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SUPPORTING INFORMATION

Unexpected C=N bond formation *via* NaI-catalyzed oxidative de-tetra-hydrogenative cross-couplings between *N*, *N*-dimethyl aniline and sulfamides

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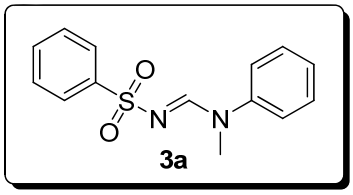
General experimental: All reactions were carried out in air. Solvents were dried and degassed by the standard methods. Benzene suflonamide, *N*,*N*-dimethyl aniline and the additives used in this reaction were obtained from commercial sources and used without further purification. *N*,*N*-disubstituted aniline derivatives were prepared according to the reference.[1] Flash column chromatography was performed using silica gel (300–400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200–300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in $CDCl_3$ on a Varian Inova-400 NMR spectrometer (300 or 400 MHz) with TMS as an internal reference. Products were characterized by comparison of ^{1}H NMR, ^{13}C NMR and TOF-MS data in the literatures.

General procedure for the preparation of benzene-substituted suflonamide.[2] To a Schlenk tube equipped with a magnetic stir bar was added benzene-substituted sulfuryl chloride (1.46 mmol) and ammonium hydroxide (4.0 mL) in air. The reaction mixture was kept stirring at 0 ^{o}C for 3-4 hours. At the end of the reaction, the aqueous layer was extracted with ether and washed with water and brine, the organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography gel (eluent: Hexanes/EtOAc = 90:10 to 80:20) to afford the pure product sulfonamide **1** in 80%~90% yield.

General procedure for the NaI-catalyzed oxidative de-tetra-hydrogenative cross-coupling reactions. To a Schlenk tube equipped with a magnetic stir bar was added sulfonamide **1** (0.5 mmol), **2** aniline (2.1 mmol), NaI (sodiumiodide, 0.01 mmol, 15.0 mg), TBHP (*tert*-butyl hydroperoxide, 5-6 M in decane, 1.5 mmol, 0.27 mL), 1,10-phenanthroline monohydrate (0.05 mmol, 9.0 mg) and ethyl acetate (2.0 mL). The reaction mixture was kept stirring at 80 ^{o}C for 12 hours. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was purified to column chromatography on silica gel (eluent: Hexanes/EtOAc = 90:10 to 80:20) to give the pure product **3**.

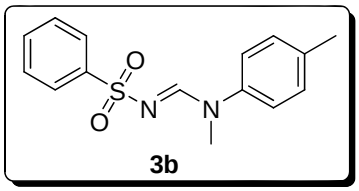
(*E*)-*N*-Methyl-*N*-phenyl-*N′*-(phenylsulfonyl)formimidamide



3a

Yellow solid; mp: 102-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.57 (s, 1H), 7.96-7.93 (m, 2H), 7.54-7.52 (m, 1H), 7.51-7.47 (m, 2H), 7.45-7.41 (m, 2H), 7.34-7.30 (m, 1H), 7.21-7.19 (m, 2H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.6, 143.2, 141.8, 132.2, 129.9, 128.9, 127.5, 126.7, 122.1, 36.1; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{14}H_{15}N_2O_2S$ 275.0854, found 275.0859.

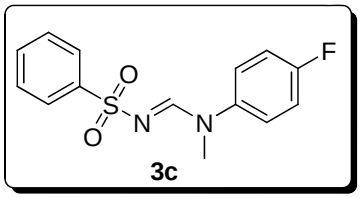
(*E*)-*N*-Methyl-*N′*-(phenylsulfonyl)-*N*-*p*-tolylformimidamide



3b

Yellow solid; mp: 105-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.55 (s, 1H), 7.97-7.95 (m, 2H), 7.56-7.54 (m, 1H), 7.53-7.49 (m, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 3.44 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.5, 141.9, 140.8, 137.5, 132.1, 130.4, 128.8, 126.7, 122.1, 36.3, 20.9; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{15}H_{17}N_2O_2S$ 289.1011, found 289.1018.

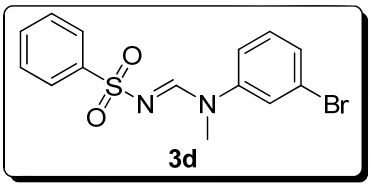
(*E*)-*N*-(4-Fluorophenyl)-*N*-methyl-*N′*-(phenylsulfonyl)formimidamide



3c

Yellow solid; mp: 120-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.51(s, 1H), 7.95 (d, *J* = 6.8 Hz, 2H), 7.59-7.55 (m, 1H), 7.53-7.49(m, 2H), 7.22-7.19 (m, 2H), 7.16-7.12 (m, 2H), 3.44(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 161.5 (d, *J* = 250.0 Hz), 158.5, 141.6, 139.4, 132.3, 128.9, 126.7, 124.4 (d, *J* = 8.6 Hz), 116.8 (d, *J* = 22.9 Hz), 36.6; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{14}H_{14}FN_2O_2S$ 293.0760, found 293.0771.

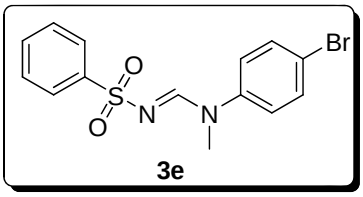
(*E*)-*N*-(3-Bromophenyl)-*N*-methyl-*N′*-(phenylsulfonyl)formimidamide



3d

Yellow solid; mp: 128-130°C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.58 (s, 1H), 7.96-7.94 (m, 2H), 7.57-7.55 (m, 1H), 7.53-7.49 (m, 2H), 7.47-7.45 (m, 1H), 7.38 (t, *J* = 6.0 Hz, 1H), 7.32-7.28 (m, 1H), 7.18-7.15 (m, 1H), 3.44(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.3, 144.3, 141.4, 132.4, 131.2, 130.4, 128.9, 126.8, 125.1, 123.4, 120.6, 36.0; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{14}H_{14}BrN_2O_2S$ 352.9959, found 352.9968.

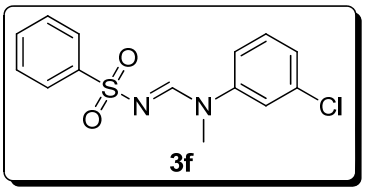
(*E*)-*N*-(4-Bromophenyl)-*N*-methyl-*N′*-(phenylsulfonyl)formimidamide



3e

Yellow solid; mp: 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.55 (s, 1H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.55-7.47 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.2, 142.2, 141.5, 133.0, 132.4, 128.9, 126.7, 123.6, 120.8, 36.0; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{14}H_{14}BrN_2O_2S$ 352.9959, found 352.9962.

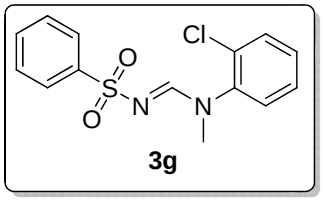
(*E*)-N-(3-Chlorophenyl)-*N*-methyl-*N′*-(phenylsulfonyl)formimidamide



3f

Yellow solid; mp: 124-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.58 (s, 1H), 7.94 (d, *J* = 7.2 Hz, 2H), 7.56-7.48 (m, 3H), 7.39-7.35 (m, 1H), 7.31-7.28 (m, 1H), 7.22(t, *J* = 2.0 Hz, 1H), 7.13-7.10 (m, 1H), 3.43(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.3, 144.2, 141.4, 135.5, 132.4, 131.0, 128.9, 127.5, 126.7, 122.2, 120.1, 36.0; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{14}H_{14}ClN_2O_2S$ 309.0465, found 309.0466.

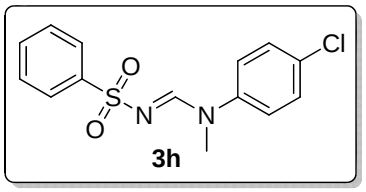
(*E*)-*N*-(2-Chlorophenyl)-*N*-methyl-*N'*-(phenylsulfonyl)formimidamide



3g

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.32 (s, 1H), 7.97-7.95 (m,2H), 7.58-7.50 (m, 4H), 7.40-7.38 (m, 2H), 7.31-7.28(m, 1H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.1, 141.7, 140.5, 132.2, 131.4, 131.0, 130.2, 128.8, 128.3, 126.8, 37.1; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{14}H_{14}ClN_2O_2S$ 309.0465, found 309.0466.

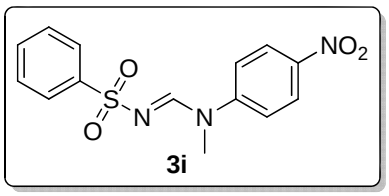
(*E*)-*N*-(4-Chlorophenyl)-*N*-methyl-*N'*-(phenylsulfonyl)formimidamide



3h

Yellow solid; mp: 110-111 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.56 (s, 1H), 7.96-7.94 (m, 2H), 7.57-7.49 (m, 3H), 7.43-7.40 (m, 2H), 7.18-7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.3, 141.7, 141.5, 133.1, 132.3, 130.0, 128.9, 126.7, 123.3, 36.1; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{14}H_{14}ClN_2O_2S$ 309.0465, found 309.0467.

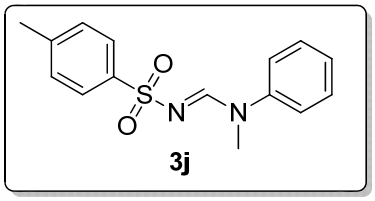
(*E*)-*N*-Methyl-*N*-(4-nitrophenyl)-*N'*-(phenylsulfonyl)formimidamide



3i

Yellow solid; mp: 128-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.70 (s, 1H), 8.20-8.17 (m, 1H), 8.10 (t, J = 2.0 Hz, 1H), 7.96-7.94 (m, 2H), 7.69-7.65 (m, 1H), 7.62-7.57 (m, 2H), 7.54-7.51 (m, 2H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.2, 149.0, 144.1, 141.0, 132.6, 131.0, 129.0, 127.3, 126.8, 121.8, 116.6, 35.9; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{14}H_{14}N_3O_4S$ 320.0705, found 320.0709.

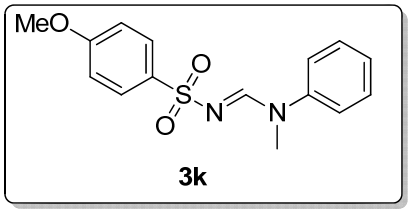
(*E*)-*N*-Methyl-*N*-phenyl-*N'*-tosylformimidamide



3j

Yellow solid; mp: 108-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.58 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.46-7.42 (m, 2H), 7.35-7.28 (m, 3H), 7.22-7.20 (m, 2H), 3.45(s, 3H), 2.43(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.4, 143.2, 142.9, 138.9, 129.9, 129.5, 127.3, 126.8, 122.1, 36.1, 21.5; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{15}H_{17}N_2O_2S$ 289.1011, found 289.1013.

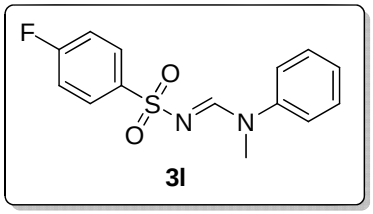
(*E*)-*N'*-(4-Methoxyphenylsulfonyl)-*N*-methyl-*N*-phenylformimidamide



3k

Yellow solid; mp: 101-104 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.56 (s, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.45-7.44 (m, 2H), 7.33-7.28 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 162.6, 158.2, 143.3, 133.6, 129.9, 128.8, 127.3, 122.0, 114.0, 55.6, 36.0; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{15}H_{17}N_2O_3S$ 305.0960, found 305.0971.

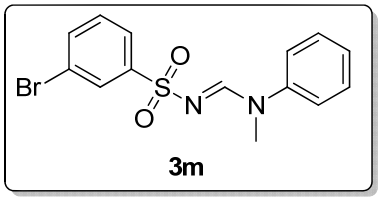
(*E*)-*N'*-(4-Fluorophenylsulfonyl)-*N*-methyl-*N*-phenylformimidamide



3l

Yellow solid; mp: 125-128 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.57 (s, 1H), 7.98-7.95 (m, 2H), 7.47-7.43 (m, 2H), 7.37-7.33 (m, 1H), 7.23-7.21 (m, 2H), 7.20-7.15 (m, 2H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.9 (d, *J* = 252 Hz), 158.5, 143.1, 137.9, 129.9, 129.5 (d, *J* = 9.2 Hz), 127.5, 122.2, 116.0 (d, *J* = 22.4 Hz), 36.2; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{14}H_{14}FN_2O_2S$ 293.0760, found 293.0769.

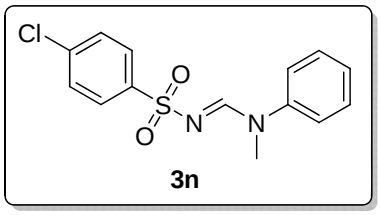
(*E*)-*N'*-(3-Bromophenylsulfonyl)-*N*-methyl-*N*-phenylformimidamide



3m

Yellow solid; mp: 99-100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.54(s, 1H), 8.07 (t, *J* = 2.0 Hz, 1H), 7.89-7.86 (m, 1H), 7.67-7.64 (m, 1H), 7.46-7.41(m, 2H), 7.37-7.32 (m, 2H), 7.23-7.20 (m, 2H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.7, 143.7, 143.0, 135.2, 130.5, 130.0, 129.7, 127.7, 125.3, 122.7, 122.2, 36.3; HRMS (TOF MS Cl^{+}) $[M+H]^{+}$ calculated for $C_{14}H_{14}BrN_2O_2S$ 352.9959, found 352.9963.

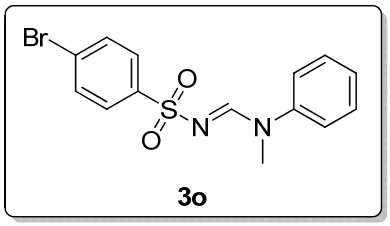
(*E*)-*N'*-(4-Chlorophenylsulfonyl)-*N*-methyl-*N*-phenylformimidamide



3n

Yellow solid; mp: 96-99 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.56 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.48-7.43 (m, 4H), 7.36-7.33 (m, 1H), 7.23-7.21 (m, 2H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.6, 143.1, 140.4, 138.6, 129.9, 129.1, 128.2, 127.6, 122.2, 36.2; HRMS (TOF MS Cl^{+}) $[M+H]^{+}$ calculated for $C_{14}H_{14}ClN_2O_2S$ 309.0465, found 309.0466.

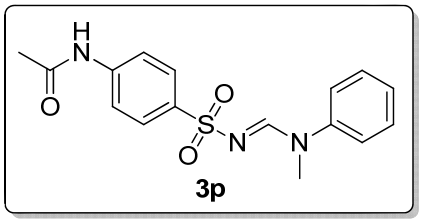
(*E*)-*N'*-(4-Bromophenylsulfonyl)-*N*-methyl-*N*-phenylformimidamide



3o

Yellow solid; mp: 105-106 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.57 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.48 -7.44 (m, 2H), 7.38-7.34 (m, 1H), 7.24-7.21 (m, 2H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.6, 143.1, 140.9, 132.1, 129.9, 128.4, 127.6, 127.1, 122.2, 36.2; HRMS (TOF MS Cl^{+}) $[M+H]^{+}$ calculated for $C_{14}H_{14}BrN_2O_2S$ 352.9959, found 352.9970.

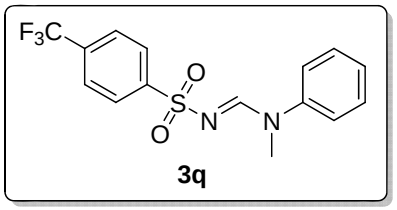
(*E*)-*N*-(4-(*N*-((Methyl(phenyl)amino)methylene)sulfamoyl)phenyl)acetamide



3p

Yellow solid; mp: 200-203 ^{o}C; ^{1}H NMR (400 MHz, DMSO) (δ, ppm) 10.32 (s, 1H), 8.48(s, 1H), 7.82-7.74 (m, 4H), 7.50-7.43 (m, 4H), 7.37-7.34 (m, 1H), 3.38 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) 169.4, 158.8, 143.5, 143.1, 136.0, 130.1, 128.0, 127.4, 122.5, 119.0, 36.0, 24.6; HRMS (TOF MS Cl^{+}) $[M+H]^{+}$ calculated for $C_{16}H_{18}N_3O_3S$ 332.1069, found 332.1078.

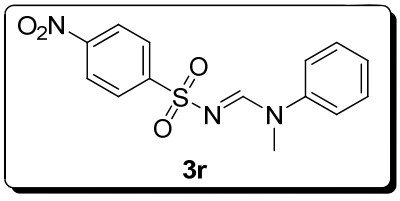
(*E*)-*N*-Methyl-*N*-phenyl-*N'*-(4-(trifluoromethyl)phenylsulfonyl)formimidamide



3q

Yellow solid; mp: 102-104 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.57 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.47-7.43 (m, 2H), 7.37-7.33 (m, 1H), 7.23-7.21 (m, 2H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.9, 145.4, 143.0, 133.8 (d, *J* = 32.7 Hz), 130.0, 127.8, 127.3, 126.0 (q, *J* = 3.7 Hz), 122.3, 36.3; HRMS (TOF MS Cl^{+}) $[M+H]^{+}$ calculated for $C_{15}H_{14}F_3N_2O_2S$ 343.0728, found 343.0730.

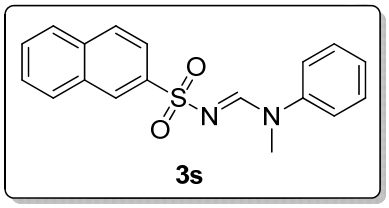
(*E*)-*N*-Methyl-*N'*-(4-nitrophenylsulfonyl)-*N*-phenylformimidamide



3r

Yellow solid; mp: 148-149 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.58 (s, 1H), 8.35 (d. *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 9.2 Hz, 2H), 7.49-7.45 (m, 2H), 7.40-7.36 (m, 1H), 7.25-7.23 (m, 2H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 159.0, 149.8, 147.6, 142.9, 130.0, 128.1, 127.9, 124.1, 122.3, 36.5; HRMS (TOF MS Cl^{+}) $[M+H]^{+}$ calculated for $C_{14}H_{14}N_3O_4S$ 320.0705, found 320.0708.

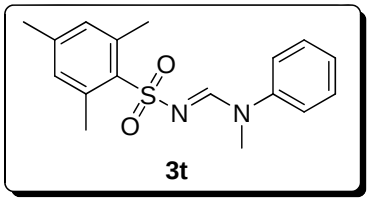
(*E*)-*N*-Methyl-*N'*-(naphthalen-2-ylsulfonyl)-*N*-phenylformimidamide



3s

Yellow solid; mp: 132-134 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.63 (s, 1H), 8.52 (s, 1H), 7.96-7.88 (m, 4H), 7.63-7.56 (m, 2H), 7.45-7.41 (m, 2H), 7.34-7.30 (m, 1H), 7.21-7.19 (m, 2H), 3.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.6, 143.2, 138.7, 134.7, 132.2, 129.9, 129.3, 129.1, 128.5, 127.9, 127.5, 127.4, 127.3, 122.6, 122.1, 36.2; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{18}H_{17}N_2O_2S$ 325.1011, found 325.1017.

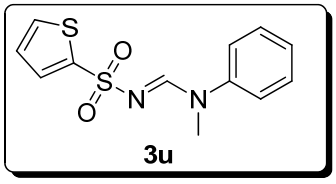
(*E*)-*N'*-(Mesitylsulfonyl)-*N*-methyl-*N*-phenylformimidamide



3t

Yellow solid; mp: 151-152 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.58 (s, 1H), 7.44-7.40 (m, 2H), 7.33-7.29 (m, 1H), 7.19-7.17 (m, 2H), 6.94 (s, 2H), 3.43 (s, 3H), 2.71 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 157.7, 143.4, 141.7, 138.8, 135.8, 131.6, 129.9, 127.2, 122.0, 36.0, 23.0, 20.9; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{17}H_{21}N_2O_2S$ 317.1324, found 317.1329.

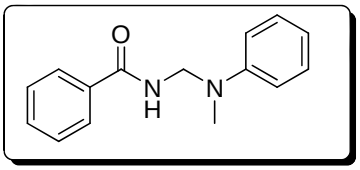
(*E*)-*N*-Methyl-*N*-phenyl-*N'*-(thiophen-2-ylsulfonyl)formimidamide



3u

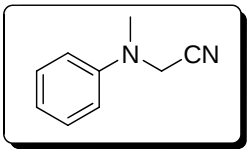
Yellow solid; mp: 105-106 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.54 (s, 1H), 7.65-7.64 (m, 1H), 7.56-7.55 (m, 1H), 7.46-7.42 (m, 2H), 7.35-7.31 (m, 1H), 7.21-7.19 (m, 2H), 7.07-7.04 (m, 1H), 3.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.6, 143.1, 143.0, 131.4, 131.2, 129.9, 127.6, 127.2, 122.2, 36.3; HRMS (TOF MS Cl^+) $[M+H]^+$ calculated for $C_{12}H_{13}N_2O_2S_2$ 281.0418, found 281.0426.

_N_-((Methyl(phenyl)amino)methyl)benzamide



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.73-7.71 (m, 2H), 7.50-7.46 (m, 1H), 7.41-7.37 (m, 2H), 7.30-7.25 (m, 2H), 6.87-6.80 (m, 3H), 6.64 (s, 1H), 5.11 (d, *J* = 5.6 Hz, 2H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.0, 147.9, 134.1, 131.7, 129.5, 128.6, 127.0, 118.3, 113.3, 58.2, 38.0.

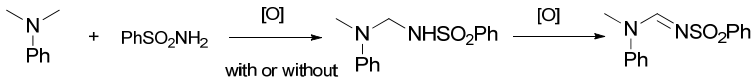
2-(Methyl(phenyl)amino)acetonitrile



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.38-7.34 (m, 2H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.19 (s, 1H), 3.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 147.8, 129.5, 120.2, 115.6, 114.9, 42.3, 39.3.

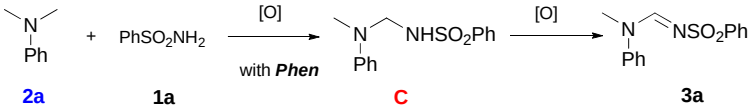
Mechanism Study of the Ligand

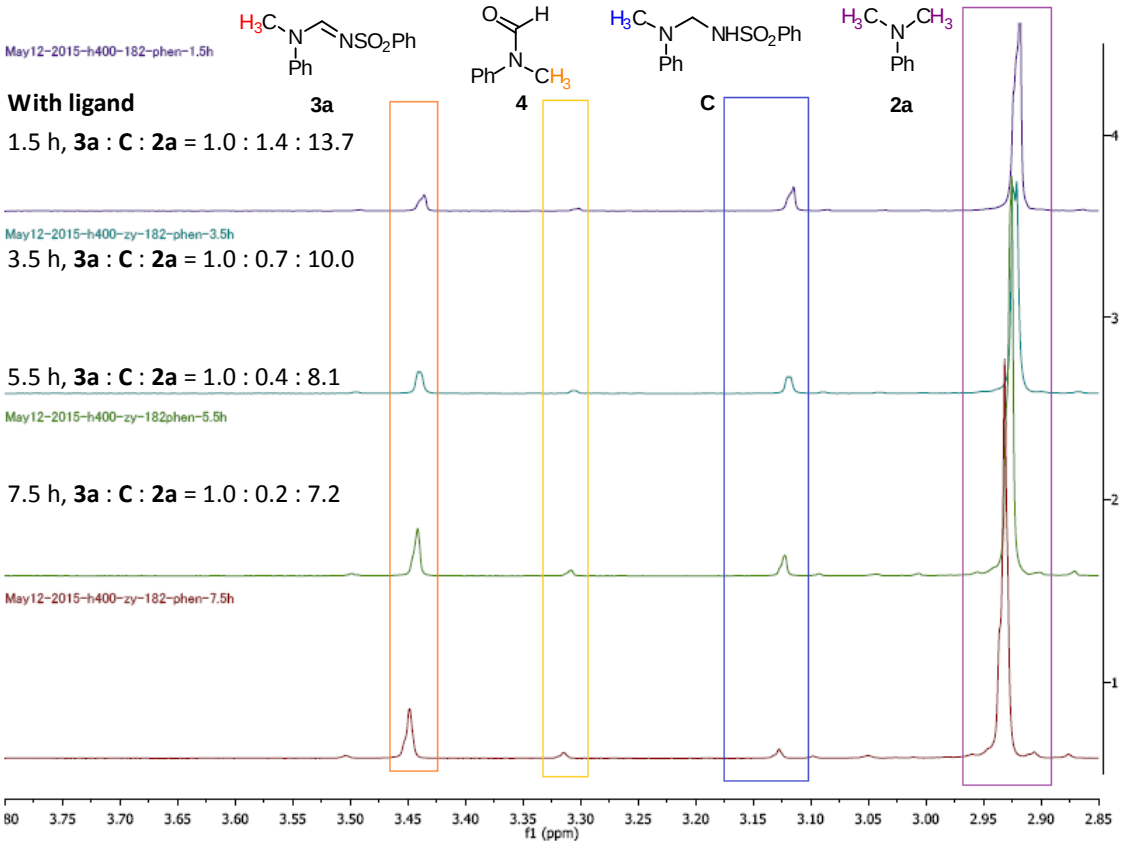
We collected the reaction conversion data at 1.5 h, 3.5 h, 5.5 h and 7.5 h for both reactions, and the results are summarized below. With these data, we found that, at various reaction times, the ratio of **3a**:**C** is almost idential either in the reaction with or without ligand (see the red part in the Table below, and determined from the ratio of integrated absorptions in ^{1}H NMR spectra that corresponded to the methyl groups with crude reaction mixture); however, the ratio of **3a**: **2a** or **C**:**2a** ***in the reaction with the ligand is higher then the one without the ligand (***see the blue part in the Table below). Although we are still not sure how exactly the ligand works in our system, according to these observation, we can confirm that the ligand assists the first part of the transforamtion to form the intermedate **C**

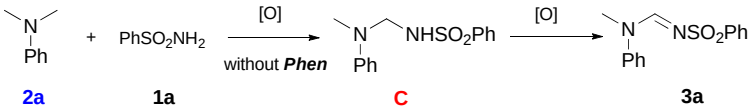


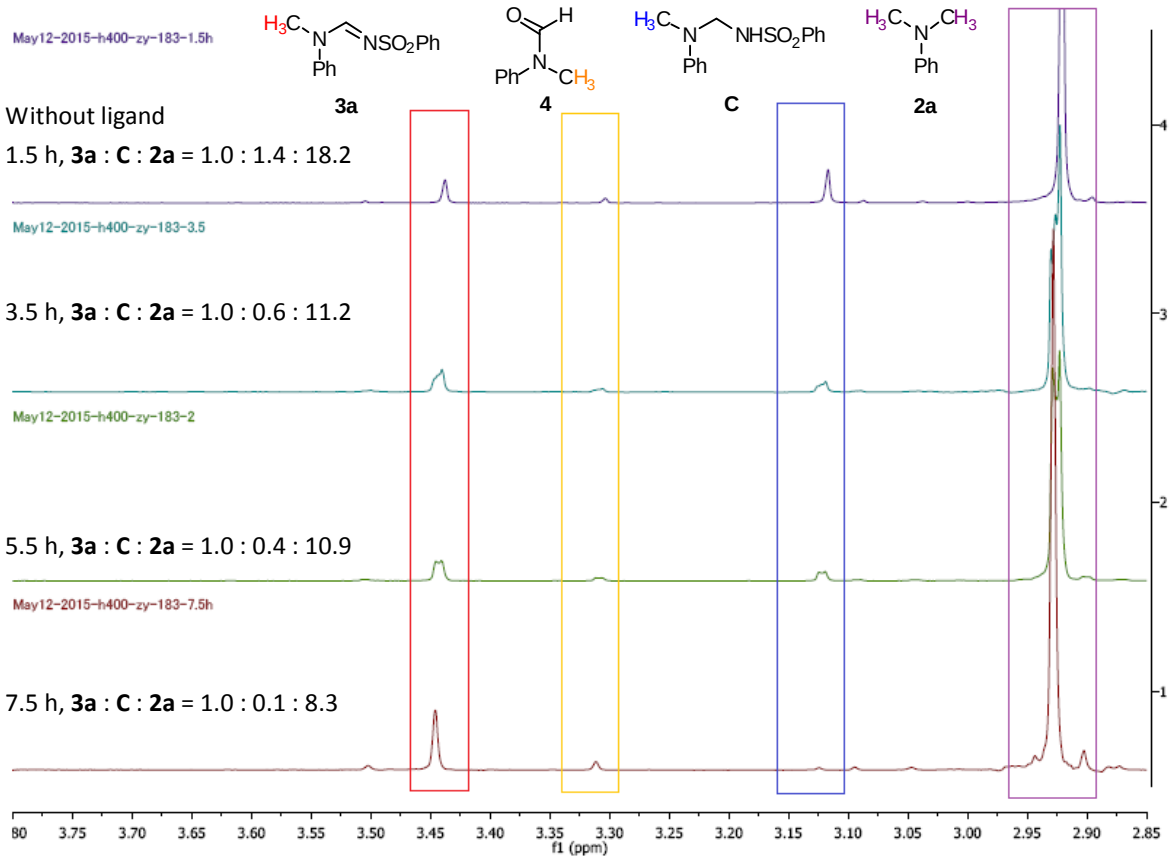
2a **1a** **C** **3a**

Time	With ligand (**3a**:**C**:**2a**)	Without ligand (**3a**:**C**:**2a**)
1.5 h	1.0:1.4:13.7	1.0:1.4:18.2
3.5 h	1.0:0.7:10.0	1.0:0.6:11.2
5.5 h	1.0:0.4:8.1	1.0:0.4:10.9
7.5 h	1.0:0.2:7.2	1.0:0.1:8.3


[O]
with *Phen*
[O]
2a
1a
C
3a

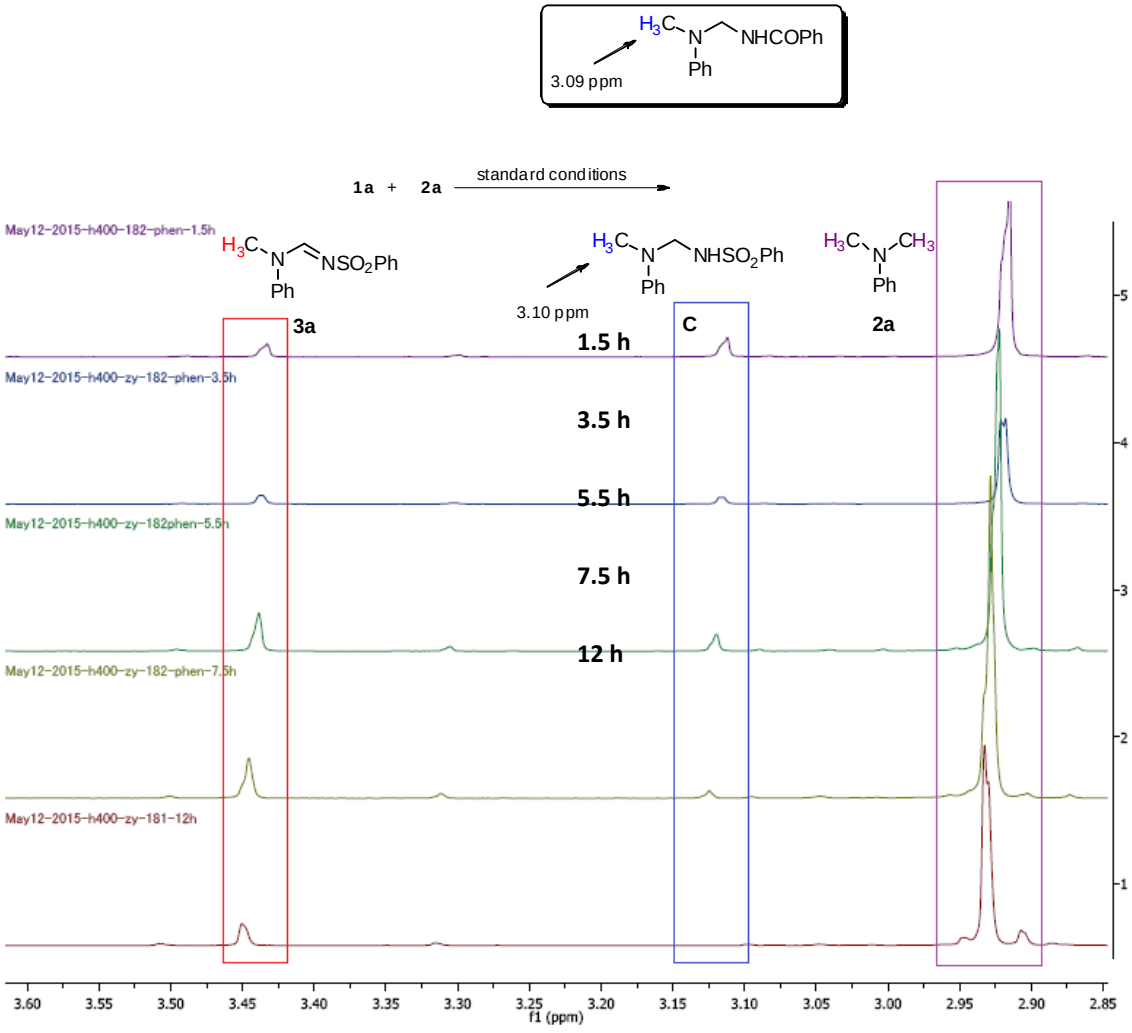

May12-2015-h400-182-phen-1.5h
With ligand
3a
4
C
2a
1.5 h, 3a : C : 2a = 1.0 : 1.4 : 13.7
May12-2015-h400-zy-182-phen-3.5h
3.5 h, 3a : C : 2a = 1.0 : 0.7 : 10.0
5.5 h, 3a : C : 2a = 1.0 : 0.4 : 8.1
May12-2015-h400-zy-182phen-5.5h
7.5 h, 3a : C : 2a = 1.0 : 0.2 : 7.2
May12-2015-h400-zy-182-phen-7.5h
f1 (ppm)


[O]
without Phen
[O]
2a
1a
C
3a

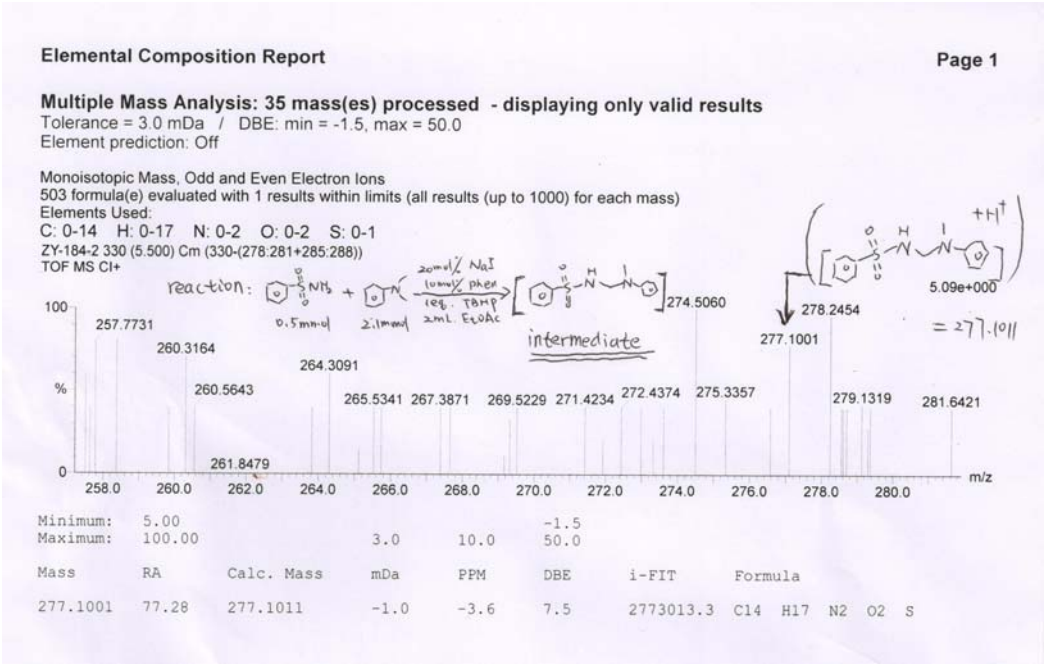

May12-2015-h400-zy-183-1.5h
3a
4
C
2a
Without ligand
1.5 h, 3a : C : 2a = 1.0 : 1.4 : 18.2
May12-2015-h400-zy-183-3.5
3.5 h, 3a : C : 2a = 1.0 : 0.6 : 11.2
May12-2015-h400-zy-183-2
5.5 h, 3a : C : 2a = 1.0 : 0.4 : 10.9
May12-2015-h400-zy-183-7.5h
7.5 h, 3a : C : 2a = 1.0 : 0.1 : 8.3
f1 (ppm)

Intermediates C Identification

Proton NMR observation:



HRMS report of the observation of the intermediate C:



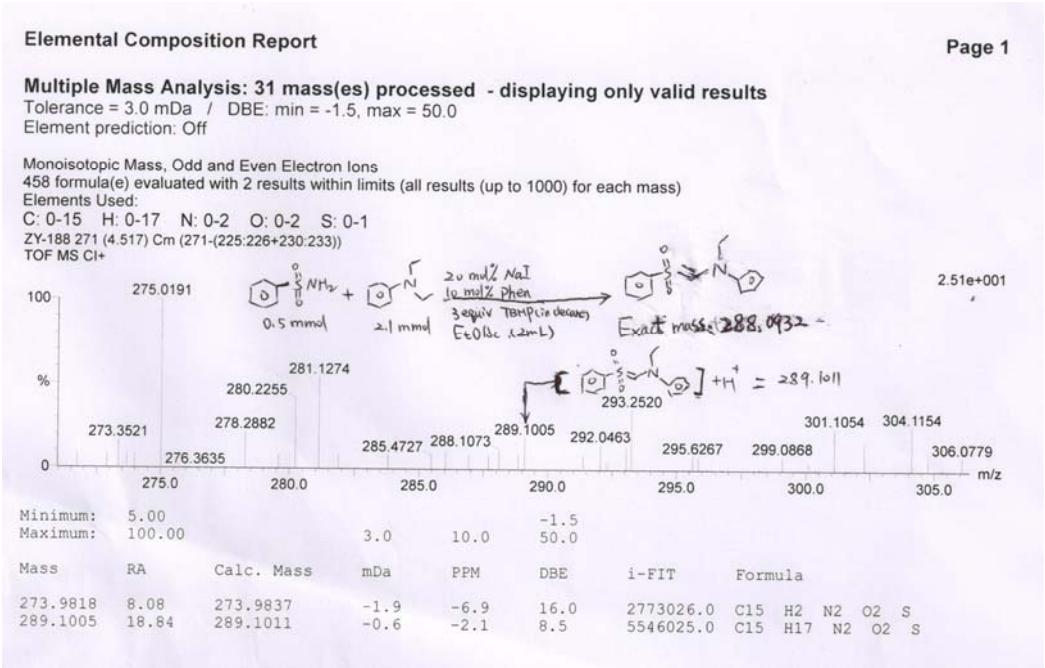
Elemental Composition Report Page 1

Multiple Mass Analysis: 35 mass(es) processed - displaying only valid results
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
503 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-14 H: 0-17 N: 0-2 O: 0-2 S: 0-1
ZY-184-2 330 (5.500) Cm (330-(278:281+285:288))
TOF MS CI+

Minimum:	5.00				-1.5		
Maximum:	100.00		3.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
277.1001	77.28	277.1011	-1.0	-3.6	7.5	2773013.3	C14 H17 N2 O2 S

HRMS Observation of the Product from *N*,*N*-Diethylaniline



Elemental Composition Report

Page 1

Multiple Mass Analysis: 31 mass(es) processed - displaying only valid results
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

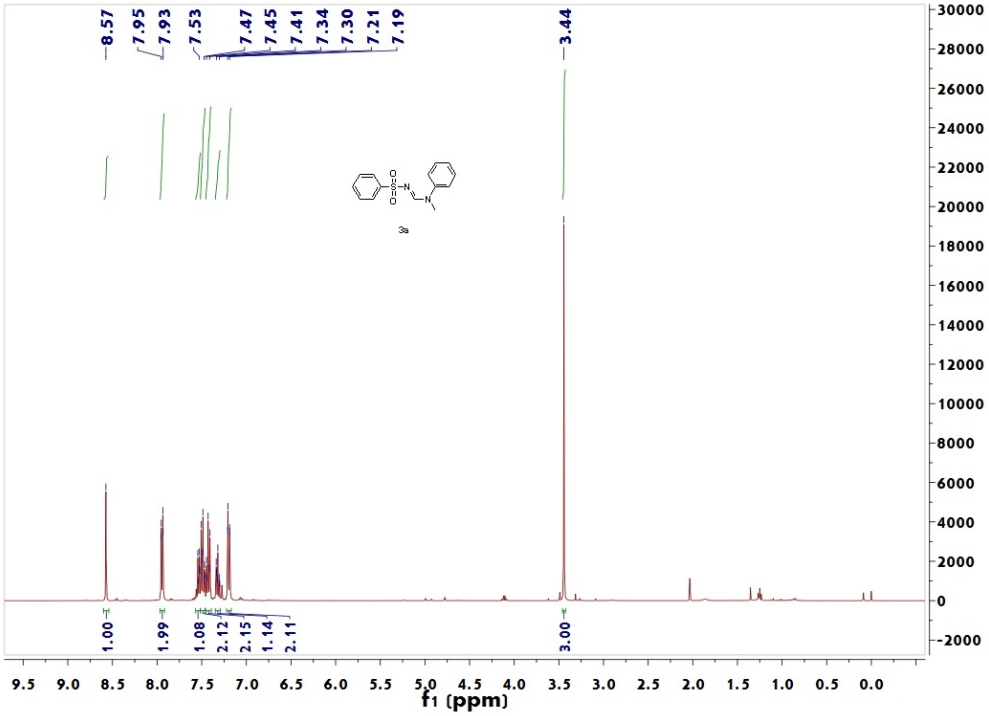
Monoisotopic Mass, Odd and Even Electron Ions
458 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-15 H: 0-17 N: 0-2 O: 0-2 S: 0-1
ZY-188 271 (4.517) Cm (271-(225:226+230:233))
TOF MS CI+

Minimum:	5.00				-1.5		
Maximum:	100.00		3.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
273.9818	8.08	273.9837	-1.9	-6.9	16.0	2773026.0	C15 H2 N2 O2 S
289.1005	18.84	289.1011	-0.6	-2.1	8.5	5546025.0	C15 H17 N2 O2 S

Reference:

1 L. S. Kristen, C. O. Allie and B. F. Matthew, *J. Am. Chem. Soc.*, 2011, **133**, 16970.

2 (a) W. J. Kerr, M. Reid and T. Tuttle, *ACS Catal.*, 2015, **5**, 402; (b) E. Yuriev, D. C. M. Kong and M. N. Iskander, *Eur. J. Med. Chem.*, 2004, **39**, 835.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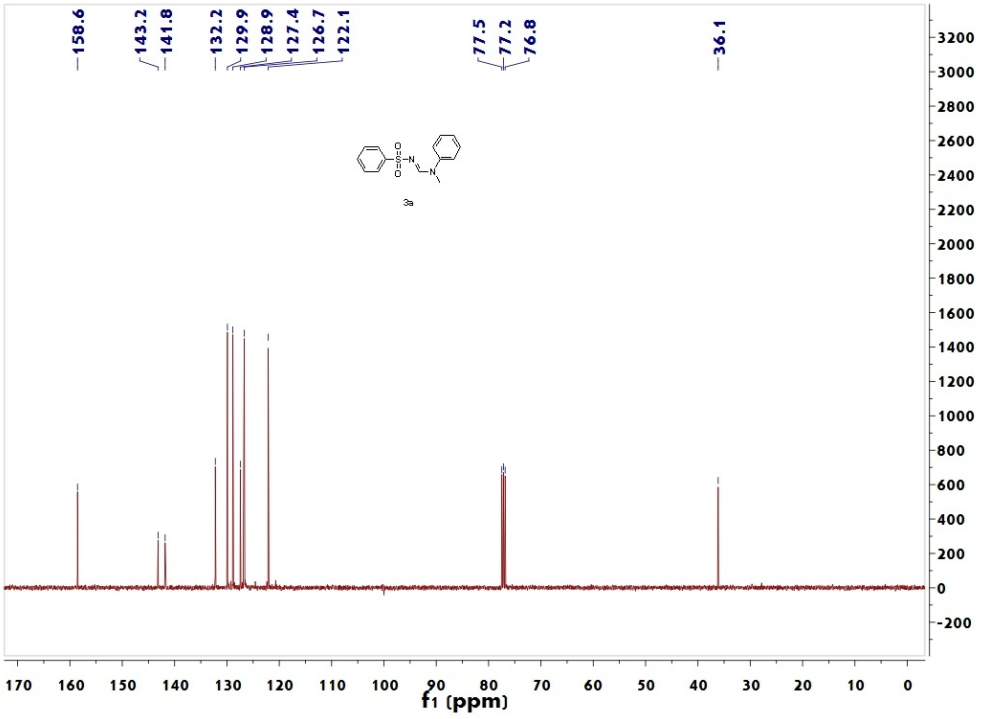
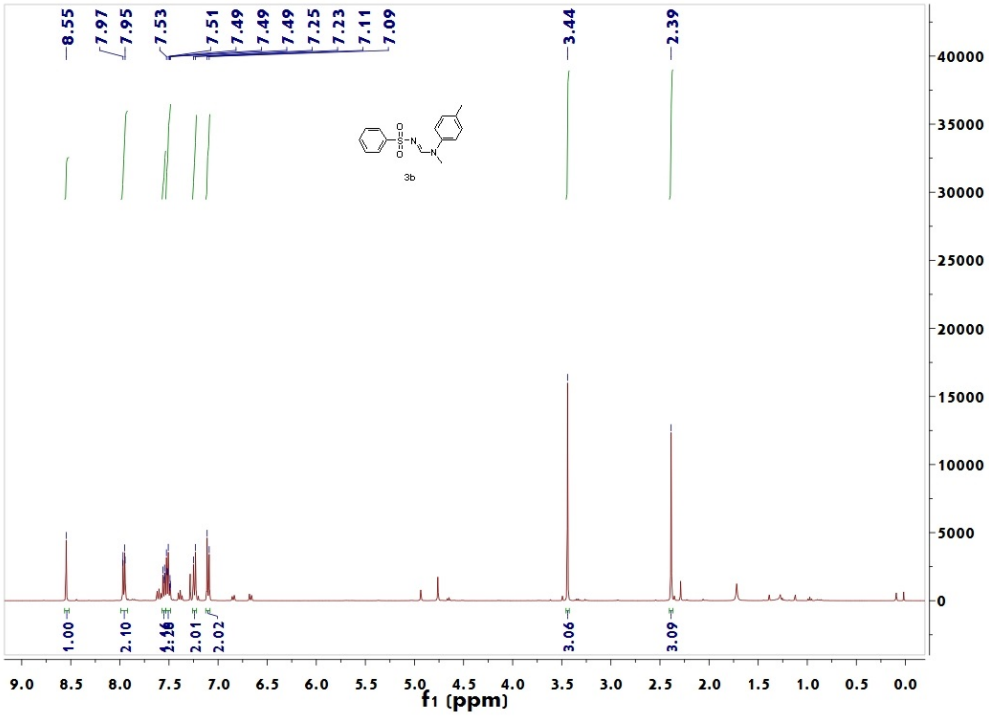
7.95
7.93
7.53
7.47
7.45
7.41
7.34
7.30
7.21
7.19
3.44
3a
1.00
1.99
1.08
2.12
2.15
1.14
2.11
3.00
f1 (ppm)


158.6
143.2
141.8
132.2
129.9
128.9
127.4
126.7
122.1
77.5
77.2
76.8
36.1
3a
f1 (ppm)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7.97
7.95
7.53
7.51
7.49
7.49
7.49
7.25
7.23
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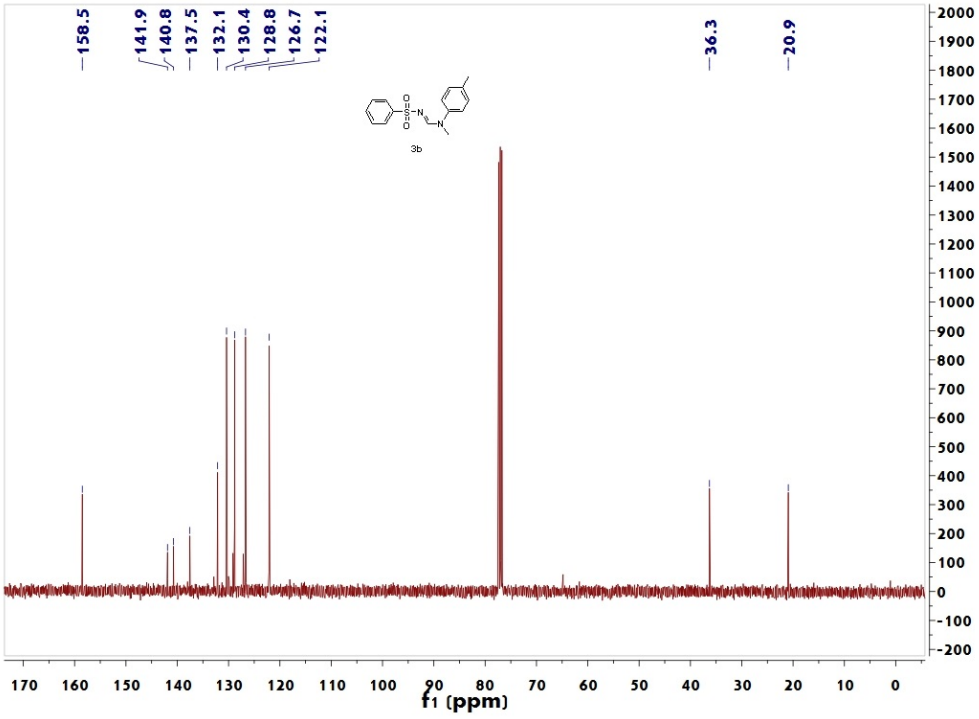
7.09
3.44
2.39
3b
1.00
2.10
2.01
2.02
3.06
3.09
f1 (ppm)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141.9
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137.5
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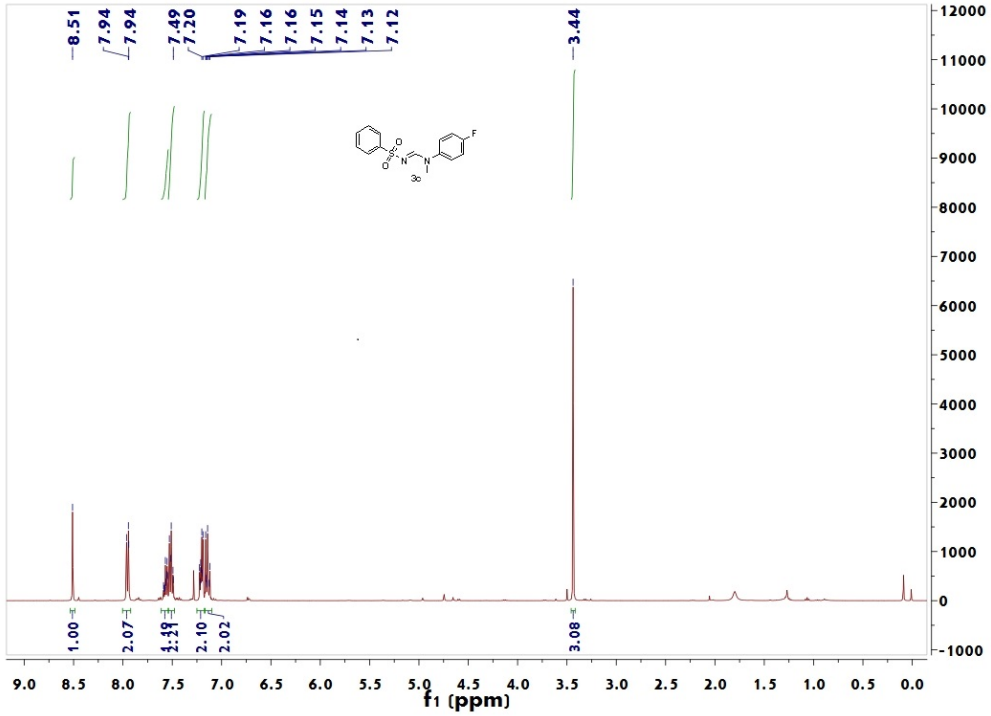
130.4
128.8
126.7
122.1
36.3
20.9
3b
f1 (ppm)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7.94
7.94
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7.14
7.13
7.12
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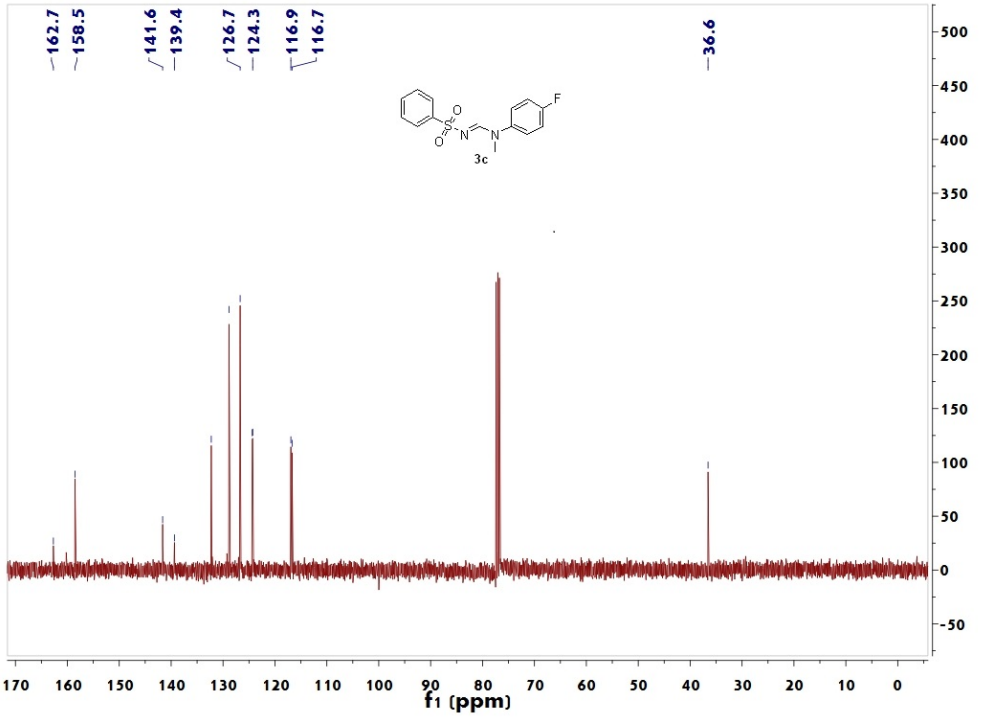
2.07
2.10
2.02
3.08
f1 (ppm)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124.3
116.9
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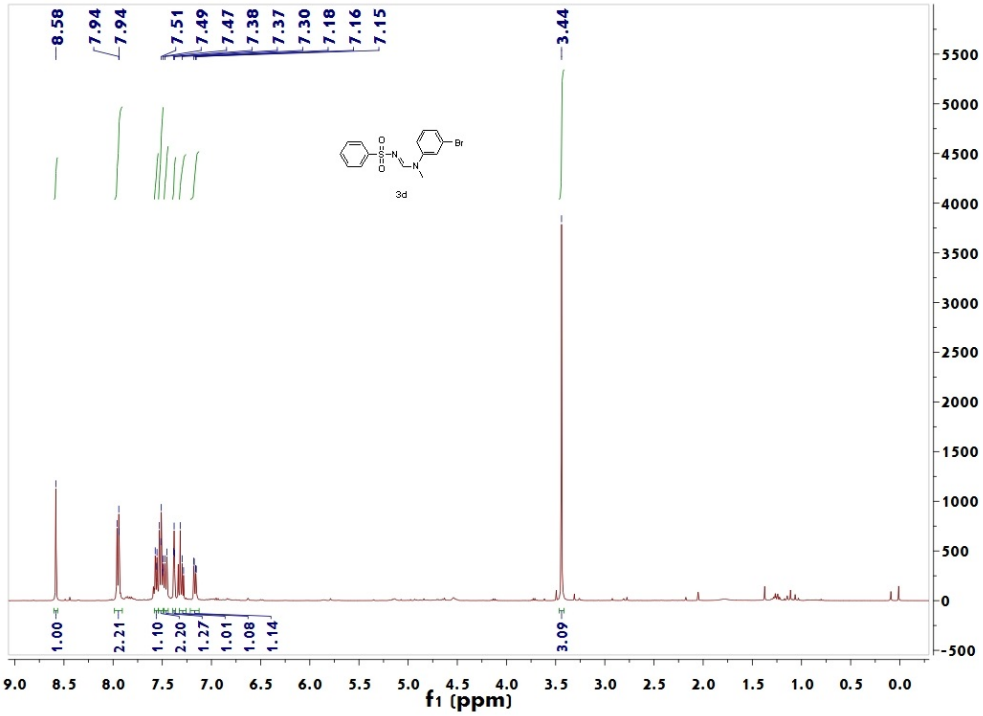
36.6
f1 (ppm)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7.94
7.94
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7.49
7.47
7.38
7.37
7.30
7.18
7.16
7.15
3.44
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3d
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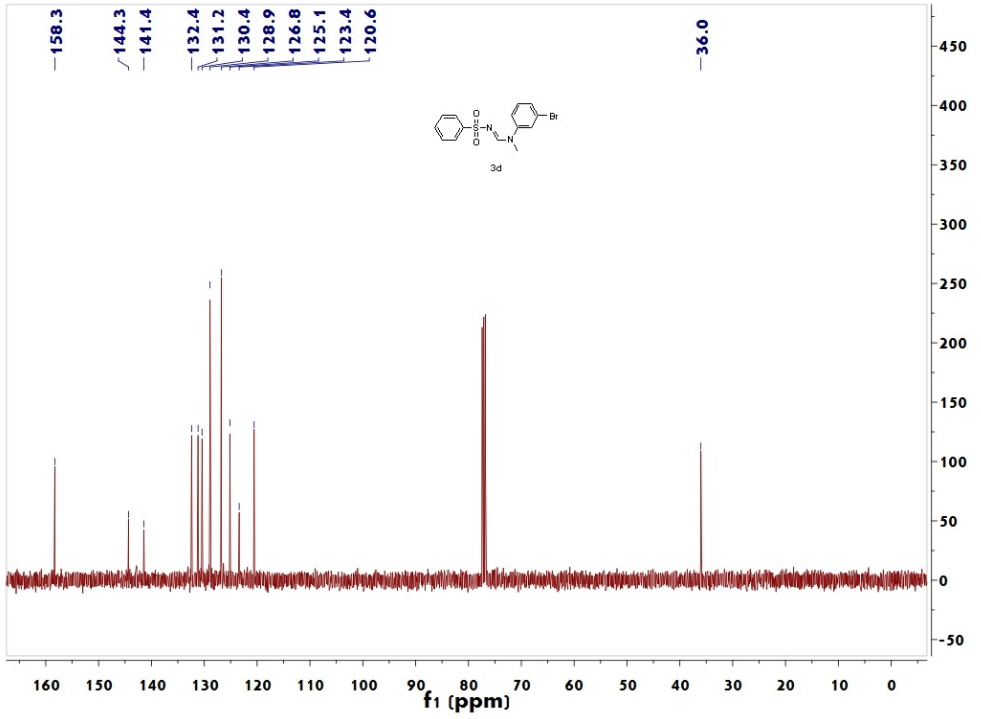
1.10
2.20
1.27
1.01
1.08
1.14
3.09
f1 (ppm)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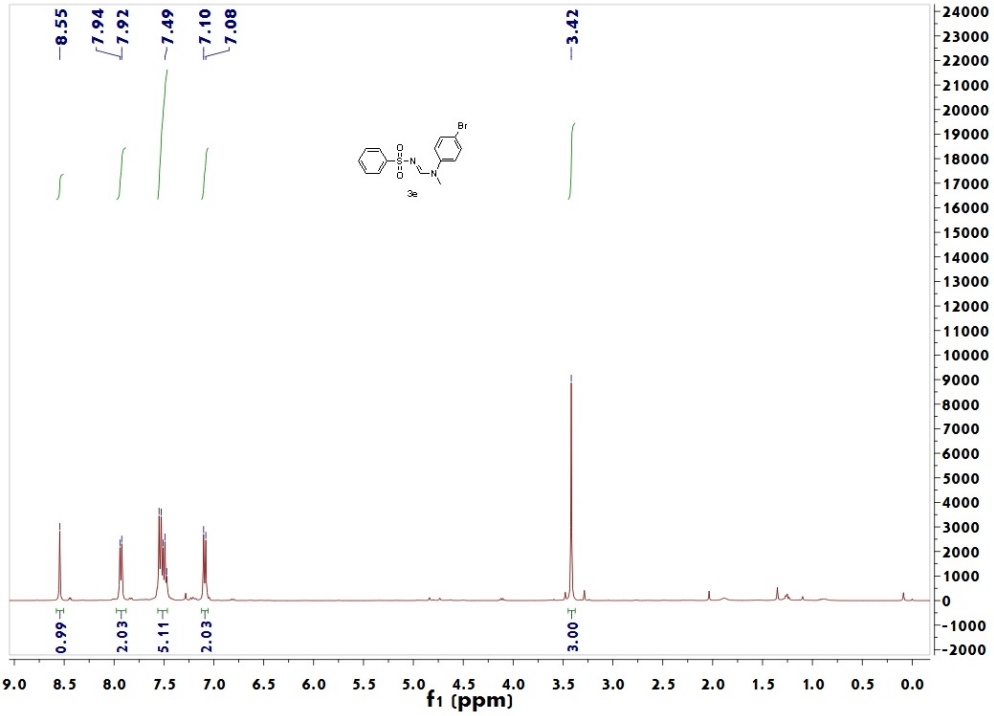
Br
3d
f1 (ppm)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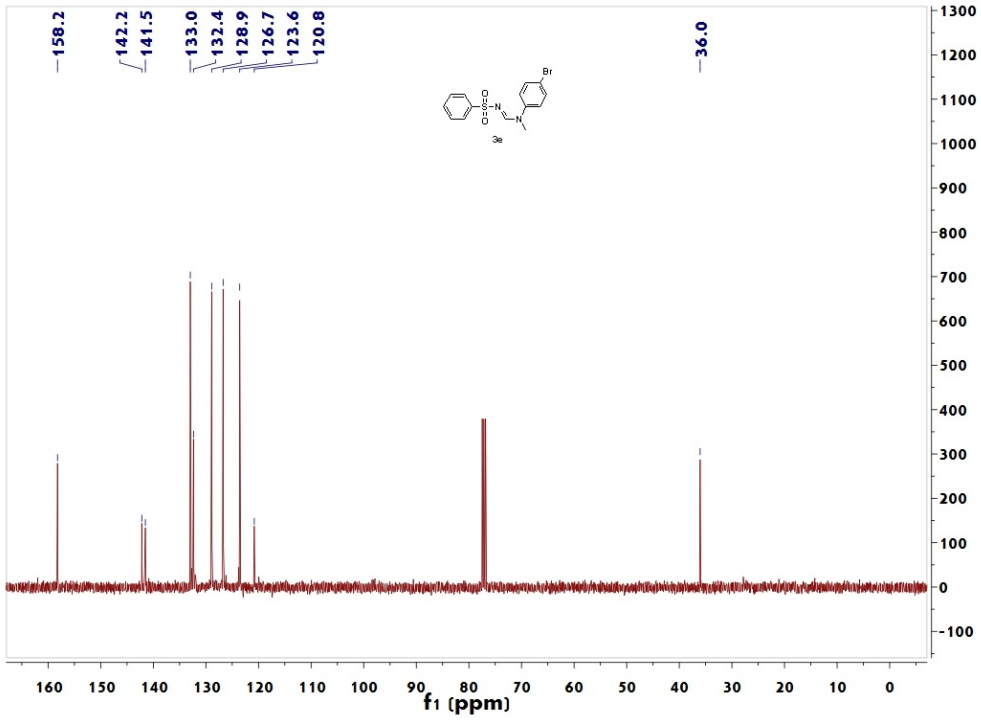
2.03
3.00
f1 (ppm)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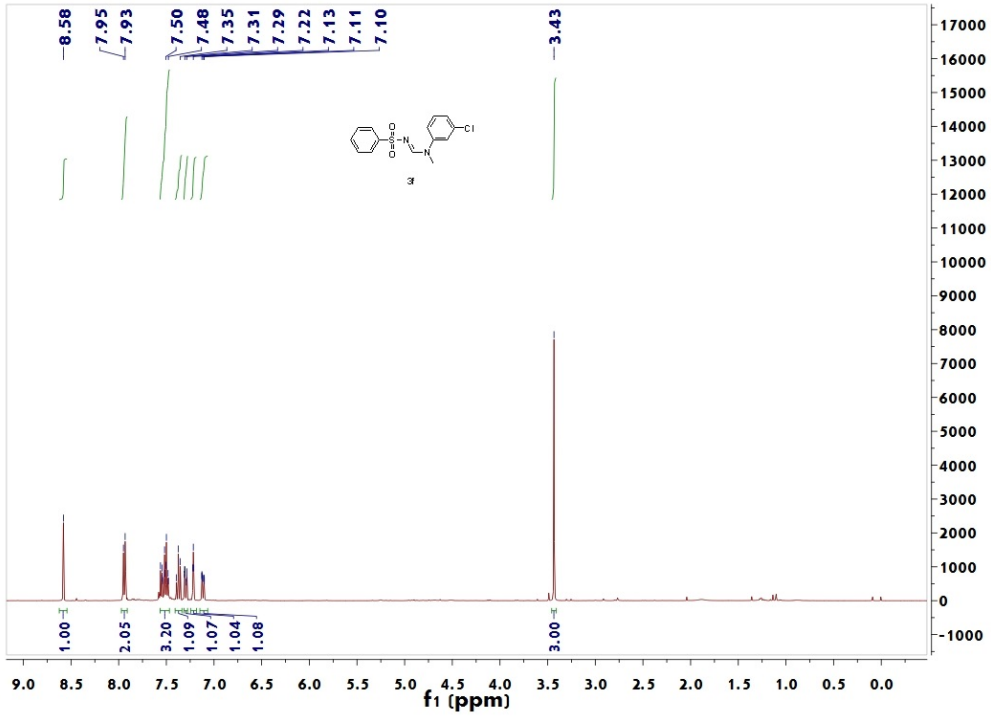
126.7
123.6
120.8
36.0
Br
3e
f1 (ppm)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7.48
7.35
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7.29
7.22
7.13
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7.10
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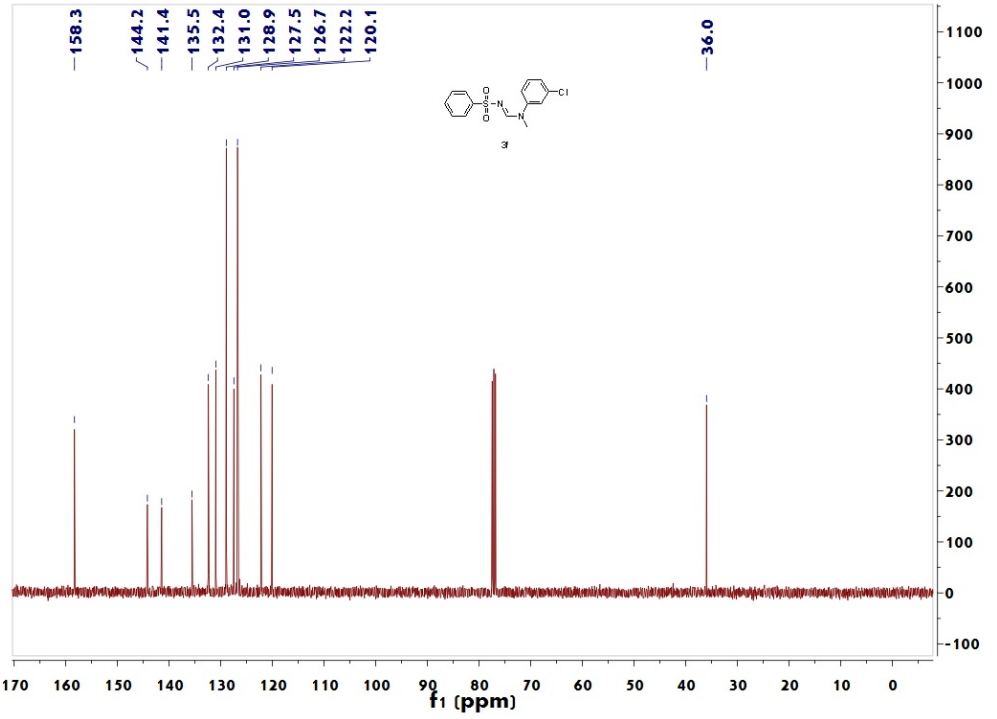
3.20
1.09
1.07
1.04
1.08
3.00
f1 (ppm)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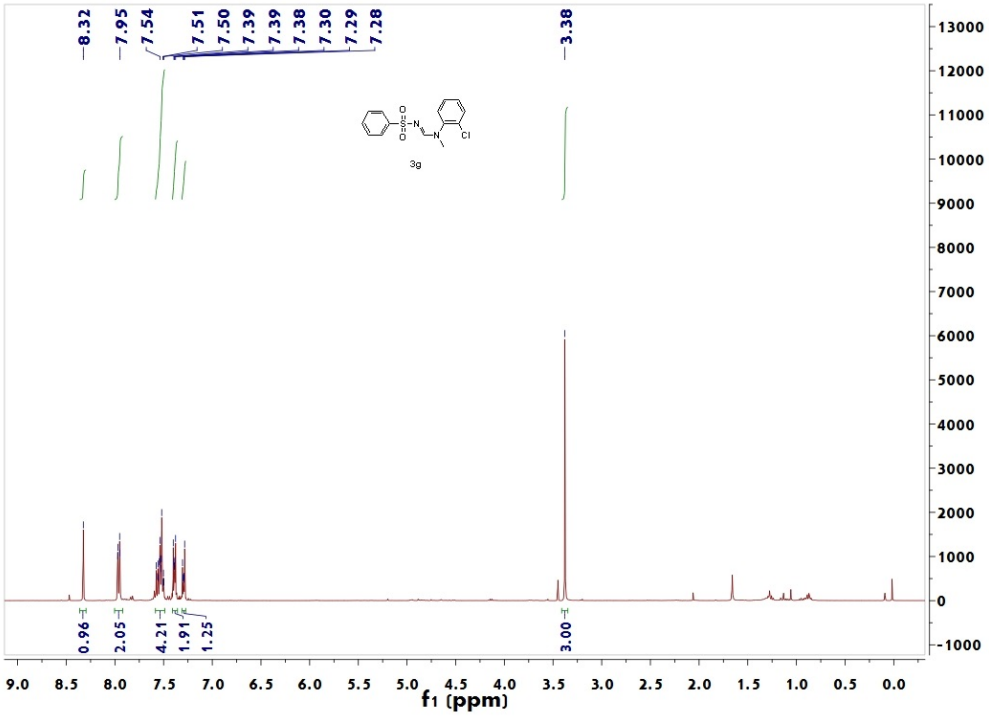
132.4
131.0
128.9
127.5
126.7
122.2
120.1
36.0
f1 (ppm)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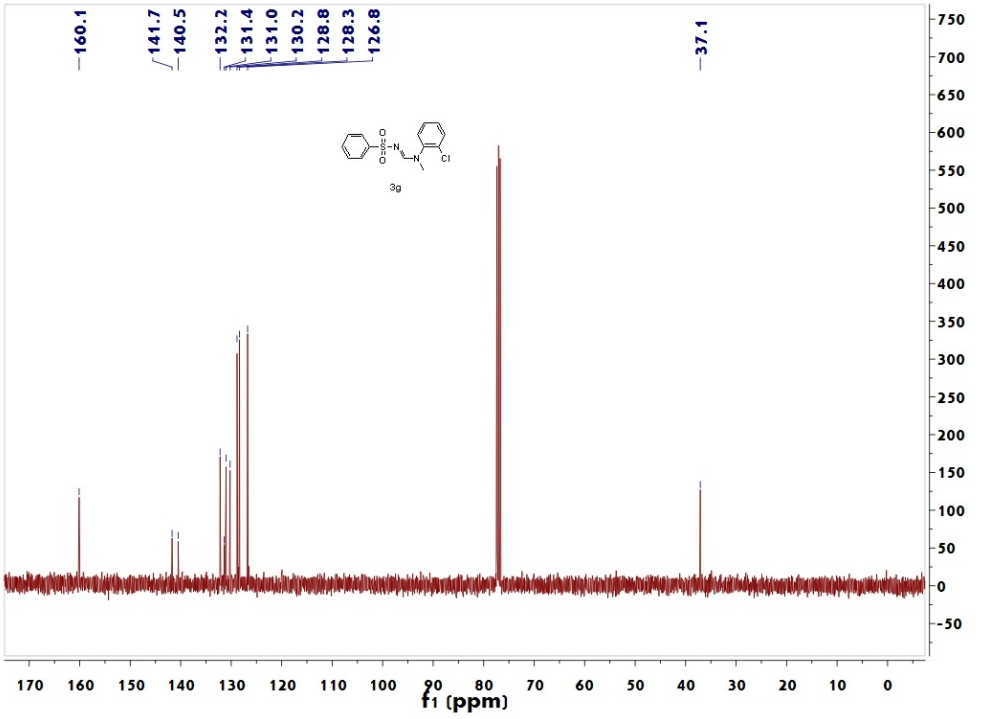
7.38
7.30
7.29
7.28
3.38
3g
0.96
2.05
4.21
1.91
1.25
3.00
f1 (ppm)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128.3
126.8
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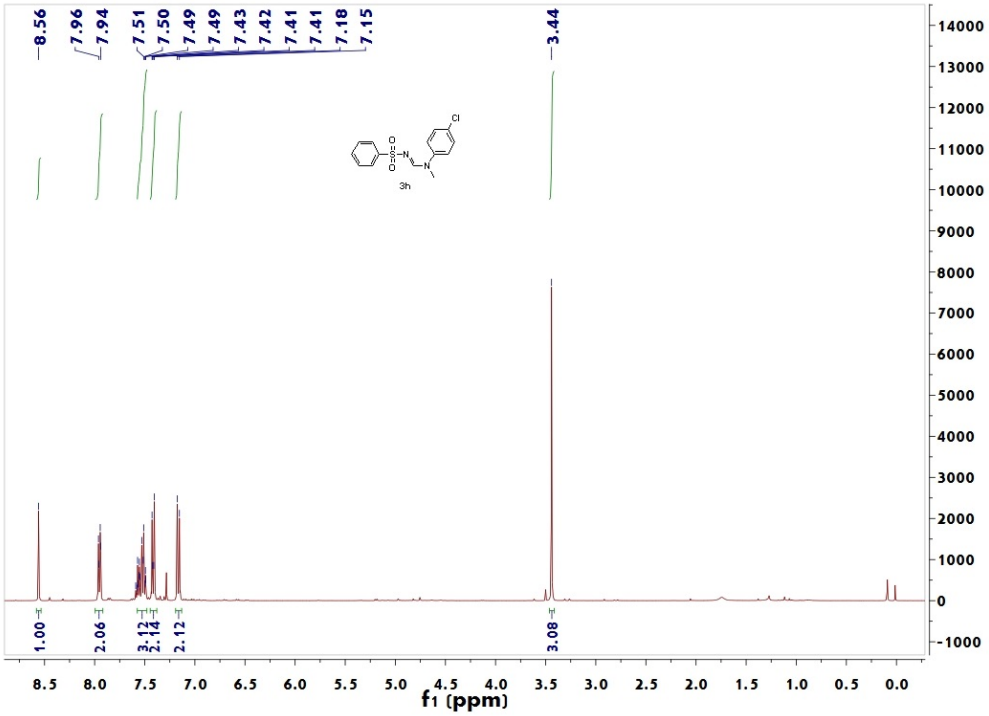
3g
f1 (ppm)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7.49
7.43
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7.41
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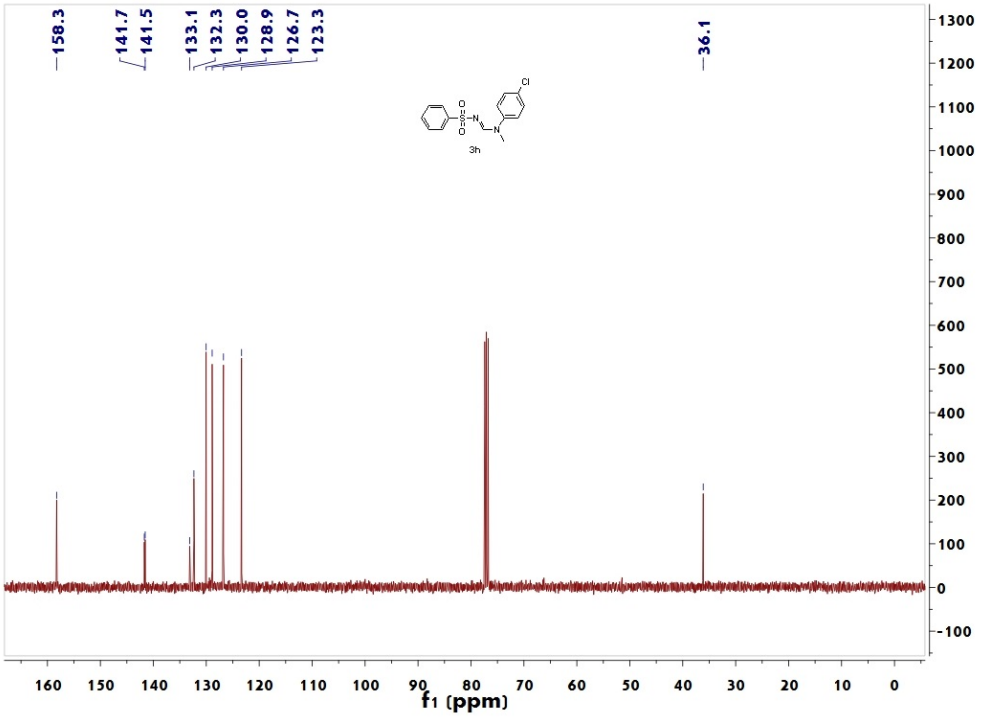
3.12
2.14
2.12
3.08
3h
f1 (ppm)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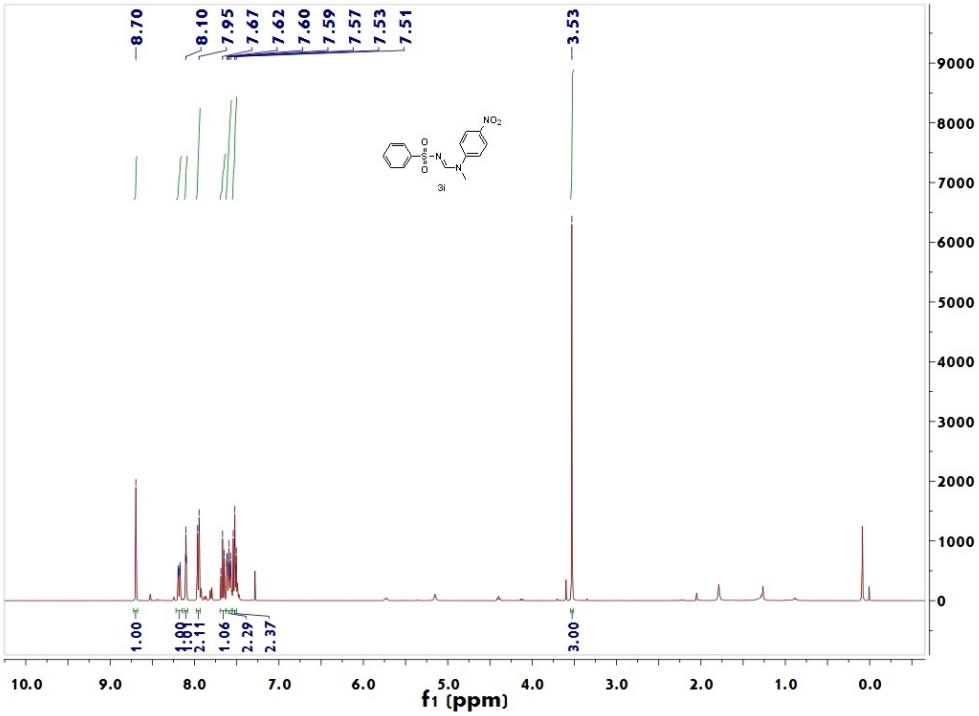
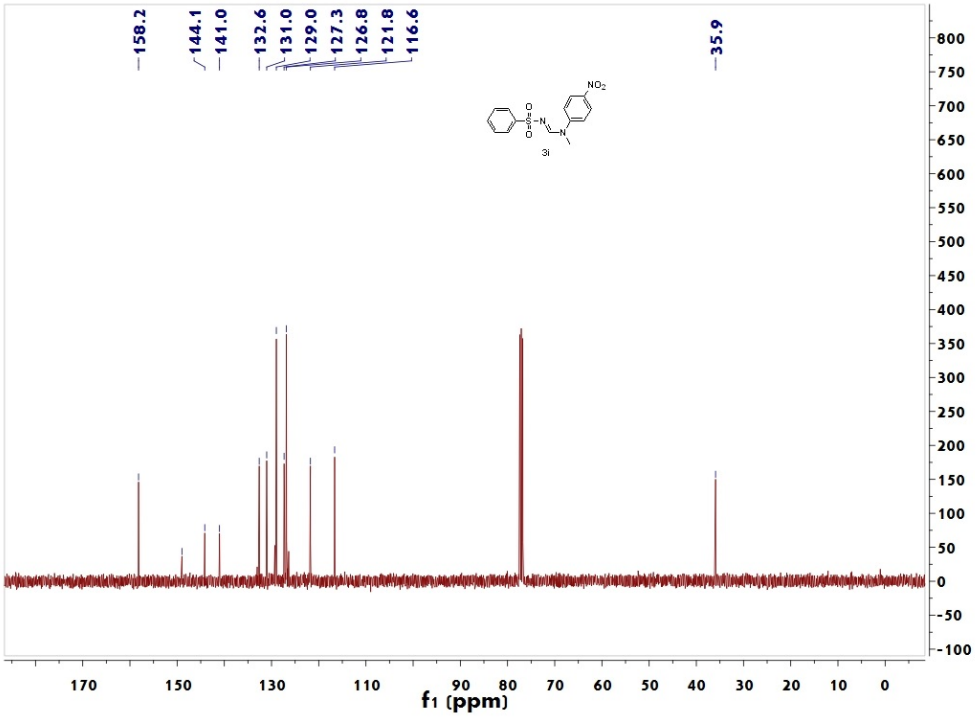
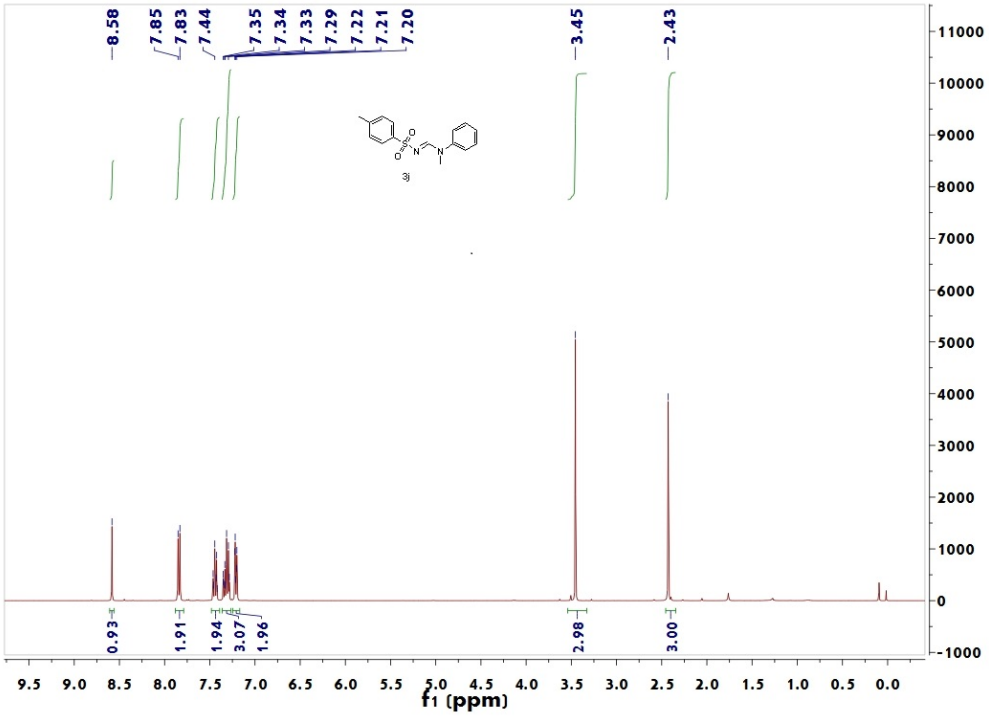
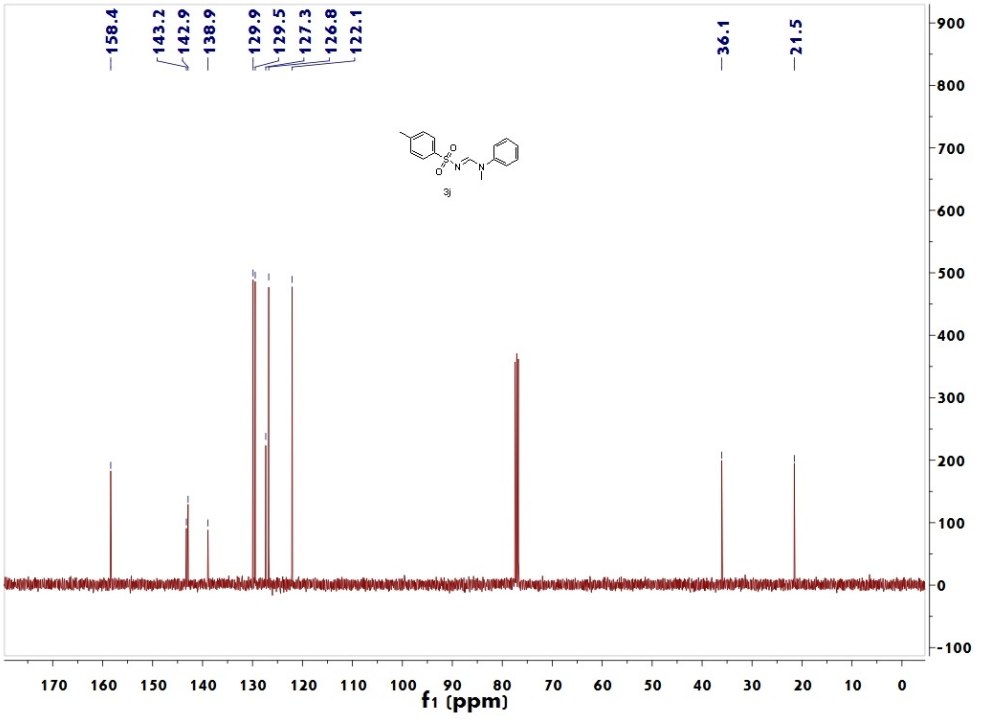
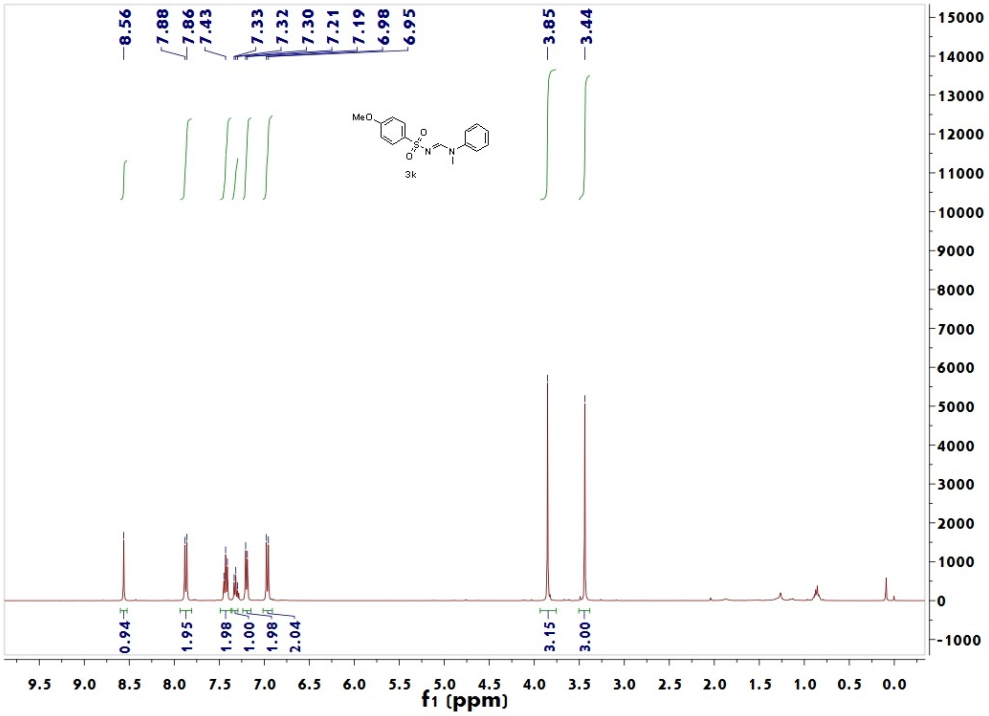
133.1
132.3
130.0
128.9
126.7
123.3
36.1
3h
f1 (ppm)

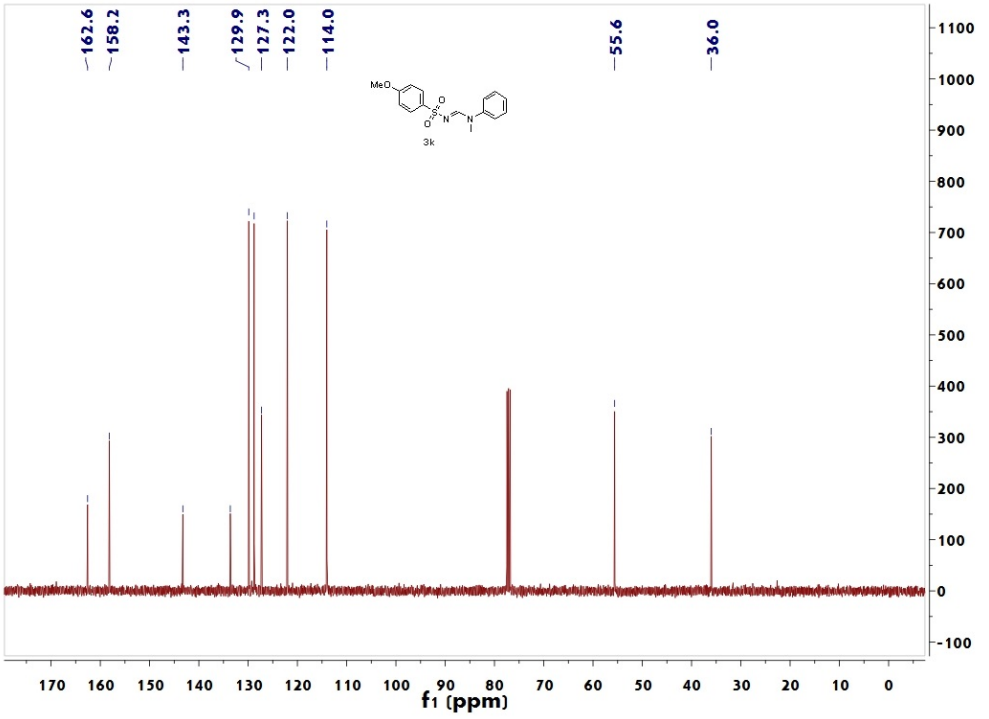

8.70
8.10
7.95
7.67
7.62
7.60
7.59
7.57
7.53
7.51
3.53
NO2
3i
1.00
1.00
2.11
1.06
2.29
2.37
3.00
f1 (ppm)

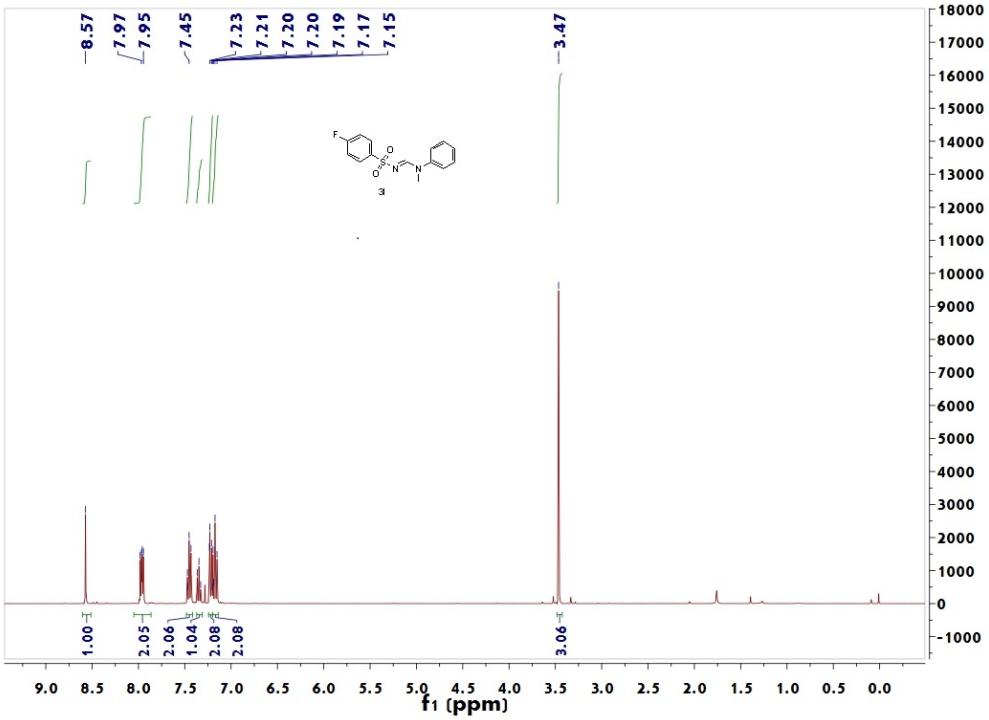

158.2
144.1
141.0
132.6
131.0
129.0
127.3
126.8
121.8
116.6
35.9
NO2
3i
f1 (ppm)

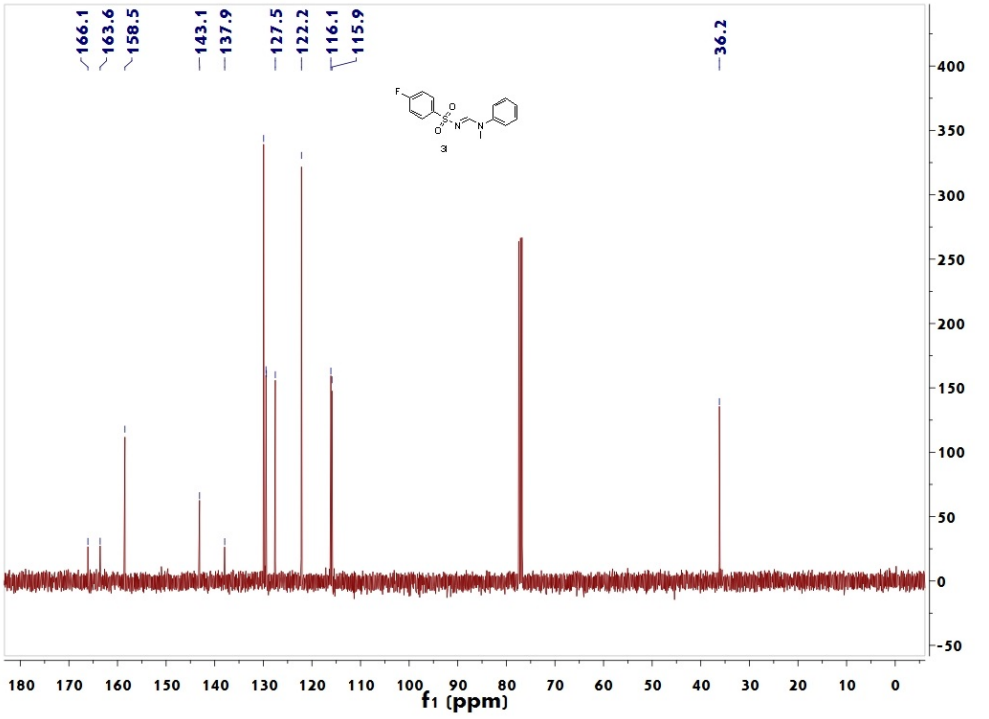

8.58
7.85
7.83
7.44
7.35
7.34
7.33
7.29
7.22
7.21
7.20
3.45
2.43
0.93
1.91
1.94
3.07
1.96
2.98
3.00
f1 (ppm)

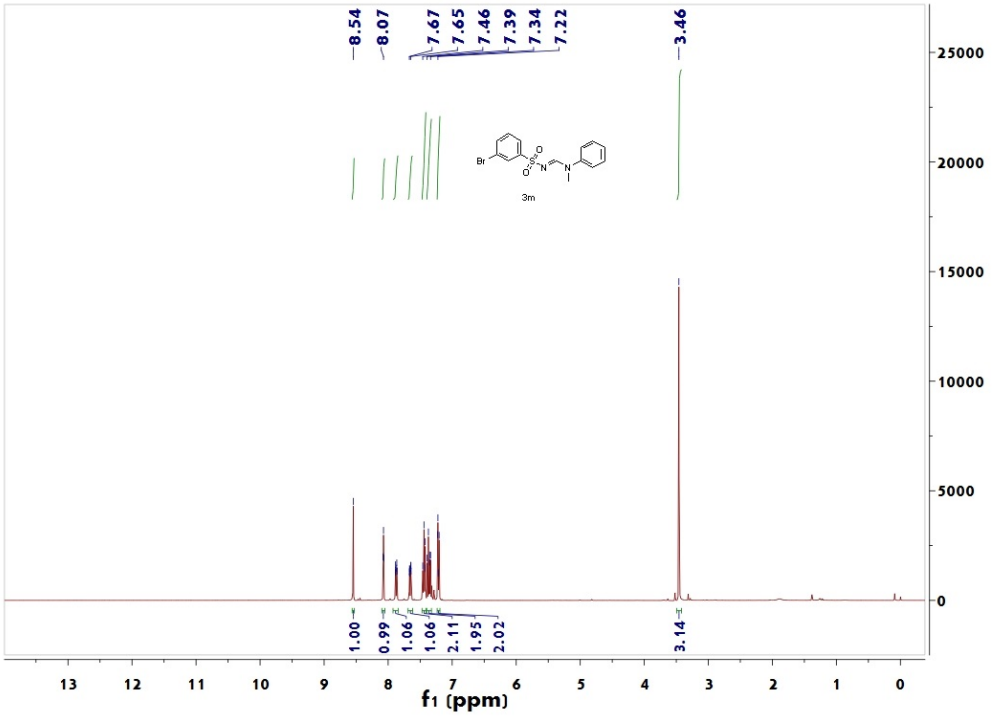

158.4
143.2
142.9
138.9
129.9
129.5
127.3
126.8
122.1
36.1
21.5
f1 (ppm)

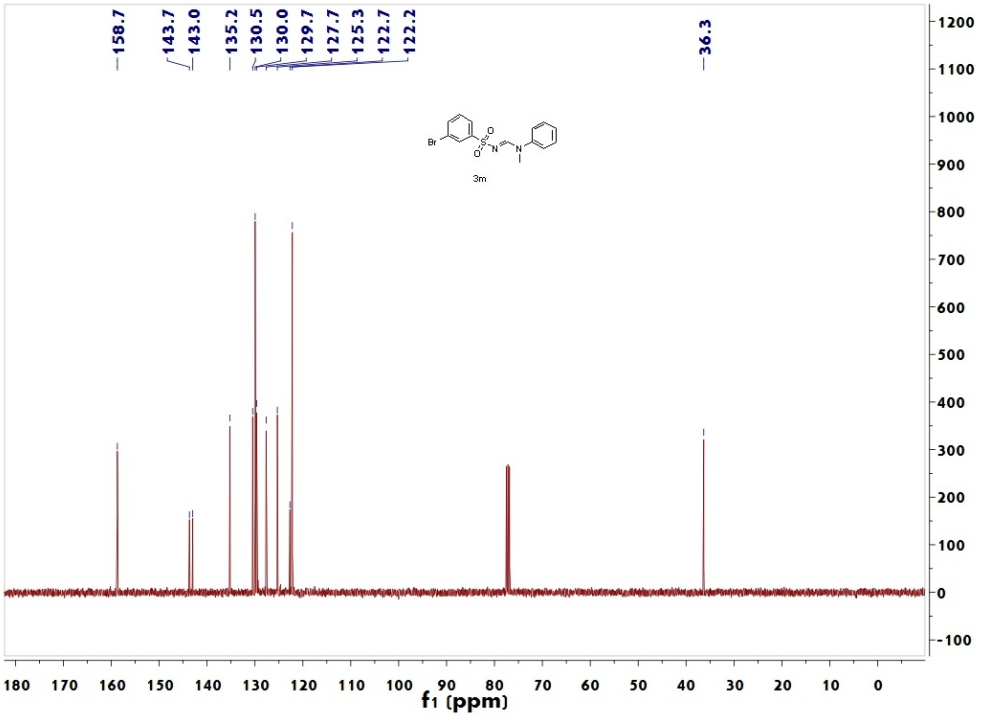

8.56
7.88
7.86
7.43
7.33
7.32
7.30
7.21
7.19
6.98
6.95
3.85
3.44
MeO
3k
0.94
1.95
1.98
1.00
1.98
2.04
3.15
3.00
f1 (ppm)

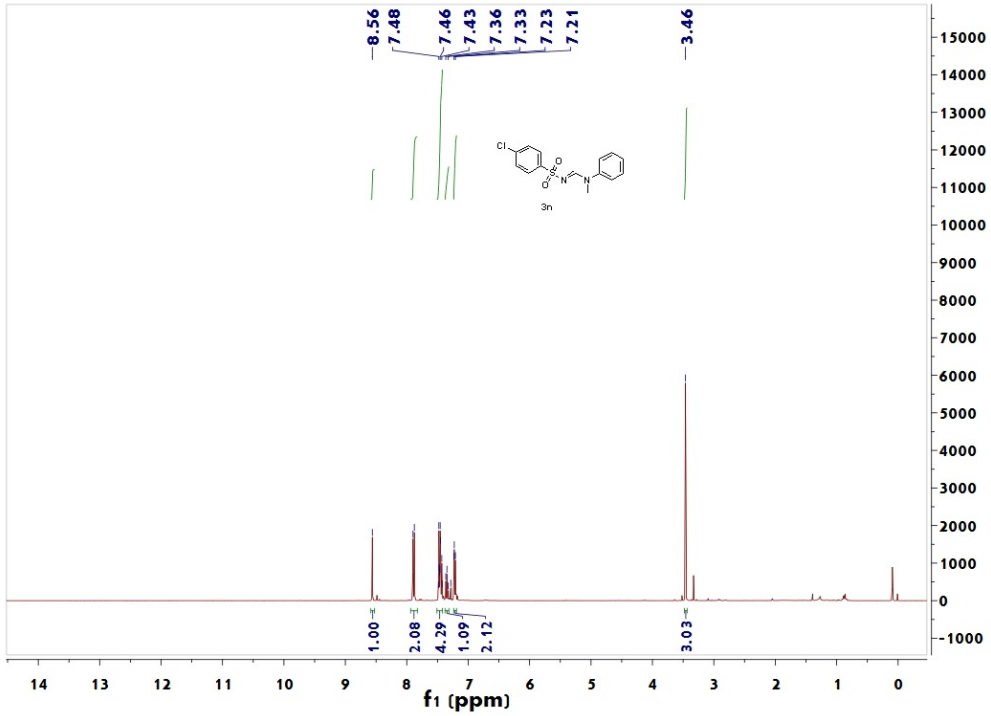

162.6
158.2
143.3
129.9
127.3
122.0
114.0
55.6
36.0
MeO
3k
f1 (ppm)

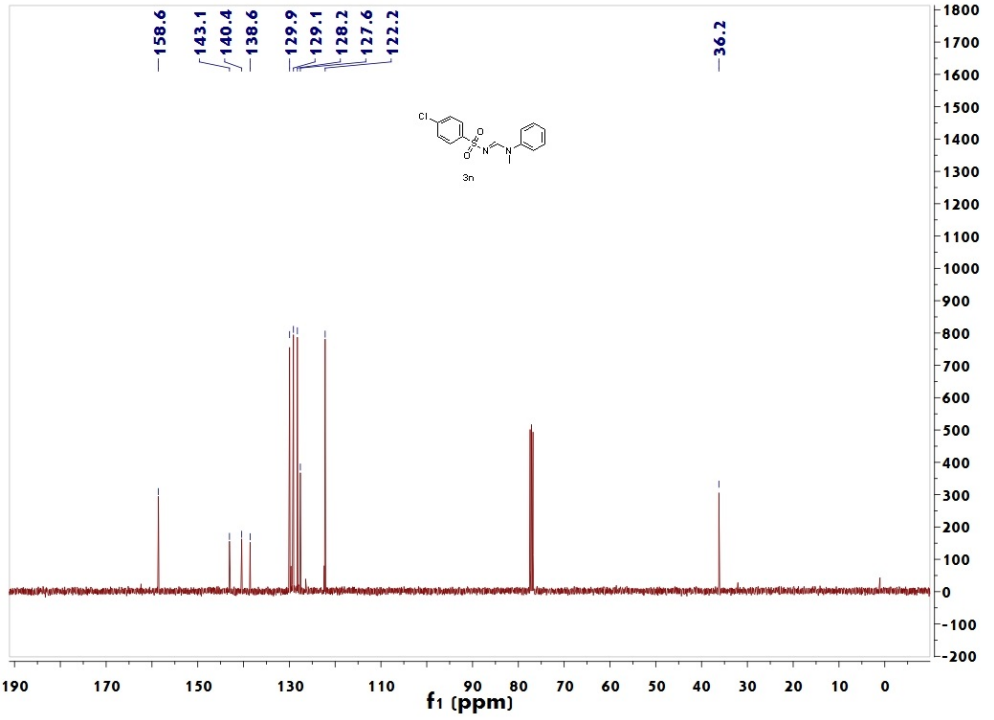

8.57
7.97
7.95
7.45
7.23
7.21
7.20
7.20
7.19
7.17
7.15
3.47
1.00
2.05
2.06
1.04
2.08
2.08
3.06
f1 (ppm)

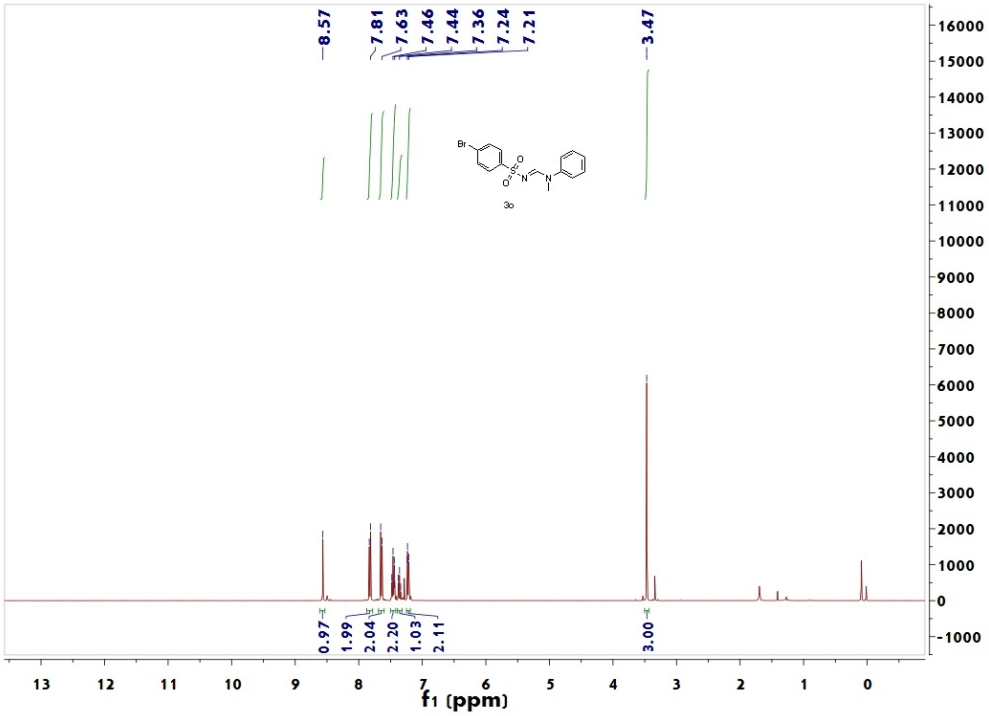

166.1
163.6
158.5
143.1
137.9
127.5
122.2
116.1
115.9
36.2
f1 (ppm)

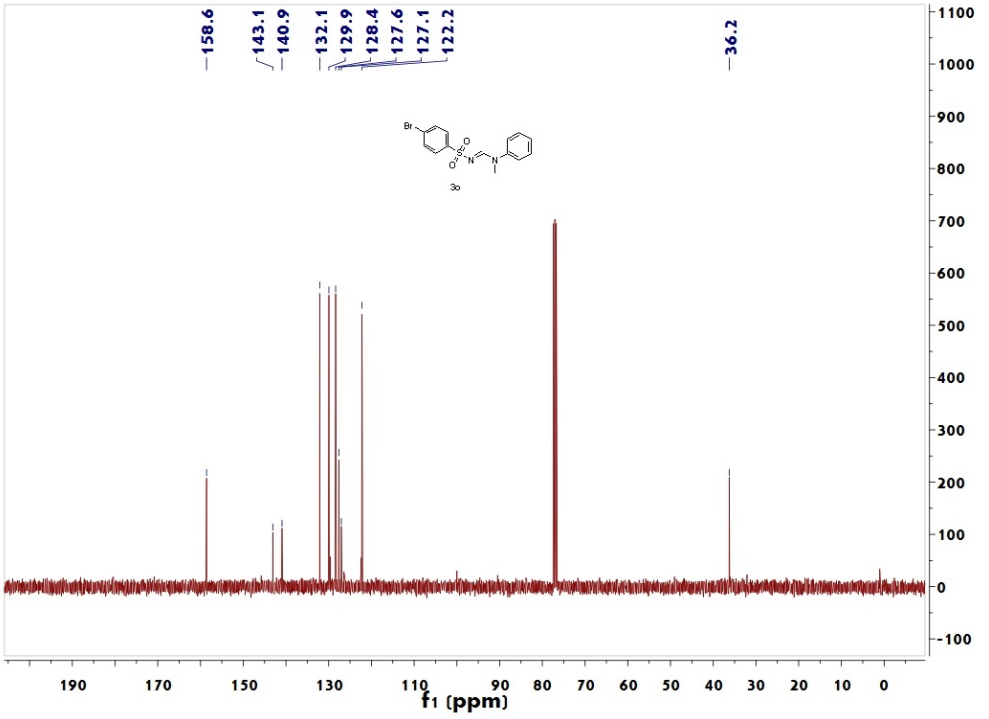

8.54
8.07
7.67
7.65
7.46
7.39
7.34
7.22
3.46
3m
1.00
0.99
1.06
1.06
2.11
1.95
2.02
3.14
f1 (ppm)

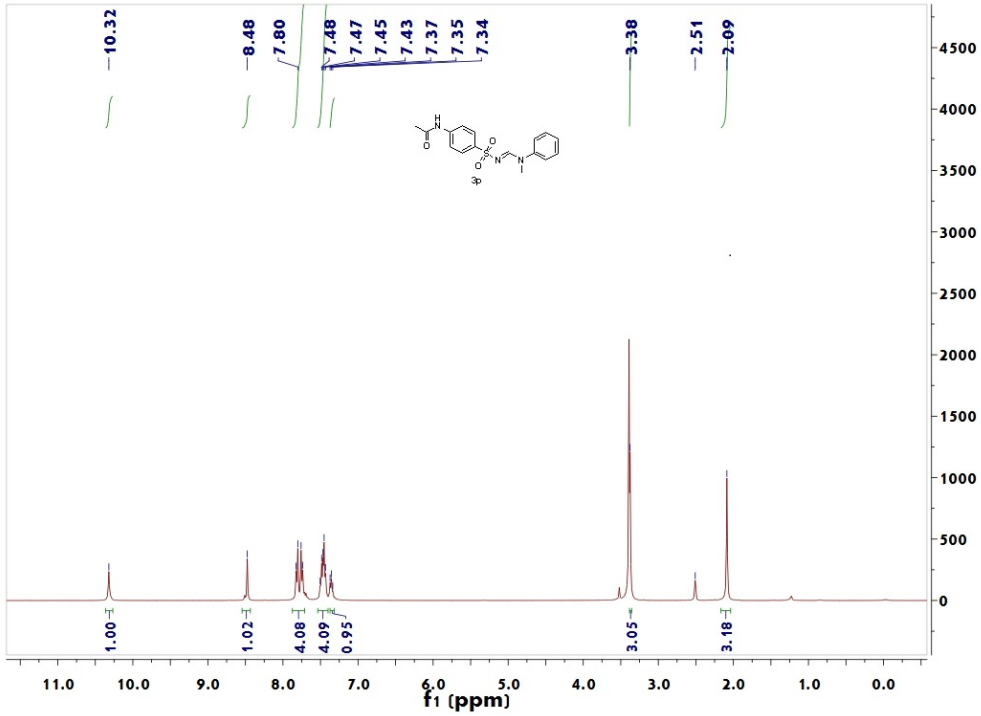

158.7
143.7
143.0
135.2
130.5
130.0
129.7
127.7
125.3
122.7
122.2
36.3
3m
f1 (ppm)

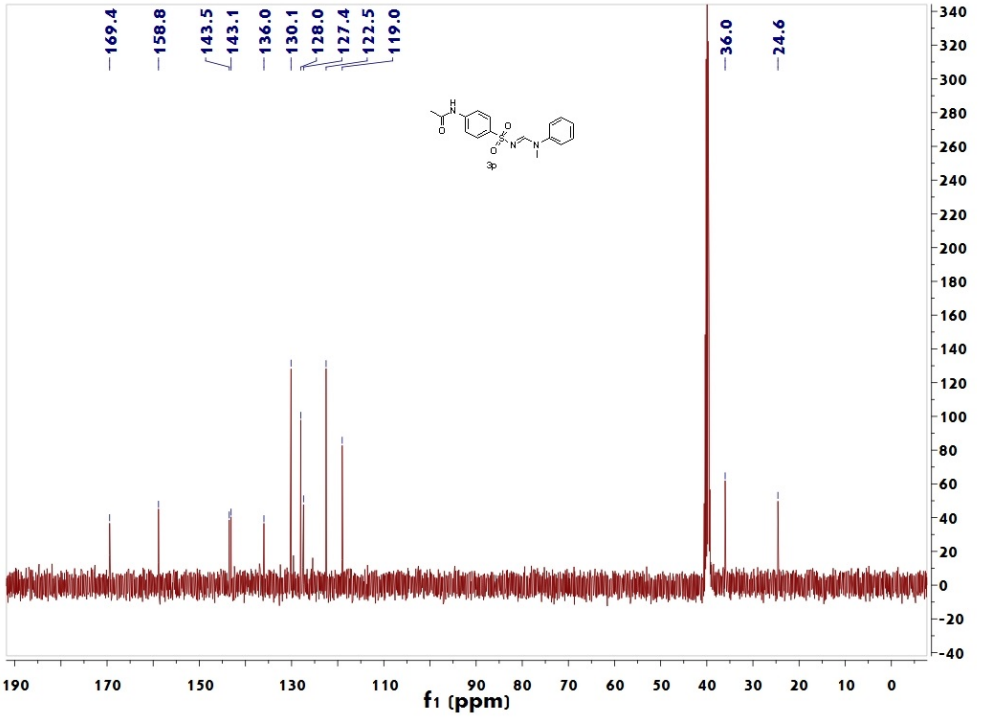

8.56
7.48
7.46
7.43
7.36
7.33
7.23
7.21
3.46
3n
1.00
2.08
4.29
1.09
2.12
3.03
f1 (ppm)

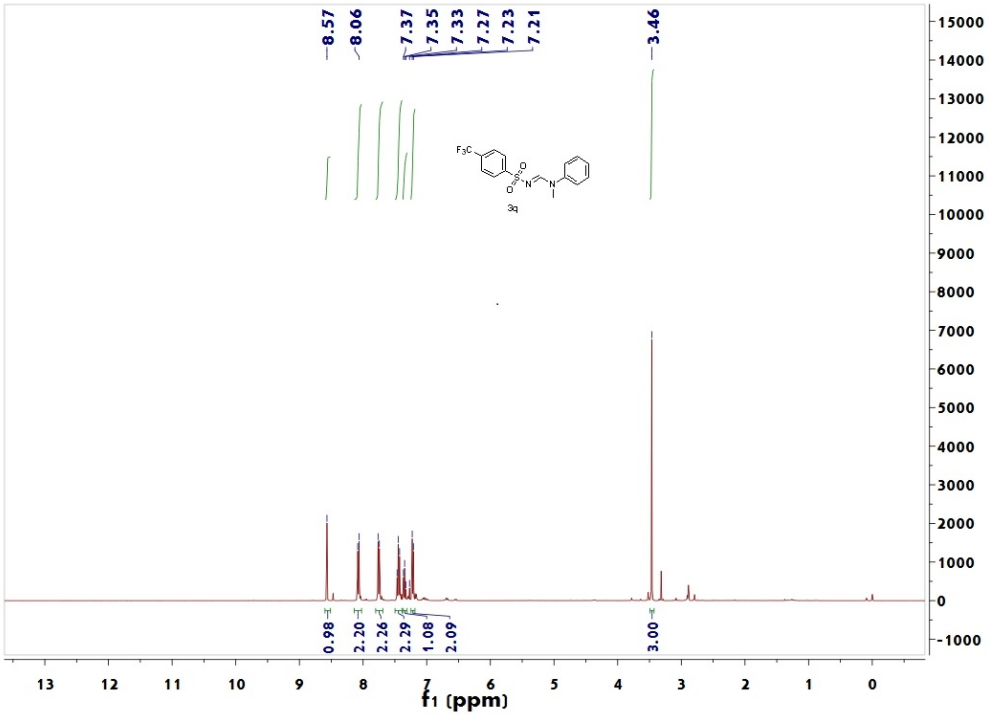

158.6
143.1
140.4
138.6
129.9
129.1
128.2
127.6
122.2
36.2
3n
f1 (ppm)

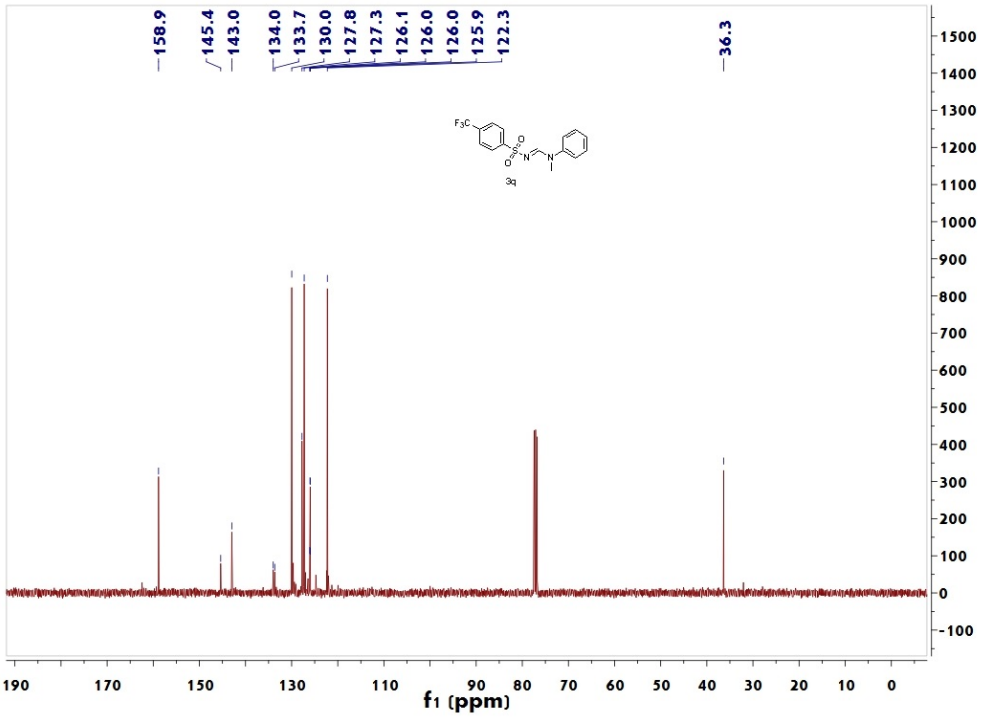

8.57
7.81
7.63
7.46
7.44
7.36
7.24
7.21
3.47
Br
O
O
S
N
N
3o
0.97
1.99
2.04
2.20
1.03
2.11
3.00
f1 (ppm)

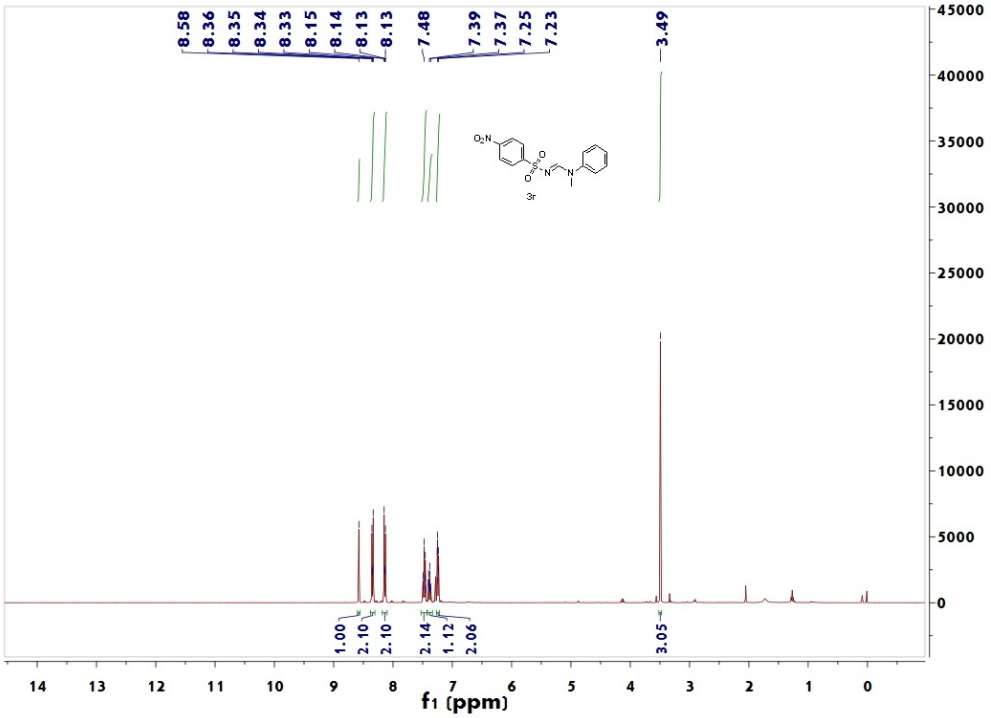

158.6
143.1
140.9
132.1
129.9
128.4
127.6
127.1
122.2
36.2
Br
O
O
S
N
N
3o
f1 (ppm)

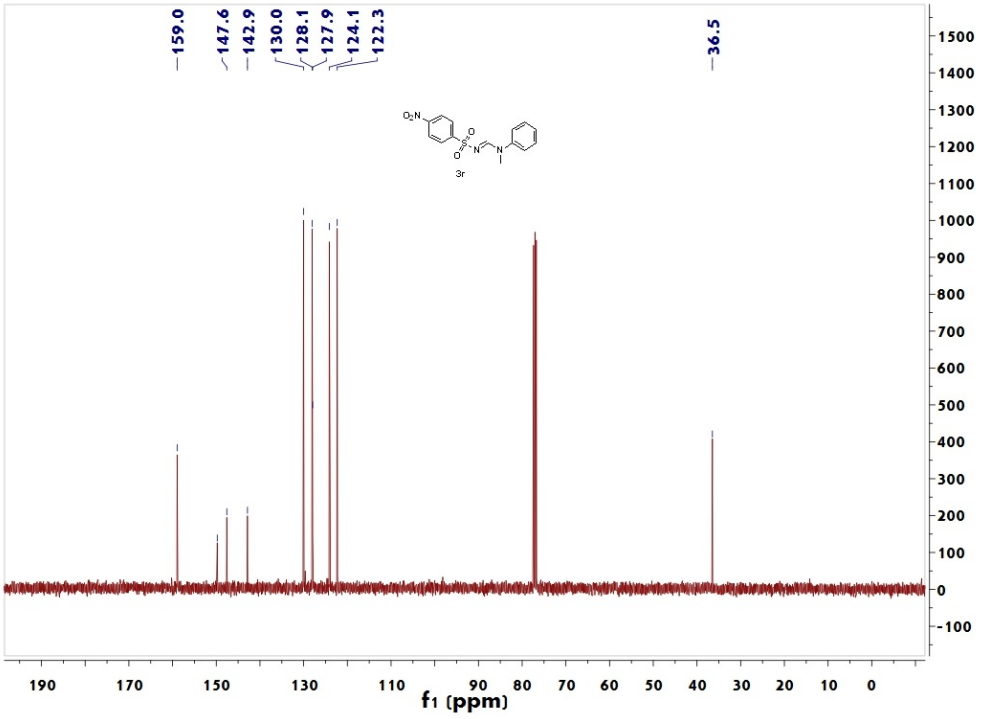

10.32
8.48
7.80
7.48
7.47
7.45
7.43
7.37
7.35
7.34
3.38
2.51
2.09
1.00
1.02
4.08
4.09
0.95
3.05
3.18
f1 (ppm)

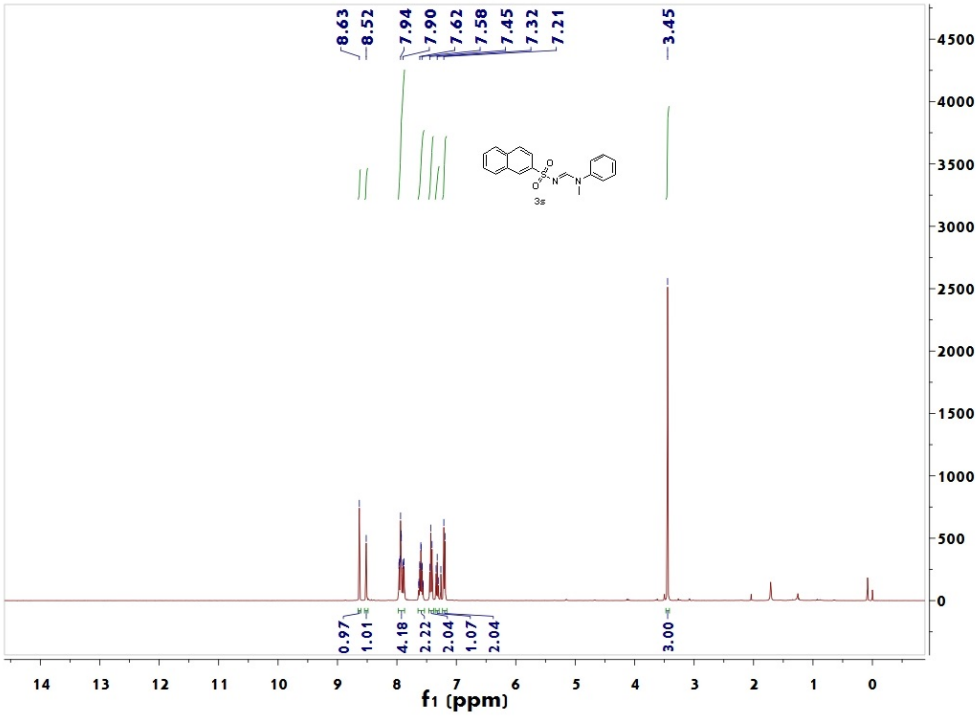

169.4
158.8
143.5
143.1
136.0
130.1
128.0
127.4
122.5
119.0
36.0
24.6
f1 (ppm)

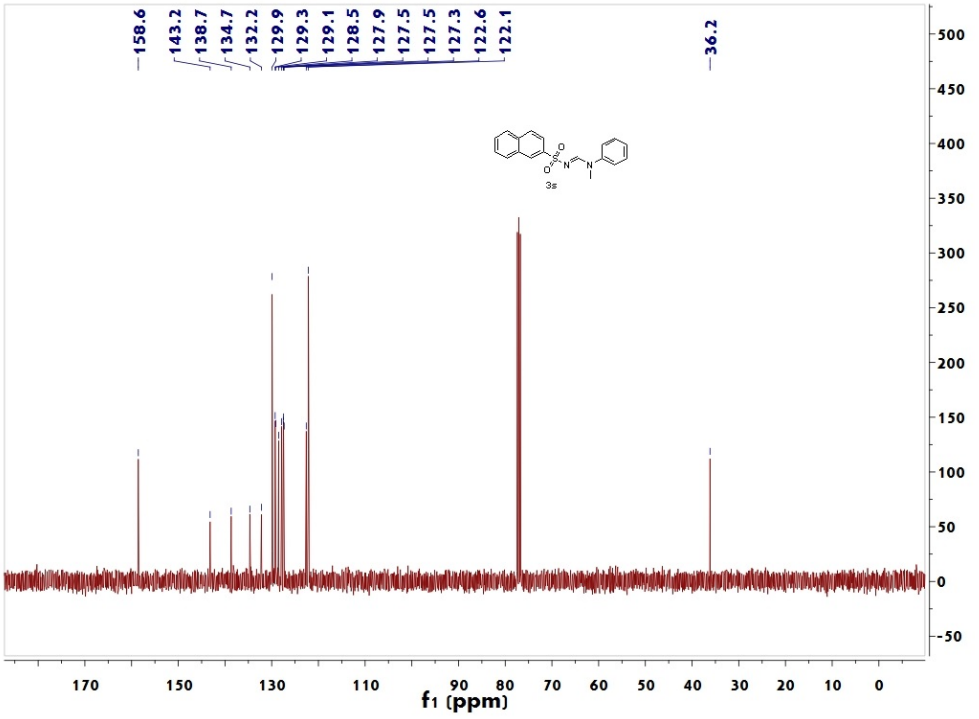

8.57
8.06
7.37
7.35
7.33
7.27
7.23
7.21
3.46
3q
0.98
2.20
2.26
2.29
1.08
2.09
3.00
f1 (ppm)

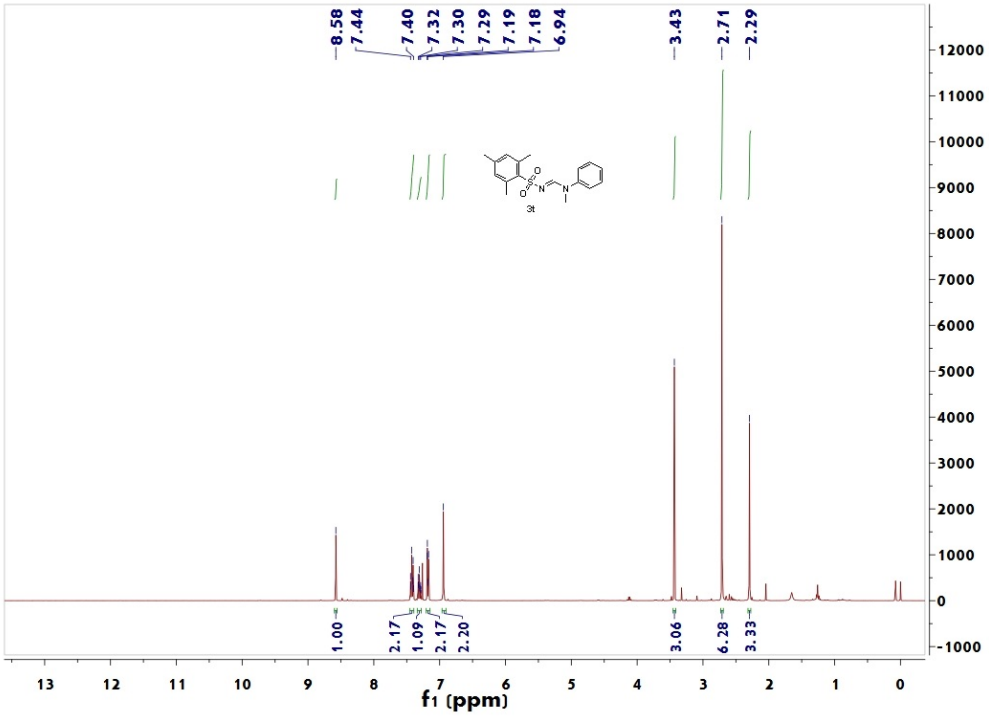

158.9
145.4
143.0
134.0
133.7
130.0
127.8
127.3
126.1
126.0
126.0
125.9
122.3
36.3
3q
f1 (ppm)

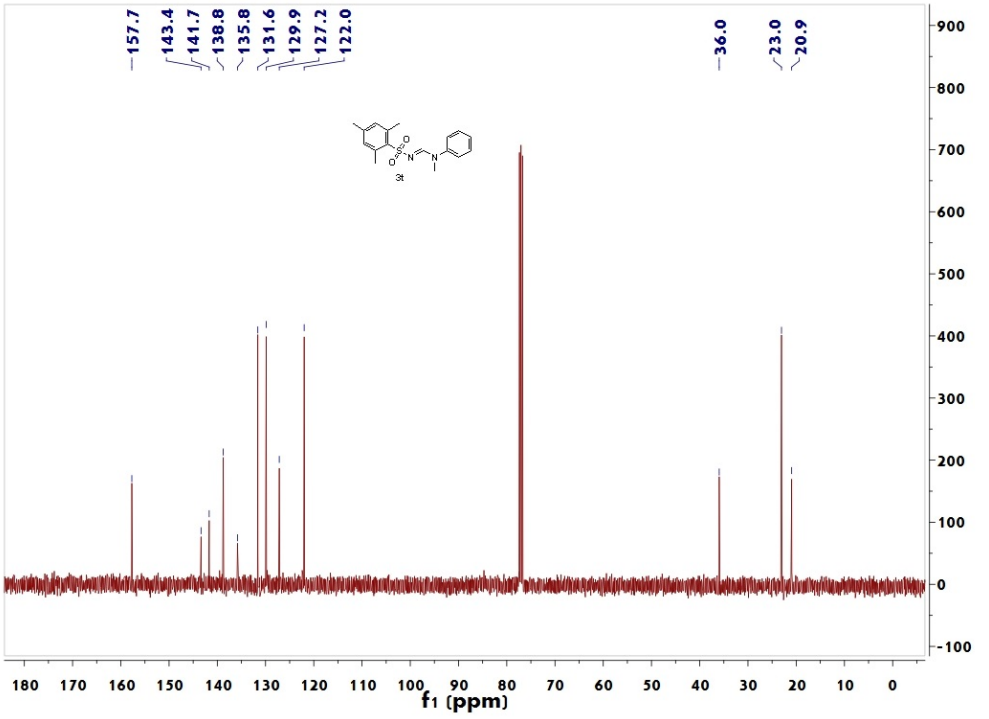

8.58
8.36
8.35
8.34
8.33
8.15
8.14
8.13
8.13
7.48
7.39
7.37
7.25
7.23
3.49
3r
1.00
2.10
2.10
2.14
1.12
2.06
3.05
f1 (ppm)

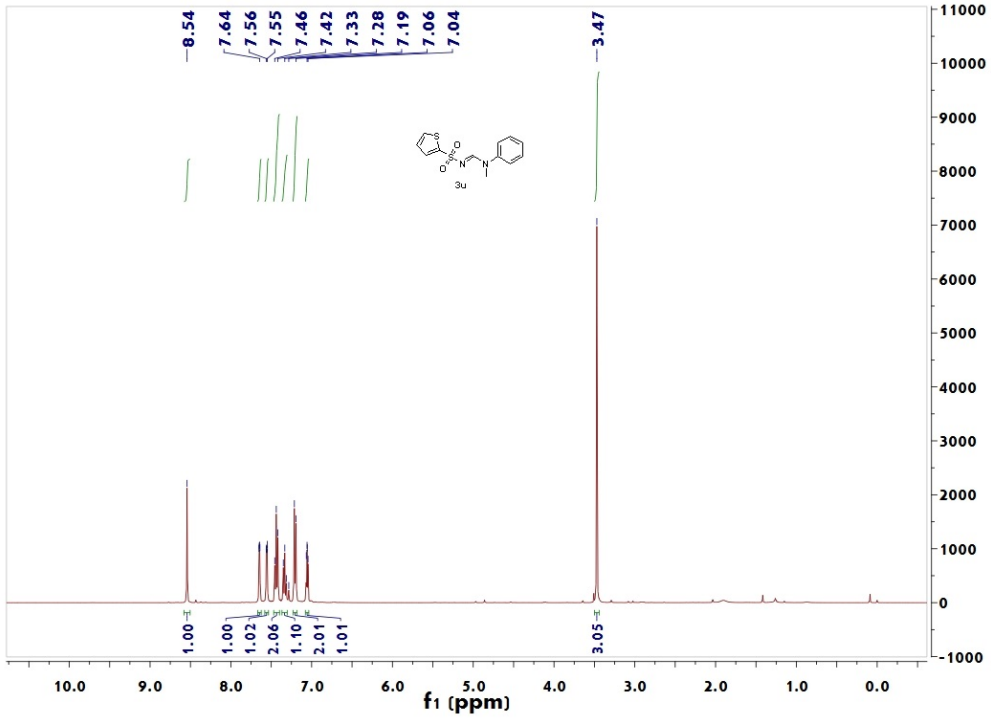

159.0
147.6
142.9
130.0
128.1
127.9
124.1
122.3
36.5
3r
f1 (ppm)


8.63
8.52
7.94
7.90
7.62
7.58
7.45
7.32
7.21
3.45
0.97
1.01
4.18
2.22
2.04
1.07
2.04
3.00
f1 (ppm)


158.6
143.2
138.7
134.7
132.2
129.9
129.3
129.1
128.5
127.9
127.5
127.5
127.3
122.6
122.1
36.2
f1 (ppm)


8.58
7.44
7.40
7.32
7.30
7.29
7.19
7.18
6.94
3.43
2.71
2.29
1.00
2.17
1.09
2.17
2.20
3.06
6.28
3.33
f1 (ppm)


157.7
143.4
141.7
138.8
135.8
131.6
129.9
127.2
122.0
36.0
23.0
20.9
f1 (ppm)


8.54
7.64
7.56
7.55
7.46
7.42
7.33
7.28
7.19
7.06
7.04
3.47
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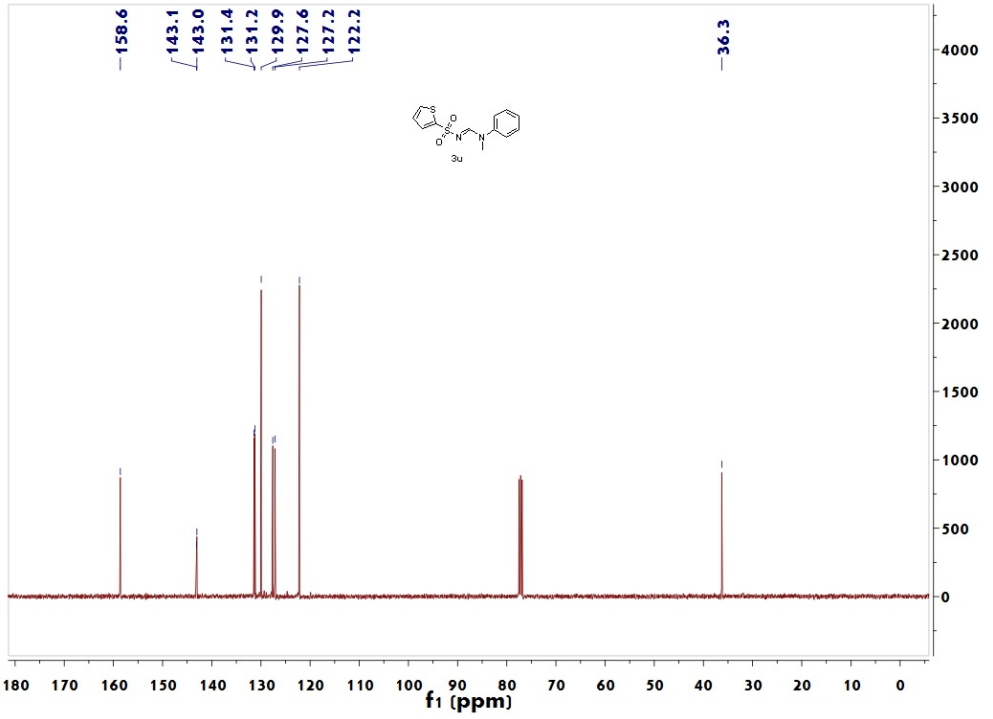
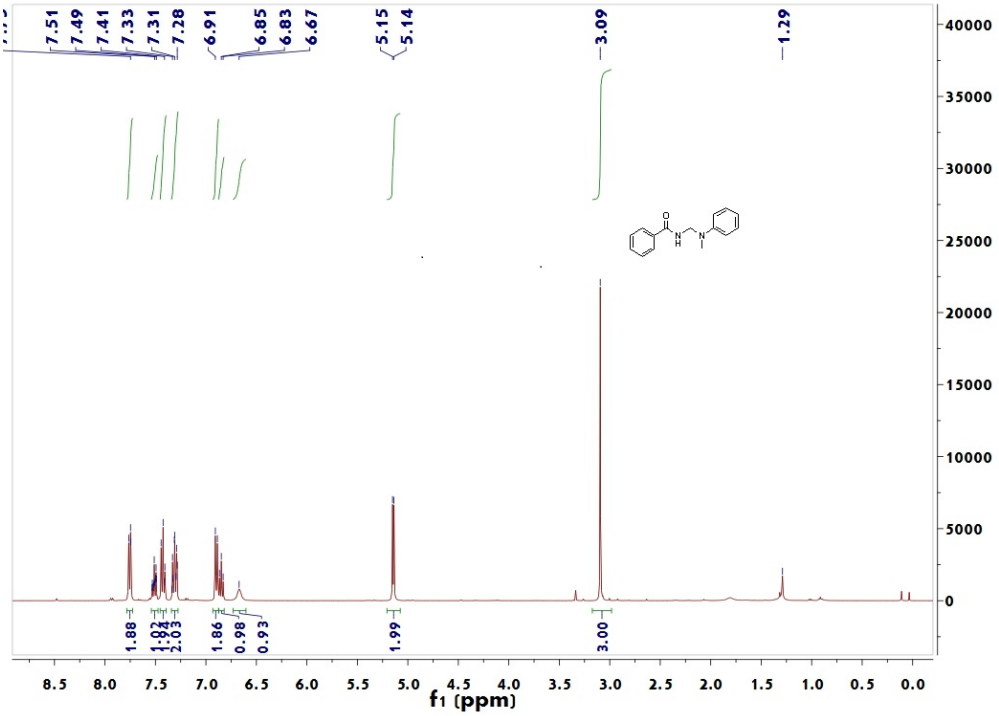
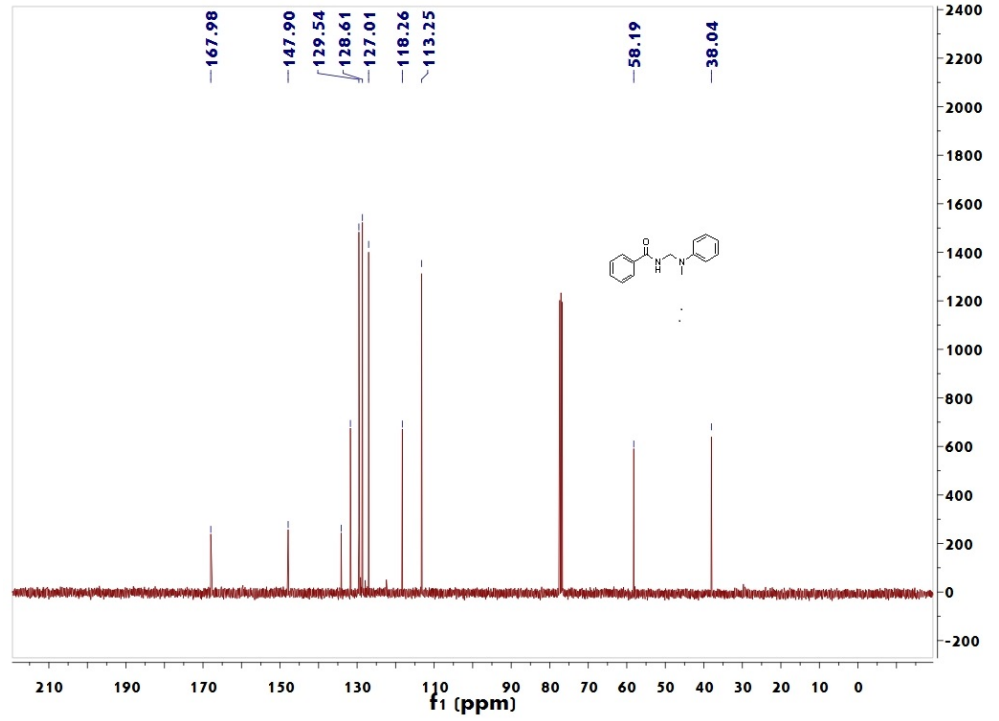
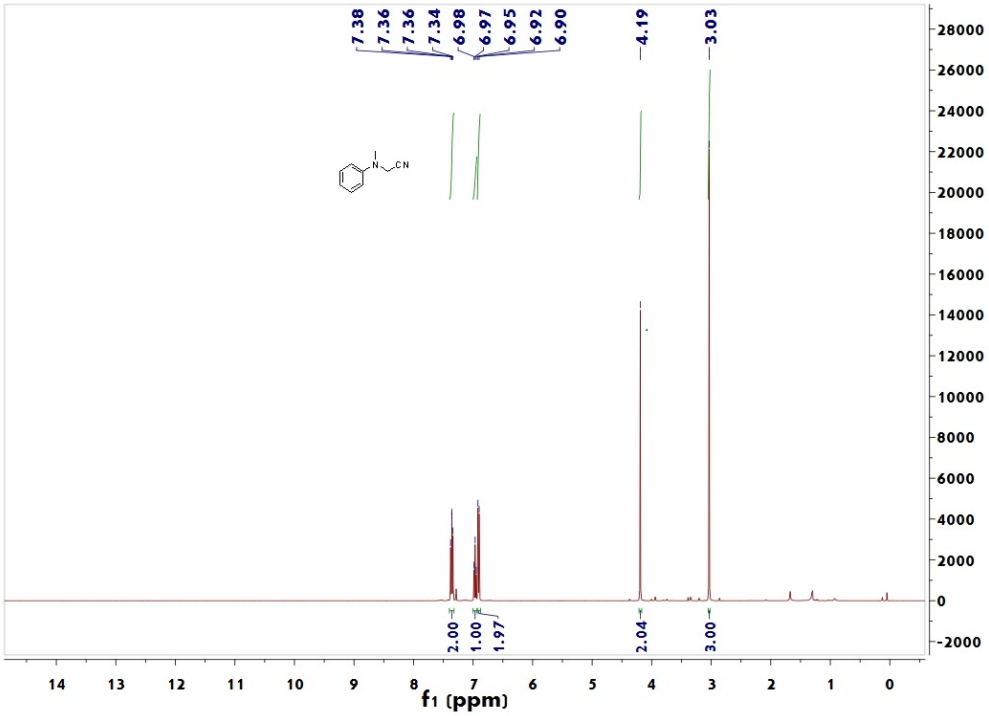
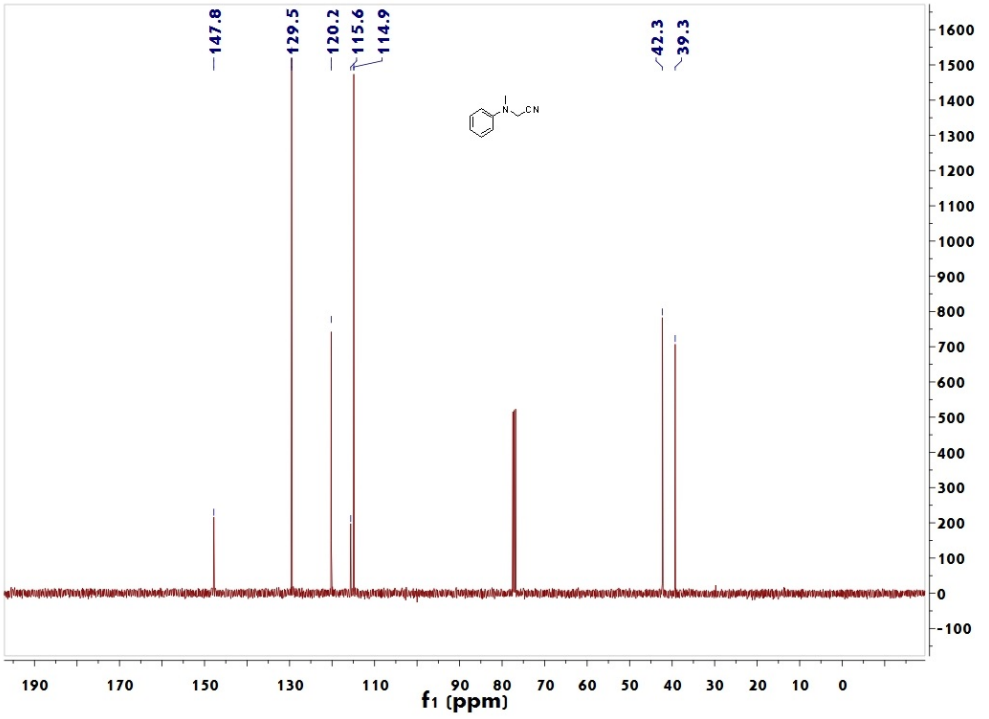
2.06
1.10
2.01
1.01
3.05
f1 (ppm)

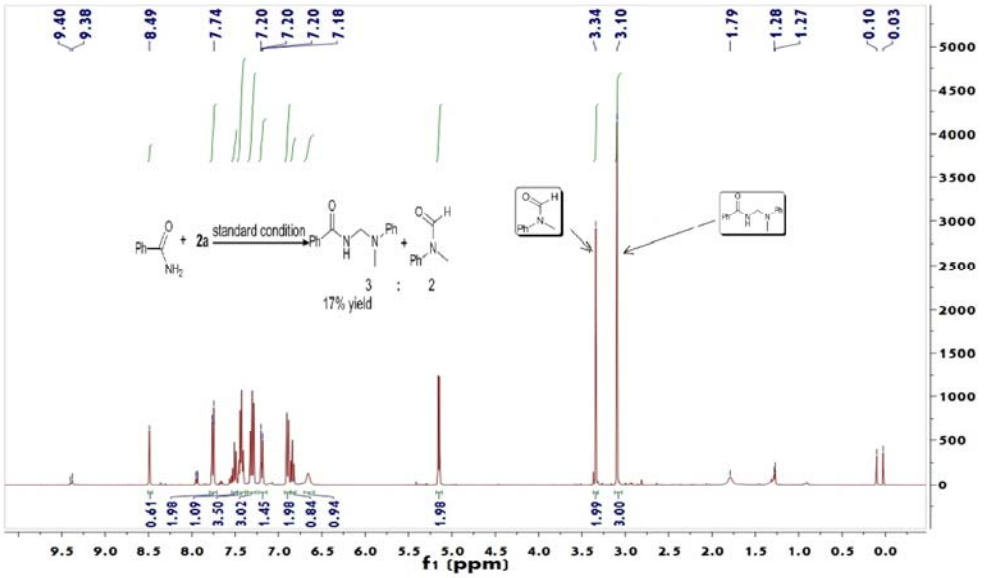

158.6
143.1
143.0
131.4
131.2
129.9
127.6
127.2
122.2
36.3
3u
f1 (ppm)


7.51
7.49
7.41
7.33
7.31
7.28
6.91
6.85
6.83
6.67
5.15
5.14
3.09
1.29
1.88
1.02
1.94
2.03
1.86
0.98
0.93
1.99
3.00
f1 (ppm)


167.98
147.90
129.54
128.61
127.01
118.26
113.25
58.19
38.04
f1 (ppm)


7.38
7.36
7.36
7.34
6.98
6.97
6.95
6.92
6.90
4.19
3.03
2.00
1.00
1.97
2.04
3.00
f1 (ppm)


147.8
129.5
120.2
115.6
114.9
42.3
39.3
f1 (ppm)


9.40
9.38
8.49
7.74
7.20
7.20
7.20
7.18
3.34
3.10
1.79
1.28
1.27
0.10
0.03
standard condition
2a
3 : 2
17% yield
0.61
1.98
1.09
3.50
3.02
1.45
1.98
0.84
0.94
1.98
1.99
3.00
f1 (ppm)