Supporting information

Black TiO_2 nanoparticles with efficient photocatalytic activity by visible-light and low temperature: Regioselective C-N bond cleavage toward the synthesis of thioureas, sulfonamides, and propargylamines

Mehdi Koohgard[a] and Mona Hosseini-Sarvari*[a]

[a]*Department of Chemistry, Shiraz University, Shiraz 7194684795, I.R. Iran.*

**Correspondence to: Mona Hosseini-Sarvari; E-mail: hossaini@shirazu.ac.ir*

Contents

1) Experimental information

General Information: TiO_2 (the mixture of anatase and rutile, specific surface area: 51-52 m^2g^{-1}, purity: ≥ 99.5, reference: PLS-TiO-P25) was purchased from a local supplier. Starting materials were purchased from commercial suppliers (Acros and Sigmaaldrich) and used without further purification. The solvents ($CHCl_3$, MDL Number: MFCD00000826, EtOH 95%, MDL Number: MFCD00003568) were used without more drying and purification. The phase evolution of the catalyst was characterized by X-ray diffraction technique using Bruker D8-advance X-ray diffractometer with Cu Ka (λ = 1.54178 Å) radiation. The distribution and morphology of the product were analyzed by JEOL, JSM-7610F Fe-SEM. UV–vis diffuse reflectance spectrum was performed with a Shimadzu UV-2450 spectrophotometer. Elemental analysis was performed on a 2400 series PerkinElmer analyzer. Brunauer–Emmett–Teller (BET) surface area, pore volume, and Barret–Joyner–Halenda (BJH) pore size distribution on the basis of nitrogen adsorption–desorption isotherms were determined with a Micromeritics ASSP 2020 equipment. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise noted, using residual solvent peaks as an internal standard or Me_4Si. The spectra were recorded using Bruker Advance DPX FT 250 MHz, Bruker Advance DPX FT 300 MHz, and Bruker Ultrashield 400 MHz spectrometry (multiplicity: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (J): in Hertz (Hz)). FT-IR spectra were obtained by a Shimadzu FT-IR 8300 spectrophotometer. The reactions were monitored by thin layer chromatography (TLC): silica gel PolyGram SIL G/UV 254 plates and visualized by UV lamp at 254 nm. The products purified by hand-made column chromatography: short columns of SiO_2 60 (230–400 mesh) in glass columns (0.5 –1.0 cm). In case of UV irradiation, the reaction was illuminated under an 8 W Xenon UV lamp (Philips), fitted with a 375 nm long-pass cut off filter, which was placed approximately 25 cm below the bottom of the glass plate under a controlled reaction temperature of 25 °C during the experiment; the intensity of UV lamp is 3.90 mW cm^{-2}. 14 W White LED (0.9 W cm^{-2}, 400-700 nm), Blue LED 14 W (0.9 W cm^{-2}, 435-500 nm), Green LED 14 W (0.9 W cm^{-2}, 520-565 nm), Red LED 14 W (0.9 W cm^{-2}, 625-780 nm) were placed in 7 cm from the reaction tube.

The box used for the reactions

Figure S1. The box containing 14 W blue LED lamp (λ > 410 nm) and the reaction setup up.

2) Calculation of band Gap

The optical band gap of the semiconductors can be calculated by using the absorption spectrum and the following equation to draw Tauc plot[1, 2].

Eq.1: $(\alpha h\nu)^{1/n} = A(h\nu - Eg)$

h: Planck's constant, ν: frequency of vibration,
α: absorption (extinction) coefficient
Eg: band gap,
A: proportionality constant
n: the value of the exponent ***n*** denotes the nature of the transition

In this study, this method was applied to estimate the band gap energy value of black TiO_2 and white TiO_2 photocatalyst which obtained from UV–Vis spectra of the coresponding semiconductors[3, 4]. Figure S2 depicts the plot of band-gap energy for black TiO_2 and white TiO_2, obtained by Tauc's equation (1) [5].

Eq.2: $[ahv]^{1/2} = A(hv-Eg)$

The calculated band-gap energy found to be 2.6 eV for black TiO_2 and 3.2 eV for white TiO_2 (anatase), respectively. Noticeably, by treatment of hydrogen with TiO_2, the band-gap of black

TiO_2 was significantly reduced.

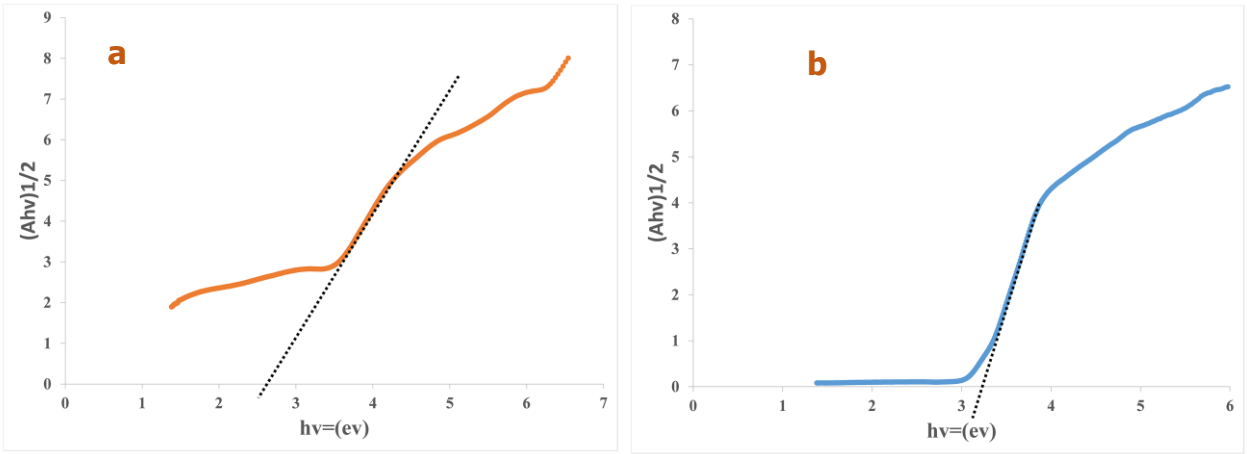


Figure S2. The plot for the band gap calculation of black TiO_2 NPs (a) and white TiO_2 NPs (b).

BJH desorption summary			**BET**
Surface Area	Pore Volume	Pore Diameter (d)	Surface Area
65.231 m^2/g	0.439 cm^3/g	34.268 nm	50.51 m^2/g

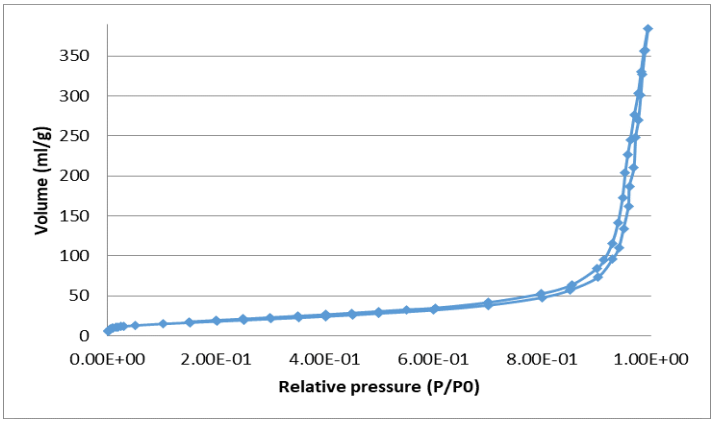
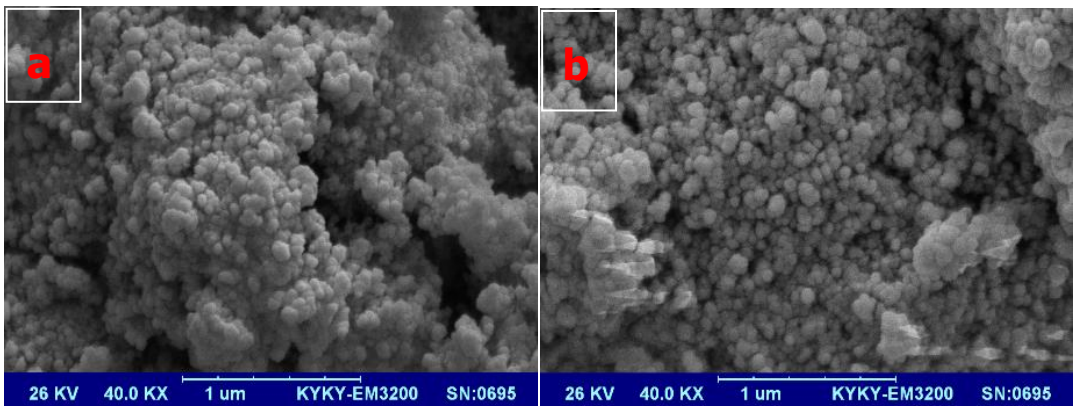


Figure. S3. BJH and BET data, the absorption and desorption isotherm diagram of black TiO_2.



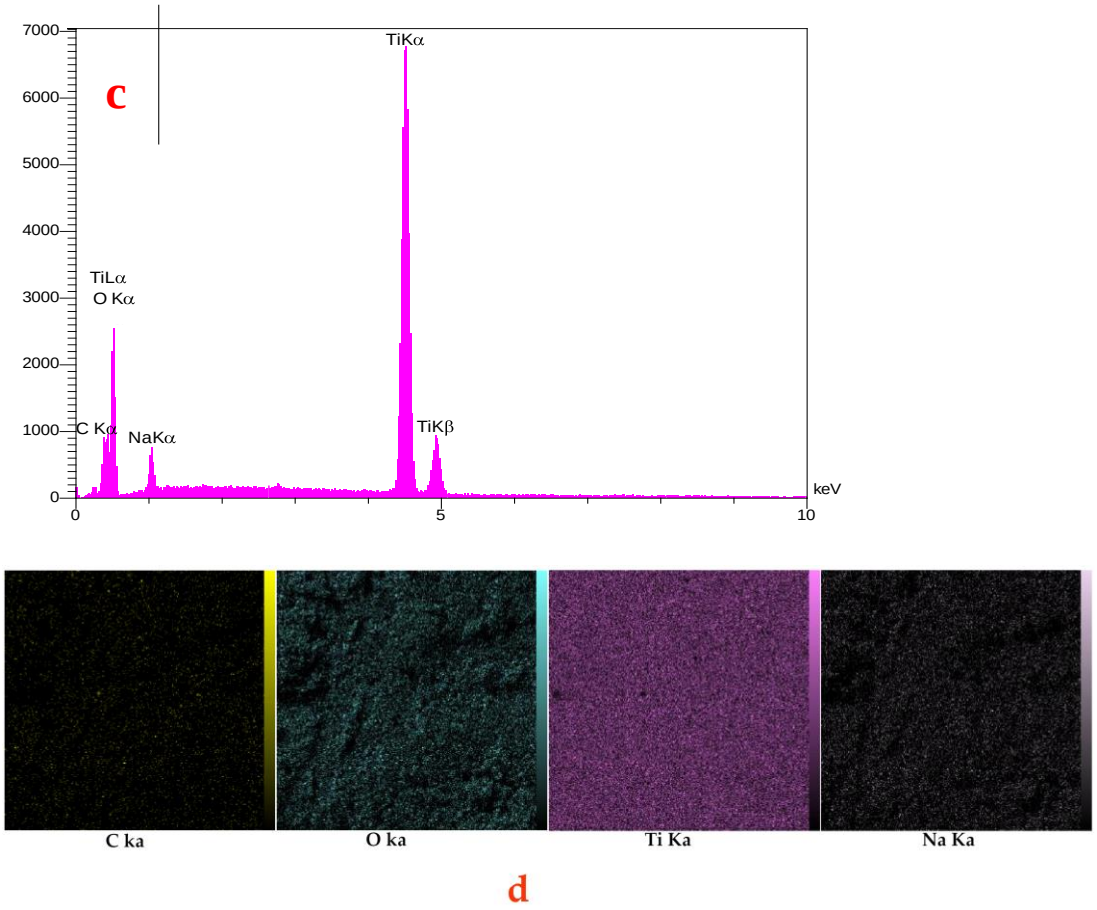
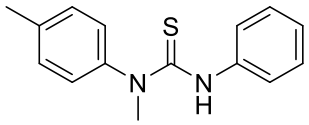


Figure. S4. SEM of black TiO_2 (a) and white TiO_2 (b), EDX (c) and mapping (d) of black TiO_2.

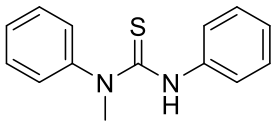
3) Characterization of compounds

1-methyl-3-phenyl-1-(p-tolyl) thiourea (3a)



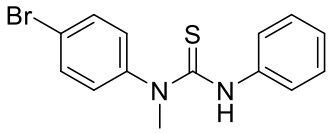
Yellow oil; IR (neat, cm^{-1}): 3371 (NH), 2589, 1519, 1334, 1210 (C=S), 1103, 1025, 763, 694, 547. ^1H NMR (250 MHz, $CDCl_3$) δ (ppm) 2.34 (s, 3H), 3.66 (s, 3H), 6.92 (s, 1H), 7.19-7.04 (m, 3H), 7.26-7.23 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 21.1, 43.5, 125.6, 125.9, 126.7, 128.5, 131.3, 139.0, 139.2, 140.1, 181.3. EA Requires for $C_{15}H_{16}N_2S$: C 70.28, H 6.29, N 10.92, S 12.51. Found: C 70.18, H 6.37, N 11.01, S 12.33.

1-methyl-1,3-diphenylthiourea (3b)[6]



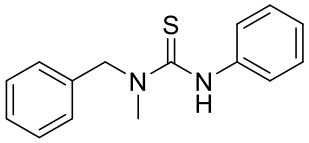
Yellow oil; IR (neat, cm^{-1}): 3355 (NH), 1589, 1504, 1342, 1211 (C=S), 1095, 1094, 763, 745, 683. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 3.66 (s, 3H), 6.90 (s, 1H), 7.15-7.06 (m, 1H), 7.39-7.18 (m, 7H), 7.49-7.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 43.6, 125.7, 126.0, 127.0, 128.6, 128.8, 130.8, 139.2, 142.9, 181.4.

1-(4-bromophenyl)-1-methyl-3-phenylthiourea (3c)



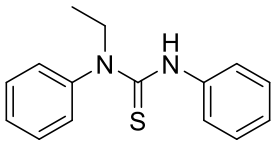
Yellow oil; IR (neat, cm^{-1}): 3213 (NH), 2902, 1597, 1515, 1491, 1386, 1271 (C=S), 1085, 822, 688. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 3.65 (s, 3H) 6.86 (s, 1H), 7.17- 7.09 (m, 3H), 7.25-7.18 (m, 4H), 7.58 (dd, *J*= 8.7 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 43.8, 125.7, 126.2, 128.7, 128.8, 134.0, 138.7, 142.5, 184.9. EA Requires for $C_{14}H_{13}BrN_2S$: C 52.35, H 4.08, N 8.72, S 9.98. Found: C 52.43, H 4.17, N 8.51, S 9.75.

1-benzyl-1-methyl-3-phenylthiourea (3e)[7]



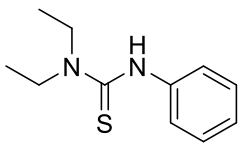
White solid; m.p. = 133-135 ºC, IR (KBr, cm^{-1}): 3232 (NH), 3028, 2812, 1643, 1597, 1496, 1423, 1330, 1247 (C=S), 1018, 860, 745, 655. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 3.16 (s, 3H), 4.97 (s, 2H), 6.98 (s, 1H), 7.19-7.16 (m, 5H), 7.24-7.20 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 44.7, 60.3, 125.3, 125.8, 127.2, 128.8, 129.0, 129.6, 136.7, 138.4, 180.3.

1-ethyl-1,3-diphenylthiourea (3f)[8]



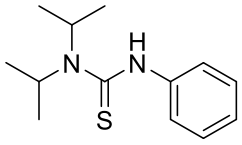
Yellow oil; IR (neat, cm^{-1}): 3242 (NH), 3031, 2912, 1654, 1597, 1496, 1434, 1319, 1247 (C=S), 1118, 860, 745, 688. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.34 (t, *J*= 7.5 Hz 3H), 4.56 (q, *J*= 5 Hz 2H), 7.30-7.06 (m, 10H), 8.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 12.7, 45.7, 125.3, 125.9, 126.7, 127.1, 127.9, 128.8, 140.0, 142.3, 178.7.

1,1-diethyl-3-phenylthiourea (3g)[9]



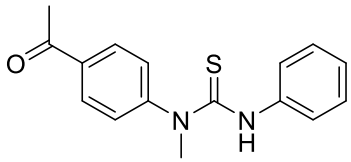
Yellow oil; IR (neat, cm^{-1}): 3229 (NH), 3038, 2975, 2931, 1695, 1518, 1452, 1404, 1350, 1137 (C=S), 1075, 1004, 910, 896, 761, 698. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 1.25 (t, *J*= 5 Hz, 6H), 3.71 (q, *J*= 7.5 Hz, 4H), 6.92 (s, 1H), 7.337.22 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 14.1, 42.2, 124.5, 125.7, 129.9, 140.8, 179.4.

1,1-diisopropyl-3-phenylthiourea (3h)[10]



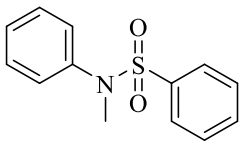
Yellow oil; IR (neat, cm^{-1}): 3216 (NH), 3041, 2952, 1677, 1512, 1413, 1129 (C=S), 1049, 916, 873, 689. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.32 (d, *J* = 6.6 Hz, 12H), 4.05 (sept, *J* = 6.4 Hz, 2H), 6.27 (s, 1H), 6.13-6.18 (m, 2H), 7.34-7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 20.9, 49.6, 124.2, 124.6, 128.7, 141.0, 155.3.

1-(4-acetylphenyl)-1-methyl-3-phenylthiourea (3j)



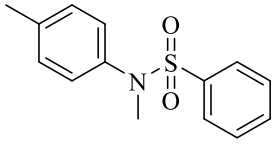
Yellow oil; IR (neat, cm^{-1}): 3383 (NH), 2565, 1793, 1511, 1326, 1216 (C=S), 1014, 759, 687, 541. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ 2.58 (s, 3H), 3.53 (s, 3H), 6.74 (s, 1H), 7.08 – 7.24 (m, 1H), 7.18 – 7.47 (m, 2H), 7.57 – 7.72 (m, 4H), 7.72 – 7.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 26.4, 37.0, 120.1, 124.2, 124.3, 128.7, 130.2, 140.3, 145.7, 179.7, 196.6. EA Requires for $C_{16}H_{16}N_2OS$: C 67.58, H 5.67, N 9.85, S 11.27. Found: C 67.68, H 5.49, N 9.71, S 11.13.

***N*-methyl-*N*-phenylbenzenesulfonamide (5a)[11]**



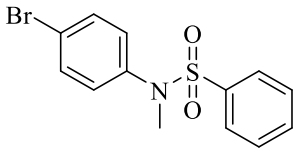
White solid; m.p. = 77-79 ºC. IR (neat, cm^{-1}): 3075, 2984, 1357, 1188, 1162. ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.10 (s, 3H), 6.97 – 7.05 (m, 2H), 7.16 – 7.27 (m, 3H), 7.32 – 7.42 (m, 2H), 7.43 – 7.55 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 36.3, 124.8, 125.6, 126.0, 126.9, 127.1, 131.0, 134.6, 139.7.

***N*-methyl-*N*-phenylbenzenesulfonamide (5b)[12]**



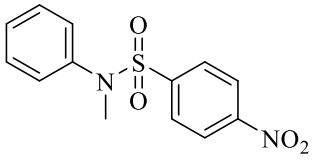
White solid; m.p. = 65-67 ºC. IR (neat, cm^{-1}): 3024, 1349. 1309. 1179. 1168. 1163. ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.15 (s, 3H), 6.95 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 7.37 – 7.50 (m, 2H), 7.53 – 7.62 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 19.2, 36.5, 124.7, 126.1, 126.9, 127.7, 129.1, 130.8, 135.5, 137.0.

N-(4-bromophenyl)-N-methylbenzenesulfonamide (5c)[13]



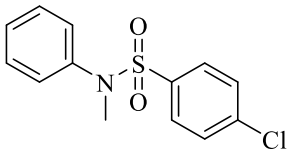
White solid; m.p. = 74-76 ºC. IR (neat, cm^{-1}): 3116, 1593, 1523, 1343, 1164, 1056. ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.07 (s, 3H), 6.85 – 6.95 (m, 2H), 7.33 – 7.54 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.99, 127.80, 128.14, 128.52, 128.89, 130.92, 132.04, 133.02, 136.04.

N-methyl-4-nitro-N-phenylbenzenesulfonamide (5e)[14]



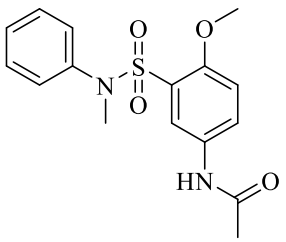
Light yellow solid; m.p. = 129-131. ºC. IR (neat, cm^{-1}): 3109, 1603, 1518, 1338, 1159, 1081. ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.07 (s, 3H), 6.89 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.56 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 38.0, 127.8, 128.1, 128.8, 128.9, 130.9, 132.0, 133.0, 136.0, 140.6.

4-chloro-N-methyl-N-phenylbenzenesulfonamide (5f)[15]



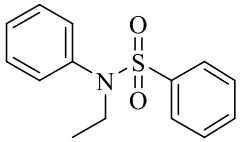
White solid; m.p. = 94-96. ºC. IR (neat, cm^{-1}): 3102, 1593, 1521, 1321, 1166, 1093. ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.11 (s, 3H), 6.94 – 6.99 (m, 2H), 7.22 – 7.26 (m, 2H), 7.40 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.47 – 7.55 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 38.7, 127.7, 127.9, 128.8, 128.8, 129.0, 129.0, 130.9, 132.5.

N-(4-methoxy-3-(N-methyl-N-phenylsulfamoyl)phenyl)acetamide (5g)



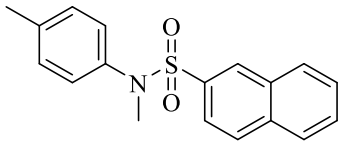
White solid; IR (neat, cm^{-1}): 3015, 1583, 1516, 1342, 1171, 1083. ^1H NMR (250 MHz, DMSO- d_6) δ 1.96 (s, 3H), 3.26 (s, 3H), 3.73 (s, 3H), 7.18- 7.11 (m, 4H), 7.22 – 7.31 (m, 2H), 7.77 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.87 (d, *J* = 2.6 Hz, 1H), 10.01 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 23.63, 38.50, 56.03, 113.14, 121.31, 125.32, 125.42, 125.92, 126.39, 128.85, 131.79, 141.13, 152.13. EA Requires for $C_{16}H_{18}N_2O_4S$: C 57.47, H 5.43, N 8.38, S 9.59. Found: C 57.39, H 5.37, N 8.33, S 9.47.

N-ethyl-N-phenylbenzenesulfonamide (5h)[16]



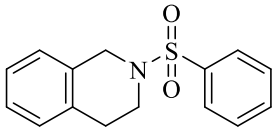
Yellowish solid; m.p. = 37-39 ºC. IR (neat, cm^{-1}): 3034, 1353, 1309. 1179. 1168. 1088. ^1H NMR (250 MHz, $CDCl_3$) δ 1.01 (t, *J* = 7.1 Hz, 3H), 3.55 (q, *J* = 7.1 Hz, 2H), 6.94 – 7.01 (m, 2H), 7.20 – 7.29 (m, 3H), 7.34 – 7.43 (m, 2H), 7.44 – 7.56 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.05, 45.62, 127.65, 127.94, 128.76, 128.81, 128.97, 129.01, 130.91, 132.54.

N-methyl-N-(p-tolyl)naphthalene-2-sulfonamide (5i)



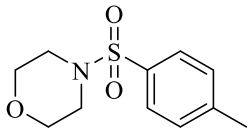
White solid; . IR (neat, cm^{-1}): 3106, 1596, 1363, 1098, 837. ^1H NMR (250 MHz, $CDCl_3$) δ 3.29 (s, 3H), 4.16 (s, 3H), 7.94 (dd, *J* = 8.5, 2.2 Hz, 2H), 8.01 – 8.08 (m, 2H), 8.42 – 8.64 (m, 3H), 8.80 – 8.90 (m, 3H), 9.15 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.08, 38.44, 123.35, 126.69, 127.46, 127.91, 128.77, 128.83, 129.15, 129.27, 129.57, 132.04, 134.84, 137.43, 138.92. EA Requires for $C_{18}H_{17}NO_2S$: C 69.43, H 5.50, N 4.50, S 10.30. Found: C 69.36, H 5.41, N 4.31, S 10.14.

2-(phenylsulfonyl)-1,2,3,4-tetrahydroisoquinoline (5j)[17]



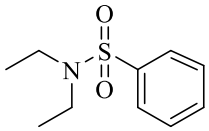
Yellowish solid; m.p. = 156-158 ºC. IR (neat, cm^{-1}): 3102, 1614, 1350, 1170. ^1H NMR (300 MHz, $CDCl_3$) δ 2.98 – 2.94 (m, 2H), 3.44 – 3.37 (m, 2H), – 4.30 (s, 2H), 6.81 – 7.30 (m, 4H), 7.64 –7.53 (m, 3H), 7.77 – 7.96 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.8, 43.7, 47.5, 126.4, 126.8, 127.7, 128.8, 129.1, 131.5, 132.8, 133.0, 136.4.

4-(phenylsulfonyl)morpholine (5k)[18]



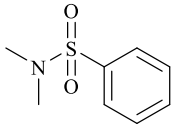
White solid; m.p. = 146-148 ºC. IR (neat, cm^{-1}): 2981, 2849, 1463, 1353, 1172. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 3H), 2.99 (t, *J* = 4.6 Hz, 4H), 3.74 (t, *J* = 4.7 Hz, 4H), 7.35 (dd, *J* = 8.1, 3.5 Hz, 2H), 7.65 (dd, *J* = 7.7, 3.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 46.0, 66.1, 127.9, 129.7, 132.1, 143.9.

N,N-diethylbenzenesulfonamide (5l)[19]



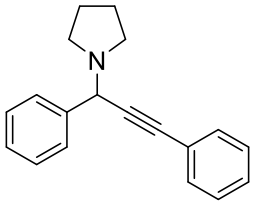
White solid; m.p. = 38-40 ºC. IR (neat, cm^{-1}): 1439, 1348, 1167, 1084. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.2 Hz, 6H), 3.18 (q, *J* = 7.1 Hz, 4H), 7.37 – 7.55 (m, 3H), 7.61 – 7.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.14, 42.02, 127.83, 129.00, 132.24, 133.67.

***N,N*-dimethylbenzenesulfonamide (5m)**[20]



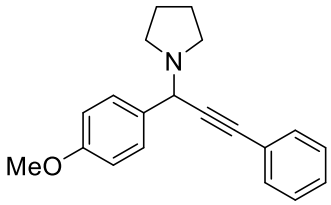
Yellowish solid; m.p. = 44-46 ºC. IR (neat, cm^{-1}): 1442, 1341, 1158, 989, 738 . ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 – 2.65 (m, 6H), 7.43 – 7.57 (m, 3H), 7.70 (dt, *J* = 8.4, 1.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.94, 127.70, 129.04, 132.75.

1-(1,3-diphenylprop-2-yn-1-yl)pyrrolidine (11a) [21]



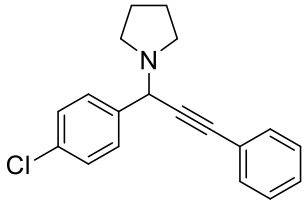
Oil. IR (KBr, cm^{-1}): ν= 2963, 2871, 2809, 2219, 1684, 1601, 1486, 1275, 1121. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.62 – 1.81 (m, 4H), 2.67 (q, *J* = 6.5, 4.3 Hz, 4H), 4.89 (s, 1H), 7.20 – 7.32 (m, 6H), 7.44-7.37 (m, 2H), 7.49 – 7.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.1, 51.9, 60.1, 84.1, 86.7, 123.1, 127.4, 128.5, 129.1, 129.4, 129.5, 132.1, 137.4.

1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (11b) [22]



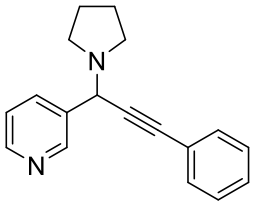
Oil. IR (KBr, cm^{-1}): ν= 2959, 2809, 2201, 1607, 1517, 1462, 1253. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.69 (t, *J* = 5.0 Hz, 4H), 2.59 (t, *J* = 6.5 Hz, 4H), 3.68 (s, 3H), 4.74 (s, 1H), 6.67 – 6.86 (m, 2H), 7.13 – 7.25 (m, 3H), 7.31 – 7.50 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.1, 51.9, 55.3, 59.9, 84.0, 86.7, 114.3, 123.1, 128.4, 128.5, 129.1, 130.4, 132.1, 159.3.

1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (11c) [23]



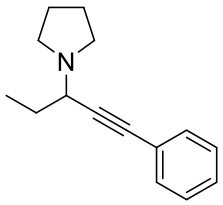
Oil. IR (KBr, cm^{-1}): ν= 2961, 2867, 2811, 2221, 1678, 1594, 1449, 1275, 761. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.80 – 1.65 (m, 4H), 2.64 (q, *J* = 6.4 Hz, 4H), 4.87 (s, 1H), 7.18 – 7.28 (m, 4H), 7.34 – 7.43 (m, 2H), 7.48 (dd, *J* = 8.8, 2.2 Hz, 2H), 7.70 – 8.0 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.0, 51.9, 59.6, 84.0, 86.7, 123.1, 128.5, 128.8, 129.0, 129.48, 132.0, 135.5, 135.6.

3-(3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-yl)pyridine (11d)



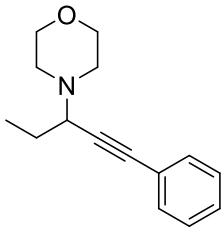
Oil. IR (KBr, cm^{-1}): ν= 2962, 2900, 2808, 2229, 1674, 1596, 1439, 1280. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.82 (t, *J* = 5.6 Hz, 4H), 2.71 (t, *J* = 5.5 Hz, 4H), 4.98 (s, 1H), 7.29 – 7.36 (m, 4H), 7.45 – 7.53 (m, 2H), 7.96 (dt, *J* = 7.9, 1.9 Hz, 1H), 8.56 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.85 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.1, 51.9, 59.3, 84.1, 86.7, 123.1, 125.0, 128.5, 129.1, 132.1, 132.3, 135.0, 148.5, 150.7. EA Requires for $C_{18}H_{18}N_2$: C 82.41, H 6.92, N 10.68. Found: C 82.38, H 6.77, N 10.41.

1-(1-phenylpent-1-yn-3-yl)pyrrolidine (11e)



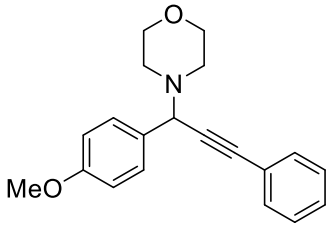
Oil. IR (KBr, cm^{-1}): ν= 2877, 2229, 1342, 1141. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.99 – 1.17 (m, 3H), 1.70 – 1.87 (m, 6H), 2.58 – 2.88 (m, 4H), 3.63 – 3.55 (m, 1H), 7.33 – 7.21 (m, 3H), 7.45 – 7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.9, 24.1, 26.2, 52.1, 56.6, 84.3, 87.1, 124.4, 128.5, 129.1, 132.1. EA Requires for $C_{15}H_{19}N$: C 84.46, H 8.98, N 6.57. Found: C 84.48, H 8.69, N 6.34.

4-(1-phenylpent-1-yn-3-yl)morpholine (11f) [24]



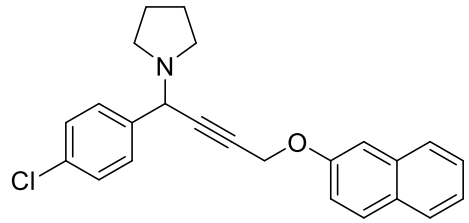
Oil. IR (KBr, cm^{-1}): ν= 2884, 2231, 1592, 1448, 1121. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.92 – 1.16 (m, 3H), 1.80 – 1.65 (m, 2H), 2.55 (dd, *J* = 9.8, 4.4 Hz, 2H), 2.72 (dd, *J* = 10.0, 4.1 Hz, 2H), 3.32 – 3.48 (m, 1H), 3.63 – 3.87 (m, 4H), 7.30 – 7.24 (m, 3H), 7.46 – 7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.9, 26.2, 51.0, 57.9, 66.8, 84.0, 86.7, 124.4, 128.5, 129.1, 132.1.

4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)morpholine (11g) [25]



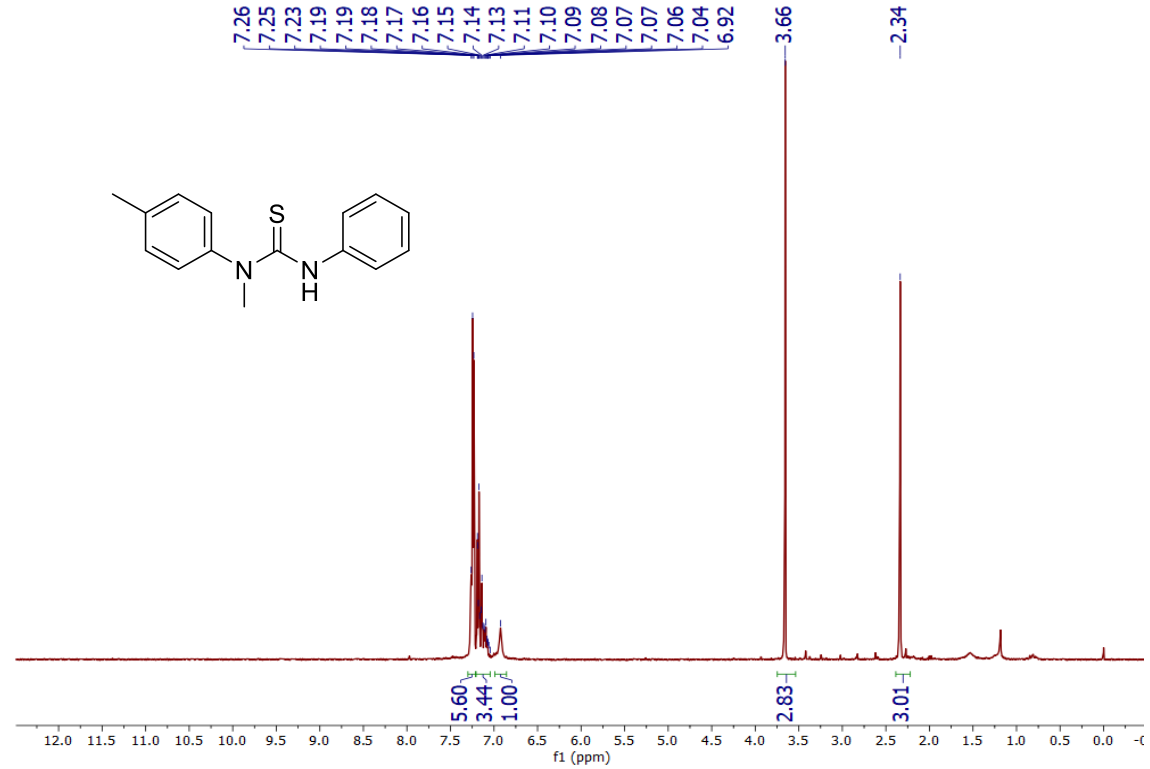
Oil. IR (KBr, cm^{-1}): ν= 2964, 2872, 2811, 2218, 1631, 1511, 1491, 1313, 1283. ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.65 – 2.59 (m, 4H), 3.76 – 3.70 (m, 4H), 3.83 – 3.79 (m, 3H), 4.76 – 4.69 (m, 1H), 6.94 – 6.87 (m, 2H), 7.35 – 7.30 (m, 3H), 7.58 – 7.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.1, 55.3, 60.3, 66.7, 84.2, 87.5, 114.3, 123.1, 128.5, 128.5, 129.1, 131.4, 132.1, 159.3.

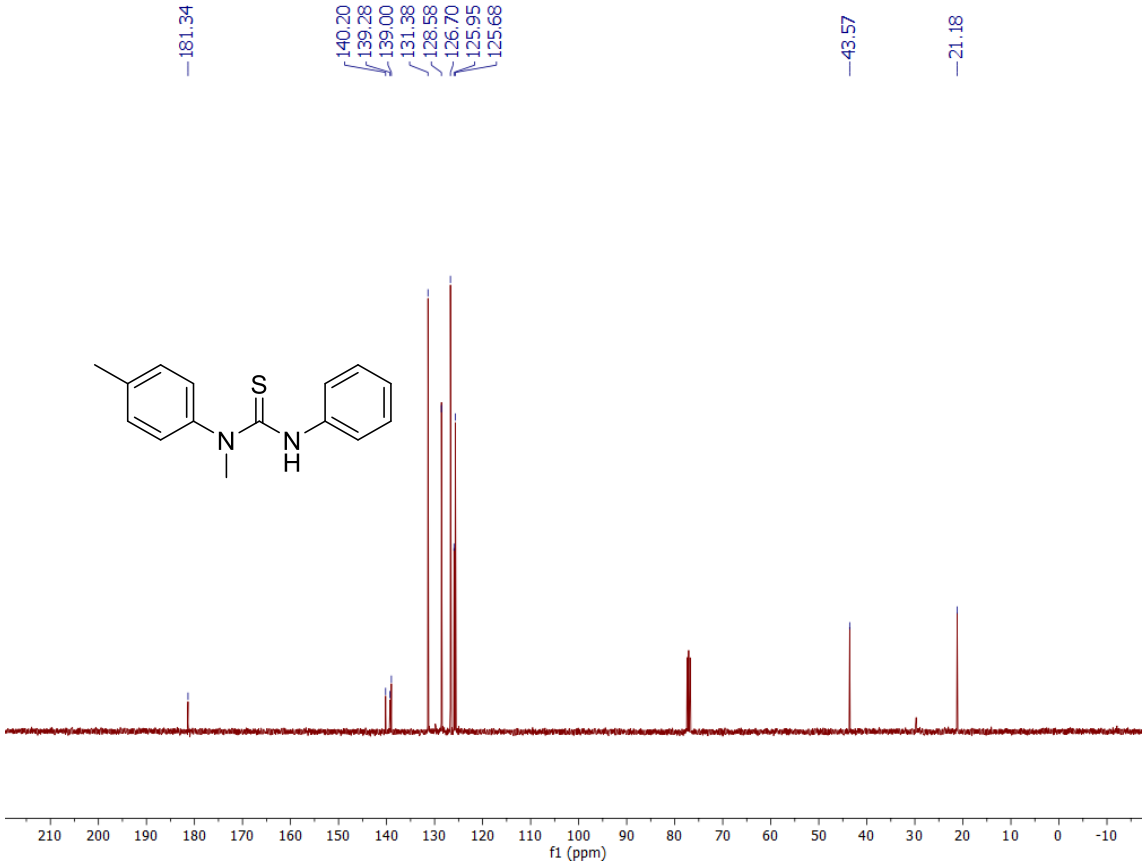
1-(1-(4-chlorophenyl)-4-(naphthalen-2-yloxy)but-2-yn-1-yl)pyrrolidine (11h)

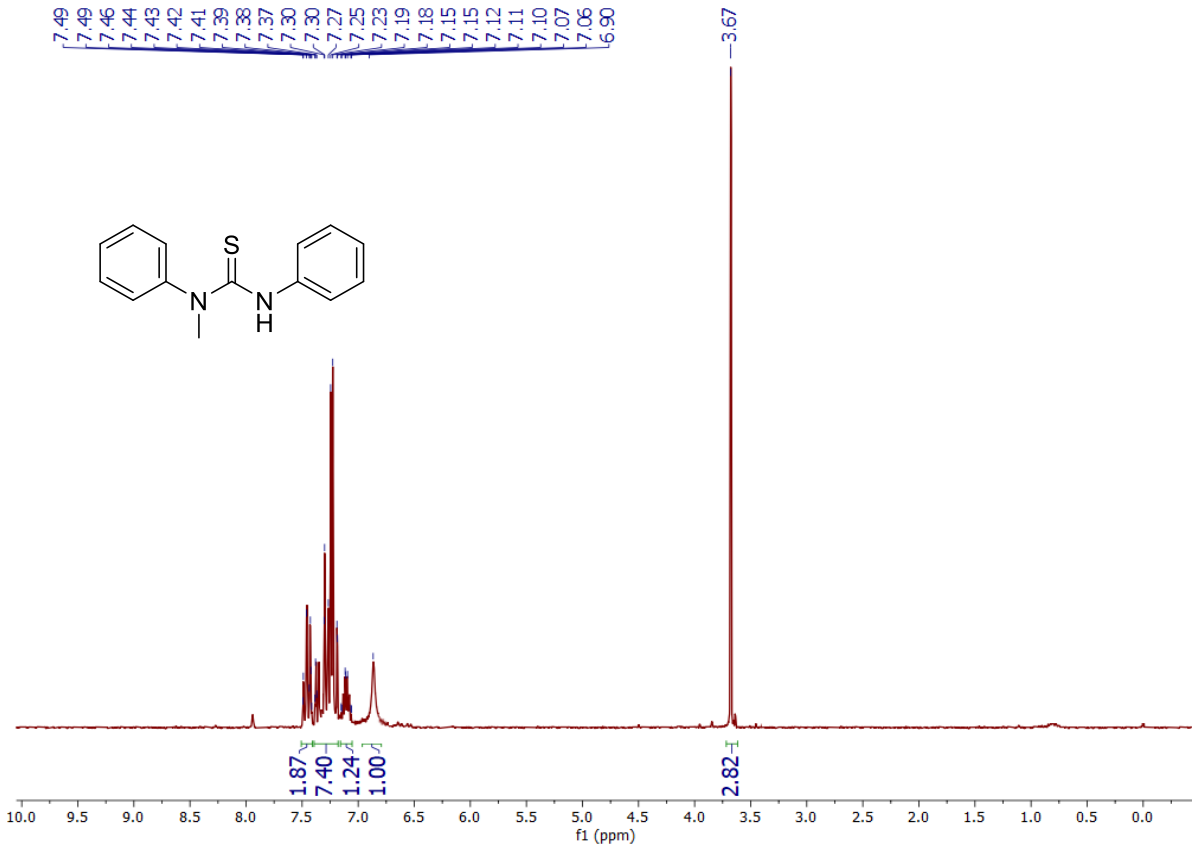


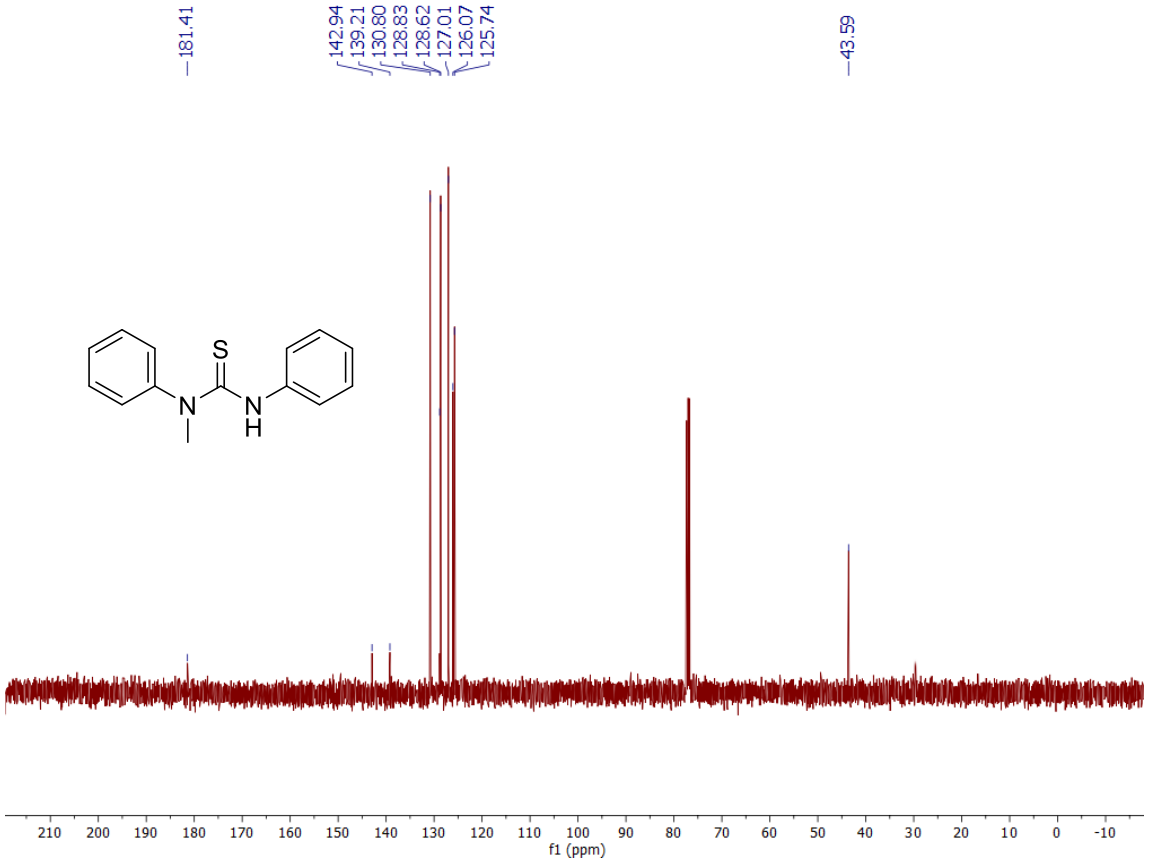
Oil. IR (KBr, cm^{-1}): ν= 2962, 2869, 2815, 2245, 1627, 1596, 1465, 1396, 840. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.66 (t, *J* = 6.5 Hz, 4H), 2.48 – 2.60 (m, 4H), 4.71 (s, 1H), 4.95 (s, 2H), 7.18 – 7.27 (m, 3H), 7.32 (d, *J* = 2.5 Hz, 1H), 7.36 – 7.52 (m, 4H), 7.69 – 7.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.1, 51.9, 54.2, 59.5, 76.1, 84.5, 111.0, 116.5, 126.2, 126.7, 127.8, 128.3, 128.5, 128.8, 129.2, 129.5, 133.0, 135.6, 136.0, 155.7. EA Requires for $C_{24}H_{22}ClNO$: C 76.69, H 5.90, N 3.73. Found: C 76.71, H 5.99, N 3.81.

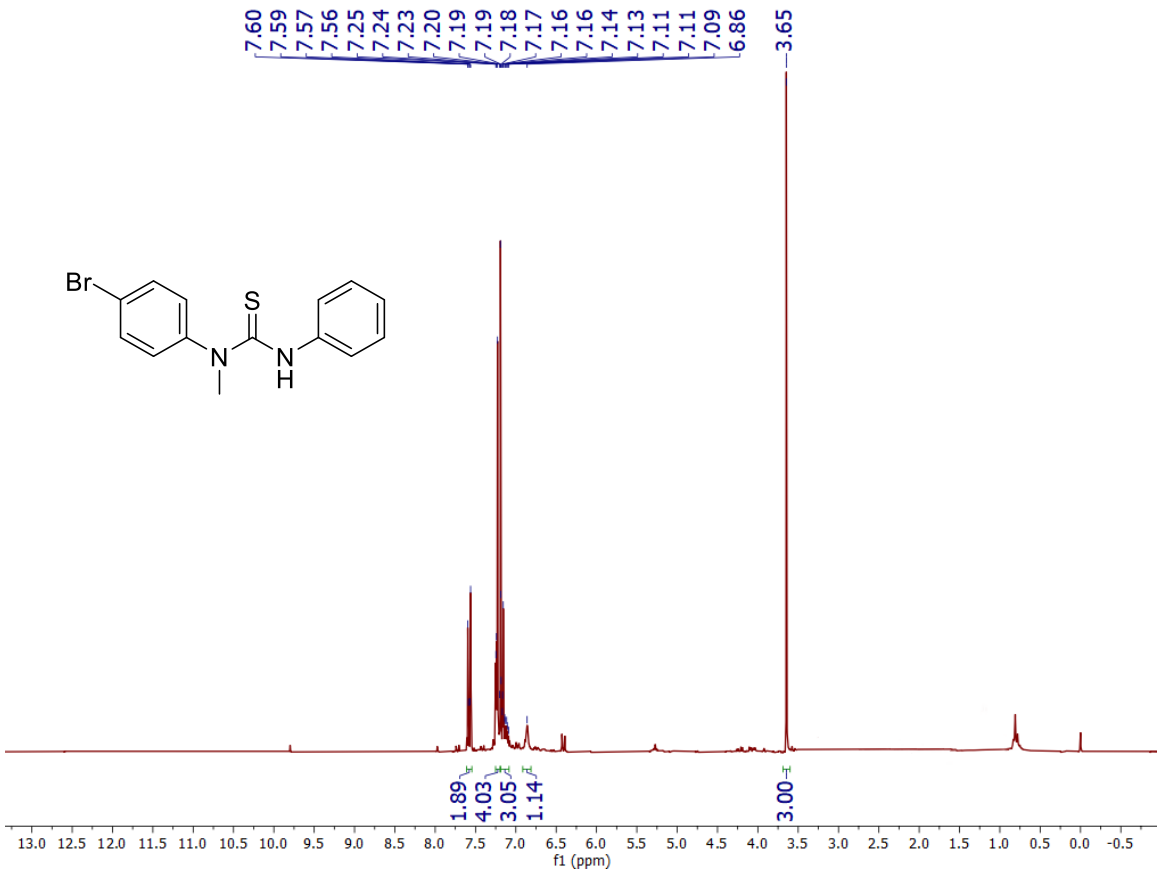
4) ^{1}H and ^{13}C NMR Spectra of Products.

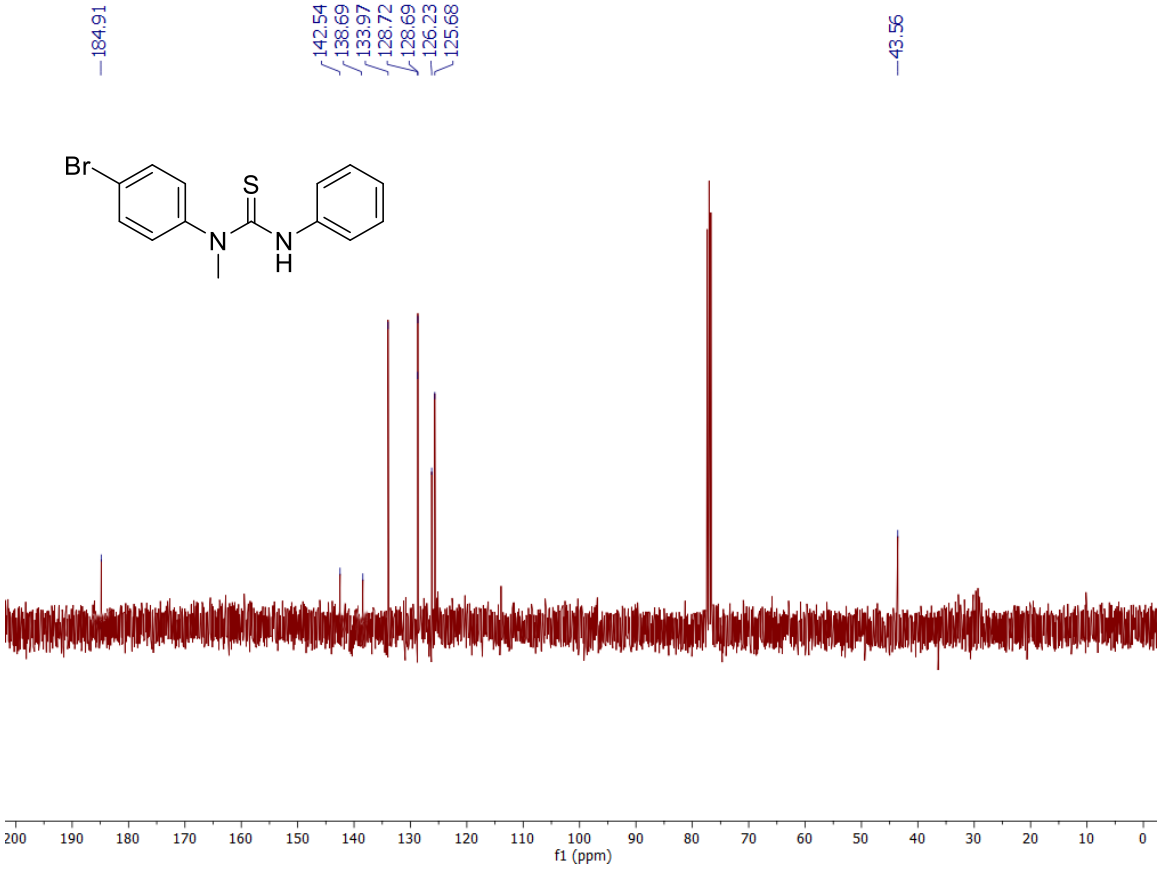


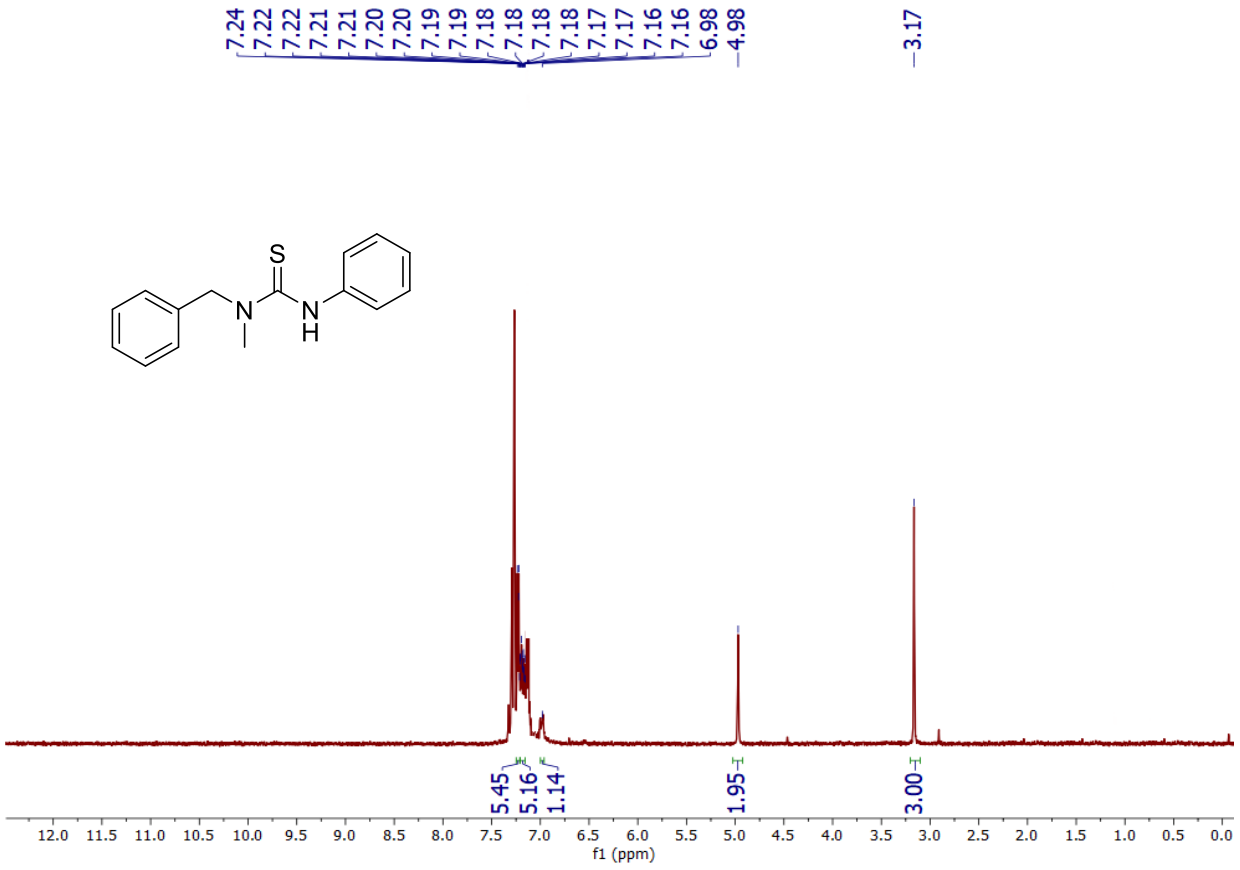


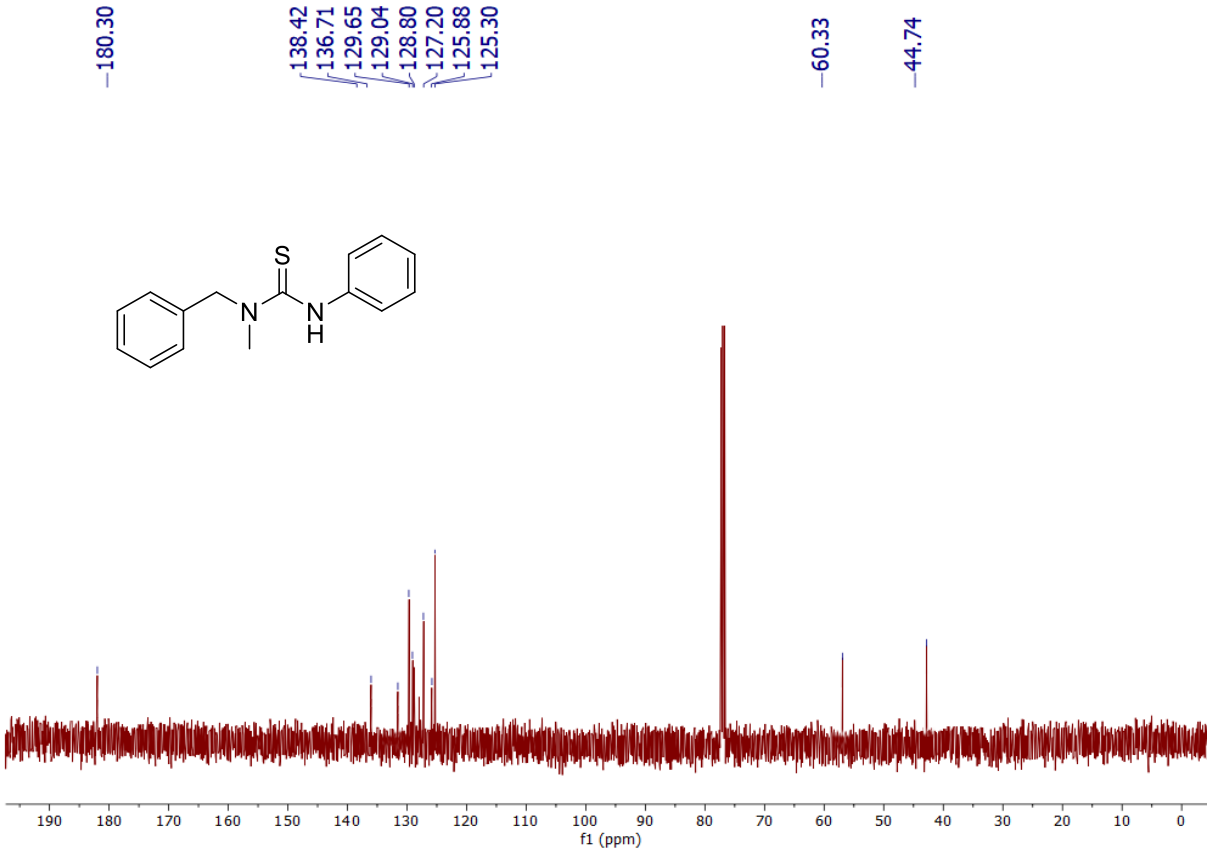

7.49
7.49
7.46
7.44
7.43
7.42
7.41
7.39
7.38
7.37
7.30
7.30
7.27
7.25
7.23
7.19
7.18
7.15
7.15
7.12
7.11
7.10
7.07
7.06
6.90
3.67
S
N
N
H
1.87
7.40
1.24
1.00
2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

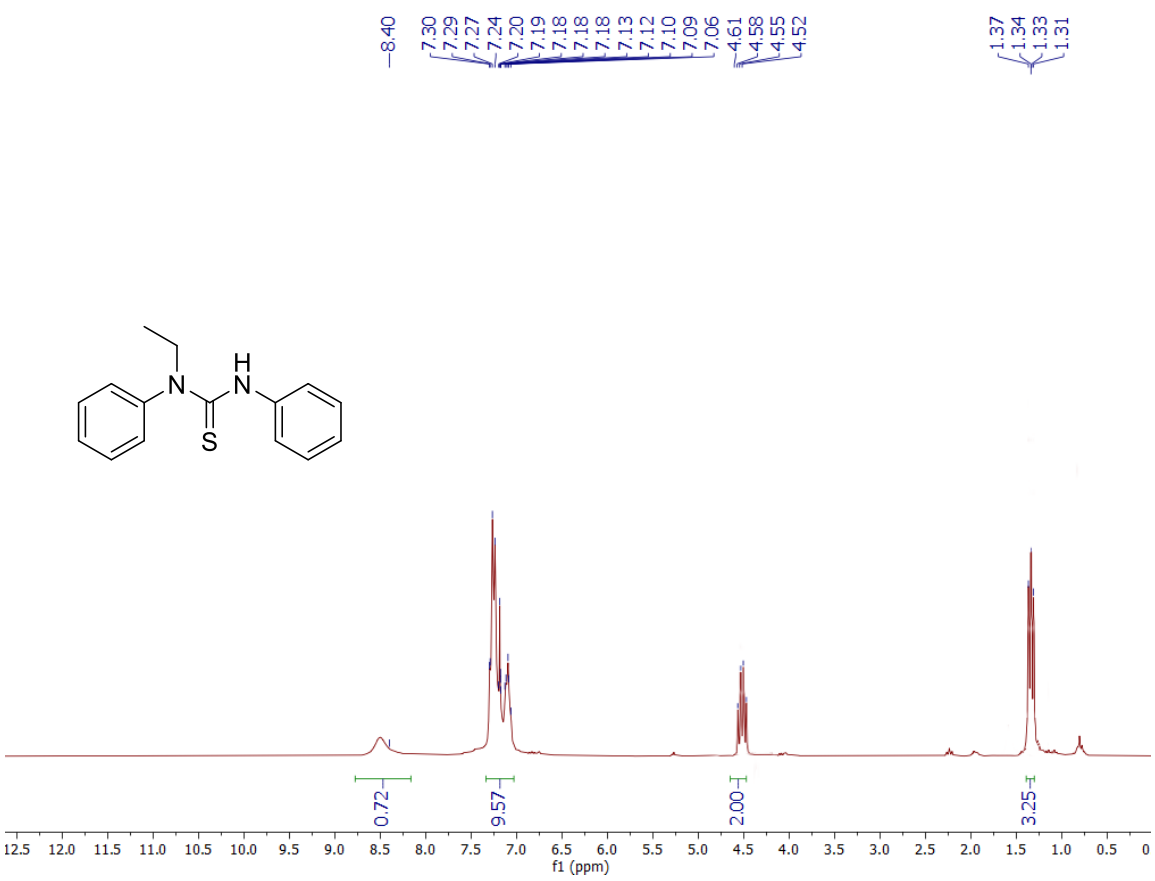

181.41
142.94
139.21
130.80
128.83
128.62
127.01
126.07
125.74
43.59
S
N
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

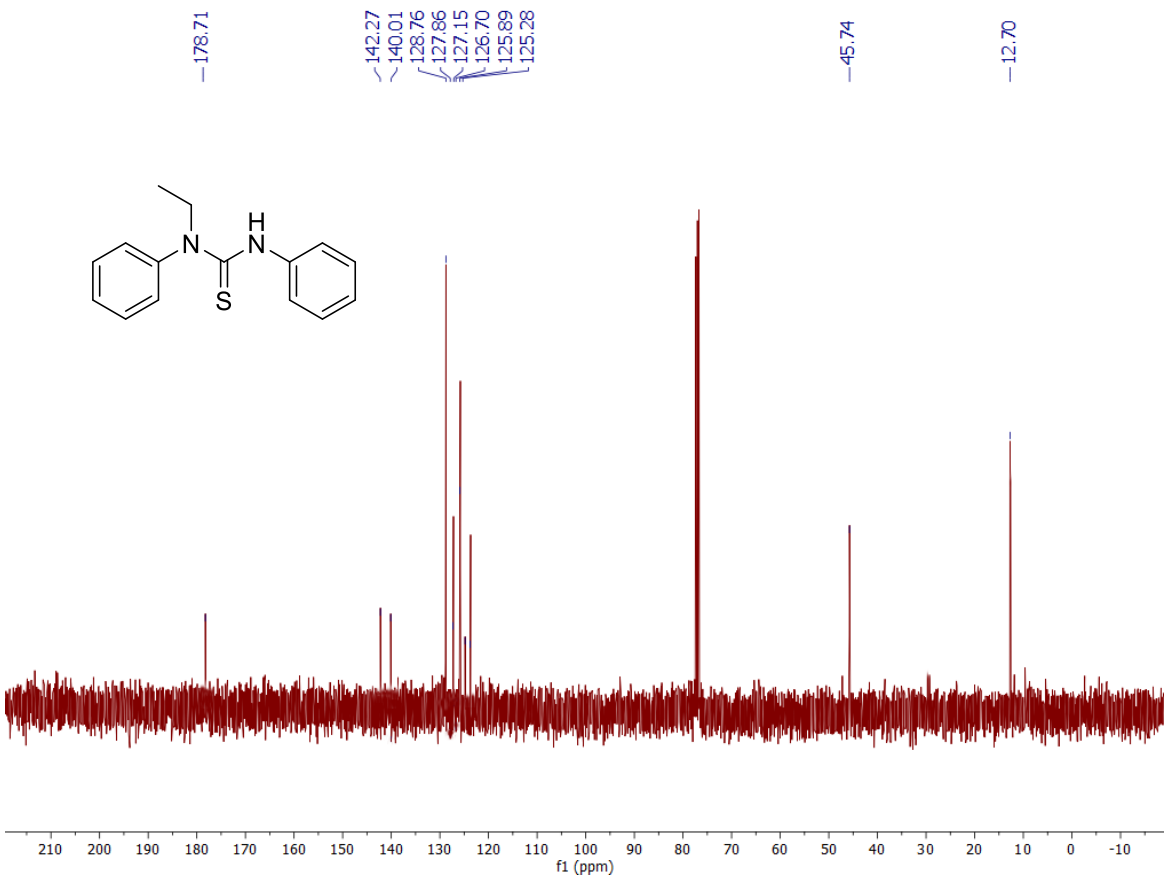

7.60
7.59
7.57
7.56
7.25
7.24
7.23
7.20
7.19
7.19
7.18
7.17
7.16
7.16
7.14
7.13
7.11
7.11
7.09
6.86
3.65
Br
S
N
N
H
1.89
4.03
3.05
1.14
3.00
f1 (ppm)

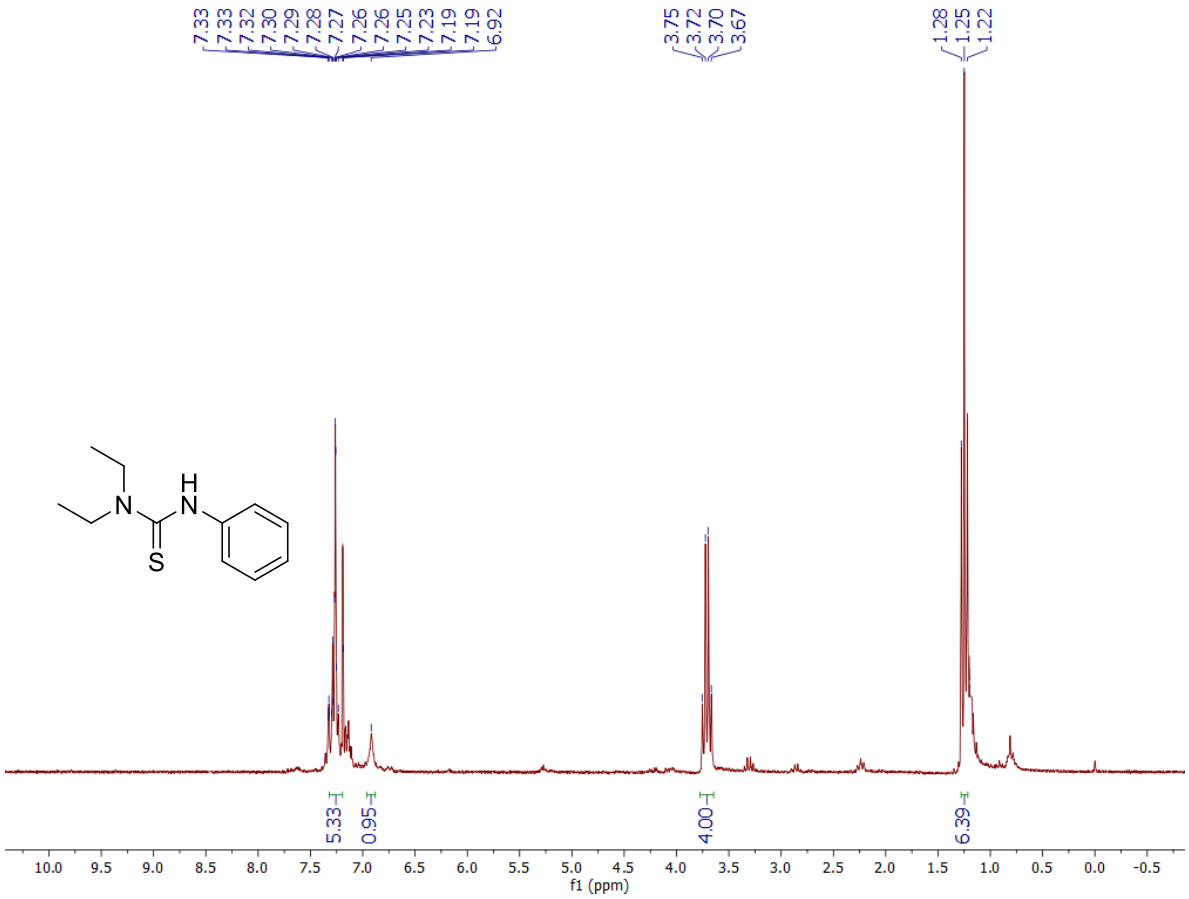

184.91
142.54
138.69
133.97
128.72
128.69
126.23
125.68
43.56
Br
S
N
N
H
f1 (ppm)

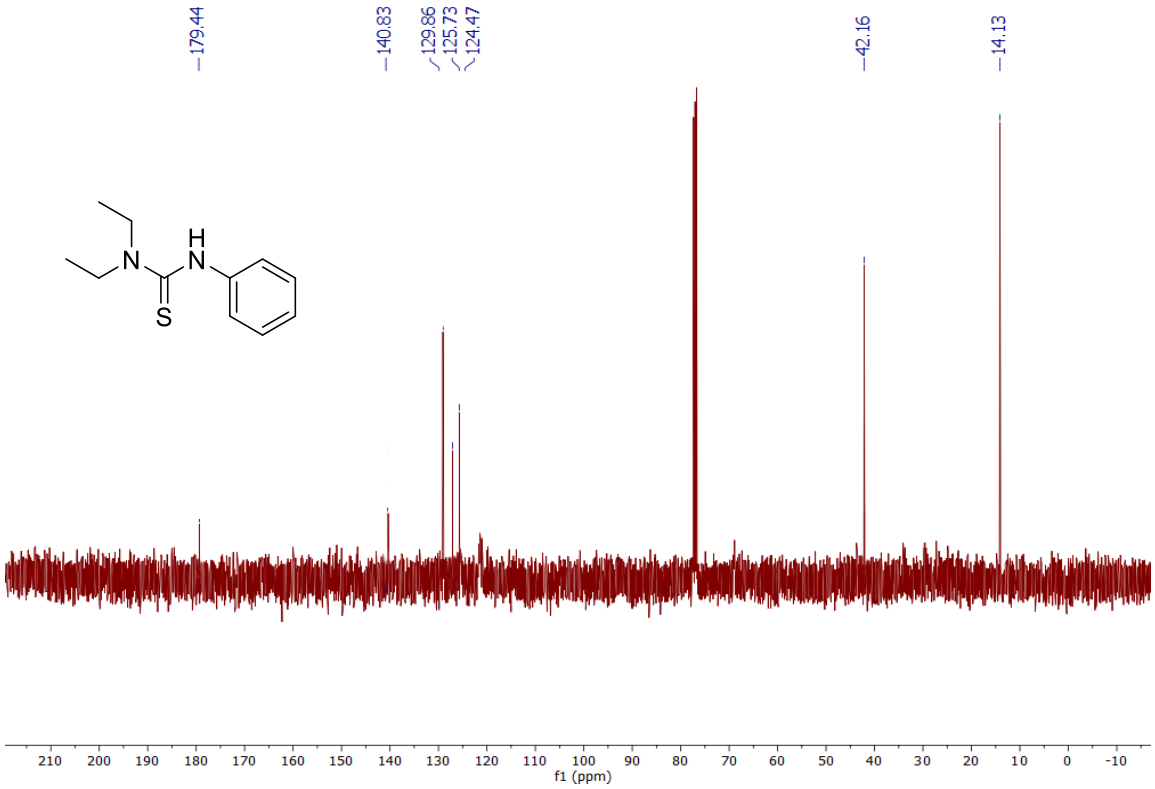

7.24
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.18
7.18
7.17
7.17
7.16
7.16
6.98
4.98
3.17
S
N
N
H
5.45
5.16
1.14
1.95
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

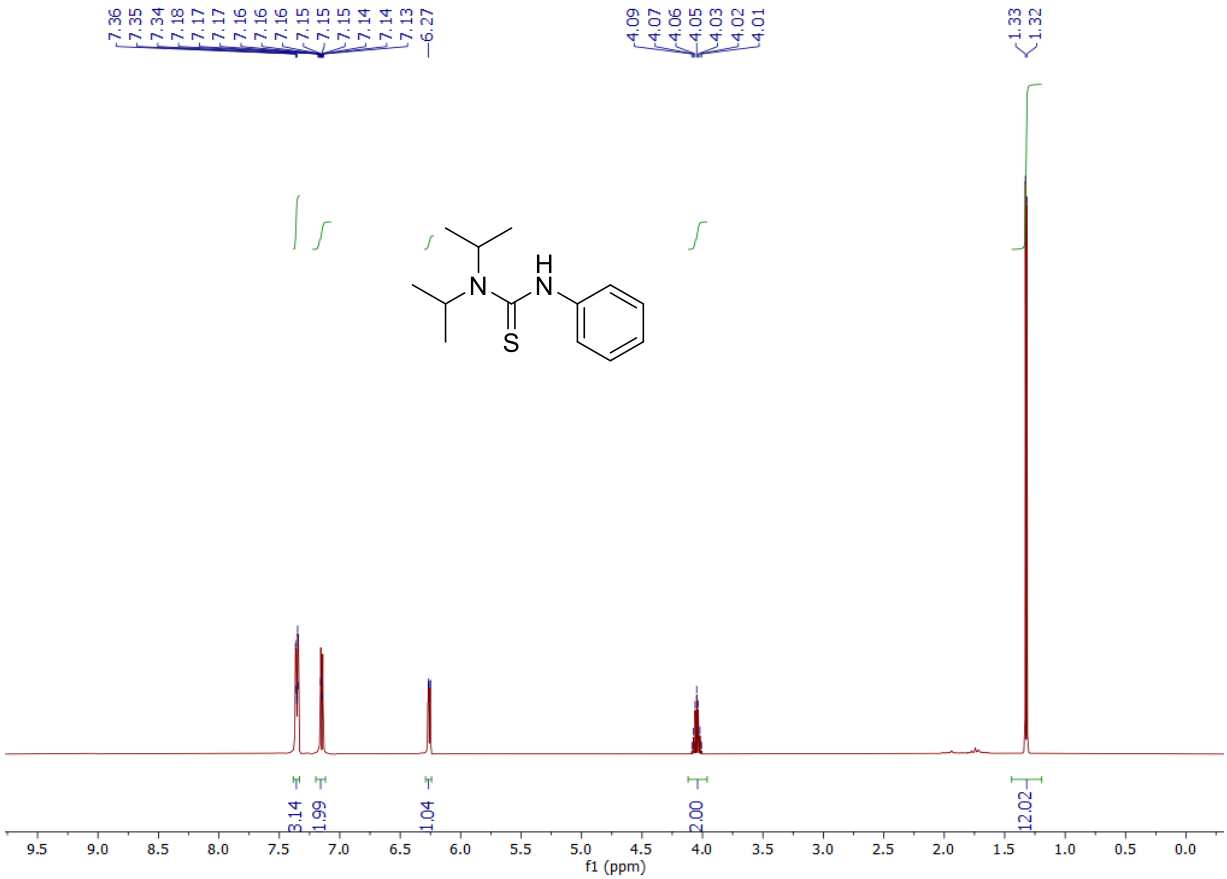

180.30
138.42
136.71
129.65
129.04
128.80
127.20
125.88
125.30
60.33
44.74
S
N
N
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

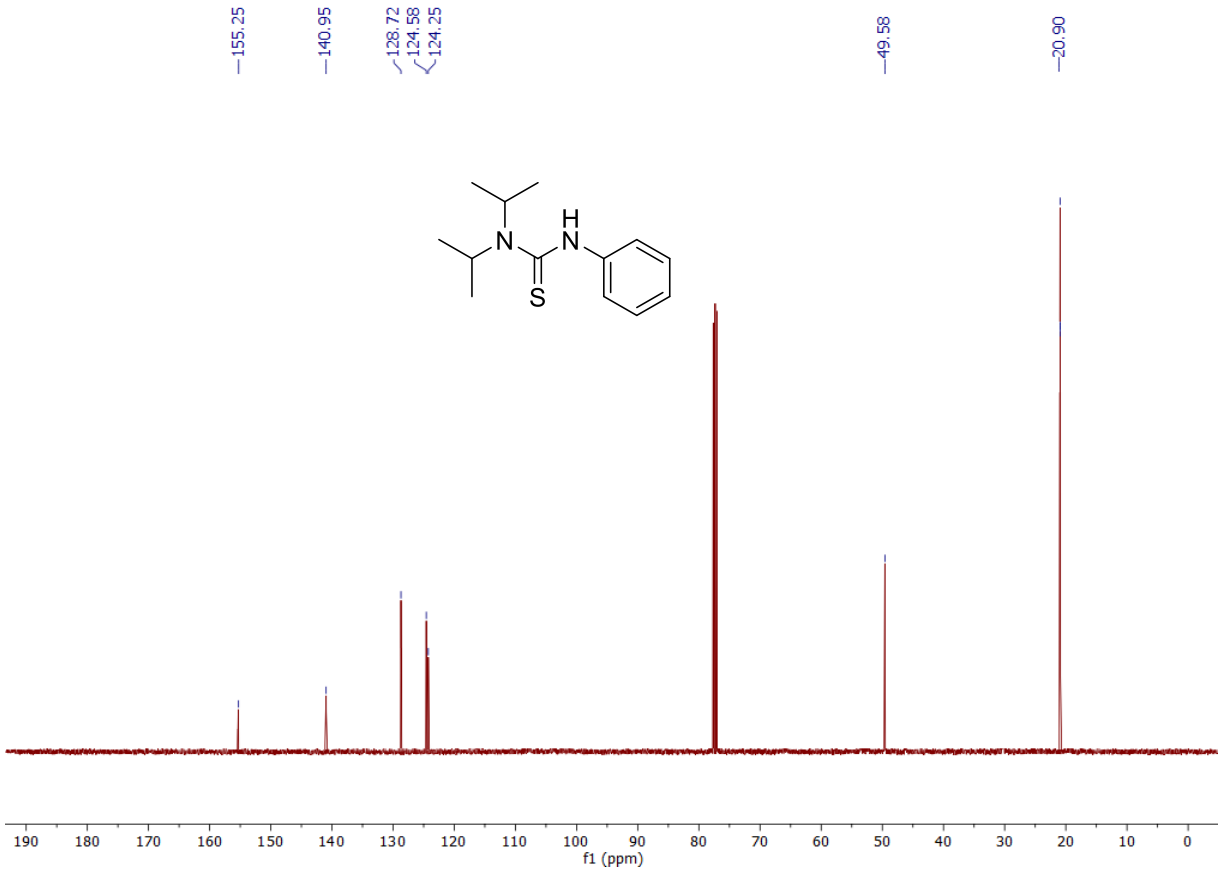

8.40
7.30
7.29
7.27
7.24
7.20
7.19
7.18
7.18
7.18
7.13
7.12
7.10
7.09
7.06
4.61
4.58
4.55
4.52
1.37
1.34
1.33
1.31
N
H
N
S
0.72
9.57
2.00
3.25
f1 (ppm)

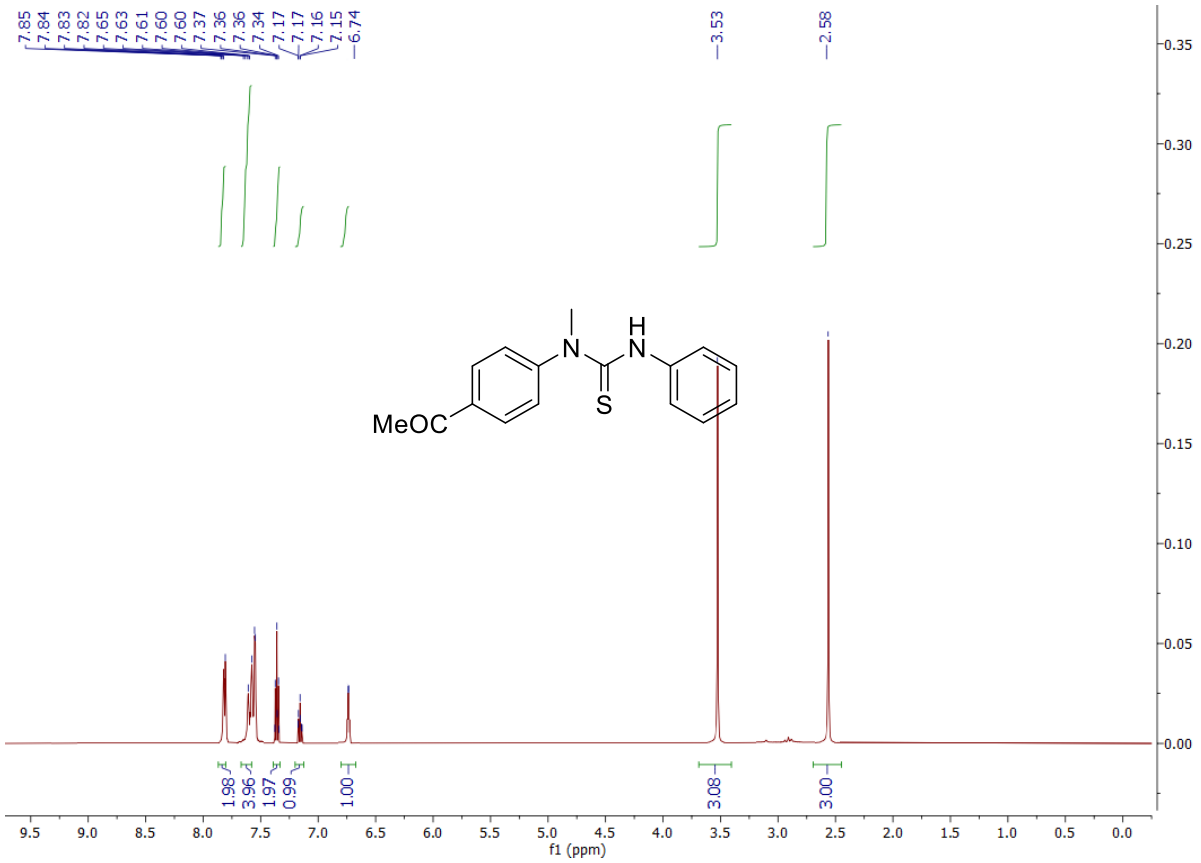

178.71
142.27
140.01
128.76
127.86
127.15
126.70
125.89
125.28
45.74
12.70
N
H
N
S
f1 (ppm)

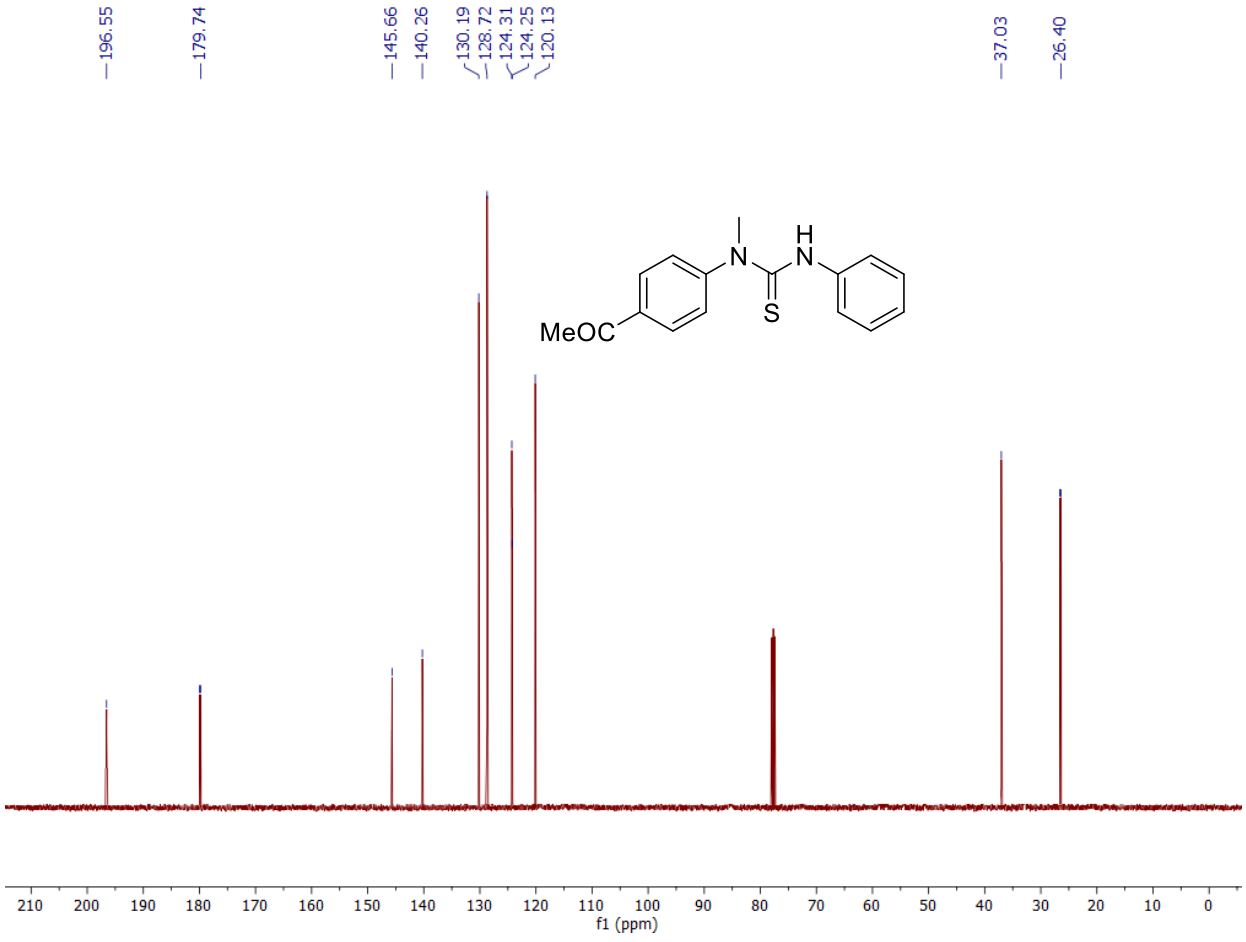

7.33
7.33
7.32
7.30
7.29
7.28
7.27
7.26
7.26
7.25
7.23
7.19
7.19
6.92
3.75
3.72
3.70
3.67
1.28
1.25
1.22
5.33
0.95
4.00
6.39
f1 (ppm)

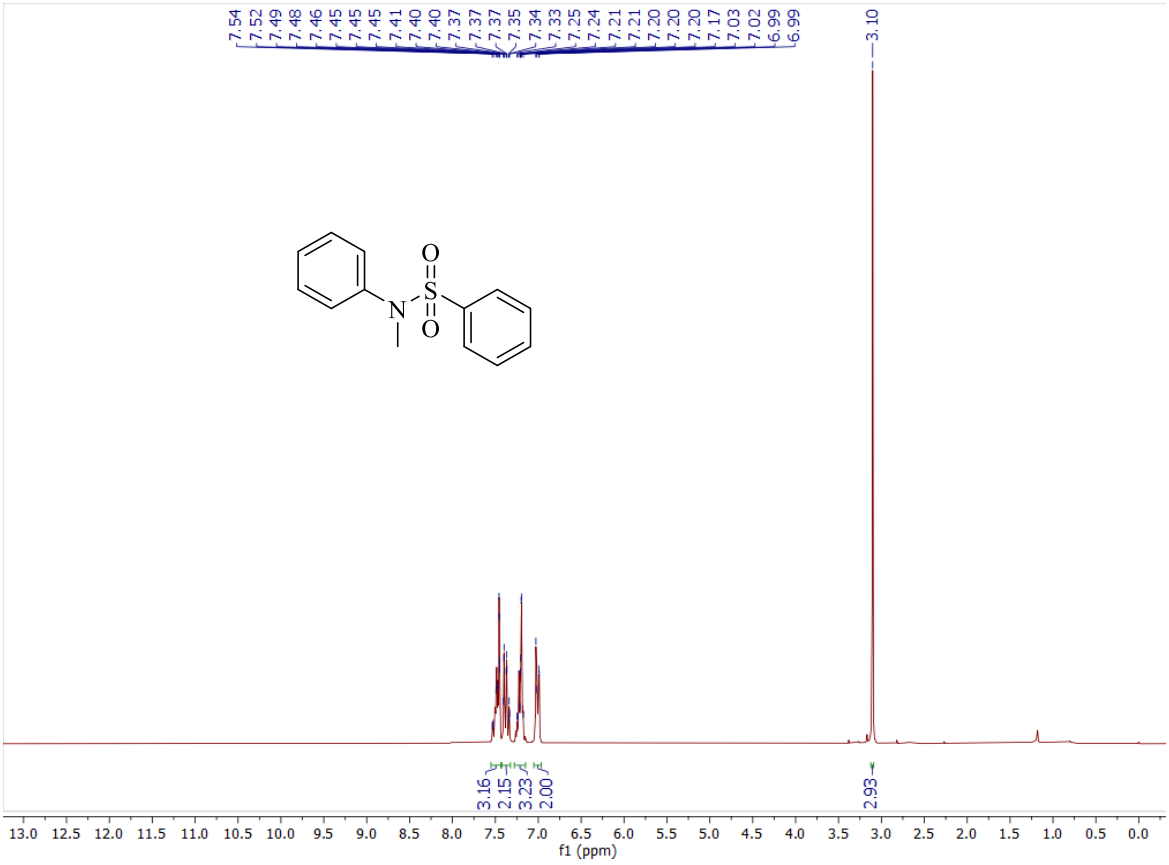

179.44
140.83
129.86
125.73
124.47
42.16
14.13
f1 (ppm)

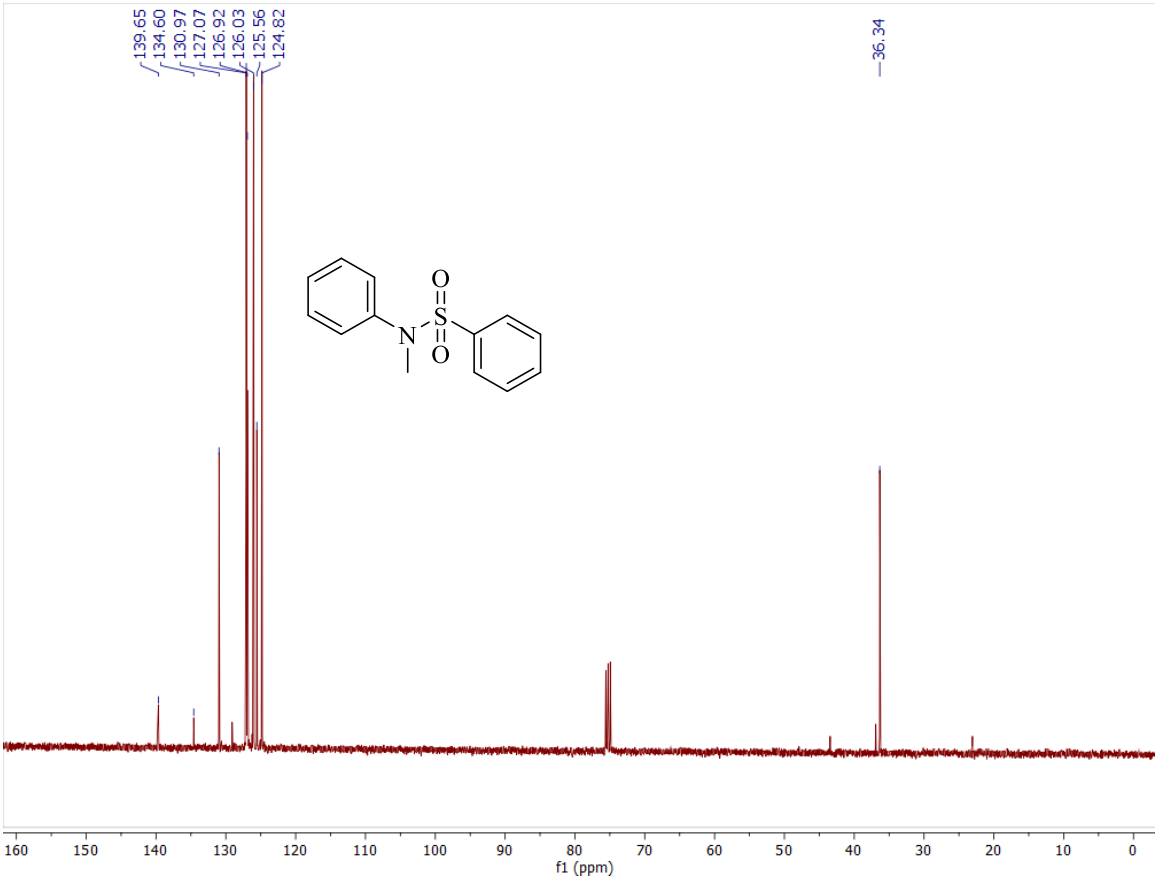

7.36
7.35
7.34
7.18
7.17
7.17
7.16
7.16
7.16
7.15
7.15
7.15
7.14
7.14
7.13
6.27
4.09
4.07
4.06
4.05
4.03
4.02
4.01
1.33
1.32
H
N
N
S
3.14
1.99
1.04
2.00
12.02
f1 (ppm)

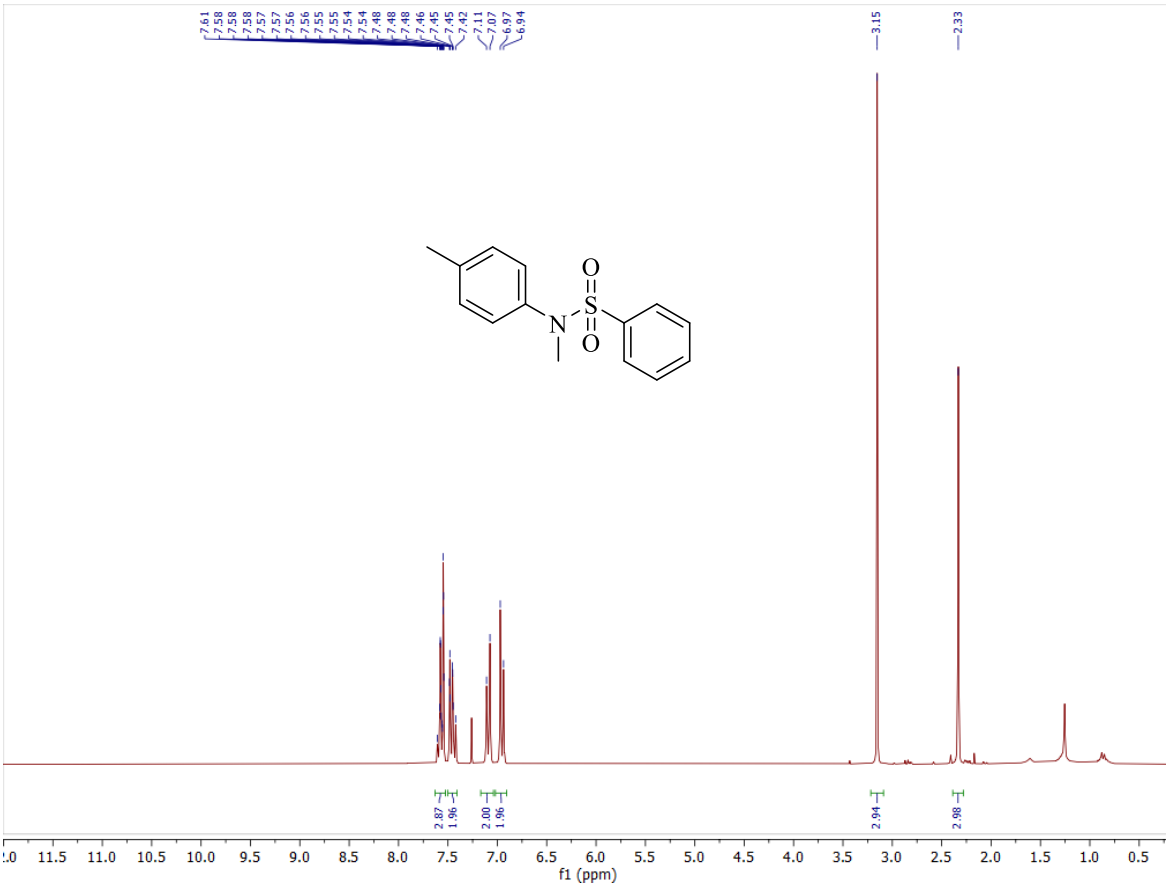

155.25
140.95
128.72
124.58
124.25
49.58
20.90
H
N
N
S
f1 (ppm)

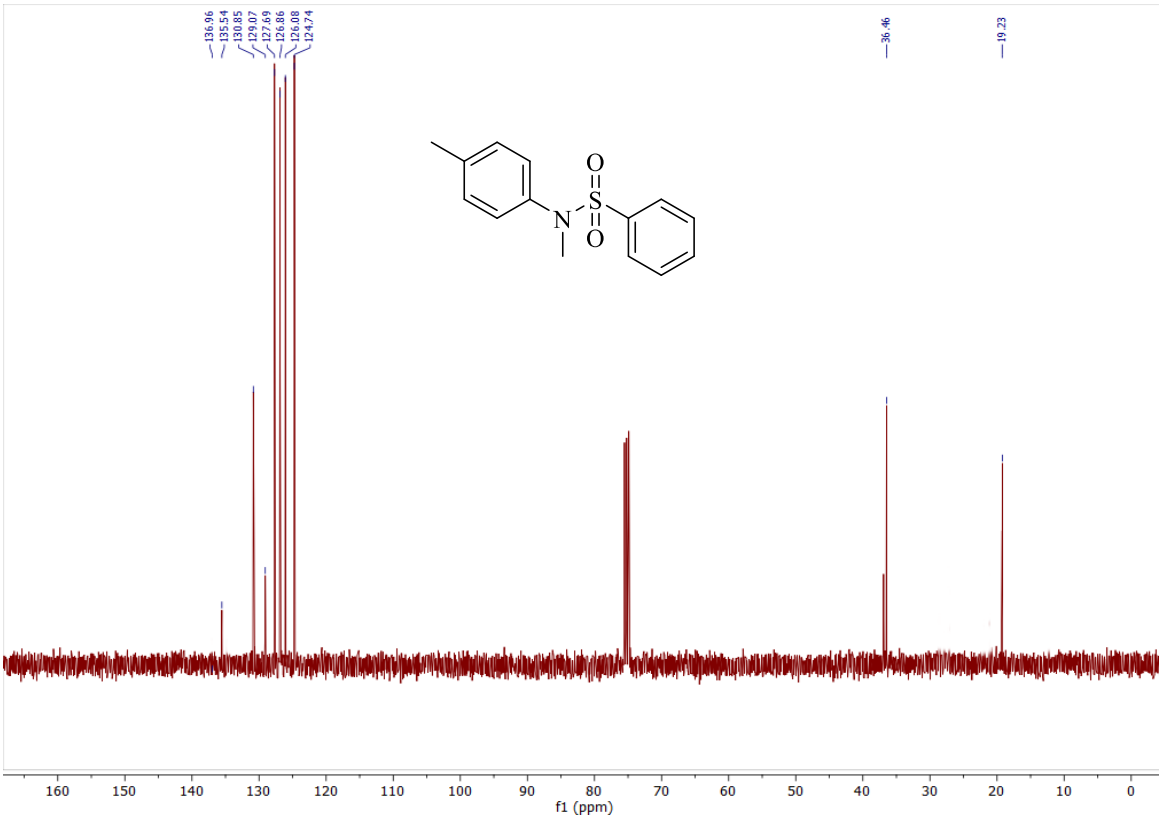

7.85
7.84
7.83
7.82
7.65
7.63
7.61
7.60
7.60
7.37
7.36
7.36
7.34
7.17
7.17
7.16
7.15
6.74
3.53
2.58
MeOC
N
H
N
S
1.98
3.96
1.97
0.99
1.00
3.08
3.00
f1 (ppm)

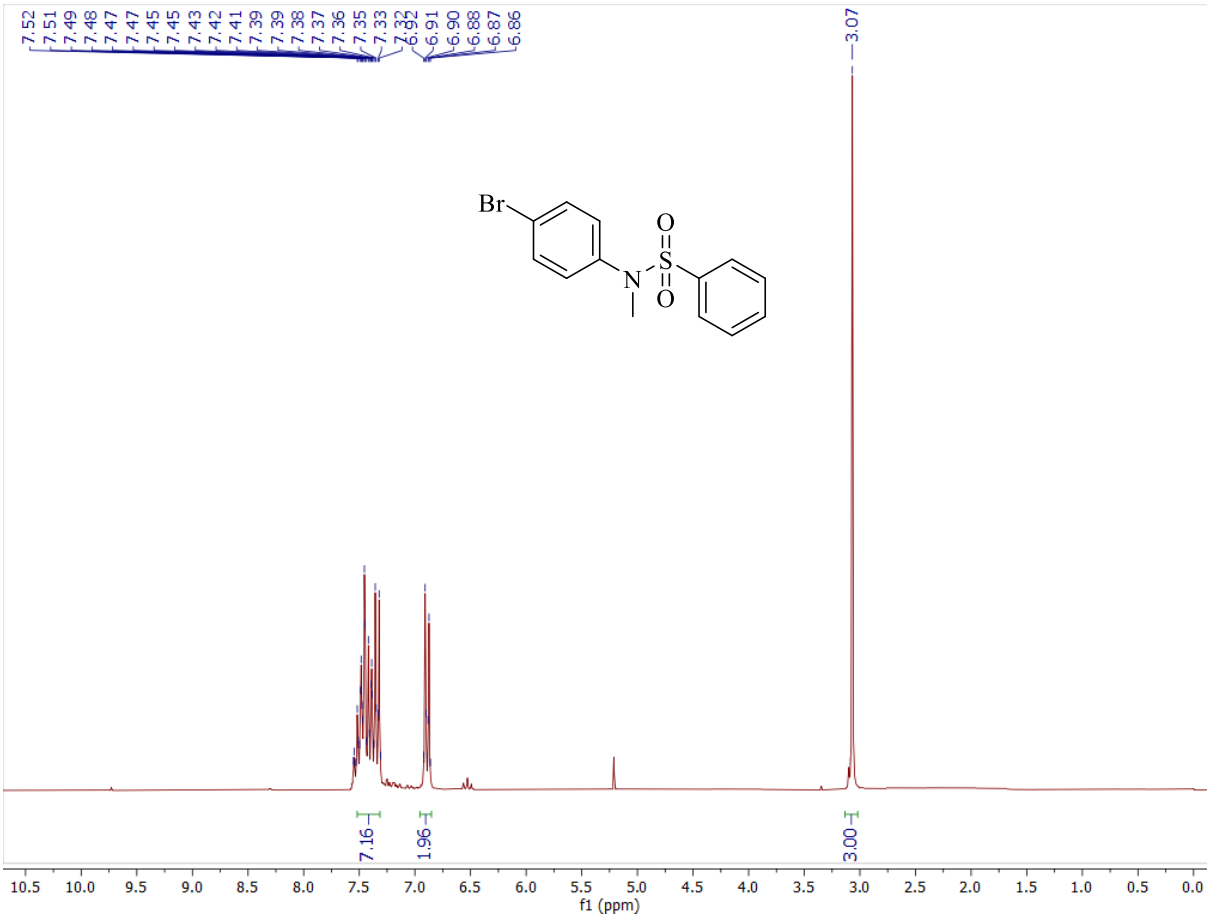

196.55
179.74
145.66
140.26
130.19
128.72
124.31
124.25
120.13
37.03
26.40
MeOC
N
H
N
S
f1 (ppm)

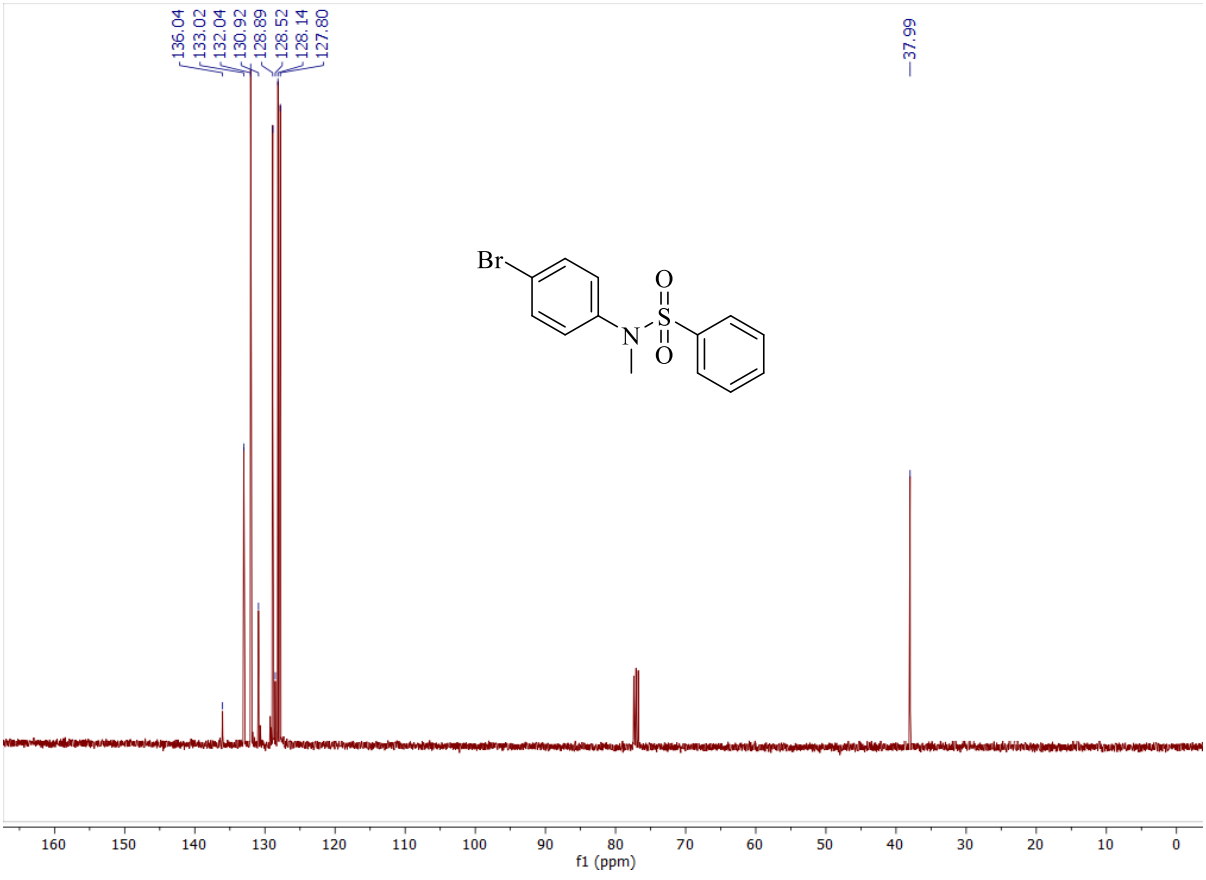

7.54
7.52
7.49
7.48
7.46
7.45
7.45
7.45
7.41
7.40
7.40
7.37
7.37
7.35
7.34
7.33
7.25
7.24
7.21
7.21
7.20
7.20
7.20
7.17
7.03
7.02
6.99
6.99
3.10
3.16
2.15
3.23
2.00
2.93
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

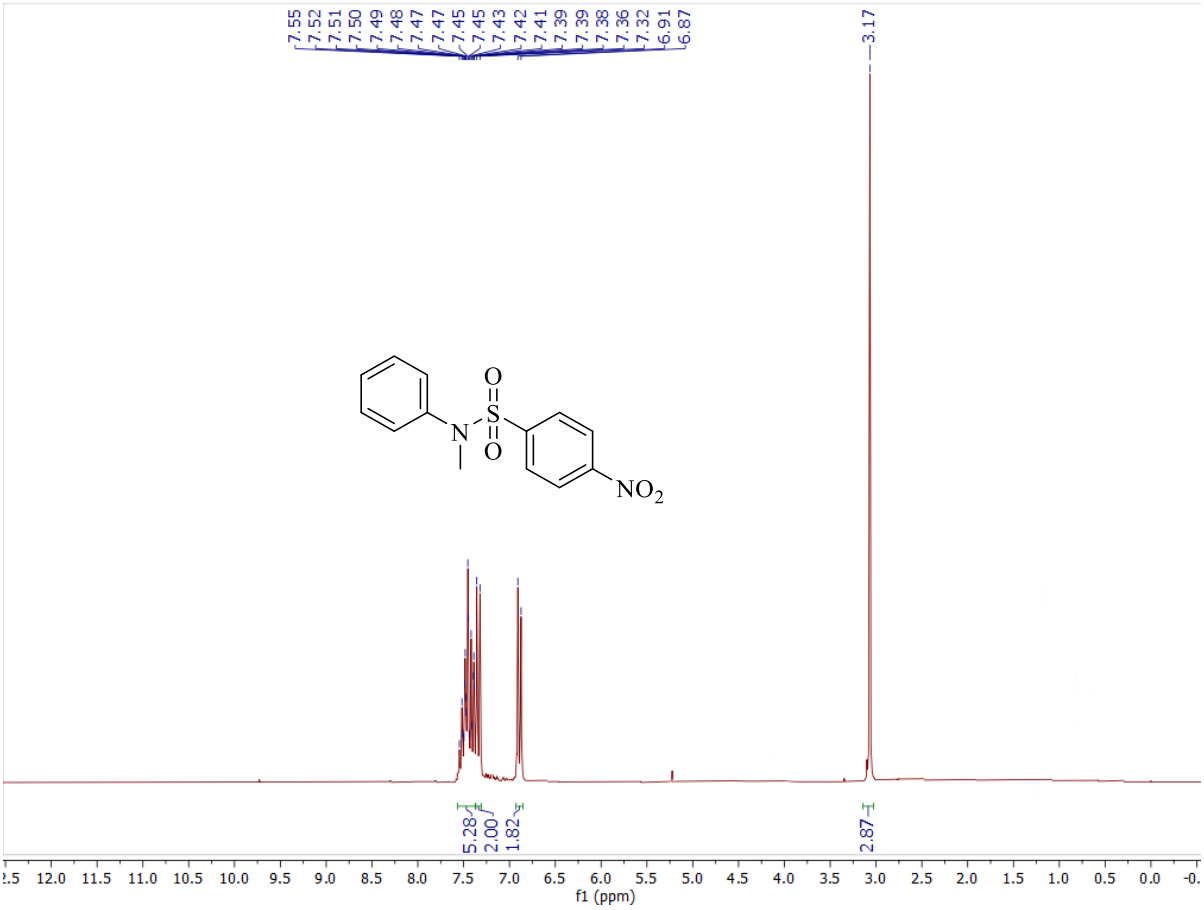

139.65
134.60
130.97
127.07
126.92
126.03
125.56
124.82
36.34
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

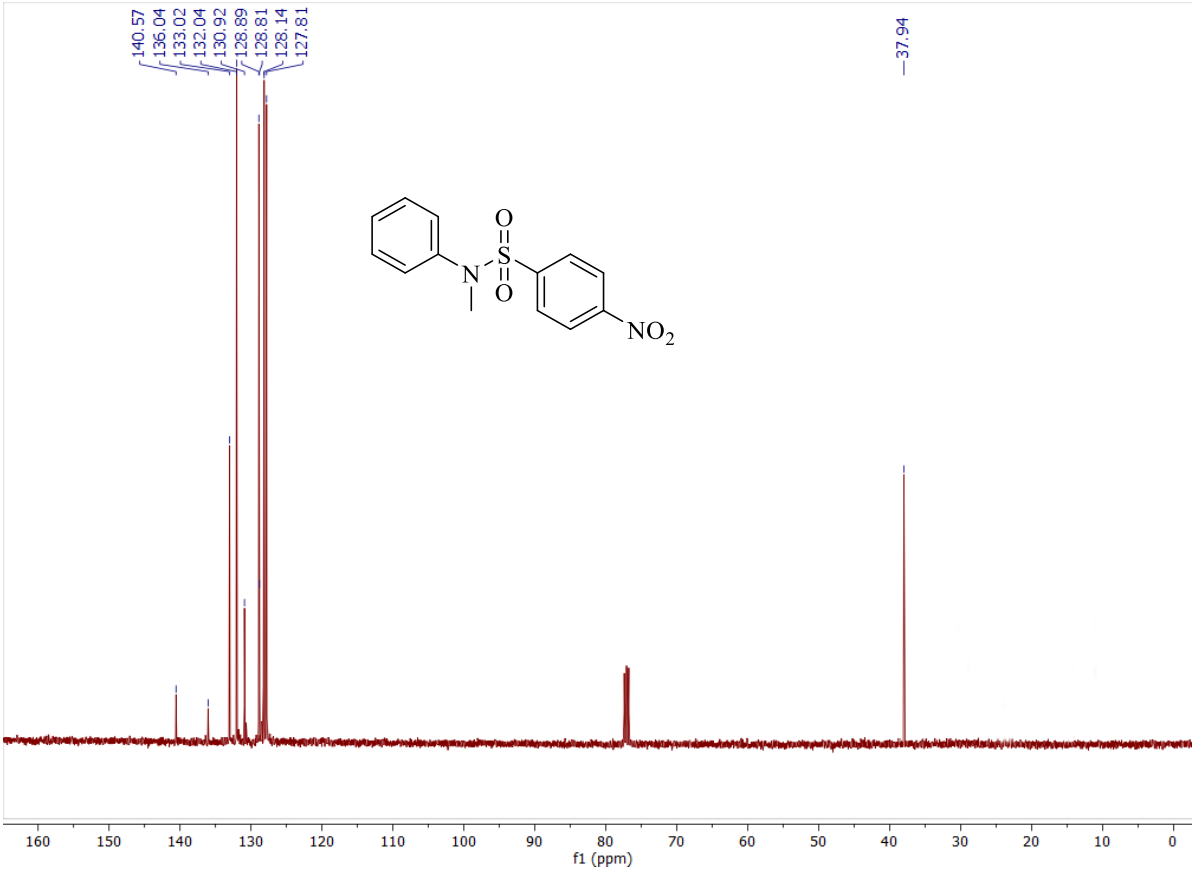

7.61
7.58
7.58
7.58
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.48
7.48
7.48
7.46
7.45
7.45
7.42
7.11
7.07
6.97
6.94
3.15
2.33
O
S
N
O
2.87
1.96
2.00
1.96
2.94
2.98
f1 (ppm)

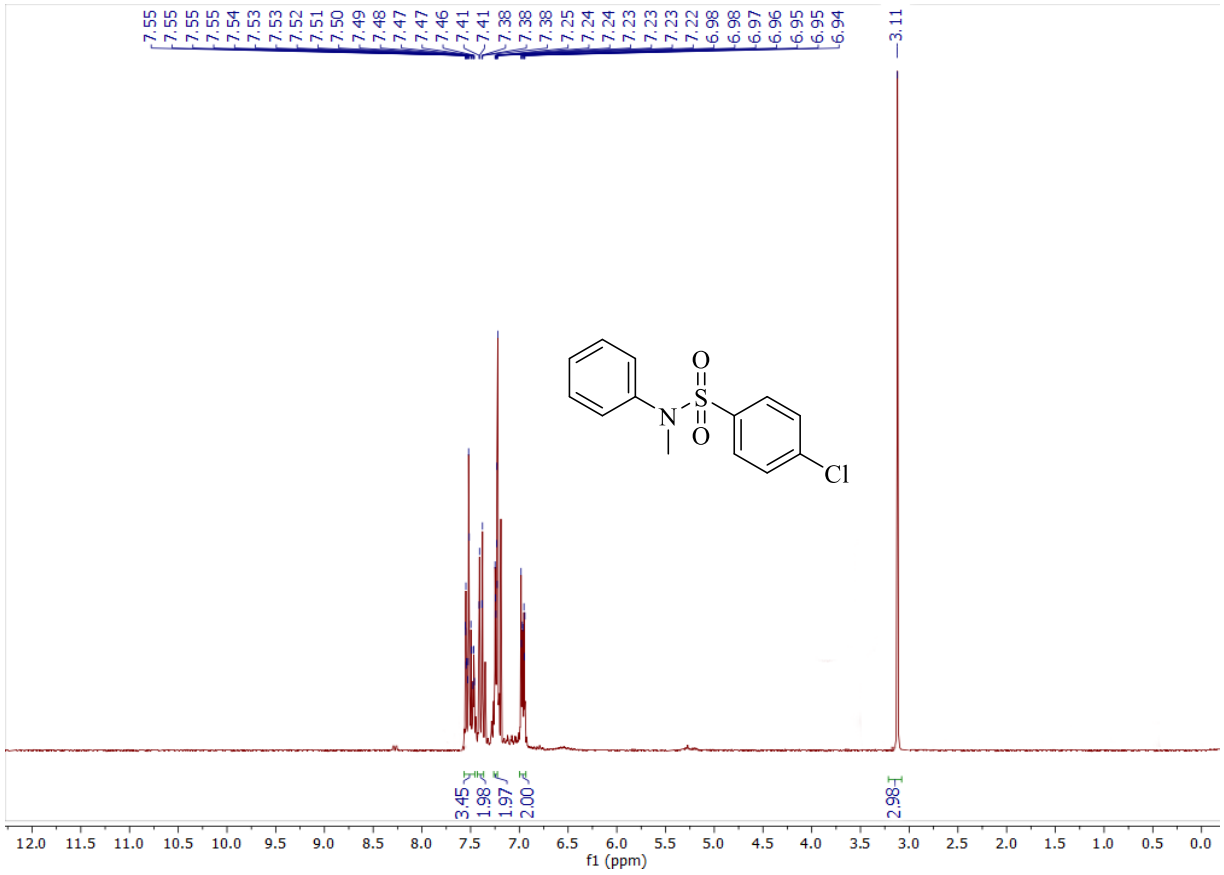

136.96
135.54
130.85
129.07
127.69
126.86
126.08
124.74
36.46
19.23
O
S
N
O
f1 (ppm)

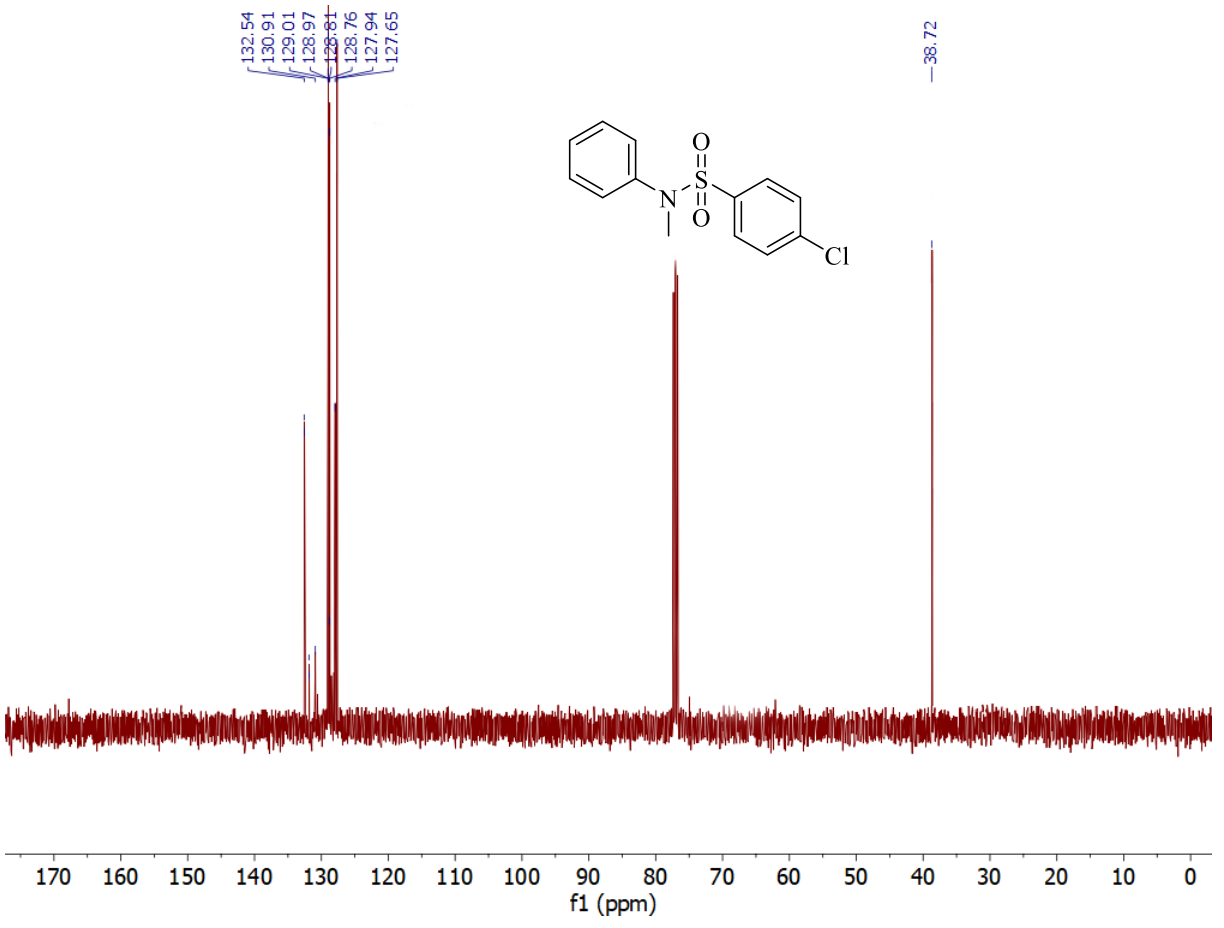

7.52
7.51
7.49
7.48
7.47
7.47
7.47
7.45
7.45
7.43
7.42
7.41
7.39
7.39
7.38
7.37
7.36
7.35
7.33
7.32
6.92
6.91
6.90
6.88
6.87
6.86
3.07
Br
O
S
O
N
7.16
1.96
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

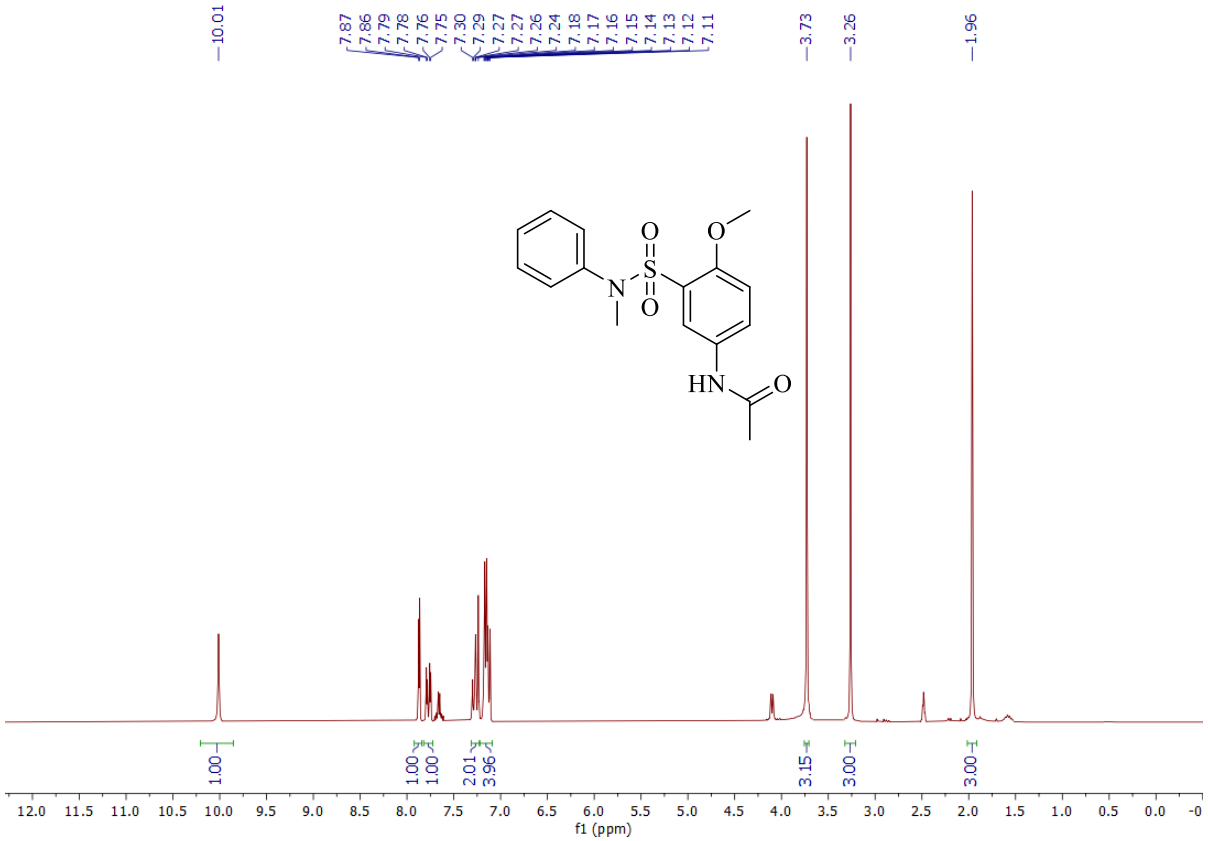

136.04
133.02
132.04
130.92
128.89
128.52
128.14
127.80
37.99
Br
O
S
O
N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

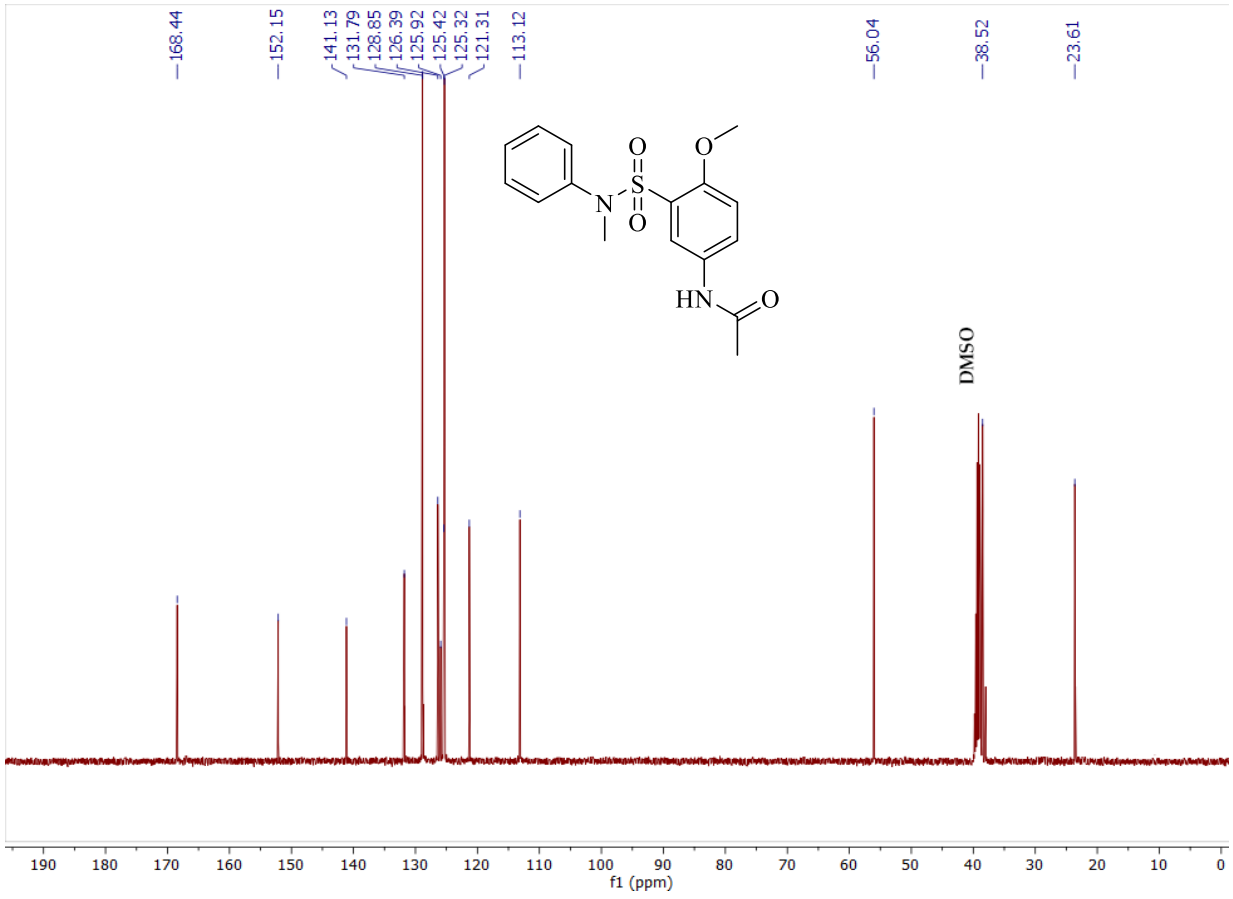

7.55
7.52
7.51
7.50
7.49
7.48
7.47
7.47
7.45
7.45
7.43
7.42
7.41
7.39
7.39
7.38
7.36
7.32
6.91
6.87
3.17
O
S
O
N
NO2
5.28
2.00
1.82
2.87
f1 (ppm)

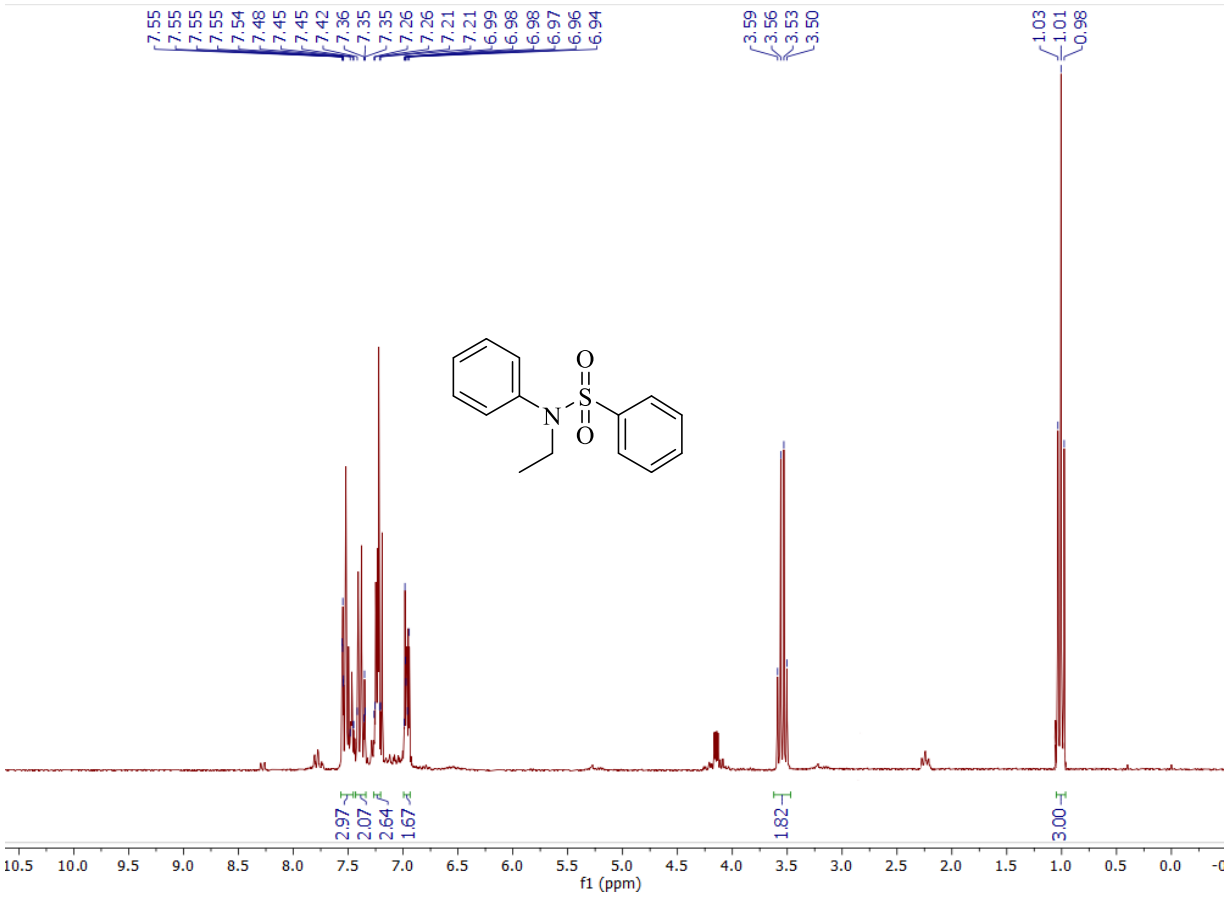

140.57
136.04
133.02
132.04
130.92
128.89
128.81
128.14
127.81
37.94
O
S
O
N
NO2
f1 (ppm)

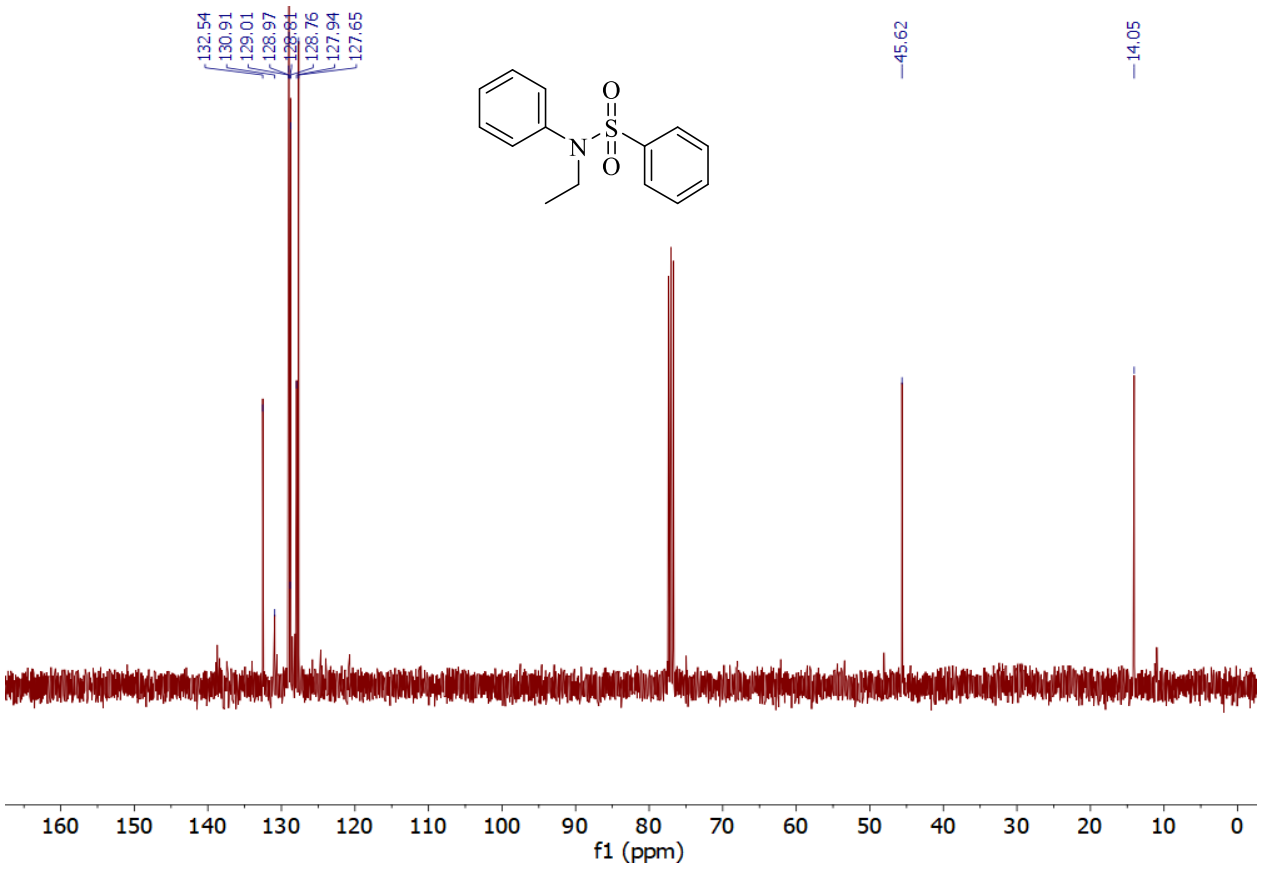

7.55
7.55
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.48
7.47
7.47
7.46
7.41
7.41
7.38
7.38
7.38
7.25
7.24
7.24
7.23
7.23
7.23
7.22
6.98
6.98
6.97
6.96
6.96
6.95
6.95
6.94
3.11
O
S
O
N
Cl
3.45
1.98
1.97
2.00
2.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

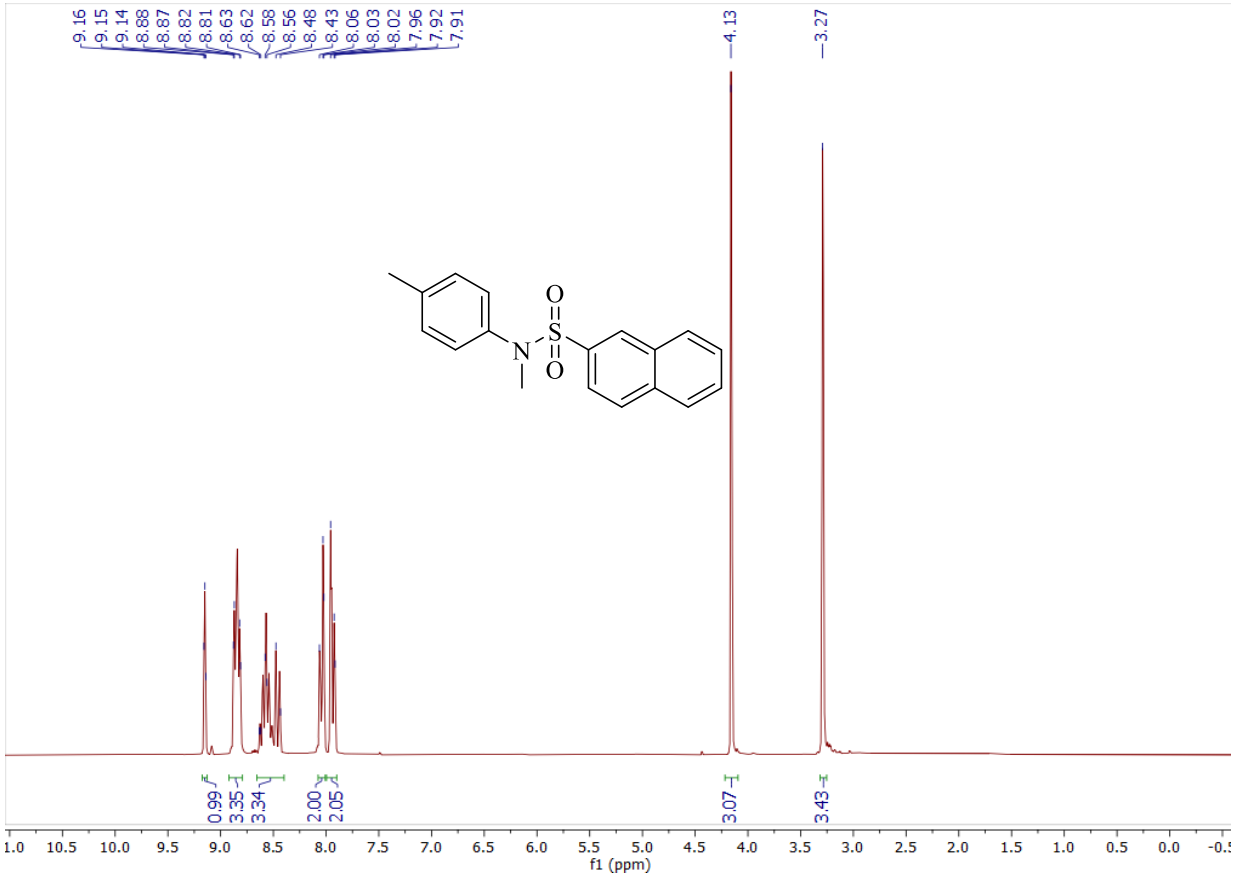

132.54
130.91
129.01
128.97
128.81
128.76
127.94
127.65
38.72
O
S
O
N
Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

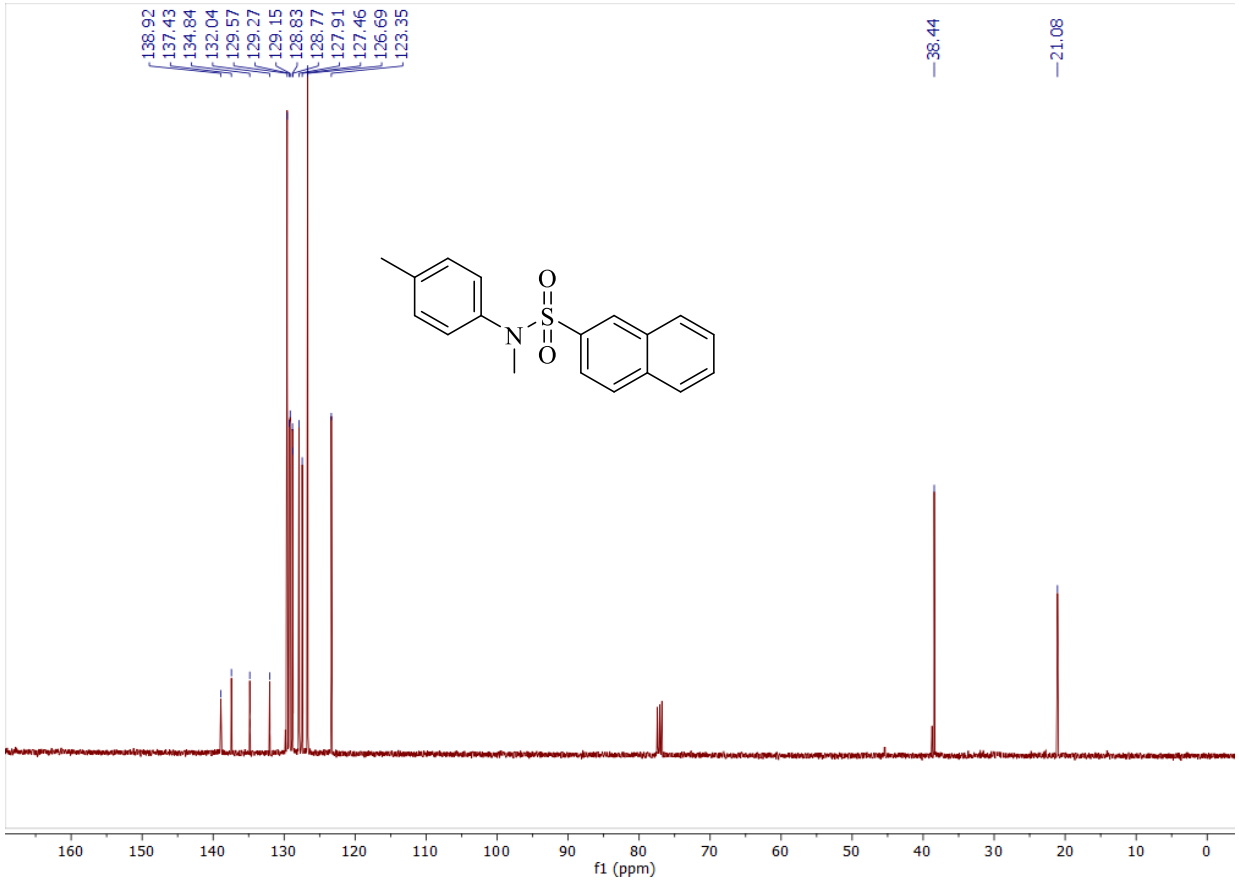

10.01
7.87
7.86
7.79
7.78
7.76
7.75
7.30
7.29
7.27
7.27
7.26
7.24
7.18
7.17
7.16
7.15
7.14
7.13
7.12
7.11
3.73
3.26
1.96
1.00
1.00
1.00
2.01
3.96
3.15
3.00
3.00
f1 (ppm)

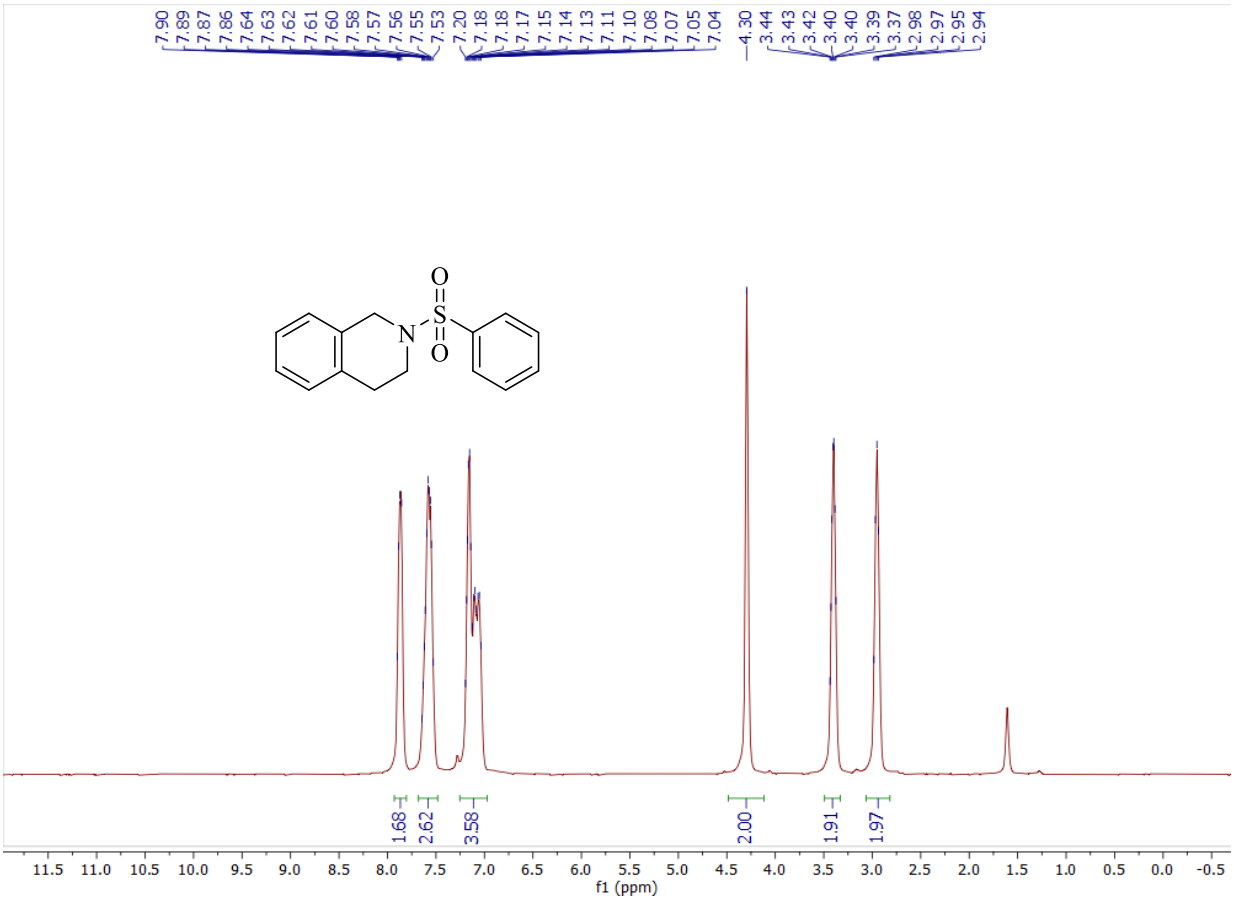

168.44
152.15
141.13
131.79
128.85
126.39
125.92
125.42
125.32
121.31
113.12
56.04
38.52
23.61
DMSO
f1 (ppm)

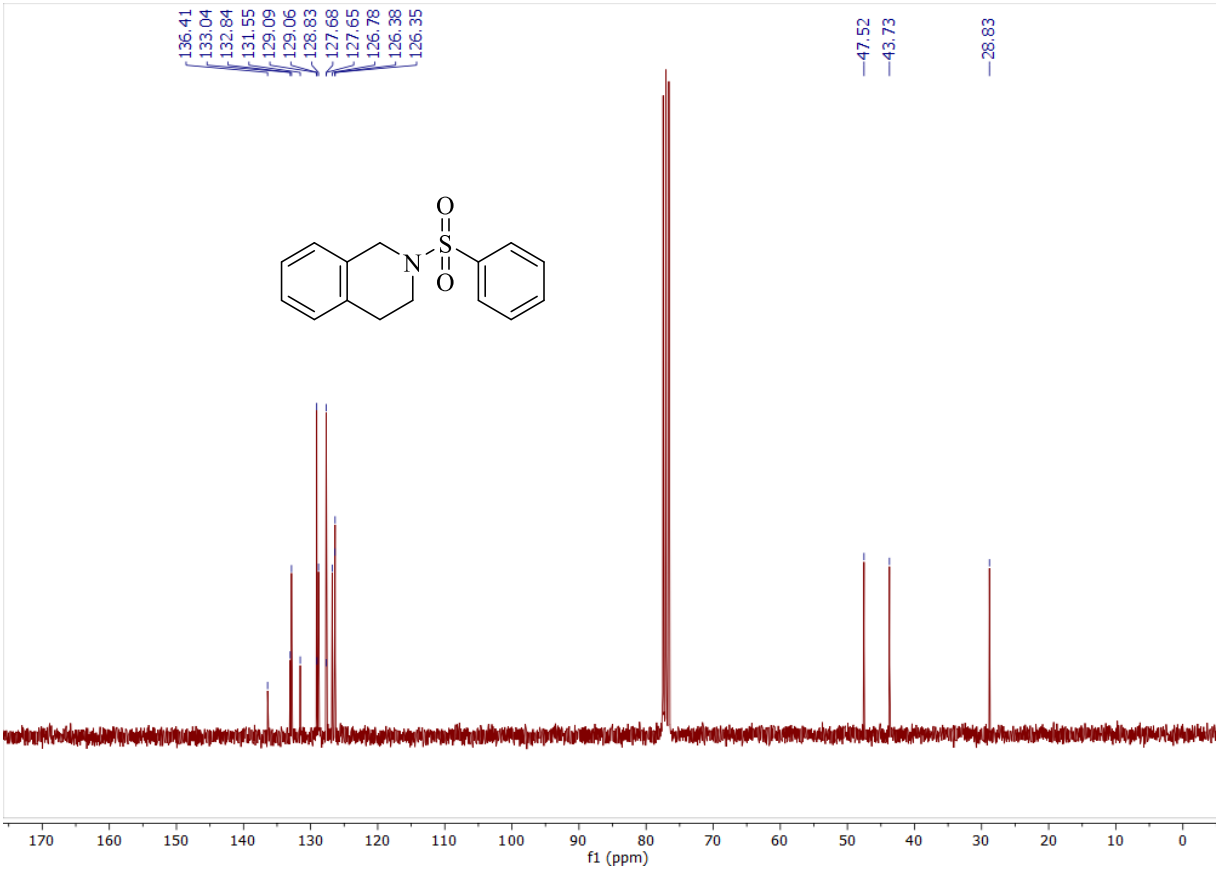

7.55
7.55
7.55
7.55
7.54
7.48
7.45
7.45
7.42
7.36
7.35
7.35
7.26
7.26
7.21
7.21
6.99
6.98
6.98
6.97
6.96
6.94
3.59
3.56
3.53
3.50
1.03
1.01
0.98
O
S
N
O
2.97
2.07
2.64
1.67
1.82
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

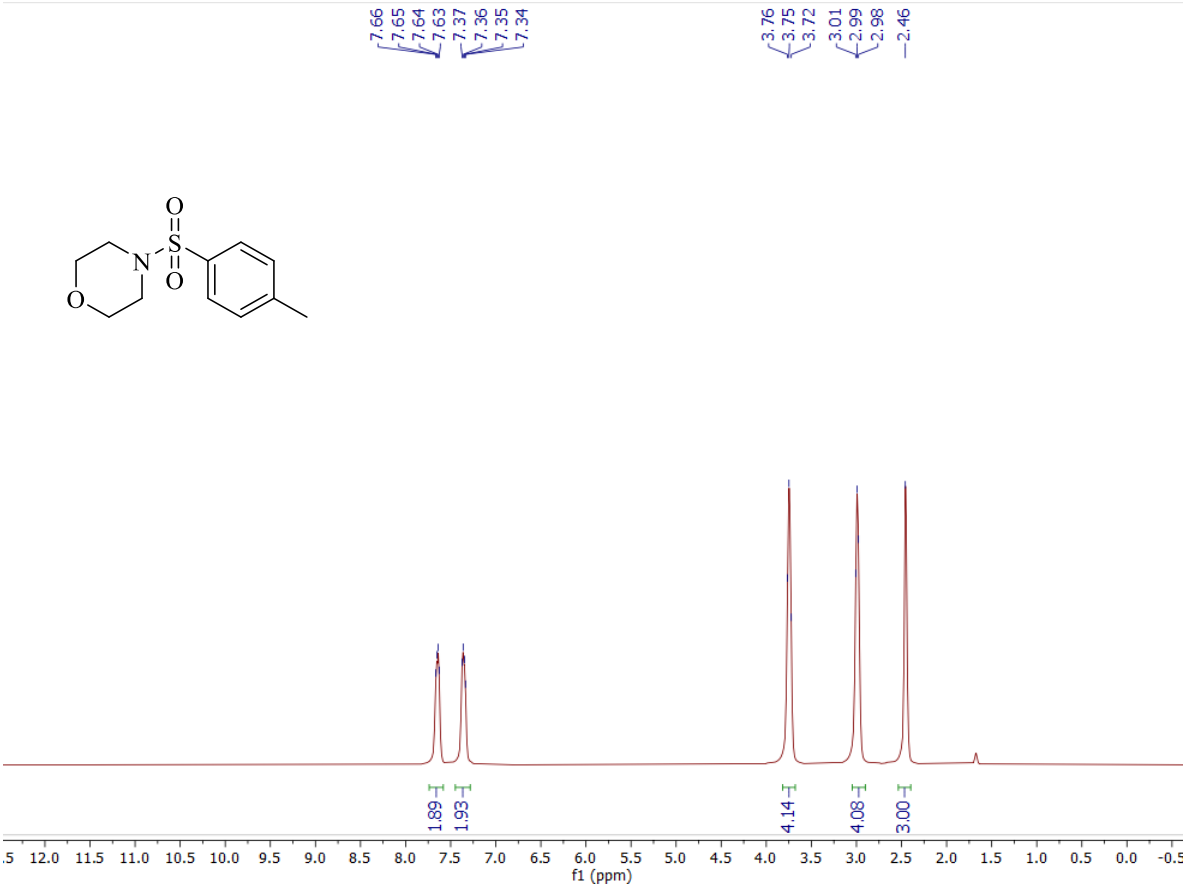

132.54
130.91
129.01
128.97
128.81
128.76
127.94
127.65
45.62
14.05
O
S
N
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

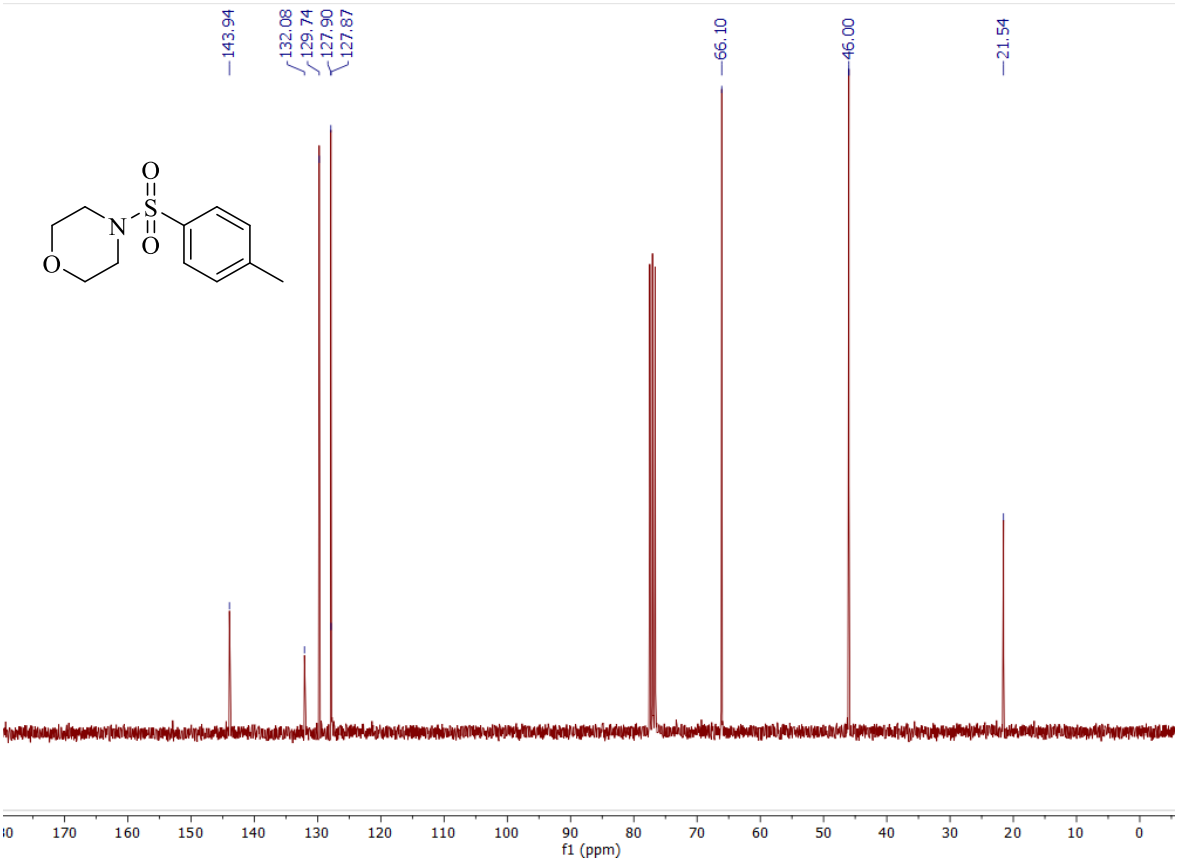

9.16
9.15
9.14
8.88
8.87
8.82
8.81
8.63
8.62
8.58
8.56
8.48
8.43
8.06
8.03
8.02
7.96
7.92
7.91
4.13
3.27
0.99
3.35
3.34
2.00
2.05
3.07
3.43
f1 (ppm)

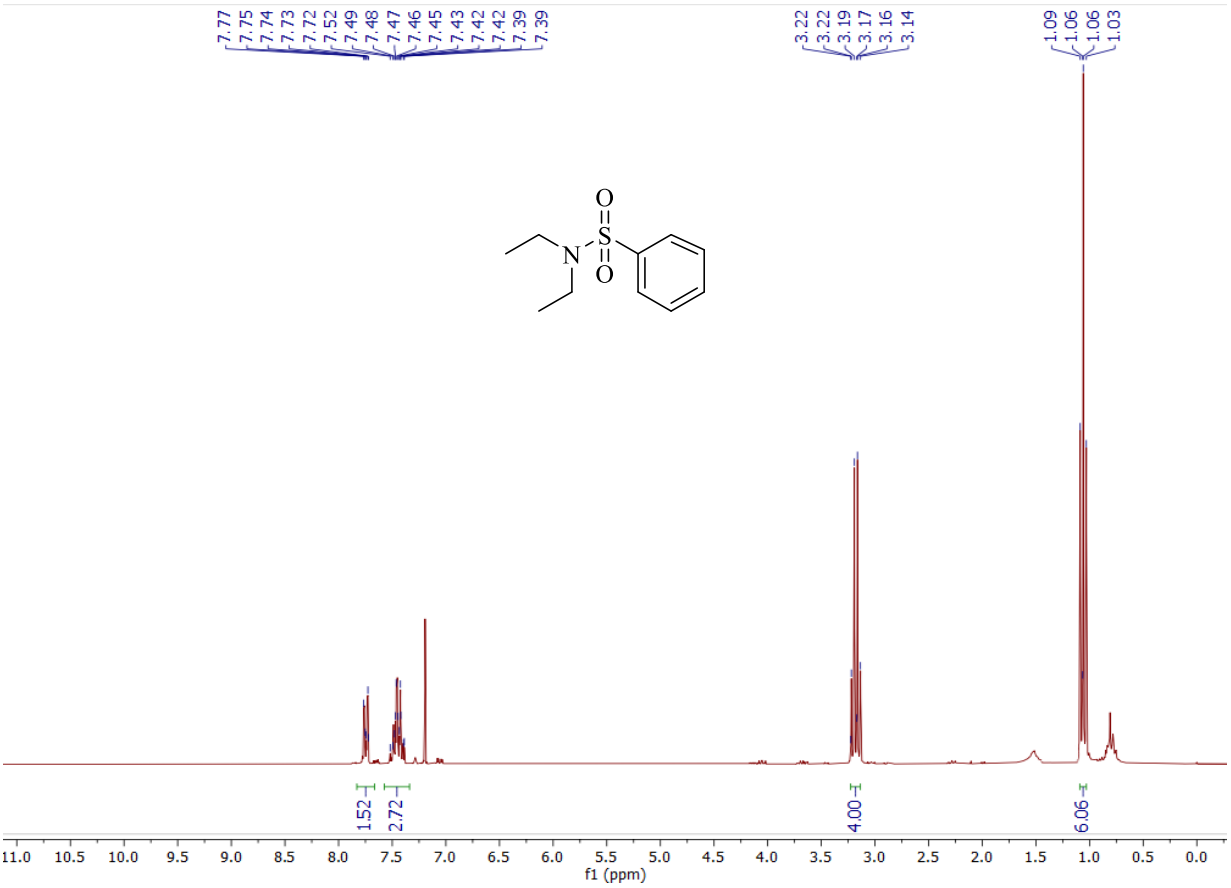

138.92
137.43
134.84
132.04
129.57
129.27
129.15
128.83
128.77
127.91
127.46
126.69
123.35
38.44
21.08
f1 (ppm)

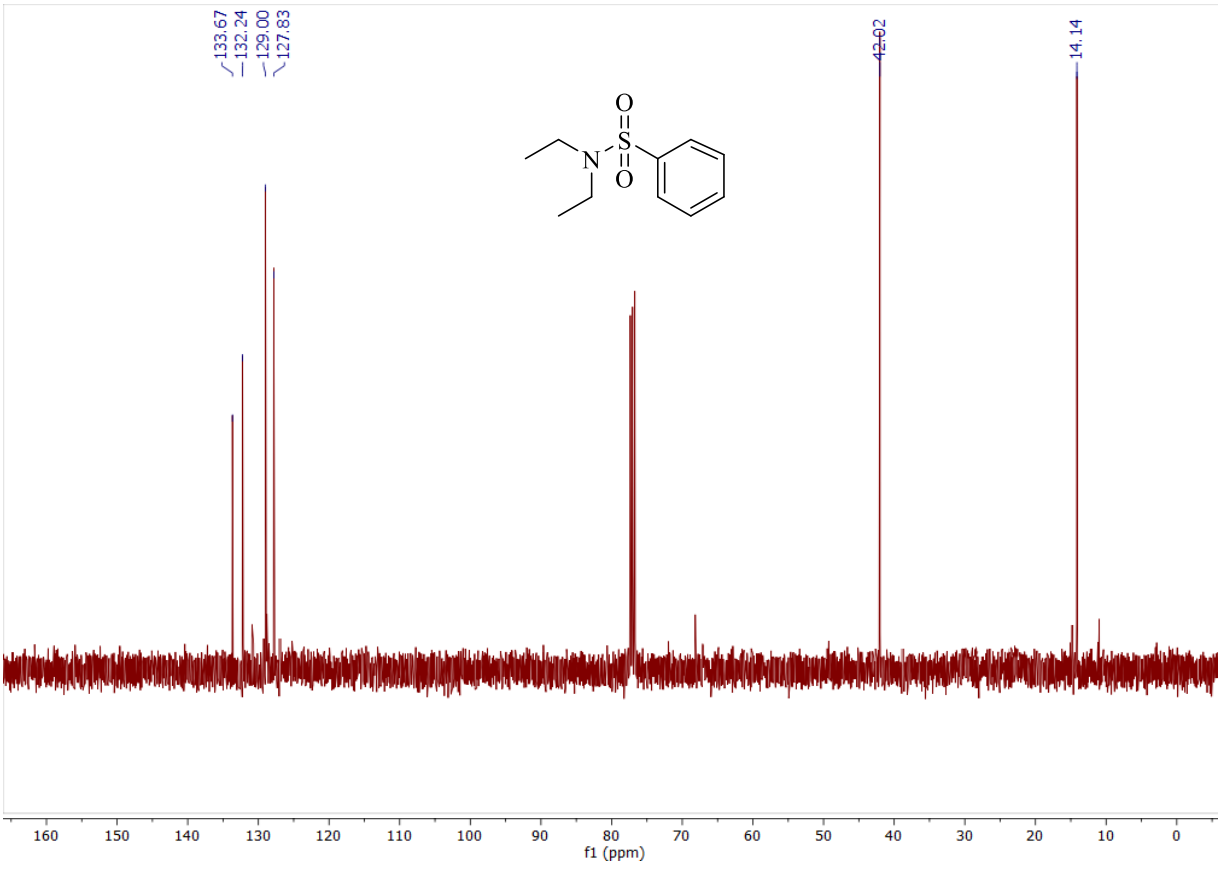

7.90
7.89
7.87
7.86
7.64
7.63
7.62
7.61
7.60
7.58
7.57
7.56
7.55
7.53
7.20
7.18
7.18
7.17
7.15
7.14
7.13
7.11
7.10
7.08
7.07
7.05
7.04
4.30
3.44
3.43
3.42
3.40
3.40
3.39
3.37
2.98
2.97
2.95
2.94
O
S
N
O
1.68
2.62
3.58
2.00
1.91
1.97
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

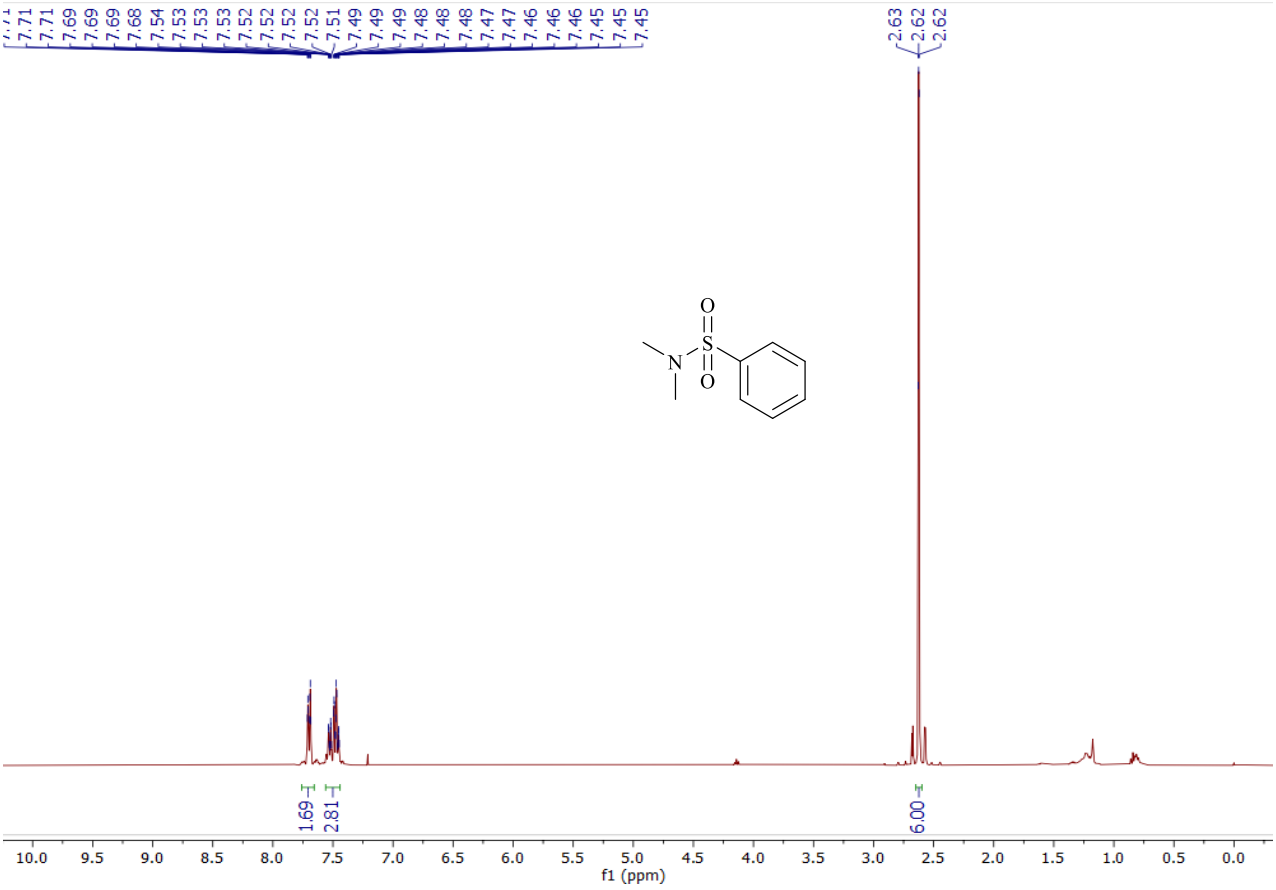

136.41
133.04
132.84
131.55
129.09
129.06
128.83
127.68
127.65
126.78
126.38
126.35
47.52
43.73
28.83
O
S
N
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

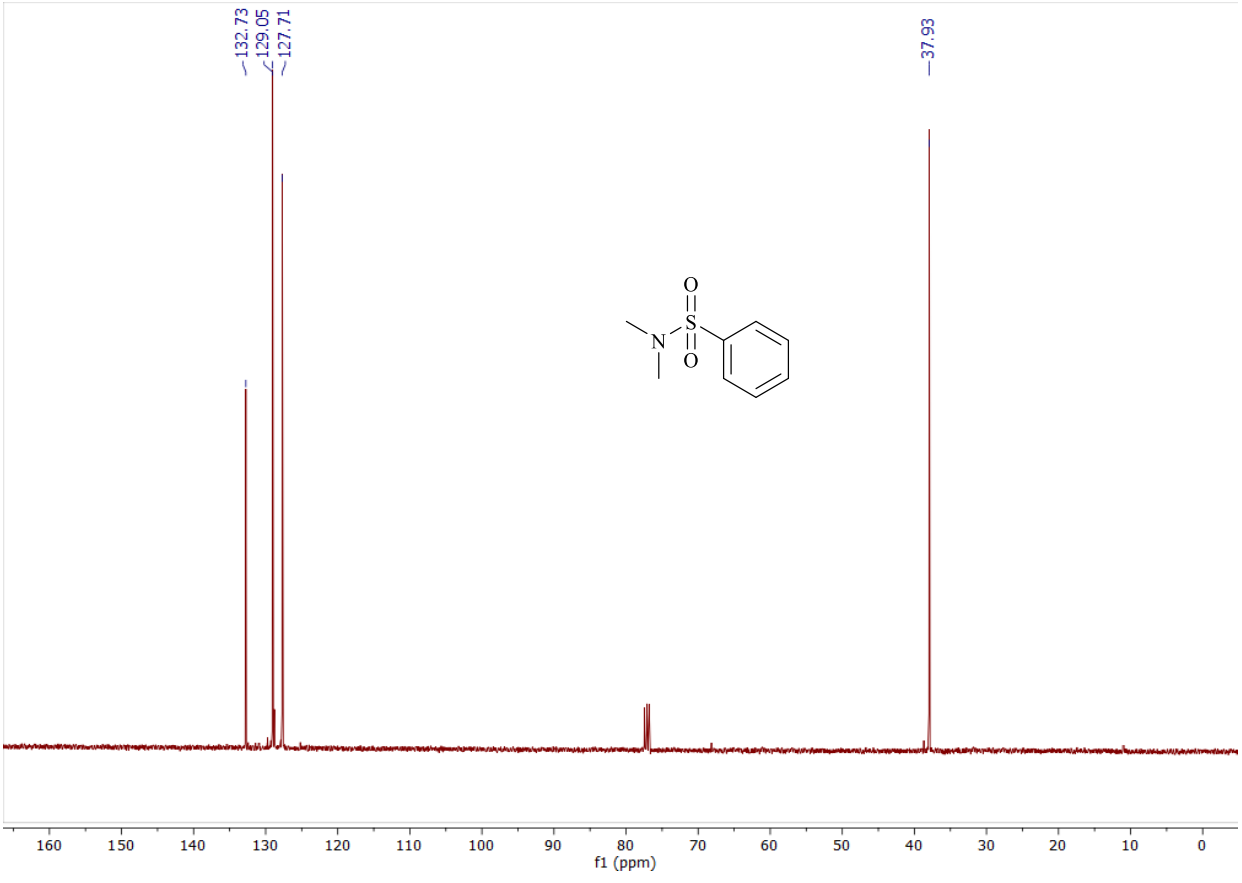

7.66
7.65
7.64
7.63
7.37
7.36
7.35
7.34
3.76
3.75
3.72
3.01
2.99
2.98
2.46
O
S
N
O
O
O
1.89
1.93
4.14
4.08
3.00
f1 (ppm)

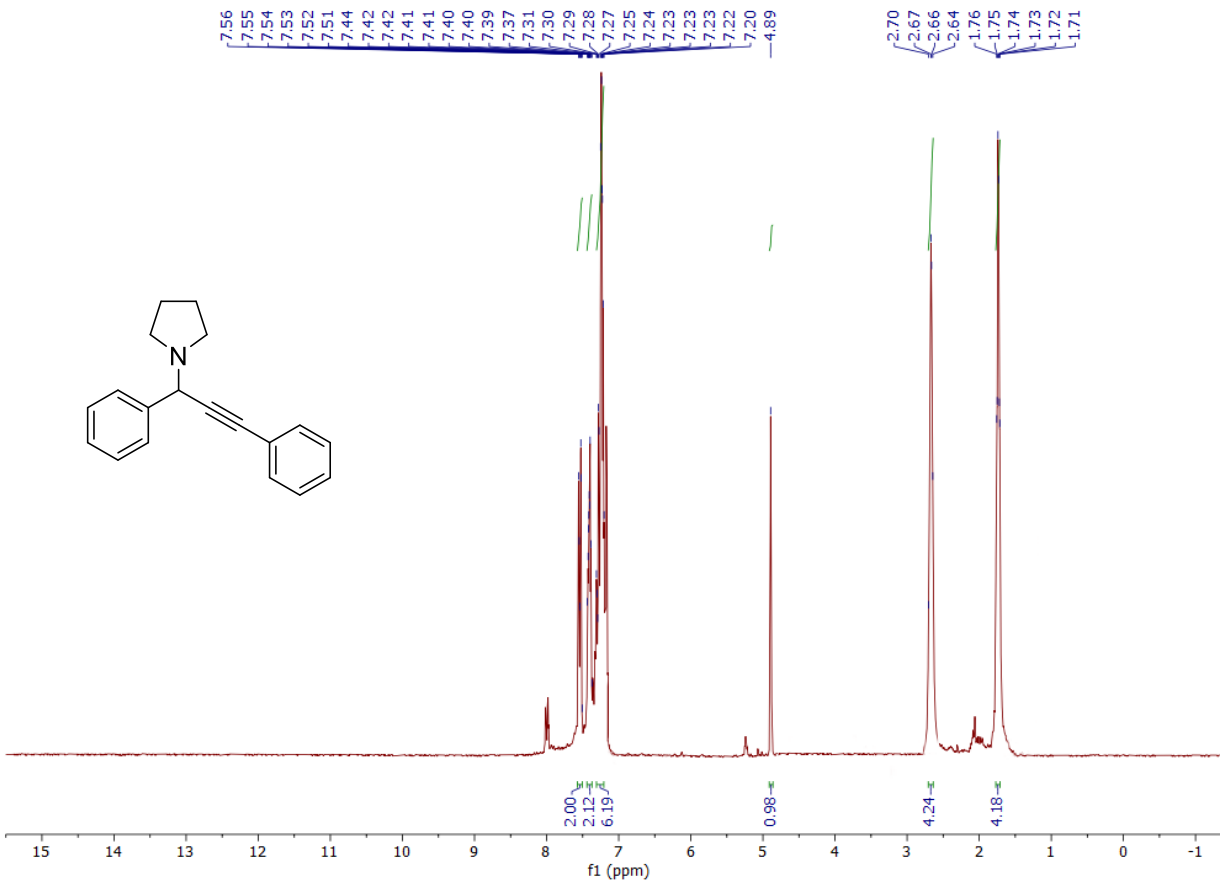

143.94
132.08
129.74
127.90
127.87
66.10
46.00
21.54
O
S
N
O
O
O
f1 (ppm)

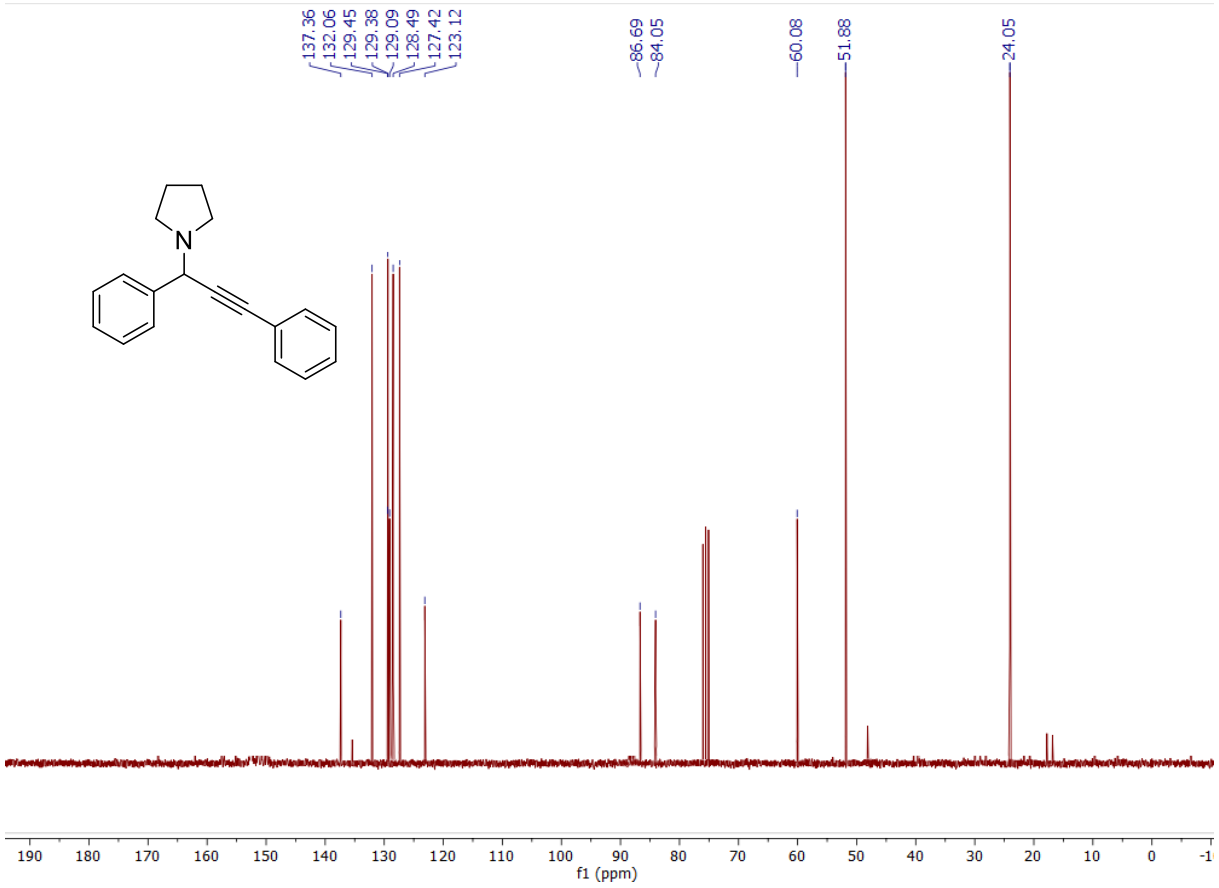

7.77
7.75
7.74
7.73
7.72
7.52
7.49
7.48
7.47
7.46
7.45
7.43
7.42
7.42
7.39
7.39
3.22
3.22
3.19
3.17
3.16
3.14
1.09
1.06
1.06
1.03
O
S
N
O
1.52
2.72
4.00
6.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

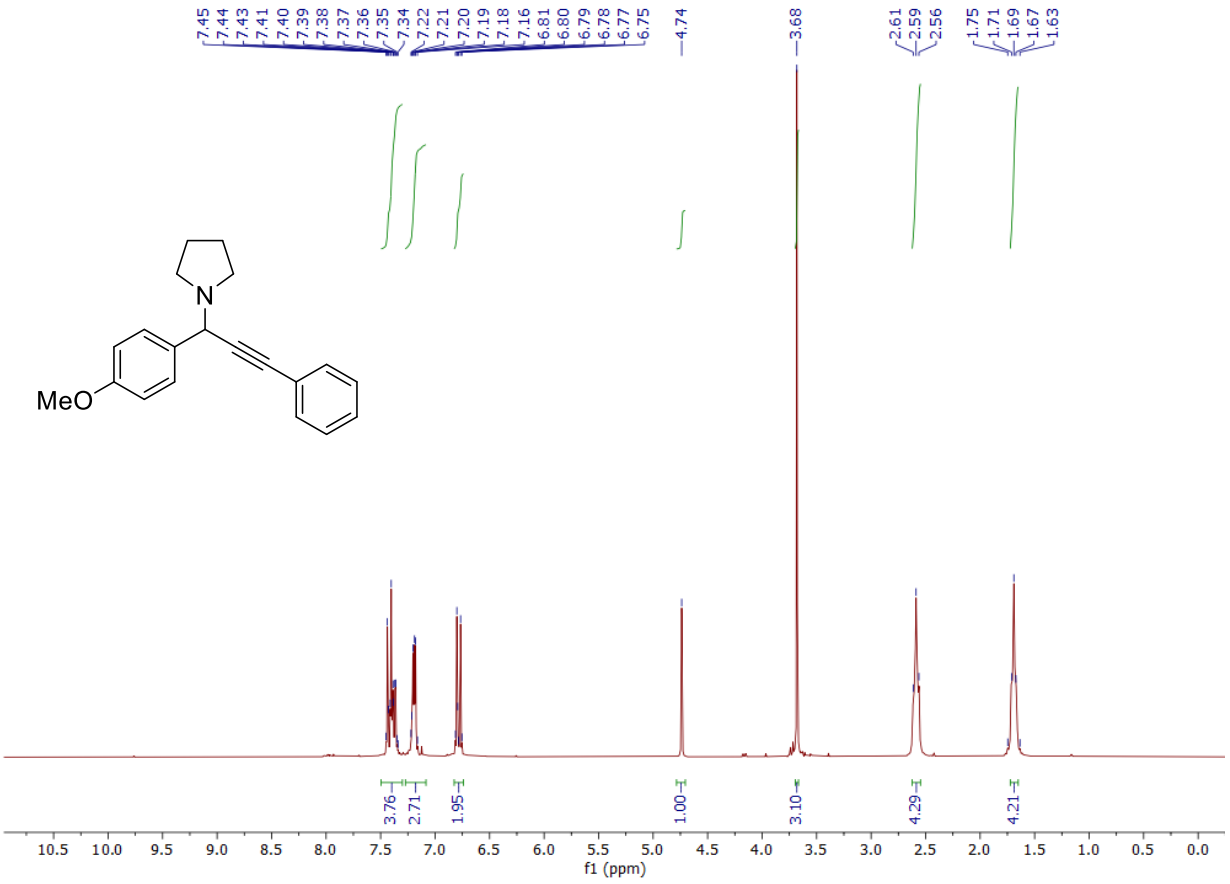

133.67
132.24
129.00
127.83
42.02
14.14
O
S
N
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

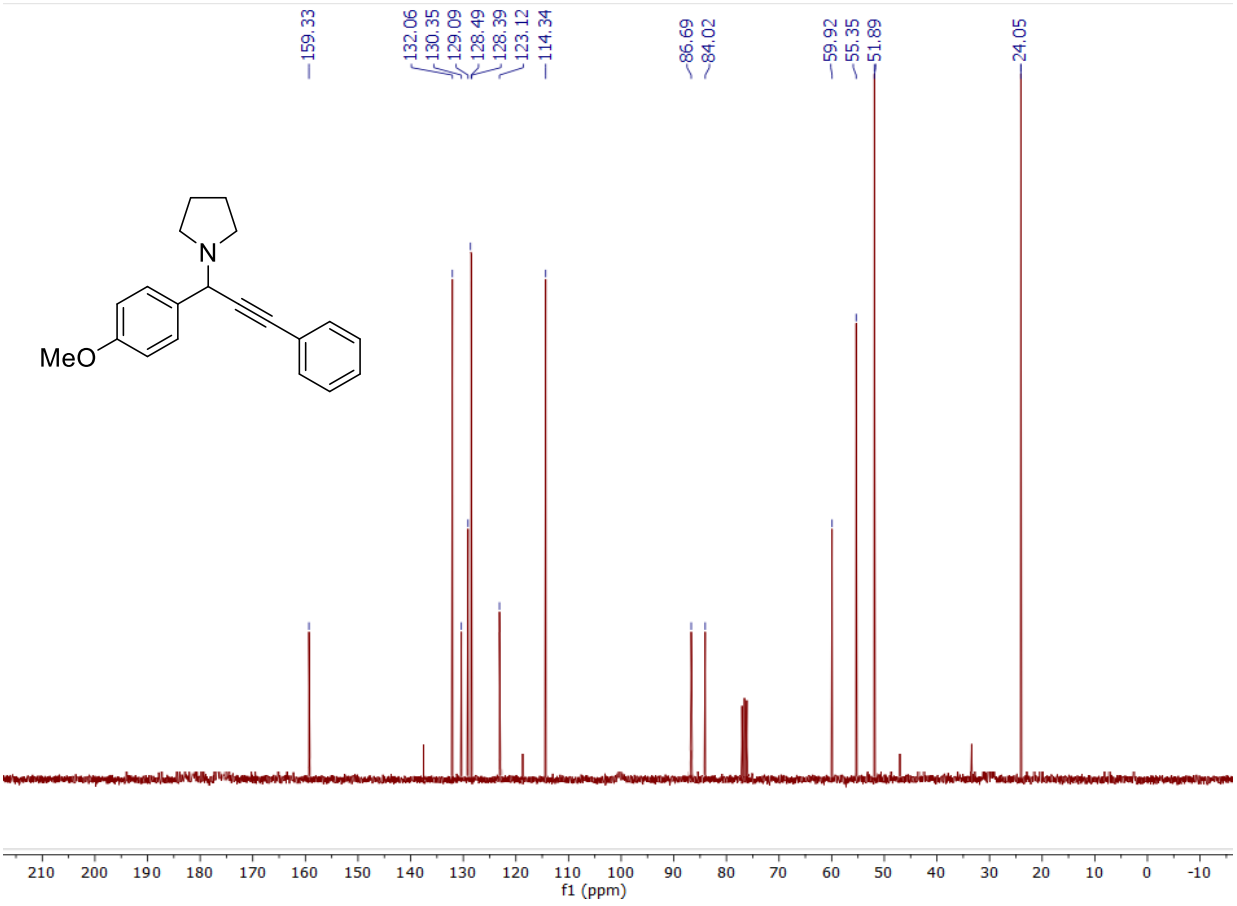

7.71
7.71
7.69
7.69
7.69
7.68
7.54
7.53
7.53
7.53
7.52
7.52
7.52
7.52
7.51
7.49
7.49
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.46
7.45
7.45
2.63
2.62
2.62
O
S
N
O
1.69
2.81
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

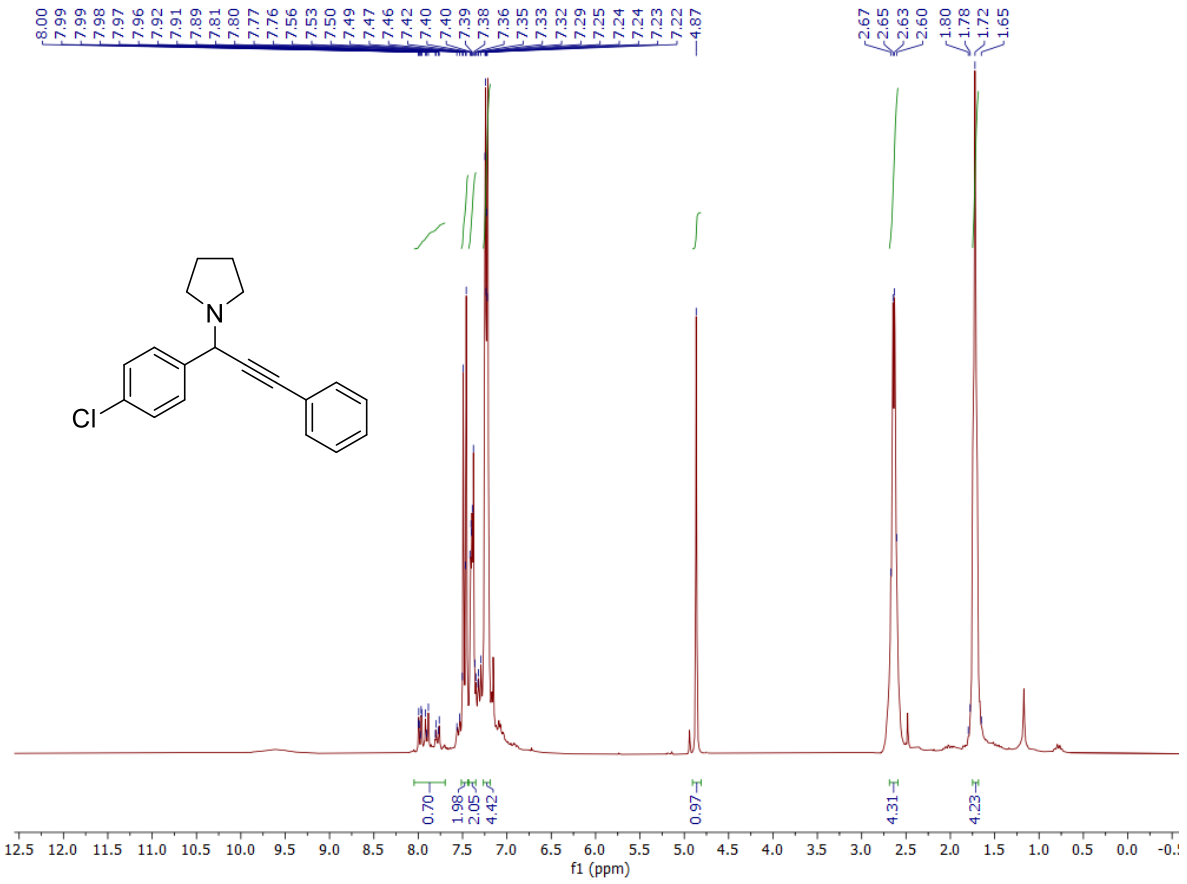

132.73
129.05
127.71
37.93
O
S
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

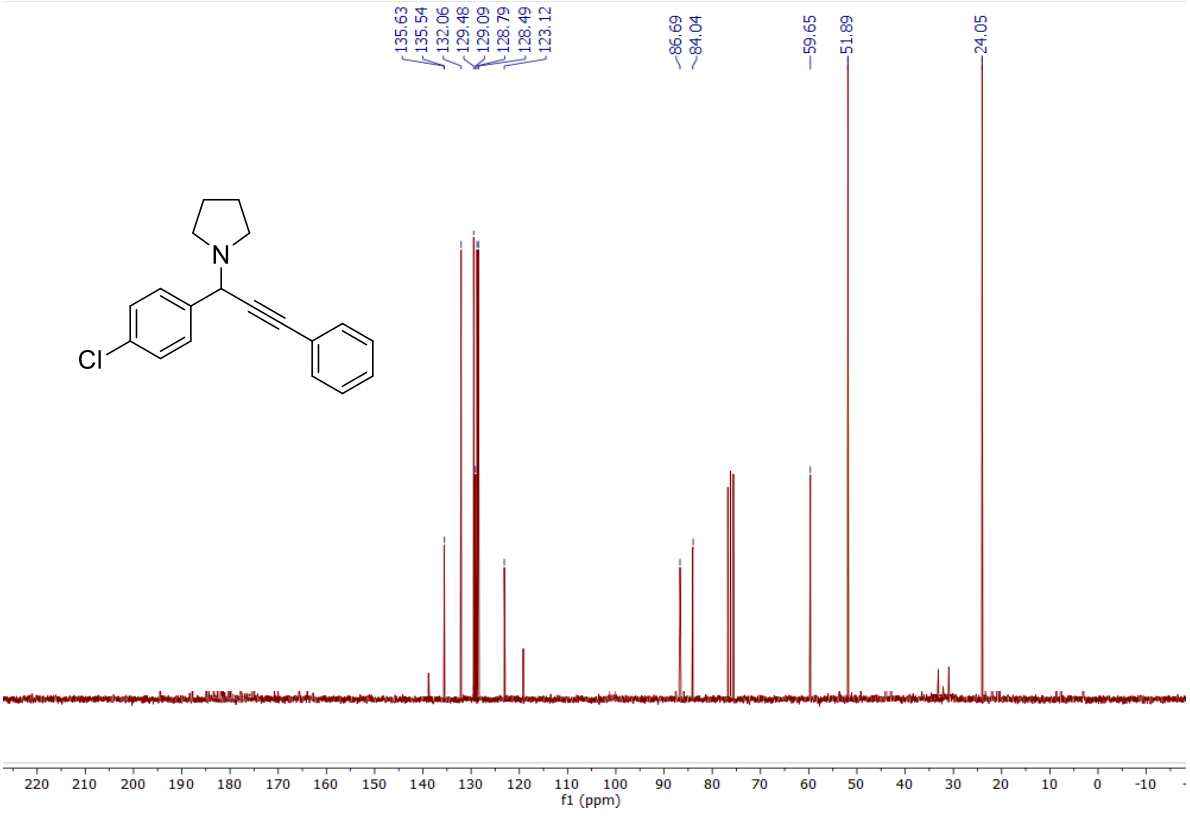

7.56
7.55
7.54
7.53
7.52
7.51
7.44
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.37
7.31
7.30
7.29
7.28
7.27
7.25
7.24
7.23
7.23
7.22
7.20
4.89
2.70
2.67
2.66
2.64
1.76
1.75
1.74
1.73
1.72
1.71
N
2.00
2.12
6.19
0.98
4.24
4.18
f1 (ppm)

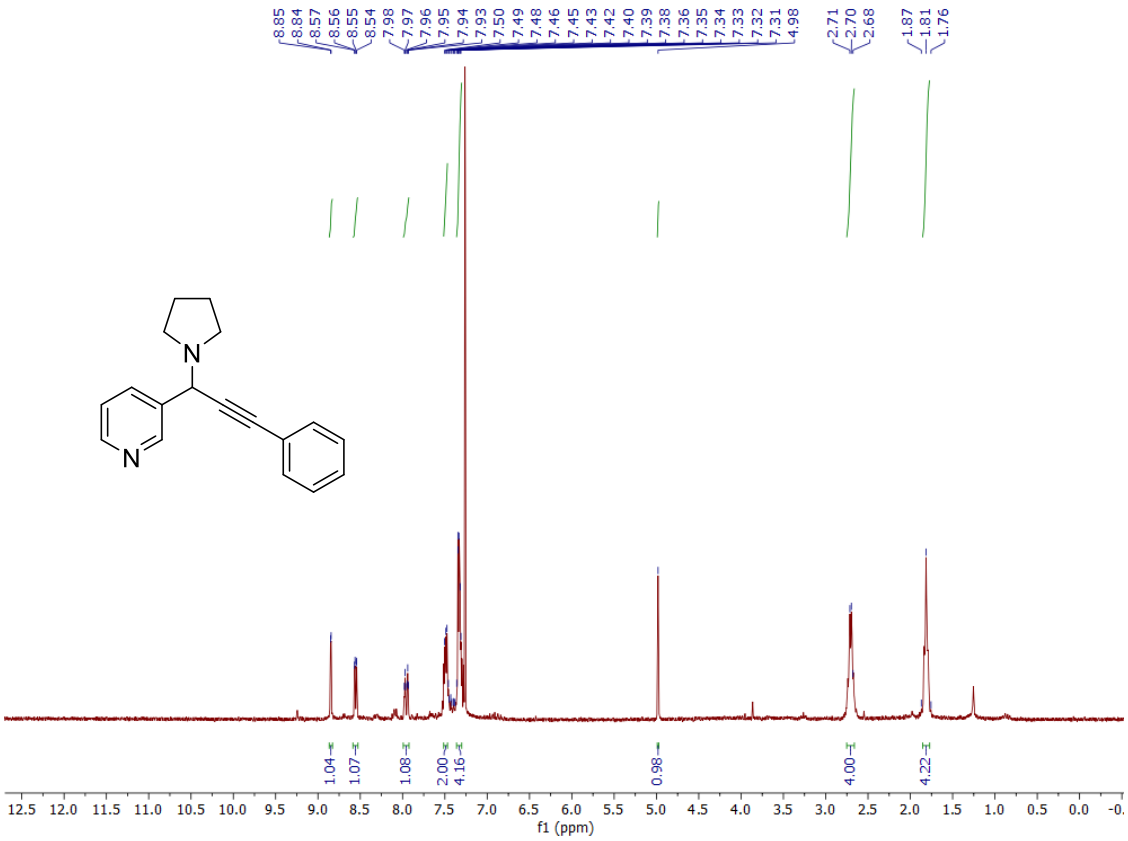

137.36
132.06
129.45
129.38
129.09
128.49
127.42
123.12
86.69
84.05
60.08
51.88
24.05
N
f1 (ppm)

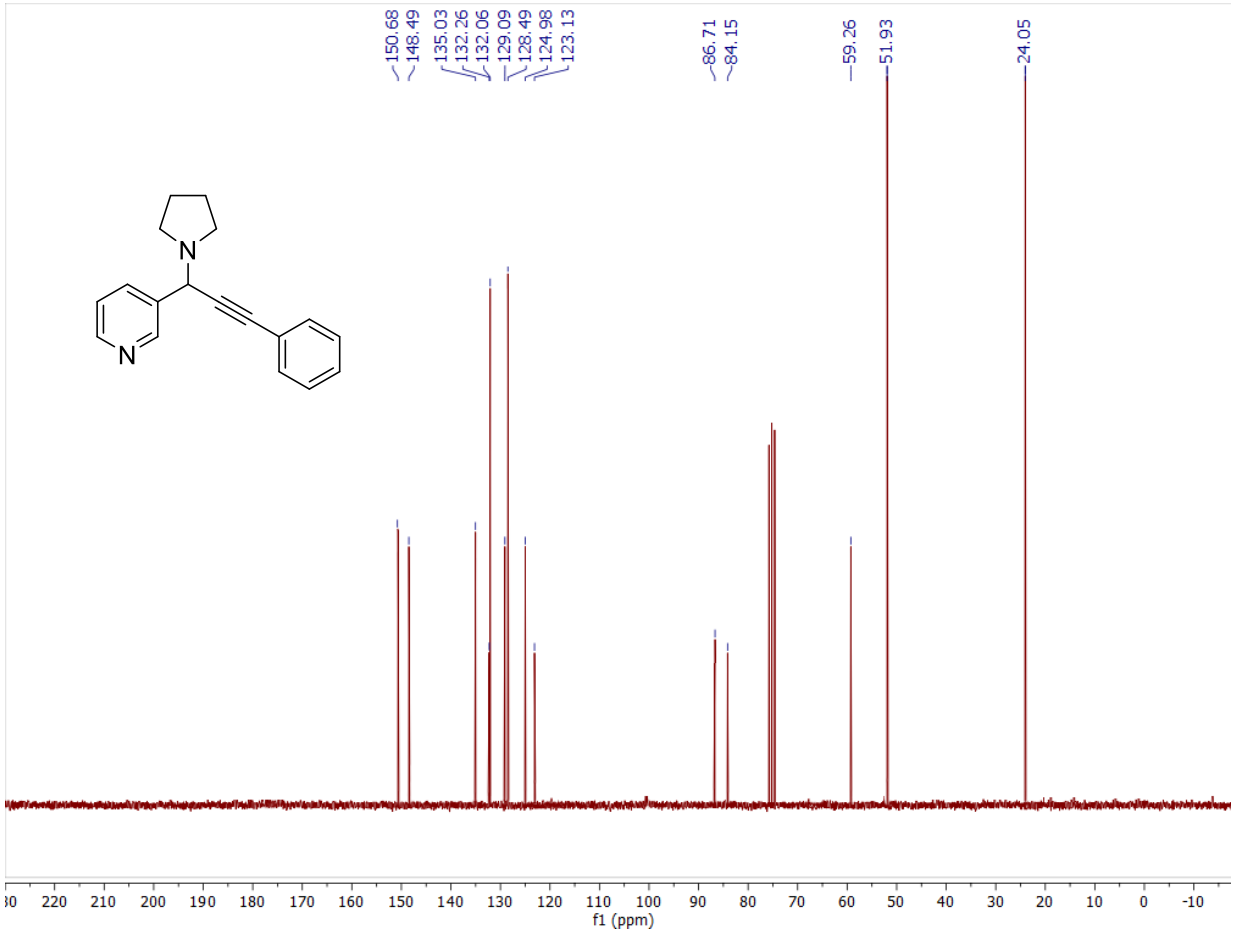

7.45
7.44
7.43
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.22
7.21
7.20
7.19
7.18
7.16
6.81
6.80
6.79
6.78
6.77
6.75
4.74
3.68
2.61
2.59
2.56
1.75
1.71
1.69
1.67
1.63
N
MeO
3.76
2.71
1.95
1.00
3.10
4.29
4.21
f1 (ppm)

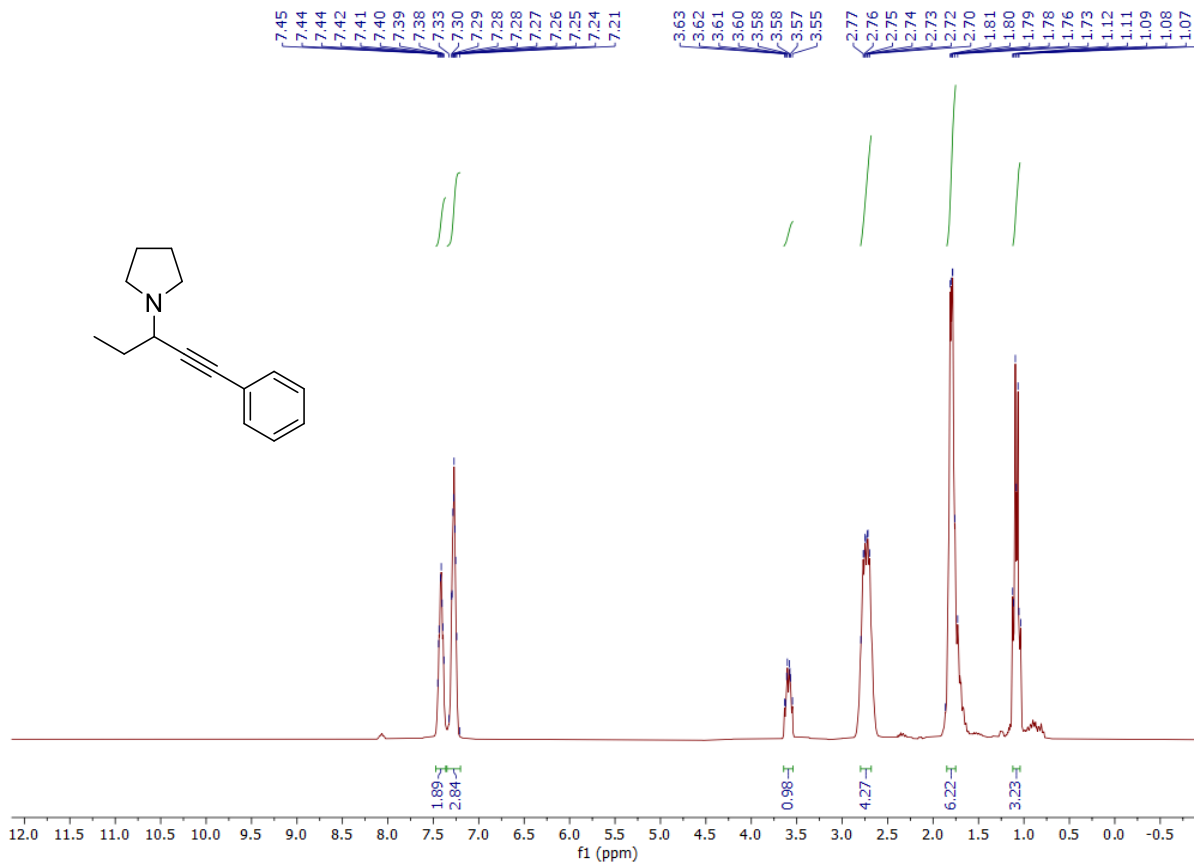

159.33
132.06
130.35
129.09
128.49
128.39
123.12
114.34
86.69
84.02
59.92
55.35
51.89
24.05
N
MeO
f1 (ppm)

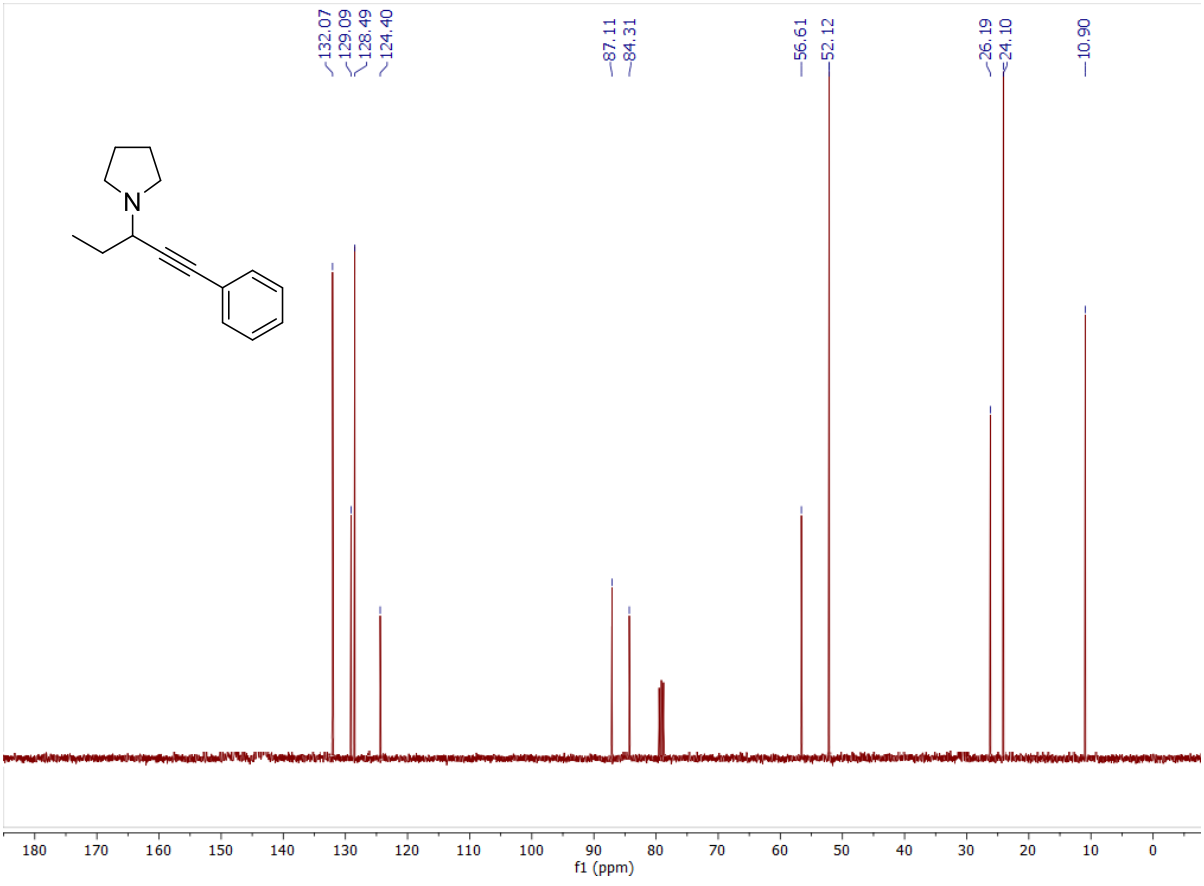

8.00
7.99
7.99
7.98
7.97
7.96
7.92
7.91
7.89
7.81
7.80
7.77
7.76
7.56
7.53
7.50
7.49
7.47
7.46
7.42
7.40
7.40
7.39
7.38
7.36
7.35
7.33
7.32
7.29
7.25
7.24
7.24
7.23
7.22
4.87
2.67
2.65
2.63
2.60
1.80
1.78
1.72
1.65
N
Cl
0.70
1.98
2.05
4.42
0.97
4.31
4.23
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

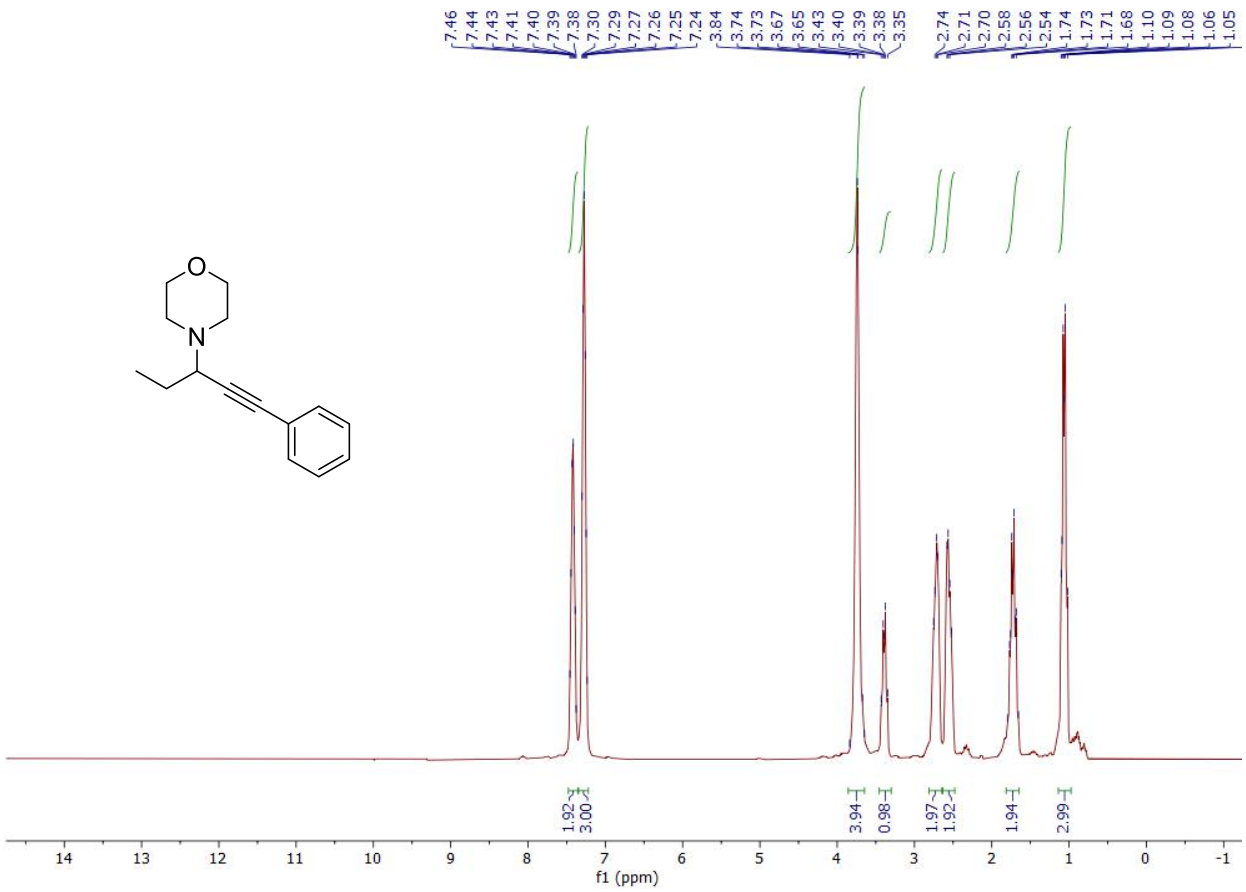

135.63
135.54
132.06
129.48
129.09
128.79
128.49
123.12
86.69
84.04
59.65
51.89
24.05
N
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

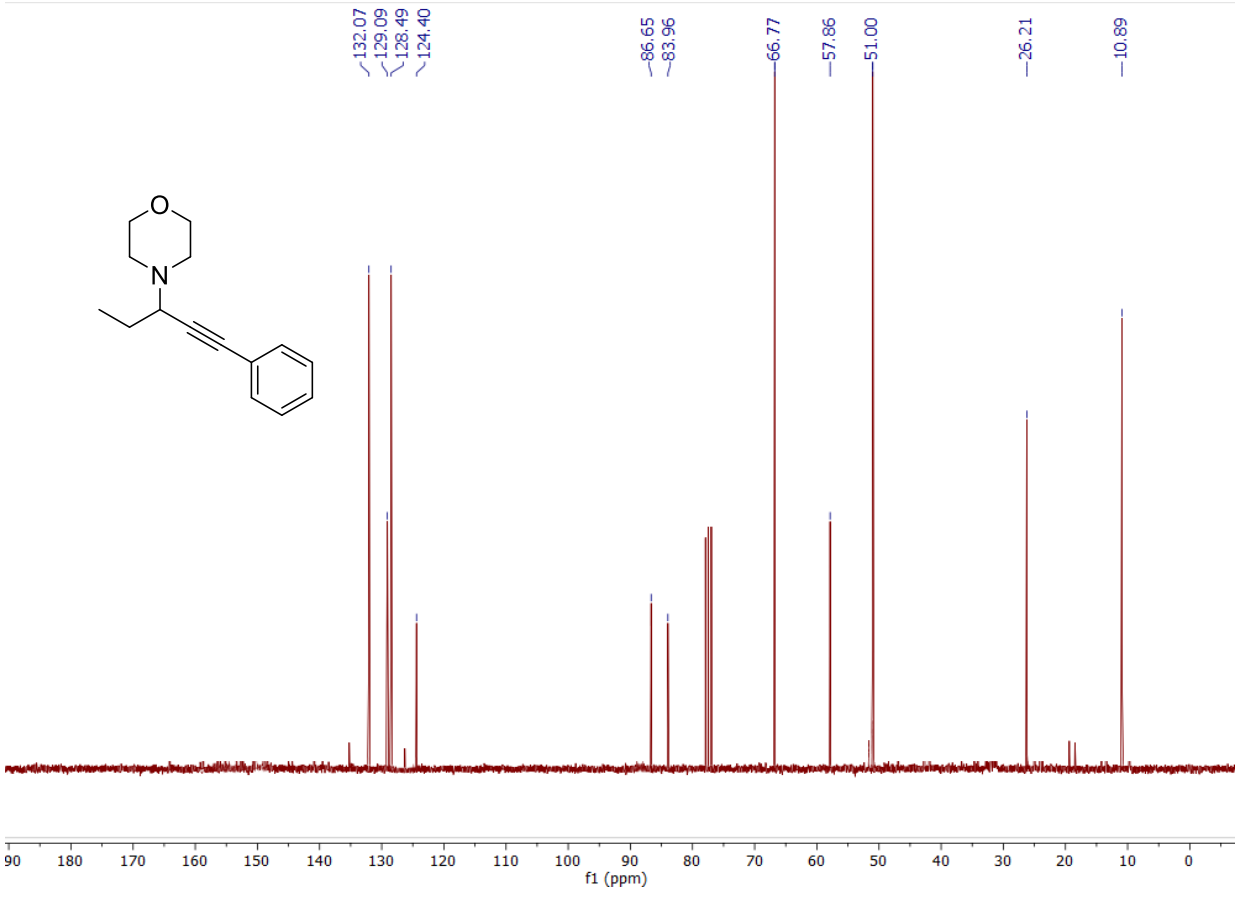

8.85
8.84
8.57
8.56
8.55
8.54
7.98
7.97
7.96
7.95
7.94
7.93
7.50
7.49
7.48
7.46
7.45
7.43
7.42
7.40
7.39
7.38
7.36
7.35
7.34
7.33
7.32
7.31
4.98
2.71
2.70
2.68
1.87
1.81
1.76
1.04
1.07
1.08
2.00
4.16
0.98
4.00
4.22
f1 (ppm)

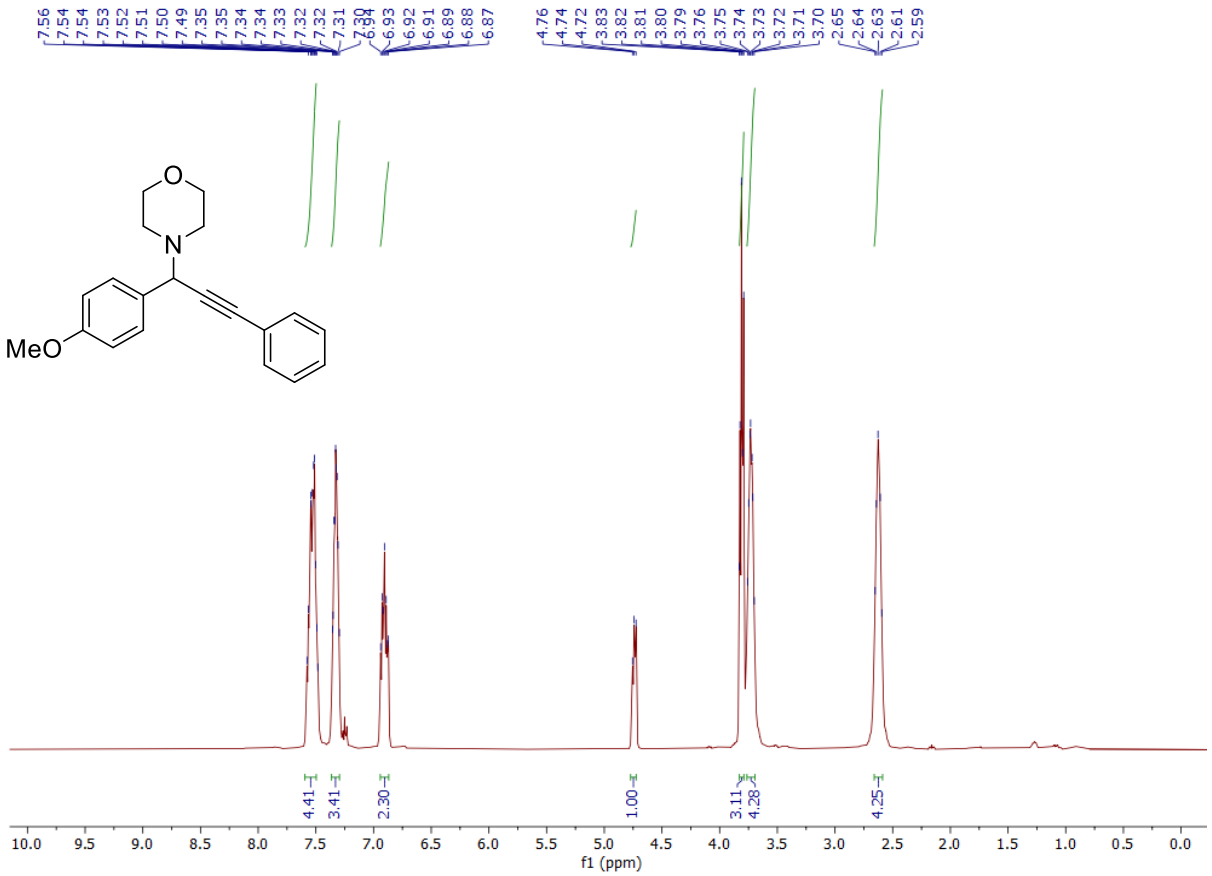

150.68
148.49
135.03
132.26
132.06
129.09
128.49
124.98
123.13
86.71
84.15
59.26
51.93
24.05
f1 (ppm)

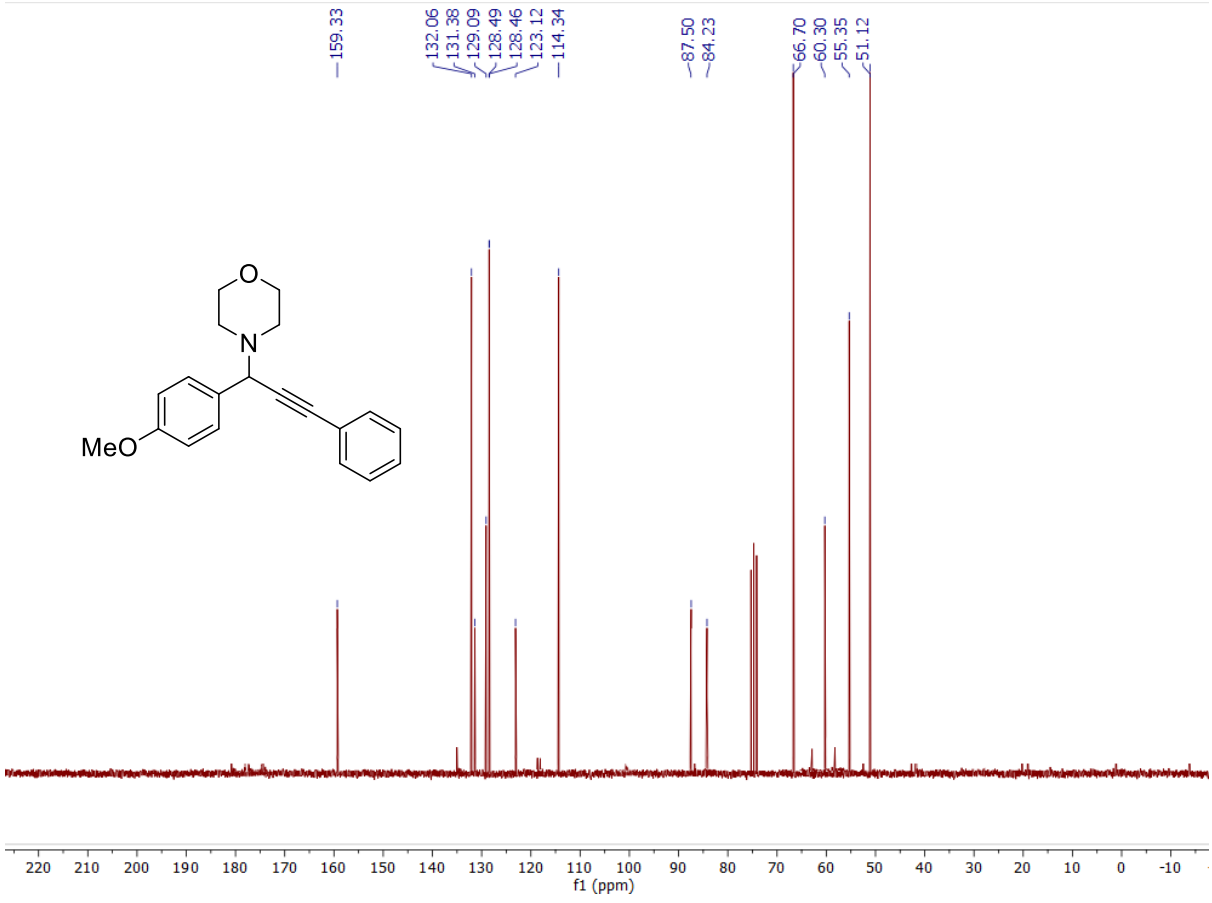

7.45
7.44
7.44
7.42
7.41
7.40
7.39
7.38
7.33
7.30
7.29
7.28
7.28
7.27
7.26
7.25
7.24
7.21
3.63
3.62
3.61
3.60
3.58
3.58
3.57
3.55
2.77
2.76
2.75
2.74
2.73
2.72
2.70
1.81
1.80
1.79
1.78
1.76
1.73
1.12
1.11
1.09
1.08
1.07
N
1.89
2.84
0.98
4.27
6.22
3.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

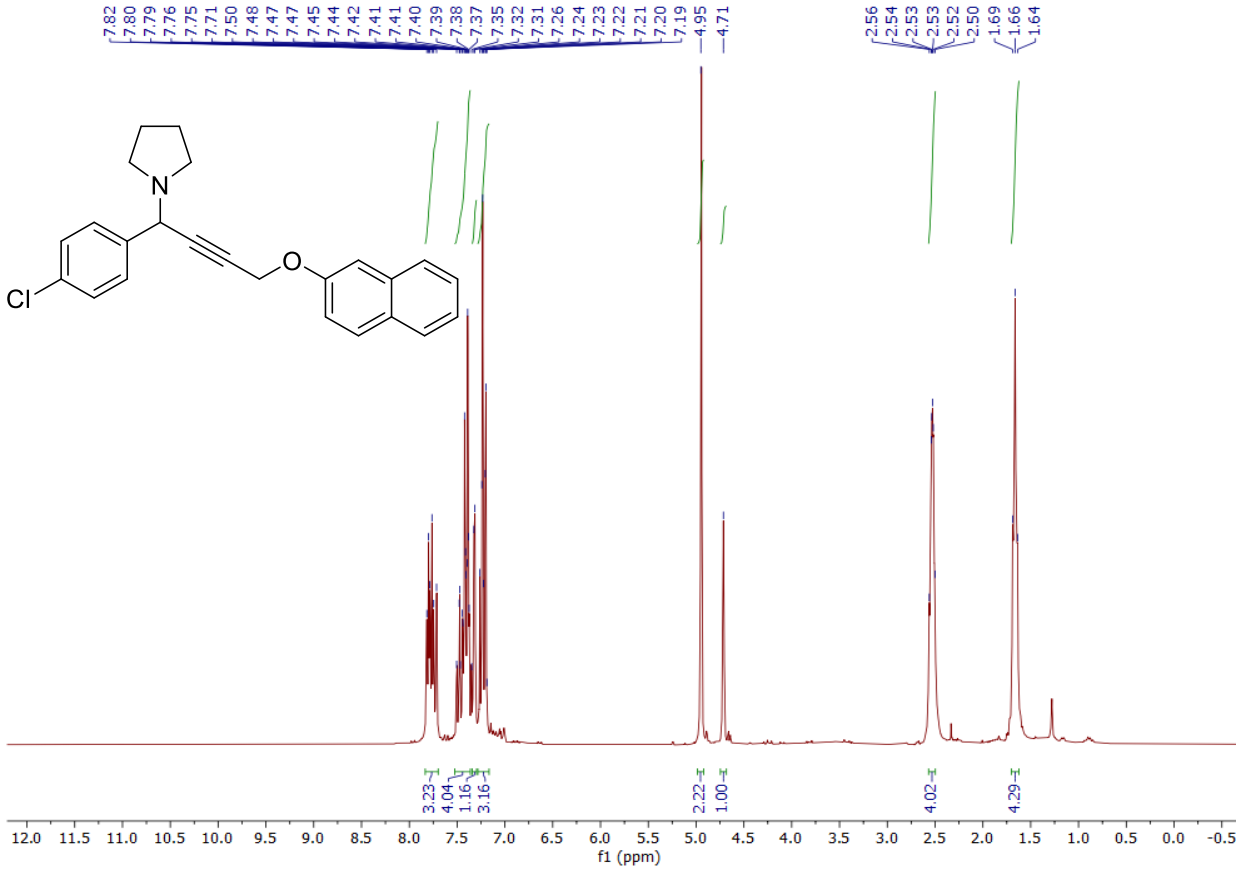

132.07
129.09
128.49
124.40
87.11
84.31
56.61
52.12
26.19
24.10
10.90
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

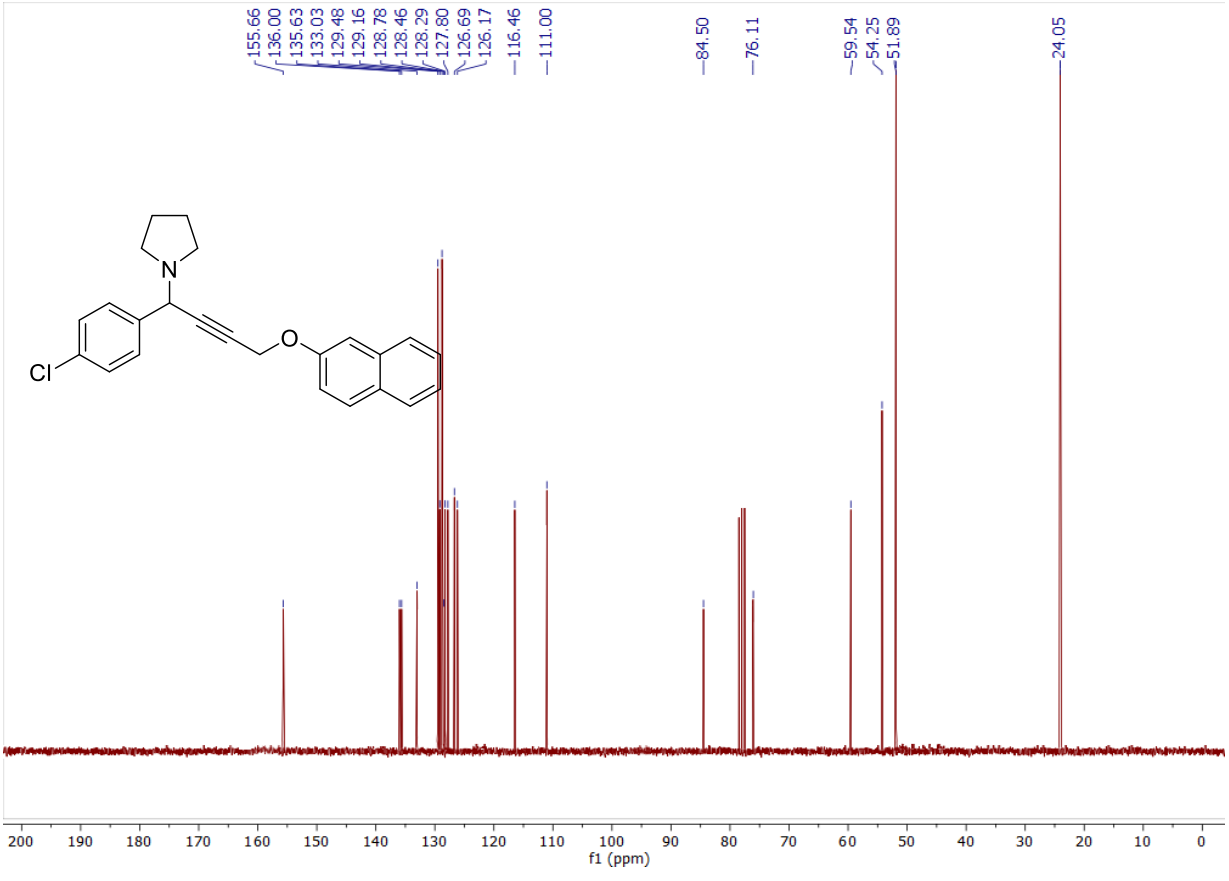

7.46
7.44
7.43
7.41
7.40
7.39
7.38
7.30
7.29
7.27
7.26
7.25
7.24
3.84
3.74
3.73
3.67
3.65
3.43
3.40
3.39
3.38
3.35
2.74
2.71
2.70
2.58
2.56
2.54
1.74
1.73
1.71
1.68
1.10
1.09
1.08
1.06
1.05
1.92
3.00
3.94
0.98
1.97
1.92
1.94
2.99
f1 (ppm)

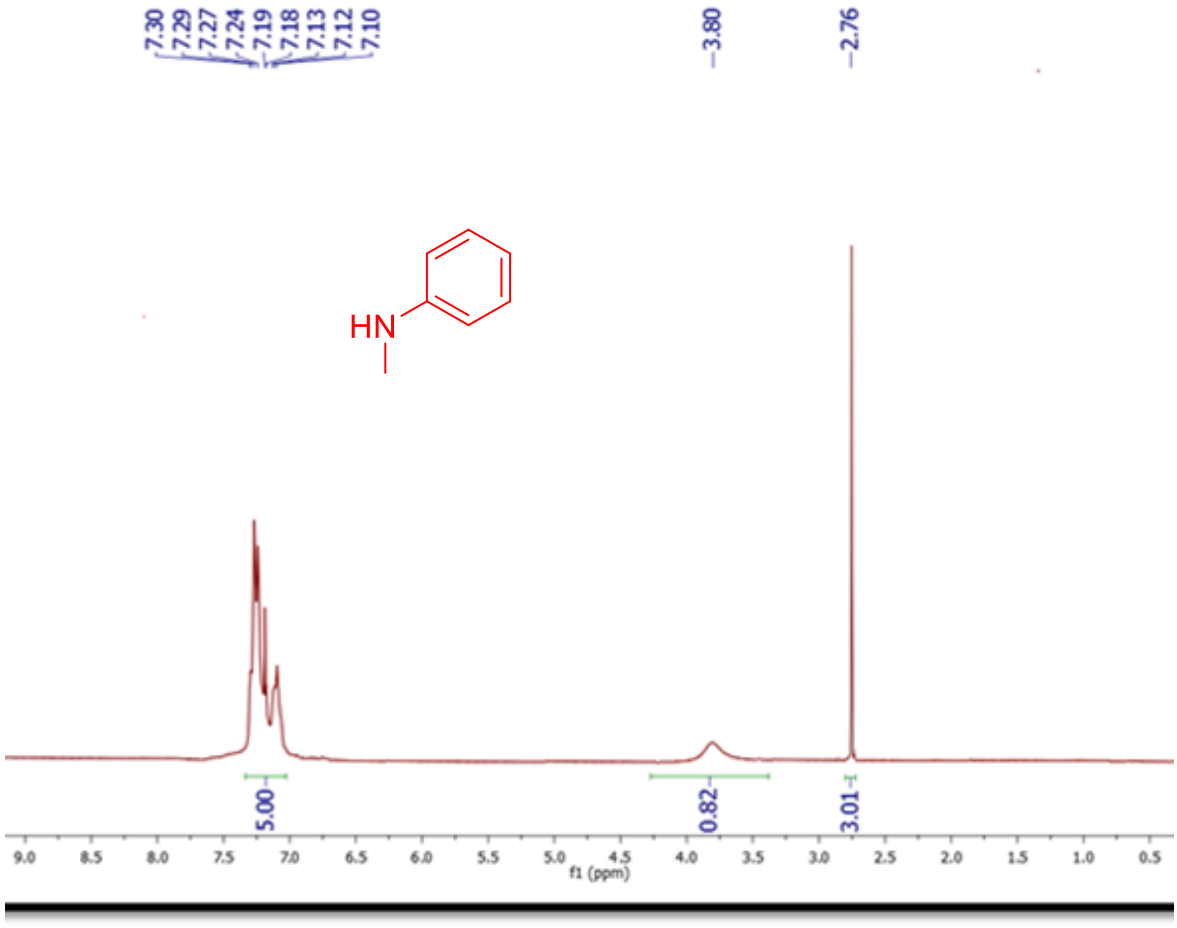

132.07
129.09
128.49
124.40
86.65
83.96
66.77
57.86
51.00
26.21
10.89
f1 (ppm)


7.56
7.54
7.54
7.53
7.52
7.51
7.50
7.49
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
6.94
6.93
6.92
6.91
6.89
6.88
6.87
4.76
4.74
4.72
3.83
3.82
3.81
3.80
3.79
3.76
3.75
3.74
3.73
3.72
3.71
3.70
2.65
2.64
2.63
2.61
2.59
O
N
MeO
4.41
3.41
2.30
1.00
3.11
4.28
4.25
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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.33
132.06
131.38
129.09
128.49
128.46
123.12
114.34
87.50
84.23
66.70
60.30
55.35
51.12
O
N
MeO
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.82
7.80
7.79
7.76
7.75
7.71
7.50
7.48
7.47
7.47
7.45
7.44
7.42
7.41
7.41
7.40
7.39
7.38
7.37
7.35
7.32
7.31
7.26
7.24
7.23
7.22
7.21
7.20
7.19
4.95
4.71
2.56
2.54
2.53
2.53
2.52
2.50
1.69
1.66
1.64
N
O
Cl
3.23
4.04
1.16
3.16
2.22
1.00
4.02
4.29
12.0 11.5 11.0 10.5 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 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


155.66
136.00
135.63
133.03
129.48
129.16
128.78
128.46
128.29
127.80
126.69
126.17
116.46
111.00
84.50
76.11
59.54
54.25
51.89
24.05
N
O
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



5) References

1. A. S. Hassanien and A. A. Akl, *Superlattices and Microstructures*, 2016, 89, 153-169.
2. S. A. Ansari and M. H. Cho, *Scientific reports*, 2016, 6, 25405.
3. R. López and R. Gómez, *Journal of sol-gel science and technology*, 2012, 61, 1-7.
4. J. Tauc, R. Grigorovici and A. Vancu, *physica status solidi (b)*, 1966, 15, 627-637.
5. M. Butler, *Journal of Applied Physics*, 1977, 48, 1914-1920.
6. K. J. Murauski, D. M. Walden, P. H. Y. Cheong and K. A. Scheidt, *Advanced synthesis & catalysis*, 2017, 359, 3713-3719.
7. M. Avalos, R. Babiano, A. Cabanillas, P. Cintas, F. J. Higes, J. L. Jiménez and J. C. Palacios, *The Journal of Organic Chemistry*, 1996, 61, 3738-3748.
8. Y. Mido, *Journal of Molecular Structure*, 1981, 72, 3-8.
9. I. S. R. Karmel, M. Tamm and M. S. Eisen, *Angewandte Chemie International Edition*, 2015, 54, 12422-12425.
10. J. Bhattacharjee, S. Das, R. K. Kottalanka and T. K. Panda, *Dalton Transactions*, 2016, 45, 17824-17832.
11. D. L. Poeira, J. Macara, H. Faustino, J. A. S. Coelho, P. M. P. Gois and M. M. B. Marques, *European Journal of Organic Chemistry*, 2019, 2019, 2695-2701.
12. X. Wang, A. Guram, M. Ronk, J. E. Milne, J. S. Tedrow and M. M. Faul, *Tetrahedron Letters*, 2012, 53, 7-10.
13. H. Toyama, H. Shirakawa, M. Komai, Y. Hashimoto and S. Fujii, *Bioorganic & Medicinal Chemistry*, 2018, 26, 4493-4501.

14. Y. Fu, Q.-Z. Li, Q.-S. Xu, H. Hügel, M.-P. Li and Z. Du, *European Journal of Organic Chemistry*, 2018, 2018, 6966-6970.
15. E. Bisz and M. Szostak, *The Journal of Organic Chemistry*, 2019, 84, 1640-1646.
16. A. R. Katritzky, G. Zhang and J. Wu, *Synthetic Communications*, 1994, 24, 205-216.
17. H. Zhu, Y. Shen, Q. Deng and T. Tu, *Chemical Communications*, 2015, 51, 16573-16576.
18. P. K. Shyam and H.-Y. Jang, *The Journal of organic chemistry*, 2017, 82, 1761-1767.
19. R. Pandya, T. Murashima, L. Tedeschi and A. G. Barrett, *The Journal of organic chemistry*, 2003, 68, 8274-8276.
20. T. Fukuda and M. Iwao, *Heterocycles*, 2012, 86, 1261-1273.
21. M. L. Kantam, S. Laha, J. Yadav and S. Bhargava, *Tetrahedron Letters*, 2008, 49, 3083-3086.
22. Z. Zarei and B. Akhlaghinia, *RSC Advances*, 2016, 6, 106473-106484.
23. A. Moaddeli and M. Abdollahi-Alibeik, *Journal of Porous Materials*, 2018, 25, 147-159.
24. M. Tajbaksh, M. Farhang, H. R. Mardani, R. Hosseinzadeh and Y. Sarrafi, *Chinese Journal of Catalysis*, 2013, 34, 2217-2222.
25. M. Gholinejad, F. Saadati, S. Shaybanizadeh and B. Pullithadathil, *RSC Advances*, 2016, 6, 4983-4991.