Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

An iodine-mediated new avenue to sulfonylation employing *N*-hydroxy aryl sulfonamide as a sulfonylating agent

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General Experimental:

All the reactions were carried out in 15 mL Ace-pressure tube with constant stirring using a Teflon-coated magnetic stirring bar. The reaction's heating source is a magnetic stirrer equipped with an oil bath and a temperature controller. Flash chromatography was performed using Merck silica gel (230-400 mesh). Thin-layer chromatography (TLC) was performed using Merck GF254 plates (thickness 0.25 mm). Visualization of spots on TLC plate was accomplished with UV. The chromatographic solvents are mentioned as v/v ratios. All the synthesized compounds were fully characterized by ^{1}H, ^{13}C NMR, and further confirmed through ESI-MS and HRMS analyses. High resolution mass spectrometry (HRMS) was recorded on a SCIEX X 500R QTOF (TOF-MS) system with turbo V ion source with twin sprayer ESI probe and twin sprayer APCI probe. NMR spectra were recorded with Bruker 500 MHz spectrometers for ^{1}H NMR, 125 MHz for ^{13}C NMR respectively. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H), $CDCl_3$ and DMSO-D_6 (^{13}C) as internal standards. Integrals are in accordance with assignments; coupling constants are given in Hz. Product yields refer to isolated yields after flash chromatography.

Reagents:

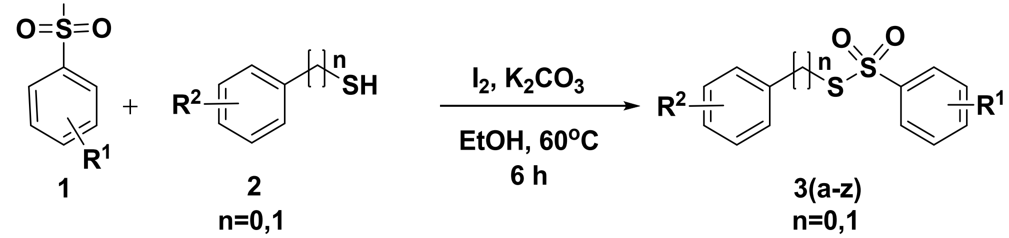
All the chemicals, including thiophenol derivatives, iodine, hydroxylamine hydrochloride, potassium carbonate, sulfonyl chloride derivatives, and other chemicals, were procured from Sigma Aldrich, Alfa Aesar and TCI Chemicals and were used as received.

Experimental Procedure

Synthesis of N-hydroxy sulfonamide:

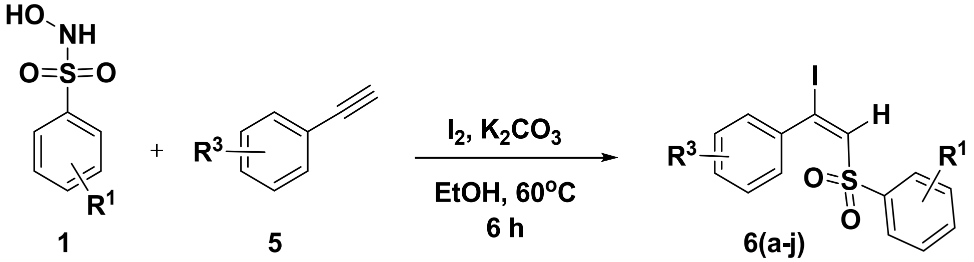
N-oxides was prepared by the reported procedure.[1]

General Procedure for the Synthesis of Thiosulfonatesfrom thiophenol



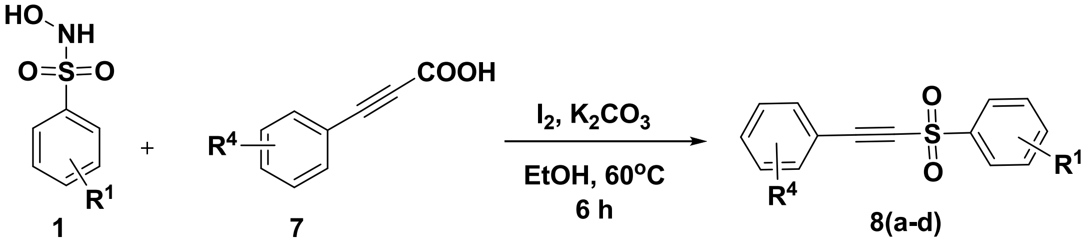
A mixture of thiophenol (1 mmol), N-hydroxy sulphonamide (1.5 mmol), iodine (1 mmol) and K_2CO_3 (1 mmol) in EtOH (3mL), placed in a 15-mL Ace-pressure tube under aerobic condition, was stirred at 60°C in an oil bath for the time 6 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was quenched by the addition of a saturated sodium thiosulfate solution. The resulting mixture was extracted with ethyl acetate (3×20 mL) and the combined organic layer was washed with water, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography.

General Procedure for the Synthesis of β-Iodovinyl Sulfones from Terminal Alkyne



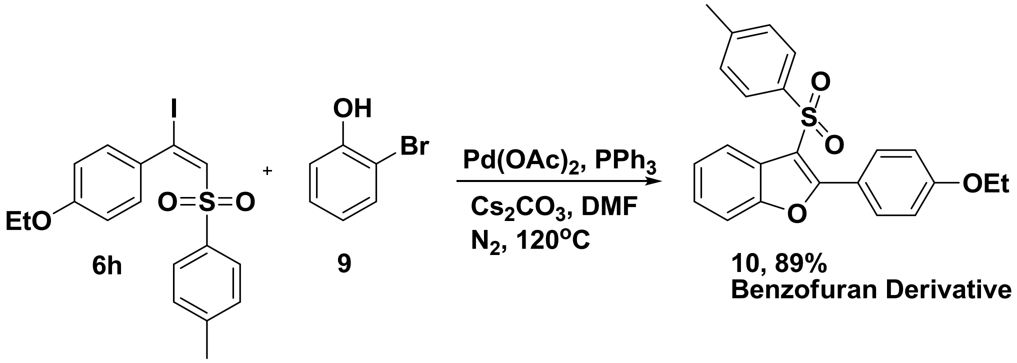
A mixture of alkynes (1 mmol), N-hydroxy sulphonamide (1.5 mmol), iodine (1.5 mmol) and K_2CO_3 (1 mmol) in EtOH (3mL), placed in a 15-mL Ace-pressure tube under aerobic condition, was stirred at 60°C in an oil bath for the time 6 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was quenched by the addition of a saturated sodium thiosulfate solution. The resulting mixture was extracted with ethyl acetate (3×20 mL) and the combined organic layer was washed with water, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography.

General Procedure for the Synthesis of Acetylenic Sulfones from Arylacetylenic acids



A mixture of Arylacetylenic acids (1 mmol), N-hydroxy sulphonamide (1.5 mmol), iodine (1 mmol) and K_2CO_3 (1 mmol) in EtOH (3mL), placed in a 15-mL Ace-pressure tube under arobic condition, was stirred at 60°C in oil bath for the time 6 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was quenched by the addition of a saturated sodium thiosulfate solution. The resulting mixture was extracted with ethyl acetate (3×20 mL) and the combined organic layer was washed with water, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography.

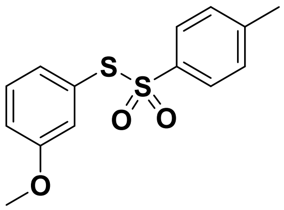
General Procedure for the Synthesis of 3-sulfonyl benzofuranderivative 10



A mixture of **6h** (1 mmol), 2-bromophenol **9** (1.5 mmol), palladium acetate (10 mol%), triphenylphosphine (20 mol%), and Cs_2CO_3 (2 mmol) in DMF (3mL), placed in a 25-mL round bottom flask, was stirred at 120°C under nitrogen atmosphere for the time 6 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature progress, and the mixture was quenchedby the addition of water (20 mL) followed by extraction withEtOAc (3×30 mL). The combined organic layers were washed with brine (3×30 mL) and dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flashchromatography (silica gel 230–400 mesh,eluted with 20% to 25% ethyl acetate/hexane).

Spectral data of the compounds:

1. **S-3-methoxyphenyl 4-methylbenzenesulfonothioate (3a)[2]**

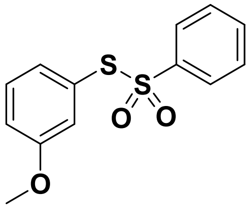


^{1}H NMR (500 MHz, CDCl$_3$) δ = 2.40 (s, 3H), 3.71 (s, 3H), 6.86-6.87 (m, 1H), 6.91-6.93 (m, 1H), 6.98-7.00 (m, 1H), 7.20-7.23 (m, 3H), 7.46-7.47 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 21.63, 55.40, 118.02, 120.88, 127.69, 128.73, 128.81, 129.38, 130.06, 140.34, 144.75, 159.85.

ESI-MS ($C_{14}H_{14}O_3S_2$): 295 [M+H]$^+$.

2. **S-3-methoxyphenyl benzenesulfonothioate (3b)[3]**

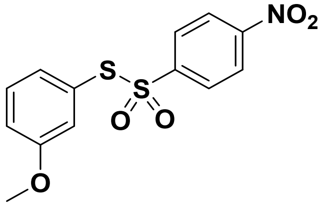


^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.70 (s, 3H), 6.84-7.00 (m, 3H), 7.20-7.23 (m, 1H), 7.41-7.44 (m, 2H), 7.56-7.59 (m, 3H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 55.44, 118.14, 120.84, 127.65, 128.76, 128.84, 130.14, 133.68, 136.59, 142.93, 159.87.

ESI-MS ($C_{13}H_{12}O_3S_2$): 281 [M+H]$^+$.

3. **S-3-methoxyphenyl 4-nitrobenzenesulfonothioate (3c)**

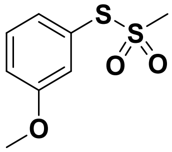


^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.79 (s, 3H), 6.90 (d, *J*=7.5 Hz, 1H), 6.98-6.99 (m, 1H), 7.06-7.08 (m, 1H), 7.28 (d, *J*=8.5 Hz, 1H), 7.78 (d, *J*=9.0 Hz, 2H), 8.28 (d, *J*=9.0 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 55.56, 118.29, 121.23, 124.10, 127.66, 128.41, 128.81, 130.48, 147.93, 150.41, 160.20.

HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{13}H_{11}NO_5S_2$: 326.0112, found: 326.0102.

4. **S-3-methoxyphenyl methanesulfonothioate (3d)**

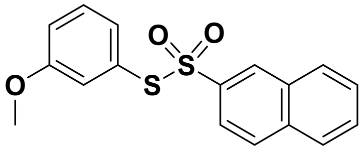


^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.19(s, 3H), 3.84 (s, 3H), 7.06-7.08 (m, 1H), 7.23-7.28 (m, 2H), 7.36-7.39 (m, 1H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 47.49, 55.59, 117.81, 121.10, 128.15, 128.74, 130.56, 160.26.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_8H_{10}O_3S_2$: 219.0171, found: 219.0142.

5. **S-3-methoxyphenyl naphthalene-2-sulfonothioate (3e)**

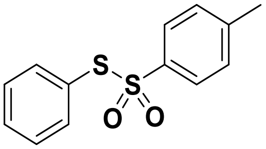


^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.52 (s, 3H), 6.78-6.79 (m, 1H), 6.88-6.90 (m, 1H), 6.96-6.98 (m, 1H), 7.14-7.17 (m, 1H), 7.56-7.59 (m, 1H), 7.63-7.70 (m, 2H), 7.78-7.80 (m, 1H), 7.88-7.92 (m, 2H), 7.97 (d, *J*=1.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 55.26, 118.25, 120.78, 122.43, 127.81, 127.94, 128.79, 128.83, 129.34, 129.46, 129.49, 130.11, 131.55, 135.11, 139.45, 159.84.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{14}O_3S_2$: 331.0418, found: 331.0417.

6. **S-phenyl 4-methylbenzenesulfonothioate (3f)^2**

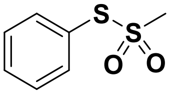


^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.43 (s, 3H), 7.21-7.22 (m, 2H), 7.33-7.39 (m, 4H), 7.44-7.50 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.69, 127.59, 128.01, 129.41, 129.43, 130.23, 131.36, 136.60, 140.26, 144.78.

ESI-MS ($C_{13}H_{12}O_2S_2$): 265 $[M+H]^+$.

7. **S-phenyl methanesulfonothioate(3g)^4**

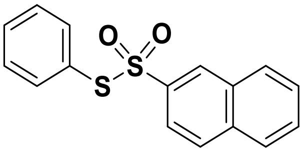


^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.18 (s, 3H), 7.46-7.56 (m, 3H), 7.70-7.73 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 47.44, 127.98, 129.92, 131.66, 136.24.

ESI-MS ($C_7H_8O_2S_2$): 188 $[M+H]^+$.

8. **S-phenyl naphthalene-2-sulfonothioate (3h)^5**

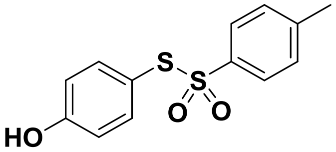


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.26-7.29 (m, 2H), 7.32-7.34 (m, 2H), 7.43.7.46 (m, 1H), 7.56-7.59 (m, 1H), 7.64-7.68 (m, 2H), 7.76-7.86 (m, 1H), 7.89-7.91 (m, 2H), 7.95 (d, *J*=1.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ =122.36, 127.80, 127.98, 128.03, 129.05, 129.32, 129.37, 129.39, 129.46, 129.48, 129.56, 131.49, 131.56, 135.12, 136.65, 139.56.

ESI-MS ($C_{16}H_{12}O_2S_2$): 301 $[M+H]^+$.

9. S-4-hydroxyphenyl 4-methylbenzenesulfonothioate (3i)[8]

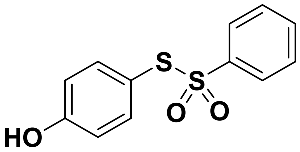


^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.41 (s, 3H), 3.50 (s, 1H), 6.76 (d, *J*=8.5 Hz, 2H), 7.19-7.23 (m, 4H), 7.45 (d, *J*=8.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.65, 116.67, 118.20, 127.63, 129.47, 138.59, 140.10, 144.78, 159.24.

ESI-MS ($C_{13}H_{12}O_3S_2$): 281 [M+H]$^+$.

10. S-4-hydroxyphenyl benzenesulfonothioate(3j)[3,4]

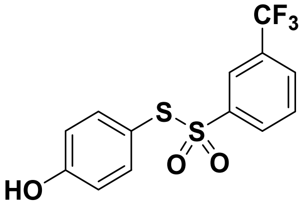


^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.50 (s, 1H), 6.75-6.78 (m, 2H), 7.18-7.20 (m, 2H), 7.42-7.45 (m, 2H), 7.56-7.59(m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ =116.69, 118.06, 127.60, 128.87, 133.65, 138.60, 142.82, 159.27.

ESI-MS ($C_{12}H_{10}O_3S_2$): 265 [M-H]$^+$.

11. S-4-hydroxyphenyl 3-(trifluoromethyl)benzenesulfonothioate (3k)

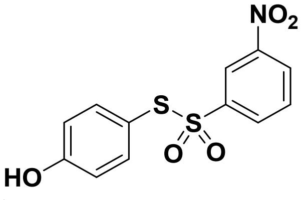


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29-7.34 (m, 3H), 7.38-7.47 (m, 3H), 7.53-7.57 (m, 2H).

13C NMR (125 MHz, $CDCl_3$) δ = 127.54, 127.84, 127.97, 128.86, 129.23, 129.29, 129.48, 129.76, 131.47, 133.73, 136.57, 142.95.

HRMS (ESI): m/z [M]$^+$ calcd for $C_{13}H_9F_3O_3S_2$: 333.9945, found: 333.9938.

12. S-4-hydroxyphenyl 3-nitrobenzenesulfonothioate(3l)

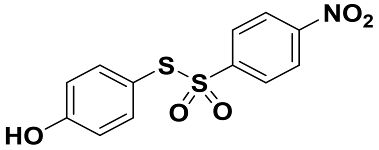


^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.50 (s, 1H), 6.75-7.77 (m, 2H), 7.32-7.39 (m, 3H), 7.63-7.66 (m, 1H), 8.23-8.30 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 116.51, 126.03, 126.10, 126.36, 127.47, 131.77, 134.14, 137.52, 145.37, 156.29.

HRMS (ESI): m/z [M+Na]$^+$calcd for $C_{12}H_9NO_5S_2$: 333.9820, found: 333.9815.

13. S-4-hydroxyphenyl 4-nitrobenzenesulfonothioate (3m)

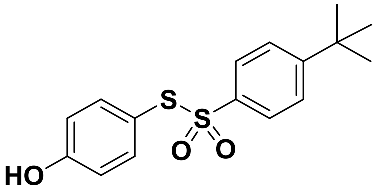


^{1}H NMR (500 MHz, $CDCl_3$+DSMO) δ = 6.66-6.74 (m, 2H), 7.01-7.07 (m, 2H), 7.60-7.65 (m, 2H), 8.13-8.18 (m, 2H), 9.60 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$+DSMO) δ = 115.24, 117.13, 123.99, 128.77, 138.29, 147.89, 150.23, 161.40.

HRMS (ESI): m/z $[M+Na]^+$calcd for $C_{12}H_9NO_5S_2$: 333.9820, found: 333.9815.

14. S-4-hydroxyphenyl 4-tert-butylbenzenesulfonothioate (3n)

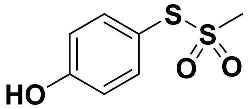


^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.32 (s, 9H), 6.76-6.78 (m, 2H), 7.18 (d, *J*=8.5 Hz, 2H), 7.43 (d, *J*=8.5 Hz, 2H), 7.50 (d, *J*=8.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 31.05, 35.33, 116.74, 117.94, 125.91, 127.47, 138.62, 139.81, 157.93, 159.39.

HRMS (ESI): m/z $[M+H]^+$calcd for $C_{16}H_{18}O_3S_2$: 323.0731, found: 323.0760.

15. S-4-hydroxyphenyl methanesulfonothioate (3o)

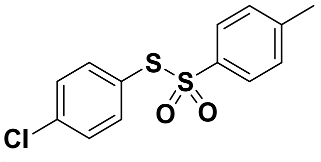


^{1}H NMR (500 MHz, $CDCl_3$+CD_3OD) δ = 3.18 (s, 3H), 6.91-6.93 (m, 2H), 7.52-7.55 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$+CD_3OD) δ = 46.16, 116.29, 116.68, 133.04, 137.92, 160.54

HRMS (ESI): m/z $[M+H]^+$calcd for $C_7H_8O_3S_2$: 204.9915, found: 204.9937 and m/z $[M+Na]^+$calcd for $C_7H_8O_3S_2$: 226.9817, found: 226.9806.

16. S-4-chlorophenyl 4-methylbenzenesulfonothioate (3p)[2]

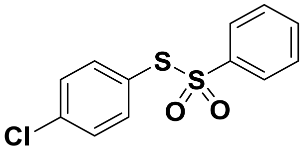


^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.49 (s, 3H), 7.22 (d, *J*=8.0 Hz, 2H), 7.28-7.32 (m, 4H), 7.46-7.47 (dd,J_1=2.0 Hz, J_2=7.0 Hz,2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.67, 126.58, 127.62, 129.53, 129.70, 137.71, 138.19, 140.25, 145.0.

ESI-MS ($C_{13}H_{11}ClO_2S_2$): 320 $[M+Na]^+$.

17. S-4-chlorophenyl benzenesulfonothioate (3q)[4]

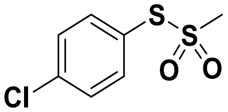


^{1}H NMR (500 MHz, CDCl$_3$) δ = 7.27-7.32 (m, 4H), 7.43-7.46 (t, *J*= 7.5 Hz, 2H), 7.58-7.61 (m, 3H)

^{13}C NMR (125 MHz, CDCl$_3$) δ = 126.38, 127.58, 128.95, 129.75, 133.84, 137.71, 138.32, 142.93

ESI-MS ($C_{12}H_9ClO_2S_2$): 285 $[M+H]^+$.

18. S-4-chlorophenyl methanesulfonothioate (3r)[4]

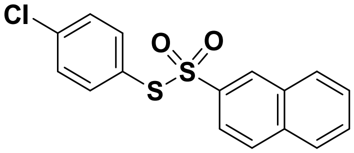


^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.19 (s, 3H), 7.45-7.47 (m, 2H), 7.62-7.65 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 47.62, 126.38, 130.22, 137.37, 138.58.

ESI-MS ($C_7H_7ClO_2S_2$): 244 $[M+Na]^+$.

19. S-4-chlorophenyl naphthalene-2-sulfonothioate (3s)

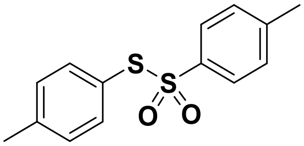


^{1}H NMR (500 MHz, CDCl$_3$) δ = 7.60-7.70 (m, 4H), 7.83-7.84 (m, 2H), 7.90-7.94 (m, 3H), 8.00 (d, *J*=1.5 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 122.29, 126.51, 127.92, 127.99, 129.32, 129.50, 129.57, 129.61, 129.74, 131.58, 135.19, 137.79, 138.33, 139.53.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{11}ClO_2S_2$: 334.9889, found: 334.9959.

20. S-p-tolyl 4-methylbenzenesulfonothioate (3t, 4a)[2,3]

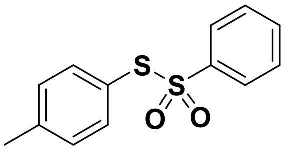


^{1}H NMR (500 MHz, CDCl$_3$) δ = 2.37 (s, 3H), 2.41 (s, 3H), 7.12 (d, *J*=8.0, 2H), 7.20-7.24(m, 4H), 7.44-7.46 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 21.50, 21.68, 124.57, 127.60, 129.38, 130.22, 136.50, 140.43, 142.08, 144.62.

ESI-MS ($C_{14}H_{14}O_2S_2$): 301 $[M+Na]^+$.

21. S-p-tolylbenzenesulfonothioate (3u)[4]

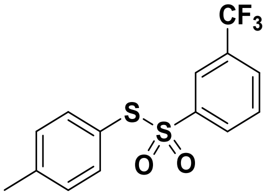


^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.37 (s, 3H), 7.12 (d, *J*=8.0, 2H), 721-7.23 (m, 2H), 7.40-7.43 (m, 2H), 7.55-7.58 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.46, 124.43, 127.57, 128.79, 129.37, 130.25, 133.53, 136.49, 142.18, 143.16.

ESI-MS ($C_{13}H_{12}O_2S_2$): 265 $[M+H]^+$.

22. S-p-tolyl 3-(trifluoromethyl)benzenesulfonothioate (3v)

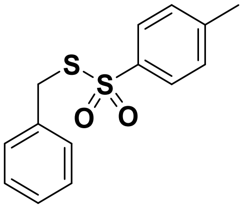


1H NMR (500 MHz, CD_3OD) δ = 2.38 (s, 3H), 7.15 (d, *J*=8.0, 2H), 7.20-7.23 (m, 2H), 7.59-7.63 (m, 2H), 7.81-8.83 (m, 2H).

^{13}C NMR (125 MHz, CD_3OD) δ = 21.40, 119.71, 121.88, 123.83, 124.05, 124.85, 124.88, 124.91, 124.94, 127.61, 129.37, 129.77, 129.99, 130.02, 130.05, 130.20, 130.49, 130.95, 131.21, 131.48, 131.75, 136.45, 142.82, 143.75.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{11}F_3O_2S_2$: 333.0186, found: 333.0225

23. S-benzyl 4-methylbenzenesulfonothioate (3w)[6,7]

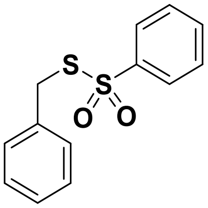


^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.43 (s, 3H), 4.25 (s, 2H), 7.13-7.28 (m, 7H), 7.72 (d, *J*=8.0, Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.63, 40.29, 127.02, 127.96, 128.78, 129.12, 129.74, 133.74, 136.51, 142.08, 144.57, 144.65.

ESI-MS ($C_{14}H_{14}O_2S_2$): 301 $[M+Na]^+$.

24. S-benzyl benzenesulfonothioate (3x)[4,7]

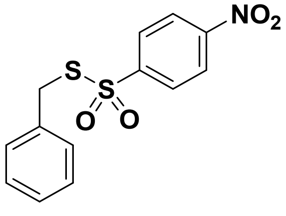


^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.27 (s, 2H), 7.16-7.23 (m, 4H), 7.33-7.49 (m, 3H), 7.55-7.60 (m, 1H), 7.82-7.84 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 40.40, 126.90, 128.04, 128.80, 129.09, 129.16, 133.51, 136.60, 144.94.

ESI-MS ($C_{13}H_{12}O_2S_2$): 265 $[M+H]^+$.

25. S-benzyl 4-nitrobenzenesulfonothioate (3y)[7]

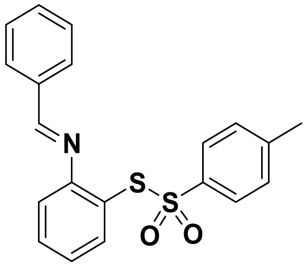


^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.34 (s, 2H), 7.15-7.21 (m, 5H), 7.84-7.86 (m, 2H), 8.18-8.21 (m, 2H)

^{13}C NMR (125 MHz, $CDCl_3$) δ = 40.98, 124.23, 127.99, 128.26, 128.83, 129.10, 133.19, 150.10, 150.17

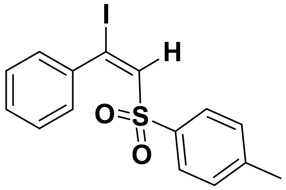
ESI-MS ($C_{13}H_{11}NO_4S_2$): 332 $[M+Na]^+$.

26. (E)-S-2-(benzylideneamino)phenyl 4-methylbenzenesulfonothioate (3z)



No reaction **(nr)**

27. (E)-1-(2-iodo-2-phenylvinylsulfonyl)-4-methylbenzene (6a)[9]

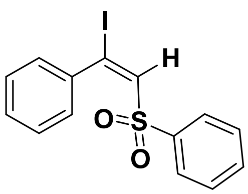


^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.39 (s, 3H), 7.17-7.23 (m, 4H), 7.26-7.31 (m, 3H), 7.35 (s, 1H), 7.44-7.46 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.62, 114.15, 127.72, 127.89, 127.92, 129.67, 129.78, 137.38, 139.69, 141.30, 144.57.

ESI-MS ($C_9H_9IO_2S$): 384 $[M+H]^+$.

28. (E)-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (6b)[9]

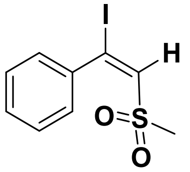


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.20-7.22 (m, 2H), 7.25-7.32 (m, 3H), 7.36-7.40 (m, 3H), 7.52-7.56 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 114.77, 127.69, 127.83, 128.00, 129.04, 129.86, 133.51, 139.60, 140.25, 141.13.

ESI-MS ($C_9H_9IO_2S$): 368 $[M-H]^+$.

29. (E)-(1-iodo-2-(methylsulfonyl)vinyl)benzene (6c)[10a]

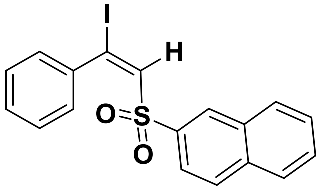


^1H NMR (500 MHz, $CDCl_3$) δ = 2.65 (s, 3H), 7.30 (s, 1H), 7.37-7.40 (m, 3H), 7.44-7.47 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 43.08, 114.88, 127.87, 128.36, 130.42, 139.47, 140.36

ESI-MS ($C_9H_9IO_2S$): 330 $[M+Na]^+$.

30. (E)-2-(2-iodo-2-phenylvinylsulfonyl)naphthalene(6d)[9]

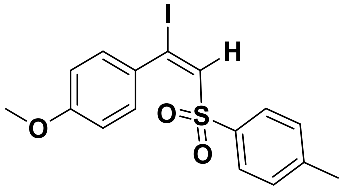


^1H NMR (500 MHz, $CDCl_3$) δ =7.17-7.25 (m, 5H), 7.46 (s, 1H), 7.55-7.66 (m, 3H), 7.77-7.78 (m, 1H), 7.85 (d, *J*=8.5 Hz, 2H), 7.99 (d, *J*=1.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 114.91, 122.41, 127.60, 127.66, 127.90, 129.36, 129.40, 129.41, 129.92, 130.02, 131.95, 135.10, 136.82, 139.48, 141.27.

ESI-MS ($C_{18}H_{13}IO_2S$): 420 $[M+H]^+$.

31. (E)-1-(2-iodo-2-(4-methoxyphenyl)vinylsulfonyl)-4-methylbenzene (6e)[9]

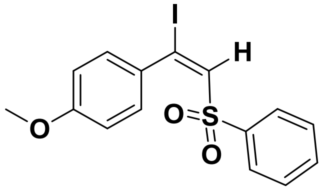


^1H NMR (500 MHz, $CDCl_3$) δ = 2.39 (s, 3H), 3.82 (s, 3H), 6.78-6.80 (m, 2H), 7.19-7.28 (m, 5H), 7.48-7.50 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.61, 55.40, 113.26, 114.87, 127.83, 129.64, 129.97, 131.89, 137.57, 140.34, 144.49, 160.87

ESI-MS ($C_{16}H_{15}IO_3S$): 412 $[M-H]^+$.

32. (E)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-4-methoxybenzene (6f)[11]

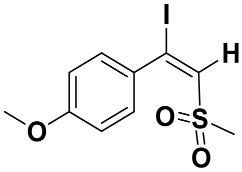


^1H NMR (500 MHz, $CDCl_3$) δ = 3.82 (s, 3H), 6.85-6.88 (m, 2H), 7.45-7.48 (m, 2H), 7.56-7.60 (m, 2H), 7.65-7.68 (m, 2H), 8.06-8.07 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 55.47, 84.65, 94.70, 109.54, 114.46, 127.28, 129.31, 133.95, 134.72, 142.18, 162.22.

ESI-MS ($C_{15}H_{13}IO_3S$): 420 [M+Na]$^+$.

33. (E)-1-(1-iodo-2-(methylsulfonyl)vinyl)-4-methoxybenzene (6g)

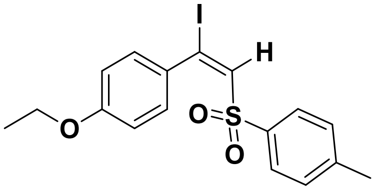


^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.27 (s, 3H), 3.84 (s, 3H), 6.86-6.92 (m, 3H), 7.50-7.53 (m, 2H)

^{13}C NMR (125 MHz, CDCl$_3$) δ = 46.91, 55.51, 109.10, 113.67, 114.59, 130.19, 134.84, 139.36

HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{10}H_{11}IO_3S$: 338.9507, found: 338.9552

34. (E)-1-ethoxy-4-(1-iodo-2-tosylvinyl)benzene (6h)[10a]

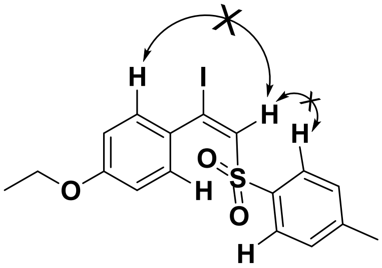


^{1}H NMR (500 MHz, CDCl$_3$) δ = 1.41-1.44 (t, *J*=7.0 Hz, 3H), 2.39 (s, 3H), 4.03-4.07 (q, *J*=7.0 Hz, 2H), 6.76-6.78 (m, 2H), 7.19-7.24 (m, 4H), 7.28 (s, 1H), 7.48 (d, *J*=8.0 Hz, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 14.72, 21.62, 63.64, 113.71, 115.06, 127.84, 129.62, 130.00, 131.66, 137.59, 140.24, 144.44, 160.26.

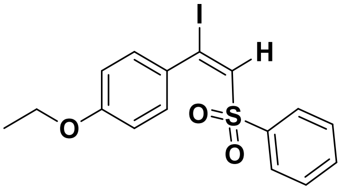
ESI-MS ($C_{17}H_{17}IO_3S$): 340 [M+Na]$^+$.

NOE of compound 6h:[10b]



To confirm the compound **6** configurations, the olefin hydrogen of the product **6h** was double irradiated and found to have no enhancement with any hydrogen of the product. It found that product **6** is E-configuration rather than Z-configuration.

35. (E)-1-ethoxy-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (6i)

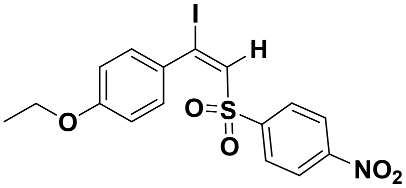


^{1}H NMR (500 MHz, CDCl$_3$) δ = 1.40-1.43 (t, *J*=7.0 Hz, 3H), 4.02-4.06 (q, *J*=7.0 Hz, 2H), 6.76 (d, *J*=9.0 Hz, 2H), 7.19-7.22 (m, 2H), 7.31 (s, 1H), 7.37-7.41(m, 2H), 7.52-7.55 (m, 1H), 7.59-7.61 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 14.73, 63.66, 113.77, 114.90, 115.65, 127.78, 128.98, 129.99, 131.58, 133.42, 140.47, 160.29.

HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{16}H_{15}IO_3S$: 414.9820, found: 414.9857.

36. (E)-1-ethoxy-4-(1-iodo-2-(4-nitrophenylsulfonyl)vinyl)benzene (6j)

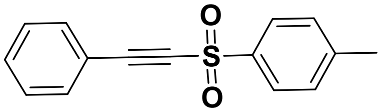


^{1}H NMR (500 MHz, CDCl$_3$) δ = 1.42-1.45 (q, *J*=7.0 Hz, 3H), 4.02-4.06 (q, *J*=7.0 Hz, 2H), 6.73-6.76 (m, 2H), 7.14-7.17 (m, 2H), 7.35 (s, 1H), 7.71-7.73(m, 2H), 8.17-8.19 (m, 2H)

^{13}C NMR (125 MHz, CDCl$_3$) δ = 14.66, 63.82, 113.88, 117.89, 124.26, 126.67, 129.17, 130.02, 131.20, 139.19, 146.08, 160.68.

HRMS (ESI): m/z [M+Na]$^+$calcd for $C_{16}H_{14}INO_5S$: 481.9671, found: 481.9648.

37. 1-methyl-4-(phenylethynylsulfonyl)benzene (8a)[11]

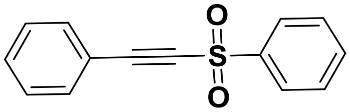


^{1}H NMR (500 MHz, CDCl$_3$) δ = 2.46 (s, 3H), 7.34-7.39 (m, 4H), 7.44-7.48 (m, 1H), 7.50-7.52 (m, 2H), 7.95-7.96 (m, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 21.72, 85.66, 92.97, 118.07, 127.50, 128.66, 129.99, 131.44, 132.72, 139.04, 145.34.

ESI-MS ($C_{15}H_{12}O_2S$): 255 [M-H]$^+$.

38. (phenylethynylsulfonyl)benzene (8b)[11]

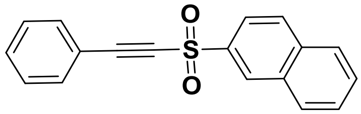


^{1}H NMR (500 MHz, CDCl$_3$) δ = 7.35-7.38 (m, 2H), 7.45-7.49 (m, 1H), 7.52-7.53 (m, 2H), 7.58-7.61 (m, 2H), 7.67-7.70 (m, 1H), 8.07-8.09 (s, 2H).

^{13}C NMR (125 MHz, CDCl$_3$) δ = 85.38, 93.50, 117.94, 127.42, 128.69, 129.37, 131.56, 132.77, 134.13, 141.90.

ESI-MS ($C_{14}H_{10}O_2S$): 243 [M+H]$^+$, 265 [M+Na]$^+$.

39. 2-(phenylethynylsulfonyl)naphthalene (8c)[11]

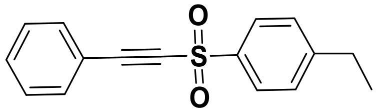


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34-7.37 (m, 2H), 7.44-7.53 (m, 3H), 7.64-7.71 (m, 2H), 7.94-8.04 (m, 4H), 8.65 (d, J=0.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 85.44, 93.76, 117.90, 122.16, 127.88, 128.07, 128.70, 129.29, 129.64, 129.71, 129.85, 131.58, 132.10, 132.79, 135.56, 138.54.

ESI-MS ($C_{18}H_{21}O_2S$): 293 $[M+H]^+$.

40. 1-ethyl-4-(phenylethynylsulfonyl)benzene (8d)

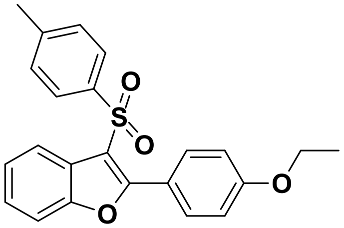


^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.26-1.29 (t, *J*=8.0 Hz, 3H), 2.73-2.78 (q, *J*=8.0 Hz, 2H), 7.35-7.46 (m, 5H), 7.51-7.53 (m, 2H), 7.97-7.99 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 15.12, 29.02, 85.56, 92.98, 118.03, 127.63, 128.68, 128.89, 131.48, 132.76, 139.02, 151.49.

HRMS (ESI): m/z $[M+H]^+$ calcd for $CC_{16}H_{14}O_2S$: 271.0748, found: 271.0776.

41. 2-(4-ethoxyphenyl)-3-tosylbenzofuran (10)[12]



^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.45-1.47 (t, *J*=7.0 Hz, 3H), 2.32 (s, 3H), 4.10-4.14 (q, *J*=7.0 Hz, 2H), 6.98-7.00 (m, 2H), 7.15 (d, *J*=8.0 Hz, 2H), 7.35-7.37 (m, 2H), 7.47-7.49 (m, 1H), 7.68 (d, *J*=8.5 Hz, 2H), 7.91-7.94 (m, 2H), 7.13-8.15 (m, 1H).

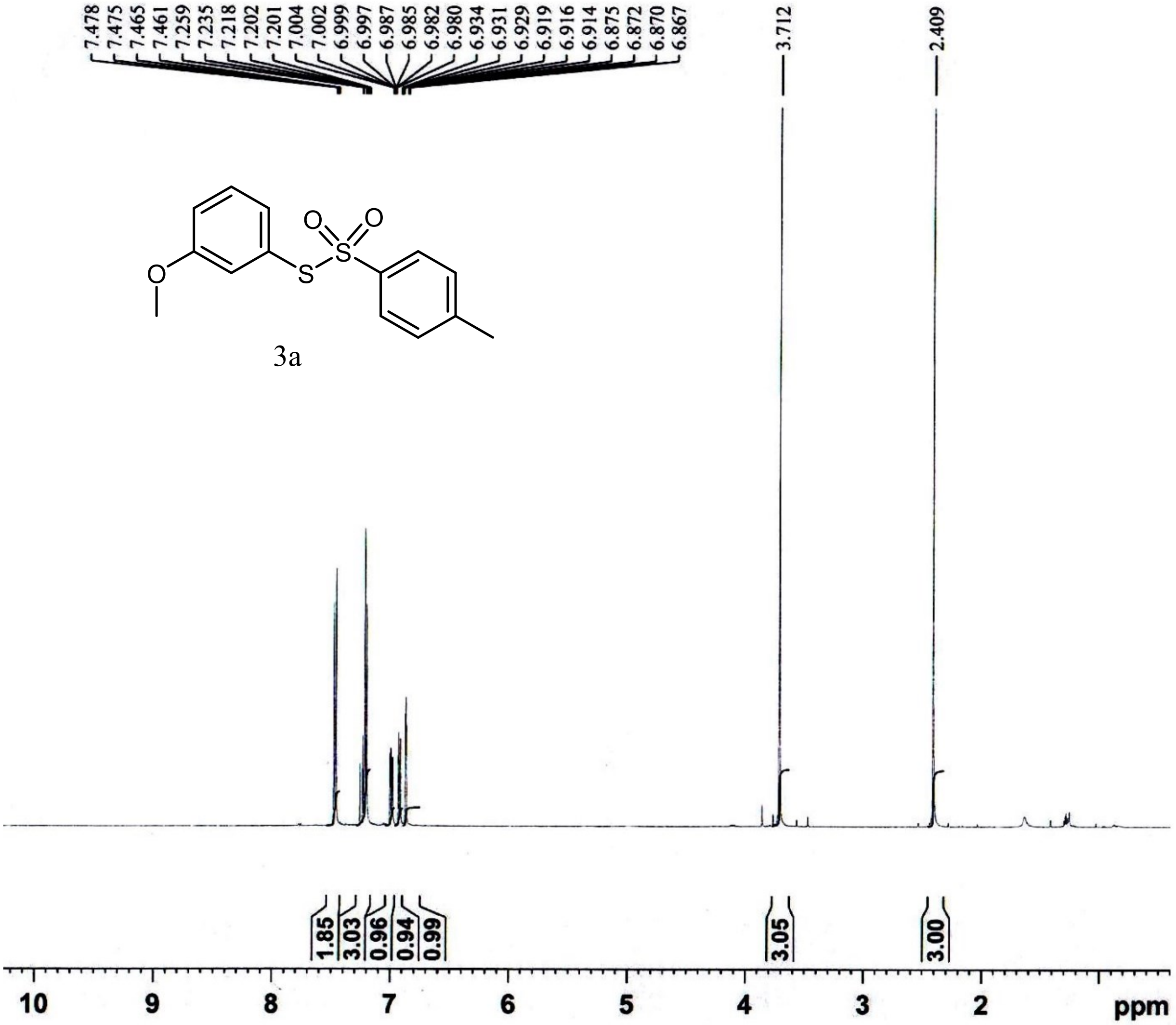
^{13}C NMR (125 MHz, $CDCl_3$) δ = 14.78, 21.55, 63.69, 111.27, 114.19, 117.27, 120.36, 121.53, 124.46, 125.59, 125.85, 126.65, 129.60, 131.79, 139.71, 144.04, 152.98, 159.07.

ESI-MS ($C_{23}H_{20}O_4S$): 393 $[M+H]^+$.

References

1. (a) S. Gupta, P. Sureshbabu, A. K. Singh, S. Sabiah and J. Kandasamy, *Tetrahedron Letters,* **2017**, *58, 909–913;* (b) L. Degennaro, A. Tota, S. De Angelis, M. Andresini, C. Cardellicchio, M. A. Capozzi, G. Romanazzi, R. Luisi, *Eur. J. Org. Chem.,* **2017,** *6486-6490*
2. G.-Y. Zhang, S.-S.Lv, A.Shoberuand J.-P. Zou, *J. Org. Chem.* 2017, **82**, 9801−9807.
3. Q. Chen, Y. Huang, X,.Wang, J.Wua and G. Yu, *Org. Biomol. Chem.*, 2018, **16**, 1713–1719.
4. P. Mampuys,Y. Zhu, S. Sergeyev, E.Ruijter, R. V. A. Orru, S. V.Doorslaer and B. U. W. Maes, *Org. Lett.* 2016, **18**, 2808−2811.

5. Z. Peng, X. Zheng, Y. Zhang, D. An and W. Dong, *Green Chem*., 2018, **20**, 1760–1764.
6. Y. Zhang, P. Ji, W. Hu, Y. WESI, H. Huang and W. Wang, *Chem. Eur. J*. 2019, **25**, 8225 – 8228.
7. R. J. Reddy, M. Waheeda and G. R. Krishna, *Org. Biomol. Chem*., 2020, **18**, 3243–3248.
8. K. Kanemoto, Y. Sugimura, S. Shimizu, S. Yoshida and T. Hosoya, *Chem. Commun.,* 2017, **53**, 10640-10643.
9. D. Luo, L. Min, W. Zheng, L. Shan, X. Wang, Y. Hu, *Chin. Chem. Lett.*, 2020, **31**, 1877–1880.
10. (a) Y. Sun, A. Abdukader, D. Lu, H. Zhang and C. Liu, *Green Chem*., 2017, **19**, 1255–1258; (b) C. Tong, B. Gan, Y. Yan, Y.-Y. Xie, *Synth. Commun*., 2017, **47**, 1927-1933.
11. (a) W. Wei, J. Wen, D. Yang, H. Jing, J. You and H. Wang, *RSC Adv*., 2015, **5**, 4416–4419; (b) L. Wanga, W. Wei, D. Yang, H. Cui, H. Yue and H. Wang, *Tetrahedron Lett*., 2017, **58**, 4799–4802.
12. R. J. Reddy, J. J. Kumar, A. H. Kumari and G. R. Krishna, *Adv. Synth. Catal.* 2020, **362**, 1317-1322.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7.235
7.218
7.202
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7.004
7.002
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6.997
6.987
6.985
6.982
6.980
6.934
6.931
6.929
6.919
6.916
6.914
6.875
6.872
6.870
6.867
3.712
2.409
O
S
S
O
O
3a
1.85
3.03
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0.94
0.99
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3.00
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8
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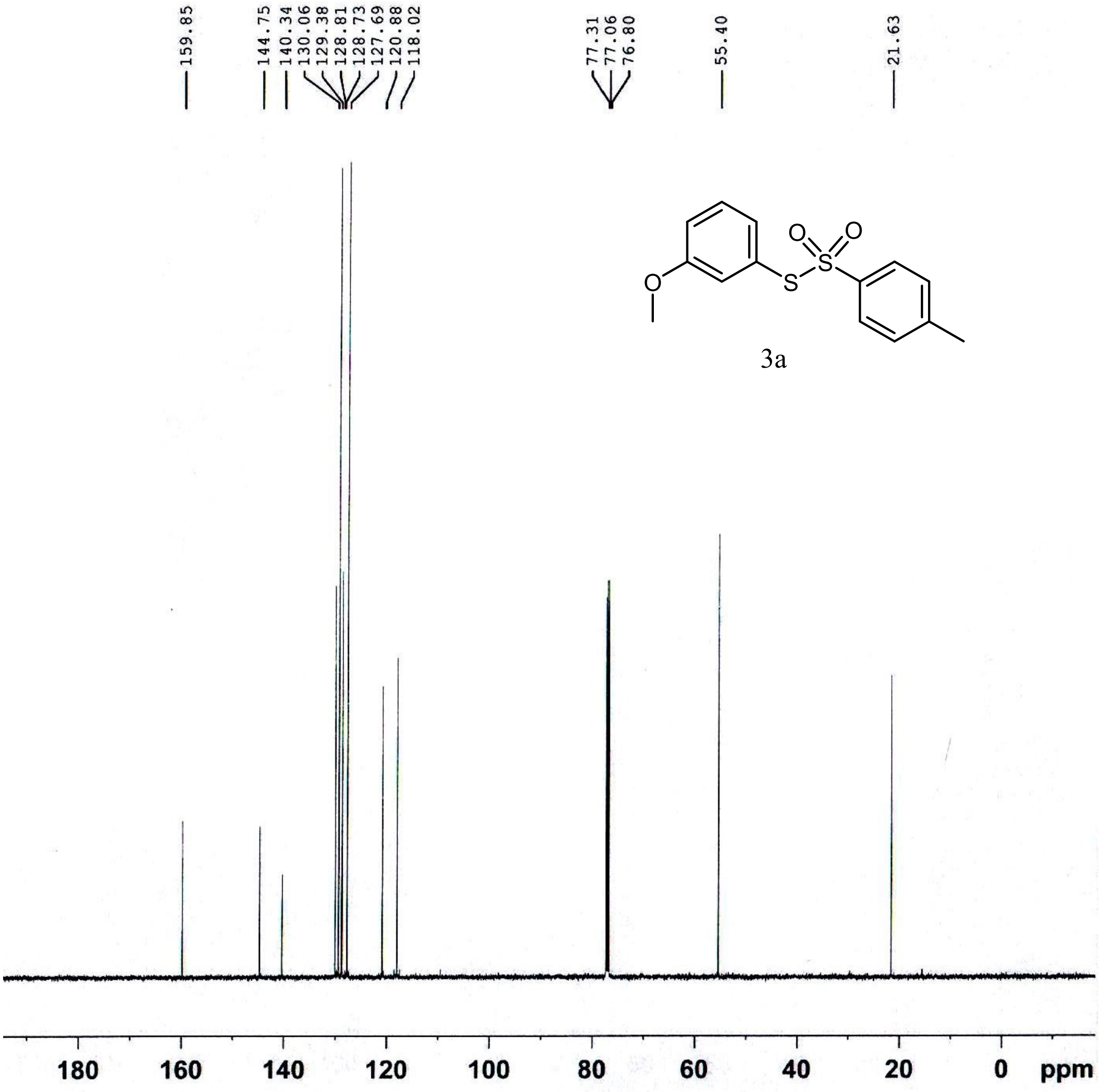
3
2
ppm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130.06
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128.81
128.73
127.69
120.88
118.02
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55.40
21.63
O
S
O
O
S
3a
180
160
140
120
100
80
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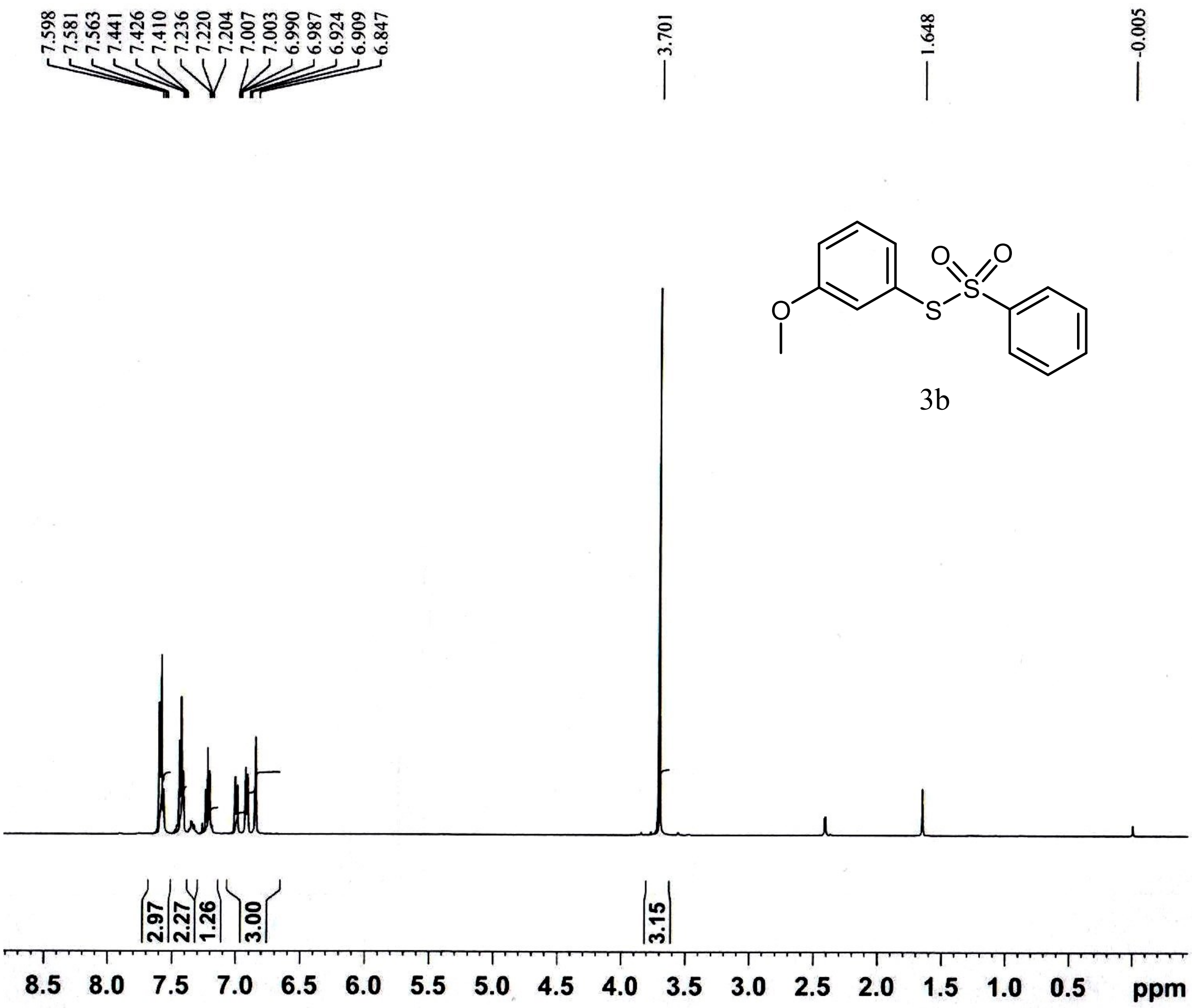
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7.003
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6.987
6.924
6.909
6.847
3.701
1.648
-0.005
O
S
S
O
O
3b
2.97
2.27
1.26
3.00
3.15
8.5
8.0
7.5
7.0
6.5
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4.0
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2.0
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1.0
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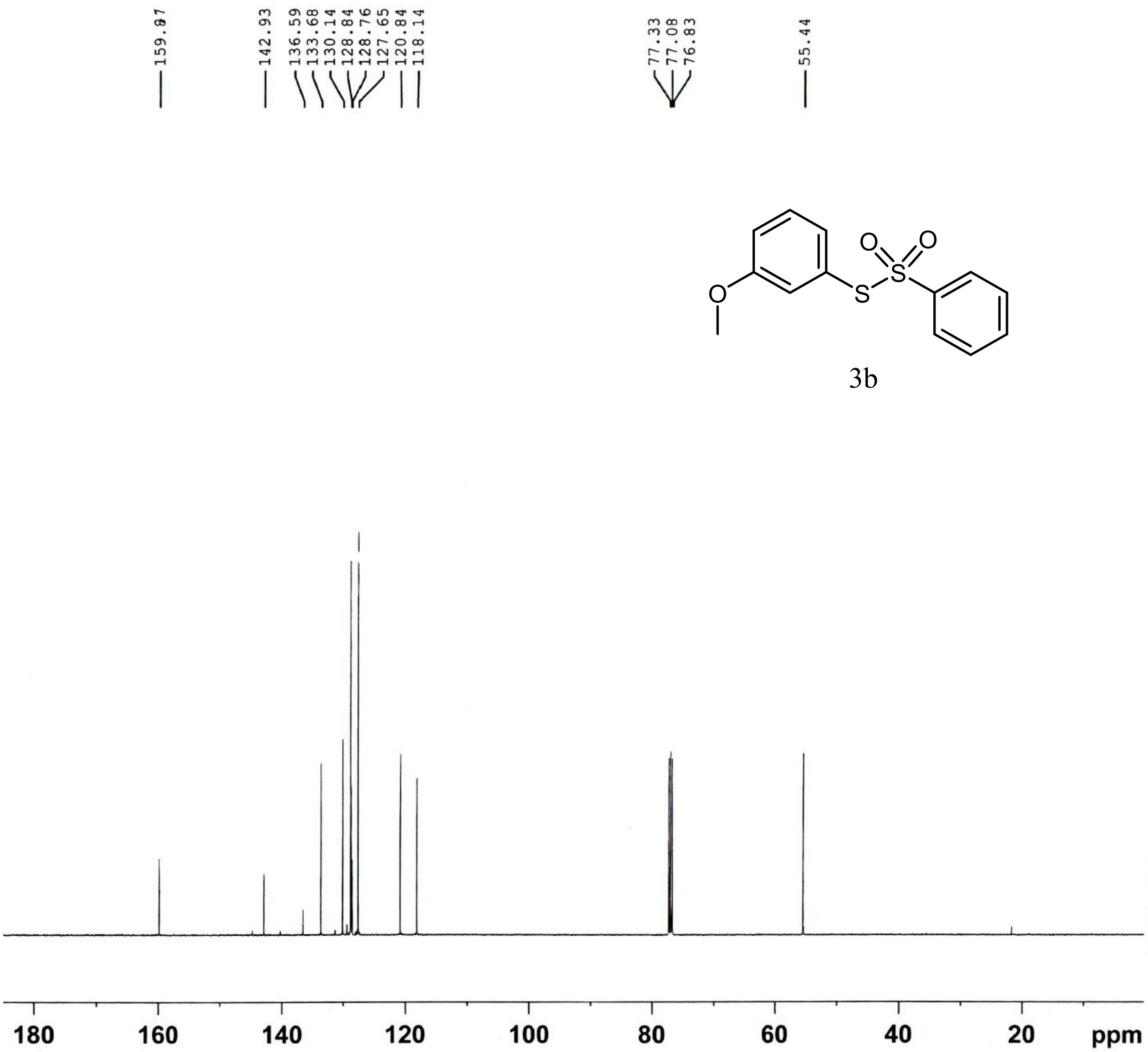
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77.33
77.08
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S
O
O
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140
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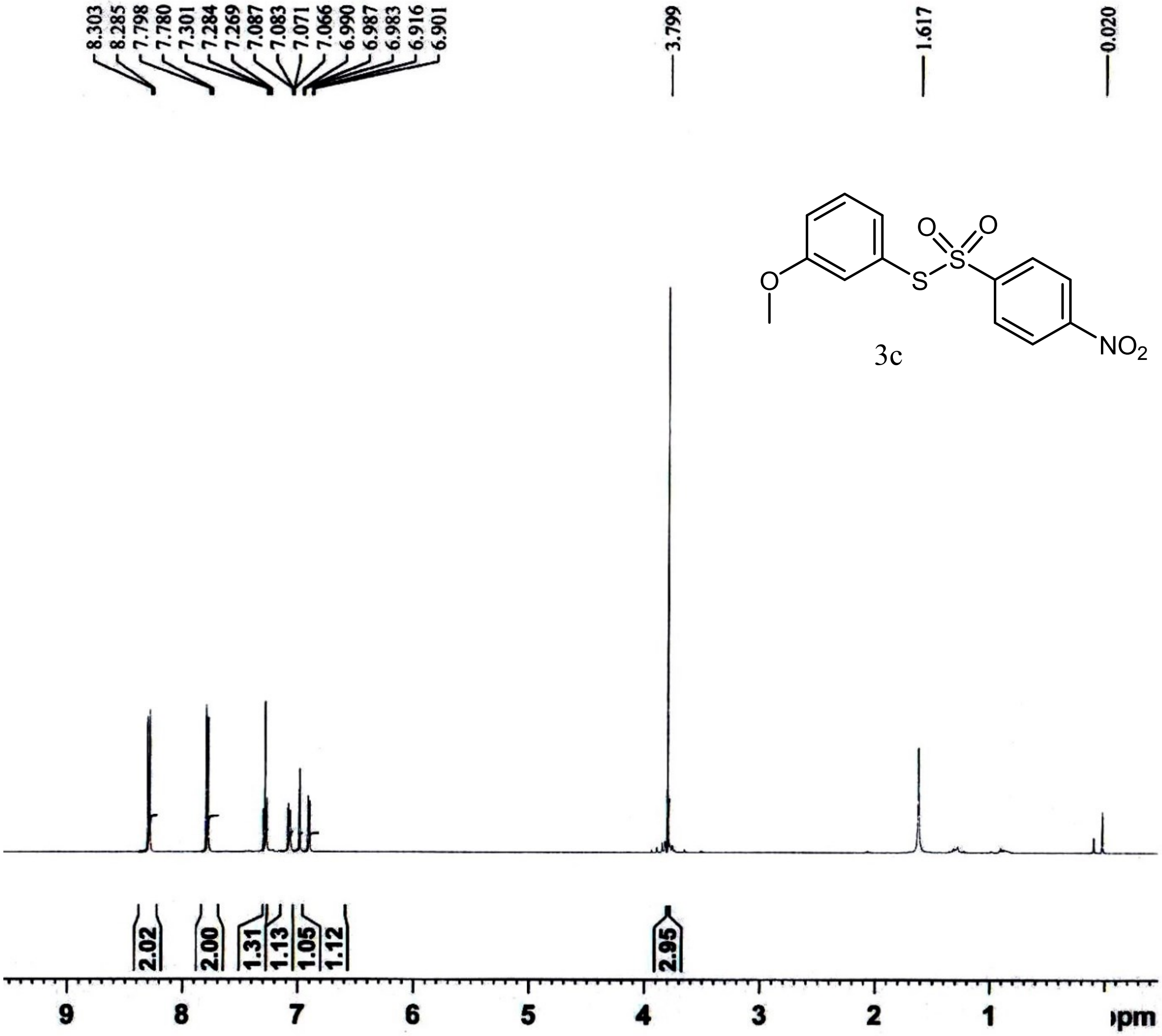
60
40
20
ppm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7.083
7.071
7.066
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6.987
6.983
6.916
6.901
3.799
1.617
0.020
O
S
O
S
O
NO2
3c
2.02
2.00
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1.13
1.05
1.12
2.95
9
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7
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3
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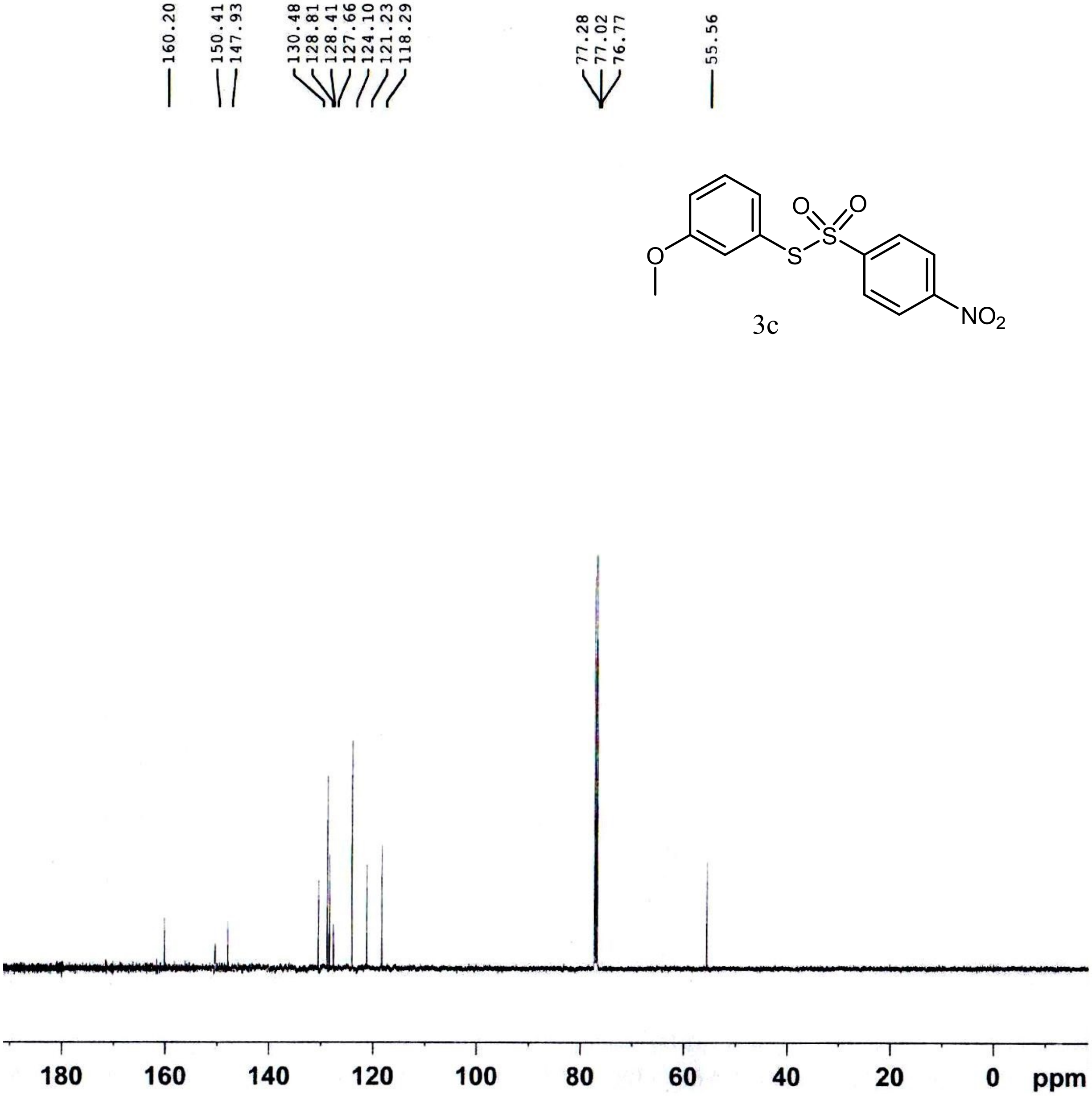
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76.77
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O
S
NO2
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100
80
60
40
20
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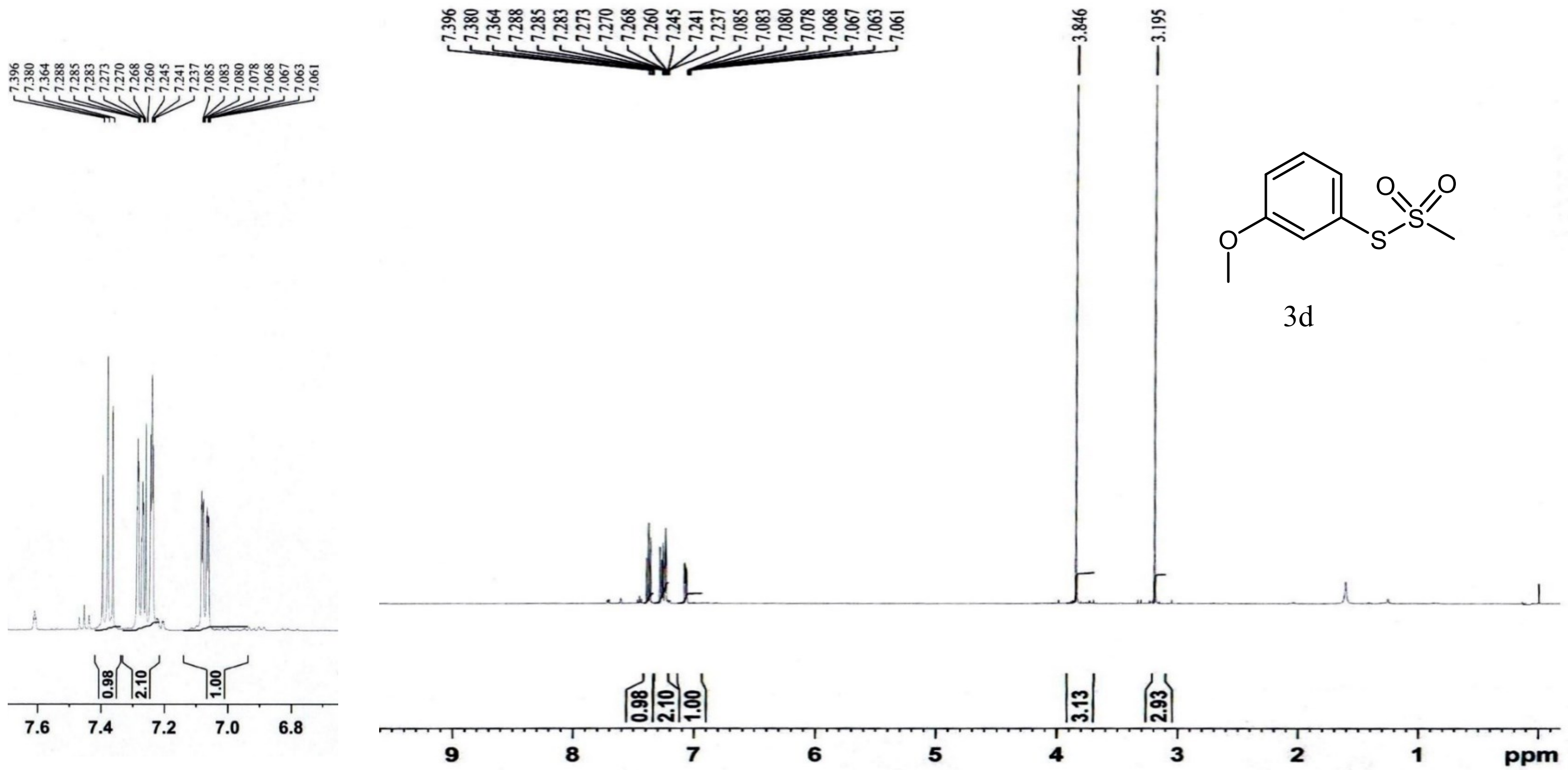
ppm

3c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7.237
7.085
7.083
7.080
7.078
7.068
7.067
7.063
7.061
3.846
3.195
0.98
2.10
1.00
3.13
2.93
7.6
7.4
7.2
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9
8
7
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5
4
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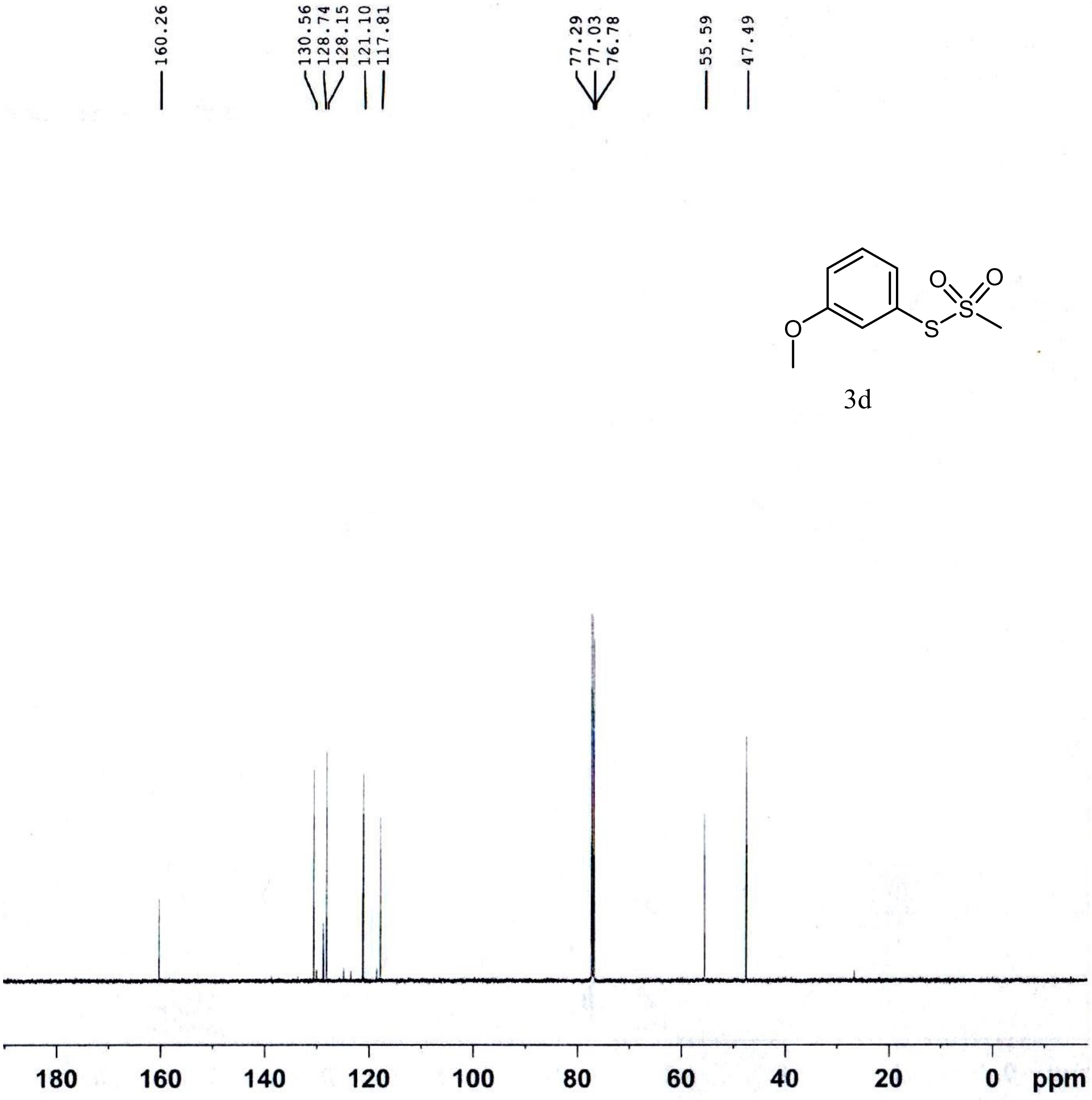
O
O
3d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77.03
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O
S
O
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80
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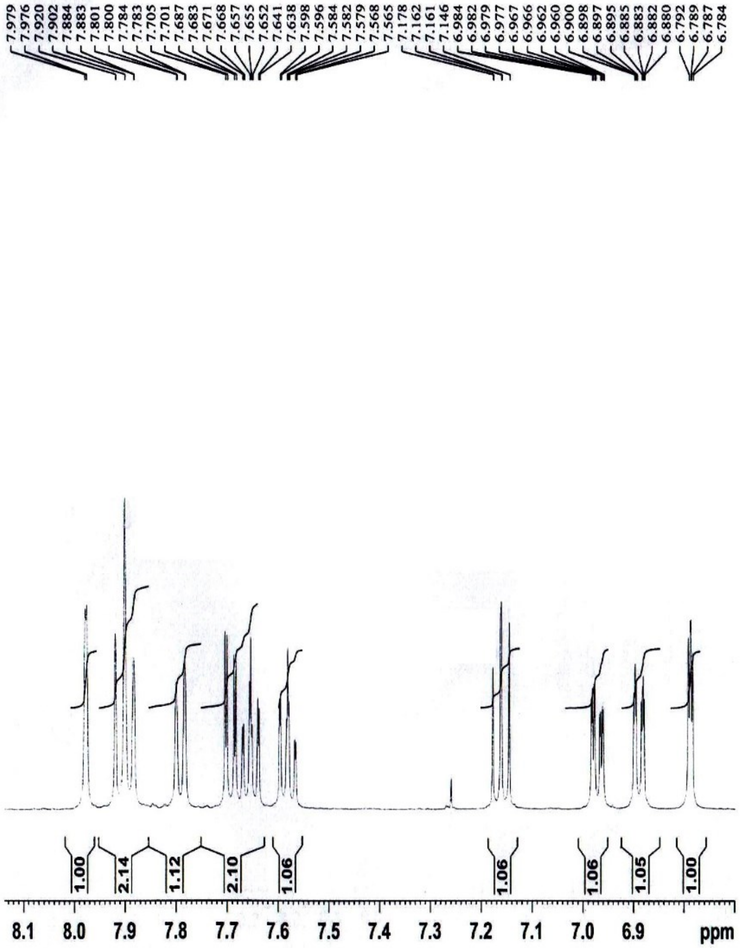
40
20
0
ppm

3d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7.800
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7.783
7.705
7.701
7.687
7.683
7.671
7.668
7.657
7.655
7.652
7.641
7.638
7.598
7.596
7.584
7.582
7.579
7.568
7.565
7.178
7.162
7.161
7.146
6.984
6.982
6.979
6.977
6.967
6.966
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6.960
6.900
6.898
6.897
6.895
6.885
6.883
6.882
6.880
6.792
6.789
6.787
6.784
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1.12
2.10
1.06
1.06
1.06
1.05
1.00
8.1
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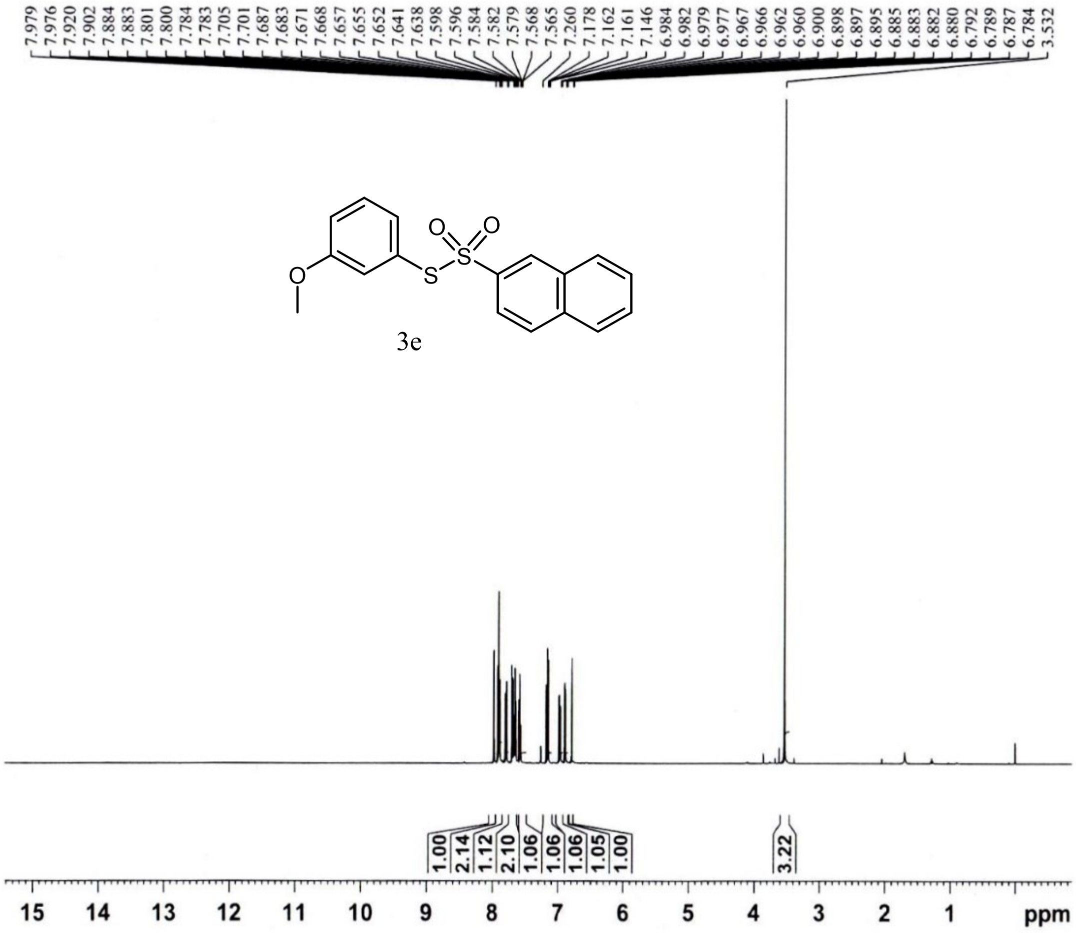
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7.701
7.687
7.683
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7.668
7.657
7.655
7.652
7.641
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7.584
7.582
7.579
7.568
7.565
7.260
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7.162
7.161
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6.979
6.977
6.967
6.966
6.962
6.960
6.900
6.898
6.897
6.895
6.885
6.883
6.882
6.880
6.792
6.789
6.787
6.784
3.532
O
S
O
S
O
3e
1.00
2.14
1.12
2.10
1.06
1.06
1.06
1.05
1.00
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15
14
13
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11
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9
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7
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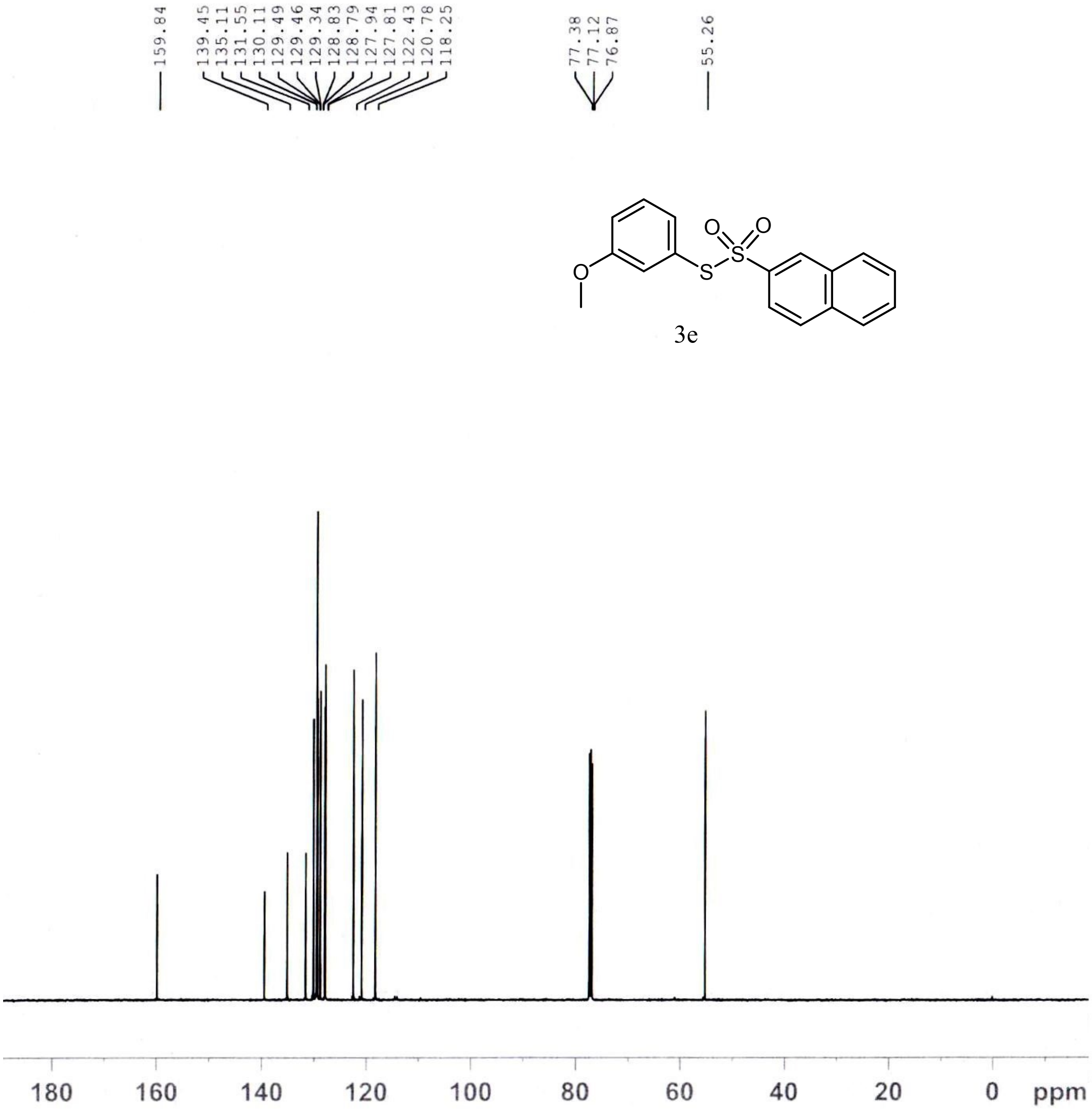
4
3
2
1
ppm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129.34
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128.79
127.94
127.81
122.43
120.78
118.25
77.38
77.12
76.87
55.26
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S
S
O
O
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140
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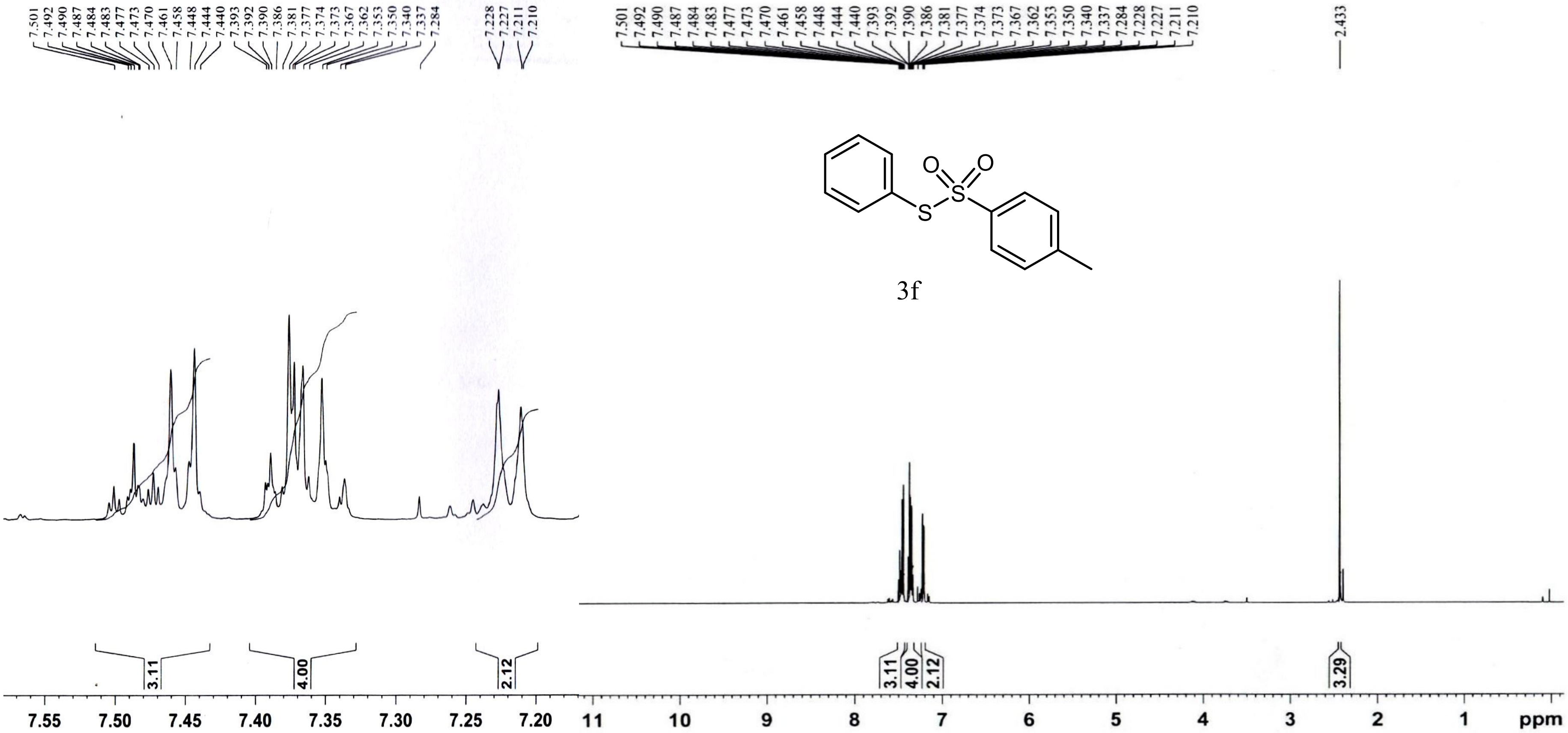
100
80
60
40
20
0
ppm

3e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7.444
7.440
7.393
7.392
7.390
7.386
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7.377
7.374
7.373
7.367
7.362
7.353
7.350
7.340
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7.284
7.228
7.227
7.211
7.210
2.433
O
O
S
S
3.11
4.00
2.12
3.29
7.55
7.50
7.45
7.40
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7.20
11
10
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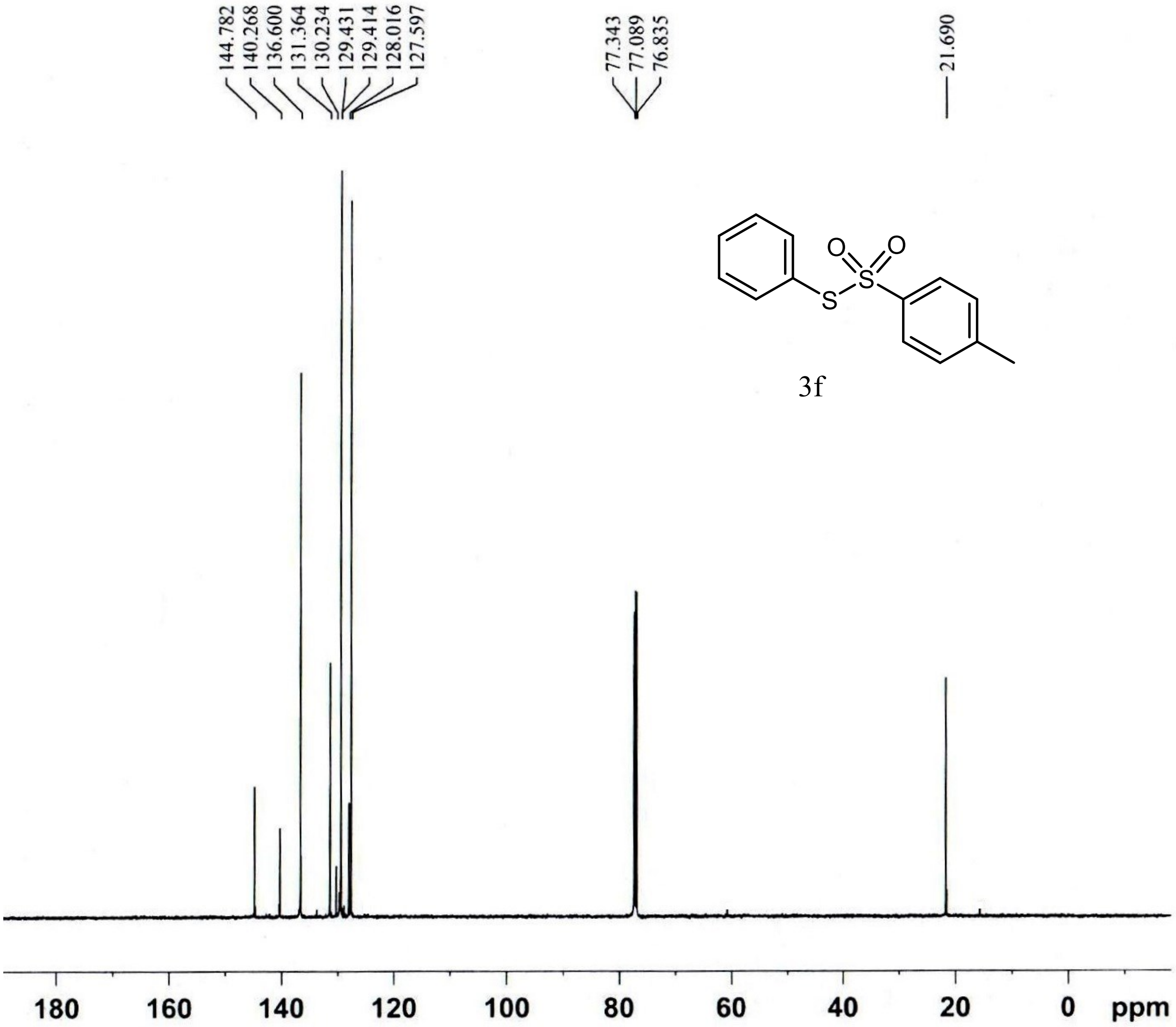
6
5
4
3
2
1
ppm

3f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136.600
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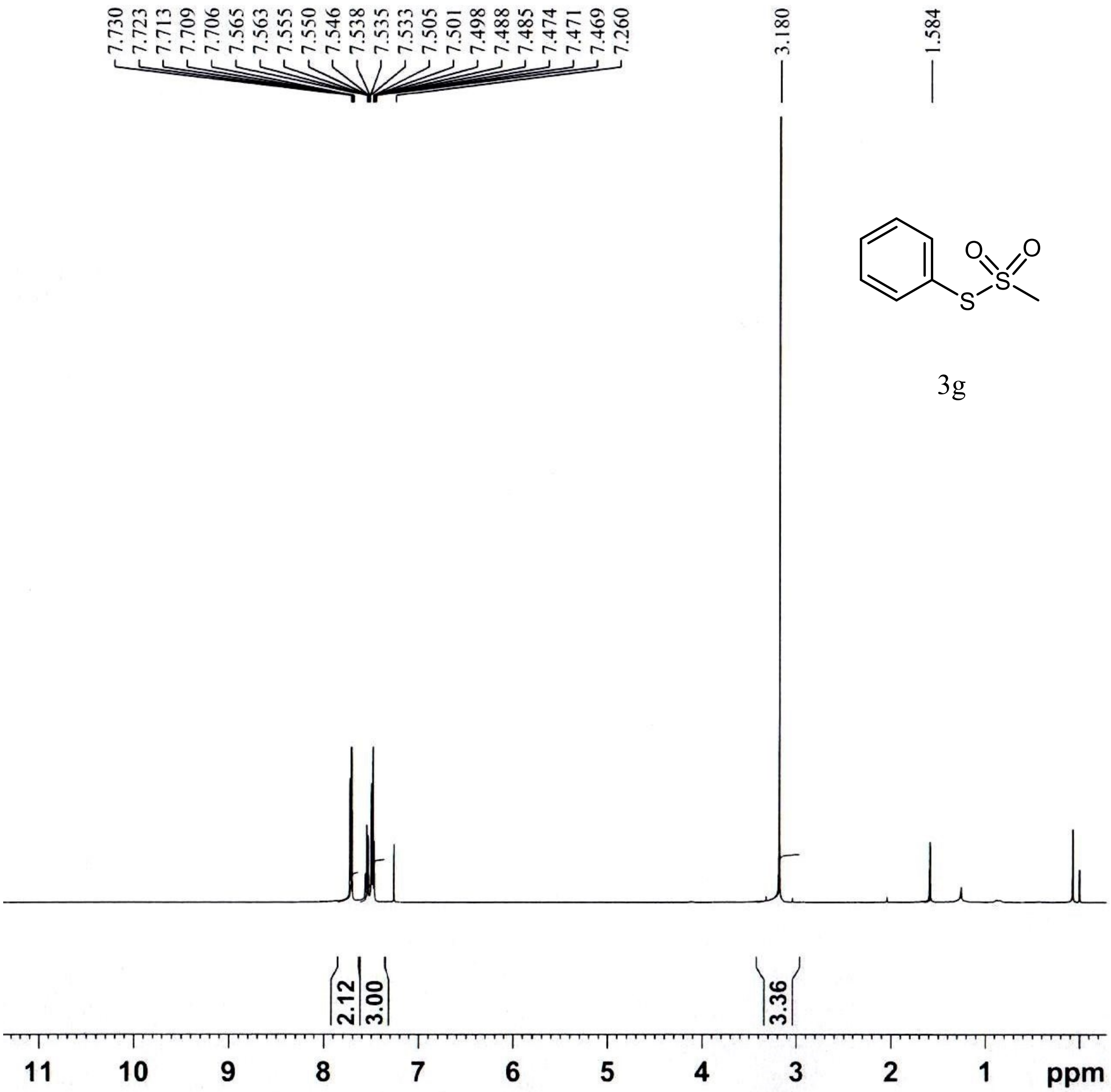
130.234
129.431
129.414
128.016
127.597
77.343
77.089
76.835
21.690
O
O
S
S
3f
180
160
140
120
100
80
60
40
20
0
ppm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7.563
7.555
7.550
7.546
7.538
7.535
7.533
7.505
7.501
7.498
7.488
7.485
7.474
7.471
7.469
7.260
3.180
1.584
S
S
O
O
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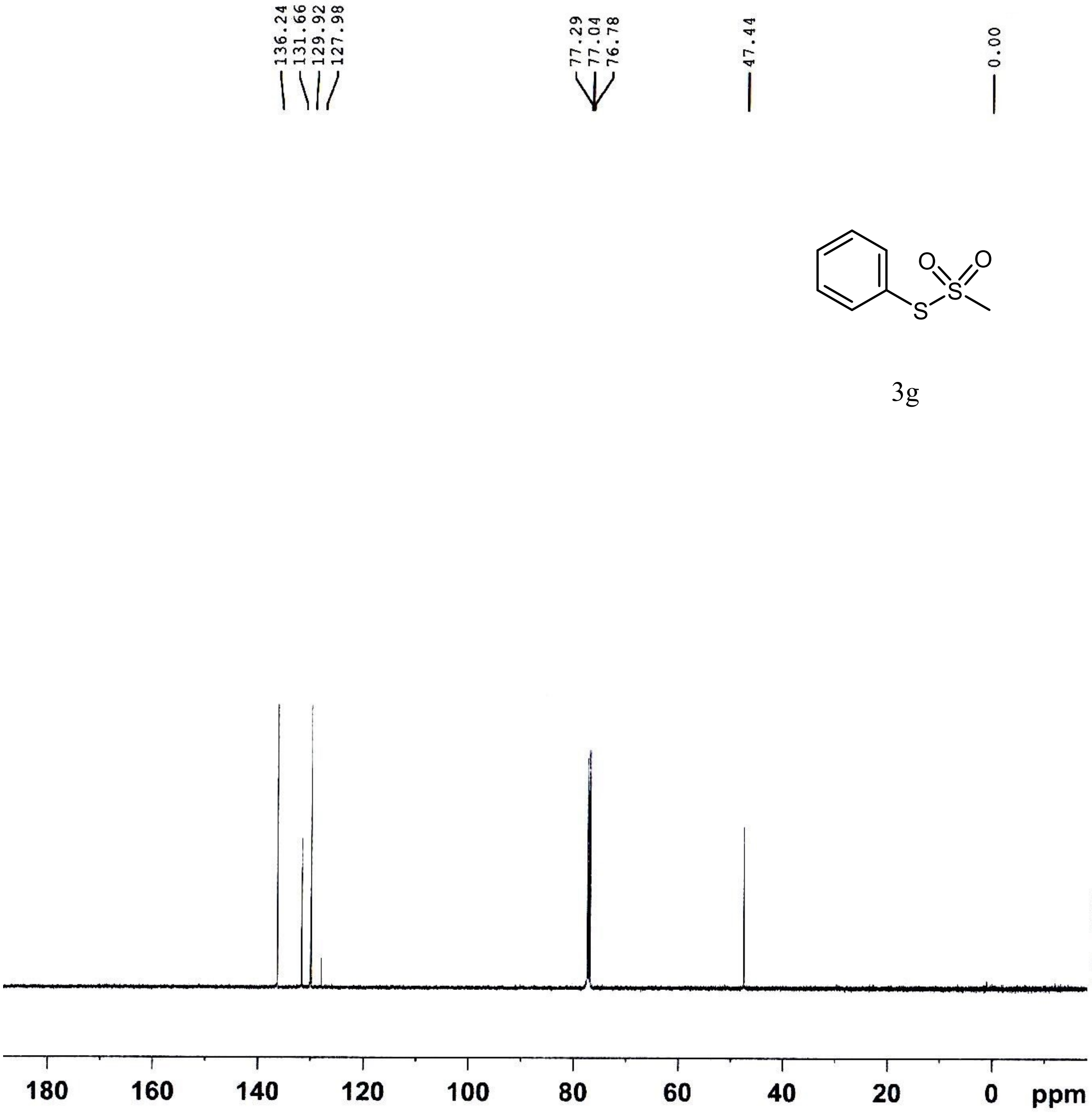
3.36
11
10
9
8
7
6
5
4
3
2
1
ppm

3g


136.24
131.66
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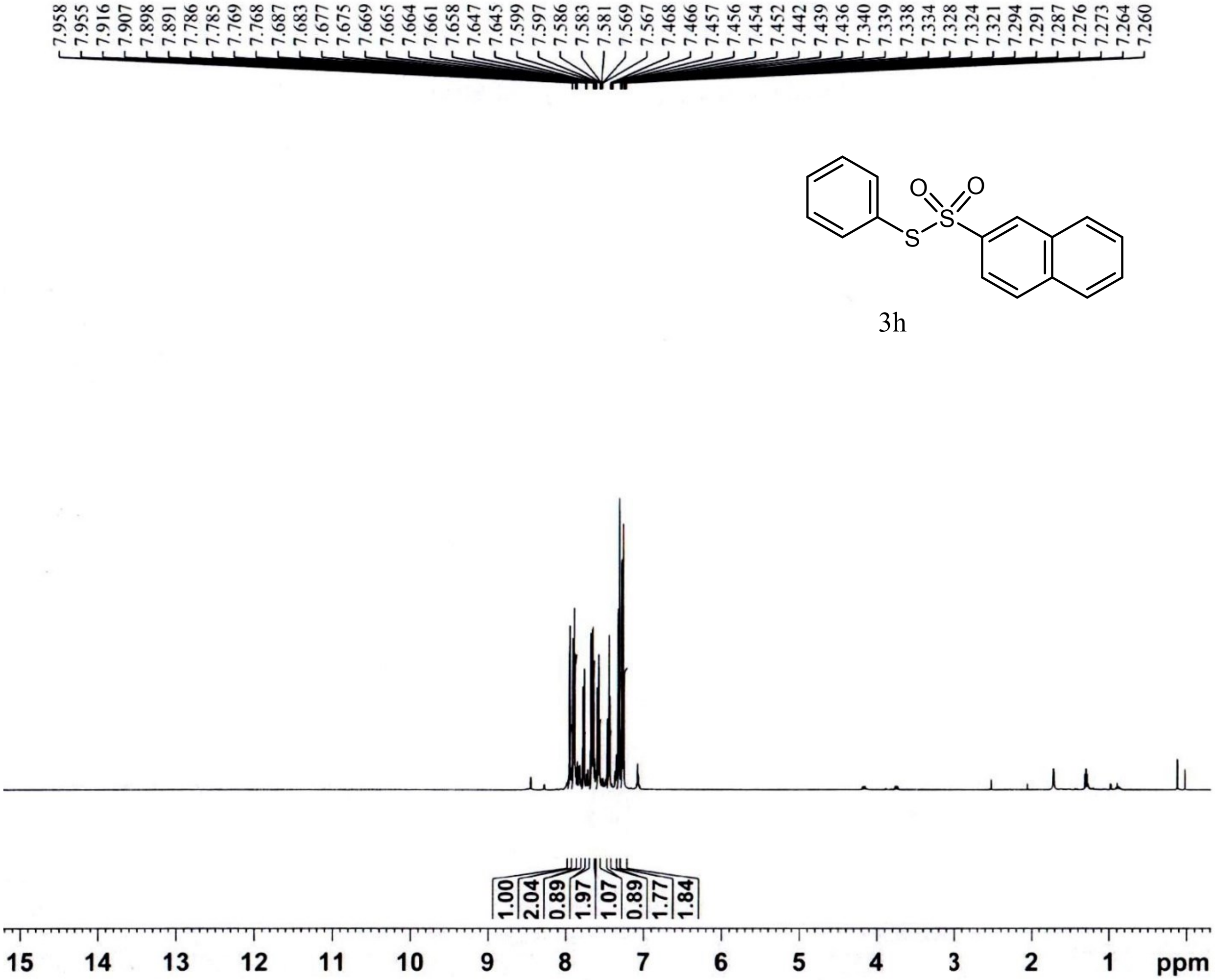
127.98
77.29
77.04
76.78
47.44
0.00
O
O
S
S
180
160
140
120
100
80
60
40
20
0
ppm

3g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7.768
7.687
7.683
7.677
7.675
7.669
7.665
7.664
7.661
7.658
7.647
7.645
7.599
7.597
7.586
7.583
7.581
7.569
7.567
7.468
7.466
7.457
7.456
7.454
7.452
7.442
7.439
7.436
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7.339
7.338
7.334
7.328
7.324
7.321
7.294
7.291
7.287
7.276
7.273
7.264
7.260
O
O
S
S
3h
1.00
2.04
0.89
1.97
1.07
0.89
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15
14
13
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11
10
9
8
7
6
5
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3
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1
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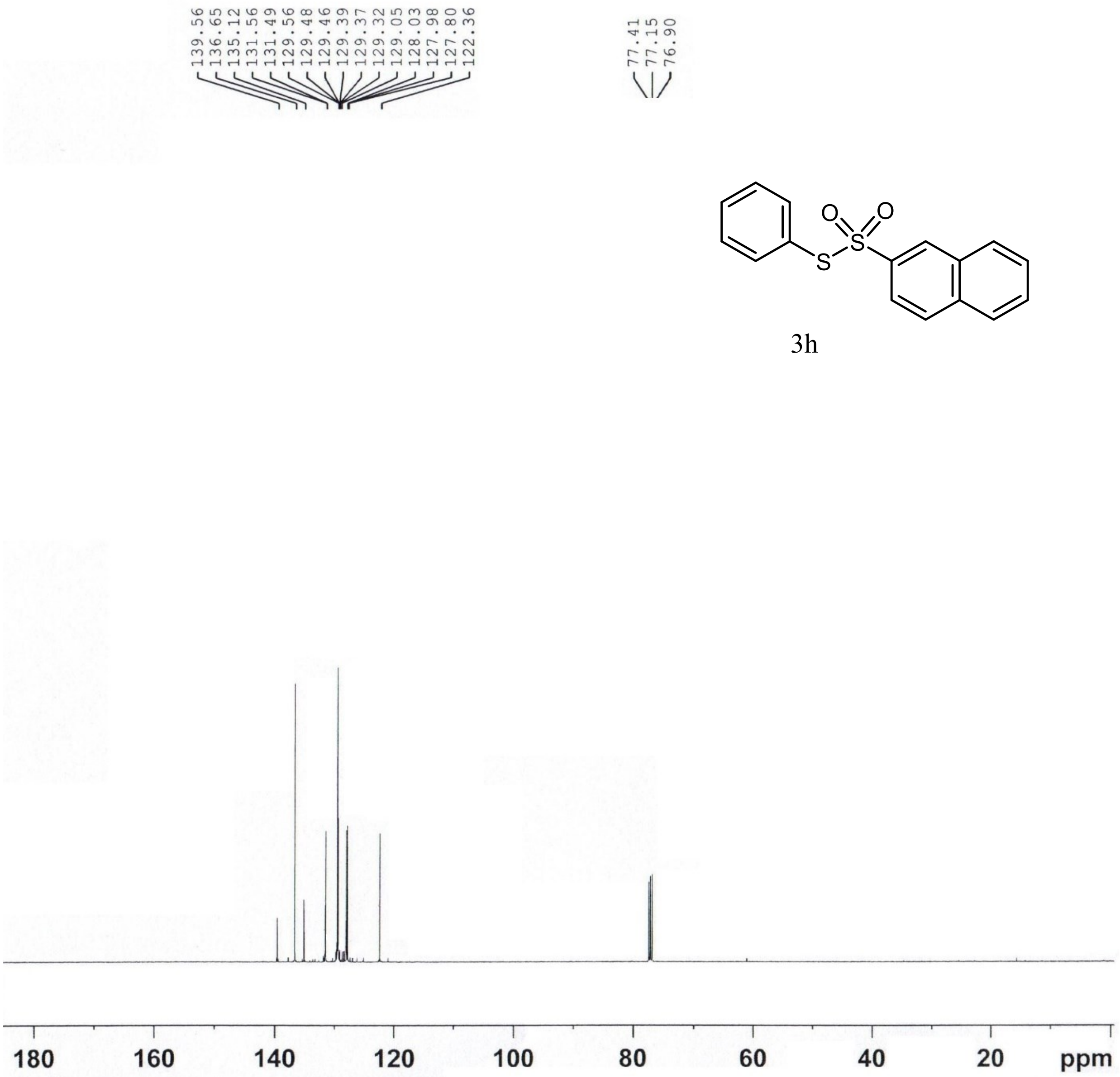
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129.37
129.32
129.05
128.03
127.98
127.80
122.36
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77.15
76.90
O
O
S
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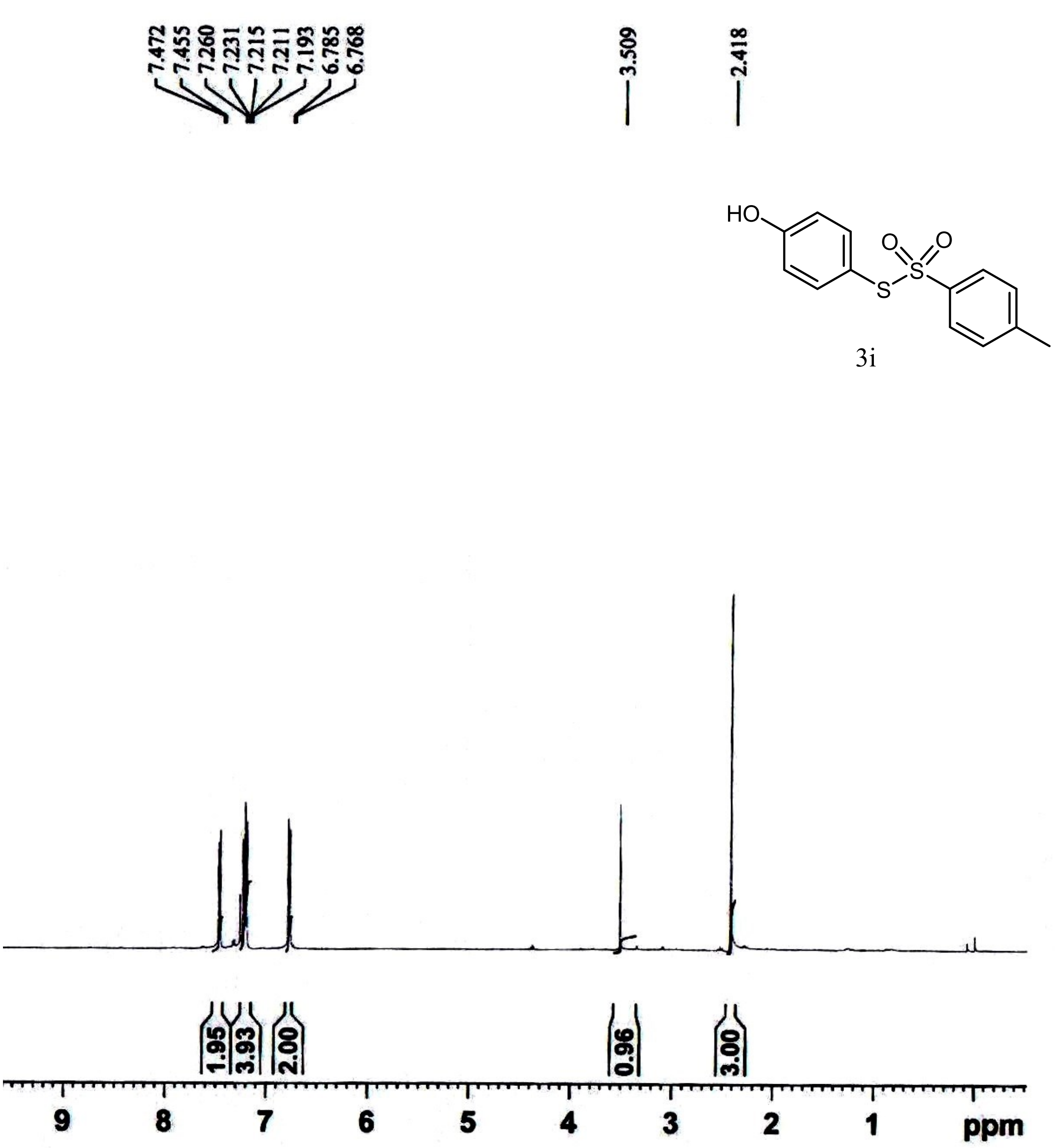
120
100
80
60
40
20
ppm

3h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7.193
6.785
6.768
3.509
2.418
HO
O
O
S
S
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7
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4
3
2
1
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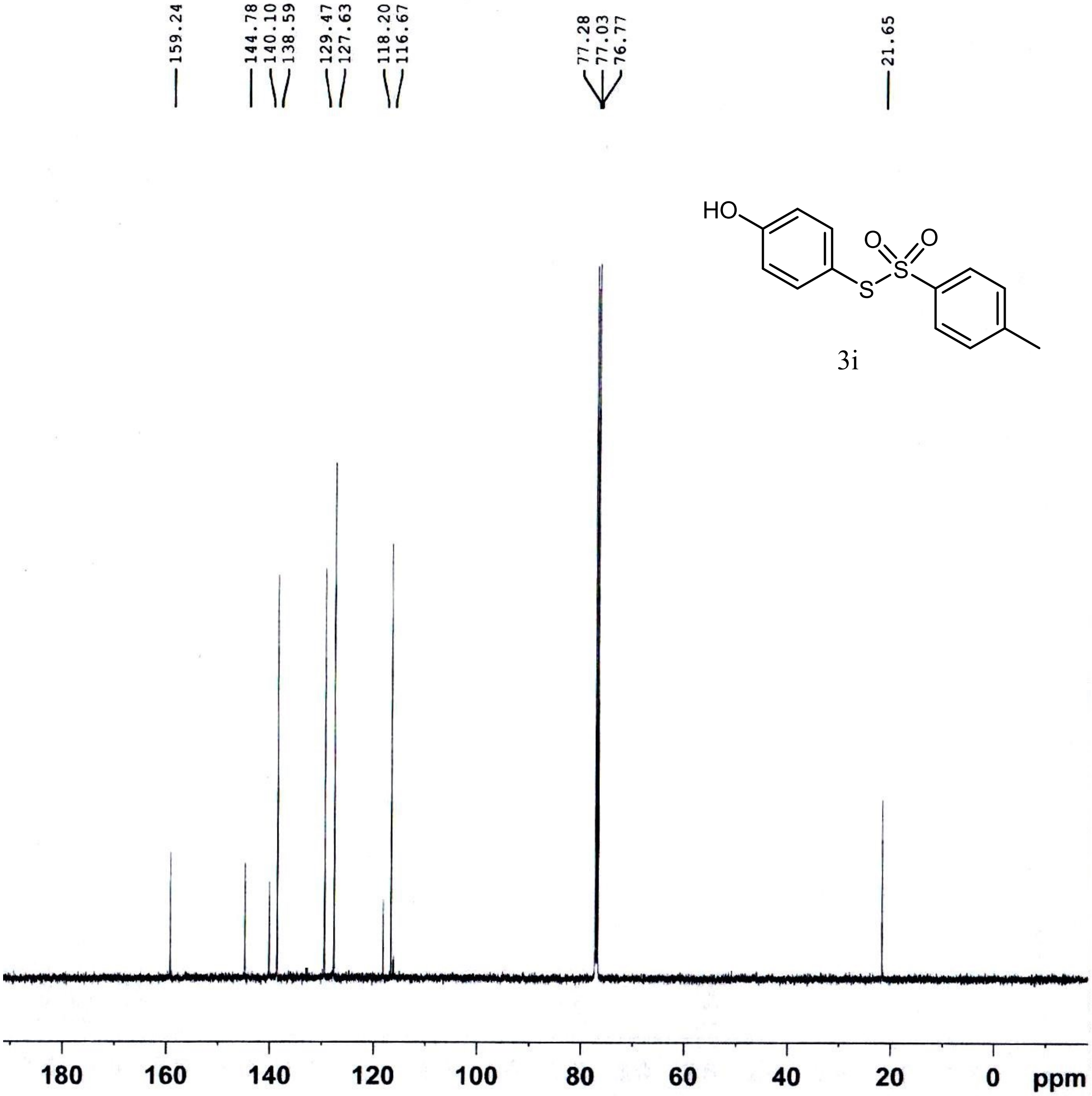
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77.03
76.77
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S
O
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100
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60
40
20
0
ppm

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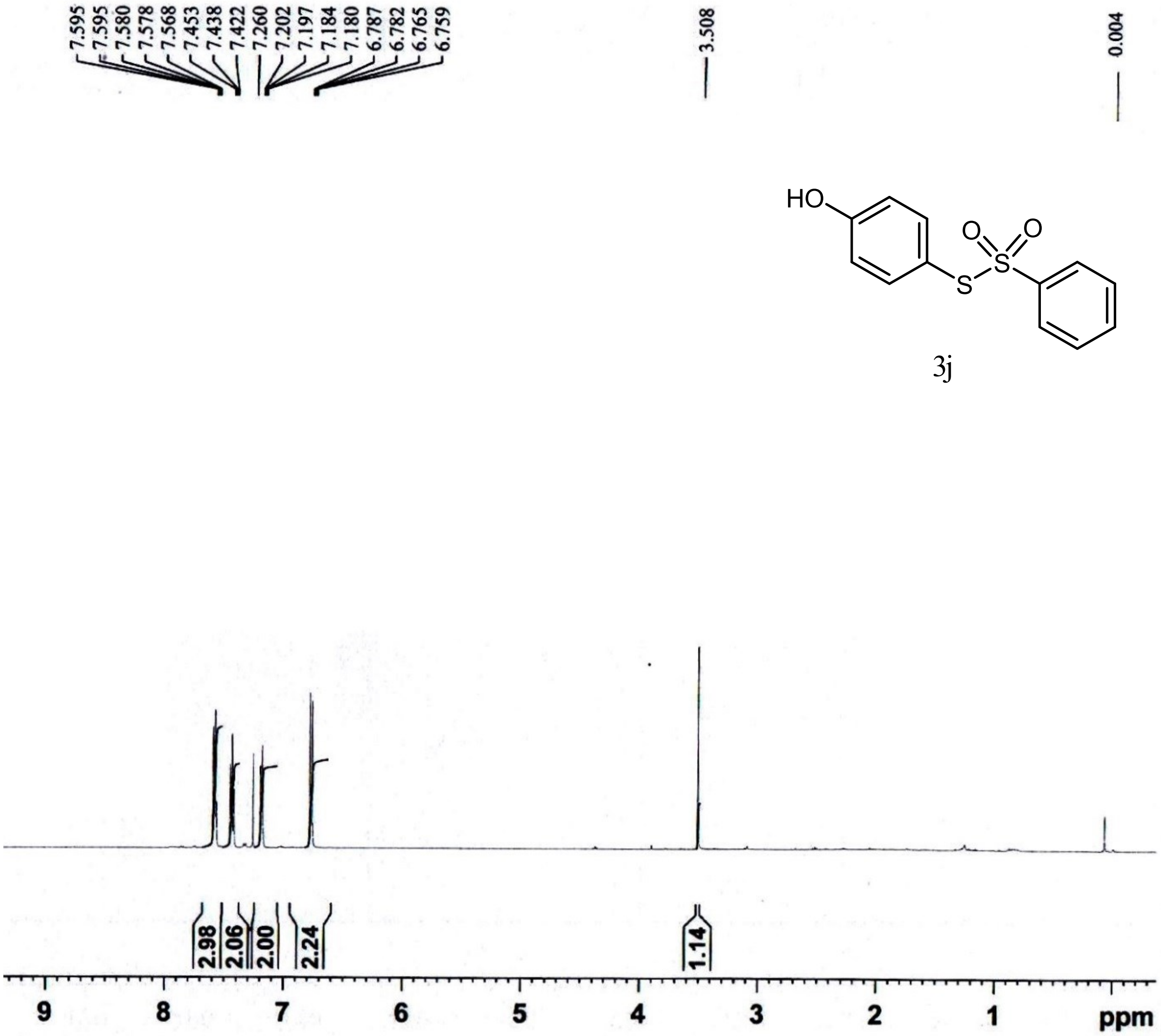
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7.180
6.787
6.782
6.765
6.759
3.508
0.004
HO
S
O
O
S
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2.00
2.24
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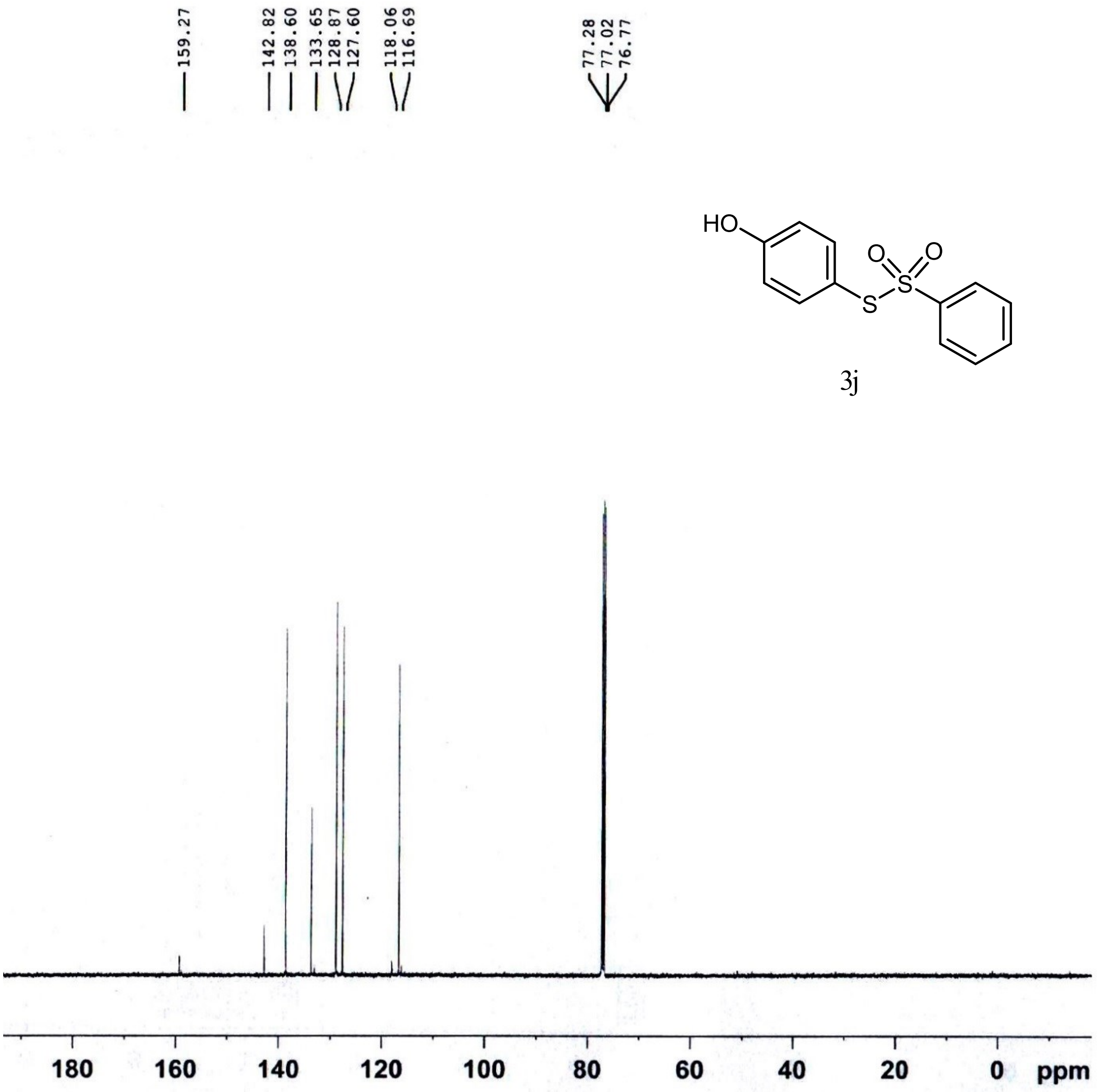
8
7
6
5
4
3
2
1
ppm

3j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116.69
77.28
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76.77
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O
O
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140
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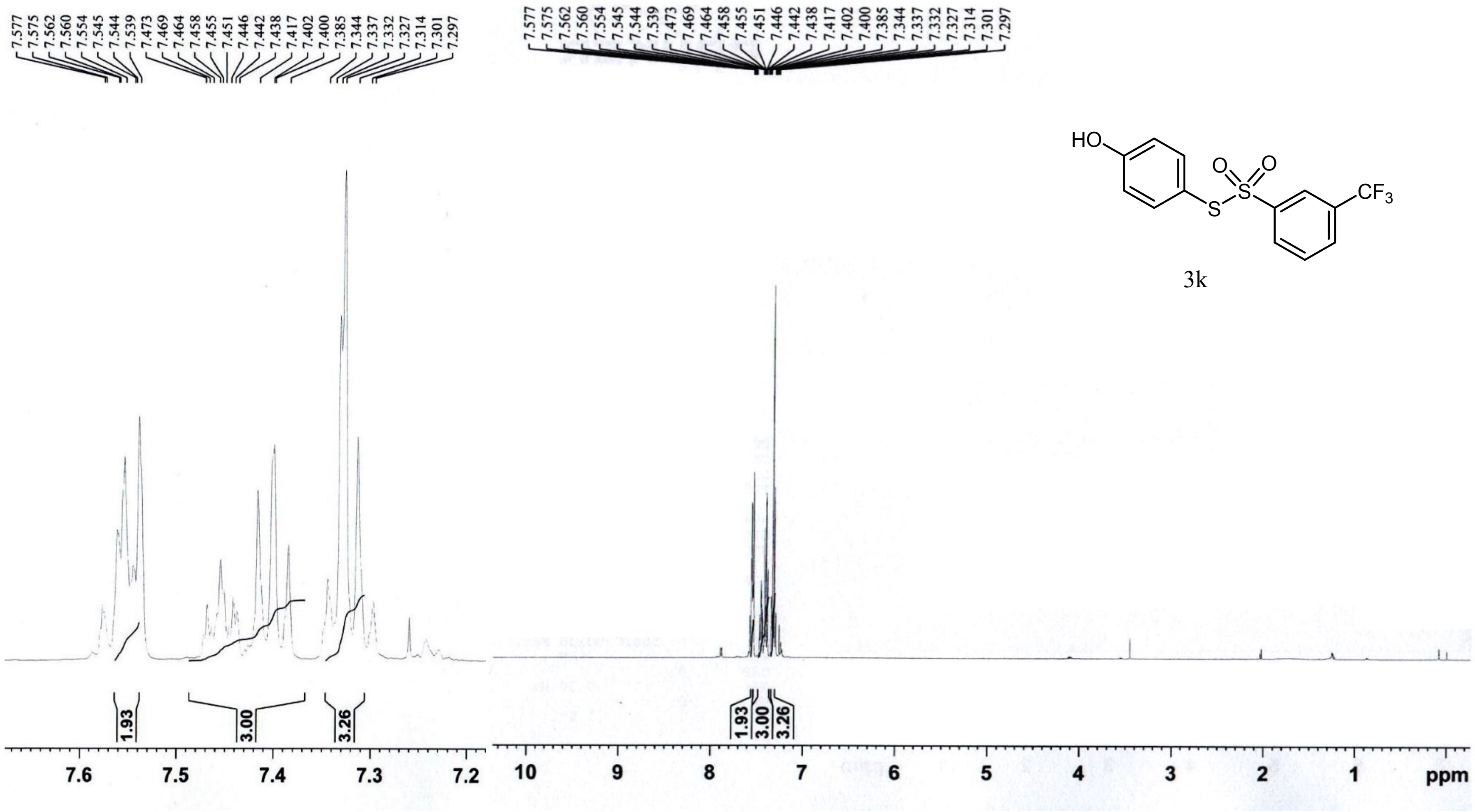
60
40
20
0
ppm

3j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1.93
3.00
3.26
7.6
7.5
7.4
7.3
7.2
7.577 7.575 7.562 7.560 7.554 7.545 7.544 7.539 7.473 7.469 7.464 7.458 7.455 7.451 7.446 7.442 7.438 7.417 7.402 7.400 7.385 7.344 7.337 7.332 7.327 7.314 7.301 7.297
1.93
3.00
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7
6
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4
3
2
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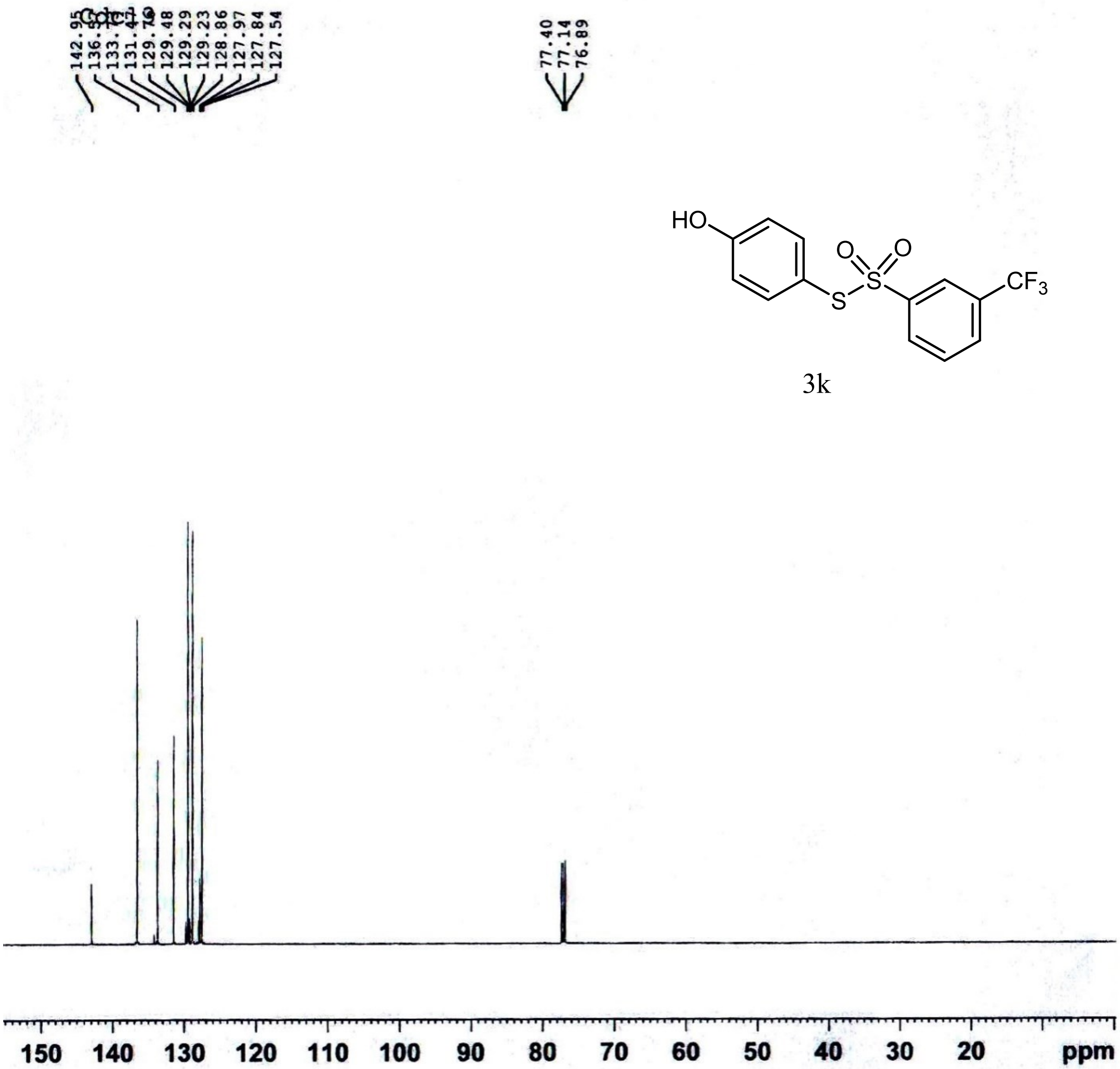
ppm
HO
O
O
S
S
CF3

3k



3k

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129.7
129.48
129.29
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128.86
127.97
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127.54
Cdcl3
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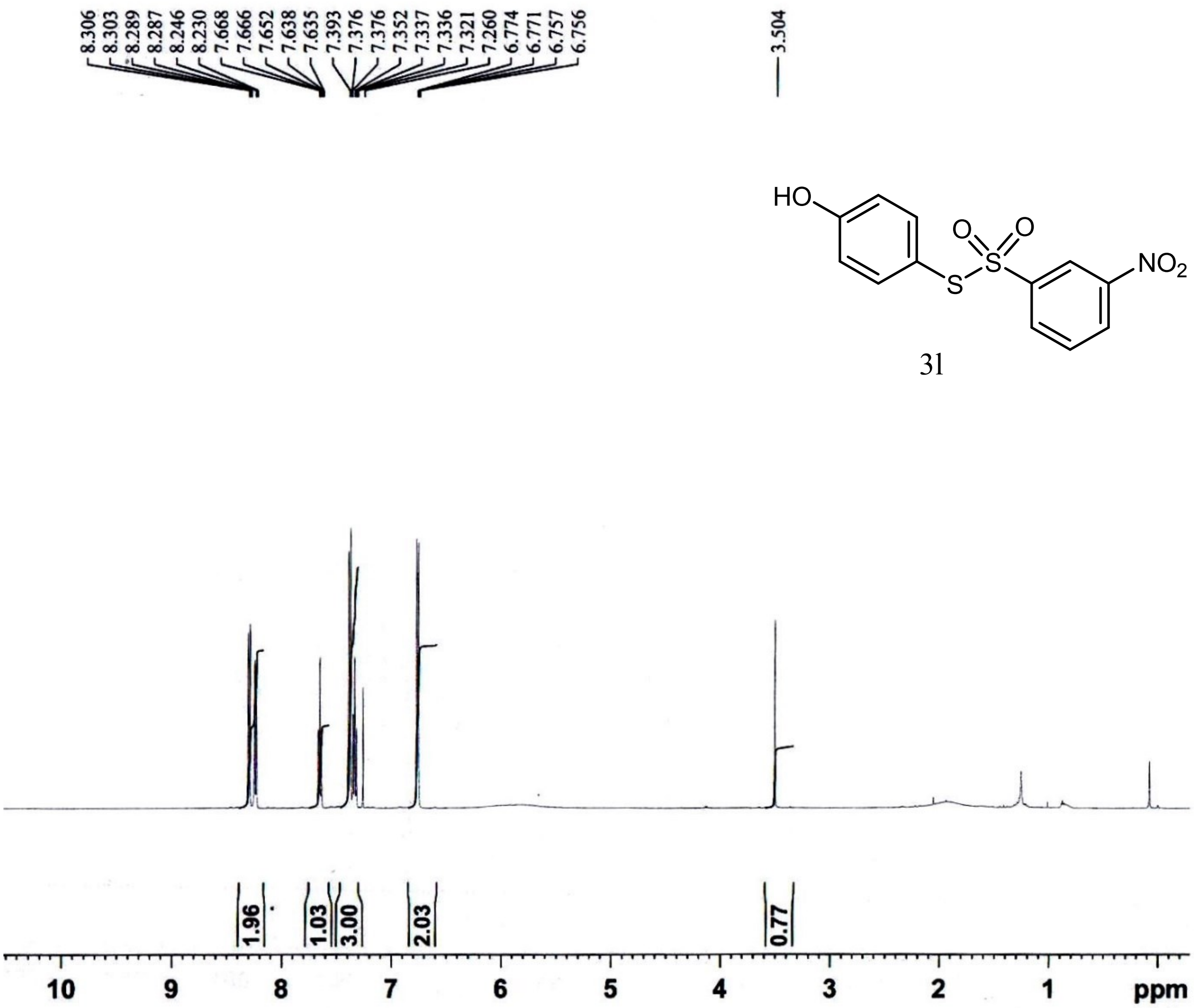
20
ppm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7.638
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7.376
7.352
7.337
7.336
7.321
7.260
6.774
6.771
6.757
6.756
3.504
HO
S
O
O
S
NO_2
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3.00
2.03
0.77
10
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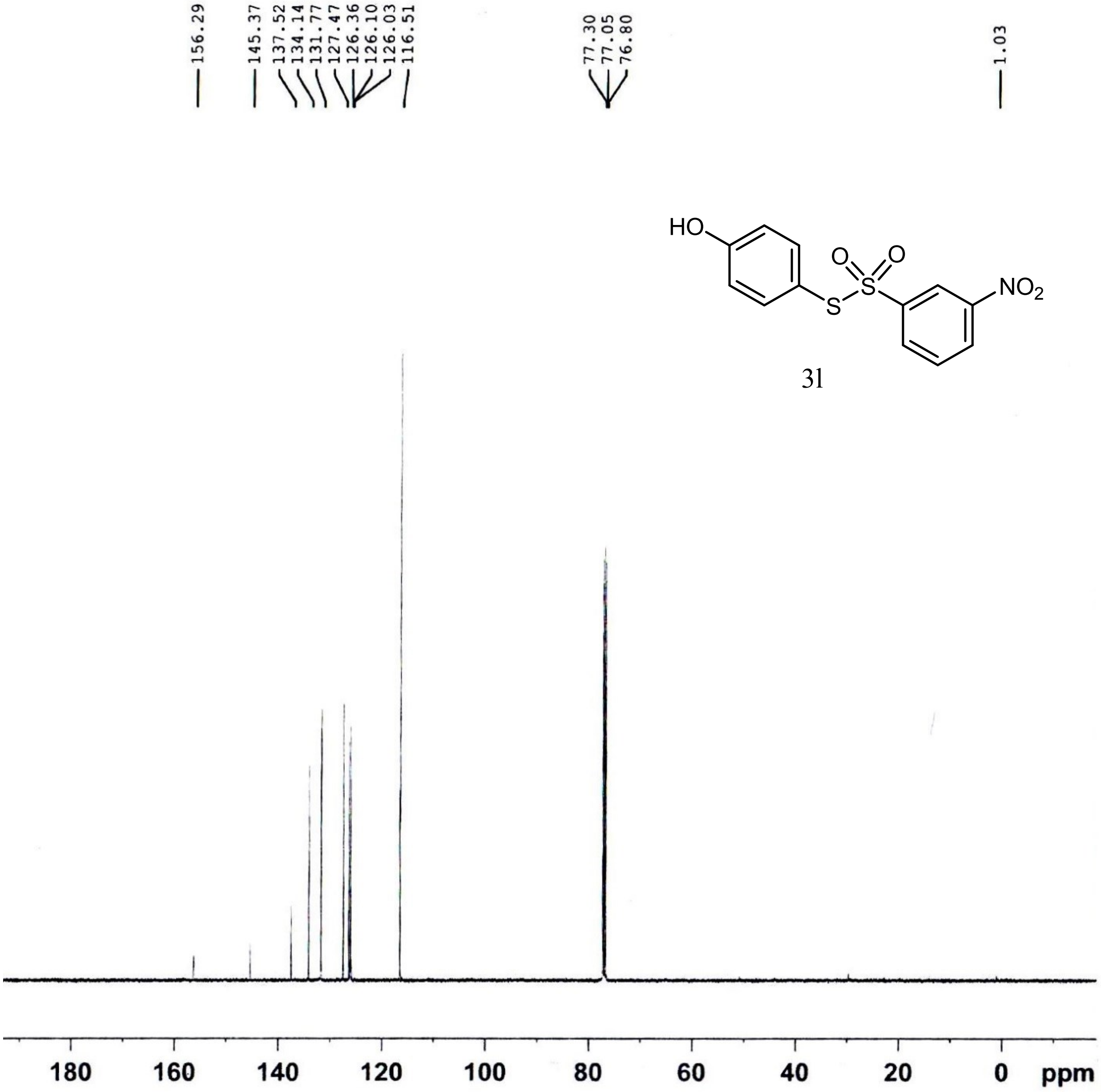
6
5
4
3
2
1
ppm

31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126.36
126.10
126.03
116.51
77.30
77.05
76.80
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O
O
NO_2
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120
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40
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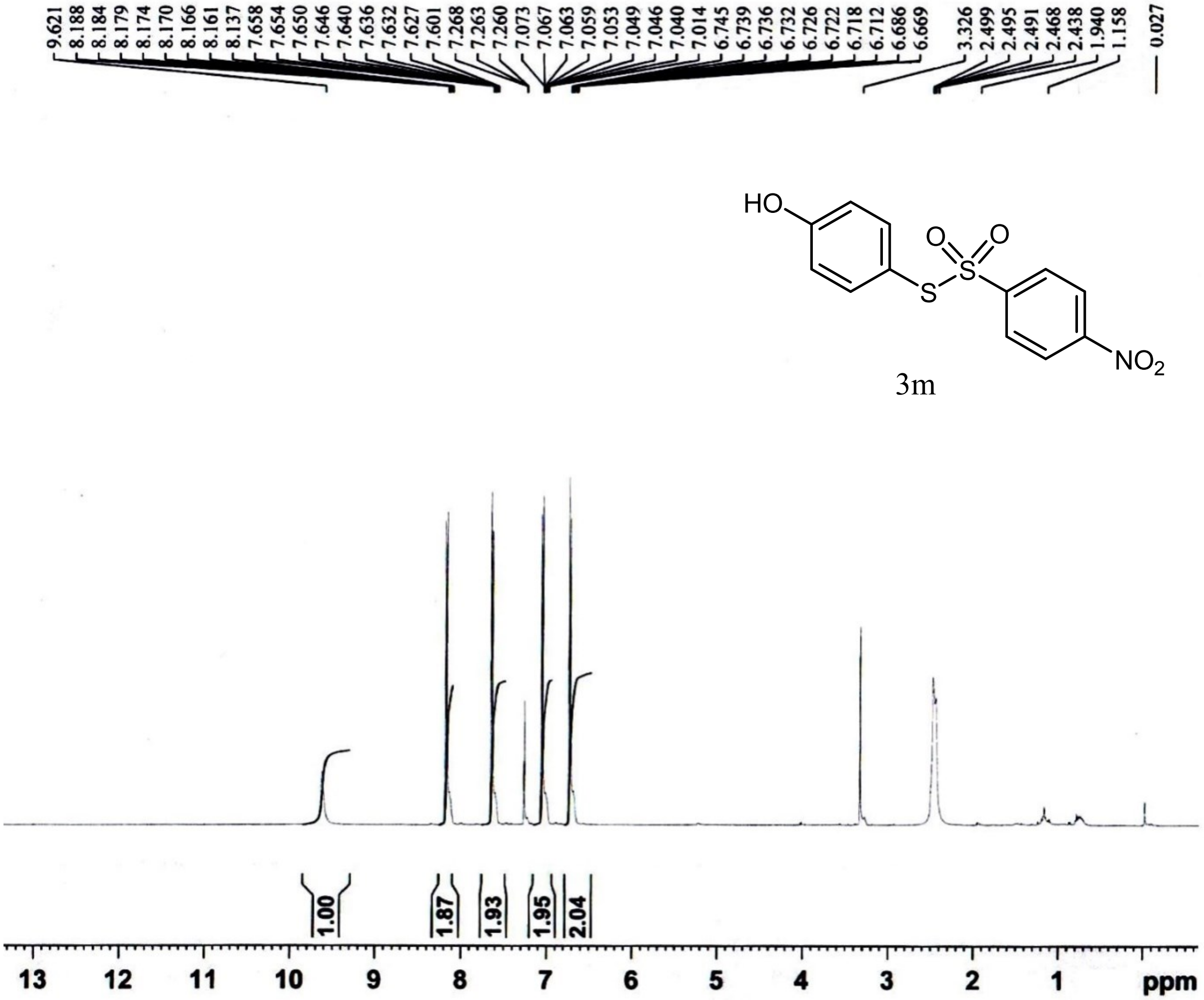
0
ppm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7.646
7.640
7.636
7.632
7.627
7.601
7.268
7.263
7.260
7.073
7.067
7.063
7.059
7.053
7.049
7.046
7.040
7.014
6.745
6.739
6.736
6.732
6.726
6.722
6.718
6.712
6.686
6.669
3.326
2.499
2.495
2.491
2.468
2.438
1.940
1.158
0.027
HO
S
O
S
O
NO2
3m
1.00
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2.04
13
12
11
10
9
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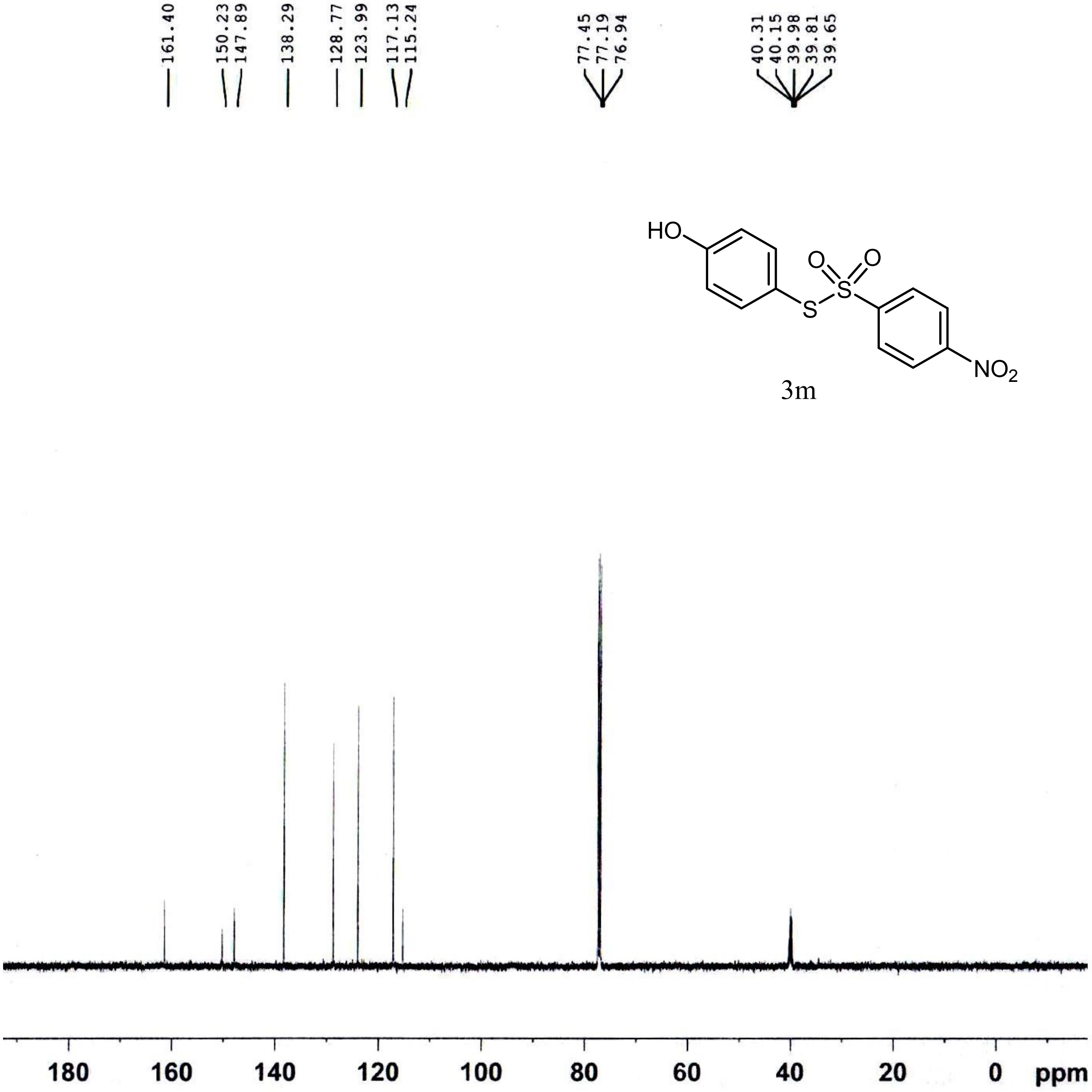
7
6
5
4
3
2
1
ppm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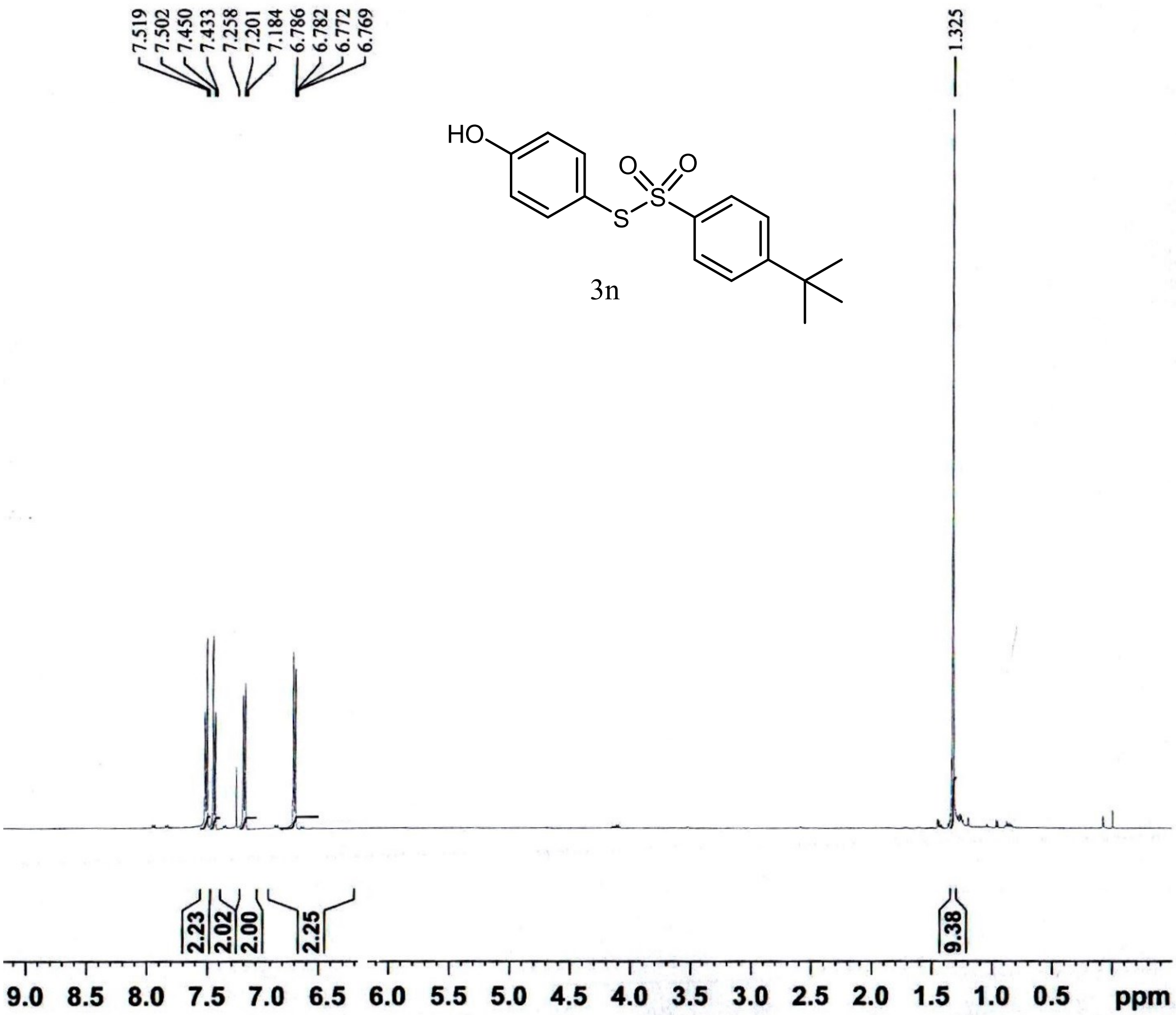
128.77
123.99
117.13
115.24
77.45
77.19
76.94
40.31
40.15
39.98
39.81
39.65
HO
S
O
O
S
NO2
180
160
140
120
100
80
60
40
20
0
ppm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6.786
6.782
6.772
6.769
1.325
HO
O
O
S
S
3n
2.23
2.02
2.00
2.25
9.38
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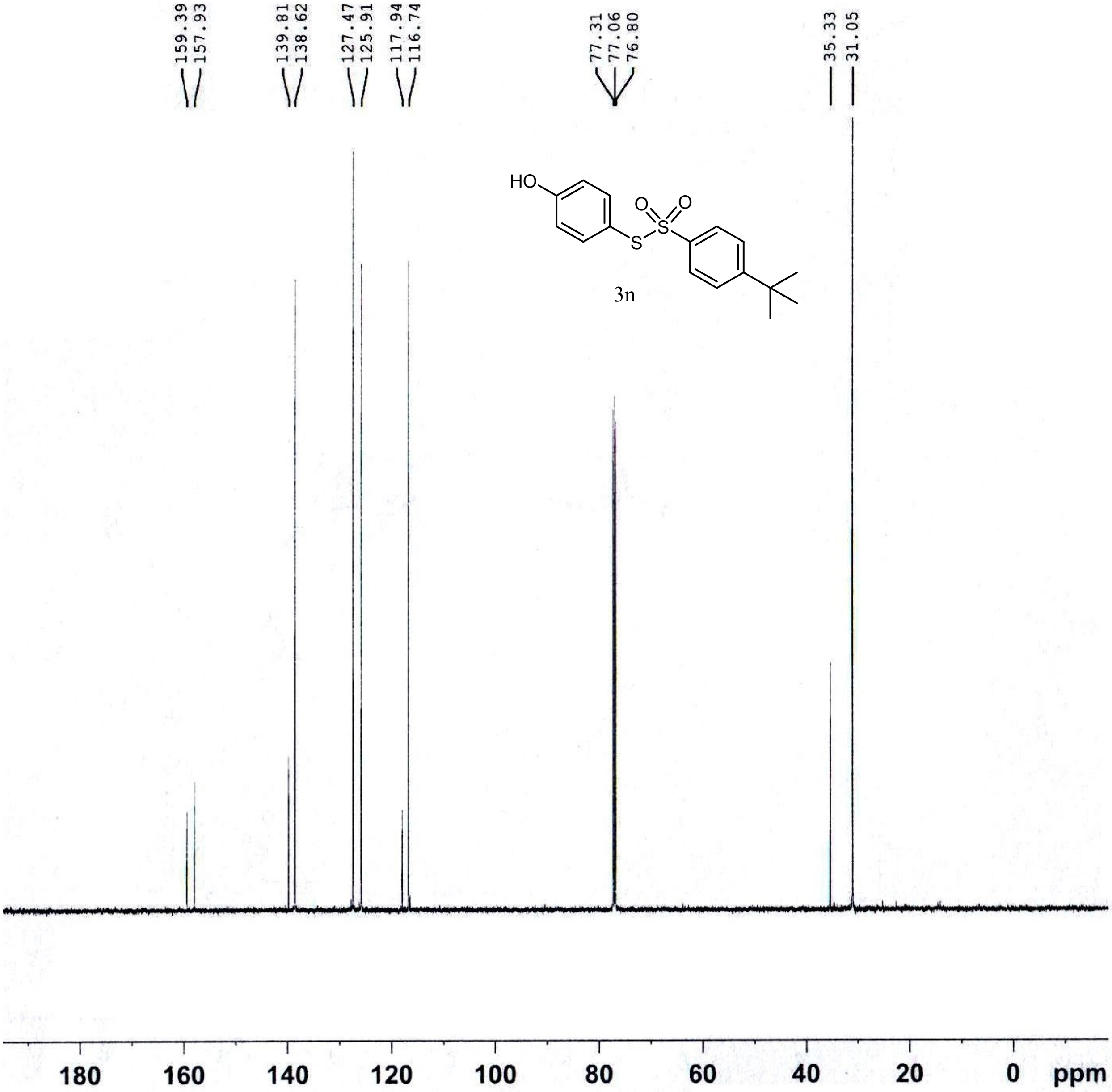
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77.06
76.80
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S
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180
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120
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80
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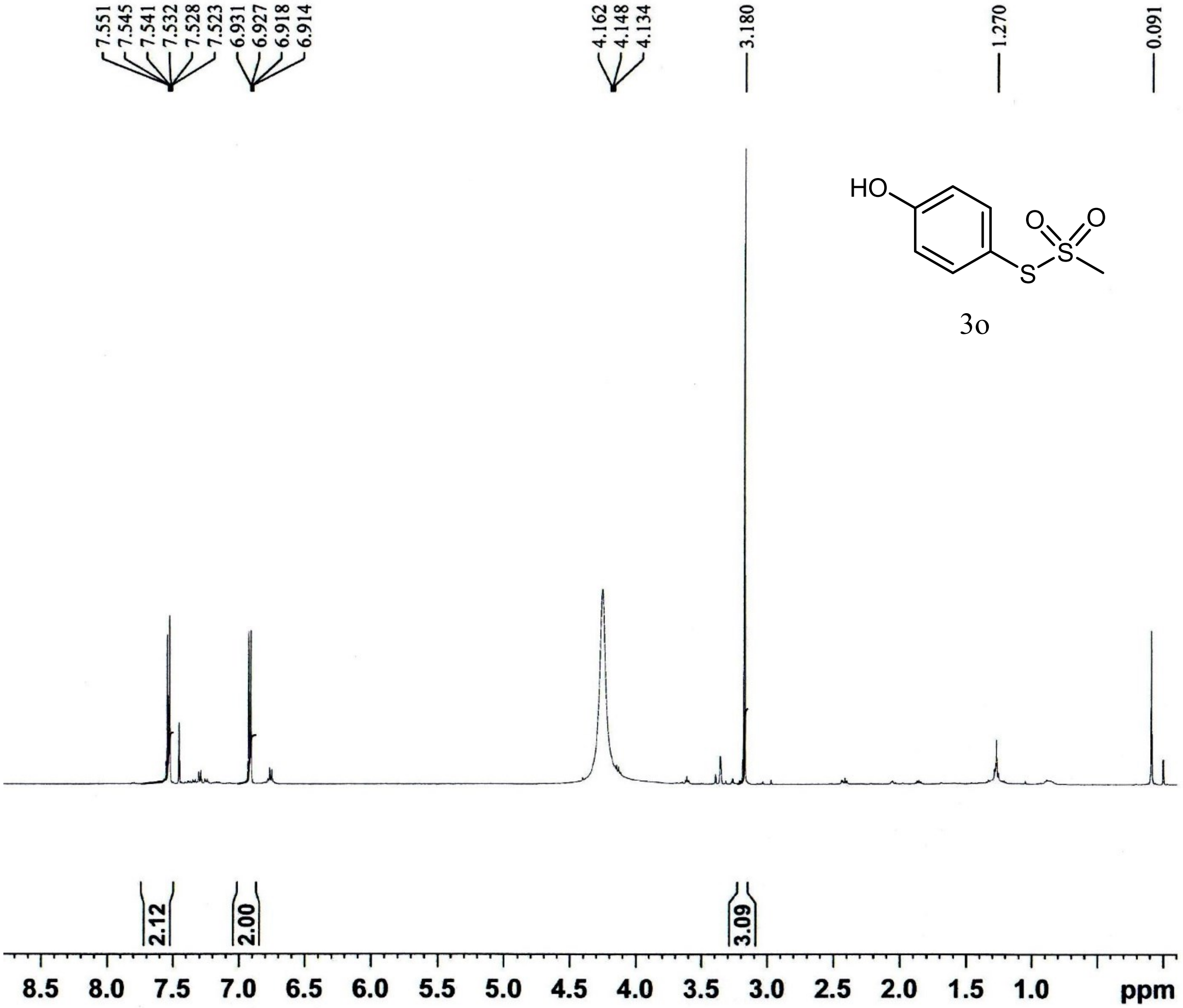
40
20
0
ppm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4.148
4.134
3.180
1.270
0.091
HO
O
O
S
S
3o
2.12
2.00
3.09
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7.5
7.0
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1.5
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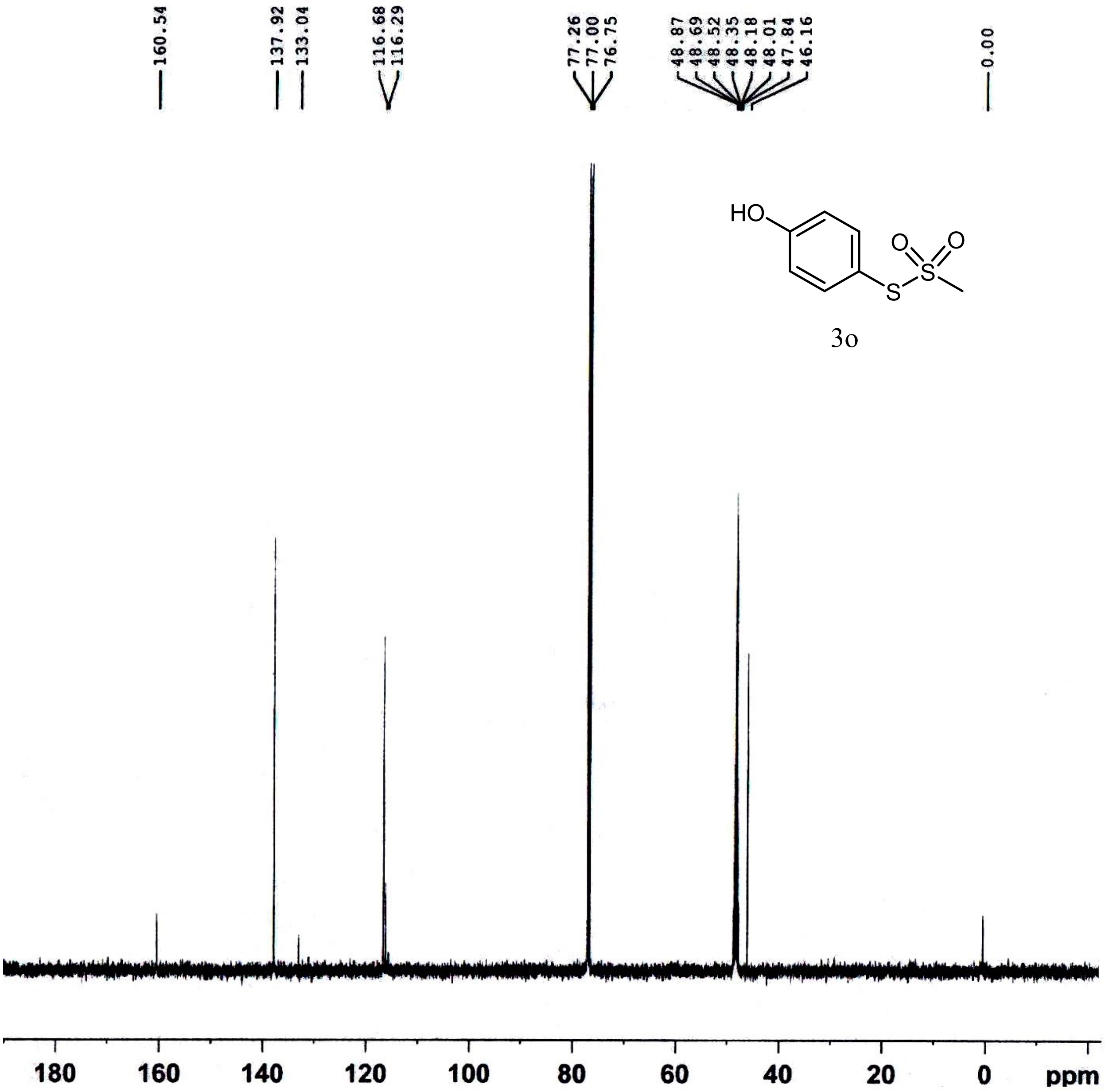
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48.01
47.84
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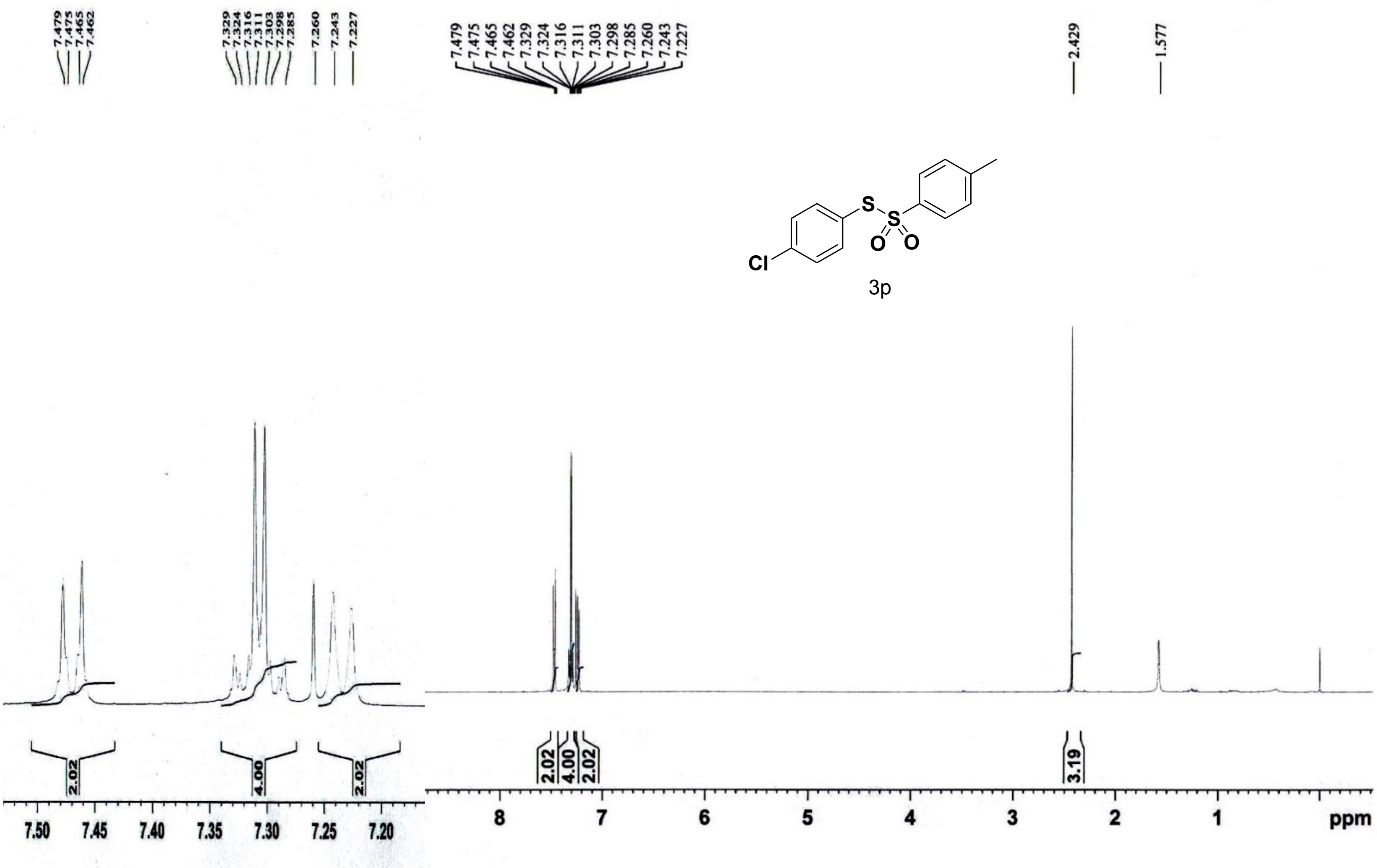
40
20
0
ppm

3o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7.303
7.298
7.285
7.260
7.243
7.227
2.429
1.577
Cl
S
S
O
O
2.02
4.00
2.02
3.19
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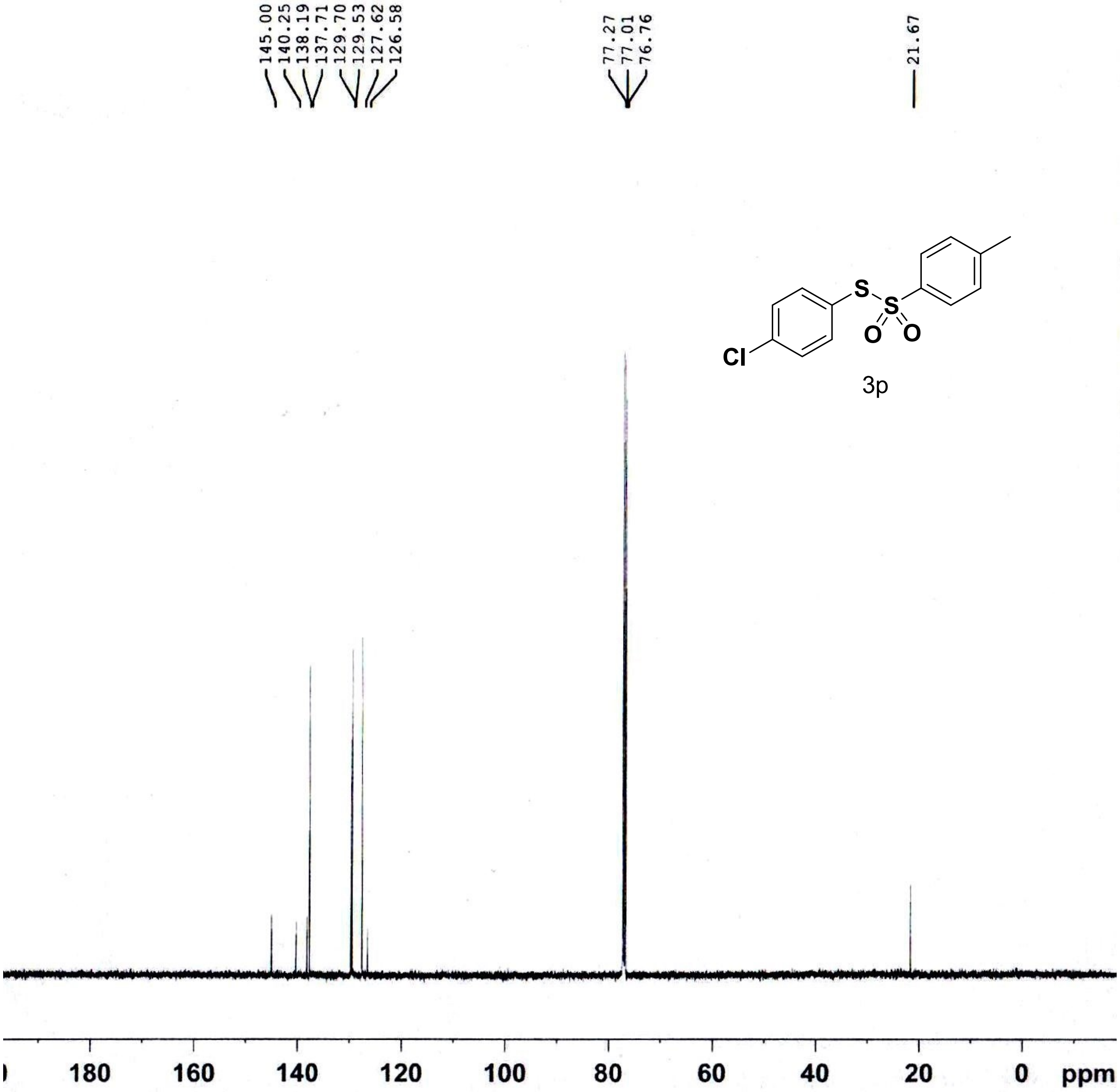
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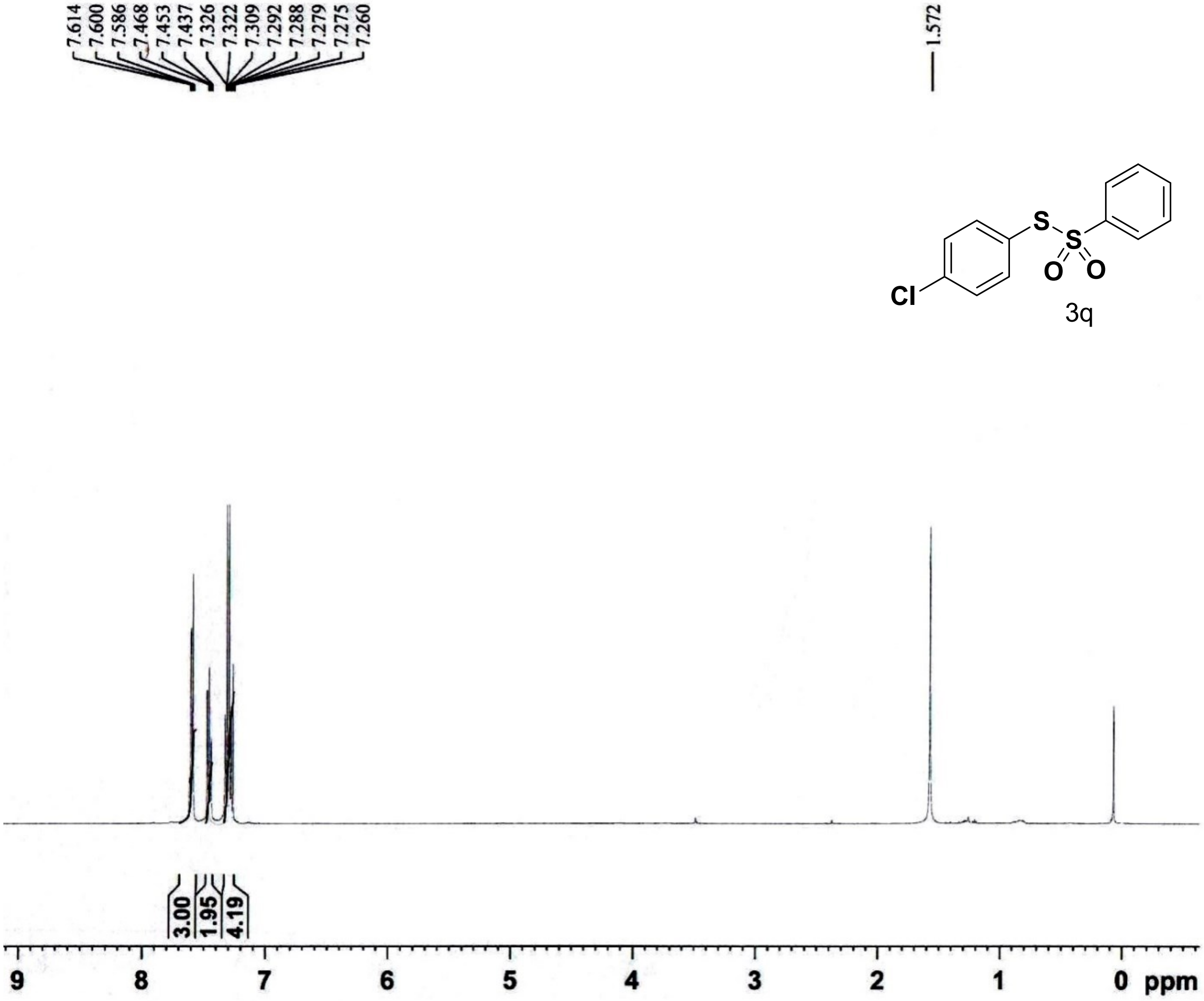
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7.275
7.260
1.572
S
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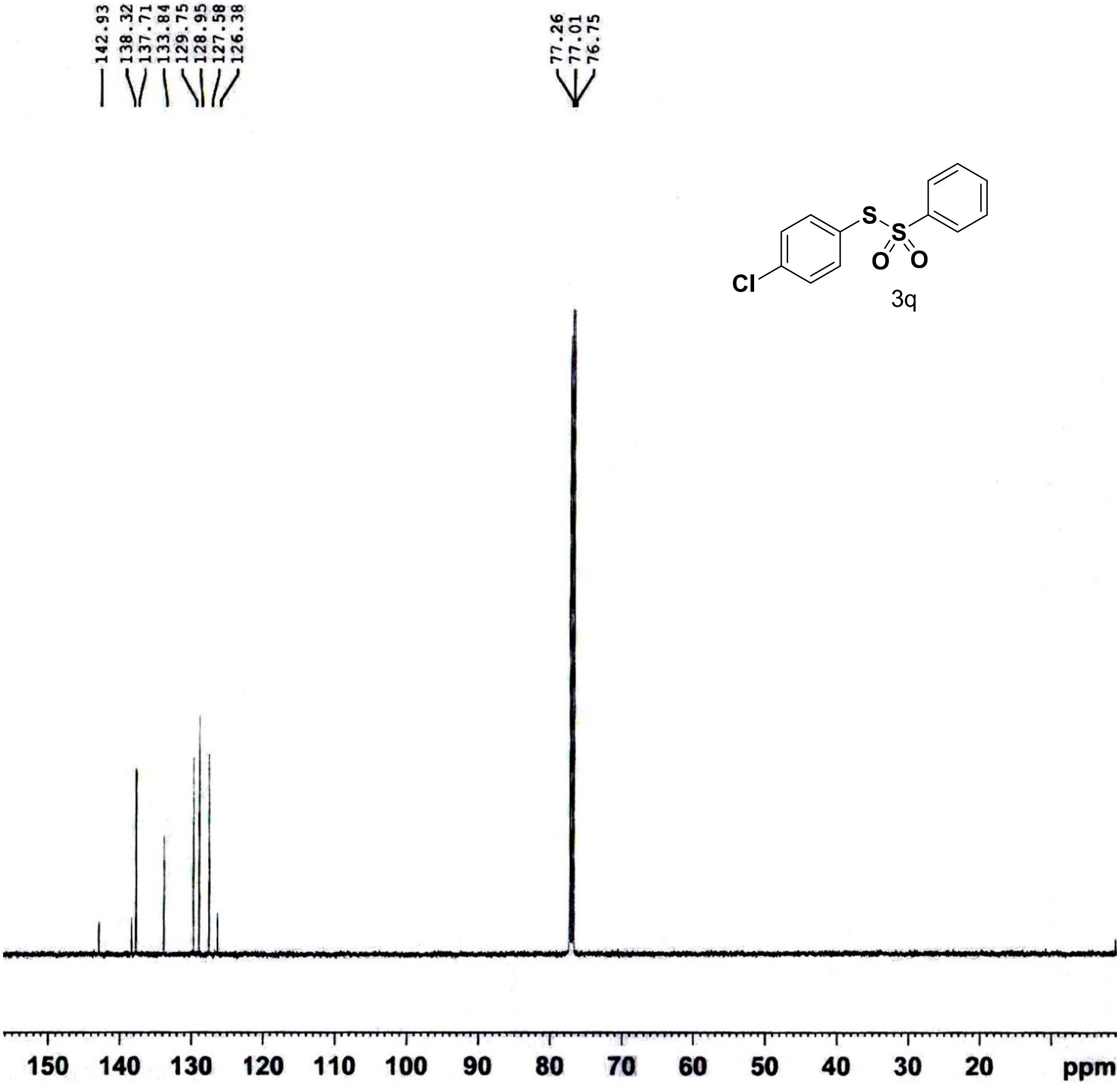
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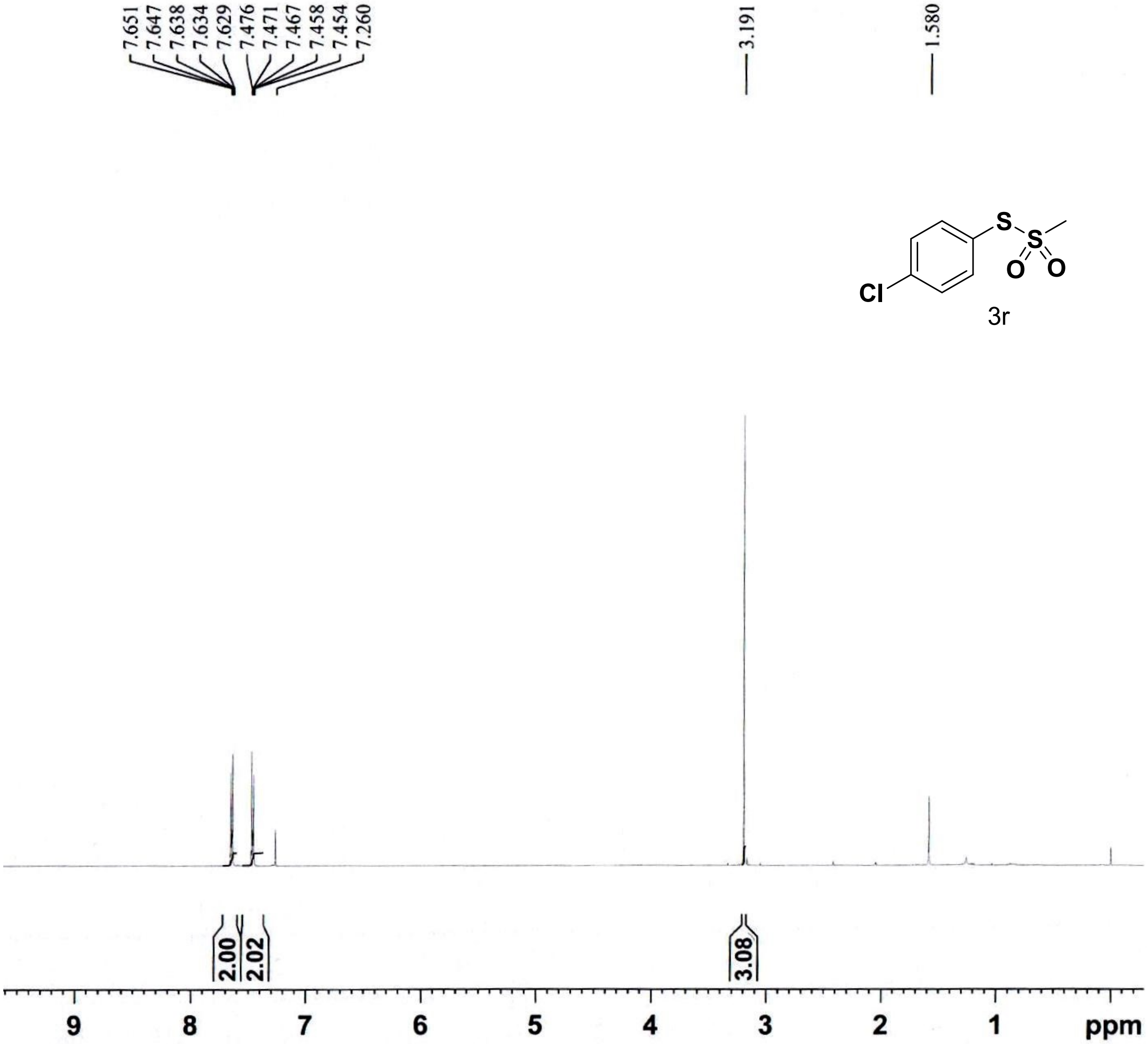
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Cl
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3
2
1
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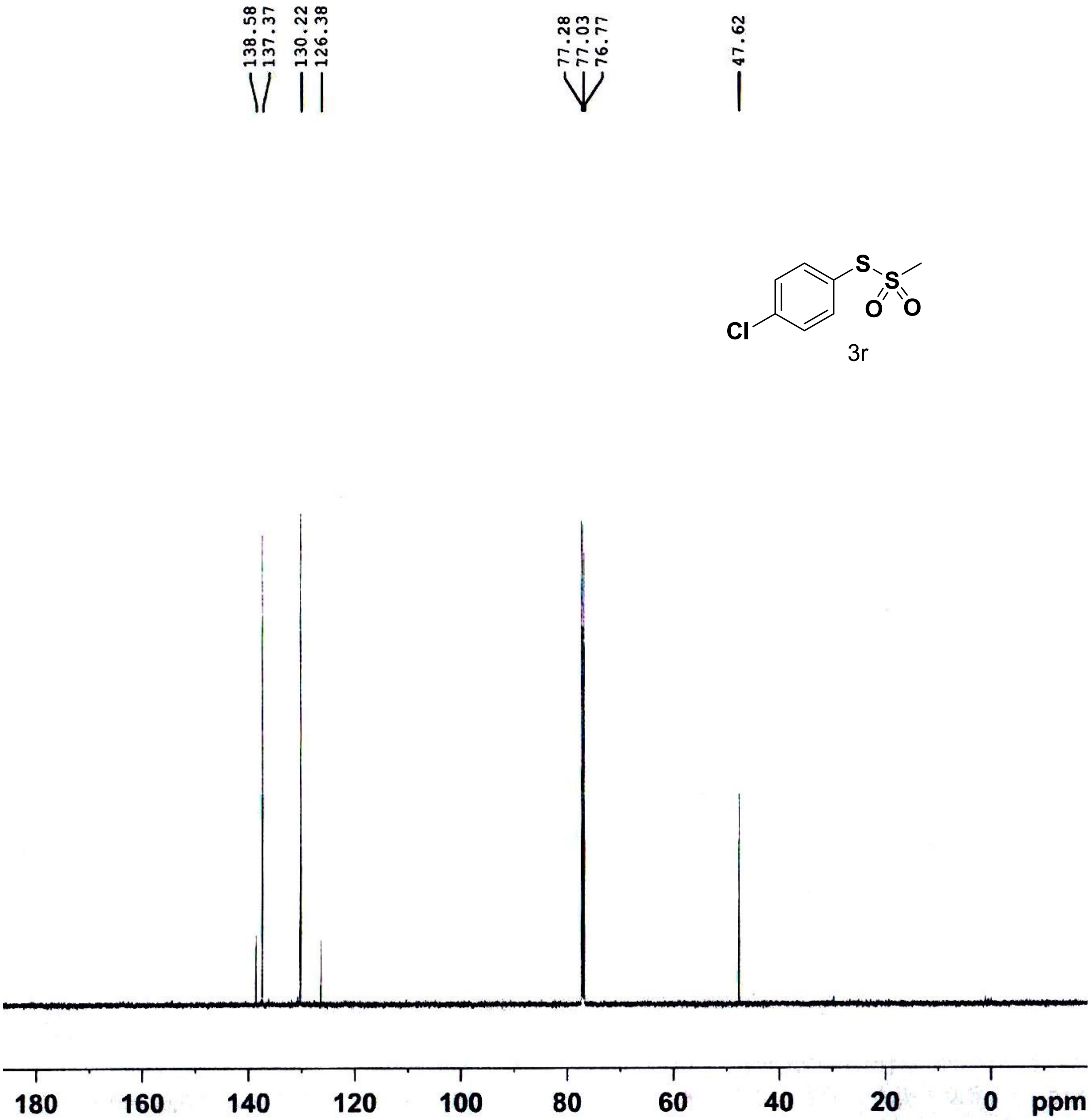
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77.03
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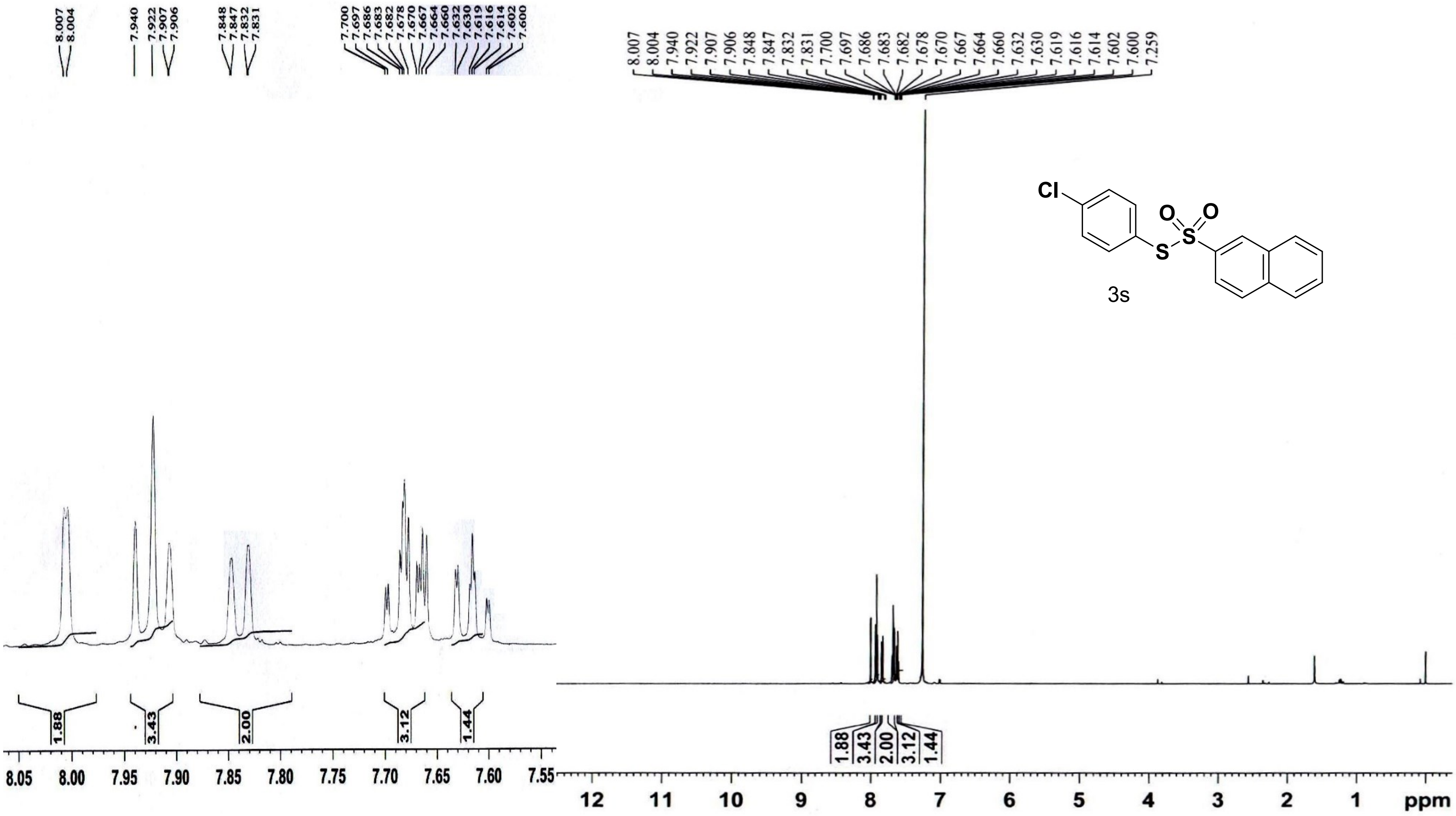
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7.697
7.686
7.683
7.682
7.678
7.670
7.667
7.664
7.660
7.632
7.630
7.619
7.616
7.614
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7.600
1.88
3.43
2.00
3.12
1.44
8.05
8.00
7.95
7.90
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7.80
7.75
7.70
7.65
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7.55
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8.004
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7.602
7.600
7.259
Cl
O
O
S
S
1.88
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1.44
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4
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ppm

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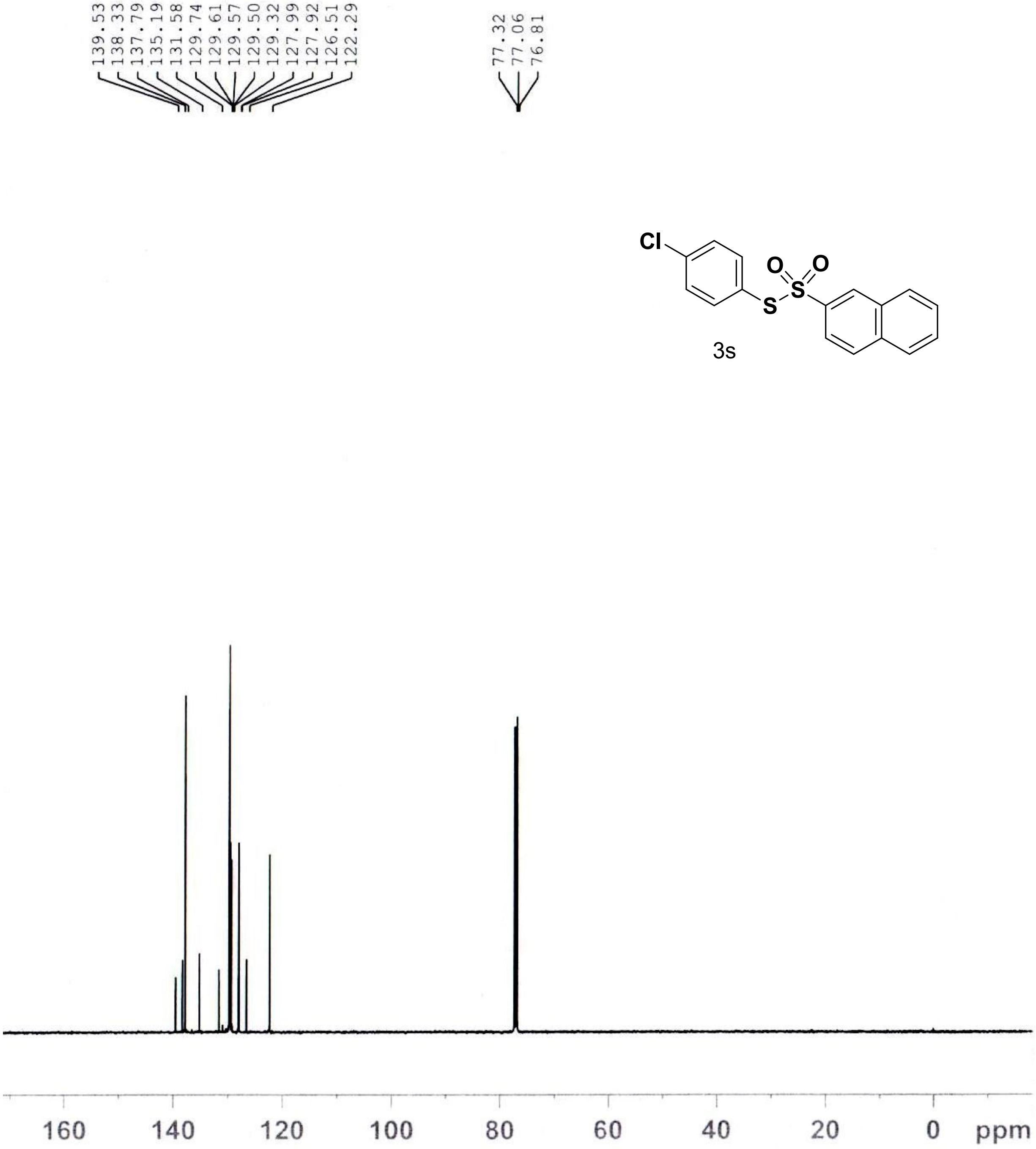
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129.57
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129.32
127.99
127.92
126.51
122.29
77.32
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Cl
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O
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20
0
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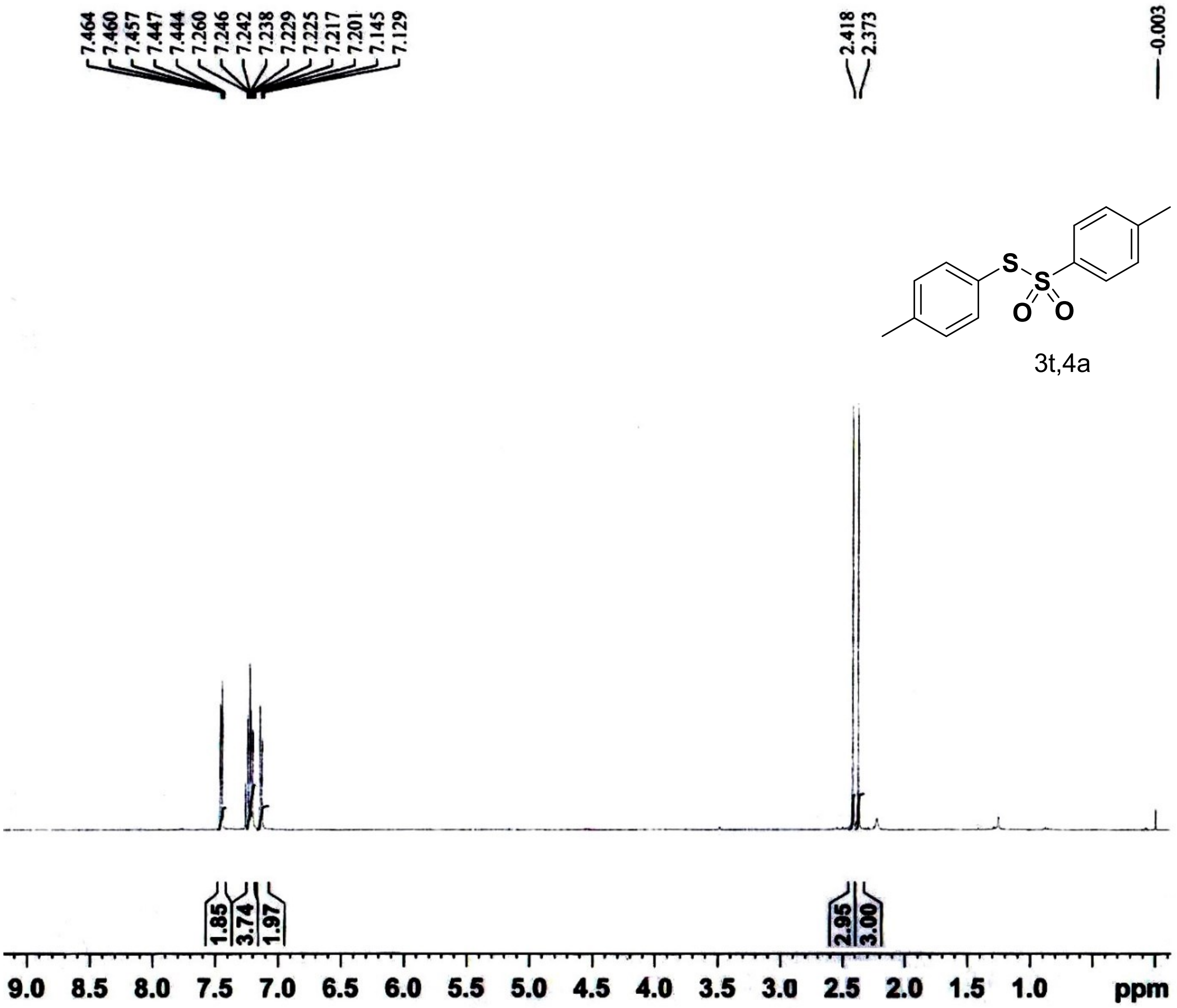
3s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7.229
7.225
7.217
7.201
7.145
7.129
2.418
2.373
-0.003
S
S
O
O
1.85
3.74
1.97
2.95
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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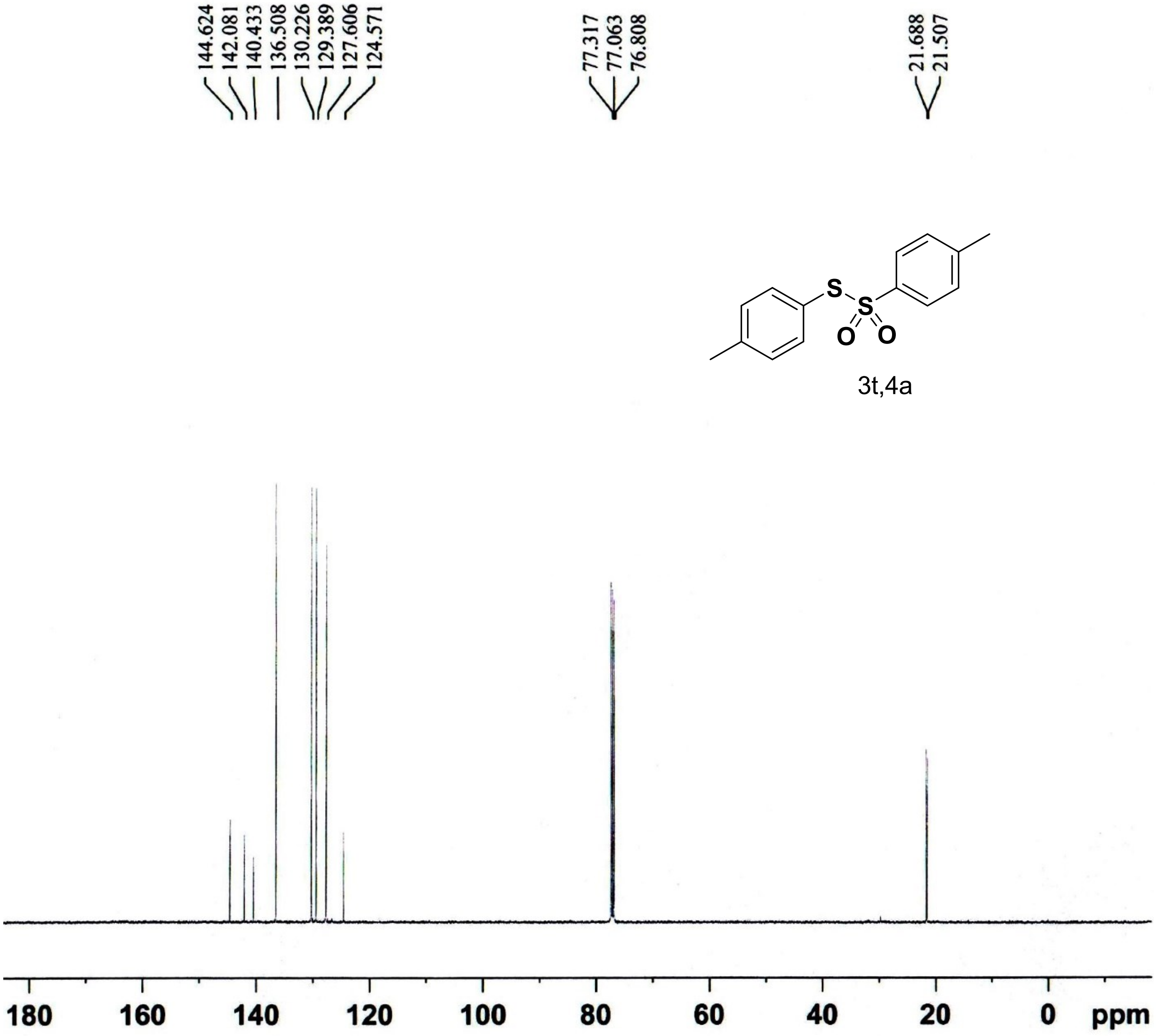
3t,4a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77.063
76.808
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O
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120
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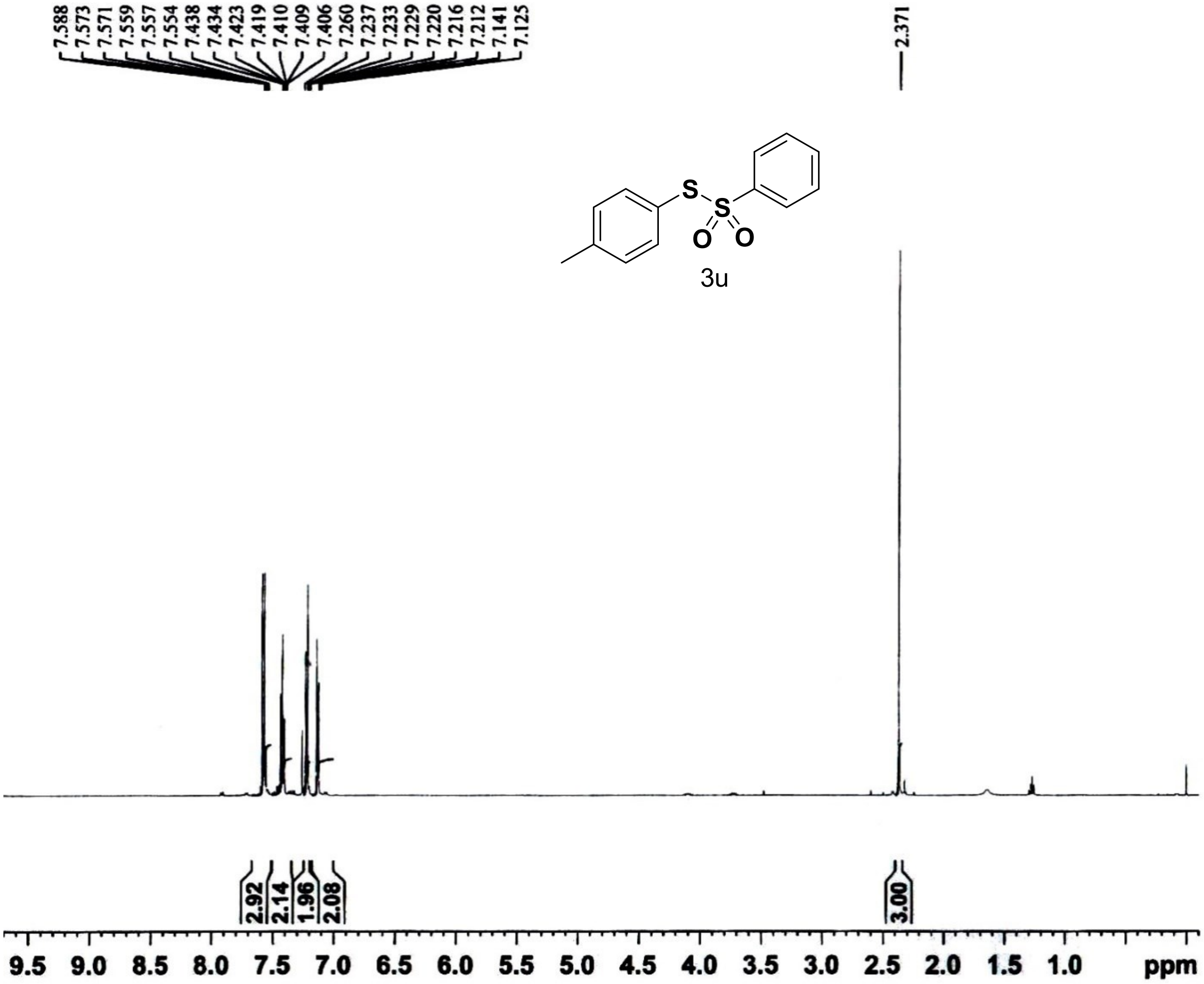
80
60
40
20
0
ppm

3t,4a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7.434
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7.419
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7.409
7.406
7.260
7.237
7.233
7.229
7.220
7.216
7.212
7.141
7.125
2.371
S
S
O
O
3u
2.92
2.14
1.96
2.08
3.00
9.5
9.0
8.5
8.0
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7.0
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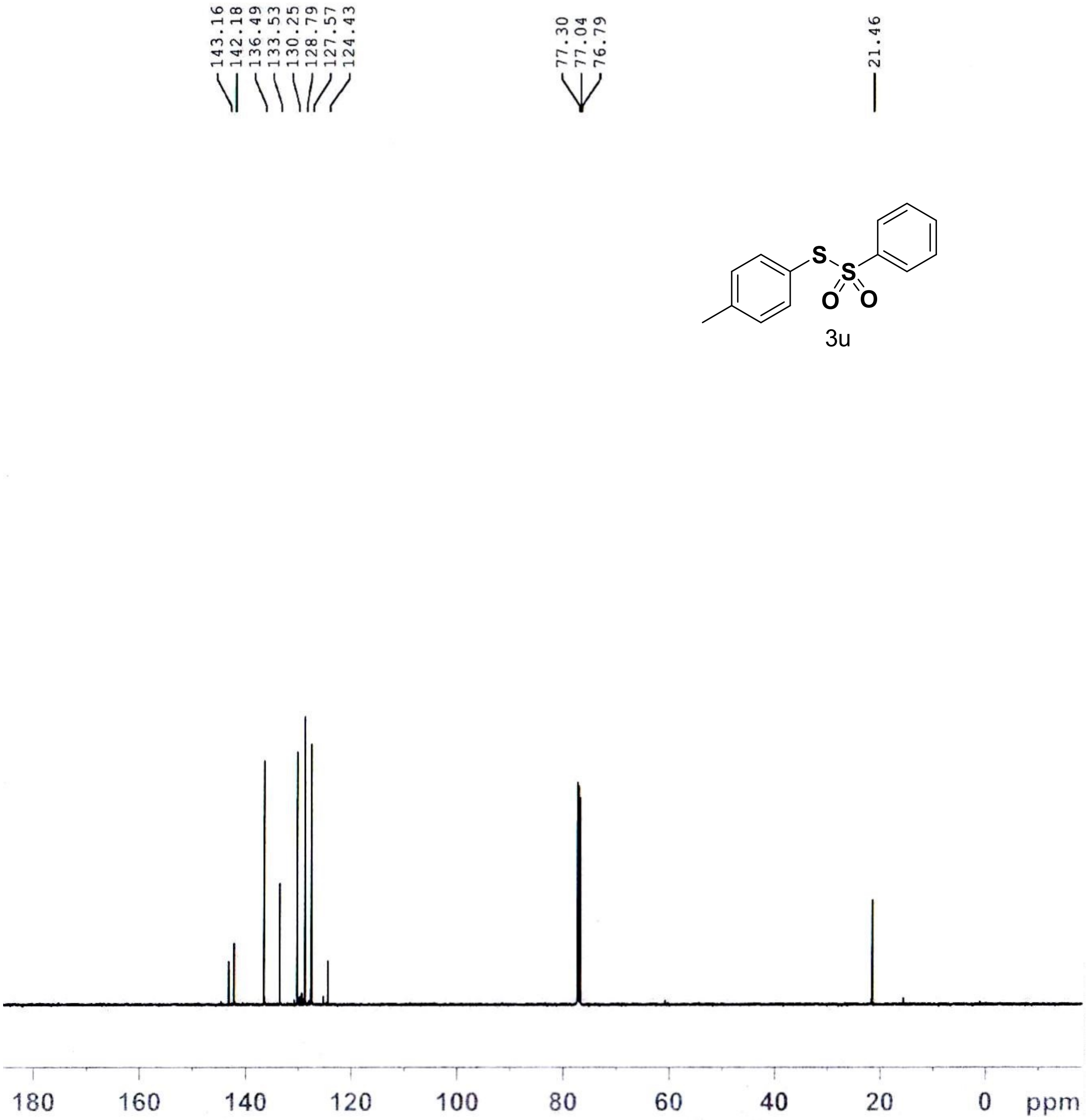
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77.04
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20
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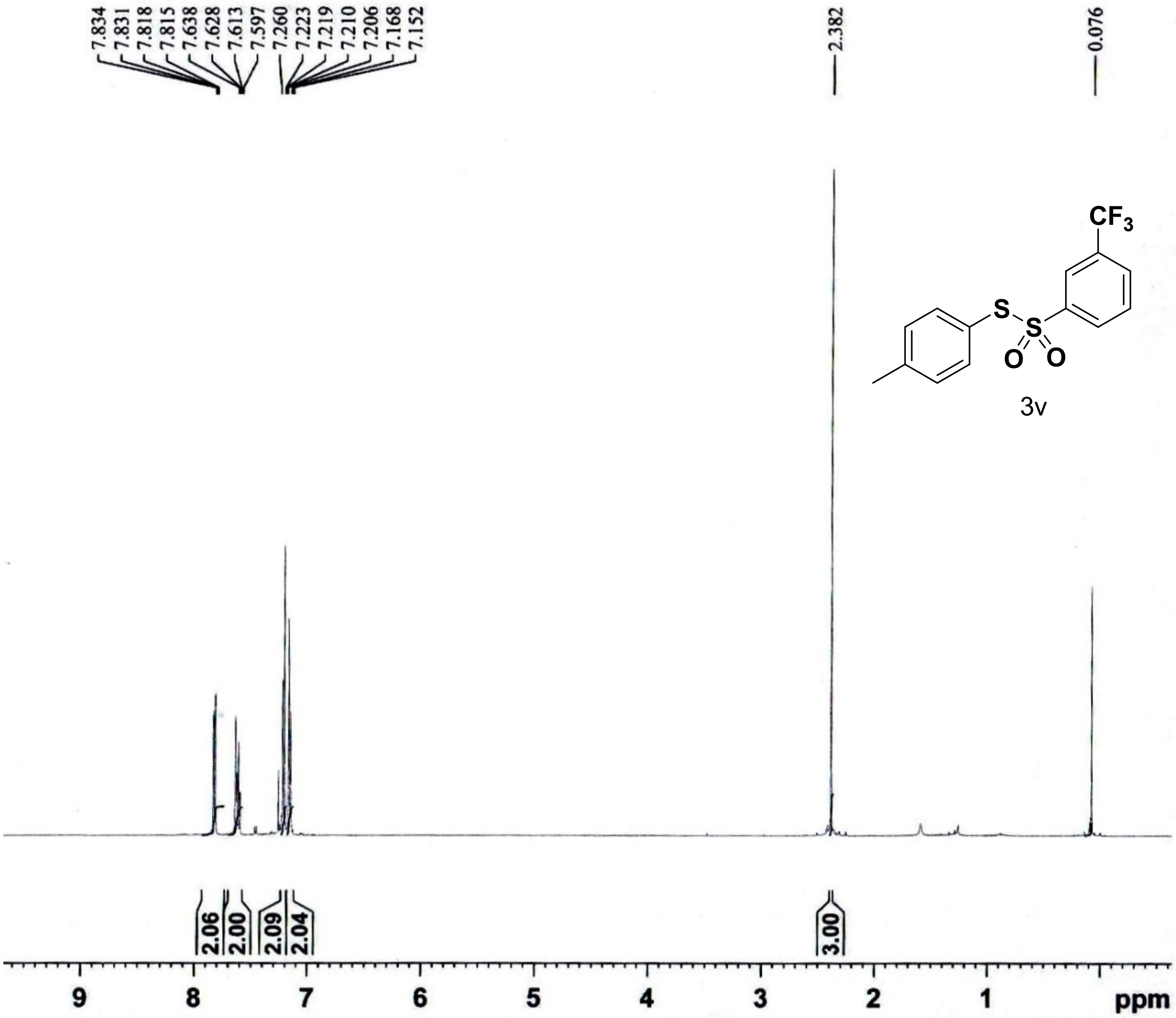
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7.210
7.206
7.168
7.152
2.382
0.076
CF3
S
S
O
O
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2.00
2.09
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9
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7
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3
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1
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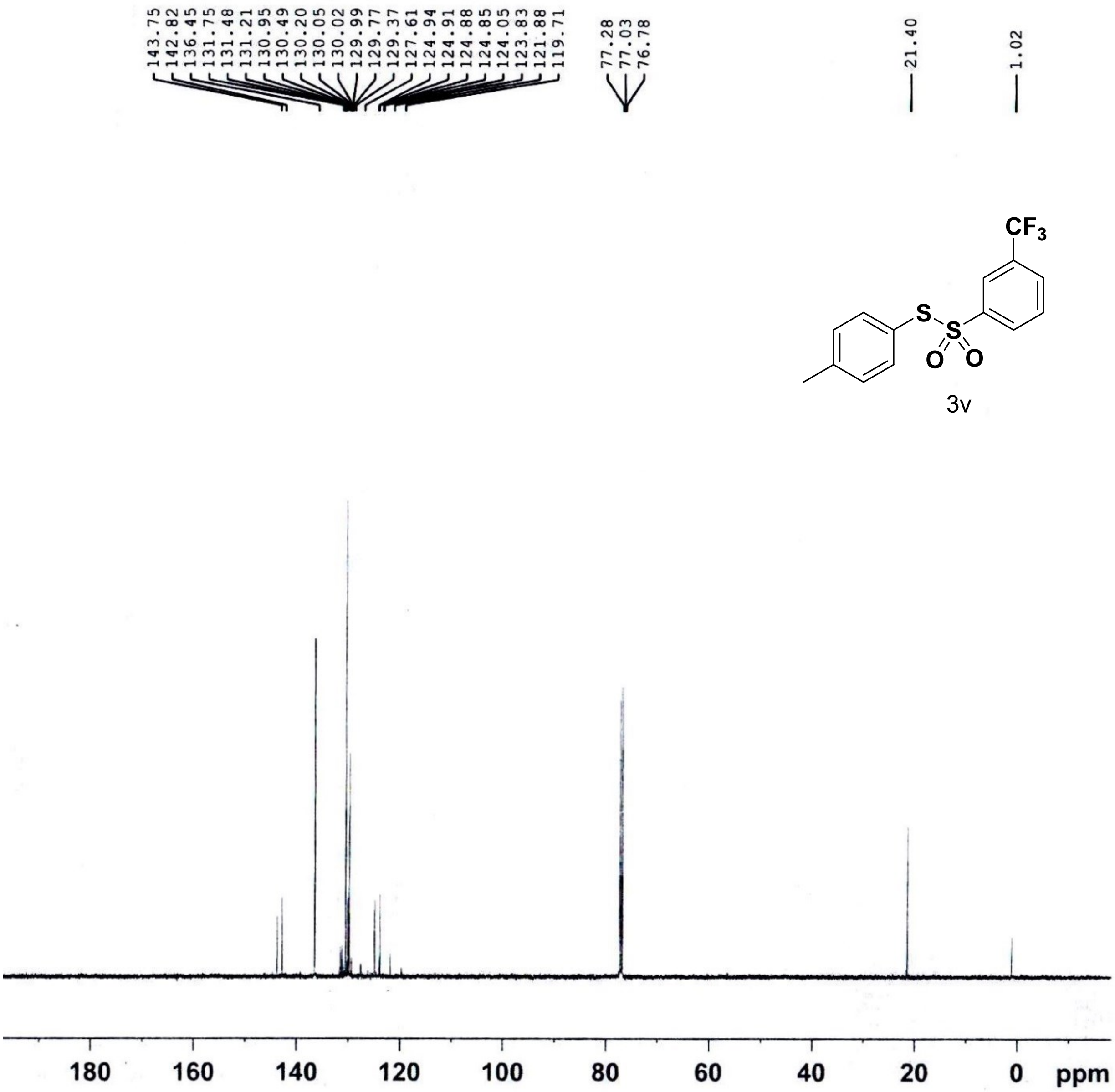
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129.77
129.37
127.61
124.94
124.91
124.88
124.85
124.05
123.83
121.88
119.71
77.28
77.03
76.78
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80
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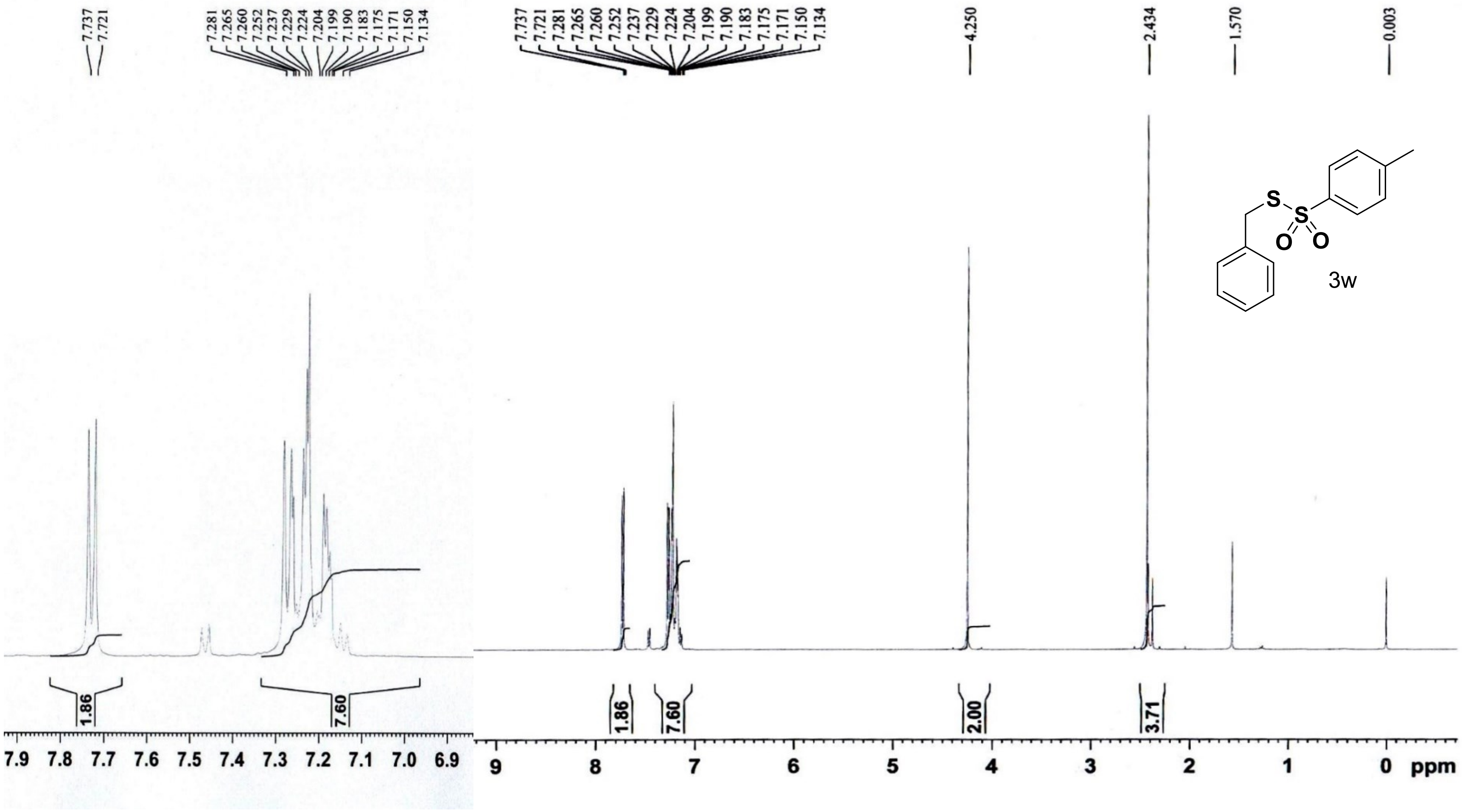
40
20
0
ppm

3v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7.183
7.175
7.171
7.150
7.134
4.250
2.434
1.570
0.003
1.86
7.60
2.00
3.71
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
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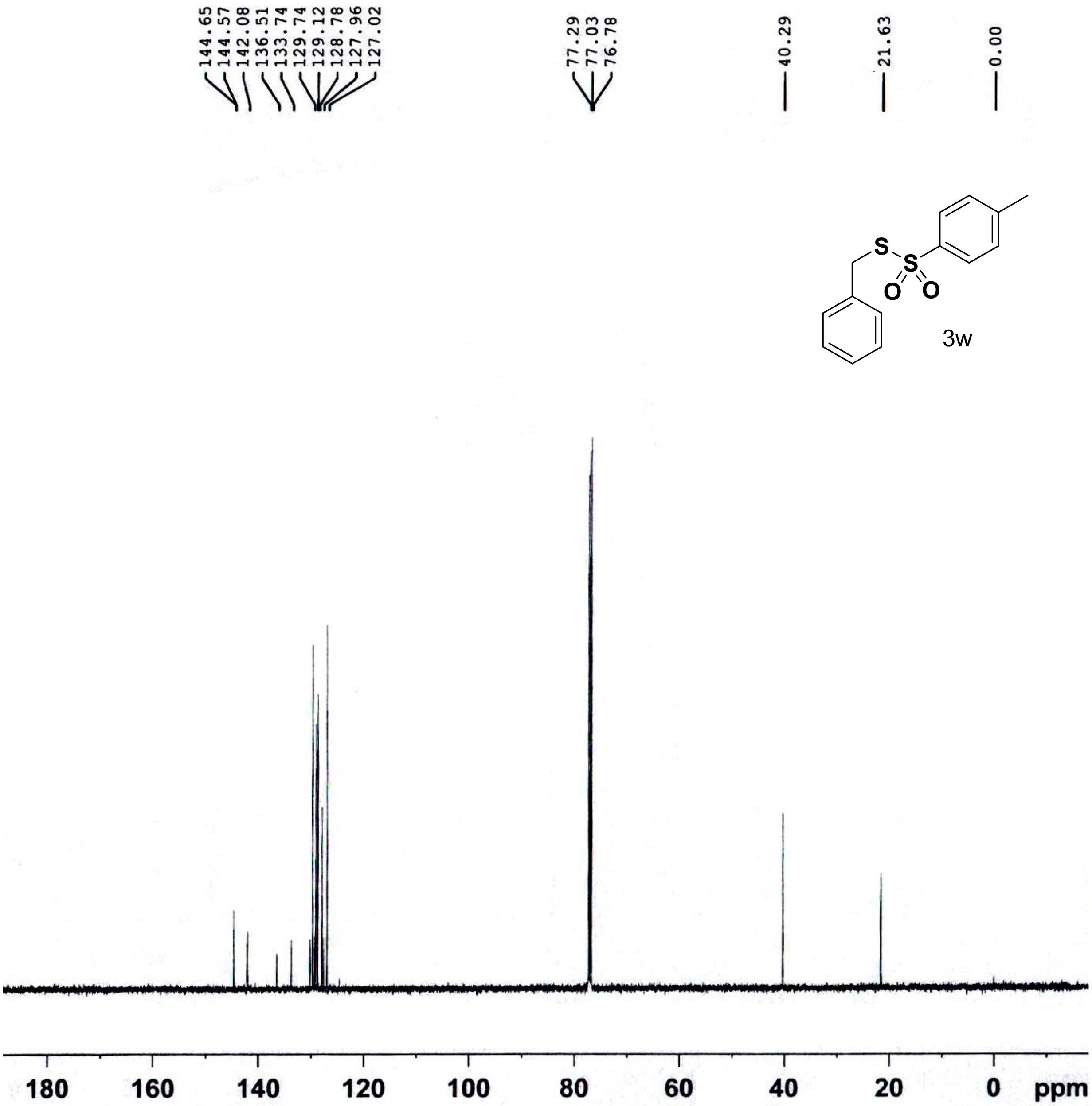
S
S
O
O
3w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127.02
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77.03
76.78
40.29
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0
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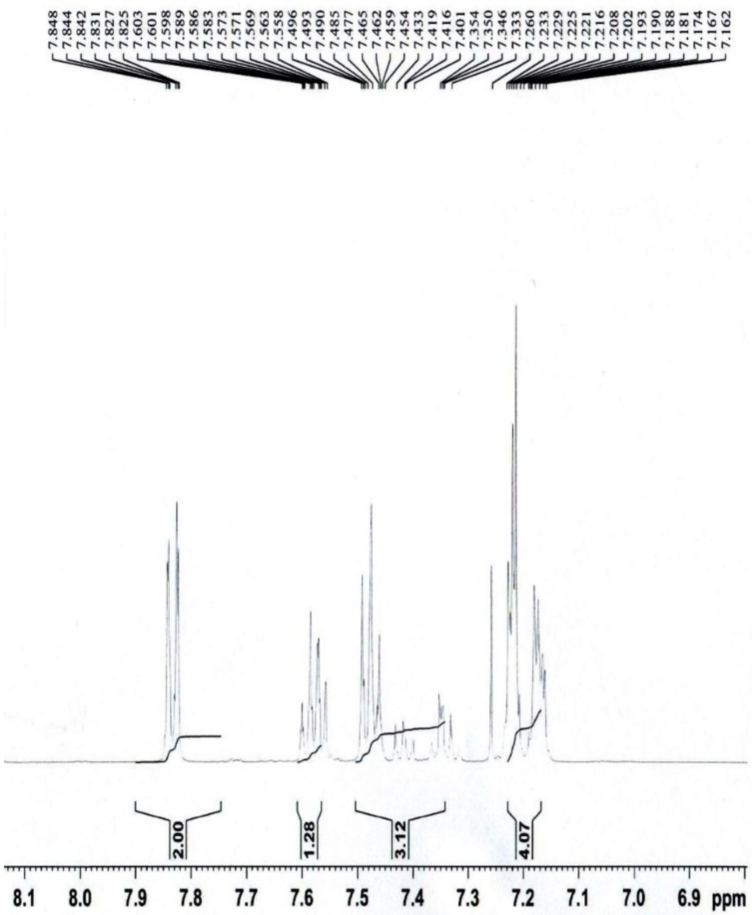
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7.571
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7.558
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7.493
7.490
7.485
7.477
7.465
7.462
7.459
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7.416
7.401
7.354
7.350
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7.333
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7.233
7.229
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7.221
7.216
7.208
7.202
7.193
7.190
7.188
7.181
7.174
7.167
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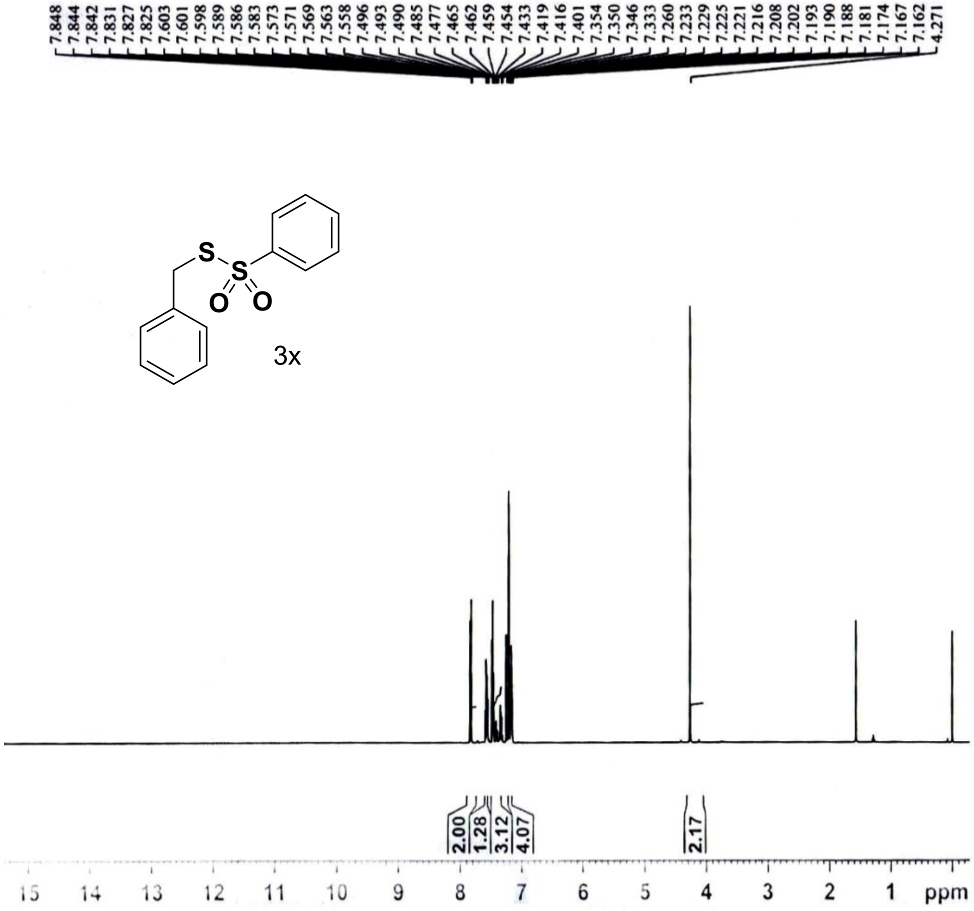
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7.571
7.569
7.563
7.558
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7.490
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7.462
7.459
7.454
7.433
7.419
7.416
7.401
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7.350
7.346
7.333
7.260
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7.229
7.225
7.221
7.216
7.208
7.202
7.193
7.190
7.188
7.181
7.174
7.167
7.162
4.271
S
S
O
O
2.00
1.28
3.12
4.07
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5
4
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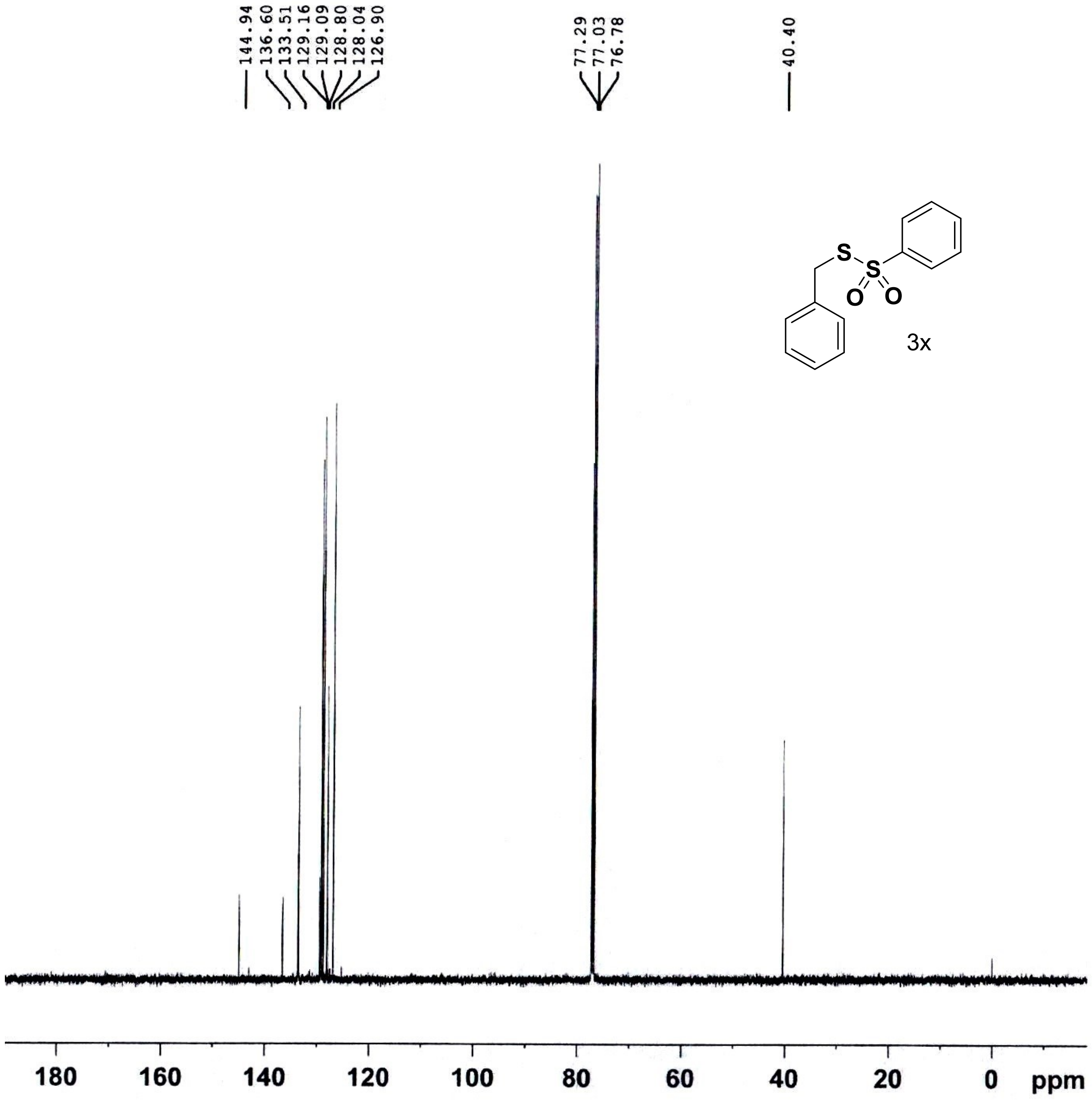
ppm

3x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77.03
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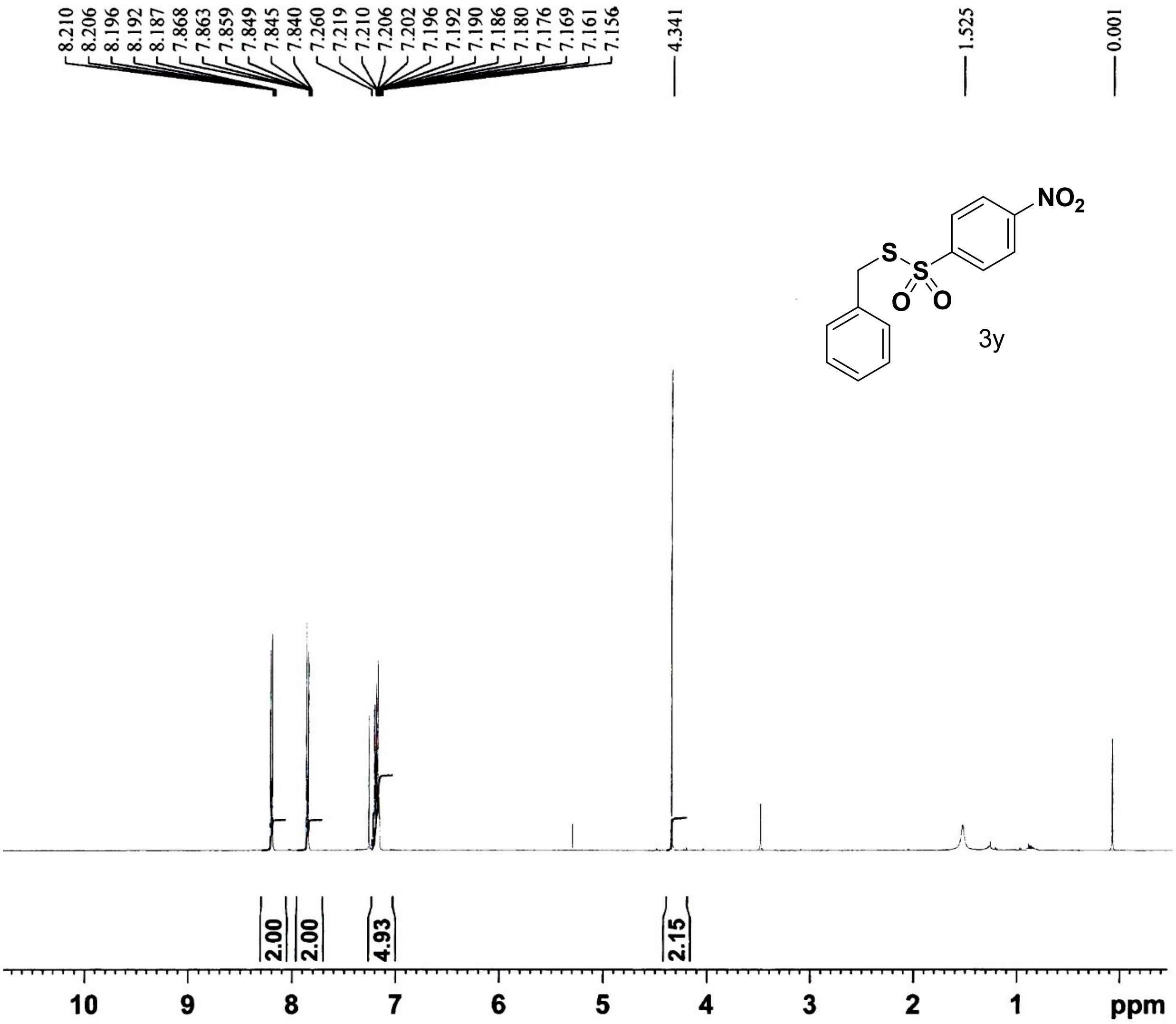
120
100
80
60
40
20
0
ppm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7.845
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7.219
7.210
7.206
7.202
7.196
7.192
7.190
7.186
7.180
7.176
7.169
7.161
7.156
4.341
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2.00
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3
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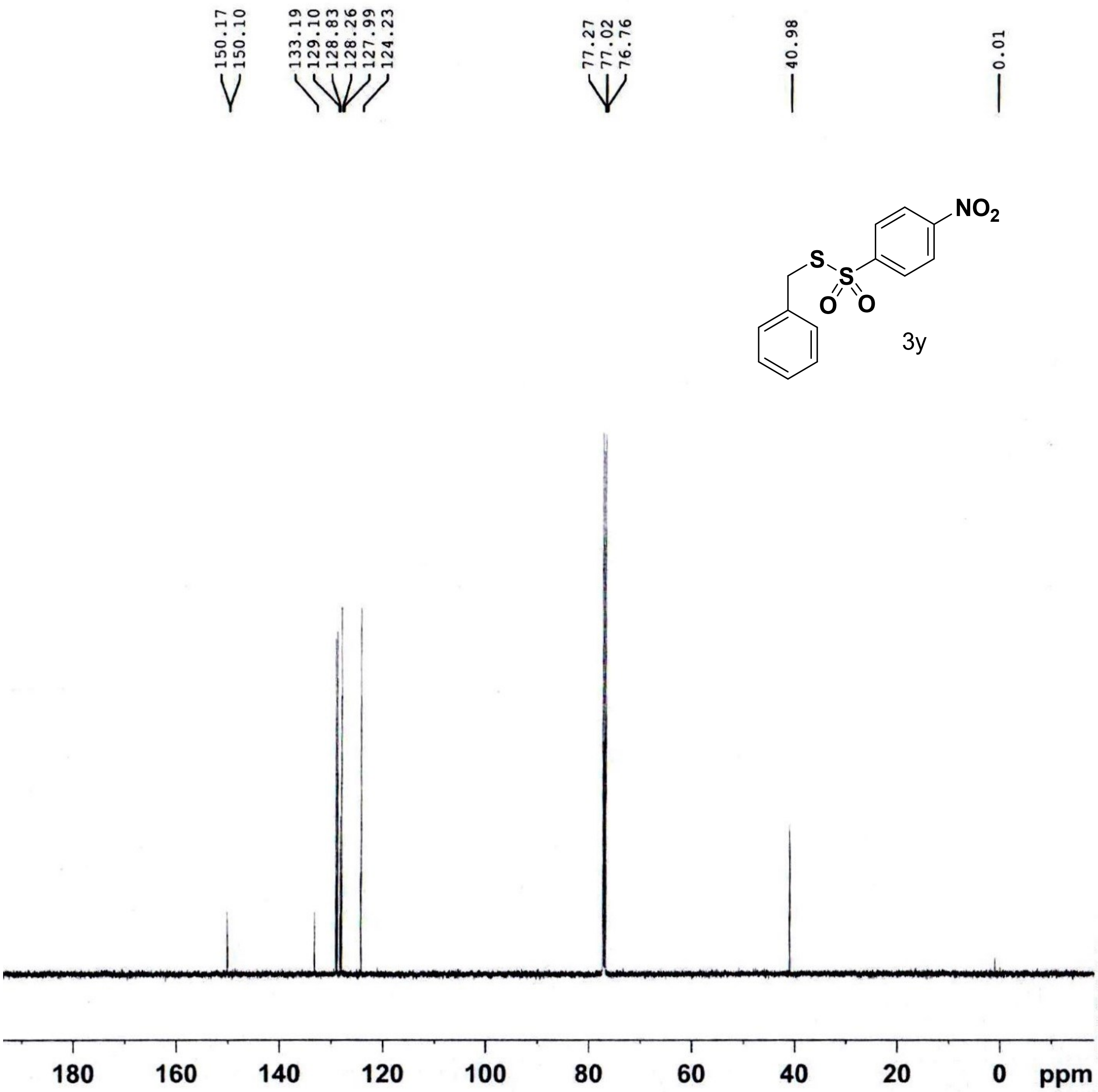
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76.76
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120
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40
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0
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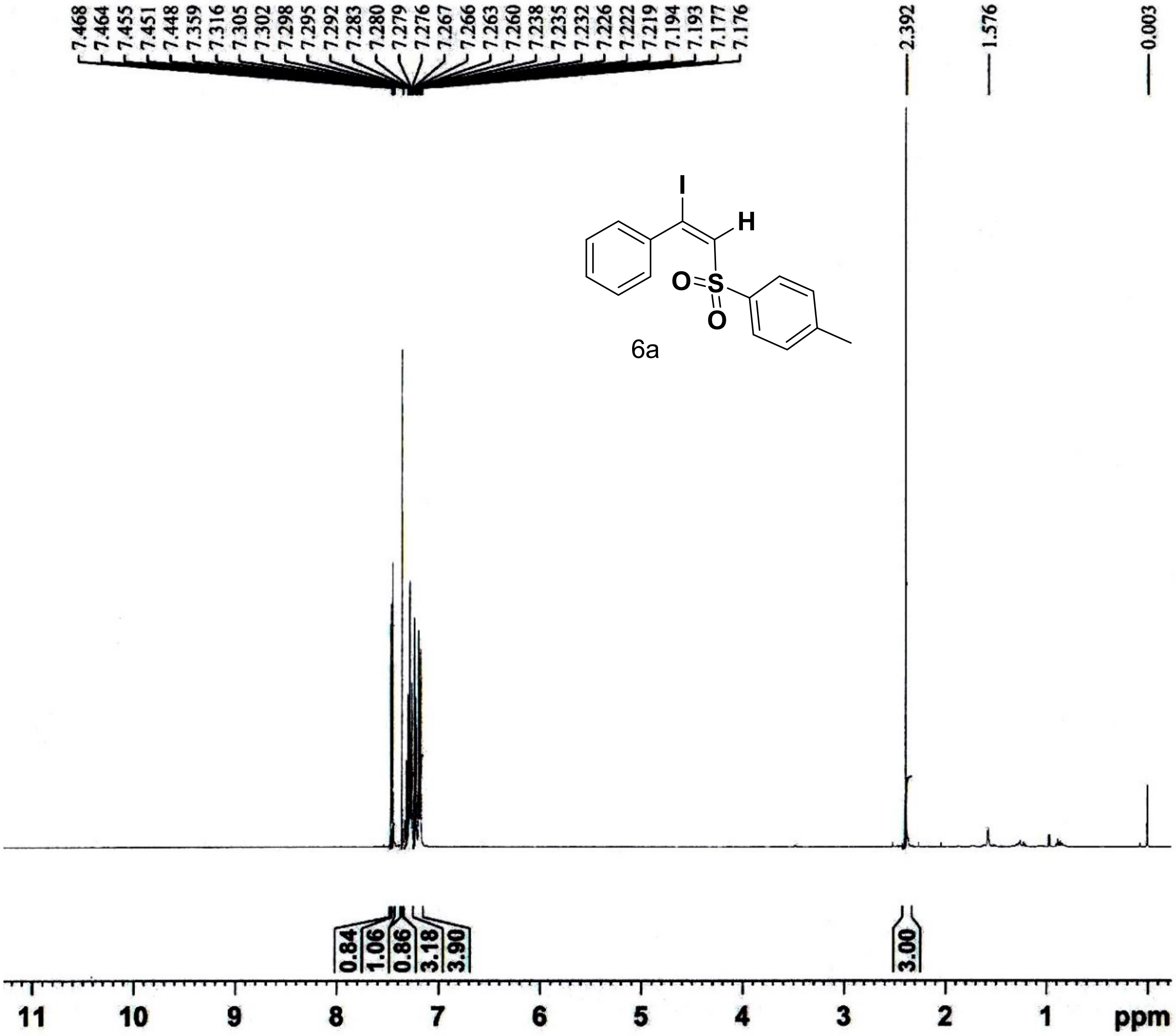
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7.279
7.276
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7.260
7.238
7.235
7.232
7.226
7.222
7.219
7.194
7.193
7.177
7.176
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1.576
0.003
I
H
O
S
O
6a
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7
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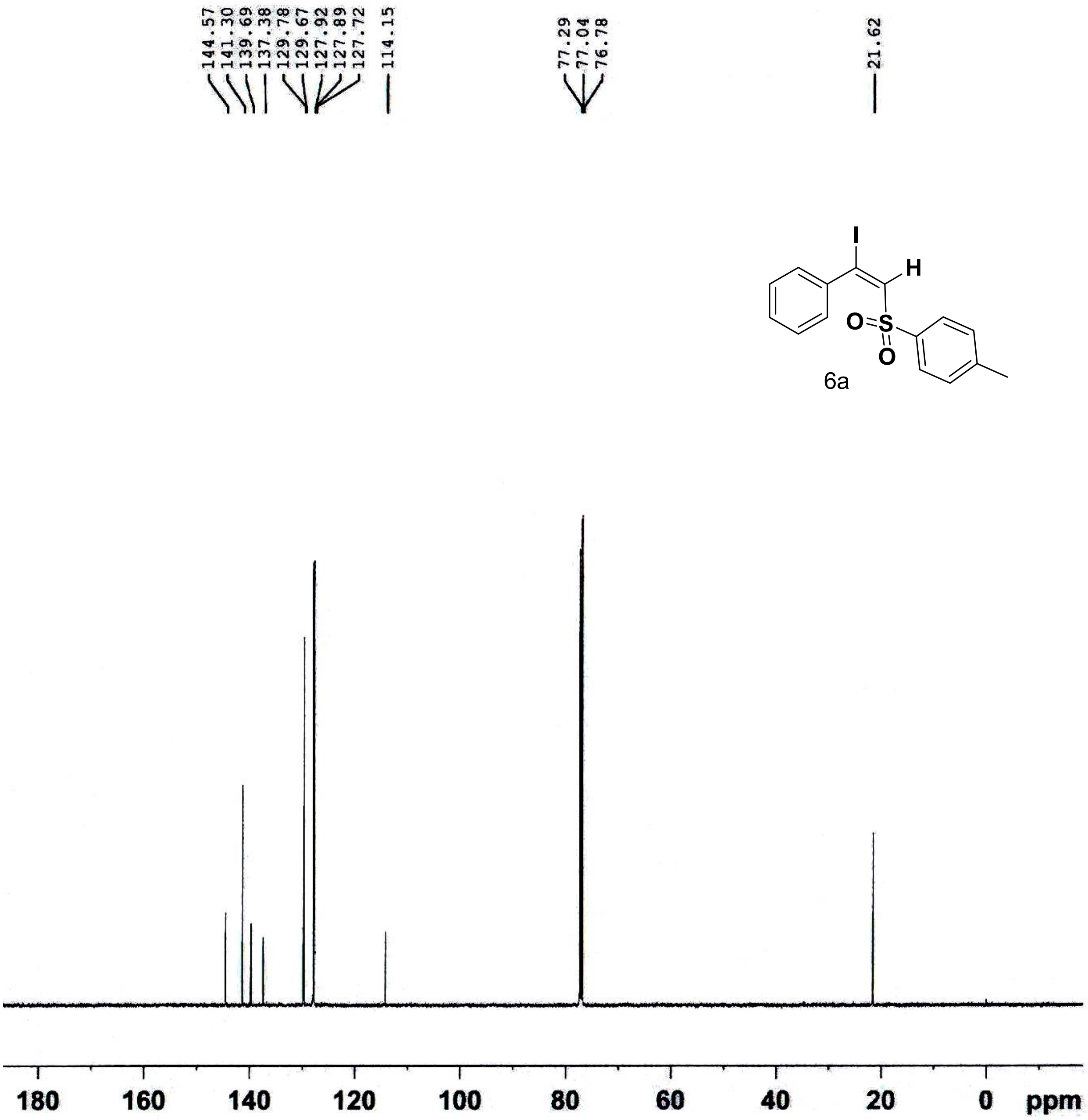
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77.04
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H
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S
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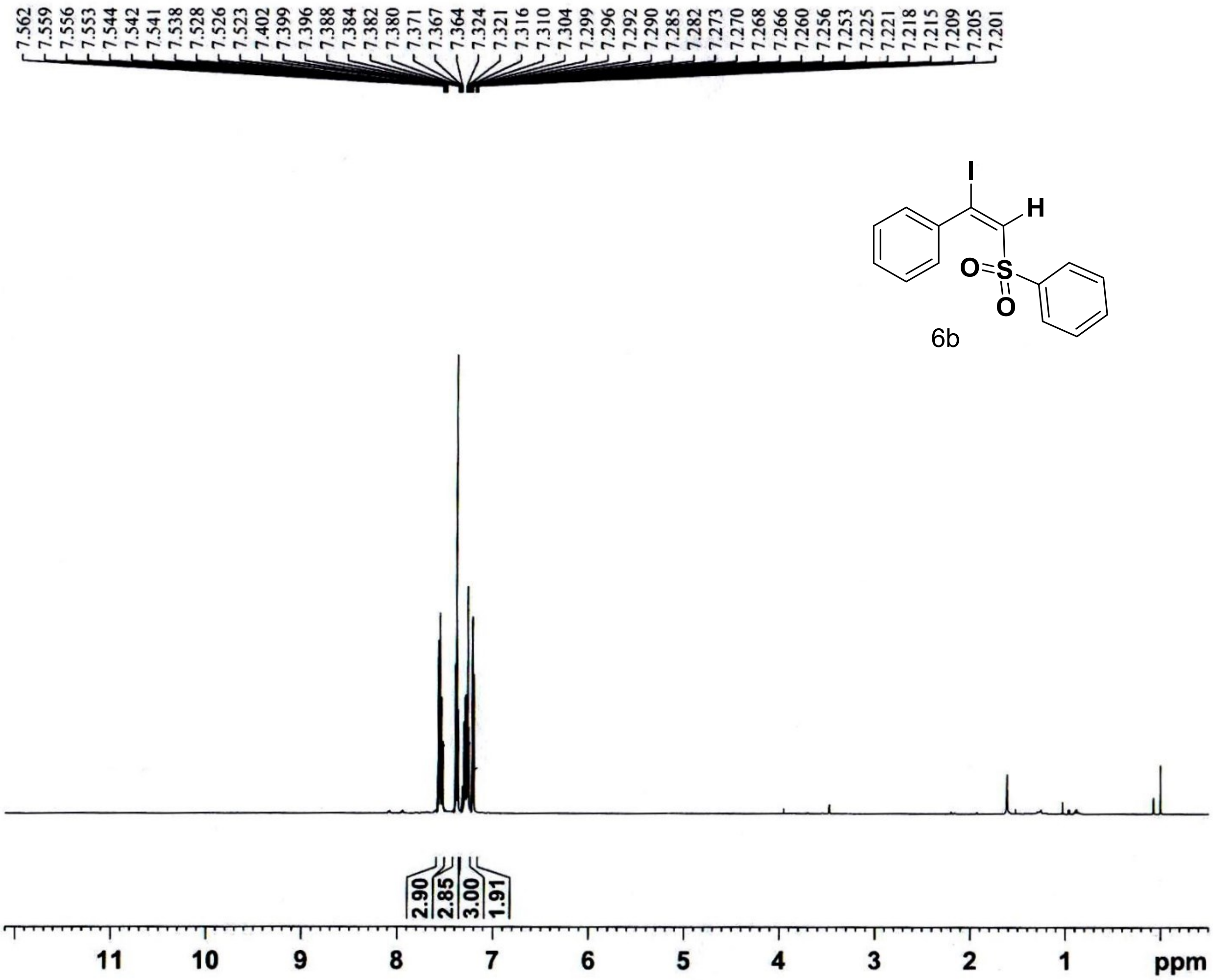
ppm

6a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7.399
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7.380
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7.321
7.316
7.310
7.304
7.299
7.296
7.292
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7.285
7.282
7.273
7.270
7.268
7.266
7.260
7.256
7.253
7.225
7.221
7.218
7.215
7.209
7.205
7.201
I
H
O
S
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3
2
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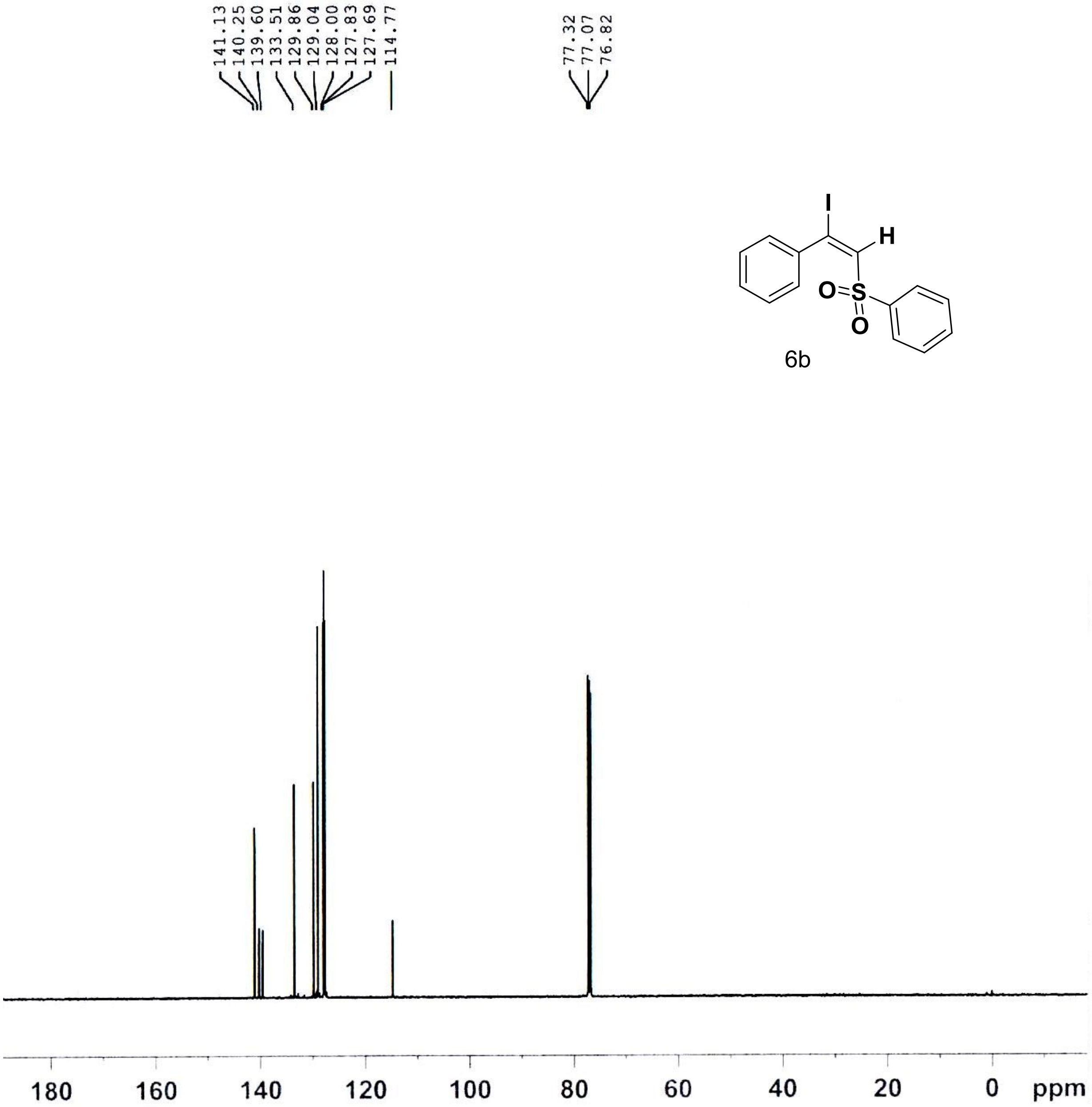
ppm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114.77
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I
H
O
S
O
6b
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120
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40
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0
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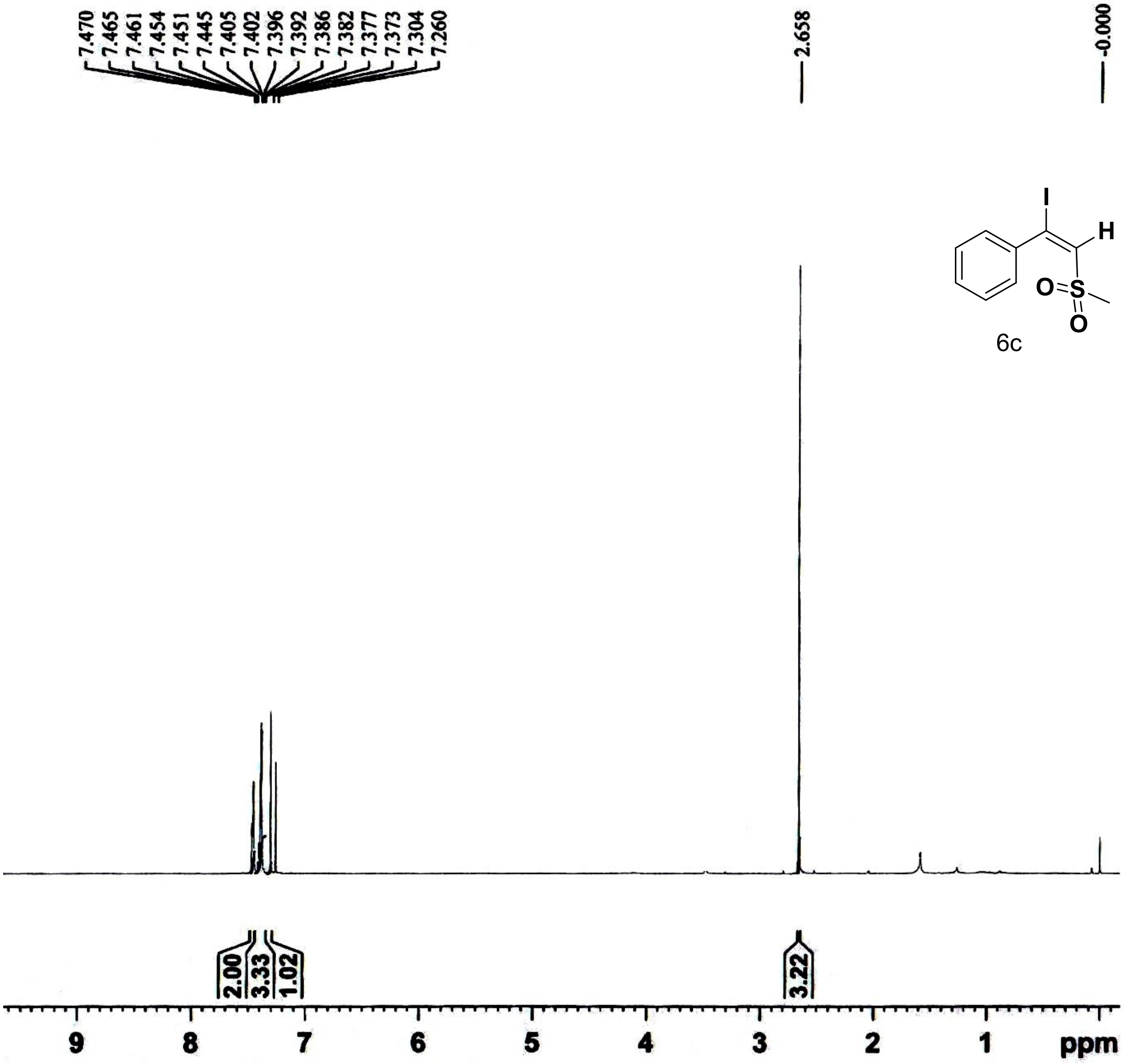
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7.377
7.373
7.304
7.260
2.658
-0.000
I
H
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2
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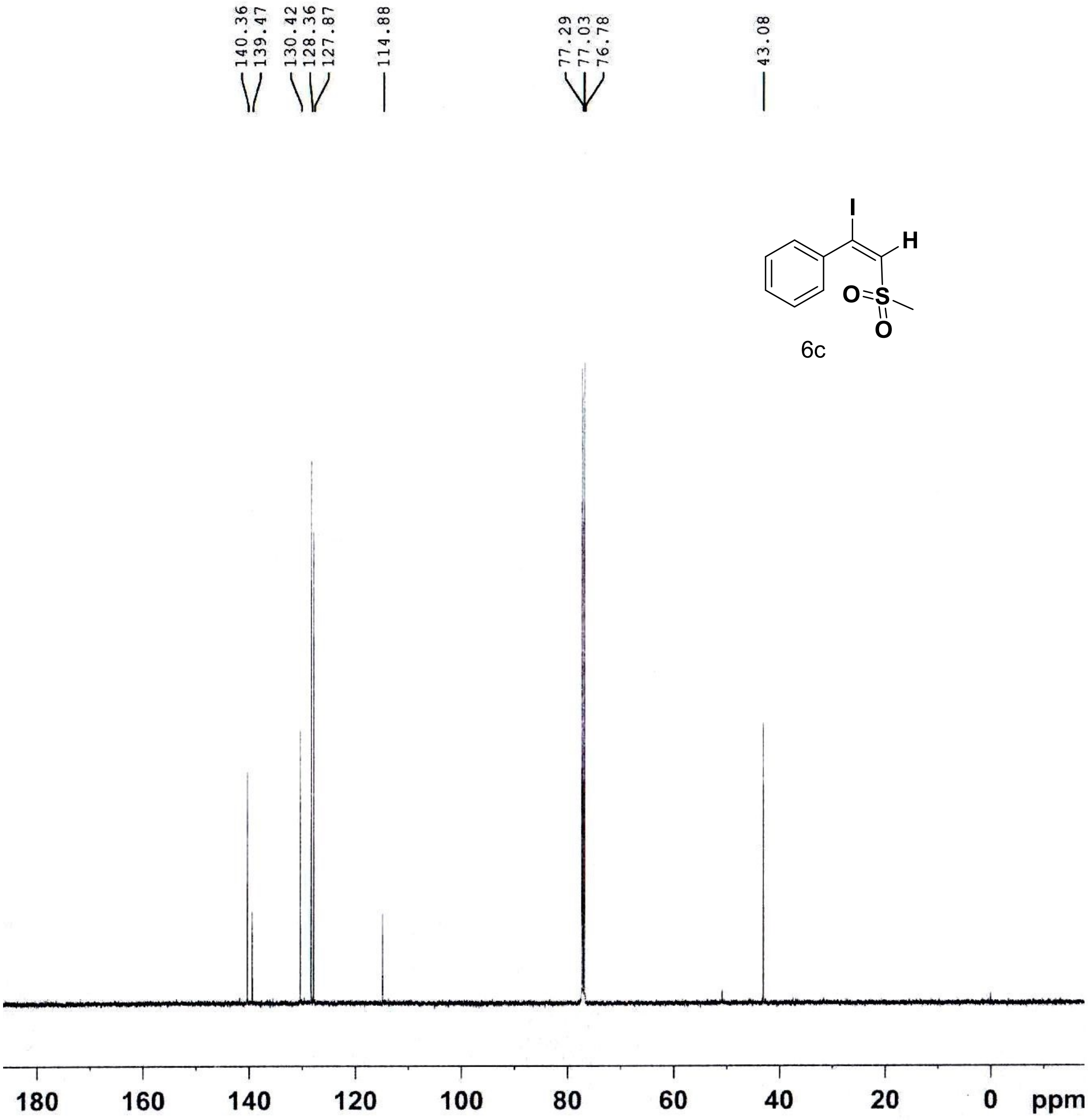
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77.03
76.78
43.08
I
H
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S
O
6c
180
160
140
120
100
80
60
40
20
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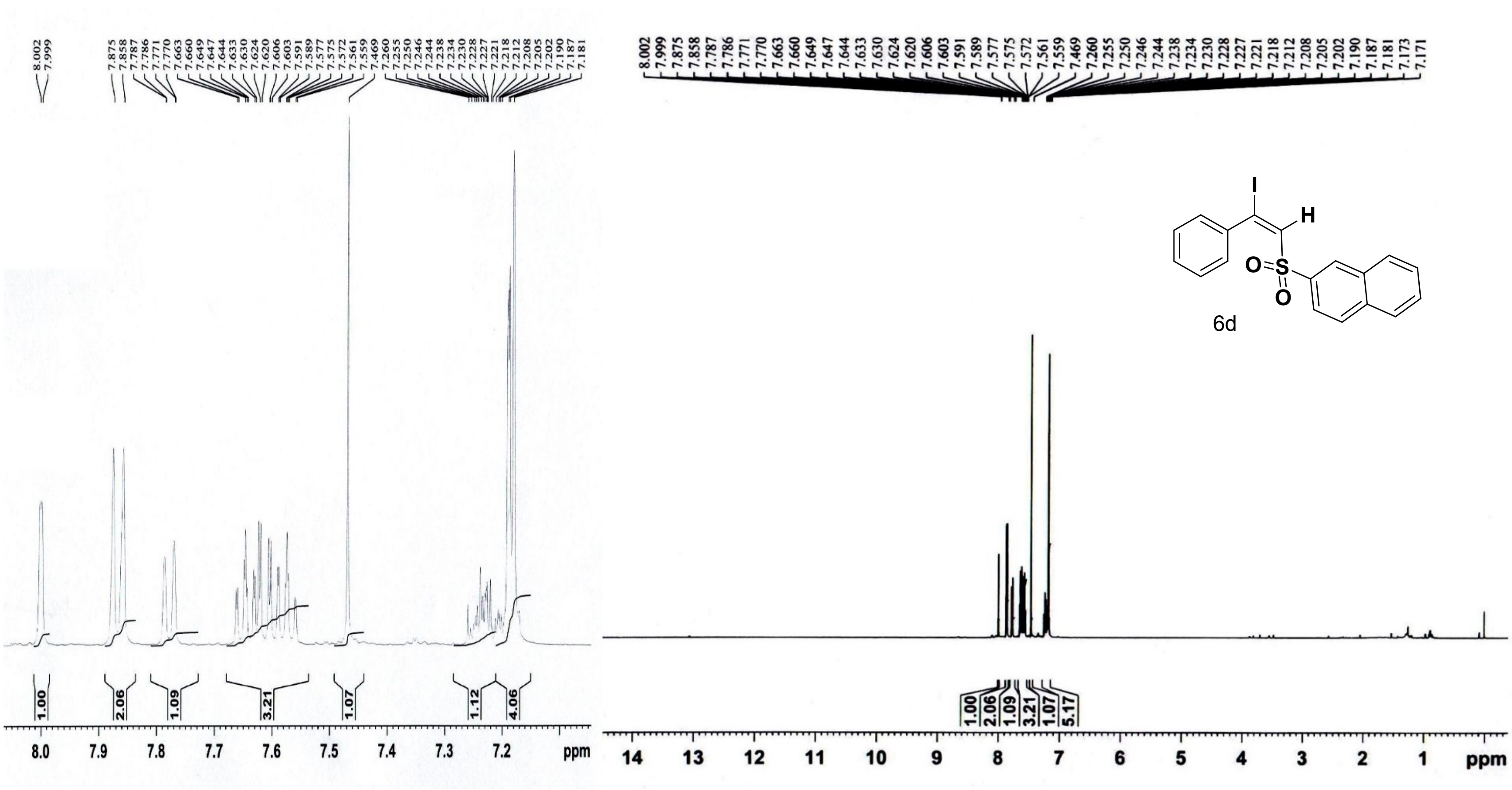
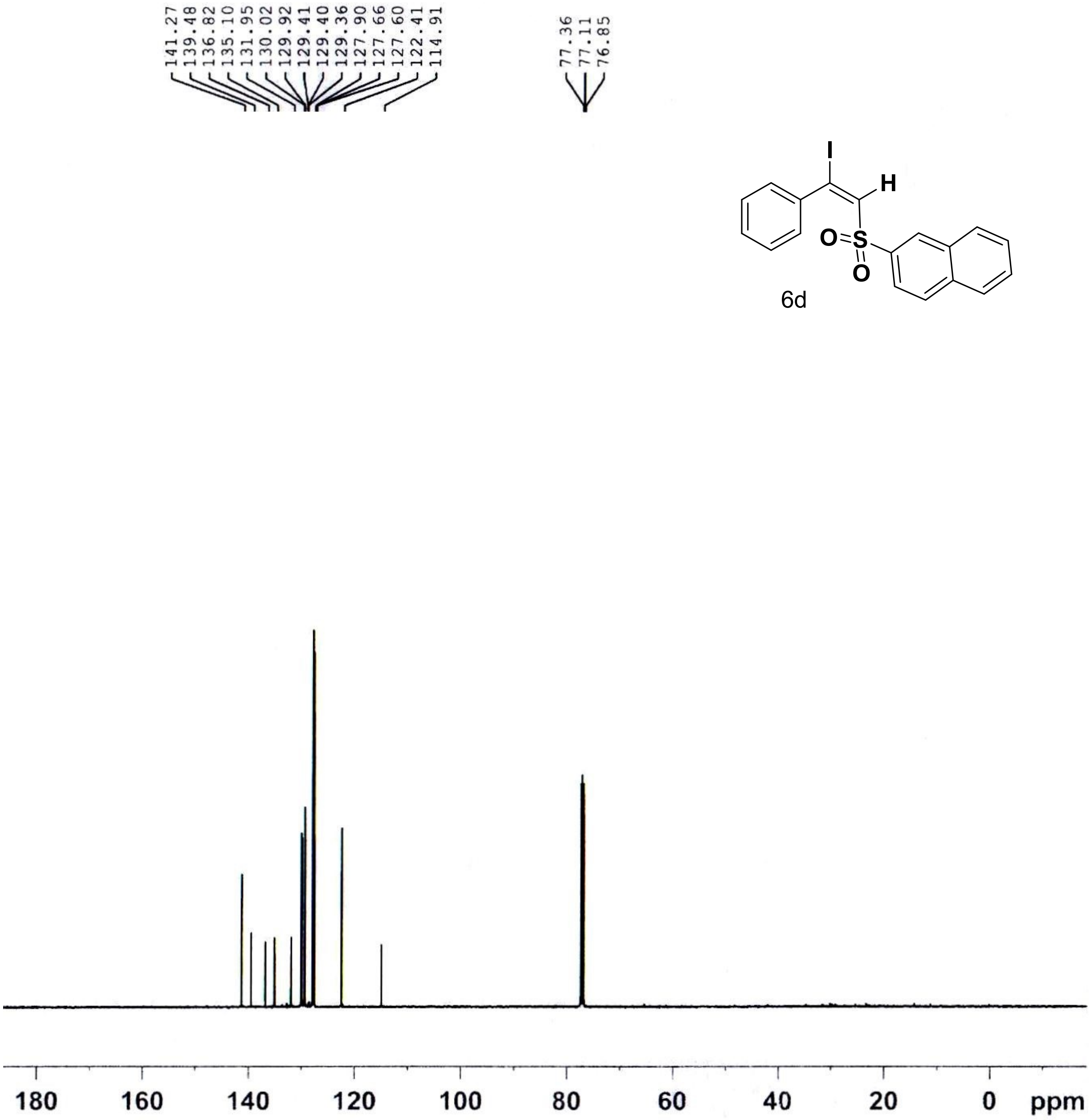
ppm


8.002 7.999 7.875 7.858 7.787 7.786 7.771 7.770 7.663 7.660 7.649 7.647 7.644 7.633 7.630 7.624 7.620 7.606 7.603 7.591 7.589 7.577 7.575 7.572 7.561 7.559 7.469 7.260 7.255 7.250 7.246 7.244 7.238 7.234 7.230 7.228 7.227 7.221 7.218 7.212 7.208 7.205 7.202 7.190 7.187 7.181
1.00 2.06 1.09 3.21 1.07 1.12 4.06
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm
8.002 7.999 7.875 7.858 7.787 7.786 7.771 7.770 7.663 7.660 7.649 7.647 7.644 7.633 7.630 7.624 7.620 7.606 7.603 7.591 7.589 7.577 7.575 7.572 7.561 7.559 7.469 7.260 7.255 7.250 7.246 7.244 7.238 7.234 7.230 7.228 7.227 7.221 7.218 7.212 7.208 7.205 7.202 7.190 7.187 7.181 7.173 7.171
I
H
O
S
O
1.00 2.06 1.09 3.21 1.07 5.17
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm

6d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129.41
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129.36
127.90
127.66
127.60
122.41
114.91
77.36
77.11
76.85
I
H
O
S
O
6d
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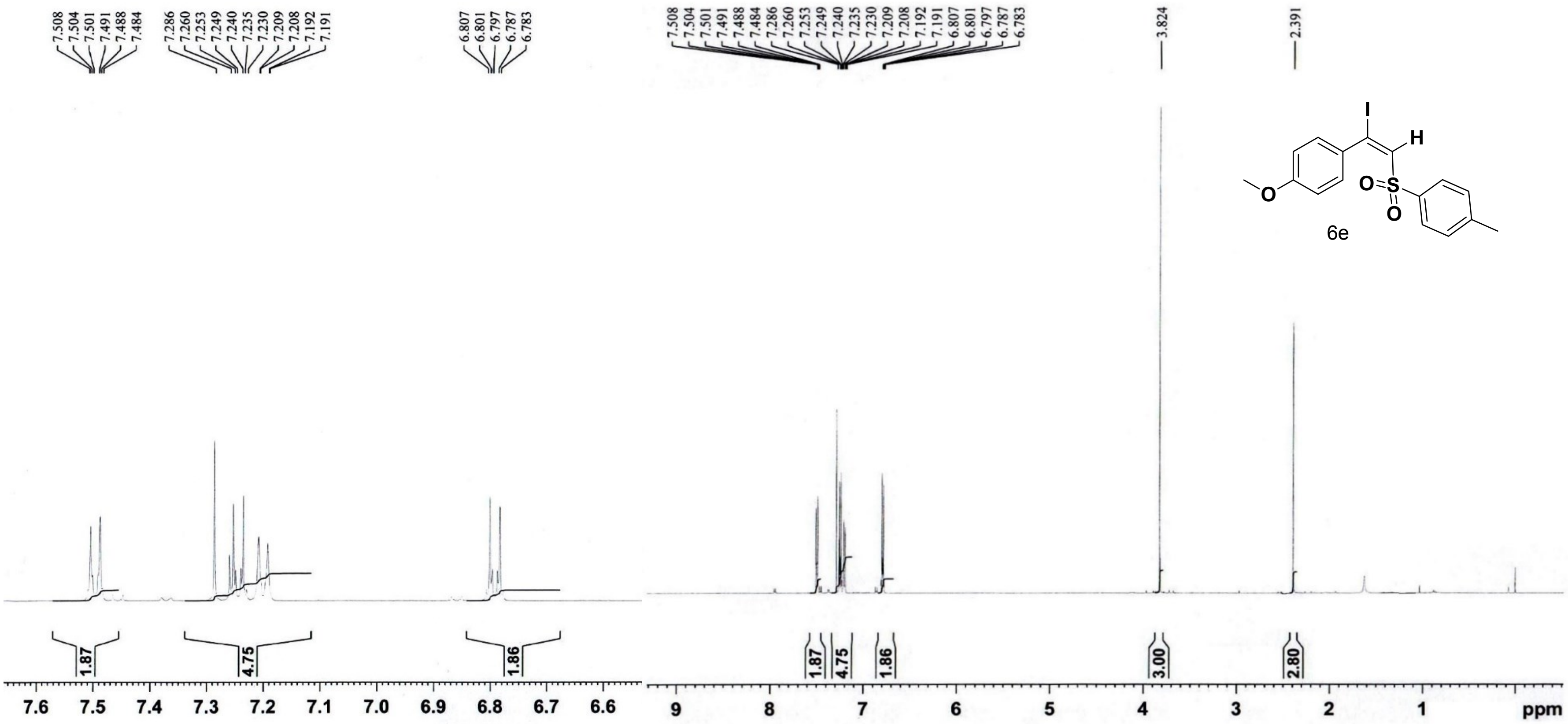
120
100
80
60
40
20
0
ppm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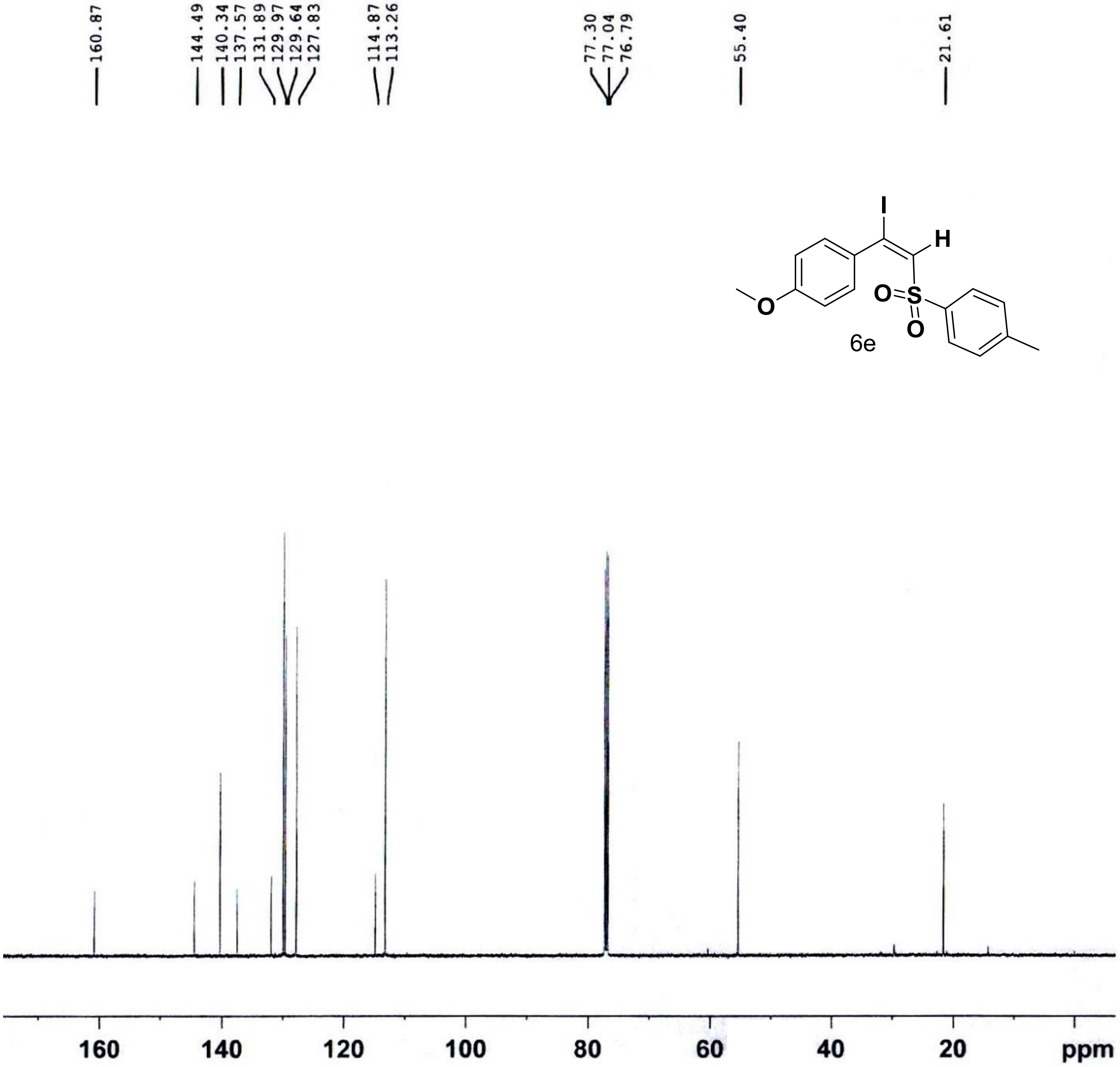
7.484
7.286
7.260
7.253
7.249
7.240
7.235
7.230
7.209
7.208
7.192
7.191
6.807
6.801
6.797
6.787
6.783
3.824
2.391
1.87
4.75
1.86
3.00
2.80
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
9
8
7
6
5
4
3
2
1
ppm
I
H
O
S
O
O
6e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127.83
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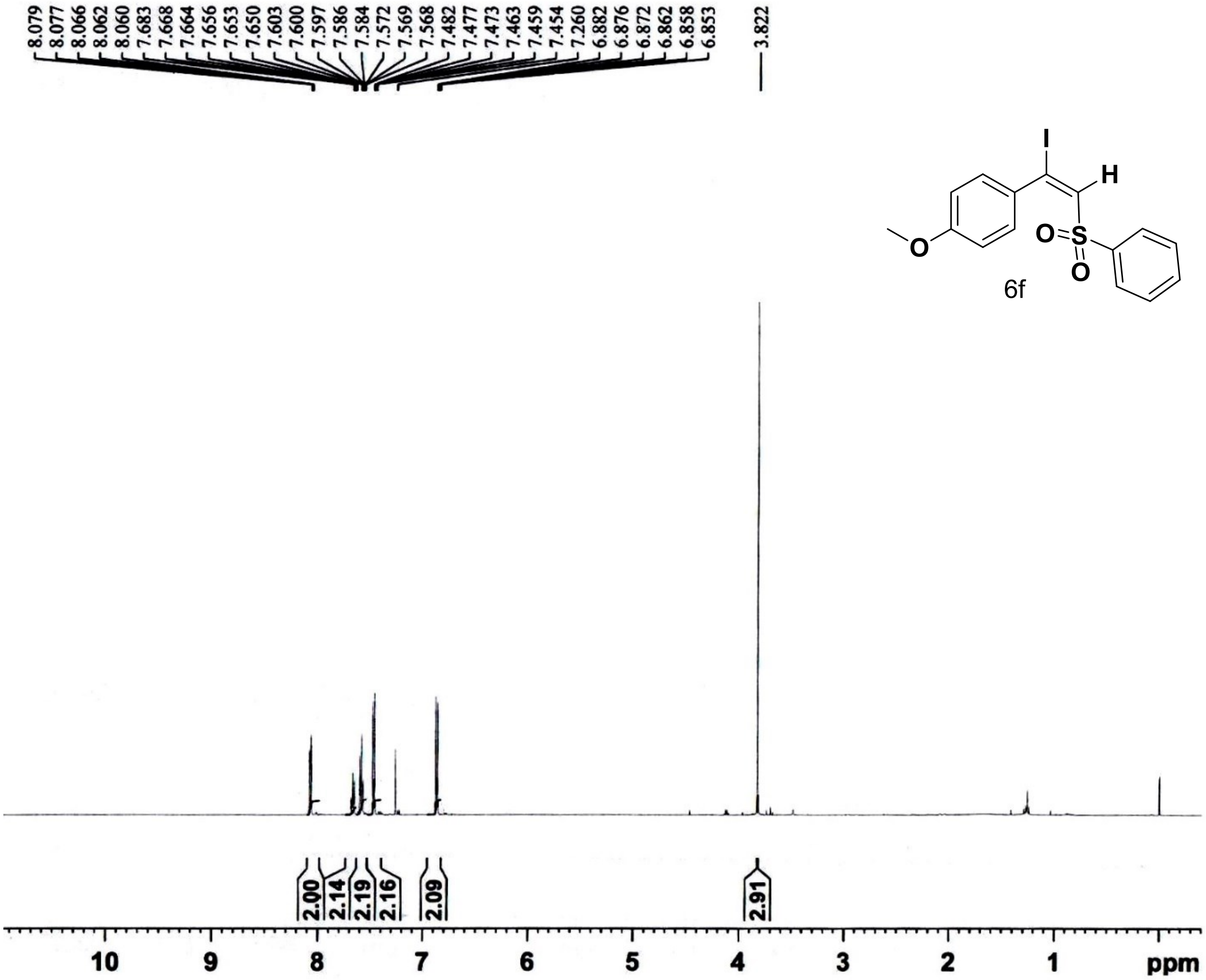
77.30
77.04
76.79
55.40
21.61
I
H
O
S
O
O
160
140
120
100
80
60
40
20
ppm

6e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8.062
8.060
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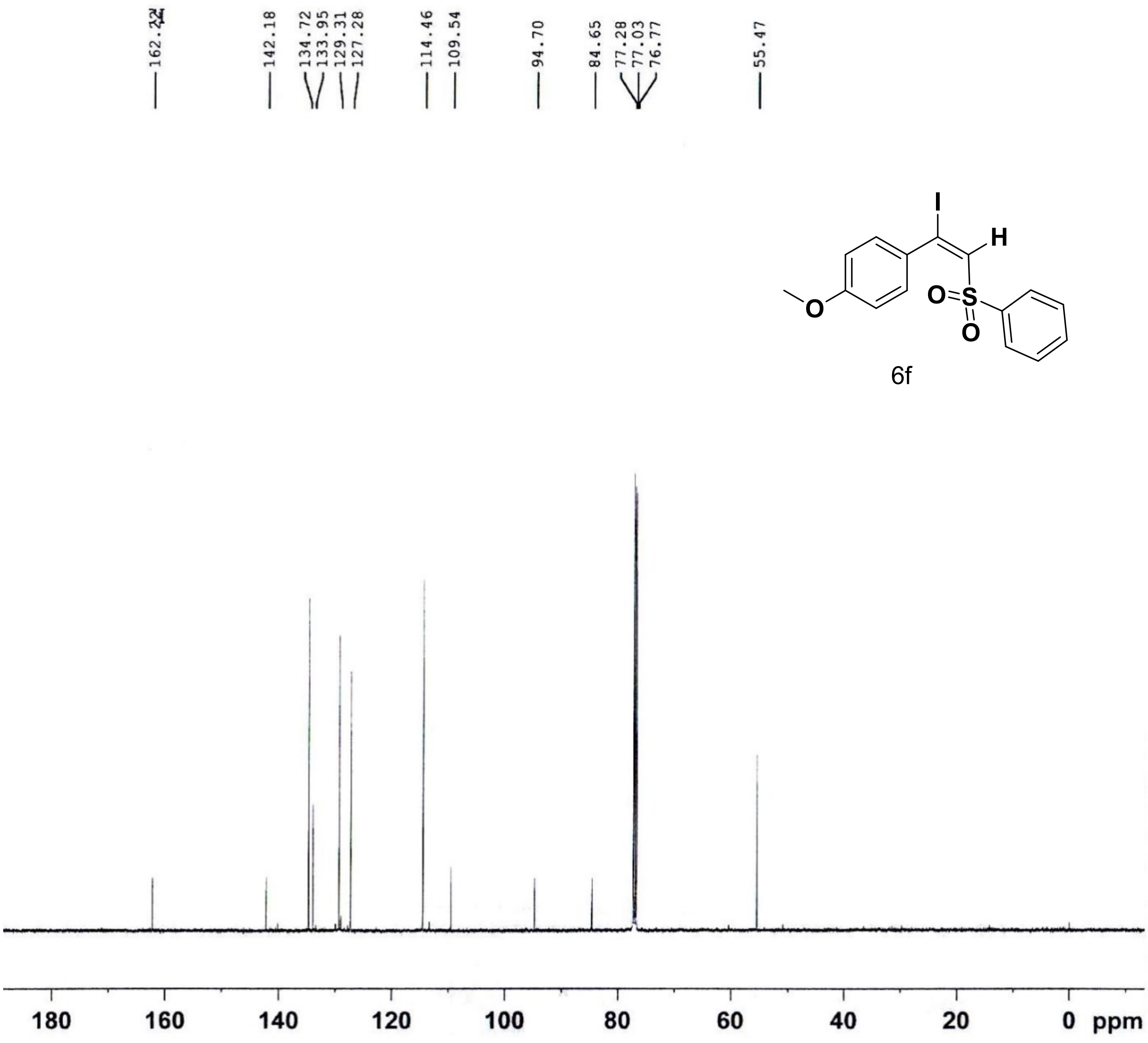
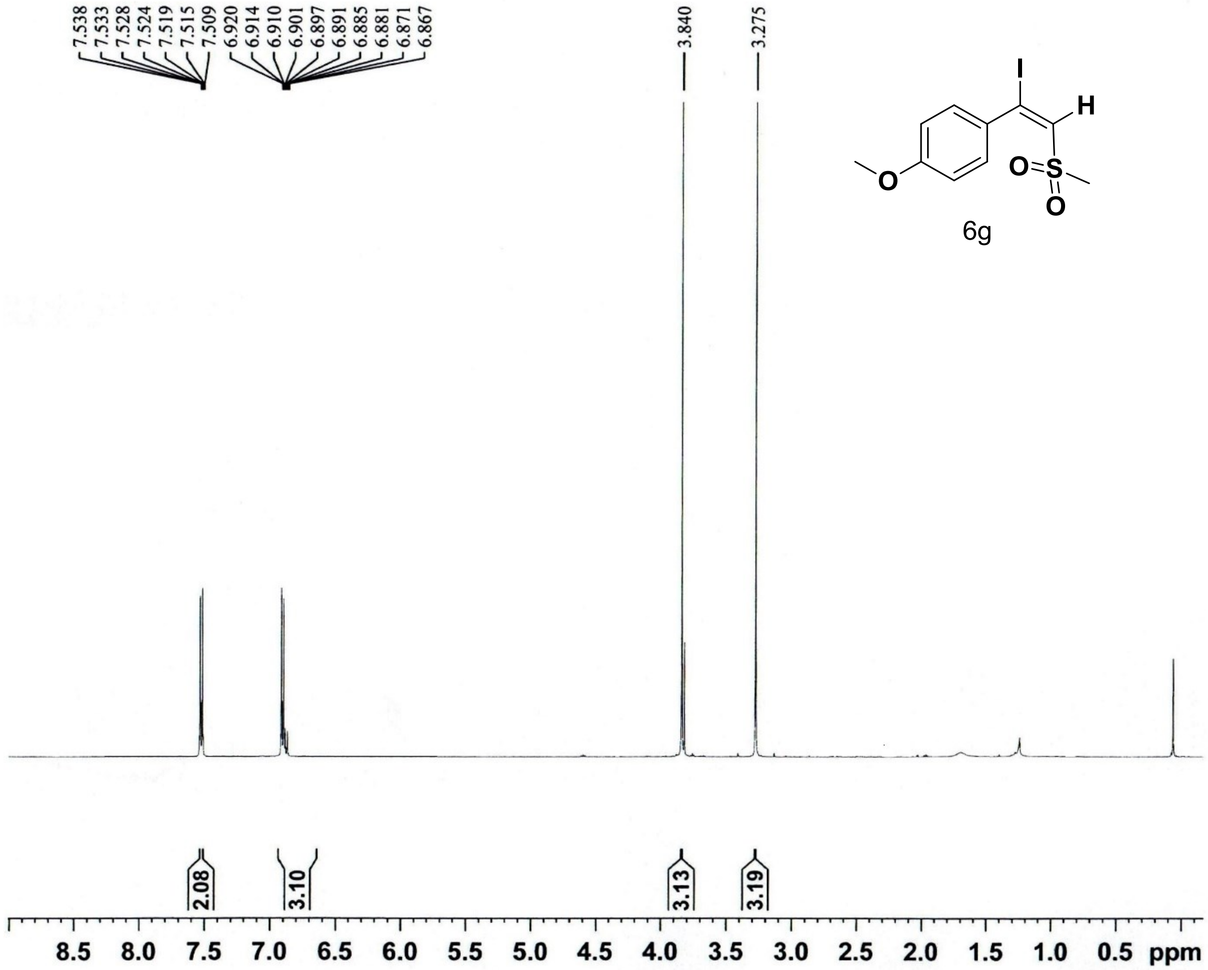
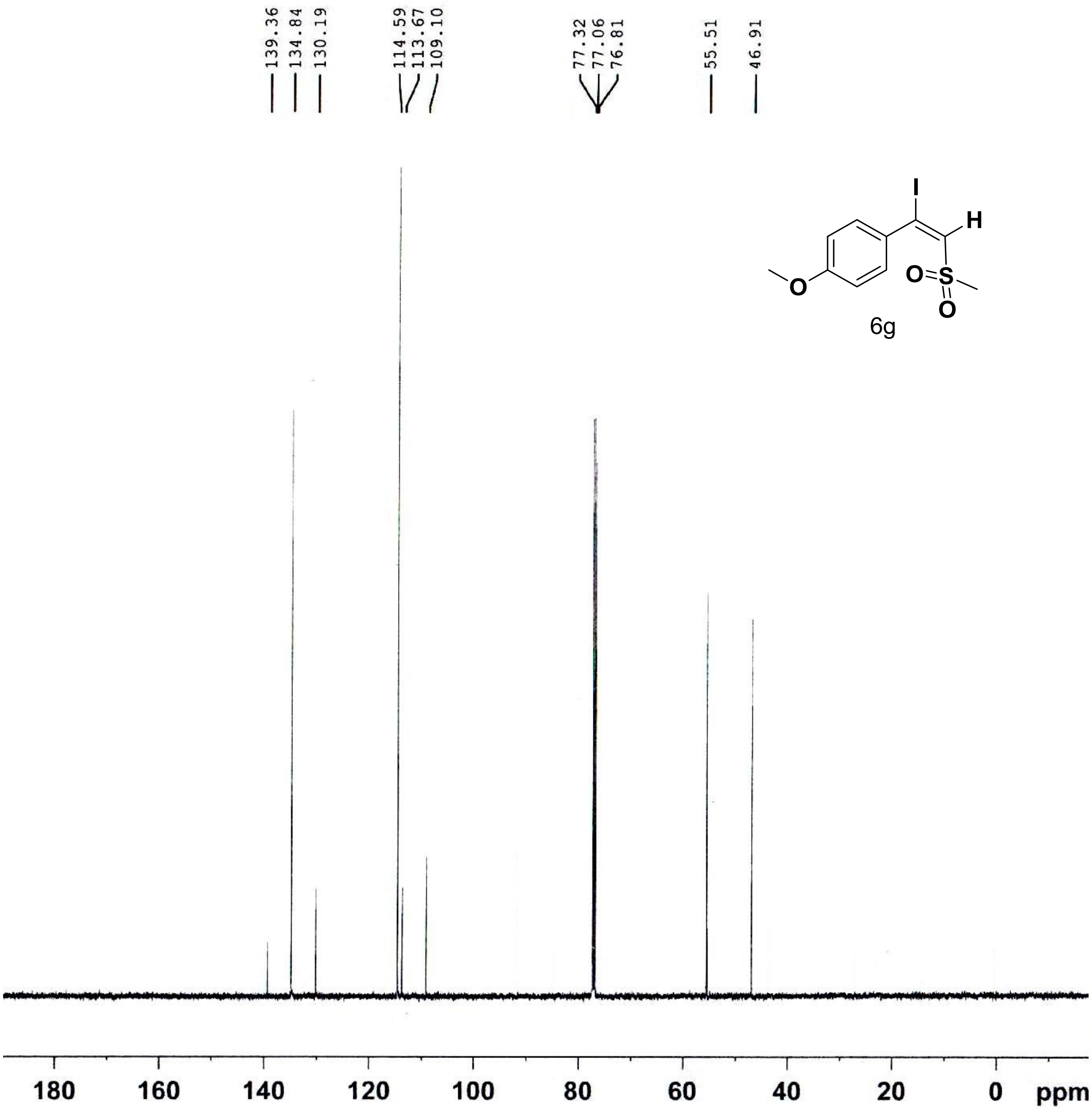
7.668
7.664
7.656
7.653
7.650
7.603
7.600
7.597
7.586
7.584
7.572
7.569
7.568
7.482
7.477
7.473
7.463
7.459
7.454
7.260
6.882
6.876
6.872
6.862
6.858
6.853
3.822
I
H
O
O
S
O
2.00
2.14
2.19
2.16
2.09
2.91
10
9
8
7
6
5
4
3
2
1
ppm

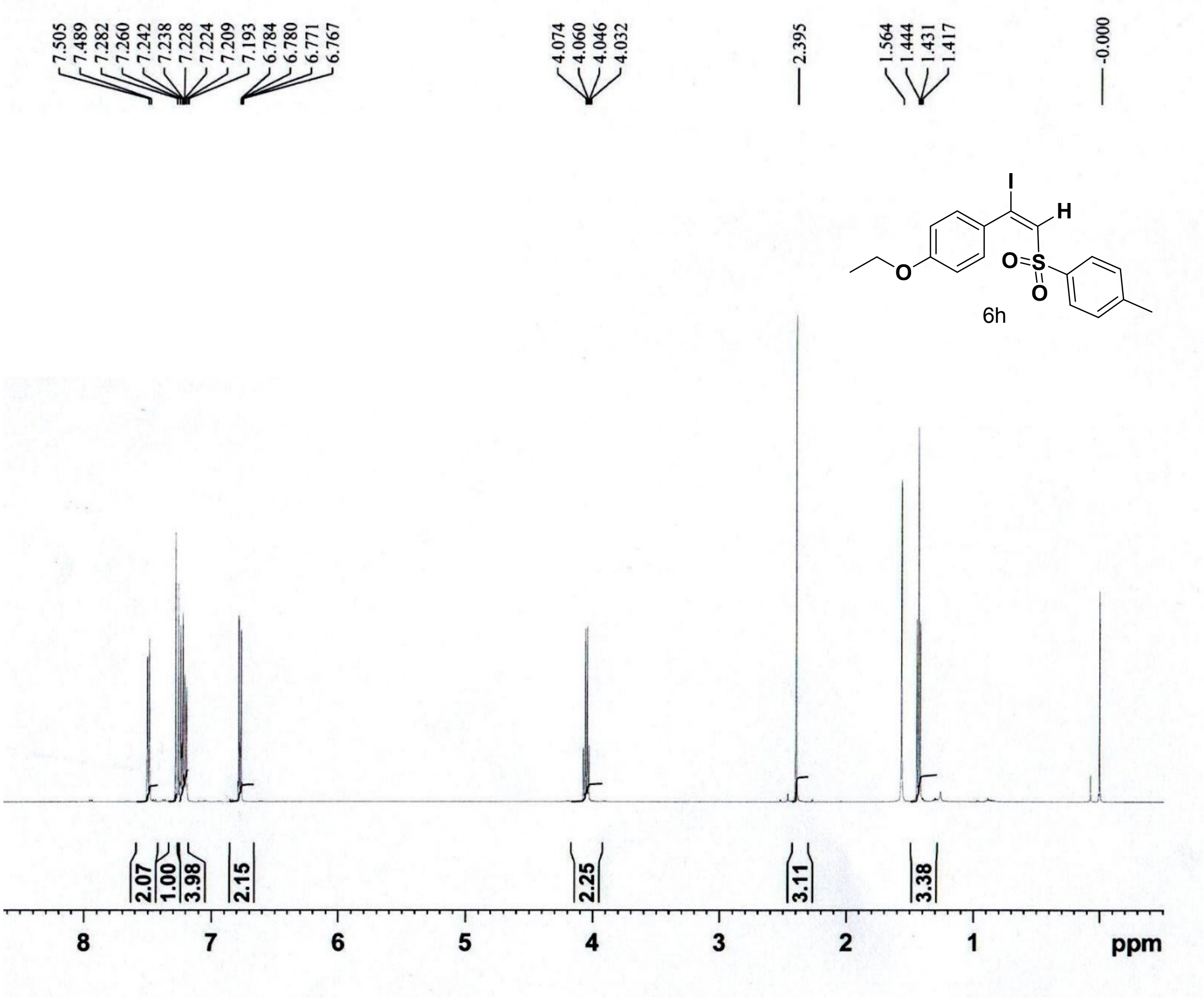
6f


162.22
142.18
134.72
133.95
129.31
127.28
114.46
109.54
94.70
84.65
77.28
77.03
76.77
55.47
I
H
O
O
S
O
6f
180
160
140
120
100
80
60
40
20
0 ppm


6g
7.538
7.533
7.528
7.524
7.519
7.515
7.509
6.920
6.914
6.910
6.901
6.897
6.891
6.885
6.881
6.871
6.867
3.840
3.275
I
H
O
O
S
O
2.08
3.10
3.13
3.19
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


139.36
134.84
130.19
114.59
113.67
109.10
77.32
77.06
76.81
55.51
46.91
I
H
O
O
S
O
180
160
140
120
100
80
60
40
20
0
ppm

6g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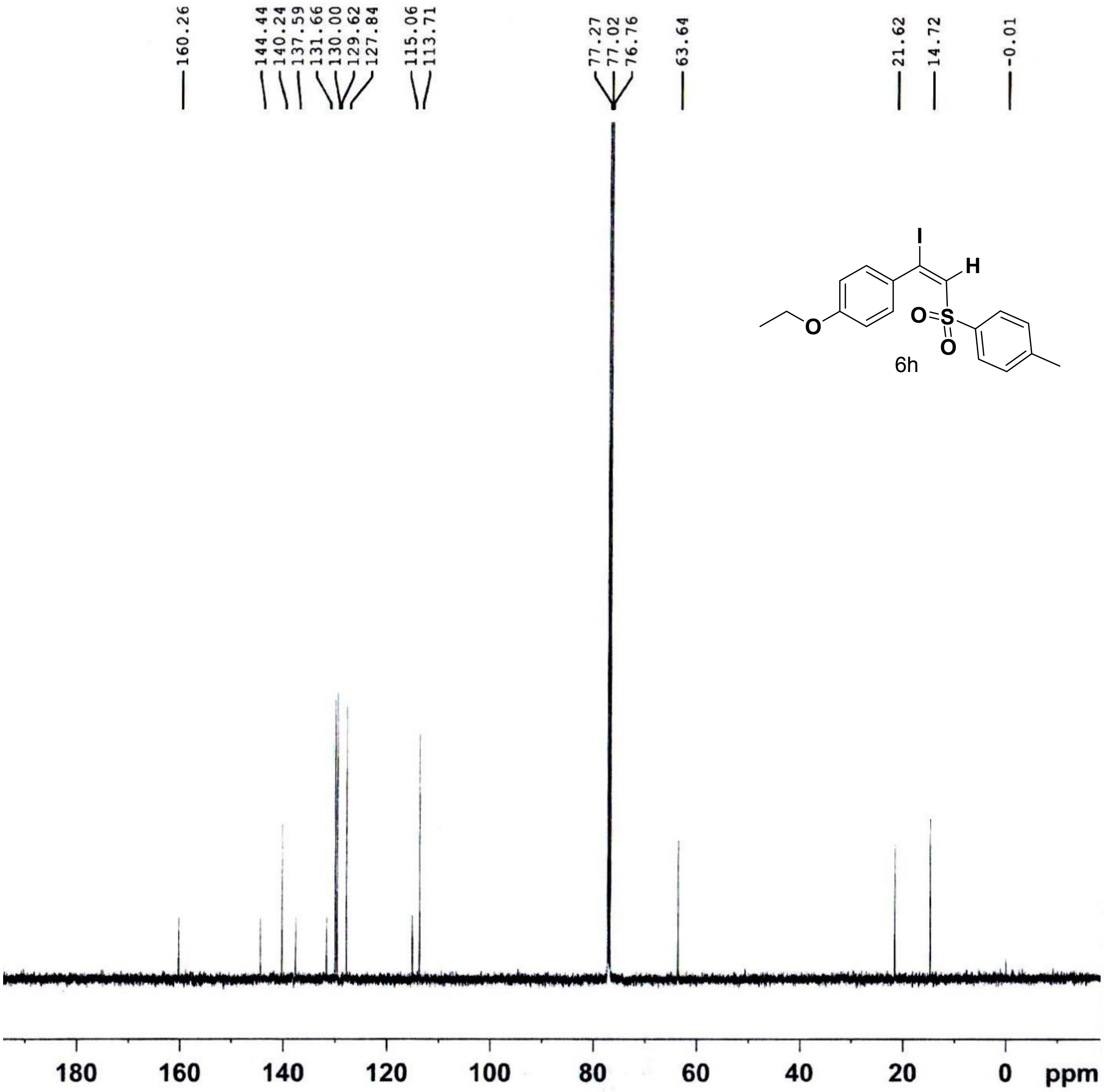
7.489
7.282
7.260
7.242
7.238
7.228
7.224
7.209
7.193
6.784
6.780
6.771
6.767
4.074
4.060
4.046
4.032
2.395
1.564
1.444
1.431
1.417
-0.000
I
H
O
O
S
O
6h
2.07
1.00
3.98
2.15
2.25
3.11
3.38
8
7
6
5
4
3
2
1
ppm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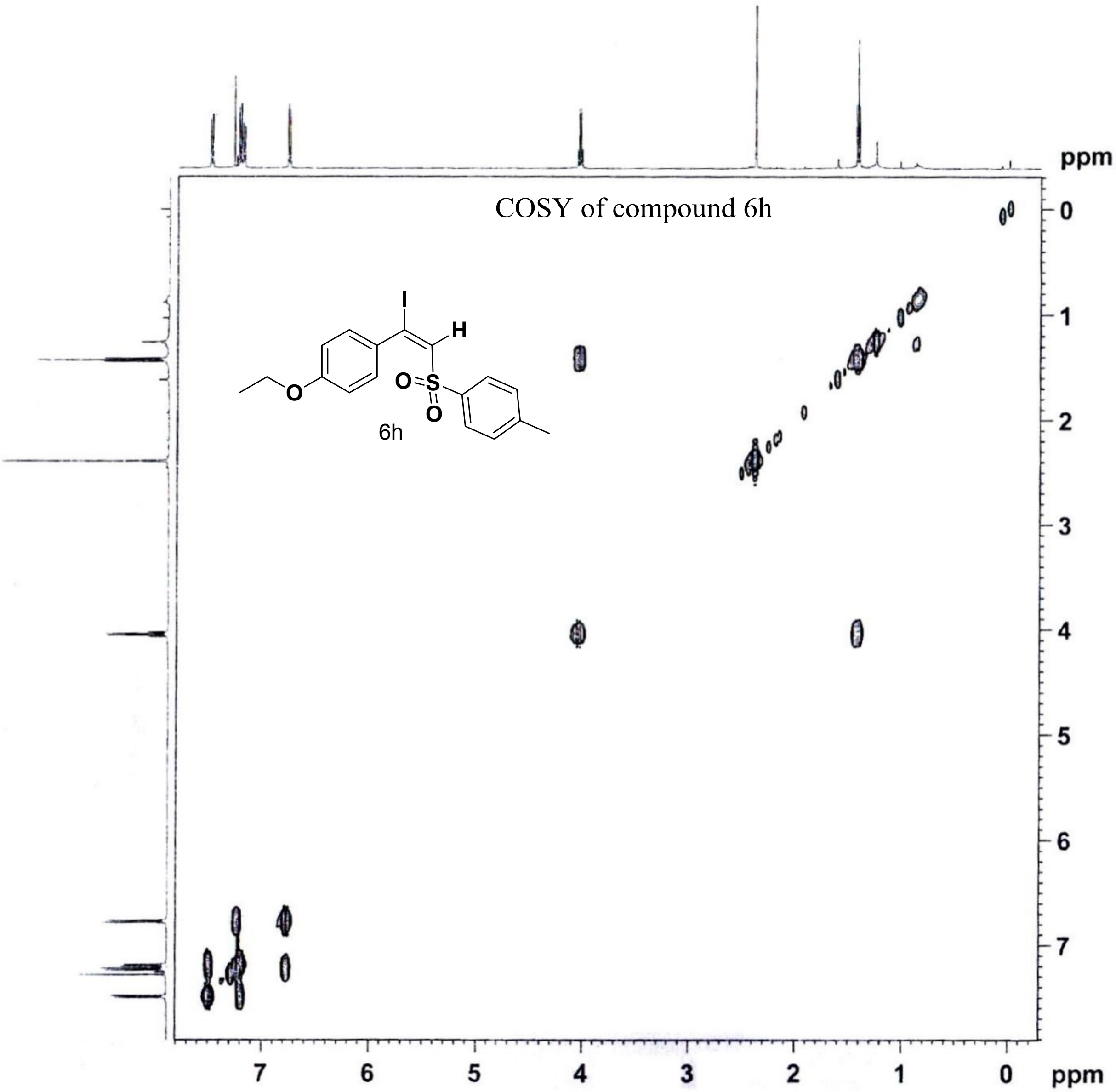
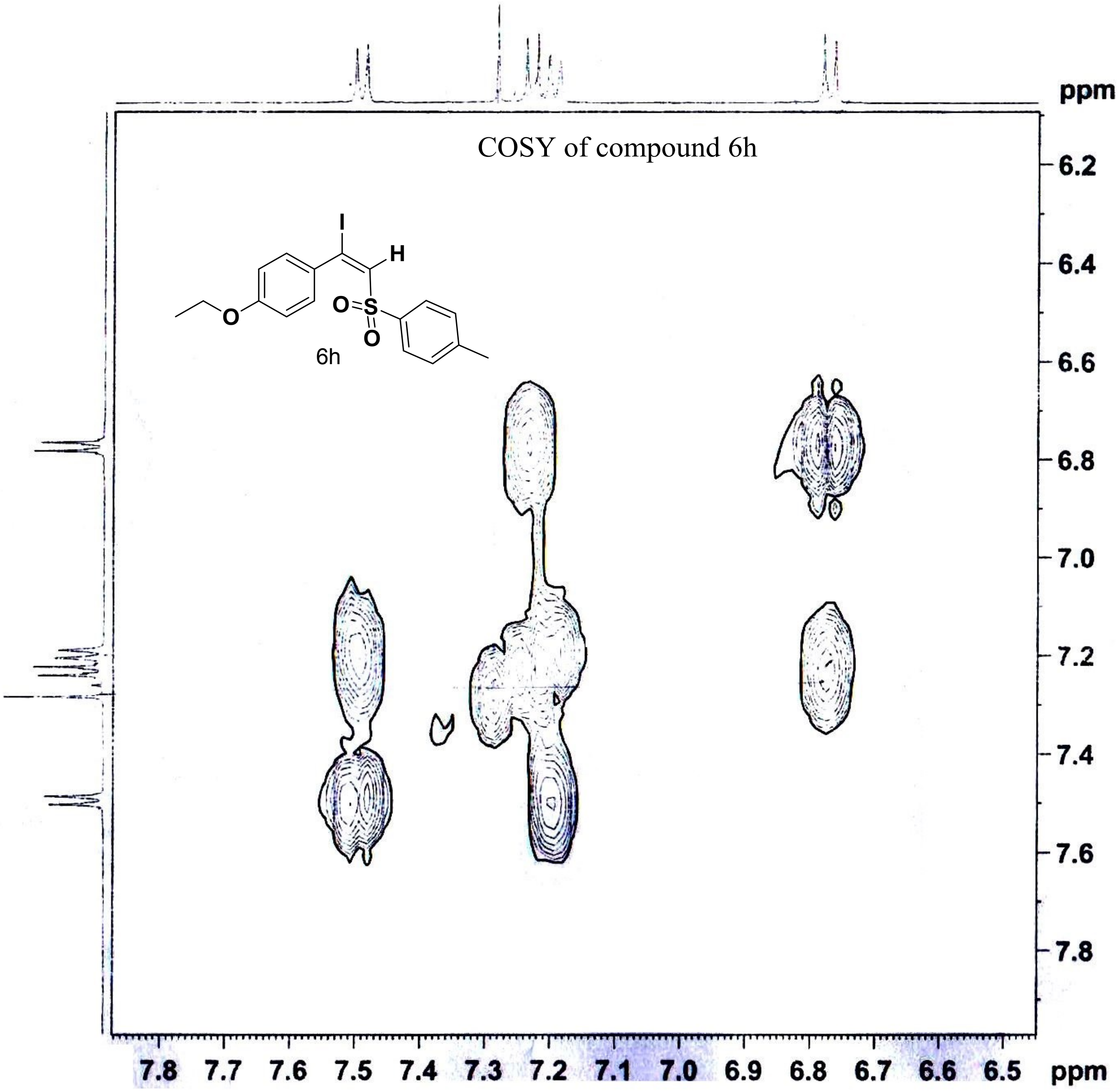
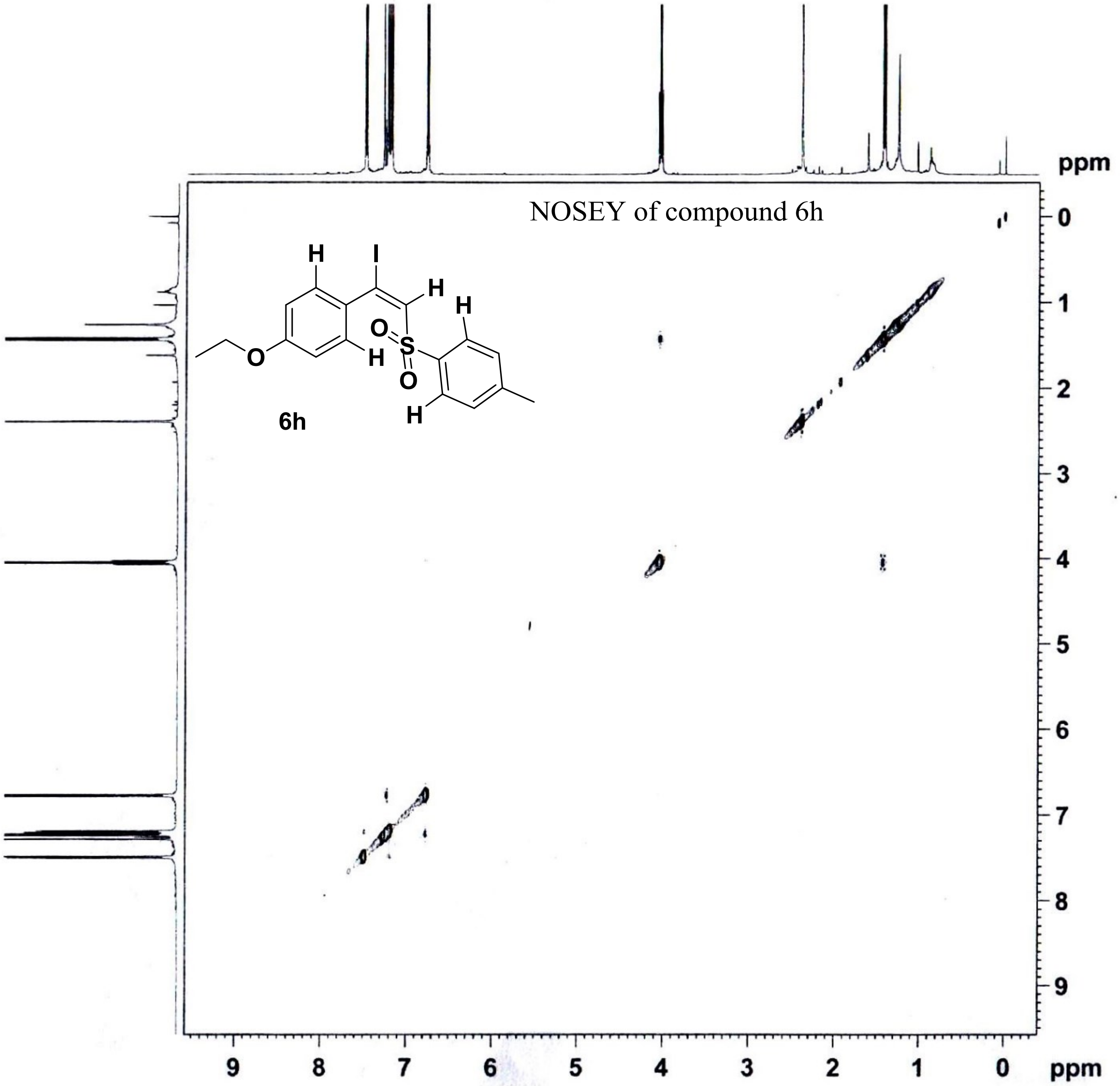
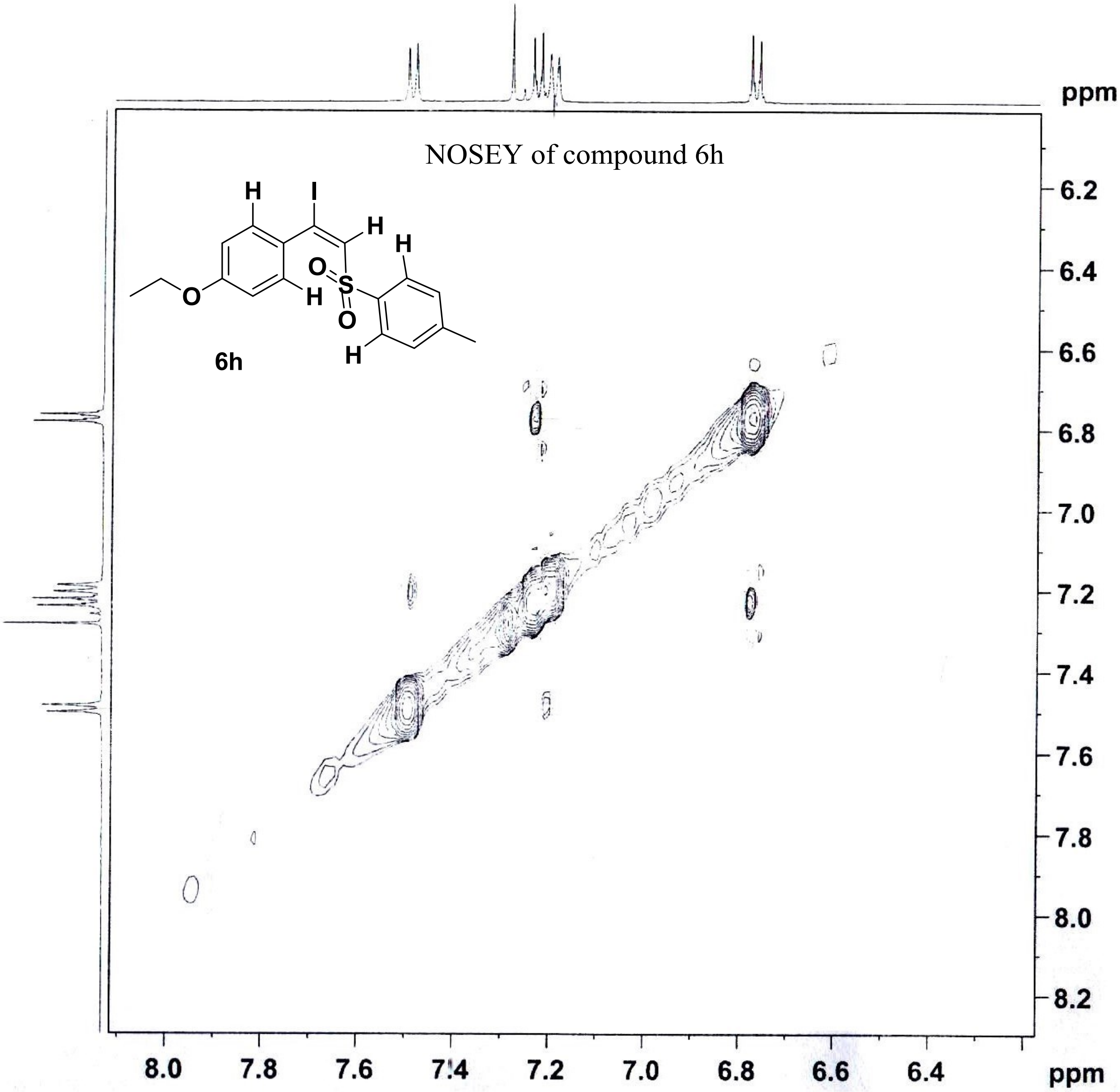
144.44
140.24
137.59
131.66
130.00
129.62
127.84
115.06
113.71
77.27
77.02
76.76
63.64
21.62
14.72
-0.01
I
H
O
S
O
O
6h
180
160
140
120
100
80
60
40
20
0
ppm

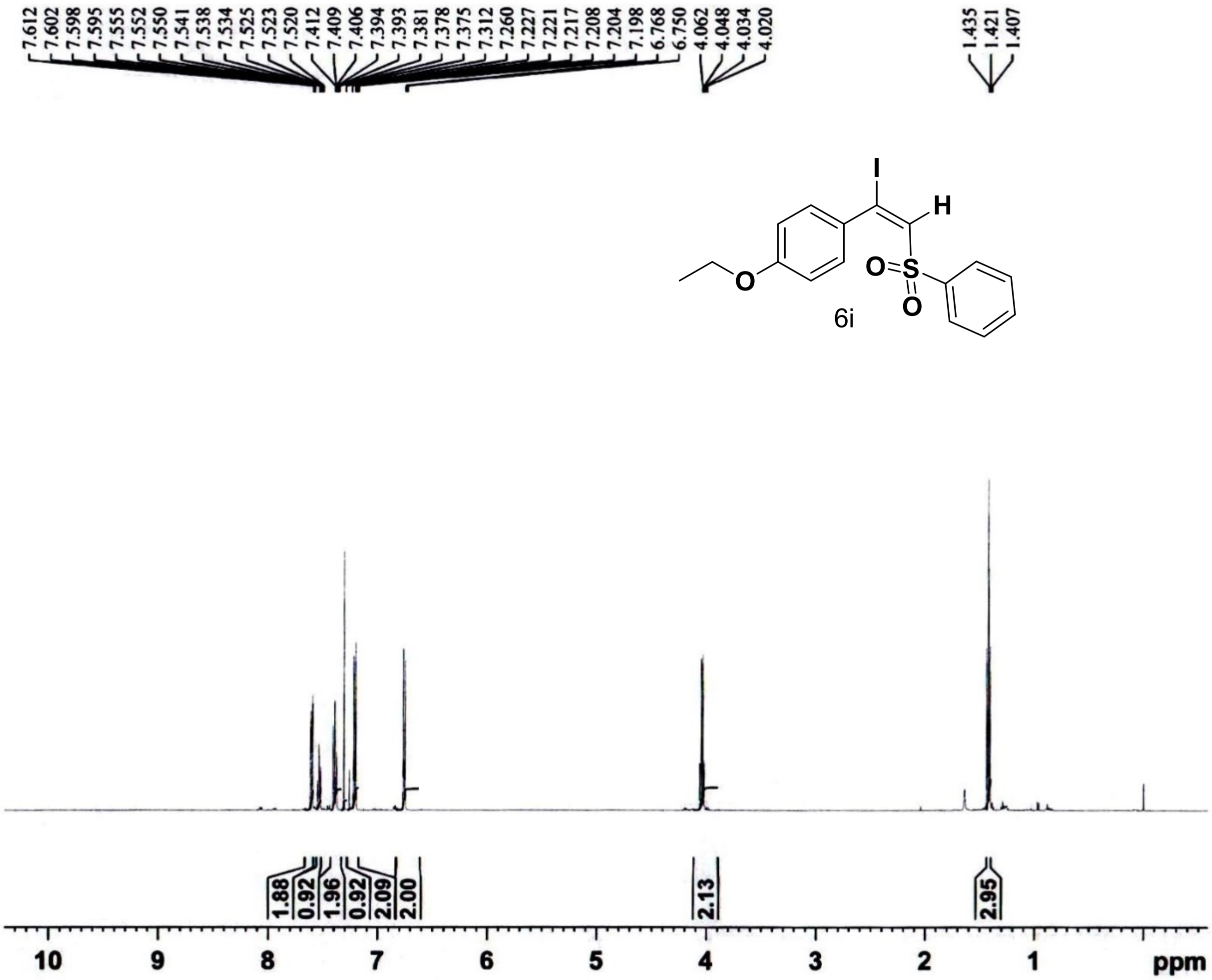

COSY of compound 6h
6h
I
H
O
O
S
O
ppm
0
1
2
3
4
5
6
7
7
6
5
4
3
2
1
0
ppm


COSY of compound 6h


NOSEY of compound 6h
ppm
0
1
2
3
4
5
6
7
8
9
9
8
7
6
5
4
3
2
1
0
ppm
H
I
H
H
O
S
O
O
H
H
6h



NOSEY of compound 6h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7.595
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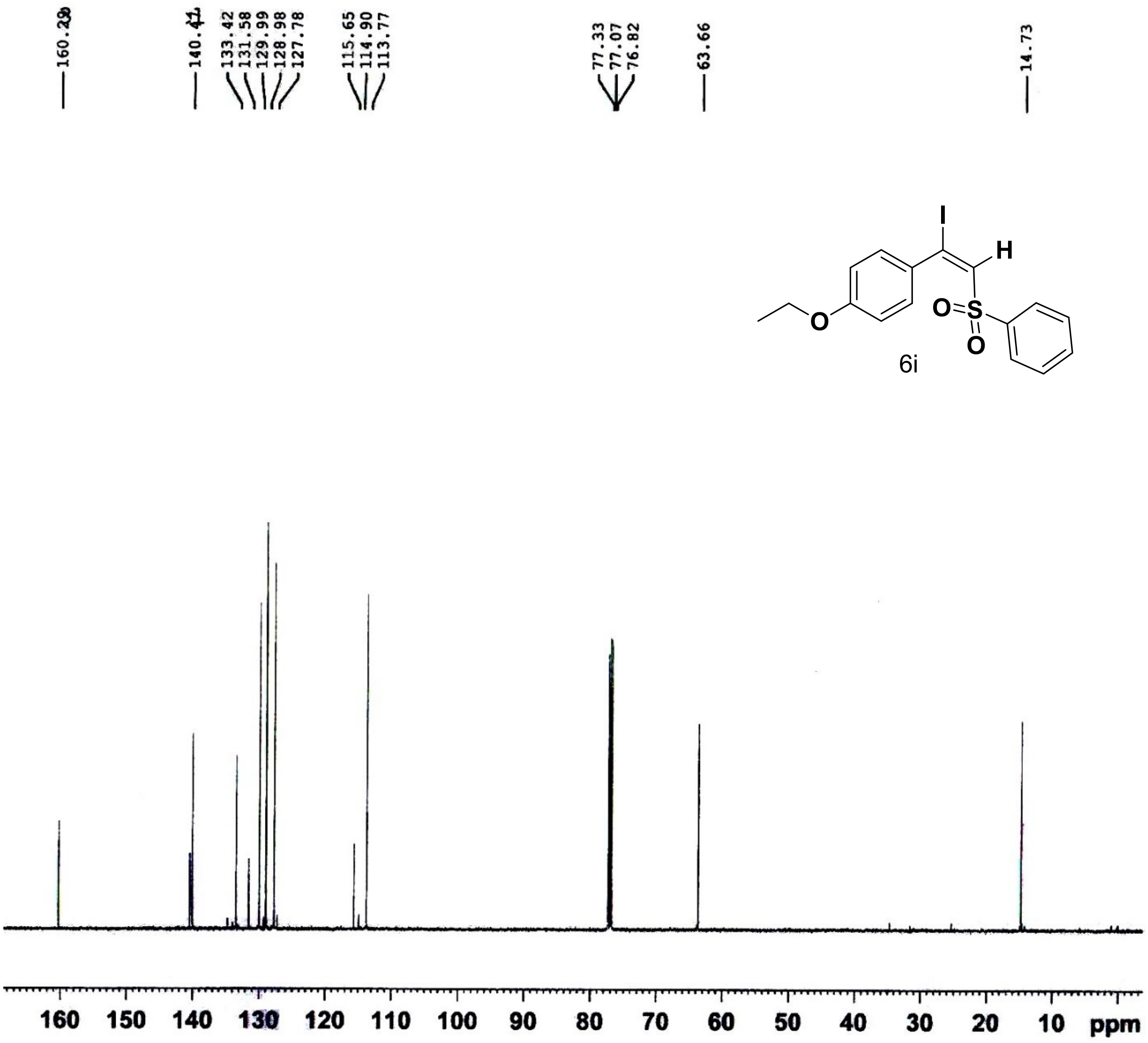
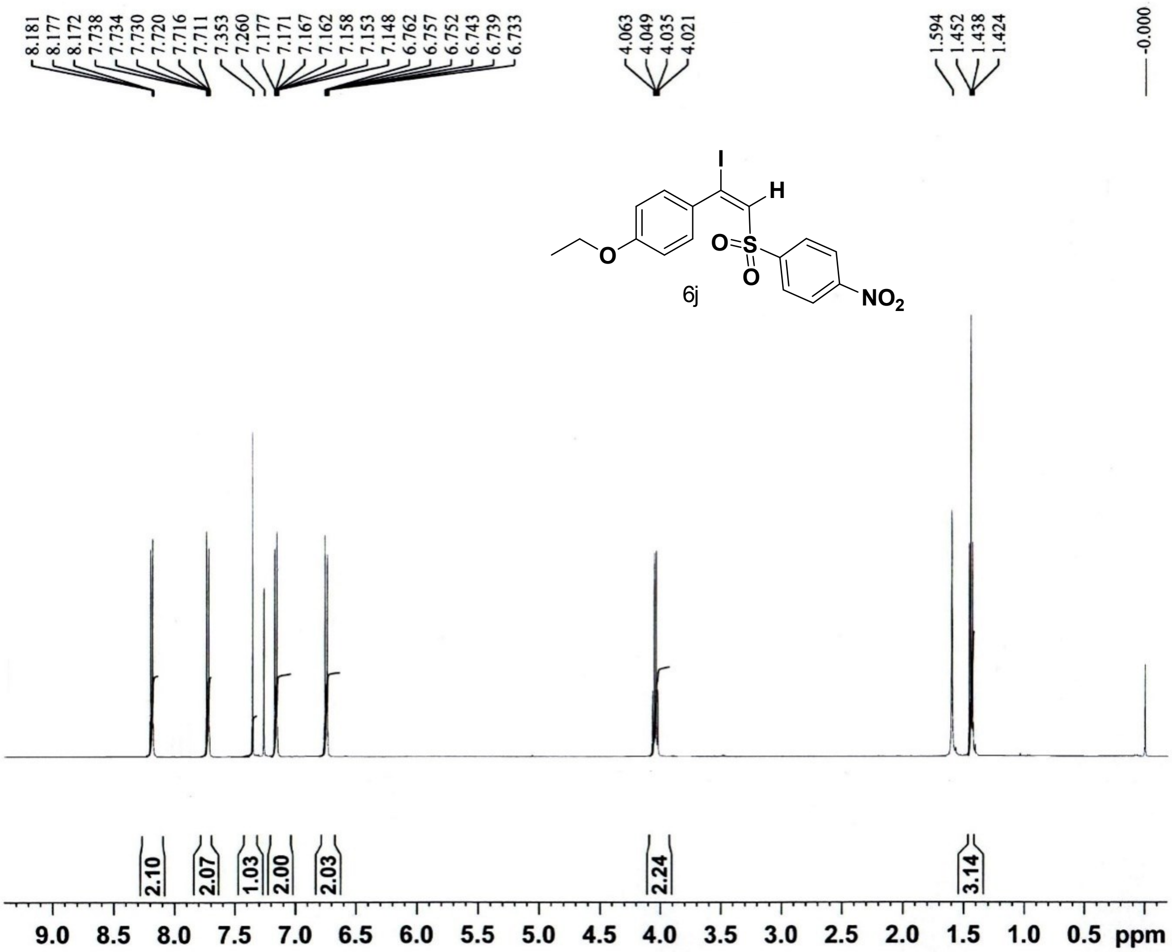
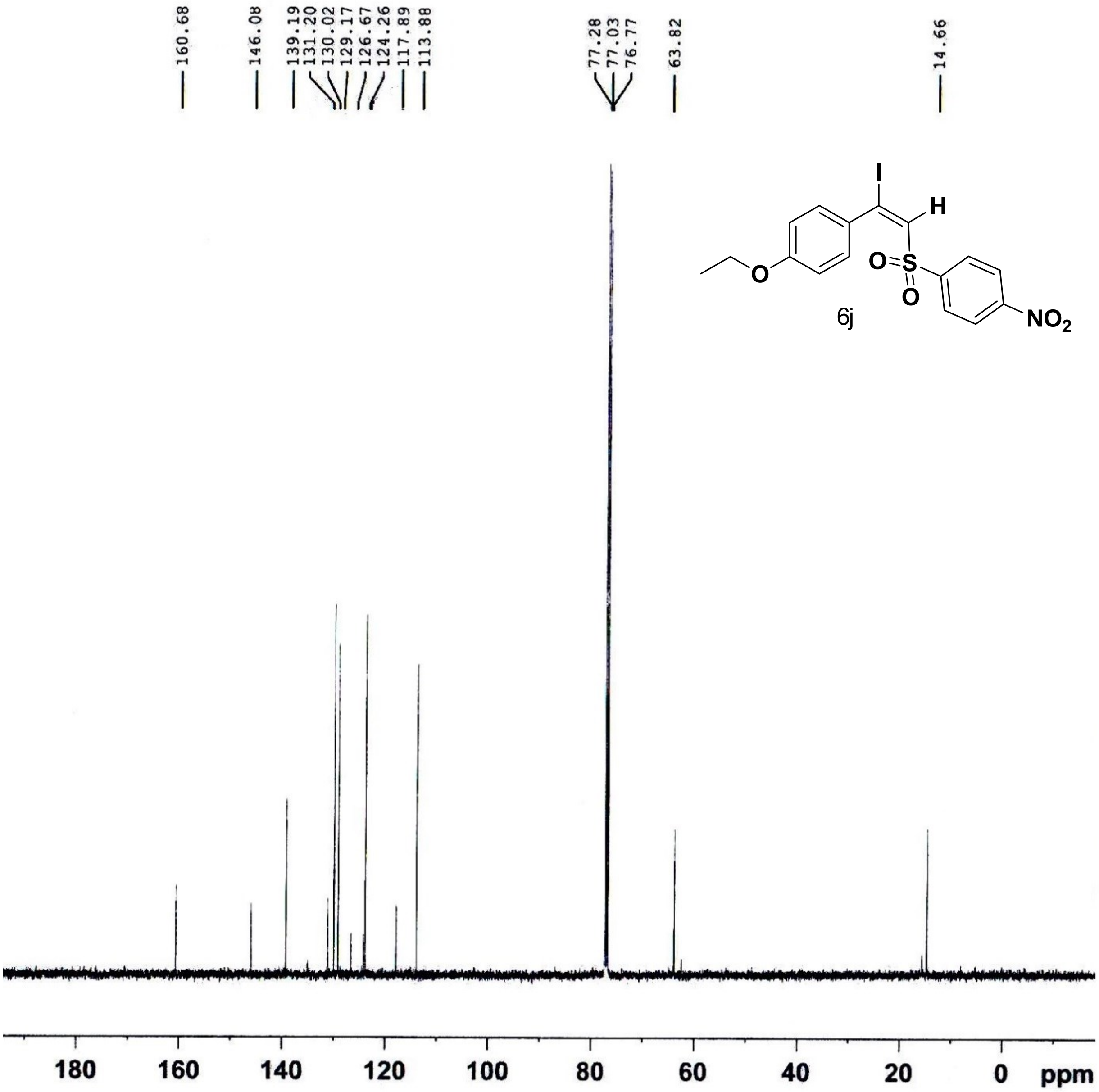
7.552
7.550
7.541
7.538
7.534
7.525
7.523
7.520
7.412
7.409
7.406
7.394
7.393
7.381
7.378
7.375
7.312
7.260
7.227
7.221
7.217
7.208
7.204
7.198
6.768
6.750
4.062
4.048
4.034
4.020
1.435
1.421
1.407
I
H
O
O
S
O
6i
1.88
0.92
1.96
0.92
2.09
2.00
2.13
2.95
10
9
8
7
6
5
4
3
2
1
ppm

160.28
140.41
133.42
131.58
129.99
128.98
127.78
115.65
114.90
113.77
77.33
77.07
76.82
63.66
14.73
I
H
O
O
S
O
6i
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.181
8.177
8.172
7.738
7.734
7.730
7.720
7.716
7.711
7.353
7.260
7.177
7.171
7.167
7.162
7.158
7.153
7.148
6.762
6.757
6.752
6.743
6.739
6.733
4.063
4.049
4.035
4.021
1.594
1.452
1.438
1.424
-0.000
I
H
O
O=S
O
NO2
6j
2.10
2.07
1.03
2.00
2.03
2.24
3.14
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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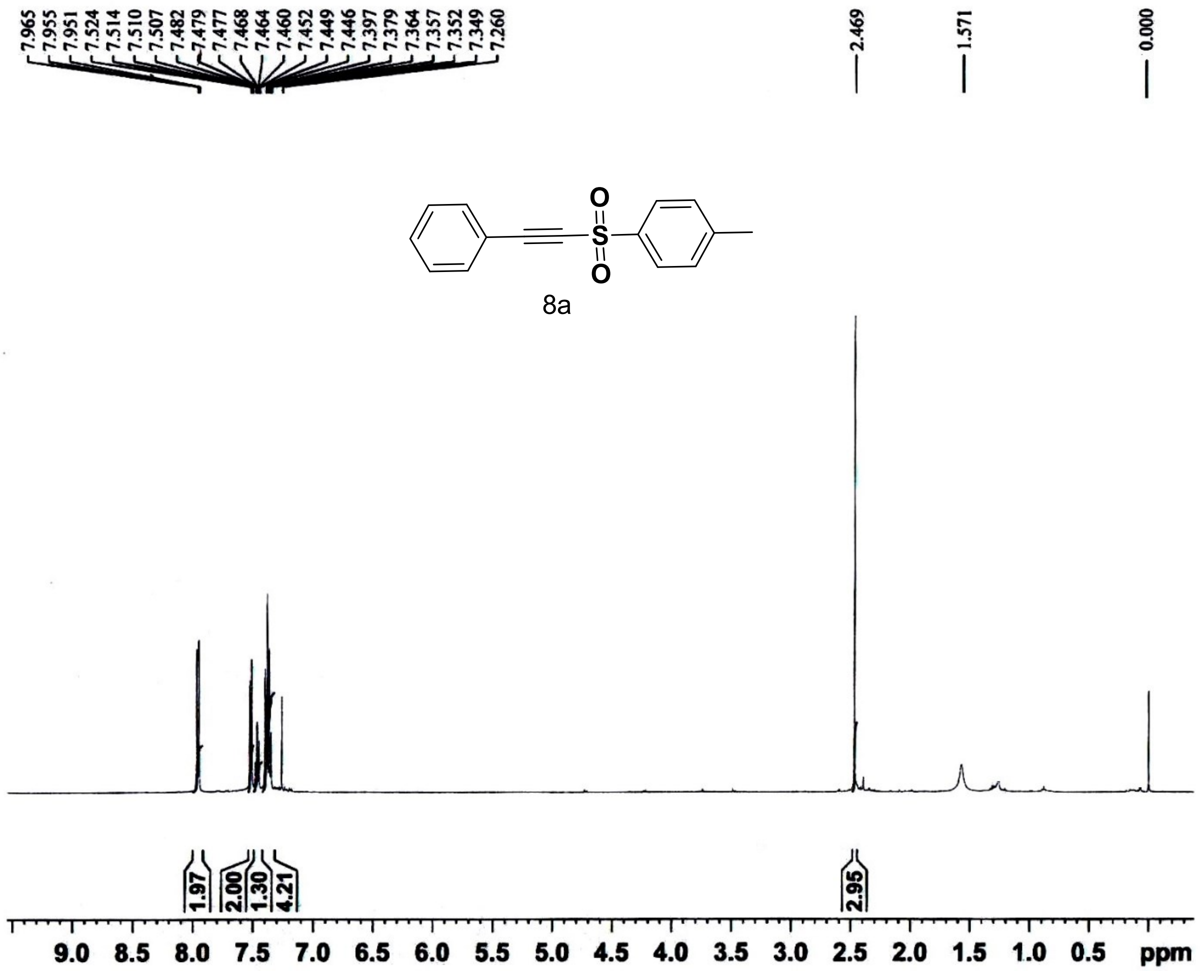
146.08
139.19
131.20
130.02
129.17
126.67
124.26
117.89
113.88
77.28
77.03
76.77
63.82
14.66
I
H
O
O
S
O
NO$_2$
6j
180
160
140
120
100
80
60
40
20
0
ppm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7.951
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7.514
7.510
7.507
7.482
7.479
7.477
7.468
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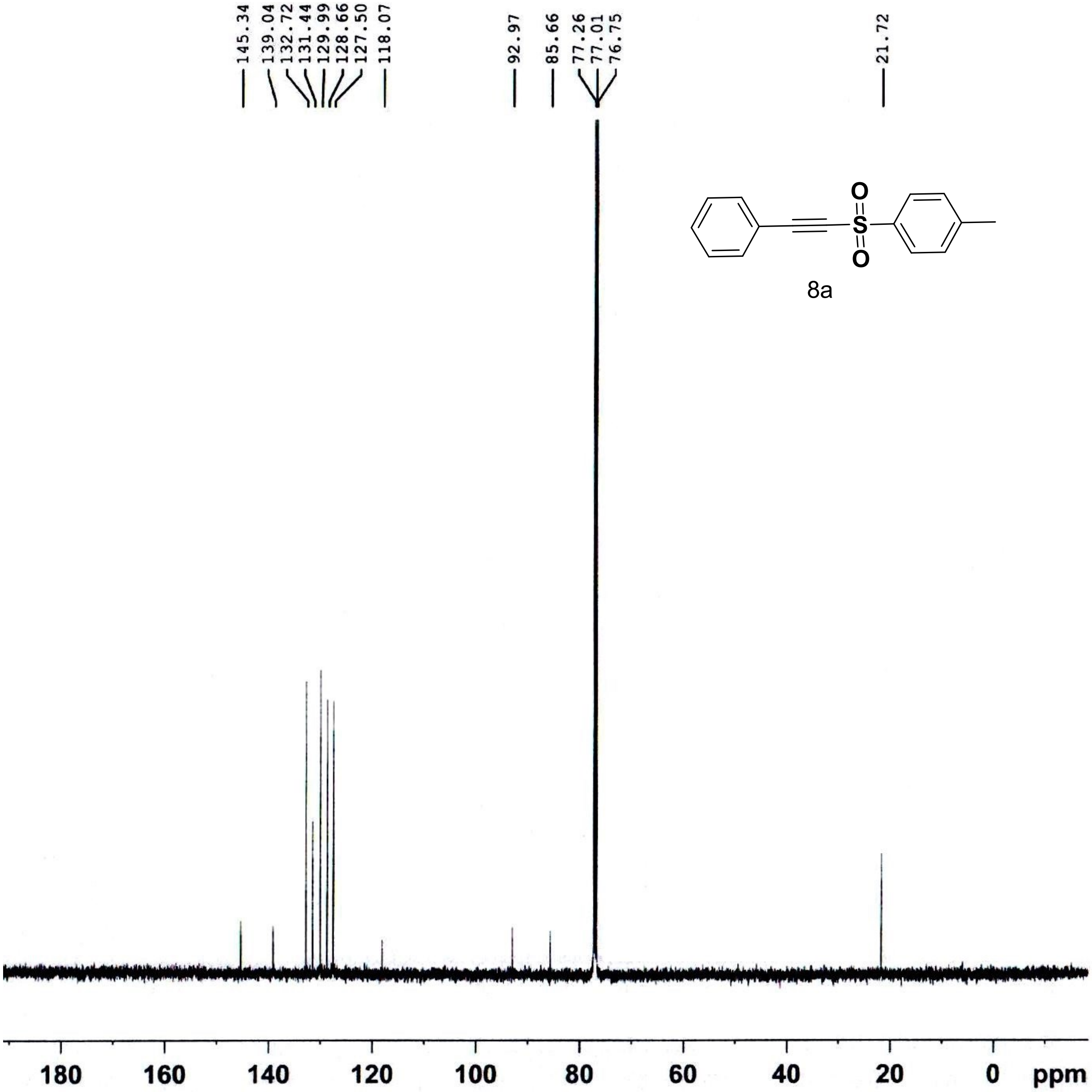
7.460
7.452
7.449
7.446
7.397
7.379
7.364
7.357
7.352
7.349
7.260
2.469
1.571
0.000
O
S
O
8a
1.97
2.00
1.30
4.21
2.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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131.44
129.99
128.66
127.50
118.07
92.97
85.66
77.26
77.01
76.75
21.72
O
S
O
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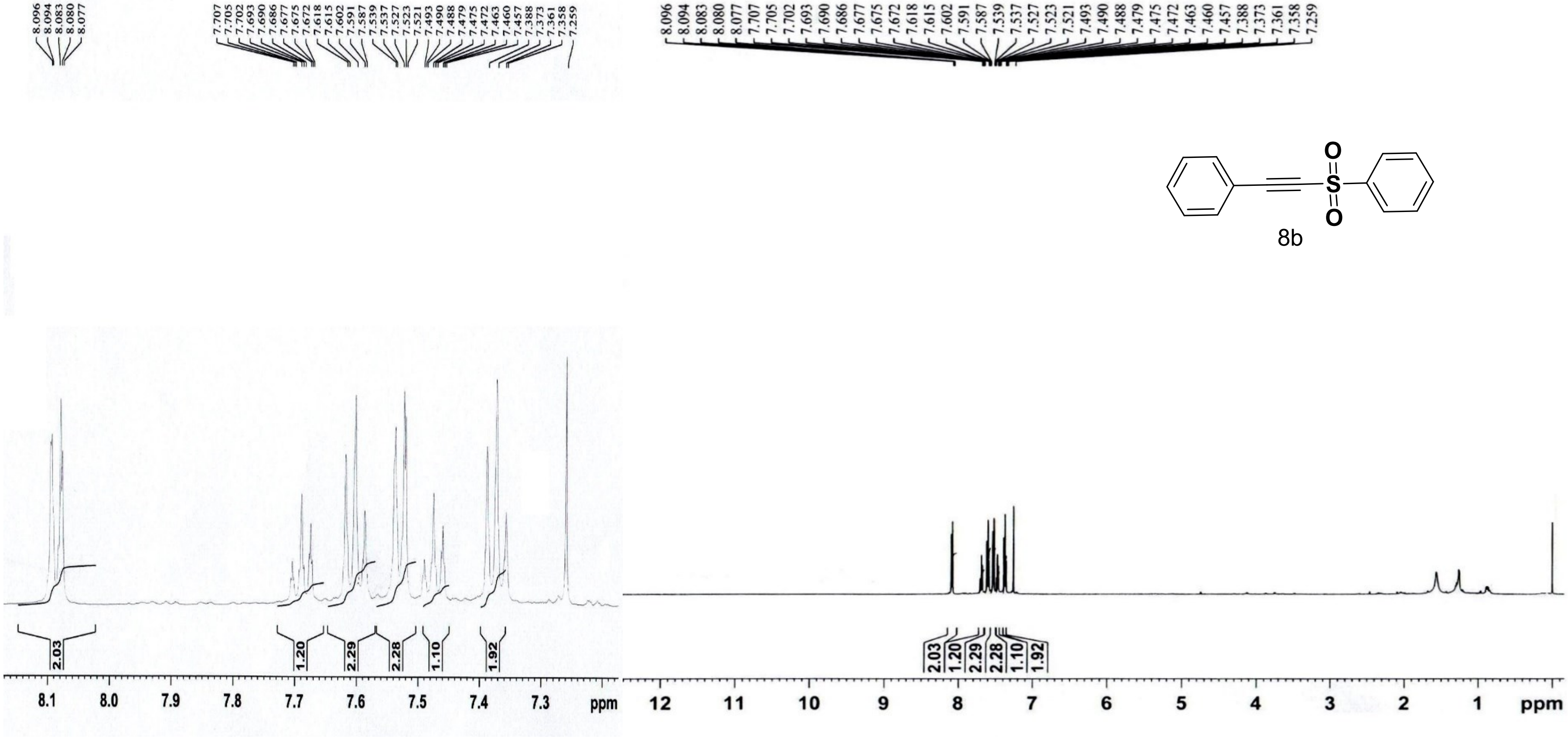
160
140
120
100
80
60
40
20
0
ppm

8a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8.080
8.077
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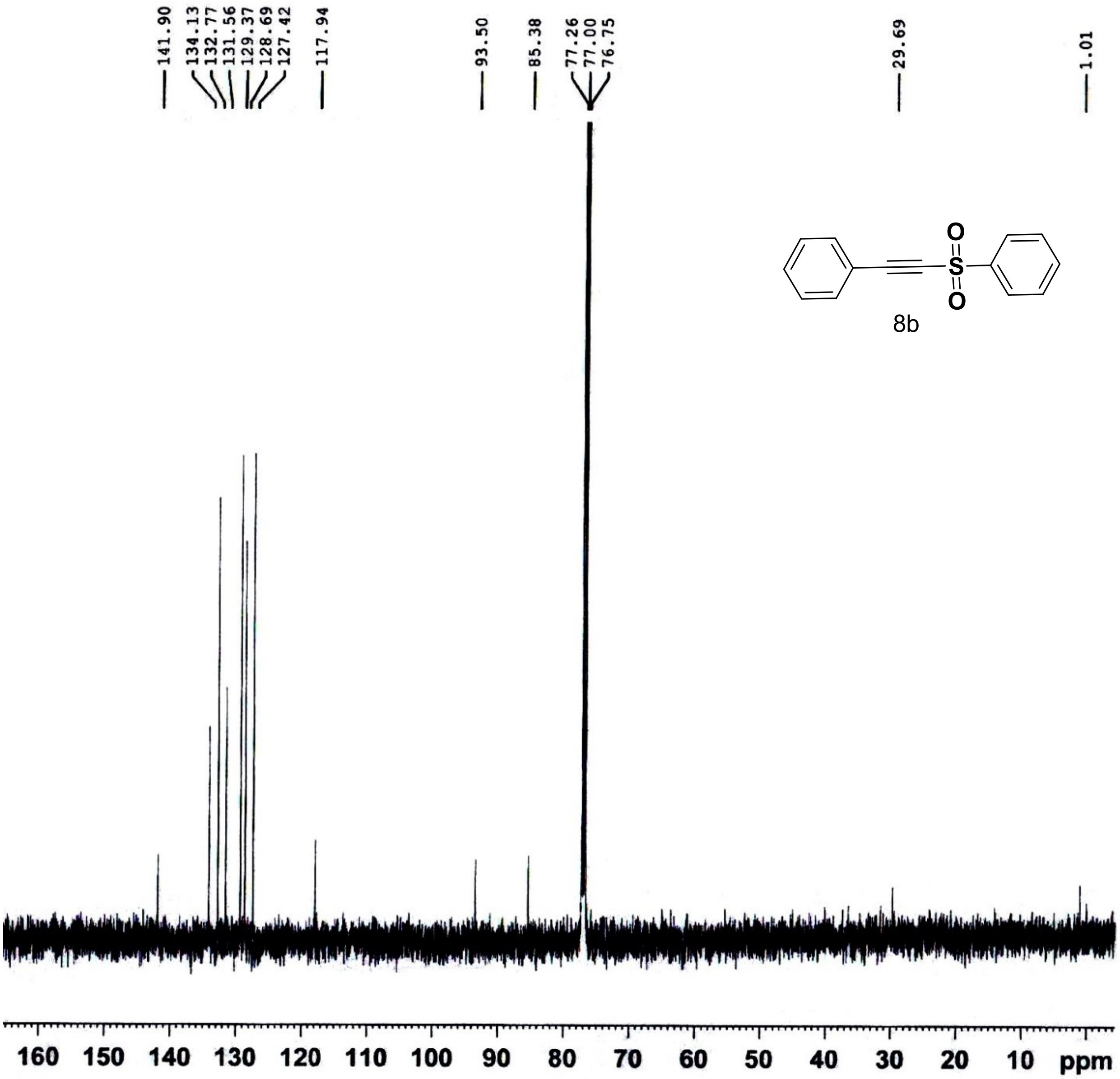
7.705
7.702
7.693
7.690
7.686
7.677
7.675
7.672
7.618
7.615
7.602
7.591
7.587
7.539
7.537
7.527
7.523
7.521
7.493
7.490
7.488
7.479
7.475
7.472
7.463
7.460
7.457
7.388
7.373
7.361
7.358
7.259
8b
2.03
1.20
2.29
2.28
1.10
1.92
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
ppm
12
11
10
9
8
7
6
5
4
3
2
1
ppm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85.38
77.26
77.00
76.75
29.69
1.01
8b
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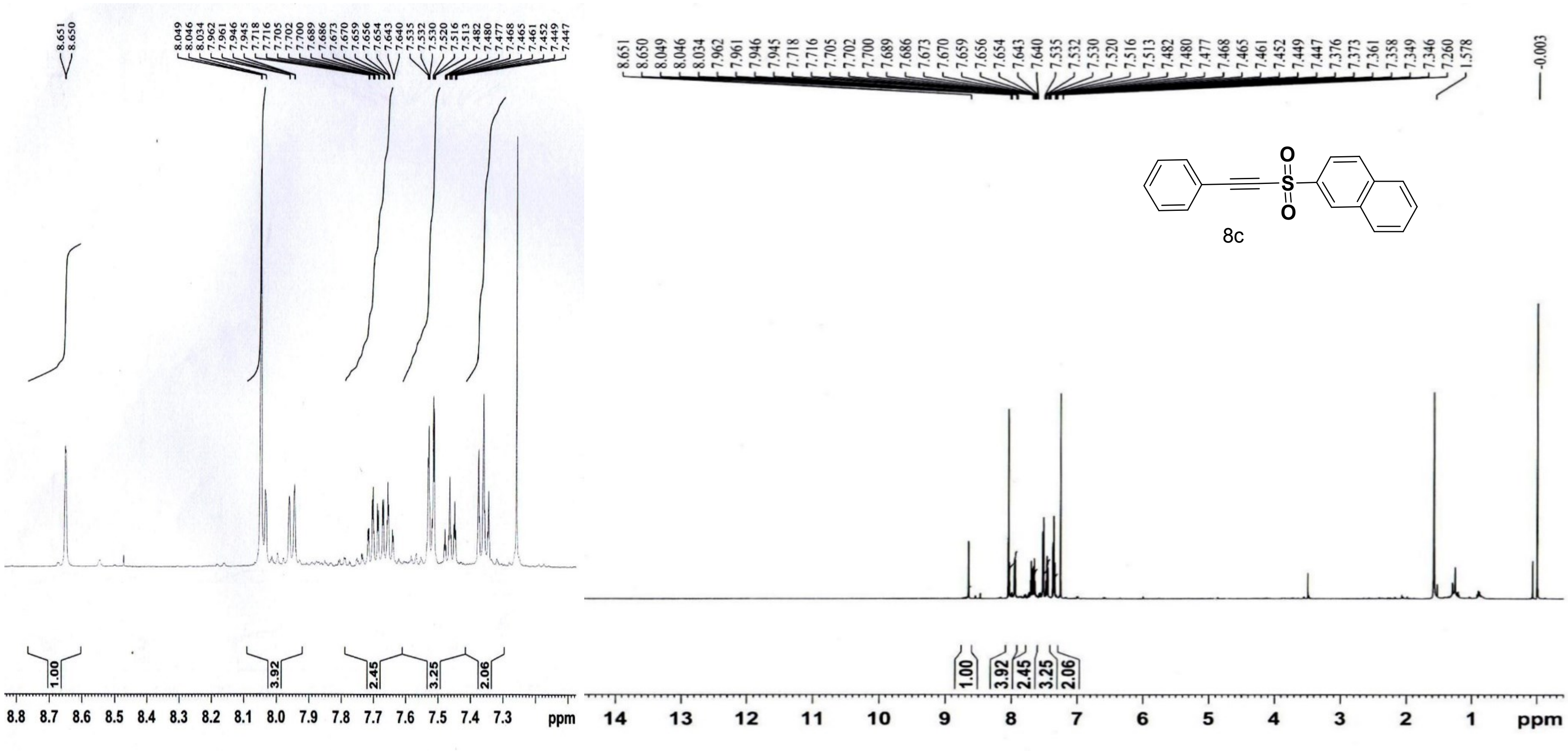
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.034
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7.961
7.946
7.945
7.718
7.716
7.705
7.702
7.700
7.689
7.686
7.673
7.670
7.659
7.656
7.654
7.643
7.640
7.535
7.532
7.530
7.520
7.516
7.513
7.482
7.480
7.477
7.468
7.465
7.461
7.452
7.449
7.447
1.00
3.92
2.45
3.25
2.06
8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
8.651
8.650
8.049
8.046
8.034
7.962
7.961
7.946
7.945
7.718
7.716
7.705
7.702
7.700
7.689
7.686
7.673
7.670
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7.656
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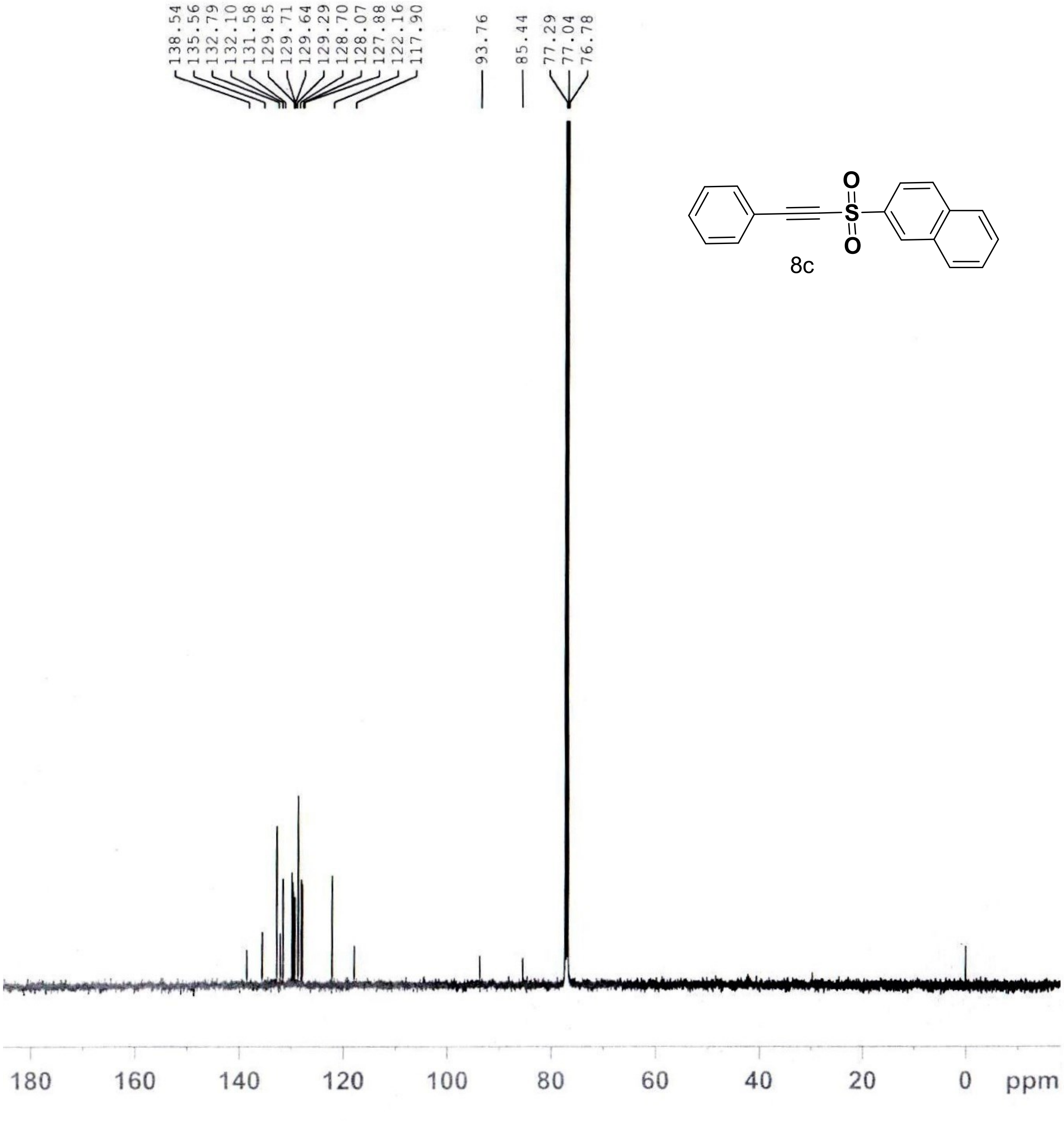
7.643
7.640
7.535
7.532
7.530
7.520
7.516
7.513
7.482
7.480
7.477
7.468
7.465
7.461
7.452
7.449
7.447
7.376
7.373
7.361
7.358
7.349
7.346
7.260
1.578
-0.003
O
S
O
1.00
3.92
2.45
3.25
2.06
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm

8c


8c

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129.71
129.64
129.29
128.70
128.07
127.88
122.16
117.90
93.76
85.44
77.29
77.04
76.78
O
S
O
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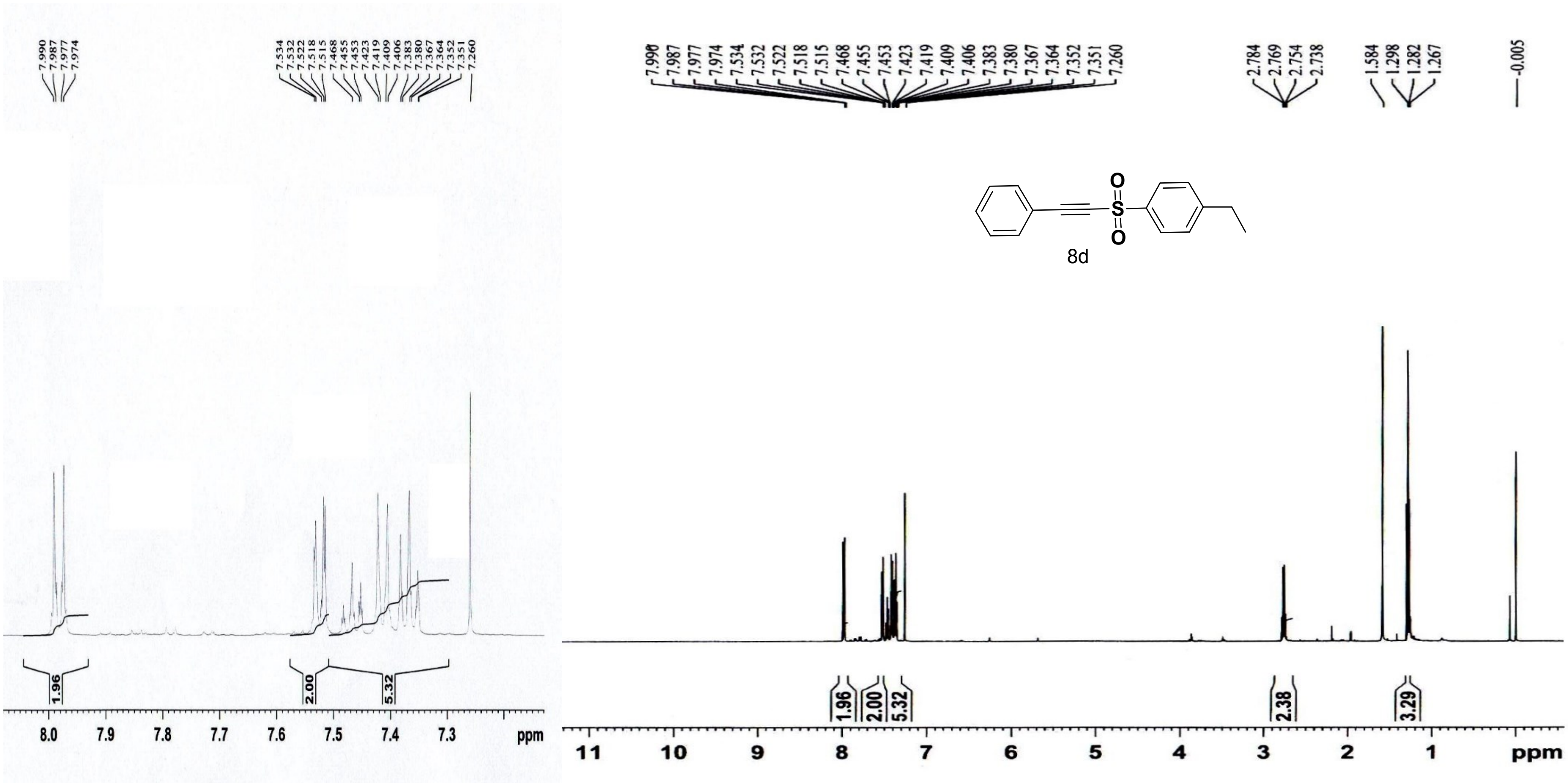
160
140
120
100
80
60
40
20
0
ppm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7.518
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7.468
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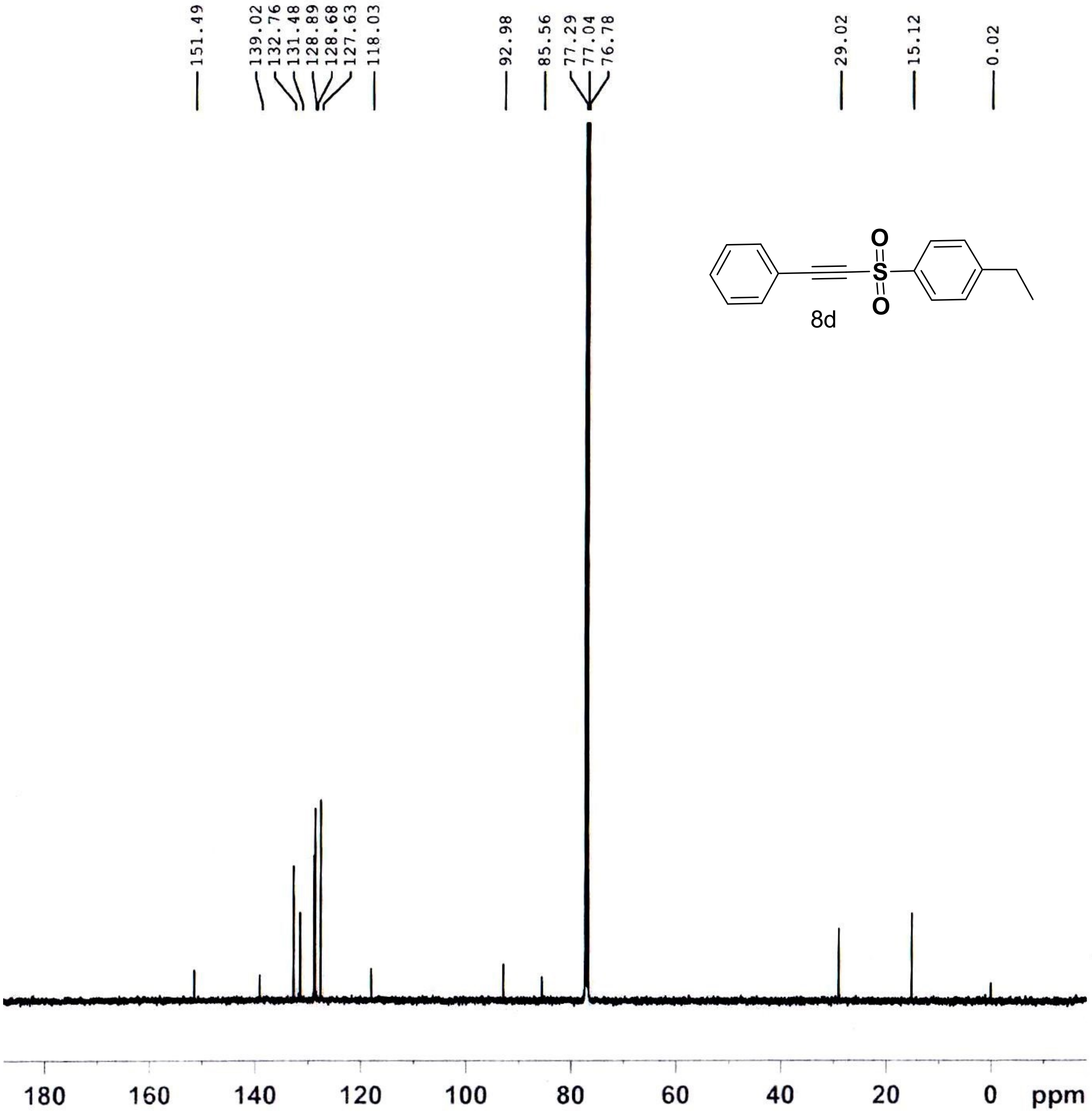
7.453
7.423
7.419
7.409
7.406
7.383
7.380
7.367
7.364
7.352
7.351
7.260
2.784
2.769
2.754
2.738
1.584
1.298
1.282
1.267
-0.005
O
S
O
1.96
2.00
5.32
2.38
3.29
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
ppm
11
10
9
8
7
6
5
4
3
2
1
ppm

8d


151.49
139.02
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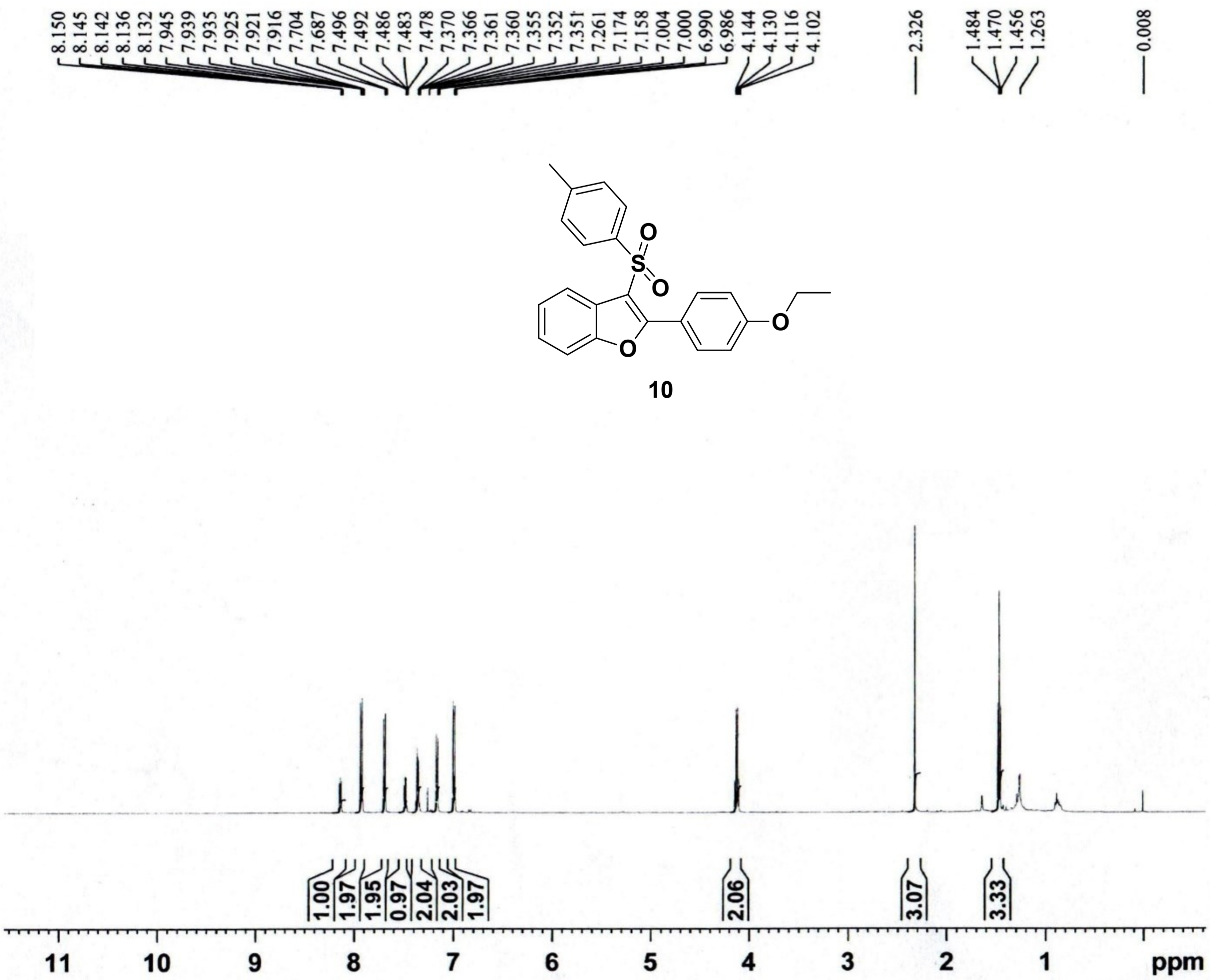
131.48
128.89
128.68
127.63
118.03
92.98
85.56
77.29
77.04
76.78
29.02
15.12
0.02
O
S
O
8d
180
160
140
120
100
80
60
40
20
0
ppm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8.142
8.136
8.132
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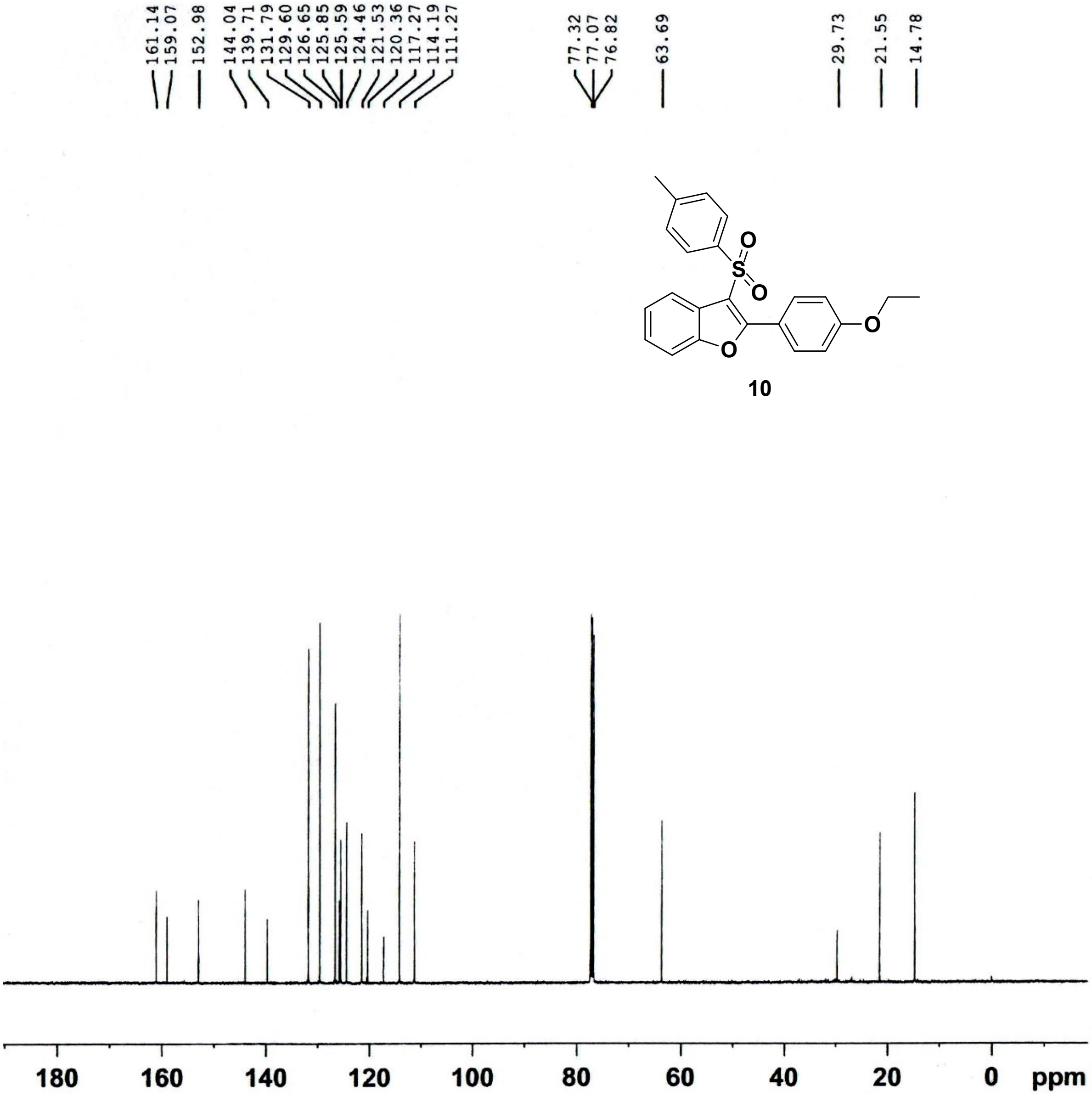
7.939
7.935
7.925
7.921
7.916
7.704
7.687
7.496
7.492
7.486
7.483
7.478
7.370
7.366
7.361
7.360
7.355
7.352
7.351
7.261
7.174
7.158
7.004
7.000
6.990
6.986
4.144
4.130
4.116
4.102
2.326
1.484
1.470
1.456
1.263
0.008
S
O
O
O
O
10
1.00
1.97
1.95
0.97
2.04
2.03
1.97
2.06
3.07
3.33
11
10
9
8
7
6
5
4
3
2
1
ppm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159.07
152.98
144.04
139.71
131.79
129.60
126.65
125.85
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124.46
121.53
120.36
117.27
114.19
111.27
77.32
77.07
76.82
63.69
29.73
21.55
14.78
O
S
O
O
O
180
160
140
120
100
80
60
40
20
0
ppm

10