SUPPORTING INFORMATION FOR

Synthesis of Sulfonimidamides from Sulfinamides by Oxidation with *N*-Chlorosuccinimide

Olga García Mancheño and Carsten Bolm*

Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, D-52056 Aachen, Germany

e-mail: Carsten.Bolm@oc.rwth-aachen.de

Table of Contents

General: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, CD_3OD or acetone-d_6 on a Varian Inova 400 or a Varian Mercury 300 spectrometer (400 and 100 MHz, and 300 and 75 MHz, respectively). Chemical shifts are given in ppm and spin-spin coupling constants, *J*, are given in Hz. Melting points were determined in open-end capillary tubes on a Büchi B-540 melting point apparatus and are uncorrected. Microanalyses were obtained with a Vario EL element analyzer. Mass spectra were acquired on a Varian MAT 212 spectrometer. IR spectra were taken on a Perkin-Elmer FT/IR 1760 and were recorded as KBr pellets or in solution. All reagents were purchased from commercial suppliers and used without further purification. Amide sodium salts were obtained upon treatment of the corresponding sulfonamide with NaH (1 equiv, 60% in mineral oil). Sulfinamides **1a-c** were prepared according to literature procedures from NH_2-free *p*-tolylsulfinamide **5** using *n*-BuLi and the corresponding anhydride,[1] or **1b** by reaction of *p*-tolylsulfinyl chloride with $BnNH_2$.

General procedure for the synthesis of sulfonimidamides 3:

To a stirring solution of sulfinamide **1** (1.0 mmol) and amine/amino salt (2.0-5.0 mmol) or H_2NCN (88.2 mg, 2.1 mmol) and *t*-BuOK (235.6 mg, 2.0 mmol) in dry acetonitrile

under argon at room temperature, NCS (160.3 mg, 1.2 mmol) was added. Once the starting material was consumed (monitored by TLC), the reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography.

***N*-(Benzoyl)-*p*-toluenesulfonimidoyl chloride (2a):**[2]

Pale yellow solid. Mp. 102-104 ºC (Lit.[2] mp. 105-106 ºC); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18-8.10 (m, 4H), 7.58 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.50-7.42 (m, 4H), 2.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9 (C=O), 146.9 (C), 140.2 (C), 134.2 (C), 133.3 (CH), 130.4 (2 x CH), 129.8 (2 x CH), 128.4 (2 x CH), 127.2 (2 x CH), 21.9 (CH_3); MS (EI+), *m/z* (relative intensity): 294 [M^+, 18], 258 [M^+-Cl, 5], 190 [$(M+H)^+$-Bz, 28], 155 [40], 105 [100].

***N*-(Benzoyl)-*N'*-(*p*-methylbenzenenesulfonyl)-*p*-toluenesulfonimidamide (3a):**

Following the general procedure, the reaction of sulfinamide **1a** with NCS and TsNHNa gave **3a** as a white solid (94%). Chromatography: gradient of ethyl acetate/pentane 1:4 to 1:1. Mp. >200 ºC (decomp.); ^{1}H NMR (400 MHz, acetone-d_6): δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 2.20 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ 173.1 (C=O), 142.6 (C), 141.5 (C), 141.0 (C), 139.8 (C), 136.7 (C), 131.5 (CH), 129.2 (2 x CH), 128.9 (2 x CH), 128.6 (2 x CH), 127.5 (2 x CH), 126.8 (2 x CH), 126.4 (2 x CH), 20.6 (CH_3), 20.5 (CH_3); IR (KBr): ν 3257, 1596, 1419, 1311, 1263, 1152, 1105, 1079, 1024 cm^{-1}; MS (ESI-), *m/z*: 427 [$(M-H)^-$]; Calcd. for $C_{21}H_{20}N_2O_4S_2 \cdot H_2O$: C, 56.48; H, 4.97 N, 6.27; found C, 56.31; H, 4.83; N, 5.90.

***N*-(Benzyl)-*N'*-(*p*-methylbenzenenesulfonyl)-*p*-toluenesulfonimidamide (3b):**

Following the general procedure, the reaction of sulfinamide **1b** with NCS and TsNHNa gave **3b** as a white solid (50%). Chromatography: gradient of ethyl acetate/pentane 1:4 to 1:1. Mp. 135-137 ºC; ^{1}H NMR (400 MHz, acetone-d_6): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.32-7.24 (m, 6H), 4.18 (AB system, *J* = 14.5 Hz, 1H), 4.12 (AB system, *J* = 14.5 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ 144.2 (C), 142.2 (C), 141.7 (C), 136.6 (C), 136.3 (C), 129.6 (2 x CH), 128.9 (2 x CH), 128.3 (CH), 128.0 (2 x CH), 127.5 (4 x CH), 126.5 (2 x CH), 46.1 (CH_2), 20.7 (CH_3), 20.6 (CH_3); IR (KBr): ν 3256, 1596, 1419, 1311, 1263, 1152, 1105, 1079 cm^{-1}; MS (EI+), *m/z* (relative intensity): 415 [$(M+H)^+$, 1], 309 [M^+-

NBn, 1], 138 [27], 106 [100]; Calcd. for $C_{21}H_{22}N_2O_3S_2$: C, 60.84; H, 5.35 N, 6.76; found C, 60.89; H, 5.28; N, 6.73.

***N*-[*tert*-Butoxycarbonyl)amino]-*N'*-(*p*-methylbenzenenesulfonyl)-*p*-toluenesulfonimidamide (3c):**

Following the general procedure, the reaction of sulfinamide **1c** with NCS and TsNHNa gave **3c** as a white solid (78%). Chromatography: gradient of ethyl acetate/pentane 1:1 to ethyl acetate. Mp. >147 ºC (decomp.); ^{1}H NMR (300 MHz, CD_3OD): δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (75 MHz, CD_3OD): δ 159.0 (C=O), 142.2 (C), 141.8 (C), 140.5 (C), 139.1 (C), 128.4 (2 x CH), 128.3 (2 x CH), 127.1 (2 x CH), 126.4 (2 x CH), 79.7 (C), 27.0 (3 x CH_3), 20.0 (CH_3); IR (KBr): ν 2979, 1646, 1299, 1152, 1091, 1050 cm^{-1}; MS (ESI-), *m/z*: 423 [$(M-H)^-$]; Calcd. for $C_{19}H_{24}N_2O_5S_2 \cdot 5/3H_2O$: C, 50.20; H, 6.06 N, 6.16; found C, 50.13; H, 5.71 N, 5.76.

***N*-(Benzoyl)-*N'*-(*p*-nitrobenzenesulfonyl)-*p*-toluenesulfonimidamide (3d):**

Following the general procedure, the reaction of sulfinamide **1a** with NCS and NsNHNa gave **3d** as a white solid (86%). Chromatography: gradient of dichloromethane/acetone 4:1 to 1:1. Mp. >240 ºC (decomp.); ^{1}H NMR (400 MHz, acetone-d_6): δ 7.90 (s, 4H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.28 (t, *J* = 8.5 Hz, 2H), 7.16-7.06 (m, 4H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ 172.8 (C=O), 150.1 (C), 148.8 (C), 142.5 (C), 140.2 (C), 136.7 (C), 131.3 (CH), 129.0 (2 x CH), 128.8 (2 x CH), 128.2 (2 x CH), 127.4 (2 x CH), 126.5 (2 x CH), 123.3 (2 x CH), 20.6 (CH_3); IR (KBr): ν 3103, 2924, 1605, 1531, 1325, 1152, 1048 cm^{-1}; MS (ESI-), *m/z*: 458 [$(M-H)^-$]; Calcd. for $C_{20}H_{17}N_3O_6S_2 \cdot 3/2\ H_2O$: C, 49.37; H, 4.14 N, 8.64; found C, 49.56; H, 4.05; N, 8.37.

***N*-(Benzoyl)-*N'*-(2-thiophenesulfonyl)-*p*-toluenesulfonimidamide (3e):**

Following the general procedure, the reaction of sulfinamide **1a** with NCS and ThphSO$_2$NHNa gave **3e** as a white solid (94%). Chromatography: gradient of dichloromethane/acetone 4:1 to 1:1. Mp. >230 ºC (decomp.); ^{1}H NMR (300 MHz, acetone-d_6): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.49 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.45-7.39 (m, 2H), 7.34-28 (br t, *J* = 7.4 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.83 (dd, *J* = 5.0, 3.7 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6): δ 173.5 (C=O), 145.8 (C), 142.8 (C), 139.8 (C), 136.8 (C), 131.6 (CH), 130.7 (CH), 130.1 (CH), 129.3 (2 x CH), 129.0 (2 x CH), 127.7 (2 x CH), 126.4 (2 x CH), 126.2 (CH), 20.5 (CH_3); IR (KBr): ν 1606, 1571, 1327, 1286, 1050 cm^{-1}; MS (ESI-), *m/z*: 419 [M^-];

Calcd. for $C_{18}H_{16}N_2O_4S_3 \cdot 4/3\ H_2O$: C, 48.63; H, 4.23 N, 6.30; found C, 48.86; H, 4.25; N, 6.01.

***N*-(Benzoyl)-*N'*-(*tert*-butylsulfonyl)-*p*-toluenesulfonimidamide (3f):**

Following the general procedure, the reaction of sulfinamide **1a** with NCS and BusNHNa gave **3f** as a white solid (50%) and sulfonimidoyl chloride **2a** (28%). Chromatography: gradient of dichloromethane/acetone 4:1 to 1:1. Mp. >200 ºC (decomp.); ^{1}H NMR (400 MHz, acetone-d_6): δ 8.11 (d, *J* = 8.2 Hz, 2H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.38-7.30 (m, 4H), 2.40 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, acetone-d_6): δ 173.0 (C=O), 142.7 (C), 141.0 (C), 136.9 (C), 131.5 (CH), 129.2 (2 x CH), 129.1 (2 x CH), 127.7 (2 x CH), 126.1 (2 x CH), 58.9 (C), 23.8 (3 x CH_3), 20.1 (CH_3); IR (KBr): ν 2929, 1598, 1556, 1346, 1100 cm^{-1}; MS (ESI-), *m/z*: 393 [$(M-H)^-$]; Calcd. for $C_{18}H_{22}N_2O_4S_2 \cdot 5/3H_2O$: C, 50.92; H, 6.01; N, 6.60; found C, 50.53; H, 5.69; N, 6.26.

***N*-(Benzoyl)-*N'*-(cyano)-*p*-toluenesulfonimidamide (3g):**

Following the general procedure, the reaction of sulfinamide **1a** with NCS, H_2NCN and *t*-BuOK gave **3g** as a white solid (85%). Chromatography: gradient of dichloromethane/acetone 4:1 to 1:1. Mp. >126 ºC (decomp.); ^{1}H NMR (300 MHz, acetone-d_6): δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.39-7.28 (m, 4H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6): δ 173.1 (C=O), 142.2 (C), 140.8 (C), 137.5 (C), 131.1 (CH), 129.1 (2 x CH), 129.0 (2 x CH), 127.6 (2 x CH), 126.6 (2 x CH), 116.0 (CN), 20.5 (CH_3); IR (KBr): ν 2183, 1603, 1567, 1328 cm^{-1}; MS (ESI-), *m/z*: 298 [$(M-H)^-$]; Calcd. for $C_{15}H_{13}N_3O_2S \cdot 5/3H_2O$: C, 54.70; H, 5.00 N, 12.76; found C, 54.31; H, 5.18; N, 13.02.

***N*-(Benzoyl)-*N'*-(phenyl)-*p*-toluenesulfonimidamide (3h):**[3]

Following the general procedure, the reaction of sulfinamide **1a** with NCS and aniline gave **3h** as a white solid (94%). Chromatography: gradient of ethyl acetate/pentane 1:10 to 1:4. Mp. 169-172 ºC (Lit.[3] mp. 173-174 ºC); ^{1}H NMR (400 MHz, acetone-d_6): δ 9.69 (br s, 1H, NH), 8.08 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.27-7.19 (m, 4H), 7.10-7.04 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ 171.4 (C=O), 144.1 (C), 136.6 (C), 136.1 (C), 131.9 (CH), 129.7 (2 x CH), 129.2 (2 x CH), 129.0 (2 x CH), 127.9 (2 x CH), 127.8 (2 x CH), 124.9 (CH), 121.5 (2 x CH), 20.6 (CH_3); IR (KBr): ν 3420, 1602, 1329, 1286, 954 cm^{-1}; MS (EI+), *m/z* (relative intensity): 350 [M^+, 63], 258

[M^+-NHPh, 81], 105 [100]; Calcd. for $C_{20}H_{18}N_2O_2S$: C, 68.55; H, 5.18 N, 7.99; found C, 68.60; H, 5.46; N, 8.11.

***N*-(Benzoyl)-*N'*,*N'*-(dimethyl)-*p*-toluenesulfonimidamide (3i):**

Following the general procedure, the reaction of sulfinamide **1a** with NCS and dimethylamine gave **3i** as a white solid (97%). Chromatography: gradient of ethyl acetate/pentane 1:4 to 1:1. Mp. 95-96 ºC; ^{1}H NMR (300 MHz, acetone-d_6): δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.50-7.41 (m, 4H), 2.84 (s, 6H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6): δ 171.4 (C=O), 144.0 (C), 136.5 (C), 133.0 (C), 131.8 (CH), 129.8 (2 x CH), 129.1 (2 x CH), 128.0 (2 x CH), 127.9 (2 x CH), 36.8 (2 x CH_3), 20.6 (CH_3); IR (KBr): ν 3015, 1636, 1454, 1283, 1142, 953 cm^{-1}; MS (EI+), *m/z* (relative intensity): 303 [M^+, 8], 259 [M^+-NMe_2, 40], 105 [100]; Calcd. for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 6.00 N, 9.26; found C, 63.66; H, 5.79; N, 9.24.

***N*-(Benzoyl)-*p*-toluenesulfonimidamide (3j):**[3]

Following the general procedure, the reaction of sulfinamide **1a** with NCS and hexamethyldisilazane gave **3j** as a white solid (89%). Chromatography: gradient of ethyl acetate/pentane 1:4 to 1:1. Mp. 137-138 ºC (Lit.[3] mp. 139-141 ºC); ^{1}H NMR (400 MHz, acetone-d_6): δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.42-7.35 (m, 4H), 7.20 (br s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ 171.7 (C=O), 143.4 (C), 139.8 (C), 136.4 (C), 131.6 (CH), 129.4 (2 x CH), 128.9 (2 x CH), 127.8 (2 x CH), 126.8 (2 x CH), 20.6 (CH_3); MS (EI+), *m/z* (relative intensity): 275 [$(M+H)^+$, 7], 197 [7], 108 [100].

General procedure for the cleavage of the *N*-benzoyl group:

To a solution of **3** (0.15 mmol) in MeOH (0.6 mL), a 10% HCl aq. solution (0.6 mL) was added at room temperature. The mixture was heated at 120 ºC in a sealed tube for 16 h. Saturated aqueous Na_2HCO_3 was added, extracted with CH_2Cl_2 (3 x 1 mL), dried over $MgSO_4$ and concentrated to dryness. The residue was purified by flash chromatography

***N*-(*p*-Toluenesulfonyl)-*p*-toluenesulfonimidamide (4):**[4]

Following the general procedure, the reaction of sulfonimidamide **3a** with 10% HCl solution in MeOH gave **4** as a white solid (73%). Chromatography: ethyl acetate/pentane 1:1. Mp. 164-165 ºC (Lit.[4] mp. 164-164.5 ºC); ^{1}H NMR (400 MHz,

acetone-d_6): δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.92 (br s, 2H, NH_2), 2.29 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ 143.8 (C), 142.0 (C), 141.7 (C), 139.3 (C), 129.4 (2 x CH), 128.8 (2 x CH), 126.8 (2 x CH), 126.4 (2 x CH), 20.6 (CH_3), 20.5 (CH_3); MS (EI+), *m/z* (relative intensity): 325 [$(M+H)^+$, 7], 308 [M^+-NH_2, 4], 261 [100], 154 [91] 108 [86].

***p*-Tolylsulfinamide (5):**[5,6]

Following the general procedure, the reaction of sulfonimidamide **3i** with 10% HCl solution in MeOH gave **5** as a white solid (87%). Chromatography: ethyl acetate/pentane 1:1. Mp. 113-114 ºC (Lit.[5] mp. 113 ºC); ^{1}H NMR (300 MHz, acetone-d_6): δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.47 (br s, 2H, NH_2), 2.41 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6): δ 142.4 (C), 141.6 (C), 129.3 (2 x CH), 126.0 (2 x CH), 20.4 (CH_3).

References

1. García-Ruano J, Alonso R, Zarzuelo MM, Noheda P: *Tetrahedron: Asymmetry*. 1995, **6:**1133-1142.

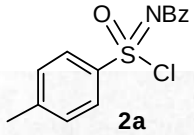
2. Levchenko ES, Berzina IN, Kirsanov AV: *Zh. Org. Khim.* 1965, **1:**1251-1255.

3. Leca D, Toussaint A, Mareau C, Fensterbank L, Lacôte E, Malacria M: *Org. Lett.* 2004, **6:**3573-3575.

4. Di Chenna PH, Robert-Peillard F, Dauban P, Dodd RH: *Org. Lett.* 2004, **6:**4503-4505.

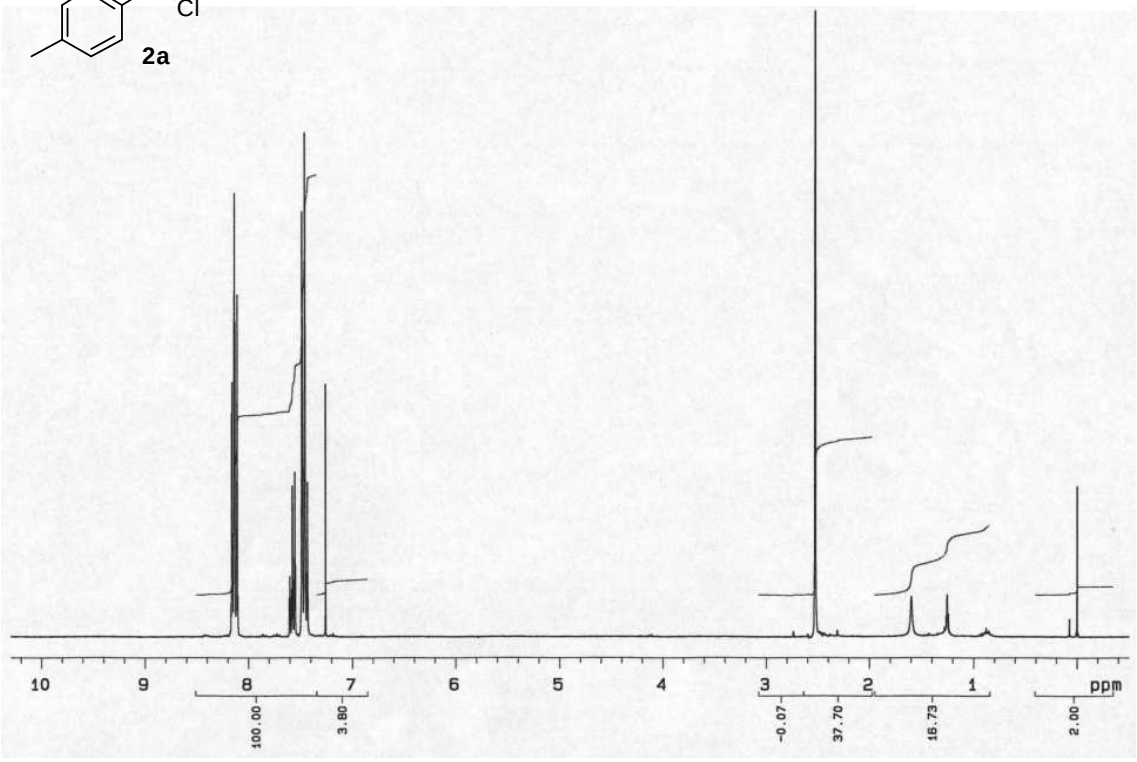
5. García Ruano JL, Alemán J, Fajardo C, Parra A: *Org. Lett.* 2005, **7:**5493-5496.

6. Davis FA, Zhang Y, Andemichae Y, Fang T, Fanelli DL, Zhang H: *J. Org. Chem.* 1999, **64:**1403-1406.

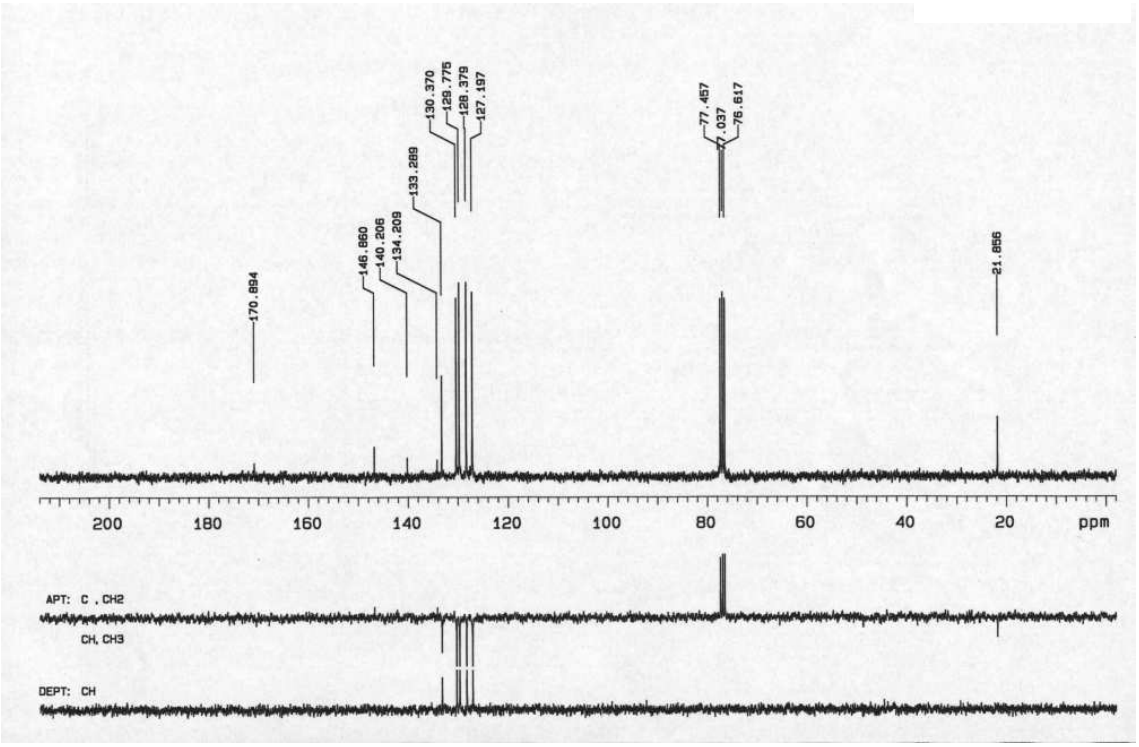


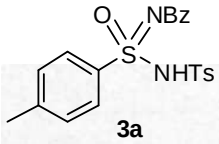
2a

300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

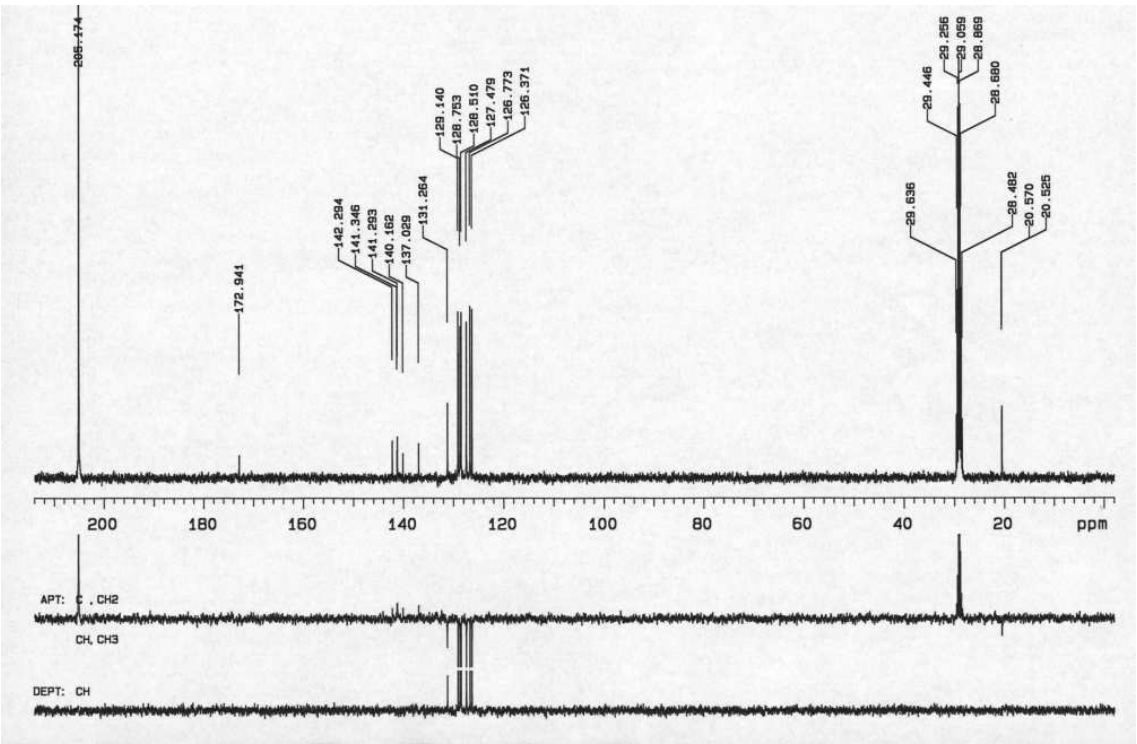




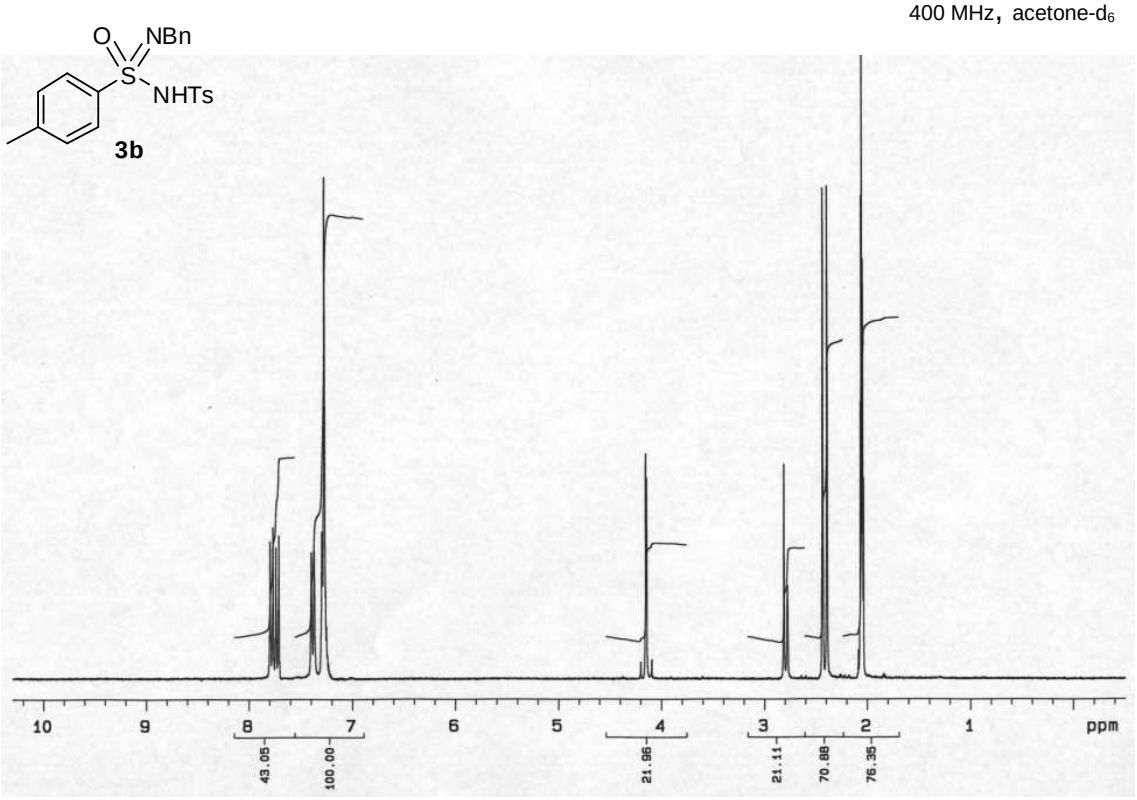
3a

400 MHz, acetone-d_6

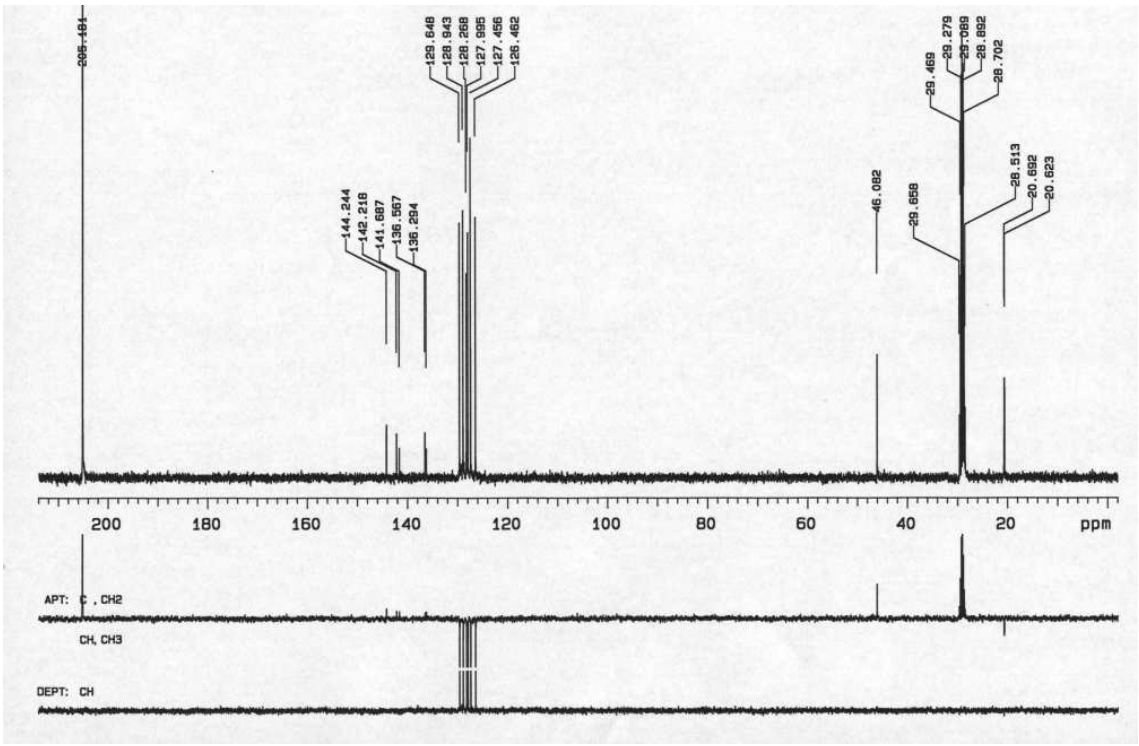
100 MHz, acetone-d_6

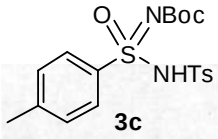


400 MHz, acetone-d_6



100 MHz, acetone-d_6

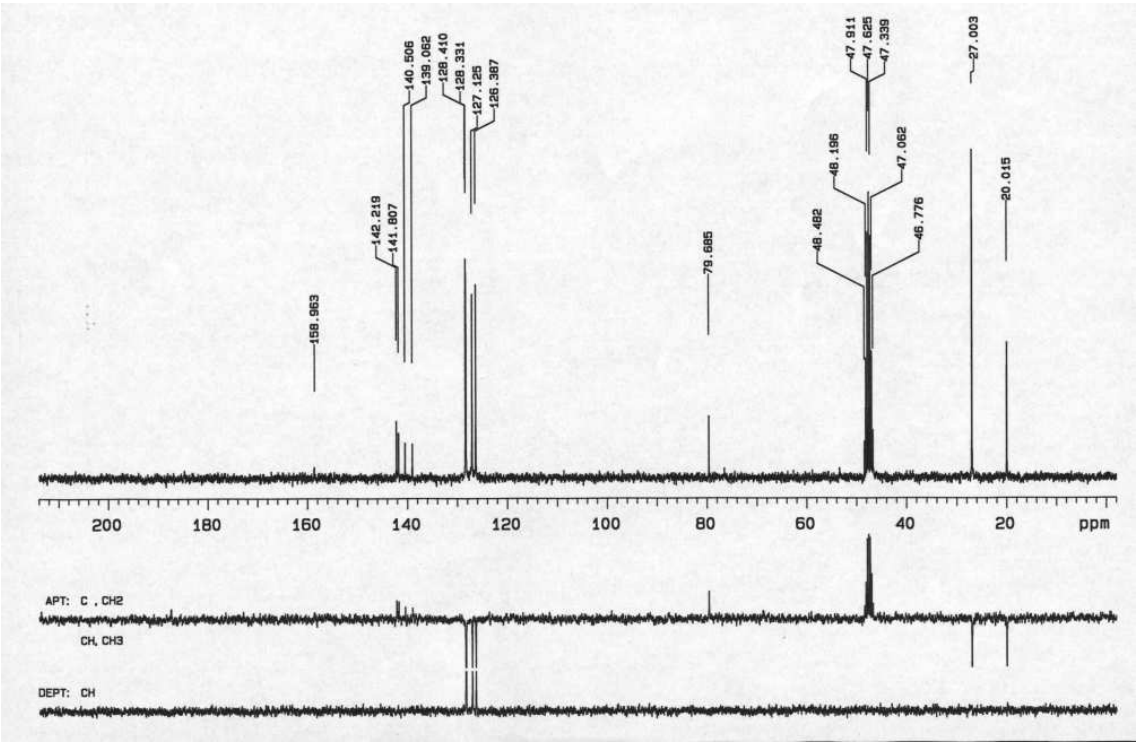




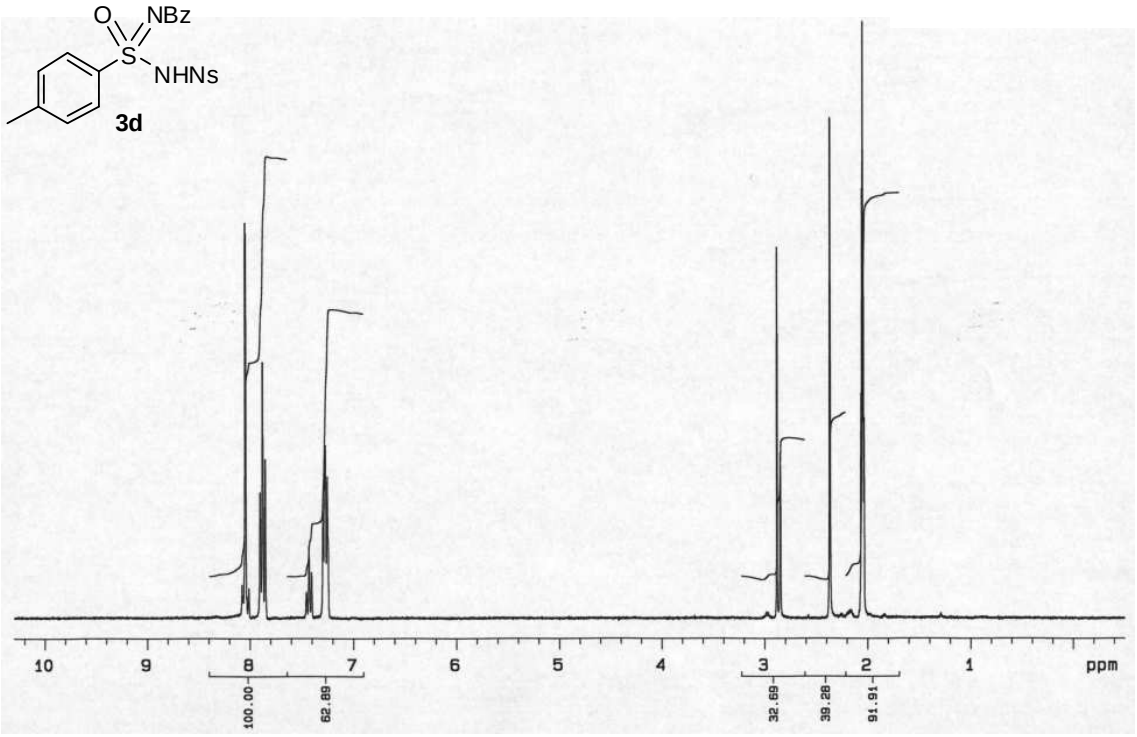
3c

300 MHz, CD_3OD

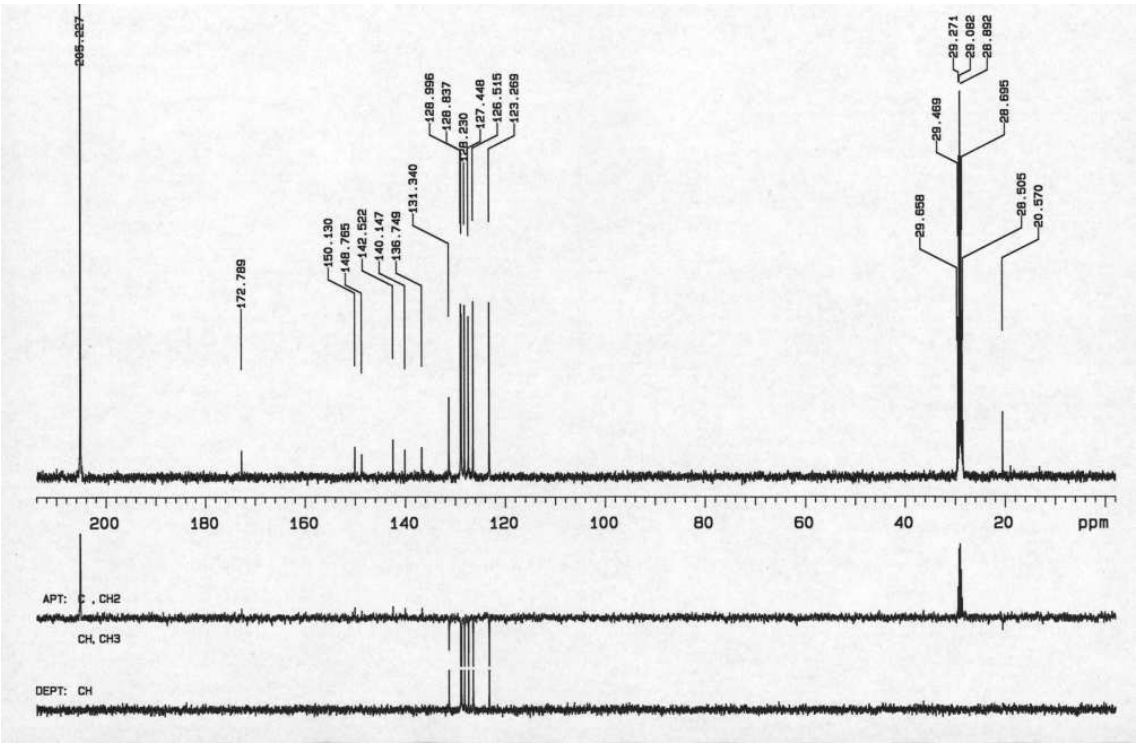
75 MHz, CD_3OD

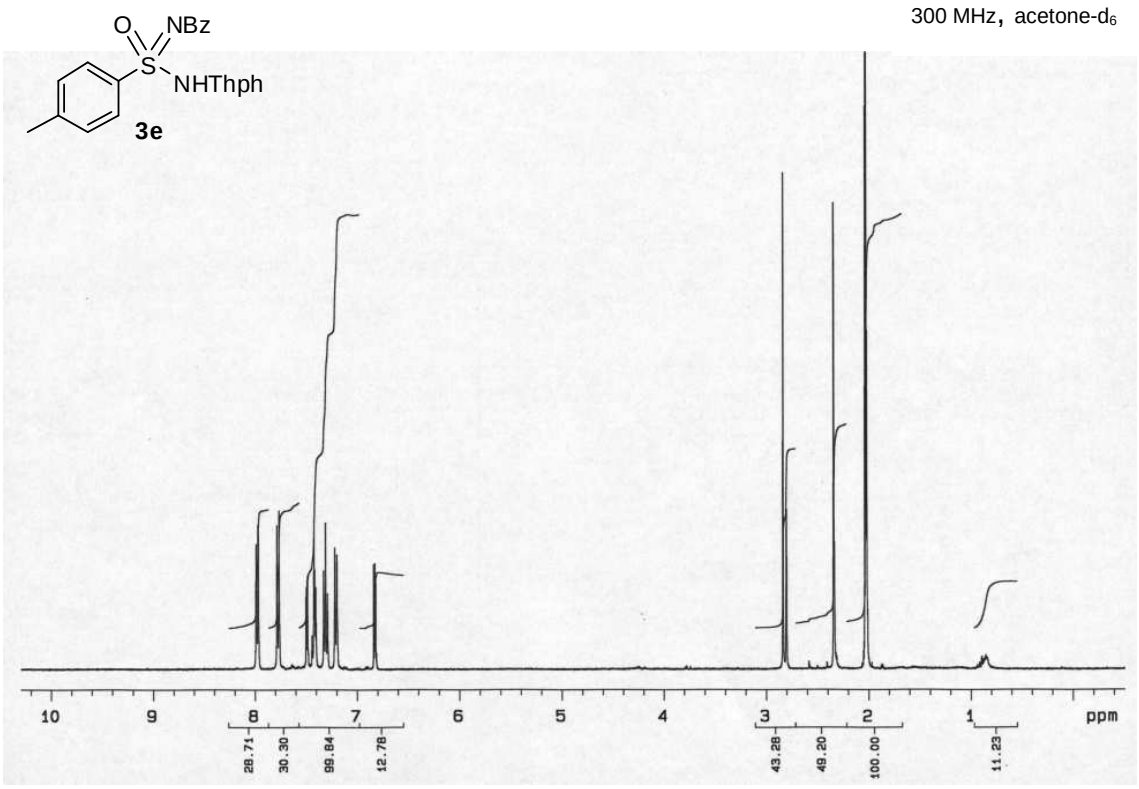


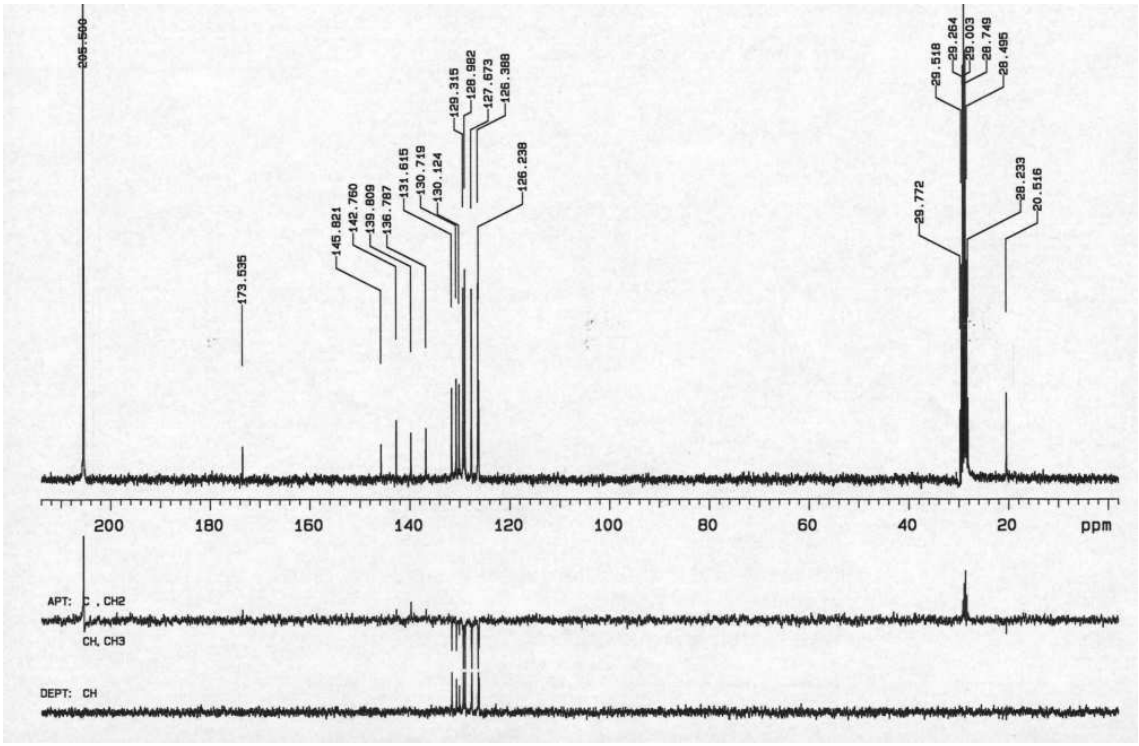
400 MHz, acetone-d_6

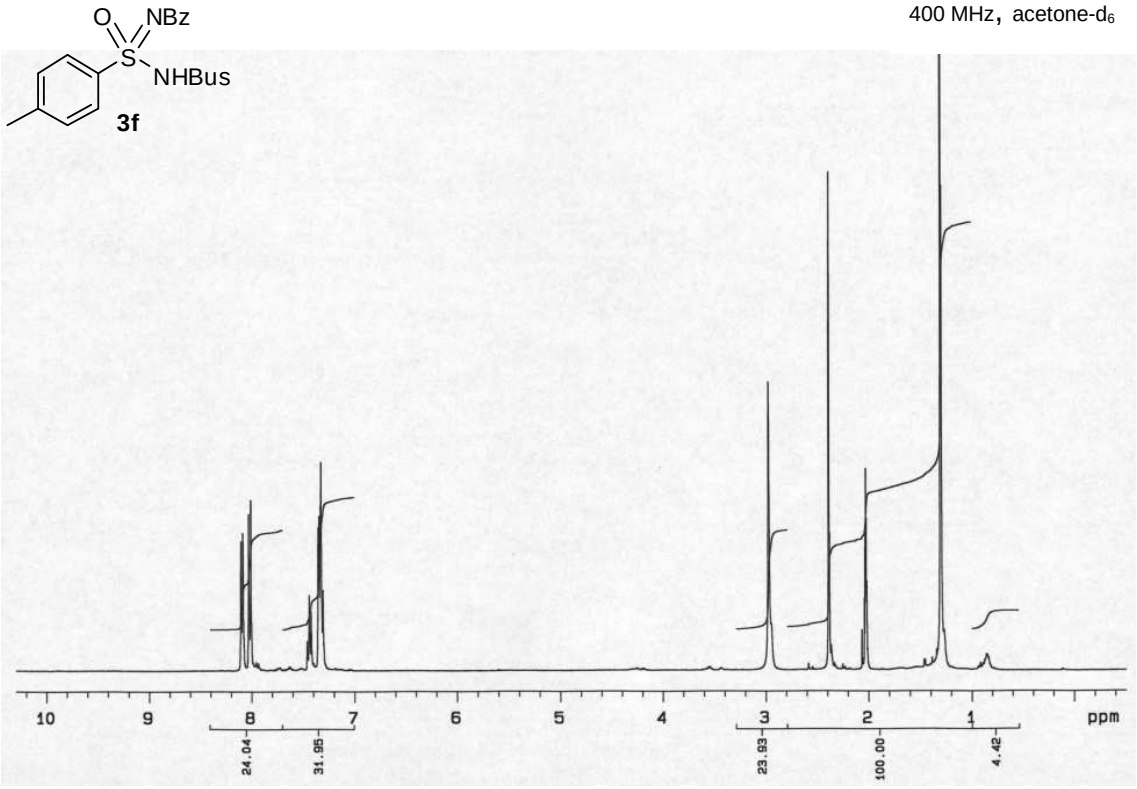


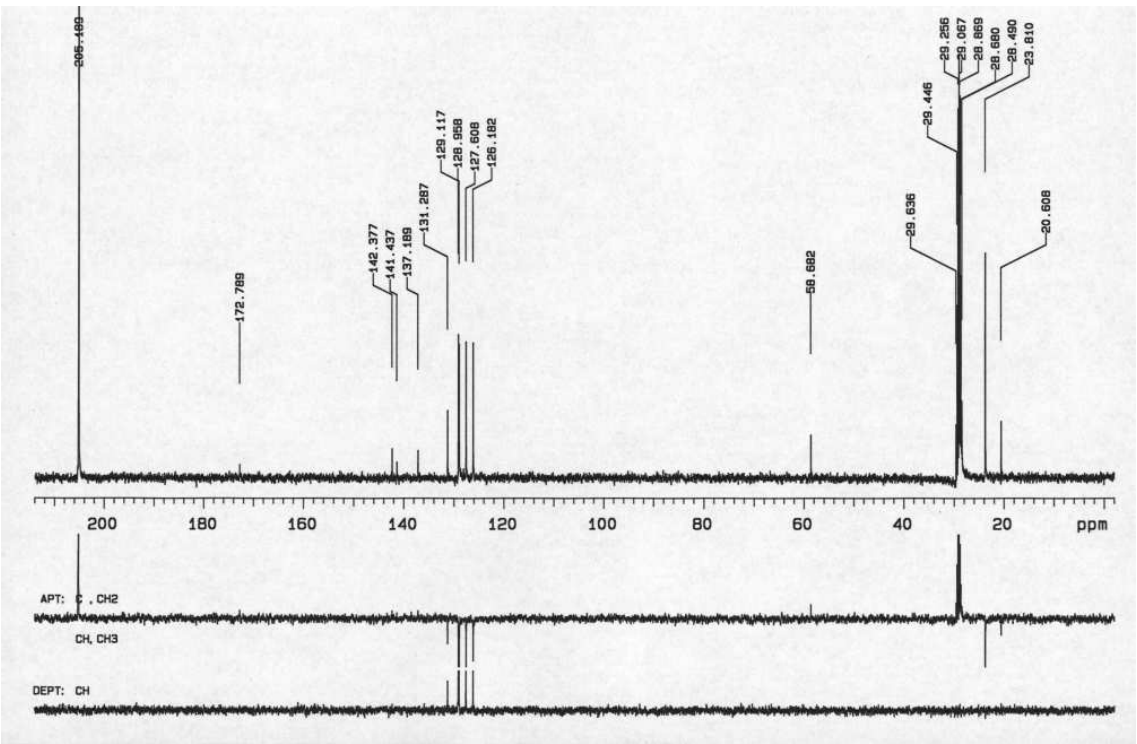
100 MHz, acetone-d_6

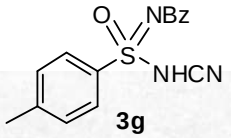



O
NBz
S
NHThph
3e
300 MHz, acetone-d6
10
9
8
7
6
5
4
3
2
1
ppm
28.71
30.30
99.84
12.78
43.28
49.20
100.00
11.23


75 MHz, acetone-d6
205.500
173.635
145.821
142.760
139.809
136.787
131.615
130.719
130.124
129.315
128.982
127.673
126.388
126.238
29.518
29.264
29.003
28.749
28.495
29.772
28.233
20.516
200
180
160
140
120
100
80
60
40
20
ppm
APT: C, CH2
CH, CH3
DEPT: CH

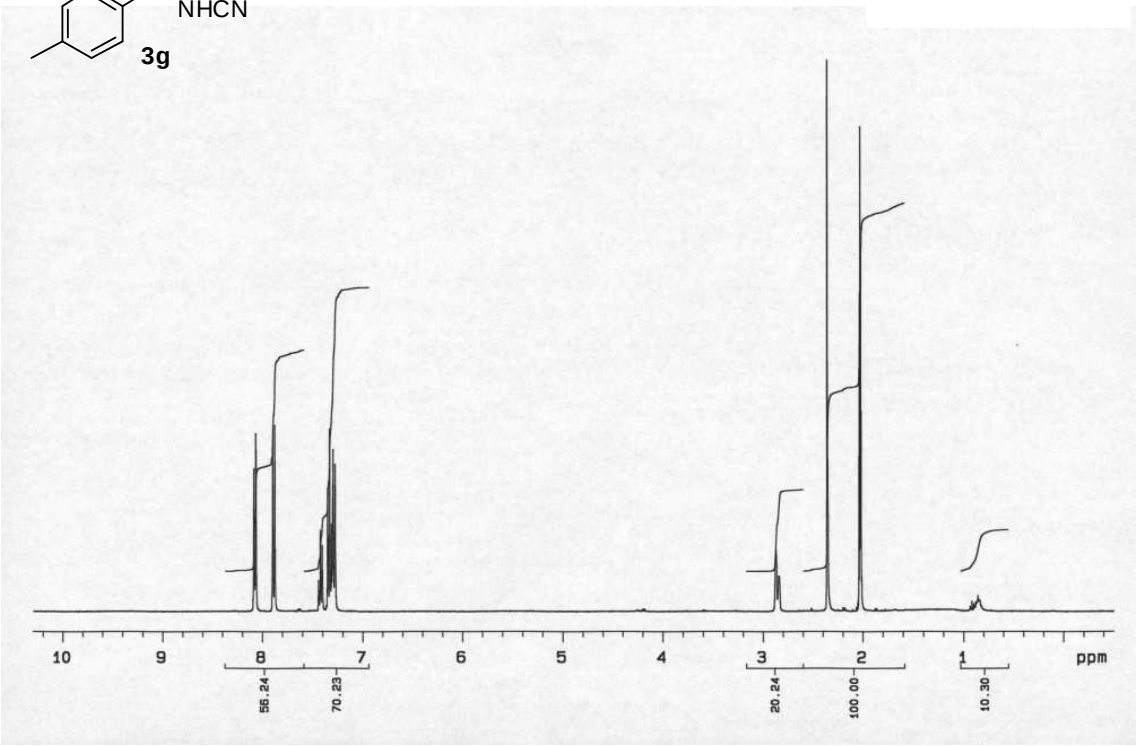

O
NBz
S
NHBus
3f
400 MHz, acetone-d6
10
9
8
7
6
5
4
3
2
1
ppm
24.04
31.95
23.93
100.00
4.42


100 MHz, acetone-d6
206.189
172.788
142.377
141.437
137.189
131.287
129.117
128.958
127.608
126.182
58.682
29.636
29.446
29.256
29.067
28.869
28.660
28.490
23.810
20.608
200
180
160
140
120
100
80
60
40
20
ppm
APT: C , CH2
CH, CH3
DEPT: CH

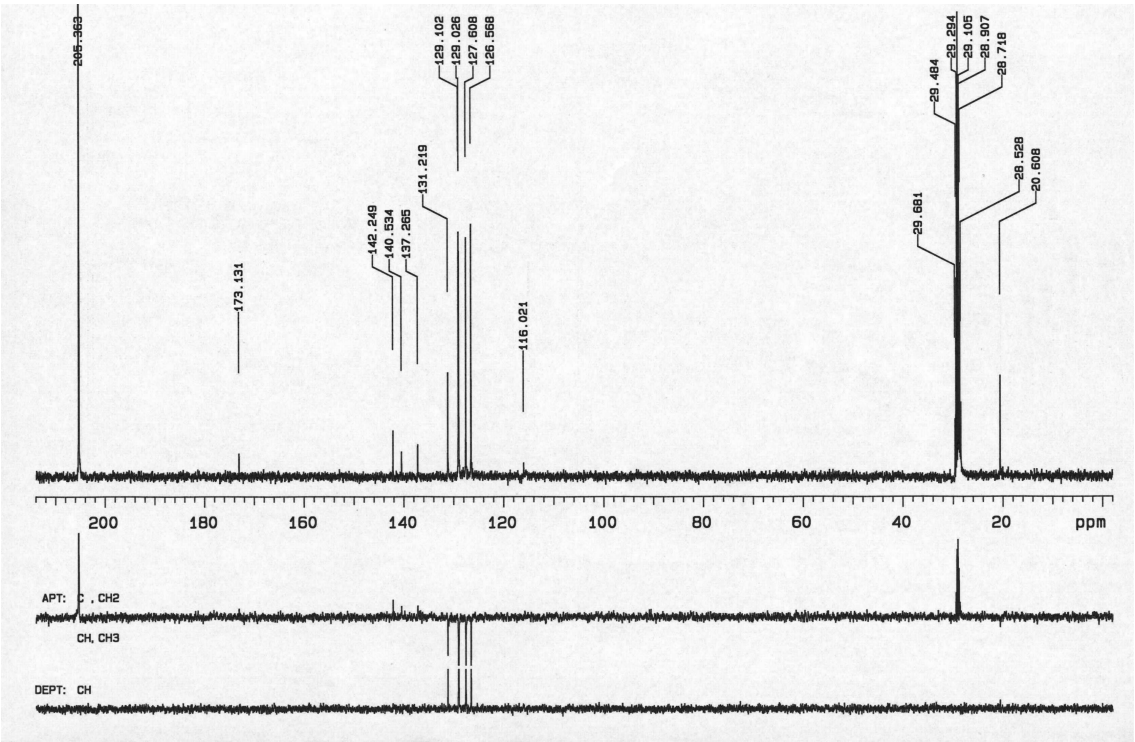


3g

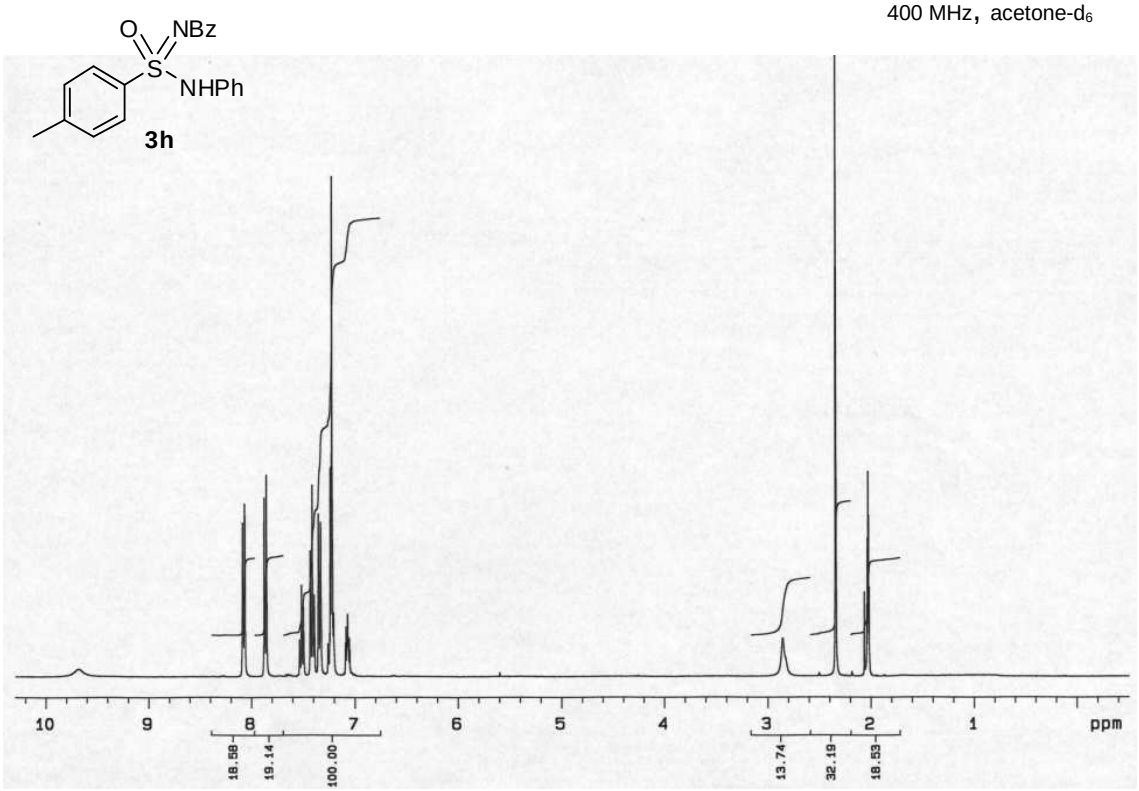
300 MHz, acetone-d_6



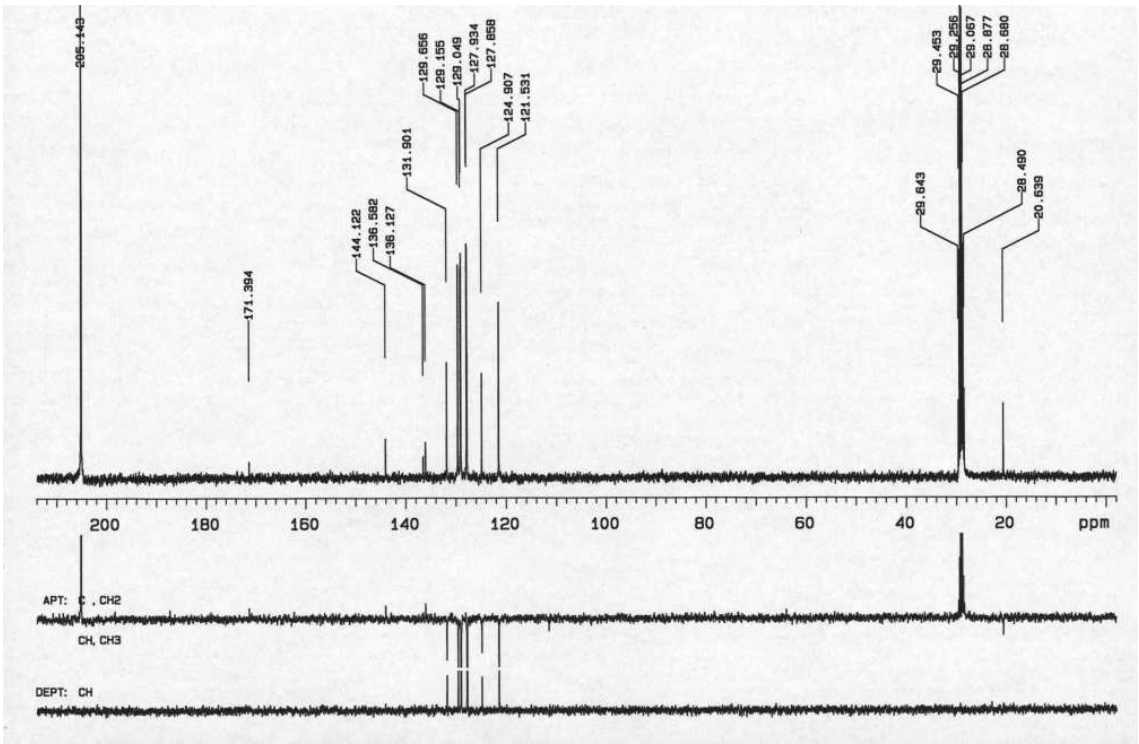
75 MHz, acetone-d_6

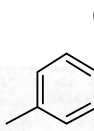


400 MHz, acetone-d_6



100 MHz, acetone-d_6

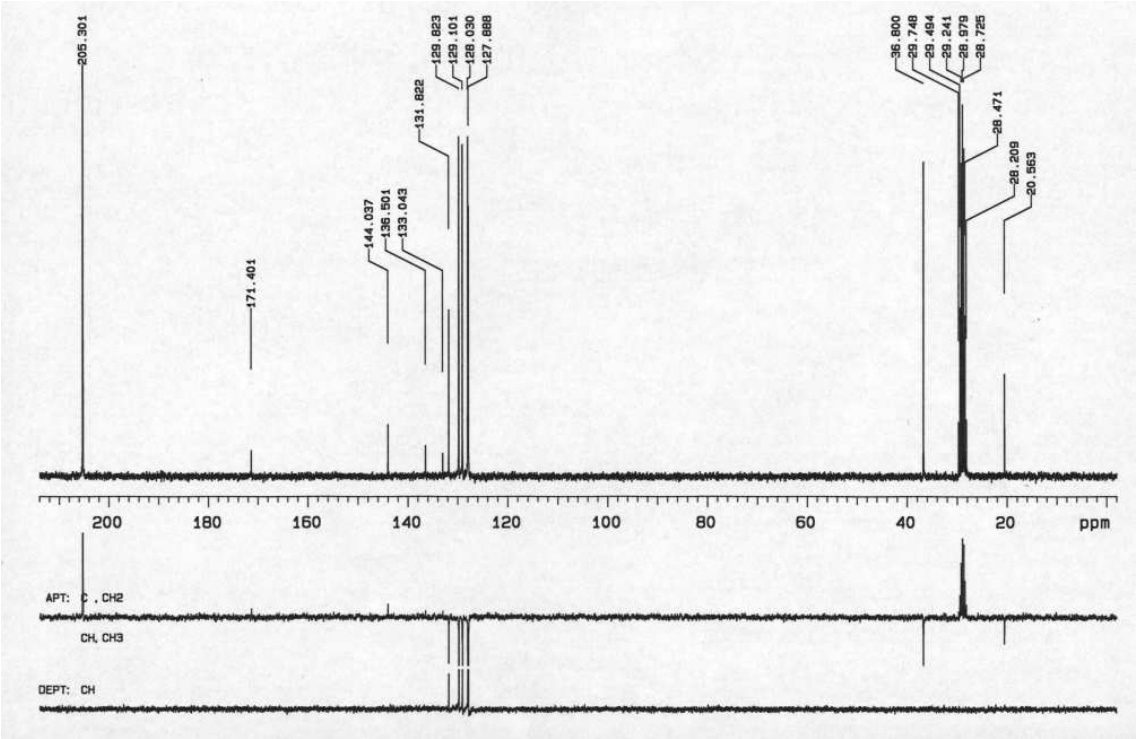


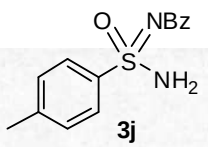


3i

300 MHz, acetone-d_6

75 MHz, acetone-d_6

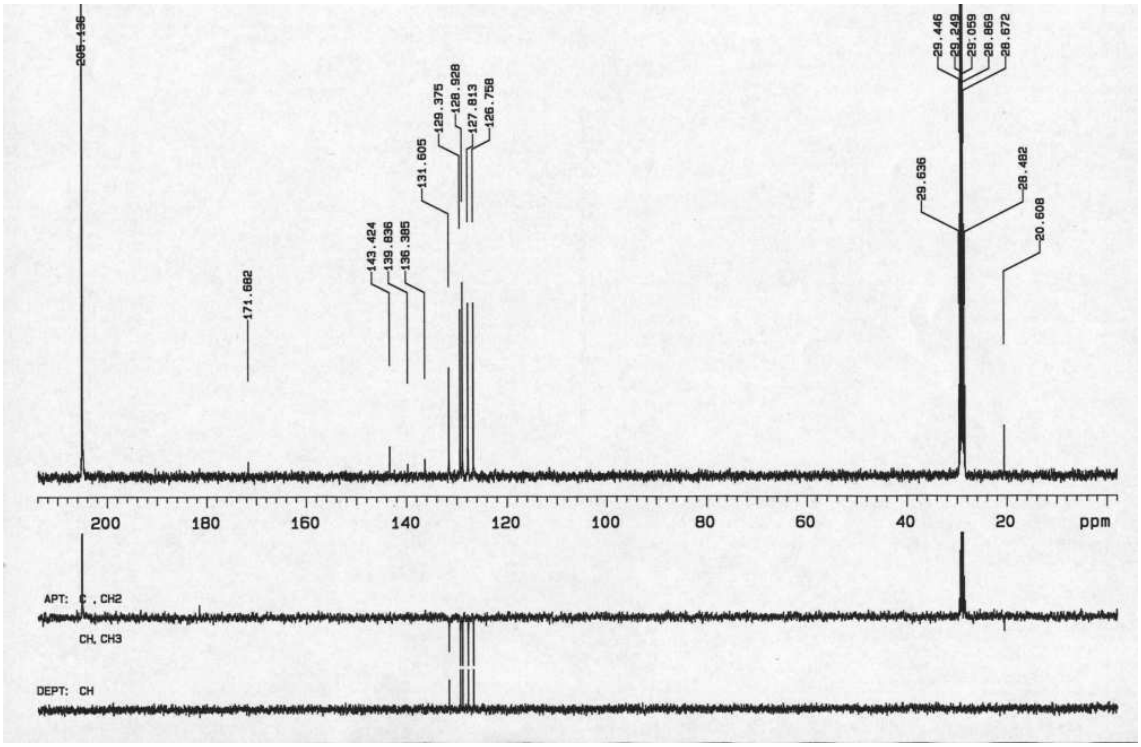


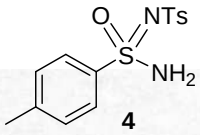


3j

400 MHz, acetone-d_6

100 MHz, acetone-d_6

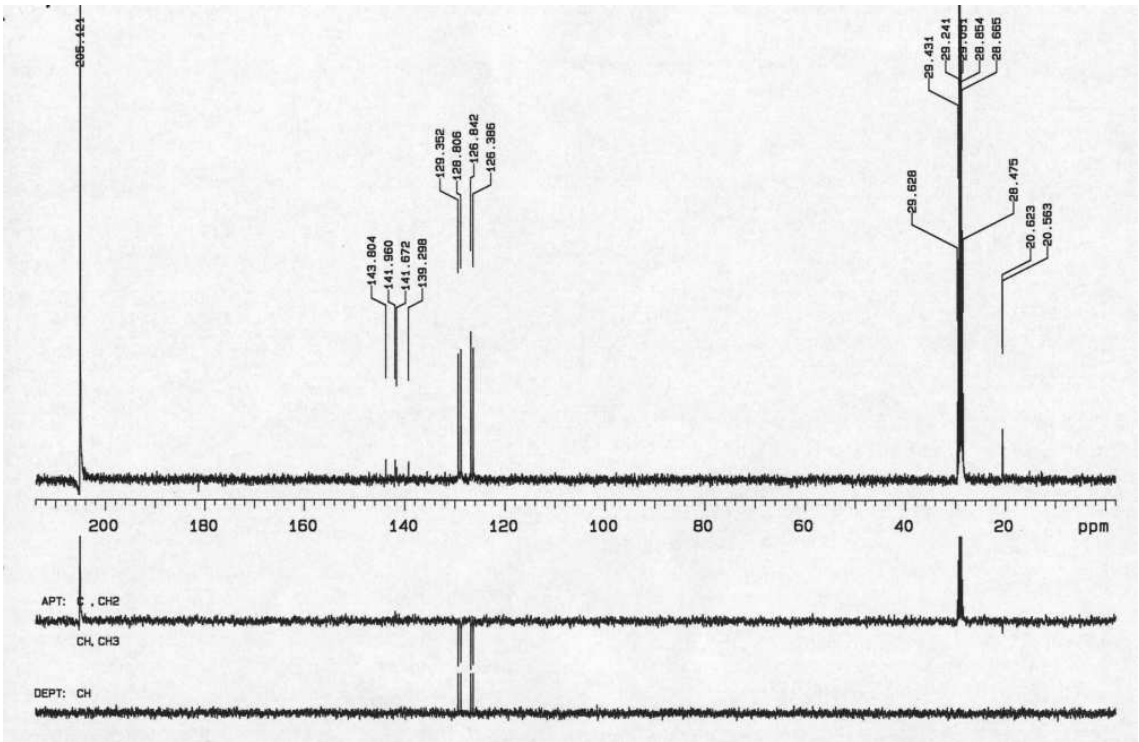


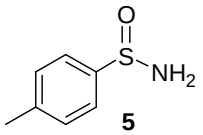


4

400 MHz, acetone-d_6

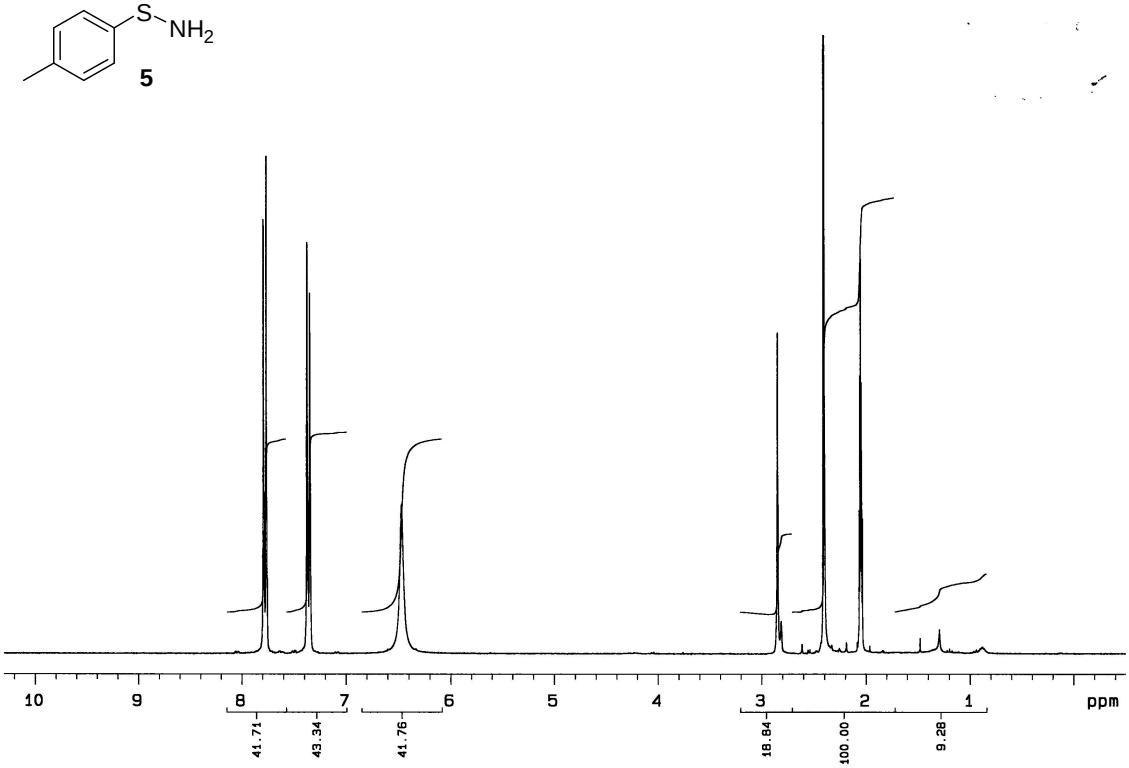
100 MHz, acetone-d_6





5

300 MHz, acetone-d_6



75 MHz, acetone-d_6