Supporting Information

Pd(II) and Cu(II) Catalyzed Oxidative Cross-Coupling of Mercaptoacetylenes and Arylboronic Acids

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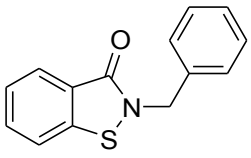
General Experimental.

^{1}H NMR and ^{13}C NMR spectra were recorded at Bruker Avance 400 MHz NMR spectrometer with solvent residual peak ($CDCl_3$: ^{1}H = 7.24 ppm, ^{13}C =77.23; $(CD_3)_2CO$: ^{1}H = 2.05 ppm, ^{13}C = 206.68 ppm; $(CD_3)_2SO$: ^{1}H = 2.50 ppm, ^{13}C = 39.51 ppm) as the internal reference unless otherwise noted. Data are reported in the following order: chemical shifts are given (δ); multiplicities are indicated b (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), app (apparent); coupling constants, *J*, are reported in Hz. Peaks in IR are reported in cm^{-1} with the following relative intensities: s (strong, 67-100%), m (medium, 40-67%), w (weak, 10-40%). HPLC analyses were carried out on an Acquity UPLC-MS Instrument (Waters Corporation), GC-MS analyses on Agilent GC-MS System (Agilent Technologies). Elemental analyses were carried out on Perkin Elmer PE 2400 Series II. High-resolution mass spectra were obtained on a LTQ Orbitrap XL (EI). IR spectra were measured with Bruker IFS 55 Equinox. Melting points were determined on Stuart SMP30 and are not corrected. Column chromatography procedures were followed using 70-230 μm silica gel. Visualization was effected with ultraviolet light.

Terminal alkynes and the palladacycle **4** were obtained from commercial sources and used without further purification. Solvents for reaction media were obtained from commercial sources, dried over 4 Å molecular sieves and titrated for water level with a Karl Fischer Coulometer (Mettler Toledo DL 32) (water content below 10 ppm).

Synthesis of *N*-thioamide and Terminal Alkyne

N-Thioamide **6,** propargyl benzoate **7** and copper(I) 3-methylsalicylate (CuMeSal) were prepared according to the previously reported procedures.[1,2]



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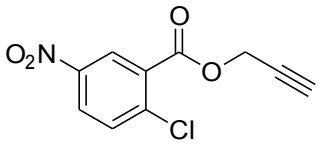

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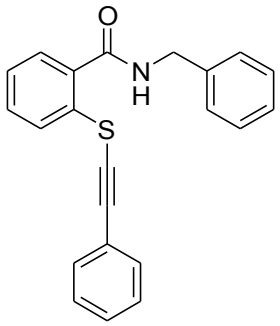
[1] Henke, A.; Srogl, J. *Chem. Commun.* **2010**, *46*, 6819–6822.
[2] Savarin, C.; Srogl, J.; Liebeskind, L. C. *Org. Lett*. **2001**, *3*, 91-93.

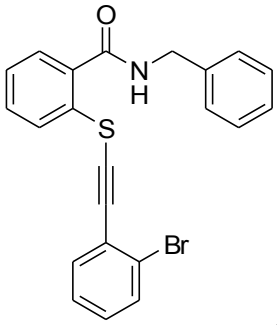
The General Method for Preparation of Mercaptoacetylenes

N-Thioamide **5** (1.5 mmol – 3.0 mmol) and AgOAc (3 mol%) were placed in a reaction tube. The tube was covered by tinfoil to protect the light-sensitive catalyst. DMF (2-3 mL) and corresponding terminal alkyne (1.2-1.3 eq) were added and the reaction tube was sealed with a cap. The resulting reaction mixture was stirred at 70-80 °C (the exact times and temperature are included for individual transformations below). The reaction progress was followed by UPLC. After the reaction was complete, it was quenched with ice cooled 5% hydrochloric acid. The precipitate was filtered, washed with water and dried or the quenched reaction mixture was extracted with ethyl acetate (3x) (in case of products which have not precipitated). The combined organic extracts were washed with brine (4x), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by recrystallization or column chromatography.

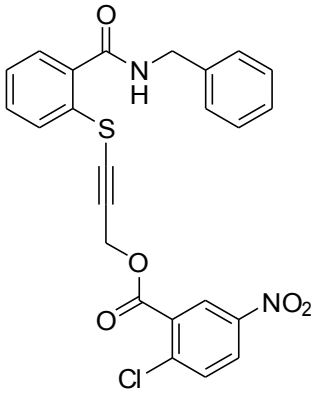


***N*-Benzyl-2-(phenylethynylthio)benzamide** (1a)[1]. The general method was followed, using *N*-thioamide **6** (720 mg; 3.0 mmol) and phenylacetylene (0.43 mL; 3.9 mmol). The reaction mixture was stirred for 46 h at 80 °C. Mercaptoacetylene **1a** was obtained as a white crystalline product after column chromatography (hexane/Et_2O/acetone 5:1:2) in 94 % yield (970 mg). M.p. 123.5-125.5 °C (EtOH/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 0.7, 8.1, 1H), 7.53 – 7.44 (m, 4H), 7.37 – 7.27 (m, *J* = 4.4, 7.5, 14.8, 8H), 7.24 – 7.19 (m, 1H), 6.33 (bs, 1H), 4.63 (d, *J* = 5.7, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 138.0, 135.4, 132.2, 132.0, 131.8, 129.0, 128.9, 128.6, 128.3, 128.2, 128.0, 127.4, 126.2, 123.2, 98.7, 77.3, 44.4.

[1] Henke, A.; Srogl, J. *Chem. Commun.* **2010**, *46*, 6819–6822.

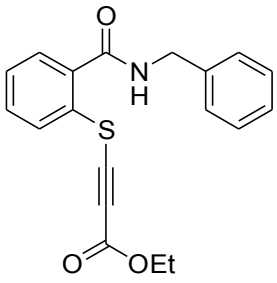


***N*-Benzyl-2-((2-bromophenyl)ethynylthio)benzamide** (1b). The general method was followed, using *N*-thioamide **6** (480 mg; 2.0 mmol) and 1-bromo-2-ethynylbenzene (0.33 mL; 2.6 mmol). The reaction mixture was stirred for 60 h at 70 °C. Mercaptoacetylene **1b** was obtained as a white crystalline product after recrystallization from EtOAc/hexane in 98 % yield (830 mg). M.p. 116.5-118 °C. ^{1}H NMR (400 MHz, Acetone-d6): δ 8.38 (bs, 1H), 8.27 (dd, *J* = 0.8, 8.1, 1H), 7.86 (dd, *J* = 1.2, 7.7, 1H), 7.72 (dd, *J* = 0.9, 8.1, 1H), 7.67 – 7.59 (m, 2H), 7.48 – 7.39 (m, 3H), 7.39 – 7.31 (m, 4H), 7.26 (apptt, *J* = 7.3, 1H), 4.62 (d, *J* = 6.0, 2H). ^{13}C NMR (101 MHz, Acetone-d6): δ 168.2, 140.8, 136.2, 134.8, 134.1, 133.4, 133.0, 131.5, 129.9, 129.9, 129.3, 129.2, 129.1, 128.5, 127.6, 126.6, 125.8, 98.2, 85.0, 44.7. IR (KBr): 3344 m (NH), 2167 w (C-C triple bond), 1643 s (CONH), 1631 s (CONH), 1523 s (CONH), 1466 m, 1455 m, 1433 m, 750 s, 704 m, 697 m. Anal. calcd for $C_{22}H_{16}BrNOS$: C, 62.56; H, 3.82; N, 3.32. Found: C, 62.23; H, 3.77; N, 3.14.

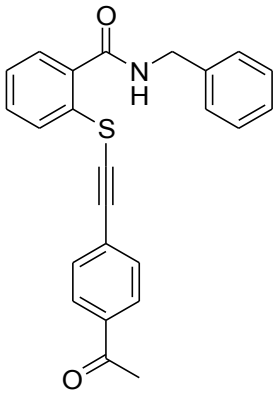


3-(2-(Benzylcarbamoyl)phenylthio)prop-2-ynyl 2-chloro-5-nitrobenzoate (1c). The general method was followed, using *N*-thioamide **6** (350 mg; 1.45 mmol) and propargyl benzoate **7** (420 mg; 1.75 mmol). The reaction mixture was stirred for 5 days at 70 °C. Mercaptoacetylene **1c** was obtained as a white crystalline product after column chromatography (hexane/Et_2O/acetone 5:1:2) in 86 % yield (600 mg). M.p. 117.5-118.5 °C (EtOH/hexane). ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.72 (d, *J* = 2.8, 1H), 8.43 (dd, *J* = 2.8, 8.8, 1H), 8.35 (bs, 1H), 8.07 (dd, *J* = 0.8, 8.1, 1H), 7.89 (d, *J* = 8.8, 1H), 7.83 (dd, *J* = 1.3, 7.7, 1H), 7.58 (ddd, *J* = 0.6, 1.4, 7.5, 1H), 7.42 – 7.30 (m, 5H), 7.25 (apptt, *J* = 7.2, 1H), 5.35 (s, 2H), 4.59 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 168.1, 164.3, 148.1, 141.2,

140.8, 135.9, 134.2, 133.7, 133.0, 132.3, 129.9, 129.2, 129.1, 129.0, 128.9, 128.5, 127.8, 127.7, 95.4, 78.7, 56.0, 44.7. IR ($CHCl_3$): 3343 w (NH), 3029 w, 3013 m, 2195 w (C-C triple bond), 1743 s (C=O), 1657 s (CONH), 1528 s (NO_2), 1519 s (CONH), 1464 m, 1455 m, 1350 s (NO_2), 1305 m, 1254 m, 1240 s, 1127 s, 1047 m, 945 w, 839 w, 701 m. Anal. calcd for $C_{24}H_{17}ClN_2O_5S$: C, 59.94; H, 3.56; N, 5.82. Found: C, 59.71; H, 3.45; N, 5.58.

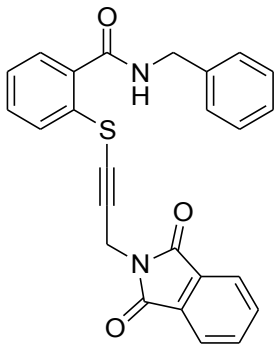


Ethyl 3-(2-(benzylcarbamoyl)phenylthio)propiolate (1d). The general method was followed, using *N*-thioamide **6** (420 mg; 1.75 mmol) and ethyl propiolate (0.23 mL; 2.30 mmol). The reaction mixture was stirred for 40 h at 70 °C. Mercaptoacetylene **1d** was obtained as an colorless oil after column chromatography (hexane/Et_2O/acetone 5:1:2) in 97 % yield (575 mg). M.p. 96-96.5 °C (EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0, 1H), 7.55 – 7.47 (m, 2H), 7.37 – 7.24 (m, 6H), 6.41 (bs, 1H), 4.60 (d, *J* = 5.7, 2H), 4.26 (q, *J* = 7.1, 2H), 1.32 (t, *J* = 7.1, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.9, 153.2, 137.8, 132.8, 132.4, 132.3, 129.1, 128.8, 128.2, 128.0, 127.3, 127.2, 92.6, 81.4, 62.2, 44.5, 14.4. IR ($CHCl_3$): 3343 w (NH), 3028 w, 3013 w, 2150 s (C-C triple bond), 1700 s (C=O), 1657 s (CONH), 1589 w, 1517 s (CONH), 1463 m, 1367 w, 1299 m, 1247 s (C-O), 1032 m, 786 m, 739 m, 701 m. Anal. calcd for $C_{19}H_{17}NO_3S$: C, 67.24; H, 5.05; N, 4.13. Found: C, 67.36; H, 4.99; N, 4.06.



2-((4-Acetylphenyl)ethynylthio)-*N*-benzylbenzamide (1e). The general method was followed, using *N*-thioamide **6** (485 mg; 2.0 mmol) and 4'-ethynylacetophenone (0.37 mL; 2.6 mmol). The reaction mixture was stirred for 40 h at 70

°C. Mercaptoacetylene **1e** was obtained as as a white crystalline product after recrystallization from EtOH/acetone in 91 % yield (700 mg). M.p. 171-172.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.28 (t, *J* = 5.9, 1H), 8.03 – 7.96 (m, 3H), 7.86 (dd, *J* = 1.2, 7.7, 1H), 7.72 (d, *J* = 8.5, 2H), 7.66 (td, *J* = 1.3, 7.7, 1H), 7.42 (td, *J* = 1.0, 7.6, 1H), 7.39 – 7.31 (m, 4H), 7.31 – 7.23 (m, 1H), 4.48 (d, *J* = 6.0, 2H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 197.1, 166.2, 139.1, 136.2, 133.3, 131.9, 131.3, 131.2, 128.4, 128.3, 128.2, 127.2, 127.0, 126.8, 126.5, 126.3, 97.6, 81.8, 42.6, 26.7. IR (KBr): 3342 m (NH), 3276 m, 3062 w, 2163 w (C-C triple bond), 1679 s (C=O), 1633 s (CONH), 1600 m, 1588 m, 1542 s (CONH), 1433 m, 1403 w, 1359 m, 1318 m, 1286 m, 1270 s, 842 w, 829 m, 746 m, 730 m, 700 m. Anal. calcd for $C_{24}H_{19}NO_2S$: C, 74.78; H, 4.97; N, 3.63. Found: C, 74.69; H, 4.89; N, 3.41.

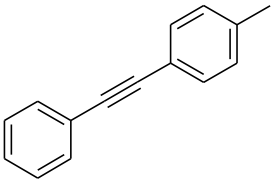


***N*-Benzyl-2-(3-(1,3-dioxoisoindolin-2-yl)prop-1-ynylthio)benzamide** (3f). The general method was followed, using *N*-thioamide **6** (440 mg; 1.8 mmol) and *N*-propargylphthalimide (440 mg; 2.4 mmol). The reaction mixture was stirred for 79 h at 80 °C. Mercaptoacetylene **1f** was obtained as as a white crystalline product after recrystallization from EtOH/hexane in 78 % yield (600 mg). M.p. 157-158.5 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.29 (bs, 1H), 8.04 (dd, *J* = 0.9, 8.1, 1H), 7.93 – 7.86 (m, 4H), 7.79 (dd, *J* = 1.3, 7.7, 1H), 7.55 (ddd, *J* = 0.7, 1.4, 7.4, 1H), 7.39 – 7.35 (m, 2H), 7.34 – 7.29 (m, 3H), 7.23 (apptt, *J* = 7.2, 1H), 4.74 (s, 2H), 4.57 (d, *J* = 6.0, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 168.3, 168.1, 140.8, 136.2, 135.9, 133.7, 133.5, 132.9, 129.8, 129.1, 129.0, 128.8, 128.4, 127.4, 124.7, 95.6, 73.2, 44.6, 29.5. IR (KBr): 3304 m (NH), 2200 w (C-C triple bond), 1770 w, 1716 s (CONCO), 1637 m (CONH), 1532 s (CONH), 1419 m, 1393 m, 1342 m, 1314 m, 1112 m, 939 m, 749 w, 739 w, 728 m, 710 w. Anal. calcd for $C_{25}H_{18}N_2O_3S$: C, 70.41; H, 4.25; N, 6.57. Found: C, 70.21; H, 4.28; N, 6.38.

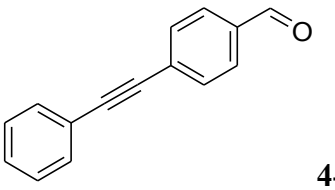
The General Protocol for Cross-Coupling Reaction

Mercaptoacetylene **1** (0.5-1.0 mmol) and corresponding boronic acid (1.1 eq), CuMeSal (3 mol%) and $Pd(dba)_2$ (1 mol %) were placed to a flask (10 ml). DMF (2-4 ml) was added and the resulting reaction mixture was stirred for 8-20 h at 45-50 °C in the presence of air. Reaction progress was followed by UPLC. After the boronic acid was consumed, the second portion of the boronic acid was added (0.2-0.4 eq.) to reach full conversion. After the reaction was complete, it was quenched with ice cooled 5% hydrochloric acid. The quenched reaction mixture was extracted with ethyl acetate (3x). The combined organic extracts were washed with brine (5x), dried over $MgSO_4$. The solvent was removed under reduced pressure and crude product was purified by column chromatography to afford both alkyne and thioether product.

Alkynes:



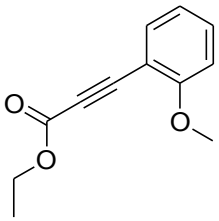
1-Methyl-4-(phenylethynyl)benzene (2a). The general method was followed, by using thioacetylene **1a** (345 mg; 1.0 mmol) and 4-tolylboronic acid (340 mg; 2.5 mmol). The reaction mixture was stirred for 22 h. Acetylene **2a** was obtained as a white solid after column chromatography (hexane/DCM 20:1) in 86 % yield (165 mg). M.p. 73-74.5 °C (MeOH/water) (lit. 72.5-74 °C).[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.50 (m, 2H), 7.43 (d, J = 8.1, 2H), 7.37 – 7.30 (m, 3H), 7.18 – 7.12 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.6, 131.8, 131.7, 129.3, 128.5, 128.3, 123.8, 120.5, 89.8, 89.0, 21.7.



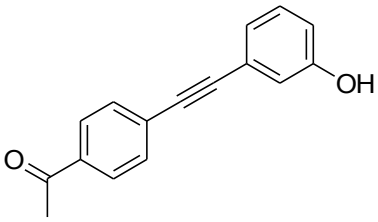
4-(Phenylethynyl)benzaldehyde (2b). The general method was followed, by using mercaptoacetylene **1a** (345 mg; 1.0 mmol) and 4-formylphenylboronic acid (450 mg; 3.0 mmol). The reaction mixture was stirred for 22 h. Acetylene **2b** was obtained as a white solid after column chromatography (hexane/Et_2O/acetone 10:1:2) in 80 % yield (165 mg). M.p. 96.5-98 °C (hexane) (lit. 96.5-98 °C)[4]. ^{1}H NMR (400 MHz, Acetone-d_6): δ 10.08 (s, 1H), 7.97 (ddd, J = 0.4, 1.6, 8.1, 2H), 7.77 (ddd, J = 0.4, 1.6, 8.1, 2H), 7.63-7.58

[3] Seyferth, D.; Damrauer, R. *J. Org. Chem.* **1966**, *31*, 1660
[4] Tolosa, J.; Kub, C.; Bunz, U. H. F. *Angew. Chem., Int. Ed.* **2009**, *48*, 4610 - 4612

(m, 2H), 7.48 – 7.42 (m, 3H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 192.8, 137.6, 133.5, 133.2, 131.0, 130.6, 130.5, 130.2, 124.0, 94.2, 89.8.

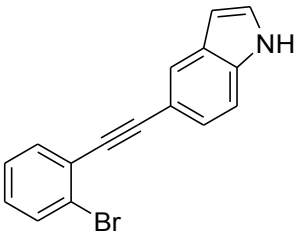


Ethyl 3-(2-methoxyphenyl)propiolate (2c). The general method was followed, by using mercaptoacetylene **1d** (330 mg; 0.97 mmol) and 2-methoxyphenylboronic acid (335 mg; 2.2 mmol). The reaction mixture was stirred for 12 h. Acetylene **2c** was obtained as a yellowish oil after column chromatography (hexane/Et_2O/acetone 7:1:2) in 75 % yield (148 mg). ^{1}H NMR (in agreement with ref)[5] (400 MHz, $CDCl_3$): δ 7.50 (dd, J = 1.8, 7.6, 1H), 7.38 (ddd, J = 0.7, 1.8, 7.5, 1H), 6.92 (td, J = 0.9, 7.6, 1H), 6.88 (d, J = 0.6, 1H), 4.27 (q, J = 7.1, 2H), 3.88 (s, 3H), 1.33 (t, J = 7.1, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.8, 154.4, 135.1, 132.4, 120.7, 111.1, 109.2, 84.8, 83.4, 62.2, 56.1, 14.3.

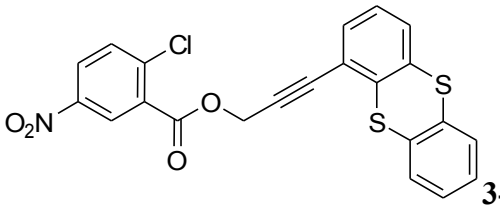


1-(4-((3-Hydroxyphenyl)ethynyl)phenyl)ethanone (2d). The general method was followed, by using mercaptoacetylene **1e** (385 mg; 1.0 mmol) and 3-hydroxyphenylboronic acid (395 mg; 2.8 mmol). The reaction mixture was stirred for 8.5 h. Acetylene **2d** was obtained as a white solid after column chromatography (hexane/Et_2O/acetone 5:1:2) in 87 % yield (205 mg). M.p. 163-164 °C (EtOH/hexan). ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.67 (bs, 1H), 8.02 (ddd, J = 0.4, 1.6, 8.2, 2H), 7.66 (ddd, J = 1.0, 2.5, 8.2, 2H), 7.26 (dd, J = 0.4, 7.8, 1H), 7.10 – 7.02 (m, 2H), 6.92 (ddd, J = 1.0, 2.5, 8.2, 1H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 197.8, 158.9, 138.1, 133.0, 131.3, 129.8, 129.1, 125.0, 124.5, 119.6, 118.0, 93.7, 89.4, 27.3. IR ($CHCl_3$): 3595 w (OH), 3012 w, 2213 w (C-C triple bond), 1641 s (C=O), 1602 s, 1591 m, 1580 m, 1441 w, 1404 w, 1360 m, 1266 s, 1179 m, 958 w, 947 w, 843 w, 831 w, 684 w. Anal. calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.35; H, 5.10.

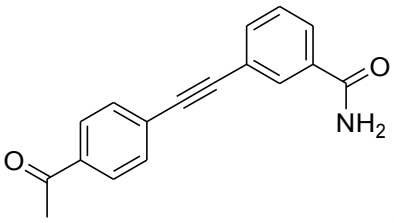
[5] Aitken, A. R.; Horsburgh, C. E. R.; McCreadie, J. G.; Seth, S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1727-1732.



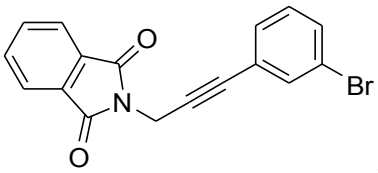
5-((2-Bromophenyl)ethynyl)-1H-indole (2e). The general method was followed, by using mercaptoacetylene **1b** (422 mg; 1.0 mmol) and 5-indolylboronic acid (484 mg; 3.0 mmol). The reaction mixture was stirred for 11 h. Acetylene **2e** was obtained as a white solid after column chromatography (hexane/Et_2O/acetone 7:1:2) in 78 % yield (230 mg). M.p. 108-109.5 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ 10.51 (bs, 1H), 7.90 – 7.85 (m, 1H), 7.71 (ddd, J = 0.3, 1.2, 8.1., 1H), 7.63 (ddd, J = 0.3, 1.7, 7.7, 1H), 7.50 (dt, J = 0.8, 8.4, 1H), 7.44 – 7.39 (m, 2H), 7.35 (dd, J = 1.5, 8.4, 1H), 7.29 (ddd, J = 0.6, 1.7, 7.5, 1H), 6.57 – 6.53 (m, 1H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 137.9, 134.5, 134.0, 130.7, 129.7, 129.0, 127.7, 127.5, 126.3, 126.2, 125.8, 114.6, 113.2, 103.4, 97.8, 86.8. IR ($CHCl_3$): 3479 w (NH), 3011 m, 2213 m (C-C triple bond), 1619 w, 1586 w, 1479 s, 1414 s, 1304 m, 1088 w, 1044 w, 1025 m, 887 m, 807 m, 699 s. Anal. calcd for $C_{16}H_{10}BrN$: C, 64.89; H, 3.40; N, 4.73. Found: C, 64.80; H, 3.35; N, 4.49.



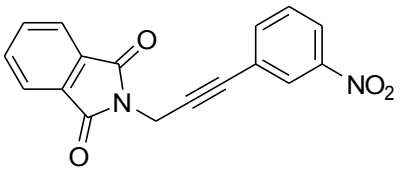
3-(Thianthren-1-yl)prop-2-ynyl 2-chloro-5-nitro-benzoate (2f). The general method was followed, by using mercaptoacetylene **1c** (315 mg; 0.65 mmol) and 1-thianthrenylboronic acid (575 mg; 2.2 mmol). The reaction mixture was stirred for 18 h. Acetylene **2f** was obtained as a yellowish solid after column chromatography (hexane/Et_2O/acetone 10:1:2) in 64 % yield (190 mg). M.p. (fast decomp.) >65 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.78 (d, J = 2.7, 1H), 8.46 (dd, J = 2.7, 8.8, 1H), 7.92 (d, J = 8.8, 1H), 7.58 – 7.53 (m, 3H), 7.51 (dd, J = 1.3, 7.7, 1H), 7.39 – 7.32 (m, 3H), 5.42 (s, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 164.2, 148.2, 141.3, 139.6, 137.0, 136.3, 135.9, 134.2, 133.2, 132.4, 130.7, 130.4, 130.1, 129.9, 129.8, 129.2, 129.0, 127.8, 123.4, 91.1, 85.2, 55.5. IR (KBr): 2242 w (C-C triple bond), 1739 s (C=O), 1609 m, 1518 s (NO_2), 1443 m, 1394 m, 1345 s (NO_2), 1309 m, 1239 s, 1128 m, 1048 s, 788 m, 747 m, 740 m. HR-MS (EI) *m/z* calcd for $C_{22}H_{12}ClNO_4S$ 452.9896, found 452.9897.



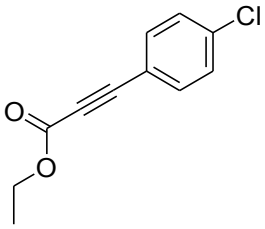
3-((4-Acetylphenyl)ethynyl)benzamide (2g). The general method was followed, by using mercaptoacetylene **1e** (290 mg; 0.75 mmol) and 3-aminocarbonylphenylboronic acid (430 mg; 2.6 mmol). The reaction mixture was stirred for 8.5 h. Acetylene **2g** was obtained as white solid after column chromatography (hexane/Et_2O/acetone 5:2:4) in 96 % yield (190 mg). M.p. 183-185 °C (decomp.). ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.14 (td, J = 0.4, 1.7, 1H), 8.04 (ddd, J = 0.5, 1.6, 8.2, 2H), 7.99 (ddd, J = 0.5, 1.7, 7.8, 1H), 7.74 (ddd, J = 0.4, 1.6, 7.8, 1H), 7.71 (ddd, J = 0.5, 1.6, 8.2, 2H), 7.61 (bs, 1H), 7.55 (td, J = 0.5, 7.8, 1H), 6.81 (bs, 1H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 197.8, 168.6, 138.4, 136.6, 135.6, 133.1, 132.2, 130.3, 129.9, 129.5, 128.8, 124.2, 92.8, 90.4, 27.3. IR (KBr): 3358 s (NH_2), 3172 m (NH_2), 2974 m, 1677 s (C=O), 1657 s (CONH), 1625 m, 1604 m, 1574 w, 1440 m, 1405 m, 1391 m, 1365 m, 1267 s, 1050 m, 964 w, 833 m. Anal. calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.19; H, 4.89; N, 5.19.



2-(3-(3-Bromophenyl)prop-2-ynyl)isoindoline-1,3-dione (2h). The general method was followed, by using mercaptoacetylene **1f** (215 mg; 0.5 mmol) and 3-bromophenylboronic acid (300 mg; 1.5 mmol). The reaction mixture was stirred for 8 h. Acetylene **2h** was obtained as a white solid after column chromatography (hexane/Et_2O/acetone 7:1:2) in 80 % yield (135 mg). M.p. 156-157 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ 7.94 – 7.87 (m, 4H), 7.58 (t, J = 1.6, 1H), 7.55 (ddd, J = 1.1, 2.0, 8.0, 1H), 7.42 (dt, J = 1.2, 7.8, 1H), 7.31 (td, J = 0.3, 7.9, 1H), 4.69 (s, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 168.2, 136.0, 135.6, 133.7, 133.3, 132.0, 131.9, 126.2, 124.7, 123.2, 86.7, 82.0, 28.7. IR ($CHCl_3$): 3020 w, 1774 m, 1723 s (CONCO), 1591 w, 1558 w, 1474 w, 1424 m, 1392 m, 1346 m, 1118 m, 943 m, 711 m. HR-MS (EI) m/z calcd for $C_{17}H_{10}BrNO_2$ 338.9895, found 338.9904.



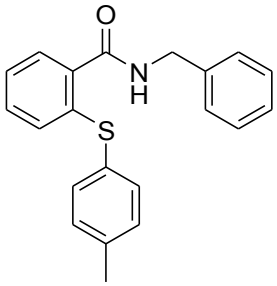
2-(3-(3-Nitrophenyl)prop-2-ynyl)isoindoline-1,3-dione (2i). The general method was followed, by using mercaptoacetylene **1f** (165 mg; 0.39 mmol) and 3-nitrophenylboronic acid (185 mg; 1.1 mmol). The reaction mixture was stirred for 6 h. Acetylene **2i** was obtained as a white solid after column chromatography (hexane/Et_2O/acetone 7:1:2) in 70 % yield (83 mg). M.p. 184-184.5 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.26 – 8.19 (m, 2H), 7.95 – 7.88 (m, 4H), 7.85 (dt, J = 1.3, 7.8, 1H), 7.71 – 7.65 (m, 1H), 4.73 (s, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 168.2, 149.8, 139.0, 136.0, 133.7, 131.6, 127.6, 125.6, 124.8, 124.7, 87.7, 81.4, 28.7. IR (KBr): 3078 w, 2974 w, 1768 m, 1710 s (CONCO), 1524 s (NO_2), 1415 s, 1391 m, 1351 s (NO_2), 1319 m, 1117 m, 936 m, 738 w, 725 m, 710 w. Anal. calcd for $C_{17}H_{10}N_2O_4$: C, 66.67; H, 3.29; N, 9.15. Found: C, 66.52; H, 3.21; N, 9.00.



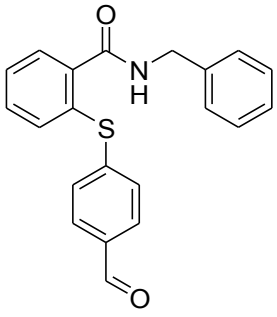
Ethyl 3-(4-chlorophenyl)propiolate (2j). The general method was followed, by using mercaptoacetylene **1d** (285 mg; 0.84 mmol) and 4-chlorophenylboronic acid (380 mg; 2.4 mmol). The reaction mixture was stirred for 9 h. Acetylene **2j** was obtained as a white solid after column chromatography (hexane/Et_2O/acetone 50:1:2) in 69 % yield (120 mg). M.p. 40-41.5 °C (hexane) (lit. 40.7-42.9 °C)[6]. ^{1}H NMR (400 MHz, Acetone-d_6): δ 7.67 (ddd, J = 0.4, 2.3, 8.4, 2H), 7.53 (ddd, J = 0.4, 2.3, 8.4, 2H), 4.27 (q, J = 7.1, 2H), 1.31 (t, J = 7.1, 3H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 154.6, 138.1, 135.8, 130.7, 119.7, 85.2, 82.8, 63.3, 14.9.

Thioethers:

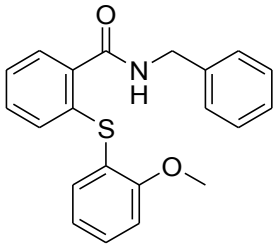
[6] Bloomfield, J.; Fuchs R. *J. Org. Chem.* **1961**, *26*, 2991-2993



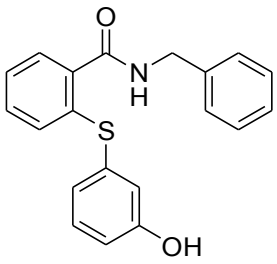
***N*-Benzyl-2-(p-tolylthio)benzamide** (3a). Thioether 3a was obtained as a white solid after column chromatography (hexane/Et_2O/acetone 10:1:2) in 83 % yield (280 mg). M.p. 124-125 °C (EtOH/hexan). ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.03 (bs, 1H), 7.56 (dd, J = 1.4, 7.6, 1H), 7.46 – 7.41 (m, 2H), 7.37 – 7.30 (m, 4H), 7.30 – 7.19 (m, 5H), 7.00 (dd, J = 1.1, 7.9, 1H), 4.60 (d, J = 6.1, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 169.1, 141.0, 139.8, 138.6, 138.3, 135.1, 132.5, 131.8, 131.6, 131.3, 129.8, 129.3, 129.1, 128.4, 127.2, 44.6, 21.8. IR (KBr): 3370 m (NH), 3060 w, 3033 w, 1641 s (CONH), 1514 s (CONH), 1493 m, 1463 w m, 1434 w, 1303 w, 1261 w, 812 m, 748 m, 740 m, 697 m. Anal. calcd for $C_{21}H_{19}NOS$: C, 75.64; H, 5.74; N, 4.20. Found: C, 75.44; H, 5.82; N, 3.99.



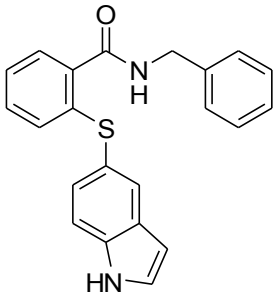
***N*-Benzyl-2-(4-formylphenylthio)benzamide** (3b). Thioether **3b** was obtained as a yellowish solid after column chromatography (grad. hexane/Et_2O/acetone 10:1:2-5:1:2) in 84 % yield (290 mg). M.p. 95.5-96 °C (EtOH/hexan). ^{1}H NMR (400 MHz, Acetone-d_6): δ 9.97 (s, 1H), 8.02 (bs, 1H), 7.81 (ddd, J = 2.2, 0.5, 8.1, 2H), 7.67 – 7.62 (m, 1H), 7.50 – 7.46 (m, 3H), 7.38 (ddd, J = 2.2, 0.5, 8.1, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.19 (m, 3H), 4.54 (d, J = 6.1, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 192.5, 168.9, 147.1, 142.7, 140.8, 136.2, 136.0, 132.2, 132.0, 131.4, 130.5, 130.1, 129.9, 129.8, 129.0, 128.3, 44.6. IR ($CHCl_3$): 3304 w (NH), 3028 m, 3012 m, 2835 w, 2741 w, 1699 s (C=O), 1661 s (CONH), 1592 s, 1564 m, 1514 s (CONH), 1463 m, 1456 m, 1388 w, 1302 m, 1285 m, 1170 m, 1082 m, 837 m, 817 m, 699 m. Anal. calcd for $C_{21}H_{17}NO_2S$: C, 72.60; H, 4.93; N, 4.03. Found: C, 72.65; H, 5.02; N, 3.86.



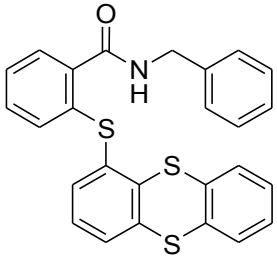
***N*-Benzyl-2-(2-methoxyphenylthio)benzamide** (3c). Thioether **3c** was obtained as a yellowish oil after column chromatography (hexane/Et_2O/acetone 7:1:2) in 64 % yield (220 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.75 (m, 1H), 7.41 (bs, 1H), 7.32 – 7.18 (m, 10H), 6.90 (td, *J* = 1.2, 7.6, 1H), 6.83 (dd, *J* = 1.0, 8.2, 1H), 4.60 (d, *J* = 5.6, 2H), 3.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9, 158.1, 138.3, 137.2, 133.5, 133.2, 133.0, 130.9, 130.1, 129.7, 128.8, 128.1, 127.6, 127.5, 123.3, 121.7, 111.5, 55.8, 44.4. IR ($CHCl_3$): 3358 w (NH), 3011 m, 2840 w, 1653 s (CONH), 1583 m, 1515 m (CONH), 1498 m, 1478 s, 1464 m, 1434 m, 1294 m, 1275 m, 1245 s, 1041 w, 1026 m, 700 m. HR-MS (ESI) *m/z* calcd for $C_{21}H_{20}NO_2S$ 350.12093, found 350.12072.



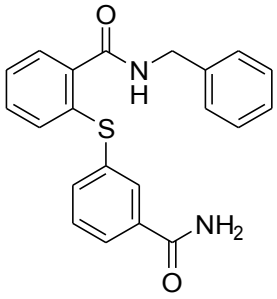
***N*-Benzyl-2-(3-hydroxyphenylthio)benzamide** (3d). Thioether **3d** was obtained as a colorless oil after column chromatography (hexane/Et_2O/acetone 5:1:2) in 93 % yield (310 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.58 (m, 1H), 7.32 – 7.24 (m, 7H), 7.24 – 7.19 (m, 2H), 7.10 (t, *J* = 7.9, 1H), 6.81 (appt, *J* = 2.0, 1H), 6.78 – 6.69 (m, 3H), 4.53 (d, *J* = 5.6, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.6, 157.4, 137.6, 136.8, 135.6, 133.8, 133.0, 131.3, 130.6, 129.3, 129.0, 128.2, 127.9, 127.6, 122.8, 118.2, 115.3, 44.7. IR (KBr): 3402 s (broad) (OH, NH), 1637 s (CONH), 1584 s, 1530 m (CONH), 1496 m, 1455 m, 1435 s, 1302 m, 1254 m, 1220 m, 995 w, 888 m, 747 m, 696 m. HR-MS (ESI) *m/z* calcd for $C_{20}H_{18}NO_2S$ 336.10528, found 336.10530.



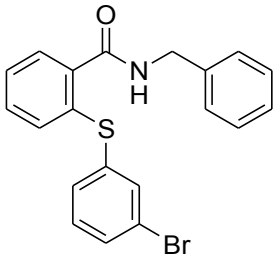
2-(1H-Indol-5-ylthio)-*N*-benzylbenzamide (3e). Thioether **3e** was obtained as a white solid after column chromatography (grad. hexane/Et_2O/acetone 7:1:2-5:1:2) in 82 % yield (295 mg). M.p. 127-128.5 °C (EtOH/hexan). ^{1}H NMR (400 MHz, Acetone-d_6): δ 10.52 (bs, 1H), 8.04 (bs, 1H), 7.85 – 7.78 (m, 1H), 7.55 – 7.50 (m, 2H), 7.50 – 7.45 (m, 2H), 7.42 (appt, J = 2.7, 1H), 7.37 – 7.31 (m, 2H), 7.28 – 7.21 (m, 2H), 7.17 (td, J = 1.6, 7.5, 1H), 7.11 (td, J = 1.3, 7.4, 1H), 6.84 (dd, J = 1.1, 7.9, 1H), 6.54 – 6.51 (m, 1H), 4.64 (d, J = 6.0, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 169.2, 141.5, 141.1, 137.9, 136.5, 131.4, 130.9, 129.8, 129.5, 129.5, 129.3, 129.1, 129.0, 128.3, 127.6, 125.9, 123.5, 114.2, 103.2, 44.6. IR ($CHCl_3$): 3438 w (NH), 3317 w (NH), 3011 m, 1655 s (CONH), 1588 m, 1512 s (CONH), 1455 m, 1433 m, 1412 m, 1247 m, 889 m, 700 m. Anal. calcd for $C_{22}H_{18}N_2OS$: C, 73.72; H, 5.06; N, 7.81. Found: C, 73.28; H, 4.95; N, 7.59.



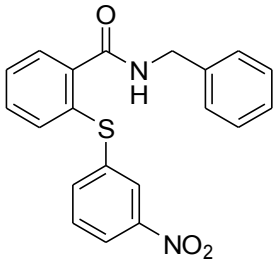
***N*-Benzyl-2-(thianthren-1-ylthio)benzamide** (3f). Thioether **3f** was obtained as a yellow solid after column chromatography (grad. hexane/Et_2O/acetone 10:1:2-7:1:2) in 79 % yield (235 mg). M.p. (fast decomp.) >53 °C. ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.15 (bs, 1H), 7.70 – 7.65 (m, 1H), 7.57 – 7.50 (m, 2H), 7.46-7.41 (m, 2H), 7.37 – 7.26 (m, 9H), 7.21 (apptt, J = 7.3, 1H), 7.05 – 6.98 (m, 1H), 4.63 (d, J = 6.1, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 169.0, 141.0, 140.0, 139.6, 137.6, 137.1, 136.8, 136.4, 136.0, 134.0, 132.4, 130.0, 130.4, 129.9, 129.8, 129.8, 129.8, 129.7, 129.6, 129.5, 129.0, 128.4, 128.3, 44.6. IR (KBr): 3330 w (NH), 3058 w, 1639 s (CONH), 1587 m, 1527 m (CONH), 1452 m, 1430 m, 1308 m, 1255 m, 748 s, 702 m. HR-MS (ESI) *m/z* calcd for $C_{26}H_{20}NOS_3$ 458.07015, found 458.07012.



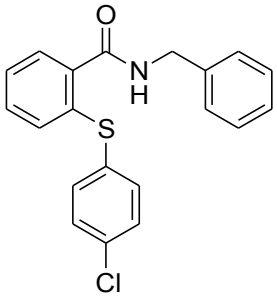
***N*-Benzyl-2-(3-carbamoylphenylthio)benzamide** (3g). Thioether **3g** was obtained as a white solid after column chromatography (grad. hexane/Et_2O/acetone 5:2:4-3:1:2) in 85 % yield (230 mg). M.p. 151-152 °C (EtOH/hexan). ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.08 (bs, 1H), 7.98 (t, J = 1.6, 1H), 7.89 (dt, J = 1.5, 7.8, 1H), 7.62 – 7.51 (m, 3H), 7.47 (td, J = 0.3, 7.8, 1H), 7.43 – 7.39 (m, 2H), 7.36 – 7.27 (m, 4H), 7.24 (apptt, J =7.3, 1H), 7.13 (m, 1H), 6.72 (bs, 1H), 4.59 (d, J = 6.0, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 169.0, 168.7, 140.9, 139.4, 137.3, 137.3, 136.7, 136.5, 132.8, 132.6, 131.8, 130.9, 129.8, 129.5, 129.1, 128.4, 128.3, 128.1, 44.6. IR (KBr): 3402 m (NH_2), 3305 m (NH), 3226 m (NH_2), 1669 m ($CONH_2$), 1647 s (CONH), 1608 m, 1565 m, 1535 m (CONH), 1422 w (C-N), 1385 w, 1305 w, 757 w, 697 w. Anal. calcd for $C_{21}H_{18}N_2O_2S$: C, 69.59; H, 5.01; N, 7.73. Found: C, 69.63; H, 5.23; N, 7.35.



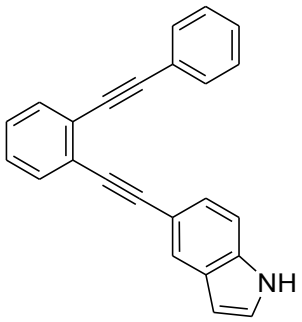
***N*-Benzyl-2-(3-bromophenylthio)benzamide** (3h). Thioether **3h** was obtained as a white solid after column chromatography (hexane/Et_2O/acetone 7:1:2) in 81 % yield (160 mg). M.p. 105-106 °C (EtOH). ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.06 (bs, 1H), 7.62 – 7.58 (m, 1H), 7.51 (td, J = 0.3, 1.8,, 1H), 7.48 (ddd, J = 0.5, 1.4, 7.6, 1H), 7.42 – 7.34 (m, 5H), 7.34 – 7.28 (m, 3H), 7.27 – 7.21 (m, 2H), 4.58 (d, J = 6.0, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 169.0, 140.9, 140.6, 140.3, 135.2, 135.1, 133.9, 132.5, 131.9, 131.8, 131.7, 129.8, 129.6, 129.1, 128.9, 128.4, 124.0, 44.6. IR ($CHCl_3$): 3435 w (NH), 3332 w (NH), 3013 m, 1658 s ($CONH_2$), 1575 m, 1561 m, 1513 s (CONH), 1461 s, 1434 w, 1290 w, 1250 w, 1068 w, 700 m. HR-MS (EI) *m/z* calcd for $C_{20}H_{16}NOSBr$ 397.0136, found 397.0142.



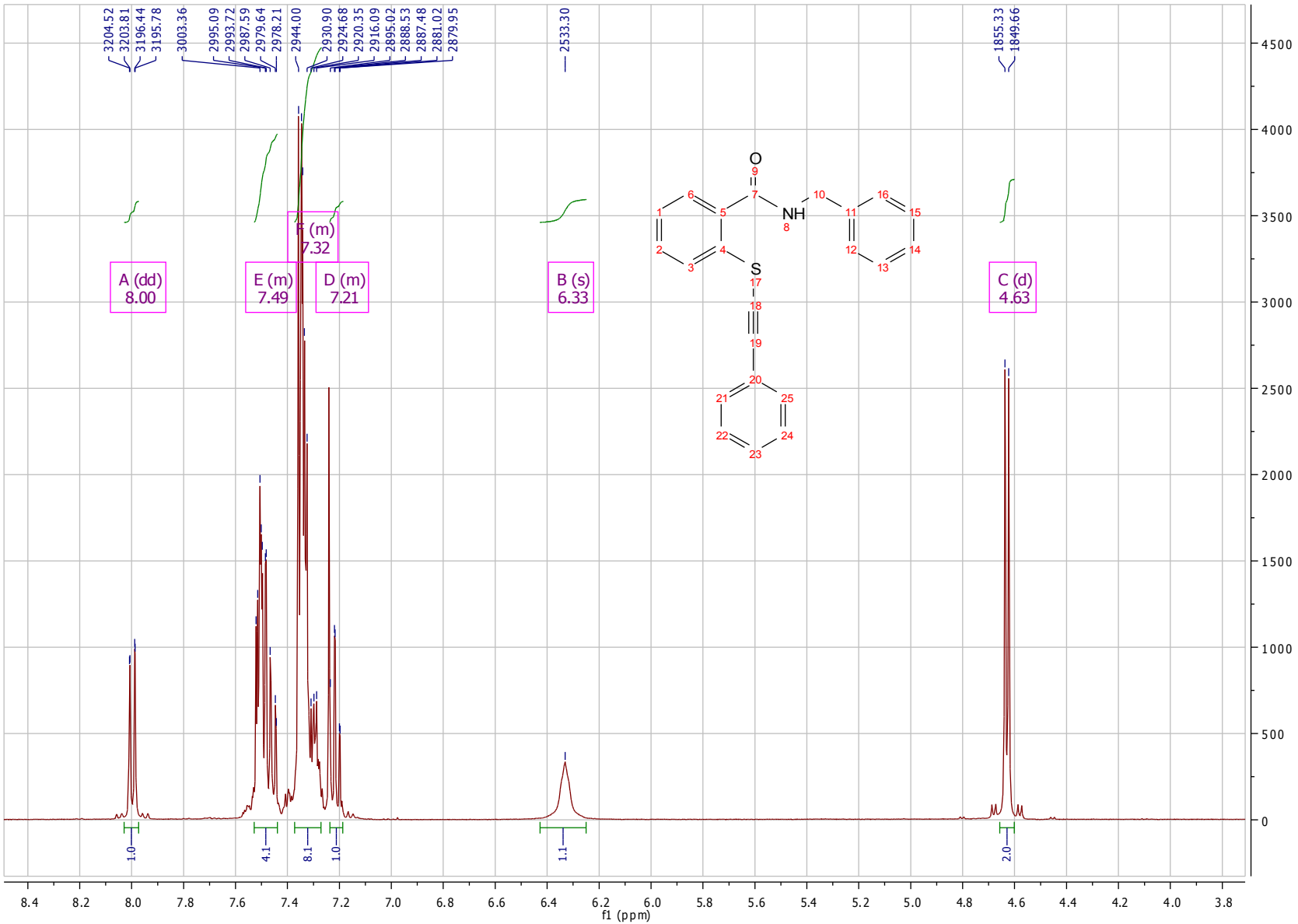
***N*-Benzyl-2-(3-nitrophenylthio)benzamide** (3i). Thioether **3i** was obtained as a white solid after column chromatography (hexane/Et_2O/acetone 7:1:2) in 82 % yield (115 mg). M.p. 137.5-138 °C (EtOH/hexan). ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.15 – 8.03 (m, 3H), 7.71 (ddd, J = 0.6, 1.1, 7.8, 1H), 7.67 – 7.59 (m, 2H), 7.48 – 7.35 (m, 5H), 7.29 (m, 2H), 7.23 (apptt, J = 7.3, 1H), 4.56 (d, J = 6.0, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 168.9, 150.4, 141.6, 141.0, 140.8, 137.8, 134.9, 133.5, 132.1, 131.8, 129.8, 129.8, 129.7, 129.1, 128.4, 126.0, 123.1, 44.6. IR (KBr): 3323 s (NH), 2974 m, 2894 w, 1633 m ($CONH_2$), 1586 w, 1535 s (NO_2), 1524 s (CONH), 1463 w, 1433 s, 1348 s (NO_2), 1310 m, 1164 w, 1086 m, 1050 m, 876 w, 732 m, 699 m, 676 m. Anal. calcd for $C_{20}H_{16}N_2O_3S$: C, 65.92; H, 4.43; N, 7.69. Found: C, 65.79; H, 4.44; N, 7.46.



***N*-Benzyl-2-(4-chlorophenylthio)benzamide** (3j). Thioether **3j** was obtained as a white solid after column chromatography (hexane/Et_2O/acetone 9:1:2) in 78 % yield (230 mg). M.p. 137.5-138 °C (EtOH/hexan). ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.04 (bs, 1H), 7.59 (ddd, J = 0.5, 1.8, 7.3, 1H), 7.43 – 7.28 (m, 10H), 7.24 (apptt, J = 7.3, 1H), 7.17 (ddd, J = 0.5, 1.3, 7.8, 1H), 4.58 (d, J = 6.0, 2H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 169.0, 140.9, 139.8, 136.3, 136.1, 135.2, 134.7, 133.0, 131.9, 130.9, 129.8, 129.5, 129.1, 128.4, 128.3, 44.6. IR (CHCl3): 3436 w (NH), 3332 w (NH), 3012 m, 1657 s ($CONH_2$), 1588 w, 1513 s (CONH), 1476 s, 1462 m, 1457 m, 1434 m, 1390 w, 1287 m, 1250 m, 1155 w, 1094 s, 825 m, 700 m, 669 s. Anal. calcd for $C_{20}H_{16}ClNOS$: C, 67.88; H, 4.56; N, 3.96. Found: C, 67.92; H, 4.44; N, 3.88.



5-((2-(Phenylethynyl)phenyl)ethynyl)-1*H*-indole (4). Alkyne **2e** (100 mg; 0.34 mmol) and one tablet of the palladium catalyst (palladium(II) acetate-X-Phos(Pd:P 1:2), loading 1μmol of Pd per tablet) were placed to a Schlenk flask (3 ml) under atmosphere of Ar. A mixture of phenylacetylene (75 μL; 0.68 mmol) and Et_3N (72 μL; 0.51 mmol) in DMA (1 mL) purged with Ar was then added to the schlenk flask and the resulting reaction mixture was stirred for 24 h at 80 °C . Reaction progress was followed by UPLC. The reaction mixture was quenched with ice cooled 5% hydrochloric acid. The quenched reaction mixture was extracted with ethyl acetate (3x). The combined organic extracts were washed with brine (5x), dried over $MgSO_4$. The solvent was removed under reduced pressure and crude product was purified by column chromatography (hexane/Et_2O/acetone 12:1:2). The product was obtained as a orange oil in 65 % yield (70 mg). ^{1}H NMR (400 MHz, Acetone-d_6): δ 10.50 (bs, 1H), 7.89 – 7.87 (m, 1H), 7.67 – 7.59 (m, 4H), 7.50 – 7.34 (m, 8H), 6.53 – 6.49 (m, 1H). ^{13}C NMR (101 MHz, Acetone-d_6): δ 137.8, 133.2, 133.0, 133.0, 130.2, 130.1, 129.9, 129.7, 129.2, 128.1, 127.7, 126.8, 126.3, 125.8, 124.8, 115.0, 113.2, 103.4, 97.5, 94.6, 89.9, 87.0. IR ($CHCl_3$): 3479 s (NH), 3064 w, 3012 m, 2208 m (C-C triple bond), 1618 w, 1600 w, 1592 w, 1495 s, 1418 s, 1444 m, 1414 s, 1344 m, 1303 m, 1083 m, 886 m, 807 m, 726 s, 691 s. HR-MS (EI) *m/z* calcd for $C_{24}H_{15}N$ 317.1204, found 317.1026.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2978.21
2944.00
2930.90
2924.68
2920.35
2916.09
2895.02
2888.53
2887.48
2881.02
2879.95
2533.30
1855.33
1849.66
A (dd)
8.00
E (m)
7.49
F (m)
7.32
D (m)
7.21
B (s)
6.33
C (d)
4.63
O
NH
S
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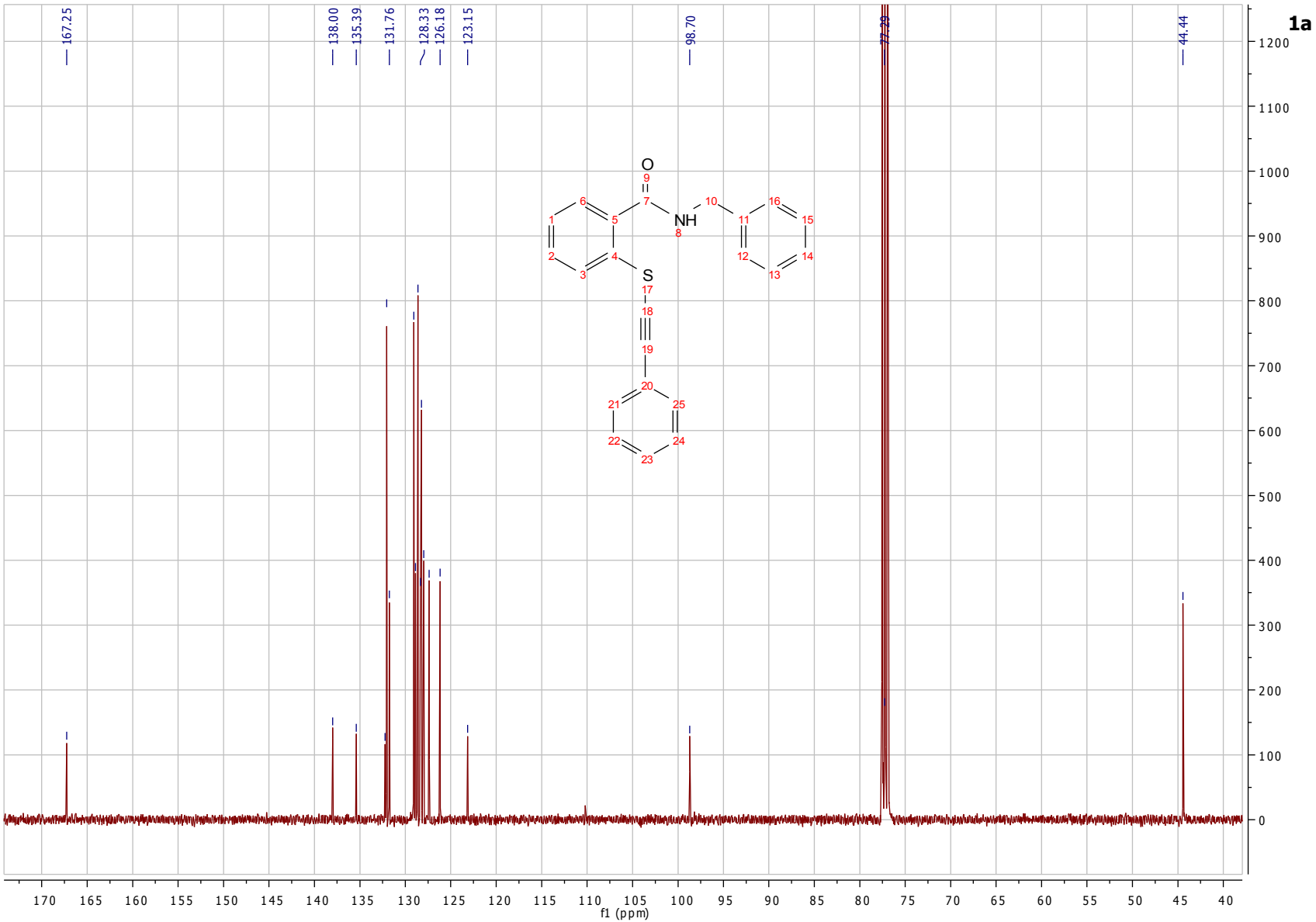
4.1
8.1
1.0
1.1
2.0
f1 (ppm)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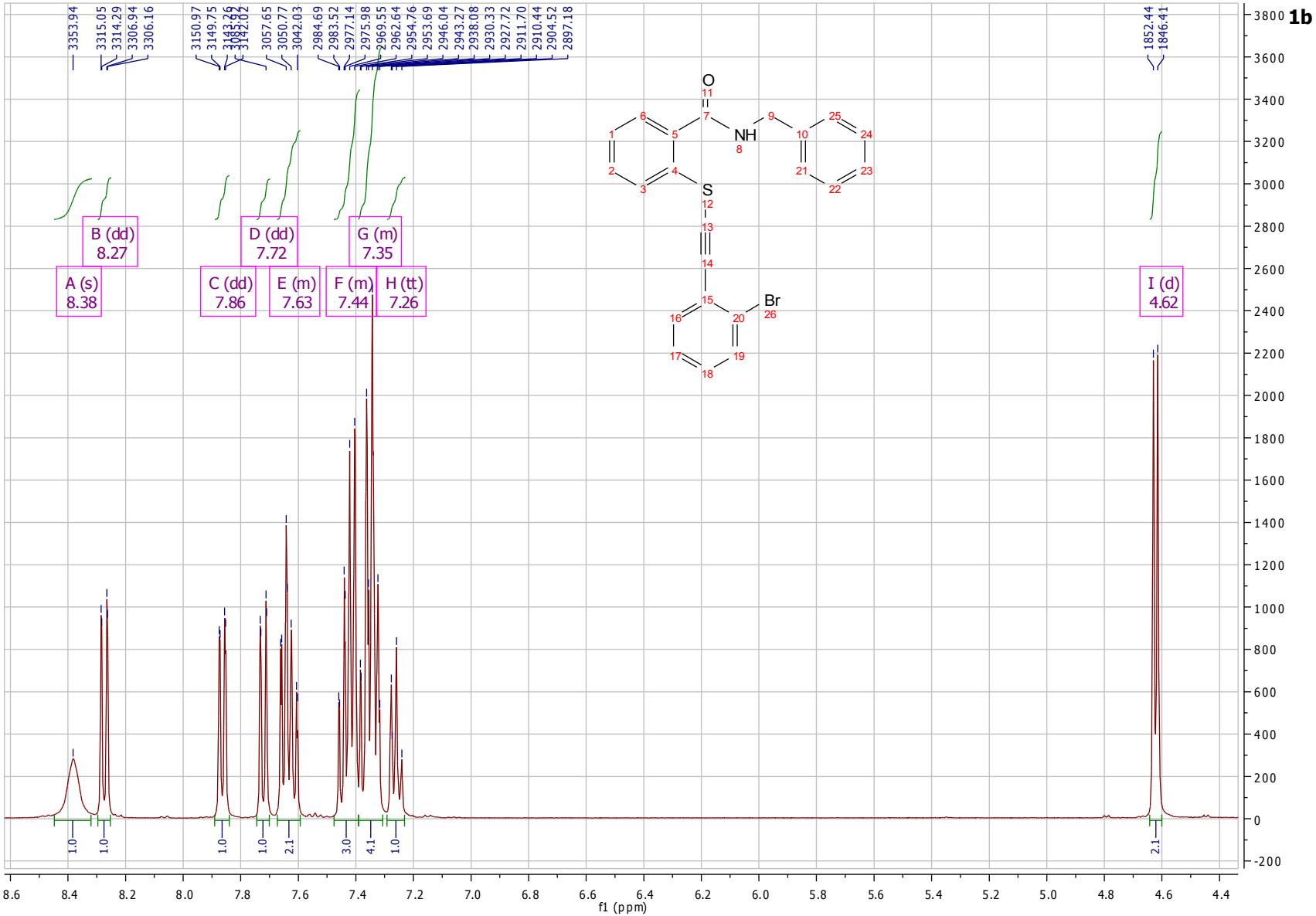
77.20
44.44
O
NH
S
f1 (ppm)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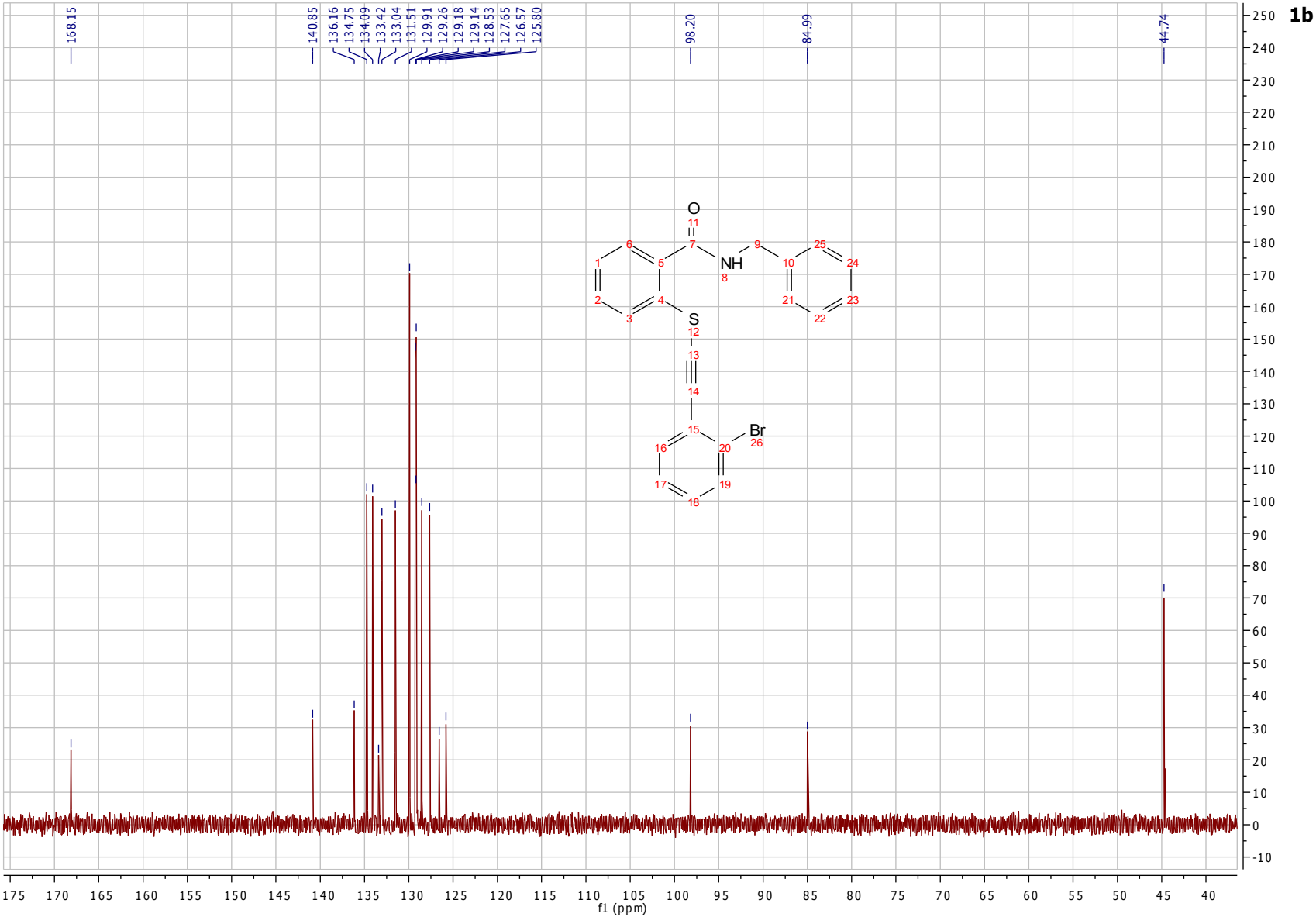
I (d) 4.62
NH
S
Br
O
f1 (ppm)

1b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131.51
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129.26
129.18
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127.65
126.57
125.80
98.20
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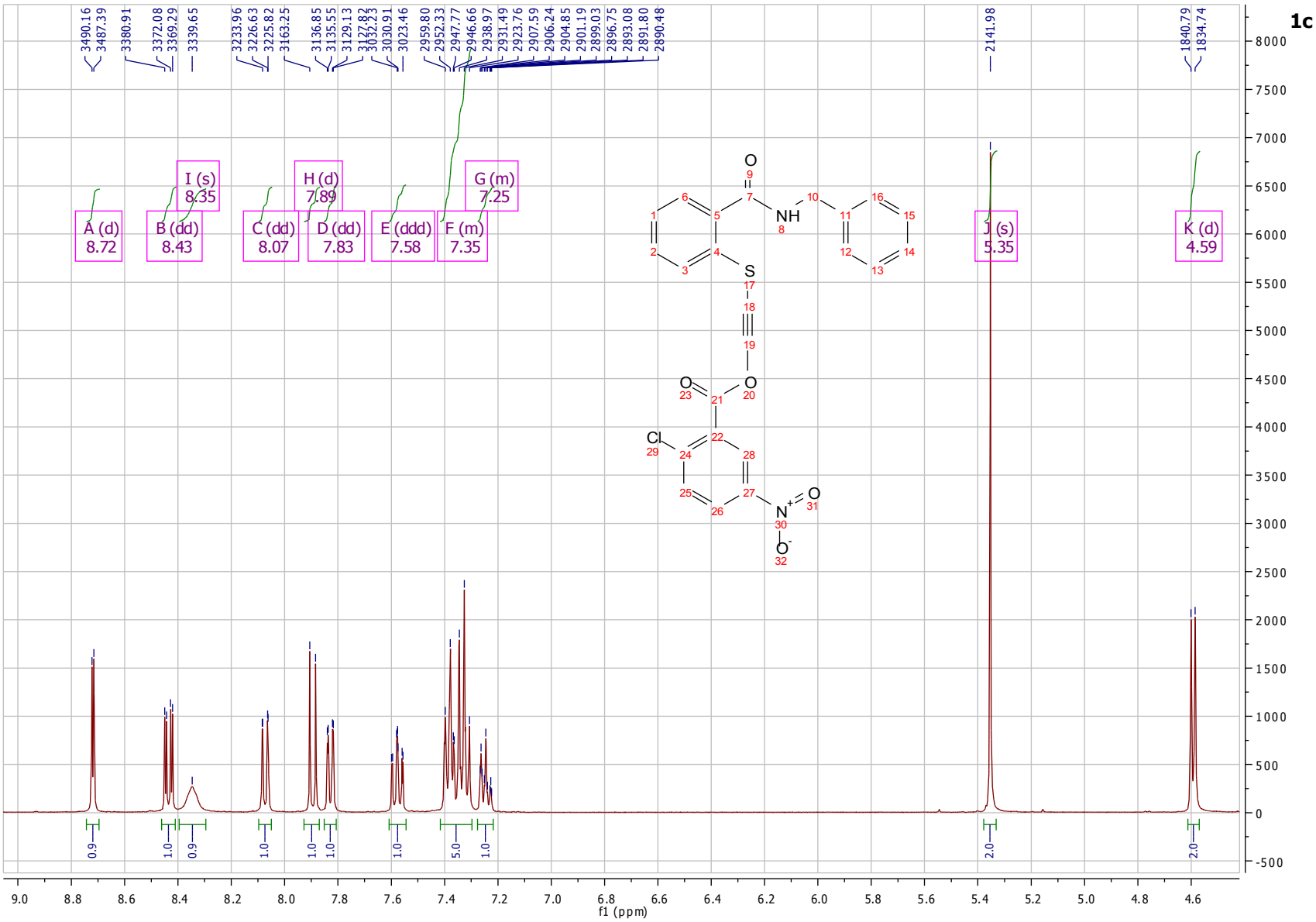
44.74
O
NH
S
Br
f1 (ppm)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C (dd) 8.07
H (d) 7.89
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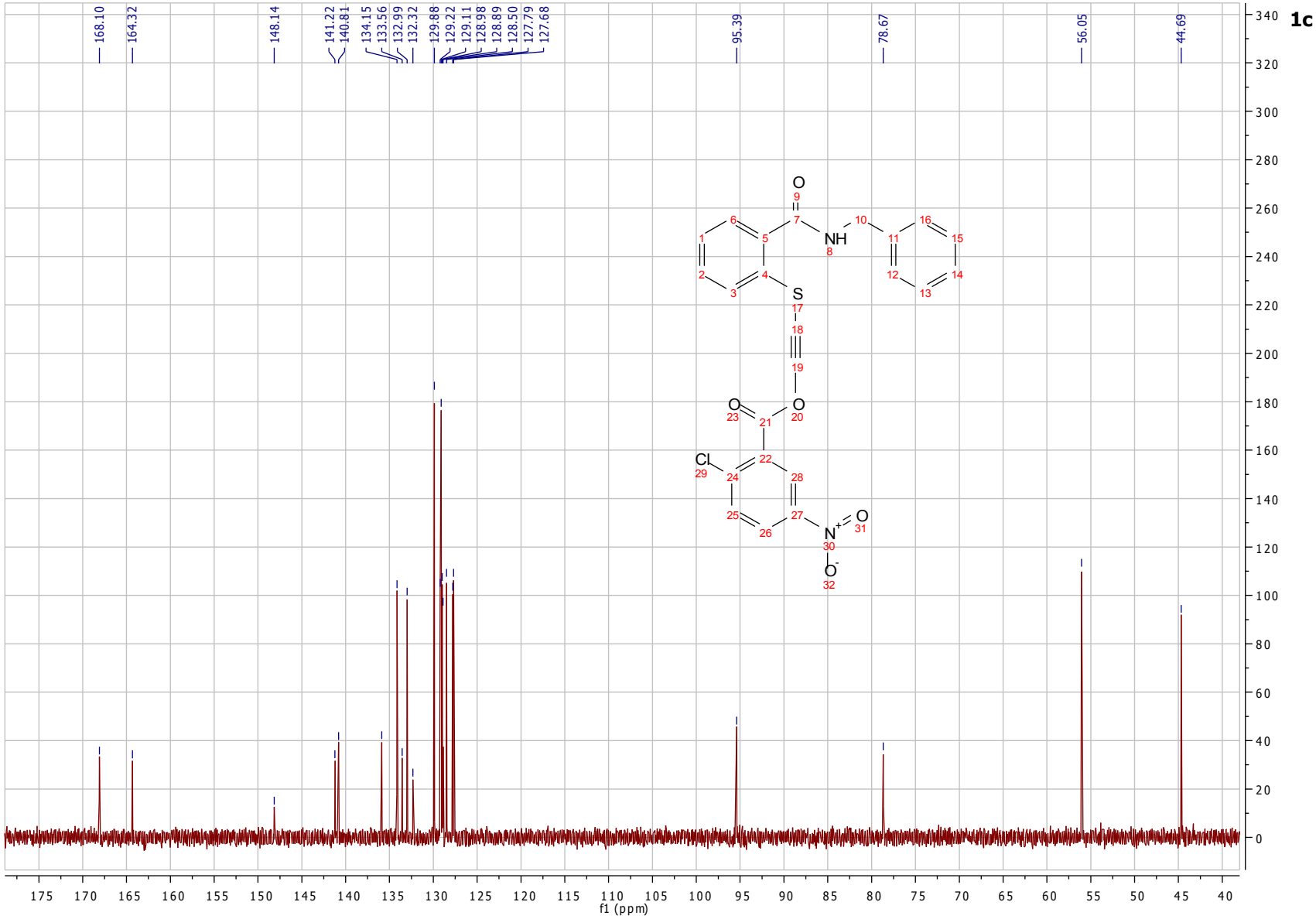
E (ddd) 7.58
G (m) 7.25
F (m) 7.35
J (s) 5.35
K (d) 4.59
f1 (ppm)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134.15
133.56
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132.32
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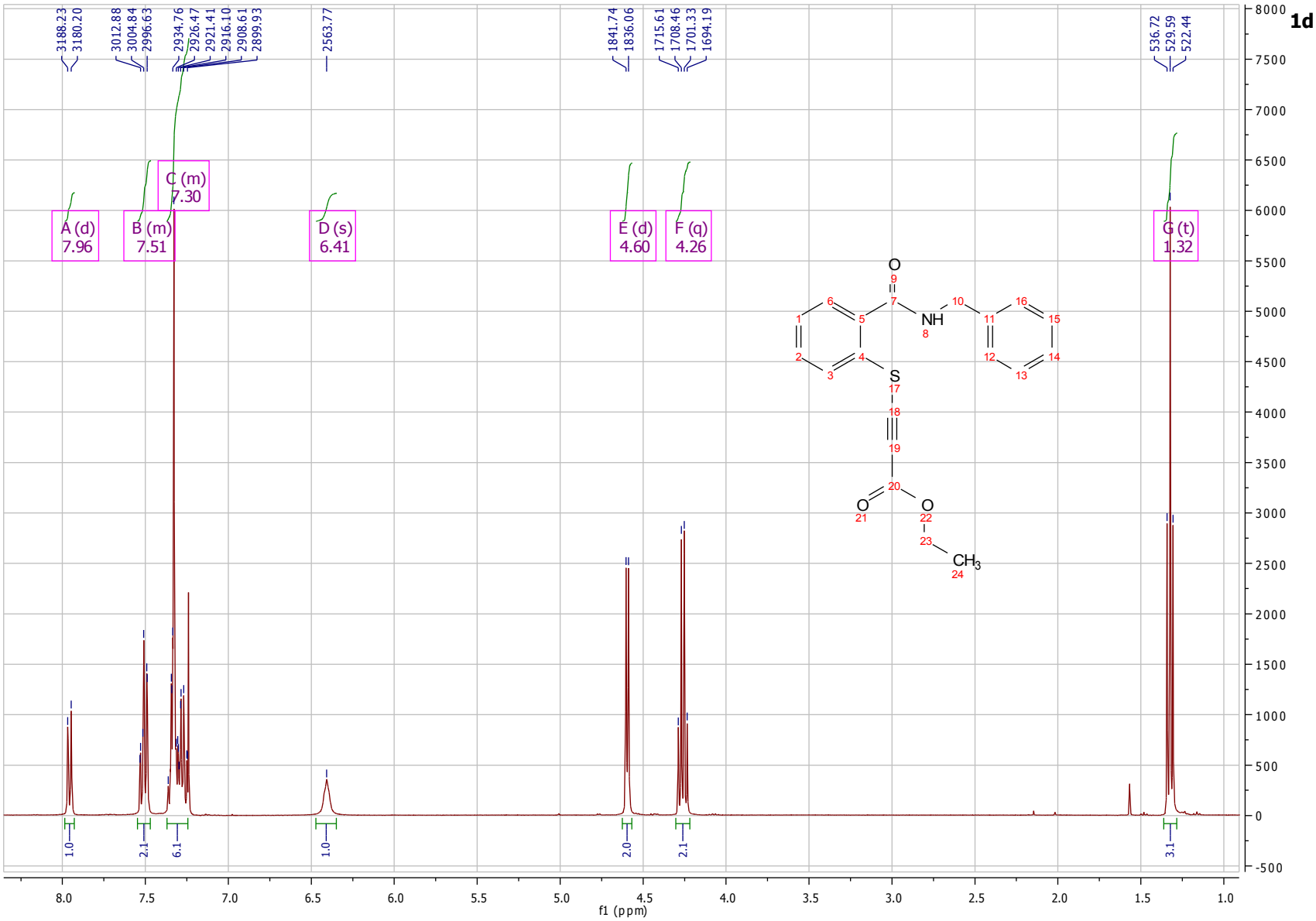
128.89
128.50
127.79
127.68
95.39
78.67
56.05
44.69
f1 (ppm)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3004.84
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2926.47
2921.41
2916.10
2908.61
2899.93
2563.77
1841.74
1836.06
1715.61
1708.46
1701.33
1694.19
536.72
529.59
522.44
A (d) 7.96
B (m) 7.51
C (m) 7.30
D (s) 6.41
E (d) 4.60
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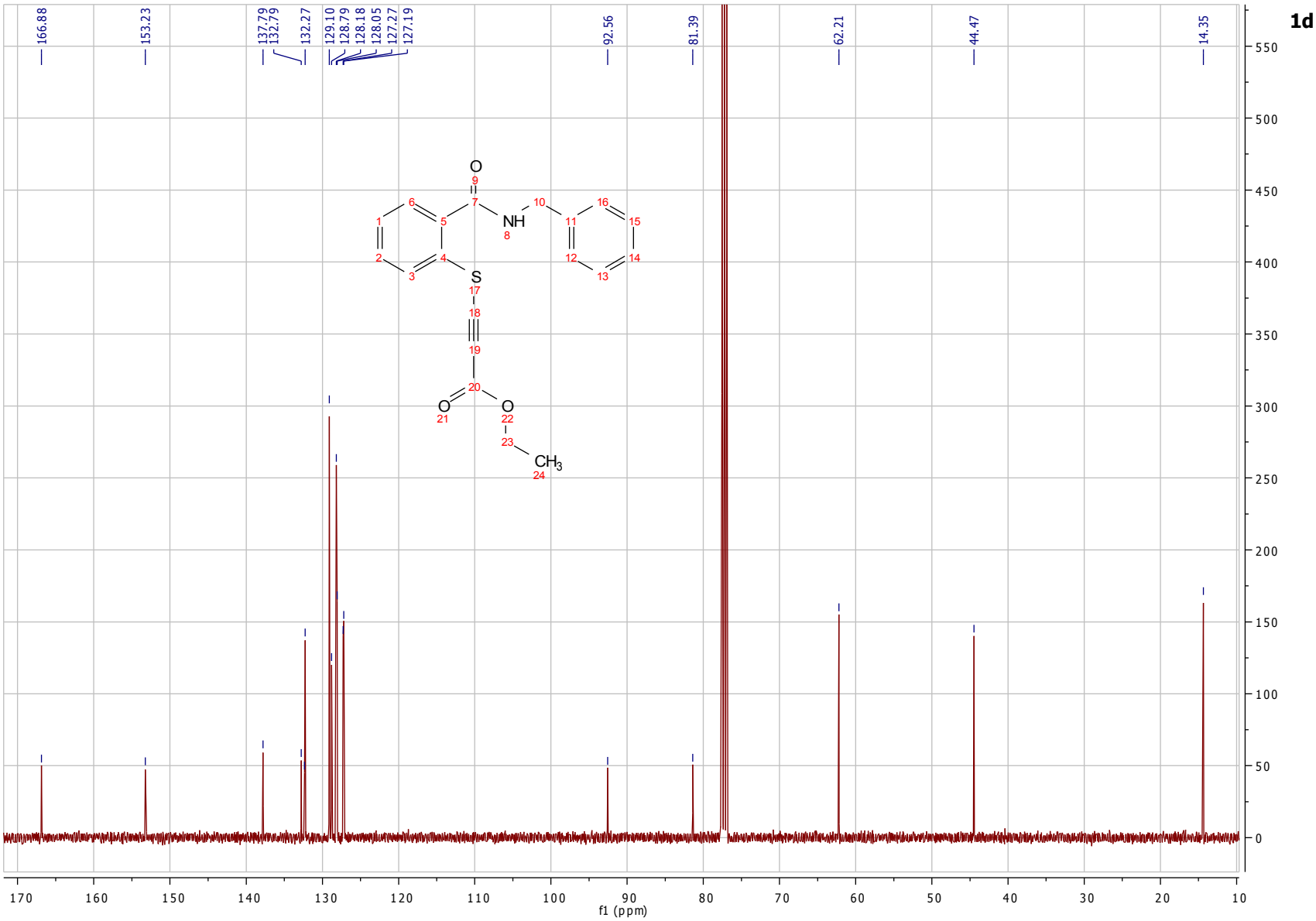
2.1
6.1
1.0
2.0
2.1
3.1
f1 (ppm)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129.10
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128.18
128.05
127.27
127.19
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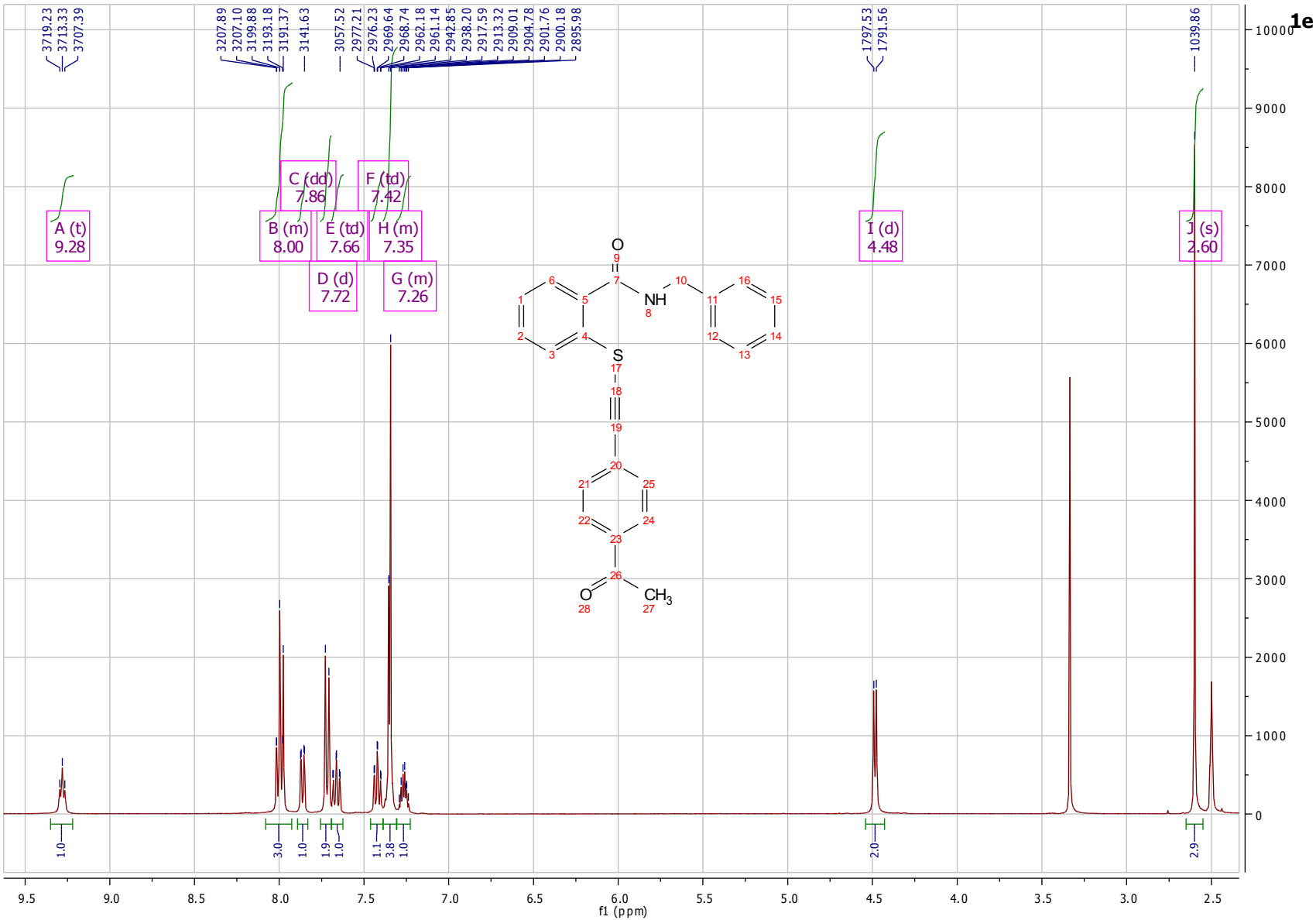
62.21
44.47
14.35
O
9
7
6
1
5
NH
8
10
16
15
11
2
4
12
14
3
13
S
17
18
19
20
O
21
O
22
23
CH3
24
f1 (ppm)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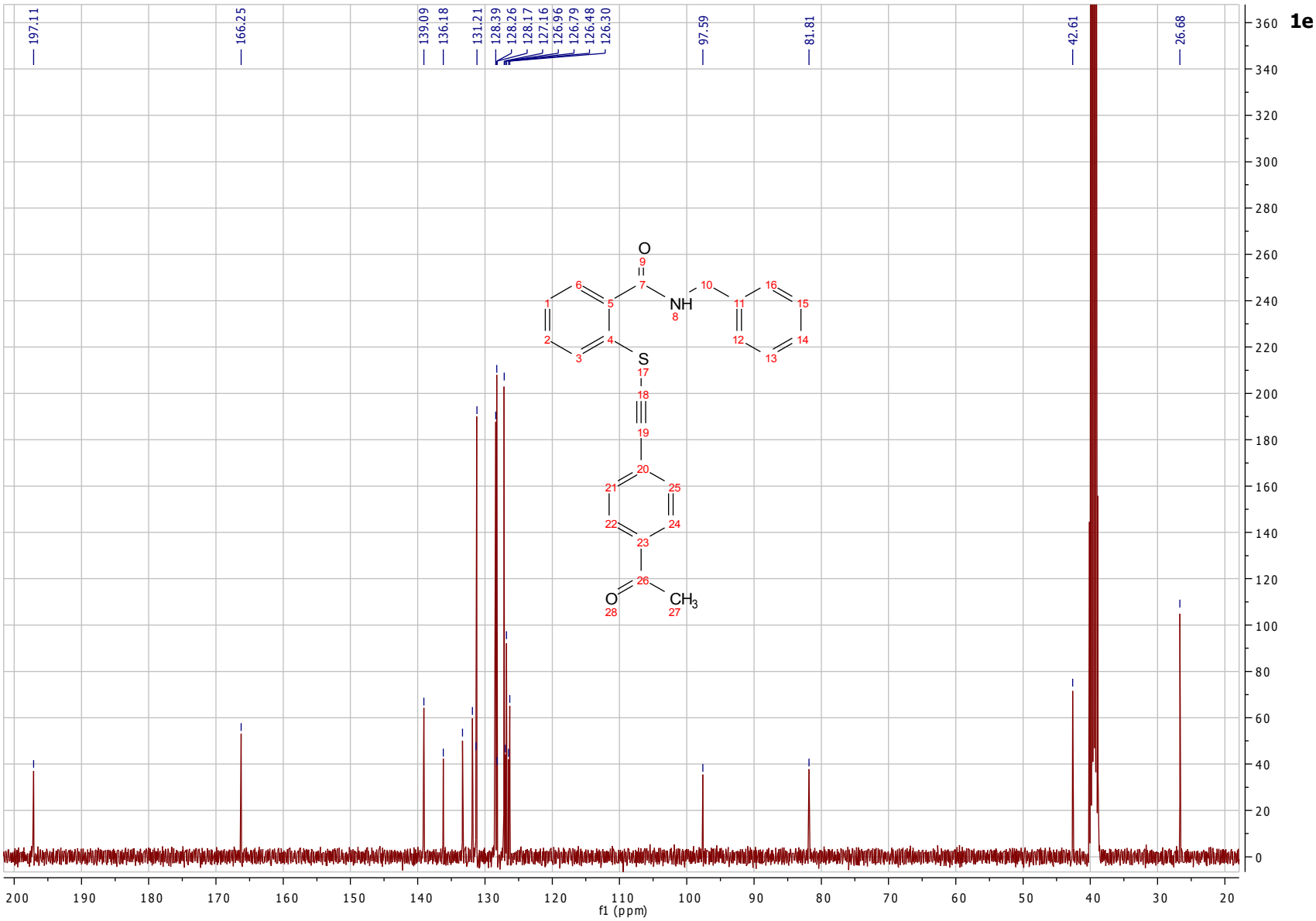
C (dd) 7.86
D (d) 7.72
E (td) 7.66
F (td) 7.42
G (m) 7.26
H (m) 7.35
I (d) 4.48
J (s) 2.60
f1 (ppm)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128.26
128.17
127.16
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126.48
126.30
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81.81
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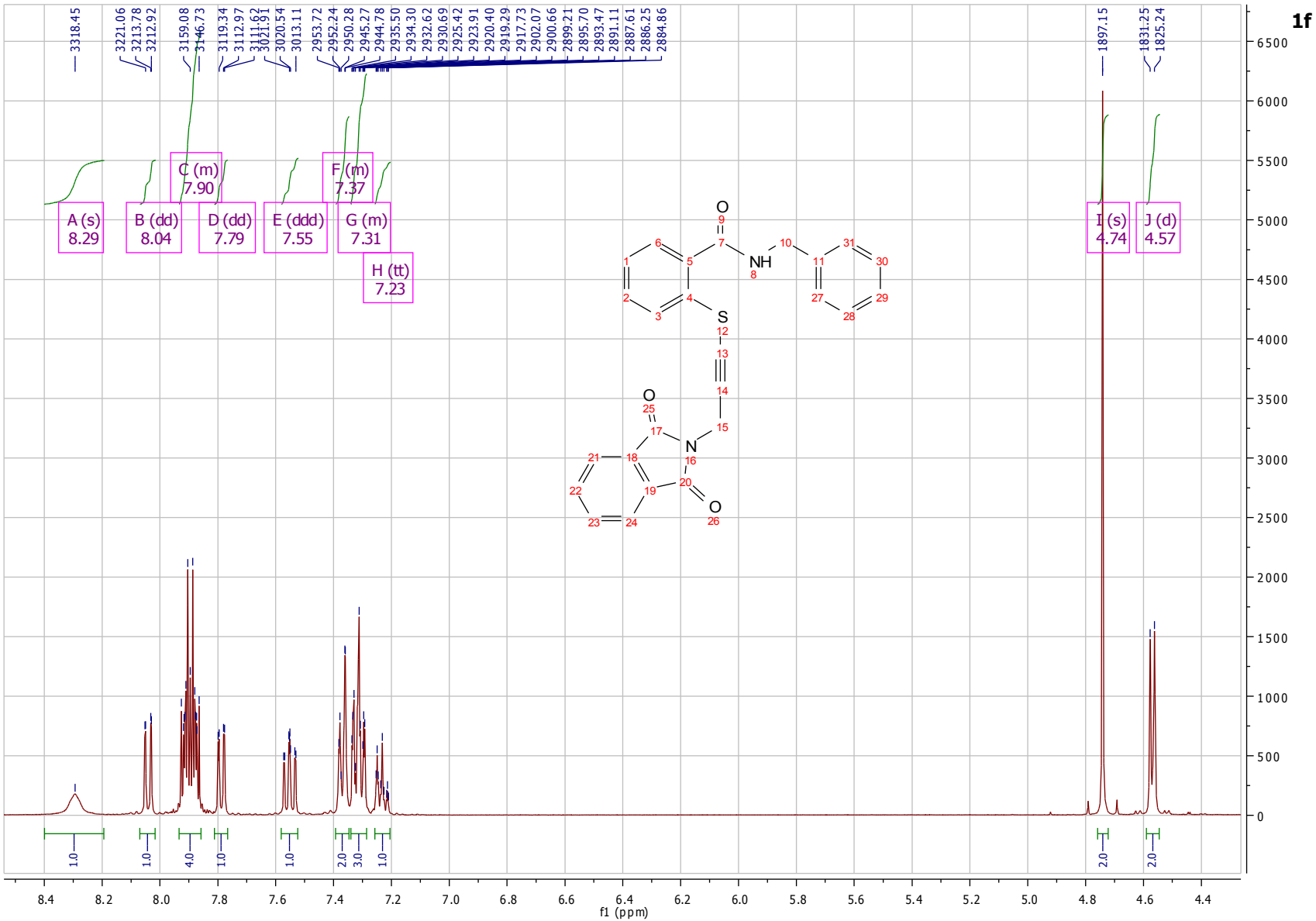
26.68
O
NH
S
CH3
f1 (ppm)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G (m) 7.31
H (tt) 7.23
I (s) 4.74
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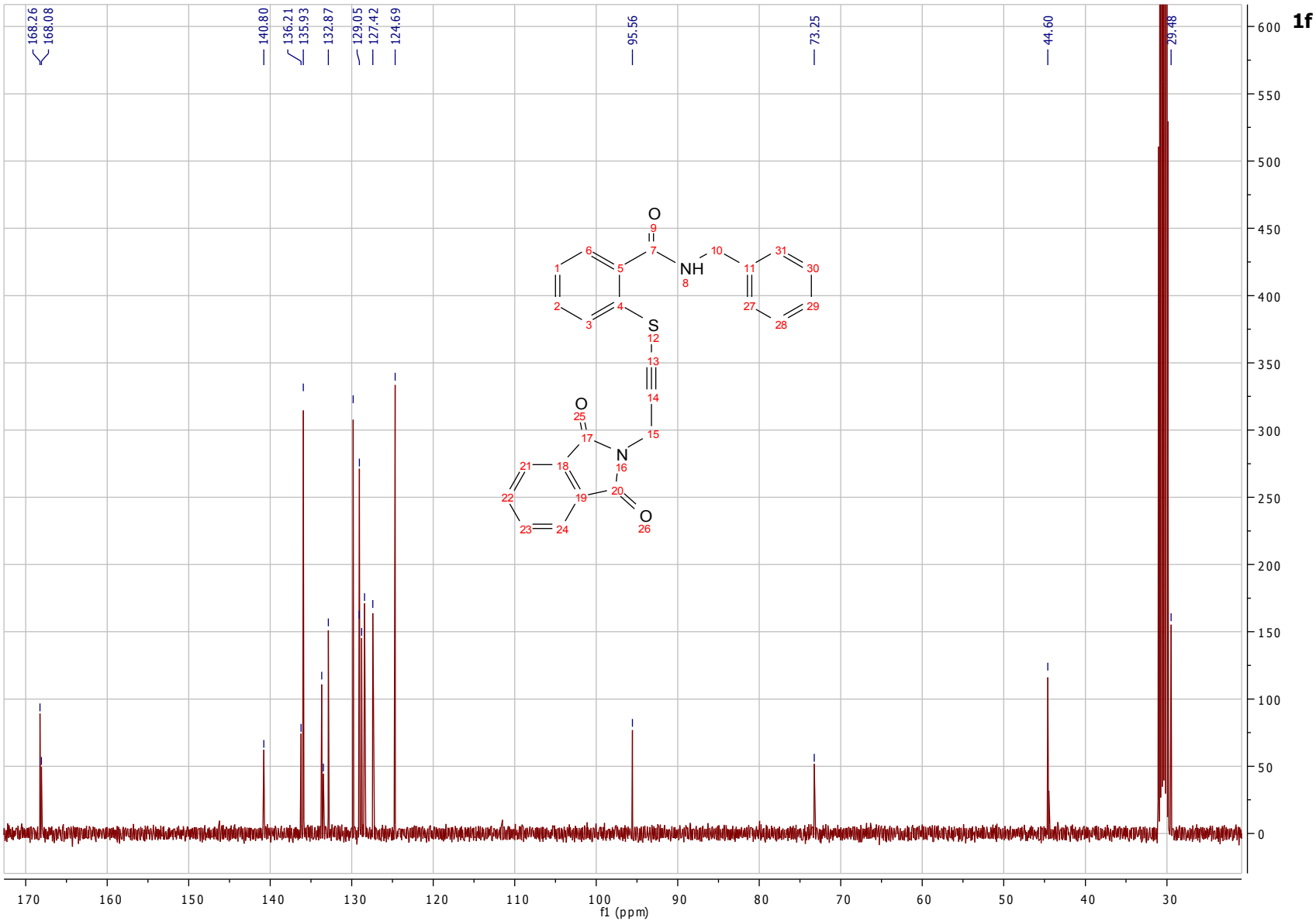
f1 (ppm)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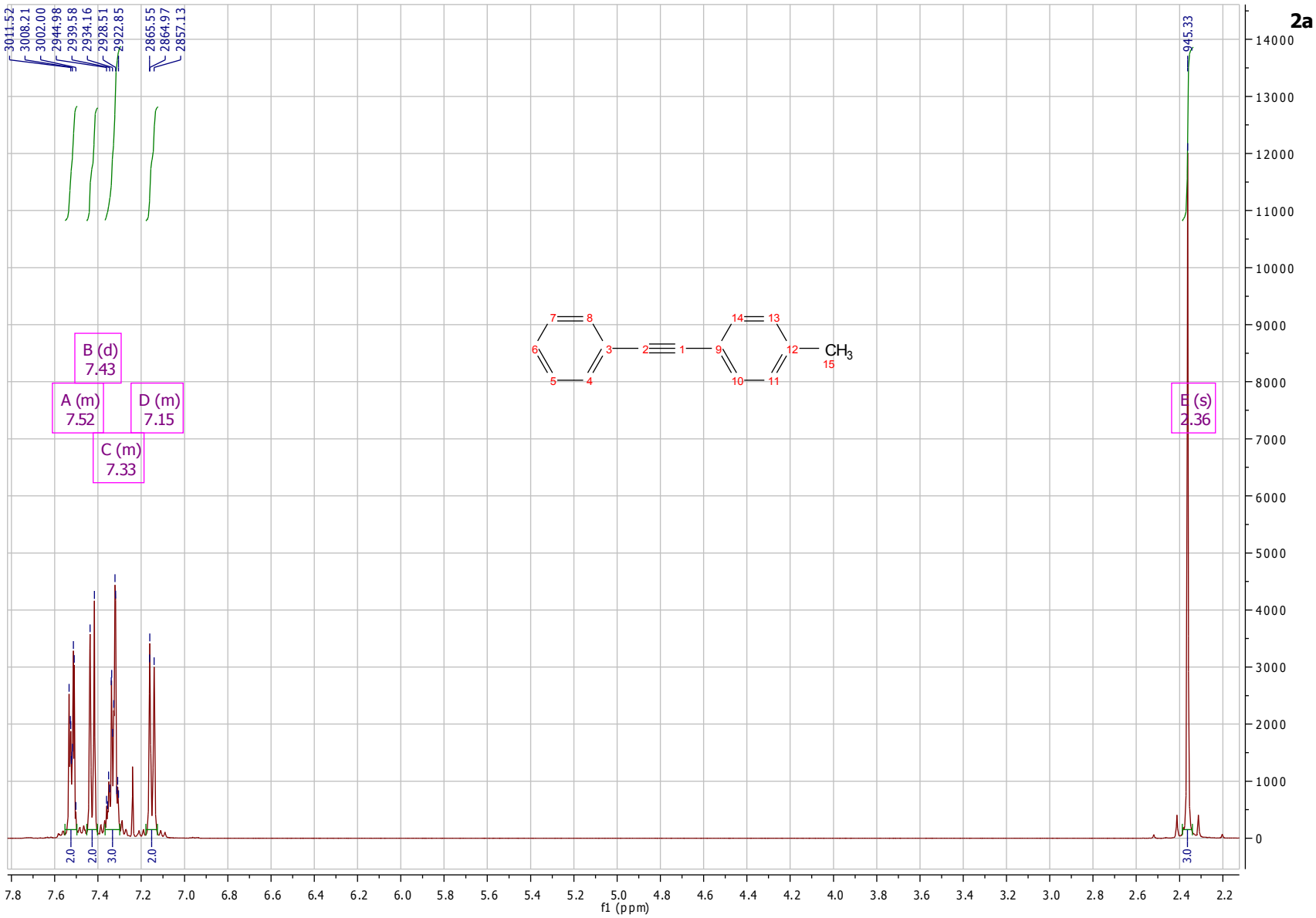
29.48
f1 (ppm)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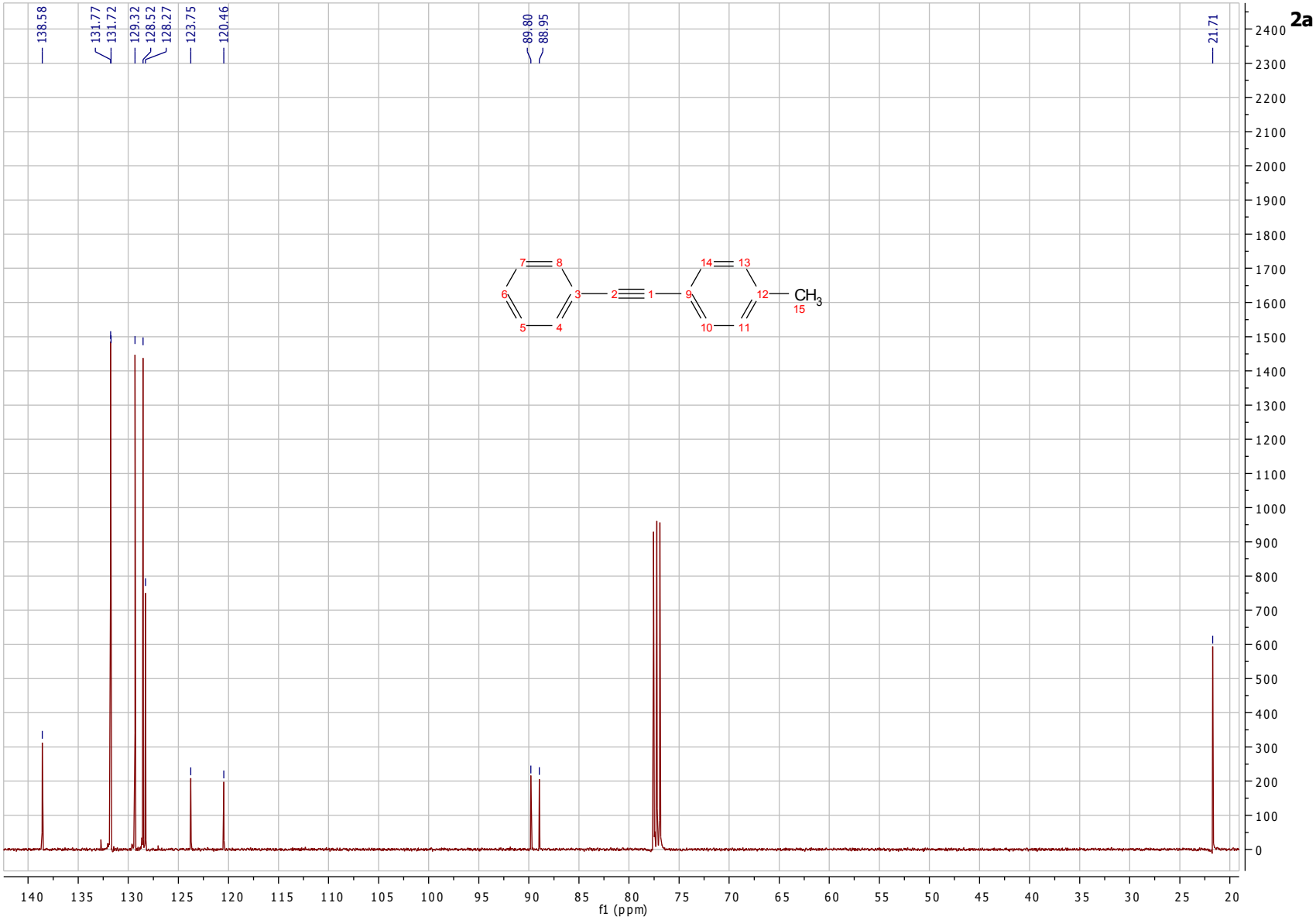
2864.97
2857.13
945.33
B (d)
7.43
A (m)
7.52
D (m)
7.15
C (m)
7.33
E (s)
2.36
CH3
f1 (ppm)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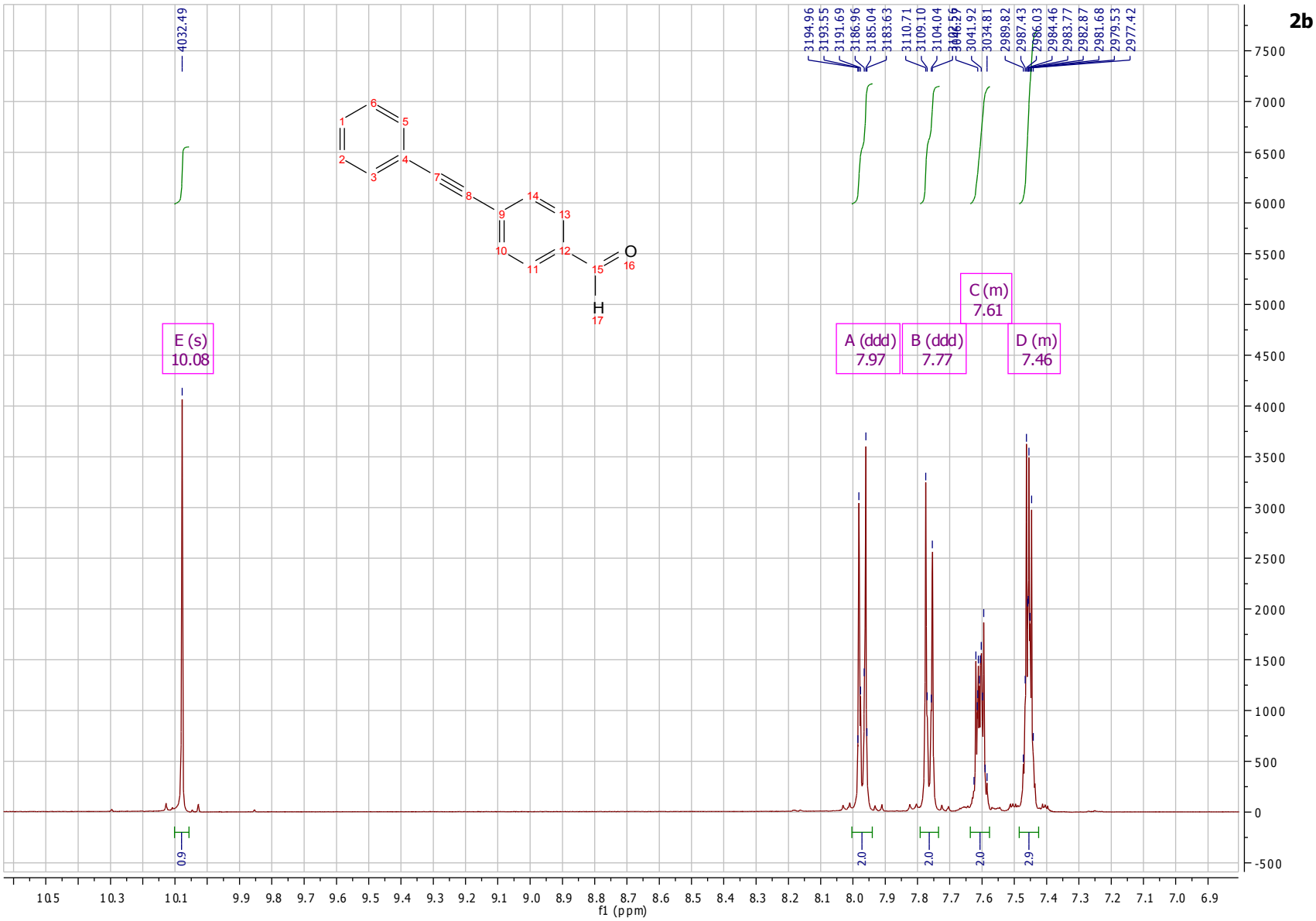
f1 (ppm)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A (ddd)
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C (m)
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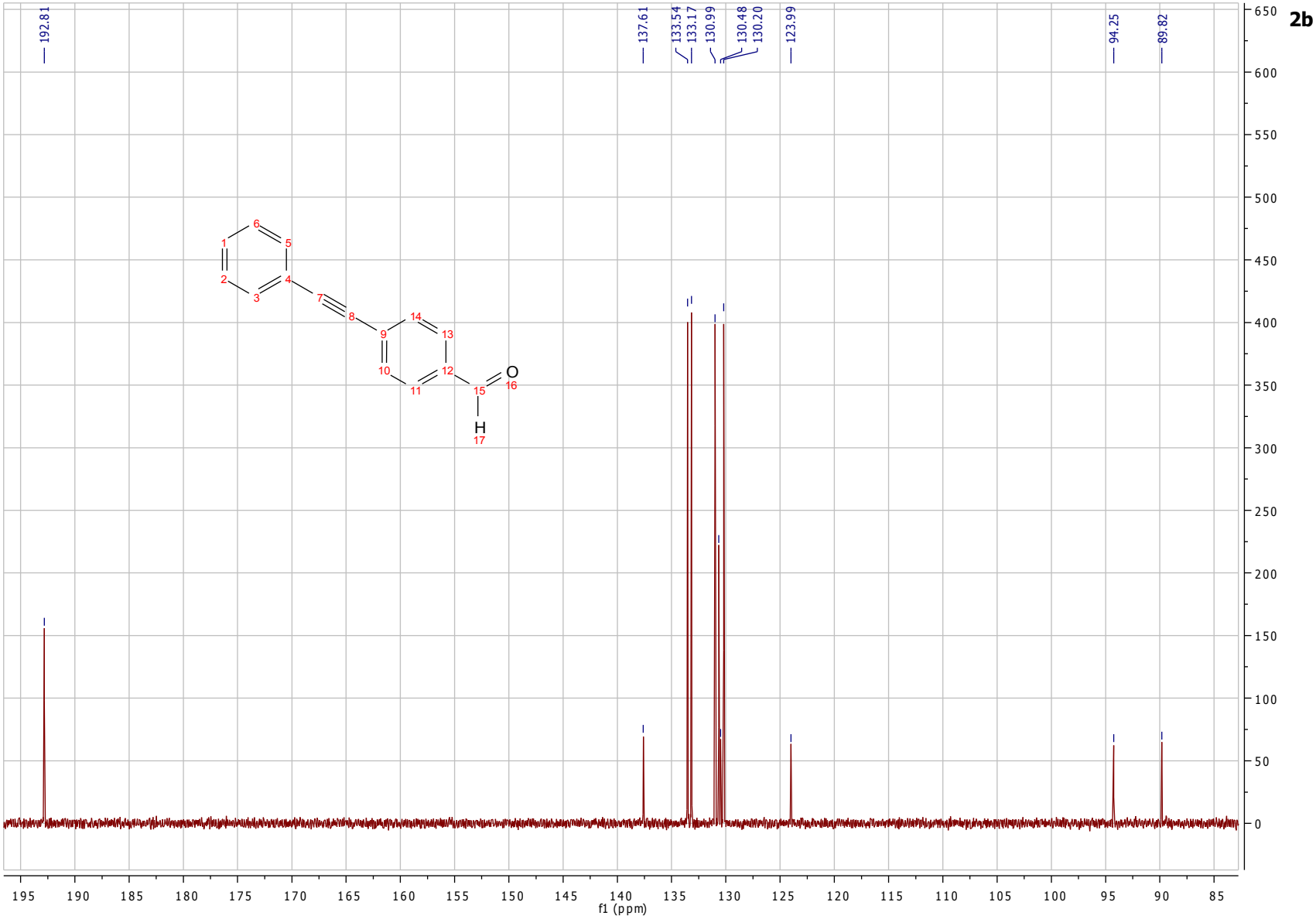
f1 (ppm)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94.25
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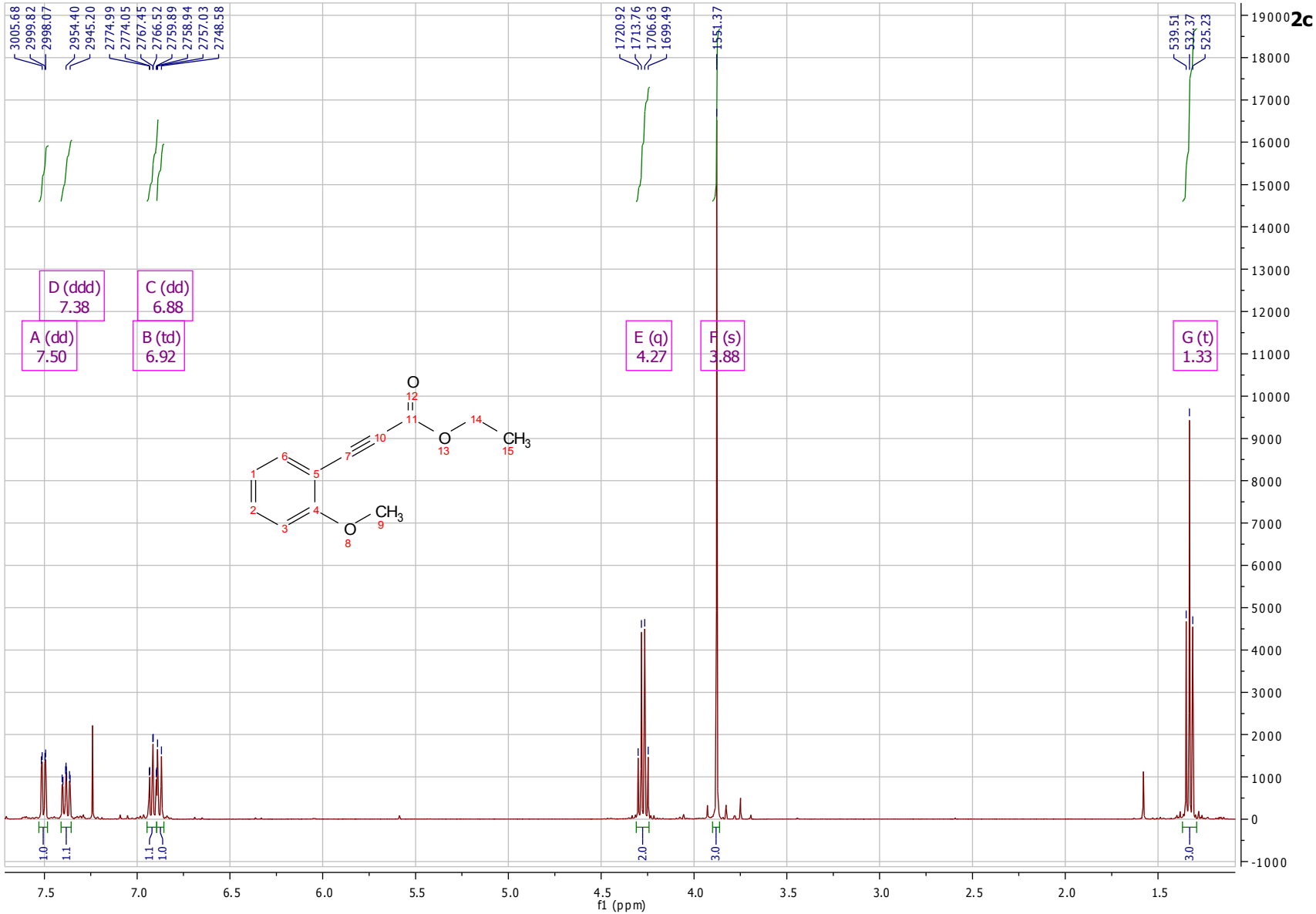
O
H
f1 (ppm)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2757.03
2748.58
1720.92
1713.76
1706.63
1699.49
1551.37
539.51
532.37
525.23
D (ddd) 7.38
C (dd) 6.88
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B (td) 6.92
E (q) 4.27
F (s) 3.88
G (t) 1.33
O
12
11
14
10
O
13
CH3
15
7
6
5
1
2
4
3
CH3
9
O
8
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1.1
1.1
1.0
2.0
3.0
3.0
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
f1 (ppm)
19000
18000
17000
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6000
5000
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1000
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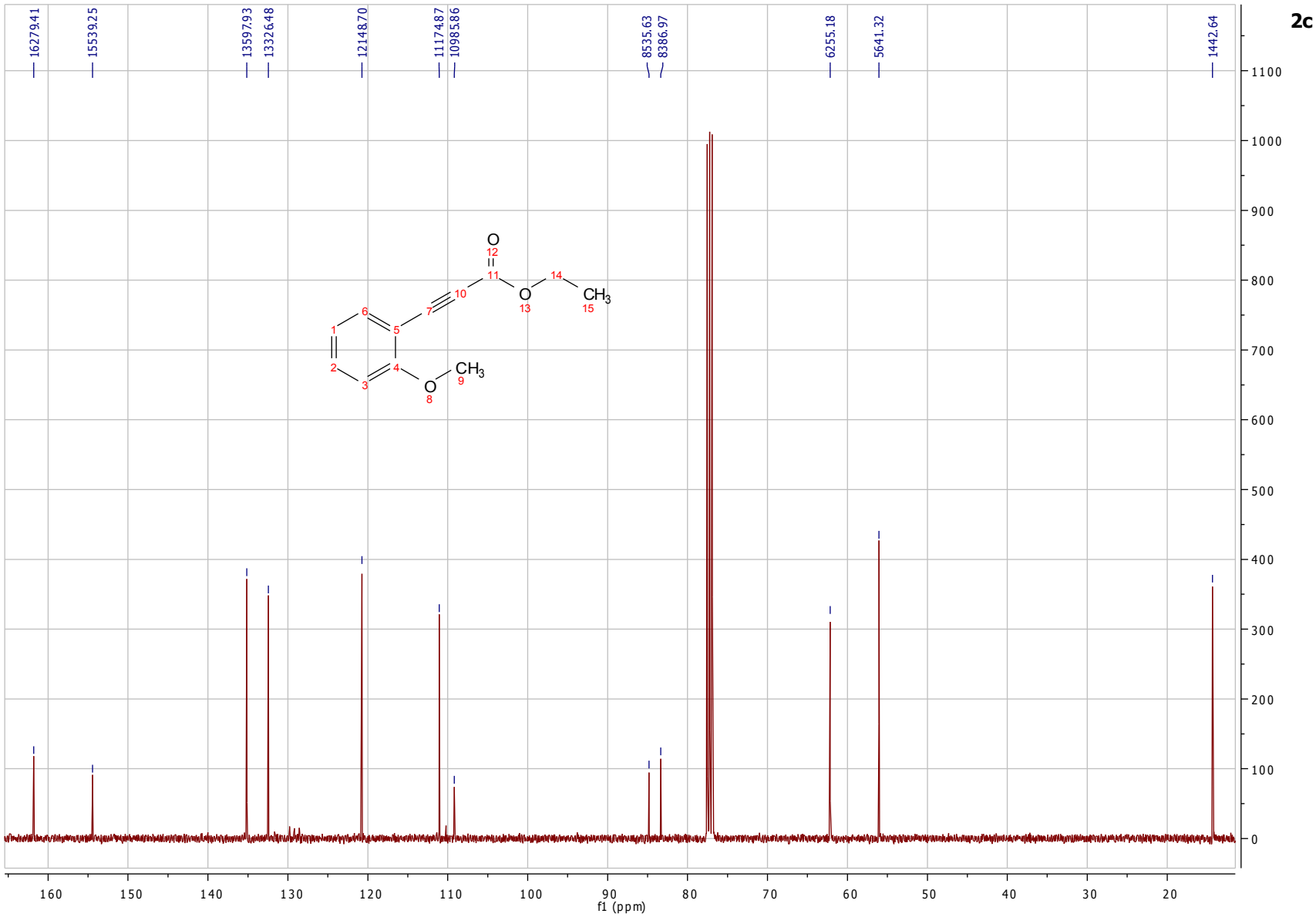
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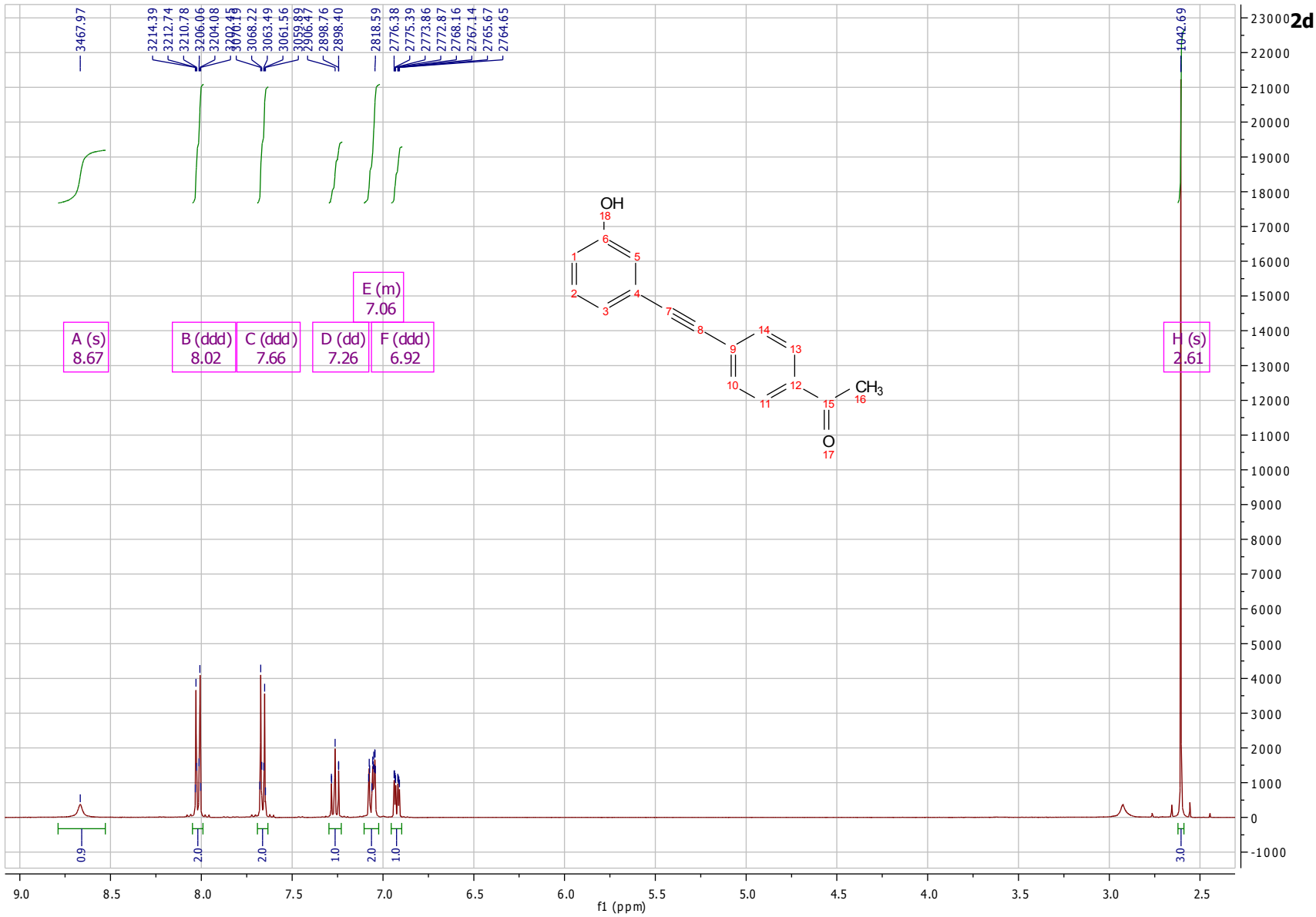
6255.18
5641.32
1442.64
O
12
11
14
10
O
13
CH3
15
7
6
5
1
2
4
3
CH3
9
O
8
1100
1000
900
800
700
600
500
400
300
200
100
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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2898.40
2818.59
2776.38
2775.39
2773.86
2772.87
2768.16
2767.14
2765.67
2764.65
1042.69
A (s) 8.67
B (ddd) 8.02
C (ddd) 7.66
D (dd) 7.26
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F (ddd) 6.92
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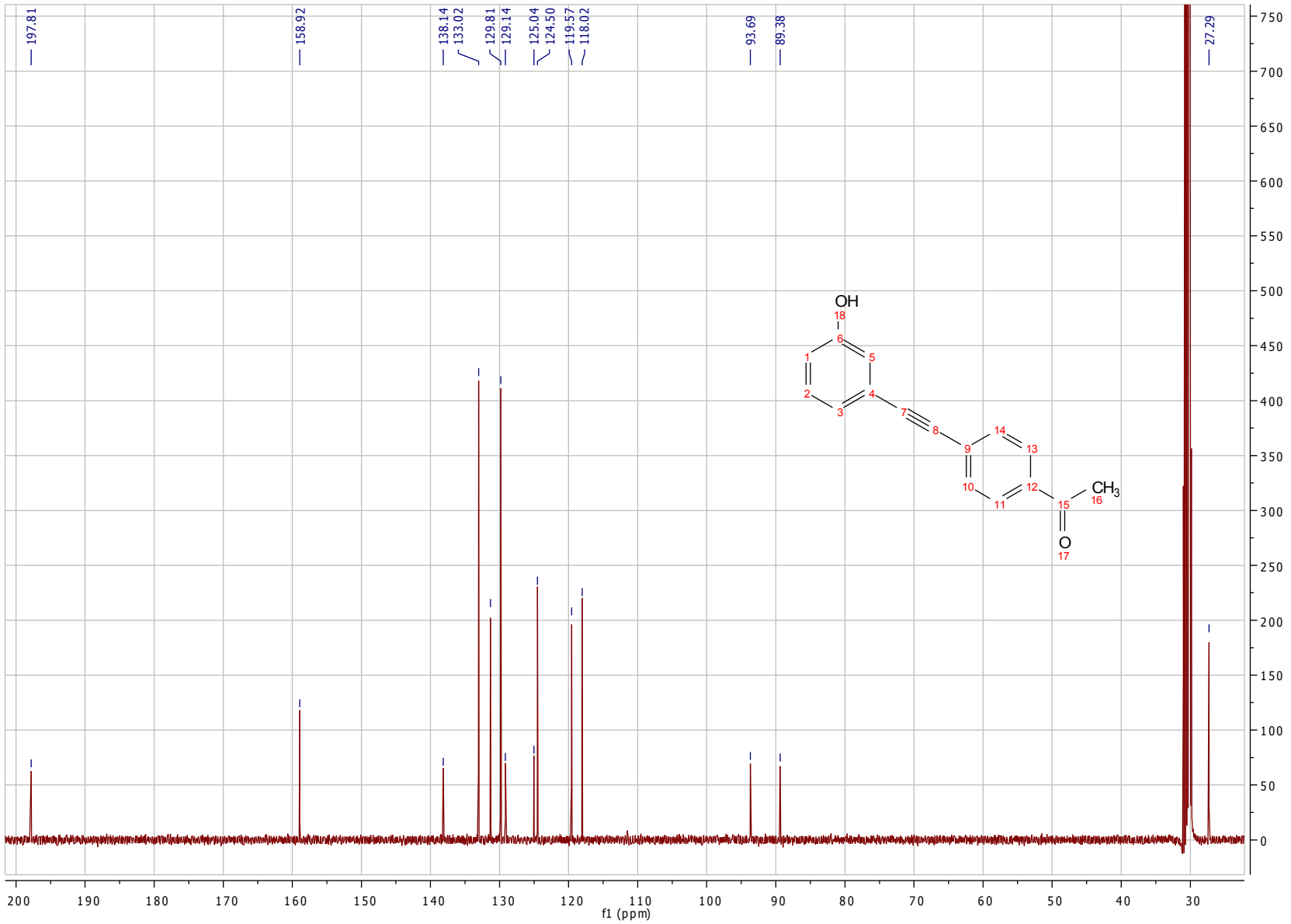
OH
18
CH3
16
O
17
f1 (ppm)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OH
18
6
5
1
2
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4
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8
9
14
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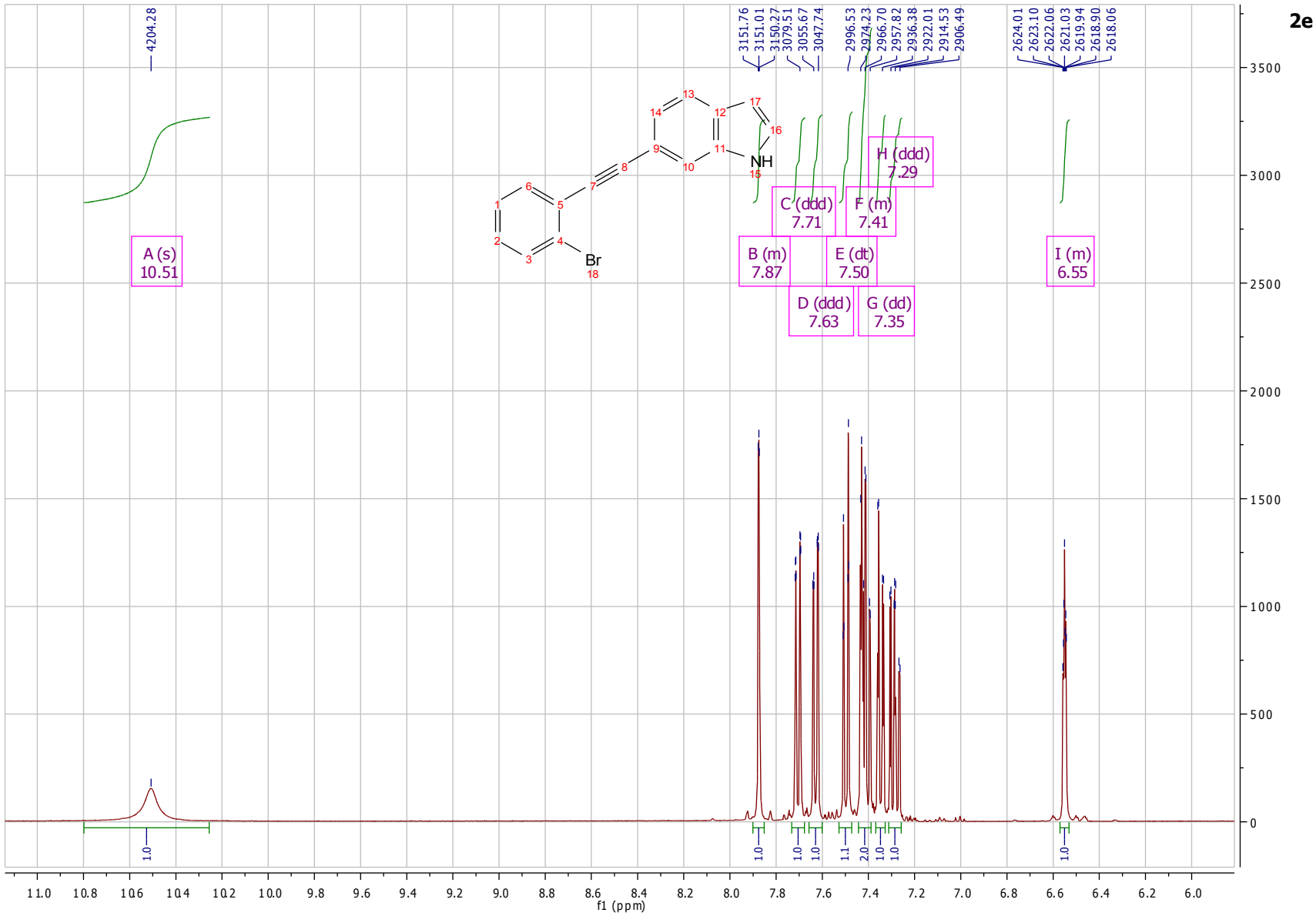
10
11
12
15
CH3
16
O
17
f1 (ppm)

2d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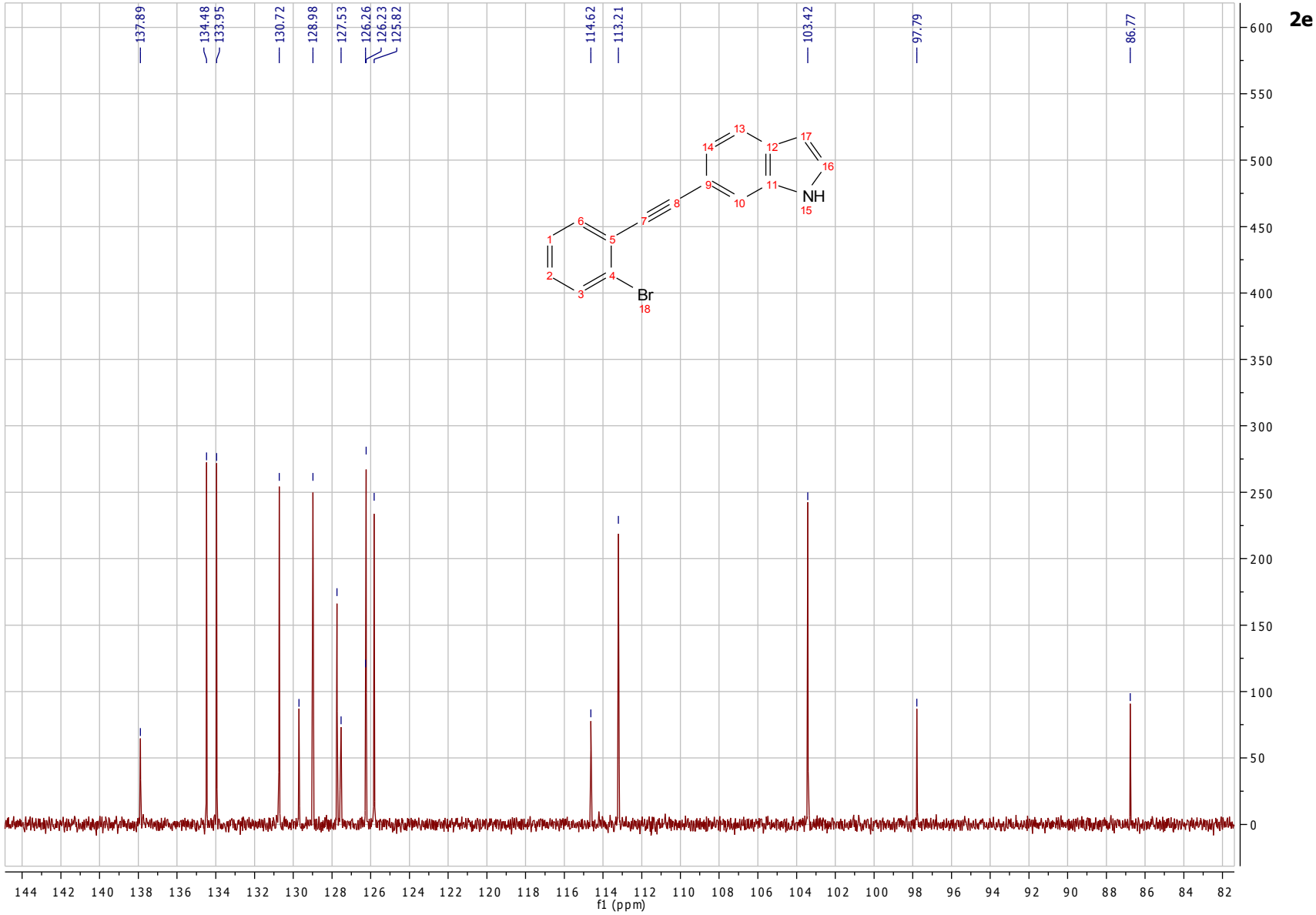
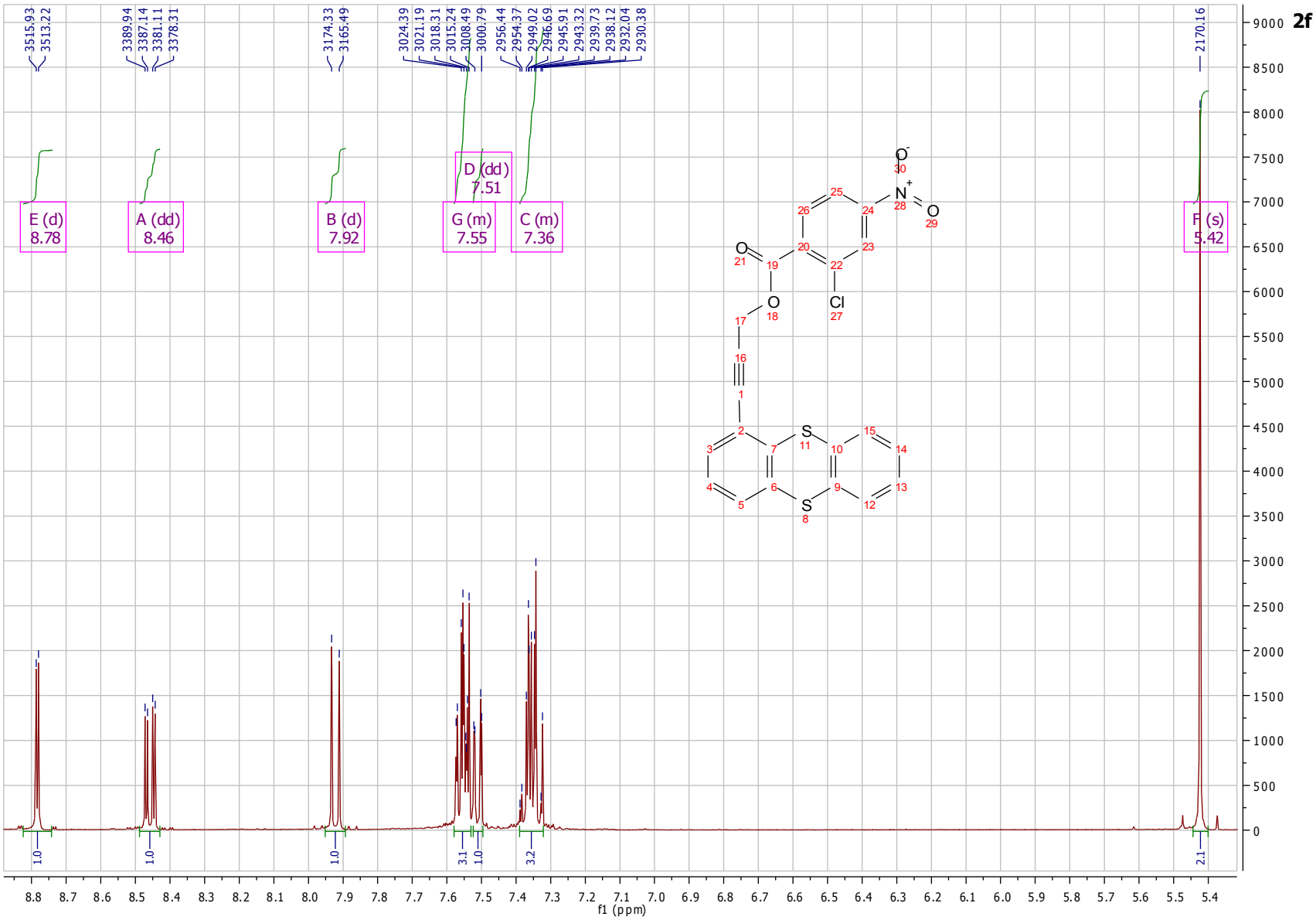
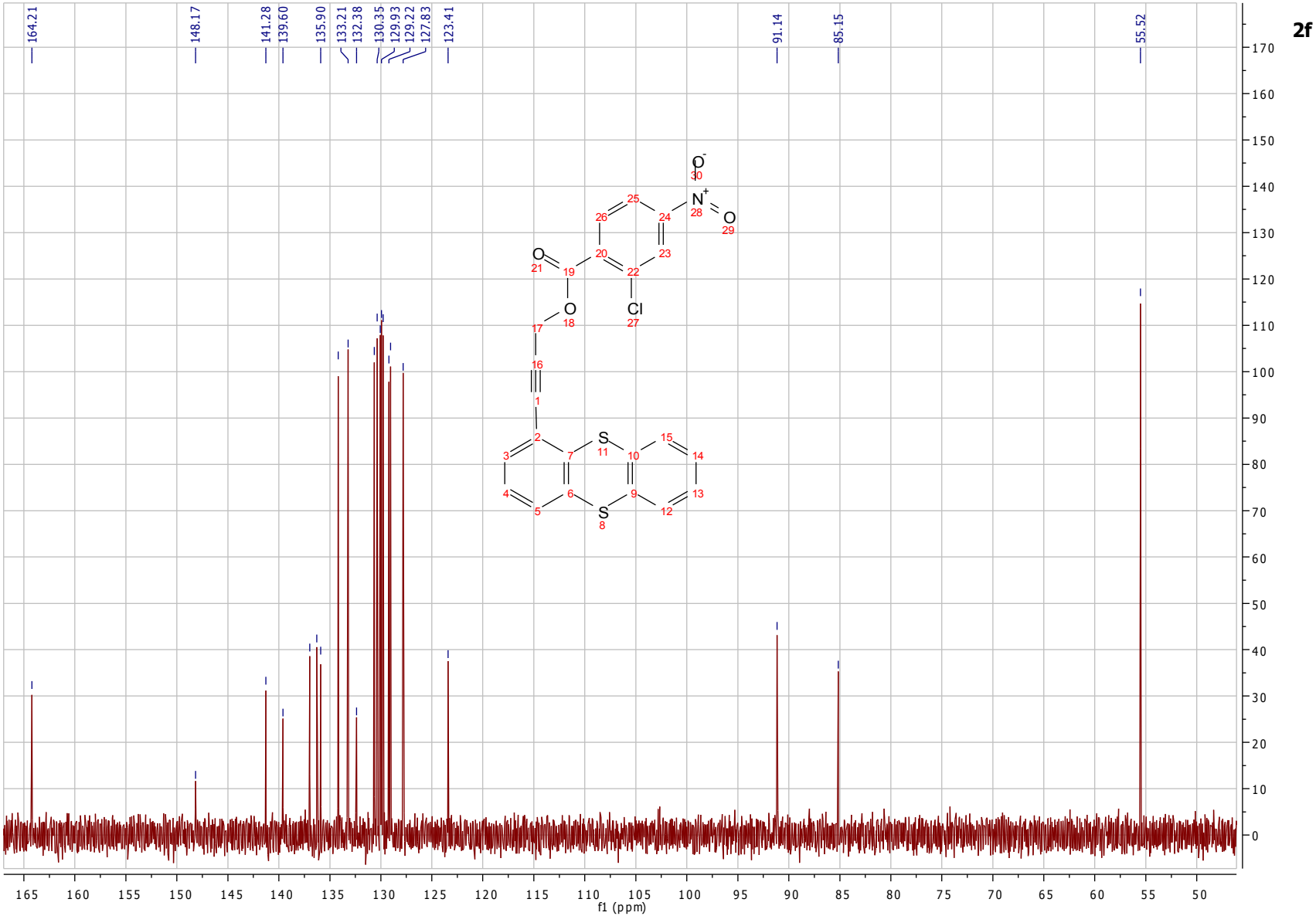
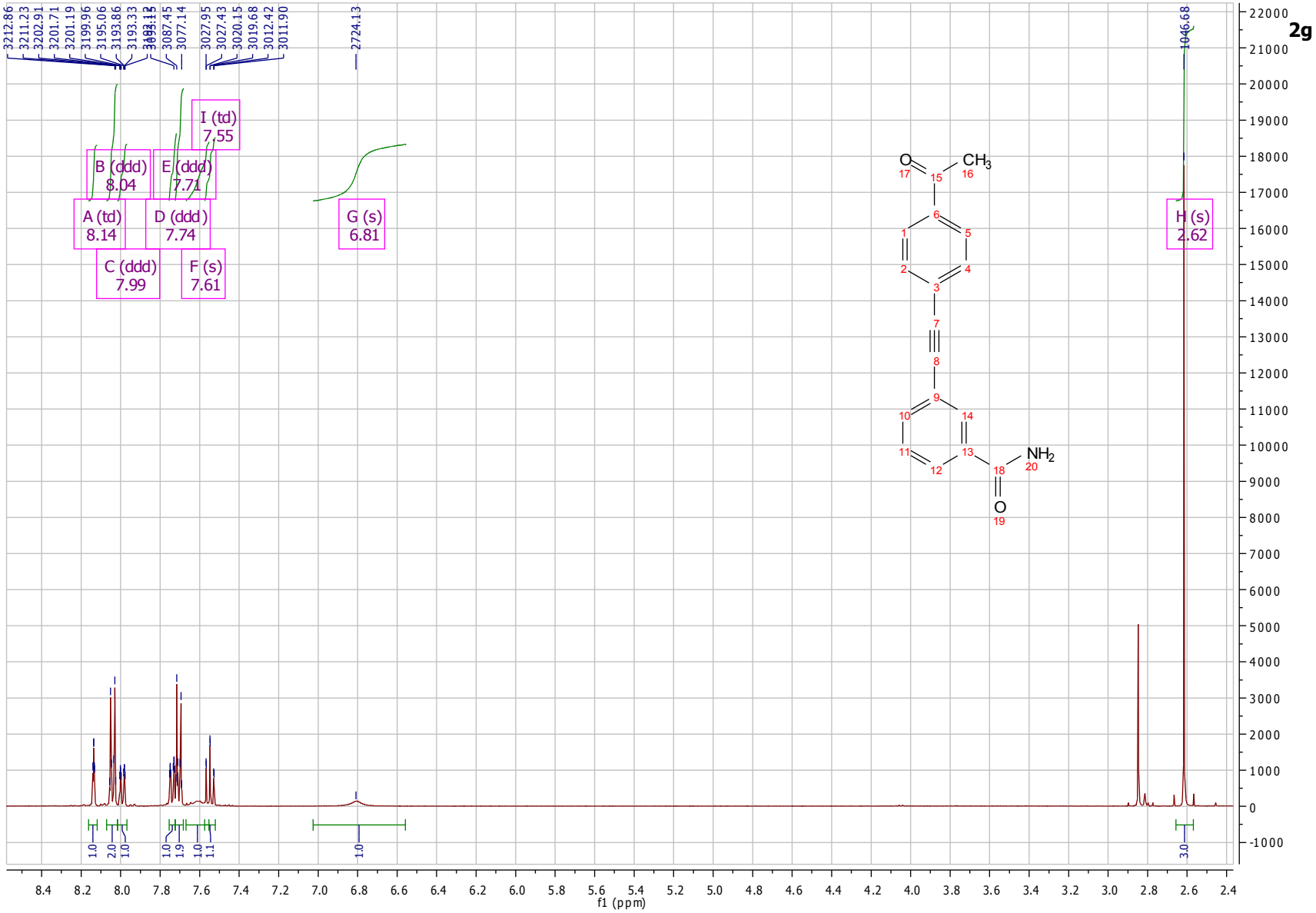
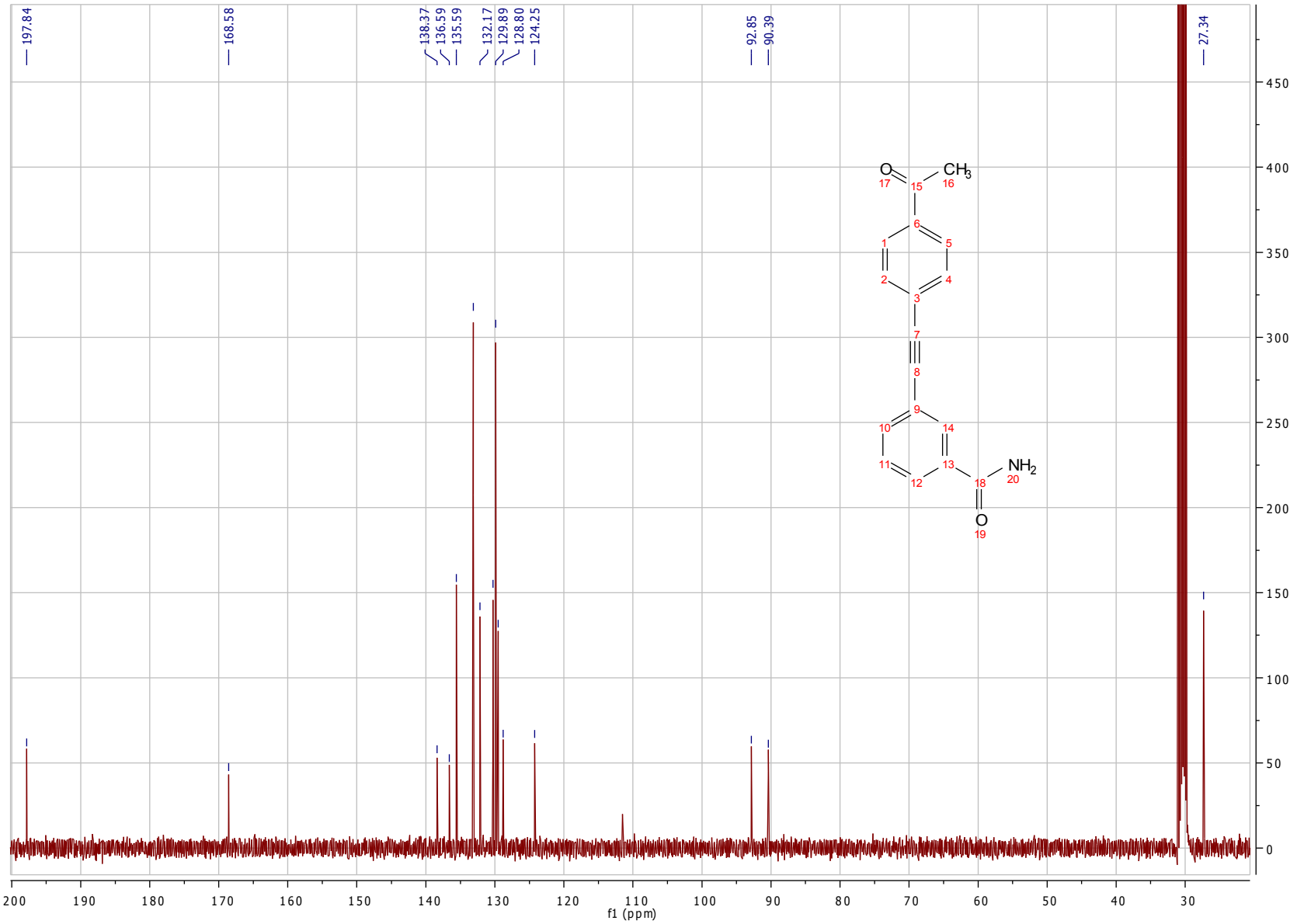
2966.70
2957.82
2936.38
2922.01
2914.53
2906.49
2624.01
2623.10
2622.06
2621.03
2619.94
2618.90
2618.06
A (s)
10.51
B (m)
7.87
C (ddd)
7.71
D (ddd)
7.63
E (dt)
7.50
F (m)
7.41
G (dd)
7.35
H (ddd)
7.29
I (m)
6.55
NH
Br
f1 (ppm)


2e
137.89
134.48
133.95
130.72
128.98
127.53
126.26
126.23
125.82
114.62
113.21
103.42
97.79
86.77
NH
Br
f1 (ppm)

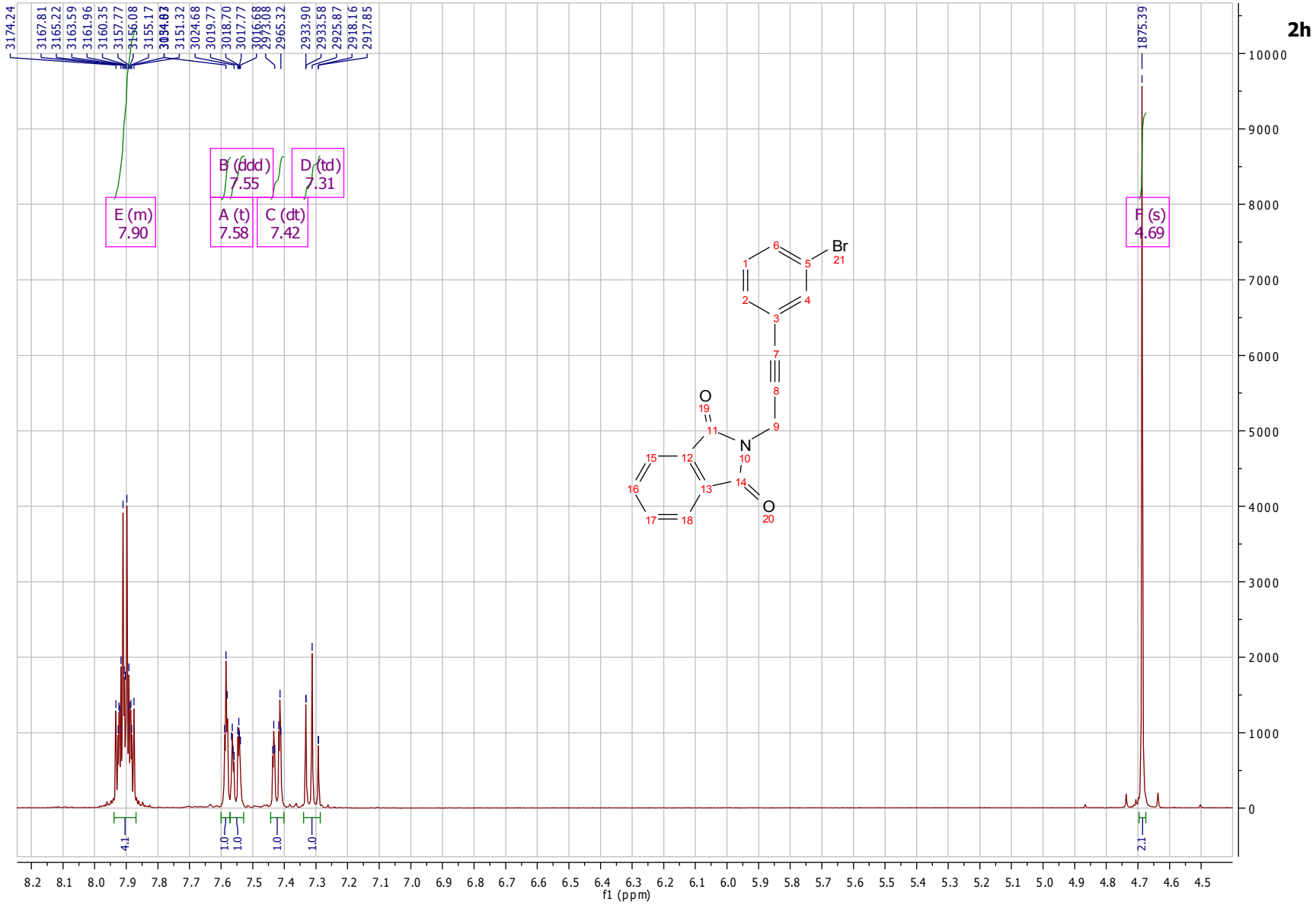

2f
E (d) 8.78
A (dd) 8.46
B (d) 7.92
D (dd) 7.51
G (m) 7.55
C (m) 7.36
F (s) 5.42
f1 (ppm)

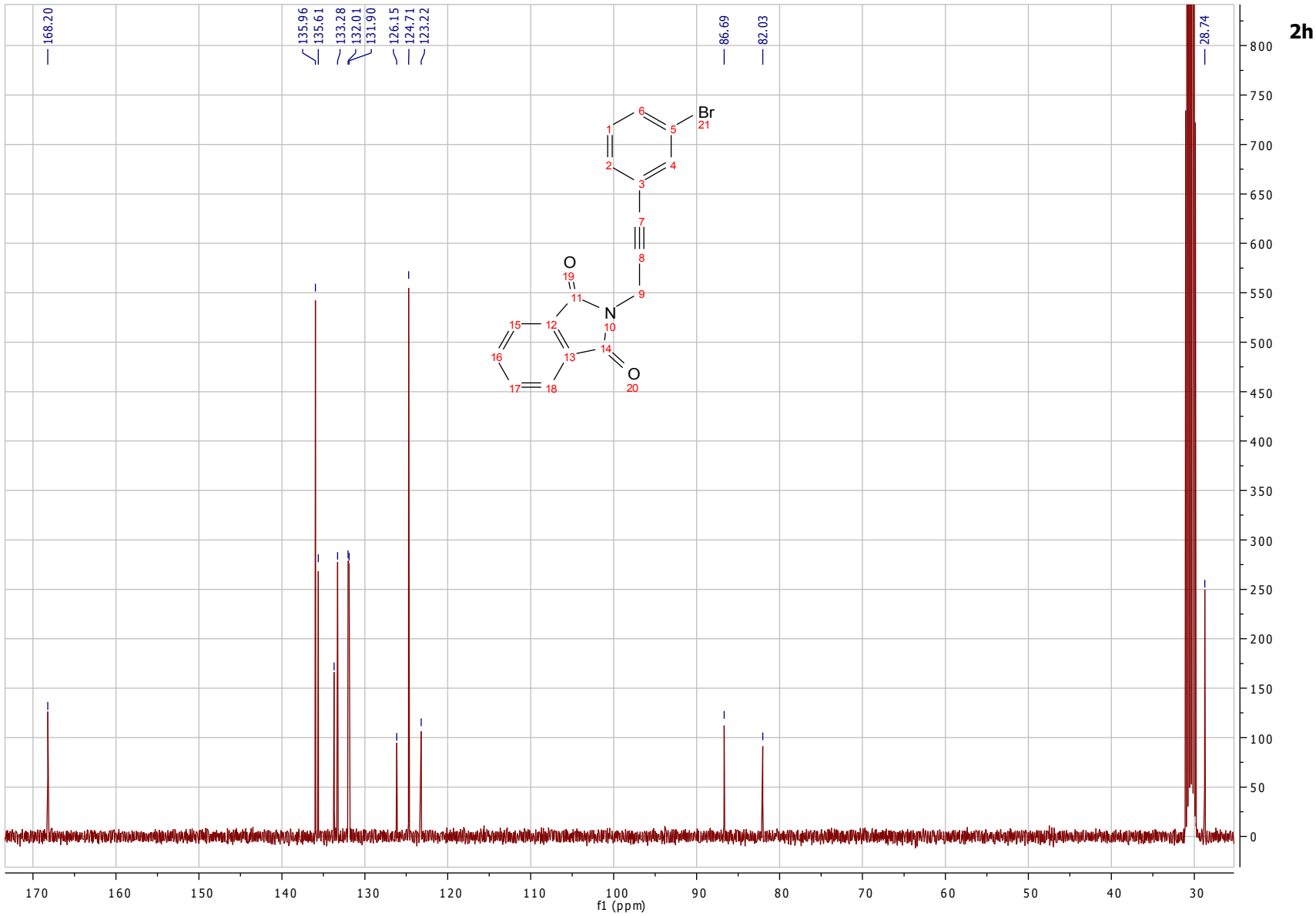

2f
164.21
148.17
141.28
139.60
135.90
133.21
132.38
130.35
129.93
129.22
127.83
123.41
91.14
85.15
55.52
f1 (ppm)

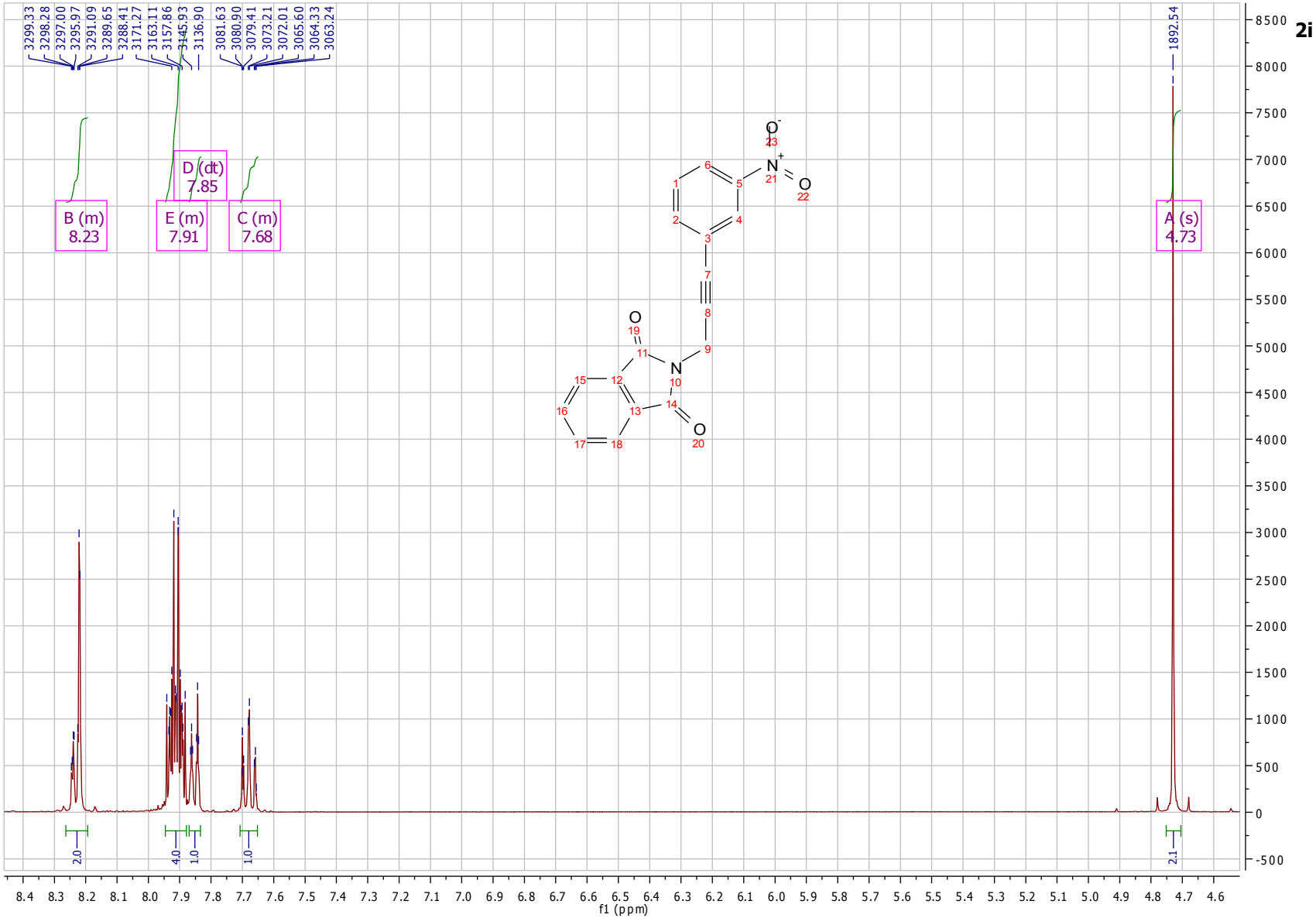

2g
I (td) 7.55
B (ddd) 8.04
E (ddd) 7.71
A (td) 8.14
D (ddd) 7.74
C (ddd) 7.99
F (s) 7.61
G (s) 6.81
H (s) 2.62
f1 (ppm)

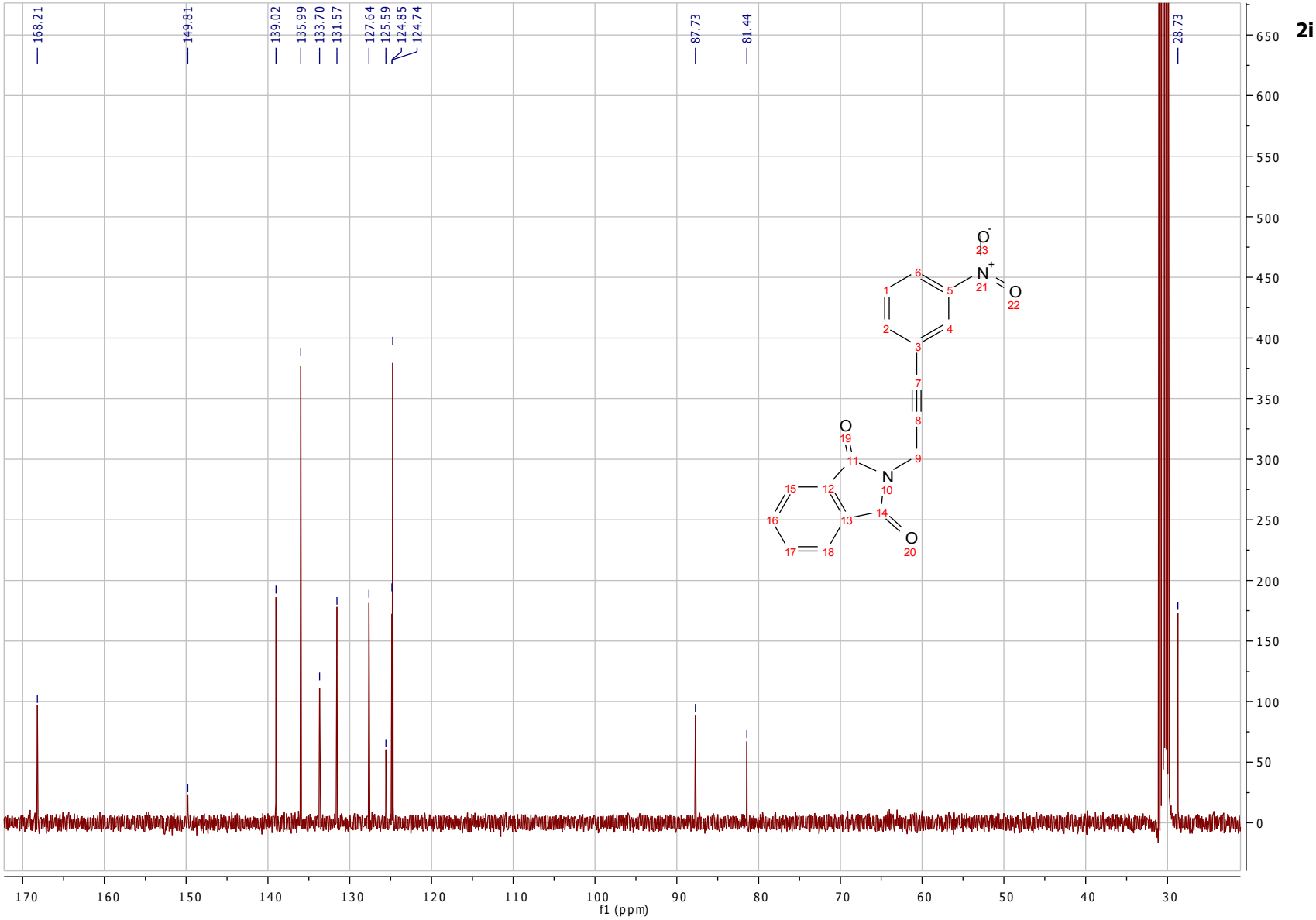

197.84
168.58
138.37
136.59
135.59
132.17
129.89
128.80
124.25
92.85
90.39
27.34
f1 (ppm)

2g

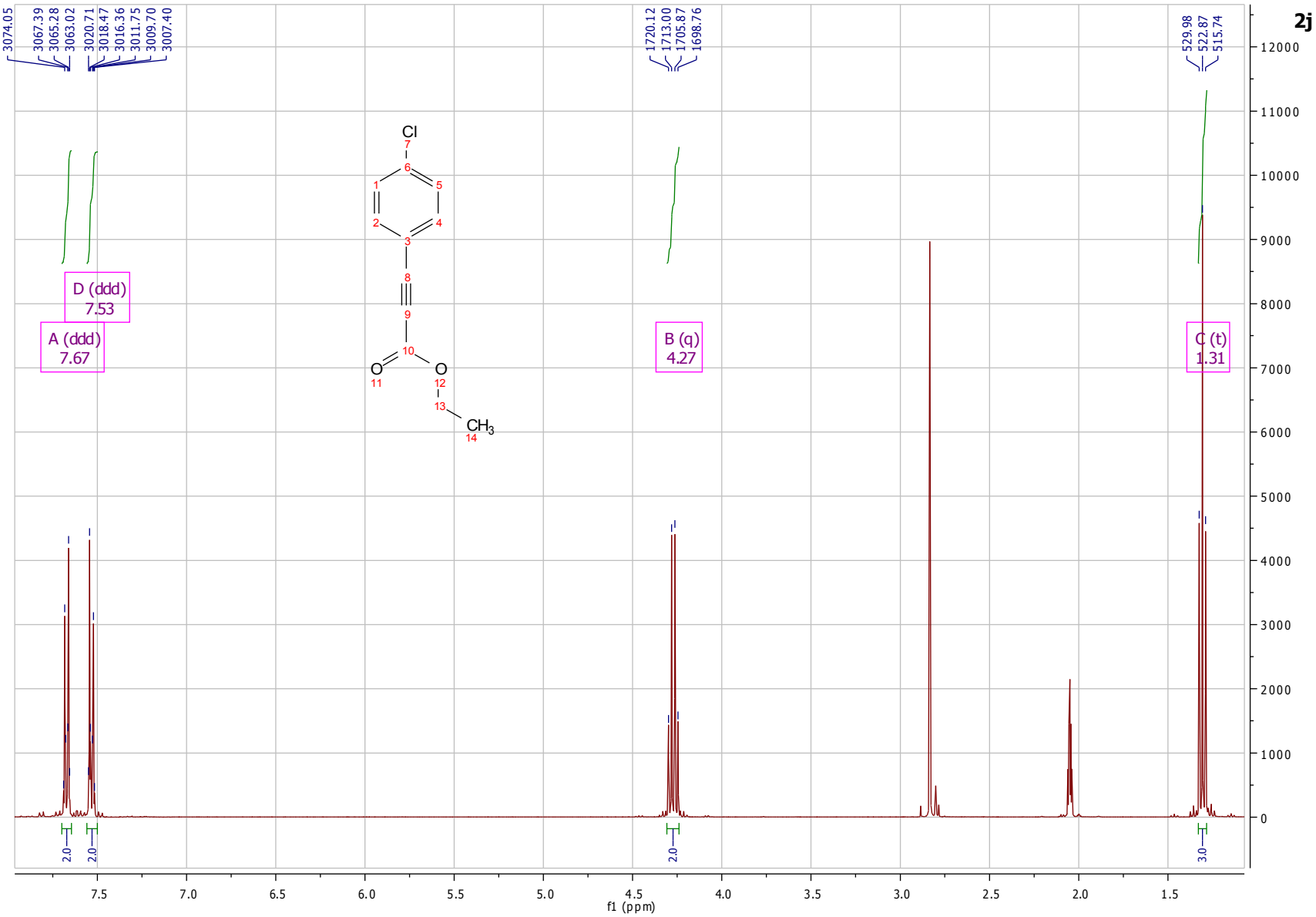

2h
E (m) 7.90
B (ddd) 7.55
D (td) 7.31
A (t) 7.58
C (dt) 7.42
F (s) 4.69
Br
O
N
O
f1 (ppm)

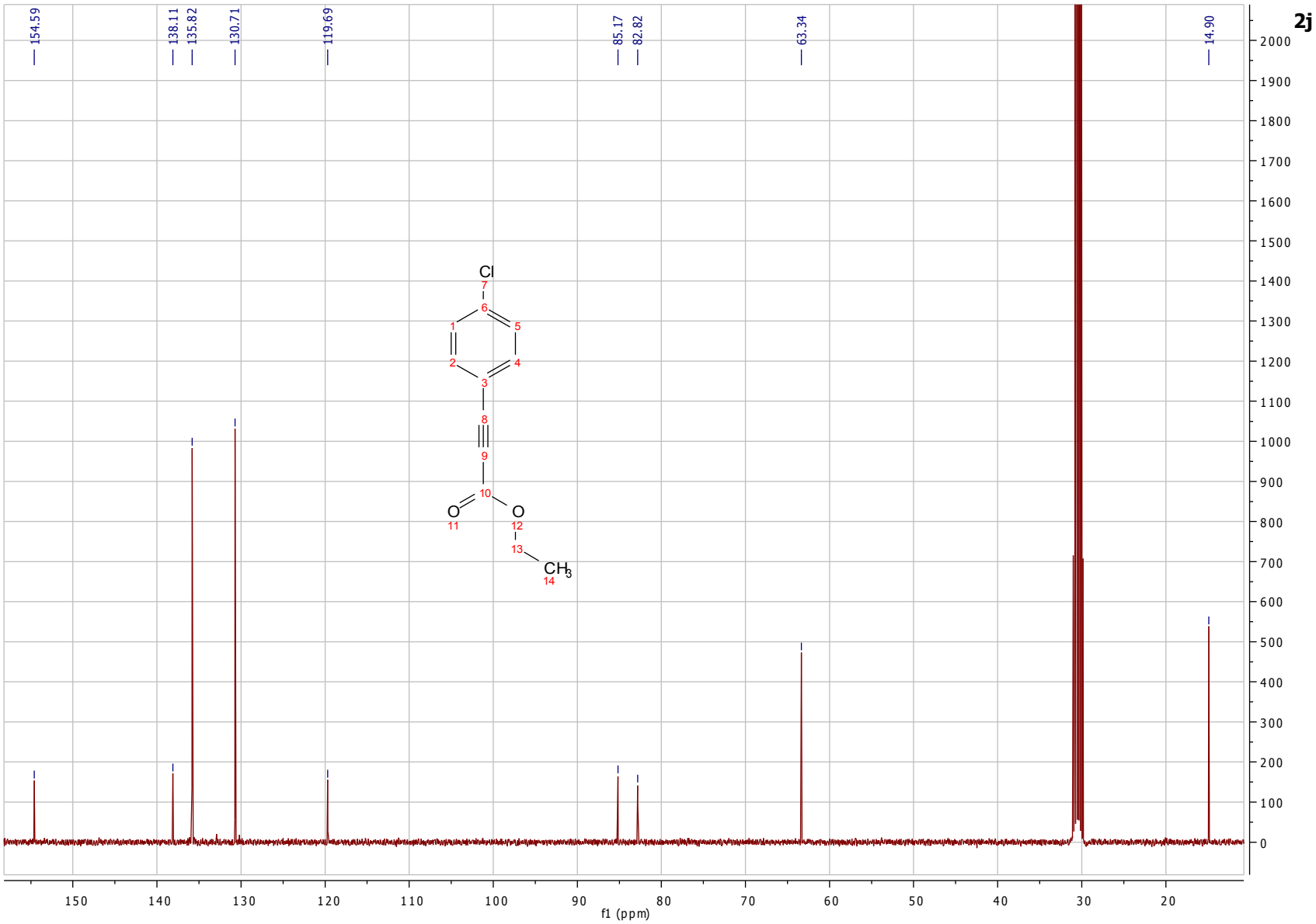

2h
168.20
135.96
135.61
133.28
132.01
131.90
126.15
124.71
123.22
86.69
82.03
28.74
Br
O
N
O
f1 (ppm)

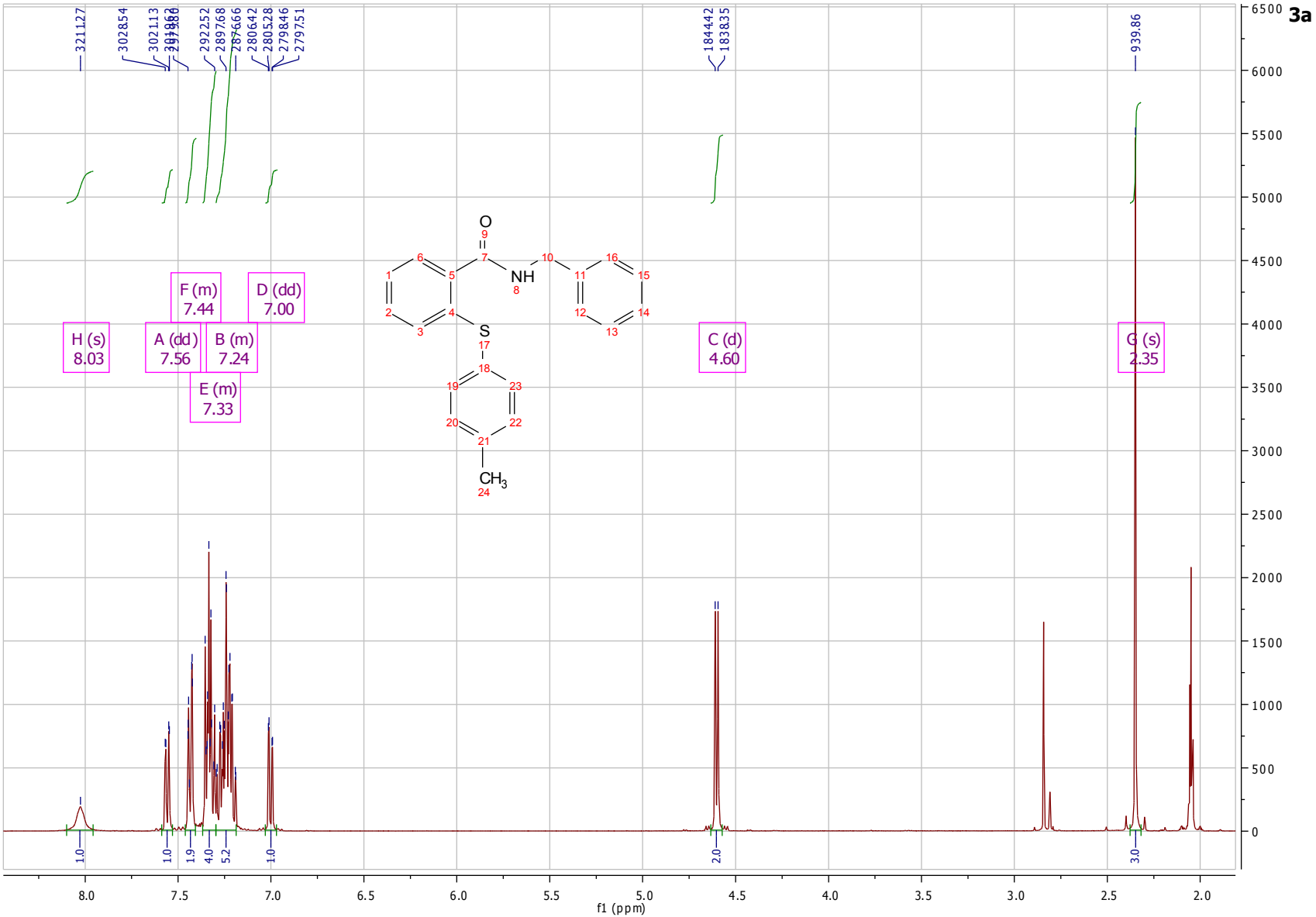

2i
3299.33
3298.28
3297.00
3295.97
3291.09
3289.65
3288.41
3171.27
3163.11
3157.86
3145.93
3136.90
3081.63
3080.90
3079.41
3073.21
3072.01
3065.60
3064.33
3063.24
1892.54
B (m)
8.23
D (dt)
7.85
E (m)
7.91
C (m)
7.68
A (s)
4.73
2.0
4.0
1.0
1.0
2.1
f1 (ppm)

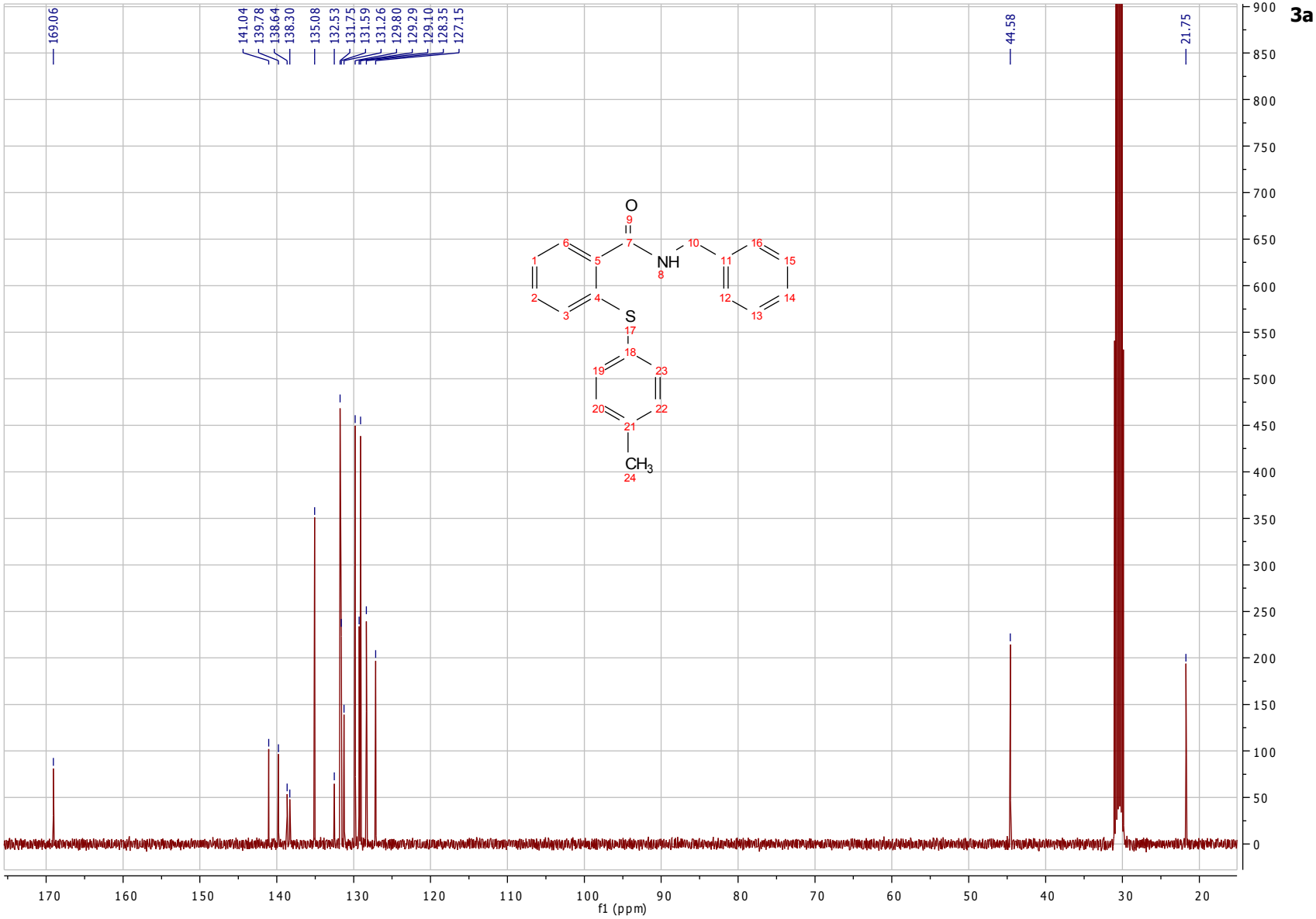

168.21
149.81
139.02
135.99
133.70
131.57
127.64
125.59
124.85
124.74
87.73
81.44
28.73
f1 (ppm)

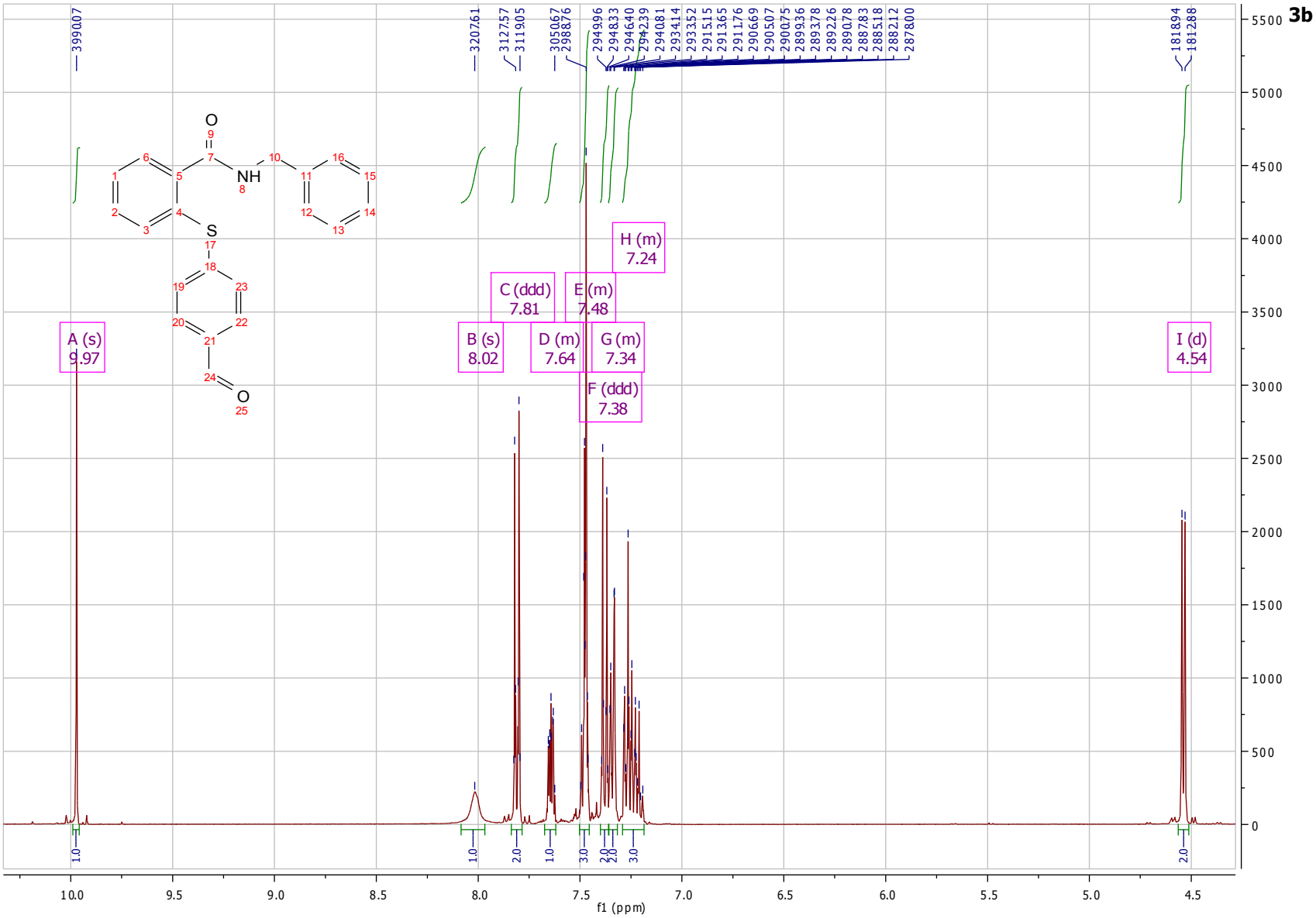
2i

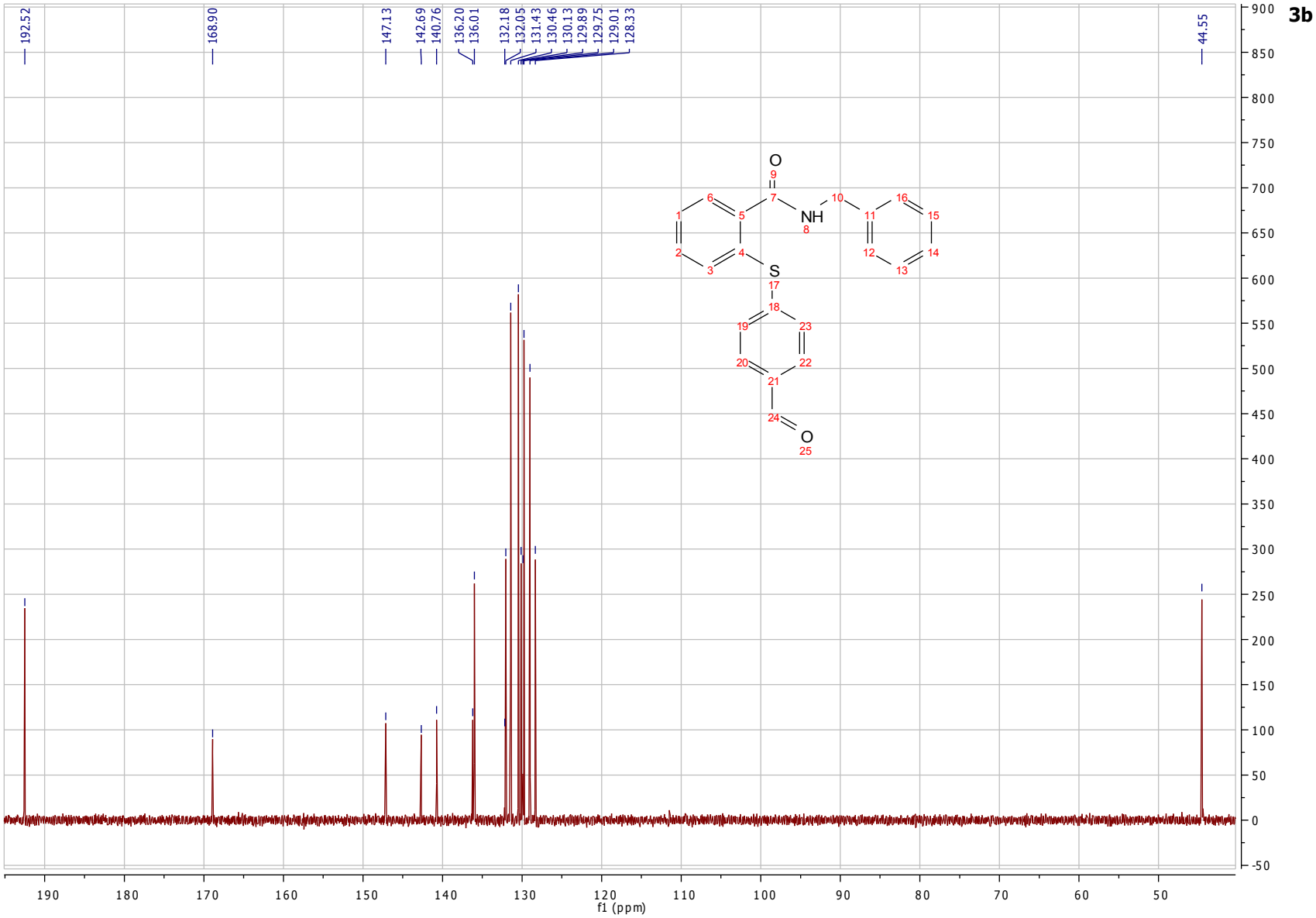

2j
3074.05
3067.39
3065.28
3063.02
3020.71
3018.47
3016.36
3011.75
3009.70
3007.40
1720.12
1713.00
1705.87
1698.76
529.98
522.87
515.74
D (ddd)
7.53
A (ddd)
7.67
B (q)
4.27
C (t)
1.31
Cl
O
O
CH3
2.0
2.0
2.0
3.0
f1 (ppm)

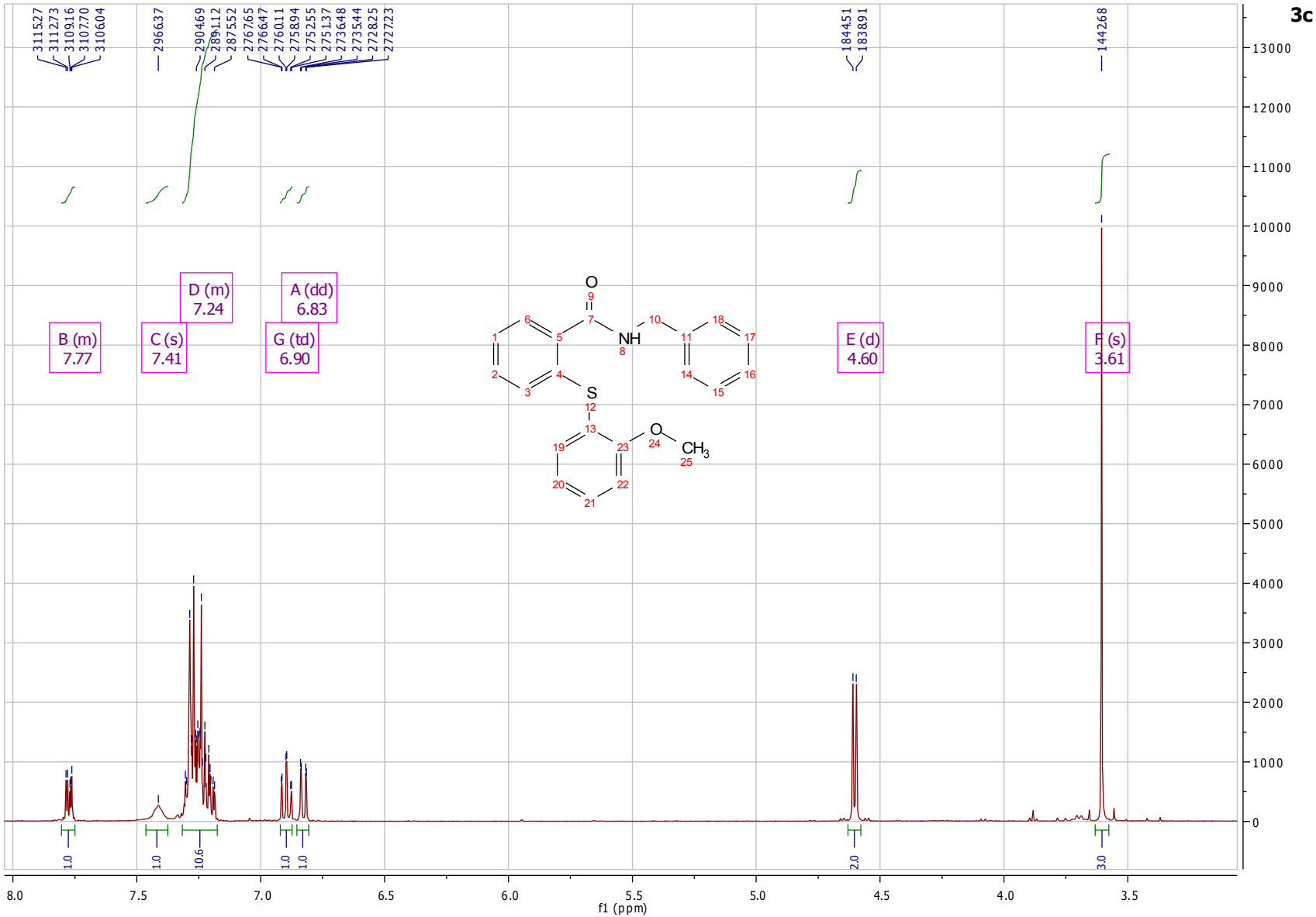

2j
154.59
138.11
135.82
130.71
119.69
85.17
82.82
63.34
14.90
Cl
O
O
CH3
f1 (ppm)

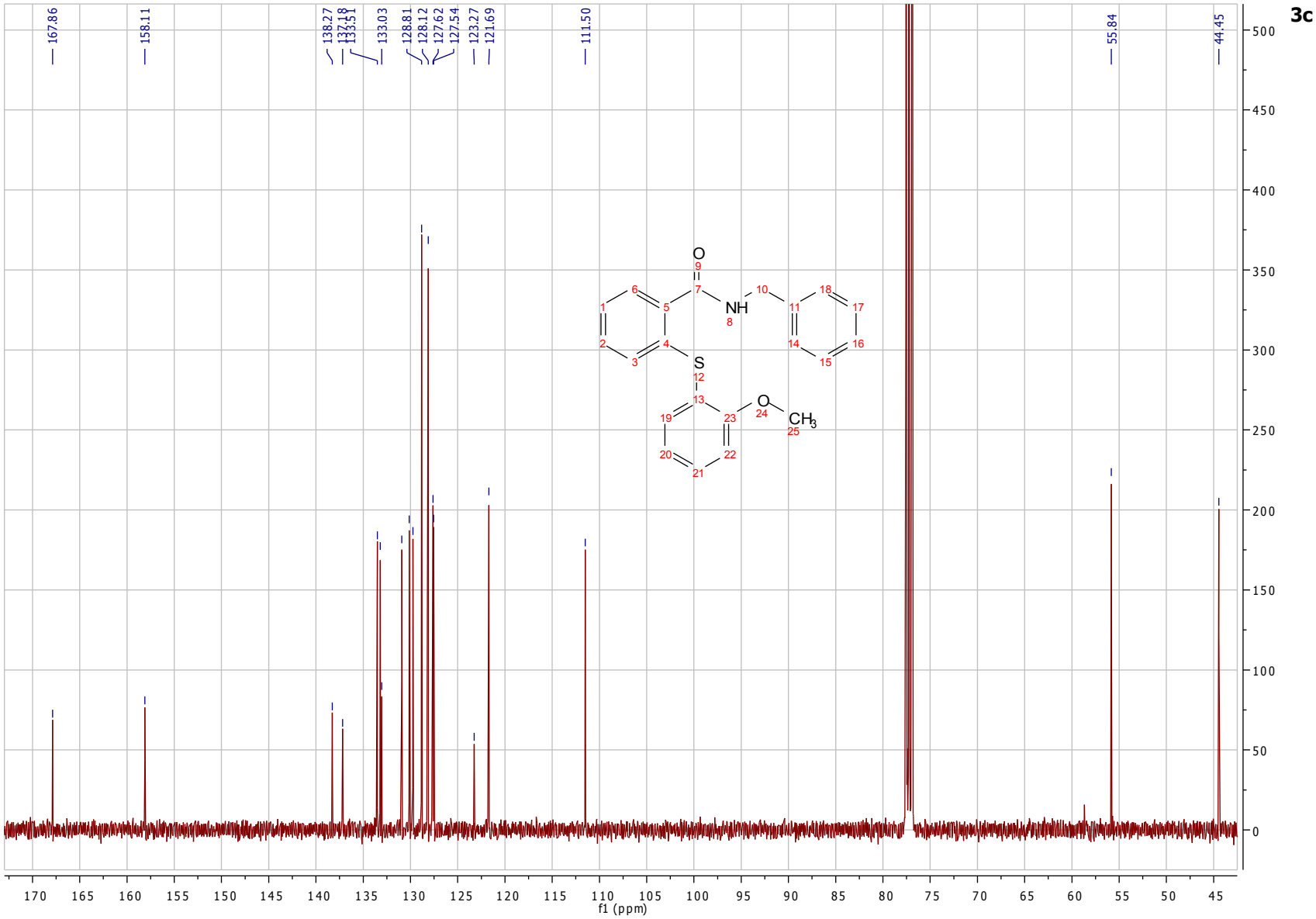

3a
H (s) 8.03
A (dd) 7.56
B (m) 7.24
E (m) 7.33
F (m) 7.44
D (dd) 7.00
C (d) 4.60
G (s) 2.35
f1 (ppm)

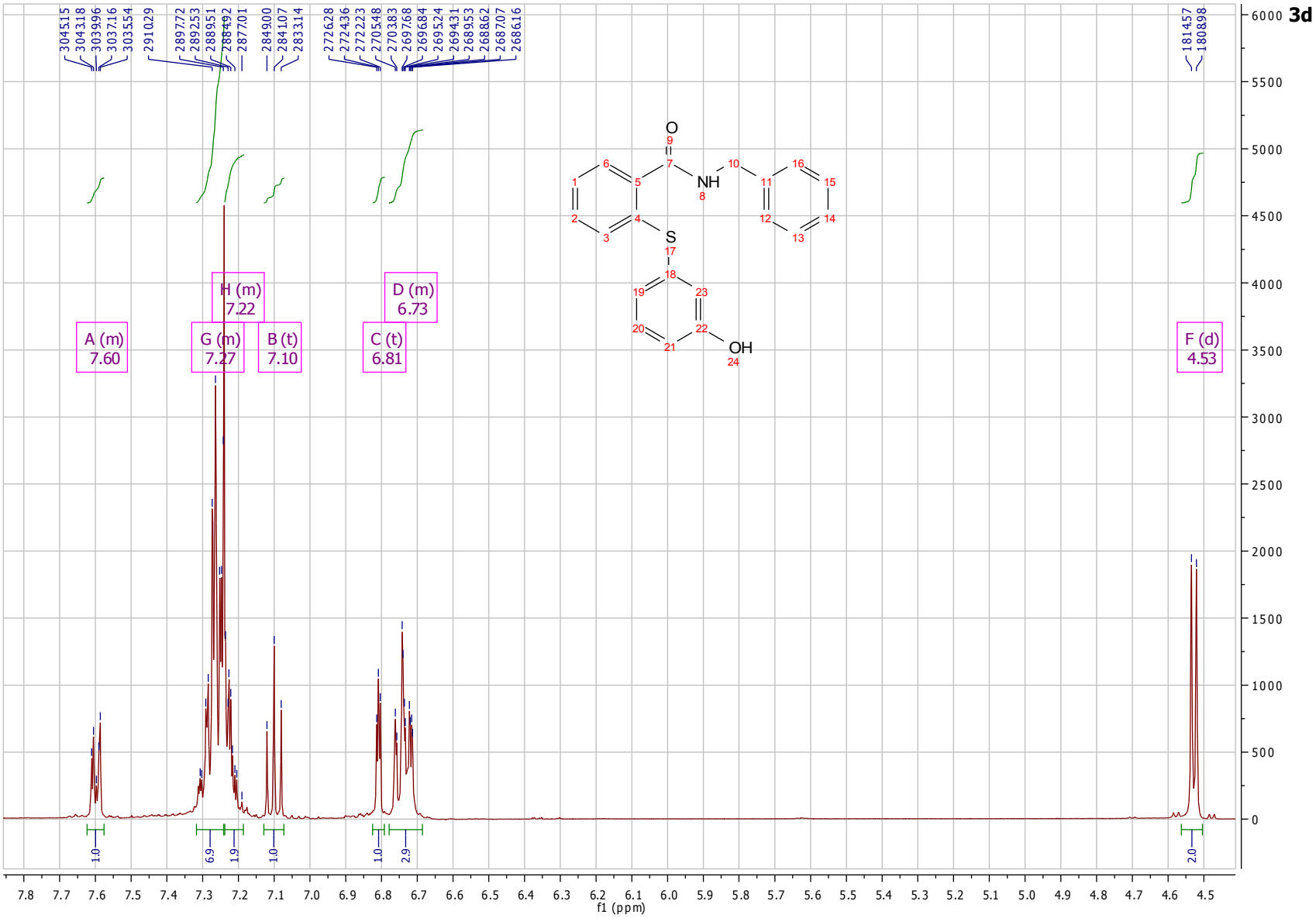

3a
169.06
141.04
139.78
138.64
138.30
135.08
132.53
131.75
131.59
131.26
129.80
129.29
129.10
128.35
127.15
44.58
21.75
O
NH
S
CH3
f1 (ppm)

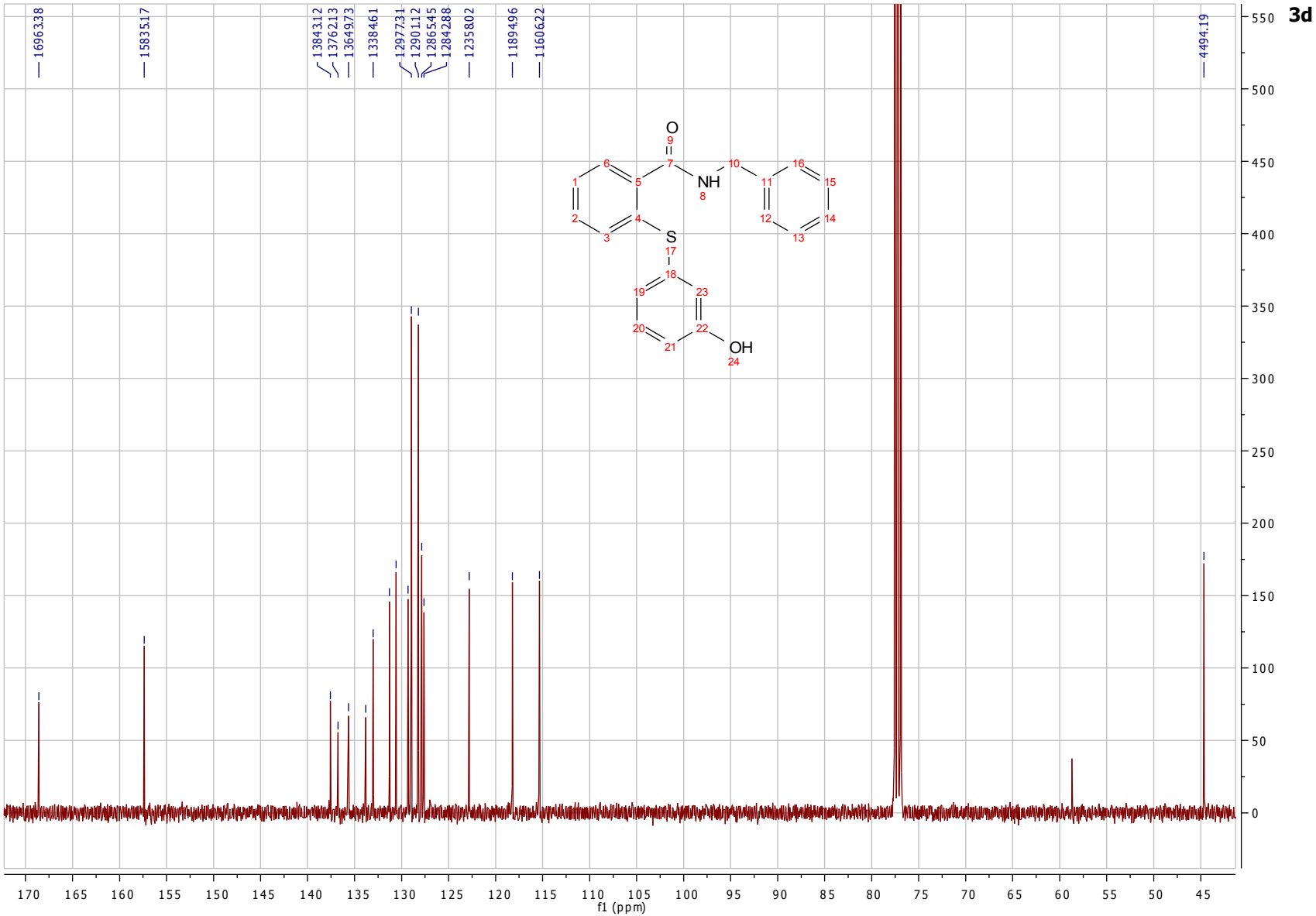

3b
A (s)
9.97
B (s)
8.02
C (ddd)
7.81
D (m)
7.64
E (m)
7.48
F (ddd)
7.38
G (m)
7.34
H (m)
7.24
I (d)
4.54
f1 (ppm)

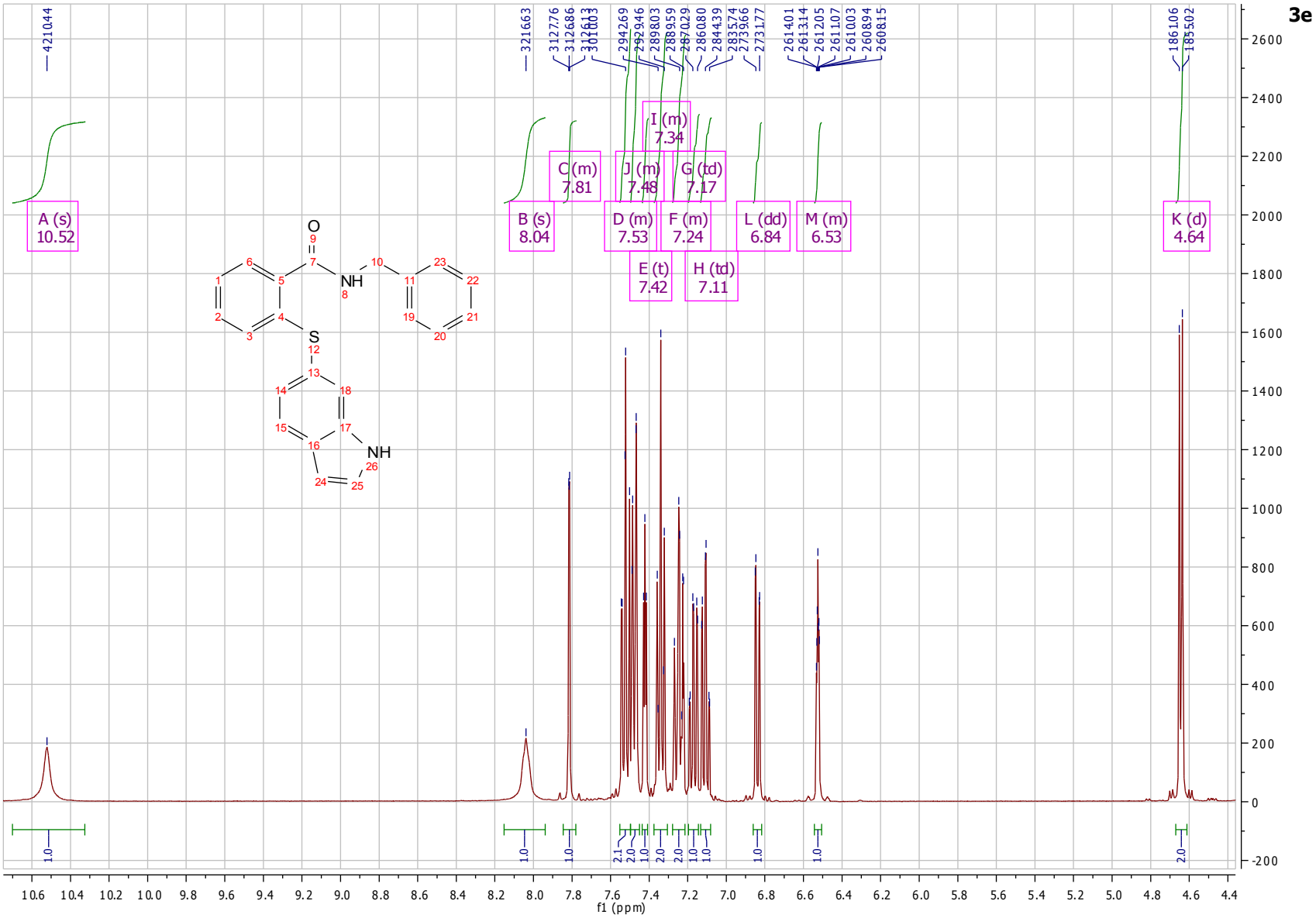

3b
192.52
168.90
147.13
142.69
140.76
136.20
136.01
132.18
132.05
131.43
130.46
130.13
129.89
129.75
129.01
128.33
44.55
O
NH
S
O
f1 (ppm)

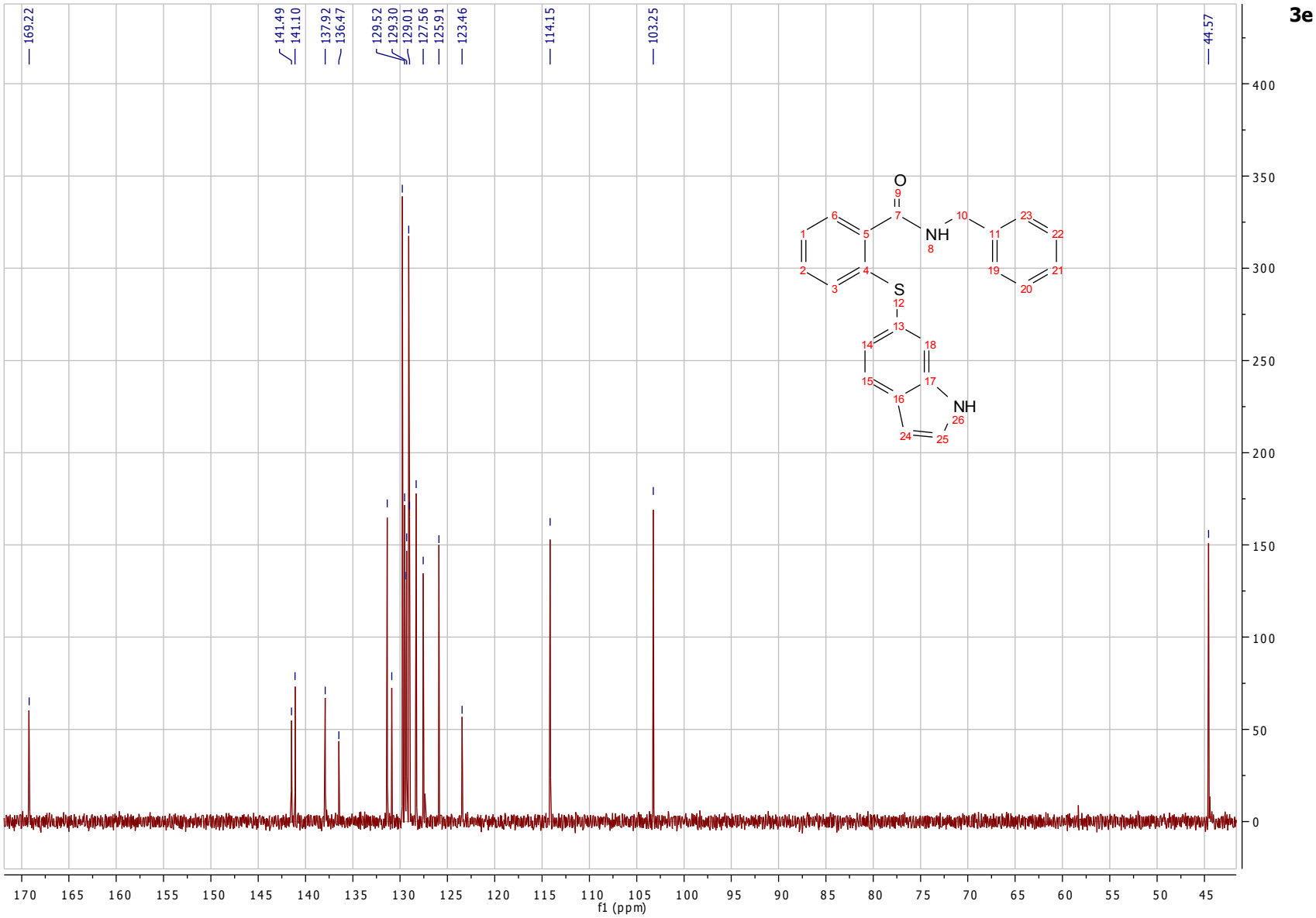

3c
311527
311273
310916
310770
310604
296637
290469
289112
287552
276765
276647
276011
275894
275255
275137
273648
273544
272825
272723
184451
183891
144268
B (m)
7.77
C (s)
7.41
D (m)
7.24
A (dd)
6.83
G (td)
6.90
E (d)
4.60
F (s)
3.61
NH
S
O
CH3
1.0
1.0
10.6
1.0
1.0
2.0
3.0
f1 (ppm)

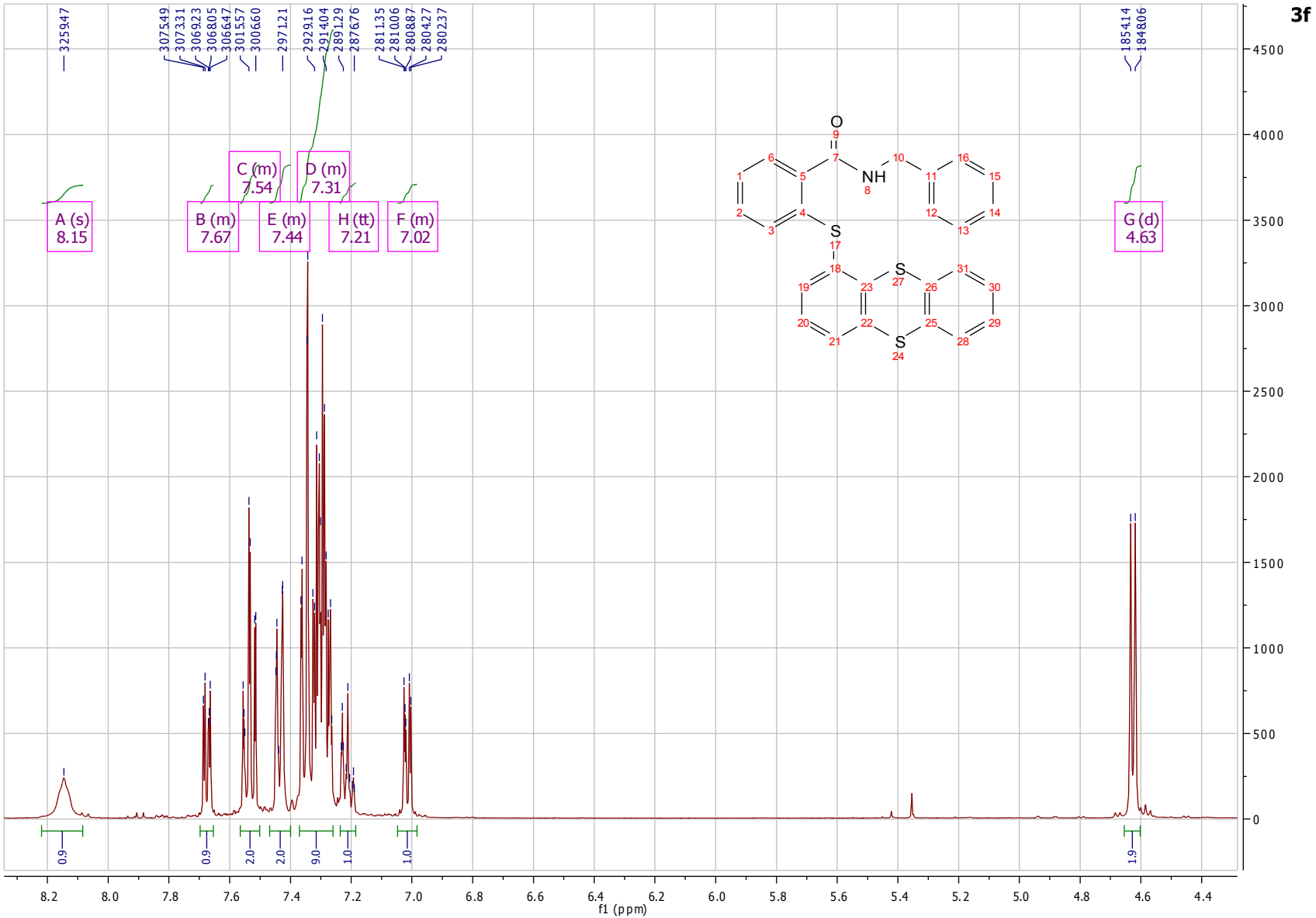

3c
167.86
158.11
138.27
133.51
133.03
128.81
128.12
127.62
127.54
123.27
121.69
111.50
55.84
44.45
f1 (ppm)

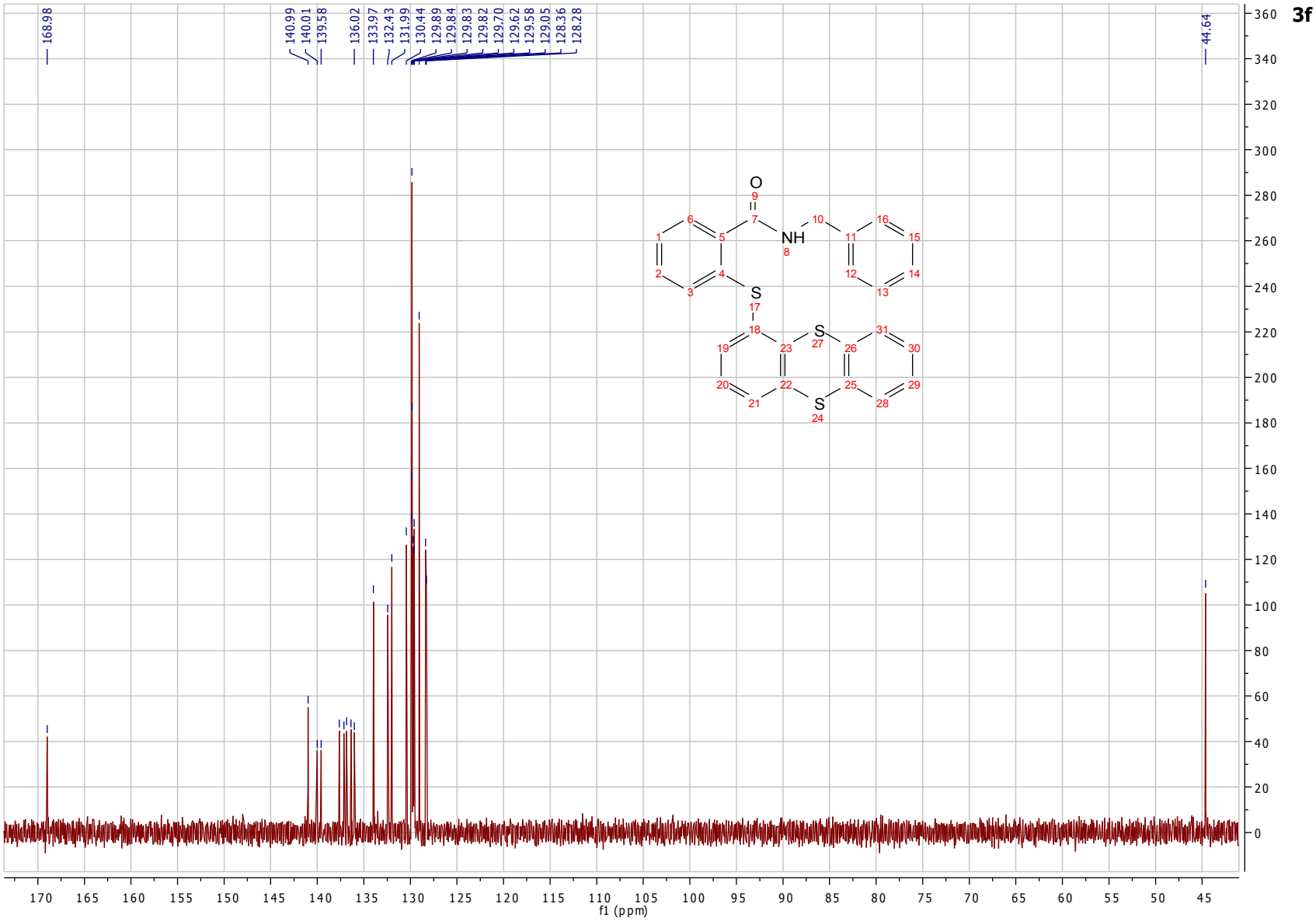

3d
A (m) 7.60
H (m) 7.22
G (m) 7.27
B (t) 7.10
D (m) 6.73
C (t) 6.81
F (d) 4.53
NH
S
OH
f1 (ppm)

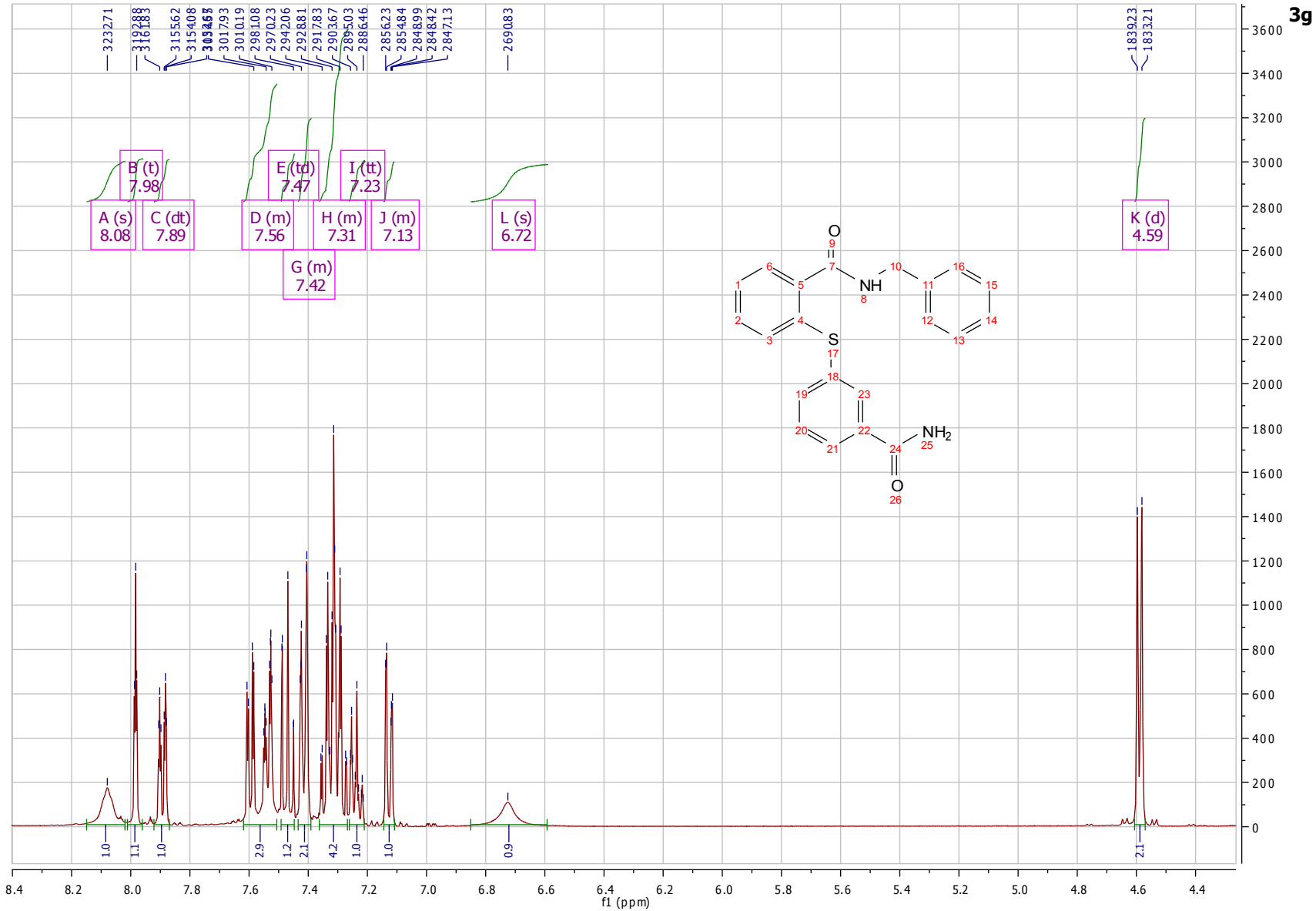

3d
169.6338
158.3517
138.4312
137.6213
136.4973
133.8461
129.7731
129.0112
128.6545
128.4288
123.5802
118.9496
116.0622
44.9419
O
NH
S
OH
f1 (ppm)

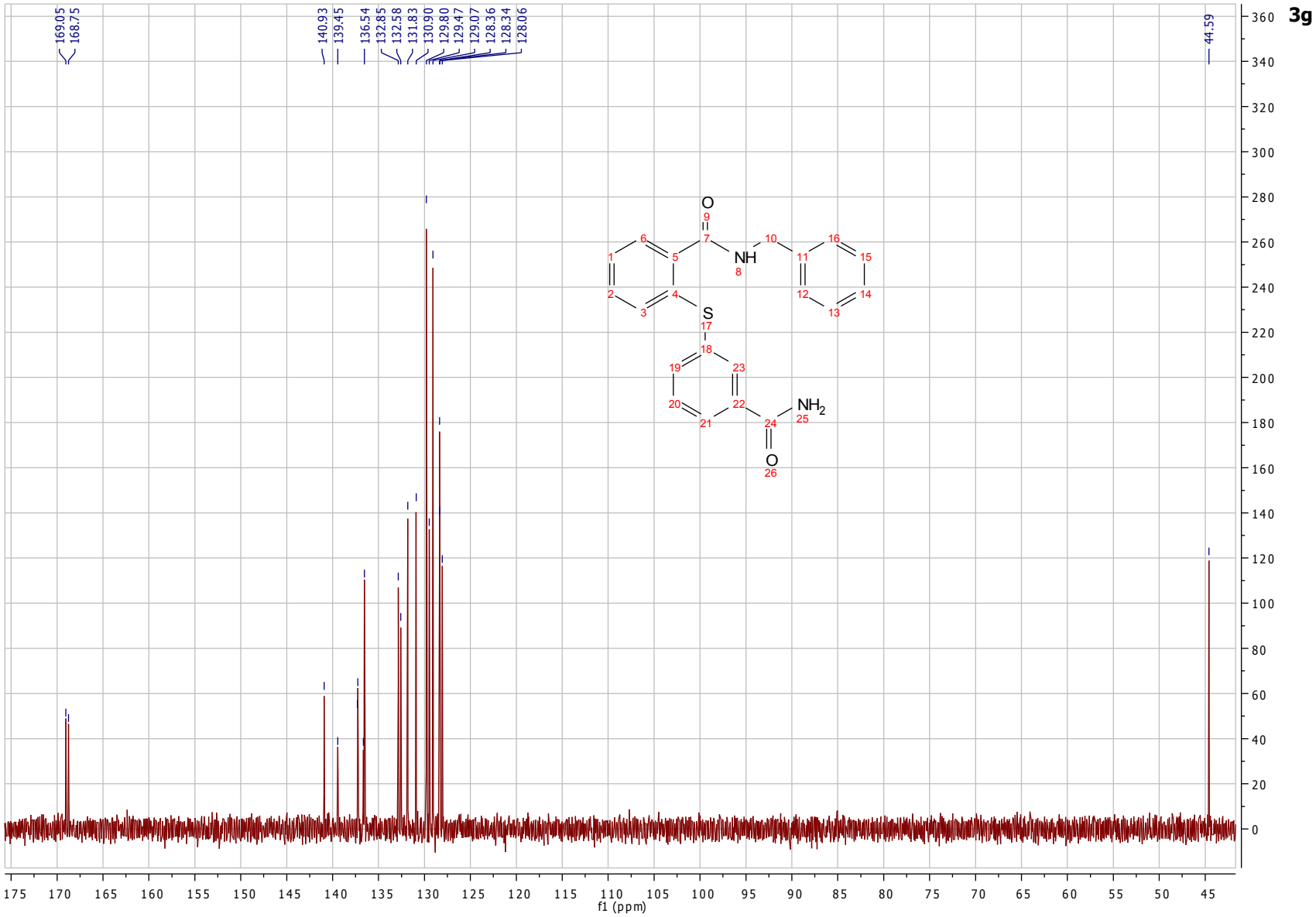

3e
A (s) 10.52
B (s) 8.04
C (m) 7.81
D (m) 7.53
E (t) 7.42
F (m) 7.24
G (td) 7.17
H (td) 7.11
I (m) 7.34
J (m) 7.48
K (d) 4.64
L (dd) 6.84
M (m) 6.53
NH
NH
O
S
f1 (ppm)

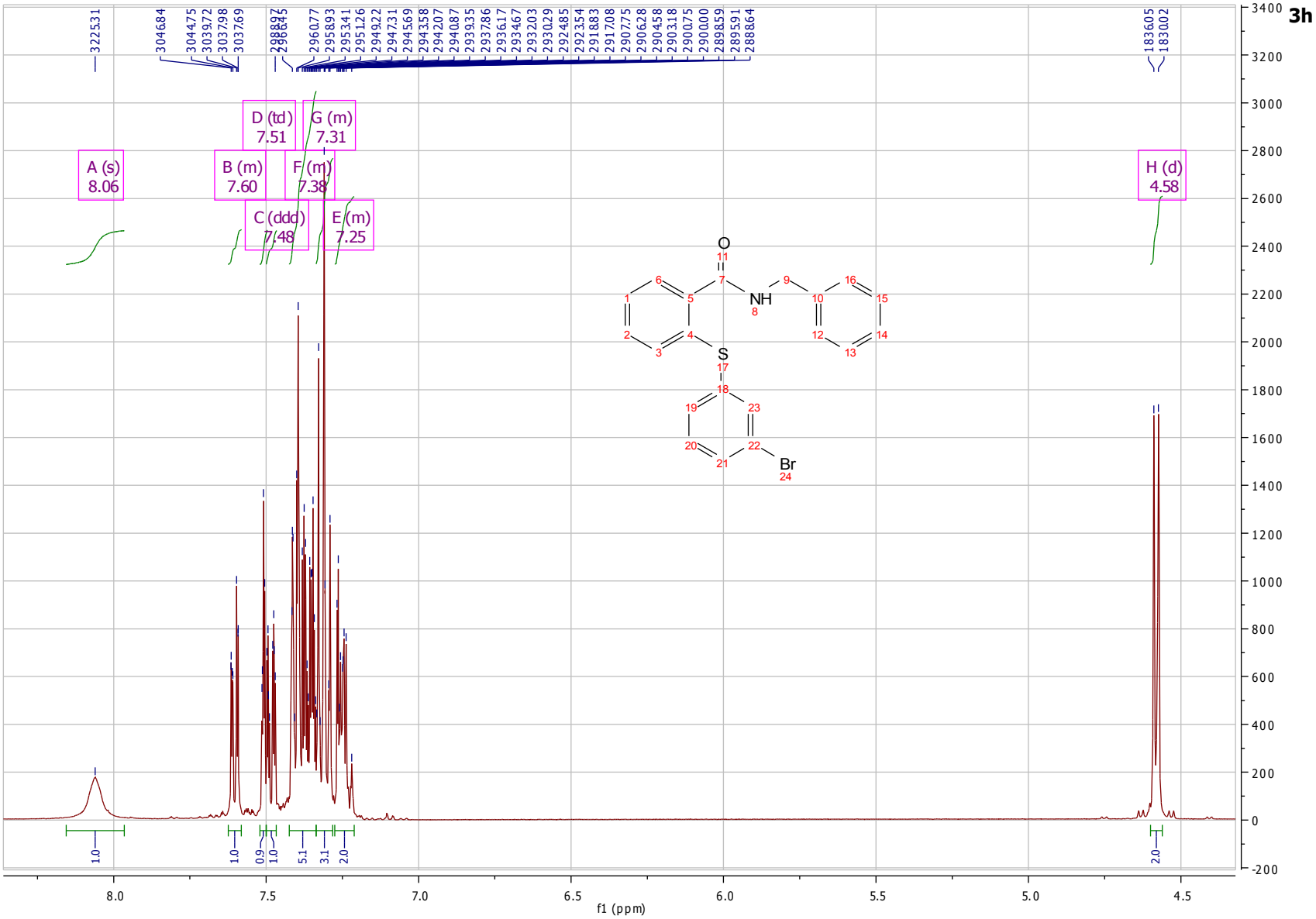

3e
169.22
141.49
141.10
137.92
136.47
129.52
129.30
129.01
127.56
125.91
123.46
114.15
103.25
44.57
O
NH
S
NH
f1 (ppm)

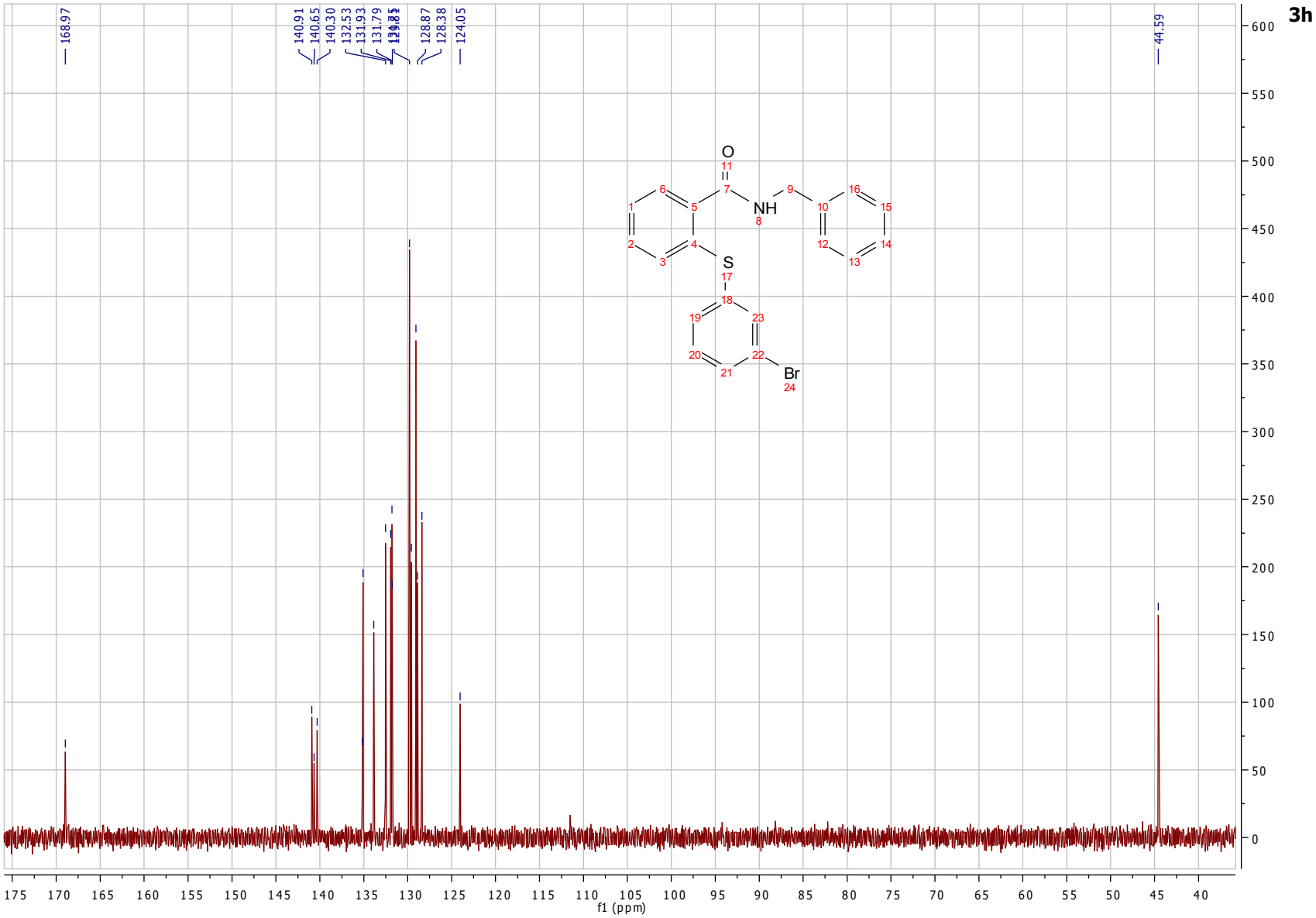

3f
A (s) 8.15
B (m) 7.67
C (m) 7.54
D (m) 7.31
E (m) 7.44
H (tt) 7.21
F (m) 7.02
G (d) 4.63
NH
S
S
S
f1 (ppm)

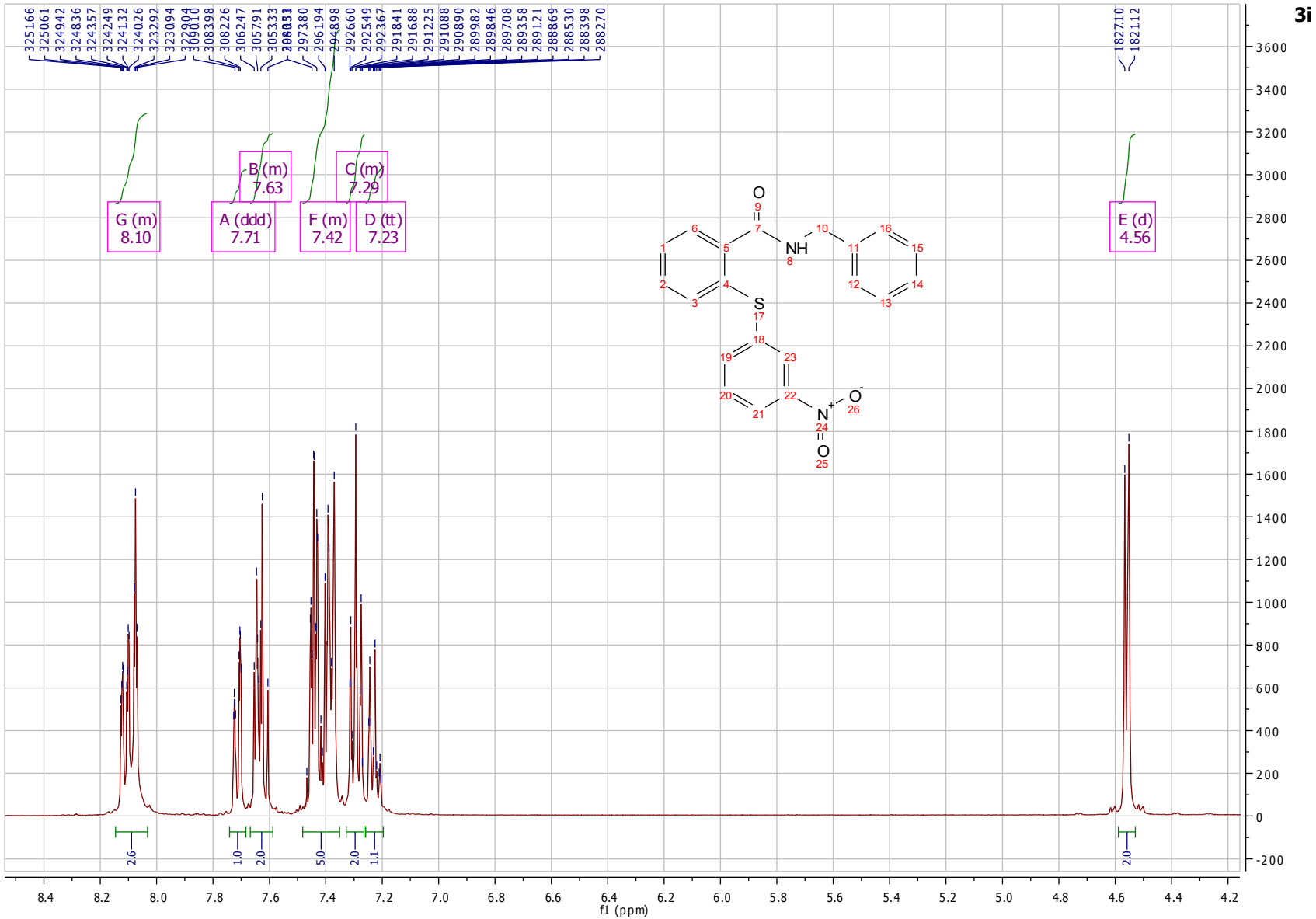

168.98
140.99
140.01
139.58
136.02
133.97
132.43
131.99
130.44
129.89
129.84
129.83
129.82
129.70
129.62
129.58
129.05
128.36
128.28
44.64
3f
O
NH
S
S
S
f1 (ppm)

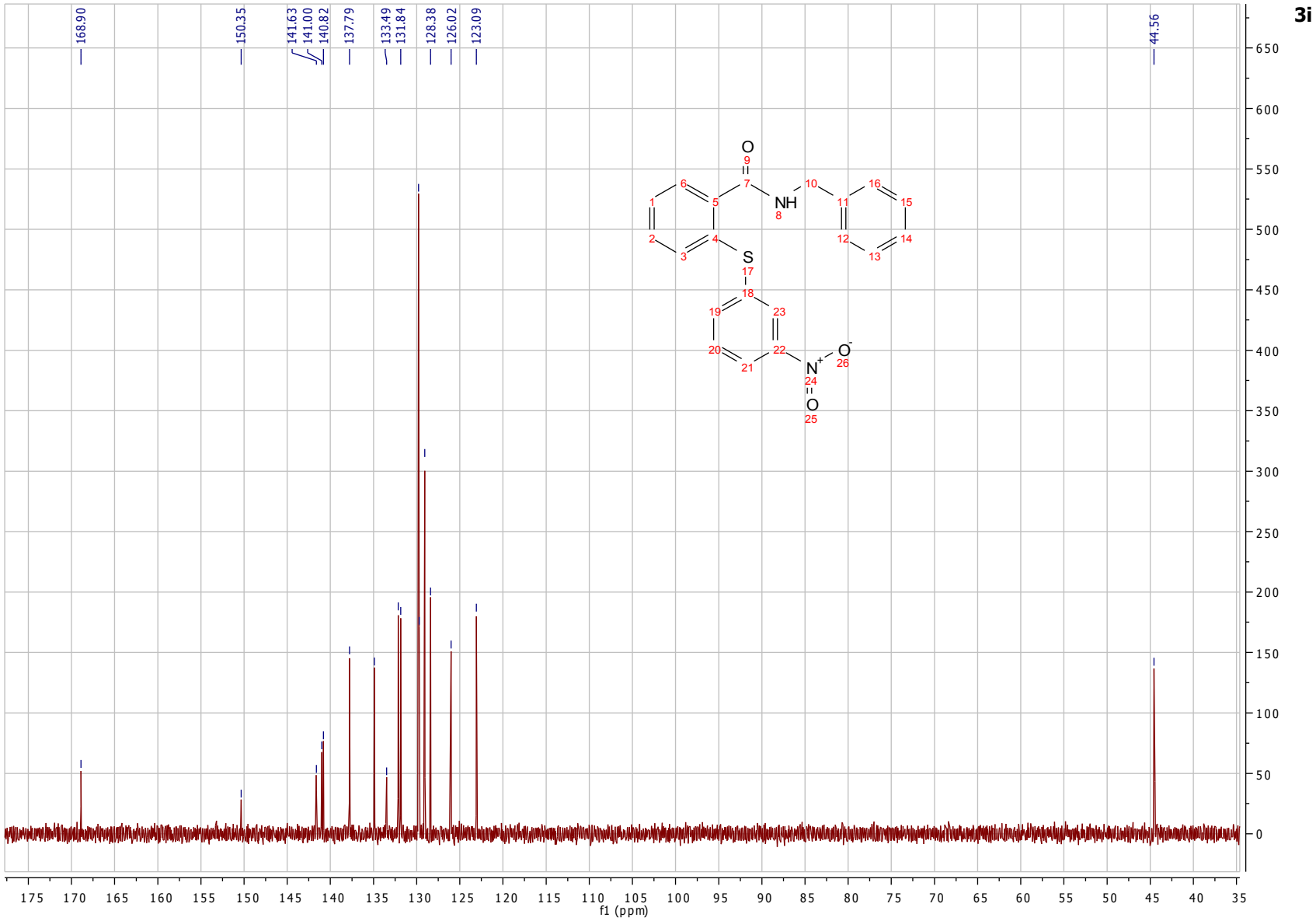

3g
A (s) 8.08
B (t) 7.98
C (dt) 7.89
D (m) 7.56
E (td) 7.47
G (m) 7.42
H (m) 7.31
I (tt) 7.23
J (m) 7.13
L (s) 6.72
K (d) 4.59
NH
S
NH2
O
f1 (ppm)

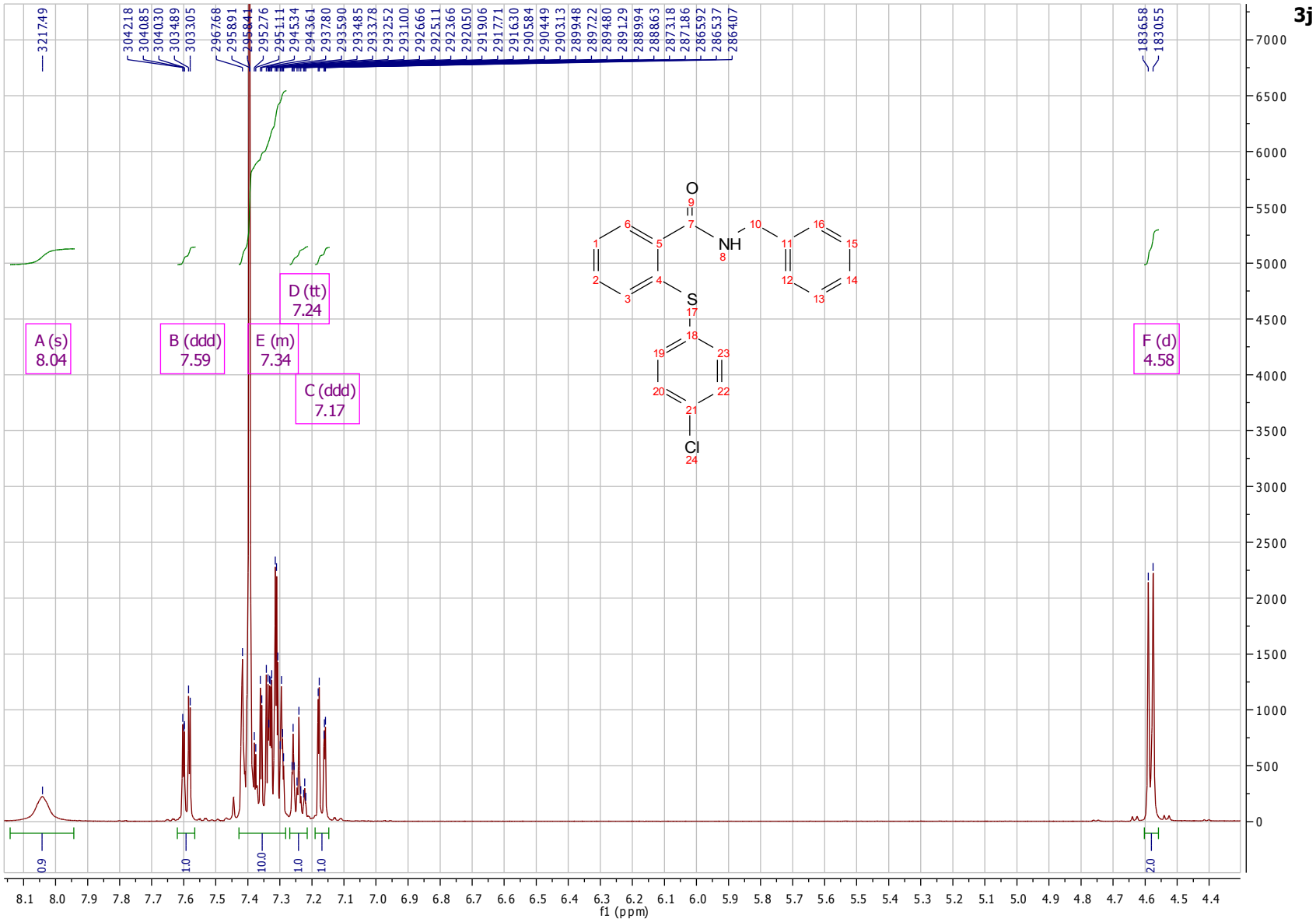

3g
169.05
168.75
140.93
139.45
136.54
132.85
132.58
131.83
130.90
129.80
129.47
129.07
128.36
128.34
128.06
44.59
O
NH
S
NH2
O
f1 (ppm)

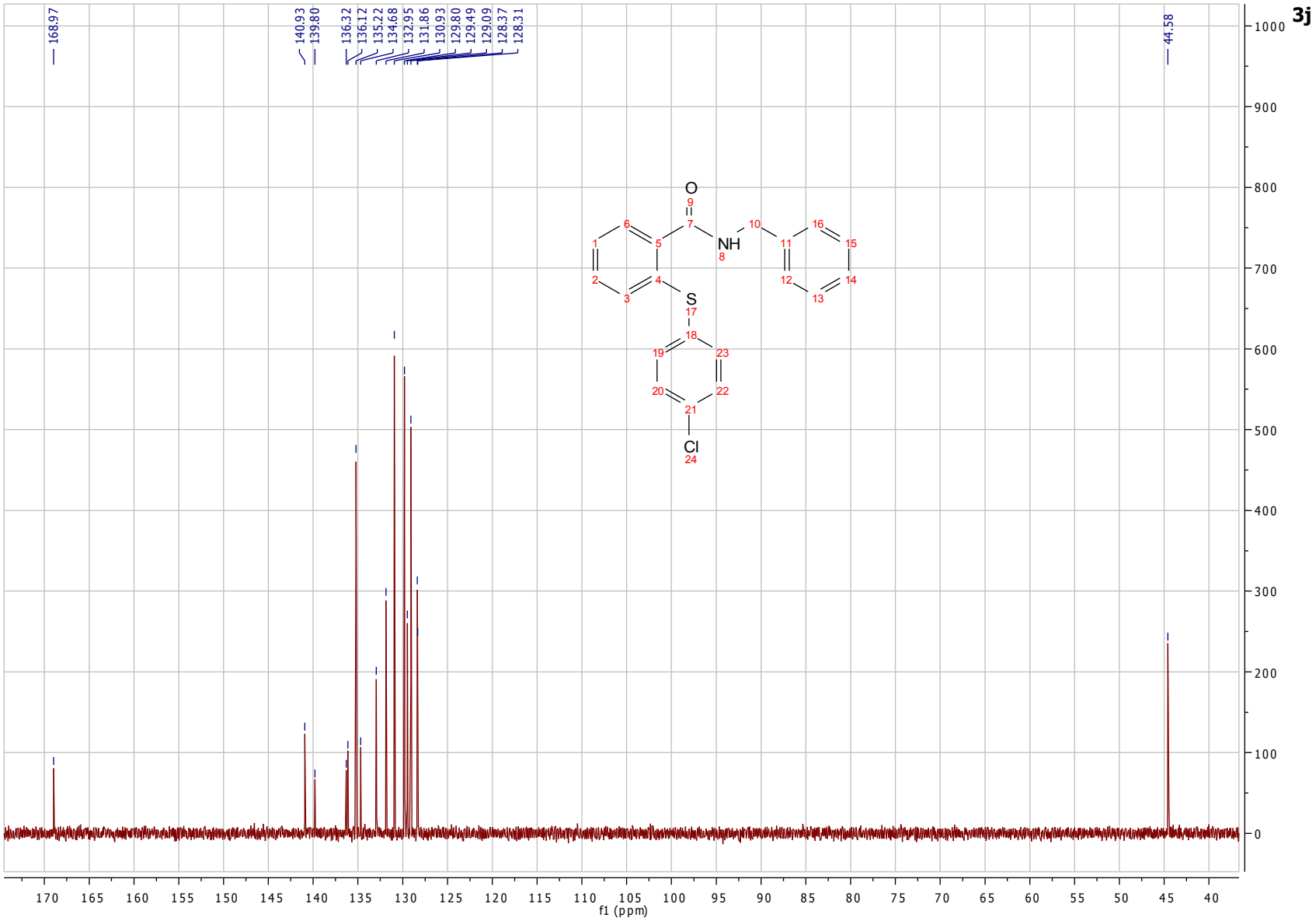

3h
A (s) 8.06
B (m) 7.60
C (ddd) 7.48
D (td) 7.51
E (m) 7.25
F (m) 7.38
G (m) 7.31
H (d) 4.58
O
NH
S
Br
f1 (ppm)

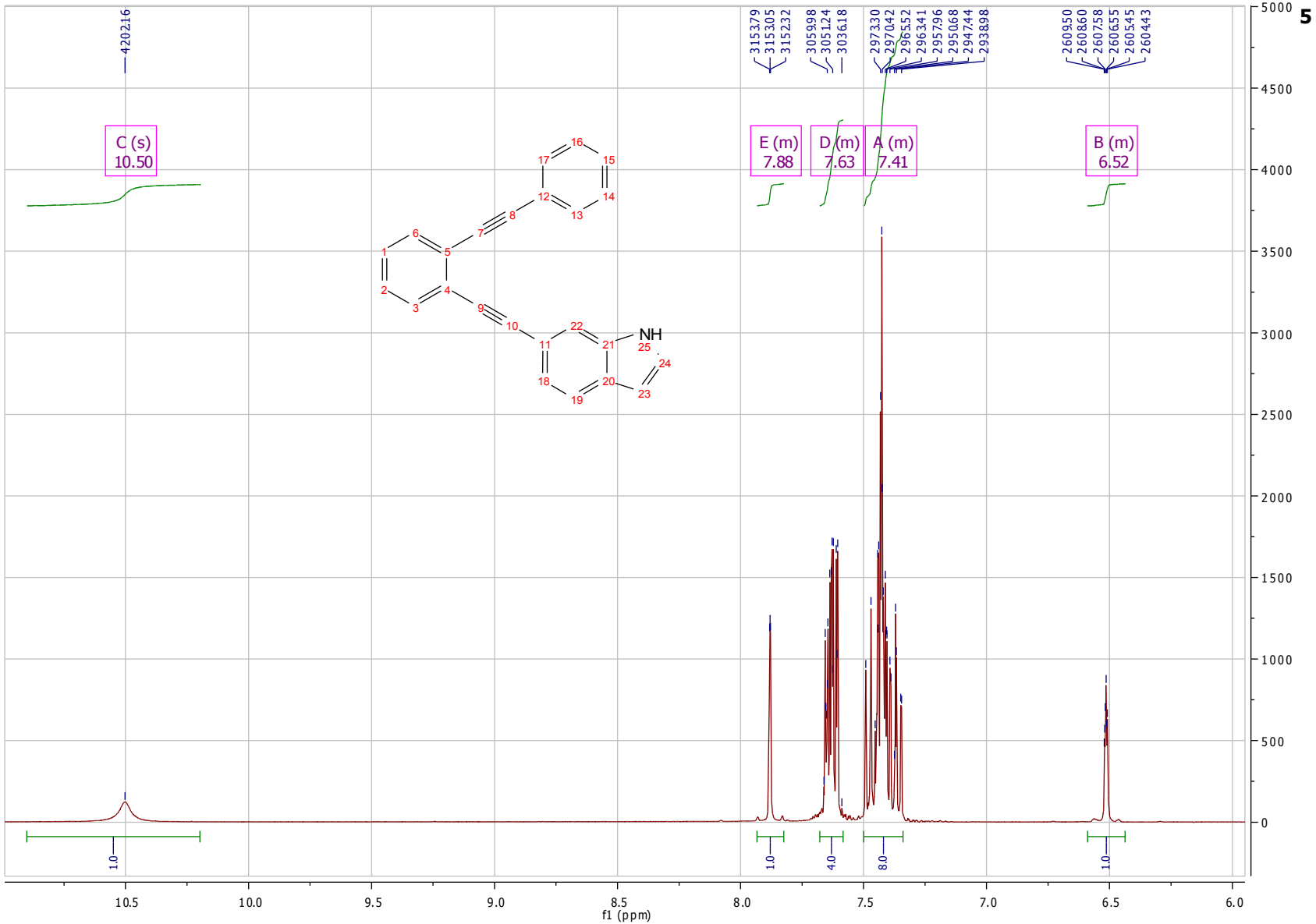

3h
168.97
140.91
140.65
140.30
132.53
131.93
131.79
128.87
128.38
124.05
44.59
O
11
7
NH
8
9
10
16
15
12
14
13
6
5
1
2
4
3
S
17
18
19
23
20
22
21
Br
24
f1 (ppm)

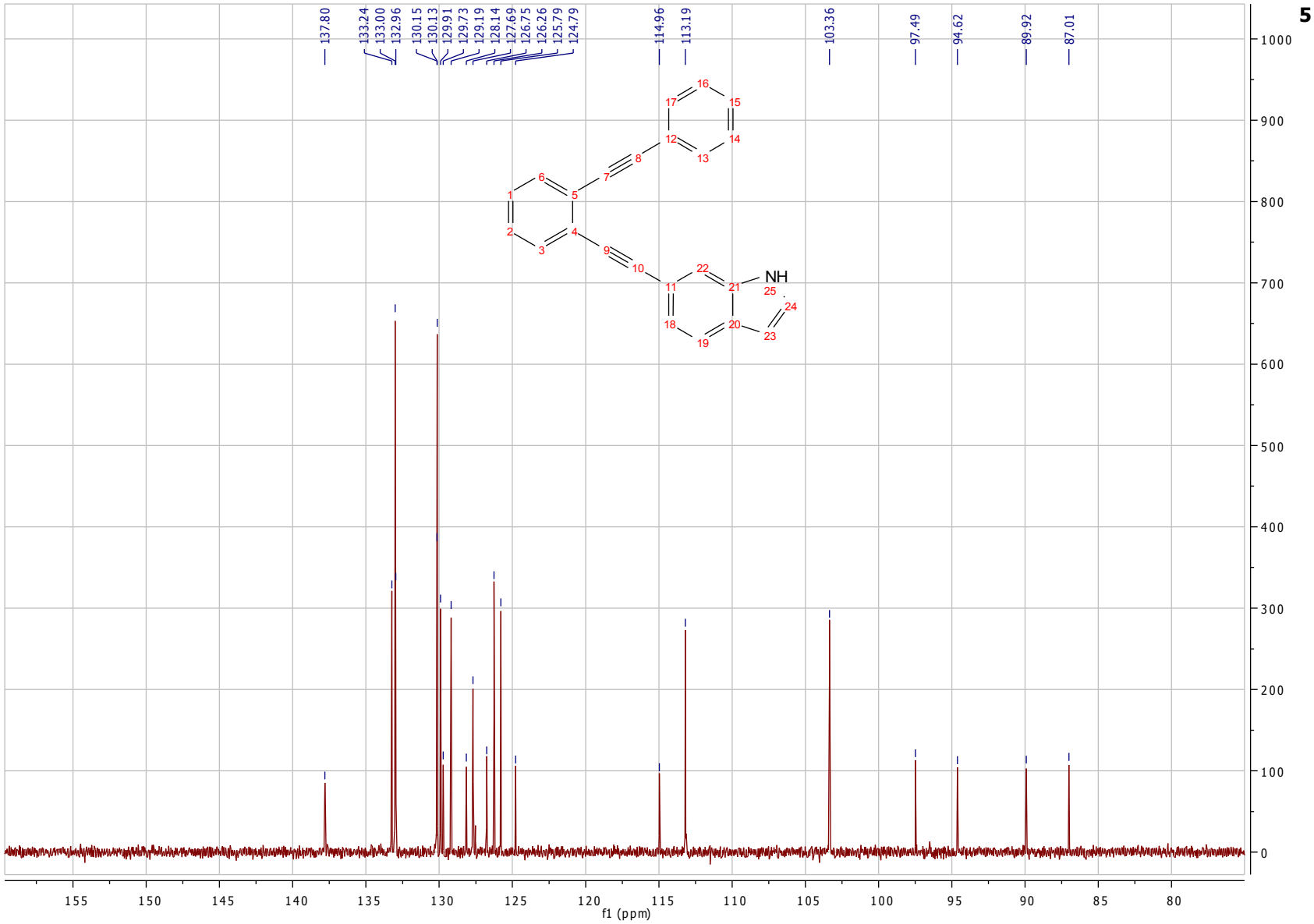

3i
G (m) 8.10
A (ddd) 7.71
B (m) 7.63
F (m) 7.42
D (tt) 7.23
C (m) 7.29
E (d) 4.56
f1 (ppm)


3i
168.90
150.35
141.63
141.00
140.82
137.79
133.49
131.84
128.38
126.02
123.09
44.56
f1 (ppm)


3j
A (s)
8.04
B (ddd)
7.59
C (ddd)
7.17
D (tt)
7.24
E (m)
7.34
F (d)
4.58
NH
S
Cl
f1 (ppm)


3j
168.97
140.93
139.80
136.32
136.12
135.22
134.68
132.95
131.86
130.93
129.80
129.49
129.09
128.37
128.31
44.58
O
NH
S
Cl
f1 (ppm)


5
C (s) 10.50
E (m) 7.88
D (m) 7.63
A (m) 7.41
B (m) 6.52
NH
f1 (ppm)


5
137.80
133.24
133.00
132.96
130.15
130.13
129.91
129.73
129.19
128.14
127.69
126.75
126.26
125.79
124.79
114.96
113.19
103.36
97.49
94.62
89.92
87.01
NH
f1 (ppm)