Supporting Information

Elemental Sulfur as Polyvalent Reagent in Redox Condensation with *o*-Chloronitrobenzenes and Benzaldehydes: Three-Component Access to 2-Arylbenzothiazoles

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General information

Reagents were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or phosphomolybdic acid and vanilline stains. Flash column chromatography was carried out using Kieselgel 35-70 μm particle sized silica gel (230-400 mesh).

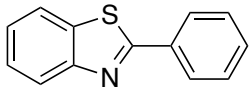
^{1}H chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm; CD_3OD, δ 3.31 ppm, DMSO-d_6, δ 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C chemical shifts are reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm; CD_3OD, 49.0 ppm DMSO-d_6, δ 39.5 ppm).

General procedure

A mixture of *o*-halonitrobenzene **1** (1 mmol), aldehyde **2** (1-1.2 mmol) and sulfur (3 mmol), *N*-methylmorpholine (4 mmol) was stirred in a closed tube under an argon atmosphere at 130 ºC for 16 h. The crude reaction mixture was purified by silica gel column chromatography (heptane/EtOAc).

Characterizations of Products

2-Phenylbenzo[d]thiazole (3aa)[1]

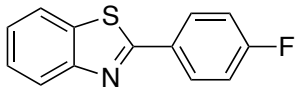


Purification of the crude mixture by column chromatography (heptane:EtOAc 97:3) afforded the product as pale yellow powder (170 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.12 (m, 3H), 7.90-7.92 (d, J = 8.0 Hz, 1H), 7.49-7.51 (m, 4H), 7.38-7.41 (t, J = 7.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 154.1, 135.1, 133.6, 131.02, 129.1, 127.6, 126.4, 125.2, 123.3, 121.6.

2-(4-Fluorophenyl)benzo[d]thiazole (3ab)[1]



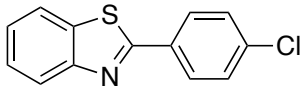
Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (140 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-8.12 (m, 3H), 7.90-7.91 (d, J = 8.0 Hz, 1H), 7.49-7.52 (m, 1H), 7.38-7.41 (m, 1H), 7.17-7.26 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 165.6, 163.6, 153.9, 135.0, 129.7, 129.6, 126.5, 125.4, 123.2, 121.6, 116.3, 116.1.

2-(4-Chlorophenyl)benzo[d]thiazole (3ac)[2]

[1] C. Yu, K. Lee, Y. You, E. J. Cho, *Adv. Synth. Catal.* **2013**, *355*, 1471.
[2] K. Inamoto, K. Nozawa, Y. Kondo, *Synlett.* **2012**, *23*, 1678.

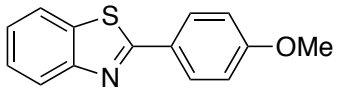


Purification of the crude mixture by column chromatography (heptane:EtOAc 97:3) afforded the product as pale yellow powder (162 mg, 66%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06-8.07 (d, J = 8.2 Hz, 1H), 7.99-8.01 (m, 2H), 7.86-7.88 (d, J = 7.9 Hz, 1H), 7.47-7.51 (m, 1H), 7.42-7.45 (m, 2H), 7.36-7.40 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 154.1, 137.1, 135.1, 132.1, 129.3, 128.7, 126.5, 125.4, 123.3, 121.7.

2-(4-Methoxyphenyl)benzo[d]thiazole (3ad)[1]

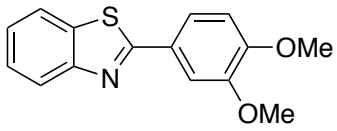


Purification of the crude mixture by column chromatography (heptane:EtOAc 97:3) afforded the product as pale yellow powder (157 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03-8.06 (m, 3H), 7.86-7.88 (d, J = 8.0 Hz, 1H), 7.46-7.49 (m, 1H), 7.34-7.37 (m, 1H), 6.99-7.02 (m, 2H), 3.88 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 162.0, 154.1, 134.8, 129.2, 126.4, 126.3, 124.9, 122.8, 121.5, 114.4, 55.5.

2-(3,4-Dimethoxyphenyl)benzo[d]thiazole (3ae)[3]



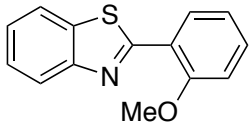
Purification of the crude mixture by column chromatography (heptane:EtOAc 97:3) afforded the product as pale yellow powder (165 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-8.07 (d, J = 8.1 Hz, 1H), 7.87-7.88 (d, J = 8.0 Hz, 1H), 7.74-7.75 (d, J = 1.7 Hz, 1H), 7.60-7.62 (m, 1H), 7.46-7.50 (m, 1H), 7.35-7.38 (m, 1H), 4.03 (s, 3H), 3.96 (s, 3H).

[3] K.E. Balsane, S.H. Gund, J.M. Nagarkar, *Catal. Commun.* **2017**, *10*, 29.

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 151.8, 149.5, 134.7, 126.4, 126.4, 125.0, 122.8, 121.5, 121.3, 111.3, 111.1, 110.0, 56.2, 56.1.

2-(2-Methoxyphenyl)benzo[d]thiazole (3af)[4]

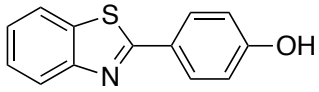


Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (160 mg, 66%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54-8.56 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 8.10-8.12 (d, J = 8.1 Hz, 1H), 7.92-7.94 (d, J = 8.1 Hz, 1H), 7.44-7.51 (m, 2H), 7.36-7.39 (m, 1H), 7.12-7.16 (m, 1H), 7.06-7.08 (d, J = 8.3 Hz, 1H), 4.05 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 157.3, 152.1, 136.1, 131.8, 129.6, 125.9, 124.6, 122.8, 122.3, 121.2, 111.8, 111.7, 55.7

4-(Benzo[d]thiazol-2-yl)phenol (3ag)[5]

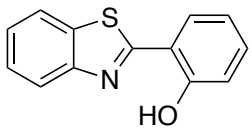


Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (140 mg, 62%).

^{1}H NMR (500 MHz, MeOD+$CDCl_3$) δ 7.91-7.95 (m, 4H), 7.47-7.50 (m, 1H), 7.36-7.39 (m, 1H), 6.91-6.94 (m, 2H).

^{13}C NMR (125 MHz, MeOD+$CDCl_3$) δ 115.6, 186.6, 169.1, 160.7, 153.5, 134.3, 128.9, 126.2, 126.1, 124.8, 124.5, 121.7, 121.4, 115.6.

2-(Benzo[d]thiazol-2-yl)phenol (3ah)[6]



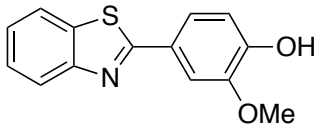
[4] J. Canivet, J. Yamaguchi, I. Ban, K. Itami, *Org. Lett.* **2009**, *11*, 1733.
[5] S. Billeau; F. Chatel; M. Robin; R. Faure; J.-P. Galy. *Magn. Reson. Chem.* **2006**; *44*, 102.
[6] T. Itoh; T. Mase. *Org. Lett.* **2007**, *9*, 3687.

Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (140 mg, 62%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97-7.98 (d, J = 8.1 Hz, 1H), 7.87-7.88 (d, J = 8.0 Hz, 1H), 7.67-7.69 (d, J = 7.9 Hz, 1H), 7.48-7.51 (t, J = 8.0 Hz, 1H), 7.37-7.41 (m, 2H), 7.11-7.12 (d, J = 8.2 Hz, 1H), 6.93-6.96 (t, J = 8.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 158.0, 151.8, 132.8, 132.6, 128.4, 126.7, 125.6, 122.2, 121.5, 119.5, 117.9, 116.8.

4-(Benzo[d]thiazol-2-yl)-2-methoxyphenol (3ai)[7]

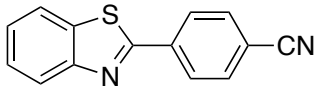


Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (155 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03-8.04 (d, J = 8.1 Hz, 1H), 7.86-7.88 (m, 1H), 7.74 ((d, J = 2.0 Hz, 1H), 7.53-7.55 (dd, J = 8.2 Hz, 2.0 Hz, 1H), 7.45-7.49 (m, 1H), 7.34-7.37 (m, 1H), 7.00-7.01 (d, J = 8.2 Hz, 1H), 4.00 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 153.9, 148.7, 147.0, 134.8, 126.3, 126.1, 124.9, 122.7, 122.0, 121.5, 114.8, 109.4, 56.2.

4-(Benzo[d]thiazol-2-yl)benzonitrile (3aj)[8]



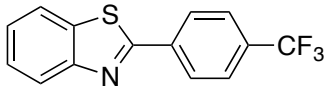
Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (145 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15-8.17 (d, J = 8.2 Hz, 2H), 8.08-8.10 (d, J = 8.2 Hz, 1H), 7.91-7.92 (d, J = 8.2 Hz, 1H), 7.73-7.75 (d, J = 8.2 Hz, 2H), 7.51-7.54 (t, J = 7.8 Hz, 1H), 7.42-7.45 (t, J = 7.8 Hz, 1H).

[7] A. Kamal; M. N. A. Khan; K. S. Reddy; Y. V. V. S. B. Sridhar. *Chem. Biol. Drug. Des.* **2008**, *71*, 78.
[8] H. Hachiya, K. Hirano, T. Satoh, M. Miura. *Org. Lett.*, **2009**, *11*, 1737.

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 154.0, 137.5, 135.3, 132.8, 127.9, 126.9, 126.1, 123.8, 121.8, 118.3, 114.1.

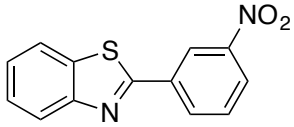
2-(4-(Trifluoromethyl)phenyl)benzo[d]thiazole (3ak)[8]



Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (207 mg, 74%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21-8.23 (d, J = 8.1 Hz, 2H), 8.11-8.13 (d, J = 8.2 Hz, 1H), 7.93-7.95 (d, J = 7.9 Hz, 1H), 7.75-7.77 (d, J = 8.2 Hz, 2H), 7.52-7.55 (m, 1H), 7.44-7.45 (m, 1H).

2-(3-Nitrophenyl)benzo[d]thiazole (3al)[9]

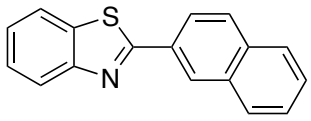


Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (160 mg, 63%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92-8.93 (m, 1H), 8.41-8.43 (m, 1H), 8.32-8.34 (m, 1H), 8.11-8.13 (d, J = 8.1 Hz, 1H), 7.94-7.95 (d, J = 8.0 Hz, 1H), 7.67-7.70 (t, J = 8.1 Hz, 1H), 7.53-7.56 (m, 1H), 7.44-7.47 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 154.0, 148.8, 135.3, 135.2, 133.0, 130.1, 126.9, 126.1, 125.2, 123.8, 122.4, 121.8.

2-(Naphthalen-2-yl)benzo[d]thiazole (3am)[9]



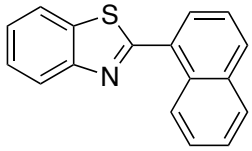
Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (157 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.21-8.23 (dd, J = 8.5 Hz, 1.8 Hz, 1H), 8.12-8.13 (d, J = 8.1 Hz, 1H), 7.92-7.98 (m, 3H), 7.86-7.90 (m, 1H), 7.53-7.57 (m, 2H), 7.50-7.53 (m, 1H), 7.39-7.42 (m, 1H).

[9] X. Zhang, W. Zeng, Y. Yang, H. Huang, Y. Liang. *Org. Lett.*, **2014**, *16*, 876.

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 154.2, 135.1, 134.7, 133.2, 131.0, 128.9, 127.9, 127.7, 127.5, 126.9, 126.4, 125.3, 124.5, 123.3, 121.7.

2-(Naphthalen-1-yl)benzo[d]thiazole (3an)[10]

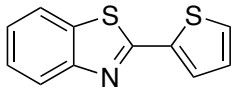


Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (175 mg, 67%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96-8.98 (d, J = 8.6 Hz, 1H), 8.22-8.24 (m, 1H), 7.97-8.01 (m, 2H), 7.93-7.96 (m, 2H), 7.62-7.66 (m, 1H), 7.55-7.60 (m, 3H), 7.44-7.48 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 154.2, 135.5, 134.1, 131.1, 130.9, 130.7, 129.5, 128.5, 127.7, 126.6, 126.3, 126.0, 125.4, 125.0, 123.6, 121.4.

2-(Thiophen-2-yl)benzo[d]thiazole (3ao)[11]



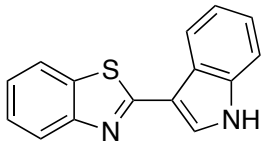
Purification of the crude mixture by column chromatography (heptane:EtOAc 93:7) afforded the product as pale yellow powder (140 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03-8.04 (d, J = 8.2 Hz, 1H), 7.83-7.85 (dd, J = 7.9 Hz, 0.5 Hz, 1H), 7.65-7.66 (dd, J = 3.8 Hz, 1.1 Hz, 1H), 7.45-7.50 (m, 2H), 7.34-7.38 (m, 1H), 7.12-7.14 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 153.6, 137.3, 134.7, 129.4, 128.7, 128.1, 126.5, 125.3, 123.0, 121.5.

2-(1H-Indol-3-yl)benzo[d]thiazole (3ap)[12]

[10] Y. Liao, H. Qi, S. Chen, P. Jiang, W. Zhou, and G. Jun Deng. *Org. Lett.*, **2012**, *14*, 6004.
[11] K-H. He, F-F. Tan, C-Z. Zhou, G-J. Zhou, X-L. Yang, Y. Li. *Angew. Chem. Int. Ed.* **2017**, *56*, 3080.
[12] M.N. Esfahani, I. M. Baltork, A.R. Khosropour, M. Moghadam, V. Mirkhani, S. Tangestaninejad. *J. Mol. Catal. A: Chem.* **2013**, *379*, 243.

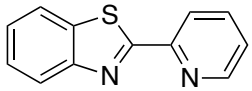


Purification of the crude mixture by column chromatography (heptane:EtOAc 90:10) afforded the product as pale yellow powder (190 mg, 76%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.93 (s, 1H, NH), 8.38-8.40 (m, 1H), 8.26 (d, J = 2.8 Hz, 1H), 8.04-8.05 (d, J = 7.8 Hz, 1H), 7.96-7.98 (d, J = 8.0 Hz, 1H), 7.52-7.54 (m, 1H), 7.47-7.49 (t, J = 7.4 Hz, 1H), 7.34-7.37 (t, J = 7.8 Hz, 1H), 7.24-7.28 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 153.7, 136.7, 133.0, 128.8, 126.1, 124.5, 124.2, 122.7, 121.7, 121.5, 121.1, 120.6, 112.3, 110.4.

2-(Pyridin-2-yl)benzo[d]thiazole (3aq)[13]

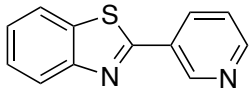


Purification of the crude mixture by column chromatography (heptane:EtOAc 97:3) afforded the product as pale yellow powder (145 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67-8.68 (d, J = 4.7 Hz, 1H), 8.36-8.37 (d, J = 7.9 Hz, 1H), 8.08-8.10 (d, J = 8.1 Hz, 1H), 7.94-7.95 (d, J = 8.1 Hz, 1H), 7.80-7.84 (m, 1H), 7.48-7.51 (m, 1H), 7.39- 7.42 (m, 1H), 7.34-7.37 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 154.3, 151.5, 149.7, 137.0, 136.2, 126.3, 125.7, 125.3, 123.6, 122.0, 120.8.

2-(Pyridin-3-yl)benzo[d]thiazole (3ar)[14]



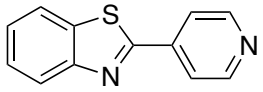
Purification of the crude mixture by column chromatography (heptane:EtOAc 90:10) afforded the product as pale yellow powder (165 mg, 78%).

[13] T.B. Nguyen; L. Ermolenko; A. Al-Mourabit. *Org. Lett.* **2013**, *15*, 4218.
[14] T.B. Nguyen; L. Ermolenko; P. Retailleau, A. Al-Mourabit. *Angew. Chem. Int. Ed.* **2014**, *53*, 13808.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.29-9.30 (d, J = 2.1 Hz, 1H), 8.71-8.72 (dd, J = 4.9 Hz, 1.5 Hz, 1H), 8.37-8.39 (m, 1H), 8.09-8.11 (d, J = 8.2 Hz, 1H), 7.92-7.93 (d, J = 8.0 Hz, 1H), 7.50-7.54 (m, 1H), 7.40-7.45 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 154.0, 151.5, 148.5, 135.0, 134.7, 129.8, 126.7, 125.8, 123.9, 123.6, 121.8.

2-(Pyridin-4-yl)benzo[d]thiazole (3as)[13]

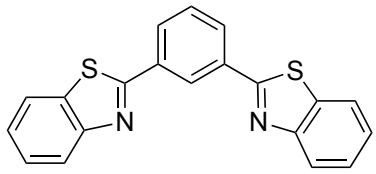


Purification of the crude mixture by column chromatography (heptane:EtOAc 90:10) afforded the product as pale yellow powder (160 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75-8.76 (d, J = 5.6 Hz, 2H), 8.11-8.12 (d, J = 8.1 Hz, 1H), 7.92-7.93 (m, 3H), 7.51-7.55 (m, 1H), 7.42-7.46 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 154.0, 150.7, 140.6, 135.3, 126.8, 126.2, 124.0, 121.9, 121.2.

1,3-*Bis*(benzo[*d*]thiazol-2-yl)benzene (3at)



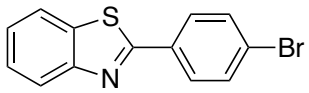
Purification of the crude mixture by column chromatography (heptane:EtOAc 9:1) afforded the product as pale orange powder (115 mg, 67%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.21 (d, J = 7.5 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 154.4, 135.4, 134.8, 130.0, 126.8, 126.8, 126.7, 125.7, 123.7, 121.9.

HRMS (ESI+) calcd for $C_{20}H_{13}N_2S_2$ $[M + H]^+$ 345.0520. Found 345.0532.

2-(4-Bromophenyl)benzo[d]thiazole (3au)[15]



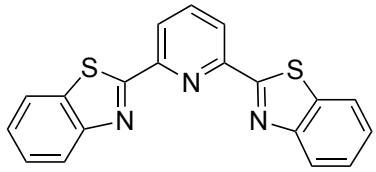
[15] H. Wang, L. Wang, J. Shang, X. Li, H. Wang, J. Gui, A. Lei, *Chem*. *Commun*. **2012**, *48*, 76.

Purification of the crude mixture by column chromatography (heptane:EtOAc 97:3) afforded the product as pale brown powder (183 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.5 Hz, 1H), 7.96-7.94 (m, 2H), 7.89 (d, J = 8.5 Hz, 1H), 7.63-7.60 (m, 2H), 7.50-7.47 (m, 1H), 7.40-7.37 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 154.1, 135.1, 132.6, 132.2, 128.9, 126.5, 125.5, 123.4, 121.7 (1 quaternary ^{13}C signal is missing due to overlap).

2,6-Bis(benzo[d]thiazol-2-yl)pyridine (3av)



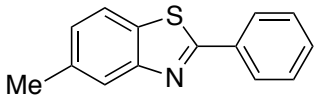
Purification of the crude mixture by column chromatography (heptane:EtOAc 3:1) afforded the product as pale brown powder (117 mg, 68%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, J = 7.7 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H), 8.00 (t, J = 7.7 Hz, 1H), 7.98 (d, J = 8.5 Hz, 2H), 7.55-7.49 (m, 2H), 7.46-7.41 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 154.6, 151.6, 138.4, 136.6, 126.6, 126.1, 124.0, 122.2, 122.2.

HRMS (ESI+) calcd for $C_{19}H_{12}N_3S_2$ $[M + H]^+$ 346,0473. Found 346.0466.

5-Methyl-2-phenylbenzo[d]thiazole (3ba)[14]

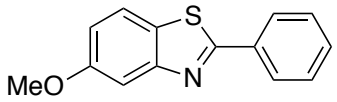


Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (180 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.10 (m, 2H), 7.90 (s, 1H), 7.76-7.77 (d, J = 8.2 Hz, 1H), 7.48-7.49 (m, 3H), 7.21-7.22 (d, J = 8.2 Hz, 1H), 2.52 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 154.6, 136.4, 133.9, 132.1, 130.8, 129.0, 127.5, 126.8, 123.3, 121.1, 21.5.

5-Methoxy-2-phenylbenzo[d]thiazole (3ca)[14]

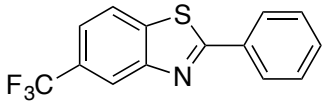


Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (150 mg, 62%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.10 (m, 2H), 7.74-7.76 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.48-7.51 (m, 3H), 7.04-7.06 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 133.5, 131.1, 129.1, 127.5, 126.7, 122.0, 121.9, 115.8, 115.7, 105.4, 55.7.

2-Phenyl-5-(trifluoromethyl)benzo[d]thiazole (3da)[14]

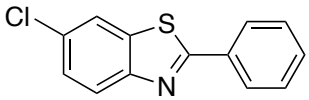


Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (195 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.08-8.10 (m, 2H), 7.98-7.99 (d, J = 8.4 Hz, 1H), 7.60-7.62 (m, 1H), 7.49-7.53 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 153.7, 138.5, 133.0, 131.6, 129.2, 128.9, 127.7, 125.3, 123.2, 122.2, 121.5, 120.4.

6-Chloro-2-phenylbenzo[d]thiazole (3ea)[16]



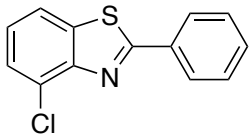
Purification of the crude mixture by column chromatography (heptane/EtOAc 95/5) afforded the product as pale yellow powder (185 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-8.08 (m, 3H), 7.78-7.80 30 (d, J = 8.0 Hz, 1H), 7.48-7.50 (m, 3H), 7.34-7.36 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 155.0, 133.3, 133.3, 132.4, 131.4, 129.1, 127.7, 125.7, 123.1, 122.3.

[16] Y. Cheng, J. Yang, Y. Qu, P. Li. *Org. Lett.*, **2012**, *14*, 98.

4-Chloro-2-phenylbenzo[d]thiazole (3fa)[15]

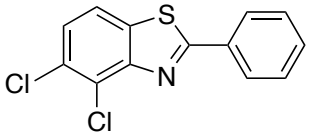


Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (150 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.10 (m, 1H), 7.96-7.97 (dd, J = 8.0 Hz, 0.5 Hz, 1H), 7.49-7.52 (m, 3H), 7.42-7.45 (t, J = 8.0 Hz, 1H), 7.36-7.38 (dd, J = 8.0 Hz, 0.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 154.7, 135.3, 133.2, 131.4, 129.1, 127.6, 127.3, 126.9, 124.9, 121.5.

4,5-Dichloro-2-phenylbenzo[d]thiazole (3ga)



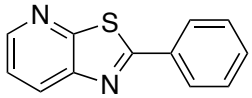
Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (180 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-8.07 (m, 2H), 7.86-7.88 (d, J = 8.7 Hz, 1H), 7.54-7.56 (d, J = 8.7 Hz, 1H), 7.49-7.51 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 152.8, 137.1, 132.9, 131.6, 129.2, 128.4, 127.6, 124.8, 122.0.

HRMS (ESI+) calcd for $C_{13}H_8Cl_2NS$ $[M + H]^+$ 279.9755. Found 279.9768.

2-Phenylthiazolo[5,4-b]pyridine (3ha)[17]



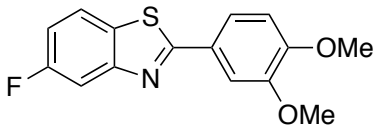
Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (130 mg, 61%).

[17] K.P. Sahasrabudhe, M.A. Estiarte, D. Tan, S. Zipfel, M. Cox, D.J. R. O'Mahony, W.T. Edwards, M.A.J. Duncton, *Journal of Heterocyclic Chemistry*, **2009**, *46*, 1125.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51-8.52 (dd, J = 4.7 Hz, 1.4 Hz, 1H), 8.21-8.23 (dd, J = 8.3 Hz, 1.5 Hz, 1H), 8.02-8.07 (m, 2H), 7.43-7.48 (m, 3H), 7.35-7.38 (dd, J = 8.2 Hz, 4.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 158.5, 147.3, 147.0, 133.4, 131.6, 130.0, 129.1, 127.6, 121.4.

2-(3,4-Dimethoxyphenyl)-5-fluorobenzo[d]thiazole (3de)[18]



Purification of the crude mixture by column chromatography (heptane:EtOAc 95:5) afforded the product as pale yellow powder (175 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.76 (dd, J = 8.7 Hz, 5.2 Hz, 1H), 7.67-7.70 (dd, J = 9.6 Hz, 2.4 Hz, 1H), 7.66 (d, J = 2.1 Hz, 1H), 7.53-7.55 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.07-7.11 (m, 1H), 6.89-6.91 (d, J = 8.4 Hz, 1H), 3.99 (s, 3H), 3.93 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 162.9, 161.0, 155.1, 155.0, 151.9, 149.4, 130.3, 126.4, 122.1, 122.1, 121.2, 113.5, 113.3, 111.1, 109.8, 109.1, 108.9, 56.1, 56.1.

[18] H. Deng, Z. Li, F. Ke, X. Zhou, *Chem. Eur. J.* **2012**, *18*, 4840.

Crystallographic data collection, structure determination and refinement

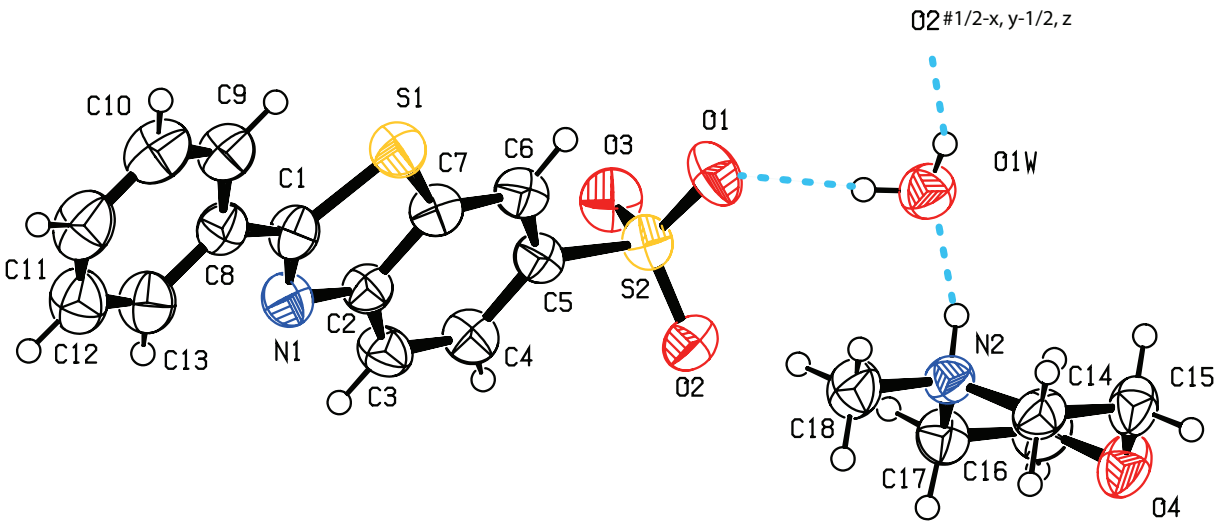
X-ray Structure Determination of **BN0654**: Performed with Rigaku diffractometer constituted by a MM007 HF rotating-anode generator, delivering copper radiation through Osmic CMF confocal optics, and a Rapid II curved Image Plate detector, on a yellow crystalline stick. Data collection and reduction software (CrystalClear 2.0 / Fs_process).[4] Crystal data: $[C_{13}\ H_8\ N\ O_3\ S_2]^-$, $[C_5\ H_{12}\ N\ O]^+$, $H_2\ O$, M 410.49 g.mol^{-1}, 0.38 x 0.11 x 0.09 mm^3, orthorhombic, space group: P bca, Cu-Kα, 1.54187 Å, T = 293 K, unit cell dimensions: a = 7.4735(1), b = 11.8551(2), c = 42.384(3) Å, V = 3755.2(3)Å^3, Z = 8, $D_{calcd.}$ = 1.452 g.cm^{-3}, absorption μ = 2.863 mm^{-1}, the θ range for data collection was 4.172 – 68.228 °, index ranges: $-7 \le h \le 9$, $-13 \le k \le 14$, $-50 \le l \le 51$. Number of reflections collected: 24217; independent reflections: 3408 (R_{int} = 0.0371). The structure was solved by intrinsic phasing methods [2] Structure refinement was performed by full-matrix least-squares methods [3] on 254 parameters, weighted refinement: $w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 5.5654P]$ with $P = [\max(F_o^2,0) + 2F_o^2]/3$ and hydrogen atoms located from difference Fourier synthesis and refined isotropically assuming a riding motion model, non-hydrogen atoms improved by anisotropic refinement. The H atom of the NH group was allowed to refine with a restrained N—H bond distance of 0.87 (2) Å and with *U*iso(H) = 1.2*U*eq(N). Goodness-of-fit on S = 1.138, final R indices: R1 = 0.0888, wR2 = 0.1523, the final difference Fourier map showed minimum and maximum values of 0.336 and -0.321 e Å^{-3}, respectively. The asymmetric unit is made of a salt of 4-methylmorpholin-4-ium 2-phenylbenzo[*d*]thiazole-6-sulfonate hydrated by one molecule of water, whose geometry has been restrained (DFIX 0.83(2) Å and DANG 1.33(4) Å instructions within SHELXL).

References

1 Rigaku. (2009) CrystalClear-SM Expert 2.0 r4 Rigaku Corporation, Tokyo, Japan.

2 Sheldrick, G. M. (2015). *Acta Crystallogr.,* **A**71, 3-8.

3 Sheldrick, G. M. (2015). *Acta Crystallogr.,* **C**71, 3-8.



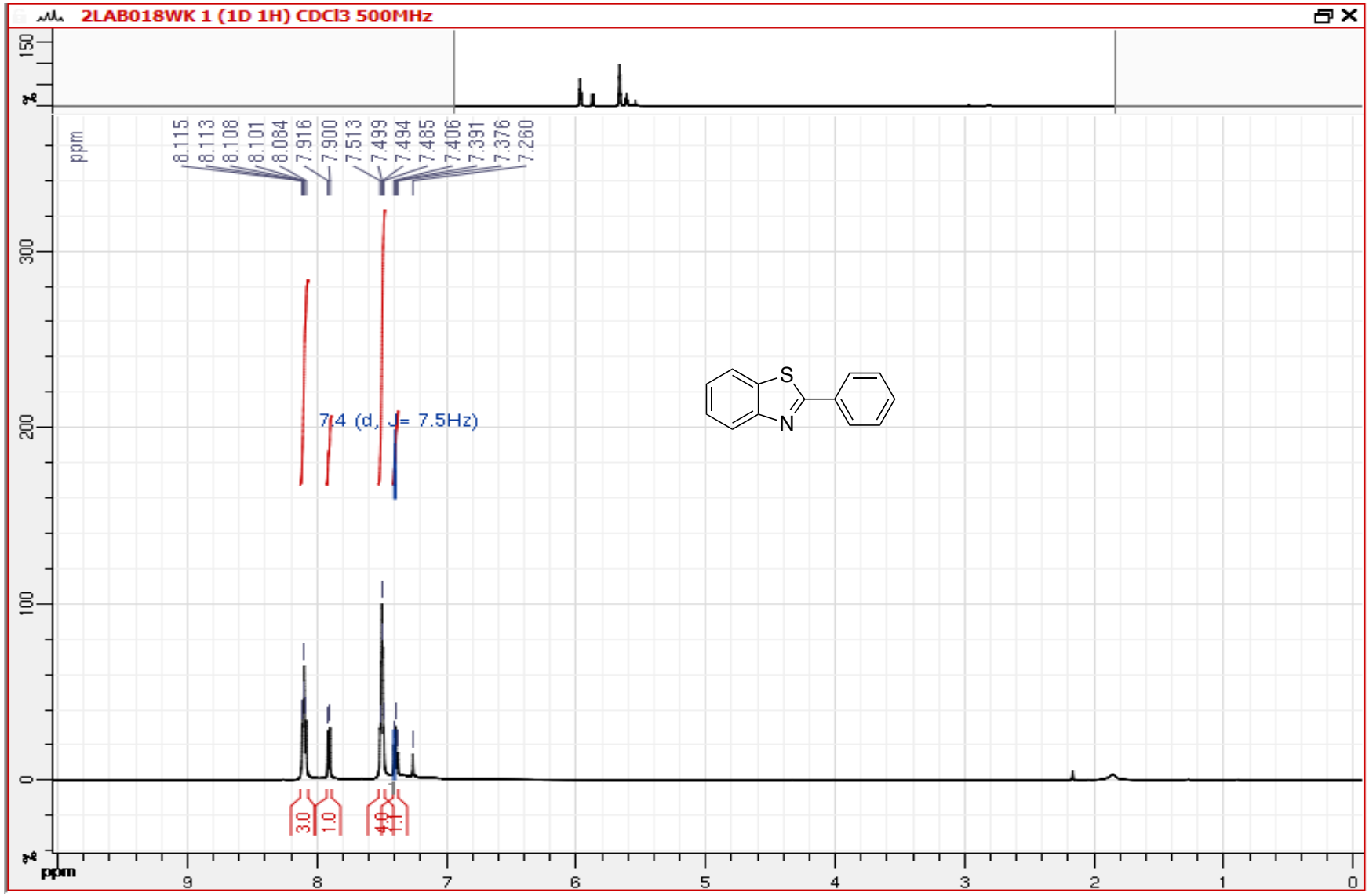
Figure

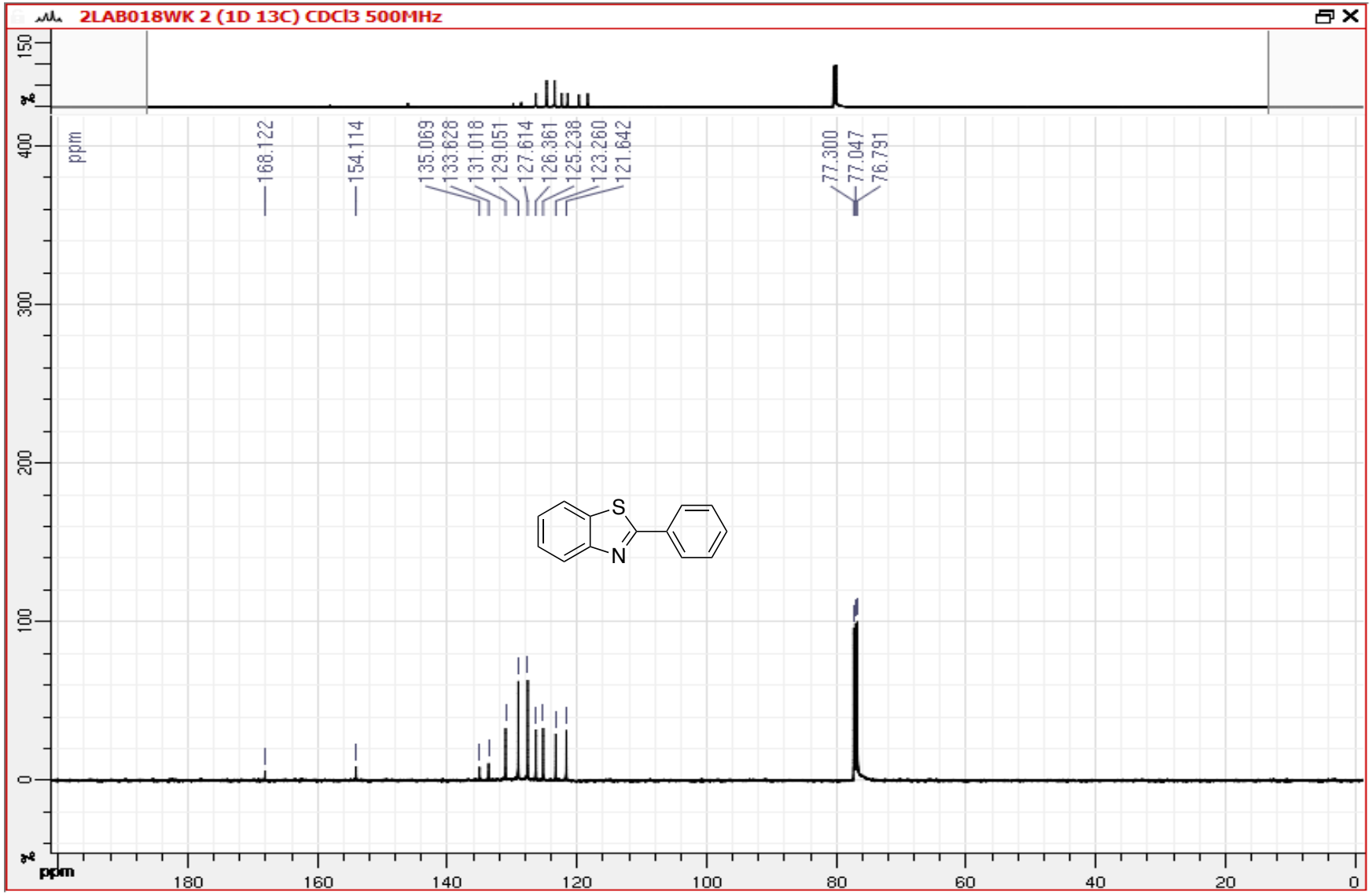
Ortep plot of **bn0654** showing the atom-numbering scheme. Ellipsoids are drawn at 50% of probability and H atoms are drawn as spheres of arbitrary radius. Cyan dotted lines indicate a partial view of the hydrogen bond network

Identification code	**bn0608p**	**bn432p**
Empirical formula	C_{16} H_{13} N O_4 S, 0.5 (C D Cl_3)	C_{21} H_{19} N_3
Formula weight	375.52	313.39
Temperature (K)	173.0 (1)	293(2)
Wavelength (Å)	0.71073	1.54187
Crystal system, Space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions a | (Å) b c β | (°)	7.5748 (3) 13.3134 (5) 16.6181 (9) 93.054 (5)	27.304 (4) 15.1588 (16) 12.886 (5) 103.06 (2)
Volume ($Å^3$)	1673.49 (13)	5196 (2)
Z, Calculated density (Mg/m^3)	4, 1.490	12, 1.202
Absorption coefficient (mm^{-1})	0.453	0.559
F(000)	772	1992
Crystal size (mm)	0.35 x 0.28 x 0.10	0.45 x 0.42 x 0.08
θ range for data collection (°)	3.740 to 28.948	3.323 to 58.930
Limiting indices	$-9 \le h \le 9$, $-17 \le k \le 15$,	$-19 \le h \le 30$, $-16 \le k \le 14$,

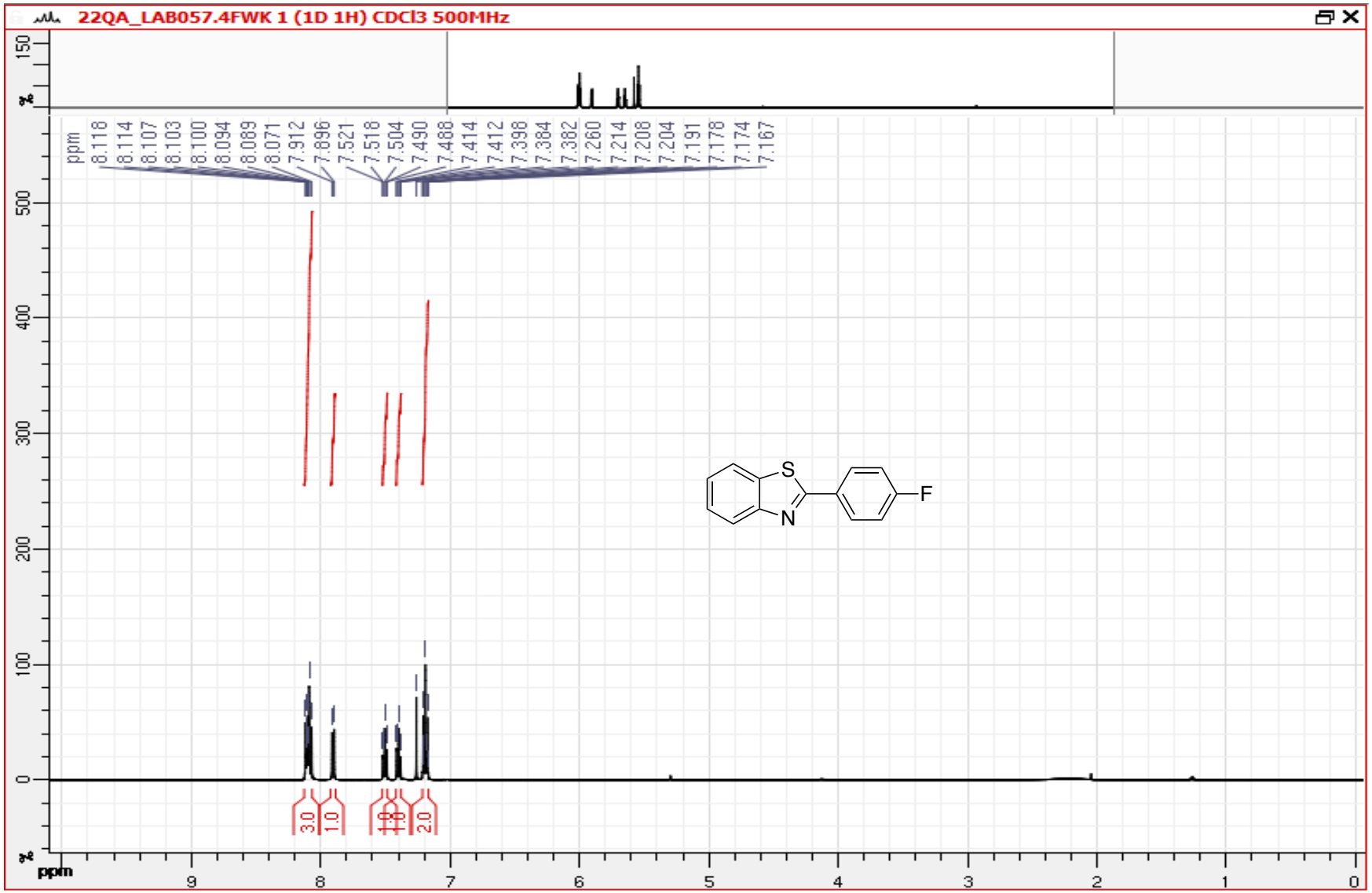
	$-22 \leq l \leq 21$	$-14 \leq l \leq 14$
Reflections collected / unique R(int)	18758 / 3906 0.0401	23759 / 7328 0.0718
Completeness to θ full (%)	99.0	98.0
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.84710	1.000 and 0.553
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3886 / 24 / 239	7318 / 63 / 660
Goodness-of-fit on F^2	1.127	0.812
Final R indices [I>2σ(I)]	R1 = 0.0579, wR2 = 0.1524	R1 = 0.0798, wR2 = 0.1846
R indices (all data)	R1 = 0.0703, wR2 = 0.1598	R1 = 0.1572, wR2 = 0.2217
Largest diff. peak and hole (e. $Å^3$)	0.921 and -0.902	0.256 and -0.175

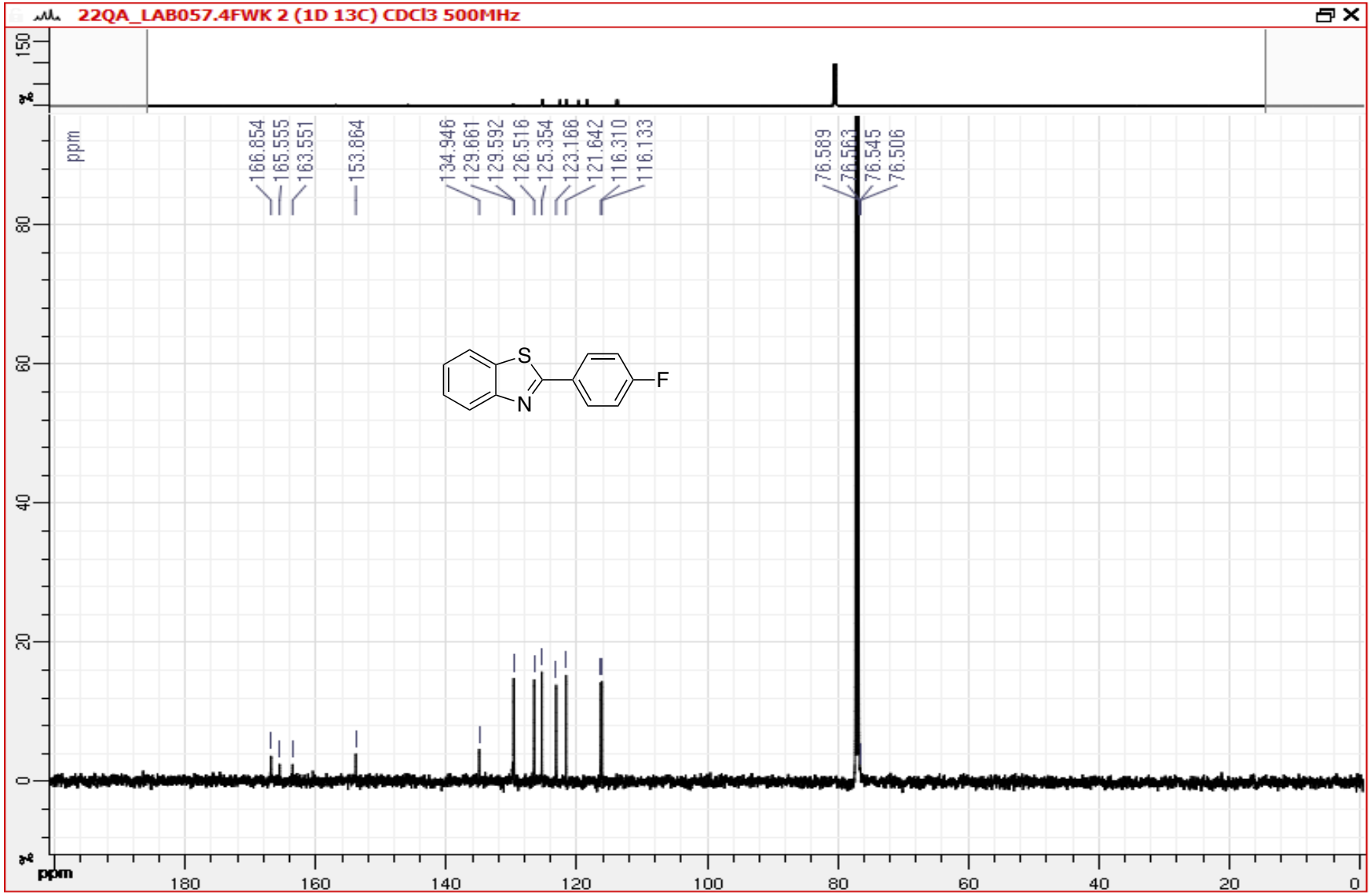
2-Phenylbenzo[d]thiazole (3aa)



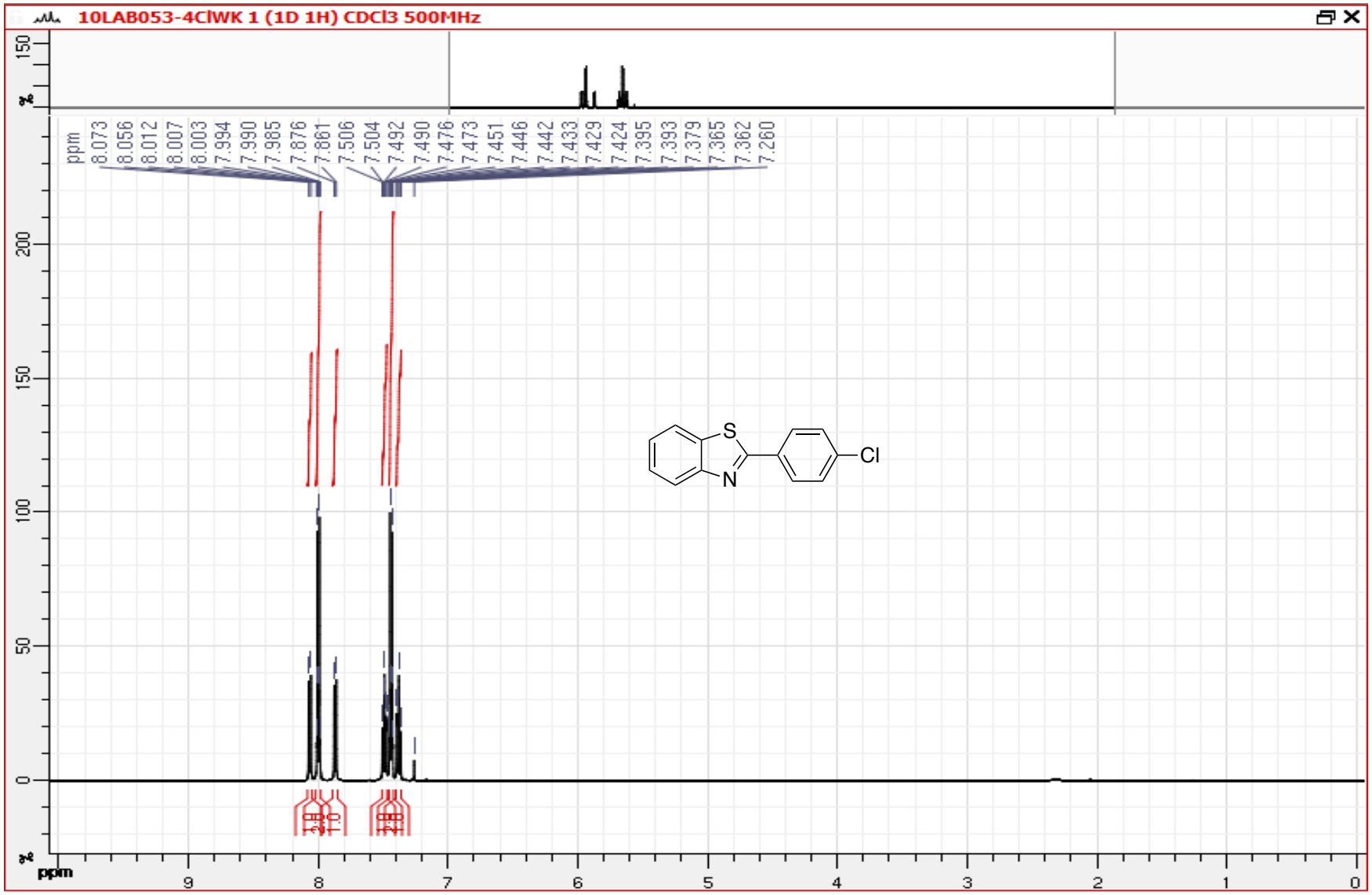

2LAB018WK 2 (1D 13C) CDCl3 500MHz
ppm
168.122
154.114
135.069
133.628
131.018
129.051
127.614
126.361
125.238
123.260
121.642
77.300
77.047
76.791
S
N

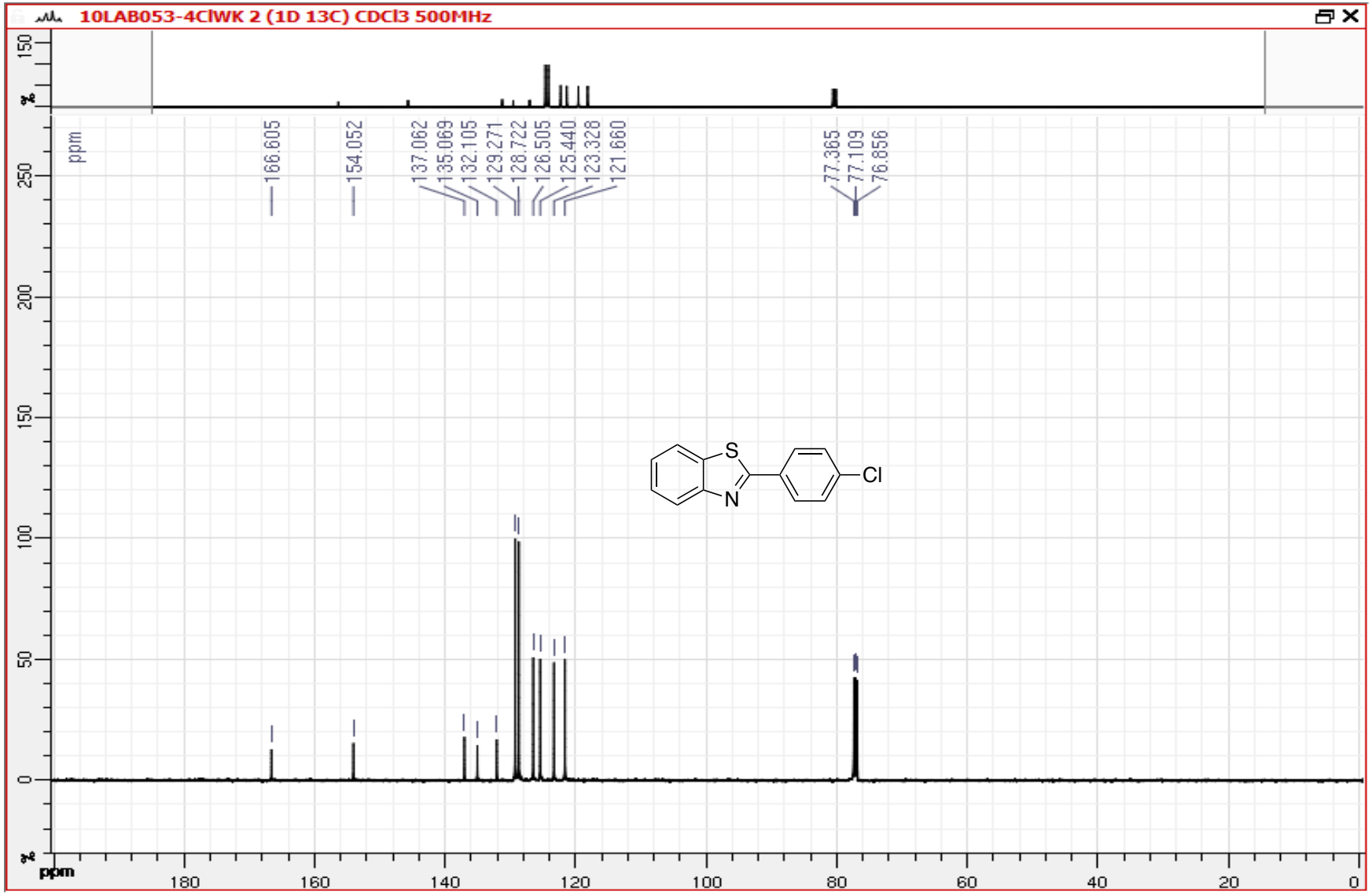
2-(4-Fluorophenyl)benzo[d]thiazole (3ab)




22QA_LAB057.4FWK 2 (1D 13C) CDCl3 500MHz
ppm
166.854
165.555
163.551
153.864
134.946
129.661
129.592
126.516
125.354
123.166
121.642
116.310
116.133
76.589
76.563
76.545
76.506
S
N
F
180
160
140
120
100
80
60
40
20
0

2-(4-Chlorophenyl)benzo[d]thiazole (3ac)

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ppm
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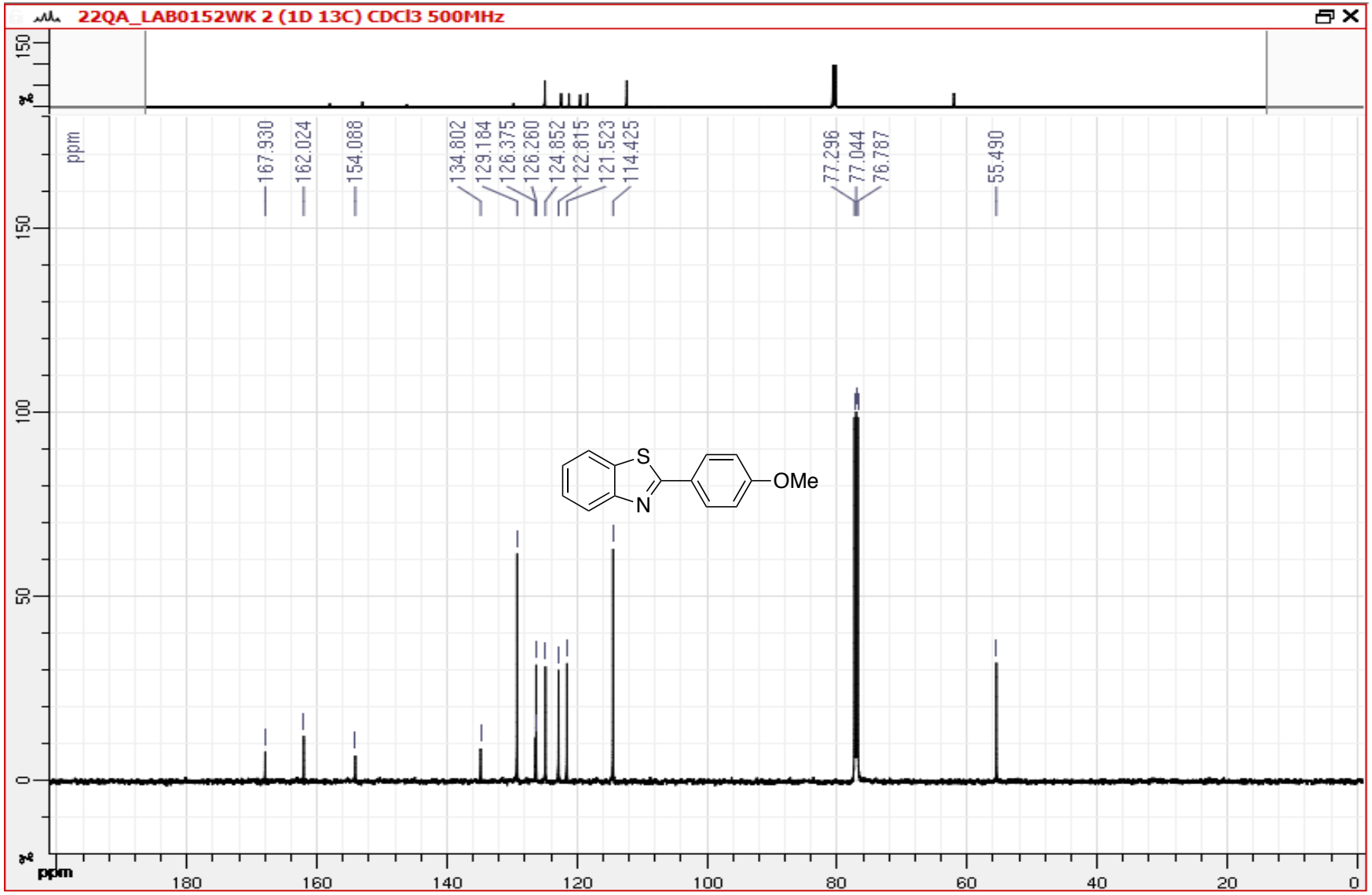
154.052
137.062
135.069
132.105
129.271
128.722
126.505
125.440
123.328
121.660
77.365
77.109
76.856
S
N
Cl
180
160
140
120
100
80
60
40
20
0

2-(4-Methoxyphenyl)benzo[d]thiazole (3ad)


22QA_LAB0152WK 2 (1D 13C) CDCl3 500MHz
ppm
167.930
162.024
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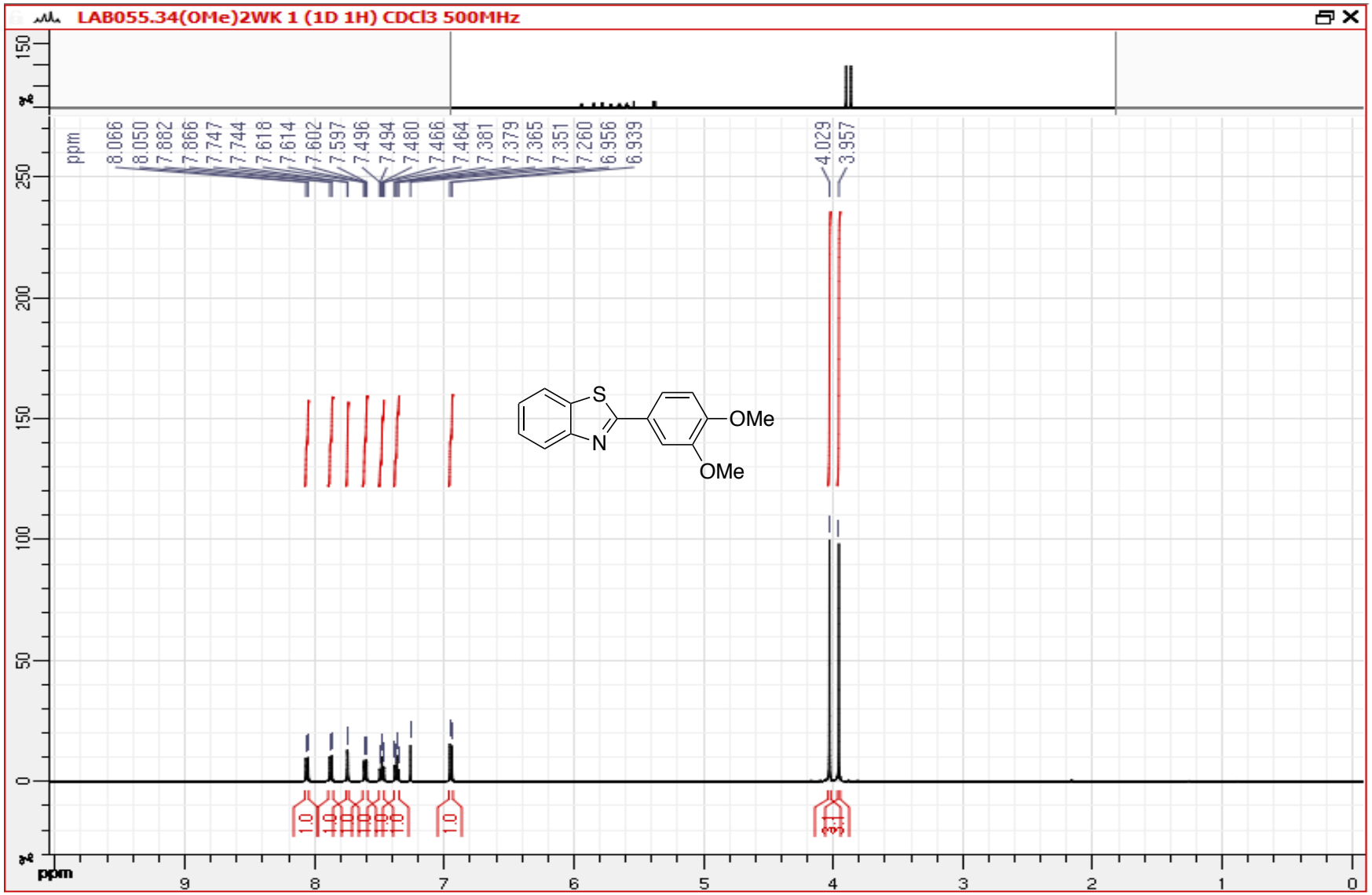
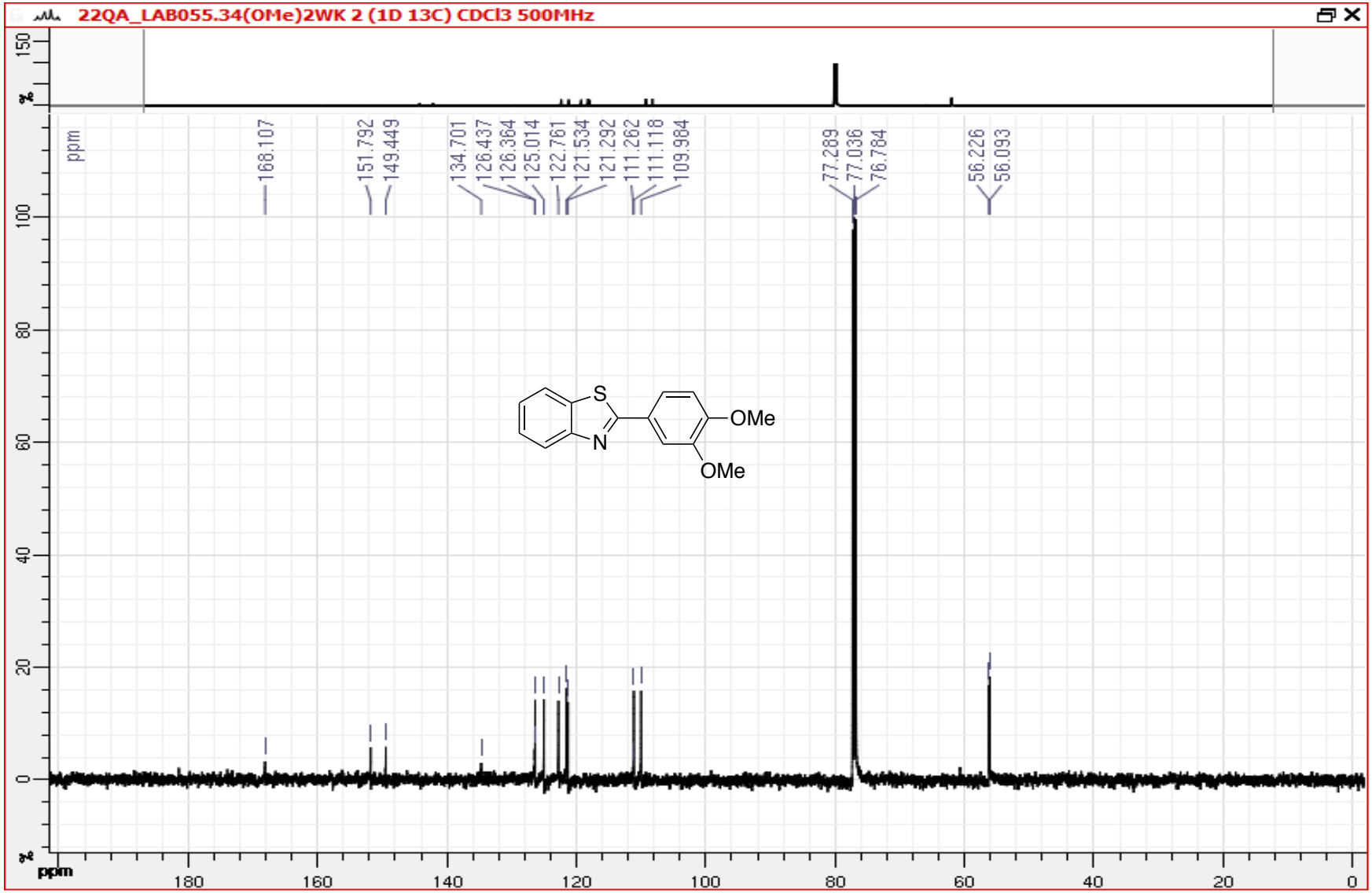
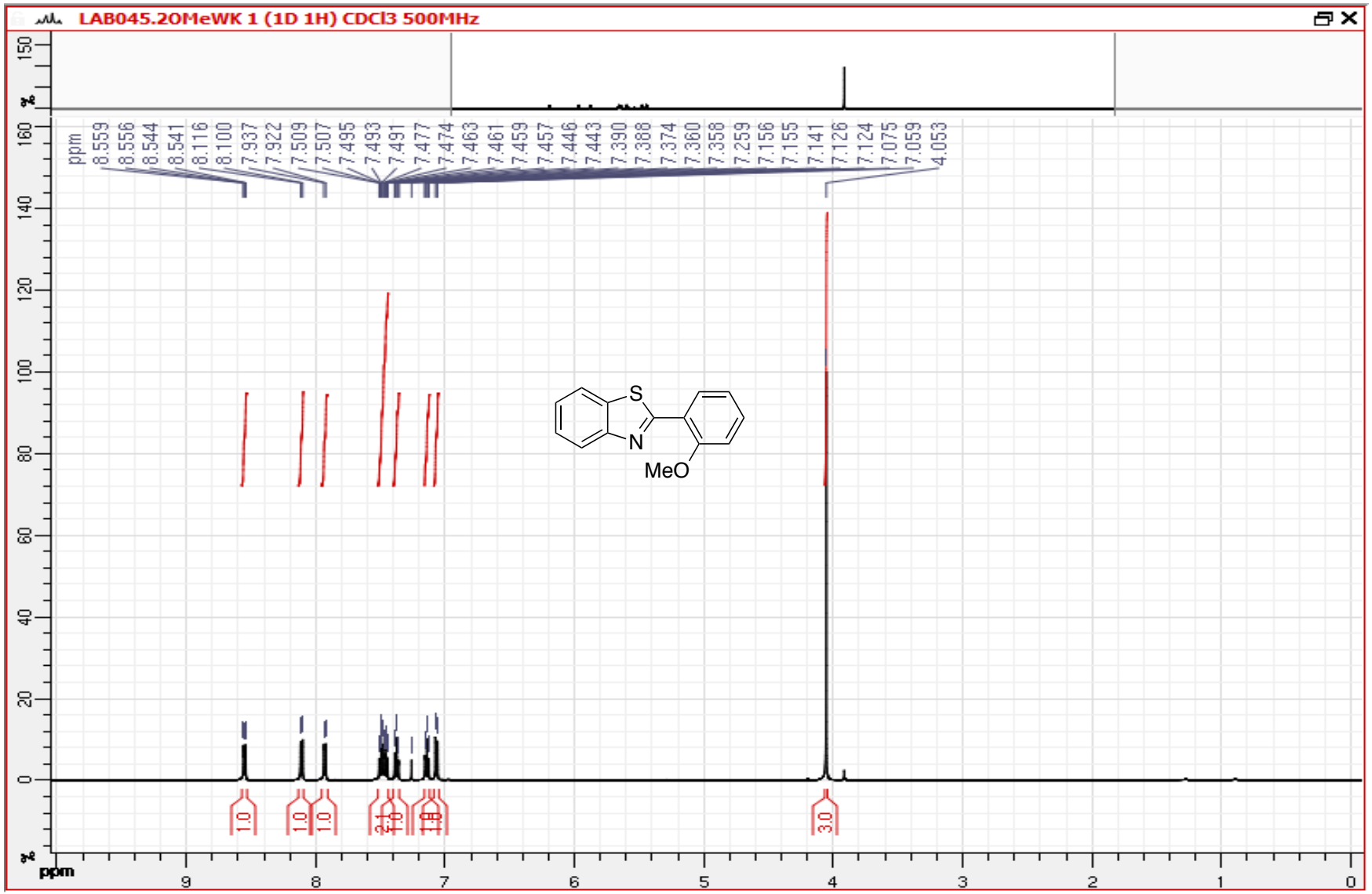
122.815
121.523
114.425
77.296
77.044
76.787
55.490
S
N
OMe
180
160
140
120
100
80
60
40
20
0

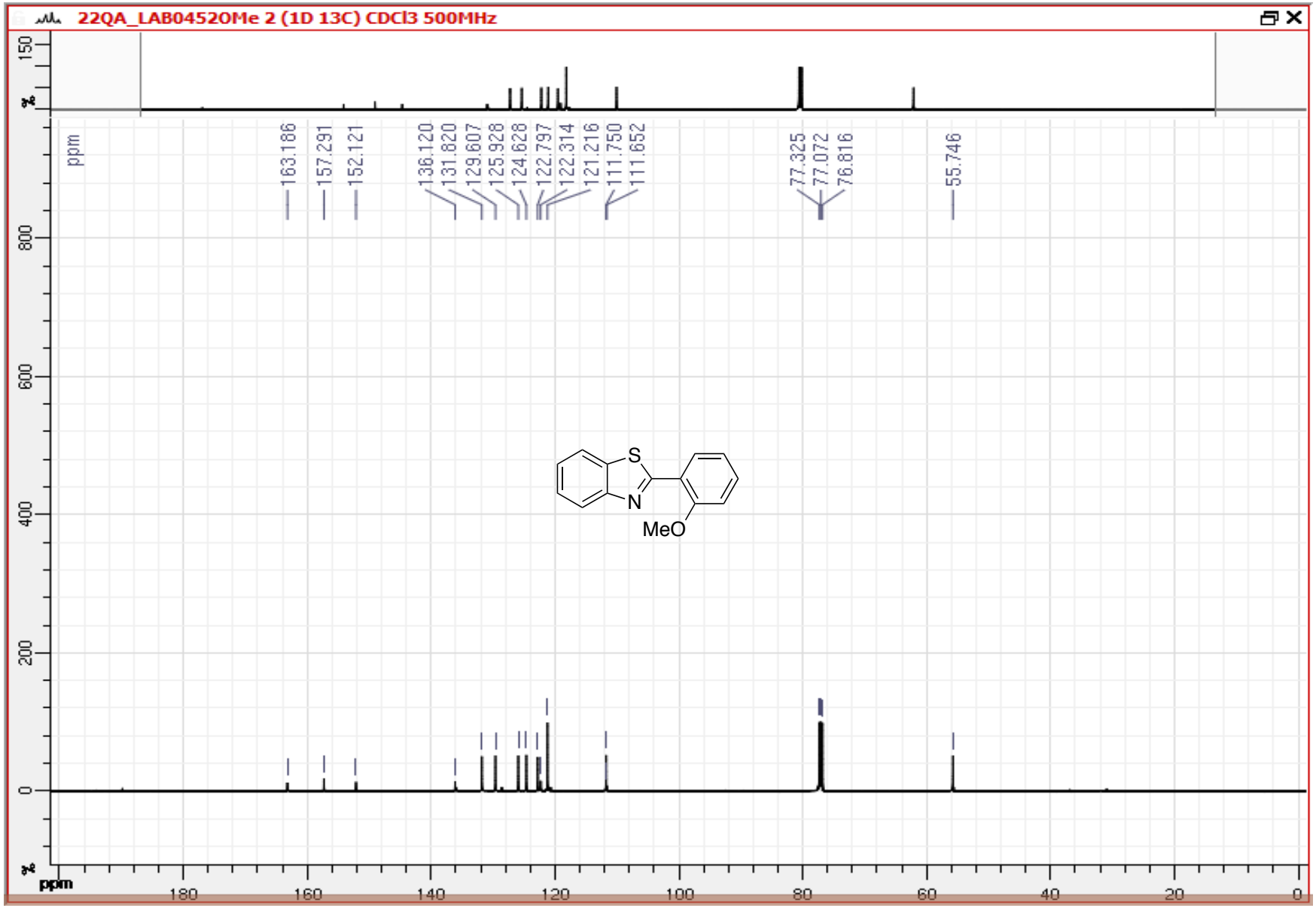
2-(3,4-Dimethoxyphenyl)benzo[d]thiazole (3ae)



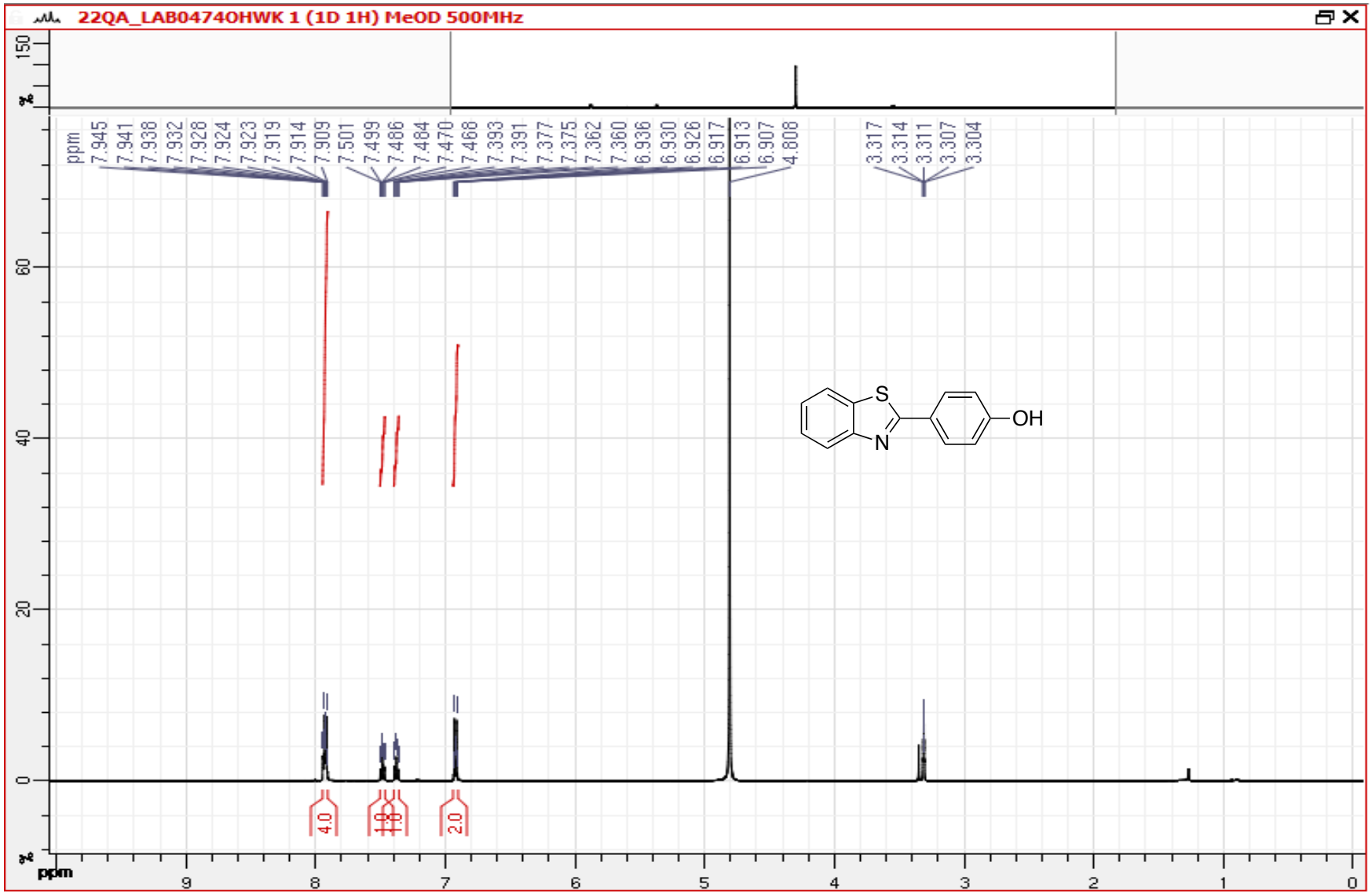

22QA_LAB055.34(OMe)2WK 2 (1D 13C) CDCl3 500MHz
ppm
168.107
151.792
149.449
134.701
126.437
126.364
125.014
122.761
121.534
121.292
111.262
111.118
109.984
77.289
77.036
76.784
56.226
56.093
S
N
OMe
OMe

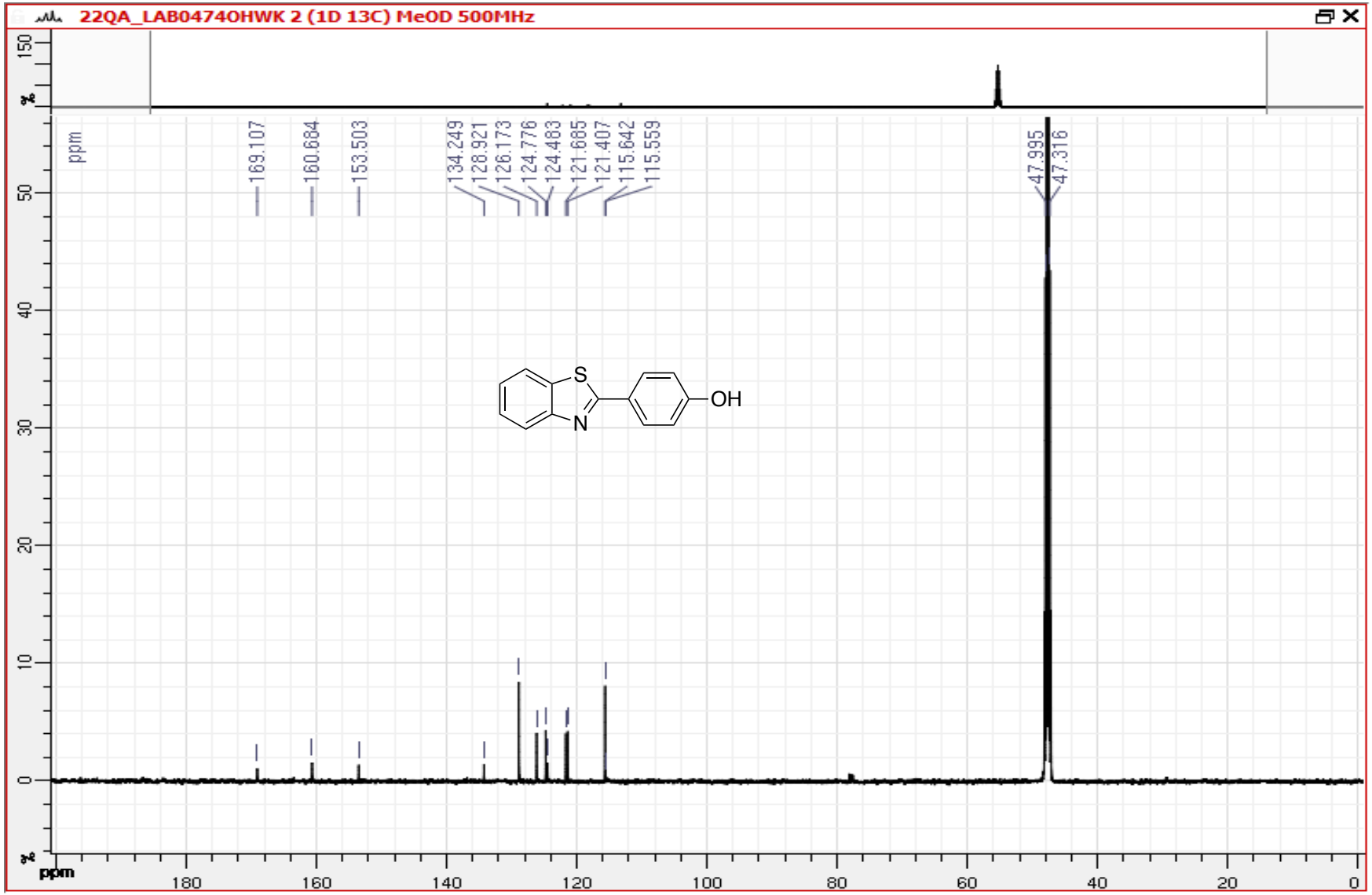
2-(2-Methoxyphenyl)benzo[d]thiazole (3af)



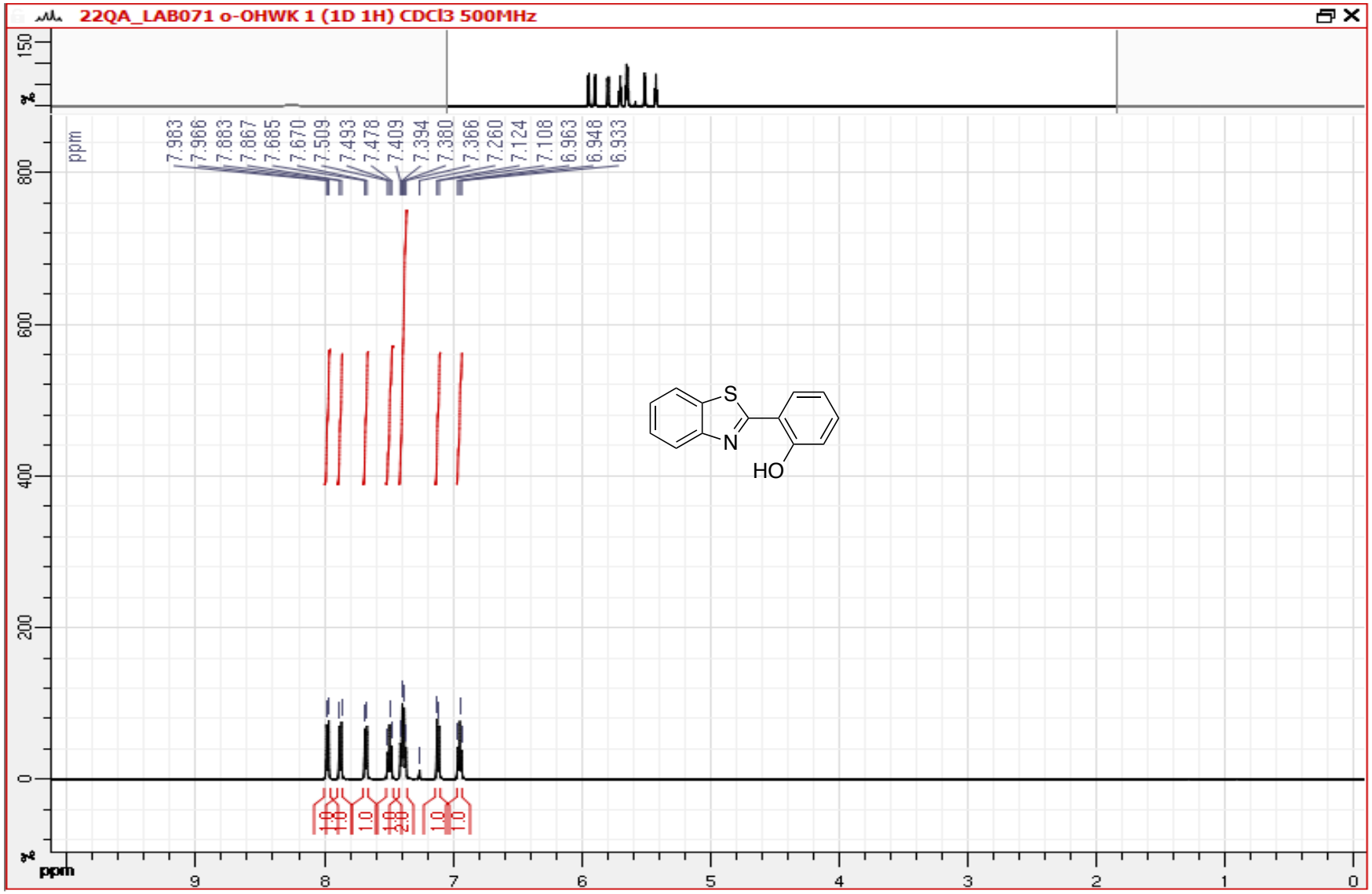

22QA_LAB04520Me 2 (1D 13C) CDCl3 500MHz
ppm
163.186
157.291
152.121
136.120
131.820
129.607
125.928
124.628
122.797
122.314
121.216
111.750
111.652
77.325
77.072
76.816
55.746
S
N
MeO
150
800
600
400
200
0
180
160
140
120
100
80
60
40
20
0

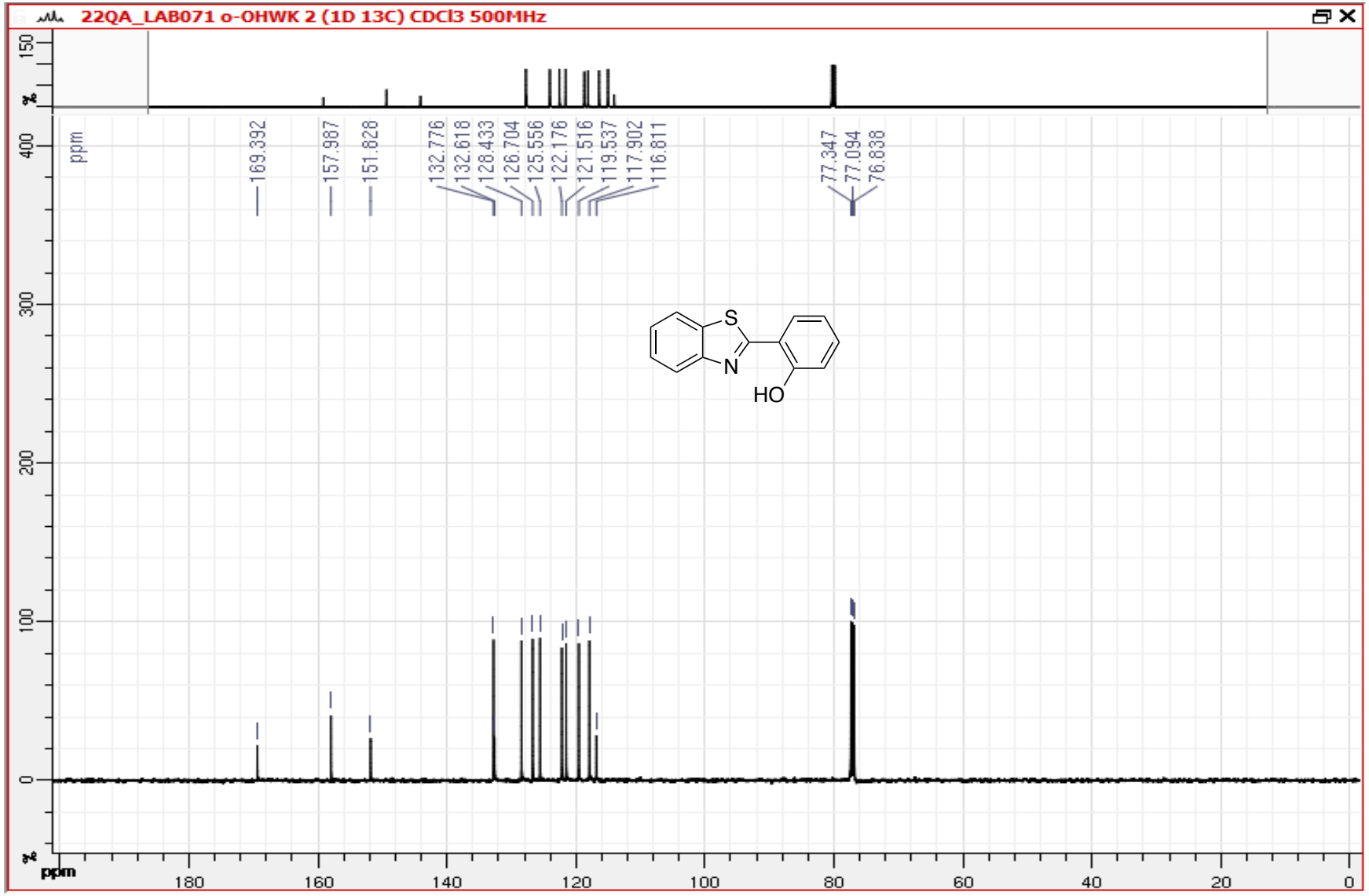
4-(Benzo[d]thiazol-2-yl)phenol (3ag)



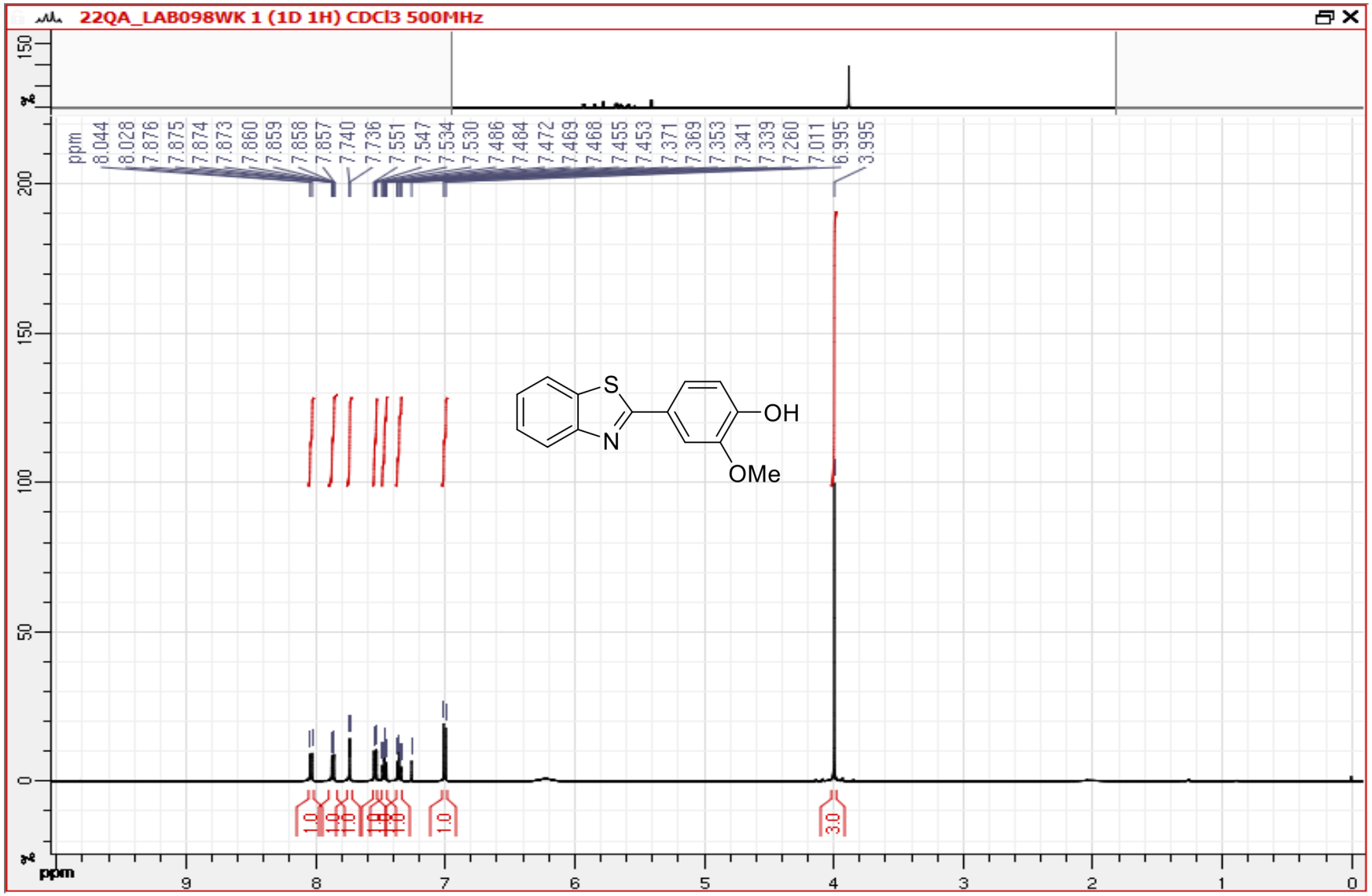

22QA_LAB0474OHWK 2 (1D 13C) MeOD 500MHz
ppm
169.107
160.684
153.503
134.249
128.921
126.173
124.776
124.483
121.685
121.407
115.642
115.559
47.995
47.316
S
N
OH
180
160
140
120
100
80
60
40
20
0

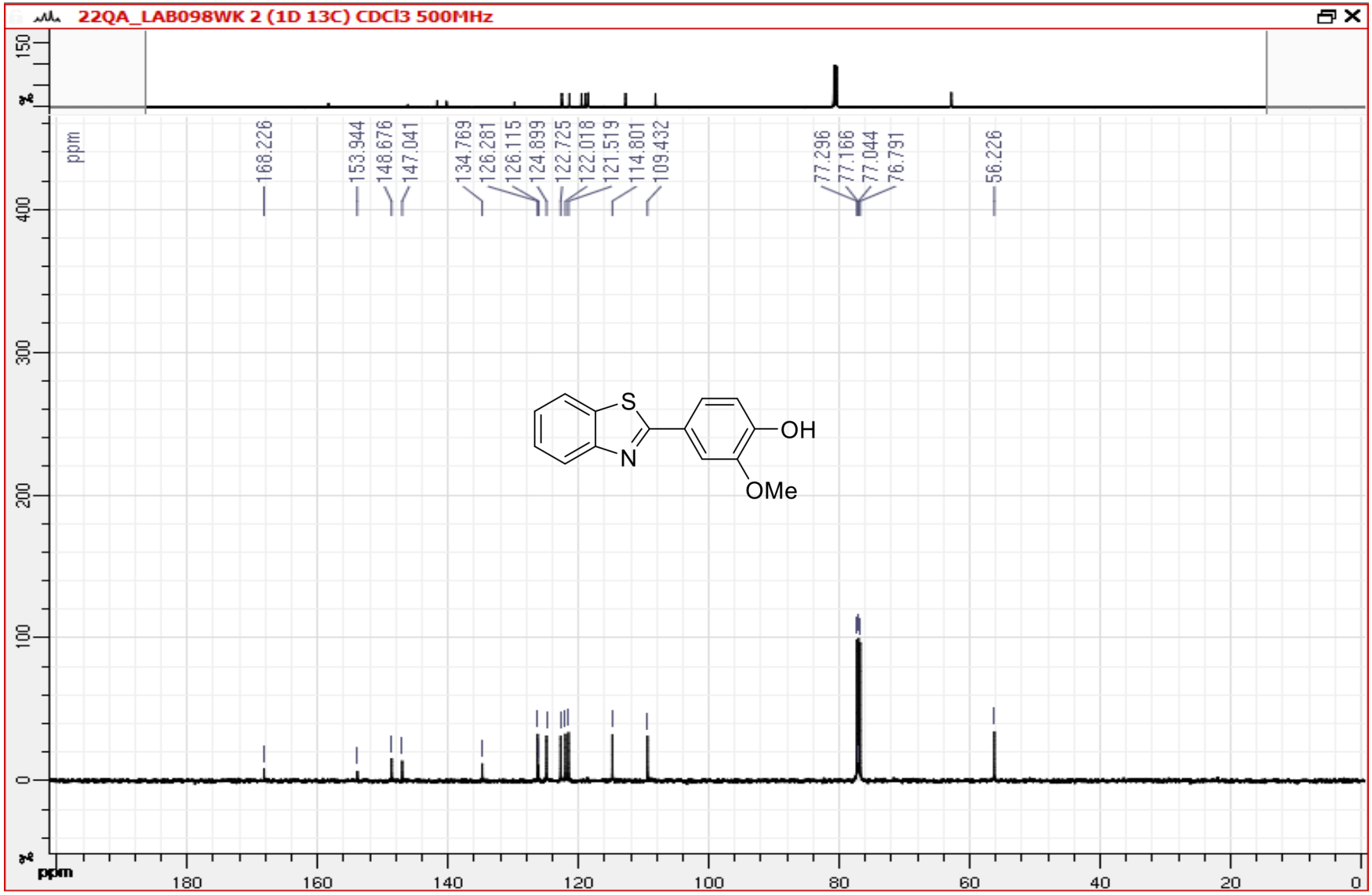
2-(Benzo[d]thiazol-2-yl)phenol (3ah)



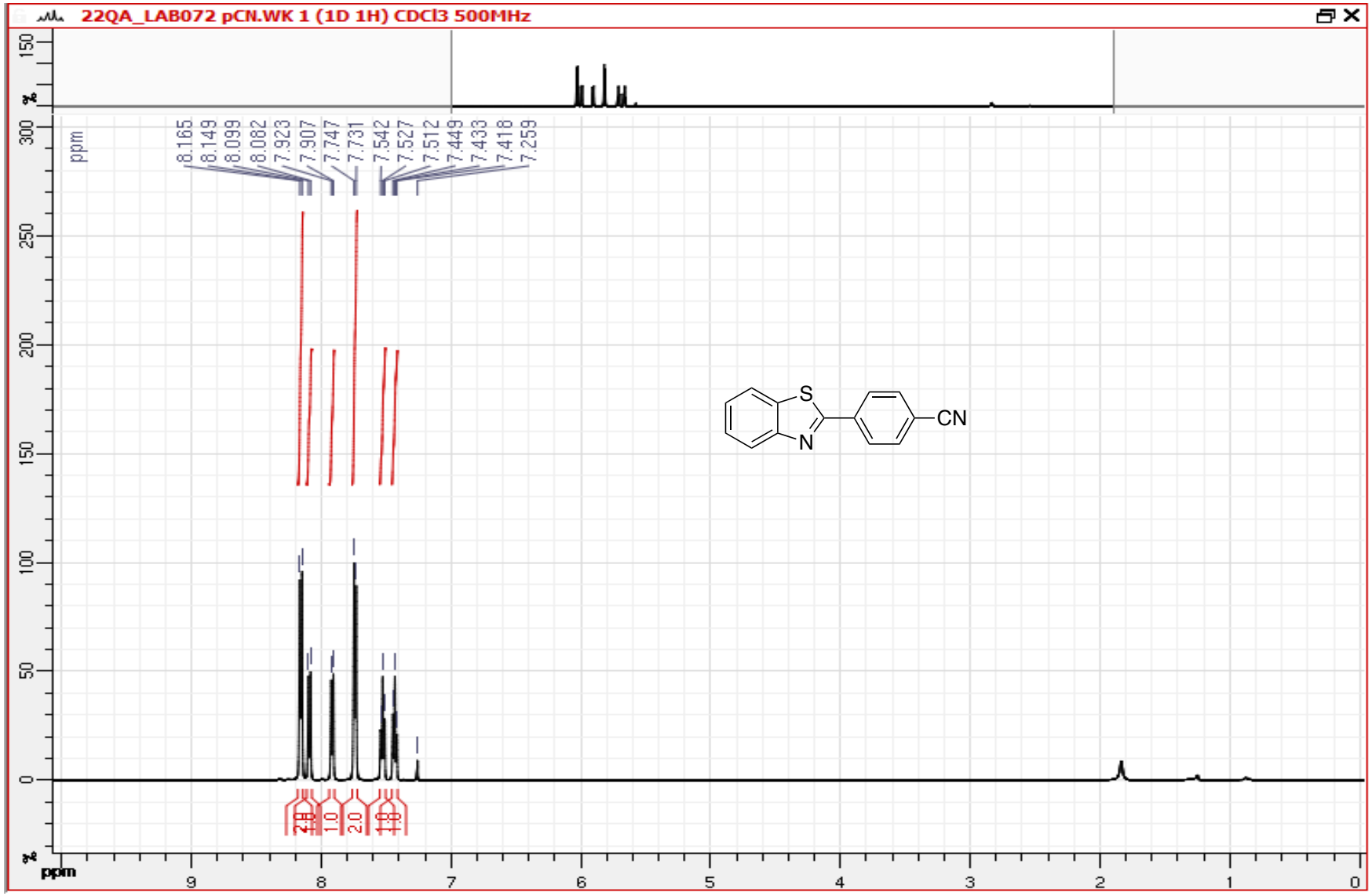

22QA_LAB071 o-OHWK 2 (1D 13C) CDCl3 500MHz
ppm
169.392
157.987
151.828
132.776
132.618
128.433
126.704
125.556
122.176
121.516
119.537
117.902
116.811
77.347
77.094
76.838
S
N
HO
150
400
300
200
100
0
180
160
140
120
100
80
60
40
20
0

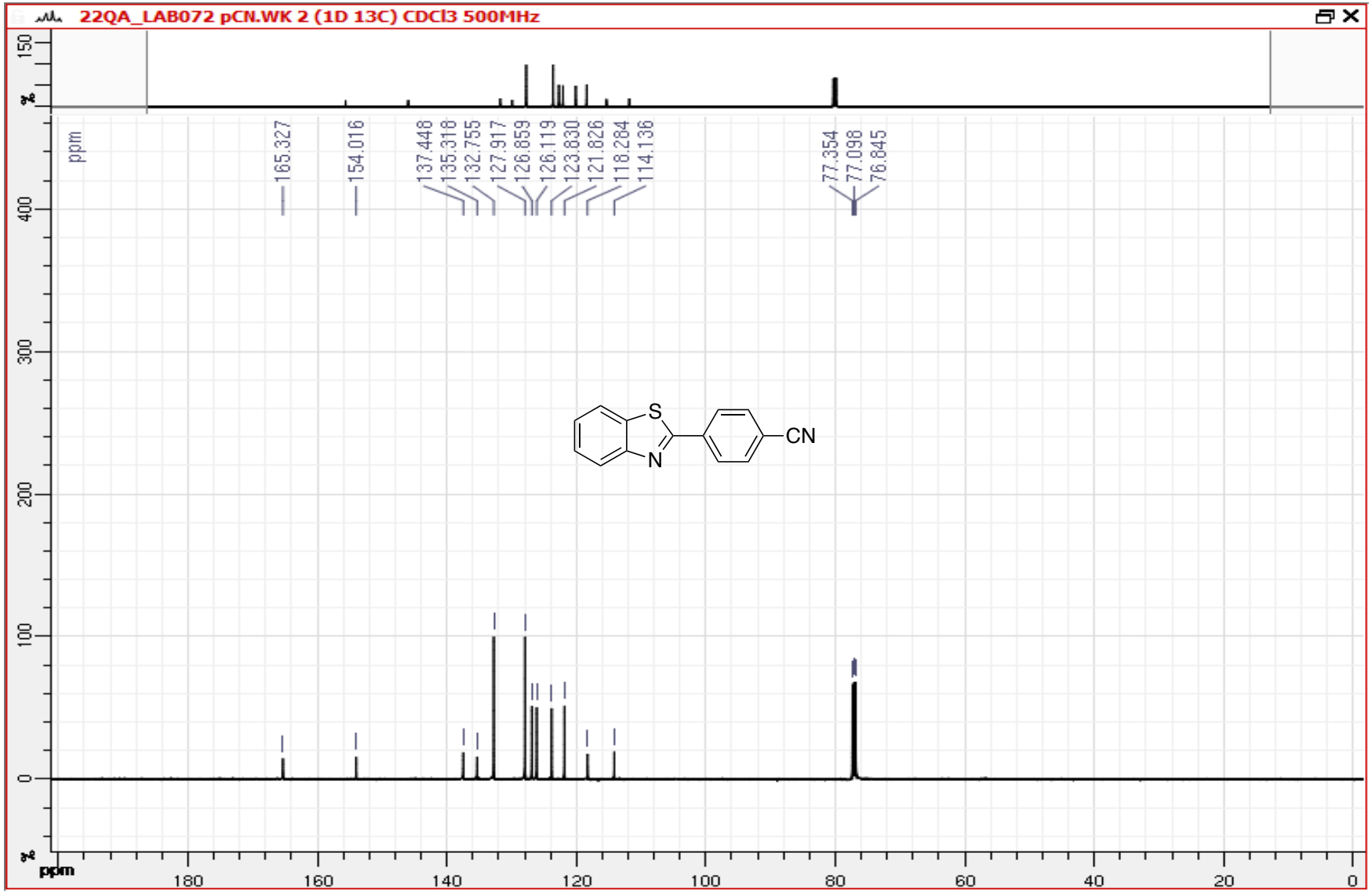
4-(Benzo[d]thiazol-2-yl)-2-methoxyphenol (3ai)



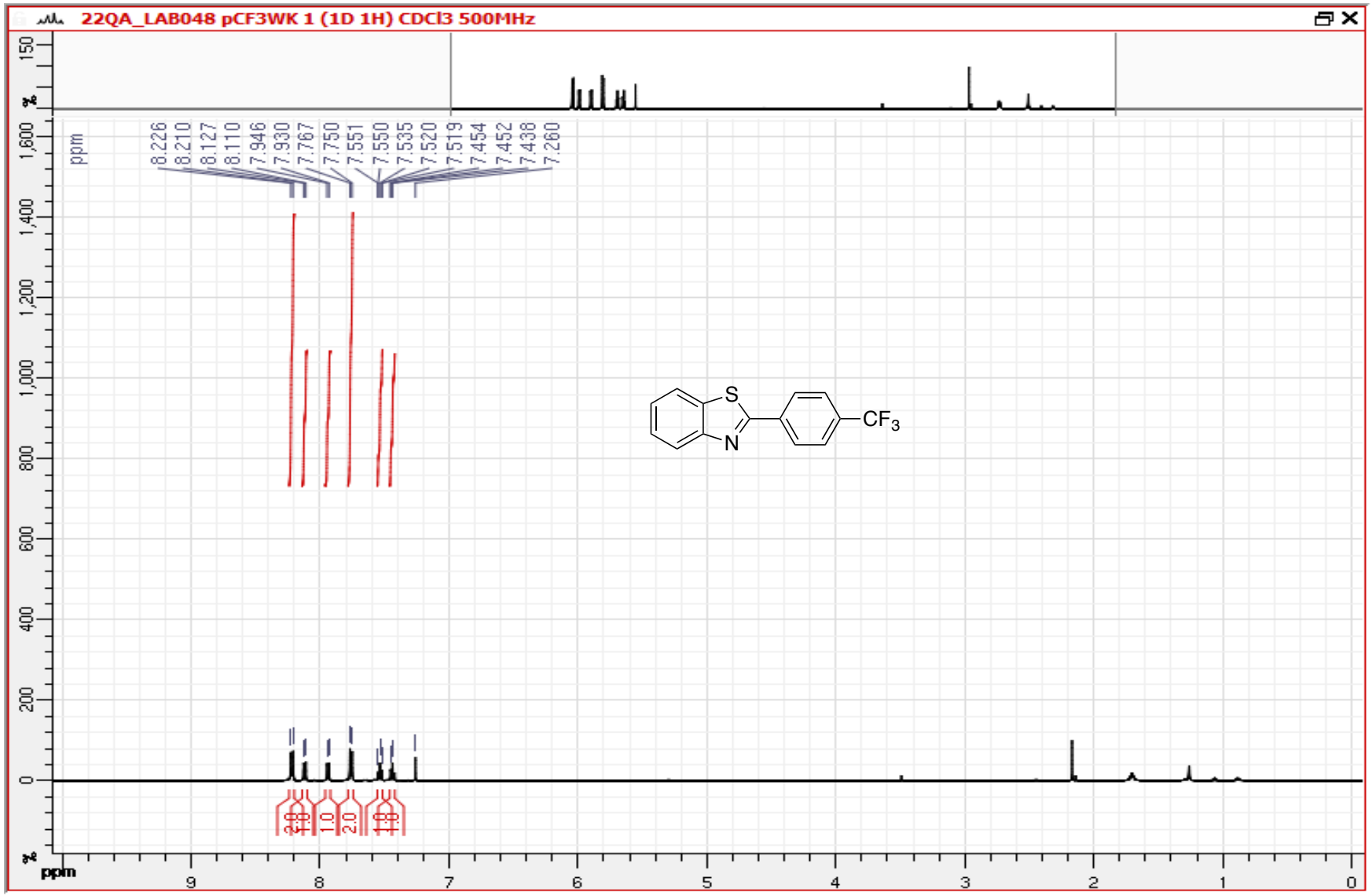

22QA_LAB098WK 2 (1D 13C) CDCl3 500MHz
ppm
168.226
153.944
148.676
147.041
134.769
126.281
126.115
124.899
122.725
122.018
121.519
114.801
109.432
77.296
77.166
77.044
76.791
56.226
S
N
OH
OMe
180
160
140
120
100
80
60
40
20
0

4-(Benzo[d]thiazol-2-yl)benzonitrile (3aj)

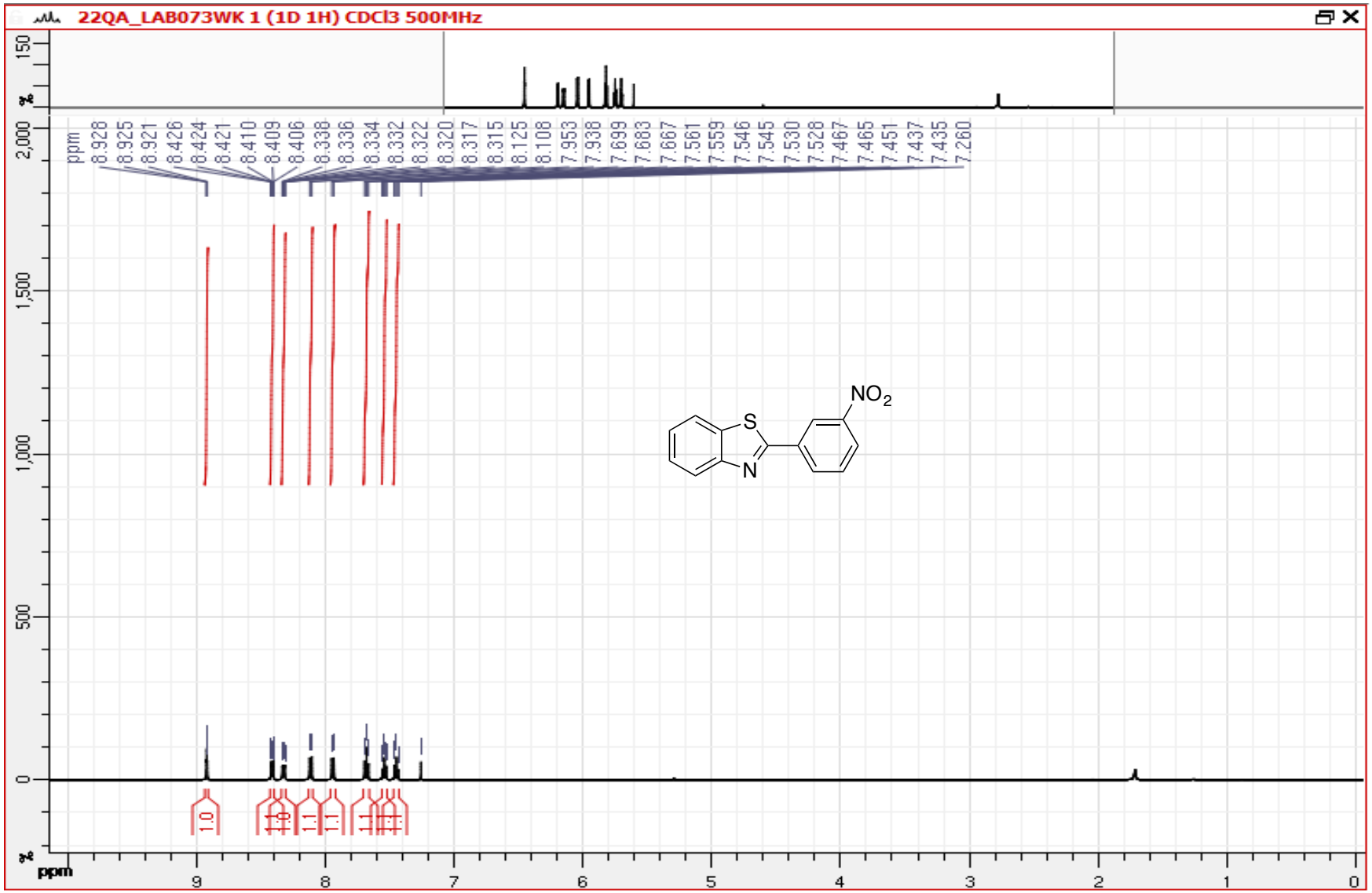


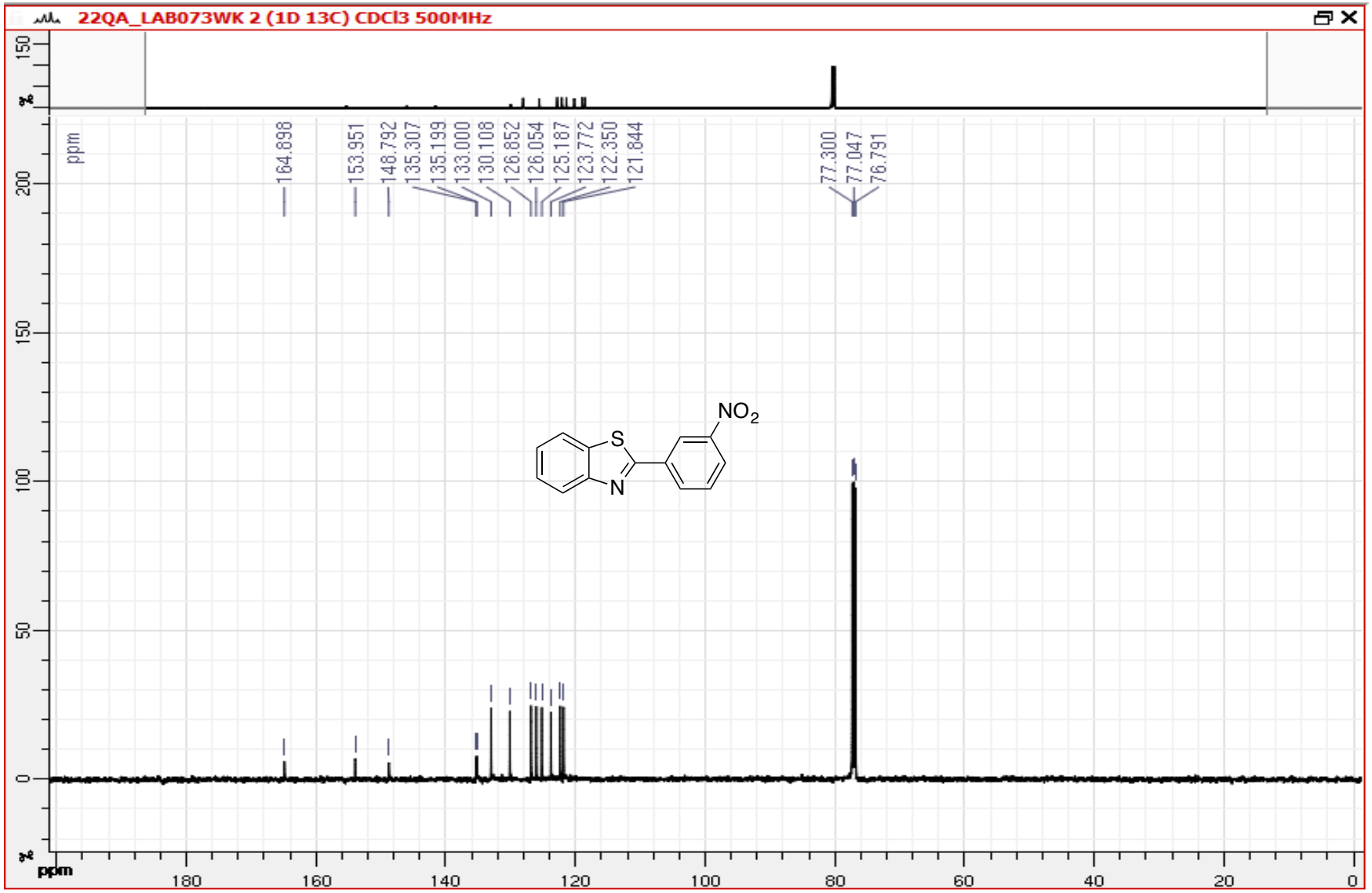

22QA_LAB072 pCN.WK 2 (1D 13C) CDCl3 500MHz
ppm
165.327
154.016
137.448
135.318
132.755
127.917
126.859
126.119
123.830
121.826
118.284
114.136
77.354
77.098
76.845
S
N
CN
180
160
140
120
100
80
60
40
20
0

2-(4-(Trifluoromethyl)phenyl)benzo[d]thiazole (3ak)

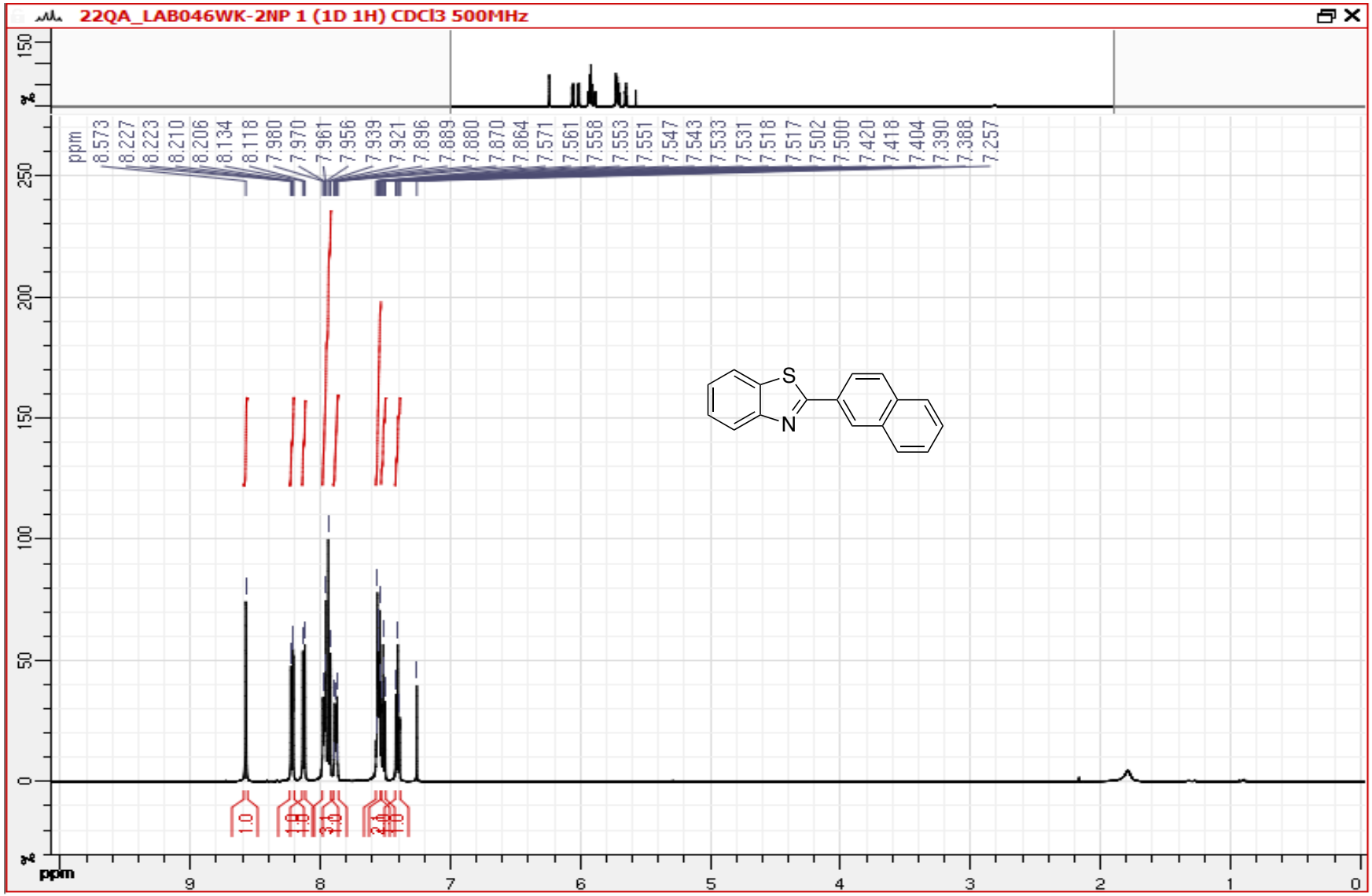


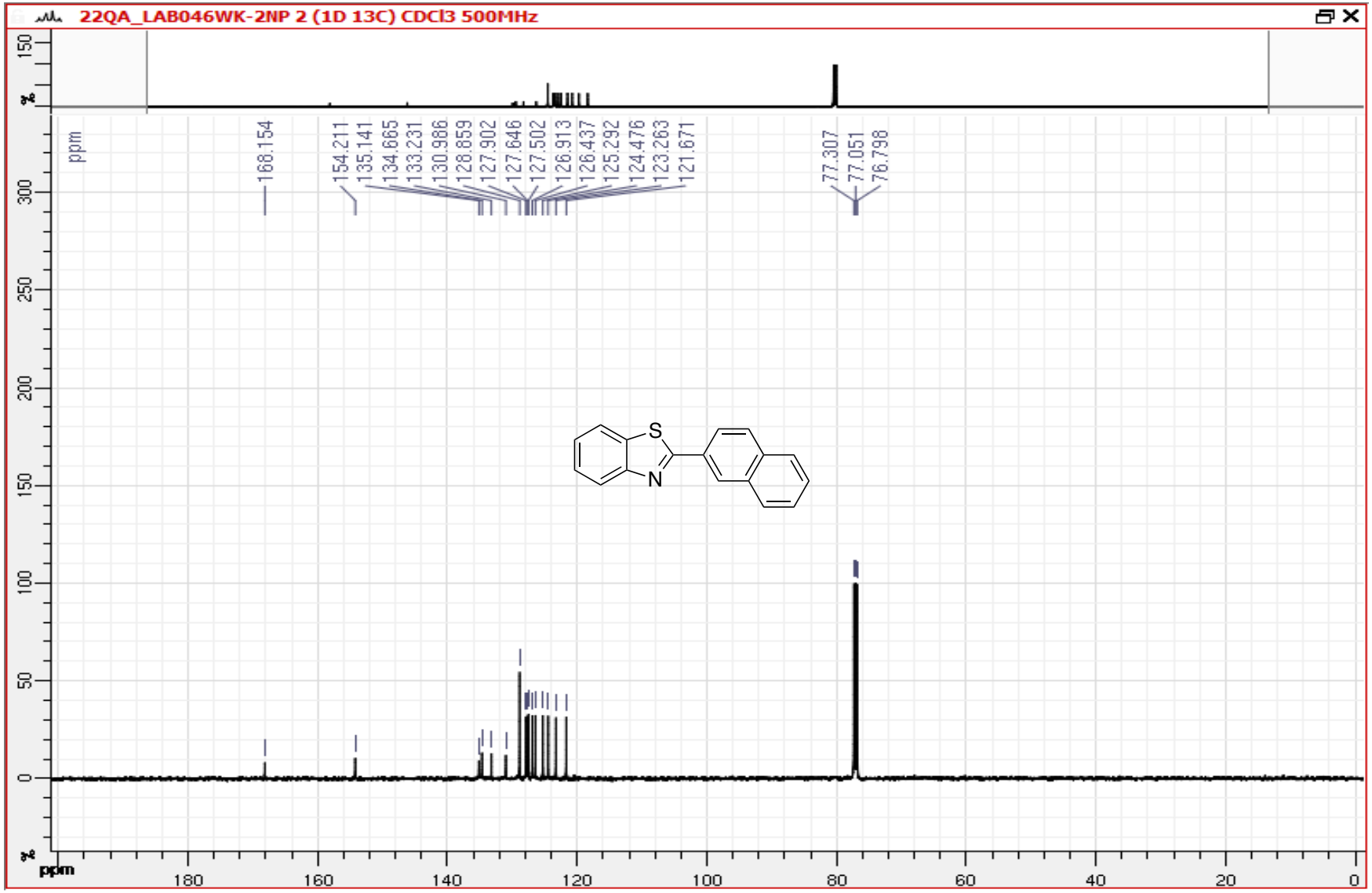
2-(3-Nitrophenyl)benzo[d]thiazole (3al)



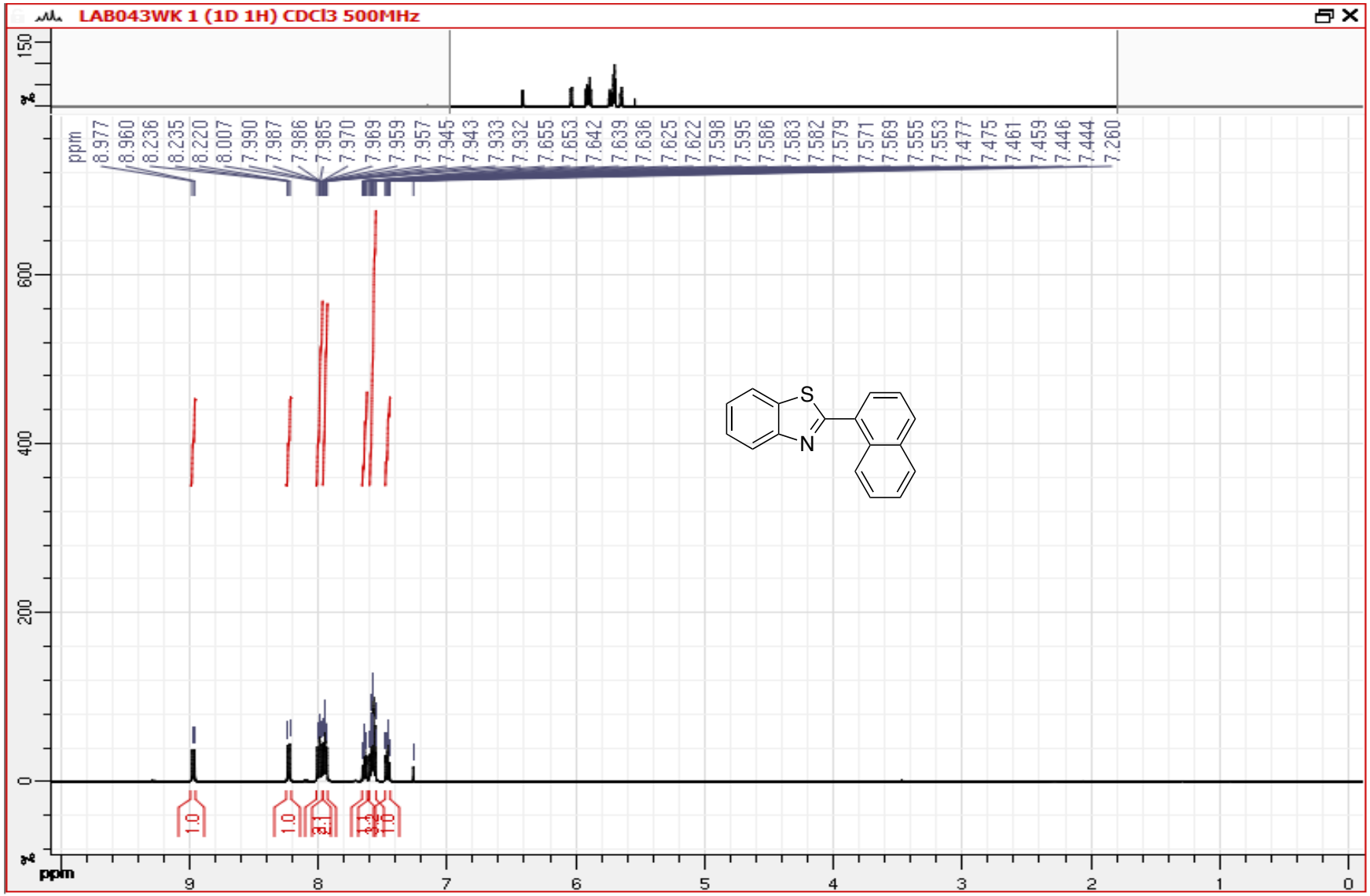

22QA_LAB073WK 2 (1D 13C) CDCl3 500MHz
ppm
164.898
153.951
148.792
135.307
135.199
133.000
130.108
126.852
126.054
125.187
123.772
122.350
121.844
77.300
77.047
76.791
NO2
S
N
180
160
140
120
100
80
60
40
20
0

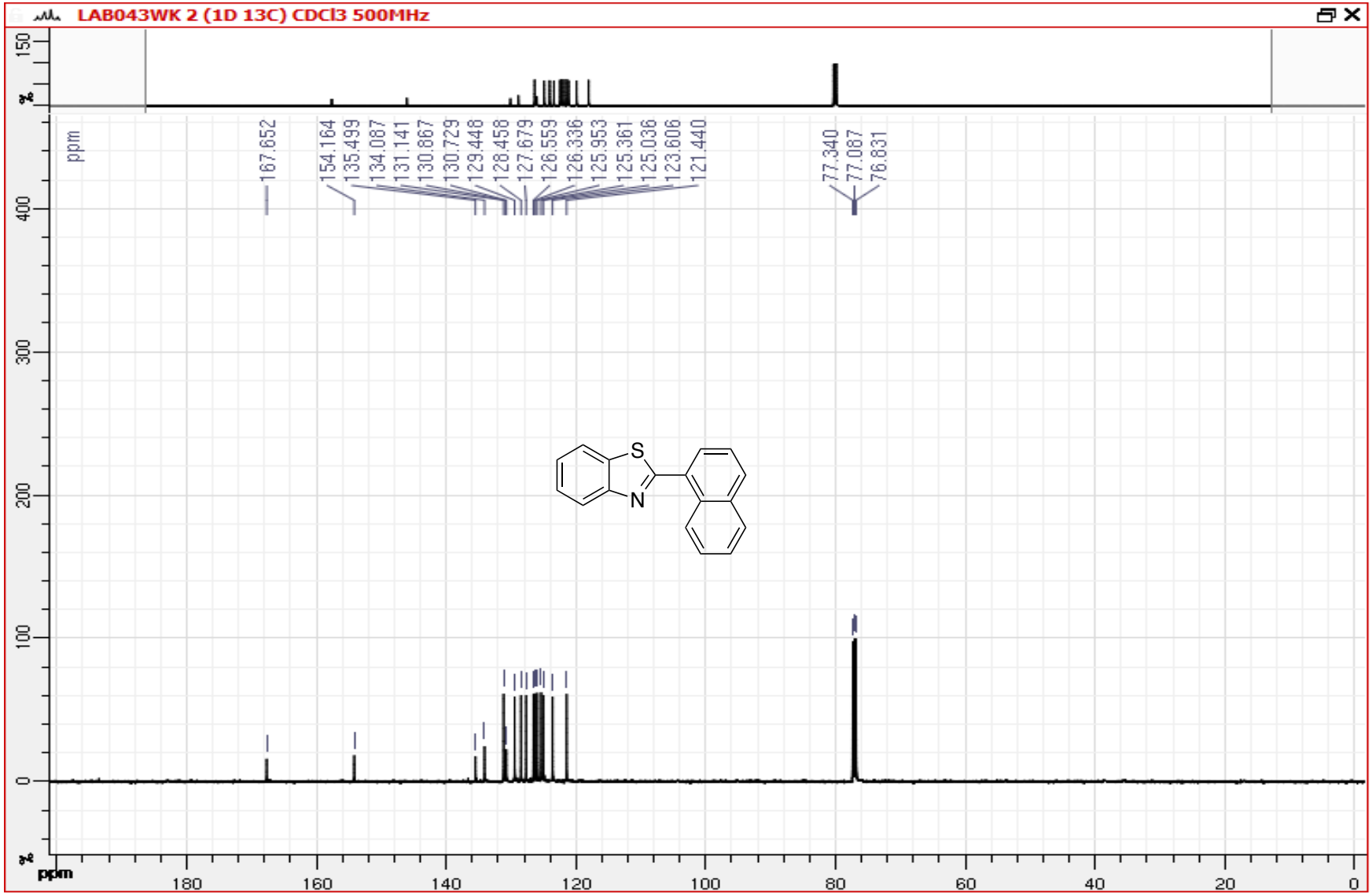
2-(Naphthalen-2-yl)benzo[d]thiazole (3am)



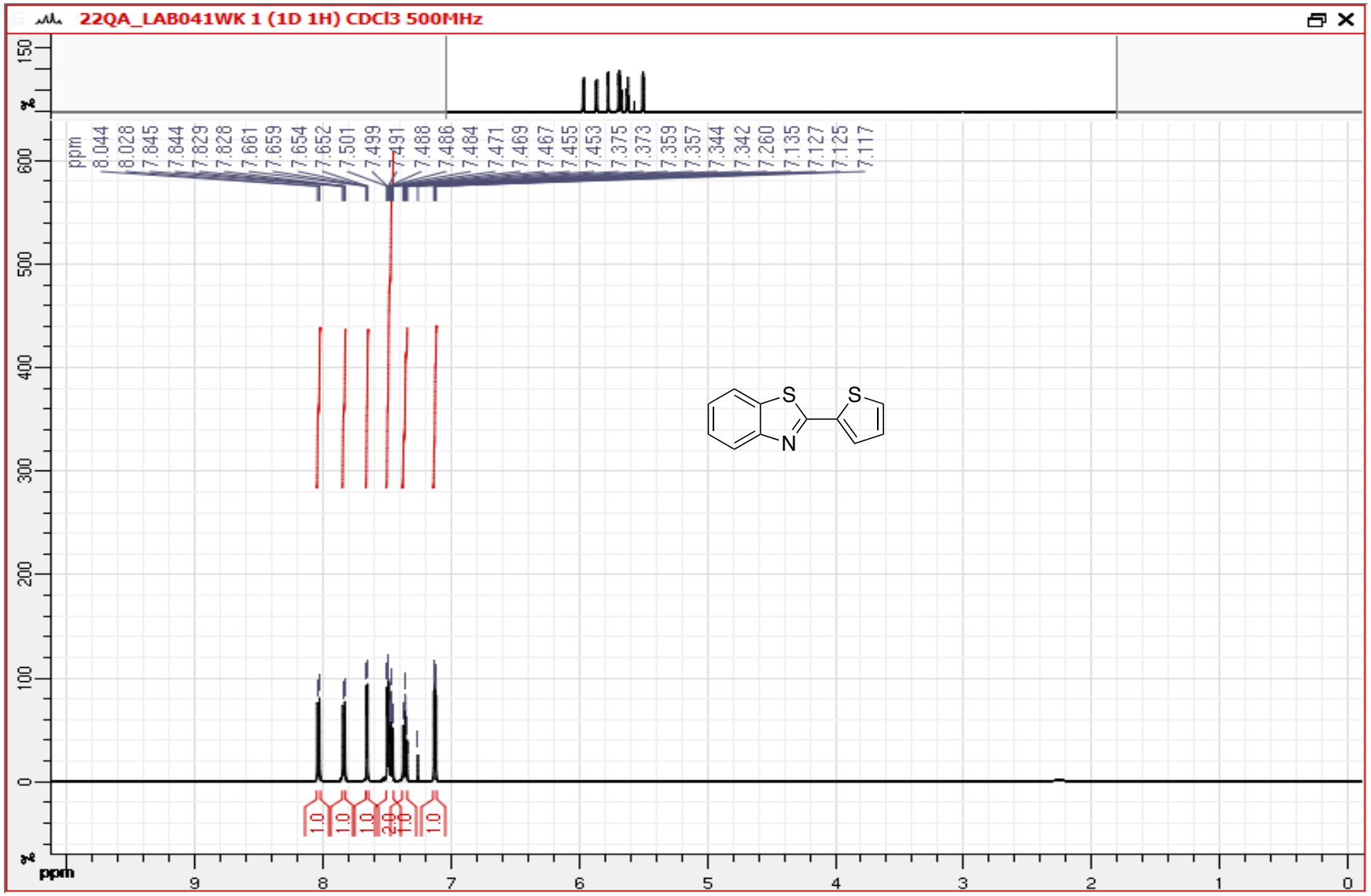

22QA_LAB046WK-2NP 2 (1D 13C) CDCl3 500MHz
ppm
168.154
154.211
135.141
134.665
133.231
130.986
128.859
127.902
127.646
127.502
126.913
126.437
125.292
124.476
123.263
121.671
77.307
77.051
76.798
S
N
180
160
140
120
100
80
60
40
20
0

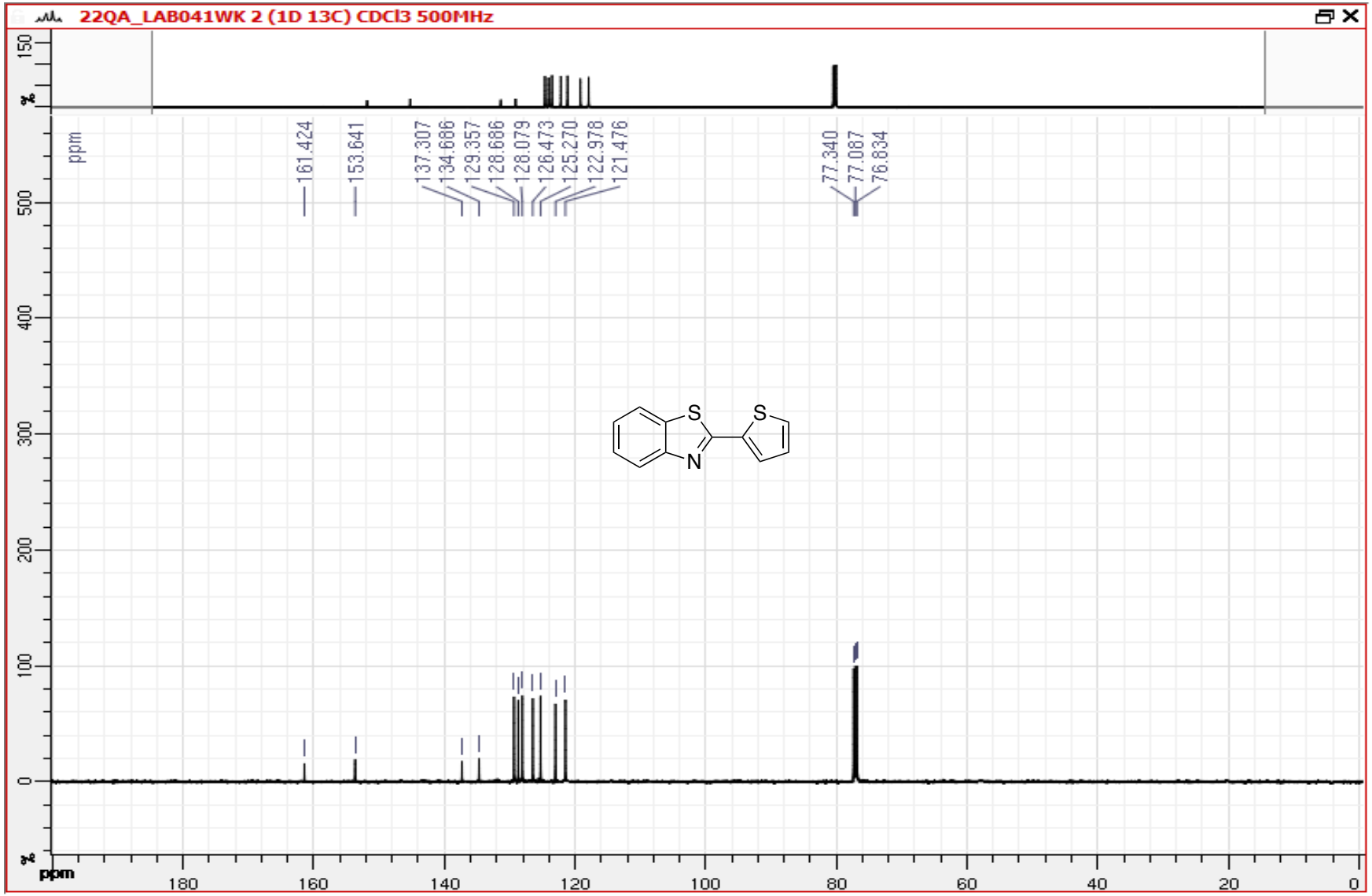
2-(Naphthalen-1-yl)benzo[d]thiazole (3an)



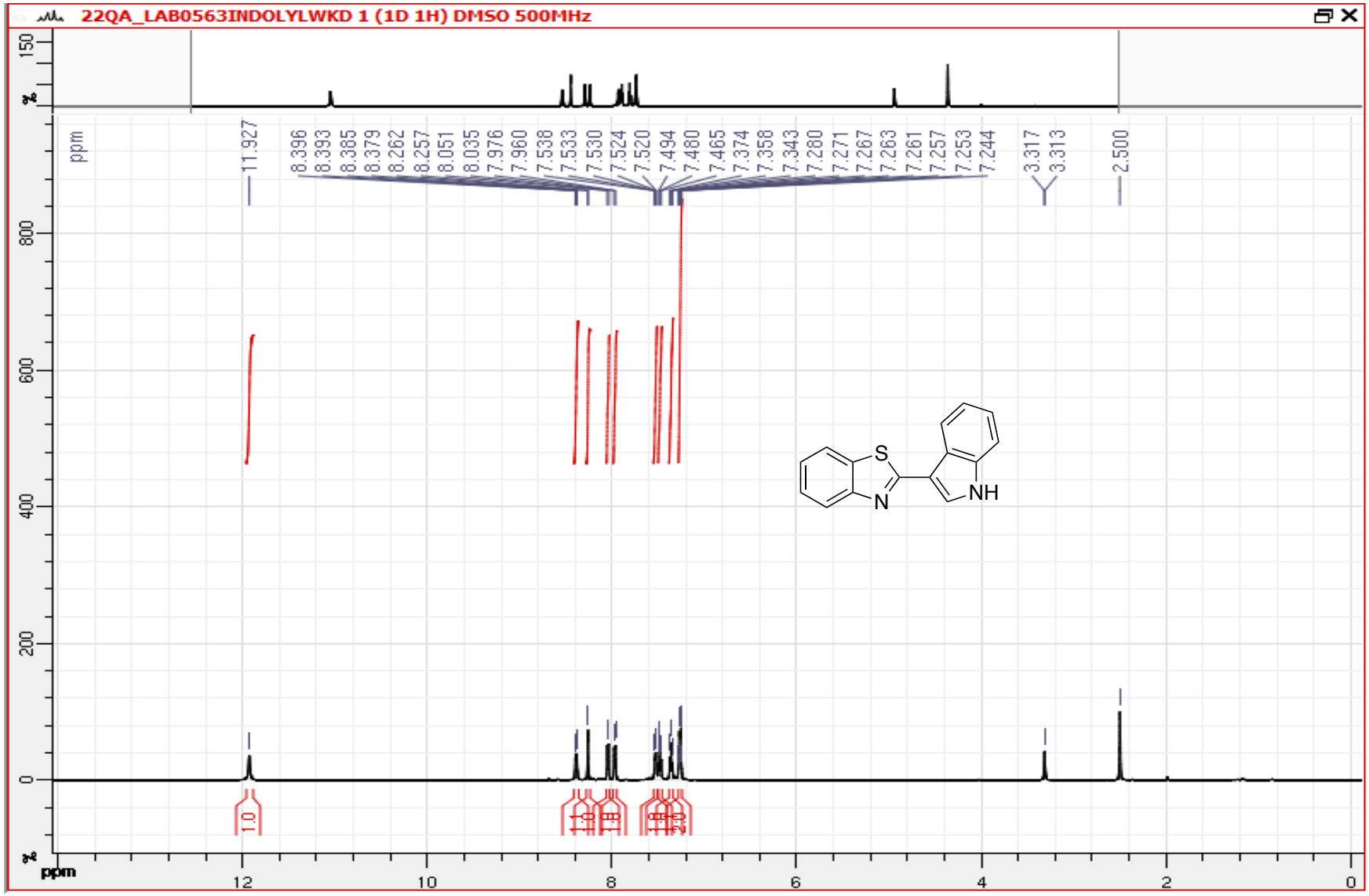

LAB043WK 2 (1D 13C) CDCl3 500MHz
ppm
167.652
154.164
135.499
134.087
131.141
130.867
130.729
129.448
128.458
127.679
126.559
126.336
125.953
125.361
125.036
123.606
121.440
77.340
77.087
76.831
S
N

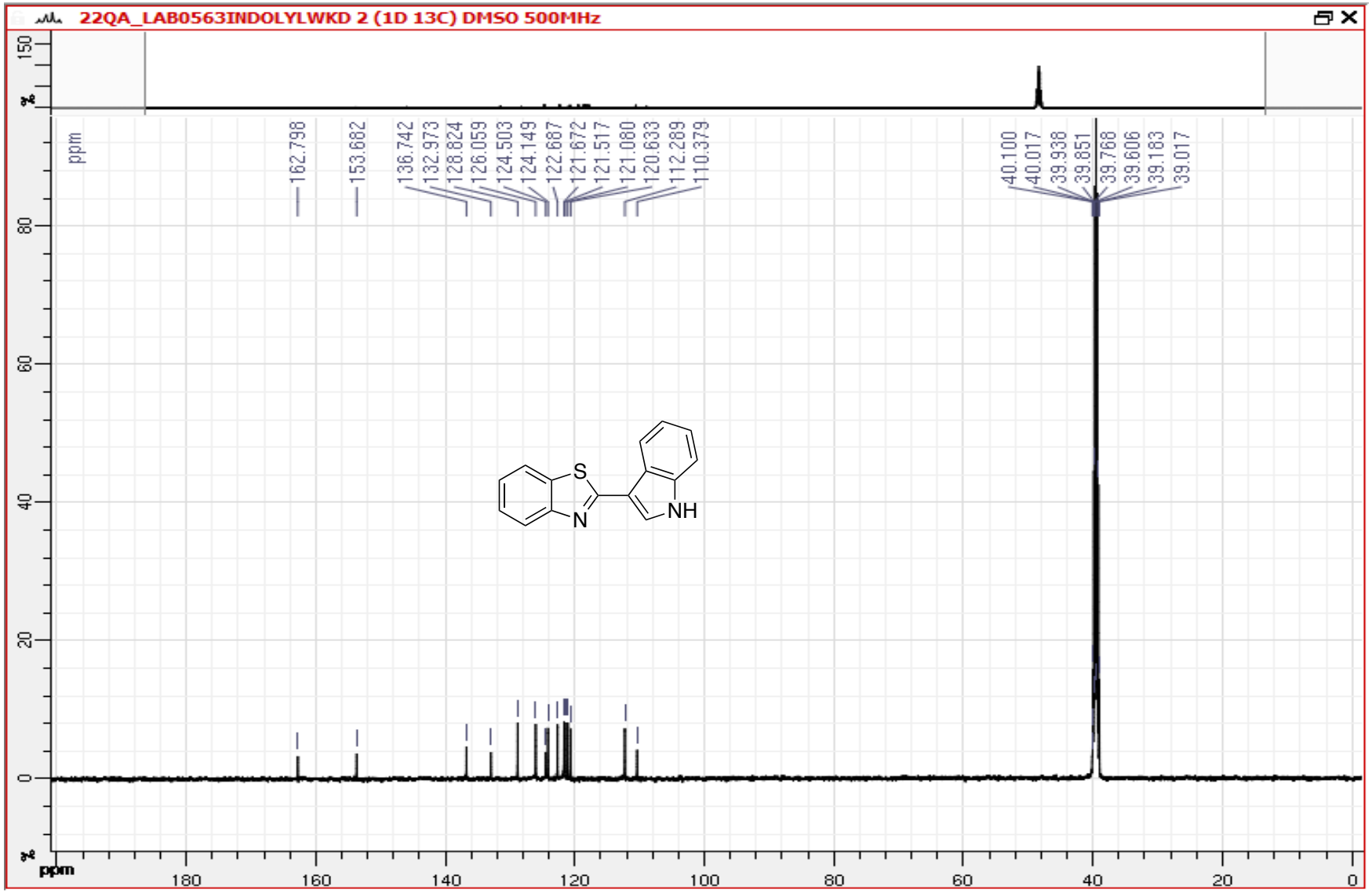
2-(Thiophen-2-yl)benzo[d]thiazole (3ao)



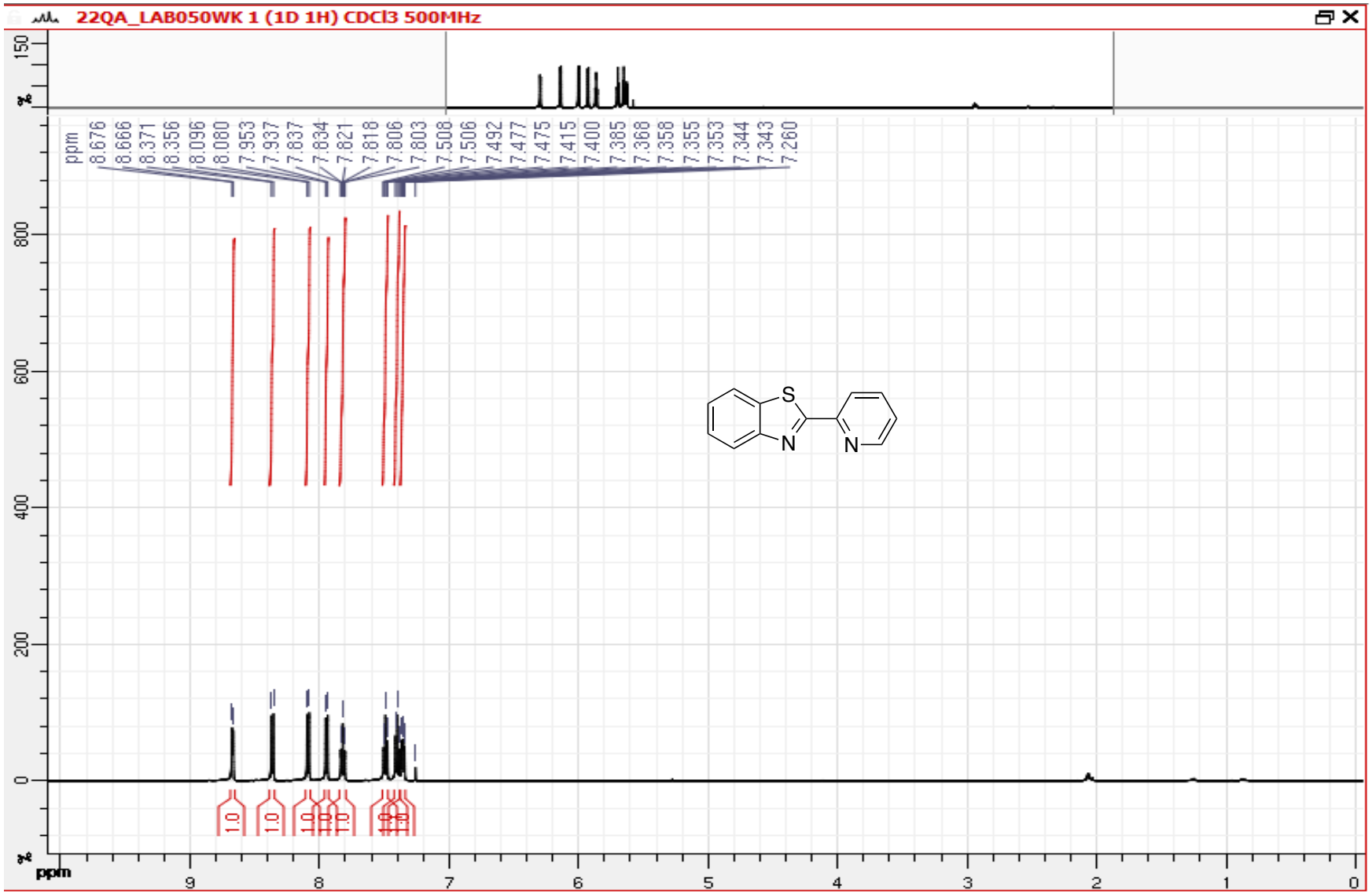

22QA_LAB041WK 2 (1D 13C) CDCl3 500MHz
ppm
161.424
153.641
137.307
134.686
129.357
128.686
128.079
126.473
125.270
122.978
121.476
77.340
77.087
76.834
S
S
N
180
160
140
120
100
80
60
40
20
0

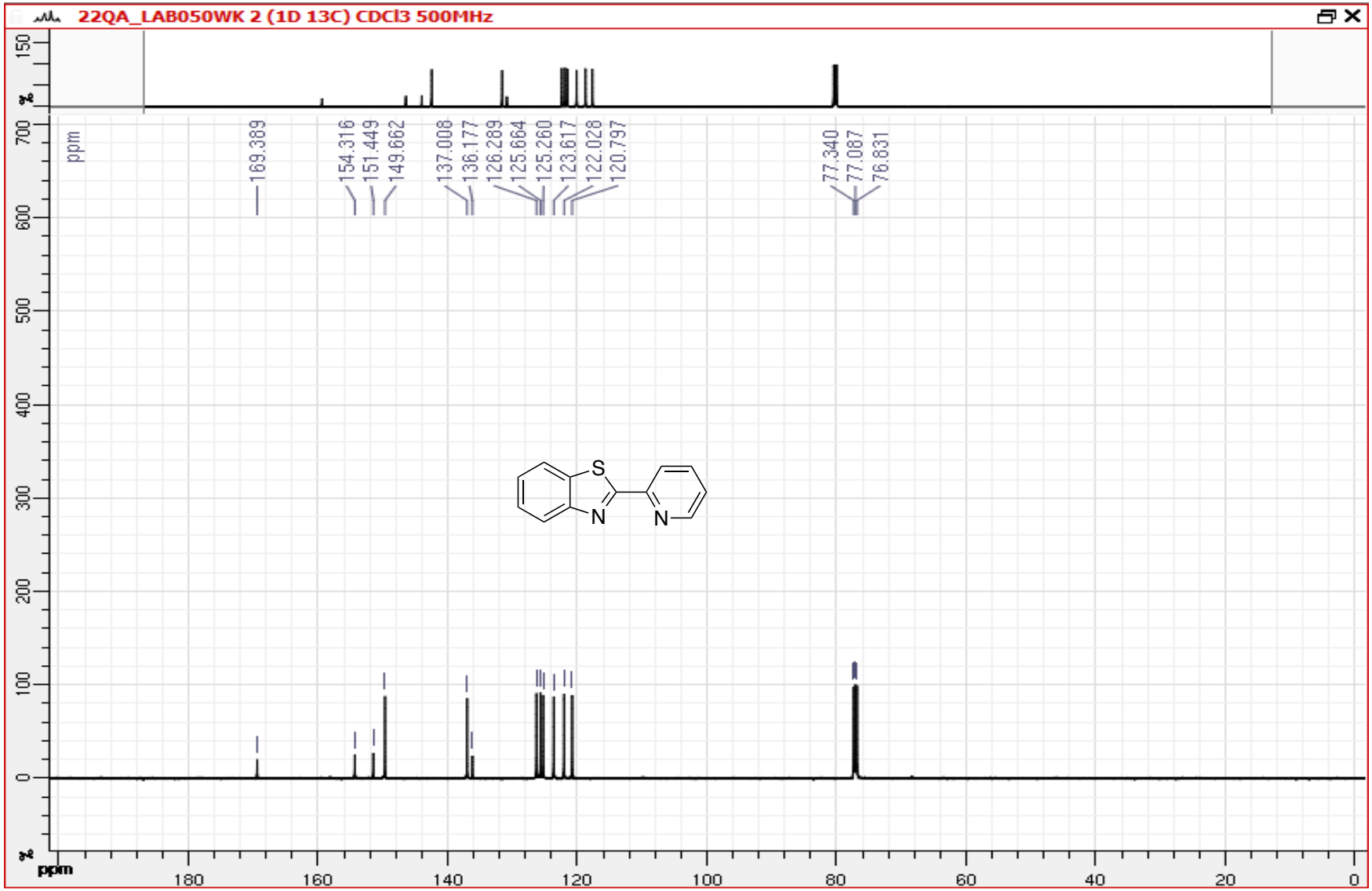
2-(1H-Indol-3-yl)benzo[d]thiazole (3ap)



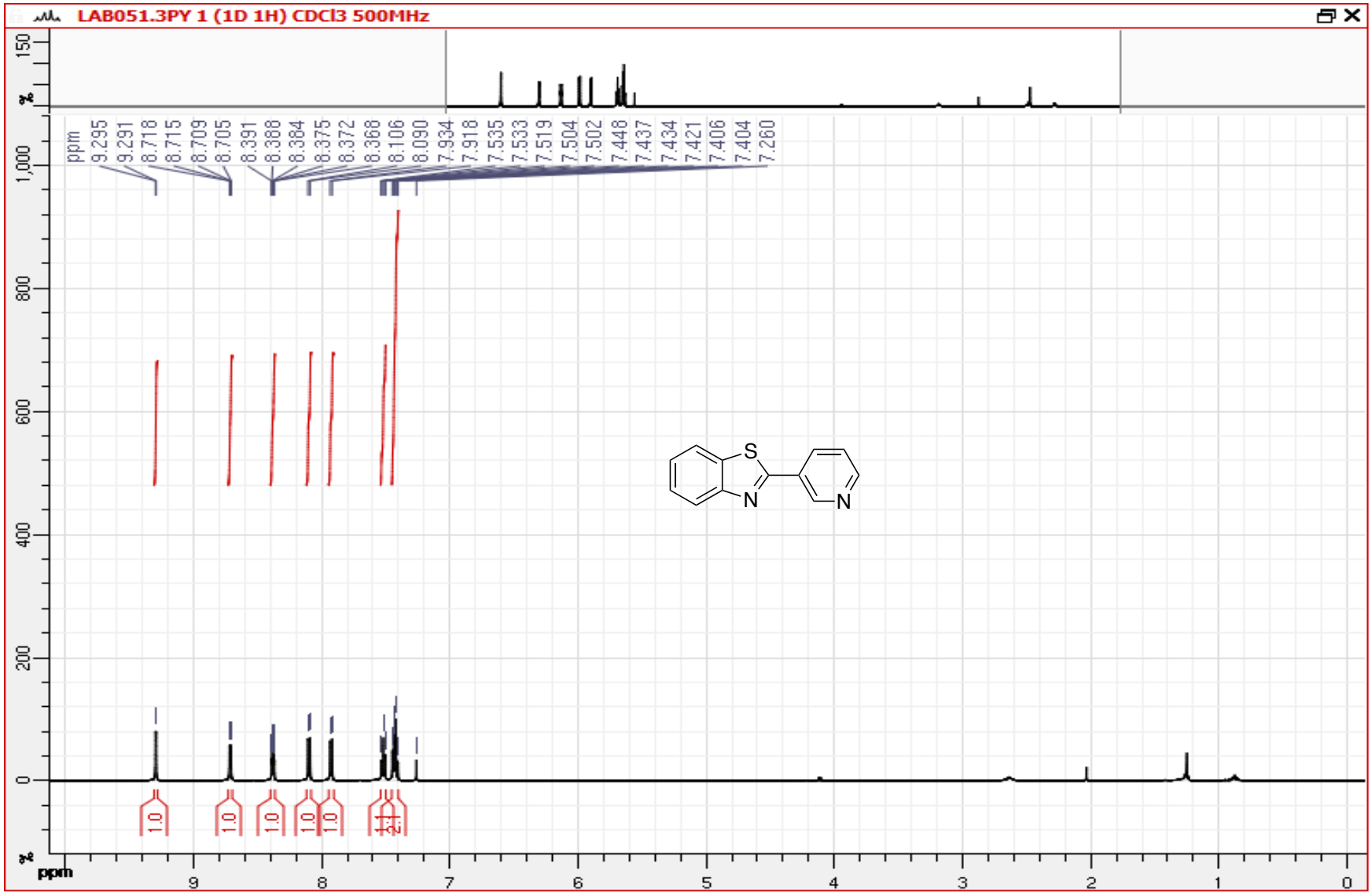

22QA_LAB0563INDOLYLWKD 2 (1D 13C) DMSO 500MHz
ppm
162.798
153.682
136.742
132.973
128.824
126.059
124.503
124.149
122.687
121.672
121.517
121.080
120.633
112.289
110.379
40.100
40.017
39.938
39.851
39.768
39.606
39.183
39.017
S
N
NH
180
160
140
120
100
80
60
40
20
0

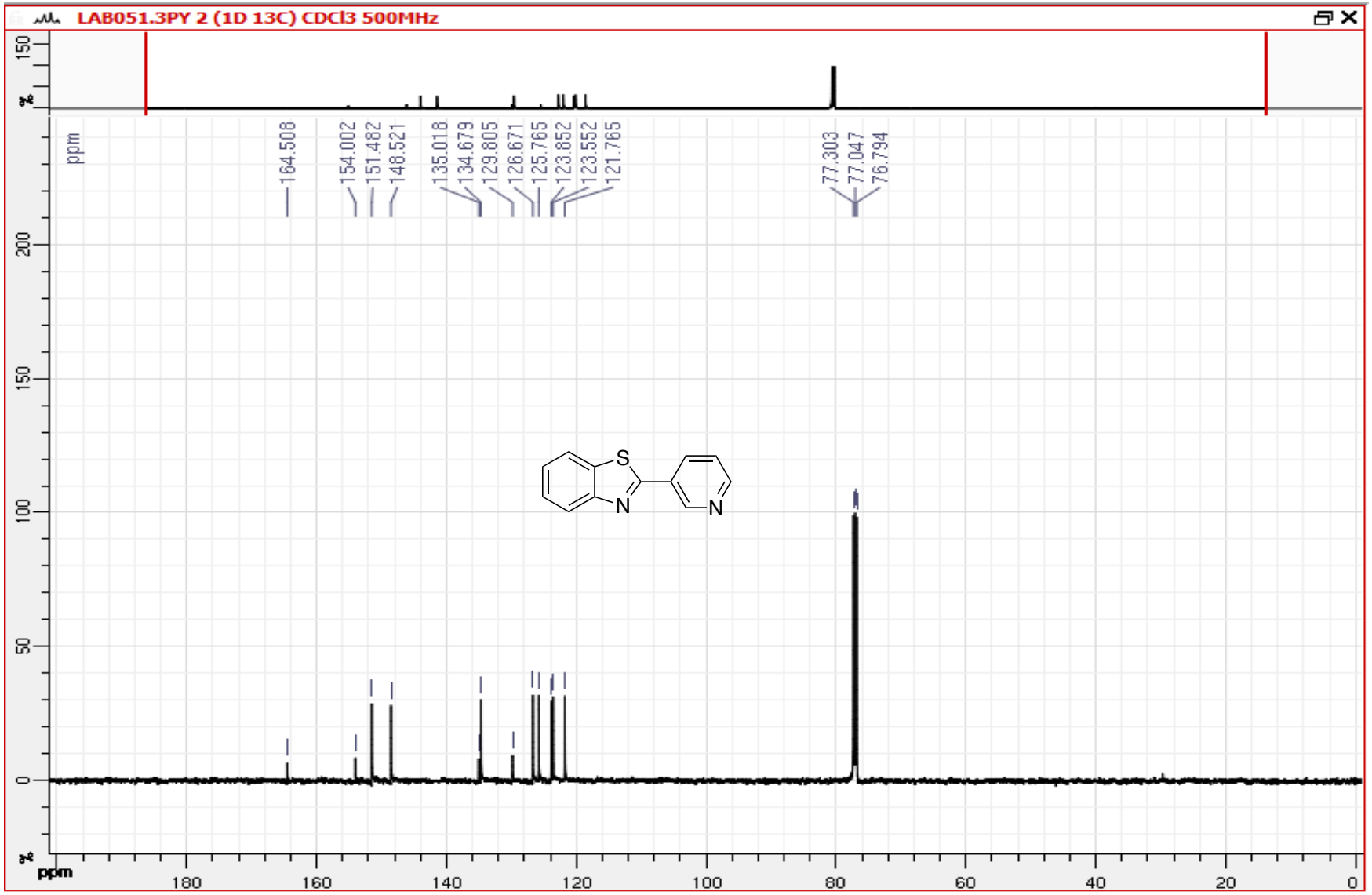
2-(Pyridin-2-yl)benzo[d]thiazole (3aq)



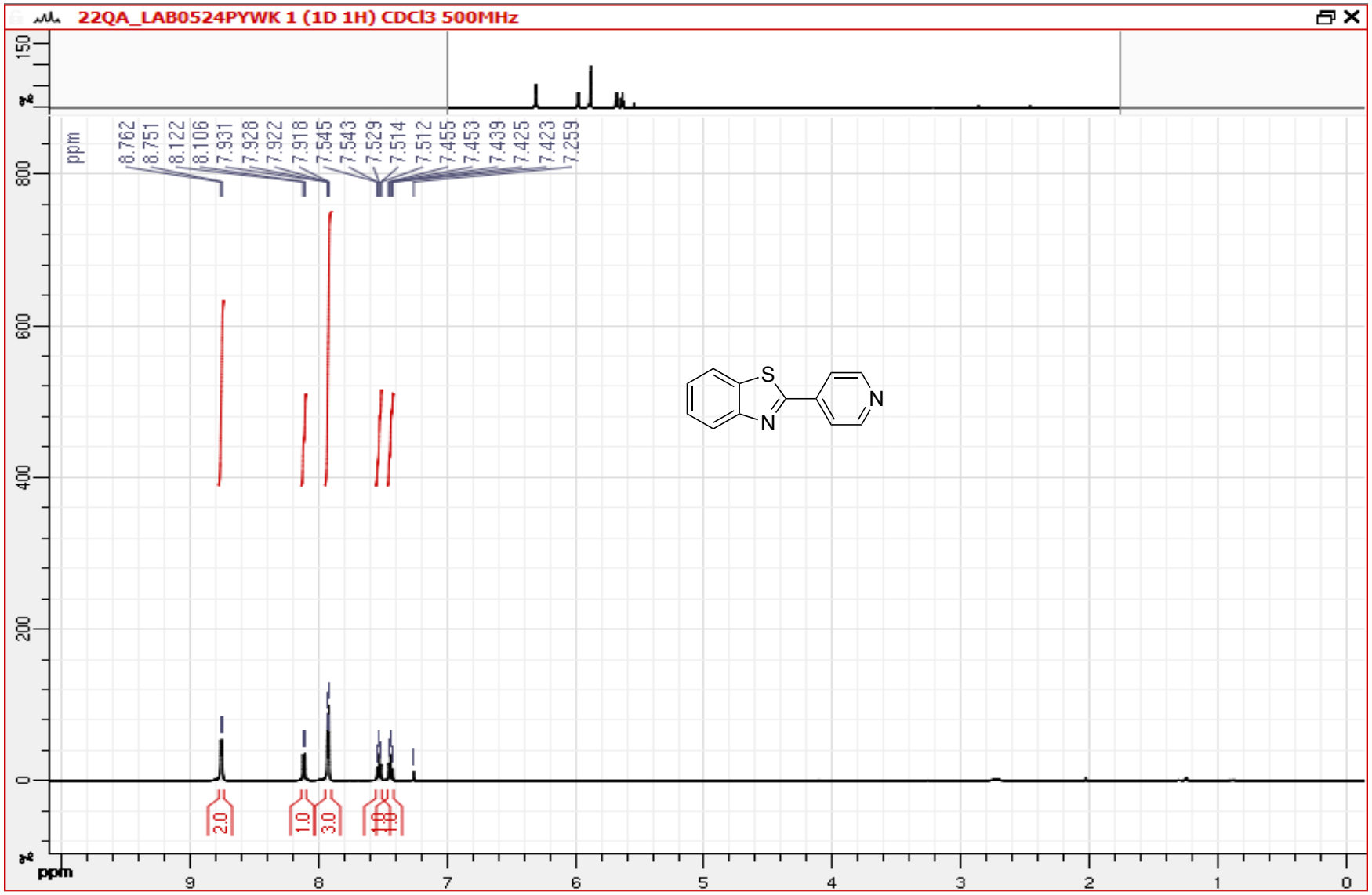

22QA_LAB050WK 2 (1D 13C) CDCl3 500MHz
ppm
169.389
154.316
151.449
149.662
137.008
136.177
126.289
125.664
125.260
123.617
122.028
120.797
77.340
77.087
76.831
S
N
N
ppm
180
160
140
120
100
80
60
40
20
0

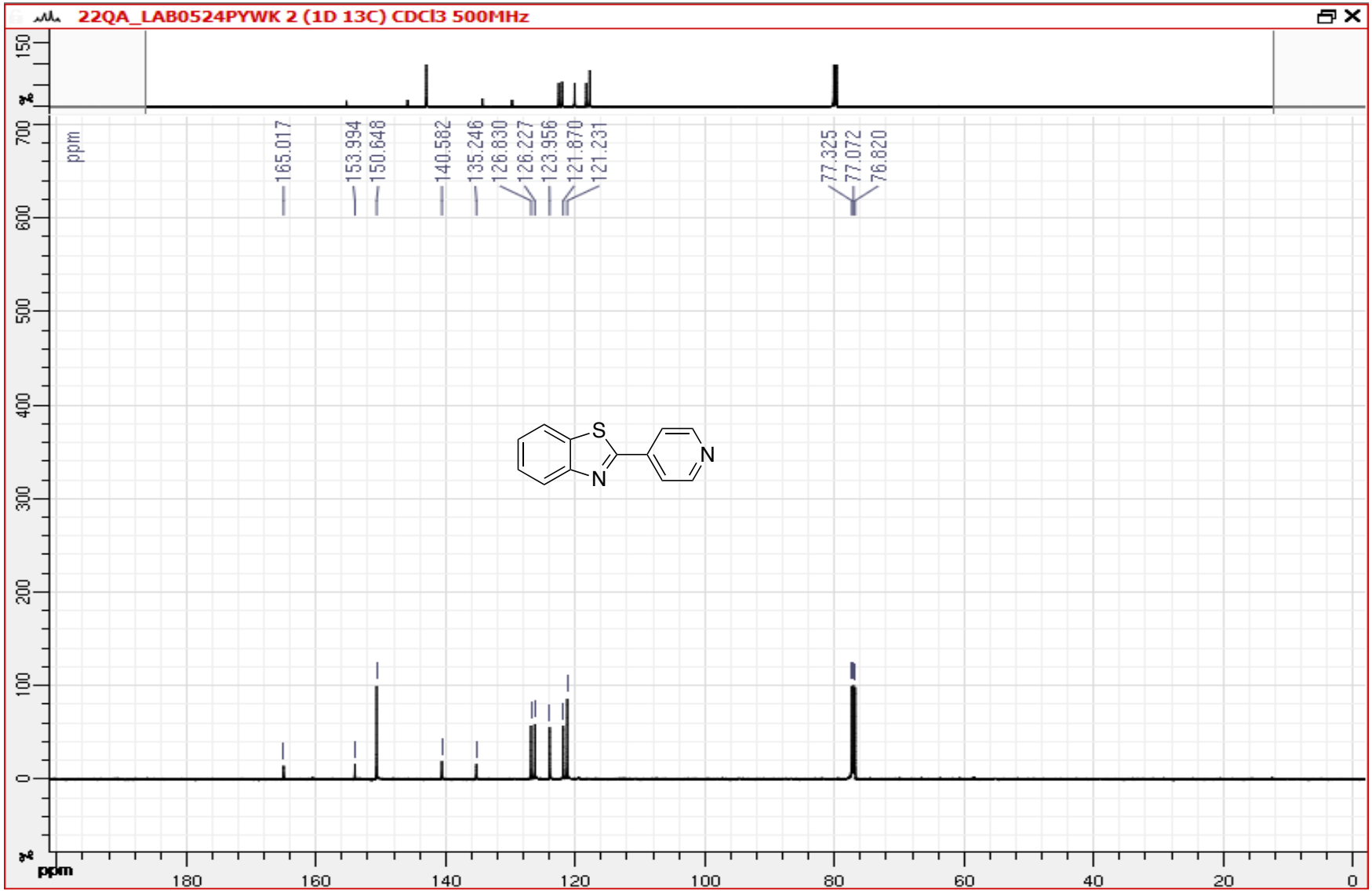
2-(Pyridin-3-yl)benzo[d]thiazole (3ar)



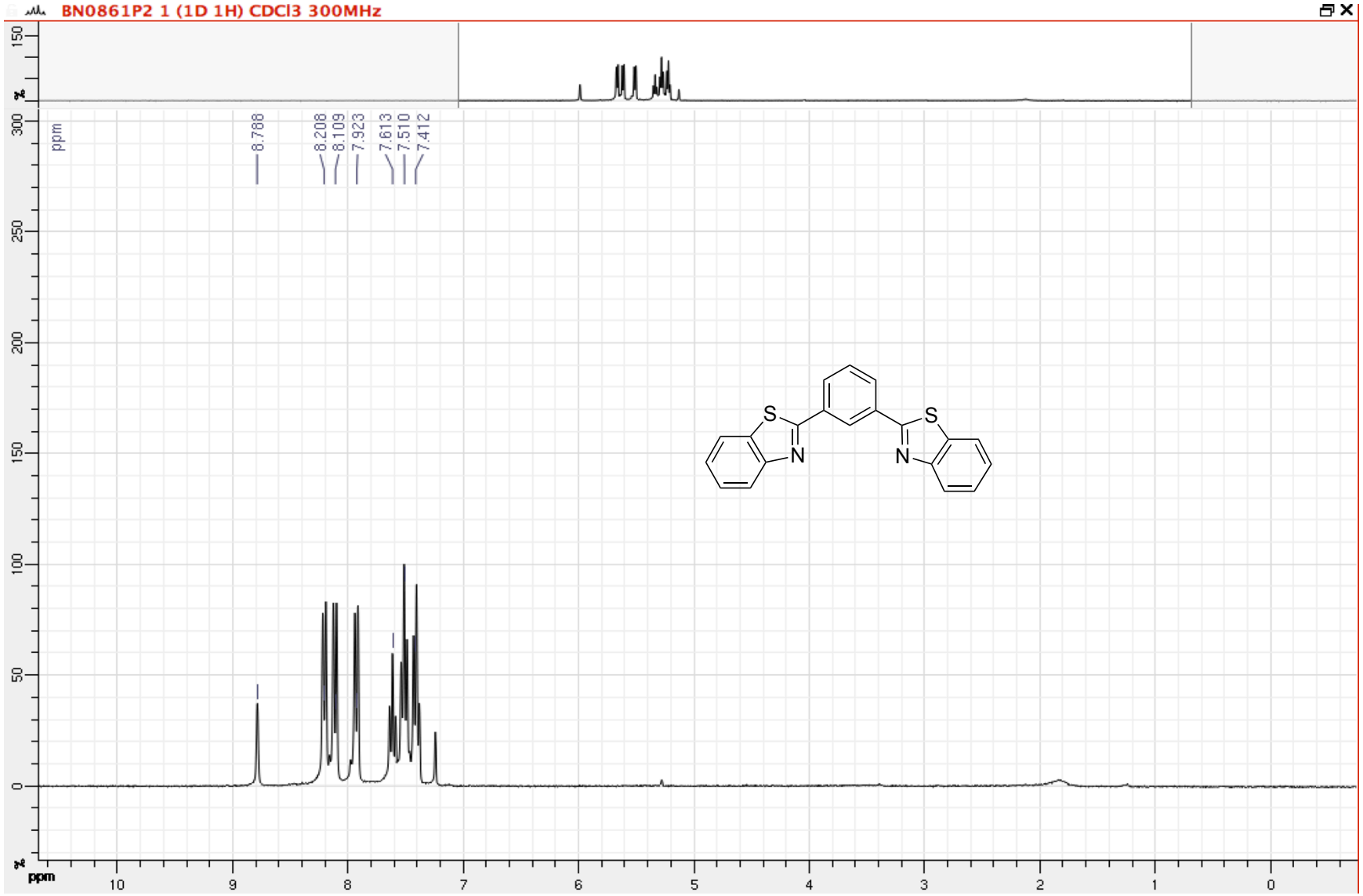

LAB051.3PY 2 (1D 13C) CDCl3 500MHz
ppm
164.508
154.002
151.482
148.521
135.018
134.679
129.805
126.671
125.765
123.852
123.552
121.765
77.303
77.047
76.794
S
N
N

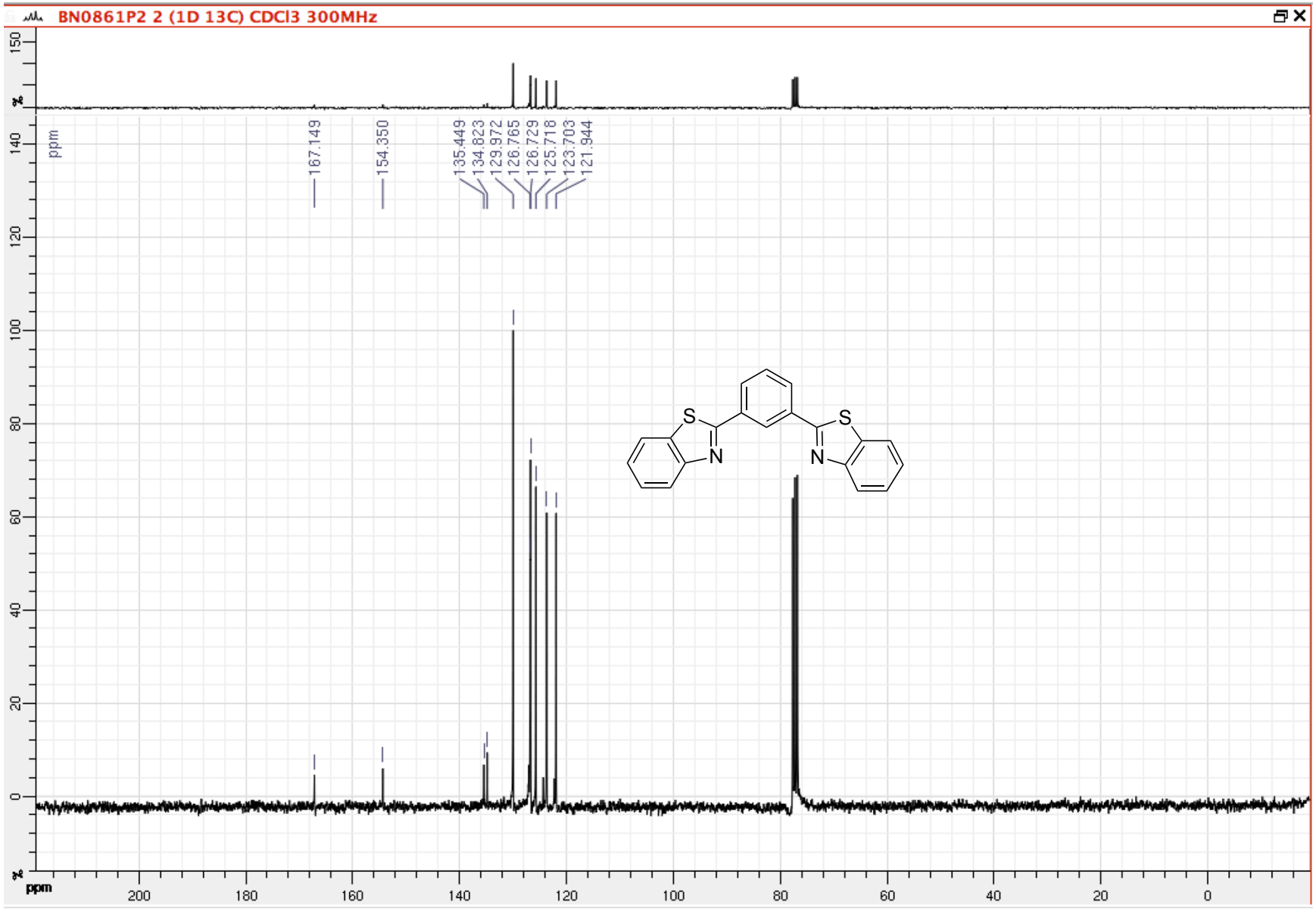
2-(Pyridin-4-yl)benzo[d]thiazole (3as)



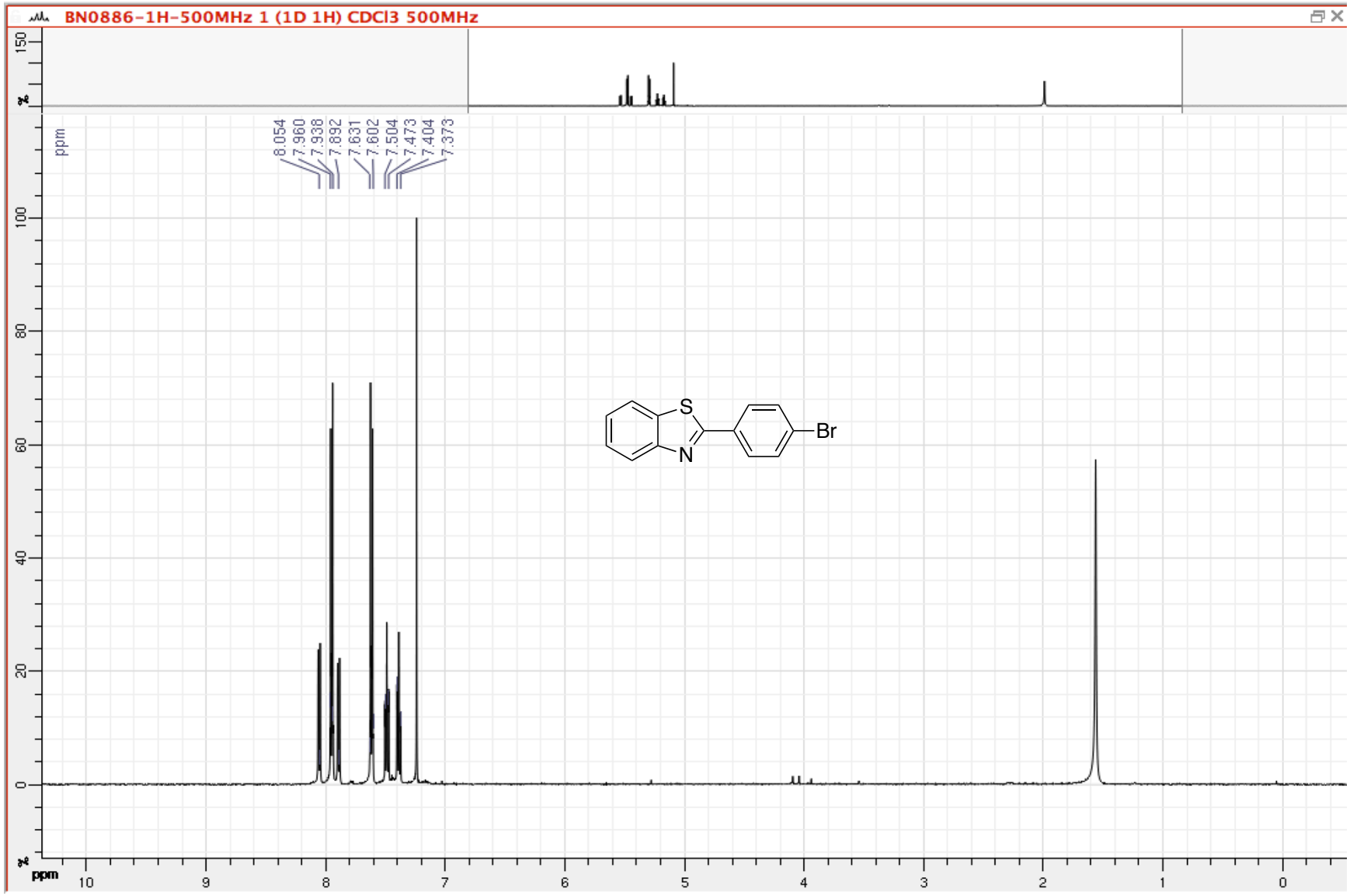

22QA_LAB0524PYWK 2 (1D 13C) CDCl3 500MHz
ppm
165.017
153.994
150.648
140.582
135.246
126.830
126.227
123.956
121.870
121.231
77.325
77.072
76.820
S
N
N
ppm
180
160
140
120
100
80
60
40
20
0

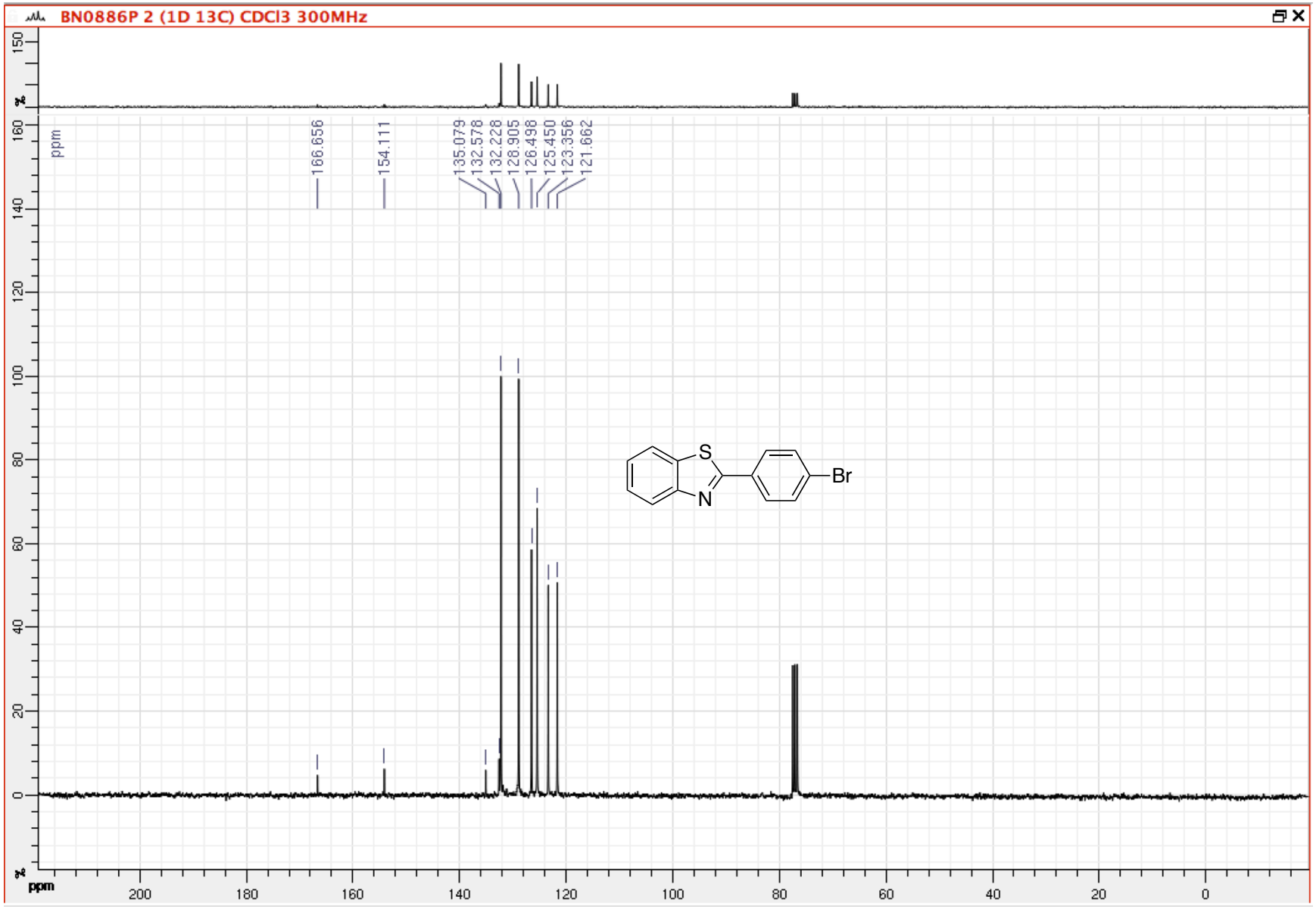
1,3-*Bis*(benzo[*d*]thiazol-2-yl)benzene (3at)



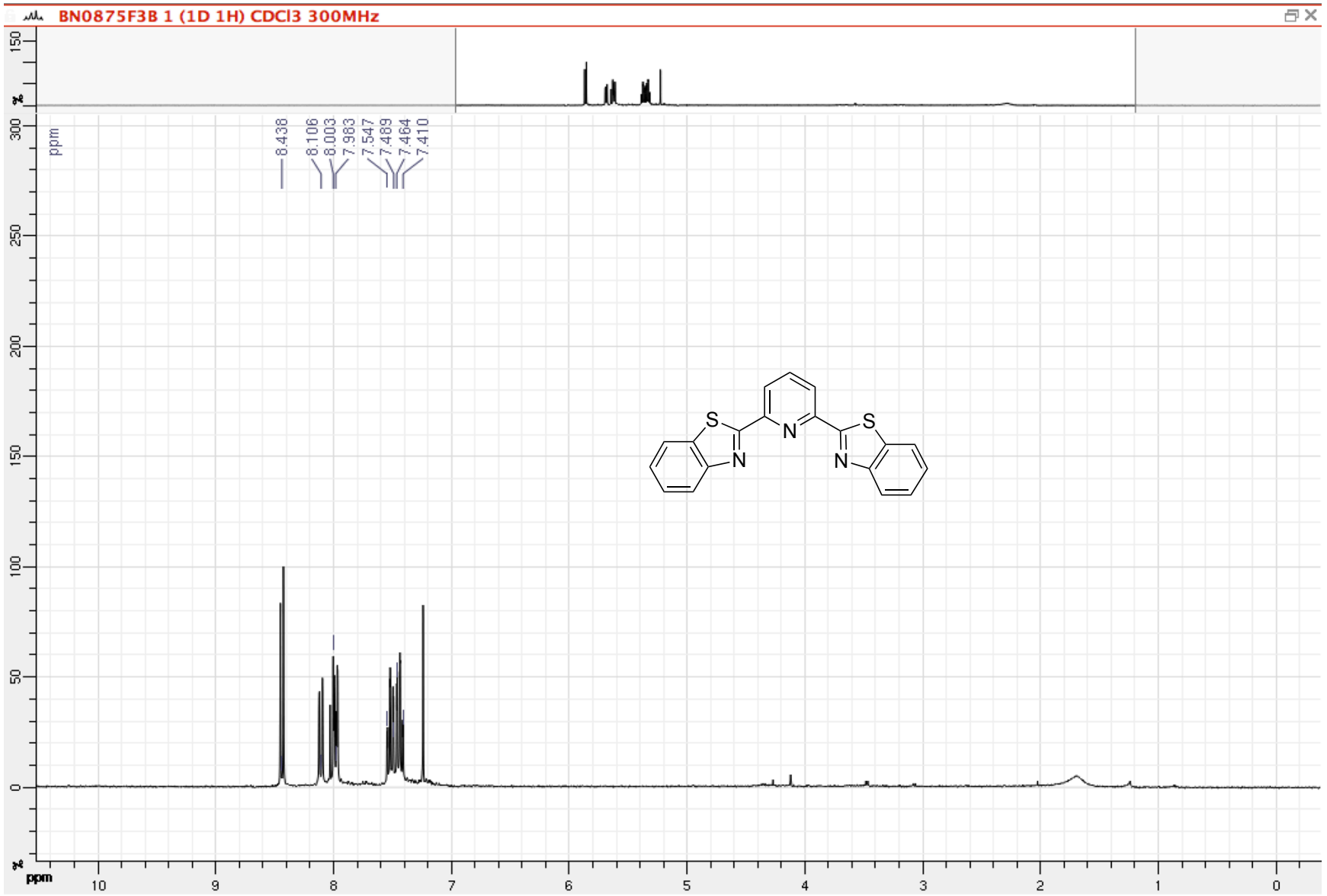

BN0861P2 2 (1D 13C) CDCl3 300MHz
ppm
167.149
154.350
135.449
134.823
129.972
126.765
126.729
125.718
123.703
121.944
S
N
S
N

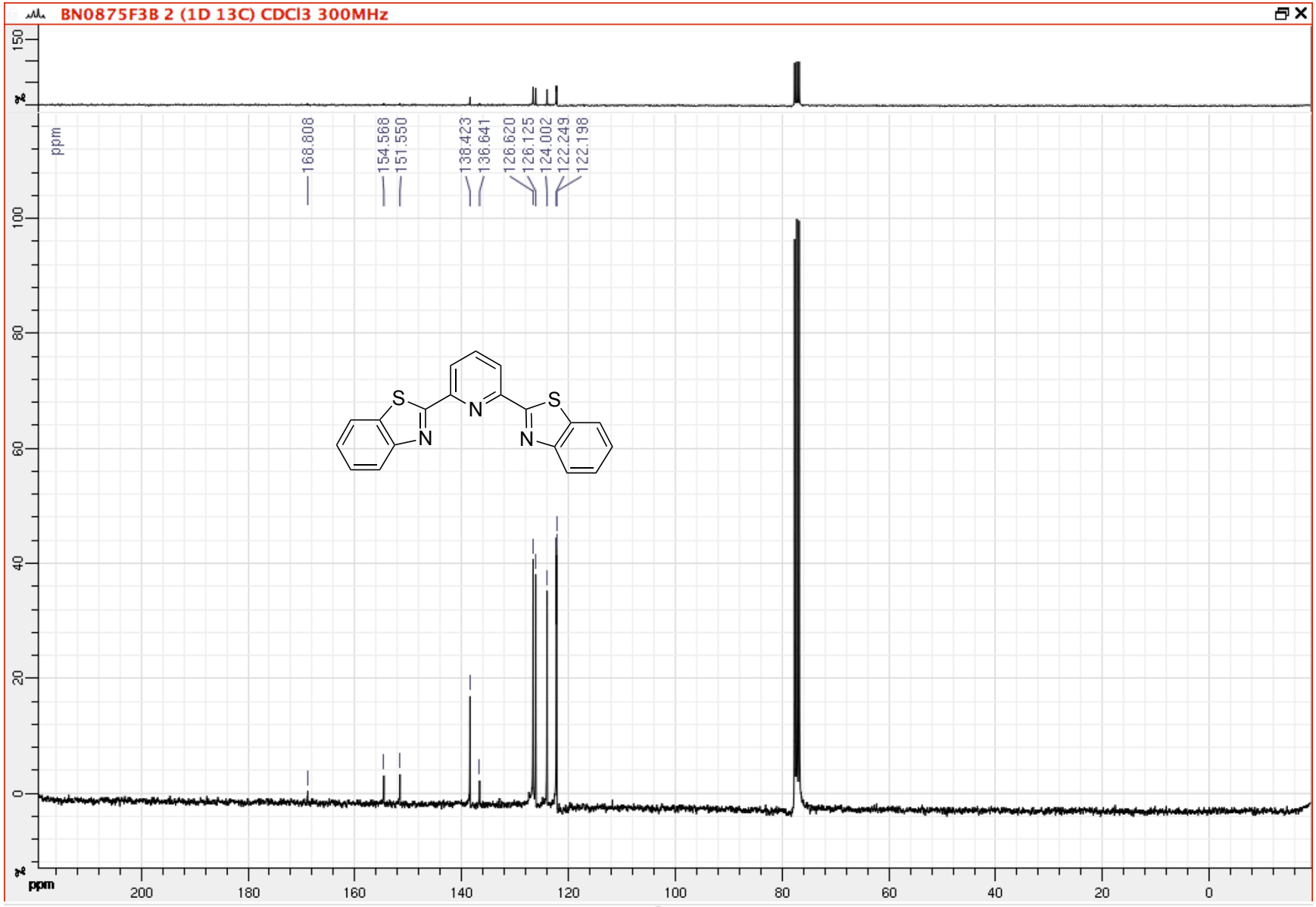
2-(4-Bromophenyl)benzo[d]thiazole (3au)



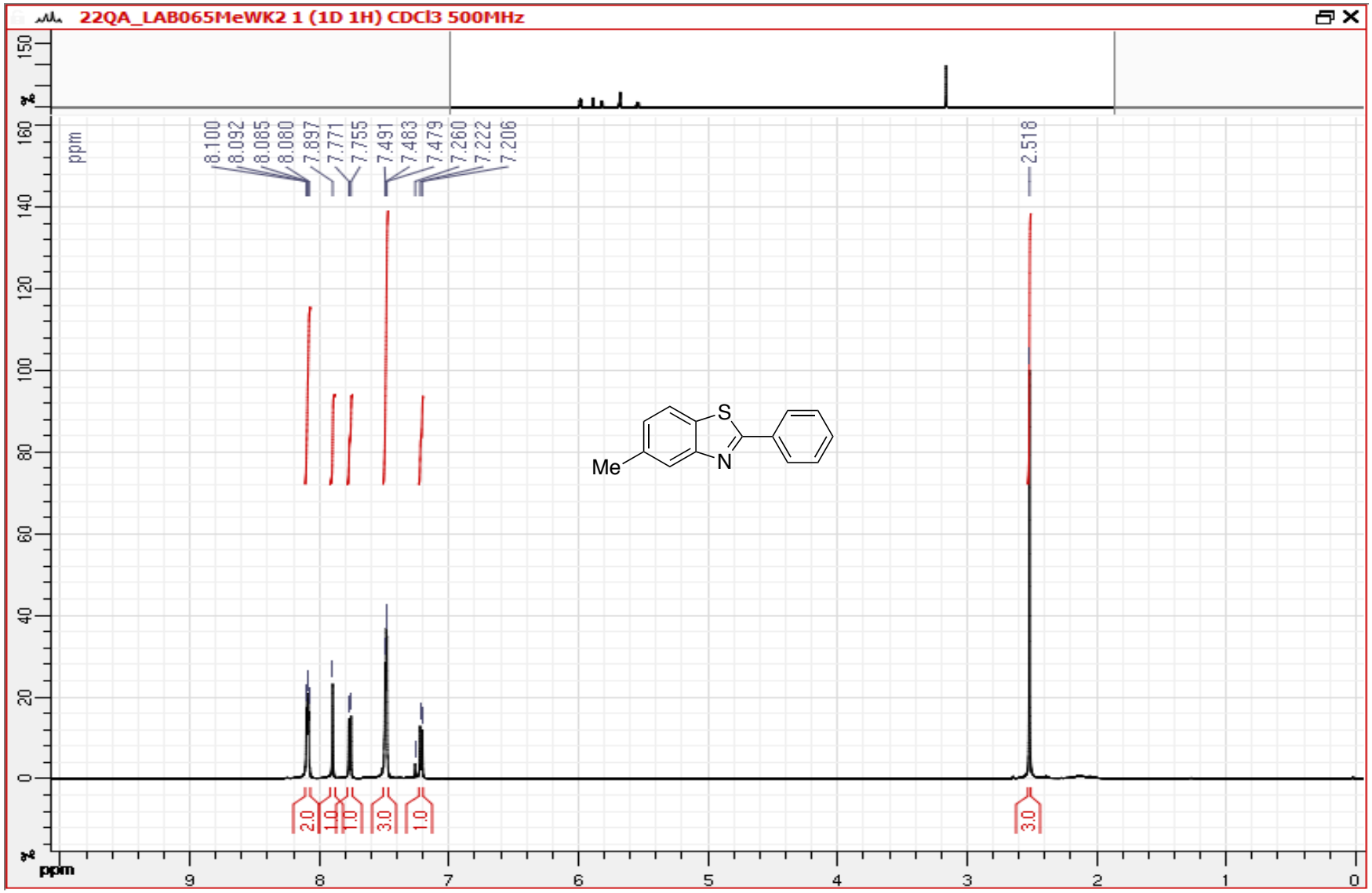

BN0886P 2 (1D 13C) CDCl3 300MHz
ppm
166.656
154.111
135.079
132.578
132.228
128.905
126.498
125.450
123.356
121.662
S
N
Br

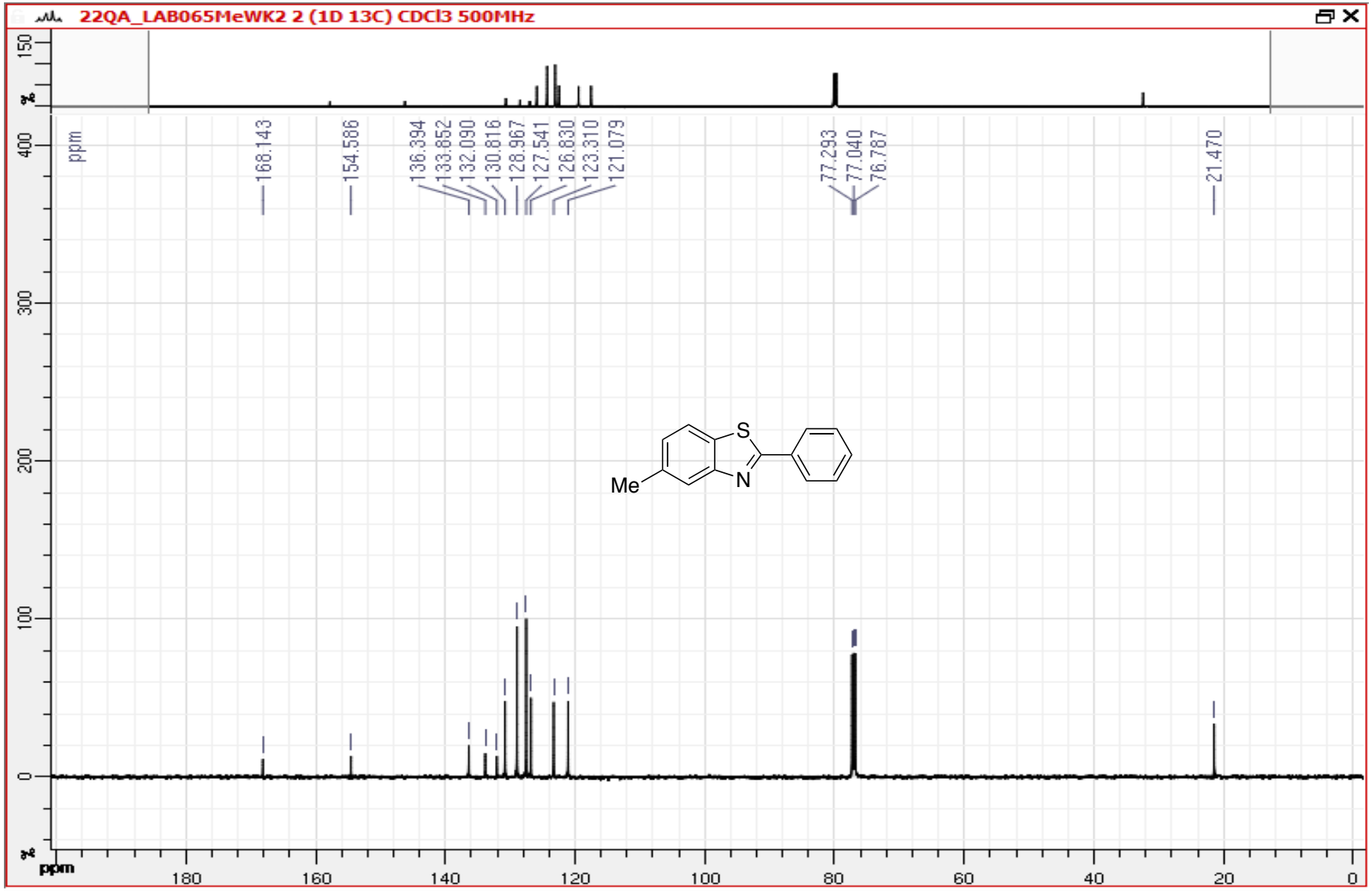
2,6-Bis(benzo[d]thiazol-2-yl)pyridine (3av)



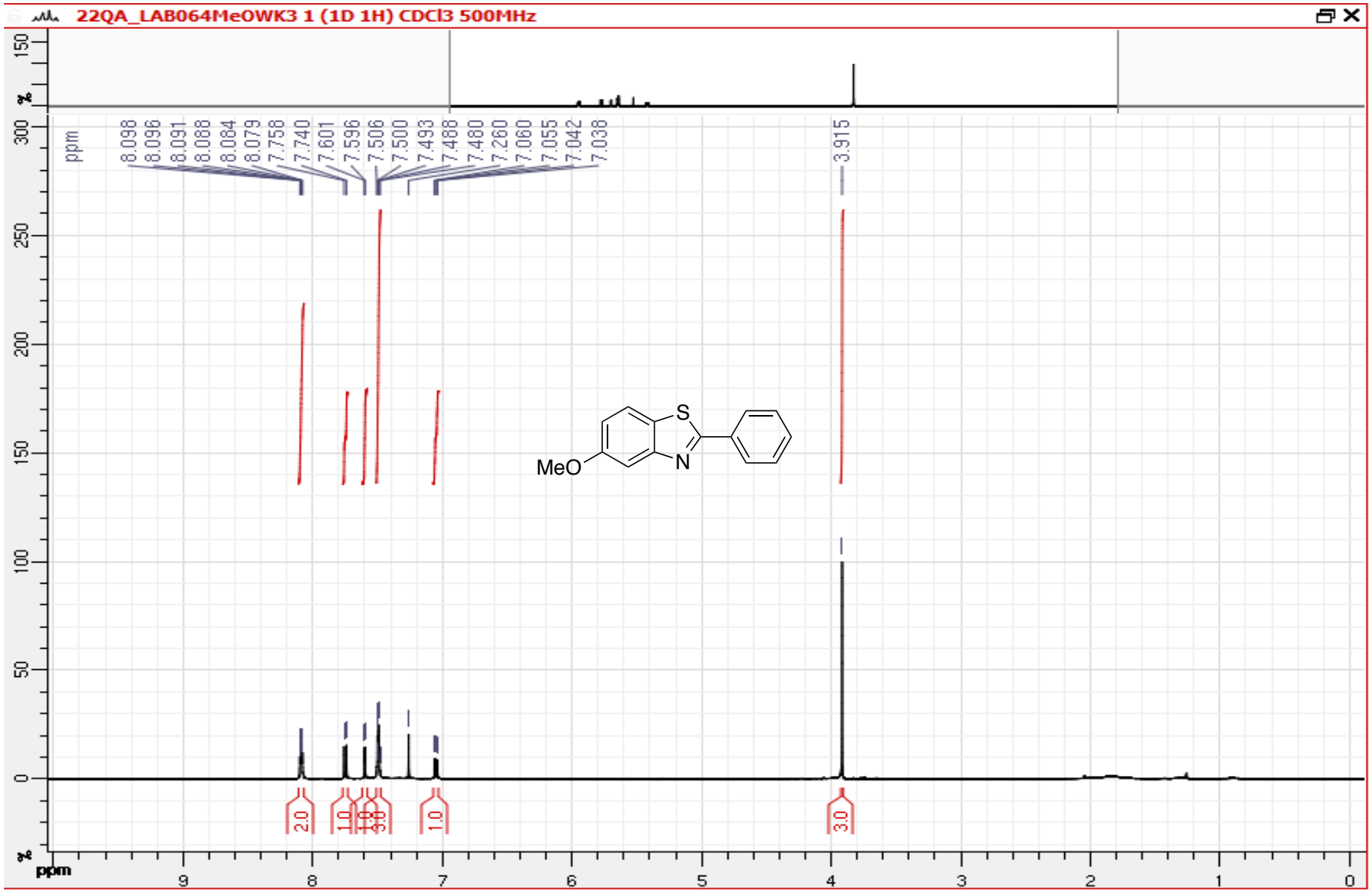

BN0875F3B 2 (1D 13C) CDCl3 300MHz
ppm
168.808
154.568
151.550
138.423
136.641
126.620
126.125
124.002
122.249
122.198
S
N
N
S
ppm
200
180
160
140
120
100
80
60
40
20
0

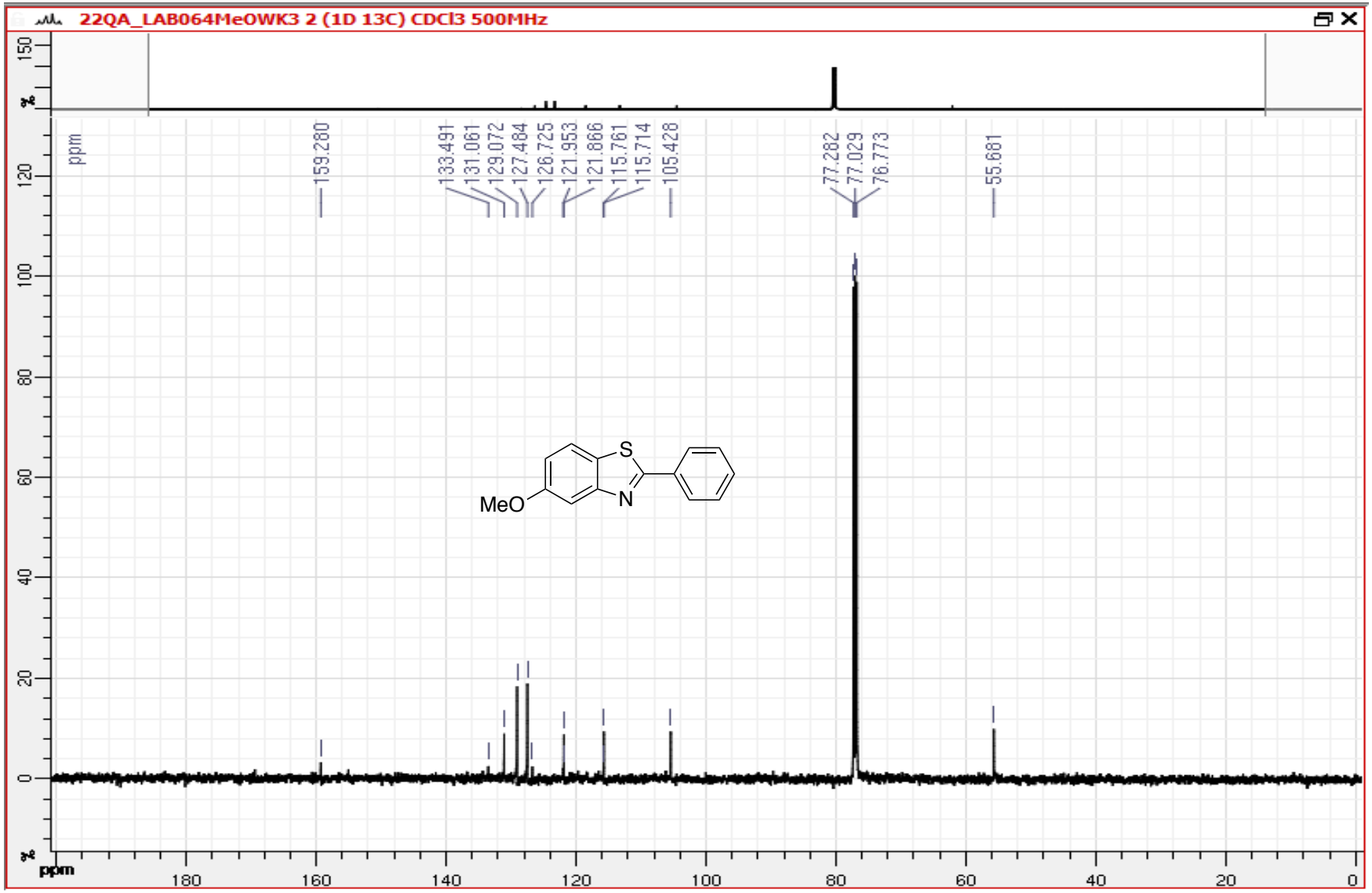
5-Methyl-2-phenylbenzo[d]thiazole (3ba)



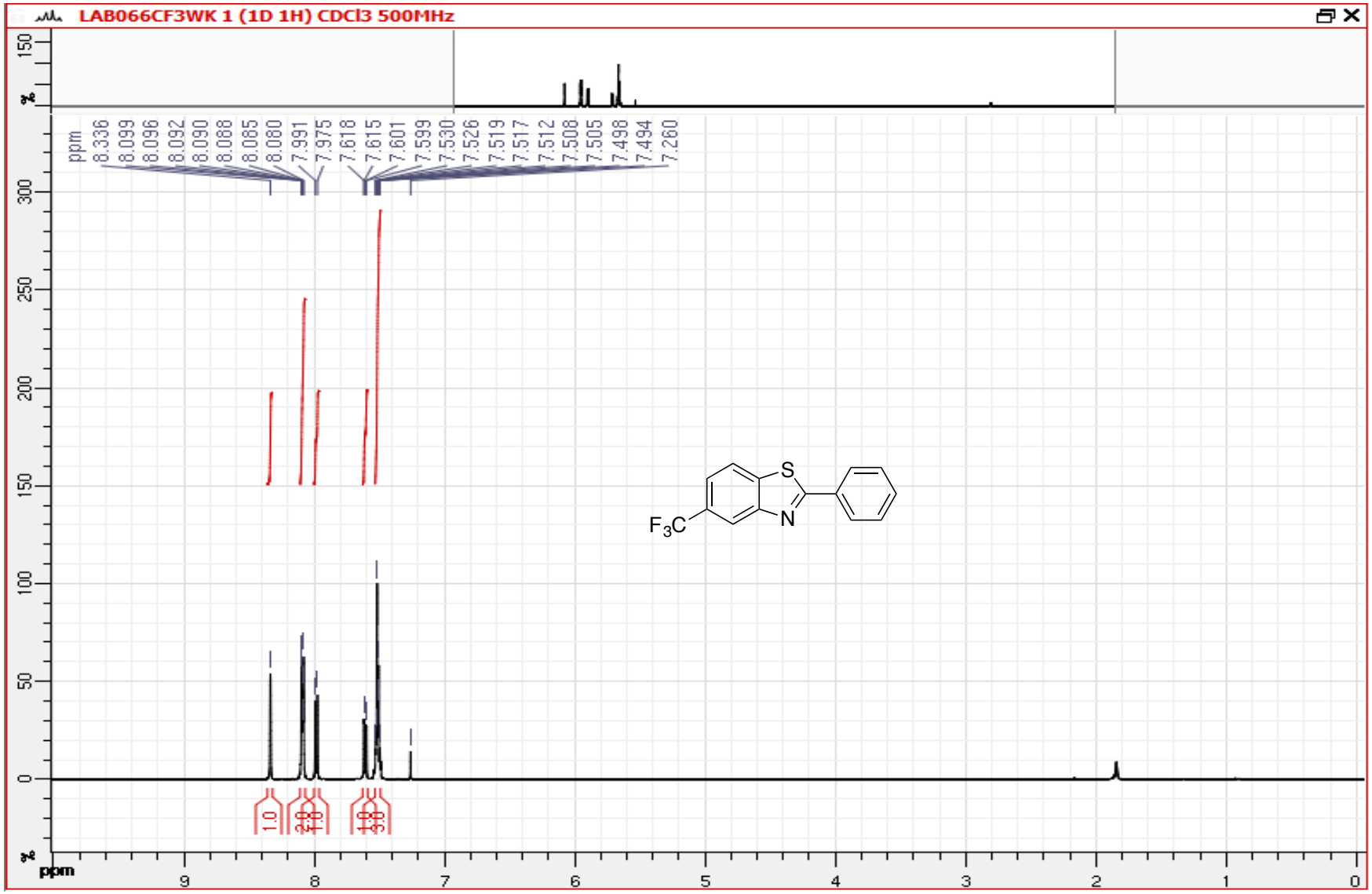

22QA_LAB065MeWK2 2 (1D 13C) CDCl3 500MHz
ppm
168.143
154.586
136.394
133.852
132.090
130.816
128.967
127.541
126.830
123.310
121.079
77.293
77.040
76.787
21.470
S
N
Me
180
160
140
120
100
80
60
40
20
0

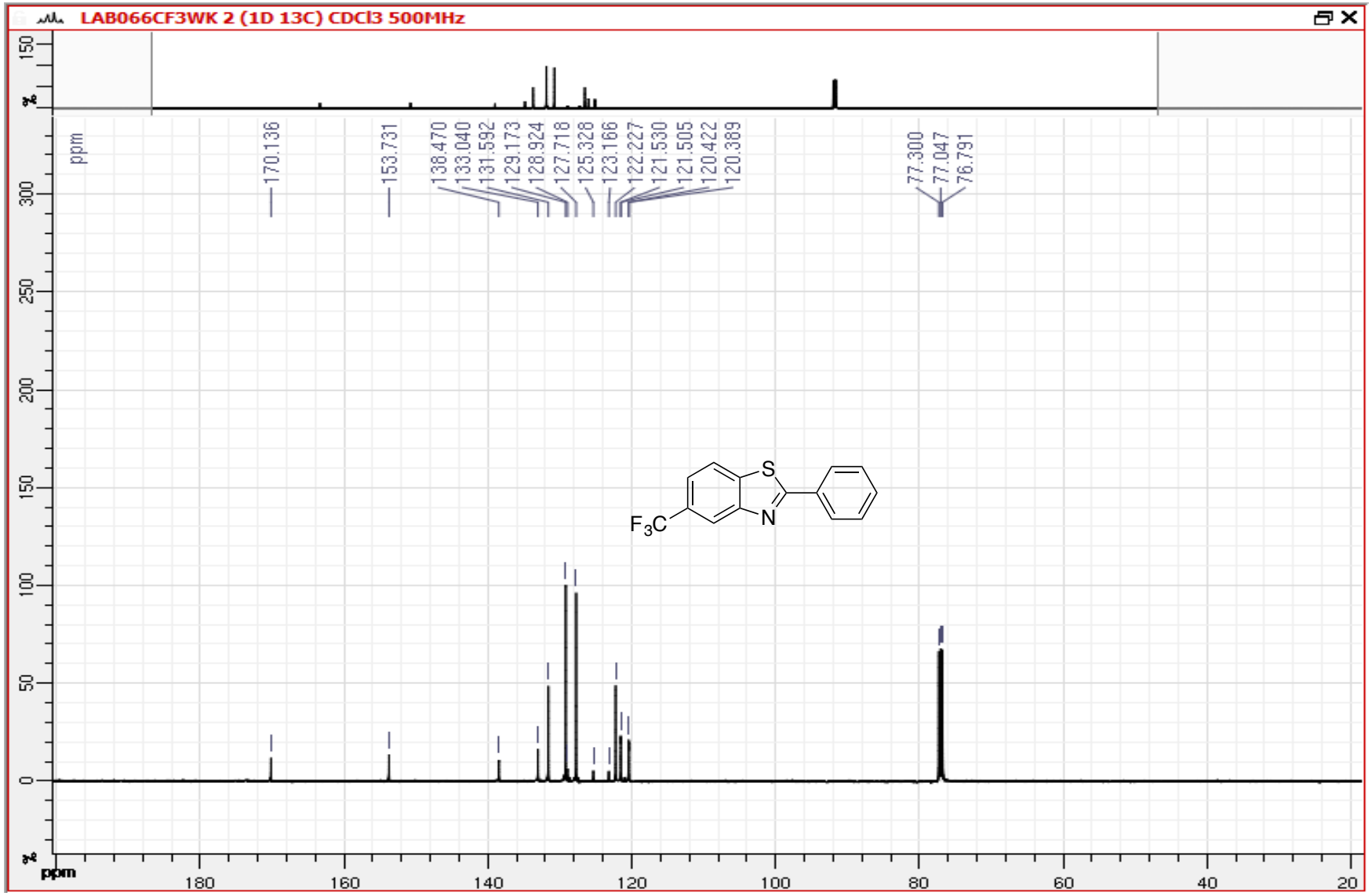
5-Methoxy-2-phenylbenzo[d]thiazole (3ca)



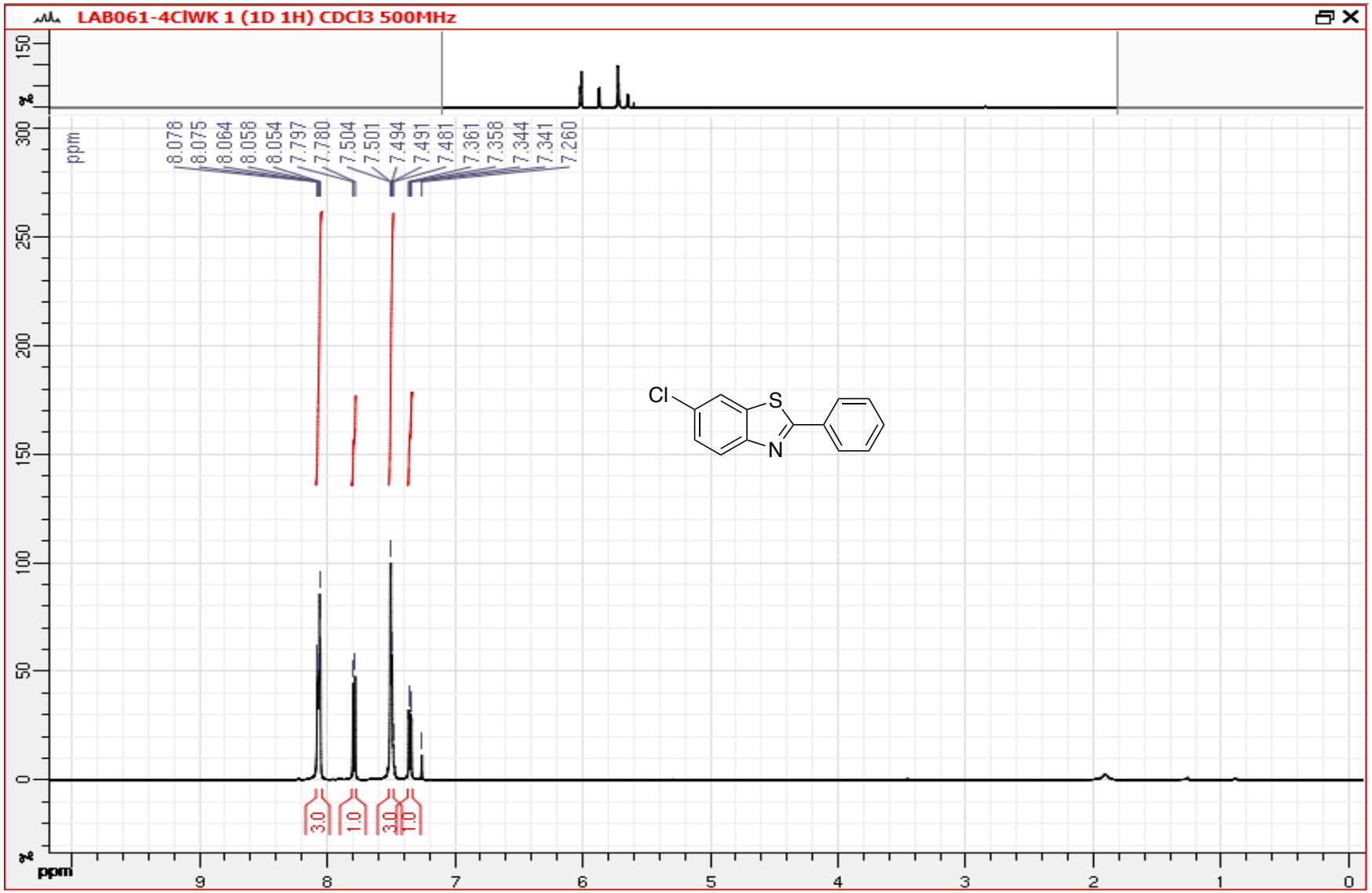

22QA_LAB064MeOWK3 2 (1D 13C) CDCl3 500MHz
ppm
159.280
133.491
131.061
129.072
127.484
126.725
121.953
121.866
115.761
115.714
105.428
77.282
77.029
76.773
55.681
MeO
S
N

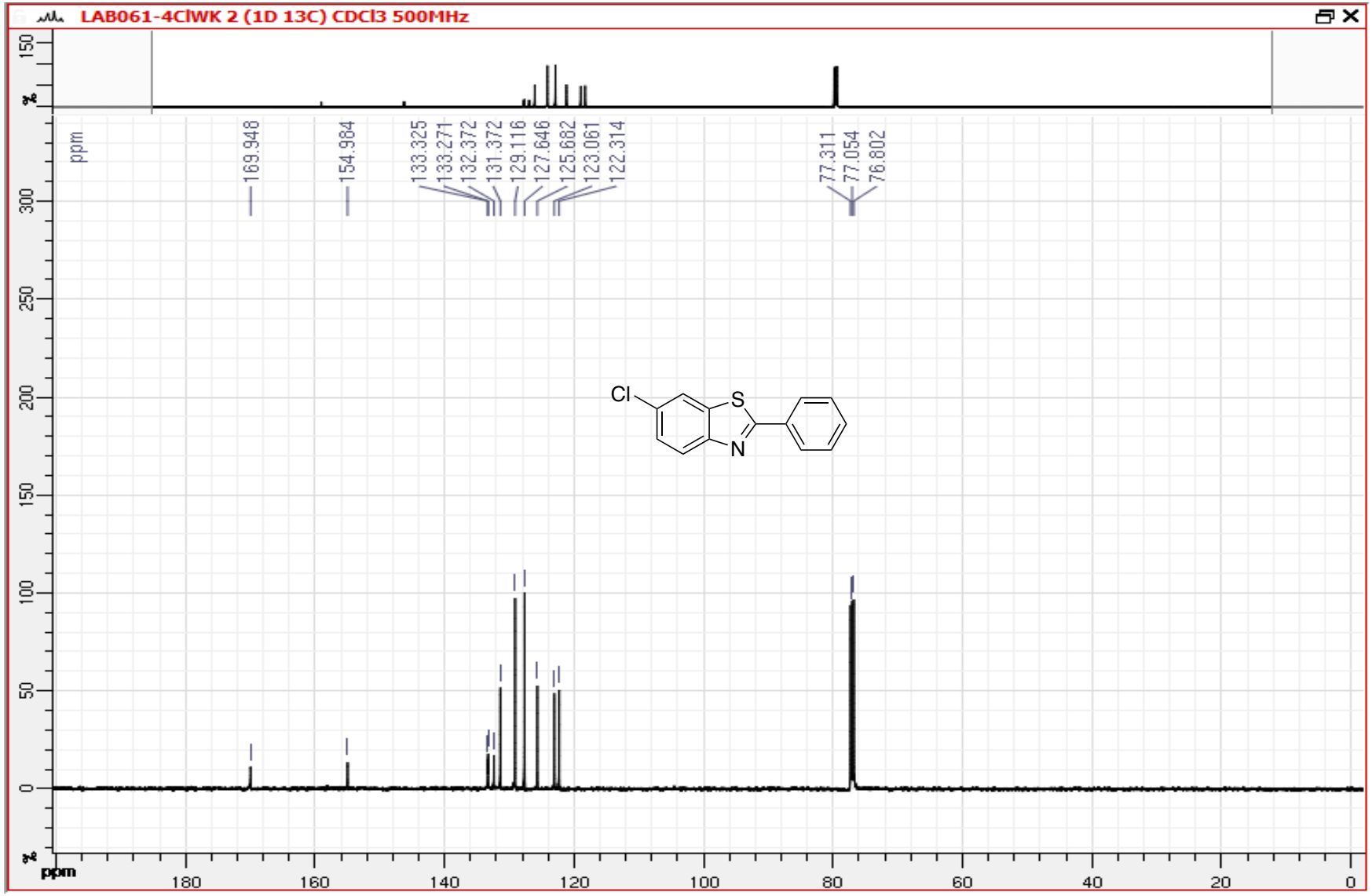
2-Phenyl-5-(trifluoromethyl)benzo[d]thiazole (3da)



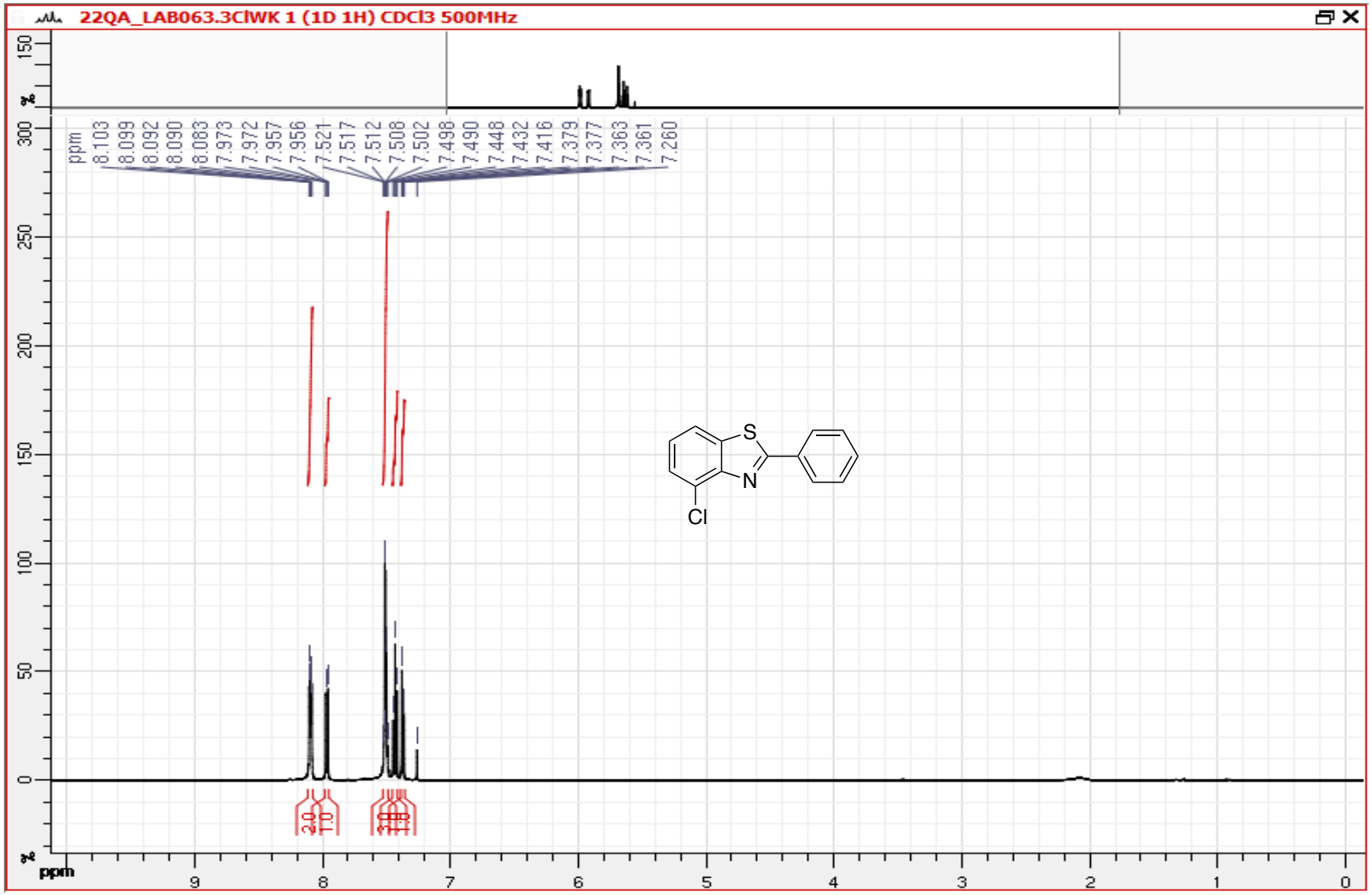

LAB066CF3WK 2 (1D 13C) CDCl3 500MHz
ppm
170.136
153.731
138.470
133.040
131.592
129.173
128.924
127.718
125.328
123.166
122.227
121.530
121.505
120.422
120.389
77.300
77.047
76.791
S
N
F3C

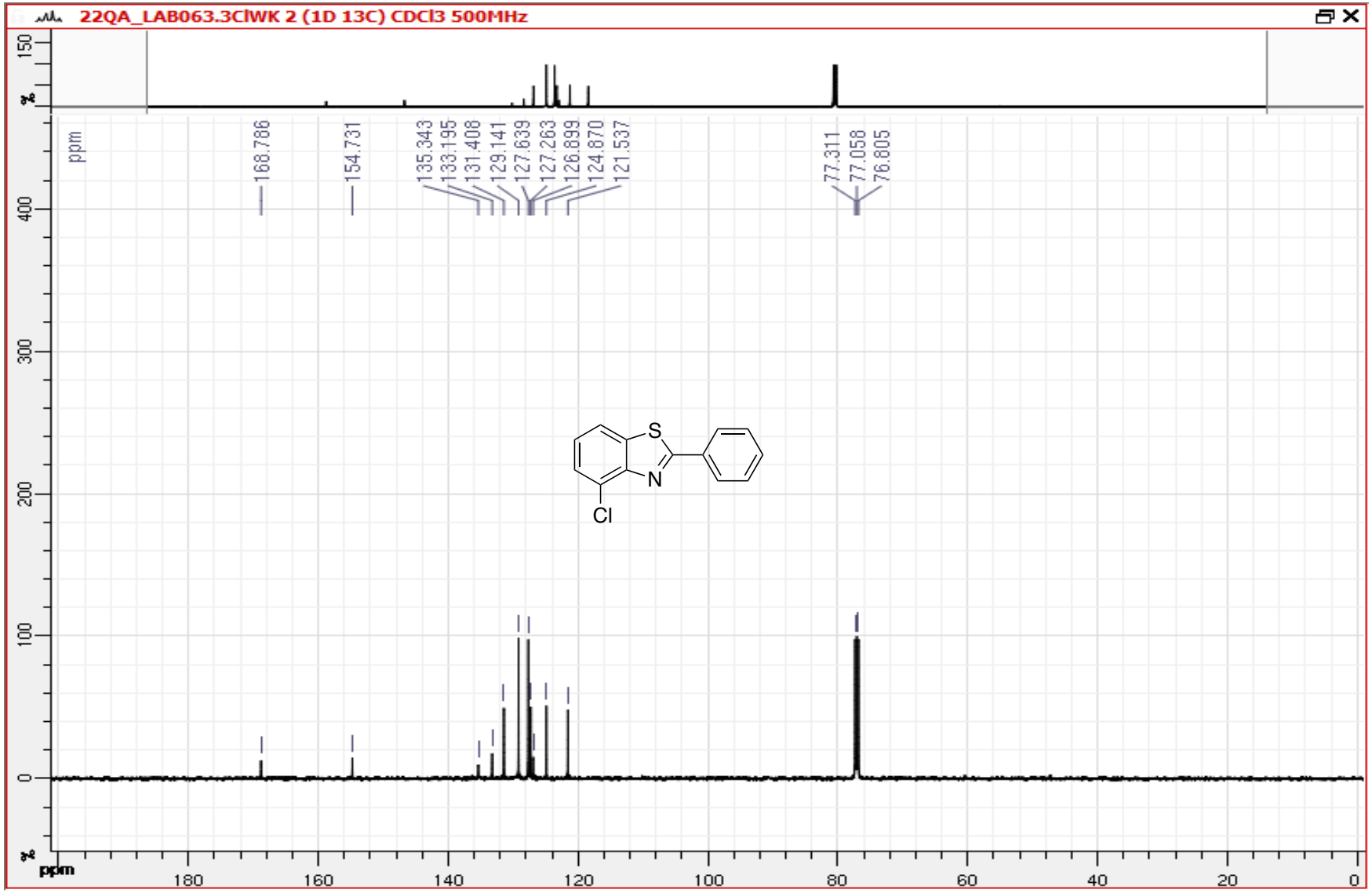
6-Chloro-2-phenylbenzo[d]thiazole (3ea)



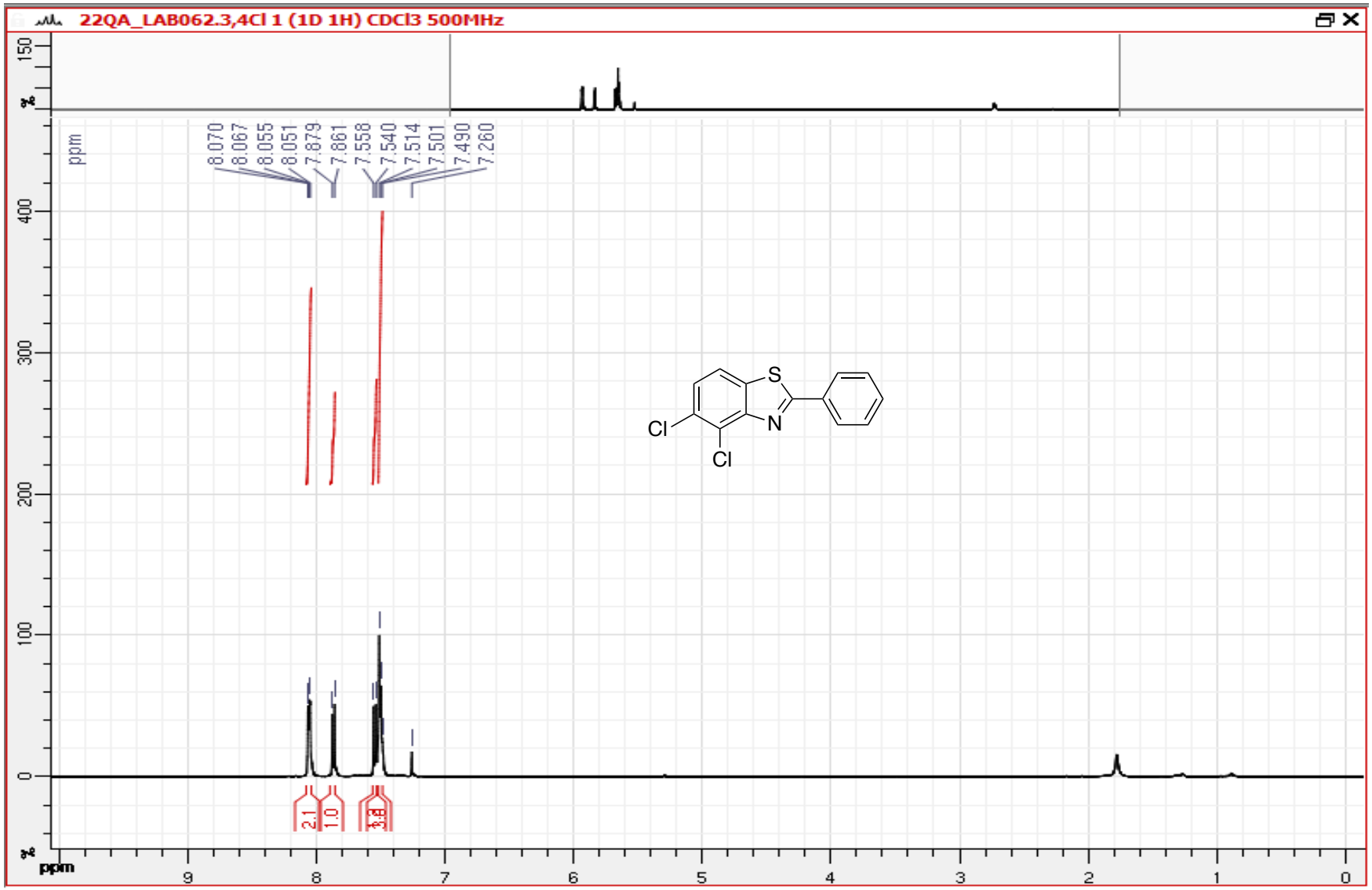

LAB061-4ClWK 2 (1D 13C) CDCl3 500MHz
ppm
169.948
154.984
133.325
133.271
132.372
131.372
129.116
127.646
125.682
123.061
122.314
77.311
77.054
76.802
Cl
S
N
180
160
140
120
100
80
60
40
20
0

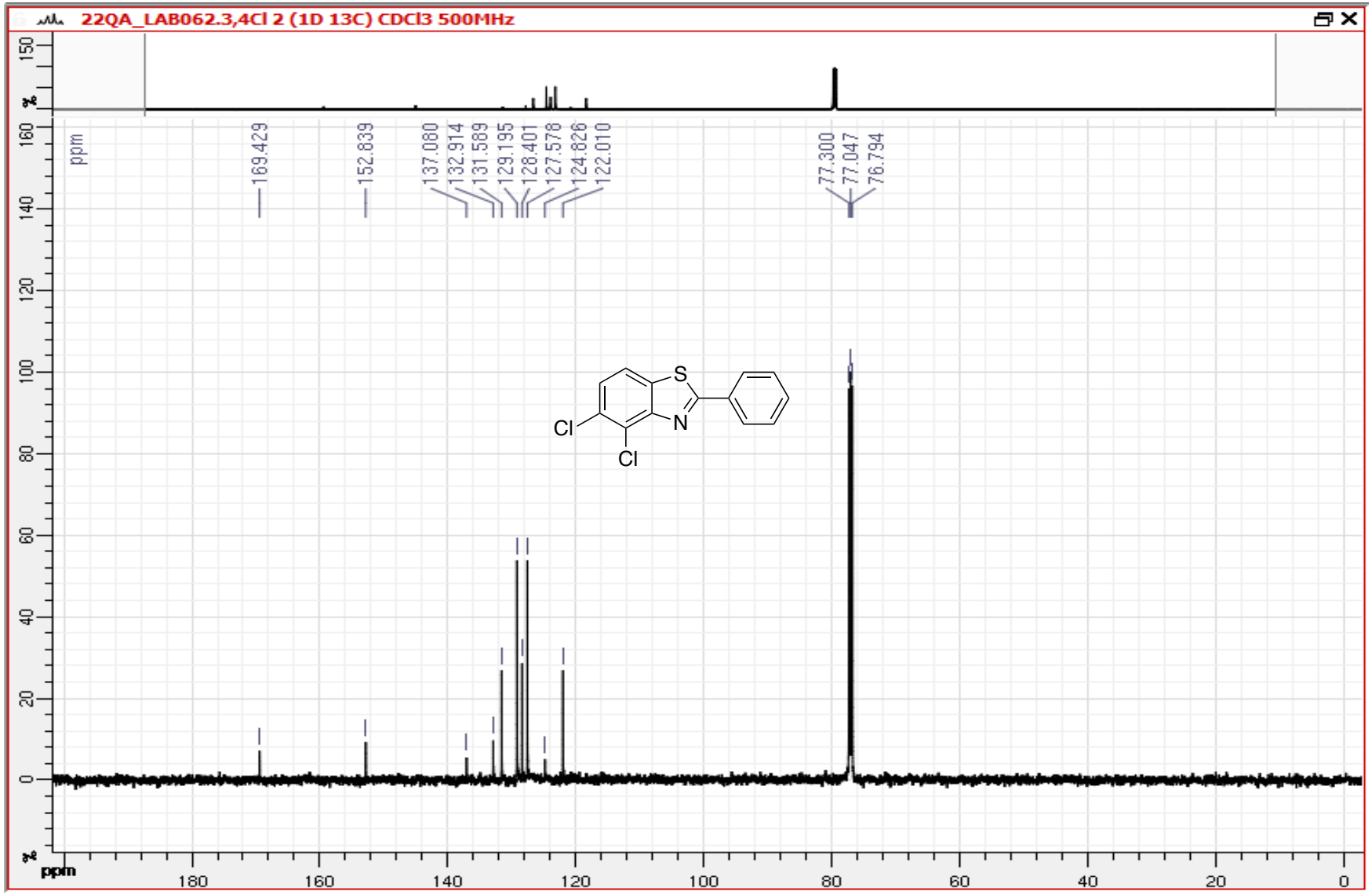
4-Chloro-2-phenylbenzo[d]thiazole (3fa)



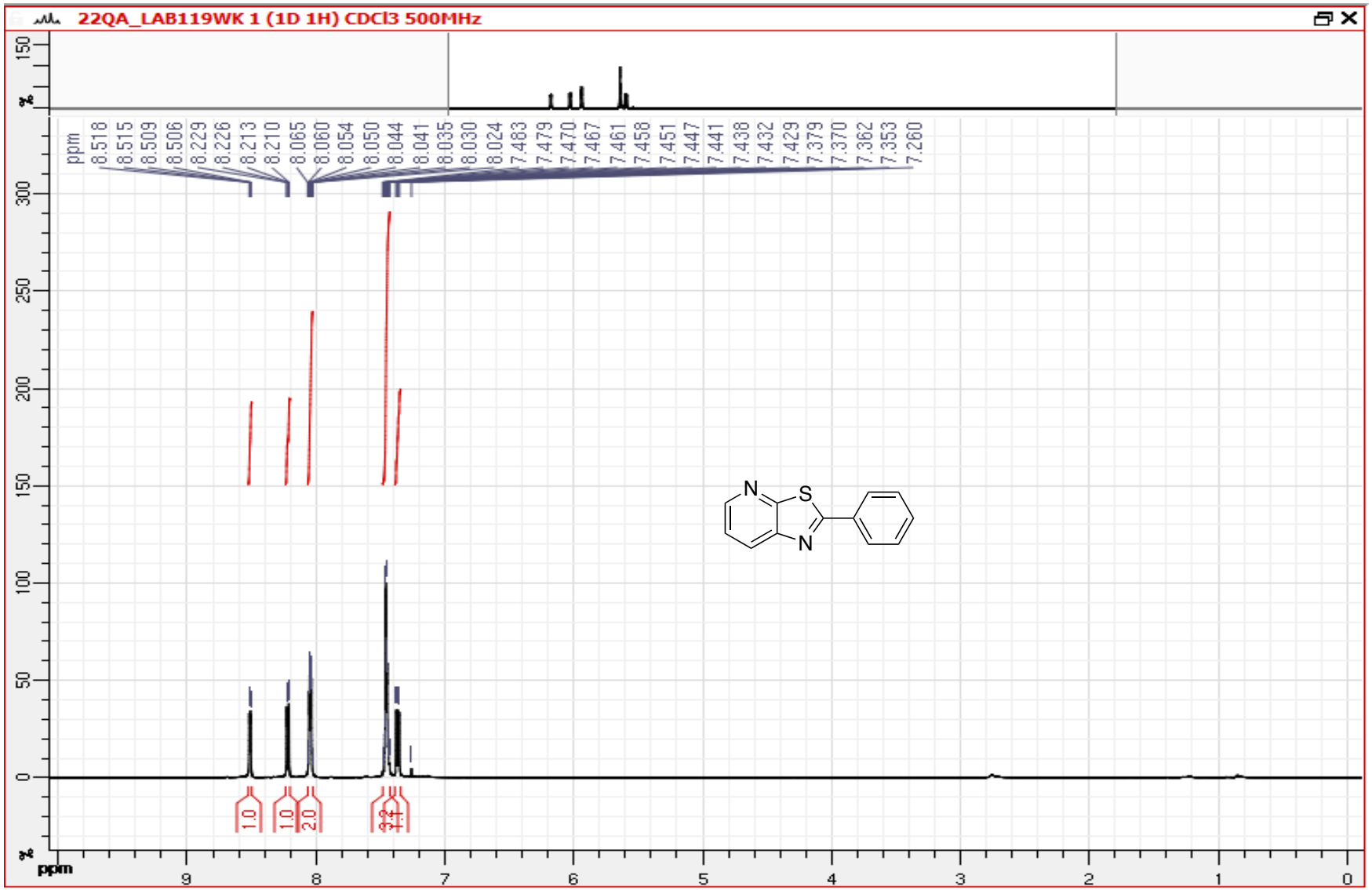

22QA_LAB063.3ClWK 2 (1D 13C) CDCl3 500MHz
ppm
168.786
154.731
135.343
133.195
131.408
129.141
127.639
127.263
126.899
124.870
121.537
77.311
77.058
76.805
S
N
Cl

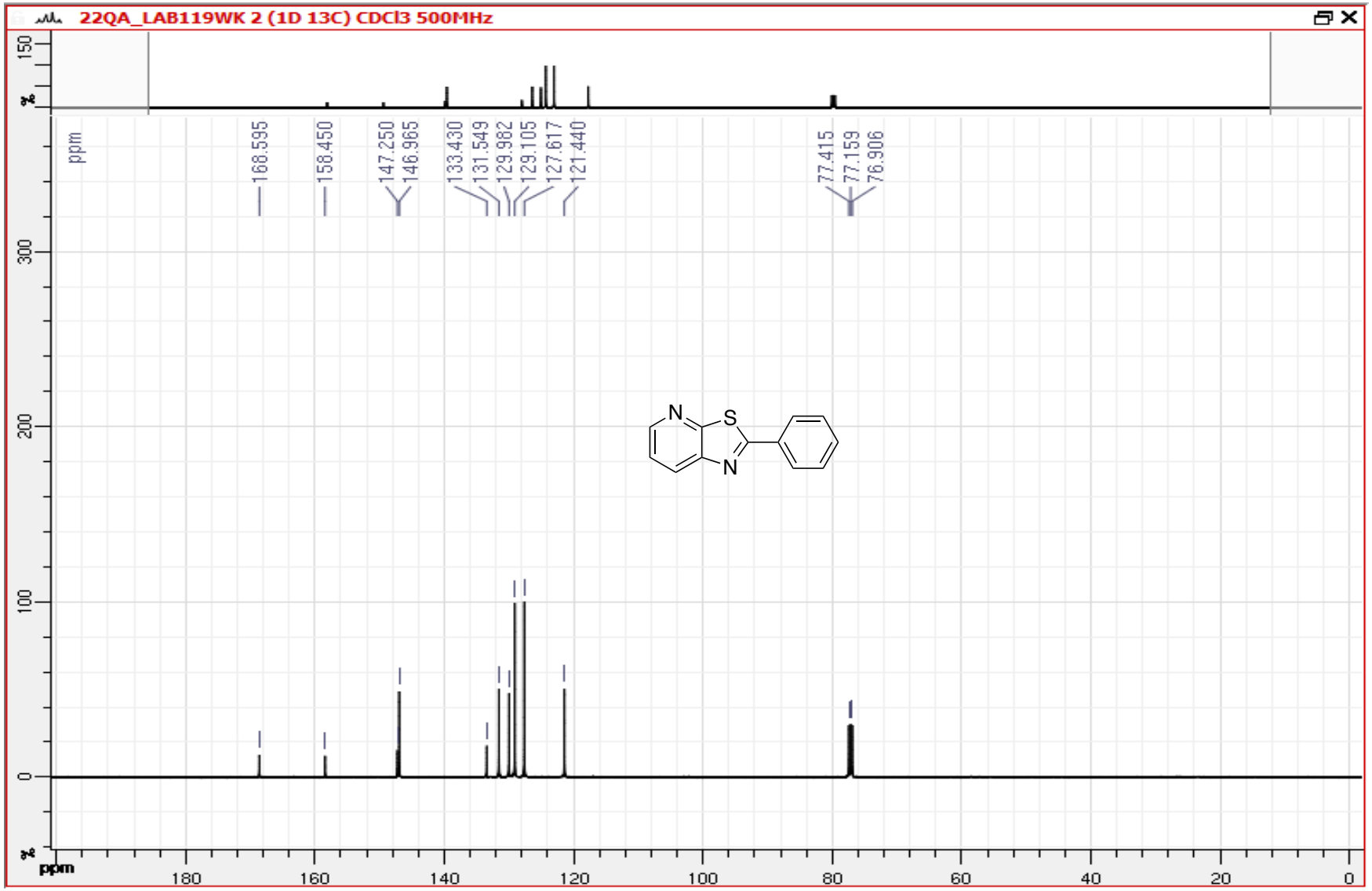
4,5-Dichloro-2-phenylbenzo[d]thiazole (3ga)



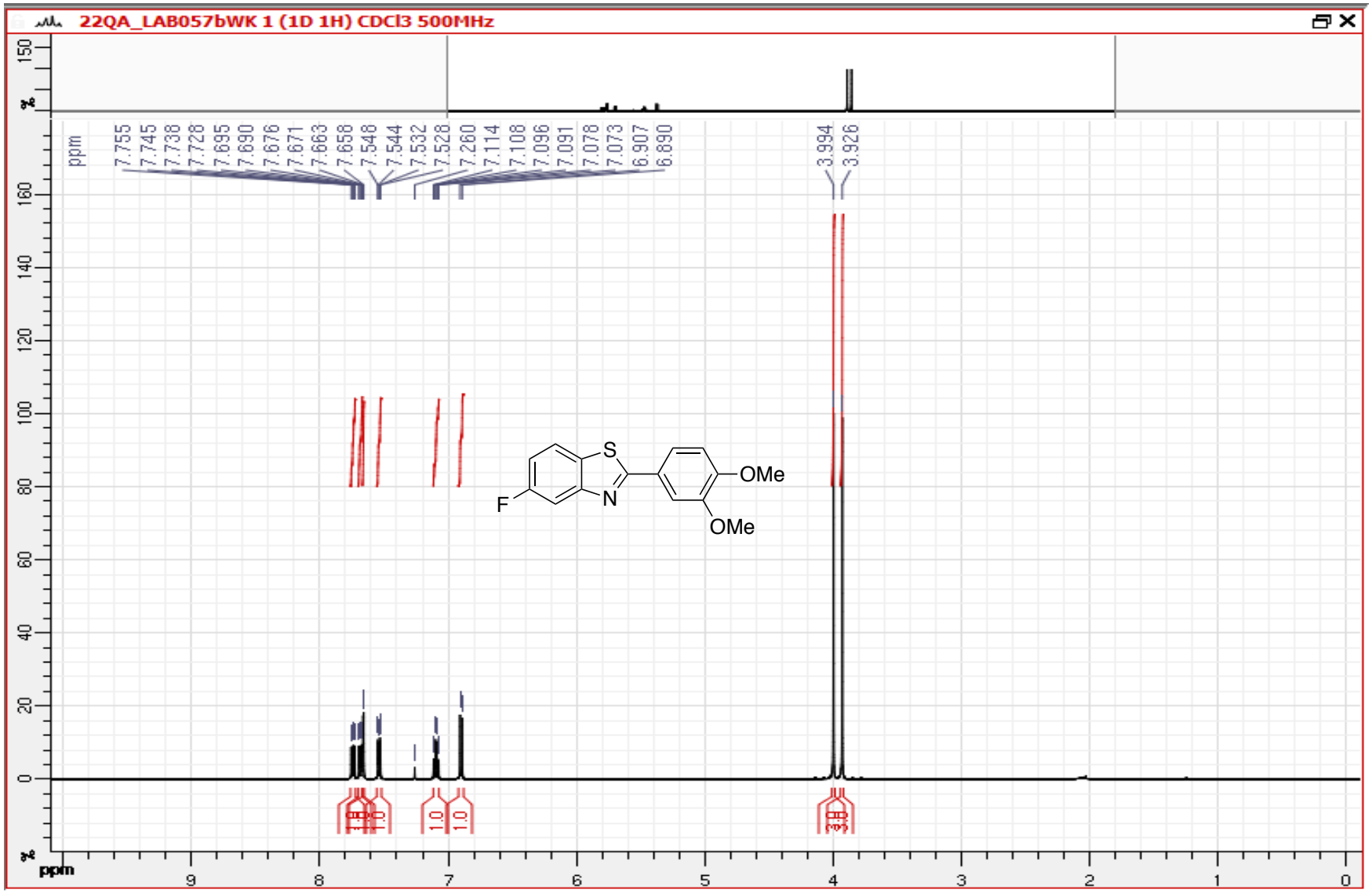

22QA_LAB062.3,4Cl 2 (1D 13C) CDCl3 500MHz
ppm
169.429
152.839
137.080
132.914
131.589
129.195
128.401
127.578
124.826
122.010
77.300
77.047
76.794
S
N
Cl
Cl
180
160
140
120
100
80
60
40
20
0

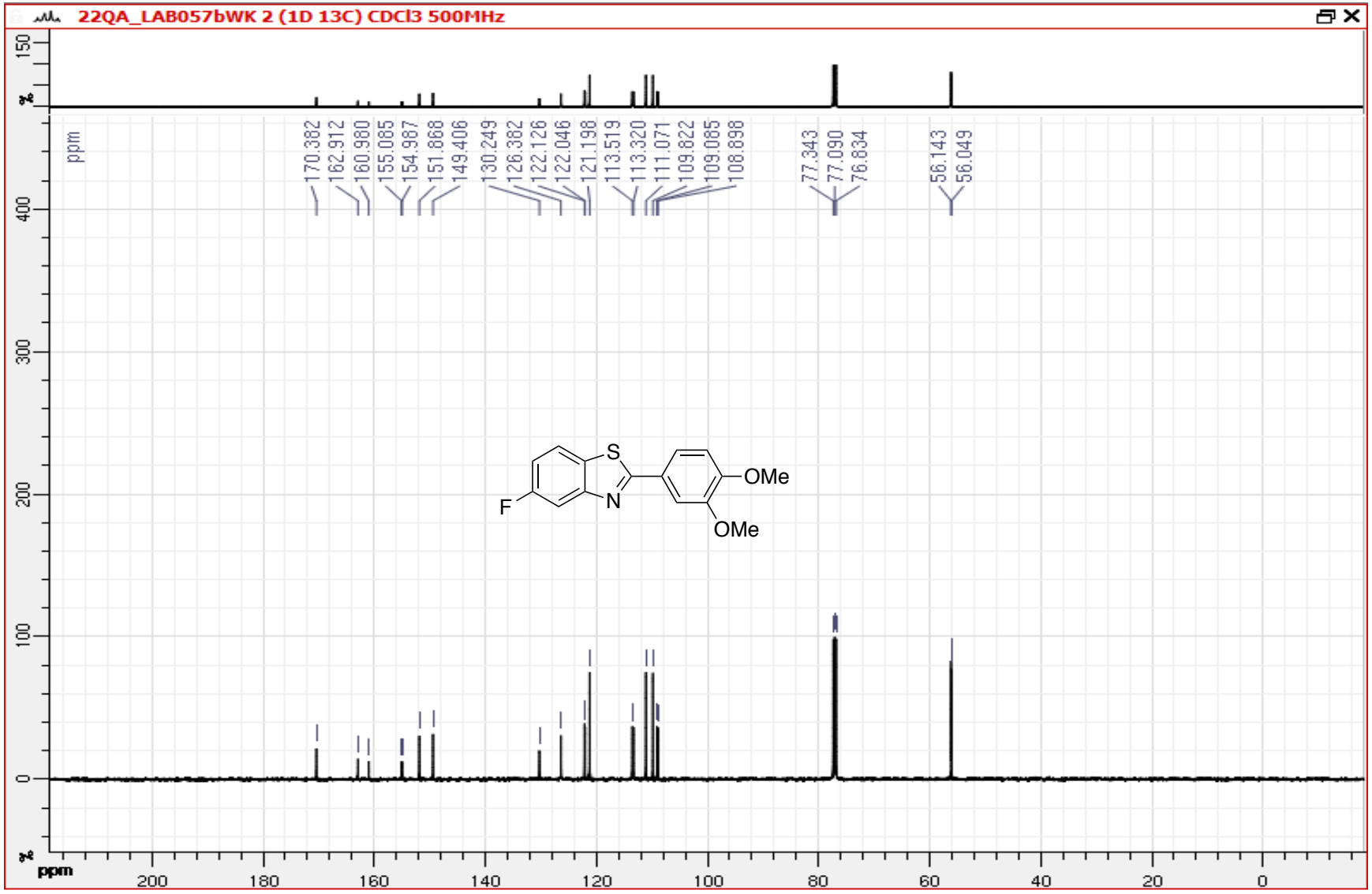
2-Phenylthiazolo[5,4-b]pyridine (3ha)




22QA_LAB119WK 2 (1D 13C) CDCl3 500MHz
ppm
168.595
158.450
147.250
146.965
133.430
131.549
129.982
129.105
127.617
121.440
77.415
77.159
76.906
N
S
N
150
300
200
100
0
180
160
140
120
100
80
60
40
20
0

2-(3,4-Dimethoxyphenyl)-5-fluorobenzo[d]thiazole (3de)




22QA_LAB057bWK 2 (1D 13C) CDCl3 500MHz
ppm
170.382
162.912
160.980
155.085
154.987
151.868
149.406
130.249
126.382
122.126
122.046
121.198
113.519
113.320
111.071
109.822
109.085
108.898
77.343
77.090
76.834
56.143
56.049
S
N
F
OMe
OMe