Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

TFA-promoted Direct C–H Sulfenylation at the C2 position of non-protected Indoles

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Table of contents

1. General experimental methods

All reactions were run under air unless otherwise specified. Trifluoroacetic acid (ReagentPlus®, 99%) and other commercially available chemicals were purchased from Aldrich and used directly without purification. CH_2Cl_2 and Et_2O were distilled over CaH_2 and sodium/benzophenone, respectively, before the use. All other solvents (DMF, CH_3CN, MeOH) were purchased from Aldrich and used directly without further purification.

NMR spectra were recorded on a Bruker AVANCE 400. ^{1}H NMR spectra were recorded at 400 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane (TMS) or residual protonated solvents as an internal standard (TMS δ 0.00 ppm, $CDCl_3$ δ 7.26 ppm, DMSO δ 2.50 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances), integration. ^{13}C NMR spectra were recorded at 100 MHz and data are reported as follows: chemical shift in ppm with the solvent as an internal indicator ($CDCl_3$ δ 77.16 ppm, DMSO δ 39.52 ppm). TLCs were performed on Merck $60F_{254}$ silica gel plates and visualized with UV lamp (254 nm), and by using a solution of phosphomolybdic acid in ethanol followed by heating. Flash column chromatographies were performed with Merck Geduran Si 60 silica gel (40-63 μm). Mass spectra with electronic impact (MS-EI) were recorded from a Shimadzu GCMS-QP 2010S. Infrared (IR) were recorded with a Bruker TENSOR^{TM} 27 (IRFT), wave-numbers are indicated in cm^{-1}. High resolution mass spectra (HRMS) were performed by the Centre Regional de Microanalyse (Université Pierre et Marie Curie VI, Paris, France). Melting points were determined on a Büchi Melting Point M-560 apparatus in open capillaries and are uncorrected.

2. Optimization of reactions conditions

General procedure

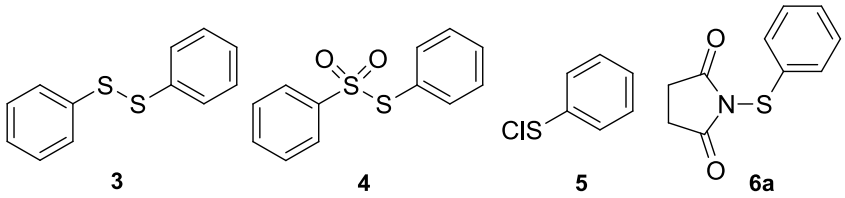
In a 10 mL oven-dried vial, equipped with a rubber septum, were added indole **1a** (35.5 mg, 0.3 mmol, 1.0 equiv) and the sulfenylating reagent **3**–**6** (0.3 mmol, 1.0 equiv). Subsequently, anhydrous solvent (0.5 M) was added into the vial, followed by the acid and the resulting solution was stirred at rt for 4 h. The reaction mixture was neutralized with a saturated solution of $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The yield of 2-(phenylsulfanyl)-1*H*-indole **2aa** was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Preparation of sulfenylating reagents (3, 4, 5, 6a)

Diphenyl disulfide **3** and *S*-phenyl benzenethiosulfonate **4** were commercially available. Phenylsulfuryl chloride **5** was prepared according to the following procedure: sulfuryl chloride (28 μL, 0.33 mmol, 1.05 equiv) was added dropwise to a solution of thiophenol (32 μL, 0.32 mmol, 1.0 equiv) and Et_3N (4 μL, 0.03 mmol, 0.1 equiv) in anhydrous CH_2Cl_2 (0.5 M) at 0 °C under argon. After stirring for 15 min, the reaction mixture was stirred for 1 h at rt and concentrated under reduced pressure at

20 °C to prevent decomposition of the sulfenyl chloride. The crude product was then used without further purification.

1-(Phenylsulfanyl)pyrrolidine-2,5-dione **6a** was synthesized according to the literature procedure (see section 3).[1]

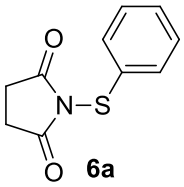


3. Preparation of *N*-thiosuccinimides (6a-6h)

General procedure

According to the literature procedure,[1] sulfuryl chloride (1.05 equiv) was added dropwise to a solution of thiol (1.0 equiv) and Et_3N (0.1 equiv) in anhydrous CH_2Cl_2 (1 M) at 0 °C under argon. After stirring for 15 min, the reaction mixture was stirred for 1 h at rt and then cooled to 0 °C. The resulting solution was transferred dropwise *via* cannula to a solution of succinimide (1.0 equiv) and Et_3N (1.3 equiv) in anhydrous CH_2Cl_2 (1 M) at 0 °C, the reaction mixture was allowed to warm to rt and stirred for 1 h. The solution was diluted with H_2O (20 mL for 5 mmol), extracted with CH_2Cl_2 (3 x 20 mL for 5 mmol), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using a mixture of PE/EtOAc or CH_2Cl_2/Et_2O as the eluent to give the desired product **6**.

1-(Phenylsulfanyl)pyrrolidine-2,5-dione (6a)[1]



Formula: $C_{10}H_9NO_2S$

Mw = 207.94 g.mol^{-1}

Compound **6a** was synthesized from thiophenol (1.04 mL, 9.89 mmol). Purification by flash column chromatography (PE/EtOAc = 7:3) afforded **6a** (1.91 g, 9.20 mmol, 93%) as a white solid. The spectral data are in agreement with the literature report.[1]

mp: 115-116 °C.

IR (neat): ν_{max} 3065, 2985, 2935, 1712, 1470, 1439, 1426, 1295, 1243, 1145, 1080, 1001 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.59 (m, 2H), 7.38-7.31 (m, 3H), 2.82 (s, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.5 (2C), 134.0, 132.5 (2C), 130.1, 129.5 (2C), 28.7 (2C).

MS: *Compound **6a** is not stable under GC/MS analysis.*

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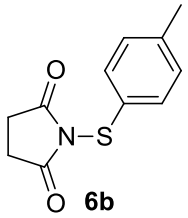
[1] P. Saravanan and P. Anbarasan, *Org. Lett.*, 2014, **16**, 848.

1-[(4-Methylphenyl)sulfanyl]pyrrolidine-2,5-dione (6b)[1]



6b

Formula: $C_{11}H_{11}NO_2S$
Mw = 221.28 g. mol^{-1}

Compound **6b** was synthesized from *p*-toluenethiol (251 mg, 1.98 mmol). Purification by flash column chromatography (PE/EtOAc = 7:3) afforded **6b** (406 mg, 1.84 mmol, 93%) as a white solid. The spectral data are in agreement with the literature report.[1]

mp: 113-115 °C.

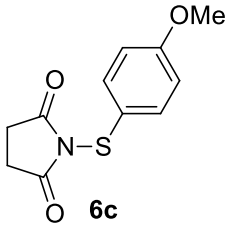
IR (neat): ν_{max} 3060, 2941, 2922, 1712, 1488, 1428, 1405, 1296, 1240, 1143, 1007 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.56 (m, 2H), 7.15-7.12 (m, 2H), 2.77 (s, 4H), 2.33 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.6 (2C), 141.0, 133.8 (2C), 130.5, 130.2 (2C), 28.7 (2C), 21.5.

MS m/z (relative intensity): 221 ($M^{+\cdot}$, 67), 139 (20), 123 (55), 79 (31), 77 (43), 70 (16), 65 (16), 55 (100).

1-[(4-Methoxyphenyl)sulfanyl]pyrrolidine-2,5-dione (6c)[1]



6c

Formula: $C_{11}H_{11}NO_3S$
Mw = 237.27 g. mol^{-1}

Compound **6c** was synthesized from 4-methoxythiophenol (0.314 mL, 2.47 mmol). Purification by flash column chromatography (PE/EtOAc = 6:4) afforded **6c** (400 mg, 1.69 mmol, 68%) as a white solid. The spectral data are in agreement with the literature report.[1]

mp: 106-110 °C.

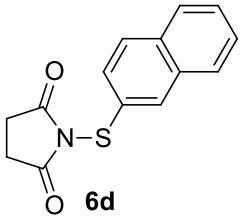
IR (neat): ν_{max} 2945, 2844, 1715, 1591, 1569, 1493, 1461, 1446, 1293, 1255, 1238, 1150, 1104, 1090, 1022, 1009 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, *J* = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.74 (s, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.7 (2C), 161.8, 137.4 (2C), 124.6, 114.8 (2C), 55.5, 28.7 (2C).

MS m/z (relative intensity): 237 ($M^{+\cdot}$, 53), 140 (17), 139 (100), 124 (10), 96 (20), 95 (18), 70 (18), 55 (41).

1-(Naphthalen-2-ylsulfanyl)pyrrolidine-2,5-dione (6d)[1]



6d

Formula: $C_{14}H_{11}NO_2S$
Mw = 257.31 g. mol^{-1}

Compound **6d** was synthesized from 2-naphthalenethiol (320 mg, 1.98 mmol). Purification by flash column chromatography (PE/EtOAc = 7:3 to 6:4) afforded **6d** (308 mg, 1.20 mmol, 61%) as a white solid. The spectral data are in agreement with the literature report.[1]

mp: 154-158 °C.

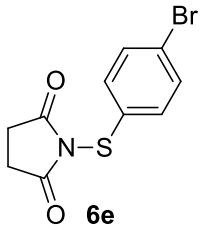
IR (neat): ν_{max} 2924, 2835, 1720, 1585, 1502, 1295, 1256, 1227, 1132, 1006 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19 (d, *J* = 1.5 Hz, 1H), 7.84-7.79 (m, 3H), 7.66 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.55-7.49 (m, 2H), 2.81 (s, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.6 (2C), 133.7, 133.3, 133.0, 131.1, 129.4, 129.2, 128.4, 127.9, 127.7, 127.1, 28.7 (2C).

MS: *Compound **6d** is not stable under GC/MS analysis.*

1-[(4-Bromophenyl)sulfanyl]pyrrolidine-2,5-dione (6e)[1]



6e

Formula: $C_{10}H_8BrNO_2S$

Mw = 286.15 g. mol^{-1}

Compound **6e** was synthesized from 4-bromothiophenol (394 mg, 1.98 mmol). Purification by flash column chromatography (PE/EtOAc = 6:4) afforded **6e** (319 mg, 1.12 mmol, 56%) as a white solid. The spectral data are in agreement with the literature report.[1]

mp: 140-144 °C.

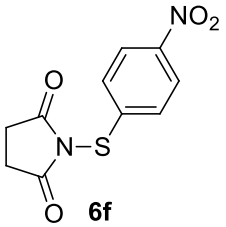
IR (neat): ν_{max} 2925, 2853, 1715, 1471, 1423, 1303, 1247, 1232, 1134, 1085, 1069, 1003 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52-7.49 (m, 2H), 7.47-7.44 (m, 2H), 2.81 (s, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.3 (2C), 134.4 (2C), 132.9, 132.7 (2C), 124.9, 28.7 (2C).

MS: *Compound **6e** is not stable under GC/MS analysis.*

1-[(4-Nitrophenyl)sulfanyl]pyrrolidine-2,5-dione (6f)[2]



6f

Formula: $C_{10}H_8N_2O_4S$

Mw = 252.25 g. mol^{-1}

Compound **6f** was synthesized from 4-nitrothiophenol (384 mg, 1.98 mmol). Purification by flash column chromatography (CH_2Cl_2/Et_2O = 100:0 to 98:2) afforded **6f** (273 mg, 1.08 mmol, 55%) as a pale yellow solid. The spectral data are in agreement with the literature report.[2]

mp: 174-176 °C.

IR (neat): ν_{max} 3105, 2951, 1728, 1598, 1583, 1514, 1342, 1294, 1248, 1221, 1086, 1006 cm^{-1}.

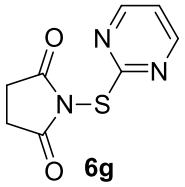
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19-8.15 (m, 2H), 7.45-7.42 (m, 2H), 2.97 (s, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.8 (2C), 147.5, 143.1, 127.7 (2C), 124.6 (2C), 28.7 (2C).

MS: *Compound **6f** is not stable under GC/MS analysis.*

[2] S. Savarin, J. Srogl and L. S. Liebeskind, *Org. Lett.*, 2002, **4**, 4309.

1-(Pyrimidin-2-ylsulfanyl)pyrrolidine-2,5-dione (6g)



6g

Formula: $C_8H_7N_3O_2S$
Mw = 209.23 g.mol^{-1}

Compound **6g** was synthesized from 2-mercaptopyrimidine (226 mg, 1.98 mmol). Purification by flash column chromatography (PE/EtOAc = 1:1) afforded **6g** (153 mg, 0.73 mmol, 37%) as a pale yellow solid.

mp: 159-162 °C.

IR (neat): ν_{max} 2957, 2954, 2853, 1719, 1556, 1428, 1376, 1306, 1239, 1185, 1143, 1007 cm^{-1}.

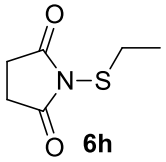
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.50 (d, *J* = 4.8 Hz, 2H), 7.04 (t, *J* = 4.8 Hz, 1H), 2.98 (s, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.1 (2C), 168.0, 158.0 (2C), 118.4, 29.0 (2C).

MS m/z (relative intensity): 209 ($M^{+\cdot}$, 44), 165 (17), 154 (54), 127 (13), 112 (62), 111 (31), 98 (17), 84 (22), 79 (44), 70 (28), 57 (26), 55 (100), 53 (43), 52 (36).

HRMS: calcd for $C_8H_8N_3O_2S$ $(M+H)^+$: 210.0332, found : 210.0331.

1-(Ethylsulfanyl)pyrrolidine-2,5-dione (6h)[3]



6h

Formula: $C_6H_9NO_2S$
Mw = 159.21 g. mol^{-1}

Compound **6h** was synthesized from ethanethiol (0.740 mL, 9.89 mmol). Purification by flash column chromatography (PE/EtOAc = 1:1) afforded **6h** (969 mg, 6.09 mmol, 62%) as a white solid. The spectral data are in agreement with the literature report.[3]

mp: 60-62 °C.

IR (neat): ν_{max} 2966, 2931, 2871, 1712, 1456, 1419, 1376, 1310, 1262, 1244, 1145, 1006 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.86 (q, *J* = 7.4 Hz, 2H), 2.82 (s, 4H), 1.20 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.3 (2C), 31.8, 28.7 (2C), 13.1.

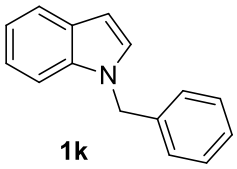
MS: *Compound **6h** is not stable under GC/MS analysis.*

[3] Y. Abe, T. Nakabayashi and J. Tsurugi, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1898.

4. Synthesis of *N*-protected indoles (1k-1n)

All reactions were performed in oven-dried flasks under argon.

1-Benzyl-1*H*-indole (1k)[4]



1k

Formula: $C_{15}H_{13}N$
Mw = 207.27 g.mol^{-1}

To a suspension of NaH (74.4 mg, 1.86 mmol, 1.1 equiv) in anhydrous DMF (8.5 mL) at 0 °C, was added indole (200 mg, 1.69 mmol, 1.0 equiv) in portions. The resulting mixture was allowed to warm to rt over 1 h, cooled to 0 °C and benzyl bromide (0.217 mL, 1.77 mmol, 1.05 equiv) was added dropwise. The solution was allowed to warm to rt and stirred overnight. The reaction mixture was quenched with H_2O (30 mL) and diluted with EtOAc (30 mL). The aqueous phase was extracted with EtOAc (3 x 30 mL) and the combined organic extracts were washed with brine (80 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (pentane/EtOAc = 100:0 to 99:1) to afford **1k** (263 mg, 1.27 mmol, 75%) as a pale yellow solid. The spectral data are in agreement with the literature report.[4]

mp: 42-43 °C.

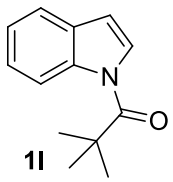
IR (neat): ν_{max} 3055, 3029, 2919, 1510, 1484, 1462, 1453, 1356, 1334, 1316, 1255, 1181, 1012 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (ddd, *J* = 7.7, 1.3, 0.8 Hz, 1H), 7.30-7.22 (m, 4H), 7.17 (m, 1H), 7.12-7.08 (m, 4H), 6.55 (dd, *J* = 3.2, 0.9 Hz, 1H), 5.31 (s, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 136.4, 128.9 (2C), 128.8, 128.4, 127.7, 126.9 (2C), 121.8, 121.1, 119.7, 109.8, 101.8, 50.2.

MS m/z (relative intensity): 207 ($M^{+\cdot}$, 28), 91 (100), 65 (21).

1-Pivaloyl-1*H*-indole (1l)[4]



1l

Formula: $C_{13}H_{15}NO$
Mw = 201.26 g.mol^{-1}

To a solution of indole (200 mg, 1.69 mmol, 1.0 equiv), DMAP (20.9 mg, 0.169 mmol, 0.1 equiv) and Et_3N (0.352 mL, 2.54 mmol, 1.5 equiv) in dry CH_2Cl_2 (3.5 mL) at 0 °C, was added pivaloyl chloride (0.252 mL, 2.03 mmol, 1.2 equiv) dropwise. The resulting solution was allowed to warm to rt and stirred overnight. The reaction mixture was concentrated under reduced pressure, the crude product was dissolved in Et_2O (15 mL) and washed with a saturated solution of NH_4Cl (15 mL). The organic layer was separated and the aqueous phase was extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column

[4] S. Islam and I. Larrosa, *Chem. Eur. J.*, 2013, **19**, 15093.

chromatography on silica gel (PE/EtOAc = 98:2) to afford **1l** (329 mg, 1.64 mmol, 97%) as a white solid. The spectral data are in agreement with the literature report.[4]

mp: 68-70 °C.

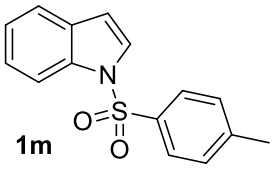
IR (neat): ν_{max} 2977, 2934, 1679, 1537, 1471, 1448, 1403, 1309, 1185, 1157, 1101, 1076 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (dq_{app}, *J* = 8.3, 0.8 Hz, 1H), 7.74 (d, *J* = 3.9 Hz, 1H), 7.57 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H), 7.37 (m, 1H), 7.28 (ddd, *J* = 7.7, 7.3, 1.1 Hz, 1H), 6.63 (dd, *J* = 3.9, 0.7 Hz, 1H), 1.53 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.1, 136.8, 129.4, 125.7, 125.1, 123.6, 120.5, 117.4, 108.3, 41.3, 28.7 (3C).

MS m/z (relative intensity): 201 ($M^{+\cdot}$, 24), 117 (66), 90 (14), 89 (16), 85 (13), 57 (100).

1-(4-Toluenesulfonyl)-1*H*-indole (1m)[5]



Formula: $C_{15}H_{13}NO_2S$

Mw = 271.33 $g.mol^{-1}$

To a suspension of NaH (81.1 mg, 2.03 mmol, 1.2 equiv) in anhydrous DMF (5 mL) at 0 °C, was added indole (200 mg, 1.69 mmol, 1.0 equiv) in one portion. The resulting mixture was stirred for 15 min at 0 °C, and a solution of tosyl chloride (358 mg, 1.86 mmol, 1.1 equiv) in anhydrous DMF (3 mL) was added dropwise to the mixture at 0 °C. The resulting solution was allowed to warm to rt and stirred for 6 h. The reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE/EtOAc = 98:2 to 95:5) to afford **1m** (438 mg, 1.61 mmol, 96%) as a pale yellow solid. The spectral data are in agreement with the literature report.[5]

mp: 81-83 °C.

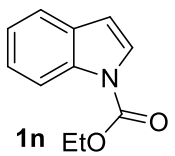
IR (neat): ν_{max} 2923, 1597, 1483, 1444, 1365, 1303, 1282, 1261, 1169, 1121, 1090, 1018 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.79-7.75 (m, 2H), 7.58 (d, *J* = 3.7 Hz, 1H), 7.53 (m, 1H), 7.32 (m, 1H), 7.25-7.19 (m, 3H), 6.66 (dd, *J* = 3.7, 0.8 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.0, 135.4, 134.9, 130.8, 130.0 (2C), 126.9 (2C), 126.4, 124.6, 123.4, 121.5, 113.6, 109.1, 21.6.

MS m/z (relative intensity): 271 ($M^{+\cdot}$, 16), 155 (23), 116 (46), 91 (100), 89 (44), 65 (36), 63 (27).

Ethyl-1-carboxylate-1*H*-indole (1n)[6]



Formula: $C_{11}H_{11}NO_2$

Mw = 189.21 $g.mol^{-1}$

To a suspension of NaH (202 mg, 5.07 mmol, 2.0 equiv) in dry THF (5 mL) at 0°C, was added indole (300 mg, 2.54 mmol, 1.0 equiv) in one portion. The reaction mixture was stirred at 0°C for 15 min,

[5] A. García-Rubia, B. Urones, R. Gómez Arrayás and J. C. Carretero, *Chem. Eur. J.*, 2010, **16**, 9676.

and ethyl chloroformate (0.375 mL, 3.8 mmol, 1.5 equiv) was added dropwise. The resulting solution was allowed to warm to rt and stirred for 6 h. The reaction mixture was diluted with H_2O (10 mL) and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (PE/EtOAc = 98:2) to afford **1n** (148 mg, 0.782 mmol, 31%) as a clear yellow oil. The spectral data are in agreement with the literature report.[6]

IR (neat): ν_{max} 2982, 1732, 1534, 1452, 1401, 1379, 1342, 1324, 1297, 1242, 1211, 1176, 1118, 1079 1044, 1016 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 3.7 Hz, 1H), 7.59 (ddd, *J* = 7.7, 1.3, 0.8 Hz, 1H), 7.35 (m, 1H), 7.26 (ddd, *J* = 7.7, 7.3, 1.1 Hz, 1H) 6.61 (dd, *J* = 3.7, 0.8 Hz, 1H), 4.51 (q, *J* = 7.1 Hz , 2H), 1.48 (t, *J* = 7.1 Hz , 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.2, 135.3, 130.6, 125.7, 124.5, 123.0, 121.1, 115.3, 108.0, 63.3, 14.5.

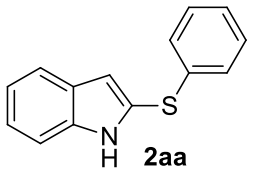
MS m/z (relative intensity): 189 ($M^{+\cdot}$, 39), 130 (66), 117 (100), 116 (37), 90 (42), 89 (57), 63 (35).

5. Synthesis of thioindoles (2aa-2na and 2ab-2ah)

General procedure

A 10 mL oven-dried vial, equipped with a rubber septum, was charged with indole **1** (1.0 equiv) and *N*-thiosuccinimide **6** (1.0 equiv). Dry CH_2Cl_2 (0.5 M) was added into the vial, followed by TFA (15 equiv), and the resulting solution was stirred at rt for 4-6 h. The reaction mixture was neutralized with a saturated solution of $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a mixture of PE/EtOAc or CH_2Cl_2/Et_2O as the eluent.

2-(Phenylsulfanyl)-1*H*-indole (2aa)[7]



2aa

Formula: $C_{14}H_{11}NS$

Mw = 225.31 $g.mol^{-1}$

Compound **2aa** was synthesized from indole **1a** (57.1 mg, 0.48 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (100 mg, 0.48 mmol). Purification by flash column chromatography (PE/EtOAc = 95:5) afforded **2aa** (86 mg, 0.38 mmol, 79%) as a white solid. The spectral data are in agreement with the literature report.[7]

mp: 74-75 °C.

IR (neat): ν_{max} 3410, 3051, 1578, 1473, 1440, 1396, 1337, 1316, 1281, 1091, 1023 cm^{-1}.

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[6] H-C. Hsu and D-R. Hou, *Tetrahedron Letters*, 2009, **50**, 7169.

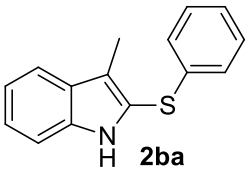
[7] P. Hamel, Y. Girard and J. G. Atkinson, *J. Org. Chem.*, 1992, **57**, 2694.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (br s, 1H), 7.54 (dd_{app}, *J* = 7.9, 1.0 Hz, 1H), 7.20 (dd_{app}, *J* = 8.2, 0.9 Hz, 1H), 7.16-7.03 (m, 7H), 6.78 (dd, *J* = 2.1, 0.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 136.8, 129.3 (2C), 128.6, 127.6 (2C), 126.4, 125.3, 123.4, 120.8, 120.4, 111.7, 111.0.

MS m/z (relative intensity): 225 ($M^{+\cdot}$, 100), 193 (22), 148 (14), 121 (17), 112 (13), 77 (18), 51 (12).

3-Methyl-2-(phenylsulfanyl)-1*H*-indole (2ba)[8]



2ba

Formula: $C_{15}H_{13}NS$
Mw = 239.34 g.mol^{-1}

Compound **2ba** was synthesized from 3-methylindole **1b** (48.4 mg, 0.36 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (75 mg, 0.36 mmol). Purification by flash column chromatography (PE/EtOAc = 95:5) afforded **2ba** (78 mg, 0.33 mmol, 90%) as a white solid. The spectral data are in agreement with the literature report.[8]

mp: 82-83 °C.

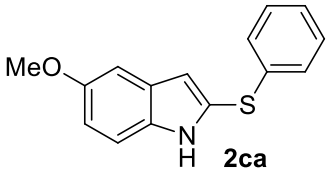
IR (neat): ν_{max} 3375, 3060, 2930, 2853, 1580, 1478, 1449, 1415, 1351, 1331, 1240, 1179, 1083 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (br s, 1H), 7.59 (ddd, *J* = 7.9, 1.1, 0.8 Hz, 1H), 7.28-7.08 (m, 6H), 7.05-7.02 (m, 2H), 2.39 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.2, 137.0, 129.2 (2C), 128.6, 126.6 (2C), 125.8, 123.6, 121.6, 120.0, 119.7, 119.6, 111.0, 9.6.

MS m/z (relative intensity): 239 ($M^{+\cdot}$, 100), 238 (48), 206 (12), 162 (16), 130 (22), 128 (17), 77 (24), 51 (16).

5-Methoxy-2-(phenylsulfanyl)-1*H*-indole (2ca)



2ca

Formula: $C_{15}H_{13}NOS$
Mw = 255.34 g.mol^{-1}

Compound **2ca** was synthesized from 5-methoxylindole **1c** (53.8 mg, 0.36 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (75 mg, 0.36 mmol). Purification by flash column chromatography (PE/EtOAc = 95:5) afforded **2ca** (74 mg, 0.29 mmol, 80%) as a yellowish solid.

mp: 61-65 °C.

IR (neat): ν_{max} 3334, 3056, 2955, 2916, 2828, 1624, 1580, 1510, 1478, 1436, 1344, 1296, 1215, 1196 1157, 1122, 1022 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (br s, 1H), 7.24-7.12 (m, 6H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.78 (dd, *J* = 2.1, 0.8 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.5, 137.0, 132.9, 129.3 (2C), 129.0, 127.5 (2C), 126.3, 125.6, 114.0, 111.8, 111.4, 102.0, 55.9.

MS m/z (relative intensity): 255 ($M^{+\cdot}$, 100), 240 (33), 212 (43), 135 (12), 77 (10), 51 (13).

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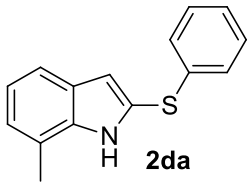
[8] F-L. Yang and S-K. Tian, *Angew. Chem., Int. Ed.*, 2013, **52**, 4929.

HRMS: calcd for $C_{15}H_{14}NOS\,(M+H)^+$: 256.0791, found : 256.0793.

7-Methyl-2-(phenylsulfanyl)-1*H*-indole (2da)



2da

Formula: $C_{15}H_{13}NS$
Mw = 239.34 g.mol^{-1}

Compound **2da** was synthesized from 7-methylindole **1d** (48.9 mg, 0.36 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (75 mg, 0.36 mmol). Purification by flash column chromatography (PE/EtOAc = 98:2) afforded **2da** (74 mg, 0.31 mmol, 85%) as a pale yellow solid.

mp: 58-60 °C.

IR (neat): ν_{max} 3406, 3052, 2915, 2853, 1581, 1477, 1440, 1415, 1338, 1248, 1101, 1084, 1023 cm^{-1}.

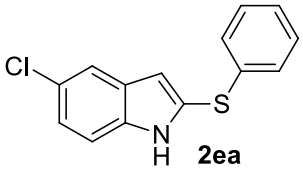
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (br s, 1H), 7.40 (m, 1H), 7.17-7.12 (m, 2H), 7.09-7.04 (m, 3H), 7.00-6.94 (m, 2H), 6.81 (d, *J* = 2.1 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.5, 137.1, 129.3 (2C), 128.1, 127.2 (2C), 126.2, 124.5, 123.9, 120.6, 120.3, 118.6, 112.7, 16.8.

MS m/z (relative intensity): 239 ($M^{+\cdot}$, 100), 238 (19), 223 (17), 207 (21), 206 (26), 162 (11), 112 (13), 91 (14), 77 (25), 51 (27).

HRMS: calcd for $C_{15}H_{14}NS\,(M+H)^+$: 240.0842, found : 240.0841.

5-Chloro-2-(phenylsulfanyl)-1*H*-indole (2ea)



2ea

Formula: $C_{14}H_{10}ClNS$
Mw = 259.75 g.mol^{-1}

Compound **2ea** was synthesized from 5-chloroindole **1e** (56.0 mg, 0.36 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (75 mg, 0.36 mmol). Purification by flash column chromatography (PE/EtOAc = 95:5) afforded **2ea** (78 mg, 0.30 mmol, 83%) as a white solid.

mp: 58-59 °C.

IR (neat): ν_{max} 3412, 3058, 1582, 1476, 1454, 1437, 1395, 1324, 1096, 1064, 1023 cm^{-1}.

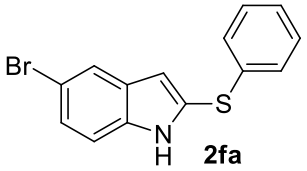
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (br s, 1H), 7.59 (m, 1H), 7.29-7.16 (m, 7H), 6.79 (dd, *J* = 2.1, 0.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.00, 135.95, 129.5, 129.4 (2C), 128.1 (2C), 127.5, 126.7, 126.1, 123.7, 120.1, 112.0, 110.7.

MS m/z (relative intensity): 259 ($M^{+\cdot}$, 100), 227 (14), 225 (13), 224 (67), 223 (58), 182 (15), 112 (53), 77 (21), 69 (13), 63 (12), 51 (47).

HRMS: calcd for $C_{14}H_{11}ClNS\,(M+H)^+$: 260.0295 and 262.0266, found : 260.0296 and 262.0266.

5-Bromo-2-(phenylsulfanyl)-1*H*-indole (2fa)



2fa

Formula: $C_{14}H_{10}BrNS$
Mw = 304.21 g.mol^{-1}

Compound **2fa** was synthesized from 5-bromoindole **1f** (71.7 mg, 0.36 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (75 mg, 0.36 mmol). Purification by flash column chromatography (PE/EtOAc = 95:5) afforded **2fa** (87 mg, 0.29 mmol, 79%) as a pale yellow solid.

mp: 61-63 °C.

IR (neat): ν_{max} 3409, 3058, 2925, 1581, 1476, 1450, 1434, 1392, 1323, 1297, 1215, 1095, 1050 cm^{-1}.

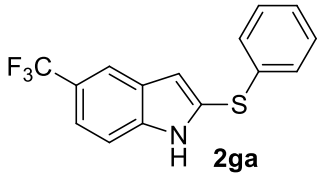
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (br s, 1H), 7.72 (d_{app}, *J* = 1.3 Hz, 1H), 7.29-7.12 (m, 7H), 6.76 (d, *J* = 1.3 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.2, 136.0, 130.2, 129.4 (2C), 128.1 (2C), 127.4, 126.7, 126.2, 123.2, 113.7, 112.4, 110.5.

MS m/z (relative intensity): 305 ($M^{+\cdot}$, 64), 303 (62), 226 (16), 225 (17), 224 (100), 223 (71), 191 (12), 147 (13), 146 (13), 120 (25), 113 (15), 112 (75), 103 (13), 88 (16), 77 (28), 76 (14), 69 (19), 65 (13), 63 (15), 62 (16), 51 (55), 50 (19).

HRMS: calcd for $C_{14}H_{11}BrNS$ $(M+H)^+$: 303.9790 and 305.9770, found : 303.9791 and 305.9770.

2-(Phenylsulfanyl)-5-(trifluoromethyl)-1*H*-indole (2ga)



2ga

Formula: $C_{15}H_{10}F_3NS$
Mw = 293.31 g.mol^{-1}

Compound **2ga** was synthesized from 5-trifluoromethylindole **1g** (95.4 mg, 0.50 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (103.6 mg, 0.50 mmol). Purification by flash column chromatography (PE/EtOAc = 95:5) afforded **2ga** (97 mg, 0.33 mmol, 66%) as a white solid.

mp: 74-78 °C.

IR (neat): ν_{max} 3412, 3064, 2925, 2851, 1579, 1478, 1440, 1404, 1344, 1329, 1267, 1185, 1158, 1098, 1052, 1023 cm^{-1}.

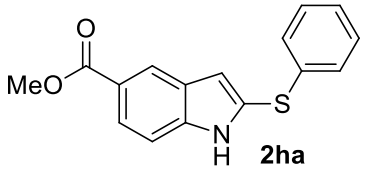
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16 (br s, 1H), 7.82 (d, *J* = 0.8 Hz, 1H), 7.36 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.26 (dd_{app}, *J* = 8.6, 0.6 Hz, 1H), 7.20-7.09 (m, 5H), 6.83 (dd, *J* = 2.1, 0.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.9, 135.6, 129.5 (2C), 128.36 (2C), 128.31, 127.9, 126.9, 125.2 (q, *J* = 271.6 Hz), 122.9 (q, *J* = 31.9 Hz), 120.0 (q, *J* = 3.4 Hz), 118.5 (q, *J* = 4.3 Hz), 111.7, 111.2.

MS m/z (relative intensity): 293 ($M^{+\cdot}$, 100), 292 (23), 274 (13), 273 (33), 261 (21), 224 (15), 223 (30), 216 (17), 145 (13), 137 (17), 112 (15), 77 (32), 69 (19), 65 (13), 51 (60), 50 (15).

HRMS: calcd for $C_{15}H_{11}F_3NS$ $(M+H)^+$: 294.0559, found : 294.0561.

Methyl-5-carboxylate-2-(phenylsulfanyl)-1*H*-indole (2ha)



2ha

Formula: $C_{16}H_{13}NO_2S$
Mw = 283.35 g.mol^{-1}

Compound **2ha** was synthesized from methyl-5-carboxylate indole **1h** (64.0 mg, 0.36 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (75 mg, 0.36 mmol). Purification by flash column chromatography (PE/EtOAc = 9:1 to 8:2) afforded **2ha** (62 mg, 0.22 mmol, 60%) as a white solid.

mp: 148-149 °C.

IR (neat): ν_{max} 3284, 2951, 1689, 1614, 1479, 1433, 1343, 1293, 1263, 1202, 1137 cm^{-1}.

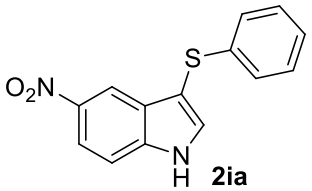
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (br s, 1H), 8.38 (m, 1H), 7.92 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.31 (dt_{app}, *J* = 8.6, 0.8 Hz, 1H), 7.28-7.17 (m, 5H), 6.93 (dd, *J* = 2.1, 0.9 Hz, 1H), 3.93 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.1, 140.2, 135.8, 129.4 (2C), 128.2 (2C) 128.1, 127.7, 126.8, 124.6, 123.7, 122.5, 112.3, 110.7, 52.1.

MS m/z (relative intensity): 283 ($M^{+\cdot}$, 100), 252 (39), 251 (17), 225 (13), 224 (60), 223 (50), 222 (13), 147 (16), 126 (20), 112 (14), 77 (26), 51 (29).

HRMS: calcd for $C_{16}H_{14}NO_2S$ $(M+H)^+$: 284.0740, found : 284.0743.

5-Nitro-3-(phenylsulfanyl)-1*H*-indole (2ia)[8]



2ia

Formula: $C_{14}H_{10}N_2O_2S$
Mw = 270.31 g.mol^{-1}

Compound **2ia** was synthesized from 5-nitroindole **1i** (82.7 mg, 0.50 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (103.6 mg, 0.50 mmol). Purification by flash column chromatography (PE/EtOAc = 9:1 to 7:3) afforded **2ia** (86 mg, 0.32 mmol, 64%) as a yellow solid. The spectral data are in agreement with the literature report.[8]

mp: 170-172 °C.

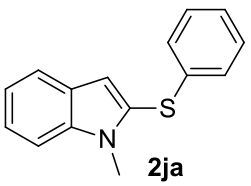
IR (neat): ν_{max} 3335, 2923, 2853, 1614, 1580, 1507, 1471, 1323, 1300, 1076 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.4 (br s, 1H), 8.25 (d, *J* = 2.2 Hz, 1H), 8.09 (s, 1H), 8.08 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.25-7.21 (m, 2H), 7.13-7.05 (m, 3H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 141.6, 140.0, 138.0, 136.6, 129.1 (2C) 128.2, 125.7 (2C), 125.4, 117.6, 114.8, 113.2, 102.7.

MS m/z (relative intensity): 270 ($M^{+\cdot}$, 100), 224 (34), 223 (37), 152 (12), 112 (23), 51 (14).

1-Methyl-2-(phenylsulfanyl)-1*H*-indole (2ja)[7]



2ja

Formula: $C_{15}H_{13}NS$
Mw = 239.34 g.mol^{-1}

Compound **2ja** was synthesized from 1-methylindole **1j** (49.0 mg, 0.36 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (75 mg, 0.36 mmol). Purification by flash column

chromatography (PE/EtOAc = 100:0 to 99:1) afforded **2ja** (70 mg, 0.29 mmol, 81%) as a white solid. The spectral data are in agreement with the literature report.[7]

mp: 76-78 °C.

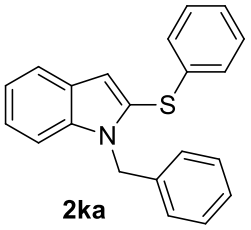
IR (neat): ν_{max} 3054, 2937, 1580, 1471, 1461, 1440, 1356, 1324, 1312, 1231, 1100, 1082, 1022 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (dt_{app}, *J* = 7.9, 0.9 Hz, 1H), 7.31-7.24 (m, 2H), 7.21-7.08 (m, 4H), 7.04-7.01 (m, 2H), 6.93 (d_{app}, *J* = 0.6 Hz, 1H), 3.66 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.8, 137.2, 129.3 (2C), 127.4, 127.2, 126.7 (2C), 125.9, 123.1, 121.0, 120.1, 111.9, 110.0, 30.0.

MS m/z (relative intensity): 239 ($M^{+\cdot}$, 100), 224 (16), 223 (15), 206 (13), 128 (10), 118 (15), 91 (14), 77 (13), 51 (12).

1-Benzyl-2-(phenylsulfanyl)-1*H*-indole (2ka)[9]



2ka

Formula: $C_{21}H_{17}NS$
Mw = 315.43 $g.mol^{-1}$

Compound **2ka** was synthesized from 1-benzylindole **1k** (79.7 mg, 0.38 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (79.7 mg, 0.38 mmol). Purification by flash column chromatography (PE 100%) afforded **2ka** (70 mg, 0.29 mmol, 81%) as a white solid. The spectral data are in agreement with the literature report.[9]

mp: 106-108 °C.

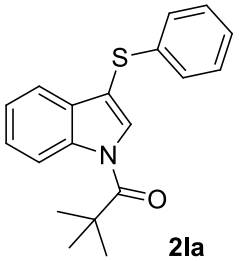
IR (neat): ν_{max} 3059, 2923, 2852, 1582, 1478, 1448, 1355, 1332, 1310, 1196, 1159, 1074 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (m, 1H), 7.23-7.04 (m, 11H), 7.01 (d, *J* = 0.6 Hz, 1H), 6.96-6.93 (m, 2H), 5.37 (s, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.5, 137.7, 136.9, 129.2 (2C), 128.6 (2C), 127.7, 127.6, 127.3, 127.1 (2C), 126.6 (2C), 126.1, 123.3, 121.1, 120.3, 112.7, 110.8, 47.3.

MS m/z (relative intensity): 315 ($M^{+\cdot}$, 24), 224 (14), 223 (17), 91 (100), 65 (20).

3-(Phenylsulfanyl)-1-(pivaloyl)-1*H*-indole (2la)



2la

Formula: $C_{19}H_{19}NOS$
Mw = 309.43 $g.mol^{-1}$

Compound **2la** was synthesized from 1-pivaloylindole **1l** (74 mg, 0.37 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (76.2 mg, 0.37 mmol). Purification by flash column chromatography (PE/EtOAc = 99:1) afforded **2la** (107 mg, 0.35 mmol, 94%) as a white solid.

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[9] P. Hamel, N. Zajac, J. G. Atkinson and Y. Girard, *J. Org. Chem.*, 1994, **59**, 6372.

mp: 80-84 °C.

IR (neat): ν_{max} 3052, 2980, 2933, 1699, 1582, 1528, 1476, 1446, 1401, 1304, 1221, 1168, 1156, 1084, 1022 cm^{-1}.

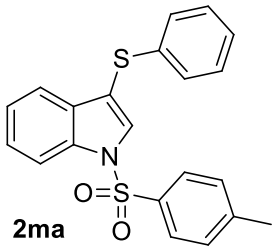
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.55 (dt_{app}, *J* = 8.4, 0.9 Hz, 1H), 8.02 (s, 1H), 7.48 (ddd, *J* = 7.8, 1.3, 0.7 Hz, 1H), 7.40 (ddd, *J* = 9.6, 7.2, 1.3 Hz, 1H), 7.29-7.18 (m, 5H), 7.14 (m, 1H), 1.55 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.9, 137.6, 136.7, 130.7, 129.7, 129.1 (2C), 127.1 (2C), 126.1, 125.8, 124.2, 119.7, 117.6, 110.7, 41.5, 28.8 (3C).

MS m/z (relative intensity): 309 ($M^{+\cdot}$, 13), 225 (24), 57 (100).

HRMS: calcd for $C_{19}H_{20}NOS$ $(M+H)^+$: 310.1260, found : 310.1260.

3-(Phenylsulfanyl)-1-[(4-toluenesulfonyl]-1*H*-indole (2ma)



Formula: $C_{21}H_{17}NO_2S_2$
Mw = 379.50 $g.mol^{-1}$

Compound **2ma** was synthesized from 1-(4-toluenesulfonyl)indole **1m** (108.5 mg, 0.4 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (82.9 mg, 0.4 mmol). Purification by flash column chromatography (PE/EtOAc = 95:5) afforded **2ma** (140 mg, 0.37 mmol, 92%) as a pale yellow solid.

mp: 79-81 °C.

IR (neat): ν_{max} 3131, 3052, 2923, 2933, 1596, 1582, 1493, 1442, 1372, 1263, 1172, 1127, 1108, 1090, 1046, 1017 cm^{-1}.

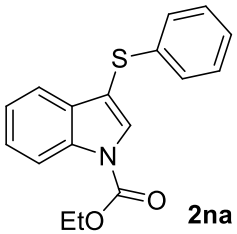
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (dt_{app}, *J* = 8.3, 0.8 Hz, 1H), 7.82 (s, 1H), 7.81-7.78 (m, 2H), 7.43 (dt_{app}, *J* = 7.9, 0.8 Hz, 1H), 7.34 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 1H), 7.26-7.08 (m, 8H), 2.36 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.5, 136.3, 135.5, 134.9, 131.1, 131.0, 130.1 (2C), 129.0 (2C), 127.3 (2C), 127.1 (2C), 125.9, 125.5, 123.9, 120.5, 113.9, 111.9, 21.7.

MS m/z (relative intensity): 379 ($M^{+\cdot}$, 16), 225 (19), 224 (100), 223 (51), 91 (24), 77 (22), 65 (19), 51 (17).

HRMS: calcd for $C_{21}H_{17}NO_2S_2Na$ $(M+Na)^+$: 402.0593, found : 402.0596.

Ethyl-1-carboxylate-3-(phenylsulfanyl)-1*H*-indole (2na)



Formula: $C_{17}H_{15}NO_2S$
Mw = 297.37 $g.mol^{-1}$

Compound **2na** was synthesized from ethyl-1-carboxylateindole **1n** (96.3 mg, 0.51 mmol) and 1-(phenylsulfanyl)pyrrolidine-2,5-dione **6a** (105.5 mg, 0.51 mmol). Purification by flash column chromatography (PE/EtOAc = 100:0 to 98:2) afforded **2na** (50 mg, 0.17 mmol, 33%) as a white solid.

mp: 73-74 °C.

IR (neat): ν_{max} 2926, 1745, 1580, 1530, 1473, 1451, 1402, 1376, 1348, 1300, 1245, 1217, 1073 cm^{-1}.

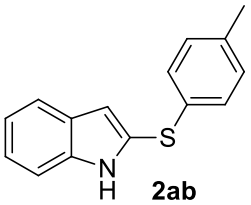
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.90 (s, 1H), 7.49 (ddd, *J* = 7.8, 1.2, 0.7 Hz, 1H), 7.37 (ddd, *J* = 8.4, 7.3, 1.1 Hz, 1H), 7.23 (ddd, *J* = 8.9, 7.0, 1.0 Hz, 1H), 7.20-7.17 (m, 4H), 7.10 (m, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.5, 136.9, 136.0, 130.9, 130.8, 129.0 (2C), 127.2 (2C), 125.7, 125.5, 123.6, 120.2, 115.5, 110.5, 63.8, 14.5.

MS m/z (relative intensity): 297 ($M^{+\cdot}$, 75), 225 (52), 224 (100), 223 (74), 193 (14), 165 (12), 148 (12), 121 (19), 120 (22), 77 (46), 51 (40).

HRMS: calcd for $C_{17}H_{16}NO_2S$ $(M+H)^+$: 298.0896, found : 298.0899.

2-[(4-Methylphenyl)sulfanyl]-1*H*-indole (2ab)[10]



2ab

Formula: $C_{15}H_{13}NS$
Mw = 239.34 g.mol^{-1}

Compound **2ab** was synthesized from indole **1a** (50 mg, 0.42 mmol) and 1-[(4-methylphenyl)sulfanyl]pyrrolidine-2,5-dione **6b** (93.5 mg, 0.42 mmol). Purification by flash column chromatography (PE/EtOAc = 98:2) afforded **2ab** (78 mg, 0.33 mmol, 77%) as a white solid. The spectral data are in agreement with the literature report.[10]

mp: 91-93 °C.

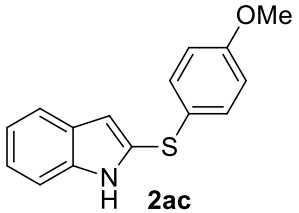
IR (neat): ν_{max} 3376, 3033, 2917, 1612, 1488, 1442, 1429, 1391, 1340, 1316, 1284, 1151, 1014 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (br s, 1H), 7.62 (ddd, *J* = 7.9, 1.8, 0.9 Hz, 1H), 7.30 (ddd, *J* = 8.2, 1.8, 0.9 Hz, 1H), 7.22 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.16-7.12 (m, 3H), 7.09-7.06 (m, 2H), 6.84 (dd, *J* = 2.1, 0.9 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 136.7, 132.7, 130.1 (2C), 128.6, 128.5 (2C), 126.4, 123.2, 120.7, 120.4, 110.9, 110.8, 21.1.

MS m/z (relative intensity): 239 ($M^{+\cdot}$, 100), 238 (20), 224 (17), 223 (20), 207 (20), 121 (14), 119 (13), 112 (12), 89 (13), 77 (16), 65 (11).

2-[(4-Methoxyphenyl)sulfanyl]-1*H*-indole (2ac)[7]



2ac

Formula: $C_{15}H_{13}NOS$
Mw = 255.34 g.mol^{-1}

Compound **2ac** was synthesized from indole **1a** (60 mg, 0.51 mmol) and 1-[(4-methoxyphenyl)sulfanyl]pyrrolidine-2,5-dione **6c** (120.3 mg, 0.51 mmol). Purification by flash column chromatography (PE/EtOAc = 95:5) afforded **2ac** (93 mg, 0.36 mmol, 72%) as a yellow oil. The spectral data are in agreement with the literature report.[7]

mp: 67-68 °C.

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[10] P. Hamel, *J. Org. Chem.*, 2002, **67**, 2854.

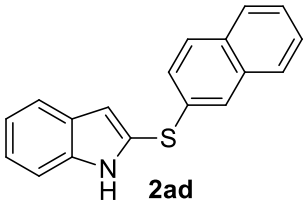
IR (neat): ν_{max} 3433, 3052, 3012, 2939, 1588, 1571, 1491, 1446, 1405, 1336, 1316, 1242, 1173, 1021, 1105 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (br s, 1H), 7.58 (dd_{app}, *J* = 7.9, 0.9 Hz, 1H), 7.27-7.23 (m, 3H), 7.18 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.11 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.83-6.79 (m, 2H), 6.75 (dd, *J* = 2.1, 0.9 Hz, 1H), 3.77 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 137.5, 131.4 (2C), 128.7, 127.9, 126.1, 123.0, 120.6, 120.3, 115.0 (2C), 110.8, 109.5, 55.5.

MS m/z (relative intensity): 255 ($M^{+\cdot}$, 100), 240 (35), 223 (16), 212 (12), 120 (12), 77 (12), 63 (13).

2-(Naphthalen-2-ylsulfanyl)-1*H*-indole (2ad)[7]



2ad

Formula: $C_{18}H_{13}NS$
Mw = 275.37 $g.mol^{-1}$

Compound **2ad** was synthesized from indole **1a** (47.4 mg, 0.4 mmol) and 1-(naphthalen-2-ylsulfanyl)pyrrolidine-2,5-dione **6d** (102.9 mg, 0.4 mmol). Purification by flash column chromatography (PE/EtOAc = 98:2 to 95:5) afforded **2ad** (93 mg, 0.34 mmol, 84%) as a white solid. The spectral data are in agreement with the literature report.[7]

mp: 116-118 °C.

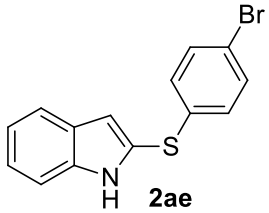
IR (neat): ν_{max} 3403, 3049, 1576, 1492, 1446, 1403, 1338, 1315, 1274, 1231, 1157 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (br s, 1H), 7.74 (m, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.65-7.62 (m, 3H), 7.45-7.38 (m, 2H), 7.28-7.20 (m, 3H), 7.14 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 6.90 (dd, *J* = 2.1, 0.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8, 133.9, 133.8, 132.0, 129.0, 128.6, 127.9, 127.3, 126.9, 126.08, 126.06, 125.9, 125.5, 123.4, 120.9, 120.5, 111.6, 111.0.

MS m/z (relative intensity): 275 ($M^{+\cdot}$, 100), 274 (39), 273 (17), 243 (14), 242 (14), 241 (13), 137 (16), 136 (13), 128 (13), 121 (16), 77 (15).

2-[(4-bromophenyl)sulfanyl]-1*H*-indole (2ae)



2ae

Formula: $C_{14}H_{10}BrNS$
Mw = 304.21 $g.mol^{-1}$

Compound **2ae** was synthesized from indole **1a** (50 mg, 0.42 mmol) and 1-[(4-bromophenyl)sulfanyl]pyrrolidine-2,5-dione **6e** (120.9 mg, 0.42 mmol). Purification by flash column chromatography (PE/EtOAc = 98:2) afforded **2ae** (119 mg, 0.39 mmol, 93%) as a white solid.

mp: 112-113 °C.

IR (neat): ν_{max} 3376, 3071, 2924, 1468, 1441, 1385, 1340, 1287, 1082, 1003 cm^{-1}.

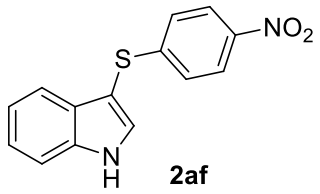
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (br s, 1H), 7.65 (ddd, *J* = 7.9, 1.1, 0.8 Hz, 1H), 7.37-7.32 (m, 3H), 7.26 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.17 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.02 (m, 2H), 6.89 (dd, *J* = 2.1, 0.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8, 136.2, 132.3 (2C), 128.9 (2C), 128.5, 124.4, 123.7, 121.0, 120.6, 120.1, 112.2, 111.1.

MS m/z (relative intensity): 303 ($M^{+\cdot}$, 83), 273 (15), 271 (15), 224 (53), 223 (75), 191 (15), 148 (49), 121 (46), 120 (14), 113 (15), 112 (100), 108 (15), 104 (20), 89 (40), 77 (55), 76 (40), 75 (27), 74 (12), 69 (18), 63 (40), 62 (13), 51 (24), 50 (38).

HRMS: calcd for $C_{14}H_{11}BrNS\,(M+H)^+$: 303.9790 and 305.9770, found : 303.9791 and 305.9767.

3-[(4-Nitrophenyl)sulfanyl]-1*H*-indole (2af)[8]



2af

Formula: $C_{14}H_{10}N_2O_2S$
Mw = 270.31 g.mol^{-1}

Compound **2af** was synthesized from indole **1a** (88.8 mg, 0.75 mmol) and 1-[(4-nitrophenyl)sulfanyl]pyrrolidine-2,5-dione **6f** (189.2 mg, 0.75 mmol). Purification by flash column chromatography (PE/EtOAc = 9:1 to 8:2) afforded **2af** (62 mg, 0.23 mmol, 30%) as a yellow solid. The spectral data are in agreement with the literature report.[8]

mp: 171-173 °C.

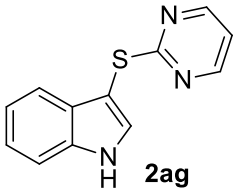
IR (neat): ν_{max} 3395, 3095, 2913, 1720, 1577, 1505, 1474, 1454, 1406, 1332, 1237, 1085, 1009 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (br s, 1H), 8.02-7.98 (m, 2H), 7.55-7.50 (m, 3H), 7.32 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.20 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.15-7.11 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.0, 145.0, 136.7, 131.4, 128.5, 125.2 (2C), 124.0 (2C), 123.7, 121.5, 119.3, 112.1, 100.2.

MS m/z (relative intensity): 270 ($M^{+\cdot}$, 100), 224 (36), 223 (47), 191 (22), 148 (48), 121 (18), 112 (21), 77 (33), 63 (14), 50 (15).

3-(Pyrimidin-2-ylsulfanyl)-1*H*-indole (2ag)



2ag

Formula: $C_{12}H_9N_3S$
Mw = 227.29 g.mol^{-1}

Compound **2ag** was synthesized from indole **1a** (48.5 mg, 0.4 mmol) and 1-(pyrimidin-2-ylsulfanyl)pyrrolidine-2,5-dione **6g** (83.7 mg, 0.4 mmol). Purification by flash column chromatography (CH_2Cl_2/Et_2O = 100:0 to 9:1) afforded **2ag** (55 mg, 0.24 mmol, 60%) as a pale orange solid.

mp: 262-266 °C.

IR (neat): ν_{max} 3158, 3112, 2913, 1562, 1551, 1454, 1426, 1378, 1183, 1126, 1104, 1006 cm^{-1}.

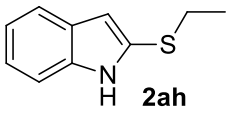
^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.64 (br s, 1H), 8.51 (d, *J* = 4.8 Hz, 2H), 7.71 (d, *J* = 2.6 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.19-7.15 (m, 2H), 7.05 (td_{app}, *J* = 7.5, 0.9 Hz, 1H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 172.2, 157.8 (2C), 136.6, 132.4, 129.2, 121.9, 120.0, 118.5, 117.5, 112.2, 97.8.

MS m/z (relative intensity): 227 ($M^{+\cdot}$, 100), 226 (45), 194 (12), 169 (25), 148 (38), 121 (27), 104 (16), 77 (44), 53 (13).

HRMS: calcd for $C_{12}H_{10}N_3S$ $(M+H)^+$: 228.0590, found : 228.0590.

2-(Ethylsulfanyl)-1*H*-indole (2ah)[11]



2ah

Formula: $C_{10}H_{11}NS$
Mw = 177.27 g.mol^{-1}

Compound **2ah** was synthesized from indole **1a** (60 mg, 0.51 mmol) and 1-(ethylsulfanyl)pyrrolidine-2,5-dione **6h** (80.7 mg, 0.51 mmol). Purification by flash column chromatography (PE/EtOAc = 95:5) afforded **2ah** (33 mg, 0.19 mmol, 37%) as a yellowish oil. The spectral data are in agreement with the literature report.[11]

IR (neat): ν_{max} 3398, 3053, 2964, 2925, 2869, 1443, 1397, 1340, 1317, 1282, 1260, 1229, 1011 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (br s, 1H), 7.59 (ddd, *J* = 8.2, 1.9, 0.8 Hz, 1H), 7.32 (ddd, *J* = 8.2, 1.8, 1.1 Hz, 1H), 7.21 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.13 (ddd, *J* = 8.2, 7.1, 0.9 Hz, 1H), 6.67 (dd, *J* = 2.1, 0.9 Hz, 1H), 2.86 (q, *J* = 7.3 Hz, 2H), 1.31 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.1, 128.80, 128.79, 122.6, 120.3, 120.2, 110.6, 108.9, 30.9, 15.3.

MS m/z (relative intensity): 177 ($M^{+\cdot}$, 86), 149 (68), 148 (100), 121 (22), 117 (19), 104 (13), 89 (13), 77 (29), 63 (11).

6. References

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[2] S. Savarin, J. Srogl, L. S. Liebeskind, *Org. Lett.*, 2002, **4**, 4309.

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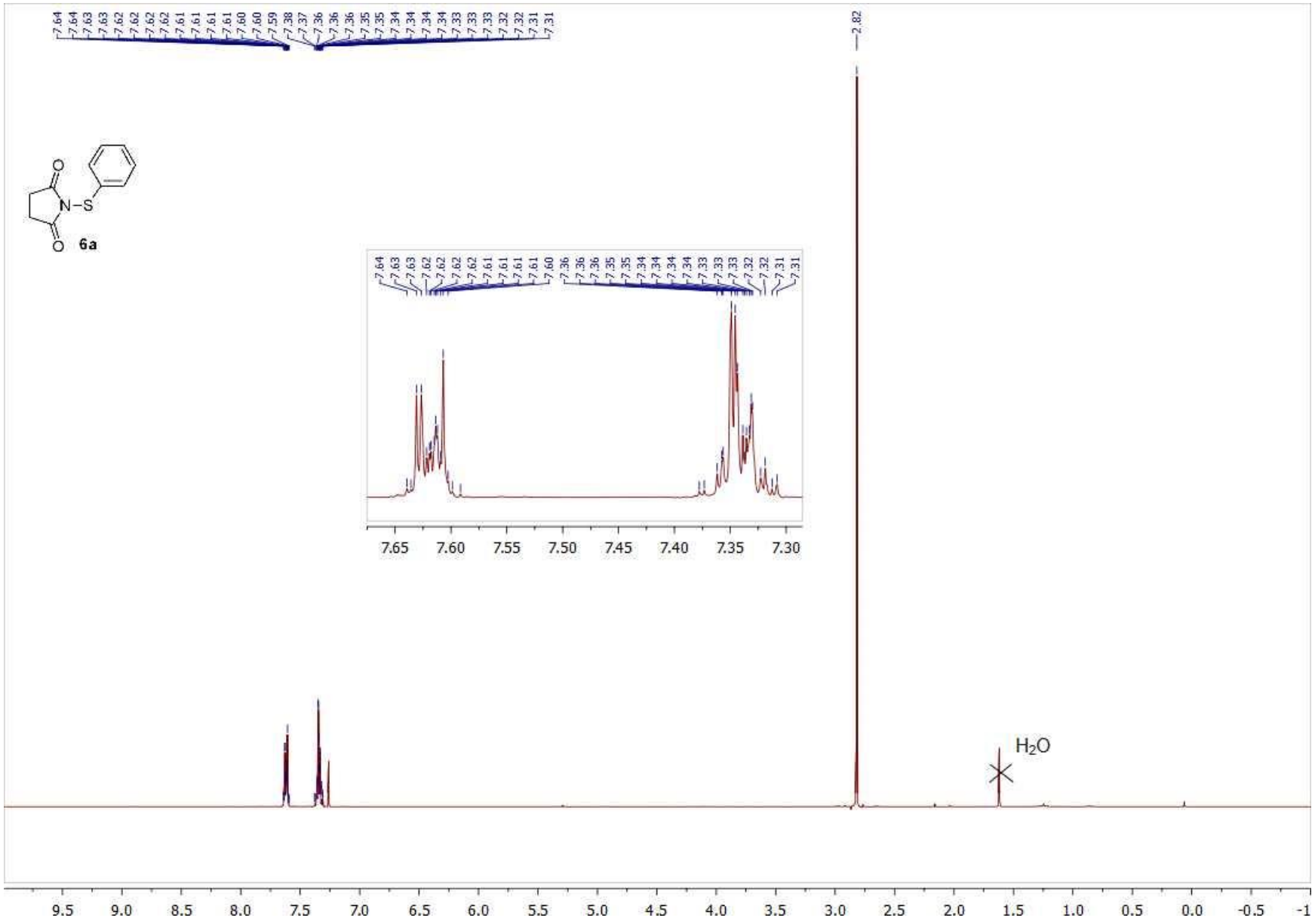
[9] P. Hamel, N. Zajac, J. G. Atkinson and Y. Girard, *J. Org. Chem.*, 1994, **59**, 6372.

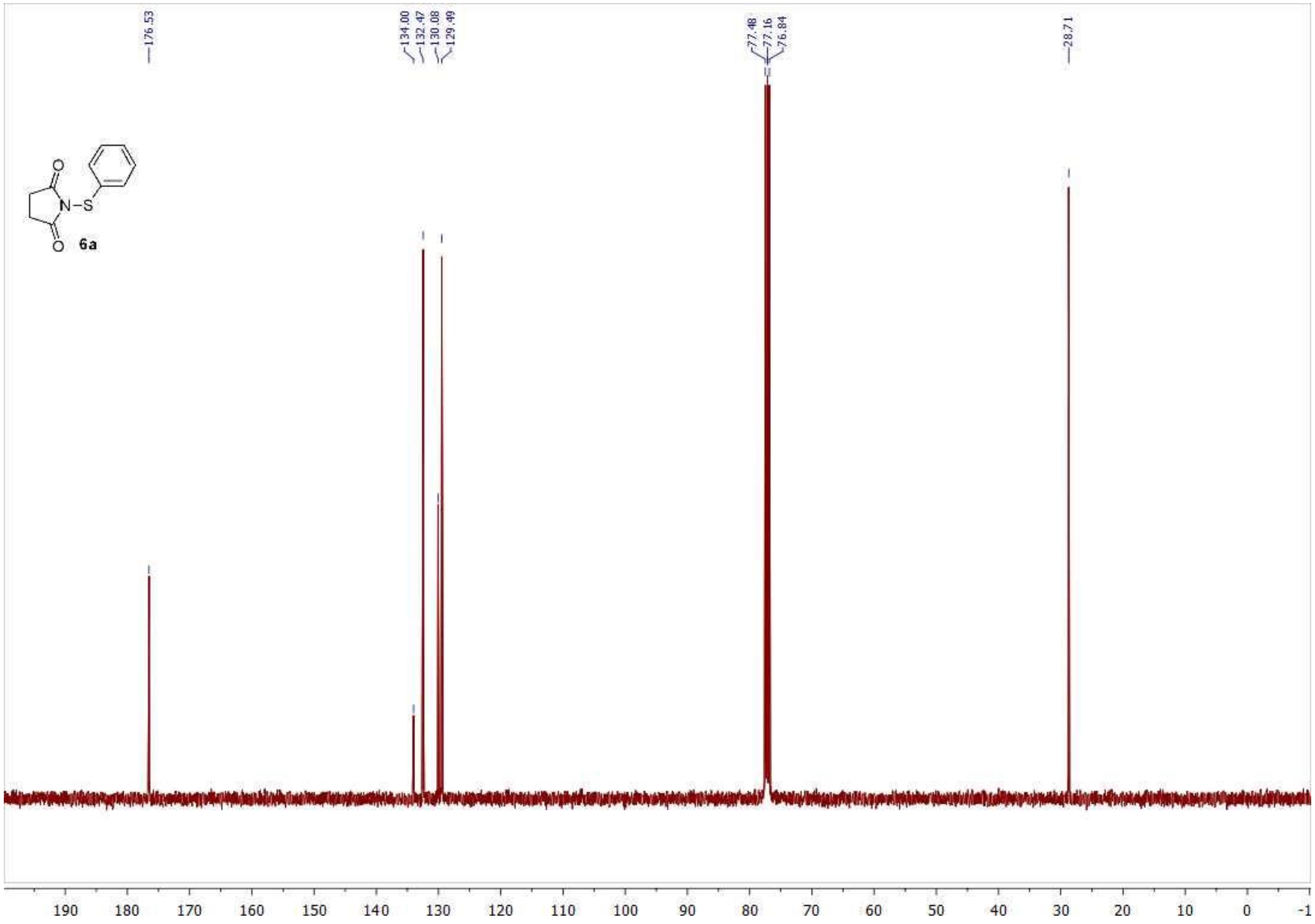
[10] P. Hamel, *J. Org. Chem.*, 2002, **67**, 2854.

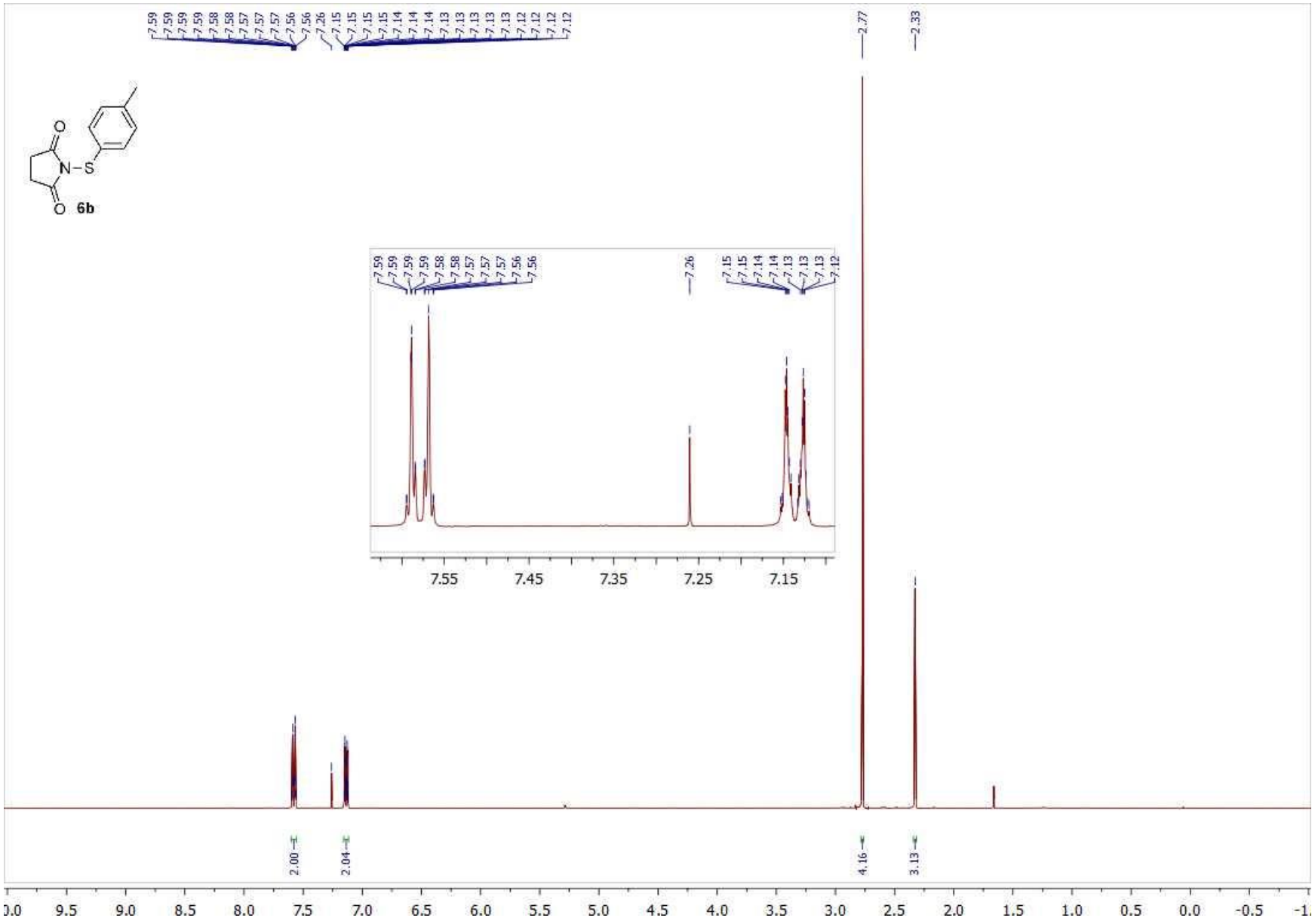
[11] M. Nakagawa and T. Hino, *Tetrahedron*, 1970, **26**, 4491.

[11] M. Nakagawa and T. Hino, *Tetrahedron*, 1970, **26**, 4491.

7. ^{1}H and ^{13}C NMR spectra of *N*-thiosuccinimides (6a-6h)


7.64 7.64 7.63 7.63 7.62 7.62 7.62 7.62 7.61 7.61 7.61 7.61 7.60 7.60 7.59 7.38 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31
2.82
O
N–S
O
6a
7.64 7.63 7.63 7.62 7.62 7.62 7.61 7.61 7.61 7.60 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.31
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30
H2O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1


176.53
134.00
132.47
130.08
129.49
77.48
77.16
76.84
28.71
N–S
O
O
6a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


6b
7.59
7.59
7.59
7.59
7.58
7.58
7.57
7.57
7.57
7.56
7.56
7.26
7.15
7.15
7.15
7.14
7.14
7.13
7.13
7.13
7.13
7.12
7.12
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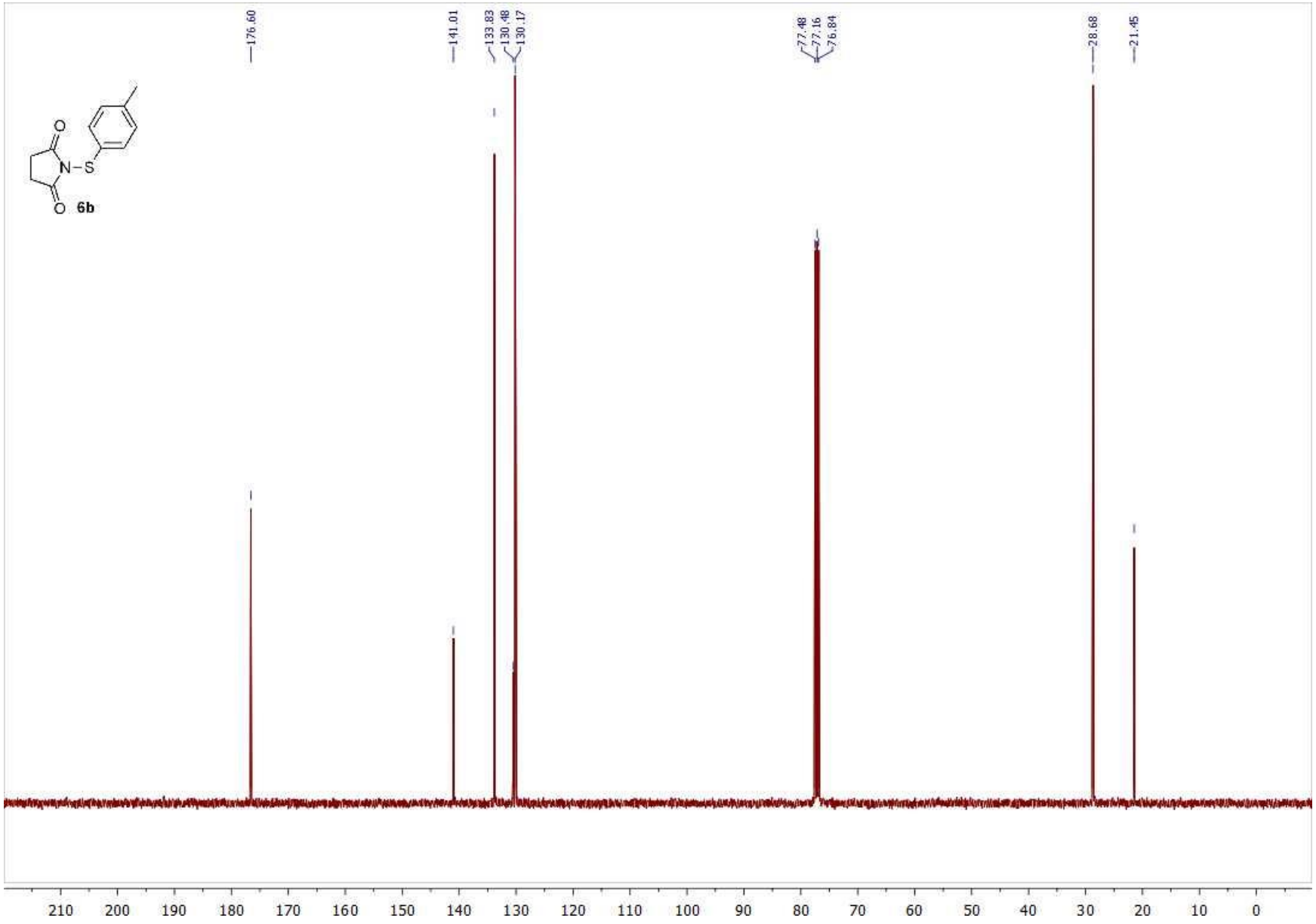
7.25
7.15
2.00
2.04
4.16
3.13


176.60
141.01
133.83
130.48
130.17
77.48
77.16
76.84
28.68
21.45
N–S
O
O
6b
210
200
190
180
170
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150
140
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60
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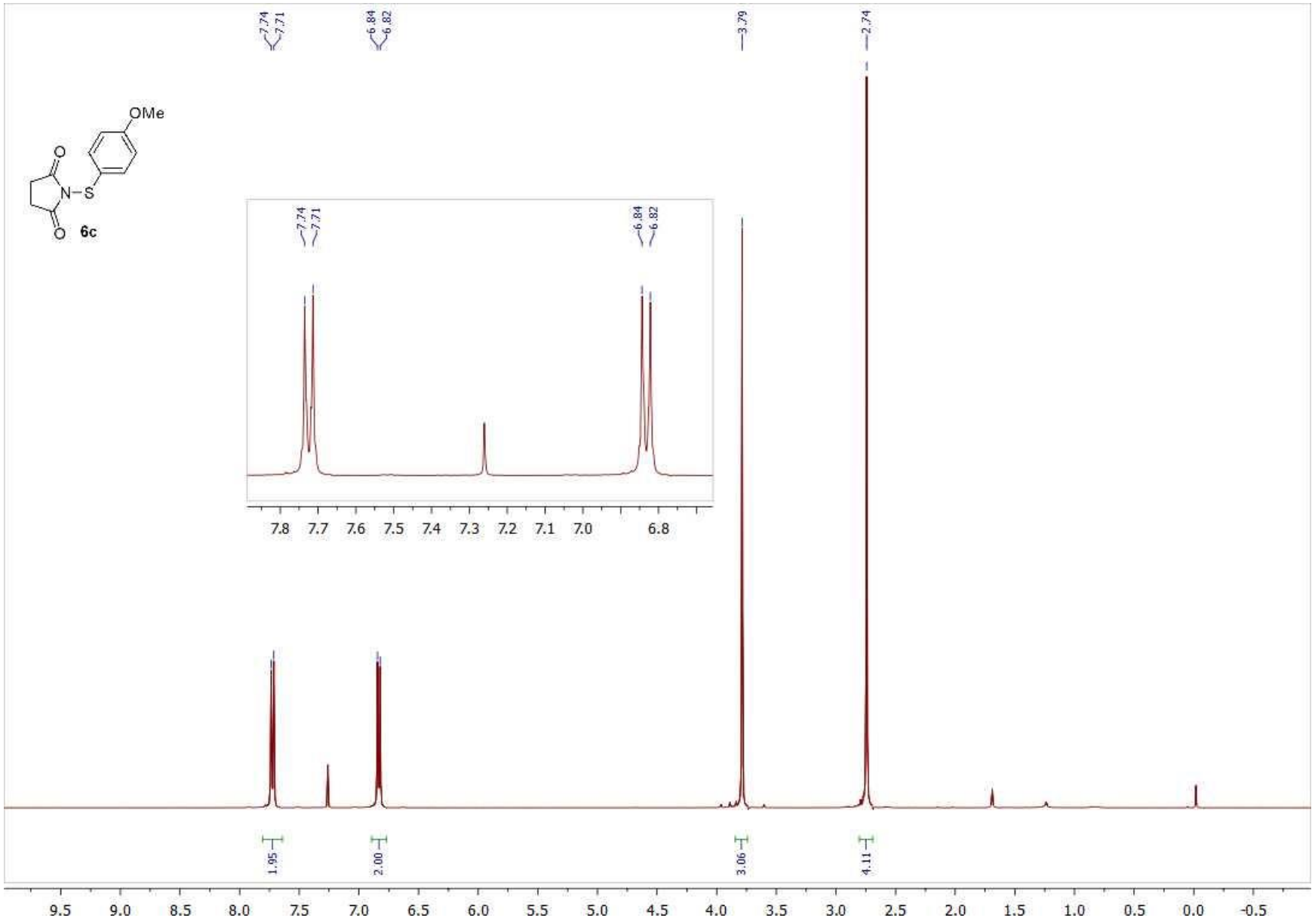
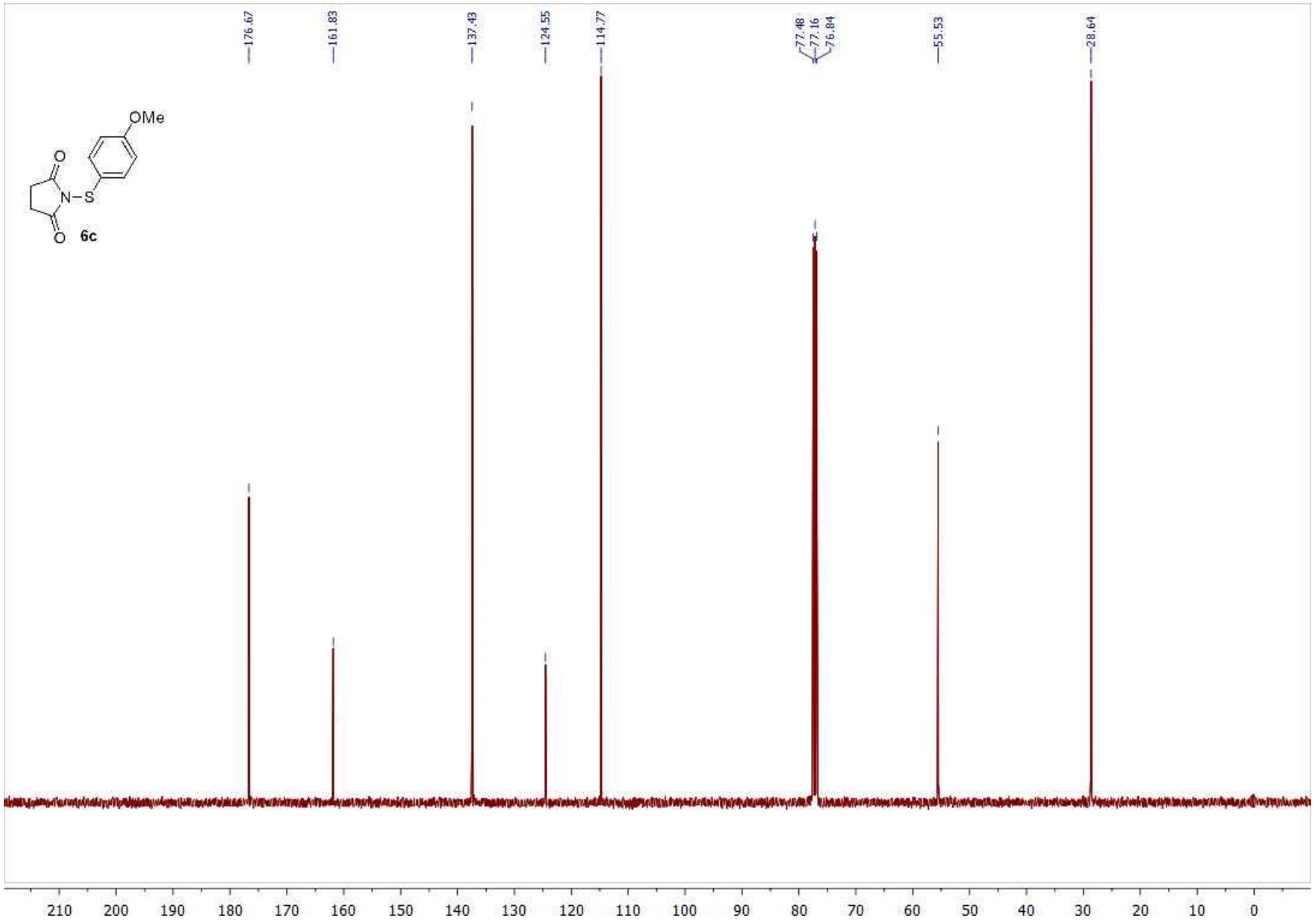
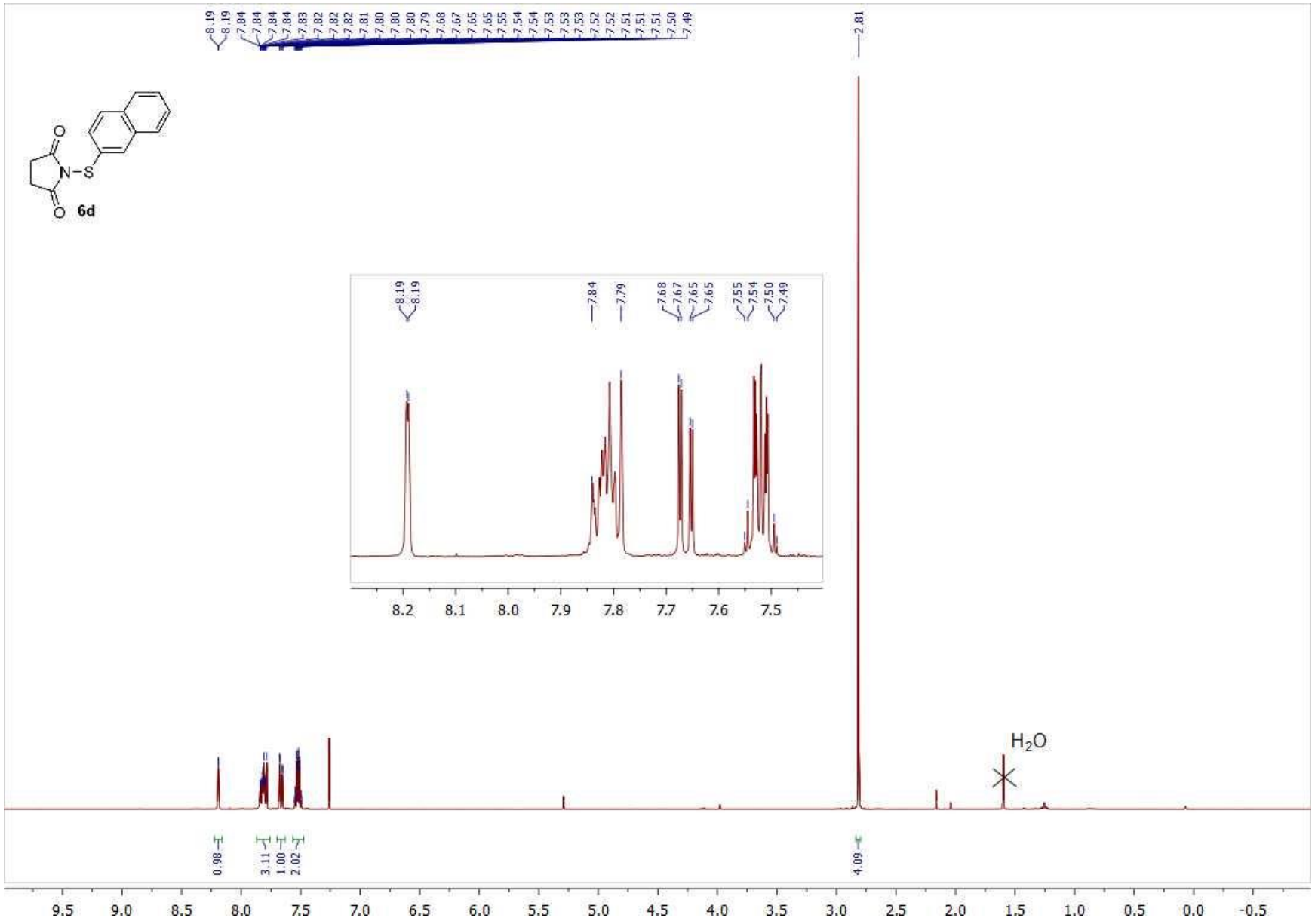
30
20
10
0


7.74
7.71
6.84
6.82
3.79
2.74
OMe
O
N–S
O
6c
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.8
1.95
2.00
3.06
4.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


176.67
161.83
137.43
124.55
114.77
77.48
77.16
76.84
55.53
28.64
OMe
O
N–S
O
6c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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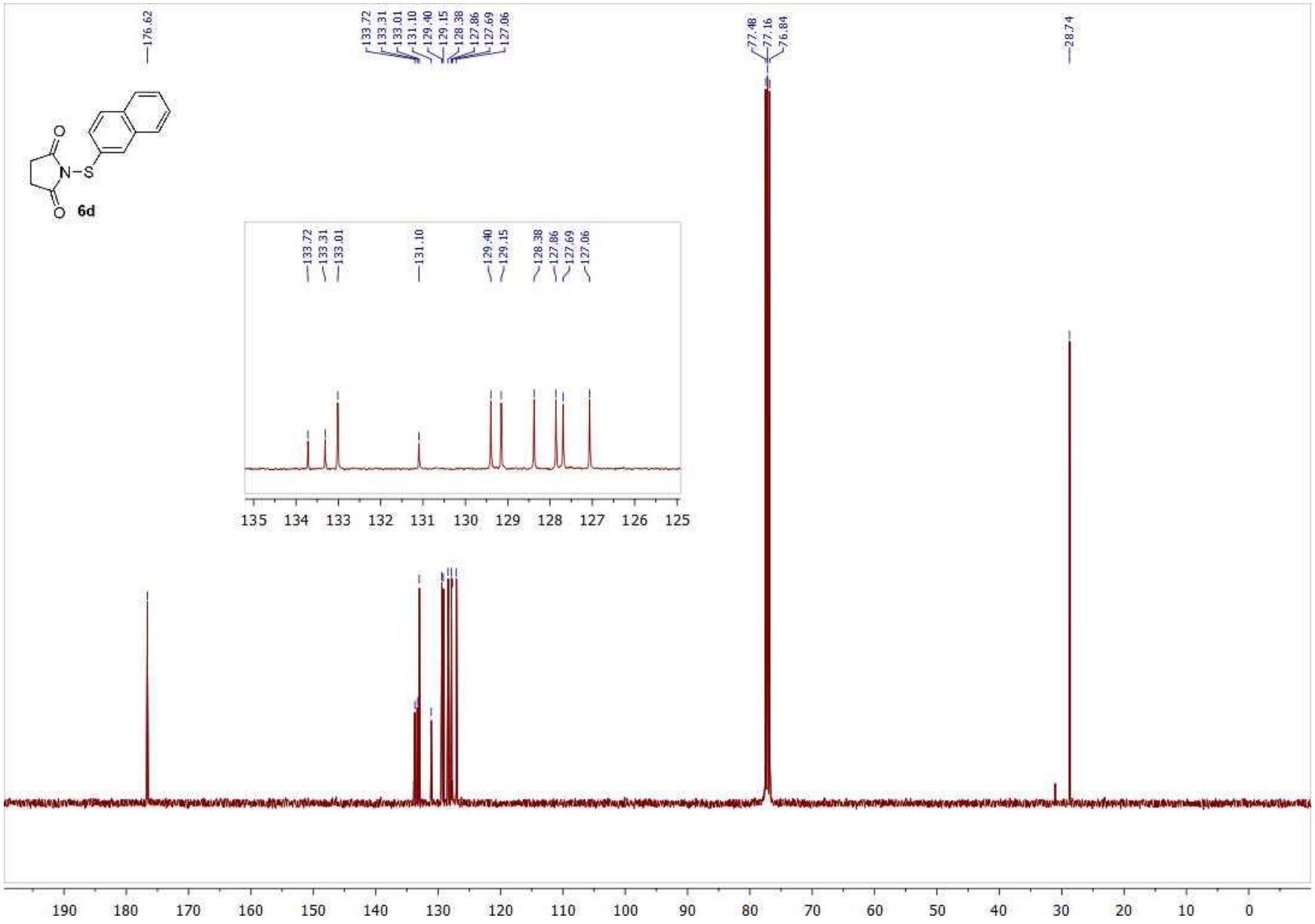
8.19
7.84
7.84
7.84
7.84
7.83
7.82
7.82
7.82
7.81
7.80
7.80
7.80
7.79
7.68
7.67
7.65
7.55
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.51
7.51
7.50
7.49
2.81
O
N–S
O
6d
8.19
8.19
7.84
7.79
7.68
7.67
7.65
7.65
7.55
7.54
7.50
7.49
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
H2O
0.98
3.11
1.00
2.02
4.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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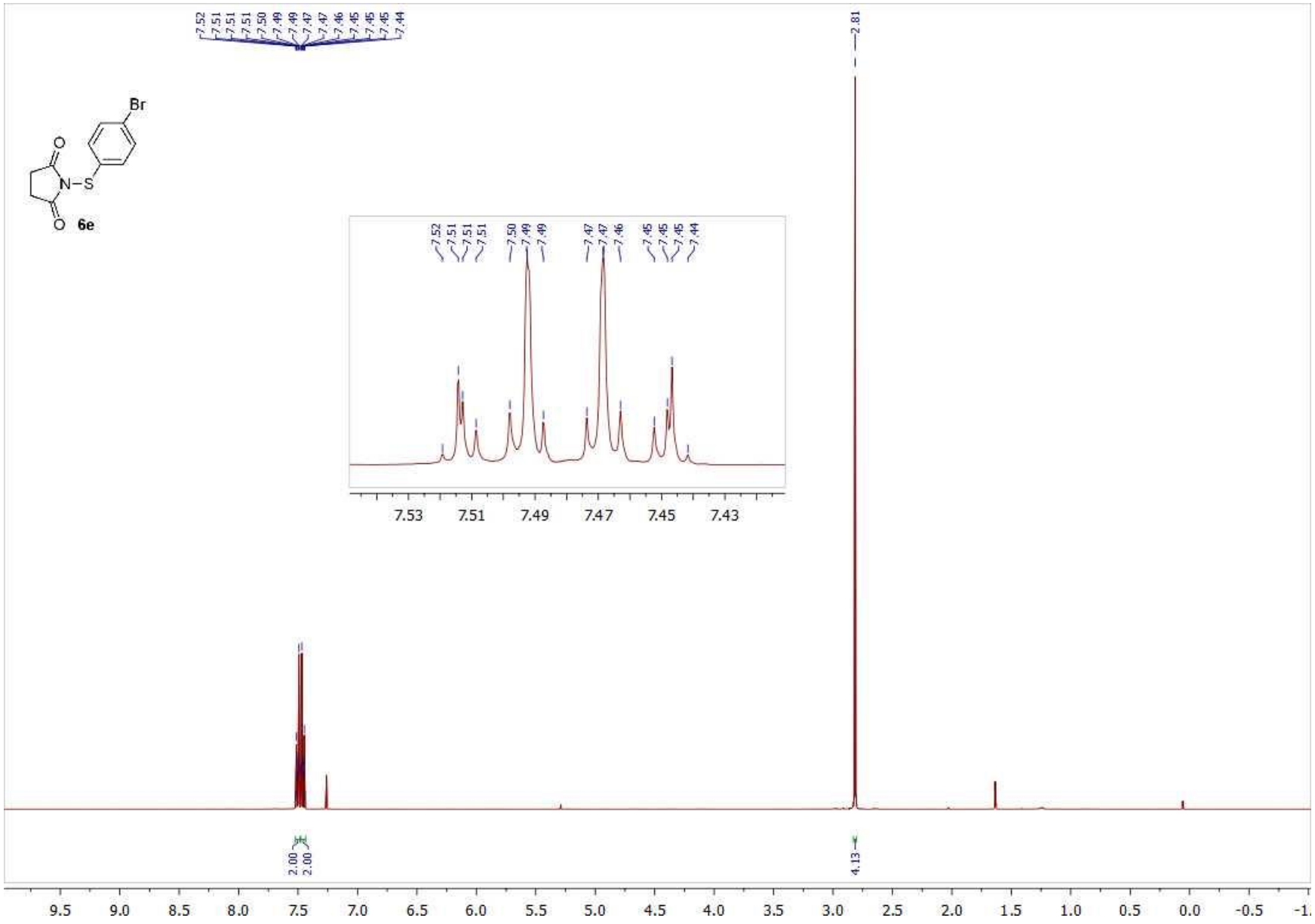
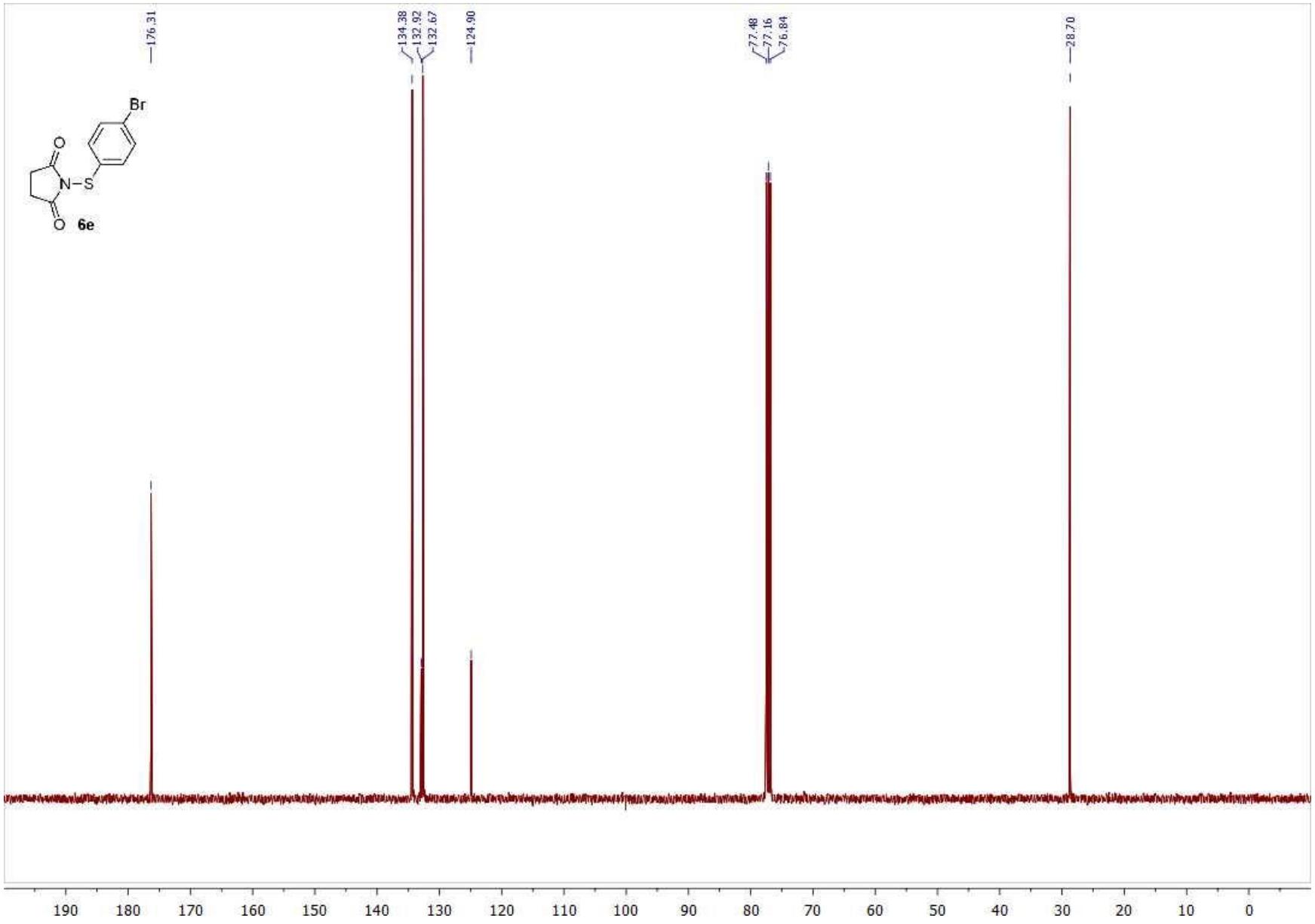
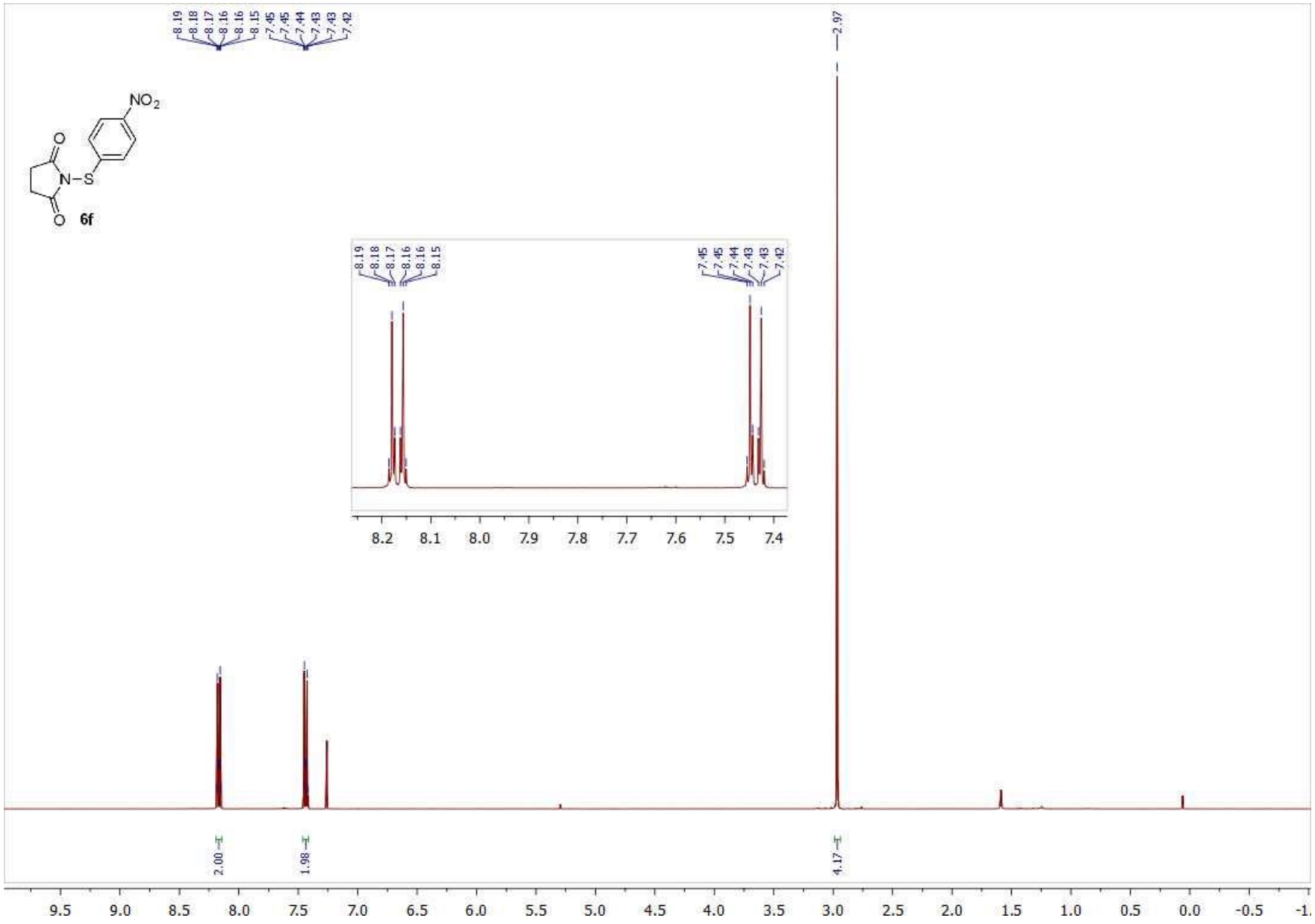
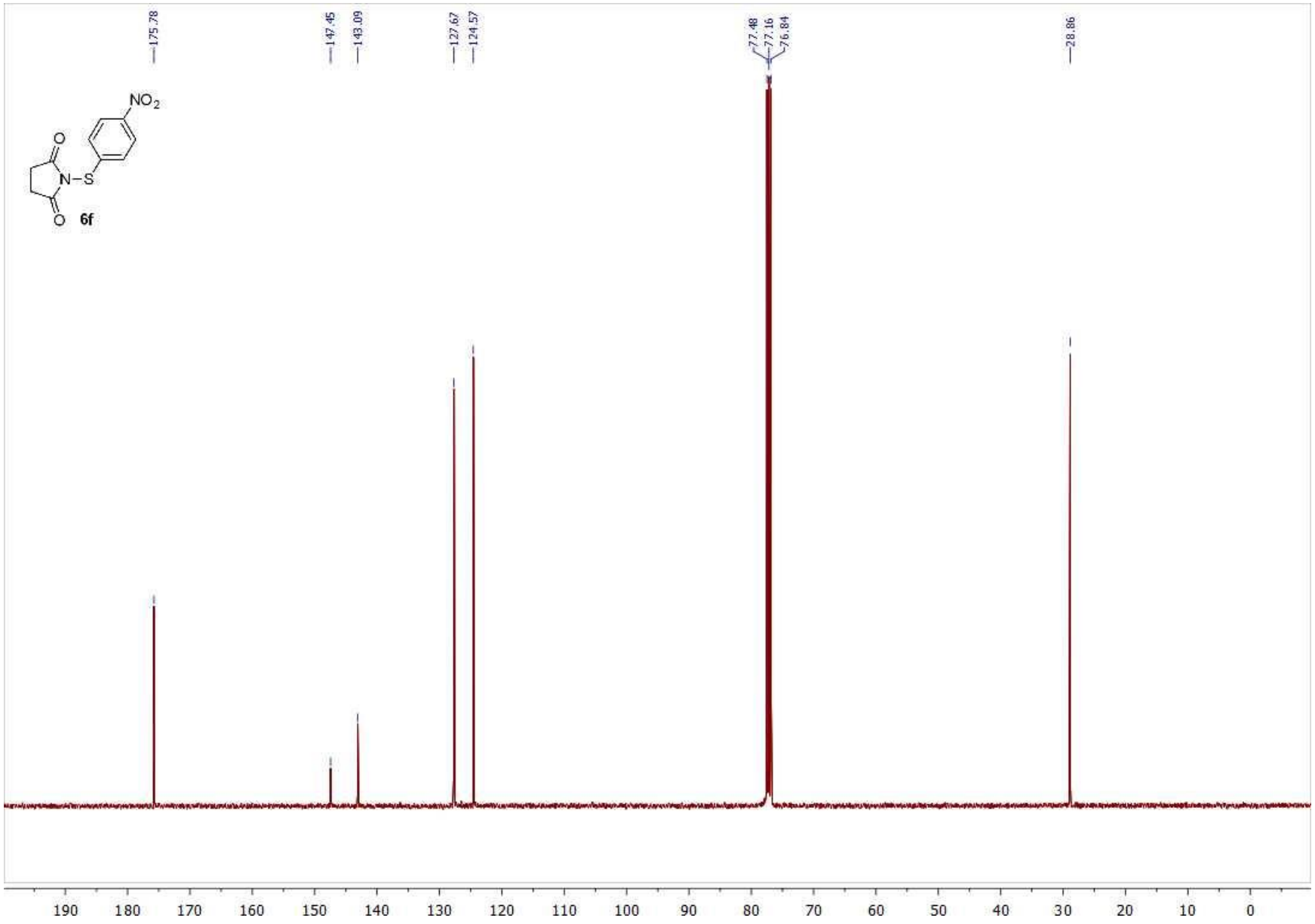
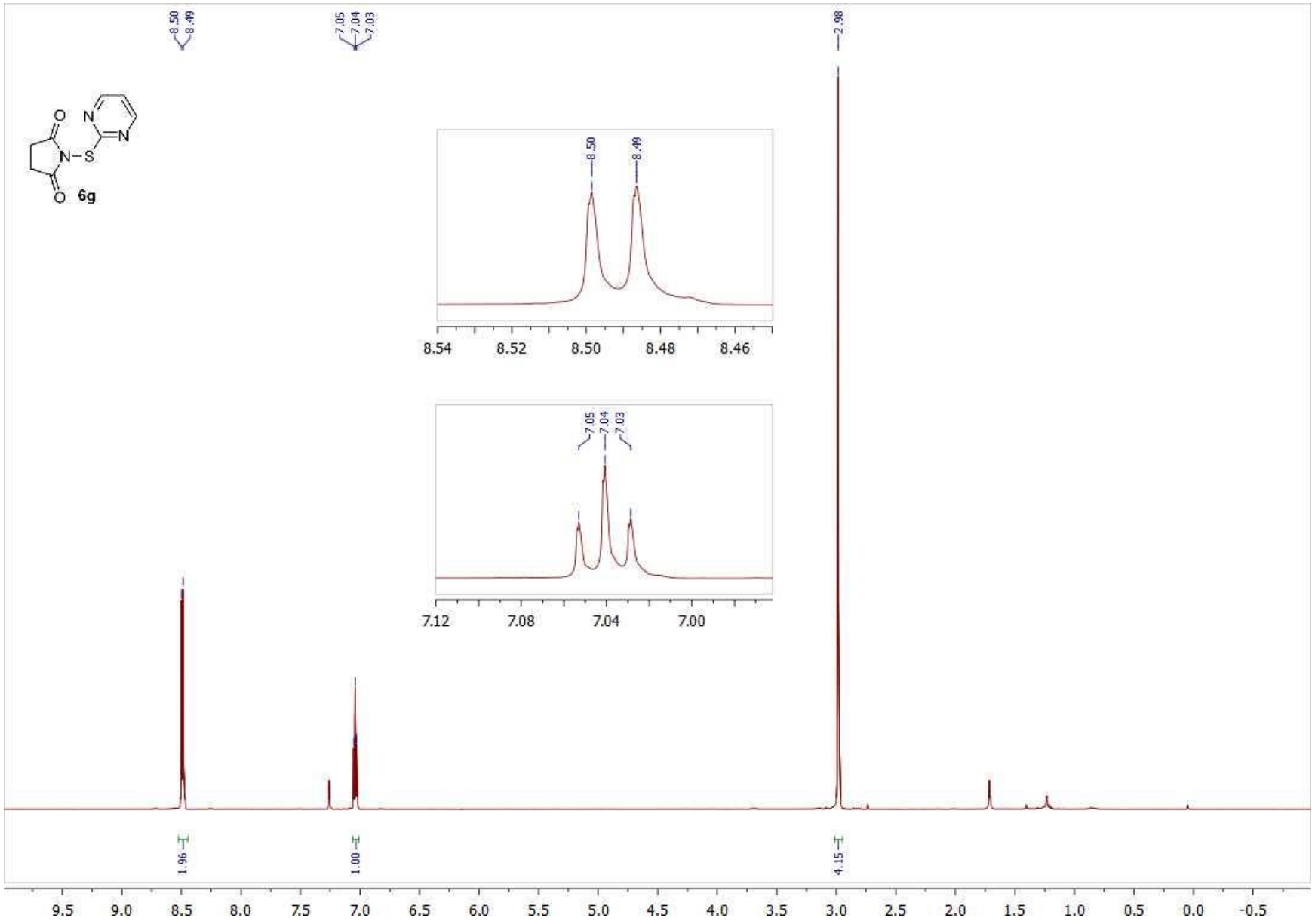
133.72
133.31
133.01
131.10
129.40
129.15
128.38
127.86
127.69
127.06
77.48
77.16
76.84
28.74
O
N–S
O
6d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
135 134 133 132 131 130 129 128 127 126 125

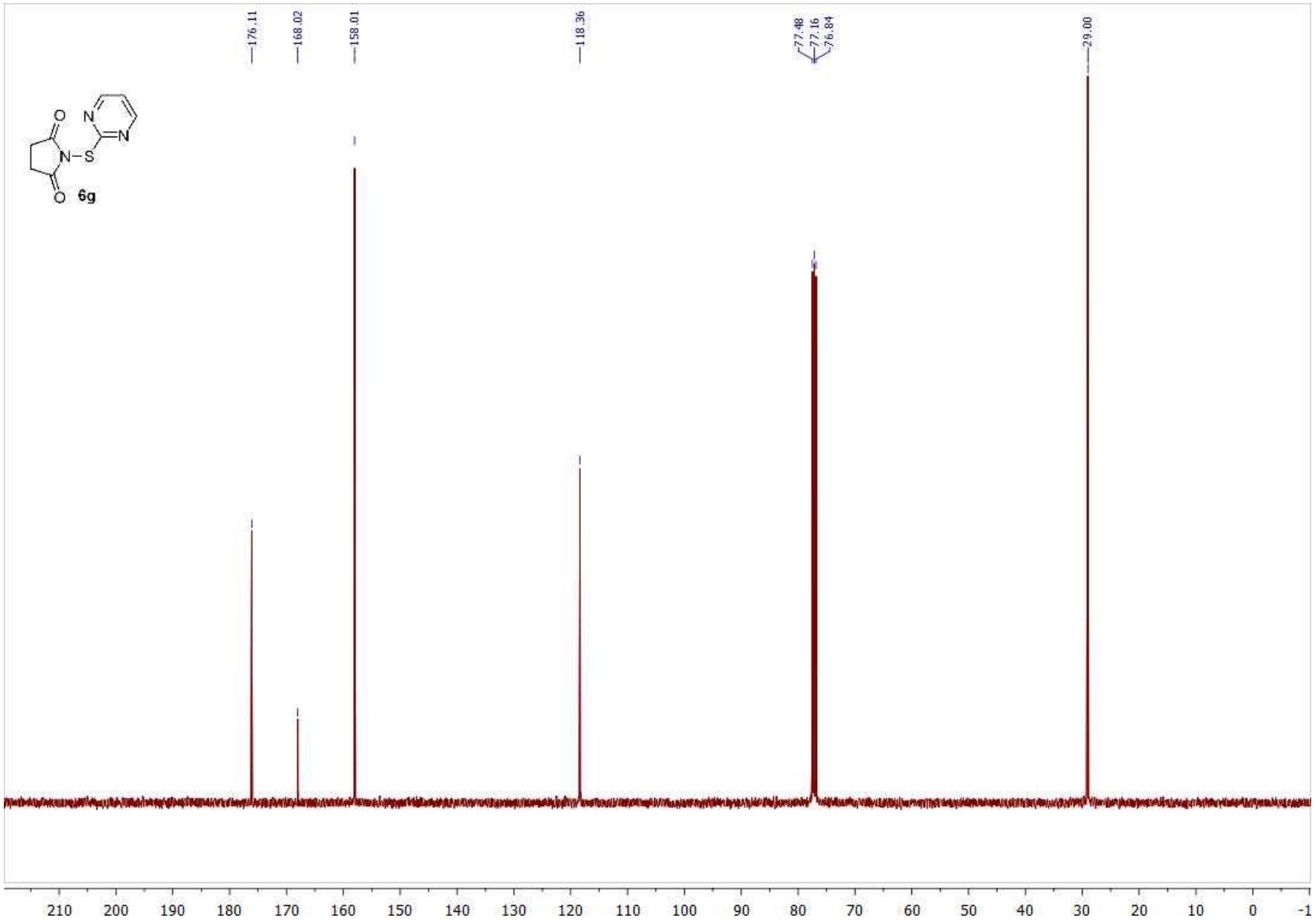

Br
O
N–S
O
6e
7.52
7.51
7.51
7.51
7.50
7.49
7.49
7.47
7.47
7.46
7.45
7.45
7.45
7.44
2.81
7.53
7.51
7.49
7.47
7.45
7.43
2.00
2.00
4.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

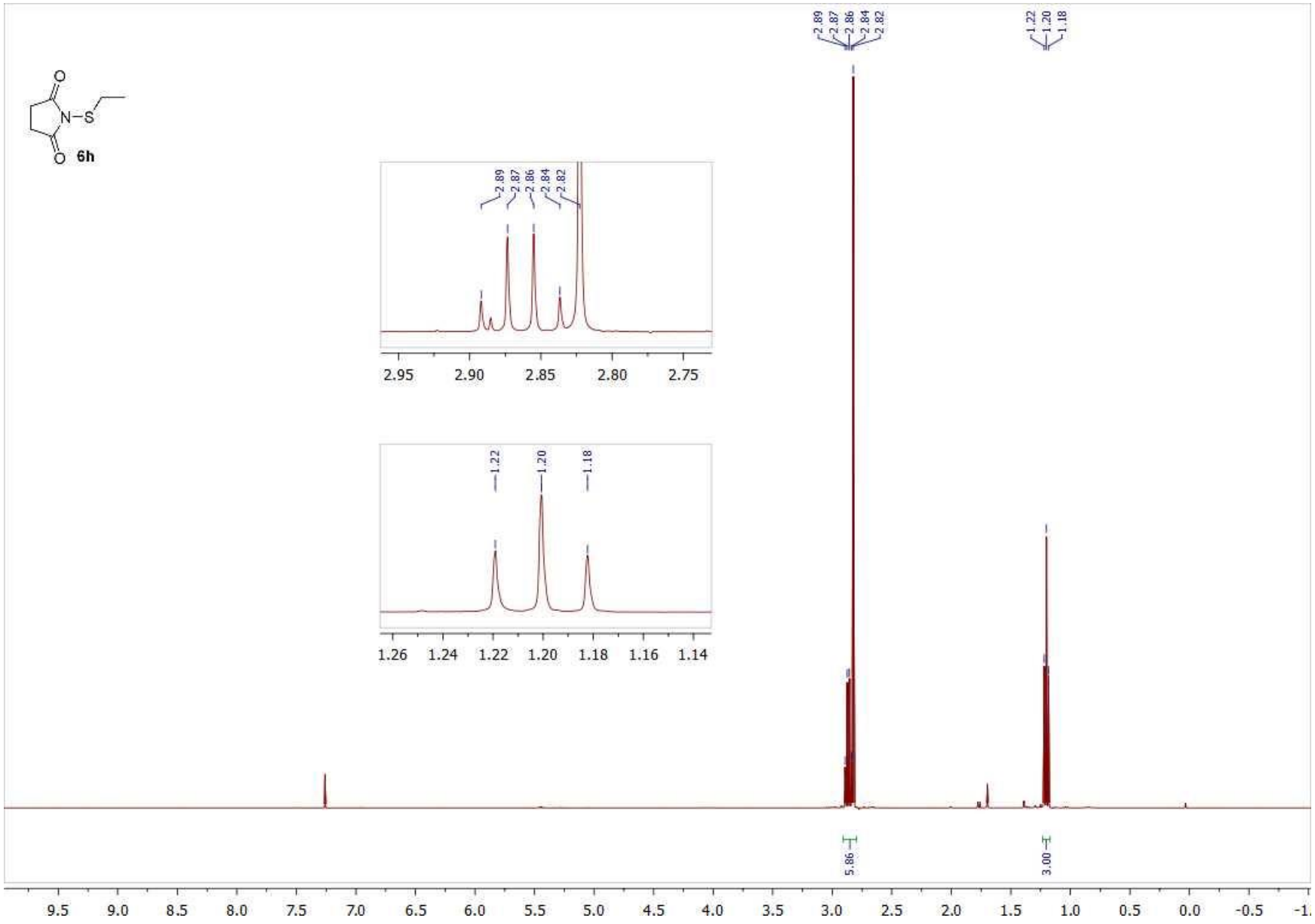

176.31
134.38
132.92
132.67
124.90
77.48
77.16
76.84
28.70
Br
O
N–S
O
6e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

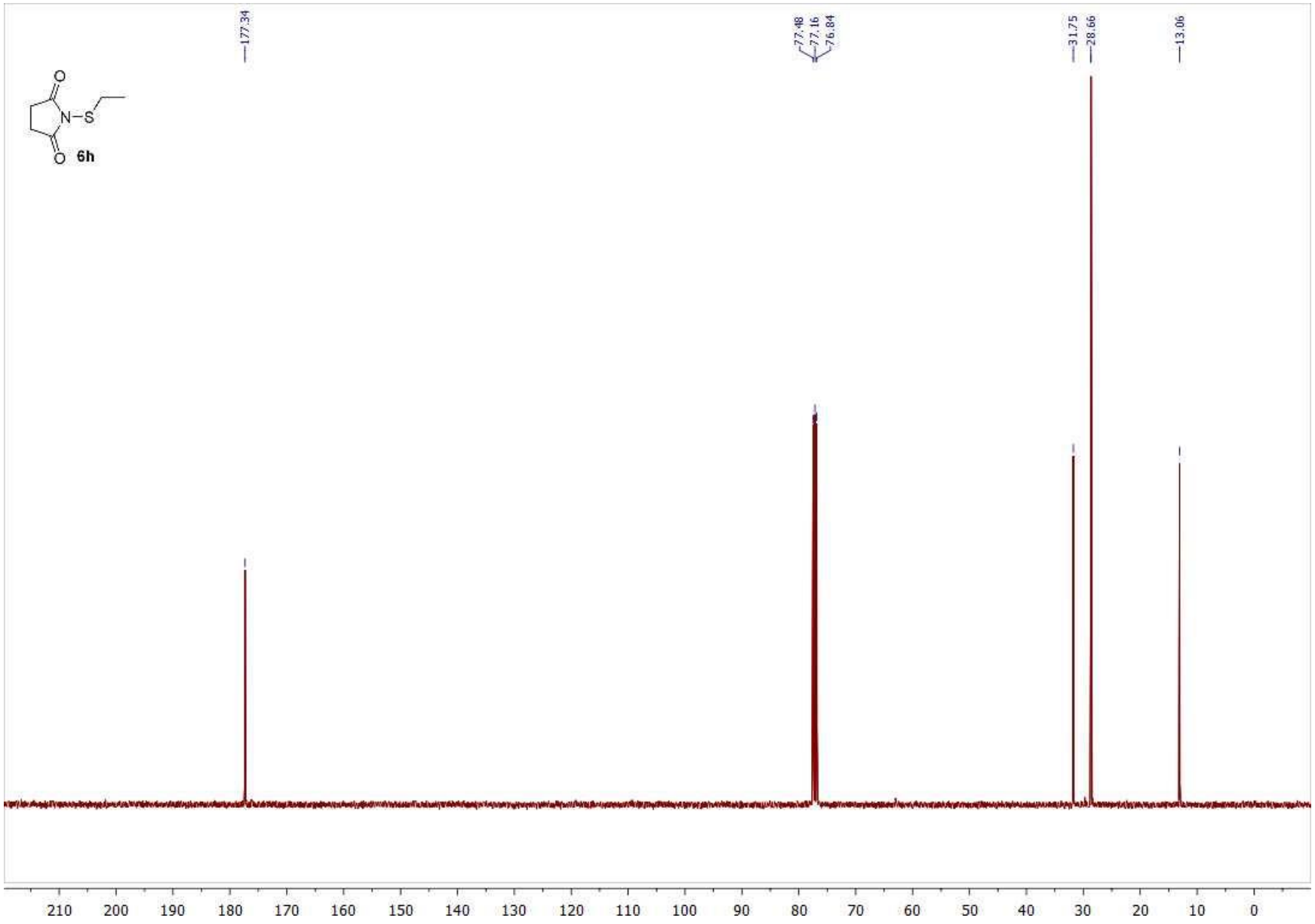

8.19
8.18
8.17
8.16
8.16
8.15
7.45
7.45
7.44
7.43
7.43
7.42
2.97
NO2
O
N–S
O
6f
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
2.00
1.98
4.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


175.78
147.45
143.09
127.67
124.57
77.48
77.16
76.84
28.86
NO2
O
N–S
O
O
6f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

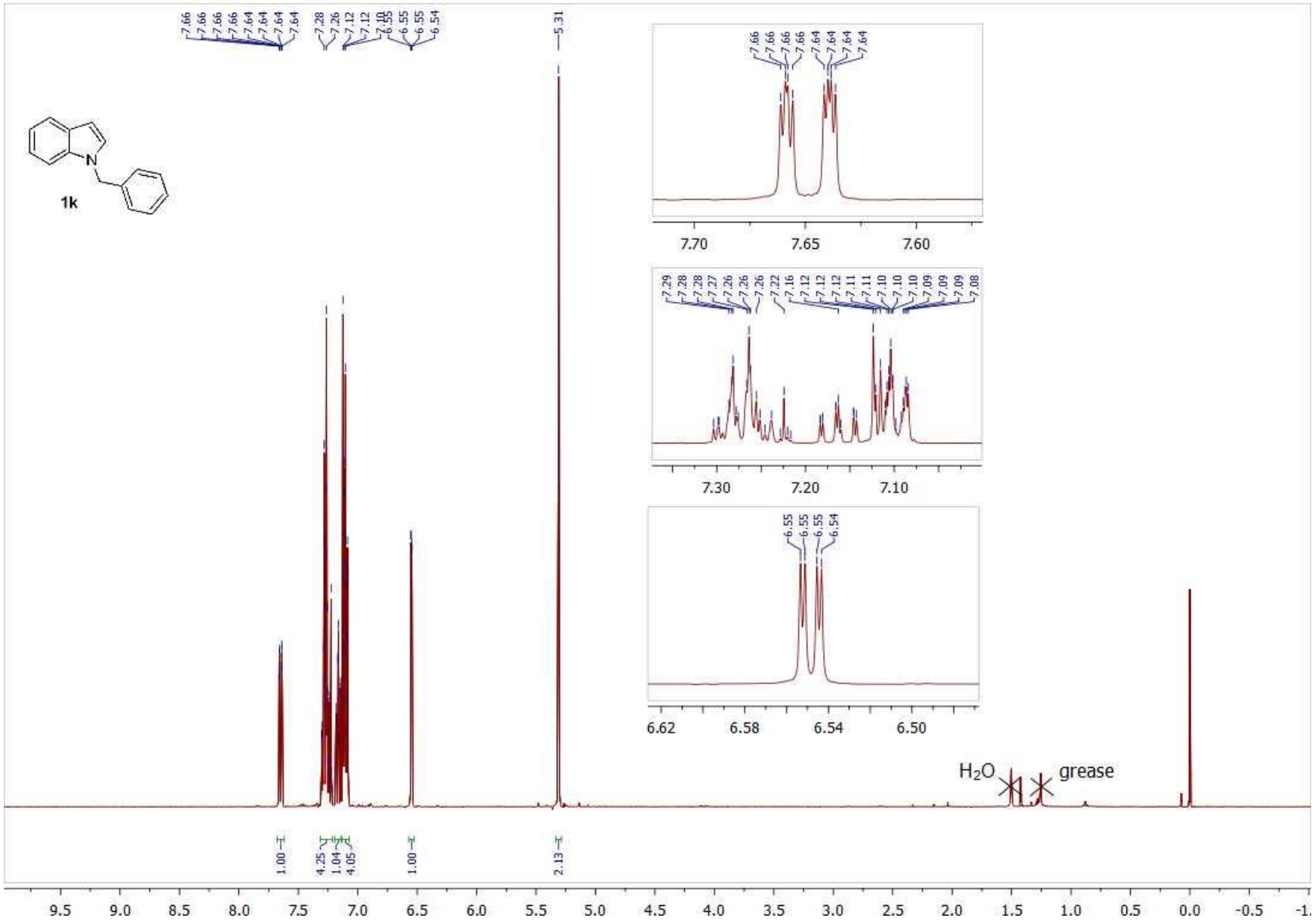

8.50
8.49
7.05
7.04
7.03
2.98
6g
8.54
8.52
8.50
8.48
8.46
7.12
7.08
7.04
7.00
1.96
1.00
4.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

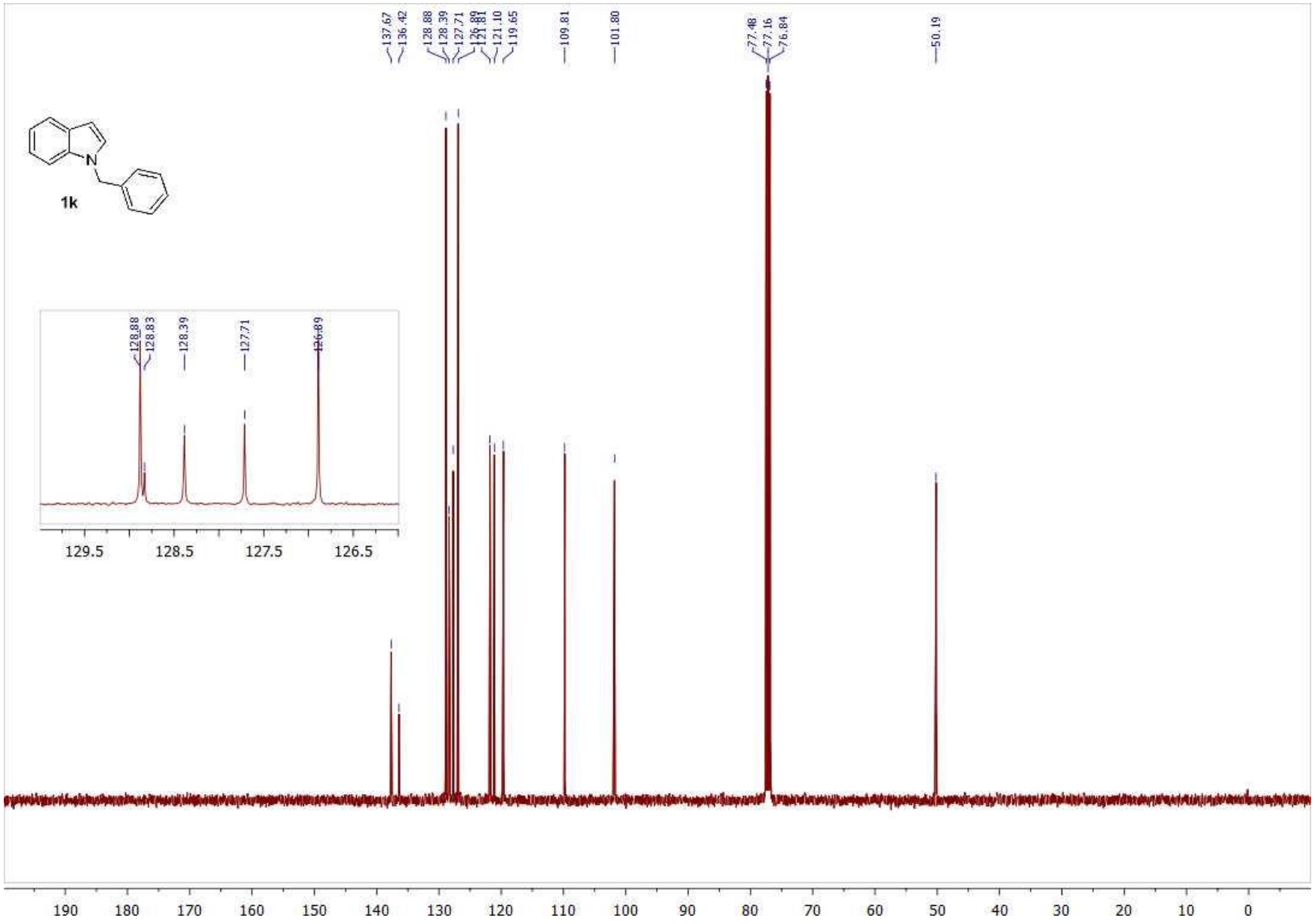

176.11
168.02
158.01
118.36
77.48
77.16
76.84
29.00
O
N
N
N–S
O
6g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

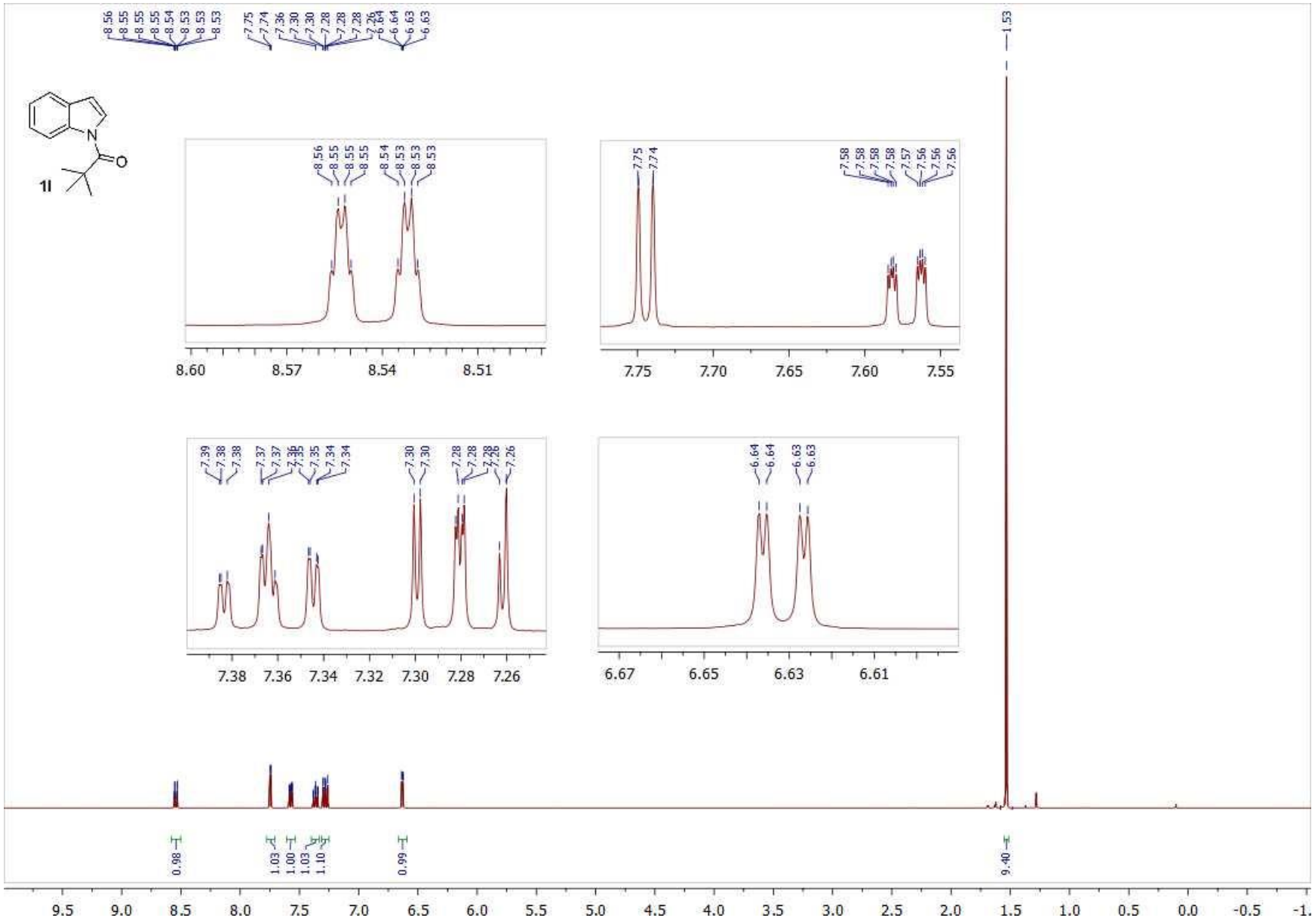

6h
2.89
2.87
2.86
2.84
2.82
1.22
1.20
1.18
2.95
2.90
2.85
2.80
2.75
1.26
1.24
1.22
1.20
1.18
1.16
1.14
5.86
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

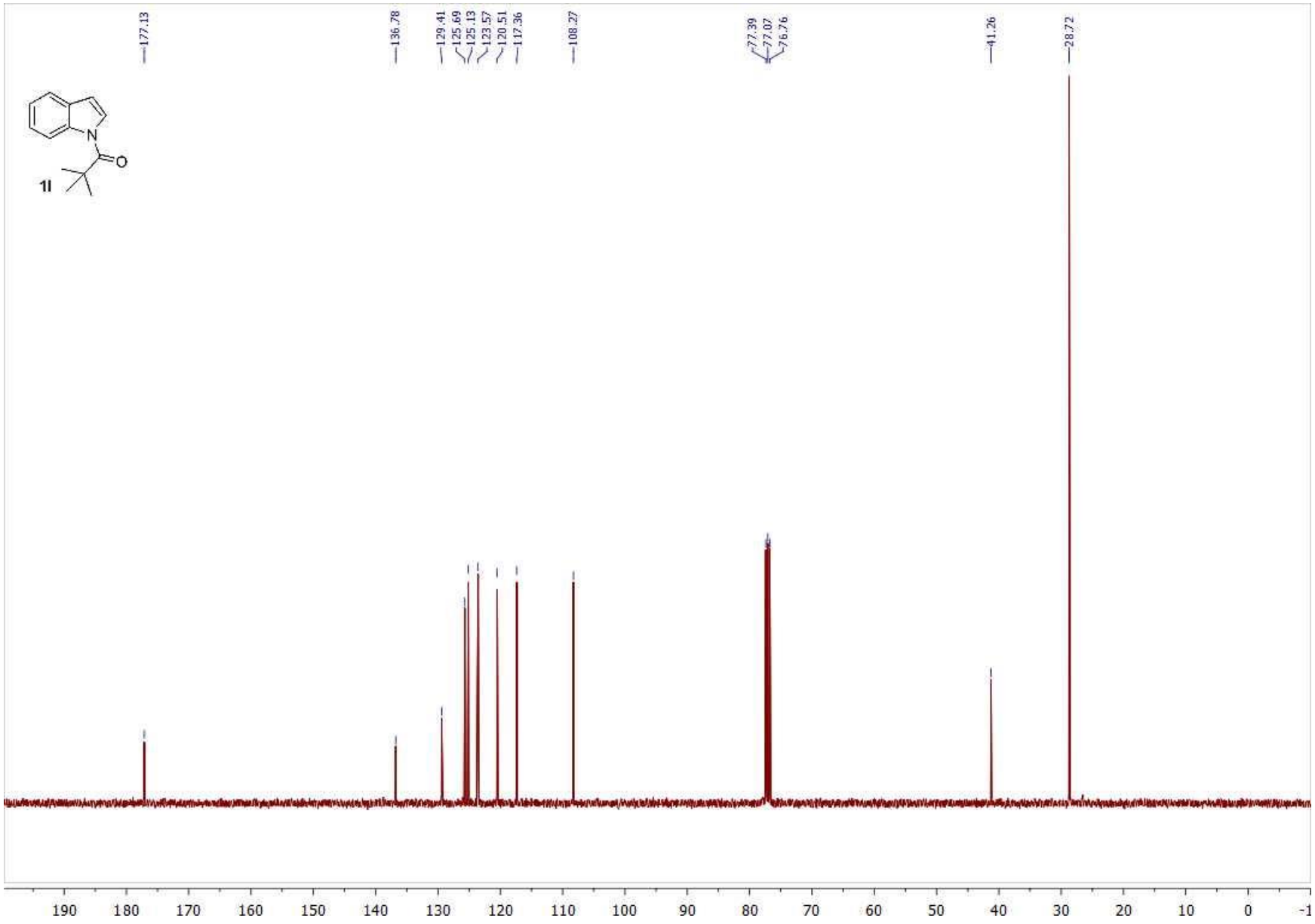

177.34
77.48
77.16
76.84
31.75
28.66
13.06
O
N–S
O
6h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

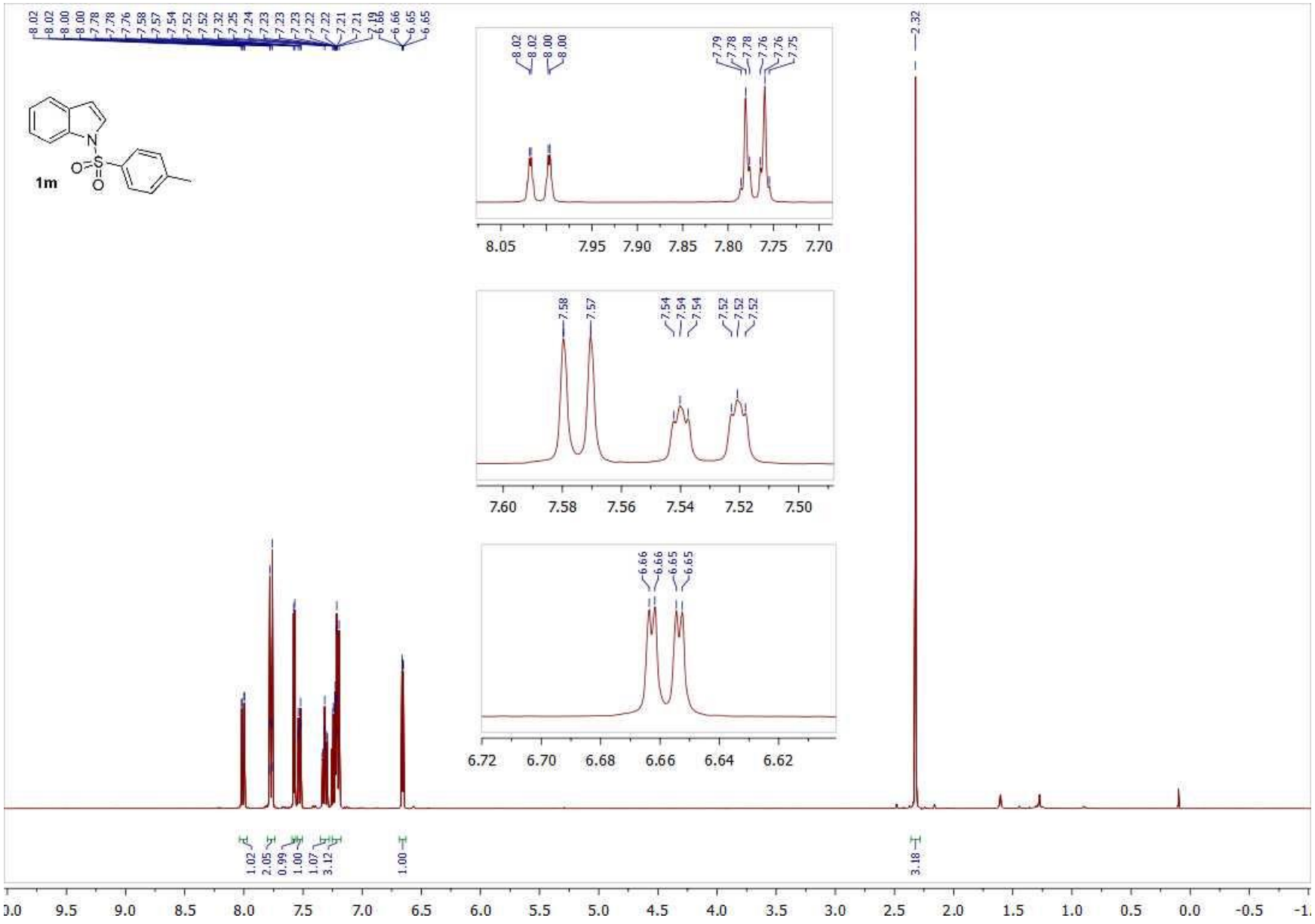
8. ^{1}H and ^{13}C NMR spectra of *N*-protected indoles (1k-1n)

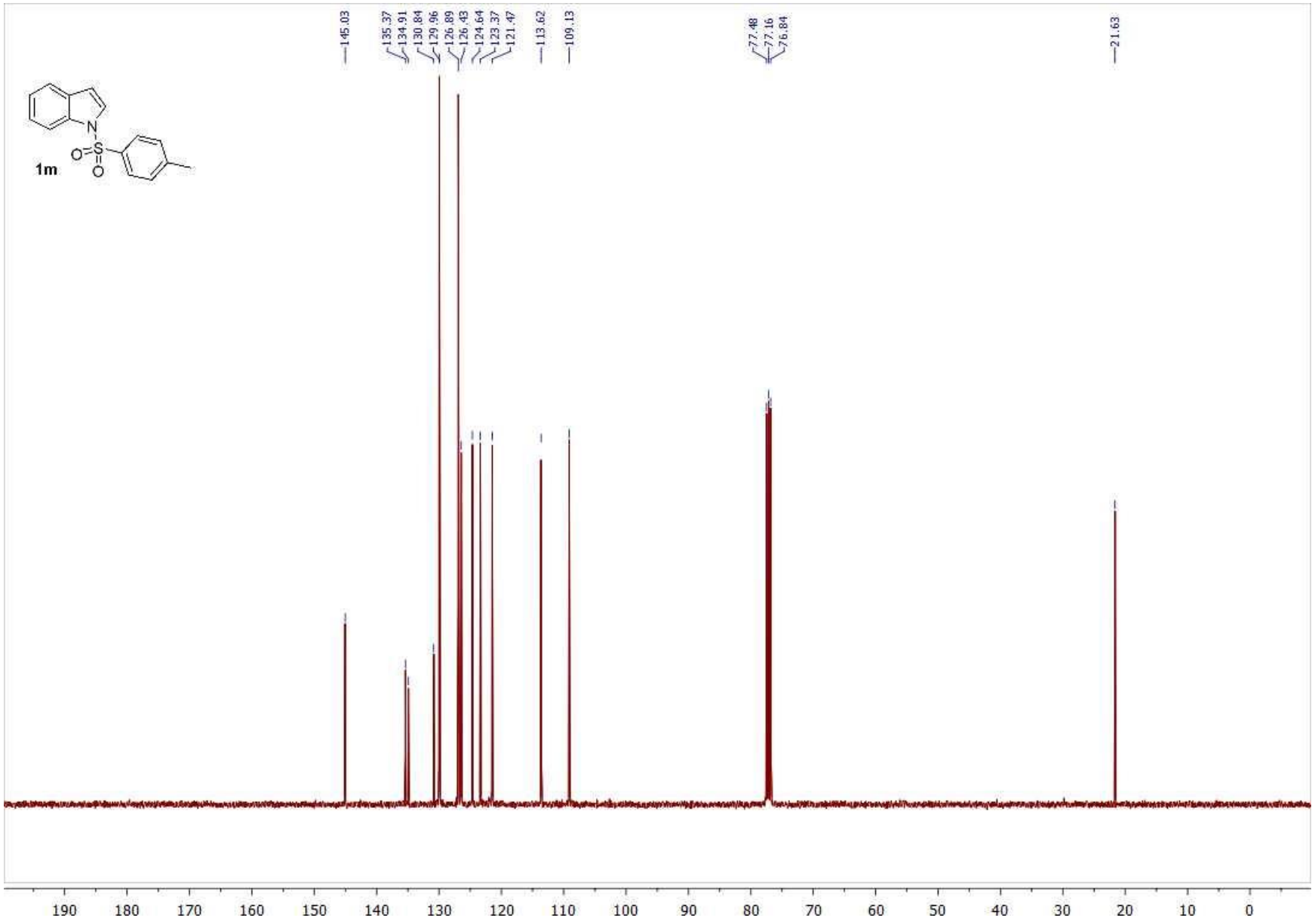

1k
7.66
7.66
7.66
7.66
7.64
7.64
7.64
7.64
7.28
7.26
7.12
7.12
7.10
6.55
6.55
6.54
5.31
7.70
7.65
7.60
7.30
7.20
7.10
6.62
6.58
6.54
6.50
H2O
grease
1.00
4.25
1.04
4.05
1.00
2.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

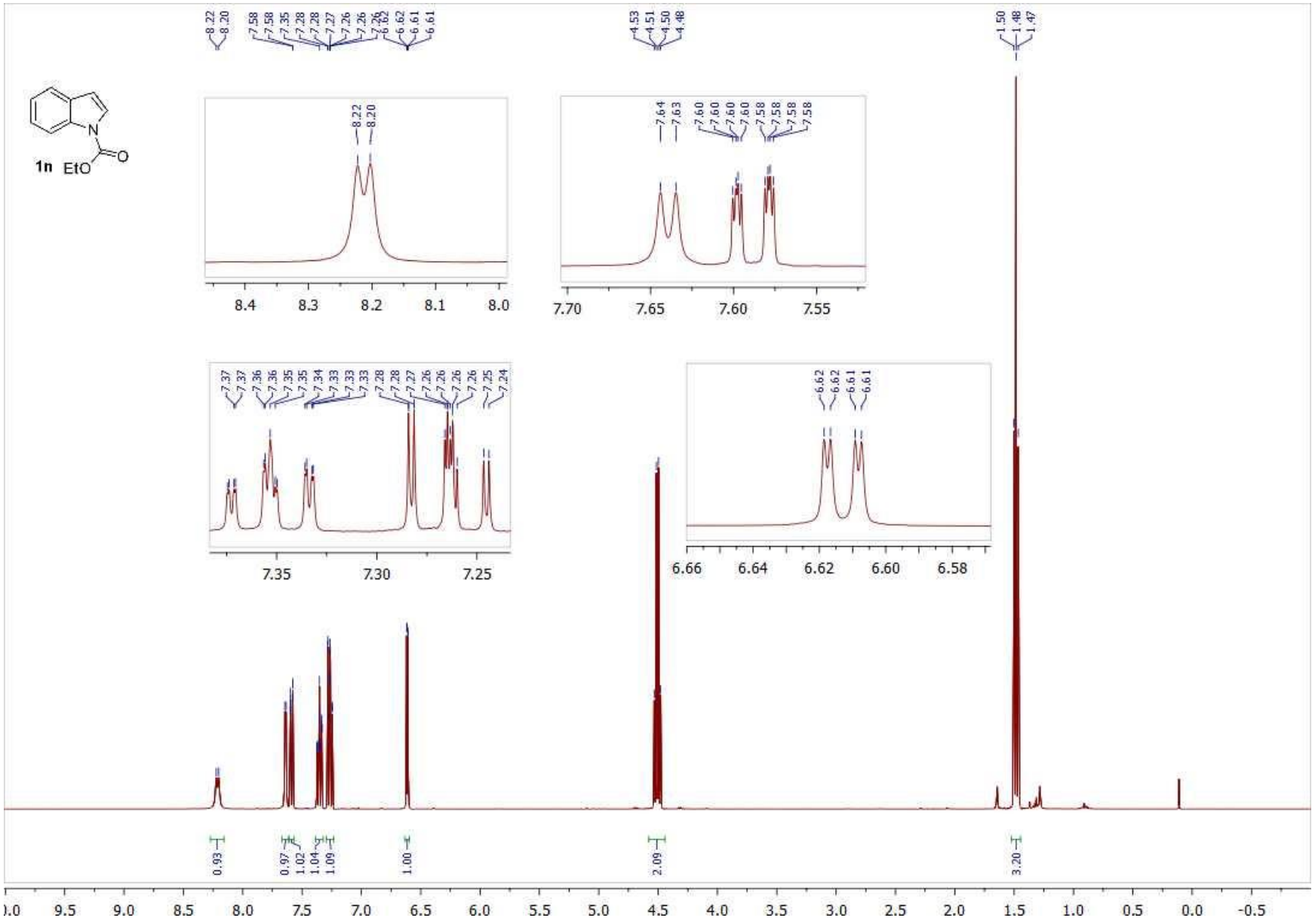

137.67
136.42
128.88
128.39
127.71
126.89
121.81
121.10
119.65
109.81
101.80
77.48
77.16
76.84
50.19
1k
N
128.88
128.83
128.39
127.71
126.89
129.5
128.5
127.5
126.5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

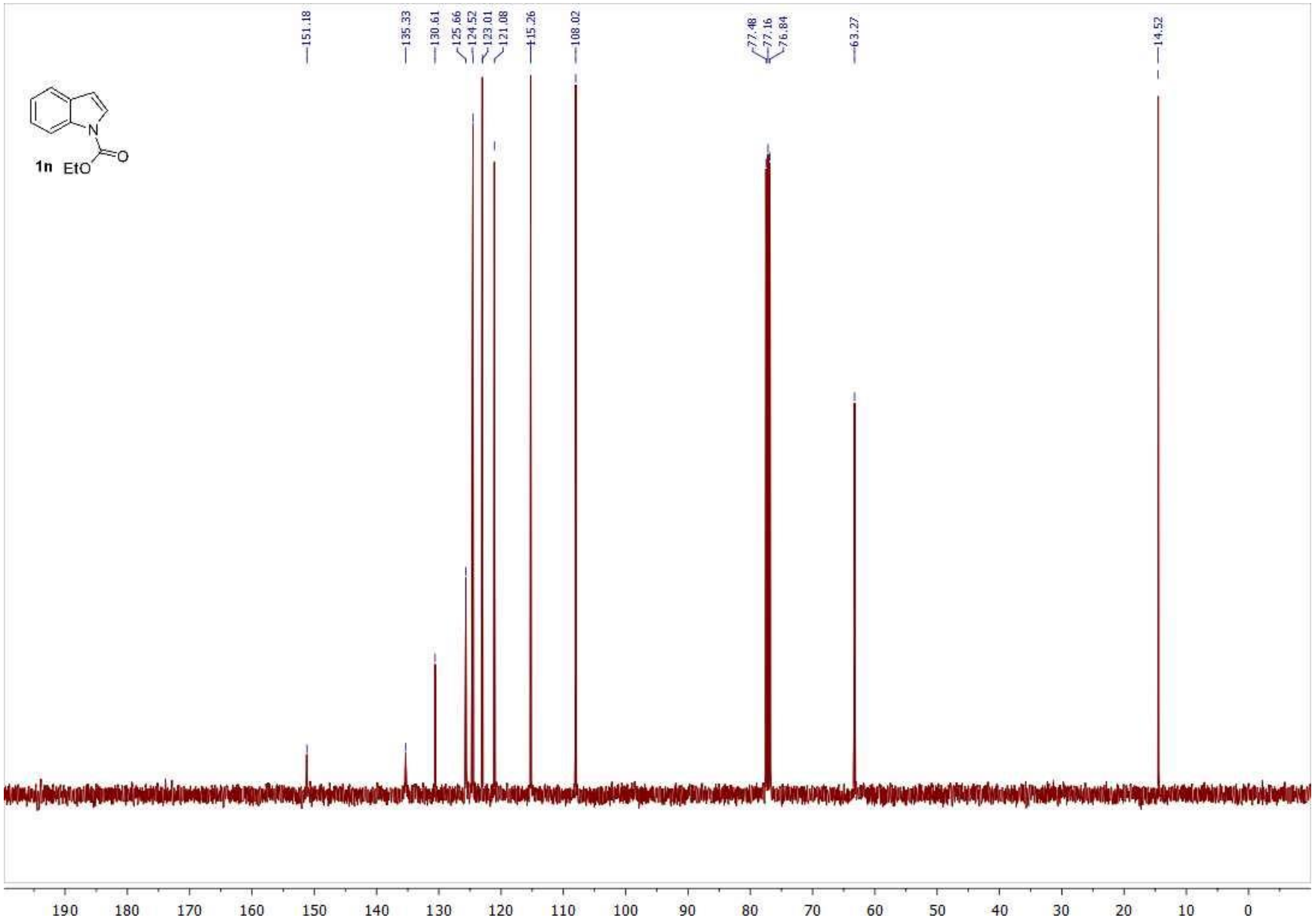

1l
8.56 8.55 8.55 8.55 8.54 8.53 8.53 8.53
7.75 7.74 7.36 7.30 7.30 7.28 7.28 7.26 6.64 6.63 6.63
1.53
8.60 8.57 8.54 8.51
7.75 7.70 7.65 7.60 7.55
7.38 7.36 7.34 7.32 7.30 7.28 7.26
6.67 6.65 6.63 6.61
0.98 1.03 1.00 1.03 1.10 0.99 9.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


177.13
136.78
129.41
125.69
125.13
123.57
120.51
117.36
108.27
77.39
77.07
76.76
41.26
28.72
1l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

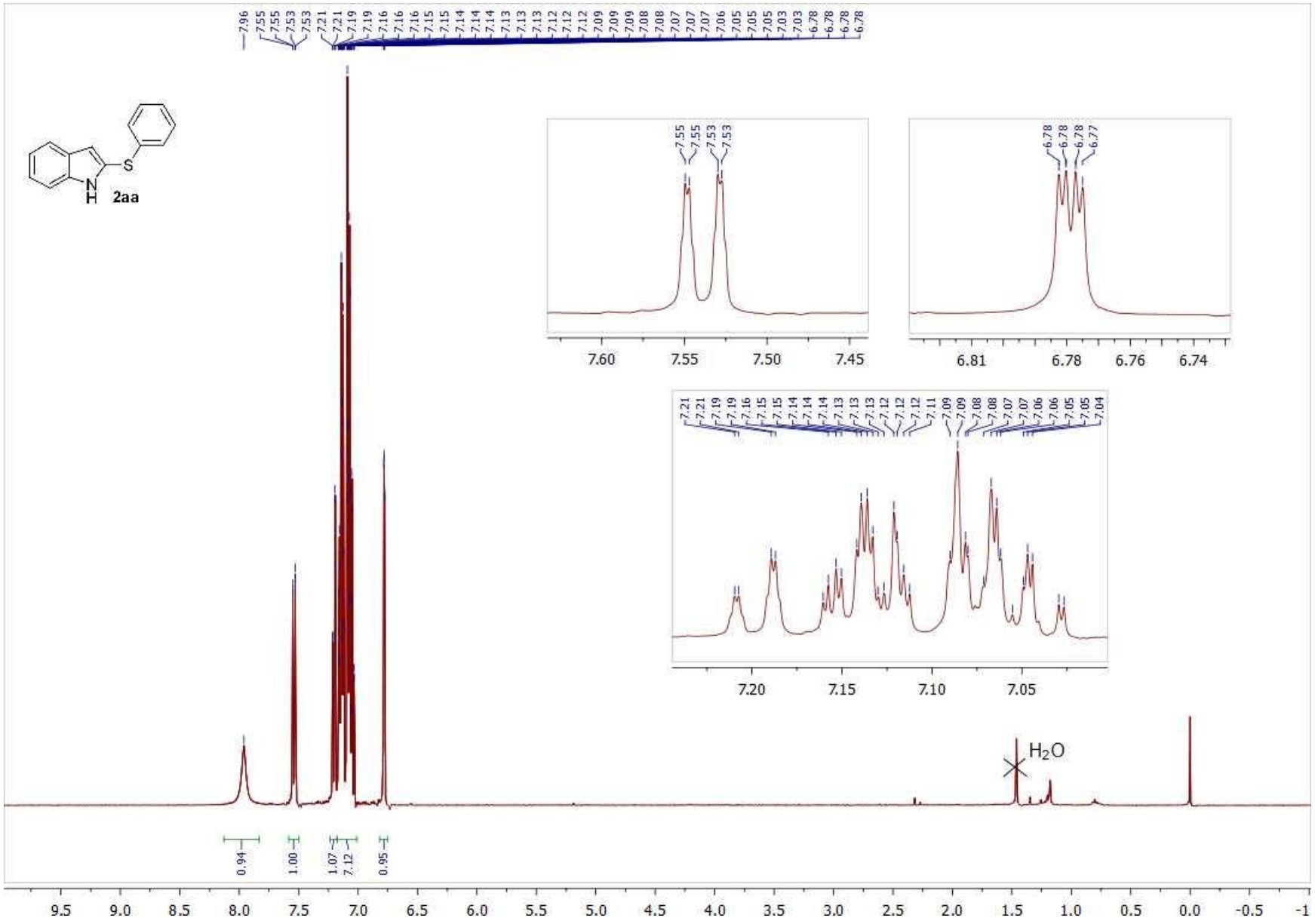

1m

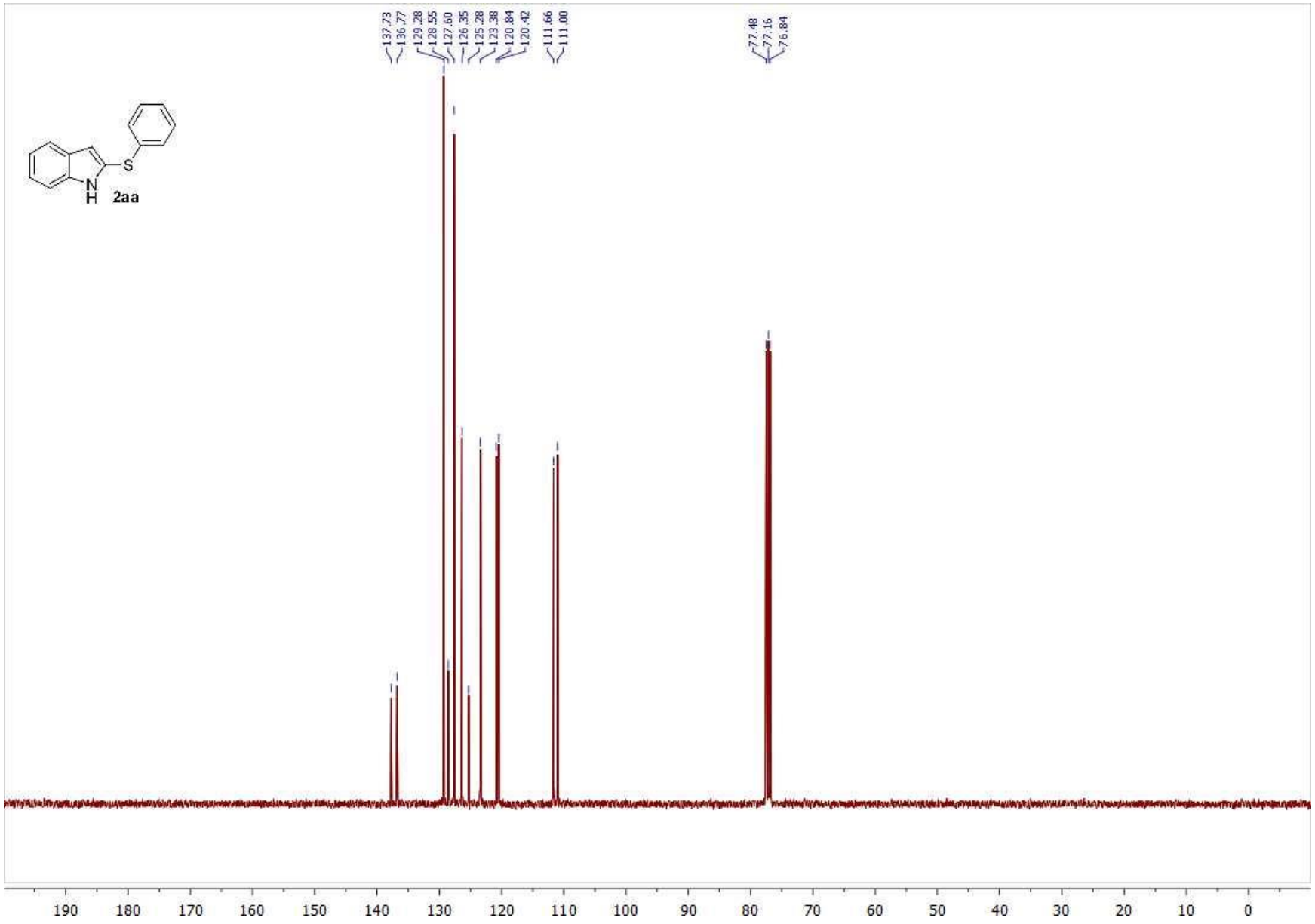

145.03
135.37
134.91
130.84
129.96
126.89
126.43
124.64
123.37
121.47
113.62
109.13
77.48
77.16
76.84
21.63
1m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

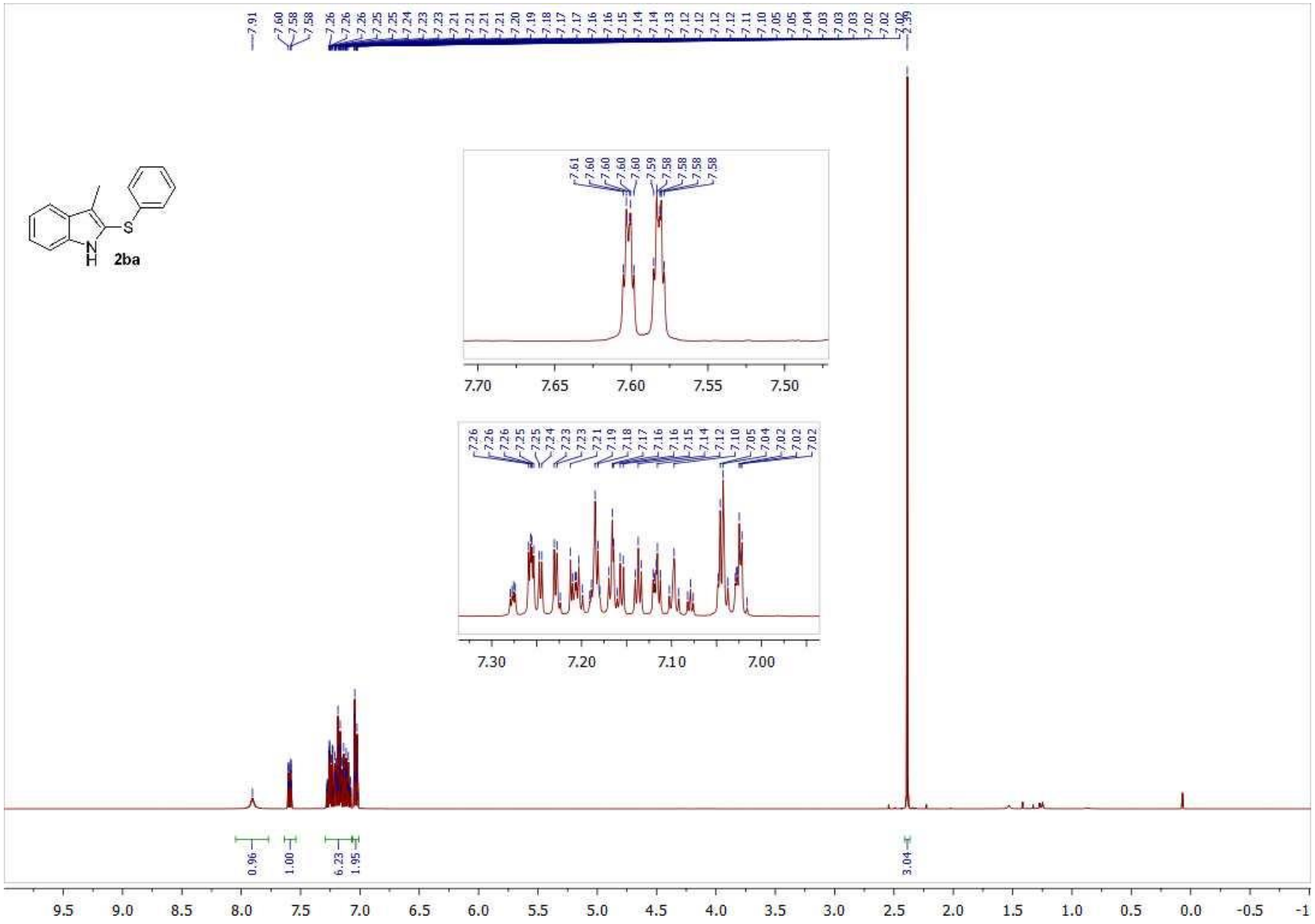

1n EtO
8.22
8.20
7.58
7.58
7.35
7.28
7.28
7.27
7.26
7.26
6.62
6.61
6.61
4.53
4.51
4.50
4.48
1.50
1.48
1.47
8.4
8.3
8.2
8.1
8.0
7.70
7.65
7.60
7.55
7.35
7.30
7.25
6.66
6.64
6.62
6.60
6.58
0.93
0.97
1.02
1.04
1.09
1.00
2.09
3.20

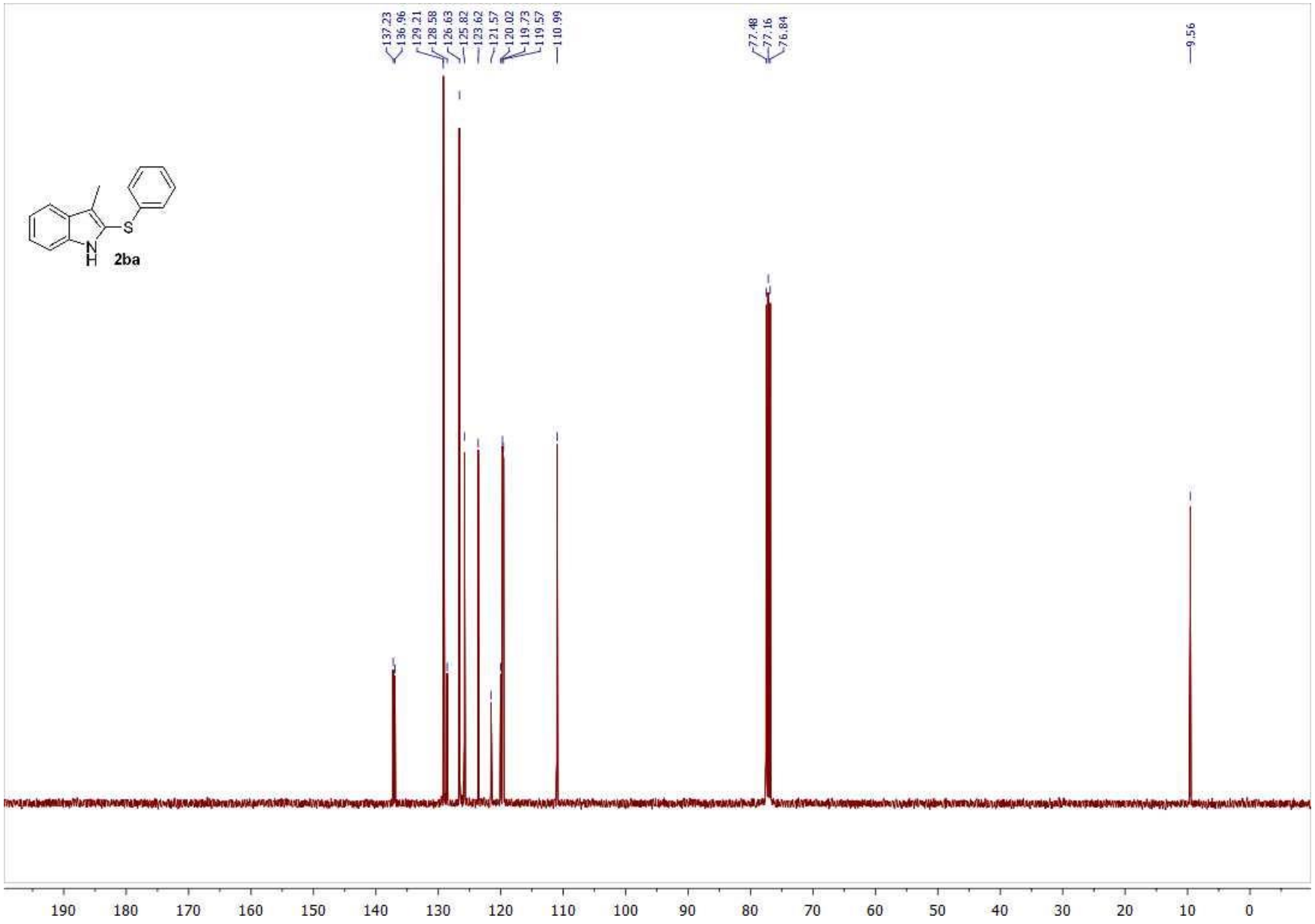

151.18
135.33
130.61
125.66
124.52
123.01
121.08
115.26
108.02
77.48
77.16
76.84
63.27
14.52
1n EtO
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

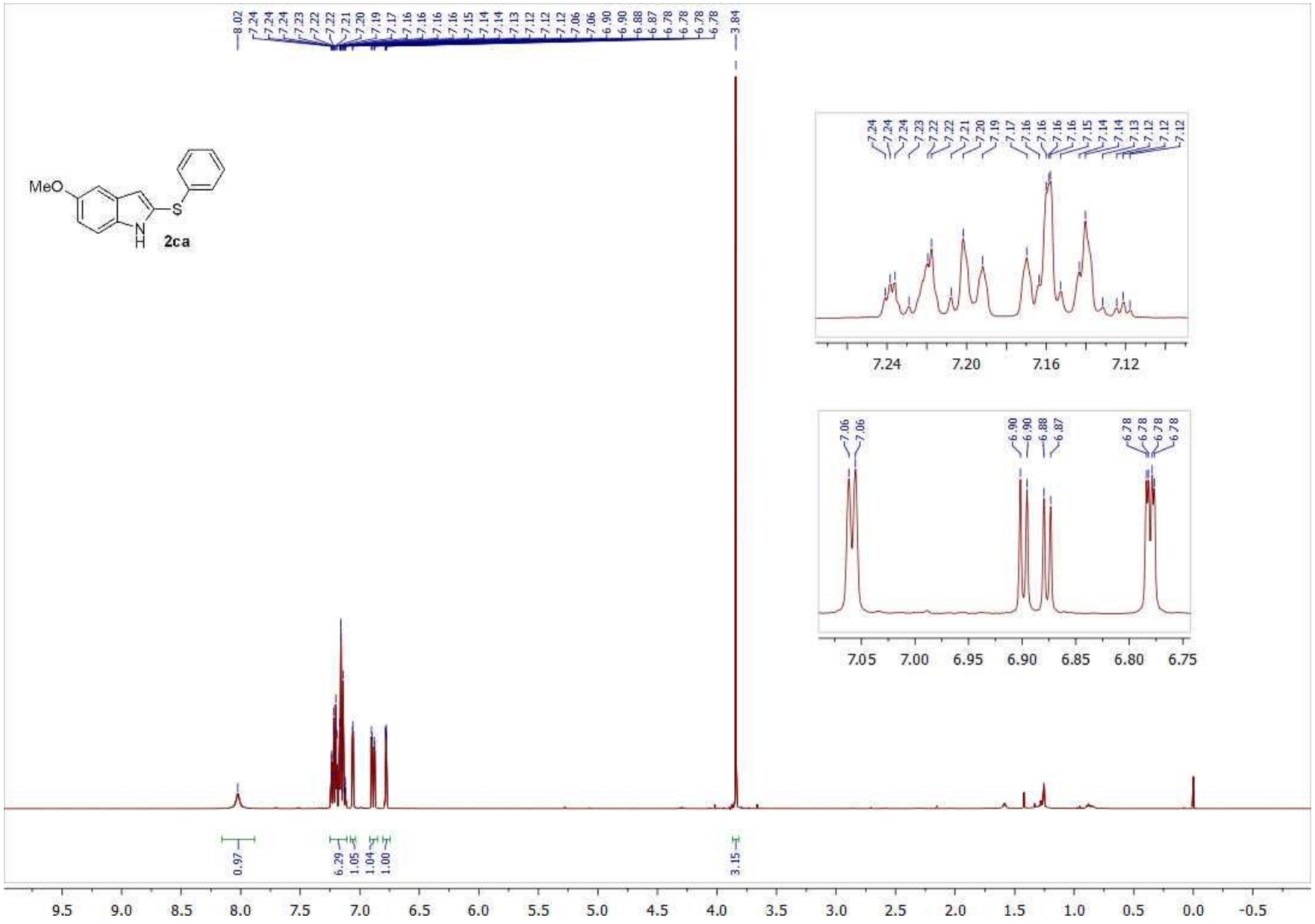
9. ^{1}H and ^{13}C NMR spectra of thioindoles (2aa-2na and 2ab-2ag)

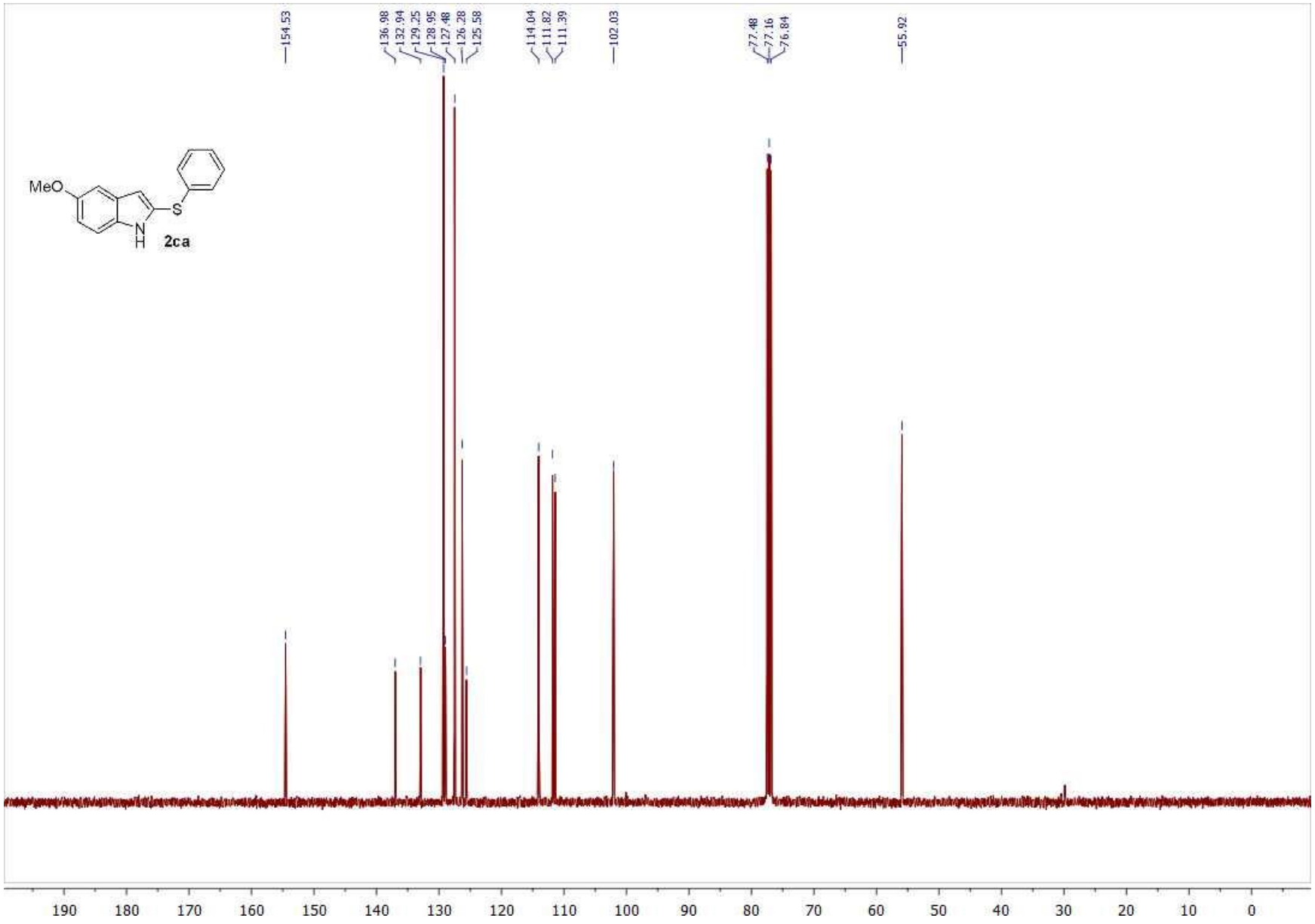

2aa
H2O


137.73
136.77
129.28
128.55
127.60
126.35
125.28
123.38
120.84
120.42
111.66
111.00
77.48
77.16
76.84
S
N
H
2aa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


2ba
7.70
7.65
7.60
7.55
7.50
7.30
7.20
7.10
7.00
0.96
1.00
6.23
1.95
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1


137.23
136.96
129.21
128.58
126.63
125.82
123.62
121.57
120.02
119.73
119.57
110.99
77.48
77.16
76.84
9.56
S
N
H
2ba
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


MeO
S
N
H
2ca
8.02
7.24
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.19
7.17
7.16
7.16
7.16
7.16
7.15
7.14
7.14
7.13
7.12
7.12
7.12
7.06
6.90
6.88
6.87
6.78
6.78
6.78
3.84
7.24
7.20
7.16
7.12
7.06
6.90
6.88
6.87
6.78
7.05
7.00
6.95
6.90
6.85
6.80
6.75
0.97
6.29
1.05
1.04
1.00
3.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


154.53
136.98
132.94
129.25
128.95
127.48
126.28
125.58
114.04
111.82
111.39
102.03
77.48
77.16
76.84
55.92
MeO
S
N
H
2ca
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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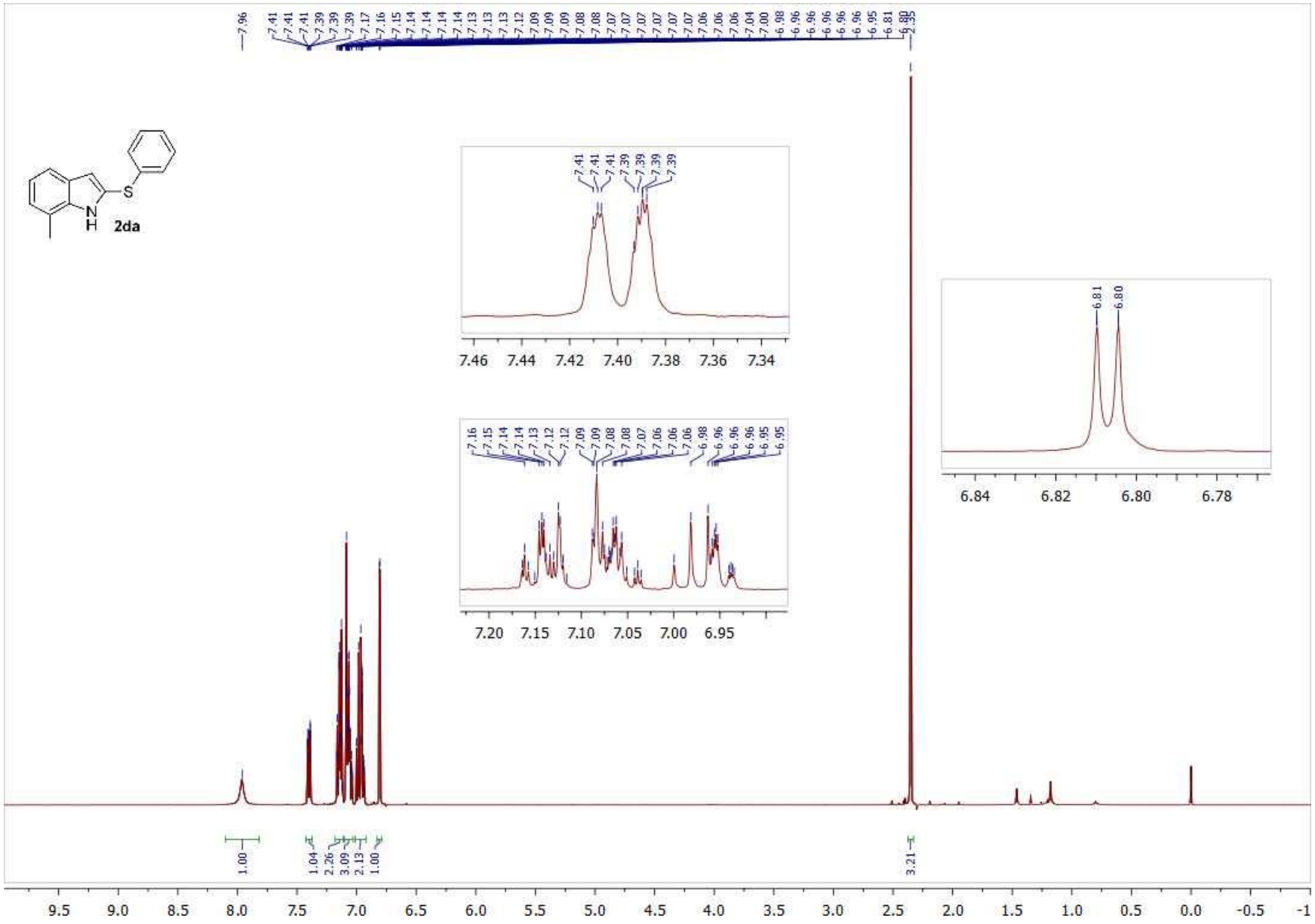
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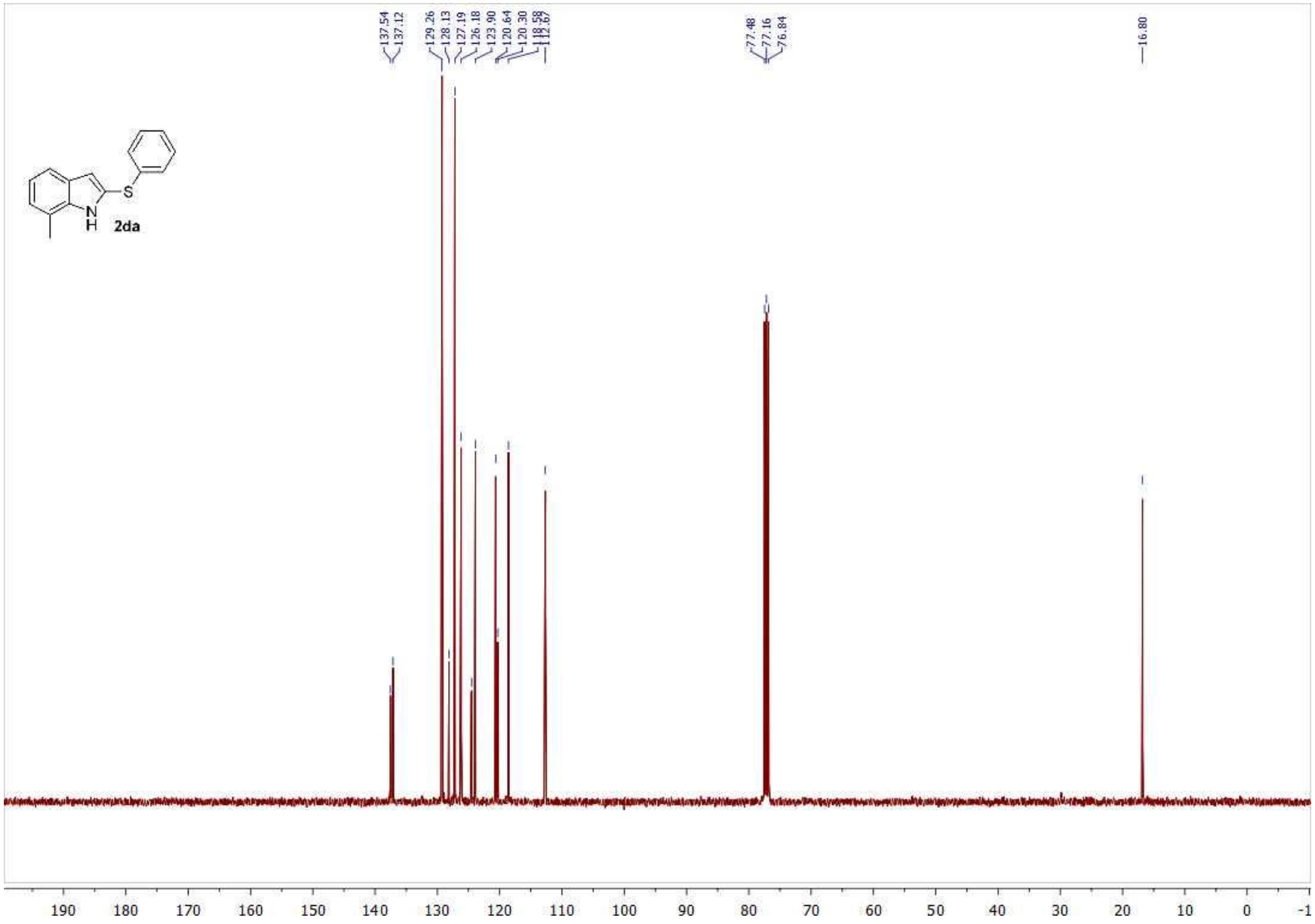
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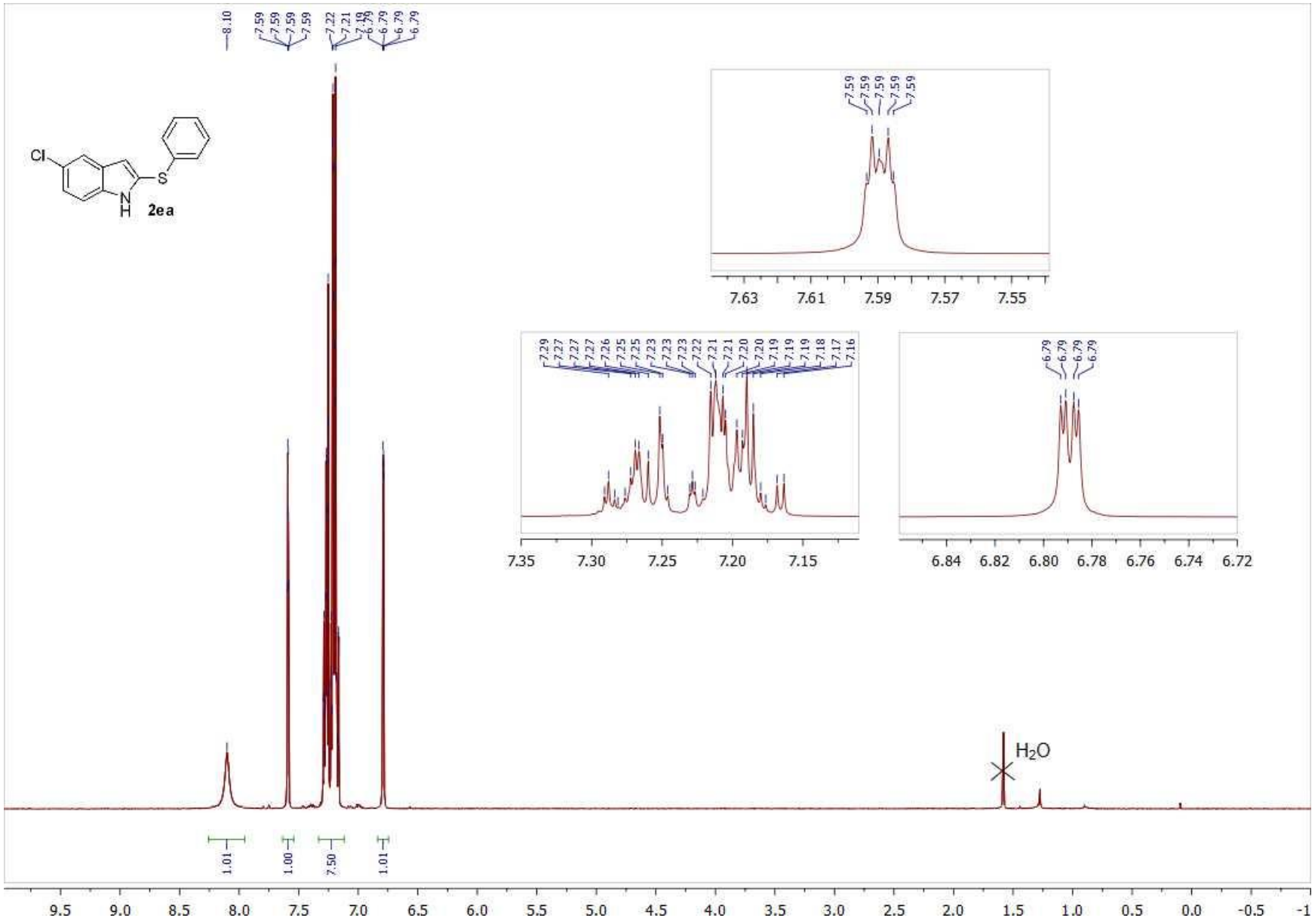
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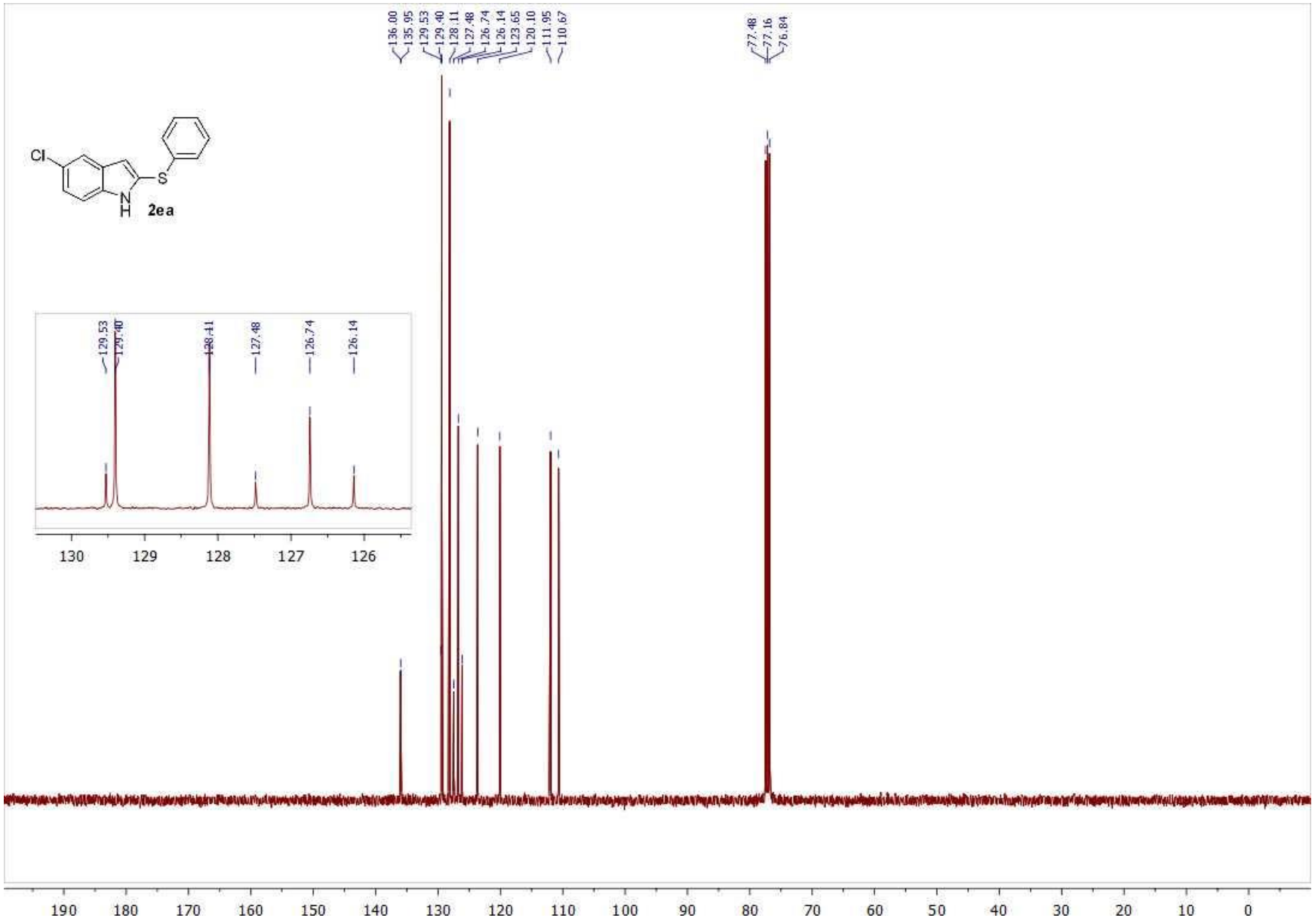
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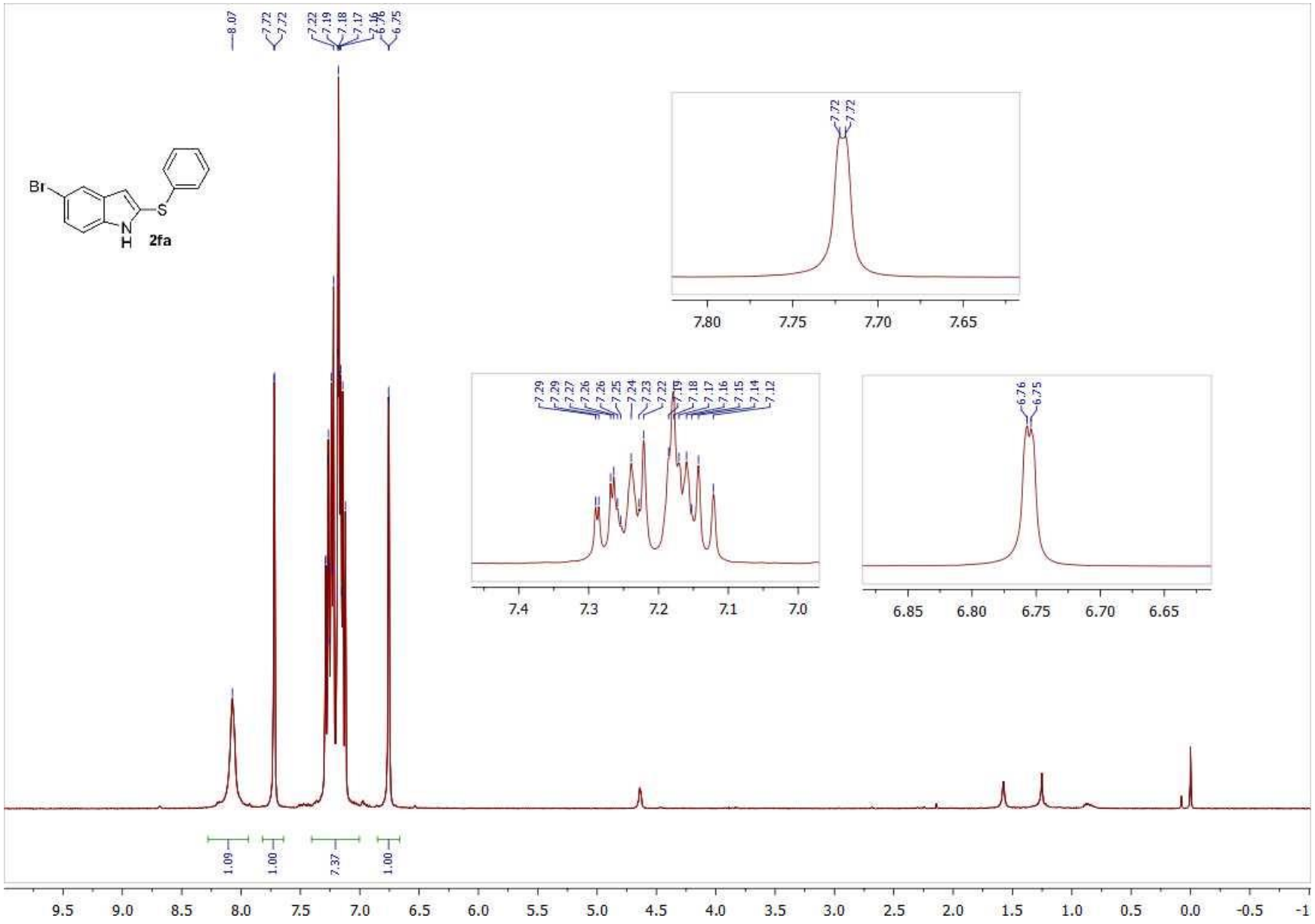
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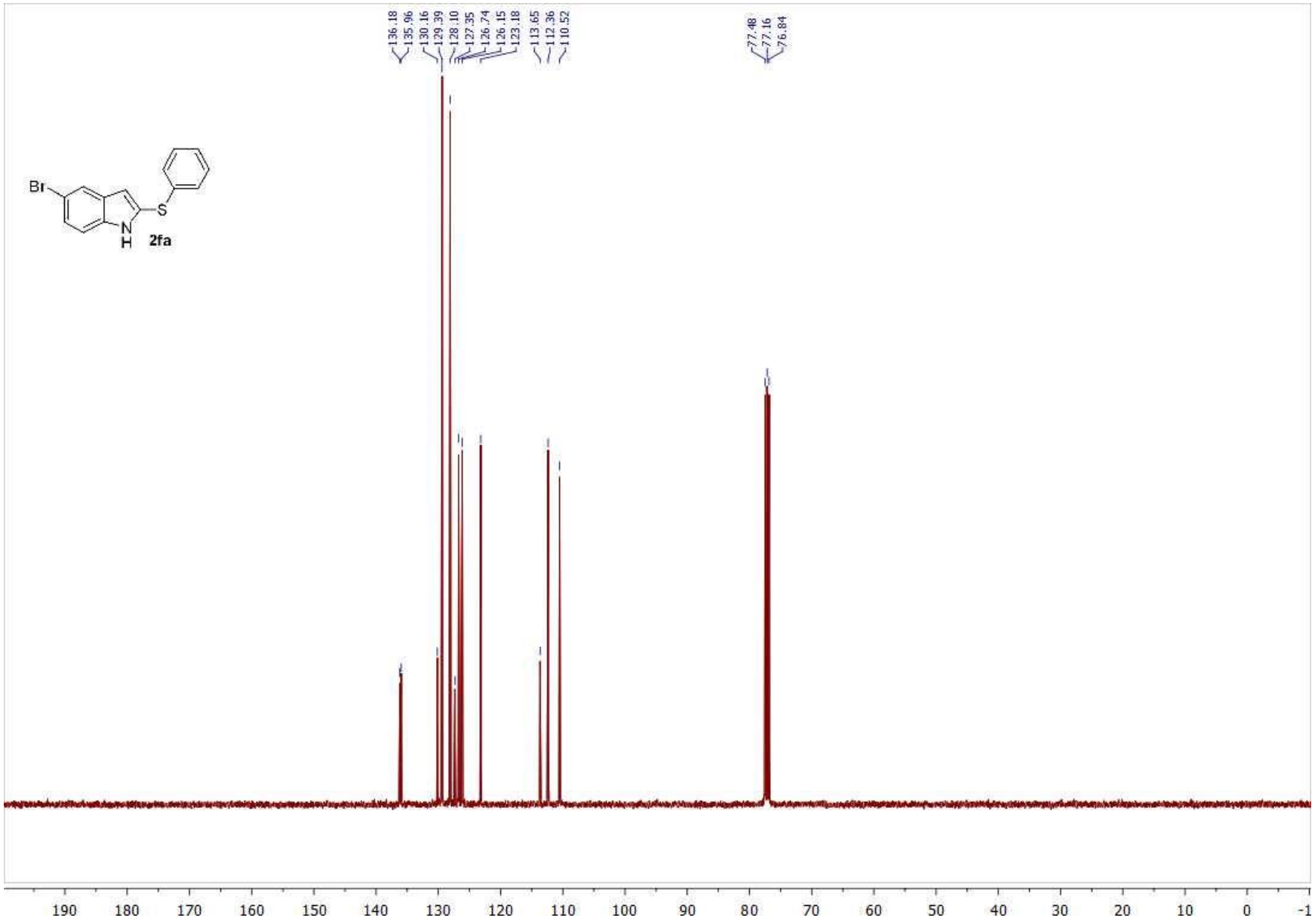
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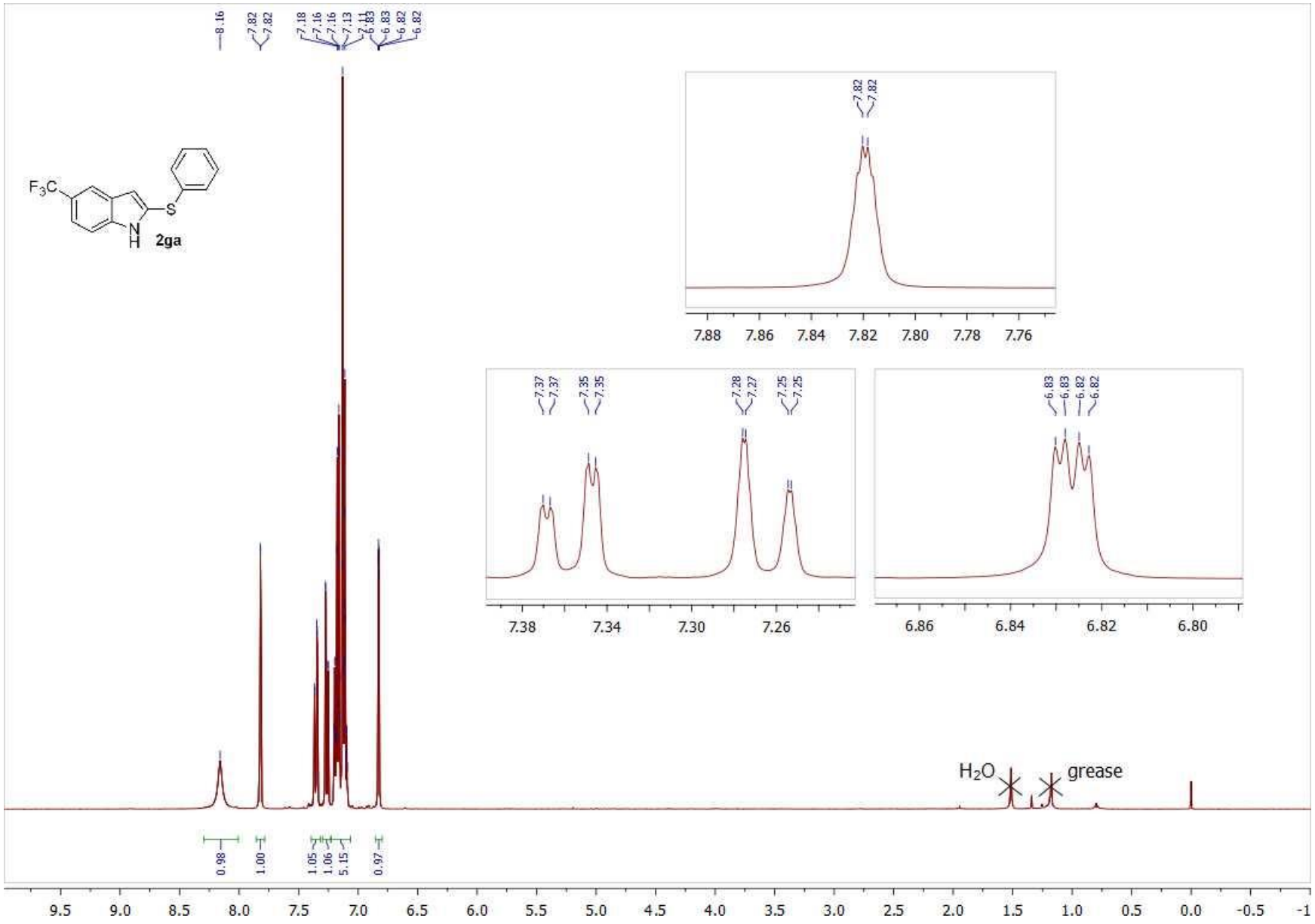
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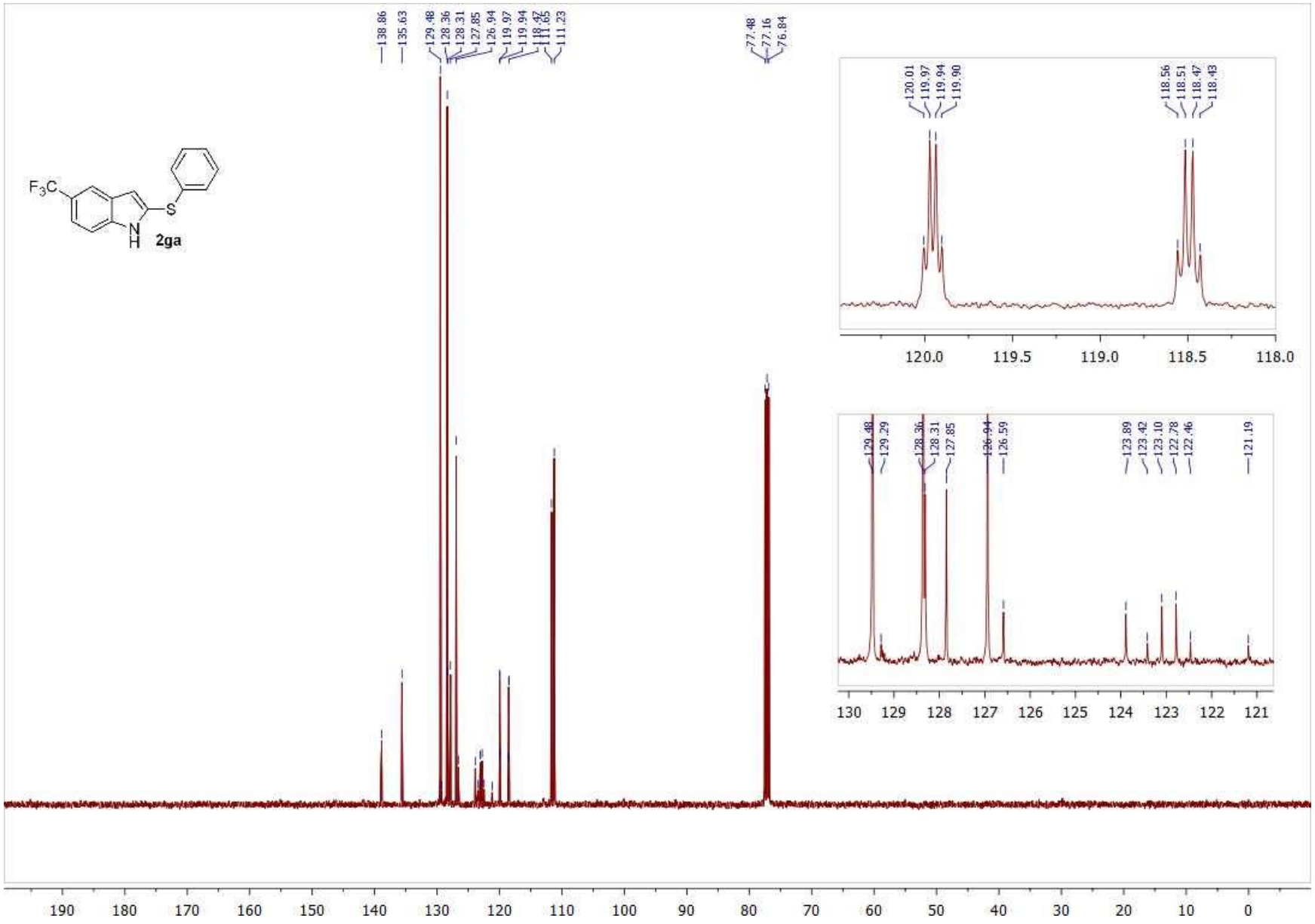
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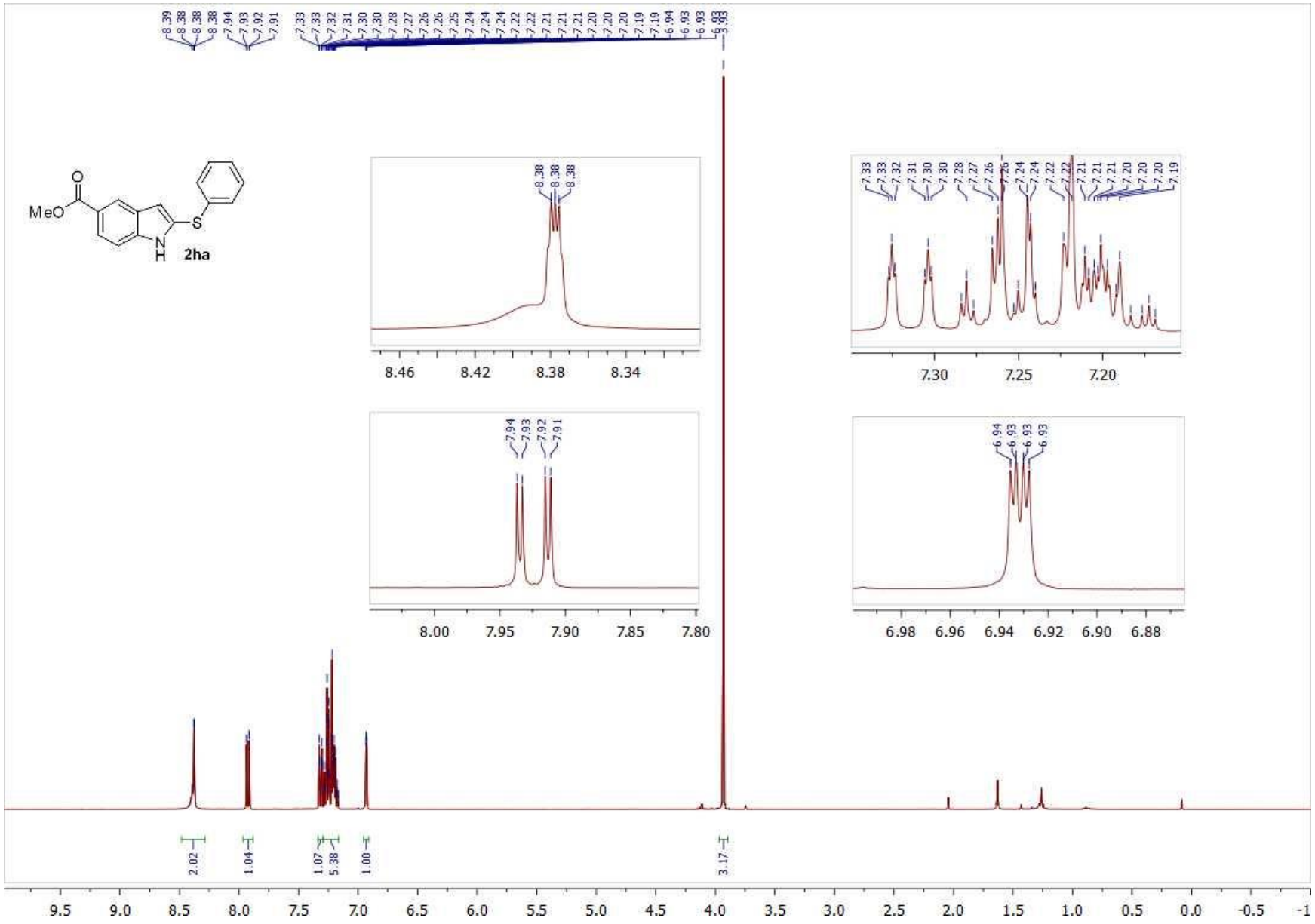
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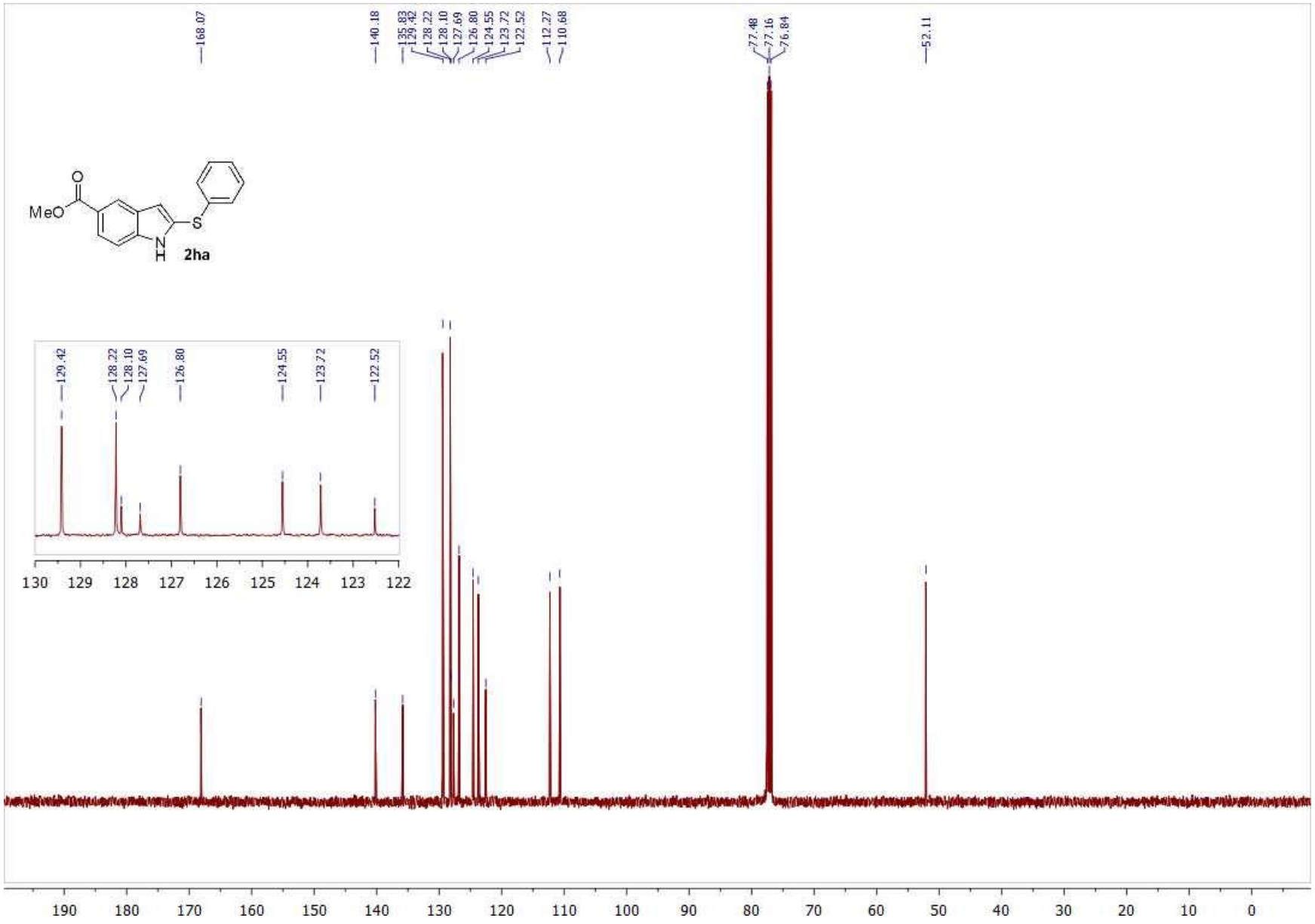
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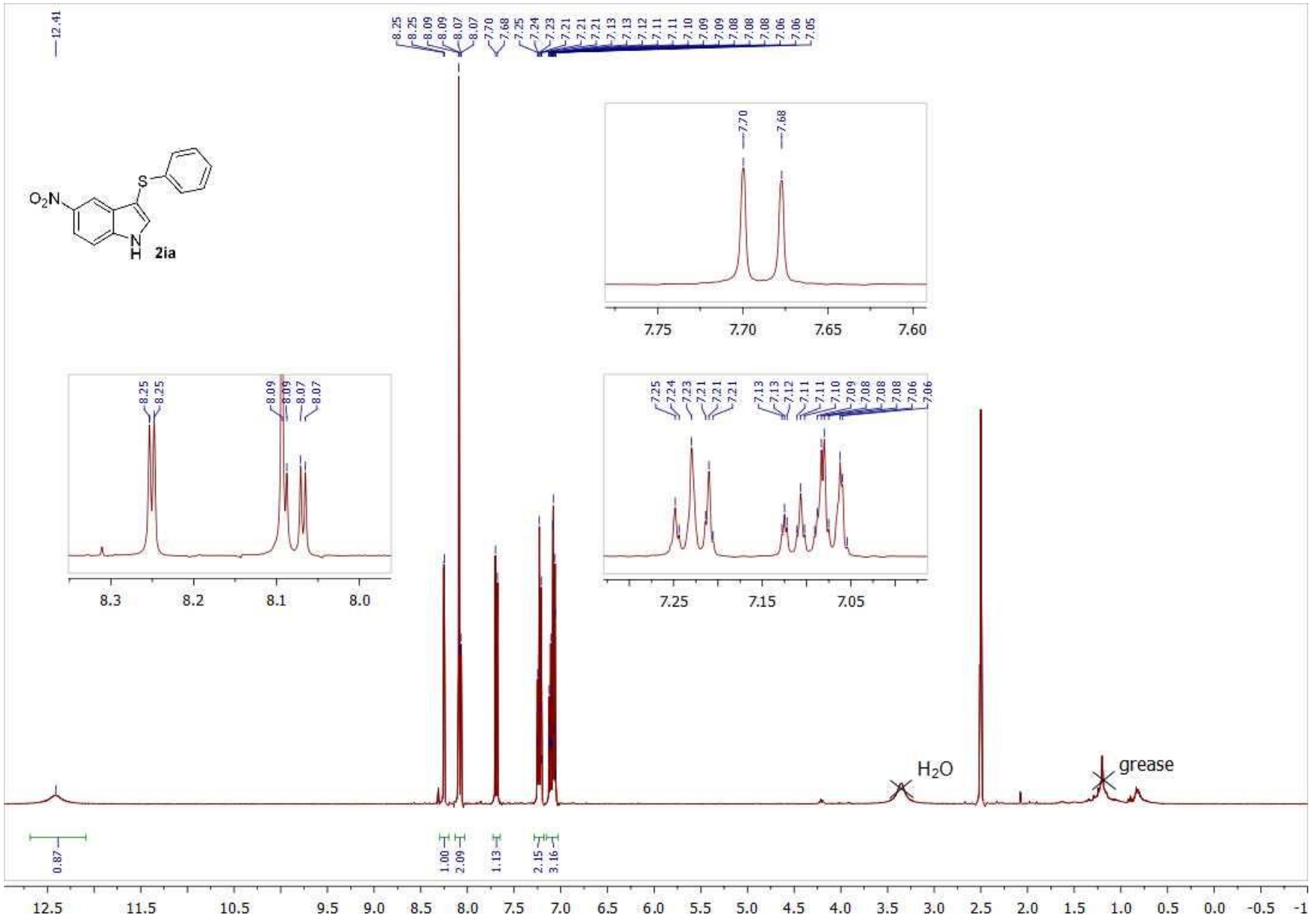
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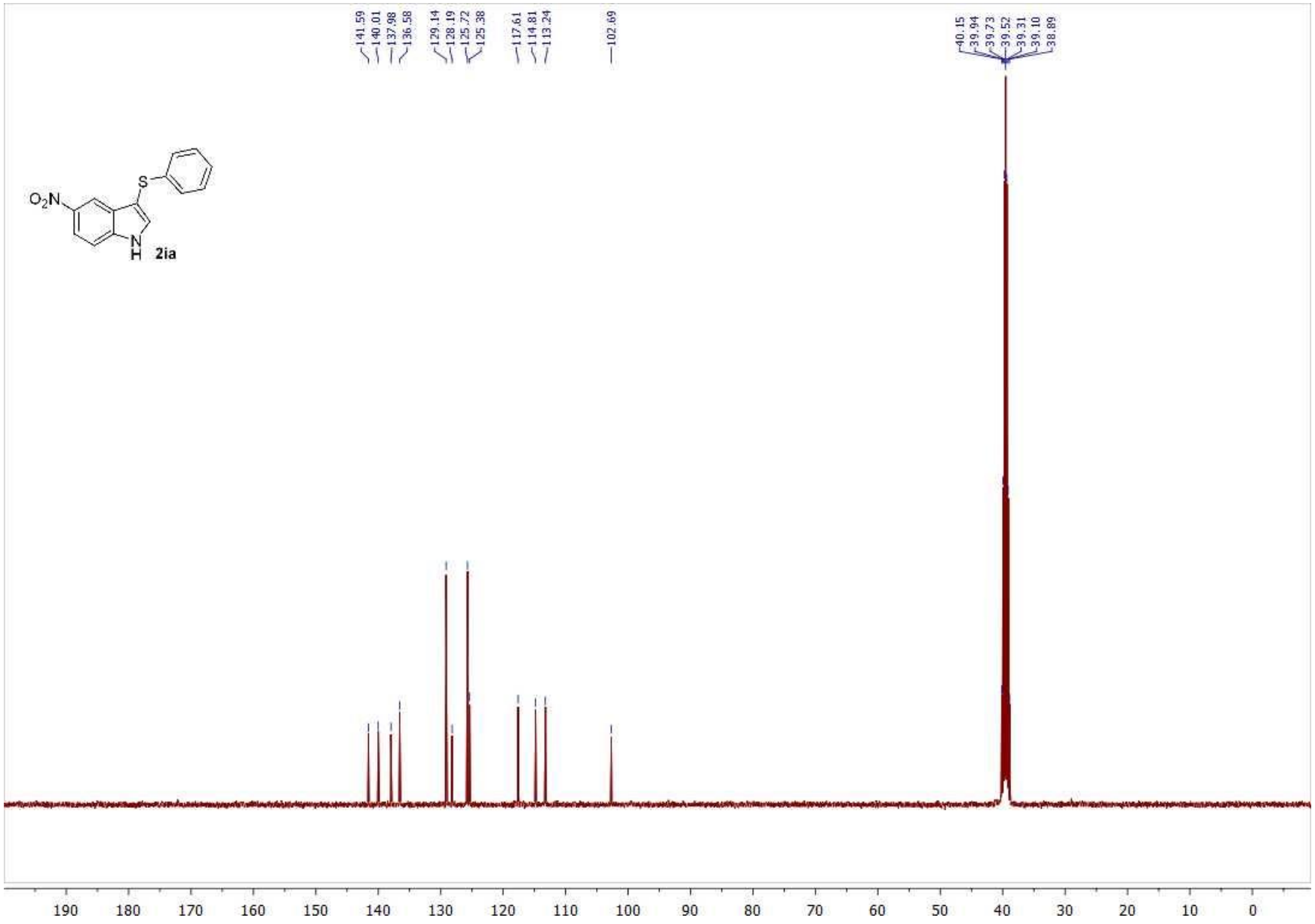
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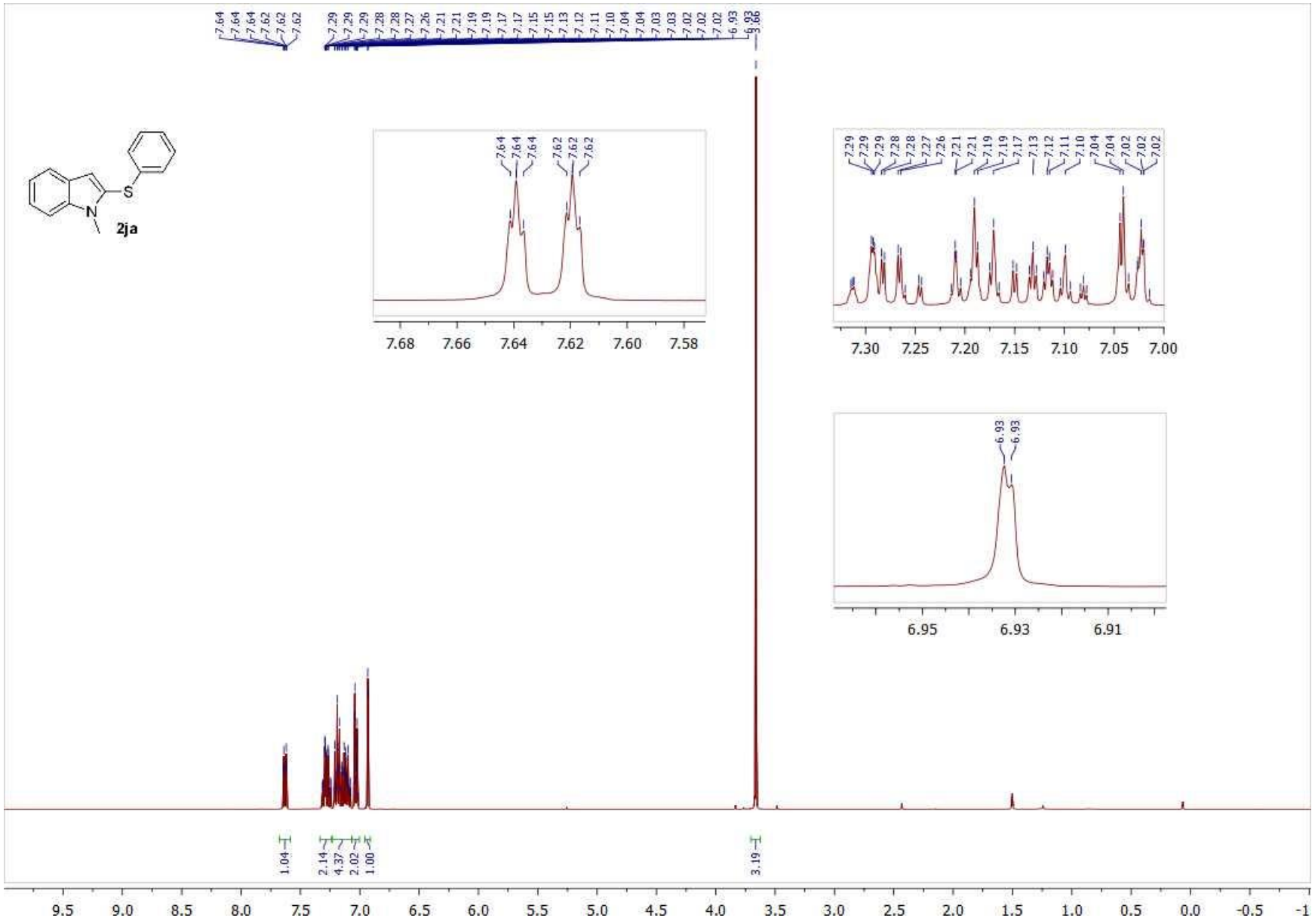
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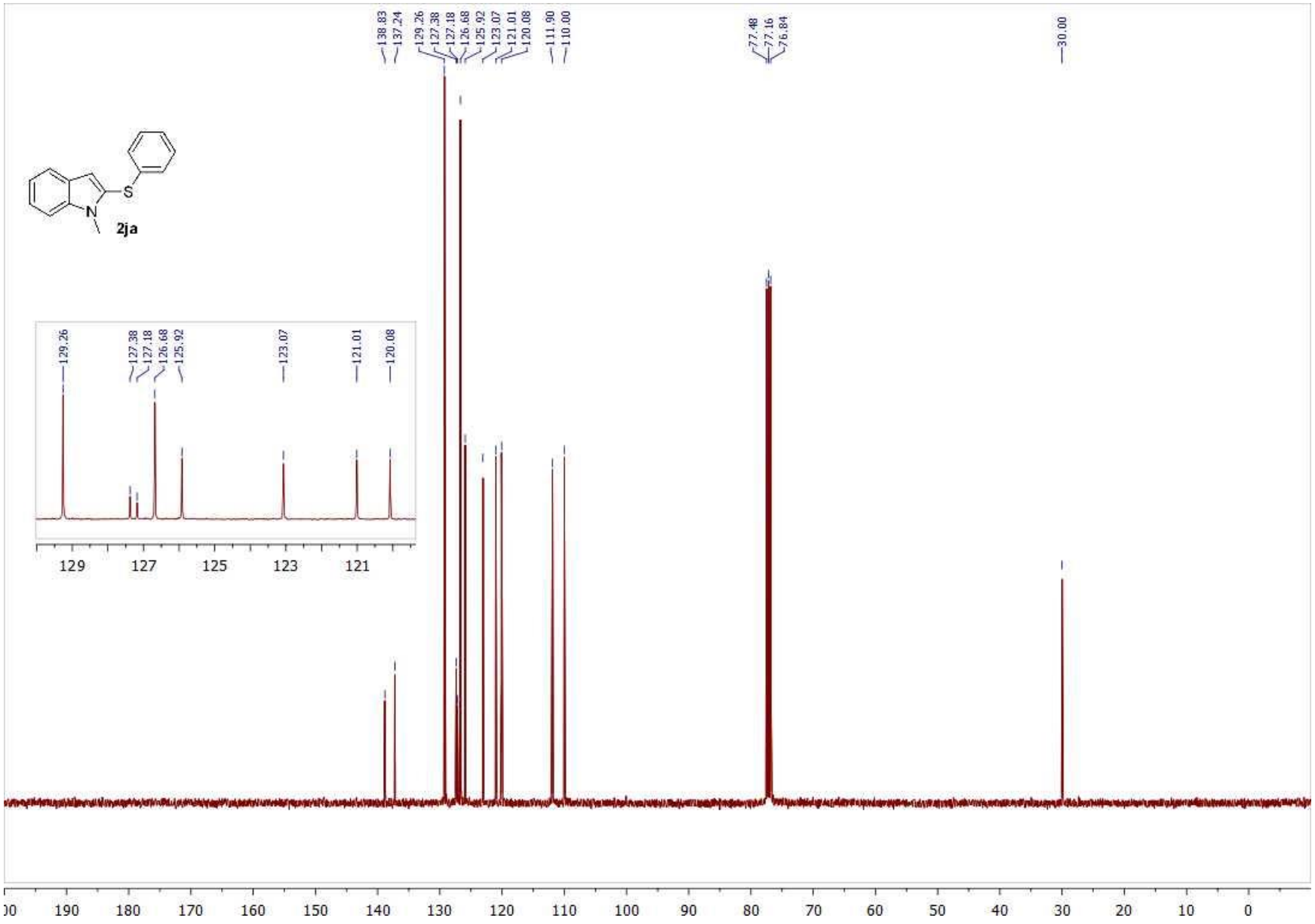
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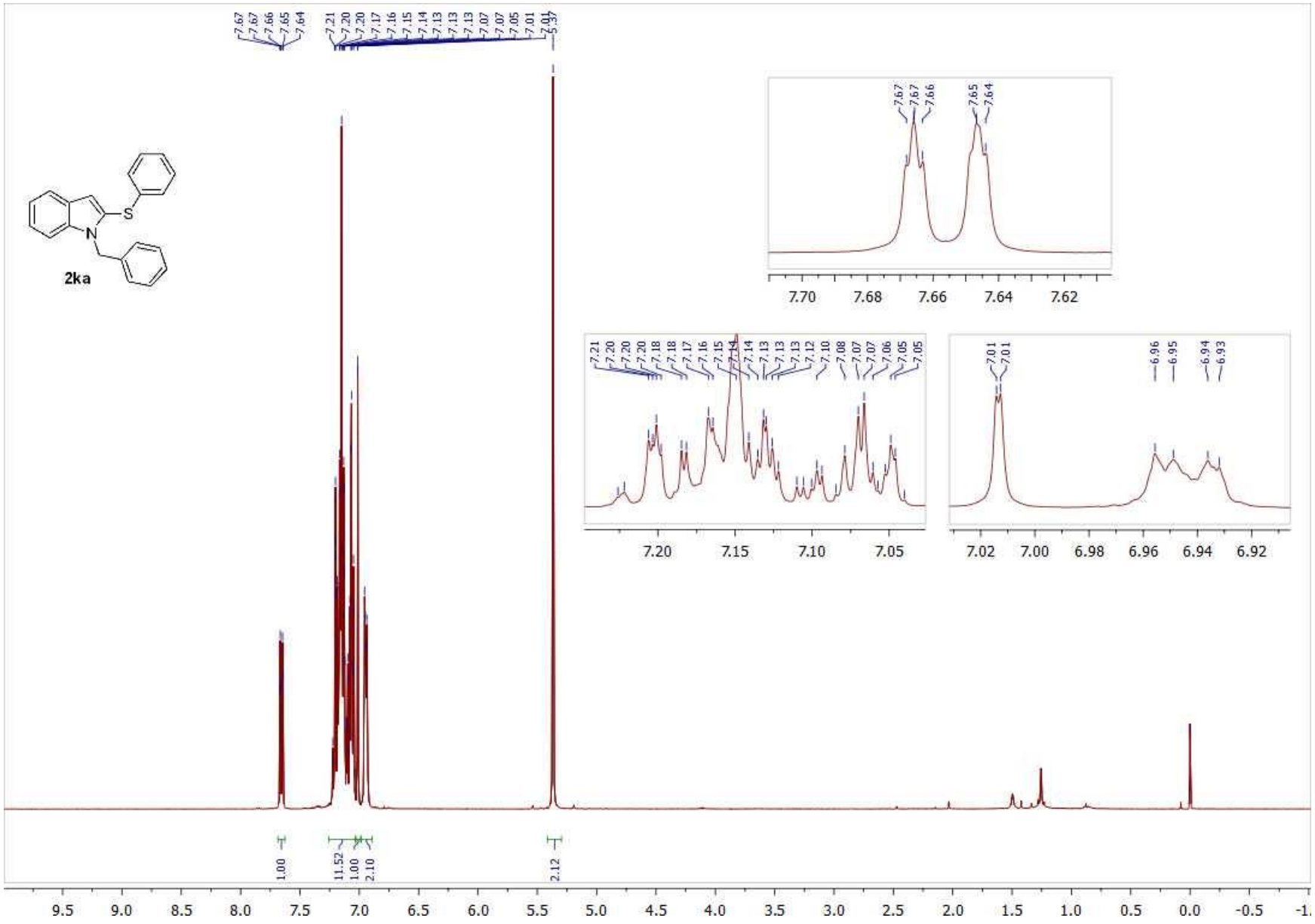
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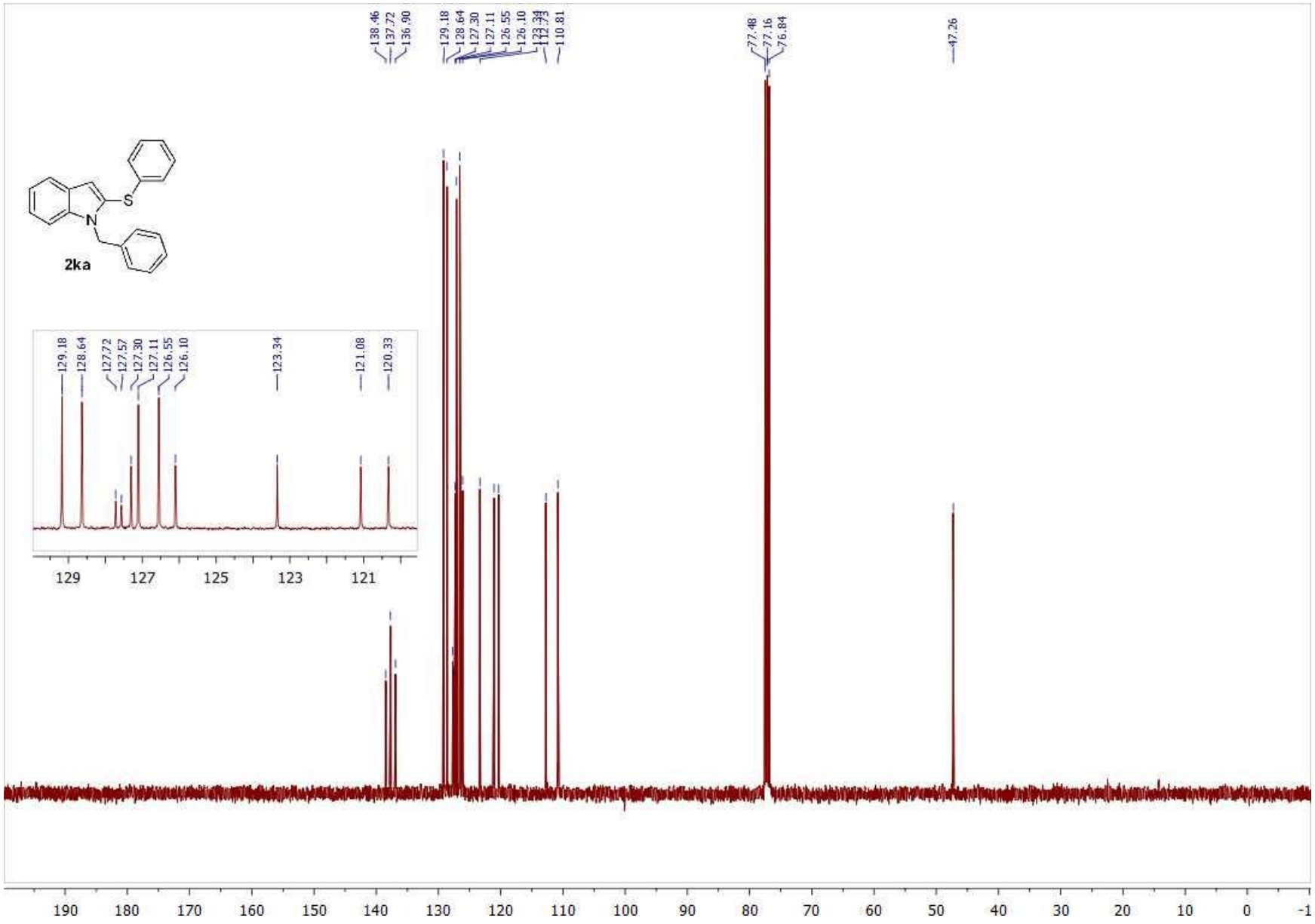
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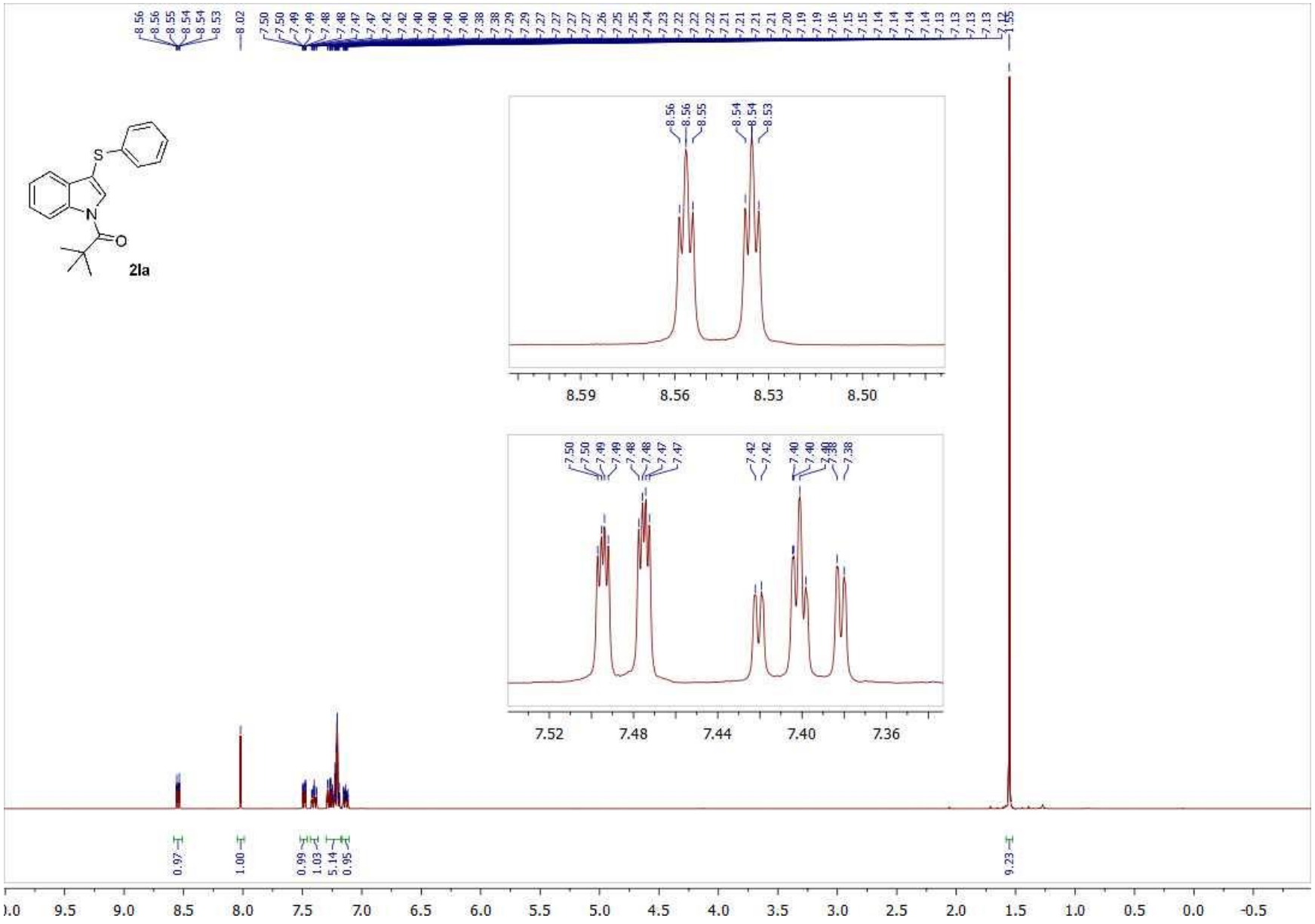
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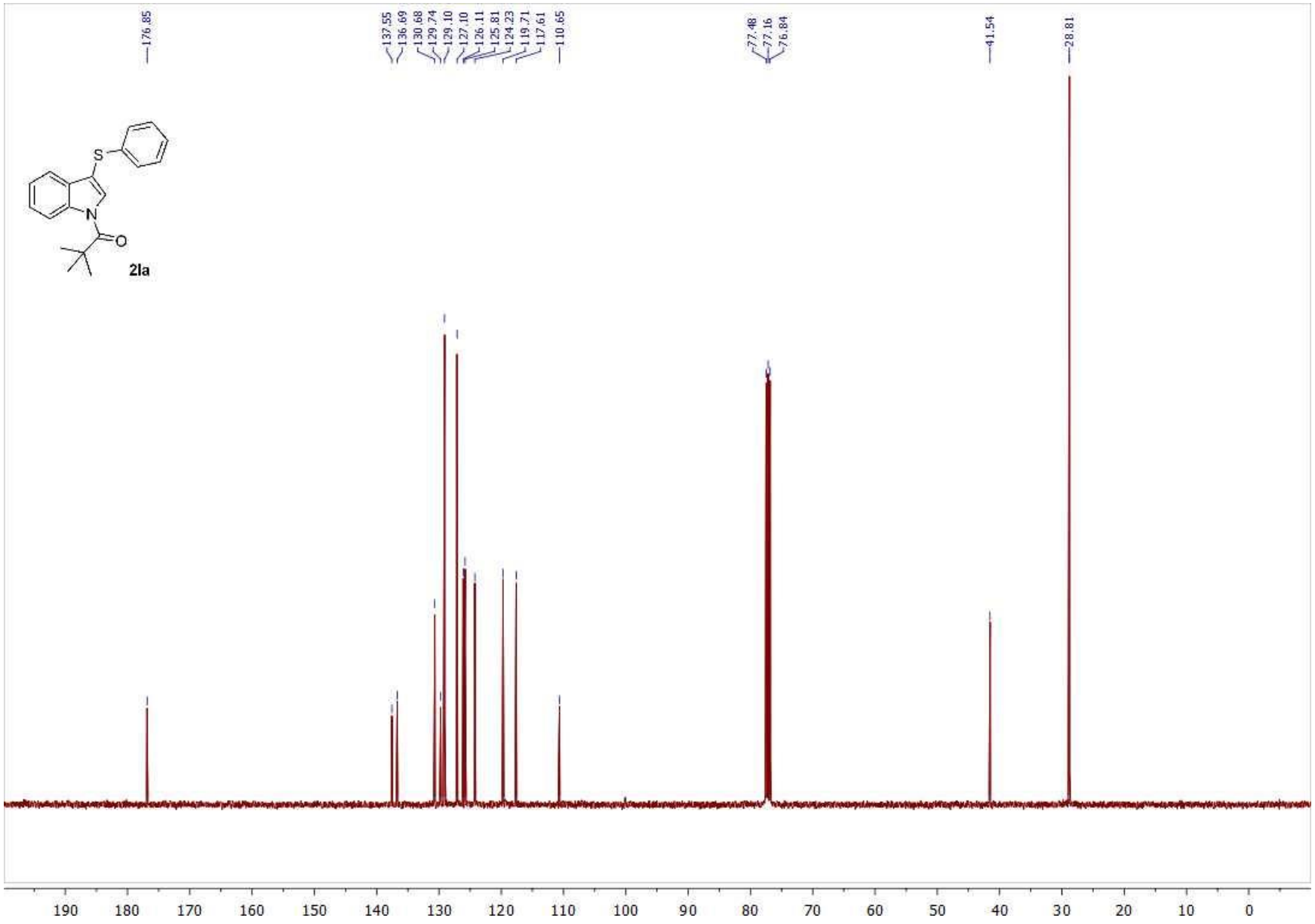
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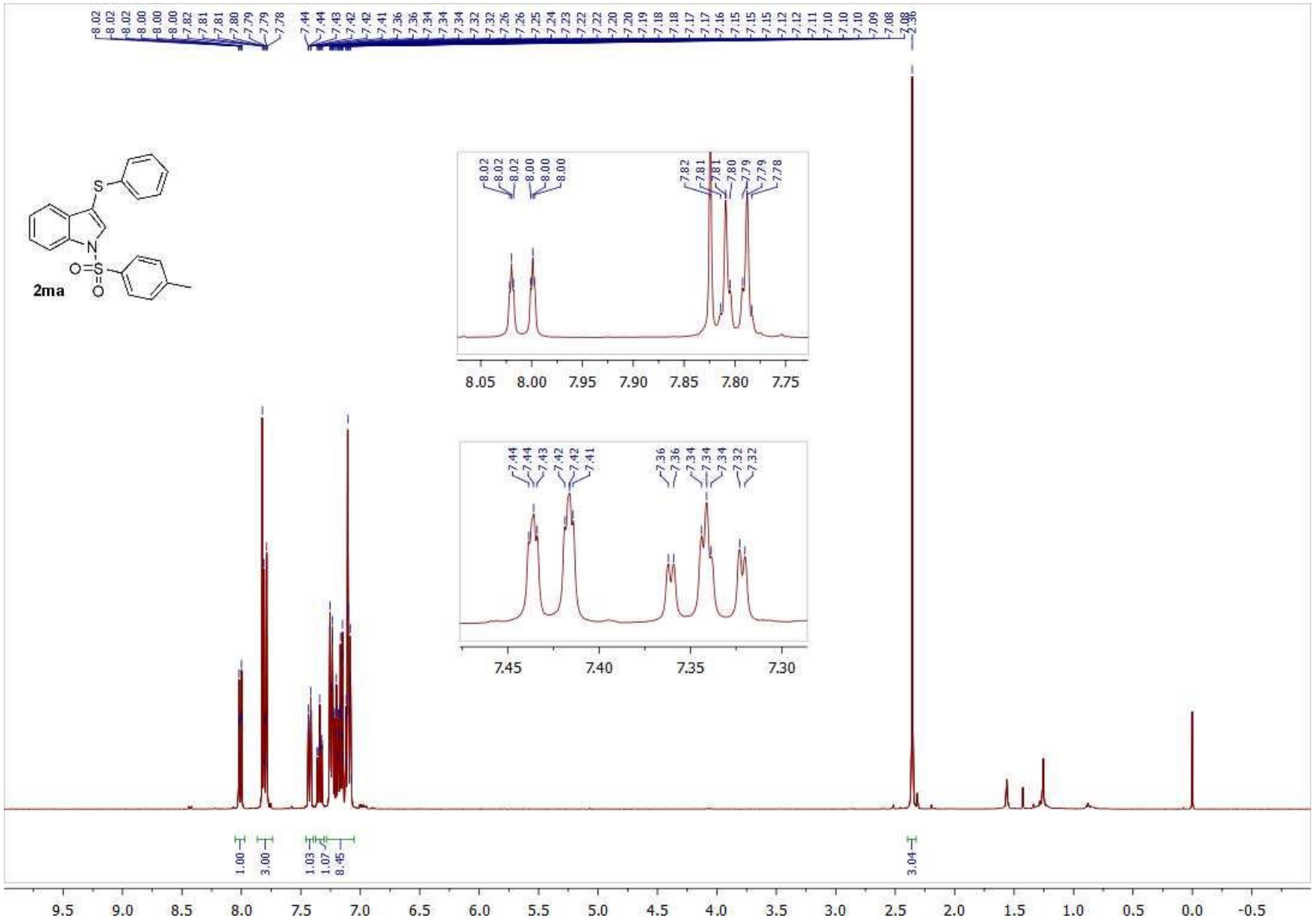
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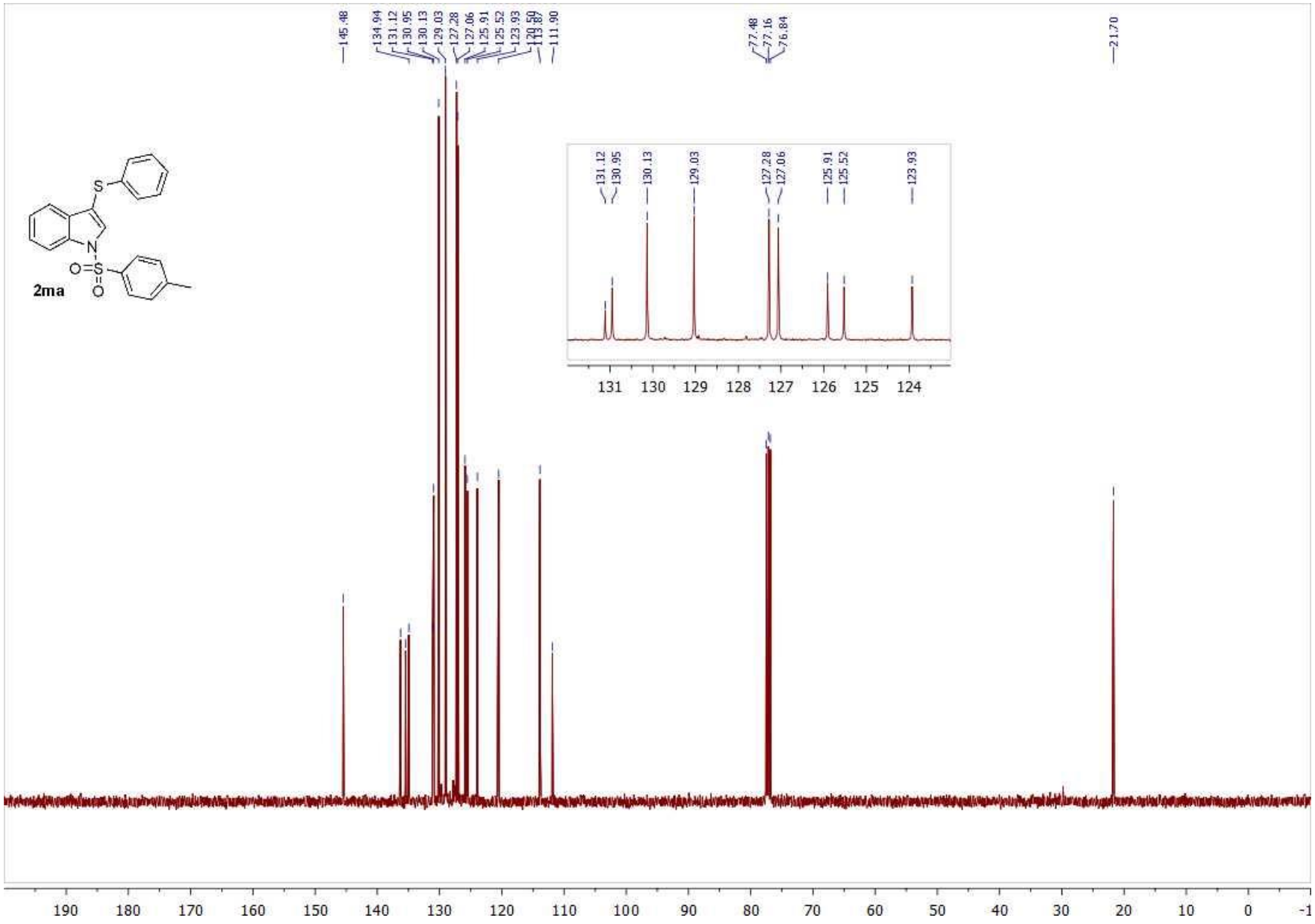
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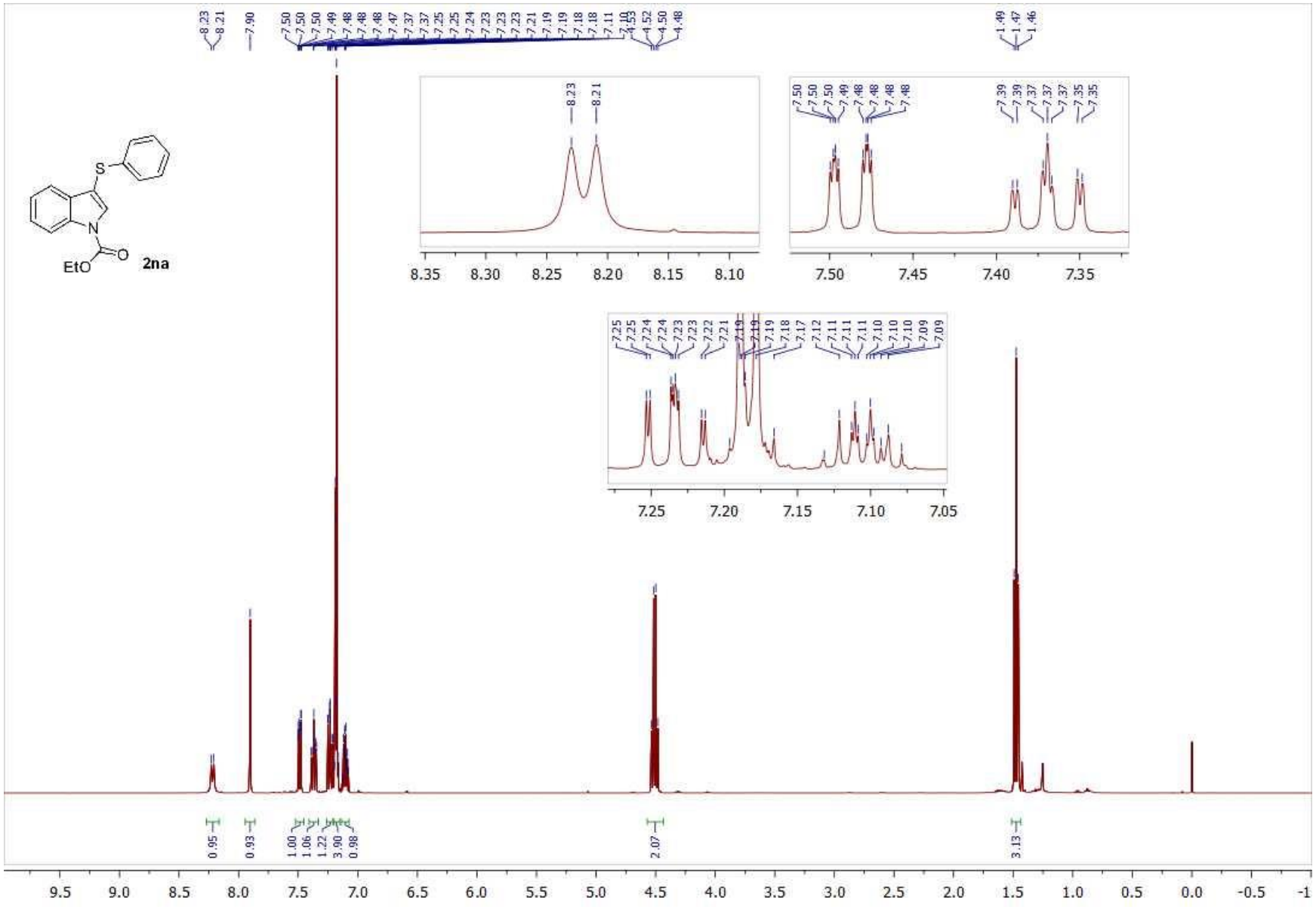
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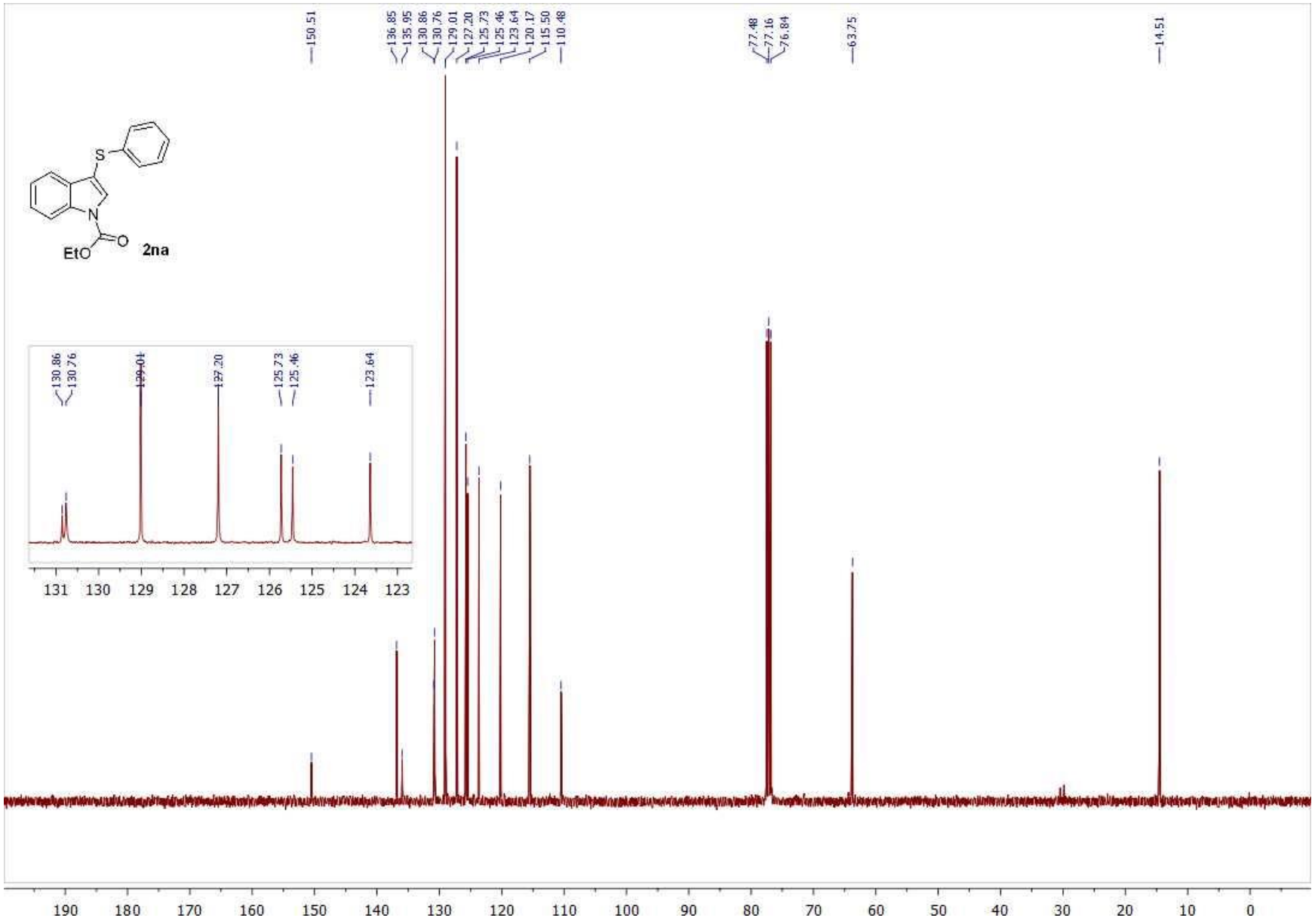
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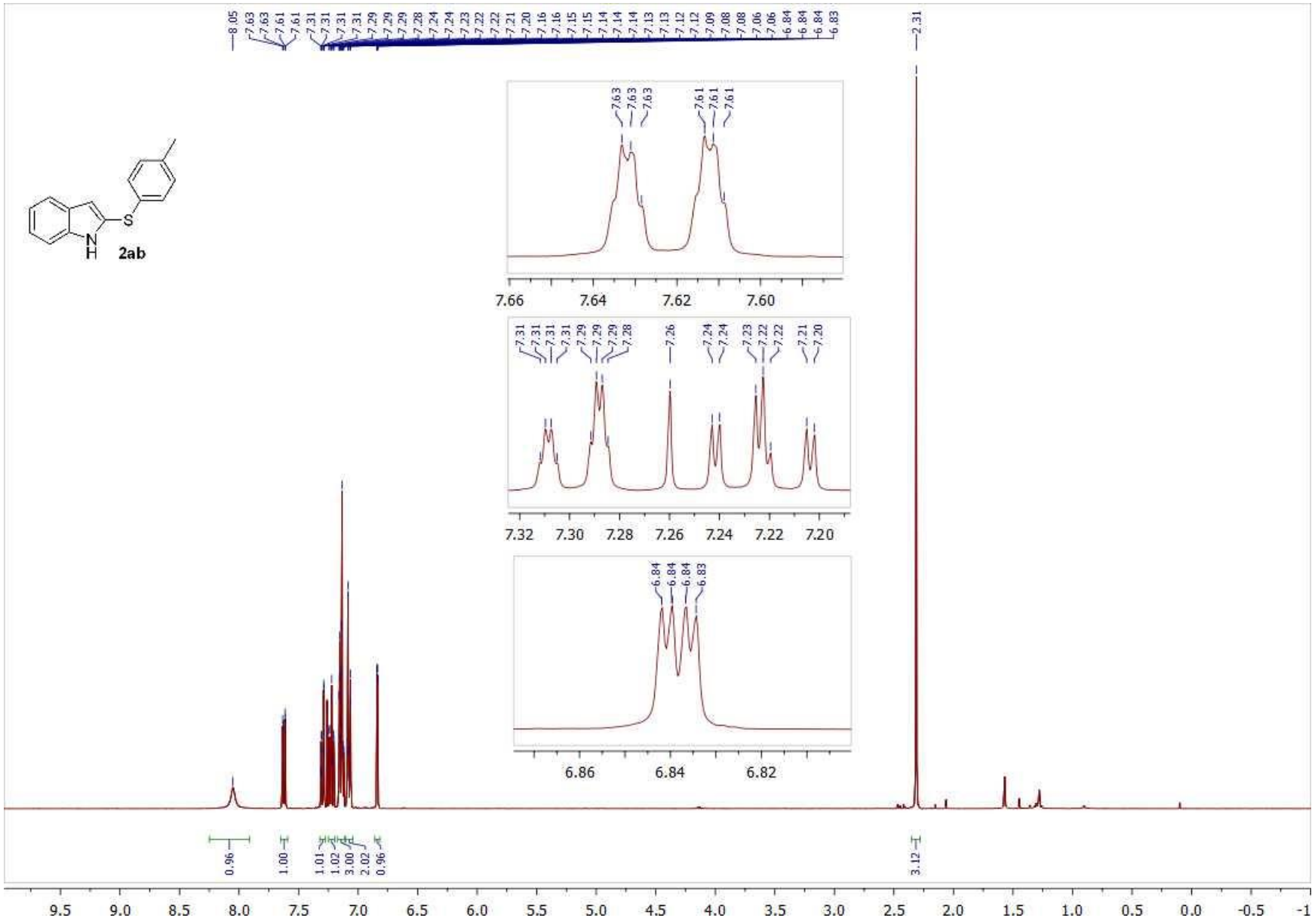
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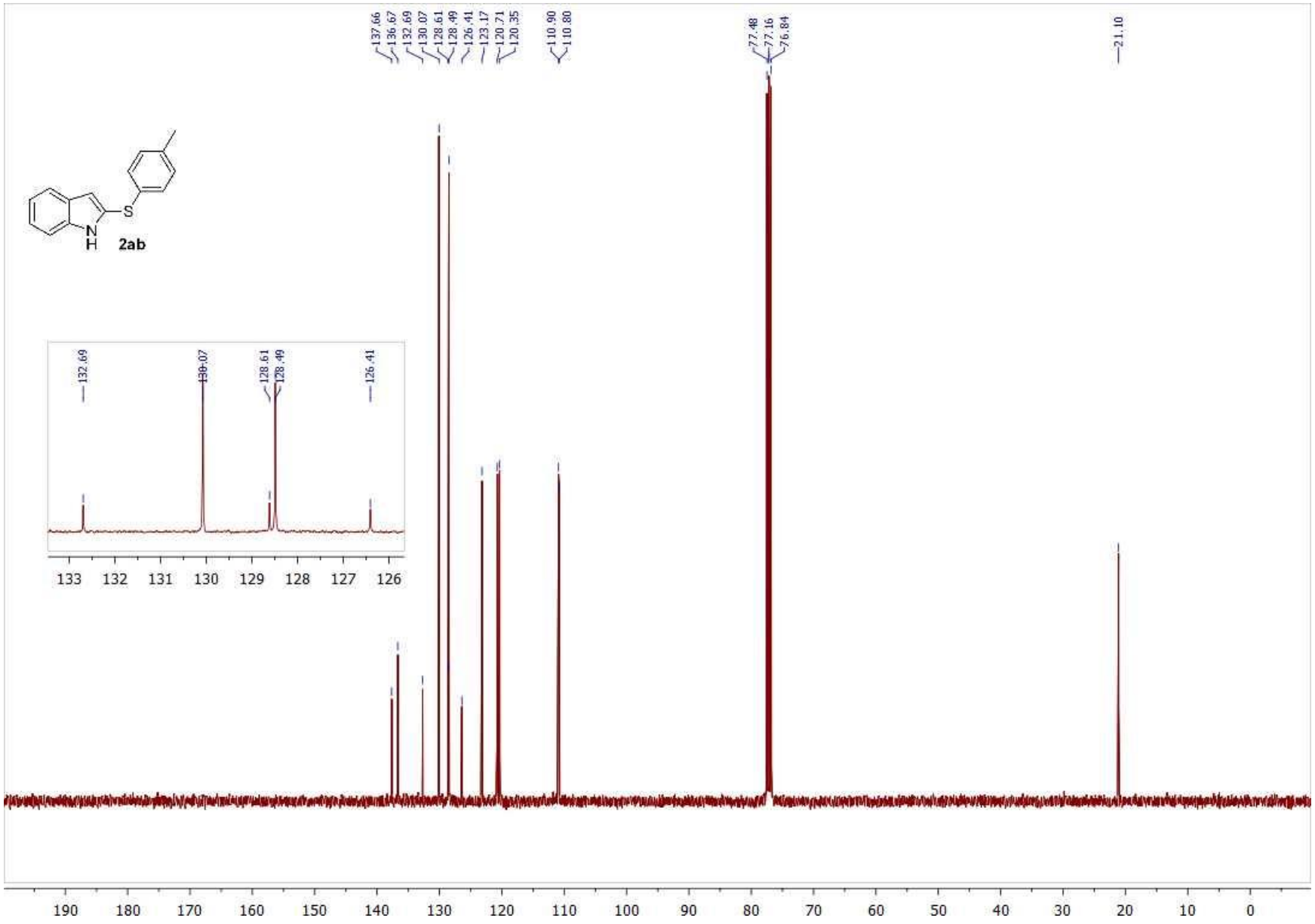
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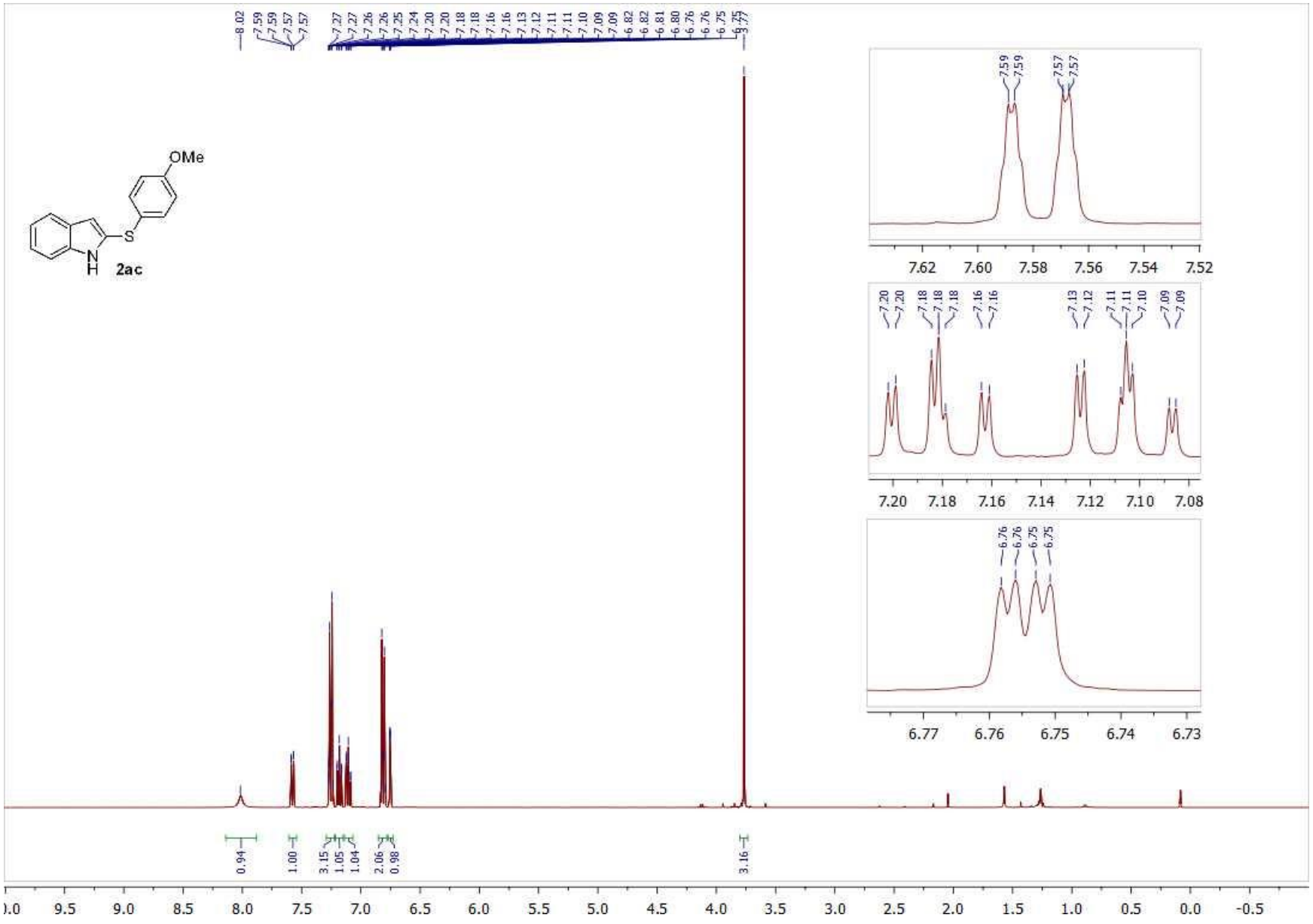
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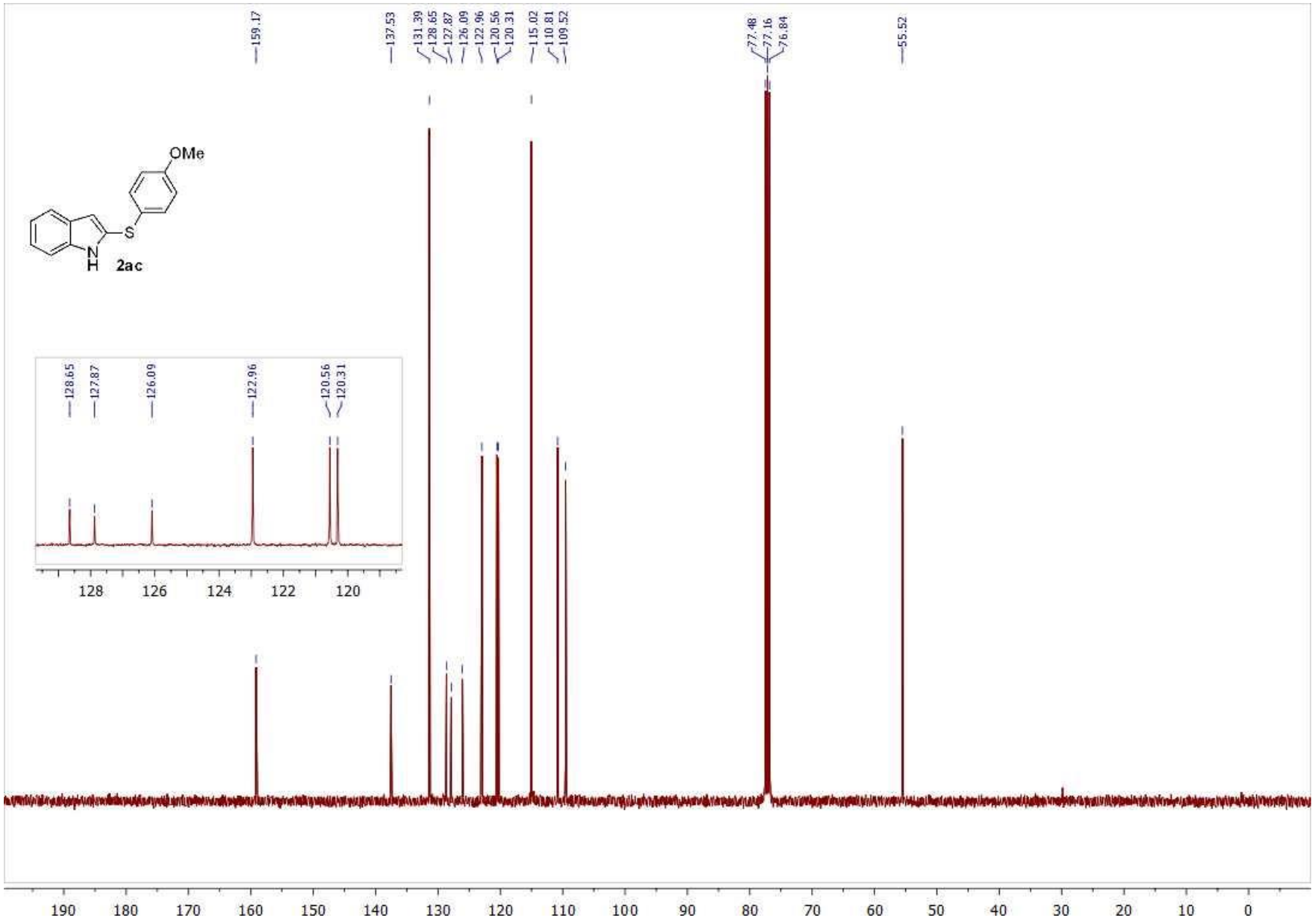
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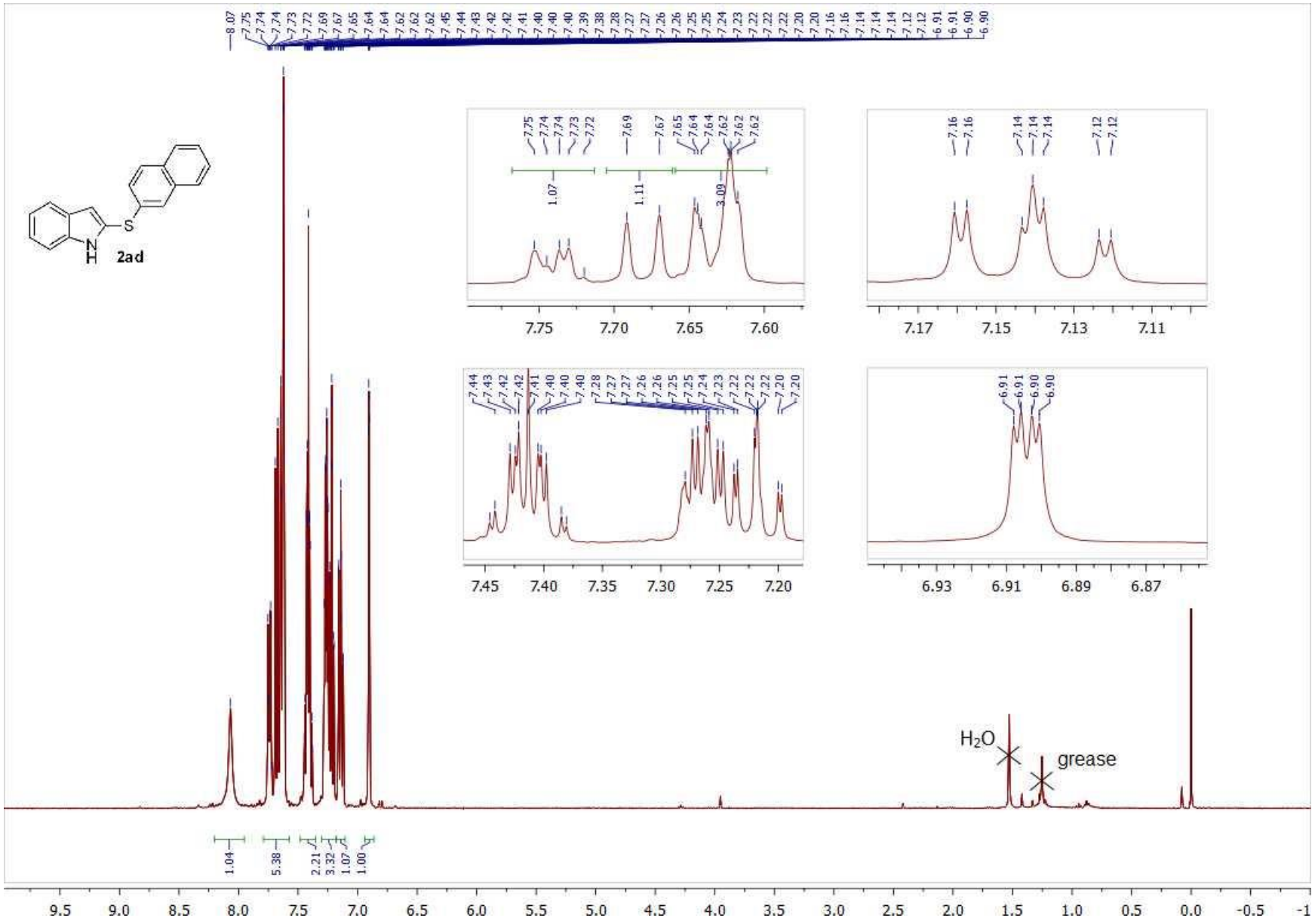
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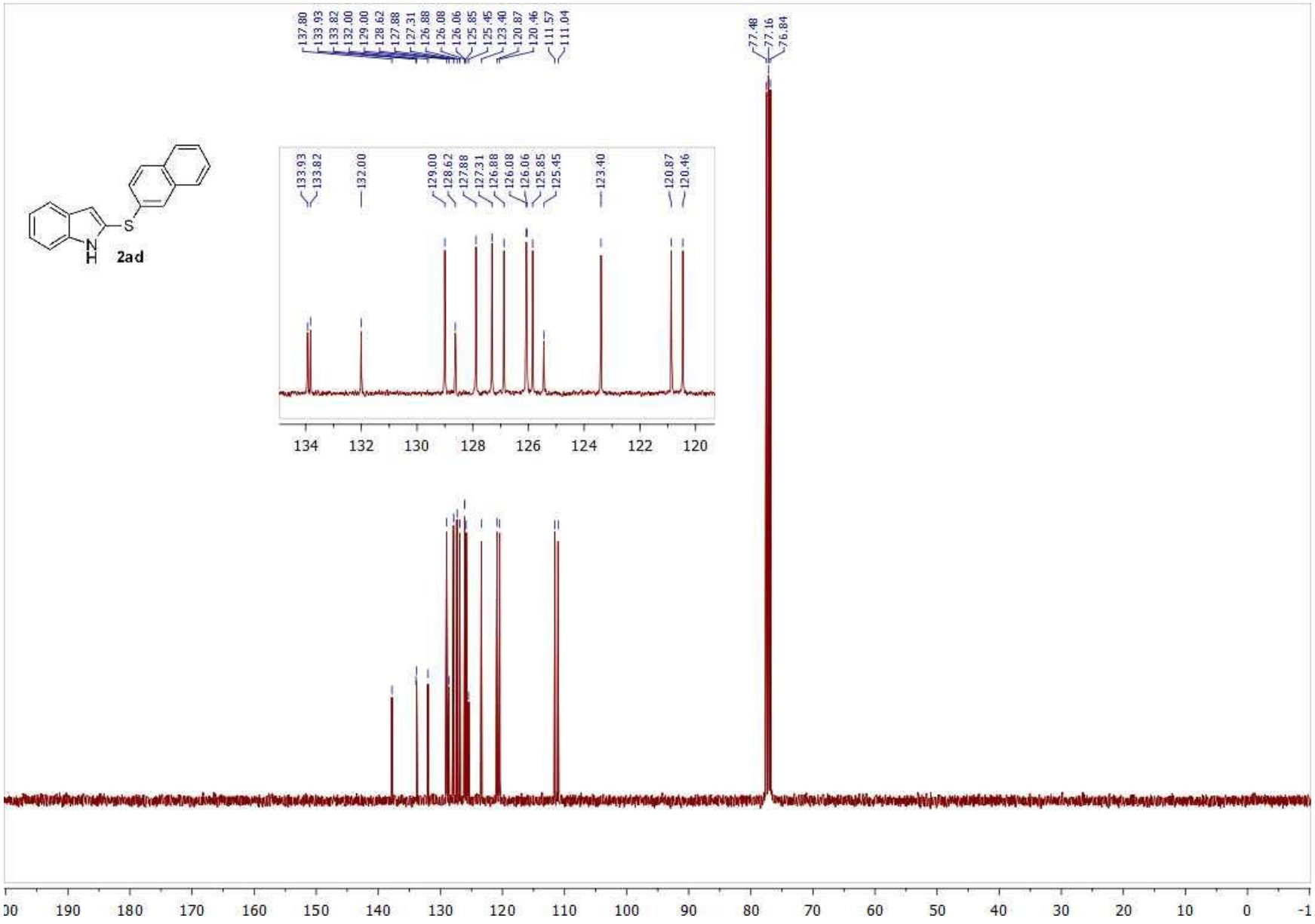
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76.84
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N
H
2ad
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128
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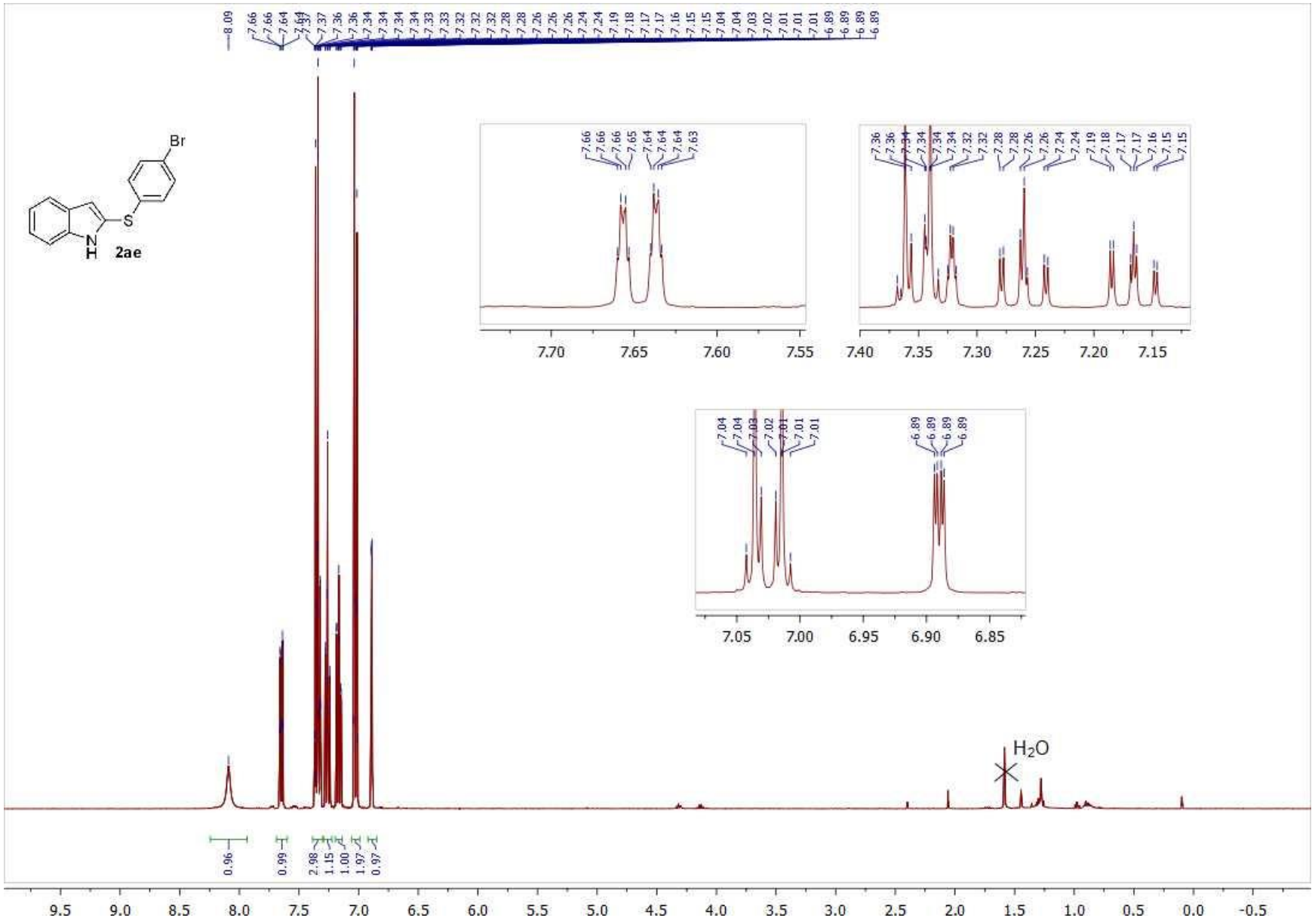
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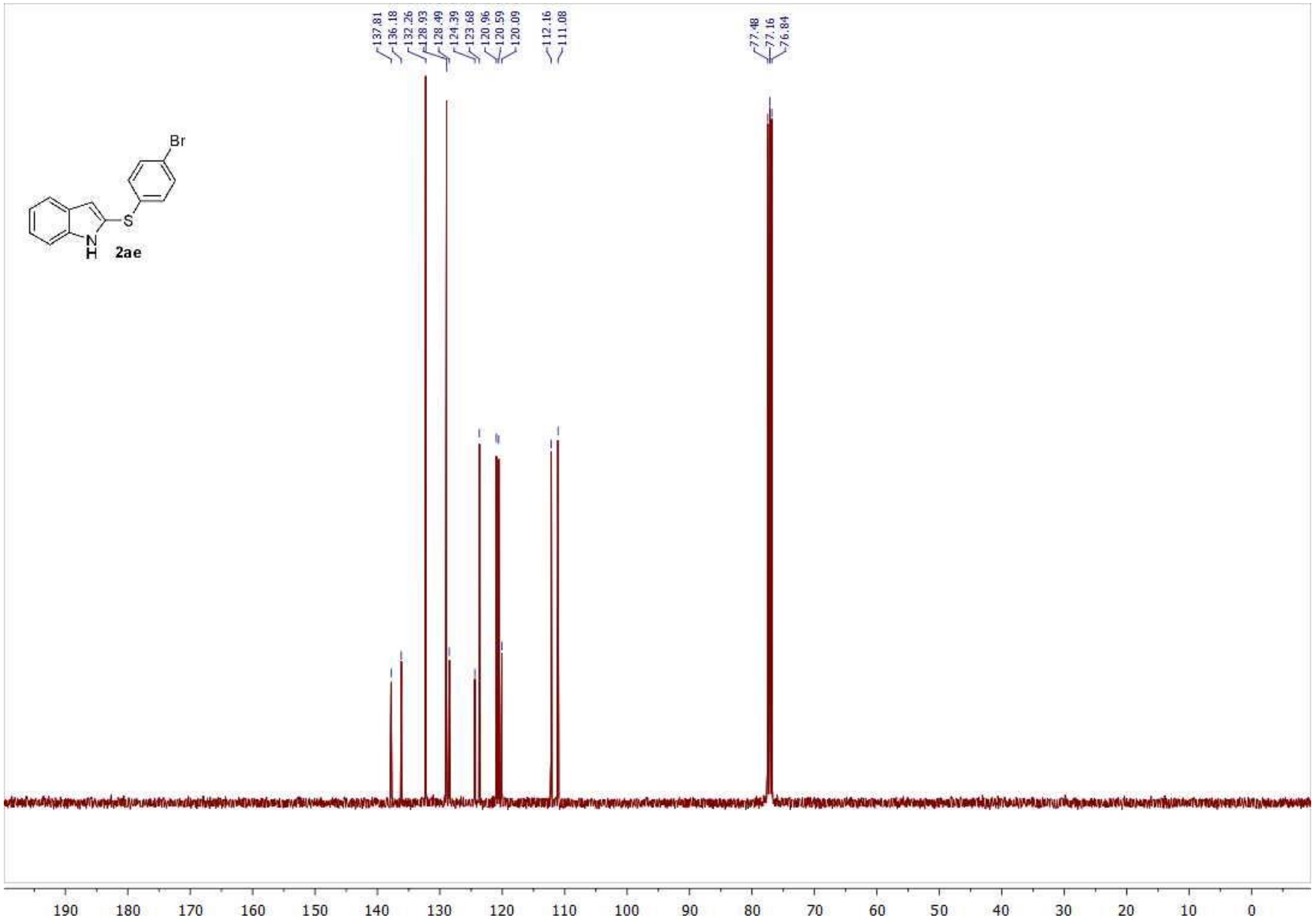
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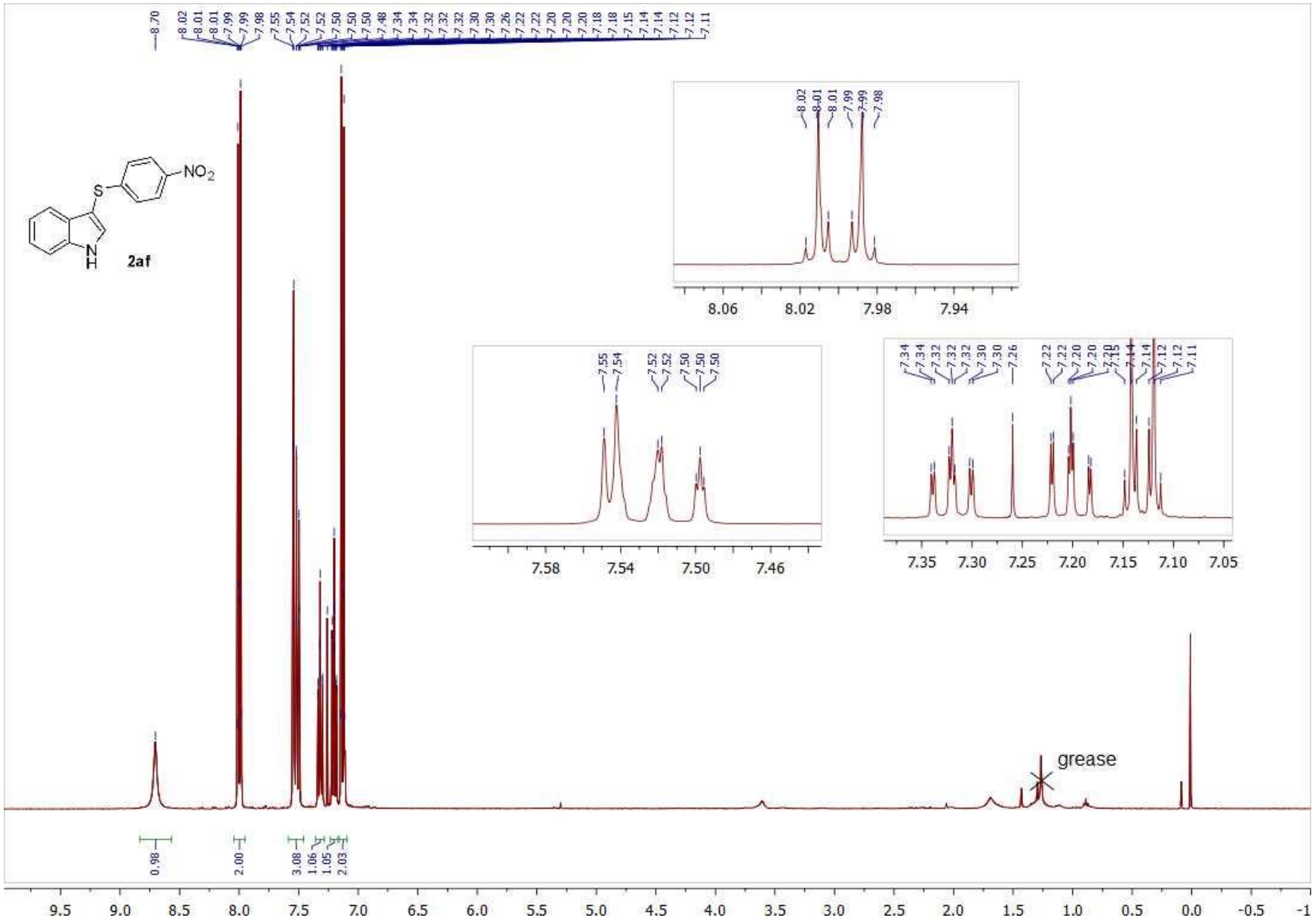
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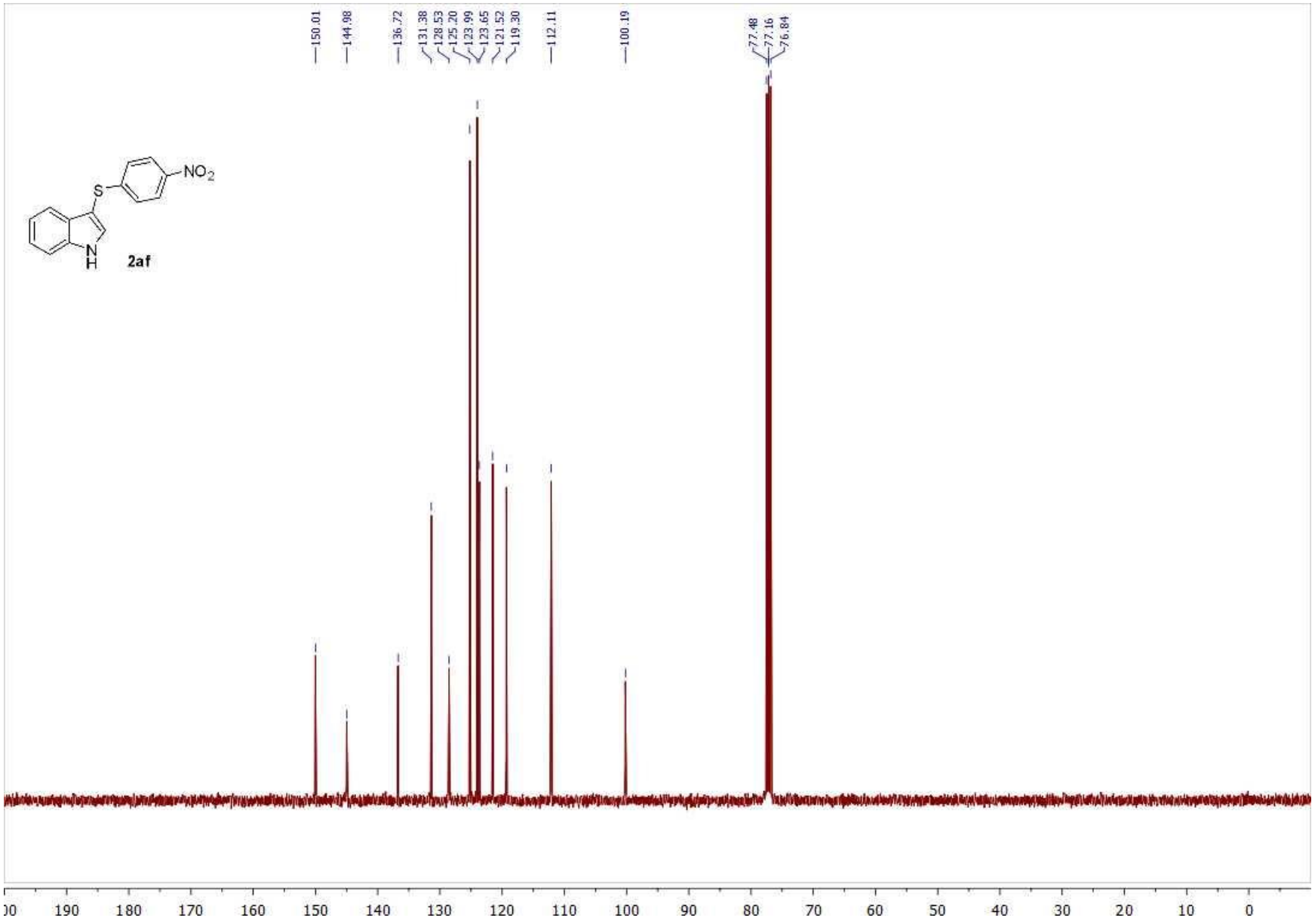
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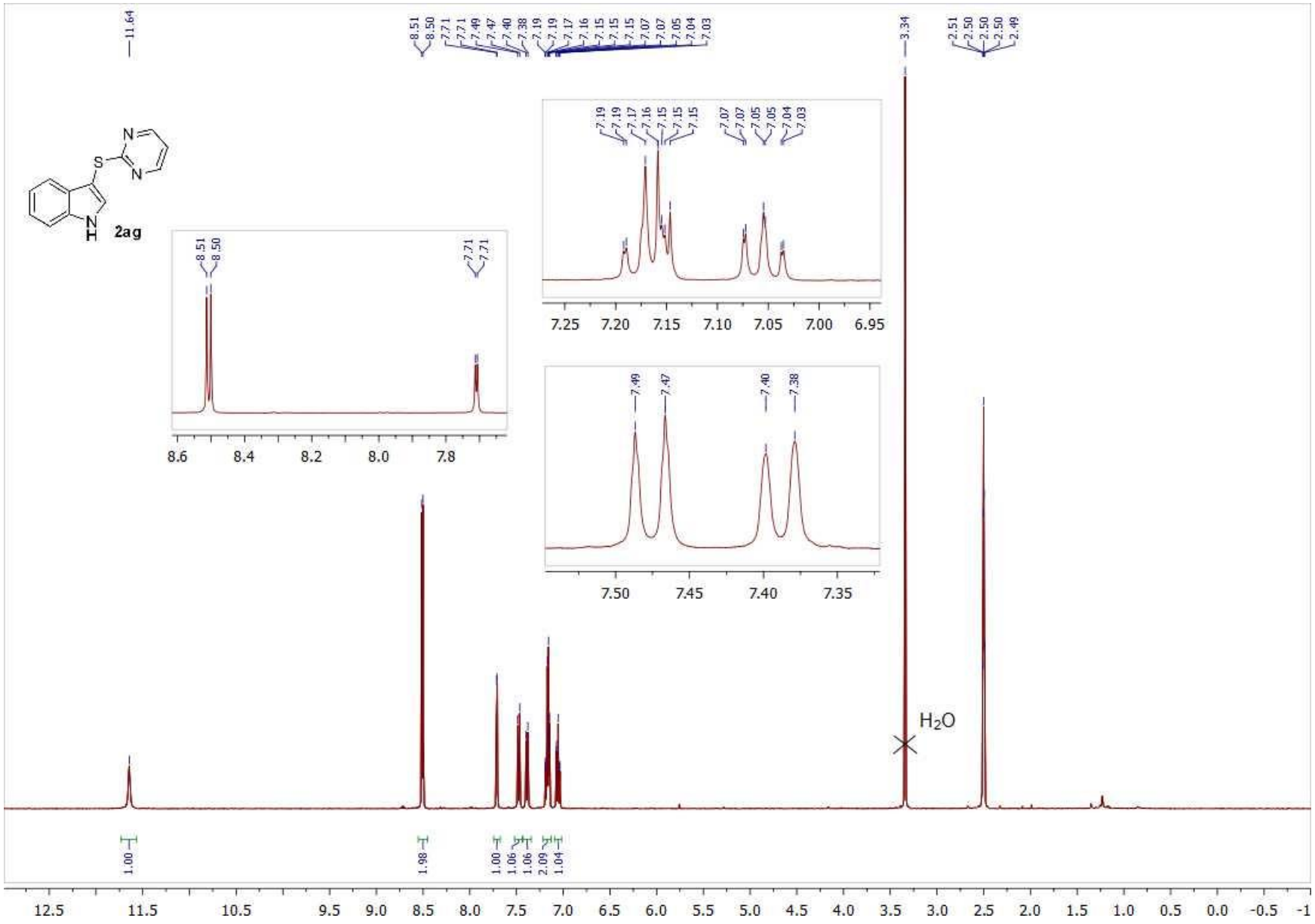
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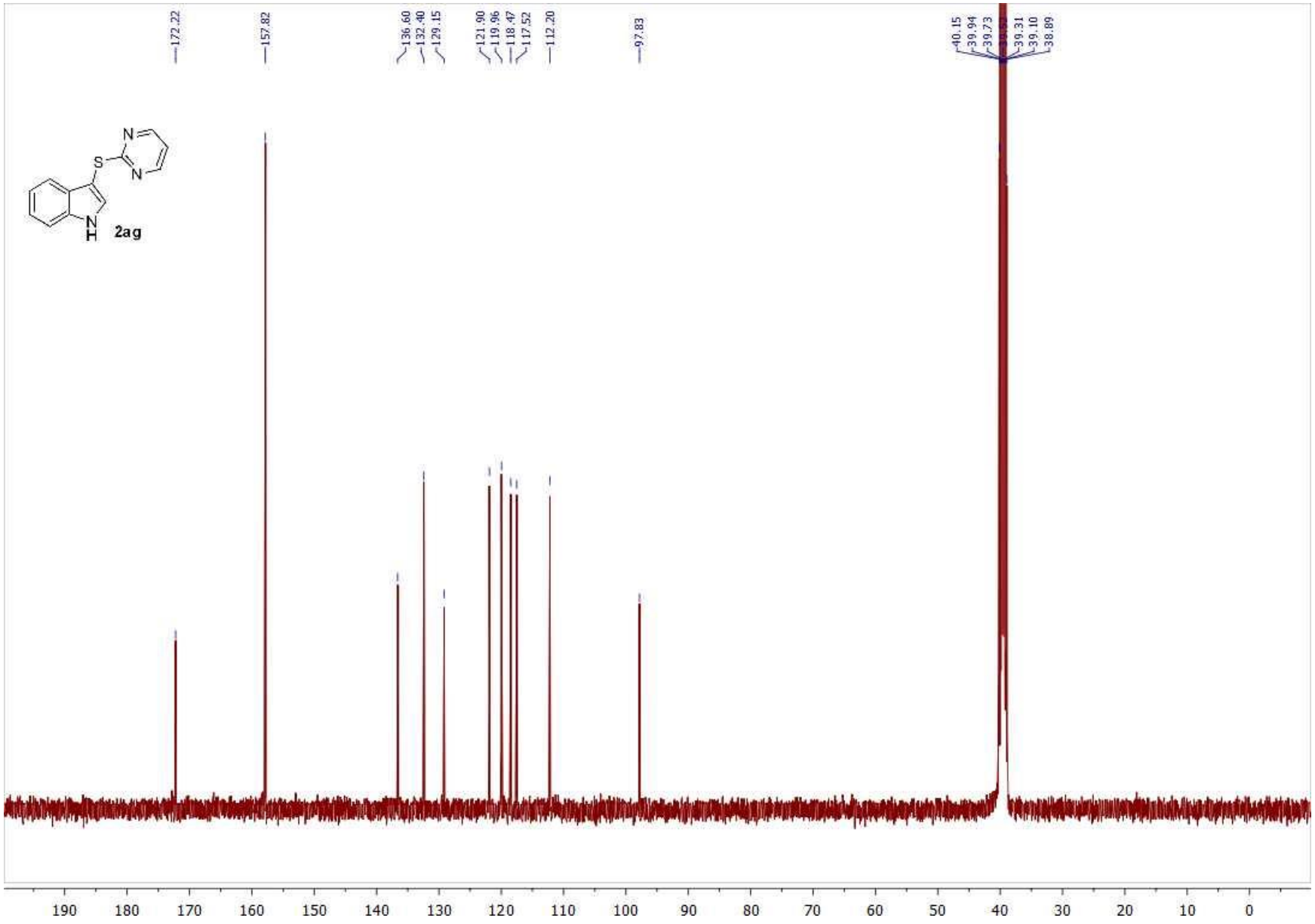
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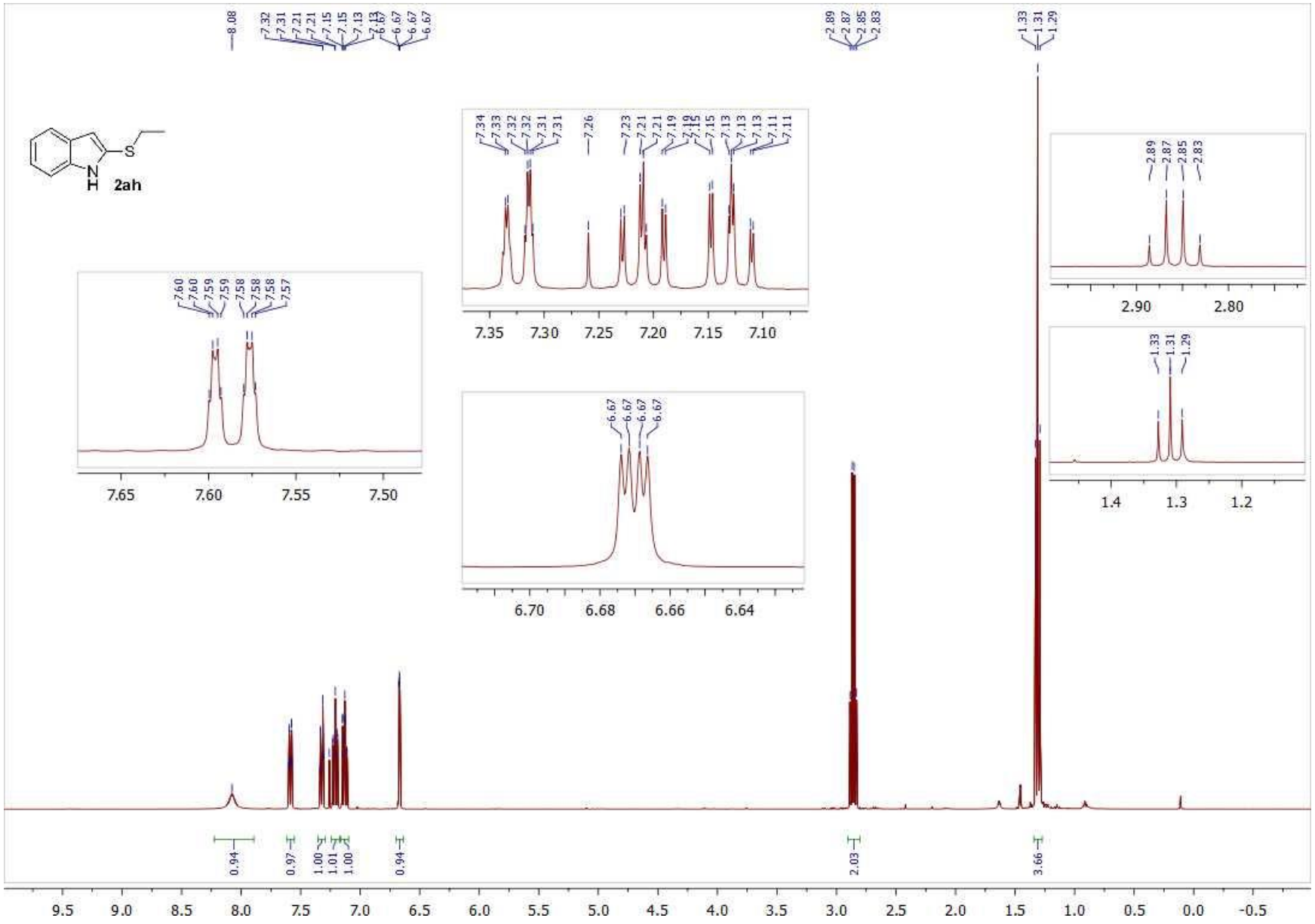
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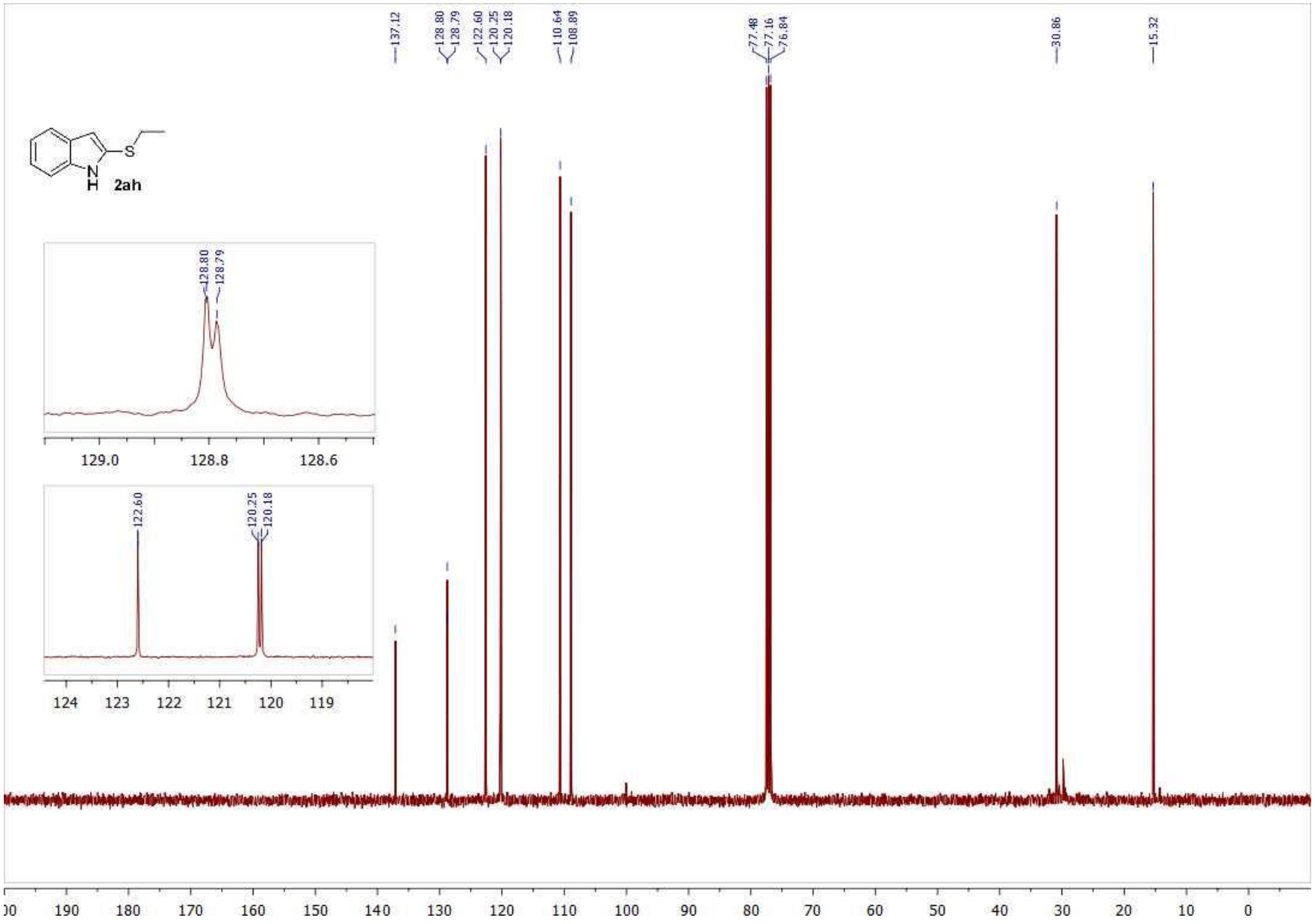
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