

## Supporting Information

### Synthesis of benzoimidazoquinazolines by cobalt-catalyzed isocyanide insertion-cyclization

F. Ahmadi and A. Bazgir\*

*Department of Chemistry, Shahid Beheshti University, General Campus, Tehran 1983963113, Iran. E-mail:*  
[a\\_bazgir@sbu.ac.ir](mailto:a_bazgir@sbu.ac.ir)

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**Materials and Methods.** Melting points were determined with a melting point Thermo Scientific 9100 apparatus and are uncorrected. IR spectra were taken with a Bomem FT-IR MB spectrometer. NMR spectra were recorded with 300 MHz Bruker DRX Avance spectrometers. MS spectra were recorded with a Finnigan LCQ mass spectrometer in negative ion mode.

All chemicals were purchased from Merck or Aldrich and were used without further purification.

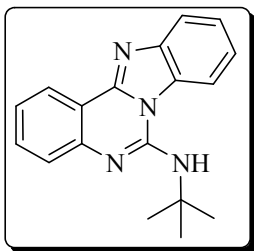
**General procedure for the synthesis of 2-(1H-benzo[d]imidazol-2-yl)aniline (1).<sup>1</sup>**

2-Aminobenzoic acid (10 mmol) dissolved in MeOH (10 mL) was added to a methanolic solution (25 mL) of o-phenylenediamine (10 mmol) with stirring at room temperature. The reaction mixture was stirred for 1 hour and then heated under reflux (6 h) to afford a dark brown solution. After filtration it was concentrated to half its volume on a water bath. Upon cooling it afforded brown microcrystalline compound, which was filtered, washed with methanol, diethyl ether and dried under vacuum.

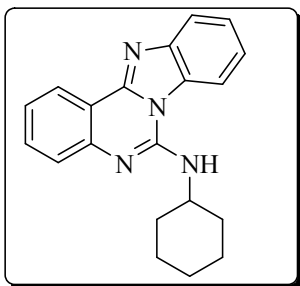
**General procedure for the synthesis of 2-(1H-tetrazol-5-yl)aniline (4).<sup>2</sup>** 2-aminobenzonitrile (0.944g, 8 mmol), sodium azide (0.624g, 10 mmol) ammonium chloride (0.512 g, 10 mmol) and DMF (5 mL) were mixed and heated at 120°C overnight. The solvent was evaporated and the residue taken up in water. The crude product was isolated by filtration and recrystallised from water to obtain the pure product.

**General procedure for the synthesis of 2-amino-benzimidamides (5):<sup>3</sup>** A corresponding amine (2 mmol) was added to a solution of isatoic anhydride (1.8 mmol) in anhydrous MeCN (6 mL), and the mixture was stirred for 2 h at room temperature and then 4 h at 50 °C. The solvent was evaporated to obtain 5.

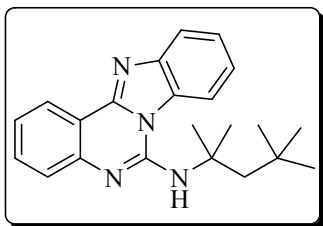
**General procedure for the synthesis of benzoimidazoquinazoline amines (3).** Isocyanide (0.5 mmol) was added to a stirred solution of 2-(1H-benzo[d]imidazol-2-yl)aniline (0.4 mmol), Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.04 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.4 mmol) and NaOAc (0.8 mmol) in DMF(1mL) at 80°C. The mixture was then kept under stirring at 80°C for 12 h. After that, the concentrated residue was purified by column chromatography over silica gel using *n*-hexane/ethyl acetate (4:1) as eluent to give the desired product 3.



**N-(tert-butyl)benzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3a).** White powder (yield 65%); m.p. 133-135°C (Lit.<sup>4</sup> m.p. 121-131 °C). IR (KBr) ( $\nu_{\max}$  /cm<sup>-1</sup>): 3436, 2972, 2919, 1633, 1606. MS (EI, 70 eV) m/z: 290 (M<sup>+</sup>). <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  8.56 (d,  $J$  = 7.9 Hz, 1H, H-Ar), 8.03 (d,  $J$  = 8.0 Hz, 1H, H-Ar), 7.81 (d,  $J$  = 8.2 Hz, 1H, H-Ar), 7.75 – 7.60 (m, 2H, H-Ar), 7.55 (t,  $J$  = 7.7 Hz, 1H, H-Ar), 7.48 – 7.32 (m, 2H, H-Ar), 5.31 (bs, 1H), 1.74 (s, 9H, CH- *t*Bu). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  149.4, 144.5, 144.2, 143.4, 131.7, 128.0, 125.6, 125.1, 124.1, 123.7, 122.4, 120.3, 115.1, 112.0, 53.1, 29.1. Anal. Calcd for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>: C, 74.46; H, 6.25; N, 19.30%. Found: C, 74.38; H, 6.30; N, 19.24.

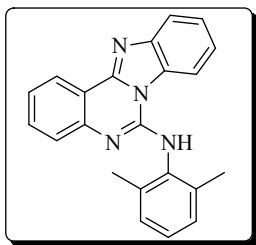


**N-cyclohexylbenzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3b).** White powder (yield 67%); m.p. 171-173°C (Lit.<sup>5</sup> m.p. 187 °C). IR (KBr) ( $\nu_{\max}$  /cm<sup>-1</sup>): 3449, 3038, 2939, 2846, 1633, 1593. MS (EI, 70 eV) m/z: 316 (M<sup>+</sup>). <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  8.54 (d,  $J$  = 7.9 Hz, 1H, H-Ar), 8.02 (d,  $J$  = 8.0 Hz, 1H, H-Ar), 7.81 (d,  $J$  = 8.1 Hz, 1H, H-Ar), 7.65 (bs, 2H, H-Ar), 7.54 (t,  $J$  = 7.7 Hz, 1H, H-Ar), 7.32-7.47 (m, 2H, H-Ar), 5.29 (d,  $J$  = 7.1 Hz, 1H), 4.35 (bs, 1H, CH-cy), 2.32 (d,  $J$  = 11.6 Hz, 2H, CH-cy), 1.95 – 1.81 (m, 2H, CH-cy), 1.80-1.69 (m, 1H, CH-cy), 1.66-1.26 (m, 5H, CH-cy). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  149.4, 144.6, 144.5, 144.4, 131.8, 128.0, 125.3, 125.1, 124.2, 123.6, 122.5, 120.3, 115.2, 112.0, 50.3, 33.1, 25.7, 24.8. Anal. Calcd for C<sub>20</sub>H<sub>20</sub>N<sub>4</sub>: C, 75.92; H, 6.37; N, 17.71%. Found: C, 75.84; H, 6.30; N, 17.66.

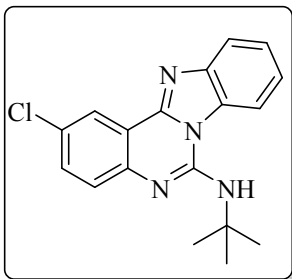


**N-(2,4,4-trimethylpentan-2-yl)benzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3c).** White powder (yield 70%); m.p. 90-92 °C. IR (KBr) ( $\nu_{\max}$  /cm<sup>-1</sup>): 3456, 2952, 2859, 1626, 1593. MS (EI, 70 eV) m/z: 346 (M<sup>+</sup>). <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  8.62 (d,  $J$  = 7.6 Hz, 1H, H-Ar), 8.07 (d,  $J$  = 9.2 Hz, 1H, H-Ar), 7.86 (d,  $J$  = 9.2 Hz, 1H, H-Ar), 7.68 (d,  $J$  = 5.2 Hz, 2H, H-Ar), 7.61 – 7.54 (m, 1H, H-Ar), 7.53 – 7.45 (m, 1H, H-Ar), 7.44-7.36 (m, 1H, H-Ar), 5.40 (bs, 1H), 2.24 (s, 2H, CH<sub>2</sub>), 1.79 (s, 6H, CH<sub>3</sub>), 1.05 (s, 9H, CH-

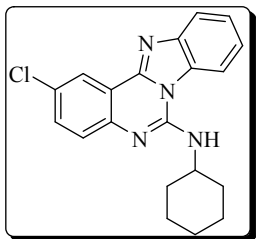
*t*Bu).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 144.3, 143.4, 143.2, 132.1, 127.7, 125.7, 125.3, 124.3, 123.8, 122.7, 119.9, 114.5, 112.1, 57.1, 50.3, 31.8, 31.6, 29.9. Anal. Calcd for  $\text{C}_{22}\text{H}_{26}\text{N}_4$ : C, 76.27; H, 7.56; N, 16.17%. Found: C, 76.36; H, 7.60; N, 16.23.



**N-(2,6-dimethylphenyl)benzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3d).** White powder (yield 67%); m.p. 270-272 °C dec. IR (KBr) ( $\nu_{\text{max}}$  / $\text{cm}^{-1}$ ): 3383, 3051, 2912, 1679, 1586. MS (EI, 70 eV)  $m/z$ : 338 ( $\text{M}^+$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.04 (bs, NH, exchange with solvent), 8.73 (d,  $J = 7.9$  Hz, 1H, H-Ar), 8.26 (d,  $J = 7.8$  Hz, 1H, H-Ar), 7.86 (d,  $J = 7.8$  Hz, 1H, H-Ar), 7.62 – 7.35 (m, 4H, H-Ar), 7.23 (t,  $J = 6.9$  Hz, 1H, H-Ar), 7.11 (d,  $J = 7.5$  Hz, 2H, H-Ar), 6.95 (t,  $J = 7.4$  Hz, 1H, H-Ar), 2.12 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  147.0, 144.3, 143.9, 137.7, 137.1, 132.5, 131.8, 129.1, 128.4, 125.0, 124.7, 123.7, 123.0, 122.7, 119.2, 116.9, 116.1, 111.6, 18.4. Anal. Calcd for  $\text{C}_{22}\text{H}_{18}\text{N}_4$ : C, 78.08; H, 5.36; N, 16.56%. Found: C, 77.98; H, 5.32; N, 16.51.

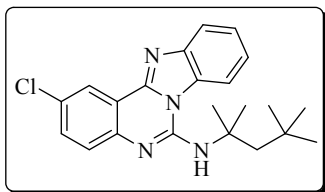


**N-(tert-butyl)-2-chlorobenzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3e).** White powder (yield 90%); m.p. 199-201 °C dec. IR (KBr) ( $\nu_{\text{max}}$  / $\text{cm}^{-1}$ ): 3449, 2972, 1633, 1606. MS (EI, 70 eV)  $m/z$ : 324 ( $\text{M}^+$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{Chloroform}-d$ )  $\delta$  8.54 (s, 1H, H-Ar), 7.98 (d,  $J = 8.0$  Hz, 1H, H-Ar), 7.85 (d,  $J = 8.0$  Hz, 1H, H-Ar), 7.65 – 7.40 (m, 4H, H-Ar), 5.51 (s, 1H), 1.75 (s, 9H,  $\text{CH}-t\text{Bu}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  148.1, 144.1, 143.5, 142.6, 131.9, 128.8, 127.8, 127.1, 125.3, 123.3, 122.8, 120.3, 115.9, 112.0, 53.3, 29.0. Anal. Calcd for  $\text{C}_{18}\text{H}_{17}\text{ClN}_4$ : C, 66.56; H, 5.28; N, 17.25%. Found: C, 66.49; H, 5.22; N, 17.21.



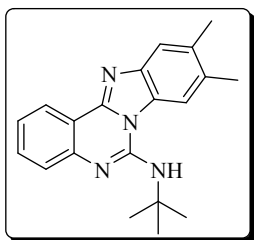
**2-chloro-N-cyclohexylbenzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3f).** White powder (yield 64%); m.p. 186-188 °C. IR (KBr)  $\nu_{\text{max}}$  (KBr) ( $\nu_{\text{max}}$  / $\text{cm}^{-1}$ ): 3443, 2919, 2853, 1626, 1600. MS (EI, 70 eV)  $m/z$ : 350 ( $\text{M}^+$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.50 (s, 1H, H-Ar), 8.01 (d,  $J = 8.1$  Hz, 1H, H-Ar), 7.80 (d,  $J = 8.2$  Hz, 1H, H-

Ar), 7.64-7.49 (m, 3H, H-Ar), 7.44 (t,  $J = 7.7$  Hz, 1H, H-Ar), 5.31 (d,  $J = 6.8$  Hz, 1H), 4.31 (bs, 1H CH-cy), 2.51 – 2.23 (m, 2H, CH<sub>2</sub>-cy), 1.99 – 1.81 (m, 2H, CH<sub>2</sub>-cy), 1.79-1.69 (m, 1H, CH<sub>2</sub>-cy), 1.67-1.25 (m, 5H, CH<sub>2</sub>-cy). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  148.21, 144.49, 143.01, 132.04, 128.85, 127.94, 126.85, 125.38, 123.49, 122.93, 120.54, 120.06, 116.12, 112.06, 50.41, 33.13, 25.74, 24.80. Anal. Calcd for C<sub>20</sub>H<sub>19</sub>ClN<sub>4</sub>: , 68.47; H, 5.46; N, 15.97%. Found: C, 68.57; H, 5.53; N, 15.91.



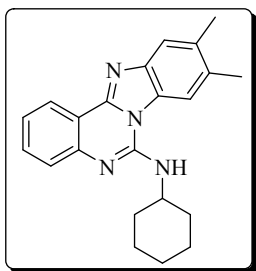
**2-chloro-N-(2,4,4-trimethylpentan-2-yl)benzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3g).** White powder (yield 62%); m.p. 143-145 °C dec. IR (KBr) ( $\nu_{\max}$  /cm<sup>-1</sup>): 3456, 2965, 2886, 1639, 1606. MS (EI, 70 eV)m/z: 380 (M<sup>+</sup>). <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  8.53 (s, 1H, H-Ar), 8.03 (d,  $J = 7.9$  Hz, 1H, H-Ar), 7.82 (d,  $J = 8.1$  Hz, 1H, H-Ar), 7.57 (bs, 3H, H-Ar), 7.47 (t,  $J = 7.9$  Hz, 1H, H-Ar), 5.39 (s, 1H),

2.21 (s, 2H, CH<sub>2</sub>), 1.77 (s, 6H, CH<sub>3</sub>), 1.03 (s, 9H, CH- *t*Bu). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  148.24, 144.02, 143.48, 142.71, 132.12, 129.06, 127.90, 127.05, 125.34, 123.59, 122.94, 120.48, 115.80, 111.85, 57.18, 50.43, 31.84, 31.58, 29.94. Anal. Calcd for C<sub>22</sub>H<sub>25</sub>ClN<sub>4</sub>. C, 69.37; H, 6.62; N, 14.71 %. Found: C, 69.31; H, 6.67; N, 14.66.

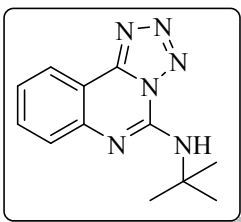


**N-(tert-butyl)-9,10-dimethylbenzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3h).** White powder (yield 91%); m.p. 225-227 °C dec. IR (KBr) ( $\nu_{\max}$  /cm<sup>-1</sup>): 3416, 2952, 2919, 1606, 1527. MS (EI, 70 eV)m/z: 318 (M<sup>+</sup>). <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  8.54 (d,  $J = 8.0$  Hz, 1H, H-Ar), 7.74 (s, 1H, H-Ar), 7.72 – 7.60 (m, 2H, H-Ar), 7.57 (s, 1H, H-Ar), 7.44 – 7.32 (m, 1H, H-Ar), 5.45 (bs, 1H), 2.47 (s, 3H, CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>), 1.76 (s,

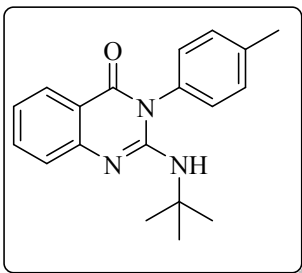
9H, CH- *t*Bu). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  148.73, 144.05, 143.56, 143.00, 134.16, 131.52, 131.31, 126.38, 125.59, 123.96, 123.52, 120.22, 115.40, 112.35, 53.04, 29.16, 21.05, 20.45. Anal. Calcd for C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>: C, 75.44; H, 6.96; N, 17.60%. Found: C, 75.35; H, 6.89; N, 17.52.



**N-cyclohexyl-9,10-dimethylbenzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3i).** White powder (yield 71%); m.p. 226-228 °C dec. IR (KBr) ( $\nu_{\max}$  / $\text{cm}^{-1}$ ): 3390, 2925, 2859, 1600, 1560. MS (EI, 70 eV)m/z: 344 (M<sup>+</sup>). <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  8.52 (d,  $J = 7.9$  Hz, 1H, H-Ar), 7.78 (s, 1H, H-Ar), 7.71 – 7.57 (m, 2H, H-Ar), 7.54 (s, 1H, H-Ar), 7.45 – 7.33 (m, 1H, H-Ar), 5.27 (d,  $J = 7.2$  Hz, 1H, H-Ar), 4.34 (bs, 1H, CH-cy), 2.50 (s, 3H, CH<sub>3</sub>), 2.47 (s, 3H, CH<sub>3</sub>), 2.37 – 2.27 (m, 1H, CH<sub>2</sub>-cy), 1.95 – 1.82 (m, 2H, CH<sub>2</sub>-cy), 1.81 – 1.69 (m, 2H, CH<sub>2</sub>-cy), 1.68 – 1.26 (m, 5H, CH<sub>2</sub>-cy). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  148.71, 144.54, 144.43, 143.22, 134.31, 131.68, 131.41, 126.46, 125.28, 124.09, 123.52, 120.41, 115.45, 112.38, 50.25, 33.20, 26.21, 24.91, 21.15, 20.77. Anal. Calcd for C<sub>20</sub>H<sub>24</sub>N<sub>4</sub>: C, 76.71; H, 7.02; N, 16.27 %. Found: C, 76.77; H, 6.97; N, 16.20.

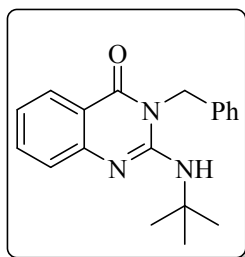


**N-(tert-butyl)tetrazolo[1,5-c]quinazolin-5-amine (6).** White powder (yield 86%); m.p. 235-237 °C dec. IR (KBr) ( $\nu_{\max}$  / $\text{cm}^{-1}$ ): 3406, 2968, 1643, 1537. MS (EI, 70 eV) m/z: 242 (M<sup>+</sup>). <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  8.44 (d,  $J = 7.8$  Hz, 1H, H-Ar), 7.80-7.72 (m, 2H, H-Ar), 7.54 (s, 1H, H-Ar), 7.46 (t, 1H,  $J = 7.0$  Hz, H-Ar), 6.16 (bs, 1H, NH), 1.69 (s, 9H, CH- *t*Bu). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  149.71, 144.97, 138.85, 133.39, 126.31, 124.64, 124.60, 111.07, 53.30, 28.77. Anal. Calcd for C<sub>12</sub>H<sub>14</sub>N<sub>6</sub>: C, 59.49; H, 5.82; N, 34.69 %. Found: C, 59.40; H, 5.86; N, 34.62.



1565, 1474. <sup>1</sup>H NMR

**2-(tert-butylamino)-3-(*p*-tolyl)quinazolin-4(3H)-one (7a).** White powder (yield 49%); m.p. 150-151 °C (Lit.<sup>6</sup> m.p. 148-150 °C). IR (KBr) ( $\nu_{\max}$  / $\text{cm}^{-1}$ ): 3407, 1652, 1562, 1475. <sup>1</sup>H NMR (300 MHz, Chloroform-*d*)  $\delta$  8.13 (d,  $J = 8.1$  Hz, 1H, H-Ar), 7.61 (t,  $J = 7.5$ , 1H, H-Ar), 7.41-7.44 (m, 1H, H-Ar), 7.38-7.40 (m, 1H, H-Ar), 7.18-7.14 (m, 3H, H-Ar), 4.01 (s, 1H, NH), 2.46 (s, 3H, CH<sub>3</sub>), 1.41 (s, 9H, CH- *t*Bu).

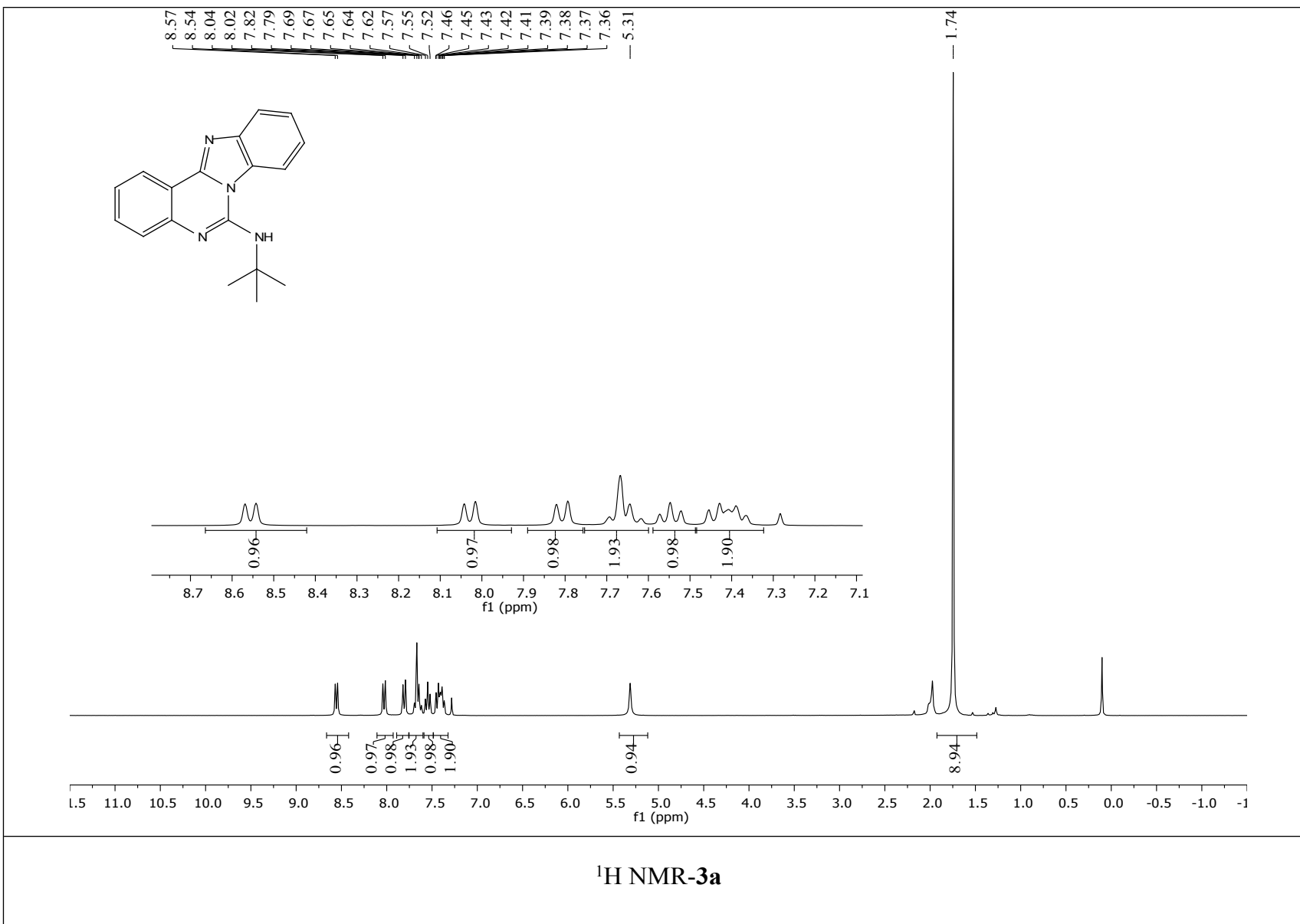


**3-benzyl-2-(tert-butylamino)quinazolin-4(3H)-one (7b).** White powder (yield 51%); m.p. 141-143 °C (Lit.<sup>6</sup> m.p. 138-140 °C). IR (KBr) ( $\nu_{\max}$  / $\text{cm}^{-1}$ ): 3432, 1682, (300 MHz, Chloroform-*d*)  $\delta$  8.20 (d,  $J = 8.1$  Hz, 1H, H-Ar), 7.63 – 7.58 (m, 1H, H-

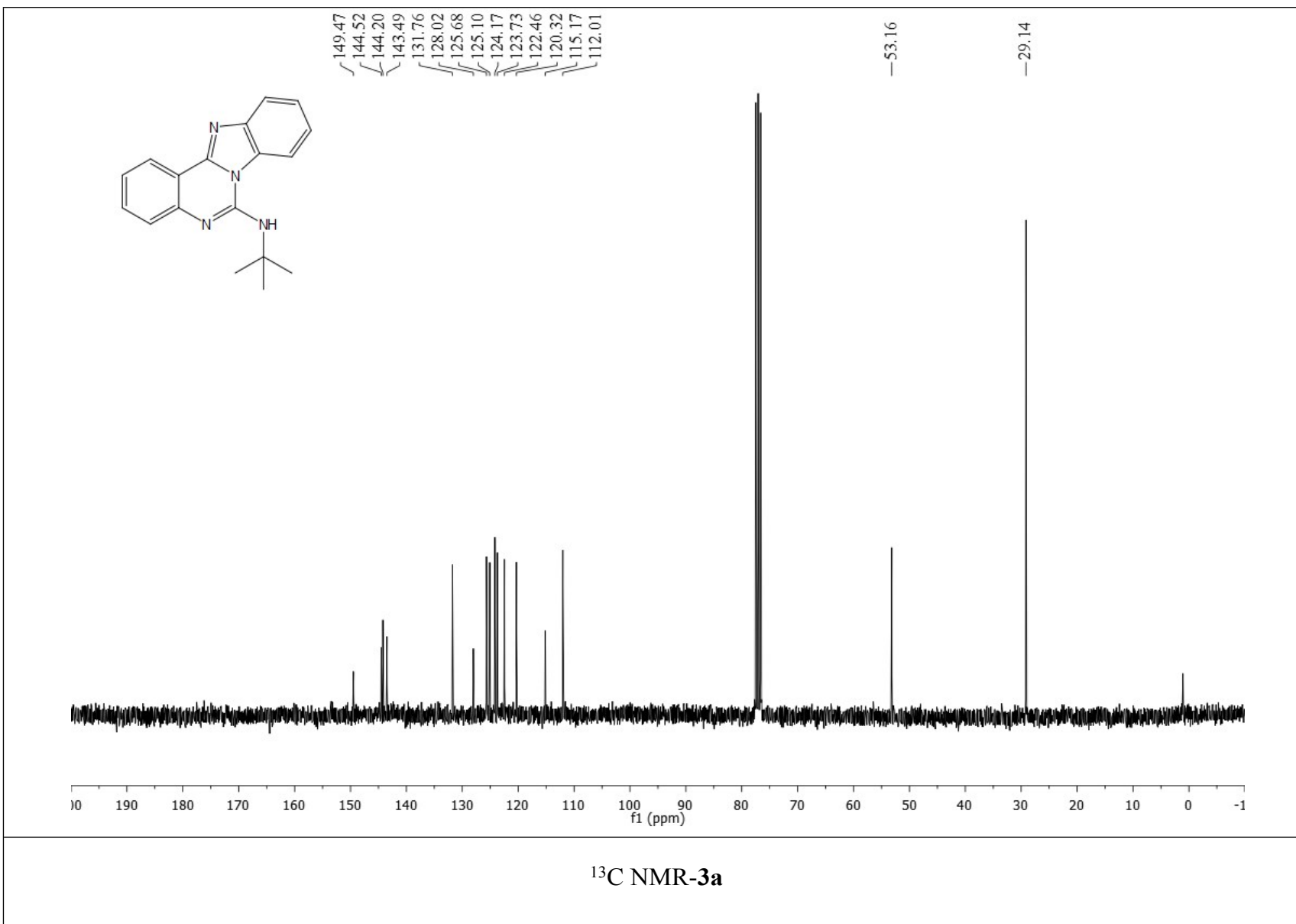
Ar), 7.41-7.34 (m, 4H, H-Ar), 7.30-7.28 (m, 2H, H-Ar), 7.20 (t,  $J = 8.1$ , 1H, H-Ar), 5.32 (s, 2H, CH<sub>2</sub>Ph), 4.35 (bs, 1H, NH), 1.34 (s, 9H, CH- *t*Bu).

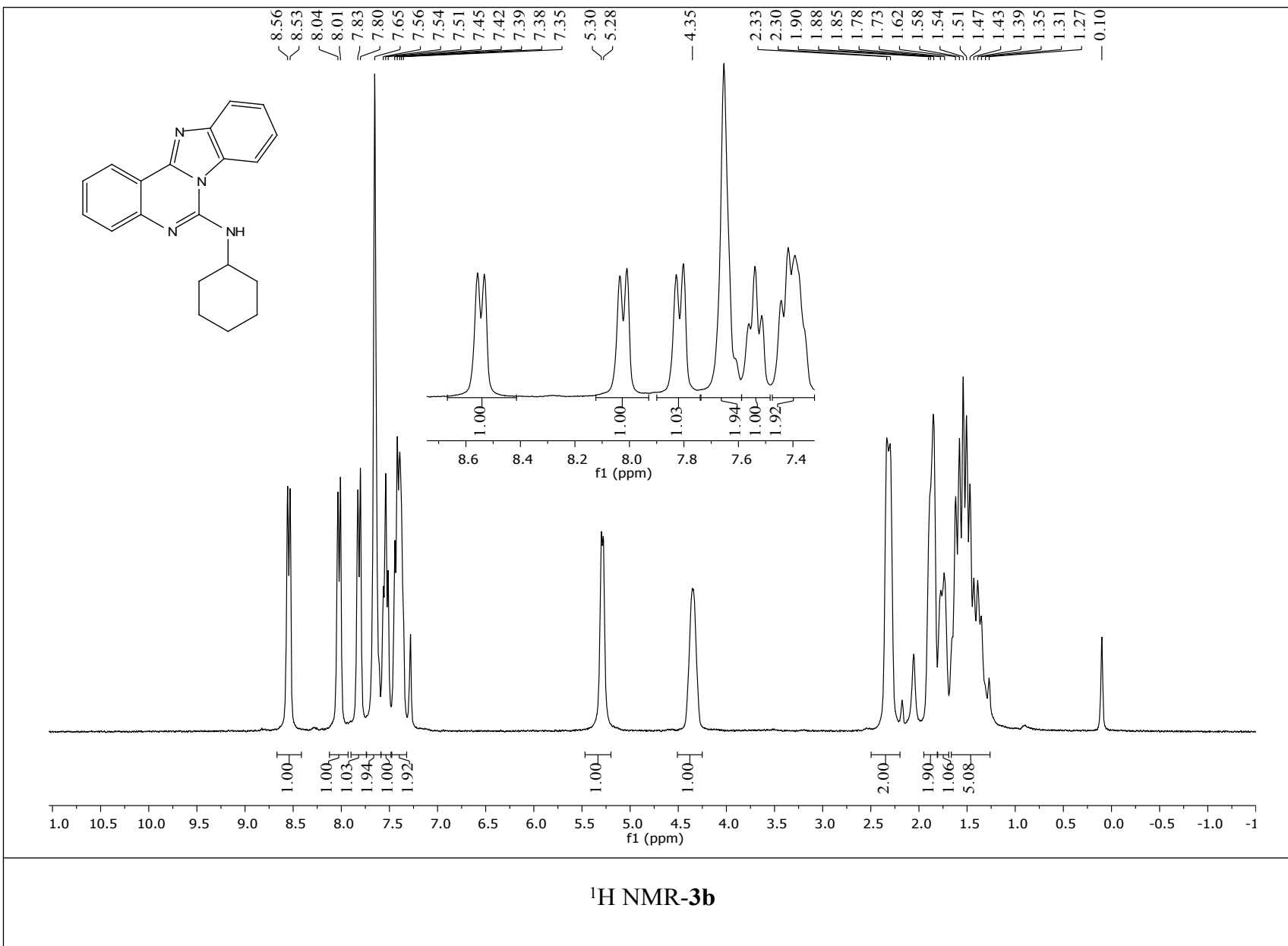
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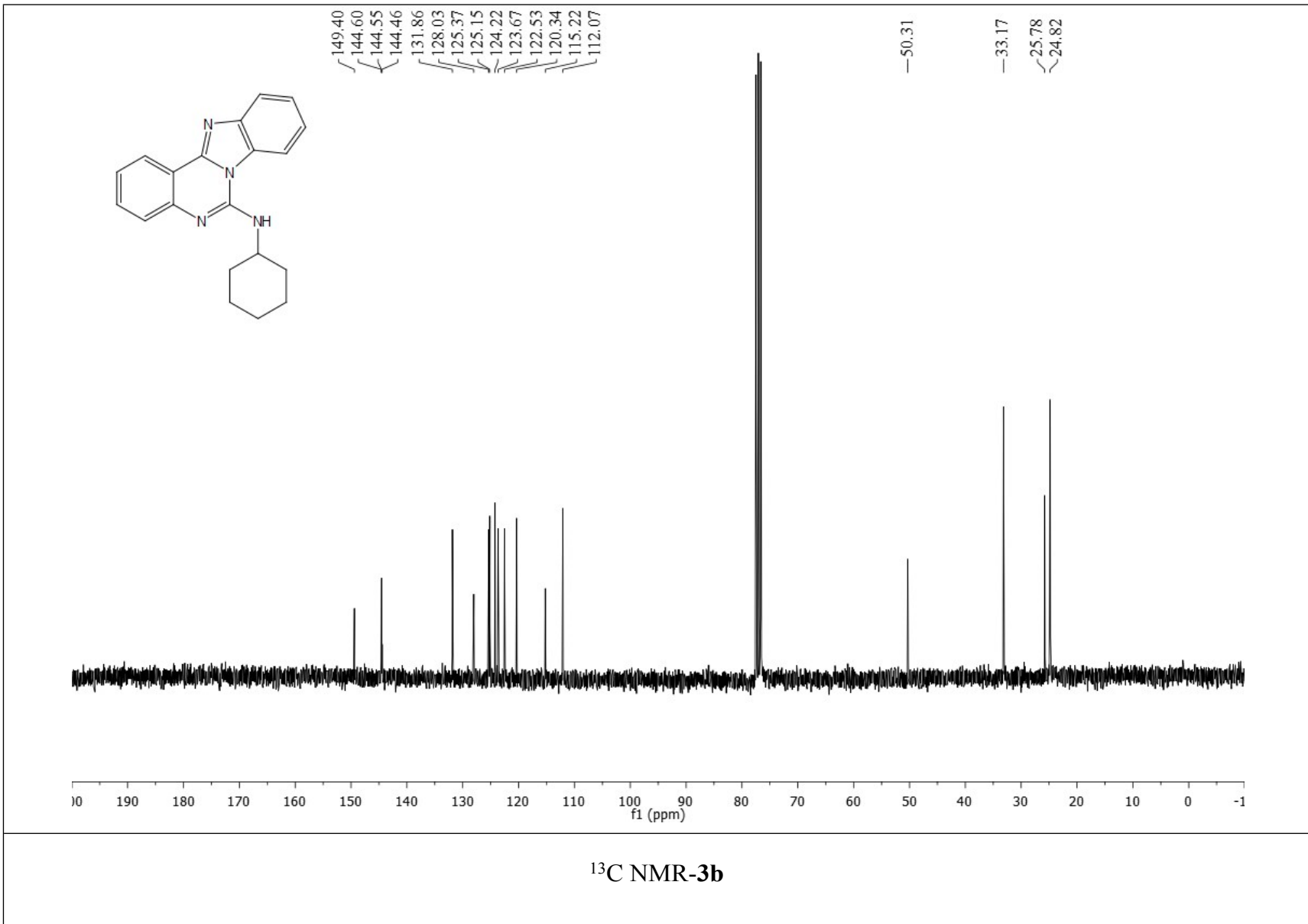
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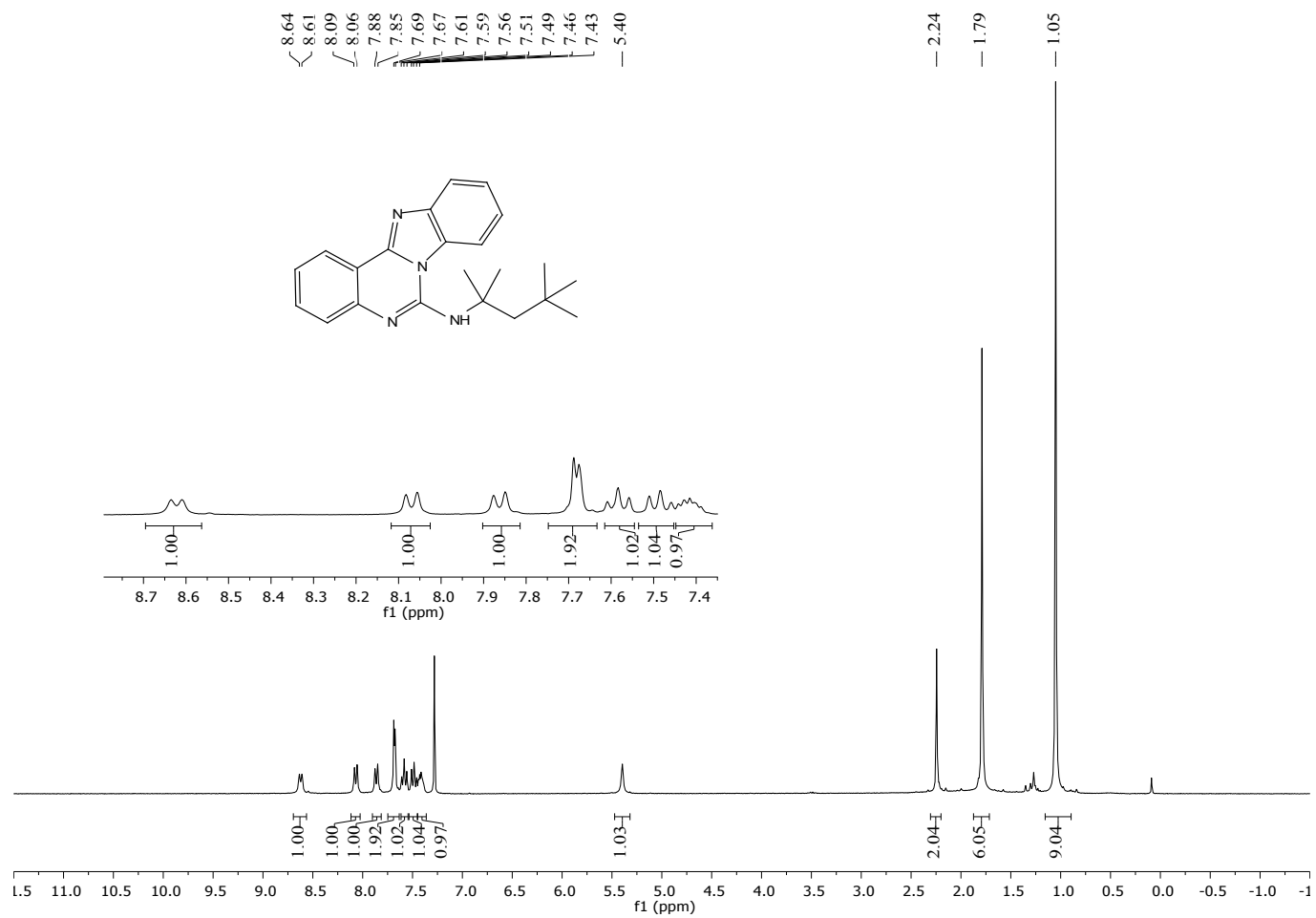




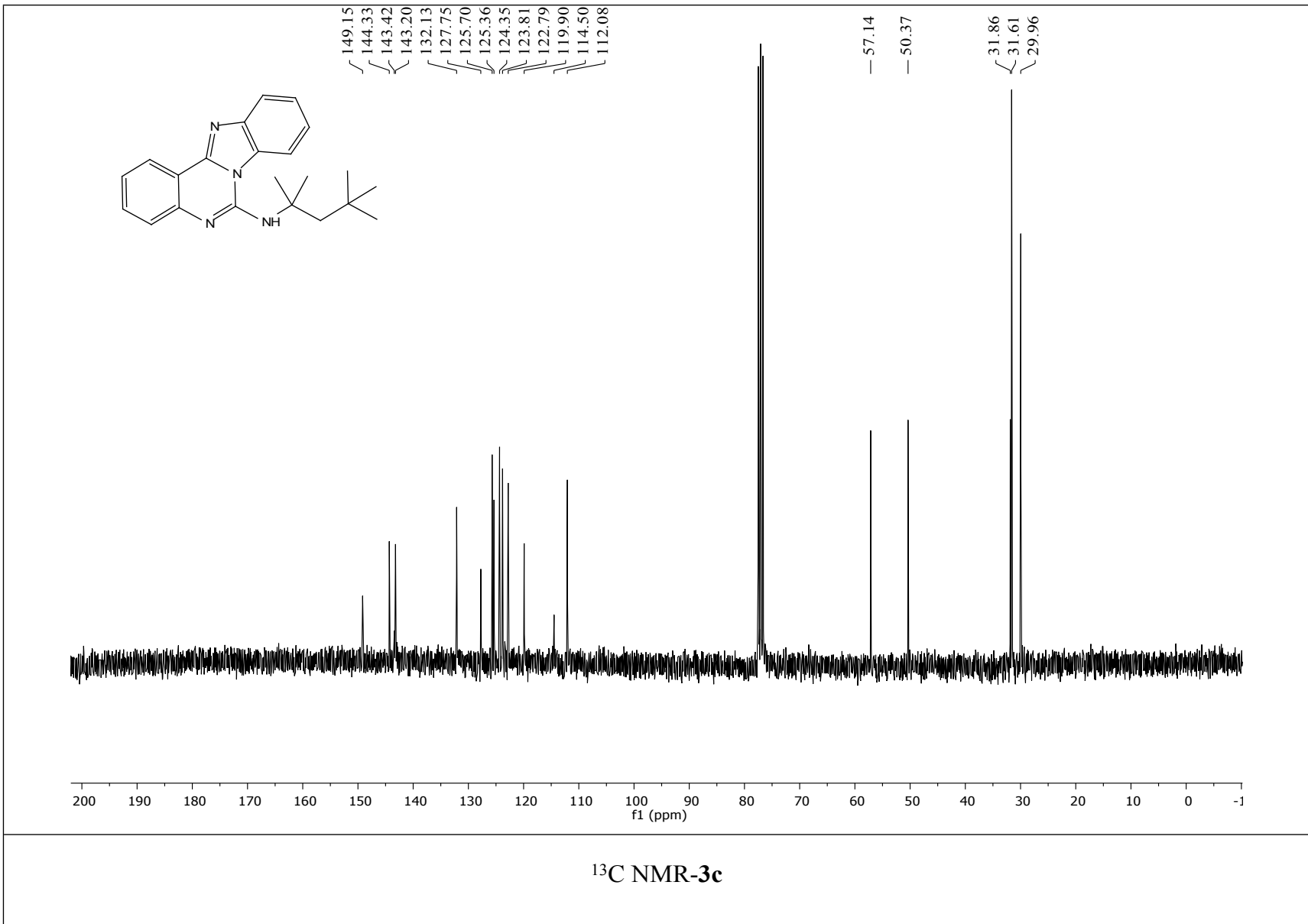


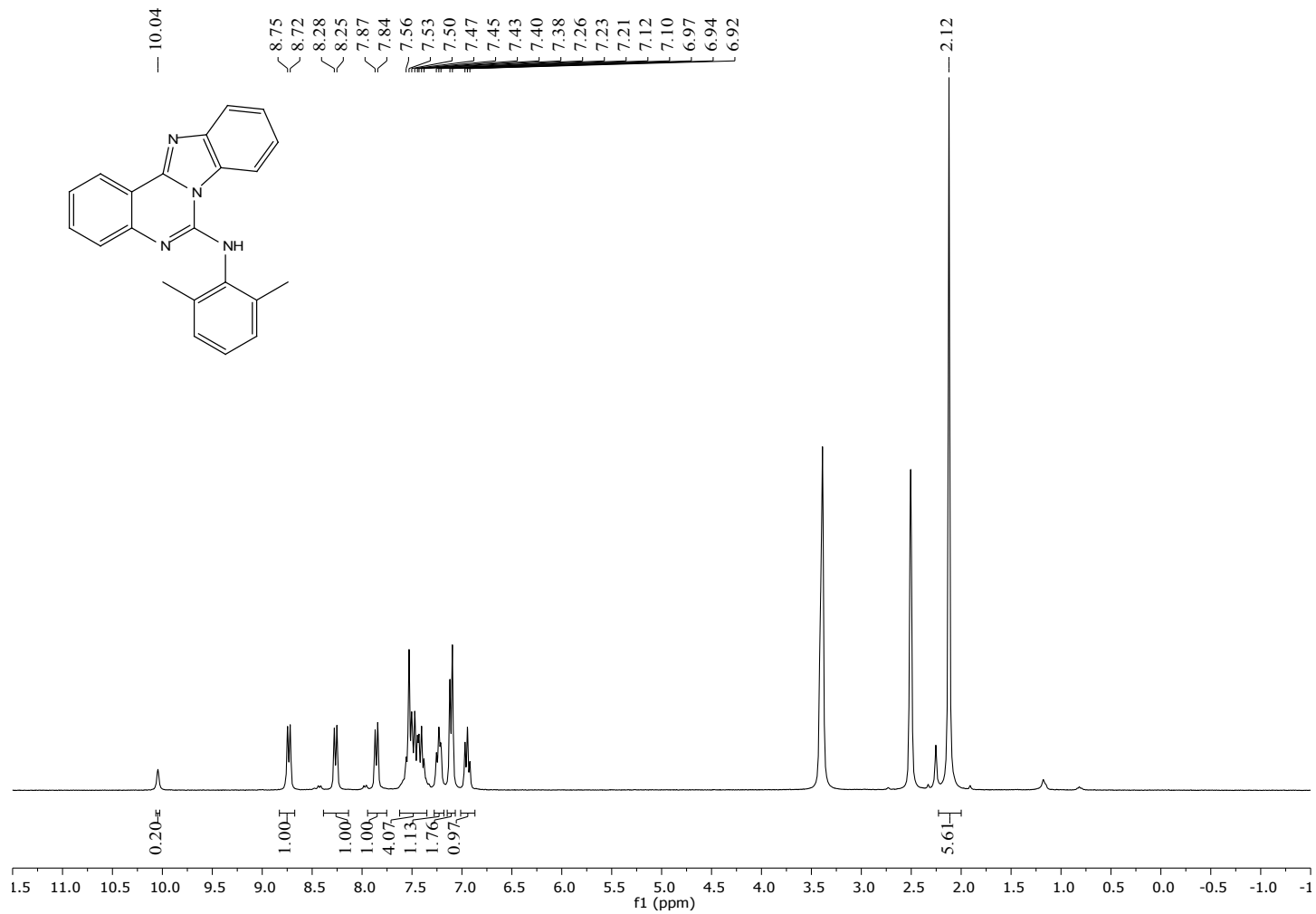




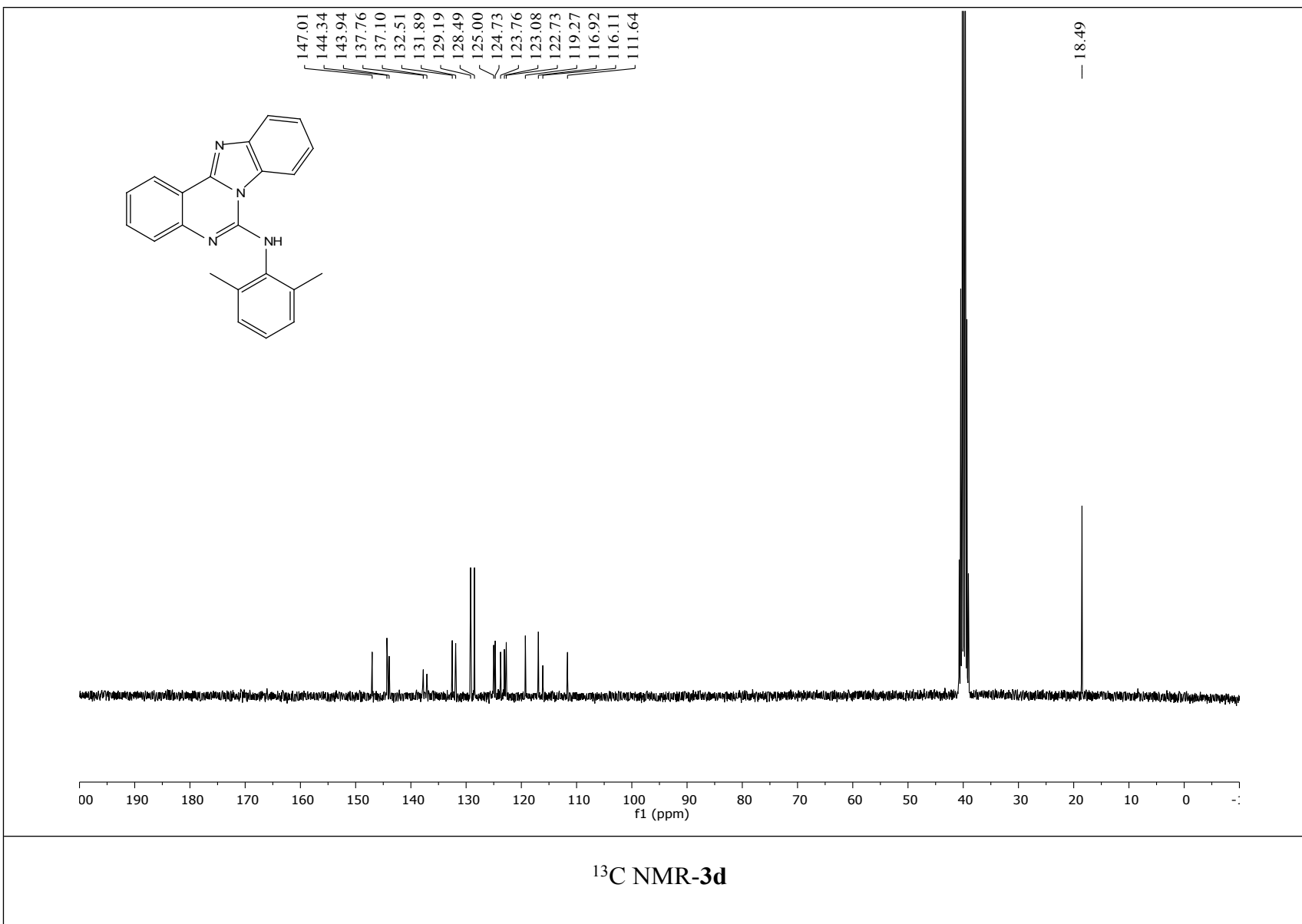


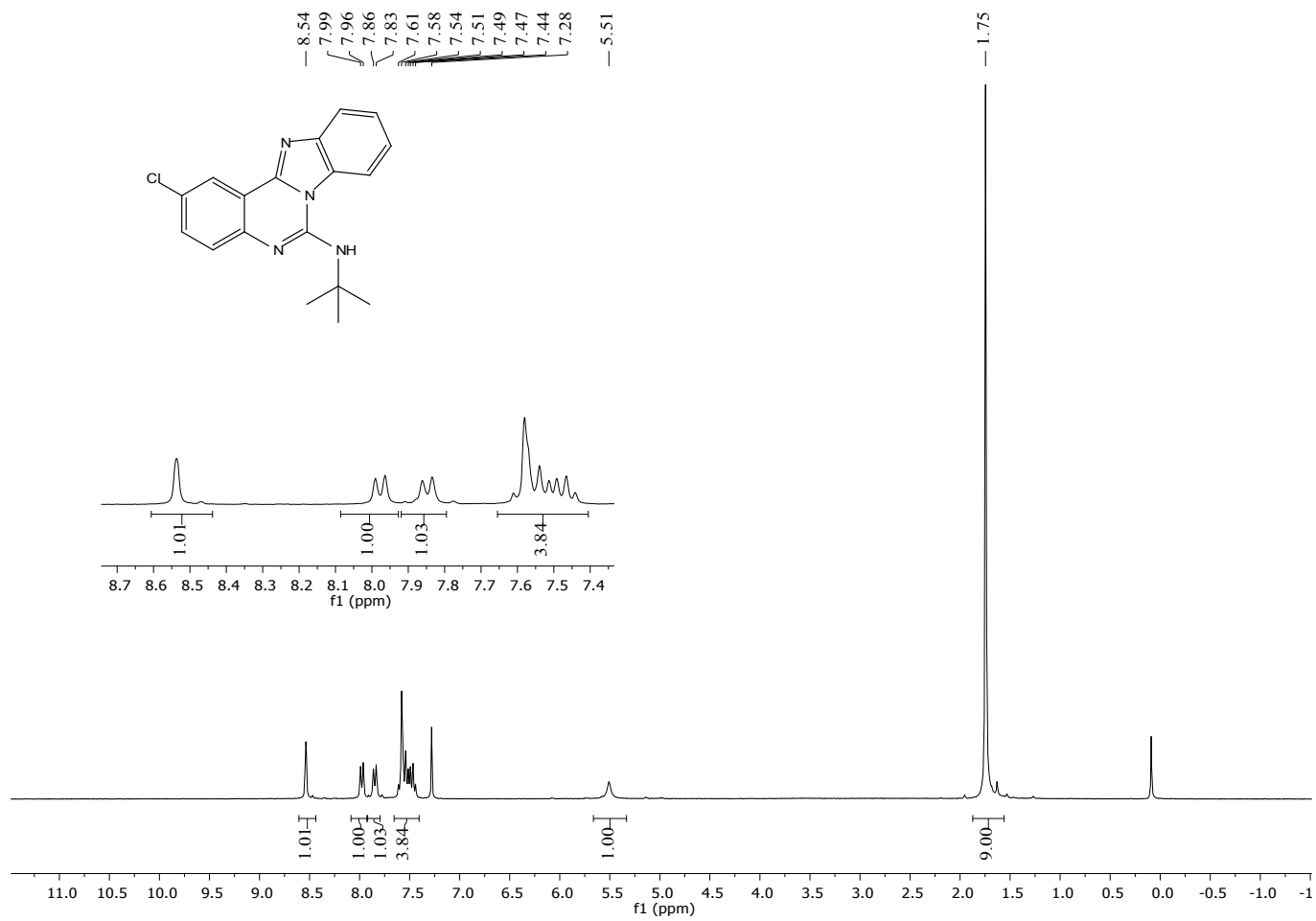
<sup>1</sup>H NMR-3c





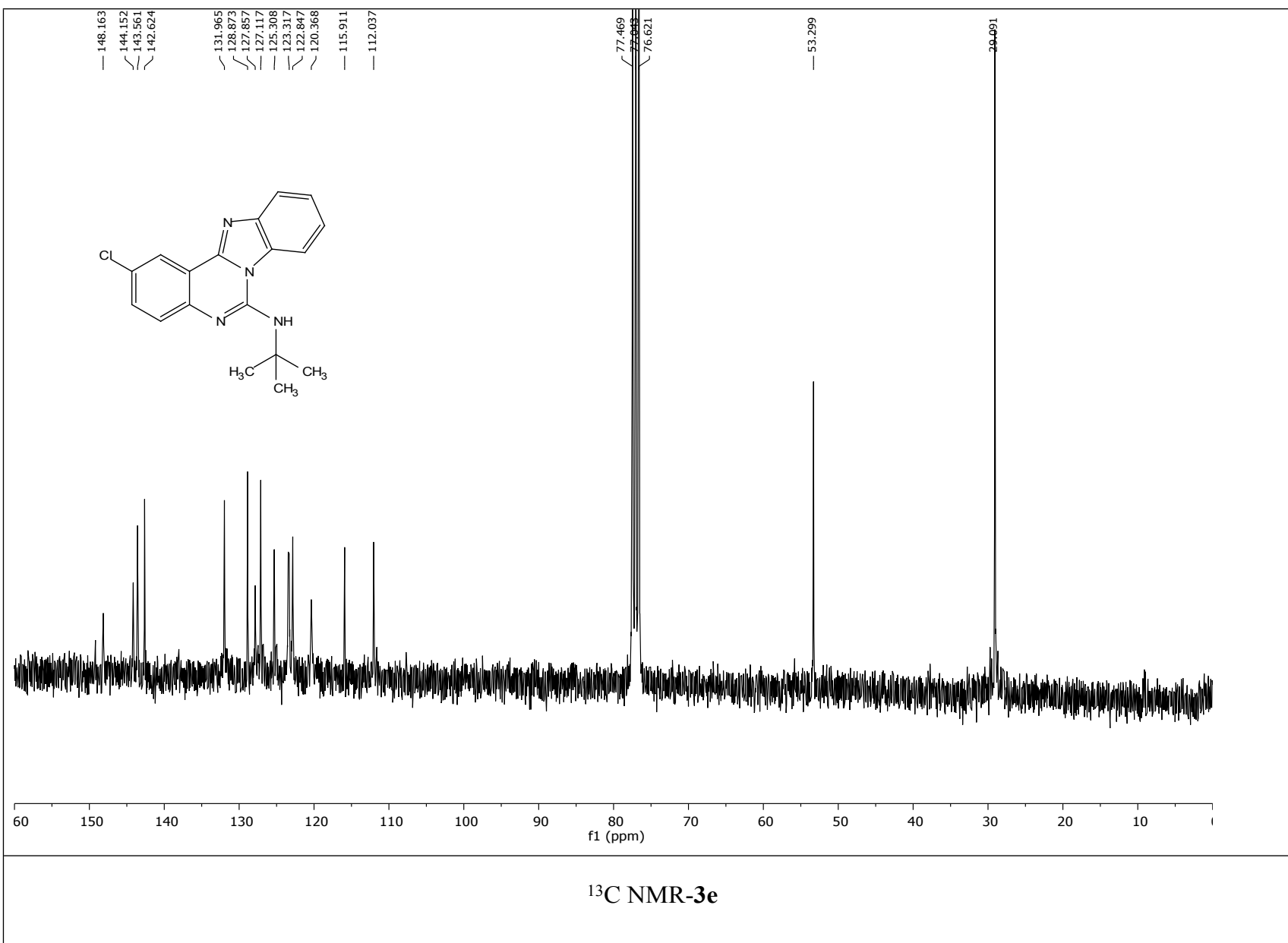
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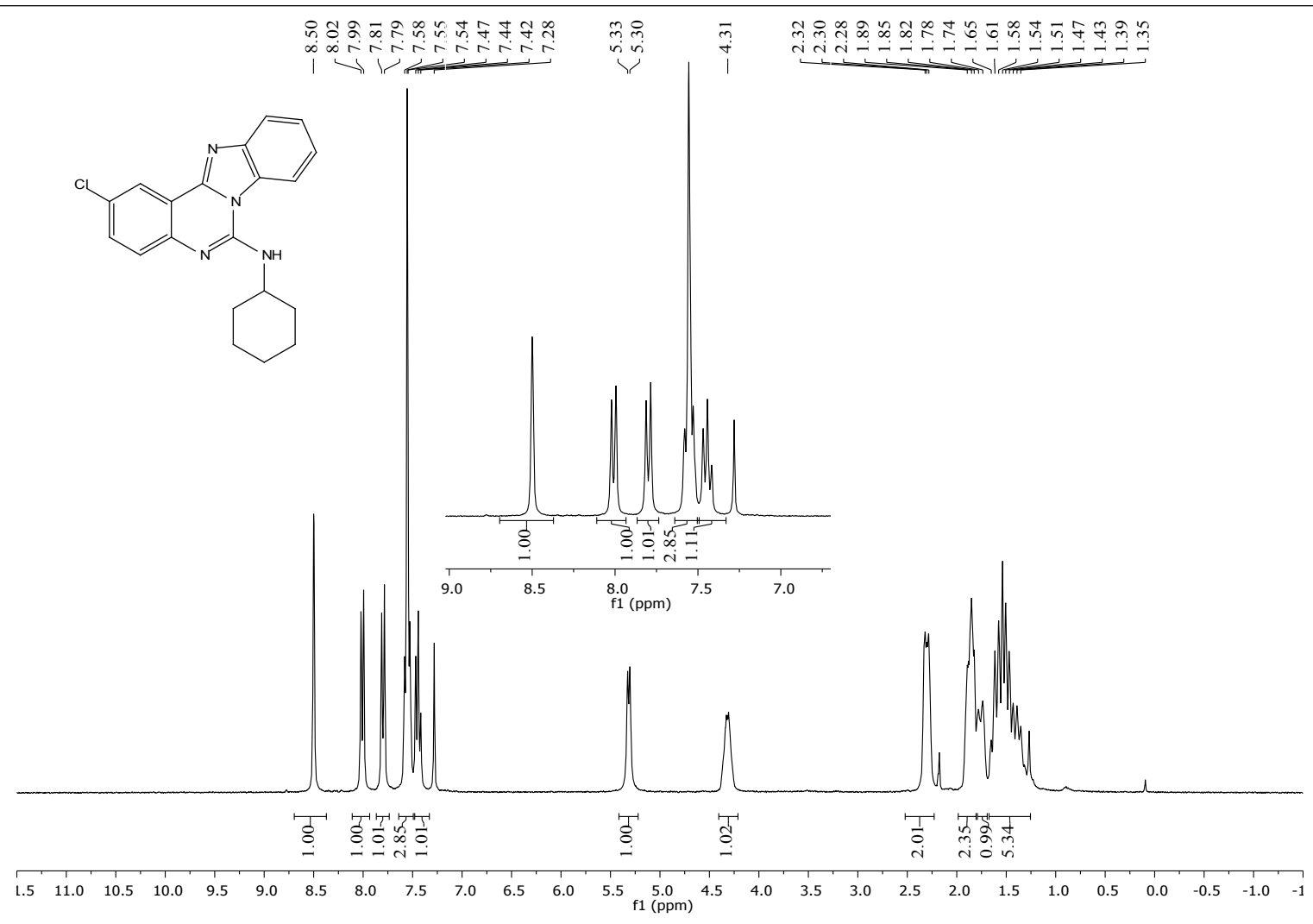




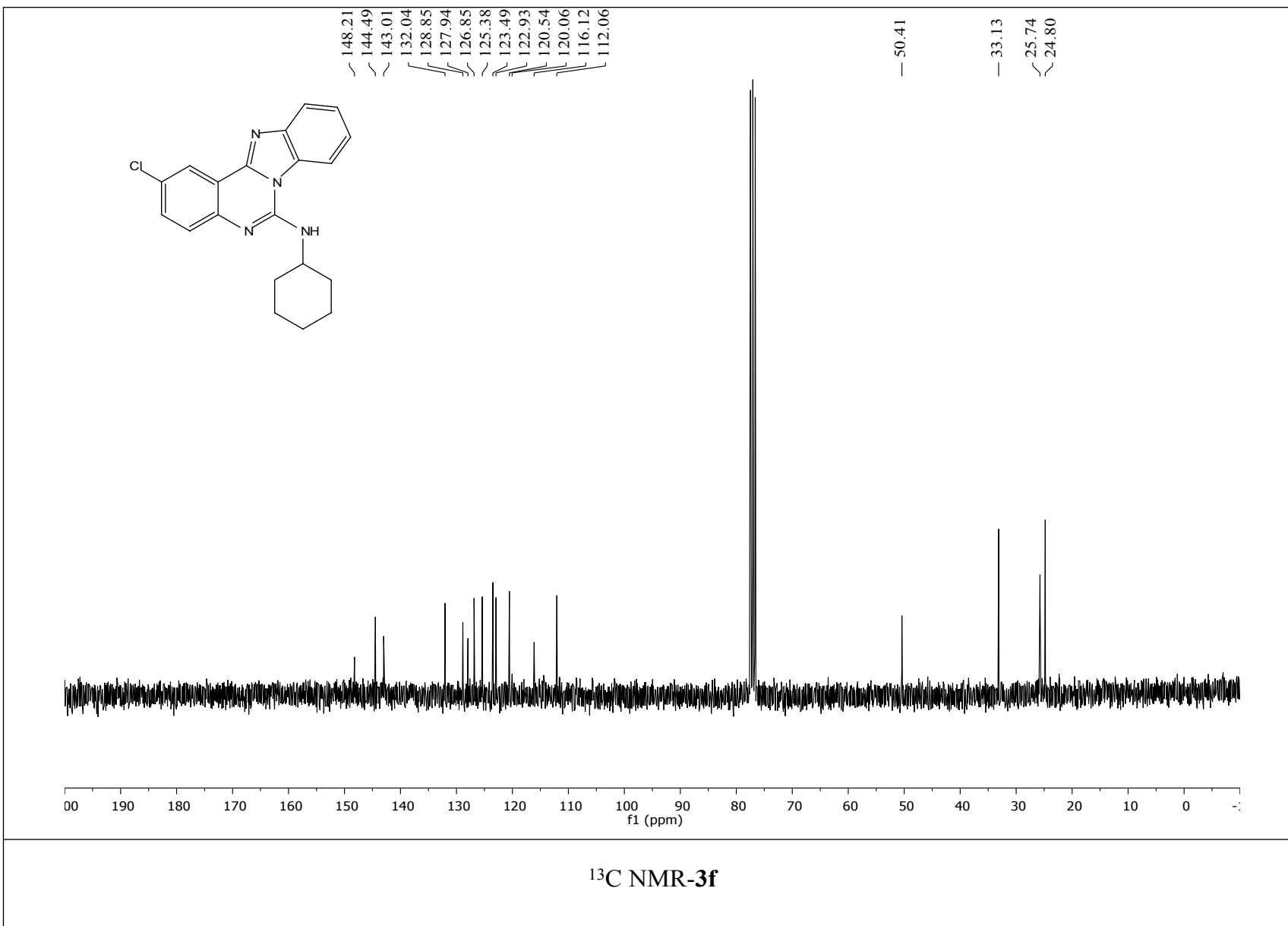
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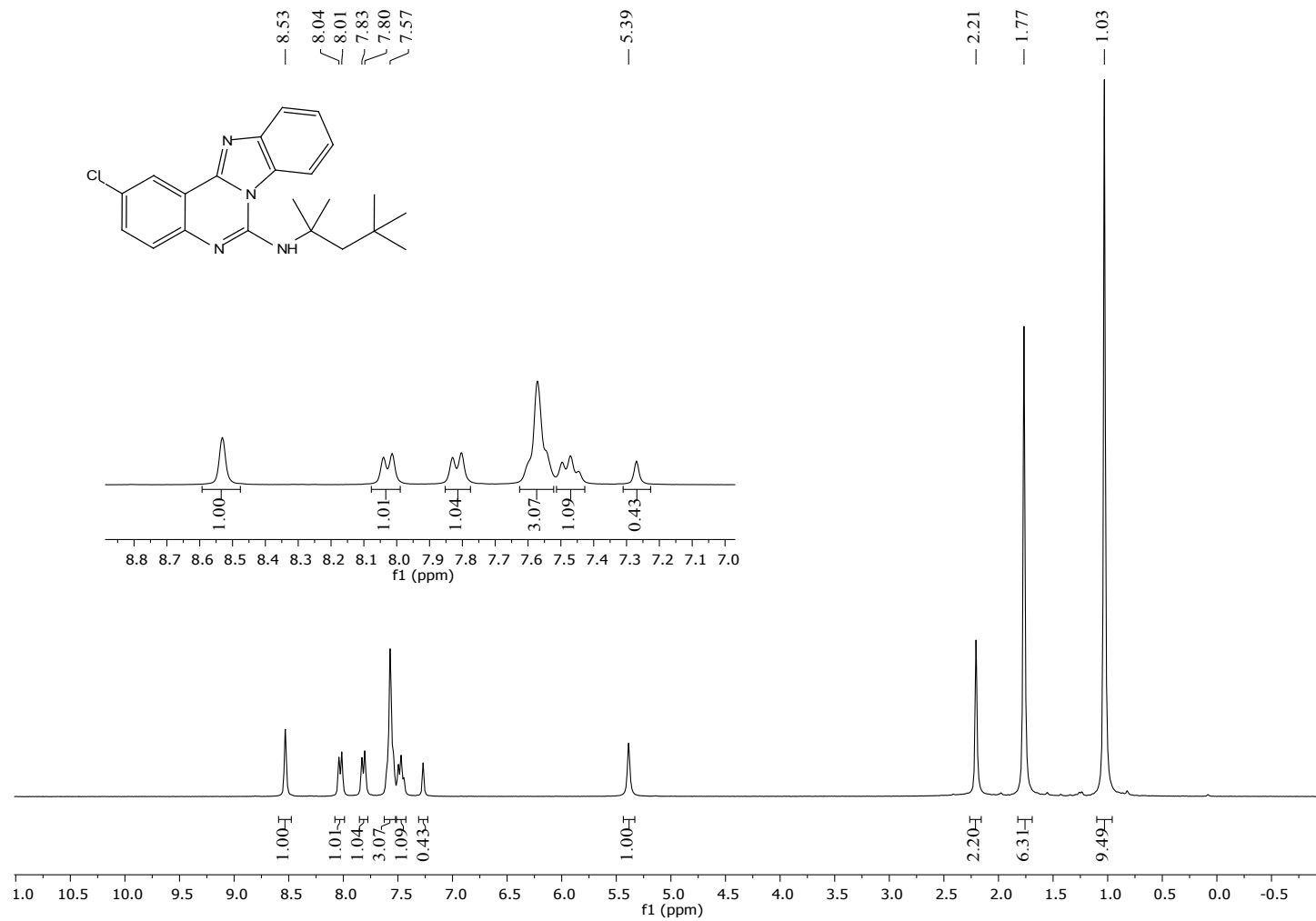




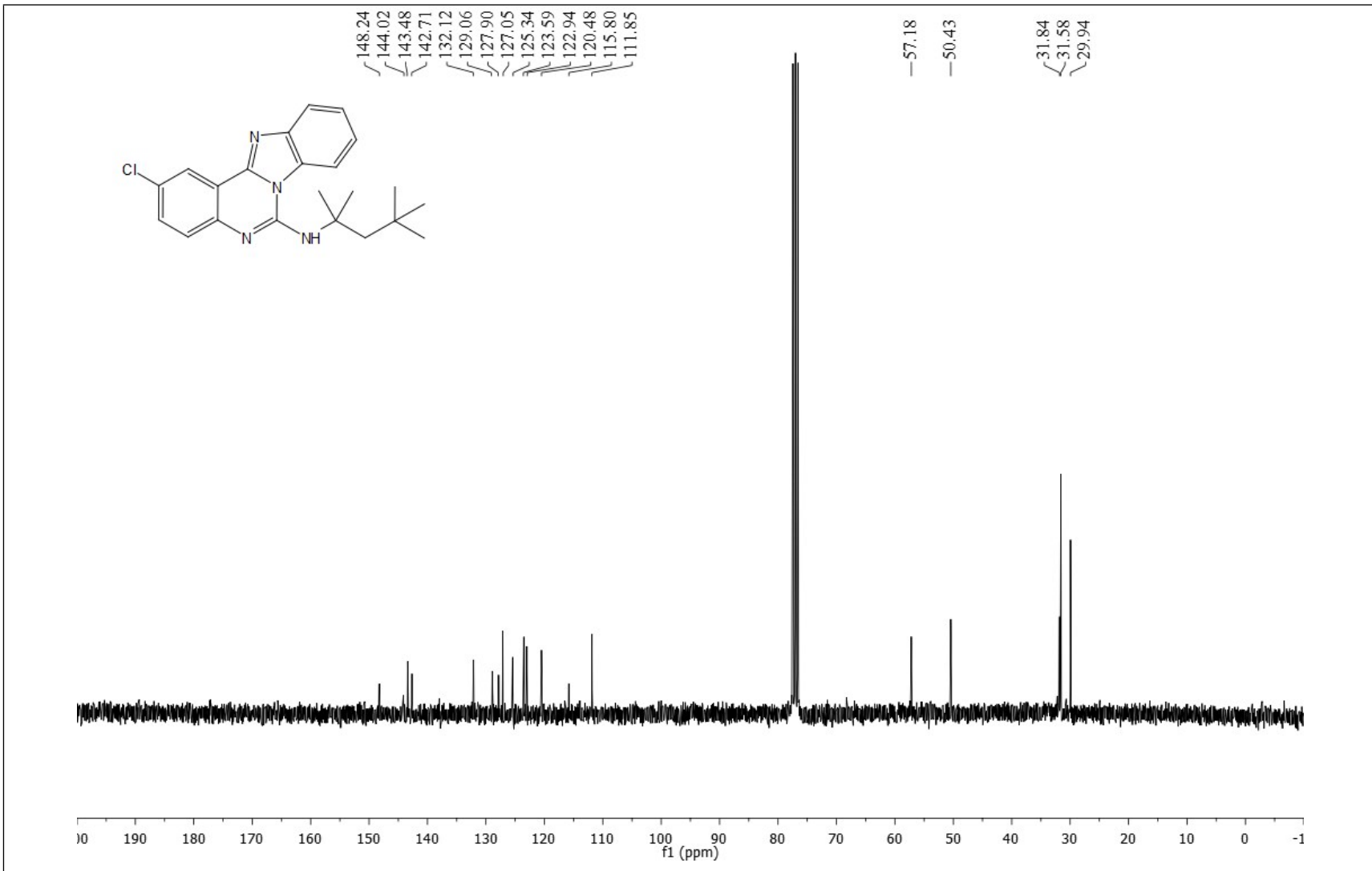


<sup>1</sup>H NMR-3f

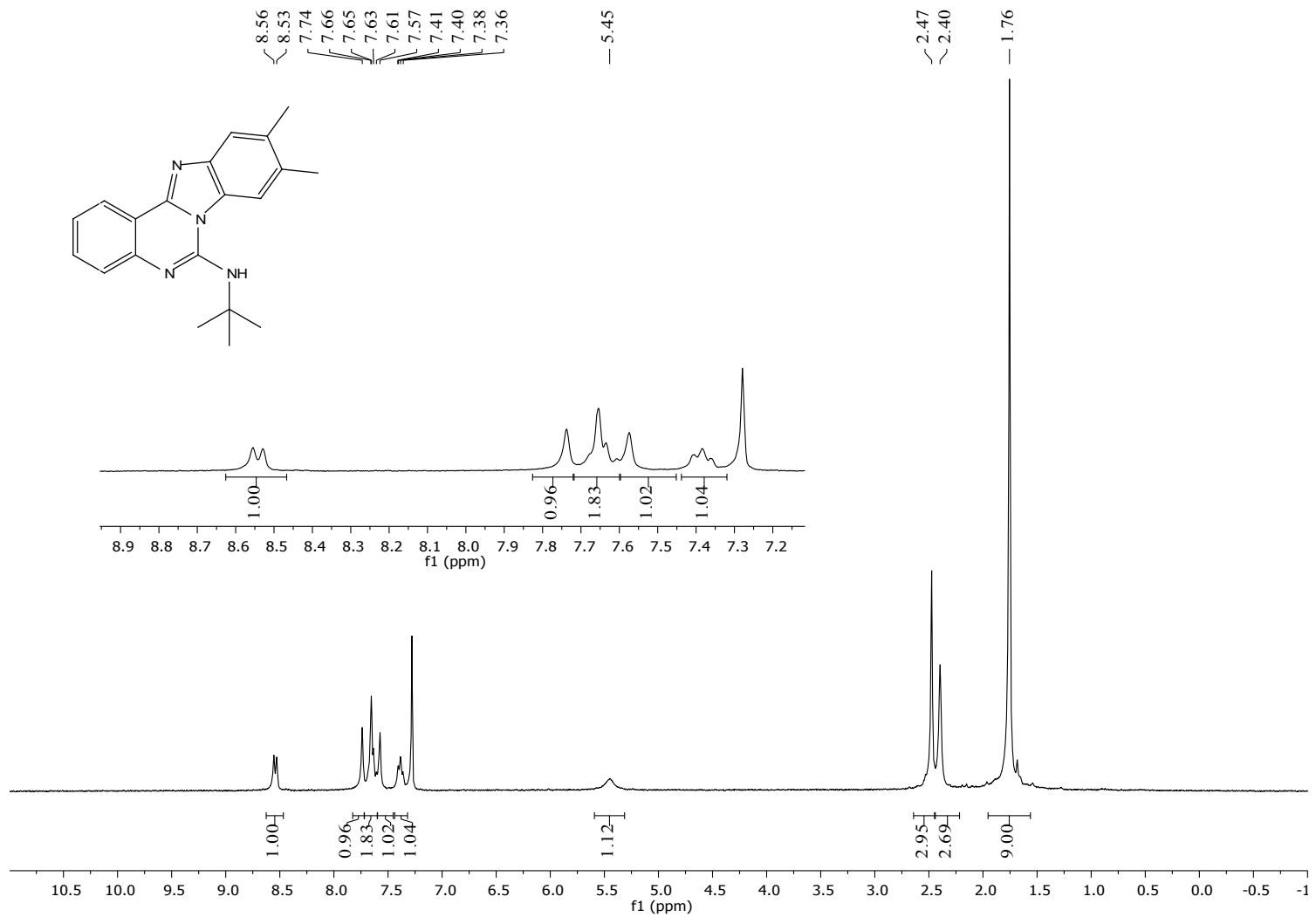




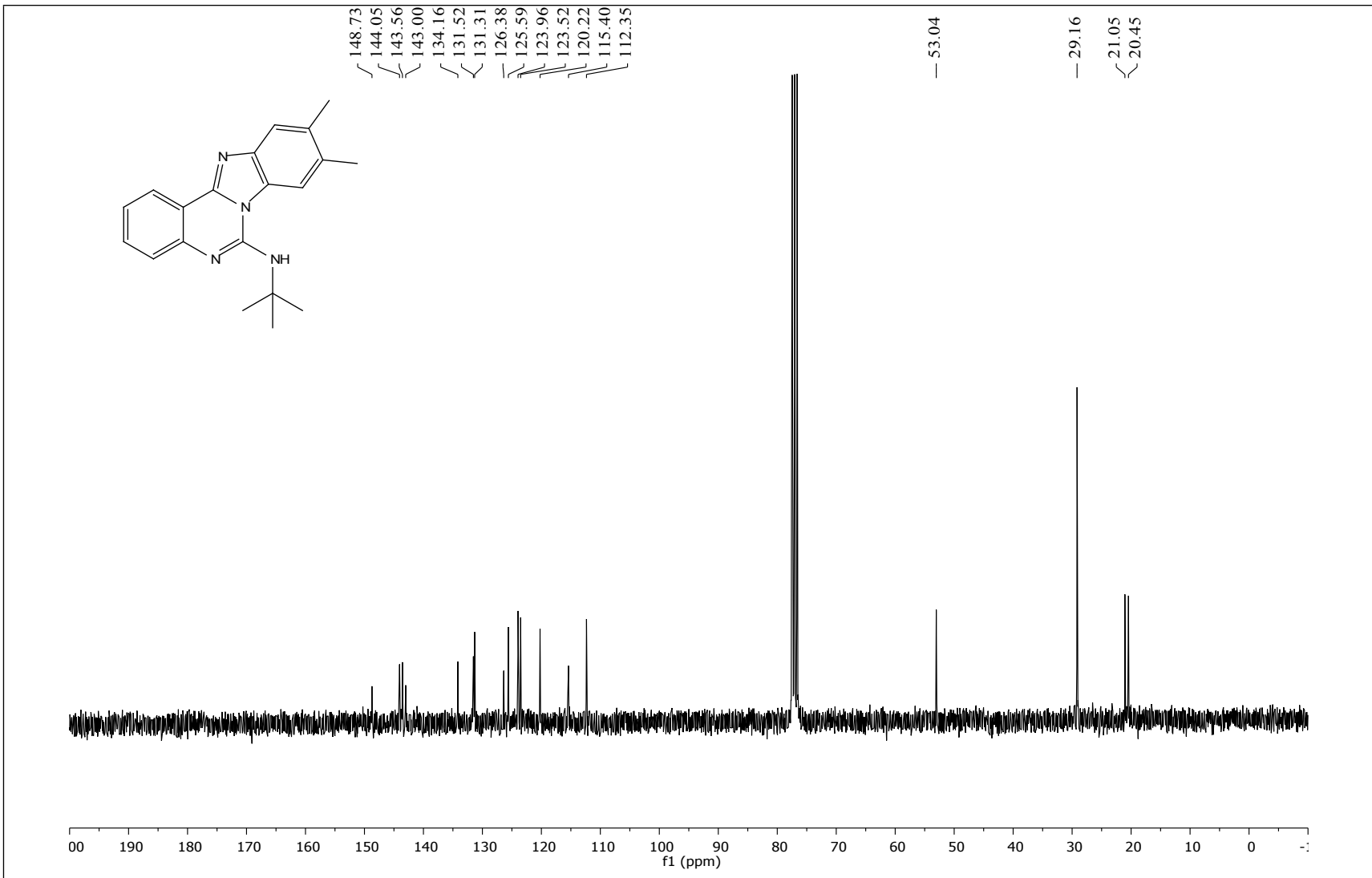
$^1\text{H}$  NMR-3g



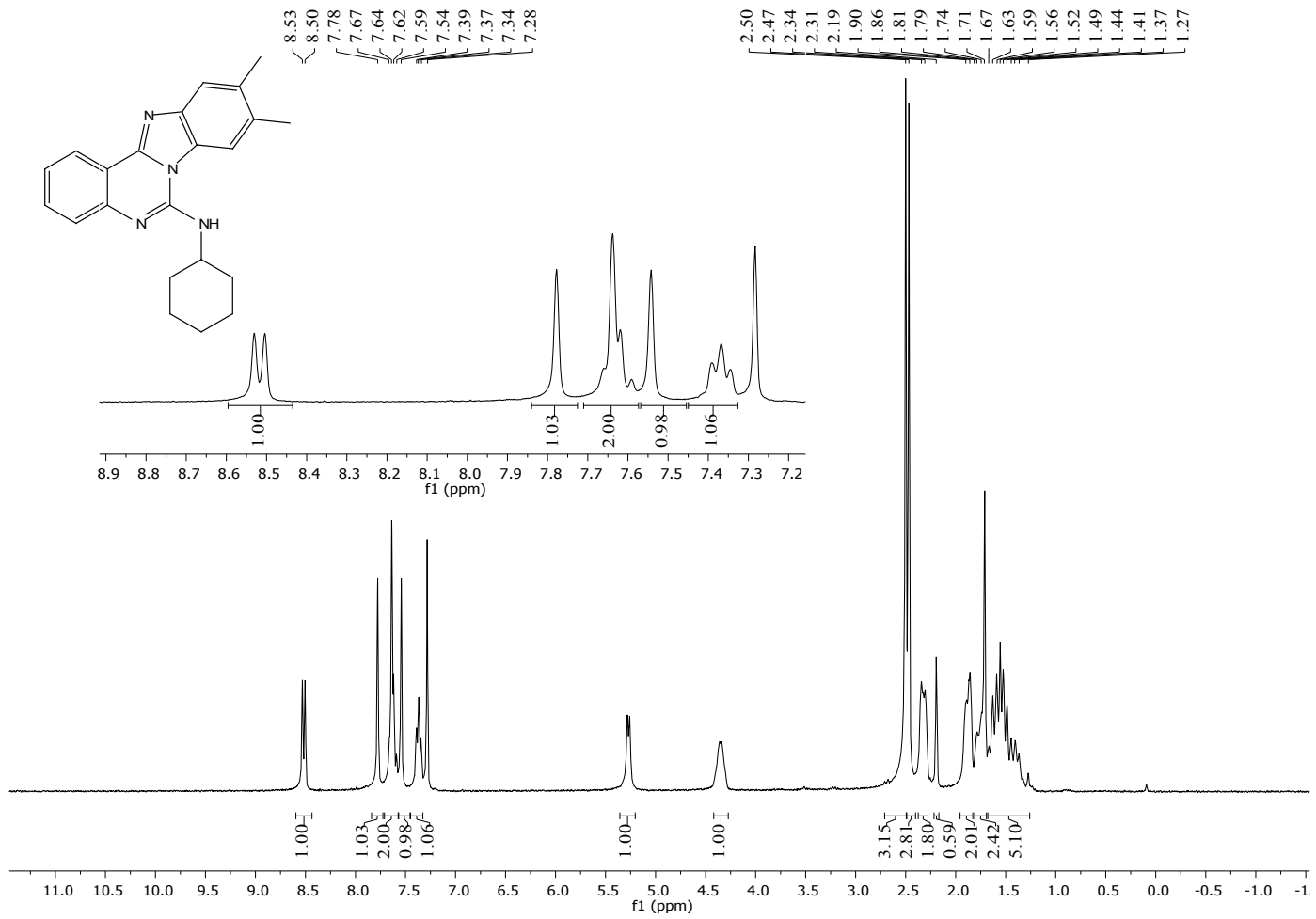
<sup>13</sup>C NMR-3g



<sup>1</sup>H NMR-3h

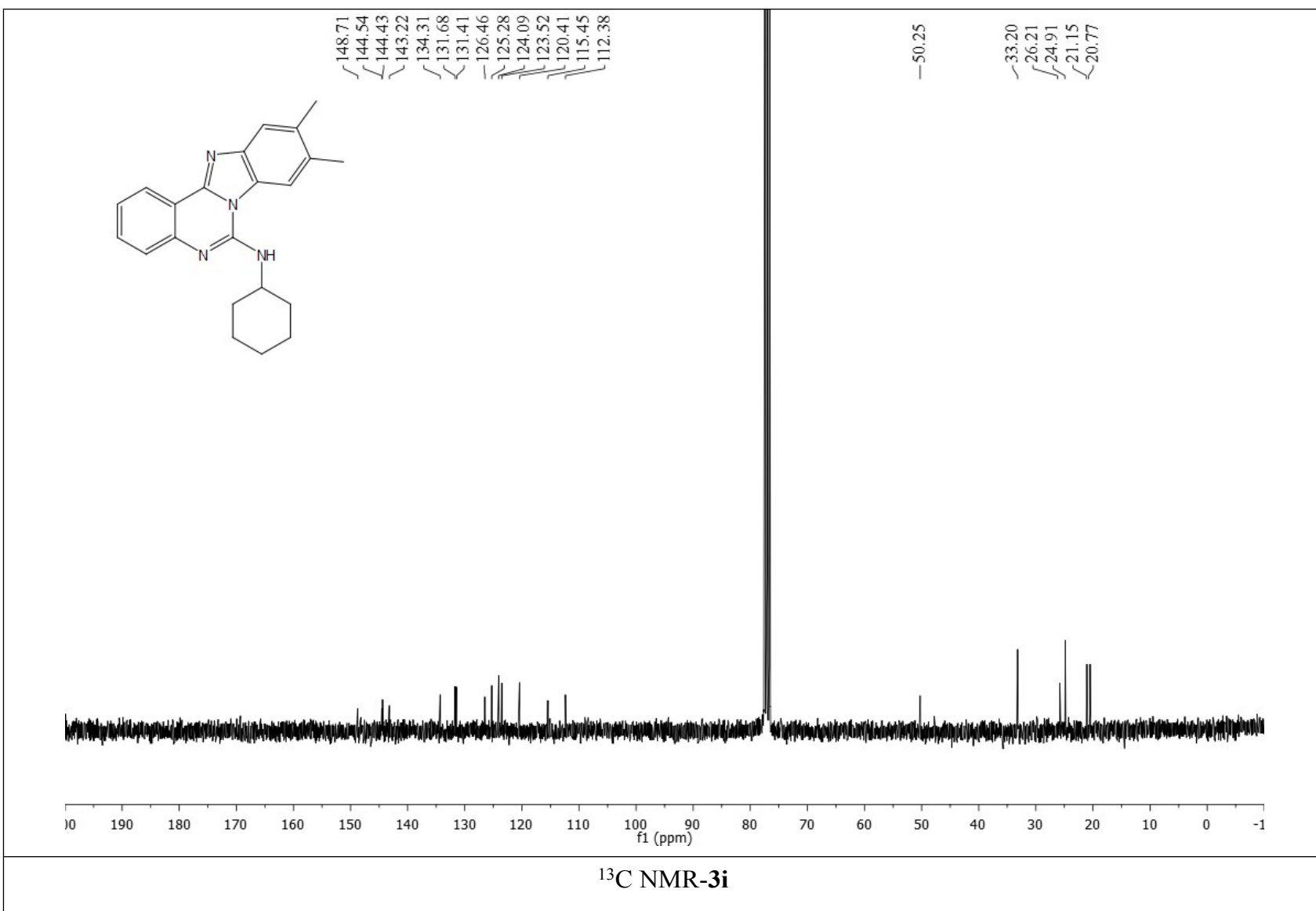


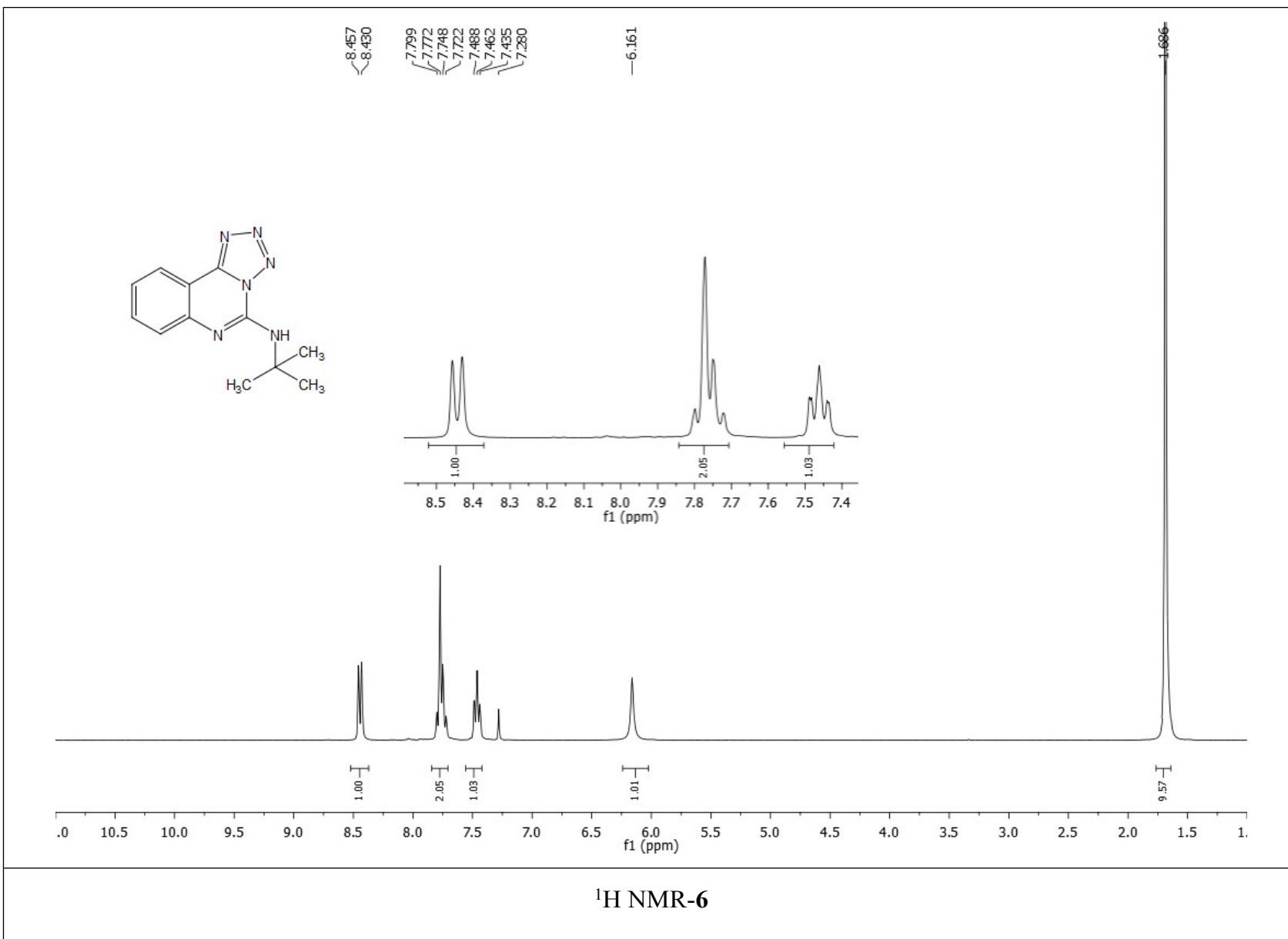
<sup>13</sup>C NMR-3h

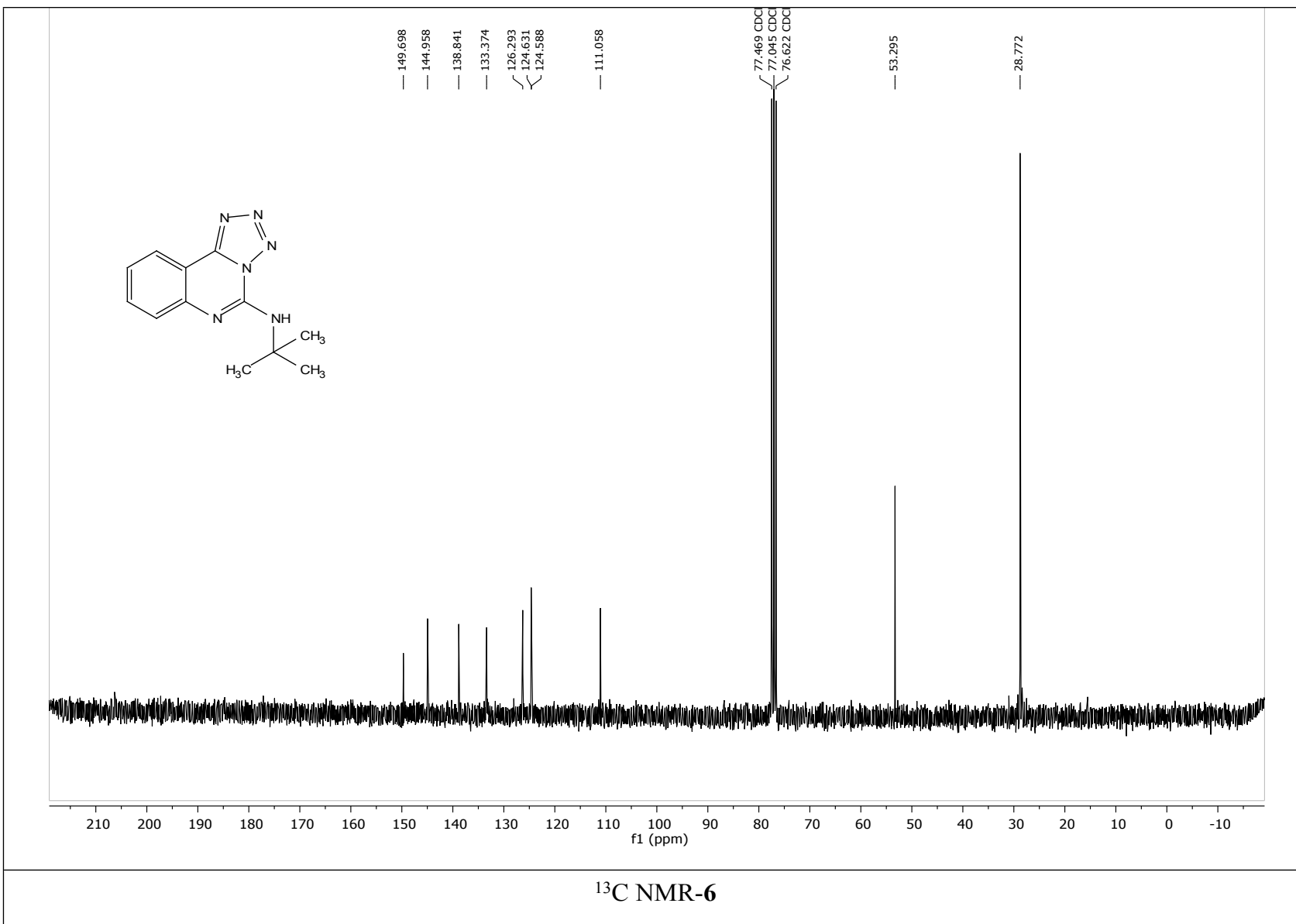


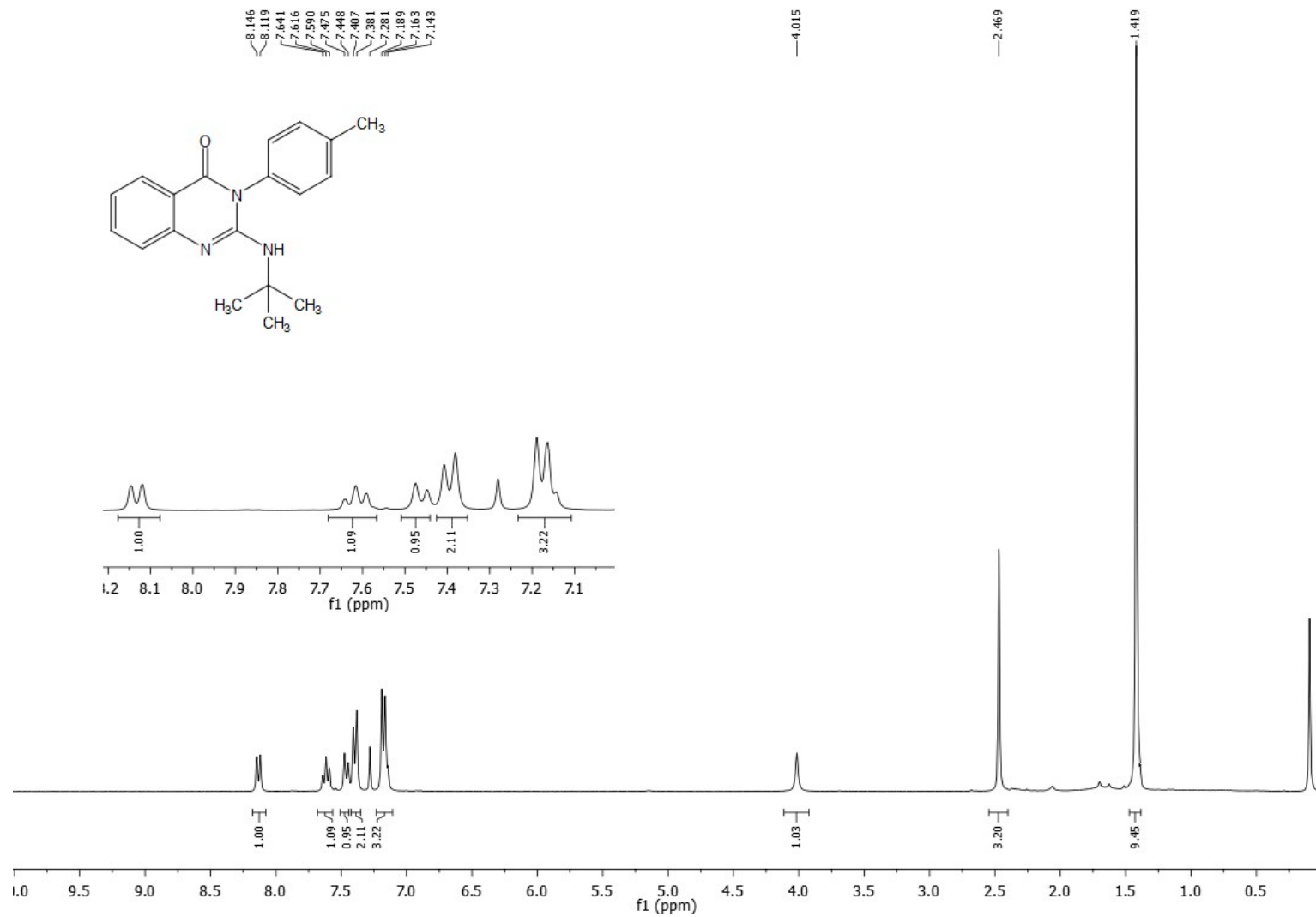
**<sup>1</sup>H NMR-3i**











<sup>1</sup>H NMR-5a

