Supporting Information

A Novel Synthetic Route to 3-Sulfenyl- and 3-Selenylindoles by *n*-Bu_4NI-Induced Electrophilic Cyclization

Yu Chen, Chul-Hee Cho, and Richard C. Larock*

Department of Chemistry, Iowa State University, Ames, IA 50011

larock@iastate.edu

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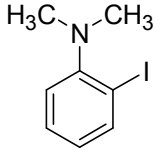
General information. All reactions were carried out in sealed 4-dram oven-dried vials. All commercially available chemicals were used as received without further purification unless otherwise indicated. Tetra-*n*-butylammonium iodide was purchased from Aldrich Chemical Co., Inc., recrystallized from acetone and diethyl ether, and dried under vaccum for 12 h before use. Pentafluorobenzenesulfenyl chloride was purchased from Acros Organics. 4-Nitrobenzenesulfenyl chloride and phenylselenenyl chloride were purchased from Aldrich Chemical Co., Inc. 2-Nitrobenzenesulfenyl chloride was purchased from Fluka Chemical Corp. Phenylsulfenyl chloride and *p*-toluenesulfenyl chloride were prepared according to literature procedures.[1] All ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively, using $CDCl_3$ as a solvent. The chemical shifts of all ^{1}H and ^{13}C NMR spectra are referenced to the residual signal of $CDCl_3$ (δ 7.26 ppm for the ^{1}H NMR spectra and δ 77.23 ppm for the ^{13}C NMR spectra). The chemical shifts of all ^{19}F NMR spectra are referenced to the signal of the internal standard hexafluorobenzene (δ -164.9 ppm). The high resolution mass spectra were recorded on a double focusing magnetic sector mass spectrometer using EI at a voltage of 70 eV. The melting points are uncorrected.

General procedure for the preparation of the *N,N*-dimethyl-*o*-iodoanilines.

These compounds were prepared according to a procedure reported by Cadogan.[2] To a solution of the corresponding *o*-iodoaniline (2.0 mmol) and iodomethane (0.85 g, 6.0 mmol) in DMF (10 mL) was added K_2CO_3 (0.55 g, 4.0 mmol). The resulting mixture was stirred at room temperature for 48 h. Water (10 mL) was added to the reaction mixture. The resulting solution was extracted with diethyl ether (3 × 10 mL). The organic layers were combined and washed with water to remove any remaining DMF and dried over anhydrous $MgSO_4$. The solvent was removed under vaccum and the residue was purified by flash column chromatography on silica gel using ethyl acetate/hexanes as the eluent.

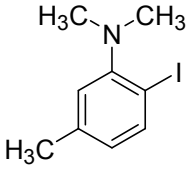
***N,N*-Dimethyl-2-iodoaniline (4a)**



4a

This compound was obtained as a yellow oil in an 81% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (s, 6H), 6.77 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.09 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.31 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.84 (dd, *J* = 7.8, 1.5 Hz, 1H). The ^{1}H NMR spectral data are in good agreement with the literature data.[3]

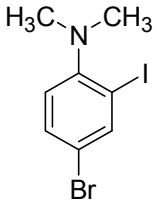
***N,N*-Dimethyl-2-iodo-5-methylaniline (4b)**



4b

This compound was obtained as a colorless oil in a 99% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.70 (s, 6H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 7.69 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 45.0, 93.1, 121.4, 126.0, 139.0, 139.7, 154.6; HRMS (EI) calcd for $C_9H_{12}IN$ 261.0014, found 261.0019.

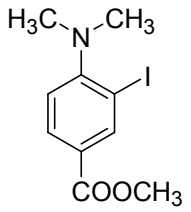
***N,N*-Dimethyl-4-bromo-2-iodoaniline (4c)**



4c

This compound was obtained as a light red oil in an 81% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.72 (s, 6H), 6.92 (d, *J* = 8.5 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.94 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.0, 97.6, 116.4, 121.5, 132.0, 142.0, 154.3; HRMS (EI) calcd for C_8H_9BrIN 324.8963, found 324.8969.

Preparation of methyl 4-dimethylamino-3-iodobenzoate (4d)

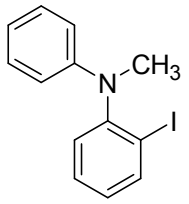


4d

This compound was prepared according to a procedure reported by Larock.[4] The product was obtained as a colorless oil in a 44% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 (s,

6H), 3.85 (s, 3H), 6.98 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 8.4, 2.0 Hz, 1H), 8.46 (d, J = 2.0 Hz, 1H). The ^{1}H NMR spectral data are in good agreement with the literature data.[4]

***N*-Methyl-*N*-phenyl-2-iodoaniline (4e)**



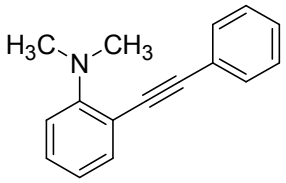
4e

This compound was prepared according to a procedure reported by Larock.[5] The product was obtained as a colorless oil in an 86% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.24 (s, 3H), 6.59 (d, J = 8.0 Hz, 2H), 6.80 (t, J = 8.0 Hz, 1H), 7.02 (dt, J = 7.8, 1.6 Hz, 1H), 7.21-7.27 (m, 3H), 7.42 (dt, J = 7.8, 1.6 Hz, 1H), 7.99 (dd, J = 8.0, 1.4 Hz, 1H). The ^{1}H NMR spectral data are in good agreement with the literature data.[5]

General procedure for preparation of the *N,N*-dialkyl-2-(1-alkynyl)anilines.

To a 4-dram oven-dried vial was added $PdCl_2(PPh_3)_2$ (18.3 mg, 0.026 mmol), CuI (3.8 mg, 0.020 mmol), 2.0 mmol of the *N,N*-dialkyl-*o*-iodoaniline, 2.2 mmol of the terminal acetylene and 6 mL of Et_3N. The resulting mixture was flushed with Ar and stirred at room temperature for the desired time. The reaction mixture was diluted with 15 mL of diethyl ether and washed with brine (15 mL). The aqueous phase was then extracted with diethyl ether (2 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under vacuum to afford the crude product, which was purified by flash column chromatography on silica gel using ethyl acetate/hexanes as the eluent.

***N,N*-Dimethyl-2-(phenylethynyl)aniline (1a)**

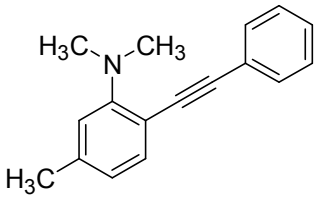


1a

This compound was obtained as a light yellow oil in an 89% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.01 (s, 6H), 6.88-6.94 (m, 2H), 7.24-7.27 (m, 1H), 7.31-7.36 (m, 3H), 7.49 (d,

J = 7.5 Hz, 1H), 7.54 (dd, *J* = 7.1, 1.1 Hz, 2H). The ^{1}H NMR spectral data are in good agreement with the literature data.[3]

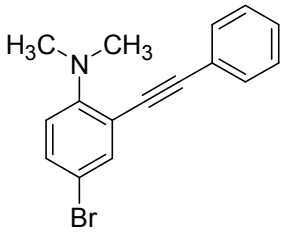
***N,N*-Dimethyl-5-methyl-2-(phenylethynyl)aniline (1b)**



1b

This compound was obtained as a light yellow oil in a 92% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.99 (s, 6H), 6.72-6.74 (m, 2H), 7.30-7.36 (m, 3H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.51-7.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 43.5, 89.2, 94.1, 112.1, 117.7, 121.4, 124.1, 127.8, 128.3, 131.2, 134.1, 139.4, 154.6; HRMS (EI) calcd for $C_{17}H_{17}N$ 235.1361, found 235.1365.

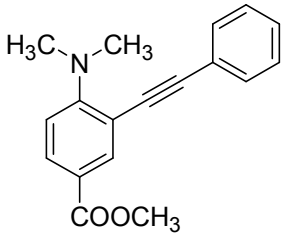
***N,N*-Dimethyl-4-bromo-2-(phenylethynyl)aniline (1c)**



1c

This compound was obtained as a light yellow oil in a 76% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (s, 6H), 6.78 (d, *J* = 8.8 Hz, 1H), 7.31-7.37 (m, 4H), 7.51-7.54 (m, 2H), 7.59 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.4, 87.7, 95.9, 112.1, 116.7, 118.5, 123.4, 128.4, 128.5, 131.4, 132.0, 136.4, 153.7; HRMS (EI) calcd for $C_{16}H_{14}BrN$ 299.0310, found 299.0314.

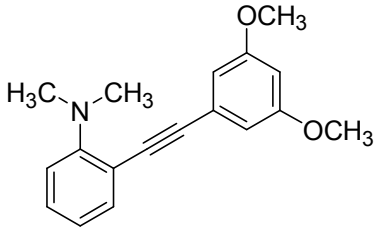
Methyl 4-dimethylamino-3-(phenylethynyl)benzoate (1d)



1d

This compound was obtained as a white solid in a 92% yield: mp 55-56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (s, 6H), 3.88 (s, 3H), 6.82 (d, *J* = 8.8 Hz, 1H), 7.32-7.37 (m, 3H), 7.51-7.53 (m, 2H), 7.87 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.16 (d, *J* = 2.0 Hz, 1H). The ^{1}H NMR spectral data are in good agreement with the literature data.[4]

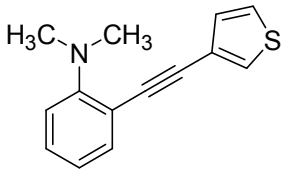
***N,N*-Dimethyl-2-(3,5-dimethoxyphenylethynyl)aniline (1e)**



1e

This compound was obtained as a light yellow oil in an 85% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (s, 6H), 3.81 (s, 6H), 6.45 (t, *J* = 2.4 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 2H), 6.87-6.94 (m, 2H), 7.23-7.28 (m, 1H), 7.49 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.4, 55.3, 88.6, 94.7, 101.3, 109.0, 114.7, 116.9, 120.4, 125.1, 129.4, 134.3, 154.7, 160.5; HRMS (EI) calcd for $C_{18}H_{19}NO_2$ 281.1416, found 281.1421.

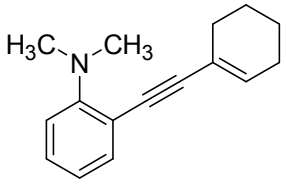
***N,N*-Dimethyl-2-(thiophen-3-ylethynyl)aniline (1f)**



1f

This compound was obtained as a light yellow oil in a 98% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (s, 6H), 6.88-6.94 (m, 2H), 7.21 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.23-7.27 (m, 1H), 7.30 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.47 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.50 (dd, *J* = 3.0, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.5, 88.4, 89.9, 115.1, 117.0, 120.5, 122.9, 125.3, 127.9, 129.2, 129.7, 134.2, 154.7; HRMS (EI) calcd for $C_{14}H_{13}NS$ 227.0769, found 227.0773.

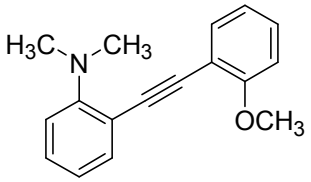
***N,N*-Dimethyl-2-(cyclohex-1-enylethynyl)aniline (1g)**



1g

This compound was obtained as a light yellow oil in an 87% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60-1.72 (m, 4H), 2.14-2.18 (m, 2H), 2.25-2.29 (m, 2H), 2.95 (s, 6H), 6.20-6.22 (m, 1H), 6.84-6.90 (m, 2H), 7.20 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.39 (dd, *J* = 7.6, 1.6 Hz, 1H). The ^{1}H NMR spectral data are in good agreement with the literature data.[6]

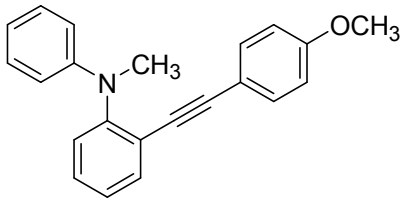
***N,N*-Dimethyl-2-(2-methoxyphenylethynyl)aniline (1h)**



1h

This compound was obtained as a colorless oil in an 82% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 6H), 3.91 (s, 3H), 6.89-6.98 (m, 4H), 7.24-7.32 (m, 2H), 7.53-7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.6, 55.7, 91.3, 93.0, 110.6, 113.2, 115.5, 116.9, 120.4, 120.5, 129.2, 129.5, 133.1, 134.4, 154.7, 159.9; HRMS (EI) calcd for $C_{17}H_{17}NO$ 251.1310, found 251.1314.

***N*-Methyl-*N*-phenyl-2-(4-methoxyphenylethynyl)aniline (1i)**



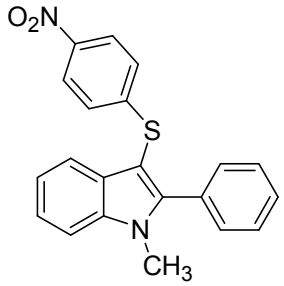
1i

This compound was obtained as a colorless oil in a 79% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 3H), 3.80 (s, 3H), 6.78-6.83 (m, 5H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.20-7.29 (m, 4H), 7.33-7.37 (m, 1H), 7.59 (dd, *J* = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.0, 55.4, 86.2, 94.9, 114.0, 115.0, 115.5, 118.1, 122.1, 125.3, 127.7, 129.0, 129.4, 133.1, 133.8, 149.2, 150.0, 159.7; HRMS (EI) calcd for $C_{22}H_{19}NO$ 313.1467, found 313.1460.

General procedure for the preparation of 3-sulfenyl- and 3-selenylindoles.

To a solution of 0.50 mmol of the *N,N*-dialkyl-2-(1-alkynyl)aniline, 0.50 mmol of *n*-Bu_4NI and 3 mL of 1,2-dichloroethane (DCE) was gradually added a solution of 1.00 mmol of arylsulfenyl or arylselenenyl chloride in 2 mL of DCE. The resulting mixture was stirred at room temperature for 5 minutes and then heated to 70 °C for the desired time. The reaction mixture was cooled to room temperature and diluted with 5 mL of dichloromethane (DCM). The mixture was then washed with 10 mL of a satd. aq. solution of NH_4Cl. The aqueous phase was extracted with diethyl ether (2 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under vacuum to yield the crude product, which was purified by flash column chromatography on silica gel using either ethyl acetate/hexanes or chloroform/hexanes as the eluent.

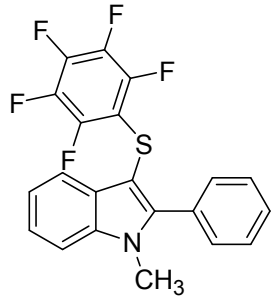
1-Methyl-3-(4-nitrophenylsulfenyl)-2-phenylindole (3a)



3a

This product was obtained as a yellow solid in a 90% yield: mp 162-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.22-7.26 (m, 1H), 7.36-7.40 (m, 3H), 7.46-7.50 (m, 4H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.0, 97.1, 110.4, 119.4, 121.6, 123.4, 124.0, 125.0, 128.6, 129.1, 129.3, 130.0, 130.5, 137.8, 144.8, 146.5, 150.6; HRMS (EI) calcd for $C_{21}H_{16}N_2O_2S$ 360.0932, found 360.0939.

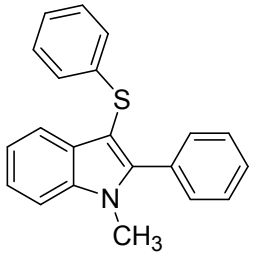
1-Methyl-3-pentafluorophenylsulfenyl-2-phenylindole (3b)



3b

This product was obtained as a colorless oil in an 87% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 7.25-7.28 (m, 1H), 7.33 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.43-7.46 (m, 2H), 7.52-7.58 (m, 3H), 7.77 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.7, 99.0, 110.1, 111.4 (t, *J* = 90.4 Hz), 119.3, 121.3, 123.0, 128.5, 129.2, 129.4, 130.5, 131.0, 137.1, 137.5 (dt, *J* = 1012 Hz, 71.6 Hz), 141.0 (dm, *J* = 1010 Hz), 146.2, 147.0 (dm, *J* = 1006 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ -164.8 (m, 2F), -157.7 (t, *J* = 24 Hz, 1F), -136.4 (dd, *J* = 28, 8 Hz, 2F); HRMS (EI) calcd for $C_{21}H_{12}F_5NS$ 405.0611, found 405.0618.

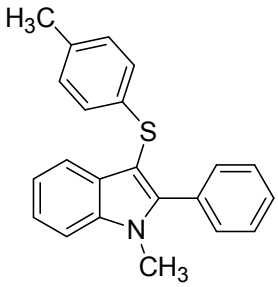
1-Methyl-2-phenyl-3-phenylsulfenylindole (3c)



3c

This product was obtained as a light yellow solid in an 87% yield: mp 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 7.08-7.12 (m, 1H), 7.13-7.15 (m, 2H), 7.19-7.23 (m, 2H), 7.26-7.30 (m, 1H), 7.39-7.43 (m, 1H), 7.46-7.53 (m, 6H), 7.75 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.9, 99.6, 110.0, 119.9, 121.1, 122.9, 124.5, 125.6, 128.4, 128.8, 128.9, 129.9, 130.6, 130.7, 137.7, 140.1, 146.0; HRMS (EI) calcd for $C_{21}H_{17}NS$ 315.1082, found 315.1087.

1-Methyl-2-phenyl-3-*p*-tolylsulfenylindole (3d)

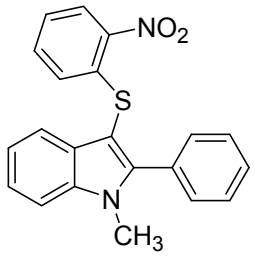


3d

This product was obtained as a white solid in a 92% yield: mp 106-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 3.75 (s, 3H), 6.96 (s, 4H), 7.20 (dt, *J* = 7.4, 0.9 Hz, 1H), 7.34 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.41-7.47 (m, 6H), 7.66 (d, *J* = 8.0 Hz, 1H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 21.1, 31.9, 100.1, 110.0, 120.0, 121.0, 122.9, 125.8, 128.4, 128.9, 129.6, 129.9, 130.7, 130.8, 134.3, 136.5, 137.7, 145.9; HRMS (EI) calcd for $C_{22}H_{19}NS$ 329.1238, found 329.1242.

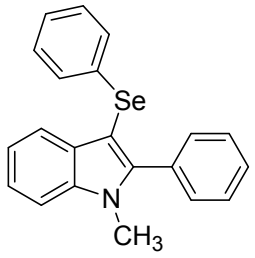
1-Methyl-3-(2-nitrophenylsulfenyl)-2-phenylindole (3e)



3e

This product was obtained as a yellow solid in a 52% yield: mp 166-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 7.00 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.23-7.27 (m, 1H), 7.35-7.38 (m, 3H), 7.43-7.44 (m, 3H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.0, 98.6, 110.3, 119.6, 121.5, 123.3, 124.4, 126.1, 127.9, 128.6, 129.2, 129.3, 130.0, 130.5, 133.5, 138.0, 141.0, 144.9, 146.9; HRMS (EI) calcd for $C_{21}H_{16}N_2O_2S$ 360.0932, found 360.0939.

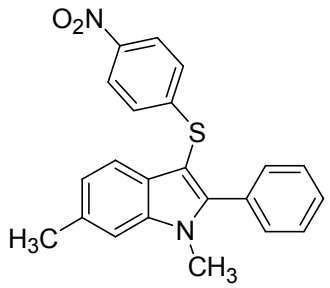
1-Methyl-2-phenyl-3-phenylselenylindole (3f)



3f

This product was obtained as a colorless oil in an 84% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 7.12-7.18 (m, 3H), 7.23-7.26 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.45-7.49 (m, 6H), 7.75 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.0, 96.5, 109.9, 120.8, 121.0, 122.9, 125.4, 128.3, 128.5, 128.8, 129.0, 130.8, 130.9, 131.3, 134.8, 137.9, 146.0; HRMS (EI) calcd for $C_{21}H_{17}NSe$ 363.0526, found 363.0532.

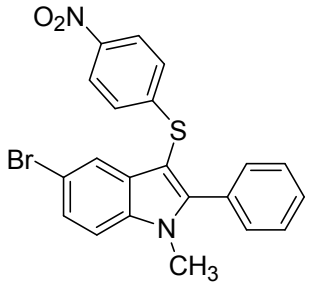
1,6-Dimethyl-3-(4-nitrophenylsulfenyl)-2-phenylindole (3g)



3g

This product was obtained as a yellow oil in a 78% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H), 3.74 (s, 3H), 7.06-7.11 (m, 3H), 7.29 (s, 1H), 7.35-7.37 (m, 2H), 7.42-7.46 (m, 4H), 7.98 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 31.9, 96.8, 110.4, 119.0, 123.3, 124.0, 124.9, 127.0, 128.5, 129.1, 130.2, 130.5, 133.5, 138.2, 144.8, 145.9, 150.8; HRMS (EI) calcd for $C_{22}H_{18}N_2O_2S$ 374.1089, found 374.1096.

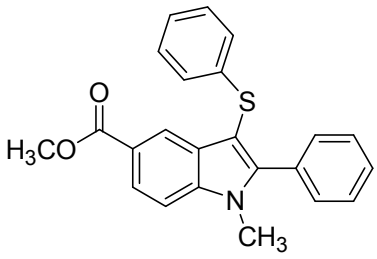
5-Bromo-1-methyl-3-(4-nitrophenylsulfenyl)-2-phenylindole (3h)



3h

This product was obtained as a yellow solid in an 85% yield: mp 123-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 7.07 (d, J = 8.8 Hz, 2H), 7.34-7.36 (m, 3H), 7.42-7.47 (m, 4H), 7.69 (s, 1H), 7.99 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.2, 96.8, 112.0, 115.1, 121.9, 124.1, 125.0, 126.4, 128.7, 129.5, 129.6, 130.4, 131.0, 136.5, 145.0, 147.7, 150.0; HRMS (EI) calcd for $C_{21}H_{15}BrN_2O_2S$ 438.0038, found 438.0046.

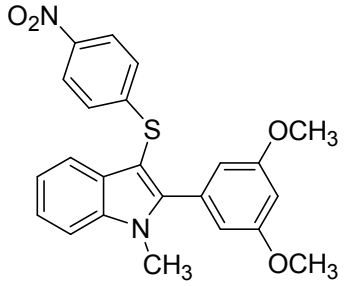
Methyl 1-methyl-2-phenyl-3-phenylsulfenylindole-5-carboxylate (3i)



3i

This product was obtained as a white solid in a 75% yield: mp 163-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.90 (s, 3H), 7.02-7.06 (m, 3H), 7.13-7.17 (m, 2H), 7.39-7.41 (m, 2H), 7.44-7.48 (m, 4H), 8.05 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.42 (dd, *J* = 1.6, 0.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.2, 52.1, 101.5, 109.9, 122.6, 123.2, 124.4, 124.8, 125.7, 128.5, 128.9, 129.2, 129.6, 130.0, 130.6, 139.8, 140.2, 147.6, 168.1; HRMS (EI) calcd for $C_{23}H_{19}NO_2S$ 373.1136, found 373.1147.

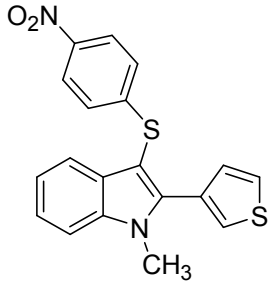
2-(3,5-Dimethoxyphenyl)-1-methyl-3-(4-nitrophenylsulfenyl)indole (3j)



3j

This product was obtained as a yellow solid in a 74% yield: mp 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 6H), 3.79 (s, 3H), 6.48 (d, *J* = 2.4 Hz, 2H), 6.54 (d, *J* = 2.0 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.0, 55.5, 97.0, 101.1, 108.7, 110.4, 119.3, 121.6, 123.4, 124.0, 125.0, 129.2, 131.7, 137.7, 144.8, 146.4, 150.8, 160.7; HRMS (EI) calcd for $C_{23}H_{20}N_2O_4S$ 420.1144, found 420.1152.

1-Methyl-3-(4-nitrophenylsulfenyl)-2-thiophen-3-ylindole (3k)

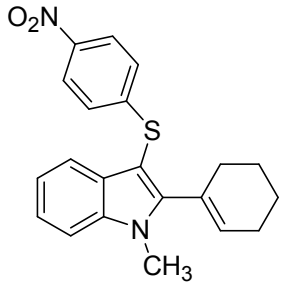


3k

This product was obtained as a yellow solid in an 85% yield: mp 162-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.20-7.25 (m, 2H), 7.36-7.41 (m, 2H), 7.43-7.45 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.0, 97.2, 110.3, 119.3, 121.6, 123.4,

124.0, 125.0, 126.2, 126.9, 128.8, 129.2, 129.9, 137.8, 141.6, 144.8, 150.6; HRMS (EI) calcd for $C_{19}H_{14}N_2O_2S_2$ 366.0497, found 366.0501.

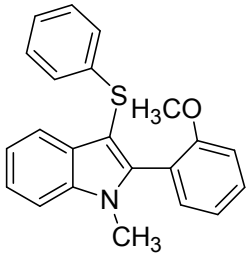
2-(Cyclohex-1-enyl)-1-methyl-3-(4-nitrophenylsulfenyl)indole (3l)



3l

This product was obtained as a light yellow oil in a 91% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67-1.78 (m, 4H), 2.20-2.24 (m, 4H), 5.81-5.83 (m, 1H), 7.08-7.11 (m, 2H), 7.14-7.19 (m, 1H), 7.28-7.33 (m, 1H), 7.39-7.42 (m, 1H), 7.46-7.49 (m, 1H), 7.96-8.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 22.7, 25.6, 29.6, 31.3, 95.2, 110.1, 119.0, 121.1, 122.8, 123.9, 124.9, 128.4, 129.1, 133.5, 137.3, 144.7, 149.2, 151.1; HRMS (EI) calcd for $C_{21}H_{20}N_2O_2S$ 364.1245, found 364.1252.

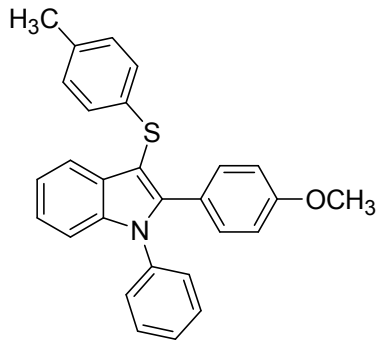
2-(2-Methoxyphenyl)-1-methyl-3-(phenylsulfenyl)indole (3m)



3m

This product was obtained as a colorless oil in a 79% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.72 (s, 3H), 7.01 (t, J = 7.2 Hz, 3H), 7.04-7.08 (m, 2H), 7.11-7.14 (m, 2H), 7.17-7.21 (m, 1H), 7.25-7.27 (m, 1H), 7.32 (dt, J = 7.6, 1.0 Hz, 1H), 7.42-7.46 (m, 2H), 7.65 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.4, 55.5, 99.7, 109.8, 111.1, 119.6, 119.8, 120.58, 120.63, 122.5, 124.3, 125.7, 128.6, 129.7, 131.0, 133.0, 137.5, 140.2, 143.7, 157.9; HRMS (EI) calcd for $C_{22}H_{19}NOS$ 345.1187, found 345.1195.

2-(4-Methoxyphenyl)-1-phenyl-3-(*p*-tolylsulfenyl)indole (3n)



3n

This product was obtained as a white solid in a 99% yield: mp 113-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.76 (s, 3H), 6.77 (dt, *J* = 8.8, 2.0 Hz, 2H), 7.01-7.03 (m, 2H), 7.06-7.08 (m, 2H), 7.18 (dt, *J* = 8.8, 2.1 Hz, 2H), 7.21-7.23 (m, 1H), 7.25-7.27 (m, 3H), 7.33-7.37 (m, 2H), 7.39-7.43 (m, 2H), 7.68-7.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 55.3, 102.0, 111.0, 113.5, 119.9, 121.6, 122.8, 123.2, 126.0, 127.6, 128.2, 129.4, 129.7, 130.2, 132.2, 134.4, 136.1, 138.1, 138.2, 145.0, 159.5; HRMS (EI) calcd for $C_{28}H_{23}NOS$ 421.1500, found 421.1509.

References:

1. Barrett, A. G. M.; Dhanak, D.; Graboski, G. G.; Taylor, S. J. *Org. Synth.* **1990**, *68*, 8-13.

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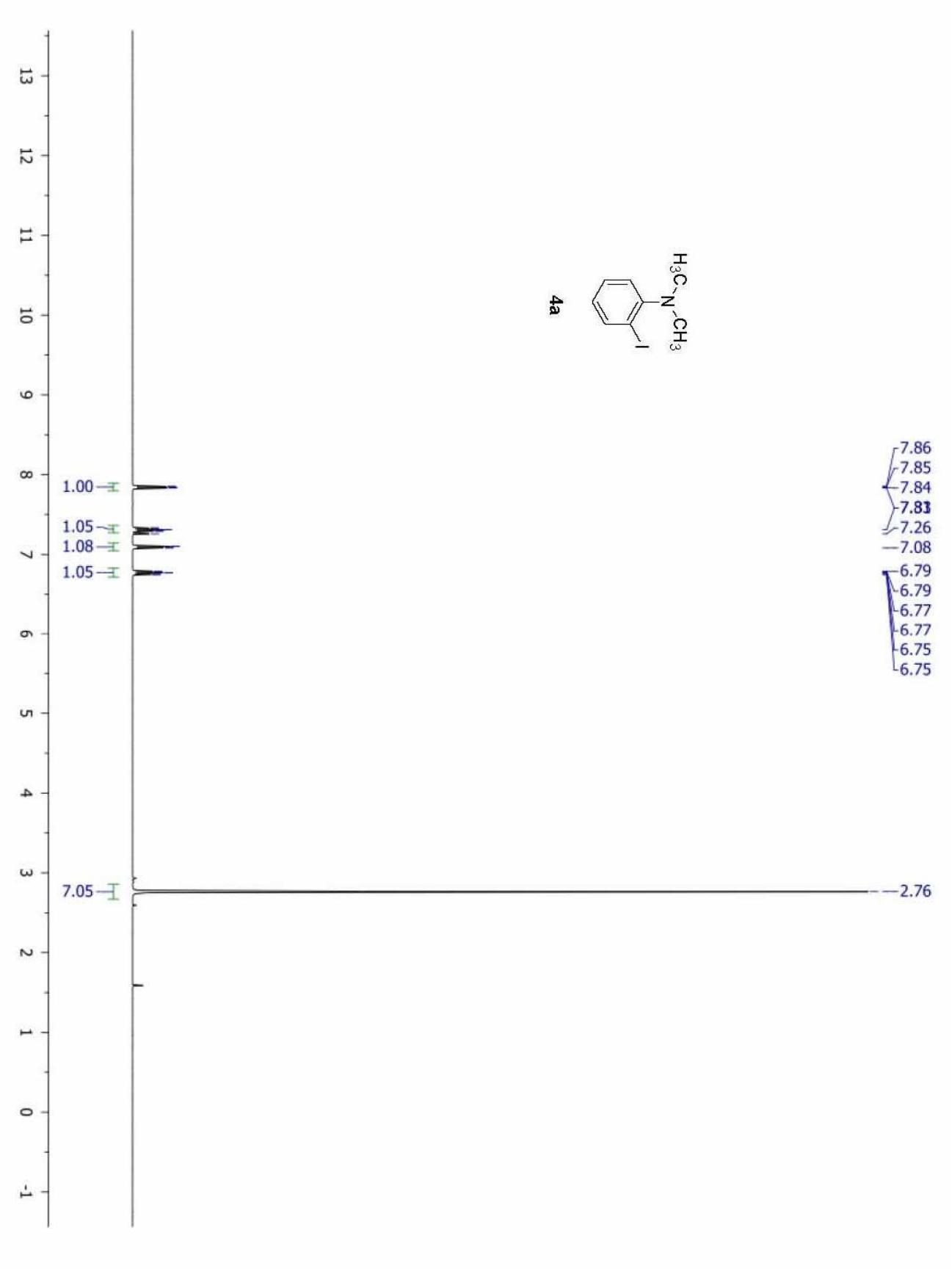
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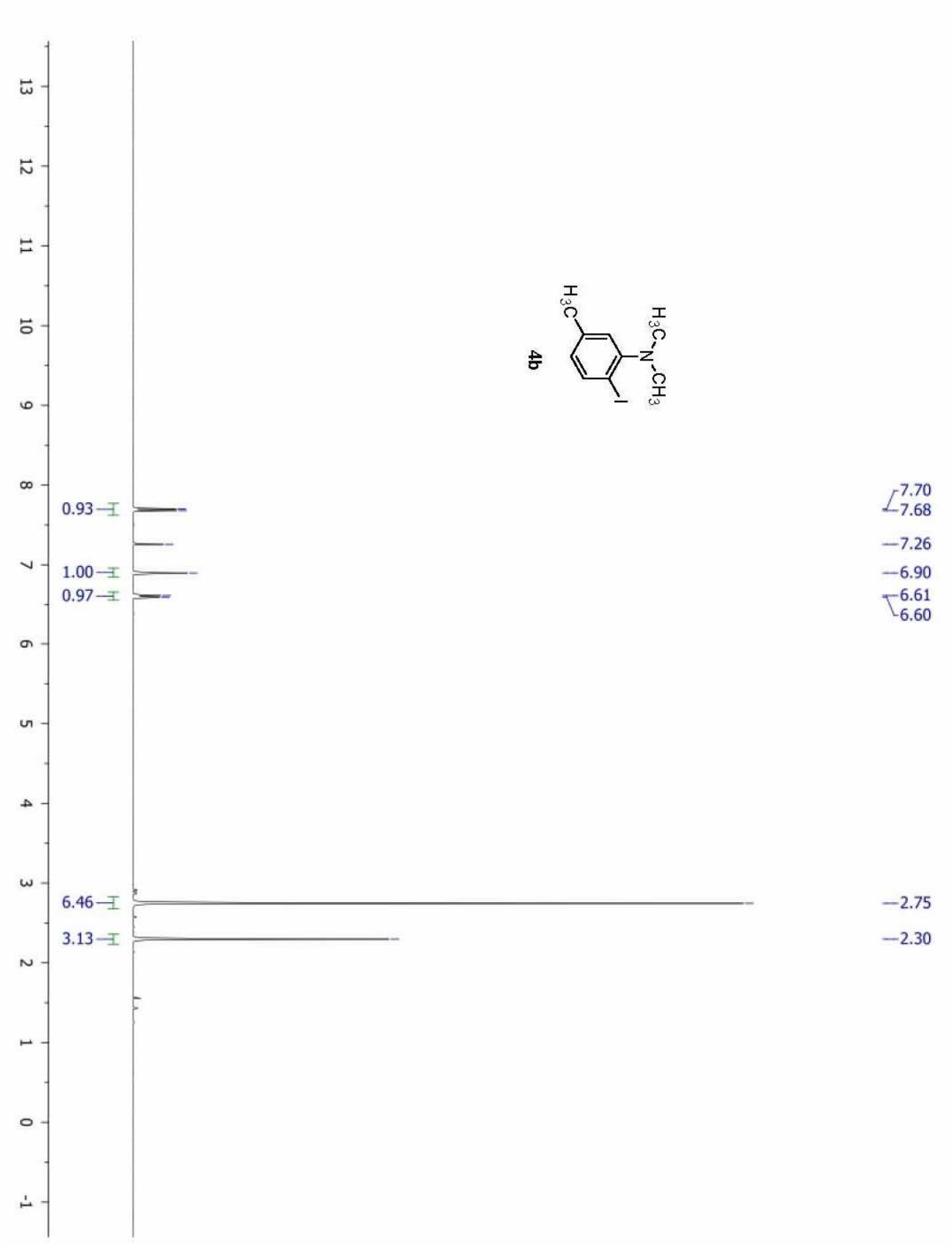
1.05
1.08
1.05
7.05
2.76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H3C
N
CH3
I
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10
9
8
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3
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0
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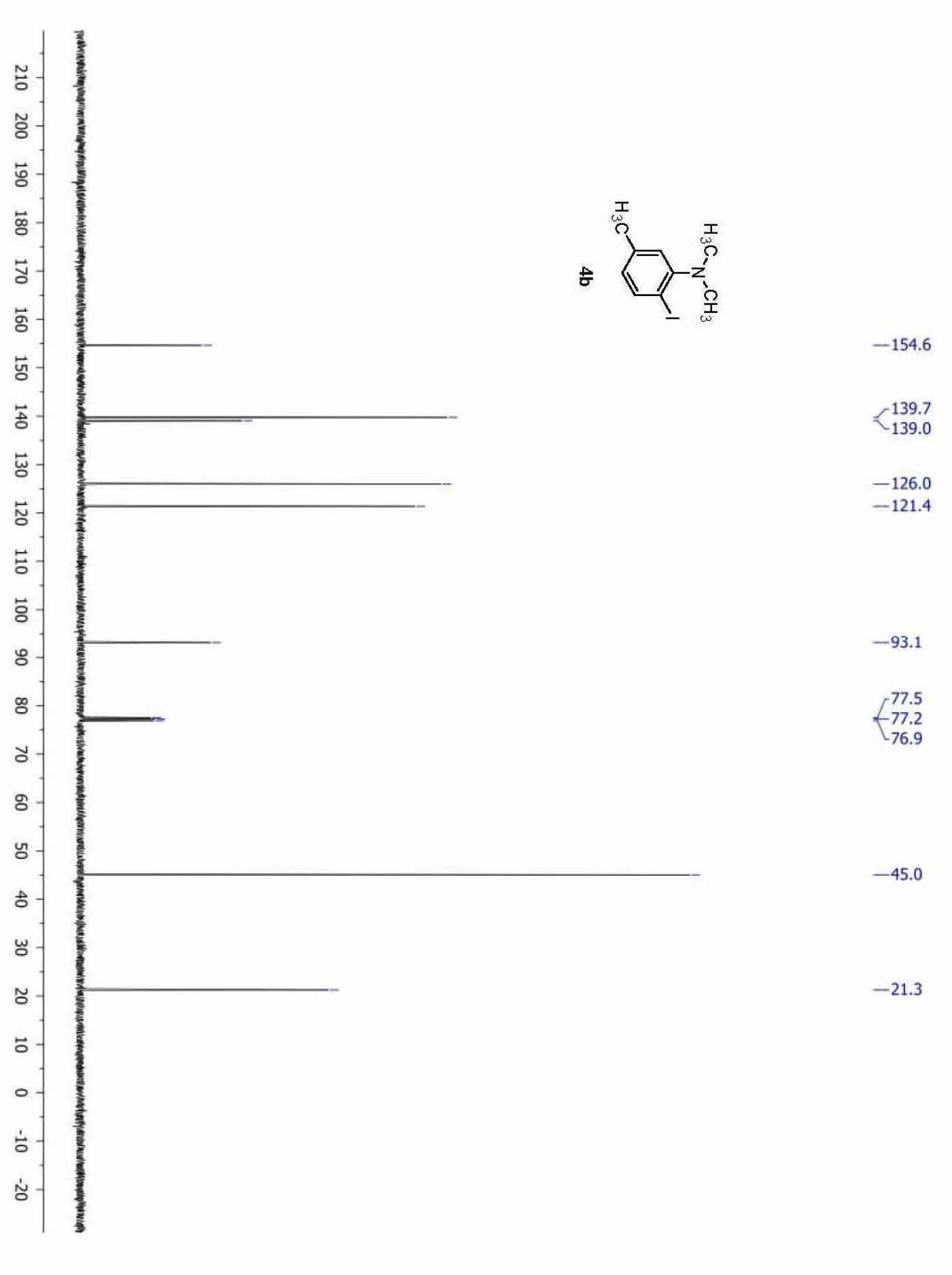
2.75
2.30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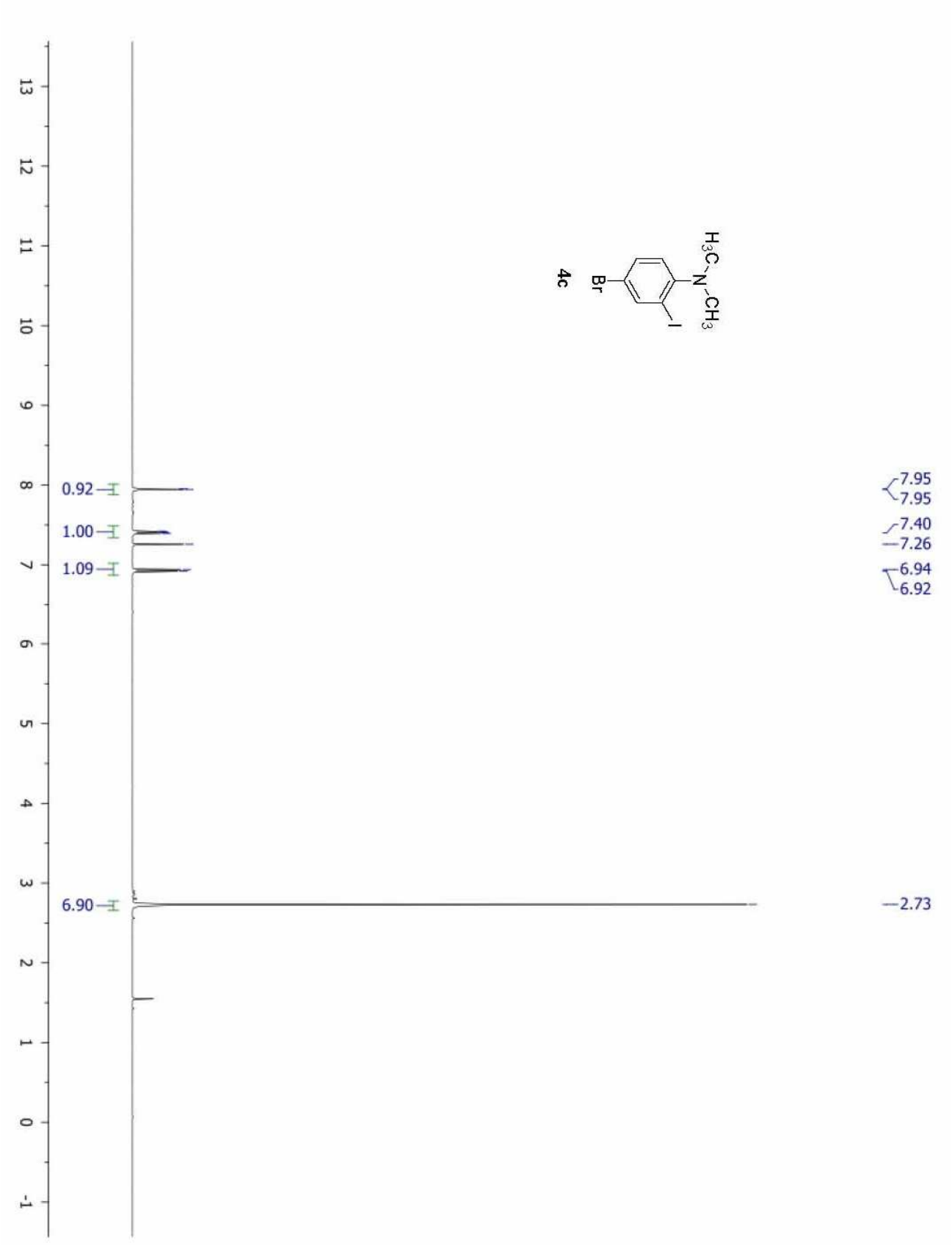
77.5
77.2
76.9
45.0
21.3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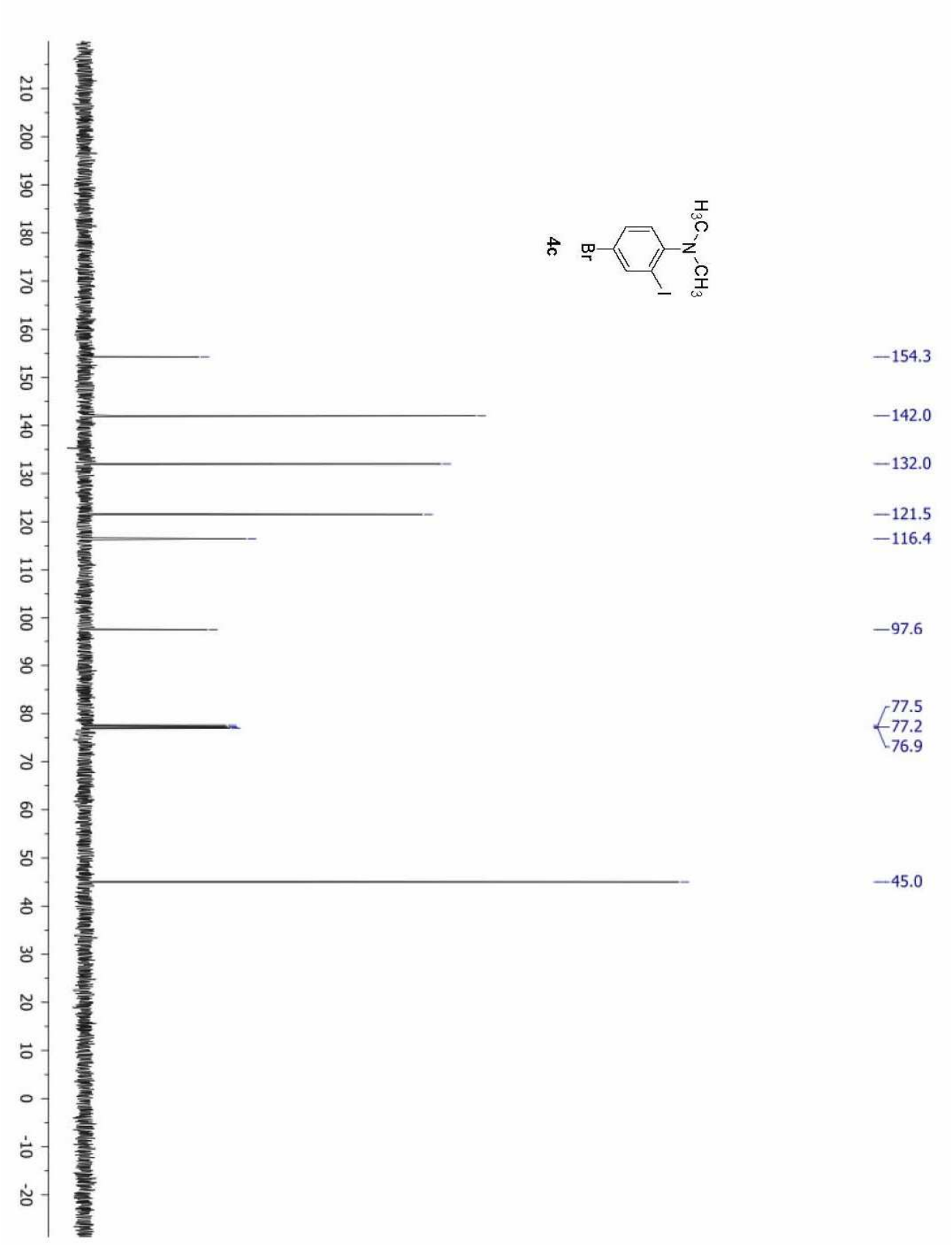
6.92
2.73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N
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76.9
45.0
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200
190
180
170
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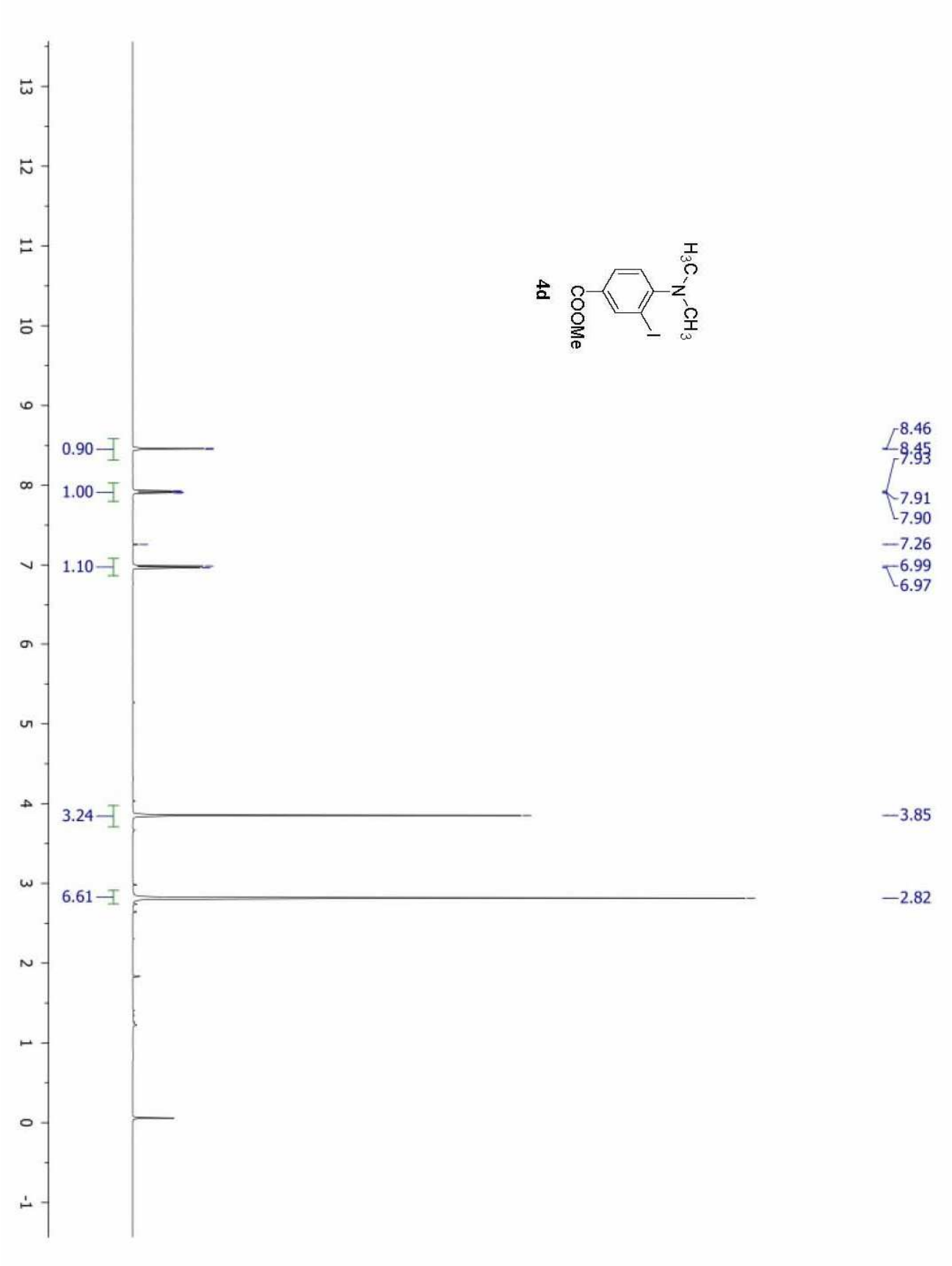
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7.26
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6.97
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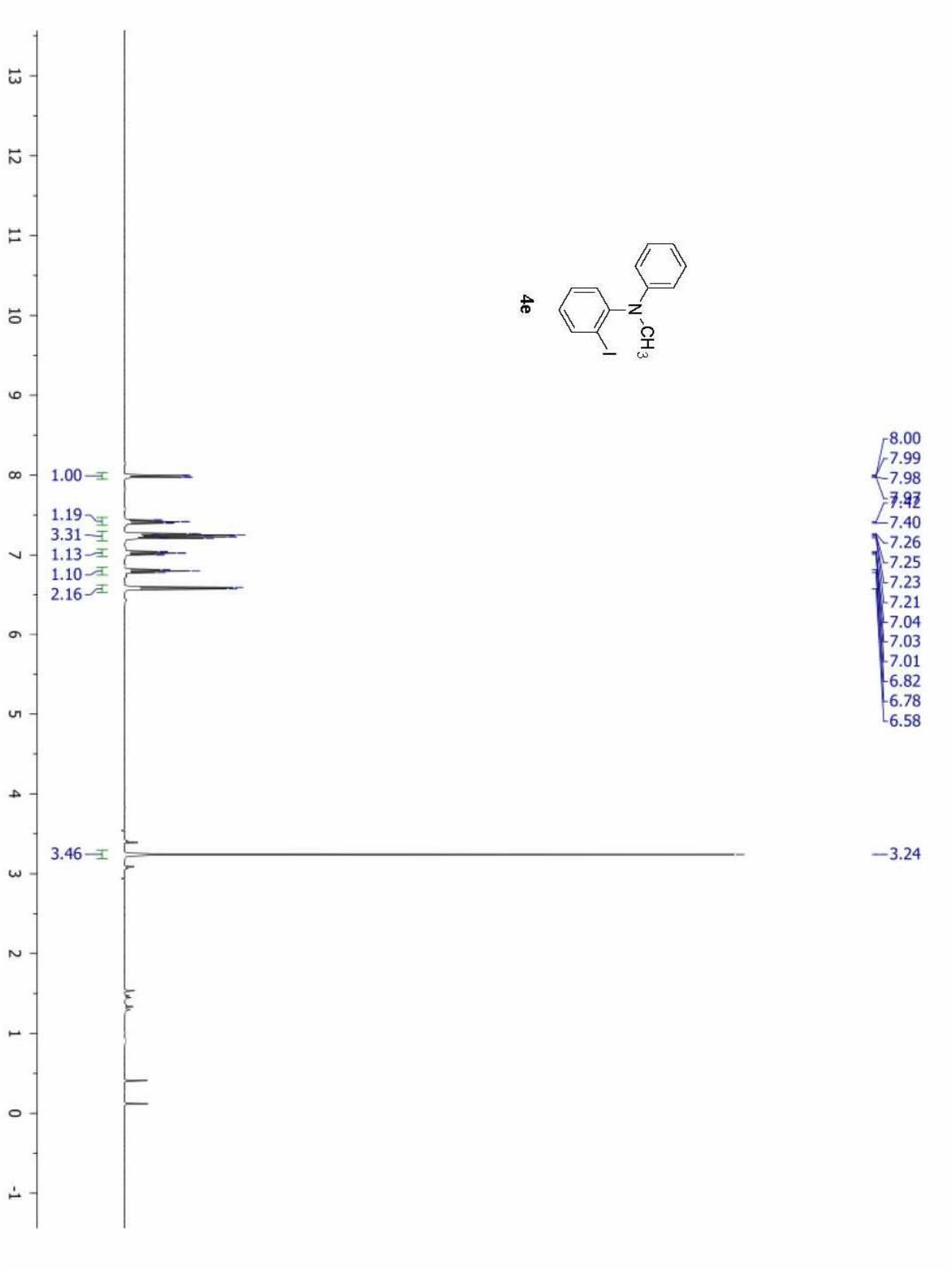
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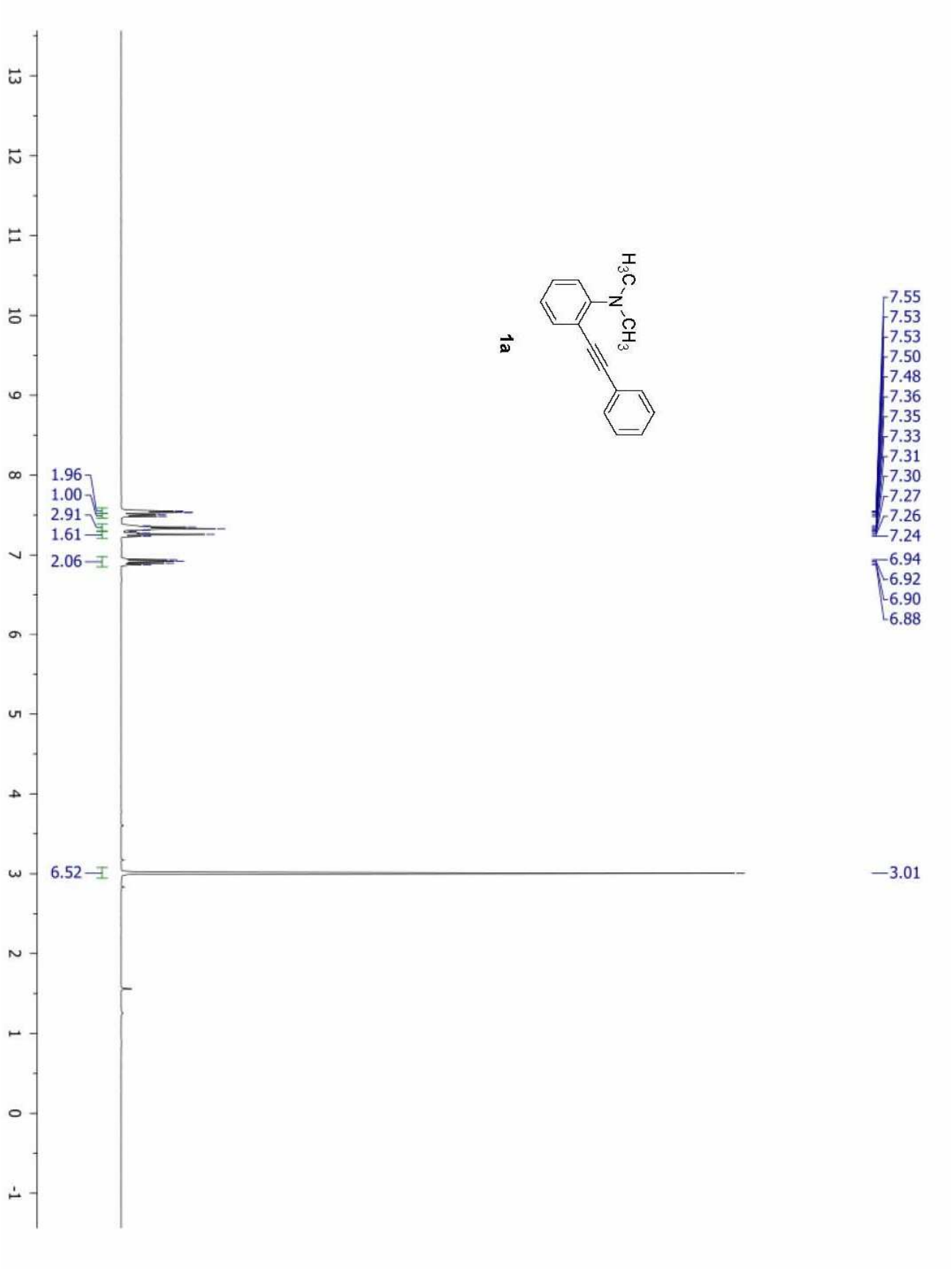
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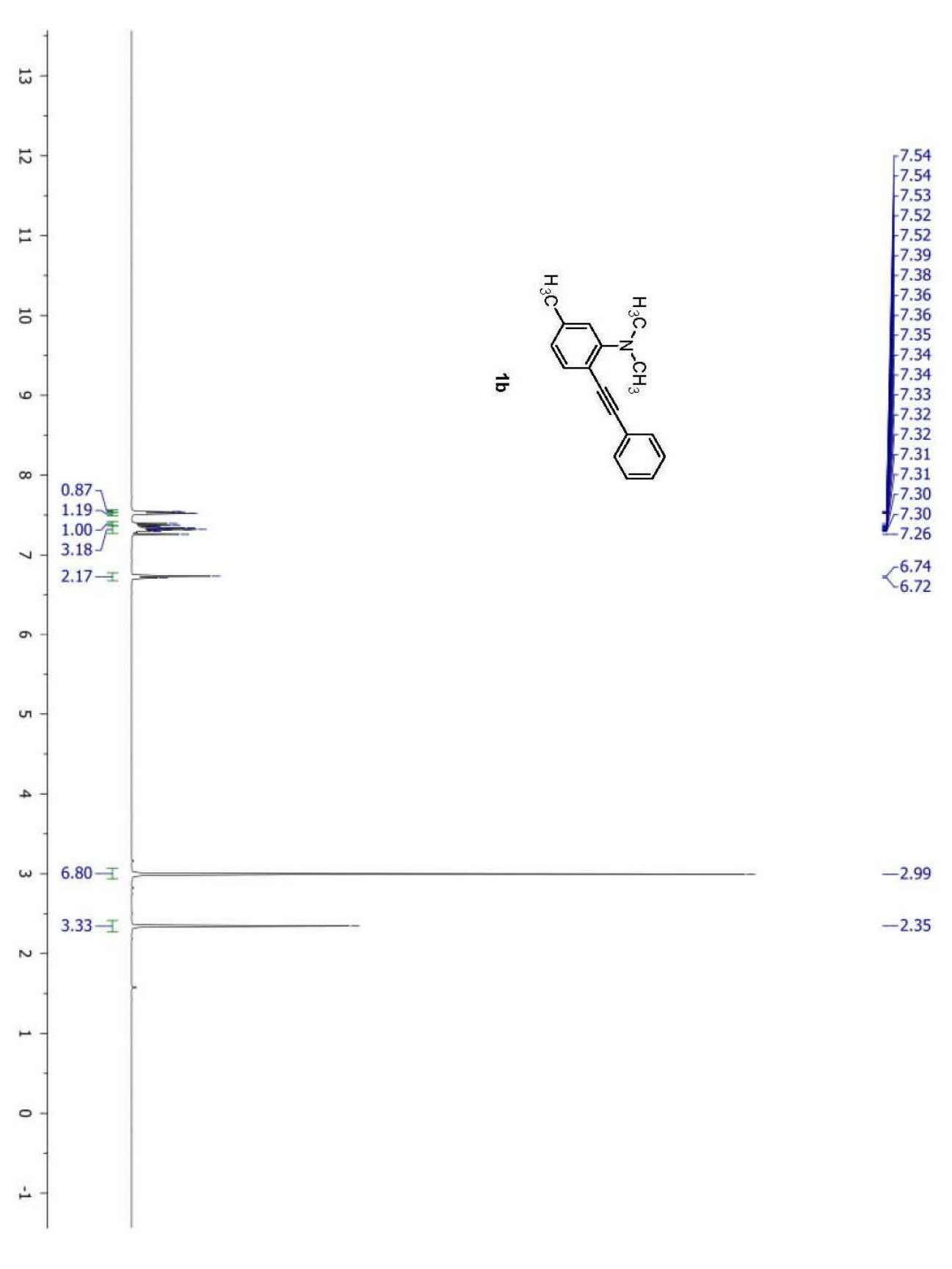
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CH3
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7.34
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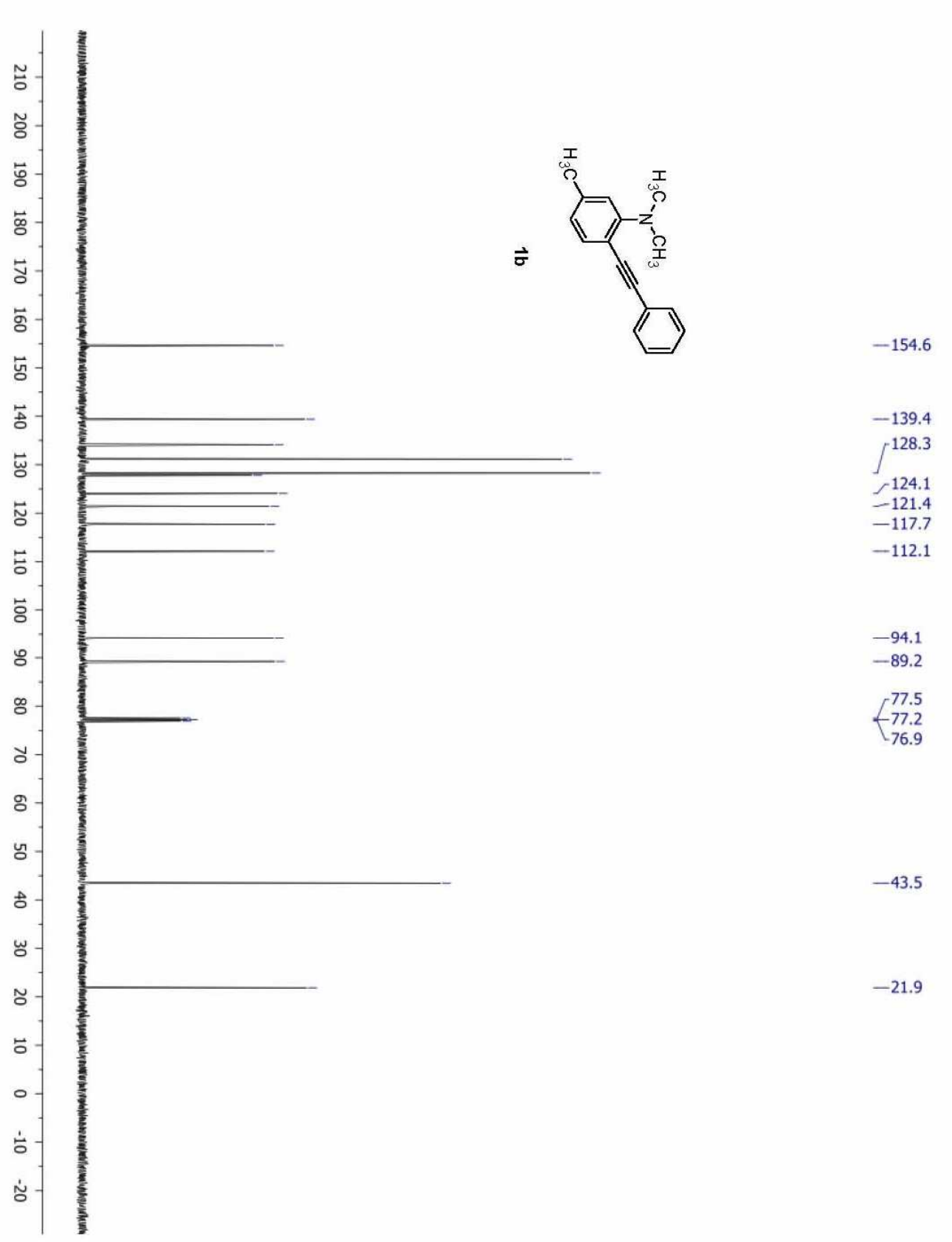
2.99
2.35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200
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180
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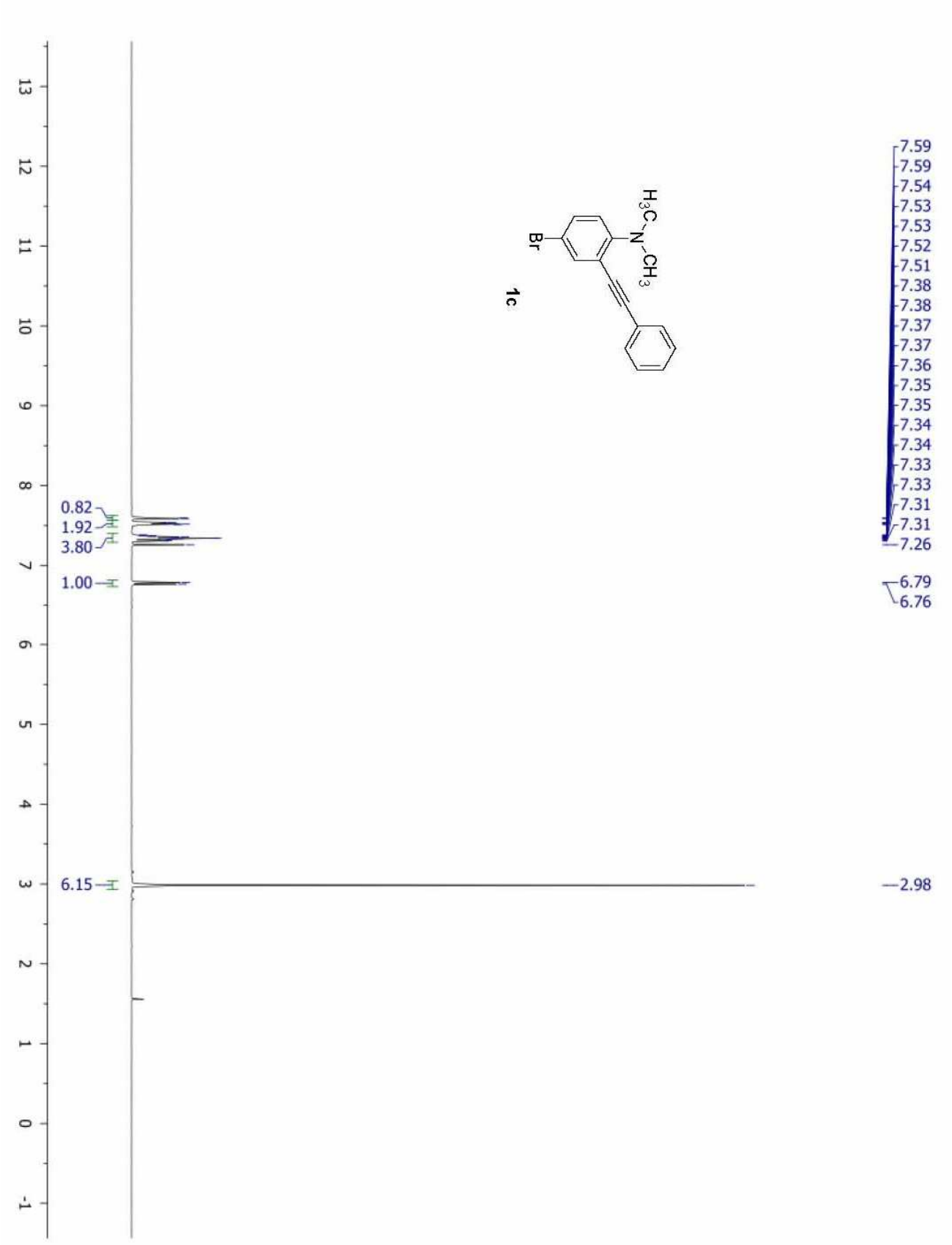
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CH3
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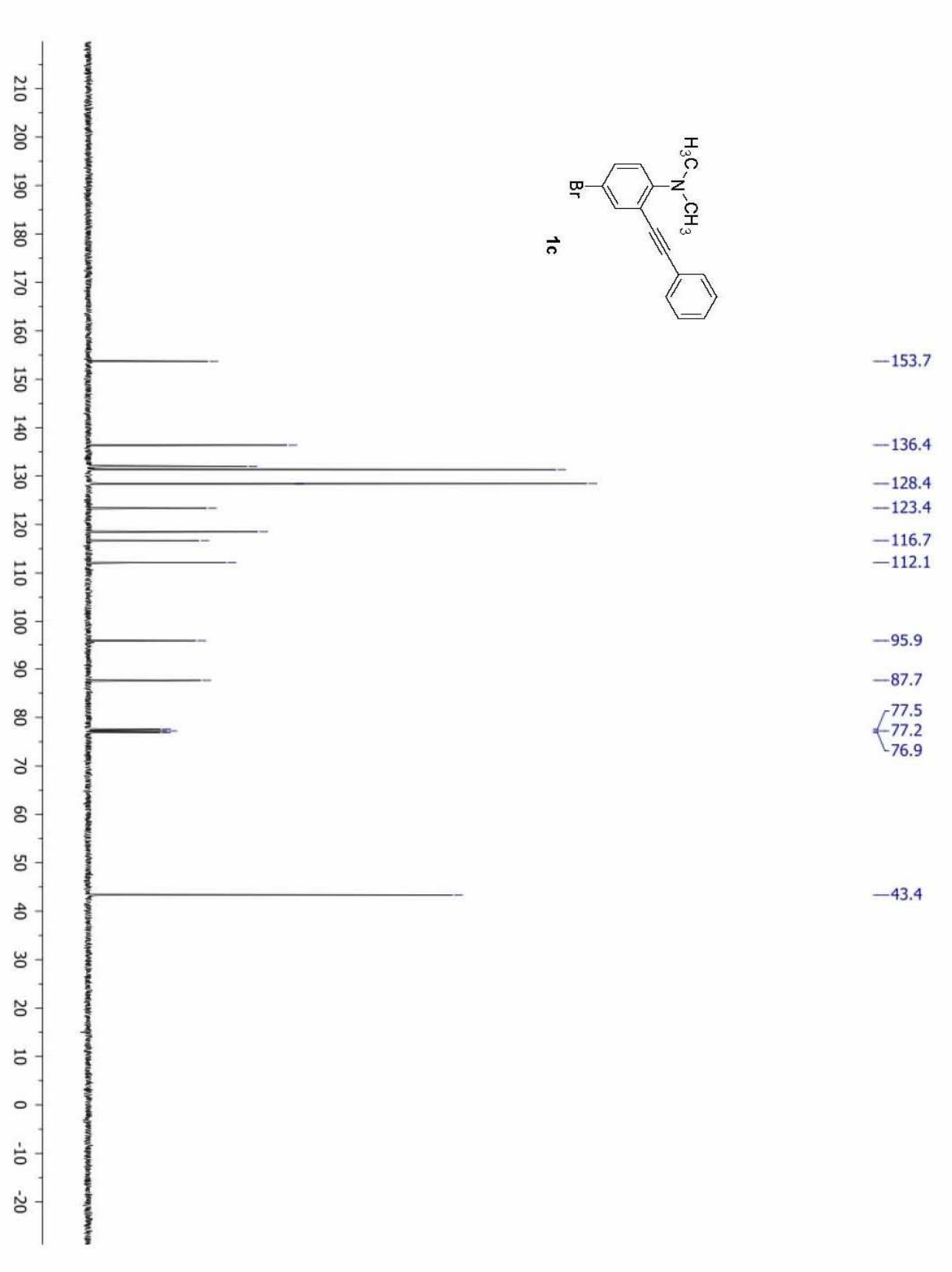
1c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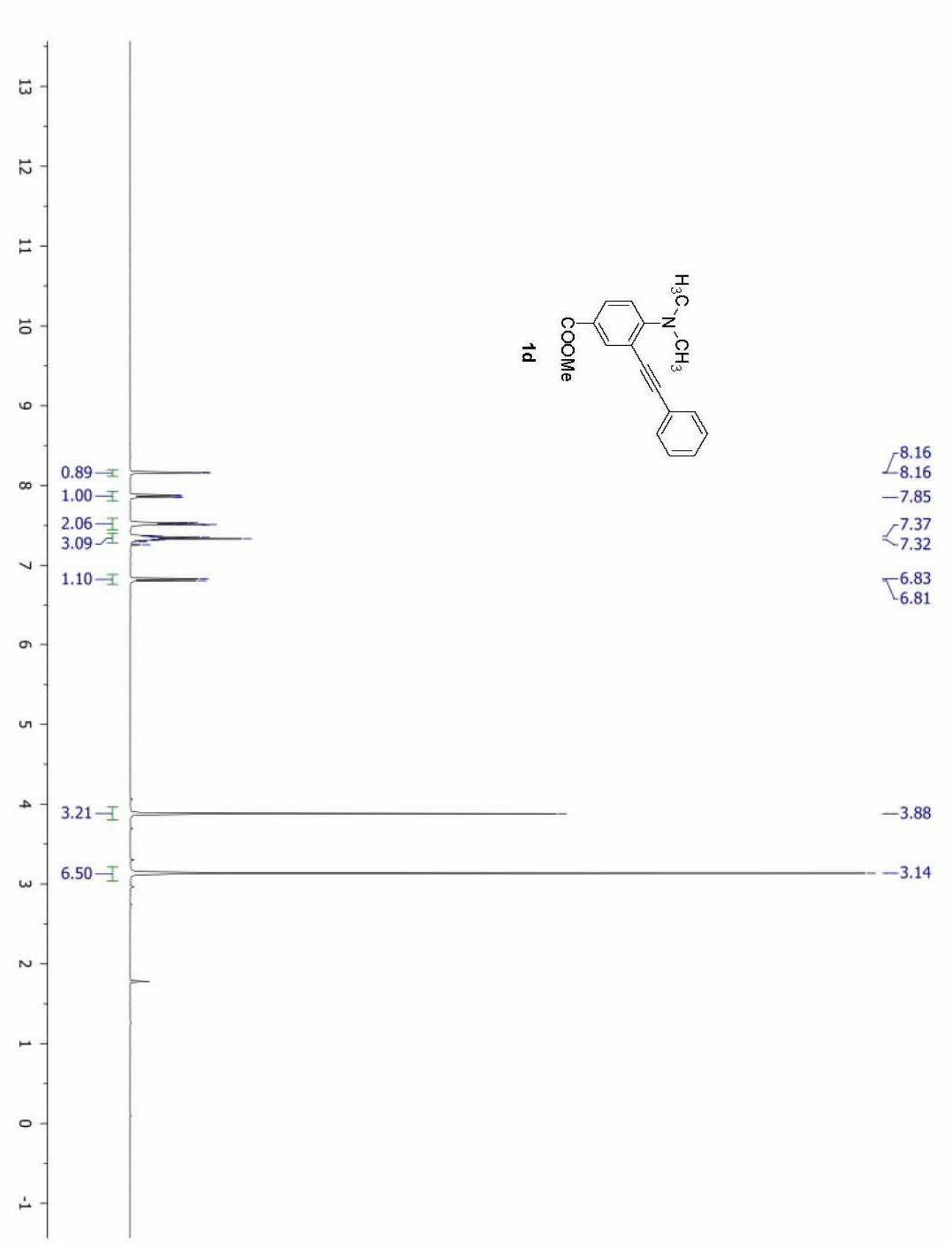
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8.16
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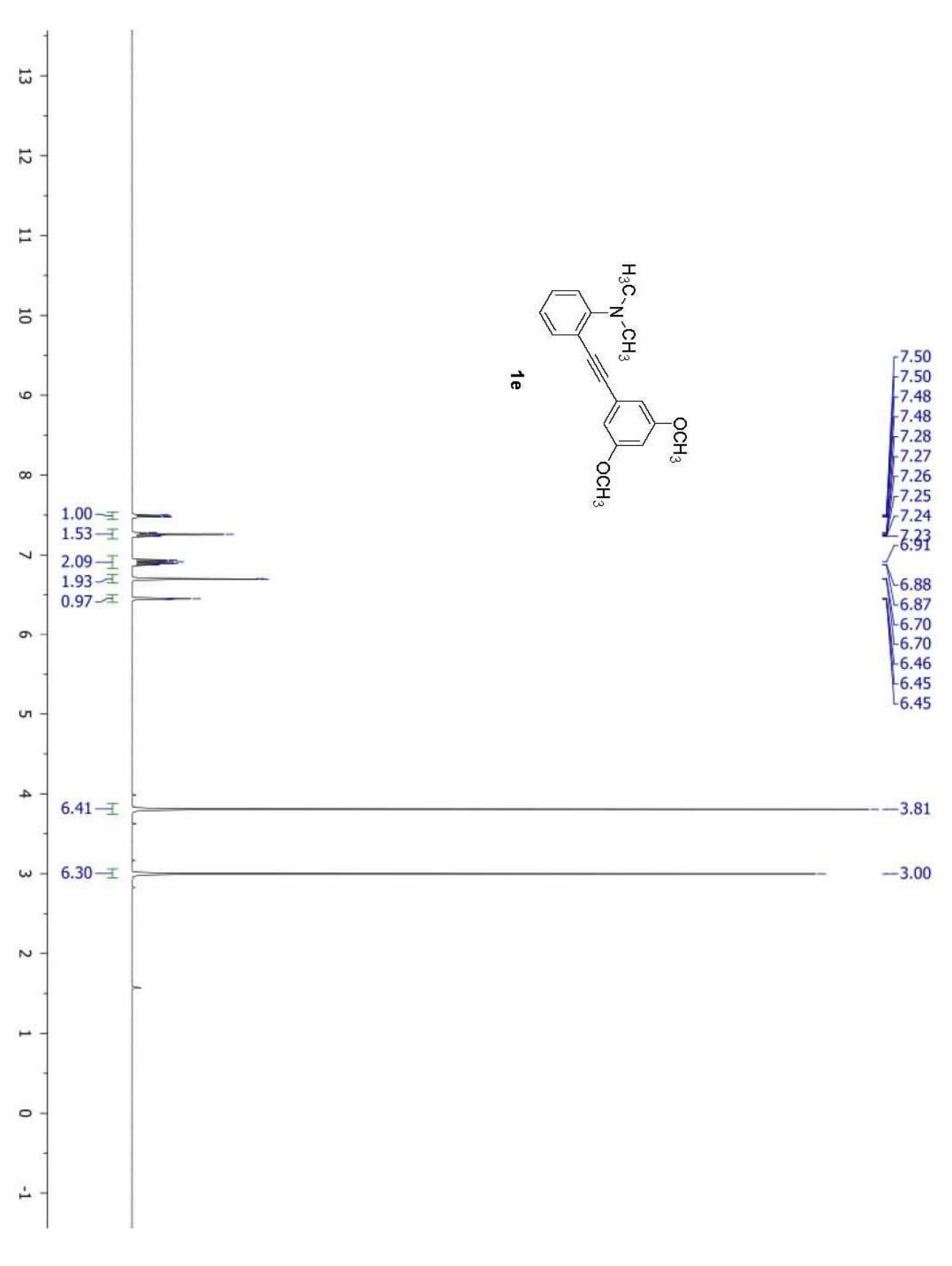
7.37
7.32
6.83
6.81
3.88
3.14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H3C
N
CH3
OCH3
OCH3
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7.50
7.48
7.48
7.28
7.27
7.26
7.25
7.24
7.23
6.91
6.88
6.87
6.70
6.70
6.46
6.45
6.45
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1.53
2.09
1.93
0.97
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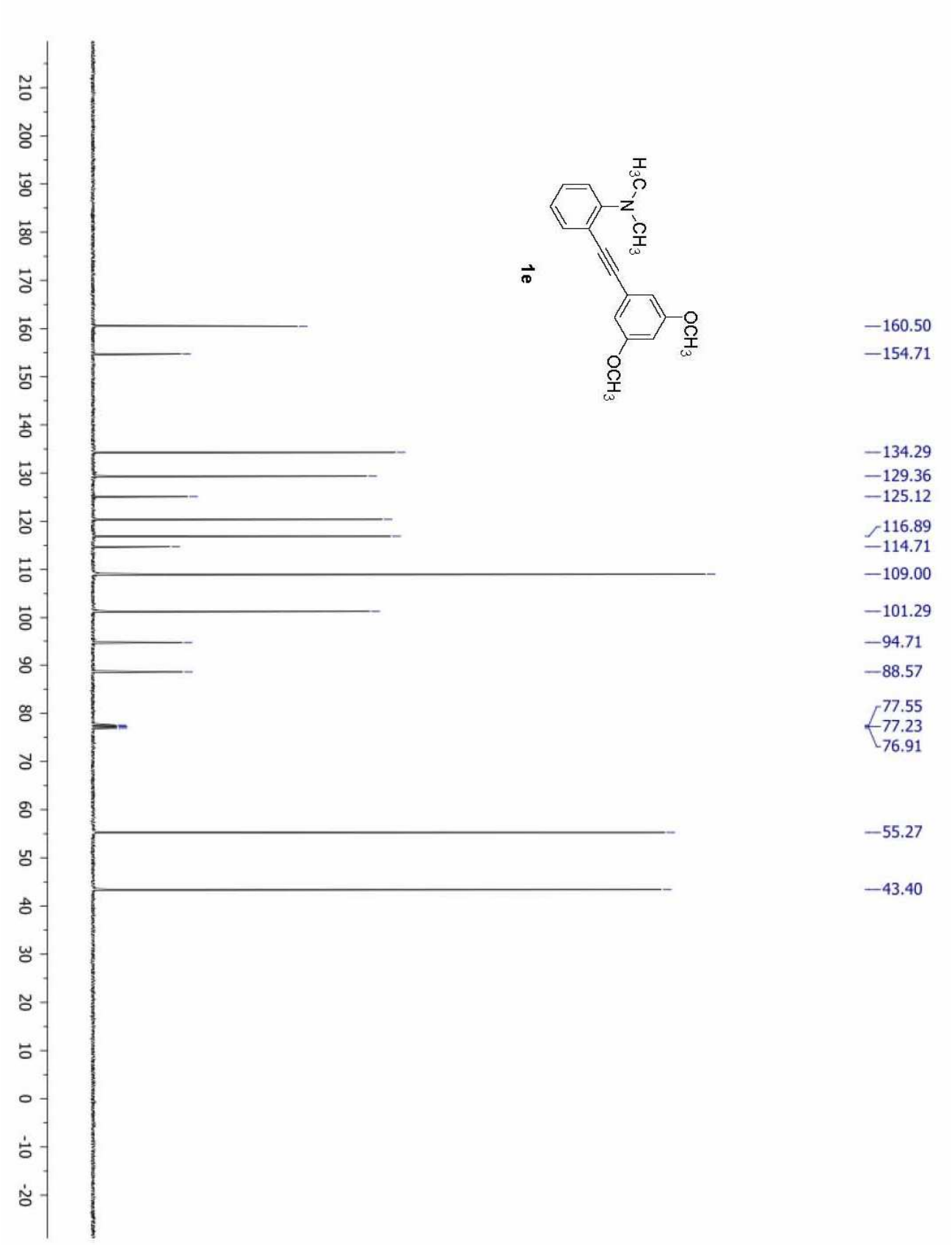
6.30
3.81
3.00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H3C
N
CH3
OCH3
OCH3
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154.71
134.29
129.36
125.12
116.89
114.71
109.00
101.29
94.71
88.57
77.55
77.23
76.91
55.27
43.40
210
200
190
180
170
160
150
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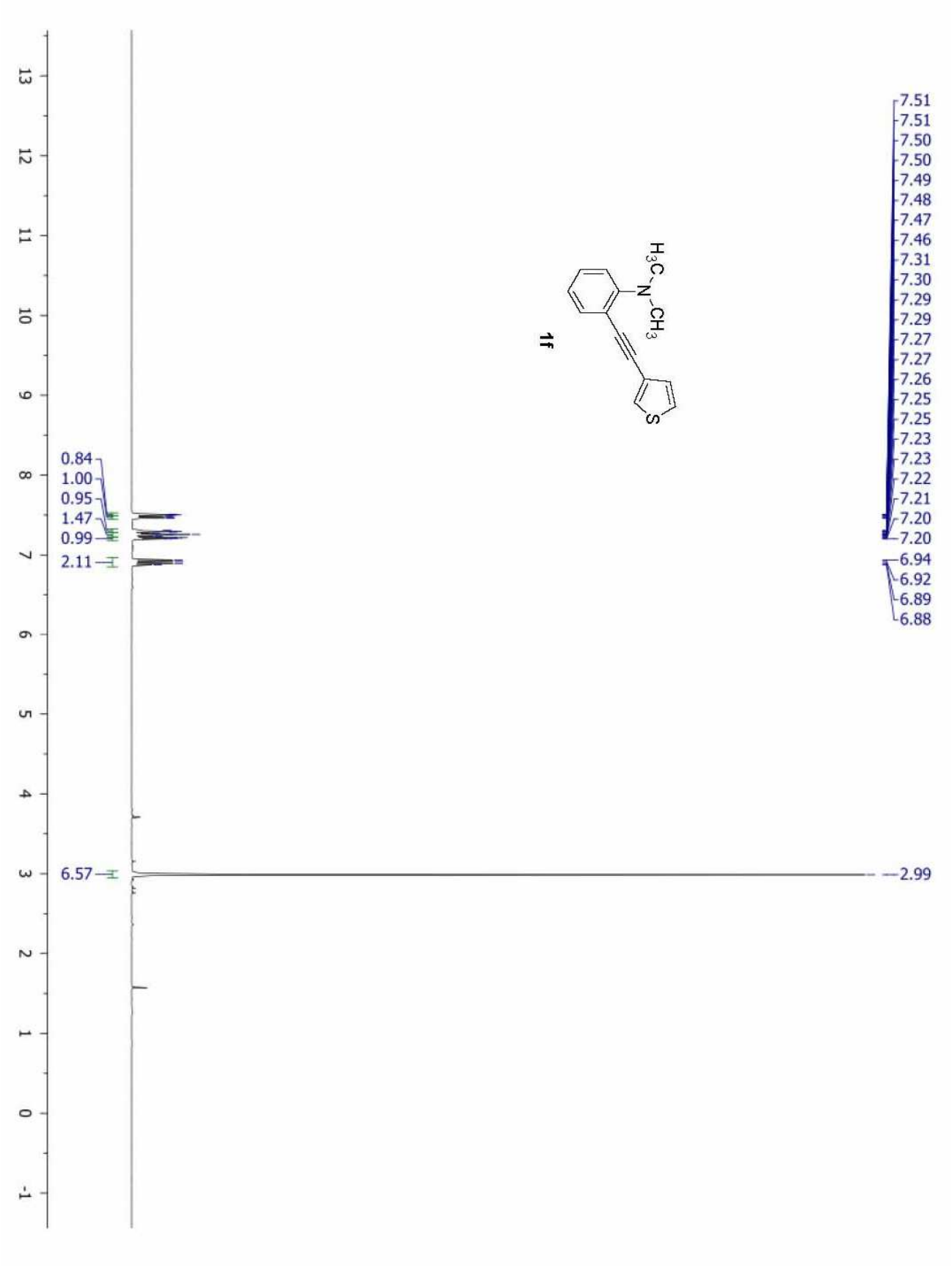
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20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7.51
7.50
7.50
7.49
7.48
7.47
7.46
7.31
7.30
7.29
7.29
7.27
7.27
7.26
7.25
7.25
7.23
7.23
7.22
7.21
7.20
7.20
6.94
6.92
6.89
6.88
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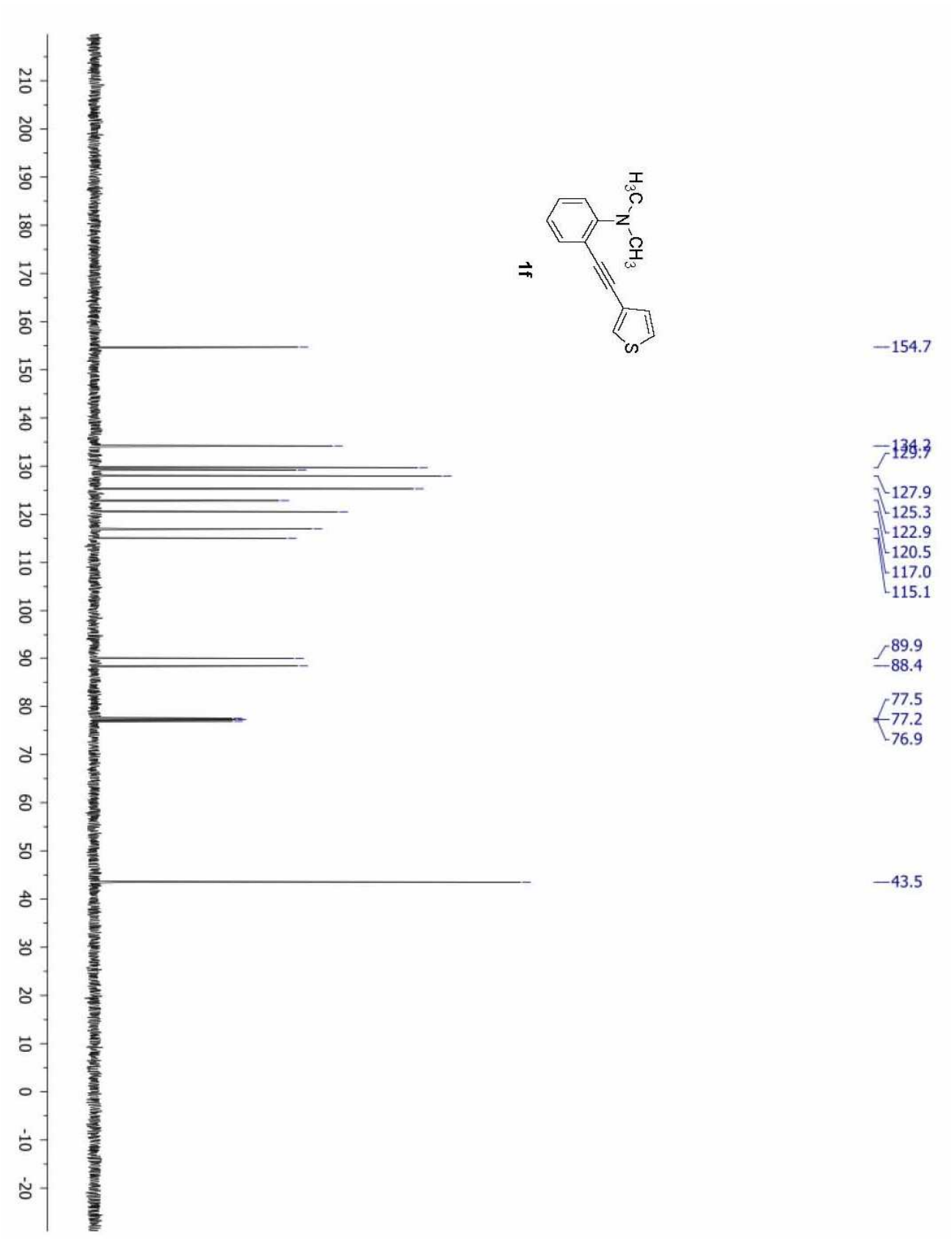
0.95
1.47
0.99
2.11
6.57
2.99
H3C
N
CH3
S
1f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200
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180
170
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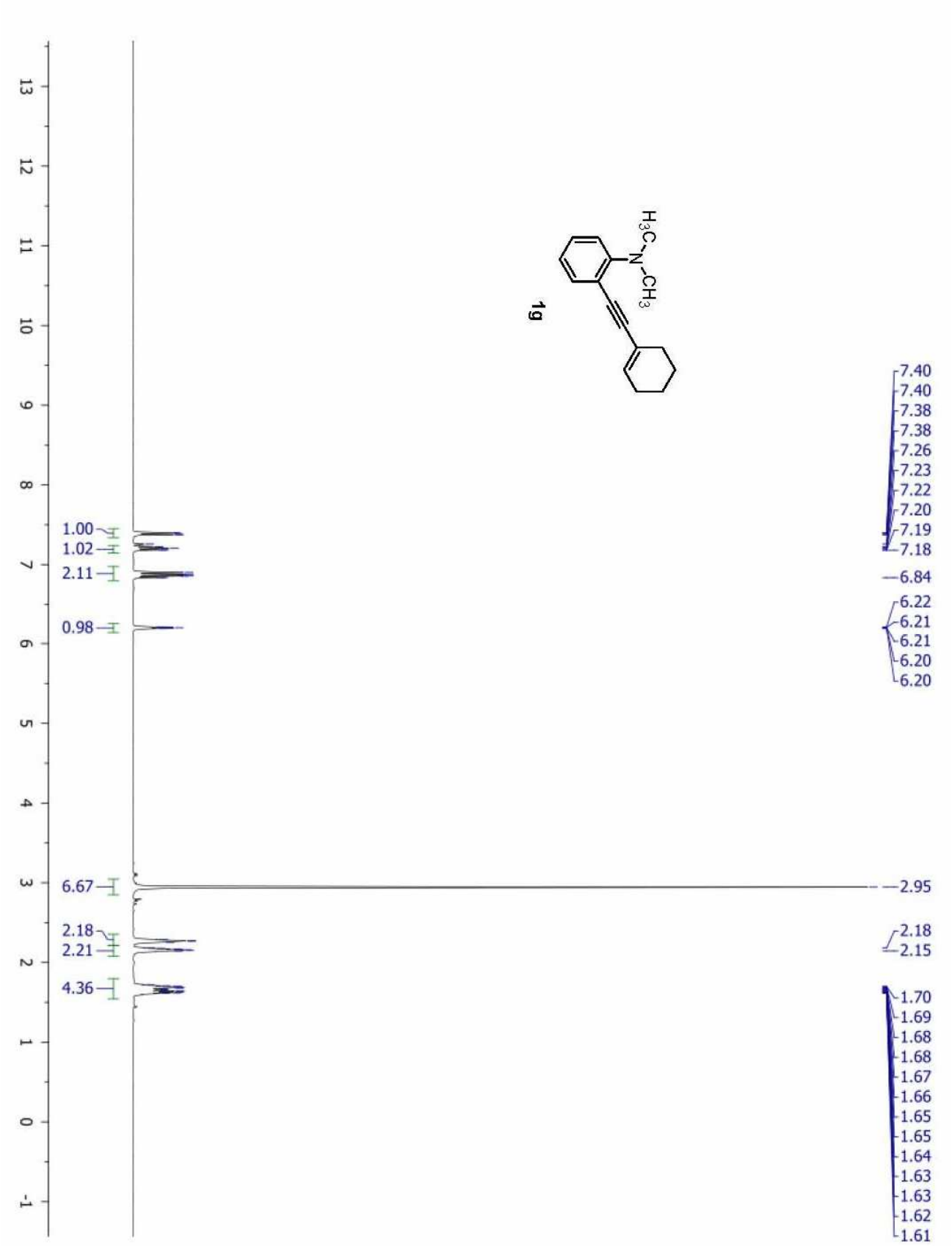
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
H3C
N
CH3
S
1f
154.7
134.2
129.7
127.9
125.3
122.9
120.5
117.0
115.1
89.9
88.4
77.5
77.2
76.9
43.5


1g
H3C
N
CH3
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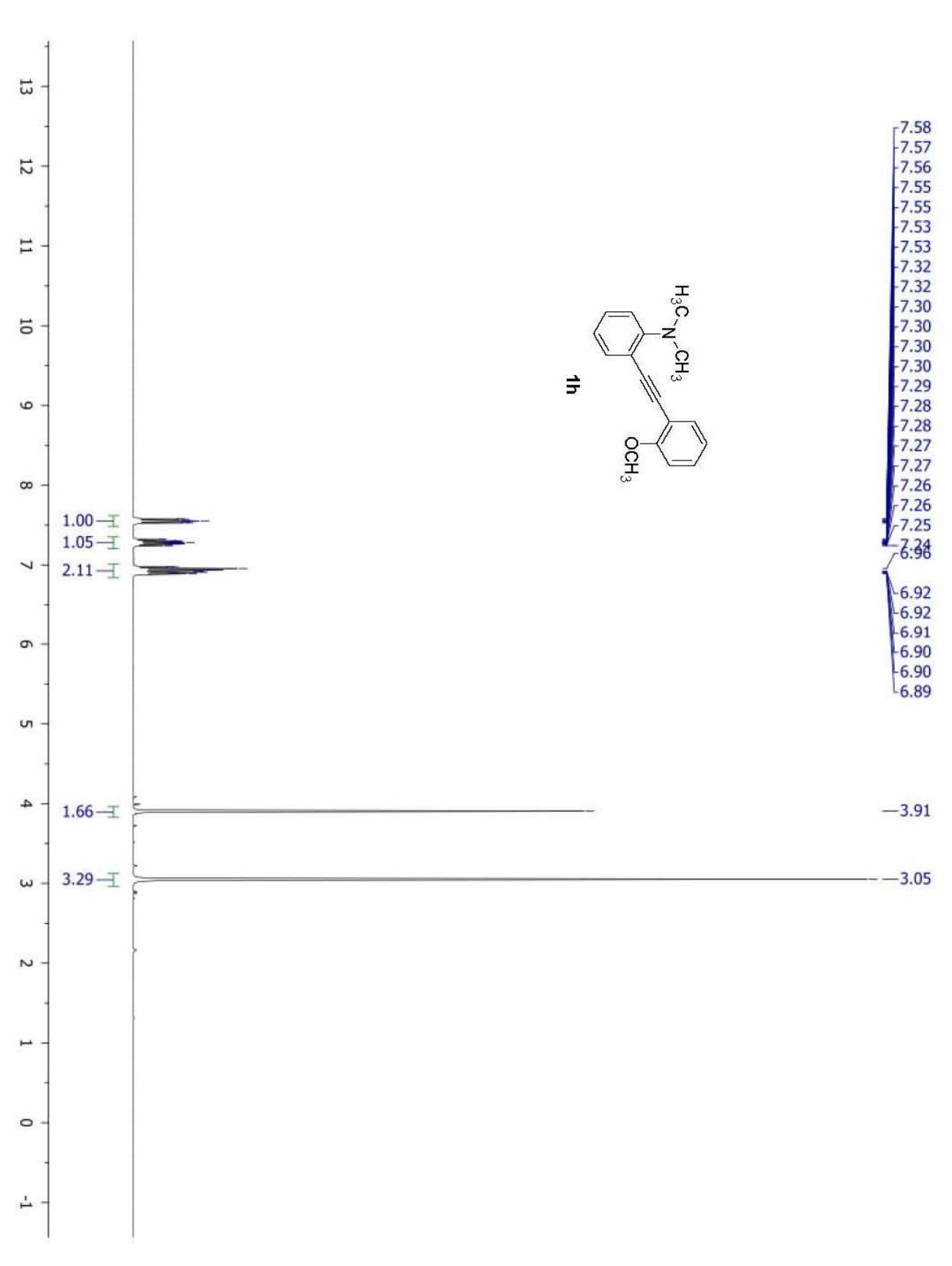
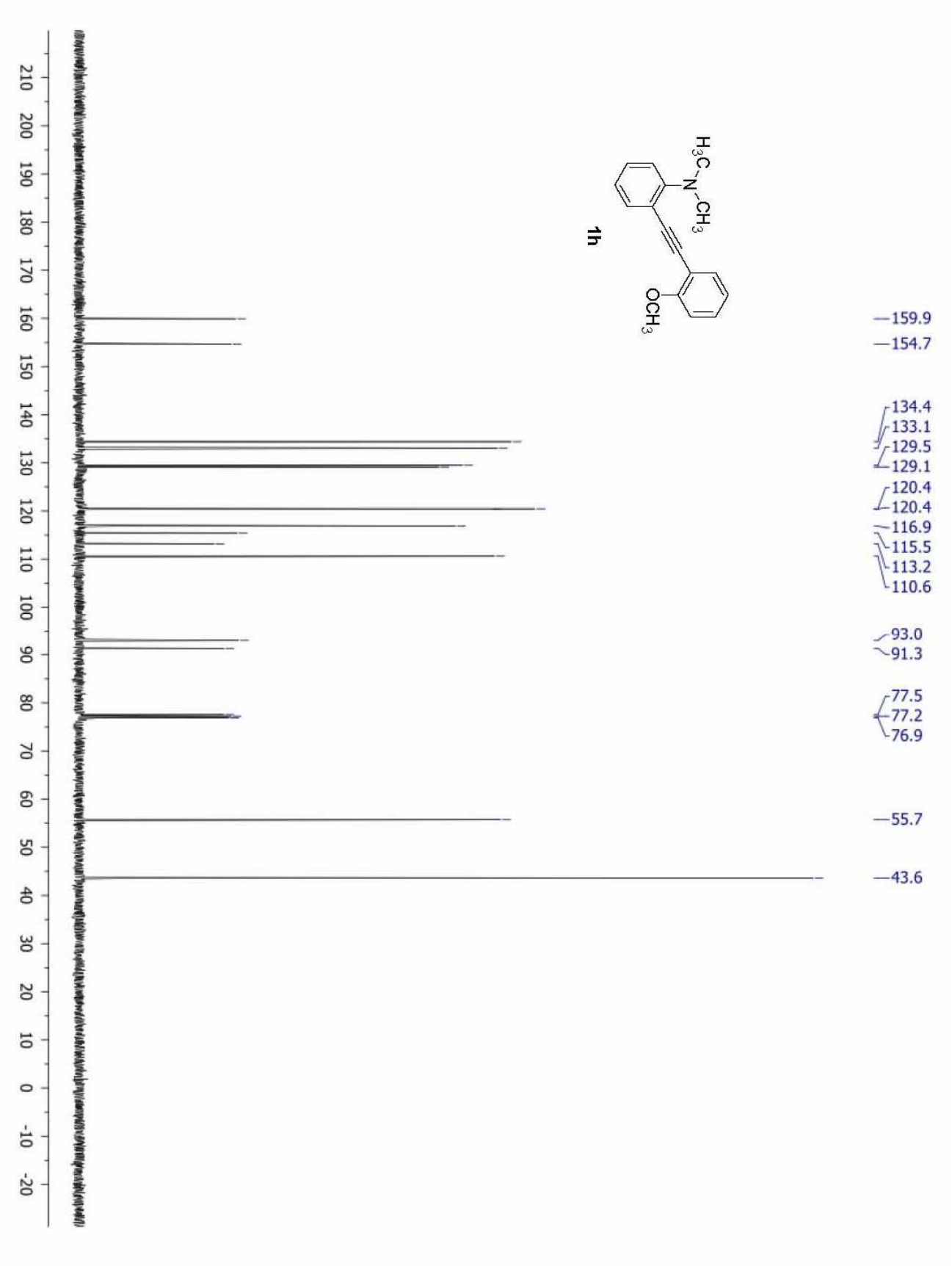
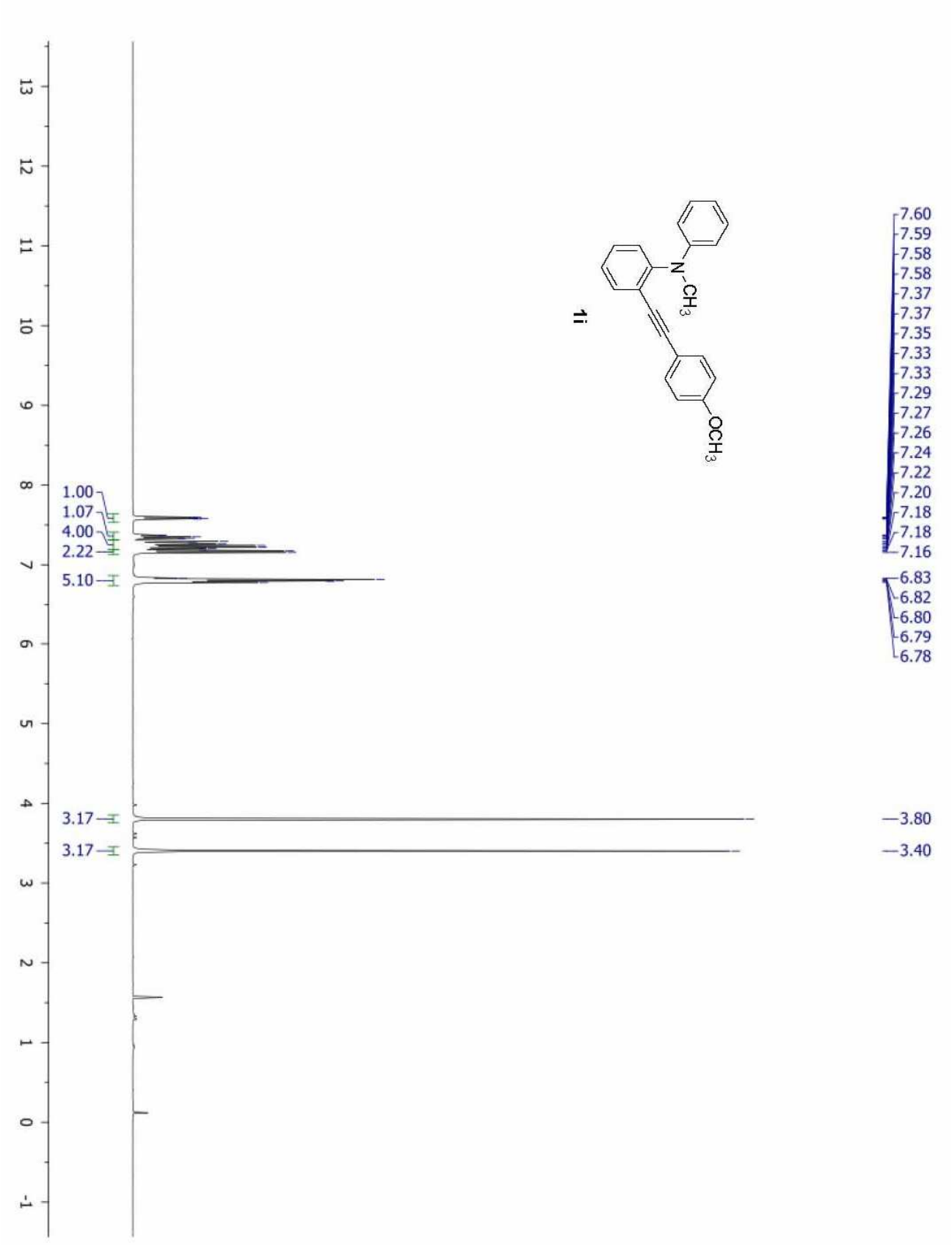
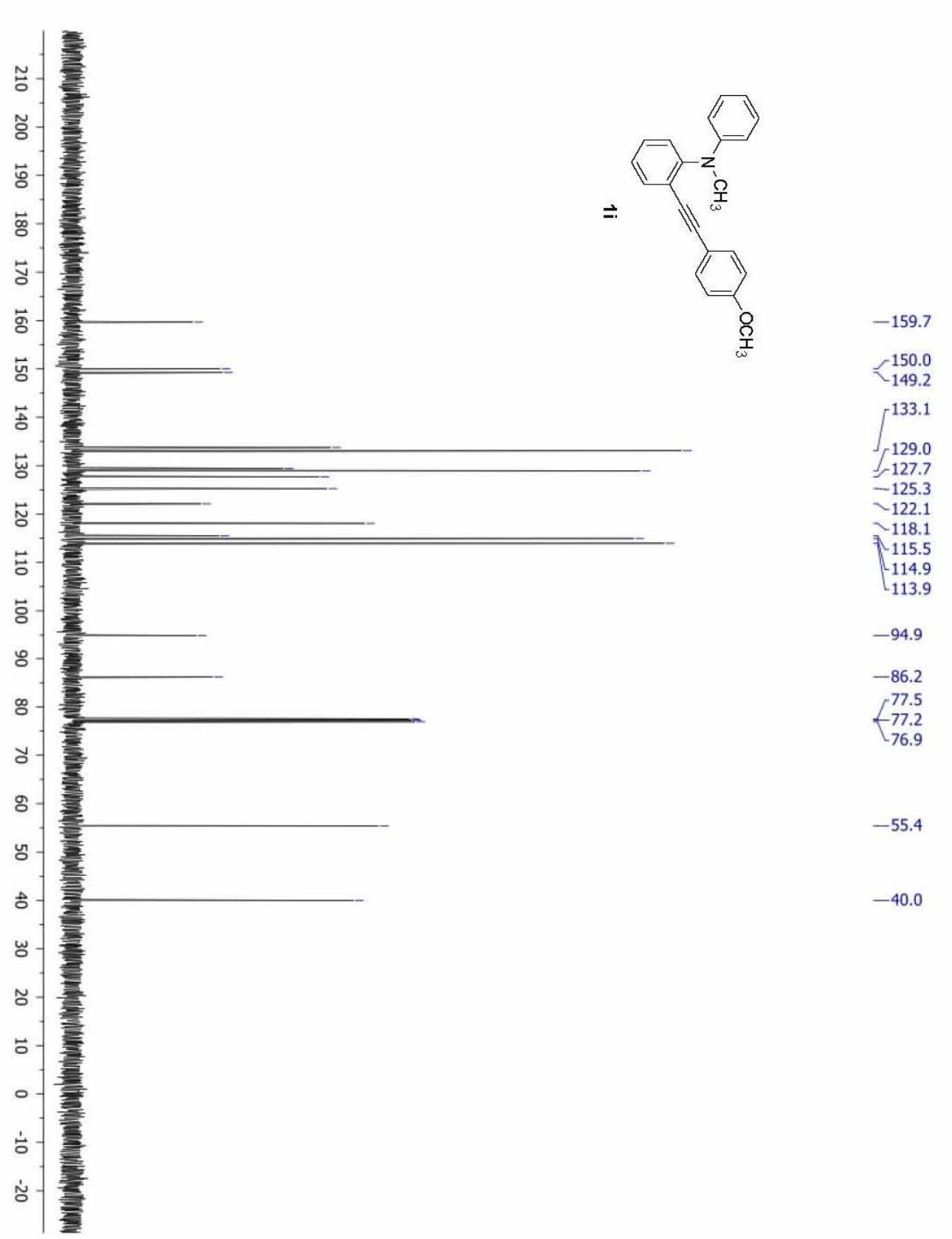
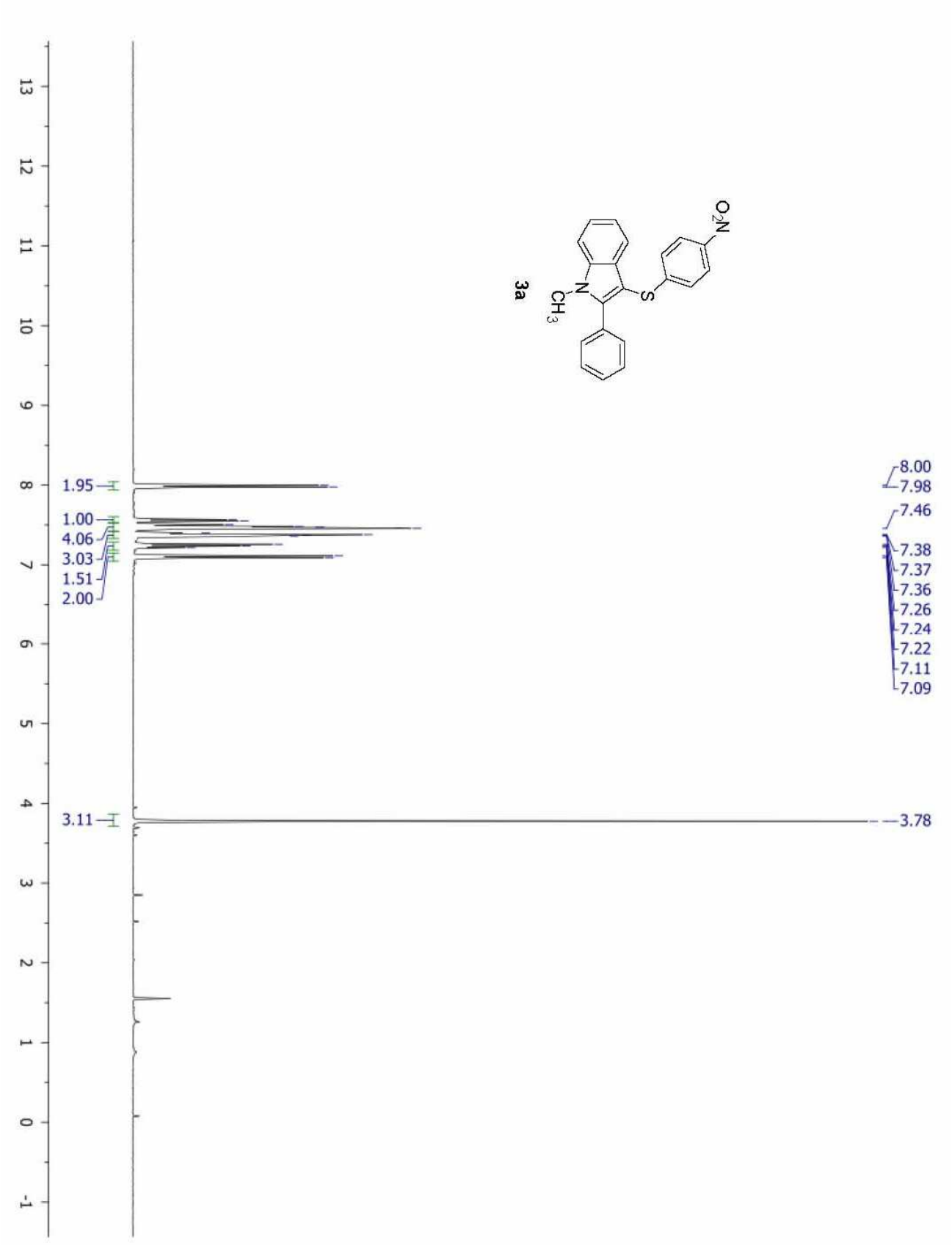
7.40
7.38
7.38
7.26
7.23
7.22
7.20
7.19
7.18
6.84
6.22
6.21
6.21
6.20
6.20
2.95
2.18
2.15
1.70
1.69
1.68
1.68
1.67
1.66
1.65
1.65
1.64
1.63
1.63
1.62
1.61
1.00
1.02
2.11
0.98
6.67
2.18
2.21
4.36

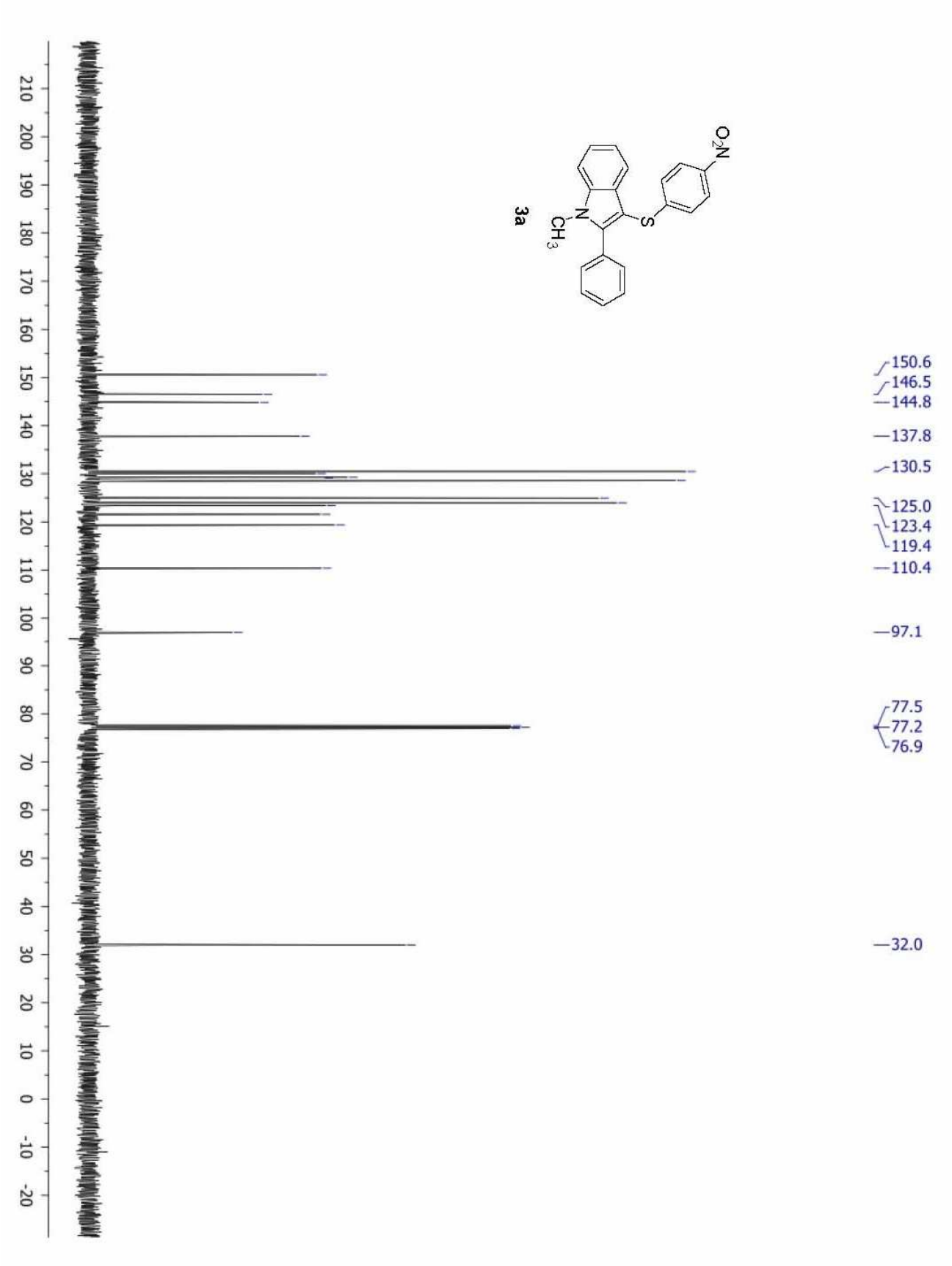

1h
7.58
7.57
7.56
7.55
7.55
7.53
7.53
7.32
7.32
7.30
7.30
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.24
6.96
6.92
6.92
6.91
6.90
6.90
6.89
1.00
1.05
2.11
1.66
3.29
3.91
3.05

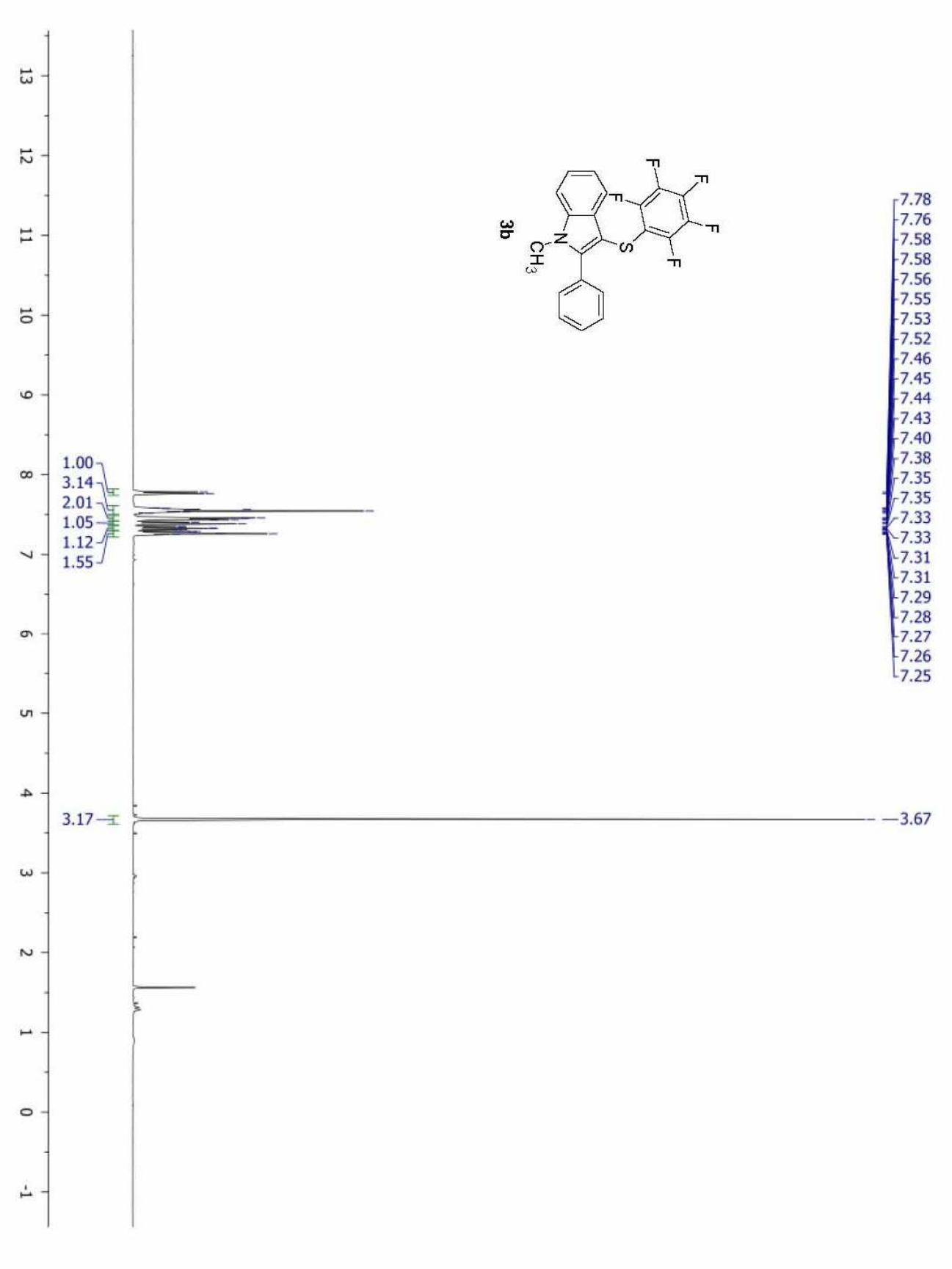

1h
159.9
154.7
134.4
133.1
129.5
129.1
120.4
120.4
116.9
115.5
113.2
110.6
93.0
91.3
77.5
77.2
76.9
55.7
43.6

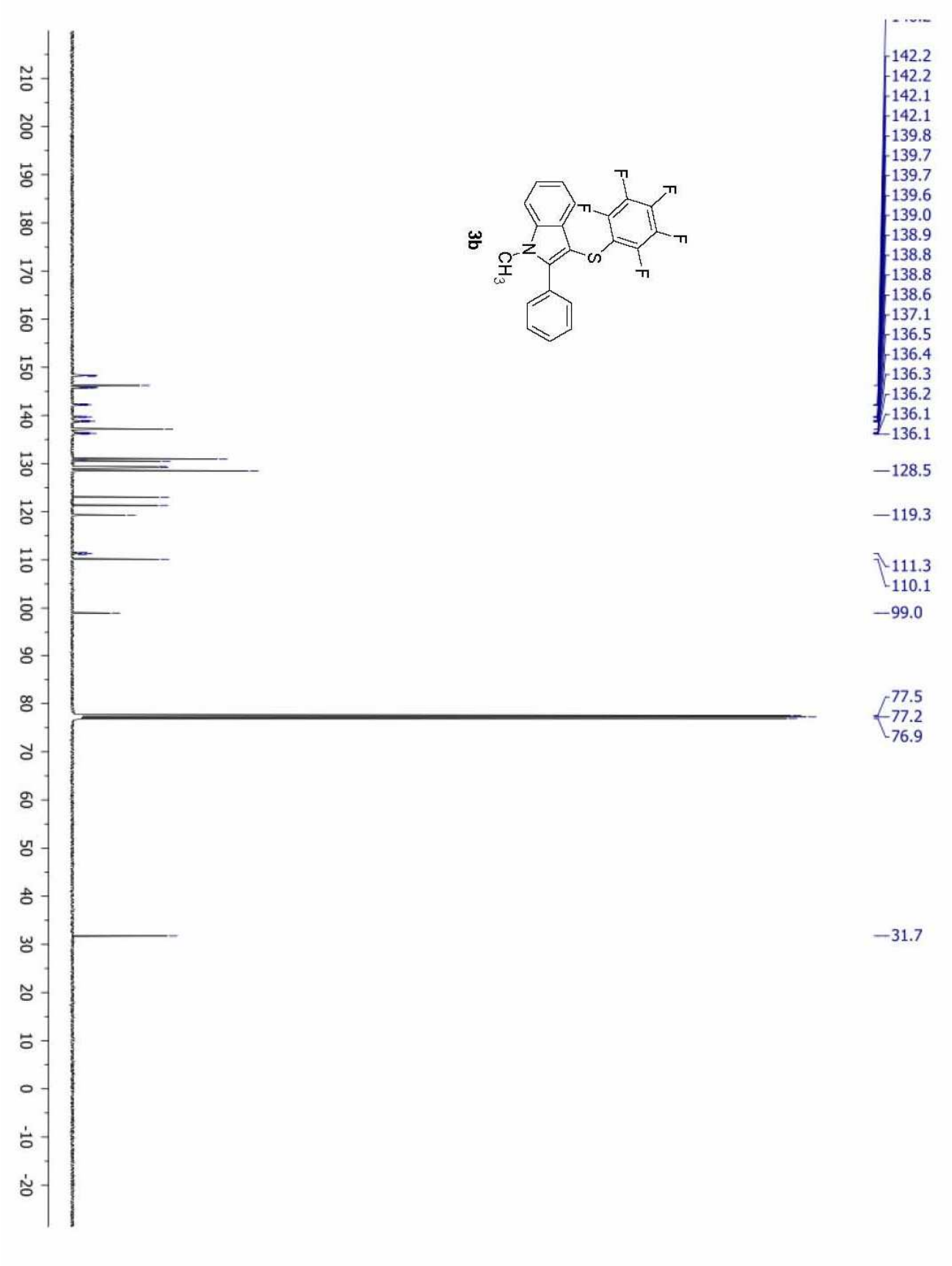

1i
N
CH3
OCH3
7.60
7.59
7.58
7.58
7.37
7.37
7.35
7.33
7.33
7.29
7.27
7.26
7.24
7.22
7.20
7.18
7.18
7.16
6.83
6.82
6.80
6.79
6.78
3.80
3.40
1.00
1.07
4.00
2.22
5.10
3.17
3.17

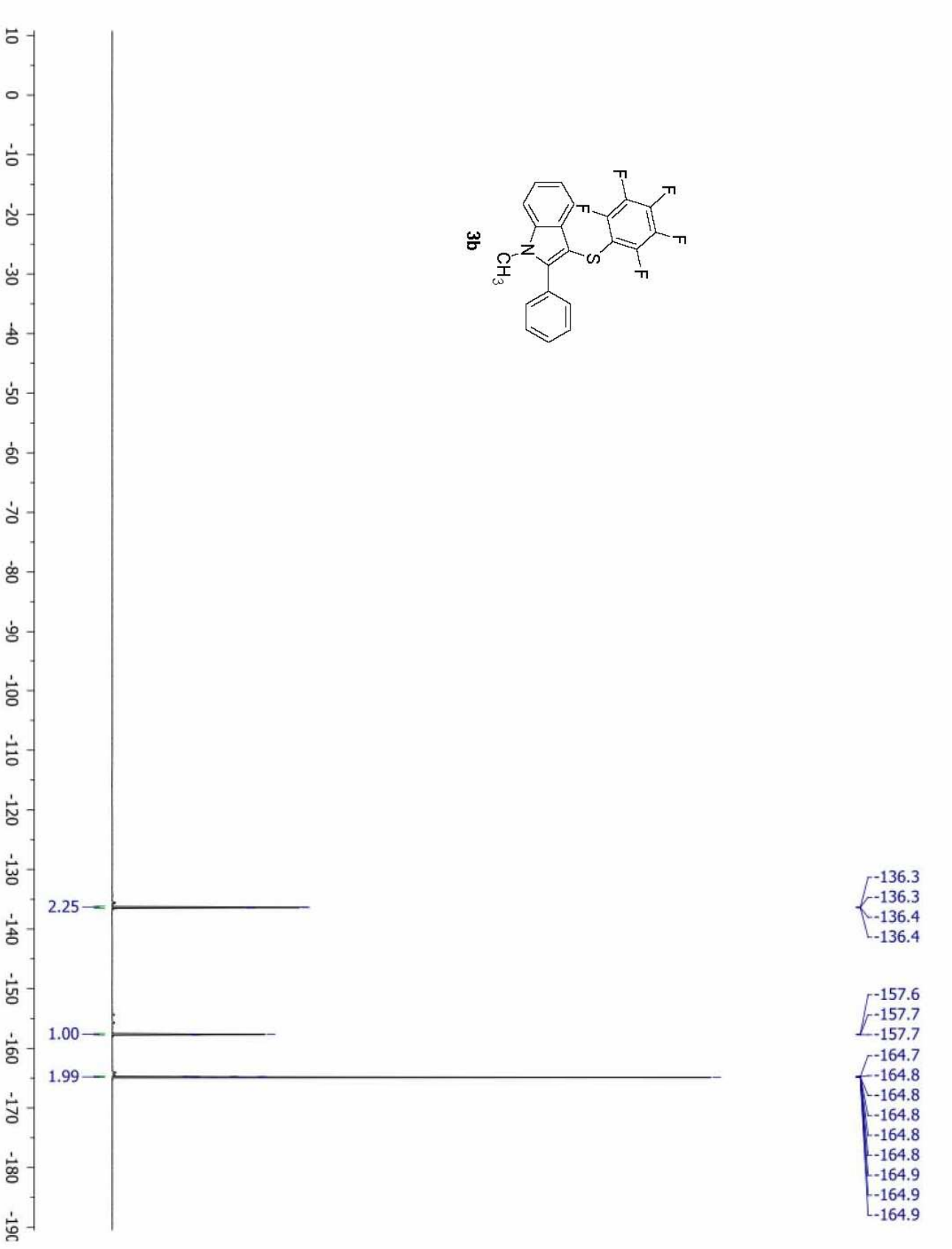

1i
N
CH3
OCH3
159.7
150.0
149.2
133.1
129.0
127.7
125.3
122.1
118.1
115.5
114.9
113.9
94.9
86.2
77.5
77.2
76.9
55.4
40.0

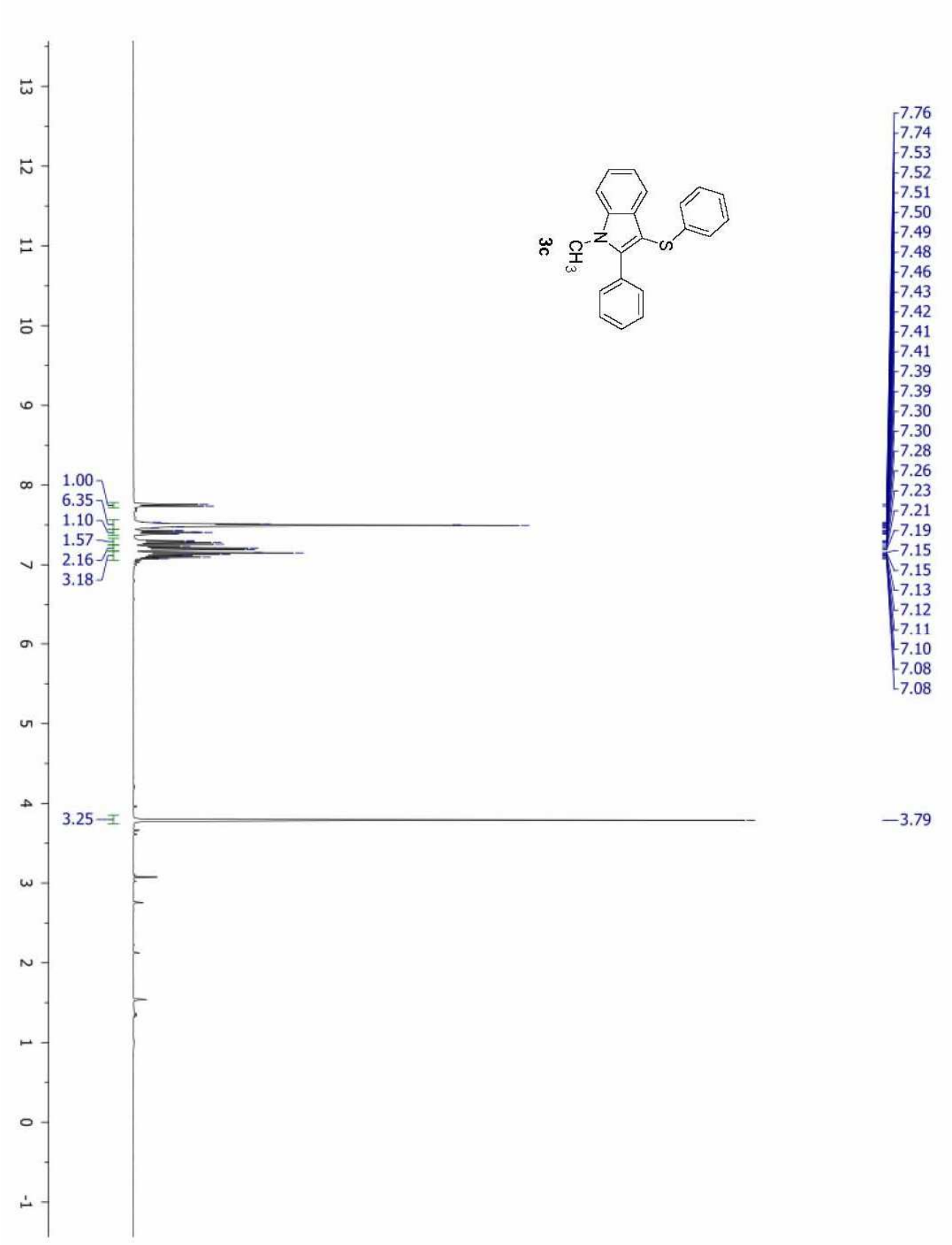

3a
1.95
1.00
4.06
3.03
1.51
2.00
3.11
8.00
7.98
7.46
7.38
7.37
7.36
7.26
7.24
7.22
7.11
7.09
3.78

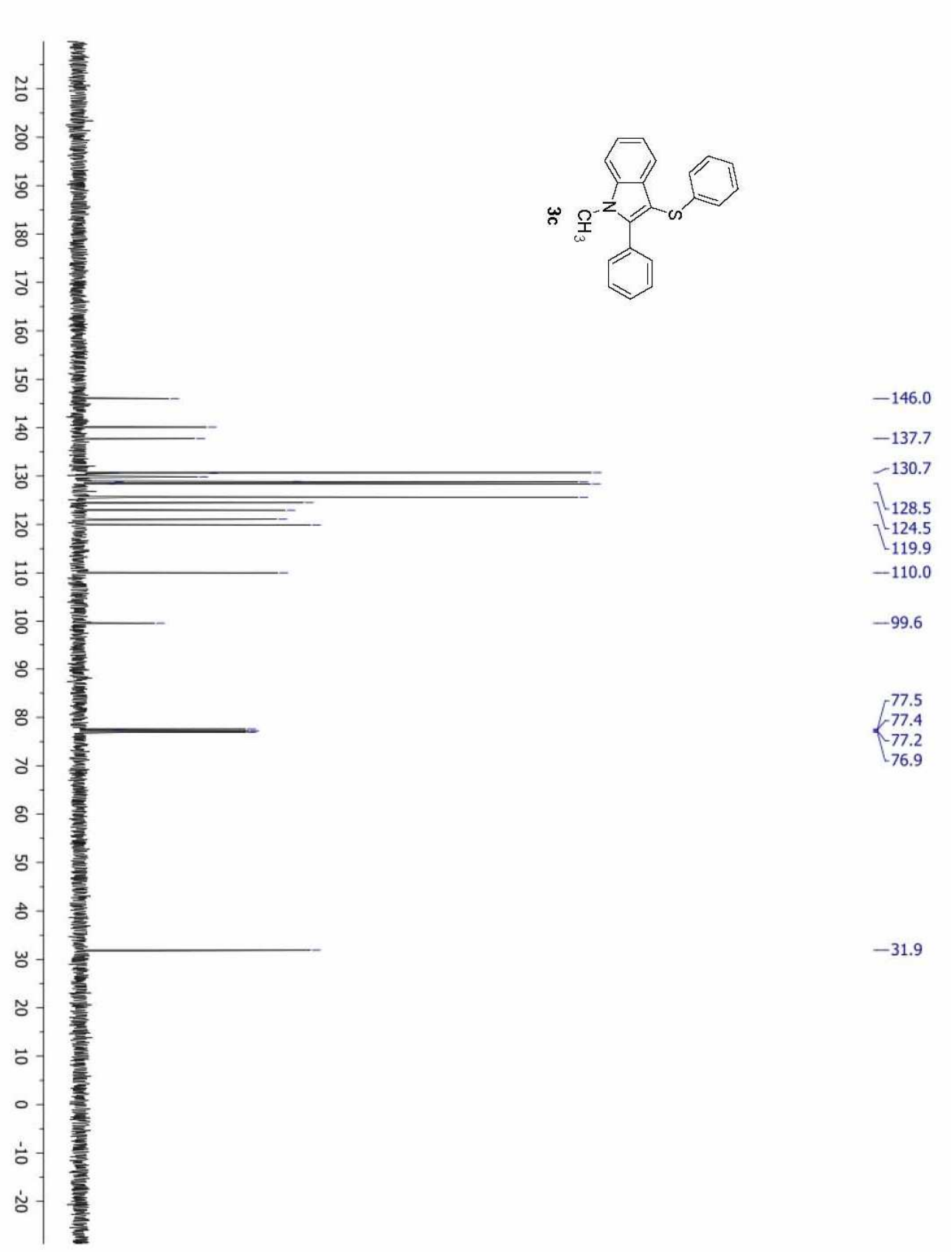

3a
150.6
146.5
144.8
137.8
130.5
125.0
123.4
119.4
110.4
97.1
77.5
77.2
76.9
32.0

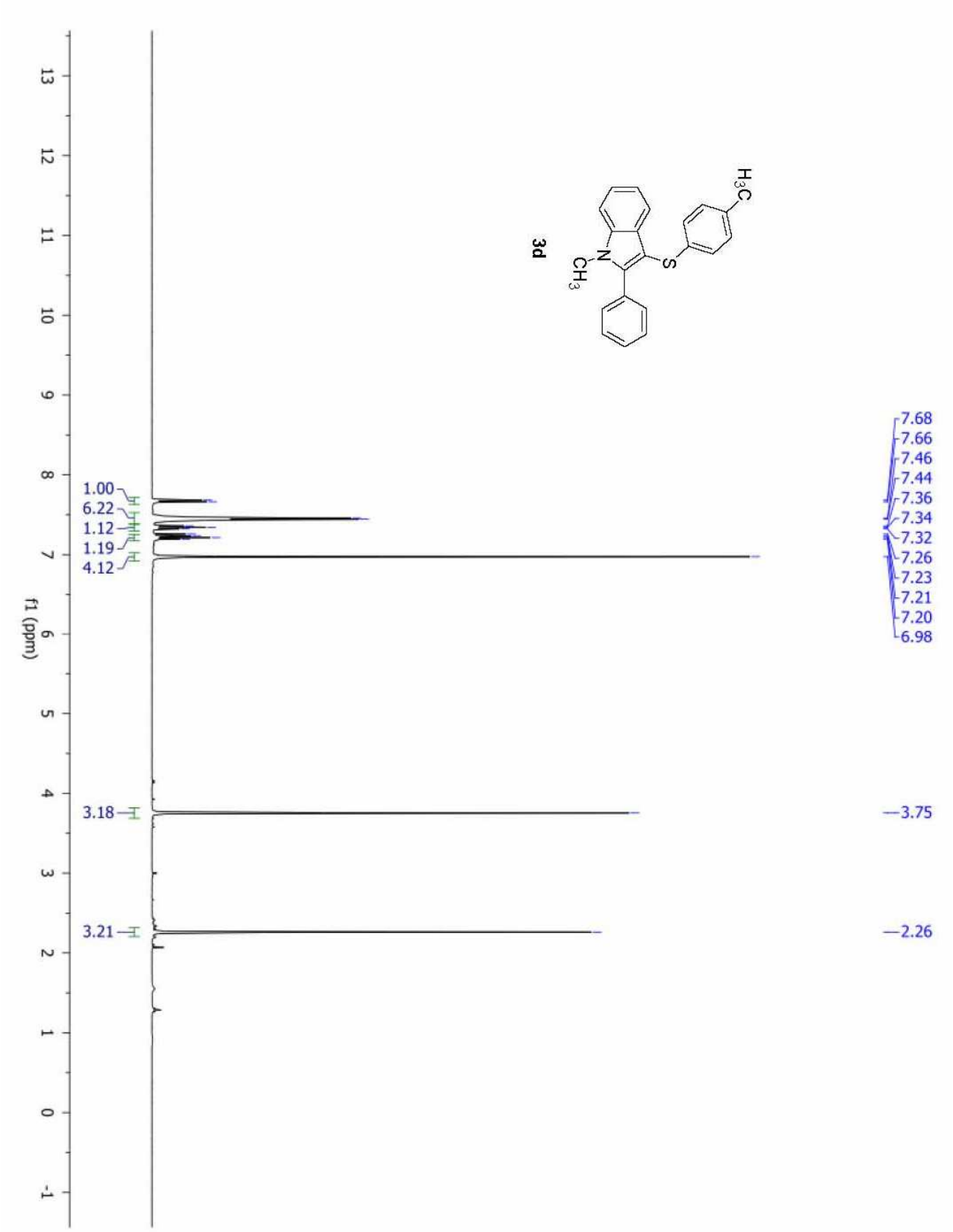

3b
F
F
F
F
F
N
CH3
S
1.00
3.14
2.01
1.05
1.12
1.55
3.17
3.67
7.78
7.76
7.58
7.58
7.56
7.55
7.53
7.52
7.46
7.45
7.44
7.43
7.40
7.38
7.35
7.35
7.33
7.33
7.31
7.31
7.29
7.28
7.27
7.26
7.25

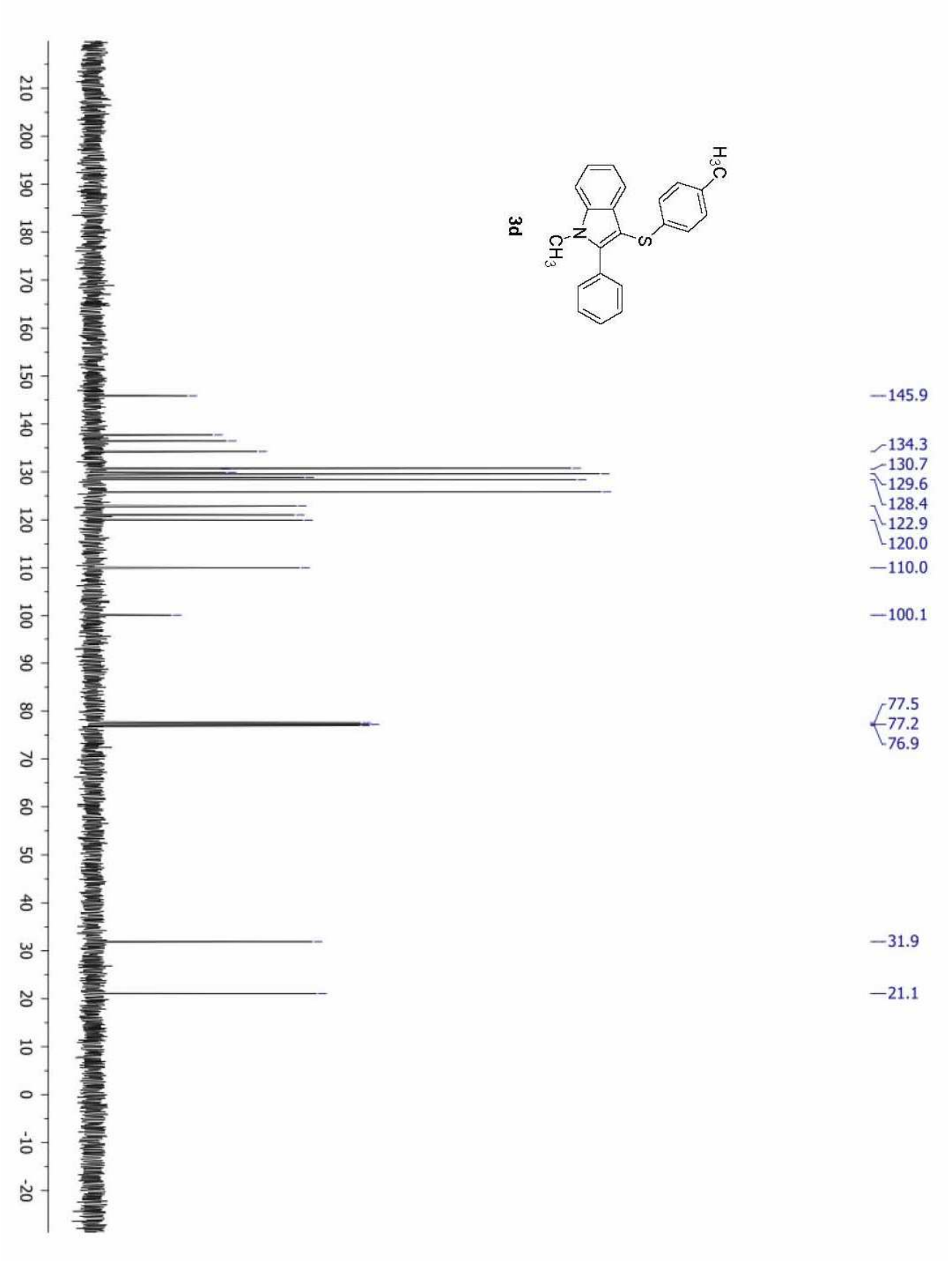

3b
142.2
142.2
142.1
142.1
139.8
139.7
139.7
139.6
139.0
138.9
138.8
138.8
138.6
137.1
136.5
136.4
136.3
136.2
136.1
136.1
128.5
119.3
111.3
110.1
99.0
77.5
77.2
76.9
31.7

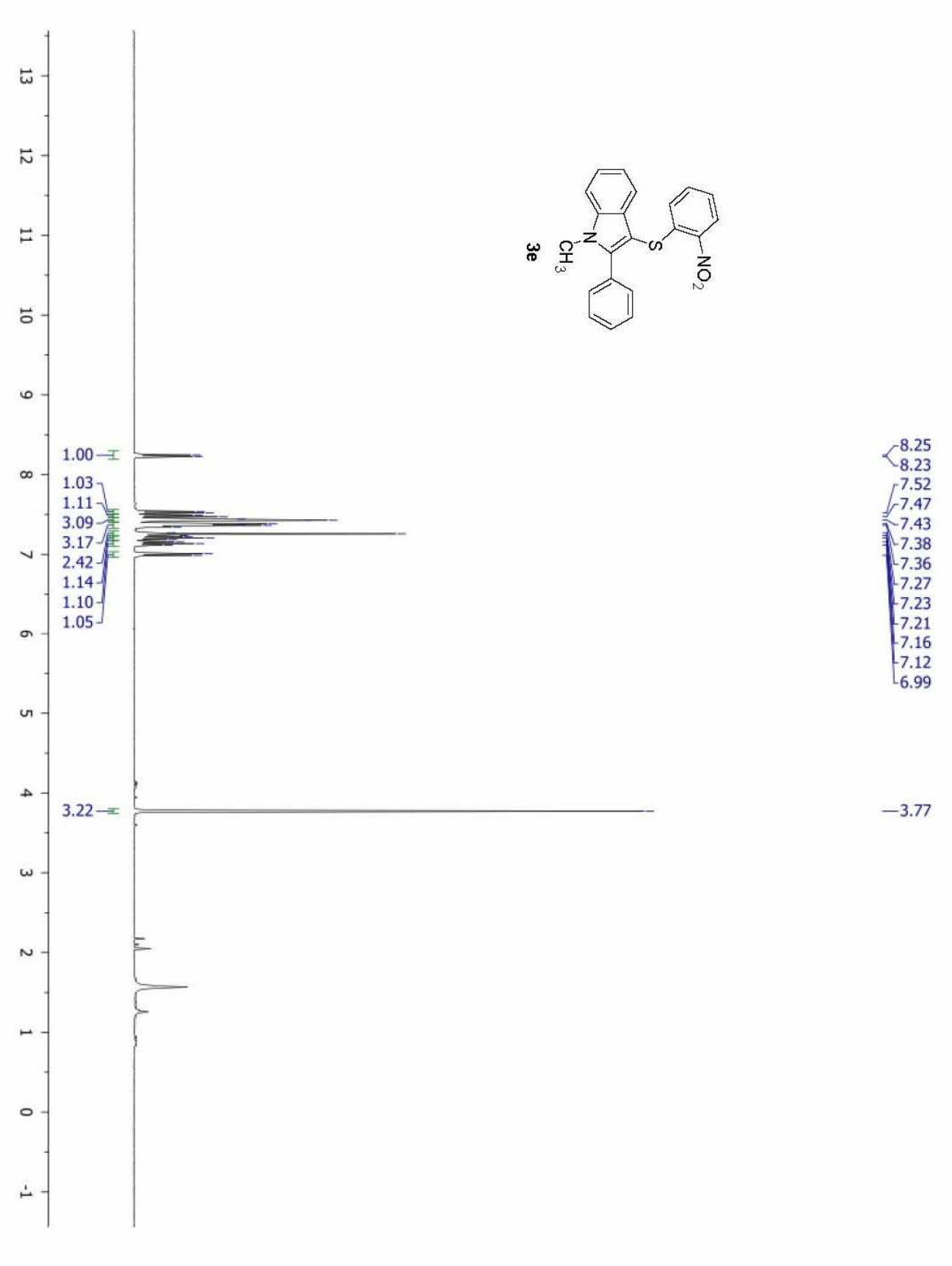

3b
F
F
F
F
F
N
CH3
S
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
2.25
1.00
1.99
-136.3
-136.3
-136.4
-136.4
-157.6
-157.7
-157.7
-164.7
-164.8
-164.8
-164.8
-164.8
-164.8
-164.9
-164.9
-164.9

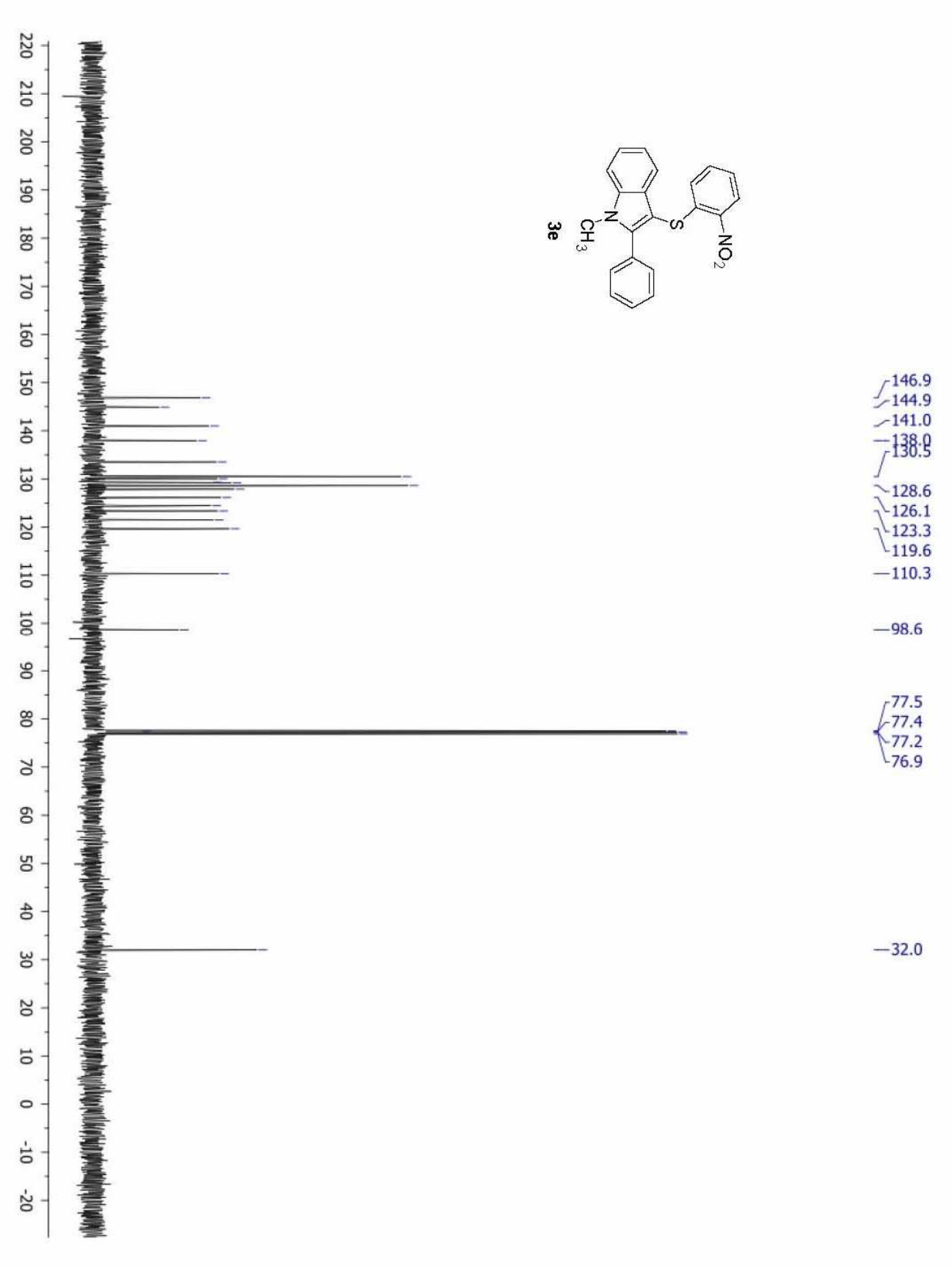

3c
N
CH3
S
7.76
7.74
7.53
7.52
7.51
7.50
7.49
7.48
7.46
7.43
7.42
7.41
7.41
7.39
7.39
7.30
7.30
7.28
7.26
7.23
7.21
7.19
7.15
7.15
7.13
7.12
7.11
7.10
7.08
7.08
1.00
6.35
1.10
1.57
2.16
3.18
3.25
3.79
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

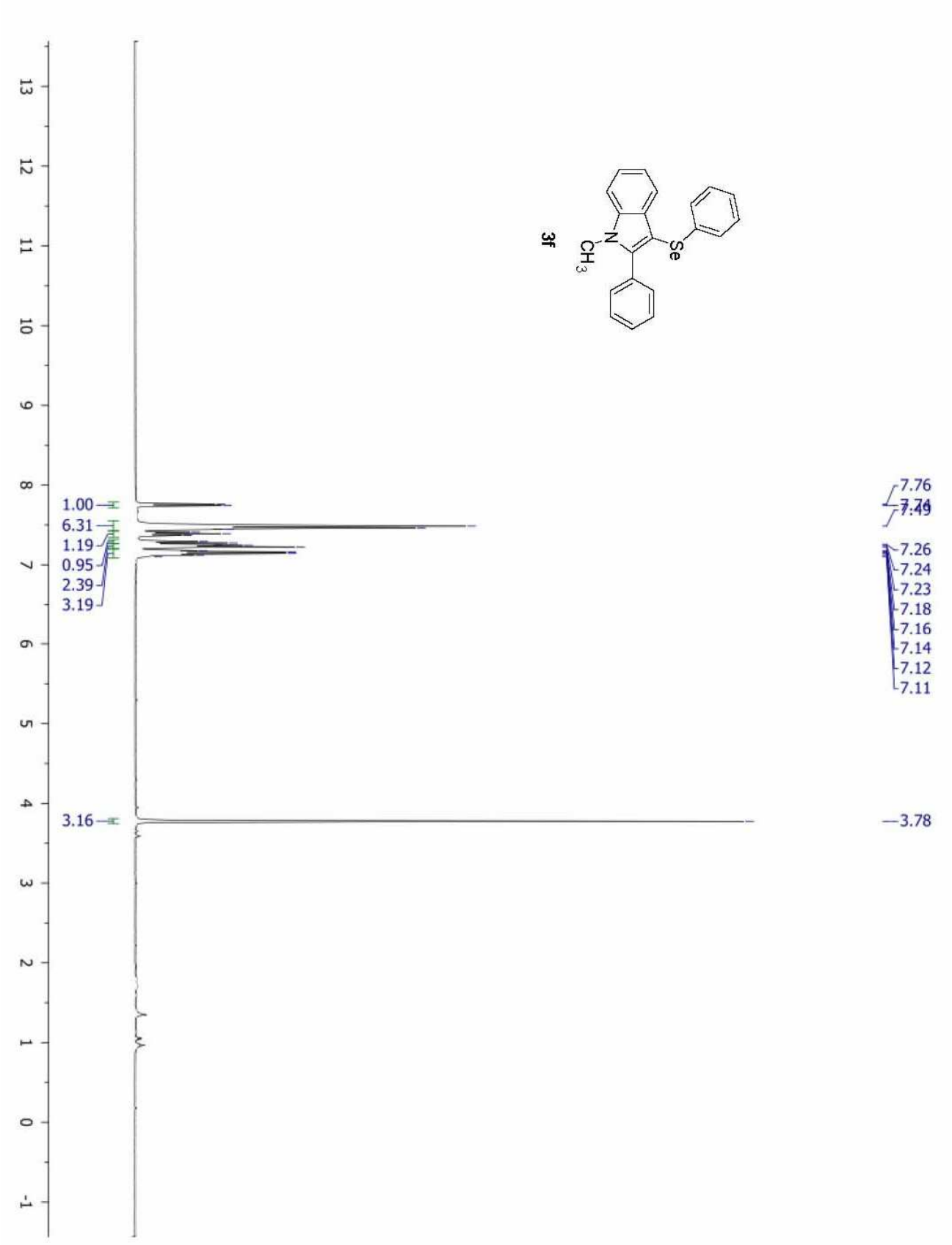

3c
N
CH3
S
146.0
137.7
130.7
128.5
124.5
119.9
110.0
99.6
77.5
77.4
77.2
76.9
31.9

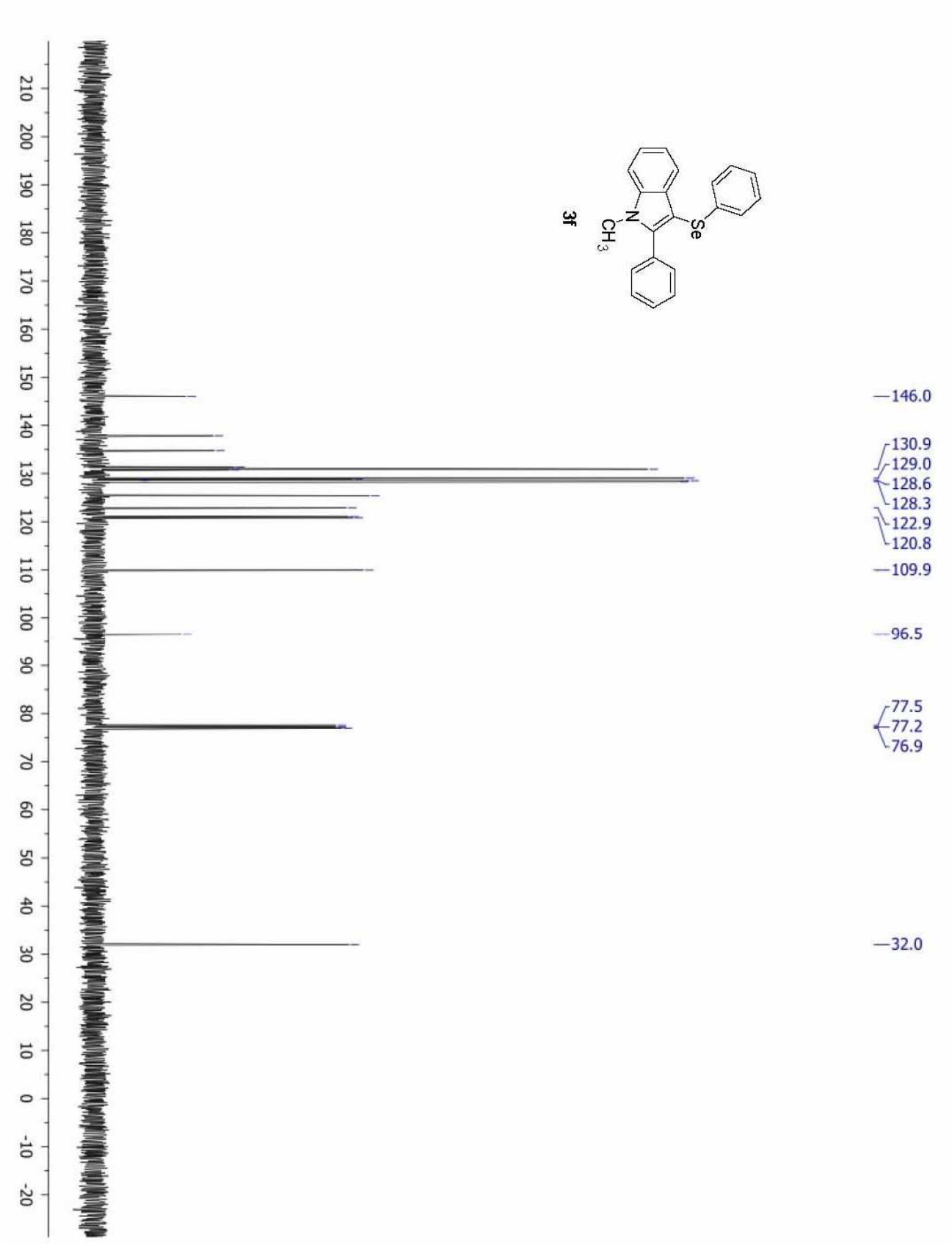

3d
H3C
N
CH3
S
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
1.00
6.22
1.12
1.19
4.12
3.18
3.21
7.68
7.66
7.46
7.44
7.36
7.34
7.32
7.26
7.23
7.21
7.20
6.98
3.75
2.26

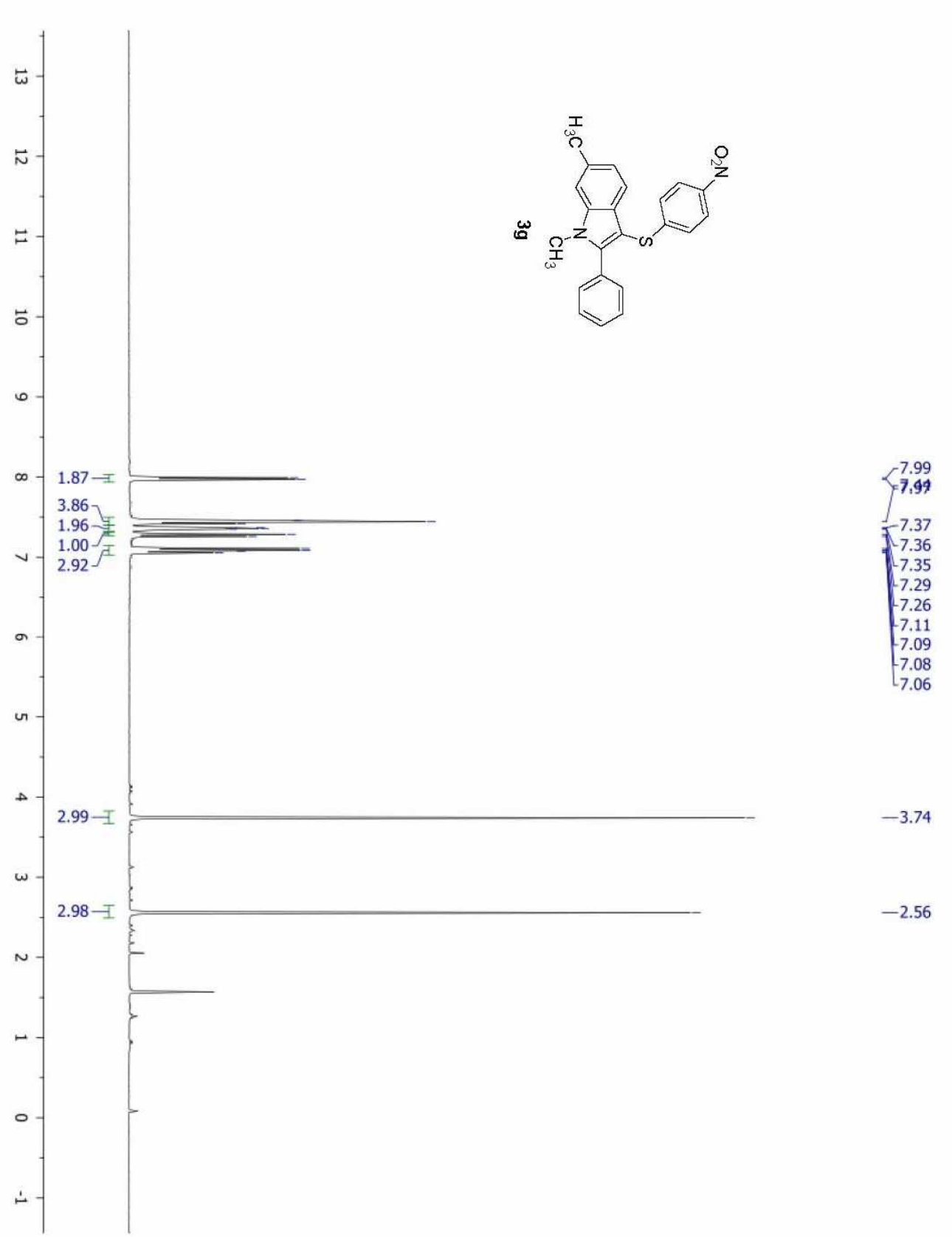

3d
145.9
134.3
130.7
129.6
128.4
122.9
120.0
110.0
100.1
77.5
77.2
76.9
31.9
21.1


3e
N
CH3
S
NO2
1.00
1.03
1.11
3.09
3.17
2.42
1.14
1.10
1.05
3.22
8.25
8.23
7.52
7.47
7.43
7.38
7.36
7.27
7.23
7.21
7.16
7.12
6.99
3.77


3e
N
CH3
S
NO2
146.9
144.9
141.0
138.0
130.5
128.6
126.1
123.3
119.6
110.3
98.6
77.5
77.4
77.2
76.9
32.0


3f
N
CH3
Se
1.00
6.31
1.19
0.95
2.39
3.19
3.16
7.76
7.74
7.49
7.26
7.24
7.23
7.18
7.16
7.14
7.12
7.11
3.78


3f
N
CH3
Se
146.0
130.9
129.0
128.6
128.3
122.9
120.8
109.9
96.5
77.5
77.2
76.9
32.0


3g
1.87
3.86
1.96
1.00
2.92
2.99
2.98
7.99
7.97
7.37
7.36
7.35
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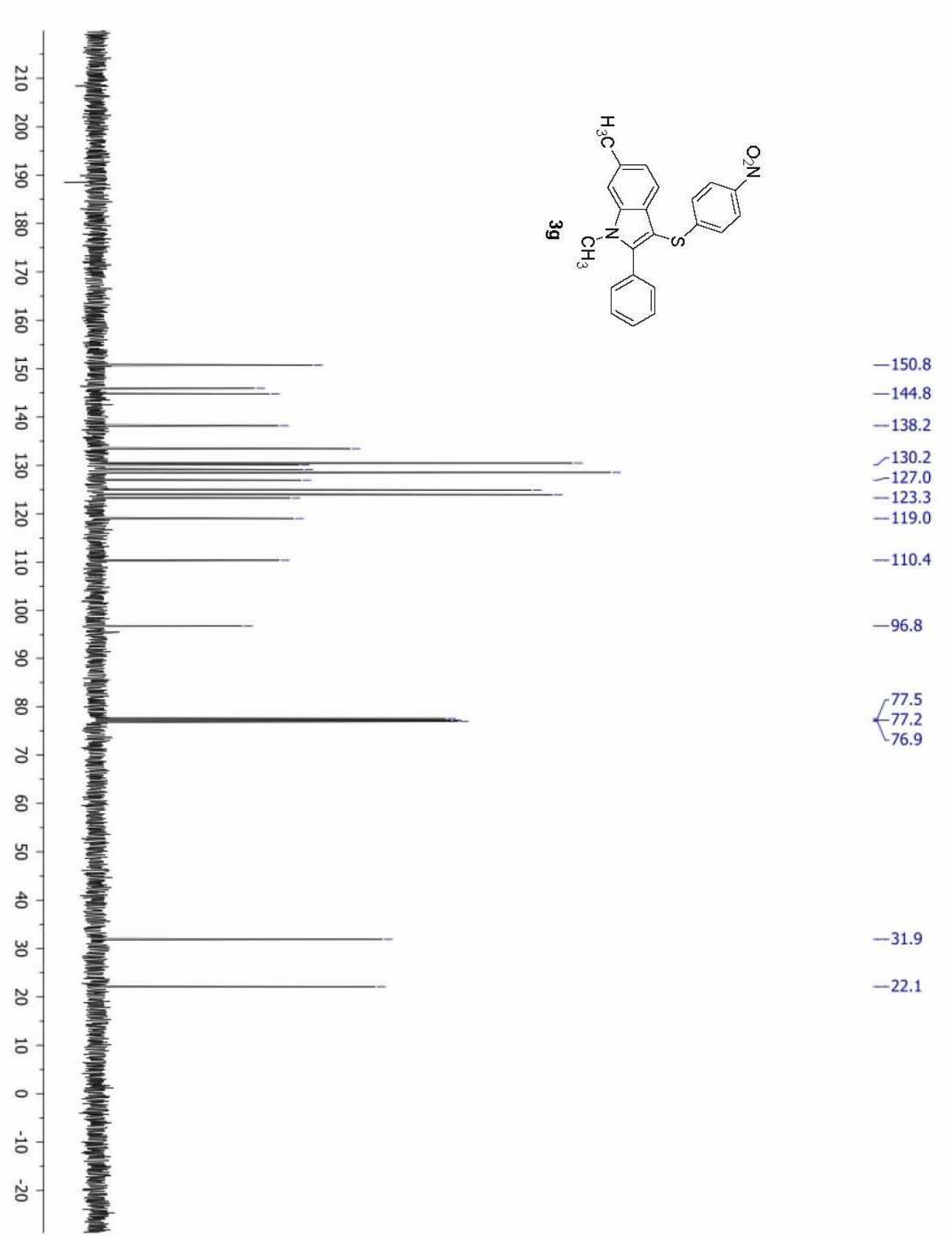
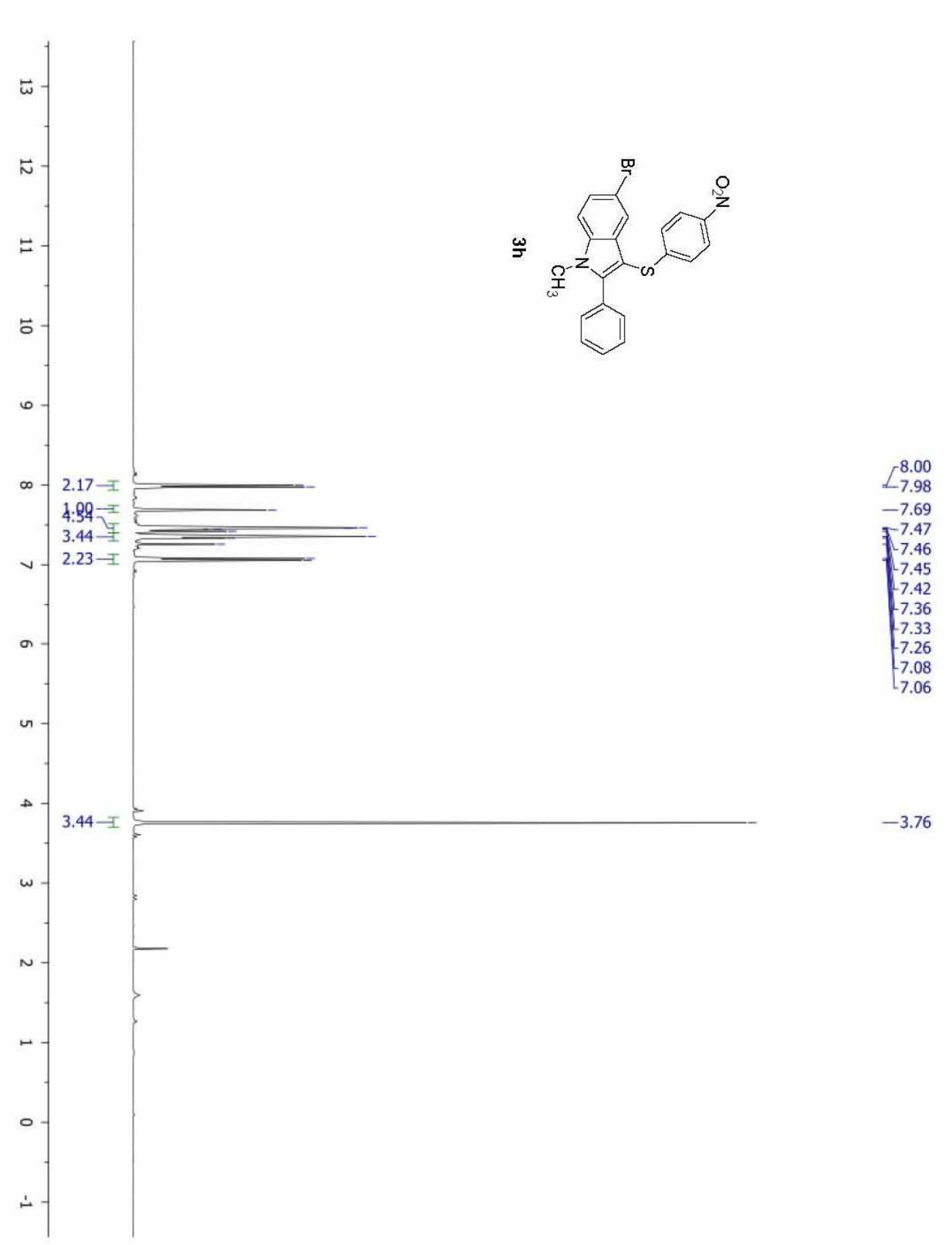
7.26
7.11
7.09
7.08
7.06
3.74
2.56


3g
150.8
144.8
138.2
130.2
127.0
123.3
119.0
110.4
96.8
77.5
77.2
76.9
31.9
22.1


3h
Br
O2N
N
CH3
S
2.17
1.00
4.34
3.44
2.23
3.44
8.00
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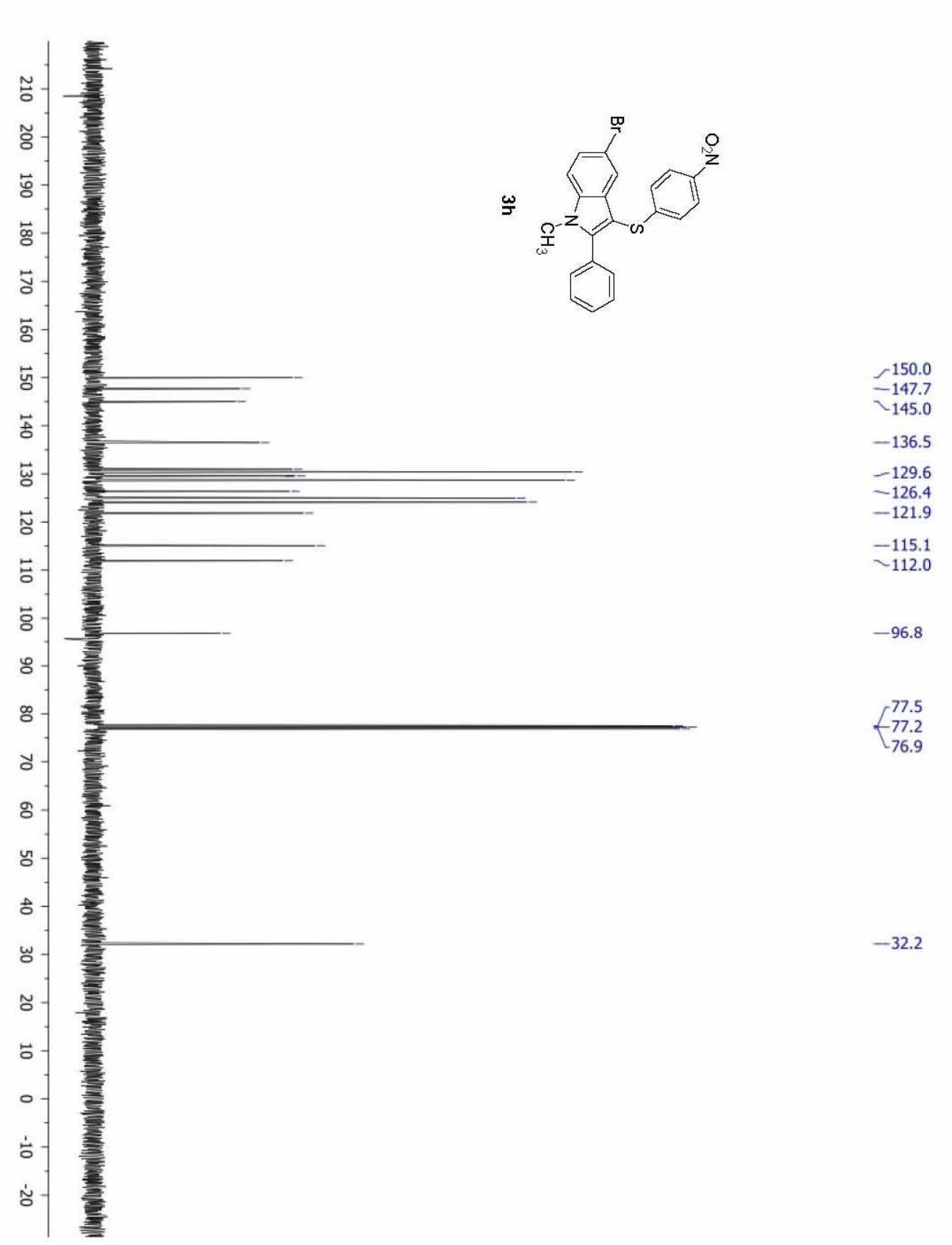
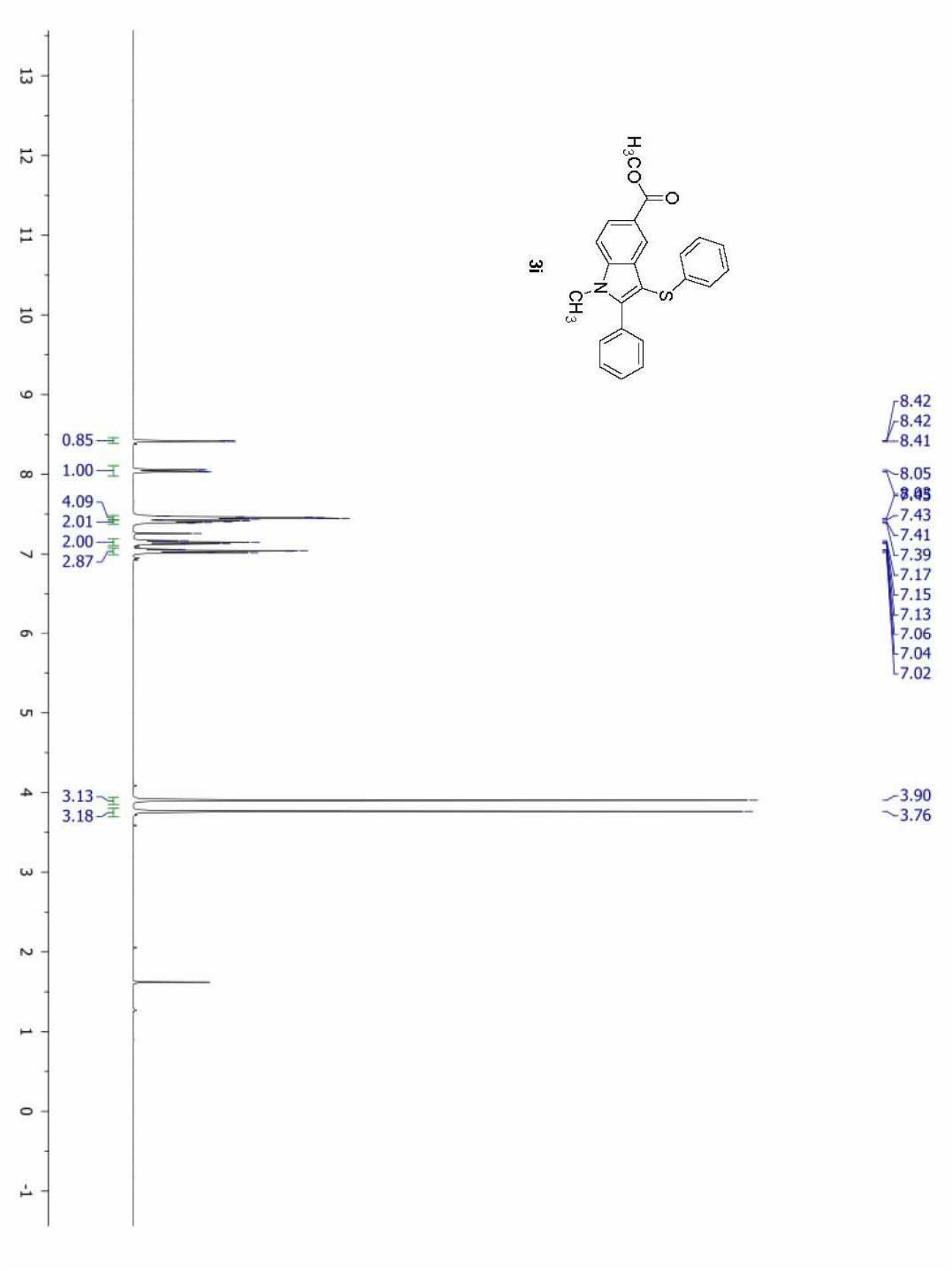
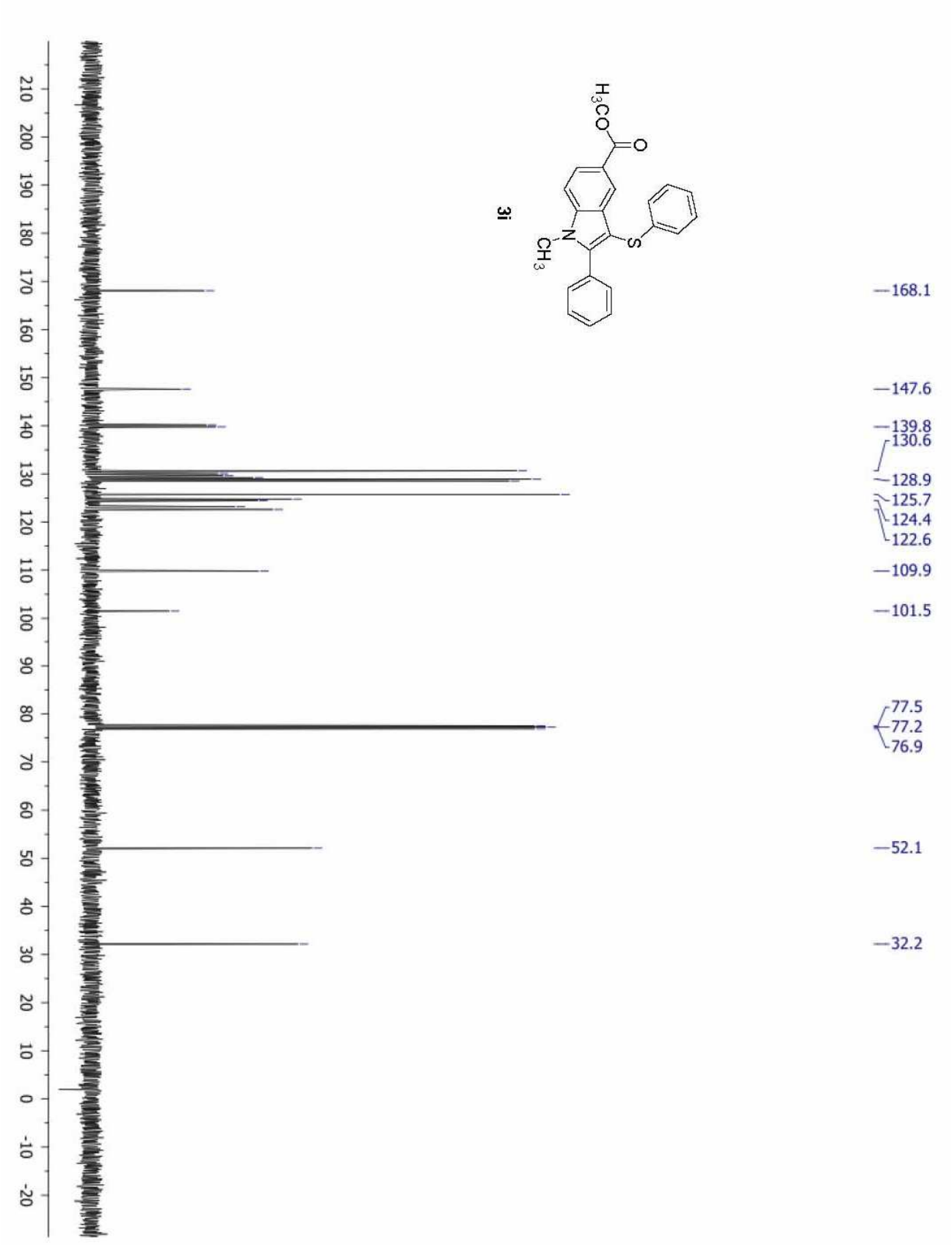
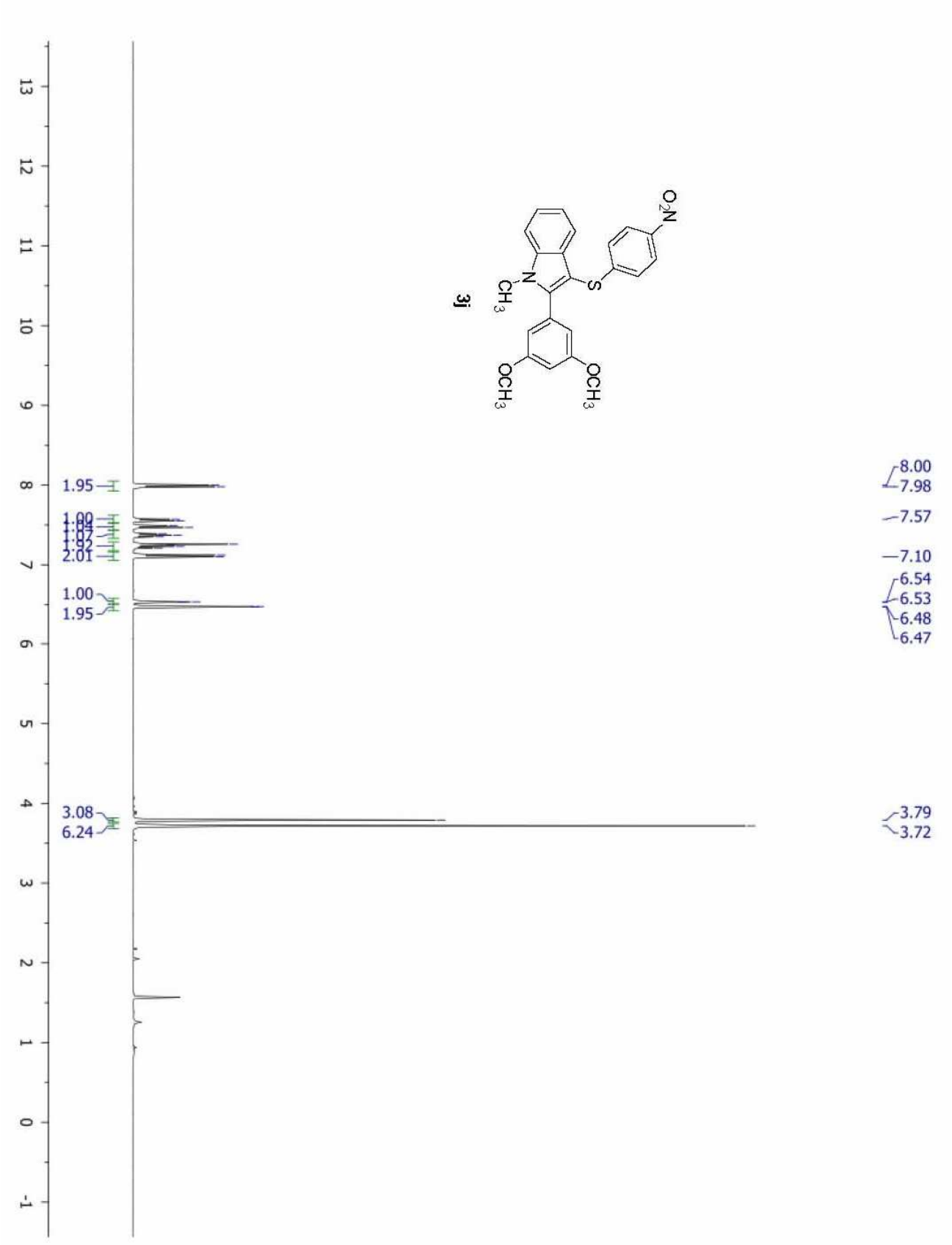
7.36
7.33
7.26
7.08
7.06
3.76


3h
Br
O2N
N
CH3
S
150.0
147.7
145.0
136.5
129.6
126.4
121.9
115.1
112.0
96.8
77.5
77.2
76.9
32.2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20


3i
H3CO
O
N
CH3
S
0.85
1.00
4.09
2.01
2.00
2.87
3.13
3.18
8.42
8.42
8.41
8.05
7.43
7.41
7.39
7.17
7.15
7.13
7.06
7.04
7.02
3.90
3.76


3i
H3CO
O
N
CH3
S
168.1
147.6
139.8
130.6
128.9
125.7
124.4
122.6
109.9
101.5
77.5
77.2
76.9
52.1
32.2


3j
O2N
N
CH3
S
OCH3
OCH3
1.95
1.00
2.01
1.00
1.95
3.08
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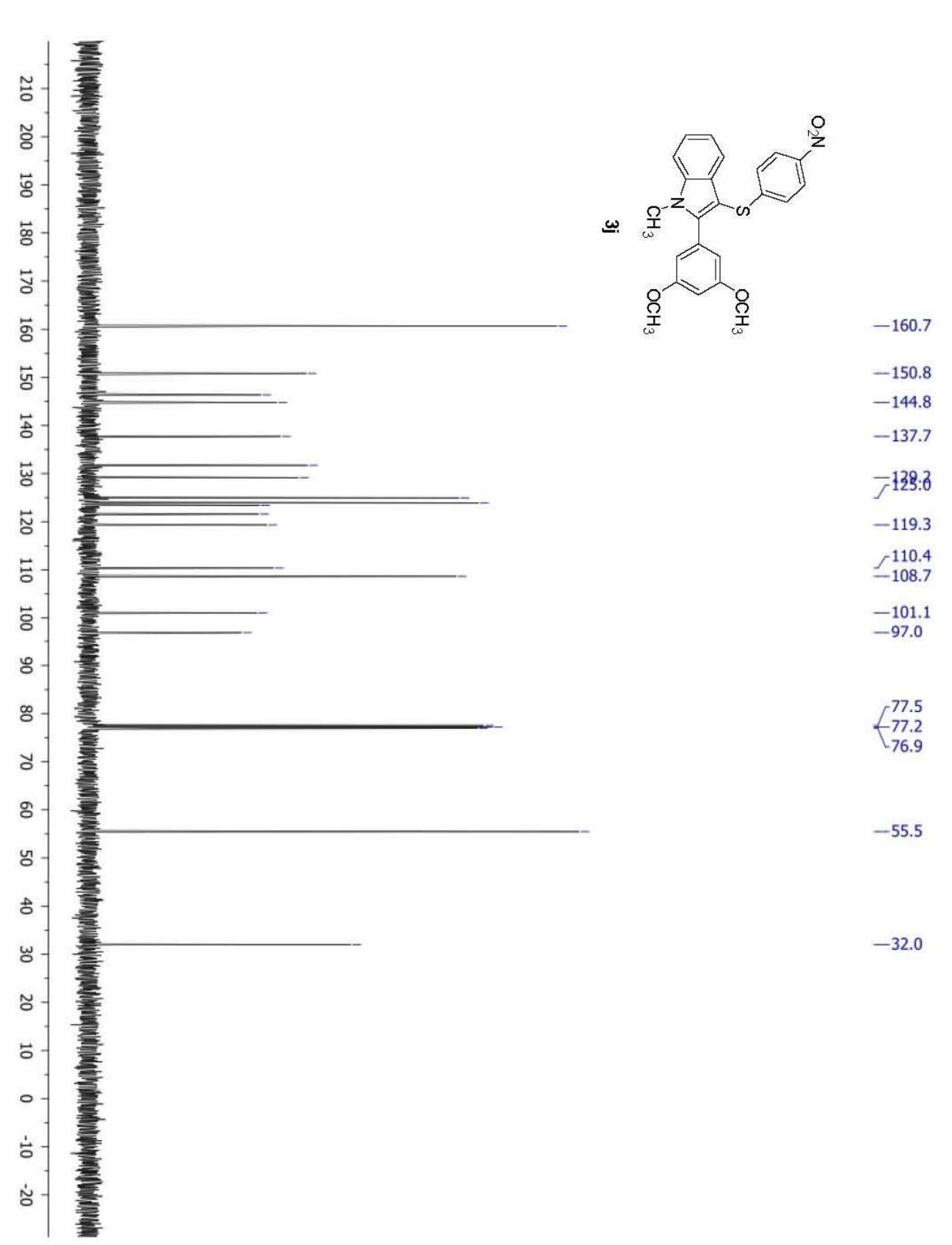
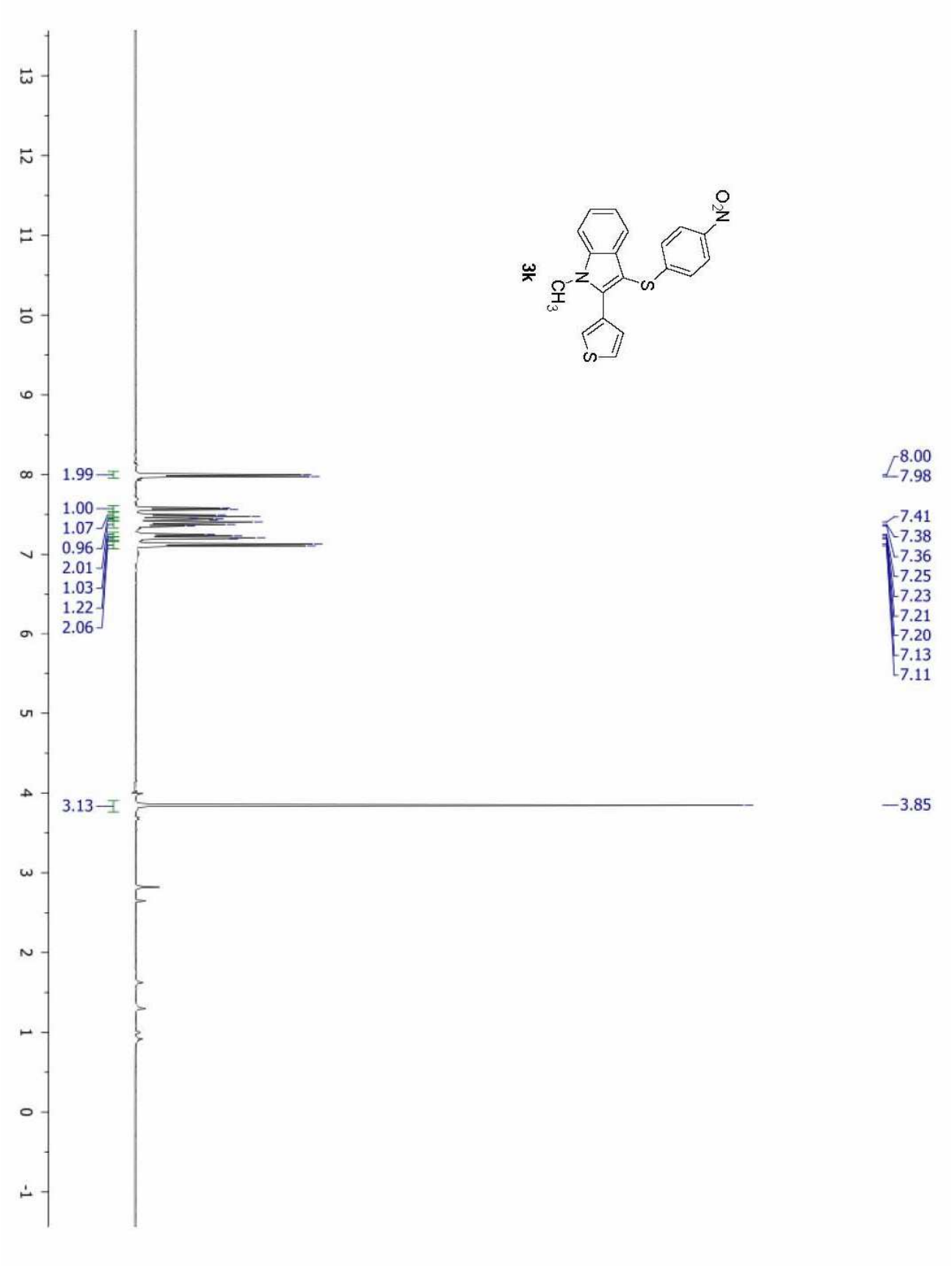
6.54
6.53
6.48
6.47
3.79
3.72


3j
O2N
N
CH3
S
OCH3
OCH3
160.7
150.8
144.8
137.7
129.2
125.0
119.3
110.4
108.7
101.1
97.0
77.5
77.2
76.9
55.5
32.0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3.13
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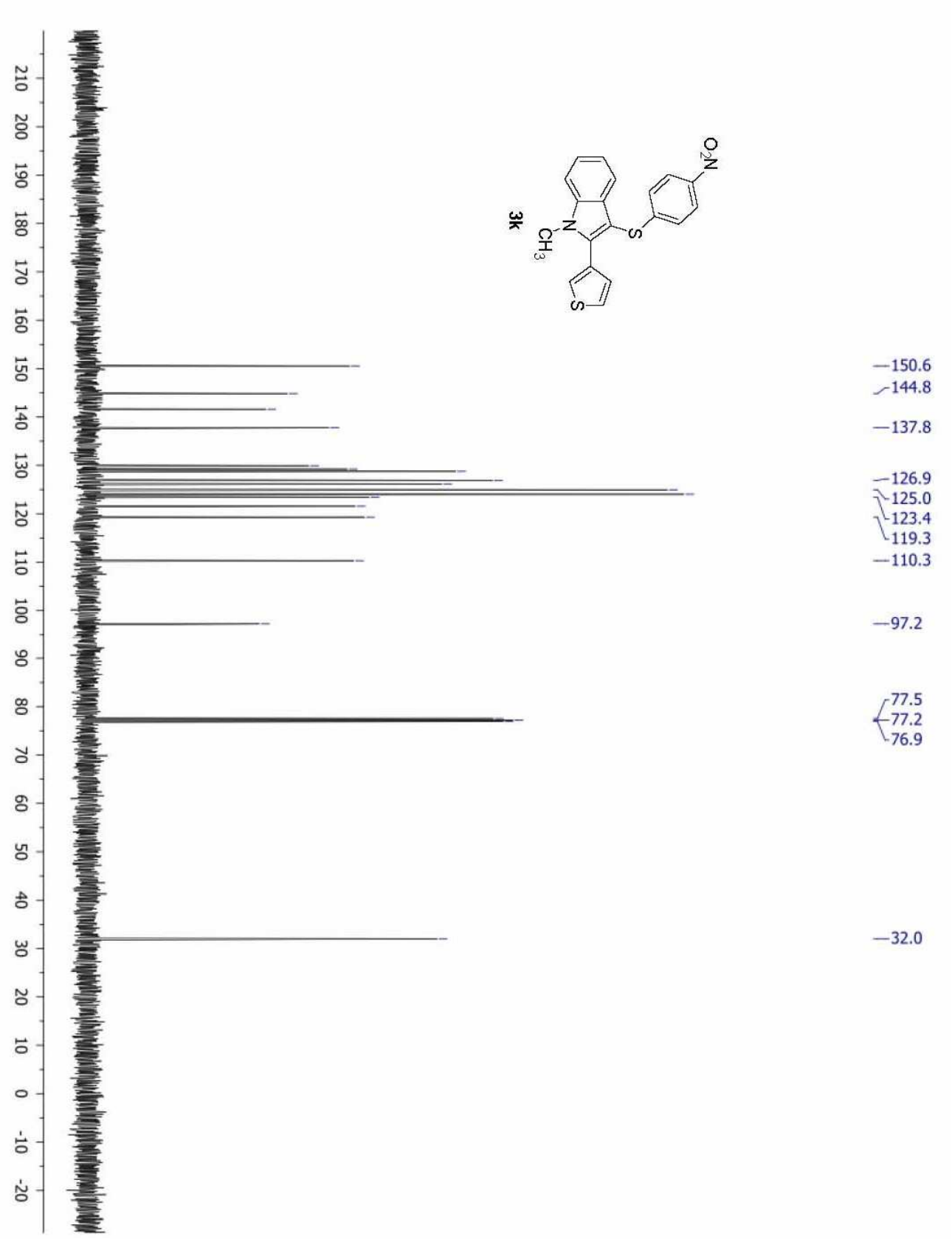
3.85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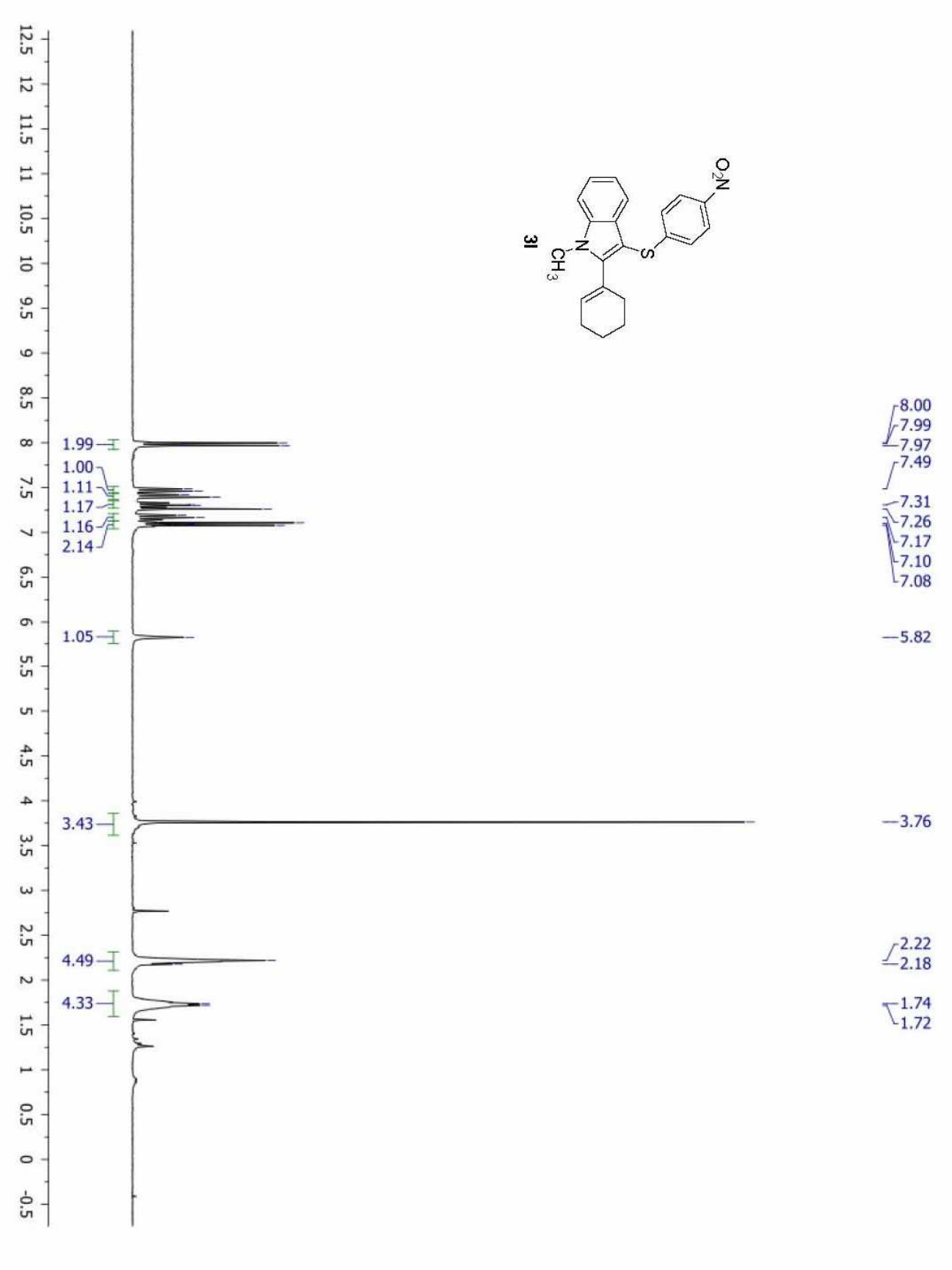
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4.33
8.00
7.99
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7.10
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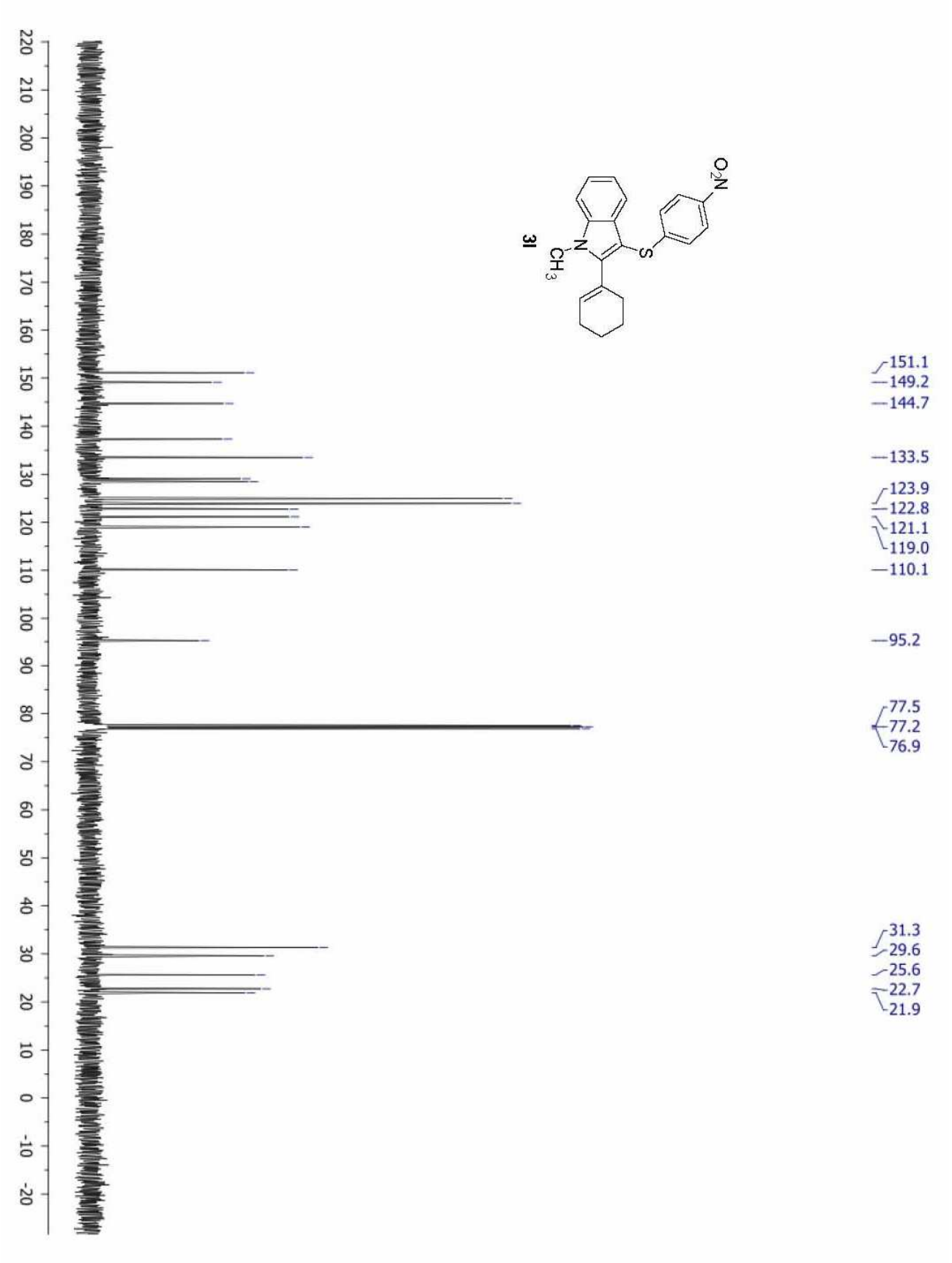
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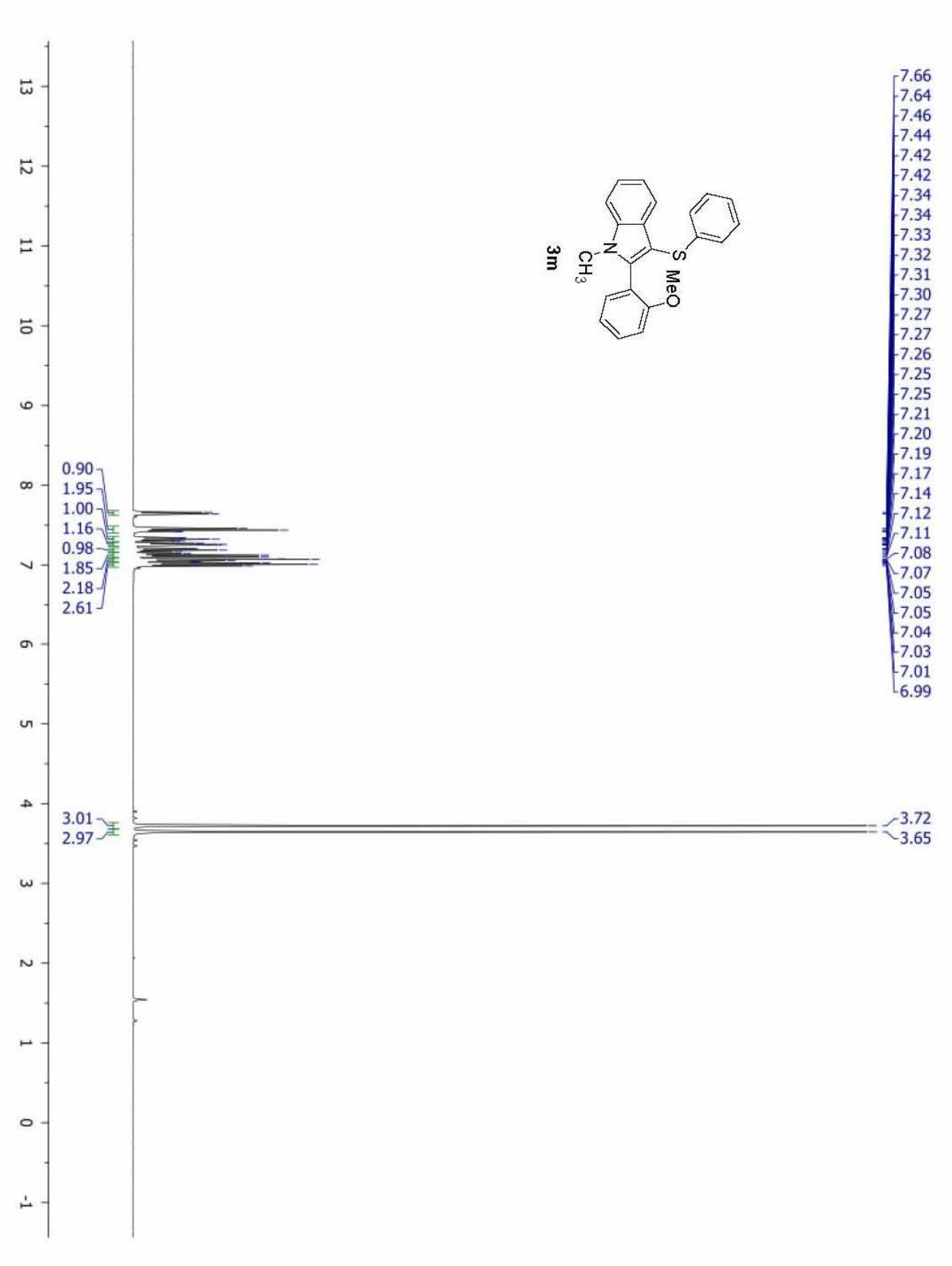
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7.33
7.32
7.31
7.30
7.27
7.27
7.26
7.25
7.25
7.21
7.20
7.19
7.17
7.14
7.12
7.11
7.08
7.07
7.05
7.05
7.04
7.03
7.01
6.99
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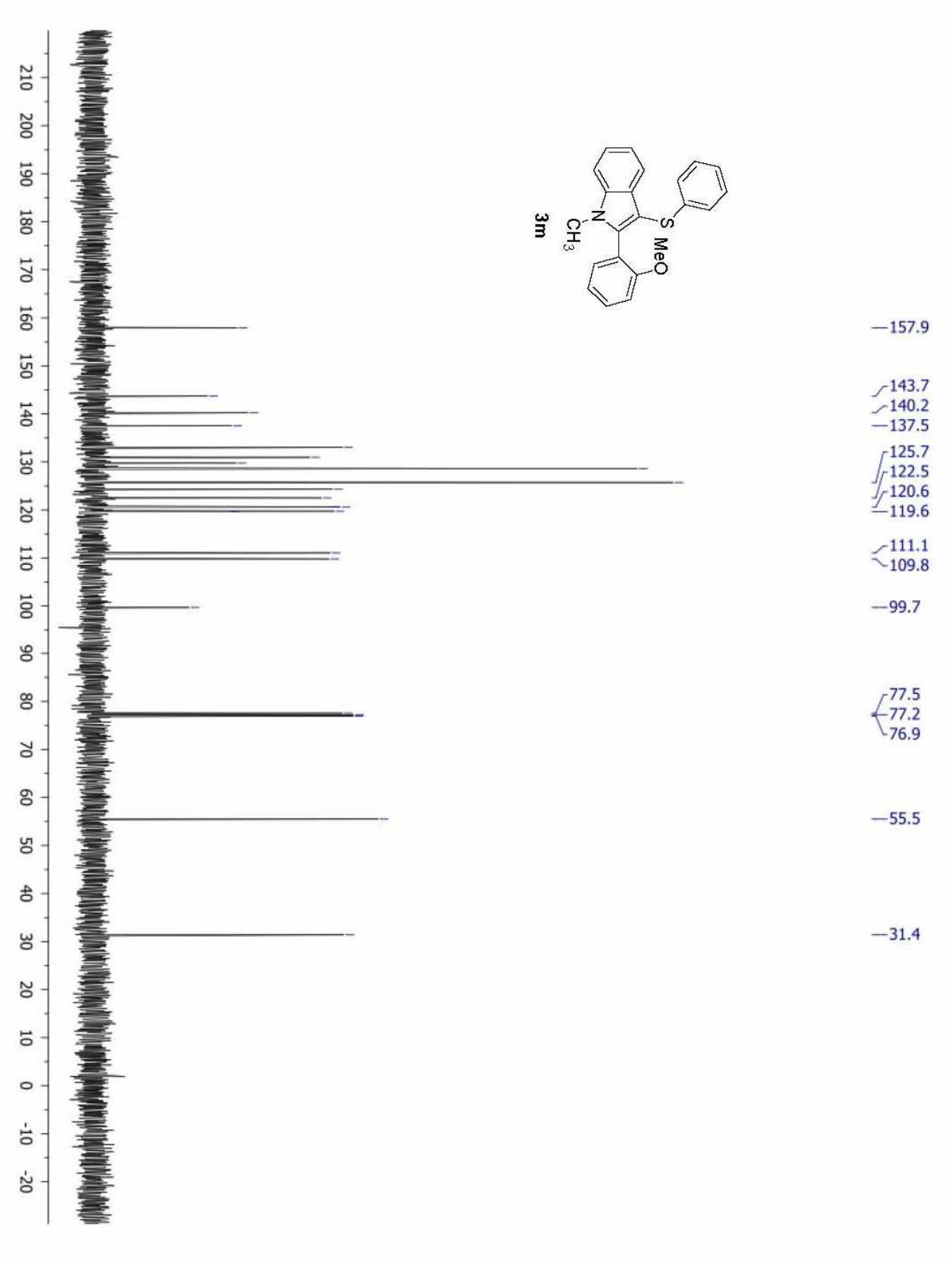
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CH3
S
MeO
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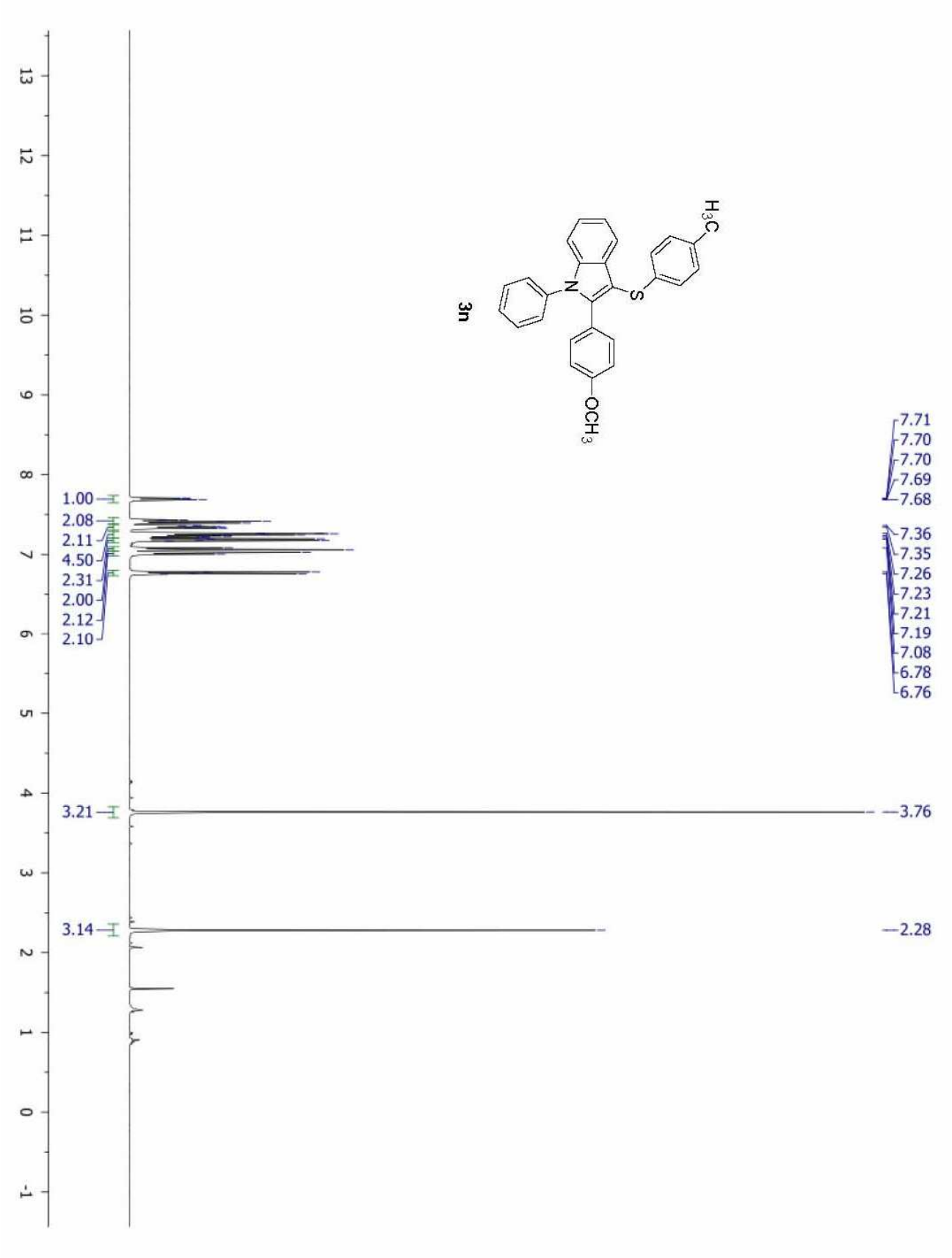
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S
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3.21
3.14
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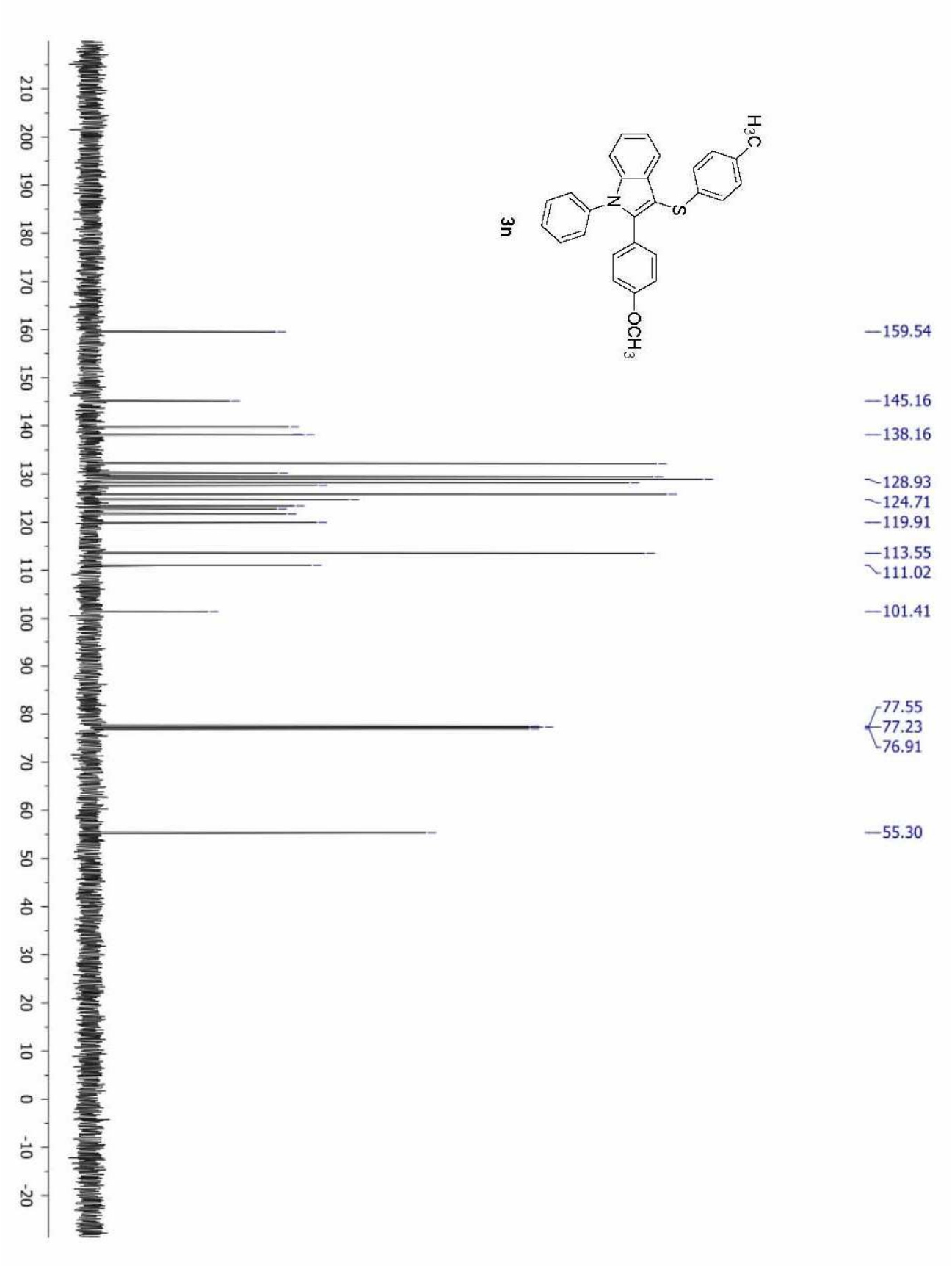
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S
OCH3
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77.23
76.91
55.30