Supporting Information

Cu and Ag catalyzed oxidative arylthiation of terminal acetylenes

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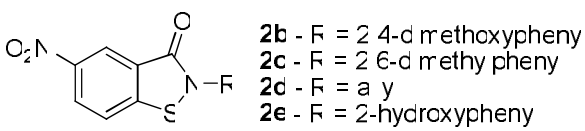
General Experimental.

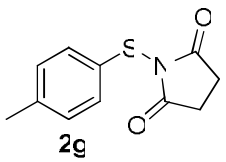
^{1}H NMR and ^{13}C NMR spectra were recorded at Bruker Avance 400 MHz NMR spectrometer with solvent residual peak ($CDCl_3$: ^{1}H = 7.24 ppm, ^{13}C =77.23; $(CD_3)_2CO$: ^{1}H = 2.05 ppm, ^{13}C = 206,68 ppm; $(CD_3)_2SO$: ^{1}H = 2.50 ppm, ^{13}C = 39.51 ppm) as the internal reference unless otherwise 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 a Boetius block and are not corrected. Column chromatography procedures were followed using 70-230 µm silica gel. Visualization was effected with ultraviolet light.

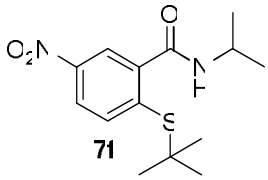
Terminal acetylenes, were obtained from commercial sources and used without further purification. Solvents such as DMF, DME for reaction media were obtained from commercial sources, dried over 4 Å molecular sieves and titrated for water level with a Karl Fischer Coulometer (Mettler Toledo DL 32) (water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

Synthesis of *N*-thioamides and Terminal Acetylenes

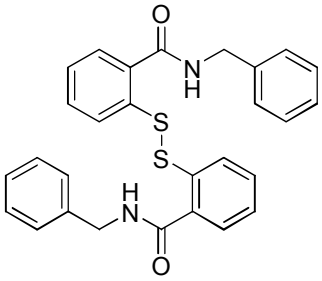
N-Thioamide **2b-2e**, *N*-Thioimide **2g**, *tert*-butylthio derivative **6f,** 2-chloro-5-nitrobenzoyl chloride and copper(I) 3-methylsalicylate (CuMeSal) were prepared according to the previously reported procedure.[1,2]



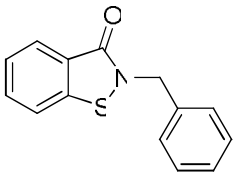




[1] Henke, A.; Srogl, J. *J. Org. Chem*. **2008**, 73, 7783–7784.
[2] Savarin, C.; Srogl, J.; Liebeskind, L. C. *Org. Lett*. **2001**, *3*, 91-93.

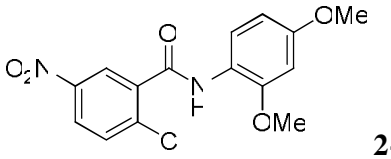


2,2'-Disulfanediylbis(*N*-benzylbenzamide) (7a). A mixture of 2,2´-dithiosalicylic acid (1.80 g; 5.86 mmol) and $SOCl_2$ (25 ml) was heated for 8 h at reflux. The excess $SOCl_2$ was evaporated and crude chloride was used in next step without a purification. Benzylamine (2,8 ml; 25.65 mmol) was disolved in dry THF (45 ml), the reaction mixture was cooled down to 0 °C under dry atmosphere and crude chloride was added stepwise. The mixture was stirred for 30 min at 0 °C and for 2.5 h at room temperature. It was poured in ice cooled 5% aqueous hydrochloric acid, the formed solid was filtered after 1 h and washed with water. Amide **7a** was obtained after drying and recrystallization from EtOH/acetone as a white crystalline product in 75 % yield (2.13 g). M.p.206.5-209 °C, (lit. 206 °C).[3] ^{1}H NMR (400 MHz, DMSO-d6): δ 9.21 (t, *J* = 6.0, 1H), 7.71 (dd, *J* = 1.2, 7.7, 1H), 7.66 (dd, *J* = 0.9, 8.1, 1H), 7.47 – 7.41 (m, 1H), 7.41 – 7.22 (m, 6H), 4.51 (d, *J* = 6.0, 2H). ^{13}C NMR (101 MHz, DMSO-d6): δ 166.8, 139.2, 136.8, 133.79, 131.1, 128.2, 127.9, 127.2, 126.8, 125.9, 125.8, 42.6.

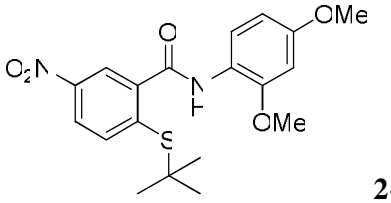


2-Benzylbenzo[d]isothiazol-3(2H)-one (2a). Disulfide **7a** (200 mg; 0.41 mmol) was dissolved in DMF (1 ml) and CuMeSal (3.0 mg; 3 mol%) was added. Reaction mixture was stirred 2 days at 60 °C. When the reaction was complete, it was poured in ice cooled 5% hydrochloric acid. It was extracted with ethyl acetate (3x15 ml). The combined organic layers were dried with $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography (hexane/Et_2O/acetone 5:1:2) to afford **2a** in 90 % yield (180 mg). M.p. 86-88,5 °C. (lit. 86-89 °C).[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.03 (m, 1H), 7.60 – 7.54 (m, 1H), 7.47 (dt, *J* = 0.8, 8.1, 1H), 7.41 – 7.36 (m, 1H), 7.36 – 7.27 (m, 5H), 5.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.6, 140.6, 136.4, 132.0, 129.0, 128.7, 128.5, 127.0, 125.7, 124.7, 120.6, 47.8.

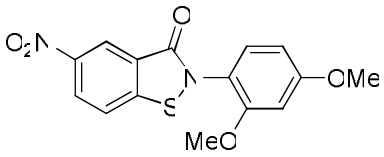
[3] Bartlett, R. G.; McClelland, E. W. *J. Chem. Soc.* **1934**, 818.
[4] Grivas, J. C. *J. Org. Chem.* **1975**, *40*, 2029.



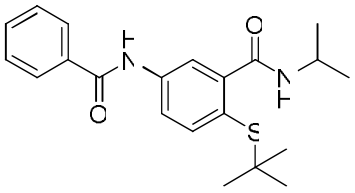
2-Chloro-*N*-(2,4-dimethoxyphenyl)-5-nitrobenzamide (8b). Amide **8b** was obtained from 2,4-dimethoxyaniline (5.0 g; 32.64 mmol) and 2-chloro-5-nitrobenzoyl chloride (6.0 g; 27.27 mmol) as a yellow-orange crystalline product after recrystallization from acetone in 89% yield (8.20 g). M.p.186-186.5 °C. ^{1}H NMR (400 MHz, DMSO-d6): δ 9.86 (s, 1H), 8.35 (d, *J* = 2.7, 1H), 8.31 (dd, *J* = 2.8, 8.8, 1H), 7.84 (d, *J* = 8.8, 1H), 7.73 (d, *J* = 8.7, 1H), 6.66 (d, *J* = 2.6, 1H), 6.56 (dd, *J* = 2.7, 8.8, 1H), 3.81 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 163.0, 157.8, 152.5, 145.9, 137.9, 137.2, 131.2, 125.4, 124.6, 123.9, 119.2, 104.2, 99.0, 55.8, 55.4. IR (KBr): 3365 m (NH), 1666 s (CONH), 1650 s (CONH), 1528 s, 1348 s (NO_2), 1305 s, 1207 s, 1107 s, 1039 s, 1024 s, 936 s, 833 s, 740 s, 613 m cm^{-1}. Anal. calcd for $C_{15}H_{13}ClN_2O_5$: C, 53.50; H, 3.89; N, 8.32. Found: C, 53.46; H, 3.76; N, 8.21.



2-(*tert*-Butylthio)-*N*-(2,4-dimethoxyphenyl)-5-nitrobenz-amide (7b). *tert*-Butylthioether **7b** was obtained from amide **8b** (7.4 g; 21.98 mmol) as a yellow crystalline product after recrystallization from acetone in 92% yield (7.9 g). M.p.161-163 °C. ^{1}H NMR (400 MHz, DMSO-d6): δ 9.81 (s, 1H), 8.33 (d, *J* = 2.6, 1H), 8.27 (dd, *J* = 2.7, 8.6, 1H), 7.89 (d, *J* = 8.6, 1H), 7.78 (d, *J* = 8.7, 1H), 6.66 (d, *J* = 2.6, 1H), 6.56 (dd, *J* = 2.6, 8.8, 1H), 3.84 (s, *J* = 20.0, 3H), 3.77 (s, *J* = 5.1, 3H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d6): δ 164.3, 157.5, 152.2, 146.5, 143.2, 139.4, 137.6, 124.4, 123.6, 122.9, 119.7, 104.3, 99.0, 55.8, 55.4, 48.5, 31.0. IR (KBr): 3215 m (NH), 3194 m (NH), 1657 s (CONH), 1536 s (CONH), 1524 s (NO_2), 1348 s (NO_2), 1286 s, 1209 s, 1158 s, 1045 m, 1034 m, 930 m, 832 m, 741 m cm^{-1}. Anal. calcd for $C_{19}H_{22}N_2O_5S$: C, 58.45; H, 5.68; N, 7.17. Found: C, 58.40; H, 5.66; N, 7.02.

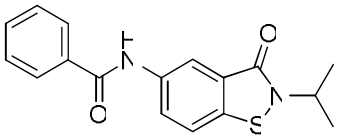


2-(2,4-Dimethoxyphenyl)-5-nitrobenzo[*d*]isothiazol-3(2*H*)-one (2b). *N*-thioamide **2b** was obtained from *tert*-butylthioether **7b** (4,0 g; 10.24 mmol) as a yellow crystalline product after recrystallization from THF/hexane in 82% yield (2.81 g). M.p. 199-200,5 °C (ethanol). ^{1}H NMR (400 MHz, DMSO-d6): δ 8.56 (d, *J* = 1.9, 1H), 8.53 (dd, *J* = 2.4, 8.9, 1H), 8.28 (d, *J* = 8.8, 1H), 7.38 (d, *J* = 8.6, 1H), 6.77 (d, *J* = 2.6, 1H), 6.65 (dd, *J* = 2.6, 8.7, 1H), 3.84 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 162.9, 161.4, 156.6, 148.1, 145.5, 130.9, 126.2, 124.1, 123.7, 121.2, 116.2, 105.4, 99.5, 56.0, 55.6. IR (KBr): 1657 s (C=O), 1518 s (NO_2), 1509 s, 1340 s (NO_2), 1282 m, 1264 s, 1208 s, 1038 m, 1025 s, 827 m, 742 m cm^{-1}. Anal. calcd for $C_{15}H_{12}N_2O_5S$: C, 54.21; H, 3.64; N, 8.34. Found: C, 53.82; H, 3.61; N, 8.19.

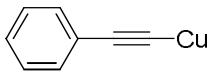


5-Benzamido-2-(tert-butylthio)-*N*-isopropylbenzamide (7f-2). *tert*-Butylthioether **7f** (7.4 g; 25.0 mmol) was dissolved in EtOH (250 ml). Charcoal (200 mg) and hydrazine hydrate (10 ml) were added and resulting reaction mixture was heated for 16 h at 50 °C under presure of Ar. After removing the solvent and excess of hydrazine by co-destialtion with ethanol (4x150 ml), the crude solid product was used without further purification in next step. The crude amine was dissolved in THF (100 ml), potassium carbonate (10 g) was added and the reaction mixture was cooled down to 0 °C. Benzoyl chloride (4.2 g; 3.5 ml) was slowly added and reaction was stirred for 6 h at 0 °C. The inorganic salts were filtered and the solvent was removed. Amide **6f-2** was obtained after drying as a white solid product in 78 % yield (7.22 g). M.p.206-208 °C (ethyl acetate/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (s, 1H), 8.36 (dd, *J* = 2.6, 8.5, 1H), 8.05 (d, *J* = 2.6, 1H), 7.96 (d, *J* = 7.4, 1H), 7.93 – 7.88 (m, 2H), 7.55 (d, *J* = 8.4, 1H), 7.52 (dt, *J* = 1.7, 2.5, 1H), 7.47 – 7.42 (m, 2H), 4.02 – 3.91 (m, 1H), 1.24 (s, 9H), 1.14 (d, *J* = 6.6, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.4, 166.3, 141.5, 141.1, 140.2, 135.0, 132.2, 128.9, 127.6, 123.5, 122.4, 121.7, 48.8, 42.4, 30.9, 22.8. IR (KBr): 3288 s (NH), 3253 m (NH), 3162 m(NH), 1672 s (CONH), 1633 s (CONH), 1590 s, 1580 s, 1538 s (CONH), 1523 s (CONH), 1468 s, 1456 s,

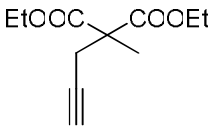
1311 s (CONH), 1258 s, 1165 m, 905 m, 893 m, 700 s cm^{-1}. Anal. calcd for $C_{21}H_{26}N_2O_2S$: C, 68.08; H, 7.07; N, 7.56. Found: C, 67.92; H, 6.92; N, 7.47.



***N*-(2-Isopropyl-3-oxo-2,3-dihydrobenzo[d]isothiazol-5-yl)benzamide** (2f). TMSCl (0.51 ml, 4.02 mmol) was added to a solution of *tert*-butylthioether **6f-2** (800 mg; 2.21 mmol) and DMSO (0.3 ml; 4.22 mmol) in dry dichloromethane (35 ml). The reaction mixture was stirred for 2 h at 0 °C and overnight at room temperature under drying tube. Hexane was added (aprox. 50 ml) and the mixture was allowed to stand for 3 h in freezer. The product was separated by filtration and washed with hexane. *N*-thioamide **2f** was obtained after drying as an yellowish crystalline product in 87 % yield (590 mg). M.p. 189-190.5 °C (ethyl acetate). ^{1}H NMR (400 MHz, DMSO-d6): δ 10.50 (s, 1H), 8.43 (d, *J* = 1.9, 1H), 8.04 (dd, *J* = 2.1, 8.8, 1H), 8.02 – 7.97 (m, 2H), 7.93 (d, *J* = 8.8, 1H), 7.65 – 7.58 (m, 1H), 7.58 – 7.52 (m, 2H), 4.84 – 4.73 (m, 1H), 1.35 (d, *J* = 6.7, 6H). ^{13}C NMR (101 MHz, DMSO-d6): δ 165.6, 163.7, 137.1, 134.6, 134.6, 131.6, 128.3, 127.6, 125.2, 124.6, 121.9, 116.1, 45.4, 21.7. IR (KBr): 3336 s (NH), 2979 m (CH_3), 1674 s, 1636 s (CONH), 1585 m, 1524 s (CONH), 1471 s, 1303 s (CONH), 1263 m, 1255 m, 888 m, 825 s, 766 m, 712 s cm^{-1}. Anal. calcd for $C_{17}H_{16}N_2O_2S$: C, 65.36; H, 5.16; N, 8.97. Found: C, 65.09; H, 5.09; N, 8.79.



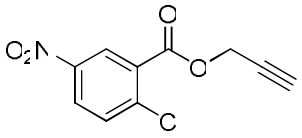
(Phenylethynyl)copper (1a) was prepared from phenylacetylene (1.07 g; 10.5 mmol) and CuI (2.02 g; 10.5 mmol) following the procedure described by Lei [5] in 32 % yield (0.55 g).



Diethyl 2-methyl-2-(prop-2-ynyl)malonate (1b) was prepared from diethyl 2-methylmalonate (1.74 g; 10 mmol) following the procedure described by Dénès and Renaud[6] in 90 % yield (1.9 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.26 – 4.11 (m, 4H), 2.76 (d, *J*

[5] Shi, W.; Luo, Y.; Luo, X.; Chao, L.; Zhang, H.; Wang, J.; Lei, A. *J. Am. Chem. Soc.* **2008**, *130*, 14713.
[6] Beaufils, F.; Dénès, F.; Renaud, P. *Org. Lett.* **2004**, *6*, 2563.

= 2.7, 2H), 1.99 (t, *J* = 2.7, 1H), 1.53 (d, *J* = 8.8, 3H), 1.23 (t, *J* = 7.1, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0, 79.5, 71.4, 61.8, 53.3, 26.0, 19.9, 14.2.



Prop-2-ynyl 2-chloro-5-nitrobenzoate (1c). The solution of propargyl acohol (0.60 ml; 10.20 mmol), pyridine (0.80 ml; 10.2 mmol) and *N*,*N*-dimethylaminopyridine (5 mg) in dry dichloromethane (25 ml) was cooled down to 0 °C under atmosphere of Ar. Chloride **5** was added stepwise. The reaction mixture was stirred for 1 h at 0 °C , washed twice with HCl (5% water solution), brine and organic layer was dried with $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography (dichloromethane) to afford **1c** in 96 % yield (1.57 g). M.p. 85.5-86.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 2.7, 1H), 8.28 (dd, *J* = 2.7, 8.8, 1H), 7.65 (d, *J* = 8.8, 1H), 4.97 (d, *J* = 2.5, 2H), 2.56 (t, *J* = 2.5, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.8, 146.4, 141.3, 132.7, 130.5, 127.4, 127.0, 76.9, 76.2, 53.8. IR ($CDCl_3$): 3308 s, 2135 w, 1746 s (C=O), 1612 s, 1577 s, 1529 s (NO_2), 1469 s, 1352 s (NO2), 1306 s, 1271 s, 1242 s, 1214 s, 1128 s, 1050 s, 983 m, 839 s, 787 m cm^{-1}. Anal. calcd for $C_{10}H_6ClNO_4$: C, 50.13; H, 2.52; N, 5.85. Found: C, 50.07; H, 2.55; N, 5.48.

Copper Catalyzed Microwave Irradiation Experiments (Method A)

All microwave irradiation experiments were carried out in a CEM-Discover microwave system operating at a frequency of 2.45 GHz. *N*-Thioamide (0.5 mmol – 1.0 mmol), CuMeSal (1-3 mol%) and corresponding acetylene (1.3-2.0 eq.) (for solid acetylene) were added to a microwave tube (10 ml). The tube was sealed with a CEM "snap-on" cap and system was purged with Ar. DMF (purged with Ar before using) (1-2 ml) and corresponding acetylene (for liquid acetylene) were added via needle and syringe trough the septum directly into the microwave tube. Resulting reaction mixture was purged with Ar and irradiated in microwave oven with gas jet cooling (the power, exact times and temperature observed are included for individual trasformations below). The reaction progress was followed by UPLC. If the catalyst was added twice (for some of these experiments), the second portion was added as a solution in dry DMF, wich was purged with Argon before using. After the reaction was completed the mixture was poured in ice cooled 5% hydrochloric acid or water (in case of pyridine derivatives) and quenched reaction mixture was stirred for 0.5-3 h. The precipitate

was filtered, washed with water and dried (for solid crude product). It was extracted with ethyl acetate (3x). The combined organic layers were dried with $MgSO_4$, filtered and solvent was evaporated (for oil crude product). The product was purified by recrystallization or column chromatography.

Copper Catalyzed Non Irradiation Experiments (Method B)

N-Thioamide (1 mmol – 4.0 mmol), CuMeSal (1-3 mol%) and corresponding acetylene (1.3-2.0 eq.) (for solid acetylene) were added to a Schlenk flask (25 ml). The flask was sealed with a Suba-Seal and system was purged with Ar. DMF (purged with Ar before using) (3 ml) and corresponding acetylene (for liquid acetylene) were added via needle and syringe trough the septum directly into the Schlenk flask. The resulting reaction mixture was purged with Ar and stirred at 50-80 °C (exact times and temperature are included for individual trasformations below). The reaction progress was followed by UPLC. It was poured in ice cooled 5% hydrochloric acid or water (in case of pyridine derivatives) and the quenched reaction mixture was stirred for 0.5-3 h. The precipitate was filtered and washed with water. After drying the crude product was purified by recrystallization or column chromatography.

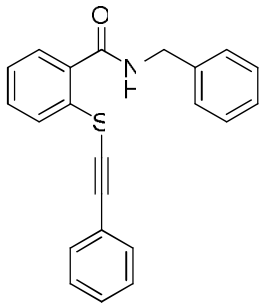
Silver Catalyzed Microwave Irradiation Experiments (Method C)

All microwave irradiation experiments were carried out in a CEM-Discover microwave system operating at a frequency of 2.45 GHz. *N*-Thioamide (0.7 mmol – 2.0 mmol), AgOAc (1-3 mol%) were added to a microwave tube (10 ml). The tube was sealed with a CEM “snap-on“ cap. DMF (1-2 ml) and corresponding acetylene (1.2-2.0 eq.) were added. The resulting reaction mixture was irradiated in microwave oven with gas jet cooling (the power, exact times and temperature observed are included for individual trasformations below). The reaction progress was followed by UPLC. If the catalyst was added twice (for some of these experiments), the second portion was added as a solid. It was poured in ice cooled 5% hydrochloric acid. The quenched reaction mixture was stirred for 0.5-1 h. The precipitate was filtered, washed with water. Product was purified by recrystallization or column chromatography.

Silver Catalyzed Non Irradiation Experiments (Method D)

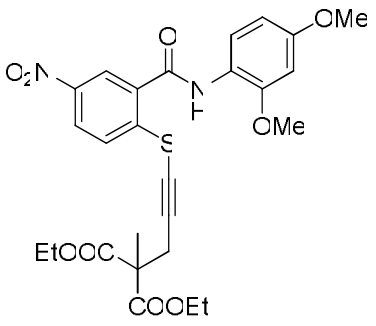
N-Thioamide (1 mmol – 1.5 mmol), AgOAc (1-3 mol%) were added to a reaction tube. DMF (1.5-3 ml) and corresponding acetylene were added and the reaction tube was sealed with a cap. The resulting reaction mixture was stirred at 50-70 °C (the exact times and temperature are included for individual trasformations below). The reaction progress was followed by UPLC. It was poured in ice cooled 5% hydrochloric acid and the quenched reaction mixture was stirred for 0.5-1 h. The precipitate was filtered and washed with water. After drying the crude product was purified by recrystallization or column chromatography.

Experiments with stoichiometric amount of phenylacetylide (1a)**.**
N-Thioamide **2d** (0.1 mmol) or *N*-thioimide **2g** (0.1 mmol) or di(4-tolyldisulfide) and phenylacetylide **1a** (0,105 mmol) were dissolved in DMF (1 mL) (poured with Ar before using) under presure of Ar. The reaction mixture was stirred for 14 h at 60 °C. The reaction progerss was folowed by HPLC.

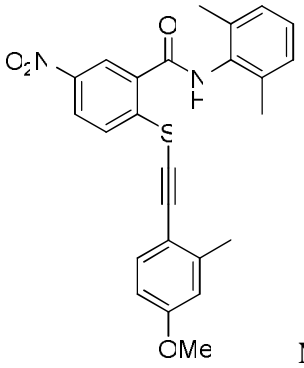


***N*-benzyl-2-(phenylethynylthio)benzamide** (3a). The Method A was followed, using *N*-thioamide **2a** (140 mg; 0.58 mmol) and phenylacetylene (0.13 ml; 1.16 mmol). The reaction mixture was irradiated under 150 W maximum microwave power to raise the internal temperature to 175 °C and the temperature was maintained for 1 h. The next portion of CuMeSal (1 mol %) was added and the reaction mixture was irradiated under 250 W maximum microwave power to raise the internal temperature to 200 °C and the temperature was maintained for 10 min. Thioacetylene **3a** was obtained as a white crystalline product after column chromatography (hexane/Et_2O/acetone 5:1:2) in 90% yield (180 mg).
The Method C was followed, using *N*-thioamide **2a** (0.49 mg; 2.00 mmol) and phenylacetylene (0.45 ml; 4.00 mmol). The reaction mixture was irradiated under 130 W maximum microwave power to raise the internal temperature to 165 °C and the temperature was maintained for 0.5 h. The next portion of AgOAc (1 mol %) was added and the reaction

mixture was irradiated under 130 W maximum microwave power to raise the internal temperature to 165 °C and the temperature was maintained for 10 min. Thioacetylene **3a** was obtained as a white crystalline product after column chromatography (CH_2Cl_2) in 88% yield (610 mg). M.p.123.5-125.5 °C. ^{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. IR (KBr): 3282 s (NH), 3078 w, 3062 w, 3032 w, 2166 w, 1635 (CONH), 1541 m (CONH), 1435 m, 1365 w, 1315 m, 752 s, 734 s, 691 s cm^{-1}. Anal. calcd for $C_{22}H_{17}NOS$: C, 76.94; H, 4.99; N, 4.08. Found: C, 76.84; H, 4.99; N, 3.93.

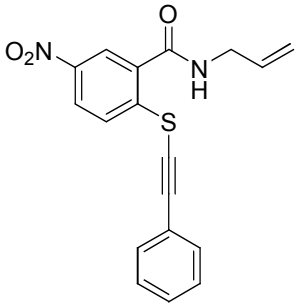


Diethyl 2-(3-(2-(2,4-dimethoxyphenylcarbamoyl)-4-nitrophenylthio)prop-2-ynyl)-2-methylmalonate (3b). The Method A was followed, using *N*-thioamide **2b** (230 mg; 0.70 mmol) and diethyl 2-methyl-2-(prop-2-ynyl)malonate (0.19 ml; 0.91 mmol). The reaction mixture was irradiated under 100 W maximum microwave power to raise the internal temperature to 150 °C and the temperature was maintained for 10 min. Thioacetylene **3b** was obtained as a yellow crystalline product after recrystallization from EtOAc/hexane in 92 % yield (350 mg). M.p. 119-120.5 °C. ^{1}H NMR (400 MHz, acetone-d6): δ 9.23 (bs, 1H), 8.67 (s, 1H), 8.37 (dd, *J* = 2.4, 8.9, 1H), 8.22 (d, *J* = 8.9, 1H), 7.94 (d, *J* = 8.7, 1H), 6.66 (d, *J* = 2.6, 1H), 6.57 (dd, *J* = 2.6, 8.8, 1H), 4.27 – 4.18 (m, 4H), 3.87 (s, 3H), 3.82 (s, 3H), 3.11 (s, 2H), 1.57 (s, 3H), 1.24 (t, *J* = 7.1, 6H). ^{13}C NMR (101 MHz, acetone-d6): δ 171.9, 164.9, 159.8, 153.6, 147.3, 146.3, 134.4, 129.6, 126.8, 125.2, 124.3, 121.6, 105.7, 100.3, 99.3, 69.9, 63.0, 57.0, 56.5, 54.7, 28.9, 21.0, 15.0. IR (KBr): 3397 m (NH), 3099 w, 3084 w, 2981 w, 2939 w, 2837 w, 2196 w, 1735 s (C=O), 1663 s (CONH), 1605 m, 1537 s (CONH), 1518 s (NO_2), 1456 m, 1417 m, 1343 s (NO_2), 1301 m, 1248 m, 1207 s, 1113 m, 1029 m cm^{-1}. Anal. calcd for $C_{26}H_{28}N_2O_9S$: C, 57.34; H, 5.18; N, 5.14. Found: C, 57.18; H, 5.19; N, 5.02.

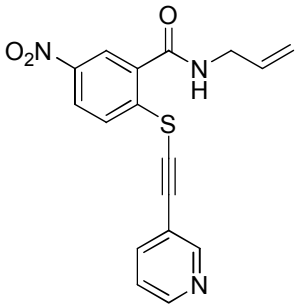


N-(2,6-dimethylphenyl)-2-((4-methoxy-2-methylphenyl)ethynyl-thio)-5-nitrobenzamide (3c). The Method A was followed, using *N*-thioamide **2c** (300 mg; 1.00 mmol) and diethyl 1-ethynyl-4-methoxy-2-methylbenzene (200 mg; 1.40 mmol). The reaction mixture was irradiated under 100 W maximum microwave power to raise the internal temperature to 150 °C and the temperature was maintained for 20 min. Thioacetylene **3c** was obtained as a yellow crystalline product after recrystallization from EtOH in 86 % yield (385 mg).

The Method D was followed, using *N*-thioamide **2c** (300 mg; 1.00 mmol) and diethyl 1-ethynyl-4-methoxy-2-methylbenzene (200 mg; 1.40 mmol). The reaction mixture was stirred for 30 h at 55 °C. Thioacetylene **3c** was obtained as a yellow crystalline product after recrystallization from EtOH in 90 % yield (400 mg). M.p. 240-241 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 2.3, 1H), 8.31 (dd, *J* = 2.3, 8.9, 1H), 8.22 (d, *J* = 8.9, 1H), 7.47 (bs, 1H), 7.44 (d, *J* = 8.5, 1H), 7.19 – 7.09 (m, 3H), 6.77 (d, *J* = 2.4, 1H), 6.71 (dd, *J* = 2.5, 8.5, 1H), 3.81 (s, 3H), 2.46 (s, 3H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d6): δ 163.5, 160.2, 145.2, 144.5, 142.6, 135.3, 134.1, 134.1, 131.4, 128.0, 127.8, 127.1, 126.2, 122.9, 115.2, 113.2, 111.9, 99.1, 76.9, 55.3, 20.6, 18.0. IR (KBr): 3222 m (NH), 3019 w, 2961 w, 2940 w, 2918 w, 2837 w, 2151 w, 1642 s (CONH), 1604 s, 1570 m, 1514 s (NO_2), 1496 s, 1467 m, 1376 w, 1342 s (NO_2), 1319 m (CONH), 1299 m, 1283 m, 1257 m, 1229 m, 1047 m, 831 m, 767 m, 739 m cm^{-1}. Anal. calcd for $C_{20}H_{18}N_2O_5S$: C, 67.25; H, 4.97; N, 6.27. Found: C, 67.19; H, 4.86; N, 6.15.

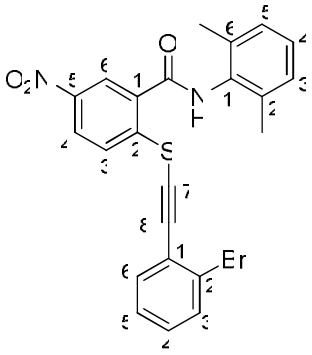


***N*-Allyl-5-nitro-2-(phenylethynylthio)benzamide** (3d). The Method B was followed, using *N*-thioamide **2d** (0.94 g; 4.00 mmol) and phenylacetylene (0.8 ml; 1.82 mmol). After 44 h at 65 °C thioacetylene **3d** was obtained as a yellow crystalline product after recrystallization from EtOH/acetone in 93% yield (1.25 g). M.p.179-180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 2.4, 1H), 8.28 (dd, *J* = 2.4, 8.9, 1H), 8.18 (d, *J* = 8.9, 1H), 7.57 – 7.49 (m, 2H), 7.40 – 7.32 (m, 3H), 6.30 (bs, 1H), 5.94 (ddt, *J* = 5.8, 10.2, 16.1, 1H), 5.36 – 5.27 (m, 1H), 5.27 – 5.21 (m, 1H), 4.10 (tt, *J* = 1.4, 5.8, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.2, 145.9, 145.6, 133.3, 132.3, 131.9, 129.6, 128.8, 128.8, 125.8, 122.3, 122.0, 118.0, 100.9, 75.2, 43.0. IR (KBr): 3290 m (NH), 3090 w, 3072 w, 3065 w, 2170 w, 1628 (CONH), 1600 m, 1532 m (CONH), 1517 s (NO_2), 1486 m, 1342 s (NO_2), 1314 m (CONH), 924 m, 757 m, 737 m 692 m cm^{-1}. Anal. calcd for $C_{18}H_{14}N_2O_3S$: C, 63.89; H, 4.17; N, 8.28. Found: C, 63.74; H, 4.08; N, 8.07.

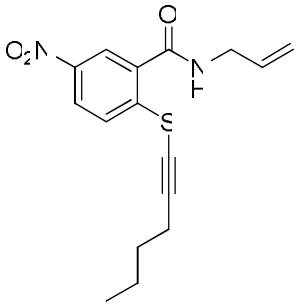


***N*-Allyl-5-nitro-2-(pyridin-3-ylethynylthio)benzamide** (3e). The Method B was followed, using *N*-thioamide **2d** (0.71 g; 3.00 mmol) and 3-ethynylpyridine (0.43 g; 4.20 mmol). After 4 days at 55 °C thioacetylene **3e** was obtained as a beige crystalline product after recrystallization from EtOH in 96 % yield (0.98 g). M.p.170-172.5 °C. ^{1}H NMR (400 MHz, DMSO-d6): δ 9.32 (t, *J* = 5.6, 1H), 8.86 (s, 1H), 8.72 (d, *J* = 2.5, 1H), 8.64 (s, 1H), 8.44 (dd, *J* = 2.5, 8.9, 1H), 8.27 (d, *J* = 8.9, 1H), 8.07 (dt, *J* = 1.7, 7.9, 1H), 7.54 – 7.45 (m, *J* = 4.8, 7.8, 1H), 5.92 (ddt, *J* = 5.3, 10.5, 17.2, 1H), 5.27 – 5.19 (m, 1H), 5.18 – 5.11 (m, 1H), 3.98 – 3.88 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d6): δ 164.4, 151.8, 149.4, 145.4, 143.1, 138.8, 134.5, 131.1, 128.2, 126.0, 123.5, 122.8, 118.7, 115.8, 96.6, 79.8, 41.7. IR (KBr): 3285 s (NH), 3089 w, 3074 w, 2173 w, 1651 s, 1637 s (CONH), 1602 m,

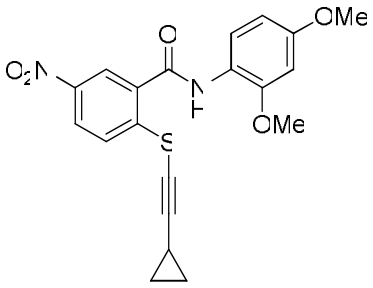
1552 s (CONH), 1512 s (NO_2), 1409 m, 1343 s (NO_2), 1314 m (CONH), 1287 m, 1248 m, 1047 m, 1022 m, 909 m, 817 m, 740 m, 703 m cm^{-1}. Anal. calcd for $C_{17}H_{13}N_3O_3S$: C, 60.17; H, 3.86; N, 12.38. Found: C, 60.20; H, 4.00; N, 12.30.



2-((2-Bromophenyl)ethynylthio)-*N*-(2,6-dimethylphenyl)-5-nitrobenzamide (3f). The Method A was followed, using *N*-thioamide **2c** (150 mg; 0.50 mmol) and 1-bromo-2-ethynylbenzene (0.09 ml; 0.70 mmol). The reaction mixture was irradiated under 120 W maximum microwave power to raise the internal temperature to 160 °C and the temperature was maintained for 15 min. Thioacetylene **3f** was obtained as an yellow crystalline product after recrystallization from EtOAc in 83 % yield (200 mg). M.p. 242-243.5 °C. ^{1}H NMR (500 MHz, DMF-d7): 10.59 (bs, 1H, NH), 9.03 (d, $J_{6,4}$ = 2,4, 1H, H-6), 8.67 (dd, $J_{4,3}$ = 8.9, $J_{4,6}$ = 2.4, 1H, H-4), 8.60 (d, $J_{3,4}$ = 8.9, 1H, H-3), 7.84 (dd, $J_{4´,3´}$ = 8.1, $J_{3´,5´}$ = 1.2, 1H, H-3´), 7.81 (dd, $J_{6´,5´}$ = 87.7, $J_{6´,4´}$ = 1.7, 1H, H-6´), 7.53 (ddd, $J_{5´,6´}$ = 7.7, $J_{5´,4´}$ = 7.4, $J_{5´,3´}$ = 1.2, 1H, H-5´), 7.45 (ddd, $J_{4´,3´}$ = 8.1, $J_{4´,5´}$ = 7.4, $J_{4´,6´}$ = 1.7, 1H, H-4´), 7.20 (s, 3H, H-3´´,4´´,5´´), 2.35 (s, 6H, 2xCH_3). ^{13}C NMR (APT) (125.7 MHz, DMF-d7): 165.1 (C=O), 147.0 (C-5), 145.0 (C-2), 136.8 (C-2´´,6´´), 135.8 (C-1´´), 134.7 (CH-6´), 133.8 (CH-3´), 132. 8 (C-1), 132.0 (CH-4´), 129.8 (CH-3), 129.1 (CH-3´´,5´´), 129.0 (CH-5´), 128.3 (CH-4´´), 127.5 (CH-4), 125.5 (C-2´), 125.2 (C-1´), 124.4 (CH-6), 99.7 (C-8), 82.2 (C-7), 18.9 (CH_3). IR (KBr): 3245 m (NH), 2974 w, 2921 w, 2175 w, 1641 s (CONH), 1601 m, 1571 m, 1514 s (CONH, NO_2), 1467 m, 1342 s (NO_2), 1317 m, 1047 m, 764 m, 751 m, 738 m cm^{-1}. Anal. calcd for $C_{23}H_{17}N_2O_3S$: C, 57.39; H, 3.56; N, 5.82. Found: C, 57.52; H, 3.70; N, 5.70.



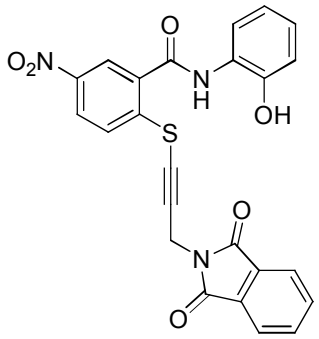
***N*-Allyl-2-(hex-1-ynylthio)-5-nitrobenzamide** (3g). The Method B was followed, using *N*-thioamide **2d** (0.71 g; 3.00 mmol) and hex-1-yne (0.45 ml; 3.60 mmol). After 3 days at 50 °C next portion of hex-1-yne (0.35 ml; 3.00 mmol) was added. After 2 days at 50 °C thioacetylene **3g** was obtained as a yellow crystalline product after column chromatography (EtOAc/hexane 1:3) in 73% yield (0.69 g). M.p.140-141.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 2.4, 1H), 8.25 (dd, *J* = 2.4, 8.9, 1H), 8.09 (d, *J* = 8.9, 1H), 6.28 (bs, 1H), 5.91 (ddt, *J* = 5.8, 10.2, 17.1, 1H), 5.32 – 5.25 (m, 1H), 5.24 – 5.19 (m, 1H), 4.07 (tt, *J* = 1.4, 5.8, 2H), 2.48 (t, *J* = 7.1, 2H), 1.64 – 1.55 (m, 2H), 1.51 – 1.40 (m, 2H), 0.94 (t, *J* = 7.3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.3, 146.7, 145.4, 133.4, 131.8, 128.4, 125.6, 122.0, 117.9, 103.6, 64.8, 42.9, 30.8, 22.2, 20.3, 13.8. IR ($CHCl_3$): 3440 m (NH), 3388 w (NH), 3343 w (NH), 3090 w, 3026 m, 3013 m, 2961 s, 2935 s, 2875 m, 2865 m, 2191 w, 1664 (CONH), 1602 s, 1573 s, 1517 s (NO_2), 1456 m, 1343 s, 1278 m, 1053 m, 918 m, 836 m, 668 m cm^{-1}. Anal. calcd for $C_{16}H_{18}N_2O_3S$: C, 60.36; H, 5.70; N, 8.80. Found: C, 60.36; H, 5.82; N, 8.73.



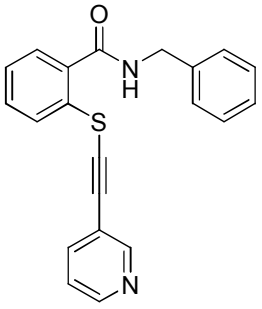
2-(Cyclopropylethynylthio)-*N*-(2,4-dimethoxyphenyl)-5-nitrobenzamide (3h). The Method B was followed, using *N*-thioamide **2b** (0.50 g; 1.50 mmol) and cyclopropylacetylene (0.19 ml; 2.25 mmol). After 41 h at 50 °C thioacetylene **3h** was obtained as a yellow crystalline product after recrystallization from acetone/EtOH in 89 % yield (535 mg).

The Method D was followed, using *N*-thioamide **2b** (0.50 g; 1.50 mmol) and cyclopropylacetylene (0.17 ml; 2.02 mmol). After 19 h at 50 °C thioacetylene **3h** was obtained as an yellow crystalline product after recrystallization from acetone/EtOH in 93 %

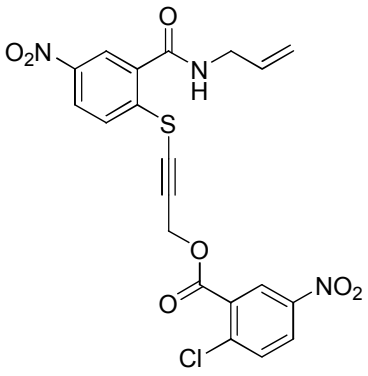
yield (555 mg). M.p. 202-203 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 2.1, 1H), 8.29 (dd, *J* = 2.4, 8.9, 1H), 8.27 – 8.22 (m, 1H), 8.16 (bs, 1H), 8.13 (d, *J* = 8.9, 1H), 6.53 – 6.48 (m, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 1.54 – 1.47 (m, 1H), 0.96 – 0.90 (m, 2H), 0.89 – 0.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.9, 157.6, 150.0, 147.1, 145.6, 132.7, 128.5, 125.6, 122.0, 121.5, 120.5, 107.2, 104.2, 99.0, 60.4, 56.1, 55.8, 9.6, 1.2. IR (KBr): 3274 m (NH), 3099 w, 3006 w, 2960 w, 2939 w, 2832 w, 2168 w, 1641 s (CONH), 1614 s, 1602 m, 1573 m, 1540 s (CONH), 1518 s (NO_2), 1503 s, 1462 s , 1454 s, 1417 s, 1341 s (NO_2), 1311 s (CONH), 1284 s, 1211 s, 1160 s, 1121 s, 1041 s, 1033 s,872 m, 836 s, 829 s, 739 m cm^{-1}. Anal. calcd for $C_{20}H_{18}N_2O_5S$: C, 60.29; H, 4.55; N, 7.03. Found: C, 60.16; H, 4.47; N, 6.89.



2-(3-(1,3-Dioxoisoindolin-2-yl)prop-1-ynylthio)-*N*-(2-hydroxy-phenyl)-5-nitrobenzamide (3i). The Method B was followed, using *N*-thioamide **2e** (288 mg; 1.00 mmol) and *N*-propargylphtalimide (240 mg; 1.30 mmol). After 40 h at 55 °C thioacetylene **3i** was obtained as an yellowish crystalline product after recrystallization from acetone/EtOH/hexane in 92 % yield (435 mg). M.p.249-251.5 °C. ^{1}H NMR (400 MHz, DMSO-d6): δ 10.18 (bs, 1H), 9.72 (bs, 1H), 8.79 (s, 1H), 8.42 (dd, *J* = 2.4, 8.9, 1H), 8.20 (d, *J* = 8.9, 1H), 7.95 – 7.90 (m, 2H), 7.90 – 7.85 (m, 2H), 7.49 (d, *J* = 7.3, 1H), 7.08 (td, *J* = 1.6, 8.0, 1H), 6.92 (dd, *J* = 1.1, 8.1, 1H), 6.82 (td, *J* = 1.3, 7.8, 1H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d6) δ 166.7, 163.6, 150.5, 145.3, 143.4, 134.6, 131.9, 131.4, 127.8, 126.7, 125.7, 125.7, 124.5, 123.6, 123.3, 118.8, 115.9, 96.2, 69.4, 28.2. IR (KBr): 3407 m (NH), 3205 m (OH), 3087 w, 1771 w (C=O), 1711 s (C=O), 1644 s (CONH), 1596 m, 1536 s (CONH), 1523 s (NO_2), 1454 s, 1418 s, 1393 s, 1346 s (NO_2), 1339 s, 1278 m, 1113 m, 939 m, 753 w, 742 w, 728 m, 712 w cm^{-1}. Anal. calcd for $C_{24}H_{15}N_3O_6S$: C, 60.88; H, 3.19; N, 8.88. Found: C, 60.74; H, 3.27; N, 8.69.

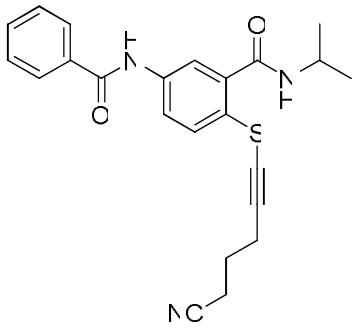


***N*-Benzyl-2-(pyridin-3-ylethynylthio)benzamide** (3j). The Method A was followed, using *N*-thioamide **2a** (170 mg; 0.70 mmol) and 3-ethynylpyridine (90 mg; 0.84 mmol). The reaction mixture was irradiated under 140 W maximum microwave power to raise the internal temperature to 175 °C. The temperature was maintained for 60 min. The next portion of CuMeSal (2 mol %) was added. The reaction mixture was irradiated under 170 W maximum microwave power to raise the internal temperature to 190 °C and the temperature was maintained for 15 min. Thioacetylene **3j** was obtained as a yellowish crystalline product after recrystallization from EtOAc/hexane in 71 % yield (170 mg). M.p. 121-123.5 °C. ^{1}H NMR (400 MHz, acetone-d6): δ 8.76 (d, *J* = 1.4, 1H), 8.58 (dd, *J* = 1.6, 4.9, 1H), 8.39 (bs, 1H), 8.10 (dd, *J* = 0.9, 8.1, 1H), 7.98 – 7.92 (m, 1H), 7.86 (dd, *J* = 1.3, 7.7, 1H), 7.65 – 7.58 (m, 1H), 7.46 – 7.31 (m, 6H), 7.26 (tt, *J* = 7.3, 1H), 4.62 (d, *J* = 6.1, 2H). ^{13}C NMR (101 MHz, acetone-d6): δ 168.2, 153.4, 150.5, 140.8, 139.8, 136.0, 133.6, 133.2, 129.9, 129.3, 129.1, 129.0, 128.5, 127.7, 124.8, 121.5, 96.5, 83.3, 44.7. IR (KBr): 3203 m (NH), 3060 w, 3033 w, 3023 w, 2867 w, 2169 w, 1640 s (CONH), 1588 m, 1535 s (CONH), 1466 m, 1410 m, 1366 w, 1265 m, 1026 w, 751 m, 697 s cm^{-1}. Anal. calcd for $C_{21}H_{16}N_2OS$: C, 73.23; H, 4.68; N, 8.13. Found: C, 73.17; H, 4.75; N, 7.97.



3-(2-(Allylcarbamoyl)-4-nitrophenylthio)prop-2-ynyl 2-chloro-5-nitrobenzoate (3k). The Method B was followed, using *N*-thioamide **2d** (0.47 g; 2.00 mmol) and prop-2-ynyl 2-chloro-5-nitrobenzoate (0.72 g; 2.80 mmol). After 4 days at 55 °C and 3 days at 80 °C thioacetylene **3k** was obtained as a yellowish crystalline product after recrystallization from EtOAc/hexane in 85 % yield (0.81 g).

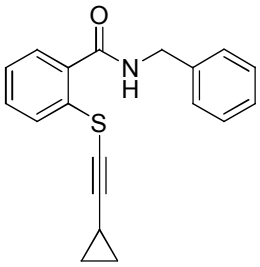
The Method D was followed, using *N*-thioamide **2d** (235 mg; 1.00 mmol) and prop-2-ynyl 2-chloro-5-nitrobenzoate (0.31 g; 1.30 mmol). After 26 h at 70 °C thioacetylene **3k** was obtained as a yellowish crystalline product after recrystallization from EtOAc/hexane in 91 % yield (435 mg). M.p.151.5-152.5 °C. ^{1}H NMR (400 MHz, acetone-d6): δ 8.73 (d, *J* = 2.8, 1H), 8.64 (d, *J* = 2.2, 1H), 8.54 – 8.41 (m, 2H), 8.40 – 8.32 (m, 2H), 7.90 (d, *J* = 8.8, 1H), 5.96 (ddt, *J* = 5.6, 10.4, 17.1, 1H), 5.39 (s, 2H), 5.32 – 5.24 (m, 1H), 5.16 – 5.10 (m, 1H), 4.08 – 4.03 (m, 2H). ^{13}C NMR (101 MHz, acetone-d6): δ 166.3, 164.3, 148.2, 147.5, 145.5, 141.3, 136.0, 134.2, 133.6, 132.2, 129.9, 129.1, 127.8, 127.0, 124.0, 117.1, 97.3, 76.8, 55.9, 43.7. IR (KBr): 3406 w (NH), 3301 m (NH), 3095 m, 3078 m, 2192 w, 1721 (C=O), 1635 (CONH), 1609 m, 1574 m, 1520 s (NO_2), 1422 m, 1410 m, 1345 s (NO_2), 1281 s (C-O), 1262 s, 1241 m, 1147 m, 1133 m, 1046 m, 950 m, 935 m, 918 m, 837 m, 741 s cm^{-1}. Anal. calcd for $C_{20}H_{14}N_3O_7S$: C, 50.48; H, 2.97; N, 8.83. Found: C, 50.26; H, 2.89; N, 8.61.



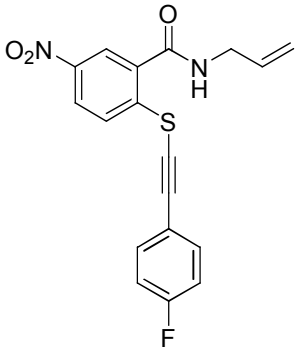
5-Benzamido-2-(5-cyanopent-1-ynylthio)-*N*-isopropyl-benzamide (3l). The Method A was followed, using *N*-thioamide **2f** (160 mg; 0.50 mmol) and hex-5-ynenitrile (0.07 ml; 0.58 mmol). The reaction mixture was irradiated under 120 W maximum microwave power to raise the internal temperature to 165 °C. The temperature was maintained for 30 min. The next portion of CuMeSal (2 mol %) and hex-5-ynenitrile (0.02 ml; 0.17 mmol) was added. The reaction mixture was irradiated under 120 W maximum microwave power to raise the internal temperature to 165 °C and the temperature was maintained for 40 min. Thioacetylene **3l** was obtained as a white crystalline product after column chromatography (hexane/Et_2O/acetone 3:1:2) in 88 % yield (180 mg).

The Method C was followed, using *N*-thioamide **2f** (225 mg; 0.70 mmol) and hex-5-ynenitrile (0.09 ml; 0.75 mmol). The reaction mixture was irradiated under 110 W maximum microwave power to raise the internal temperature to 160 °C. The temperature was maintained for 20 min. The next portion of AgOAc (1 mol %) and hex-5-ynenitrile (0.03 ml; 0.26 mmol) was added. The reaction mixture was irradiated under 130 W maximum microwave power to raise the internal temperature to 175 °C and the temperature was

maintained for 1 h. Conversion was 22 % (according HPLC). Product was not isolated. M.p. 130.5-131 °C. ^{1}H NMR (400 MHz, acetone-d6): δ 9.68 (s, 1H), 8.11 (d, *J* = 2.3, 1H), 8.03 – 7.98 (m, 2H), 7.94 (dd, *J* = 2.3, 8.7, 1H), 7.87 (d, *J* = 8.7, 1H), 7.63 – 7.49 (m, 4H), 4.25 – 4.14 (m, 1H), 2.71 – 2.63 (m, *J* = 7.1, 12.7, 4H), 2.01 – 1.93 (m, 2H), 1.26 (d, *J* = 6.6, 6H). ^{13}C NMR (101 MHz, acetone-d6): δ 166.9, 166.5, 138.4, 136.0, 134.7, 132.7, 129.5, 129.4, 128.5, 128.4, 123.6, 120.3, 120.1, 98.3, 70.0, 42.7, 25.6, 22.8, 19.9, 16.6. IR ($CHCl_3$): 3431 m (NH), 3312 m (NH), 3065 w, 3013 s, 2976 m, 2941 w, 2252 w (CN), 2190 w, 1651 s (CONH), 1601 m, 1580 s, 1525 s (CONH), 1490 s, 1468 s, 1400 s, 1309 s (CONH), 1251 m, 1171 m, 1046 m, 1028 m, 821 m, 709 s cm^{-1}. Anal. calcd for $C_{23}H_{23}N_3O_2S$: C, 68.12; H, 5.72; N, 10.36. Found: C, 67.84; H, 5.65; N, 10.25.

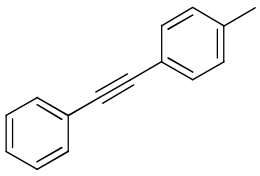


***N*-Benzyl-2-(cyclopropylethynylthio)benzamide** (3m). The Method D was followed, using *N*-thioamide **2a** (0.30 g; 1.24 mmol) and cyclopropylacetylene (0.22 ml; 2.60 mmol). After 60 h at 70 °C thioacetylene **3m** was obtained as an yellowish crystalline product after recrystallization from EtOH/hexane in 97 % yield (370 mg). M.p. 116-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6, 1H), 7.47 – 7.41 (m, 2H), 7.33 (d, *J* = 4.4, 4H), 7.31 – 7.25 (m, 1H), 7.17 (td, *J* = 1.1, 7.6, 1H), 6.29 (s, 1H), 4.59 (d, *J* = 5.7, 2H), 1.52 – 1.43 (m, 1H), 0.91 – 0.79 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 138.0, 136.2, 132.2, 131.5, 129.0, 128.2, 128.0, 127.9, 127.4, 125.9, 104.6, 62.0, 44.4, 9.4, 1.2. IR (ATR): 3266 m (NH), 3011 w, 2944 w, 2185 w, 2162 w, 1625 s (CONH), 1524 s, 1496 m, 1451 m, 1432 m, 1306 m, 1281 m, 1263 m, 1156 w, 1028 m, 987 m, 836 w, 811 w, 789 w, 740 m, 732 m, 704 s, 665 s, 650 s, 602 s cm^{-1}. Anal. calcd for $C_{19}H_{17}NOS$: C, 74.24; H, 5.57; N, 4.56.03. Found: C, 74.25; H, 5.50; N, 4.44.



***N*-Allyl-2-((4-fluorophenyl)ethynylthio)-5-nitrobenzamide** (3n). The Method D was followed, using *N*-thioamide **2d** (0.74 g; 3.14 mmol) and 1-ethynyl-4-fluorobenzene (0.45 ml; 3.93 mmol). After 27 h at 70 °C thioacetylene **3n** was obtained as an yellowish crystalline product after recrystallization from EtOH in 94 % yield (1.05 g). M.p. 196.5-197.5 °C. ^{1}H NMR (400 MHz, acetone-d6): δ 8.64 (d, *J* = 2.4, 1H), 8.48 (s, 1H), 8.42 (dd, *J* = 2.4, 8.9, 1H), 8.35 (d, *J* = 8.9, 1H), 7.72 – 7.66 (m, 2H), 7.28 – 7.20 (m, 2H), 6.04 – 5.93 (m, 1H), 5.29 (m,, 1H), 5.14 (m, 1H), 4.11 – 4.05 (m, 2H). ^{13}C NMR (101 MHz, acetone-d6): δ 165.8, 164.0 (d, $^{1}J_{C\text{-}F}$= 249), 146.8, 145.6, 135.5, 135.2 (d, $^{2}J_{C\text{-}F}$= 8.7), 132.9, 129.3, 126.6, 123.4, 119.6 (d, $^{3}J_{C\text{-}F}$= 2.9), 117.0, 116.7 (d, $^{4}J_{C\text{-}F}$= 22.5), 99.8, 76.9, 43.1. IR (ATR): 3282 w (NH), 3074 w, 2166 w, 1634 s (CONH), 1599 m, 1546 m, 1514 m, 1503 s, 1456 m, 1339 s, 1316 m, 1283 m, 1258 m, 1233 m, 1154 m, 1051 m, 996 m, 926 m, 915 m, 834 s , 793 m, 736 m, 532 s cm^{-1}. HR-MS (EI) *m/z* calcd for $C_{18}H_{13}N_2O_3SF$ 356.0623, found 356.0631.

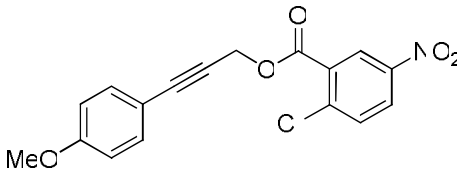
The General Method for Preparation of Acetylenes and Regeneration of *N*-thioamide



1-Methyl-4-(phenylethynyl)benzene (5a). Thioacetylene **3d** (340 mg; 1.00 mmol) and 4-methylphenylboronic acid (185 mg; 1.30 mmol), CuMeSal (262 mg; 1.2 eq) and $Pd(PPh_3)_4$ (59 mg; 5 mol %) were added to a Schlenk flask (25 ml). The flask was sealed with a Suba-Seal and system was purged with Ar (3x). DME (8 ml) was added via needle and syringe trough the septum directly into the Schlenk flask. Resulting reaction

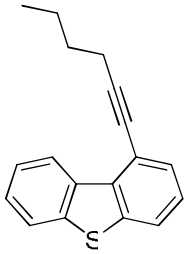
mixture was purged with Ar (3x) and stirred for 16-18 h at 40-45 °C under the presure of Ar. Reaction progres was followed by UPLC. Reaction mixture was diluted with ethyl acetate (10 ml) and black solid filtered through Celite. The solvent was removed in rotatory evaporator and crude product was purified by column chromatography (hexane/dichloromethane 30:1) to afford pure acetylene **5a** as an white crystalline product in 85 % yield (165 mg). M.p.73-74.5 °C (MeOH/water) (lit. 72.5-74 °C).[7] ^{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.

The black solid was transfered back to the Schlenk flask, DMF (5 ml) and LiCl (1.5 eq) were added. The black solid was completely disolved to form a dark red solution after 10 min. The reaction mixture was stirred for 1 h at room temperature in the presence of the air. The mixture was poured in ice cooled HCl (5 % water solution). The precipitate was filtered and washed with water. After drying the crude product was purified by column chromatography (EtOAc/hexane 1:3->1:2) to afford *N*-thioamide **2d** in 59 % yield (140 mg) which showed identical spectroscopic properties as the one previously reported.[1]

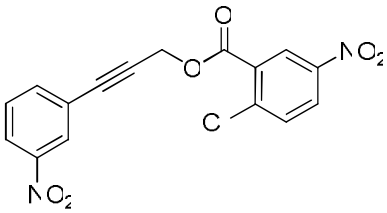


3-(4-Methoxyphenyl)prop-2-ynyl 2-chloro-5-nitro-benzoate (5b). The general method was followed, by using thioacetylene **3k** (200 mg; 0.42 mmol) and 4-methoxyphenylboronic acid (83 mg; 0.55 mmol). Acetylene **5b** was obtained as a colorless oil after column chromatography (hexane/Et_2O/acetone 7:1:2) in 83 % yield (120 mg). ^{1}H NMR (400 MHz, acetone-d6): δ 8.71 (d, *J* = 2.8, 1H), 8.44 (dd, *J* = 2.8, 8.8, 1H), 7.90 (d, *J* = 8.8, 1H), 7.46 – 7.40 (m, 2H), 6.98 – 6.92 (m, 2H), 5.27 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, acetone-d6): δ 164.2, 162.0, 148.1, 141.2, 134.8, 134.1, 132.5, 128.9, 127.7, 115.7, 115.4, 88.3, 82.8, 56.4, 55.8. IR ($CHCl_3$): 3108 w, 3087 w, 3030 w, 3012 w, 2958 w, 2938 w, 2841 w, 2230 m, 1742 s (C=O), 1609 s, 1576 m, 1530 s (NO_2), 1511 s, 1467 m, 1351 s (NO_2), 1306 s, 1294 s, 1270 s, 1250 s, 1174 m, 1129 s, 1049 s, 1035 s, 943 m, 836 s, 743 s cm^{-1}. HR-MS (EI) *m/z* calcd for $C_{17}H_{12}ClNO_5$ 345.0404, found 345.0414.

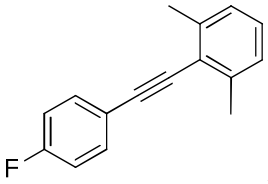
[7] Seyferth, D.; Damrauer, R. *J. Org. Chem.* **1966**, *31*, 1660
[1] Henke, A.; Srogl, J. *J. Org. Chem*. **2008**, 73, 7783–7784.



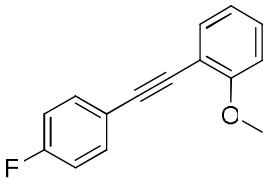
1-(Hex-1-ynyl)dibenzo[b,d]thiophene (5c). The general method was followed, by using thioacetylene **3g** (200 mg; 0.63 mmol) and 4-dibenzothiophenboronic acid (185 mg; 0.82 mmol). Acetylene **5c** was obtained as an colorless oil after column chromatography (hexane/EtOAc 50:1) in 69 % yield (115 mg). ^{1}H NMR (400 MHz, acetone-d6): δ 8.34 – 8.30 (m, 1H), 8.28 (dd, *J* = 1.3, 7.7, 1H), 8.05 – 7.99 (m, 1H), 7.58 – 7.46 (m, 4H), 2.58 (t, *J* = 6.9, 2H), 1.72 – 1.63 (m, 2H), 1.63 – 1.54 (m, 2H), 0.99 (q, *J* = 7.3, 3H). ^{13}C NMR (101 MHz, acetone-d6): δ 143.7, 140.8, 137.4, 137.0, 130.9, 128.8, 126.4, 126.3, 124.5, 123.6, 122.6, 120.4, 97.6, 79.8, 32.3, 23.3, 20.3, 14.6. IR ($CHCl_3$): 3070 m, 3011 s, 2961 s, 2935 s, 2874 m, 2864 m, 2228 w, 1576 w, 1442 s, 1386 s, 1305 m, 1251 s, 1101 m, 1047 m, 1022 m, 798 m cm^{-1}. HR-MS (EI) *m/z* calcd for $C_{18}H_{16}S$ 264.0973, found 264.0977.



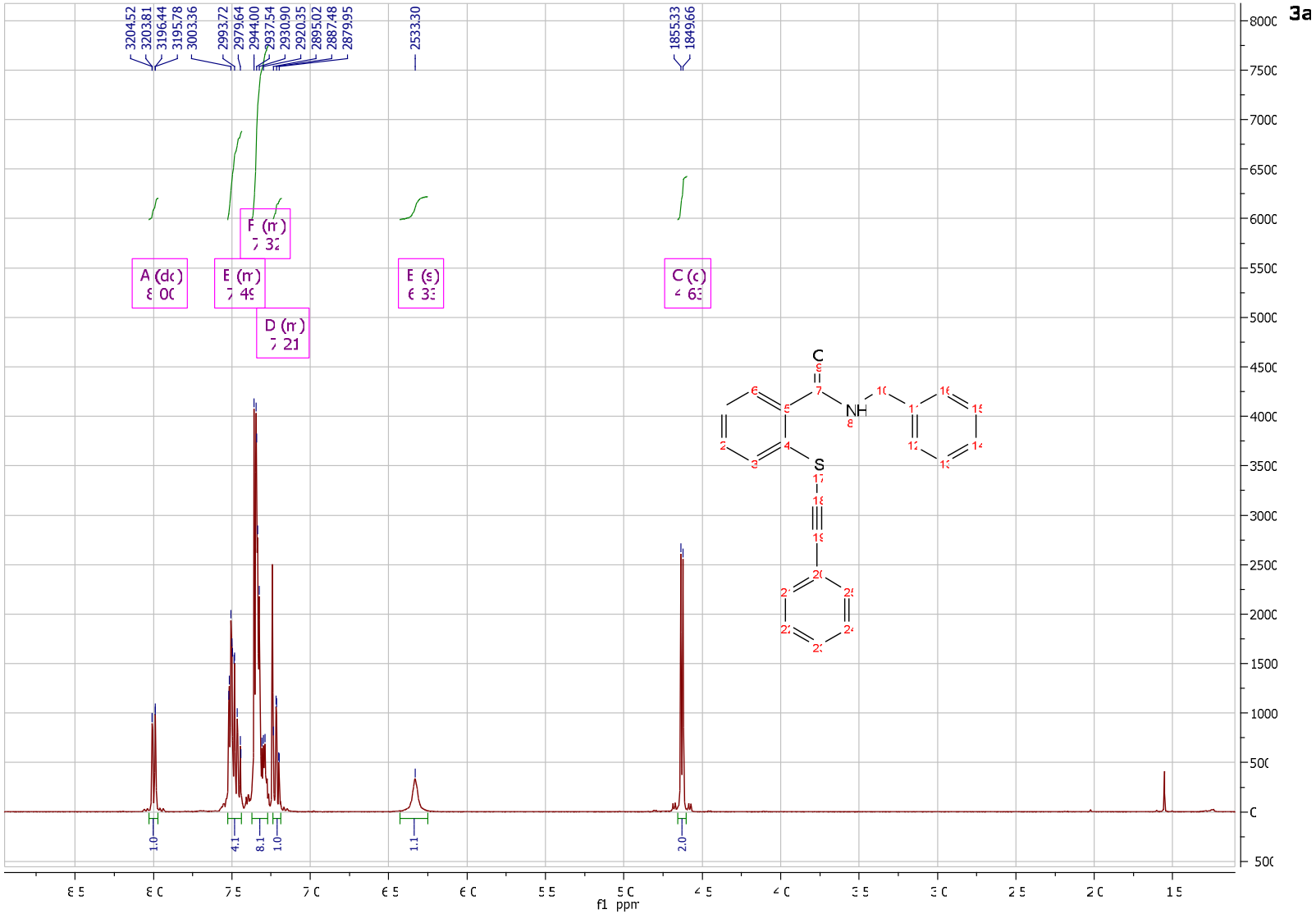
3-(3-Nitrophenyl)prop-2-ynyl 2-chloro-5-nitro-benzoate (5d). The general method was followed, by using thioacetylene **3k** (200 mg; 0.42 mmol) and 3-nitrophenylboronic acid (92 mg; 0.55 mmol). Acetylene **5d** was obtained as an white solid after column chromatography (hexane/Et_2O/acetone 8:1:2) in 66 % yield (100 mg). M.p. 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 2.7, 1H), 8.33 – 8.27 (m, 2H), 8.19 (ddd, *J* = 1.1, 2.3, 8.3, 1H), 7.79-7.75 (m, 1H), 7.67 (d, *J* = 8.8, 1H), 7.52 (t, *J* = 8.0, 1H), 5.21 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.9, 148.4, 146.5, 141.4, 137.8, 132.8, 130.4, 129.7, 127.5, 127.1, 127.0, 124.0, 123.9, 85.2, 84.8, 54.2. IR (ATR): 3109 w, 3089 w, 1722 s (C=O), 1607 s, 1516 s (NO_2), 1463 m, 1348 s (NO_2), 1304 s, 1136 s, 1046 s, 945 m, 921 s, 836 s, 805 m, 781 m, 734 s, 697 m, 668 s, 655 m, 595 m cm^{-1}. HR-MS (EI) *m/z* calcd for $C_{16}H_9N_2O_6Cl$ 360.0148, found 360.0149.



2-((4-Fluorophenyl)ethynyl)-1,3-dimethylbenzene (5e). The general method was followed, by using thioacetylene **3n** (300 mg; 0.84 mmol) and 2,6-dimethylphenylboronic acid (164 mg; 1.09 mmol). Acetylene **5e** was obtained as a colorless oil after column chromatography (hexane/Et_2O/acetone 40:1:2) in 58 % yield (110 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.47 (m, 2H), 7.12 (dd, *J* = 6.3, 8.6, 1H), 7.07 – 7.01 (m, 4H), 2.49 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.7 (d, $^1J_{C\text{-}F}$= 249), 140.4, 133.4 (d, $^2J_{C\text{-}F}$= 8.3), 128.0, 127.0, 123.0, 120.2 (d, $^4J_{C\text{-}F}$= 3.5), 115.8 (d, $^3J_{C\text{-}F}$= 22.1), 96.9, 87.0 (d, $^5J_{C\text{-}F}$= 1.3), 21.3. IR (ATR): 3064 w, 2918 w, 1599 w, 1505 s, 1467 w, 1228 s, 1154 m, 1091 w, 831 s, 804 m, 767 s, 731 w, 592 w, 524 m, 481 m cm^{-1}. HR-MS (EI) *m/z* calcd for $C_{16}H_{13}F$ 224.0998, found 224.1001.



1-((4-Fluorophenyl)ethynyl)-2-methoxybenzene (5f). The general method was followed, by using thioacetylene **3n** (300 mg; 0.84 mmol) and 2-methoxyphenylboronic acid (166 mg; 1.09 mmol). Acetylene **5f** was obtained as a yellowish oil after column chromatography (hexane/Et_2O/acetone 10:1:2) in 76 % yield (145 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.49 (m, 2H), 7.47 (dd, *J* = 1.7, 7.6, 1H), 7.30 (ddd, *J* = 1.7, 7.5, 8.4, 1H), 7.05 – 6.98 (m, 2H), 6.92 (td, *J* = 1.0, 7.5, 1H), 6.89 (d, *J* = 8.4, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.7(d, $^1J_{C\text{-}F}$= 249), 160.2, 133.8, 133.7(d, $^2J_{C\text{-}F}$= 8.3), 130.0, 120.7, 120.0 (d, $^4J_{C\text{-}F}$= 3.5), 115.7 (d, $^3J_{C\text{-}F}$= 22.1), 112.6, 111.0, 92.5, 85.66 (d, $^5J_{C\text{-}F}$= 1.4), 56.1. IR (ATR): 3072 w, 2943 w, 2836 w, 1595 w, 1575 w, 1506 s , 1488 m, 1461 m, 1434 m, 1274 m, 1219 s, 1155 m, 1105 m, 1022 m, 833 s, 747 s, 526 m, 485 s cm^{-1}. HR-MS (EI) *m/z* calcd for $C_{15}H_{11}OF$ 226.0790, found 226.0794.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2979.64
2944.00
2937.54
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2920.35
2895.02
2887.48
2879.95
2533.30
1855.33
1849.66
A (dd)
8.00
B (m)
7.49
D (m)
7.21
F (m)
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4.1
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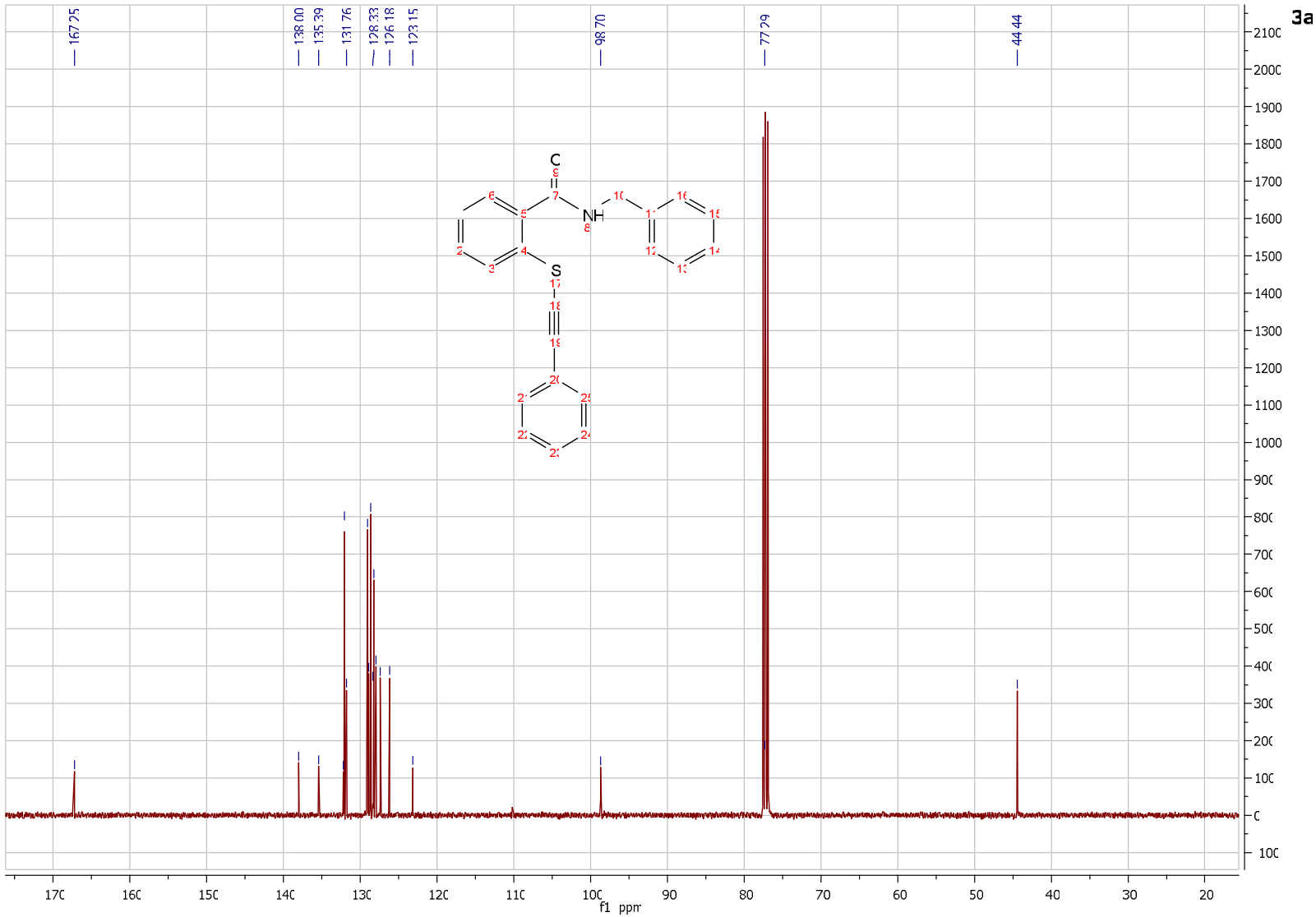
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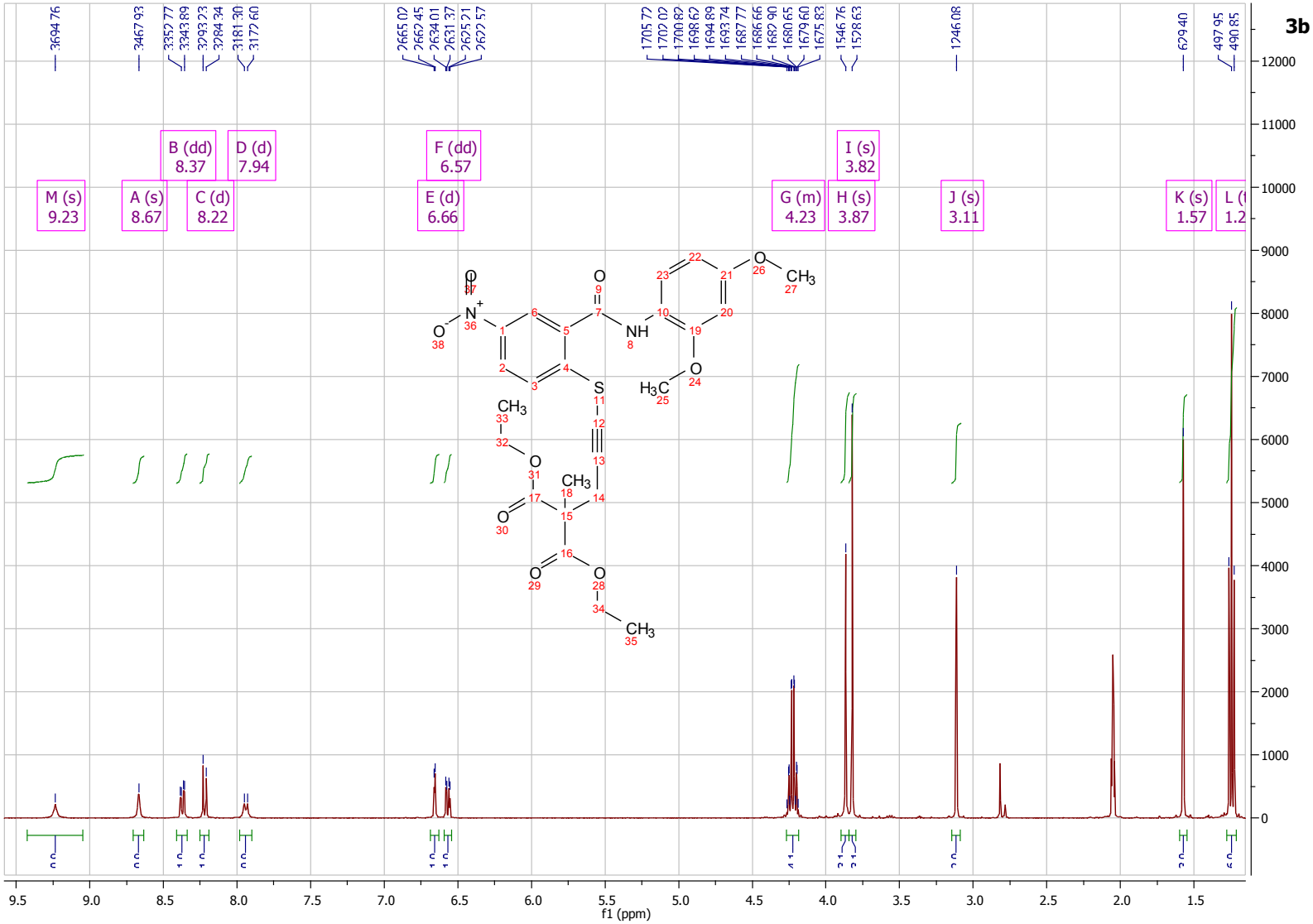
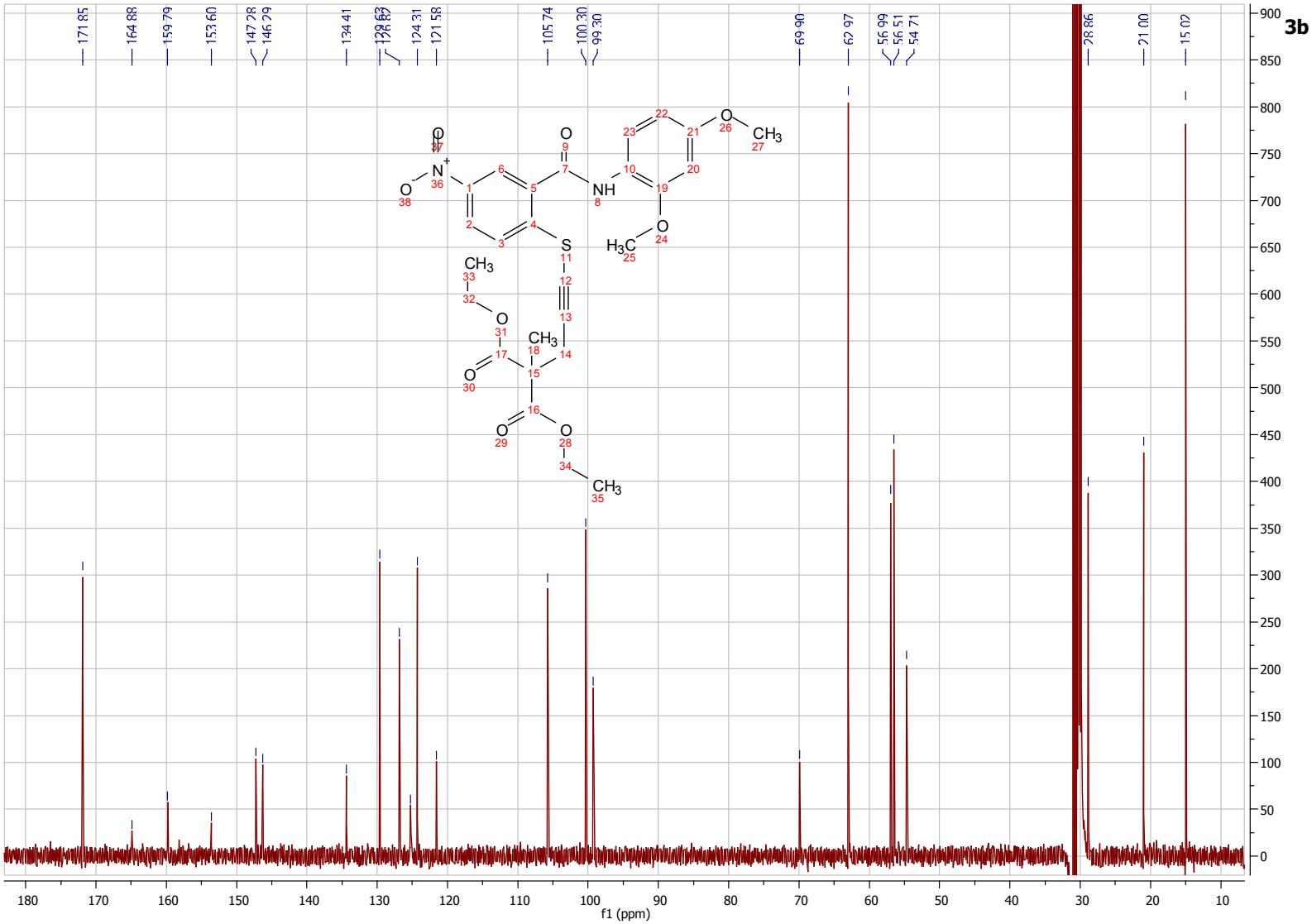
123.15
98.70
77.29
44.44
NH
S
f1 ppm


3b
M (s) 9.23
A (s) 8.67
B (dd) 8.37
C (d) 8.22
D (d) 7.94
E (d) 6.66
F (dd) 6.57
G (m) 4.23
H (s) 3.87
I (s) 3.82
J (s) 3.11
K (s) 1.57
f1 (ppm)


3b
171.85
164.88
159.79
153.60
147.28
146.29
134.41
124.31
121.58
105.74
100.30
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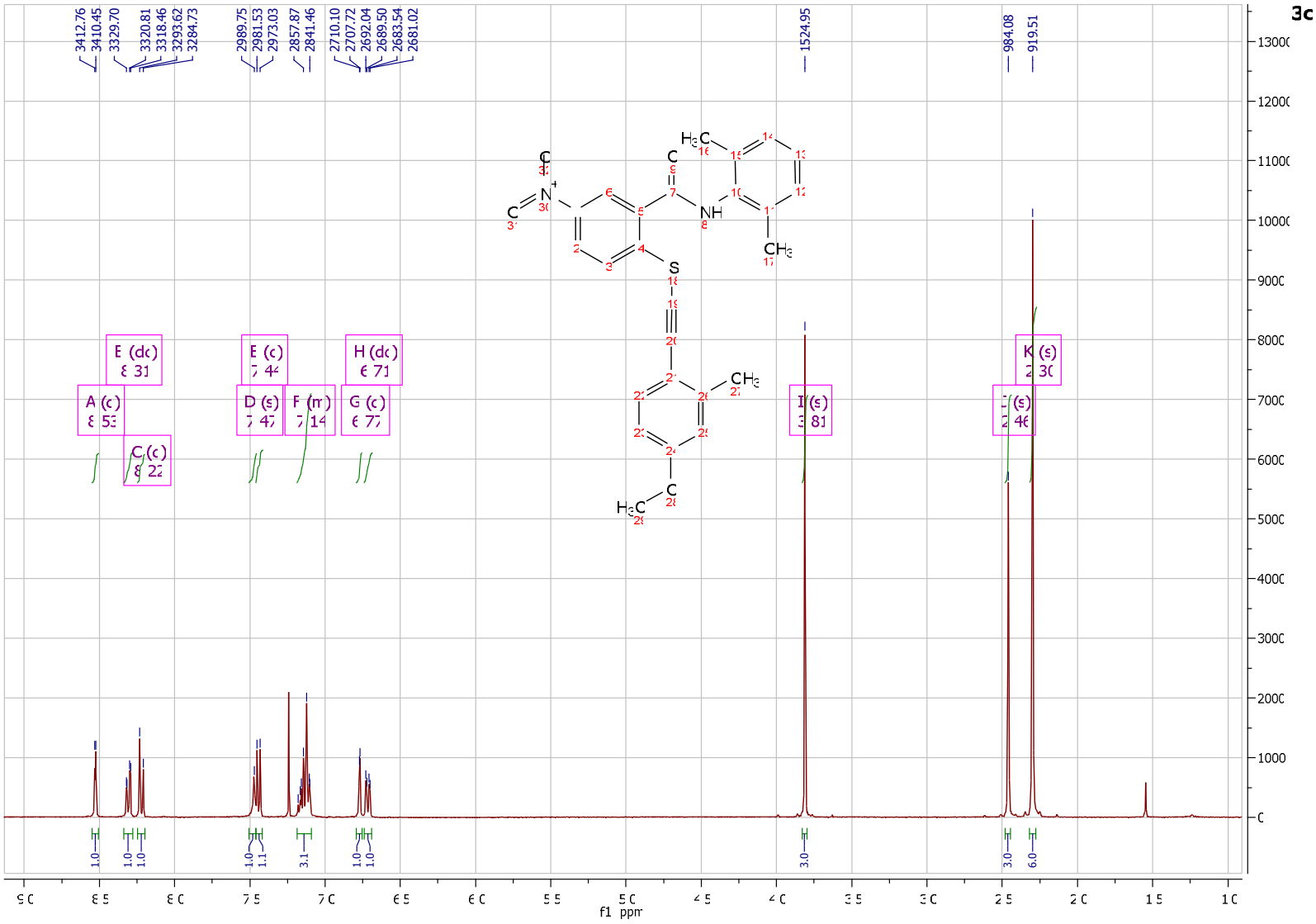
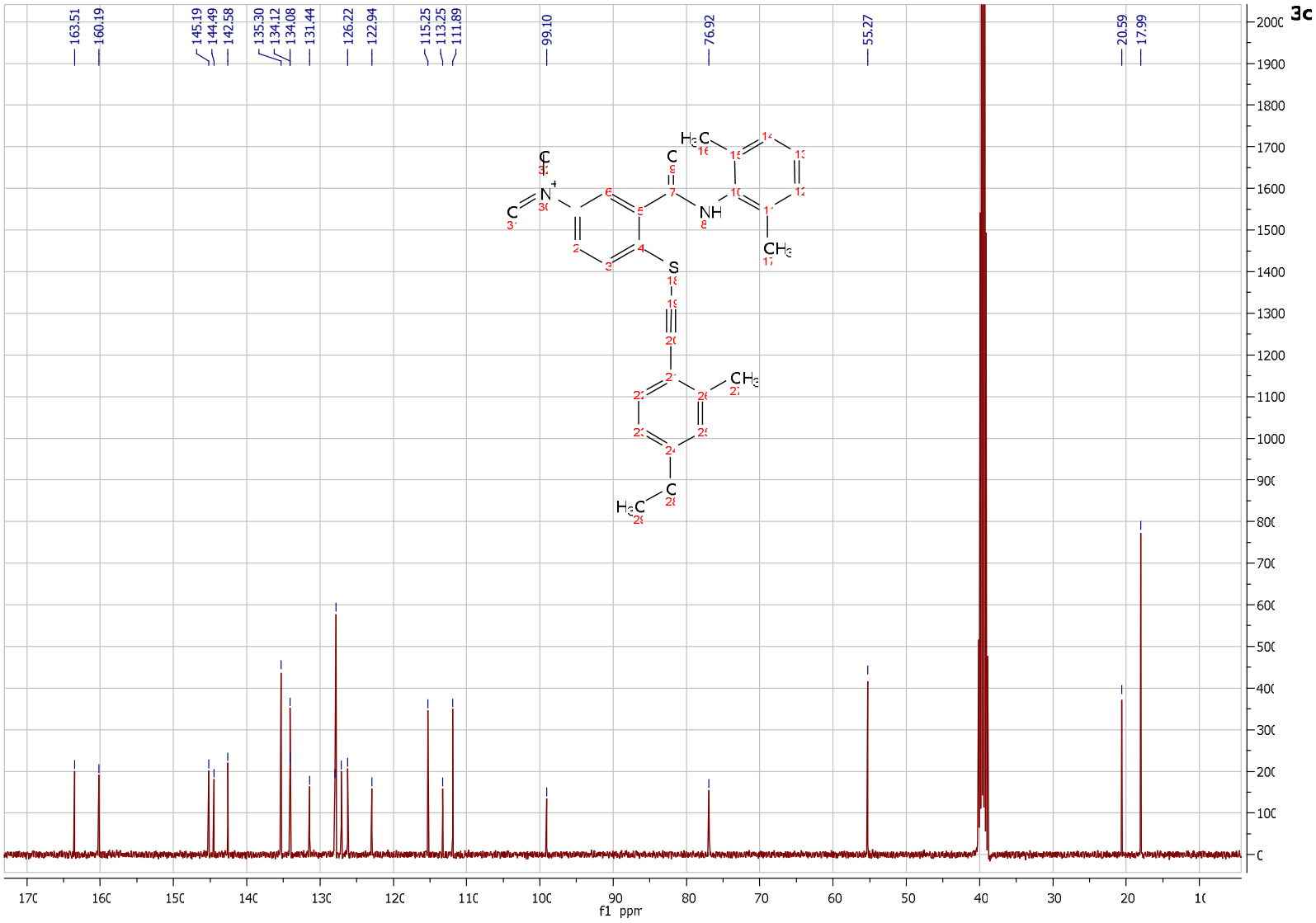
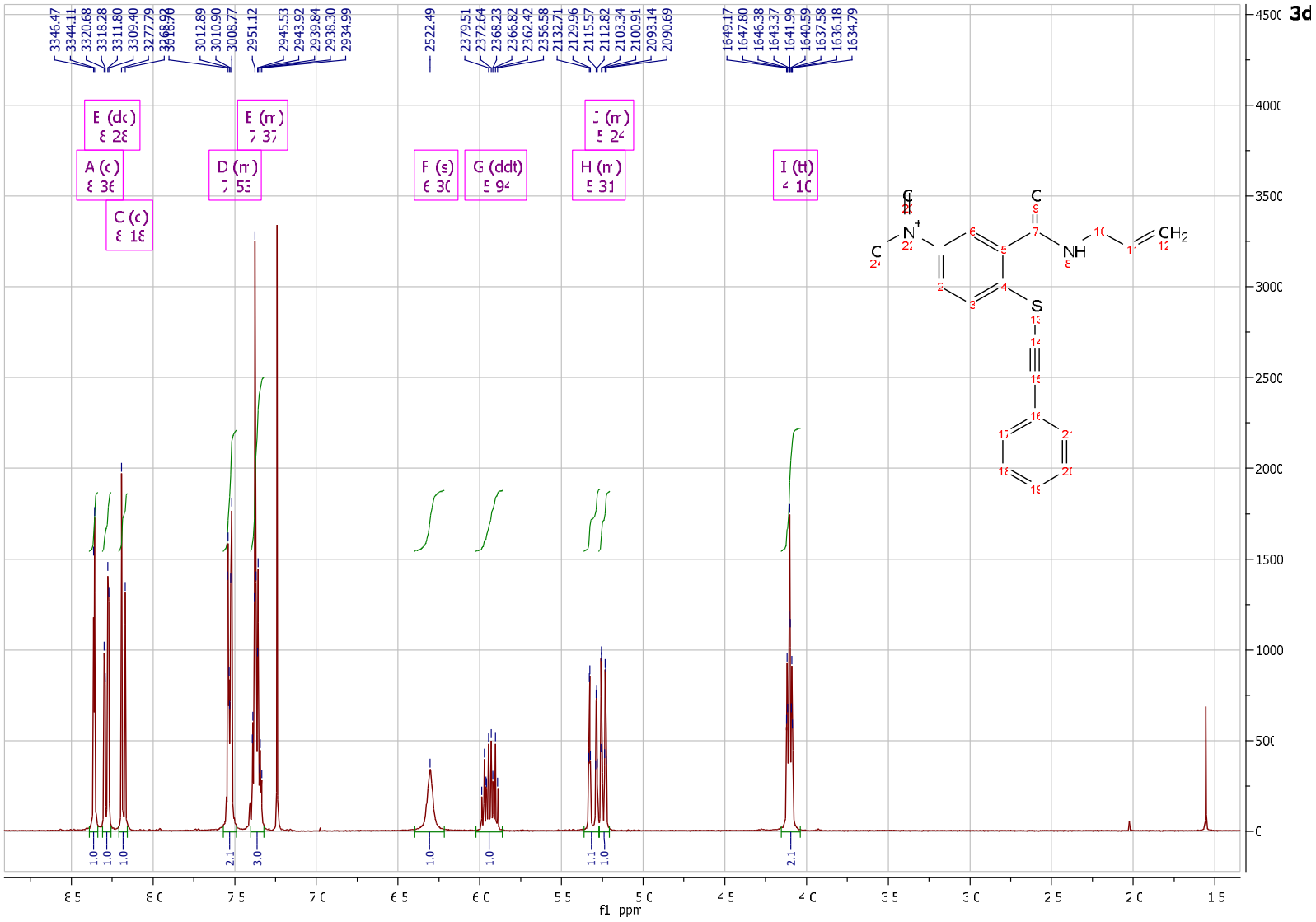
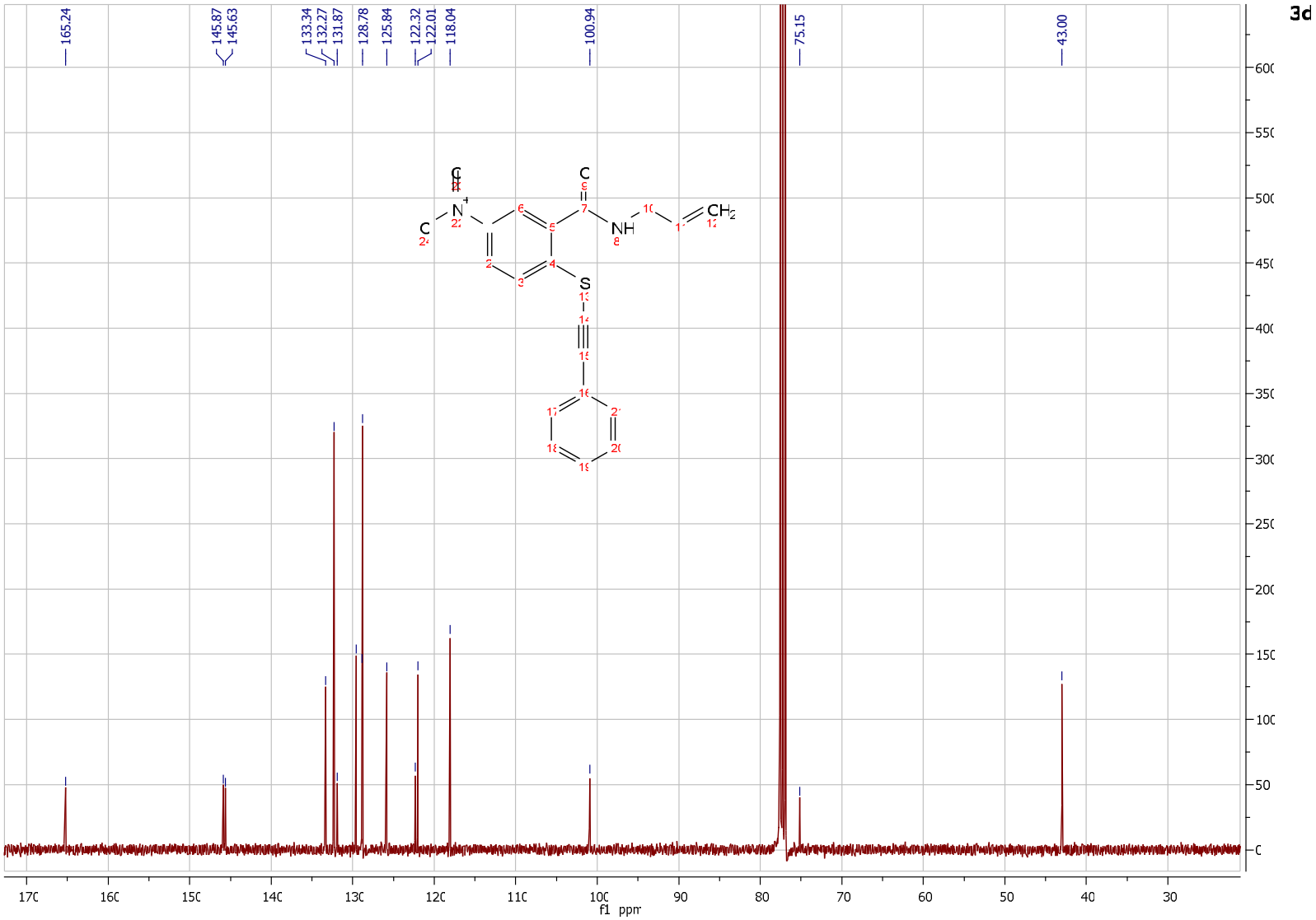
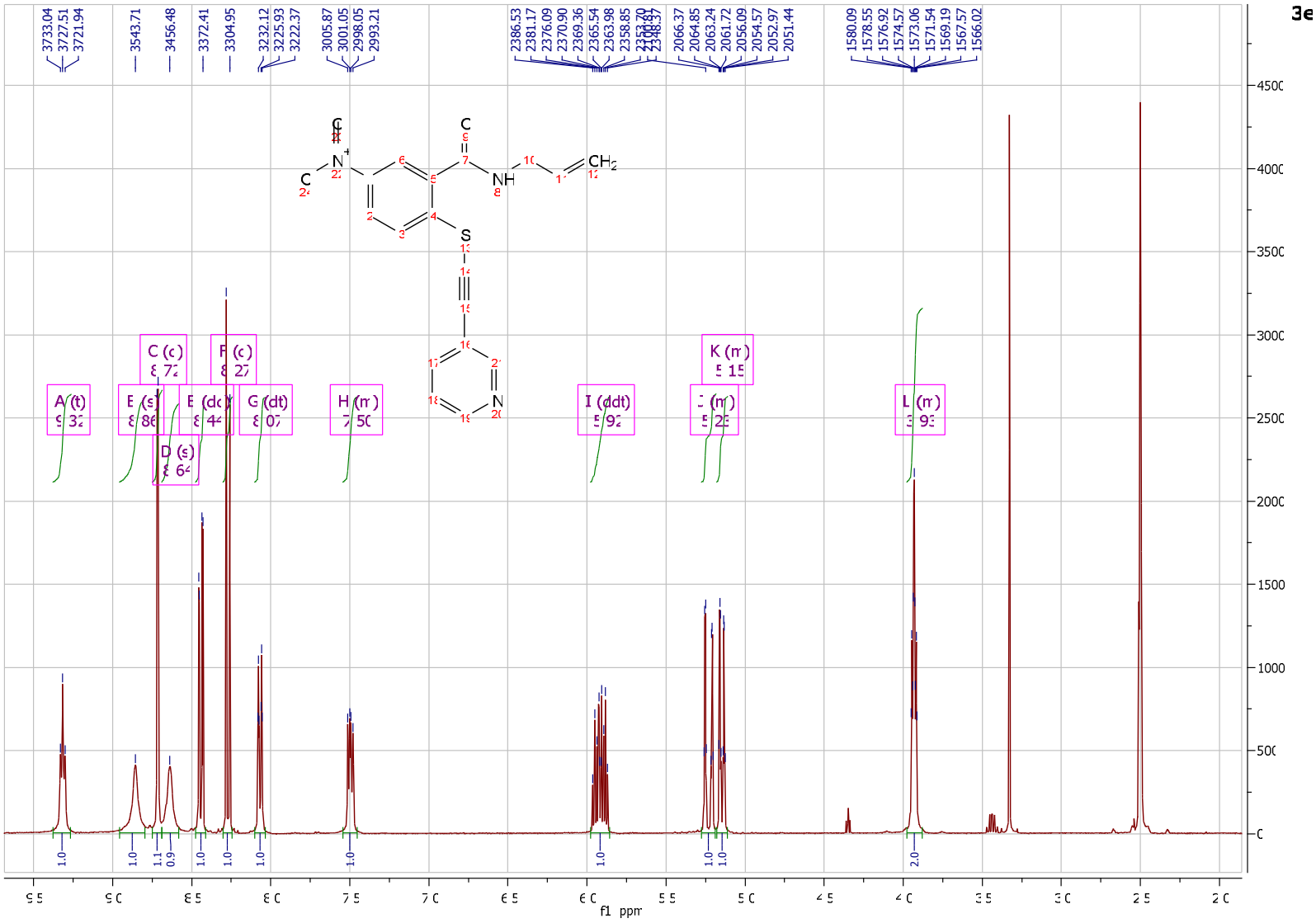
56.51
54.71
28.86
21.00
15.02
f1 (ppm)

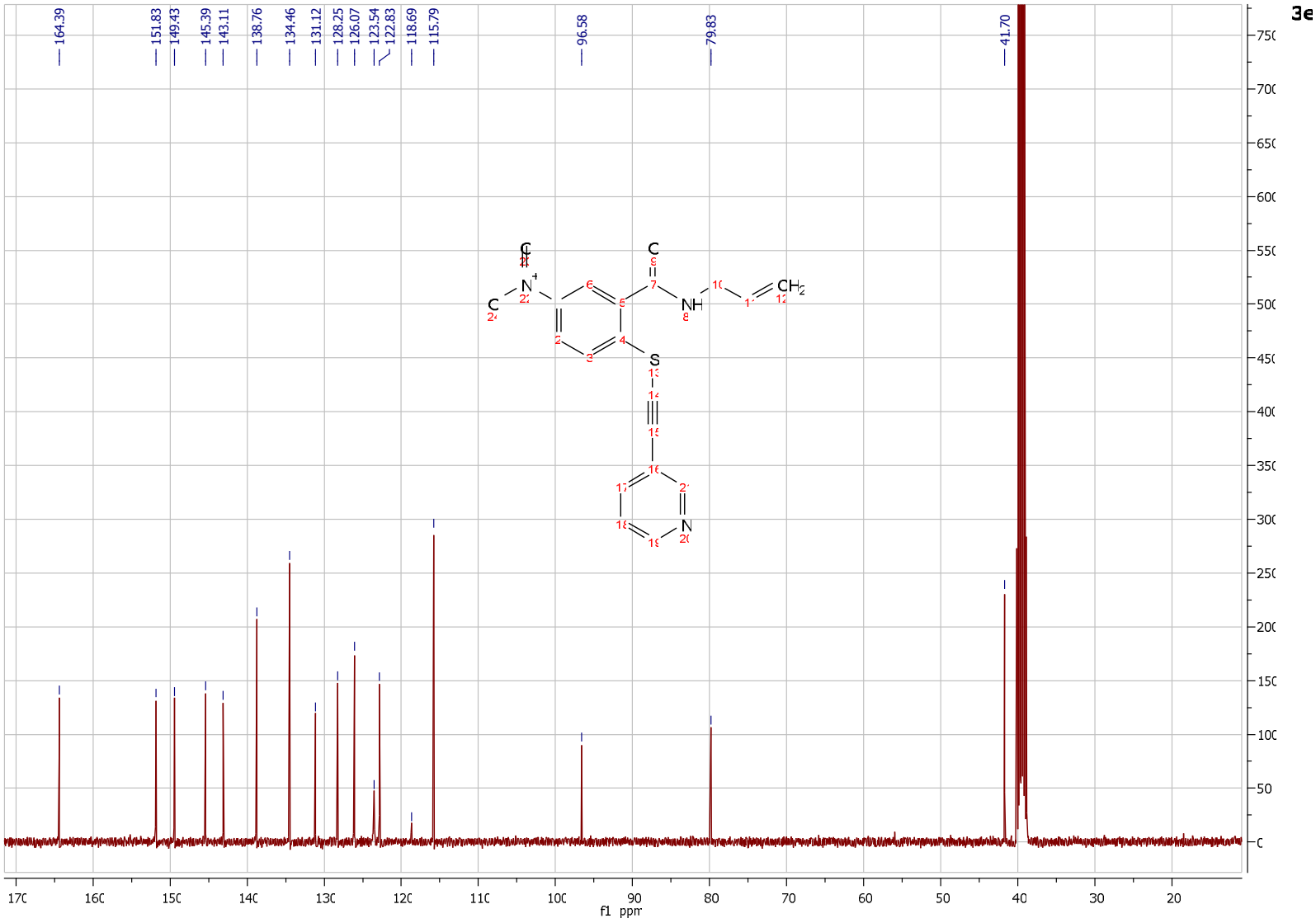

3c
3412.76
3410.45
3329.70
3320.81
3318.46
3293.62
3284.73
2989.75
2981.53
2973.03
2857.87
2841.46
2710.10
2707.72
2692.04
2689.50
2683.54
2681.02
1524.95
984.08
919.51
A (c)
C (c)
E (dd)
D (s)
F (m)
E (d)
G (d)
H (dd)
I (s)
K (s)
f1 ppm

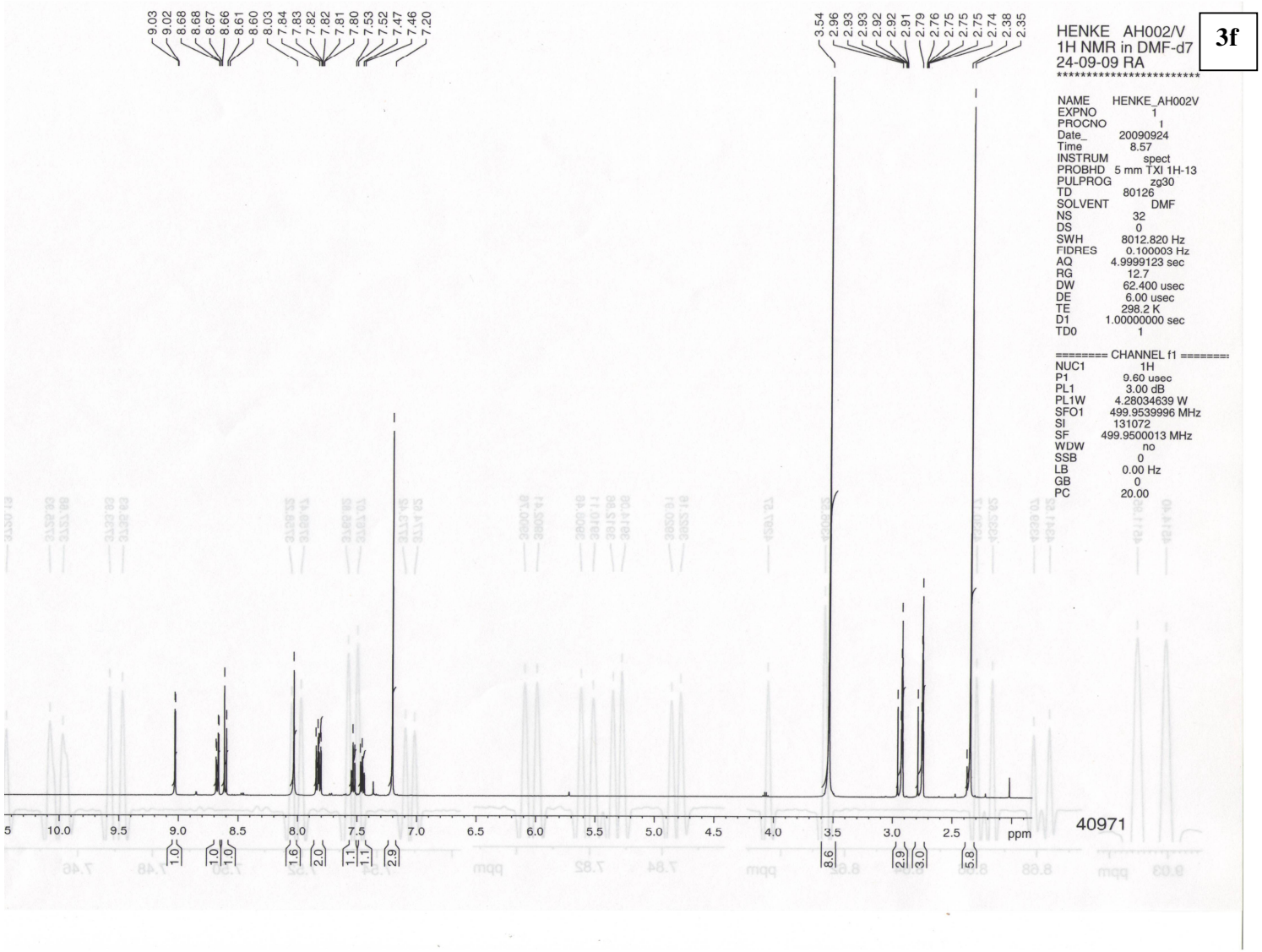

3c
163.51
160.19
145.19
144.49
142.58
135.30
134.12
134.08
131.44
126.22
122.94
115.25
113.25
111.89
99.10
76.92
55.27
20.59
17.99
f1 ppm

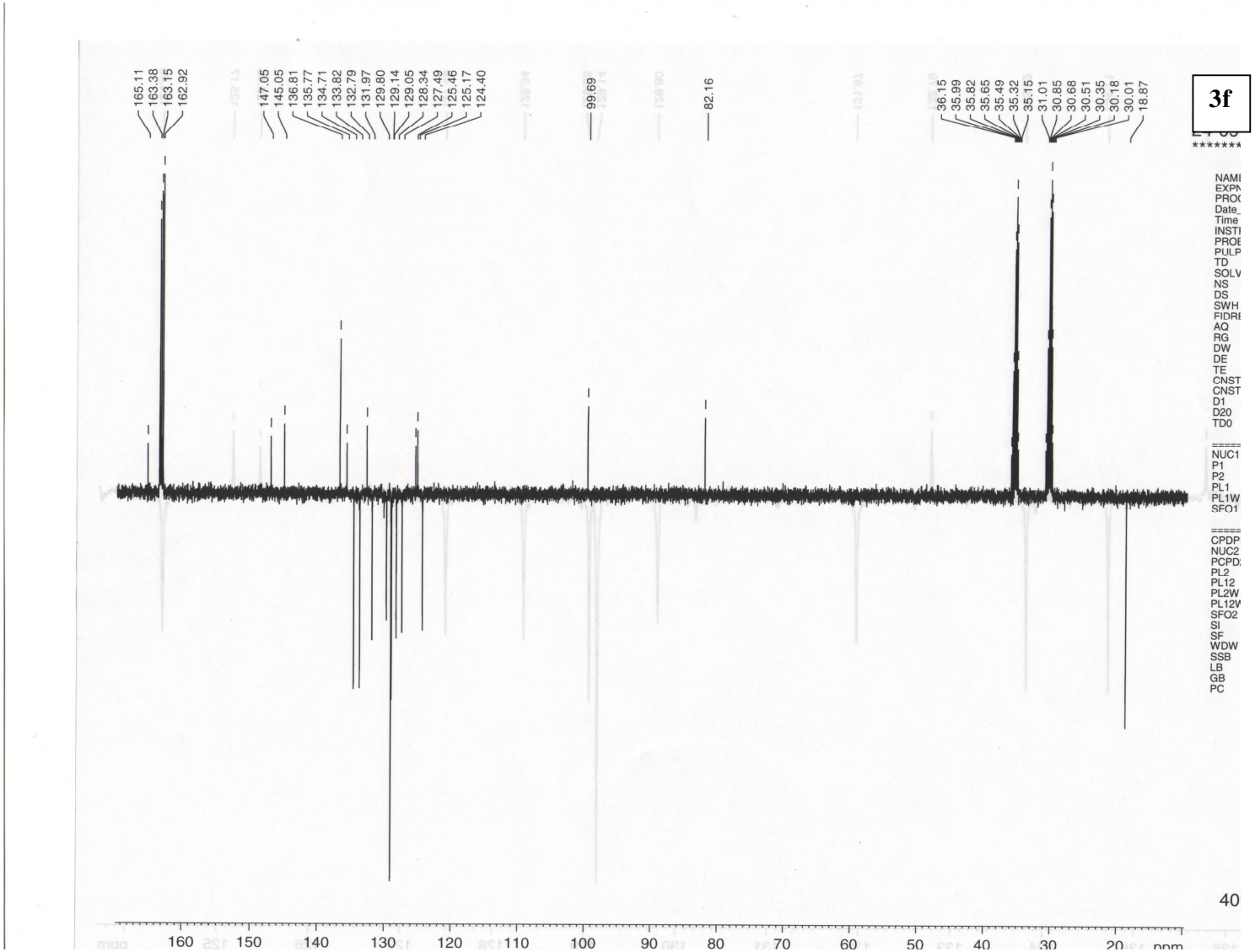

3d
f1 ppm

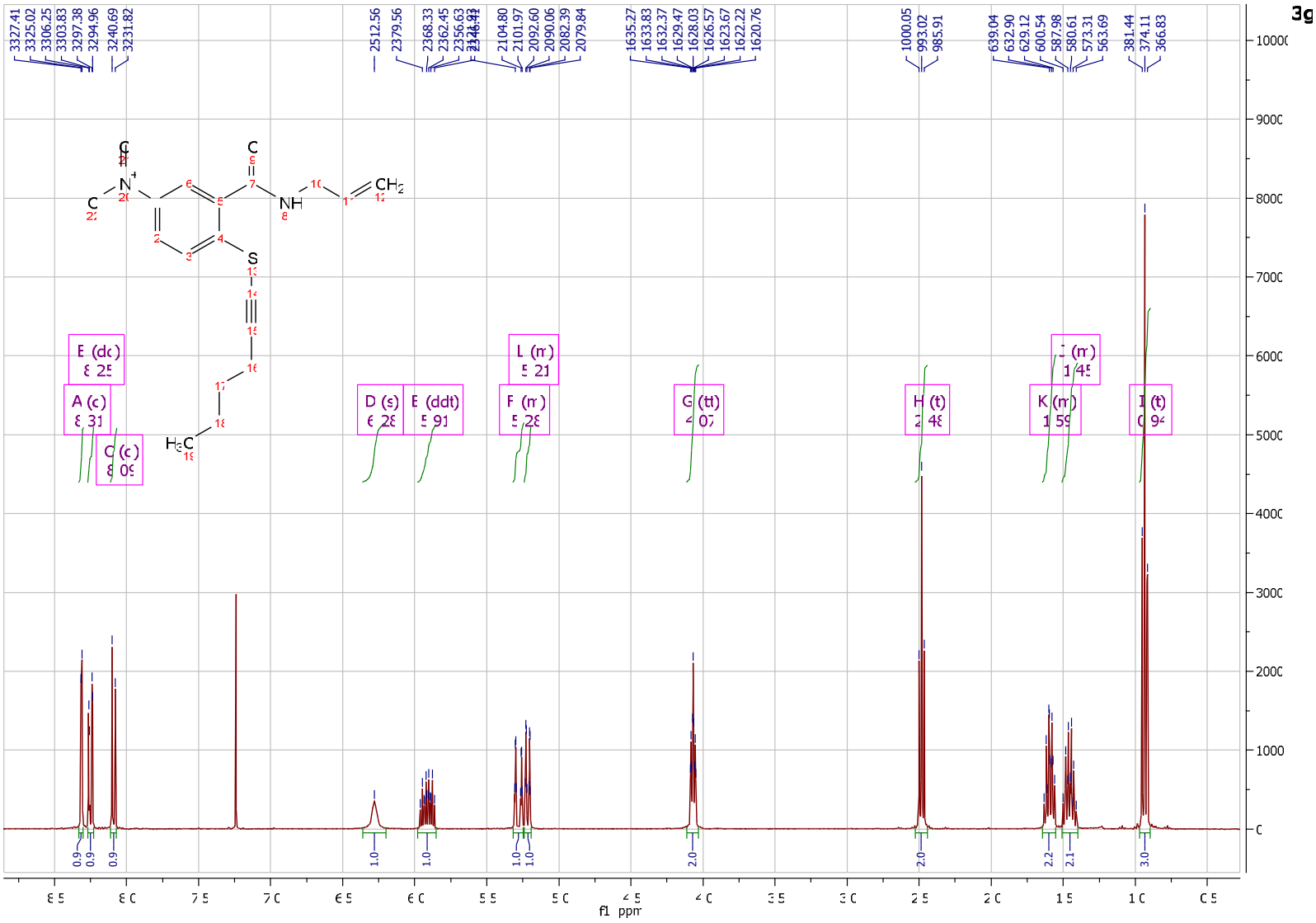

3d
165.24
145.87
145.63
133.34
132.27
131.87
128.78
125.84
122.32
122.01
118.04
100.94
75.15
43.00
f1 ppm

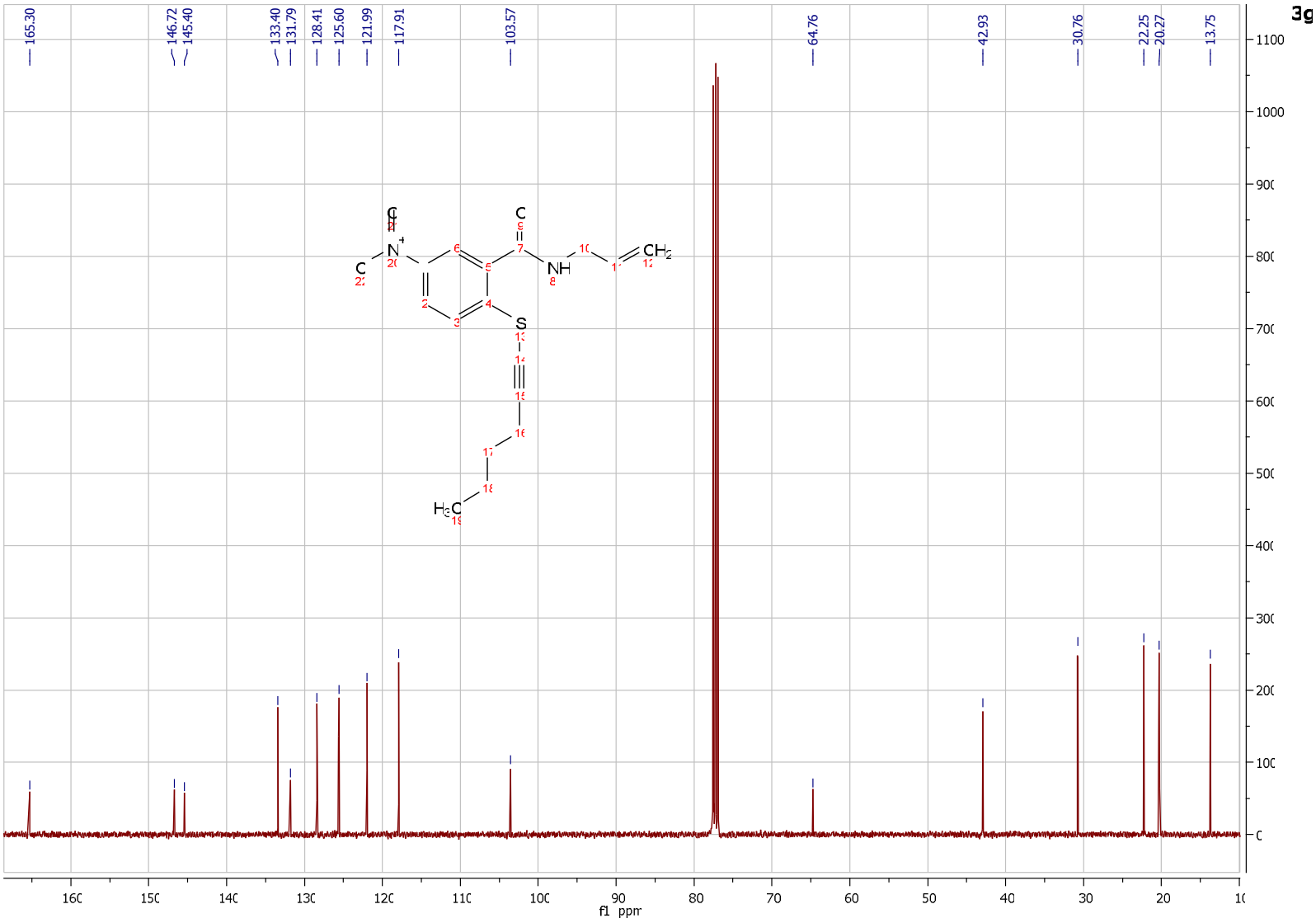

3733.04
3727.51
3721.94
3543.71
3456.48
3372.41
3304.95
3232.12
3225.93
3222.37
3005.87
3001.05
2998.05
2993.21
2386.53
2381.17
2376.09
2370.90
2369.36
2365.54
2363.98
2358.85
2066.37
2064.85
2063.24
2061.72
2056.09
2054.57
2052.97
2051.44
1580.09
1578.55
1576.92
1574.57
1573.06
1571.54
1569.19
1567.57
1566.02
NH
S
N
CH2
A (t)
C (c)
F (c)
K (m)
H (m)
I (ddt)
L (m)
D (s)
G (dt)
1.0
1.1
0.9
2.0
f1 ppm

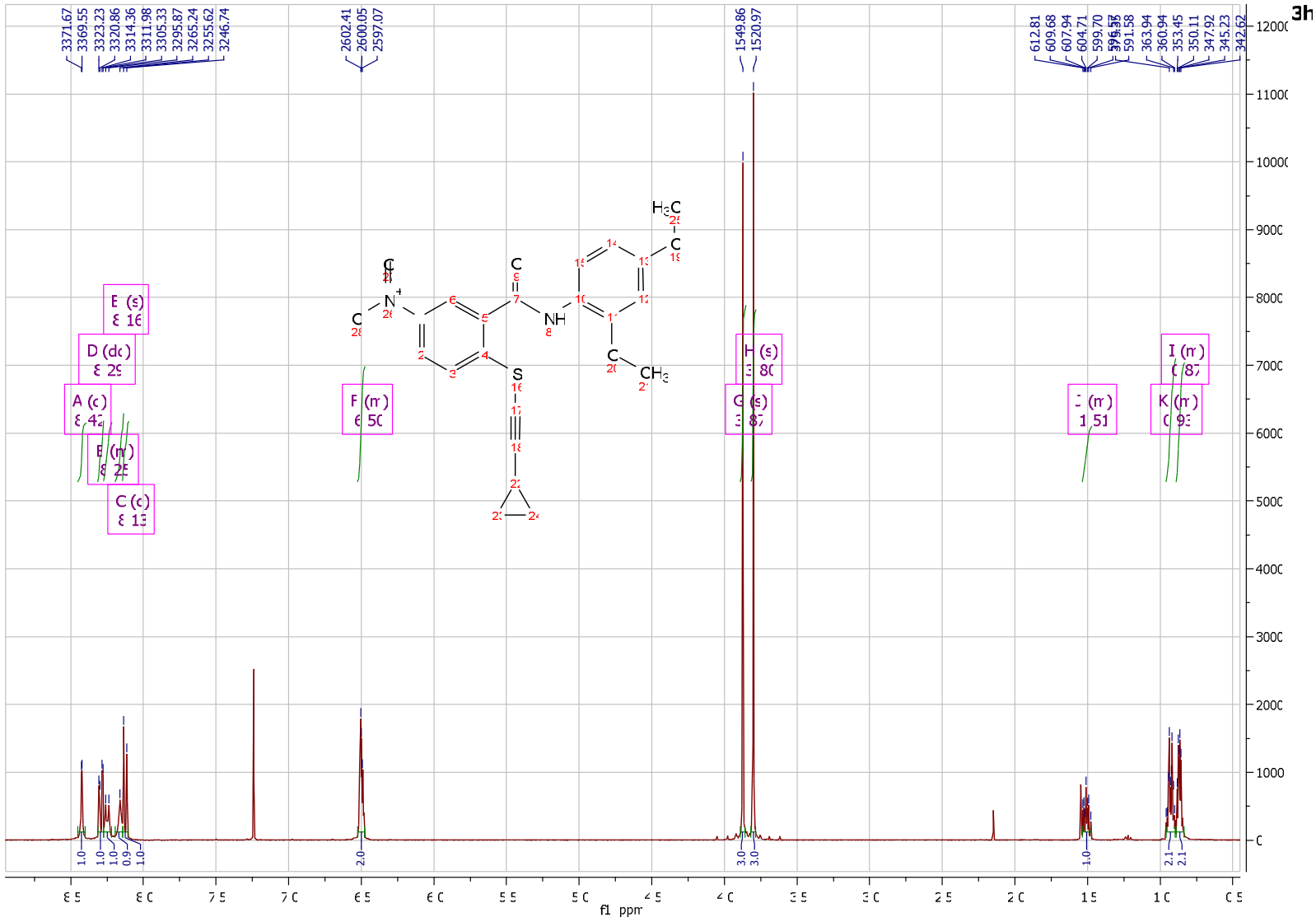

3e
164.39
151.83
149.43
145.39
143.11
138.76
134.46
131.12
128.25
126.07
123.54
122.83
118.69
115.79
96.58
79.83
41.70
f1 ppm

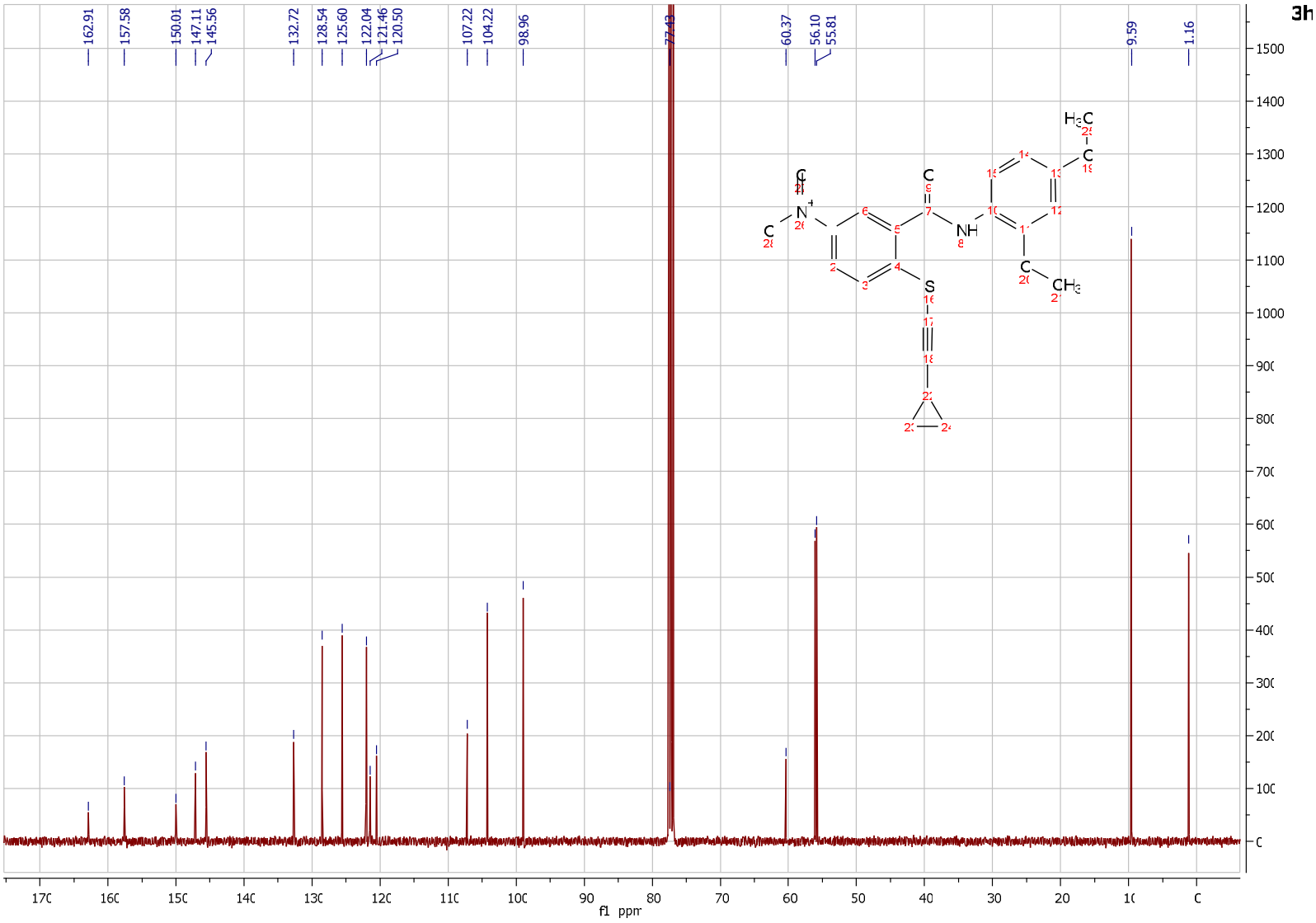

9.03
9.02
8.68
8.68
8.67
8.66
8.61
8.60
8.03
7.84
7.83
7.82
7.82
7.82
7.81
7.80
7.53
7.52
7.47
7.46
7.20
3.54
2.96
2.93
2.93
2.92
2.92
2.91
2.79
2.76
2.75
2.75
2.75
2.74
2.38
2.35
HENKE AH002/V
1H NMR in DMF-d7
24-09-09 RA
****
NAME HENKE_AH002V
EXPNO 1
PROCNO 1
Date_ 20090924
Time 8.57
INSTRUM spect
PROBHD 5 mm TXI 1H-13
PULPROG zg30
TD 80126
SOLVENT DMF
NS 32
DS 0
SWH 8012.820 Hz
FIDRES 0.100003 Hz
AQ 4.9999123 sec
RG 12.7
DW 62.400 usec
DE 6.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 3.00 dB
PL1W 4.28034639 W
SFO1 499.9539996 MHz
SI 131072
SF 499.9500013 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 20.00
3f
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
1.0
1.0
1.0
1.6
2.0
1.1
1.1
2.9
8.6
2.9
3.0
5.8
40971


3f
165.11
163.38
163.15
162.92
147.05
145.05
136.81
135.77
134.71
133.82
132.79
131.97
129.80
129.14
129.05
128.34
127.49
125.46
125.17
124.40
99.69
82.16
36.15
35.99
35.82
35.65
35.49
35.32
35.15
31.01
30.85
30.68
30.51
30.35
30.18
30.01
18.87
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


3g
f1 ppm


3g
165.30
146.72
145.40
133.40
131.79
128.41
125.60
121.99
117.91
103.57
64.76
42.93
30.76
22.25
20.27
13.75
NH
CH2
S
f1 ppm


3371.67
3369.55
3323.23
3320.86
3314.36
3311.98
3305.33
3295.87
3265.24
3255.62
3246.74
2602.41
2600.05
2597.07
1549.86
1520.97
612.81
609.68
607.94
604.71
599.70
591.58
363.94
360.94
353.45
350.11
347.92
345.23
342.62
3h
f1 ppm


162.91
157.58
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147.11
145.56
132.72
128.54
125.60
122.04
121.46
120.50
107.22
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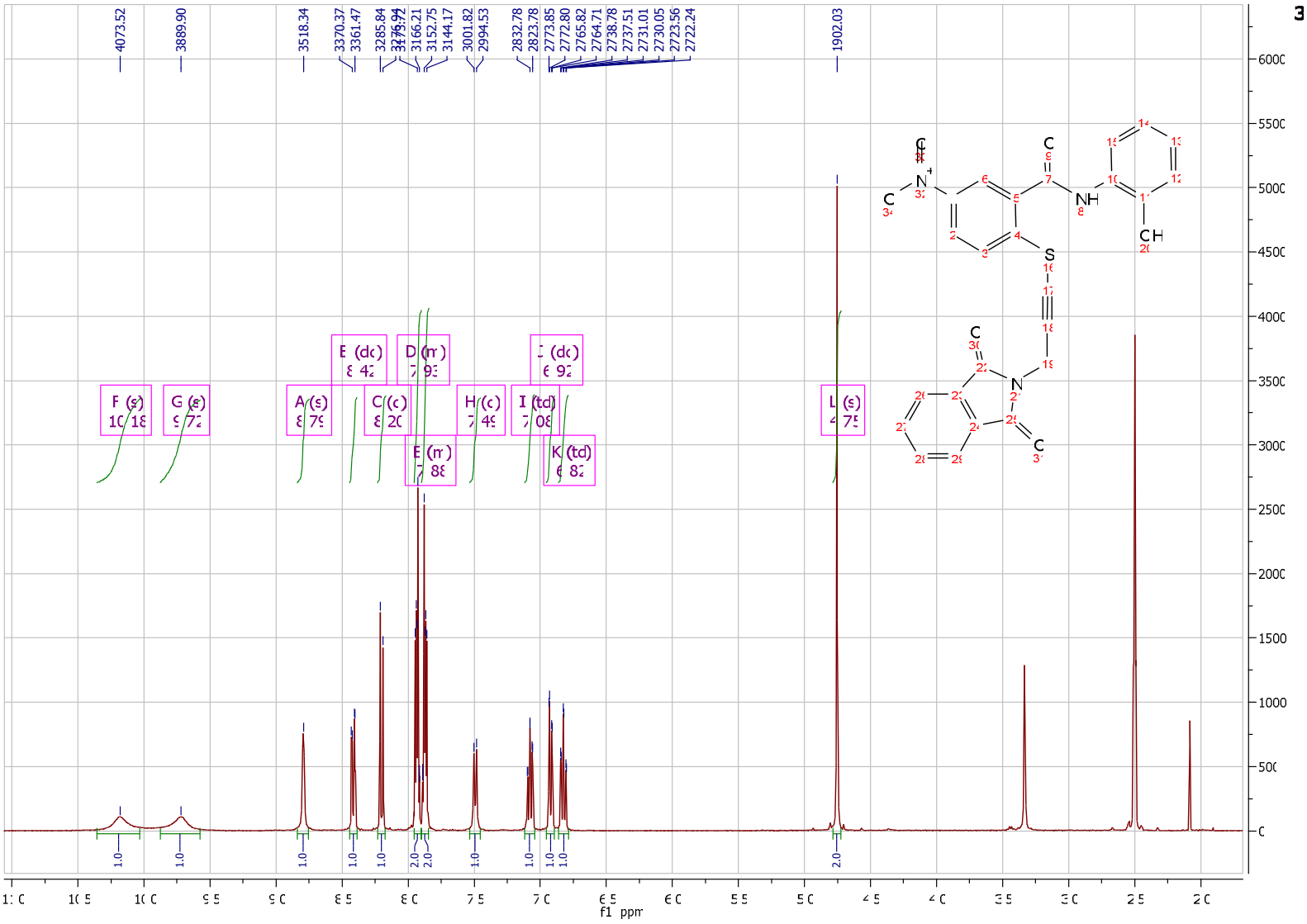
98.96
77.43
60.37
56.10
55.81
9.59
1.16
3h
f1 ppm


4073.52
3889.90
3518.34
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3361.47
3285.84
3166.21
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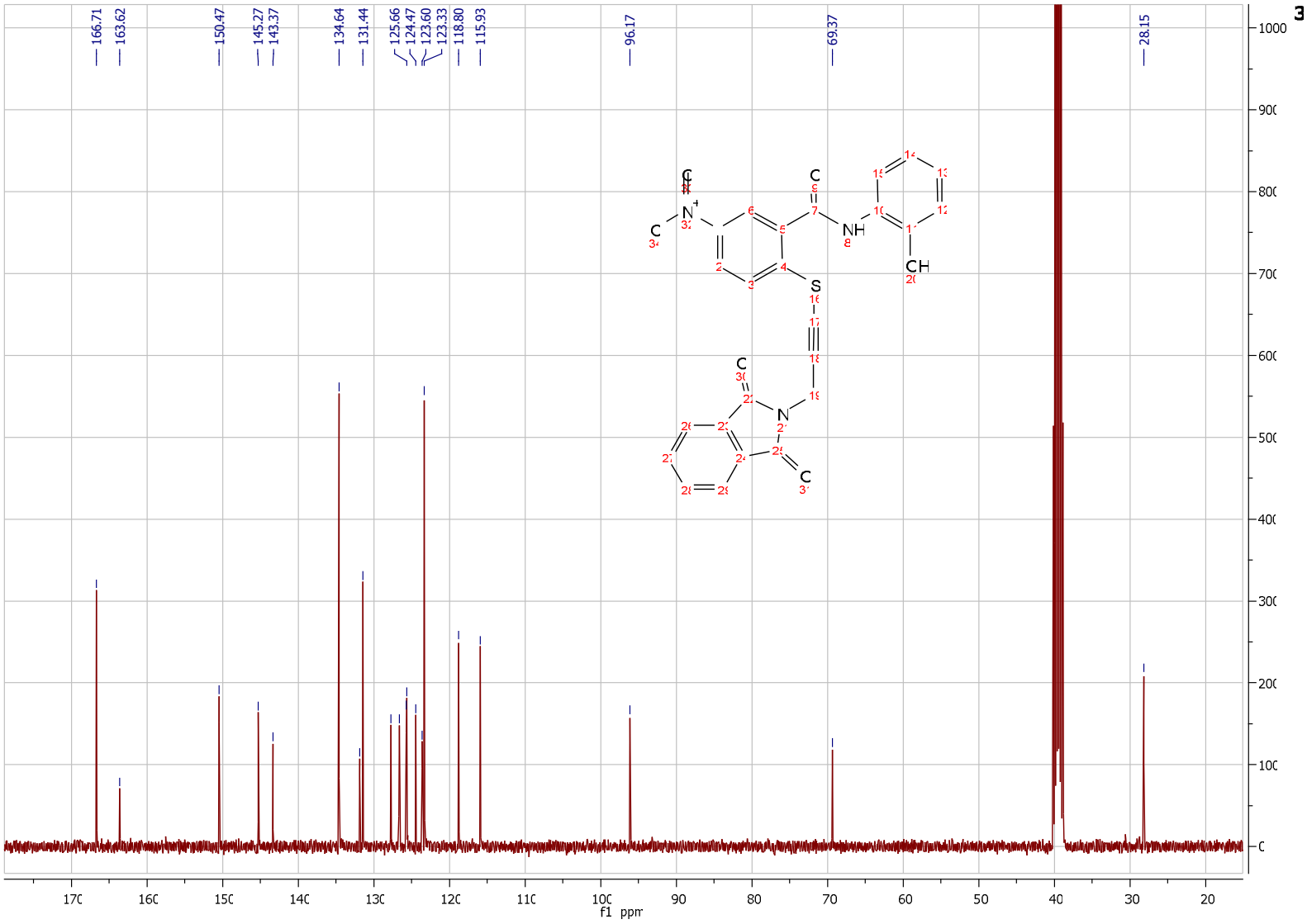
3144.17
3001.82
2994.53
2832.78
2823.78
2773.85
2772.80
2765.82
2764.71
2738.78
2737.51
2731.01
2730.05
2723.56
2722.24
1902.03
F (s)
G (s)
A (s)
E (dd)
D (m)
C (d)
E (m)
H (d)
I (td)
J (dd)
K (td)
L (s)
NH
CH
S
f1 ppm


166.71
163.62
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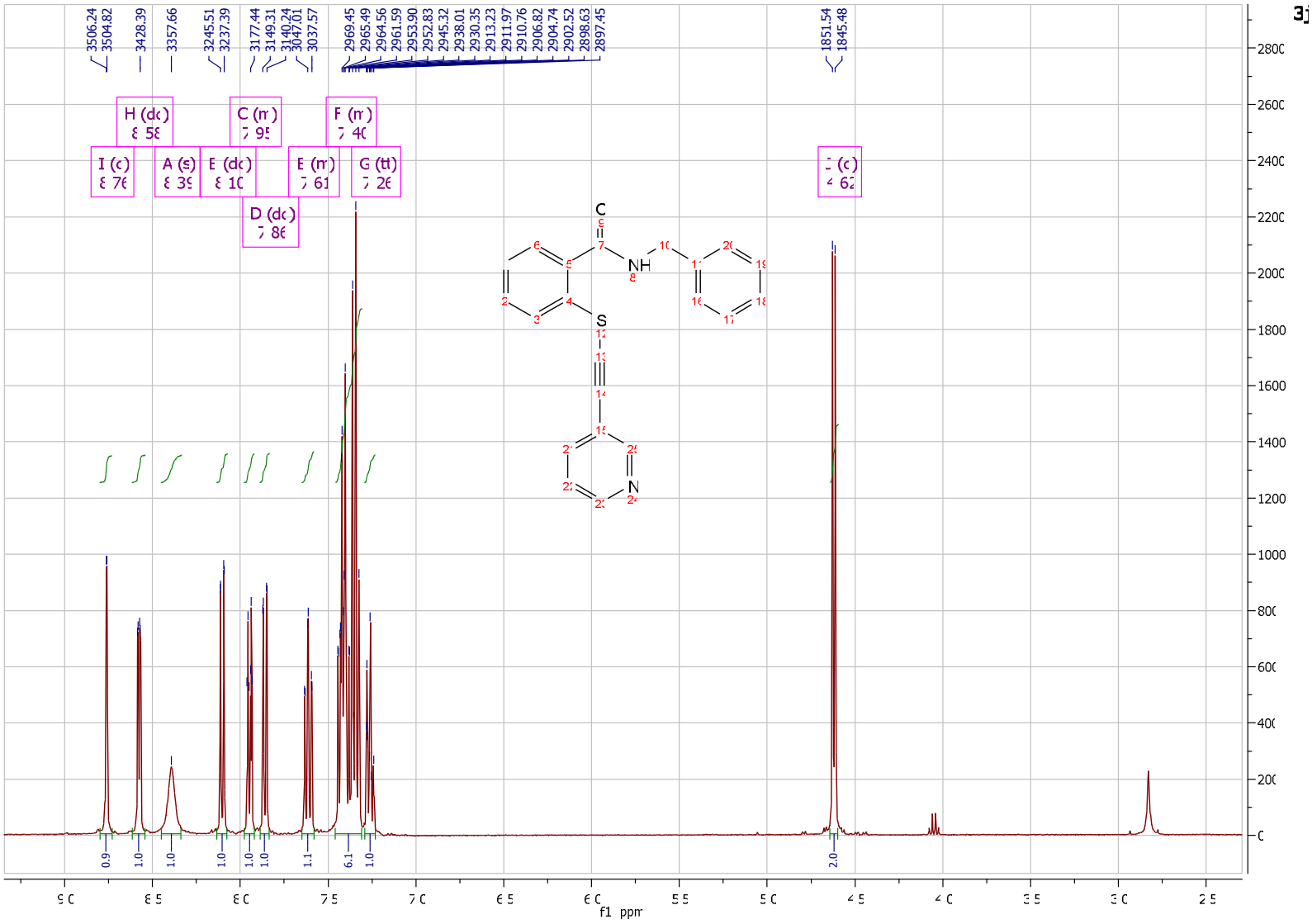
145.27
143.37
134.64
131.44
125.66
124.47
123.60
123.33
118.80
115.93
96.17
69.37
28.15
f1 ppm


3506.24
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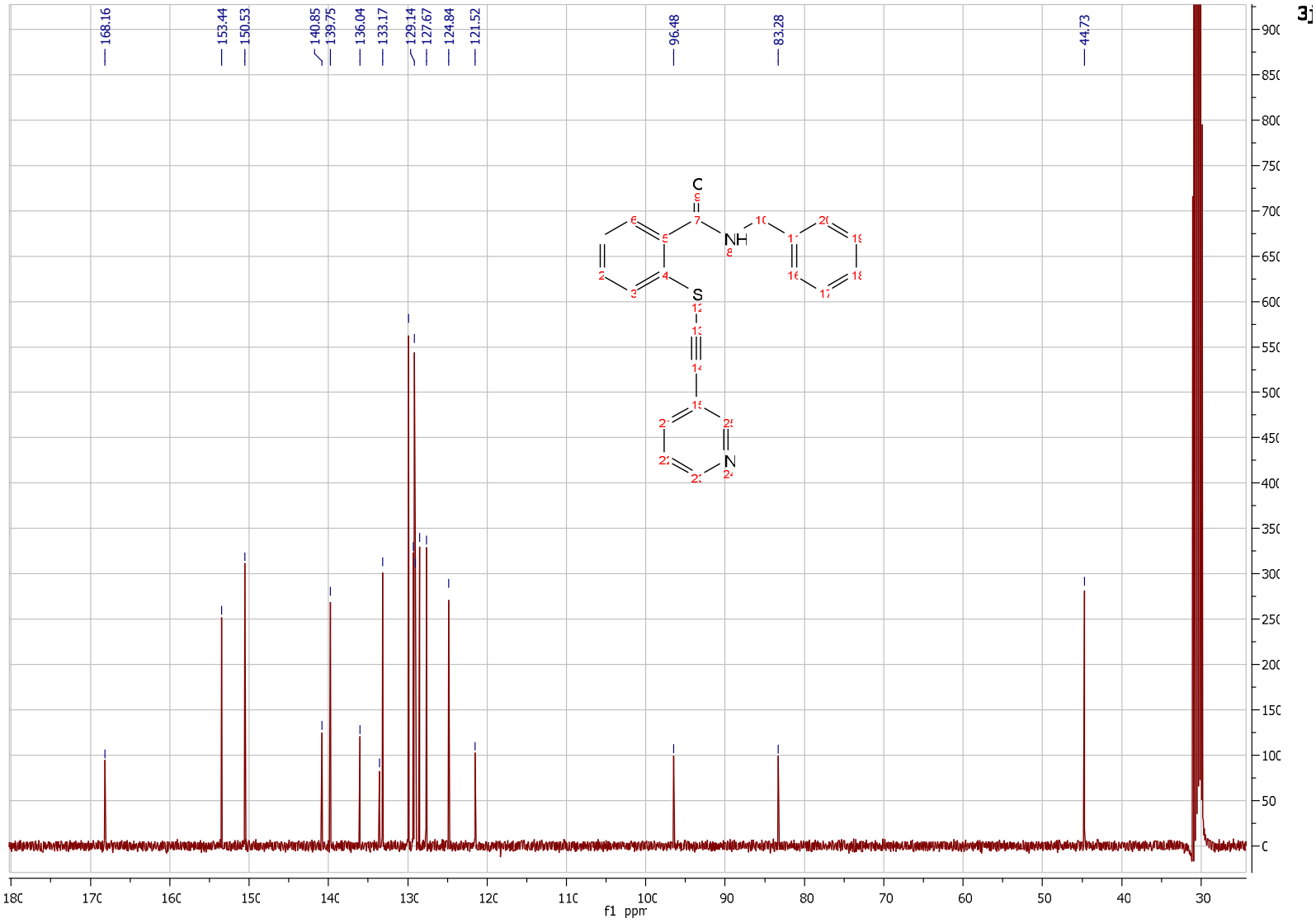
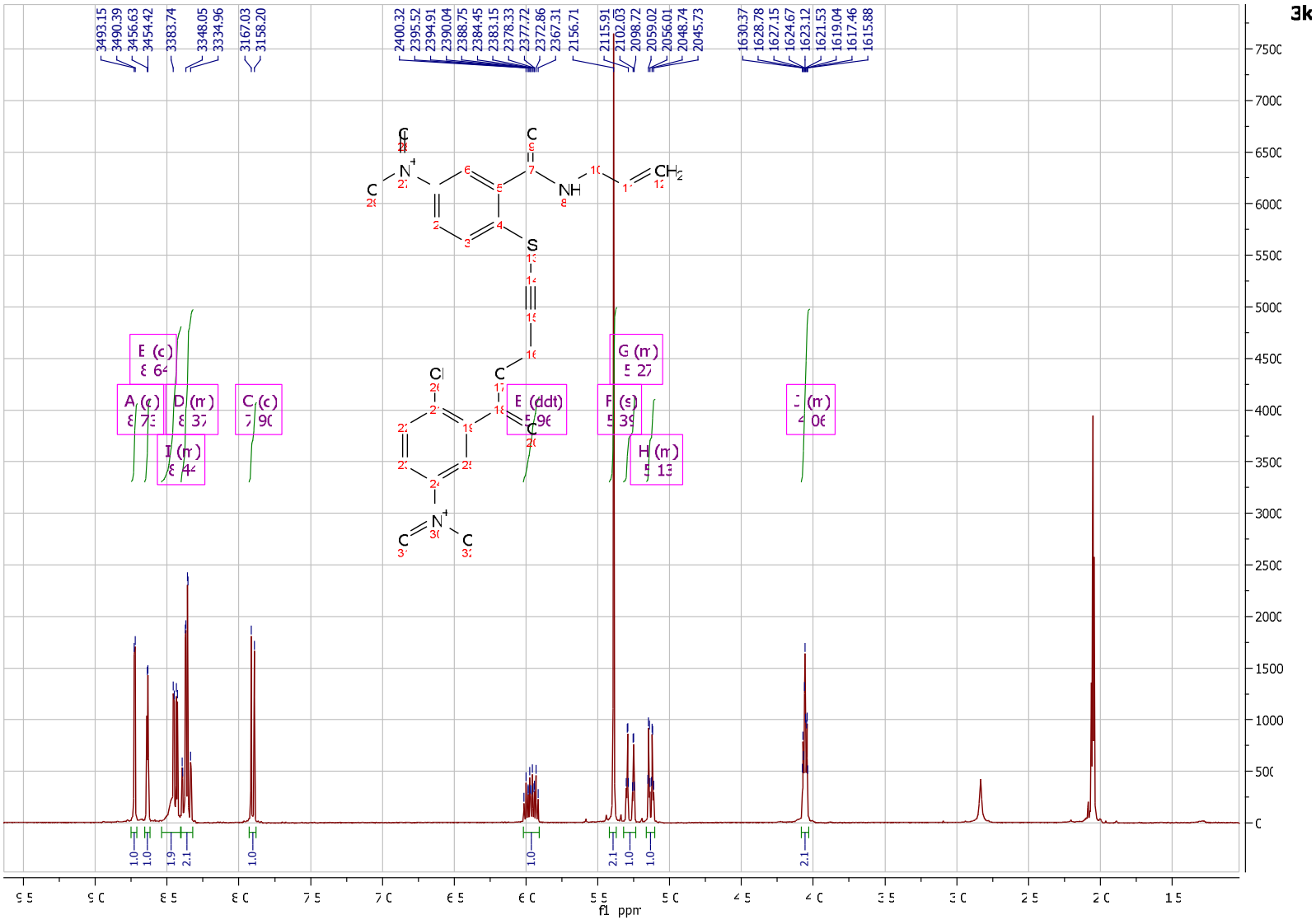
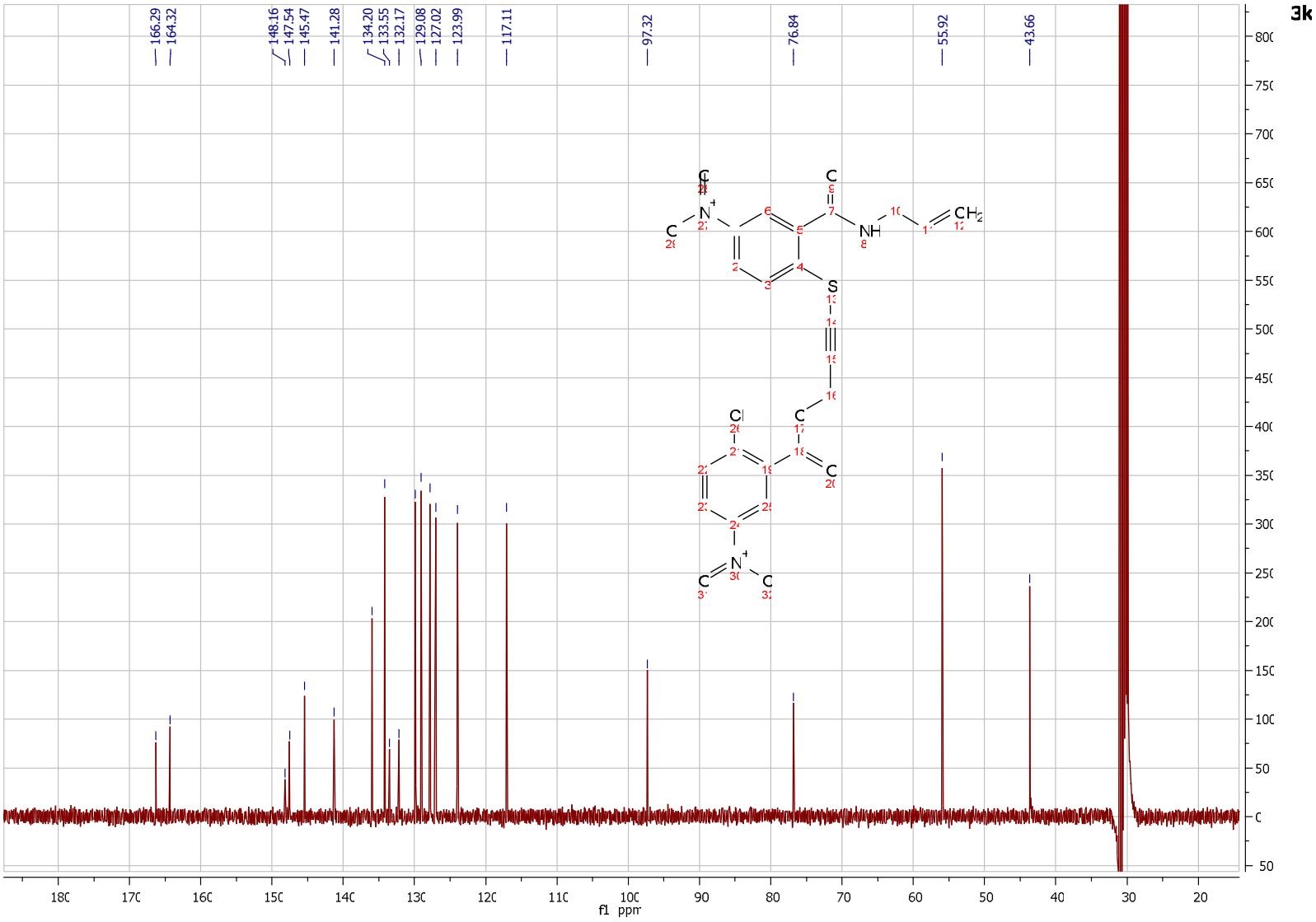
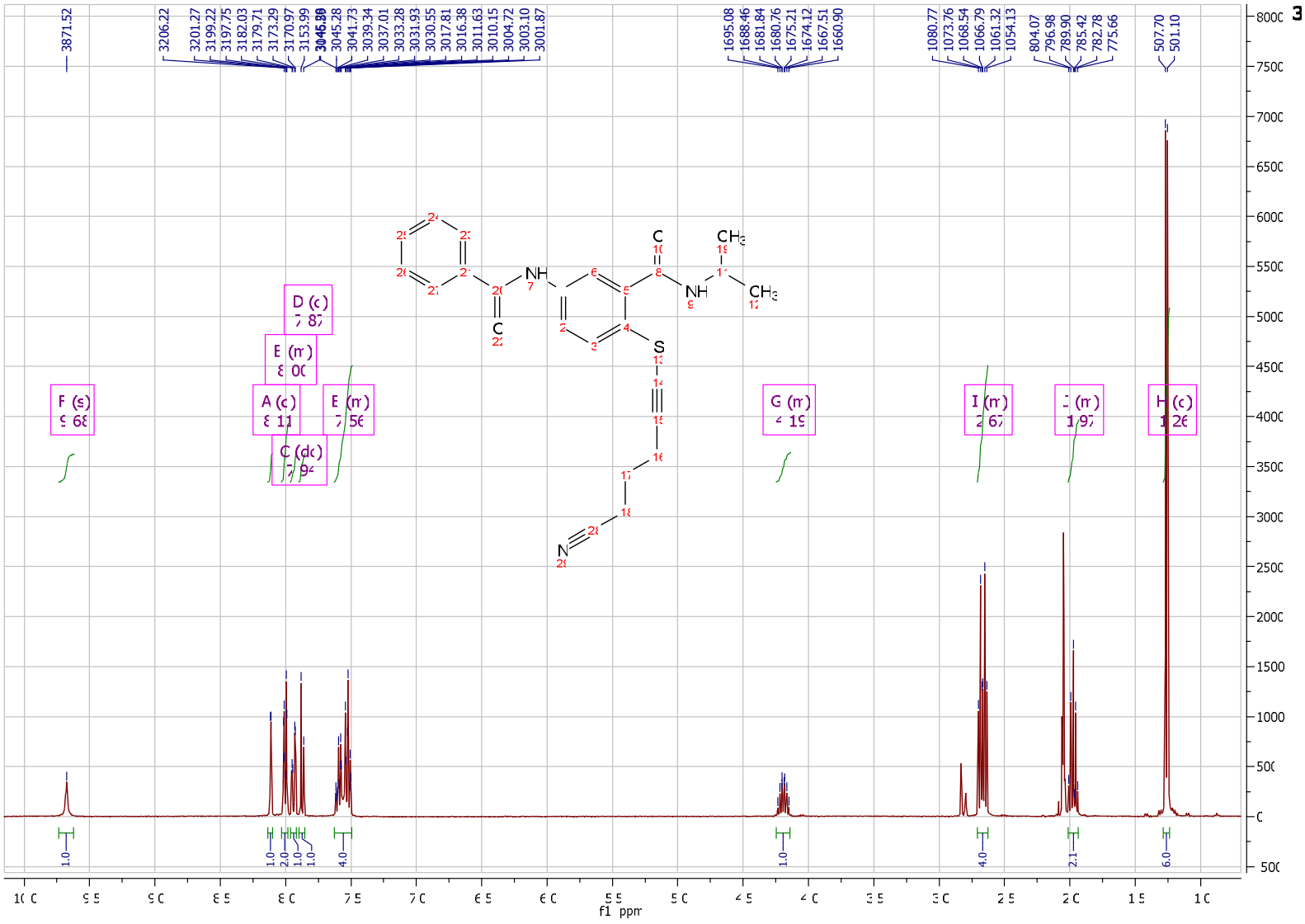
3245.51
3237.39
3177.44
3149.31
3140.24
3047.01
3037.57
2969.45
2965.49
2964.56
2961.59
2953.90
2952.83
2945.32
2938.01
2930.35
2913.23
2911.97
2910.76
2906.82
2904.74
2902.52
2898.63
2897.45
1851.54
1845.48
H (dd)
8 58
C (m)
7 95
F (m)
7 40
I (d)
8 76
A (s)
8 35
B (dd)
8 10
E (m)
7 61
G (tt)
7 26
D (dd)
7 86
J (d)
4 62
NH
S
N
0.9
1.0
1.0
1.0
1.0
1.0
1.1
6.1
1.0
2.0
f1 ppm


168.16
153.44
150.53
140.85
139.75
136.04
133.17
129.14
127.67
124.84
121.52
96.48
83.28
44.73
f1 ppm


3k
f1 ppm


3k
166.29
164.32
148.16
147.54
145.47
141.28
134.20
133.55
132.17
129.08
127.02
123.99
117.11
97.32
76.84
55.92
43.66
f1 ppm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3197.75
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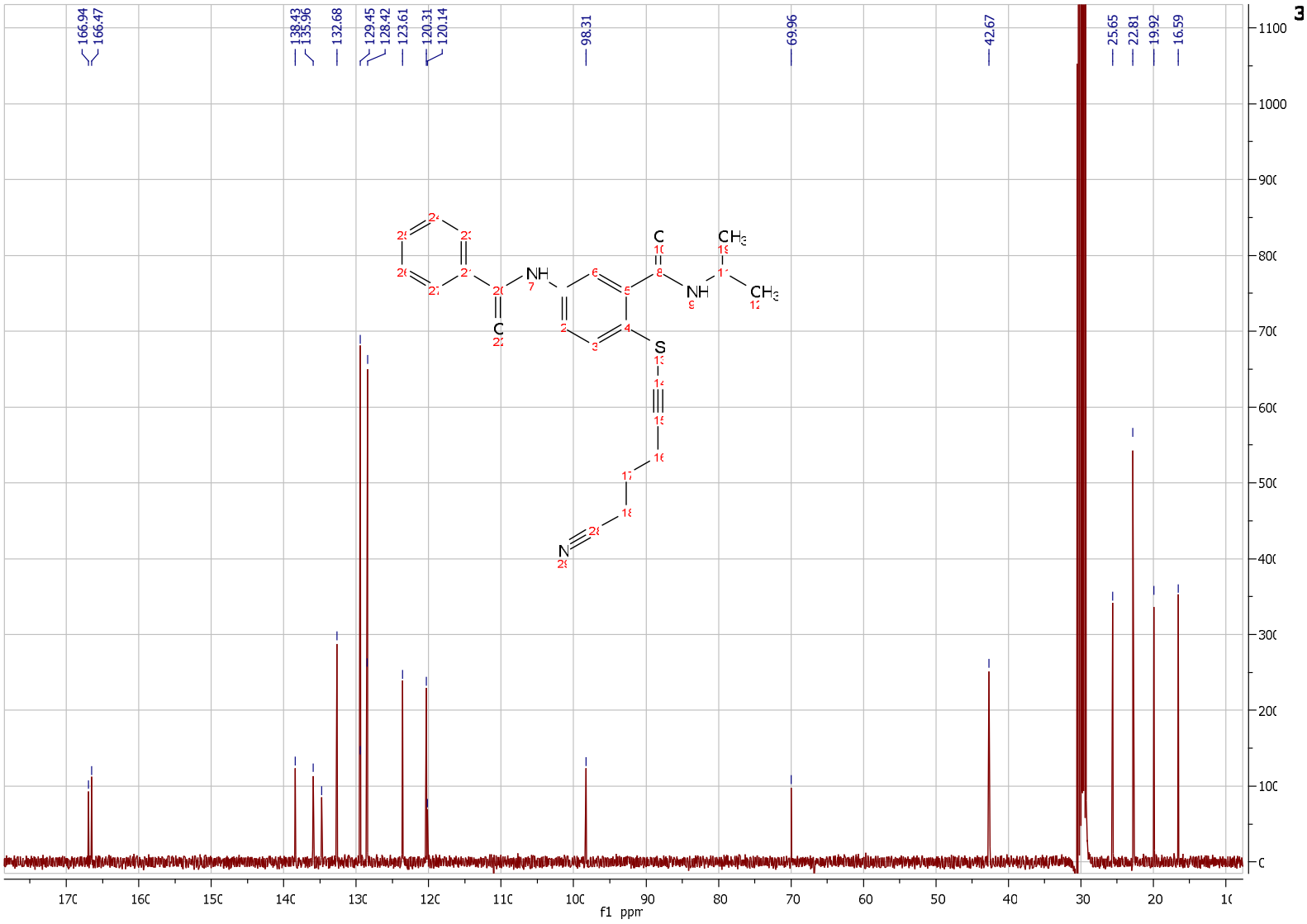
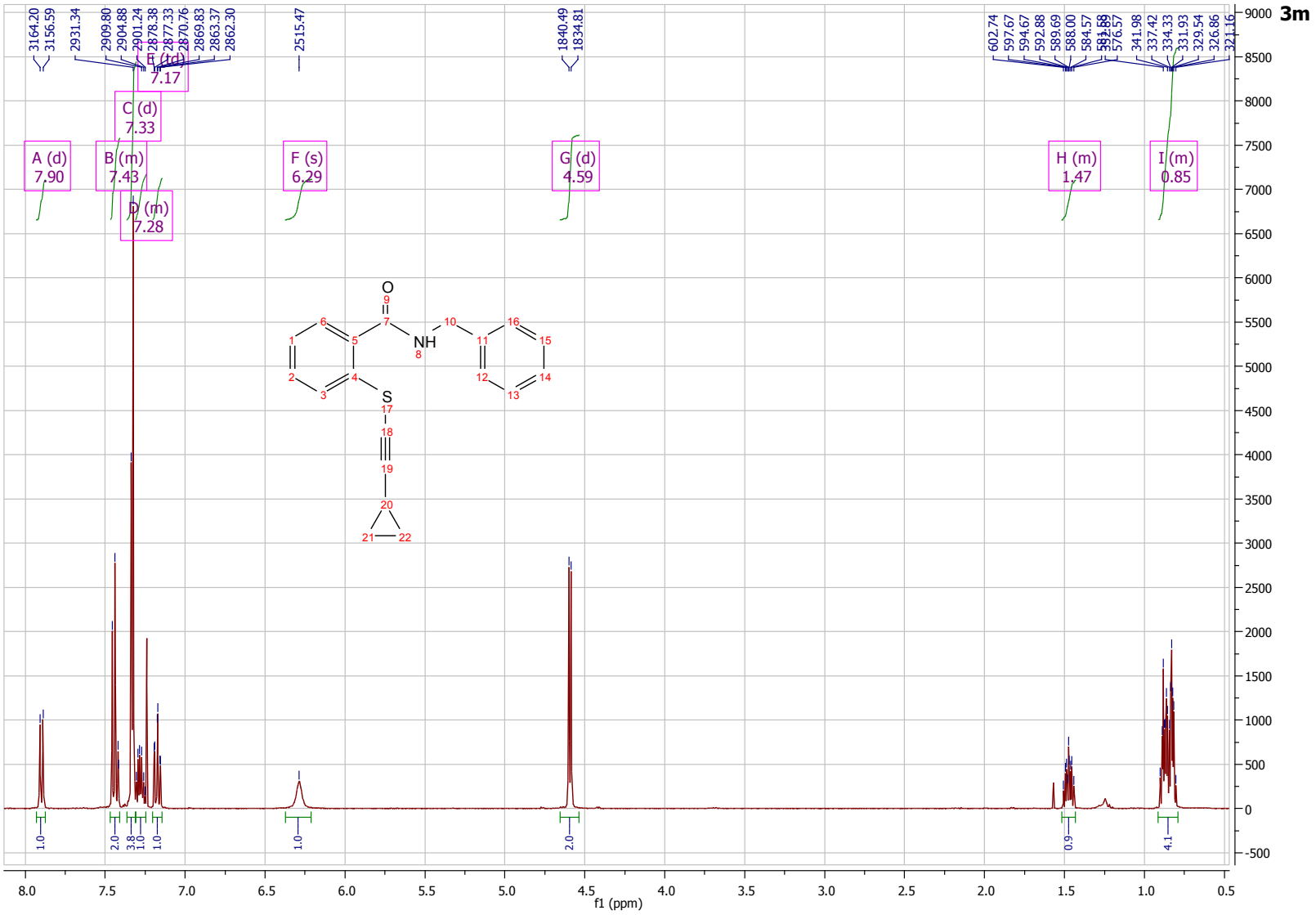
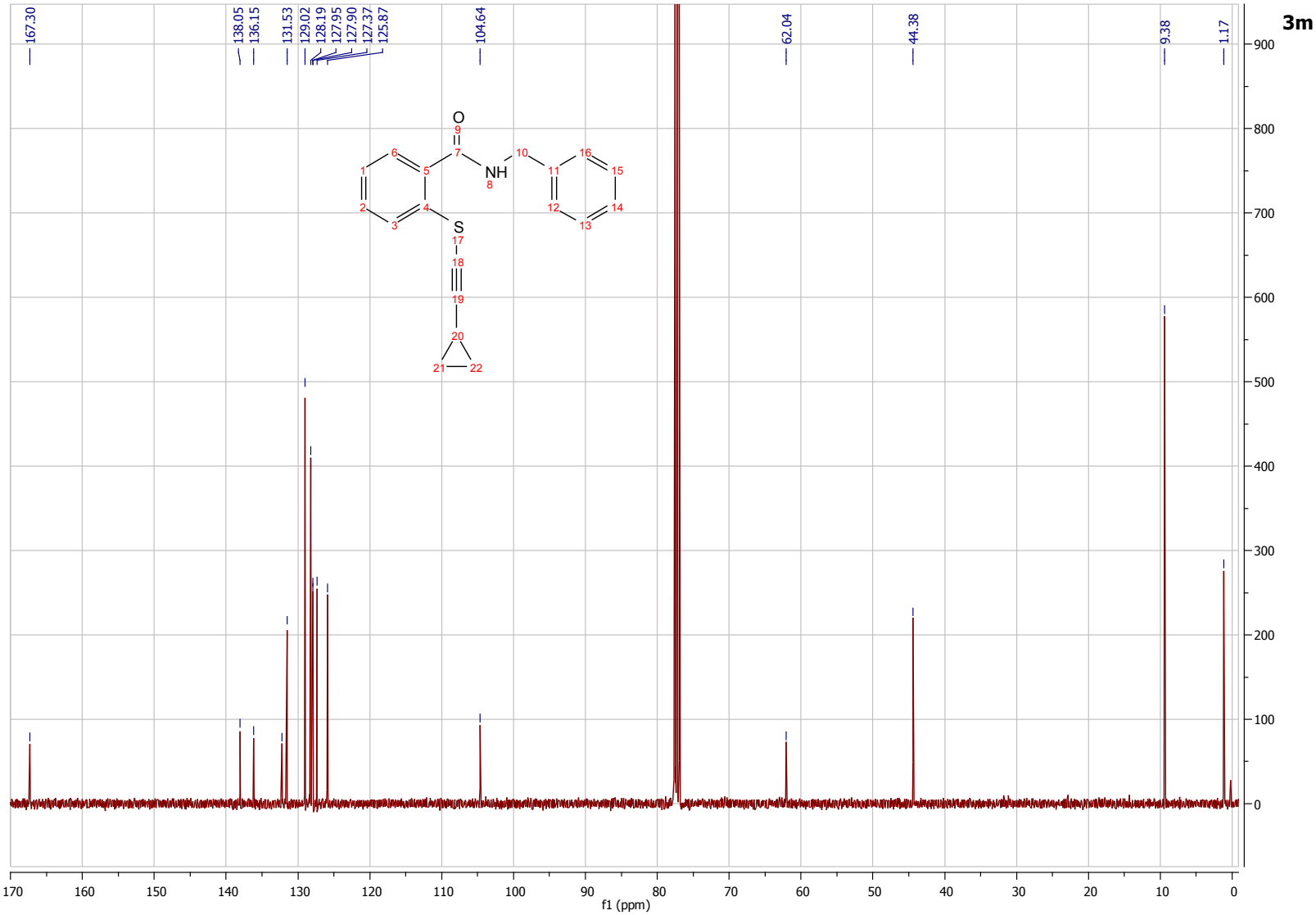
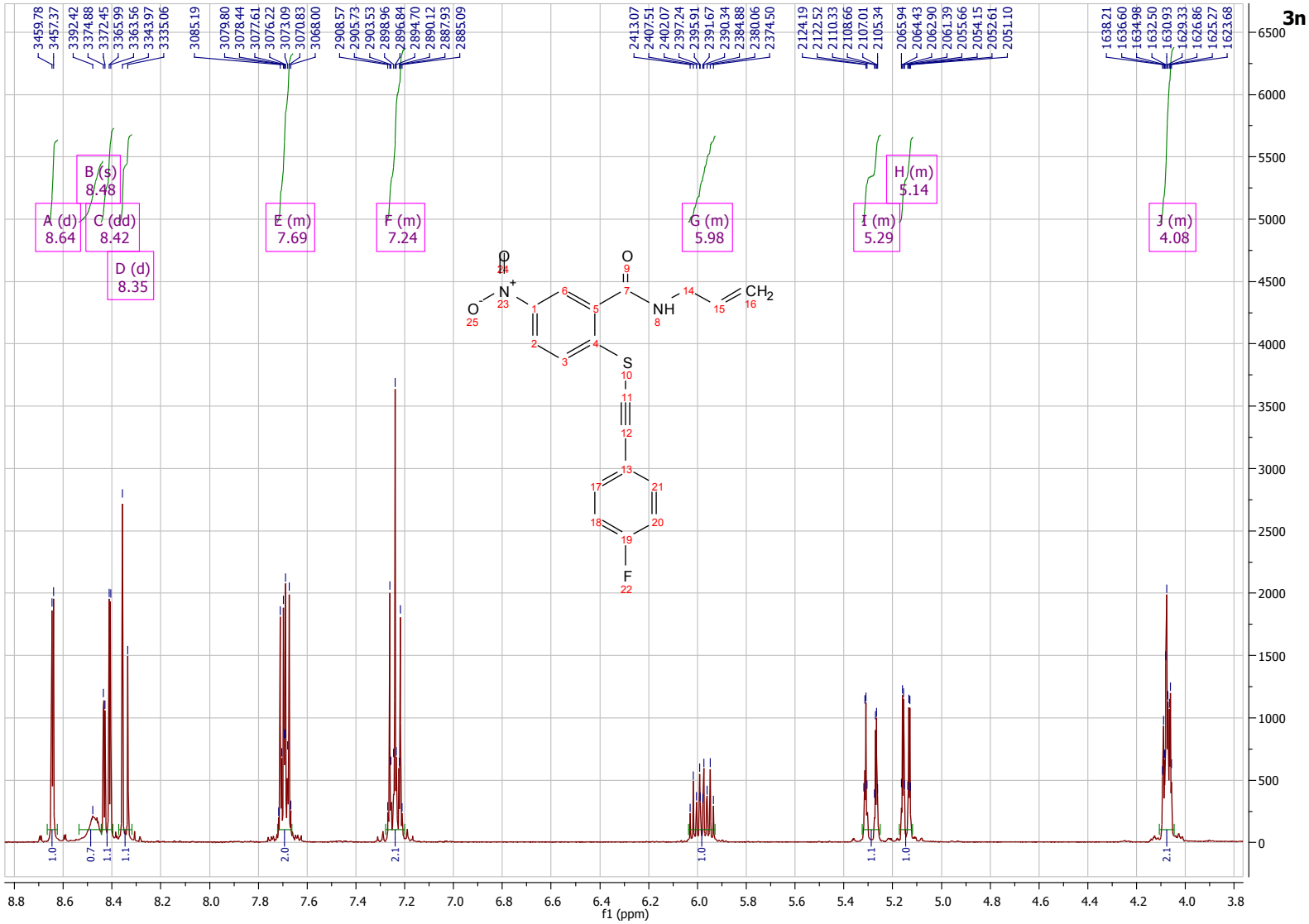
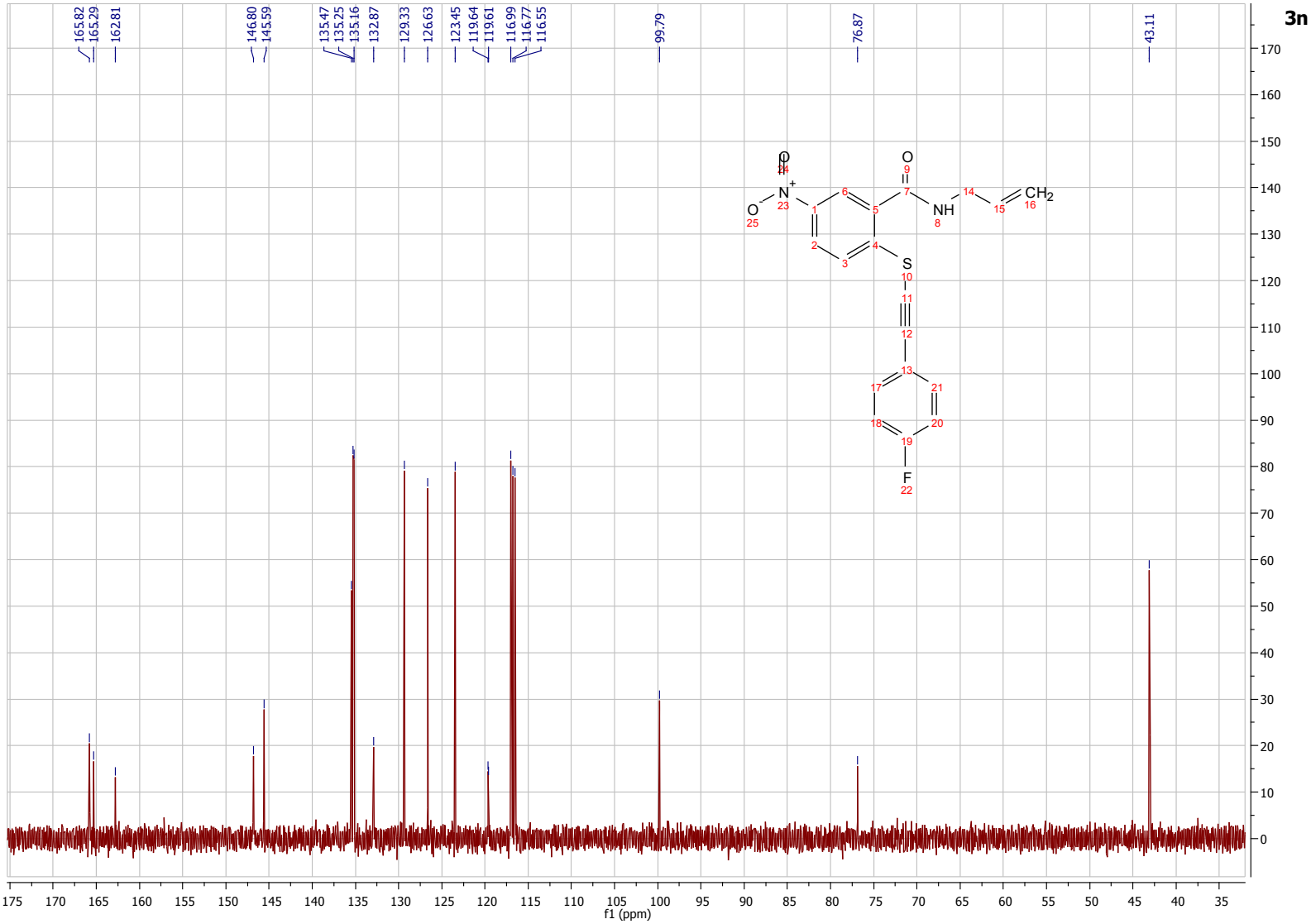
3179.71
3173.29
3170.97
3153.99
3045.28
3041.73
3039.34
3037.01
3033.28
3031.93
3030.55
3017.81
3016.38
3011.63
3010.15
3004.72
3003.10
3001.87
1695.08
1688.46
1681.84
1680.76
1675.21
1674.12
1667.51
1660.90
1080.77
1073.76
1068.54
1066.79
1061.32
1054.13
804.07
796.98
789.90
785.42
782.78
775.66
507.70
501.10
D (d)
7.87
E (m)
8.00
F (s)
9.68
A (d)
8.11
E (m)
7.56
C (dd)
7.94
G (m)
4.19
I (m)
2.67
J (m)
1.97
H (d)
1.26
NH
NH
CH3
CH3
O
O
S
N
f1 ppm

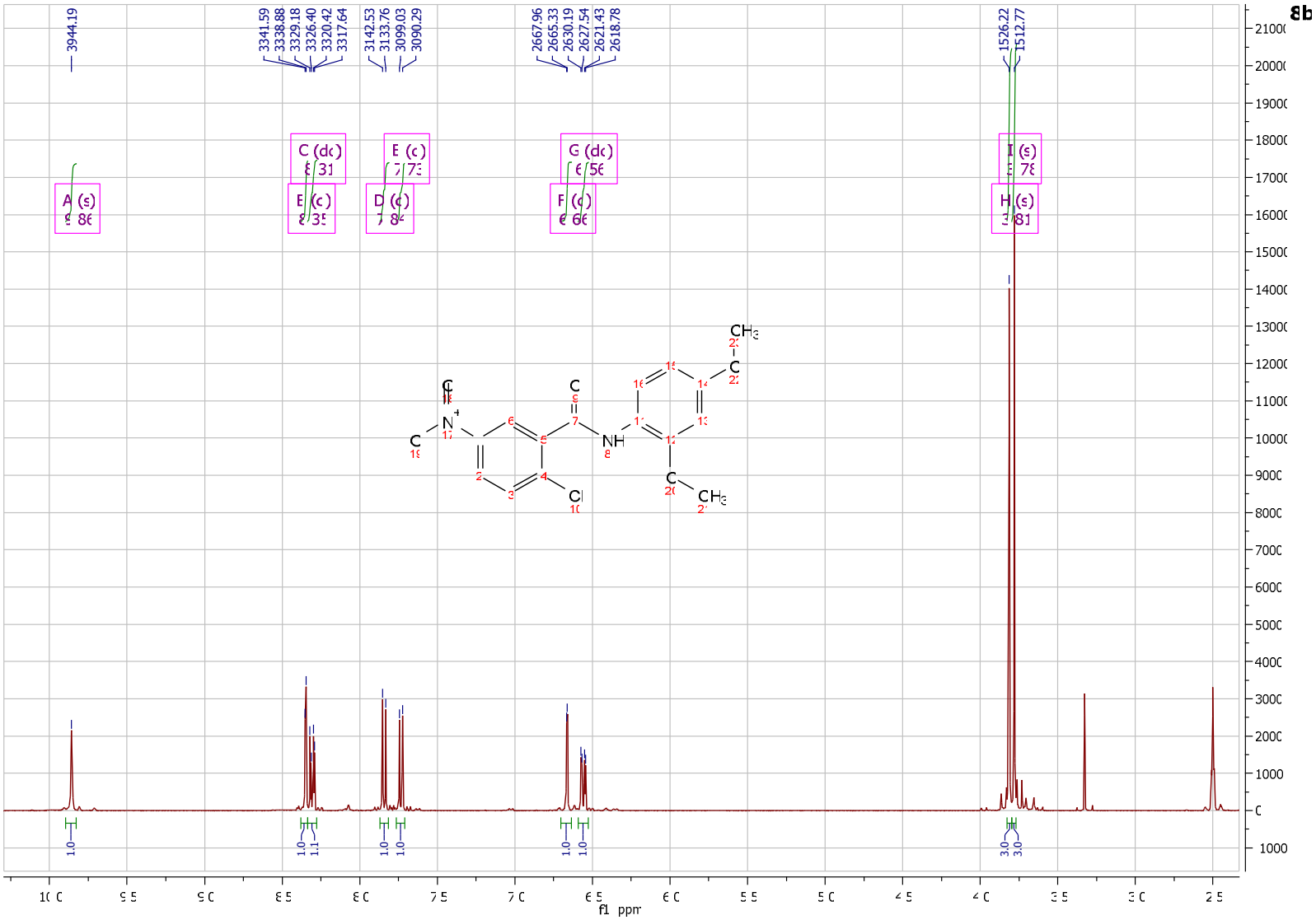

166.94
166.47
138.43
135.96
132.68
129.45
128.42
123.61
120.31
120.14
98.31
69.96
42.67
25.65
22.81
19.92
16.59
NH
NH
CH3
CH3
S
N
f1 ppm

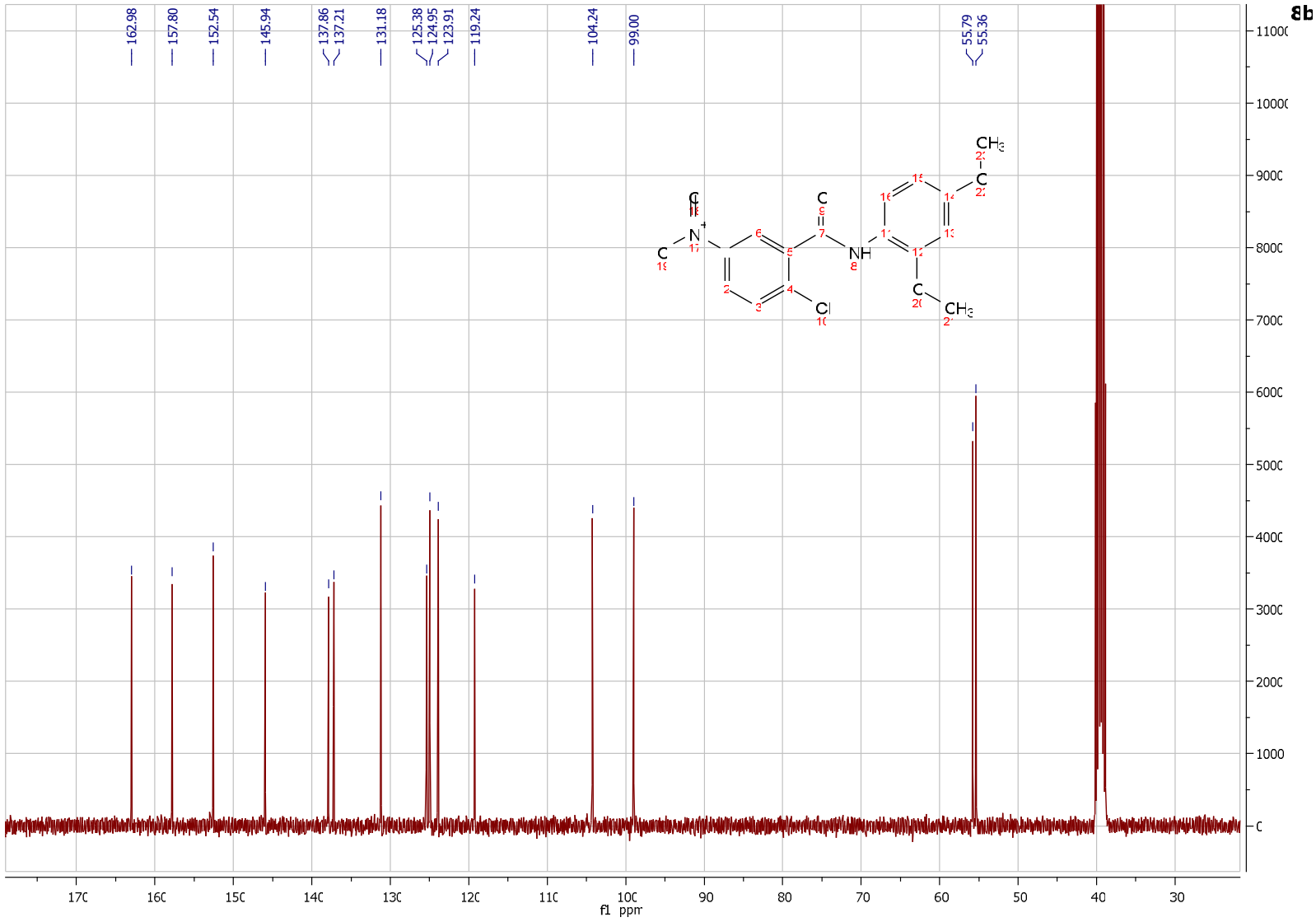

3m
A (d) 7.90
B (m) 7.43
C (d) 7.33
D (m) 7.28
E (td) 7.17
F (s) 6.29
G (d) 4.59
H (m) 1.47
I (m) 0.85
NH
S
O
f1 (ppm)

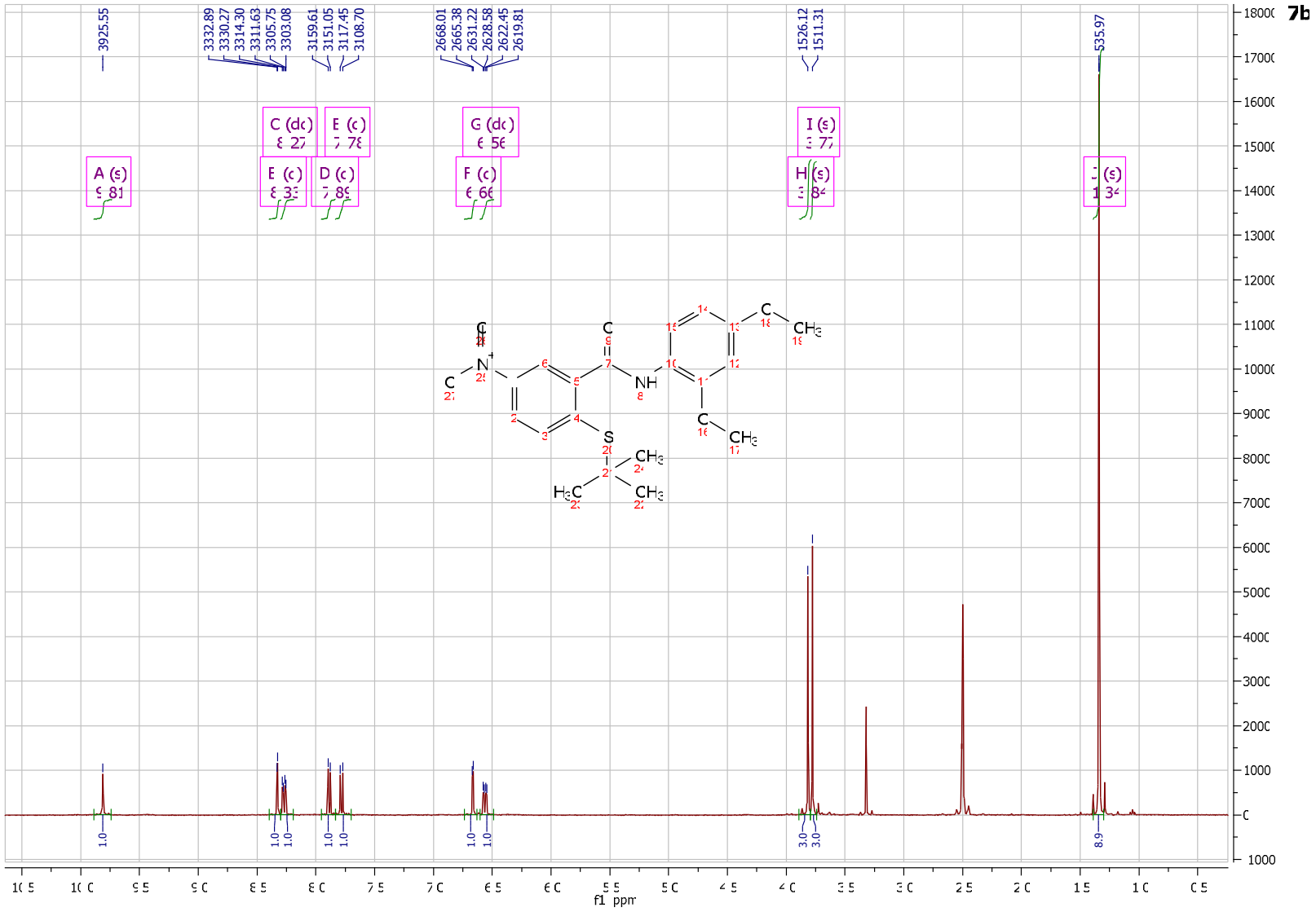

3m
167.30
138.05
136.15
131.53
129.02
128.19
127.95
127.90
127.37
125.87
104.64
62.04
44.38
9.38
1.17
O
NH
S
f1 (ppm)

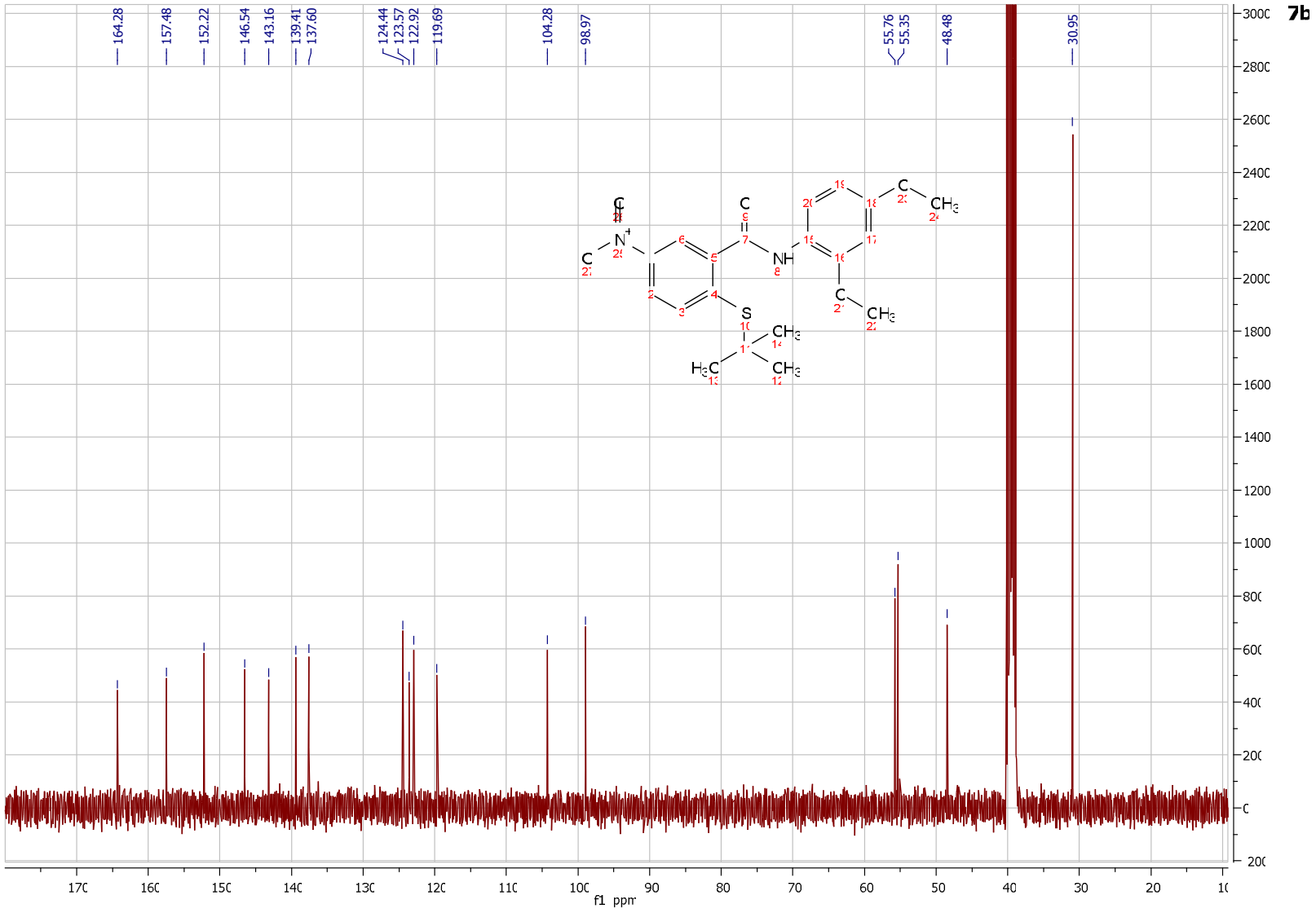

3n
A (d) 8.64
B (s) 8.48
C (dd) 8.42
D (d) 8.35
E (m) 7.69
F (m) 7.24
G (m) 5.98
H (m) 5.14
I (m) 5.29
J (m) 4.08
f1 (ppm)

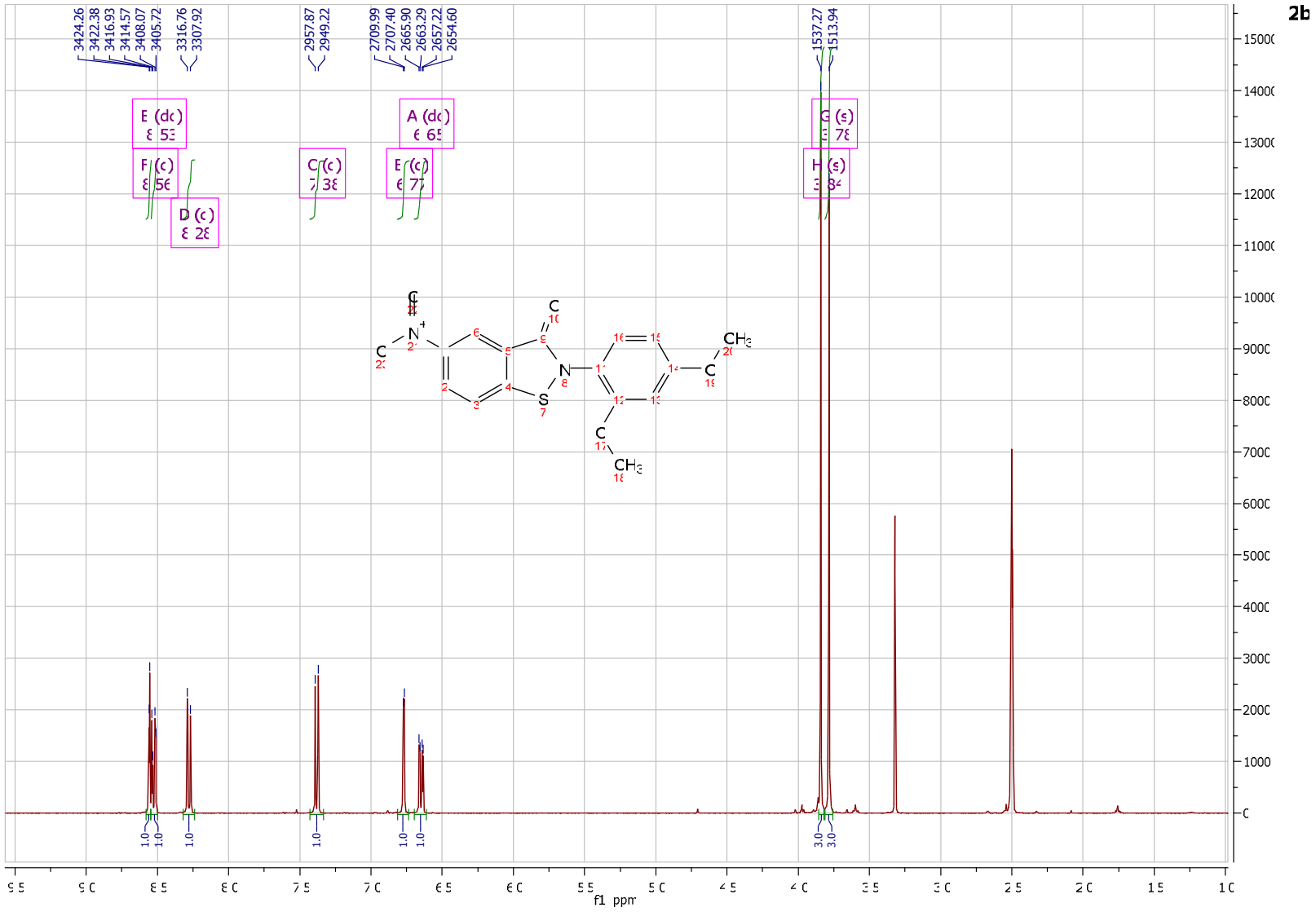

3n
165.82
165.29
162.81
146.80
145.59
135.47
135.25
135.16
132.87
129.33
126.63
123.45
119.64
119.61
116.99
116.77
116.55
99.79
76.87
43.11
f1 (ppm)

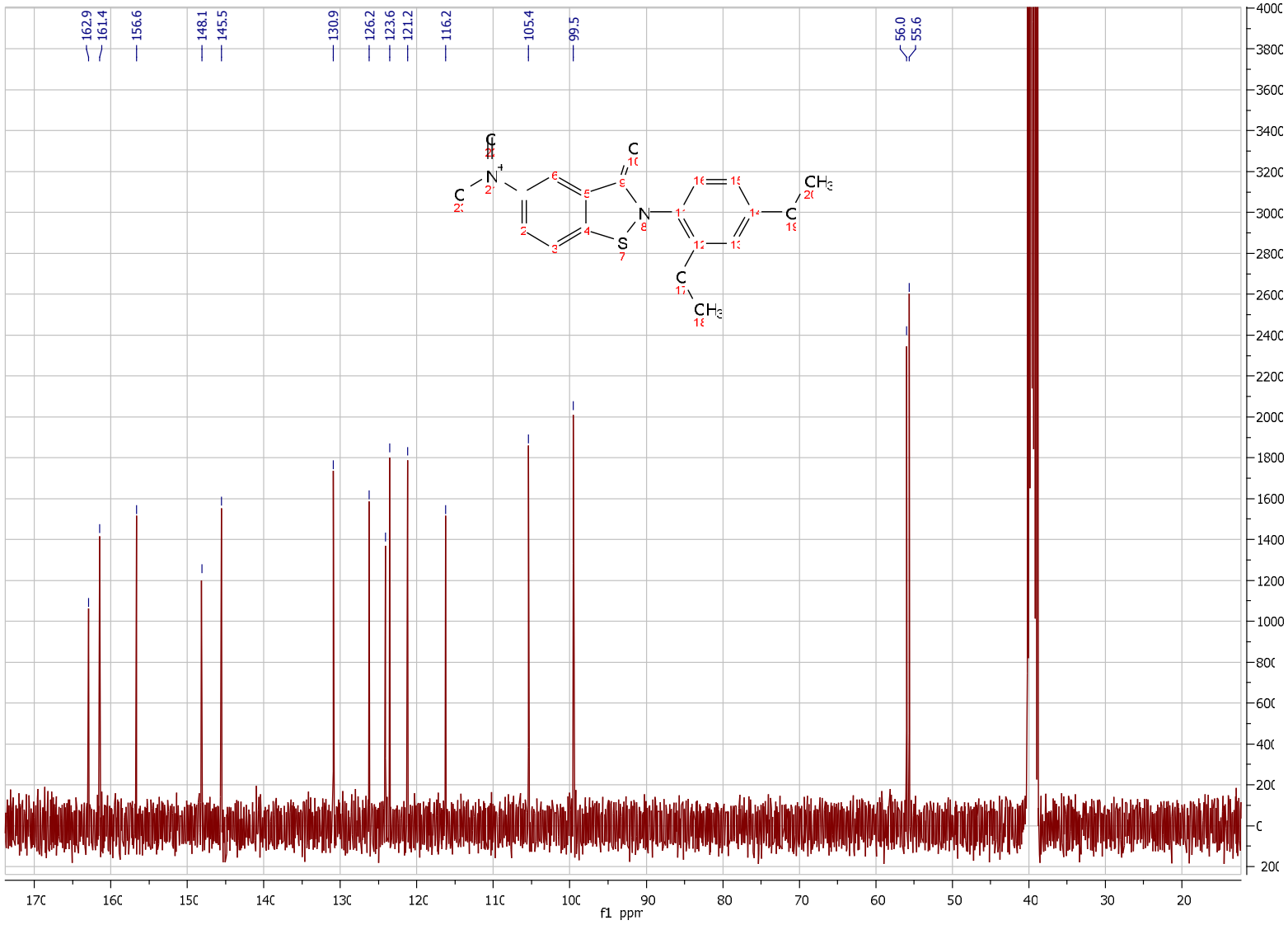

8b
3944.19
3341.59
3338.88
3329.18
3326.40
3320.42
3317.64
3142.53
3133.76
3099.03
3090.29
2667.96
2665.33
2630.19
2627.54
2621.43
2618.78
1526.22
1512.77
A (s)
C (dd)
E (d)
G (dd)
I (s)
f1 ppm

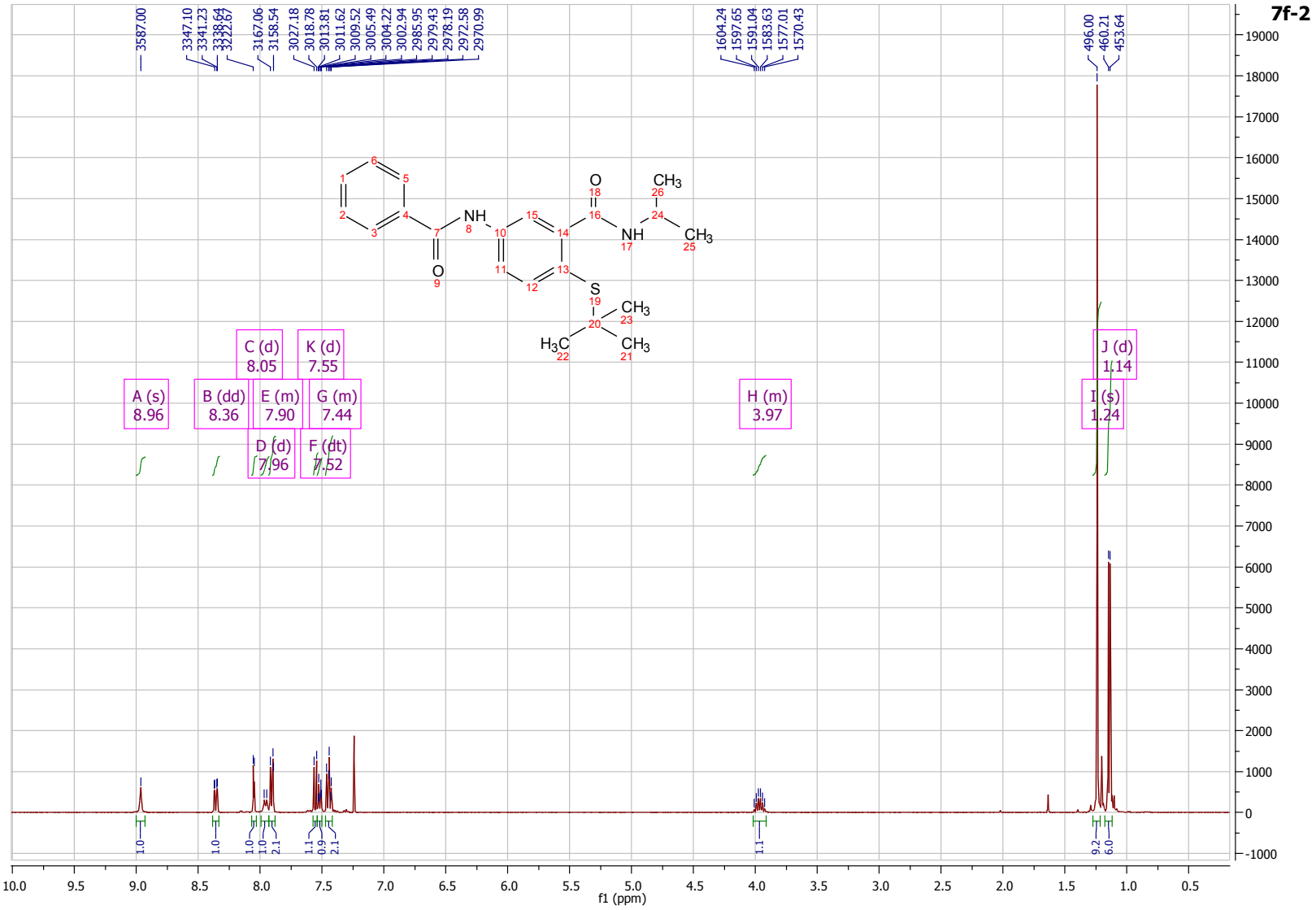

8b
162.98
157.80
152.54
145.94
137.86
137.21
131.18
125.38
124.95
123.91
119.24
104.24
99.00
55.79
55.36
f1 ppm

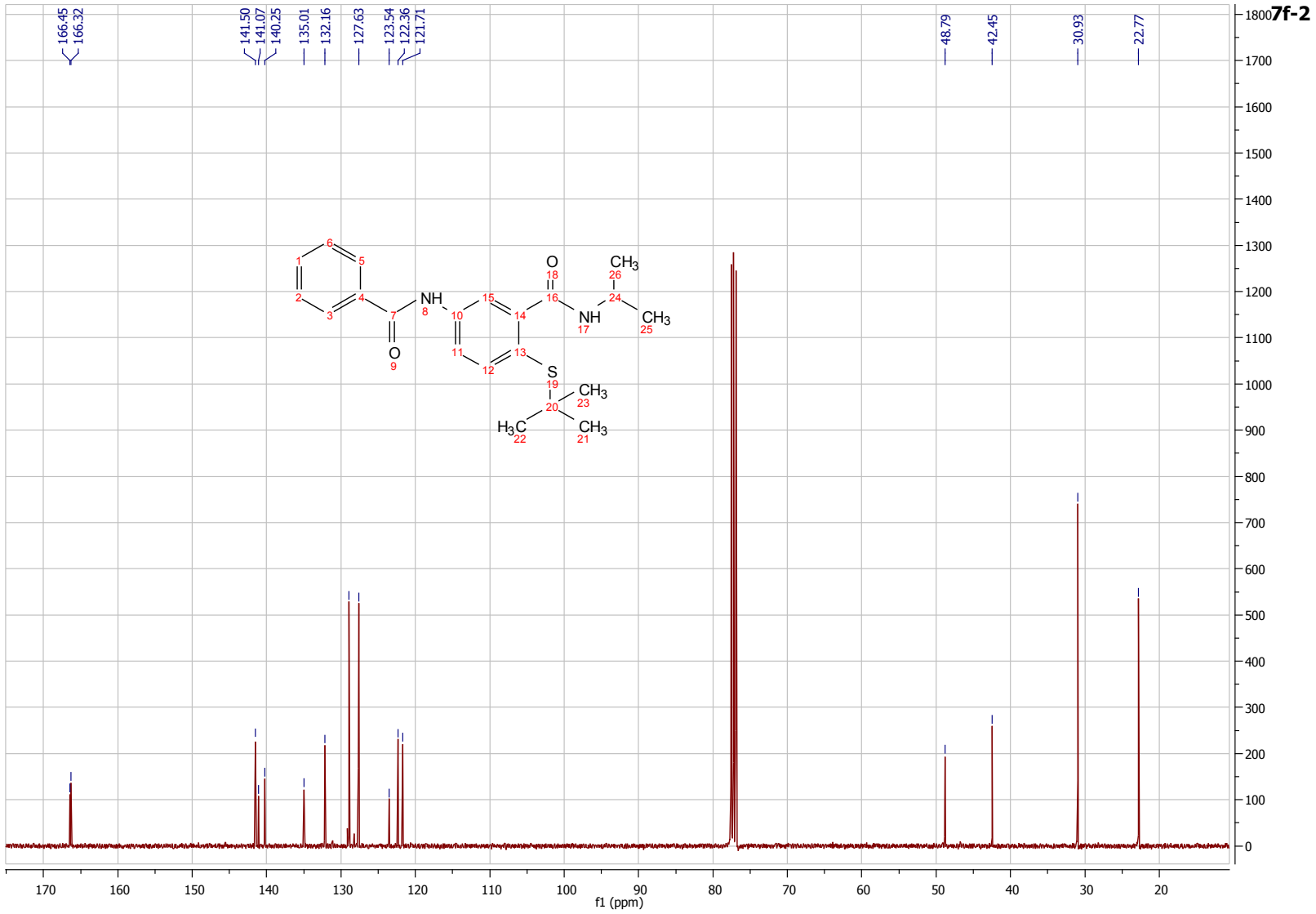

7b
3925.55
3332.89
3330.27
3314.30
3311.63
3305.75
3303.08
3159.61
3151.05
3117.45
3108.70
2668.01
2665.38
2631.22
2628.58
2622.45
2619.81
1526.12
1511.31
535.97
A (s)
C (dd)
E (c)
E (c)
D (d)
F (d)
I (s)
H (s)
J (s)
NH
S
f1 ppm

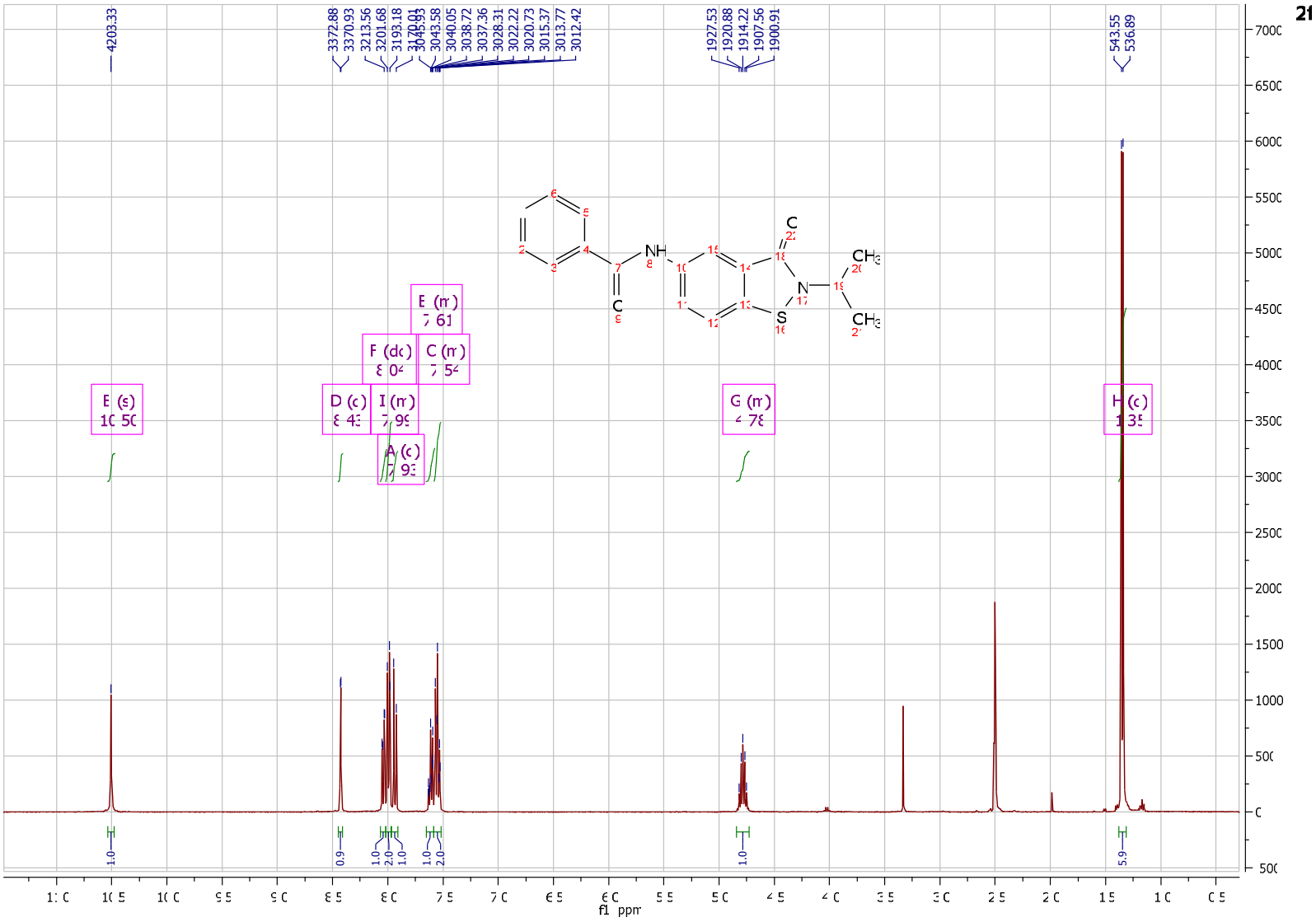

7b
164.28
157.48
152.22
146.54
143.16
139.41
137.60
124.44
123.57
122.92
119.69
104.28
98.97
55.76
55.35
48.48
30.95
f1 ppm

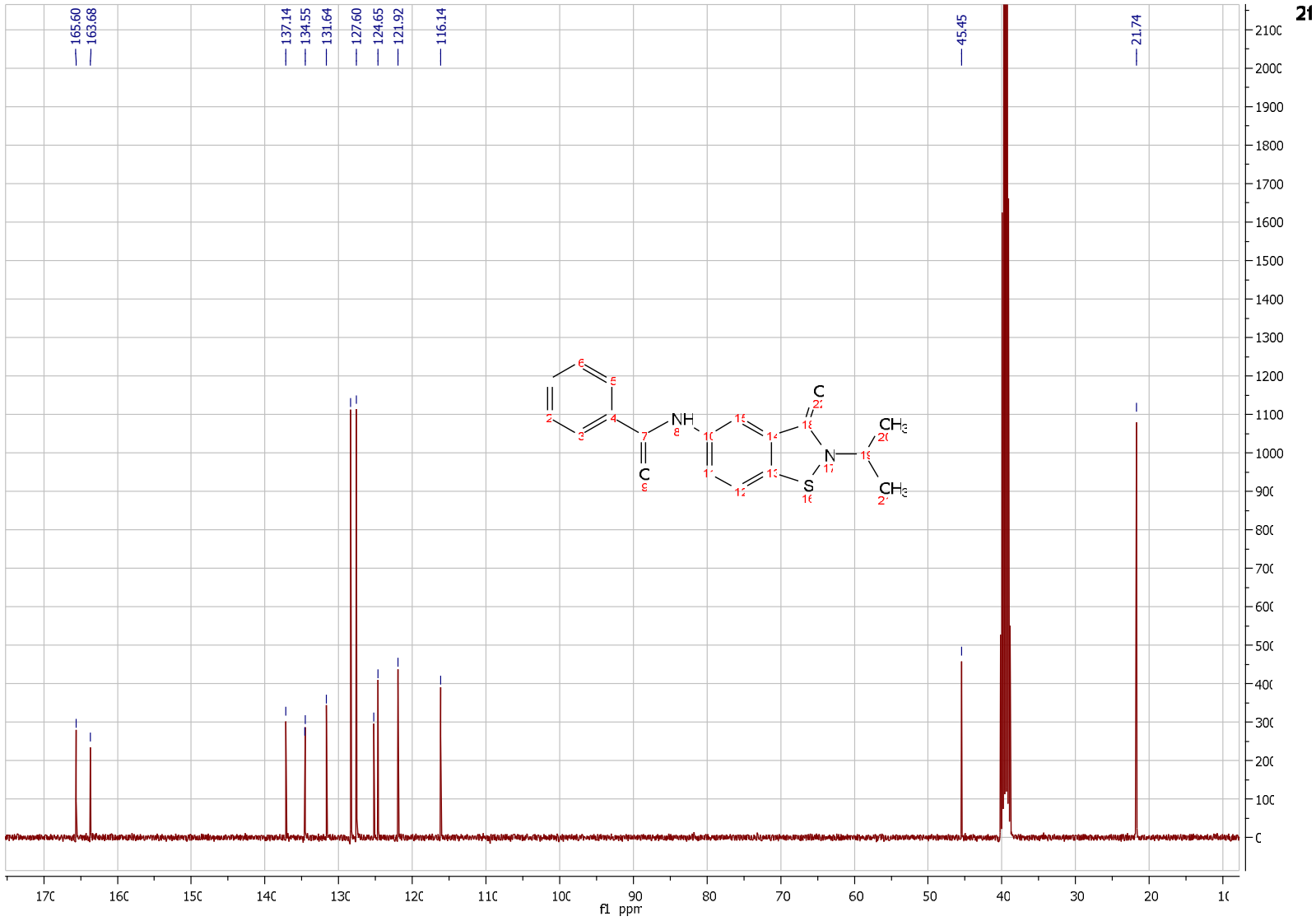

2b
3424.26
3422.38
3416.93
3414.57
3408.07
3405.72
3316.76
3307.92
2957.87
2949.22
2709.99
2707.40
2665.90
2663.29
2657.22
2654.60
1537.27
1513.94
f1 ppm

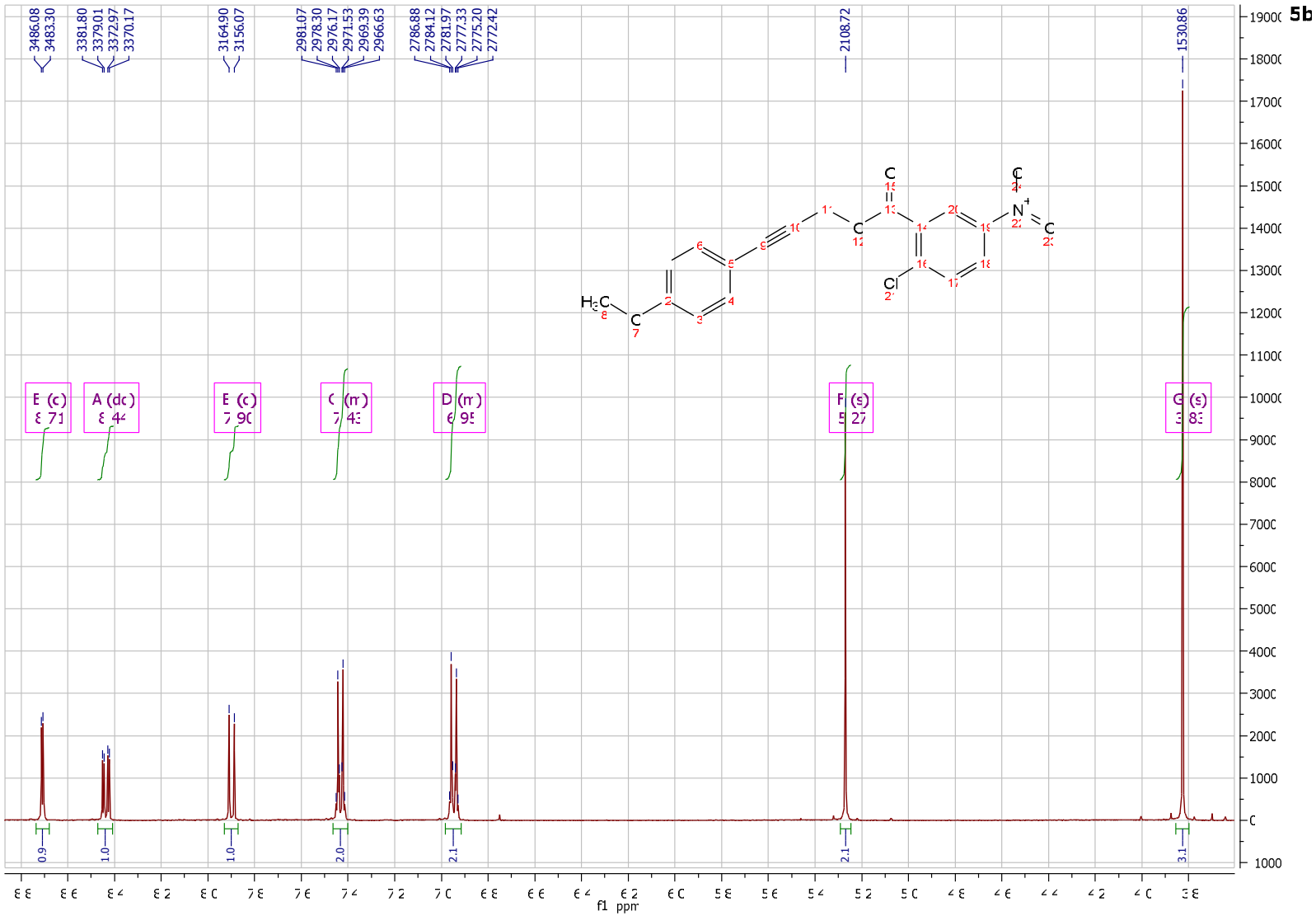

2b
162.9
161.4
156.6
148.1
145.5
130.9
126.2
123.6
121.2
116.2
105.4
99.5
56.0
55.6
f1 ppm

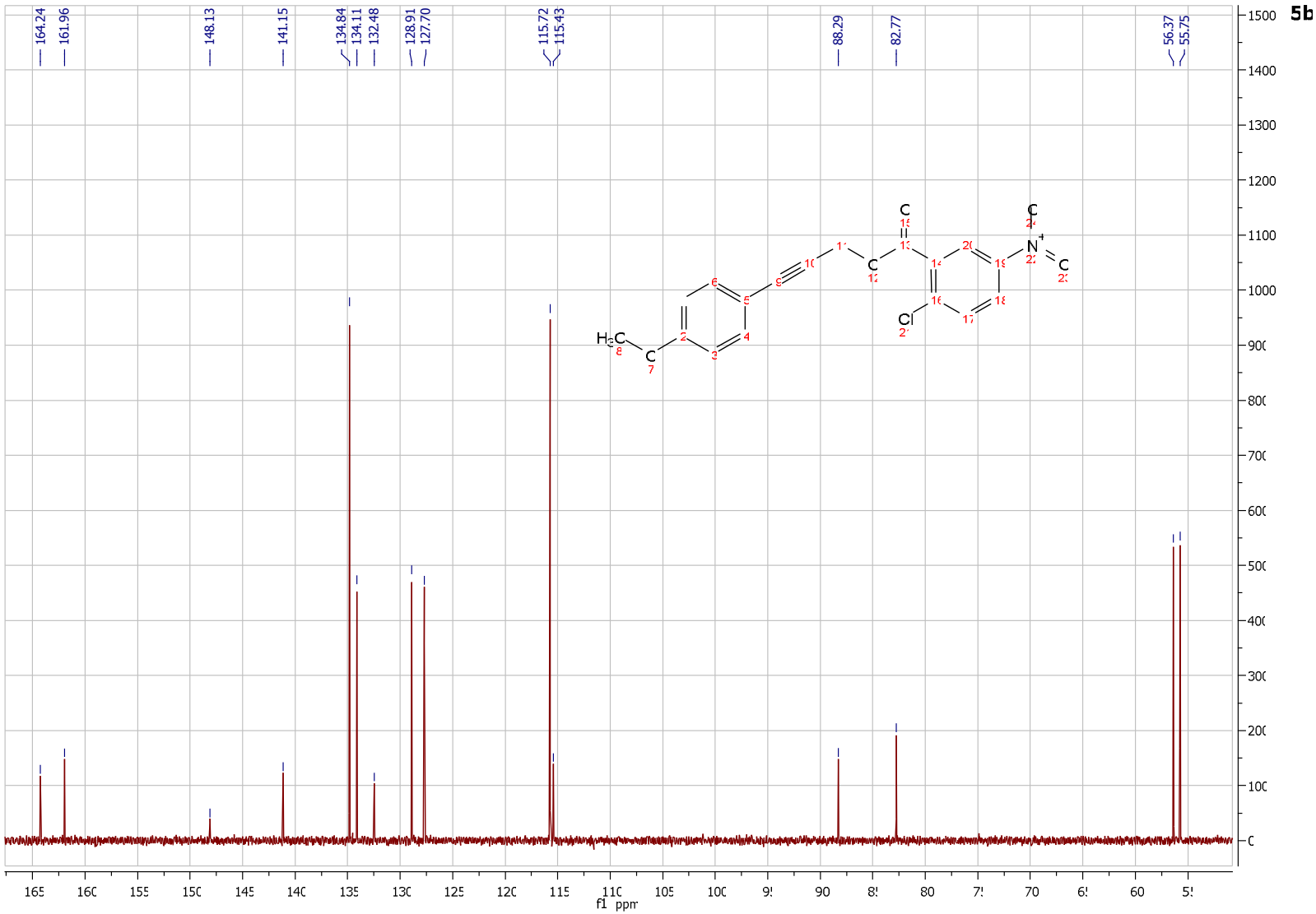

7f-2
3587.00
3347.10
3341.23
3338.64
3322.67
3167.06
3158.54
3027.18
3018.78
3013.81
3011.62
3009.52
3005.49
3004.22
3002.94
2985.95
2979.43
2978.19
2972.58
2970.99
1604.24
1597.65
1591.04
1583.63
1577.01
1570.43
496.00
460.21
453.64
A (s) 8.96
B (dd) 8.36
C (d) 8.05
D (d) 7.96
E (m) 7.90
F (dt) 7.52
G (m) 7.44
H (m) 3.97
I (s) 1.24
J (d) 1.14
K (d) 7.55
f1 (ppm)

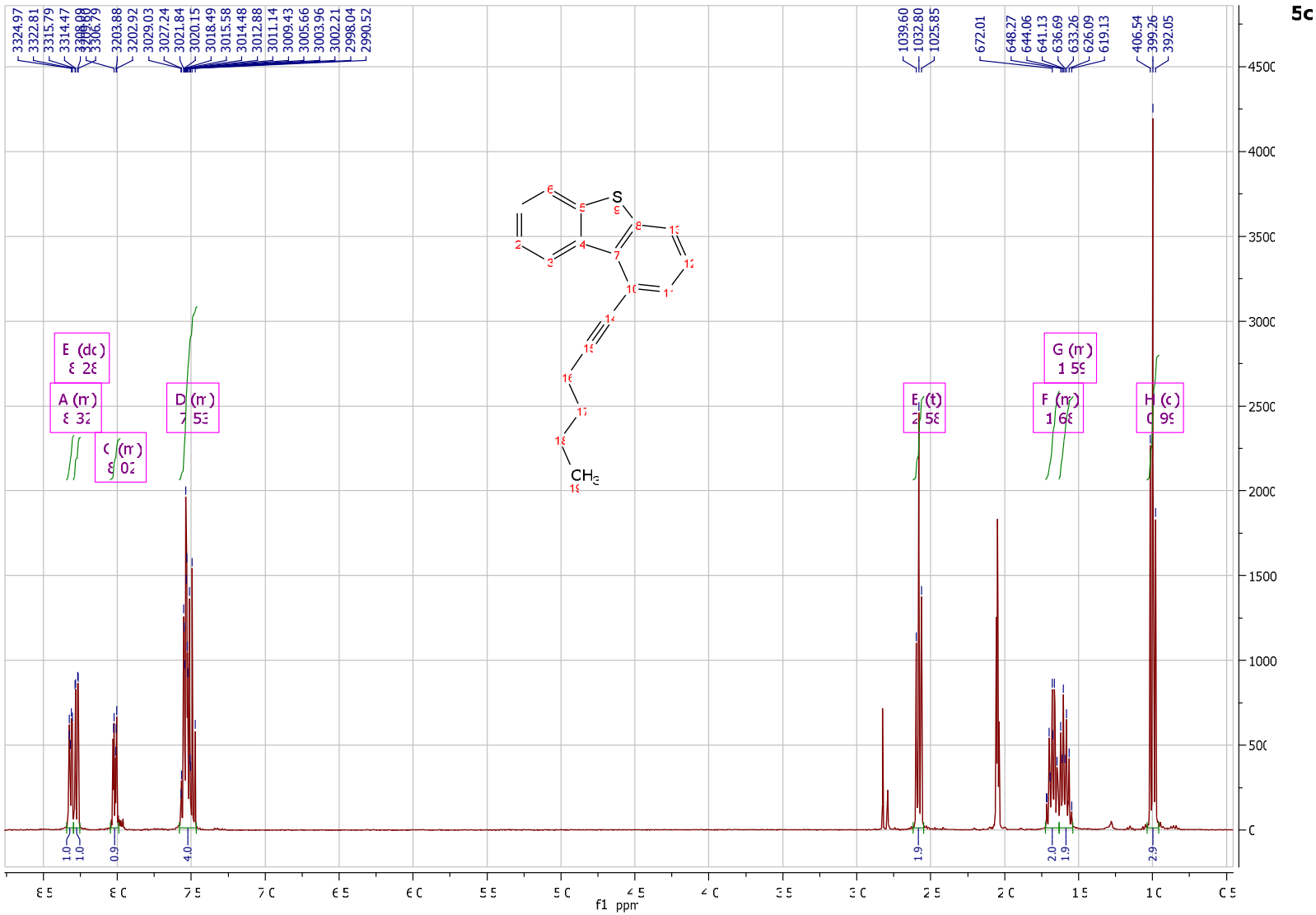

7f-2
166.45
166.32
141.50
141.07
140.25
135.01
132.16
127.63
123.54
122.36
121.71
48.79
42.45
30.93
22.77
f1 (ppm)

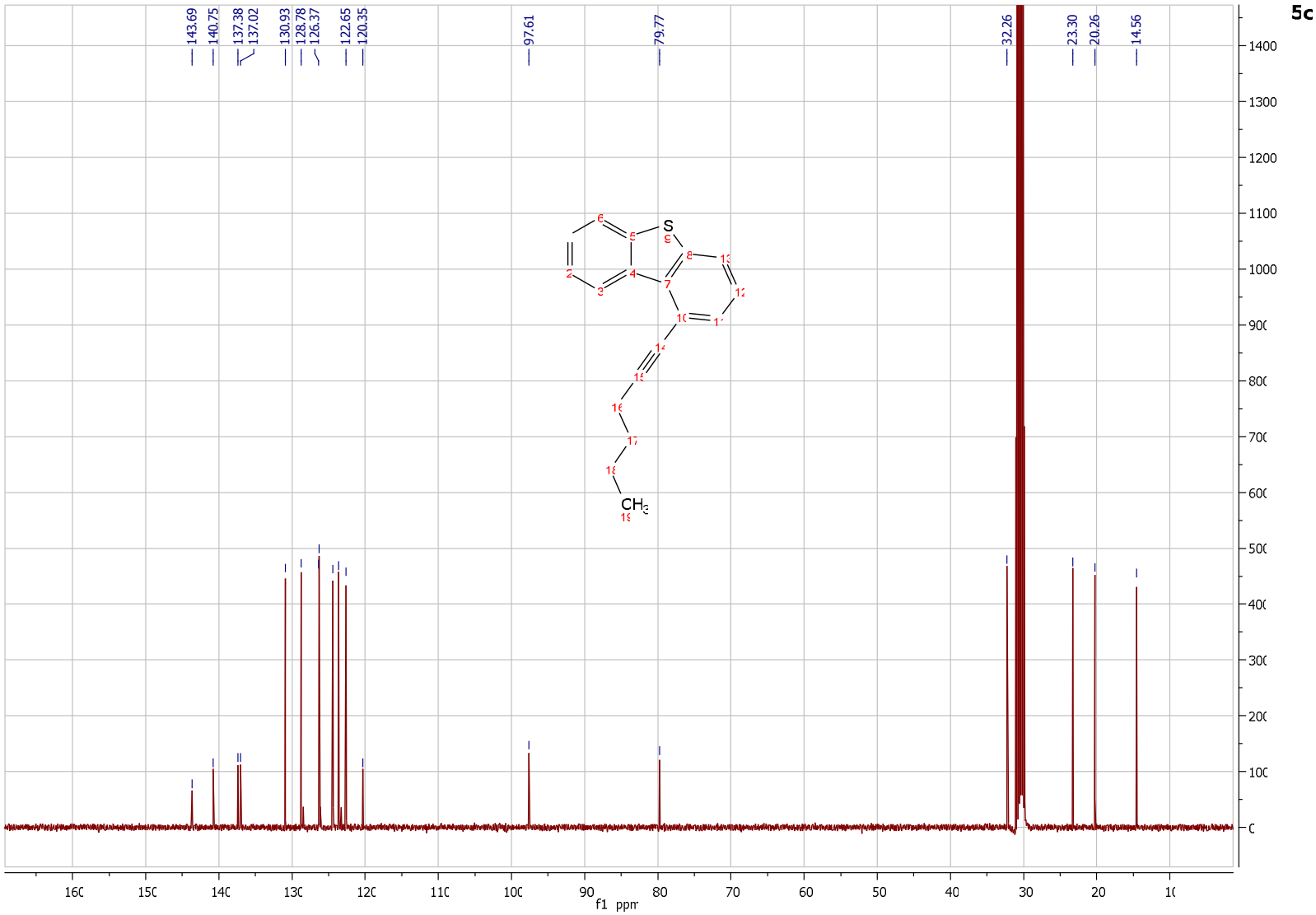

21
4203.33
3372.88
3370.93
3213.56
3201.68
3193.18
3043.58
3040.05
3038.72
3037.36
3028.31
3022.22
3020.73
3015.37
3013.77
3012.42
1927.53
1920.88
1914.22
1907.56
1900.91
543.55
536.89
E (s)
D (c)
I (m)
A (c)
F (dd)
C (m)
E (m)
G (m)
H (c)
NH
CH3
CH3
N
S
f1 ppm

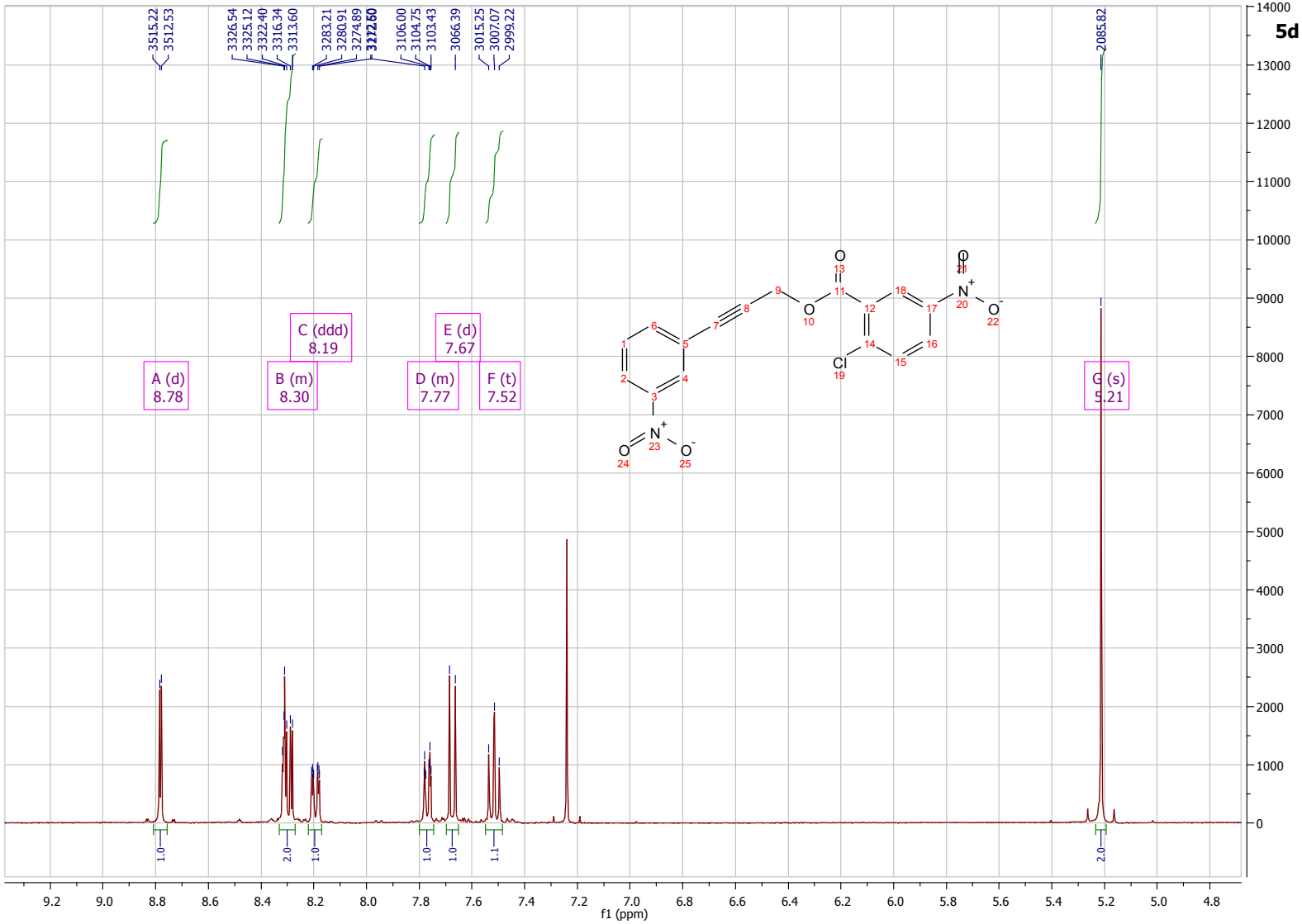

21
165.60
163.68
137.14
134.55
131.64
127.60
124.65
121.92
116.14
45.45
21.74
NH
N
S
CH3
CH3
f1 ppm

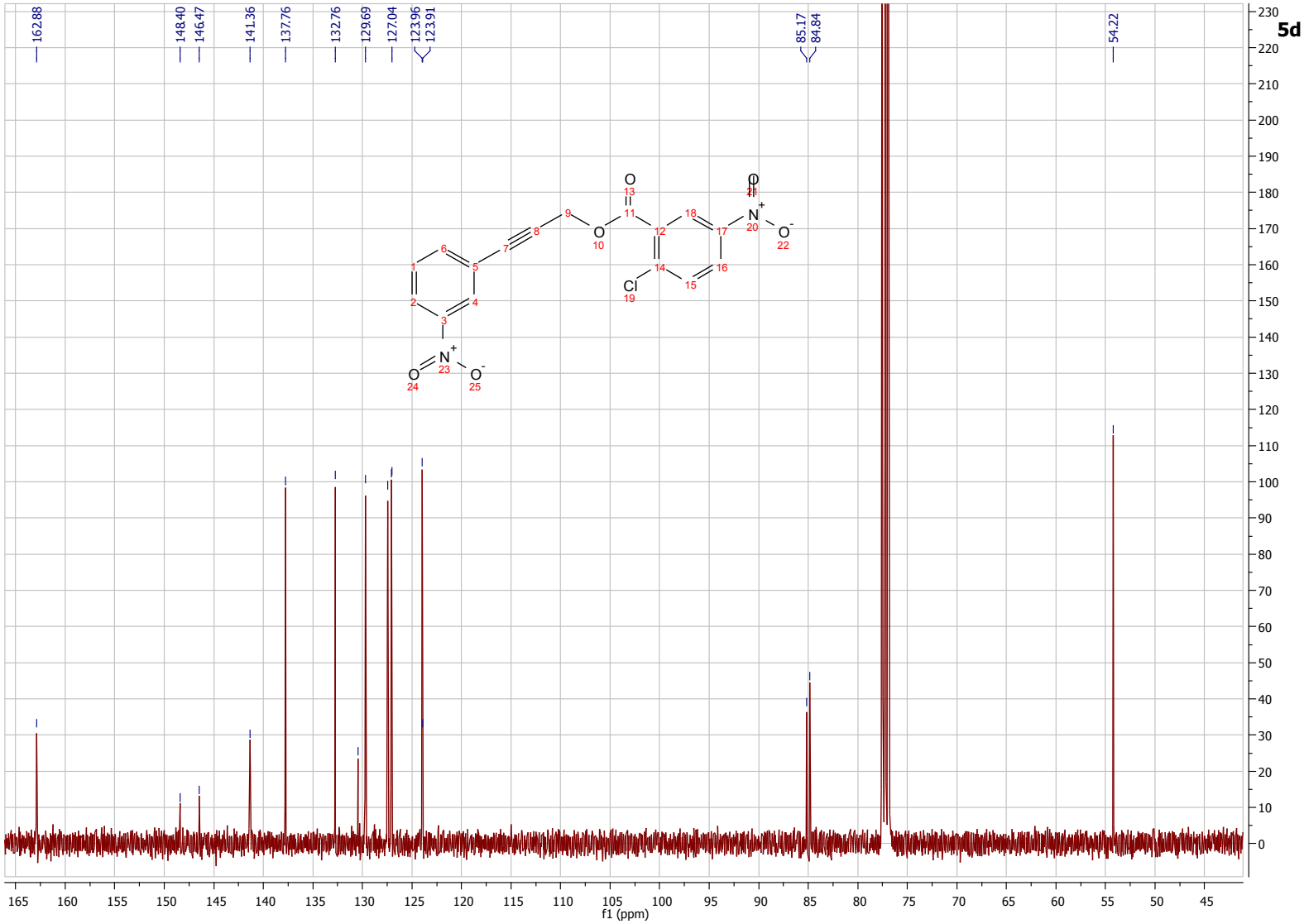

5b
3486.08
3483.30
3381.80
3379.01
3372.97
3370.17
3164.90
3156.07
2981.07
2978.30
2976.17
2971.53
2969.39
2966.63
2786.88
2784.12
2781.97
2777.33
2775.20
2772.42
2108.72
1530.86
f1 ppm

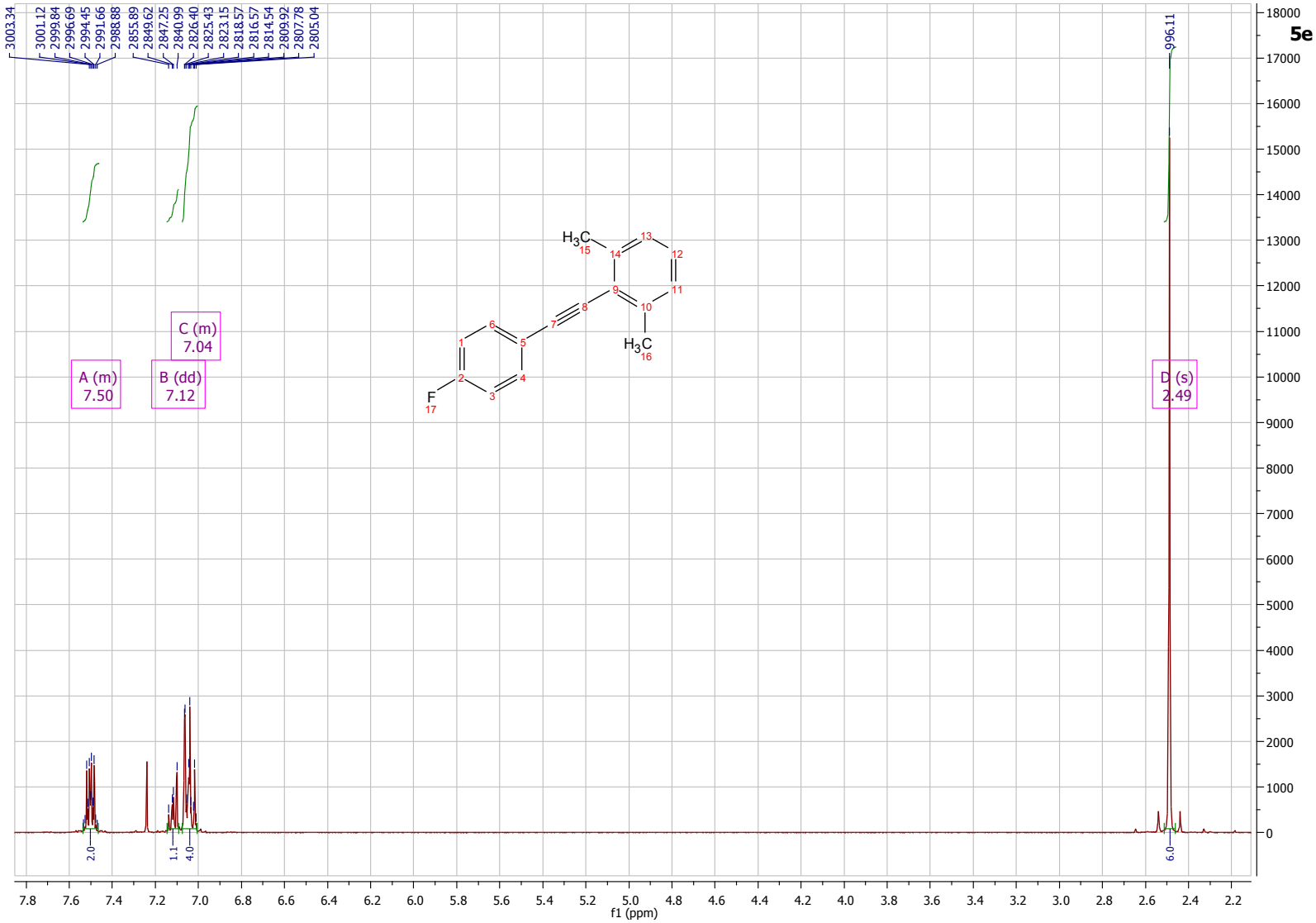

164.24
161.96
148.13
141.15
134.84
134.11
132.48
128.91
127.70
115.72
115.43
88.29
82.77
56.37
55.75
5b
f1 ppm

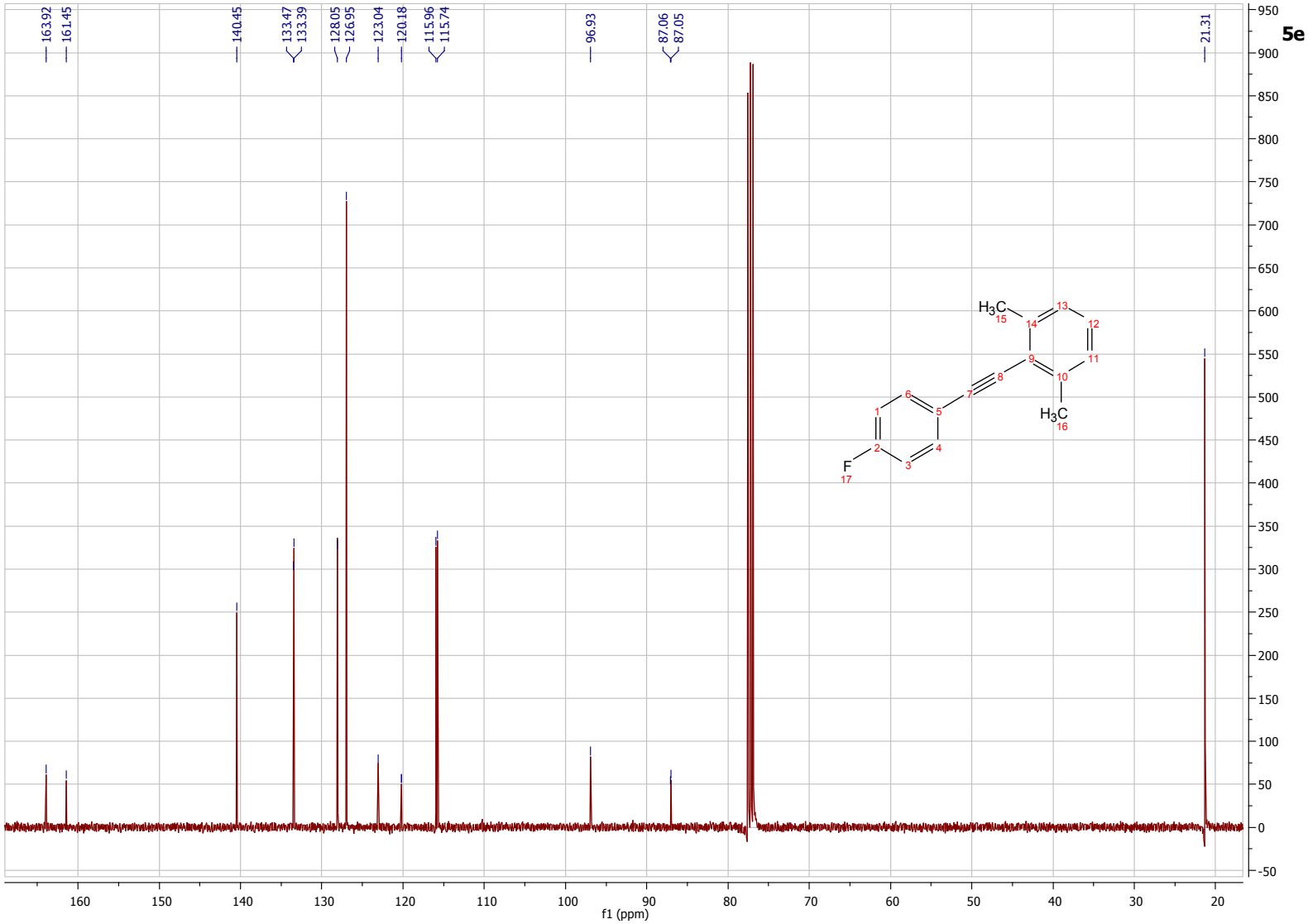

5c
f1 ppm

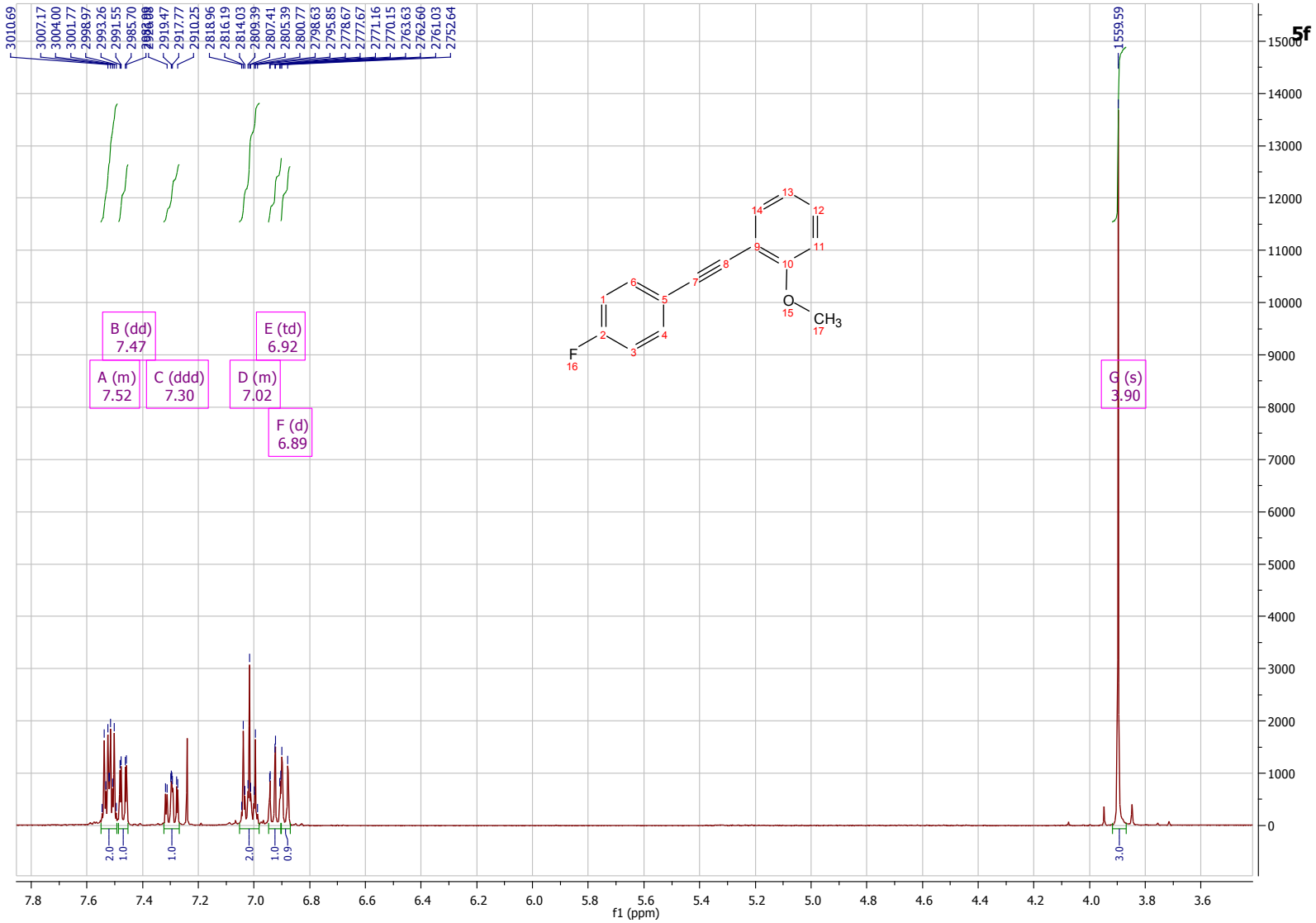

5c
143.69
140.75
137.38
137.02
130.93
128.78
126.37
122.65
120.35
97.61
79.77
32.26
23.30
20.26
14.56
S
CH3
f1 ppm

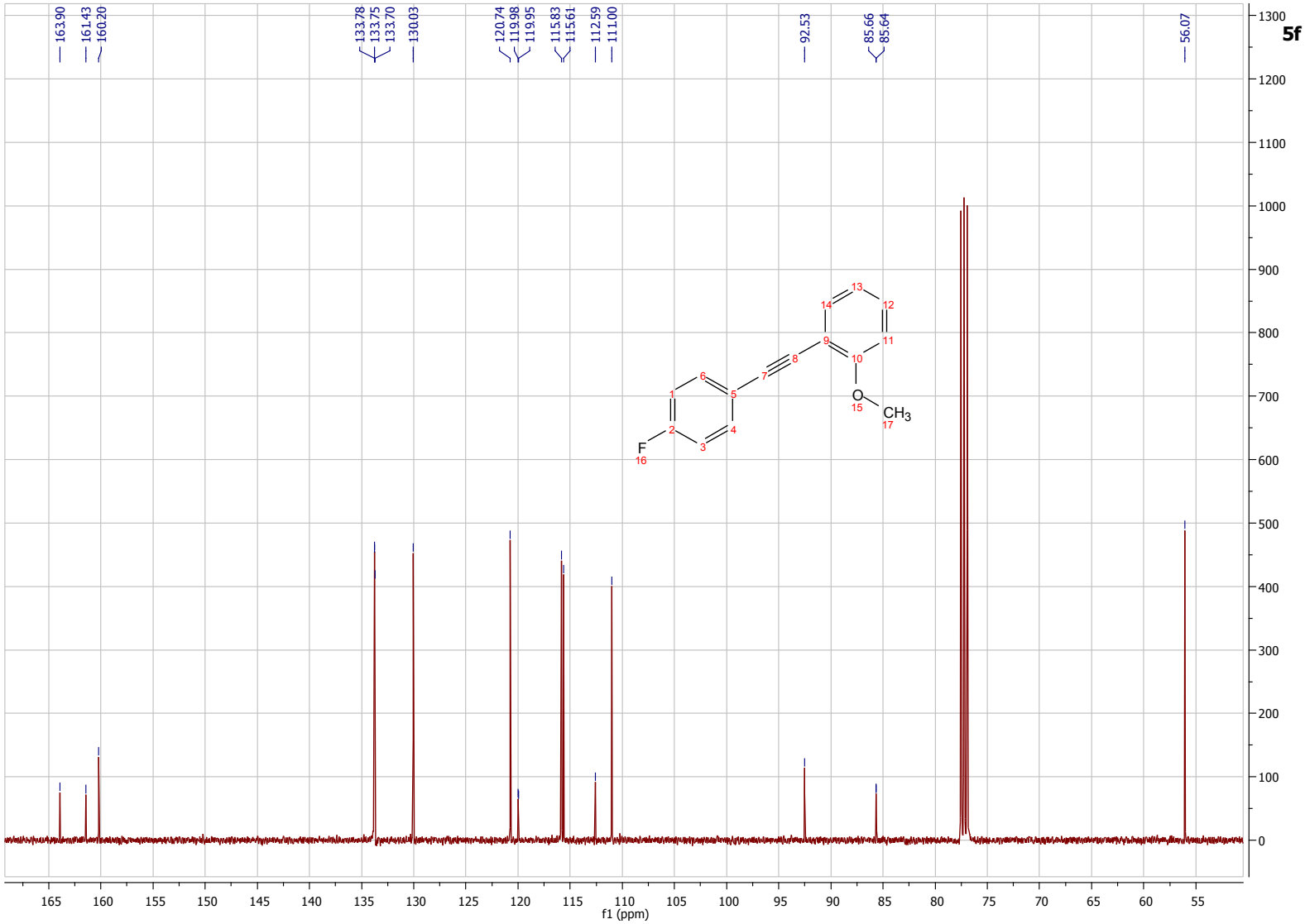

5d
A (d)
8.78
B (m)
8.30
C (ddd)
8.19
D (m)
7.77
E (d)
7.67
F (t)
7.52
G (s)
5.21
f1 (ppm)


5d
162.88
148.40
146.47
141.36
137.76
132.76
129.69
127.04
123.96
123.91
85.17
84.84
54.22
f1 (ppm)


5e
A (m)
7.50
B (dd)
7.12
C (m)
7.04
D (s)
2.49
f1 (ppm)


5e
163.92
161.45
140.45
133.47
133.39
128.05
126.95
123.04
120.18
115.96
115.74
96.93
87.06
87.05
21.31
f1 (ppm)


5f
B (dd)
7.47
A (m)
7.52
C (ddd)
7.30
E (td)
6.92
D (m)
7.02
F (d)
6.89
G (s)
3.90
f1 (ppm)


5f
163.90
161.43
160.20
133.78
133.75
133.70
130.03
120.74
119.98
119.95
115.83
115.61
112.59
111.00
92.53
85.66
85.64
56.07
f1 (ppm)