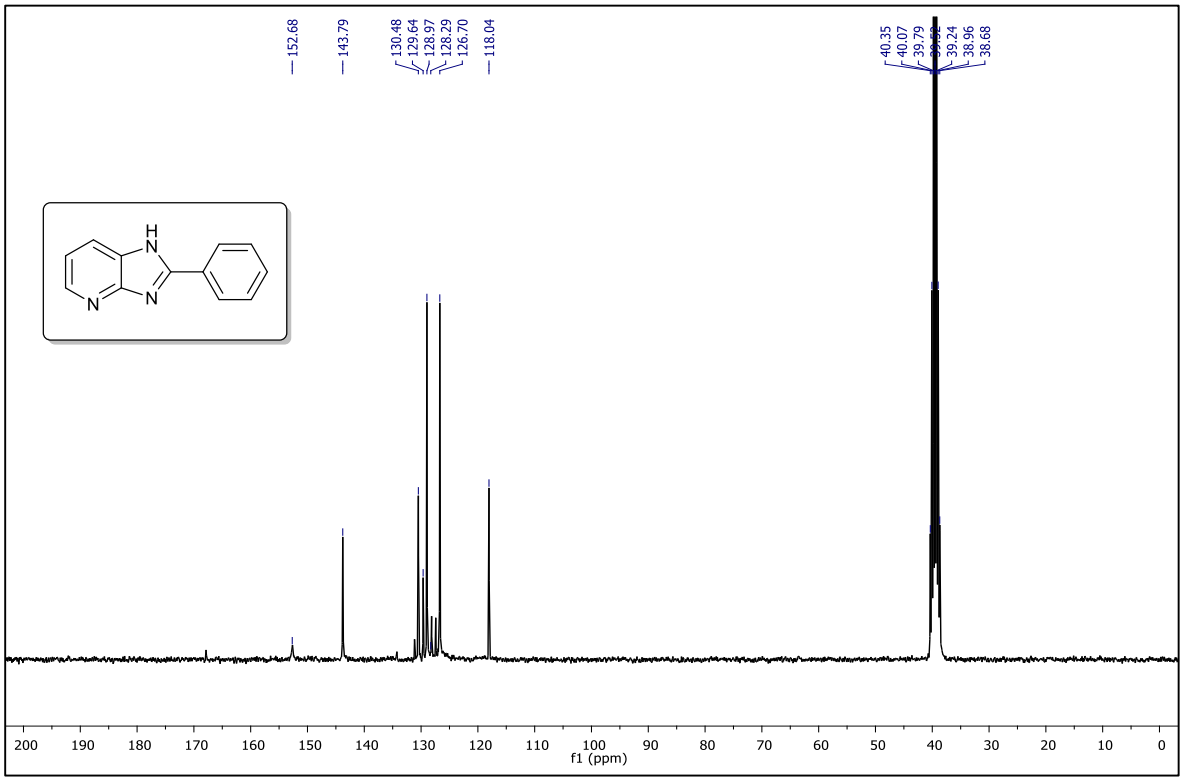
1.14
3.21
1.17
f1 (ppm)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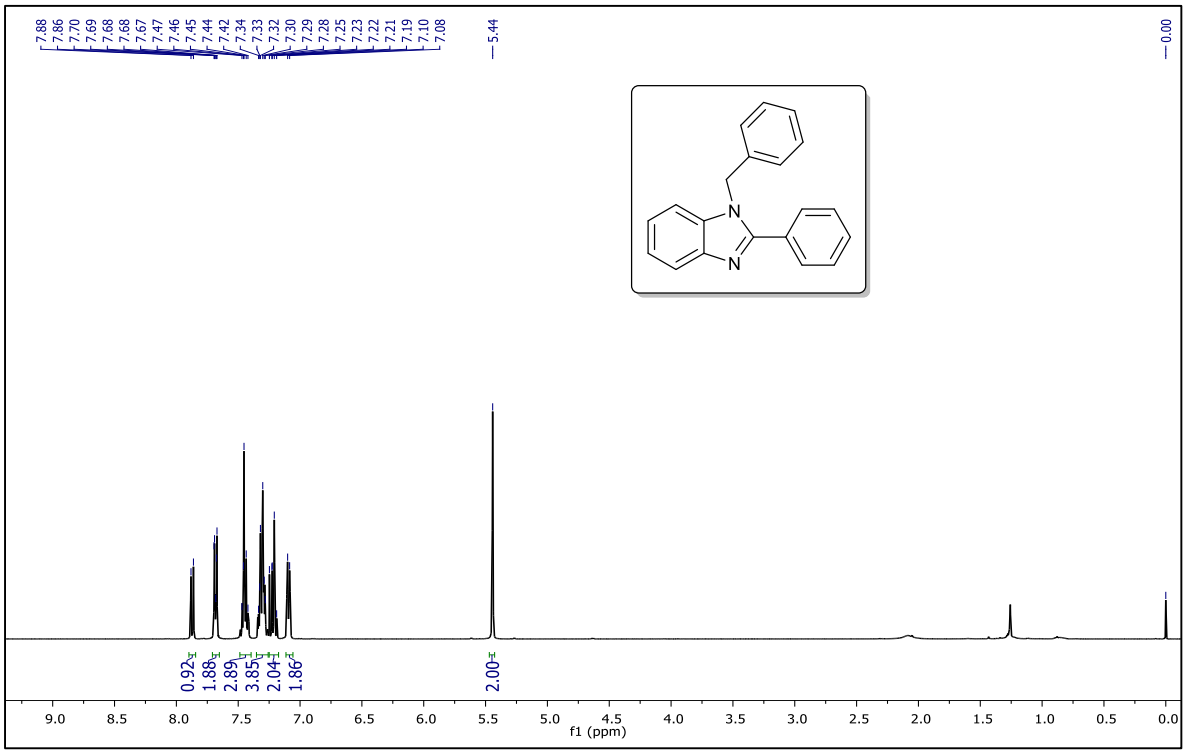
40.07
39.79
39.52
39.24
38.96
38.68
f1 (ppm)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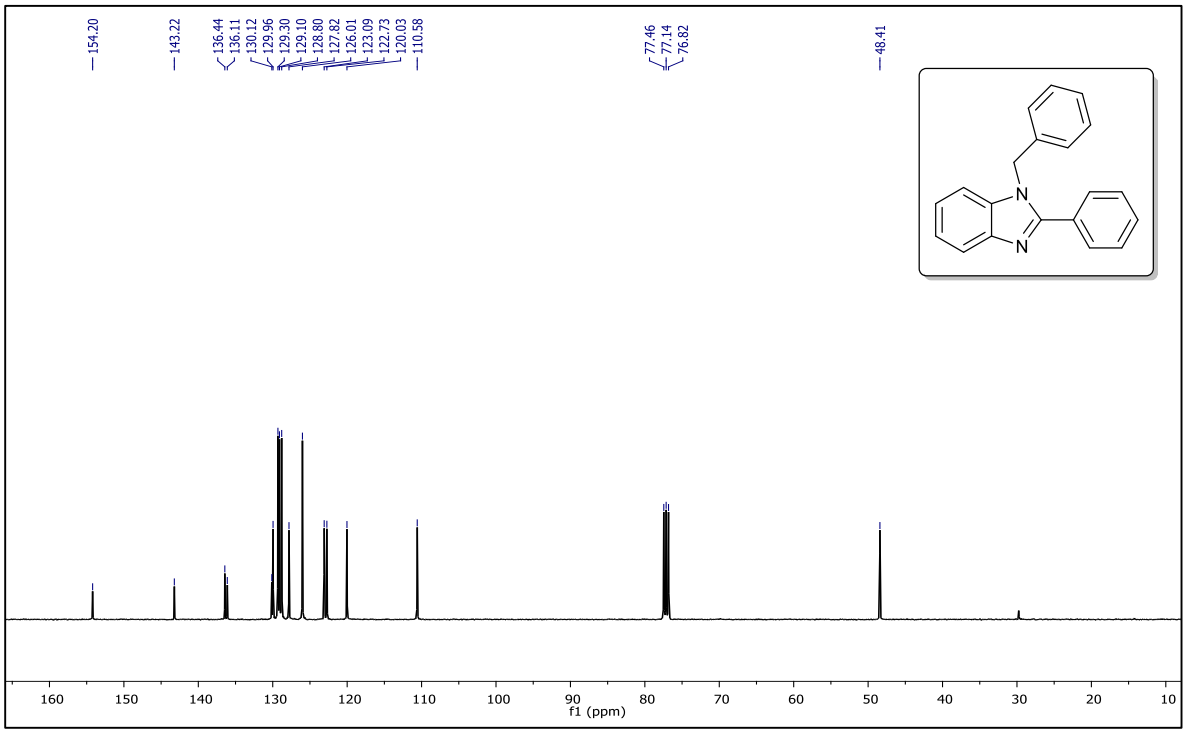
7.33
7.32
7.30
7.29
7.28
7.25
7.23
7.22
7.21
7.19
7.10
7.08
5.44
0.00
N
N
0.92
1.88
2.89
3.85
2.04
1.86
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.10
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127.82
126.01
123.09
122.73
120.03
110.58
77.46
77.14
76.82
48.41
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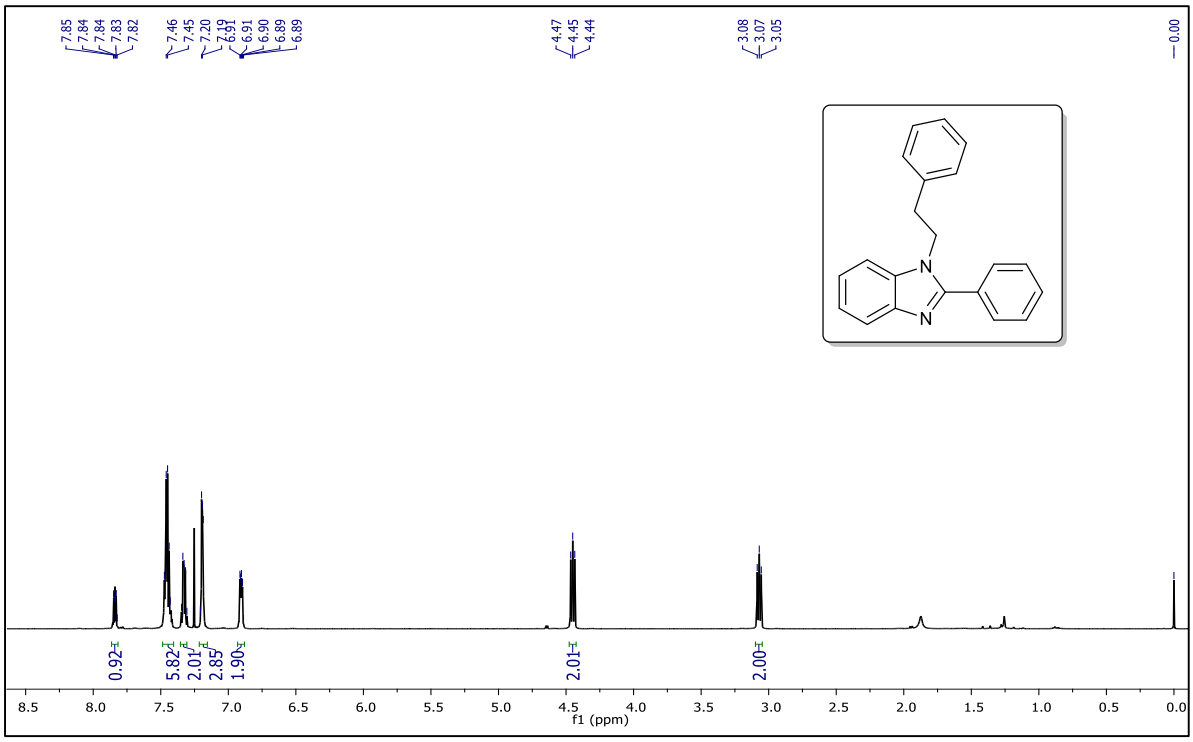
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.20
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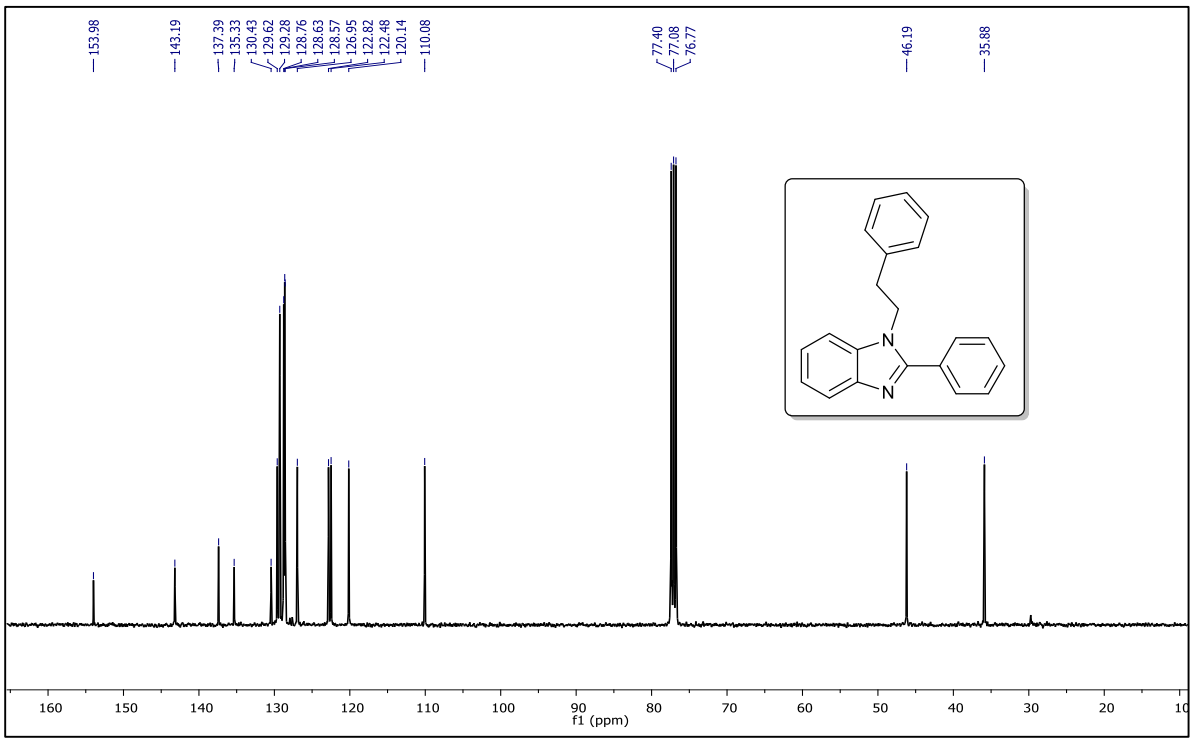
6.91
6.90
6.89
6.89
4.47
4.45
4.44
3.08
3.07
3.05
0.00
0.92
5.82
2.01
2.85
1.90
2.01
2.00
f1 (ppm)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128.76
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128.57
126.95
122.82
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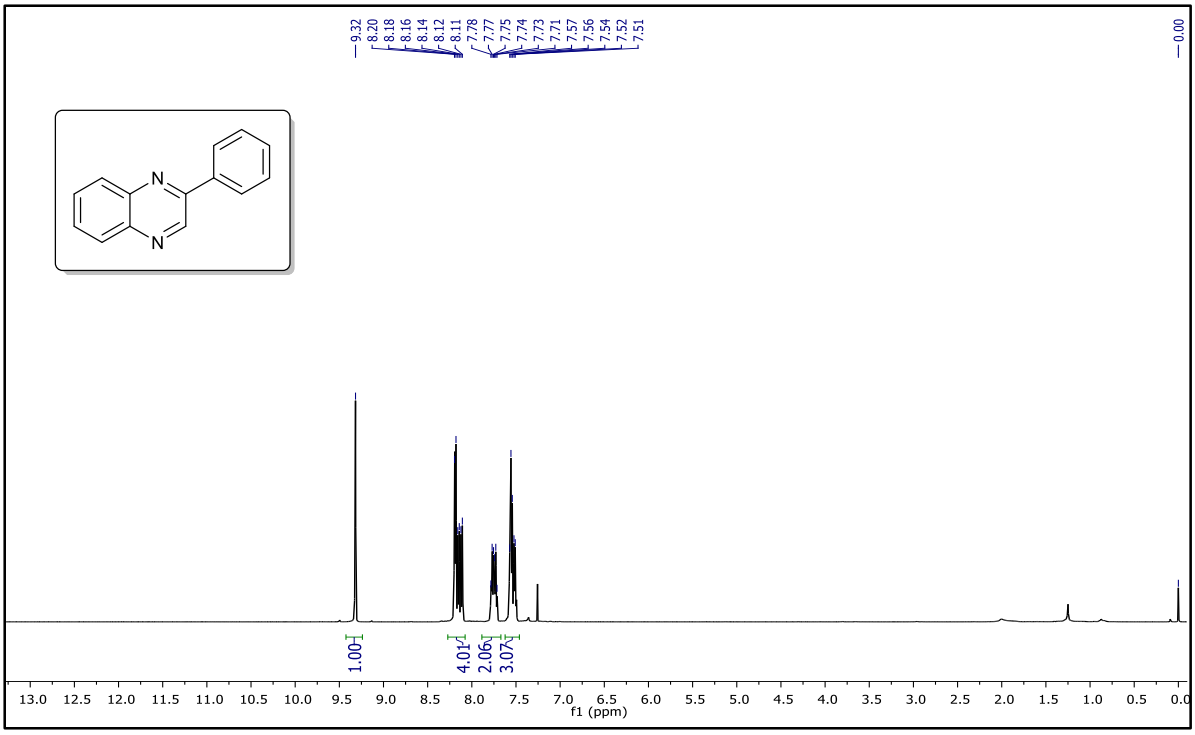
120.14
110.08
77.40
77.08
76.77
46.19
35.88
f1 (ppm)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8.11
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7.74
7.73
7.71
7.57
7.56
7.54
7.52
7.51
0.00
1.00
4.01
2.06
3.07
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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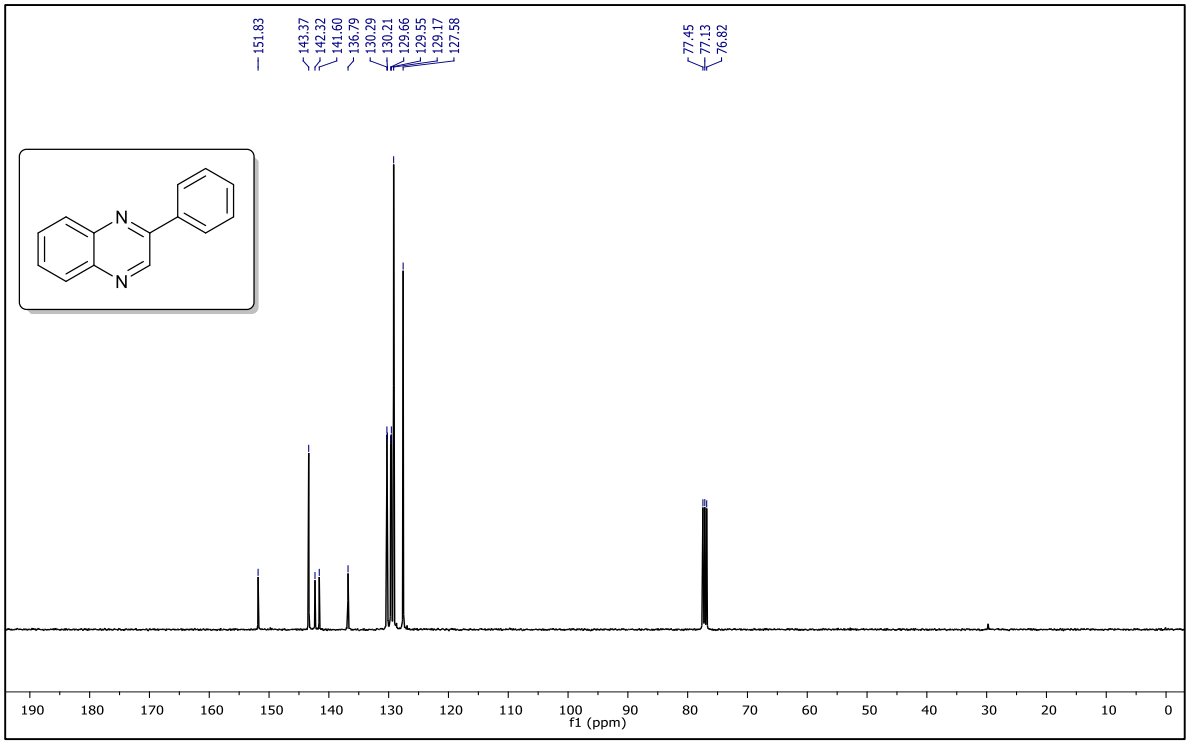
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129.66
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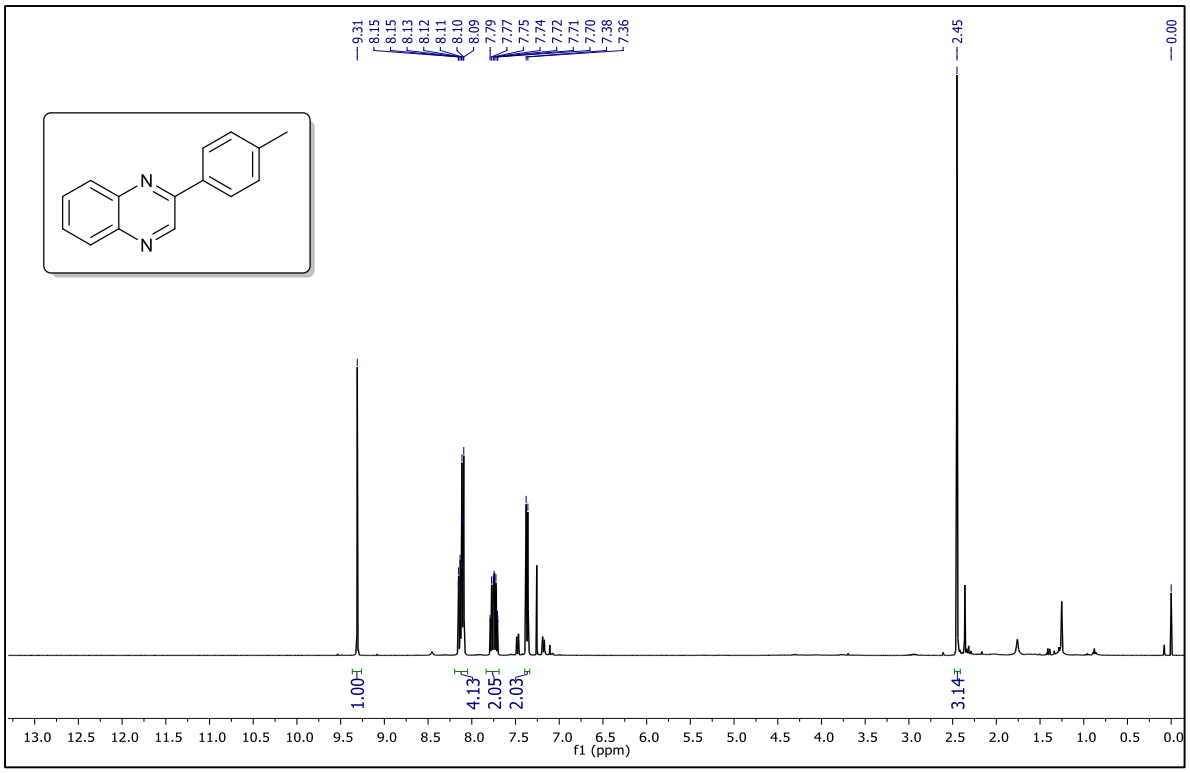
127.58
77.45
77.13
76.82
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.77
7.75
7.74
7.72
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7.36
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0.00
1.00
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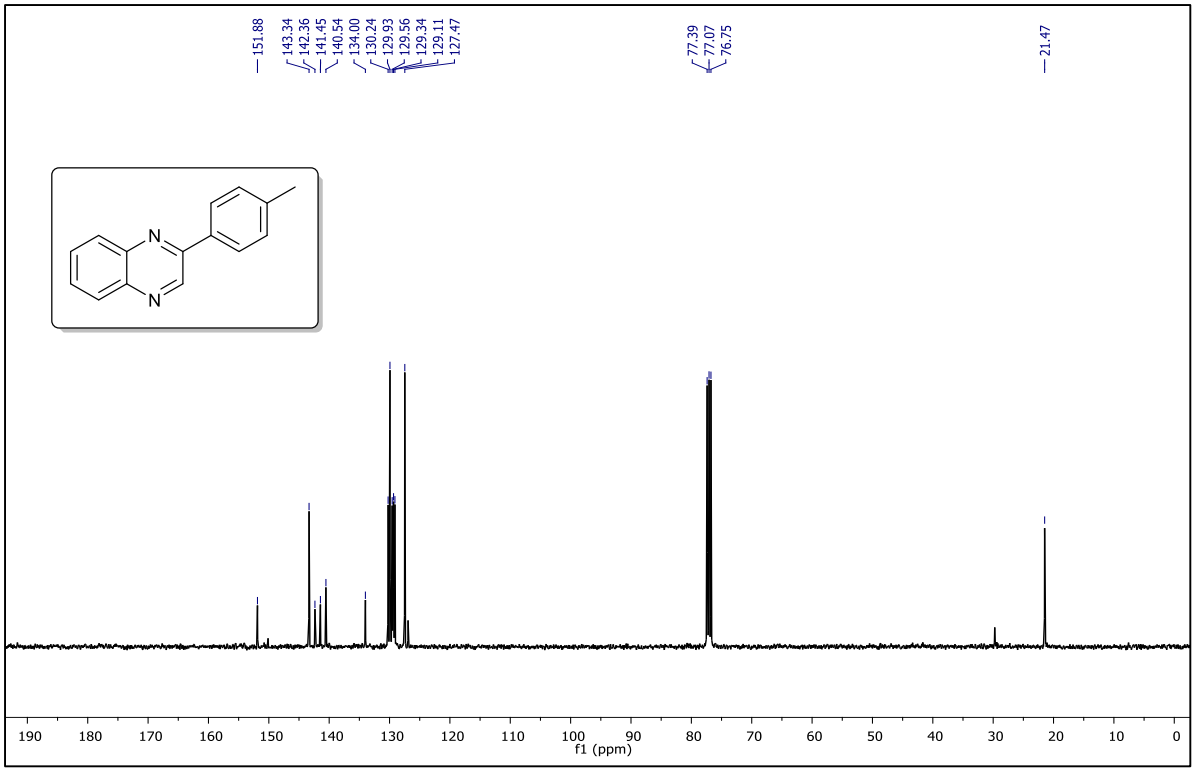
2.05
2.03
3.14
f1 (ppm)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129.11
127.47
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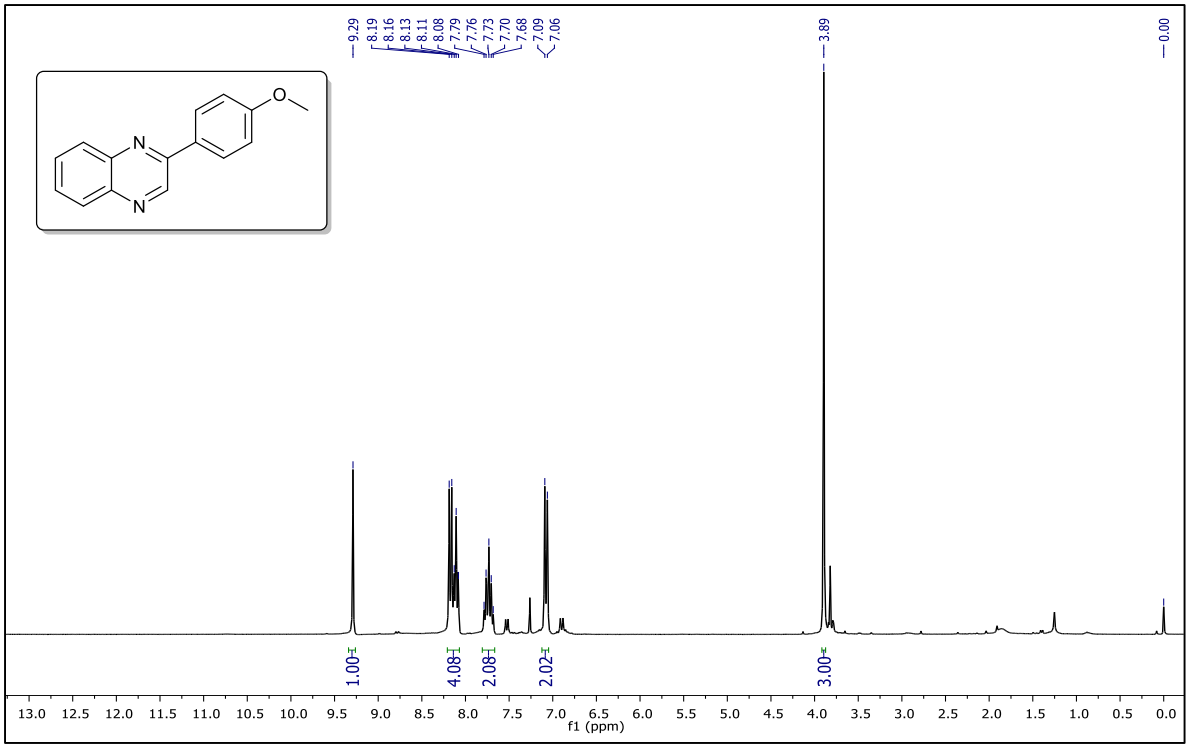
77.07
76.75
21.47
f1 (ppm)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8.08
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7.76
7.73
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7.68
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7.06
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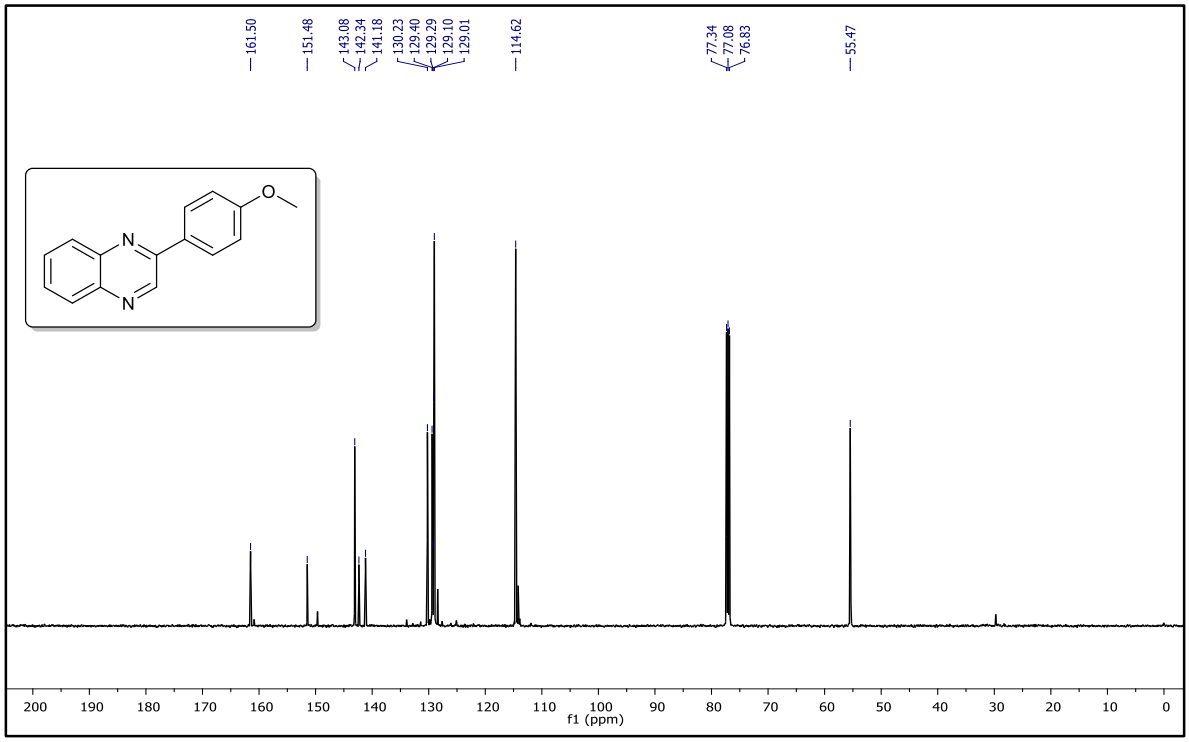
1.00
4.08
2.08
2.02
3.00
f1 (ppm)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130.23
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129.29
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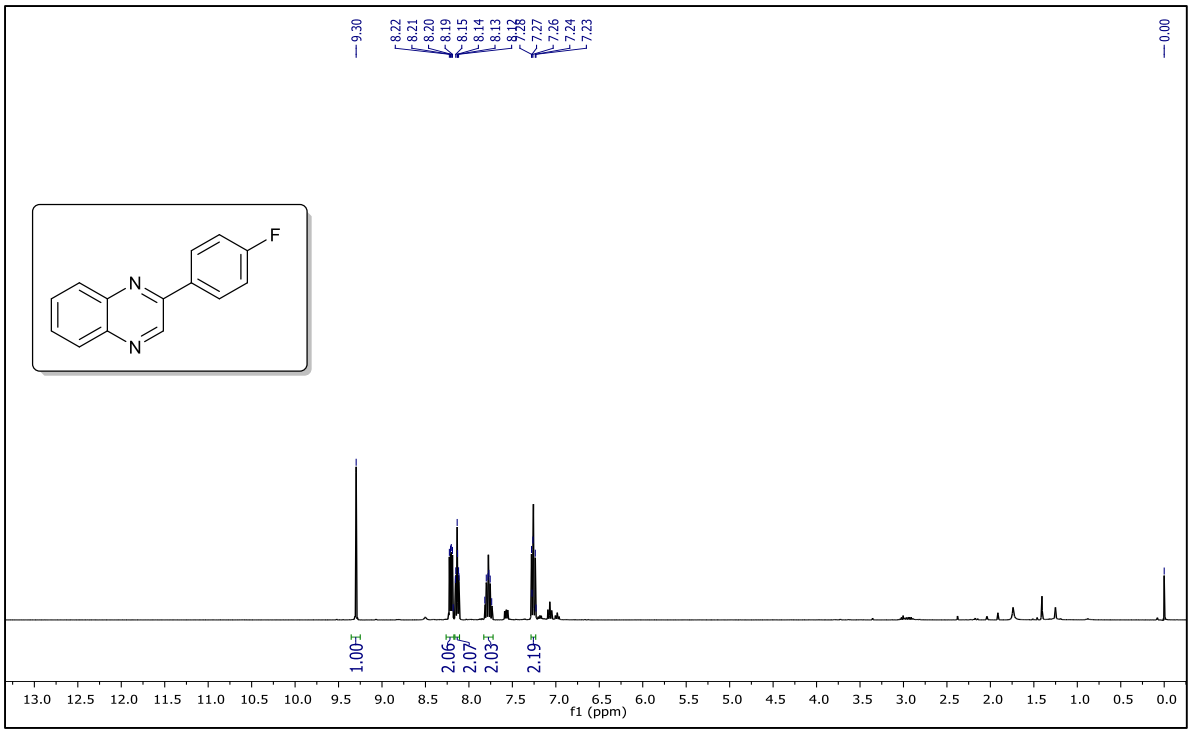
114.62
77.34
77.08
76.83
55.47
f1 (ppm)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7.26
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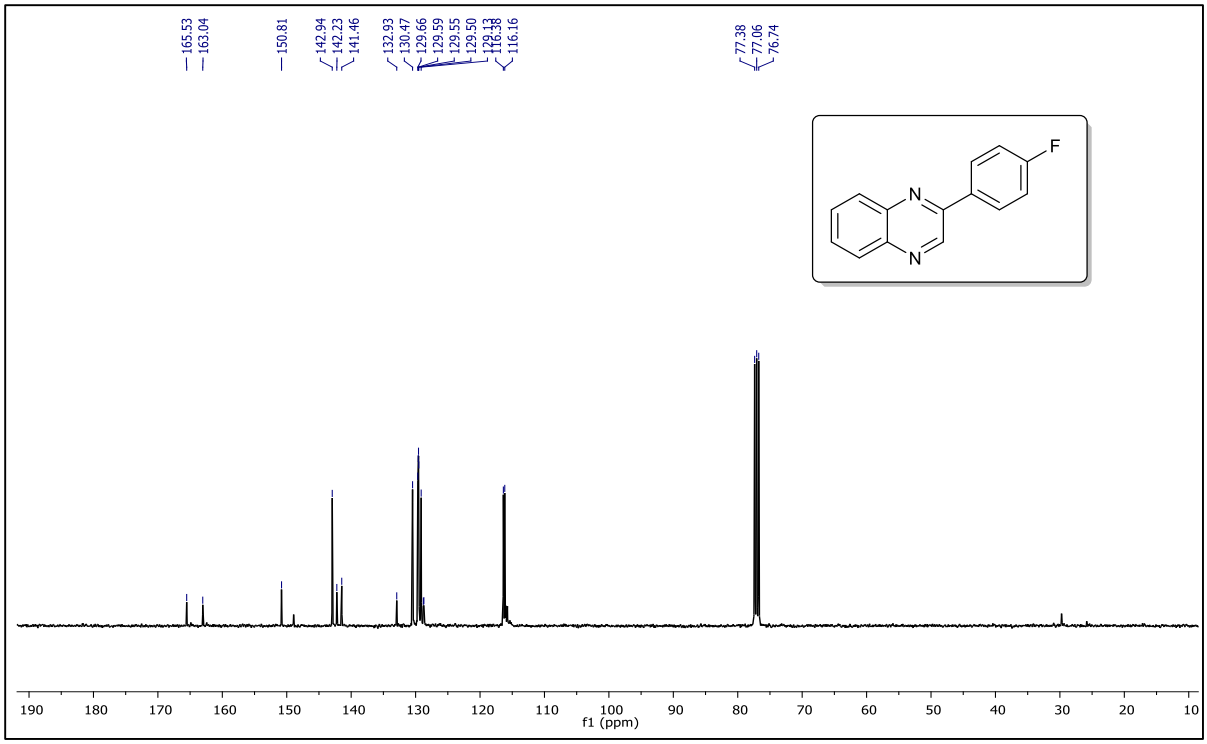
7.23
0.00
F
N
N
1.00
2.06
2.07
2.03
2.19
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.59
129.55
129.50
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116.16
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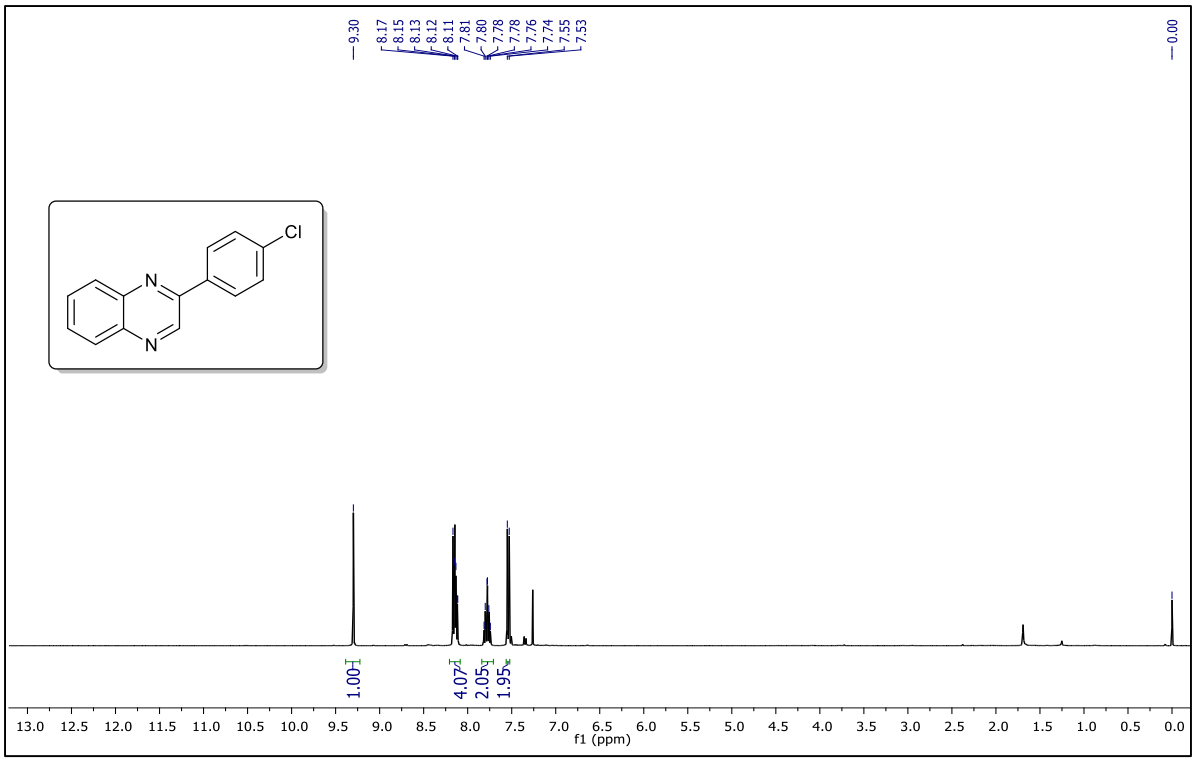
77.06
76.74
F
N
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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8.13
8.12
8.11
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7.80
7.78
7.78
7.76
7.74
7.55
7.53
0.00
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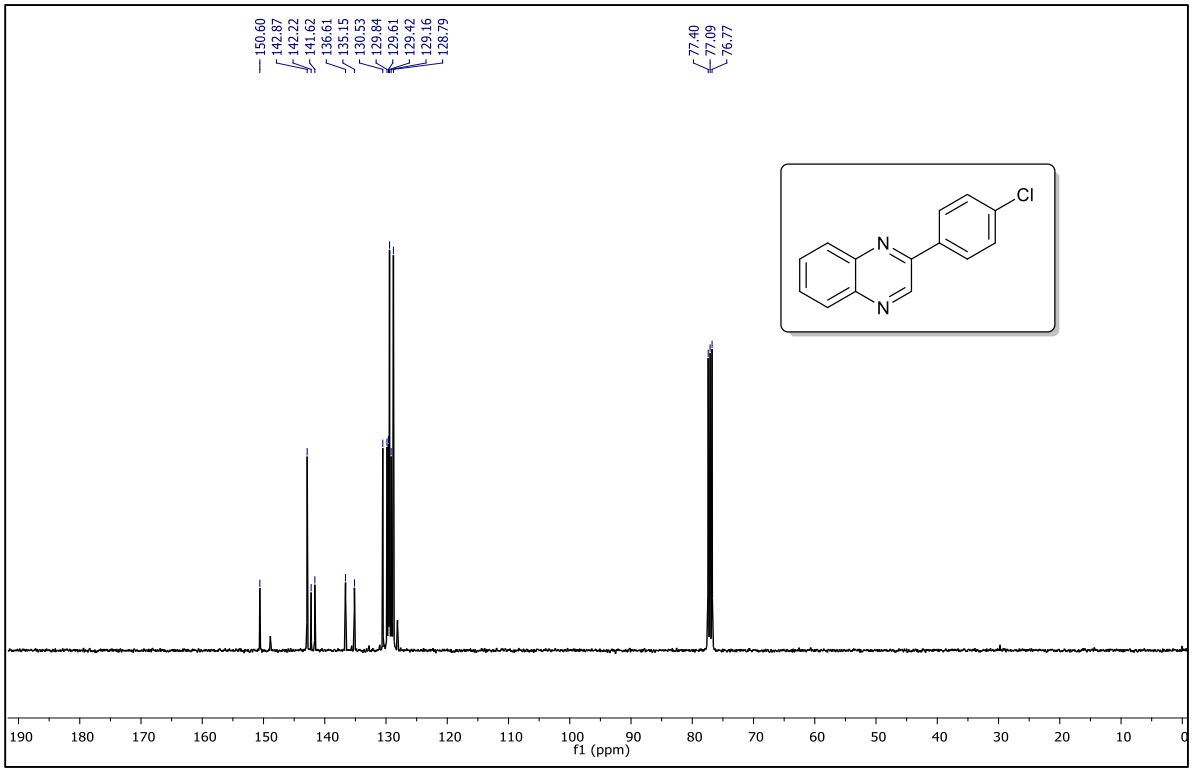
N
1.00
4.07
2.05
1.95
f1 (ppm)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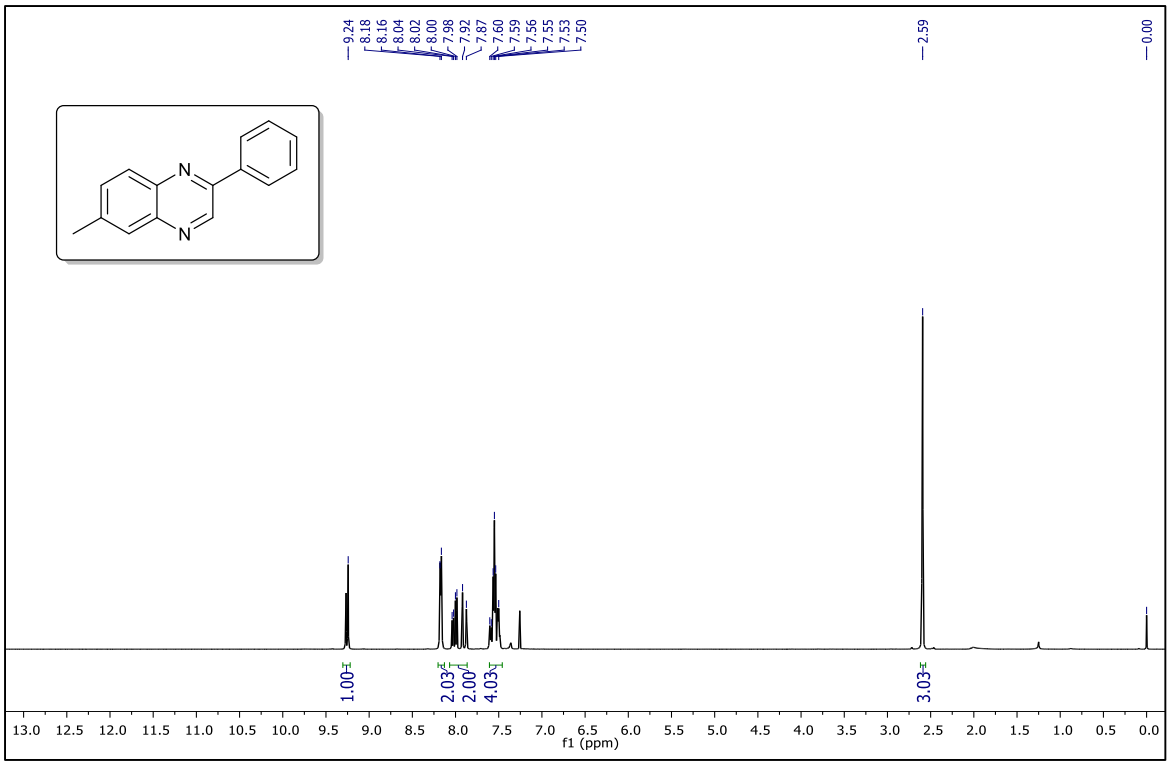
129.16
128.79
77.40
77.09
76.77
Cl
N
N
f1 (ppm)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8.02
8.00
7.98
7.92
7.87
7.60
7.59
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7.50
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0.00
1.00
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2.00
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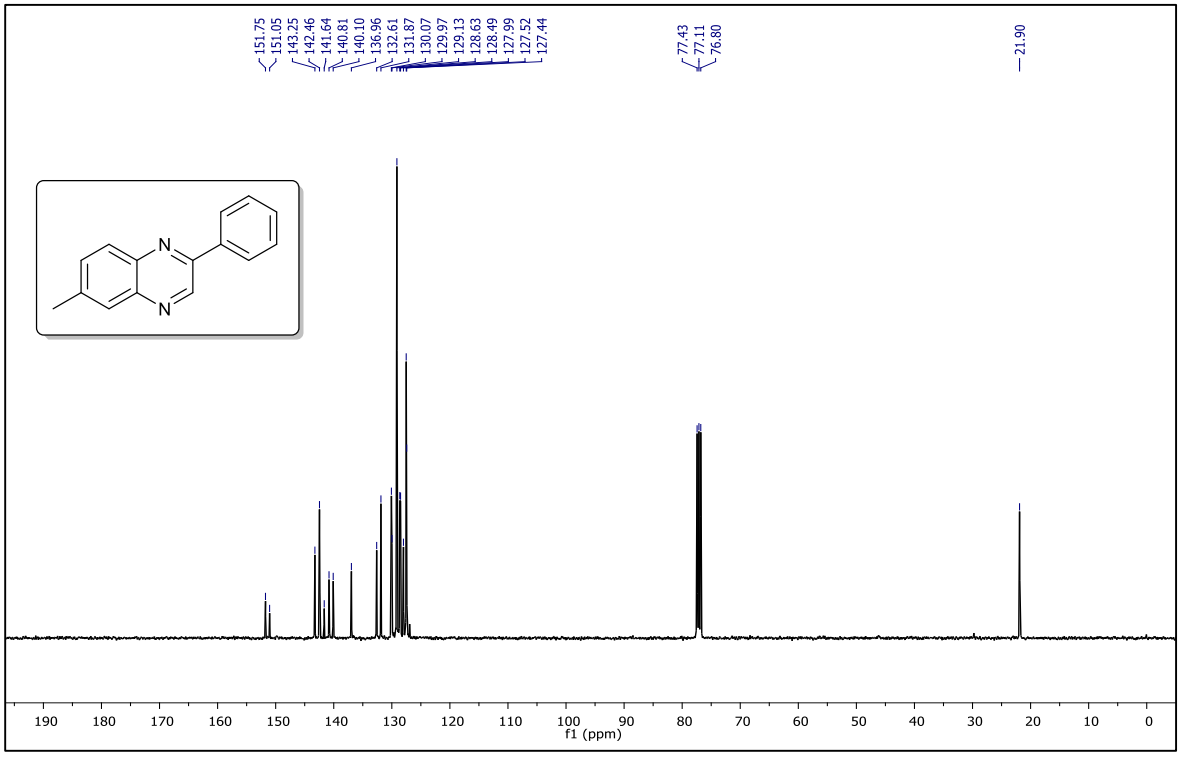
3.03
f1 (ppm)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130.07
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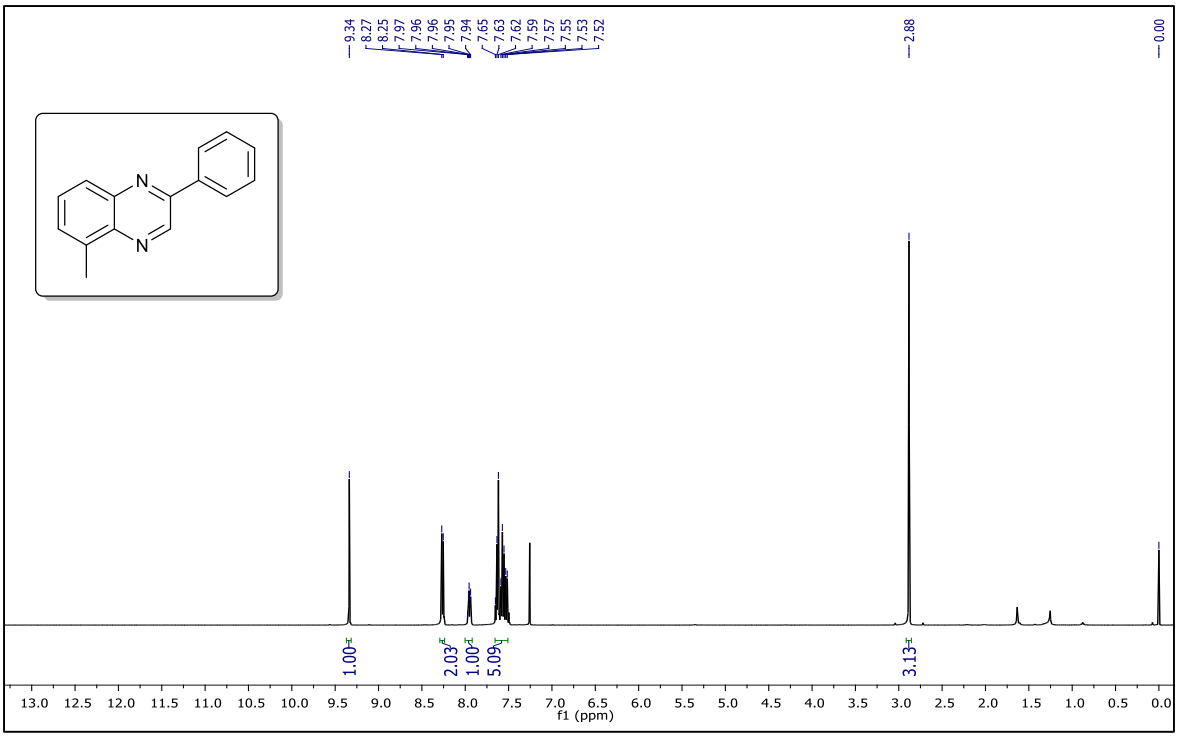
77.11
76.80
21.90
f1 (ppm)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7.96
7.95
7.94
7.65
7.63
7.62
7.59
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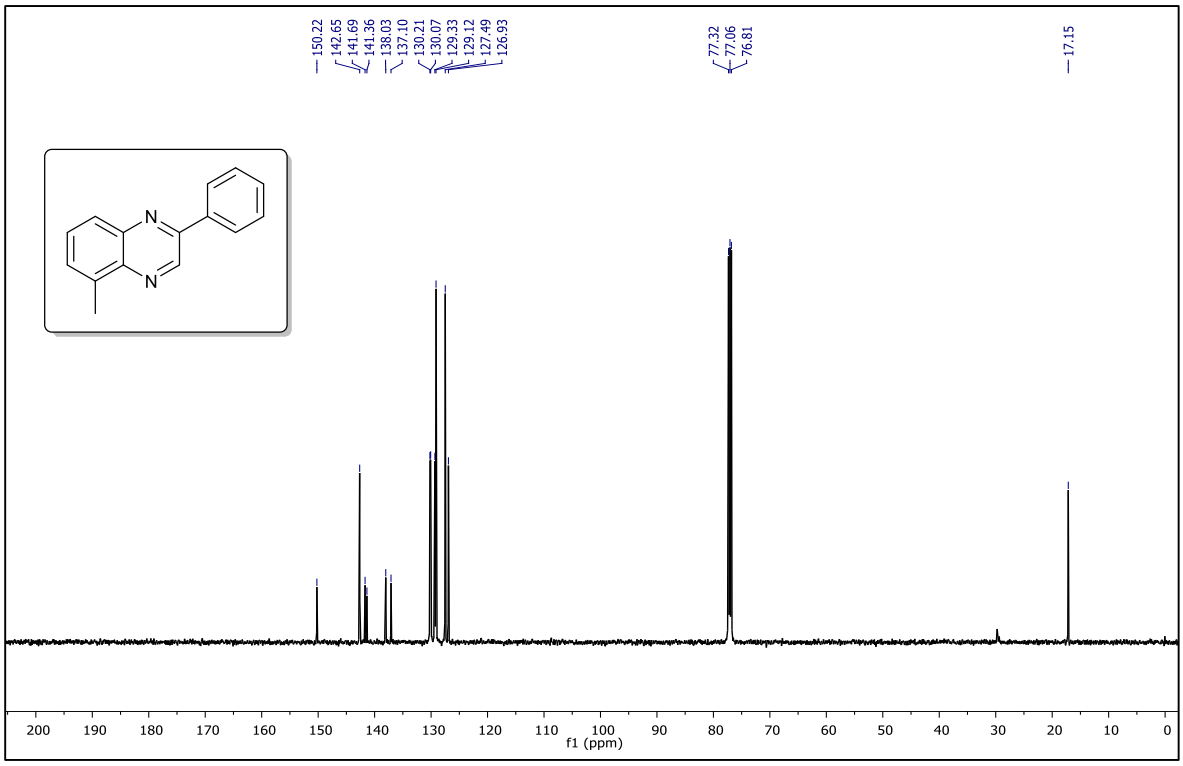
7.55
7.53
7.52
2.88
0.00
1.00
2.03
1.00
5.09
3.13
f1 (ppm)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138.03
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129.12
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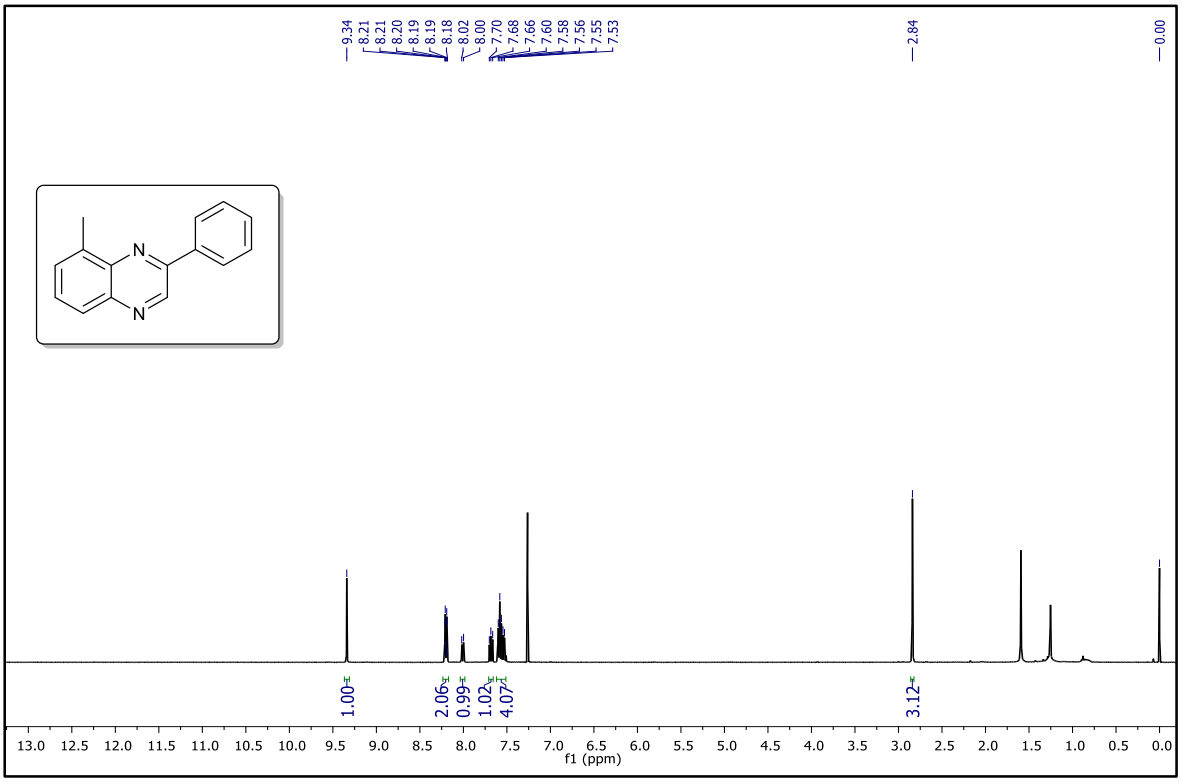
77.32
77.06
76.81
17.15
f1 (ppm)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8.19
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8.02
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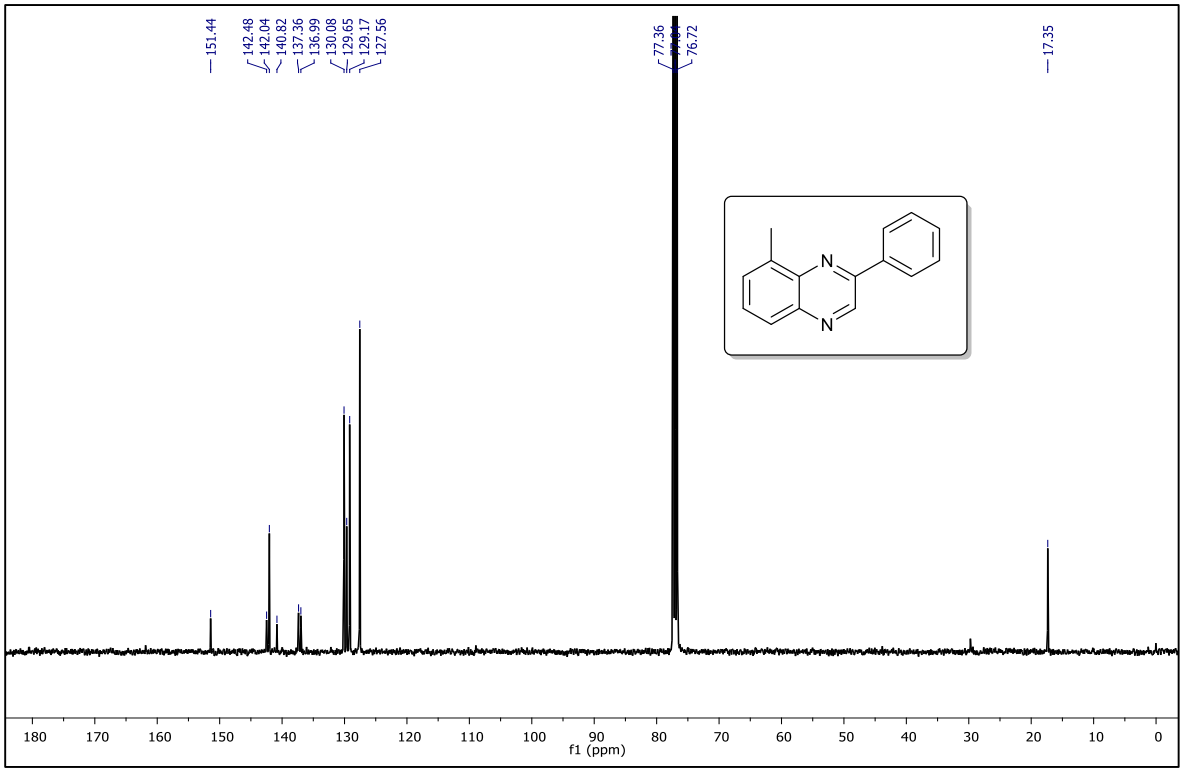
7.66
7.60
7.58
7.56
7.55
7.53
2.84
0.00
N
N
1.00
2.06
0.99
1.02
4.07
3.12
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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76.72
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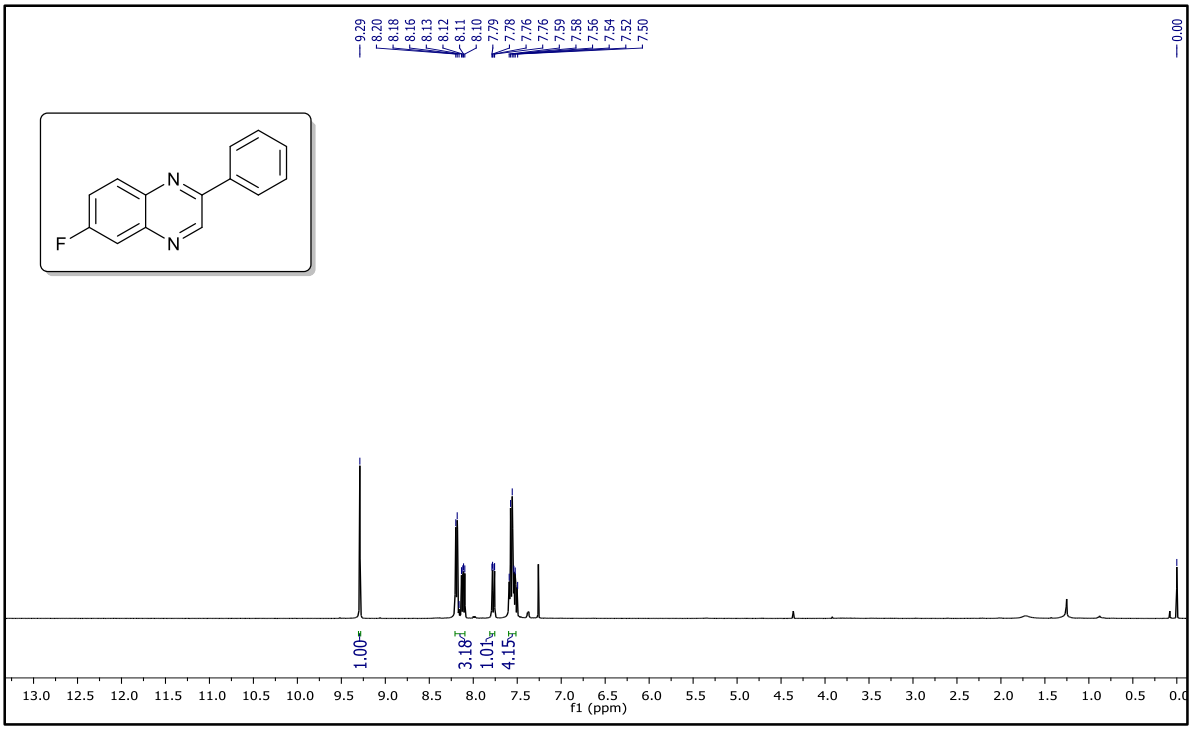
f1 (ppm)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8.10
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7.78
7.76
7.76
7.59
7.58
7.56
7.54
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7.50
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N
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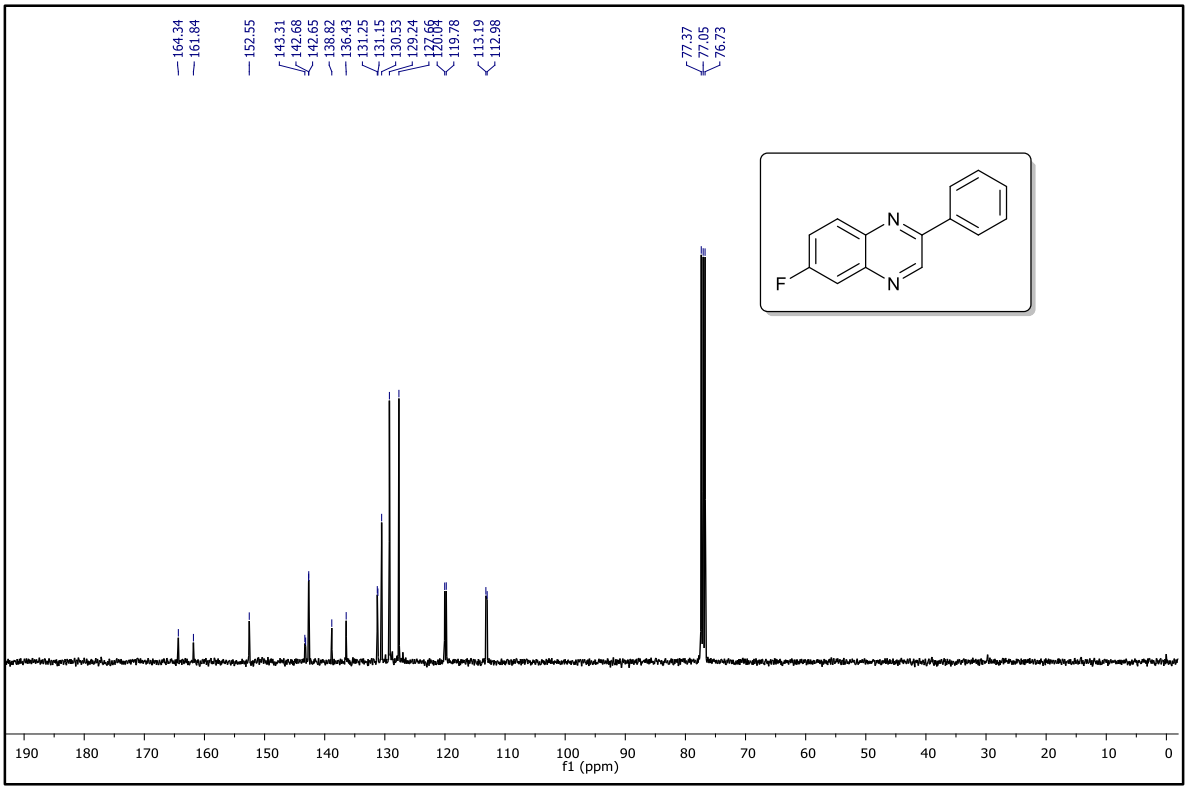
3.18
1.01
4.15
f1 (ppm)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112.98
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77.05
76.73
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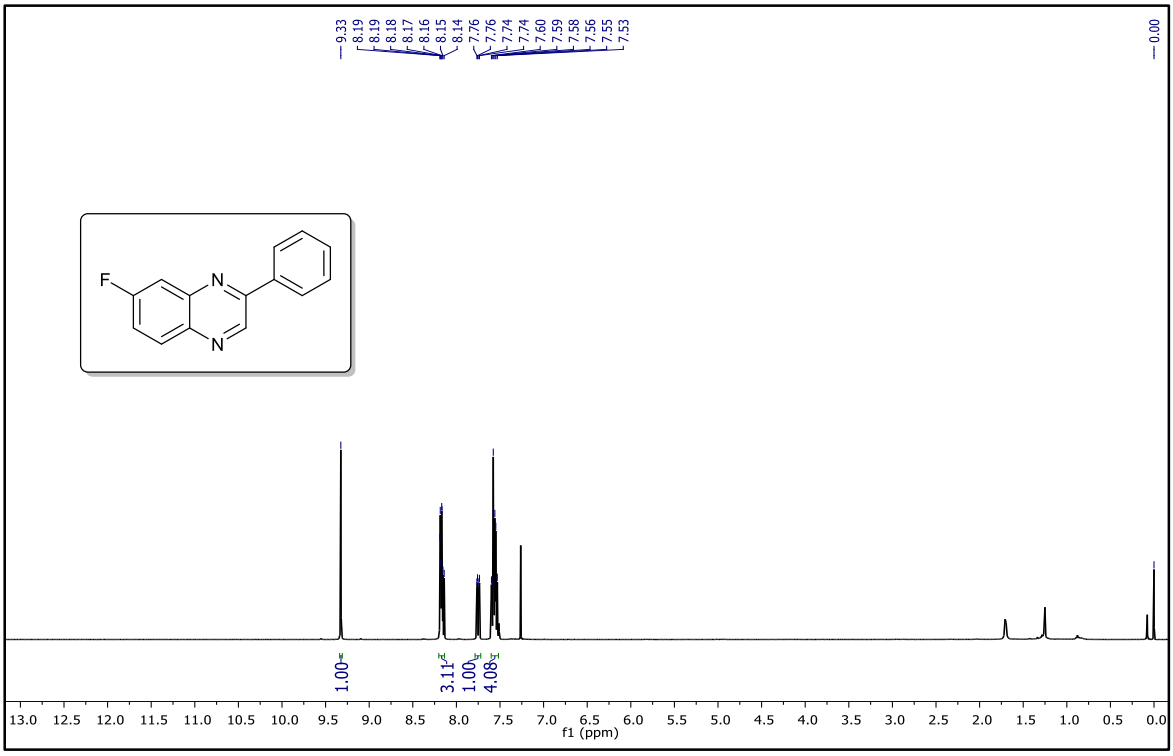
F
N
f1 (ppm)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8.14
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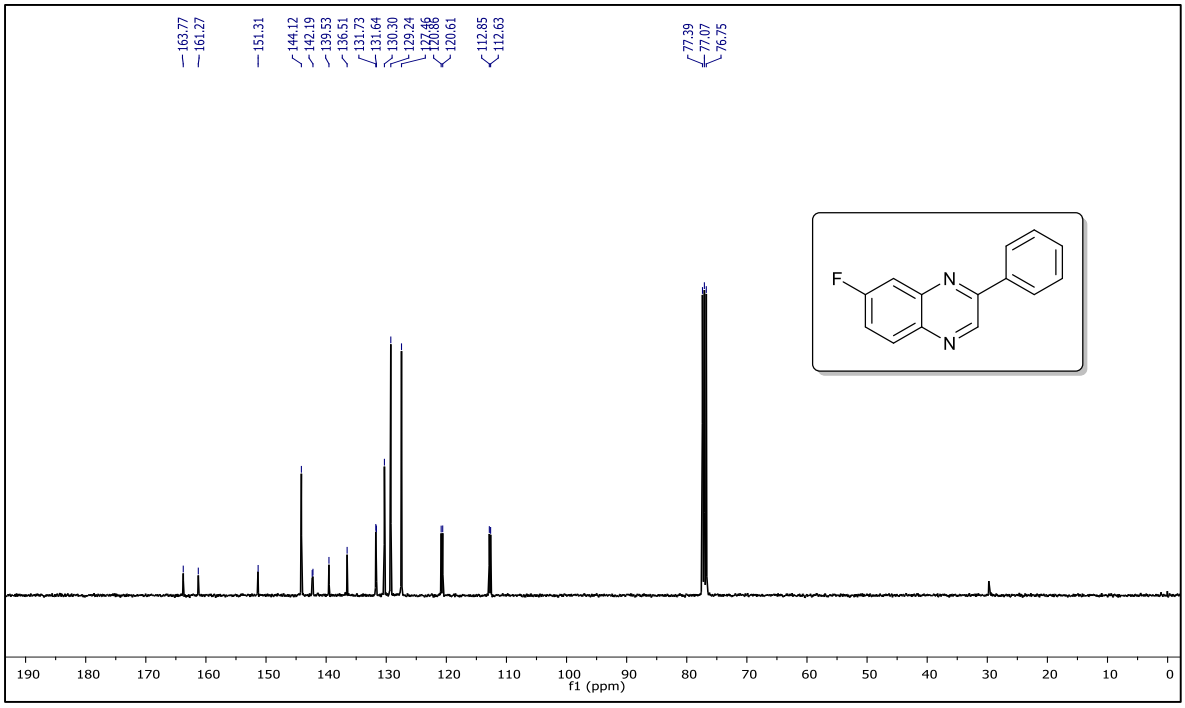
7.76
7.74
7.74
7.60
7.59
7.58
7.56
7.55
7.53
0.00
F
N
N
1.00
3.11
1.00
4.08
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.46
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120.61
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112.63
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77.07
76.75
F
N
N
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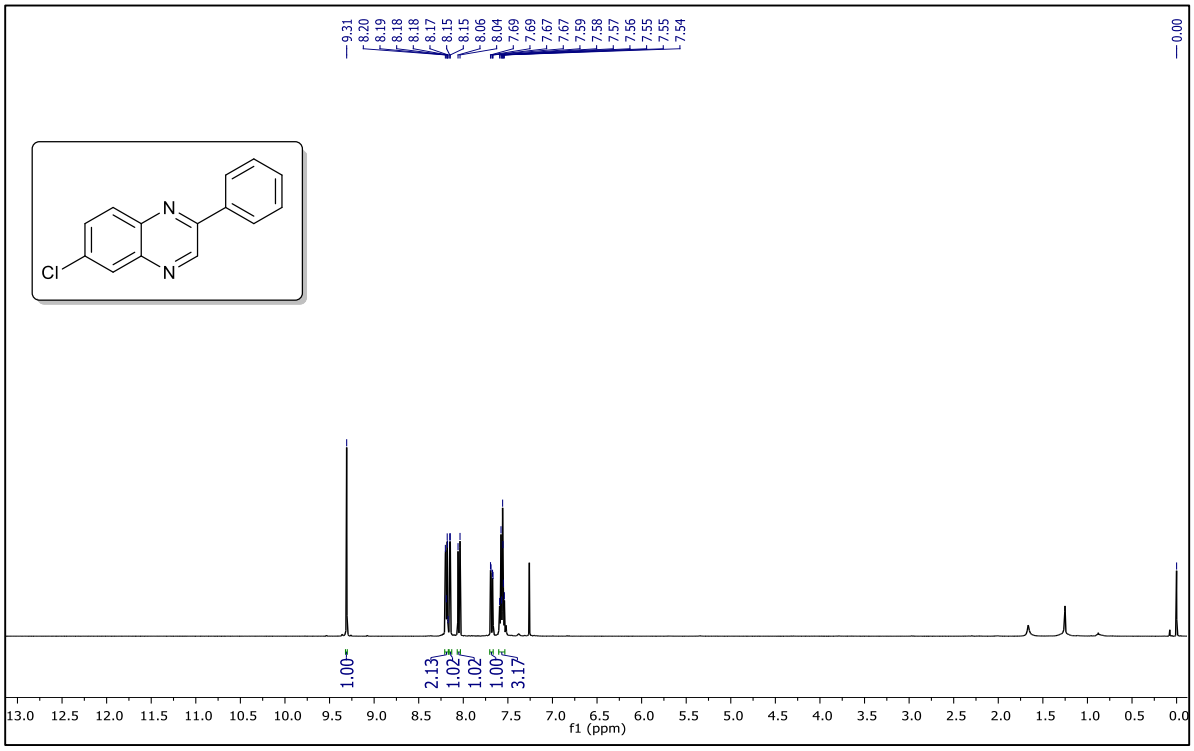
f1 (ppm)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7.67
7.67
7.59
7.58
7.57
7.56
7.55
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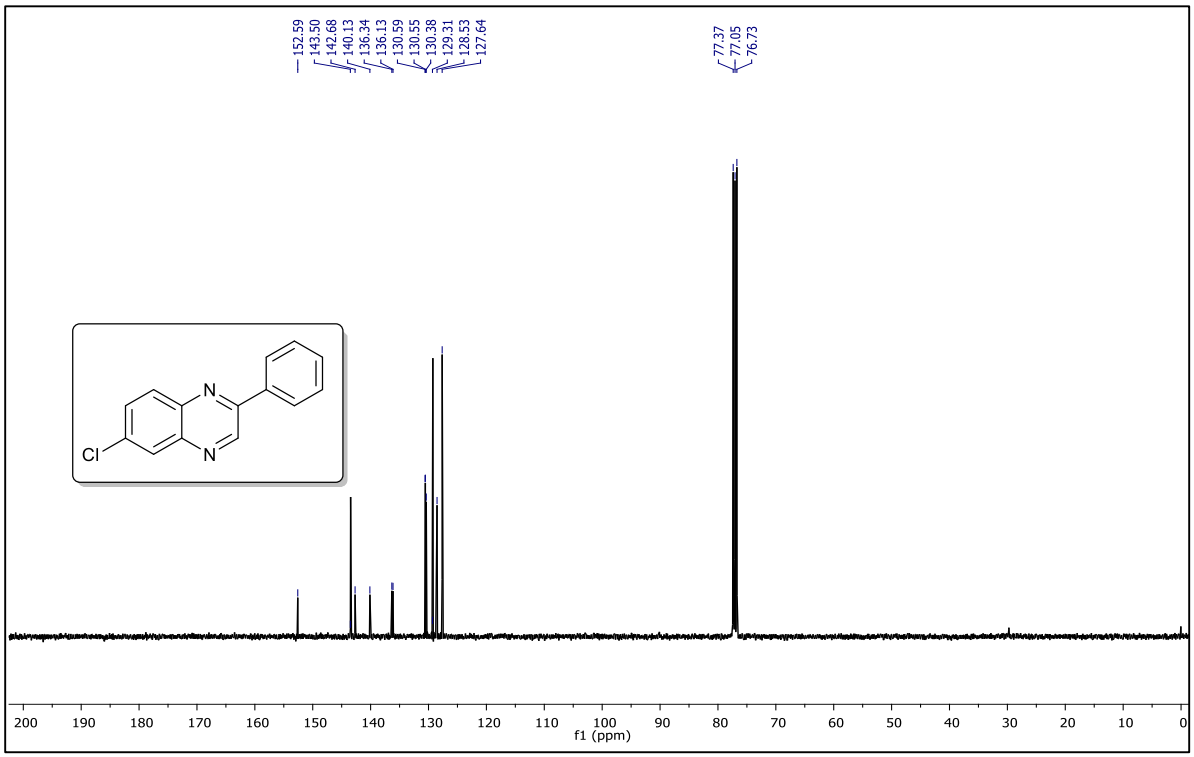
1.02
1.00
3.17
f1 (ppm)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127.64
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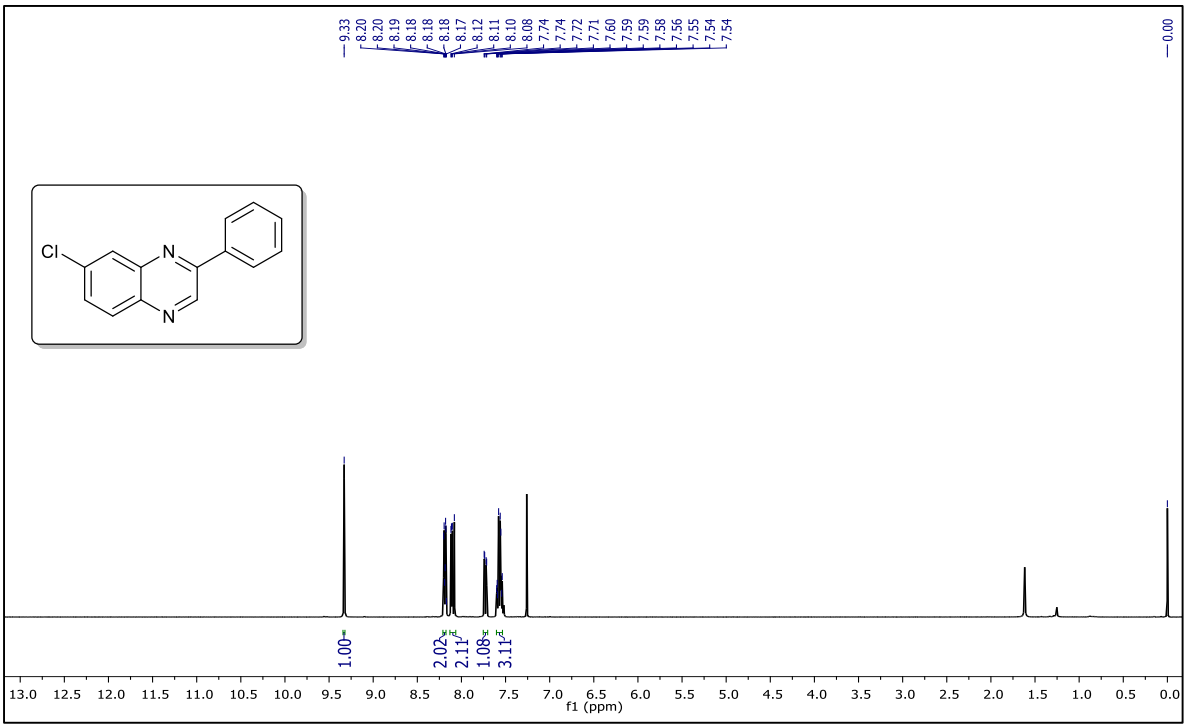
77.05
76.73
N
N
Cl
f1 (ppm)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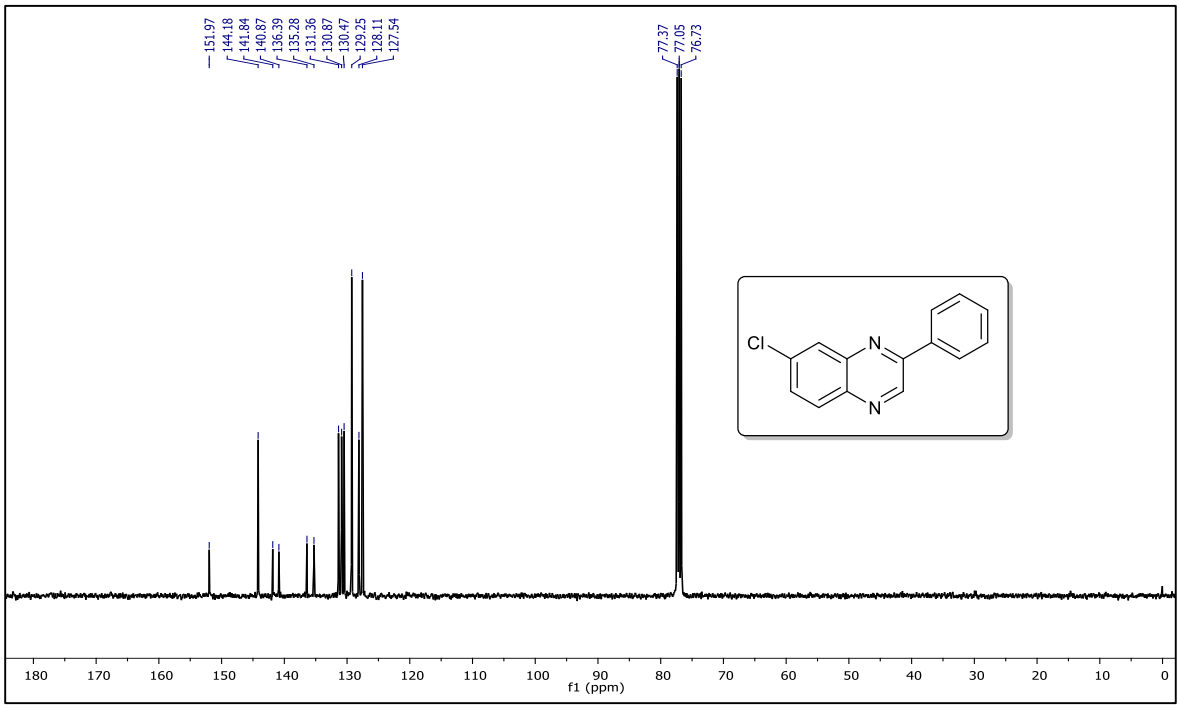
8.10
8.08
7.74
7.74
7.72
7.71
7.60
7.59
7.59
7.58
7.56
7.55
7.54
7.54
0.00
Cl
N
N
1.00
2.02
2.11
1.08
3.11
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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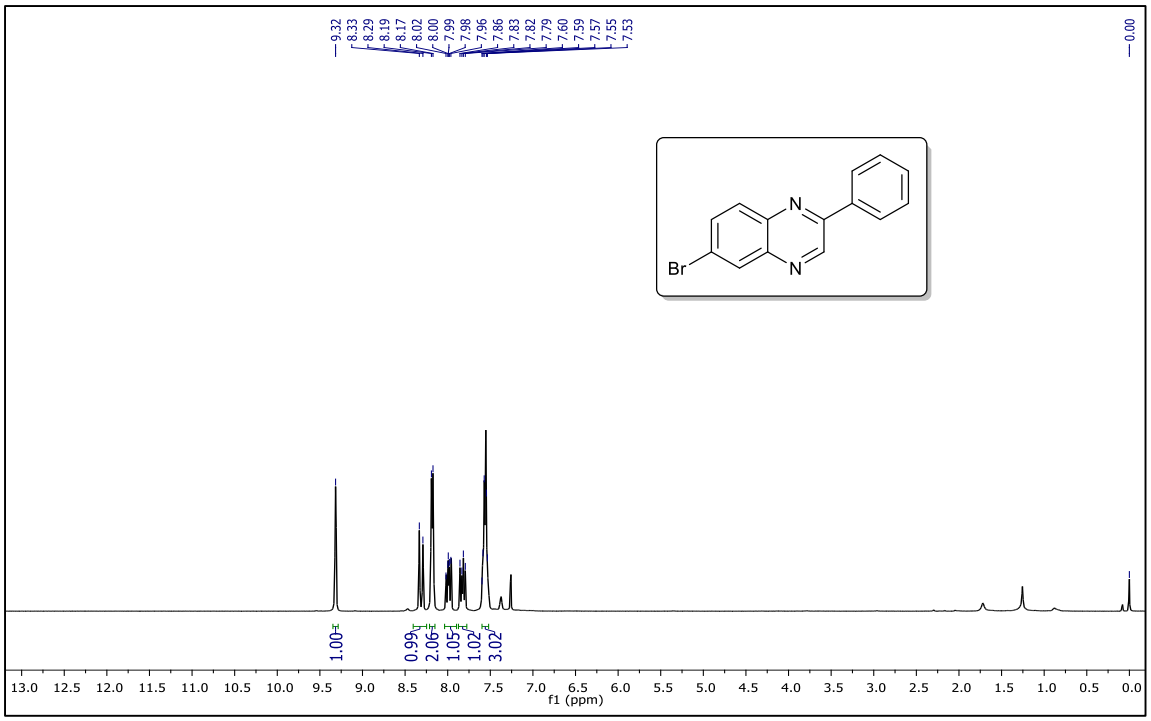
77.05
76.73
Cl
N
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.96
7.86
7.83
7.82
7.79
7.60
7.59
7.57
7.55
7.53
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1.00
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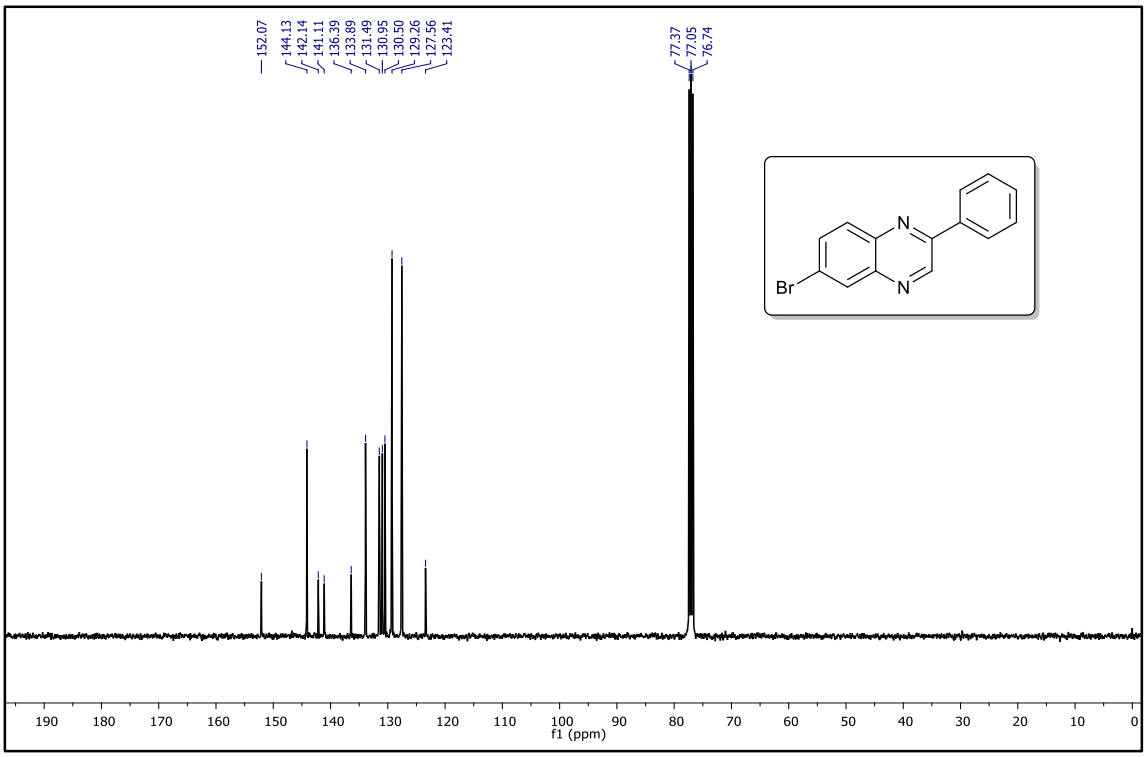
2.06
1.05
1.02
3.02
f1 (ppm)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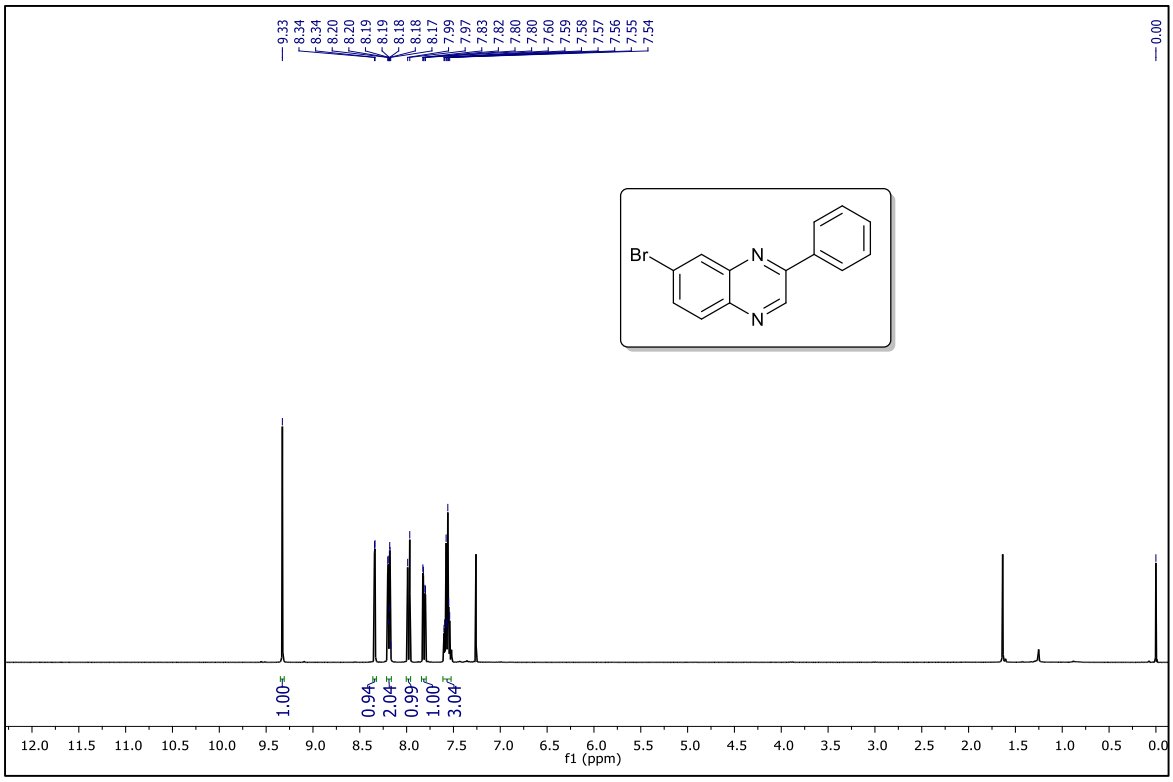
Br
N
N
f1 (ppm)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8.18
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8.17
7.99
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7.82
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7.60
7.59
7.58
7.57
7.56
7.55
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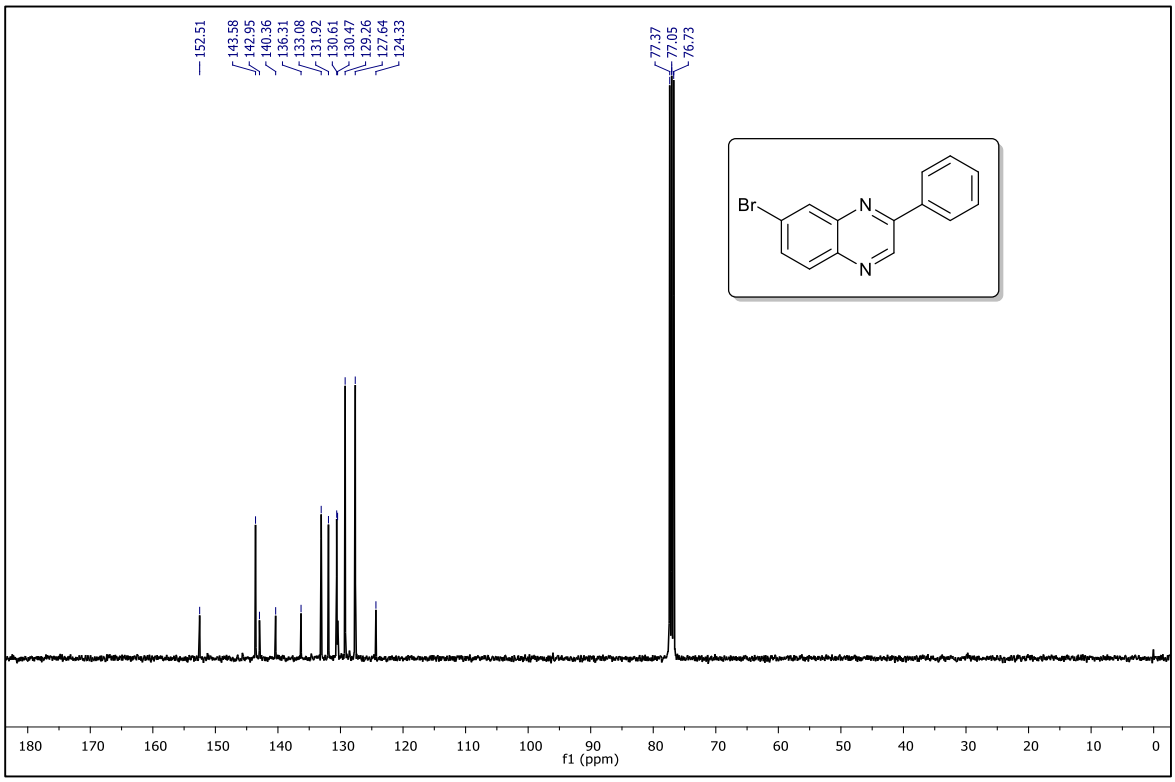
0.99
1.00
3.04
f1 (ppm)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127.64
124.33
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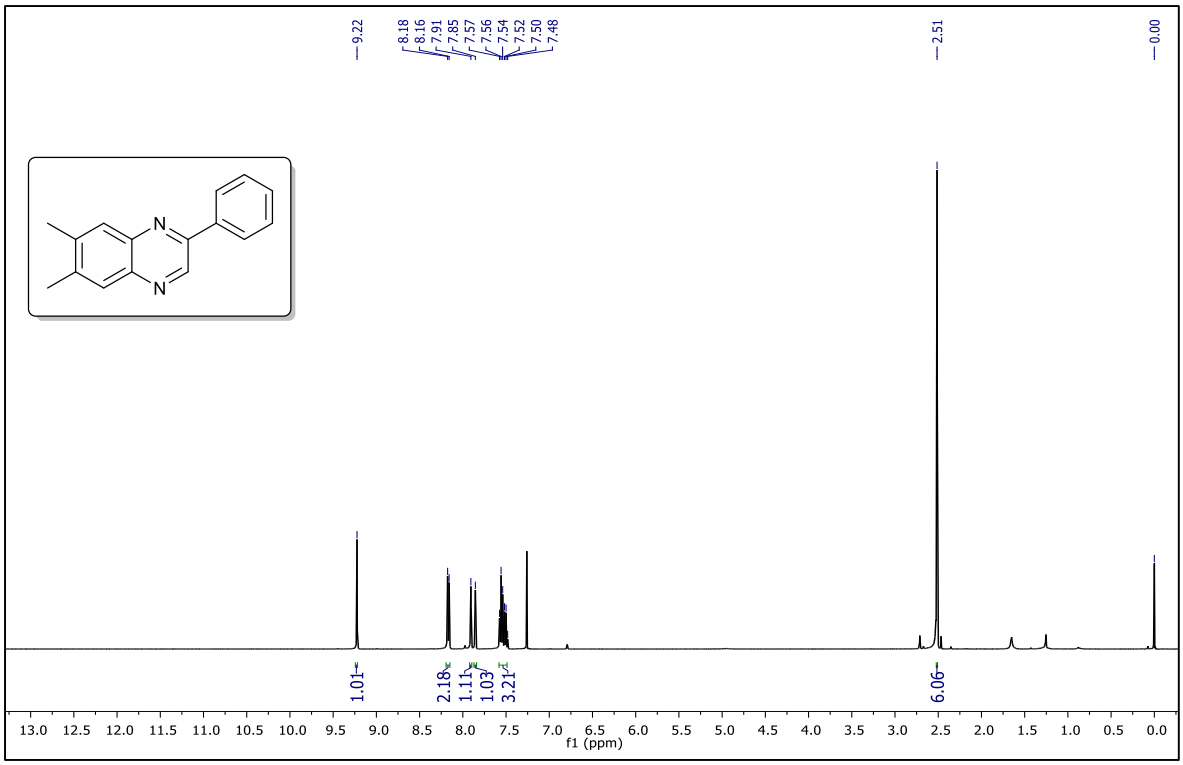
77.05
76.73
Br
N
N
f1 (ppm)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7.56
7.54
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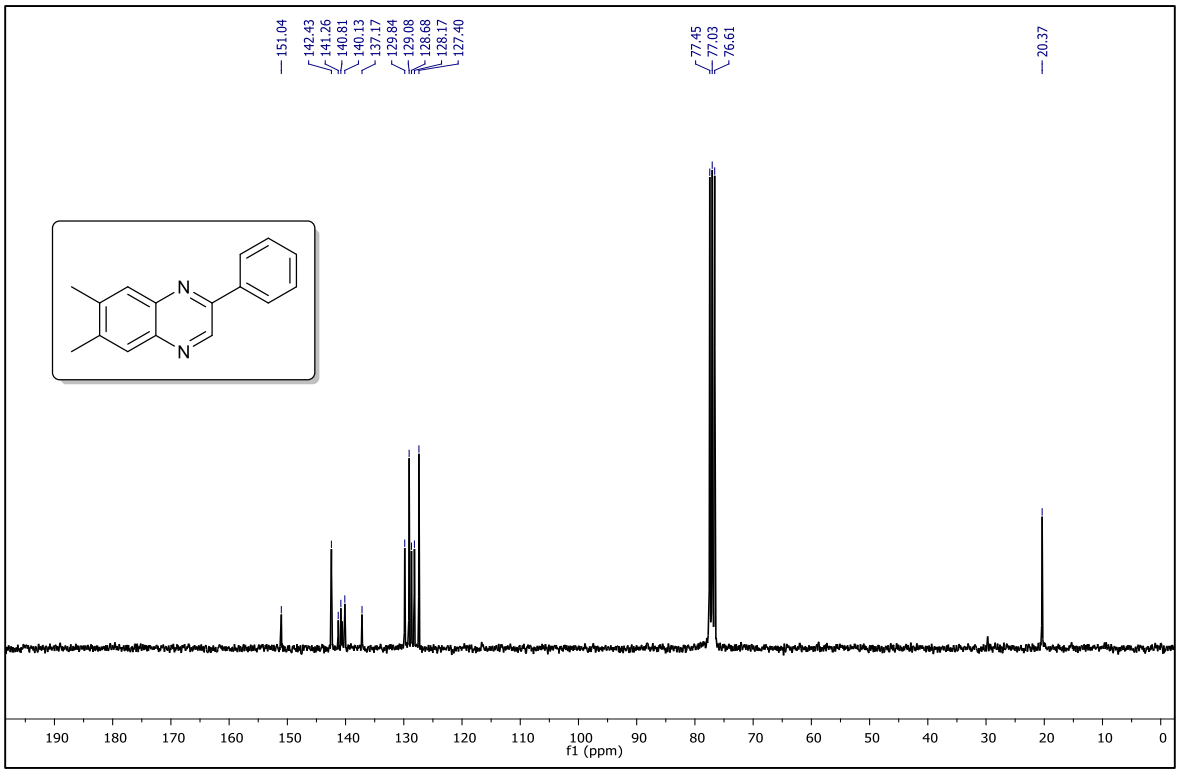
1.01
2.18
1.11
1.03
3.21
6.06
f1 (ppm)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77.03
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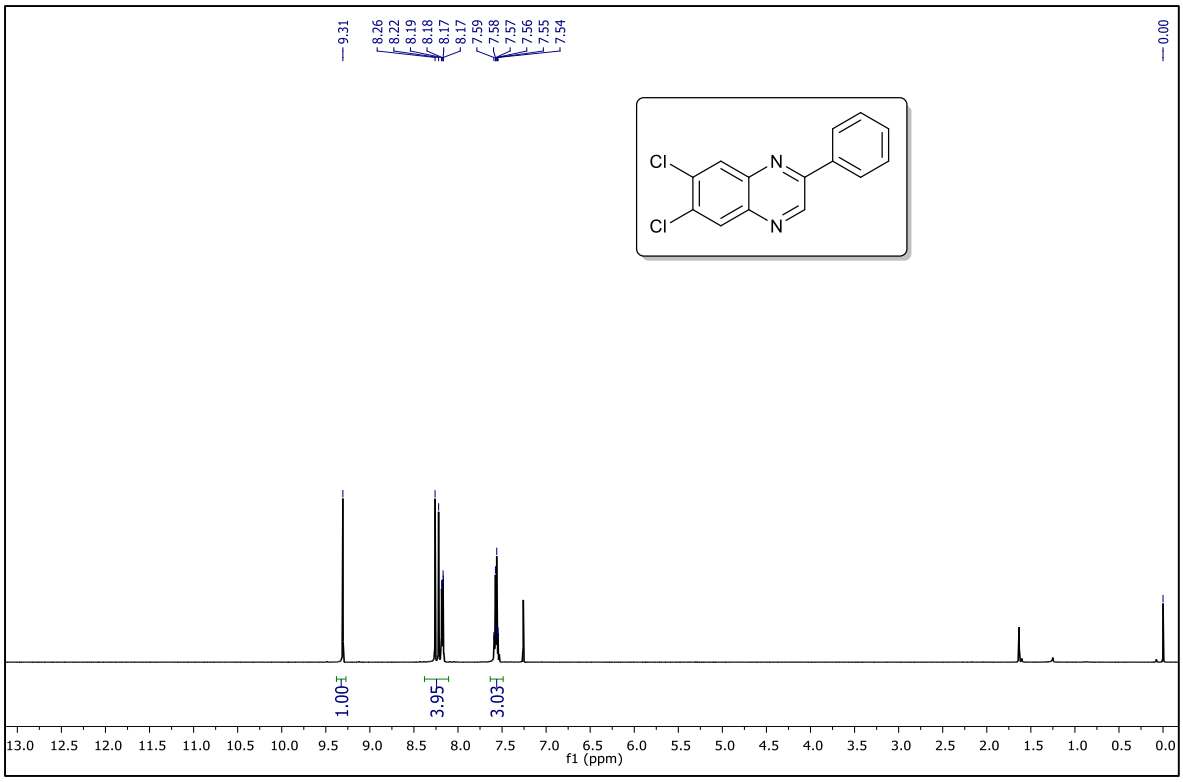
20.37
f1 (ppm)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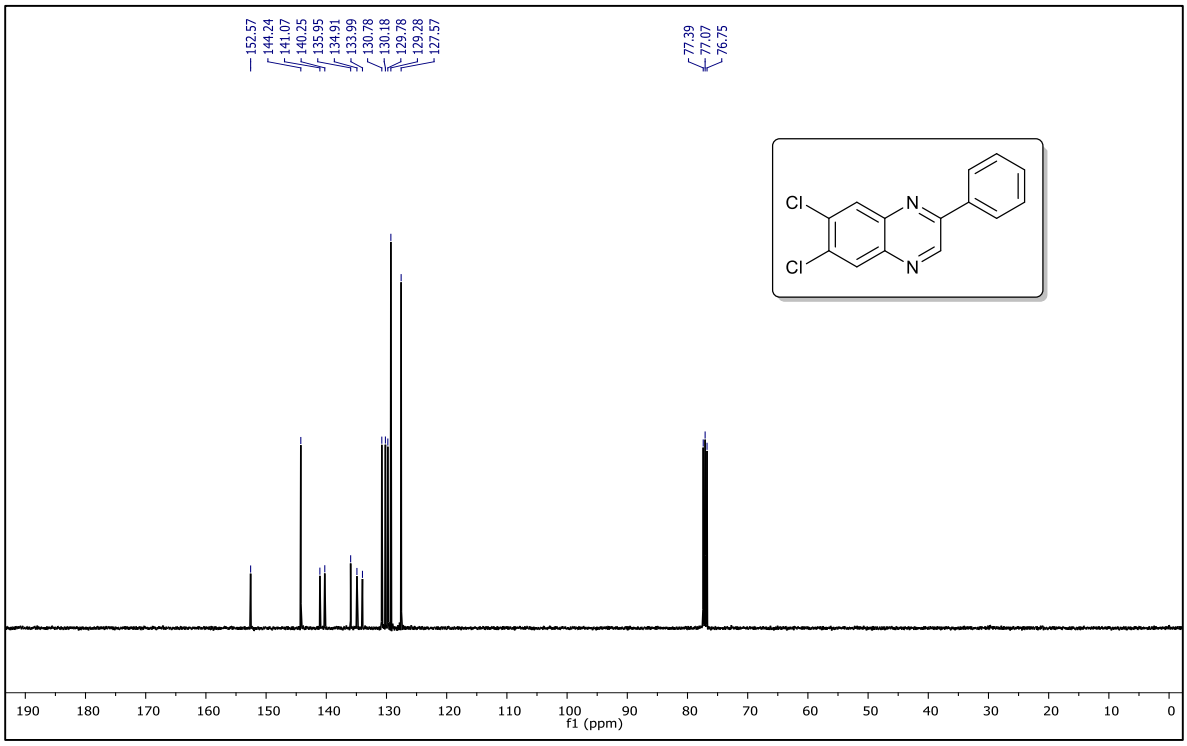
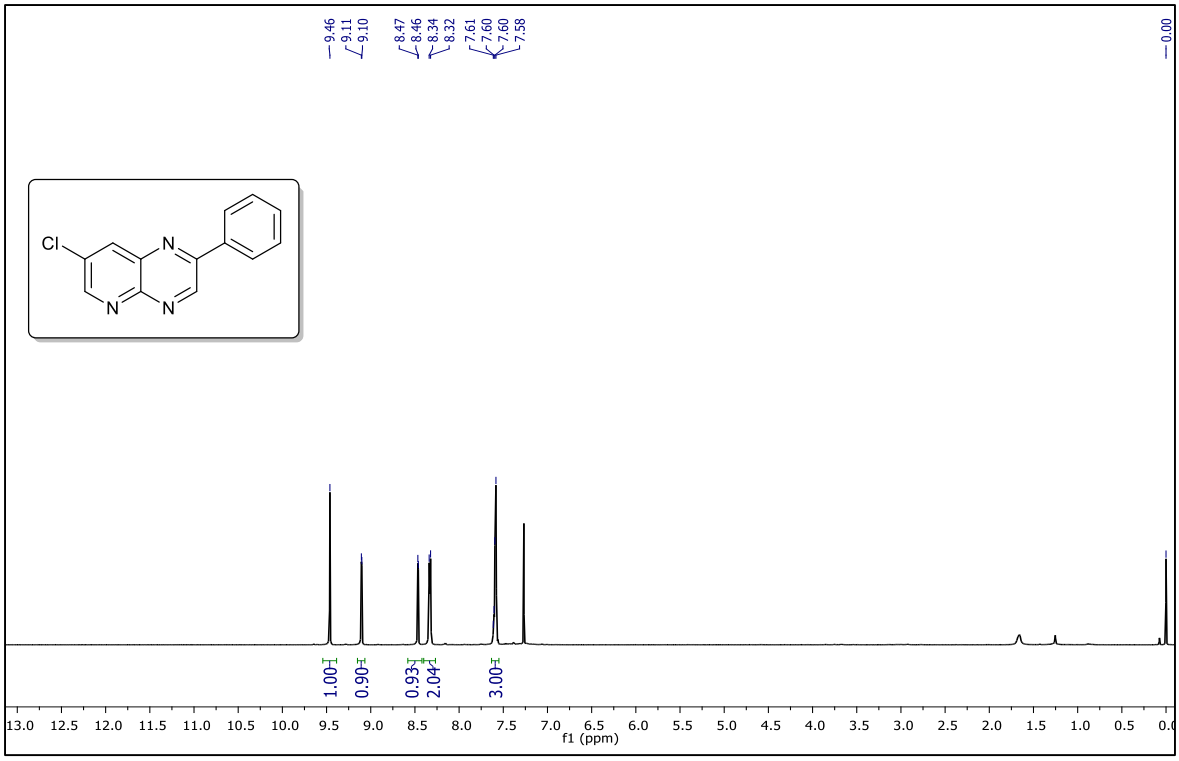
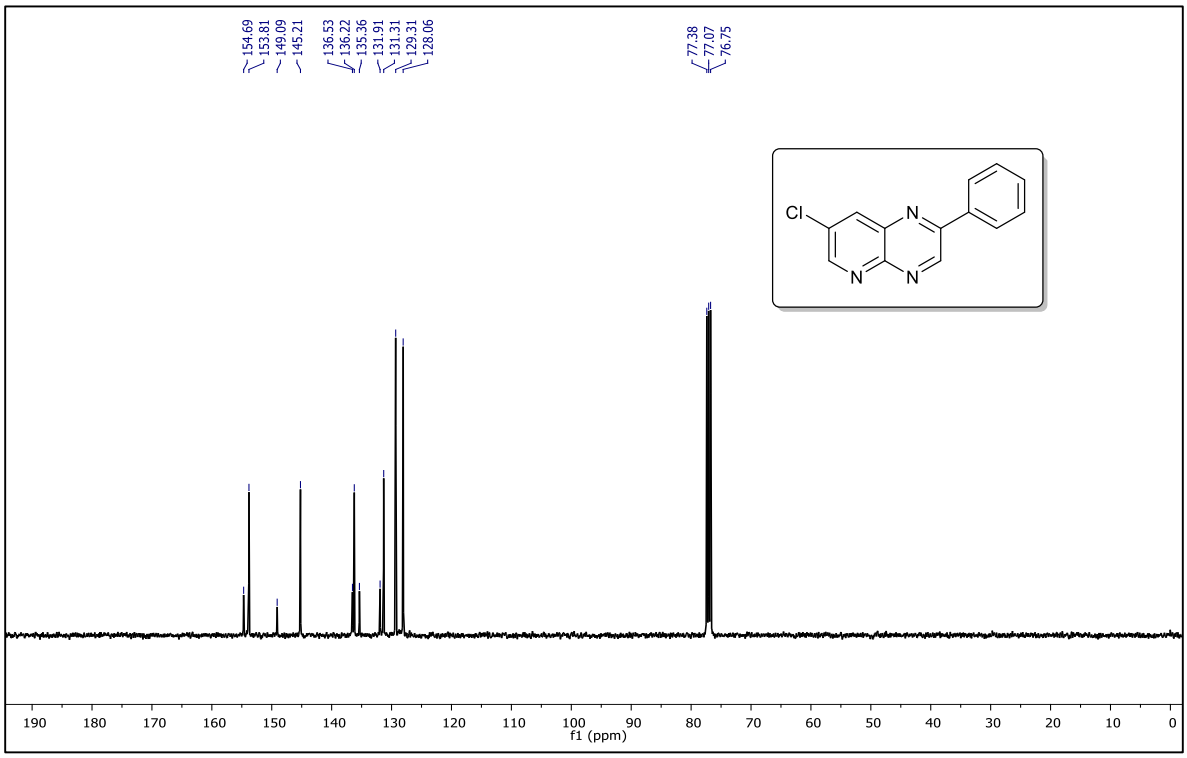
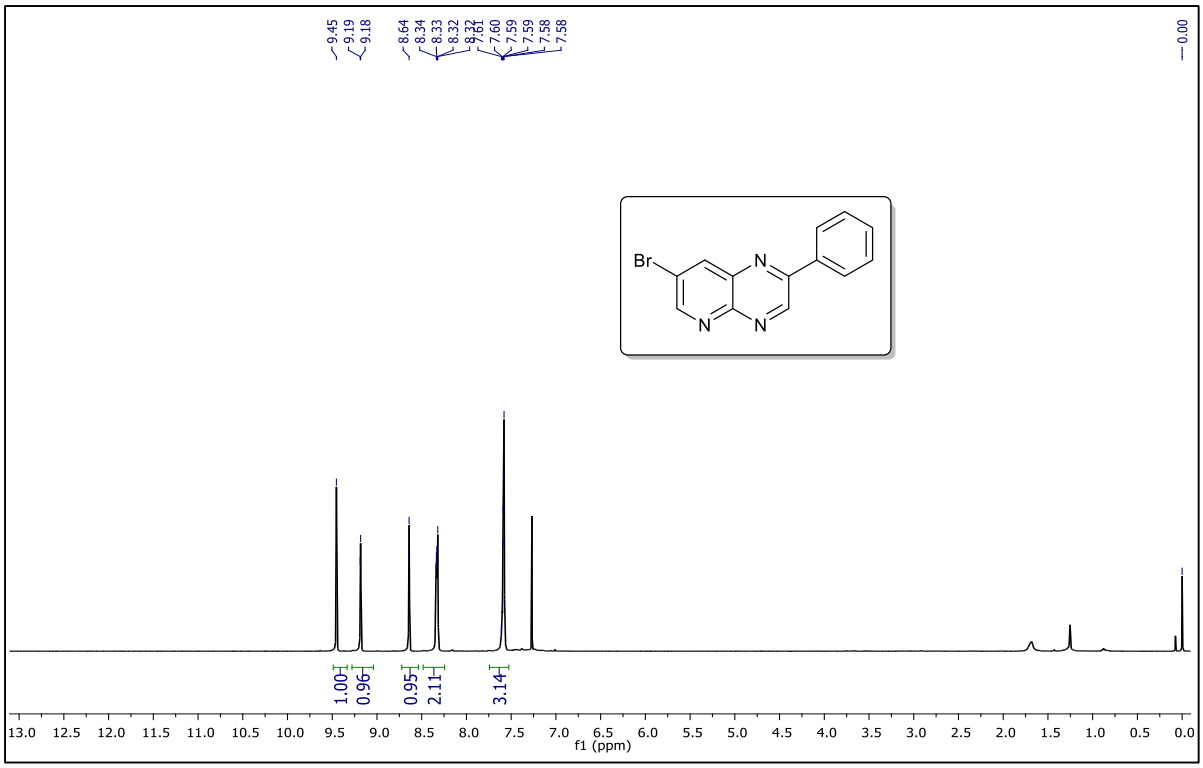
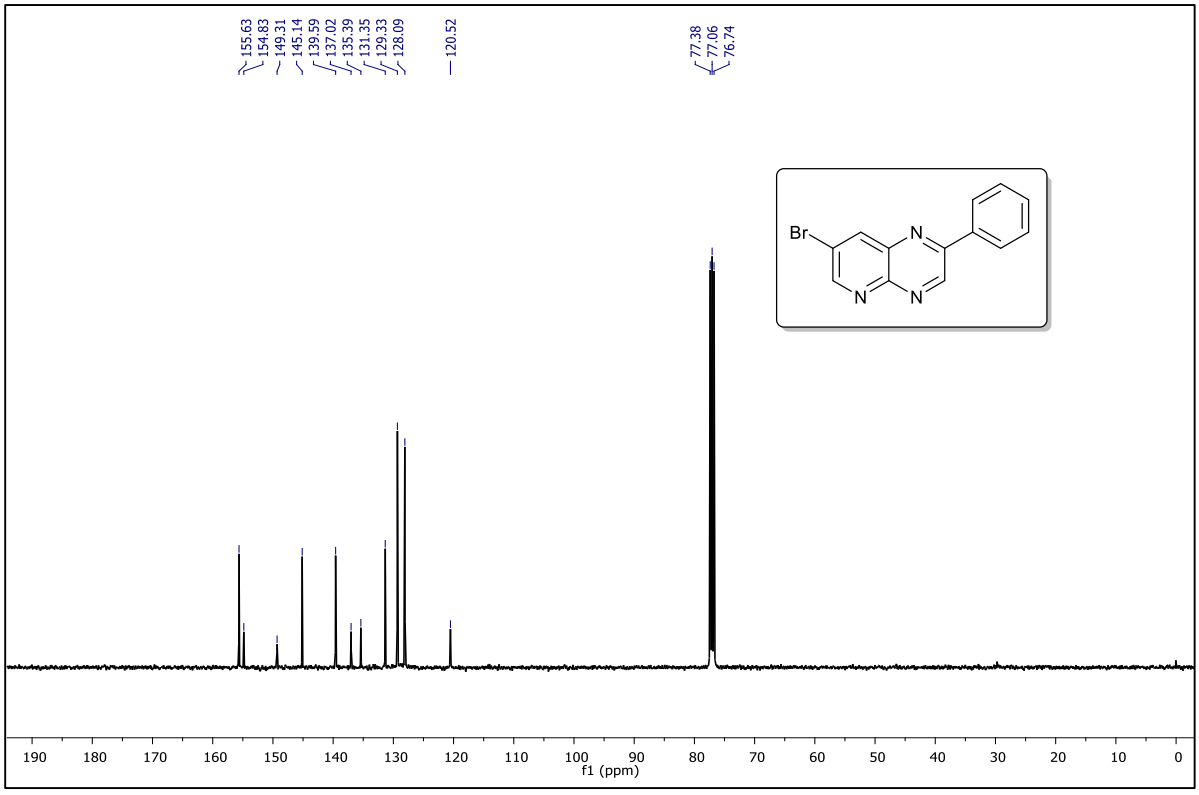
8.17
7.59
7.58
7.57
7.56
7.55
7.54
0.00
Cl
Cl
N
N
1.00
3.95
3.03
f1 (ppm)


152.57
144.24
141.07
140.25
135.95
134.91
133.99
130.78
130.18
129.78
129.28
127.57
77.39
77.07
76.75
Cl
Cl
N
N
f1 (ppm)


9.46
9.11
9.10
8.47
8.46
8.34
8.32
7.61
7.60
7.60
7.58
0.00
Cl
N
N
N
1.00
0.90
0.93
2.04
3.00
f1 (ppm)


154.69
153.81
149.09
145.21
136.53
136.22
135.36
131.91
131.31
129.31
128.06
77.38
77.07
76.75
Cl
N
N
N
f1 (ppm)


9.45
9.19
9.18
8.64
8.34
8.33
8.32
8.32
7.61
7.60
7.59
7.59
7.58
7.58
0.00
Br
N
N
N
1.00
0.96
0.95
2.11
3.14
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.63
154.83
149.31
145.14
139.59
137.02
135.39
131.35
129.33
128.09
120.52
77.38
77.06
76.74
Br
N
N
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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