Visible-Light-Induced Thiol-ene/Air Oxidation Tandem Reaction for Sulfoxide Synthesis: A Photocatalyst-free and Metal-free Approach

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Contents

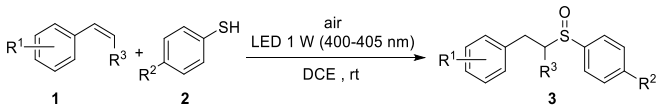
1. General Information

All solvents and reagents were obtained from commercial sources and were purified according to standard procedures. Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances.

NMR spectra were recorded on a Bruker 400 MHz spectrometer (^{1}H, ^{13}C and ^{19}F). Chemical shifts were reported in ppm from $CDCl_3$ or DMSO-d_6 with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were recorded on Bruker-Tensor 27; Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra were determined on a Bruker micro TOF-II, Agilent 5975 CMSD and Agilent 6224 TOF LC/MS mass spectrometer.

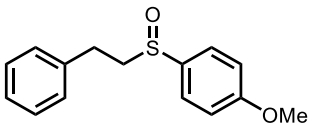
The photocatalytic reactions were performed on PhotoSyn-10 parallel photoreactor (purchased from Shanghai Quanhuan Technology Co., Ltd.). Emission spectra of the blue LED lamp (maximum emission at λ = 405 nm). Wavelength: 400 nm–405 nm.

2. General Experimental Procedure

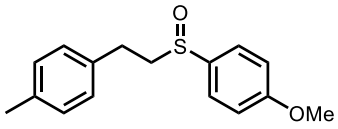


2a (0.54 mmol) was added to a solution of **1a** (0.3 mmol) in DCE (2 mL) in the open air and light irradiation at room temperature. The reaction was stirred at room temperature for the time indicated each case. The crude product was purified by flash column chromatography to give the product **3**.

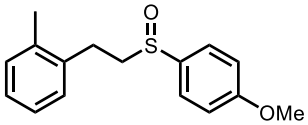
3. Spectral Data of Products



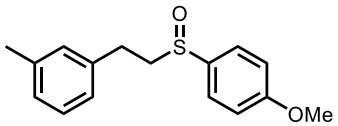
1-methoxy-4-(phenethylsulfinyl)benzene (3a),[1] 12 h, yield 82%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.22 – 7.16 (m, 3H), 7.02 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 3.08 – 3.00 (m, 3H), 2.94 – 2.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 138.8, 134.4, 128.7, 128.5, 126.6, 126.0, 114.8, 58.4, 55.5, 28.3. IR (neat): 3563, 2939, 1592, 1494, 1248, 1087, 1024, 829, 700 cm^{-1}. HRMS Calculated for $C_{15}H_{17}O_2S$ $[M+H]^+$ 261.0944, found 261.0946.



1-methoxy-4-((4-methylphenethyl)sulfinyl)benzene (3b), 12 h, yield 73%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.10 – 7.01 (m, 6H), 3.84 (s, 3H), 3.04 – 2.95 (m, 3H), 2.89 – 2.82 (m, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 136.3, 135.8, 134.5, 129.4, 128.4, 126.0, 114.9, 58.6, 55.6, 28.0, 21.1. IR (neat): 2923, 1593, 1513, 1248, 1038, 1023, 822, 514 cm^{-1}. HRMS Calculated for $C_{16}H_{19}O_2S$ $[M+H]^+$ 275.1100, found 275.1104.

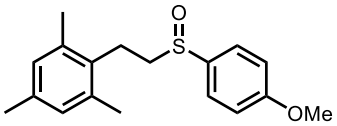


1-(2-((4-methoxyphenyl)sulfinyl)ethyl)-2-methylbenzene (3c), 12 h, yield 80%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.12 – 7.11 (m, 4H), 7.03 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H), 3.04 – 2.84 (m, 4H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 137.1, 136.1, 134.5, 130.6, 129.0, 126.9, 126.4, 126.0, 114.9, 57.0, 55.6, 25.6, 19.2. IR (neat): 2941, 1593, 1492, 1455, 1302, 1248, 1094, 1035, 822, 740, 451 cm^{-1}. HRMS Calculated for $C_{16}H_{19}O_2S$ $[M+H]^+$ 275.1100, found 275.1103.

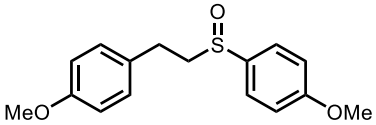


1-(2-((4-methoxyphenyl)sulfinyl)ethyl)-3-methylbenzene (3d), 12 h, yield 74%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 7.4

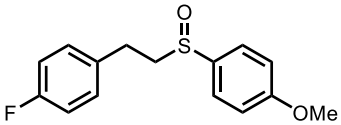
Hz, 1H), 7.03 – 6.95 (m, 5H), 3.84 (s, 3H), 3.05 – 2.95 (m, 3H), 2.90 – 2.81 (m, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 138.8, 138.4, 134.5, 129.4, 128.7, 127.5, 126.1, 125.6, 114.9, 58.5, 55.6, 28.3, 21.4. IR (neat): 2913, 1592, 1494, 1457, 1302, 1248, 1086, 1024, 822, 795, 525 cm^{-1}. HRMS Calculated for $C_{16}H_{19}O_2S$ $[M+H]^+$ 275.1100, found 275.1102.



2-(2-((4-methoxyphenyl)sulfinyl)ethyl)-1,3,5-trimethylbenzene (3e), 12 h, yield 64%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.80 (s, 2H), 3.86 (s, 3H), 2.99 – 2.76 (m, 4H), 2.22 (s, 3H), 2.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 136.2, 136.0, 134.3, 132.4, 129.2, 126.0, 114.8, 55.6, 54.9, 21.2, 20.8, 19.6. IR (neat): 2910, 1591, 1495, 1461, 1299, 1250, 1090, 1021, 828, 796, 520 cm^{-1}. HRMS Calculated for $C_{18}H_{23}O_2S$ $[M+H]^+$ 303.1413, found 303.1418.

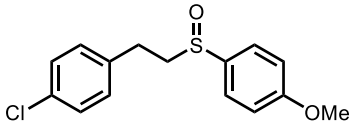


1-methoxy-4-((4-methoxyphenethyl)sulfinyl)benzene (3f), 24 h, yield 85%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H), 3.76 (s, 3H), 3.05 – 2.92 (m, 3H), 2.88 – 2.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 158.4, 134.6, 130.8, 129.6, 126.0, 114.9, 114.2, 58.8, 55.6, 55.3, 27.6. IR (neat): 2938, 1593, 1510, 1494, 1301, 1243, 1175, 1086, 1025, 822, 523 cm^{-1}. HRMS Calculated for $C_{16}H_{19}O_3S$ $[M+H]^+$ 291.1049, found 291.1051.

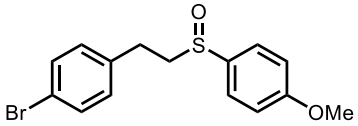


1-fluoro-4-(2-((4-methoxyphenyl)sulfinyl)ethyl)benzene (3g), 12 h, yield 79%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.13 – 7.10 (m, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.95 (t, *J* = 8.5 Hz, 2H), 3.84 (s, 3H), 3.05 – 2.97 (m, 3H), 2.91 – 2.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ162.1, 161.7 (d, *J* = 244.9 Hz),

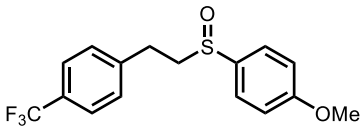
134.6 (d, J = 3.2 Hz), 134.3, 130.1 (d, J = 7.9 Hz), 126.0, 115.6 (d, J = 21.3 Hz), 114.9, 58.5, 55.6, 27.6. IR (neat): 2938, 1593, 1508, 1495, 1302, 1249, 1024, 825, 524 cm^{-1}. HRMS Calculated for $C_{15}H_{16}FO_2S$ $[M+H]^+$ 279.0850, found 279.0850.



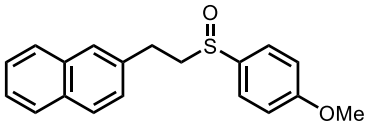
1-chloro-4-(2-((4-methoxyphenyl)sulfinyl)ethyl)benzene (3h), 12 h, yield 76%, light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H), 3.03 – 2.96 (m, 3H), 2.89 – 2.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 137.3, 134.2, 132.5, 130.0, 128.9, 126.0, 114.9, 58.1, 55.6, 27.7. IR (neat): 2922, 1593, 1489, 1247, 1088, 1040, 821, 804, 506 cm^{-1}. HRMS Calculated for $C_{15}H_{16}ClO_2S$ $[M+H]^+$ 295.0554, found 295.0557.



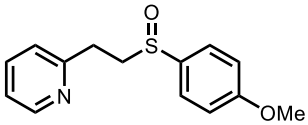
1-bromo-4-(2-((4-methoxyphenyl)sulfinyl)ethyl)benzene (3i), 18 h, yield 57%, light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.05 – 7.01 (m, 4H), 3.84 (s, 3H), 3.04 – 2.97 (m, 3H), 2.88 – 2.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 137.9, 134.2, 131.9, 130.4, 126.0, 120.6, 115.0, 58.1, 55.6, 27.8. IR (neat): 2922, 1593, 1487, 1303, 1248, 1040, 822, 798, 494 cm^{-1}. HRMS Calculated for $C_{15}H_{16}BrO_2S$ $[M+H]^+$ 339.0049, found 339.0051.



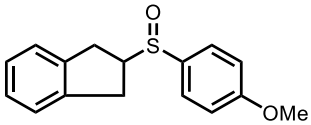
1-methoxy-4-((4-(trifluoromethyl)phenethyl)sulfinyl)benzene (**3j),** 18 h, yield 75%, light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 4H), 7.29 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 3.86 (s, 3H), 3.16 – 3.09 (m, 1H), 3.06 – 3.02 (m, 2H), 2.98 – 2.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 143.1, 134.1, 129.1 (q, J = 32.4 Hz), 129.0, 126.0, 125.7 (q, J = 3.7 Hz), 124.2 (q, J = 271.9 Hz), 115.0, 57.8, 55.6, 28.1. IR (neat): 2949, 1497, 1324, 1249, 1161, 1110, 1068, 1026, 833, 524 cm^{-1}. HRMS Calculated for $C_{16}H_{16}F_3O_2S$ $[M+H]^+$ 329.0818, found 329.0821.



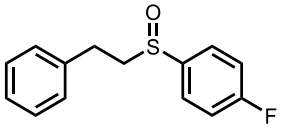
2-(2-((4-methoxyphenyl)sulfinyl)ethyl)naphthalene (3k), 12 h, yield 77%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 3H), 7.62 – 7.58 (m, 3H), 7.47 – 7.41 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 2H), 3.84 (s, 3H), 3.23 – 3.02 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 136.4, 134.5, 133.6, 132.3, 128.5, 127.7, 127.6, 127.0, 126.9, 126.3, 126.1, 125.7, 114.9, 58.4, 55.6, 28.5. IR (neat): 2906, 1593, 1492, 1241, 1123, 1087, 1043, 815, 525, 473 cm^{-1}. HRMS Calculated for $C_{19}H_{19}O_2S$ $[M+H]^+$ 311.1100, found 311.1102.



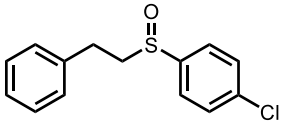
2-(2-((4-methoxyphenyl)sulfinyl)ethyl)pyridine (3l), 12 h, yield 62%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 3H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.10 – 7.07 (m, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.29 – 3.11 (m, 3H), 3.07 – 3.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 158.5, 149.4, 136.7, 134.4, 126.0, 123.4, 121.7, 114.8, 56.1, 55.5, 30.3. IR (neat): 3441, 1592, 1495, 1437, 1303, 1249, 1173, 1087, 1022, 830, 755, 528 cm^{-1}. HRMS Calculated for $C_{14}H_{16}NO_2S$ $[M+H]^+$ 262.0896, found 262.0901.



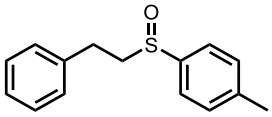
2-((4-methoxyphenyl)sulfinyl)-2,3-dihydro-1H-indene (3m), 12 h, yield 50%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.6 Hz, 2H), 7.20 – 7.14 (m, 4H), 7.02 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H), 3.68 – 3.61 (m, 1H), 3.54 (dd, *J* = 16.8, 6.0 Hz, 1H), 3.14 – 3.04 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 140.6, 140.4, 134.1, 127.1, 127.0, 126.8, 124.8, 124.4, 114.8, 64.1, 55.6, 33.5, 32.5. IR (neat): 3842, 3718, 2314, 1651, 1496, 1242, 1087, 1033, 833, 686, 478, 462 cm^{-1}. HRMS Calculated for $C_{16}H_{17}O_2S$ $[M+H]^+$ 273.0944, found 273.0937.



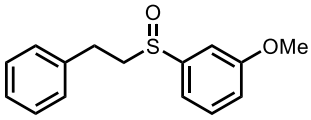
1-fluoro-4-(phenethylsulfinyl)benzene (**3n**),[1] 12 h, yield 75%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.16 (m, 2H), 3.12 – 2.86 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (d, *J* = 251.4 Hz), 139.1 (d, *J* = 3.0 Hz), 138.6, 128.9, 128.6, 126.9, 126.4 (d, *J* = 8.8 Hz), 116.7 (d, *J* = 22.5 Hz), 58.6, 28.2. IR (neat): 3676, 3029, 1588, 1490, 1220, 1083, 1153, 1038, 833, 699, 520, 470 cm^{-1}. HRMS Calculated for $C_{14}H_{14}FOS$ $[M+H]^+$ 249.0744, found 249.0746.



1-chloro-4-(phenethylsulfinyl)benzene (3o),[1] 12 h, yield 73%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.16 (m, 3H), 3.13 – 2.98 (m, 3H), 2.91 – 2.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 138.5, 137.3, 129.6, 128.9, 128.6, 126.9, 125.5, 58.4, 28.1. IR (neat): 2926, 1599, 1472, 1454, 1087, 1036, 1008, 818, 738, 698, 504, 490 cm^{-1}. HRMS Calculated for $C_{14}H_{14}ClOS$ $[M+H]^+$ 265.0448, found 265.0452.

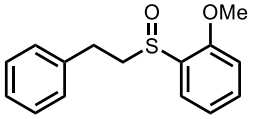


1-methyl-4-(phenethylsulfinyl)benzene (3p),[1] 12 h, yield 82%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.22 – 7.16 (m, 3H), 3.10 – 3.02 (m, 3H), 2.94 – 2.87 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 140.2, 138.9, 130.0, 128.8, 128.6, 126.7, 124.2, 58.3, 28.3, 21.5. IR (neat): 2920, 1599, 1494, 1454, 1084, 1038, 1014, 809, 751, 699, 509 cm^{-1}. HRMS Calculated for $C_{15}H_{17}OS$ $[M+H]^+$ 245.0995, found 245.0997.



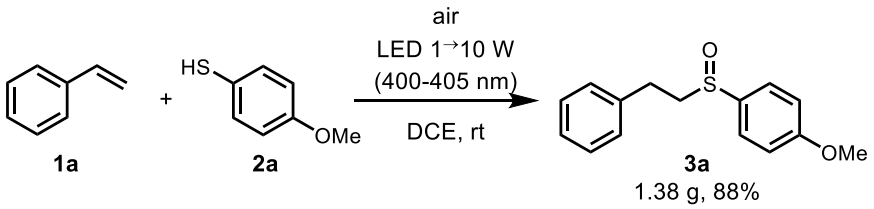
1-methoxy-3-(phenethylsulfinyl)benzene (3q), 12 h, yield 80%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.9 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.17 (m, 4H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 3.14 – 2.99 (m, 3H), 2.96 – 2.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 145.2, 138.8,

130.3, 128.8, 128.6, 126.8, 117.5, 116.1, 108.5, 58.4, 55.7, 28.3. IR (neat): 3017, 2932, 1588, 1475, 1278, 1243, 1030, 749, 685 cm^{-1}. HRMS Calculated for $C_{15}H_{17}O_2S$ $[M+H]^+$ 261.0944, found 261.0942.



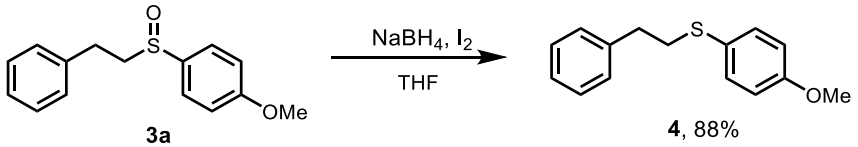
1-methoxy-2-(phenethylsulfinyl)benzene (3r), 12 h, yield 67%, light yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.21 – 7.16 (m, 4H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H), 3.35 – 3.28 (m, 1H), 3.19 – 3.12 (m, 1H), 3.08 – 3.01 (m, 1H), 2.89 – 2.82 (m, 1H). IR (neat): 3485, 3000, 2931, 1579, 1472, 1430, 1268, 1234, 1061, 1030, 749, 698 cm^{-1}. HRMS Calculated for $C_{15}H_{17}O_2S$ $[M+H]^+$ 261.0944, found 261.0942.

4. Gram scale experiment of 3a



2a (10.8 mmol) was added to a solution of **1a** (6 mmol) in DCE (20 mL) in the open air and light irradiation at room temperature. Light irradiation with a 400-405 nm LED light source (1W) for 2 d, then light irradiation with a 400-405 nm LED light source (10W) for 4 d. After evaporating the solvent, the crude product was purified by flash column chromatography with an eluent (PE/EA = 4/1) to give the product **3a** 1.38 g, 88%.

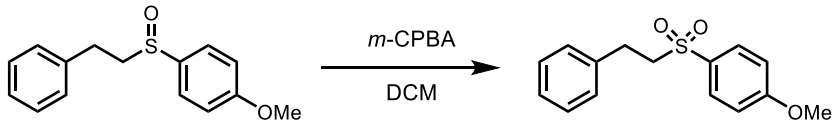
5. Chemical transformations of 3a



To a solution of the **3a** (0.15 mmol) and I_2 (0.18 mmol) in THF (2 mL) was slowly

added $NaBH_4$ (0.15 mmol). The mixture was stirred at r.t. for 10 min, the reaction was quenched with a 10% aq solution of NaOH (2 mL). The aqueous layer was extracted with DCM (3 × 10 mL), and the combined organic extracts were washed successively with 5% aq $Na_2S_2O_3$ (5 mL) and H_2O (2 × 10 mL). The resulting organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. Further purification of the product was achieved by column chromatography with an eluent (PE/EA = 20/1) to give **4** as a yellow oil (32 mg, 88% yield).[2]

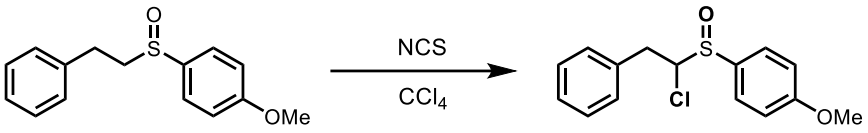
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.23 – 7.15 (m, 3H), 6.85 (d, *J* = 8.2 Hz, 2H), 3.79 (s, 3H), 3.08 – 3.04 (m, 1H), 2.88 – 2.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 140.4, 133.3, 128.5, 128.5, 126.4, 126.3, 114.6, 55.3, 37.2, 35.9. IR (neat): 2923, 1591, 1492, 1454, 1283, 1241, 1172, 1029, 823, 696 cm^{-1}. HRMS Calculated for $C_{15}H_{17}OS$ $[M+H]^+$ 245.0995, found 245.0997.



3a **5**, 94%

At 0 °C, m-chloroperbenzoic acid (0.2 mmol) was added portion wise to a solution of **3a** (0.1 mmol) in CH_2Cl_2 (2 mL). The resulting solution was allowed to warm to room temperature and stirred for 2 h. saturated aqueous $NaHCO_3$ was added to the reaction mixture and the resulting solution was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with an eluent (PE/EA = 5/1) to give **5** as a white solid (26 mg, 94% yield).[3]

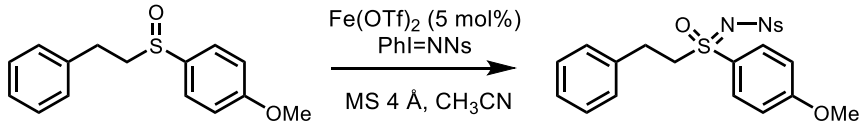
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.18 (m, 3H), 7.11 (d, *J* = 7.4 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 3.35 – 3.31 (m, 2H), 3.05 – 3.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 137.7, 130.6, 130.4, 128.9, 128.4, 127.0, 114.6, 57.9, 55.8, 29.0. IR (neat): 2925, 1595, 1498, 1451, 1285, 1262, 1179, 1147, 1023, 742, 592, 531 cm^{-1}. HRMS Calculated for $C_{15}H_{17}O_3S$ $[M+H]^+$ 277.0893, found 277.0896.



3a **6**, 88%

N-Chlorosuccinimide (0.22 mmol) was added to a solution of the sulfoxide **3a** (0.2mmol) in 2 mL of carbon tetrachloride and the suspension was stirred at room temperature for 24 h. The precipitate (succinimide) was filtered off and the solvent was evaporated. The residue was purified by silica gel column chromatography with an eluent (PE/EA = 4/1) to afford **6** as a yellow oil (52 mg, 88%) (about 93:7 diastereomeric mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 2H), 7.34 – 7.24 (m, 5H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.67 (dd, *J* = 9.8, 3.9 Hz, 0.93H), 4.54 – 4.52 (m, 0.07H), 3.87 (s, 3H), 3.63 (dd, *J* = 14.2, 3.9 Hz, 1H), 3.16 (dd, *J* = 14.3, 10.0 Hz, 0.07H), 2.68 (dd, *J* = 14.0, 10.1 Hz, 0.93H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 135.6, 129.6, 129.4, 128.8, 127.7, 127.5, 114.5, 76.6, 55.6, 36.8. IR (neat): 3025, 1588, 1490, 1451, 1302, 1248, 1168, 1083, 1048, 827, 695 cm^{-1}. HRMS Calculated for $C_{15}H_{16}O_2ClS$ $[M+H]^+$ 295.0554, found 295.0550.



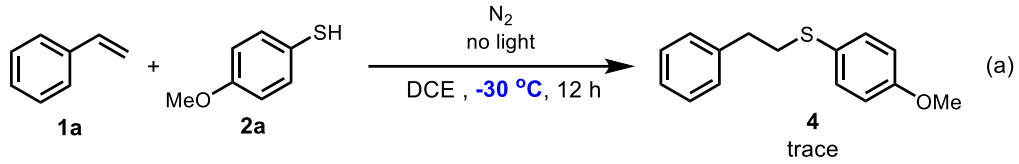
3a **7**, 89%

A mixture of sulfoxide 1 (0.30 mmol), $Fe(OTf)_2$, 4Å MS (0.5 g/mmol), and PhI=NNs (0.39 mmol) in CH_3CN (3.0 mL) was stirred at room temperature for 1h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography with an eluent (PE/EA = 4/1) to afford the corresponding sulfoximines **7** as a yellow oil (123 mg, 89%).

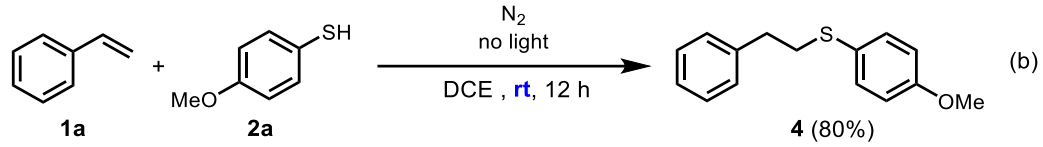
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.07 (d, *J* = 8.2 Hz, 4H), 3.91 (s, 3H), 3.81 – 3.67 (m, 2H), 2.99 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 149.8, 149.3, 136.1, 130.6, 129.0, 128.5, 128.2, 127.4, 126.7, 124.1, 115.3, 59.8, 56.0, 28.9.

IR (neat): 3092, 1586, 1522, 1492, 1345, 1300, 1259, 1150, 1085, 1055, 1010, 746, 614 cm^{-1}. HRMS Calculated for $C_{15}H_{16}O_2ClS$ $[M+H]^+$ 461.0836, found 461.0835.

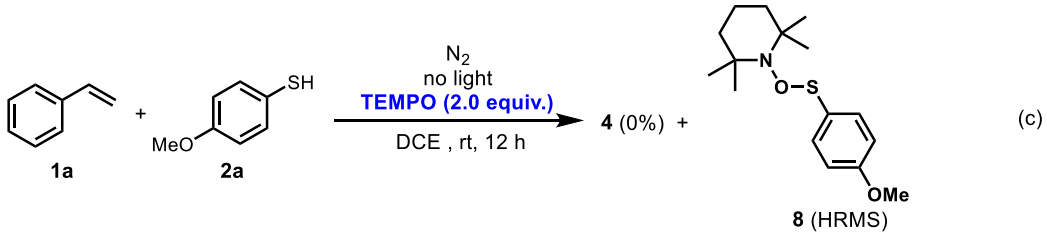
6. Mechanistic studies



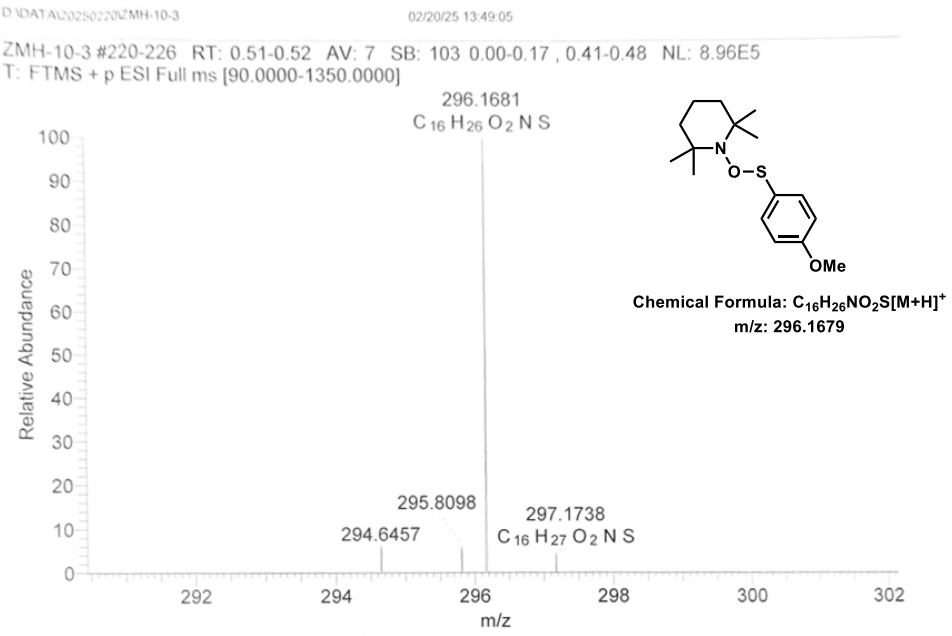
At -30 °C, **2a** (0.54 mmol) was added to a solution of **1a** (0.3 mmol) in DCE (2 mL) under N_2, the reaction mixture was stirred for 12 h. After completion of the reaction, the reaction mixture was quenched by the addition of TEMPO (0.6 mmol). The resulting solution was allowed to warm to room temperature and stirred for 10 min. The solution was concentrated in vacuum, only a trace amount of desired product **4** was detected..



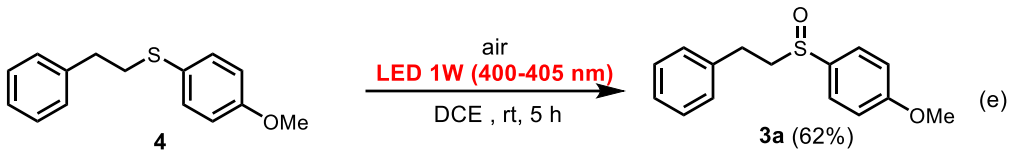
At room temperature, **2a** (0.54 mmol) was added to a solution of **1a** (0.3 mmol) in DCE (2 mL) under N_2, the reaction mixture was stirred for 12 h. After completion of the reaction, the reaction mixture was purified by flash column chromatography with an eluent (PE/EA = 20/1) to give the product **4**.



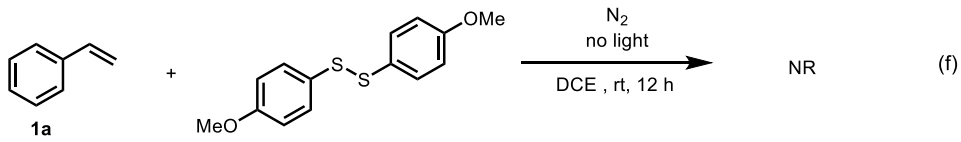
At room temperature, **2a** (0.54 mmol) was added to a solution of **1a** (0.3 mmol) and TEMPO (0.6 mmol) in DCE (2 mL) under N_2, the reaction mixture was stirred for 12 h. The reaction mixture was detected by HRMS.



To a solution of **4** (0.1 mmol) in DCE (1 mL) in the open air at room temperature. The reaction was stirred at room temperature for 5 h. The reaction mixture was detected by TLC.



To a solution of **4** (0.1 mmol) in DCE (1 mL) in the open air and light irradiation at room temperature. The reaction was stirred at room temperature for 5 h. The reaction mixture was purified by flash column chromatography with an eluent (PE/EA = 4/1) to give the product **3a**.



At room temperature, diphenyl disulfide (0.3 mmol) was added to a solution of **1a** (0.3 mmol) in DCE (2 mL) under N_2, the reaction mixture was stirred for 12 h. The reaction mixture was detected by TLC.

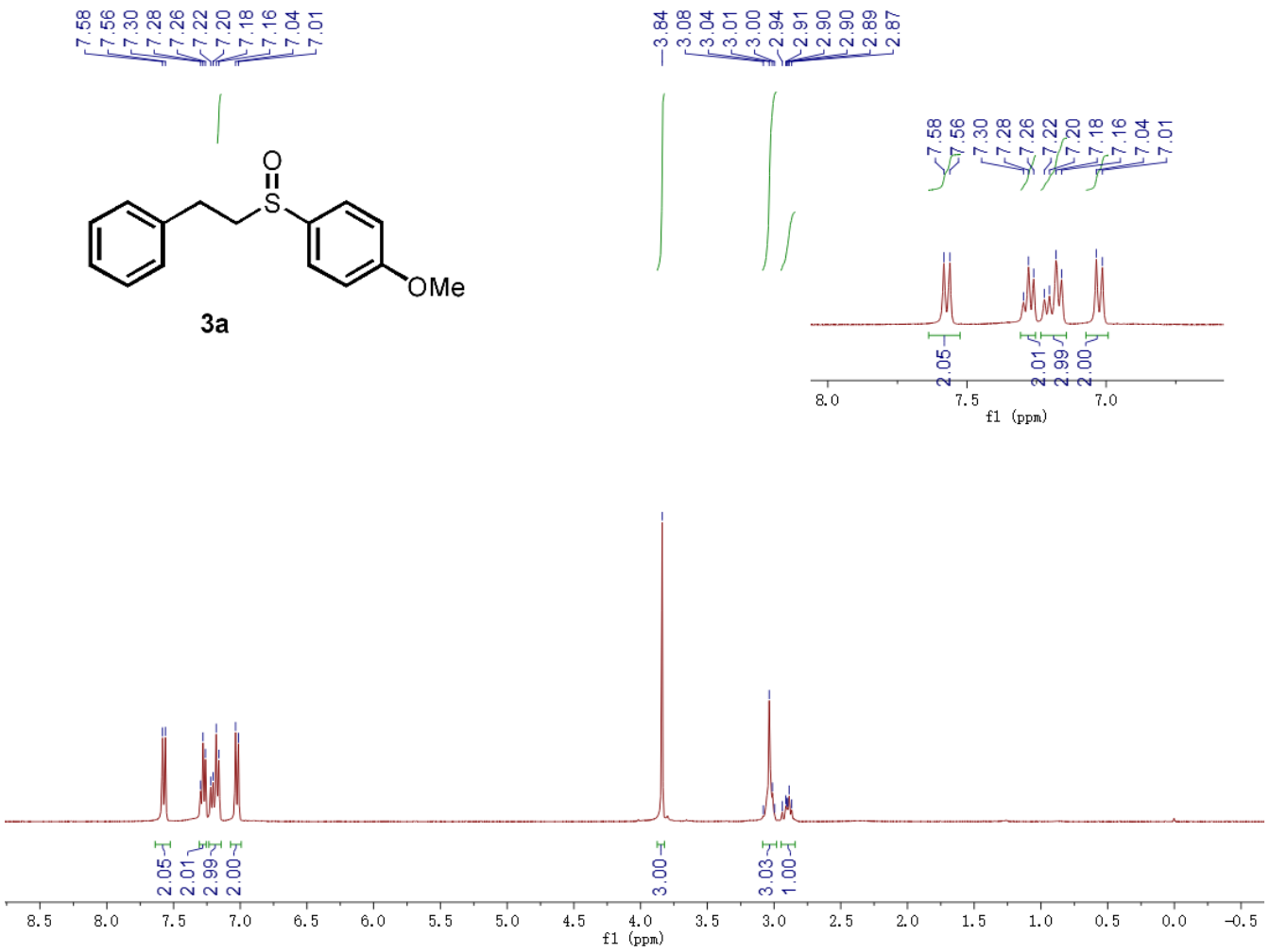
7. References

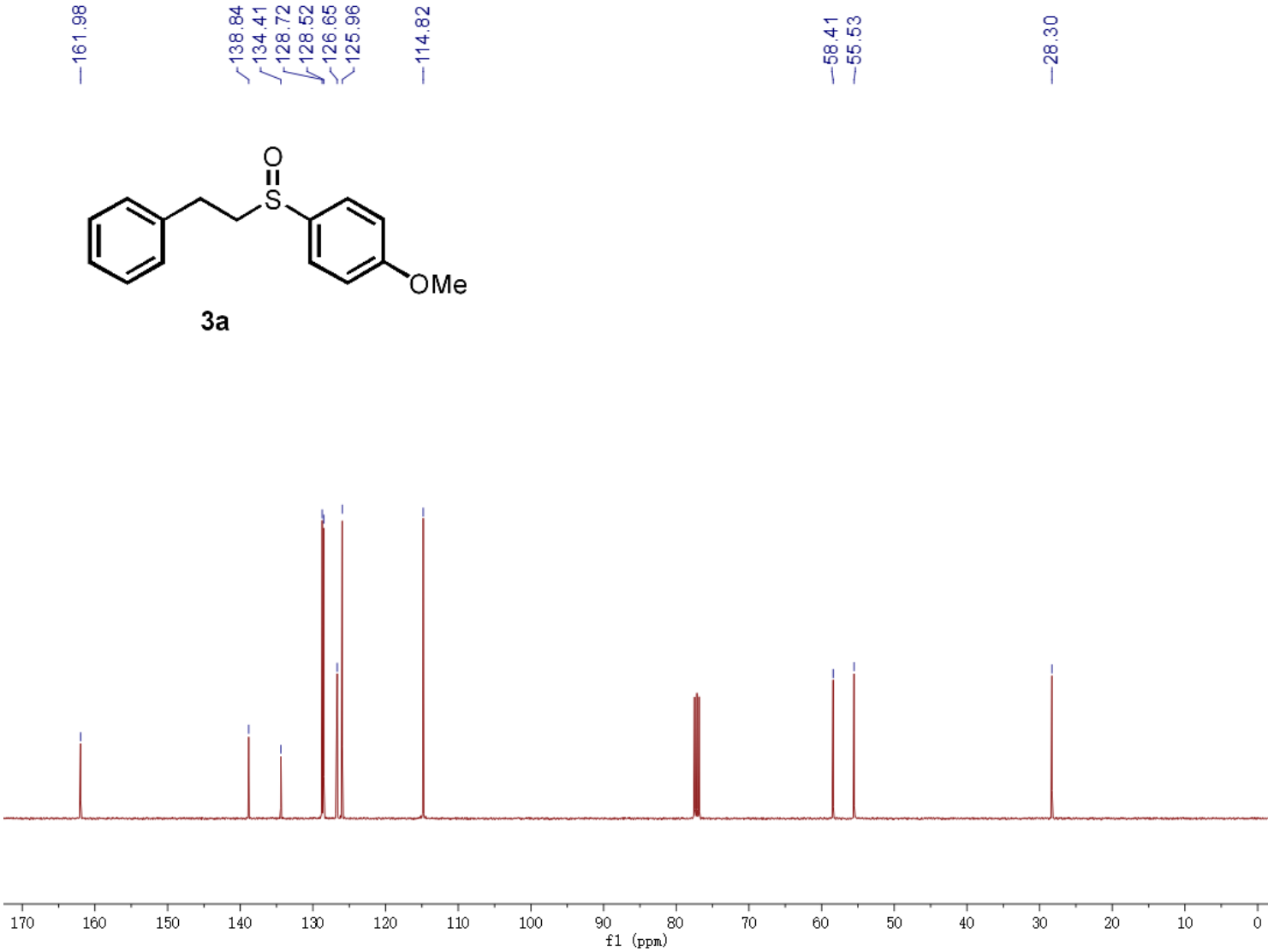
(1) Cui, H., Wei, W., Yang, D., Zhang, Y., Zhao, H., Wang, L., Wang, H. *Green Chem.* 2017, **19**, 3520.

(2) Movassagh B., Navidi M. *ARKIVOC* 2008, (xv), 47.

(3)Andrei Shavnya, Steven B. Coffey, Aaron C. Smith and Vincent Mascitti. *Org. Lett.* 2013, **15**, 24, 6226–6229

8. ^{1}H NMR and ^{13}C NMR Spectra of Products

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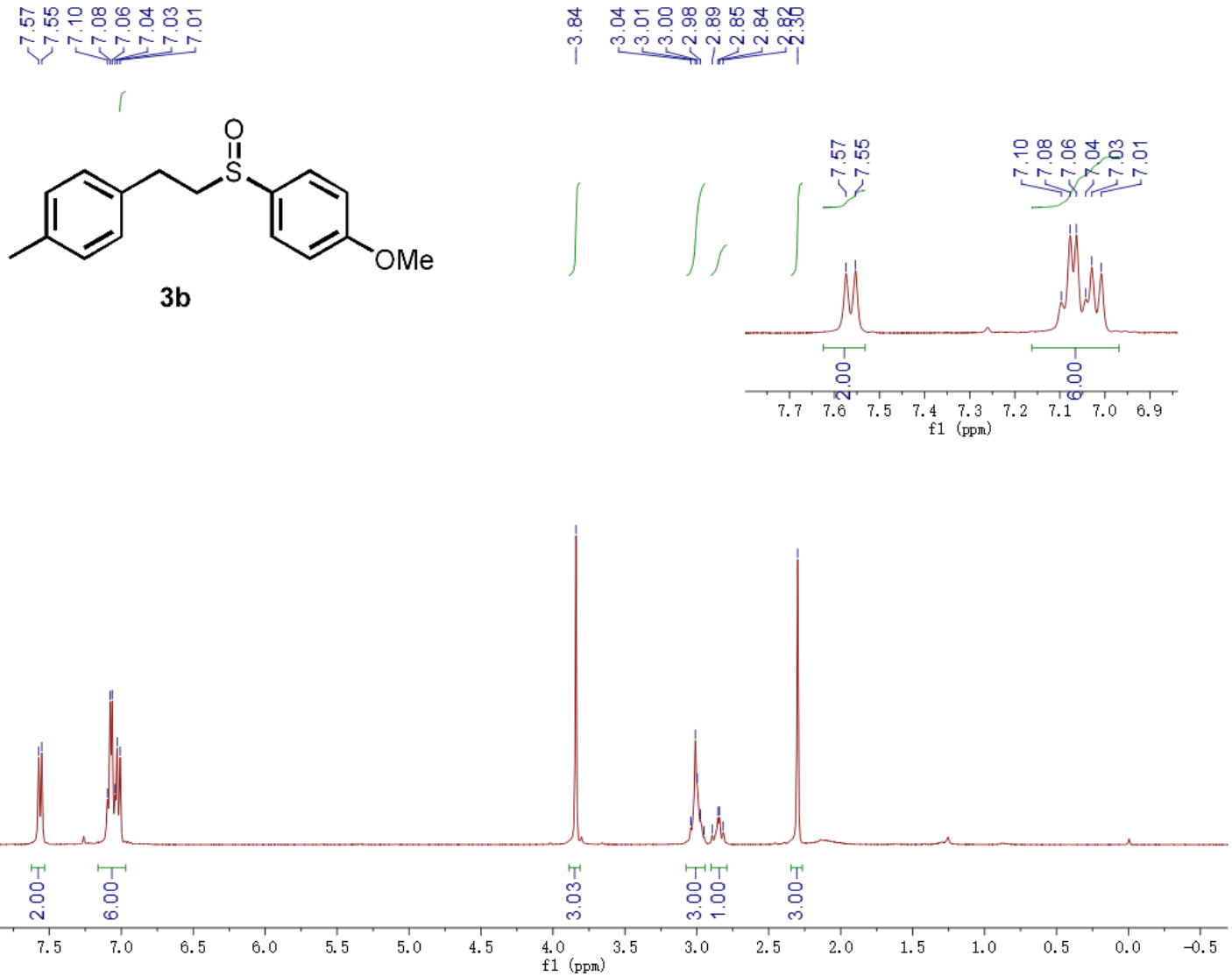
134.41
128.72
128.52
126.65
125.96
114.82
58.41
55.53
28.30
O
S
OMe
3a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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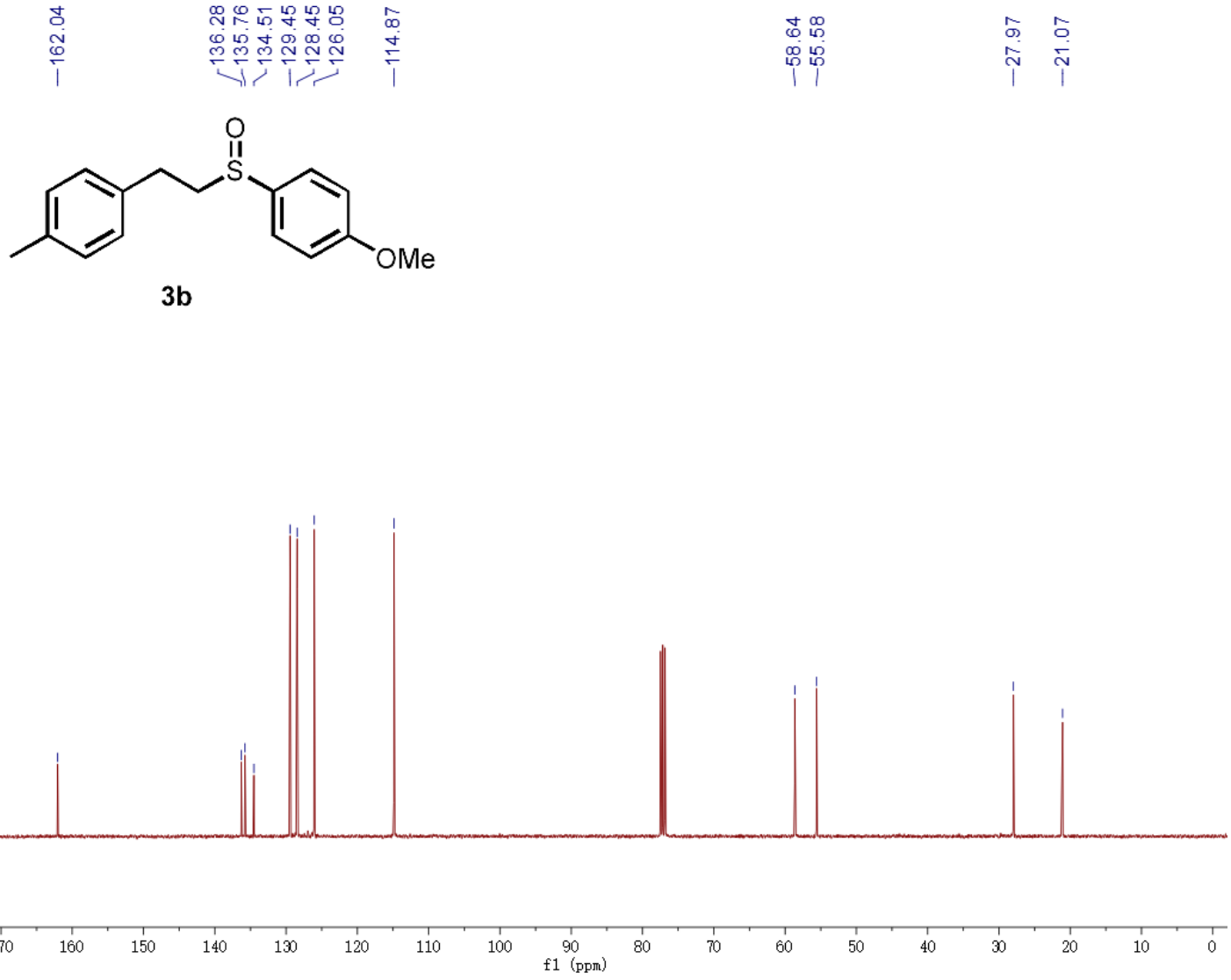
7.55
7.10
7.08
7.06
7.04
7.03
7.01
3.84
3.04
3.01
3.00
2.98
2.89
2.85
2.84
2.82
2.80
O
S
OMe
3b
2.00
6.00
f1 (ppm)
2.00
6.00
3.03
3.00
1.00
3.00
f1 (ppm)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55.58
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S
OMe
3b
80
170
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150
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130
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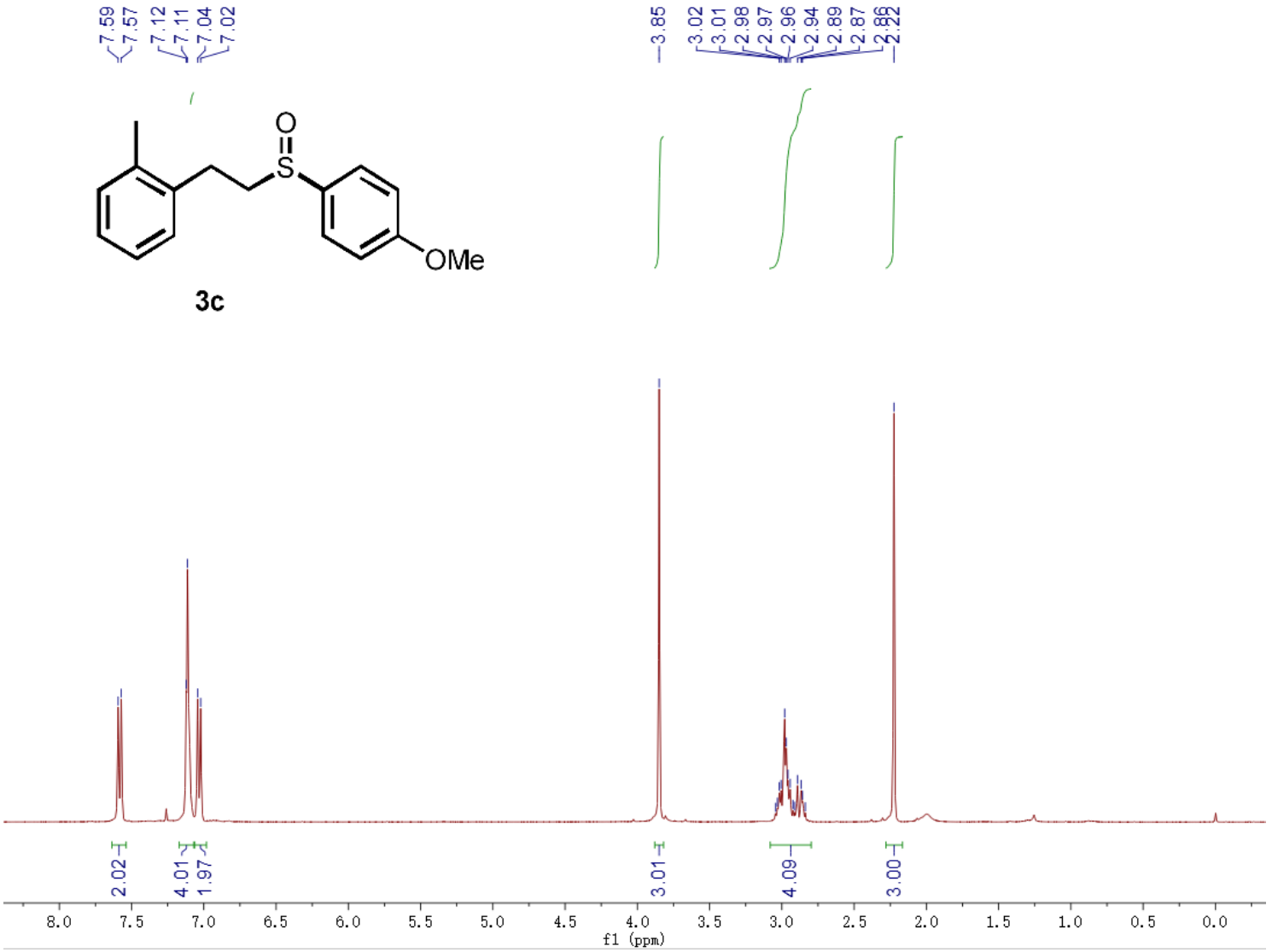
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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3.02
3.01
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2.97
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2.94
2.89
2.87
2.86
2.82
O
S
OMe
3c
2.02
4.01
1.97
3.01
4.09
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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1.5
1.0
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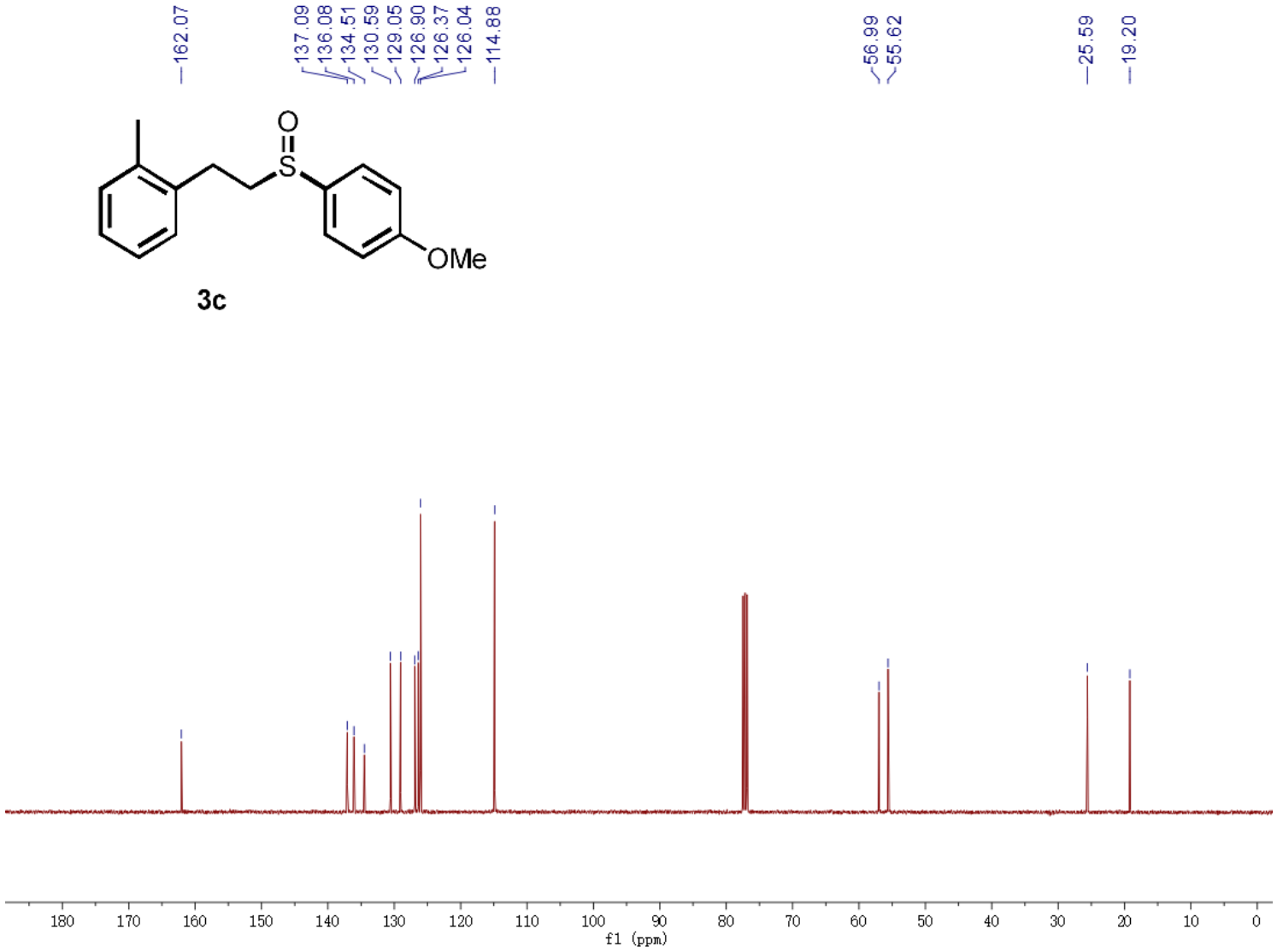
0.0
f1 (ppm)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25.59
19.20
O
S
OMe
3c
180
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50
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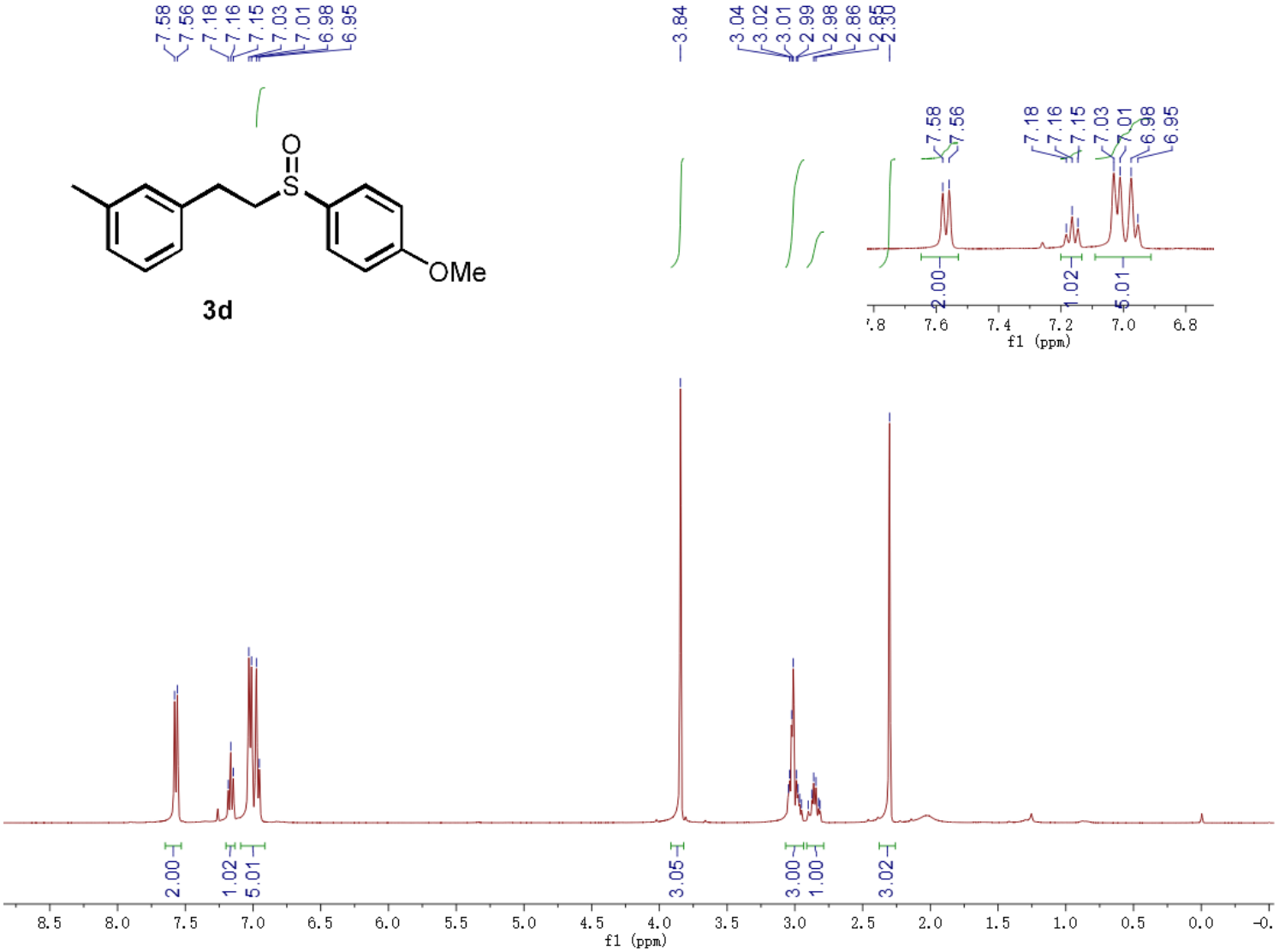
f1 (ppm)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7.03
7.01
6.98
6.95
3.84
3.04
3.02
3.01
2.99
2.98
2.86
2.85
2.30
O
S
OMe
3d
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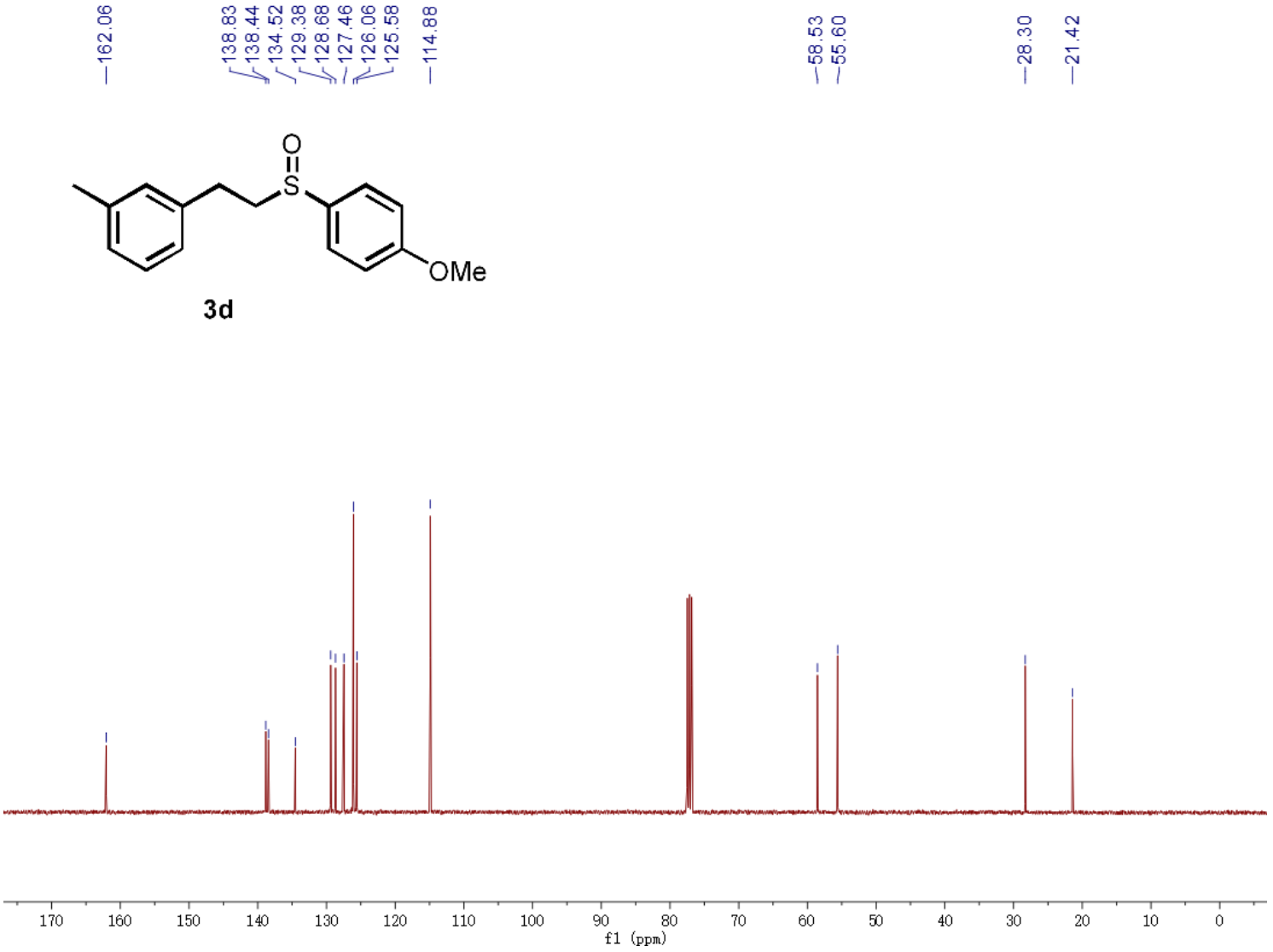
1.02
5.01
3.05
3.00
1.00
3.02
f1 (ppm)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114.88
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21.42
O
S
OMe
3d
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50
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10
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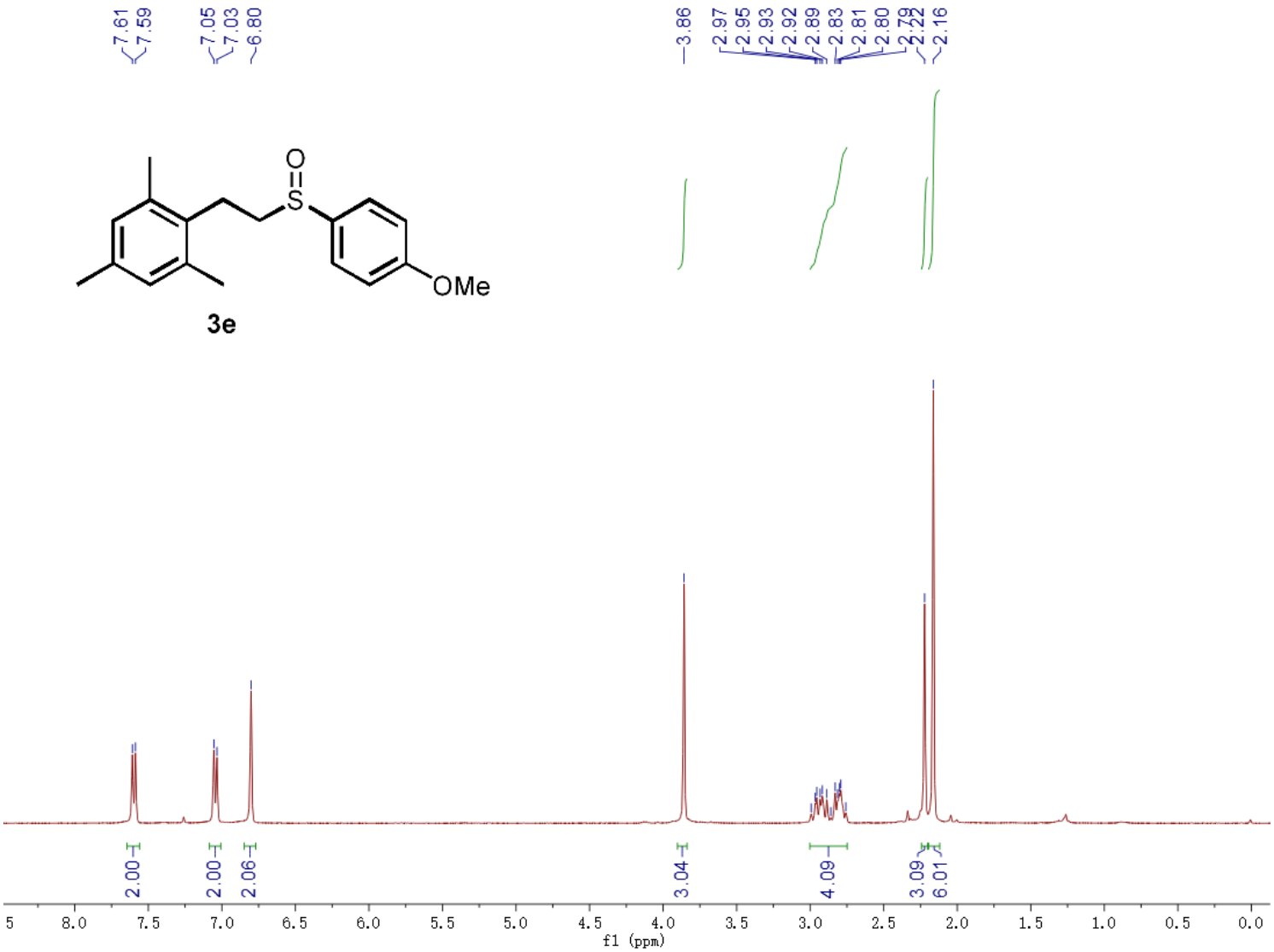
f1 (ppm)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2.80
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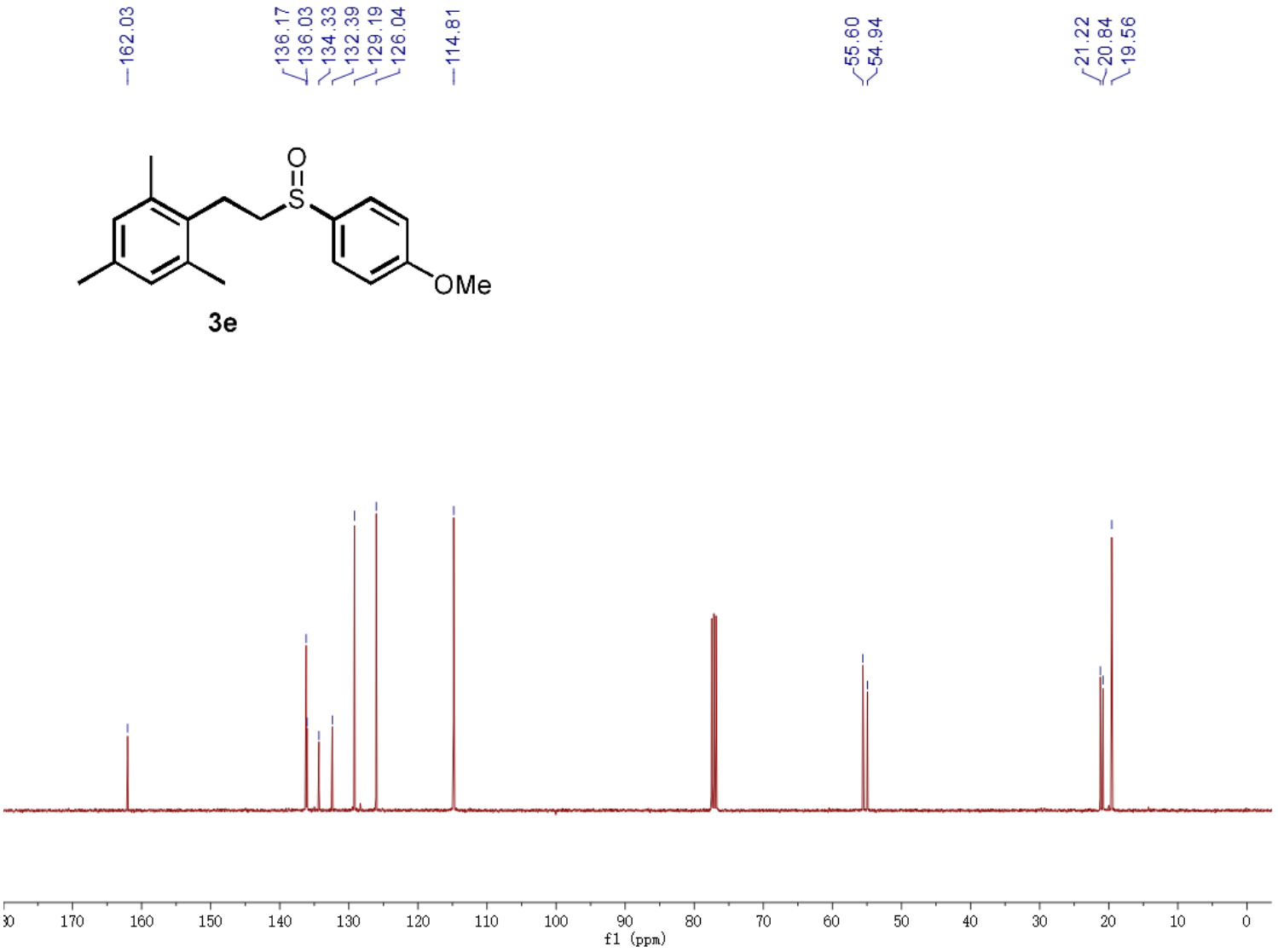
f1 (ppm)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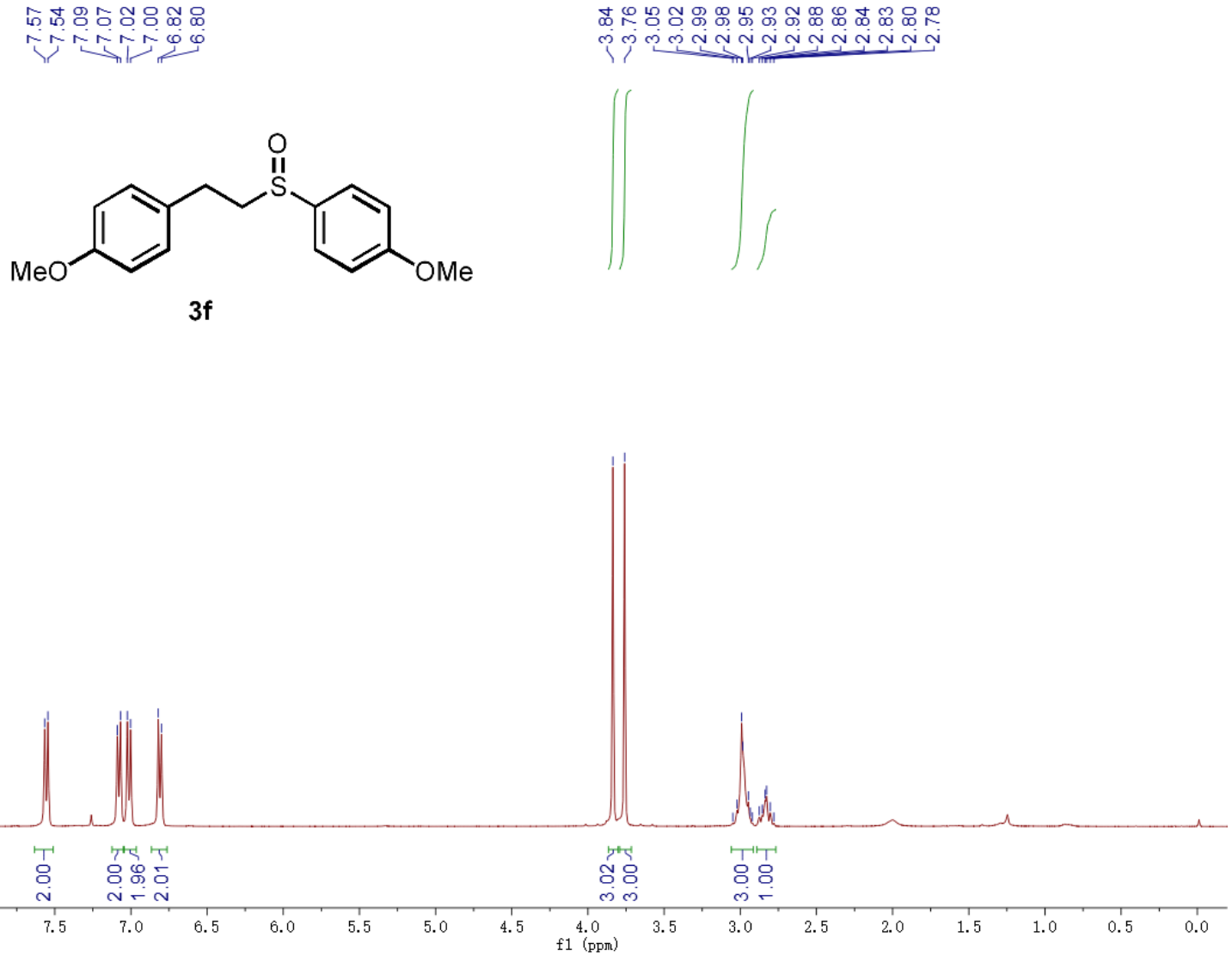
S
OMe
3e
f1 (ppm)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2.98
2.95
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2.92
2.88
2.86
2.84
2.83
2.80
2.78
O
S
MeO
OMe
3f
2.00
2.00
1.96
2.01
3.02
3.00
3.00
1.00
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
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2.0
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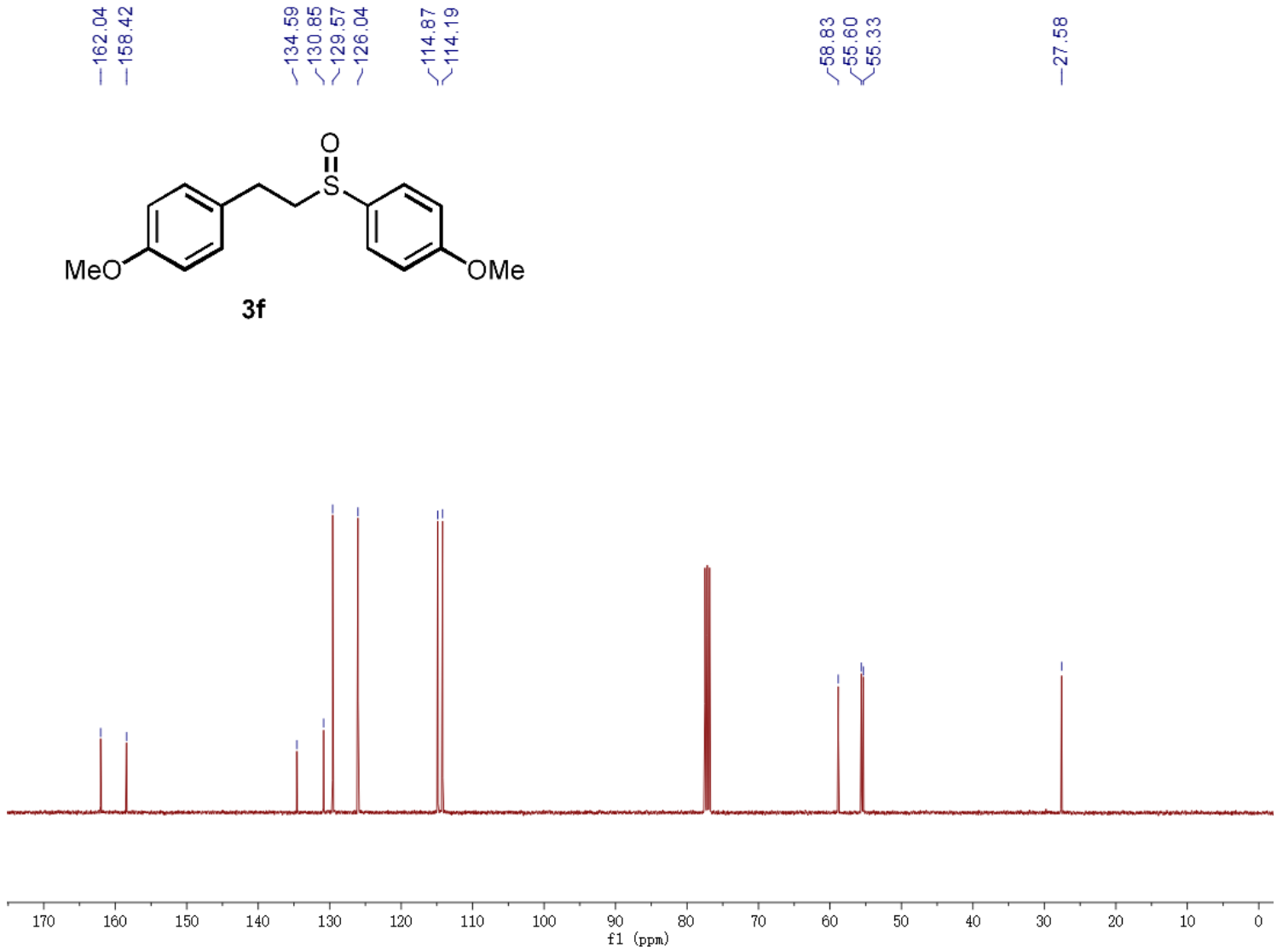
f1 (ppm)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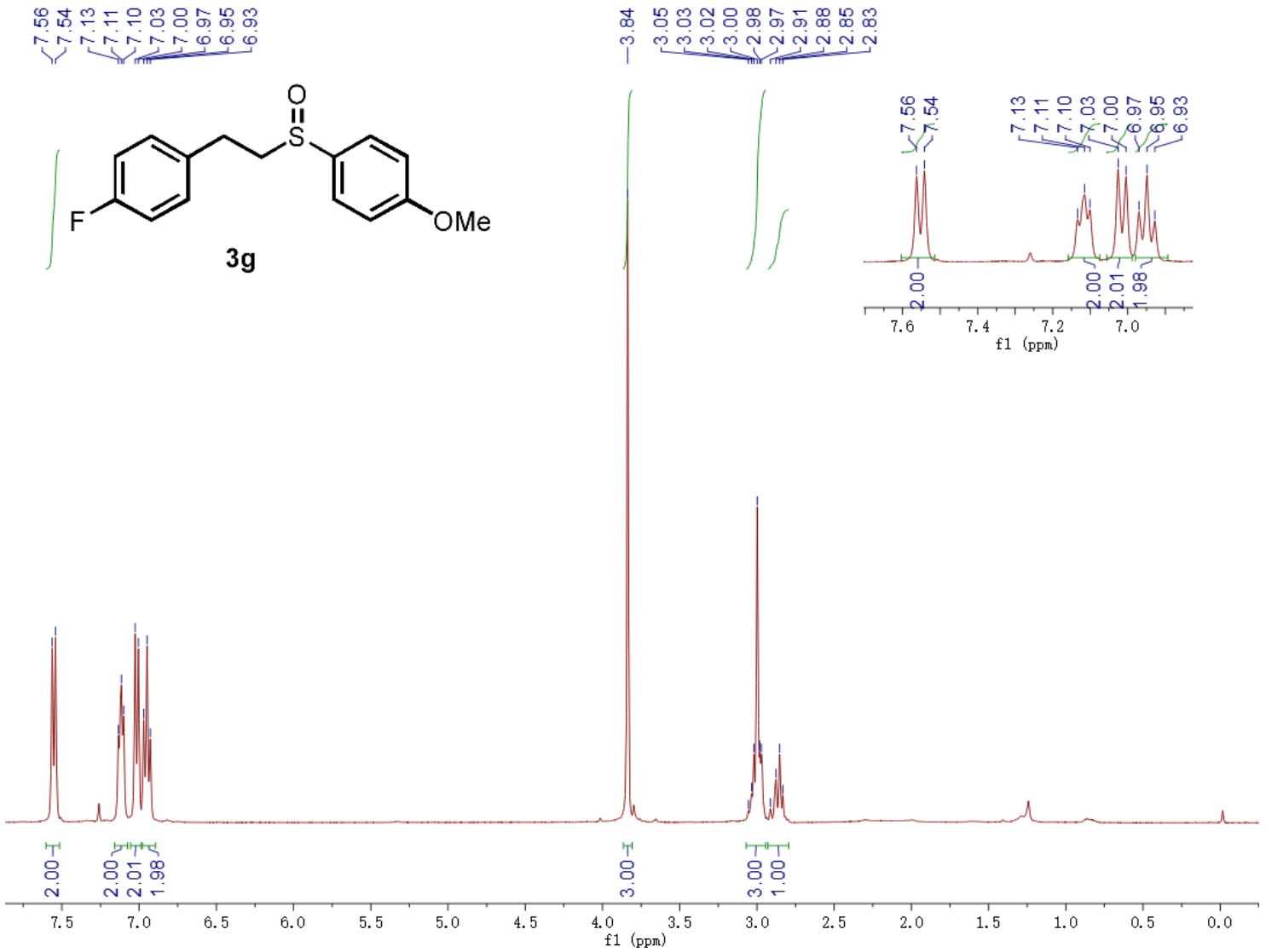
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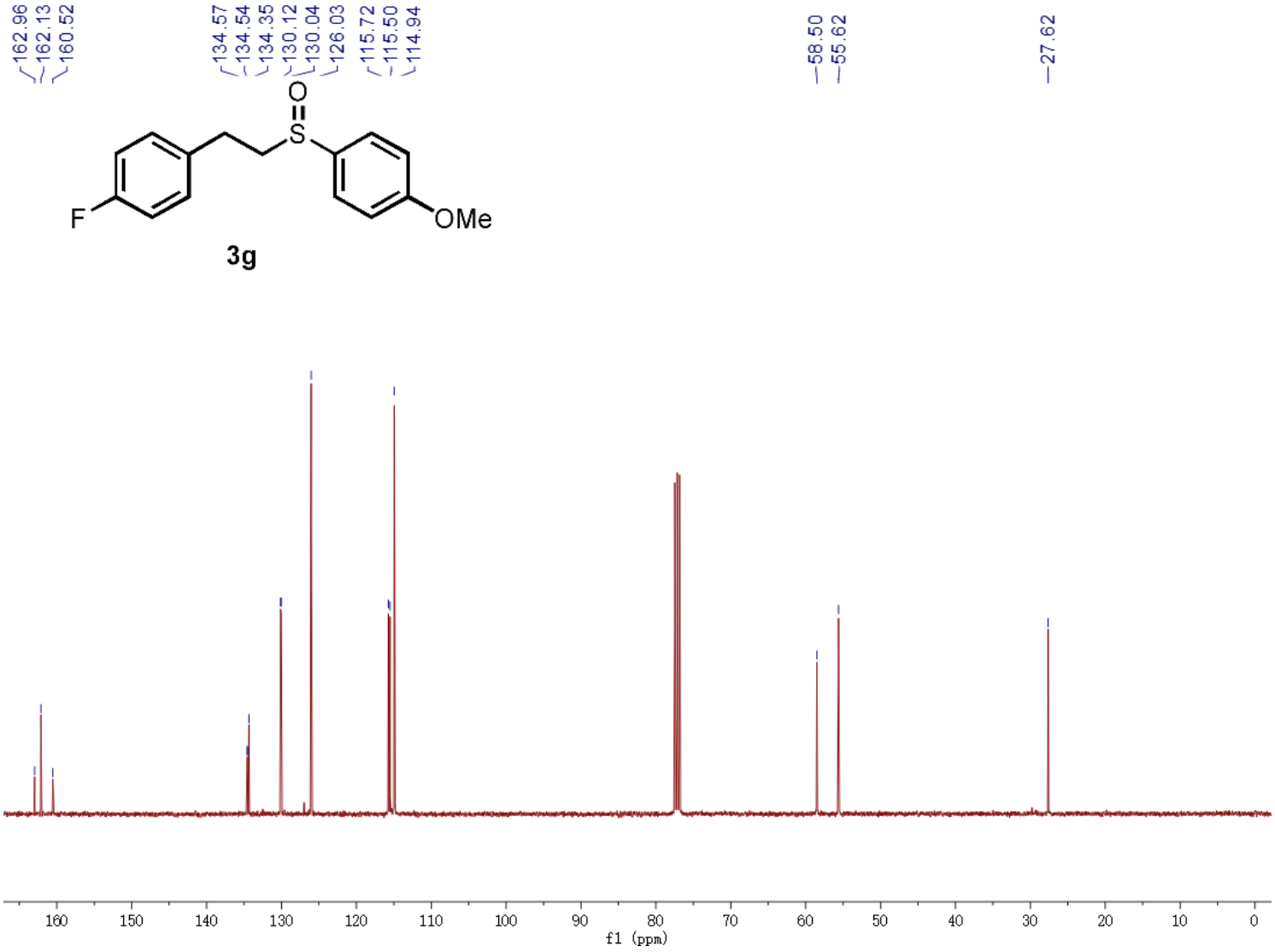
f1 (ppm)
7.6
7.4
7.2
7.0
f1 (ppm)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126.03
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114.94
58.50
55.62
27.62
O
S
F
OMe
3g
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130
120
110
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90
80
70
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50
40
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20
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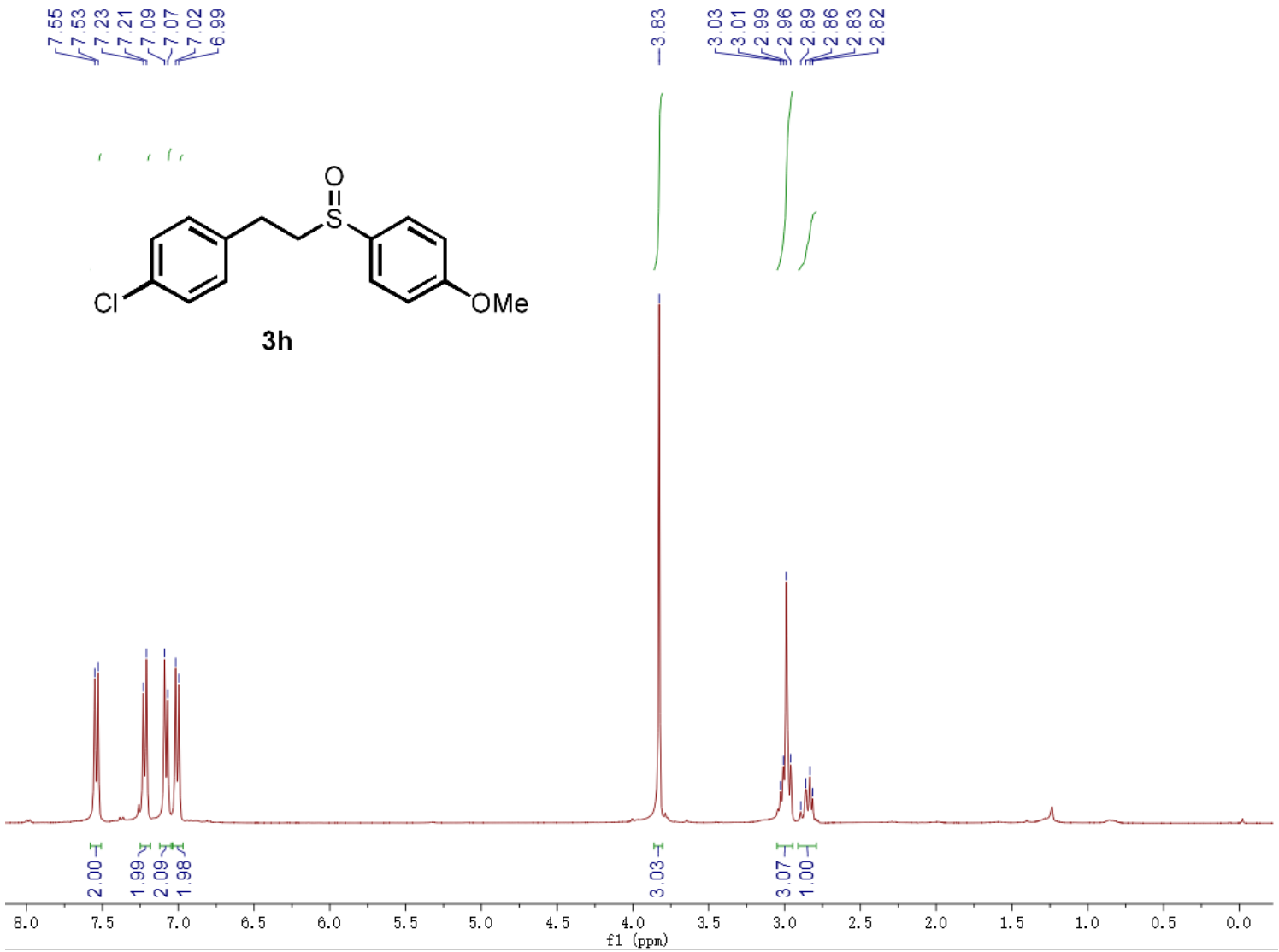
f1 (ppm)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7.02
6.99
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3.03
3.01
2.99
2.96
2.89
2.86
2.83
2.82
O
S
Cl
OMe
3h
2.00
1.99
2.09
1.98
3.03
3.07
1.00
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
1.5
1.0
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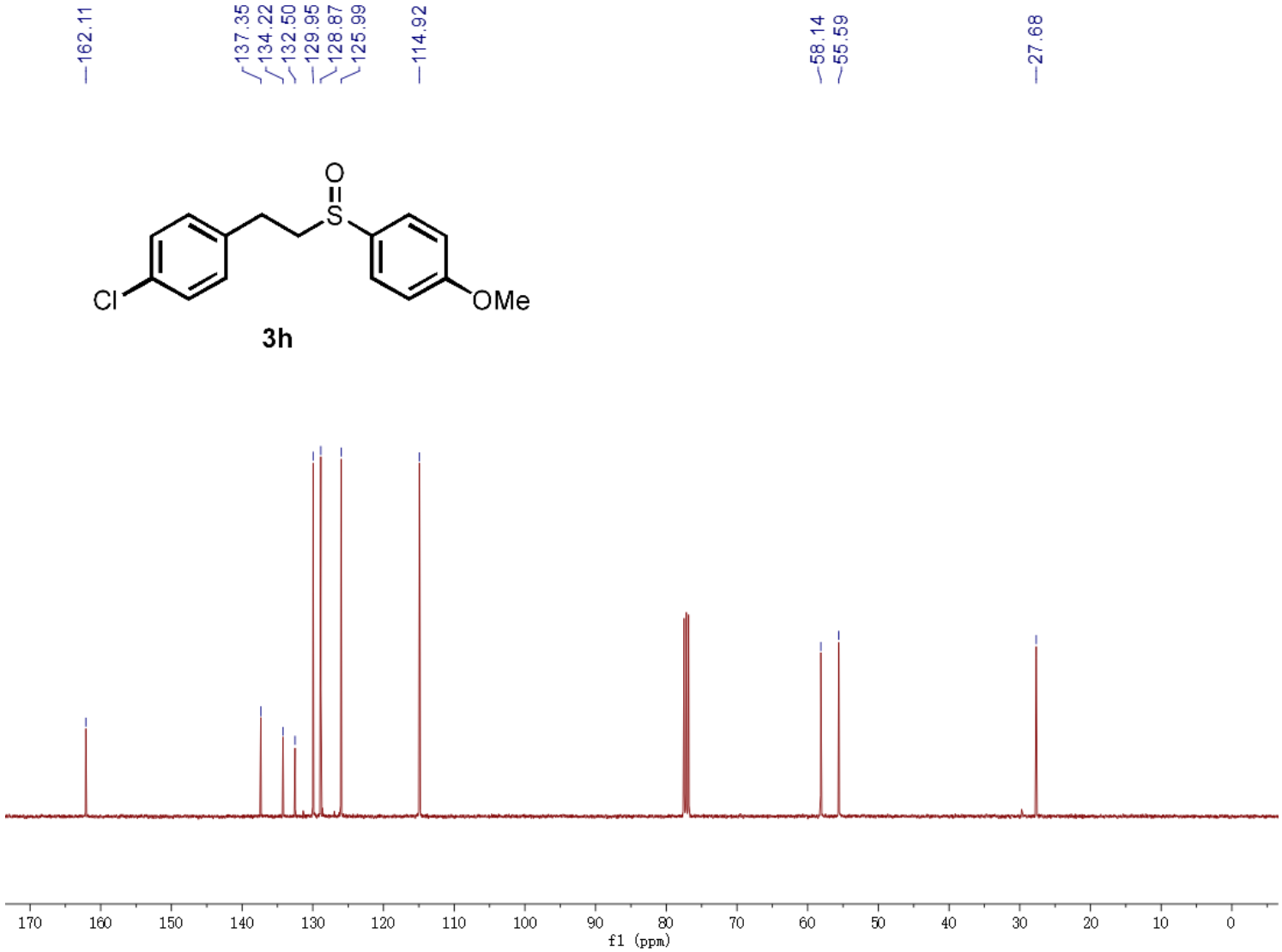
0.0
f1 (ppm)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Cl
OMe
3h
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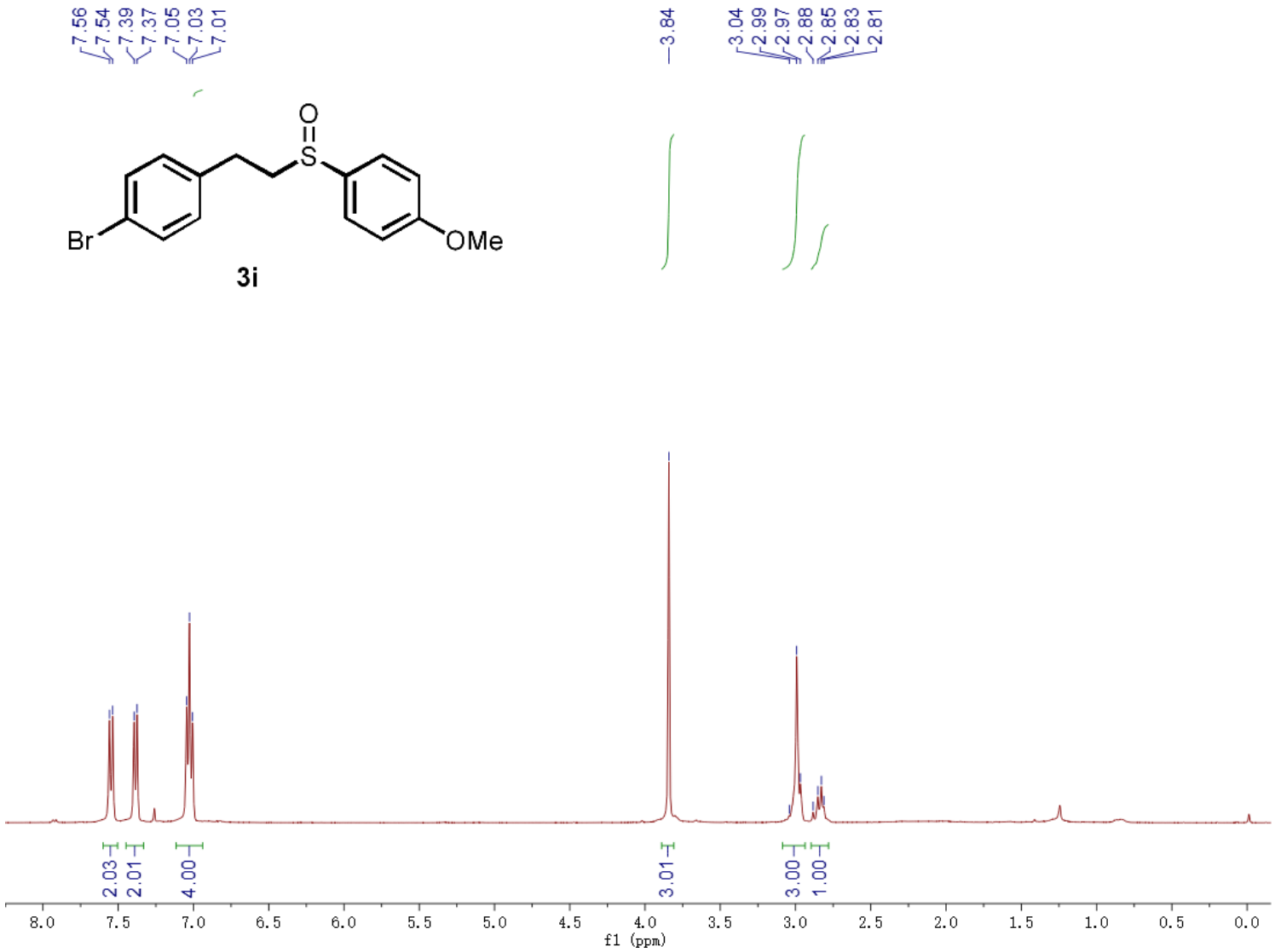
f1 (ppm)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2.97
2.88
2.85
2.83
2.81
O
S
Br
OMe
3i
2.03
2.01
4.00
3.01
3.00
1.00
8.0
7.5
7.0
6.5
6.0
5.5
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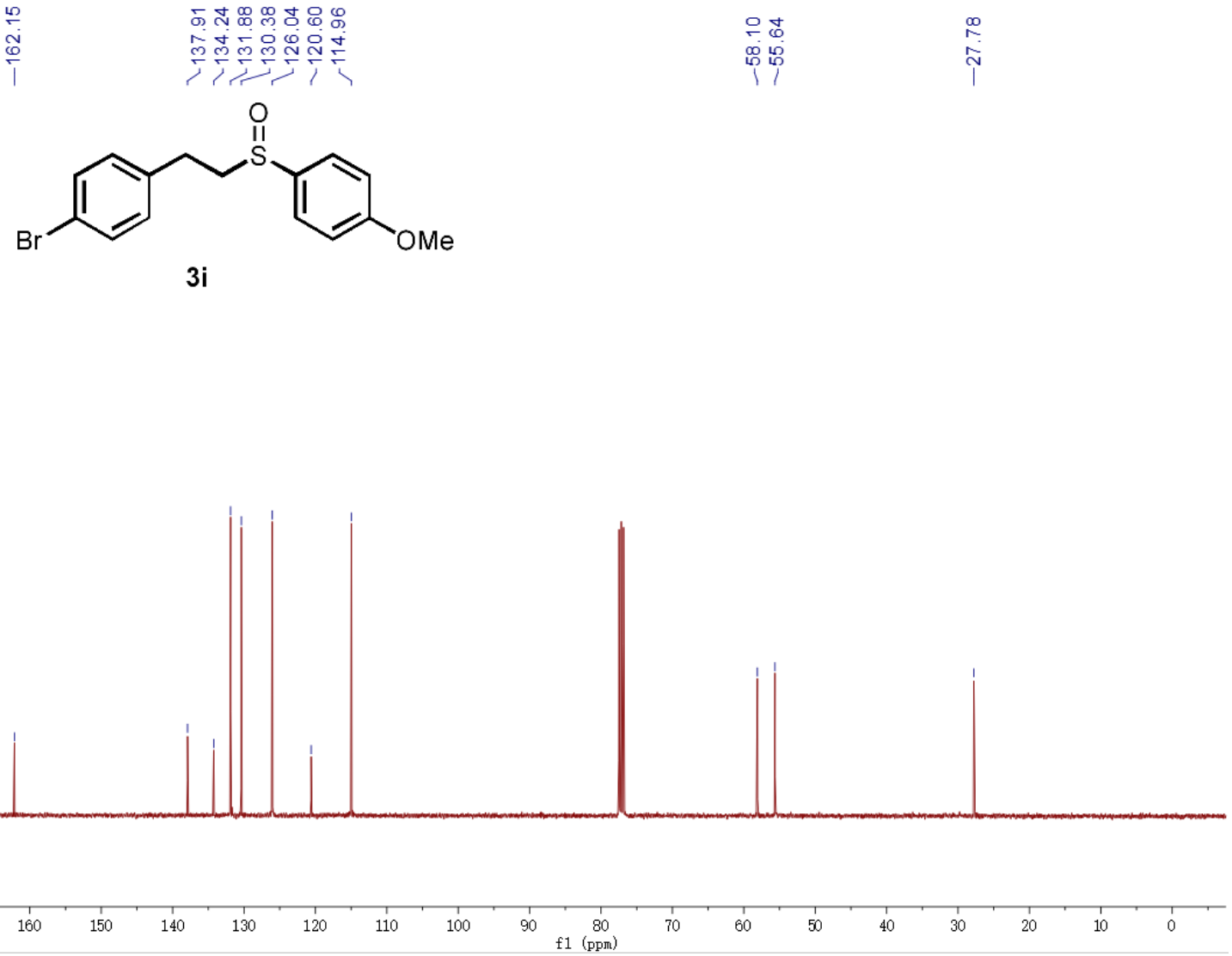
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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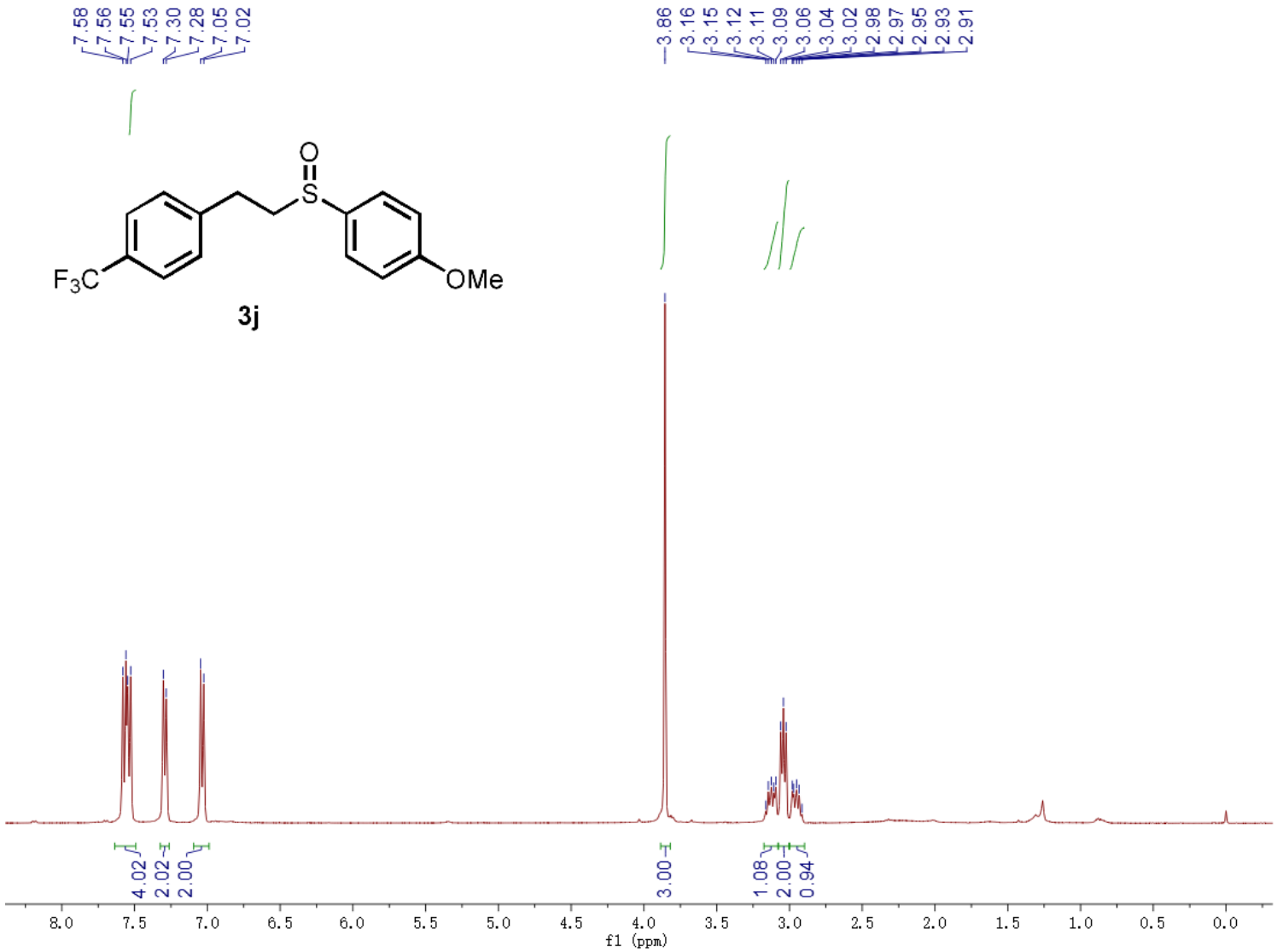
27.78
O
S
Br
OMe
3i
f1 (ppm)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3.11
3.09
3.06
3.04
3.02
2.98
2.97
2.95
2.93
2.91
O
S
F3C
OMe
3j
4.02
2.02
2.00
3.00
1.08
2.00
0.94
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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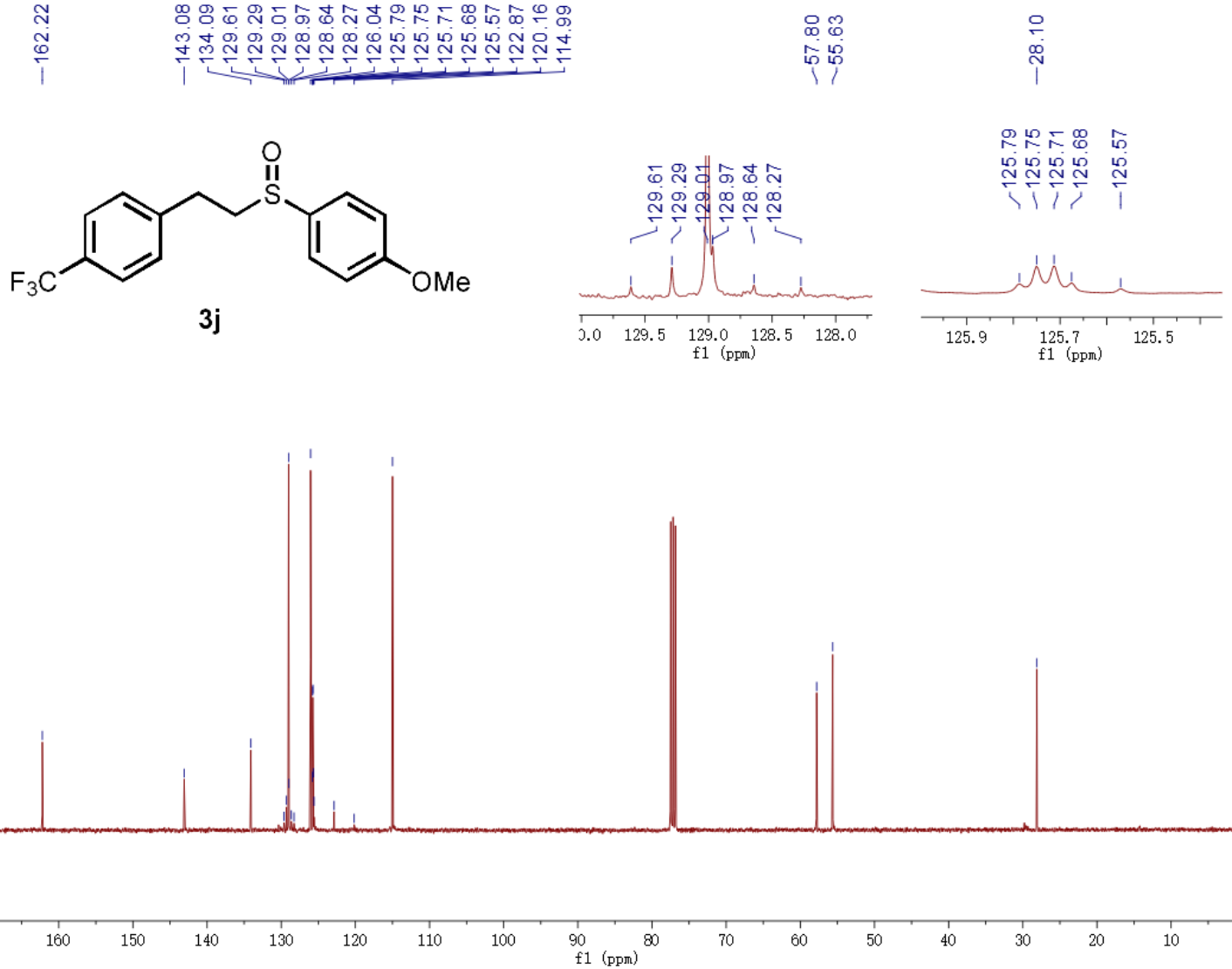
0.0
f1 (ppm)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128.64
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126.04
125.79
125.75
125.71
125.68
125.57
122.87
120.16
114.99
57.80
55.63
28.10
O
S
F3C
OMe
3j
129.61
129.29
129.01
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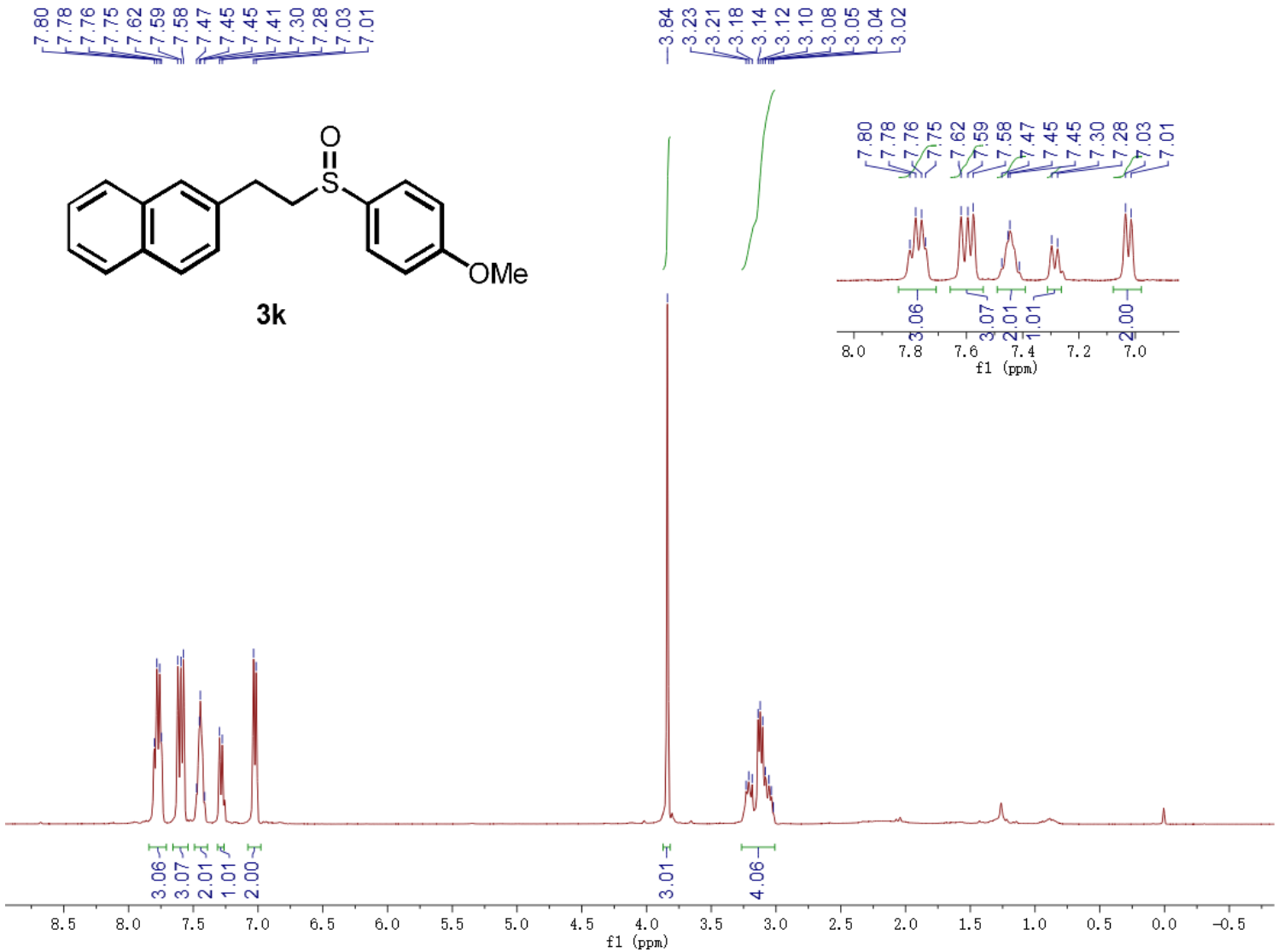
128.27
f1 (ppm)
125.79
125.75
125.71
125.68
125.57
f1 (ppm)
f1 (ppm)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7.58
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7.45
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7.30
7.28
7.03
7.01
3.84
3.23
3.21
3.18
3.14
3.12
3.10
3.08
3.05
3.04
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3.06
3.07
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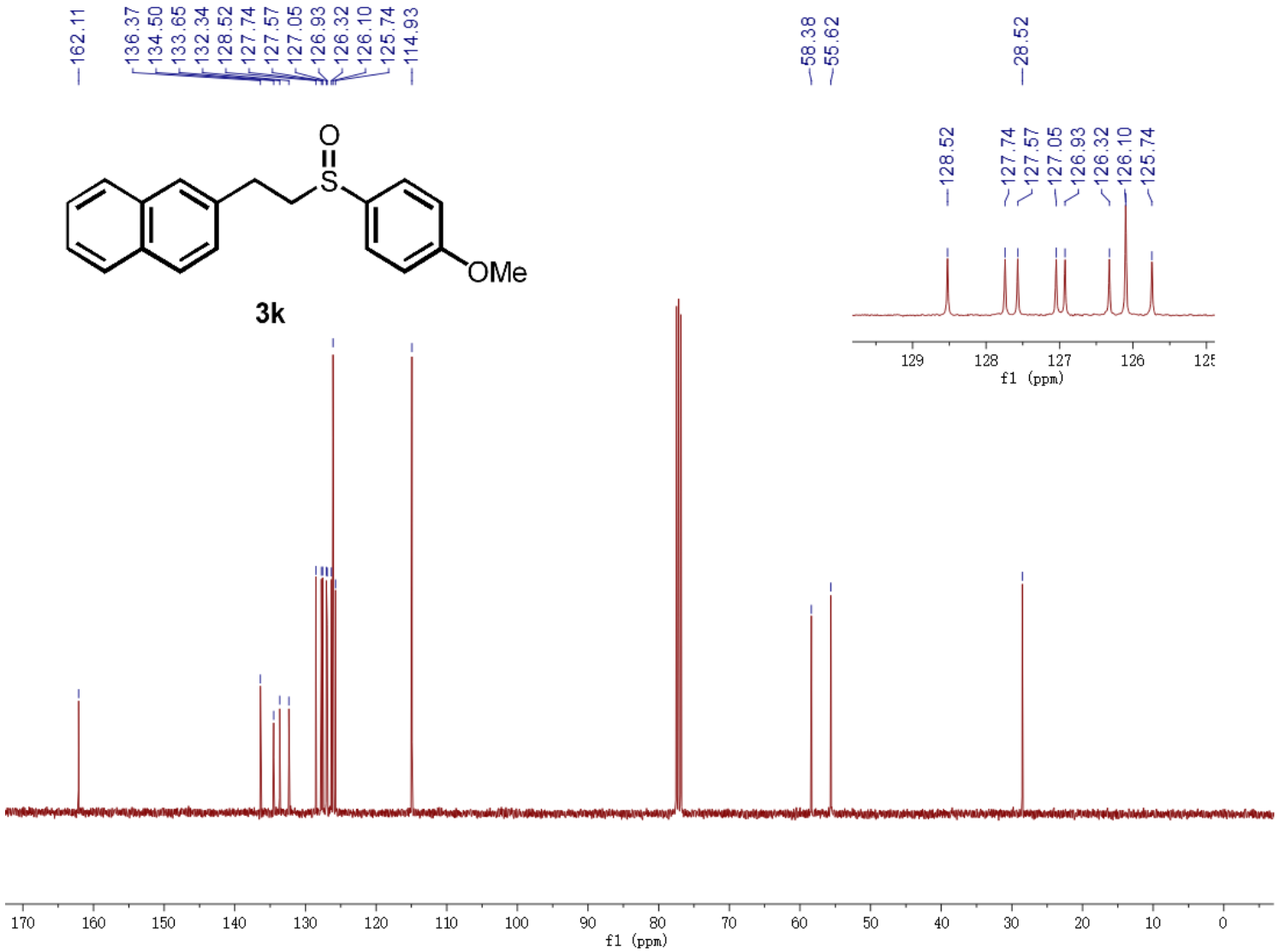
1.01
2.00
3.01
4.06
f1 (ppm)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125.74
114.93
58.38
55.62
28.52
O
S
OMe
3k
128.52
127.74
127.57
127.05
126.93
126.32
126.10
125.74
129
128
127
126
f1 (ppm)
170
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130
120
110
100
90
80
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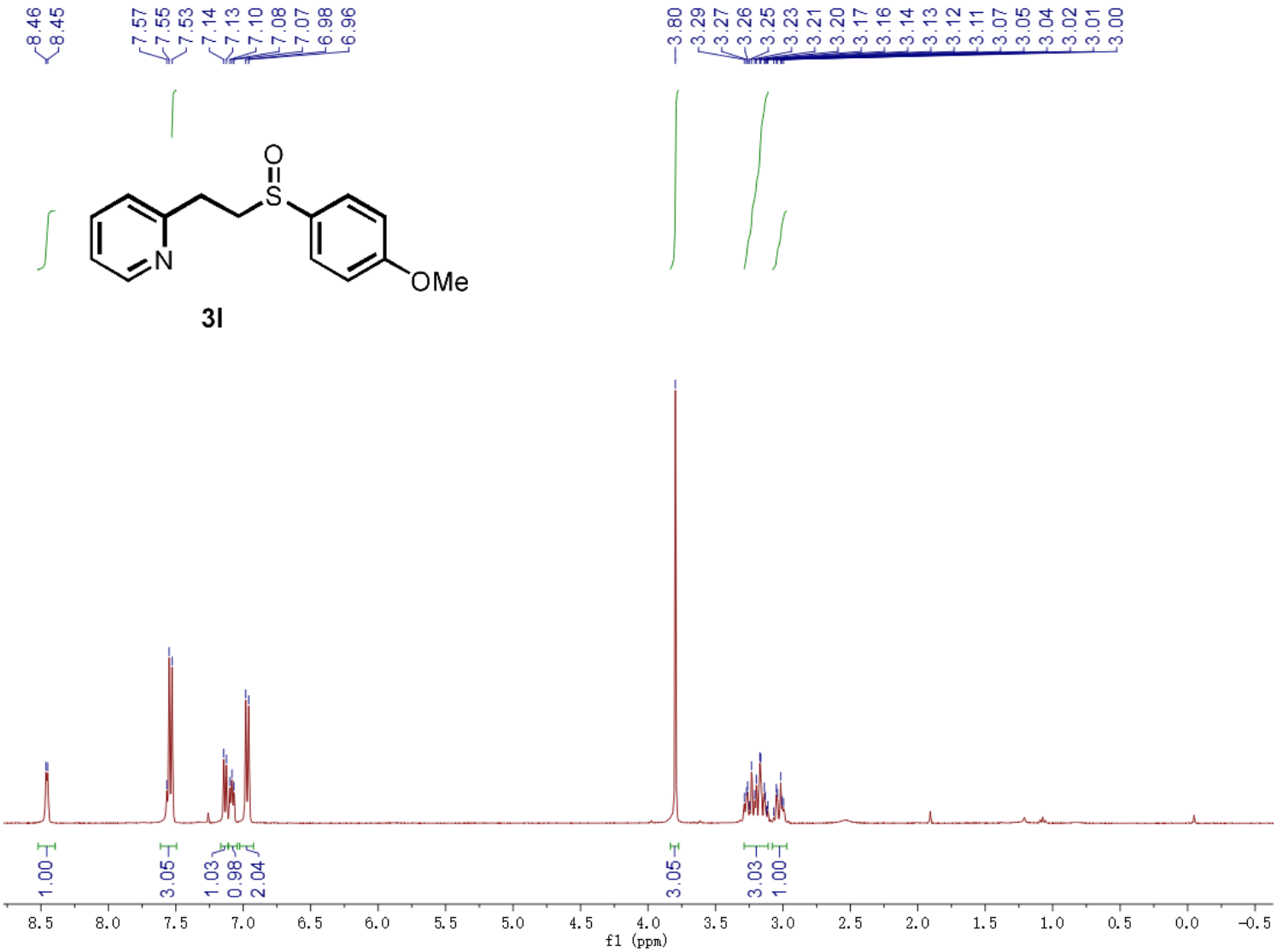
50
40
30
20
10
0
f1 (ppm)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7.07
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6.96
3.80
3.29
3.27
3.26
3.25
3.23
3.21
3.20
3.17
3.16
3.14
3.13
3.12
3.11
3.07
3.05
3.04
3.02
3.01
3.00
O
S
N
OMe
3l
1.00
3.05
1.03
0.98
2.04
3.05
3.03
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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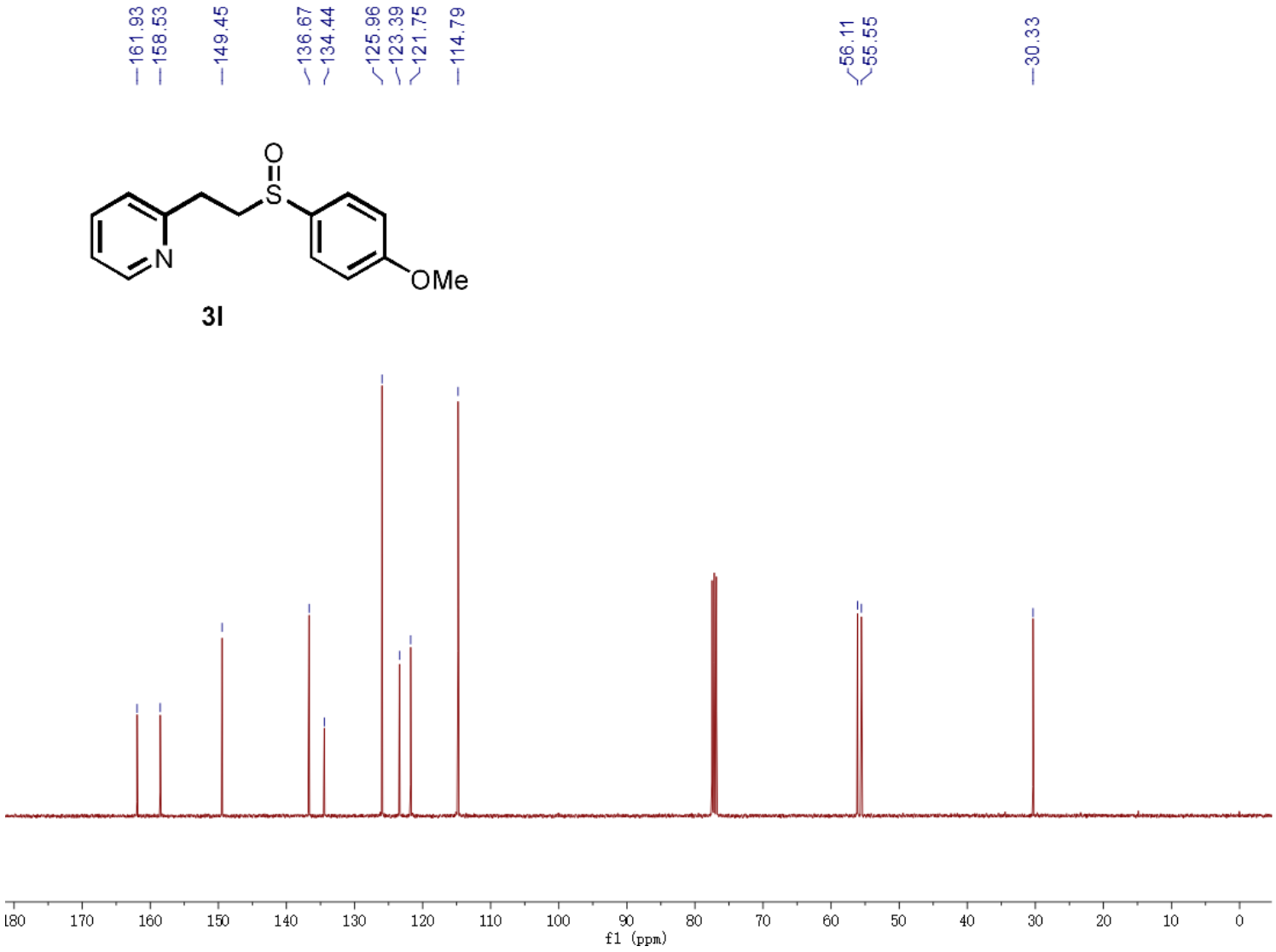
-0.5
f1 (ppm)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56.11
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30.33
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S
N
OMe
3l
180
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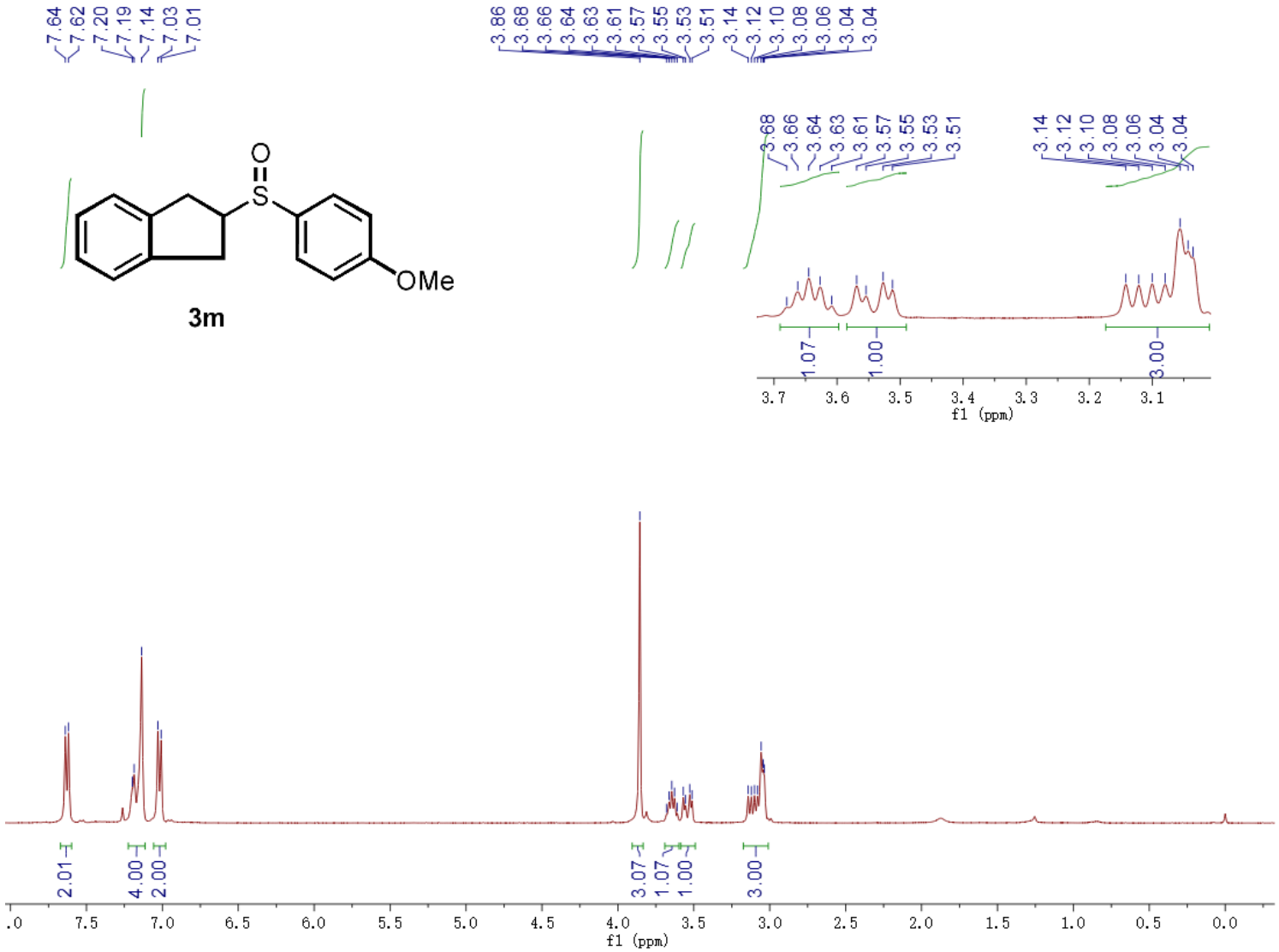
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.01
3.86
3.68
3.66
3.64
3.63
3.61
3.57
3.55
3.53
3.51
3.14
3.12
3.10
3.08
3.06
3.04
3.04
O
S
OMe
3m
1.07
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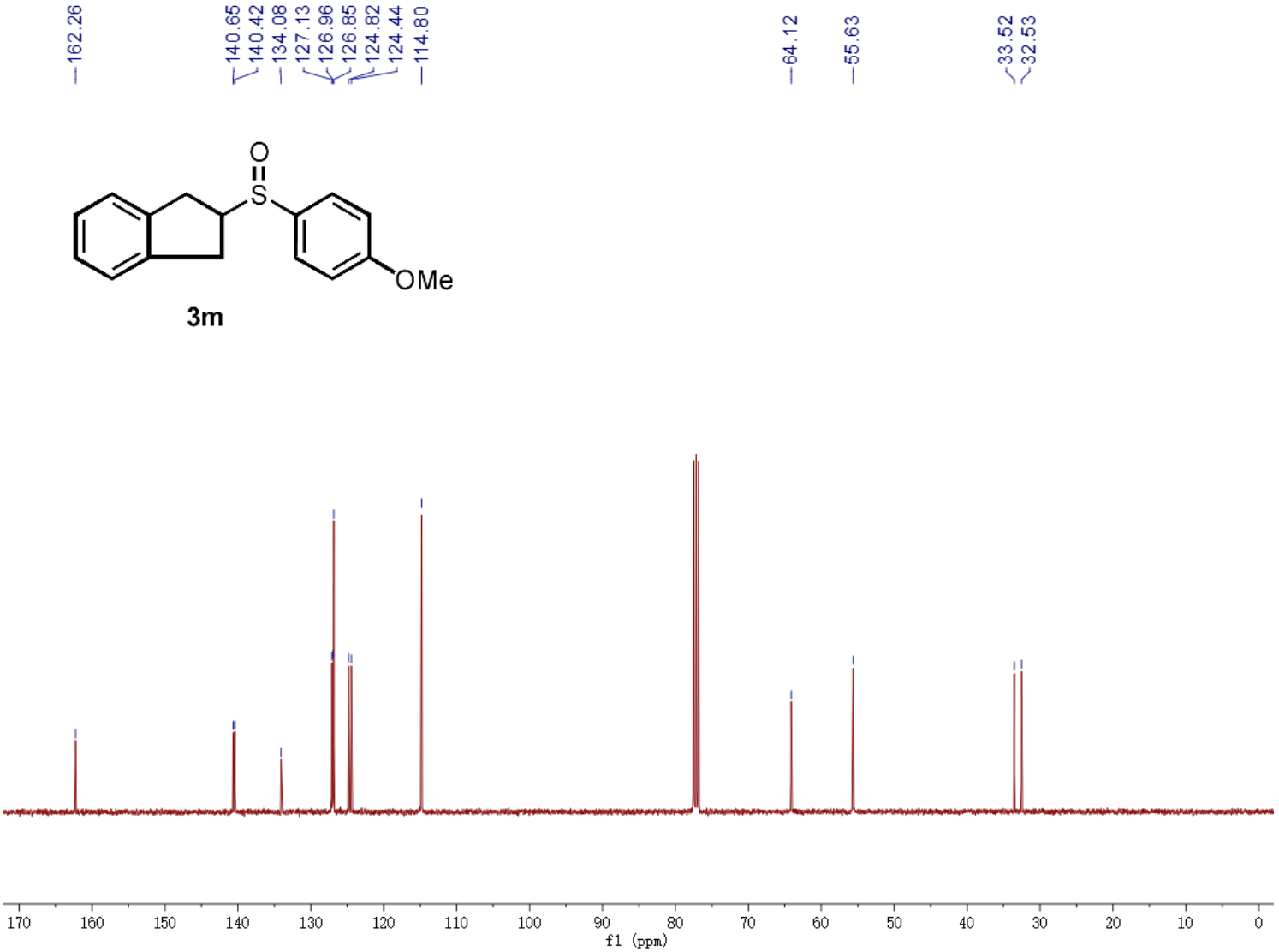
3.00
f1 (ppm)
2.01
4.00
2.00
3.07
1.07
1.00
3.00
f1 (ppm)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124.82
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114.80
64.12
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33.52
32.53
O
S
OMe
3m
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130
120
110
100
90
80
70
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50
40
30
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10
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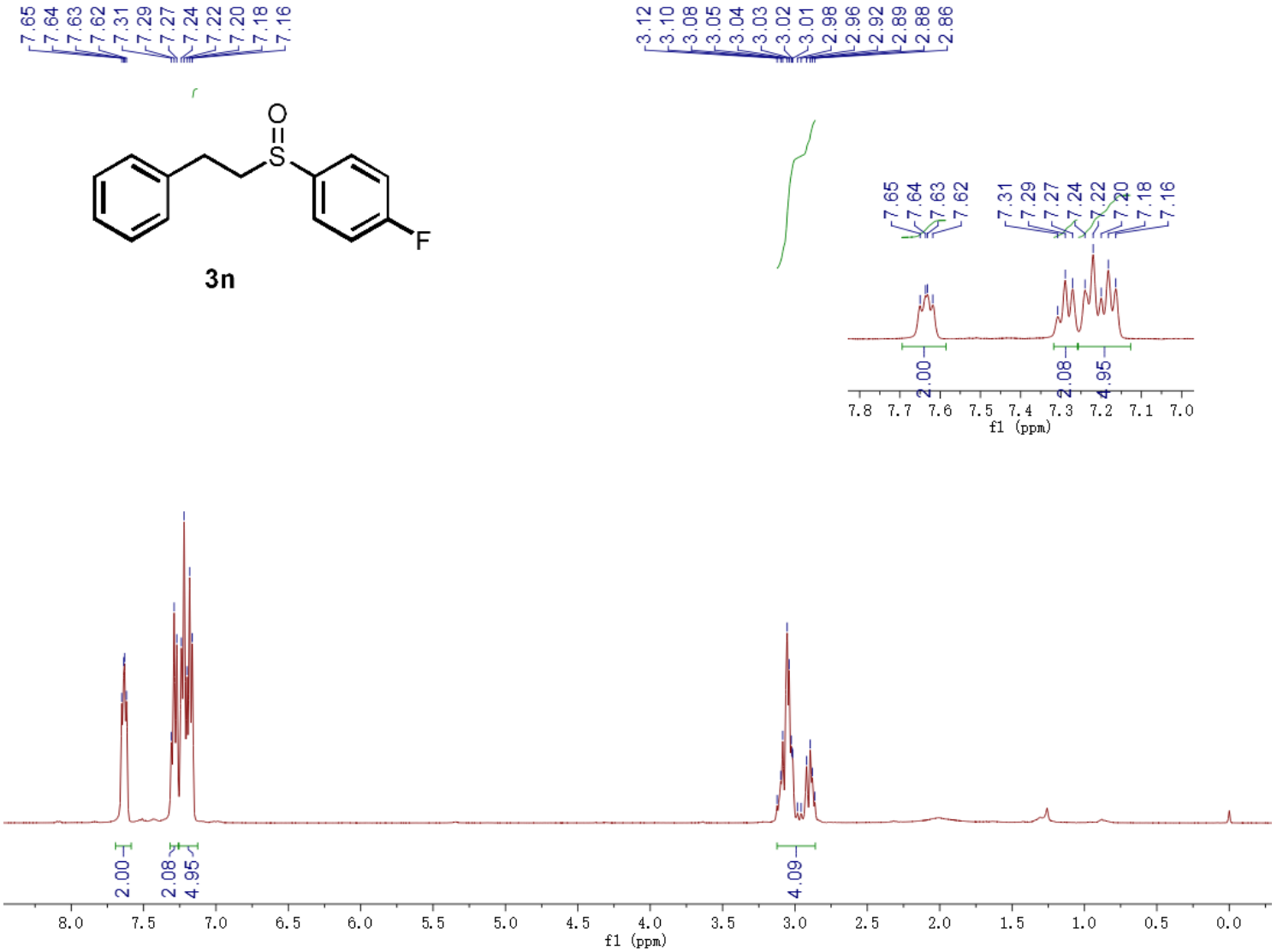
f1 (ppm)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7.20
7.18
7.16
3.12
3.10
3.08
3.05
3.04
3.03
3.02
3.01
2.98
2.96
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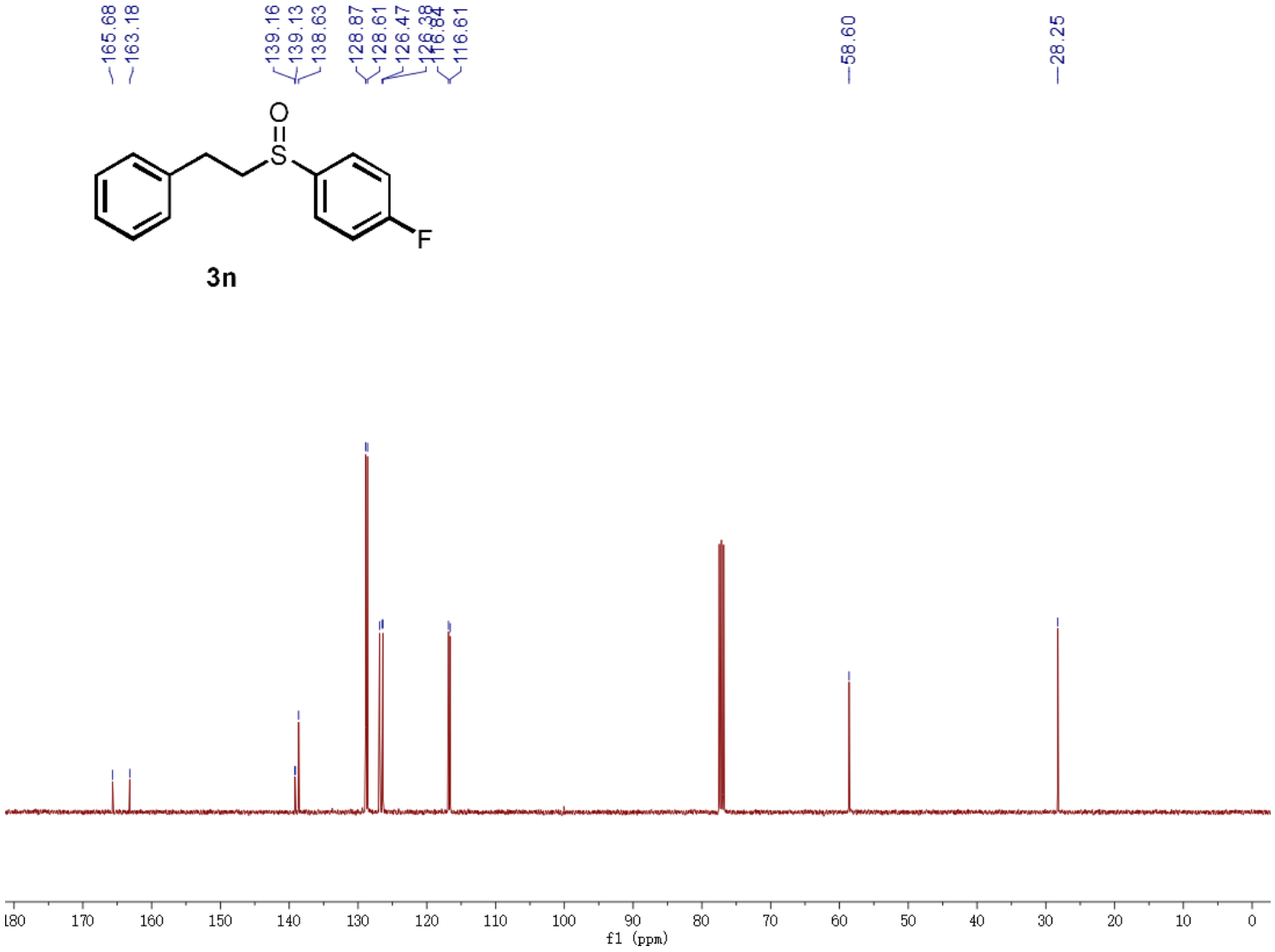
2.88
2.86
O
S
F
3n
2.00
2.08
4.95
4.09
f1 (ppm)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116.84
116.61
58.60
28.25
O
S
F
3n
180
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160
150
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130
120
110
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90
80
70
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50
40
30
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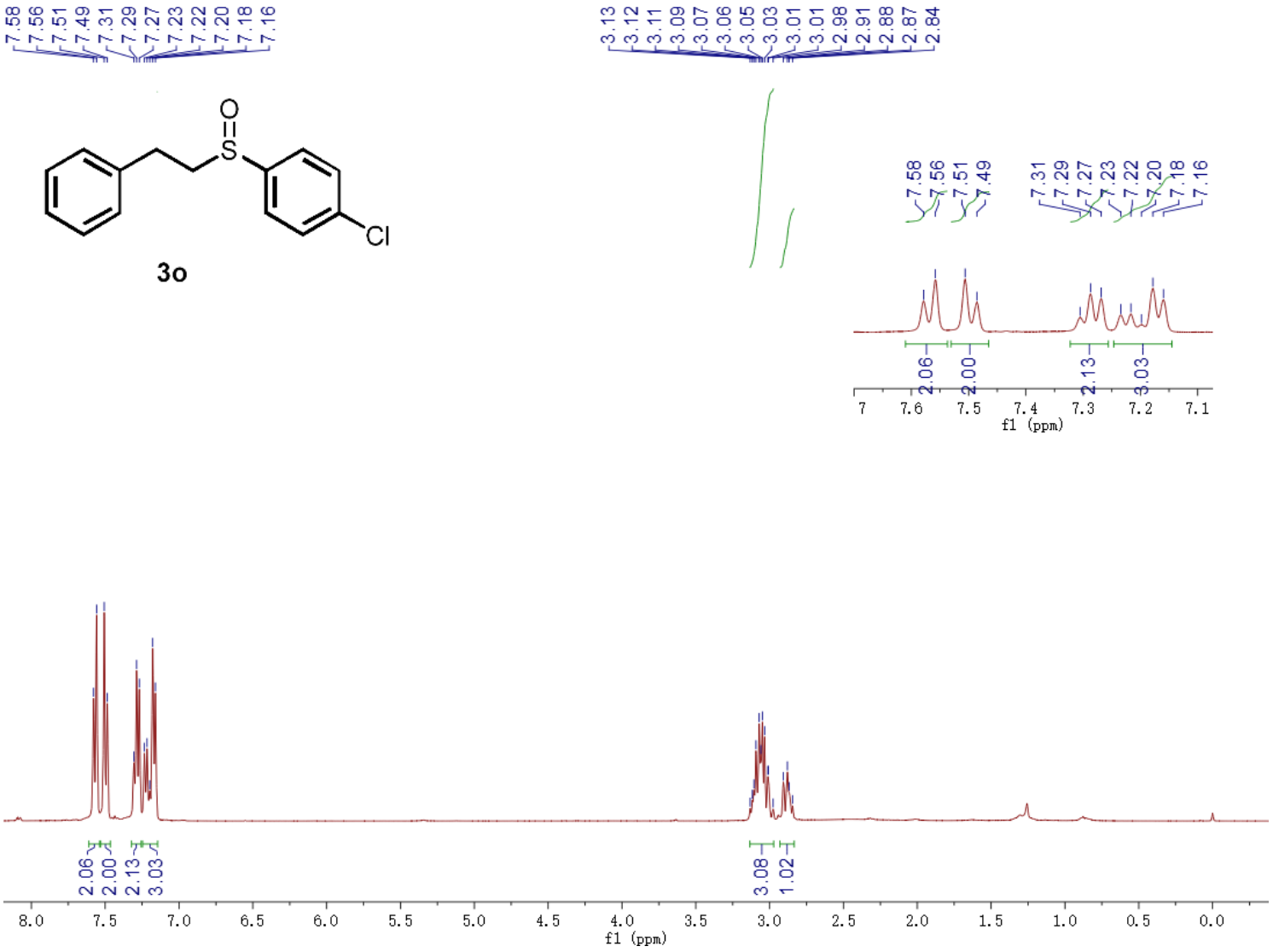
10
0
f1 (ppm)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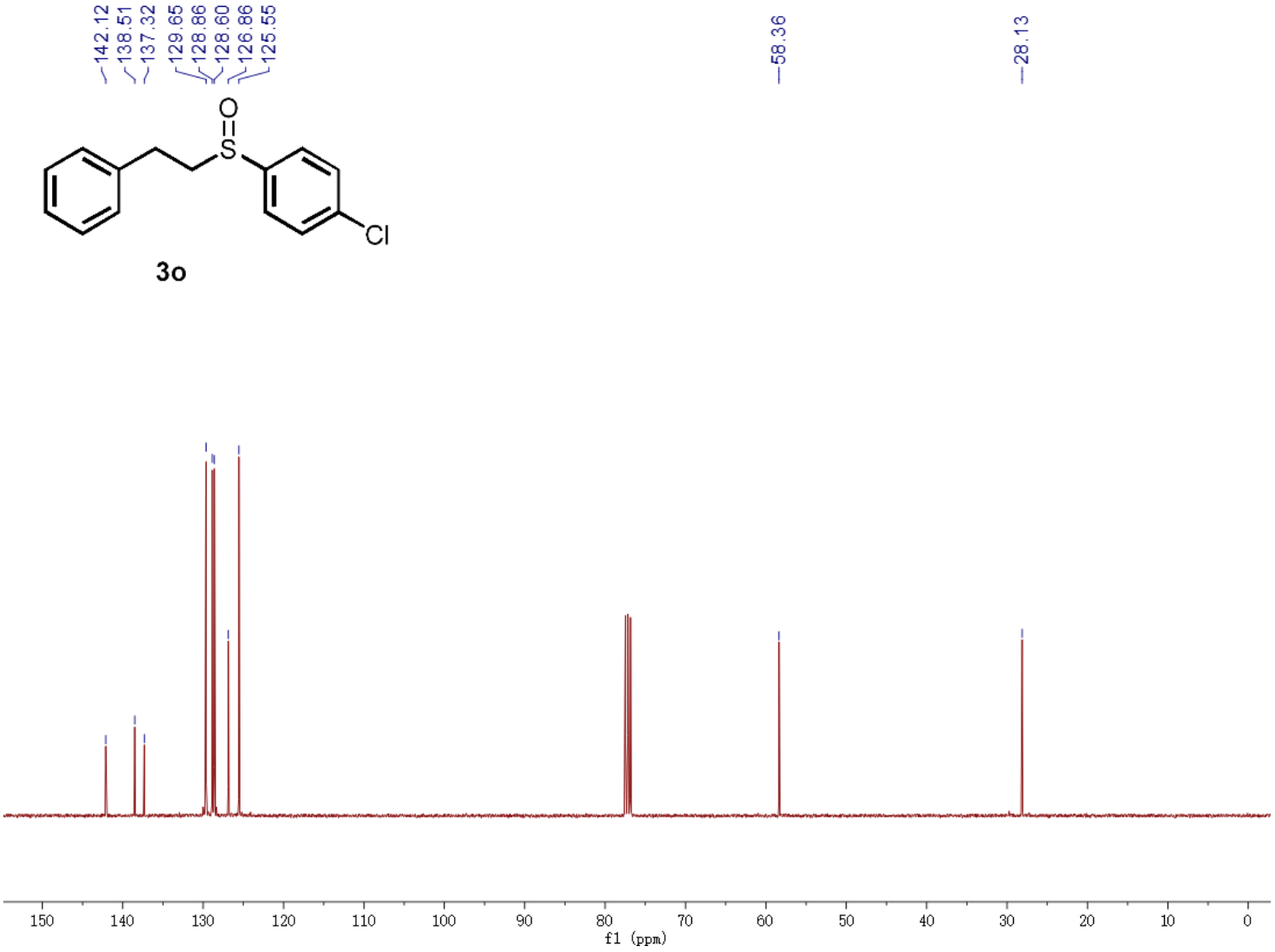
7.16
3.13
3.12
3.11
3.09
3.07
3.06
3.05
3.03
3.01
3.01
2.98
2.91
2.88
2.87
2.84
O
S
Cl
3o
2.06
2.00
2.13
3.03
f1 (ppm)
3.08
1.02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28.13
O
S
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50
40
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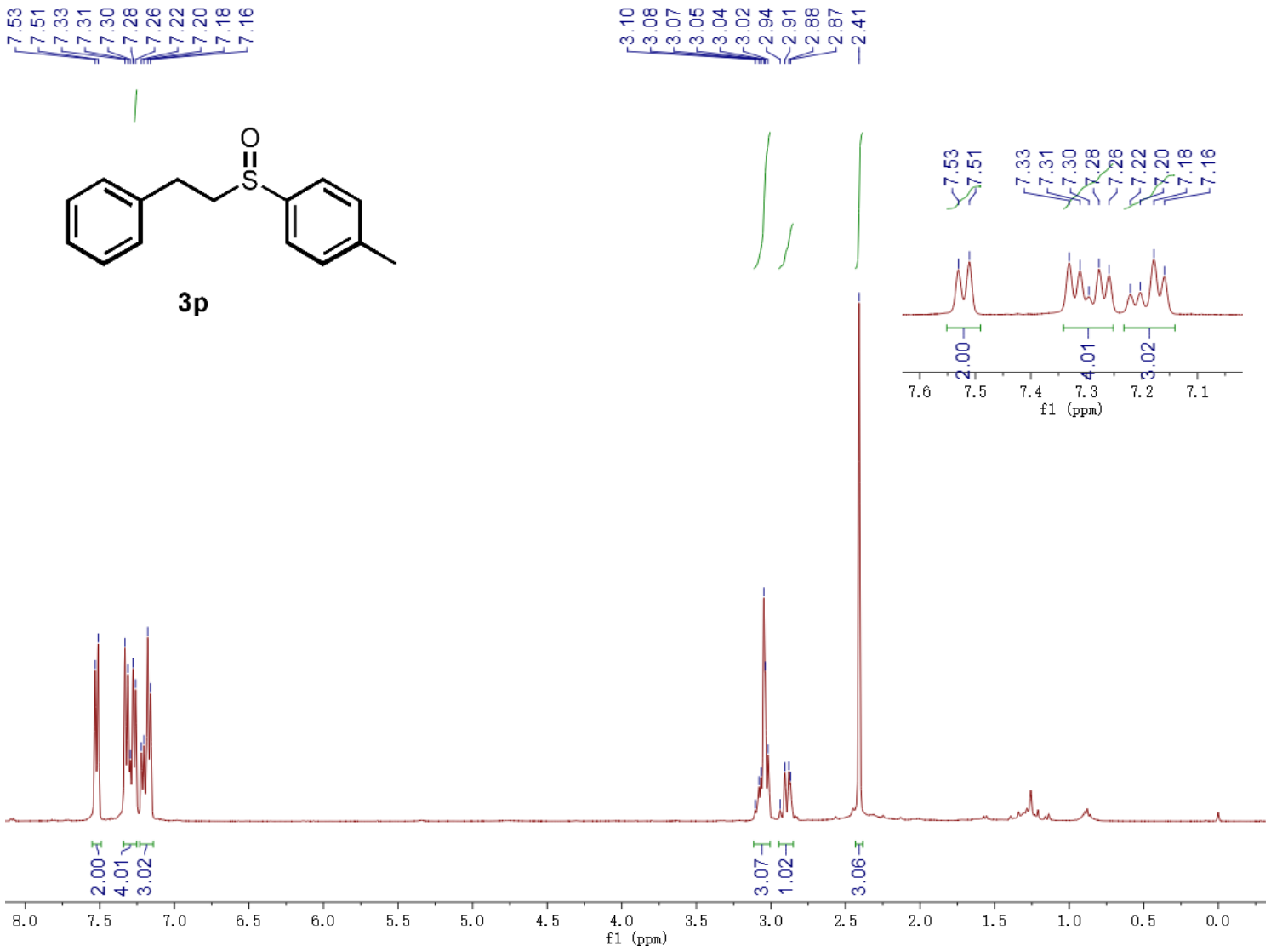
10
0
f1 (ppm)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7.20
7.18
7.16
3.10
3.08
3.07
3.05
3.04
3.02
2.94
2.91
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O
S
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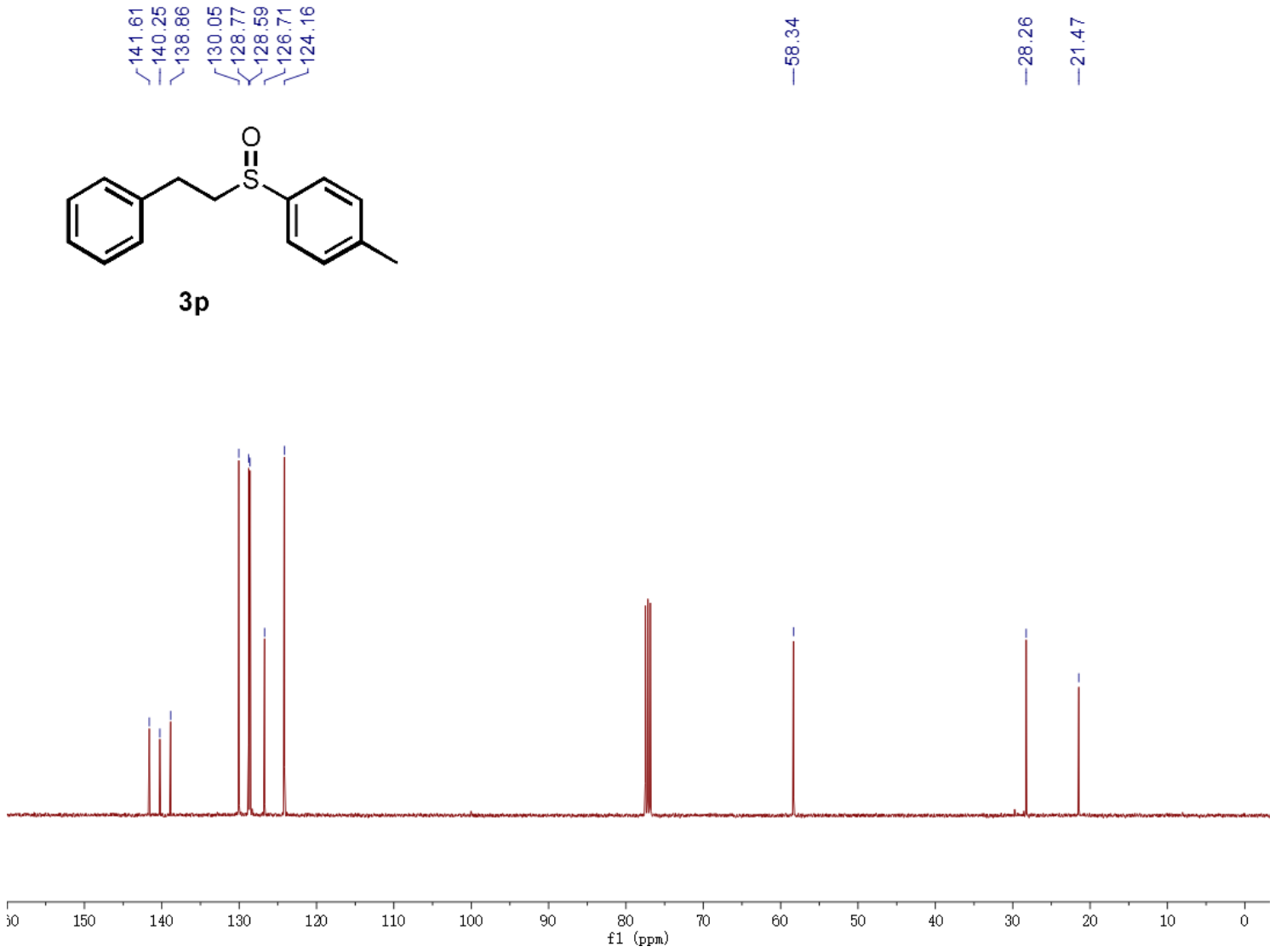
4.01
3.02
3.07
1.02
3.06
f1 (ppm)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124.16
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28.26
21.47
O
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110
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90
80
70
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50
40
30
20
10
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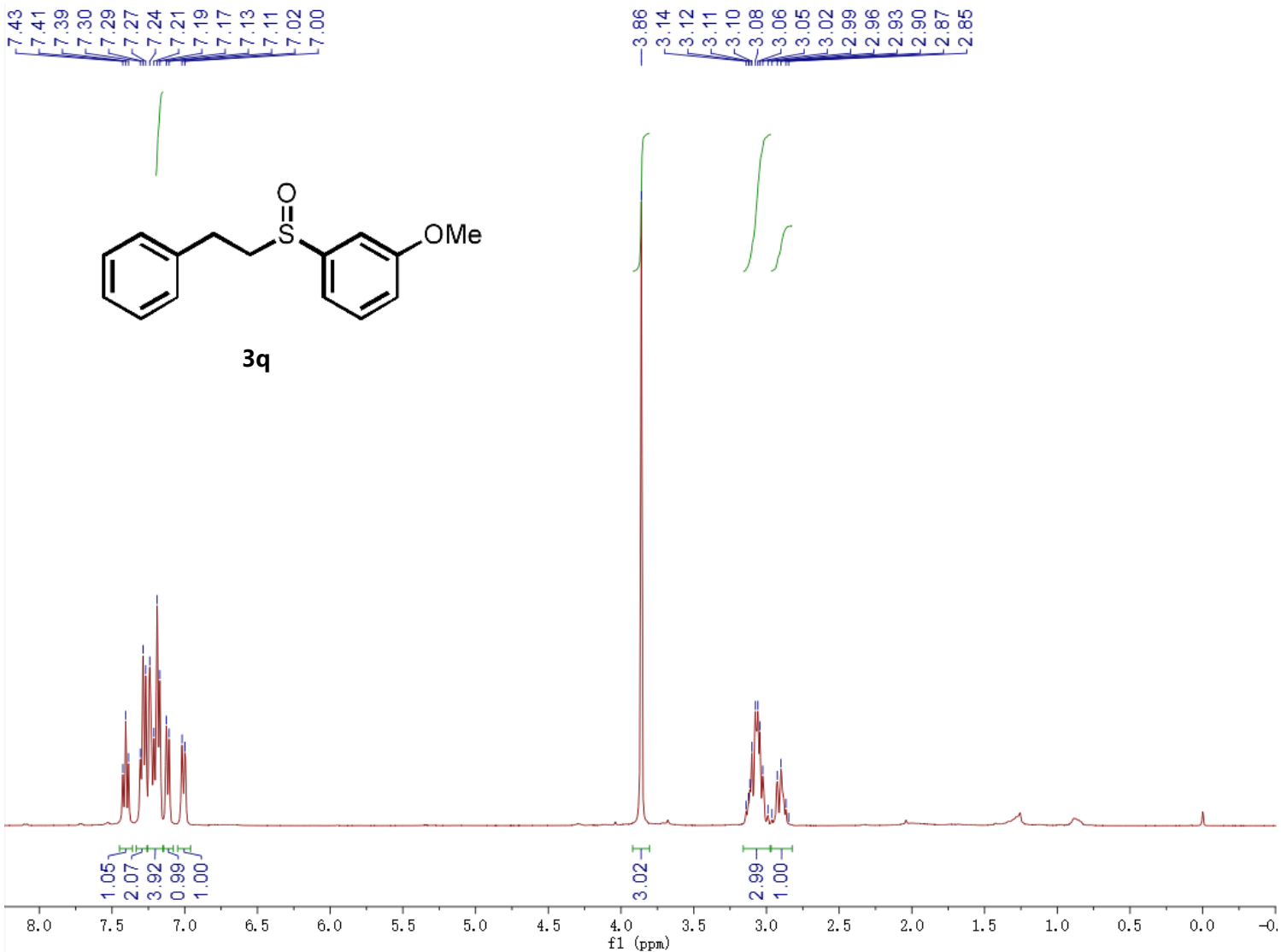
f1 (ppm)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7.11
7.02
7.00
3.86
3.14
3.12
3.11
3.10
3.08
3.06
3.05
3.02
2.99
2.96
2.93
2.90
2.87
2.85
O
S
OMe
3q
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2.07
3.92
0.99
1.00
3.02
2.99
1.00
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7.0
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6.0
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2.0
1.5
1.0
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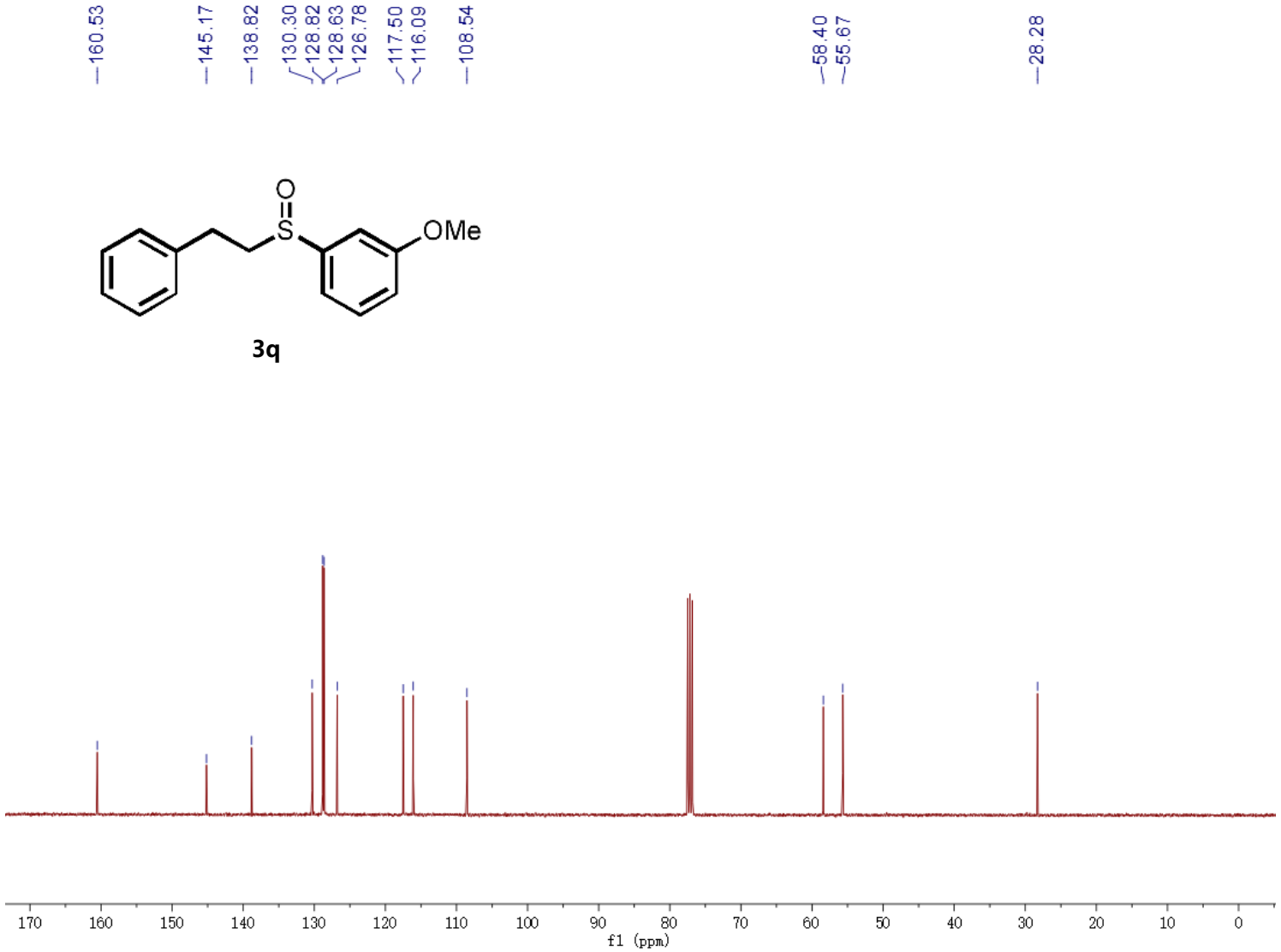
0.0
f1 (ppm)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O
S
OMe
3q
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50
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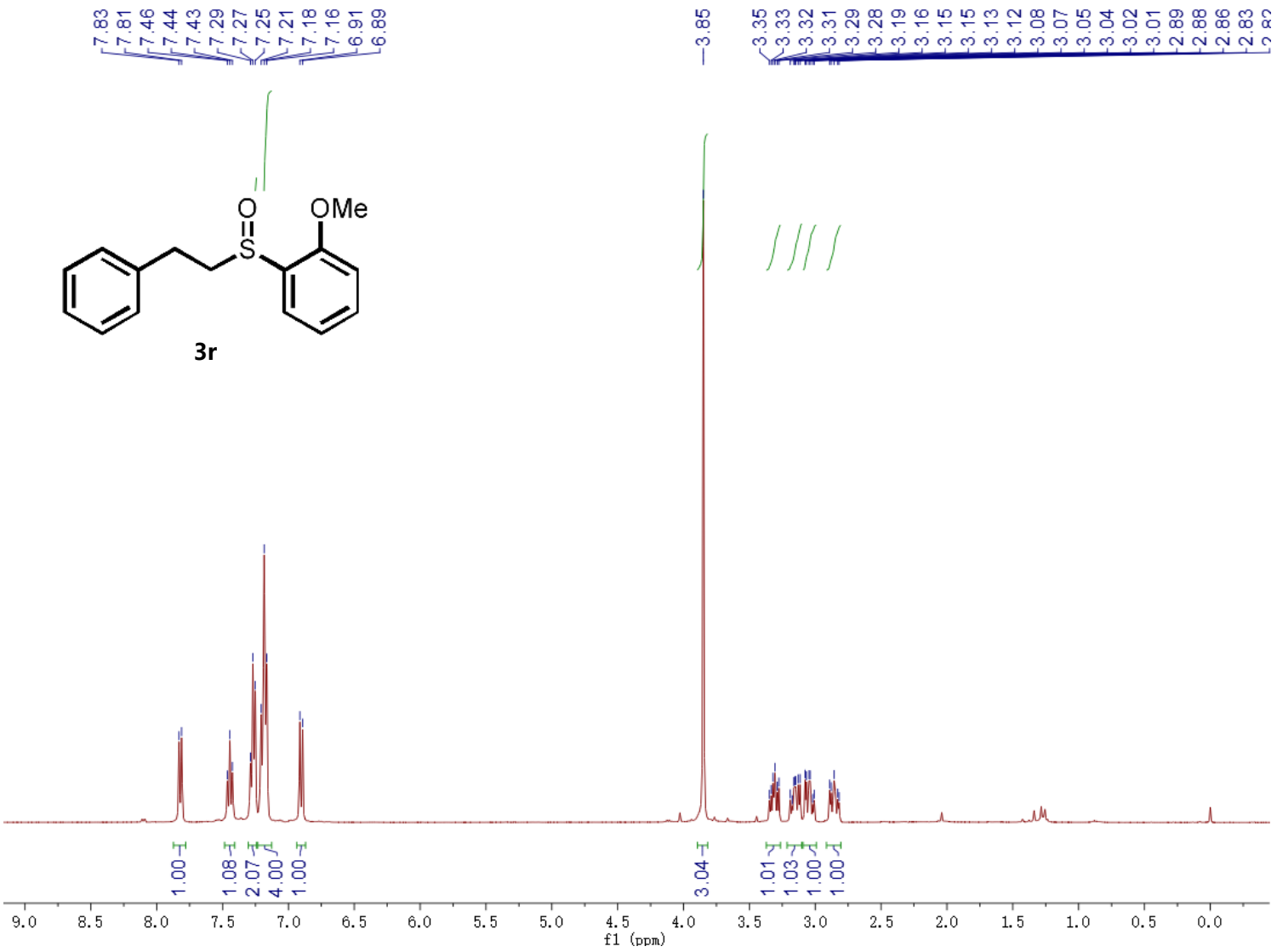
10
0
f1 (ppm)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3.35
3.33
3.32
3.31
3.29
3.28
3.19
3.16
3.15
3.15
3.13
3.12
3.08
3.07
3.05
3.04
3.02
3.01
2.89
2.88
2.86
2.83
O
S
OMe
1.00
1.08
2.07
4.00
1.00
3.04
1.01
1.03
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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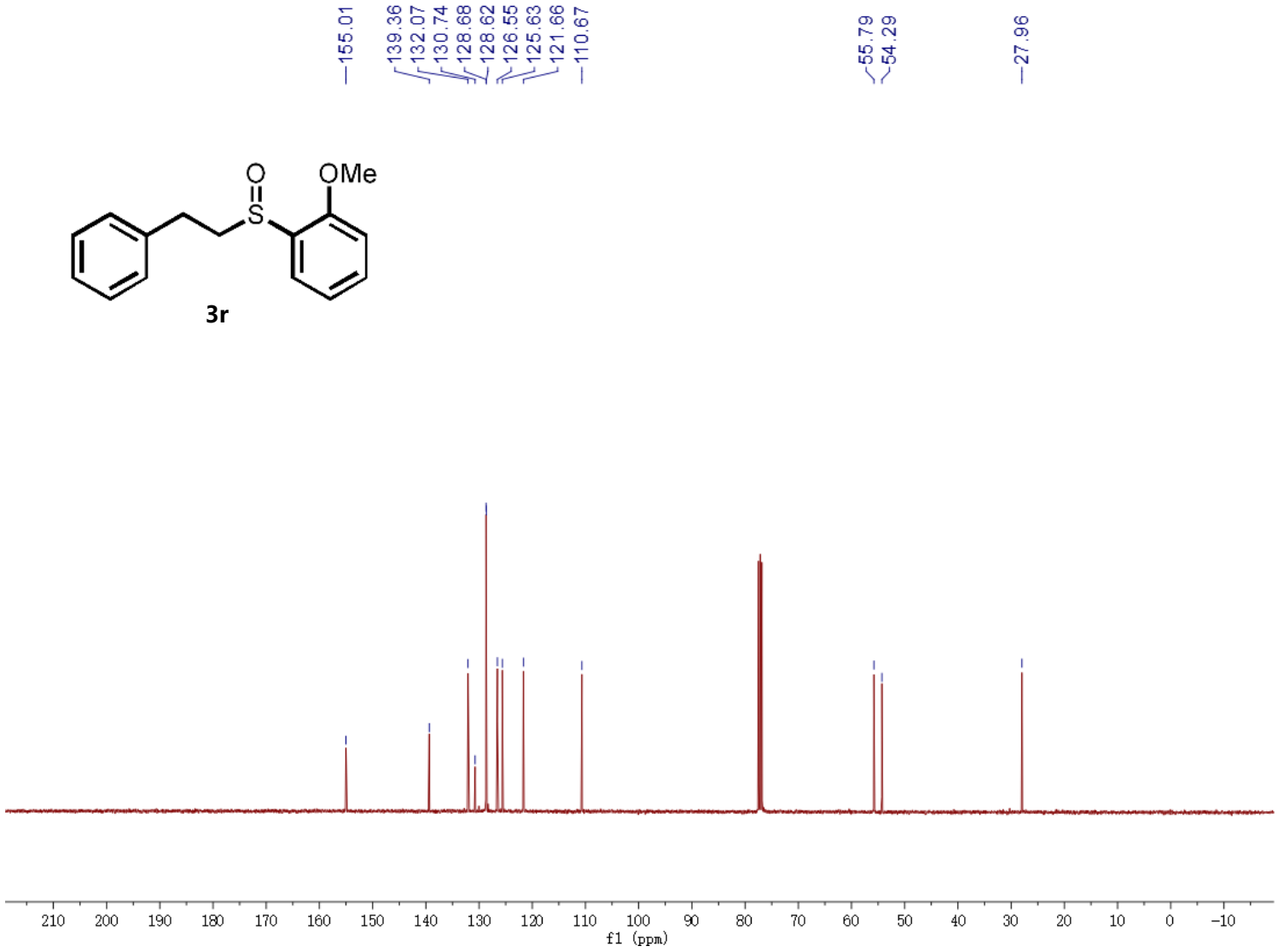
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3r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54.29
27.96
O
OMe
S
3r
210
200
190
180
170
160
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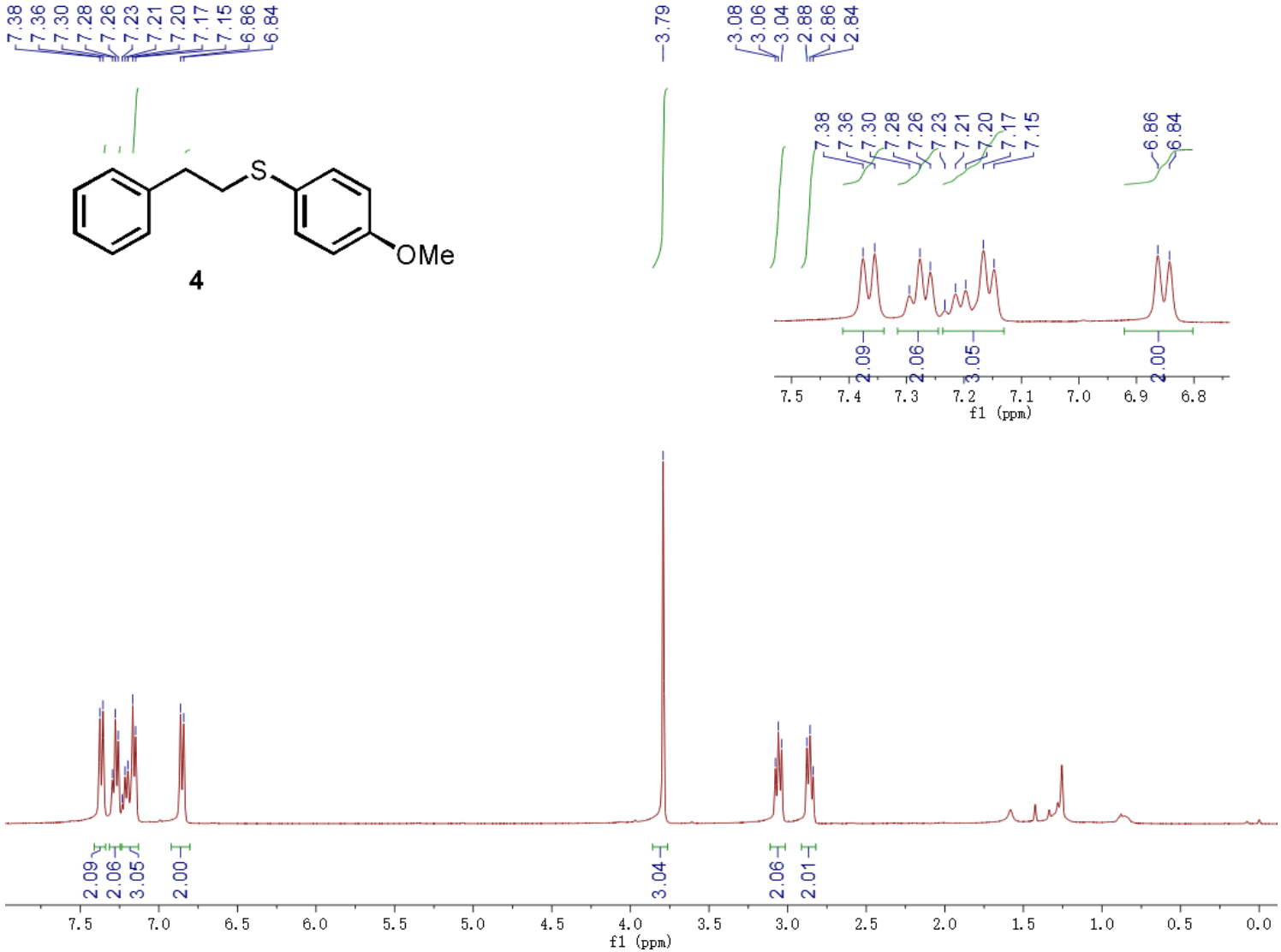
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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3.79
3.08
3.06
3.04
2.88
2.86
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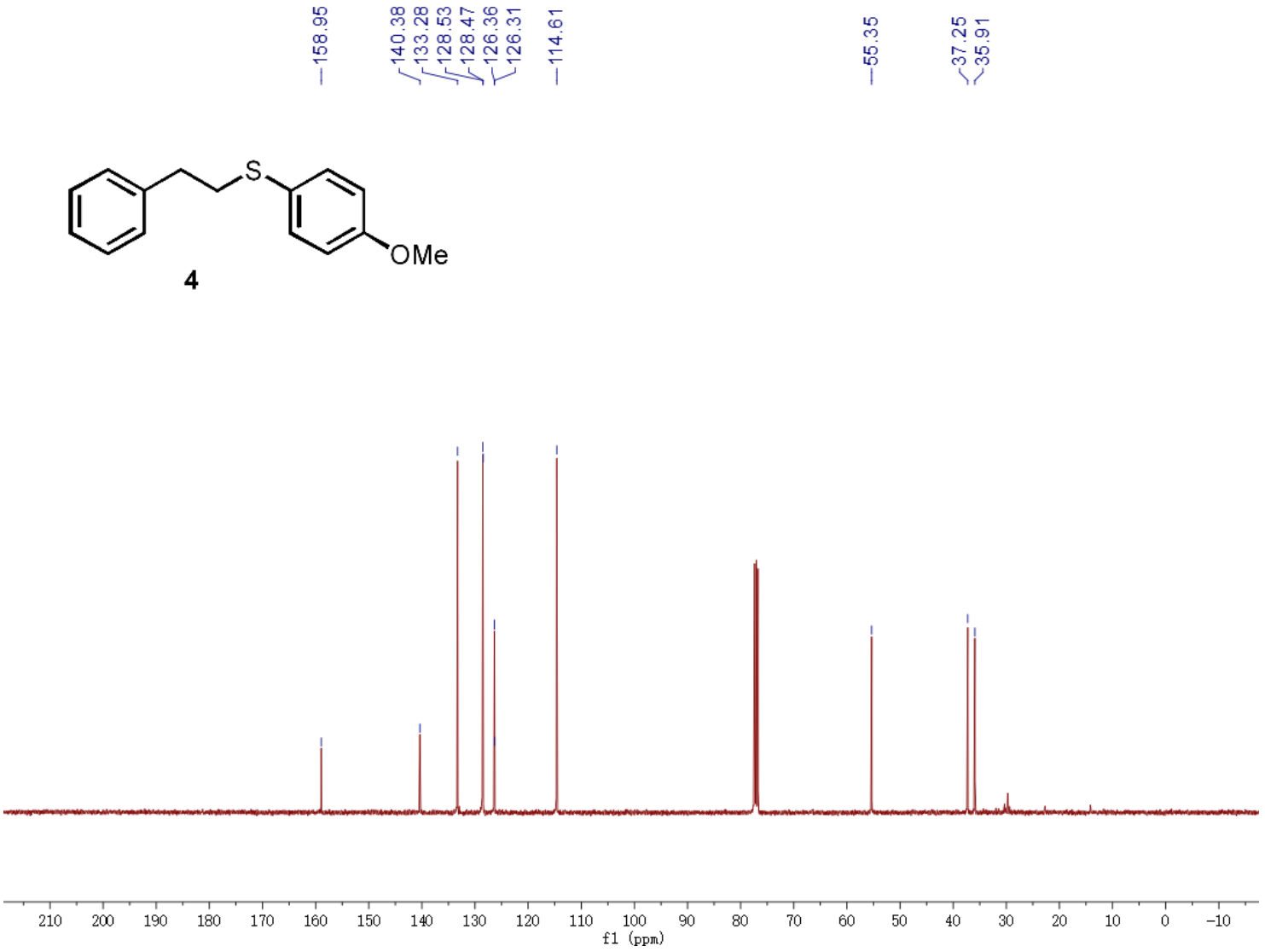
4
2.09
2.06
3.05
2.00
3.04
2.06
2.01
f1 (ppm)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126.31
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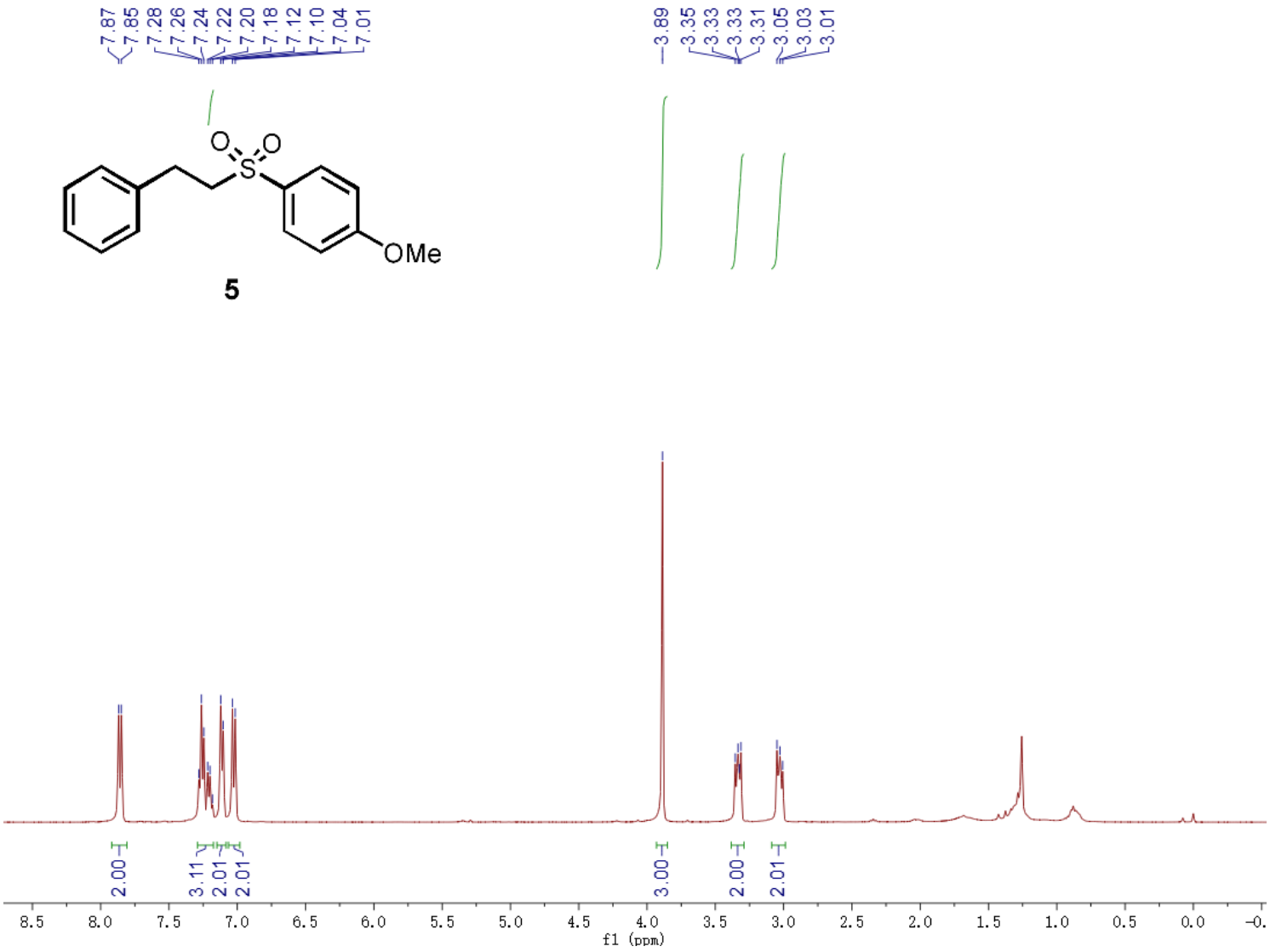
35.91
S
OMe
4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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3.35
3.33
3.33
3.31
3.05
3.03
3.01
O
O
S
OMe
5
2.00
3.11
2.01
2.01
3.00
2.00
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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2.0
1.5
1.0
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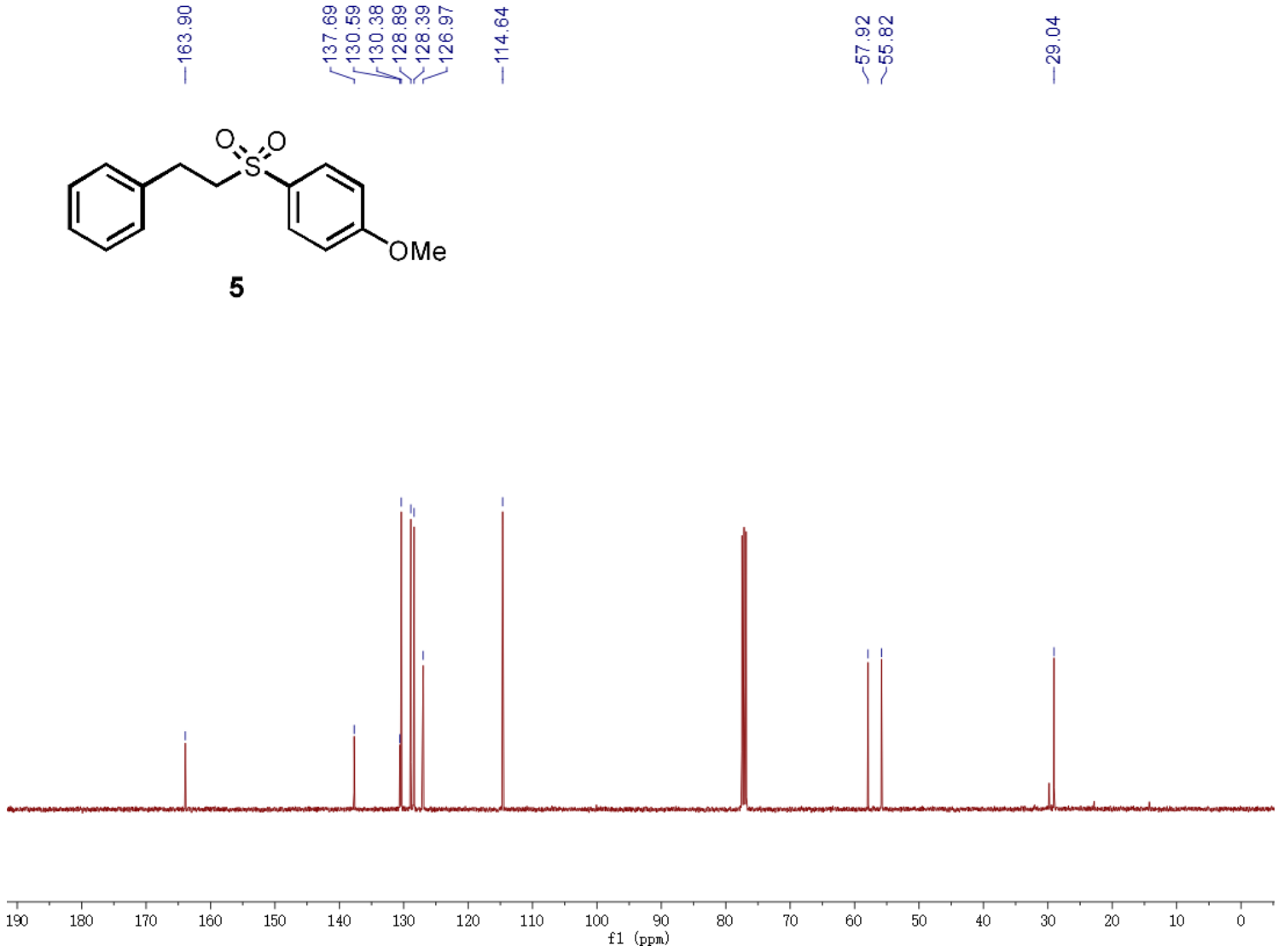
-0.
f1 (ppm)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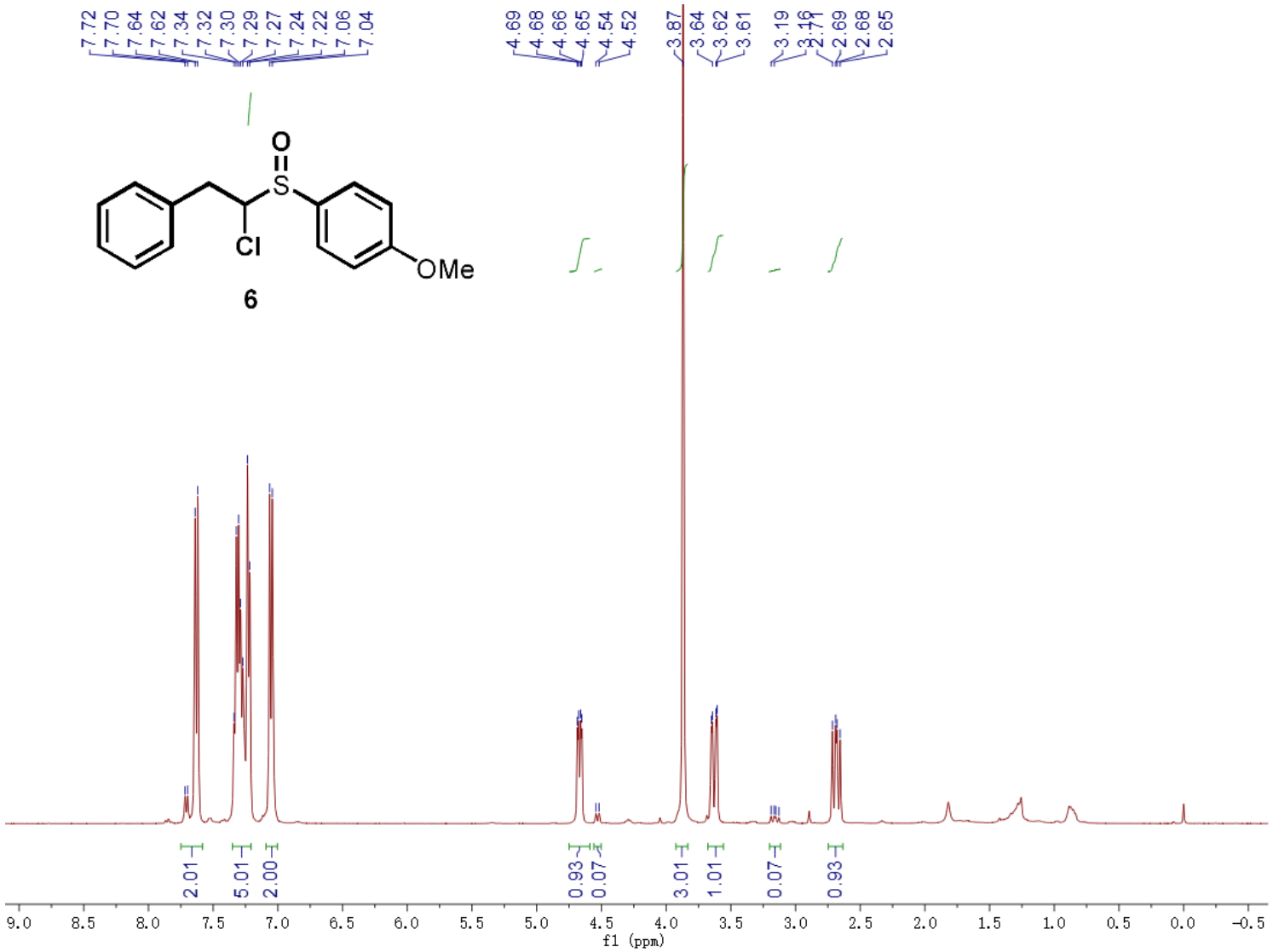
137.69
130.59
130.38
128.89
128.39
126.97
114.64
57.92
55.82
29.04
O
O
S
OMe
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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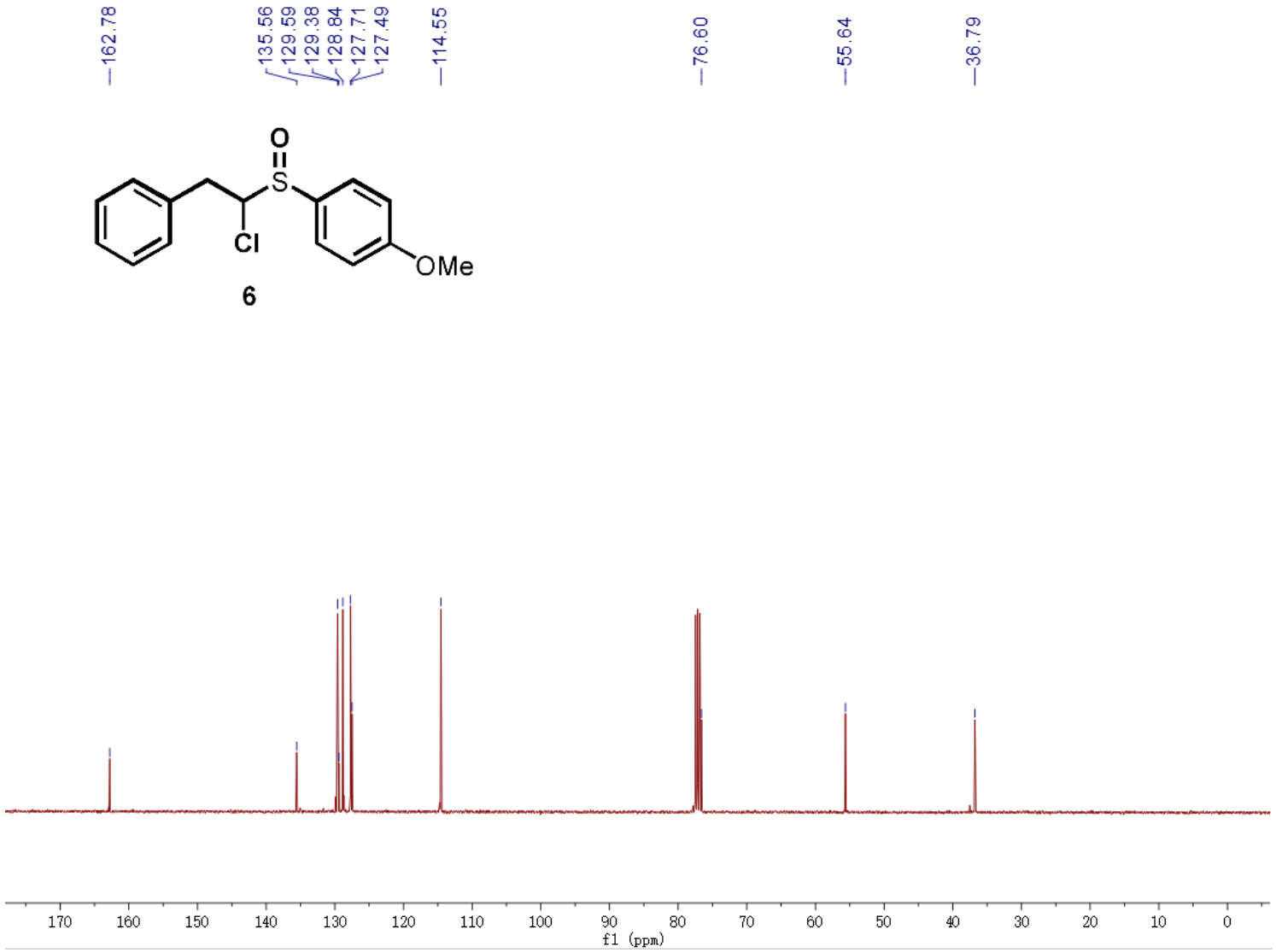
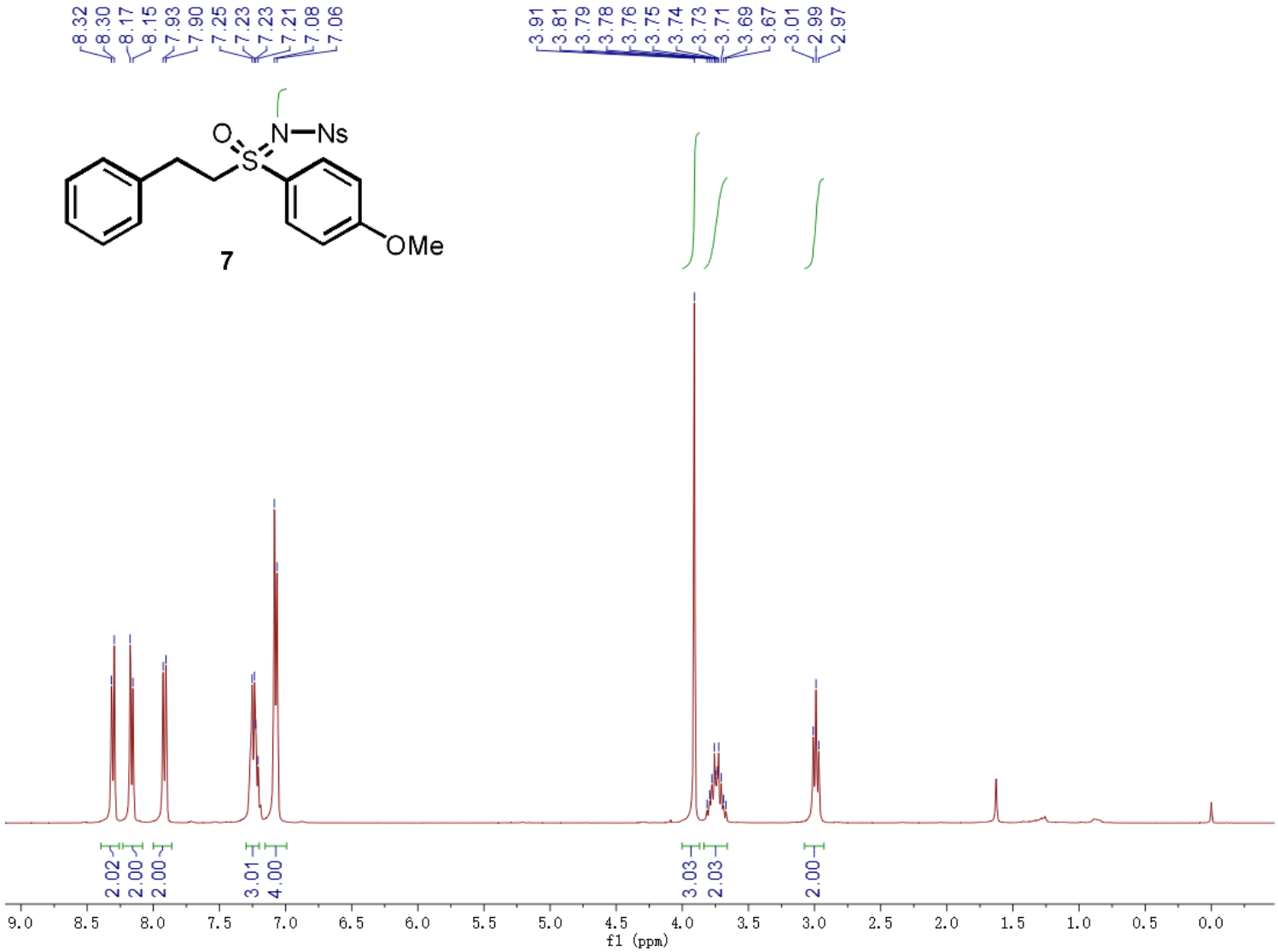
7.62
7.34
7.32
7.30
7.29
7.27
7.24
7.22
7.06
7.04
4.69
4.68
4.66
4.65
4.54
4.52
3.87
3.64
3.62
3.61
3.19
3.16
2.71
2.69
2.68
2.65
O
S
Cl
OMe
6
2.01
5.01
2.00
0.93
0.07
3.01
1.01
0.07
0.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


162.78
135.56
129.59
129.38
128.84
127.71
127.49
114.55
76.60
55.64
36.79
O
S
Cl
OMe
6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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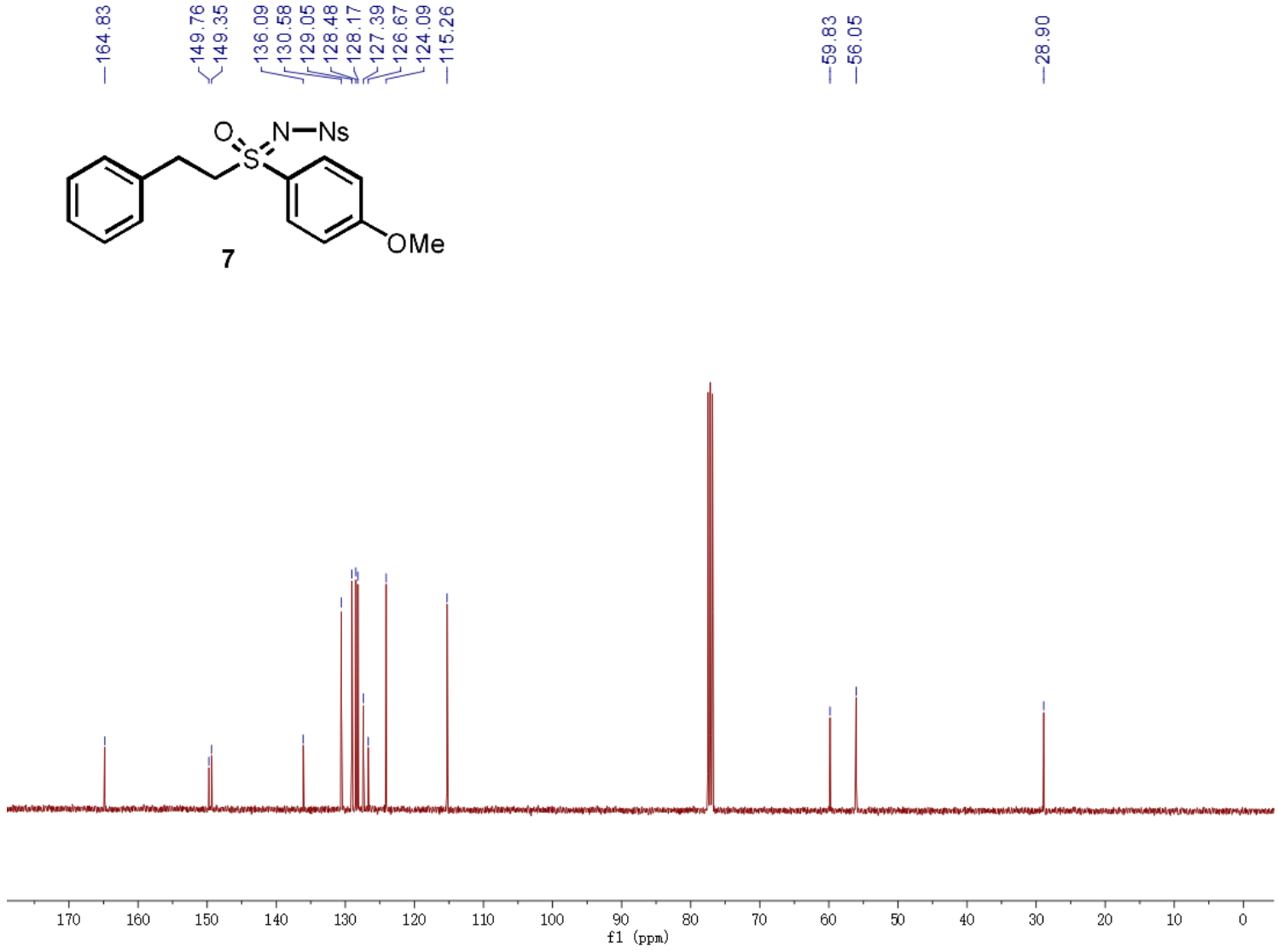
8.30
8.17
8.15
7.93
7.90
7.25
7.23
7.23
7.21
7.08
7.06
3.91
3.81
3.79
3.78
3.76
3.75
3.74
3.73
3.71
3.69
3.67
3.01
2.99
2.97
O
S
N
Ns
OMe
7
2.02
2.00
2.00
3.01
4.00
3.03
2.03
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.83
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149.35
136.09
130.58
129.05
128.48
128.17
127.39
126.67
124.09
115.26
59.83
56.05
28.90
O
S
N
Ns
OMe
7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)