Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Regioselective thiolation of electron rich arenes and heterocycle under recyclable catalytic media

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General Experimental:

All the reactions were carried out in 15 mL Ace-pressure tube with constant stirring using Teflon-coated magnetic stirring bar. Column chromatography was performed using Merck silica gel (100-200 mesh). Thin layer chromatography (TLC) was performed using Merck GF_{254} plates (thickness 0.25 mm). Visualization of spots on TLC plate was accomplished with UV light and by staining in I_2 chamber. ^1H and ^{13}C NMR were recorded on 300/500 MHz and 125 MHz Brucker FTNMR spectrometer. NMR chemical shifts are expressed in δ values with reference to tetramethylsilane (TMS) as internal standard. Product yields refer to isolated yields after column chromatography.

Reagents:

All the chemicals including sulphonyl hydrazides, 1-Butyl-3-methylimidazolium Bromide, 1-Butyl-3-methylimidazolium chloride, 1-Butyl-3-methylimidazolium iodide, 1-Ethyl-3-methylimidazolium chloride, 1-Ethyl-3-methylimidazolium hydrogen sulphate, tetrabutyl ammonium iodide, tetrabutylammonium fluoride, iodine, carvacrol, and other phenols were procured from Sigma-Aldrich and Alfa aesar, and were used as received. Thymol was isolated from *trachyspermum ammi* and used after purification.

General procedure for the preparation of diaryl sulfides (C-S bond):

A mixture of phenols **1** (1 mmol), arylsulfonyl hydrazides **2** (1.2 mmol) and [Bmim][Br] (2 mmol), placed in a 15-mL Ace-pressure tube, was stirred at 140°C for the stipulated period of time. After completion of the reaction (monitored through TLC), the mixture was cooled to room temperature and the reaction mixture was treated with EtOAc (5 mL) and water (10 mL). This was extracted with ethyl acetate (3 ×10 mL) and the combined organic phase was dried over Na_2SO_4, and the organic phase was concentrated under rotary vacuum evaporator and the crude product was purified by column chromatography using a mixture of ethyl acetate/n-hexane as eluent to afford the desired unsymmetrical diaryl sulfides **3**.

Recyclability of ionic liquids:

The recyclability of the ionic liquid was investigated with the same set of optimized reaction condition as a model reaction (Table 1, entry 6, Product **3a**). Upon completion of the reaction, the product was isolated via standard work up procedure, while the aqueous layer containing [Bmim][Br] was dried to remove water at 60°C under vacuum and then washed with diethyl ether. The recovered ionic liquid was reused for four to five times without significant loss of the activity. The results were represented in Figure 1.

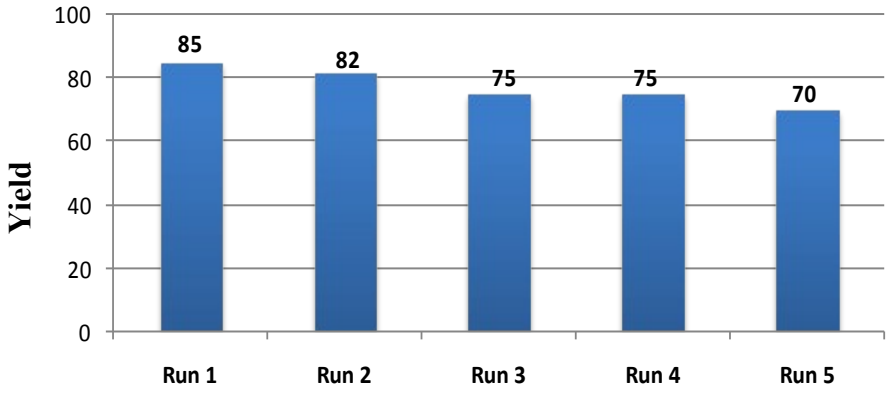
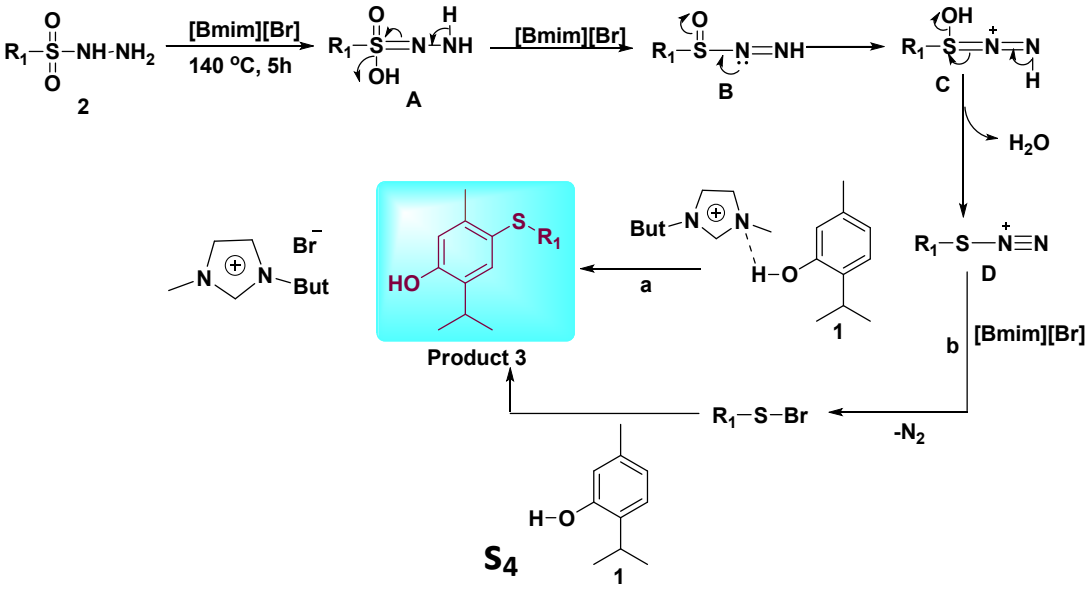


Figure 1: Recyclability of ionic liqiud

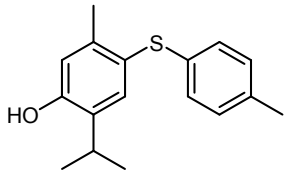
Mechanism:

On the basis of existing literature and based on my previous work,[1] we proposed a plausible mechanism for para- sulfanylation of thymol, which is outlined in scheme 4. Initially, sulfonyl hydrazide (2) is transformed to form D in the presence of [Bmim][Br]. In the next step D is attacked by the thymol through electrophilic aromatic substitution and gave desired product **3** through the path **a** or path **b**.



Spectral data of the compounds:

1. **2-Isopropyl-5-methyl-4-(*p*-tolylthio)phenol (3a)**



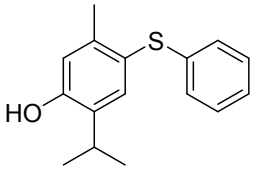
Brown viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.33 (s, 1H, ArH), 7.03 (d, *J* = 8.0 Hz, 2H, ArH), 6.96 (d, *J* = 1.5 Hz, 2H, ArH), 6.68 (s, 1H, ArH), 4.93 (s, 1H, OH), 3.17-3.11 (m, 1H, CH), 2.28 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 1.23 (d, *J* = 6.5 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 153.49, 140.78, 134.92, 134.29, 133.04, 129.64, 127.06, 123.14, 117.65, 26.89, 22.52, 20.89, 20.31.

EI-MS ($C_{17}H_{20}OS$): 272 [M], 273 $[M+H]^+$.

2. **2-Isopropyl-5-methyl-4-(phenylthio)phenol (3b)**



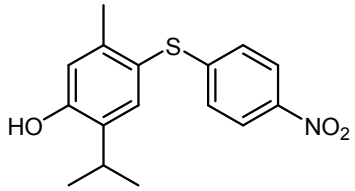
Brown viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.39 (s, 1H, ArH), 7.28-7.21 (m, 2H, ArH), 7.13-7.05 (m, 1H, ArH), 7.05-7.04 (m, 2H, ArH), 6.73 (s, 1H, ArH), 4.99 (s, 1H, OH), 3.21-3.15 (m, 1H, CH), 2.30 (s, 3H, CH_3), 1.27 (d, *J*= 6.5 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 153.77, 141.23, 138.85, 134.81, 133.21, 128.86, 126.43, 124.93, 122.30, 117.73, 26.88, 22.54, 22.50, 20.33.

ESI-MS ($C_{16}H_{18}OS$): 259 $[M+H]^+$.

3. **2-Isopropyl-5-methyl-4-((4-nitrophenyl)thio)phenol (3c)**



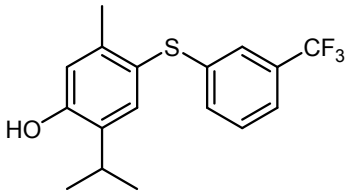
Yellow solid. Mp: 110-111°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.05-8.02 (m, 2H, ArH), 7.37 (s, 1H, ArH), 7.03-7.00 (m, 2H, ArH), 6.78 (s, 1H, ArH), 5.09 (s, 1H, OH), 3.21-3.15 (m, 1H, CH), 2.26 (s, 3H, CH_3), 1.25 (d, *J*= 7.0 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 155.27, 149.92, 144.83, 141.80, 135.35, 134.19, 124.95, 124.0, 118.91, 118.18, 26.89, 22.49, 20.19.

ESI-MS ($C_{16}H_{17}NO_3S$): 303 [M], 302$[M-H]^-$.

4. 2-Isopropyl-5-methyl-4-((3-(trifluoromethyl)phenyl)thio)phenol (3d)



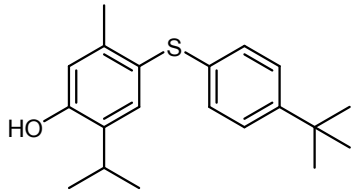
Colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.37 (s, 1H, ArH), 7.30-7.26 (m, 3H, ArH), 7.11 (d, *J*= 7.5 Hz, 1H, ArH), 6.74 (s, 1H, ArH), 5.13 (br s, 1H, OH), 3.18-3.14 (m, 1H, CH), 2.27 (s, 3H, CH_3), 1.24 (d, *J*= 7.0 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 154.30, 141.43, 140.89, 135.08, 133.69, 131.64 (q), 129.13, 128.96, 124.97, 122.55, 121.48, 121.45, 120.76, 117.96, 26.86, 22.48, 20.25.

EI-MS ($C_{17}H_{17}F_3OS$): 326 [M], 327 $[M+H]^+$.

5. 4-(4-Tert-butylphenylthio)-2-isopropyl-5-methylphenol (3e)



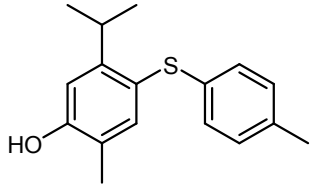
Colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.28 (s, 1H, ArH), 7.17 (d, *J*= 8.1 Hz, 2H, ArH), 6.90 (d, *J*= 8.4 Hz, 2H, ArH), 6.60 (s, 1H, ArH), 4.96 (br s, 1H, CH), 3.14-3.01 (m, 1H, CH), 2.22 (s, 3H, CH_3), 1.19 (s, 9H, 3×CH_3), 1.15 (d, *J* = 7.2 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 153.61, 148.15, 141.06, 135.11, 134.61, 133.06, 126.42, 125.90, 122.79, 117.62, 34.34, 31.30, 26.88, 22.52, 20.39.

EI-MS ($C_{20}H_{26}OS$): 314 [M], 315 $[M+H]^+$.

6. 5-Isopropyl-2-methyl-4-(*p*-tolylthio)phenol (3f)



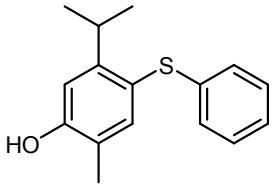
Brown viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.26 (s, 1H, ArH), 7.03 (d, *J* = 8.0 Hz, 2H, ArH), 6.98-6.95 (m, 2H, ArH), 6.79 (s, 1H, ArH), 5.12 (br s, 1H, OH), 3.53-3.48 (m, 1H, CH), 2.28 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 1.14 (d, *J* = 6.5 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 154.92, 151.59, 138.61, 135.80, 134.94, 129.60, 127.28, 122.30, 121.96, 112.88, 30.62, 23.76, 20.89, 15.12.

EI-MS ($C_{17}H_{20}OS$): 272 [M], 273 $[M+H]^+$.

7. 5-Isopropyl-2-methyl-4-(phenylthio)phenol (3g)



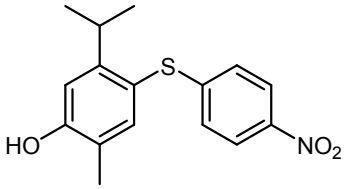
Brown viscous liquid

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.30 (s, 1H, ArH), 7.20-7.17 (m, 2H, ArH), 7.09-7.01 (m, 3H, ArH), 6.79 (s, 1H, ArH), 4.90 (br s, 1H, OH), 3.51-3.45 (m, 1H, CH), 2.19 (s, 3H, CH_3), 1.13 (d, *J*= 7.0 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 155.20, 152.11, 139.77, 139.21, 128.78, 126.59, 124.90, 122.40, 121.08, 113.01, 30.70, 23.79, 15.11.

ESI-MS ($C_{16}H_{18}OS$): 259 $[M+H]^+$.

8. 5-Isopropyl-2-methyl-4-((4-nitrophenyl)thio)phenol (3h)



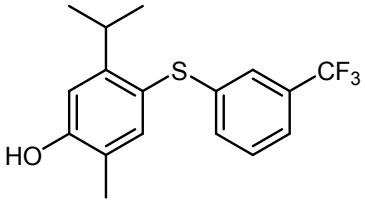
Yellow viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.03 (dd, *J*= 2.0, 7.0 Hz, 2H, ArH), 7.31 (s, 1H, ArH), 7.03 (dd, *J*= 2.0, 7.0 Hz, 2H, ArH), 6.86 (s, 1H, ArH), 5.05 (s, 1H, OH), 3.37-3.31 (m, 1H, CH), 2.23 (s, 3H, CH_3), 1.14 (d, *J*= 7.0 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 156.31, 152.88, 150.71, 144.80, 139.78, 125.07, 123.94, 123.27, 117.91, 113.55, 30.95, 23.83, 15.15.

EI-MS ($C_{16}H_{17}NO_3S$): 303 [M], 304 $[M+H]^+$.

9. 5-Isopropyl-2-methyl-4-((3-(trifluoromethyl)phenyl)thio)phenol (3i)



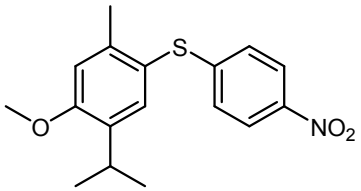
Brown viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm)**:** 7.31-7.24 (m, 4H, ArH), 7.12 (d, *J*= 7.0 Hz, 1H, ArH), 6.83 (s, 1H, ArH), 5.00 (br s, 1H, OH), 3.43-3.38 (m, 1H, CH), 2.21 (s, 3H, CH_3), 1.13 (d, *J*= 7.0 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 155.78, 152.55, 141.74, 139.53, 131.56 (q), 129.07, 129.0, 124.98, 122.85, 122.54, 121.44, 121.40, 119.32, 113.34, 30.81, 23.78, 15.12.

EI-MS ($C_{17}H_{17}F_3OS$): 326 [M], 327 $[M+H]^+$.

10. (5-Isopropyl-4-methoxy-2-methylphenyl)(4-nitrophenyl)sulfane (3j)



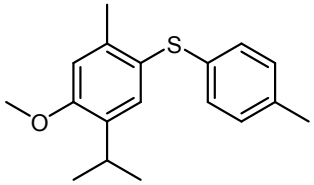
Yellow solid. Mp: 104-105°C.

1H NMR (500 MHz, $CDCl_3$, δ ppm): 8.04 (d, *J*= 8.5 Hz, 2H, ArH), 7.36 (s, 1H, ArH), 7.02 (d, *J* = 8.5 Hz, 2H, ArH), 6.84 (s, 1H, ArH), 3.88 (s, 3H, OCH_3), 3.30-3.25 (m, 1H, CH), 2.33 (s, 3H, CH_3), 1.20 (d, *J*= 7.0 Hz, 6H, 2×CH_3).

13C NMR (125 MHz, $CDCl_3$, δ ppm): 158.61, 149.92, 144.81, 141.78, 136.65, 134.65, 124.97, 124.0, 118.65, 113.10, 55.48, 26.59, 22.57, 20.74.

EI-MS ($C_{17}H_{19}NO_3S$): 317 [M], 318 $[M+H]^+$.

11. (5-Isopropyl-4-methoxy-2-methylphenyl)(*p*-tolyl)sulfane (3k)



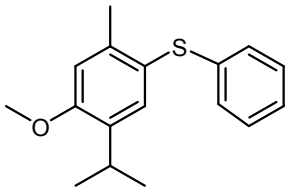
Colorless viscous liquid.

^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 7.34 (s, 1H, ArH), 7.04 (d, *J* = 8.0 Hz, 2H, ArH), 6.97 (m, 2H, ArH), 6.78 (s, 1H, ArH), 3.85 (s, 3H, OCH_3), 3.29-3.23 (m, 1H, CH), 2.36 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 1.19 (d, *J*= 6.5 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 157.42, 140.52, 135.70, 135.06, 134.86, 133.67, 129.63, 127.13, 122.60, 112.79, 55.44, 26.58, 22.63, 20.84.

EI-MS ($C_{18}H_{22}OS$): 286 [M], 287 $[M+H]^+$.

12. (5-Isopropyl-4-methoxy-2-methylphenyl)(phenyl)sulfane (3l)



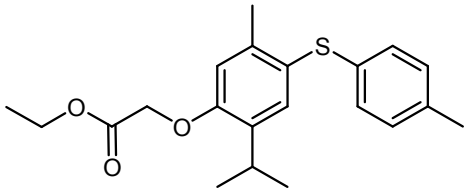
Yellow viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.35 (s, 1H, ArH), 7.21-7.18 (m, 2H, ArH), 7.10-7.01 (m, 3H, ArH)), 6.79 (s, 1H, ArH), 3.85 (s, 3H, OCH_3), 3.28-3.23 (m, 1H, CH), 2.35 (s, 3H, CH_3), 1.19 (d, *J*= 7.0 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 157.64, 141.01, 138.97, 135.81, 134.16, 128.82, 126.45, 124.86, 121.69, 112.79, 55.43, 26.55, 22.62, 20.86.

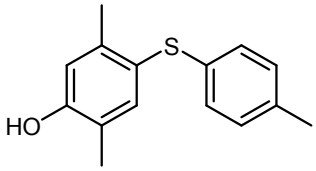
EI-MS ($C_{17}H_{20}OS$): 272 [M], 273 $[M+H]^+$.

13. Ethyl 2-(2-isopropyl-5-methyl-4-(p-tolylthio)phenoxy)acetate (3m)



No reaction

14. 2,5-Dimethyl-4-(*p*-tolylthio)phenol (3n)



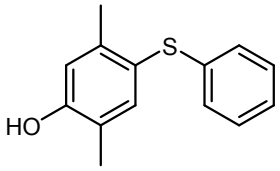
White solid. Mp: 96-97°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.25 (s, 1H, ArH), 7.04 (d, *J*= 8.0 Hz, 2H, ArH), 6.98 (d, *J*=8.5 Hz, 2H, ArH), 6.70 (s, 1H, ArH), 4.84 (br s, 1H, OH), 2.28 (s, 6H, 2×CH_3), 2.20 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 154.41, 141.03, 138.18, 135.11, 134.76, 129.69, 127.44, 123.16, 122.27, 117.24, 20.93, 20.40, 15.13.

EI-MS ($C_{15}H_{16}OS$): 244 [M], 245 $[M+H]^+$.

15. 2,5-Dimethyl-4-(phenylthio)phenol (3o)



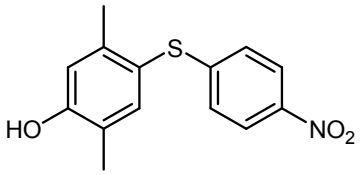
Colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.30 (s, 1H, ArH), 7.21-7.18 (m, 2H, ArH), 7.09-7.01 (m, 3H, ArH), 6.73 (s, 1H, ArH), 4.91 (s, 1H, OH), 2.28 (s, 3H, CH_3), 2.20 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 154.80, 141.58, 138.85, 138.79, 129.23, 128.85, 127.83, 126.62, 124.99, 122.42, 122.12, 117.30, 20.40, 15.11.

ESI-MS ($C_{14}H_{14}OS$): 229 $[M-H]^-$.

16. 2,5-Dimethyl-4-((4-nitrophenyl)thio)phenol (3p)



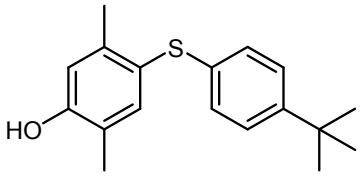
Yellow solid. Mp: 156-157°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.04-8.01 (m, 2H, ArH), 7.33 (s, 1H, CH_3), 7.02-7.0 (m, 2H, ArH), 6.80 (s, 1H, ArH), 5.13 (s, 1H, OH), 2.27 (s, 3H, CH_3), 2.23 (s, 1H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 155.89, 149.73, 144.85, 142.34, 139.56, 125.05, 124.01, 123.25, 118.99, 117.73, 20.27, 15.13.

ESI-MS ($C_{14}H_{13}NO_3S$): 274 $[M-H]^-$.

17. 4-((4-(*Tert*-butyl)phenyl)thio)-2,5-dimethylphenol(3q)



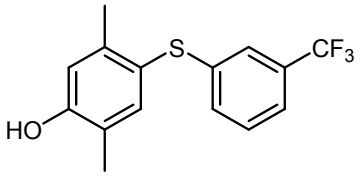
Colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.29 (s, 1H, ArH), 7.24 (dd, *J*= 2.0, 6.5 Hz, 2H, ArH), 6.99 (d, *J* = 0.5 Hz, 1H, ArH), 6.97 (s, 1H, ArH), 6.72 (s, 1H, ArH), 5.06 (br s, 1H, OH), 2.31 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 1.28 (s, 9H, 3×CH_3)

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 154.60, 148.26, 141.34, 138.57, 135.03, 126.71, 125.93, 122.69, 122.35, 117.21, 34.35, 31.31, 20.48, 15.15.

ESI-MS ($C_{18}H_{22}OS$): 285 $[M-H]^-$.

18. 2,5-Dimethyl-4-(3-(trifluoromethyl)phenylthio)phenol (3r)



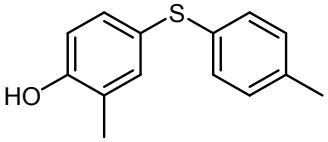
White solid. Mp: 98-99°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.32-7.26 (m, 4H, ArH), 7.10 (d, *J*= 7.5 Hz, 1H, ArH), 6.76 (s, 1H, ArH), 4.89 (s, 1H, OH), 2.27 (s, 3H, CH_3), 2.22 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 155.31, 141.95, 140.77, 139.26, 131.37 (q), 129.15, 129.04, 122.79, 122.63, 121.54, 121.51, 120.52, 117.53, 20.33, 15.10.

EI-MS ($C_{15}H_{13}F_3OS$): 298 [M], 299 $[M+H]^+$.

19. 2-Methyl-4-(*p*-tolylthio)phenol (3s)



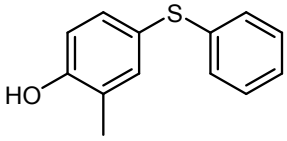
Colorless viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.23 (s, 1H, ArH), 7.22-7.11 (m, 3H, ArH), 7.07 (d, *J* = 8.5 Hz, 2H, ArH), 6.74 (d, *J* = 8.0 Hz, 1H, ArH), 4.82 (s, 1H, OH), 2.30 (s, 3H, CH_3), 2.21 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 153.83, 136.02, 135.84, 134.51, 132.17, 129.75, 129.23, 125.38, 125.01, 115.82, 20.99, 15.66.

ESI-MS ($C_{14}H_{14}OS$): 229 $[M-H]^-$.

20. 2-Methyl-4-(phenylthio)phenol (3t)[2]



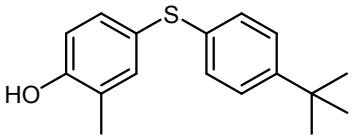
Yellow viscous liquid

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.28-7.20 (m, 4H, ArH), 7.17-7.11 (m, 3H, ArH), 6.77 (d, *J* = 8.5 Hz, 1H, ArH), 4.90 (s, 1H, OH), 2.23 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 154.25, 138.75, 136.78, 133.13, 128.90, 128.12, 125.68, 125.19, 124.10, 115.94, 16.65.

ESI-MS ($C_{13}H_{12}OS$): 215 $[M-H]^-$.

21. 4-((4-(*Tert*-butyl)phenyl)thio)-2-methylphenol (3u)



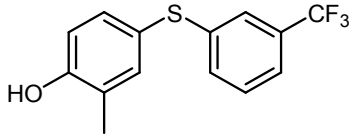
Colorless viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.28-7.25 (m, 3H, ArH), 7.21 (dd, *J*= 2.0, 8.5 Hz, 1H, ArH), 7.14 (d, *J*= 8.5 Hz, 2H, ArH), 6.75 (d, *J* = 8.5 Hz, 1H, ArH), 4.98 (br s, 1H, OH), 2.23 (s, 3H, CH_3), 1.29 (s, 9H, 3×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 154.03, 149.10, 136.37, 134.85, 132.69, 128.36, 126.02, 125.10, 124.77, 115.88, 34.43, 31.30, 15.69.

EI-MS ($C_{17}H_{20}OS$): 272 [M], 273 $[M+H]^+$.

22. 2-Methyl-4-(3-(trifluoromethyl)phenylthio)phenol (3v)



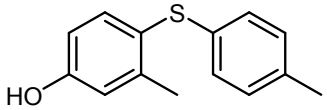
Yellow viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.37-7.29 (m, 4H, ArH), 7.25-7.23 (m, 2H, ArH), 6.81 (d, *J*= 8.5 Hz, 1H, ArH), 5.00 (s, 1H, OH), 2.25 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 154.88, 140.97, 137.49, 133.92, 131.39, 131.13, 130.31, 129.17, 125.61, 123.80, 123.77, 122.21, 122.08, 122.05 116.25, 15.65.

EI-MS ($C_{14}H_{11}F_3OS$): 284 [M], 285 $[M+H]^+$.

23. 3-Methyl-4-(*p*-tolylthio)phenol (3w)



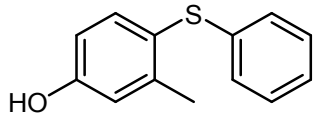
Brown viscous liquid

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.33 (d, *J*= 8.0 Hz, 1H, ArH), 7.05 (d, *J*= 8.0 Hz, 2H, ArH), 7.00 (m, 2H, ArH), 6.77 (d, *J*= 2.5 Hz, 1H, ArH), 6.67 (dd, *J*= 3.0, 8.5 Hz, 2H, ArH), 5.04 (br s, 1H, OH), 2.32 (s, 3H, CH_3), 2.29 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 156.04, 143.46, 136.70, 135.40, 134.30, 129.75, 127.88, 123.99, 117.67, 113.83, 20.93, 20.88.

EI-MS ($C_{14}H_{14}OS$): 230 [M], 231 $[M+H]^+$.

24. 3-Methyl-4-(phenylthio)phenol (3x)[2]



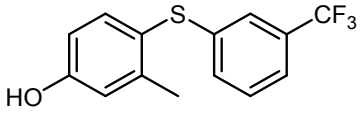
Colorless viscous liquid

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.39 (d, *J*= 8.0 Hz, 1H, ArH), 7.22-7.19 (m, 2H, ArH), 7.11-7.08 (m, 1H, ArH), 7.04-7.03 (m, 2H, ArH), 6.80 (d, *J*= 2.5 Hz, 1H, ArH), 6.69 (dd, *J*= 3.0 Hz, 8.0 Hz, 1H, ArH), 4.92 (br s, 1H, OH), 2.32 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 156.42, 144.17, 138.40, 137.56, 128.91, 126.95, 125.21, 122.92, 117.77, 113.93, 20.91.

ESI-MS ($C_{13}H_{12}OS$): 239 $[M+Na]^+$.

25. 3-Methyl-4-(3-(trifluoromethyl)phenylthio)phenol (3y)



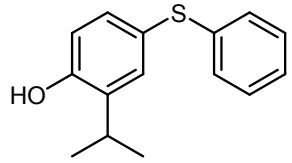
Brown viscous liquid

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.43 (d, *J*= 8.0 Hz, 1H, ArH), 7.33-7.26 (m, 3H, ArH), 7.12 (d, *J*= 7.5 Hz, 1H, ArH), 6.83 (d, *J*= 2.5 Hz, 1H, ArH), 6.73 (dd, *J*= 2.5, 8.0 Hz, 1H, ArH), 5.11 (s, 1H, OH), 2.32 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 156.96, 144.66, 140.46, 138.20, 131.70 (q), 129.27, 124.93, 122.84, 121.70, 121.73, 121.20, 118.05, 114.28, 20.85.

EI-MS ($C_{14}H_{11}F_3OS$): 284 [M], 285 $[M+H]^+$.

26. 2-Msopropyl-4-(phenylthio)phenol (3z)



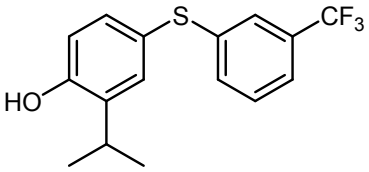
Brown viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.34 (d, *J*= 2.0 Hz, 1H, ArH), 7.24-7.11 (m, 6H, ArH), 6.74 (d, *J*= 8.0 Hz, 1H, ArH), 4.93 (s, 1H, OH), 3.21-3.16 (m, 1H, CH), 1.24 (d, *J*= 6.5 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 153.20, 138.85, 135.79, 132.68, 132.62, 128.90, 127.87, 125.59, 124.22, 116.39, 27.15, 22.42.

ESI-MS ($C_{15}H_{16}OS$): 243 $[M-H]^-$.

27. 2-Isopropyl-4-(3-(trifluoromethyl)phenylthio)phenol (3aa)



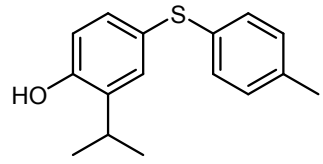
Colorless viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.36-7.30 (m, 3H, ArH), 7.26-7.21 (m, 3H, ArH), 6.79 (d, *J*= 8.0 Hz, 1H, ArH), 5.02 (s, 1H, OH), 3.23-3.16 (m, 1H, CH), 1.25 (d, *J*= 7.0 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 153.82, 141.09, 136.31, 133.37, 133.31, 131.39, 130.07, 129.15, 124.93, 123.52, 123.49, 122.36, 121.96, 116.68, 27.12, 22.38.

ESI-MS ($C_{16}H_{15}F_3OS$): 311 $[M-H]^-$.

28. 2-Isopropyl-4-(*p*-tolylthio)phenol (3ab)



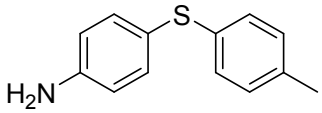
Brown viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.30 (d, *J*= 2.0 Hz, 1H, ArH), 7.13-7.10 (m, *J*= 8.0 Hz, 3H, ArH), 7.06 (d, *J*= 8.0 Hz, 2H, ArH), 6.71 (d, *J*= 8.0 Hz, 1H, ArH), 4.92 (s, 1H, OH), 3.20-3.14 (m, 1H, CH), 2.29 (s, 3H, CH_3), 1.23 (d, *J*= 6.5 Hz, 6H, 2×CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 152.83, 135.88, 135.63, 134.60, 131.72, 131.70, 129.71, 128.95, 125.44, 116.29, 27.16, 22.41, 20.96.

EI-MS ($C_{16}H_{18}OS$): 258 [M], 259 $[M+H]^+$.

29. 4-(p-tolylthio)aniline (3ac)[3a]



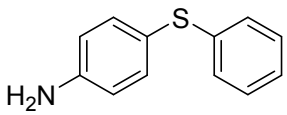
Brown solid. Mp: 70-71°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.29-7.26 (m, 2H, ArH), 7.10-7.03 (m, 4H, ArH), 6.67-6.64 (m, 2H, ArH), 3.76 (br s, 2H, NH_2), 2.29 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 146.65, 135.56, 135.47, 135.33, 129.64, 128.31, 121.79, 115.84, 20.94

EI-MS ($C_{13}H_{13}NS$): 215 [M], 216 $[M+H]^+$.

30. 4-(phenylthio)aniline (3ad)[3b]



White solid. Mp: 92-93°C

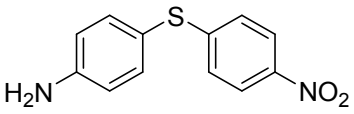
^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.32-7.30 (m, 2H, ArH), 7.22-7.19 (m, 2H, ArH), 7.13-7.08 (m, 3H, ArH), 6.69 (dd, *J*= 2.0, 8.5 Hz, 2H, ArH), 3.83 (br s, 2H, NH_2).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 146.99, 139.66, 136.09, 128.77, 127.26 125.21, 120.48, 115.84.

EI-MS ($C_{12}H_{11}NS$): 201 $[M+H]^+$

.

31. 4-(4-nitrophenylthio)aniline (3ae)[3b]

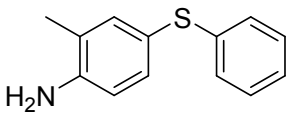


Yellow solid. Mp: 137-138°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.03 (d, *J*= 9.0 Hz, 2H, ArH), 7.34 (d, *J*= 8.5 Hz, 2H, ArH), 7.09 (d, *J*= 9.0 Hz, 2H, ArH), 6.74 (d, *J*= 8.5 Hz, 2H, ArH), 3.96 (br s, 2H,

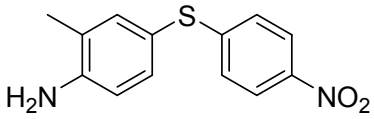
NH_2). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 151.04, 148.36, 144.83, 137.24, 125.24, 123.89, 116.45, 116.15. EI-MS ($C_{12}H_{10}N_2O_2S$): 246 [M], 247$[M+H]^+$.

32. 2-methyl-4-(phenylthio)aniline (3af)[3c]



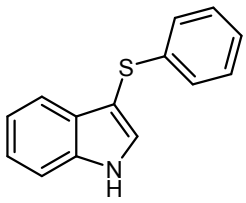
Brown solid. Mp: 59-60°C. ^1H NMR (500 MHz, $CDCl_3$, δ ppm): 7.24-7.19 (m, 4H, ArH), 7.13-7.08 (m, 3H, ArH), 6.68 (dd, *J*= 8.0 Hz, 1H, ArH), 3.78 (br s, 2H, NH_2), 2.15 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 145.35, 139.94, 137.02, 133.88, 128.81, 128.78, 127.18, 125.14, 123.29, 120.17, 115.87, 17.23. EI-MS ($C_{13}H_{13}NS$): 216 $[M+H]^+$.

33. 2-methyl-4-(4-nitrophenylthio)aniline (3ag)[3b]



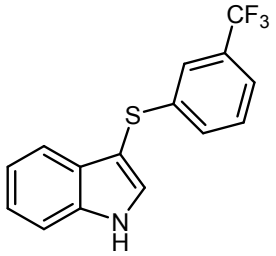
Yellow solid. Mp: 121-122 °C.
^1H NMR (500 MHz, $CDCl_3$, δ ppm): 8.03 (dd, *J*= 2.0, 7.0 Hz, 2H, ArH), 7.26-7.21 (m, 2H, ArH), 7.09 (dd, *J*= 2.0, 7.0 Hz, 2H, ArH), 6.74 (d, *J*= 8.0 Hz, 1H, ArH) 3.89 (br s, 2H, NH_2), 2.18 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 151.24, 146.61, 144.78, 137.88, 134.88, 125.23, 123.87, 123.70, 116.28, 115.87, 17.23. ESI-MS ($C_{13}H_{12}N_2O_2S$): 261 $[M+H]^+$.

34. 3-(Phenylthio)-1*H*-indole (5a)[4]



White solid. Mp: 150-151°C.
^1H NMR (500 MHz, $CDCl_3$, δ ppm): 8.41 (br s, 1H, NH), 7.62 (d, *J*= 8.0 Hz, 1H, ArH), 7.50 (d, *J*= 2.5 Hz, 1H, ArH), 7.45 (d, *J*= 8.5 Hz, 1H, ArH), 7.29-7.26 (m, 1H, ArH), 7.18-7.03 (m, 6H, ArH).
^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 139.22, 136.51, 130.64, 129.13, 128.69, 125.87, 124.77, 123.07, 120.92, 119.70, 111.55, 102.95.
EI-MS ($C_{14}H_{11}NS$): 226 $[M+H]^+$.

35. 3-(3-(Trifluoromethyl)phenylthio)-1*H*-indole (5b)[5]



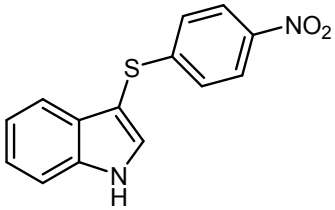
Brown viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.48 (br s, 1H, NH), 7.63 (dd, *J*= 1.0, 7.5 Hz, 1H, ArH), 7.54 (d, *J*= 3.0 Hz, 1H, ArH), 7.49 (s, 1H, ArH), 7.48 (s, 1H, ArH), 7.44 (s, 1H, ArH), 7.34-7.31 (m, 2H, ArH), 7.28-7.21 (m, 2H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 141.0, 136.56, 131.01, 129.06 (q), 123.34, 122.36, 122.33, 121.53, 121.50, 121.20, 119.41, 111.76, 101.59.

EI-MS ($C_{15}H_{10}F_3NS$): 294 $[M+H]^+$.

36. 3-(4-Nitrophenylthio)-1*H*-indole (5c)[4]



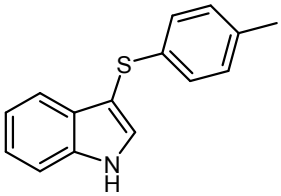
Brown solid. Mp: 176-177°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.63 (br s, 1H, NH), 8.01-7.98 (m, 2H, ArH), 7.55-7.49 (m, 3H, ArH), 7.33-7.26 (m, 1H, ArH), 7.21-7.11 (m, 3H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 149.82, 144.93, 136.61, 131.21, 128.45, 125.11, 123.88, 123.58, 121.44, 119.23, 111.97, 100.23.

EI-MS ($C_{14}H_{10}N_2O_2S$): 270[M], 271$[M+H]^+$.

37. 3-(*p*-Tolylthio)-1*H*-indole (5d)[4]

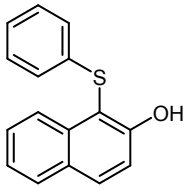


White solid. Mp: 123-124°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.36 (br s, 1H, NH), 7.62 (d, *J*= 8.0 Hz, 1H, ArH), 7.48 (d, *J*= 2.5 Hz, 1H, ArH), 7.44 (d, *J*= 8.0 Hz, 1H, ArH), 7.27-7.24 (m, 1H, ArH), 7.17-7.14 (m, 1H, ArH), 7.04 (dd, *J*= 2.0, 7.0 Hz, 2H, ArH), 6.98 (d, *J*= 8.0 Hz, 2H, ArH), 2.25 (s, 3H, CH_3).

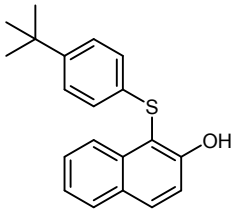
^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 136.48, 135.48, 134.65, 130.38, 129.48, 129.14, 126.29, 122.99, 120.84, 119.73, 111.51, 103.62, 20.86.
EI-MS ($C_{15}H_{13}NS$): 239 [M], 240 $[M+H]^+$.

38. 1-(Phenylthio)naphthalen-2-ol (7a)[6]



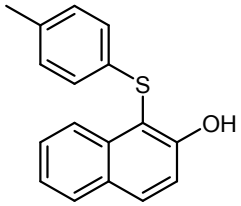
White solid. Mp: 52-53°C.
^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.24 (d, *J*= 8.0 Hz, 1H, ArH), 7.93 (d, *J*= 9.0 Hz, 1H, ArH), 7.83 (d, *J*= 8.0 Hz, 1H, ArH), 7.52-7.49 (m, 1H, ArH), 7.40-7.31 (m, 2H, ArH), 7.20-7.16 (m, 2H, ArH), 7.13-7.10 (m, 1H, ArH), 7.05-7.03 (m, 2H, ArH).
^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 157.03, 135.47, 135.39, 132.86, 129.52, 129.21, 128.60, 127.98, 126.40, 125.92, 124.72, 123.89, 116.90, 108.07.
EI-MS ($C_{16}H_{12}OS$): 252 [M], 253 $[M+H]^+$.

39. 1-(4-tert-butylphenylthio)naphthalen-2-ol (7b)[6]



White solid. Mp: 71-72°C.
^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.28 (d, *J*= 8.0 Hz, 1H, ArH), 7.91 (d, *J*= 9.0 Hz, 1H, ArH), 7.83 (d, *J*= 8.5 Hz, 1H, ArH), 7.52-7.49 (m, 1H, ArH), 7.39-7.34 (m, 2H, ArH), 7.23-7.19 (m, 3H, ArH, OH), 7.00-6.97 (m, 2H, ArH).
^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 156.92, 149.14, 135.57, 132.68, 131.81, 129.48, 128.55, 127.89, 127.78, 126.30, 126.28, 126.15, 124.84, 123.82, 116.85, 108.57, 34.39, 31.29, 31.23.
EI-MS ($C_{20}H_{20}OS$): 308 [M], 309 $[M+H]^+$.

40. 1-(p-tolylthio)naphthalen-2-ol (7c)[6]



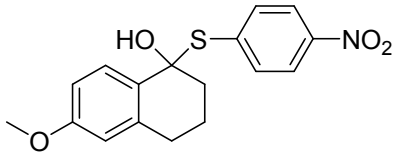
White solid. Mp: 80-81°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.24 (d, *J*= 8.5 Hz, 1H, ArH), 7.90 (d, *J*= 9.0 Hz, 1H, ArH), 7.82 (d, *J*= 8.0 Hz, 1H, ArH), 7.51-7.47 (m, 1H, ArH), 7.38-7.32 (m, 2H, ArH), 7.20 (br s, 1H, OH), 7.0-6.94 (m, 4H, ArH), 2.24 (s, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 156.88, 135.90, 135.45, 132.65, 131.75, 129.96, 129.49, 128.55, 127.89, 126.70, 124.75, 123.80, 116.84, 108.71, 20.89.

EI-MS ($C_{17}H_{14}OS$): 266 [M], 267 $[M+H]^+$.

41. 6-methoxy-1-(4-nitrophenylthio)-1,2,3,4-tetrahydronaphthalen-1-ol (9a)



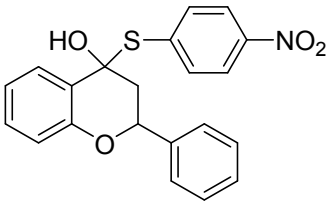
Yellow solid. Mp: 191-192°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.38-8.35 (m, 2H, ArH), 8.24-8.21 (m, 2H, ArH), 7.90 (d, *J*= 9.0 Hz, 1H, ArH), 7.47 (br s, 1H, OH), 6.78 (dd, *J*= 2.5, 9.0 Hz, 1H, ArH), 6.60 (d, *J*= 2.5 Hz, 1H, ArH), 3.80 (s, 3H, OCH_3), 2.71 (t, *J*= 6.0 Hz, 2H, CH_2), 2.46 (t, *J*= 6.5 Hz, 2H, CH_2), 1.92-1.87 (m, 2H, CH_2).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 161.06, 154.29, 150.39, 144.10, 141.85, 129.51, 126.68, 124.13, 123.88, 113.29, 112.67, 55.31, 29.71, 25.44, 21.41.

EI-MS ($C_{17}H_{17}NO_4S$): 331 [M], 332 $[M+H]^+$.

42. 4-(4-nitrophenylthio)-2-phenylchroman-4-ol (9b)



White solid. Mp: 171-172°C.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.36 (dd, *J*= 2.0, 7.0 Hz, 2H, ArH), 8.20 (dd, *J*= 2.0, 7.0 Hz, 2H, ArH), 7.89 (dd, *J*= 1.5, 8.0 Hz, 1H, ArH), 7.63 (br s, 1H, OH), 7.43-7.30 (m, 6H, ArH), 7.02-6.94 (m. 2H, ArH), 5.10-5.07 (m. 1H, CH), 3.04-3.00 (m. 1H, CH), 2.65.04-2.59 (m. 1H, CH).

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): 157.41, 150.50, 150.06, 143.68, 138.94, 132.46, 129.50, 128.90, 128.86, 126.04, 124.67, 124.23, 122.02, 118.79, 118.08, 76.79, 32.50

ESI-MS ($C_{21}H_{17}NO_4S$): 379 [M], 380 $[M+H]^+$.

References:

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3. (a) Duan, Z. Ranjit, S. Liu, X. *Org. Lett.* **2010**, *12*, 2430-2433. (b) Tian, H.; Yang, H.; Zhu, C.; Fu, H. *Adv. Synth. Catal.* **2015**, *357*, 1-9. (c) Fang, X. L.; Tang, R. Y.; Zhang, X. G.; Li, J. H. *Synthesis* **2011**, *7*, 1099-1105.
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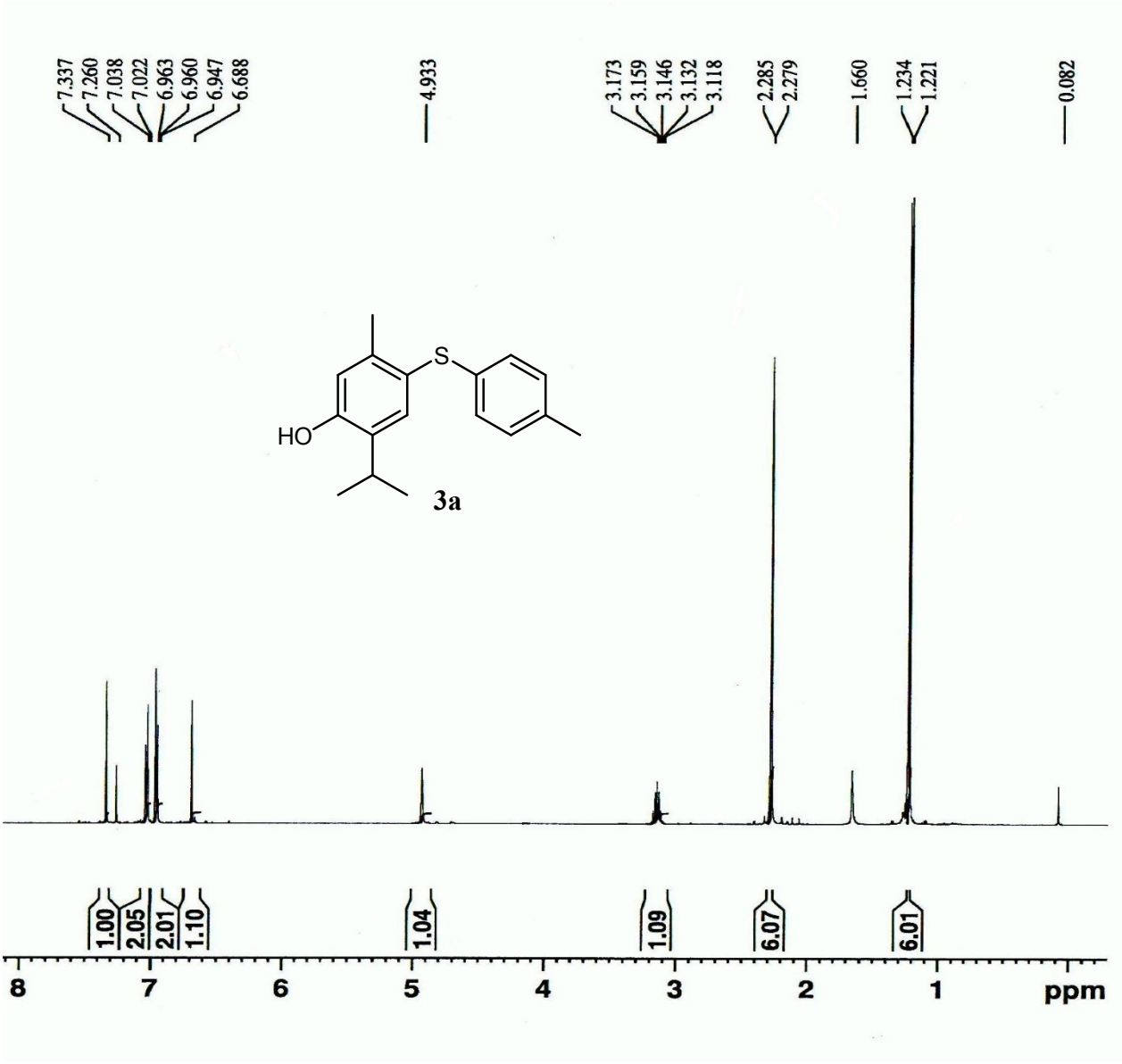
5. Kumaraswamy, G.; Raju, R.; Narayanarao, V. *RSC Adv.,* 2015, **5**, 22718-22723.
6. Kang, X.; Yan, R.; Yu, G.; Pang, X.; Liu, X.; Li, X.; Xiang, L.; Huang, G. *J. Org. Chem.*, **2014**, *79*, 10605–10610.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6.947
6.688
4.933
3.173
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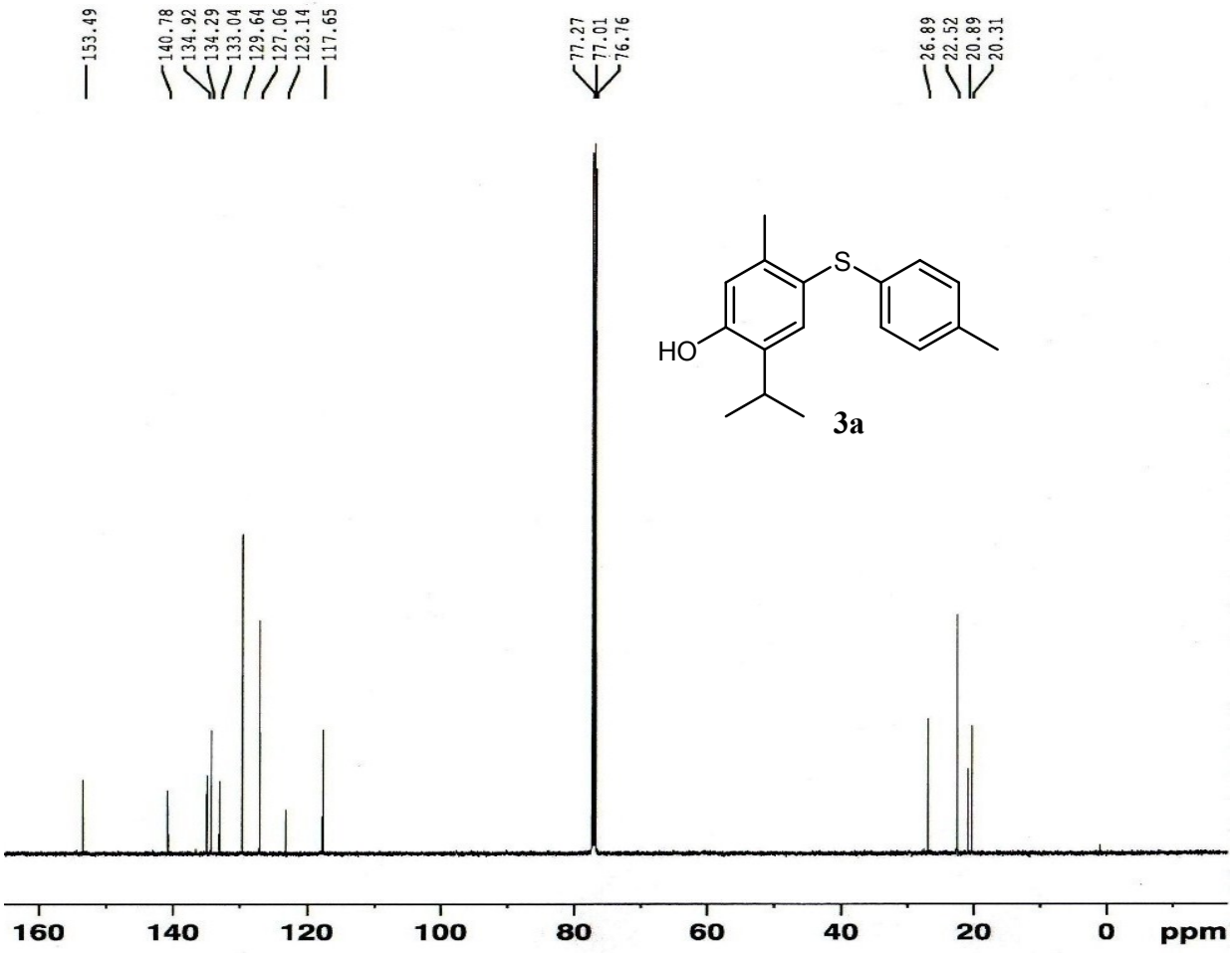
3.146
3.132
3.118
2.285
2.279
1.660
1.234
1.221
0.082
HO
S
3a
1.00
2.05
2.01
1.10
1.04
1.09
6.07
6.01
8
7
6
5
4
3
2
1
ppm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123.14
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77.27
77.01
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20.31
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HO
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80
60
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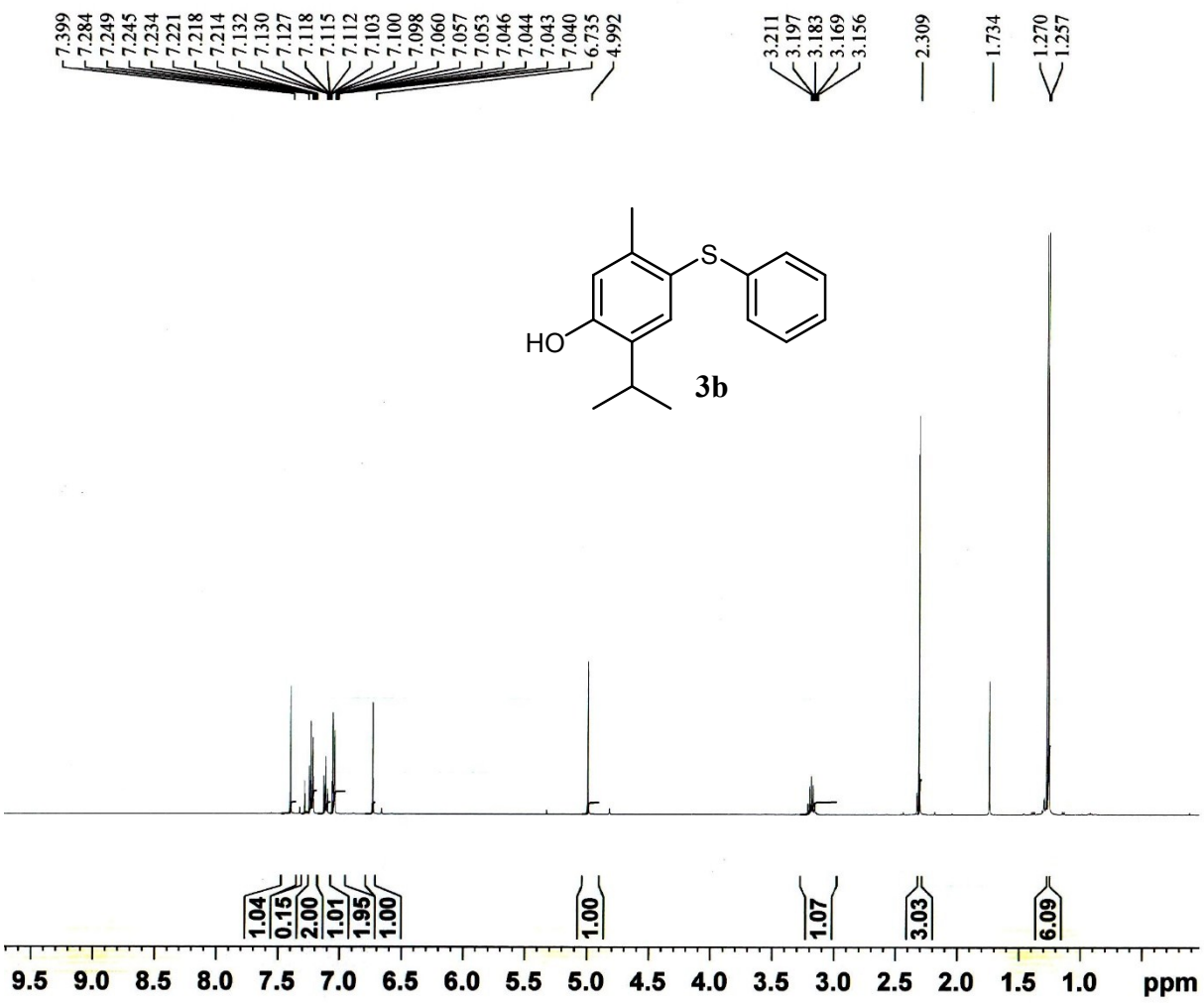
20
0
ppm

3a

[]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7.115
7.112
7.103
7.100
7.098
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7.057
7.053
7.046
7.044
7.043
7.040
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3.197
3.183
3.169
3.156
2.309
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1.257
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3b
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0.15
2.00
1.01
1.95
1.00
1.00
1.07
3.03
6.09
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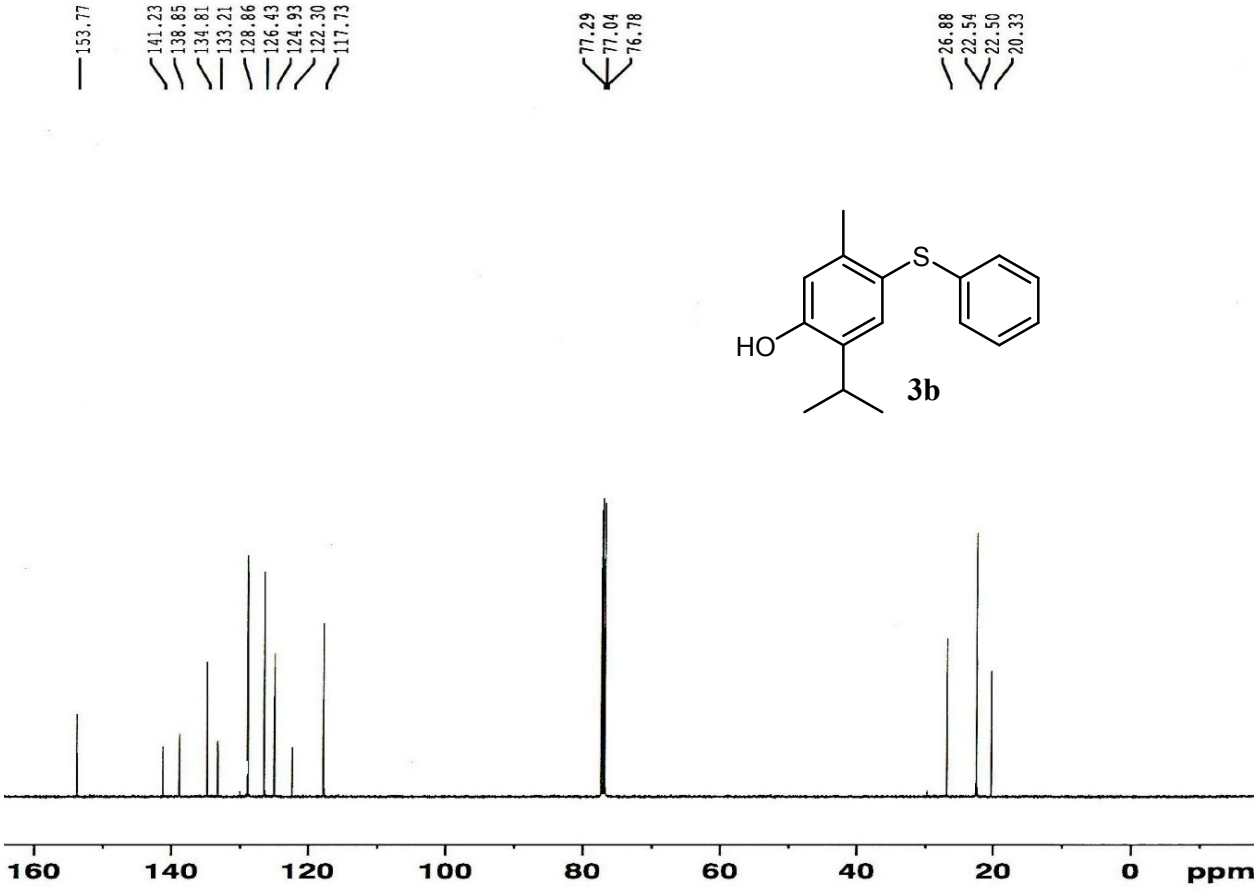
ppm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76.78
26.88
22.54
22.50
20.33
S
HO
160
140
120
100
80
60
40
20
0
ppm

3b


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8.046
8.042
8.032
8.028
8.023
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7.260
7.030
7.024
7.020
7.010
7.006
7.001
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3.199
3.185
3.171
3.157
2.263
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1.241
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NO2
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0.22
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6.03
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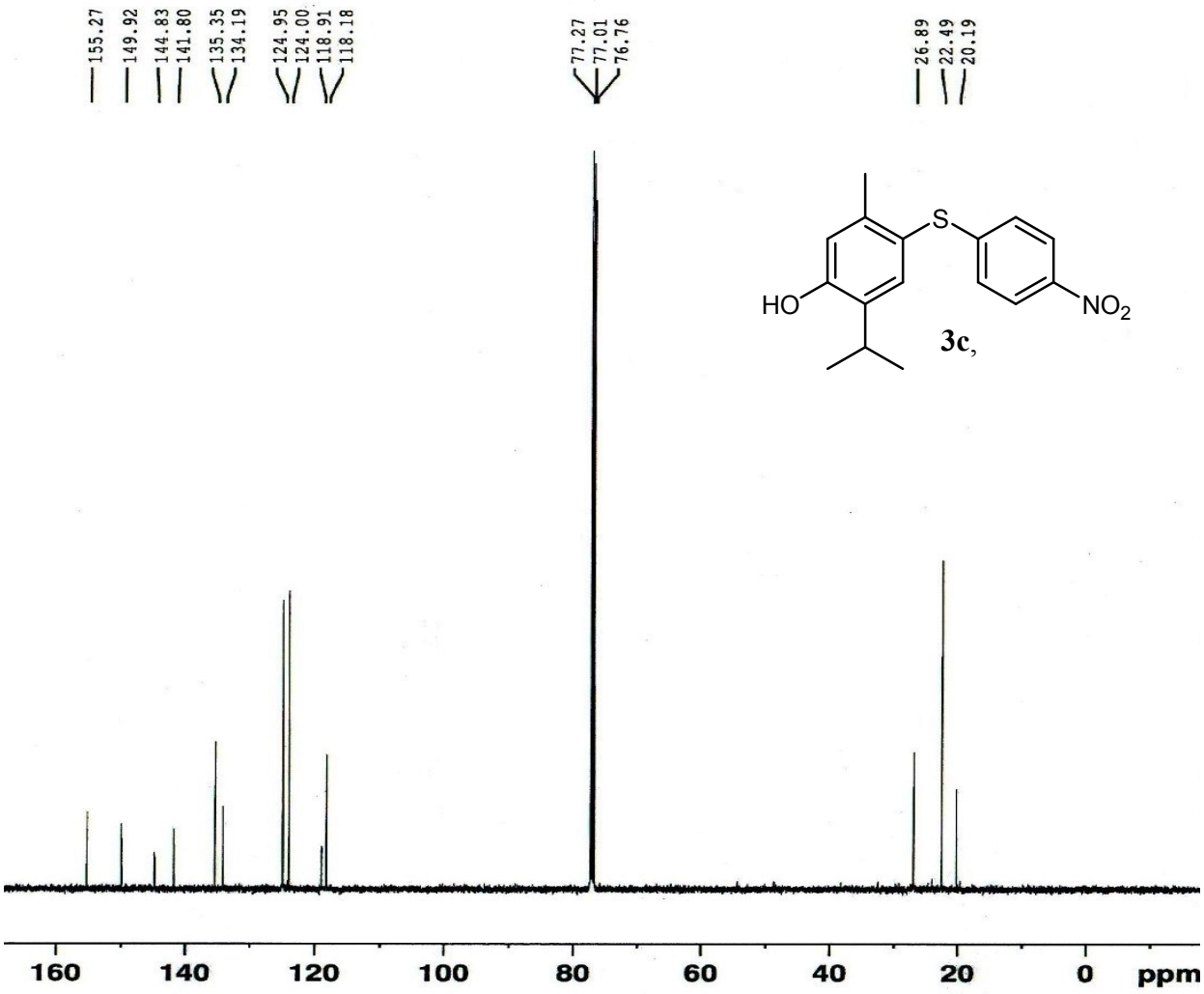
ppm

3c,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76.76
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NO2
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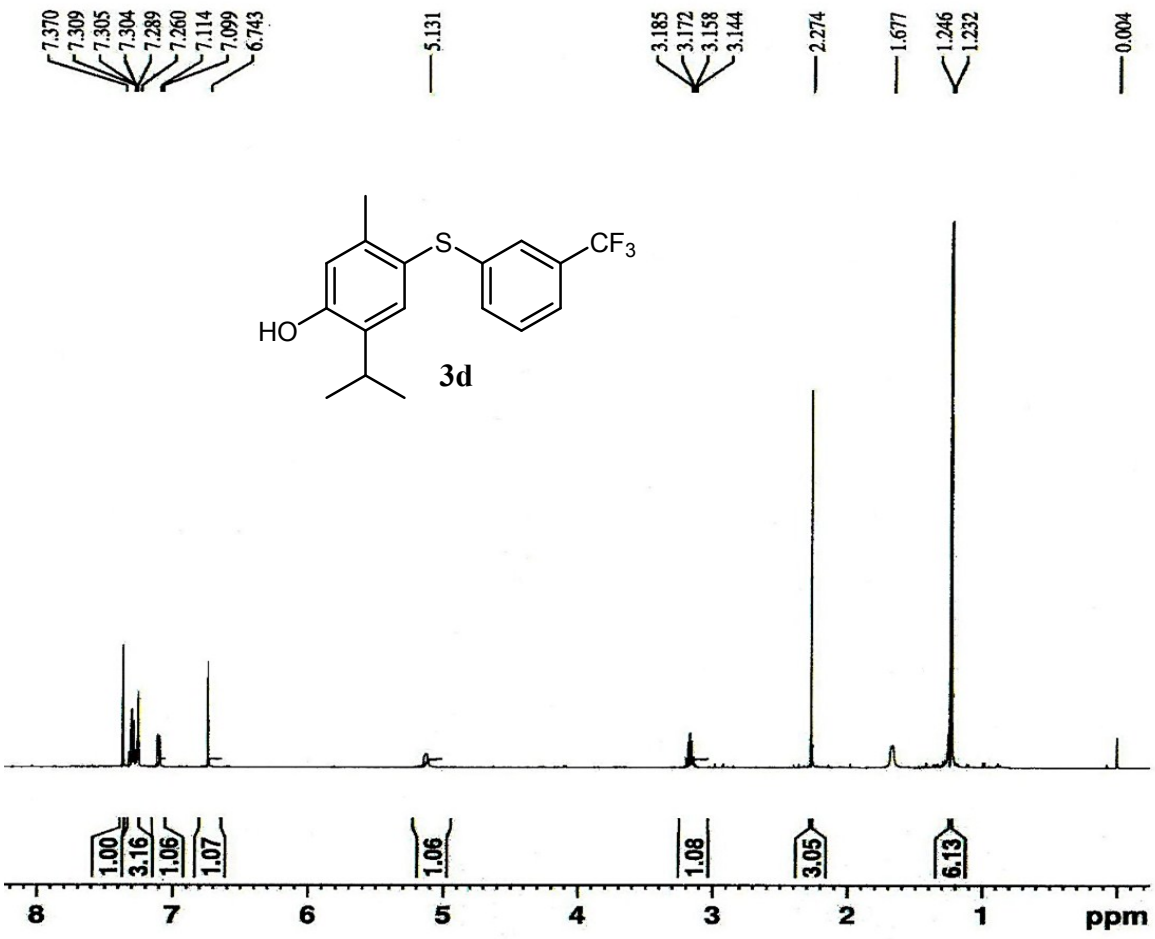
ppm

3c,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1.06
1.08
3.05
6.13
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7
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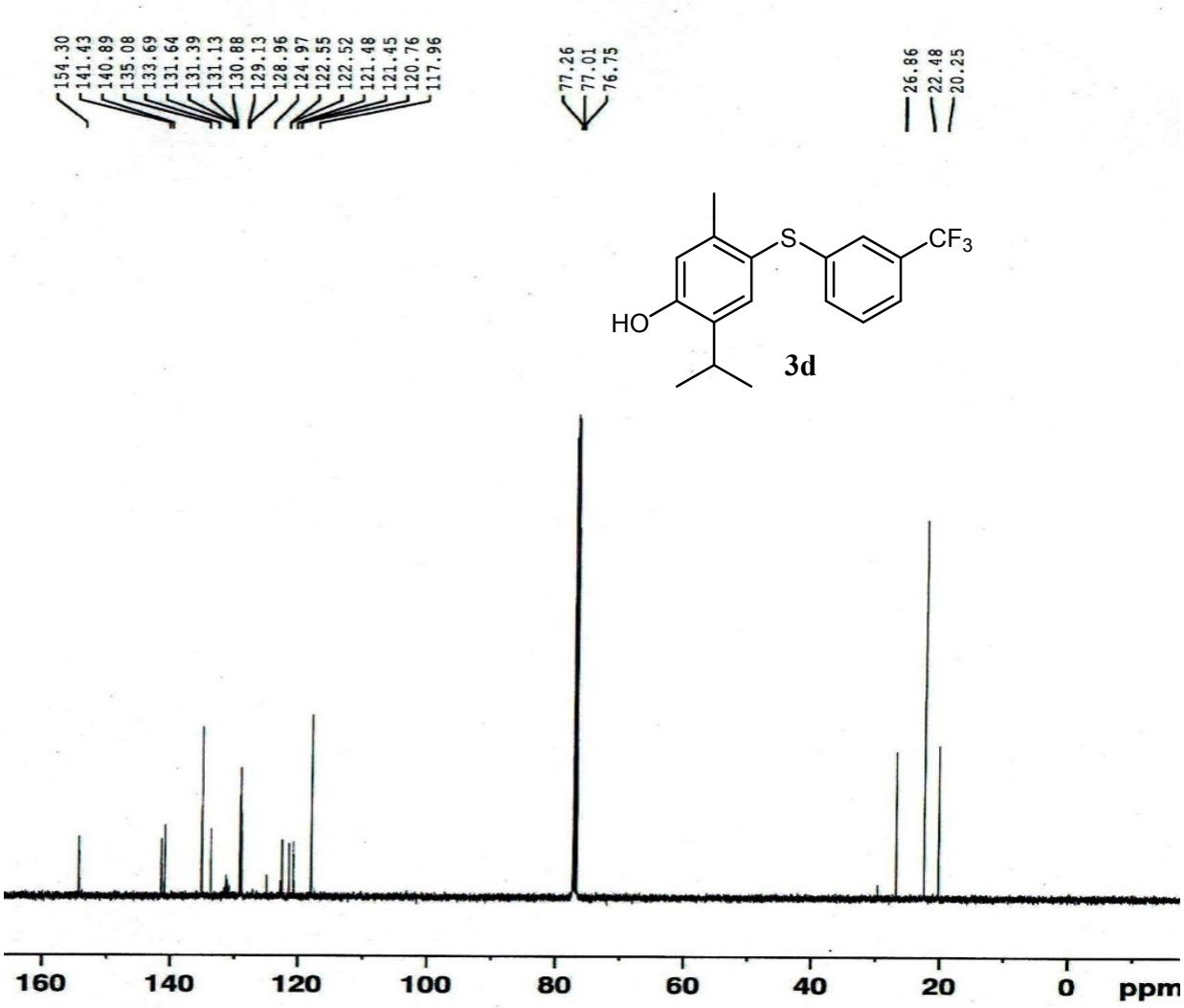
3
2
1
ppm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129.13
128.96
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122.55
122.52
121.48
121.45
120.76
117.96
77.26
77.01
76.75
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20.25
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CF3
HO
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0
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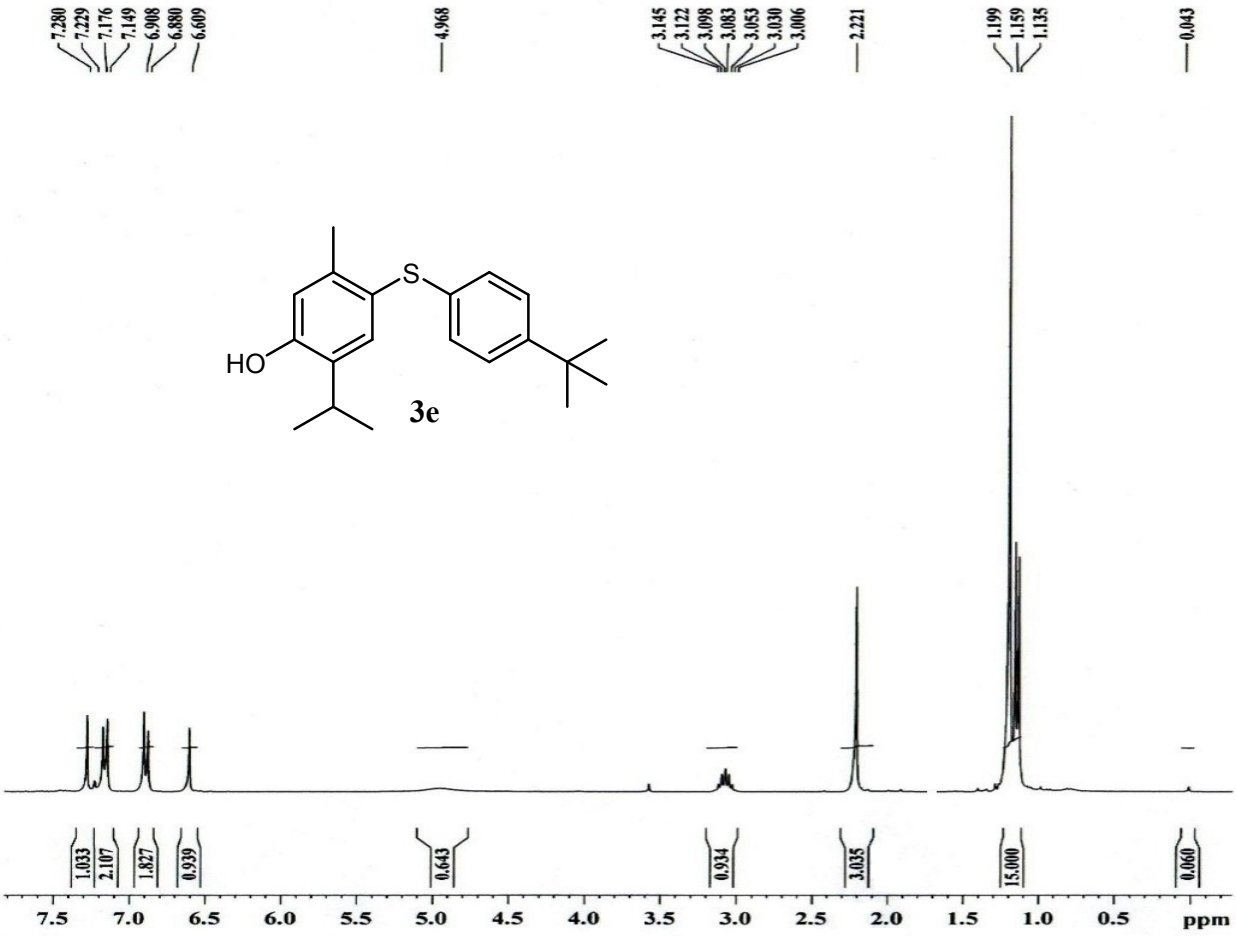
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15.000
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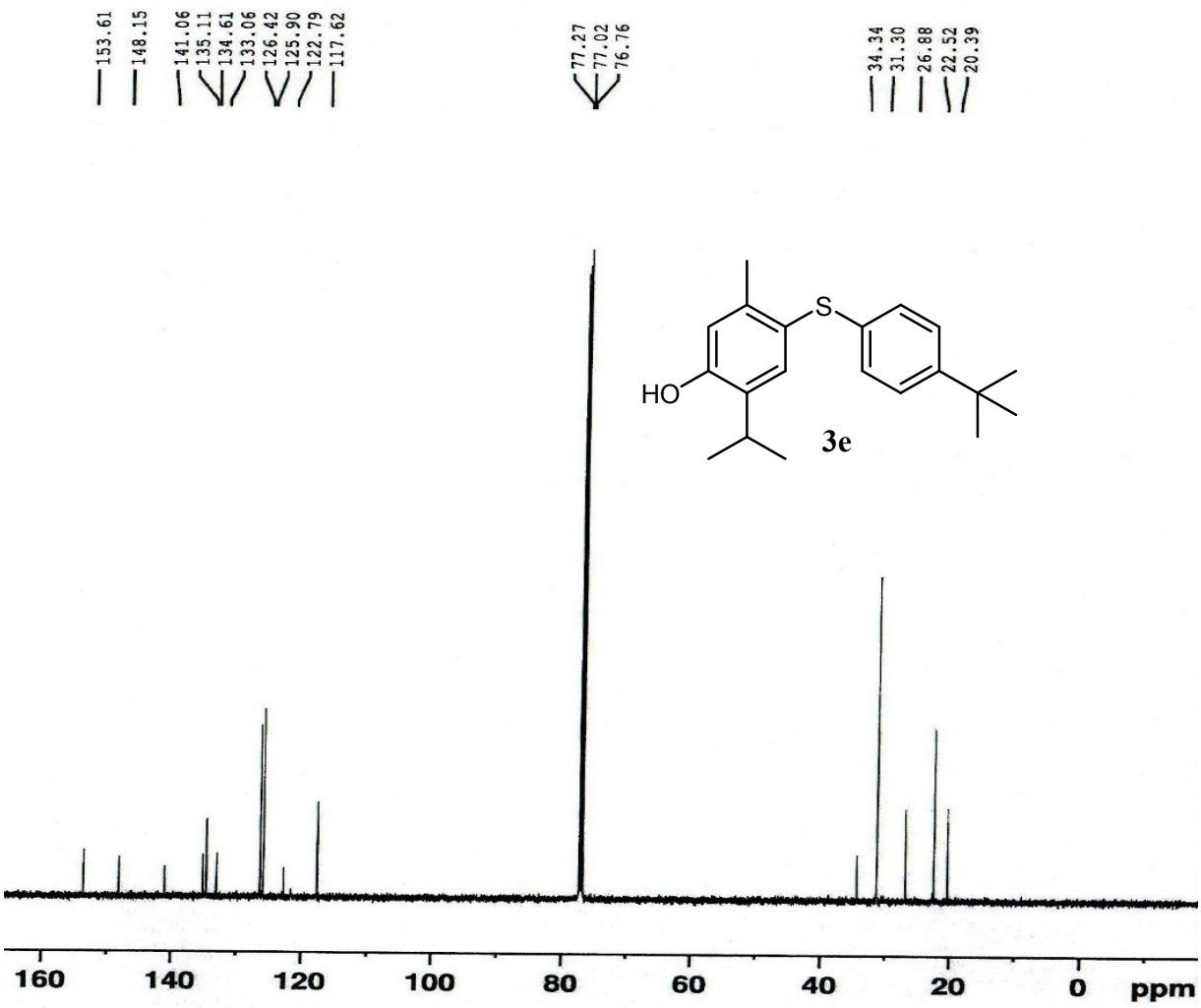
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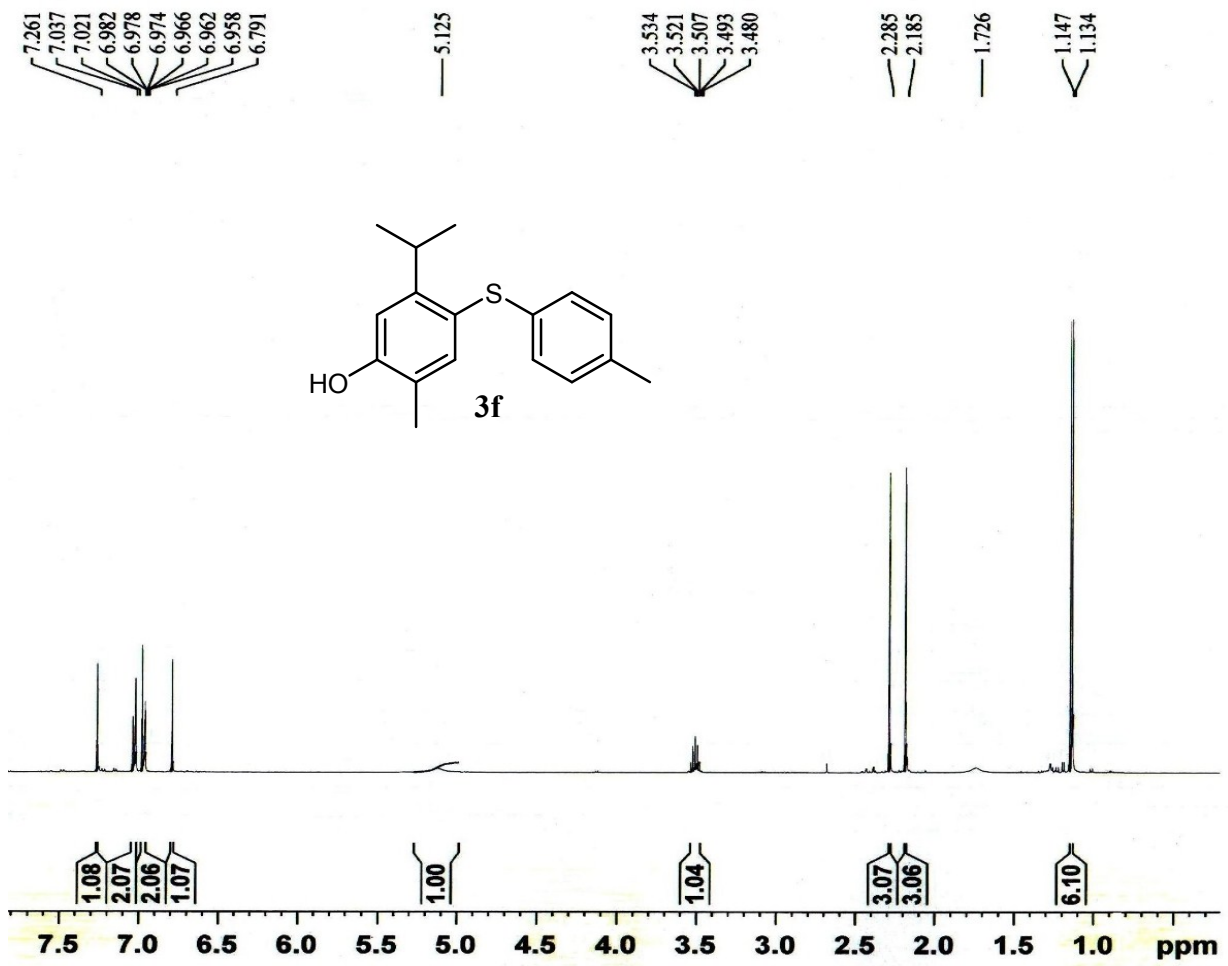
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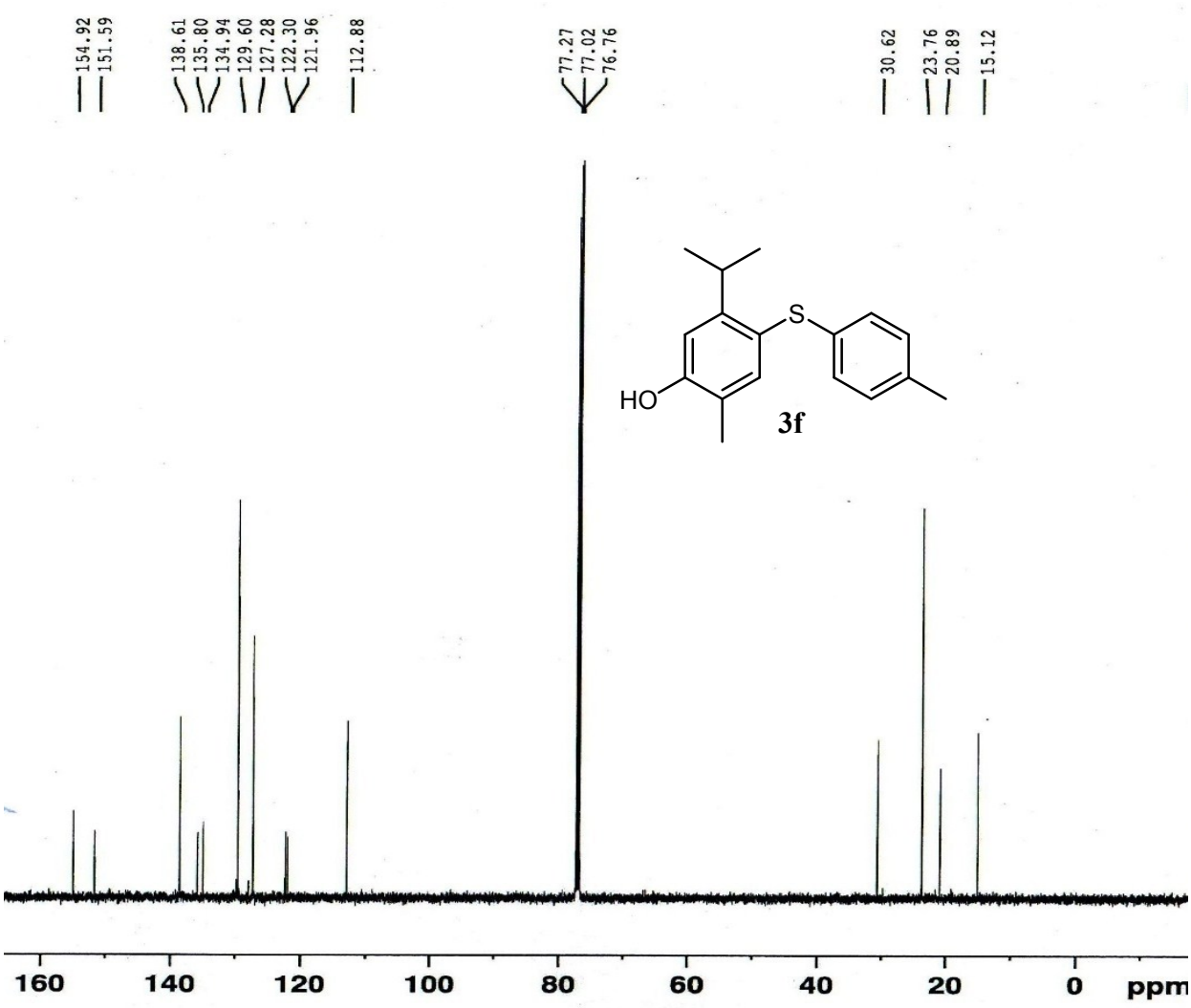
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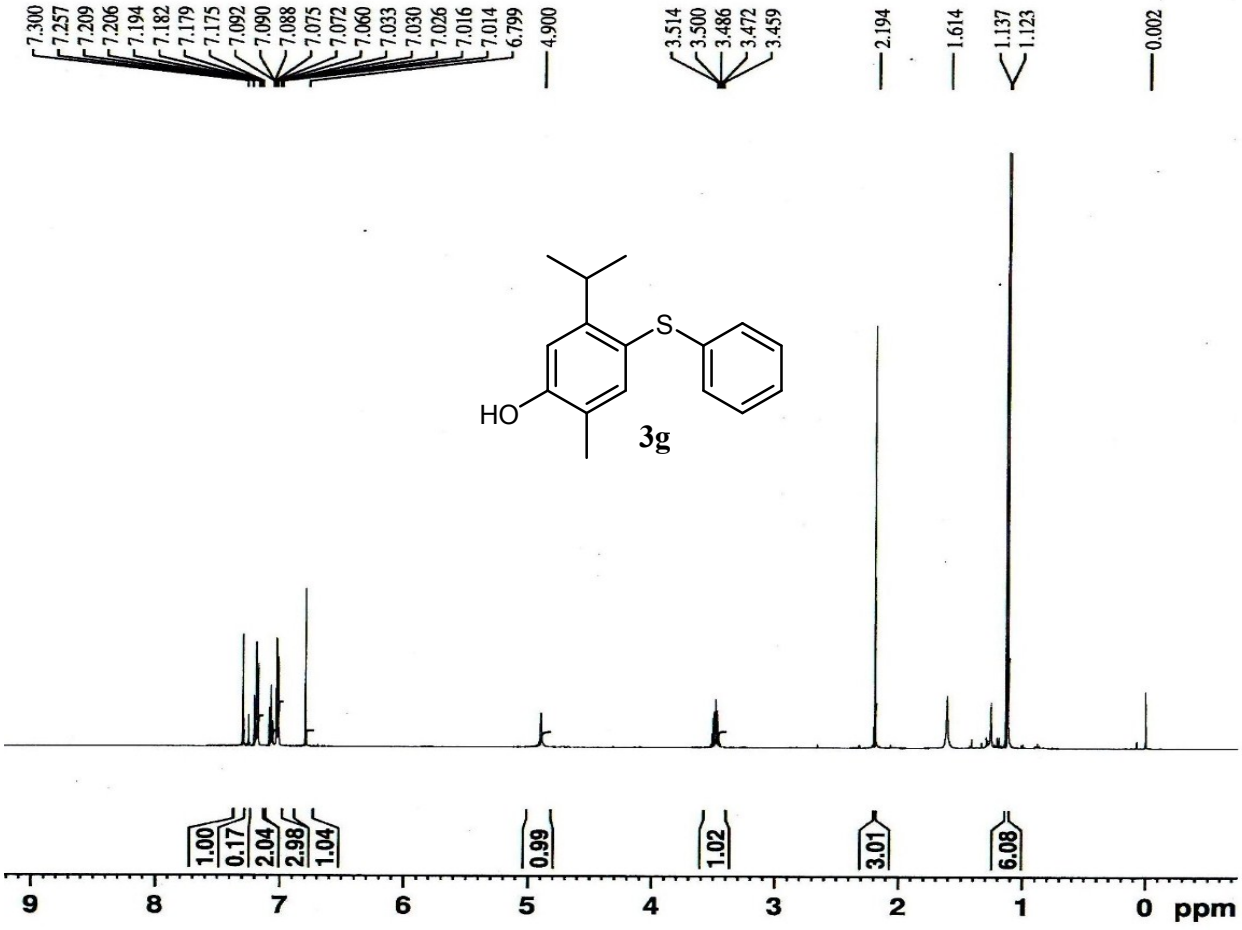
ppm

3f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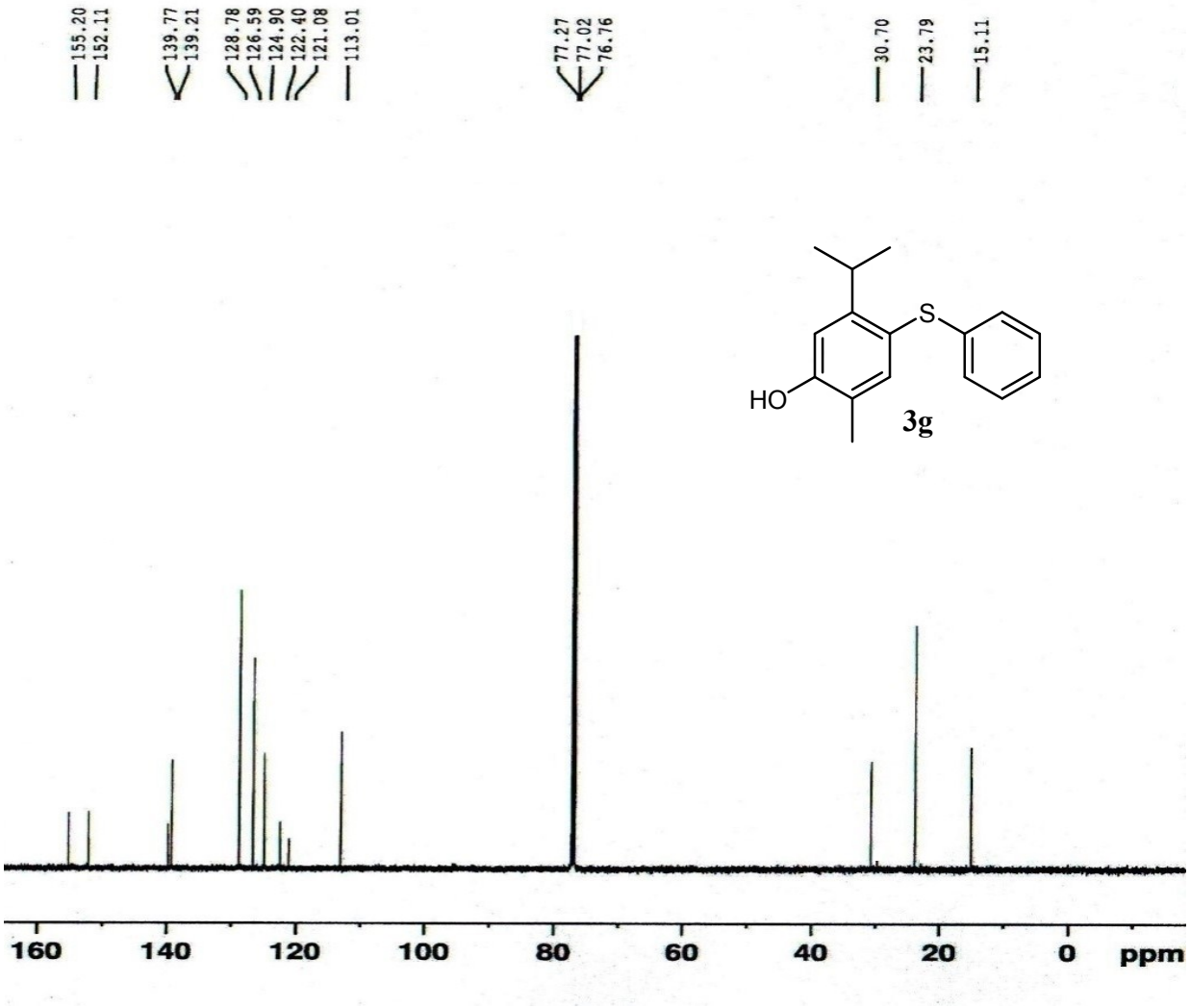
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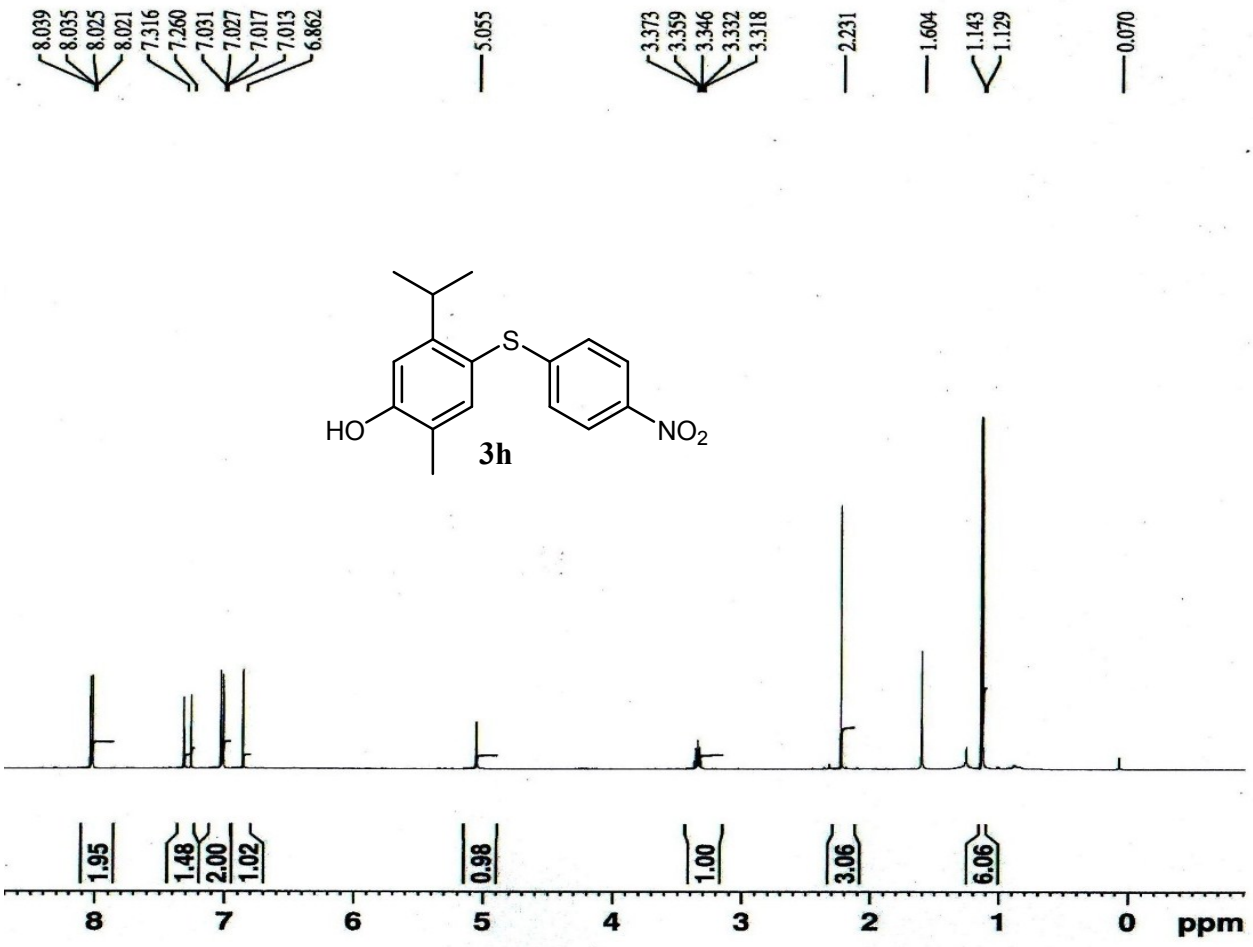
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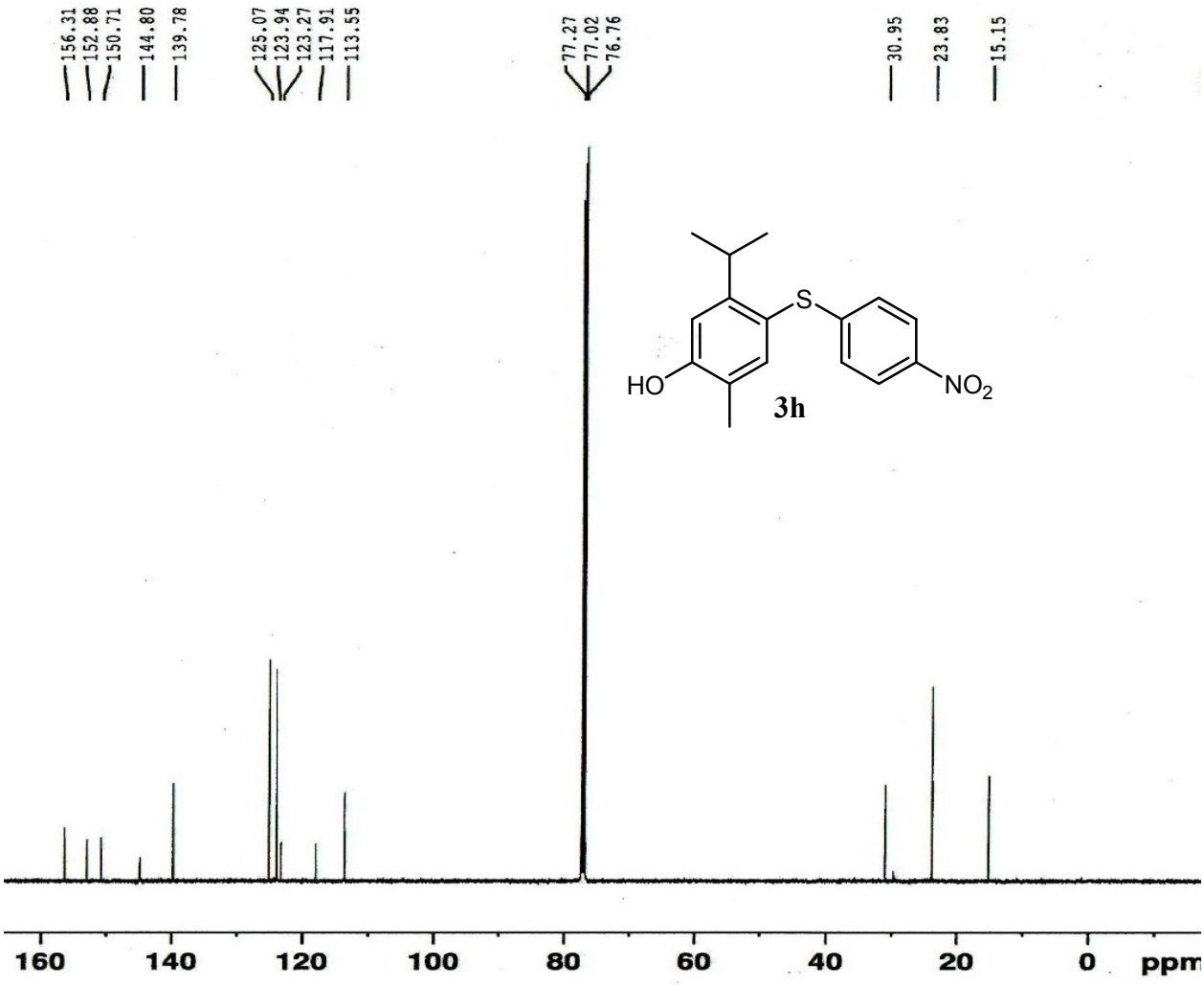
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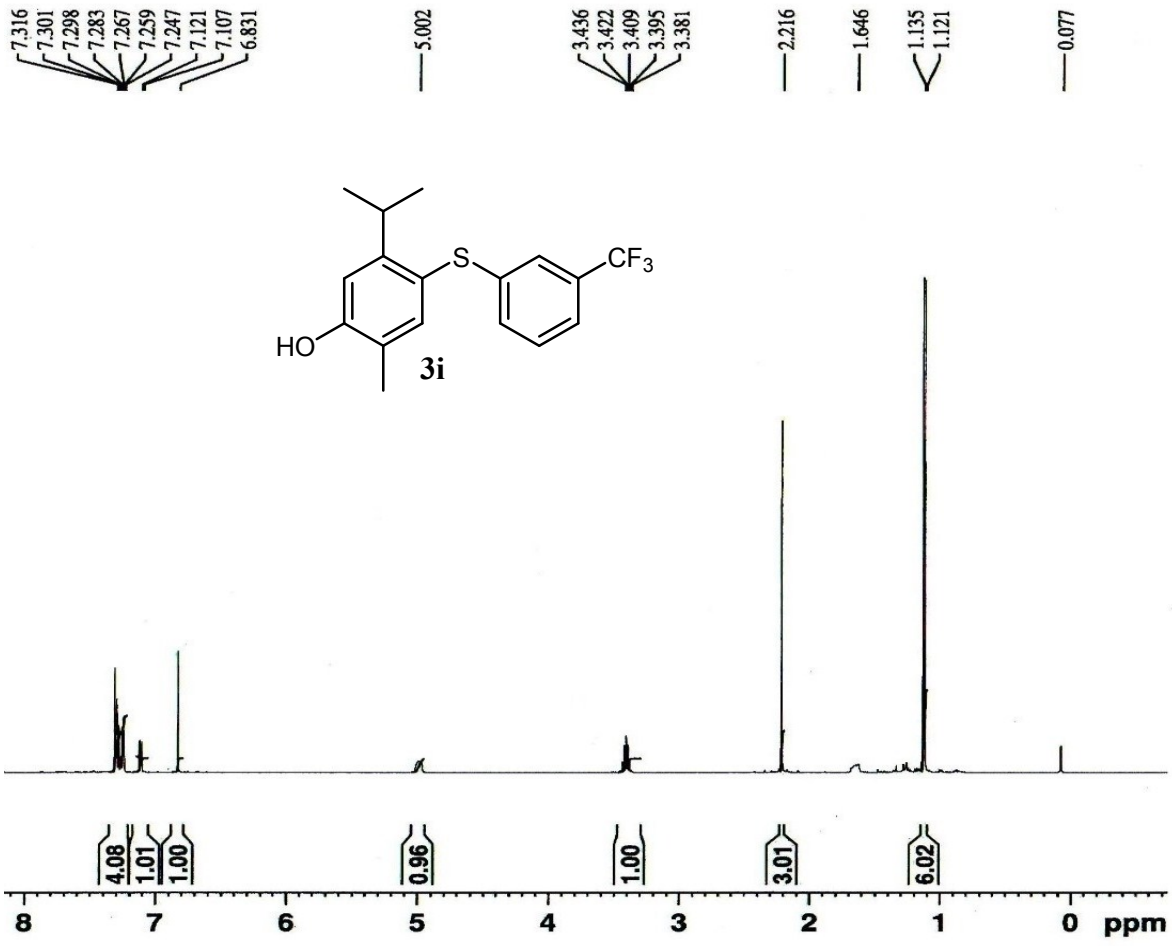
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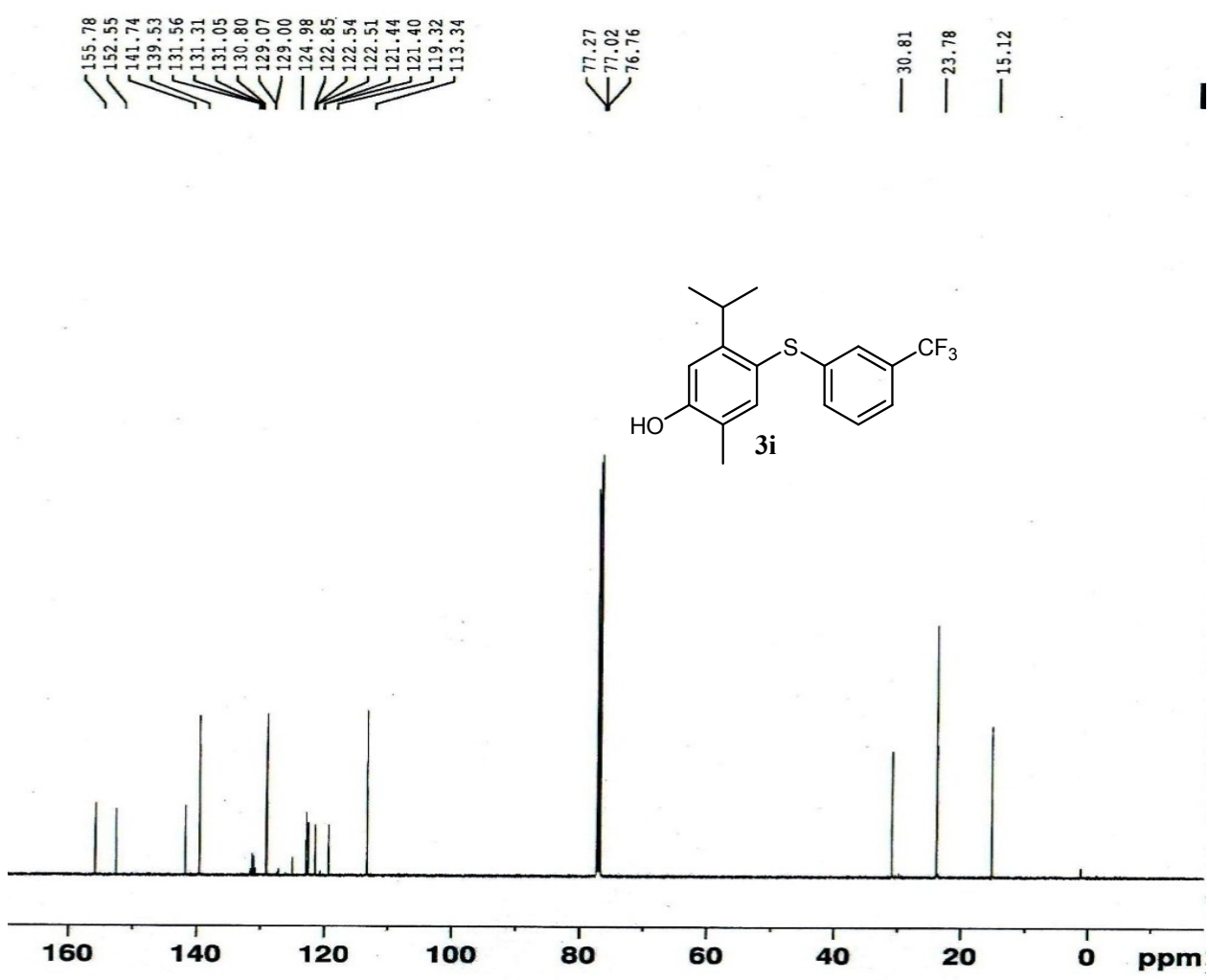
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23.78
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S
CF3
3i
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120
100
80
60
40
20
0
ppm


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NO2
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3.08
1.09
3.00
6.09
8
7
6
5
4
3
2
1
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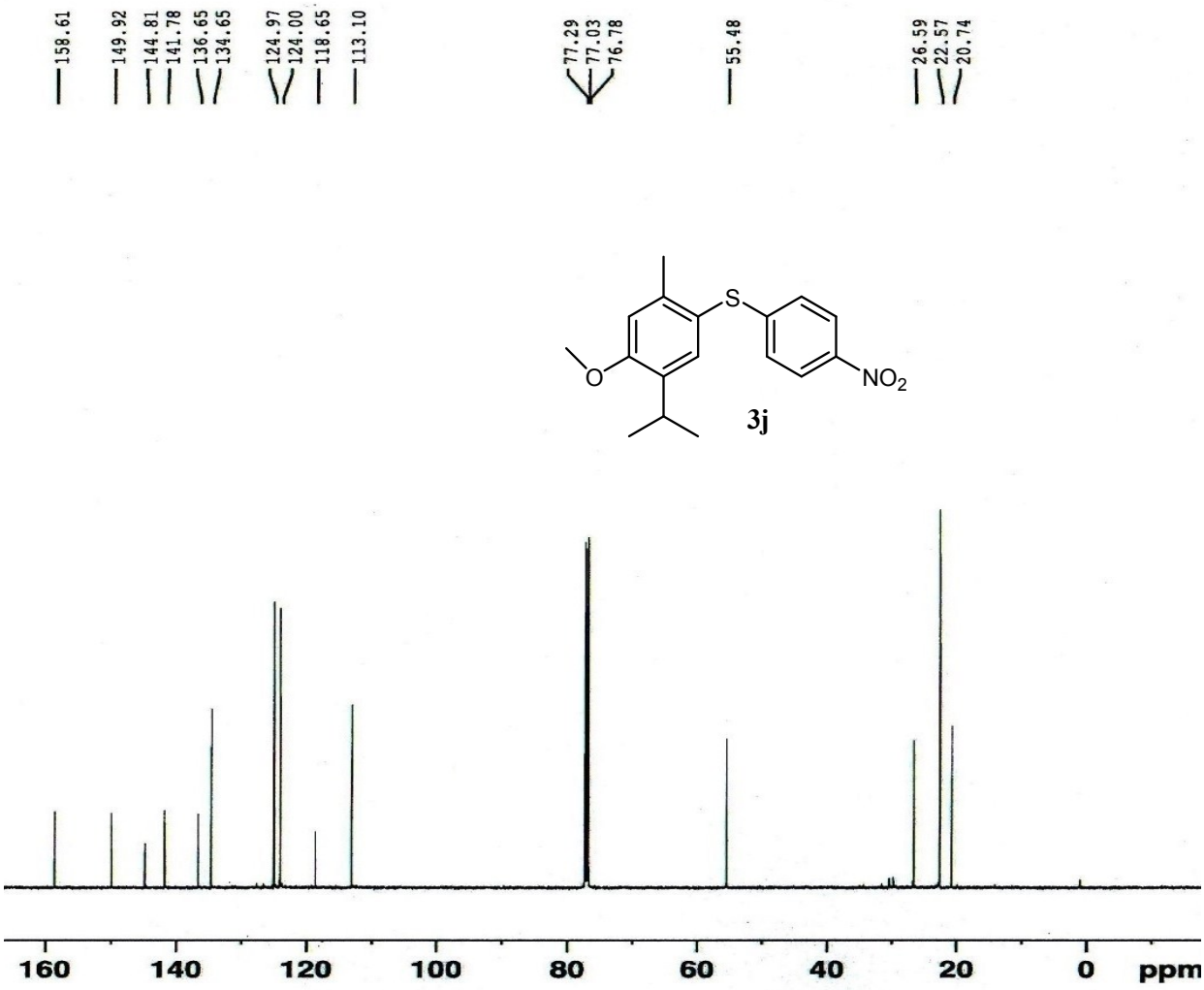
3j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76.78
55.48
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20.74
S
O
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80
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20
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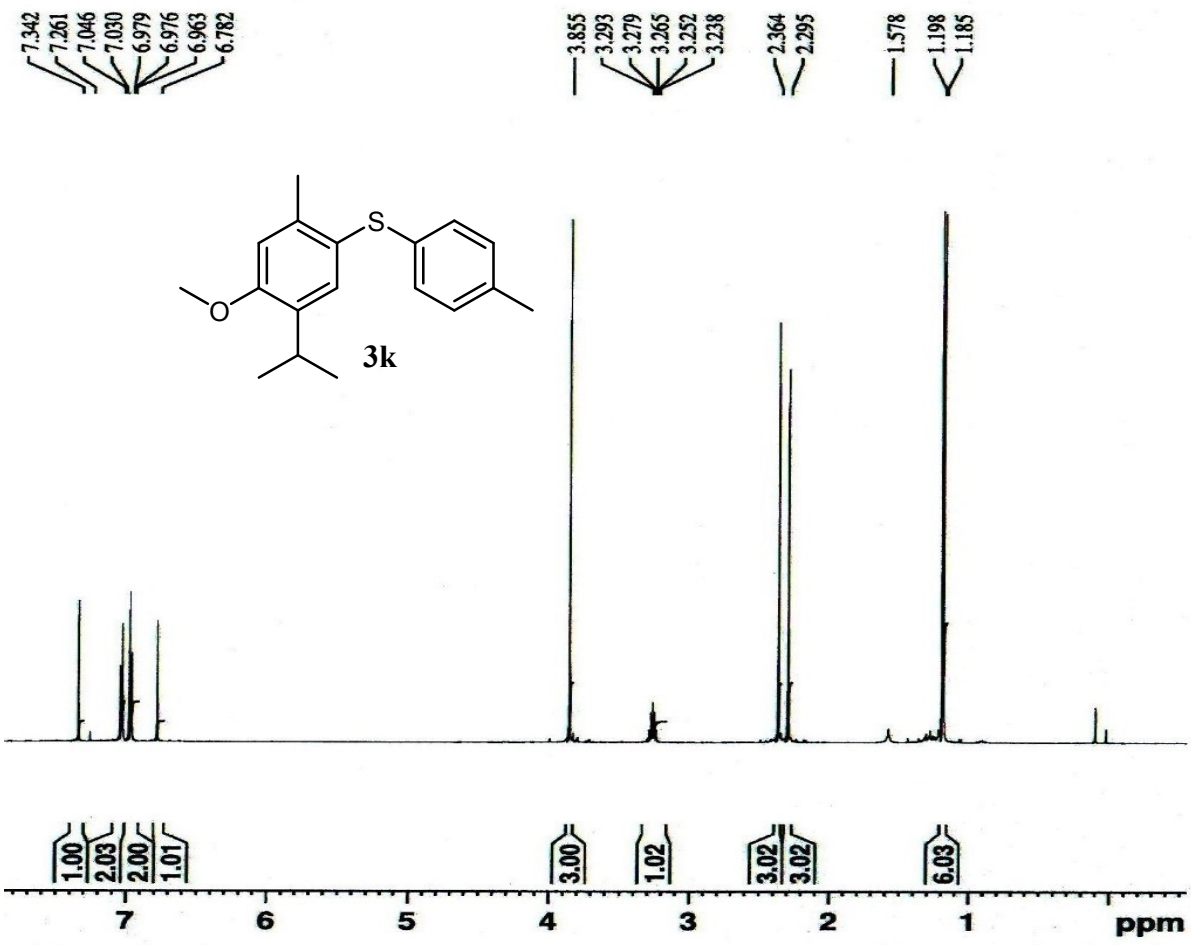
ppm

3j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3.252
3.238
2.364
2.295
1.578
1.198
1.185
S
O
3k
1.00
2.03
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3.00
1.02
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7
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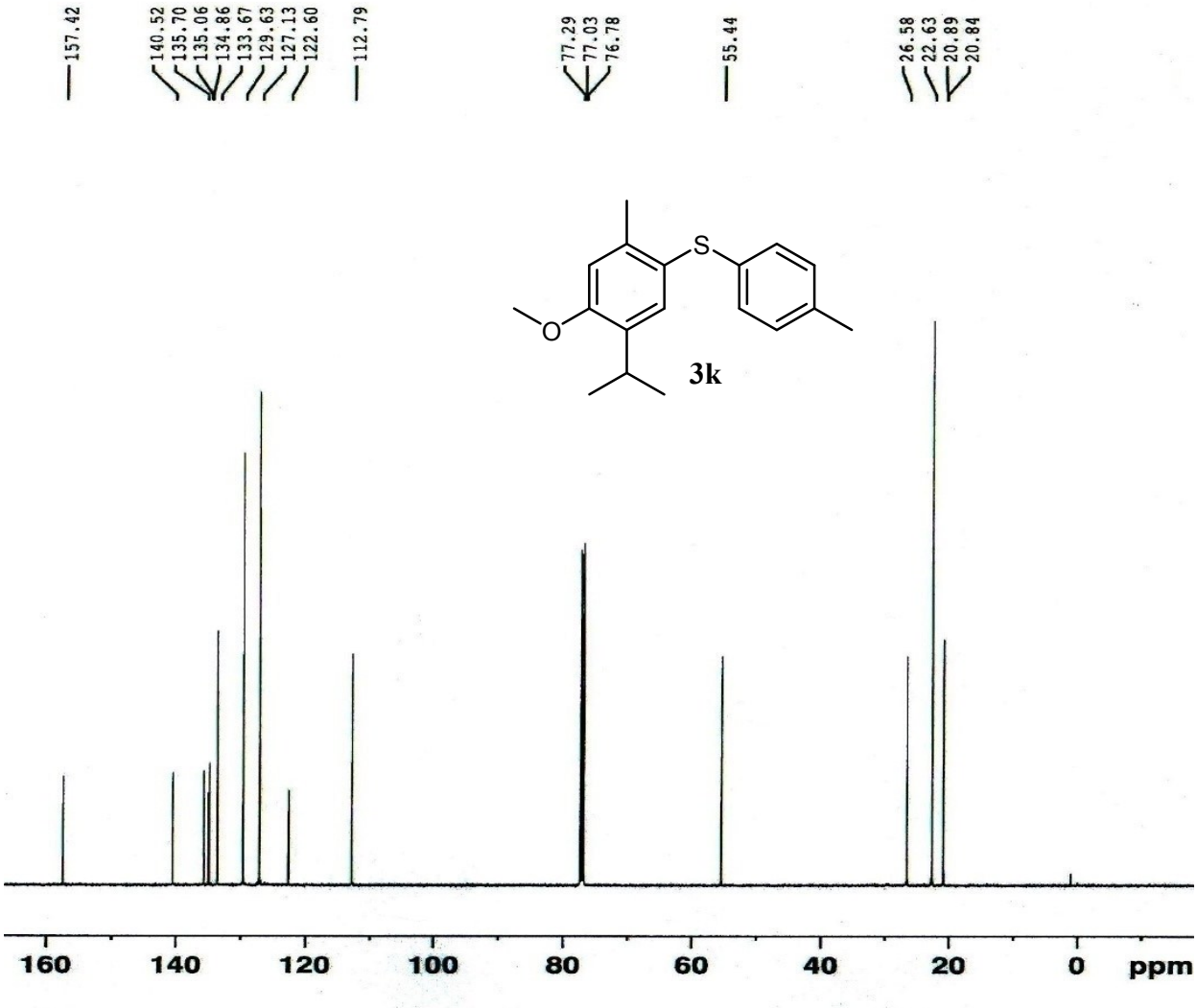
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127.13
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76.78
55.44
26.58
22.63
20.89
20.84
S
O
3k
160
140
120
100
80
60
40
20
0
ppm


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7.215
7.203
7.191
7.188
7.100
7.097
7.095
7.083
7.080
7.070
7.068
7.066
7.031
7.028
7.014
7.012
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3.288
3.274
3.260
3.247
3.233
2.353
1.565
1.193
1.179
S
O
1.04
2.03
1.03
2.00
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5
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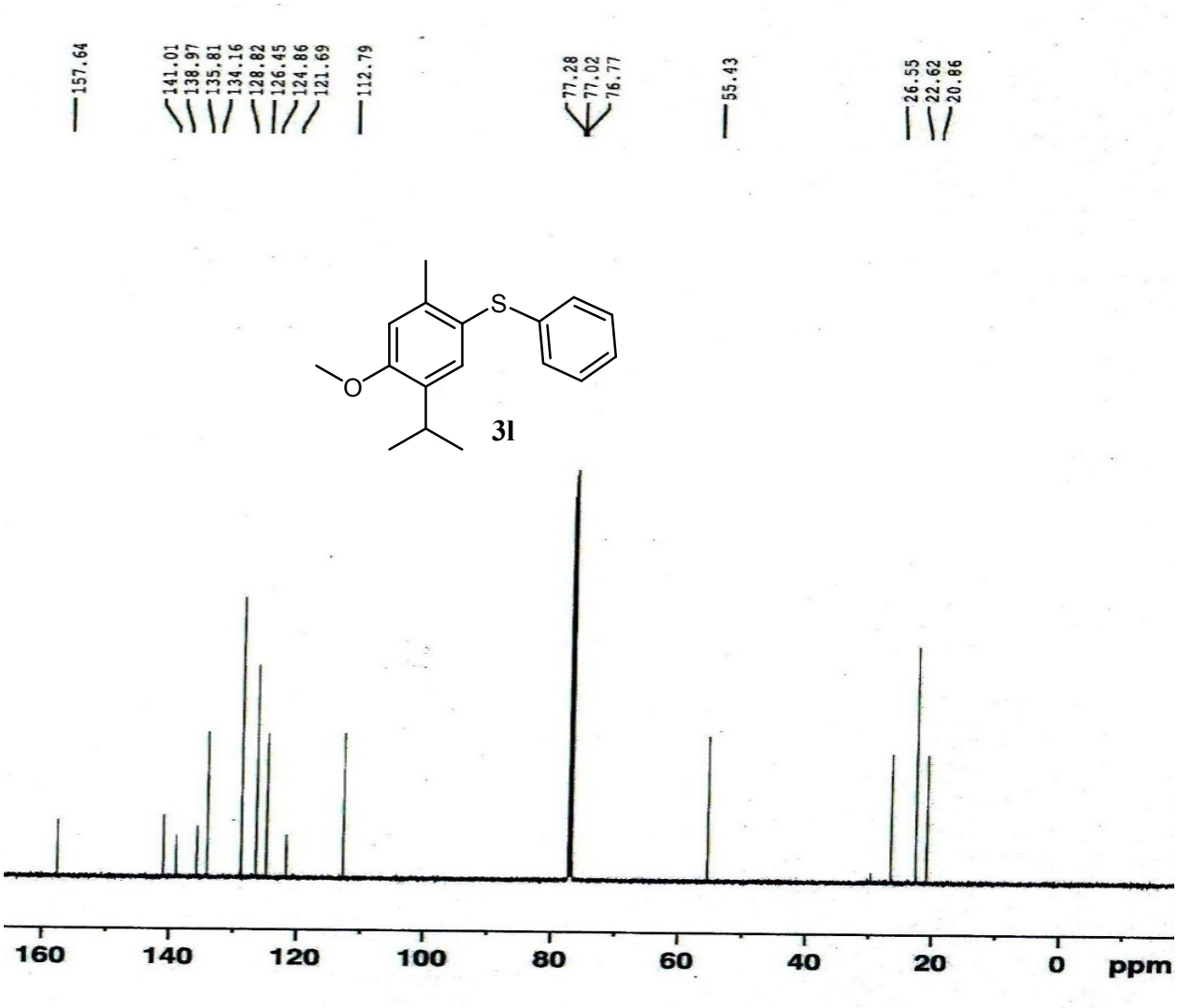
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77.28
77.02
76.77
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O
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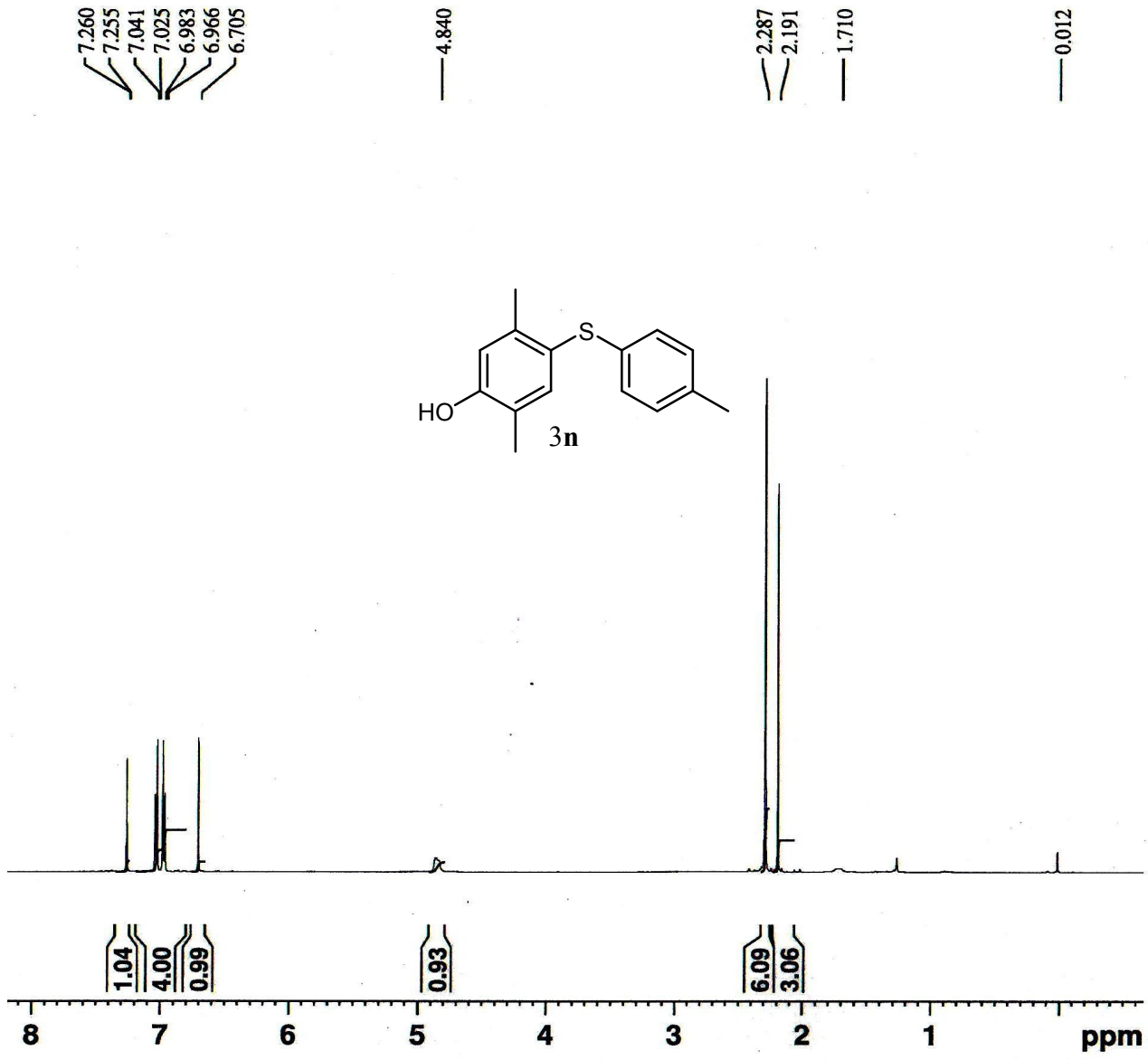
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4.840
2.287
2.191
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0.012
HO
S
3n
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0.99
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8
7
6
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3
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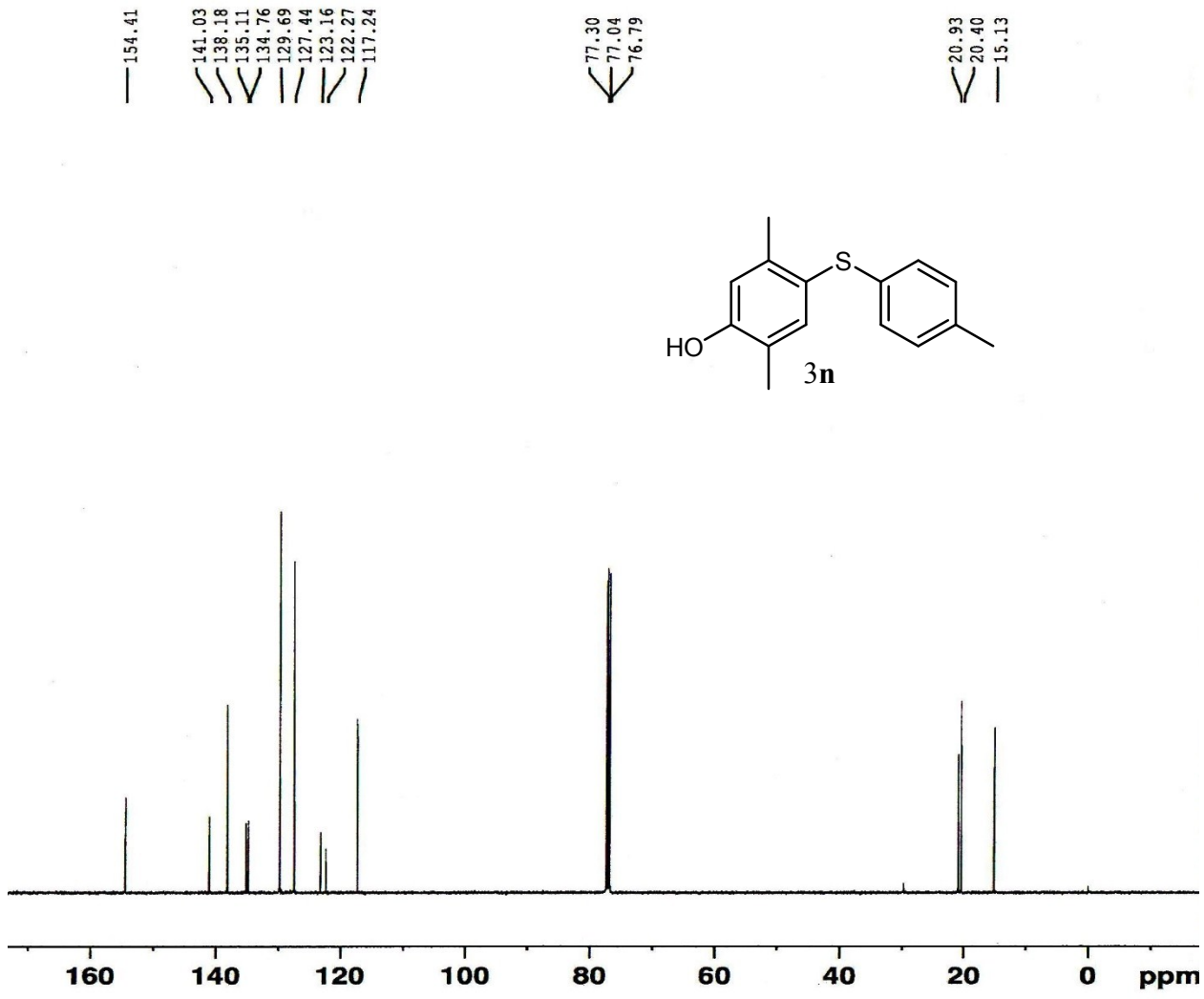
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127.44
123.16
122.27
117.24
77.30
77.04
76.79
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20.40
15.13
HO
S
3n
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120
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80
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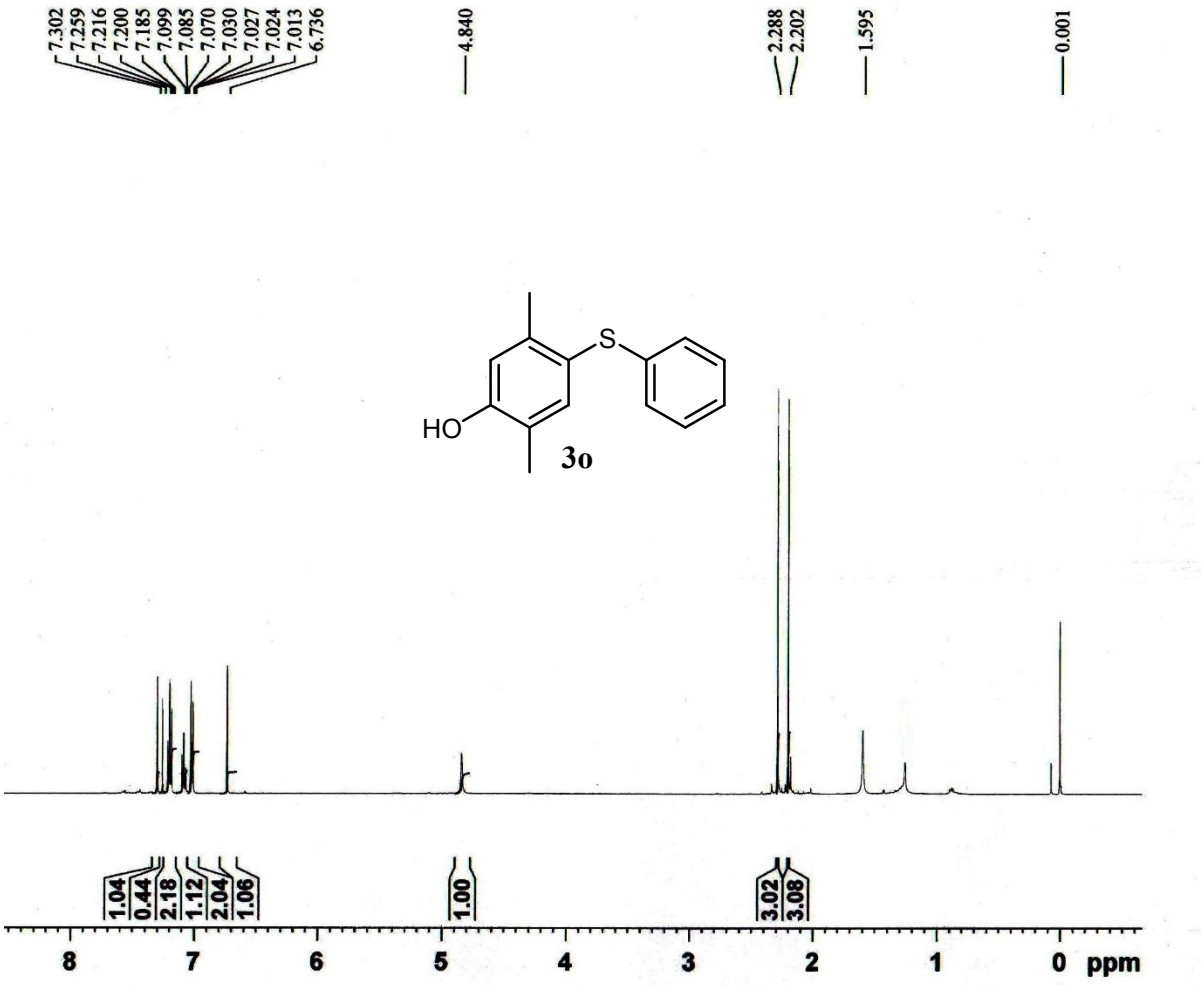
40
20
0
ppm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7.070
7.030
7.027
7.024
7.013
6.736
4.840
2.288
2.202
1.595
0.001
S
HO
3o
1.04
0.44
2.18
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2.04
1.06
1.00
3.02
3.08
8
7
6
5
4
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2
1
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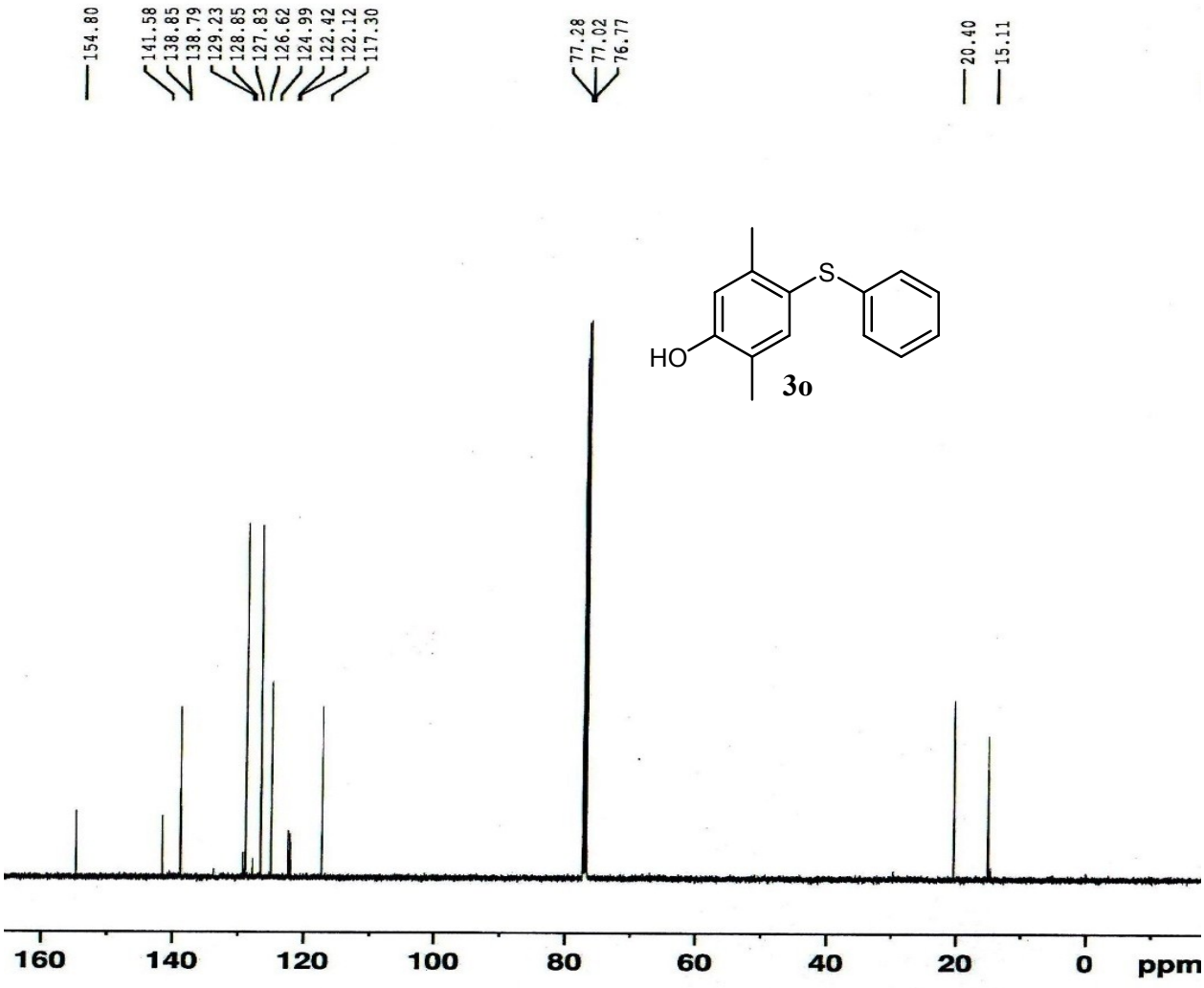
ppm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128.85
127.83
126.62
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122.42
122.12
117.30
77.28
77.02
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20.40
15.11
S
HO
3o
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120
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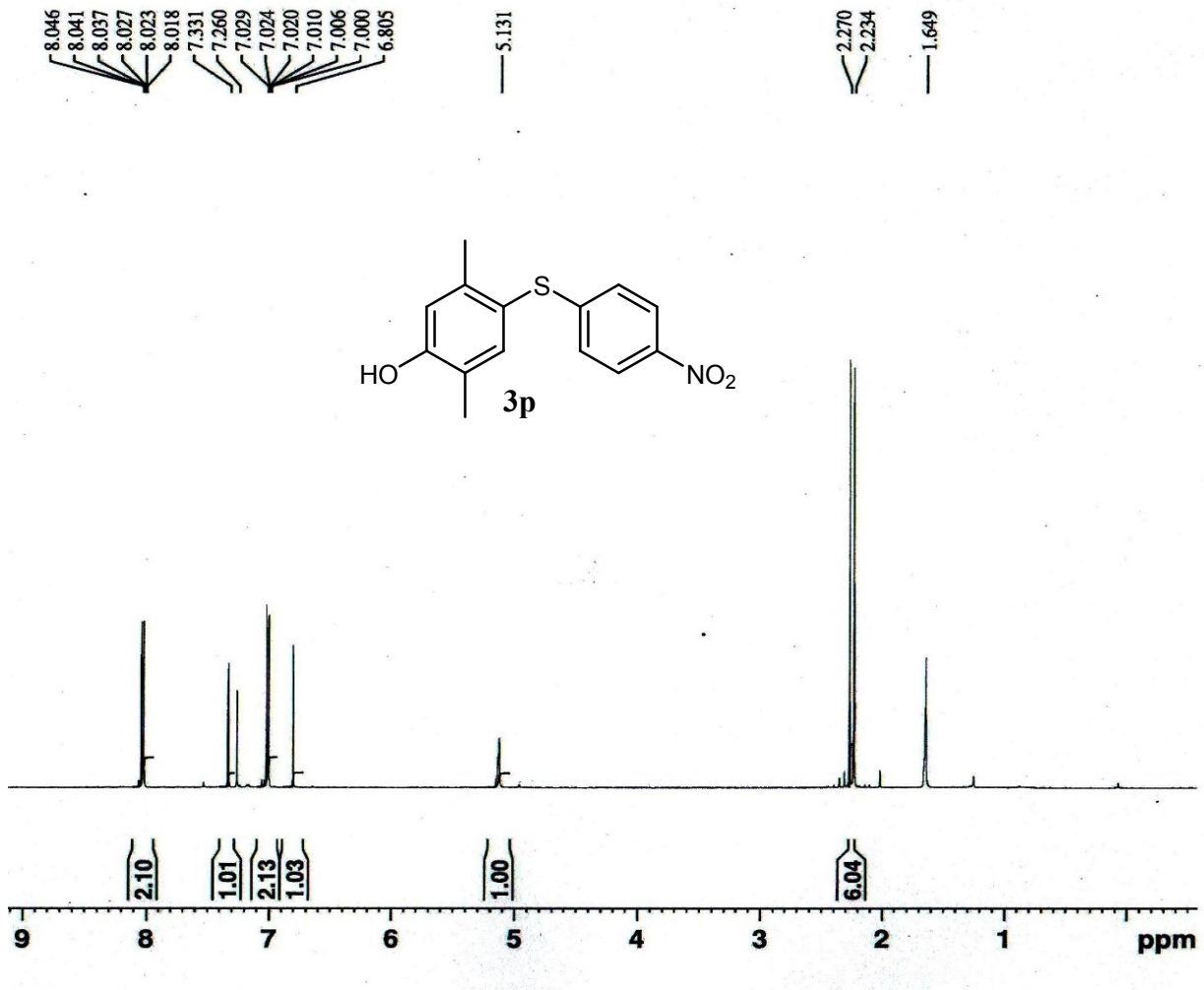
40
20
0
ppm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7.029
7.024
7.020
7.010
7.006
7.000
6.805
5.131
2.270
2.234
1.649
HO
S
NO2
3p
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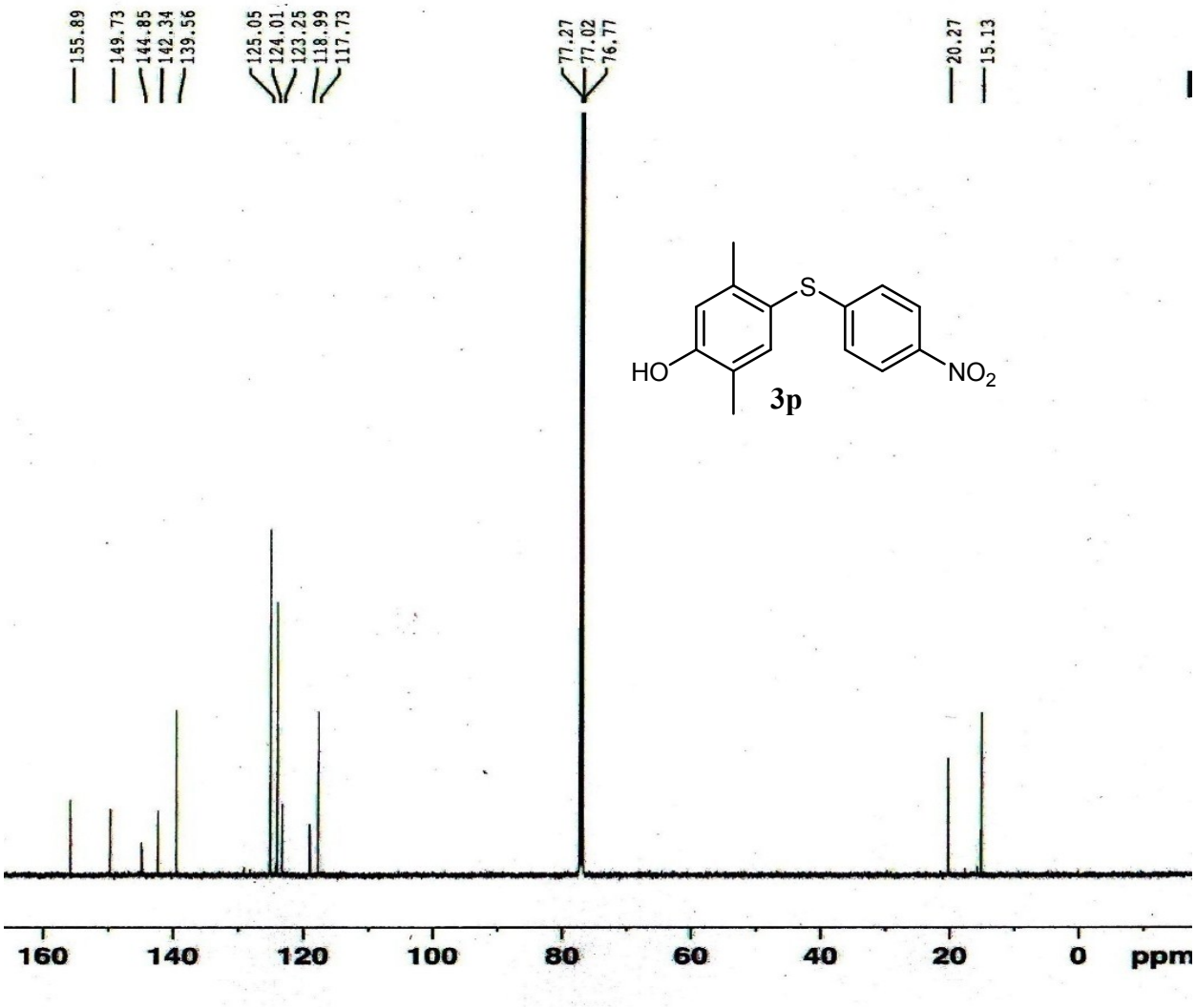
2.13
1.03
1.00
6.04
9
8
7
6
5
4
3
2
1
ppm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123.25
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77.27
77.02
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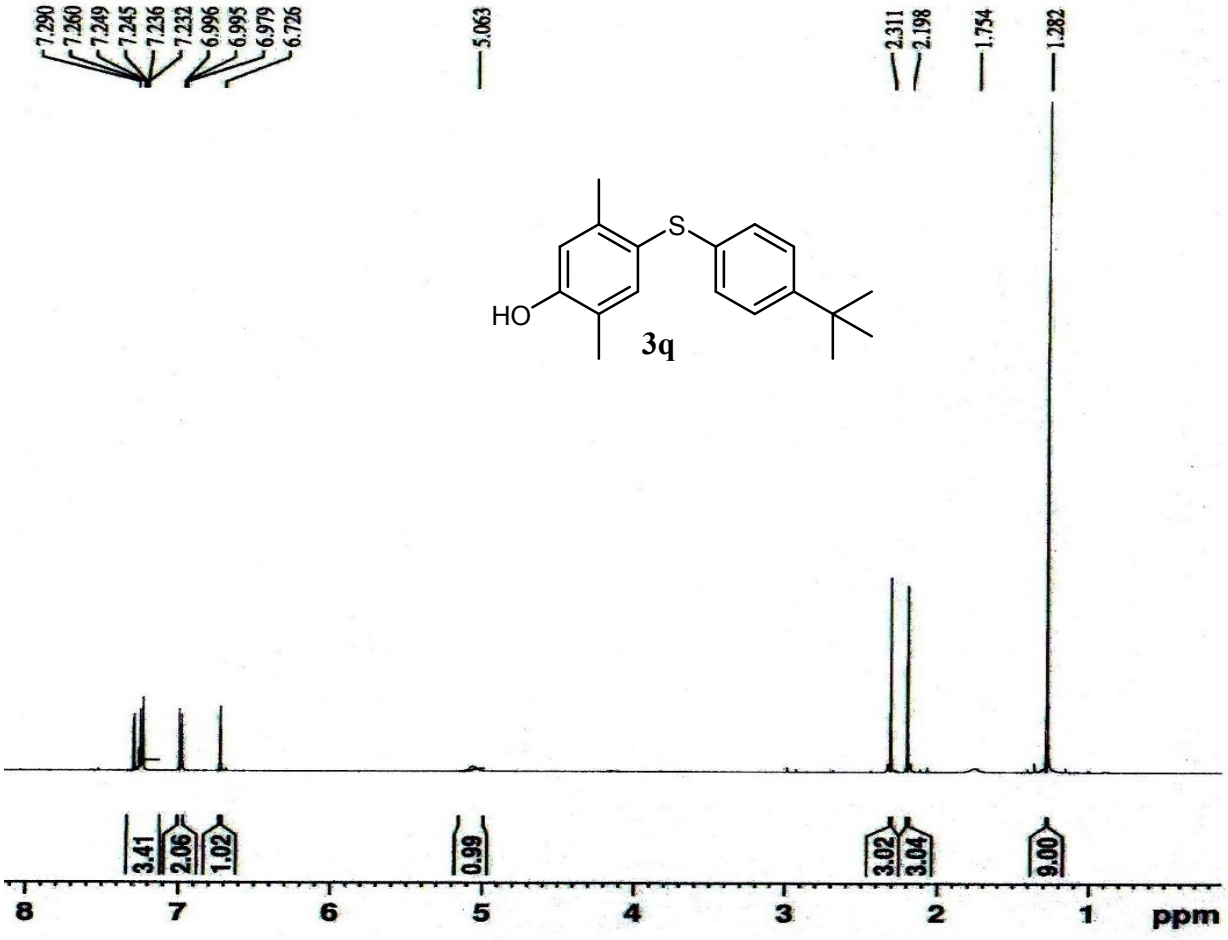
20.27
15.13
HO
S
NO2
3p
160
140
120
100
80
60
40
20
0
ppm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7.232
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6.995
6.979
6.726
5.063
2.311
2.198
1.754
1.282
HO
S
3q
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1.02
0.99
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3.04
9.00
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7
6
5
4
3
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1
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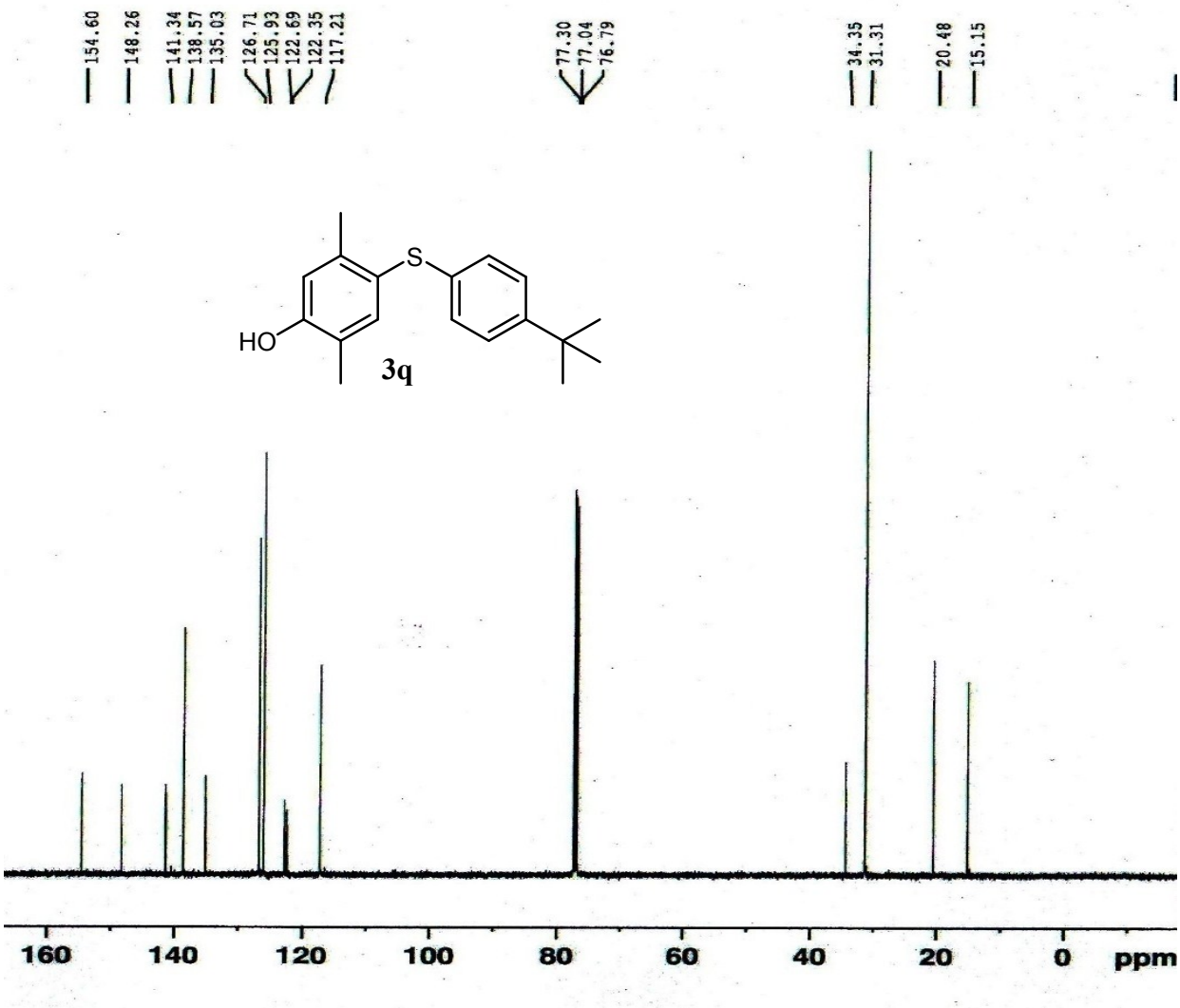
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122.69
122.35
117.21
77.30
77.04
76.79
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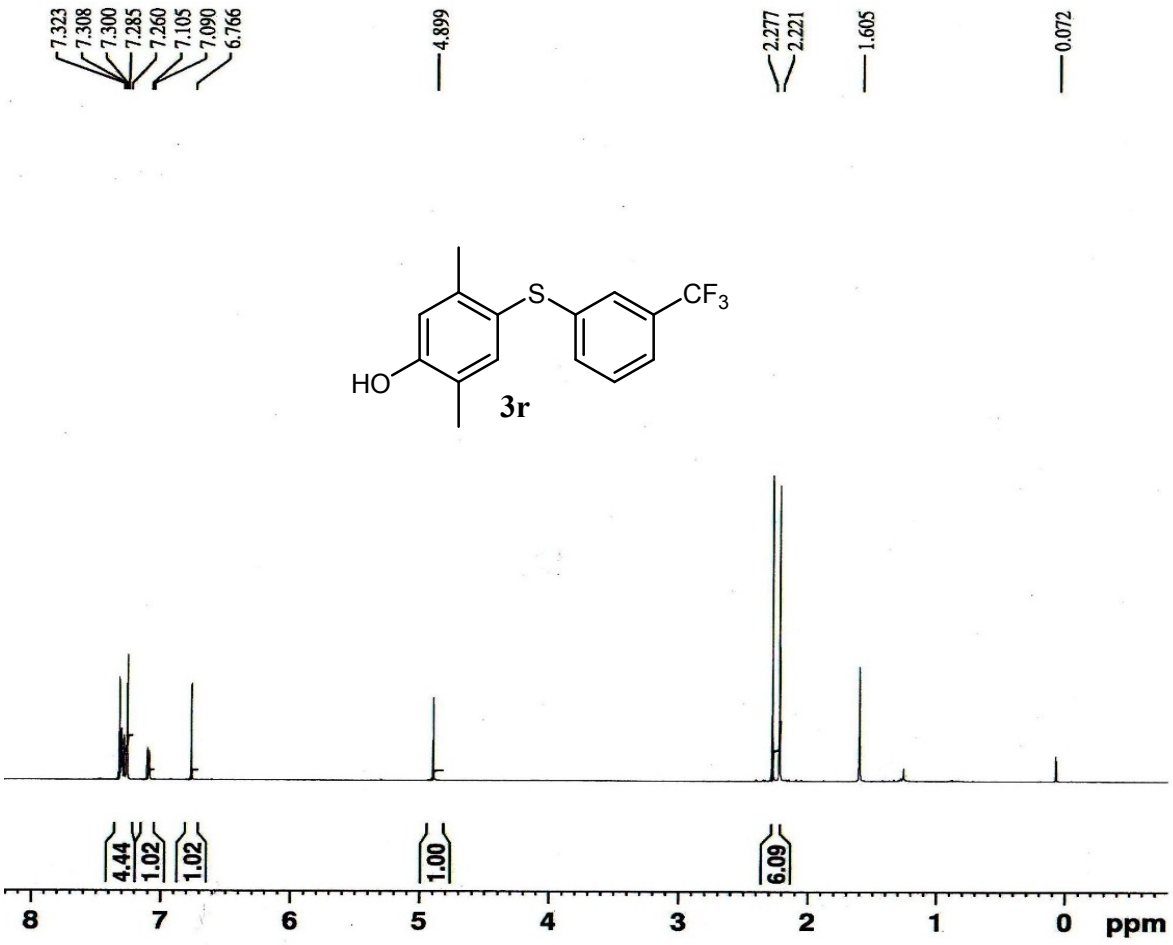
15.15
HO
S
160
140
120
100
80
60
40
20
0
ppm

3q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1.605
0.072
S
CF3
HO
3r
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1.02
1.02
1.00
6.09
8
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6
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4
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2
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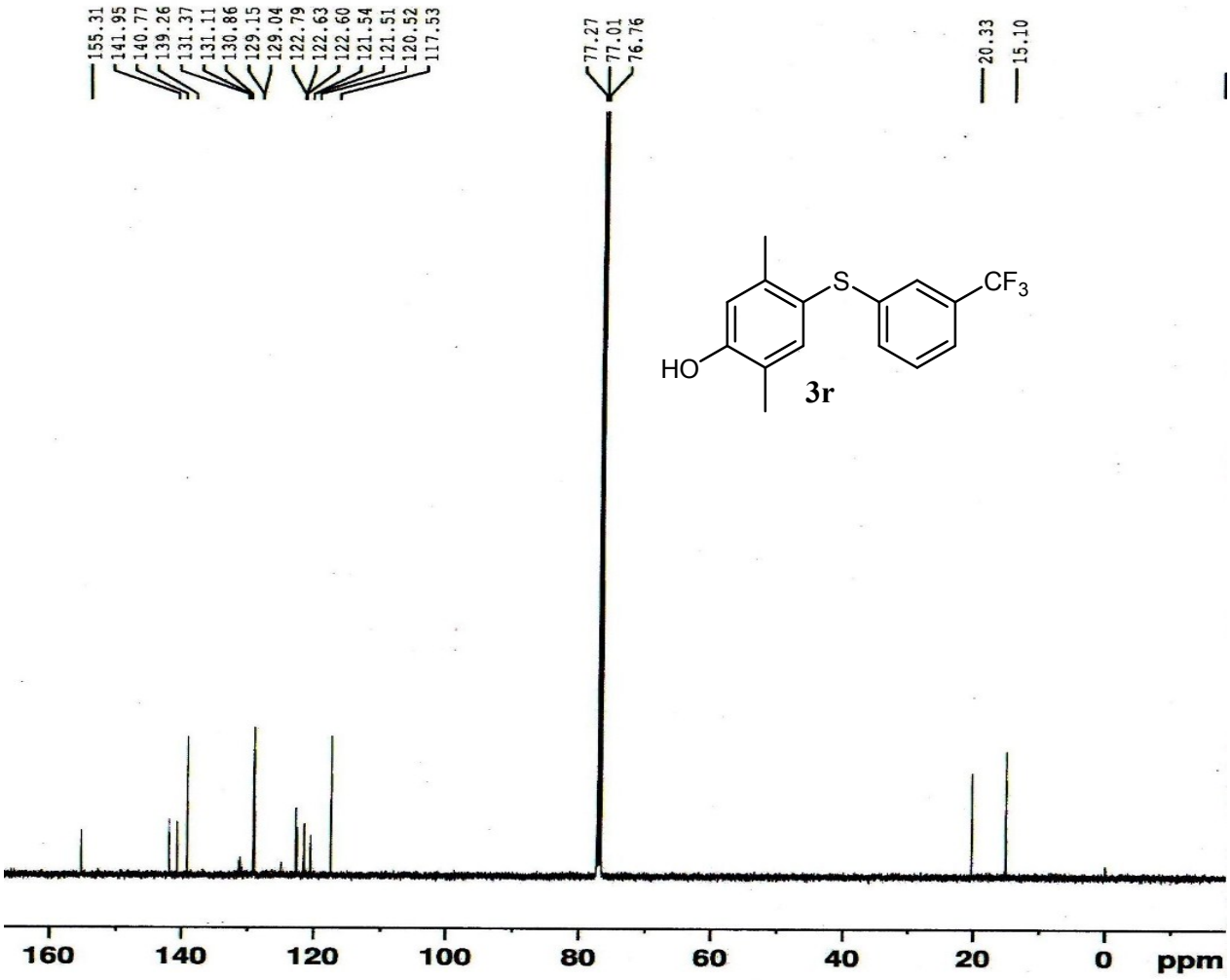
0
ppm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122.63
122.60
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117.53
77.27
77.01
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S
CF3
HO
3r
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120
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40
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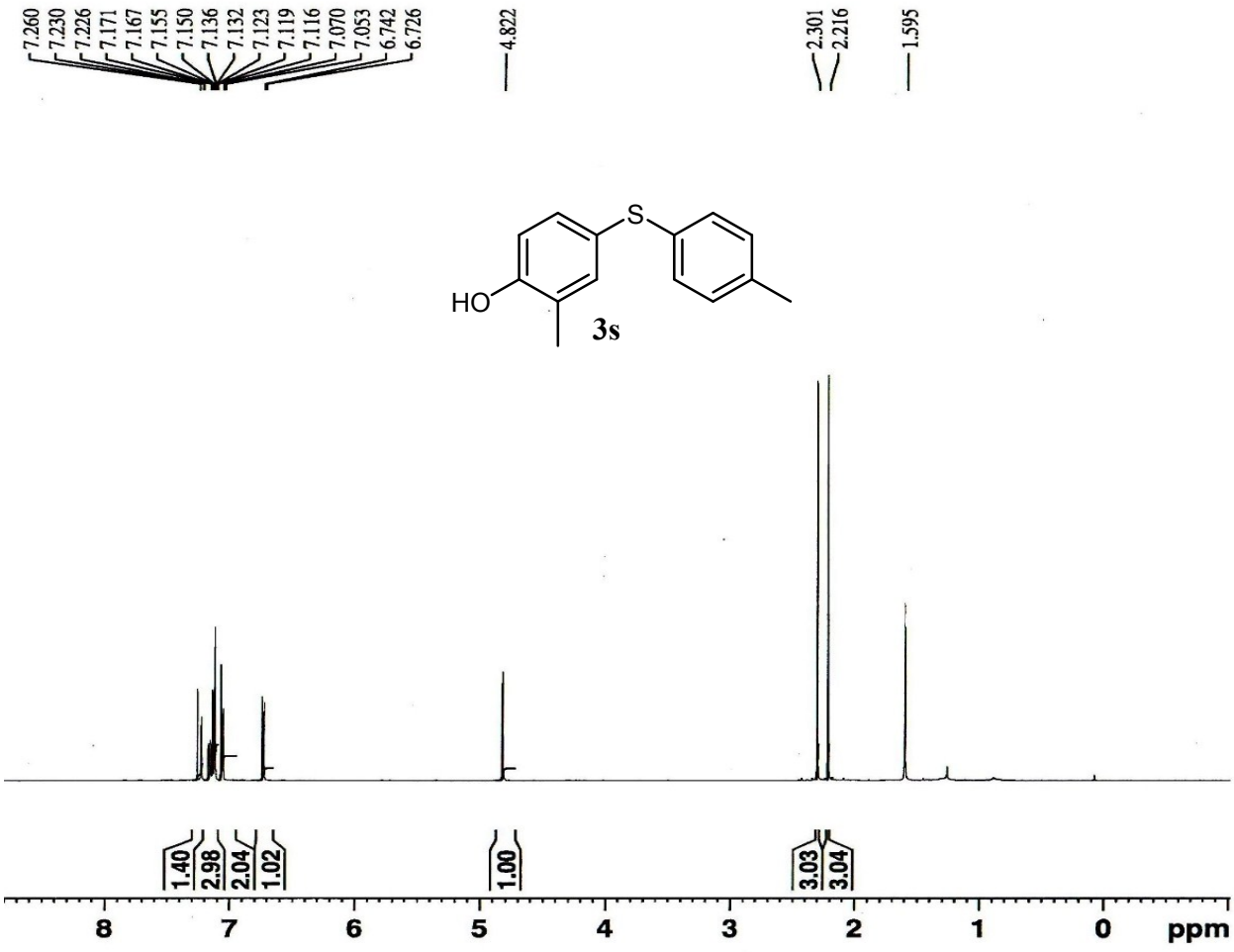
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7.132
7.123
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7.116
7.070
7.053
6.742
6.726
4.822
2.301
2.216
1.595
HO
S
3s
1.40
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1.00
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6
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2
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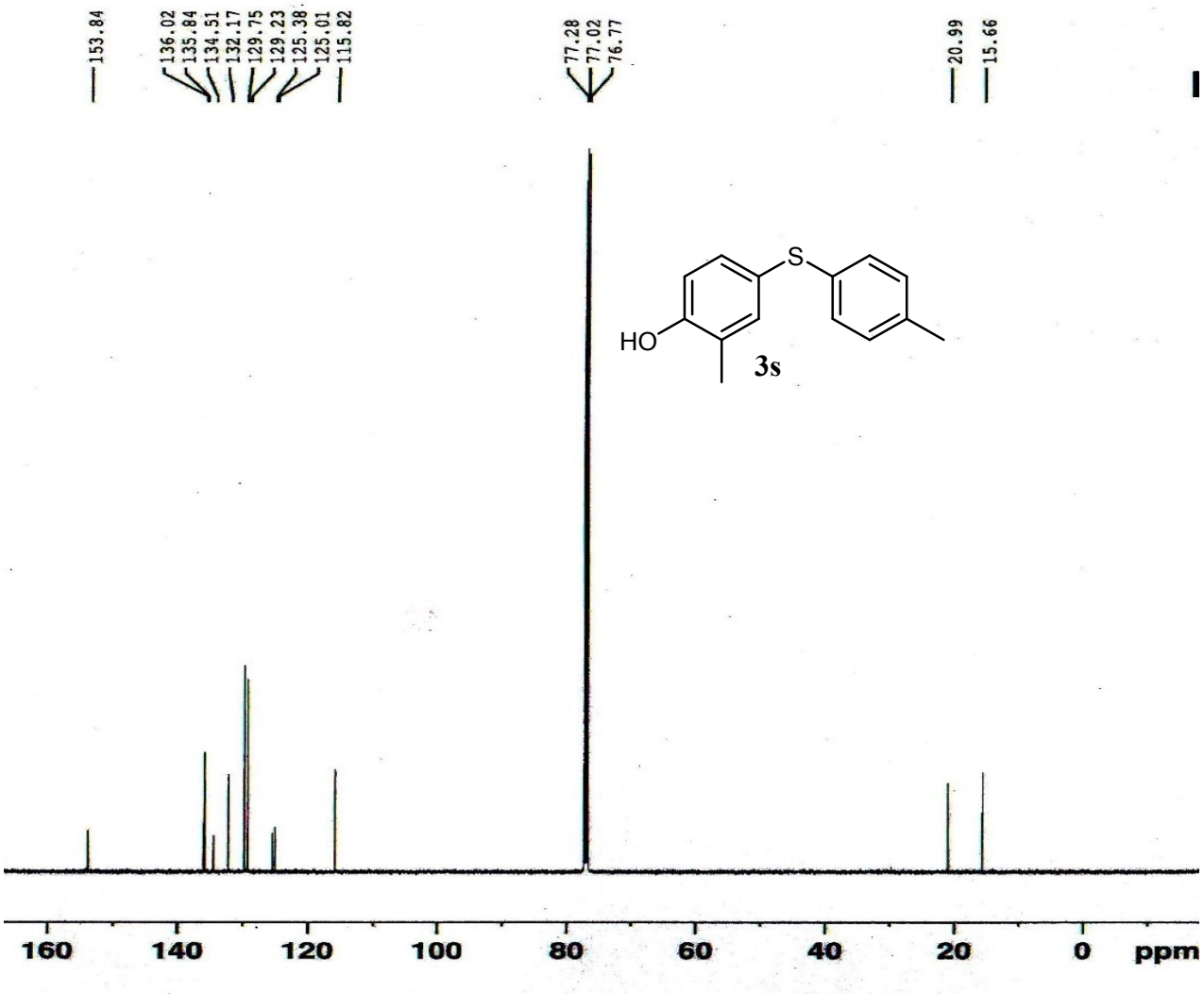
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125.38
125.01
115.82
77.28
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15.66
HO
S
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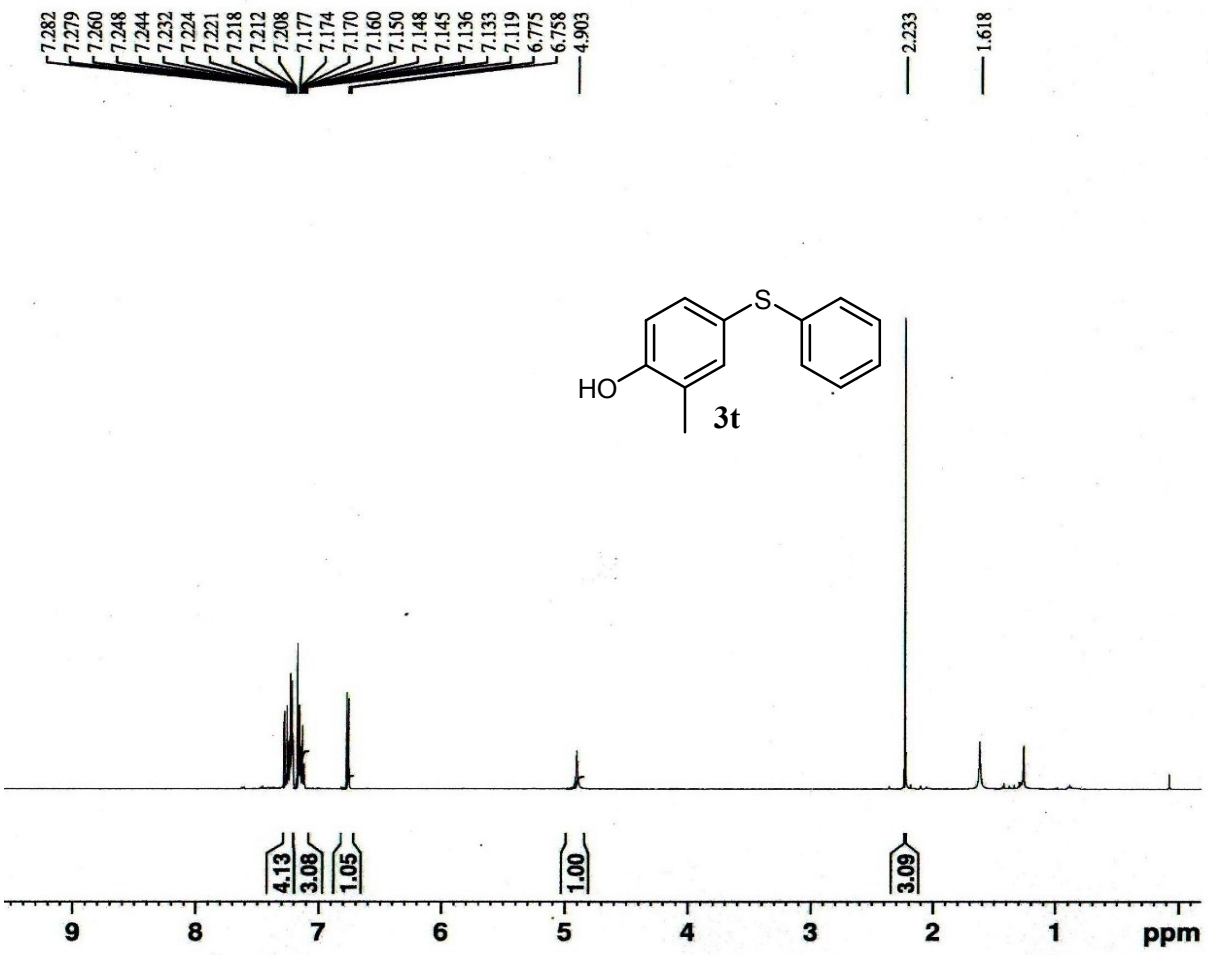
120
100
80
60
40
20
0
ppm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7.174
7.170
7.160
7.150
7.148
7.145
7.136
7.133
7.119
6.775
6.758
4.903
2.233
1.618
HO
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1.05
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7
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3
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1
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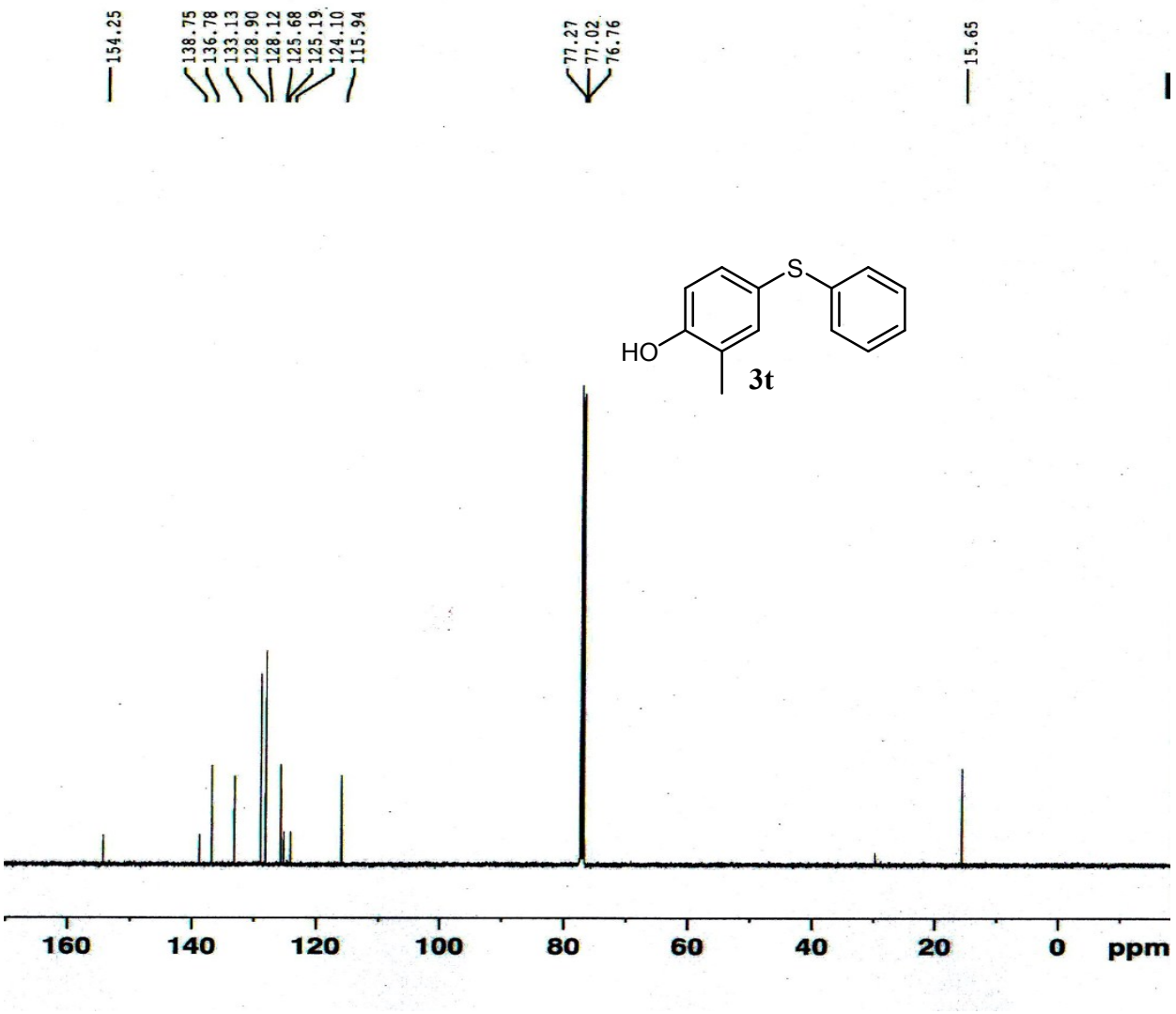
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125.19
124.10
115.94
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15.65
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120
100
80
60
40
20
0
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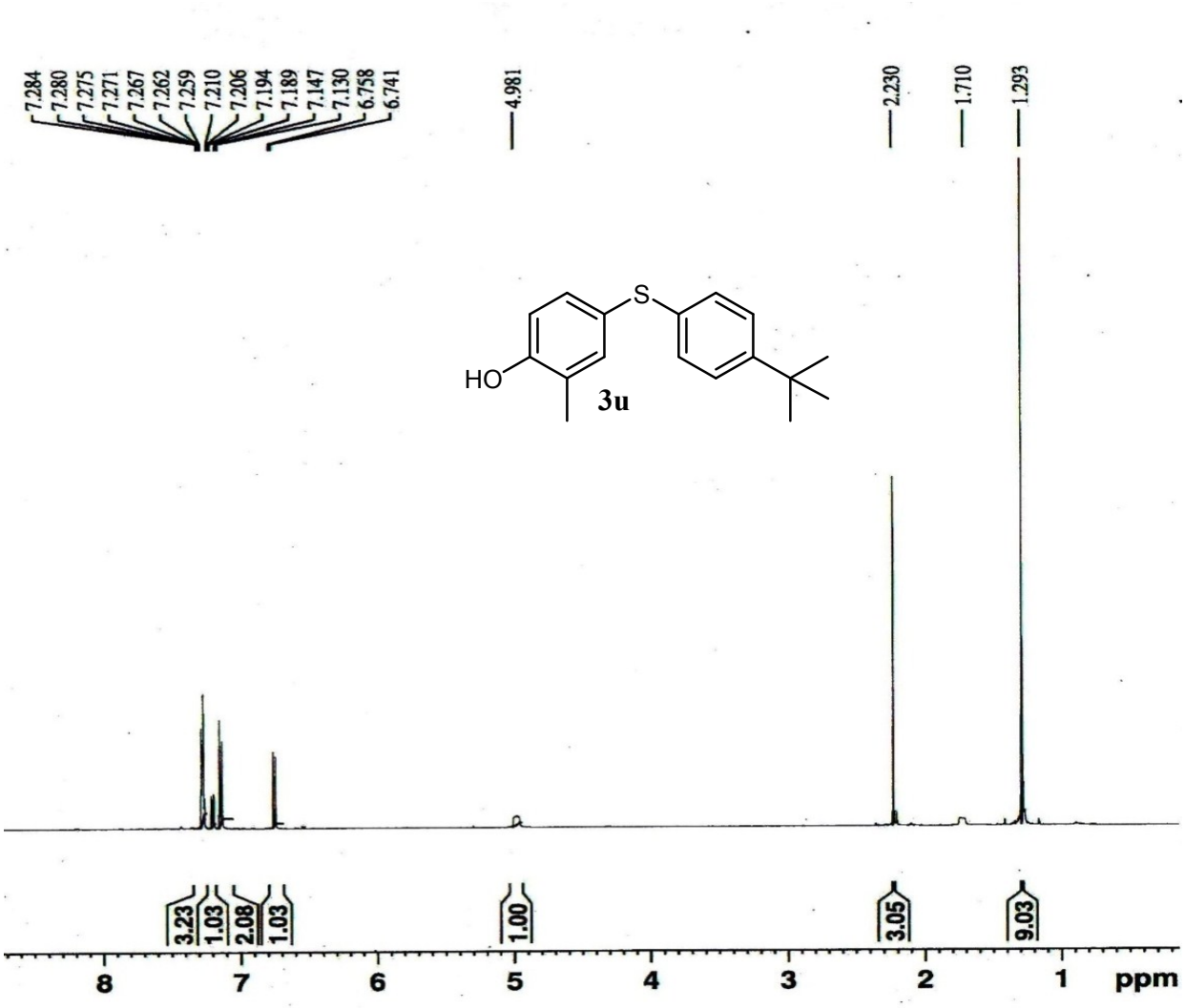
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7.147
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6.758
6.741
4.981
2.230
1.710
1.293
HO
S
3u
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1.00
3.05
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7
6
5
4
3
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1
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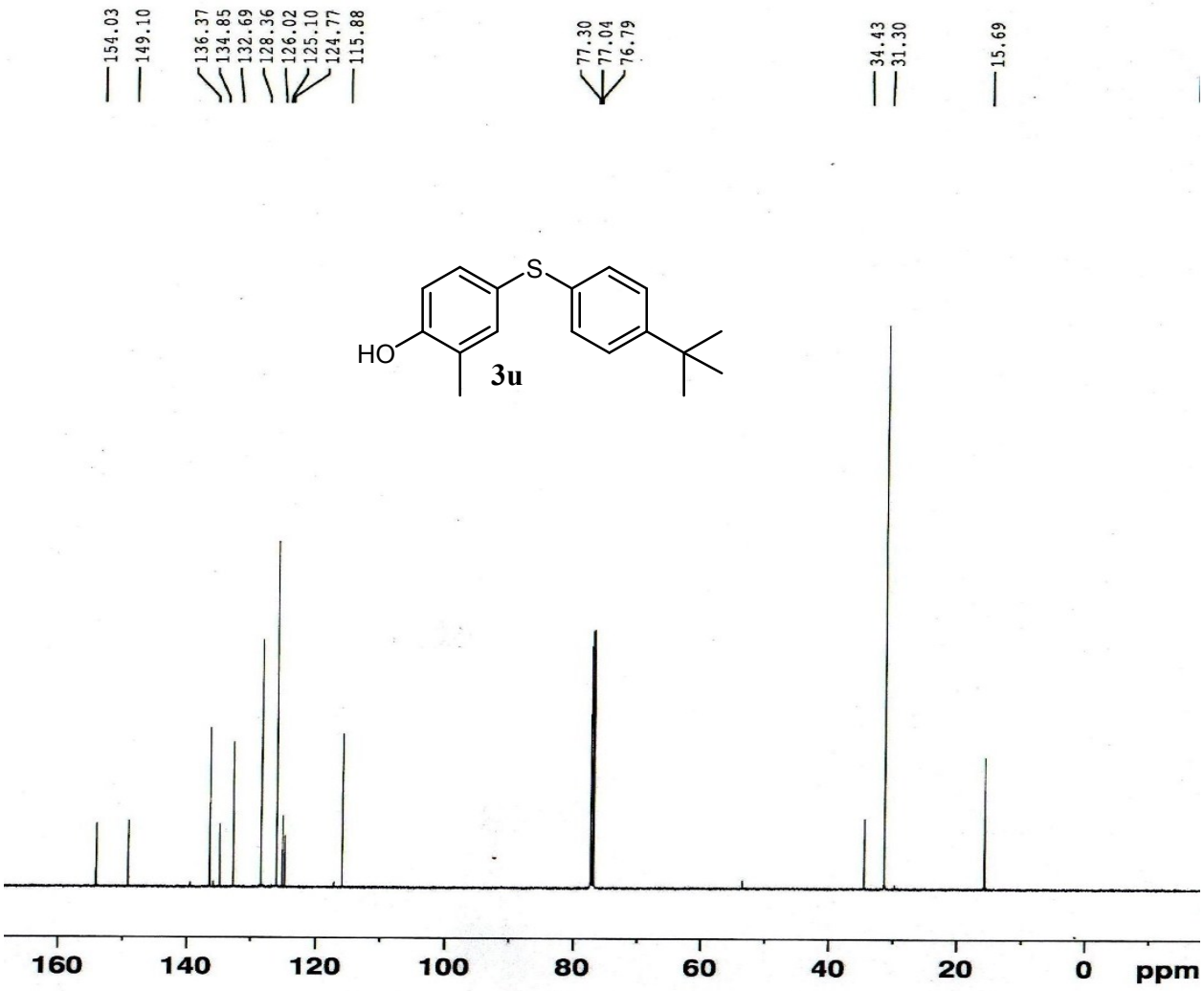
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128.36
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125.10
124.77
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77.04
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15.69
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S
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120
100
80
60
40
20
0
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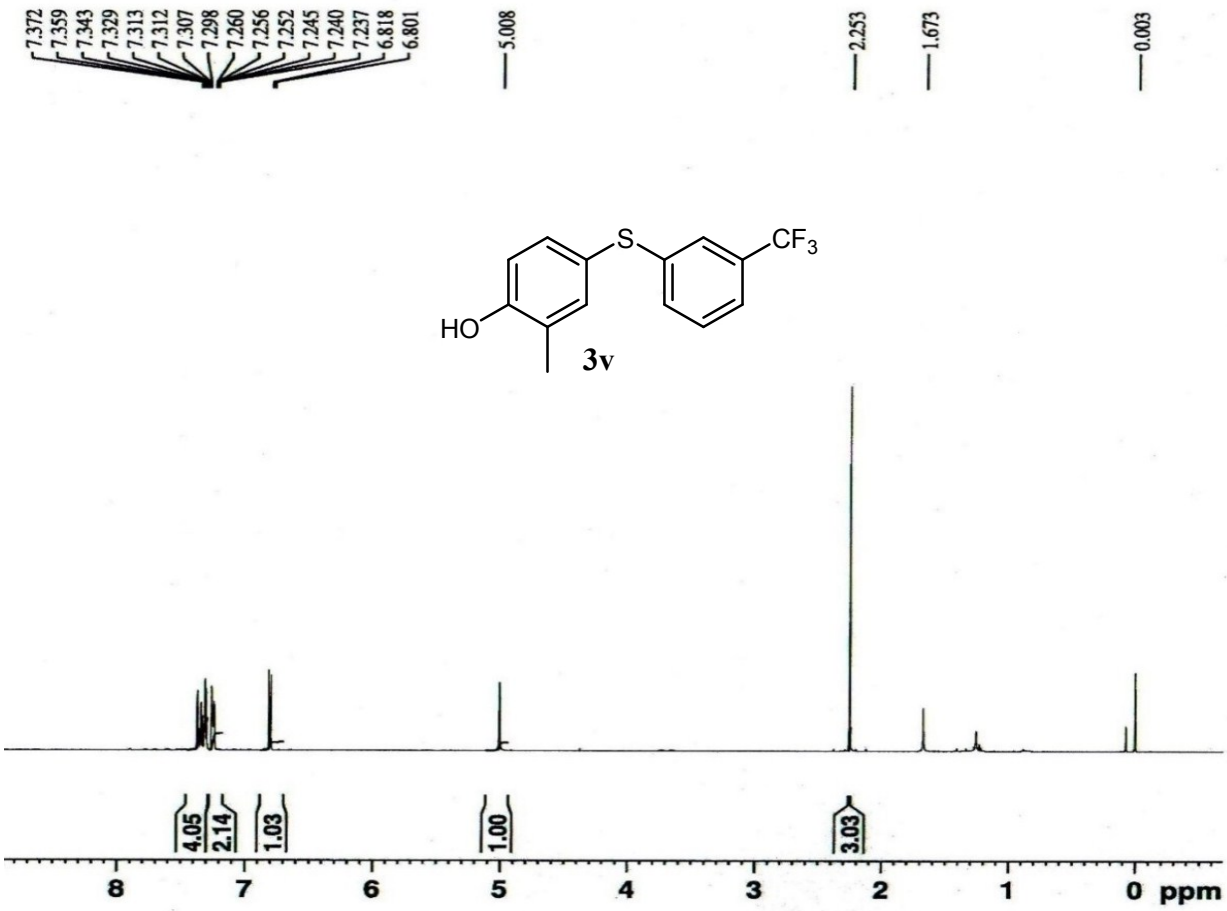
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7.245
7.240
7.237
6.818
6.801
5.008
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S
CF3
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7
6
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3
2
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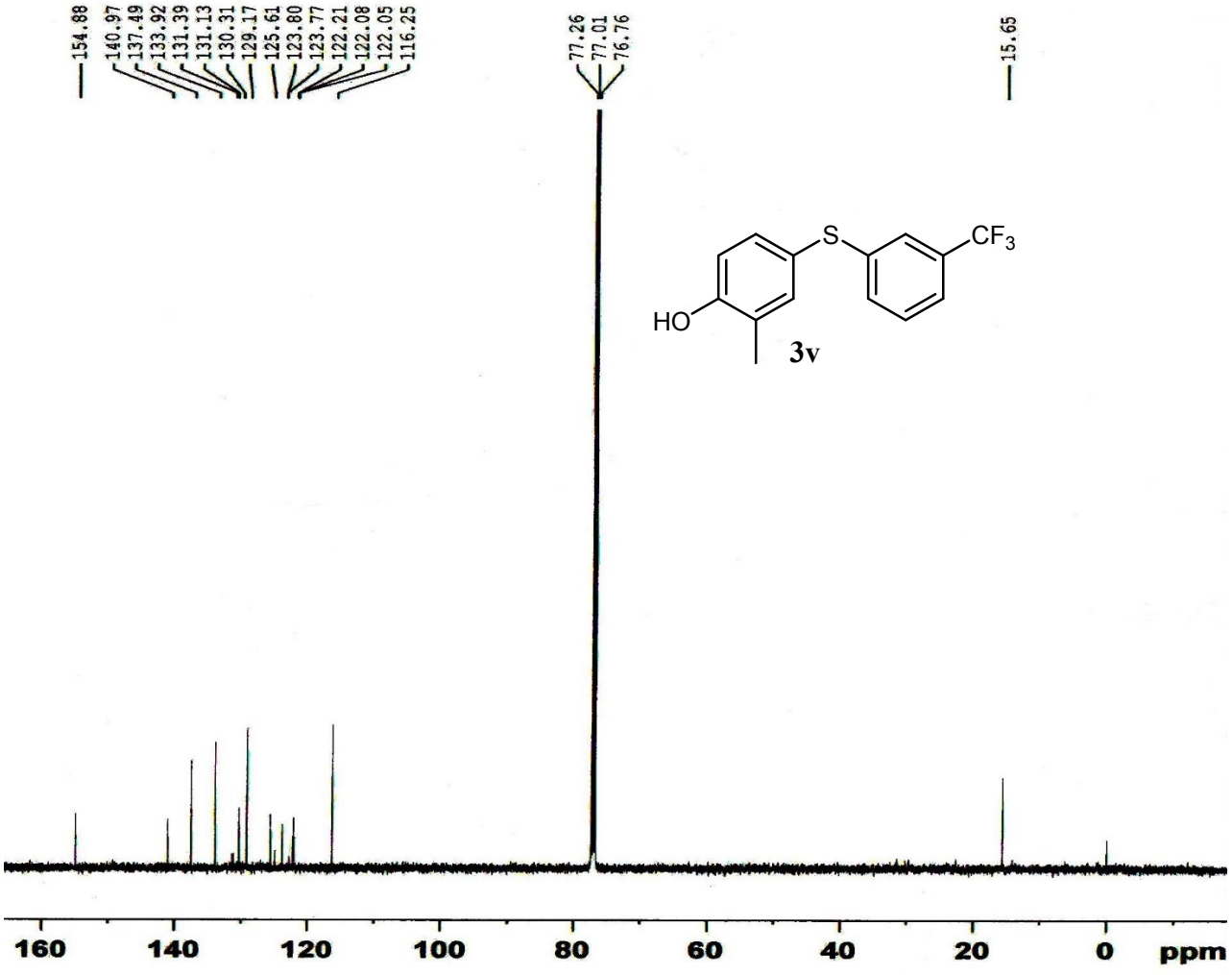
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122.21
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122.05
116.25
77.26
77.01
76.76
15.65
S
CF3
HO
3v
160
140
120
100
80
60
40
20
0
ppm


7.337
7.321
7.259
7.051
7.035
7.006
7.002
6.998
6.989
6.985
6.774
6.769
6.672
6.666
6.655
6.650
5.046
2.328
2.290
1.726
0.083
HO
S
3w
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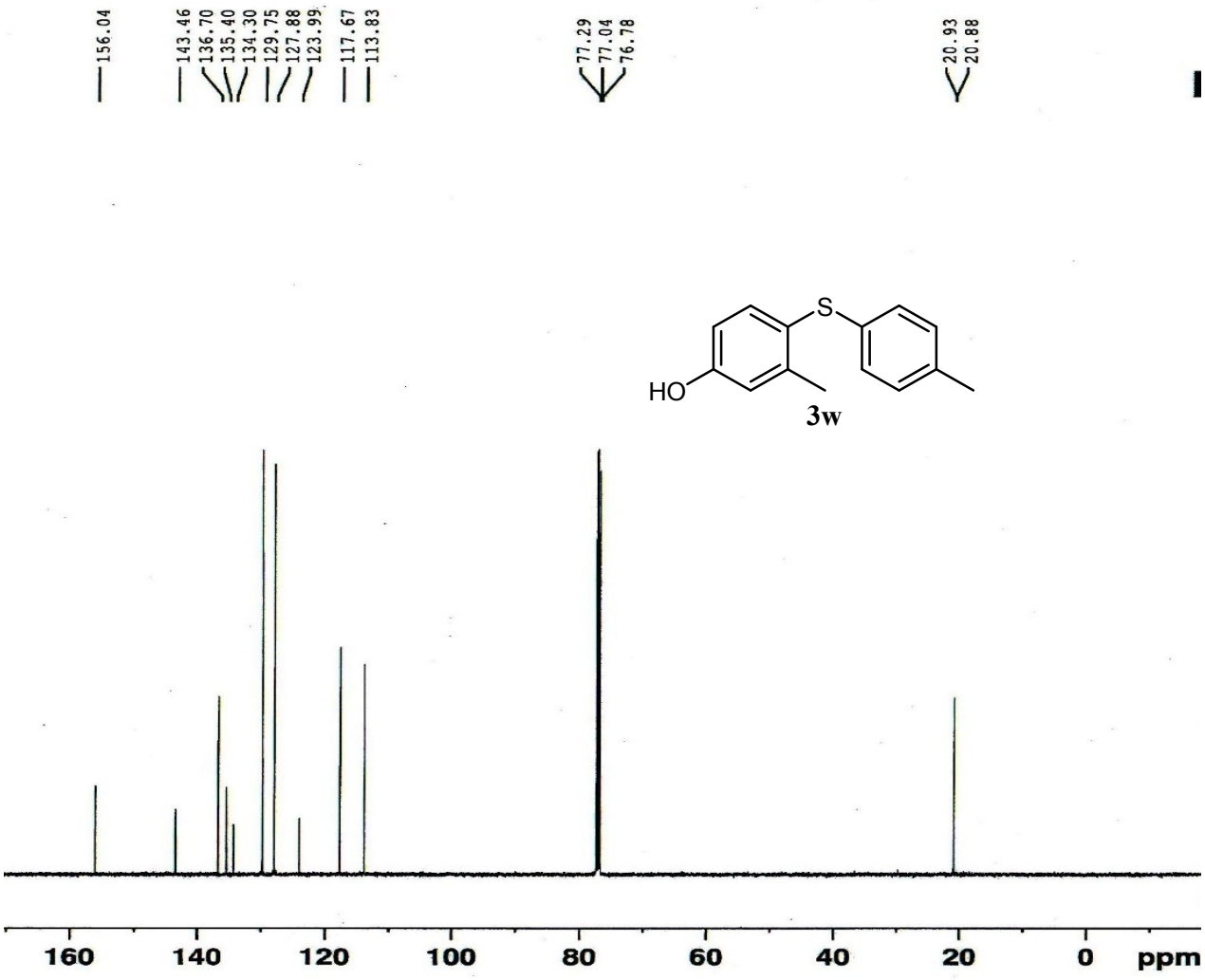
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20.88
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100
80
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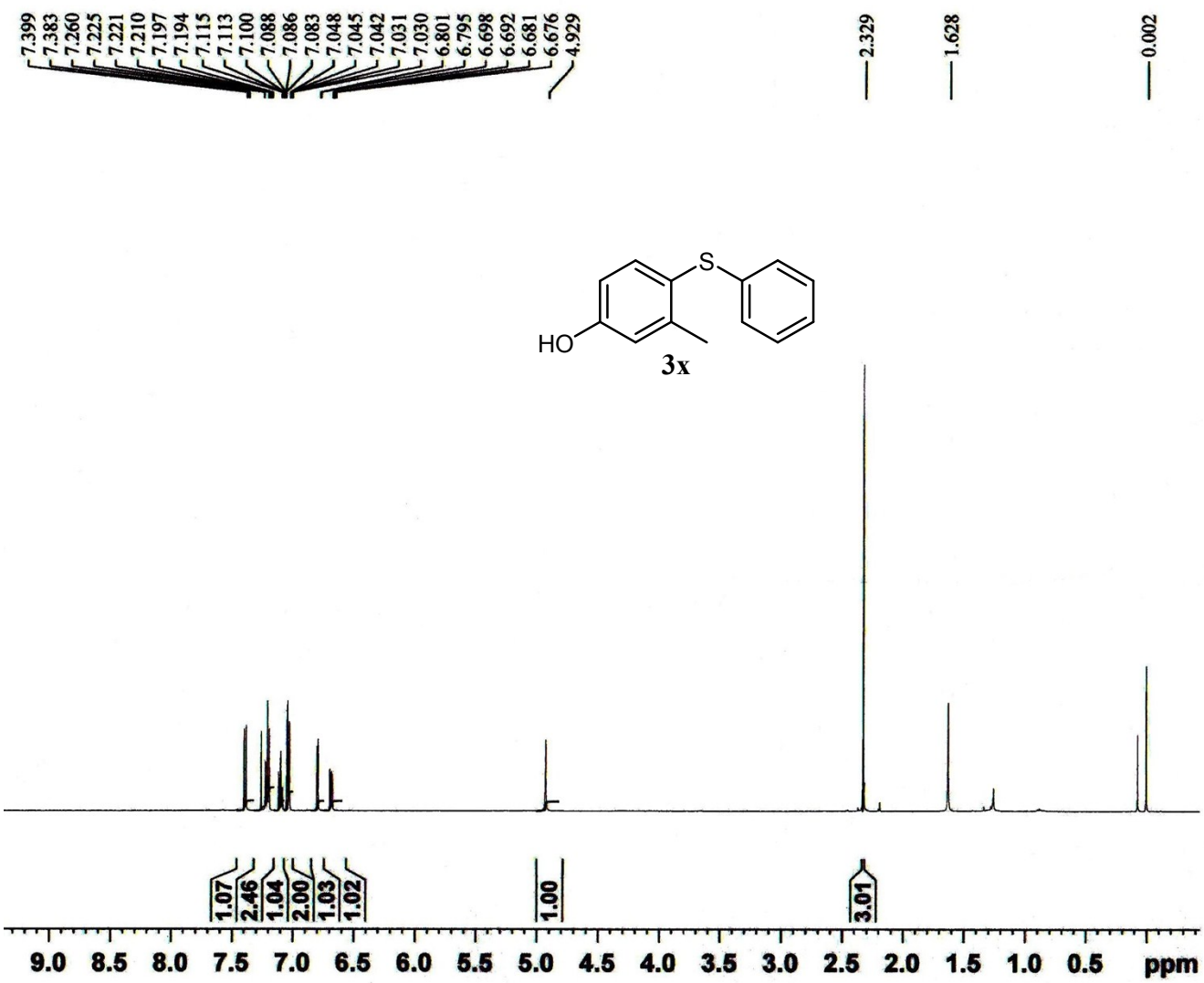
40
20
0
ppm

3w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7.113
7.100
7.088
7.086
7.083
7.048
7.045
7.042
7.031
7.030
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6.795
6.698
6.692
6.681
6.676
4.929
2.329
1.628
0.002
S
HO
3x
1.07
2.46
1.04
2.00
1.03
1.02
1.00
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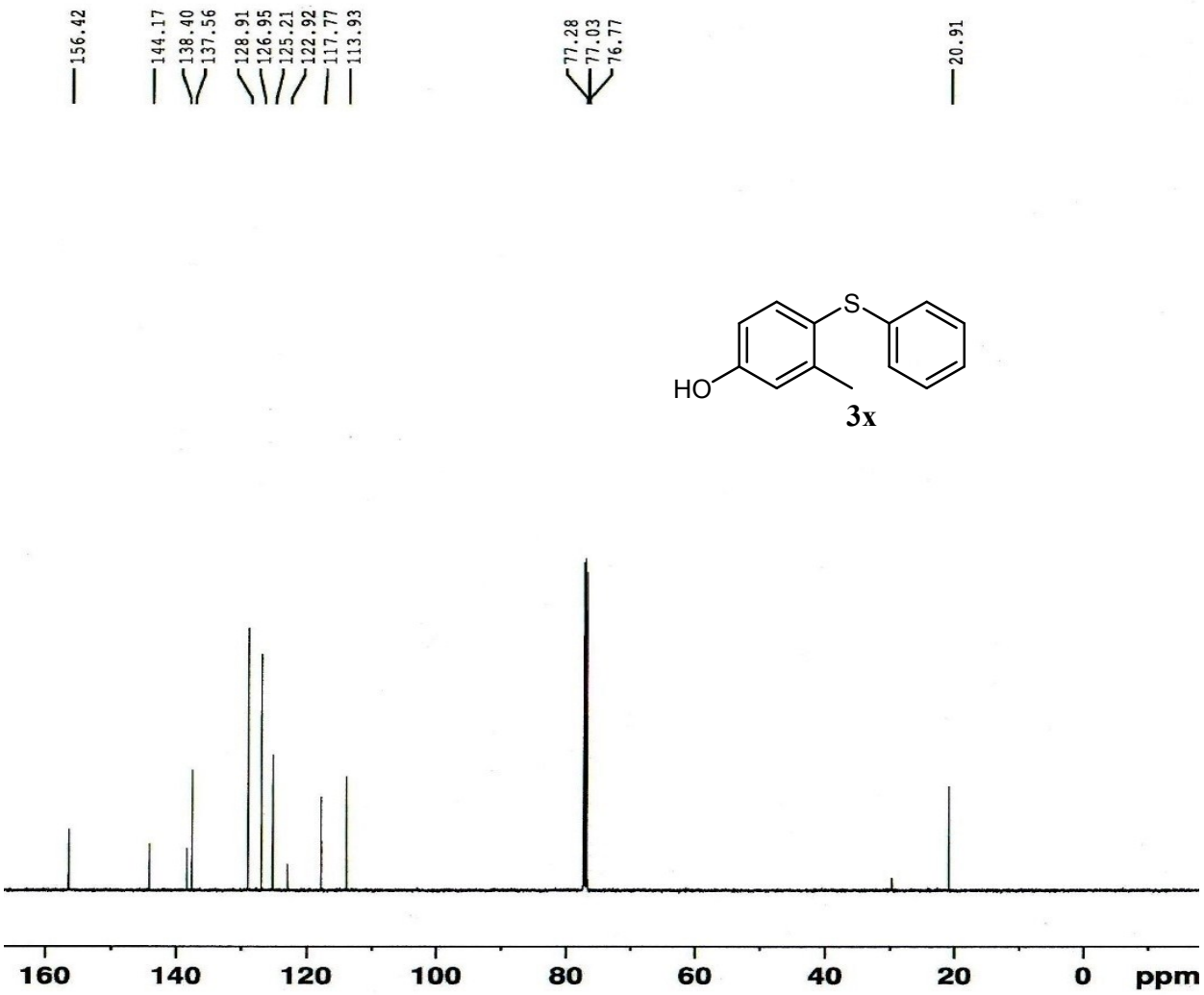
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113.93
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20.91
S
HO
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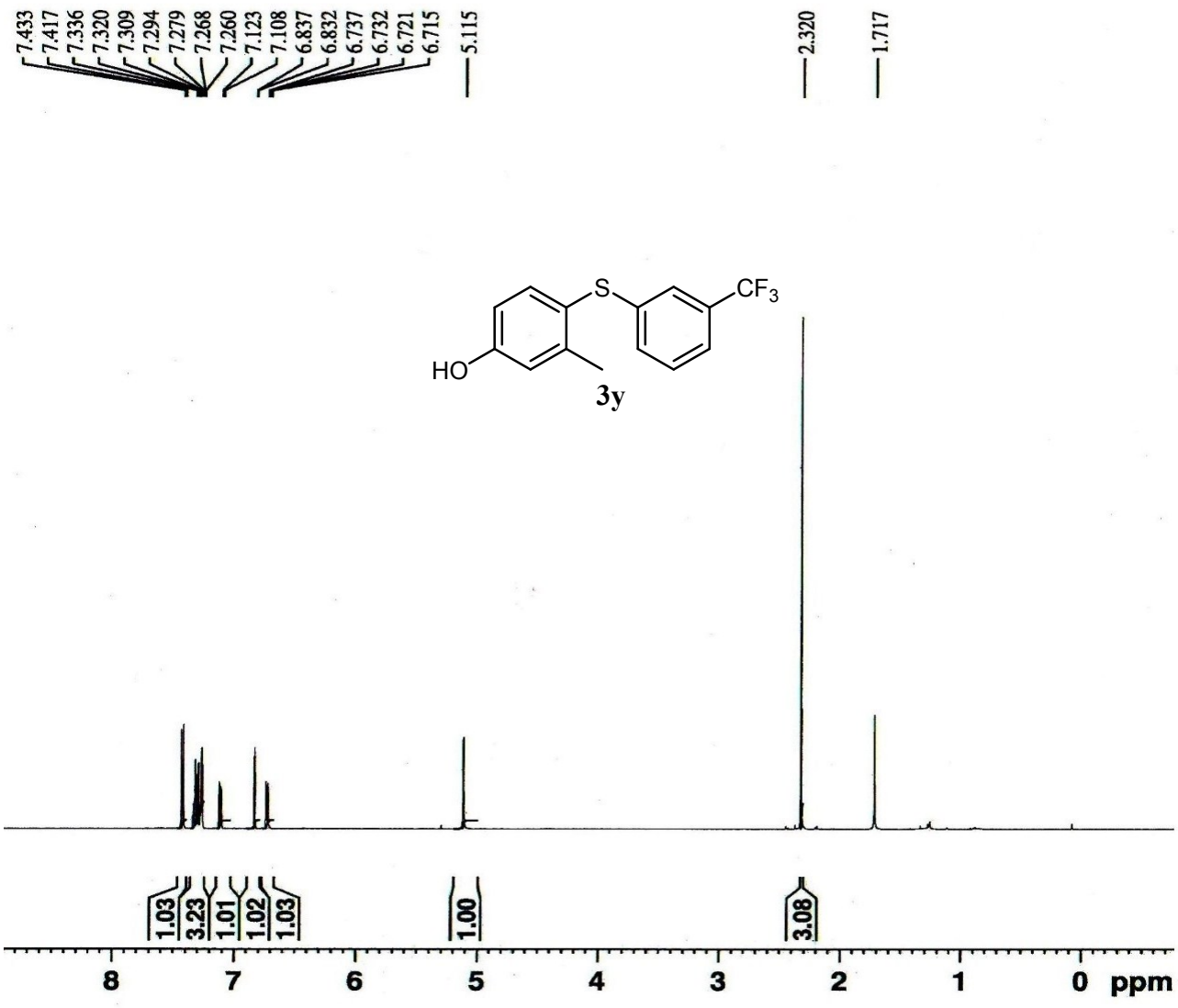
140
120
100
80
60
40
20
0
ppm

3x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6.832
6.737
6.732
6.721
6.715
5.115
2.320
1.717
S
CF3
HO
3y
1.03
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1.03
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8
7
6
5
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2
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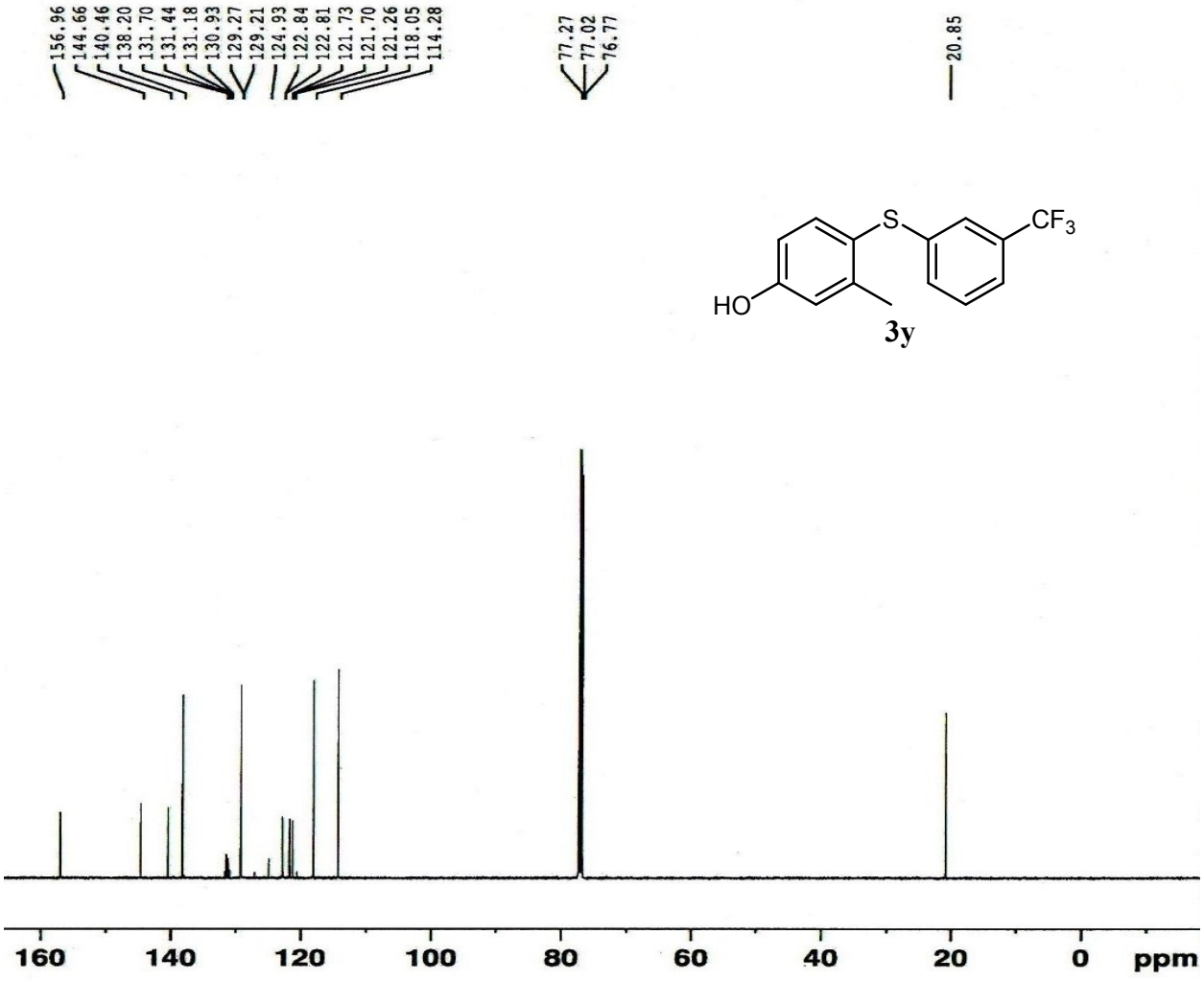
0
ppm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129.21
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121.70
121.26
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114.28
77.27
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S
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120
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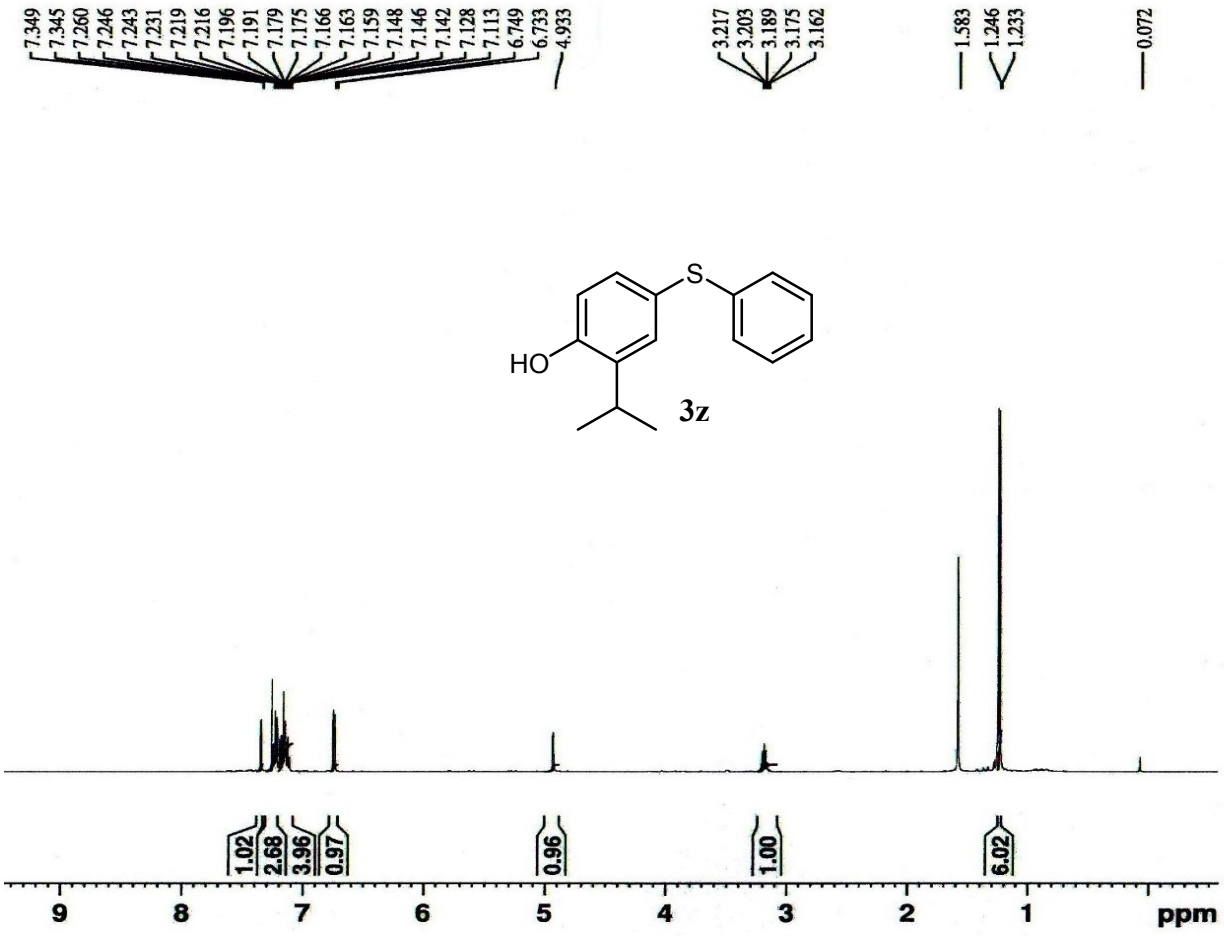
20
0
ppm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7.146
7.142
7.128
7.113
6.749
6.733
4.933
3.217
3.203
3.189
3.175
3.162
1.583
1.246
1.233
0.072
S
HO
3z
1.02
2.68
3.96
0.97
0.96
1.00
6.02
9
8
7
6
5
4
3
2
1
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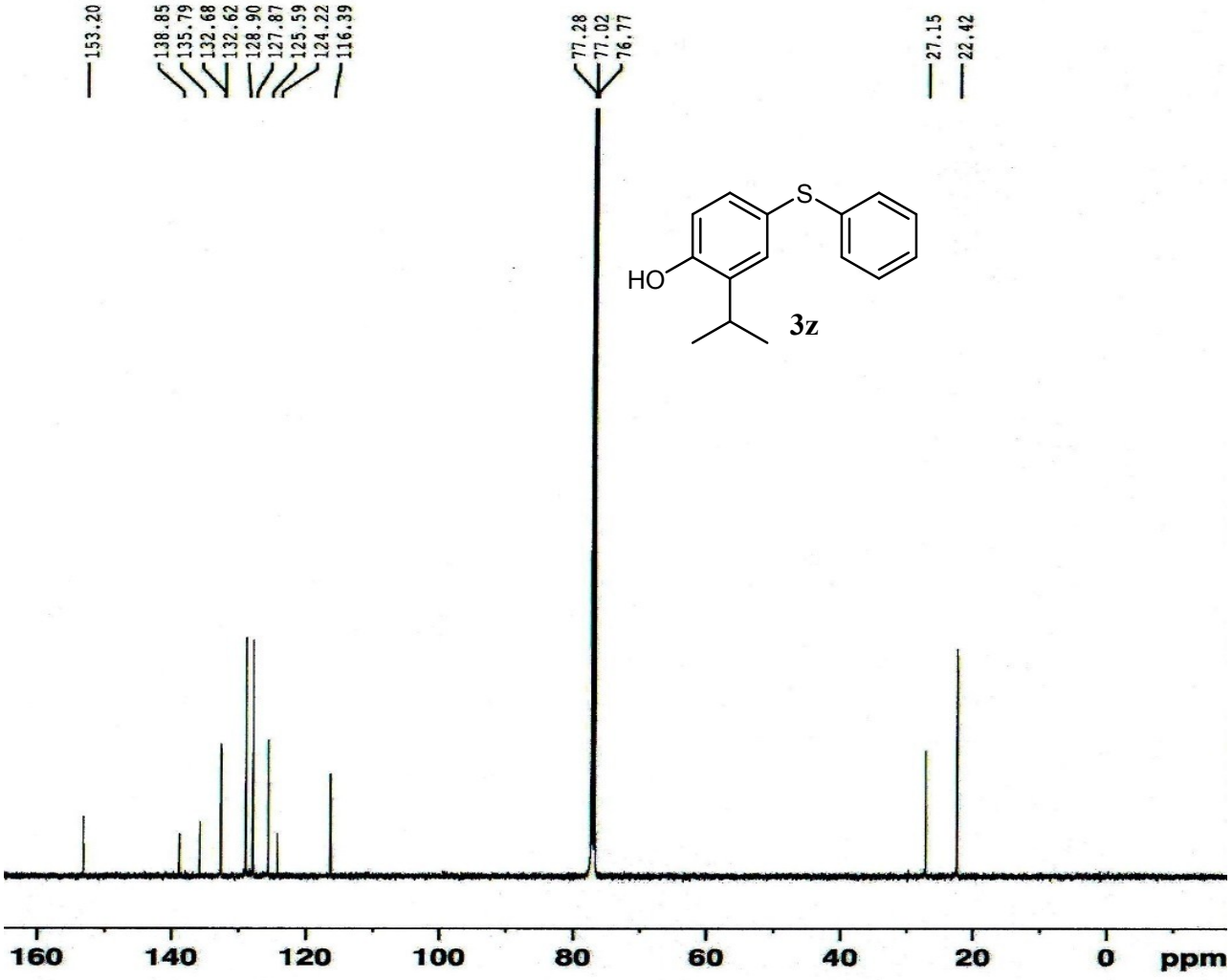
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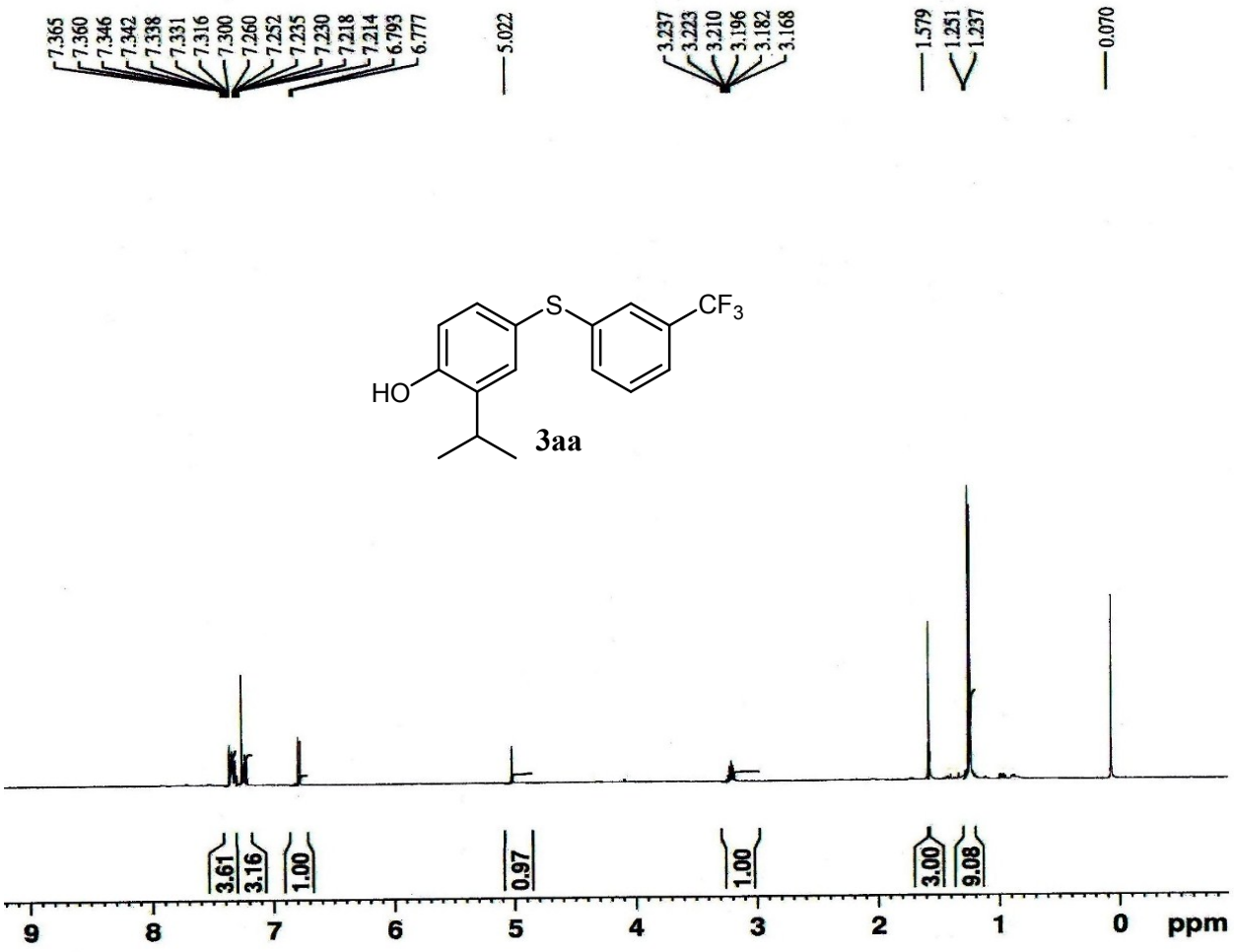
138.85
135.79
132.68
132.62
128.90
127.87
125.59
124.22
116.39
77.28
77.02
76.77
27.15
22.42
S
HO
3z
160
140
120
100
80
60
40
20
0
ppm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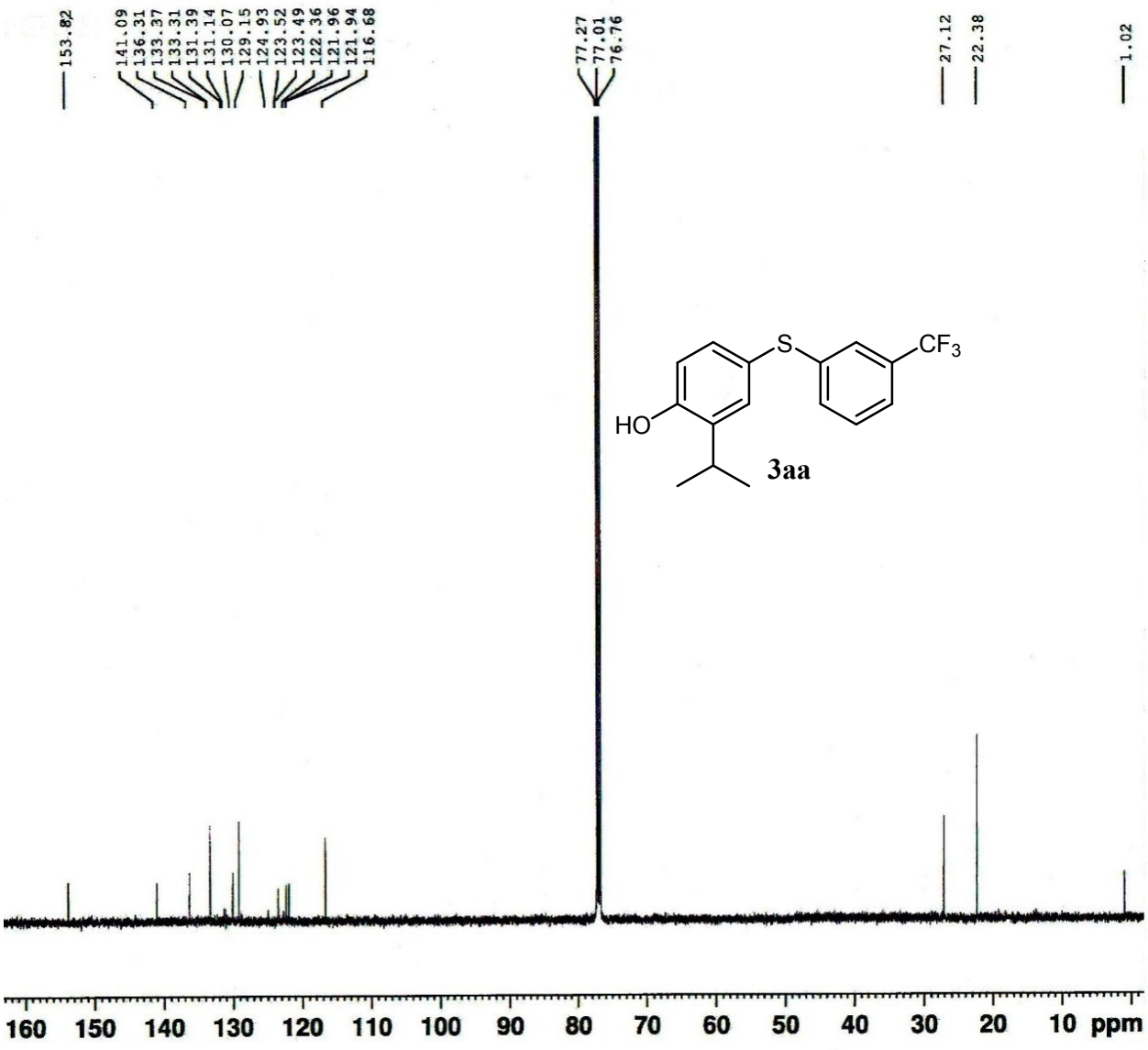
7.300
7.260
7.252
7.235
7.230
7.218
7.214
6.793
6.777
5.022
3.237
3.223
3.210
3.196
3.182
3.168
1.579
1.251
1.237
0.070
S
CF3
HO
3aa
3.61
3.16
1.00
0.97
1.00
3.00
9.08
9
8
7
6
5
4
3
2
1
0
ppm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141.09
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130.07
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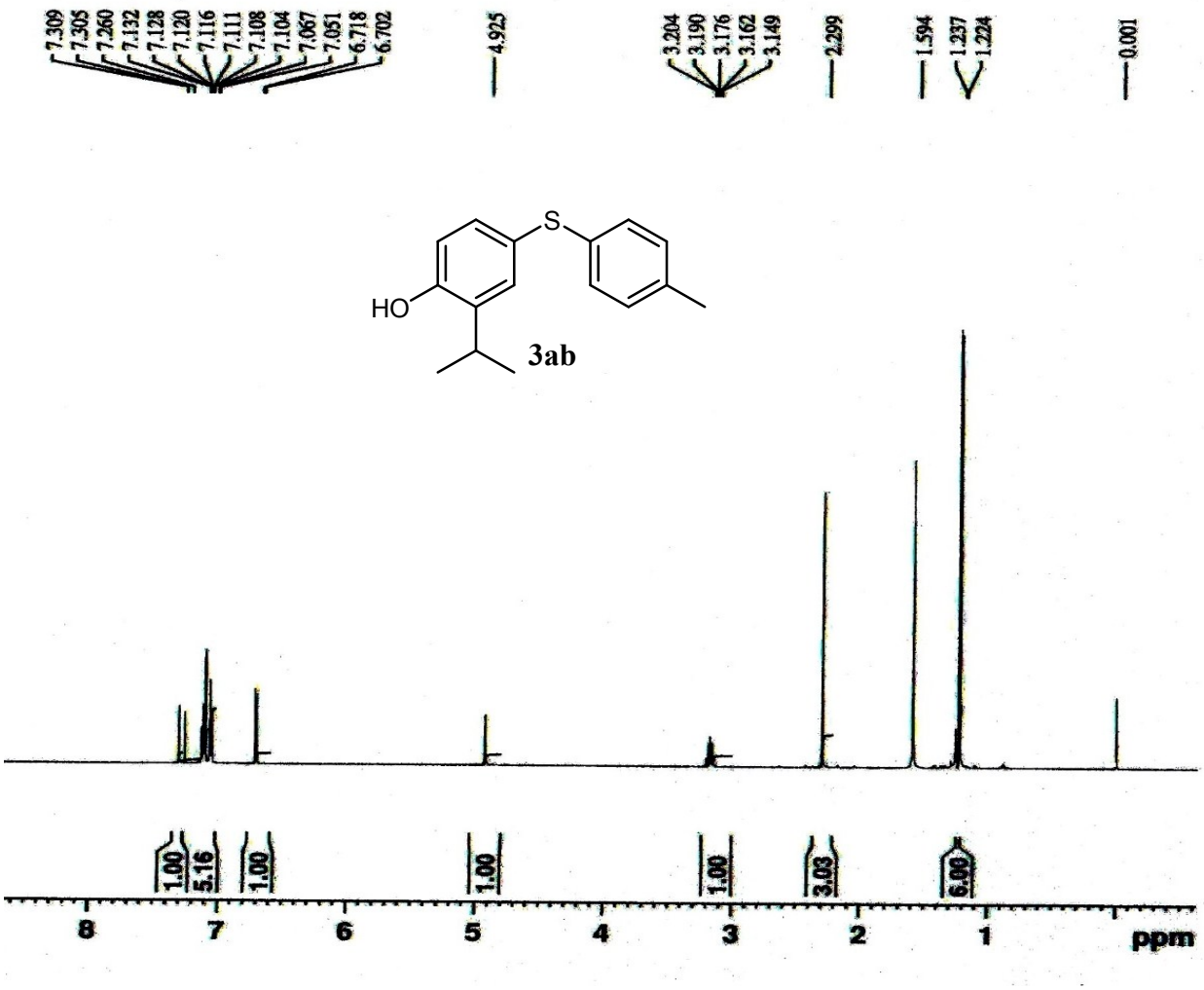
124.93
123.52
123.49
122.36
121.96
121.94
116.68
77.27
77.01
76.76
27.12
22.38
1.02
S
CF3
HO
3aa
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.260
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7.128
7.120
7.116
7.111
7.108
7.104
7.067
7.051
6.718
6.702
4.925
3.204
3.190
3.176
3.162
3.149
2.299
1.594
1.237
1.224
0.001
HO
S
3ab
1.00
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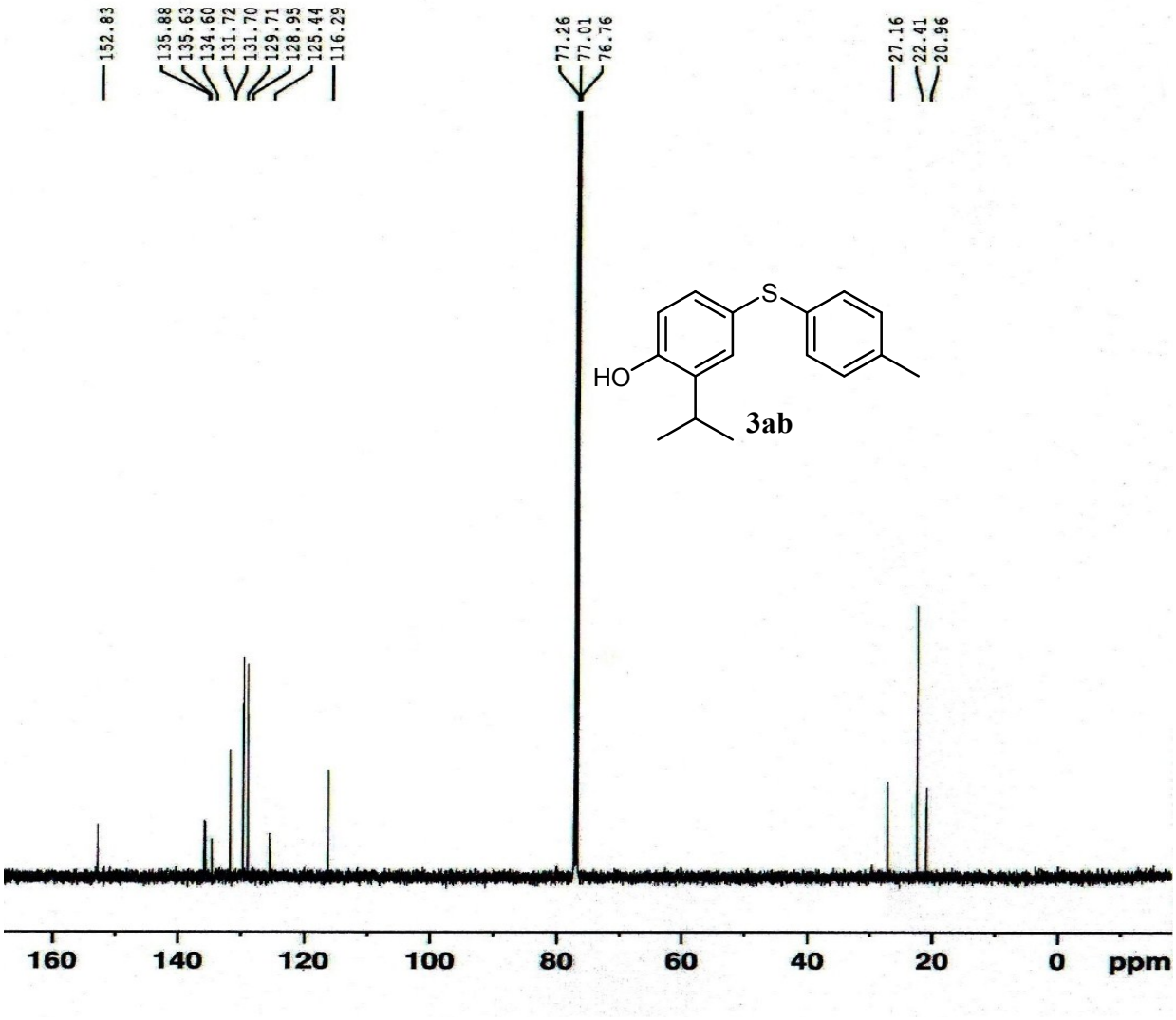
1.00
1.00
1.00
3.03
6.00
8
7
6
5
4
3
2
1
ppm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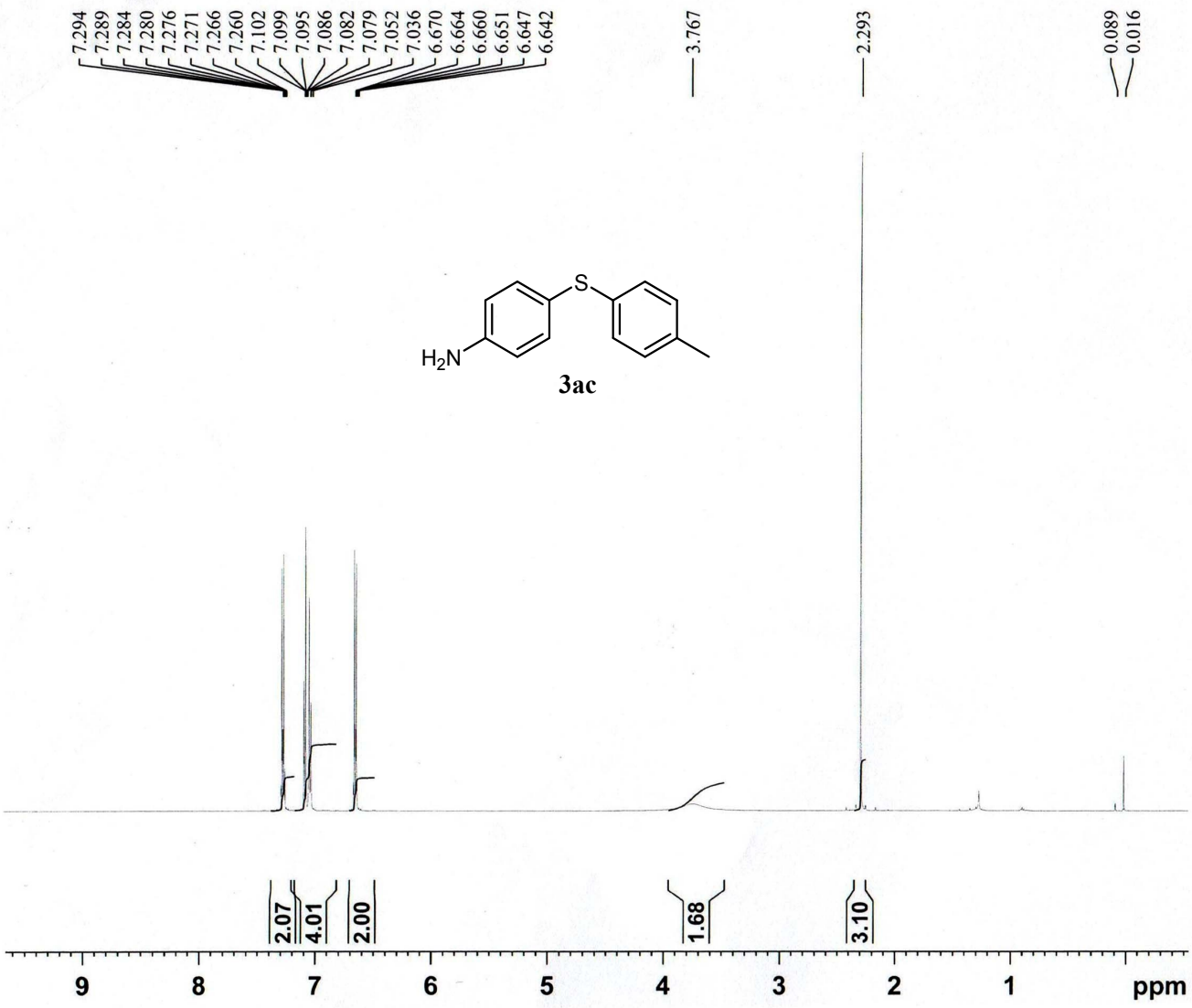
135.63
134.60
131.72
131.70
129.71
128.95
125.44
116.29
77.26
77.01
76.76
27.16
22.41
20.96
S
HO
3ab
160
140
120
100
80
60
40
20
0
ppm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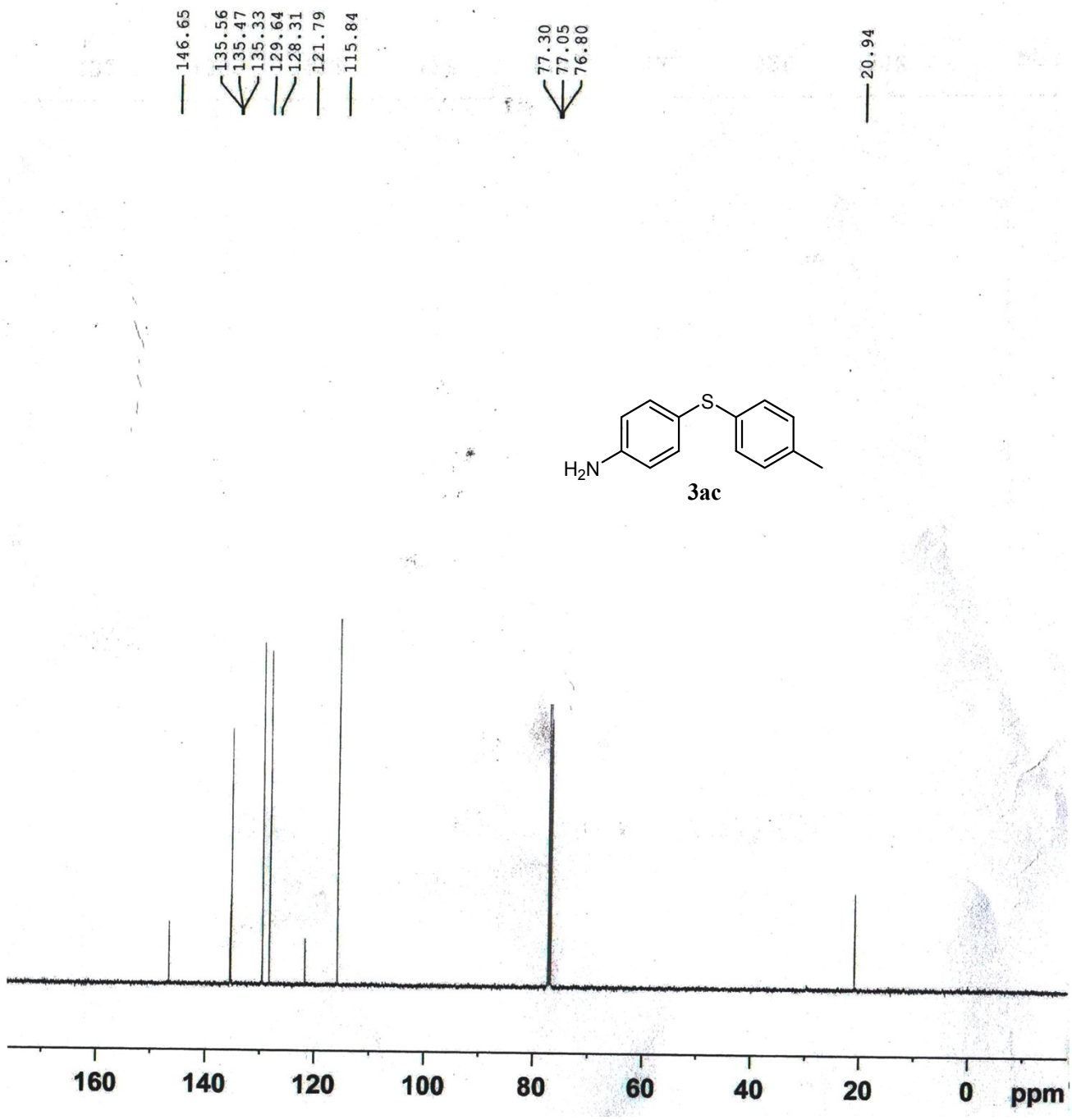
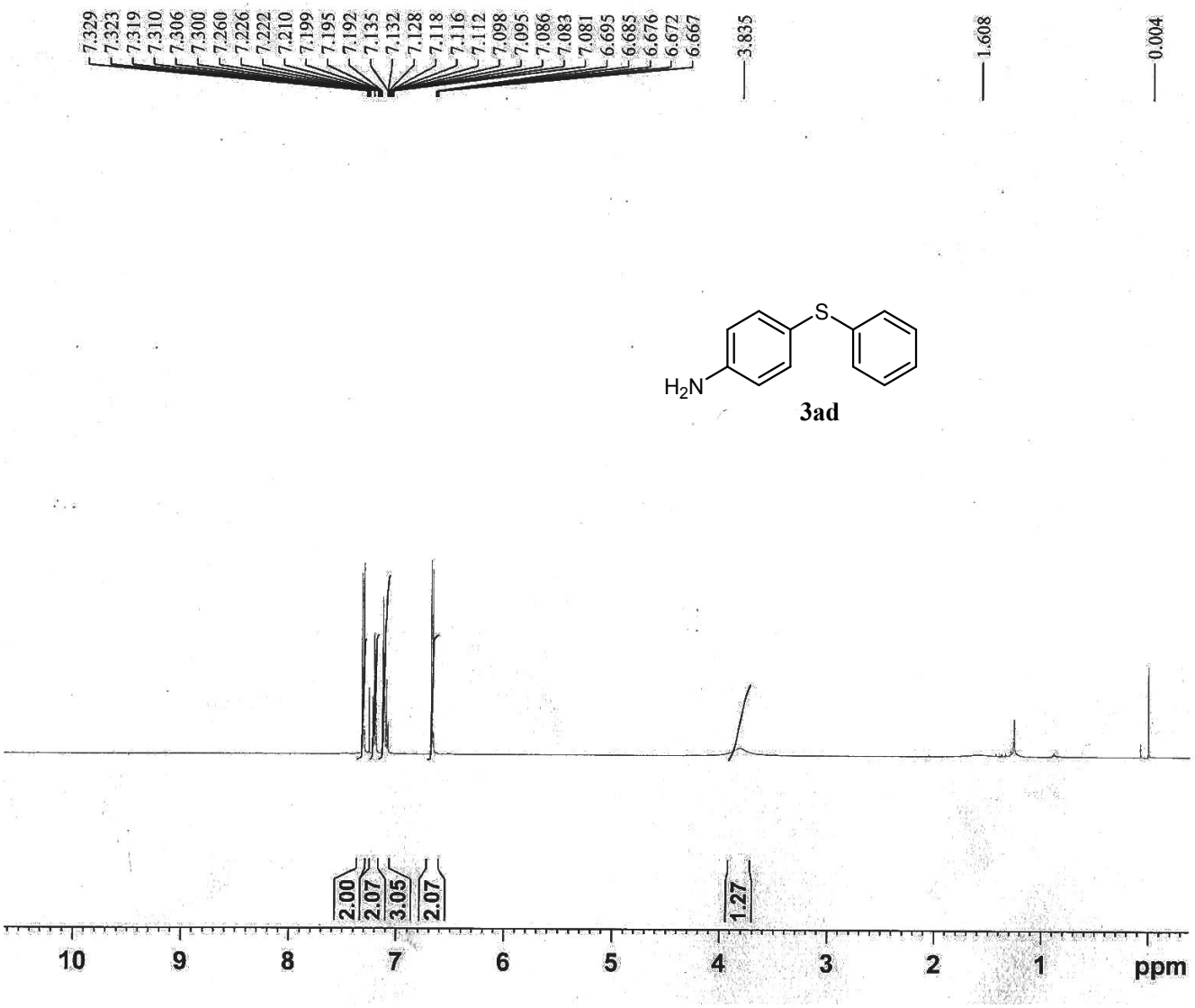
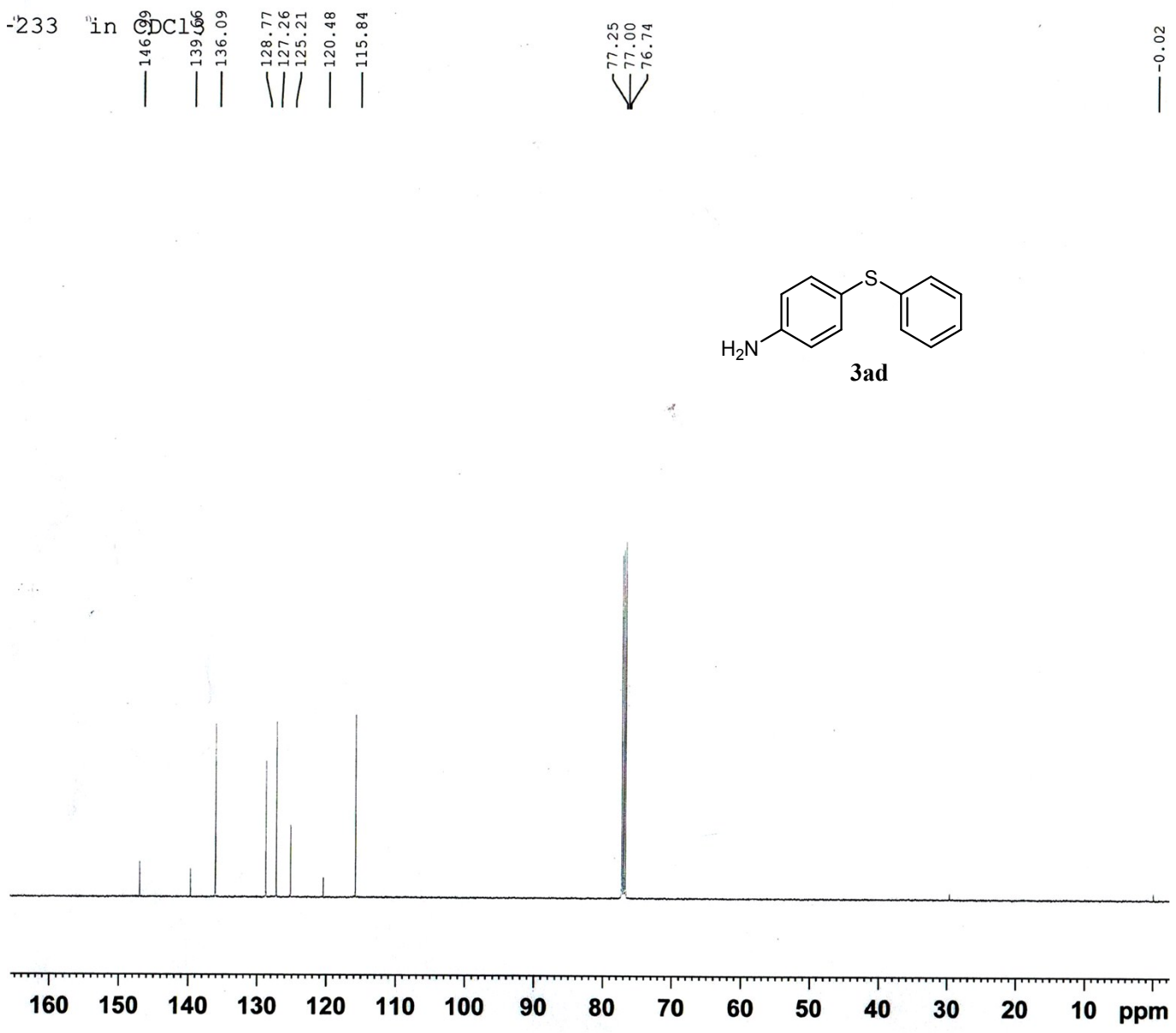
7.289
7.284
7.280
7.276
7.271
7.266
7.260
7.102
7.099
7.095
7.086
7.082
7.079
7.052
7.036
6.670
6.664
6.660
6.651
6.647
6.642
3.767
2.293
0.089
0.016
S
H2N
2.07
4.01
2.00
1.68
3.10
9
8
7
6
5
4
3
2
1
ppm

3ac

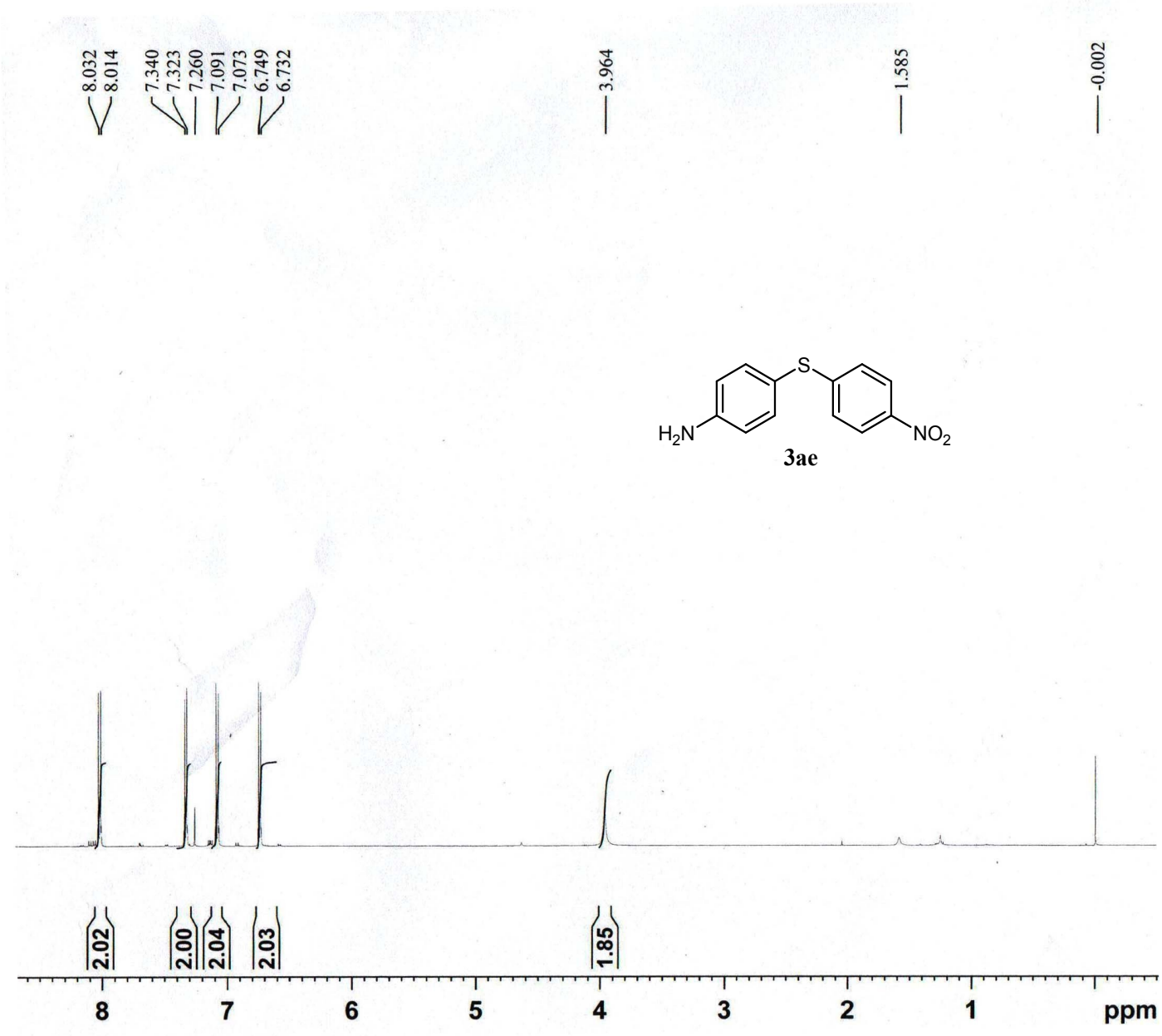

146.65
135.56
135.47
135.33
129.64
128.31
121.79
115.84
77.30
77.05
76.80
20.94
S
H2N
160
140
120
100
80
60
40
20
0
ppm

3ac

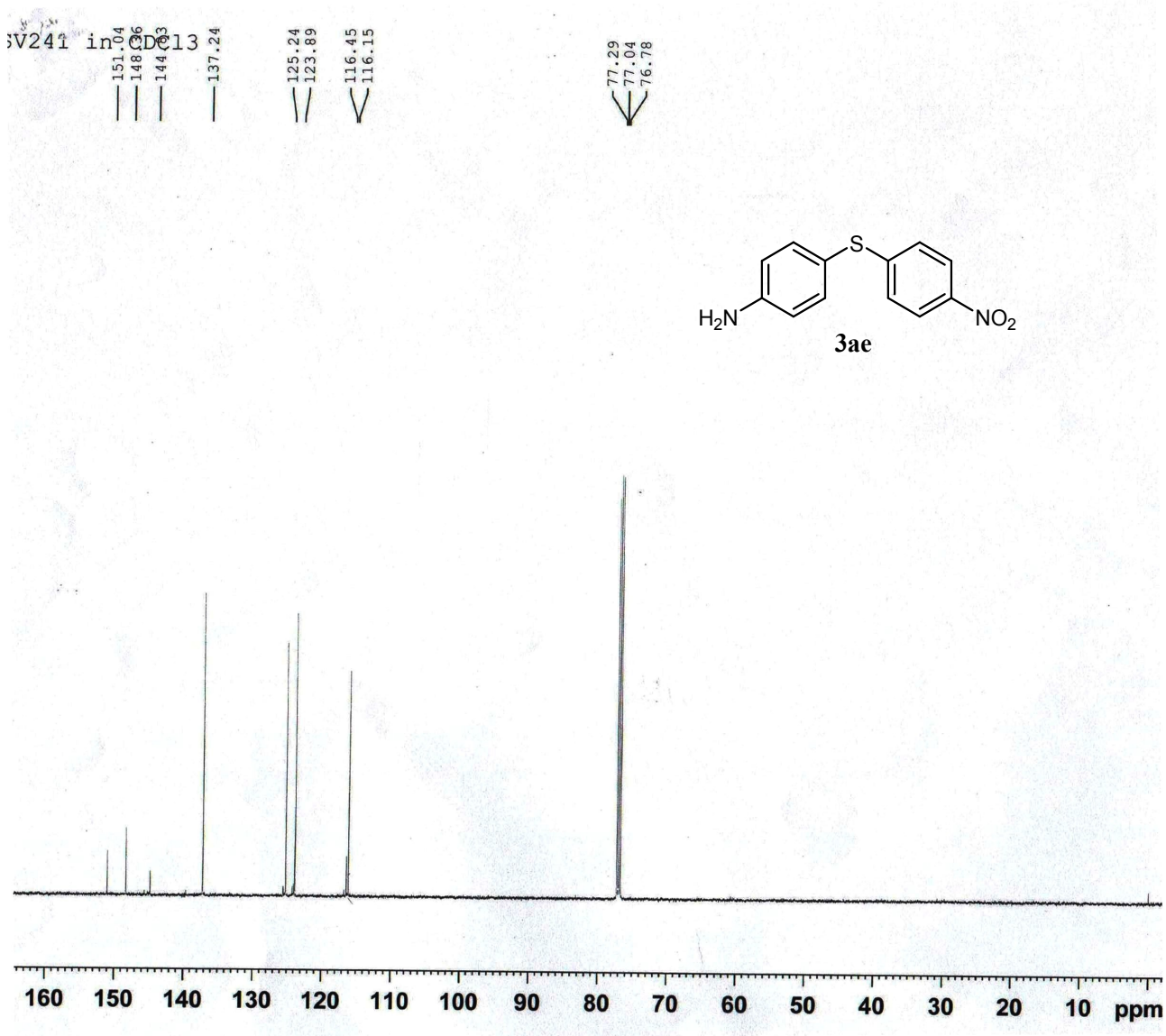

7.329
7.323
7.319
7.310
7.306
7.300
7.260
7.226
7.222
7.210
7.199
7.195
7.192
7.135
7.132
7.128
7.118
7.116
7.112
7.098
7.095
7.086
7.083
7.081
6.695
6.685
6.676
6.672
6.667
3.835
1.608
0.004
S
H2N
3ad
2.00
2.07
3.05
2.07
1.27
10
9
8
7
6
5
4
3
2
1
ppm

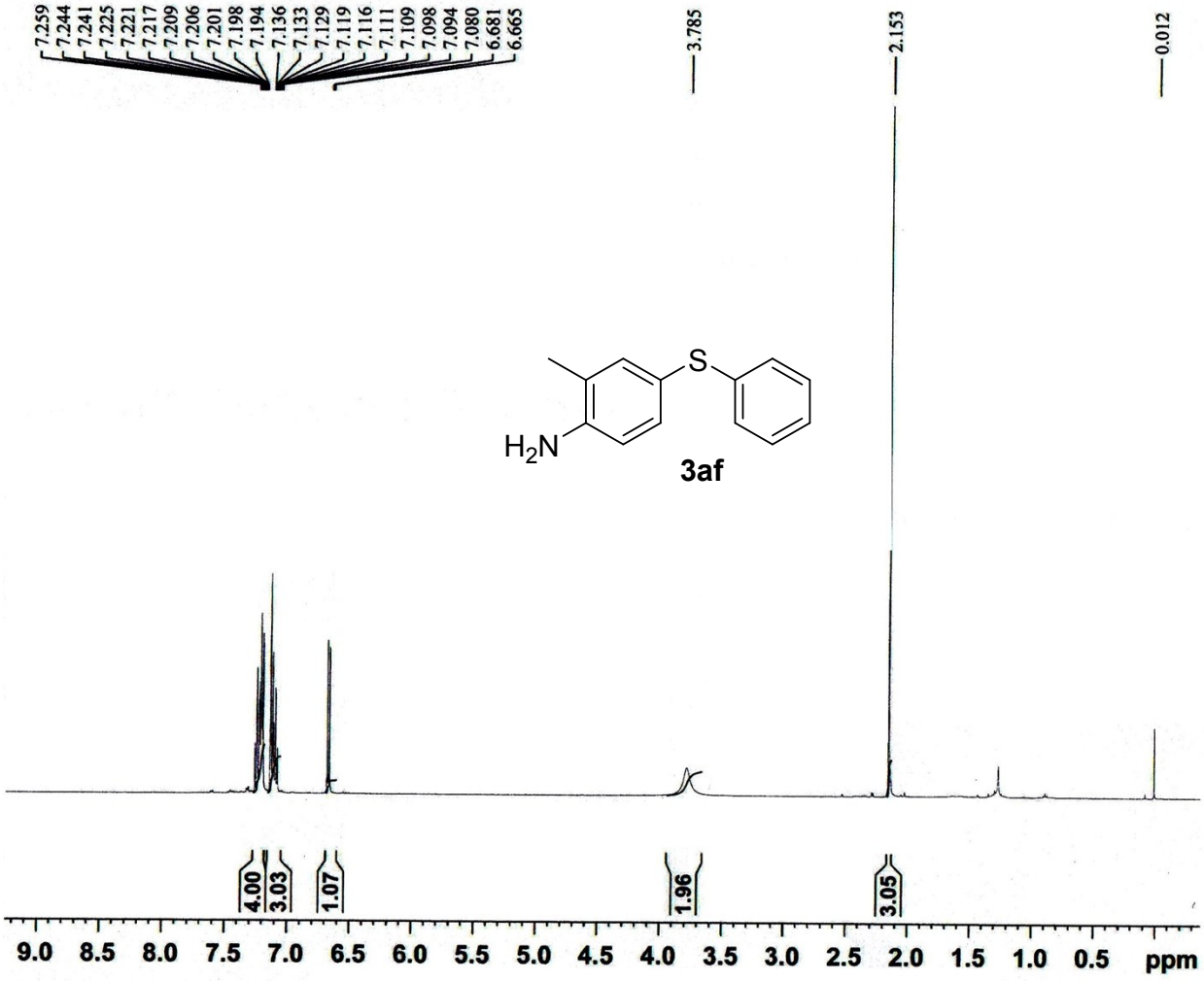

-233 in CDCl3
146.99
139.66
136.09
128.77
127.26
125.21
120.48
115.84
77.25
77.00
76.74
-0.02
S
H2N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

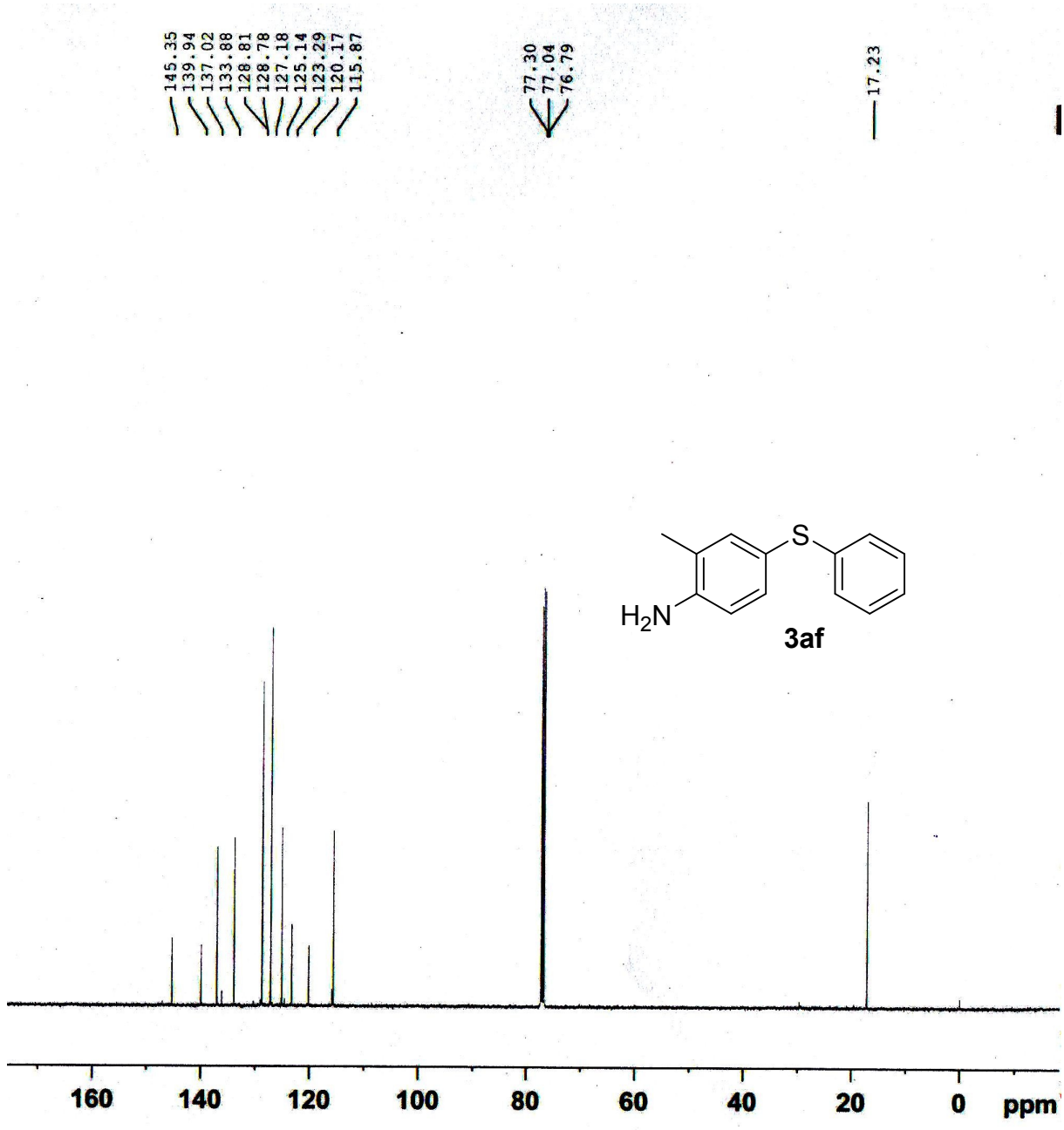
3ad


8.032
8.014
7.340
7.323
7.260
7.091
7.073
6.749
6.732
3.964
1.585
-0.002
S
H_2N
NO_2
2.02
2.00
2.04
2.03
1.85
8
7
6
5
4
3
2
1
ppm

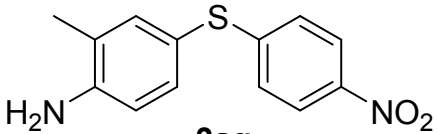
3ae


SV241 in CDCl3
151.04
148.06
144.03
137.24
125.24
123.89
116.45
116.15
77.29
77.04
76.78
S
H2N
NO2
3ae
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

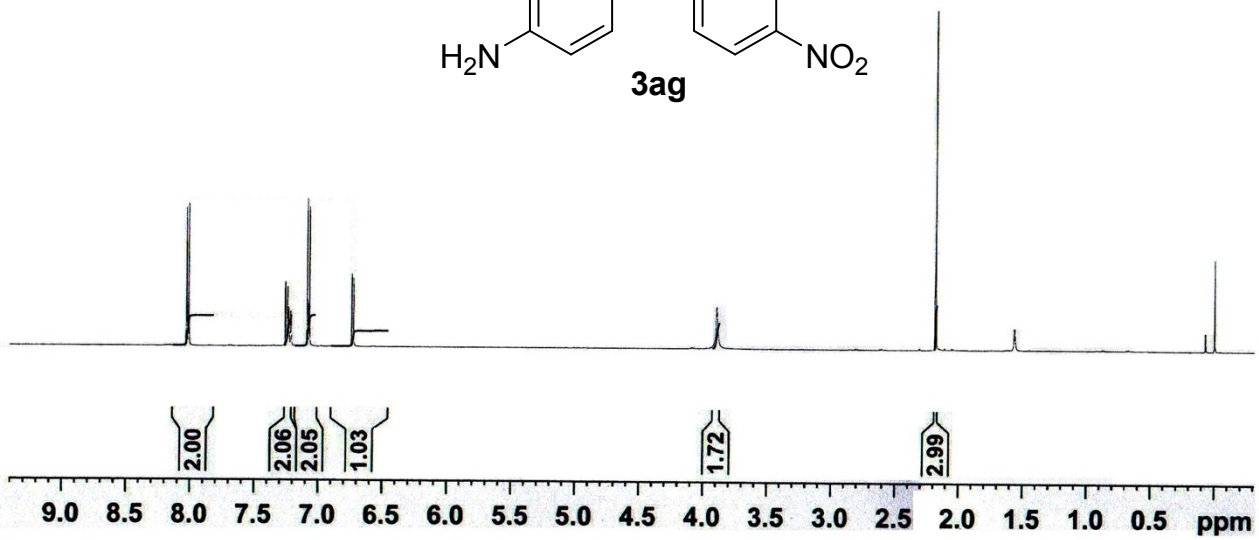

7.259
7.244
7.241
7.225
7.221
7.217
7.209
7.206
7.201
7.198
7.194
7.136
7.133
7.129
7.119
7.116
7.111
7.109
7.098
7.094
7.080
6.681
6.665
3.785
2.153
0.012
S
H2N
3af
4.00
3.03
1.07
1.96
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

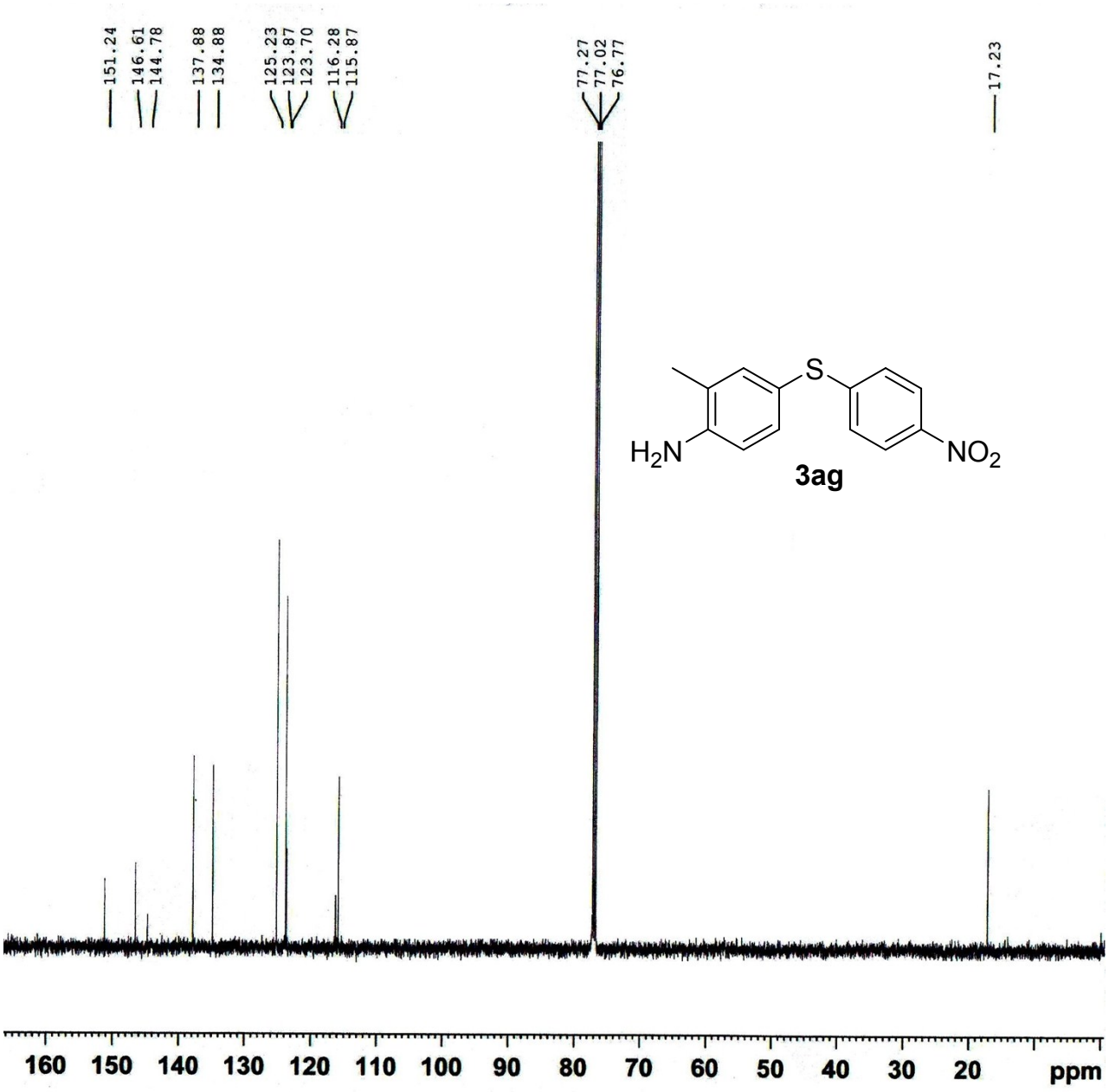

145.35
139.94
137.02
133.88
128.81
128.78
127.18
125.14
123.29
120.17
115.87
77.30
77.04
76.79
17.23
S
H2N
3af
160
140
120
100
80
60
40
20
0
ppm


8.036
8.031
8.027
8.022
8.017
8.013
8.008
7.260
7.244
7.235
7.231
7.218
7.214
7.096
7.091
7.087
7.082
7.077
7.073
7.068
6.743
6.727
3.894
2.183
-0.000


S
H2N
NO2

3ag


2.00
2.06
2.05
1.03
1.72
2.99
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 ppm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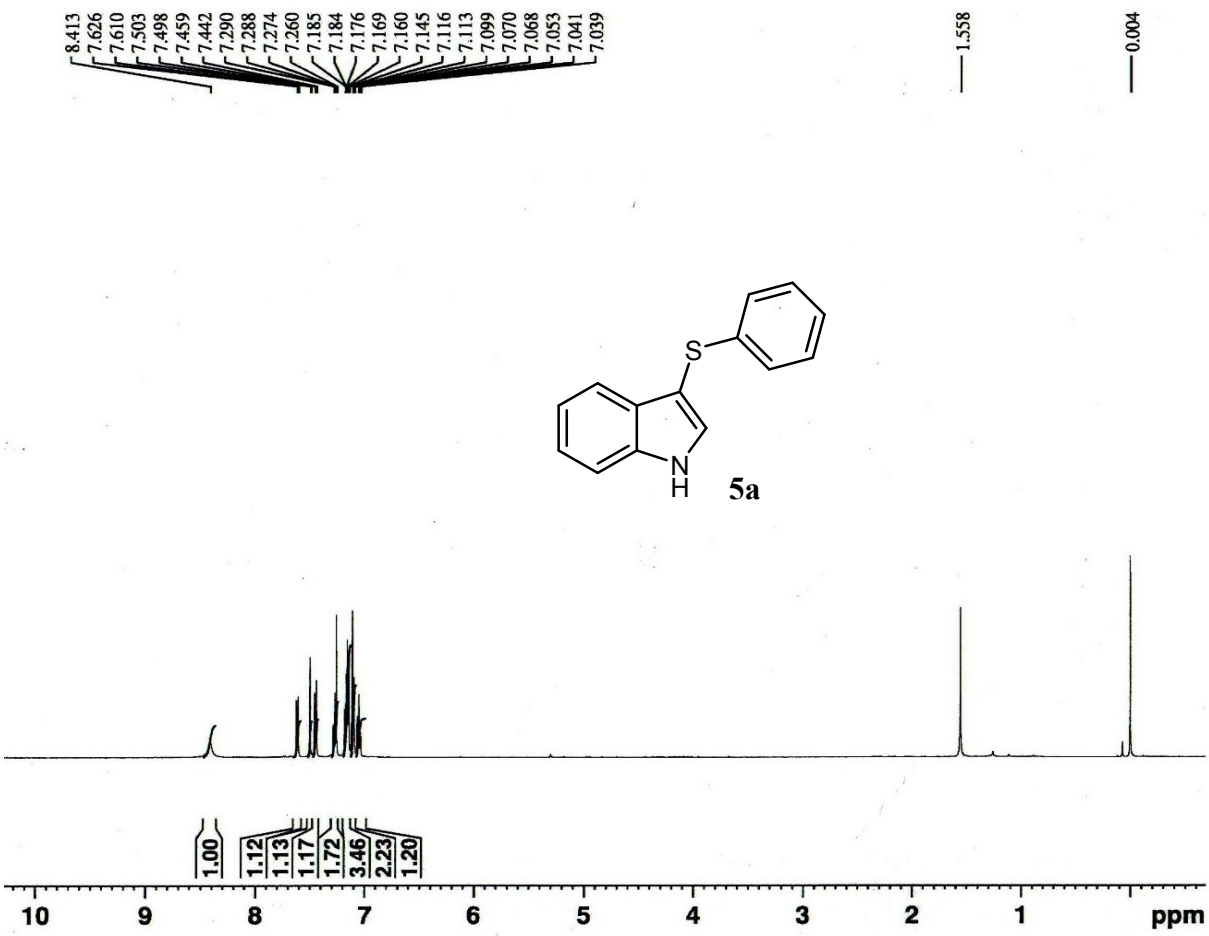
146.61
144.78
137.88
134.88
125.23
123.87
123.70
116.28
115.87
77.27
77.02
76.77
17.23
S
H2N
NO2
3ag
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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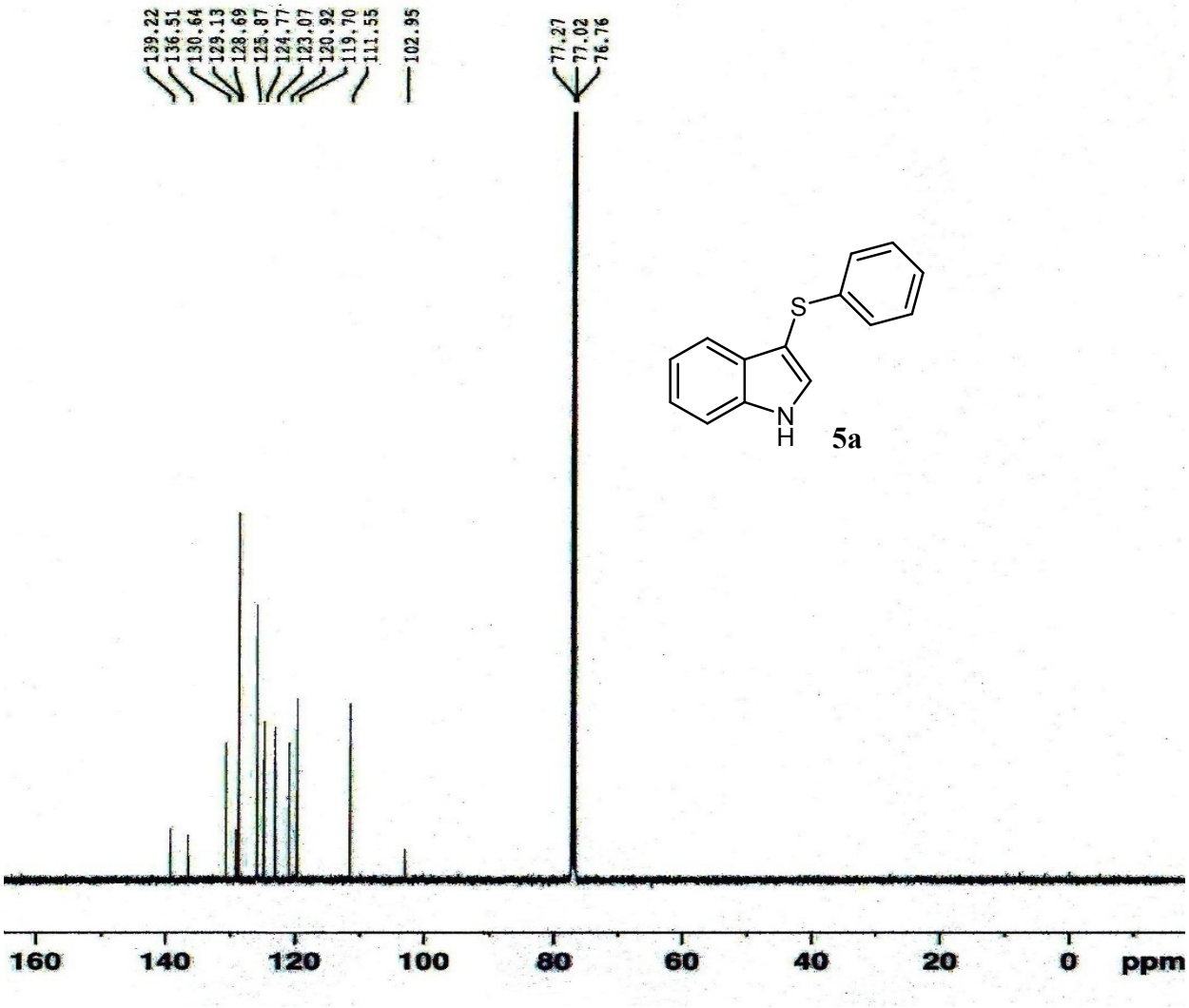
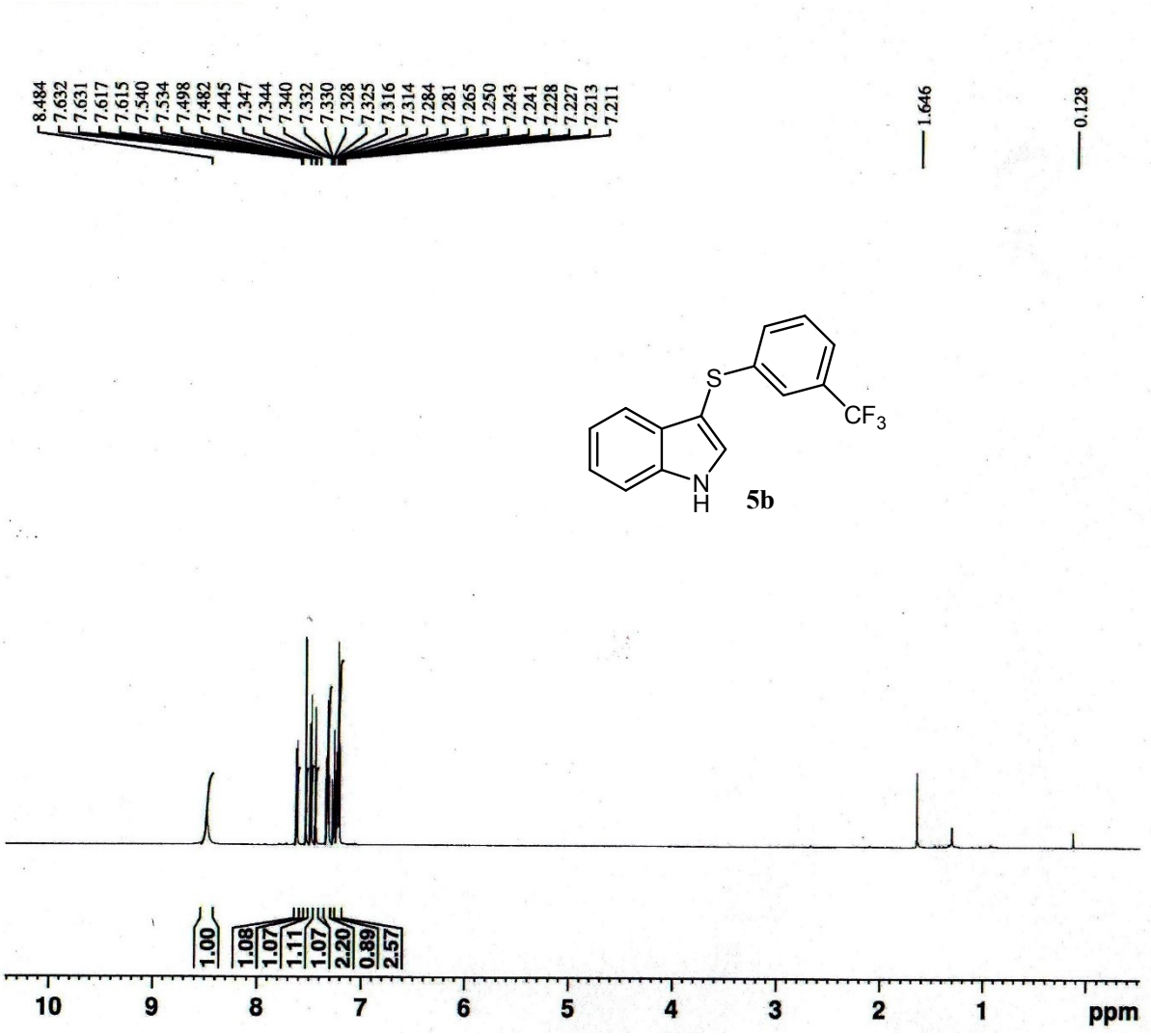
7.626
7.610
7.503
7.498
7.459
7.442
7.290
7.288
7.274
7.260
7.185
7.184
7.176
7.169
7.160
7.145
7.116
7.113
7.099
7.070
7.068
7.053
7.041
7.039
1.558
0.004
S
N
H
5a
1.00
1.12
1.13
1.17
1.72
3.46
2.23
1.20
10
9
8
7
6
5
4
3
2
1
ppm


139.22
136.51
130.64
129.13
128.69
125.87
124.77
123.07
120.92
119.70
111.55
102.95
77.27
77.02
76.76
S
N
H
160
140
120
100
80
60
40
20
0
ppm

5a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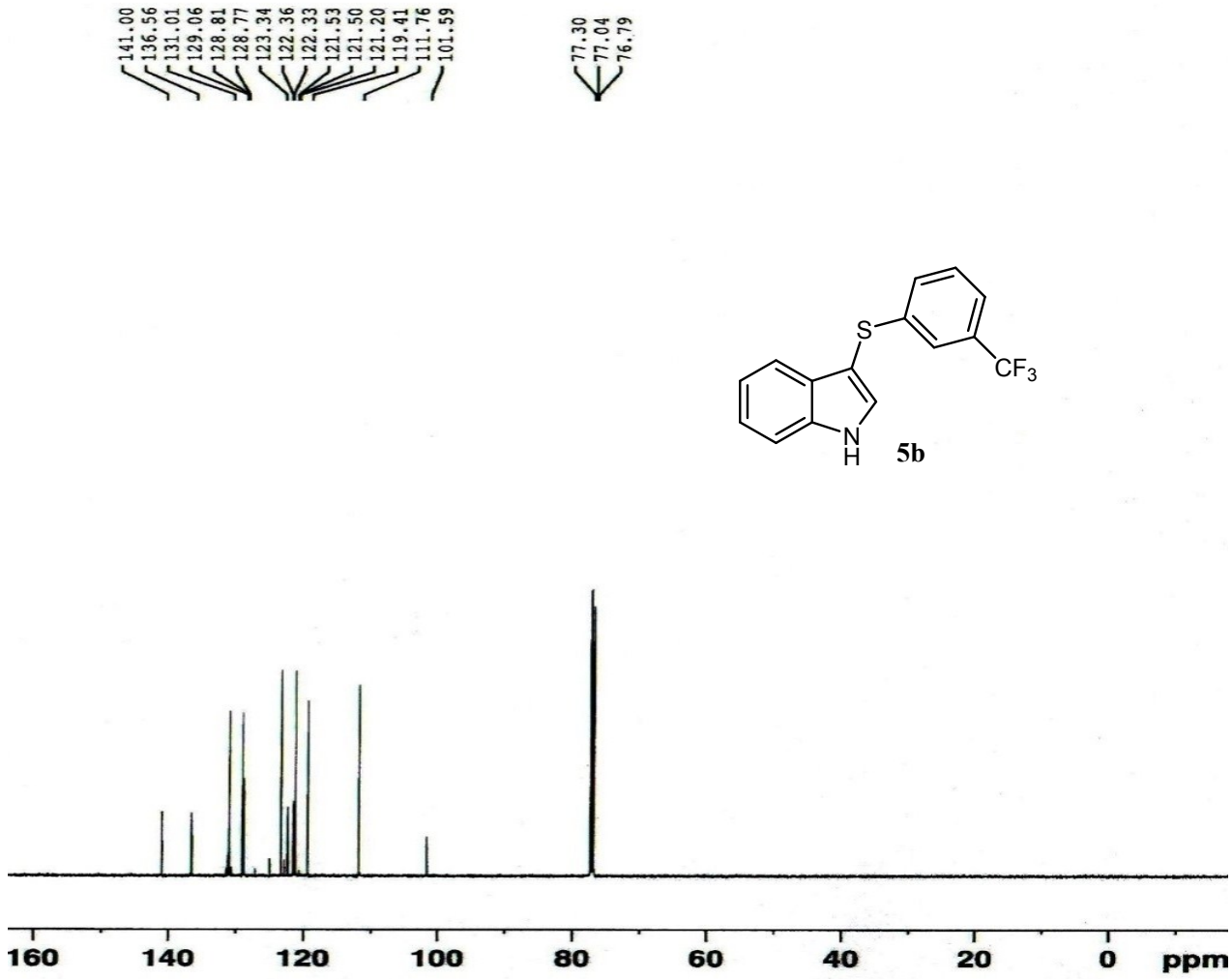
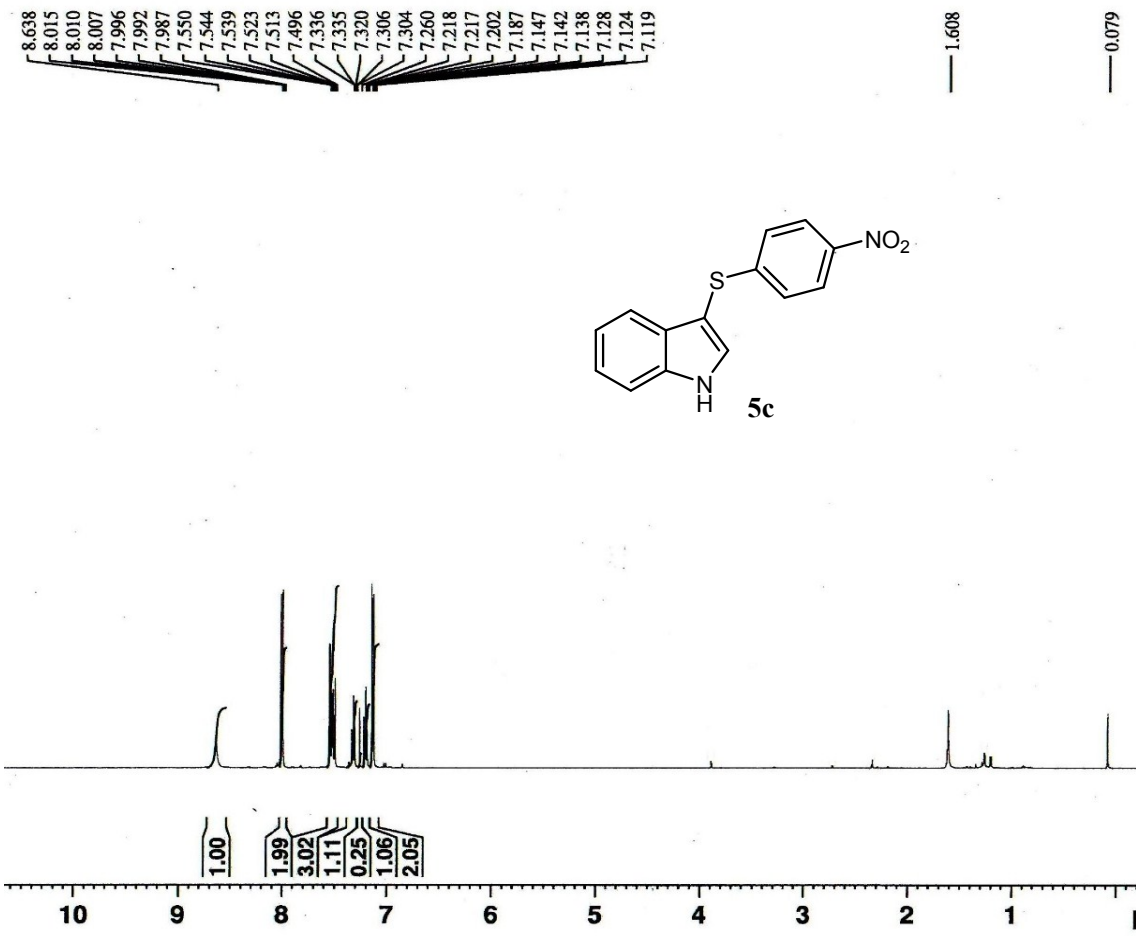
7.631
7.617
7.615
7.540
7.534
7.498
7.482
7.445
7.347
7.344
7.340
7.332
7.330
7.328
7.325
7.316
7.314
7.284
7.281
7.265
7.250
7.243
7.241
7.228
7.227
7.213
7.211
1.646
0.128
S
CF3
N
H
5b
1.00
1.08
1.07
1.11
1.07
2.20
0.89
2.57
10
9
8
7
6
5
4
3
2
1
ppm


141.00
136.56
131.01
129.06
128.81
128.77
123.34
122.36
122.33
121.53
121.50
121.20
119.41
111.76
101.59
77.30
77.04
76.79
S
CF3
N
H
5b
160
140
120
100
80
60
40
20
0
ppm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8.010
8.007
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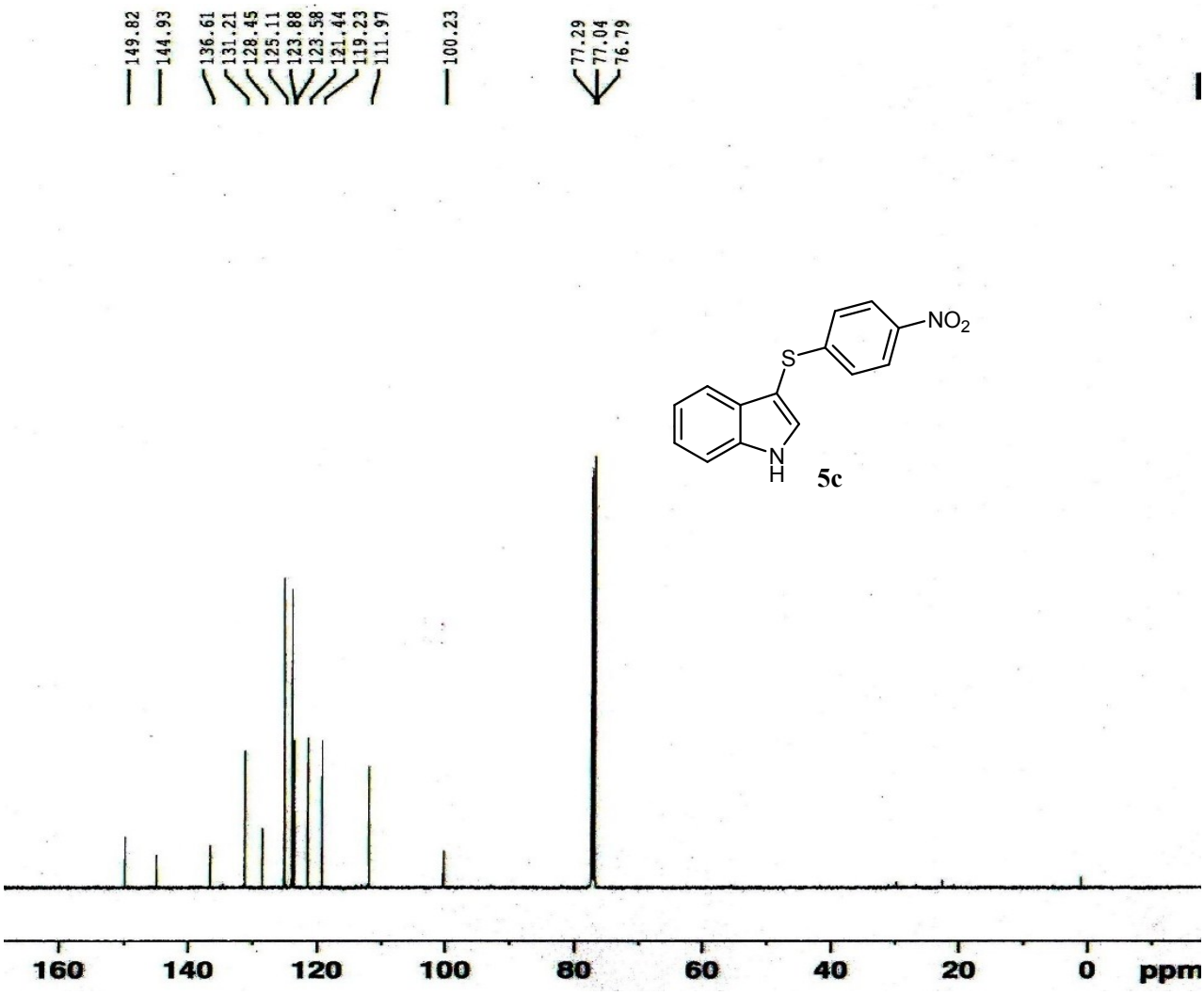
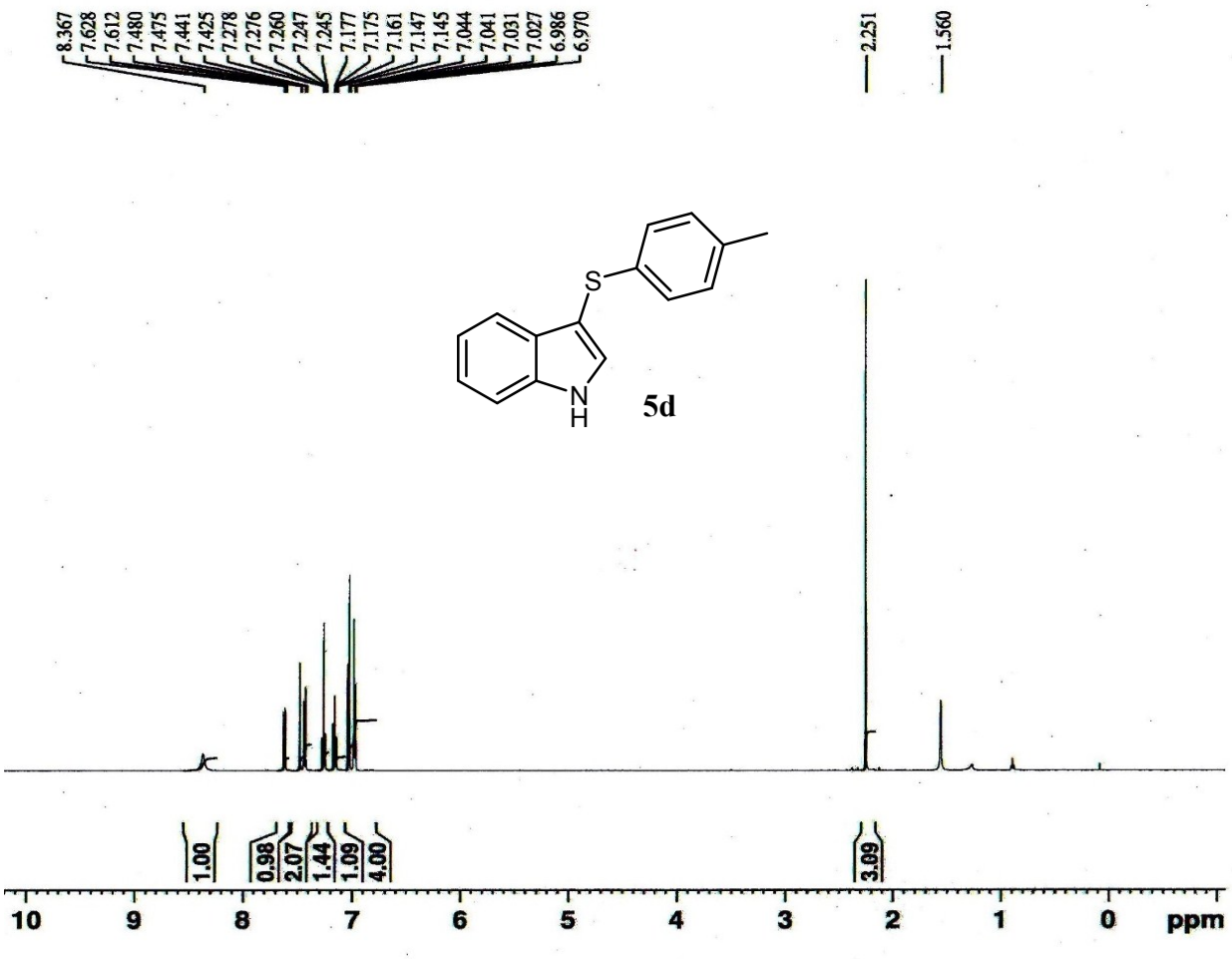
7.992
7.987
7.550
7.544
7.539
7.523
7.513
7.496
7.336
7.335
7.320
7.306
7.304
7.260
7.218
7.217
7.202
7.187
7.147
7.142
7.138
7.128
7.124
7.119
1.608
0.079
NO2
S
N
H
5c
1.00
1.99
3.02
1.11
0.25
1.06
2.05
10
9
8
7
6
5
4
3
2
1
ppm


149.82
144.93
136.61
131.21
128.45
125.11
123.88
123.58
121.44
119.23
111.97
100.23
77.29
77.04
76.79
NO2
S
N
H
5c
160
140
120
100
80
60
40
20
0
ppm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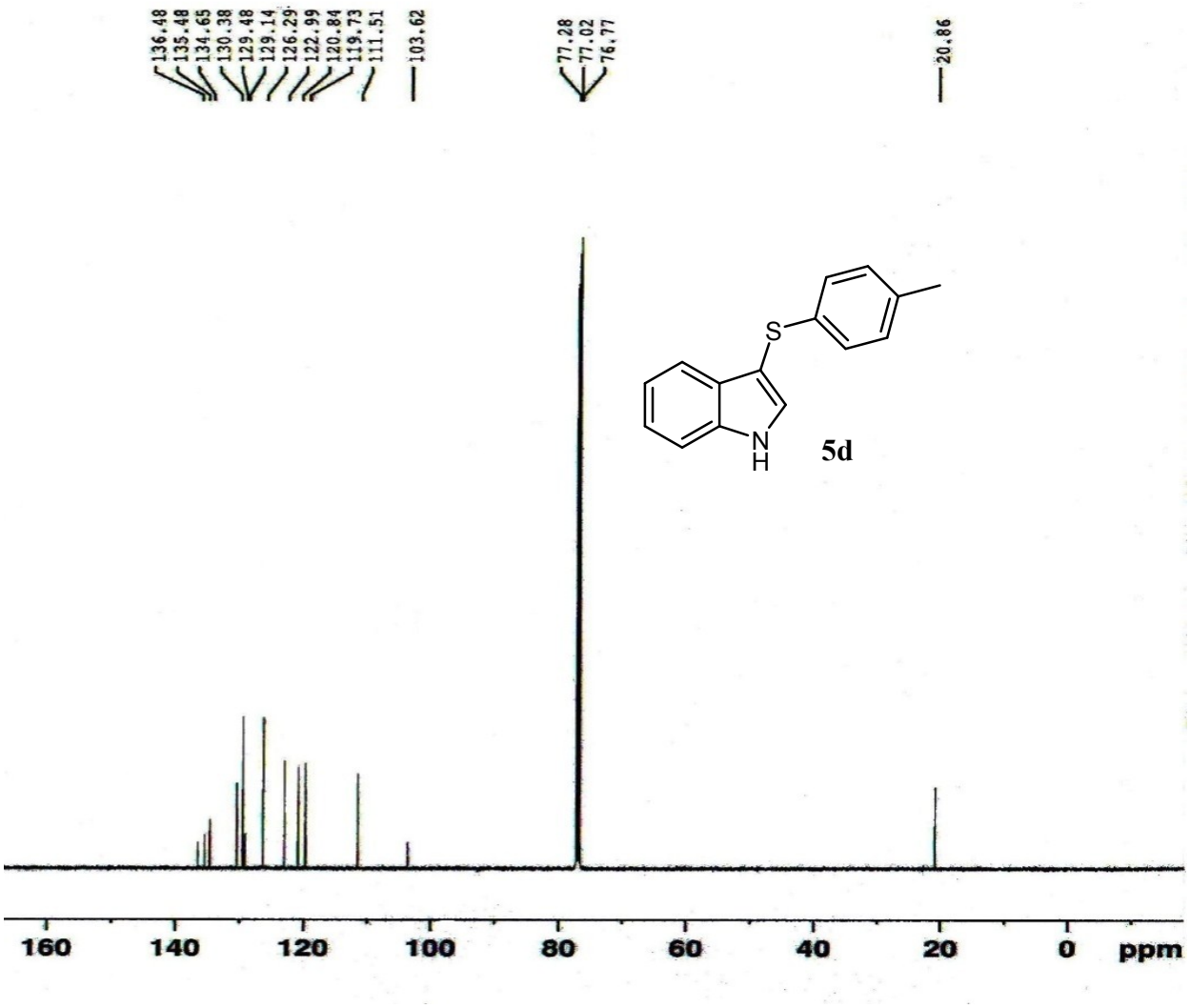
7.425
7.278
7.276
7.260
7.247
7.245
7.177
7.175
7.161
7.147
7.145
7.044
7.041
7.031
7.027
6.986
6.970
2.251
1.560
S
N
H
5d
1.00
0.98
2.07
1.44
1.09
4.00
3.09
10
9
8
7
6
5
4
3
2
1
0
ppm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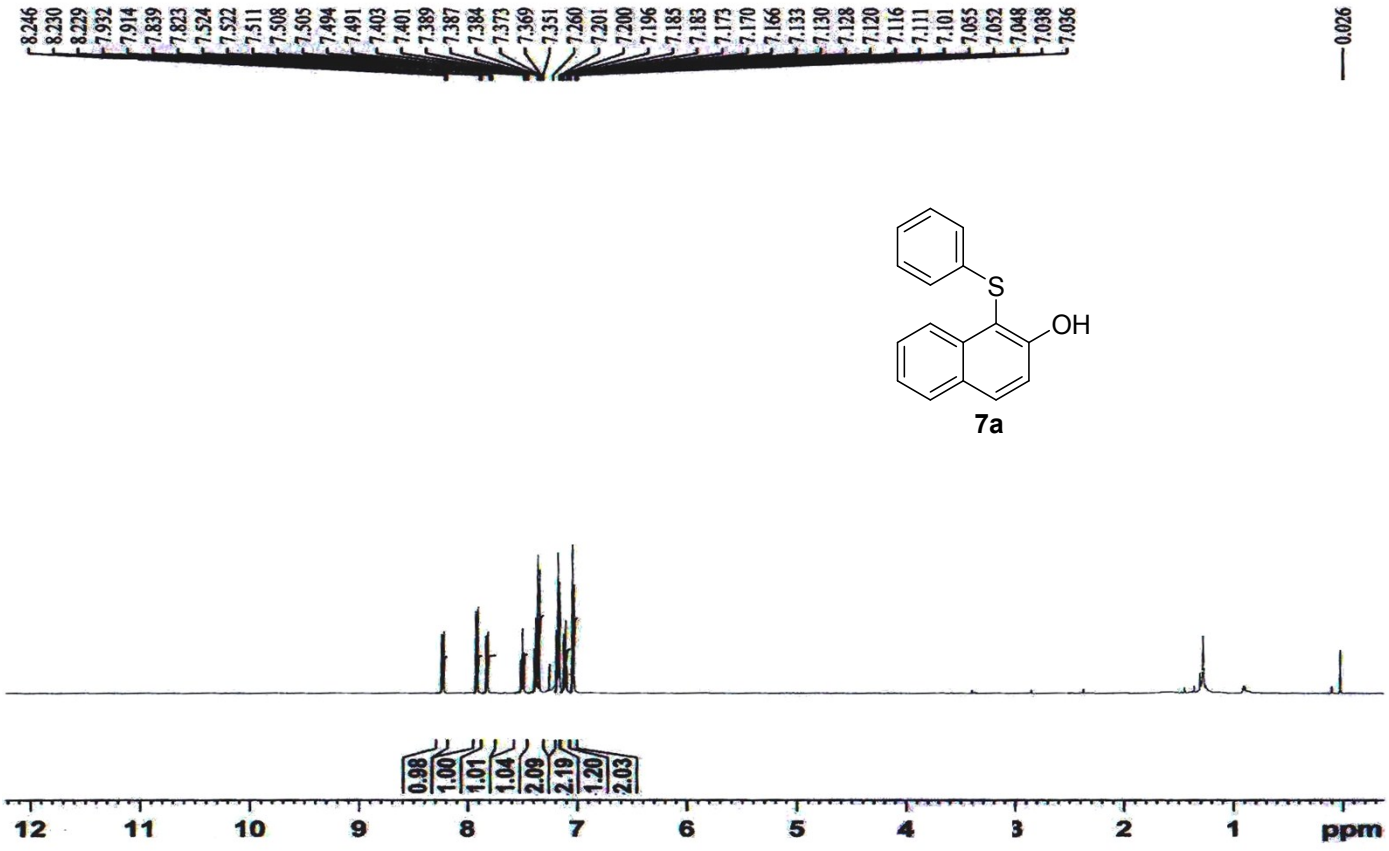
135.48
134.65
130.38
129.48
129.14
126.29
122.99
120.84
119.73
111.51
103.62
77.28
77.02
76.77
20.86
S
N
H
160
140
120
100
80
60
40
20
0
ppm

5d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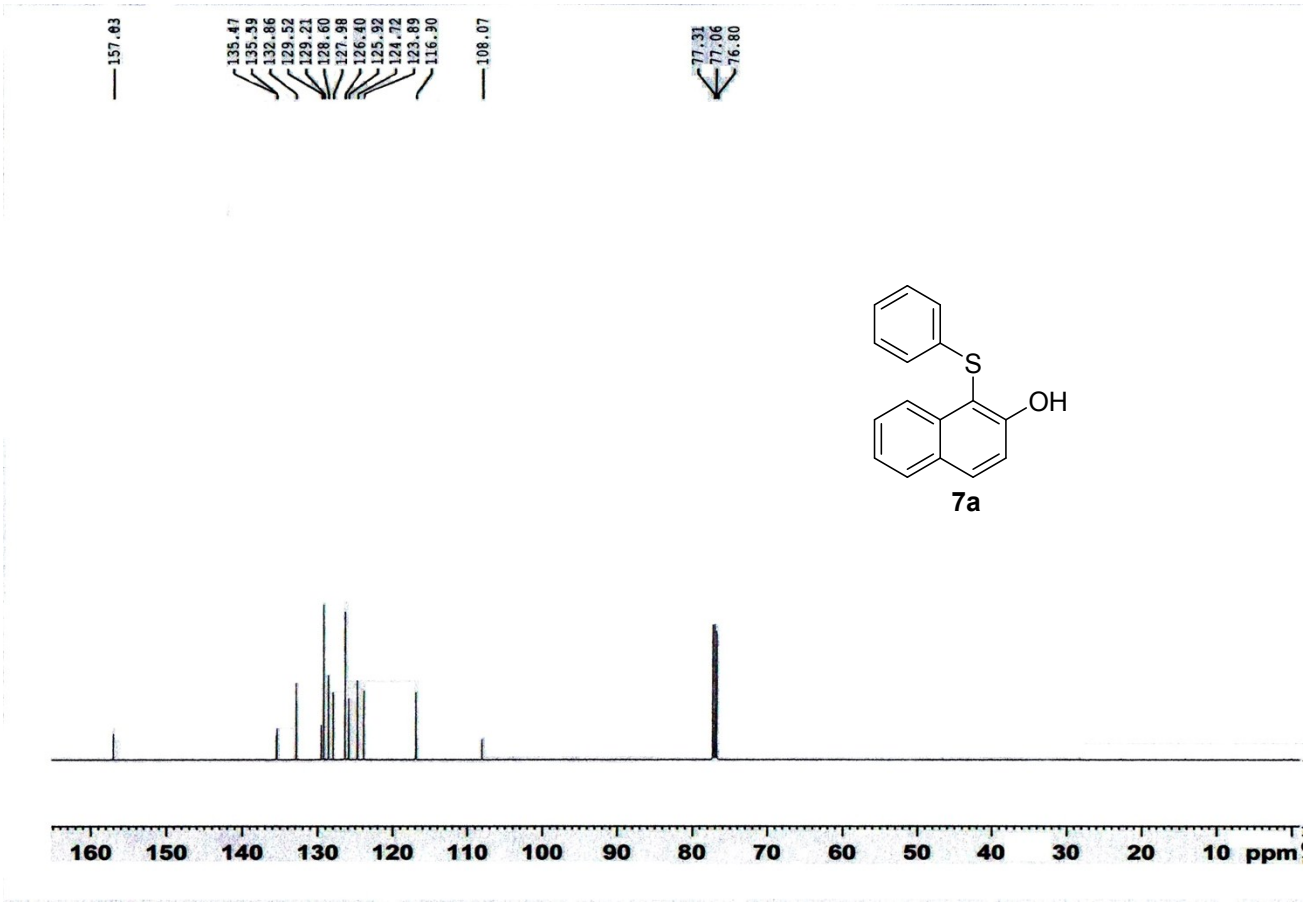
8.230
8.229
7.932
7.914
7.839
7.823
7.524
7.522
7.511
7.508
7.505
7.494
7.491
7.403
7.401
7.389
7.387
7.384
7.373
7.369
7.351
7.260
7.201
7.200
7.196
7.185
7.183
7.173
7.170
7.166
7.133
7.130
7.128
7.120
7.116
7.111
7.101
7.055
7.052
7.048
7.038
7.036
0.026
S
OH
7a
0.98
1.00
1.01
1.04
2.09
2.19
1.20
2.03
12
11
10
9
8
7
6
5
4
3
2
1
ppm


157.03
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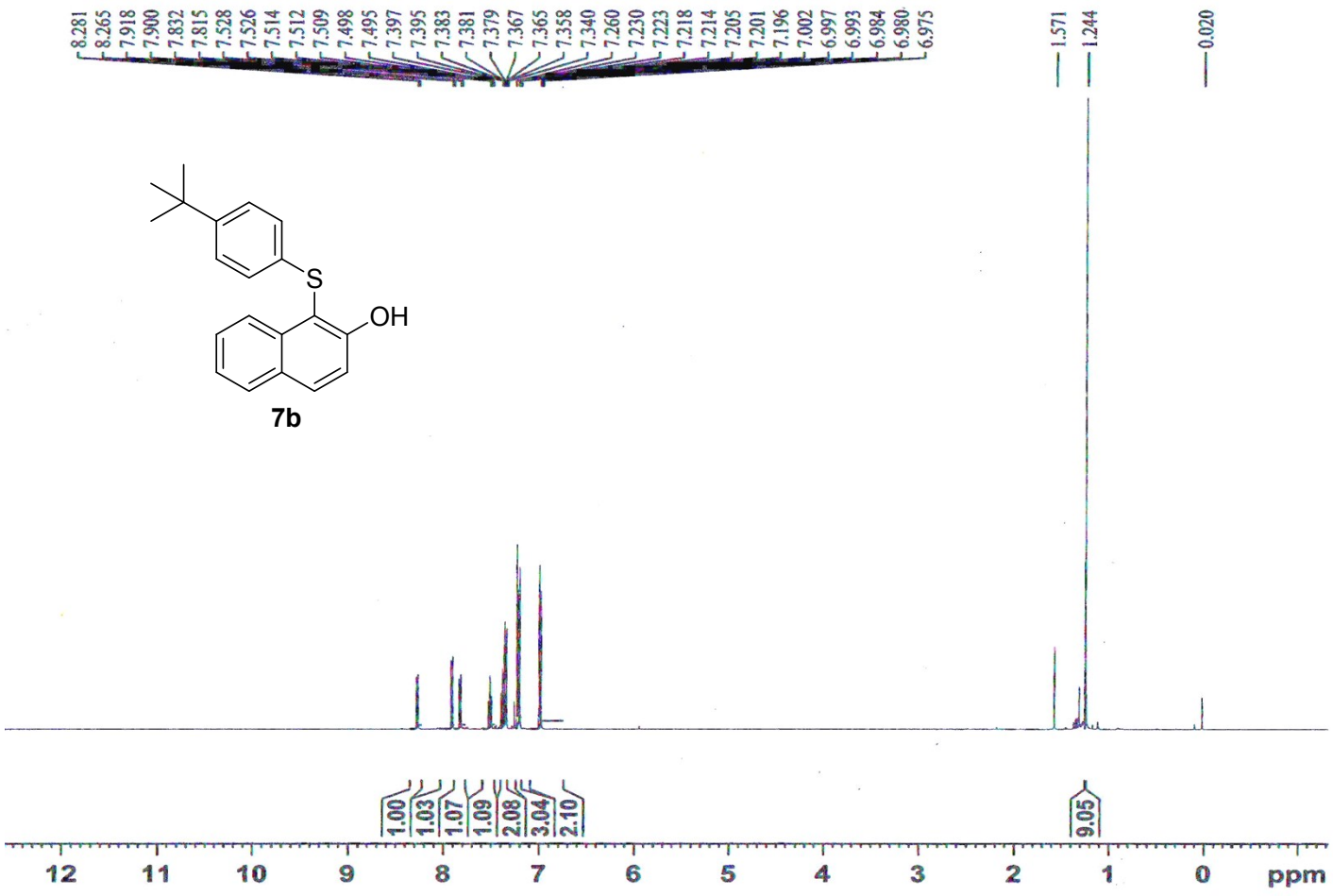
135.59
132.86
129.52
129.21
128.60
127.98
126.40
125.92
124.72
123.89
116.30
108.07
77.31
77.06
76.80
S
OH
7a
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.900
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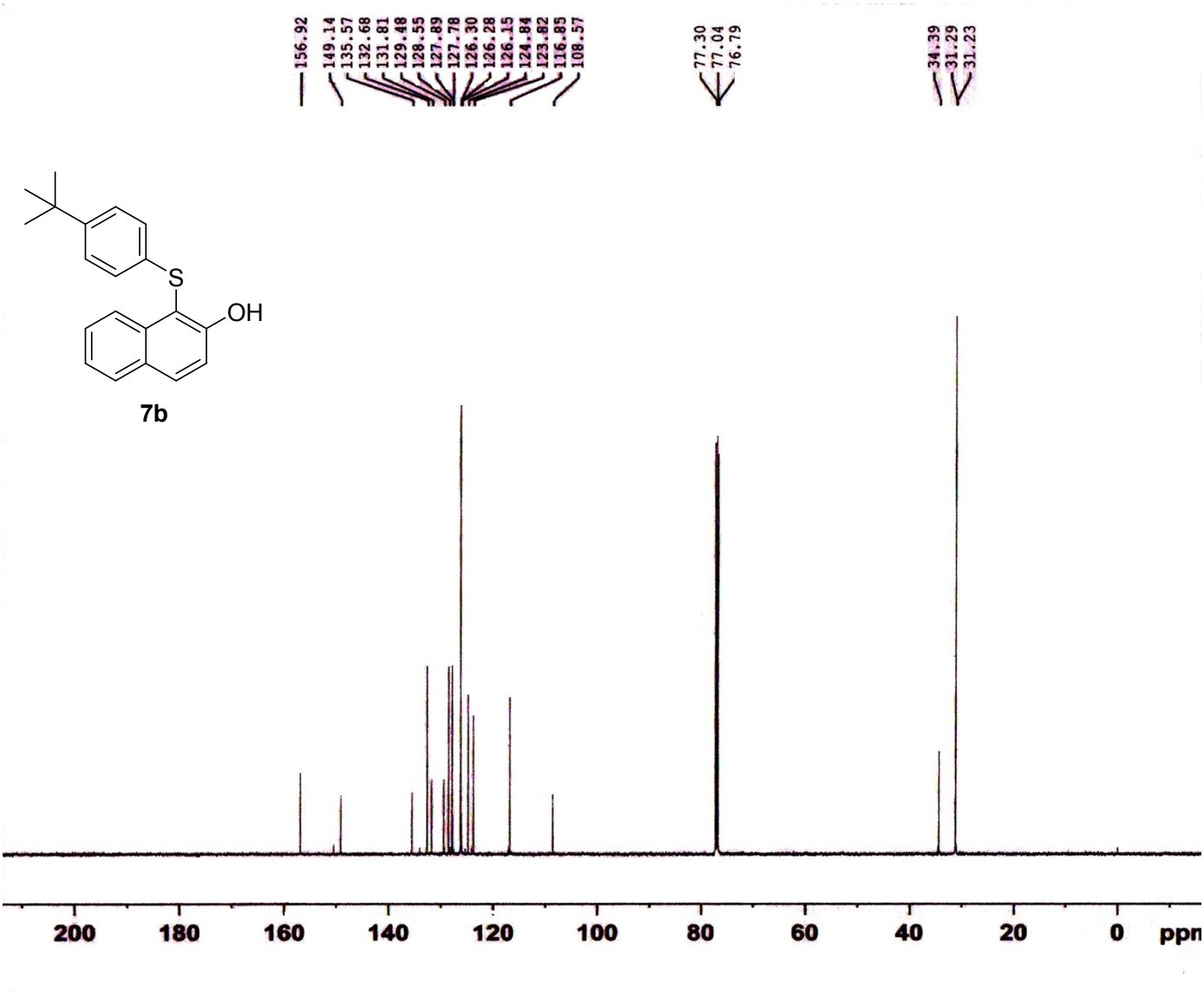
7.526
7.514
7.512
7.509
7.498
7.495
7.397
7.395
7.383
7.381
7.379
7.367
7.365
7.358
7.340
7.260
7.230
7.223
7.218
7.214
7.205
7.201
7.196
7.002
6.997
6.993
6.984
6.980
6.975
1.571
1.244
0.020
S
OH
7b
1.00
1.03
1.07
1.09
2.08
3.04
2.10
9.05
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm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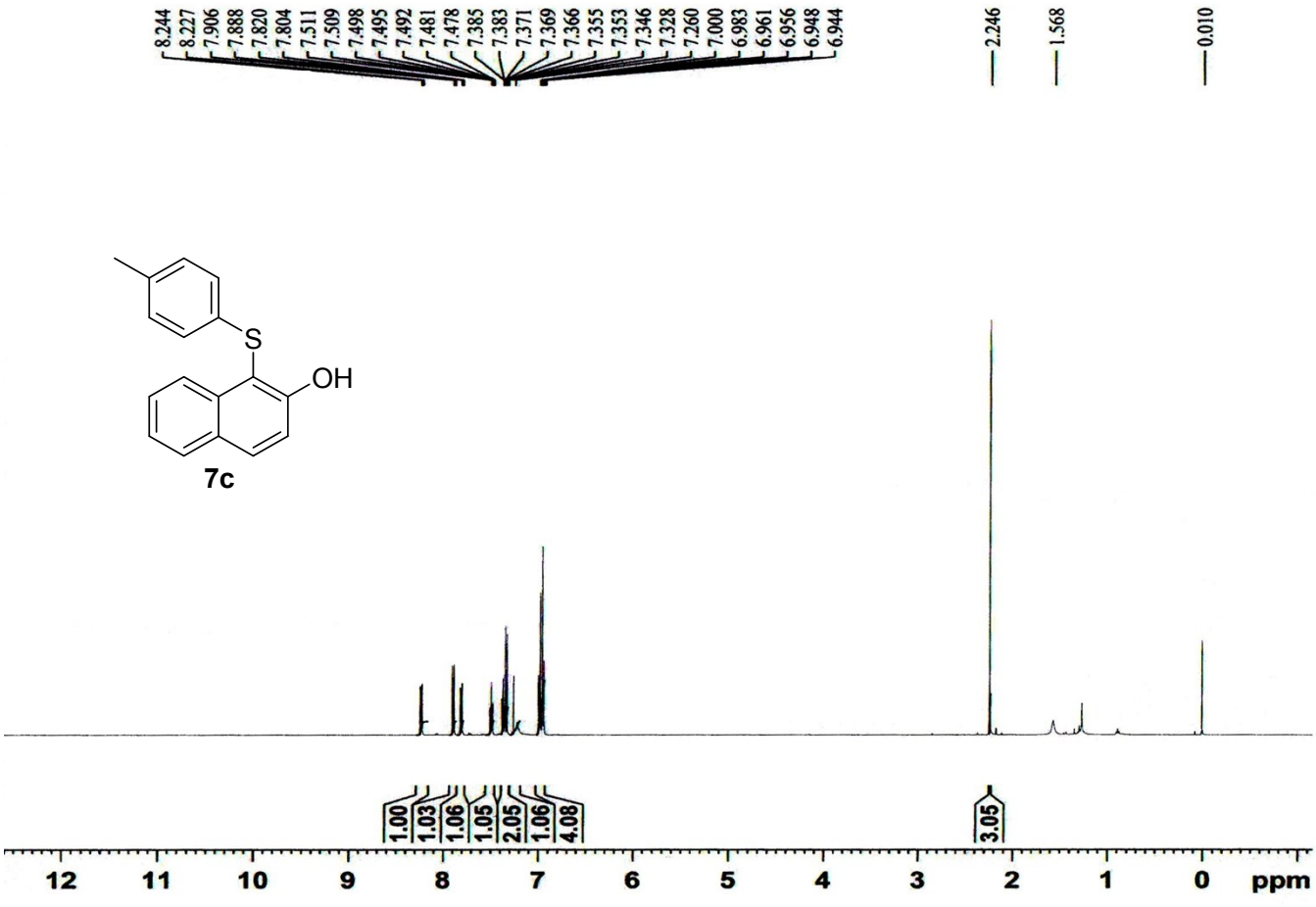
135.57
132.68
131.81
129.48
128.55
127.89
127.78
126.30
126.28
126.15
124.84
123.82
116.85
108.57
77.30
77.04
76.79
34.39
31.29
31.23
S
OH
200
180
160
140
120
100
80
60
40
20
0
ppm

7b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8.227
7.906
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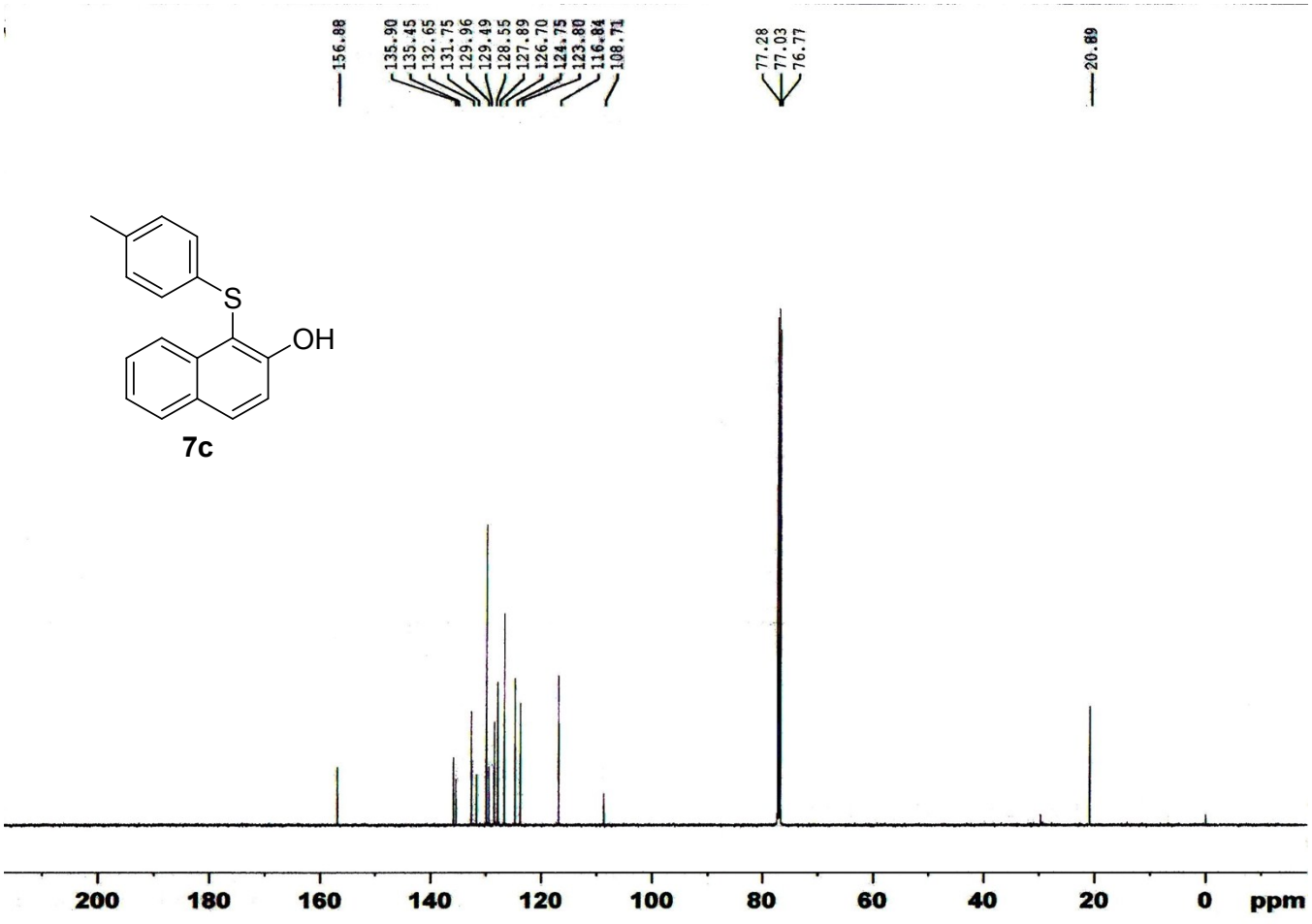
7.820
7.804
7.511
7.509
7.498
7.495
7.492
7.481
7.478
7.385
7.383
7.371
7.369
7.366
7.355
7.353
7.346
7.328
7.260
7.000
6.983
6.961
6.956
6.948
6.944
2.246
1.568
0.010
S
OH
7c
1.00
1.03
1.06
1.05
2.05
1.06
4.08
3.05
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm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131.75
129.96
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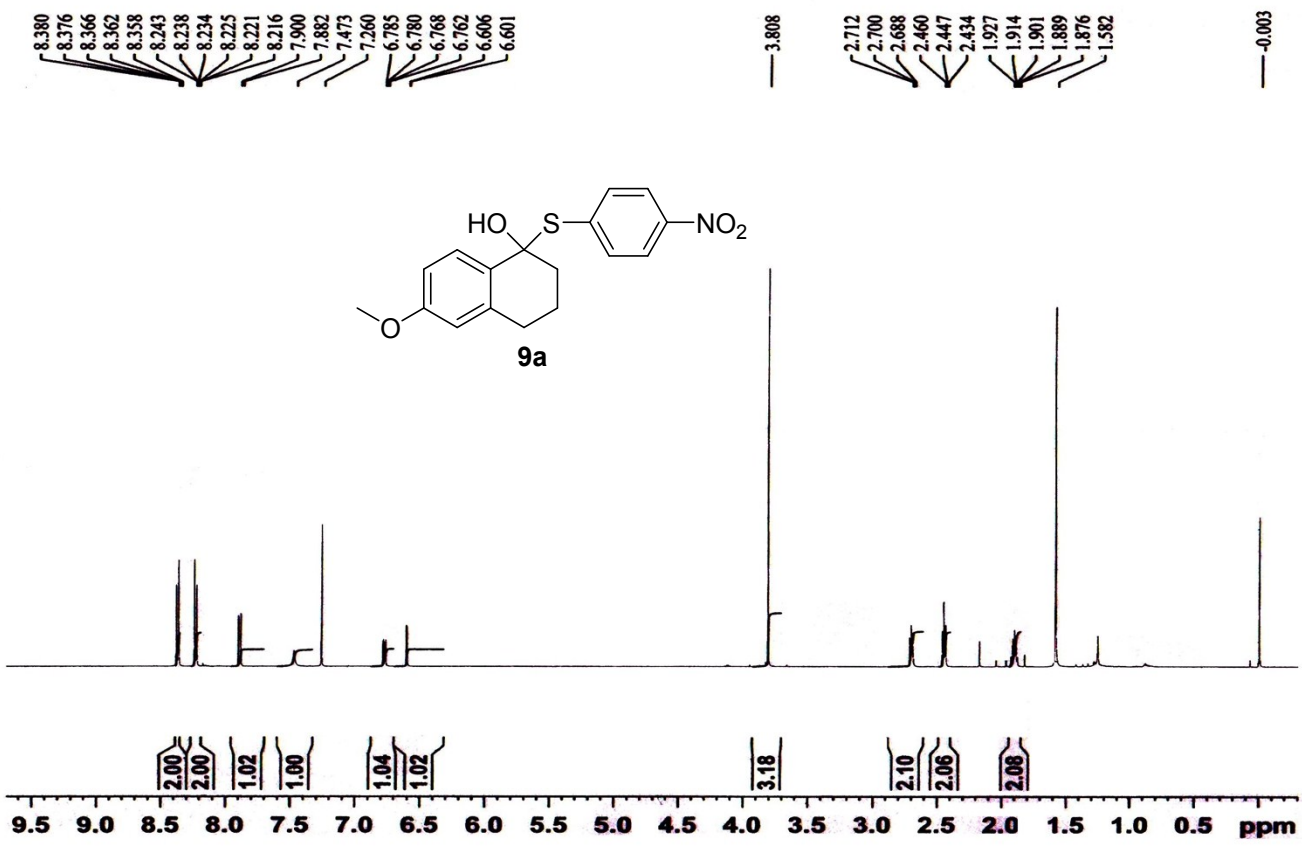
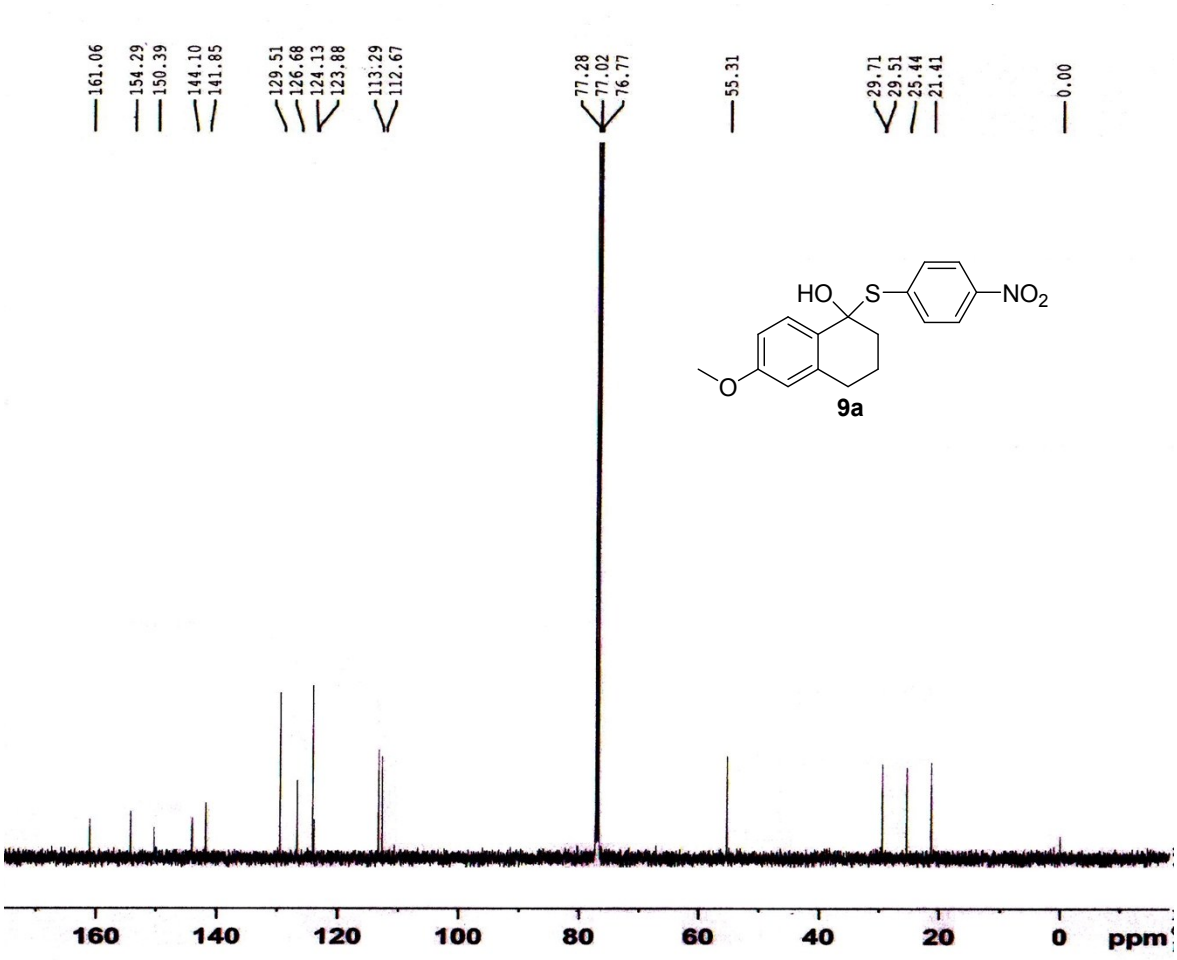
128.55
127.89
126.70
124.75
123.80
116.84
108.71
77.28
77.03
76.77
20.89
S
OH
200
180
160
140
120
100
80
60
40
20
0
ppm

7c


8.380
8.376
8.366
8.362
8.358
8.243
8.238
8.234
8.225
8.221
8.216
7.900
7.882
7.473
7.260
6.785
6.780
6.768
6.762
6.606
6.601
3.808
2.712
2.700
2.688
2.460
2.447
2.434
1.927
1.914
1.901
1.889
1.876
1.582
-0.003
HO
S
NO2
O
9a
2.00
2.00
1.02
1.00
1.04
1.02
3.18
2.10
2.06
2.08
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 ppm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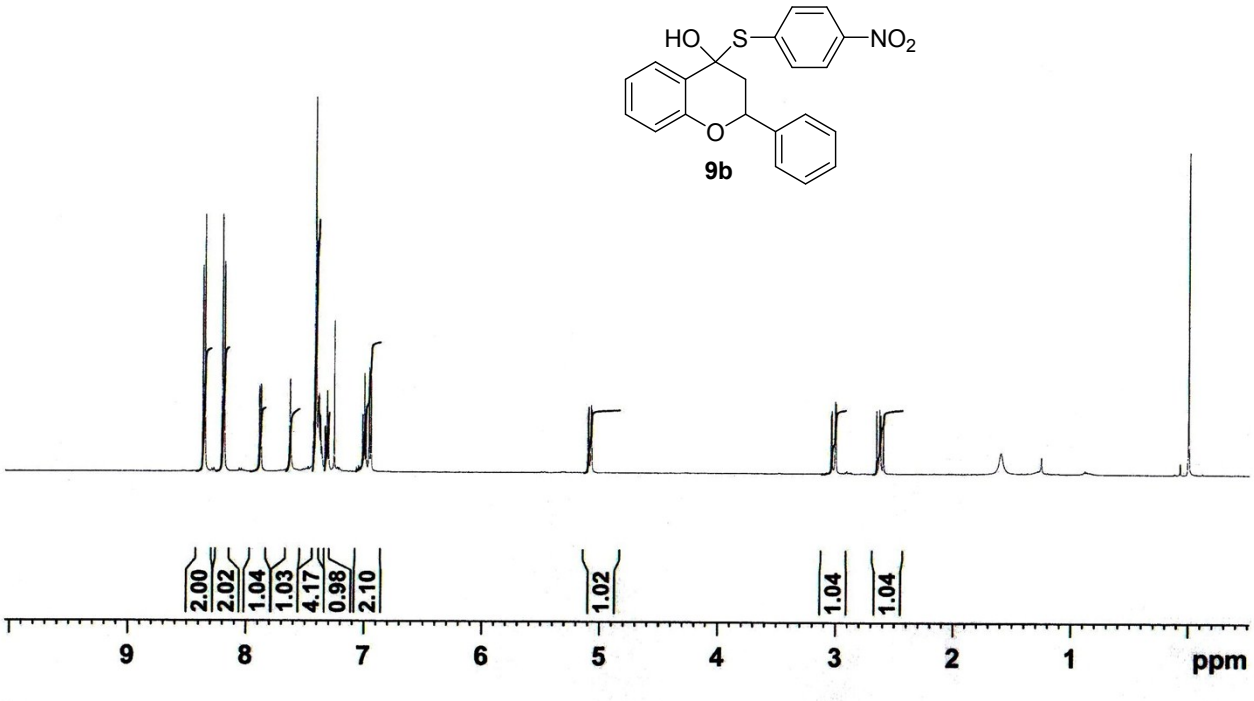
154.29
150.39
144.10
141.85
129.51
126.68
124.13
123.88
113.29
112.67
77.28
77.02
76.77
55.31
29.71
29.51
25.44
21.41
0.00
HO
S
NO2
O
9a
160
140
120
100
80
60
40
20
0
ppm


8.369
8.365
8.355
8.351
8.205
8.201
8.190
8.187
7.893
7.890
7.877
7.874
7.633
7.436
7.424
7.420
7.411
7.400
7.397
7.395
7.392
7.387
7.382
7.376
7.374
7.337
7.334
7.323
7.320
7.318
7.306
7.303
7.258
7.021
7.019
7.004
6.990
6.988
6.964
6.962
6.947
6.946
5.105
5.099
5.080
5.074
3.041
3.035
3.008
3.002
2.656
2.631
2.623
2.598
-0.000


HO
S
NO2
O
9b
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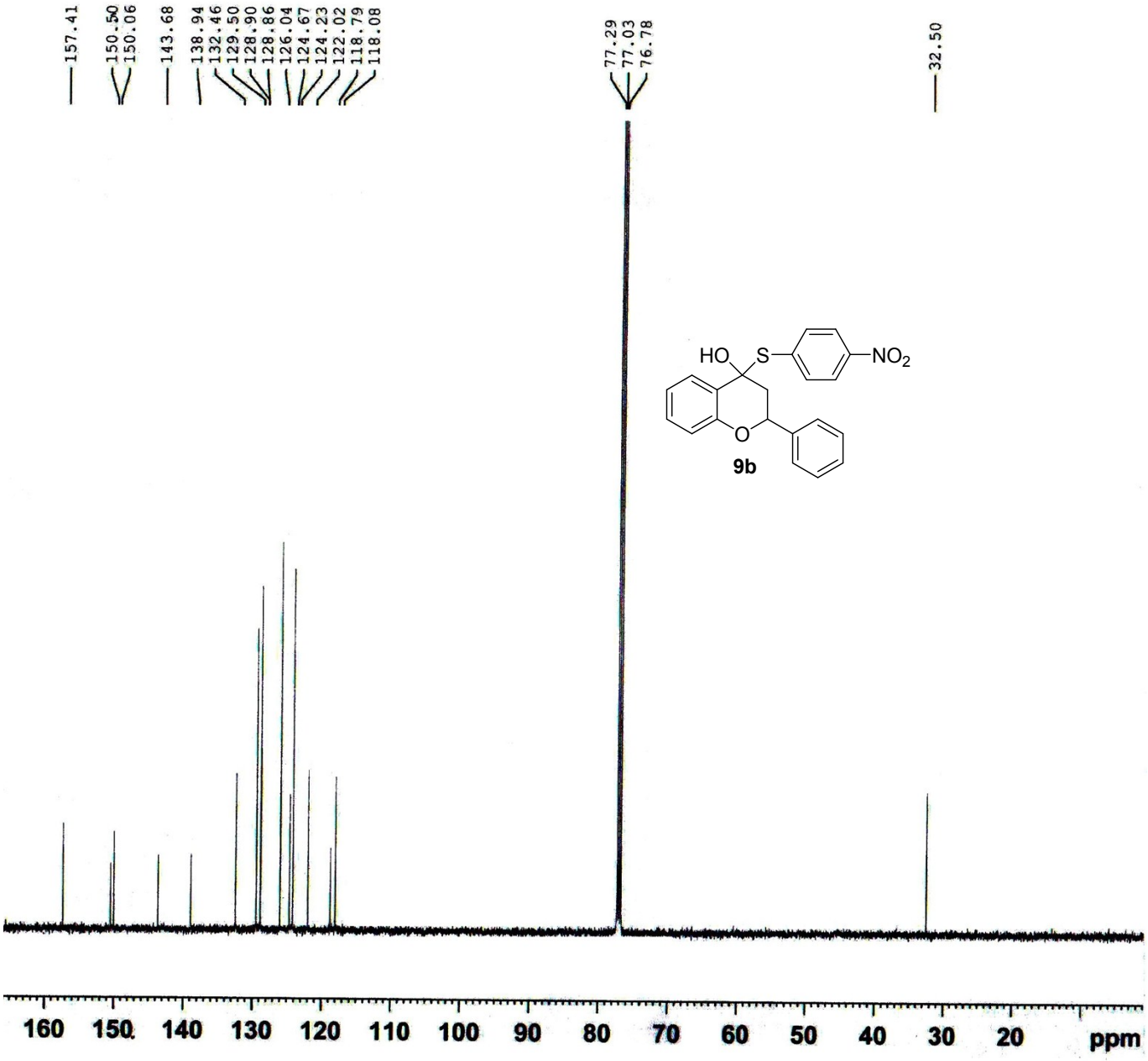
2.02
1.04
1.03
4.17
0.98
2.10
1.02
1.04
1.04
9
8
7
6
5
4
3
2
1
ppm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150.06
143.68
138.94
132.46
129.50
128.90
128.86
126.04
124.67
124.23
122.02
118.79
118.08
77.29
77.03
76.78
32.50
HO
S
NO2
O
9b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm