Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A novel carbamoyl radical based dearomatizing spiroacylation process.

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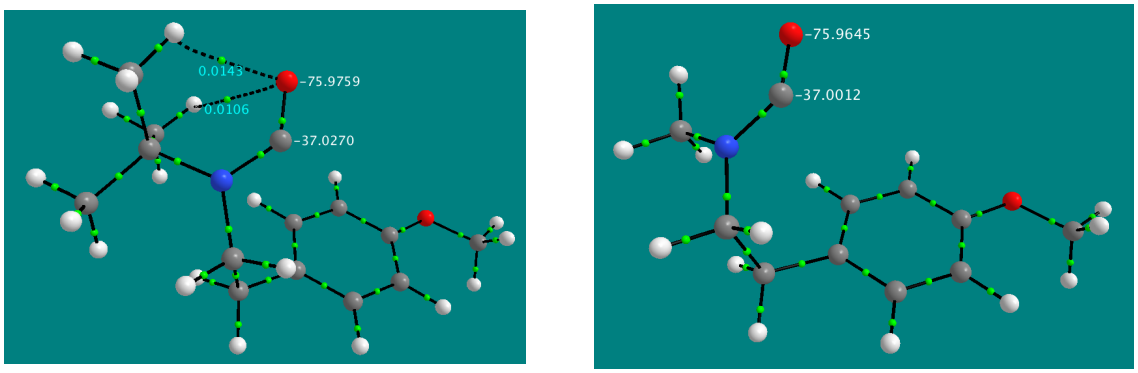
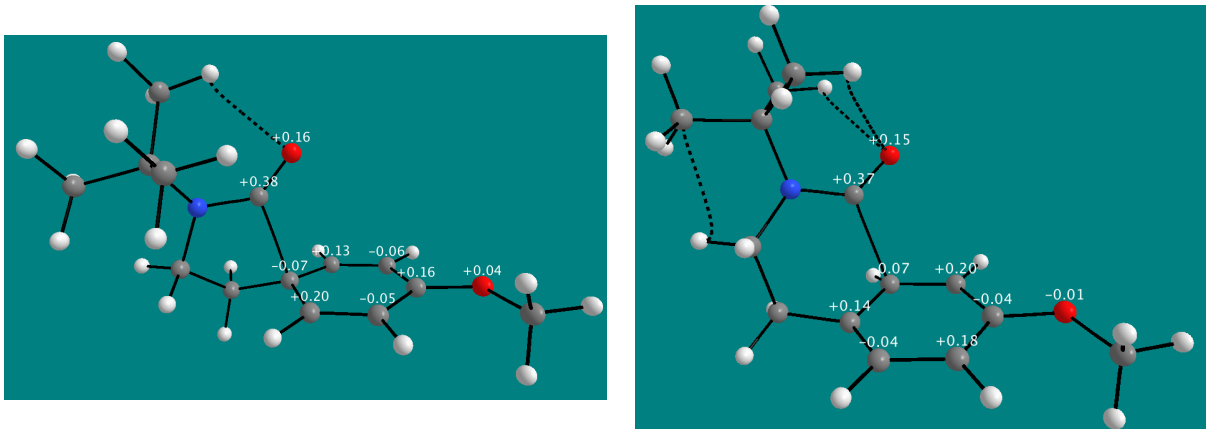


a) b)

Figure S1. Atomic energies of carbamoyl group of radical 31.



a) b)

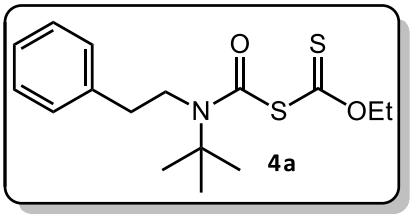
Figure S2. Radial delocalization as described by atomic spin populations at the transition state of spirocyclization and six-membered ring formation of carbamoyl radical 31.

General Information

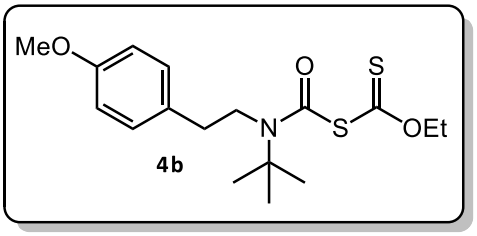
All solvents were dried and distilled prior to use by standard procedures. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC), carried out on 0.25 mm silica gel plates using UV light as visualizing agent and vanillin for staining. Column chromatography was performed using silica gel 60 (particle size 0.04−0.063 mm / 230-400 mesh ASTM). Unless stated otherwise, all of the yields refer to isolated products after flash column chromatography. **Proton nuclear magnetic resonance** (1H NMR) spectra were recorded using 300 MHz equipment. For 1H NMR spectra, chemical shifts (δ) are referenced from TMS (0.00 ppm). Coupling constants (*J*) are reported in Hz. For multiplicities the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet. **Carbon nuclear magnetic resonance** (13C NMR) spectra were recorded using an NMR spectrometer at 75 MHz. For 13C NMR spectra, chemical shifts (δ) are given from CDCl3 (77.0 ppm). **Infrared spectra** were obtained on a Nicolet Magna 750 FT-IR spectrometer and the absorptions are given in wavenumbers (cm-1). The low- and high-resolution **mass spectra** were obtained on a JEOL JMS-AX505HA.

General procedure for the preparation of carbamoylxanthates:

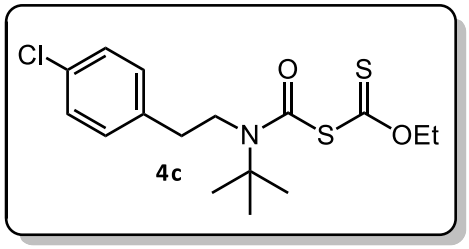
To a stirred solution of triphosgene (0.7 mmol) in CH_2Cl_2 (5.0 mL), at 0 ºC the corresponding N-*tert*-butylphenethylamine (1.0 mmol) was added followed by dropwise addition of Et_3N (3.4 mmol). The mixture was stirred for 10 min at rt. The solvent was removed under reduced pressure to give the crude carbamoyl chloride. This compound was used in the next step without further purification. A solution of the crude carbamoyl chloride in acetonitrile (5.0 mL) was treated with the O-ethylxanthic acid, potassium salt (1.0 mmol). The reaction was stirred for 15 min, at rt, quenched with water, and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent removed under reduced pressure. The carbamoylxanthate was purified by a silica gel column chromatography to afford the pure xanthate.



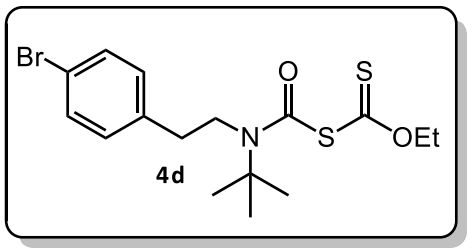
***N*-phenethyl – *N* -*tert*-butylcarbamoyl-*O*-ethyldithiocarbonate.** This residue was purified by flash chromatography (98:2 hexane/EtOAc) to give **4a** (94%) as yellow oil. **IR** (film) ν/cm^{-1}: 3025, 2979, 2933, 1689, 1235, 1039; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.35-7.18 (m, 5H), 4.69 (q, *J*=7.1 Hz, 2H), 3.63-3.57 (m, 2H), 2.91-2.85 (m, 2H), 1.52 (s, 9H), 1.46 (t, *J*=7.0, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.2, 158.8, 137.6, 128.6, 128.5, 126.7, 70.5, 69.9, 48.9, 38.3, 28.5, 13.4; The structure was confirmed as its spirodienone.



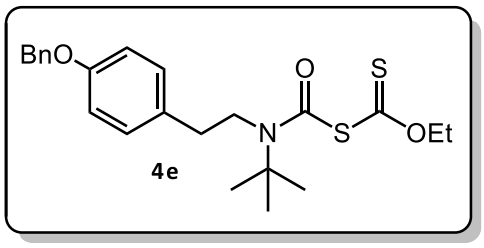
***N* - (4-methoxyphenethyl) – *N* – *tert* – butylcarbamoyl -*O*-ethyldithiocarbonate.** This residue was purified by flash chromatography (90:10 hexane/EtOAc) to give **4b** (92%) as yellow oil. **IR** (film) ν/cm^{-1}: 2979, 2934, 2835, 1688, 1512, 1246, 1038; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.13 (d, *J*=8.5 Hz, 2H), 6.86 (d, *J*=8.5 Hz, 2H), 4.69 (q, *J*=7.0 Hz, 2H), 3.78 (s, 3H), 3.60-3.54 (m, 2H), 2.85-2.80 (m, 2H), 1.52 (s, 9H), 1.46 (t, *J*=7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.3, 158.7, 158.4, 129.6, 129.5, 114.0, 70.5, 59.8, 55.1, 49.1, 37.4, 28.5, 13.4. The structure was confirmed as its spirodienone.



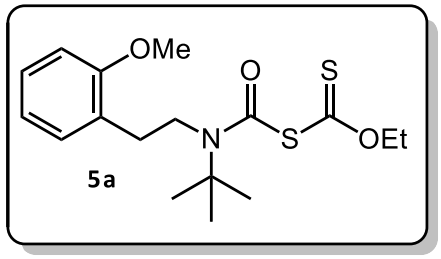
***N* - (4-chlorophenethyl) – *N* – tert - butylcarbamoyl - *O*-ethyldithiocarbonate.** This residue was purified by flash chromatography (98:2 hexane/EtOAc) to give **4c** (91%) as yellow oil. **IR** (film) ν/cm^{-1}: 2979, 2933, 2869, 1689, 1235, 1000; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.29 (d, *J*=8.3 Hz, 2H), 7.15 (d, *J*=8.3 Hz, 2H), 4.69 (q, *J*=7.1 Hz, 2H), 3.60-3.55 (m, 2H), 2.88-2.83 (m, 2H), 1.52 (s, 9H), 1.44 (t, *J*=7.1, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 206.9, 158.8, 136.0, 132.6, 129.9, 128.8, 70.7, 60.0, 48.7, 37.7, 28.6, 13.4. The structure was confirmed as its spirodienone.



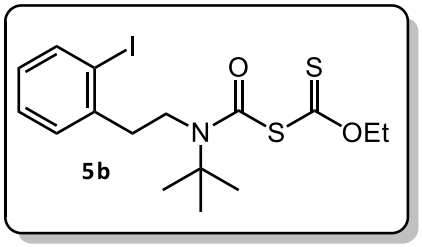
***N* - (4-bromophenethyl) – *N* – tert – butylcarbamoyl - *O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (98:2 hexane/EtOAc) to give **4d** (93%) as yellow oil. **IR** (film) ν/cm^{-1}: 2979, 2932, 2868, 1689, 1234, 1041, 999; **^{1}H NMR** (200 MHz, $CDCl_3$) δ/ppm: 7.45 (d, *J*= 8.4 Hz, 2H), 7.10 (d, *J*=8.4 Hz, 2H), 4.71 (q, *J*=7.0 Hz, 2H), 3.61-3.53 (m, 2H), 2.88-2.80 (m, 2H), 1.52 (s, 9H), 1.45 (t, *J*=7.2 Hz, 3H); **^{13}C NMR** (50 MHz, $CDCl_3$) δ/ppm: 206.9, 158.7, 136.5, 131.7, 130.28, 120.6, 70.7, 59.9, 48.5, 37.7, 28.5, 13.4. The structure was confirmed as its spirodienone.



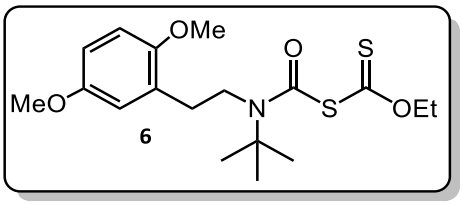
***N* - (4-benziloxyphenethyl) – *N* – tert – butylcarbamoyl - *O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (98:2 hexane/EtOAc) to give **4e** (90%) as yellow oil. **IR** (film) ν/cm^{-1}: 2935, 2834, 1689, 1590, 1515, 1237, 1007, 809; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.43-7.34 (m, 5H), 7.12 (d, *J*= 8.7 Hz, 2H), 7.93 (d, *J*= 9.0, 2H), 5.03 (s, 2H), 4.69 (q, *J*= 7.1, 2H), 4.59 (m, 2H), 2.84 (m, 2H), 1.51 (s, 9H), 1.43 (t, 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.3, 158.8, 157.6, 136.8, 129.9, 129.5, 128.5, 127.8, 127.3, 115.0, 70.6, 69.8, 49.1, 37.4, 28.5, 13.4. The structure was confirmed as its spirodienone.



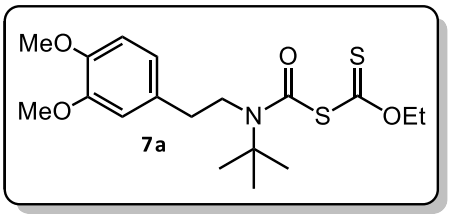
***N* - (2-methoxyphenethyl) – *N* – tert-butylcarbamoyl - *O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (90:10 hexane/EtOAc) to give **5a** (87%) as yellow oil. **IR** (film) ν/cm^{-1}: 2979, 2935, 2835, 1737, 1688, 1512, 1247, 1039; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.24-7.13 (m, 2H), 6.91-6.83 (m, 2H), 4.68 (q, *J*=7.1, 2H), 3.83 (s, 3H), 3.59-3.56 (dd, 2H), 2.91-2.85 (dd, 2H), 1.53 (s, 9H), 1.45 (t, *J*=7.1, 3H) ; **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.7, 158.7, 157.3, 130.3, 127.9, 125.9, 120.4, 110.0, 70.3, 59.8, 54.9, 47.1, 33.2, 28.3, 13.3. The structure was confirmed as its spirodienone.



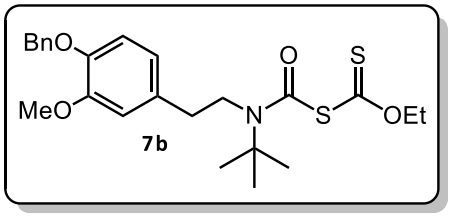
***N* - (2-iodophenethyl) – *N* – tert-butylcarbamoyl - *O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (98:2 hexane/EtOAc) to give **5b** (90%) as yellow oil. **IR** (film) ν/cm^{-1}: 3025, 2979, 2933, 1689, 1235, 1039. **^{1}H NMR** (200 MHz, $CDCl_3$) δ/ppm: 7.34-7.18 (m, 4H), 4.72 (q, *J*=7.4, 2H), 3.66-3.56 (dd, *J*=8.4, 2H), 2.92-2.84 (dd, *J*=8.8, 2H), 1.53 (s, 9H), 1.48 (t, *J*=7.4, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.1, 158.7, 137.5, 129.0, 128.4, 126.6, 98.6, 70.5, 59.8, 48.8, 38.2, 29.1, 13.4. The structure was confirmed as its spirodienone.



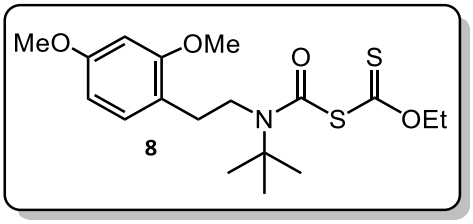
***N* - (2,5-dimethoxyphenethyl) – *N* - tert-butylcarbamoyl – *O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (90:10 hexane/EtOAc) to give **6** (91%) as yellow oil. **IR** (film) ν/cm^{-1}: 2978, 2833, 1738, 1687, 1502, 1224, 1029, 805; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.79-6.72 (m, 3H), 4.68 (q, *J*= 7.1 Hz, 2H), 3.78 (s, 3H), 3.75 (s, 3H), 3.61-3.56 (m, 2H), 2.88-2.82 (m, 2H), 1.53 (s, 9H), 1.43 (t, *J*= 7.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.7, 158.7, 153.3, 151.5, 127.0, 116.6, 111.8, 110.9, 70.3, 59.8, 55.4, 47.1, 33.4, 28.3, 13.3. The structure was confirmed as its spirodienone.



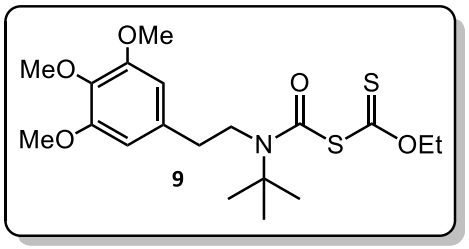
***N* - (3,4-dimethoxyphenethyl) – *N* – tert-butylcarbamoyl - *O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (90:10 hexane/EtOAc) to give **7a** (96%) as yellow oil. **IR** (film) ν/cm^{-1}: 2978, 2963, 2935, 2834, 1689, 1515, 1237, 1007; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.83 (dd, *J*= 1.9, 6.7 Hz, 1H), 6.76 (dd, *J*= 2.0, 7.0 Hz, 1H), 6.72 (s, 1H), 4.7 (q, *J*= 7.0 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.63 (dd, *J*= 8.2 Hz, 2H), 2.85 (dd, *J*= 8.3 Hz, 2H), 1.53 (s, 9H), 1.44 (t, *J*= 7.08, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.3, 158.8, 149.0, 147.9, 130.2, 120.5, 111.8, 111.4, 70.6, 59.9, 55.8, 49.2, 38.0, 28.6, 13.5. The structure was confirmed as its spirodienone.



***N* - (4-benziloxy-3-methoxyphenethyl) – *N* - tert–butyl - carbamoyl-*O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (98:2 hexane/EtOAc) to give **7b** (90%) as yellow oil. **IR** (film) ν/cm^{-1}: 2961, 2939, 2839, 1639, 1602, 1279, 1194, 1074, 994, 858, **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.43-7.25 (m, 5H), 6.82 (d, *J*= 8.1, 1H), 6.74 (d, *J*= 8.1 Hz, 1H), 6.67 (dd, *J*= 1.8, 8.1 Hz, 1H), 5.1 (s, 2H), 4.68 (q, *J*= 7.2 Hz, 2H), 3.88 (s, 3H), 3.61 (dd, *J*= 8.3, 2H), 2.83 (dd, *J*= 8.5 Hz, 2H), 1.51 (s, 9H), 1.43 (t, *J*=7.1, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.3, 158.7, 149.7, 147.0, 137.0, 130.8, 128.4, 127.7, 127.1, 120.5, 114.3, 112.4, 70.0, 70.6, 59.9, 55.9, 49.1, 37.9, 28.6, 13.4. The structure was confirmed as its spirodienone.

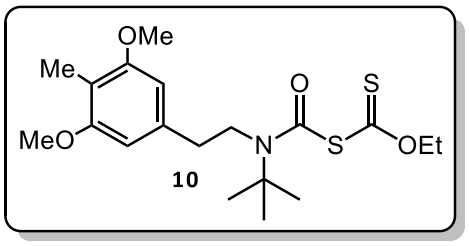


***N* - (2,4-dimethoxyphenethyl) – *N* - tert-butylcarbamoyl - *O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (90:10 hexane/EtOAc) to give **8** (93%) as yellow oil. **IR** (film) ν/cm^{-1}: 2966, 2935, 2836, 1738, 1688, 1613, 1463, 1209, 1000, **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.06 (d, *J*= 8.4 Hz, 1H), 6.43 (s, 1H), 6.43 (d, *J*= 7.8 Hz, 1H), 4.69 (q, *J*= 7.0 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.57-3.52 (m, 2H), 2.84-2.78 (m, 2H), 1.52 (s, 9H), 1.44 (t, *J*= 7.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.9, 159.8, 158.8, 158.3, 130.6, 118.4, 104.0, 98.3, 70.4, 59.8, 55.2, 55.0, 47.4, 32.7, 28.5, 13.4. The structure was confirmed as its spirodienone.

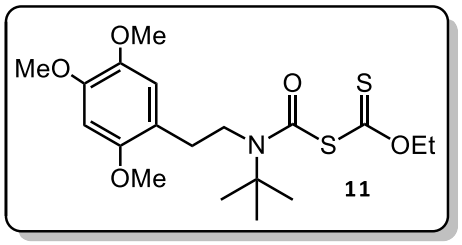


***N* - (3,4,5-trimethoxyphenethyl)-*N*-tert-butylcarbamoyl-*O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (90:10 hexane/EtOAc) to give **9** (90%) as yellow oil. **IR** (film) ν/cm^{-1}: 2964, 2937, 2836, 1688, 1590, 1460, 1238, 1128, 1010, 733; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.41 (s, 2H), 4.69 (q, *J*= 7.1 Hz, 2H), 3.86 (s, 6H), 3.82 (s, 3H), 3.63-3.60 (m, 2H), 2.85-2.80 (m, 2H), 1.53 (s, 9H), 1.44 (t, *J*= 7.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.2,

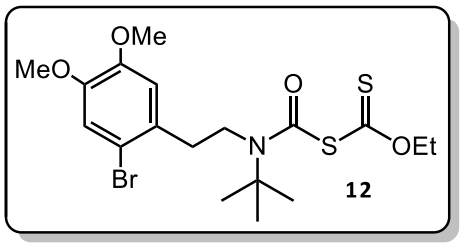
158.6, 153.2, 136.7, 133.3, 105.4, 70.6, 60.7, 59.9, 56.0, 49.0, 38.6, 28.5, 13.4. The structure was confirmed as its spirodienone.



N - (2,4-dimethoxy-3-methylphenethyl) – N - tert-butyl - carbamoyl-O-ethyldithiocarbonate: This residue was purified by flash chromatography (90:10 hexane/EtOAc) to give **10** (86%) as yellow oil. **IR** (film) ν/cm^{-1}: 2962, 2938, 2835, 1688, 1602, 1488, 1237, 1110, 1001; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.02 (d, *J*= 8.4, 1H), 6.61 (d, *J*= 8.3, 1H), 4.70 (q, *J*= 7.1, 2H), 3.81 (s, 3H), 3.74 (s, 3H), 3.60-3.54 (m, 2H), 2.85-2.80 (m, 2H), 2.15 (s, 3H), 1.53 (s, 9H), 1.44 (t, *J*= 7.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.7, 158.9, 157.9, 157.4, 127.4, 122.7, 119.8, 106.2, 70.5, 60.7, 60.0, 55.5, 48.2, 33.1, 28.6, 9.2. The structure was confirmed as its spirodienone.

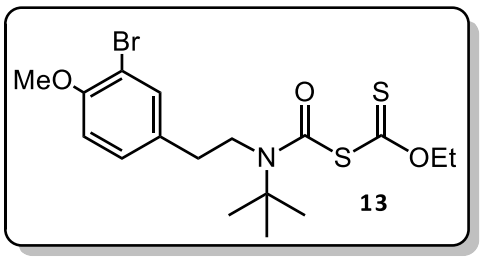


***N* - (2,4,5-trimethoxyphenethyl)-*N*-tert-butylcarbamoyl-*O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (90:10 hexane/EtOAc) to give **11** (93%) as yellow oil. **IR** (film) ν/cm^{-1} 2963, 2934, 2832, 1687, 1516, 1221, 1206, 1042, 856; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.7 (s, 1H), 6.50 (s, 1H), 4.69 (q, *J*= 7.1 Hz, 2H), 3.88 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 3.58-3.53 (m, 2H), 2.84-2.78 (m, 2H), 1.52 (s, 9H), 1.44 (t, *J*= 7.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.9, 158.8, 151.6, 148.5, 142.8, 117.3, 114.6, 97.3, 70.5, 59.9, 56.7, 55.9, 47.5, 32.9, 28.5, 13.5. The structure was confirmed as its spirodienone.

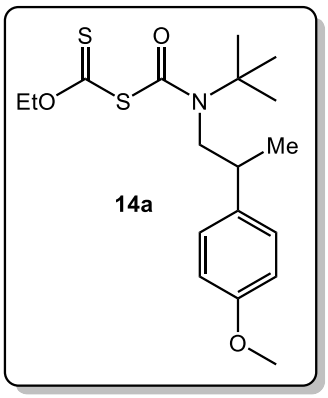


***N* - (2-bromo-4,5-dimethoxyphenethyl) – *N* –tert - butylcarbamoyl-*O*-ethyldithiocarbonate:** This residue was purified by flash chromatography (95:5 hexane/EtOAc) to give **12** (89%) as yellow oil. **IR** (film) ν/cm^{-1}: 2978, 2935, 2840, 1687, 1600, 1509, 1216, 1006; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.98 (s, 1H), 6.82 (s, 1H), 4.69 (q, *J*=7.5 Hz, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 3.62-3.53 (m, 2H), 3.00-2.93 (m, 2H), 1.54 (s, 9H), 1.44 (t, *J*= 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$)

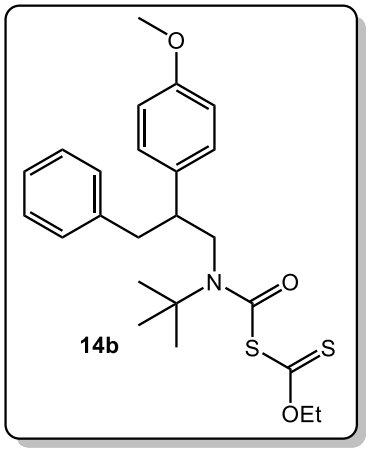
δ/ppm: 207.9, 158.5, 151.1, 148.5, 135.3, 129.3, 119.1, 115.2, 113.1, 60.0, 56.0, 55.8, 47.4, 38.0, 28.5, 13.4. The structure was confirmed as its spirodienone.



N-(3-bromo-4-methoxyphenethyl)-N-tert-butylcarbamoyl-O-ethyldithiocarbonate: This residue was purified by flash chromatography (95:5 hexane/EtOAc) to give **13** (88%) as yellow oil. **IR** (film) ν/cm^{-1}: 2978, 2936, 2838, 1688, 1603, 1498, 1255, 1236, 1043, 812; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.36 (d, *J*= 2.1 Hz, 1H), 7.14 (dd, *J*= 2.1, 8.3 Hz, 1H), 8.86 (d, *J*= 8.3, 1H), 4.7 (q, *J*= 7.0 Hz, 2H), 3.55-3.53 (m, 2H), 2.83-2.78 (m, 2H), 1.52 (s, 9H), 1.45 (t, *J*= 7.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.0, 158.8, 154.7, 133.2, 131.2, 128.6, 112.1, 111.7, 70.7, 60.0, 56.2, 56.2, 48.8, 37.0, 28.6, 13.5. The structure was confirmed as its spirodienone.

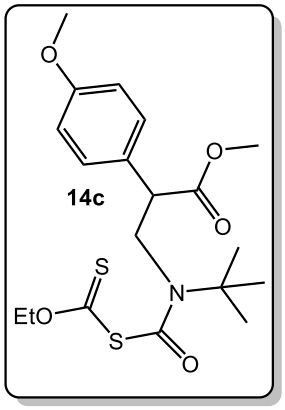


N-tert-butyl-N-(2-(4-methoxyphenyl)propyl)-carbamoyl-O-ethyl-dithiocarbonate: This residue was purified by flash chromatography (95:5 hexane/EtOAc) to give **14a** (94%) as yellow oil. **IR** (film) ν/cm^{-1}: 2979, 2934, 2835, 1688, 1512, 1246, 1030; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.14 (d, *J*= 9.0, 2H), 6.86 (d, *J*= 8.7, 2H), 4.66-4.55 (m, 2H), 3.77 (s, 6H), 3.68-3.54 (m, 2H), 3.03-2.91 (m, 1H), 1.43 (s, 9H), 1.41 (t, *J*= 7.2, 3H), 1.29 (d, *J*= 7.1, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.6, 159.1, 158.4, 134.8, 128.3, 113.9, 70.3, 60.0, 55.1, 54.4, 40.6, 28.4, 18.0, 13.4. The structure was confirmed as its spirodienone.

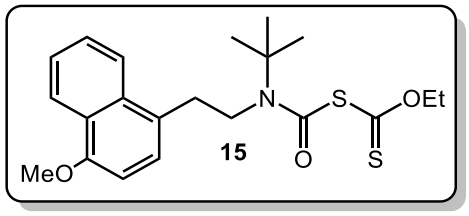


N-tert-butyl – N - (2-(4-methoxyphenyl) – 3 - phenylpropyl)-carbamoyl-O-ethyldithiocarbonate: This residue was purified by flash chromatography (95:5 hexane/EtOAc) to give **14b** (96%) as yellow oil. **IR** (film) ν/cm^{-1}: 2978, 2932, 1683, 1512, 1249, 1108, 1034; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.20-7.11 (m, 3H), 7.06 (d, *J*=8.6 Hz, 2H), 6.99 (d, *J*=6.6 Hz, 2H), 6.82 (d, *J*=8.6 Hz, 2H), 4.64 (q, *J*=7.1, 2H), 3.77 (s, 3H), 3.72-3.70 (m, 2H), 3.09-2.86 (m, 3H),

1.41 (t, *J*=7.2, 3H), 1.38 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.7, 159.3, 158.5, 139.5, 132.5, 129.3, 128.9, 128.1, 126.6, 113.9, 70.4, 60.1, 55.1, 53.1, 49.0, 39.3, 29.6, 28.5, 13.4. The structure was confirmed as its spirodienone.

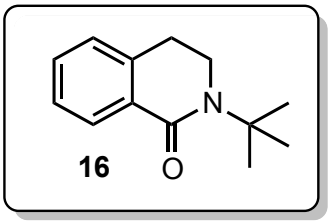


Methyl-3-(tert-butyl(((ethoxycarbonothioyl)thio)carbonyl)amino)-2-(4-methoxyphenyl)propanoate: This residue was purified by flash chromatography (98:2 hexane/EtOAc) to give **14c** (90%) as yellow oil. **IR** (film) ν/cm^{-1}: 2978, 2837, 1734, 1686, 1610, 1512, 1178, 1033; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.20 (d, *J*= 8.7, 2H), 6.85 (d, *J*= 8.6, 2H), 4.61 (q, *J*= 7.1, 2H), 4.20-4.13 (m, 1H), 4.88-4.77 (m, 2H), 3.74 (s, 3H), 3.64 (s, 3H), 1.37 (t, *J*= 7.2, 3H), 1.37 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 207.4, 172.4, 159.2, 159.2, 129.4, 127.3, 114.1, 70.3, 60.1, 55.0, 52.1, 50.1, 28.4, 13.3. The structure was confirmed as its spirodienone.

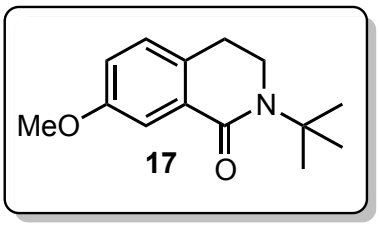


N - (2-(4-methoxynaphthalen-1-yl) ethyl) – N – tert - butylcarbamoyl-O-ethyldithiocarbonate: This residue was purified by flash chromatography (98:2 hexane/EtOAc) to give **15** (92%) as yellow oil. **IR** (film) ν/cm^{-1} 3070, 2975, 2935, 1738, 1687, 1640, 1362, 1221, 1048; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm 7.59 (d, *J*= 6.8 Hz, 1H), 7.29 (d, *J*= 6.3 Hz, 1H), 7.22-7.00 (m, 2H), 5.2 (d, *J*= 3.0 Hz, 1H), 4.99 (d, *J*= 2.9 Hz, 1H), 4.68 (q, *J*= 7.1 Hz, 2H), 3.71 (s, 3H), 3.44-3.35 (m, 2H), 2.46-2.37 (m, 1H), 2.00-1.91 (m, 1H), 1.46 (s, 9H), 1.39 (t, *J*= 7.0 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 2011.7, 173.6, 152.4, 138.2, 129.7, 128.8, 128.5, 126.9, 123.9, 122.4, 96.0, 69.7, 54.6, 53.5, 42.1, 29.9, 27.3, 13.4. The structure was confirmed as its spirodienone.

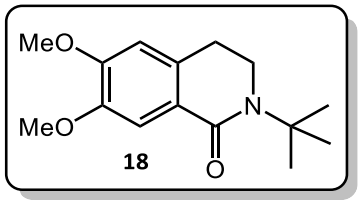
General procedure for the preparation of 3,4-dihydroisoquinolinones 16-18 under microwave heating: A solution of the corresponding xanthate (1 mmol) in toluene (5 mL) was irradiated in a CEM microwave (250 W) at 100 °C, then, dilauroyl peroxide (1.5 equiv) was added portionwise (0.3 equiv/5min), the organic solvent was removed under reduced pressure and the crude residue was purified by chromatography on a silica gel column. Microwave reactions were conducted using a CEM Discover Synthesis™ Unit (CEM Corp., Matthews, NC).



2-(tert-butyl)-3,4-dihydroisoquinolin-1(2H)-one: This residue was purified by flash chromatography (95:5 hexane/EtOAc) to give **16** (14%) as white solid. **IR** (film) ν/cm^{-1} 2960, 2837, 1633, 1601; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 8.08 (d, *J*= 6.0 Hz, 1H), 7.38-7.33 (m, 2H), 7.15 (d, *J*= 6.0 Hz, 1H), 3.60 (t, *J*= 6.0 Hz, 2H), 2.93 (t, *J*= 6.0 Hz, 2H), 1.55 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 161.1, 138.1, 131.1, 128.2, 126.8, 126.2, 42.3, 28.9. **MS** (EI), m/z (M+): 203.11.



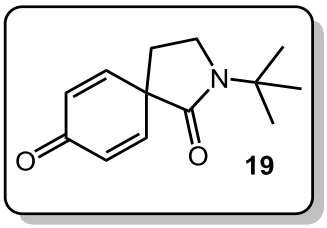
2-(tert-butyl)-7-methoxy-3,4-dihydroisoquinolin-1(2H)-one: This residue was purified by flash chromatography (95:5 hexane/EtOAc) to give **17** (10%) as yellow pale solid. **IR** (film) ν/cm^{-1} 2964, 2835, 1633, 1600; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.02 (s, 1H), 6.95 (d, *J*= 6.0 Hz, 1H), 6.84 (d, *J*= 6.0 Hz, 1H), 3.82 (s, 3H), 3.57 (t, *J*= 6.0 Hz, 2H), 2.85 (t, *J*= 6.0 Hz, 2H), 1.53 (s, 9H); **^{13}C NMR** (50 MHz, $CDCl_3$) δ/ppm: 162.0, 158.6, 130.4, 129.6, 127.3, 119.0, 111.1, 55.9, 42.5, 28.9, 28.4; **MS** (DART), m/z (M+): 233.02.



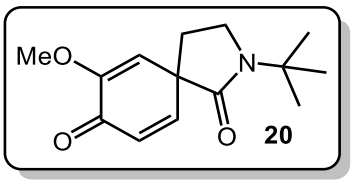
2-(tert-butyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2H)-one: This residue was purified by flash chromatography (90:1 hexane/EtOAc) to give **18** (55%) as white solid. **IR** (sol.) ν/cm^{-1}: 2961, 2939, 2839, 1639, 1602; **^{1}H NMR** (200 MHz, $CDCl_3$) δ/ppm: 7.61 (s, 1H), 6.61 (s, 1H) 3.91 (s, 1H), 3.90 (s, 1H) 3.60-3.53 (m, 2H), 2.88-2.81 (m, 2H), 1.54 (s, 9H); **^{13}C NMR** (50 MHz, $CDCl_3$) δ/ppm: 165.6, 151.3, 147.7, 131.7, 124.06, 110.4, 108.4, 57.1 55.9, 42.5, 28.9, 28.9. **MS** (DART), m/z (M+): 263.15.

Typical Procedure for Radical spirocyclisation.

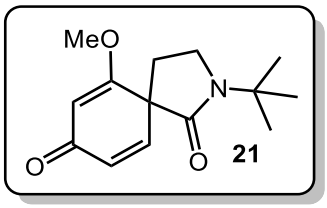
A solution of xanthate (1 mmol) in CH_2Cl_2 (20 mL) at -5 °C was added Et_3B (1.0 M in THF) stepwise (0.5 mmol/40 min), in an open-flask system. At the end of this time, the organic solvent was removed under reduced pressure and the crude residue was purified by chromatography on a silica gel column (ethyl acetate/hexane 50:50) to furnish the desired product.



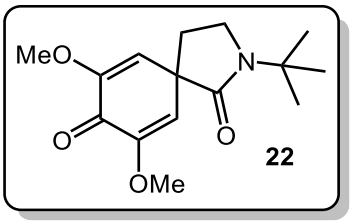
2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-diene-1,8-dione: white solid (65% from **4b**); **IR** (neat) ν/cm^{-1}: 3003, 2981, 2877, 1694, 1664, 1627, 1404, 1237,1096; **^{1}H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.78 (d, *J*= 10.0 Hz, 2H), 6.38 (d, *J*= 10.1 Hz, 2H), 3.61 (dd, *J*= 6.5, 6.9 Hz, 2H), 2.24 (dd, *J*= 6.7, 6.6 Hz, 2H), 1.40 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 185.4, 169.5, 146.7, 130.7, 55.1, 53.7, 42.3, 30.2, 27.5; **MS ESI+** (m/z, M+1): calc. for $C_{13}H_{18}NO_2$: 220.1337, found: 220.1339.



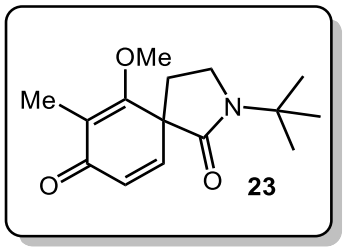
2 - (tert-butyl)-7-methoxy-2-azaspiro[4.5]deca - 6,9-diene- 1,8 - dione: Pale yellow oil (80% from **7b**); **IR** (neat) ν/cm^{-1}: 2979, 2934, 2876, 1690, 1668, 1641, 1237; **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.79 (dd, *J*= 2.5, 9.7 Hz, 1H), 6.42 (d, *J*= 9.8 Hz, 1H), 5.66 (d, *J*= 2.6 Hz, 1H), 3.68 (s, 3H), 3.64 (dd, *J*= 2.6, 6.0 Hz, 2H), 2.30 (dd, *J*= 2.7, 6.0 Hz, 2H), 1.42 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 180.6, 170.5, 152.8, 146.5, 130.2, 114.4, 55.1, 54.9, 53.8, 42.2, 31.3, 27.6; **MS ESI+** (m/z, M+1): calc. for $C_{14}H_{20}NO_3$: 250.1443, found: 250.1437.



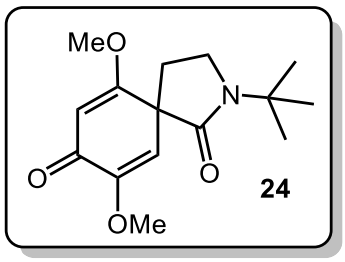
2-(tert-butyl)-6-methoxy-2-azaspiro[4.5]deca-6,9-diene-1,8-dione: white solid (64% from **8**); **IR** (neat) ν/cm^{-1}: 2983, 2942, 2910, 1693, 1658, 1597, 1367; **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.51 (d, *J*= 9.7 Hz, 1H), 6.25 (dd, *J*= 1.4, 9.8 Hz, 1H), 5.61 (d, *J*= 1.4 Hz, 1H), 3.72 (s, 3H), 3.61-3.53 (m, 2H), 2.49-2.40 (m, 1H), 2.16-2.07 (m, 1H), 1.38 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 187.7, 174.2, 169.5, 143.1, 129.0, 103.3, 55.8, 55.1, 43.1, 28.9, 27.3; **MS ESI+** (m/z, M+1): calc. for $C_{14}H_{20}NO_3$: 250.1443, found: 250.1433.



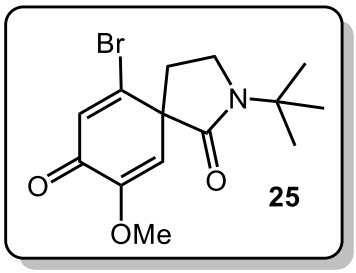
2 - (tert-butyl)- 7,9 –dimethoxy -2-azaspiro[4.5]deca-6,9-diene-1,8-dione: white solid (82% from **9**); **IR** (neat) ν/cm^{-1}: 2957, 2922, 2852, 1665, 1615, 1110; **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 5.68 (s, 2H), 3.69 (s, 6H), 3.65 (dd, *J*= 6.5 Hz, 2H), 2.30 (dd, *J*= 6.5 Hz, 2H), 1.44 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 176.1, 171.6, 152.3, 114.3, 55.3, 55.0, 50.8, 42.2, 32.4, 27.5; **MS ESI+** (m/z, M+1): calc. for $C_{15}H_{22}NO_4$: 280.1548, found: 280.1349.



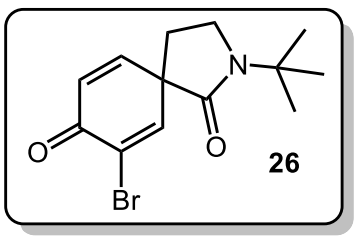
2 - (tert-butyl)-6-methoxy - 7 - methyl-2-azaspiro[4.5]deca-6,9-diene-1,8-dione: Pale yellow oil (66% from **10**); **IR** (neat) ν/cm^{-1}: 2998, 2878, 1689, 1658, 1609, 1237; **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.54 (d, *J*= 9.7, 1H), 6.29 (d, *J*= 9.7, 1H), 3.84 (s, 3H), 3.63-3.55 (m, 2H), 2.55-2.46 (m, 1H), 2.08-2.01 (m, 1H), 1.89 (s, 3H), 1.41 (s, 9H), **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 188.6, 169.9, 143.1, 128.6, 121.7, 61.2, 56.4, 55.0, 43.0, 28.1, 27.4, 9.3; . **MS ESI+** (m/z, M+1): calc. for $C_{15}H_{22}NO_3$: 264.1599, found: 264.1595.



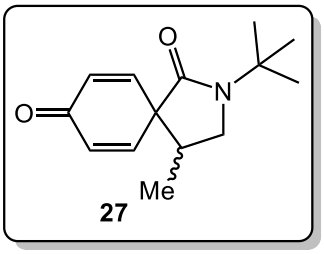
2-(tert-butyl)-6,9-dimethoxy-2-azaspiro[4.5]deca-6,9-diene-1,8-dione: Pale yellow solid (93% from **11**); **IR** (neat) ν/cm^{-1}: 2908, 2848, 1693, 1644, 1609, 1022; **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 5.56 (s, 1H), 5.30 (s, 1H), 3.65 (s, 3H), 3.59 (s, 3H), 3.54-3.46 (m, 2H), 2.41-2.38 (m, 1H), 2.09-2.04 (m, 1H), 1.33 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 182.2, 174.5, 170.6, 151.2, 110.5, 102.9, 56.2, 55.0, 54.6, 43.1, 30.2, 27.3; **MS ESI+** (m/z, M+1): calc. for $C_{15}H_{22}NO_4$: 280.1548, found: 280.1547.



6-bromo-2-(tert-butyl)-9-methoxy-2-azaspiro[4.5]deca-6,9-diene-1,8-dione: Pale yellow solid (72% from **12**); **IR** (neat) ν/cm^{-1}: 2930, 2855, 1690, 1667, 1210; **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.78 (s, 1H), 5.74 (s, 1H), 3.68 (s, 1H), 3.65-3.52 (m, 2H), 2.69-2.61 (m, 1H), 2.30-2.26 (m, 1H), 1.44 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 178.6, 169.0, 151.4, 147.8, 134.1, 115.6, 59.1, 55.4, 55.1, 42.8, 30.8, 27.4; **MS ESI+** (m/z, M+1): calc. for C14H19BrNO$_3$: 328.0548, found: 328.0555.



7-bromo-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-diene-1,8-dione (25): white solid (67% from **12**); **IR** (neat) ν/cm^{-1}: 3008, 2930, 2857, 1694, 1671, 1289, **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.22 (d, *J*= 2.7 Hz, 1H), 6.83 (dd, *J*= 2.6, 9.8 Hz, 1H), 6.5 (d, *J*= 9.8, 1H), 3.66 (dd, *J*= 6.7 Hz, 2H), 2.3 (dd, *J*= 6.7 Hz, 2H), 1.43 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 178.3, 168.1, 146.8, 129.3, 126.5, 56.8, 55.5, 42.3, 30.1, 27.4; **MS ESI+** (m/z, M+1): calc. for C13H17BrNO$_2$: 298.0442, found: 298.0440.



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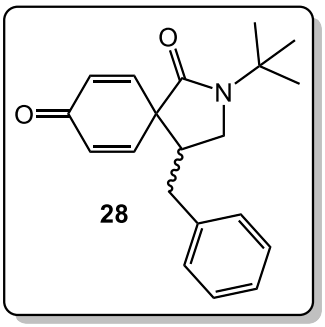
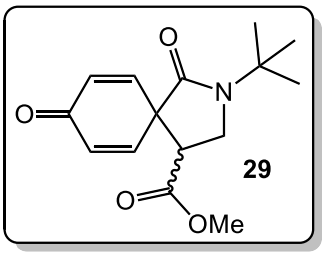
2-(tert-butyl)-4-methyl-2-azaspiro[4.5]deca-6,9-diene-1,8-dione: Pale yellow oil (66% from **14a**), **IR** (neat) ν/cm^{-1}: 3039. 2976, 2937, 1688, 1661, 1622, 1404, 1246; **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.75 (d, *J*= 10.0 Hz, 2H), 6.49-6.41 (m, 1H), 3.74-3.68 (m, 1H), 3.28-3.21 (m, 2H), 1.41 (s, 9H), 1.38 (d, *J*= 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 185.6, 166.2, 148.1, 142.5, 132.4, 132.0, 55.1, 49.7, 38.6, 29.6, 27.7, 13.1; **MS ESI+** (m/z, M+1): calc. for $C_{14}H_{19}NO_2$: 234.141, found: 234.119.



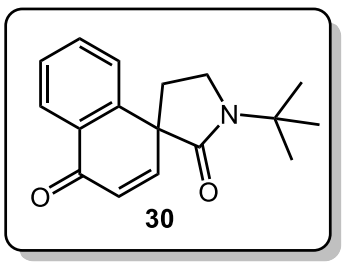
28

4-benzyl-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-diene-1,8-dione: white solid (62% from **14b**); **IR** (neat) ν/cm^{-1}: 3026, 2975, 2932, 1692, 1661, 1625, 1505, 1242. **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 7.27-7.18 (m, 3H), 7.05 (d, *J*= 6.3 Hz, 2H), 6.86 (dd, *J*= 10.1 Hz, 1H), 6.68 (dd, *J*=10.0 Hz, 1H), 6.48 (dd, *J*= 10.0 Hz, 1H), 6.35 (dd, *J*= 10.0 Hz, 1H), 3.54-3.48 (m, 1H), 3.37-3.31 (m, 1H), 2.86-2.72 (m, 1H), 2.61-2.52 (m, 2H), 1.35 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 185.5, 169.4, 148.0, 142.0, 137.9, 132.1, 132.4, 128.6, 128.3, 126.8, 57.6, 55.2, 48.0, 45.2, 35.2, 27.6; **MS ESI+** (m/z, M+1): calc. for $C_{20}H_{23}NO_2$: 310.172, found: 310.1486.



29

Methyl-2-(tert-butyl)-1,8-dioxo-2-azaspiro[4.5]deca-6,9-diene-4-carboxylate: white solid (70% from **14c**); **IR** (neat) ν/cm^{-1}: 2958, 2921, 2852, 1736, 1695, 1665, 1628, 1406, 1202; **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 6.80 (dd, *J*= 9.9 Hz, 1H), 6.72 (dd, *J*= 10.2 Hz, 1H), 6.50 (dd, *J*= 9.9, 1H), 6.39 (dd, *J*= 9.9 Hz, 1H), 3.95-3.89 (m, 1H), 3.77 (m, 1H), 3.61 (s, 3H), 3.54-3.42 (m, 2H), 1.42 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 185.0, 169.3, 167.2, 147.1, 140.9, 132.2, 131.8, 55.6, 55.6, 52.5, 46.9, 43.7, 27.5; **MS ESI+** (m/z, M+1): calc. for $C_{15}H_{19}NO_4$: 278.1324, found: 278.1290.

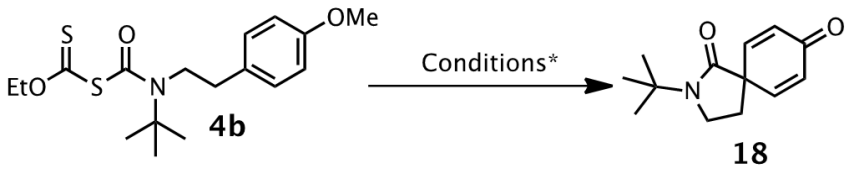


30

1' - (tert-butyl)-4H-spiro[naphthalene-1,3'-pyrrolidine]-2',4-dione: Pale yellow oil (73% from **14**), **IR** (neat) ν/cm^{-1}: 3007, 2929, 1690, 1664, 1243; **1H NMR** (300 MHz, $CDCl_3$) δ/ppm: 8.20 (dd, *J*= 1.1, 8.9 Hz, 1H), 7.59 (t, *J*= 7.8 Hz, 1H), 7.43 (t, *J*= 8.7 Hz, 1H), 7.35 (d, *J*= 8.1

Hz, 1H), 6.92 (d, J=10.0 Hz, 1H), 6.56 (d, J=10.1 Hz, 1H), 3.79-3.73 (m, 2H), 2.57-2.41 (m, 2H), 1.47 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ/ppm: 184.3, 172.2, 147.0, 144.4, 133.0, 131.9, 129.4, 127.6, 126.8, 126.0, 55.1, 53.4, 42.9, 33.4, 29.6, 27.6; **MS ESI+** (m/z, M+1): calc. for $C17H20NO_2$: 270.1494, found: 270.1496.

Table of optimization:



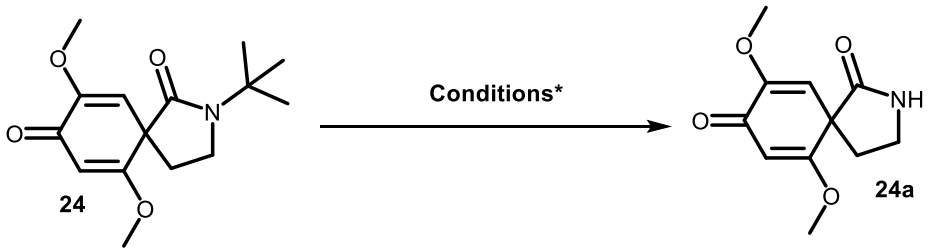
Entry	Oxidant*	Et_3B	Solvent	Temperature	Time	Yield
1	___	2.0	CH_2Cl_2	25 ºC	14 h.	32%
2	___	2.0	CH_2Cl_2	25 ºC	4 h.	35%
3	$FeSO_4$[a]	2.0	THF	25 ºC	4 h.	30%
4	$FeSO_4$[a]	2.0	CH_2Cl_2-EtOH-H_2O	25 ºC	14 h.	32%
5	$FeSO_4$[a]	2.0	CH_2Cl_2-EtOH-H_2O	25 ºC	4 h.	34%
6	$Fe_2(SO_4)_3$[a]	2.0	THF	25 ºC	4 h.	___
7	$Fe_2(SO_4)_3$[b]	2.0	THF	25 ºC	4 h.	18%
8	Cu(2-etylhexanoate)$_2$[a]	2.0	THF	25 ºC	4 h.	___
9	Cu(2-etylhexanoate)$_2$[b]	2.0	THF	25 ºC	4 h.	12%
10	CuI_2[a]	2.0	CH_2Cl_2	25 ºC	4 h.	___
11	CuI_2[b]	2.0	CH_2Cl_2	25 ºC	4 h.	21%
12	___	2.0	CH_2Cl_2[1]	25 ºC	4 h.	35%
13	___	2.0	CH_2Cl_2[1]	25 ºC	4 h.	38%
14	___	2.0	CH_2Cl_2[1]	-5 ºC	4 h.	62%
15	___	2.0	CH_2Cl_2[1]	-40 ºC	4 h.	NR
16	___	2.0	CH_2Cl_2[1]	-78 ºC	4 h.	NR

17	___	2.0	CH_2Cl_2[1]	25 ºC	4 h.	65%

Oxidant*: a) 1.0 eq. b) 0.1 eq.

CH_2Cl_2[1:] 0.05M (In all of the above cases the concentration was 0.2M)

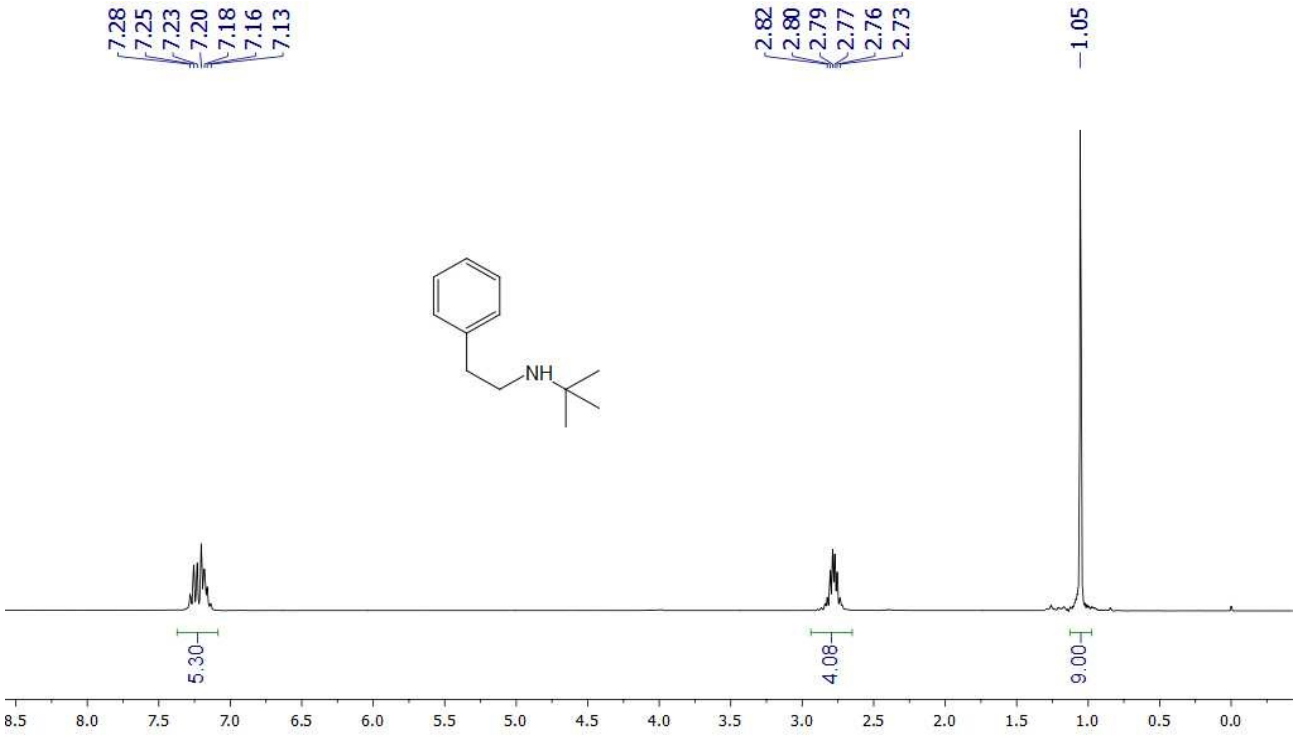
Table of conditions for deprotection of N-*t*-Bu:

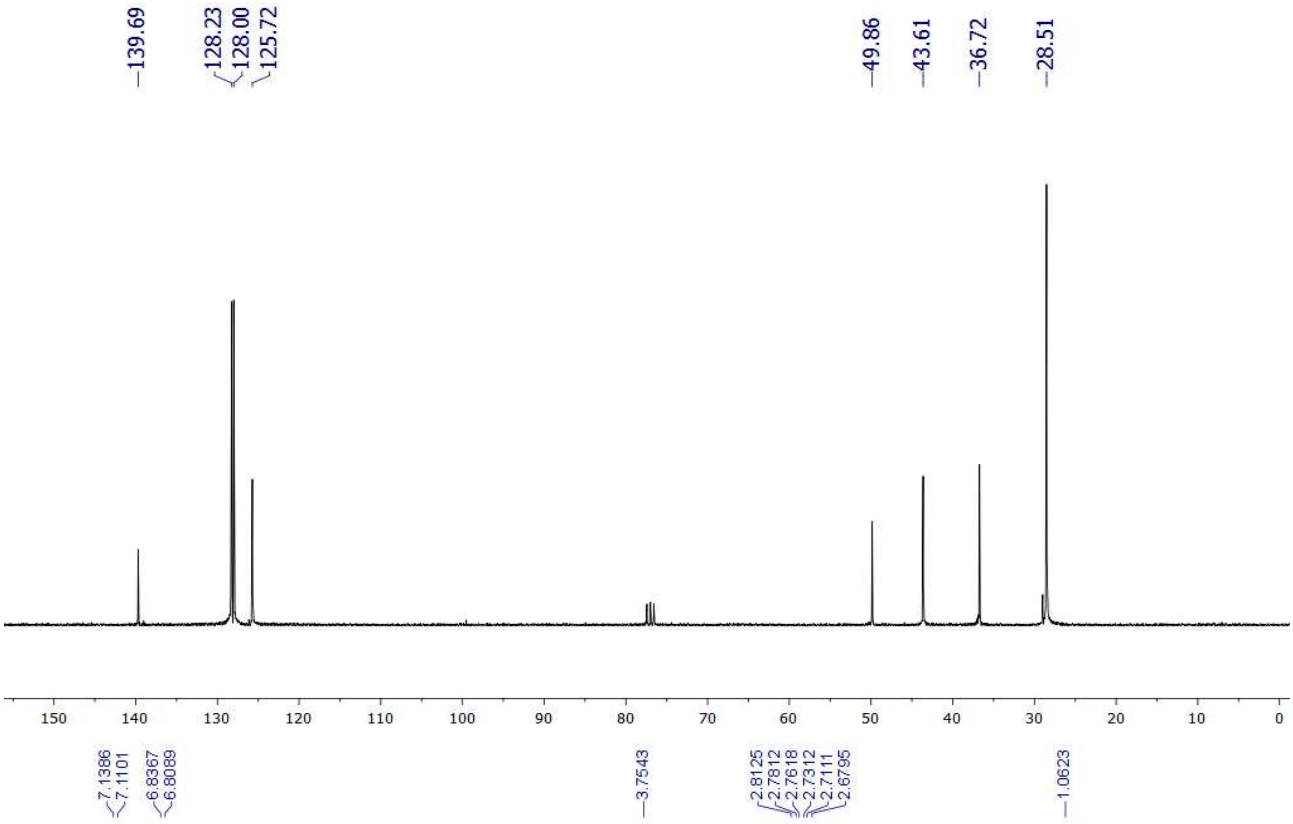


Entry	Acid	Temperature	Time	Product **23a**
1	TFA	72.4° C	1 h.	____
2	TFA	25° C	30 min	**24**
3	TFA	25° C	12 h.	___
4	H_2SO_4	55° C	1 h.	___
5	H_2SO_4	25° C	12 h.	___
6	$BF_3{\cdot}2CH_3COOH$	25° C	24 h.	**24**
7	$BF_3{\cdot}2CH_3COOH$	25° C	72 h.	**24**
8	$BF_3{\cdot}2CH_3COOH$	40° C	4 h.	**24**
9	$BF_3{\cdot}2CH_3COOH$	60° C	4 h.	___
10	$BF_3{\cdot}2CH_3COOH$	60° C	30 min.	___

* In all cases, the acid was used as solvent, following the methodologies found in literature.

a) Lopez-Valdez, G,; Olguin-Uribe, S,; Miranda, L. *Tetrahedron Lett.* **2007**, *48*, 8285. b) Diabla, F,; Montiel, J,; Martínez-Laporta, A,; Bonjoch, J. *Tetrahedron Lett.* **2013**, 5*4*, 2619. c) Dawidowsky, M,; Herold, F,; Wilczek, M,; Turlo, J,; Chodkowski, A,; Gomolka, A,; Kleps, J. *Tetrahedron.* **2012**, *68*, 8222.

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80
70
60
50
40
30
20
10
0
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7.1101
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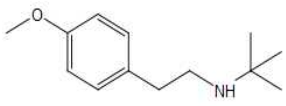
2.7312
2.7111
2.6795
1.0623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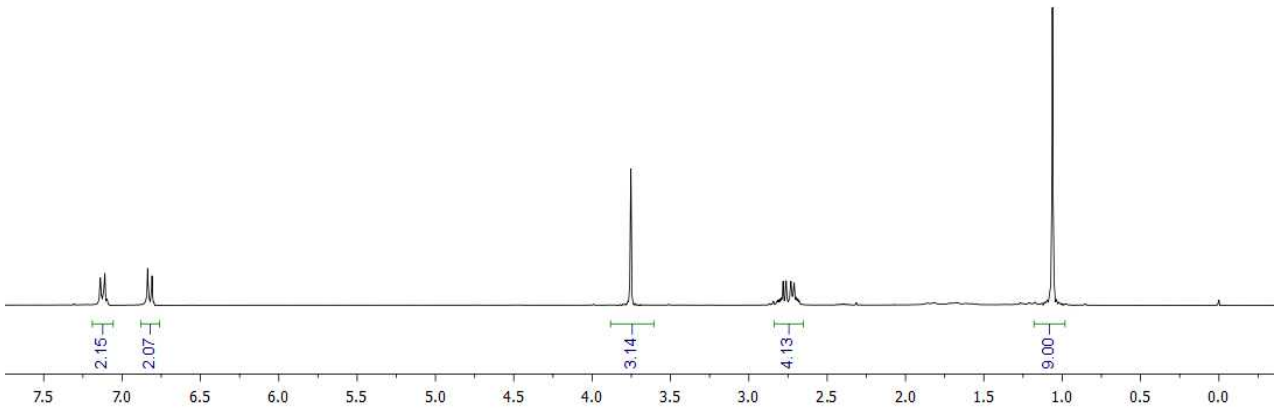
NH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6.5
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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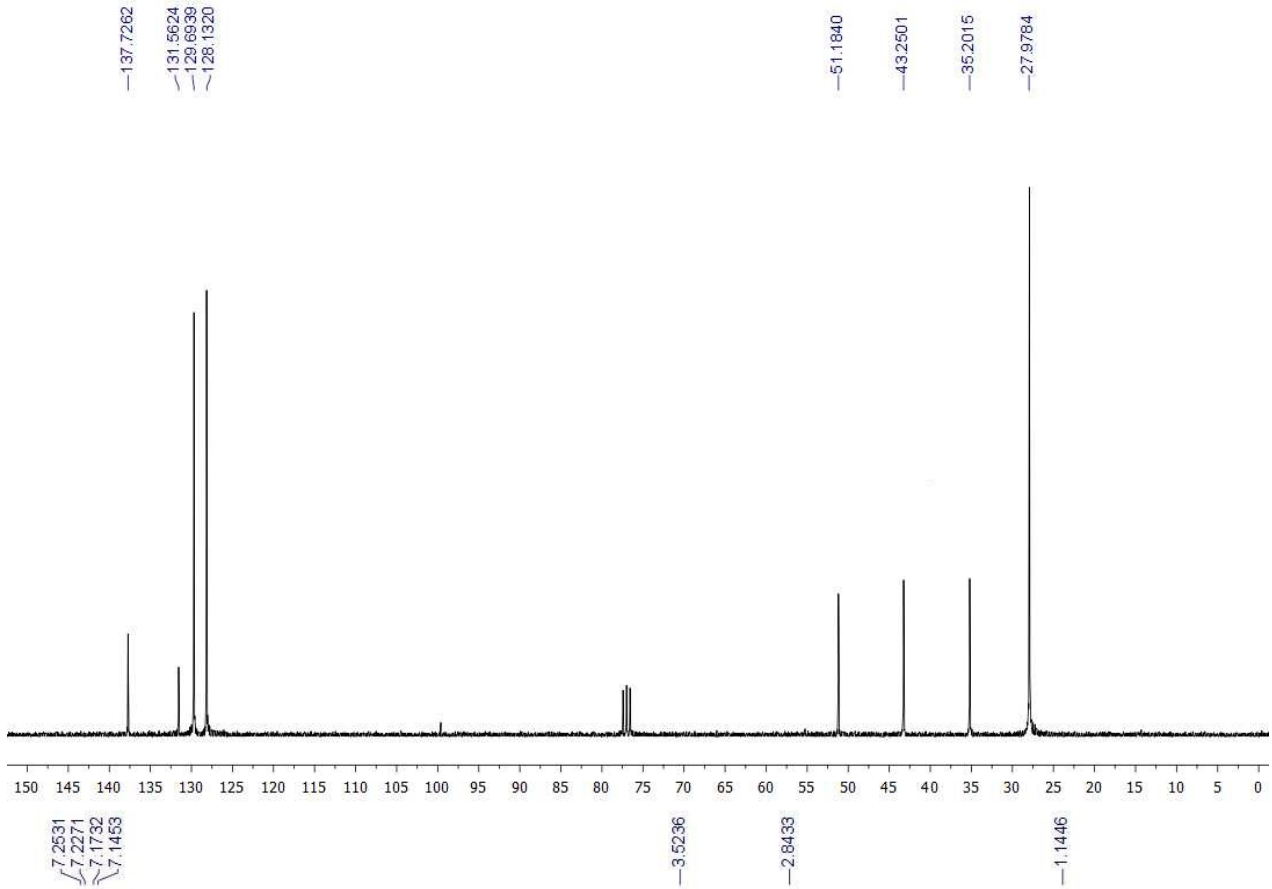
0.0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128.1320
51.1840
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35.2015
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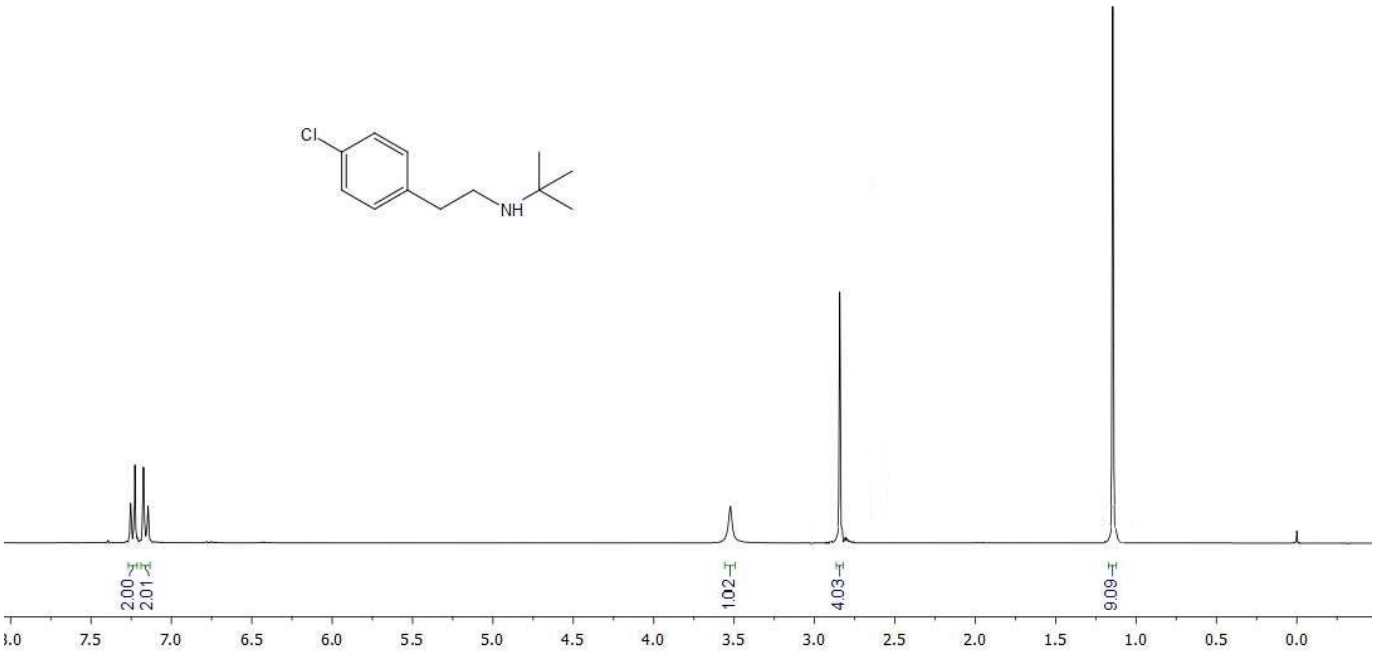
7.2271
7.1732
7.1453
3.5236
2.8433
1.1446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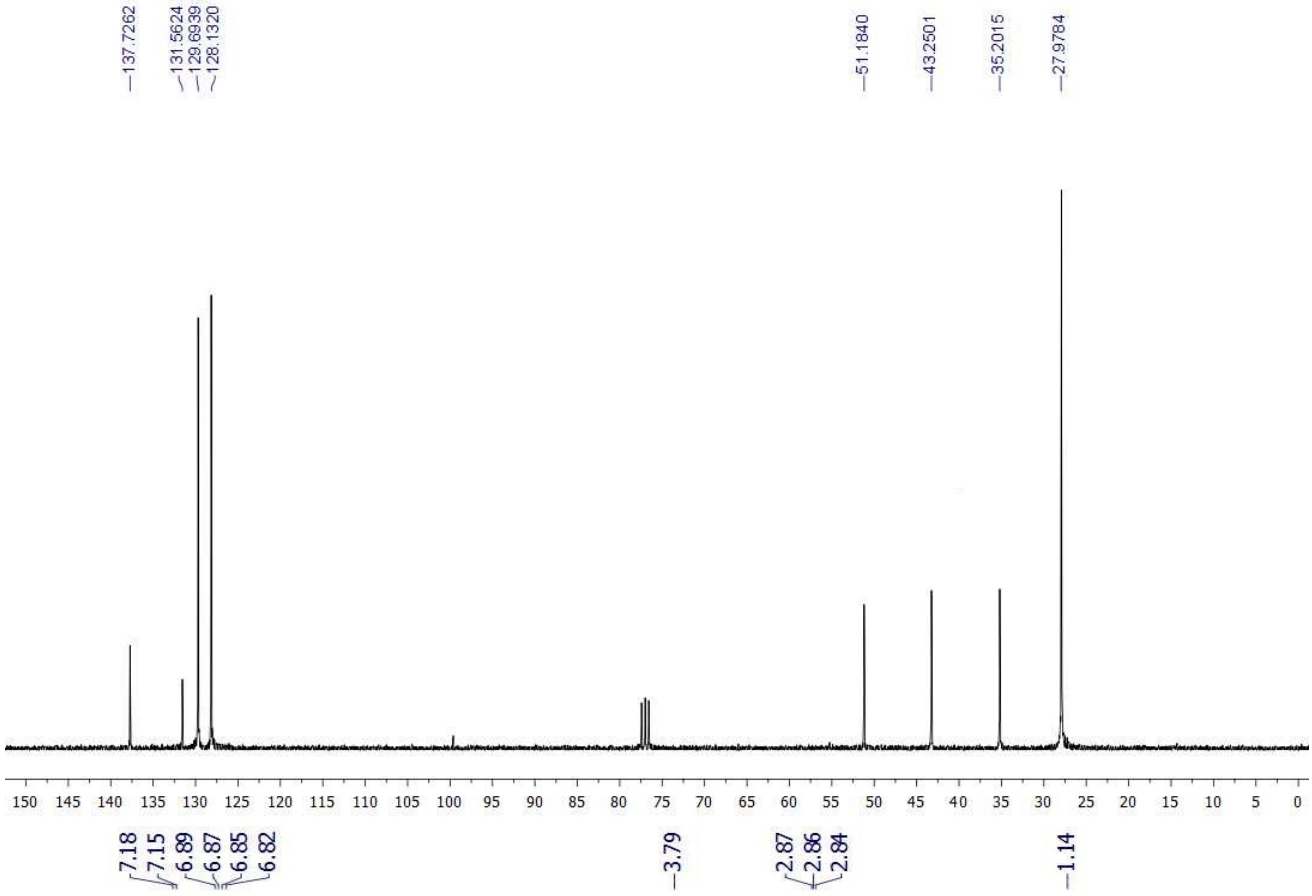
4.03
9.09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131.5624
129.6939
128.1320
51.1840
43.2501
35.2015
27.9784
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
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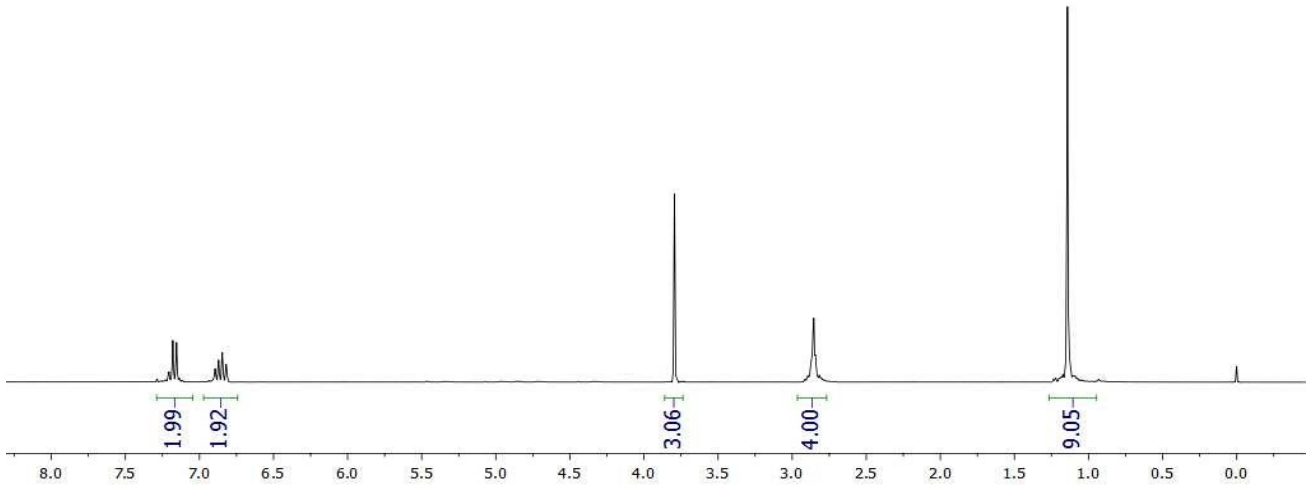
7.15
6.89
6.87
6.85
6.82
3.79
2.87
2.86
2.84
1.14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1.92
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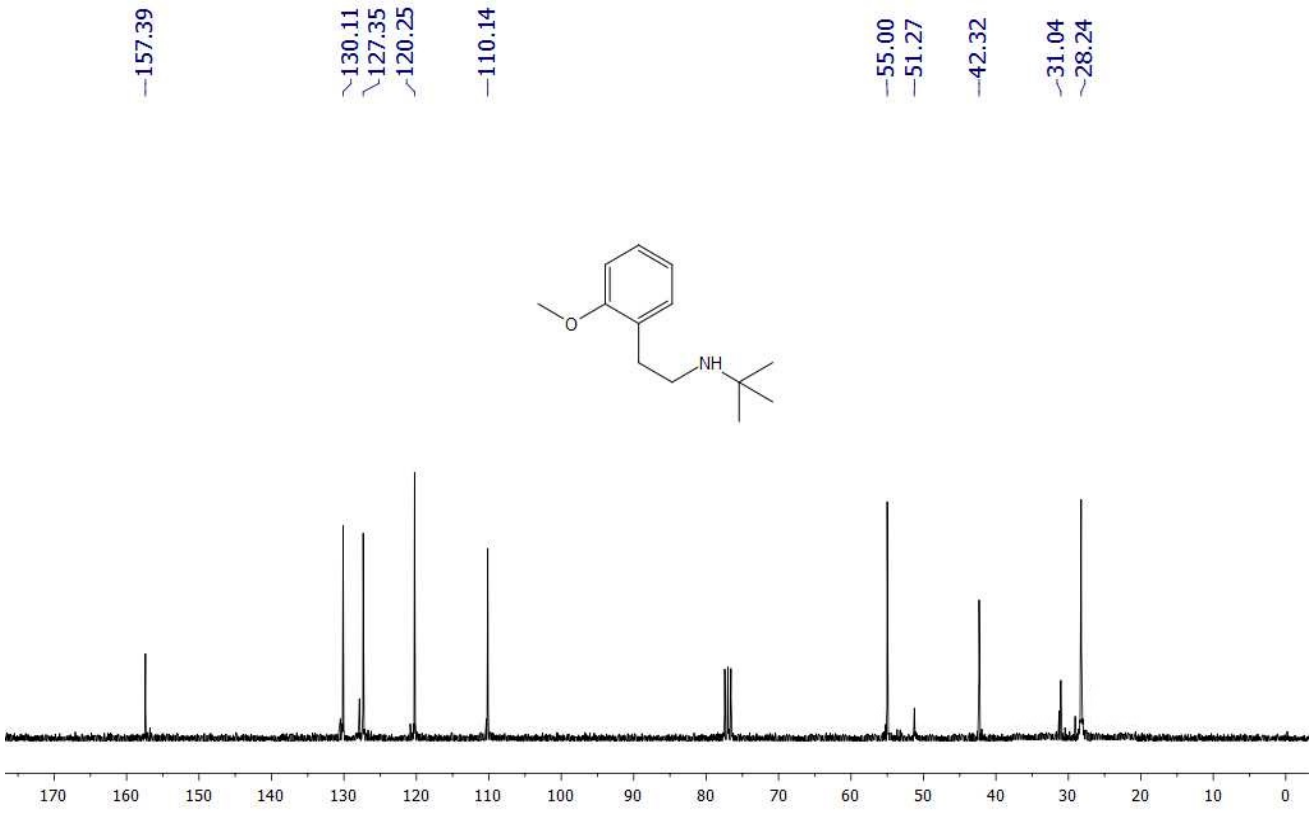
4.00
9.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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51.27
42.32
31.04
28.24
O
NH
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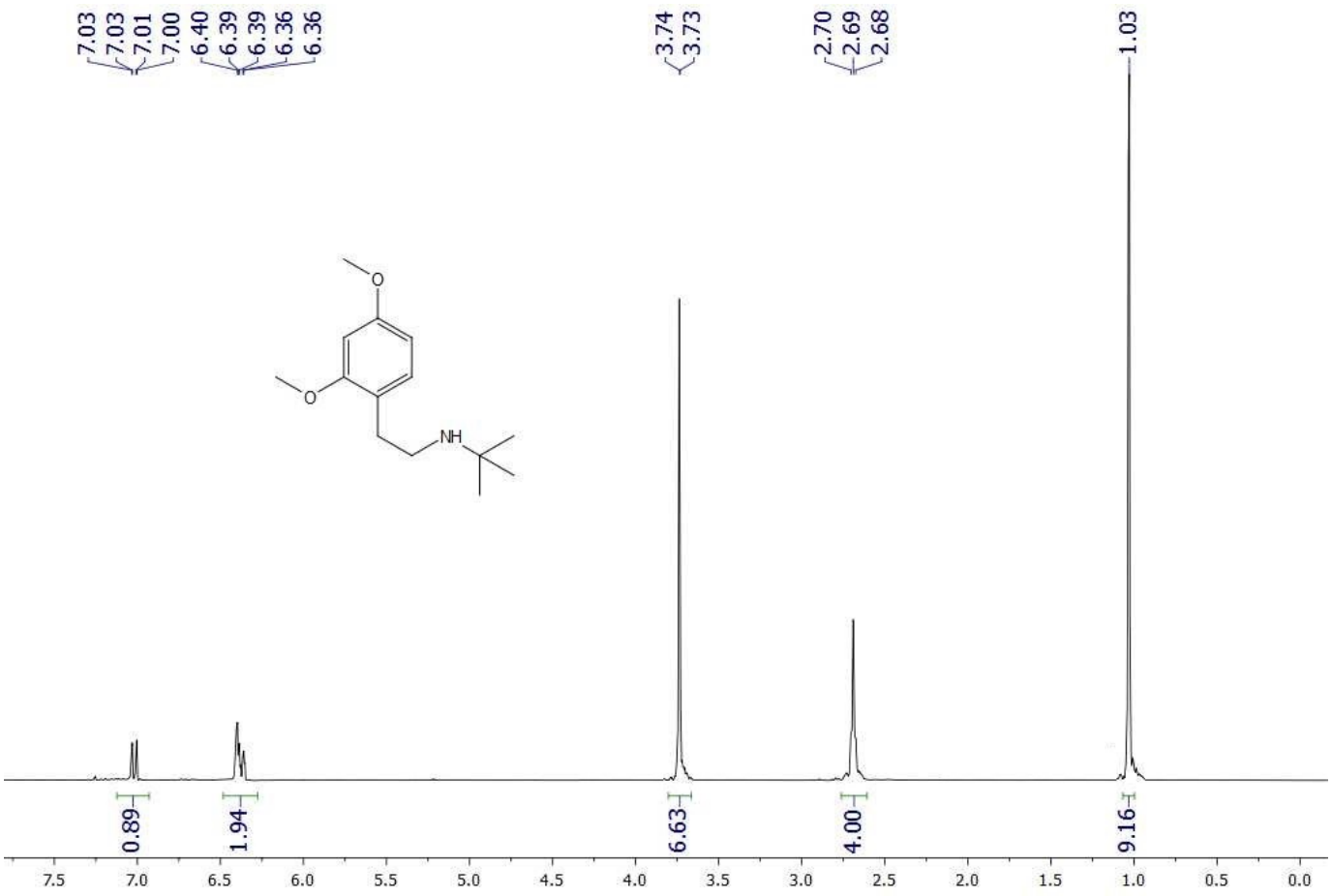
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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3.73
2.70
2.69
2.68
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O
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6.63
4.00
9.16
7.5
7.0
6.5
6.0
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2.0
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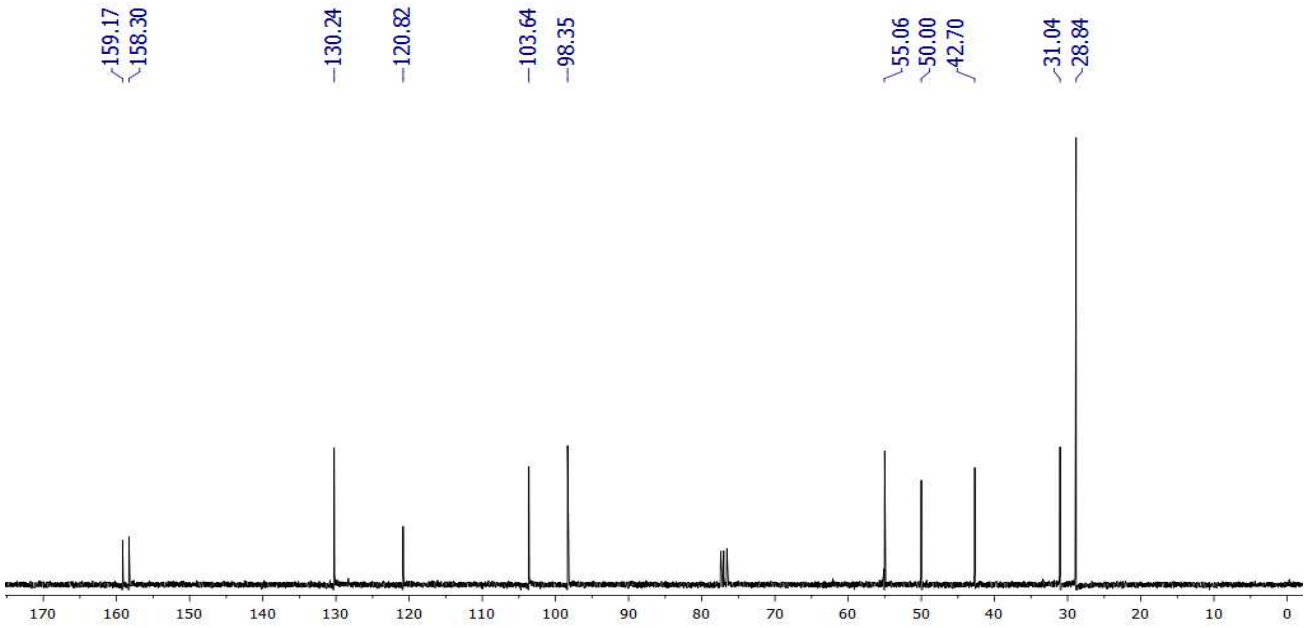
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98.35
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50.00
42.70
31.04
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70
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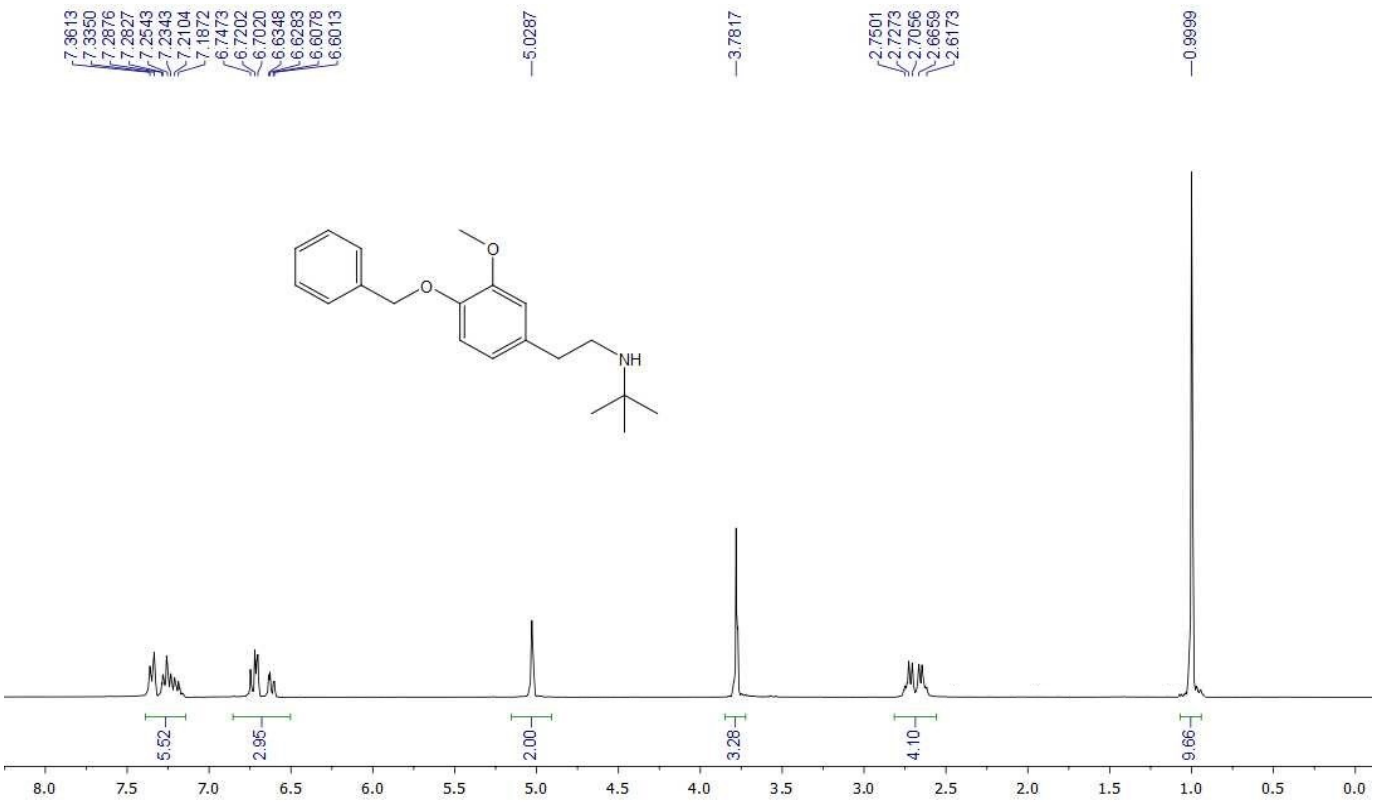
30
20
10
0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7.2343
7.2104
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6.7202
6.7020
6.6348
6.6283
6.6078
6.6013
5.0287
3.7817
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2.7273
2.7056
2.6659
2.6173
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O
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9.66
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7.5
7.0
6.5
6.0
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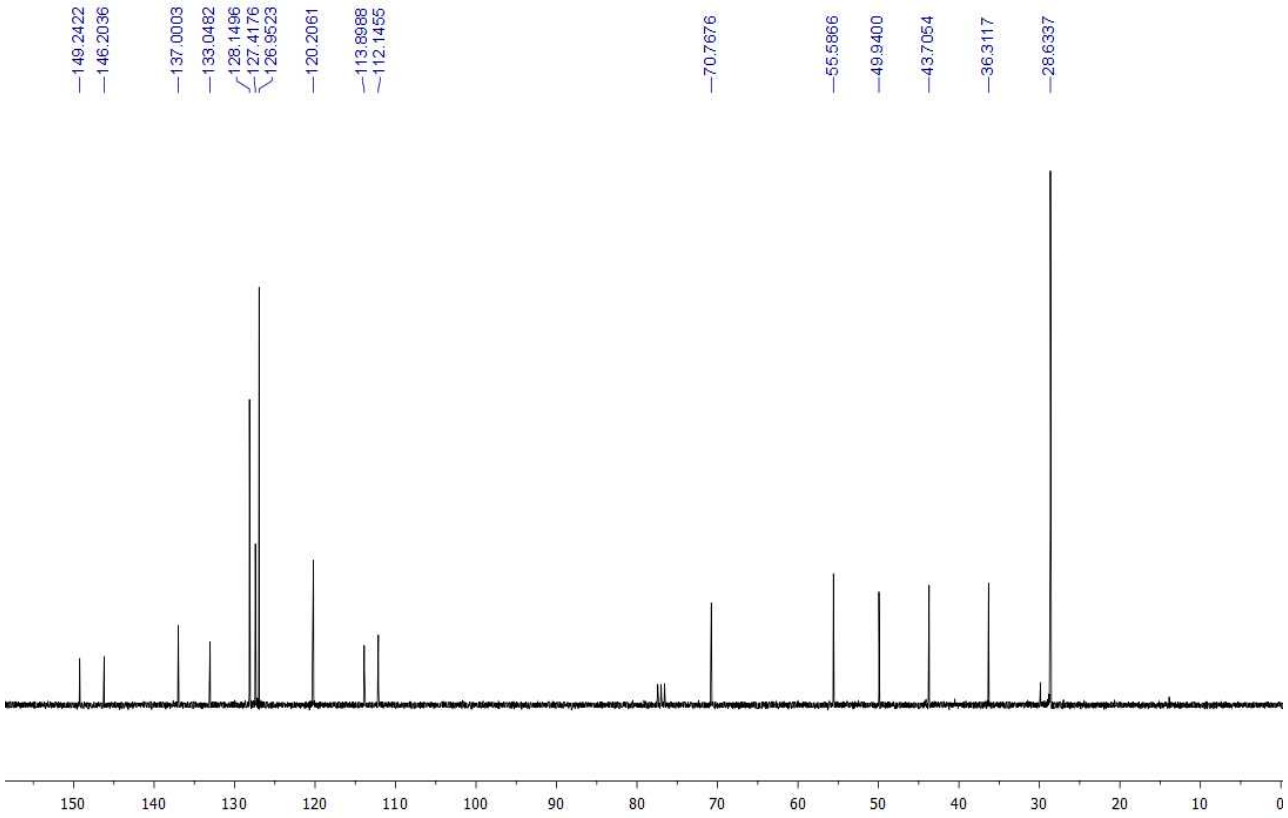
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55.5866
49.9400
43.7054
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10
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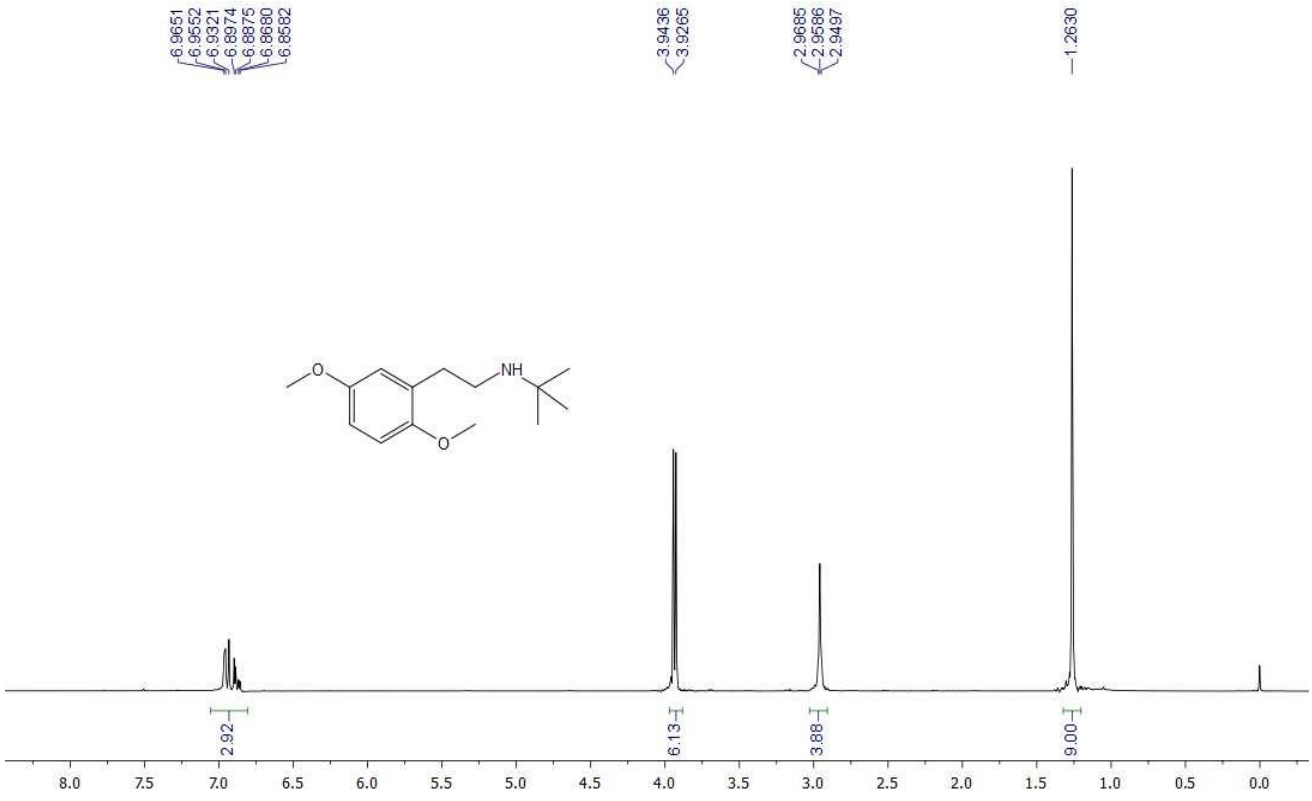
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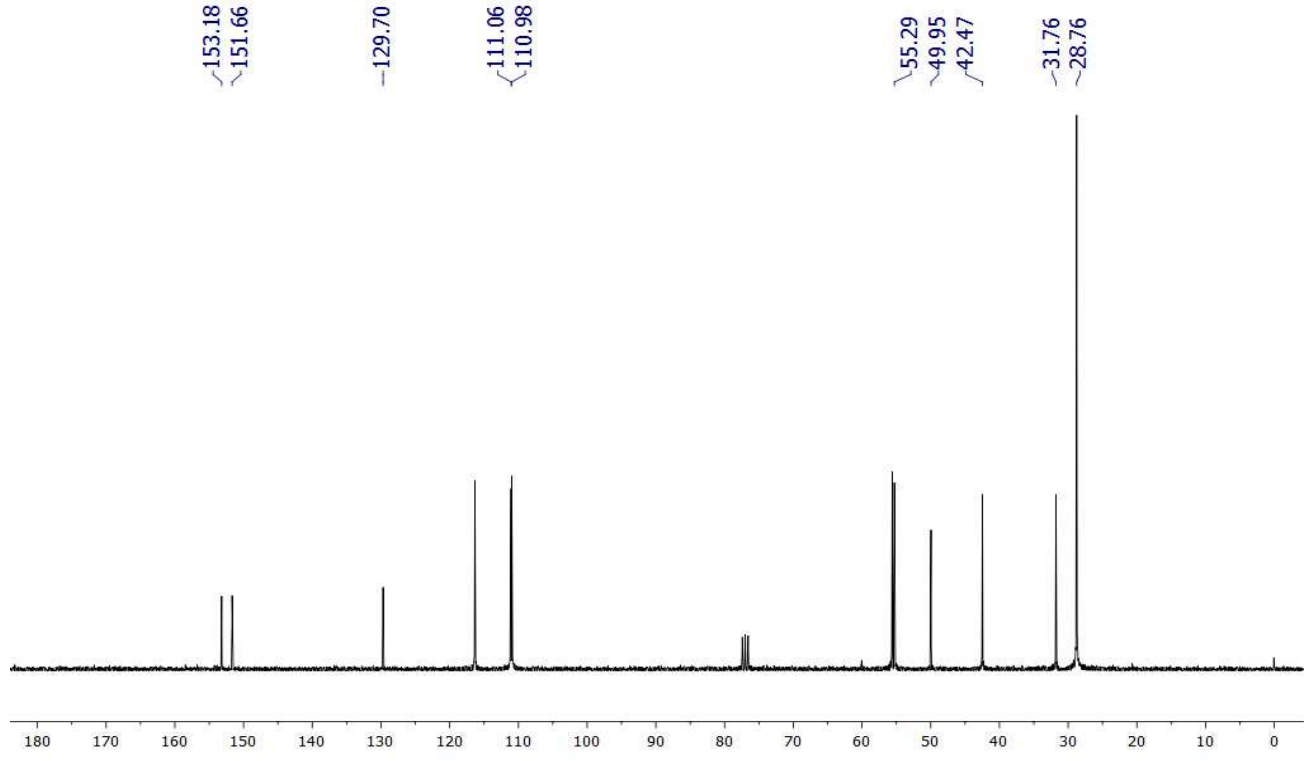
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70
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10
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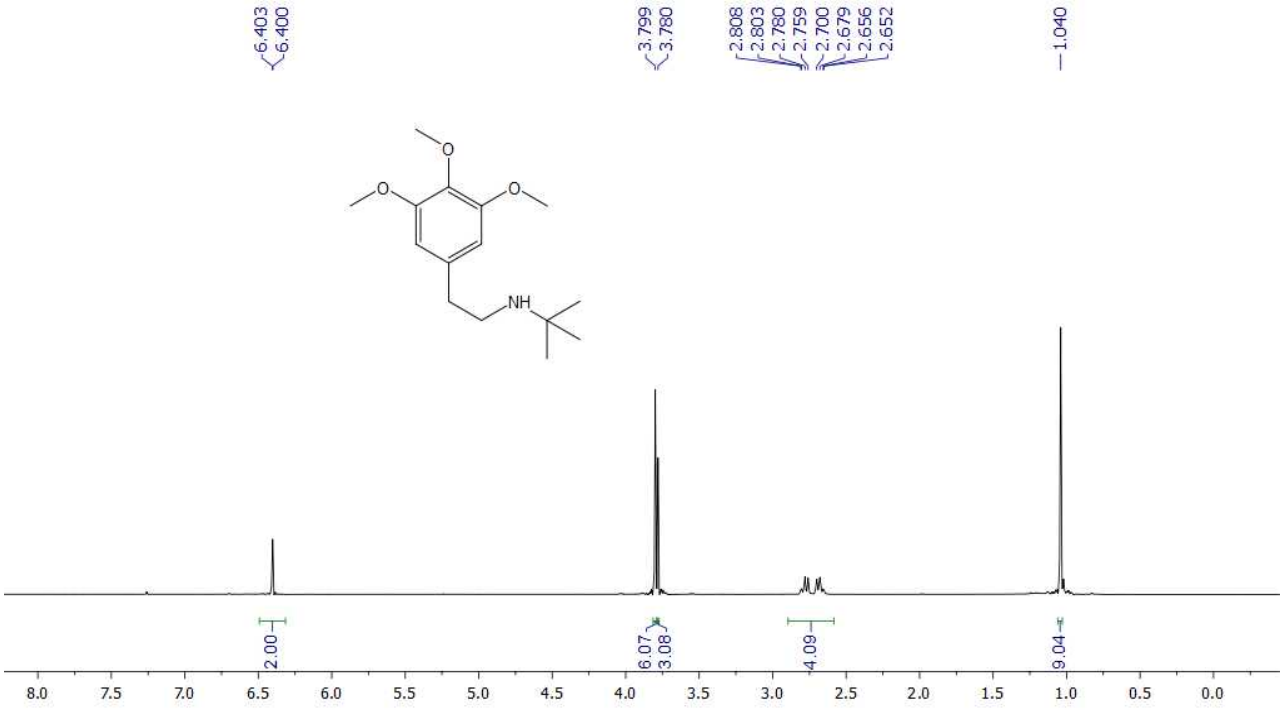
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3.08
4.09
9.04
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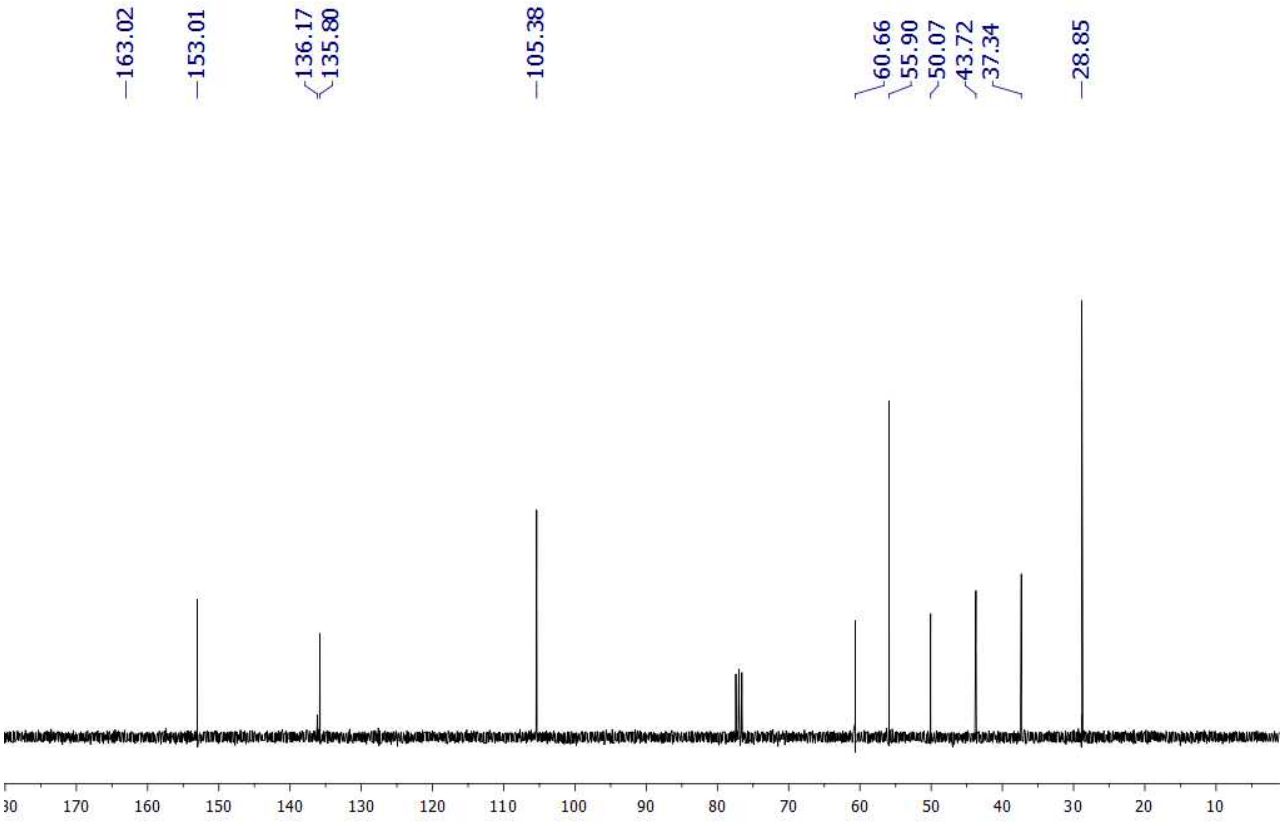
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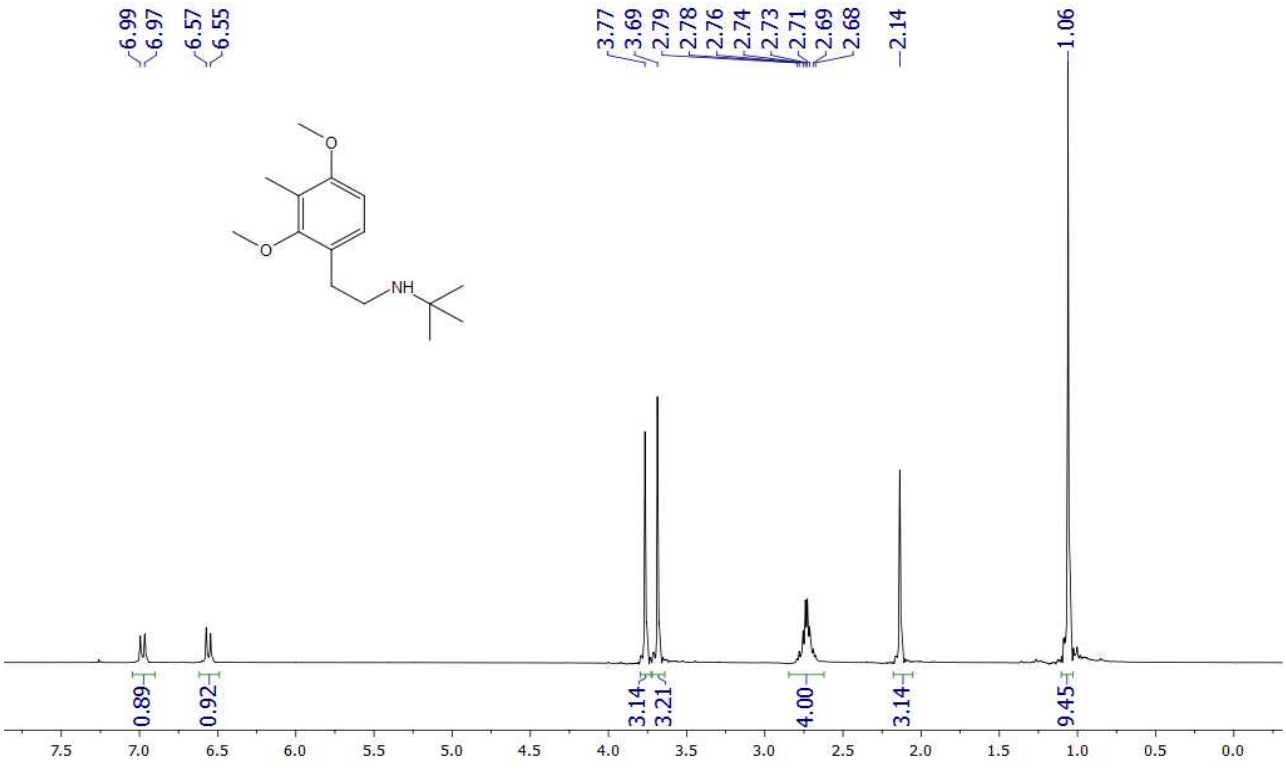
30
20
10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2.68
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7.0
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6.0
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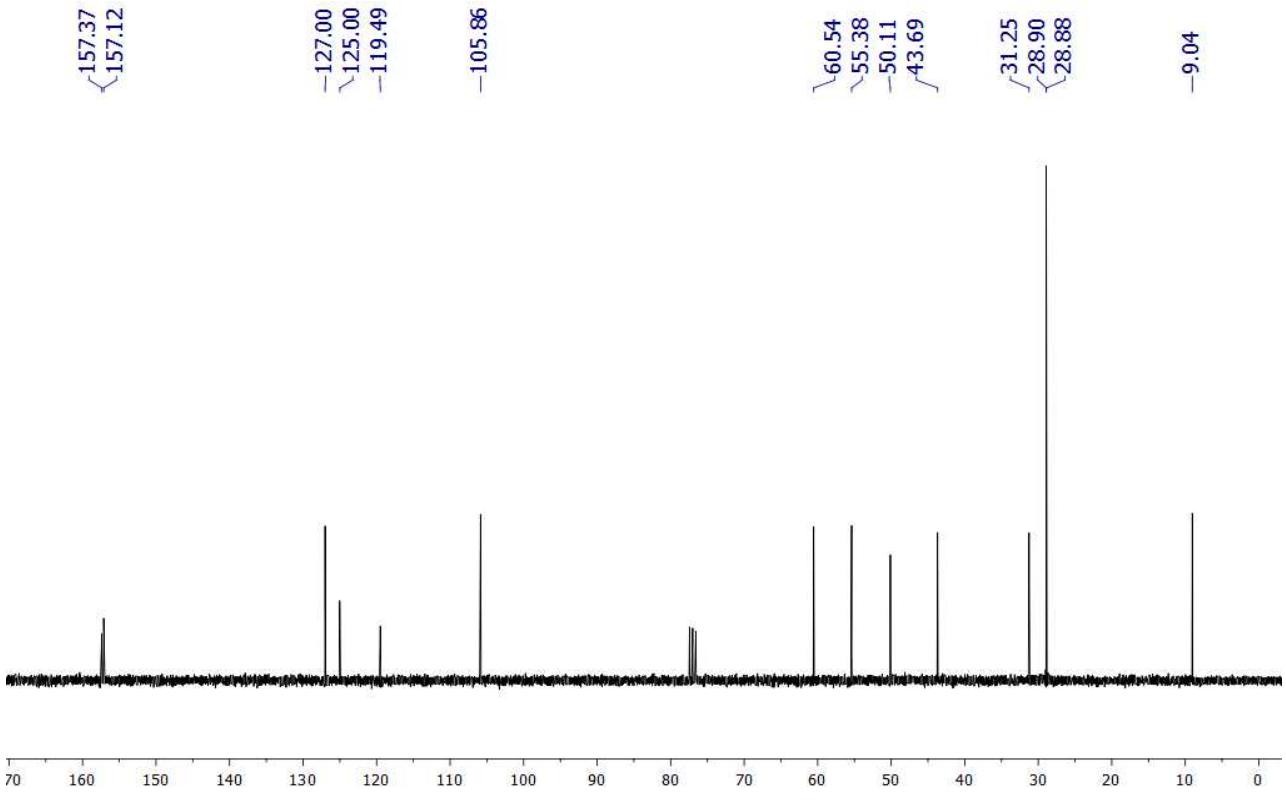
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10
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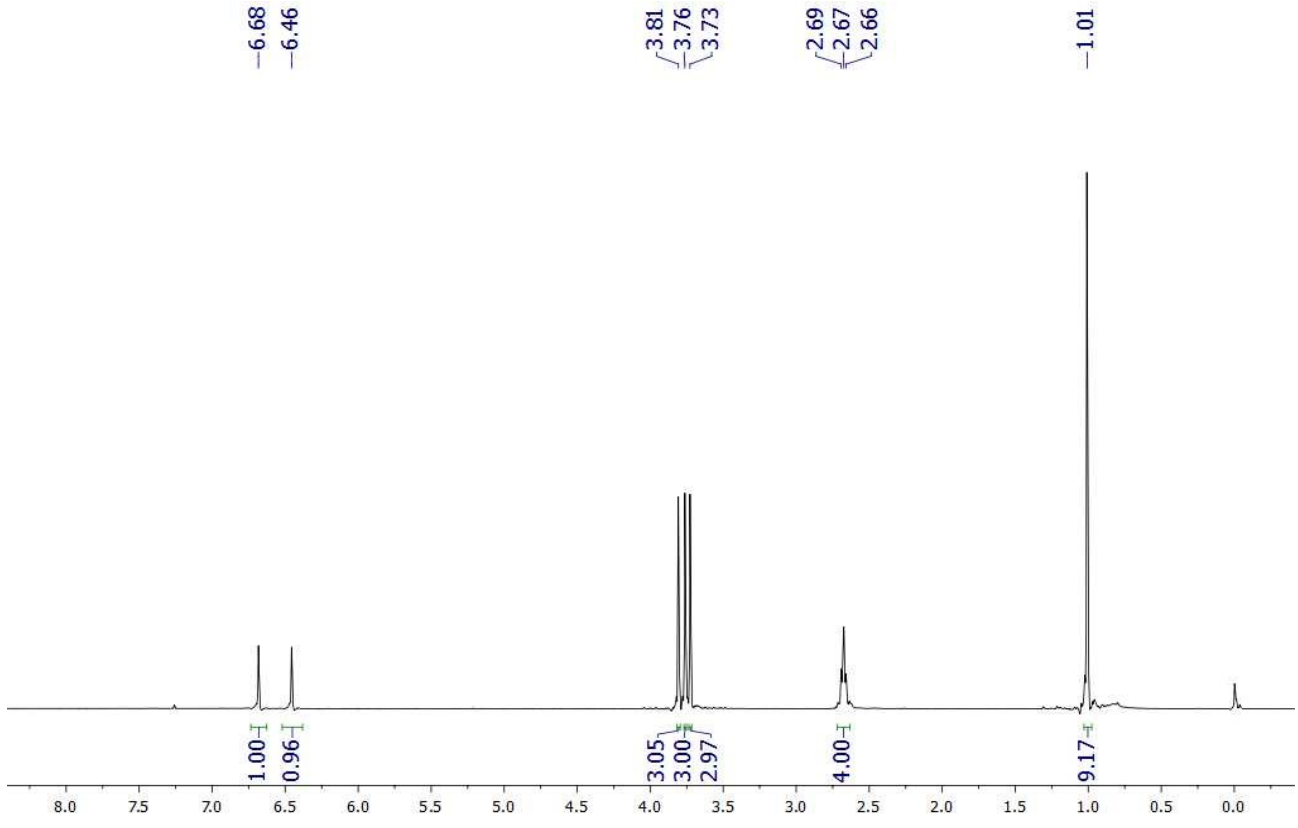
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3.00
2.97
4.00
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7.0
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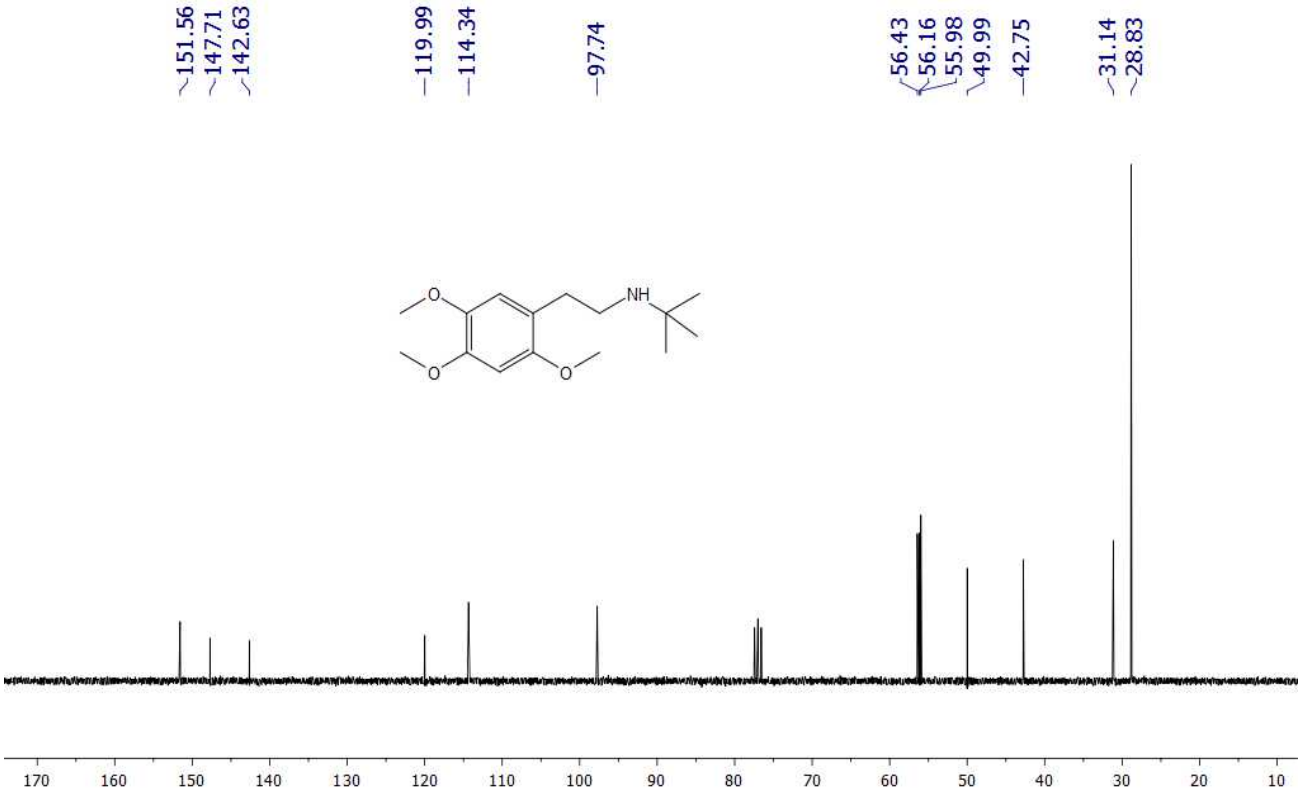
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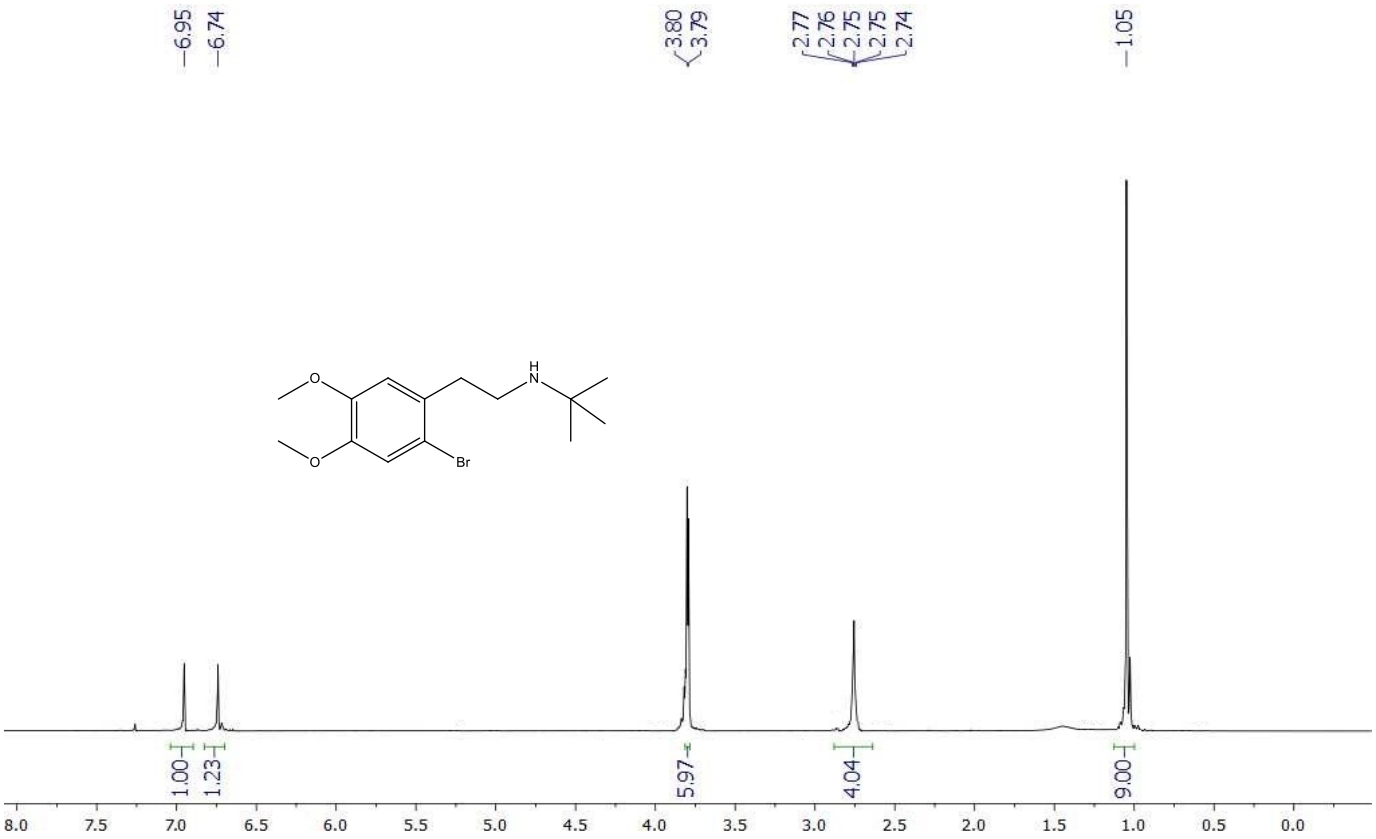
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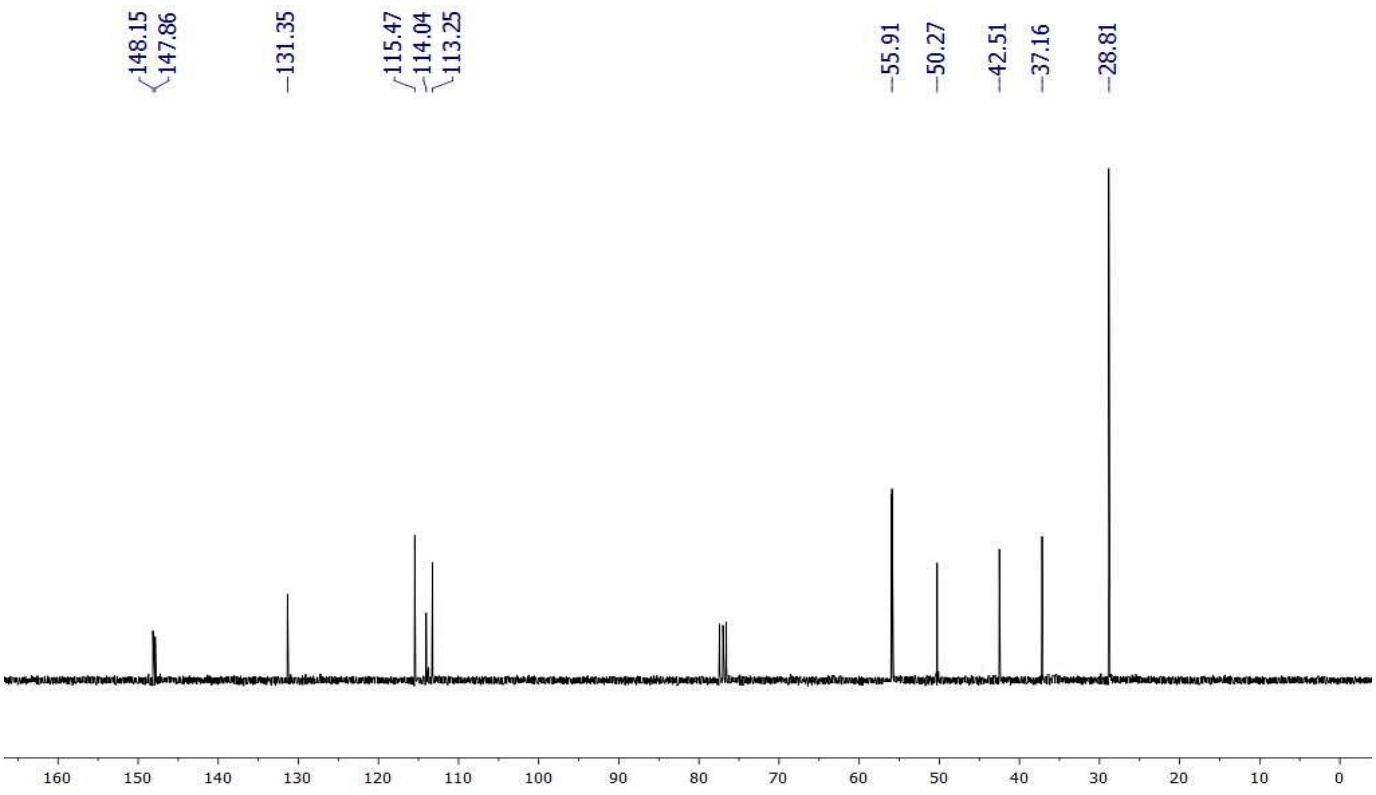
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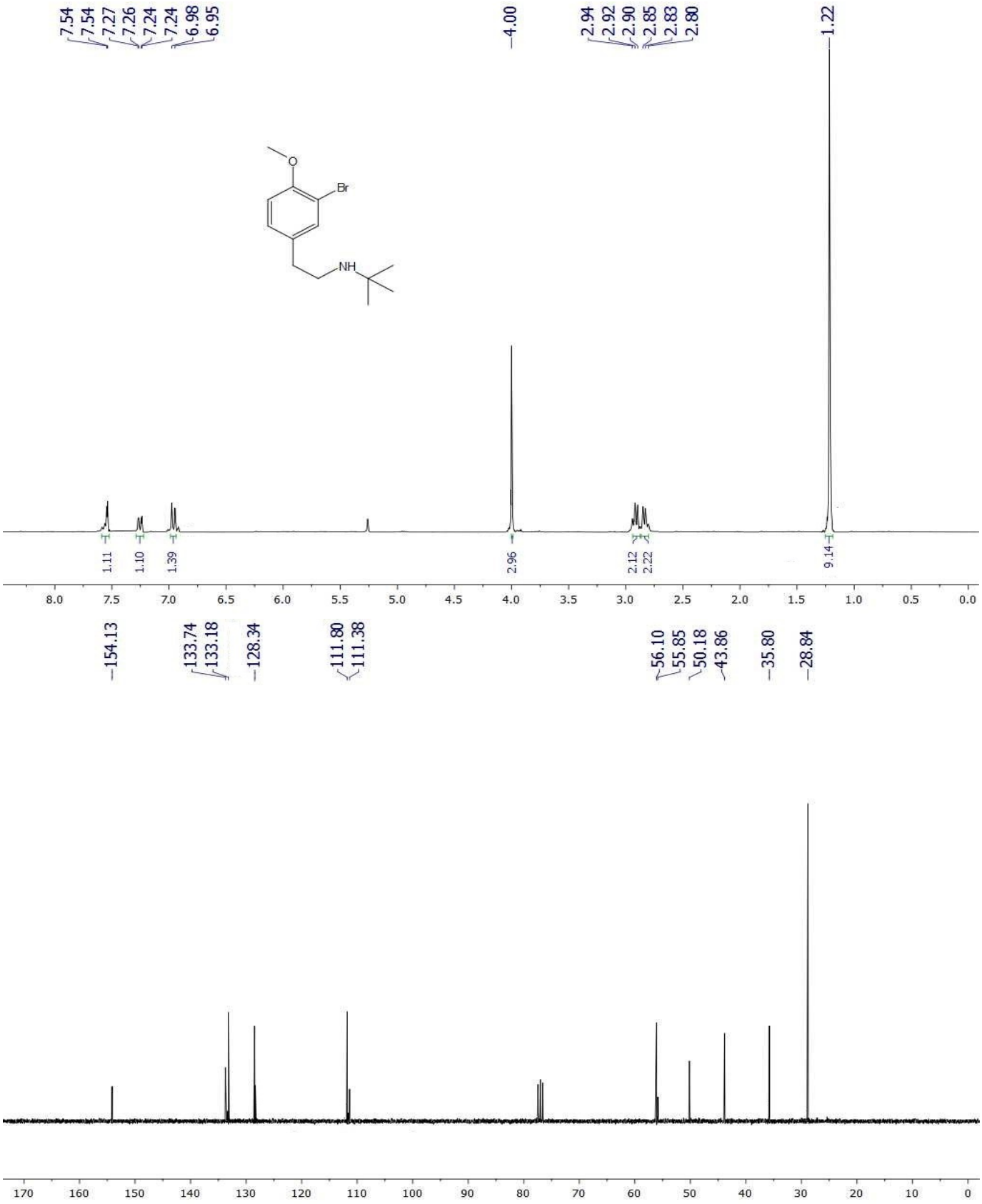
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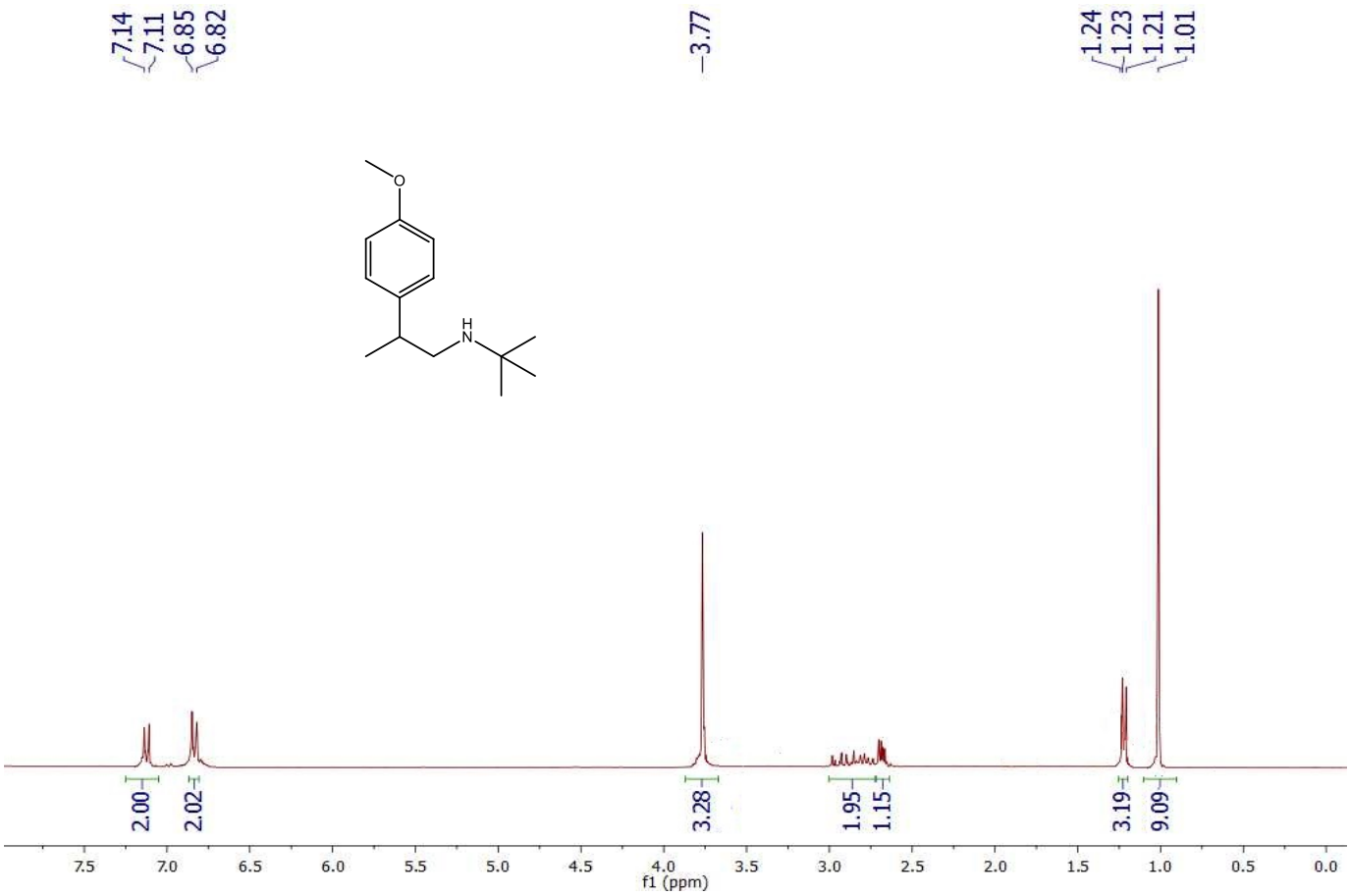
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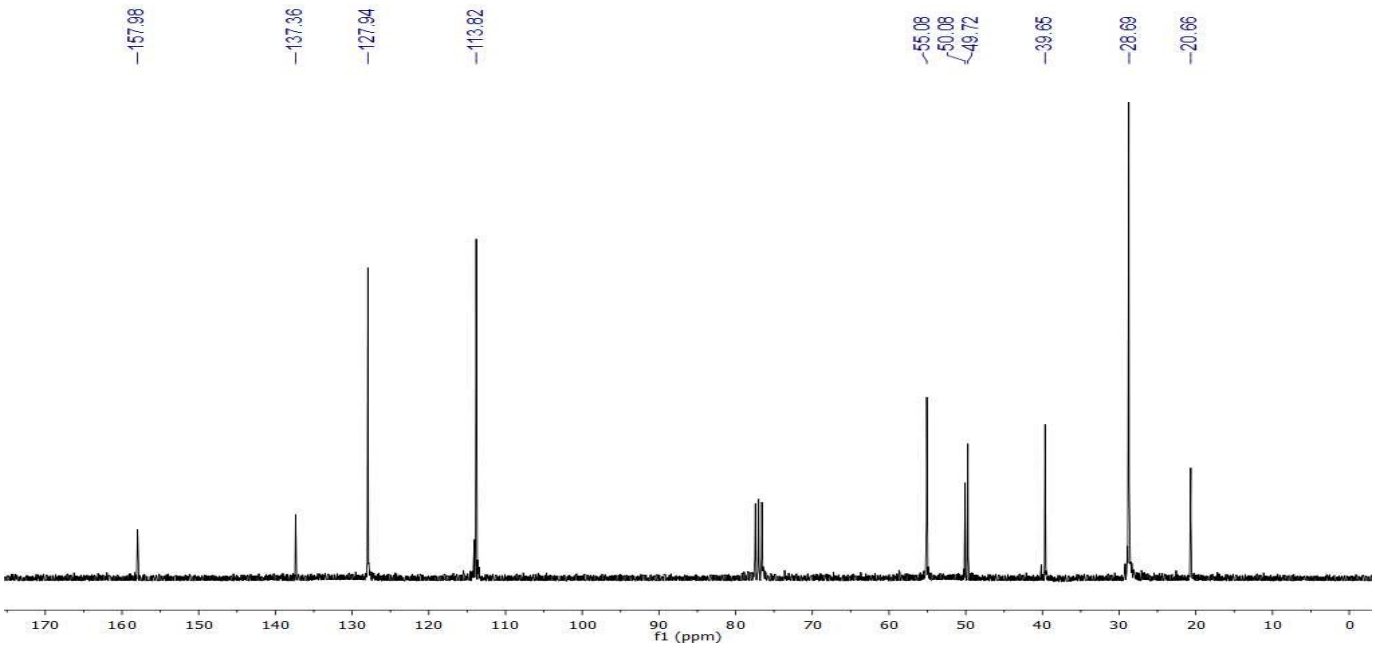
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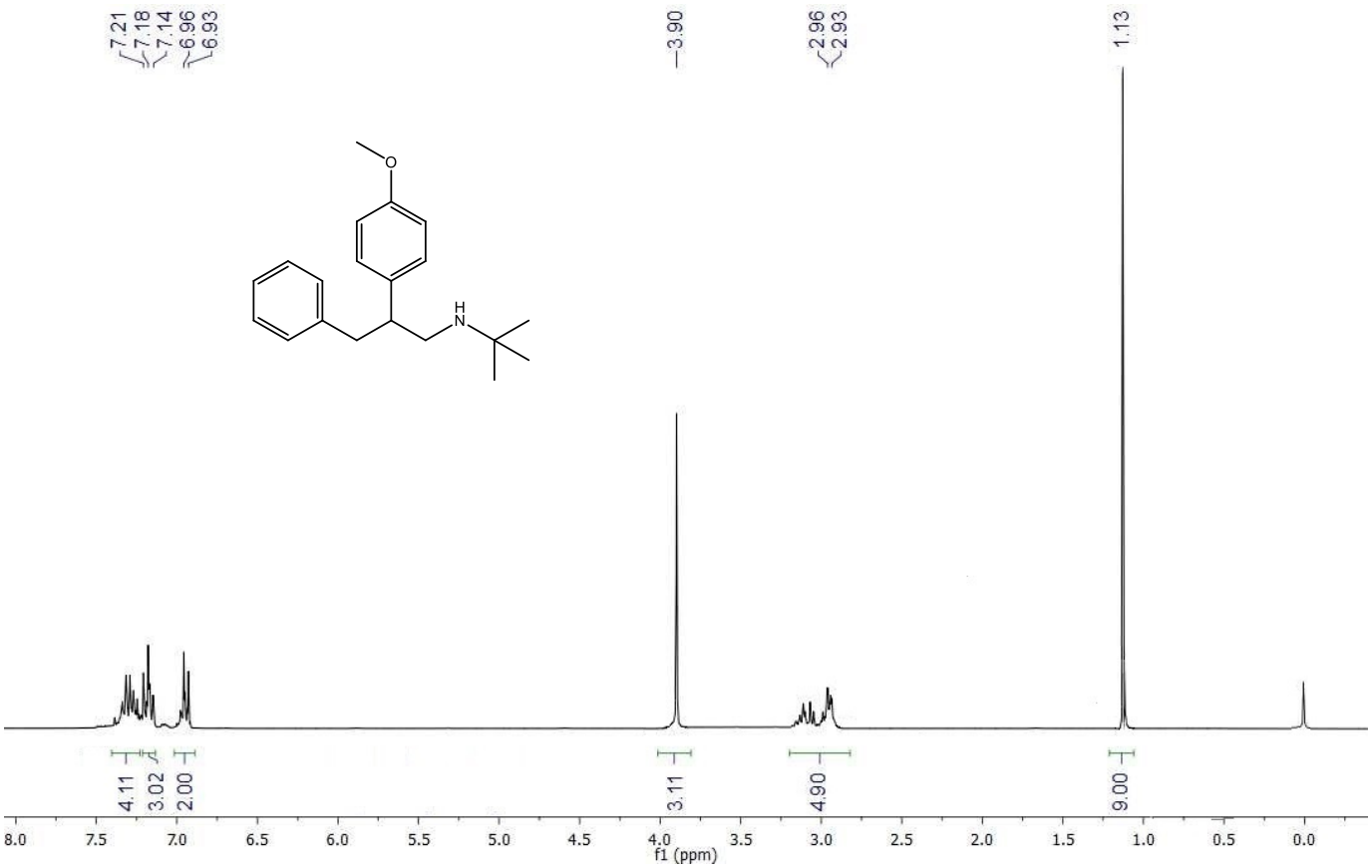
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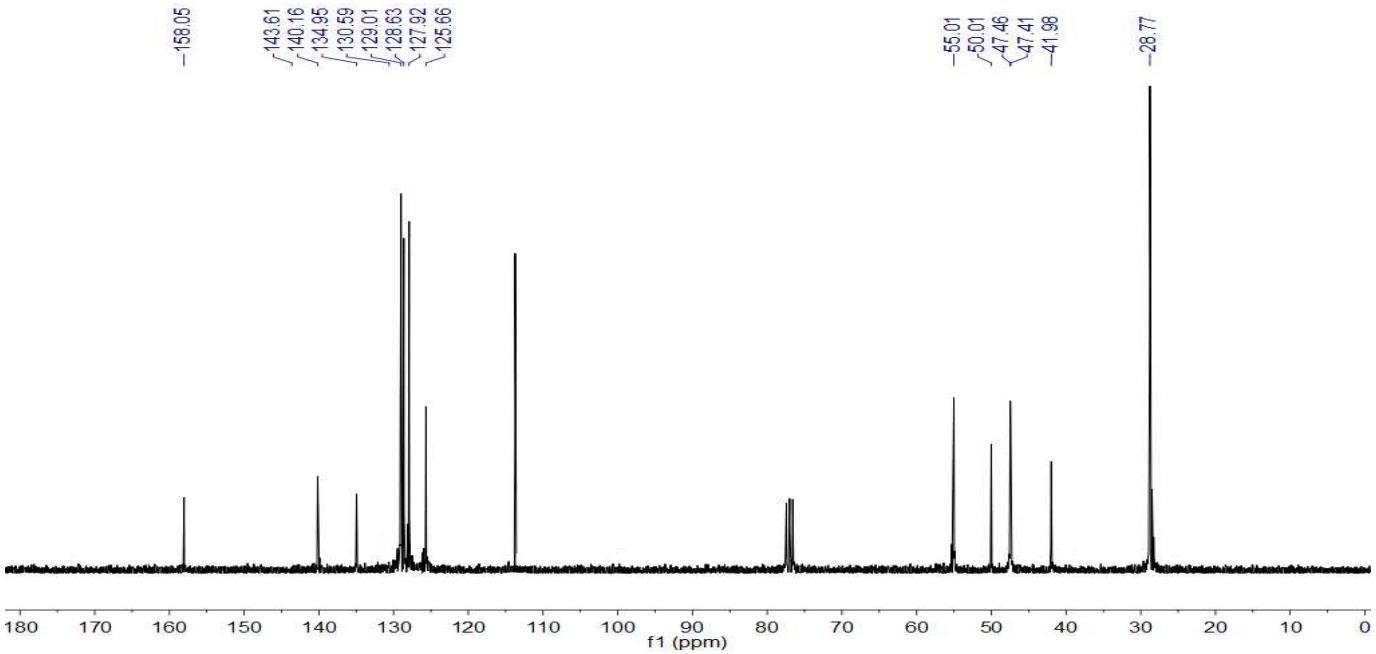
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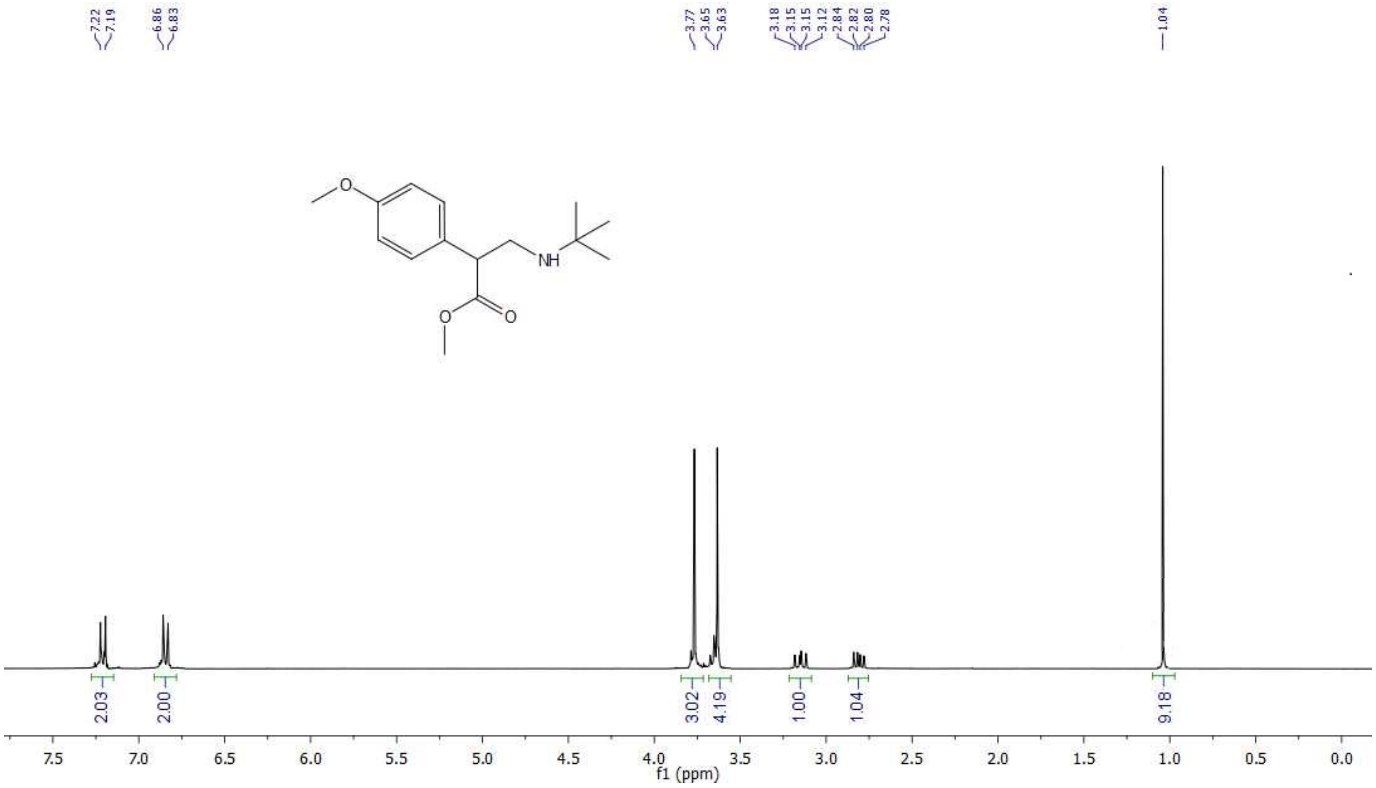
f1 (ppm)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2.80
2.78
1.04
O
NH
O
O
2.03
2.00
3.02
4.19
1.00
1.04
9.18
7.5
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6.5
6.0
5.5
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2.0
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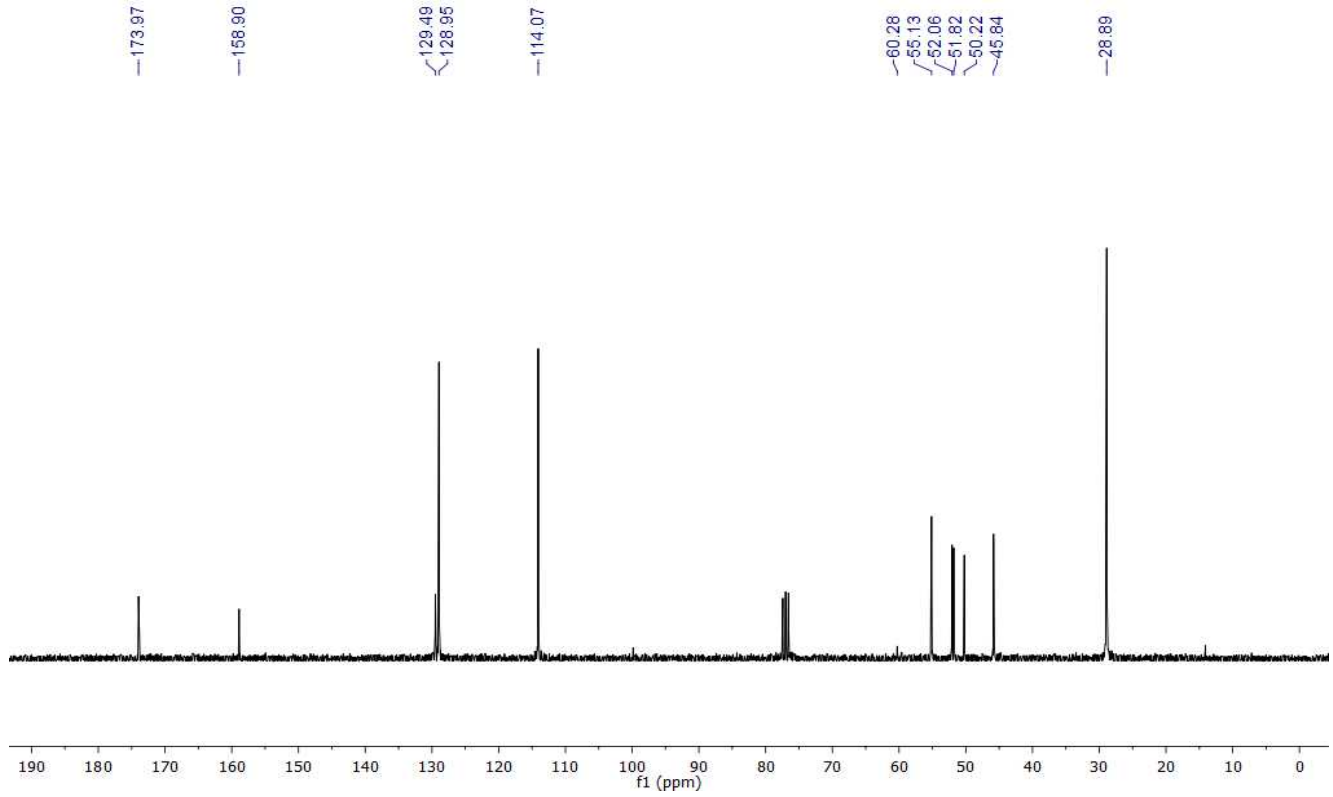
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180
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140
130
120
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90
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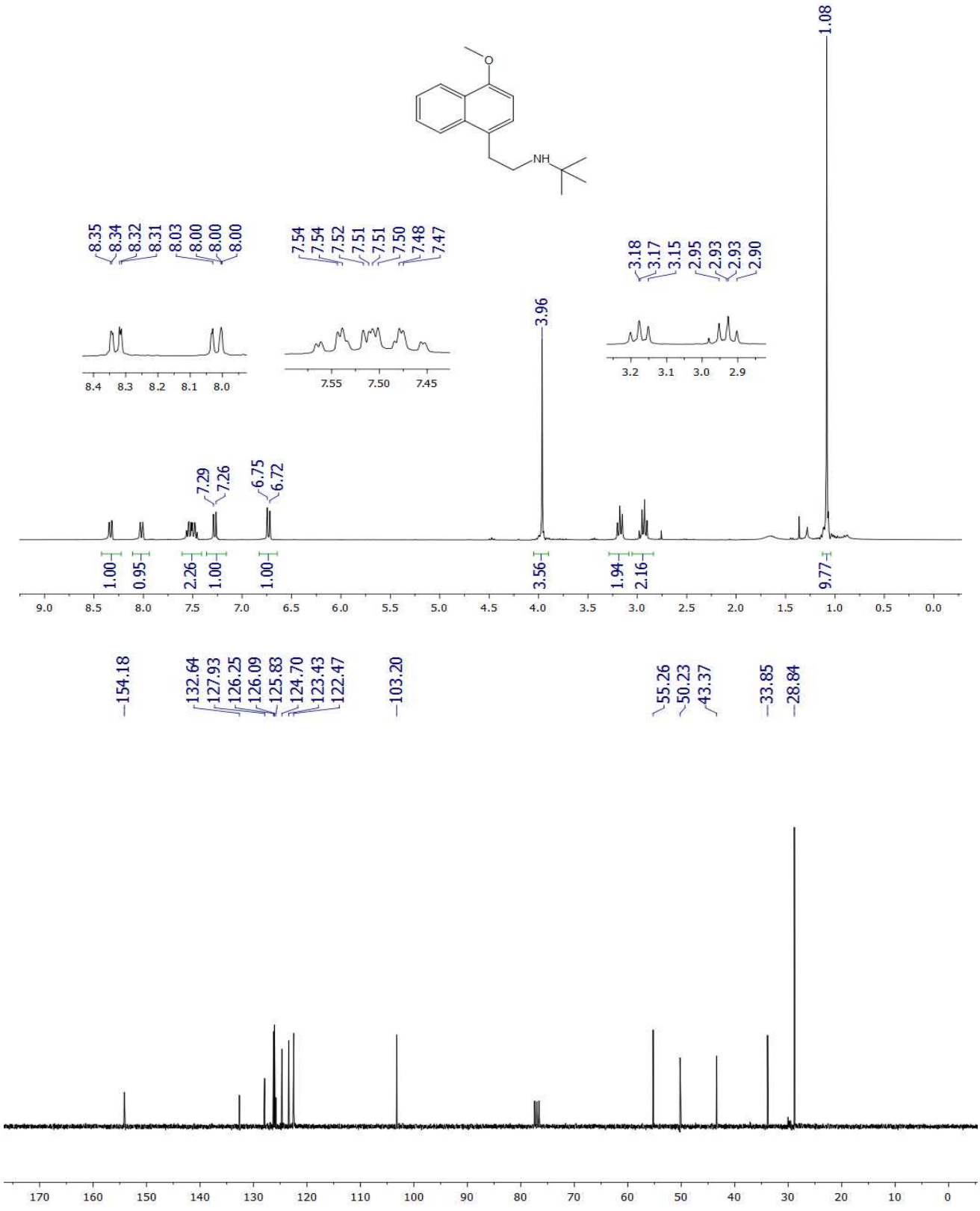
f1 (ppm)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7.51
7.51
7.50
7.48
7.47
3.18
3.17
3.15
2.95
2.93
2.93
2.90
3.96
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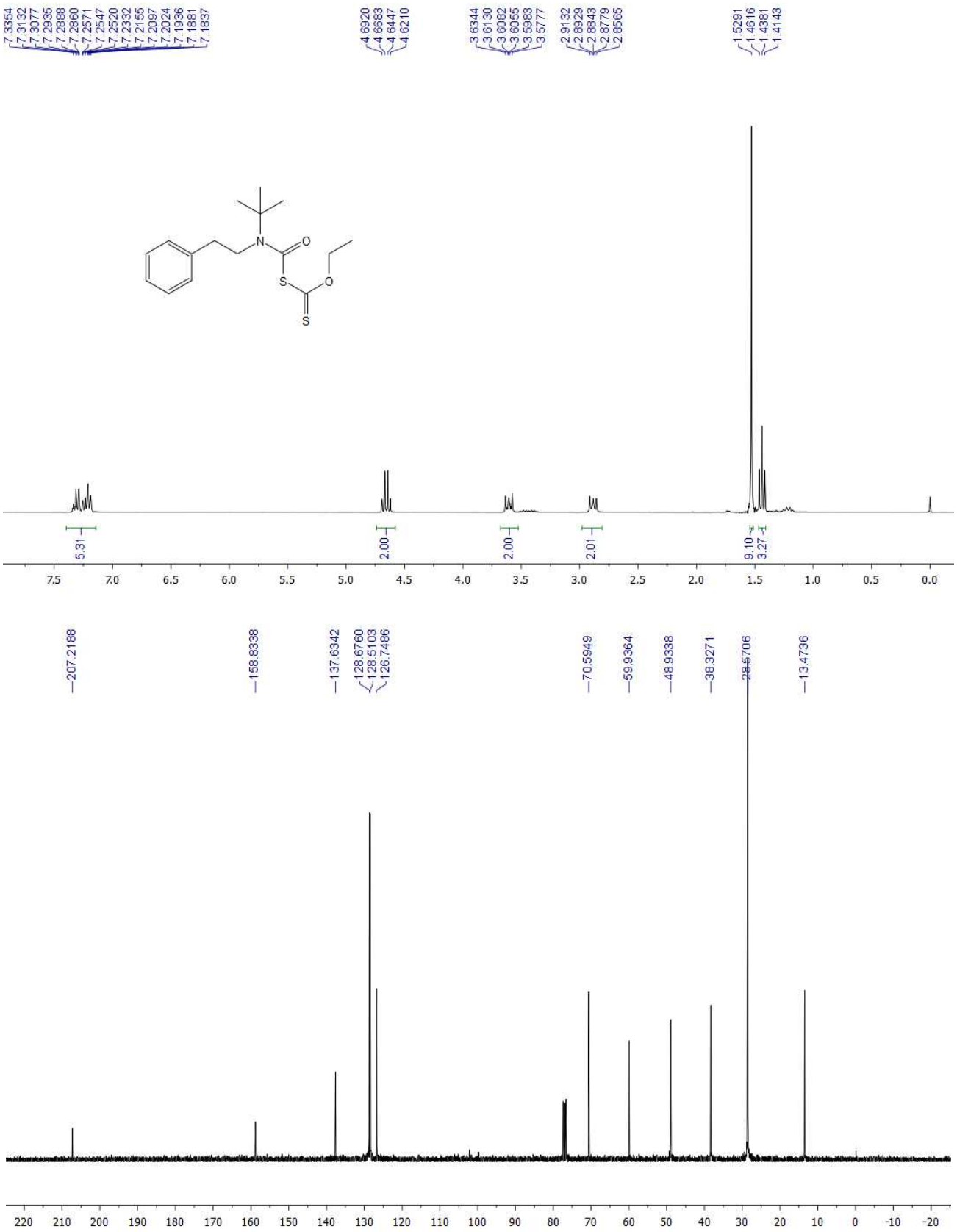
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7.1837
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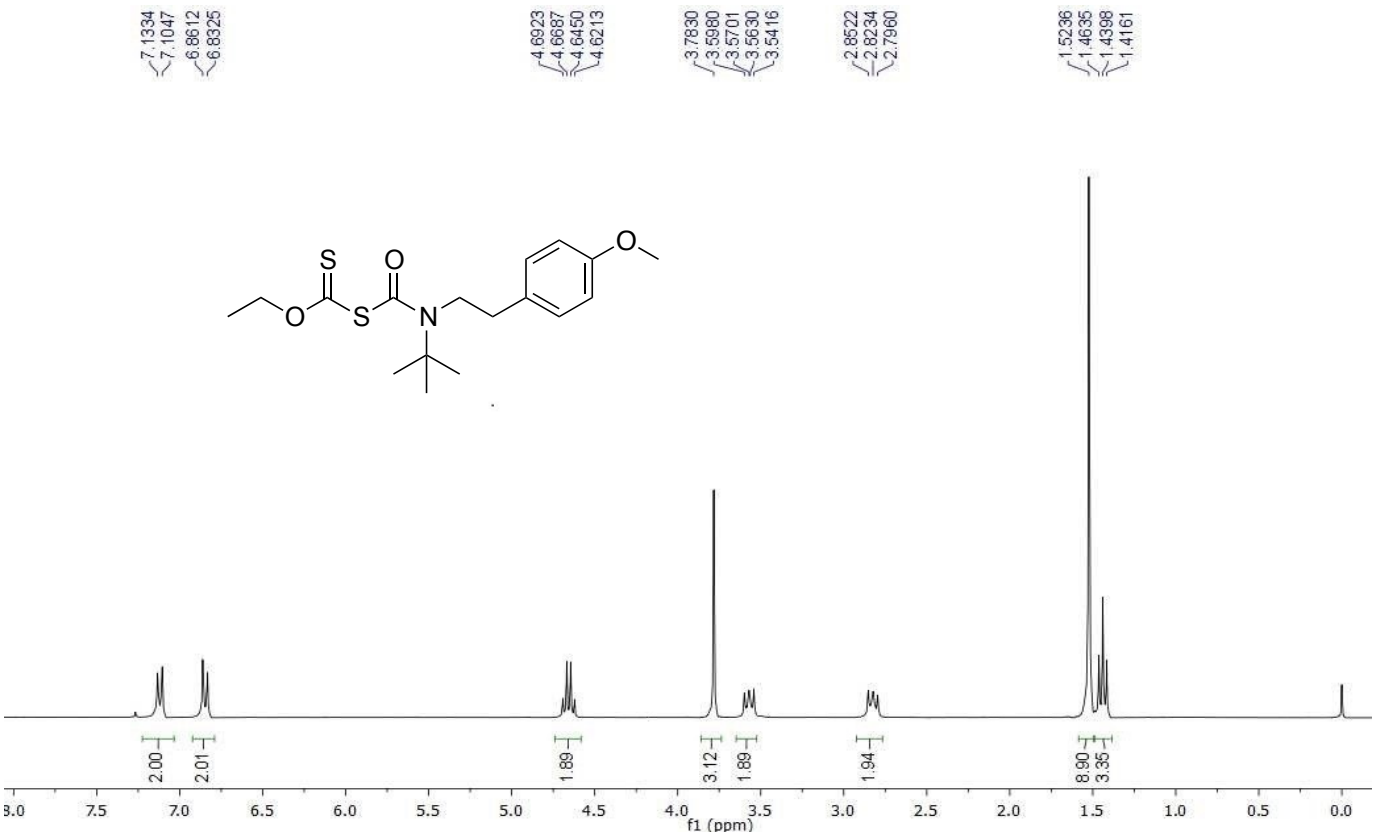
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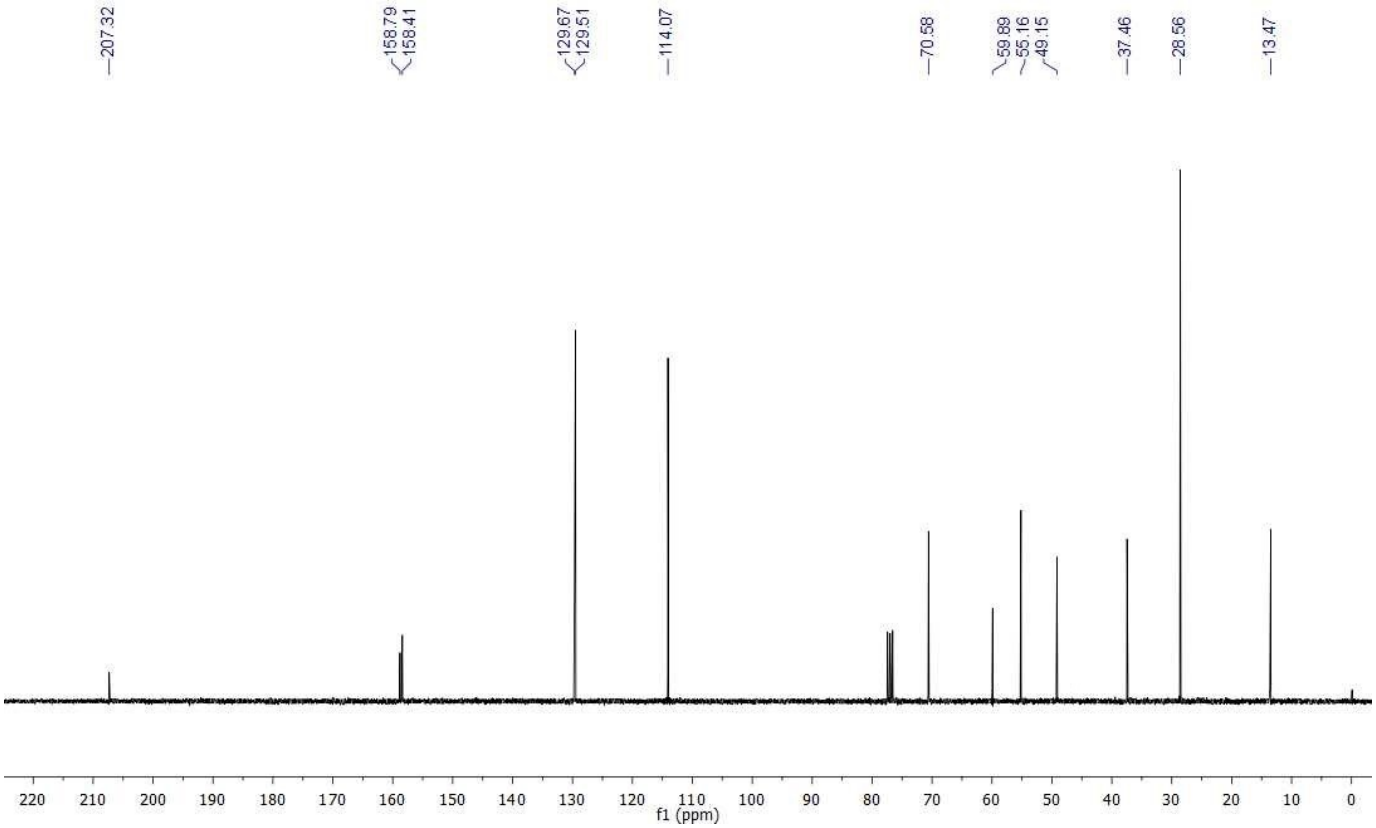
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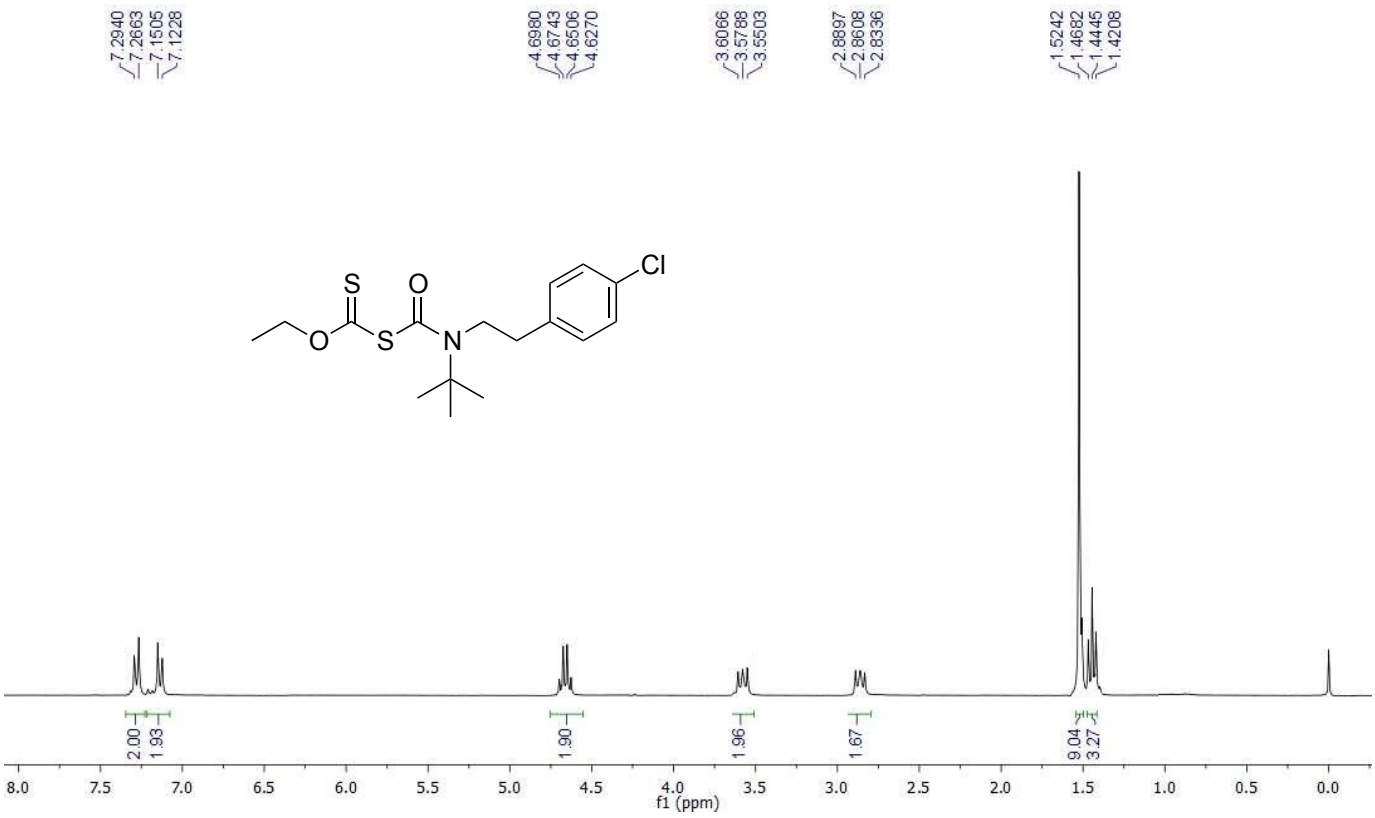
f1 (ppm)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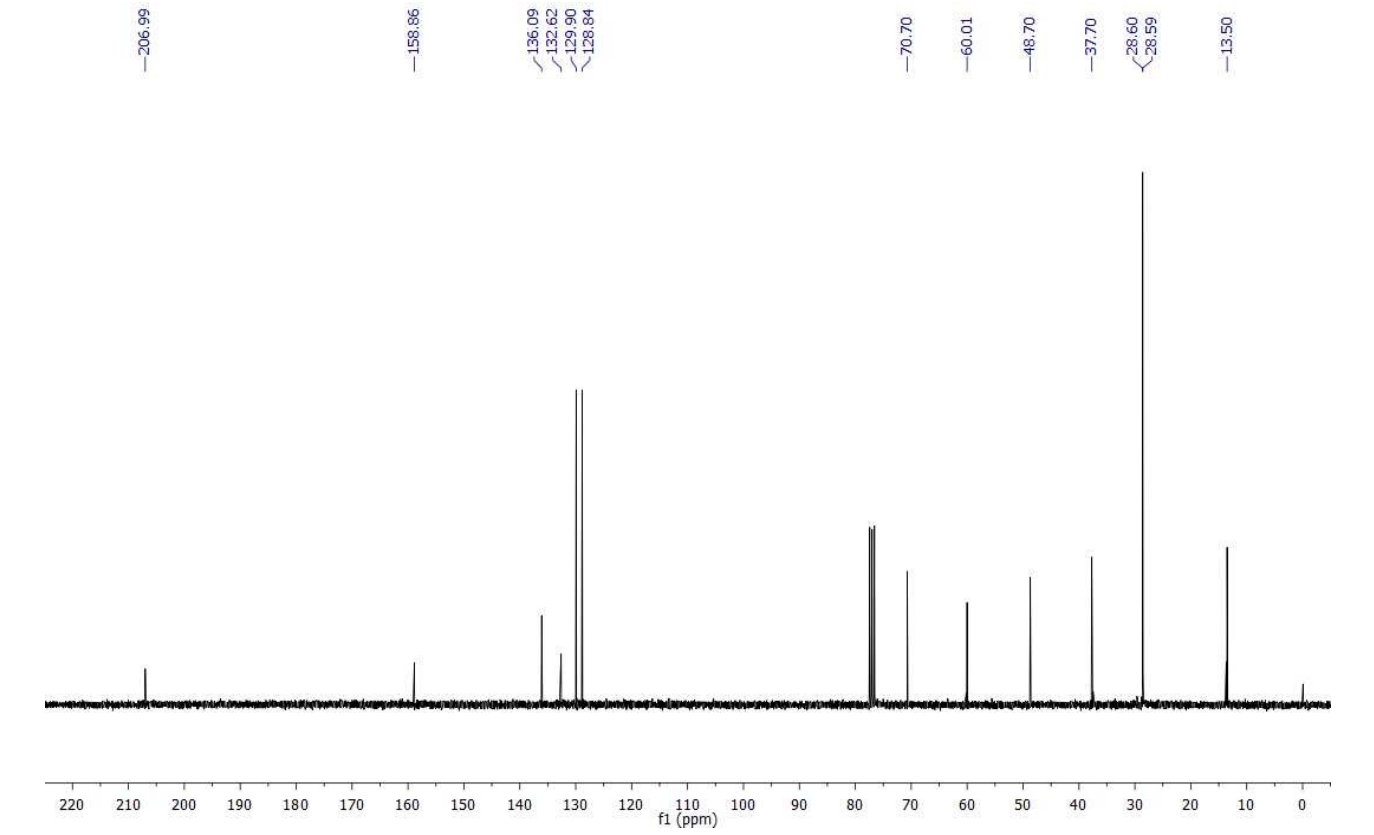
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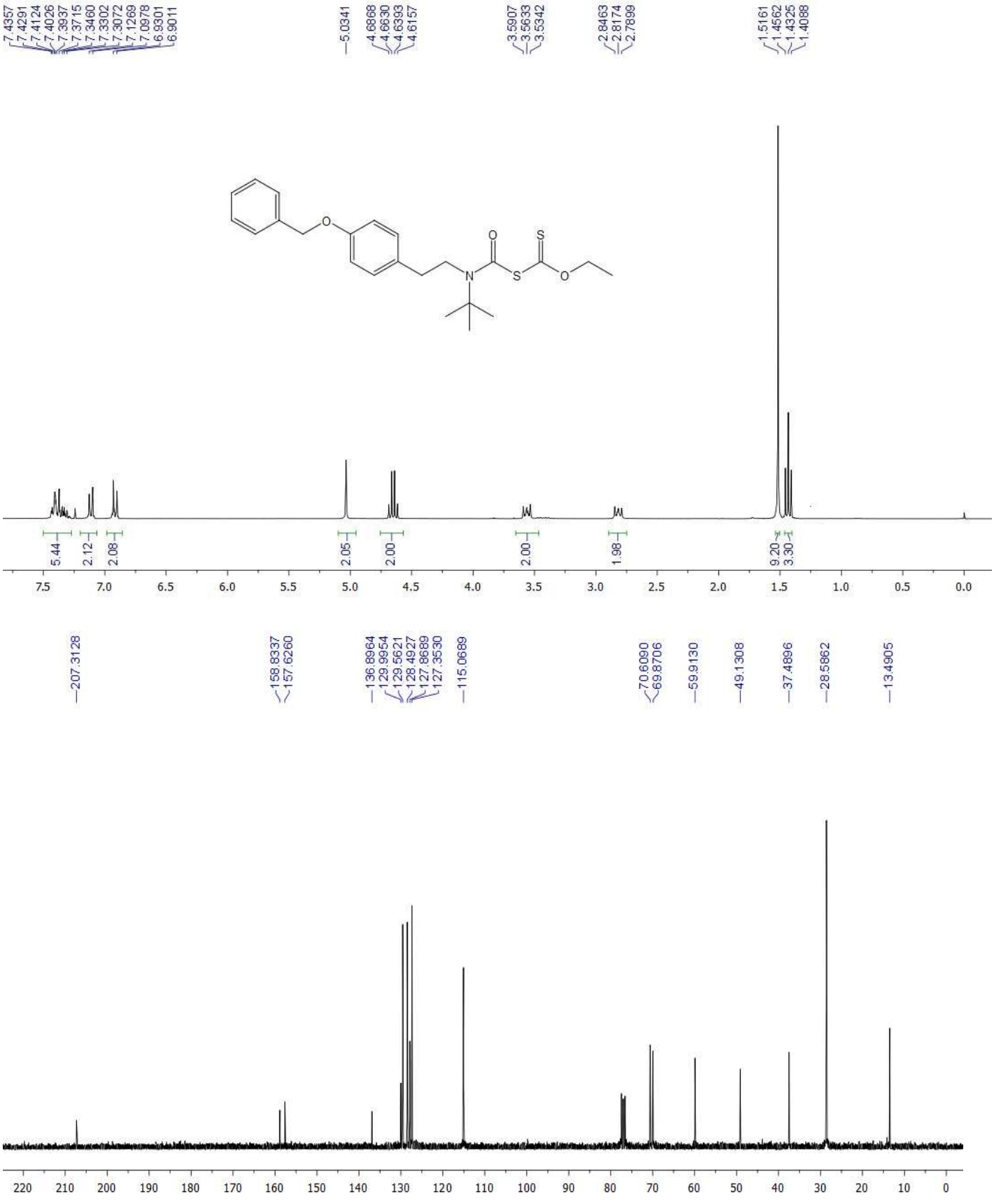
f1 (ppm)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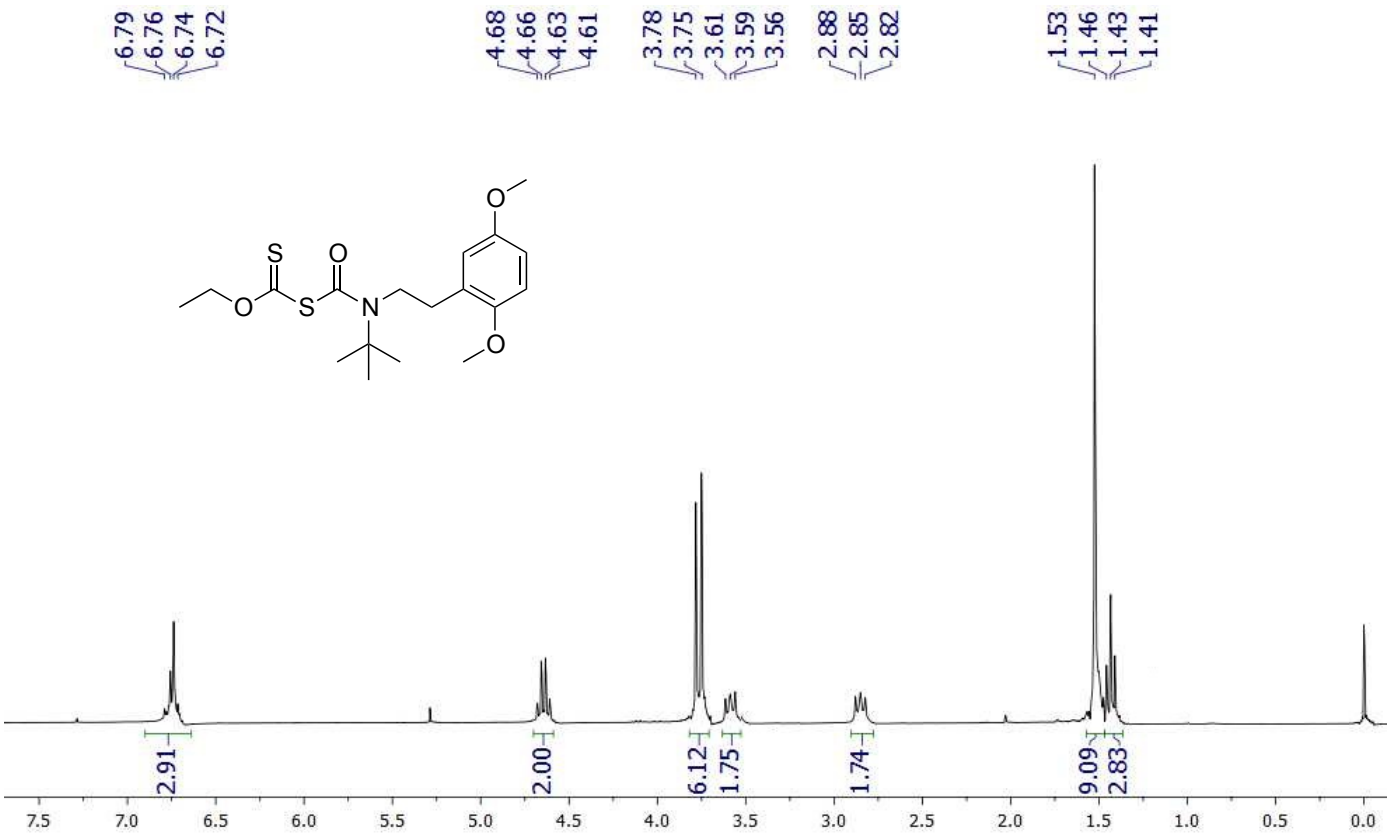
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1.46
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1.41
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O
S
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O
O
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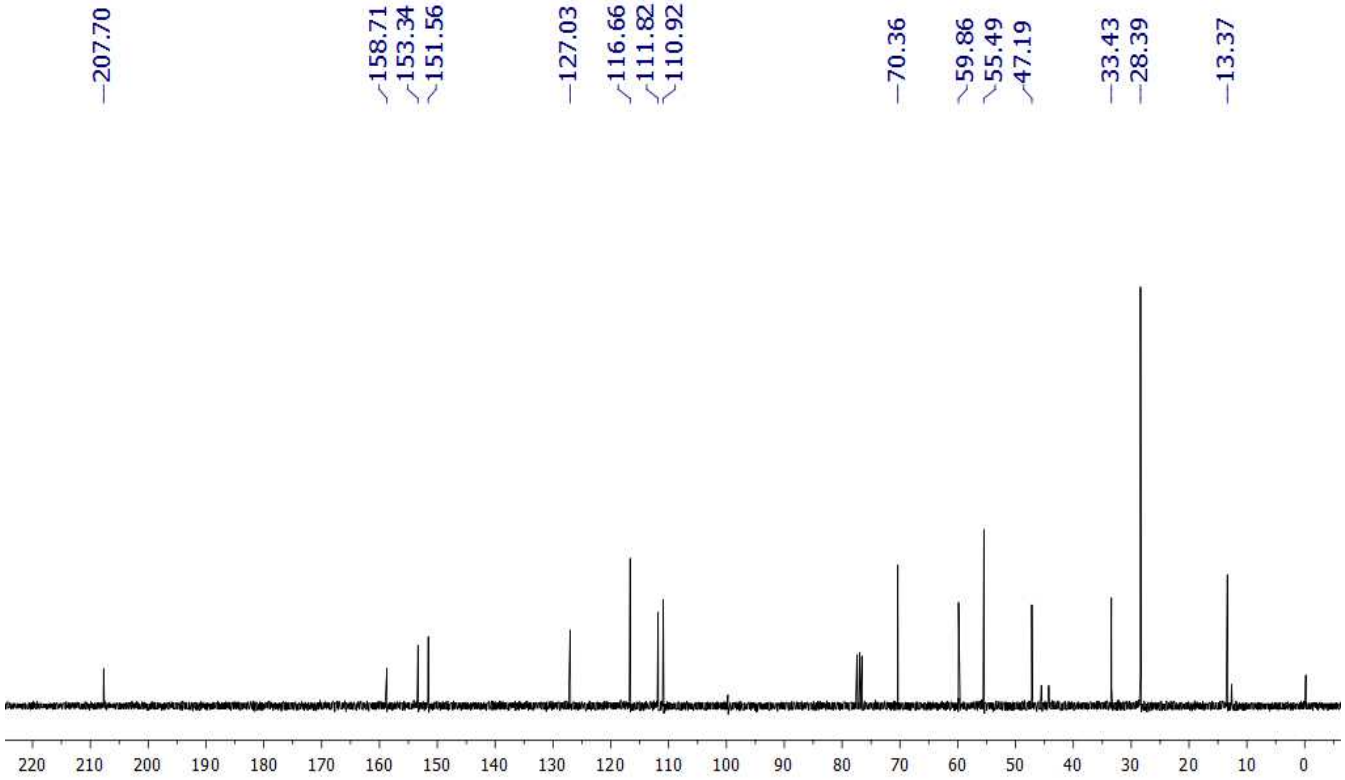
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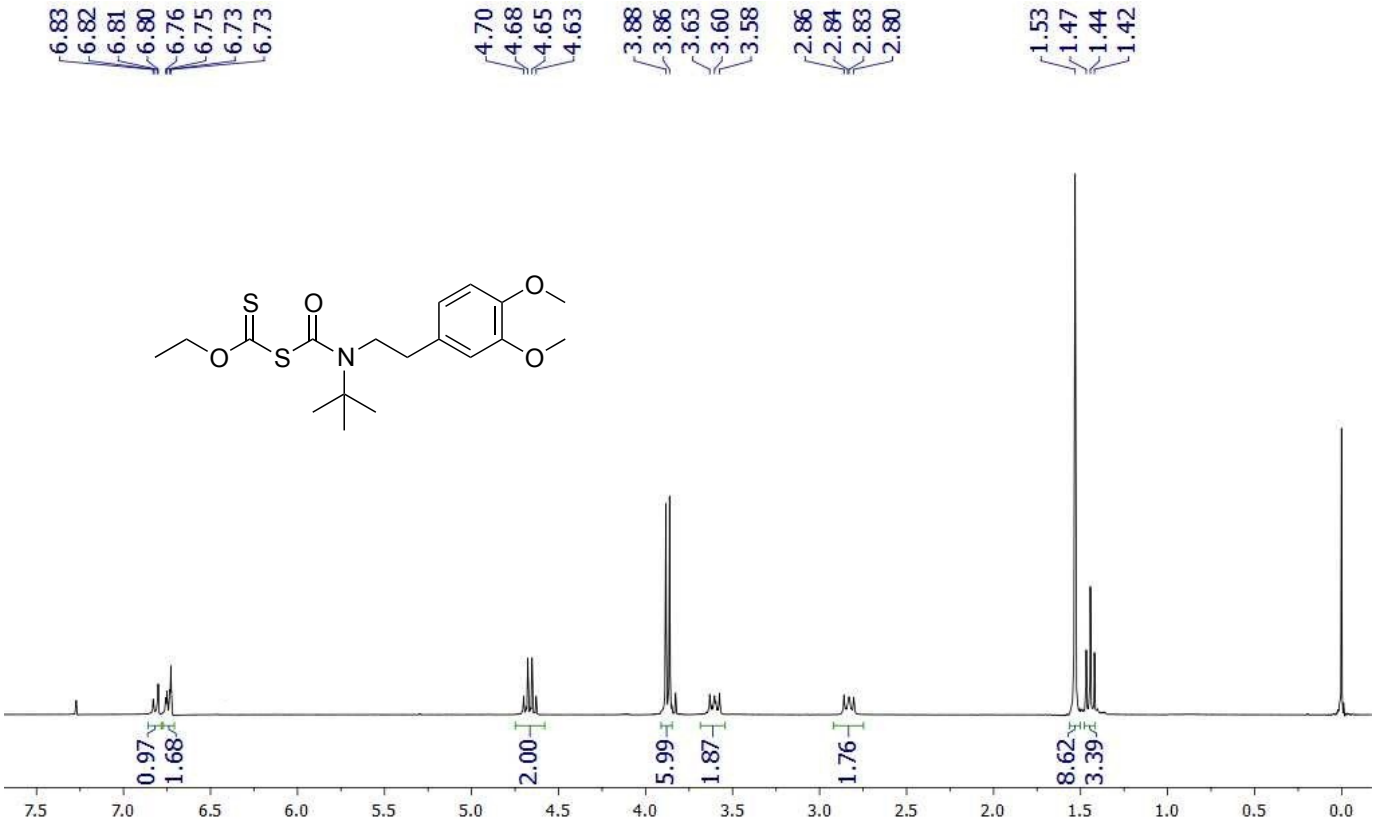
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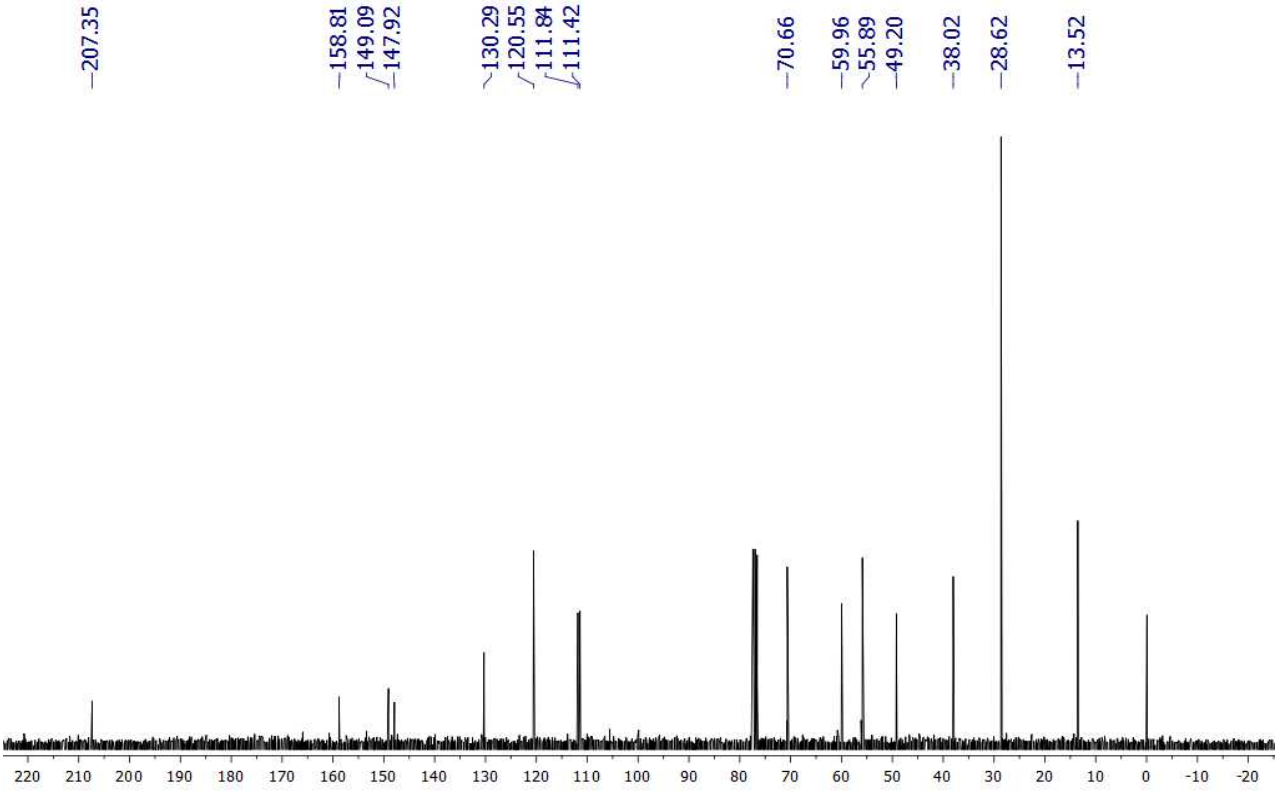
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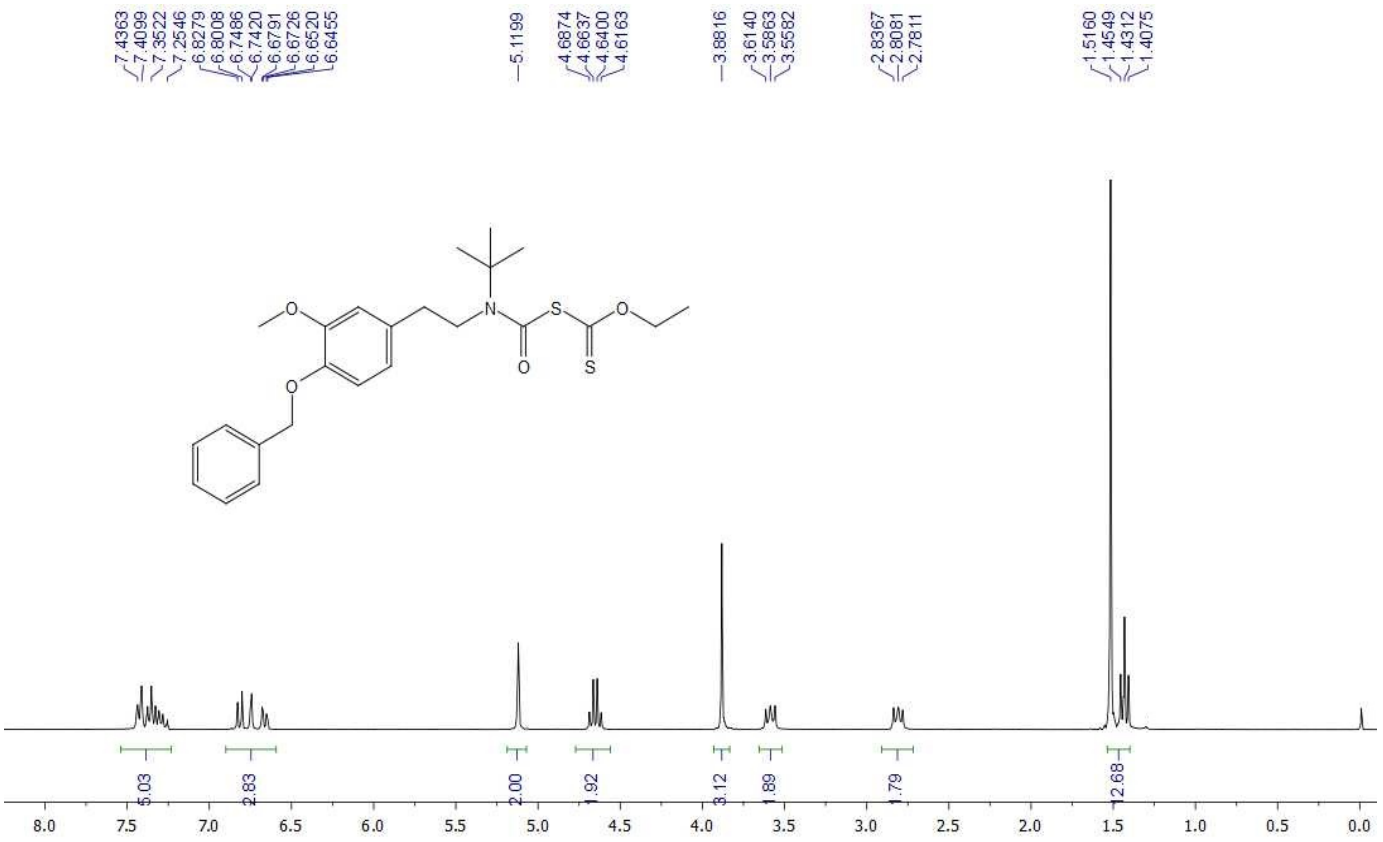
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O
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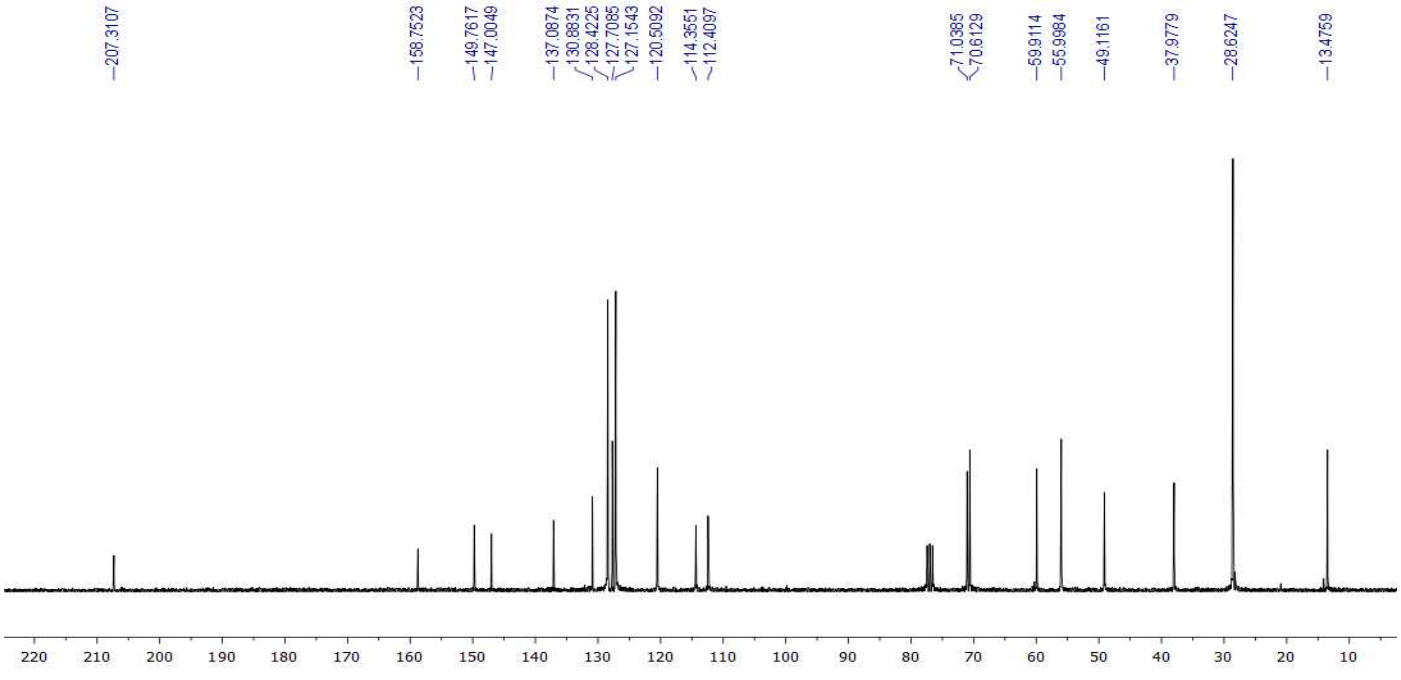
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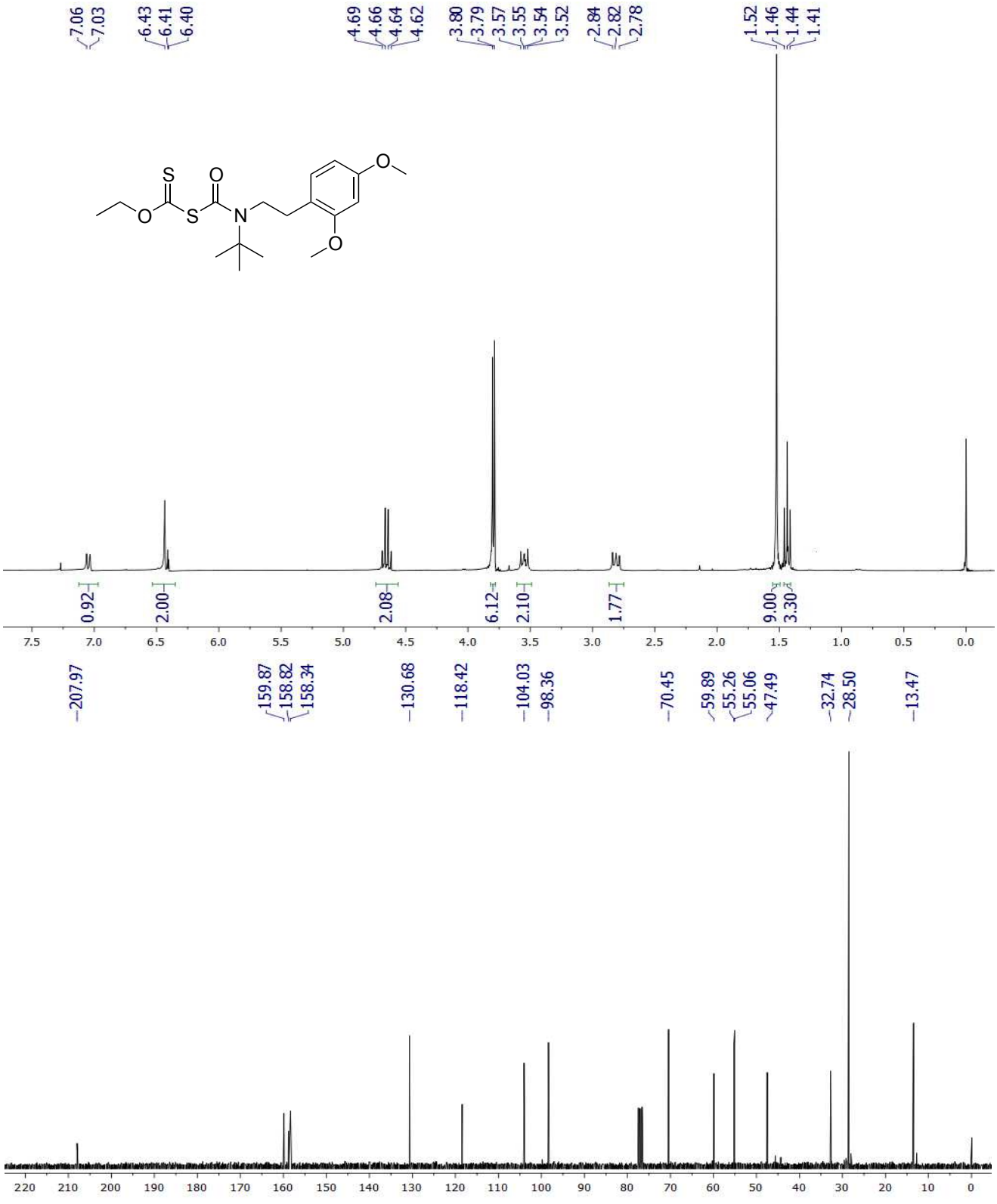
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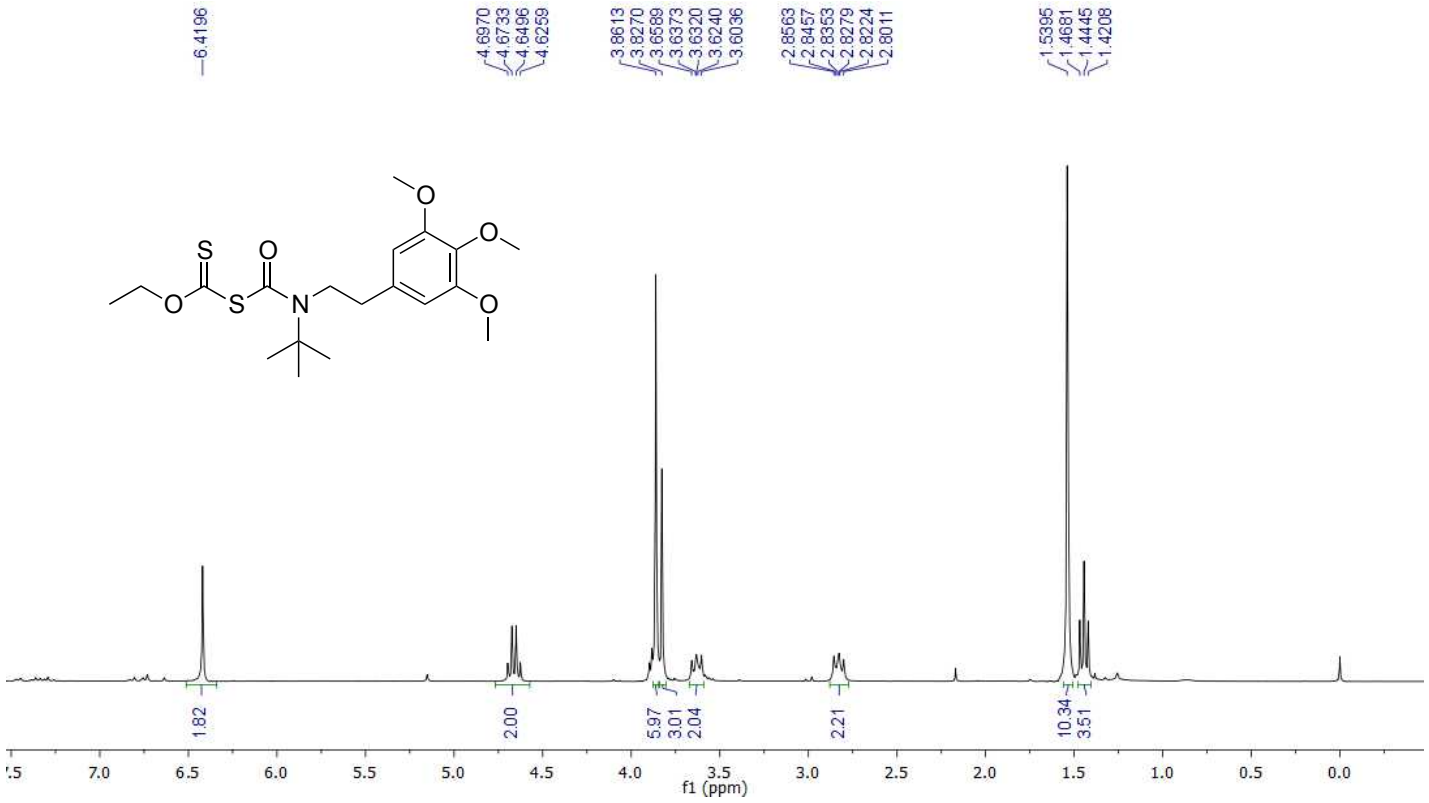
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2.8011
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2.04
2.21
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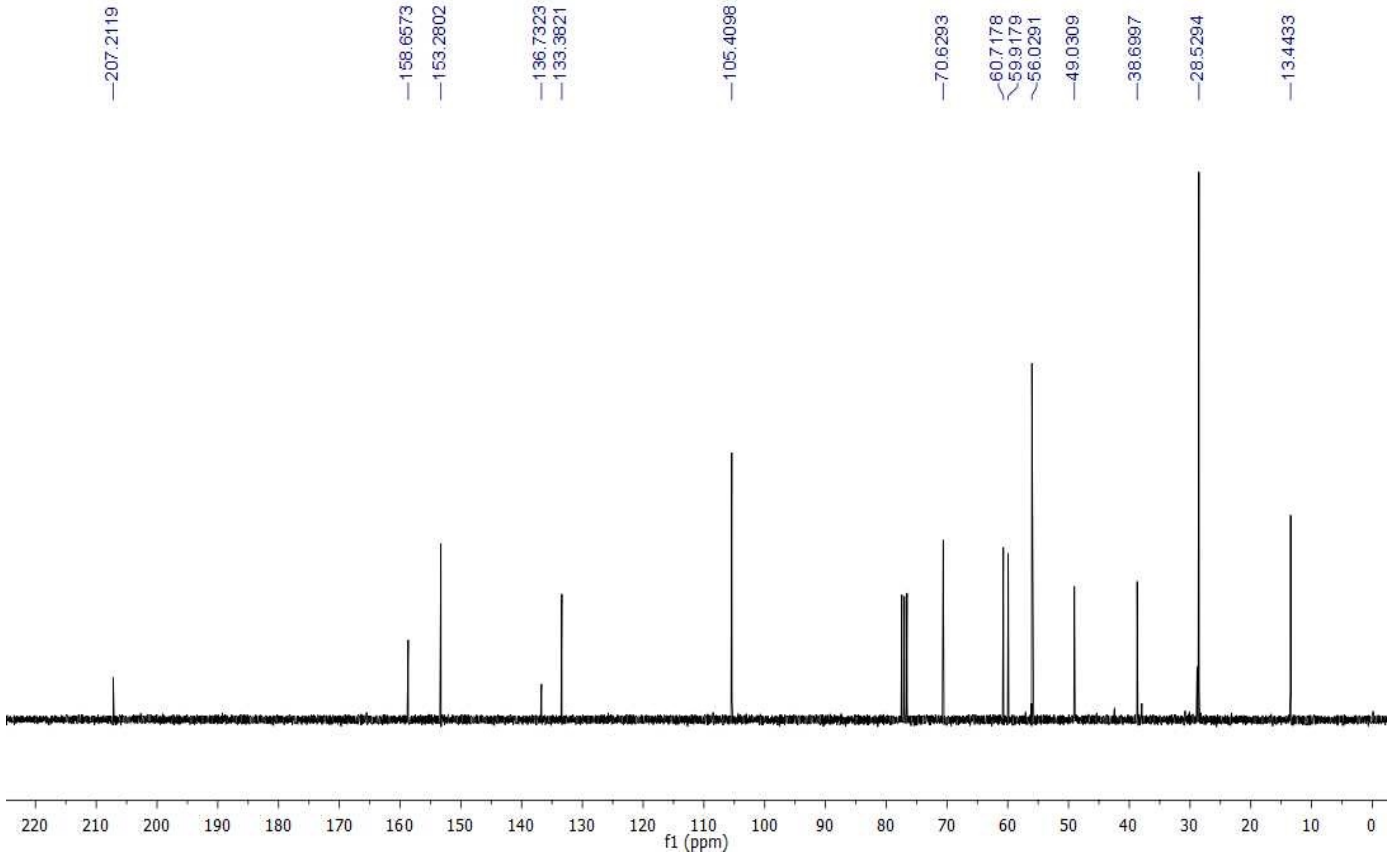
f1 (ppm)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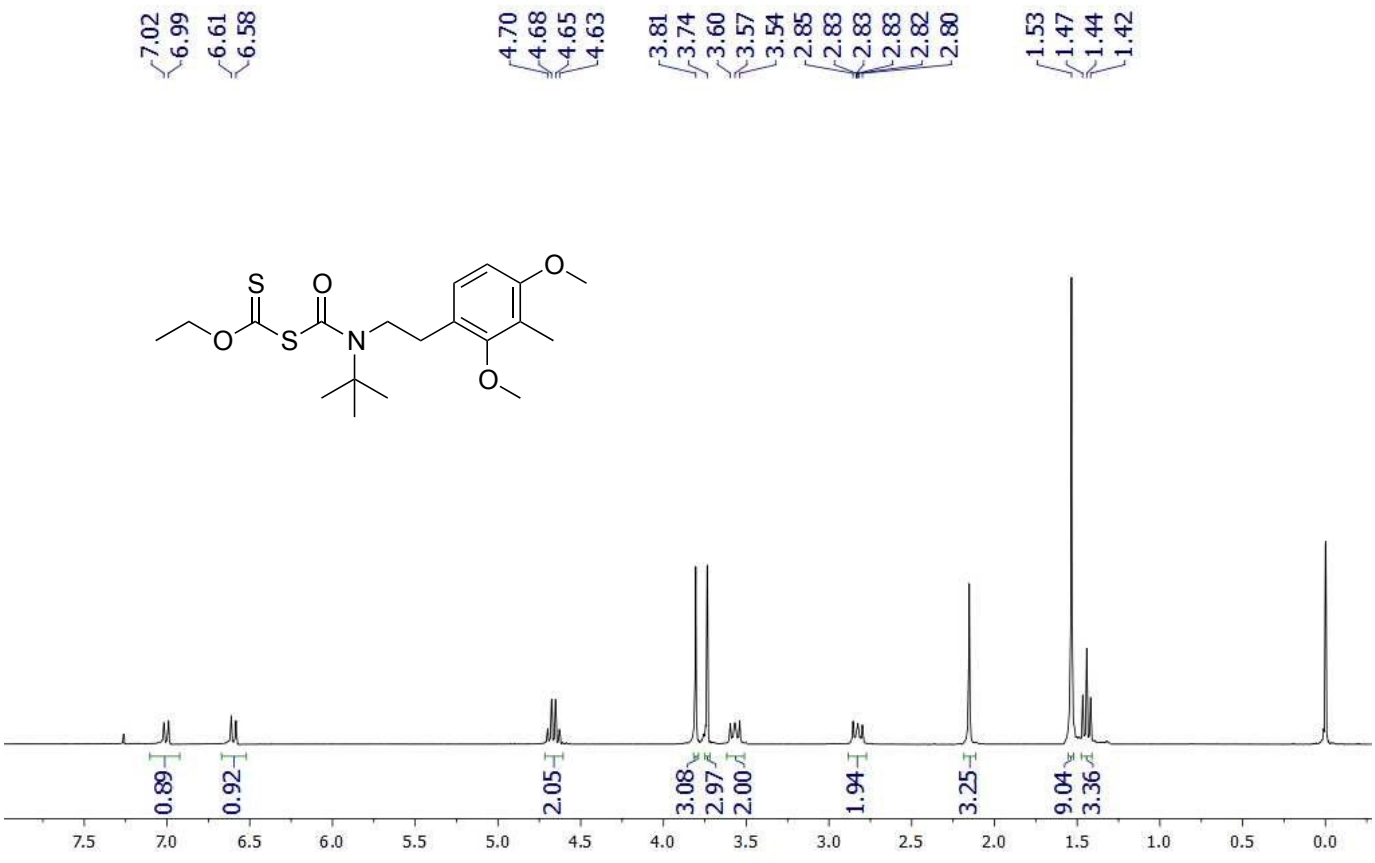
f1 (ppm)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3.54
2.85
2.83
2.83
2.83
2.82
2.80
1.53
1.47
1.44
1.42
S
O
O
S
N
O
O
0.89
0.92
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3.08
2.97
2.00
1.94
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9.04
3.36
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6.0
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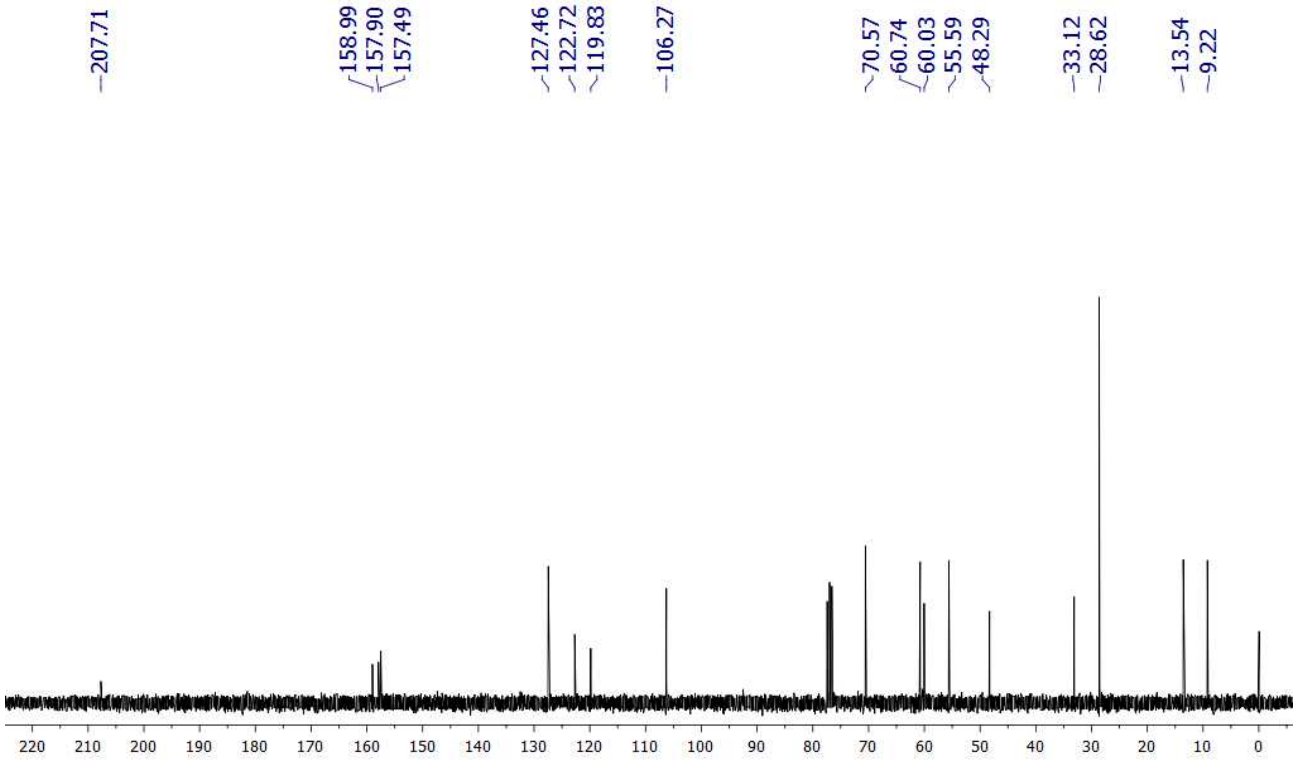
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55.59
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9.22
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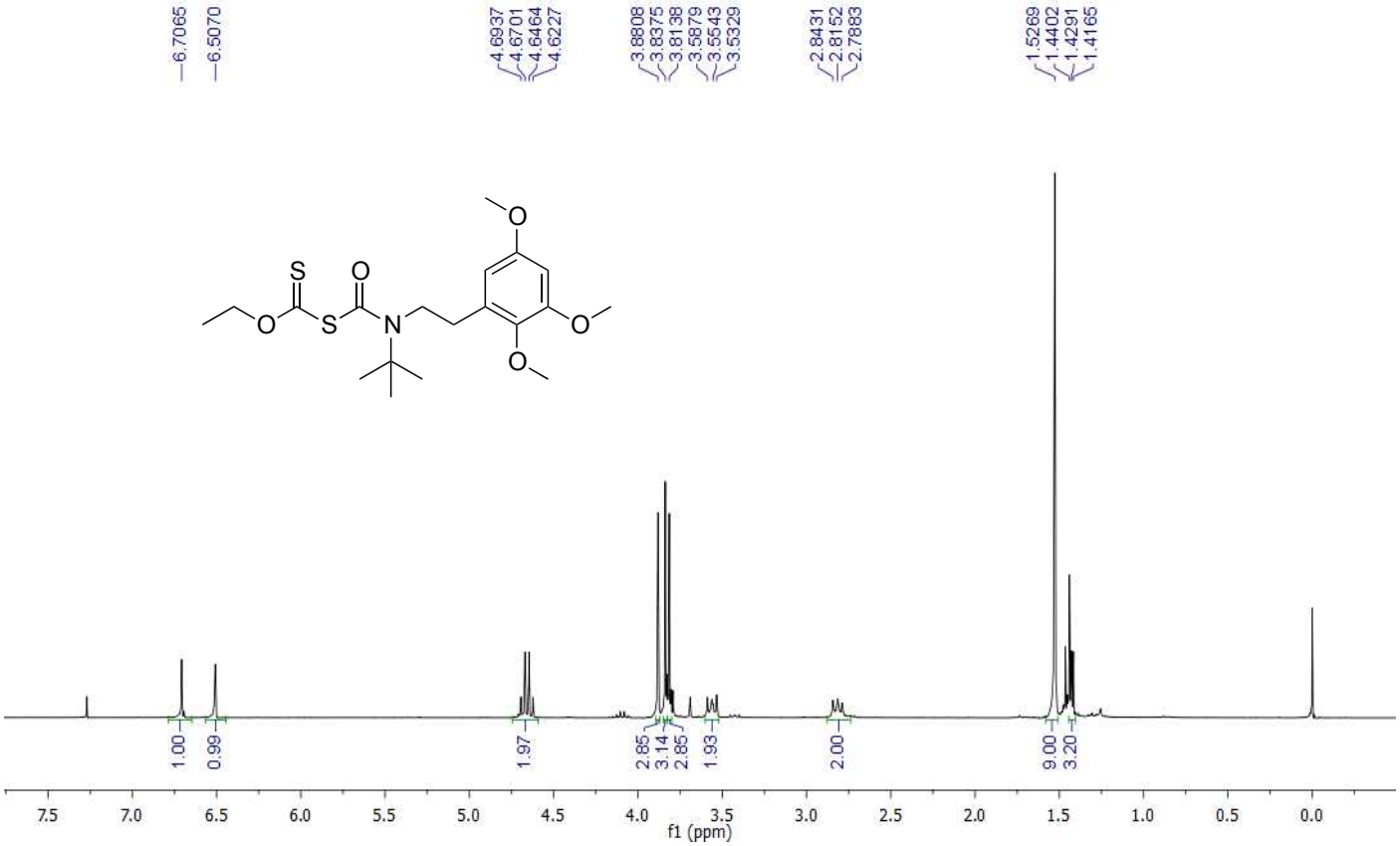
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3.5543
3.5329
2.8431
2.8152
2.7883
1.5269
1.4402
1.4291
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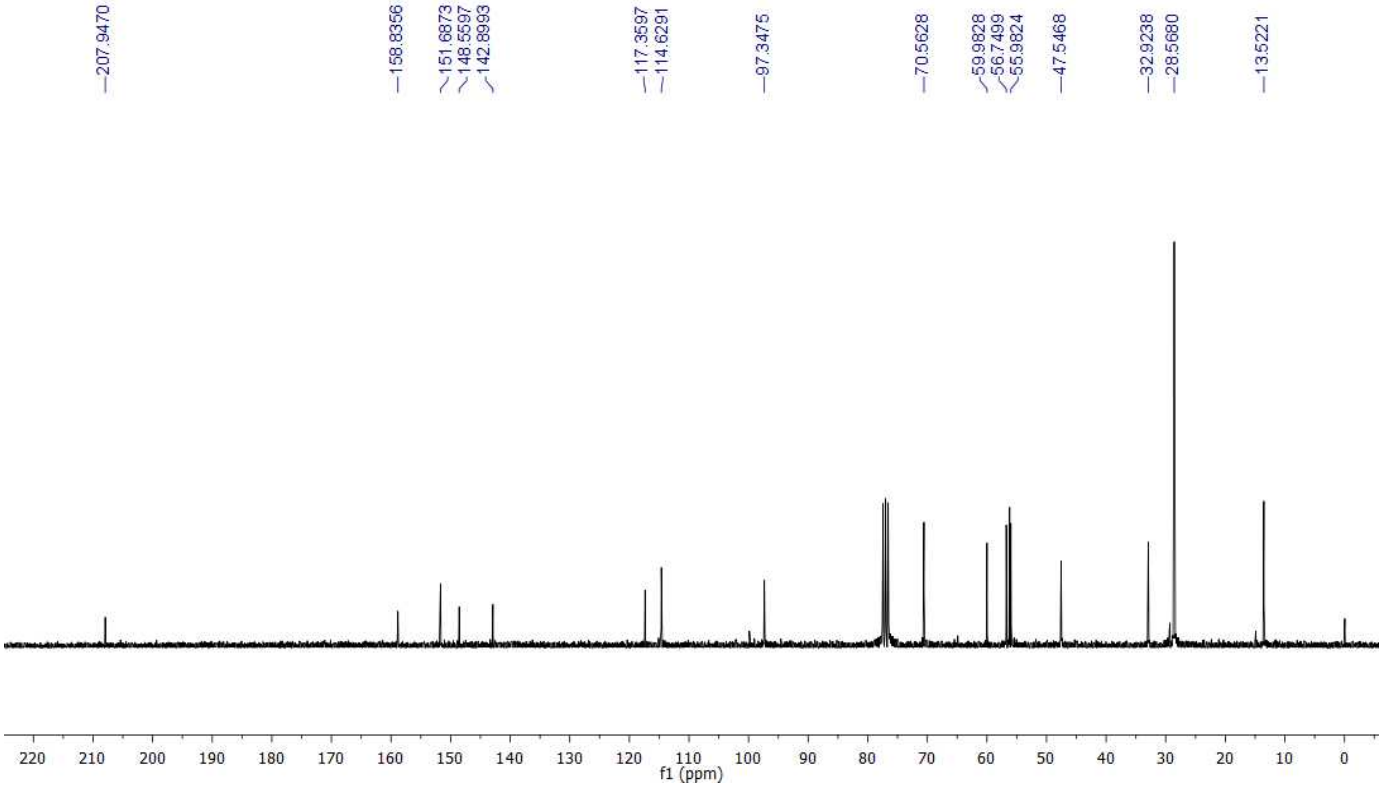
1.93
2.00
9.00
3.20
f1 (ppm)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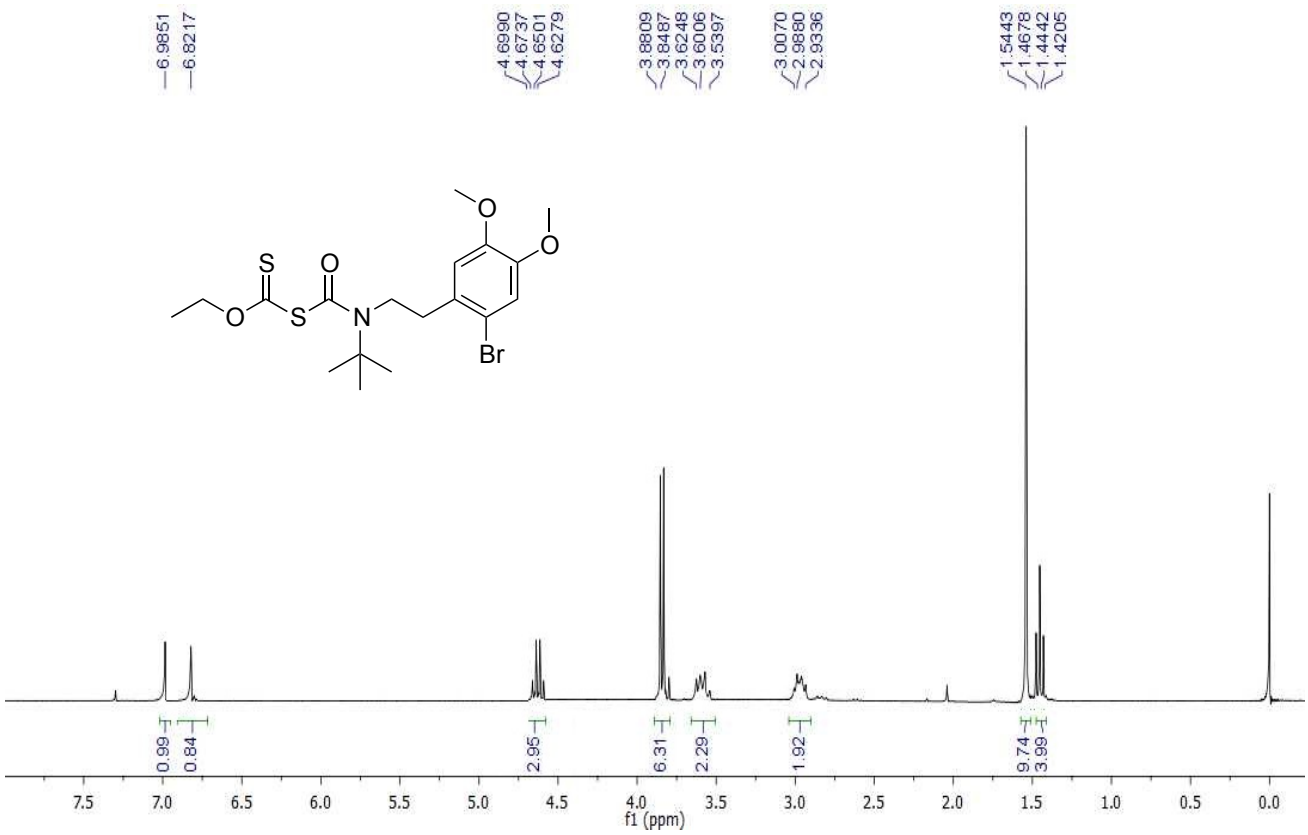
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3.0070
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2.9336
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1.4678
1.4442
1.4205
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O
S
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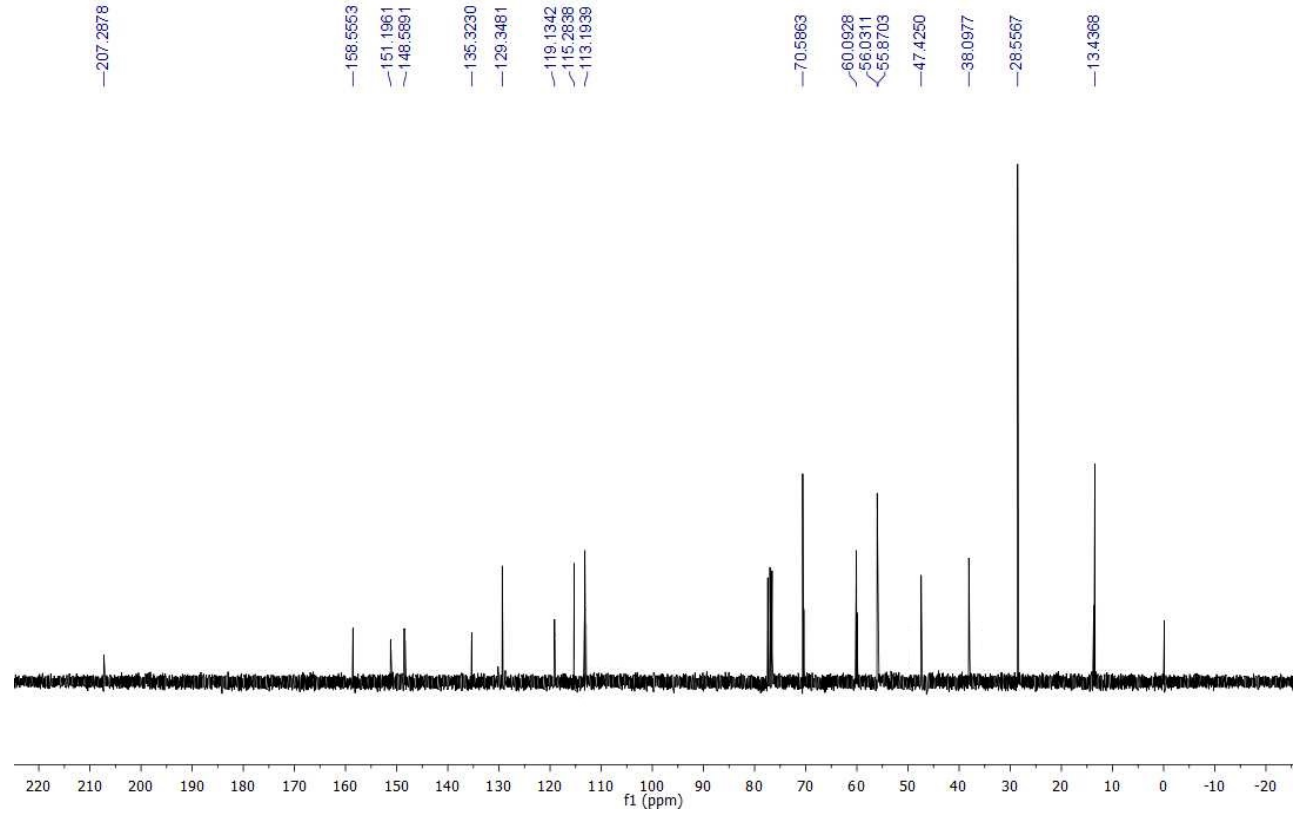
0.84
2.95
6.31
2.29
1.92
9.74
3.99
f1 (ppm)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38.0977
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13.4368
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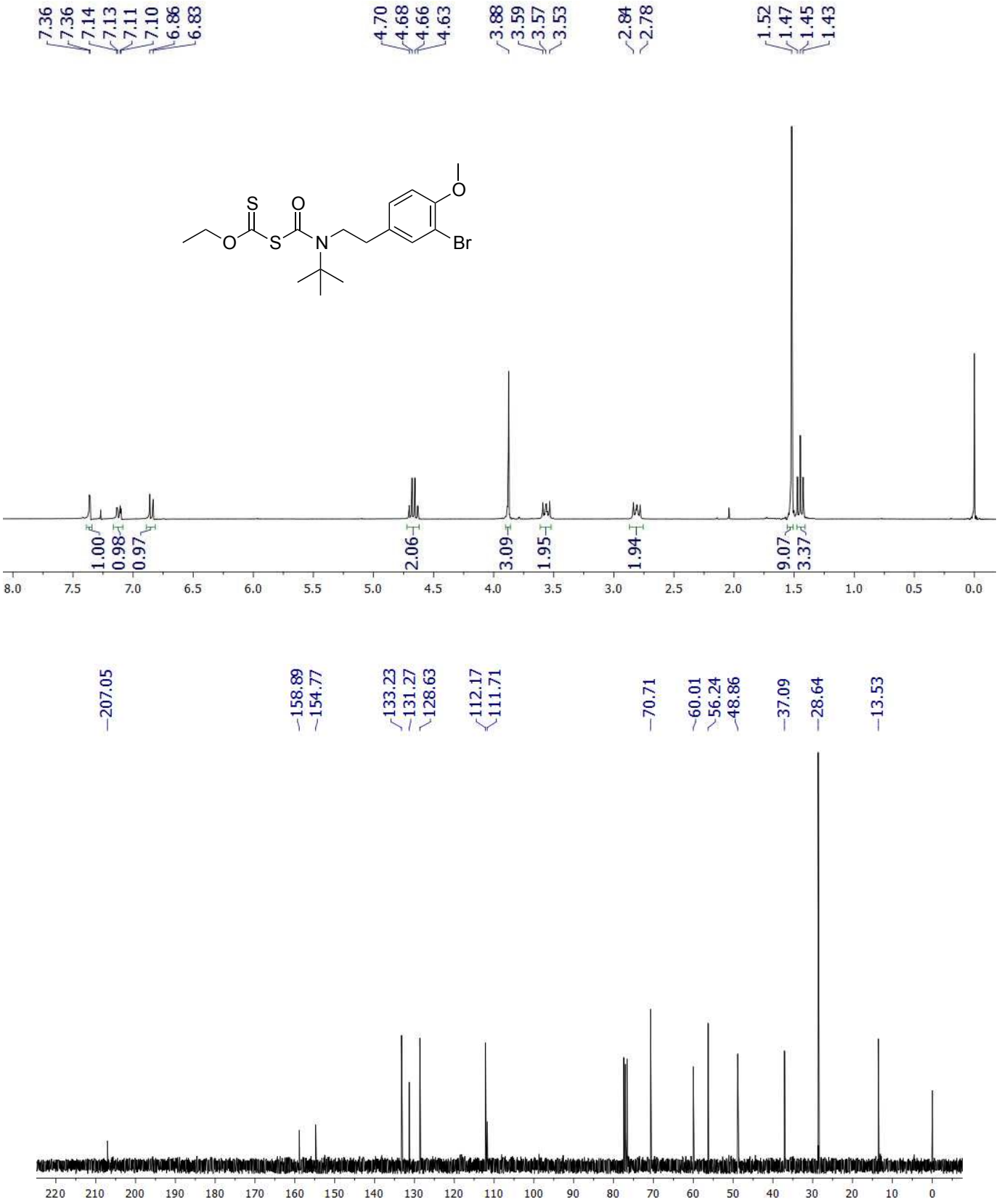
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4.63
3.88
3.59
3.57
3.53
2.84
2.78
1.52
1.47
1.45
1.43
S
O
O
S
N
Br
1.00
0.98
0.97
2.06
3.09
1.95
1.94
9.07
3.37
207.05
158.89
154.77
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56.24
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37.09
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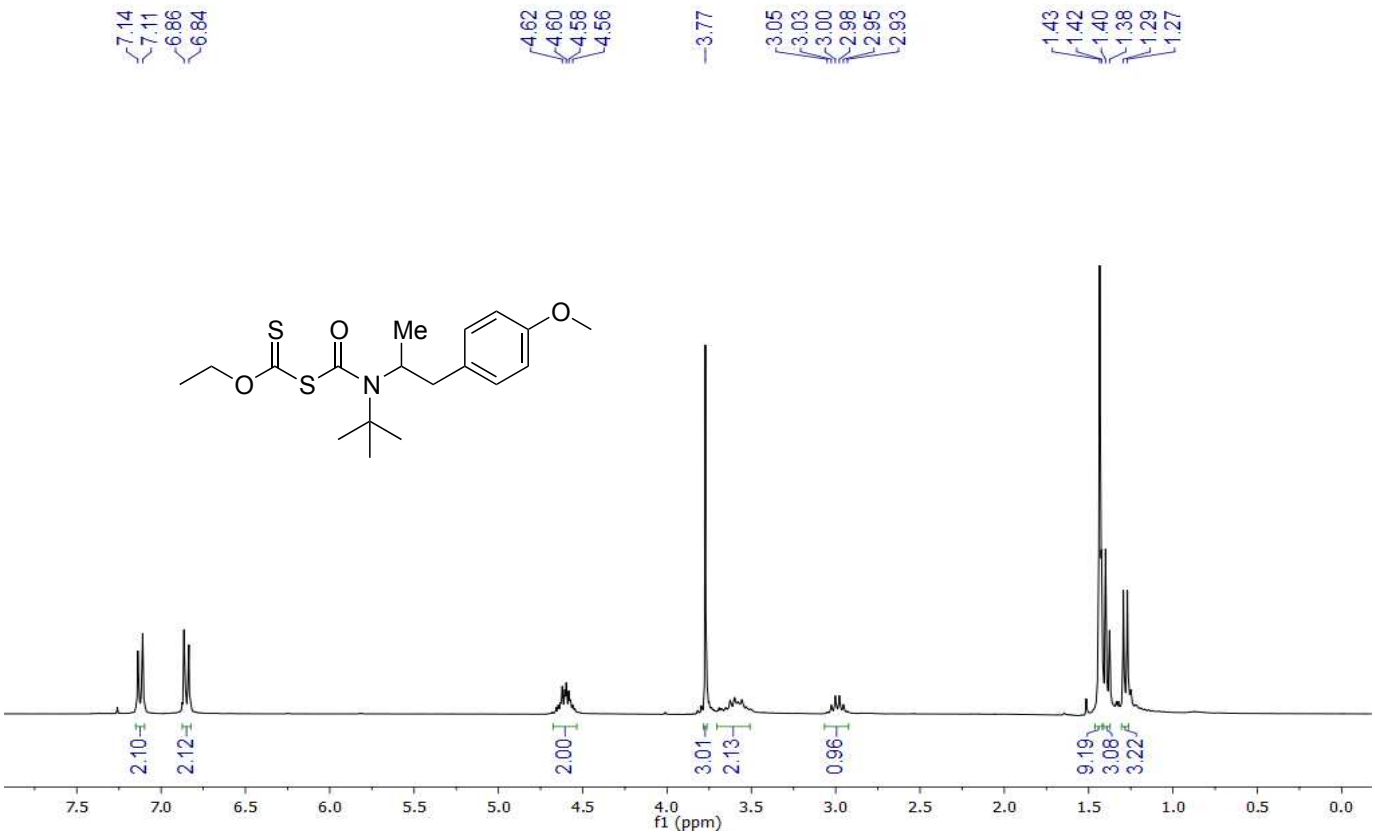
13.53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4.56
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3.05
3.03
3.00
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2.93
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1.42
1.40
1.38
1.29
1.27
S
O
Me
O
O
S
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2.12
2.00
3.01
2.13
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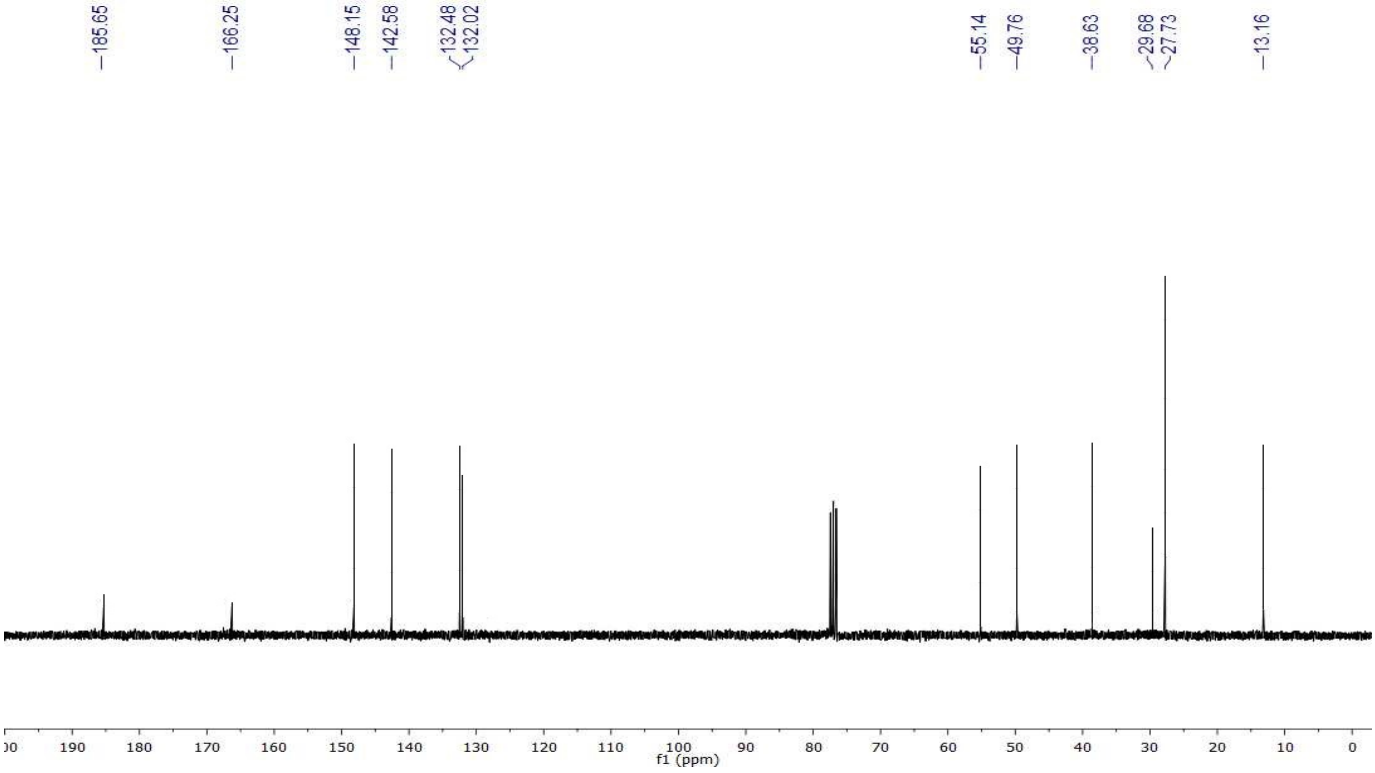
9.19
3.08
3.22
f1 (ppm)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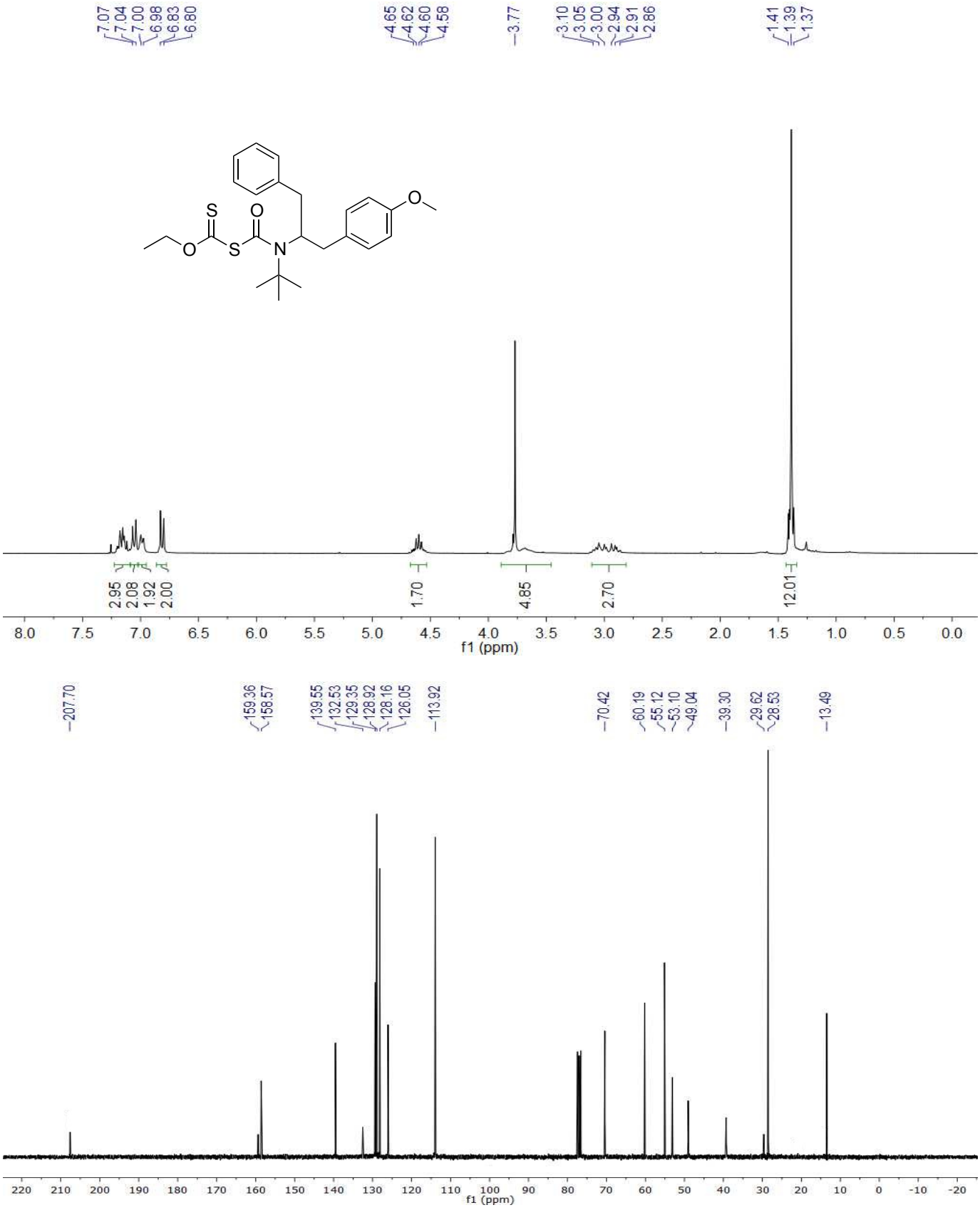
132.02
55.14
49.76
38.63
29.68
27.73
13.16
f1 (ppm)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6.83
6.80
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4.62
4.60
4.58
3.77
3.10
3.05
3.00
2.94
2.91
2.86
1.41
1.39
1.37
S
O
O
S
N
O
2.95
2.08
1.92
2.00
1.70
4.85
2.70
12.01
f1 (ppm)
207.70
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158.57
139.55
132.53
129.35
128.92
128.16
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113.92
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60.19
55.12
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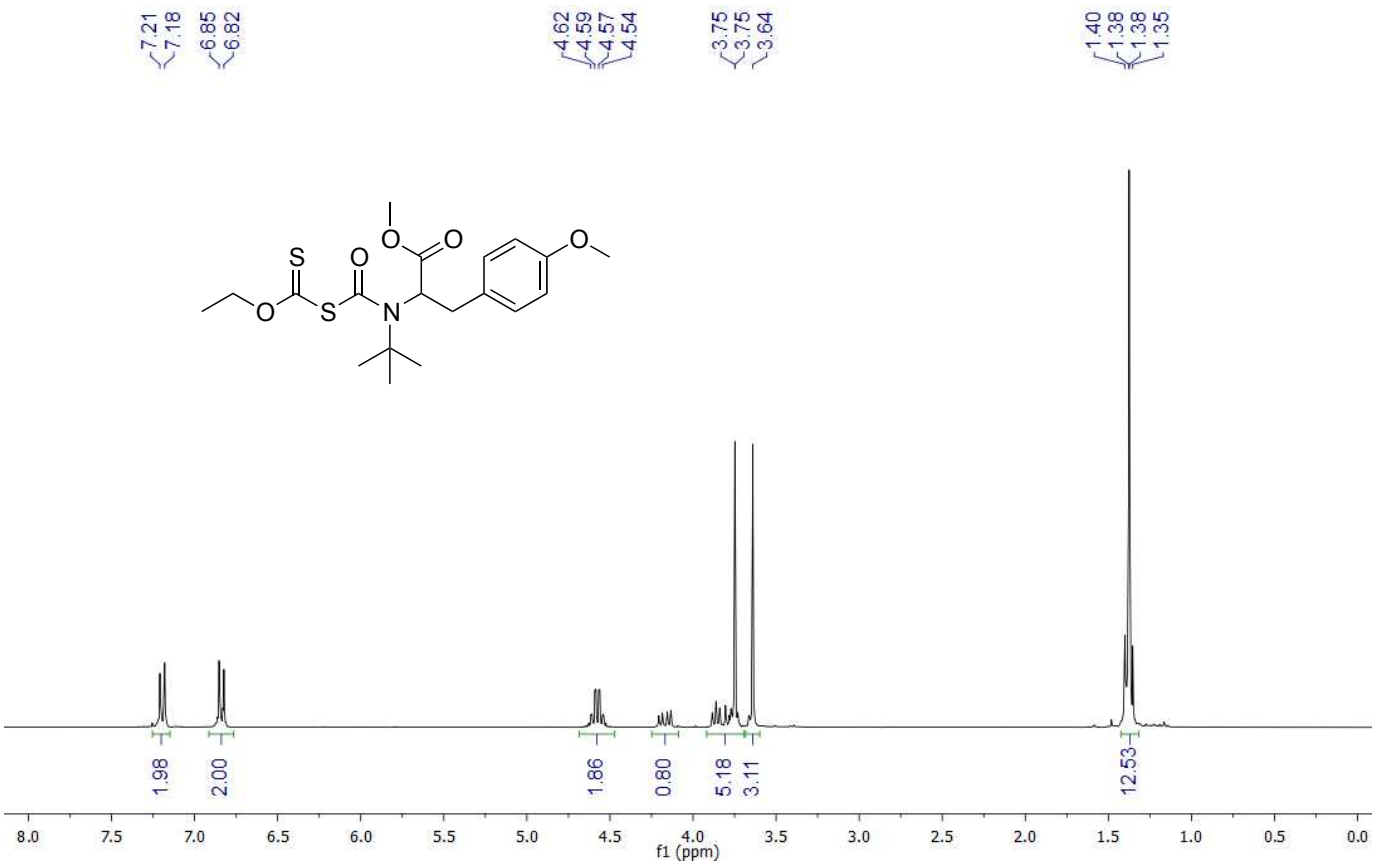
28.53
13.49
f1 (ppm)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4.54
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3.75
3.64
1.40
1.38
1.38
1.35
S
O
O
O
O
S
N
O
1.98
2.00
1.86
0.80
5.18
3.11
12.53
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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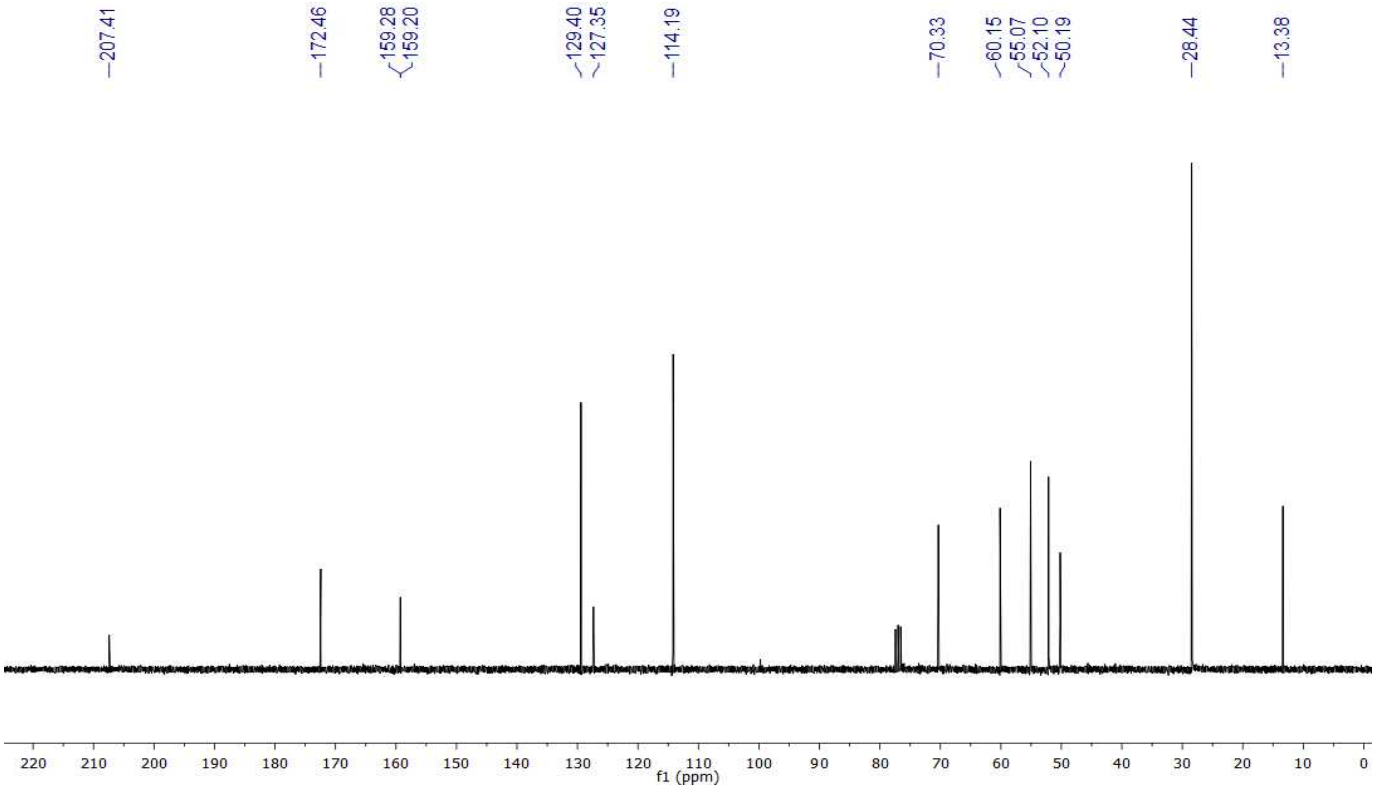
0.0
f1 (ppm)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70.33
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55.07
52.10
50.19
28.44
13.38
220
210
200
190
180
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150
140
130
120
110
100
90
80
70
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50
40
30
20
10
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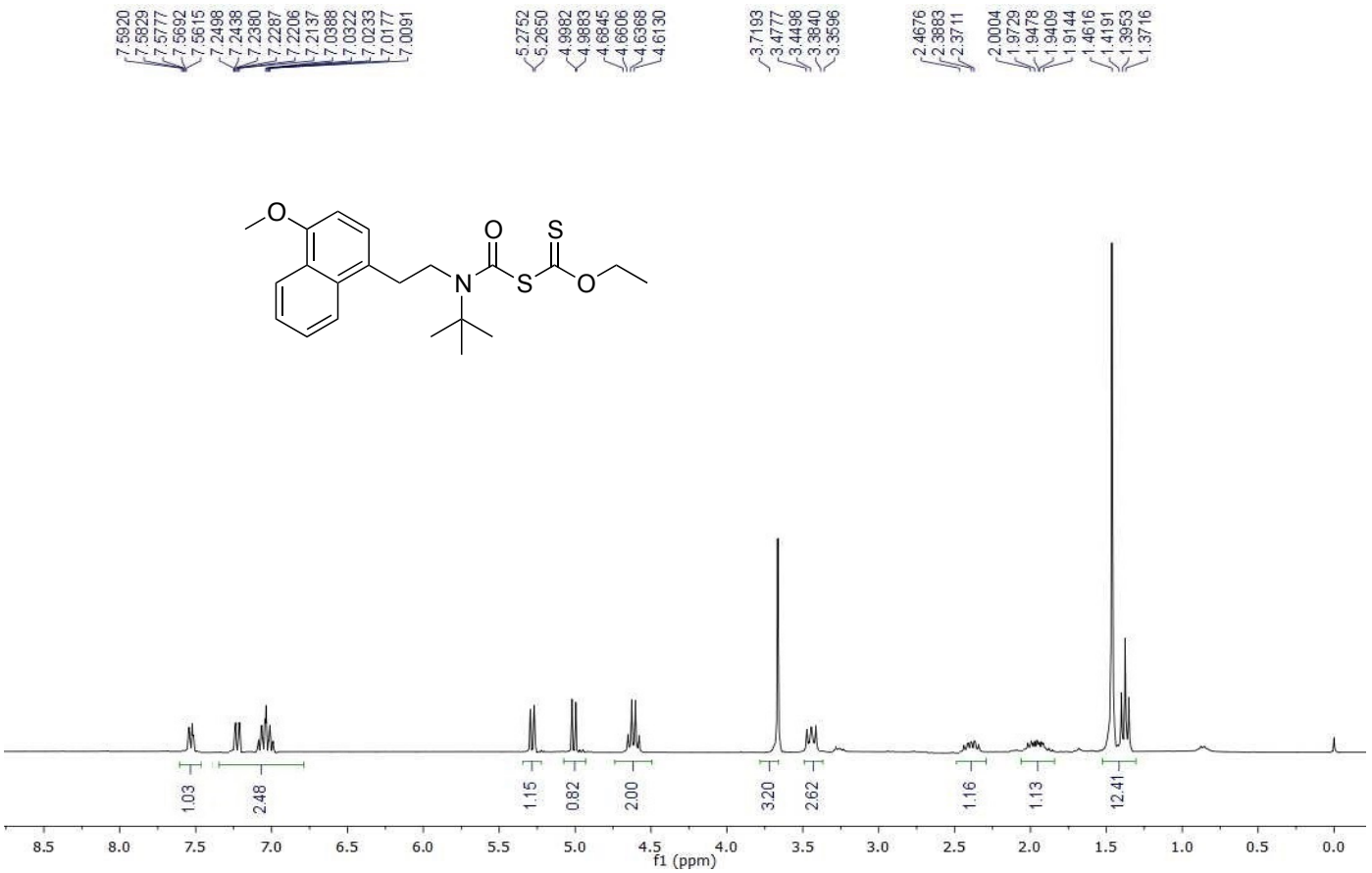
f1 (ppm)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7.0388
7.0322
7.0233
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7.0091
5.2752
5.2650
4.9982
4.9883
4.6845
4.6606
4.6368
4.6130
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3.4777
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3.3840
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2.3883
2.3711
2.0004
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1.9409
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1.4616
1.4191
1.3953
1.3716
O
O
S
N
S
O
1.03
2.48
1.15
0.82
2.00
3.20
2.62
1.16
1.13
12.41
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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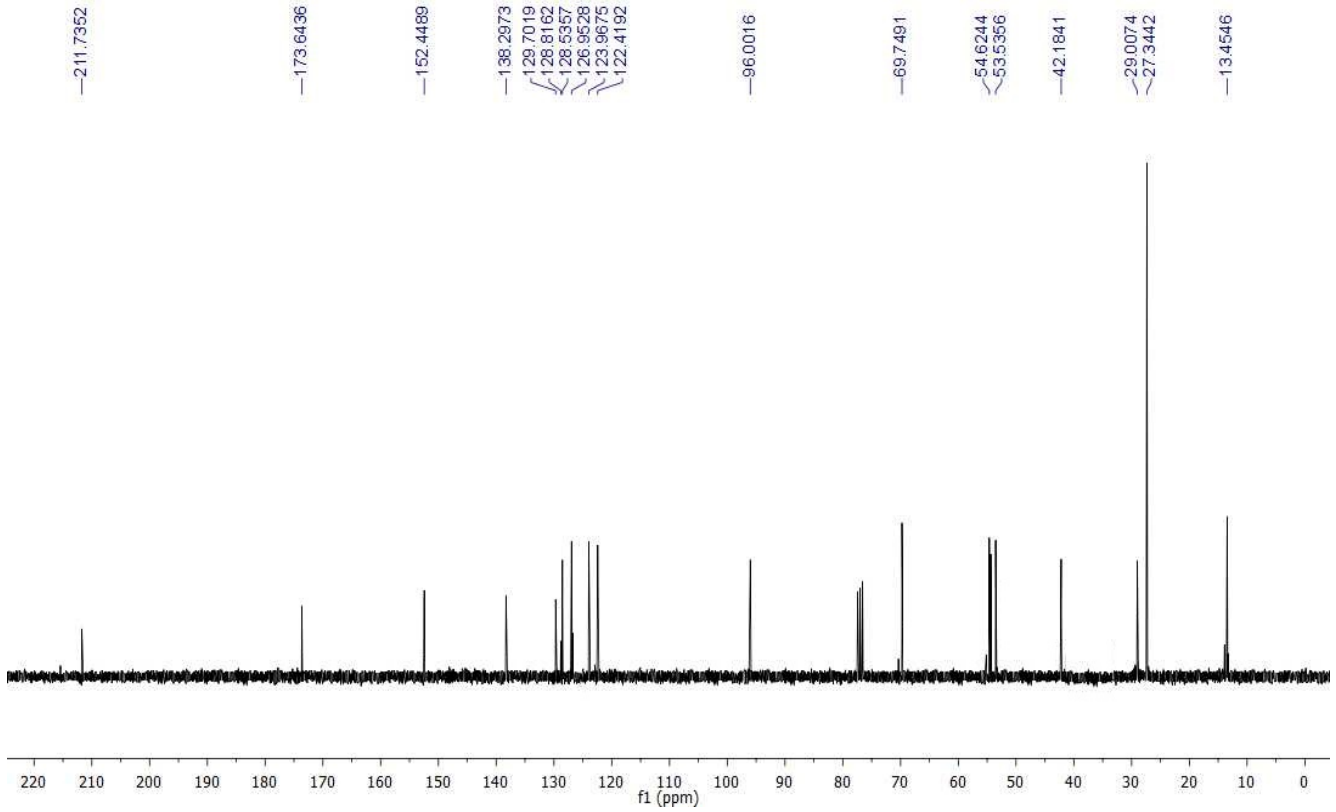
0.0
f1 (ppm)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53.5356
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29.0074
27.3442
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200
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180
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50
40
30
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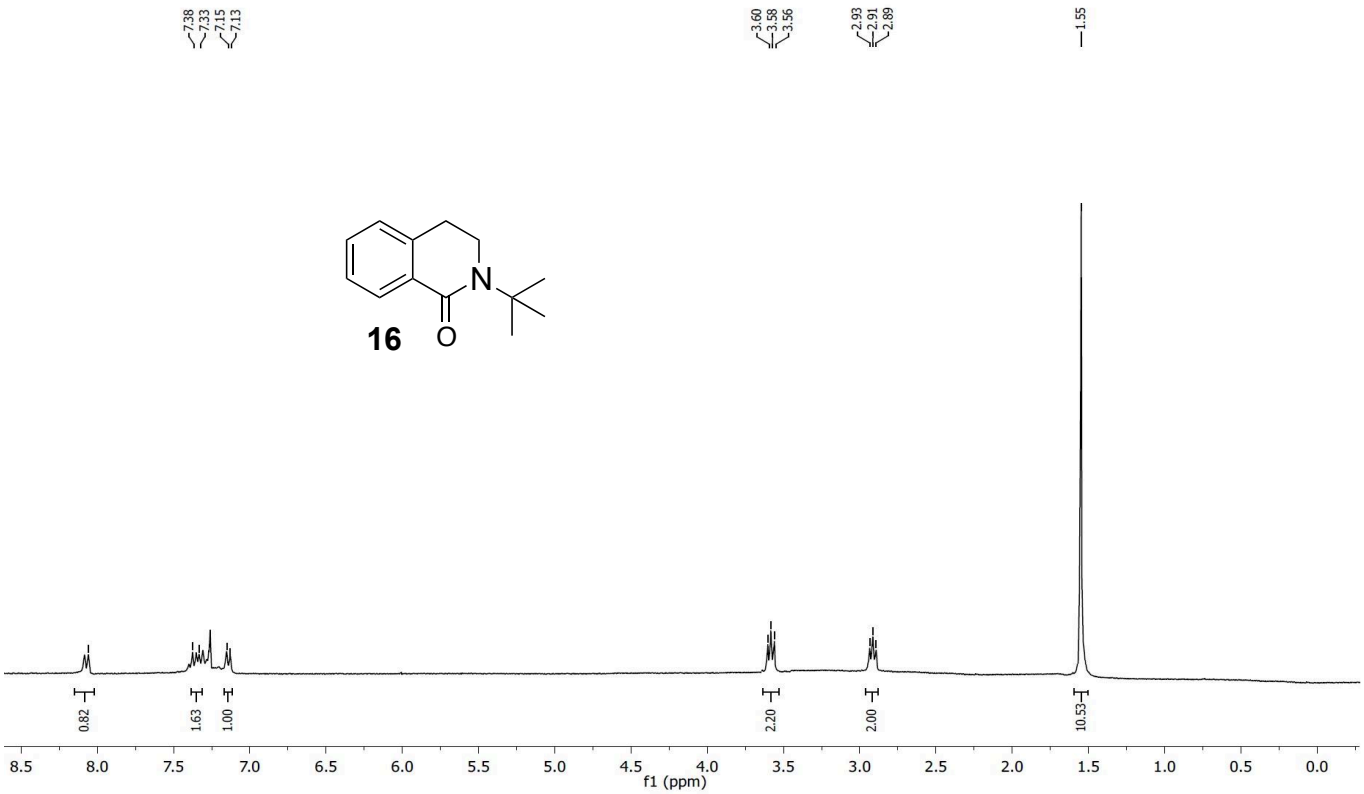
f1 (ppm)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2.89
1.55
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O
16
0.82
1.63
1.00
2.20
2.00
10.53
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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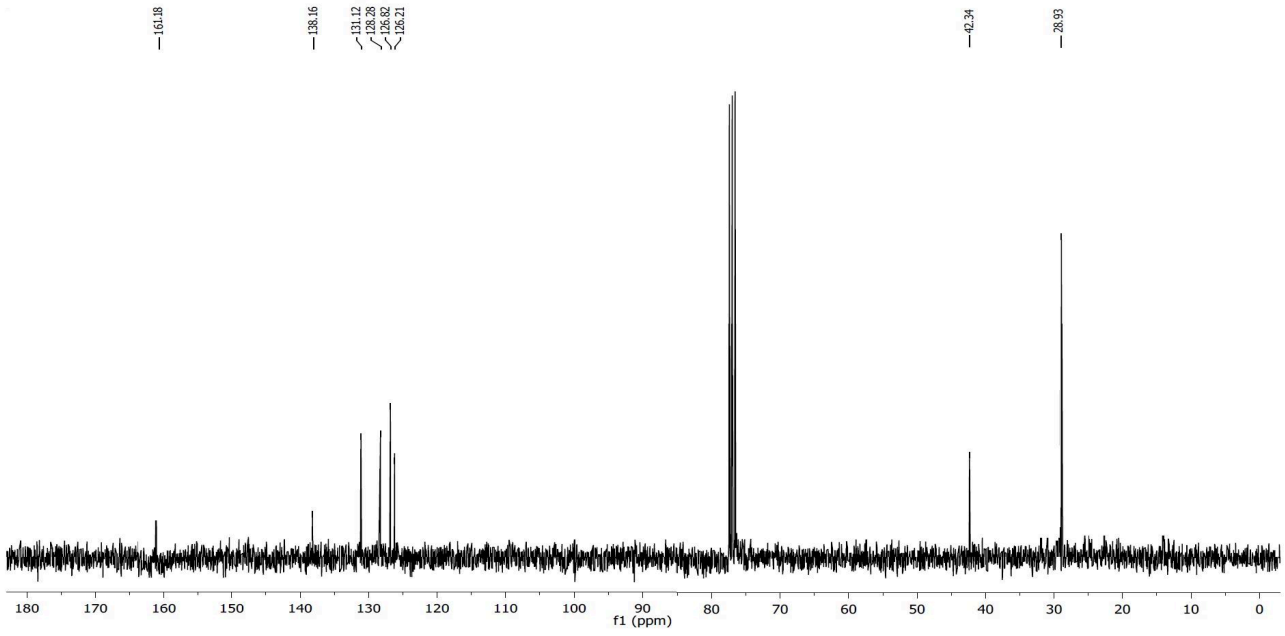
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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180
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120
110
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70
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50
40
30
20
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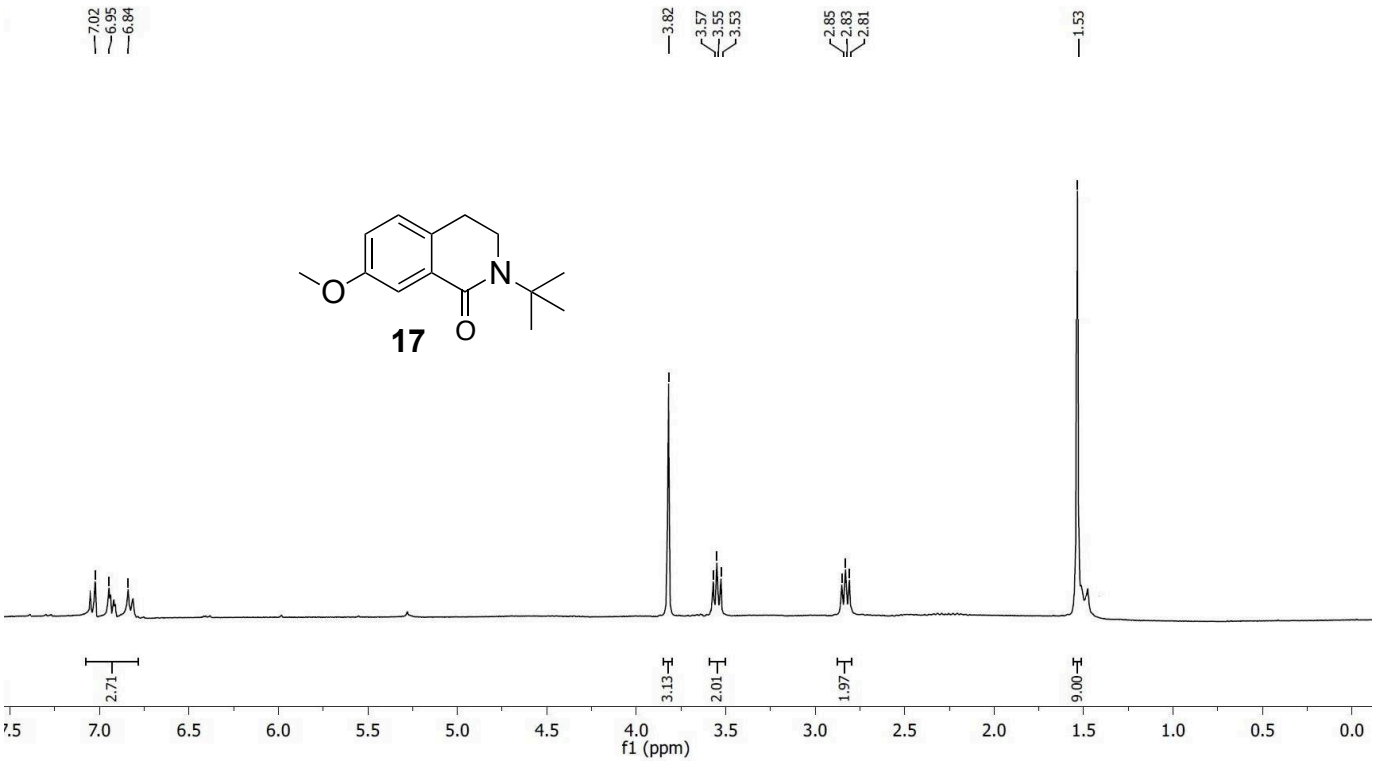
f1 (ppm)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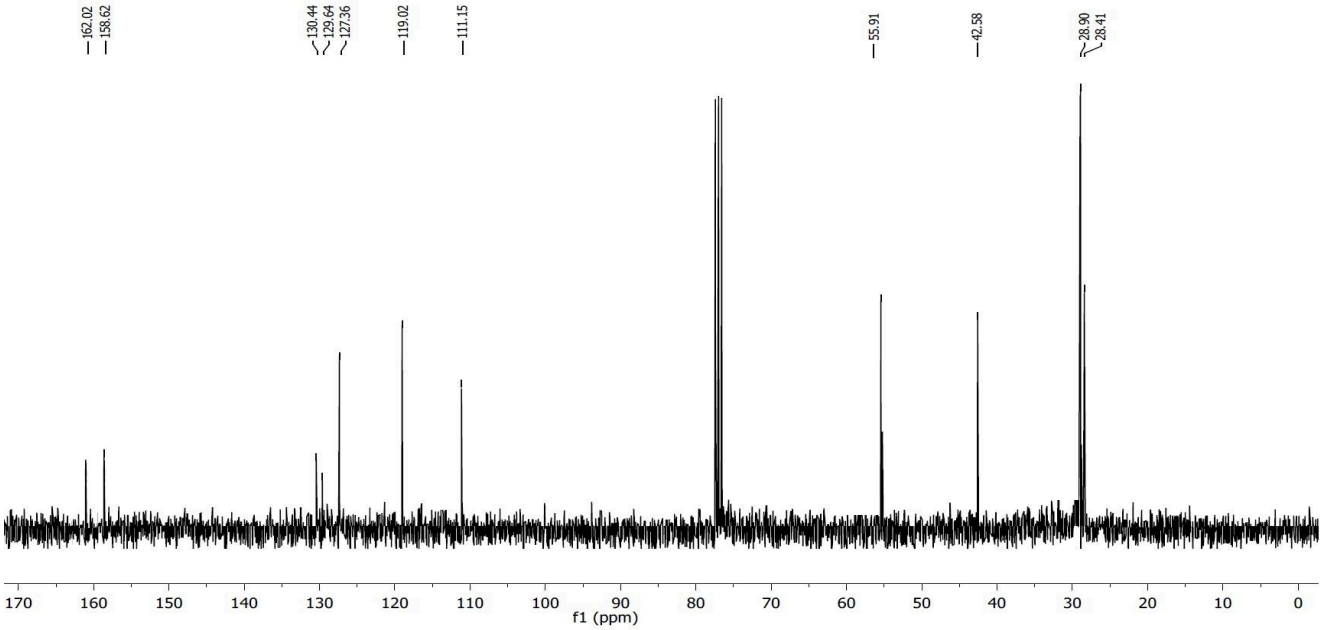
9.00
f1 (ppm)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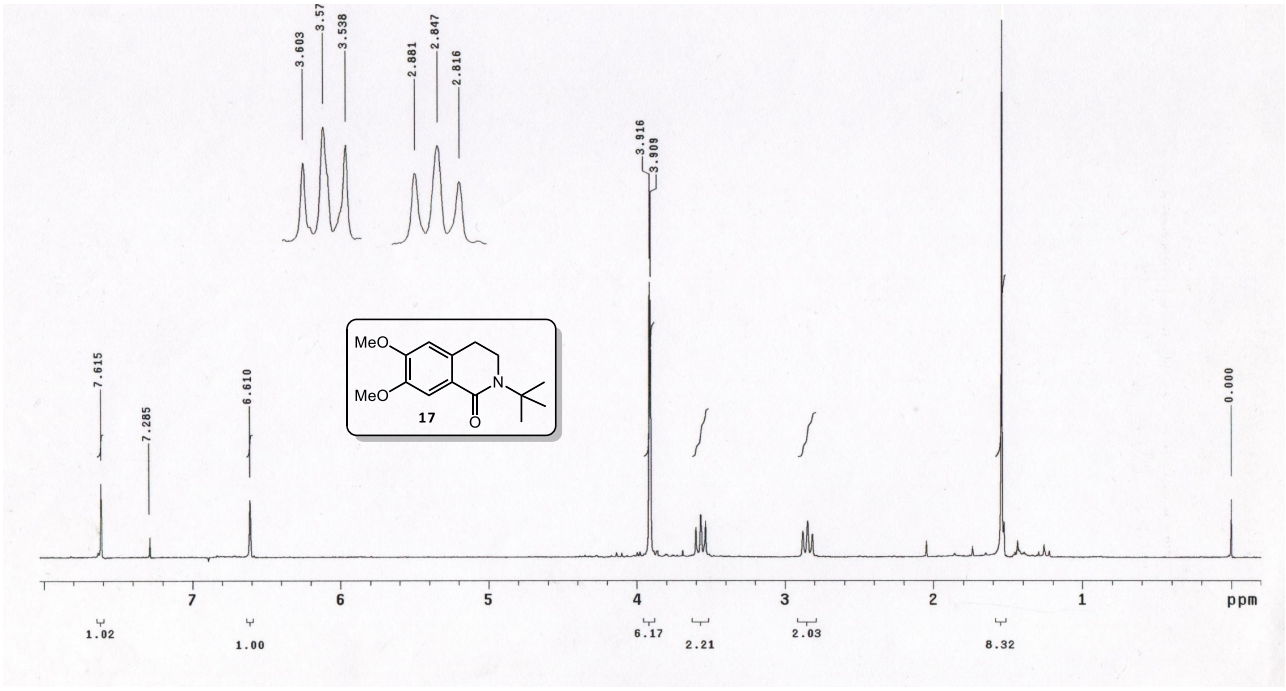
28.41
f1 (ppm)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3.909
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7.285
6.610
0.000
MeO
MeO
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O
7
6
5
4
3
2
1
ppm
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1.00
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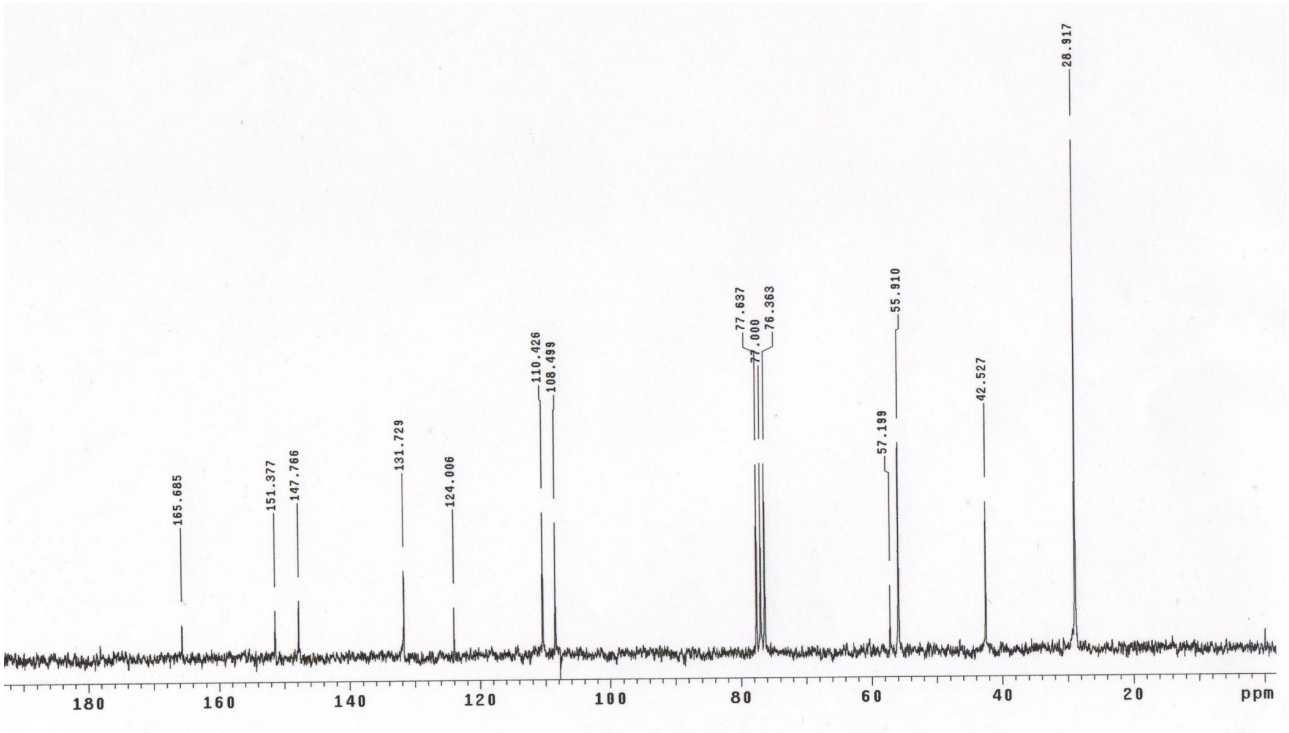
2.21
2.03
8.32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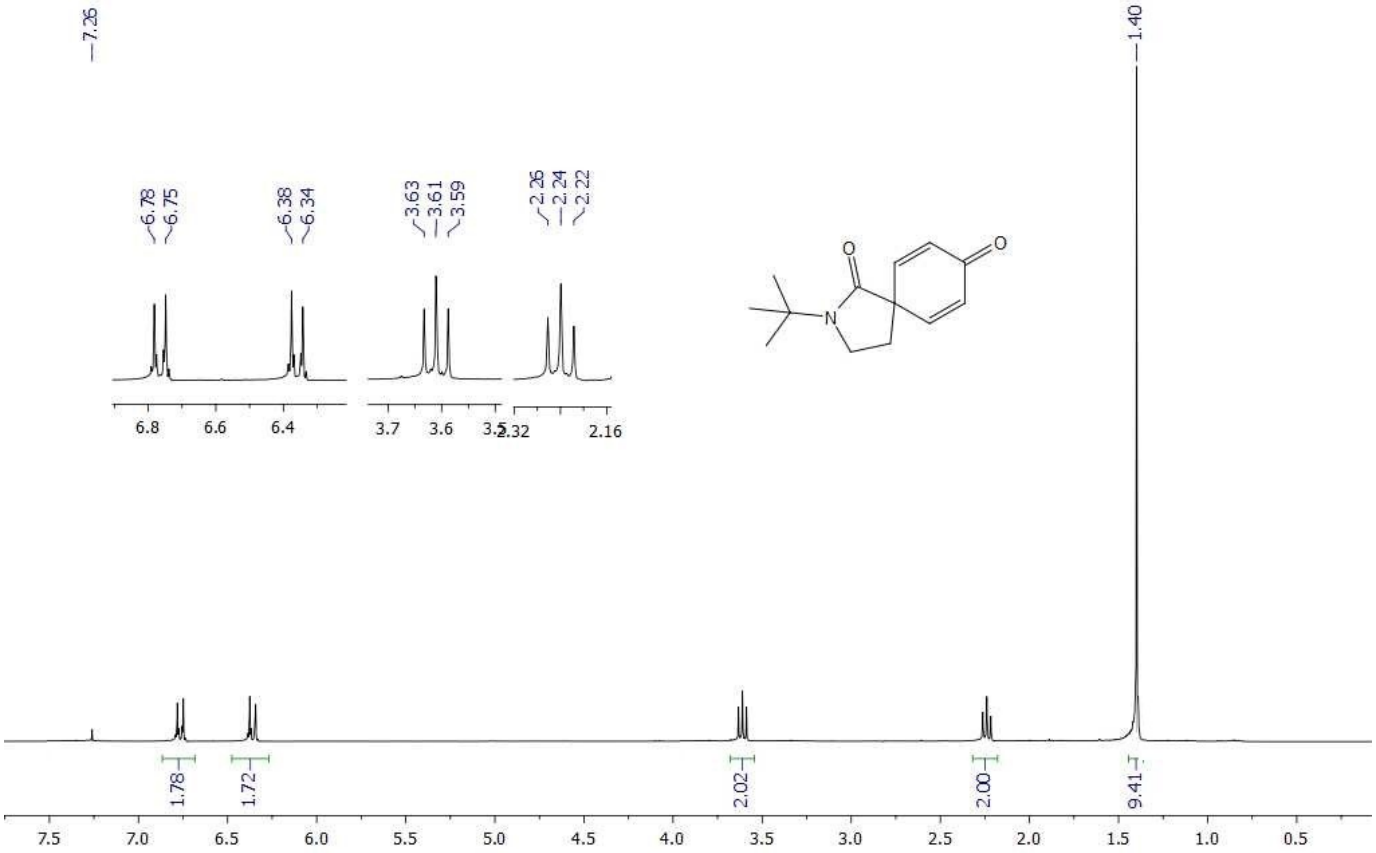
20
ppm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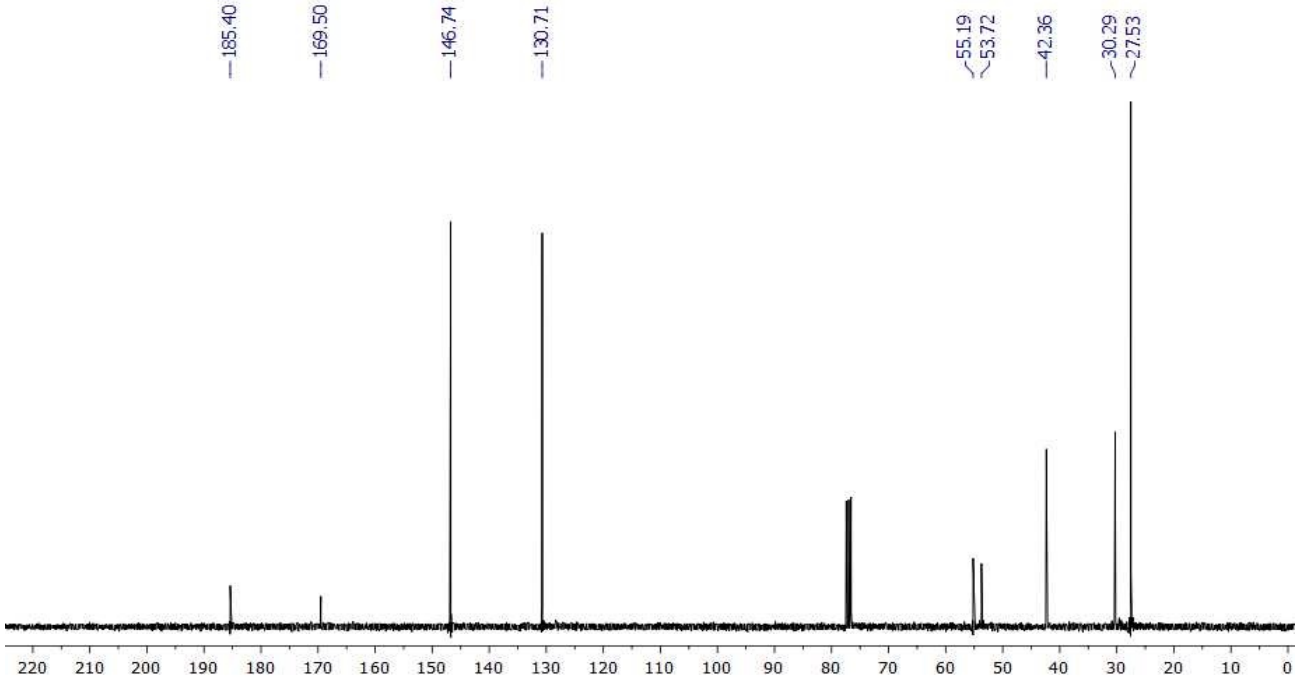
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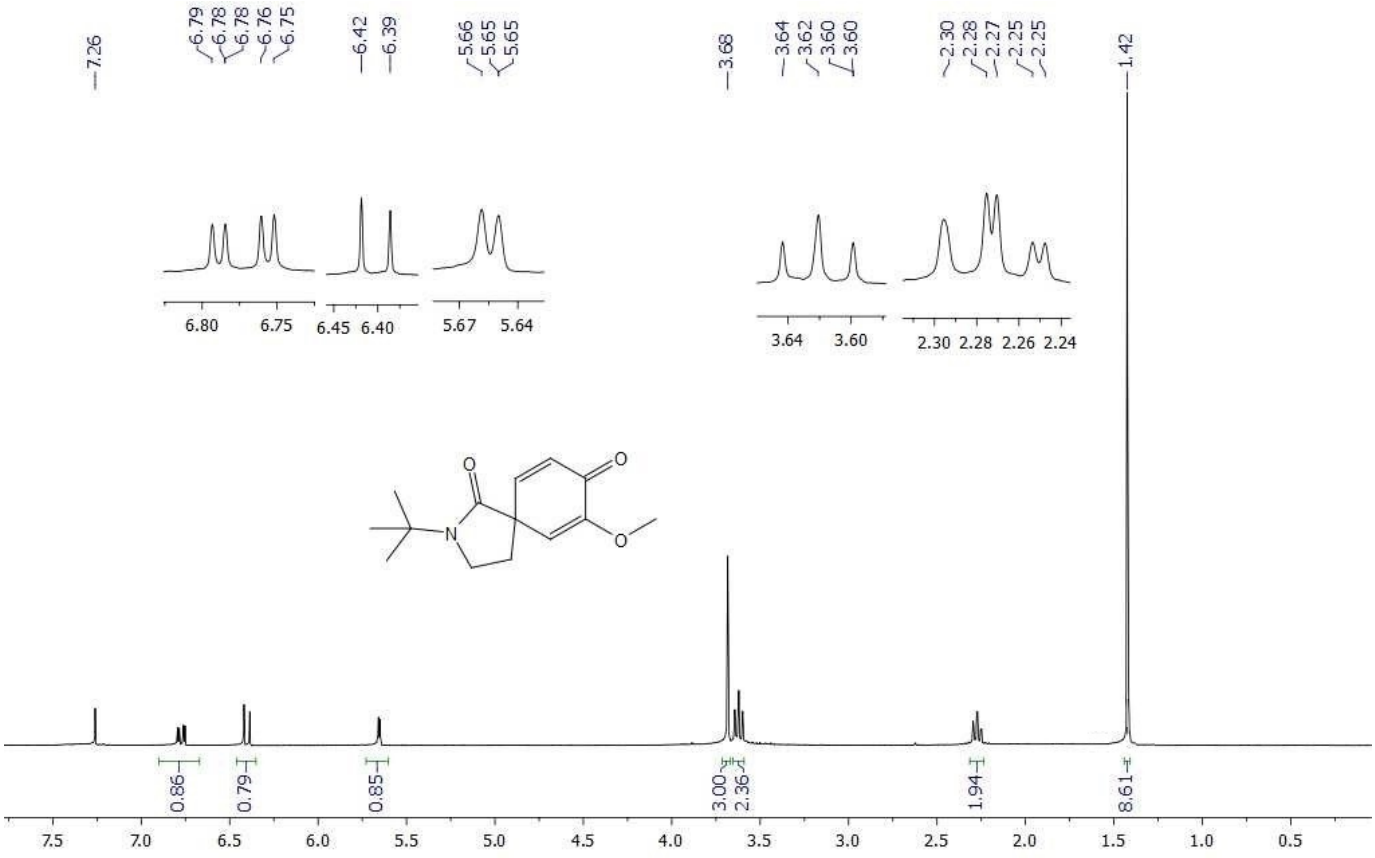
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3.62
3.60
3.60
2.30
2.28
2.27
2.25
2.25
1.42
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6.75
6.45
6.40
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2.24
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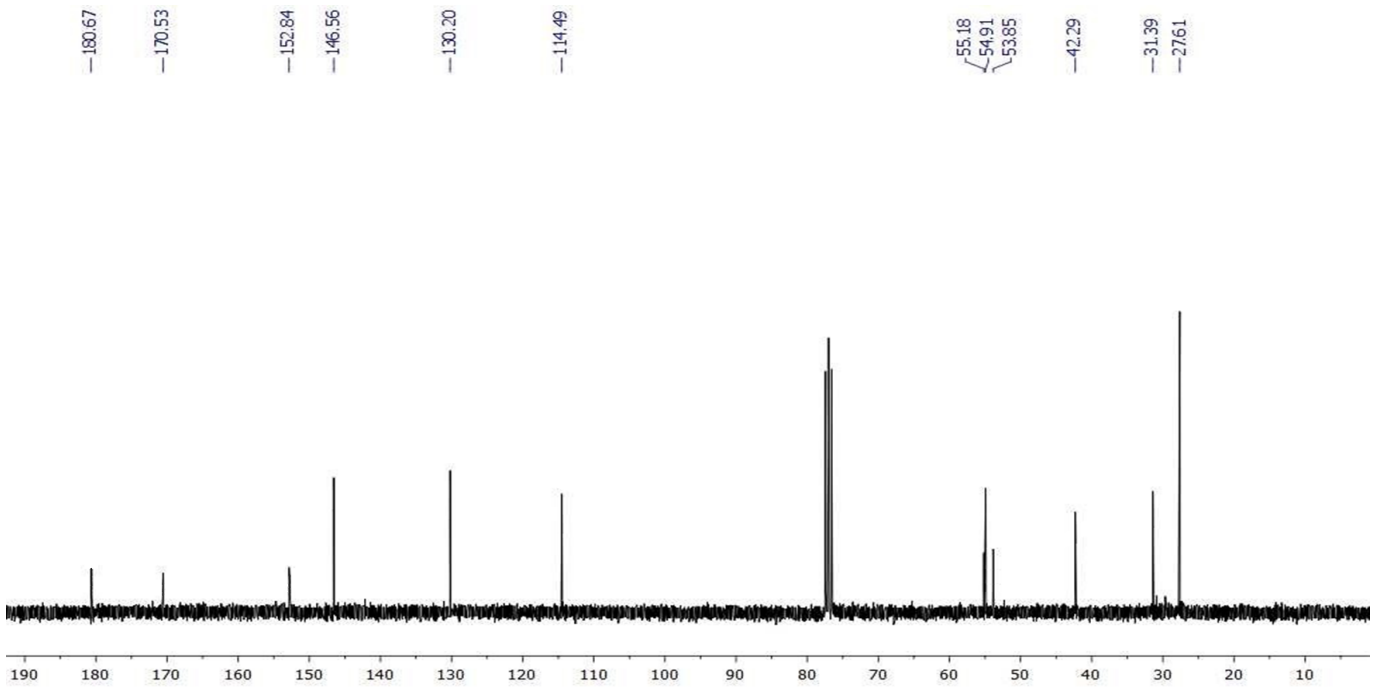
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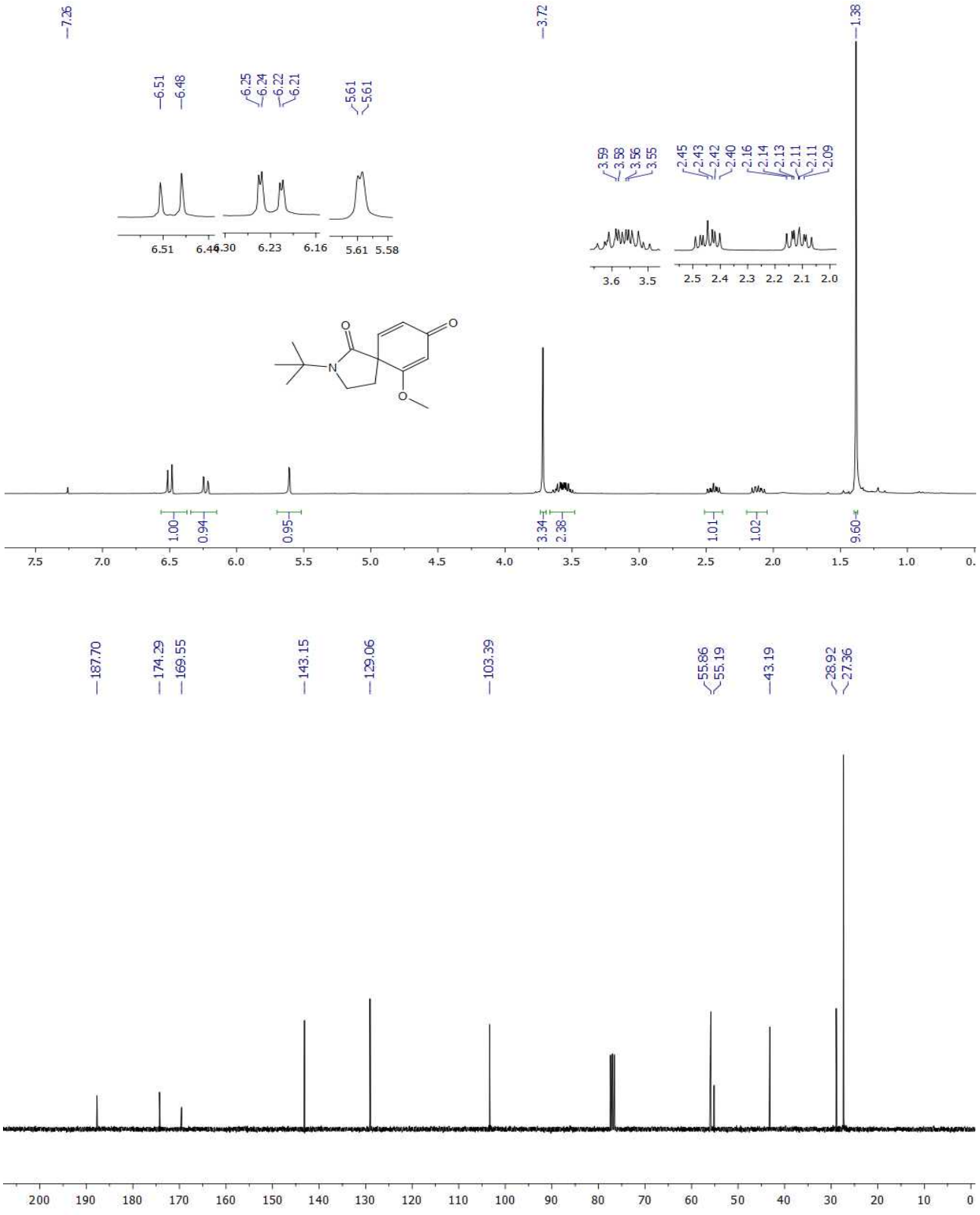
10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2.45
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2.14
2.13
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2.11
2.09
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O
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0.95
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1.02
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2.0
1.5
1.0
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0.0
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114.34
55.31
55.09
50.89
42.22
32.45
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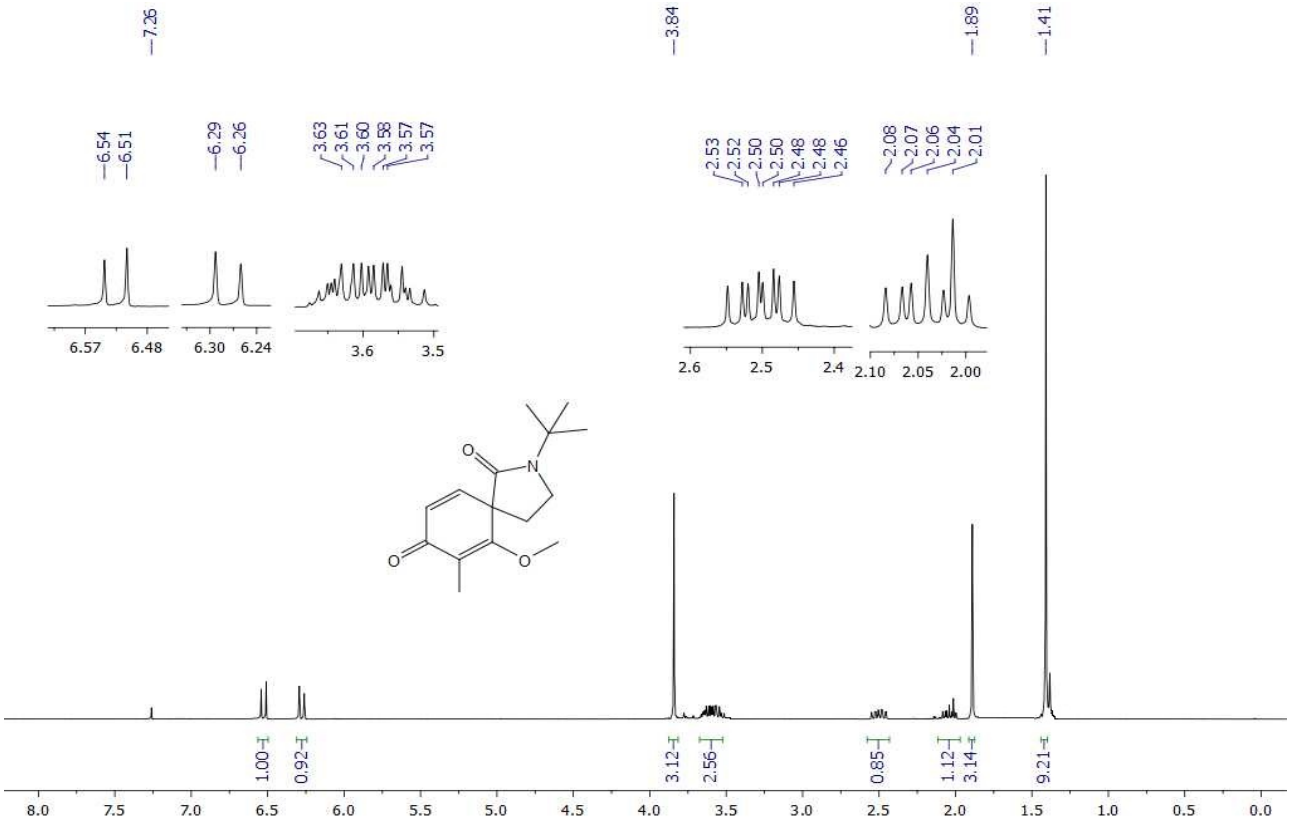
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3.57
3.57
2.53
2.52
2.50
2.50
2.48
2.48
2.46
2.08
2.07
2.06
2.04
2.01
6.57
6.48
6.30
6.24
3.6
3.5
2.6
2.5
2.4
2.10
2.05
2.00
O
N
O
O
1.00
0.92
3.12
2.56
0.85
1.12
3.14
9.21
8.0
7.5
7.0
6.5
6.0
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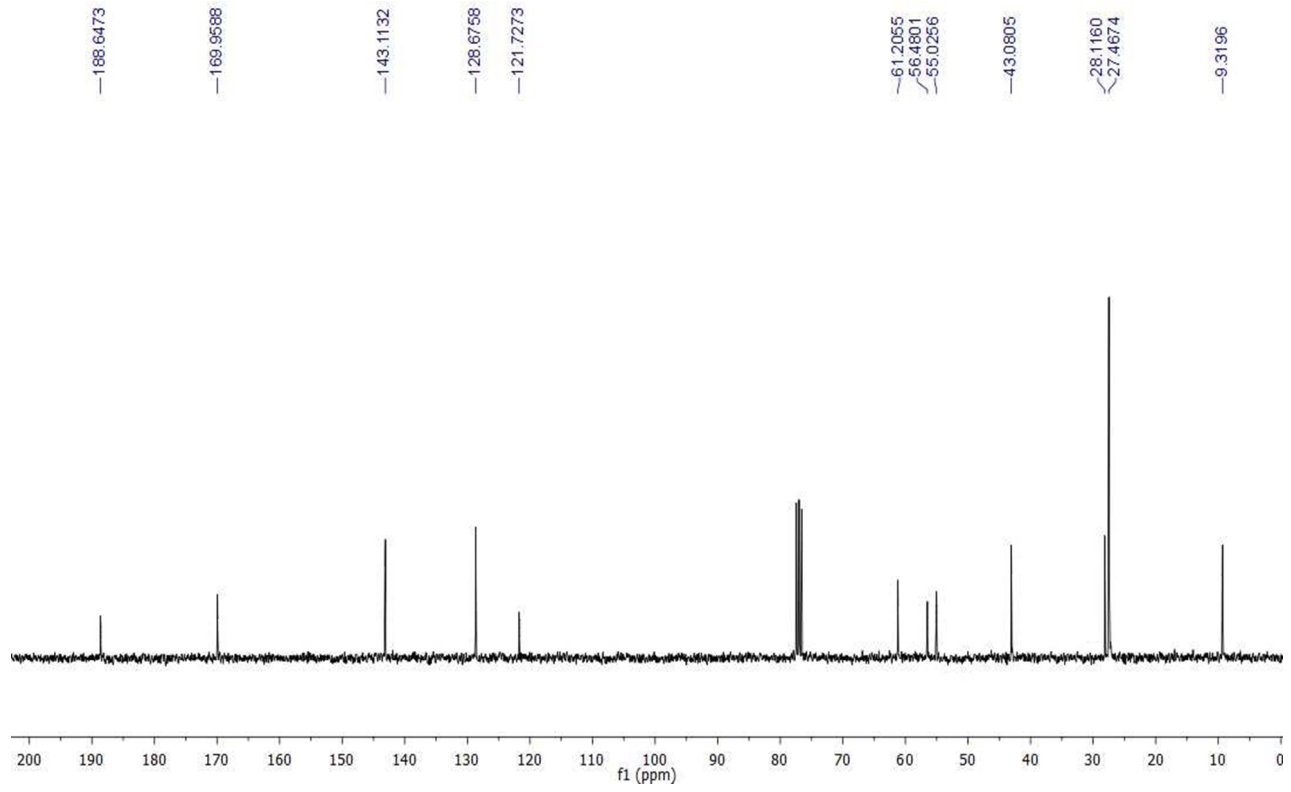
0.0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56.4801
55.0256
43.0805
28.1160
27.4674
9.3196
200
190
180
170
160
150
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130
120
110
100
90
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70
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50
40
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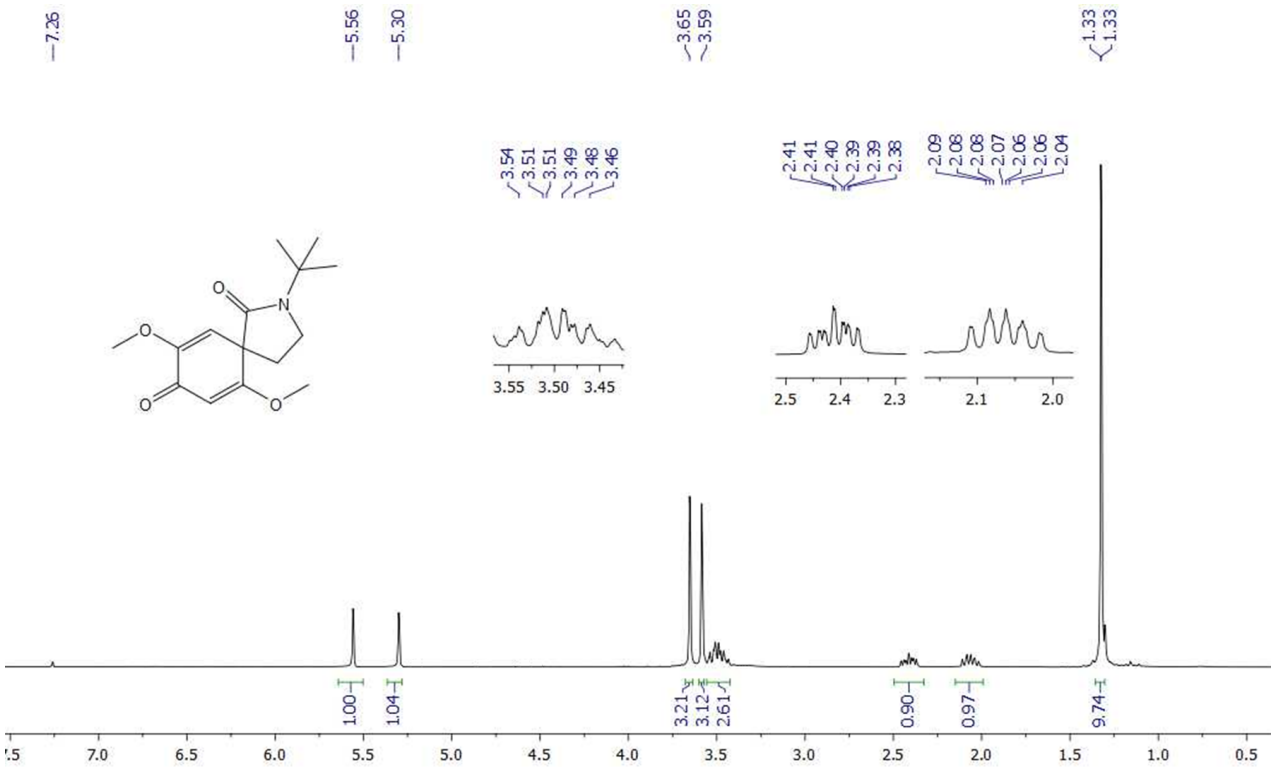
f1 (ppm)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3.54
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3.49
3.48
3.46
2.41
2.41
2.40
2.39
2.39
2.38
2.09
2.08
2.08
2.07
2.06
2.06
2.04
3.55 3.50 3.45
2.5 2.4 2.3
2.1 2.0
1.00
1.04
3.21
3.12
2.61
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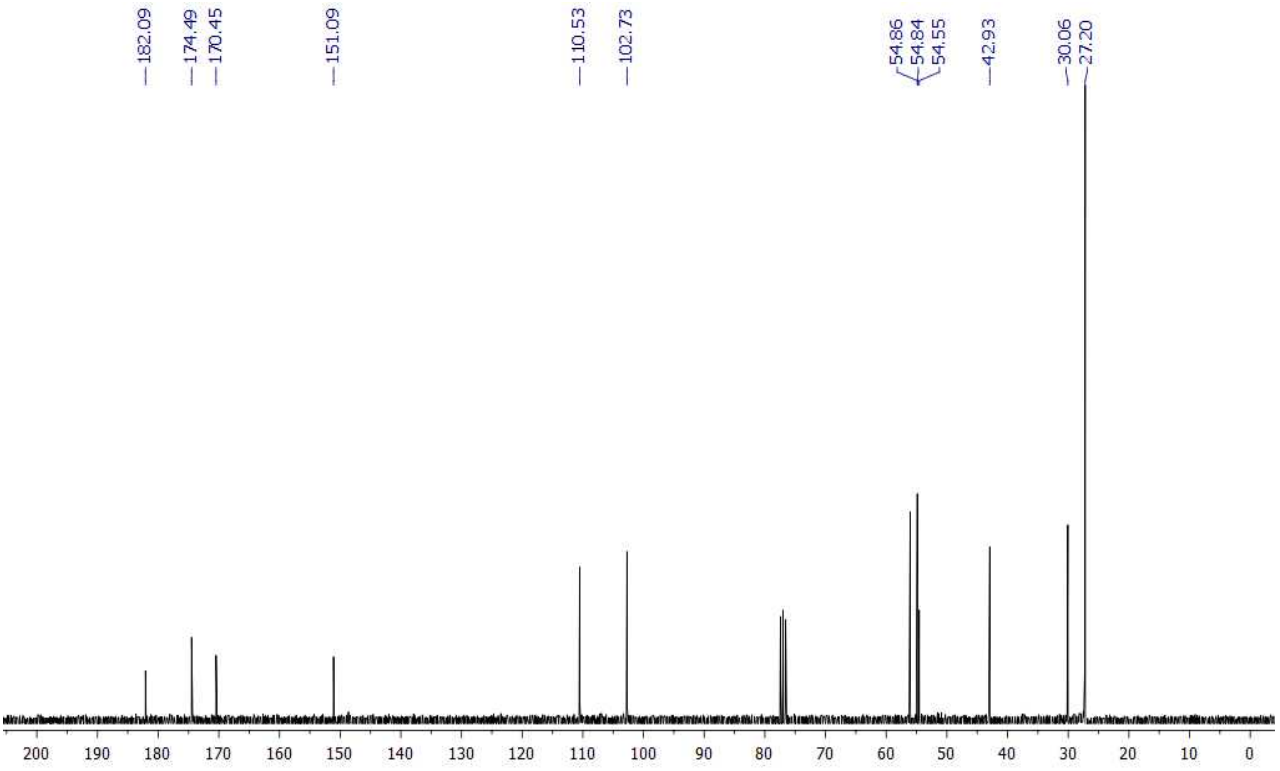
0.97
9.74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151.09
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54.84
54.55
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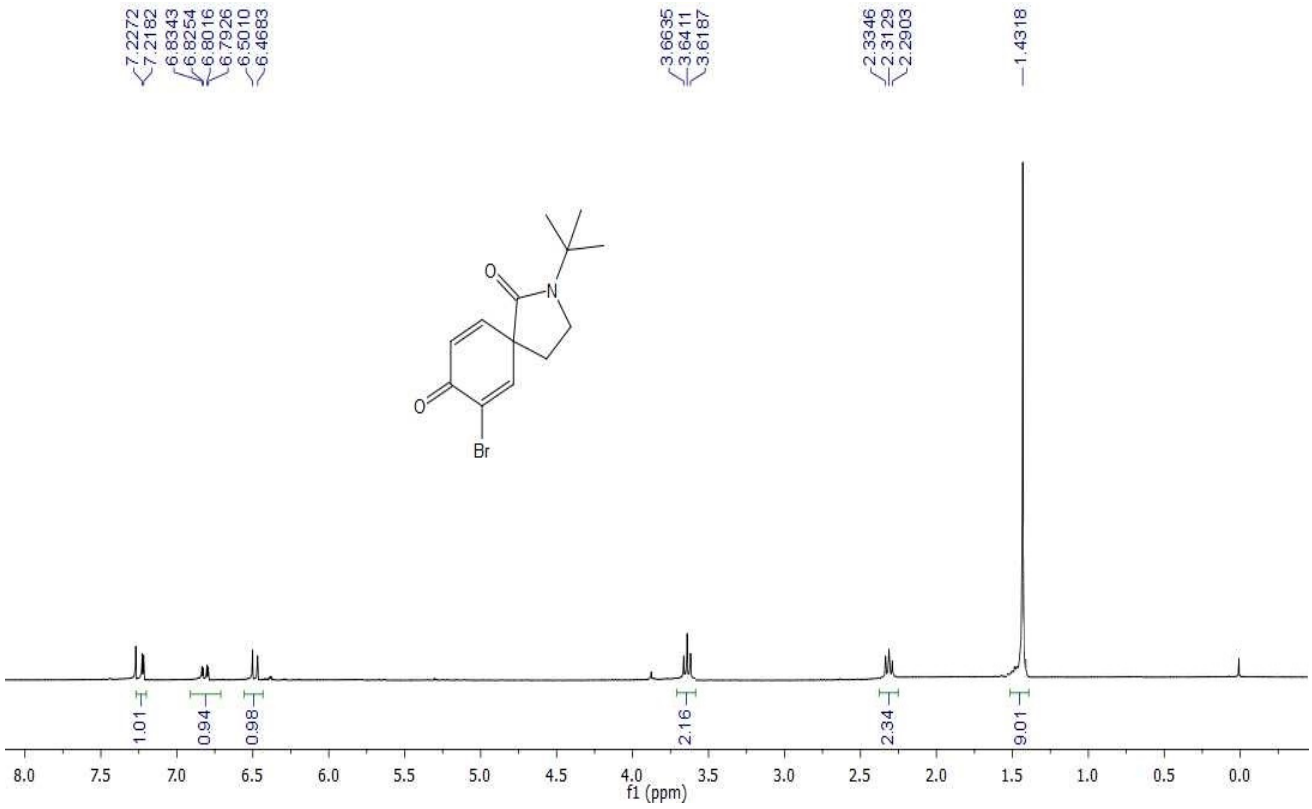
27.20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3.6411
3.6187
2.3346
2.3129
2.2903
1.4318
O
N
O
Br
1.01
0.94
0.98
2.16
2.34
9.01
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
1.5
1.0
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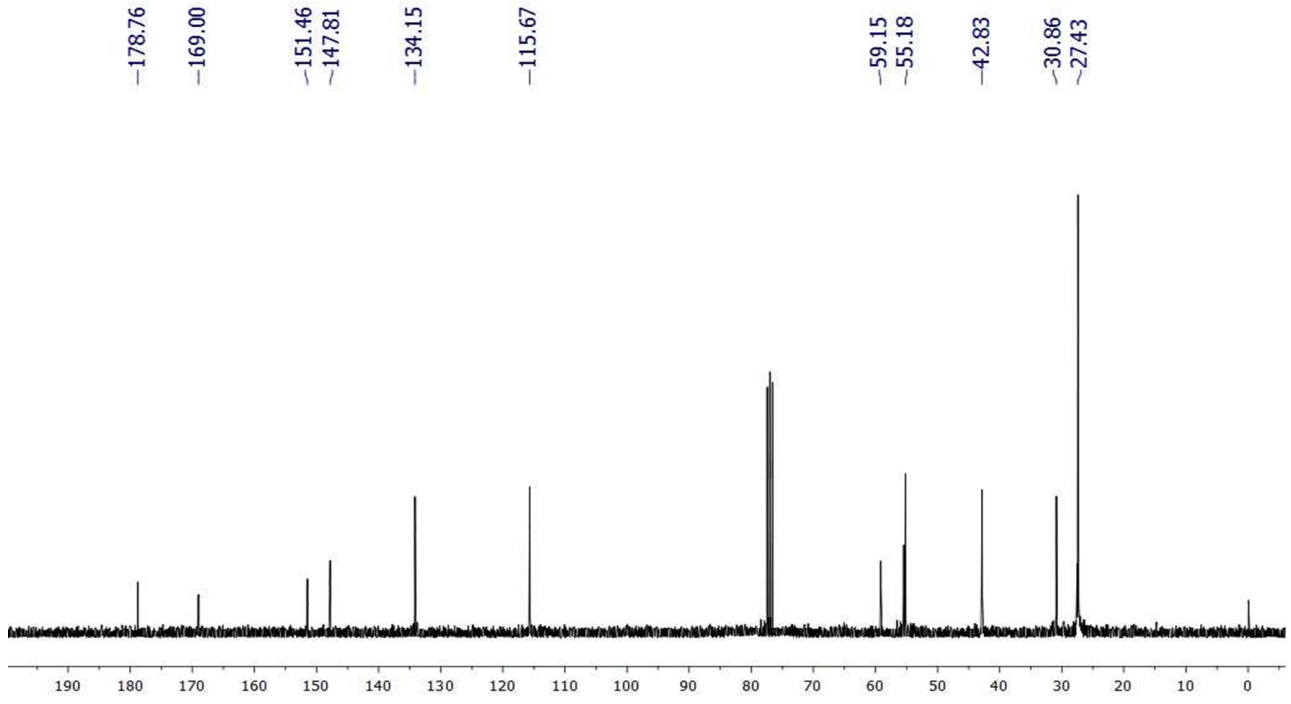
0.0
f1 (ppm)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55.18
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30.86
27.43
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150
140
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120
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70
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30
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10
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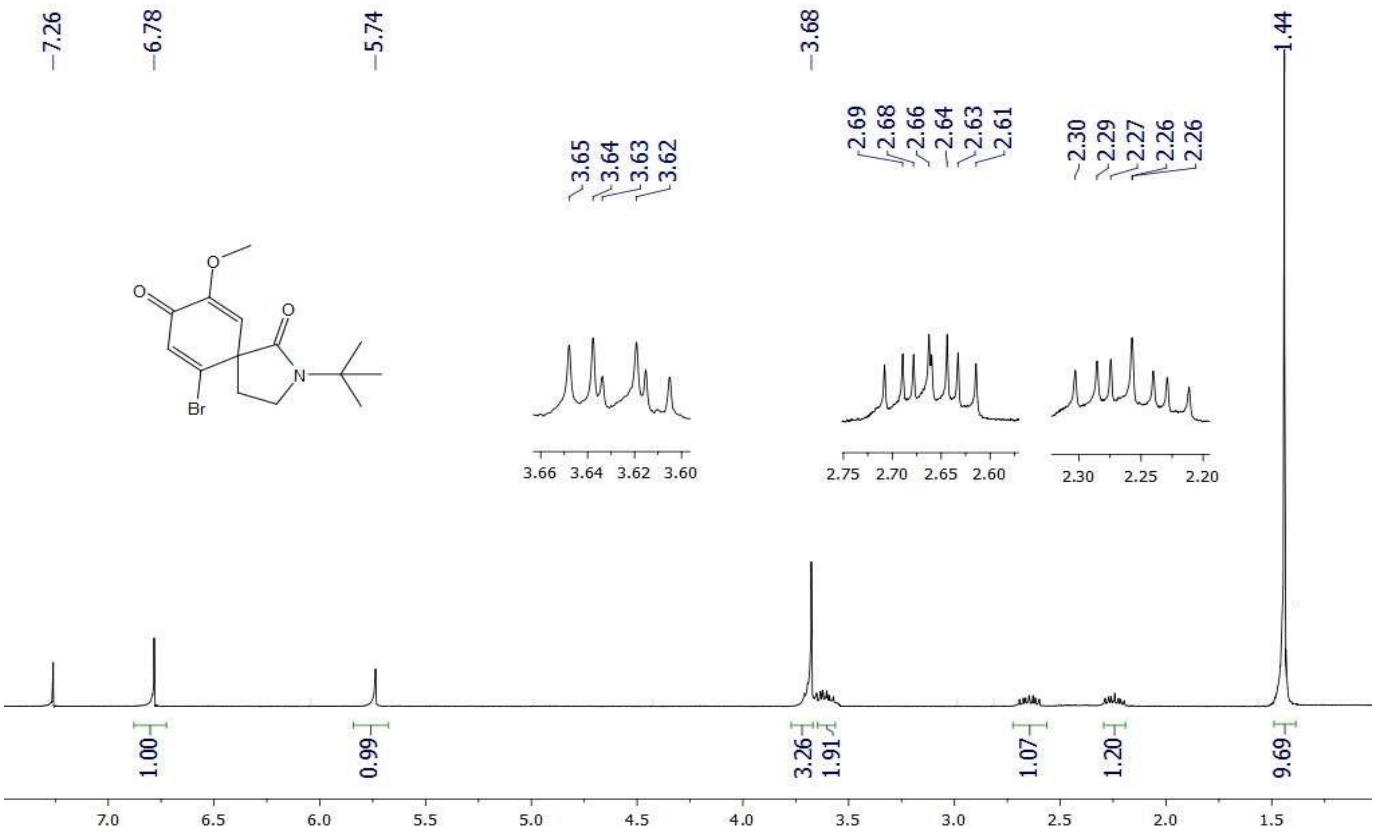
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3.63
3.62
2.69
2.68
2.66
2.64
2.63
2.61
2.30
2.29
2.27
2.26
2.26
O
O
O
N
Br
1.00
0.99
3.26
1.91
1.07
1.20
9.69
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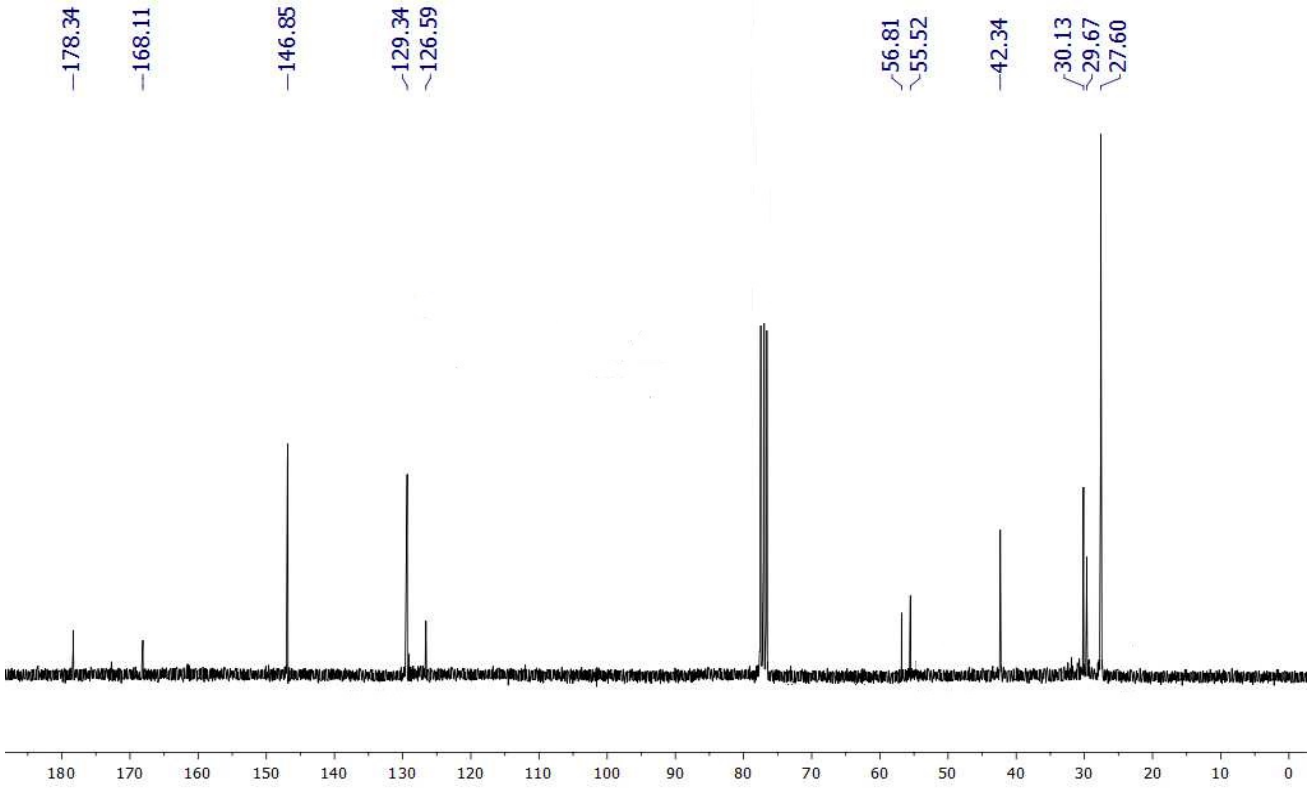
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5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42.34
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29.67
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150
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110
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80
70
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50
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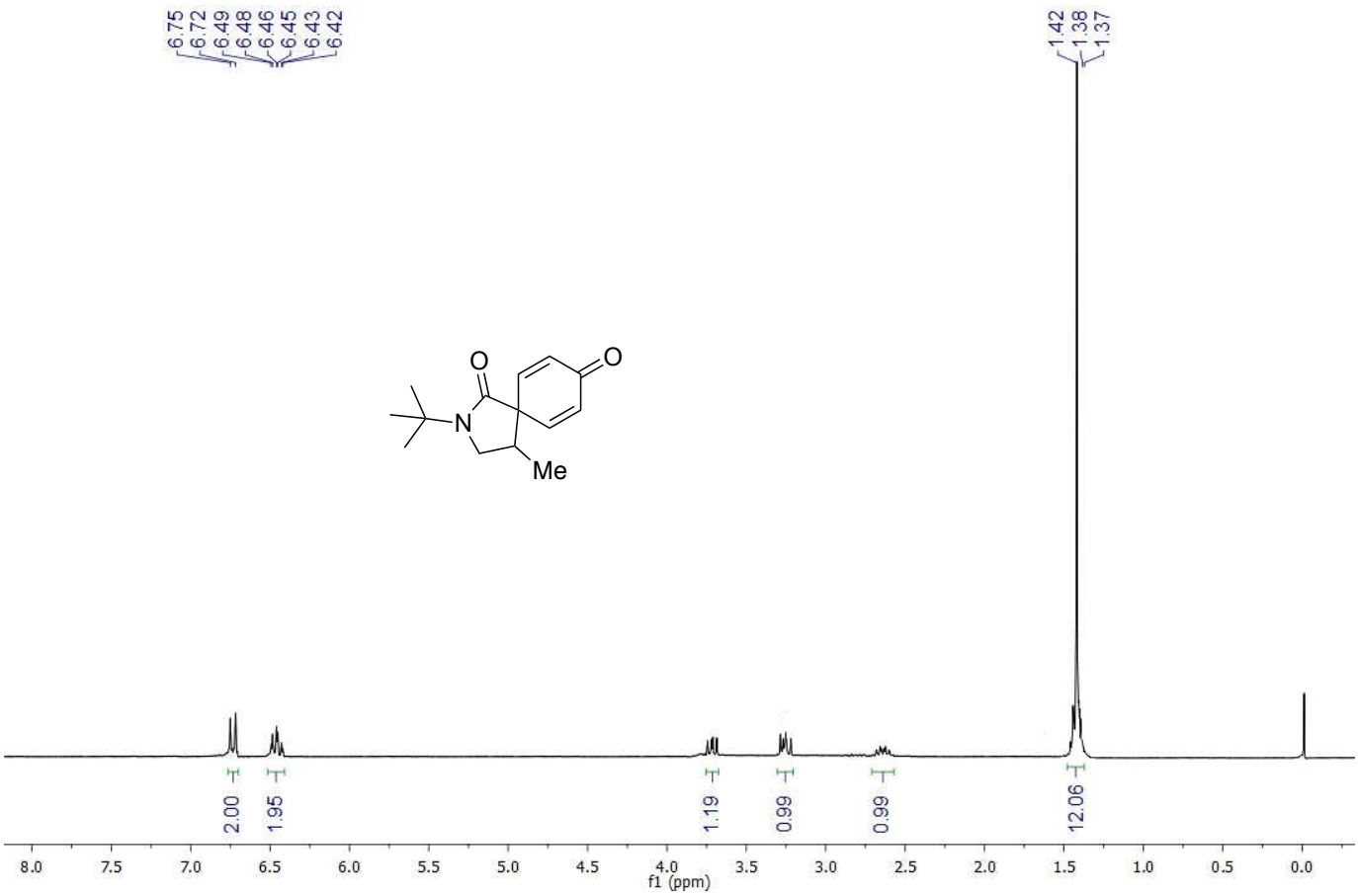
30
20
10
0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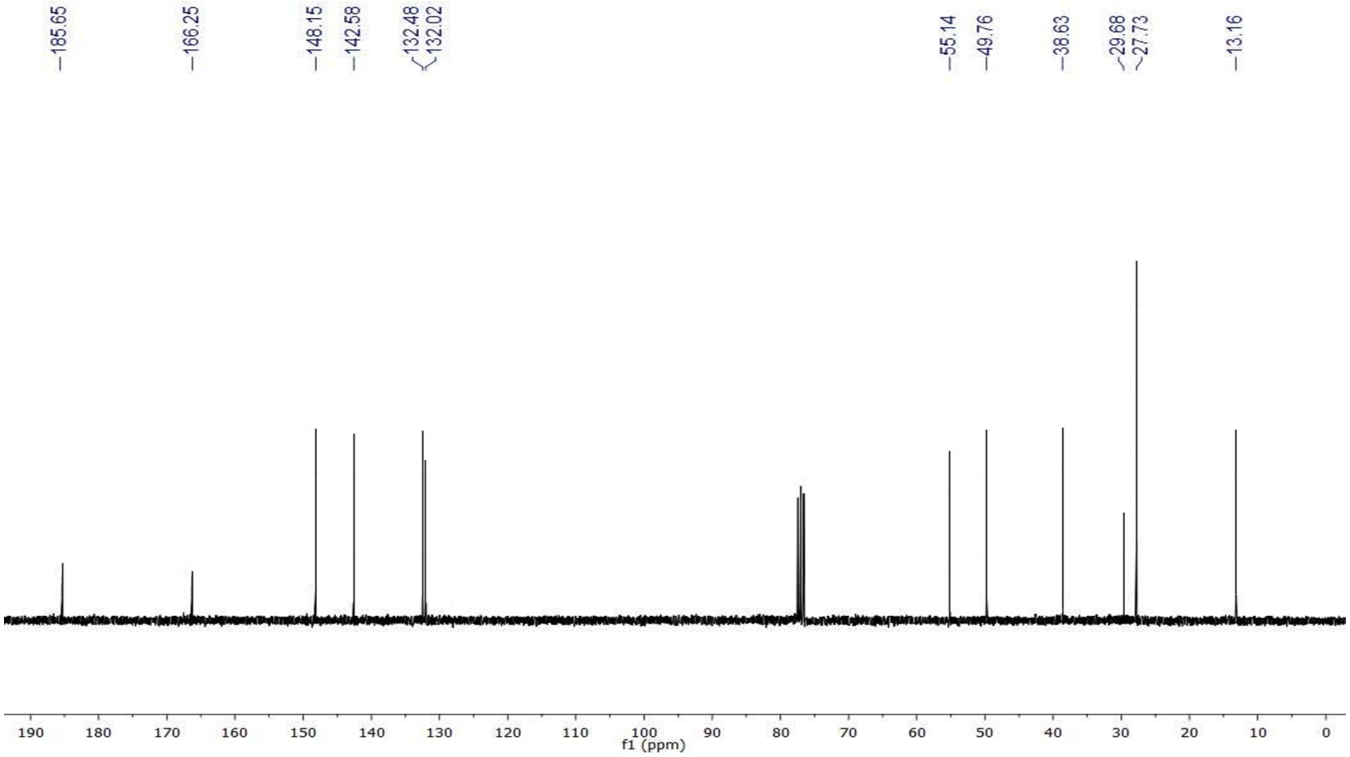
6.72
6.49
6.48
6.46
6.45
6.43
6.42
1.42
1.38
1.37
O
O
N
Me
2.00
1.95
1.19
0.99
0.99
12.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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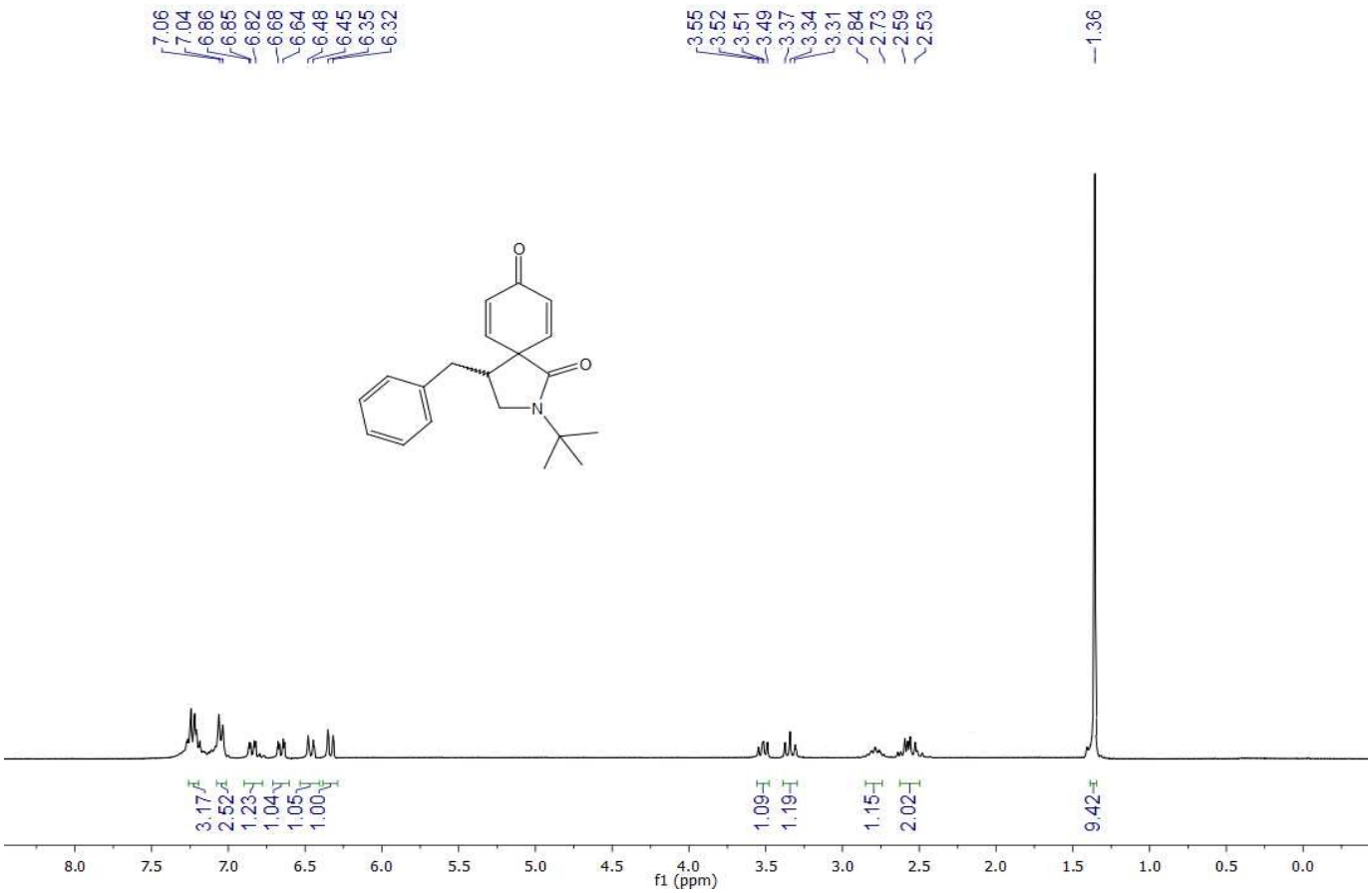
142.58
132.48
132.02
55.14
49.76
38.63
29.68
27.73
13.16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.68
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3.52
3.51
3.49
3.37
3.34
3.31
2.84
2.73
2.59
2.53
1.36
O
O
N
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2.52
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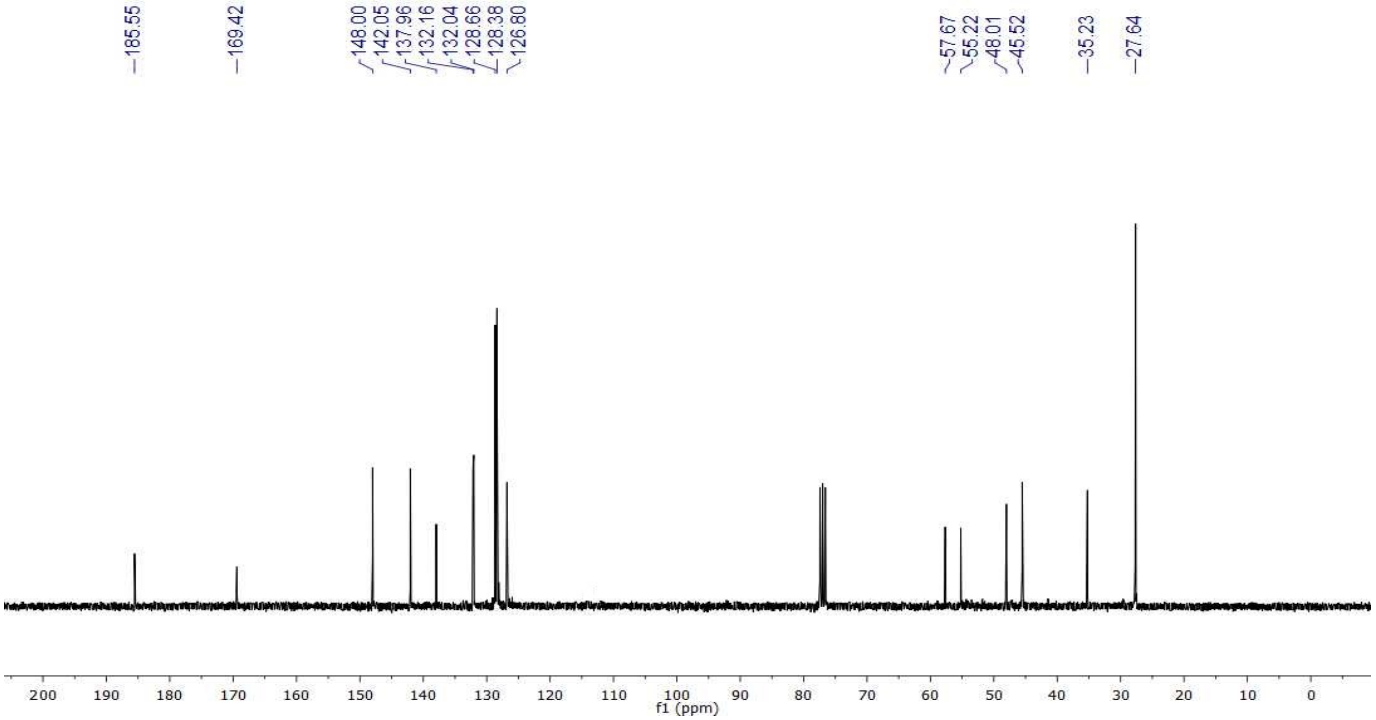
1.04
1.05
1.00
1.09
1.19
1.15
2.02
9.42
f1 (ppm)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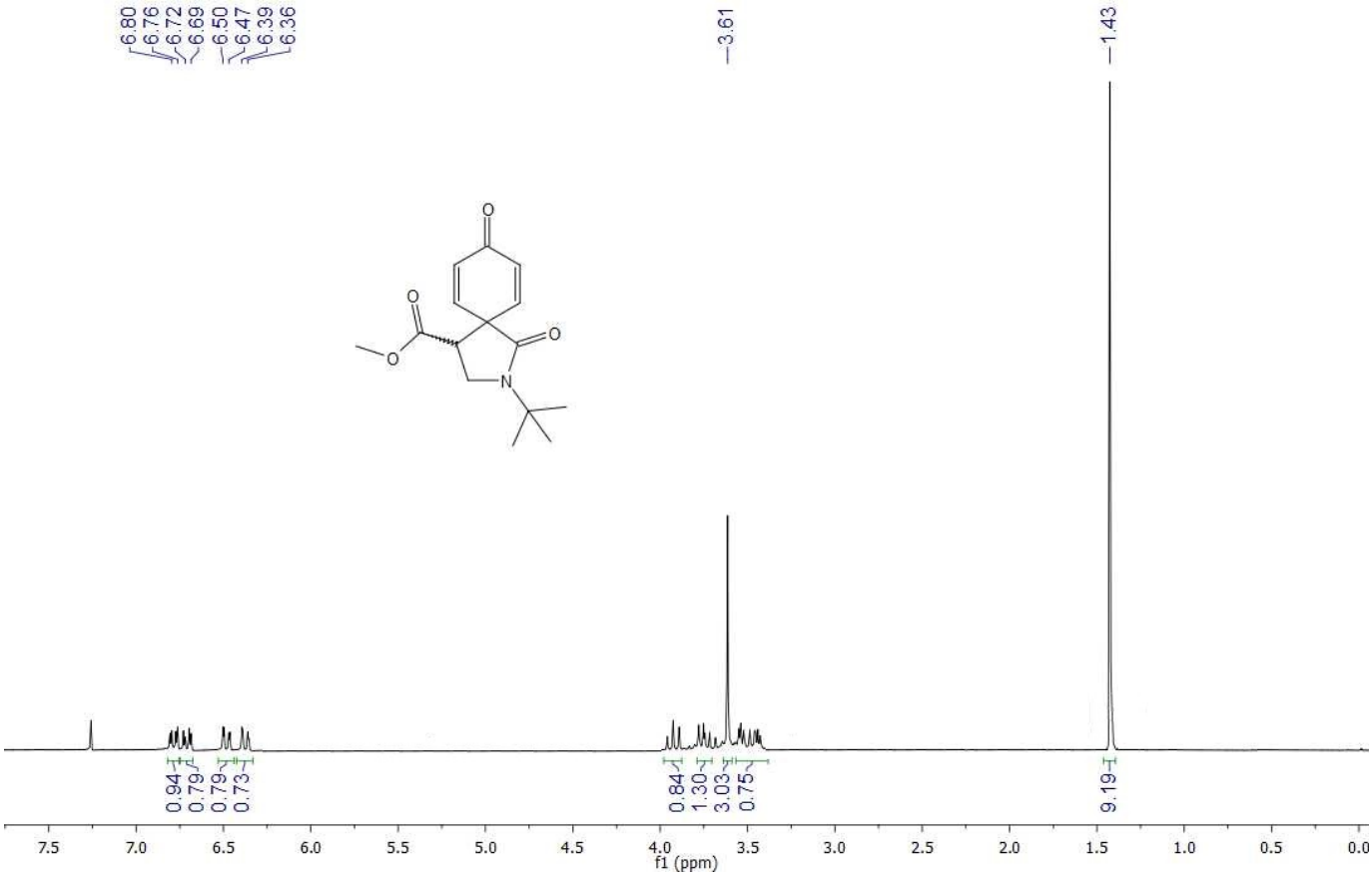
45.52
35.23
27.64
f1 (ppm)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O
O
O
N
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0.79
0.79
0.73
0.84
1.30
3.03
0.75
9.19
7.5
7.0
6.5
6.0
5.5
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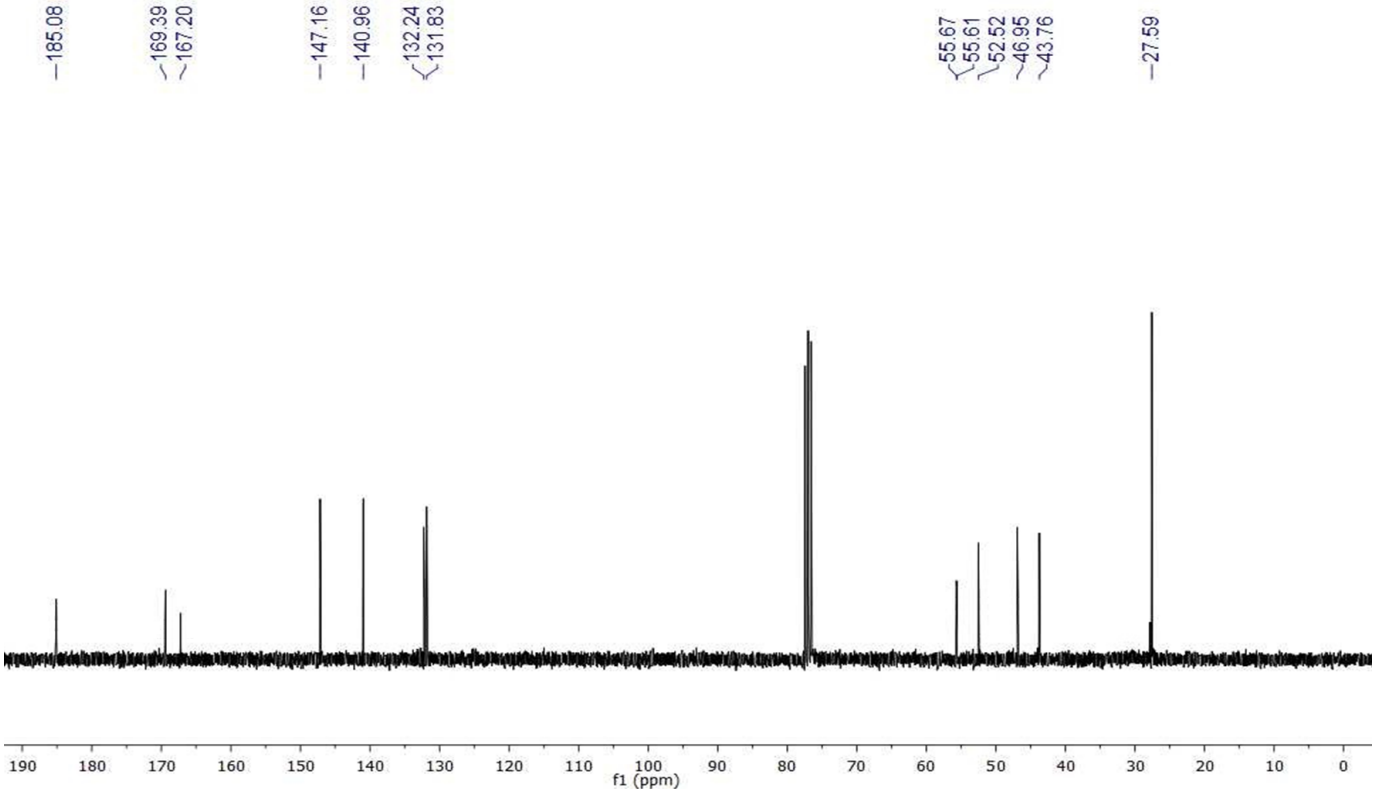
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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27.59
190
180
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140
130
120
110
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90
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40
30
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10
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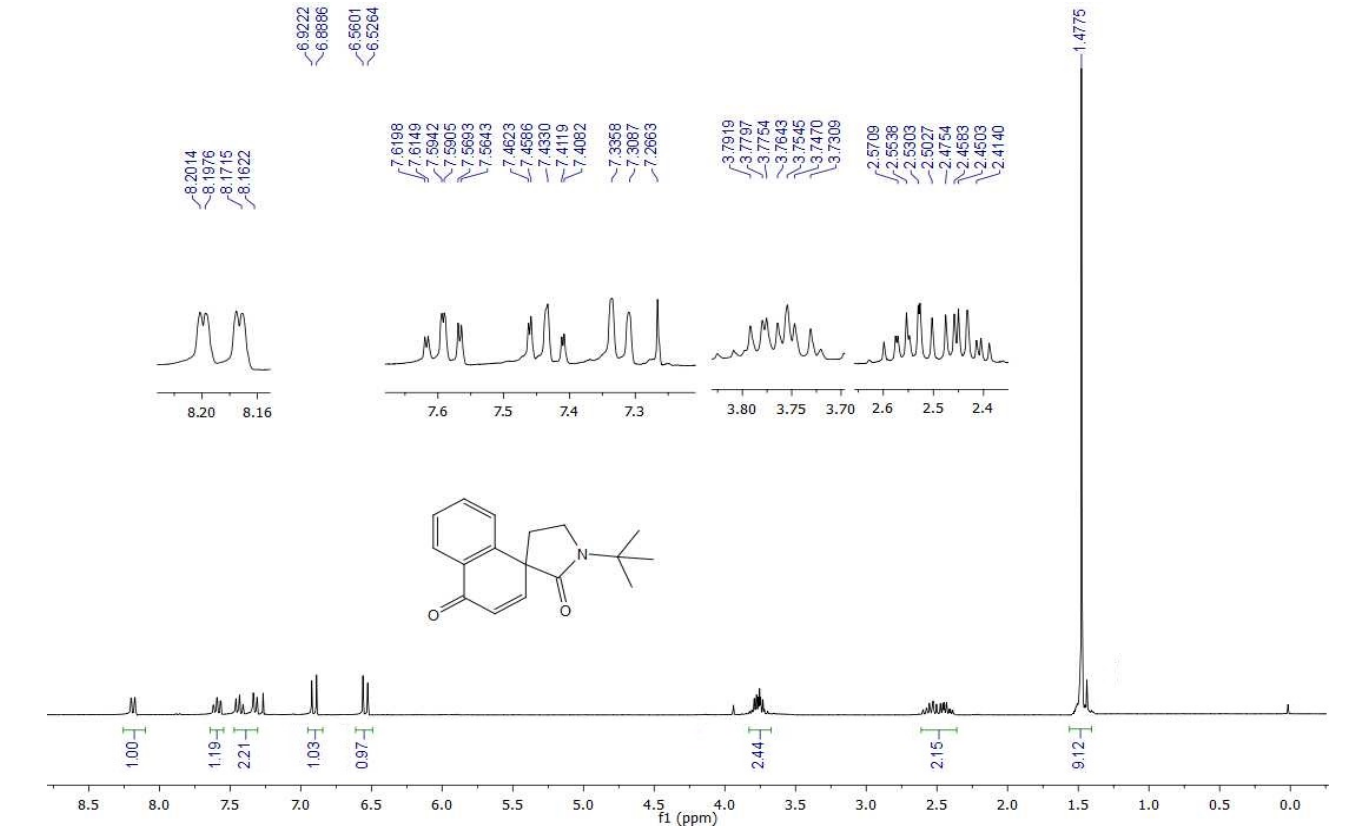
f1 (ppm)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7.5643
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7.3358
7.3087
7.2663
3.7919
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3.7643
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3.7309
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2.5538
2.5303
2.5027
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2.4503
2.4140
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8.20
8.16
7.6
7.5
7.4
7.3
3.80
3.75
3.70
2.6
2.5
2.4
O
N
O
1.00
1.19
2.21
1.03
0.97
2.44
2.15
9.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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1.5
1.0
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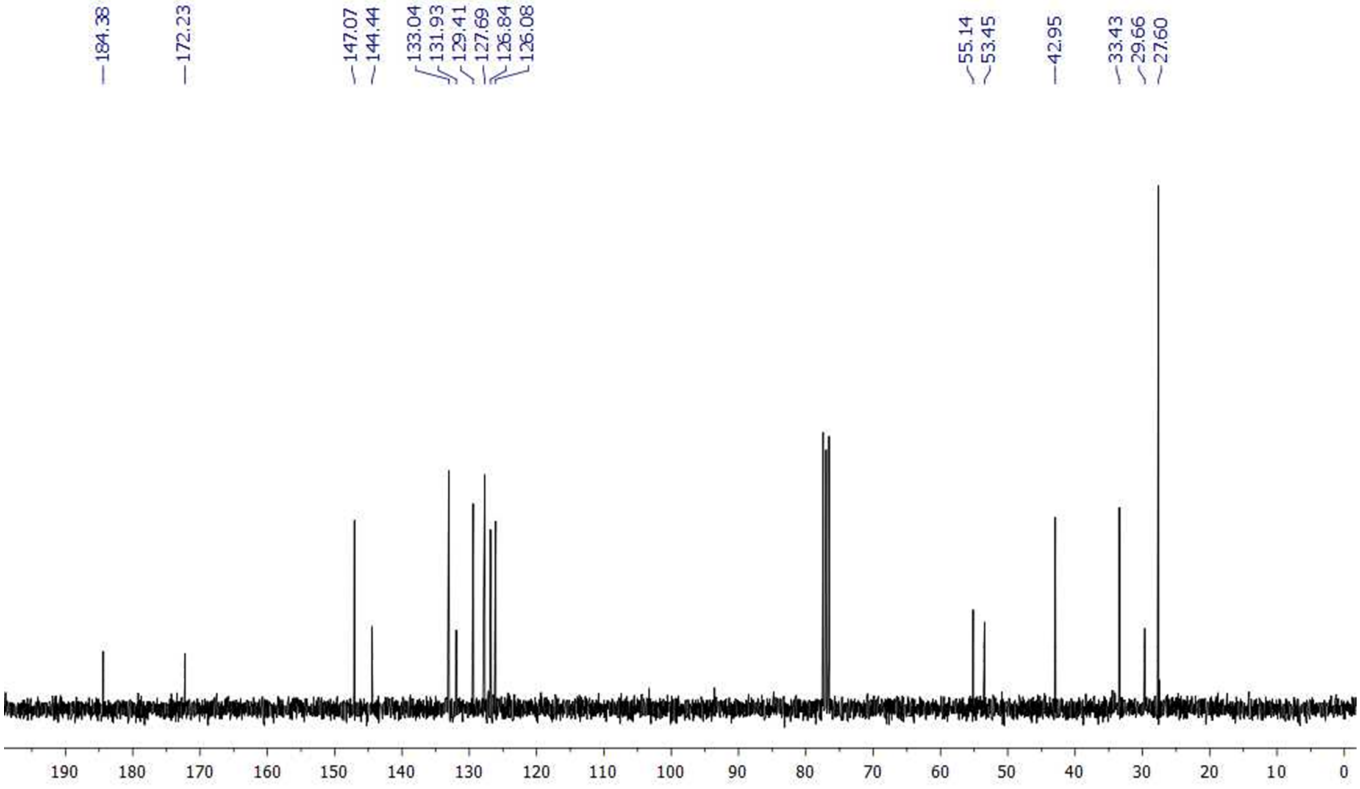
f1 (ppm)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33.43
29.66
27.60
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120
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100
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50
40
30
20
10
0