Supporting Information for

A General Method for the Preparation of *N*-Sulfonyl Aldimines and Ketimines.

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Experimental section.

General Methods.

^{1}H NMR and ^{13}C NMR spectra were acquired at 200 or 300 MHz at 75 or 100 MHz respectively. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 and 77.0 ppm). Mass spectra (MS) were determined at ionizing voltage of 70 eV. All reactions were carried out in anhydrous solvents and under argon atmosphere. THF and CH_2Cl_2 were distilled from sodium-benzophenone and P_2O_5 respectively. Flash column chromatography was performed using silica gel Merk-60 (230-400 mesh). All reagents were purchased from Aldrich. MP-carbonate resin was purchased from Argonaut.

Methyl 4-methylphenylsulfinate (9).[1] Over a solution of *p*-tolyldisulfure **8** (0.08 mol, 20 g) in MeOH (200 mL), NBS (0.12 mol) was slowly added at room temperature. The reaction mixture was stirred for 10 min., whereupon it was diluted with CH_2Cl_2 (200 mL), and washed several times with $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4, the solvent eliminated, to obtain a colourless oil in quantitative yield. ^{1}H NMR (300 MHz): δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 3.42 (s, 3H), 2.38 (s, 3H).

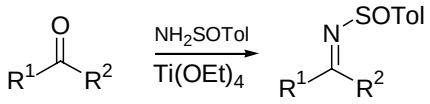
***p*-Toluenesulfinamide (2).**[2] Over a solution of methyl *p*-tolylsufinate (**9**) (0.058 mol, 10 g) in THF (150) mL at –78 ºC, 88 mL a 1M solution of LHMDS (88 mmol) in THF were added. Then, the temperature was elevated to rt and the reaction mixture stirred for 2h, whereupon it was quenched with 50 mL a sat. solution of saturated NH_4Cl and stirred for 1 h. The reaction was extracted with AcOEt (2x100 mL), dried over anhydrous Na_2SO_4, and the solvent was eliminated. The obtained brown solid was crystallized from hexane, obtaining sulfonamide **2**, as a yellow solid in 92% yield;

1 Brownbridge, P.; Jowett, I. C. *Synthesis* **1987**, 252.
2 Davis, F. A.; Zhang, Y.; Andemichae, Y.; Fang, T.; Fanelli, D. L.; Zhang, H. *J. Org. Chem.* **1999**, *64*, 1403.

mp:113 ºC (Lit. 113 ºC); ^{1}H NMR (200 Mhz): δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 2H), 4.58 (bs, 2H), 2.38 (s, 3H).

General Procedure for Synthesis of Racemic p-*Tolylsulfinimines.*

p-Tolylsulfinimines **4a**, **4b**, **4f**, were prepared as following Davis´ procedure.[2] The rest of sulfinylimines of Table 1 were prepared as follows:



In a 50 mL two-neck round-bottomed flask fitted with a condenser, septum, argon inlet, and magnetic stirring bar were charged with racemic *p*-toluensulfonamide (**2)** 200 mg (1.30 mmol), the corresponding aldehyde (1.30 mmol) or ketone (6.50 mmol) in 20 mL of CH_2Cl_2, and $Ti(OEt)_4$ (5.2 mmol). The solution was heated under reflux and monitored by TLC. When the reaction was finished 5 mL, of MeOH were added, and some drops of $NaHCO_3$, until precipitation of the titanium salts. Then it was filtered through anhydrous Na_2SO_4, washed with EtOAc, and the organic layer concentrated.. The crude was chromatographied (eluent indicated in each case) to obtain the corresponding *p*-tolylsulfinimine **4c-t**.

***N*-(Naphthalen-2-ylmethylidene)-*p*-toluenesulfinamide (4c).**[3] Reaction time: 12h; Yield: 94%. Flash chromatography; 1:3 (EtOAc/hexane). Yellow solid; mp: 86-88 ºC; (Lit. 86-88 ºC); ^{1}H NMR (200 MHz): δ 9.35 (s, 1H), 8.98 (d, *J* = 7.9 Hz, 1H), 8.07-7.88 (m, 4H), 7.72-7.51 (m, 4H), 7.32 (d, *J* = 8.3 Hz, 2H), 2.39 (s, 3H).

***N*-(*o*-Bromobenzylidene)-*p*-toluenesulfinamide (4d).**[4] Reaction time: 10h; Yield: 91%; Flash chromatography; 1:4 (EtOAc/hexane). Yellow solid; mp: 104-105 ºC (Lit.

3 García Ruano, J. L.; Alemán, J.; Soriano, F.J. *Org. Lett*. **2004**, *5*, 677.

104-106 ºC); ^{1}H NMR (300 MHz): δ 9.15 (s, 1H), 8.03 (d, *J* = 9.6 Hz, 1H), 7.65-7.62 (m, 3H), 7.38-7.28 (m, 4H), 2.39 (s, 3H).

***N*-(*p*-Nitrilebenzylidene)-*p*-toluenesulfinamide (4e).**[3] Reaction time: 10h; Yield: 81%. Flash chromatography; 1:2 (EtOAc/hexane). White solid; mp: 158-160 ºC (Lit. 159-160 ºC); ^{1}H NMR (300 MHz): δ 8.76 (s, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 2.40 (s, 3H).

***N*–α–Phenyl-(benzylidene)-*p*-toluenesulfinamide (4j).**[4] Reaction time: 8h; Yield: 79%. Flash chromatography; 1:3 (EtOAc/hexane). White solid; ^{1}H NMR (300 MHz): δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.70–7.10 (m, 10H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.40 (s, 3H).

***N*–α–Methyl-(benzylidene)-*p*-toluenesulfinamide (4k).**[6] Reaction time: 10h; Yield: 78%. Flash chromatography; 1:4 (EtOAc/hexane). White solid. mp: 103.5-140.5 ºC (Lit. 104-105 ºC); ^{1}H NMR (200 MHz): δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.36-7.20 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.72 (s, 3H), 2.38 (s, 3H).

***N*–α–Methyl-(4-methoxybenzylidene)-*p*-toluenesulfinamide (4l).**[5] Reaction time: 36h; Yield: 73%. Flash chromatography; 1:3 (EtOAc/hexane). White solid. mp: 91-92 ºC (Lit. 91.5-92.5 ºC); ^{1}H NMR (200 MHz): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 2.73 (s, 3H), 2.39 (s, 3H).

***N*–α–Methyl-(4-nitrilebenzylidene)-*p*-toluenesulfinamide (4m).** Reaction time: 8h; Yield: 77%. Flash chromatography; 1:4 (EtOAc/hexane).White solid; mp: 141-142 ºC; IR (NaCl): 2960, 2242, 1610, 1597, 1556, 1097 cm^{-1}; ^{1}H NMR (300 MHz): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.71-7.65 (m, 4H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.78 (s, 3H), 2.39 (s, 3H);

4 Annunziata, R.; Cinquini, M.; Cozzi, F. *J. Chem. Soc. Perkin Trans I* **1982**, *2*, 339.
5 Davis, F. A.; Lee, S.; Zhang, H. ; Fanelli, D. L. *J. Org. Chem.* **2000**, *65*, 8704.

^{13}C NMR (75 MHz): δ 171.5, 142.6, 142.1, 141.8, 132.1 (2C), 129.9 (2C), 127.8, 125.1, 117.9, 114.9, 21.4, 19.9; MS (FAB) *m/z* 283 (M+1, 11), 282 (54), 153 (49), 139 (100), 135 (35); HRMS [M+1]: Calcd. for $C_{16}H_{15}N_2OS$: 283.0905; found, 283.0900.

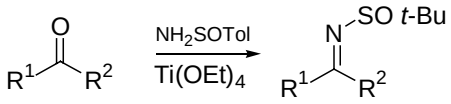
(1,2,2-Trimethylpropylidene)-*p*-toluenesulfinamide (4n).[6] Reaction time: 6h; Yield: 48%. Flash chromatography; 1:6 (EtOAc/hexane). Colorless oil; ^{1}H NMR (300 MHz): δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.41 (s, 3H), 2.32 (s, 3H), 1.14 (s, 9H).

(1,2-Dimethylpropylidene)-*p*-toluenesulfinamide (4o). Reaction time: 4h; Yield: 65%. Flash chromatography; 1:1 (EtOAc/hexane). Colorless Oil; IR (NaCl): 2970, 2929, 1615, 1462, 1098 cm^{-1}; ^{1}H NMR (300 MHz): δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.55 (sept, *J* =6.9 Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 1.11 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz): δ 186.6, 143.3, 141.5, 129.6, 125.0, 40.8, 21.3, 20.6, 19.3, 19.2.

***N*-(*S*)-*p*-Tolylsulfinylaldimine of (1*S*, 2*R*)-2-(*tert*-Butyldiphenylsililoxy)methyl-1-formylciclopropane (4t).**[6] Reaction time: 12h; Yield: 65%. Flash chromatography; 1:3 (EtOAc/hexane). Colorless Oil; $[\alpha]_D^{20}$ +276.2 (c=0.66, $CHCl_3$): IR (NaCl): 2956, 2857, 1607, 1427, 1109 cm^{-1}; ^{1}H NMR (300 MHz): δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.68-7.62 (m, 4H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.42-7.39 (m, 6H), 7.26 (d, *J* = 8.3 Hz, 2H), 3.93 (dd, *J* = 11.4, 6.0 Hz 1H), 3.63 (dd, *J* = 11.4, 8.1 Hz, 1H), 2.38 (s, 3H), 2.10-2.05 (m, 1H), 1.75-1.65 (m, 1H), 1.25-1.20 (m, 2H), 1.04 (s, 9H); ^{13}C NMR (75 MHz): δ 167.5, 142.3, 141.4, 133.7, 129.7, 127.8, 127.7, 124.5, 63.0, 26.8, 24.9, 22.2, 21.4, 19.1, 13.3.

*Synthesis of N-t-butanesulfinyl aldimines and ketimines **5***

Sulfinilimines **5a**, **5p**, **5g** were prepared following Ellman´s procedure.[7] The rest of sulfinylimines of Table 2 were prepared as follows.



In a 50 mL two-neck round-bottomed flask fitted with a condenser, septum, argon inlet, and magnetic stirring bar was charged with racemic *t*-Butylsulfonamide (**3**) 200 mg (1.30 mmol), the corresponding aldehyde (1.30 mmol) or ketone (1.4 mmol) in of CH_2Cl_2 (20 mL), and finally $Ti(OEt)_4$ (2.6 mmol) was added. The solution was heated under reflux and monitored by TLC. When the reaction was finished 5 mL of MeOH and some drops of $NaHCO_3$ were added, until precipitation of the titanium salts. Then it was filtered through a short pad of anhydrous Na_2SO_4, washed with EtOAc, and the organic layer concentrated. The crude was chromatographied (eluent indicated in each case), to obtain the corresponding *t*-Butylsulfinimine **5a-u**.

***N*–α–Methyl-(4-methoxybenzylidene)-*t*-butanesulfinamide (5l).** Under the above described conditions sulfinilimine **5l** was obtained in 30% yield. This yield could be improved using 5.85 mmol of $Ti(OEt)_4$, 2.6 mmol of the corresponding ketone and 1.3 mmol of sulfonamide **3**. Reaction time: 20 h; Yield: 62%. Flash chromatography; 1:2 (EtOAc/hexane). Colorless oil; IR (NaCl): 2963, 1591, 1562, 1257. 1055 cm^{-1}; ^1H NMR (300 MHz): δ 7.88 (d, *J* = 9.1 Hz, 2H); 6.90 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 3H), 2.72 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (75 MHz): δ 162.5, 129.2, 128.4, 128.1, 113.7, 57.1, 55.4, 22.4, 22.1, 19.6.

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6 The corresponding aldehyde **1t** was synthesized as described by: Kazuta, Y.; Matsuda, A.; Shuto, S. *J. Org. Chem.* **2002**, *67*, 1669.

7 Ellman: Liu, G.; Cogan, D.A.; Owens, T. D.; Tang, T. P.; Ellman, J. A. *J. Org. Chem.* **1999**, *64*, 1278.

***N*–α–Methyl-(4-nitrilebenzylidene)-*t*-butanesulfinamide (5m).** Reaction time: 4 h; Yield: 73%. Flash chromatography; 1:2 (EtOAc/hexane). Colorless oil; IR (NaCl): 2925, 2230, 1610, 1598, 1064 cm^{-1}; ^{1}H NMR (300 MHz): δ 7.94 (d, *J* = 8.6 Hz, 2H); 7.72 (d, *J* = 8.6 Hz, 2H), 2.78 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (75 MHz): δ 178.6, 141.6, 132.4, 128.3, 117.8, 116.1, 59.5, 29.6, 23.9.

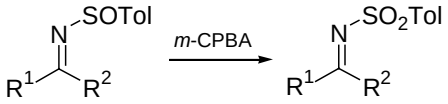
***N*-(1-Methylpropylidene)-*t*-butanesulfinamide (5r).** Reaction time: 24 h; Yield 73%. This compound was obtained as a Z/E mixture of isomers (1:4). Colorless oil; *E isomer*: ^{1}H NMR (300 MHz): δ 2.31 (q, *J* = 7.5 Hz, 2H), 2.21 (s, 3H), 1.14 (s, 9H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz): δ 185.6, 182.4, 55.8, 36.2, 29.3, 21.7, 9.4; *Z isomer*: ^{1}H NMR (300 MHz): δ 2.31 (q, *J* = 7.5 Hz, 2H), 2.07 (s, 3H), 1.14 (s, 9H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz): δ 182.4, 55.8, 36.2, 29.3, 22.3, 13.7.

***N*-[1-(1-Pyridineethylidine)-*t*-butanesulfonamide (5s).** Reaction time: 18 h; Yield: 58%; colourless oil; IR (NaCl): 3473, 2962, 1609, 1579, 1566, 1072 cm^{-1}; ^{1}H NMR (300 MHz): δ 8.63 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.73 (td, *J* = 7.5Hz, 1.8 Hz, 1H), 7.35 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 2.84 (s, 3H), 1.31 (s, 9H);. ^{13}C NMR (75 MHz): δ 177.6, 155.2, 148.7, 136.4, 125.6, 121.8, 57.5, 22.4, 18.5.

***N-tert*butylsulfinylketimine of (2*S*, 5*S*)-5-isopropenyl-2-methylcyclohexanone (5u/5u').** The starting ketone (+)-dihydrocarvone **1u** was purchased from Aldrich as a mixture of epimers at C2 that was separated by flash chromatography [1:20 to 1:10 (EtOAc/hexane)]. Reaction time: 7 h; Yield: 65%. Flash chromatography; gradient from 1:50 to 1:10 (EtOAc/hexane). Colorless oil; *Compound **5u**; Rf*= 0.6 (9:1 hexane/AcOEt); $[\alpha]_D^{20}$= -215.6 (c=1.1, $CHCl_3$): IR (NaCl): 3315, 2955, 2928 1624, 1475, 1071 cm^{-1}; ^{1}H NMR (300 MHz): δ 4.64 (m, 2H), 3.53 (ddd, *J* = 12.4, 4.5, 3.1, 1H), 2.35-2.15 (m, 2H), 2.05-1.95 (m, 1H), 1.85 (t, *J* = 12.5 2.1, 1H), 1.85-1.75 (m, 1H), 1.64 (s, 3H), 1.55-1.20 (m, 2H), 1.14 (s, 9H), 0.98 (d, J = 6.4 Hz, 3H); ^{13}C NMR

(75 MHz): δ 189.3, 147.5, 109.3, 56.1, 47.0, 43.6, 39.1, 36.0, 30.7, 22.0, 20.5, 16.1; *Compound* ***5u´****;Rf*=0.4 (9:1 hexane/AcOEt);. $[\alpha]_D^{20}$= +159.6 (c=1.0, $CHCl_3$): IR (NaCl): 3317, 3082, 2965, 2929, 1621, 1475, 1360, 1074 cm^{-1}; ^1H NMR (300 MHz): δ 4.65 (m, 2H), 3.48 (d, *J* = 10.2, 1H), 2.34-2.28 (m, 2H), 2.15-1.98 (m, 2H), 1.85-1.77 (m, 1H), 1.64 (m, 3H), 1.50-1.20 (m, 2H), 1.15 (s, 9H), 1.00 (d, *J* = 6.5 Hz, 3H): ^{13}C NMR (75 MHz): δ 189.8, 147.2, 109.7, 55.8, 46.2, 43.3, 39.0, 35.7, 30.7, 21.9, 20.2, 16.2.

Typical procedure for the oxidation of p-*Tolylsulfinylimine to* p-*Tolylsulfonylimine (Table 1).*



To a solution of the corresponding sulfinylimine **5** (0.4 mmol) in CH_2Cl_2 (2 mL) dry *m*-CPBA was added at rt in one portion. When the reaction was completed (less than 1 minute), the reaction was diluted with 4 mL of CH_2Cl_2, washed with 3x5 mL of saturated solution of $NaHCO_3$. Finally, the organic layer was dried over anhydrous Na_2SO_4 and the solvent evaporated, obtaining the corresponding pure sulfonylimines **6** without further purification.

***N*-Benzylidene-*p*-toluenesulfonamide (6a).**[8] Yield: Quant. White solid; mp: 114-115 ºC (Lit. 112-113 ºC); ^{1}H NMR (300 MHz): δ 9.05 (s, 1H), 7.90-7.48 (m, 4H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H).

***N*-(3-Methoxybenzylidene)-*p*-toluenesulfonamide (6b)**. Yield: Quant. White solid; mp: 78-79 ºC; ^{1}H NMR (300 MHz): δ 8.97 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.45-7.31 (m, 5H), 7.13 (ddd, *J* = 8.1, 2.5, 1.4 Hz, 1H), 3.80 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (75 MHz): δ 170.1, 160.0, 144.6, 133.6, 130.0, 129.9 (2C), 128.0, 125.2, 122.1, 113.3, 55.5, 21.6.

***N*-(2-Naphthylmethylene)-*p*-toluenesulfonamide (6c).**[9] Yield: 95%. White solid; mp: 80-81 ºC; ^{1}H NMR (300 MHz): δ 9.61 (s, 1H), 8.16-8.08 (m, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.93-7.89 (m, 1H), 7.70-7.50 (m, 4H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.43 (s,3H).

***N*-(2-Bromobenzylidene)-*p*-toluenesulfonamide (6d).** Yield: Quant.; white solid; mp: 140-141 ºC; IR (NaCl): 1645, 1597, 1430, 1319, 1157 cm^{-1} ; ^{1}H NMR (300 MHz):

[8] Chemia, F.; Hebbe, V.; Normant, J.-F. *Synthesis*, **2000**, *1*, 75.
[9] Jennings, W. B.; Lovely, C. J. *Tetrahedron Lett.* **1988**, *39*, 6223.

δ 9.42 (s, 1H), 8.13 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.64 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.45-7.28 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz): δ 169.1, 144.9, 135.7, 134.5, 133.7, 131.1, 130.5, 129.5, 127.9, 127.9, 126.3, 21.6.

***N*-(4-Nitrilebenzylidene)-*p*-toluenesulfonamide (6e).**[10] Yield: 85%; ^{1}H NMR (300 MHz): δ 9.03 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 2.45(s, 3H).

(*E*)-2-[(*p*-Toluensulfonyl)imino]-4-phenyl-3-butene (6f).[11] Yield: 95%. White solid; mp: 110-111 ºC (Lit. 109-110 ºC); ^{1}H NMR (300 MHz): δ 8.78 (d, *J* = 9.4 Hz, 1H), 7.85 (d, *J* =8.4 Hz, 2H), 7.60-7.35 (m, 6H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.96 (dd, *J* = 15.9, 9.4 Hz, 1H), 2.41 (s, 3H).

***N*-Butylidene-*p*-toluenesulfonamide (6g).**[12] In this case, *m*-CPBA was added to a solution of sulfinylimine **4g** previously heated at 45 ºC. Yield: 96%. Colorless oil; ^{1}H NMR (300 MHz): δ 8.57 (t, *J* = 4.5 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 2.60-2.40 (m, 2H), 2.42 (s, 3H), 1.80-1.60 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz): δ 178.3, 144.6, 134.5, 129.7, 127.9, 37.6, 21.5, 17.9, 13.4.

***N*-*Iso*butylidene-*p*-toluenesulfonamide (6h).**[13] In this case, *m*-CPBA was added to a solution of sulfinylimine **4h** previously heated at 45 ºC. Yield: Quant.; White solid; mp: 116-118 ºC (Lit. 114-115 ºC ; ^{1}H NMR (300 MHz): δ 8.49 (d, *J* = 4.1 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 2.73-2.69 (m, 1H), 2.43 (s, 3H), 1.15 (d, *J* = 6.9 Hz, 6H).

10 Klein, M.; Ugi, I; *Chem. Sciences* **1992**, *47*, 887.
11 Boger, D. L.; Corbett, W. L. *J. Org. chem.* **1992**, *57*, 4777.
12 Chemia, F.; Hebbe, V.; Normant, J.-F. *Synthesis*, **2000**, *1*, 75.
13 Lee, K. Y.; Lee, C. C.; Kim, J. N. *Tetrahedron Letters*, **2003**, *44*, 1231.

***N*-(2,2-Dimethylpropylidine)-*p*-toluenesulfonamide (6i).**[14] Yield: 96 %; White solid; ^{1}H NMR (300 MHz): δ 8.43 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 2.43 (s, 3H), 1.12 (s, 9H).

***N*-(Diphenylmethylene)-*p*-toluenesulfionamide (6j).**[15] Yield: 88%. White solid; ^{1}H NMR (300 MHz): δ 7.70-7.30 (m, 10H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.39 (s, 3H).

***N*-(1-Phenylethylidine)-*p*-toluenesulfonamide (6k).**[16] Yield: 96%. White solid; ^{1}H NMR (300 MHz): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.54-7.35 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.99 (s, 3H), 2.45 (s, 3H).

***N*-[1-(4-Methoxyphenyl)ethylidine)]-*p*-toluenesulfonamide (6l).** Yield: 84%; IR (NaCl): 2932, 1639, 1431, 1325, 1151 cm^{-1}; ^{1}H NMR (300 MHz): δ 7.93-7.88 (m, 4H), 7.33 (dd, *J* = 8.6, 0.6 Hz, 2H), 6.88 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 3H), 2.94 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz): δ 163.9, 143.2, 139.1, 130.6 (2C), 129.4 (2C), 127.0, 113.9, 55.5, 21.5, 20.7.

***N*-[1-(4-Nitrilephenyl)ethylidine)-*p*-toluenesulfonamide (6m).** Yield: 90%; ^{1}H NMR (300 MHz): δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 6.33 (d, *J* = 8.3 Hz, 2H), 2.96 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz): δ 177.6, 143.9, 141.2, 137.9, 132.2, 129.5, 128.5, 127.1, 117.7, 116.0, 21.5, 21.0.

***N*-(1,2,2-Trimethylpropylidine)-*p*-toluenesulfonamide (6n).**[17] Yield: 90 %; white solid; mp: 119-120ºC; ^{1}H NMR (200 MHz): δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 2.52 (s, 3H), 2.41 (s, 3H), 1.12 (s, 9 H).

***N*-(1,2-Dimethylpropylidine)-*p*-toluenesulfonamide (6o).** Yield: 90 %; colourless oil; ^{1}H NMR (300 MHz): δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.60-2.40 (m,

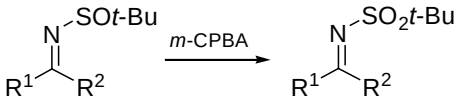
14 Trost, B. M.; Christopher, M. *J. Org. Chem.* **1991**, *56*, 6468.
15 Lee, K. Y.; Lee, C. C.; Kim, J. N. *Tetrahedron Letters*, **2003**, *44*, 1231.
16 Wolfe, J.; Ney, J. E. *Org. Lett*. **2003**, *5*, 4607.

1H), 2.55 (s, 3H), 2.42 (s, 3H), 1.12 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz): δ 193.7,143.4, 138.6, 129.7, 126.4, 41.5, 21.9, 21.5, 19.2.

***N*-*p*-Tolylsulfonyl aldimine of (1*S*, 2*R*)-2-(*tert*-Butyldiphenylsililoxy)methyl-1-formylciclopropane (6t).** Yield: 96%; colorless oil; $[\alpha]_D^{20}$ -8.2 (c=1.00, $CHCl_3$); IR (NaCl): 2929, 2856, 1704, 1612, 1427, 1326, 1159 cm^{-1}; ^{1}H NMR (300 MHz): δ 8.43 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.66-7.60 (m, 4H), 7.47-7.30 (m, 6H), 7.25 (d, J = 8.3 Hz, 2H), 3.98 (dd, *J* = 11.7, 4.8 Hz, 1H), 3.63 (dd, *J* = 11.7, 8.0 Hz, 1H), 2.40 (s, 3H), 2.10-2.01 (m, 1H), 1.80-1.70 (m, 1H), 1.35-1.20 (m, 2H), 1.02 (s, 9H); ^{13}C NMR (75 MHz): δ 179.2, 144.1, 135.6, 135.5, 129.8, 129.7, 127.9, 127.8, 127.7 (2C), 62.1, 29.7, 26.9, 26.8, 22.8, 21.6, 19.1, 14.5.

Oxidation of N-t-*Butanesulfinylimine to* N-t-*Butanesulfonylimine.(Table 2).*

Sulfonylimines **7a-t** were prepared under identical condition described for *p*-tolyl derivatives **6** (table 1).



***N*-Benzylidene-*t*-butanesulfonamide (7a).**[18] Yield: Quant; ^{1}H NMR (300 MHz): δ 9.05 (s, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.68-7.51 (m, 3H), 1.50 (s, 9H).

***N*-*Furan*-2-*ylmethylene*-*t*-butanesulfonamide (7p).** In this case, the treatment of the crude with a sat. solution of $NaHCO_3$ afforded sulfonylimine **7p** contaminated with a 15 % of *m*-chlorobenzoic acid, which was eliminated by using MP-carbonate resin as scavenger.[19] Yield: Quant. Orange solid; mp: 88.0-90.0 ºC; IR (NaCl): 2985, 1637, 1606, 1542, 1533, 1301, 1152; ^{1}H NMR (300 MHz): δ 8.77 (s, 1H), 7.77 (d, *J* = 3.6 Hz,

17 Sugihara, Y.; Iimura, S.; Nakayama, J. *J. Chem. Comm.* **2002**, *2*, 134.
18 Artman, G. D.; Bartolozzi, A.; Franck, R. W.; Weinreb, S. M. *Synlett* **2001**, 232.
19 Parlow, J.J.; Naing, W.; South, M.S.; Flynn, D.L. *Tetrahedron Lett* **1997**, *38*, 7959.

1H), 7.34 (d, *J* = 3.6 Hz, 1H), 6.67 (dd, *J* = 3.6, 1.7 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (75 MHz): δ 150.3, 149.6, 149.3, 124.2, 113.6, 58.4, 24.0.

***N*-Butylidene-*t*-butanesulfonamide (7g).** Yield: 84%[20]; colorless Oil; ^{1}H NMR (300 MHz): δ 8.63 (t, *J* = 4.5 Hz, 1H), 2.60-2.40 (m, 2H), 1.80-1.60 (m, 2H), 1.40 (s, 9H), 1.02 (t, *J* = 7.3 Hz, 3H).

***N*-(Diphenylmethylene)-*t*-butanesulfonamide (7j).** Yield: Quant.; colourless oil; ^{1}H NMR (300 MHz): δ 7.60-7.38 (m, 10H), 1.56 (s, 9H); ^{13}C NMR (75 MHz): 180.3, 135.1, 134.3, 133.6, 130.5, 130.1, 129.2, 127.8, 127.3, 59.3, 24.1.

***N*-(1-Phenylethylidine)-*t*-butanesulfonamide (7k).[21]** Yield: Quant.; colourless oil; ^{1}H NMR (300 MHz): δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.08, 2H), 2.91 (s, 3H), 1.55 (s, 9H).

***N*-[1-(4-Methoxyphenyl)ethylidine]-*t*-butanesulfonamide (7l).** Yield: Quant.; colourless oil; IR (NaCl): 2931, 1593, 1565, 1290, 1120 cm^{-1} ; ^{1}H NMR (300 MHz): δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.87 (s, 3H), 1.54 (s, 9H);. ^{13}C NMR (75 MHz): δ 176.0, 133.4, 130.3, 130.2, 113.9, 59.0, 55.5, 29.7, 24.0.

***N*-[1-(4-Nitrilephenyl)ethylidine)-*t*-butanesulfonamide (7m).** Yield: Quant.; white solid; mp: 99-101 ºC; IR (NaCl): 2929, 2227, 1612, 1556, 1479, 1295, 1124 cm^{-1}; ^{1}H NMR (300 MHz): δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 2.91 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (75 MHz): δ 178.6, 133.6, 132.4, 128.3, 117.8, 116.0, 59.5, 29.6, 23.9.

***N*-Cyclohexylidine-*t*-butanesulfonamide (7q).**[20] Yield: 90 %; colourless oil; ^{1}H NMR (300 MHz): δ 2.93 (t, *J* = 7.8 Hz, 2H), 2.38 (t, *J* = 6.4 Hz, 2H), 1.90-1.80 (m, 4H), 1.70-

20 This compound was obtained in a mixture of 90% *N*-Sulfonylimine and 10% of starting material.
21 Chen, Y.-C.; Wu, T.-F.; Deng, J.-G.; Liu, H.; Cui, X.; Zhu, J.; Jiang, Y.-Z.; Choi, M. C. K.; Chan, A. S. C. *J. Org, Chem.* **2002**, *67*, 5301.

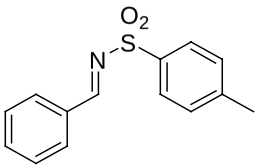
1.64 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (75 MHz): δ 193.4, 58.6, 40.3, 36.0, 27.9, 27.1, 24.9, 23.8.

***N*-(1-Methylpropylidene)-*t*-butanesulfonamide (7r).** Yield: Cuant. Colorless oil; *E isomer*: ^{1}H NMR (300 MHz): δ 2.51 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 1.47 (s, 9H), 1.09 (t, *J* = 7.2 Hz, 3H);. ^{13}C NMR (75 MHz): 178.0, 60.1, 31.9, 29.7, 22.7,14.1.

***N*-[1-(1-Pyridin)ethylidine)-*t*-butanesulfonamide (7s).** Yield: 80%; White solid; mp: 90-91 ºC; IR (NaCl): 2922, 1624, 1577, 1566, 1292 cm^{-1} ; ^{1}H NMR (300 MHz): δ 8.70 (bd, *J* = 4.7 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.79 (td, *J* = 7.8, 1.7 Hz, 1H), 7.44 (ddd, *J* = 7.8, 4.7, 1.0 Hz, 1H), 3.02 (s, 3H), 1.55 (s, 9H);. ^{13}C NMR (75 MHz): δ 181.7, 154.5, 149.1, 136.6, 126.6, 121.9, 59.2, 29.7, 23.9.

***N*-*tert*butylsulfonylketimine of (2*S*, 5*S*)-5-isopropenyl-2-methylcyclhexanone (7u).** Both diastereoisomers **5u** and **5u'** were oxidized following the procedure described above giving **7u** in 83% yield. White solid; mp: 101-102 ºC; $[\alpha]_D^{20}$ +58.2 (c=1.1, $CHCl_3$): IR (NaCl): 3400, 2920, 1610, 1320, 1152 cm^{-1}; ^{1}H NMR (300 MHz): δ 4.76 (m, 2H), 3.64 (dt, *J* = 12.4, 12.5 Hz, 1H), 2.50-2.32 (m, 2H), 2.19 (t, *J* = 12.8 Hz, 1H), 2.18-2.10 (m, 1H), 1.91-1.85 (m, 1H), 1.74 (s, 3H), 1.65-1.50 (m, 1H), 1.48 (s, 9H), 1.44-1.32 (m, 1H), 1.05 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz): δ 175.2, 147.2, 109.9, 59.0, 47.1, 43.9, 41.5, 36.3, 30.7, 23.9, 20.5, 16.1.

Representative NMR of some sulfonyl-imines.



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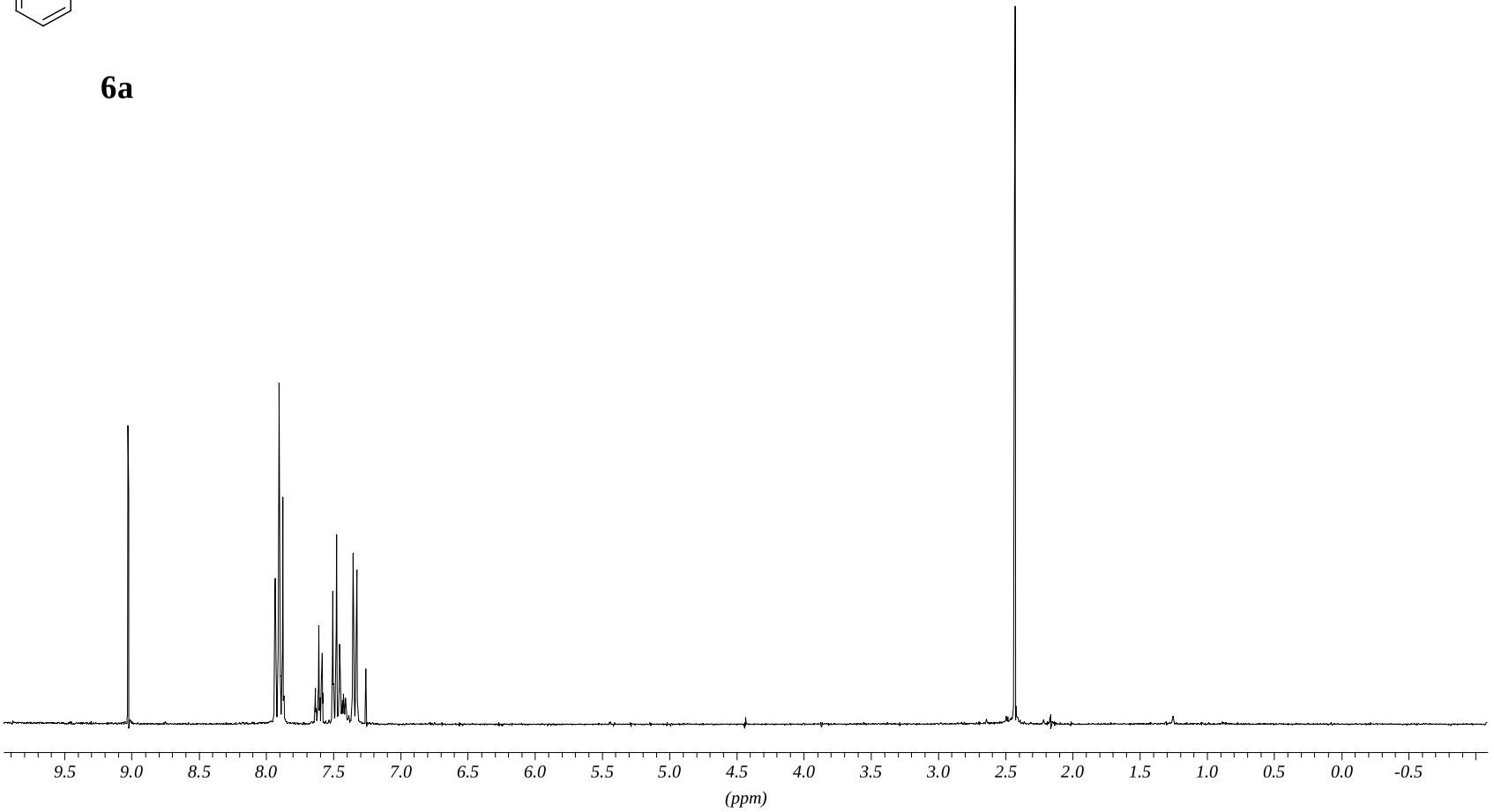

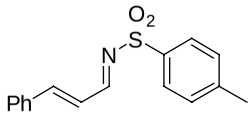
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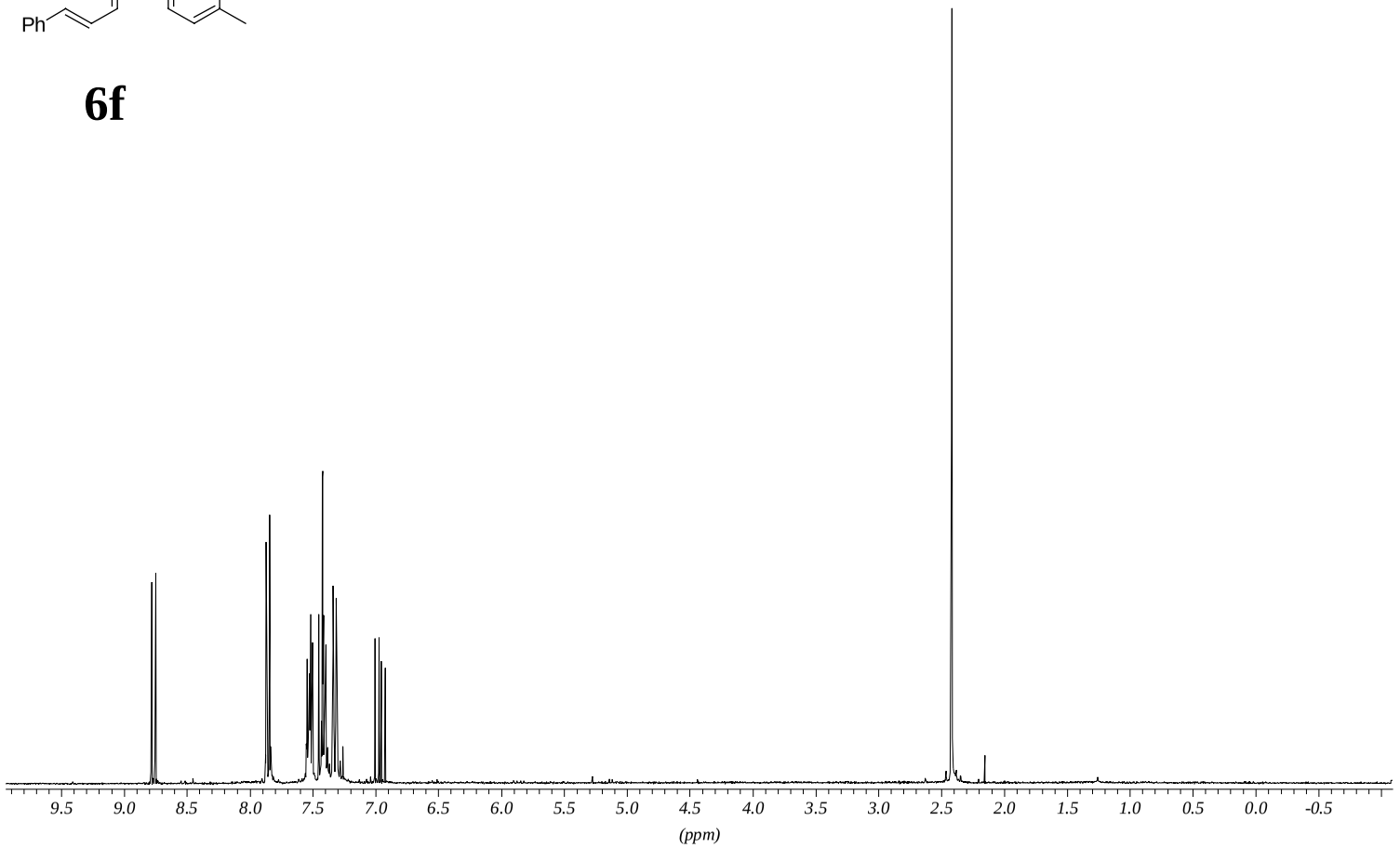
N
Ph

6f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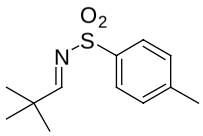
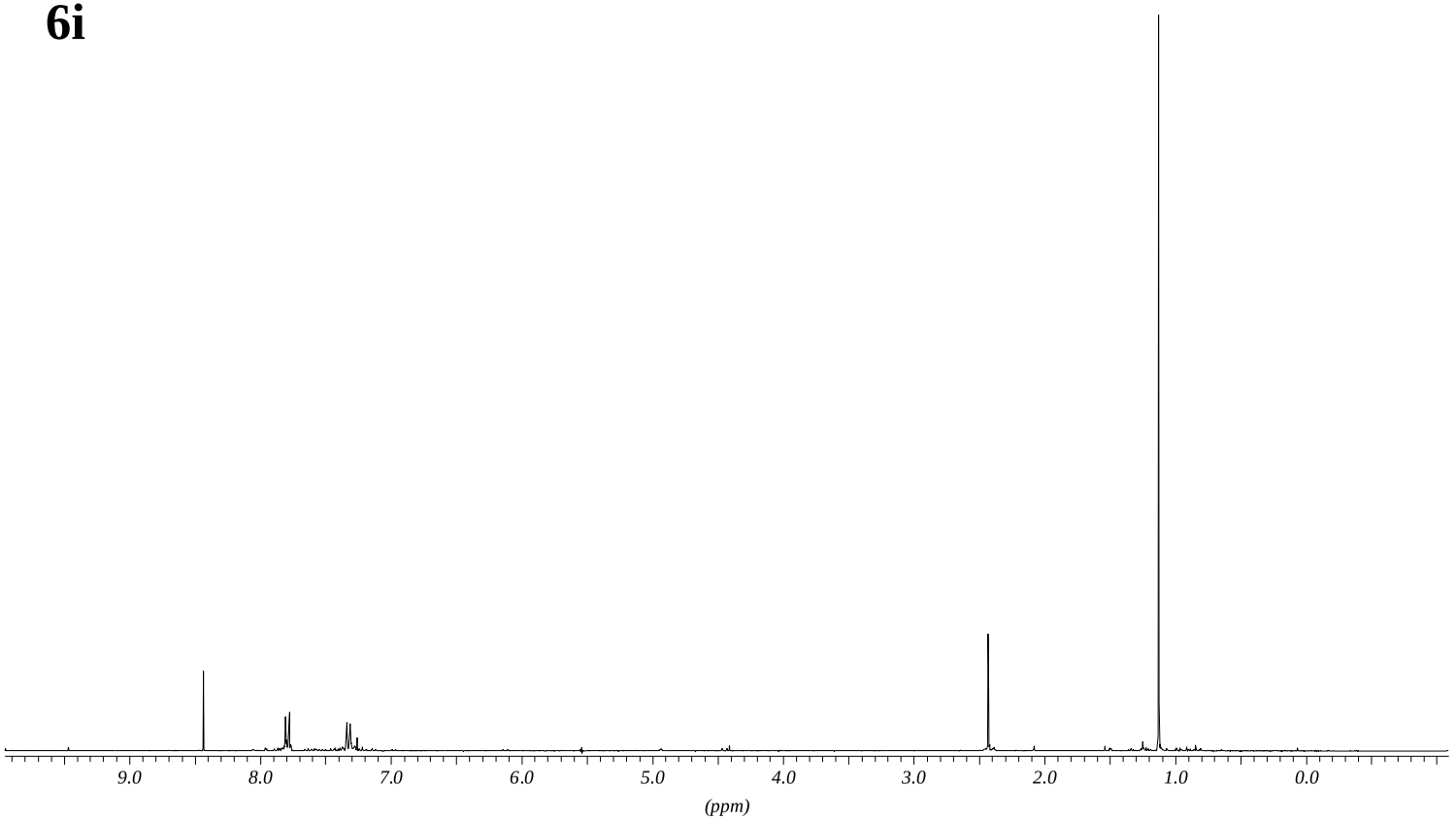
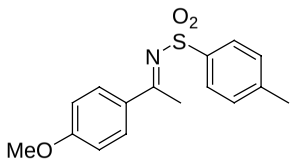


6i

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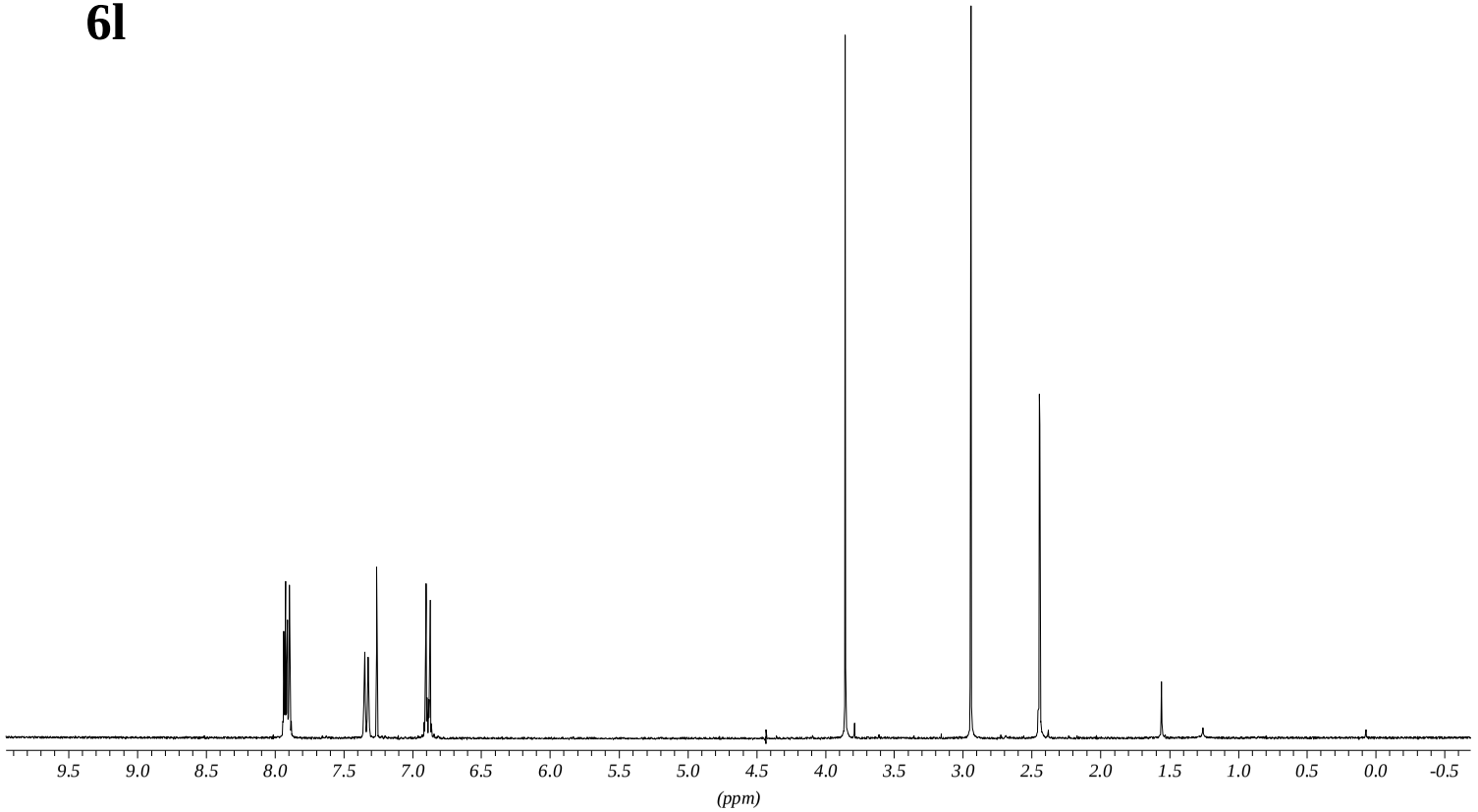
S
MeO

6l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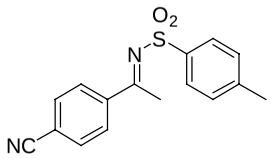

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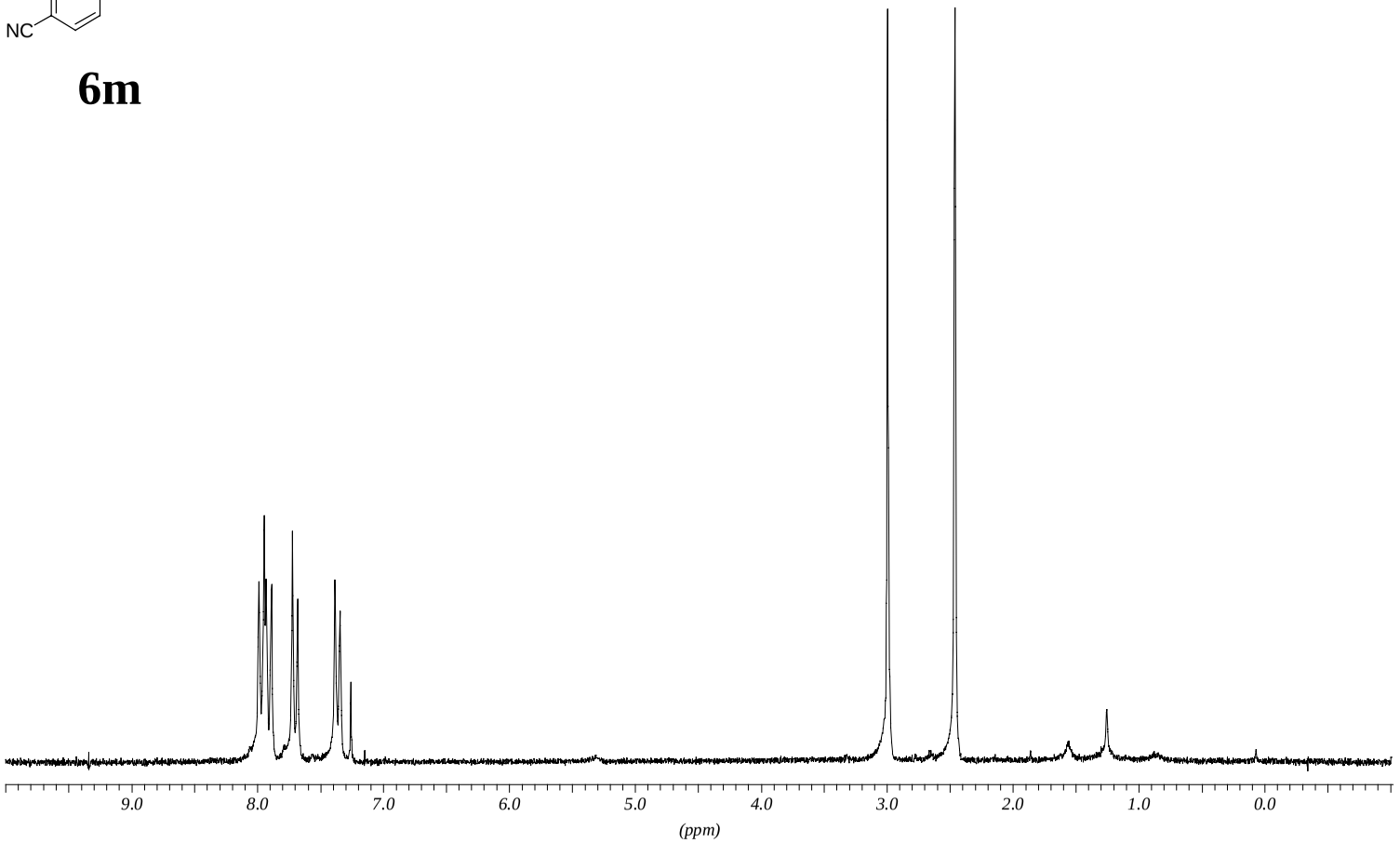

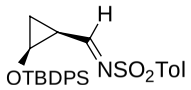

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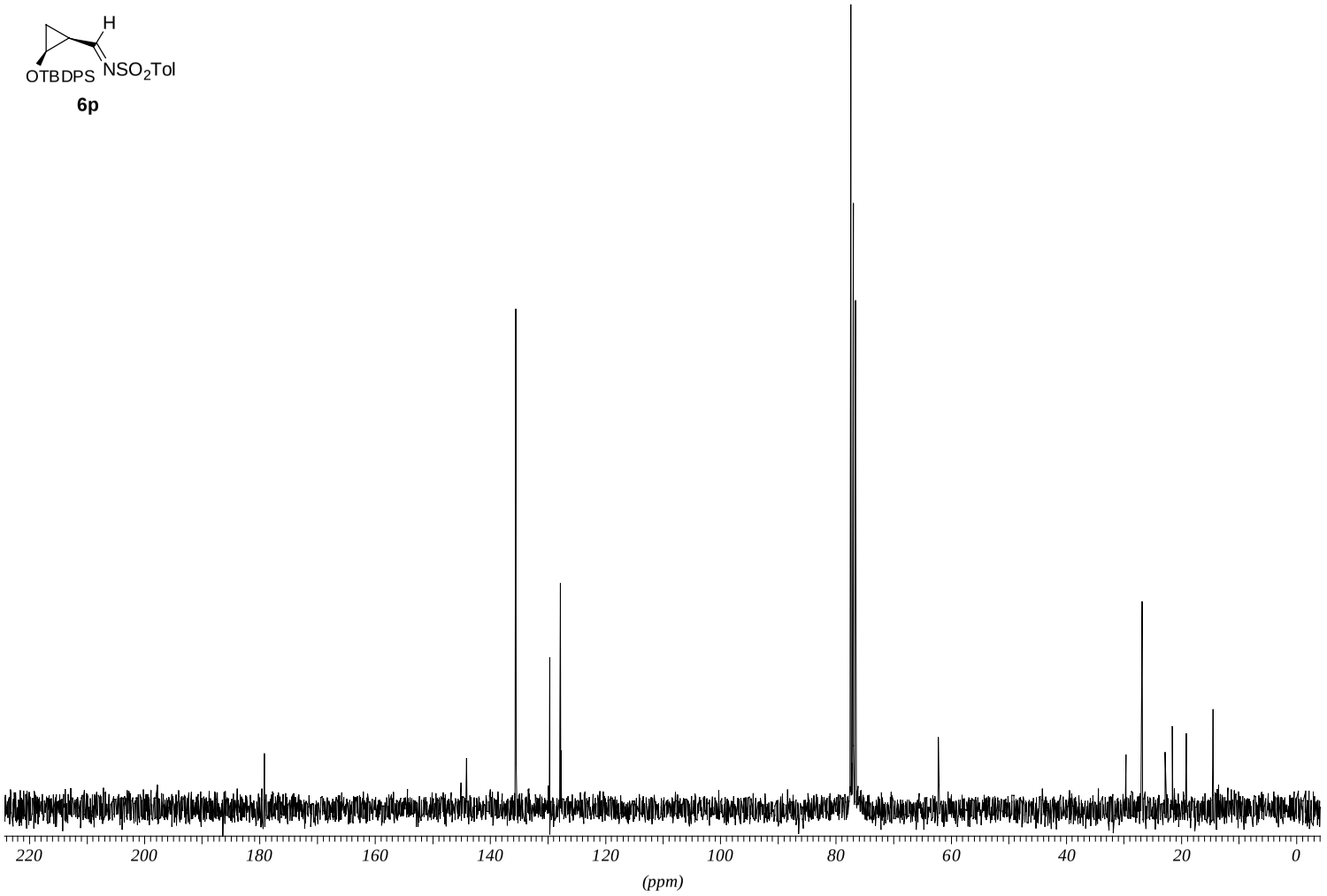
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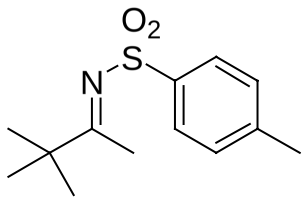

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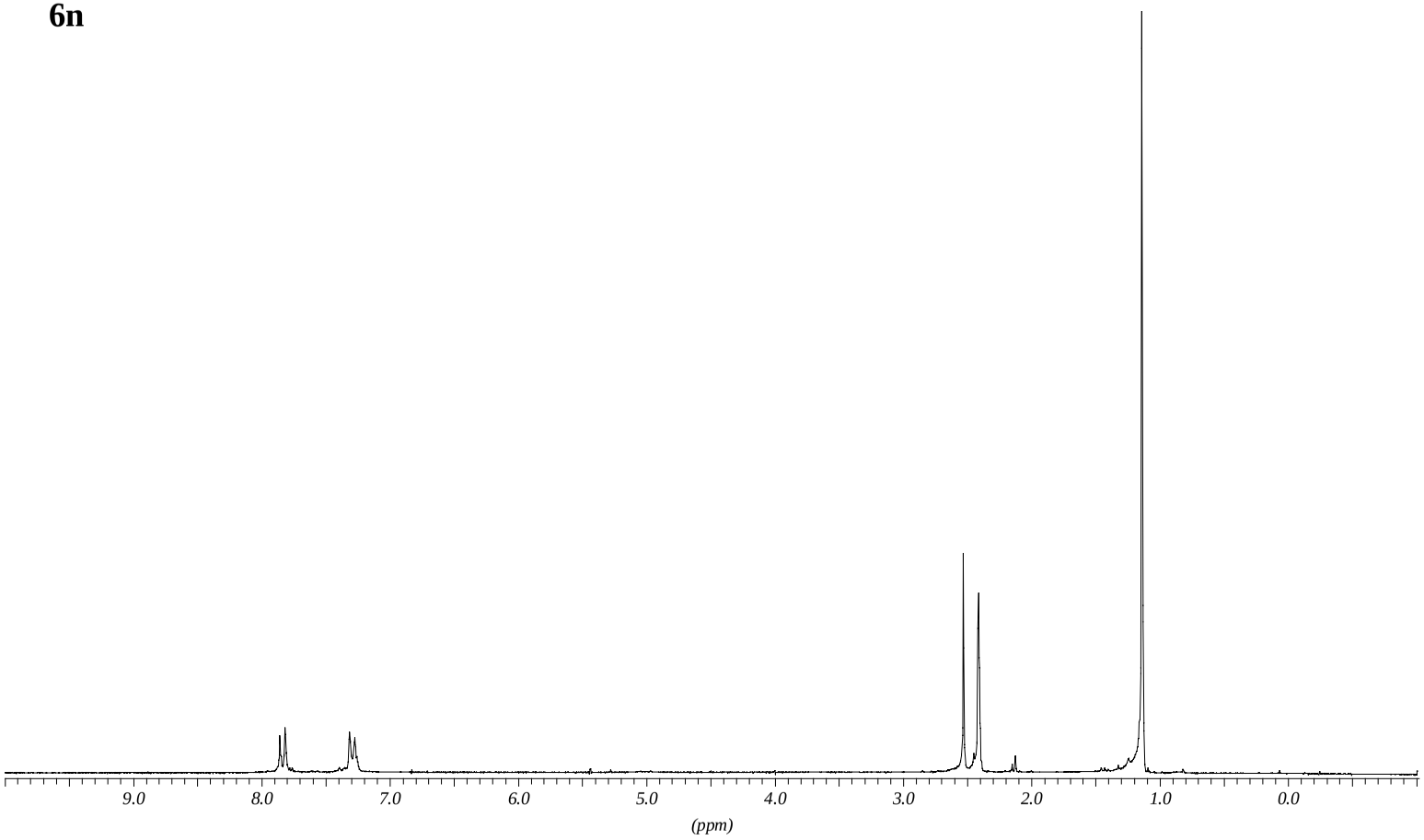
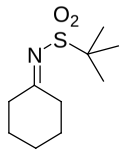
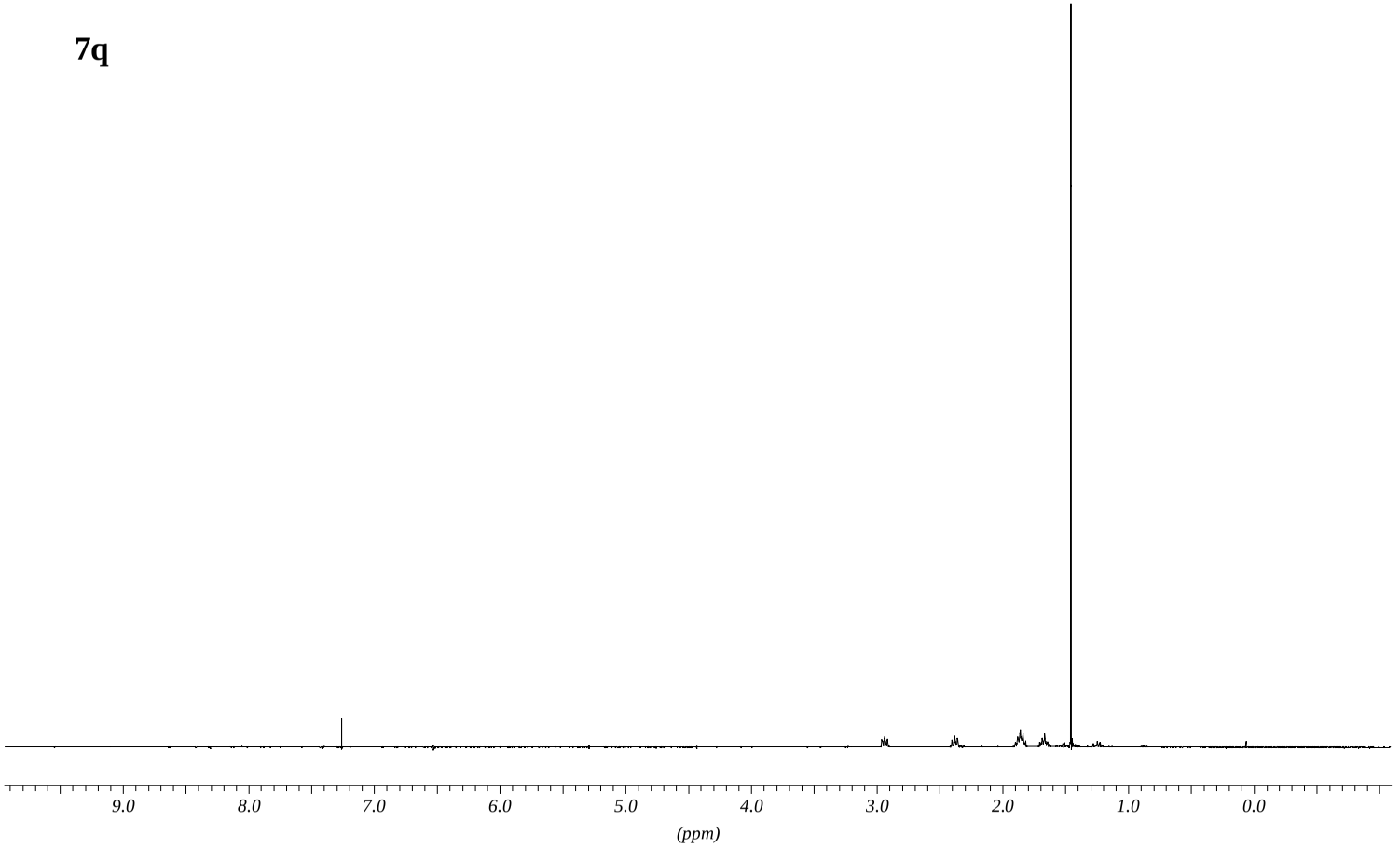
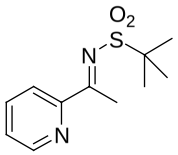




7q





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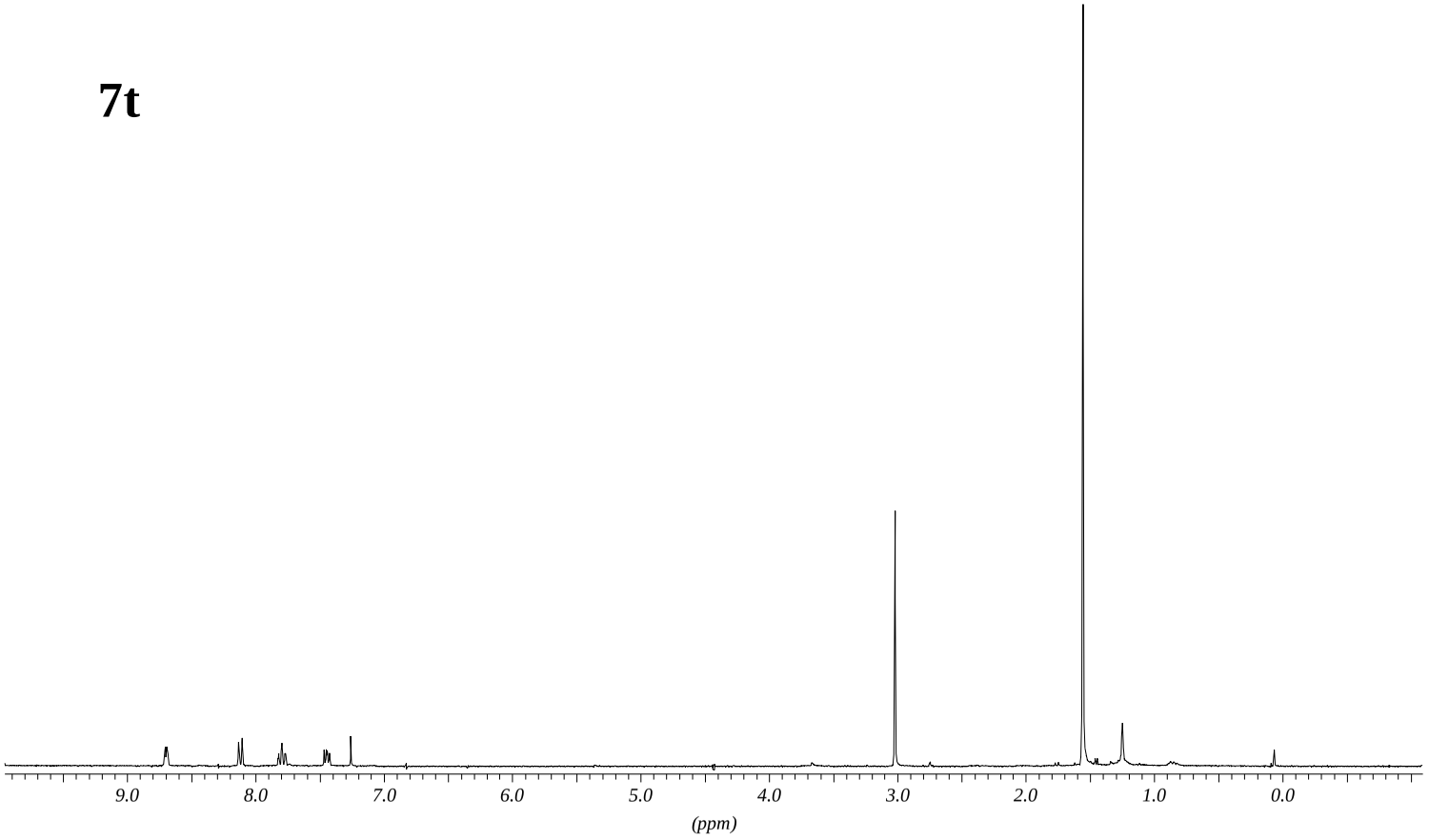

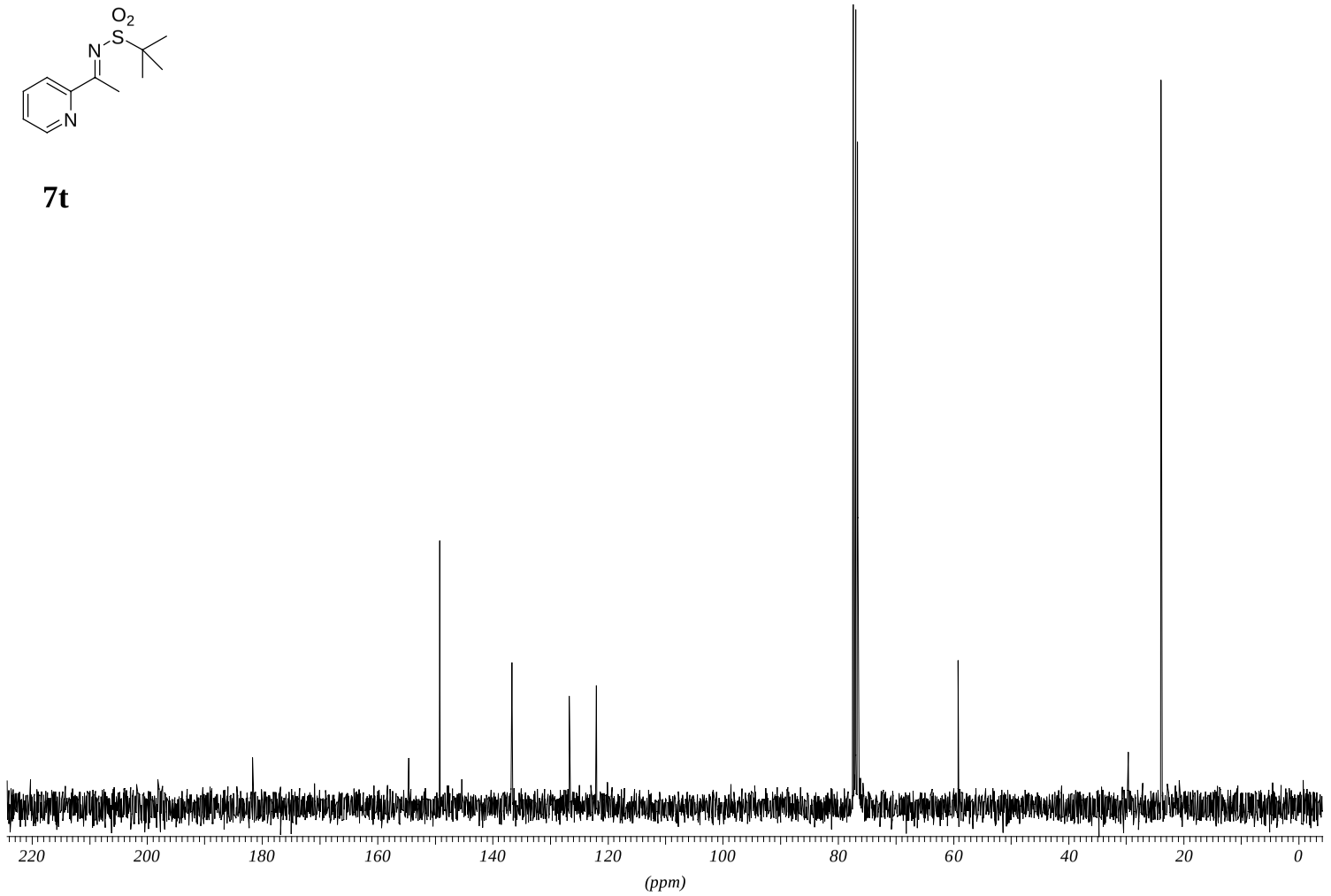
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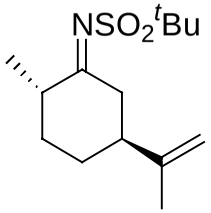

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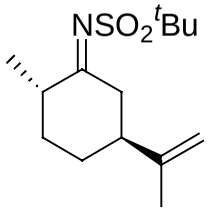

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