Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Metal-free Synthesis of N-Sulfonylformamidines *via* Skeletal Reconstruction of Sulfonyl Oximonitriles

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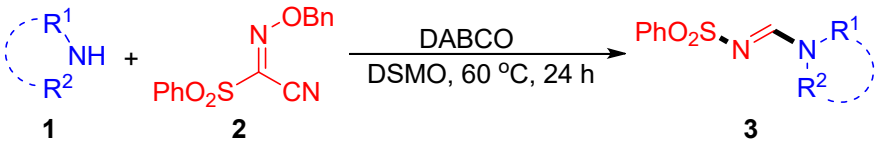
General information:

^{1}H, and ^{13}C were recorded at Bruker 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, 77.16 ppm; $(CD_3)_2SO$: 2.50 ppm, 39.52 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). Infrared spectra were obtained with a AVATAR 360 FT-IR spectrometer. X-ray structural analysis was conducted on the XtaLAB mini. The high resolution ESI-MS spectra were obtained with a Waters Vion IMS QTof high resolution mass spectrometer.

Materials: All commercially available reagents and solvent were used without further purification. Analytical thin layer chromatography was performed on 0.25 mm silica gel plates. Silica gel (200-300 mesh) was used for flash chromatography. Sulfonyl Oximonitriles were prepared according to the literatures.[1]

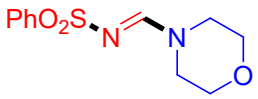
General procedure for the domino reaction of sulfonyl oximonitriles with secondary amines:



1 **2** **3**

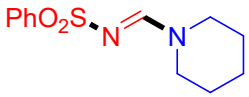
To a 10 mL Schlenk charged with sulfonyl oximonitriles **2** (0.2 mmol), DABCO (33.7 mg, 0.3 mmol) and secondary amines **1** (0.8 mmol) was added DMSO (1.0 mL) *via* a syringe. Then, the reaction mixture was vigorously stirred at 60 °C for 24 h. After the reaction was complete, the mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and washed with saturated brine (15 mL), dried anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford the desired products **3**.

(*E*)-*N*-(morpholinomethylene)benzenesulfonamide (3a):



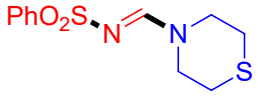
78% yield, white solid, mp 133–134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.50 (t, *J* = 4.8 Hz, 2H), 3.69 (s, 4H), 3.76 (t, *J* = 4.8 Hz, 2H), 7.45–7.49 (m, 2H), 7.51–7.55 (m, 1H), 7.88–7.91 (m, 2H), 8.20 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 142.1, 132.1, 128.9, 126.6, 66.9, 66.0, 50.4, 44.3; **IR** (KBr) ν 2920, 2850, 1615, 1445, 1344, 1147, 1088, 858 cm^{-1}; **HRMS** (ESI): calcd for $C_{11}H_{15}N_2O_3S$ $[M+H]^+$ 255.0798, found 255.0523.

(*E*)-*N*-(piperidin-1-ylmethylene)benzenesulfonamide (3b):



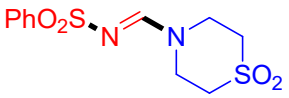
66% yield, white solid, mp 118–119 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.53–1.57 (m, 2H), 1.61–1.68 (m, 4H), 3.39 (t, *J* = 5.6 Hz, 2H), 3.57 (t, *J* = 5.6 Hz, 2H), 7.41–7.50 (m, 3H), 7.86 (dd, *J* = 7.6 Hz, 0.8 Hz, 2H), 8.11 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 142.6, 131.8, 128.7, 126.4, 51.9, 44.7, 26.4, 24.8, 23.9; **IR** (KBr) ν 2941, 2860, 1614, 1446, 13361, 1338, 1148, 1089, 928, 874 cm^{-1}; **HRMS** (ESI): calcd for $C_{12}H_{17}N_2O_2S$ $[M+H]^+$ 253.1005, found 253.1083.

(*E*)-*N*-(thiomorpholinomethylene)benzenesulfonamide (3c):



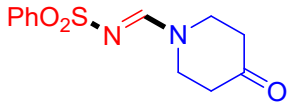
73% yield, white solid, mp 137–138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.63 (t, *J* = 5.6 Hz, 2H), 2.70 (t, *J* = 5.2 Hz, 2H), 3.72 (t, *J* = 5.2 Hz, 2H), 3.91 (t, *J* = 5.2 Hz, 2H), 7.44–7.48 (m, 2H), 7.49–7.53 (m, 1H), 7.85–7.88 (m, 2H), 8.18 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2, 142.1, 132.1, 128.9, 126.6, 53.4, 46.4, 28.3, 26.9; **IR** (KBr) ν 2920, 2851, 1607, 1446, 1352, 1283, 1146, 1089, 891 cm^{-1}; **HRMS** (ESI): calcd for $C_{11}H_{15}N_2O_2S_2$ $[M+H]^+$ 271.0569, found 271.0264.

(*E*)-*N*-((1,1-dioxidothiomorpholino)methylene)benzenesulfonamide (3d):



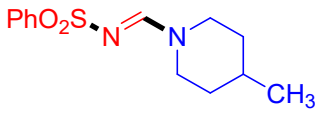
45% yield, white solid, mp 227–228 °C; **^{1}H NMR** (400 MHz, DMSO-D6) δ 3.21 (t, *J* = 5.2 Hz, 2H), 3.39 (t, *J* = 5.2 Hz, 2H), 3.93 (t, *J* = 4.8 Hz, 2H), 4.00 (t, *J* = 4.8 Hz, 2H), 7.53–7.62 (m, 3H), 7.79–7.82 (m, 2H), 8.36 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-D6) δ 159.8, 142.3, 132.1, 129.0, 126.0, 50.7, 49.9, 48.1, 41.3; **IR** (KBr) ν 2926, 2852, 1638, 1446, 1276, 1147, 1025, 991 cm^{-1}; **HRMS** (ESI): calcd for $C_{11}H_{15}N_2O_4S_2$ $[M+H]^+$ 303.0468, found 303.0558.

(*E*)-*N*-((4-oxopiperidin-1-yl)methylene)benzenesulfonamide (3e):



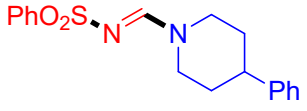
48% yield, white solid, mp 171–172 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.52 (t, *J* = 6.4 Hz, 2H), 2.58 (t, *J* = 6.4 Hz, 2H), 3.81 (t, *J* = 6.4 Hz, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 7.45–7.5 (m, 3H), 7.87–7.90 (m, 2H), 8.34 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.6, 158.2, 141.8, 132.3, 128.9, 126.6, 48.9, 42.2, 41.1, 39.8; **IR** (KBr) ν 2921, 2851, 1699, 1605, 1449, 1337, 1275, 1145, 1085, 883, 750 cm^{-1}; **HRMS** (ESI): calcd for $C_{12}H_{15}N_2O_3S$ $[M+H]^+$ 267.0798, found 267.0858.

(*E*)-*N*-((4-methylpiperidin-1-yl)methylene)benzenesulfonamide (3f):



71% yield, white solid, mp 76–77 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.94 (d, *J* = 6.4 Hz, 3H), 1.07–1.23 (m, 2H), 1.60–1.70 (m, 2H), 1.73–1.79 (m, 1H), 2.78 (dt, *J* = 13.2 Hz, 3.2 Hz, 1H), 3.25 (dt, *J* = 12.8 Hz, 3.2 Hz, 1H), 3.54–3.58 (m, 1H), 4.36–4.41 (m, 1H), 7.41–7.50 (m, 3H), 7.85–7.92 (m, 2H), 8.11 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 142.6, 131.8, 128.7, 126.4, 51.3, 44.0, 34.4, 32.9, 30.7, 21.5; **IR** (KBr) ν 2926, 2870, 1614, 1446, 1336, 1147, 1088, 921, 872 cm^{-1}; **HRMS** (ESI): calcd for $C_{13}H_{19}N_2O_2S$ $[M+H]^+$ 267.1162, found 267.1106.

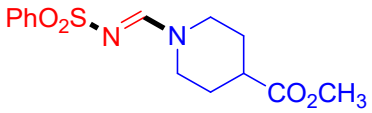
(*E*)-*N*-((4-phenylpiperidin-1-yl)methylene)benzenesulfonamide (3g):



72% yield, white solid, mp 154–155 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.64–1.80 (m, 2H), 1.91–1.94 (m, 1H), 1.99–2.02 (m, 1H), 2.75–2.83 (m, 1H), 2.90 (dt, *J* = 13.2 Hz,

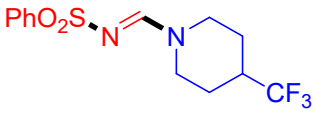
3.2 Hz, 1H), 3.43 (dt, *J* = 13.2 Hz, 2.8 Hz, 1H), 3.70–3.75 (m, 1H), 4.59–4.64 (m, 1H), 7.16–7.18 (m, 2H), 7.21–7.25 (m, 1H), 7.30–7.34 (m, 2H), 7.45–7.54 (m, 3H), 7.90–7.93 (m, 2H), 8.20 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 144.1, 142.5, 131.9, 128.8, 126.9, 126.7, 126.6, 51.6, 44.4, 42.3, 33.7, 32.2; **IR** (KBr) ν 2922, 2850, 1614, 1446, 1334, 1283, 1146, 1088, 877, 753 cm^{-1}; **HRMS** (ESI): calcd for $C_{18}H_{21}N_2O_2S$ $[M+H]^+$ 329.1318, found 329.0892.

(*E*)-methyl 1-(((phenylsulfonyl)imino)methyl)piperidine-4-carboxylate (3h):



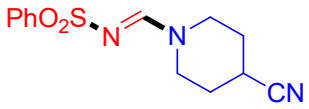
68% yield, white solid, mp 101–102 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.65–1.84 (m, 2H), 1.94–2.05 (m, 2H), 2.58–2.65 (m, 1H), 3.07–3.14 (m, 1H), 3.30–3.37 (m, 1H), 3.65 (dt, *J* = 13.2 Hz, 4.0 Hz, 1H), 3.69 (s, 3H), 4.22 (dt, *J* = 13.2 Hz, 4.0 Hz, 1H), 7.44–7.53 (m, 3H), 7.86–7.88 (m, 2H), 8.16 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 157.6, 142.3, 131.9, 128.8, 128.5, 52.1, 49.9, 42.8, 40.1, 28.3, 27.0; **IR** (KBr) ν 2922, 2850, 1732, 1611, 1447, 1334, 1285, 1147, 1089, 883 cm^{-1}; **HRMS** (ESI): calcd for $C_{14}H_{19}N_2O_4S$ $[M+H]^+$ 311.1060, found 311.1178.

(*E*)-*N*-((4-(trifluoromethyl)piperidin-1-yl)methylene)benzenesulfonamide (3i):



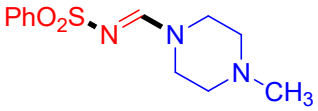
72% yield, white solid, mp 118–119 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.45–1.64 (m, 2H), 1.91–1.94 (m, 1H), 1.98–2.02 (m, 1H), 2.24–2.38 (m, 1H), 2.81 (dt, *J* = 13.2 Hz, 3.2 Hz, 1H), 3.30 (dt, *J* = 12.8 Hz, 3.2 Hz, 1H), 3.70–3.74 (m, 1H), 4.51–4.55 (m, 1H), 7.43–7.52 (m, 3H), 7.85–7.92 (m, 2H), 8.17 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 142.1, 132.1, 128.8, 127.9, 126.6 (q, $J_{C\text{-}F}$ = 276.8 Hz), 126.5, 49.4, 42.3, 40.0 (q, $J_{C\text{-}F}$ = 28.0 Hz), 25.0, 23.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -73.68 (s, 3F); **IR** (KBr) ν 2921, 2850, 1614, 1447, 1337, 1286, 1148, 1084, 1000, 883 cm^{-1}; **HRMS** (ESI): calcd for $C_{13}H_{16}F_3N_2O_2S$ $[M+H]^+$ 321.0879, found 320.9936.

(*E*)-*N*-((4-cyanopiperidin-1-yl)methylene)benzenesulfonamide (3j):



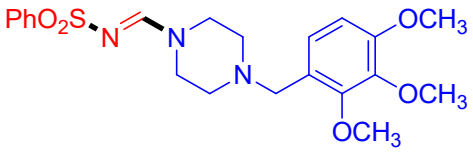
70% yield, white solid, mp 159–160 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.85–2.03 (m, 4H), 2.95–3.01 (m, 1H), 3.45–3.51 (m, 1H), 3.63–3.70 (m, 1H), 3.72–3.81 (m, 2H), 7.45–7.55 (m, 3H), 7.86–7.88 (m, 2H), 8.17 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 141.9, 132.2, 128.9, 126.6, 120.0, 48.3, 41.3, 28.9, 27.5, 25.9; **IR** (KBr) ν 2921, 2851, 1610, 1447, 1345, 1280, 1147, 1088, 881, 752 cm^{-1}; **HRMS** (ESI): calcd for $C_{13}H_{16}N_3O_2S$ $[M+H]^+$ 278.0958, found 278.0611.

(*E*)-*N*-((4-methylpiperazin-1-yl)methylene)benzenesulfonamide (3k):



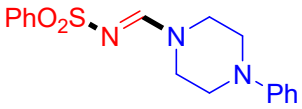
61% yield, white solid, mp 64–65 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.40 (t, *J* = 5.2 Hz, 2H), 2.47 (t, *J* = 5.2 Hz, 2H), 3.48 (t, *J* = 5.2 Hz, 2H), 3.67 (t, *J* = 5.2 Hz, 2H), 7.43–7.53 (m, 3H), 7.86–7.89 (m, 2H), 8.14 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 142.2, 132.0, 128.8, 126.5, 54.9, 53.7, 50.3, 46.0, 43.7; **IR** (KBr) ν 2920, 2850, 1613, 1447, 1345, 1285, 1145, 1089, 884 cm^{-1}; **HRMS** (ESI): calcd for $C_{12}H_{18}N_3O_2S$ $[M+H]^+$ 268.1114, found 268.0936.

(*E*)-*N*-((4-(2,3,4-trimethoxybenzyl)piperazin-1-yl)methylene)benzenesulfonamide (3l):



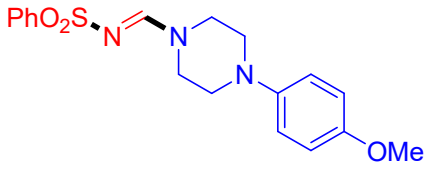
62% yield, white solid, mp 81–82 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.44 (t, *J* = 5.2 Hz, 2H), 2.51 (t, *J* = 4.8 Hz, 2H), 3.44 (t, *J* = 5.2 Hz, 2H), 3.47 (s, 2H), 3.63 (t, *J* = 4.8 Hz, 2H), 3.82–3.87 (m, 9H), 6.61 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 7.41–7.50 (m, 3H), 7.84–7.86 (m, 2H), 8.13 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 153.2, 152.6, 142.4, 142.3, 131.8, 128.7, 126.4, 125.1, 122.8, 107.0, 61.2, 60.8, 56.2, 56.0, 52.7, 51.5, 50.6, 43.9; **IR** (KBr) ν 2922, 2849, 1613, 1495, 1446, 1345, 1283, 1149, 1091, 999, 882 cm^{-1}; **HRMS** (ESI): calcd for $C_{21}H_{28}N_3O_5S$ $[M+H]^+$ 434.1744, found 434.0912.

(*E*)-*N*-((4-phenylpiperazin-1-yl)methylene)benzenesulfonamide (3m):



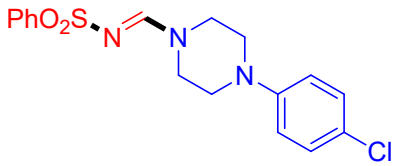
81% yield, white solid, mp 126–127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.18 (t, *J* = 5.2 Hz, 2H), 3.25 (t, *J* = 5.2 Hz, 2H), 3.63 (t, *J* = 5.2 Hz, 2H), 3.82 (t, *J* = 5.2 Hz, 2H), 6.90–6.95 (m, 3H), 7.26–7.31 (m, 2H), 7.45–7.56 (m, 3H), 7.89–7.94 (m, 2H), 8.24 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 150.5, 142.2, 132.1, 129.4, 128.9, 126.6, 121.4, 117.3, 50.4, 50.3, 49.1, 43.8; **IR** (KBr) ν 2921, 2850, 1614, 1496, 1446, 1343, 1287, 1230, 1147, 1089, 1016, 883 cm^{-1}; **HRMS** (ESI): calcd for $C_{17}H_{20}N_3O_2S$ $[M+H]^+$ 330.1271, found 330.1410.

(*E*)-*N*-((4-(4-methoxyphenyl)piperazin-1-yl)methylene)benzenesulfonamide (3n):



90% yield, white solid, mp 128–129 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.05 (t, *J* = 4.8 Hz, 2H), 3.12 (t, *J* = 4.8 Hz, 2H), 3.62 (t, *J* = 5.2 Hz, 2H), 3.76 (s, 3H), 3.81 (t, *J* = 5.2 Hz, 2H), 6.86 (dd, *J* = 18.4 Hz, 9.2 Hz, 4H), 7.45–7.54 (m, 3H), 7.89–7.92 (m, 2H), 8.22 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 155.0, 144.8, 142.3, 132.0, 128.8, 126.6, 119.6, 114.7, 55.6, 51.7, 50.6, 50.5, 44.0; **IR** (KBr) ν 2920, 2834, 1610, 1512, 1446, 1346, 1298, 1247, 1148, 1089, 1019, 885 cm^{-1}; **HRMS** (ESI): calcd for $C_{18}H_{22}N_3O_3S$ $[M+H]^+$ 360.1376, found 360.1419.

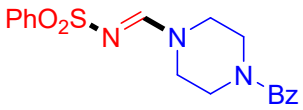
(*E*)-*N*-((4-(4-chlorophenyl)piperazin-1-yl)methylene)benzenesulfonamide (3o):



82% yield, white solid, mp 148–149 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.14 (t, *J* = 5.2 Hz, 2H), 3.21 (t, *J* = 5.2 Hz, 2H), 3.63 (t, *J* = 5.2 Hz, 2H), 3.80 (t, *J* = 5.2 Hz, 2H), 6.83 (dd, *J* = 12.0 Hz, 3.2 Hz, 2H), 7.22 (dd, *J* = 12.0 Hz, 3.6 Hz, 2H), 7.45–7.54 (m, 3H), 7.88–7.94 (m, 2H), 8.24 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 149.1, 142.1, 132.1, 129.3, 128.9, 126.6, 126.3, 118.5, 50.3, 50.2, 49.0, 43.7; **IR** (KBr) ν

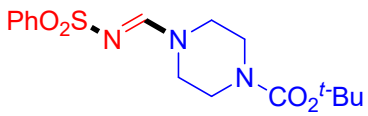
2921, 2850, 1614, 1496, 1446, 1348, 1285, 1233, 1149, 1089, 1017, 885 cm^{-1}; **HRMS** (ESI): calcd for $C_{17}H_{19}ClN_3O_2S$ $[M+H]^+$ 364.0881, found 364.0839.

(*E*)-*N*-((4-benzoylpiperazin-1-yl)methylene)benzenesulfonamide (3p):



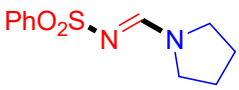
73% yield, white solid, mp 161–162 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.51–3.67 (m, 8H), 7.37–7.54 (m, 8H), 7.87 (d, *J* = 8.0 Hz, 2H), 8.25 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 158.1, 141.9, 134.6, 132.2, 130.5, 128.9, 128.8, 127.1, 126.6, 50.2, 43.9; **IR** (KBr) ν 2921, 2851, 1606, 1446, 1346, 1284, 1147, 1090, 1006, 878 cm^{-1}; **HRMS** (ESI): calcd for $C_{18}H_{20}N_3O_3S$ $[M+H]^+$ 358.1220, found 358.1142.

(*E*)-tert-butyl 4-(((phenylsulfonyl)imino)methyl)piperazine-1-carboxylate (3q):



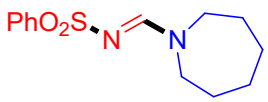
69% yield, white solid, mp 198–199 °C; **^{1}H NMR** (400 MHz, DMSO-D6) δ 1.40 (s, 9H), 3.36–3.41 (m, 4H), 3.50–3.56 (m, 4H), 7.54–7.59 (m, 3H), 7.78 (d, *J* = 6.8 Hz, 2H), 8.32 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-D6) δ 158.7, 153.7, 142.7, 131.9, 129.0, 126.0, 79.5, 49.2, 43.1, 28.0; **IR** (KBr) 1645, 1615, ν 2921, 2850, 1446, 1347, 1283, 1149, 1025, 994 cm^{-1}; **HRMS** (ESI): calcd for $C_{16}H_{24}N_3O_4S$ $[M+H]^+$ 354.1482, found 354.1285.

(*E*)-*N*-(pyrrolidin-1-ylmethylene)benzenesulfonamide (3r):



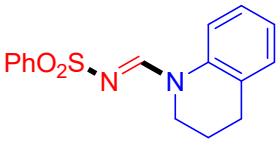
57% yield, white solid, mp 124–125 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.92–1.98 (m, 4H), 3.47 (t, *J* = 6.8 Hz, 2H), 3.58 (t, *J* = 6.4 Hz, 2H), 7.42–7.51 (m, 3H), 7.89 (dd, *J* = 8.0 Hz, 1.2 Hz, 2H), 8.32 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.0, 142.6, 131.8, 128.8, 126.6, 50.1, 46.6, 25.1, 24.4; **IR** (KBr) ν 2922, 2850, 1614, 1446, 1348, 1282, 1147, 1089, 894, 852 cm^{-1}; **HRMS** (ESI): calcd for $C_{11}H_{15}N_2O_2S$ $[M+H]^+$ 239.0849, found 239.0946.

(*E*)-*N*-(azepan-1-ylmethylene)benzenesulfonamide (3s):



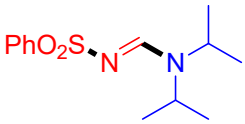
78% yield, white solid, mp 60–61 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.51–1.57 (m, 4H), 1.69–1.76 (m, 4H), 3.47 (t, *J* = 6.0 Hz, 2H), 3.52 (t, *J* = 6.0 Hz, 2H), 7.40–7.49 (m, 3H), 7.84–7.91 (m, 2H), 8.17 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 142.7, 131.7, 128.7, 126.3, 52.9, 47.4, 29.7, 27.8, 26.8, 25.9; **IR** (KBr) ν 2923, 2852, 1604, 1445, 1340, 1297, 1145, 1088, 905, 839, 750 cm^{-1}; **HRMS** (ESI): calcd for $C_{13}H_{19}N_2O_2S$ $[M+H]^+$ 267.1162, found 267.0795.

(*E*)-*N*-((3,4-dihydroquinolin-1(2H)-yl)methylene)benzenesulfonamide (3t):



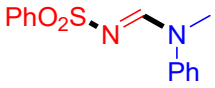
66% yield, white solid, mp 149–150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.93–1.99 (m, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 3.87 (t, *J* = 6.4 Hz, 2H), 7.11–7.26 (m, 4H), 7.46–7.55 (m, 3H), 7.91–7.94 (m, 2H), 8.86 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 141.7, 137.4, 132.3, 129.9, 129.7, 128.9, 127.7, 126.7, 125.8, 117.3, 44.7, 26.9, 22.0; **IR** (KBr) ν 2923, 2849, 1610, 1589, 1572, 1498, 1446, 1339, 1303, 1149, 1088, 1018, 927, 856, 740 cm^{-1}; **HRMS** (ESI): calcd for $C_{16}H_{17}N_2O_2S$ $[M+H]^+$ 301.1005, found 301.1123.

(*E*)-*N*,*N*-diisopropyl-*N'*-(phenylsulfonyl)formimidamide (3u):



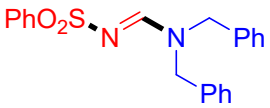
82% yield, white solid, mp 108–109 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.21 (d, *J* = 6.8 Hz, 6H), 1.30 (d, *J* = 6.8 Hz, 6H), 3.63–3.73 (m, 1H), 4.46–4.57 (m, 1H), 7.42–7.50 (m, 3H), 7.84–7.87 (m, 2H), 8.24 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 142.8, 131.7, 128.7, 126.3, 48.6, 48.0, 23.6, 19.6; **IR** (KBr) ν 2978, 2922, 2850, 1602, 1453, 1338, 1282, 1144, 1087, 891, 839 cm^{-1}; **HRMS** (ESI): calcd for $C_{13}H_{21}N_2O_2S$ $[M+H]^+$ 269.1318, found 269.1325.

(*E*)-*N*-methyl-N-phenyl-N'-(phenylsulfonyl)formimidamide (3v):



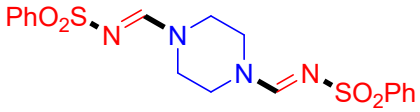
68% yield, oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.44 (s, 3H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.39–7.44 (m, 2H), 7.47–7.56 (m, 3H), 7.92–7.95 (m, 2H), 8.57 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.6, 143.2, 141.8, 132.2, 129.9, 128.9, 127.5, 126.7, 122.1, 36.2; **IR** (KBr) ν 2927, 2852, 1604, 1575, 1447, 1338, 1299, 1148, 1086, 892, 778 cm^{-1}; **HRMS** (ESI): calcd for $C_{13}H_{21}N_2O_2S$ $[M+H]^+$ 275.0849, found 275.0484.

(*E*)-*N*,*N*-dibenzyl-*N'*-(phenylsulfonyl)formimidamide (3w):



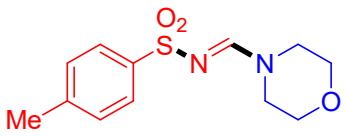
44% yield, white solid, mp 125–126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.36 (s, 2H), 4.53 (s, 2H), 7.10–7.12 (m, 2H), 7.14–7.17 (m, 2H), 7.23–7.25 (m, 1H), 7.27–7.30 (m, 2H), 7.35–7.41 (m, 3H), 7.47–7.57 (m, 3H), 7.91–7.94 (m, 2H), 8.51 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 142.3, 134.5, 134.0, 132.0, 129.3, 128.9, 128.8, 128.7, 128.3, 128.0, 126.5, 55.2, 48.6; **IR** (KBr) ν 2922, 2852, 1601, 1582, 1496, 1446, 1283, 1148, 1002, 999, 875 cm^{-1}; **HRMS** (ESI): calcd for $C_{21}H_{21}N_2O_2S$ $[M+H]^+$ 365.1318, found 365.0957.

(*N*,*N'E*,*N*,*N'E*)-*N*,*N'*-(piperazine-1,4-diylbis(methanylylidene))dibenzenesulfonamide (3x):



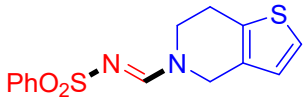
38% yield, white solid, mp 114–115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.56–2.70 (m, 4H), 3.45–3.57 (m, 2H), 3.65–3.74 (m, 2H), 4.89 (s, 1H), 7.38–7.55 (m, 8H), 7.86–7.94 (m, 2H), 8.17 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 142.0, 132.2, 131.9, 129.5, 129.2, 128.9, 127.9, 126.6, 114.7, 61.9, 50.0, 49.4, 48.7, 43.4; **IR** (KBr) ν 2921, 2850, 1614, 1447, 1349, 1282, 1147, 1088, 1000, 887 cm^{-1}; **HRMS** (ESI): calcd for $C_{18}H_{21}N_4O_4S_2$ $[M+H]^+$ 421.0999, found 421.0718.

(*E*)-4-methyl-*N*-(morpholinomethylene)benzenesulfonamide (3y):



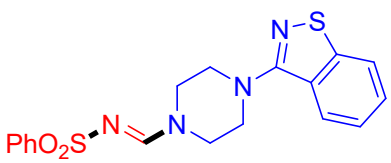
58% yield, white solid, mp 123–124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.93–2.98 (m, 2H), 3.12–3.18 (m, 2H), 3.66–3.76 (m, 4H), 7.26 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.6, 139.3, 129.8, 126.3, 67.1, 53.5, 45.8, 21.5; **IR** (KBr) ν 2924, 2852, 1613, 1456, 1275, 1260, 1181, 1105, 1011, 749 cm^{-1}; **HRMS** (ESI): calcd for $C_{12}H_{17}N_2O_3S$ $[M+H]^+$ 269.0954, found 270.3235.

***N*-((6,7-dihydrothieno[3,2-c]pyridin-5(4H)-yl)methylene)benzenesulfonamide (3aa):**



45% yield, white solid, mp 184–185 °C; *E*/*Z* = 2:1, *E*-configuration: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.99 (t, *J* = 5.6 Hz, 2H), 3.79 (t, *J* = 5.6 Hz, 2H), 4.69 (s, 2H), 6.75 (d, *J* = 5.2 Hz, 1H), 7.16 (d, *J* = 5.2 Hz, 1H), 7.44–7.49 (m, 3H), 7.83–7.90 (m, 2H), 8.35 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 142.2, 132.1, 131.8, 129.9, 128.8, 126.6, 124.8, 124.5, 48.7, 44.5, 25.6; *Z*-configuration: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.91 (t, *J* = 5.6 Hz, 0.97H), 3.97 (t, *J* = 5.6 Hz, 0.93H), 4.58 (s, 0.94H), 6.78 (d, *J* = 5.2 Hz, 0.44H), 7.18 (d, *J* = 6.0 Hz, 0.46H), 7.49–7.53 (m, 1.43H), 7.91–7.94 (m, 0.93H), 8.37 (s, 0.45H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.4. 142.3, 133.4, 132.0, 130.0, 128.8, 126.6, 124.5, 124.2, 50.6. 42.0. 24.2; **IR** (KBr) ν 2921, 2851, 1607, 1564, 1446, 1349, 1286, 1149, 1088, 887, 836 cm^{-1}; **HRMS** (ESI): calcd for $C_{14}H_{15}N_2O_2S_2$ $[M+H]^+$ 307.0569, found 307.0658.

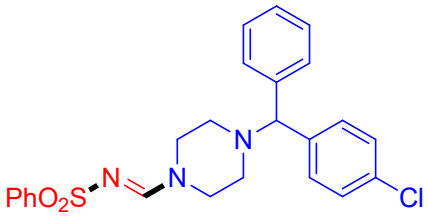
(*E*)-*N*-((4-(benzo[d]isothiazol-3-yl)piperazin-1-yl)methylene)benzenesulfonamide (3ab):



79% yield, white solid, mp 123–124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.53–3.56 (m,

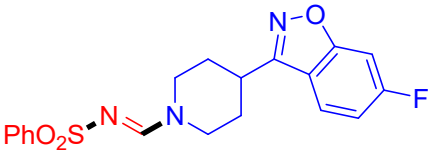
2H), 3.61–3.64 (m, 2H), 3.71–3.73 (m, 2H), 3.88–3.90 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.46–7.55 (m, 4H), 7.82–7.86 (m, 2H), 7.89–7.91 (m, 2H), 8.28 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7, 157.9, 153.0, 142.1, 132.1, 128.9, 128.0, 127.6, 126.6, 124.4, 123.4, 120.8, 50.2, 50.1, 49.3, 43.6; **IR** (KBr) ν 2921, 2850, 1610, 1561, 1493, 1446, 1345, 1285, 1117, 1089, 1012, 882 cm^{-1}; **HRMS** (ESI): calcd for $C_{18}H_{19}N_4O_2S_2$ $[M+H]^+$ 387.0944, found 387.1051.

(*E*)-*N*-((4-((4-chlorophenyl)(phenyl)methyl)piperazin-1-yl)methylene)benzenesulfonamide (3ac):



72% yield, white solid, mp 149–150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.39 (t, J = 5.2 Hz, 2H), 2.44–2.47 (m, 2H), 3.47 (t, J = 5.2 Hz, 2H), 3.60–3.70 (m, 2H), 4.26 (s, 1H), 7.19–7.35 (m, 9H), 7.43–7.53 (m, 3H), 7.85–7.88 (m, 2H), 8.13 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 142.3, 141.1, 140.3, 133.2, 132.0, 129.2, 129.1, 129.0, 128.8, 127.8, 127.7, 126.6, 75.0, 51.8, 50.8, 50.7, 44.0; **IR** (KBr) ν 2921, 2818, 1614, 1487, 1446, 1347, 1284, 1148, 1089, 999, 891 cm^{-1}; **HRMS** (ESI): calcd for $C_{24}H_{25}ClN_3O_2S$ $[M+H]^+$ 454.1351, found 454.0895.

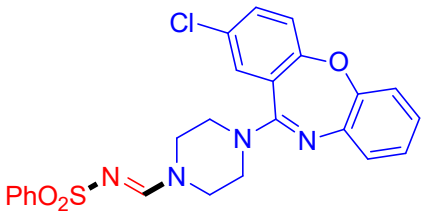
(*E*)-*N*-((4-(6-fluorobenzo[d]isoxazol-3-yl)piperidin-1-yl)methylene)benzenesulfonamide (3ad):



71% yield, white solid, mp 121–122 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.92–2.02 (m, 1H), 2.05–2.26 (m, 3H), 3.19–3.26 (m, 1H), 3.37–3.45 (m, 1H), 3.48–3.55 (m, 1H), 3.83 (dt, J = 13.6 Hz, 3.6 Hz, 1H), 4.44 (dt, J = 13.6 Hz, 3.6 Hz, 1H), 7.09 (dt, J = 8.8 Hz, 2.4 Hz, 1H), 7.27 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.45–7.54 (m, 3H), 7.59–7.62 (m, 1H), 7.88–7.91 (m, 2H), 8.23 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4 (d, $J_{C\text{-}F}$ = 250.1 Hz), 164.0 (d, $J_{C\text{-}F}$ = 13.6 Hz), 159.5, 157.7, 142.2, 132.1, 128.9, 126.6, 122.1

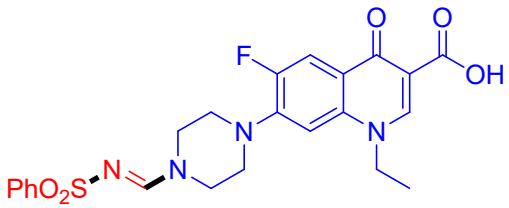
(d, $J_{C\text{-}F}$ = 11.0 Hz), 116.9, 113.0 (d, $J_{C\text{-}F}$ = 25.4 Hz), 97.8 (d, $J_{C\text{-}F}$ = 26.5 Hz), 50.3, 43.2, 33.5, 30.4, 29.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.59 (s, 1F); **IR** (KBr) ν 2929, 2853, 1611, 1495, 1447, 1354, 1273, 1147, 1088, 997, 882 cm^{-1}; **HRMS** (ESI): calcd for $C_{19}H_{19}FN_3O_3S$ $[M+H]^+$ 388.1126, found 388.0735.

(*E*)-*N*-((4-(2-chlorodibenzo[b,f][1,4]oxazepin-11-yl)piperazin-1-yl)methylene)benzenesulfonamide (3ae):



76% yield, white solid, mp 187–188 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.52–3.77 (m, 8H), 7.00–7.05 (m, 1H), 7.08–7.14 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 2.8 Hz, 1H), 7.41 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.45–7.54 (m, 3H), 7.88–7.91 (m, 2H), 8.27 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 158.3, 157.9, 151.7, 142.1, 139.5, 133.2, 132.1, 130.7, 128.8, 128.7, 127.2, 126.6, 126.0, 125.4, 124.5, 123.0, 120.3, 49.9, 47.6, 46.7, 43.5; **IR** (KBr) ν 2921, 2851, 1607, 1559, 1470, 1346, 1300, 1284, 1237, 1147, 1090, 1009, 883 cm^{-1}; **HRMS** (ESI): calcd for $C_{24}H_{22}ClN_4O_3S$ $[M+H]^+$ 481.1096, found 481.1226.

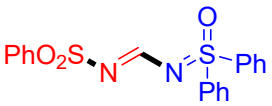
(*E*)-1-ethyl-6-fluoro-4-oxo-7-(4-(((phenylsulfonyl)imino)methyl)piperidin-1-yl)-1,4-dihydroquinoline-3-carboxylic acid (3af):



52% yield, white solid, mp 215–216 °C; **^{1}H NMR** (400 MHz, DMSO-D6) δ 1.38 (t, *J* = 7.2 Hz, 3H), 2.59–2.62 (m, 2H), 2.73–2.76 (m, 2H), 3.32–3.36 (m, 4H), 4.53 (q, *J* = 14.0 Hz, 6.8 Hz, 2H), 5.50 (s, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.42–7.51 (m, 5H), 7.86 (d, *J* = 13.2 Hz, 1H), 8.89 (s, 1H), 15.31 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-D6) δ 176.2, 166.2, 153.0 (d, $J_{C\text{-}F}$ = 248.1 Hz), 148.5, 145.4 (d, $J_{C\text{-}F}$ = 10.2 Hz), 137.2, 133.0, 129.1, 129.0, 127.9, 119.6 (d, $J_{C\text{-}F}$ = 7.4 Hz), 115.9, 111.2 (d, $J_{C\text{-}F}$ = 22.8 Hz), 107.1,

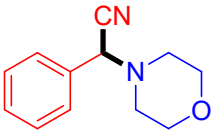
106.3 (d, $J_{C\text{-}F}$ = 2.8 Hz), 60.7, 49.4, 49.3, 49.2, 48.9, 14.4; **^{19}F NMR** (376 MHz, DMSO-D6) δ -121.41 (s, 1F); **IR** (KBr) ν 3402, 2922, 2851, 1687, 1628, 1476, 1275, 1260, 1025, 999, 750 cm^{-1}; **HRMS** (ESI): calcd for $C_{23}H_{24}FN_4O_5S$ $[M+H]^+$ 487.1446, found 487.1013.

(*E*)-*N*-(dibenzenesulfonimidoylmethylene)benzenesulfonamide (3ag):



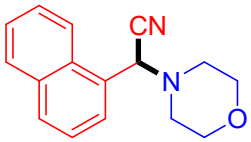
48% yield, white solid, mp 111–112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.41 (m, 2H), 7.46–7.55 (m, 5H), 7.60–7.64 (m, 2H), 7.76–7.79 (m, 2H), 7.95–7.98 (m, 4H), 8.79 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8, 141.0, 138.5, 134.4, 132.3, 129.9, 128.7, 127.7, 126.9; **IR** (KBr) ν 3065, 2922, 2852, 1633, 1538, 1448, 1308, 1283, 1227, 1152, 1088, 839, 809, 734 cm^{-1}; **HRMS** (ESI): calcd for $C_{19}H_{17}N_2O_3S_2$ $[M+H]^+$ 385.0675, found 385.0252.

2-morpholino-2-phenylacetonitrile (4a):



41% yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.58 (t, J = 4.4 Hz, 4H), 3.67–3.77 (m, 4H), 4.82 (s, 1H), 7.35–7.43 (m, 3H), 7.52–7.55 (m, 2H); **IR** (KBr) ν 2921, 2853, 1613, 1445, 1345, 1285, 1147, 1089, 1025, 945, 859 cm^{-1}.

2-morpholino-2-(naphthalen-1-yl)acetonitrile (4c):

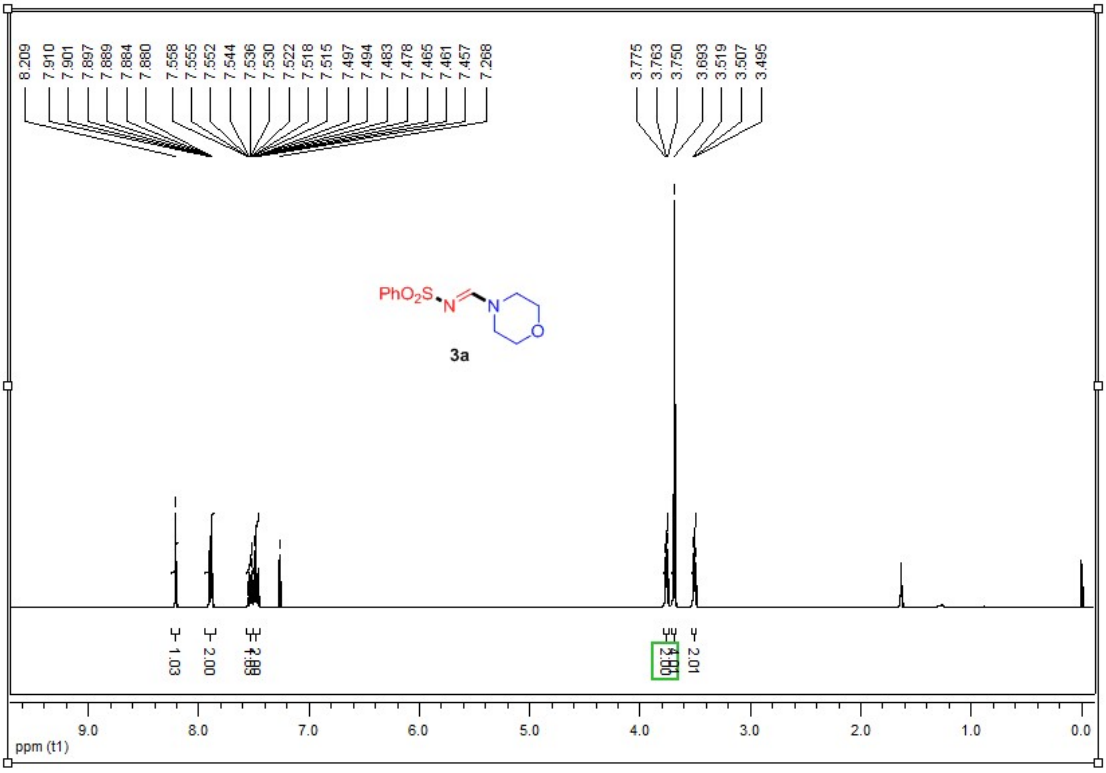


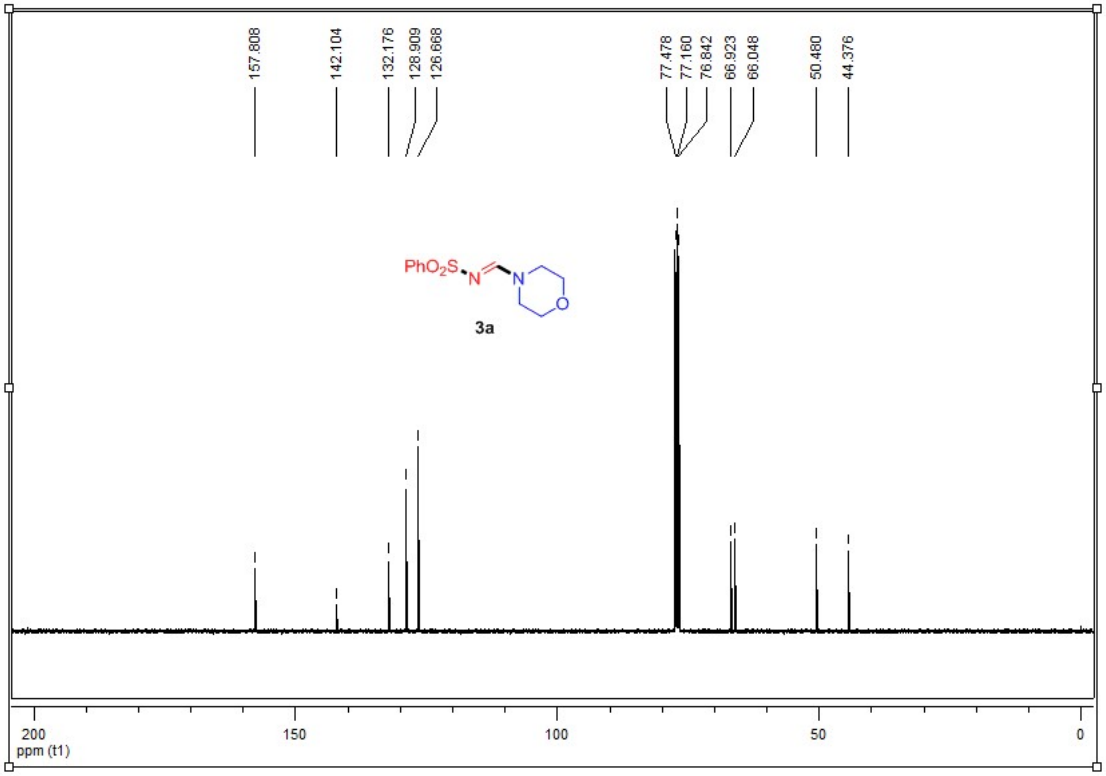
42% yield, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.61–2.62 (m, 2H), 2.68–2.72 (m, 2H), 3.61–3.65 (m, 2H), 3.68–3.73 (m, 2H), 5.42 (s, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.52–7.60 (m, 2H), 7.79 (d, J = 7. 2 Hz, 1H), 7.90 (d, J = 7.6 Hz, 2H), 8.13 (d, J = 8.4 Hz, 1H); **IR** (KBr) ν 2922, 2859, 1614, 1446, 1345, 1285, 1148, 1089, 1025, 954, 859 cm^{-1}.

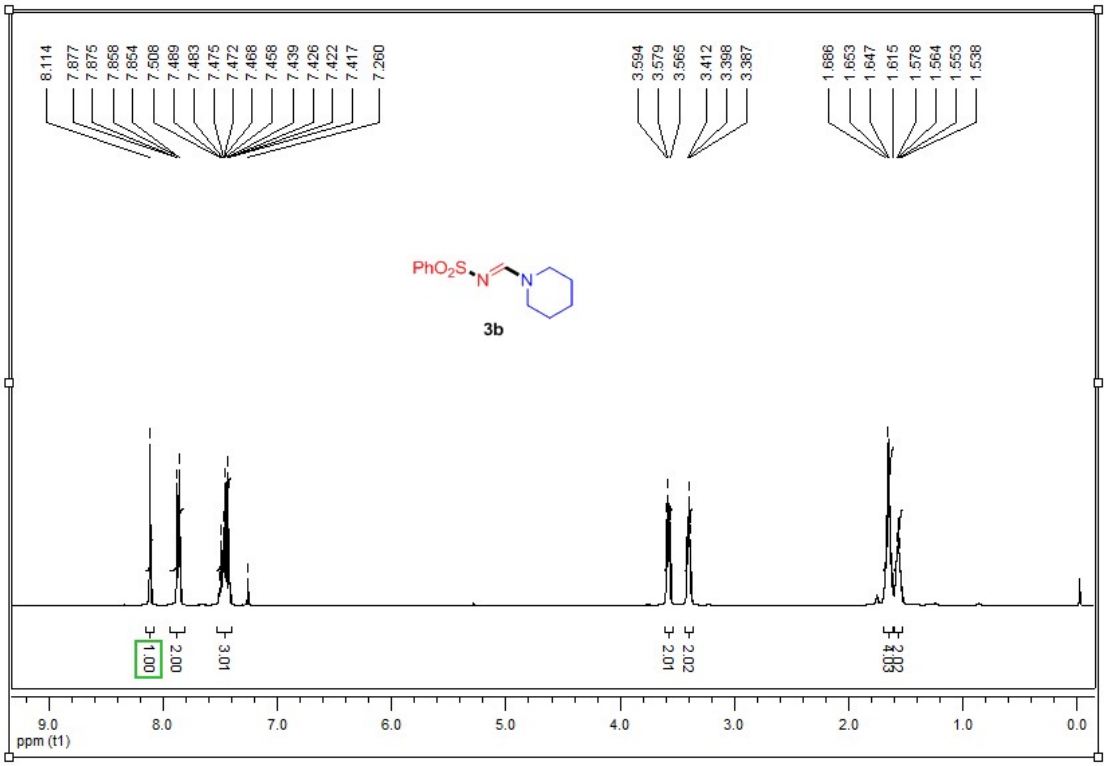
Reference:

[1] (a) B. Gaspar, E. M. Carreira, *J. Am. Chem. Soc.*, **2009**, *131*, 13214; (b) Y. Zhu, X. Wen, S. Song, N. Jiao, *ACS Catal.*, **2016**, *6*, 6465.

Copies of NMR spectra of the products:



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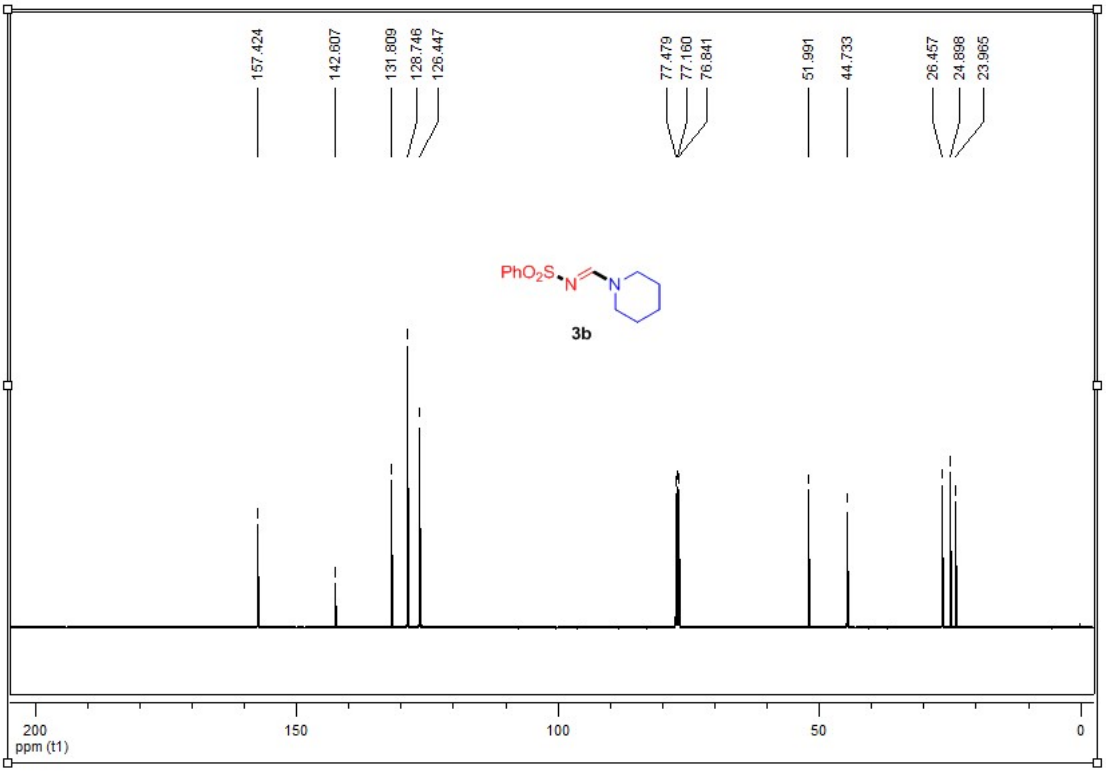
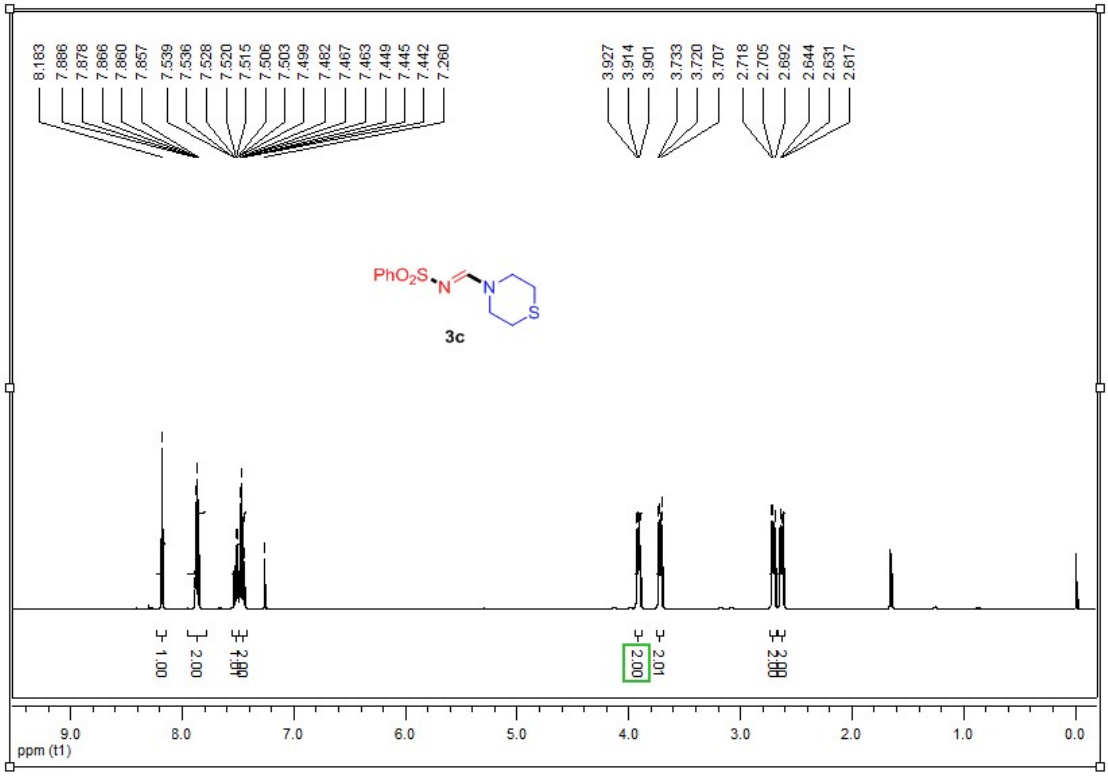
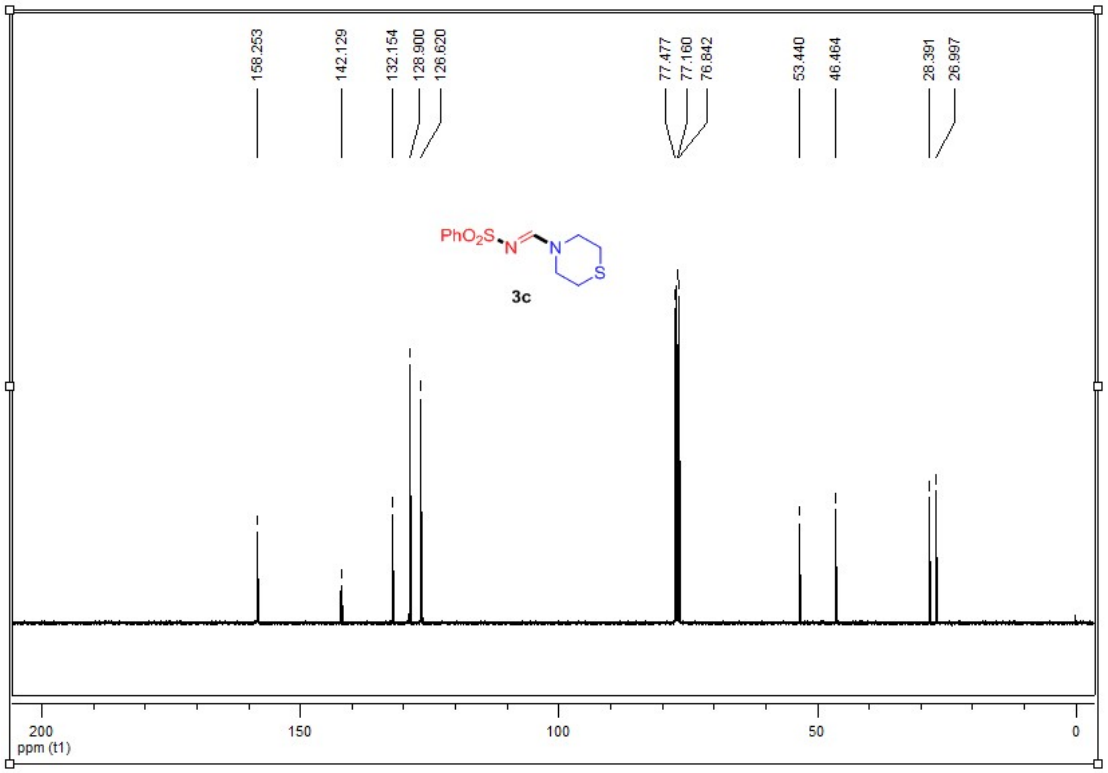
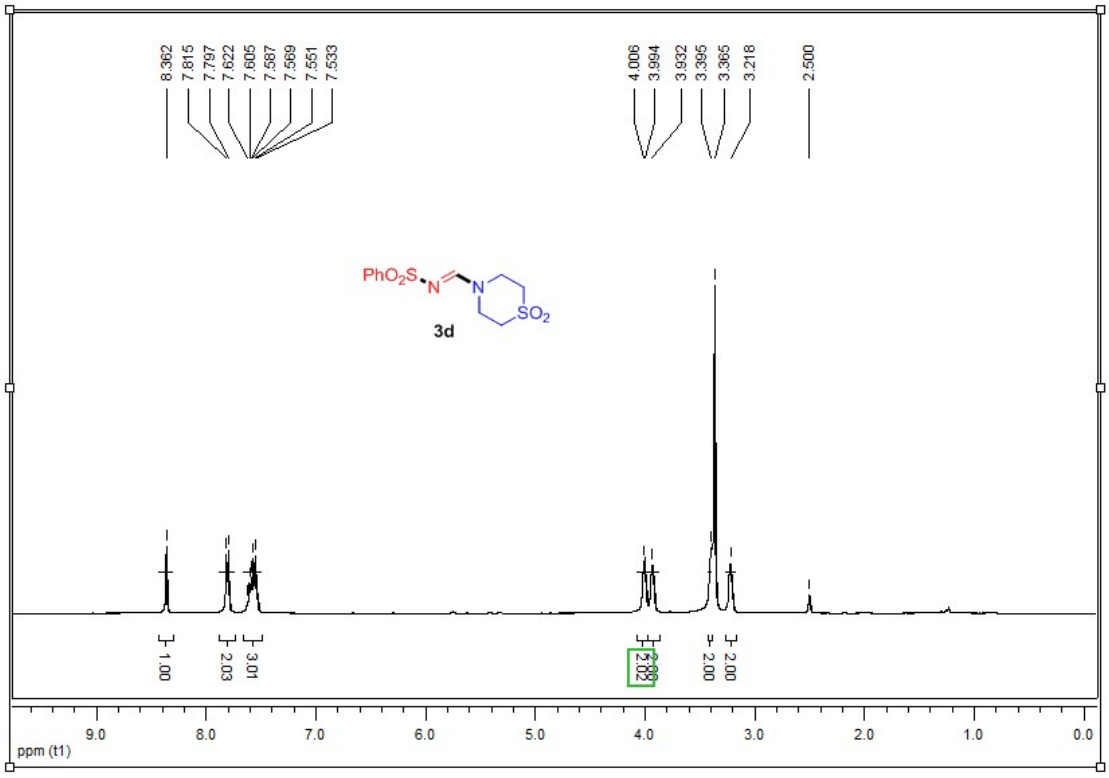
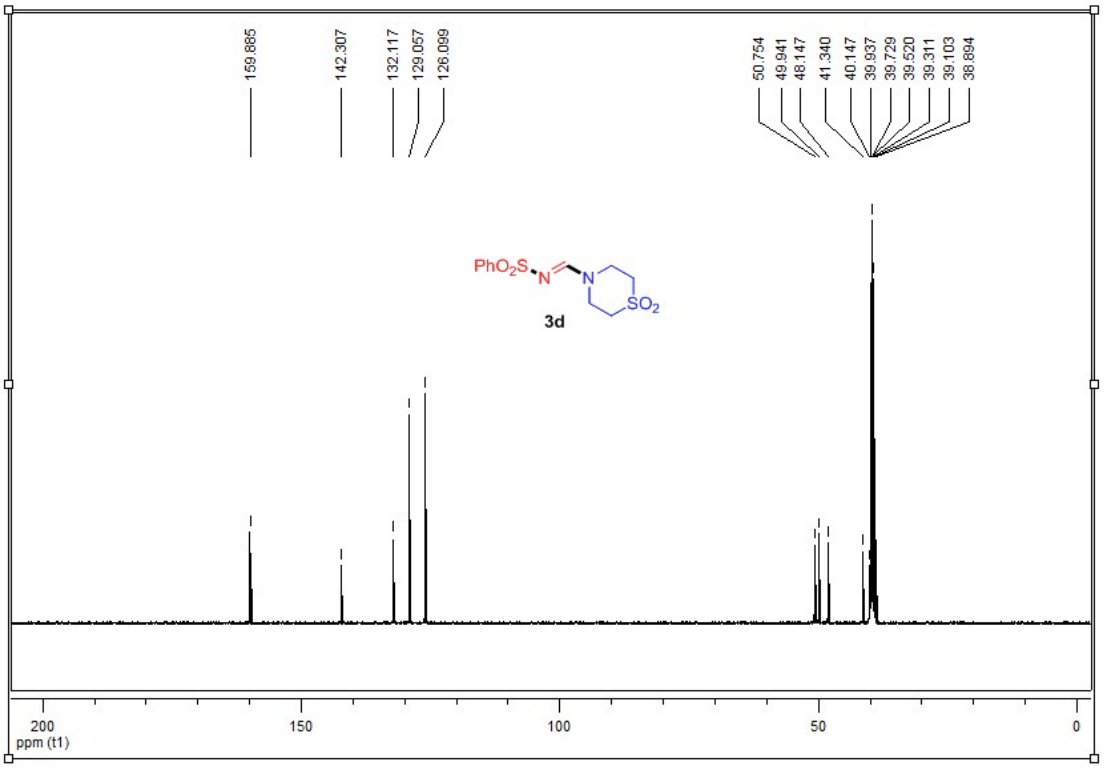
7.875
7.858
7.854
7.508
7.489
7.483
7.475
7.472
7.468
7.458
7.439
7.426
7.422
7.417
7.260
3.594
3.579
3.565
3.412
3.398
3.387
1.686
1.653
1.647
1.615
1.578
1.564
1.553
1.538
PhO2S
N
N
3b
1.00
2.00
3.01
2.01
2.02
4.03
2.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

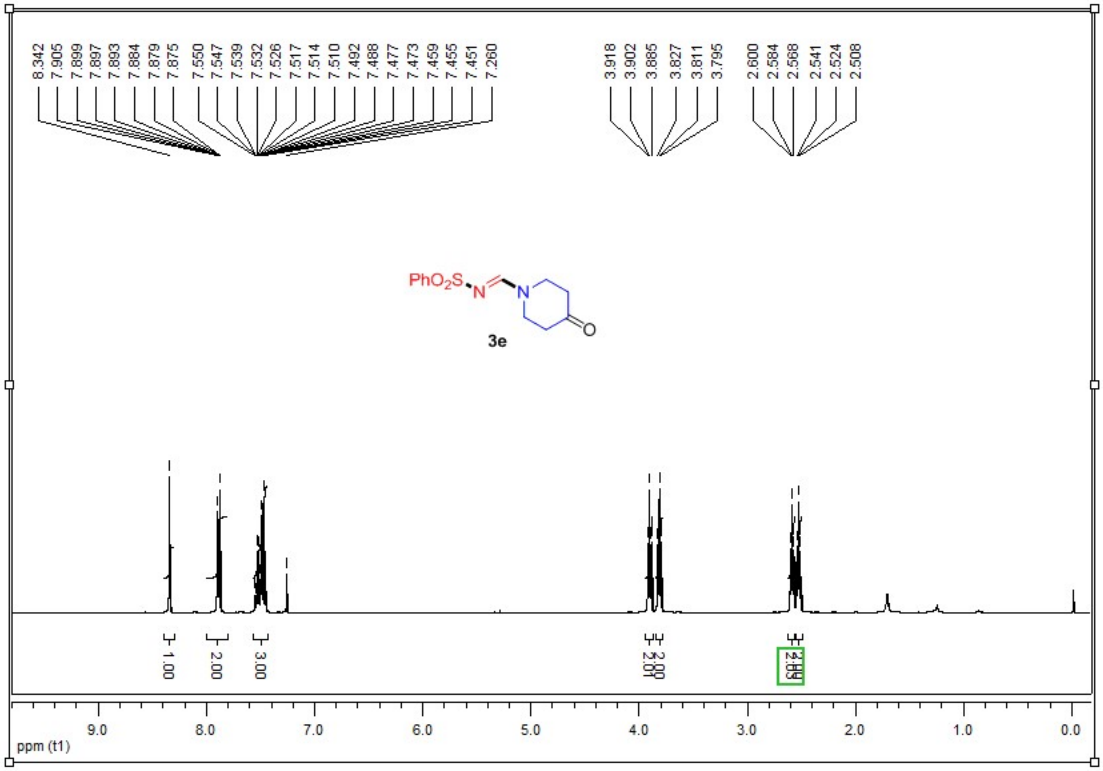

157.424
142.607
131.809
128.746
126.447
77.479
77.160
76.841
51.991
44.733
26.457
24.898
23.965
PhO2S
N
N
3b
200
150
100
50
0
ppm (t1)


8.183
7.886
7.878
7.866
7.860
7.857
7.539
7.536
7.528
7.520
7.515
7.506
7.503
7.499
7.482
7.467
7.463
7.449
7.445
7.442
7.260
3.927
3.914
3.901
3.733
3.720
3.707
2.718
2.705
2.692
2.644
2.631
2.617
PhO2S
N
N
S
3c
1.00
2.00
4.88
2.00
2.01
2.88
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


158.253
142.129
132.154
128.900
126.620
77.477
77.160
76.842
53.440
46.464
28.391
26.997
PhO2S
N
N
S
3c
200
150
100
50
0
ppm (t1)


8.362
7.815
7.797
7.622
7.605
7.587
7.569
7.551
7.533
4.006
3.994
3.932
3.395
3.365
3.218
2.500
PhO2S
N
N
SO2
3d
1.00
2.03
3.01
2.02
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


159.886
142.307
132.117
129.057
126.099
50.754
49.941
48.147
41.340
40.147
39.937
39.729
39.520
39.311
39.103
38.894
PhO2S
N
N
SO2
3d
200
150
100
50
0
ppm (t1)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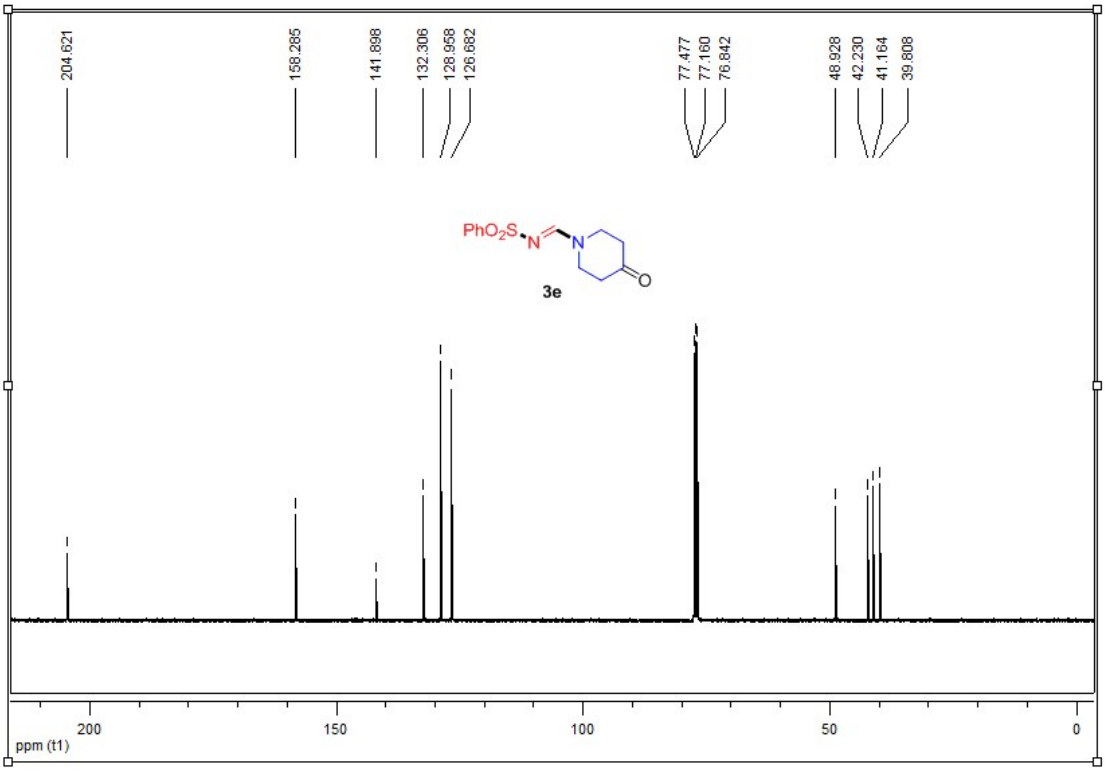
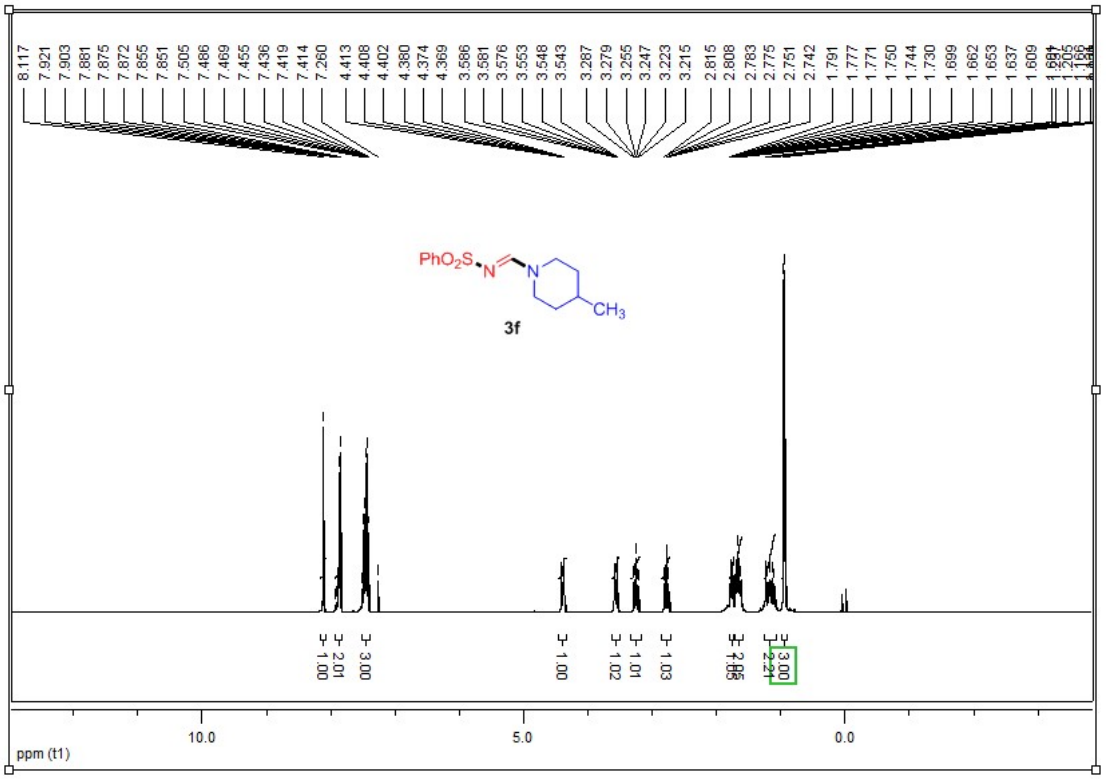
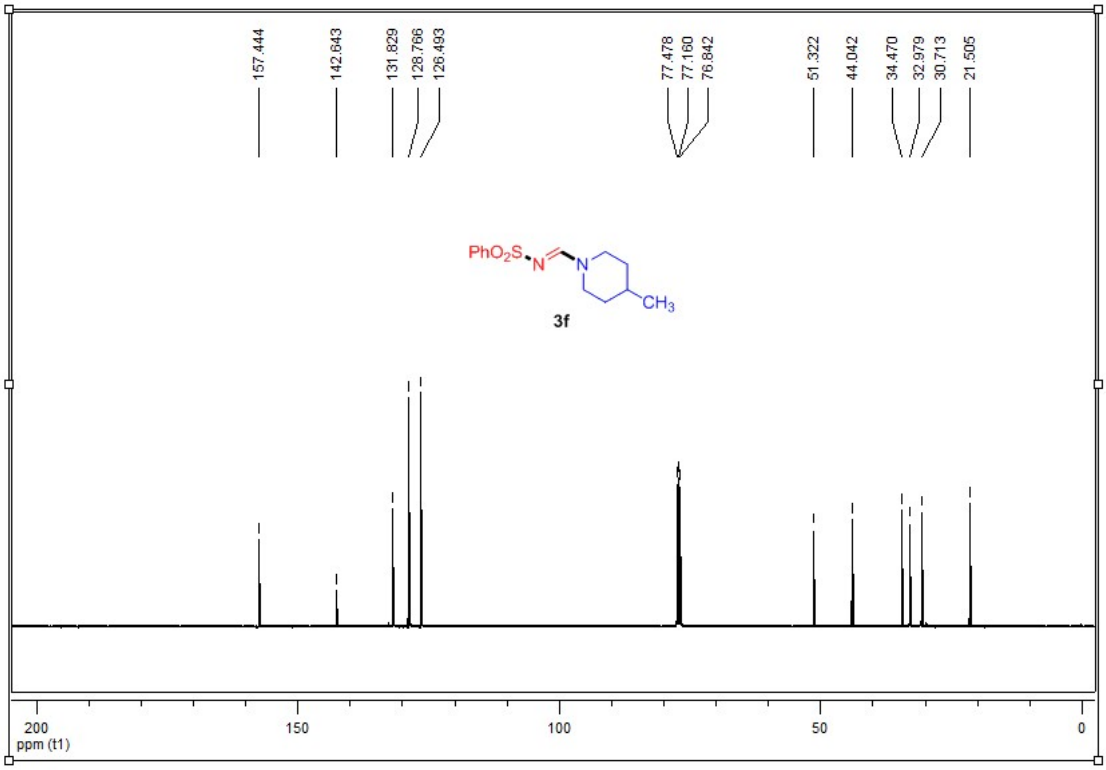
7.905
7.899
7.897
7.893
7.884
7.879
7.875
7.550
7.547
7.539
7.532
7.526
7.517
7.514
7.510
7.492
7.488
7.477
7.473
7.459
7.455
7.451
7.260
3.918
3.902
3.885
3.827
3.811
3.795
2.600
2.584
2.568
2.541
2.524
2.508
PhO2S
N
N
O
3e
1.00
2.00
3.00
2.00
2.89
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


204.621
158.285
141.898
132.306
128.958
126.682
77.477
77.160
76.842
48.928
42.230
41.164
39.808
PhO2S
N
N
O
3e
200
150
100
50
0
ppm (t1)


8.117
7.921
7.903
7.881
7.875
7.872
7.855
7.851
7.505
7.486
7.469
7.455
7.436
7.419
7.414
7.260
4.413
4.408
4.402
4.380
4.374
4.369
3.586
3.581
3.576
3.553
3.548
3.543
3.287
3.279
3.255
3.247
3.223
3.215
2.815
2.808
2.783
2.775
2.751
2.742
1.791
1.777
1.771
1.750
1.744
1.730
1.699
1.662
1.653
1.637
1.609
PhO2S
N
N
CH3
3f
1.00
2.01
3.00
1.00
1.02
1.01
1.03
2.06
2.24
3.00
10.0
5.0
0.0
ppm (t1)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77.478
77.160
76.842
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44.042
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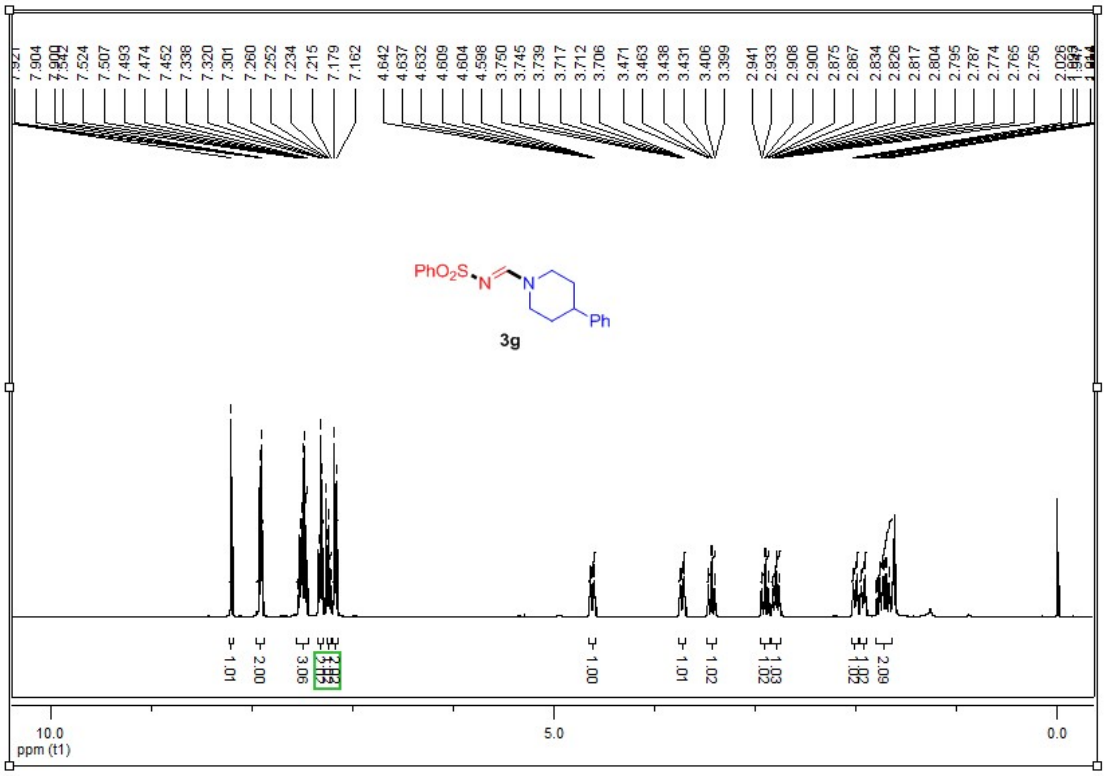
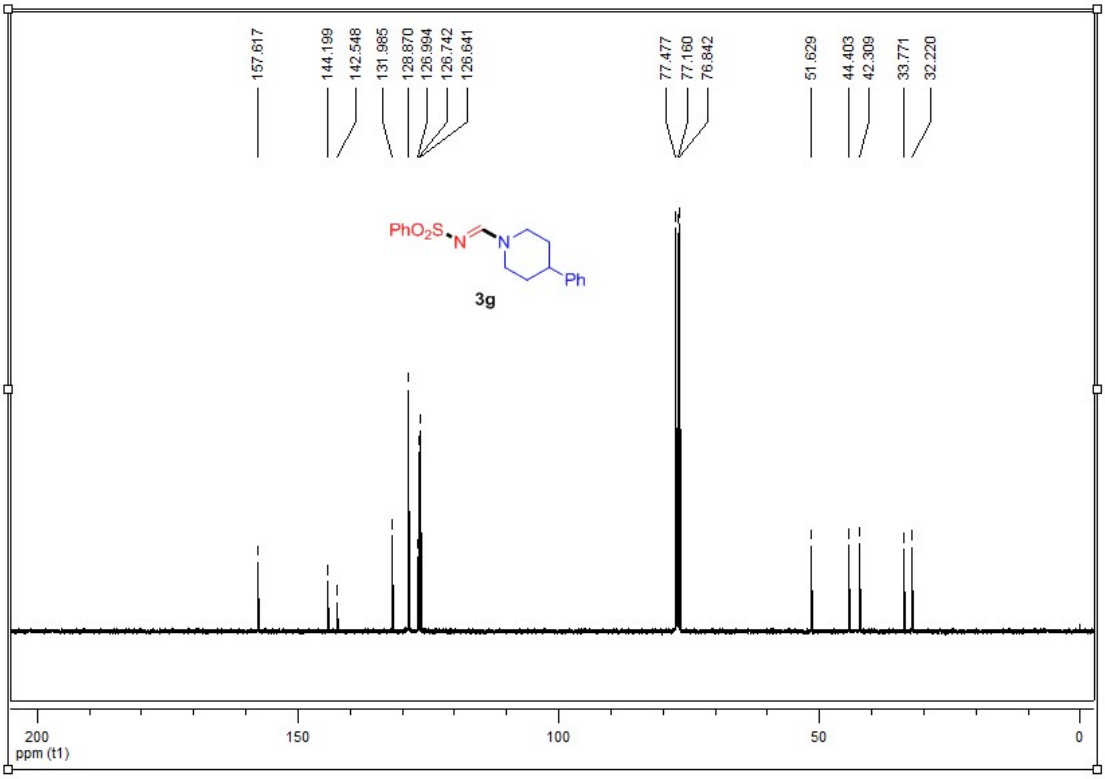
30.713
21.505
PhO2S
N
N
CH3
3f
200
150
100
50
0
ppm (t1)


7.921
7.904
7.524
7.507
7.493
7.474
7.452
7.338
7.320
7.301
7.260
7.252
7.234
7.215
7.179
7.162
4.642
4.637
4.632
4.609
4.604
4.598
3.750
3.745
3.739
3.717
3.712
3.706
3.471
3.463
3.438
3.431
3.406
3.399
2.941
2.933
2.908
2.900
2.875
2.867
2.834
2.826
2.817
2.804
2.795
2.787
2.774
2.765
2.756
PhO2S
N
N
Ph
3g
1.01
2.00
1.06
1.00
1.01
1.02
1.03
1.02
2.09
10.0
ppm (t1)
5.0
0.0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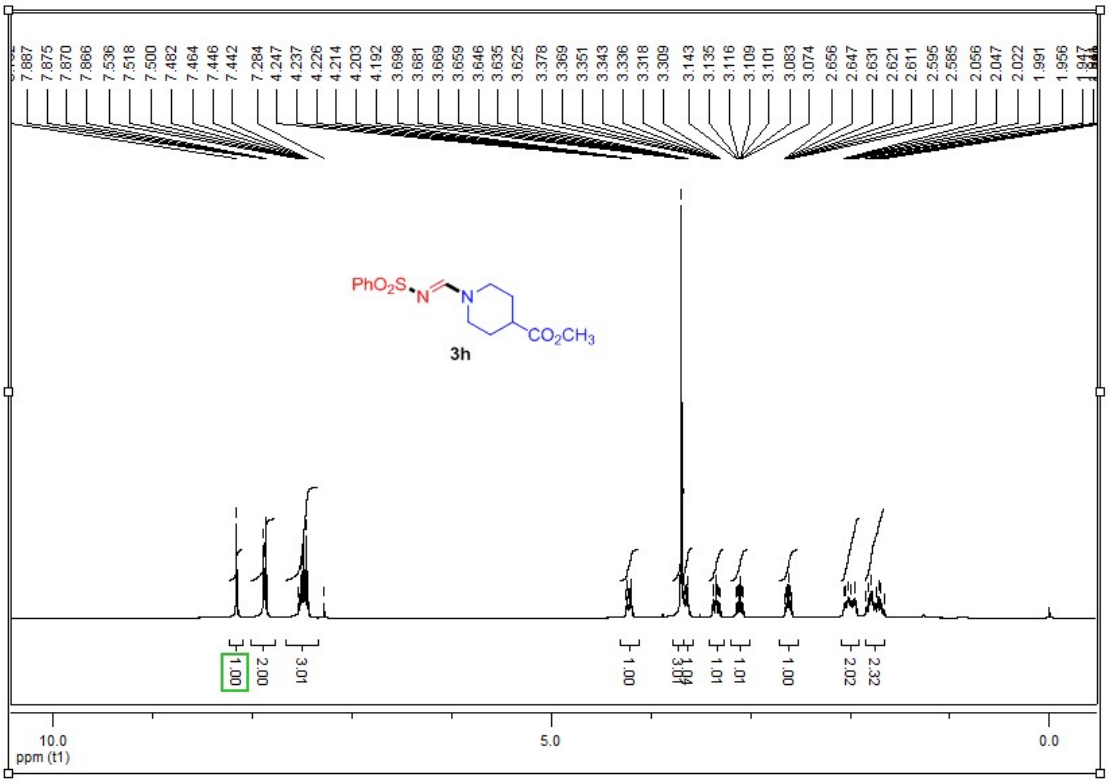
128.870
126.994
126.742
126.641
77.477
77.160
76.842
51.629
44.403
42.309
33.771
32.220
PhO2S
N
N
Ph
3g
200
ppm (t1)
150
100
50
0


7.887
7.875
7.870
7.866
7.536
7.518
7.500
7.482
7.464
7.446
7.442
7.284
4.247
4.237
4.226
4.214
4.203
4.192
3.698
3.681
3.669
3.659
3.646
3.635
3.625
3.378
3.369
3.351
3.343
3.336
3.318
3.309
3.143
3.135
3.116
3.109
3.101
3.083
3.074
2.656
2.647
2.631
2.621
2.611
2.595
2.585
2.056
2.047
2.022
1.991
1.956
PhO2S
N
N
CO2CH3
3h
1.00
2.00
3.01
1.00
1.01
1.01
1.00
2.02
2.32
10.0
ppm (t1)
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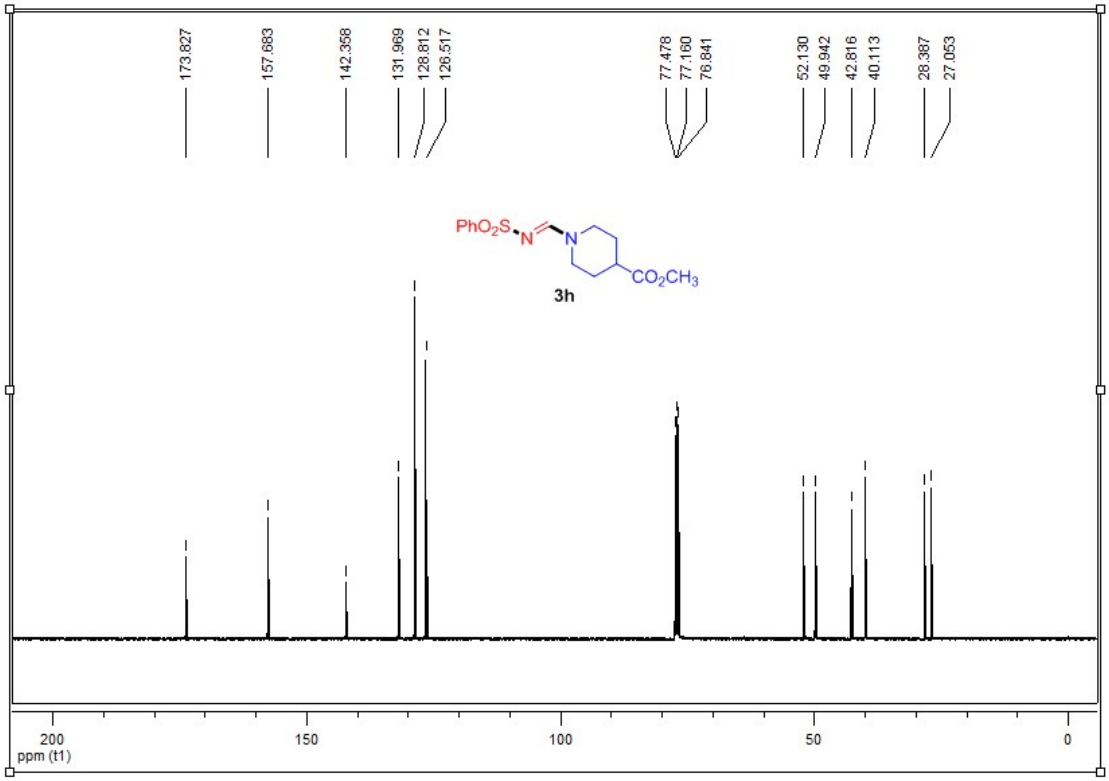
0.0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128.812
126.517
77.478
77.160
76.841
52.130
49.942
42.816
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28.387
27.053
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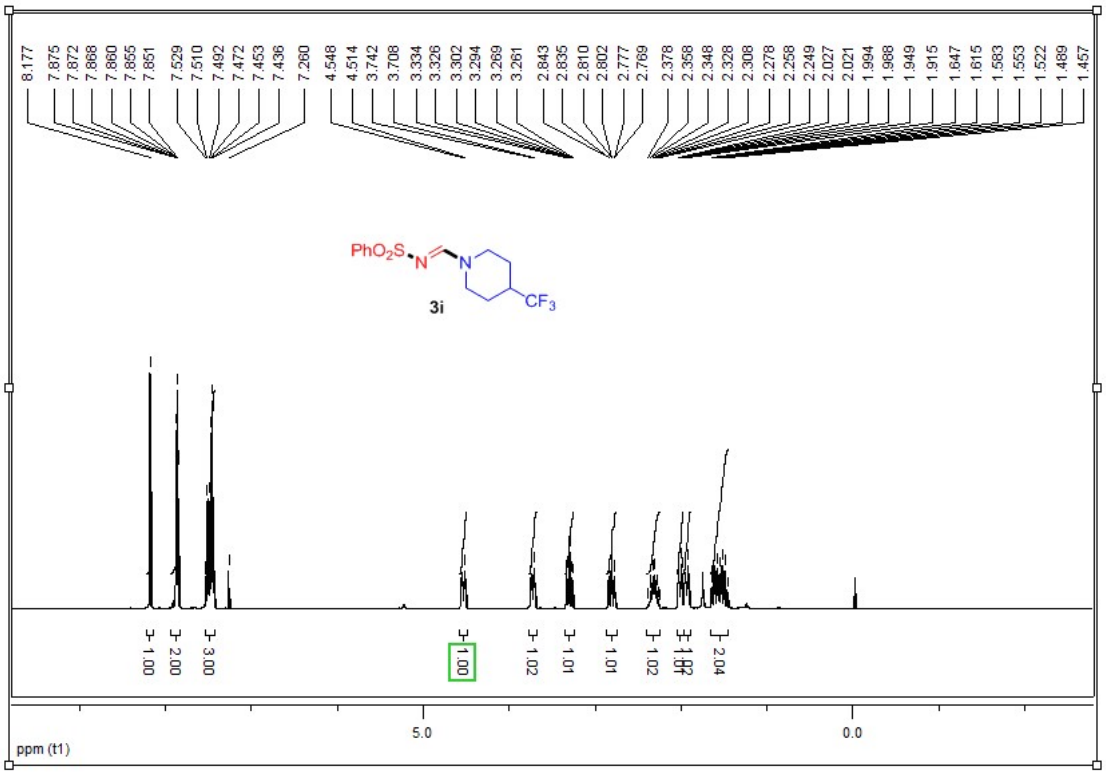
N
N
CO2CH3
3h
200
ppm (t1)
150
100
50
0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7.851
7.529
7.510
7.492
7.472
7.453
7.436
7.260
4.548
4.514
3.742
3.708
3.334
3.326
3.302
3.294
3.269
3.261
2.843
2.835
2.810
2.802
2.777
2.769
2.378
2.358
2.348
2.328
2.308
2.278
2.258
2.249
2.027
2.021
1.994
1.988
1.949
1.915
1.647
1.615
1.583
1.553
1.522
1.489
1.457
PhO2S
N
N
CF3
3i
3.00
2.00
3.00
1.00
1.02
1.01
1.01
1.02
1.82
2.04
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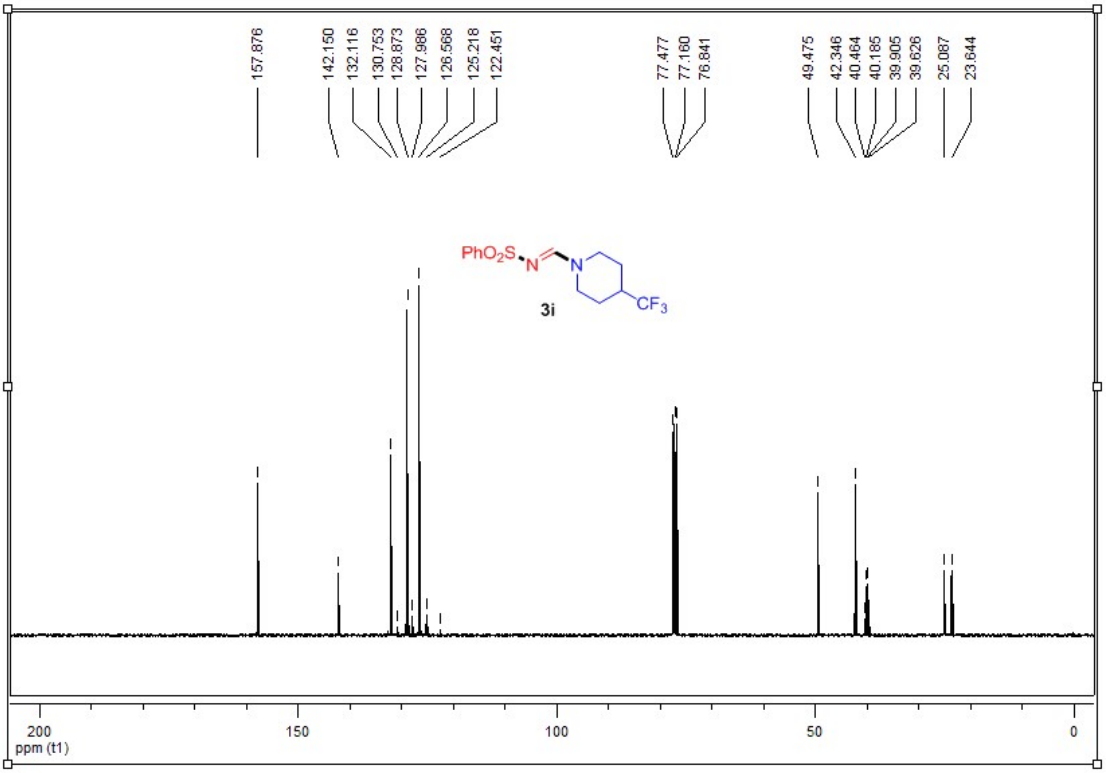
0.0
ppm (t1)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125.218
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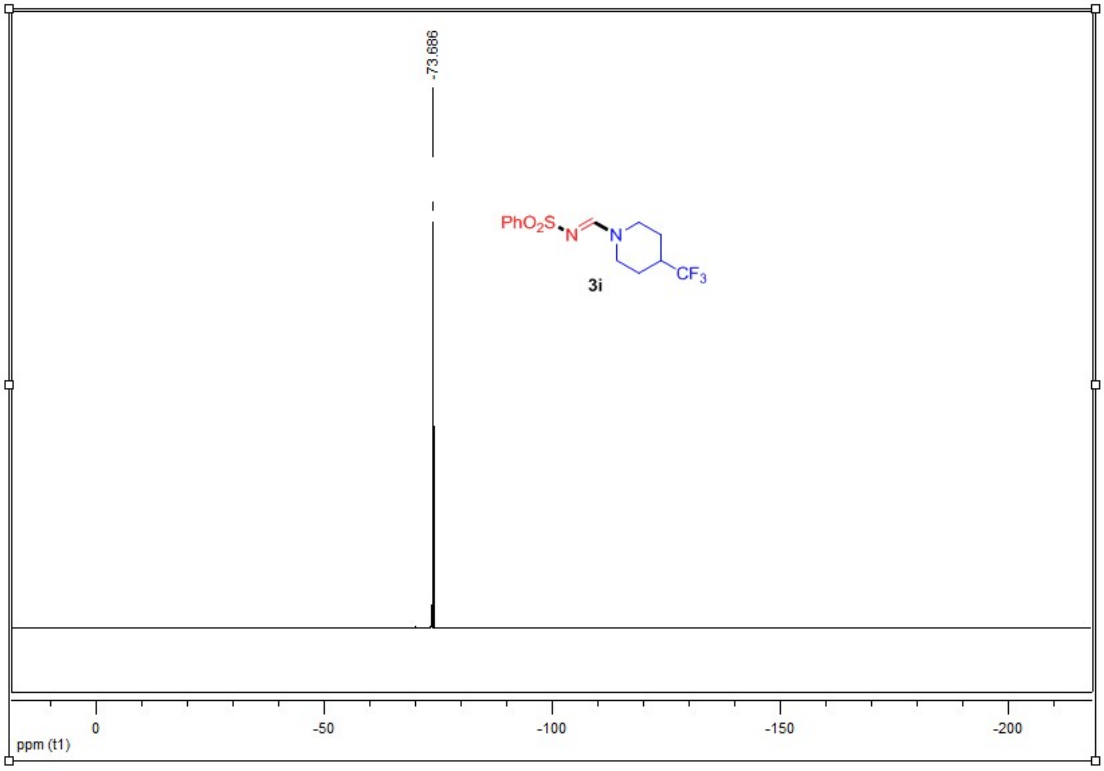
77.477
77.160
76.841
49.475
42.346
40.464
40.185
39.905
39.626
25.087
23.644
PhO2S
N
N
CF3
3i
200
150
100
50
0
ppm (t1)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N
CF3
3i
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-50
-100
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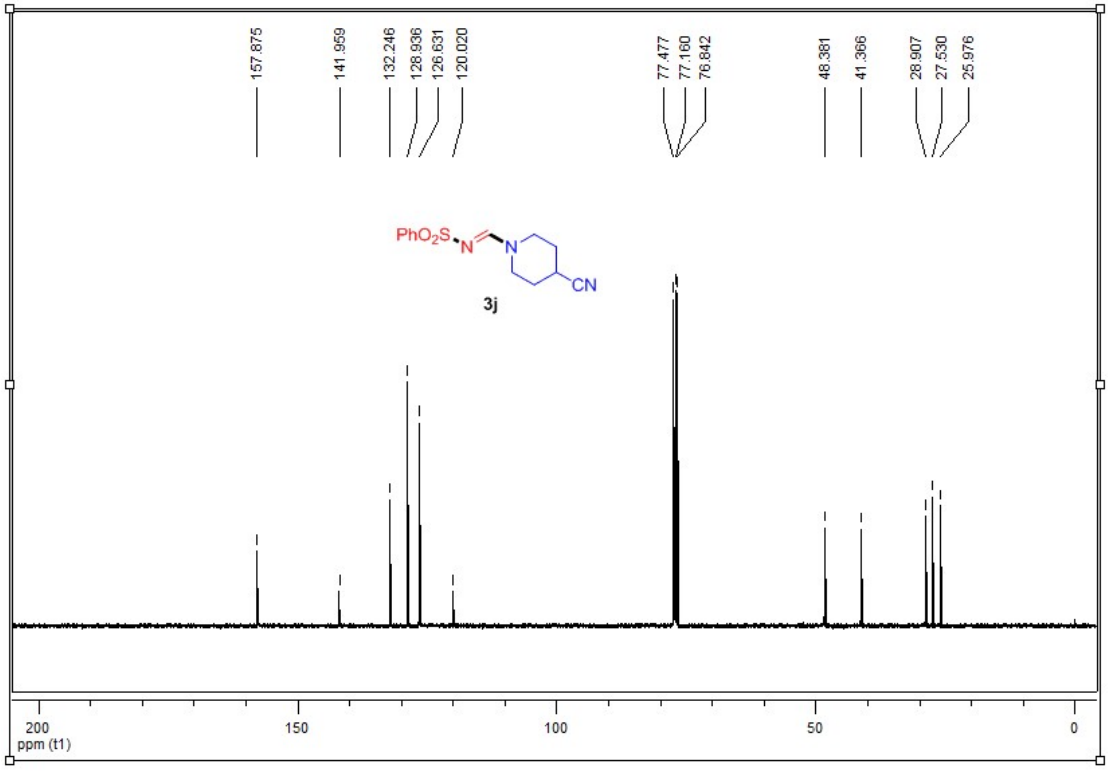
-200
ppm (t1)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77.160
76.842
48.381
41.366
28.907
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25.976
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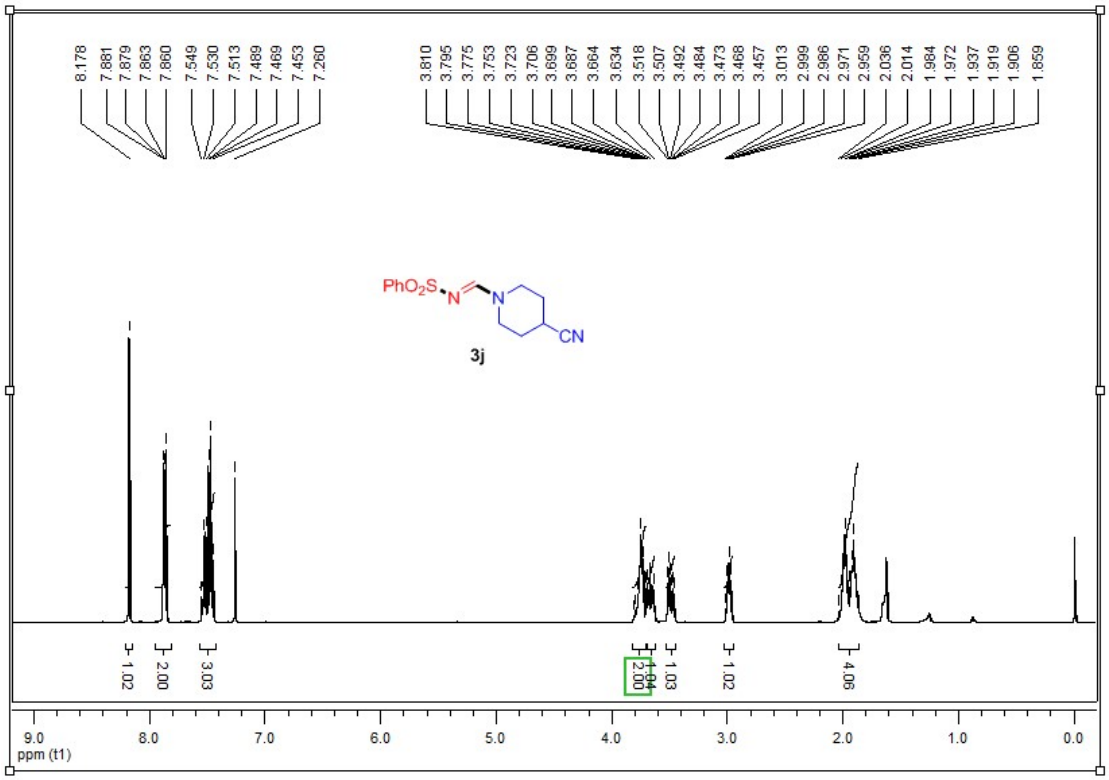
N
N
CN
3j
200
150
100
50
0
ppm (t1)


8.178
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7.860
7.549
7.530
7.513
7.489
7.469
7.453
7.260
3.810
3.795
3.775
3.753
3.723
3.706
3.699
3.687
3.664
3.634
3.518
3.507
3.492
3.484
3.473
3.468
3.457
3.013
2.999
2.986
2.971
2.959
2.036
2.014
1.984
1.972
1.937
1.919
1.906
1.859
PhO2S
N
N
CN
3j
1.02
2.00
3.03
2.00
1.03
1.02
4.06
9.0
8.0
7.0
6.0
5.0
4.0
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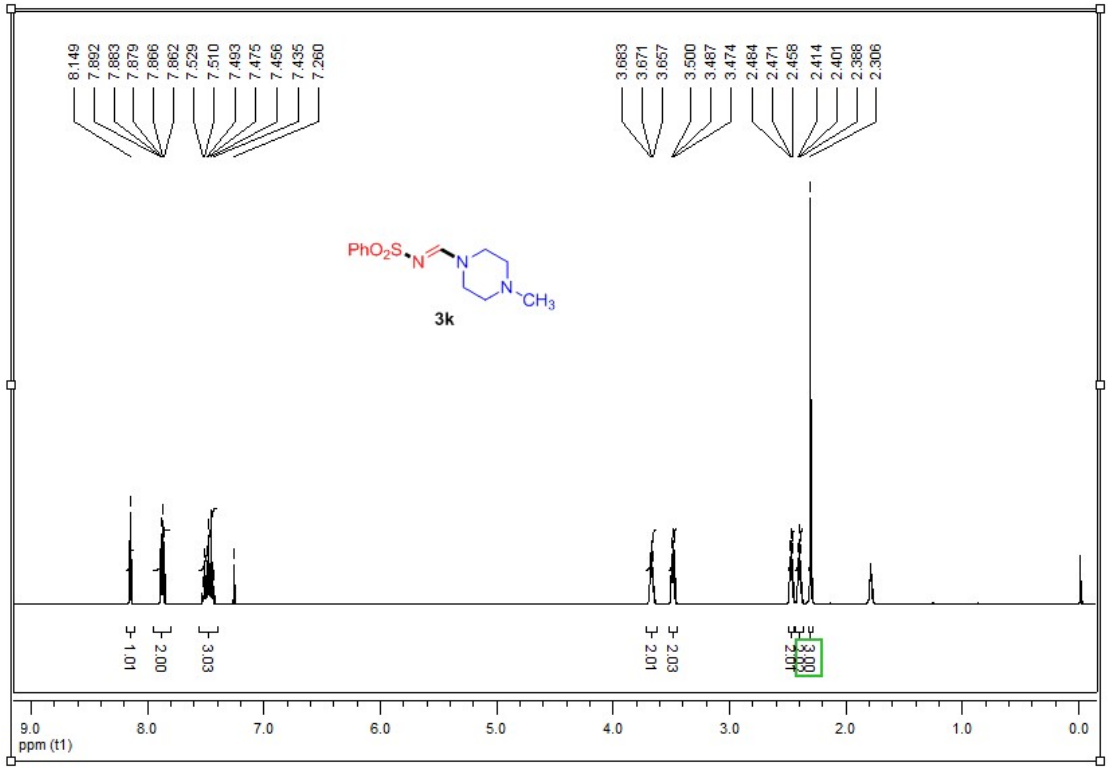
2.0
1.0
0.0
ppm (t1)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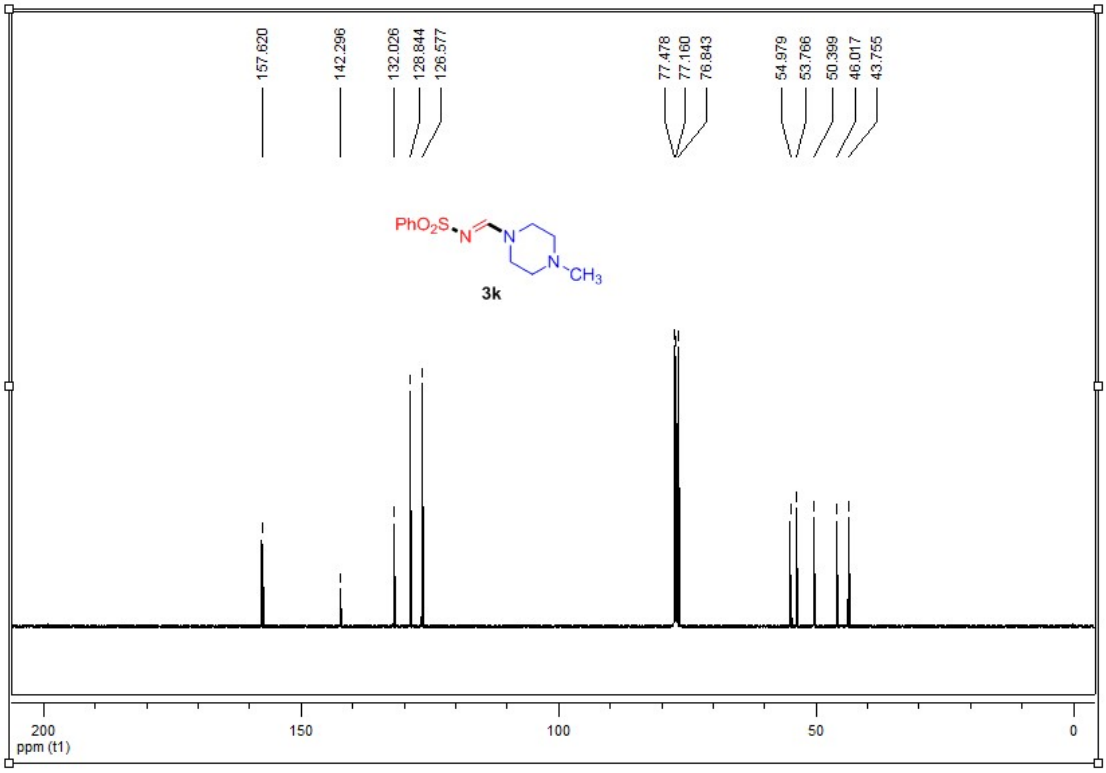
7.529
7.510
7.493
7.475
7.456
7.435
7.260
3.683
3.671
3.657
3.500
3.487
3.474
2.484
2.471
2.458
2.414
2.401
2.388
2.306
PhO2S
N
N
N
CH3
3k
1.01
2.00
3.03
2.01
2.03
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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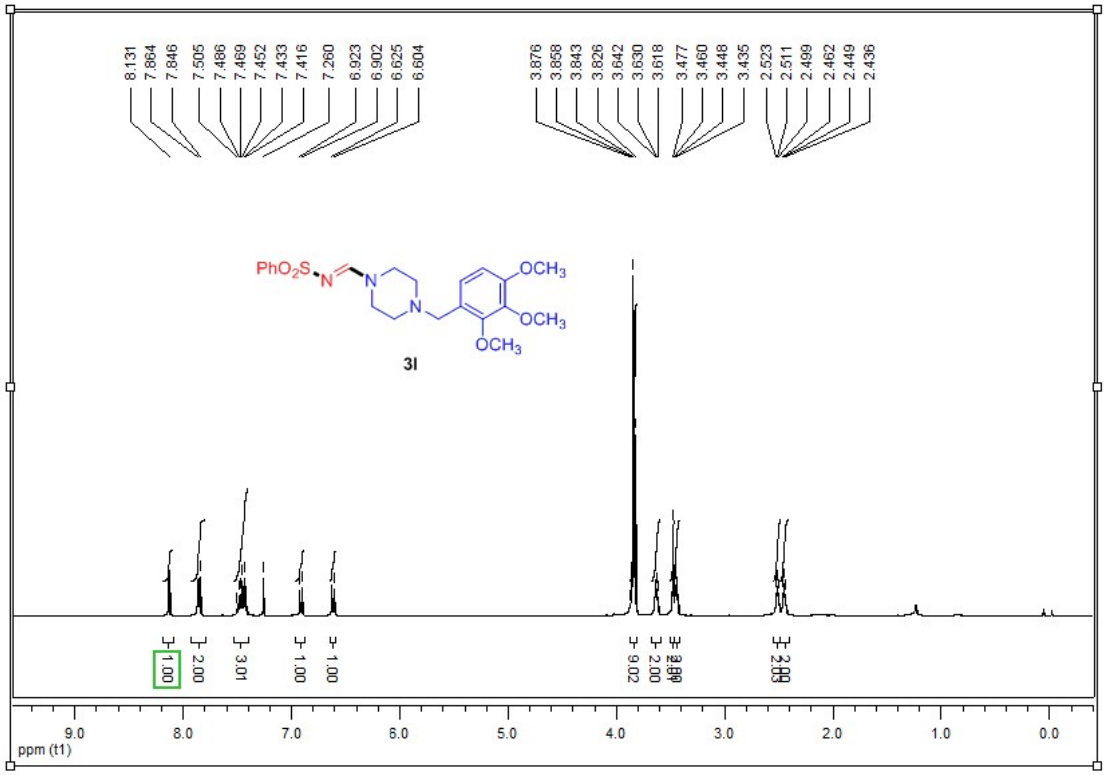
142.296
132.026
128.844
126.577
77.478
77.160
76.843
54.979
53.766
50.399
46.017
43.755
PhO2S
N
N
N
CH3
3k
200
150
100
50
0
ppm (t1)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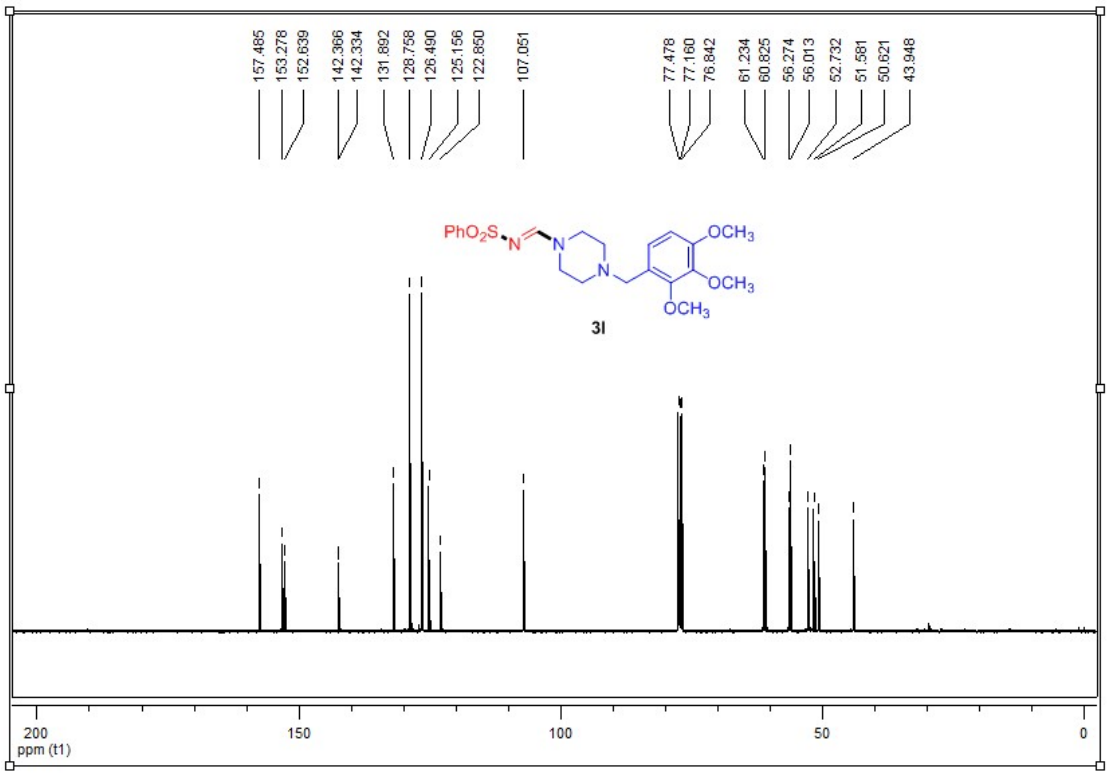
7.864
7.846
7.505
7.486
7.469
7.452
7.433
7.416
7.260
6.923
6.902
6.625
6.604
3.876
3.858
3.843
3.826
3.642
3.630
3.618
3.477
3.460
3.448
3.435
2.523
2.511
2.499
2.462
2.449
2.436
PhO2S
N
N
N
OCH3
OCH3
OCH3
3l
1.00
2.00
3.01
1.00
1.00
9.02
2.00
3.89
2.89
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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153.278
152.639
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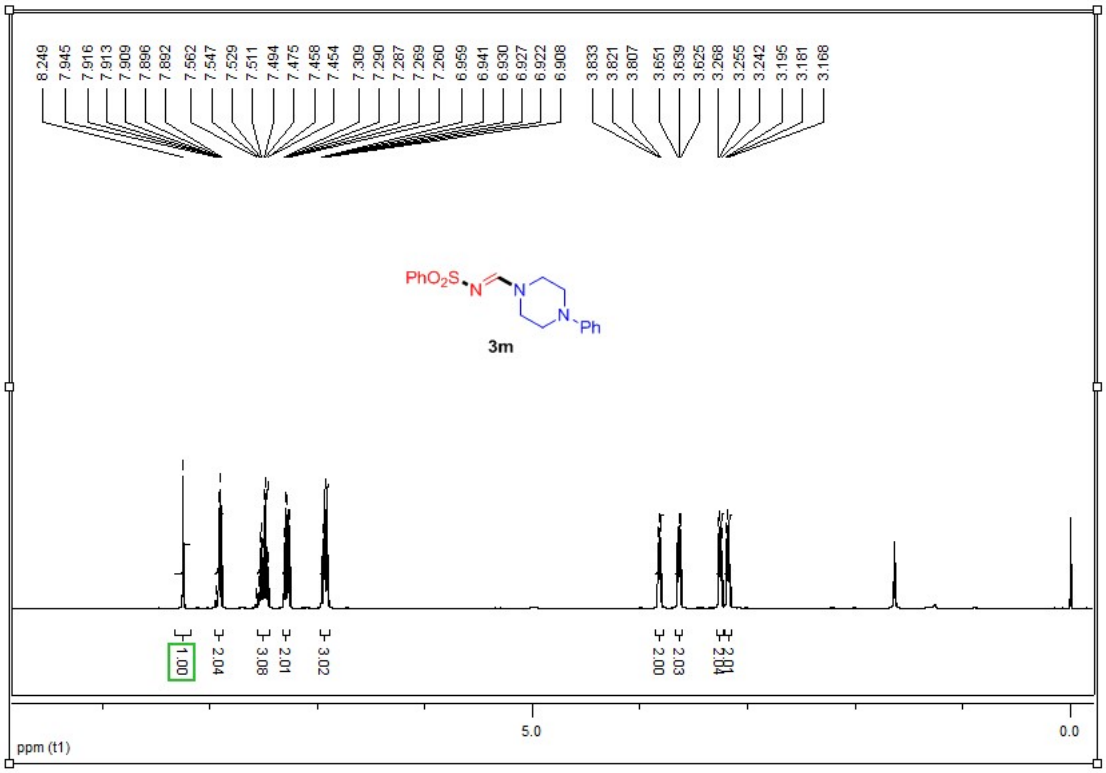
142.334
131.892
128.758
126.490
125.156
122.850
107.051
77.478
77.160
76.842
61.234
60.825
56.274
56.013
52.732
51.581
50.621
43.948
PhO2S
N
N
N
OCH3
OCH3
OCH3
3l
200
150
100
50
0
ppm (t1)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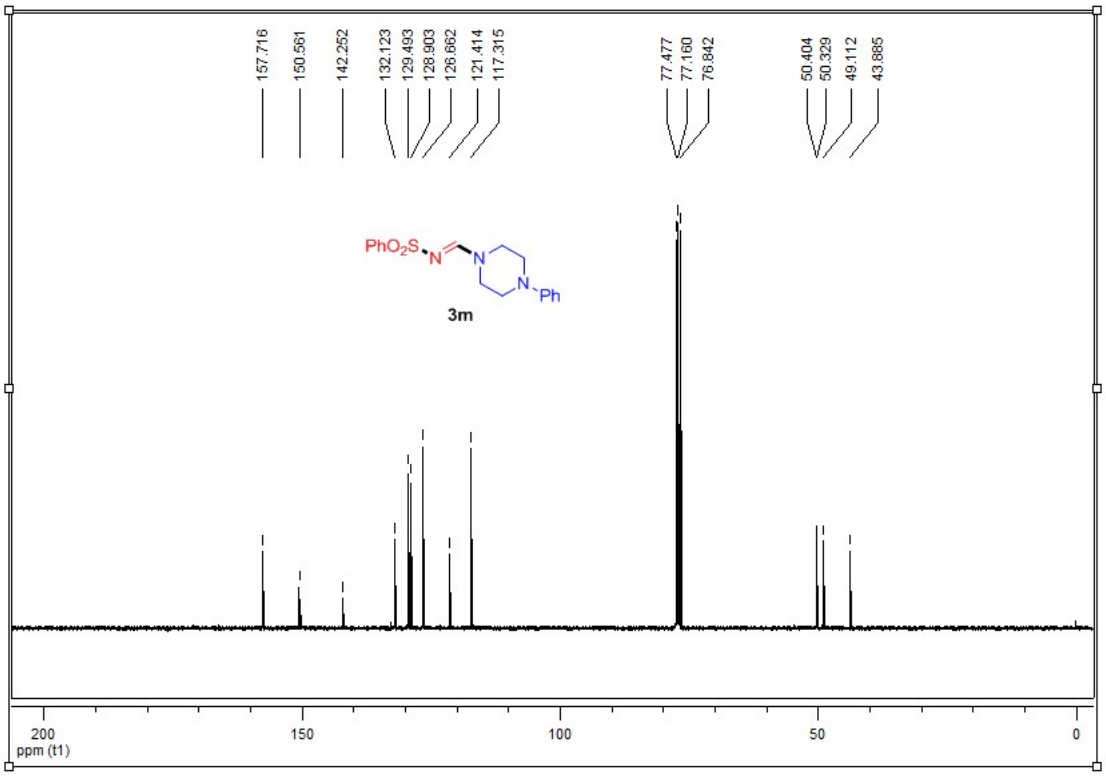
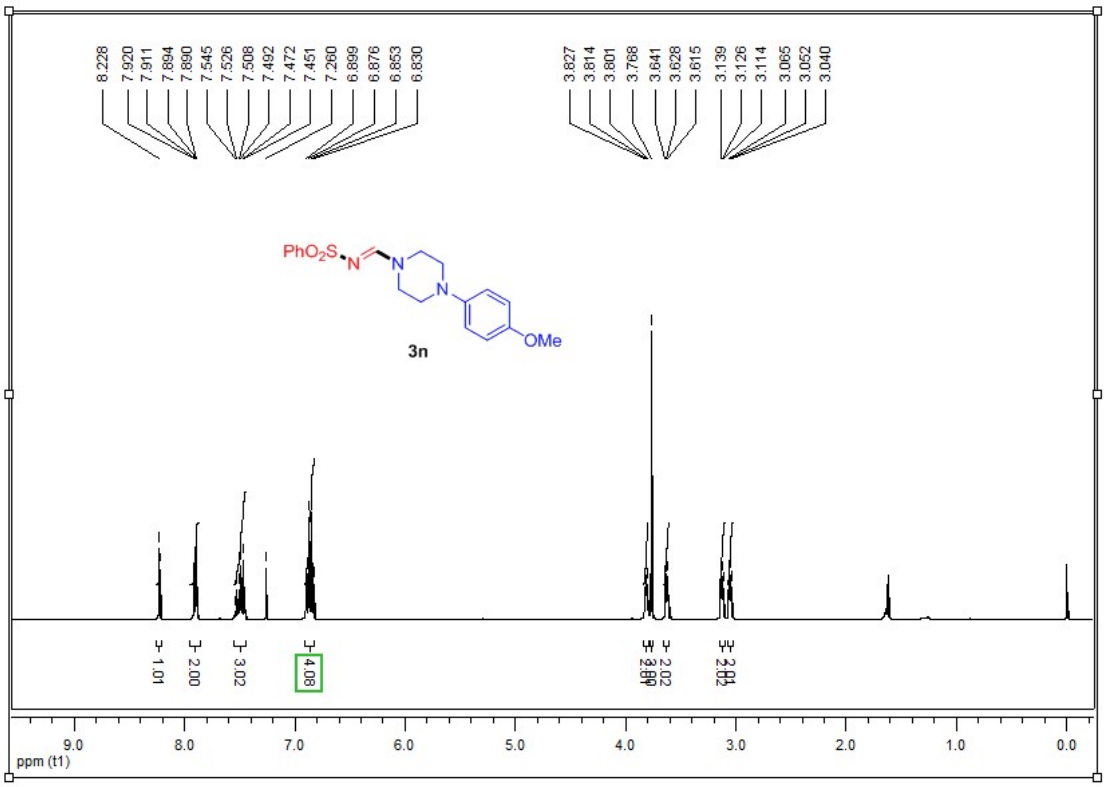
7.945
7.916
7.913
7.909
7.896
7.892
7.562
7.547
7.529
7.511
7.494
7.475
7.458
7.454
7.309
7.290
7.287
7.269
7.260
6.959
6.941
6.930
6.927
6.922
6.908
3.833
3.821
3.807
3.651
3.639
3.625
3.268
3.255
3.242
3.195
3.181
3.168
PhO2S
N
N
N
Ph
3m
1.00
2.04
3.08
2.01
3.02
2.00
2.03
2.01
5.0
0.0
ppm (t1)


157.716
150.561
142.252
132.123
129.493
128.903
126.662
121.414
117.315
77.477
77.160
76.842
50.404
50.329
49.112
43.885
PhO2S
N
N
N
Ph
3m
200
150
100
50
0
ppm (t1)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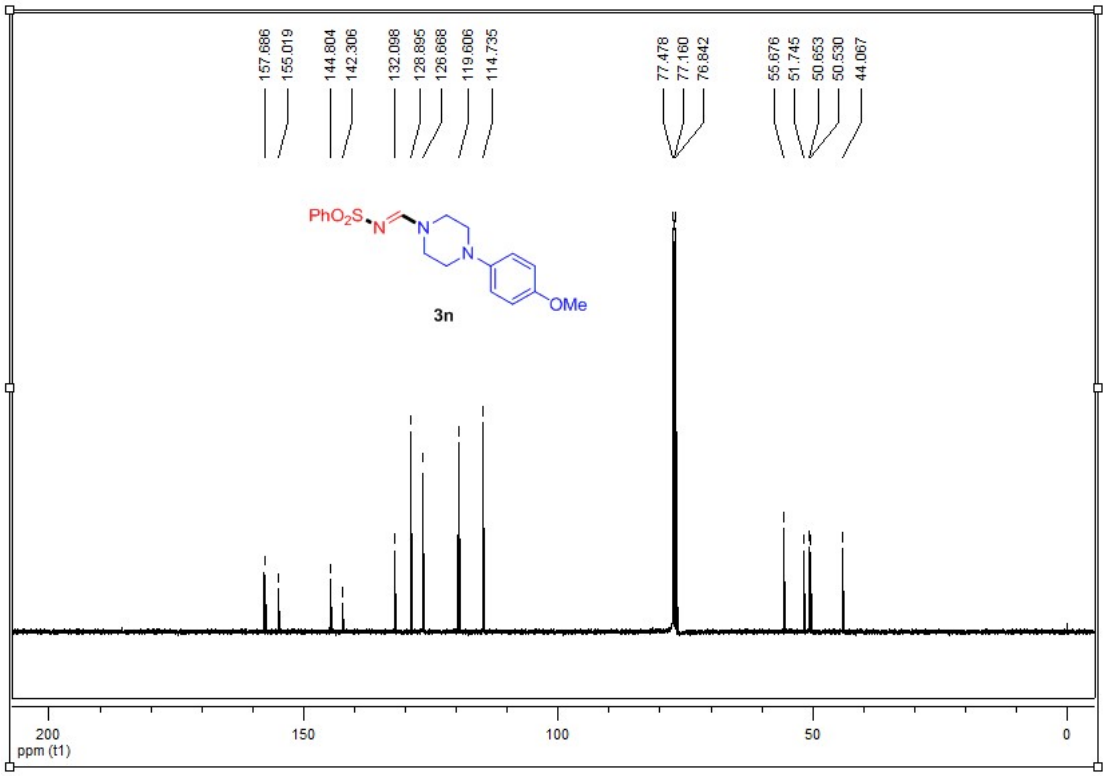
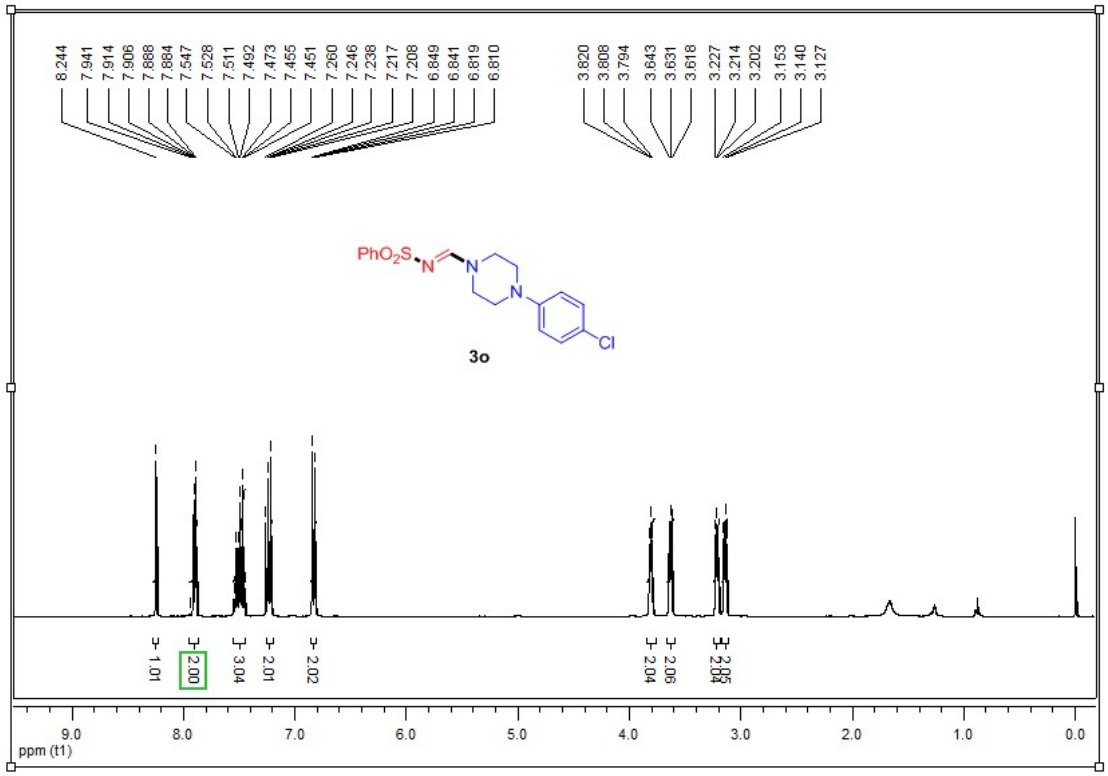
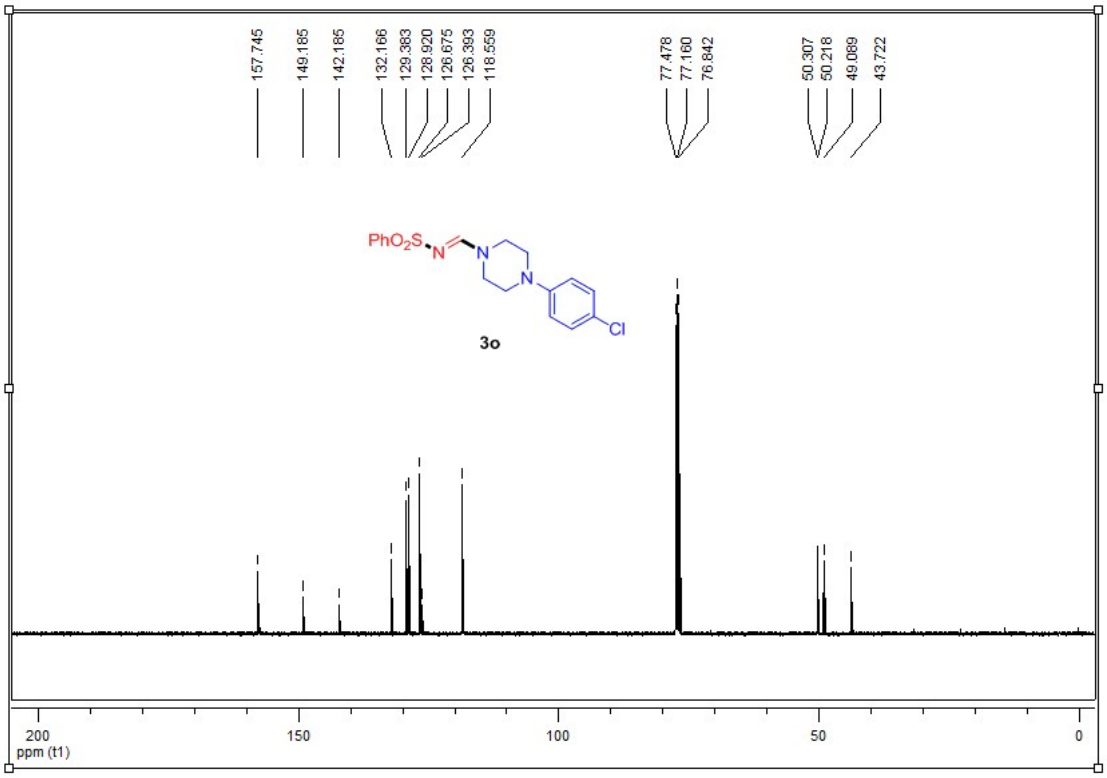
7.920
7.911
7.894
7.890
7.545
7.526
7.508
7.492
7.472
7.451
7.260
6.899
6.876
6.853
6.830
3.827
3.814
3.801
3.768
3.641
3.628
3.615
3.139
3.126
3.114
3.065
3.052
3.040
PhO2S
N
N
N
OMe
3n
1.01
2.00
3.02
4.08
2.02
2.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


157.686
155.019
144.804
142.306
132.098
128.895
126.668
119.606
114.735
77.478
77.160
76.842
55.676
51.745
50.653
50.530
44.067
PhO2S
N
N
N
OMe
3n
200
150
100
50
0
ppm (t1)


8.244
7.941
7.914
7.906
7.888
7.884
7.547
7.528
7.511
7.492
7.473
7.455
7.451
7.260
7.246
7.238
7.217
7.208
6.849
6.841
6.819
6.810
3.820
3.808
3.794
3.643
3.631
3.618
3.227
3.214
3.202
3.153
3.140
3.127
PhO2S
N
N
N
Cl
3o
1.01
2.00
3.04
2.01
2.02
2.04
2.06
2.05
2.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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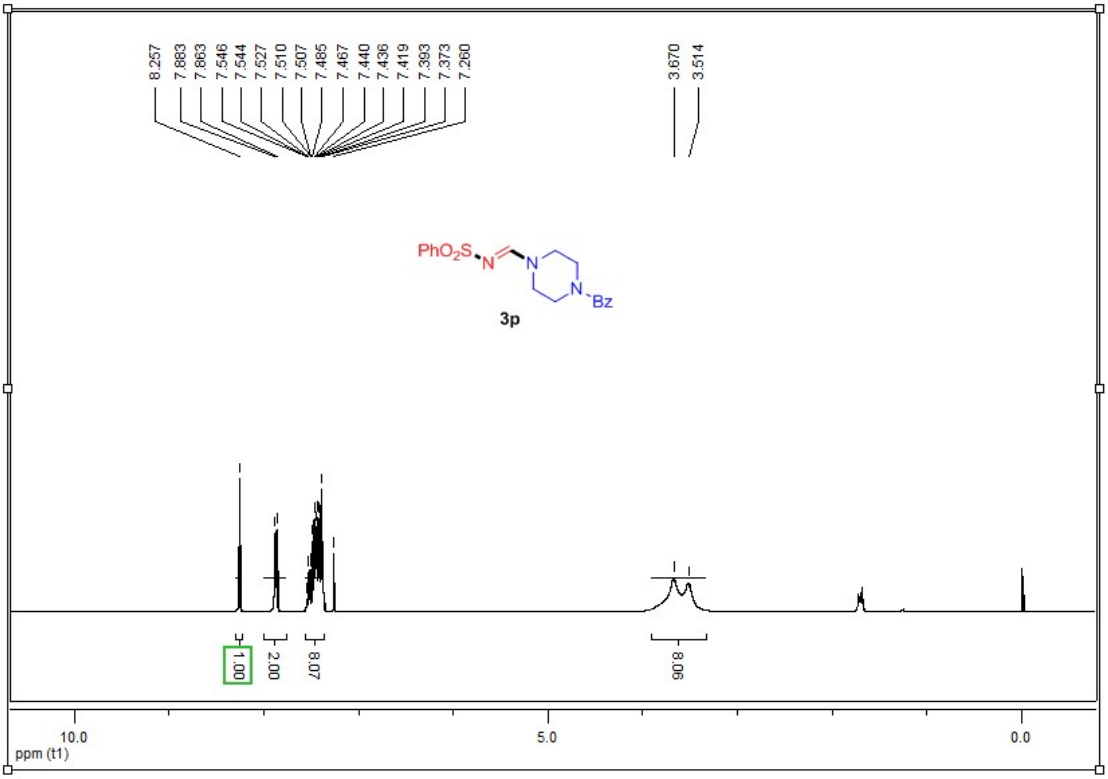
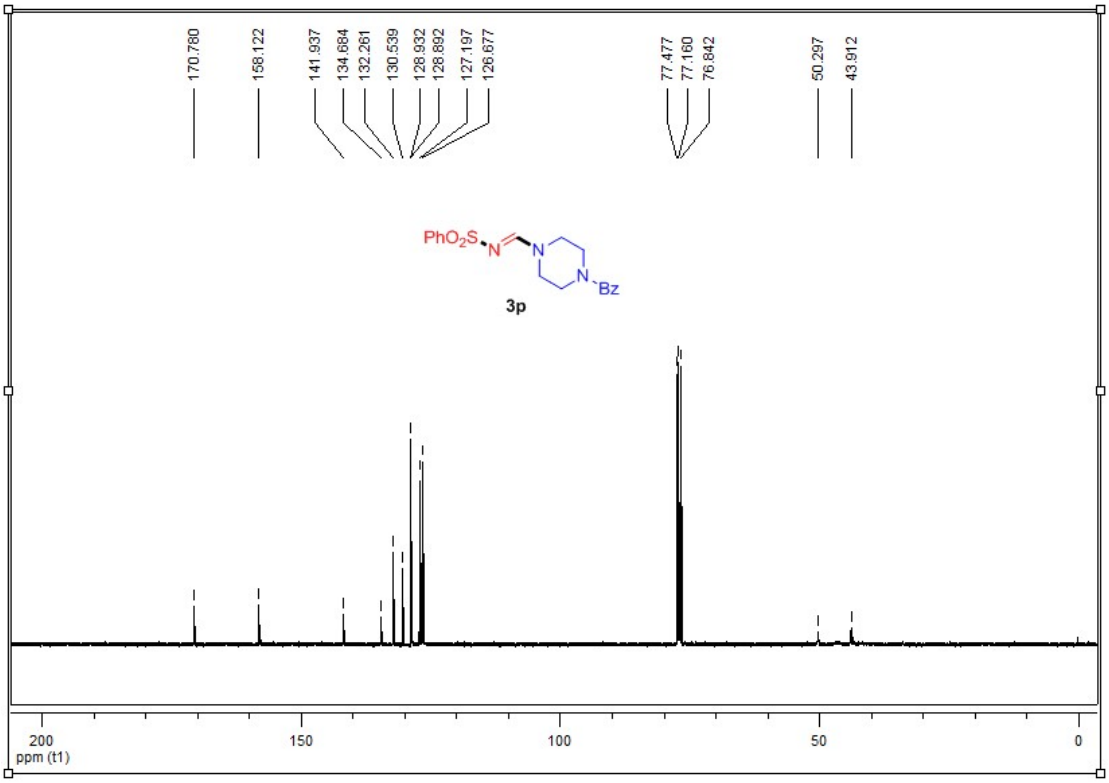
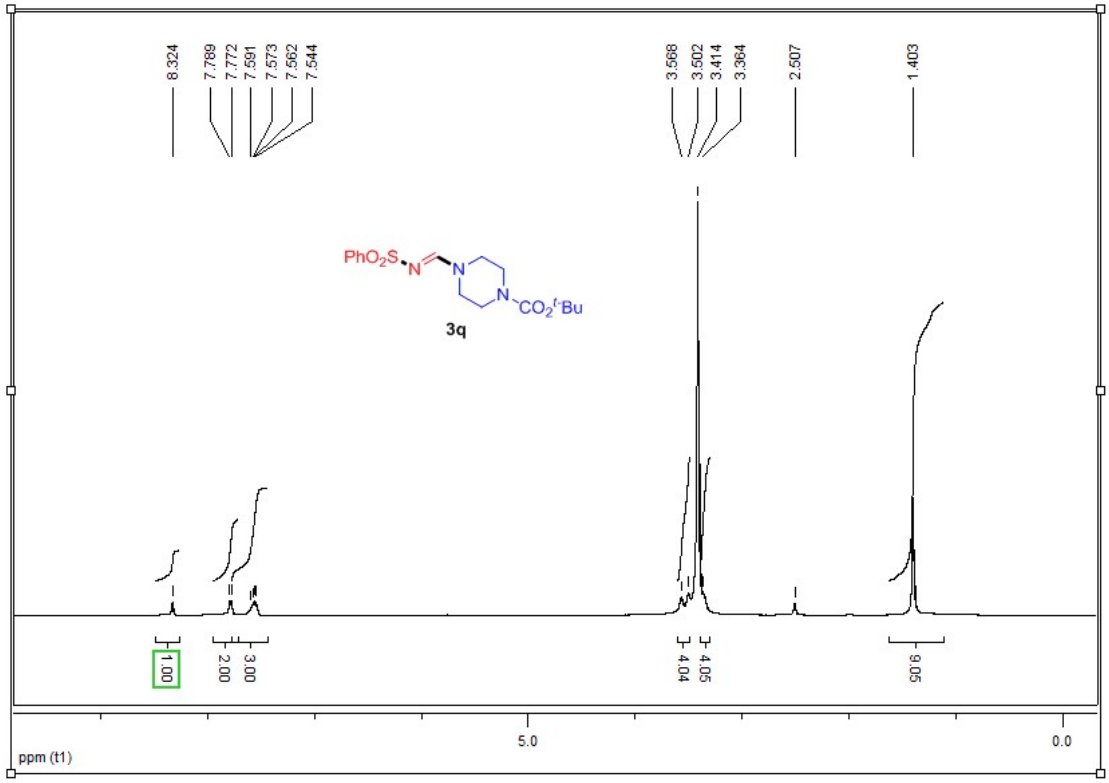
149.185
142.185
132.166
129.363
128.920
126.675
126.393
118.559
77.478
77.160
76.842
50.307
50.218
49.089
43.722
PhO2S
N
N
N
Cl
3o
200
150
100
50
0
ppm (t1)


8.257
7.883
7.863
7.546
7.544
7.527
7.510
7.507
7.485
7.467
7.440
7.436
7.419
7.393
7.373
7.260
3.670
3.514
PhO2S
N
N
N
Bz
3p
1.00
2.00
8.07
8.06
10.0
5.0
0.0
ppm (t1)


170.780
158.122
141.937
134.684
132.261
130.539
128.932
128.892
127.197
126.677
77.477
77.160
76.842
50.297
43.912
PhO2S
N
N
N
Bz
3p
200
150
100
50
0
ppm (t1)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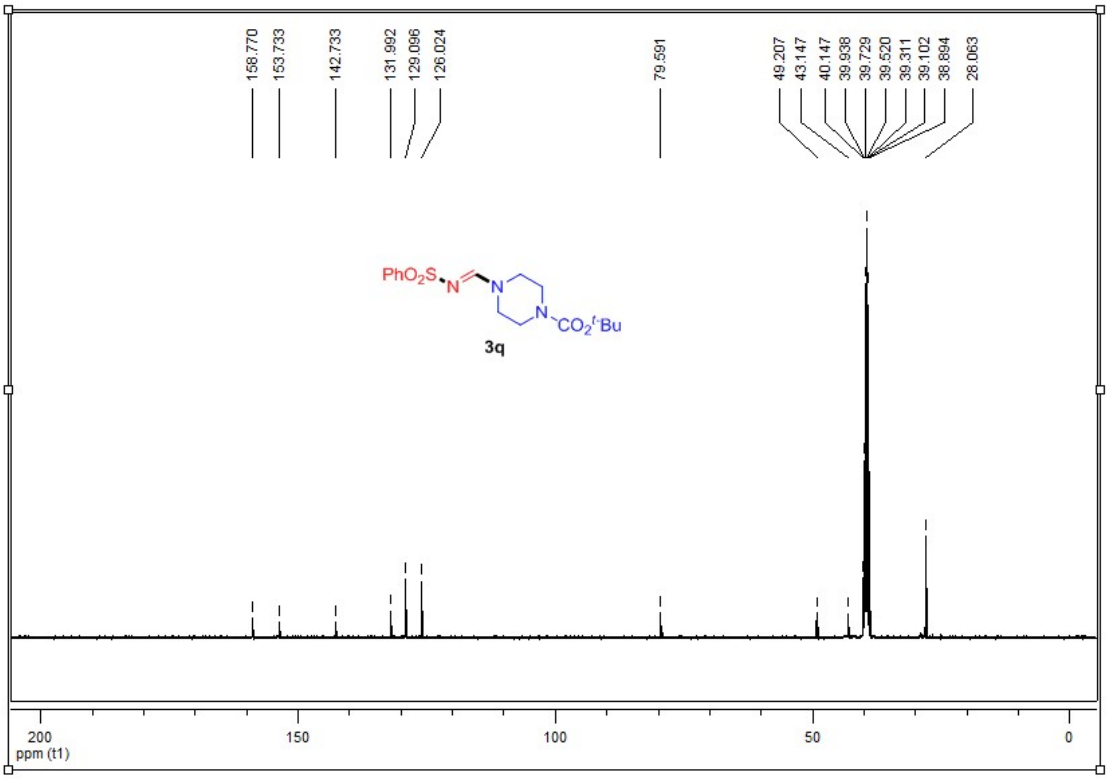
7.789
7.772
7.591
7.573
7.562
7.544
3.568
3.502
3.414
3.364
2.507
1.403
PhO2S
N
N
N
CO2tBu
3q
1.00
2.00
3.00
4.04
4.05
9.06
5.0
0.0
ppm (t1)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153.733
142.733
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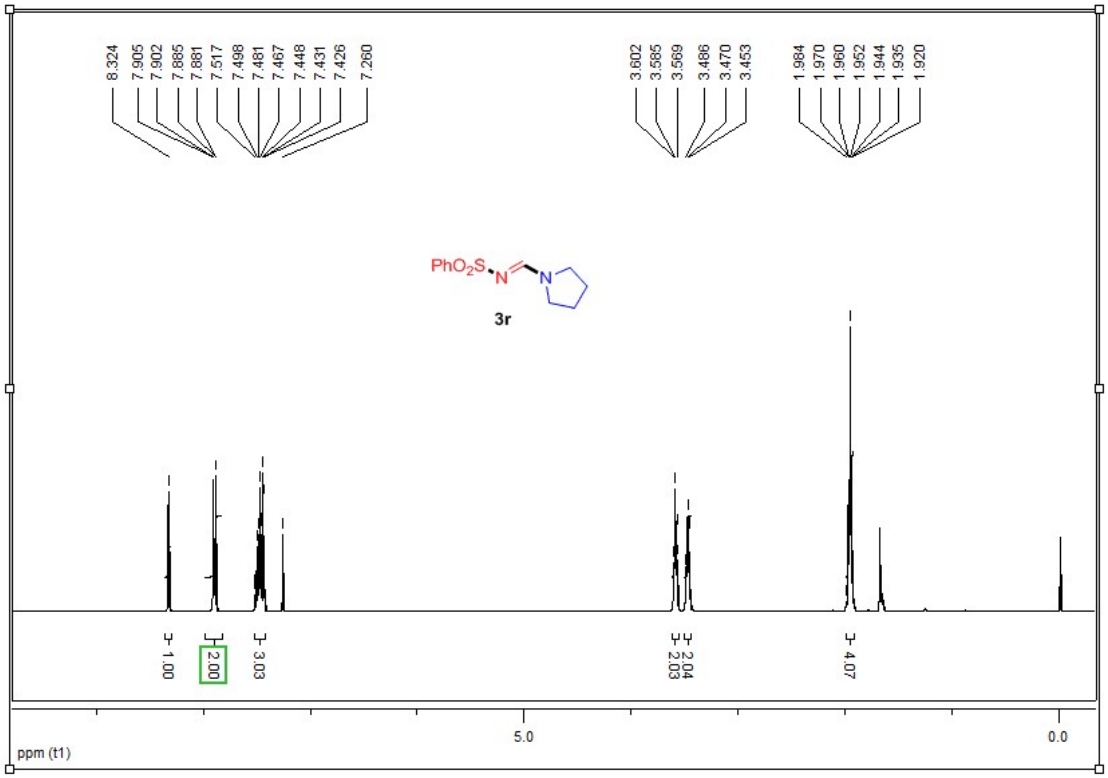
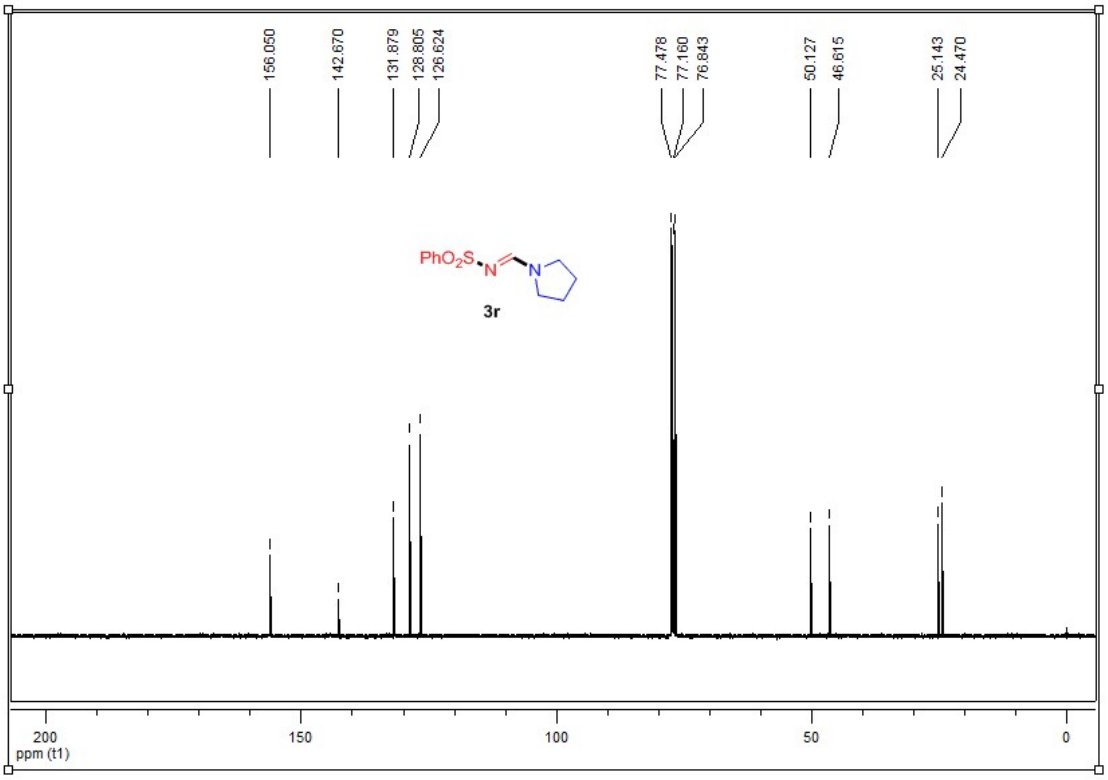
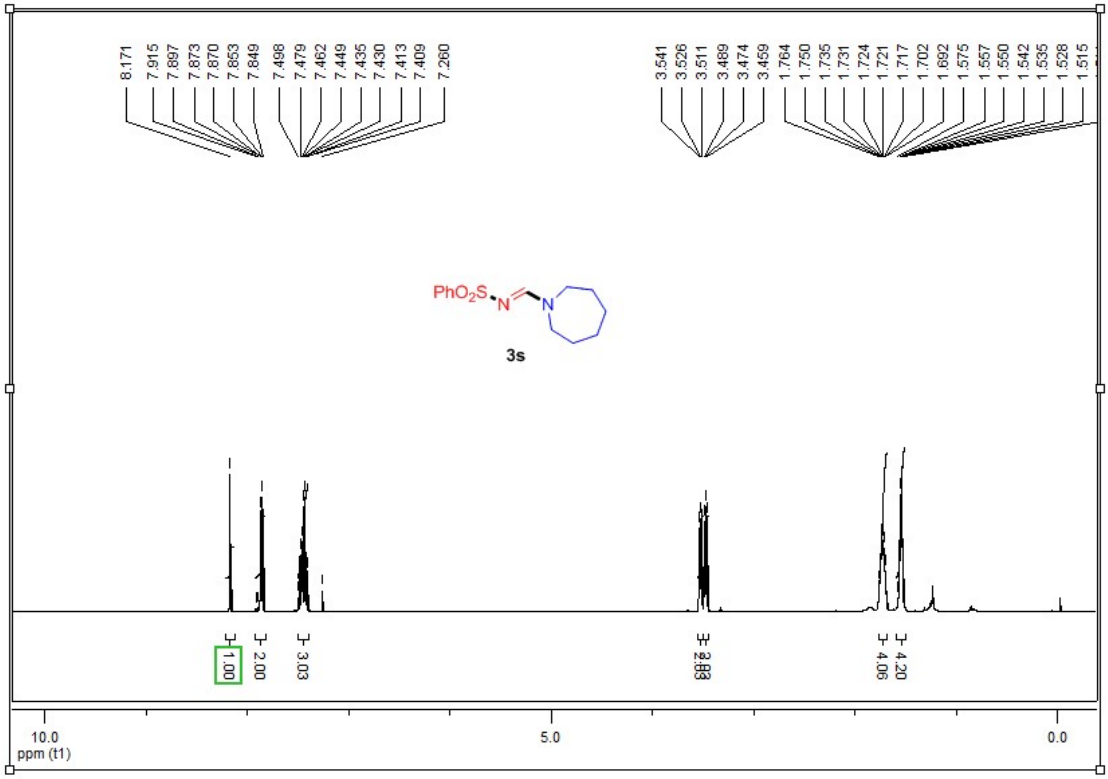
126.024
79.591
49.207
43.147
40.147
39.938
39.729
39.520
39.311
39.102
38.894
28.063
PhO2S
N
N
N
CO2tBu
3q
200
150
100
50
0
ppm (t1)


8.324
7.905
7.902
7.885
7.881
7.517
7.498
7.481
7.467
7.448
7.431
7.426
7.260
3.602
3.585
3.569
3.486
3.470
3.453
1.984
1.970
1.960
1.952
1.944
1.935
1.920
PhO2S
N
N
3r
1.00
2.00
3.03
2.04
2.03
4.07
5.0
0.0
ppm (t1)


156.050
142.670
131.879
128.805
126.624
77.478
77.160
76.843
50.127
46.615
25.143
24.470
PhO2S
N
N
3r
200
ppm (t1)
150
100
50
0


8.171
7.915
7.897
7.873
7.870
7.853
7.849
7.498
7.479
7.462
7.449
7.435
7.430
7.413
7.409
7.260
3.541
3.526
3.511
3.489
3.474
3.459
1.764
1.750
1.735
1.731
1.724
1.721
1.717
1.702
1.692
1.575
1.557
1.550
1.542
1.535
1.528
1.515
PhO2S
N
N
3s
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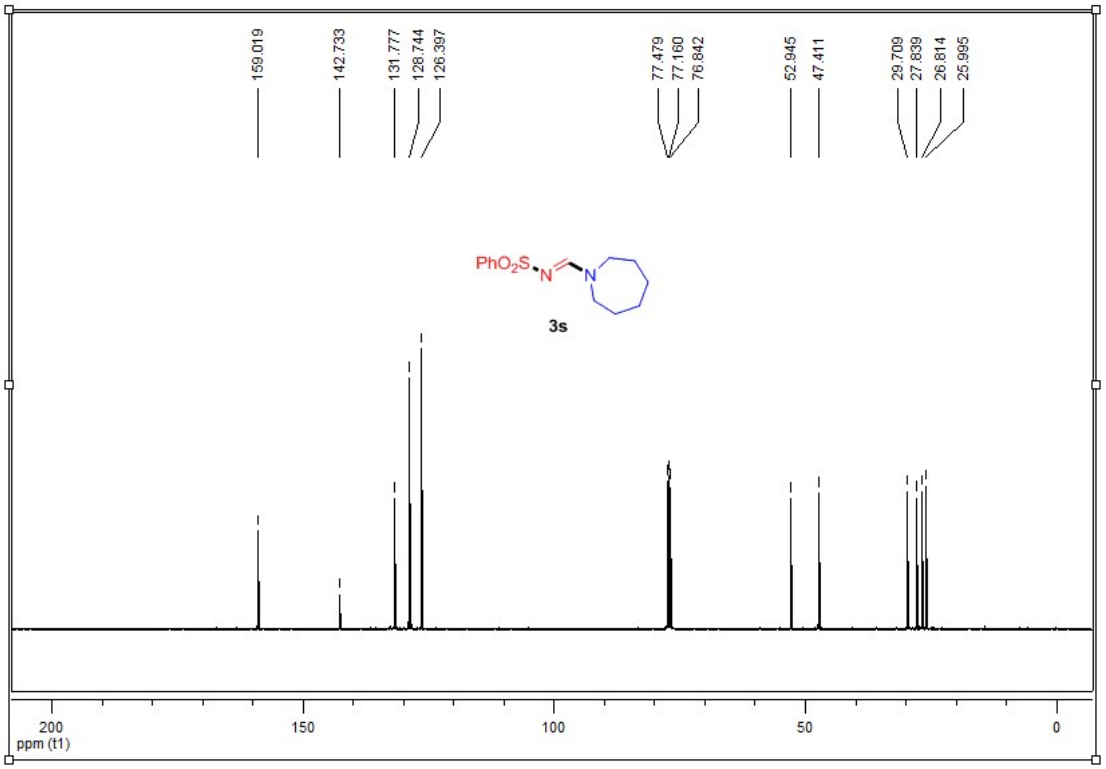
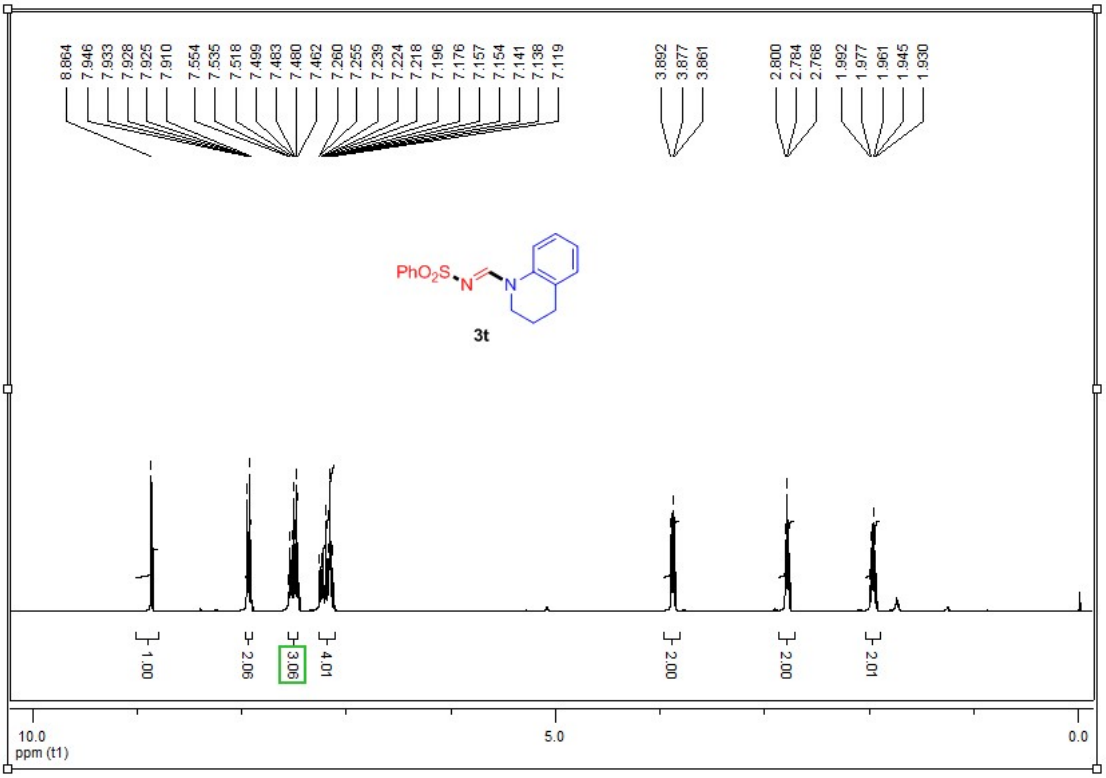
2.00
3.03
8.88
4.06
4.20
10.0
ppm (t1)
5.0
0.0


159.019
142.733
131.777
128.744
126.397
77.479
77.160
76.842
52.945
47.411
29.709
27.839
26.814
25.995
PhO2S
N
N
3s
200
150
100
50
0
ppm (t1)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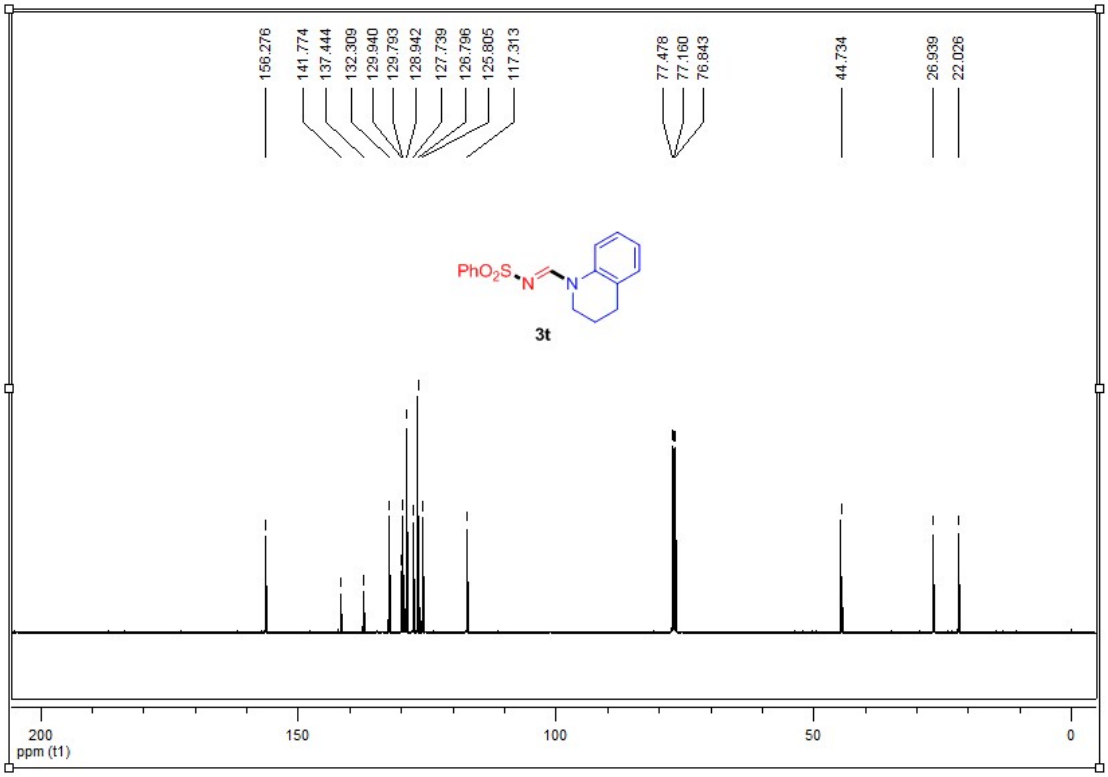
7.910
7.554
7.535
7.518
7.499
7.483
7.480
7.462
7.260
7.255
7.239
7.224
7.218
7.196
7.176
7.157
7.154
7.141
7.138
7.119
3.892
3.877
3.861
2.800
2.784
2.768
1.992
1.977
1.961
1.945
1.930
PhO2S
N
N
3t
1.00
2.06
3.06
4.01
2.00
2.00
2.01
10.0
5.0
0.0
ppm (t1)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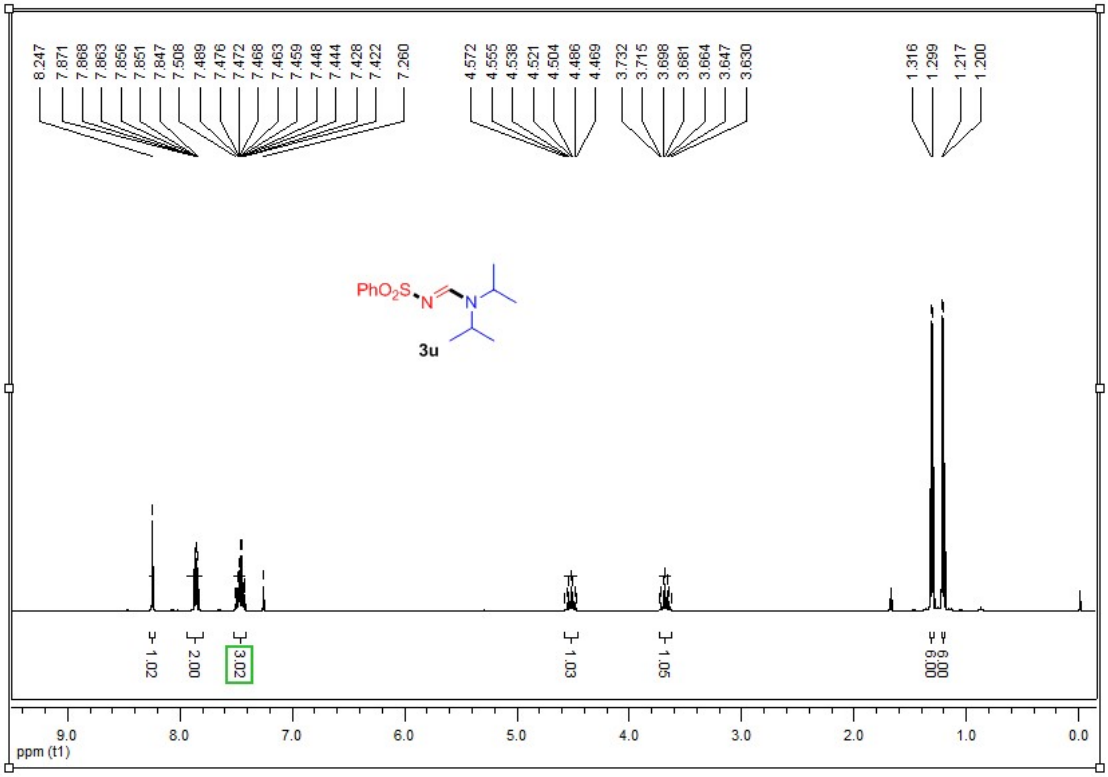
141.774
137.444
132.309
129.940
129.793
128.942
127.739
126.796
125.805
117.313
77.478
77.160
76.843
44.734
26.939
22.026
PhO2S
N
N
3t
200
150
100
50
0
ppm (t1)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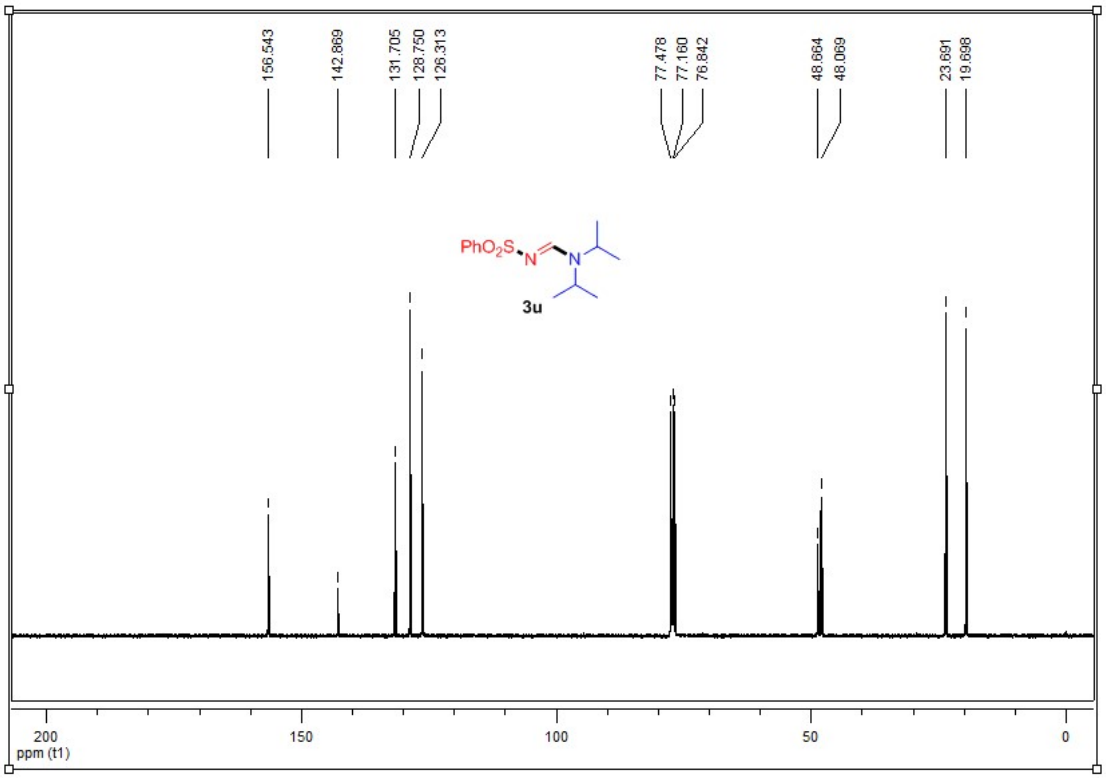
7.856
7.851
7.847
7.508
7.489
7.476
7.472
7.468
7.463
7.459
7.448
7.444
7.426
7.422
7.260
4.572
4.555
4.538
4.521
4.504
4.486
4.469
3.732
3.715
3.698
3.681
3.664
3.647
3.630
1.316
1.299
1.217
1.200
PhO2S
N
N
3u
1.02
2.00
2.02
1.03
1.06
6.00
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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142.869
131.705
128.750
126.313
77.478
77.160
76.842
48.664
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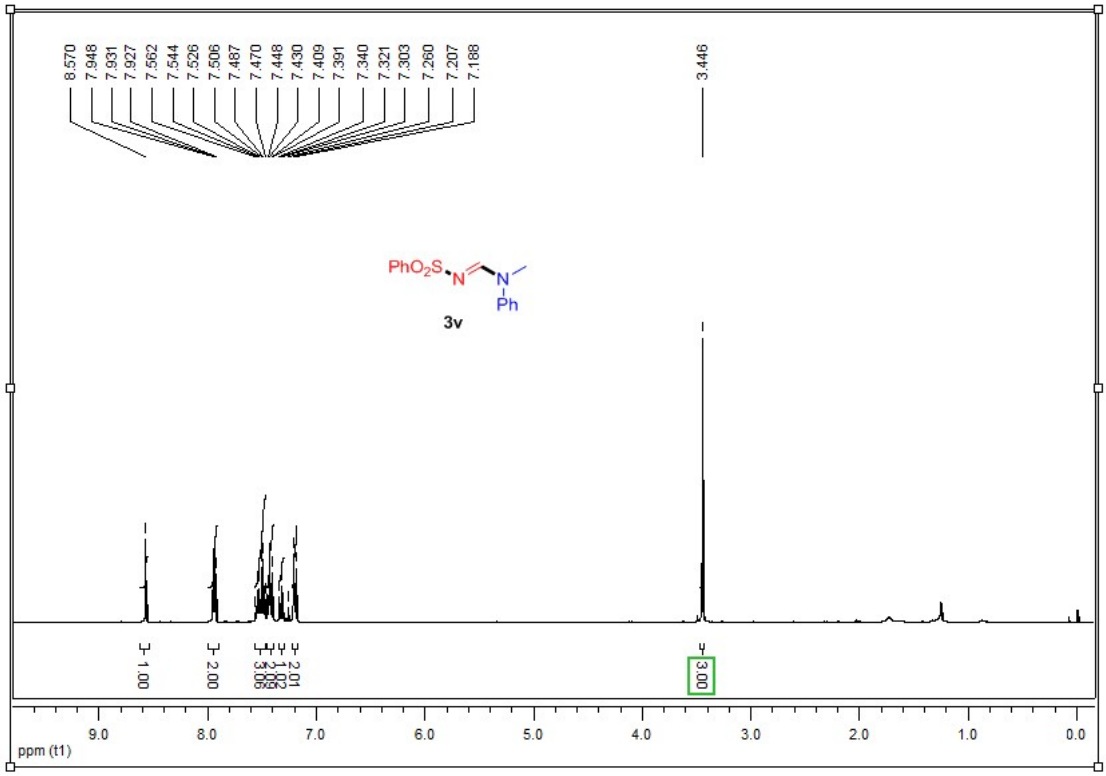
23.691
19.698
PhO2S
N
N
3u
200
150
100
50
0
ppm (t1)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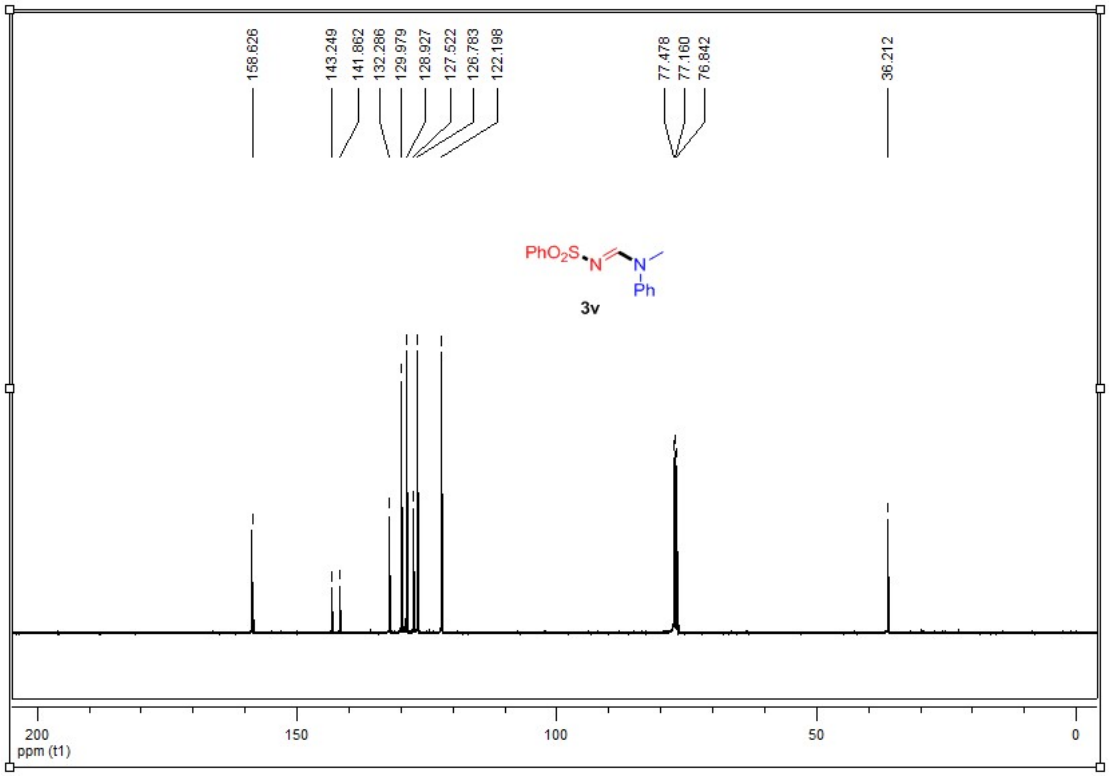
7.931
7.927
7.562
7.544
7.526
7.506
7.487
7.470
7.448
7.430
7.409
7.391
7.340
7.321
7.303
7.260
7.207
7.188
3.446
PhO2S
N
N
Ph
3v
1.00
2.00
2.01
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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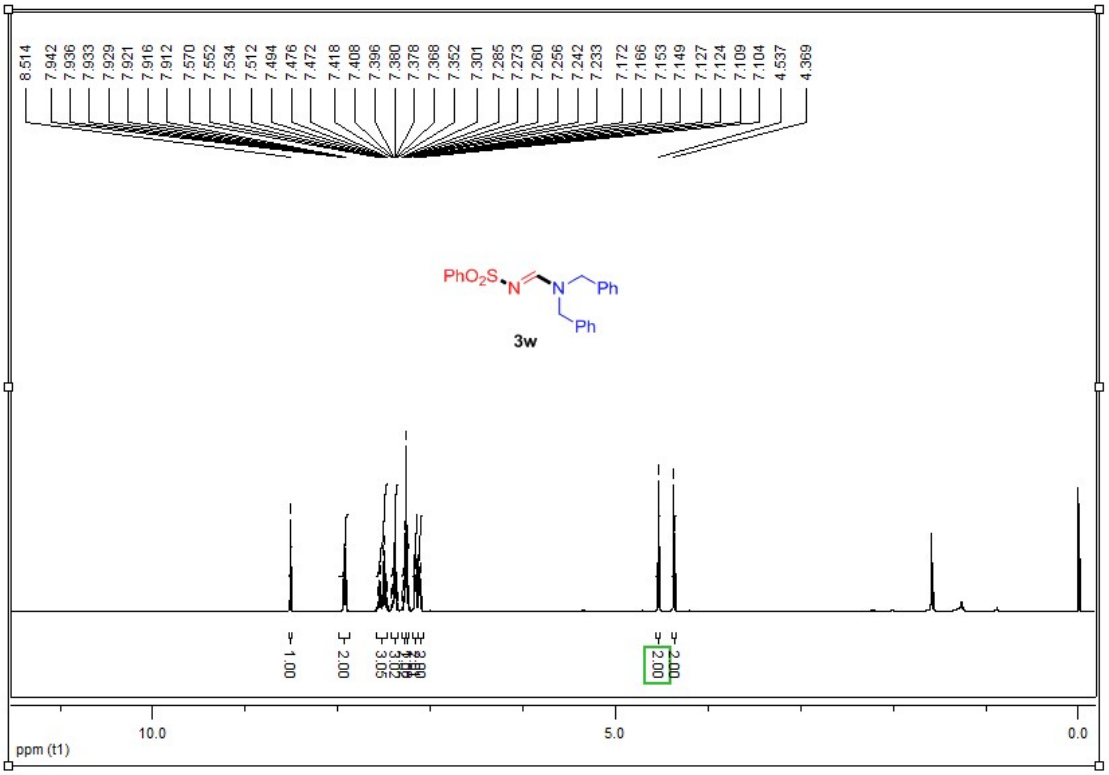
141.862
132.266
129.979
128.927
127.522
126.783
122.198
77.478
77.160
76.842
36.212
PhO2S
N
N
Ph
3v
200
150
100
50
0
ppm (t1)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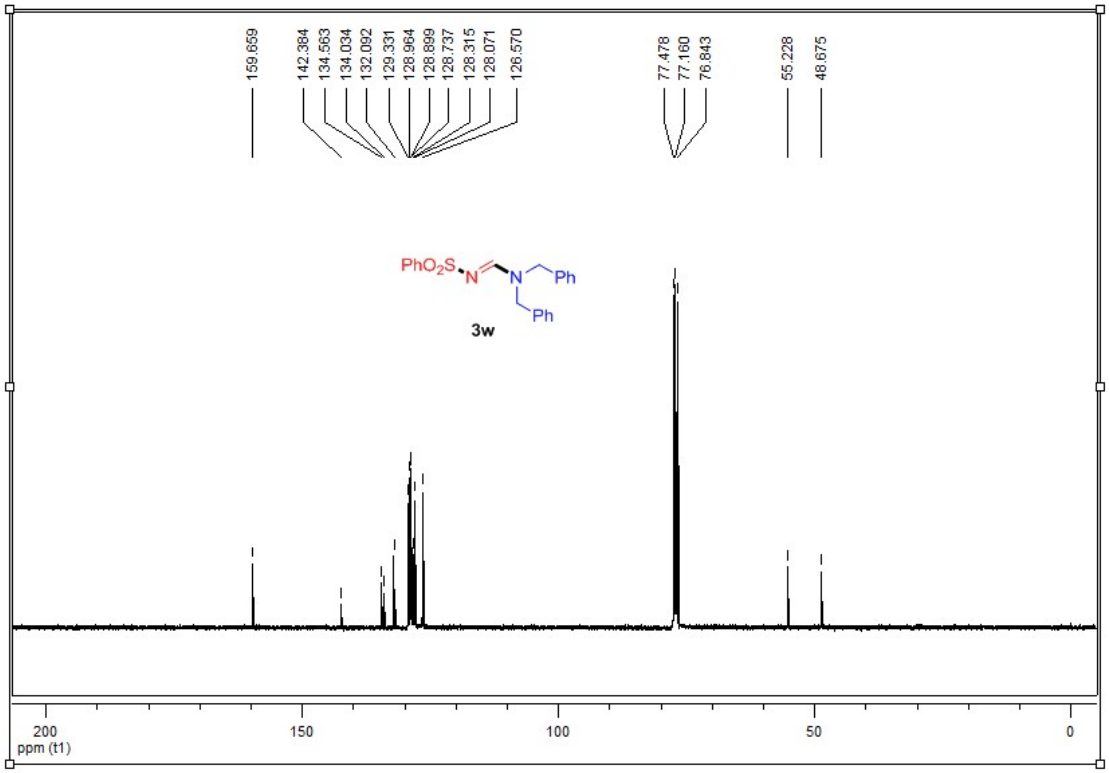
7.933
7.929
7.921
7.916
7.912
7.570
7.552
7.534
7.512
7.494
7.476
7.472
7.418
7.408
7.396
7.380
7.378
7.368
7.352
7.301
7.285
7.273
7.260
7.256
7.242
7.233
7.172
7.166
7.153
7.149
7.127
7.124
7.109
7.104
4.537
4.369
PhO2S
N
N
Ph
Ph
3w
1.00
2.00
3.05
2.00
10.0
5.0
0.0
ppm (t1)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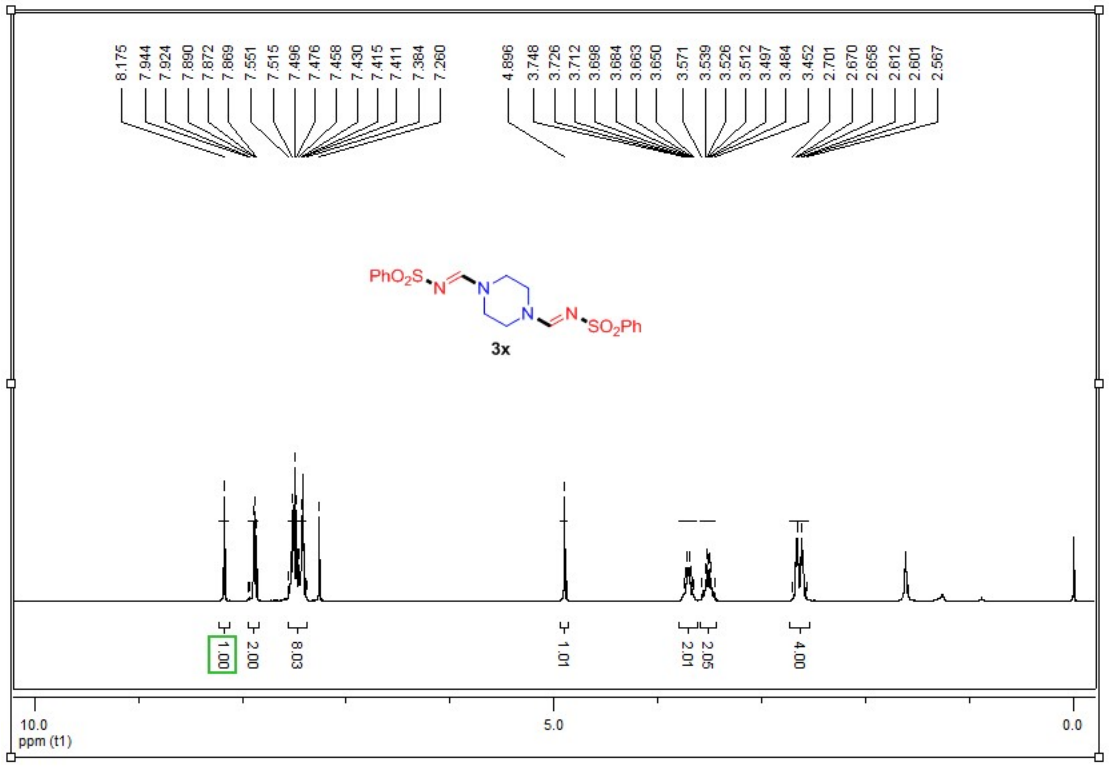
134.563
134.034
132.092
129.331
128.964
128.899
128.737
128.315
128.071
126.570
77.478
77.160
76.843
55.228
48.675
PhO2S
N
N
Ph
Ph
3w
200
150
100
50
0
ppm (t1)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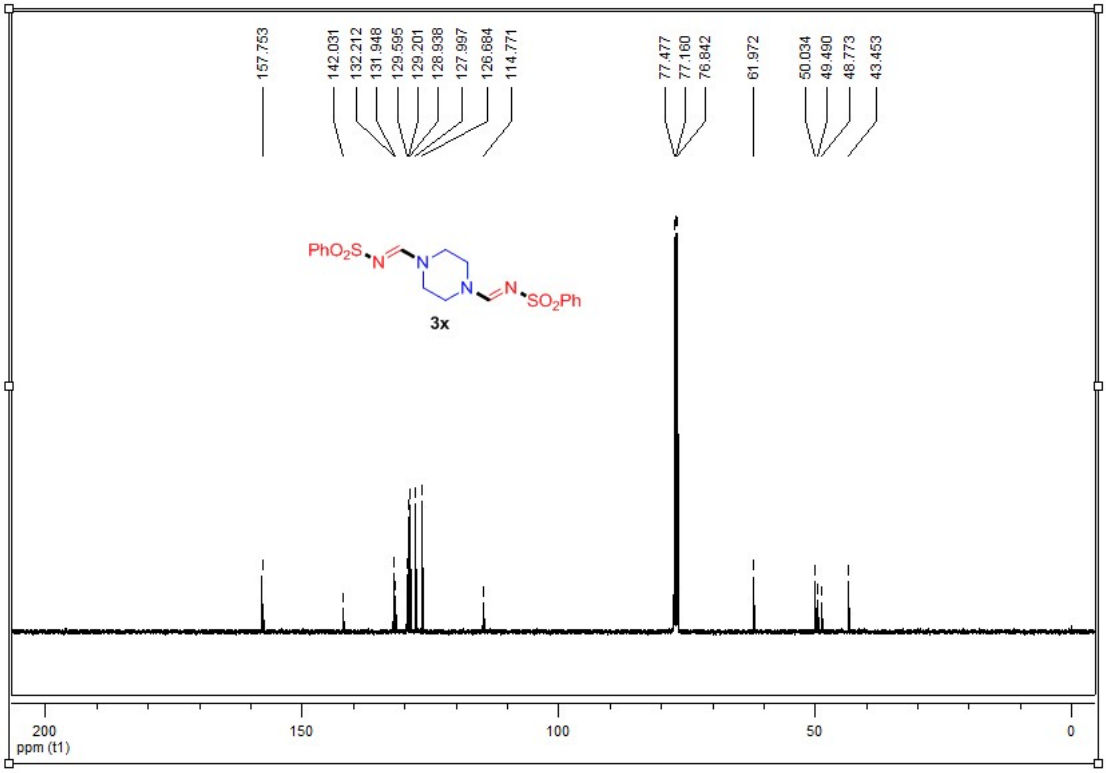
7.515
7.496
7.476
7.458
7.430
7.415
7.411
7.384
7.260
4.896
3.748
3.726
3.712
3.698
3.684
3.663
3.650
3.571
3.539
3.526
3.512
3.497
3.484
3.452
2.701
2.670
2.658
2.612
2.601
2.567
PhO2S
N
N
N
SO2Ph
3x
1.00
2.00
8.03
1.01
2.01
2.05
4.00
10.0
5.0
0.0
ppm (t1)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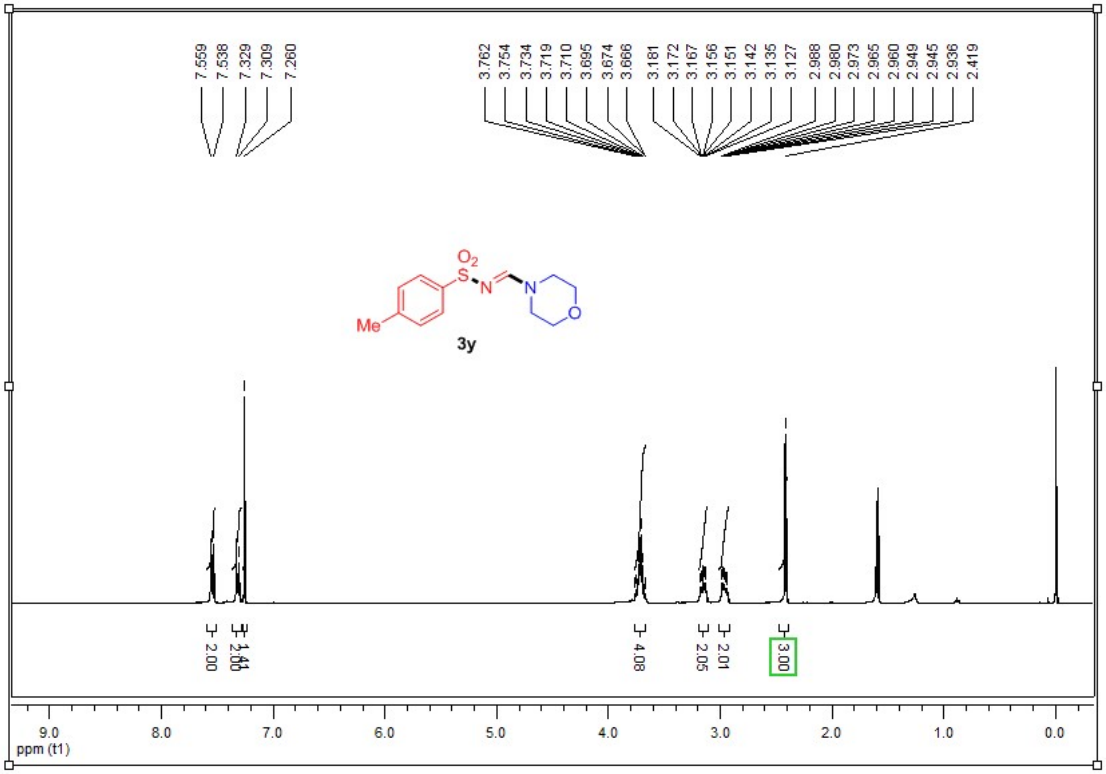
129.201
128.938
127.997
126.684
114.771
77.477
77.160
76.842
61.972
50.034
49.490
48.773
43.453
PhO2S
N
N
N
SO2Ph
3x
200
150
100
50
0
ppm (t1)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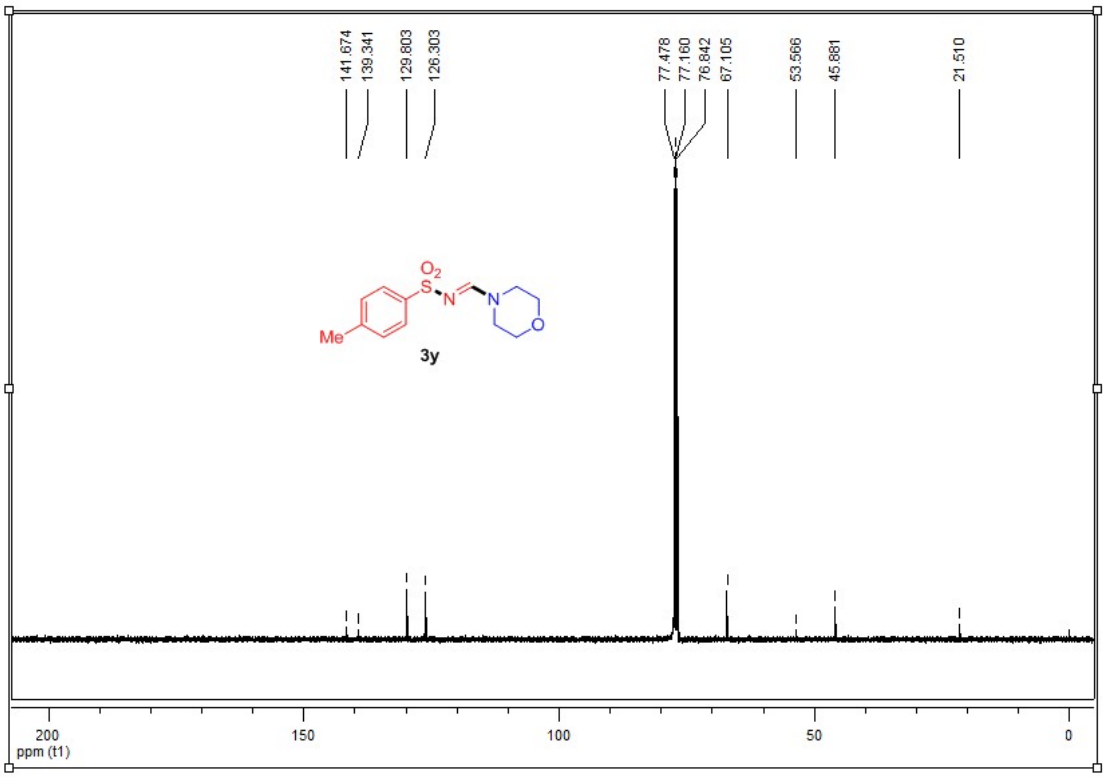
7.538
7.329
7.309
7.260
3.762
3.754
3.734
3.719
3.710
3.695
3.674
3.666
3.181
3.172
3.167
3.156
3.151
3.142
3.135
3.127
2.988
2.980
2.973
2.965
2.960
2.949
2.945
2.936
2.419
O2
S
N
N
O
Me
3y
2.00
4.08
2.05
2.01
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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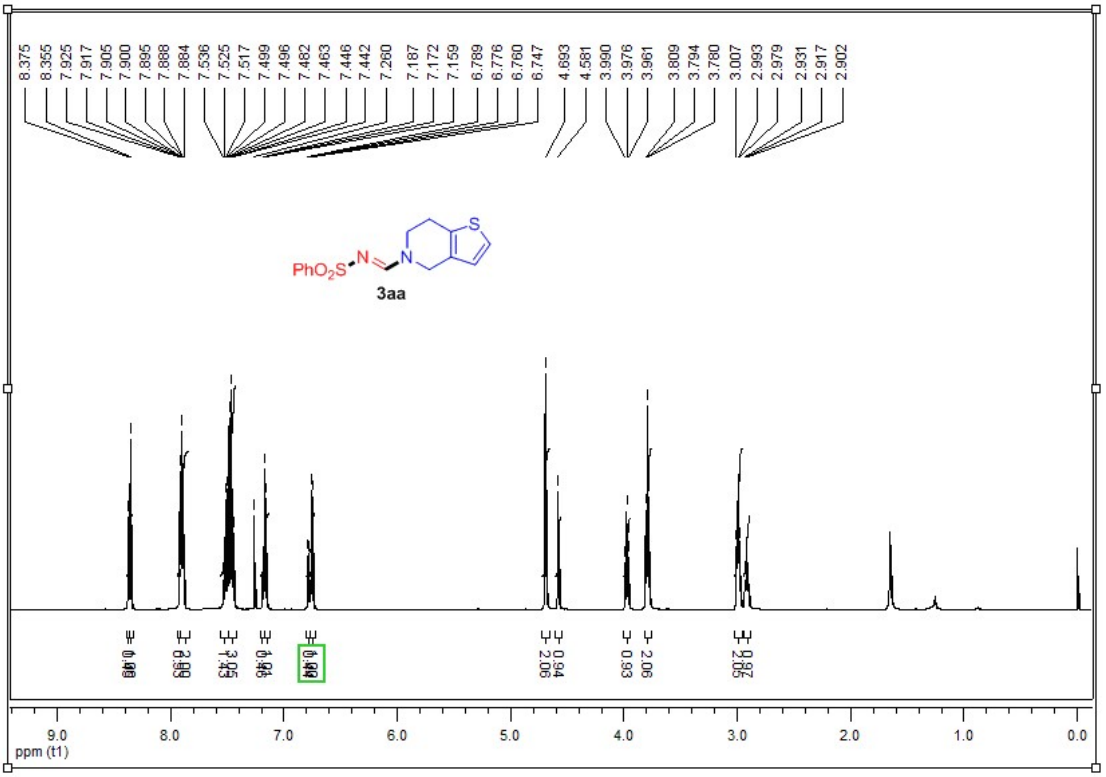
139.341
129.803
126.303
77.478
77.160
76.842
67.105
53.566
45.881
21.510
Me
3y
200
150
100
50
0
ppm (t1)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8.355
7.925
7.917
7.905
7.900
7.895
7.888
7.884
7.536
7.525
7.517
7.499
7.496
7.482
7.463
7.446
7.442
7.260
7.187
7.172
7.159
6.789
6.776
6.760
6.747
4.693
4.581
3.990
3.976
3.961
3.809
3.794
3.780
3.007
2.993
2.979
2.931
2.917
2.902
PhO2S
3aa
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7.0
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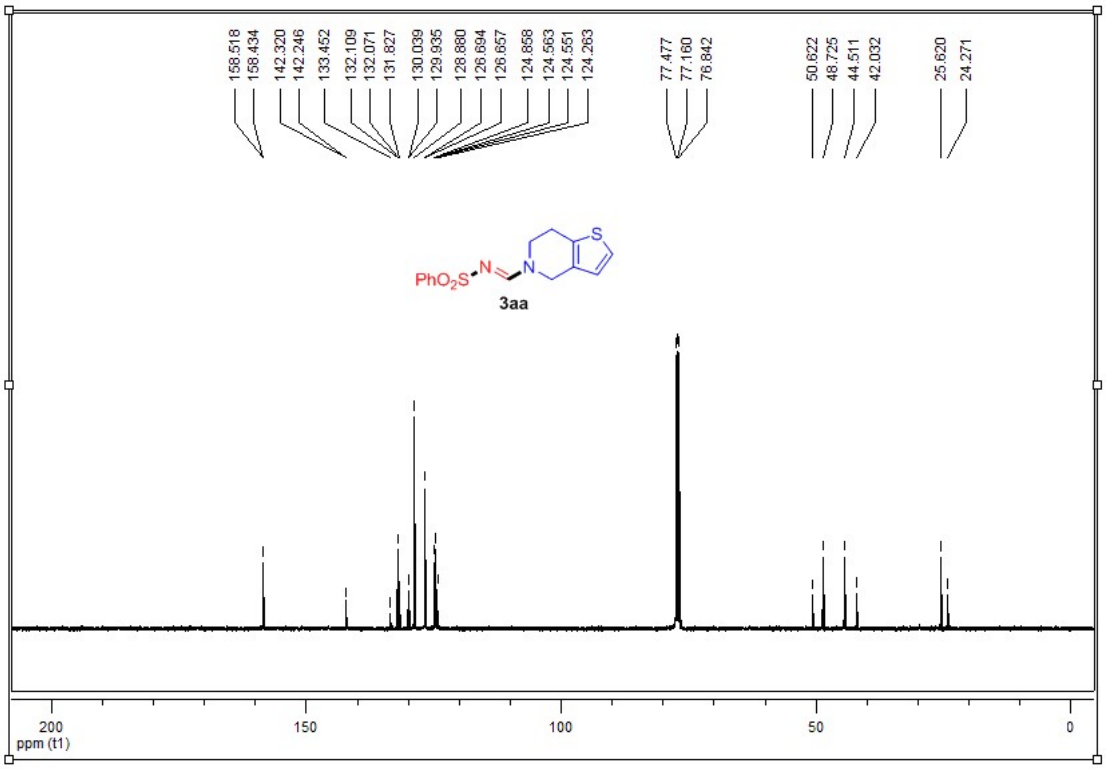
2.0
1.0
0.0
ppm (t1)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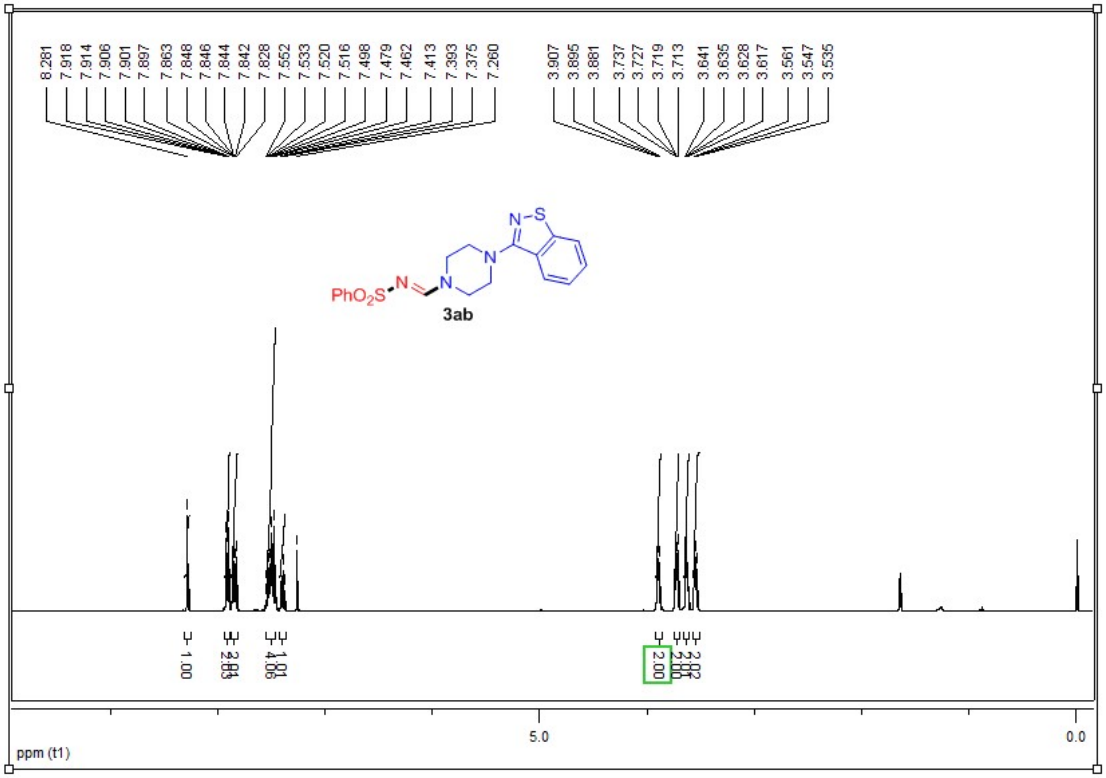
158.434
142.320
142.246
133.452
132.109
132.071
131.827
130.039
129.935
128.880
126.694
126.657
124.858
124.563
124.551
124.263
77.477
77.160
76.842
50.622
48.725
44.511
42.032
25.620
24.271
PhO2S
N
S
3aa
200
150
100
50
0
ppm (t1)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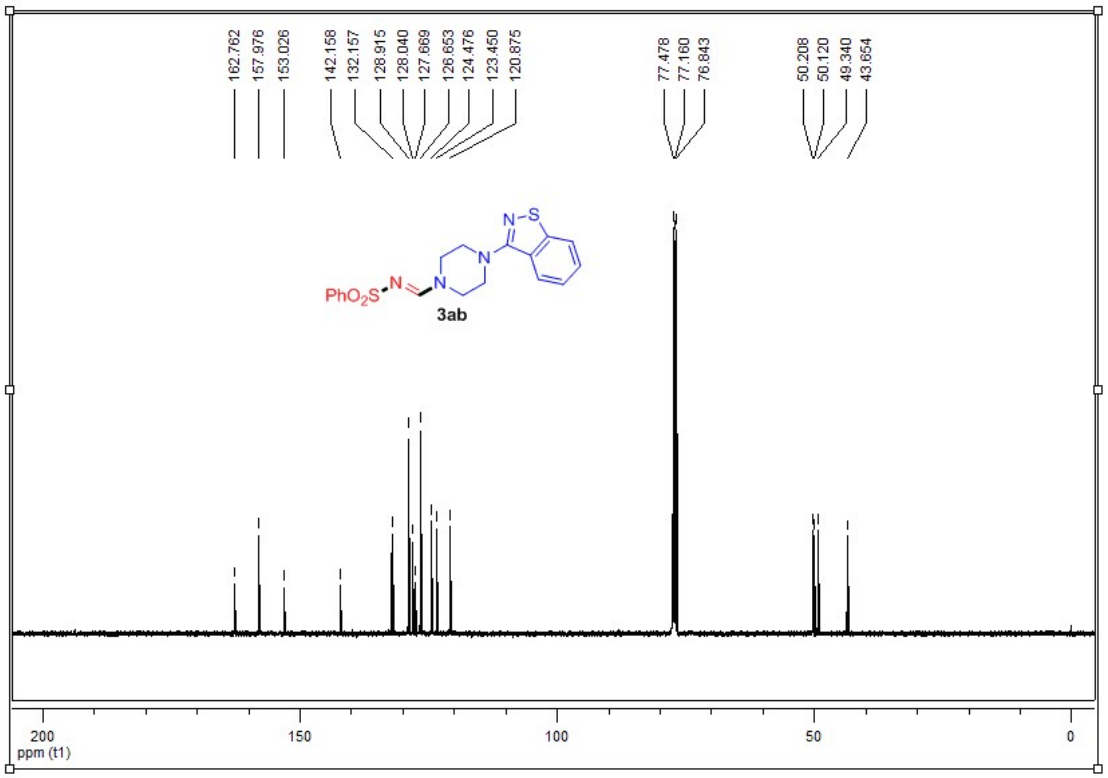
7.918
7.914
7.906
7.901
7.897
7.863
7.848
7.846
7.844
7.842
7.828
7.552
7.533
7.520
7.516
7.498
7.479
7.462
7.413
7.393
7.375
7.260
3.907
3.895
3.881
3.737
3.727
3.719
3.713
3.641
3.635
3.628
3.617
3.561
3.547
3.535
PhO2S
N
S
3ab
1.00
3.88
4.06
2.00
5.0
0.0
ppm (t1)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157.976
153.026
142.158
132.157
128.915
128.040
127.669
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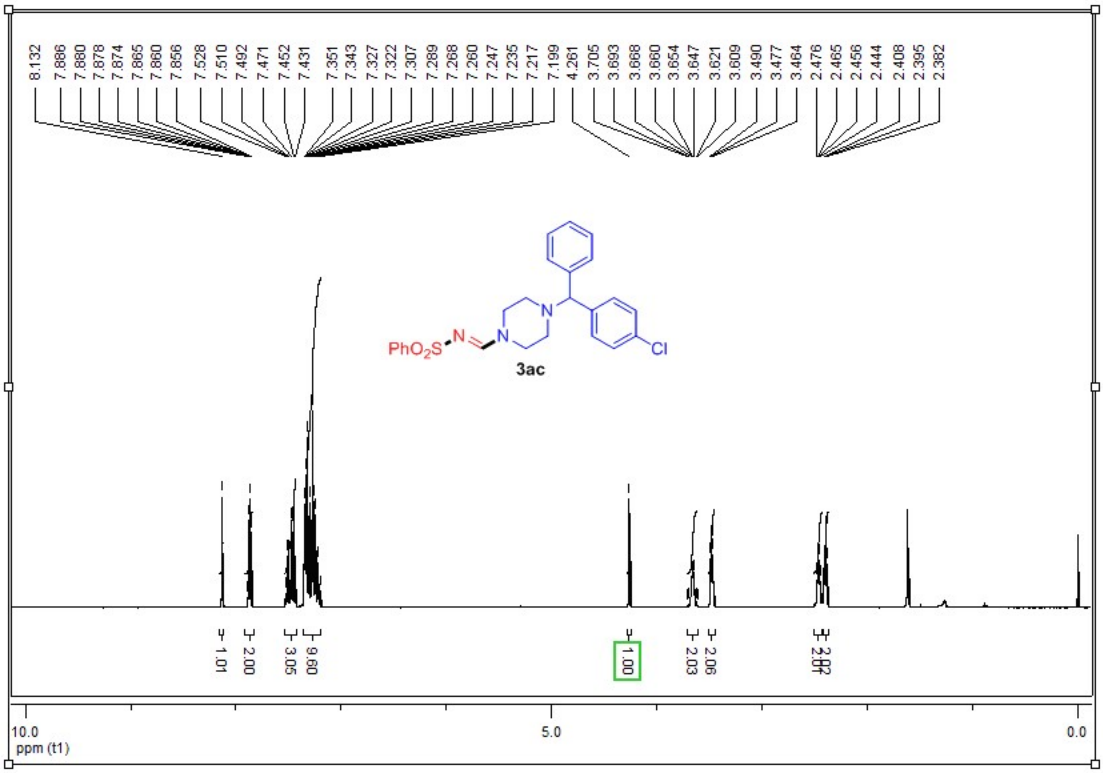
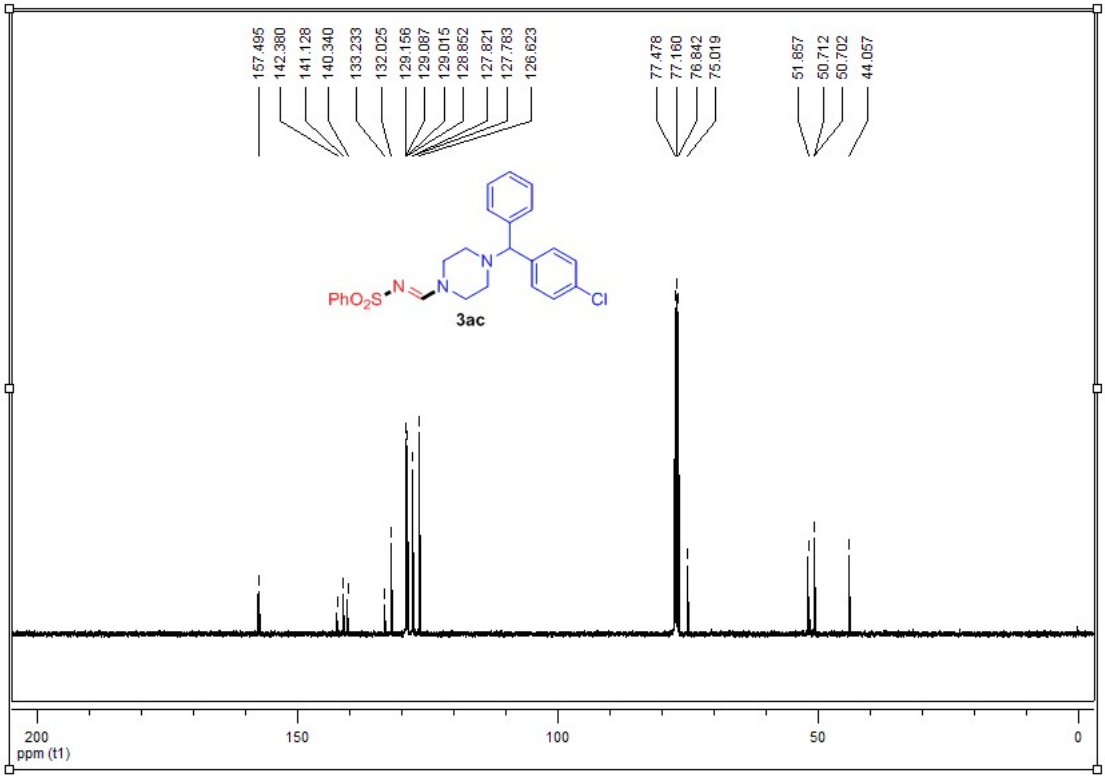
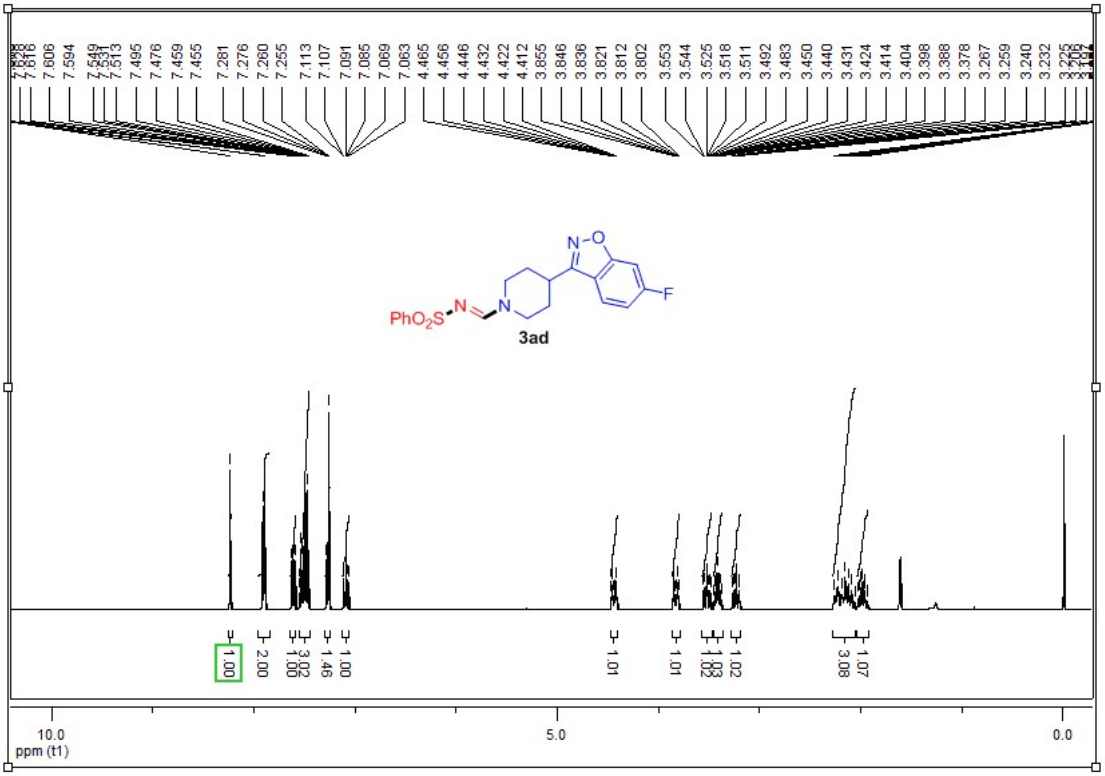
124.476
123.450
120.875
77.478
77.160
76.843
50.208
50.120
49.340
43.654
3ab
200
150
100
50
0
ppm (t1)


8.132
7.886
7.880
7.878
7.874
7.865
7.860
7.856
7.526
7.510
7.492
7.471
7.452
7.431
7.351
7.343
7.327
7.322
7.307
7.289
7.268
7.260
7.247
7.235
7.217
7.199
4.261
3.705
3.693
3.668
3.660
3.654
3.647
3.621
3.609
3.490
3.477
3.464
2.476
2.465
2.456
2.444
2.408
2.395
2.382
3ac
1.01
2.00
3.05
6.80
1.00
2.03
2.06
3.82
10.0
5.0
0.0
ppm (t1)


157.495
142.380
141.128
140.340
133.233
132.025
129.156
129.087
129.015
128.852
127.821
127.783
126.623
77.478
77.160
76.842
75.019
51.857
50.712
50.702
44.057
PhO2S
N
N
Cl
3ac
200
150
100
50
0
ppm (t1)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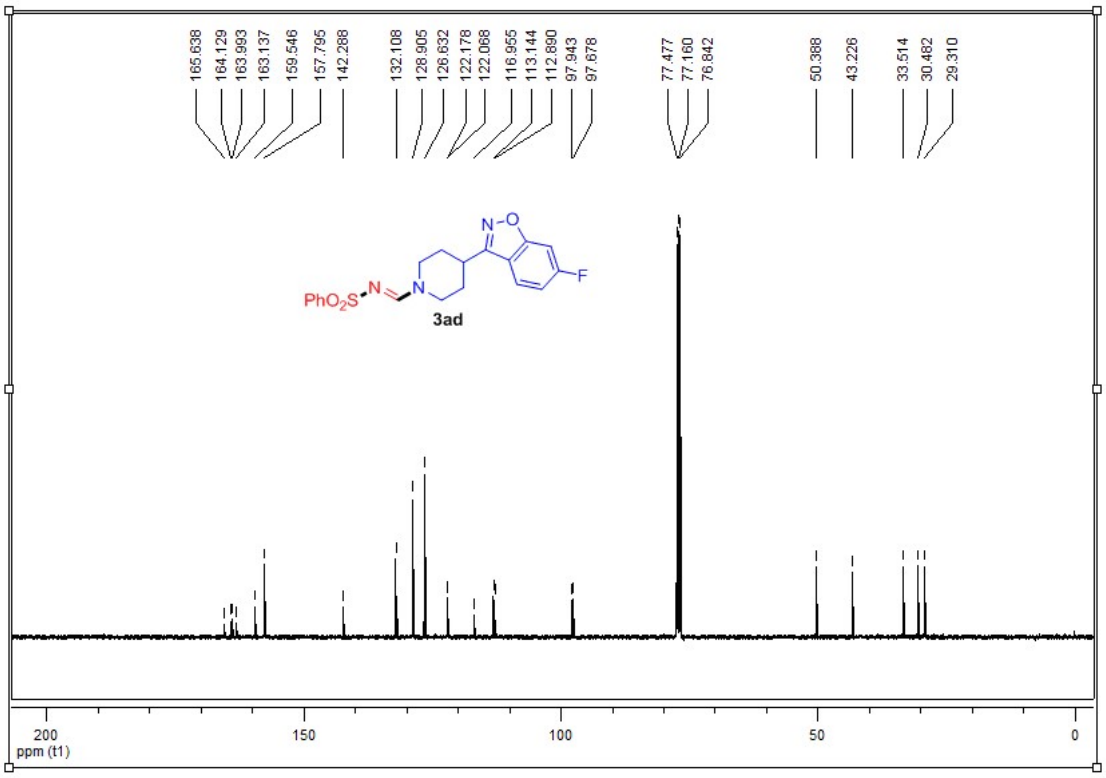
7.594
7.549
7.531
7.513
7.495
7.476
7.459
7.455
7.281
7.276
7.260
7.255
7.113
7.107
7.091
7.085
7.069
7.063
4.465
4.456
4.446
4.432
4.422
4.412
3.855
3.846
3.836
3.821
3.812
3.802
3.553
3.544
3.525
3.518
3.511
3.492
3.483
3.450
3.440
3.431
3.424
3.414
3.404
3.398
3.388
3.378
3.267
3.259
3.240
3.232
N
O
F
PhO2S
N
N
3ad
1.00
2.00
3.02
1.06
1.46
1.00
1.01
1.01
1.02
3.08
1.07
10.0
5.0
0.0
ppm (t1)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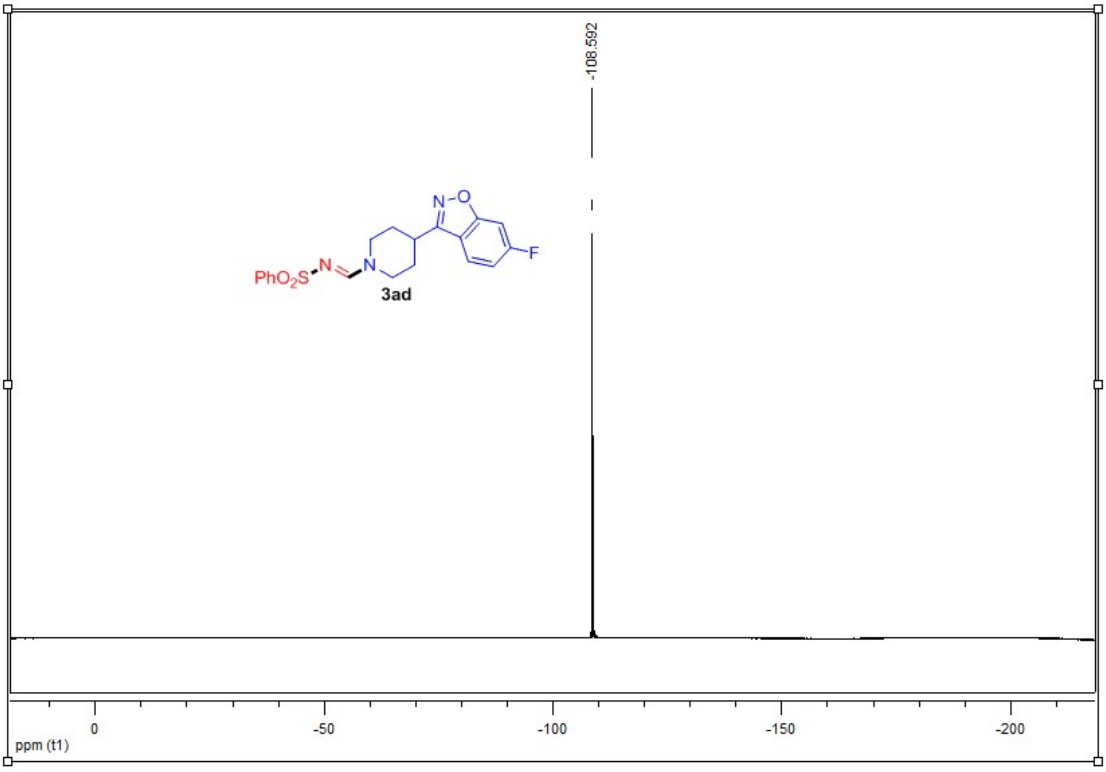
164.129
163.993
163.137
159.546
157.795
142.288
132.108
128.905
126.632
122.178
122.068
116.955
113.144
112.890
97.943
97.678
77.477
77.160
76.842
50.388
43.226
33.514
30.482
29.310
PhO2S
N
O
F
3ad
200
150
100
50
0
ppm (t1)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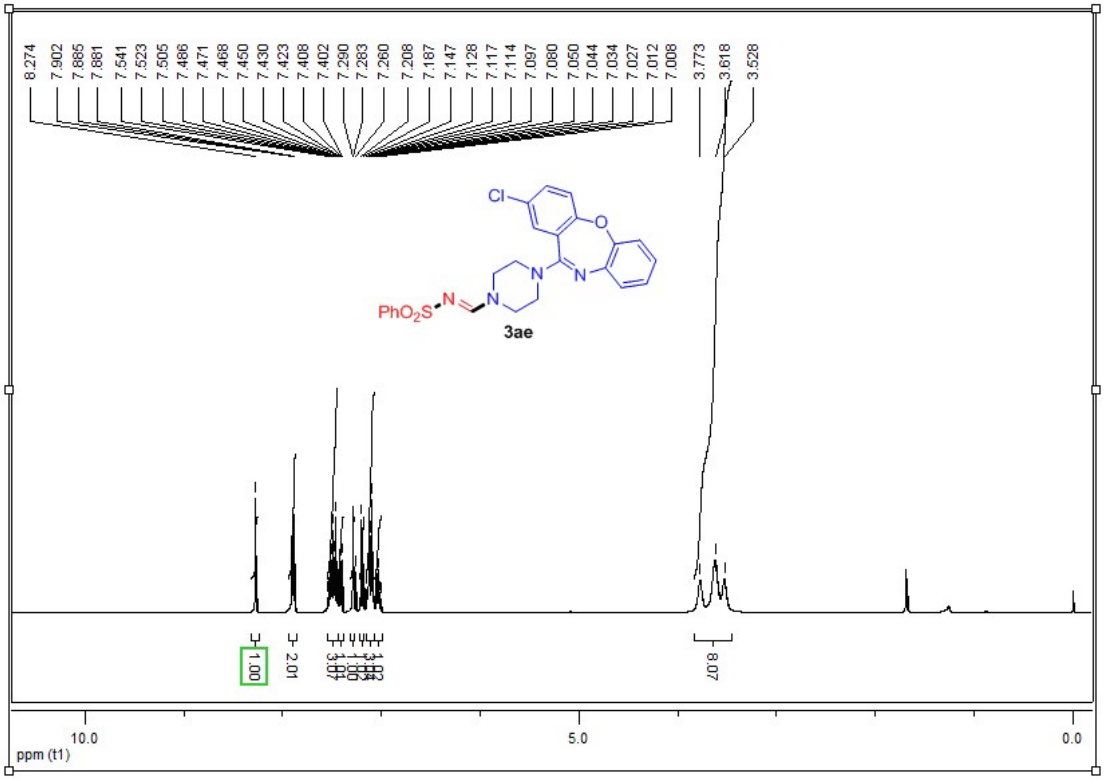
PhO2S
N
O
F
3ad
0
-50
-100
-150
-200
ppm (t1)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7.885
7.881
7.541
7.523
7.505
7.486
7.471
7.468
7.450
7.430
7.423
7.408
7.402
7.290
7.283
7.260
7.208
7.187
7.147
7.128
7.117
7.114
7.097
7.080
7.050
7.044
7.034
7.027
7.012
7.008
3.773
3.618
3.528
Cl
O
N
N
N
PhO2S
3ae
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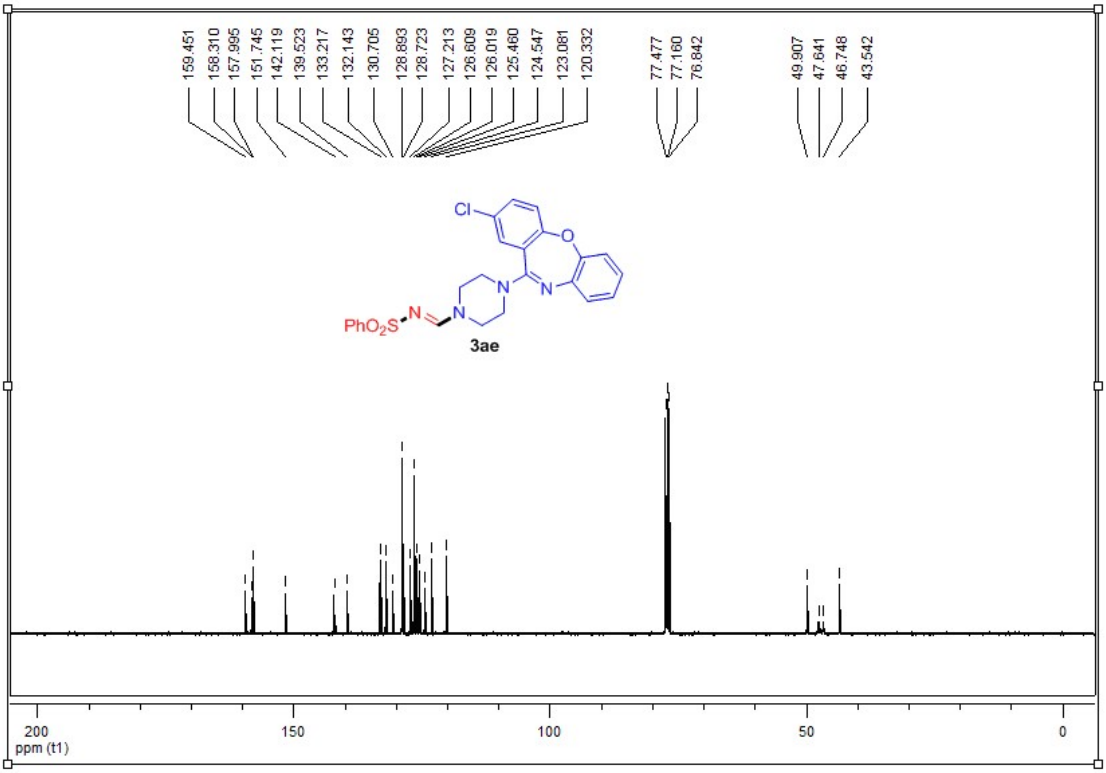
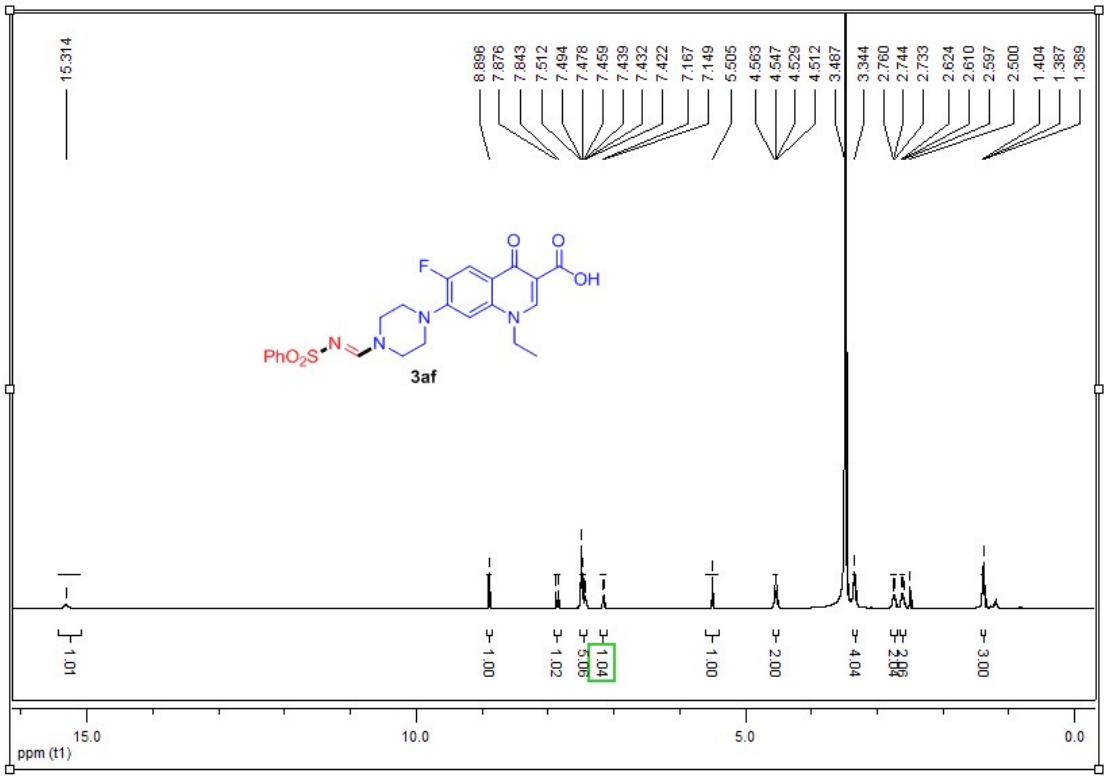
2.01
3.07
8.07
10.0
5.0
0.0
ppm (t1)


159.451
158.310
157.995
151.745
142.119
139.523
133.217
132.143
130.705
128.893
128.723
127.213
126.609
126.019
125.460
124.547
123.081
120.332
77.477
77.160
76.842
49.907
47.641
46.748
43.542
Cl
O
N
N
N
PhO2S
3ae
200
150
100
50
0
ppm (t1)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8.896
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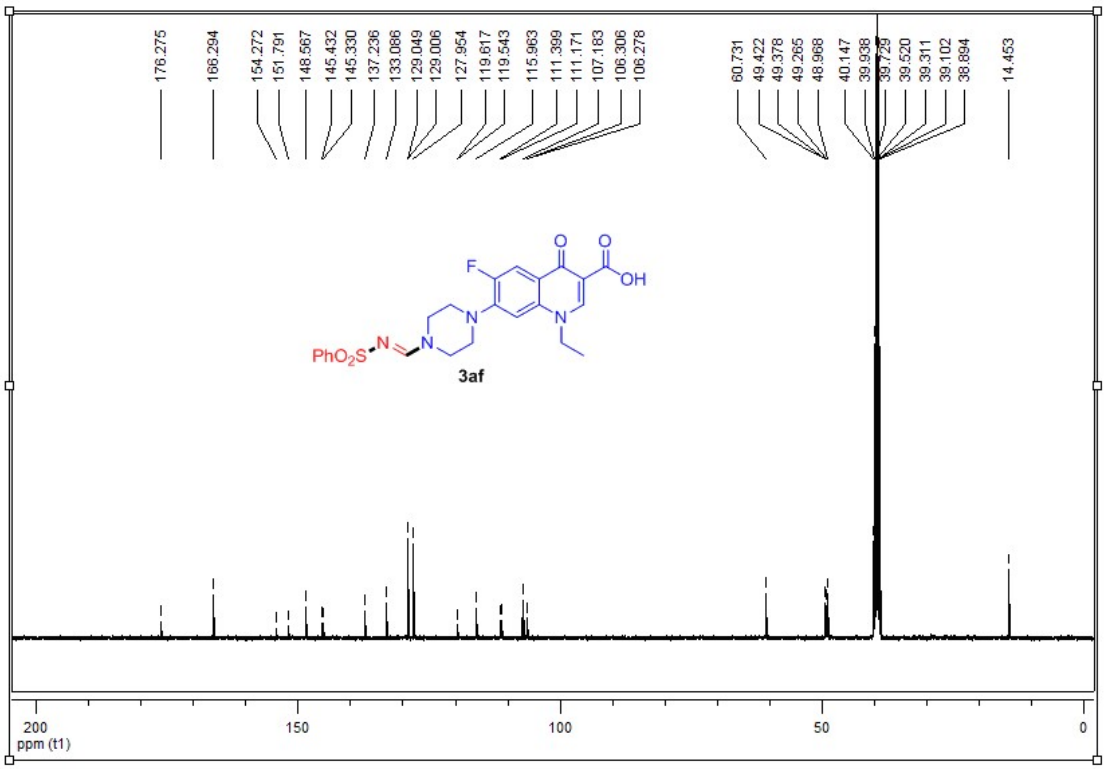
7.843
7.512
7.494
7.478
7.459
7.439
7.432
7.422
7.167
7.149
5.505
4.563
4.547
4.529
4.512
3.487
3.344
2.760
2.744
2.733
2.624
2.610
2.597
2.500
1.404
1.387
1.369
3af
1.01
1.00
1.02
5.06
1.04
1.00
2.00
4.04
2.05
3.00
15.0
10.0
5.0
0.0
ppm (t1)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148.567
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137.236
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129.049
129.006
127.954
119.617
119.543
115.963
111.399
111.171
107.183
106.306
106.278
60.731
49.422
49.378
49.265
48.968
40.147
39.938
39.729
39.520
39.311
39.102
38.894
14.453
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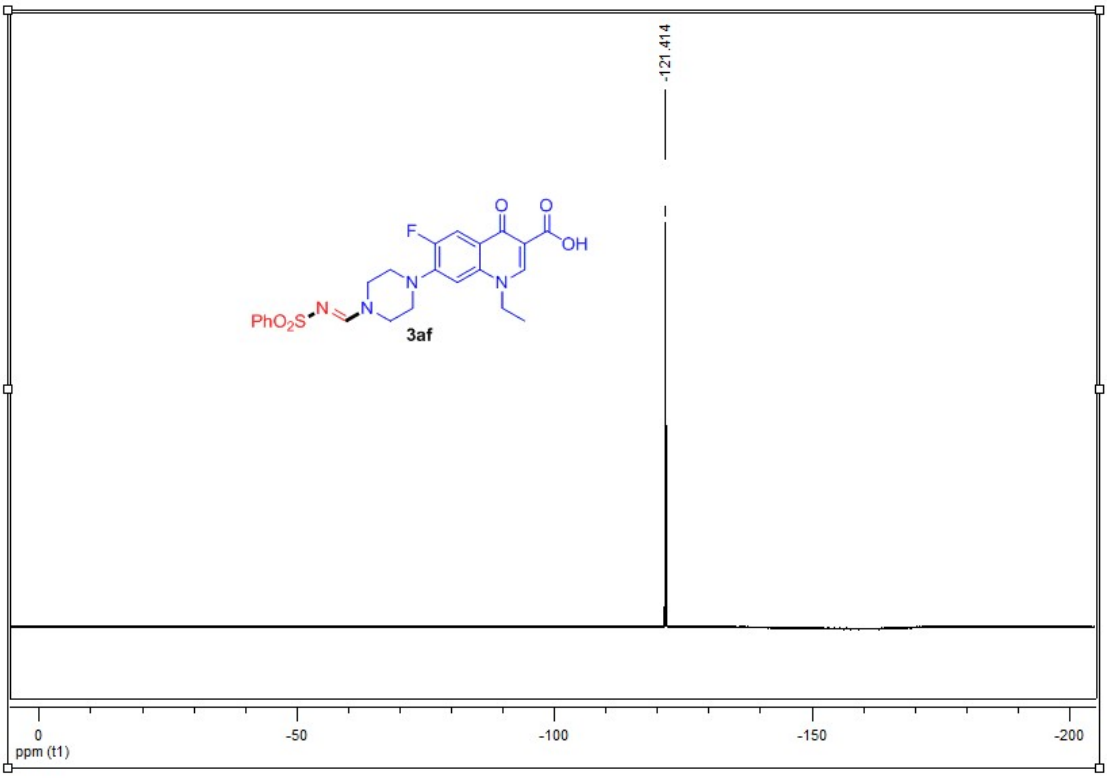
200
150
100
50
0
ppm (t1)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0
-50
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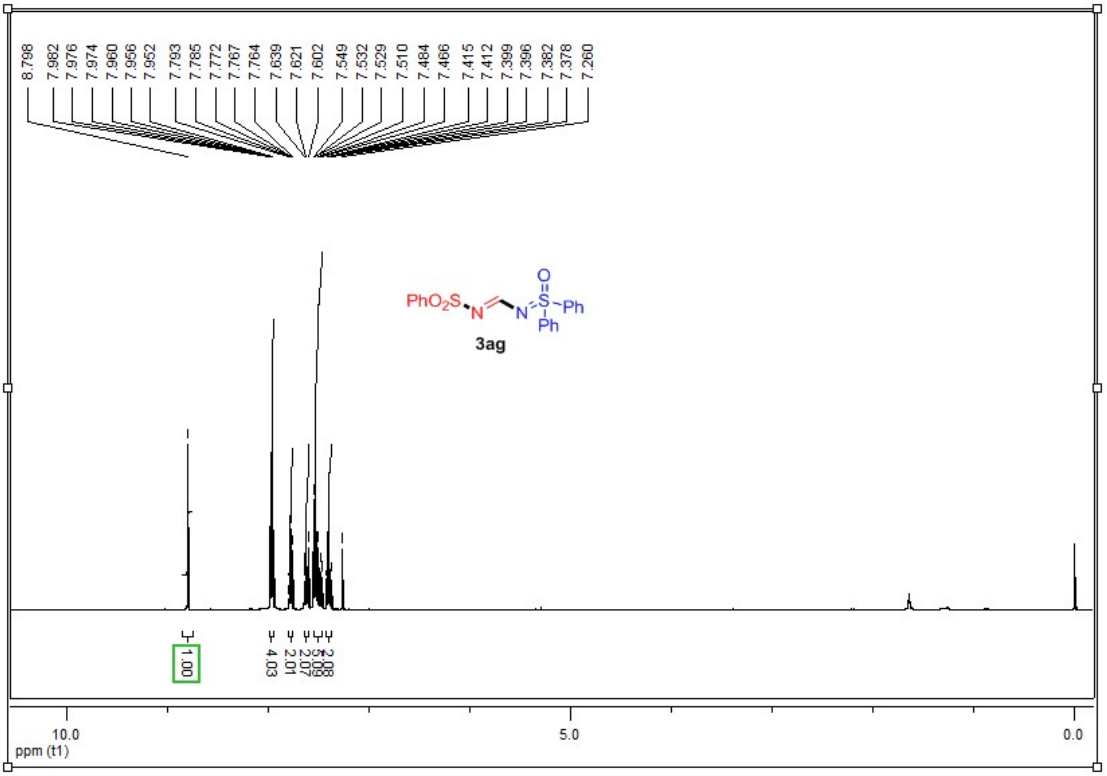
-150
-200
ppm (t1)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7.974
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7.793
7.785
7.772
7.767
7.764
7.639
7.621
7.602
7.549
7.532
7.529
7.510
7.484
7.466
7.415
7.412
7.399
7.396
7.382
7.378
7.260
3ag
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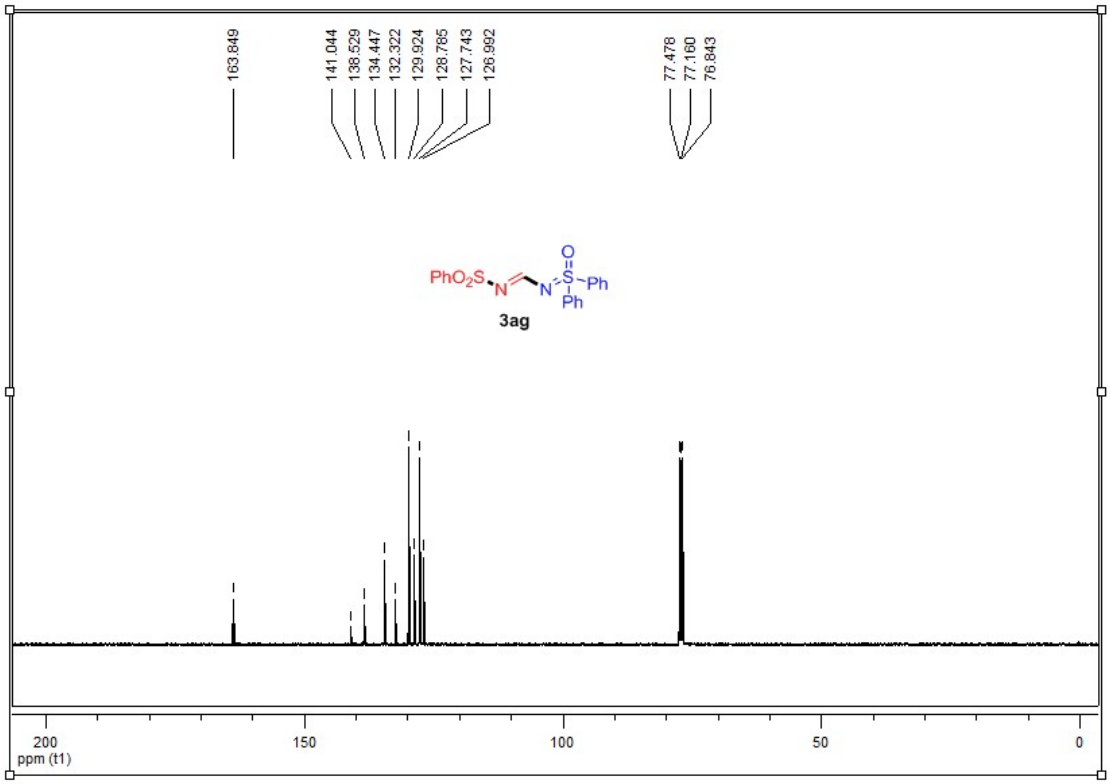
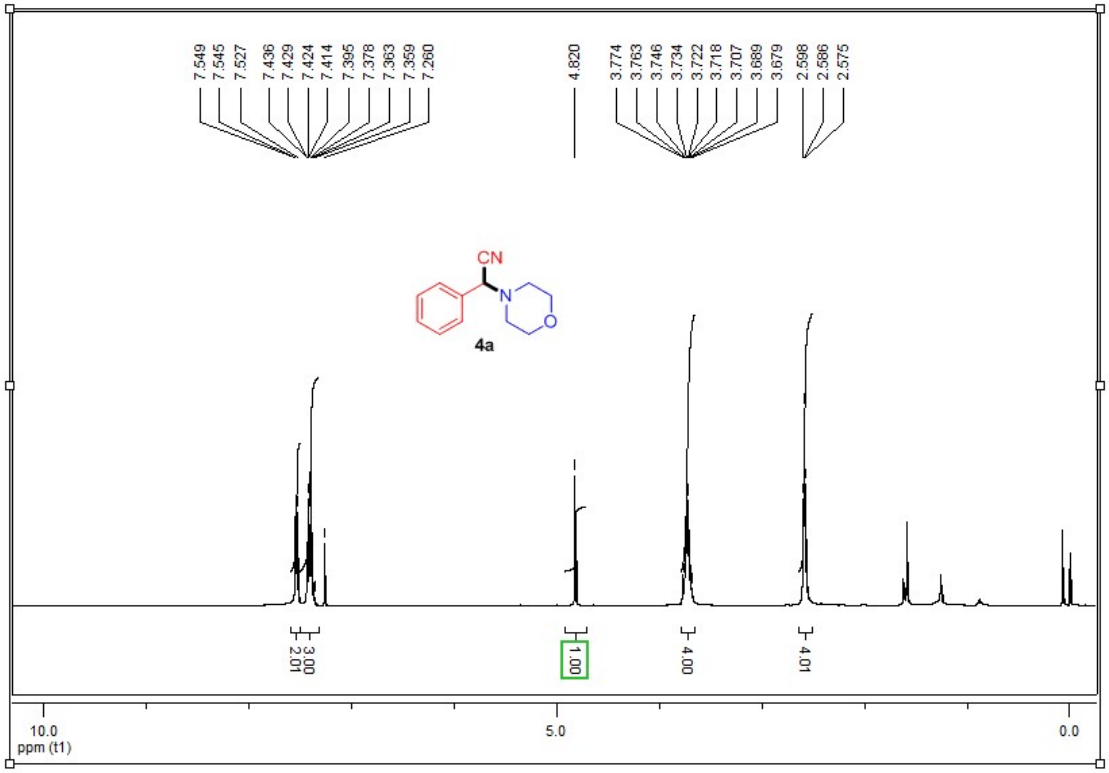
4.03
2.01
2.09
2.09
2.08
10.0
5.0
0.0
ppm (t1)


163.849
141.044
138.529
134.447
132.322
129.924
128.785
127.743
126.992
77.478
77.160
76.843
PhO2S
N
N
O
S
Ph
Ph
3ag
200
150
100
50
0
ppm (t1)


7.549
7.545
7.527
7.436
7.429
7.424
7.414
7.395
7.378
7.363
7.359
7.260
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3.734
3.722
3.718
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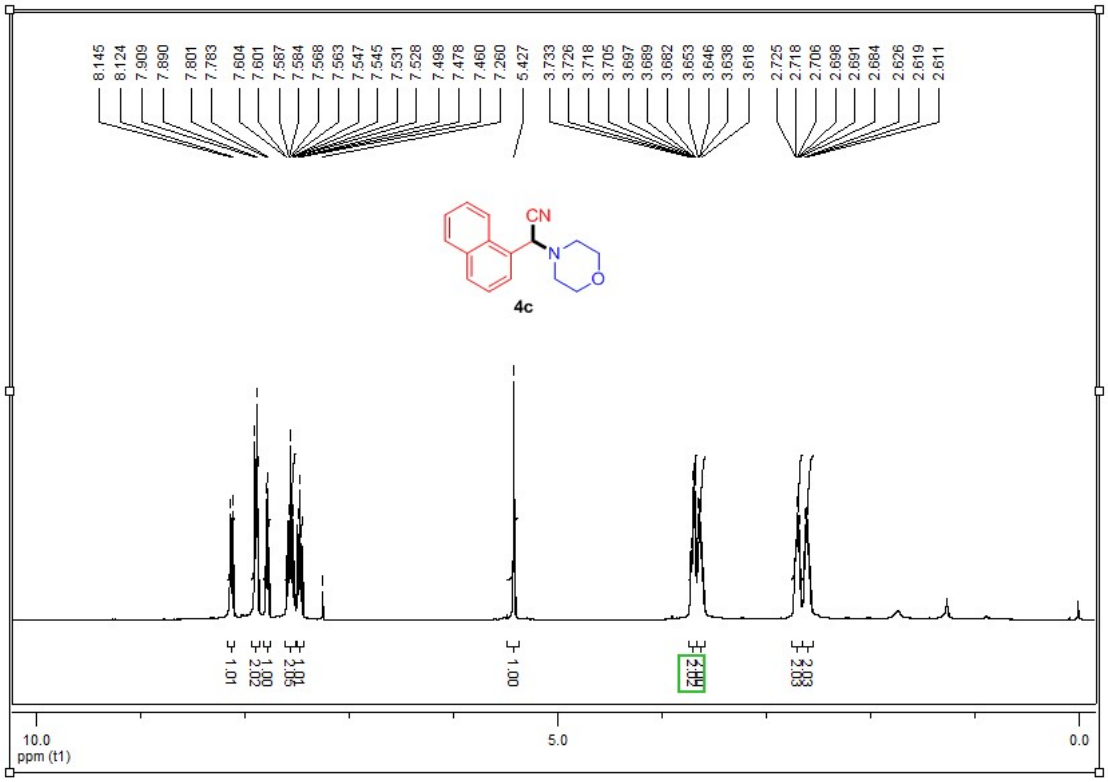
3.689
3.679
2.598
2.586
2.575
CN
N
O
4a
2.01
3.00
1.00
4.00
4.01
10.0
5.0
0.0
ppm (t1)


8.145
8.124
7.909
7.890
7.801
7.783
7.604
7.601
7.587
7.584
7.568
7.563
7.547
7.545
7.531
7.528
7.498
7.478
7.460
7.260
5.427
3.733
3.726
3.718
3.705
3.697
3.689
3.682
3.653
3.646
3.638
3.618
2.725
2.718
2.706
2.698
2.691
2.684
2.626
2.619
2.611
CN
N
O
4c
1.01
2.02
1.00
2.03
10.0
ppm (t1)
5.0
0.0

Crystallographic data for the product 3a and 4a:

(1) CCDC 1961175 contains the supplementary crystallographic data for the product **3a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

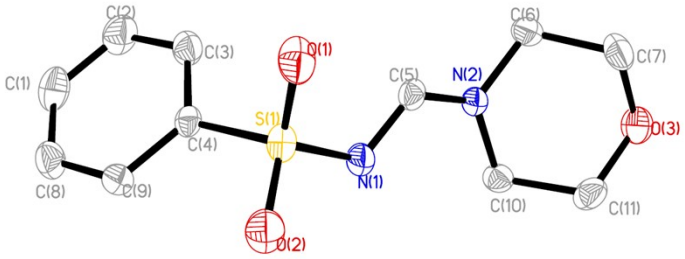


Table 1. Crystal data and structure refinement for 3a.

Empirical formula	C11 H14 N2 O3 S
Formula weight	254.30
Temperature	297(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pccn
Unit cell dimensions	a = 9.6000(5) A alpha = 90 deg. b = 31.4072(17) A beta = 90 deg. c = 7.9432(5) A gamma = 90 deg.
Volume	2394.9(2) Å ^{3}
Z, Calculated density	8, 1.411 Mg/m^3
Absorption coefficient	0.269 mm^{-1}
F(000)	1072
Crystal size	0.32 x 0.23 x 0.11 mm
Theta range for data collection	2.88 to 27.53 deg.
Limiting indices	-12<=h<=12, -40<=k<=40, -8<=l<=10
Reflections collected / unique	34779 / 2756 [R(int) = 0.1109]
Completeness to theta = 25.03	99.6 %
Max. and min. transmission	0.9711 and 0.9190
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2756 / 0 / 154
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0592, wR2 = 0.0997
R indices (all data)	R1 = 0.1127, wR2 = 0.1154

Largest diff. peak and hole	0.218 and -0.318 e.A^{-3}

(2) CCDC 2058393 contains the supplementary crystallographic data for the product **4a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

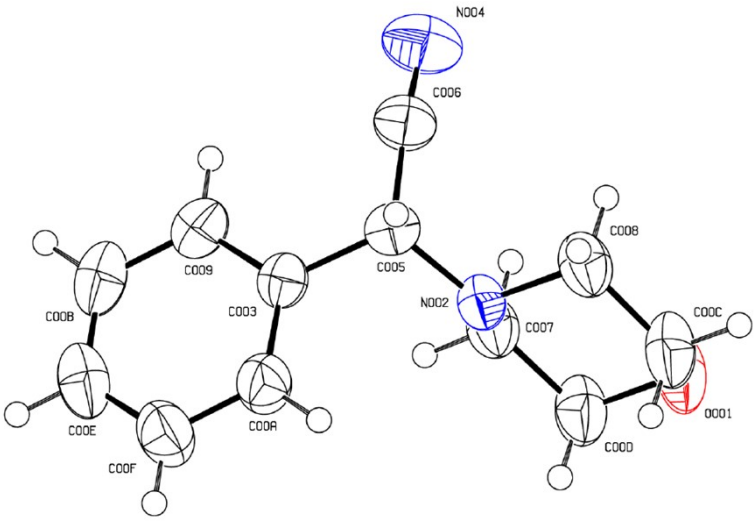


Table 1. Crystal data and structure refinement for 4a.

Empirical formula	C12 H14 N2 O
Formula weight	202.25
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pccn
Unit cell dimensions	a = 5.4098(6) A alpha = 83.534(9) deg. b = 10.0948(11) A beta = 83.027(9) deg. c = 10.8060(11) A gamma = 76.485(10) deg.
Volume	567.36(11) Å ^{3}
Z, Calculated density	2, 1.184 Mg/m^3
Absorption coefficient	0.077 mm^{-1}
F(000)	216
Crystal size	0.30 x 0.24 x 0.12 mm
Theta range for data collection	3.81 to 24.99 deg.
Limiting indices	-6<=h<=6, -11<=k<=10, -12<=l<=12
Reflections collected / unique	3698 / 1987 [R(int) = 0.0222]
Completeness to theta = 25.03	99.5 %

Max. and min. transmission	0.9711 and 0.9190
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1987 / 0 / 136
Goodness-of-fit on F^2	0.978
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.1387
R indices (all data)	R1 = 0.0691, wR2 = 0.1557
Largest diff. peak and hole	0.147 and -0.185 $e.A^{-3}$