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Supporting Information

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A Ligand Library Approach to the Highly Efficient Rhodium/Phosphoramidite Catalyzed Asymmetric Arylation of *N,N*-dimethylsulfamoyl Protected Aldimines

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General remarks: All air and moisture sensitive manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. ^{1}H-NMR, ^{31}P-NMR, and ^{13}C-NMR spectra were recorded on a Varian 400 (400, 162, and 101 MHz) in $CDCl_3$. Mass spectra (HRMS) were recorded on an AEI MS-902. Optical rotations were measured on a Schmidt and Haensch Polartronic MH8. Ligand libraries were synthesized using a Zinsser Lissy liquid handling robot equipped with 4 probes and placed inside a glove box. Whatman PKP 2 mL 96-well filter plates in combination with the UniVac 3 vacuum manifold were used to perform the parallel filtration of the ligand library.[1] Screening of the ligand libraries was performed in a parallel reactor consisting of an aluminum block on a magnetical stirrer/heater containing 32 10 mL vials equiped with magnetic stirring bar, screwcap, and septum. Microwave assisted chemistry was performed in a CEM focused Microwave Synthesis System, model Discover. $Rh(acac)(C_2H_4)_2$ was purchased from Strem and used without further purification. 1,3-Diaminopropane was distilled from calcium hydride. All other chemicals were purchased from Acros and used as received unless stated otherwise. *N,N*-dimethylsulfamoyl amide was readily prepared from commercial dimethylsulfamoyl chloride and 30% aqueous ammonia.[2] Flash chromatography was performed using silica gel 60 Å (Merck, 230-400 mesh).

Synthesis of sulfamoylimines 5

Substrates **5a-i** were synthesized according to a literature procedure.[3] 20 mmol of the corresponding benzaldehyde and 2,54 g (20,5 mmol) of *N,N*-dimethylsulfamide were dissolved in 80 mL of toluene and water was azeotropically distilled for 16 h using a Dean-Stark apparatus. After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 and filtered. After evaporation of the solvent under reduced pressure, the crude product was crystallized from isopropanol. Spectral data of **5d**, **5e** and **5i** was in accordance with literature.[3]

***N*-(Dimethylsulfamoyl)-4-chlorobenzaldimine 5a** Yield: 70%; mp 120.5-122.1°C; ^{1}H NMR ($CDCl_3$) δ = 8.83 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 2.85 (s, 6H); ^{13}C NMR ($CDCl_3$) δ

= 169.10, 140.88, 131.89 (2), 130.80, 129.52 (2), 38.26 (2); HRMS calcd for $C_9H_{11}{}^{37}ClN_2O_2S$: *m/z* 248.0203, found: 248.0200.

***N*-(Dimethylsulfamoyl)-4-fluorobenzaldimine 5b** Yield: 74%; mp 113.6-114.8°C; ^1H NMR ($CDCl_3$) δ = 8.87 (s, 1H), 7.99-7.95 (m, 2H), 7.21 (m, 2H), 2.89 (2s, 6H); ^{13}C NMR ($CDCl_3$) δ = 169.01, 166.55 (d, J_{CF} = 257.9 Hz), 133.27 (2d, J_{CF} = 9.8 Hz), 128.79 (d, J_{CF} = 2.5 Hz), 116.58 (2d, J_{CF} = 23.2 Hz), 38.29 (2); HRMS calcd for $C_9H_{11}FN_2O_2S$: *m/z* 230.0525, found: 230.0534.

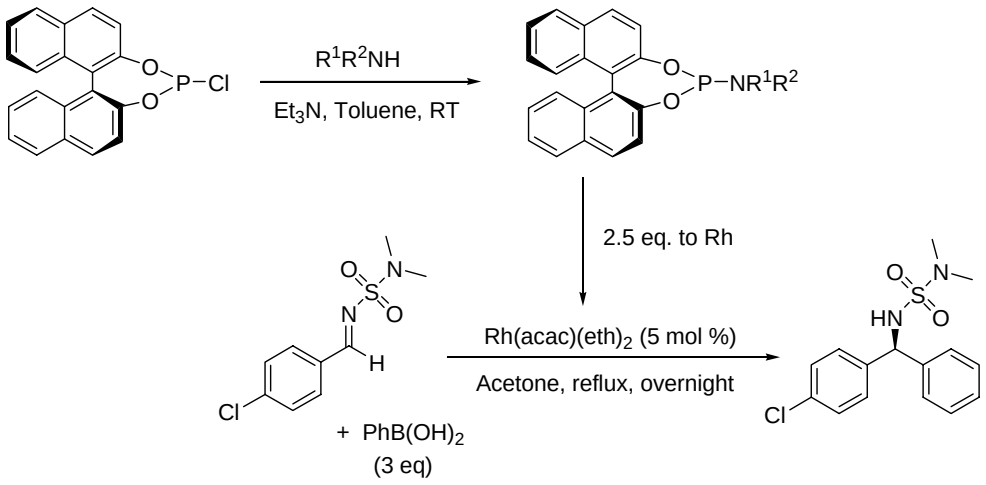
***N*-(Dimethylsulfamoyl)-4-(trifluoromethyl)benzaldimine 5c** Yield: 67%; mp 105.5-106.6°C; ^1H NMR ($CDCl_3$) δ = 8.96 (s, 1H), 8.08 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 2.92 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 169.07, 135.65 (q, J_{CF} = 32.2 Hz), 135.64, 131.12 (2), 126.28 (q, J_{CF} = 3.8 Hz), 123.53 (2q, J_{CF} = 273 Hz), 38.47 (2); HRMS calcd for $C_{10}H_{11}N_2O_2F_3S$: *m/z* 280.0493, found: 280.0488.

***N*-(Dimethylsulfamoyl)-2-methylbenzaldimine 5f** Yield: 46%; mp 71.5-72.7°C; ^1H NMR ($CDCl_3$) δ = 9.19 (s, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.49 (m, 1H), 7.36-7.30 (m, 2H), 2.89 (s, 6H), 2.63 (s, 3H); ^{13}C NMR (THF-d^8) δ = 169.99, 142.47, 134.53, 132.44, 132.05, 131.50, 127.32, 38.47, 20.10 (2); HRMS calcd for $C_{10}H_{14}N_2O_2S$: *m/z* 226.0776, found: 226.0784.

***N*-(Dimethylsulfamoyl)-3-fluorobenzaldimine 5g** Yield: 50%; mp 58.0-60.3°C; ^1H NMR ($CDCl_3$) δ = 8.88 (s, 1H), 7.67-7.70 (m, 2H), 7.55-7.49 (m, 1H), 7.36-7.31 (m, 1H), 2.89 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 169.35 (d, J_{CF} = 3.1 Hz), 163.06 (d, J_{CF} = 249.2 Hz), 134.74 (d, J_{CF} = 7.7 Hz), 131.03 (d, J_{CF} = 8.4 Hz), 127.63 (d, J_{CF} = 3.1 Hz), 121.72 (d, J_{CF} = 21.5 Hz), 116.27 (d, J_{CF} = 22.2 Hz), 38.47 (2); HRMS calcd for $C_9H_{11}FN_2O_2S$: *m/z* 230.0525, found: 230.0530.

***N*-(Dimethylsulfamoyl)-2-thienaldimine 5h** Yield: 78%; mp 110.6-111.1°C; ^1H NMR ($CDCl_3$) δ = 8.97 (d, *J* = 1.1 Hz, 1H), 7.77-7.75 (m, 2H), 7.22 (dd, *J* = 5.1 Hz, *J* = 4.0 Hz, 1H), 2.81 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 162.89, 138.52, 138.34, 135.80, 128.94, 39.55; HRMS calcd for $C_7H_{10}N_2O_2S_2$: *m/z* 218.0184, found: 218.0161.

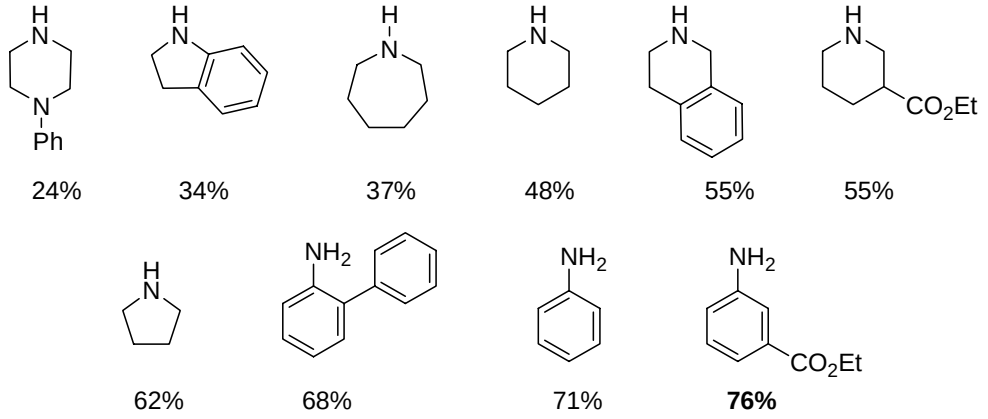
Parallel synthesis and *in situ* screening of phosphoramidite ligand Libraries



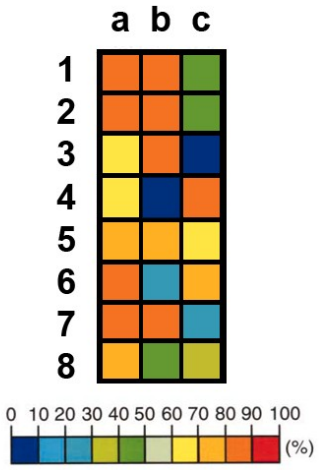
Synthesis of primary and secondary libraries. The preparation of ligand libraries was adapted from a previously reported procedure.[2] Stock solutions were prepared by dissolving the proper amounts of every reagent necessary for the library synthesis in dry toluene (all by weight). For the phosphorochloridite and the triethylamine a concentration of 0.5 M was used. For the amines/alcohols 1.0 M stock solutions were prepared. In the case of chiral amines the racemic amine was used. Using the liquid handling robot, 100 µL of the phosphorochloridite solution and 100 µL of the triethylamine solution were transferred into each of 24 wells of the Whatman PKP filter plate. Next, 50 µL of each of the 24 amine/alcohol solutions was added to the corresponding well. The microplate was placed on an orbital shaker and vortexed for 2 hours at room temperature. The microplate was then placed onto the vacuum manifold and filtration was performed upon application of vacuum. The filtrates, *i.e.* 24 solutions of different ligands in dry toluene were collected and stored into a 96-well polypropylene microplate.

Screening of the library. Stock solutions were prepared in dioxane (primary library) or acetone (secondary library) containing the Rh precursor, $Rh(acac)(eth)_2$ at a concentration of 0.05 M, and the imine **5a** at a concentration of 0.05 M. Using the liquid handling robot 62.5 µL of the ligand solutions (0.0125 mmol) was transferred from the microplate into 24 vials, equipped with stirring bars. Then 100 µL of the $Rh(acac)(eth)_2$ (0.005 mmol) and 2 mL of imine stock solution (0.1 mmol) was added to each of the 24 vials. After the addition of 36.3 mg (0.3 mmol) of phenylboronic acid (**6n)** the vials were capped and transferred to the parallel reactor. The reactions were left stirring overnight at reflux. After evaporating the solvent, the obtained solids were analyzed by chiral HPLC (*vide infra*) in order to determine the enantioselectivity.

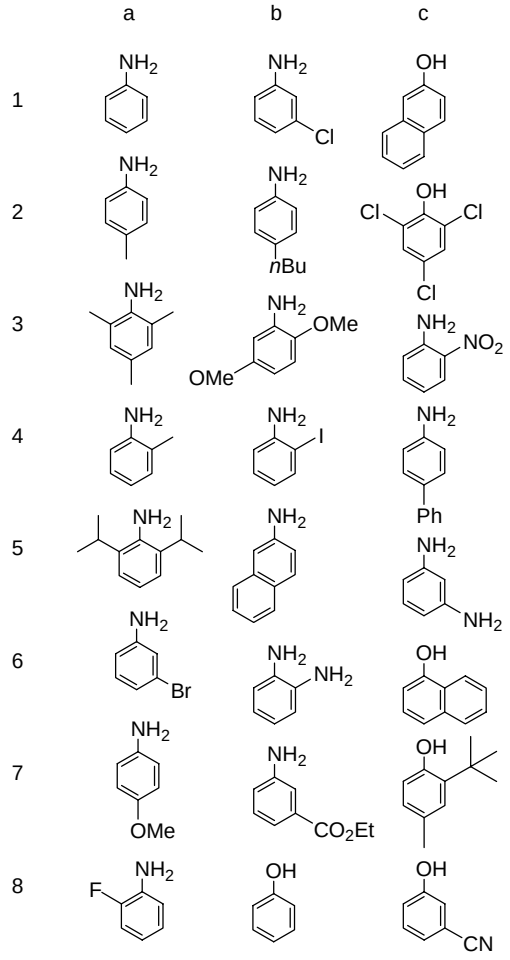
Enantioselectivities obtained with the primary ligand library. Relevant results of the screening of a divers library of amines are listed in the figure below with ascending enantioselectivity. Results in which racemic product or low yields were obtained have been discluded.



Enantioselectivities obtained with the secondary ligand library. A more specific library was screened based on the results from the first generation library. Enantioselectivities obtained in this second generation library of phosphoramidites and phosphites are listed in the figure below. Results in which racemic product or low yields were obtained have been discluded.



	a	b	c
1	84%	85%	48%
2	83%	80%	43%
3	62%	81%	ND
4	69%	ND	84%
5	71%	79%	68%
6	85%	20%	74%
7	**87%**	86%	25%
8	78%	47%	38%



ND : Not Determined

(yield to low for ee determination)

Synthesis of phosphoramidite ligand 4b

(*R*)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-α;3,4-α']dinaphthalen-4-yl)-(4-methoxy-phenyl)-amine (4b) 1.55 gram (5.4 mmol) of *bis*-β-naphthol was dissolved in 5 mL of PCl_3 and heated at reflux for 8 hours. Excess of PCl_3 was removed by distillation. The residual solid was subjected to an azeotropic distillation with toluene (5 mL) and dried under vacuum until a white foam was obtained (1.87 g, y = 99%). This solid was dissolved in 3 mL of dry toluene and added to a solution of 665 mg *p*-anisidine (5.4 mmol) in 3 mL of dry THF and 1 mL of triethylamine. The resulting suspension was stirred for 4 hours at room temperature. After filtration over celite and removal of the solvent under reduced pressure, the residual oil was chromatographed over silica (pentane/EtOAc 9/1) and filtered over a plug of neutral aluminum oxide (pentane/EtOAc 9/1). Yield: 61%; ^{1}H NMR (C_6D_6) δ = 7.44-7.68 (m, 6H), 7.12-7.26 (m, 2H), 6.92-7.01 (m, 2H), 6.65-6.79 (m, 2H), 4.83 (d, J = 4.0 Hz), 3.29 (s, 3H); ^{13}C NMR (C_6D_6) δ = 155.73 (2), 149.6, 147.86 (2d, J_{CP} = 3.7 Hz), 134.3 (2d, J_{CP} = 15.9 Hz), 133.38, 131.84 (2d, J_{CP} = 29.3 Hz), 130.42 (2d, J_{CP} = 69.6 Hz), 128.66 (2d, J_{CP} = 8.5 Hz), 127.24 (2d, J_{CP} = 13.4 Hz), 126.66 (2), 125.17 (2d, J_{CP} = 2.4 Hz), 122.44 (2d, J_{CP} = 70.8 Hz), 120.52 (2d, J_{CP} = 11.0 Hz), 115.03 (2), 55.02; ^{31}P NMR (C_6D_6) δ = 148.47; HRMS calcd for $C_{27}H_{20}NO_3P$: *m/z* 437.1201, found: 437.1181.

Catalytic arylboronic acid addition reactions

General procedure for Table 1, entries 1-11. In a flame dried Schlenk tube flushed with nitrogen, 1.55 mg (6.0 µmol, 3 mol%) of $Rh(acac)(C_2H_4)_2$ and 14.0 µmol (7 mol%) of one of the enantiomers of phosphoramidite **4** were dissolved in 2 mL of acetone. After stirring for 15 min at room temperature, 0.2 mmol of substrate **5** and 0.26 mmol of arylboronic acid **6** (1.3 equiv) were added and the resulting mixture was stirred at 40°C. After 4 h the reaction mixture was cooled to RT and the solvent evaporated under reduced pressure. Products were purified by column chromatography using eluent conditions reported for TLC.

***N*-(Dimethylsulfamoyl)-C-(4-chlorophenyl)-*C*-phenylmethyleneamine 7an** Obtained as a solid in 95% isolated yield (table 1, entry 2);

mp 118.9-120.8°C; TLC conditions (Heptane/EtOAc: 80/20) R_f = 0.30; ^{1}H NMR ($CDCl_3$) δ = 7.32-7.21 (m, 9H), 5.55 (d, *J* = 6.6 Hz, 1H), 4.66 (d, *J* = 6.6 Hz, 1H), 2.54 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 140.88, 139.91, 133.63, 128.88 (2), 128.83, 128.77 (2) 128.04 (2), 127.30 (2), 60.98, 37.63 (2); HRMS calcd for $C_{15}H_{17}N_2O_2S^{37}Cl$: *m/z* 324.0699, found: 324.0696; Anal. calcd for $C_{15}H_{17}N_2O_2SCl$: 55.46 (C), 5.28 (H), 8.62 (N), 9.87 (S), found: 55.35 (C), 5.28 (H), 8.32 (N), 9.83 (S); The ee was determined on a Chiralcel OD-H column with heptane : isopropanol = 90 : 10, flow = 0.5 mL/ min. Retention times: 14.0 and 16.9 min; $[\alpha]^{20}_D$ + 3.8 (*c* 2.9, $CHCl_3$) (table 1, entry 2, 95% ee).

***N*-(Dimethylsulfamoyl)-*C*-(4-fluorophenyl)-*C*-phenylmethyleneamine 7bn** Obtained as a solid in 81% isolated yield (table 1, entry 3); mp 110.8-111.2°C; TLC conditions (Heptane/EtOAc: 80/20) R_f = 0.35; ^{1}H NMR ($CDCl_3$) δ = 7.32-7.21 (m, 7H), 6.97 (m, 2H), 5.55 (d, *J* = 7.0 Hz, 1H), 5.01 (d, *J* = 7.0 Hz, 1H), 2.52 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 162.33 (d, J_{CF} = 247.9 Hz), 141.33, 137.43 (d, J_{CF} = 3.0 Hz), 129.30 (d, J_{CF} = 8.4 Hz), 128.99 (2), 128.08 (2), 127.46 (2), 115.72 (2d, J_{CF} = 21.5 Hz), 61.07, 37.77; HRMS calcd for $C_{15}H_{17}N_2O_2FS$: *m/z* 308.0995, found: 308.0988; Anal. calcd for $C_{15}H_{17}N_2O_2FS$: 58.45 (C), 5.56 (H), 9.09 (N), 10.40 (S), found: 58.05 (C), 5.67 (H), 9.02 (N), 10.40 (S); The ee was determined on a Chiralcel OD-H column with heptane : isopropanol = 90 : 10, flow = 0.5 mL/ min. Retention times: 13.8 and 15.6 min; $[\alpha]^{20}_D$ + 0.8 (c 2.5, $CHCl_3$) (table 1, entry 3, 93% ee).

***N*-(Dimethylsulfamoyl)-*C*-(4-trifluoromethylphenyl)-*C*-phenylmethyleneamine 7cn** Obtained as a solid in 98% isolated yield (table 1, entry 4); mp 105.5-106.6°C; TLC conditions (Heptane/EtOAc: 80/20) R_f = 0.30; ^{1}H NMR ($CDCl_3$) δ = 7.56 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.34-7.21 (m, 5H), 5.62 (d, *J* = 7.0 Hz, 1H), 5.02 (d, *J* = 7.0 Hz, 1H), 2.54 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 145.18, 140.42, 129.84 (q, J_{CF} = 32.2 Hz), 128.91, 128.11, 127.59 (2), 127.24 (2), 125.53 (2q, J_{CF} = 3.8 Hz), 123.82 (q, J_{CF} = 272.2 Hz), 61.11, 37.53 (2); HRMS calcd for $C_{16}H_{17}N_2O_2F_3S$: *m/z* 358.0963, found: 358.0955; Anal. calcd for $C_{16}H_{17}N_2O_2F_3S$: 53.64 (C), 4.78 (H), 7.82 (N), 8.95 (S), found: 53.80 (C), 5.17 (H), 7.48 (N), 10.40 (S); The ee was determined on a Chiralcel OD-H column with heptane : isopropanol = 90 : 10, flow = 0.5 mL/ min.

Retention times: 12.2 and 16.0 min; $[\alpha]^{20}_{D}$ – 6.9 (*c* 2.8, $CHCl_3$) (table 1, entry 4, 94% ee).

***N*-(Dimethylsulfamoyl)-*C*-(4-methoxyphenyl)-*C*-phenylmethyleneamine 7dn and 7io** Obtained as an oil in 72% (**7dn**, table 1, entry 5) and 97% (**7io**, table 1, entry 7) isolated yield; TLC conditions (Heptane/EtOAc: 80/20) R_f = 0.26; ^{1}H NMR ($CDCl_3$) δ = 7.29-7.15 (m, 7H), 6.81 (d, *J* = 12.6 Hz, 2H), 5.53 (d, *J* = 6.9 Hz, 1H), 4.92 (d, *J* = 6.9 Hz, 1H), 2.51 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 159.19, 141.78, 133.72, 128.81, 128.78 (2), 127.79 (2), 127.46 (2), 114.17 (2), 61.16, 37.75 (2); HRMS calcd for $C_{16}H_{20}N_2O_3S$: *m/z* 320.1194, found: 320.1185; The ee was determined on a Chiralcel OD-H column with heptane : isopropanol = 90 : 10, flow = 0.5 mL/ min. Retention times: 18.3 and 21.0 min; $[\alpha]^{20}_{D}$ -13.7 (*c* 2.8, $CHCl_3$) (table 1, entry 7, 92% ee).

***N*-(Dimethylsulfamoyl)-*C*-(4-methylphenyl)-*C*-phenylmethyleneamine 7en and 7ip** Obtained as a solid in 77% (**7en**, table 1, entry 6) and 81% (**7ip**, table 1, entry 8) isolated yield. mp 75.9-76.8°C. TLC conditions (Heptane/EtOAc: 80/20) R_f = 0.39. ^{1}H NMR ($CDCl_3$) δ = 7.30-7.19 (m, 5H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.53 (d, *J* = 7.0 Hz, 1H), 4.88 (d, *J* = 7.0 Hz, 1H), 2.51 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 141.76, 138.63, 137.66, 129.55, 128.83 (2), 127.83 (2), 127.52 (2), 127.46 (2), 61.51, 37.78, 21.22 (2); HRMS calcd for fragment $C_{14}H_{14}N$: *m/z* 196.1126, found: 196.1127; The ee was determined on a Chiralcel OD-H column with heptane : isopropanol = 90 : 10, flow = 0.5 mL/ min. Retention times: 12.8 and 14.5 min; $[\alpha]^{20}_{D}$ -7.3 (*c* 1.9, $CHCl_3$) (table 1, entry 8, 94% ee).

***N*-(Dimethylsulfamoyl)-*C*-(2-methylphenyl)-*C*-phenylmethyleneamine 7fn** Obtained as an oil in 91% isolated yield (table 1, entry 9); TLC conditions (Heptane/EtOAc: 80/20) R_f = 0.37; ^{1}H NMR ($CDCl_3$) δ = 7.43-7.18 (m, 9H), 5.84 (d, *J* = 6.6 Hz, 1H), 4.82 (d, *J* = 6.6 Hz, 1H), 2.55 (s, 6H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$) δ = 140.94, 139.36, 135.71, 131.02, 128.88, 127.93, 127.85 (2), 127.82 (2), 127.11, 126.42, 58.31, 37.71, 19.63 (2); HRMS calcd for $C_{16}H_{20}N_2O_2S$: *m/z* 304.1245, found: 304.1235; The ee was determined on a Chiralpak AS column with heptane : isopropanol = 90 : 10, flow = 1.0 mL/ min; Retention times: 12.0 and 13.9 min; $[\alpha]^{20}_{D}$ -15.5 (*c* 0.8, $CHCl_3$) (table 1, entry 9, 87% ee).

***N*-(Dimethylsulfamoyl)-*C*-(3-fluorophenyl)-*C*-phenylmethyleneamine 7gn** Obtained as a solid in 91% isolated yield (table 1, entry 10); mp 103.6-105.4°C; TLC conditions (Heptane/EtOAc: 80/20) R_f = 0.39; ^{1}H NMR ($CDCl_3$) δ = 7.39-7.29 (m, 6H), 7.14 (m, 1H), 7.05 (m, 1H), 6.99 (m, 1H), 5.62 (d, *J* = 6.6 Hz, 1H), 4.86 (d, *J* = 6.4 Hz, 1H), 2.60 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 163.05 (d, J_{CF} = 246.9 Hz), 144.15 (d, J_{CF} = 15.9 Hz), 140.97, 130.42 (d, J_{CF} = 8.4 Hz), 129.06, 128.23, 127.52, 123.22 (d, J_{CF} = 3.1 Hz), 114.84 (d, J_{CF} = 20.8 Hz), 114.58 (d, J_{CF} = 22.2 Hz), 61.29 (d, J_{CF} = 2.3 Hz), 37.79 (2); HRMS calcd for $C_{15}H_{17}N_2O_2FS$: *m/z* 308.0995, found: 308.0992; Anal. calcd for $C_{15}H_{17}N_2O_2FS$: 58.45 (C), 5.56 (H), 9.09 (N), 10.40 (S), found: 58.1 (C), 5.52 (H), 8.92 (N); The ee was determined on a Chiralcel AD column with heptane : isopropanol = 95 : 5, flow = 1.0 mL/ min. Retention times: 16.6 and 19.6 min; $[\alpha]^{20}_D$ - 7.4 (*c* 2.5, $CHCl_3$) (table 1, entry 10, 93% ee).

***N*-(Dimethylsulfamoyl)-*C*-(2-thienyl)-*C*-phenylmethyleneamine 7hn** Obtained as a solid in 81% isolated yield (table 1, entry 11); mp 81.1-82.9°C; TLC conditions (Heptane/EtOAc: 80/20) R_f = 0.33; ^{1}H NMR ($CDCl_3$) δ = 7.43-7.33 (m, 5H), 7.27-7.25 (m, 1H), 6.95 (dd, *J* = 5.1 Hz, *J* = 3.7 Hz, 1H), 6.81 (m, 1H), 5.83 (d, *J* = 7.0 Hz, 1H), 4.94 (br s, 1H), 2.62 (s, 6H); ^{13}C NMR ($CDCl_3$) δ = 145.61, 141.28, 128.93, 128.38, 127.26, 127.07, 126.18, 125.81, 57.93, 37.77 (2); HRMS calcd for fragment $C_{11}H_{10}NS$: *m/z* 188.0534, found: 188.0530; The ee was determined on a Chiralcel OJ column with heptane : isopropanol = 90 : 10, flow = 1.0 mL/min. Retention times: 16.9 and 24.2 min; $[\alpha]^{20}_D$ + 12.0 (*c* 2.3, $CHCl_3$) (table 1, entry 11, 91% ee).

Procedure for Table 1, entry 12. In a flame dried Schlenk tube flushed with nitrogen, 10.3 mg (40.4 µmol, 1 mol%) of $Rh(acac)(C_2H_4)_2$ and 44.2 mg (101.0 µmol, 2.5 mol%) of phosphoramidite (*R*)-**4b** was dissolved in 10 mL of acetone. After stirring for 15 min at room temperature, 1 gram (4.0 mmol) of substrate **5a** and 634 mg of phenylboronic acid (5.2 mmol, 1.3 equiv) were added and the resulting mixture was stirred at 45°C. After 16 h the reaction mixture was cooled to RT and the solvent evaporated under reduced pressure. Products were purified by column chromatography using eluent conditions reported for TLC

(*vide supra*). The product **7an** was obtained as a white solid with 94% ee and 92% isolated yield.

Removal of the *N,N*-dimethylsulfamoyl group

***C*-(4-Chloro-phenyl)-*C*-phenyl-methylamine 8an.** A 50 mL flask equipped with a reflux condenser was charged with 1 mmol of amine **7an** (94% ee) in 2 mL of dry 1,3-diaminopropane. The mixture was heated with a microwave synthesis system for 2 h, during which it was gently refluxing. After cooling to RT, the mixture was diluted with 50 mL of CH_2Cl_2 and extracted with 50 mL of water. After extraction of the water layer with 2 x 50 mL of CH_2Cl_2, the combined organic layers were dried on Na_2SO_4. The product was obtained as a colorless oil in 96% yield after removal of the solvent under reduced pressure. ^{1}H NMR ($CDCl_3$) δ = 7.19-7.29 (m, 9H), 5.14 (s, 1H), 1.87 (bs, 2H); ^{13}C NMR ($CDCl_3$) δ = 145.13, 143.98, 132.62, 128.58, 128.53 (2), 128.25 (2), 127.17 (2), 126.76 (2), 59.13; HRMS calcd for $C_{13}H_{12}N^{37}Cl$: *m/z* 217.0658, found: 217.0651; $[\alpha]^{20}_D$ -9.7 (*c* 1.1, EtOH) (95%), literature: $[\alpha]^{20}_D$ +10.8 (*c* 2.2, EtOH) for (*S*)-**8an**.[4] Retention of ee was shown by chiral HPLC (*vide supra*) after reprotection with *N,N*-dimethylsulfamoyl chloride in THF in the presence of an equivalent of triethylamine.

References

[1] a)L. Lefort, J. A. F. Boogers, A. H. M. de Vries, J. G. de Vries, *Org. Lett.* **2004**, *6*, 1733; b) A. Duursma, L. Lefort, J. A. F. Boogers, A. H. M. de Vries, J. G. de Vries, A. J. Minnaard, B. L. Feringa, *Org. Biomol. Chem.* **2004**, *2*, 1682.

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[3] M. Huisman, R. ten Have, A. M. van Leusen, *Synth. Commun.* **1997**, *27*, 945.

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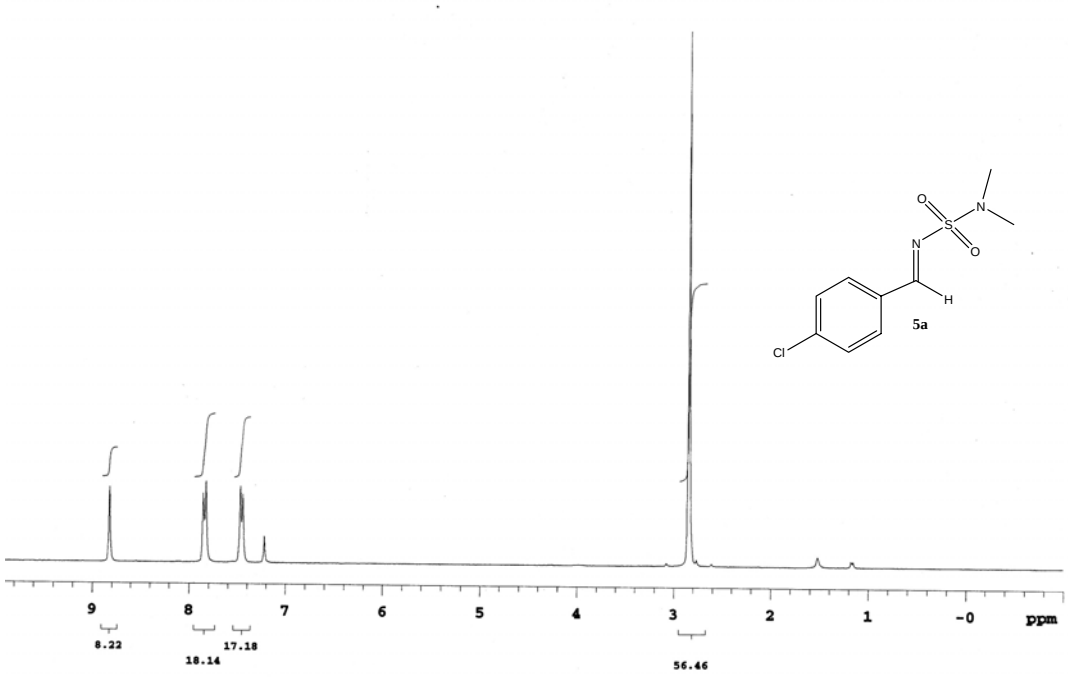
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S
N
O
N
H
Cl
5a
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8
7
6
5
4
3
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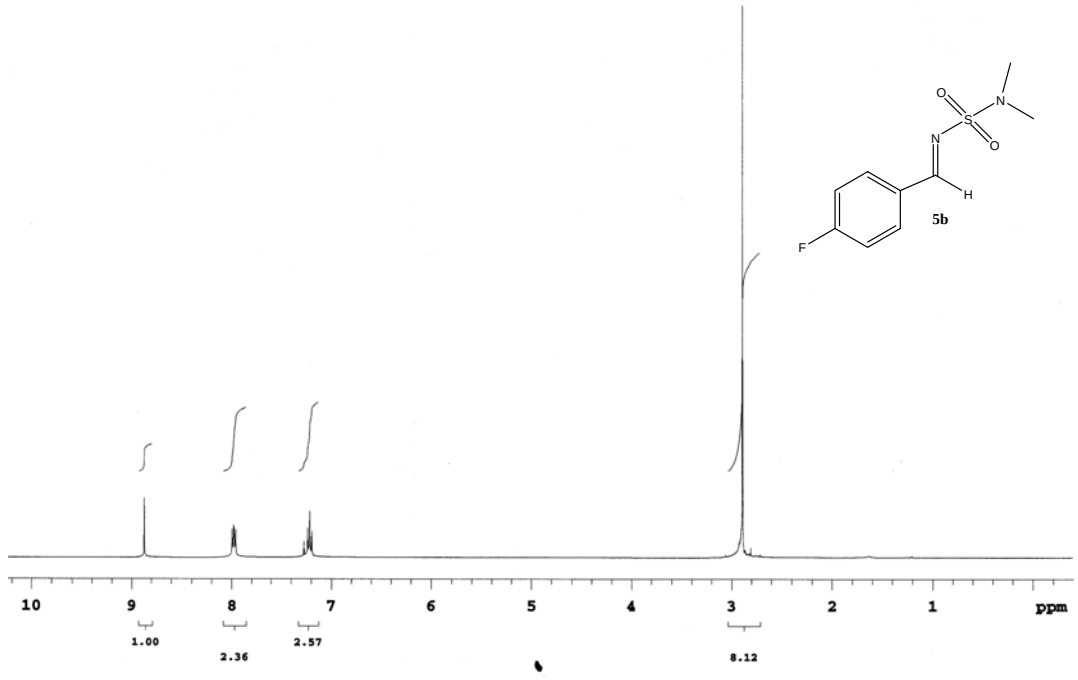
18.14
17.18
56.46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N
O
N
H
F
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8
7
6
5
4
3
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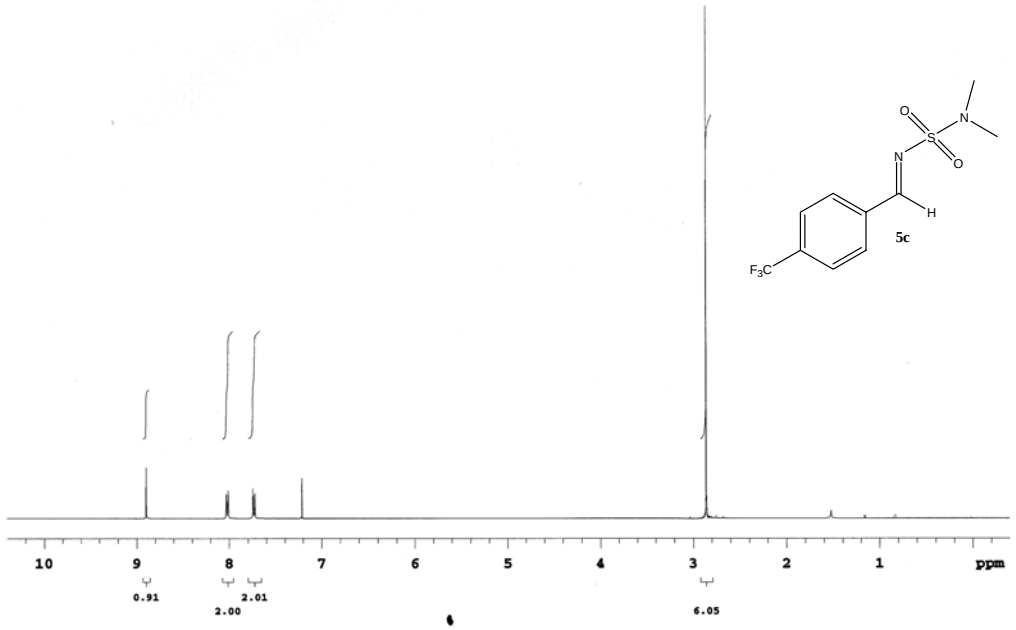
8.12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N
O
N
H
F3C
5c
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8
7
6
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4
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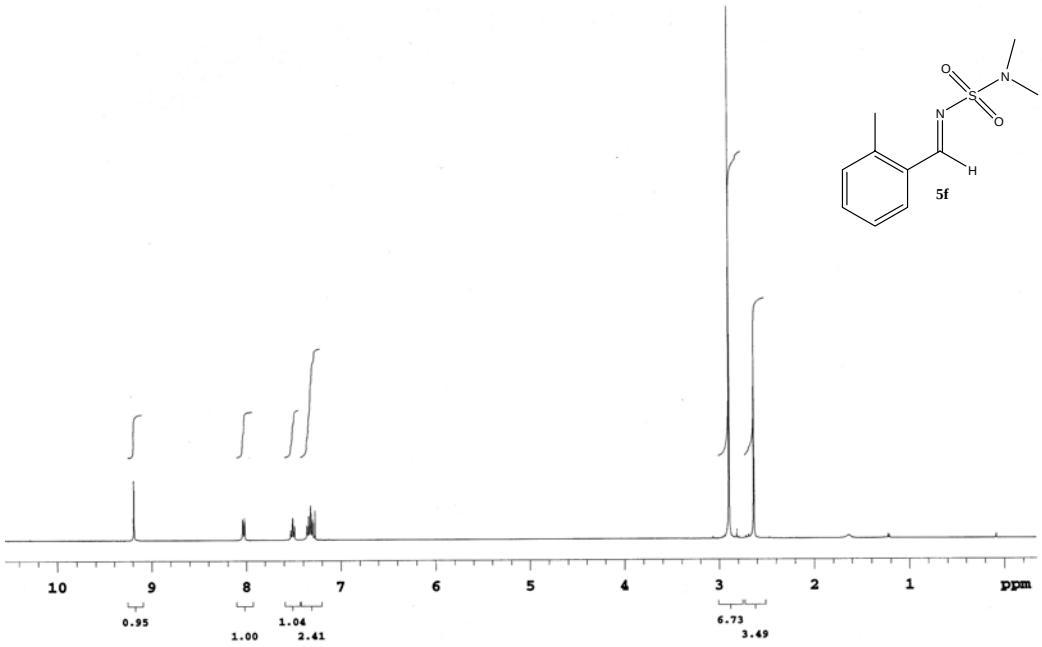
2.01
6.05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S
N
O
N
H
5f
10
9
8
7
6
5
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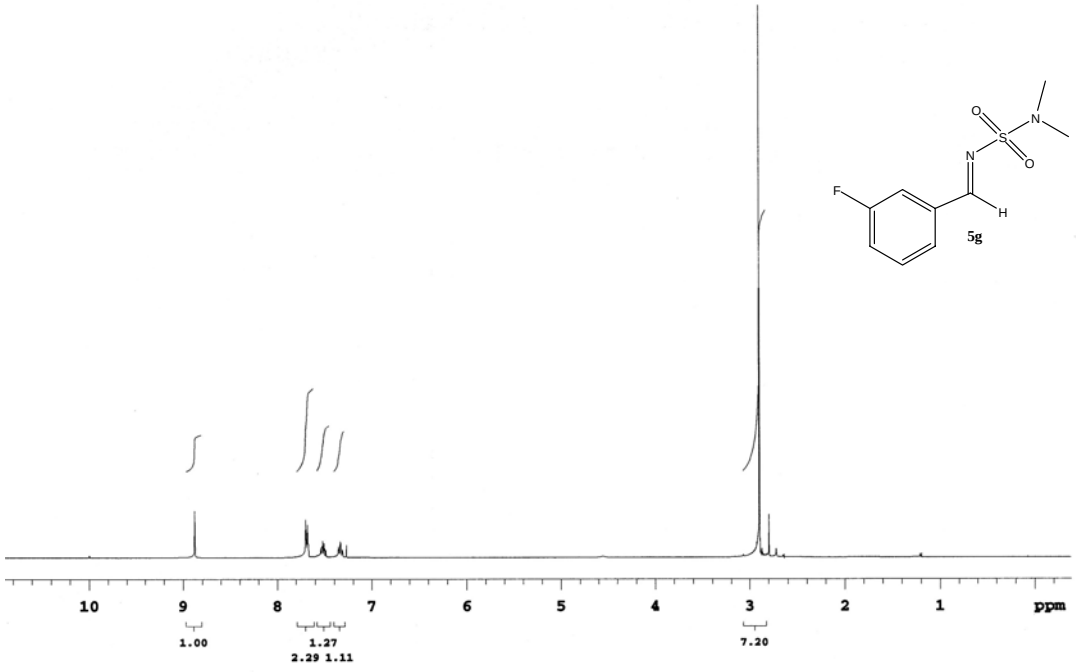
3.49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N
S
O
N
F
H
10
9
8
7
6
5
4
3
2
1
ppm
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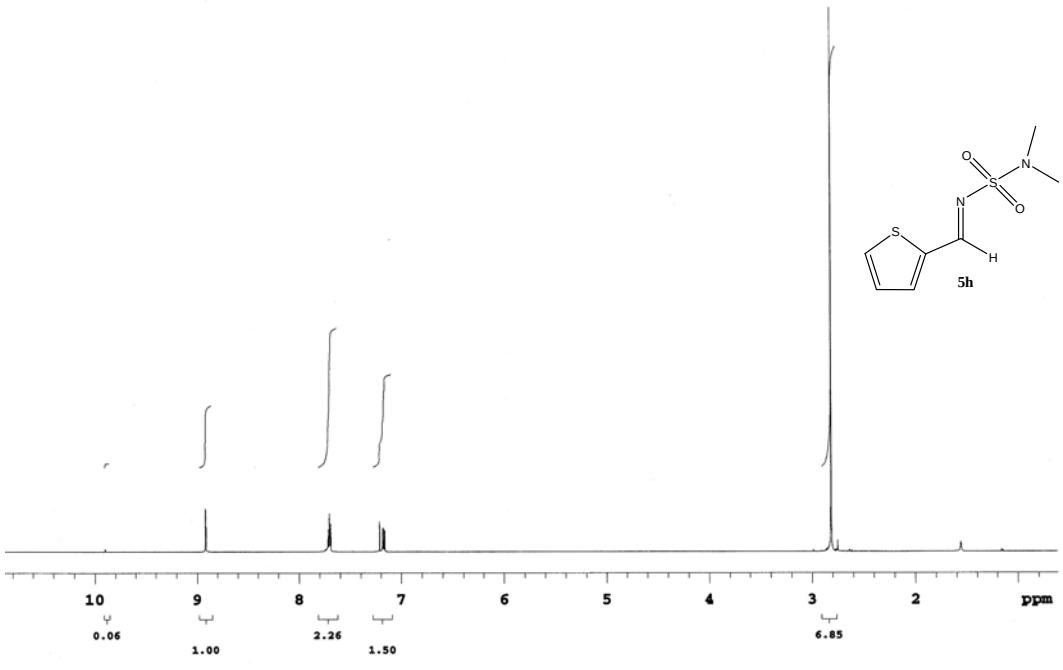
1.27
2.29 1.11
7.20

5g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S
O
N
S
H
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5
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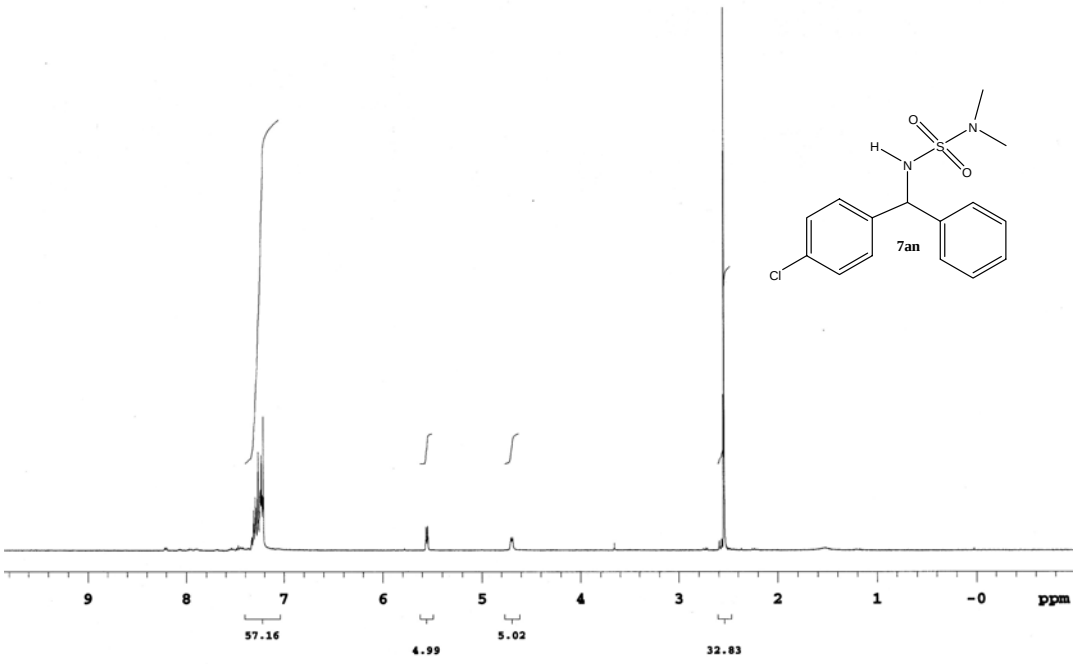
1.50
6.85

5h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Cl
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7
6
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4
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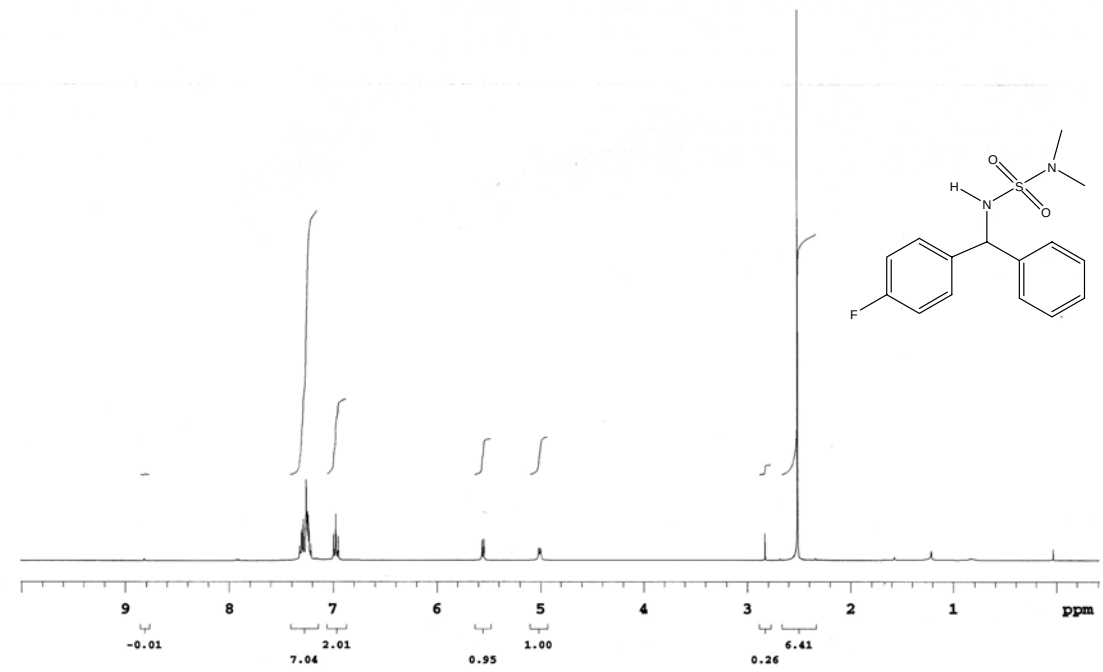
32.83


F
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8
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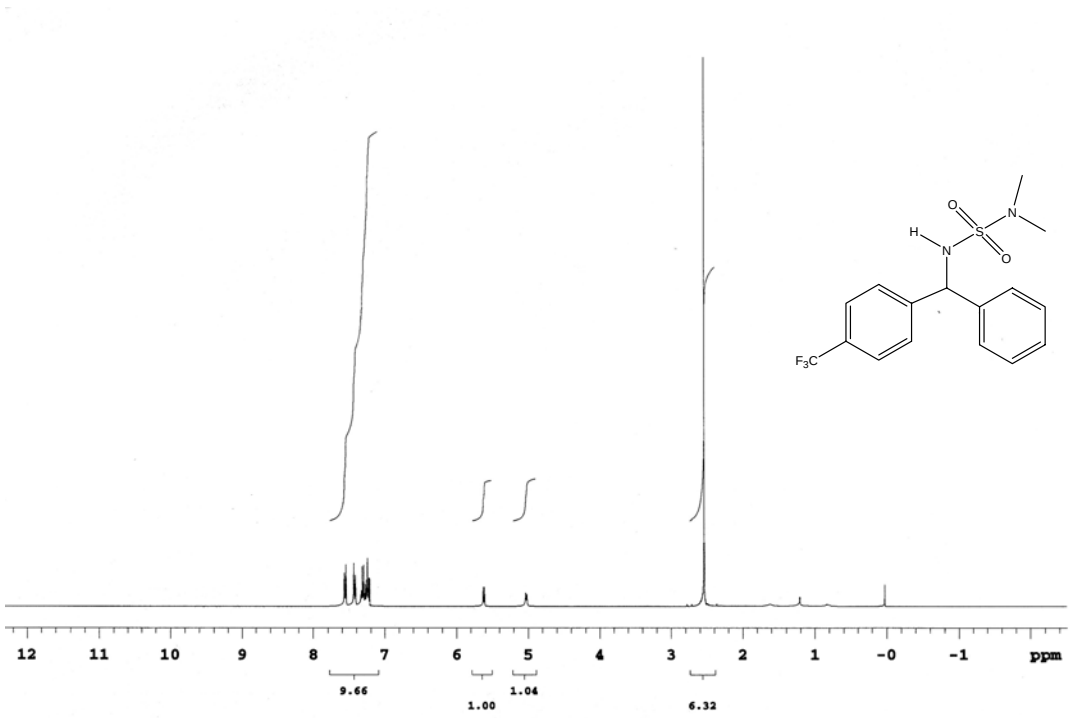
6.41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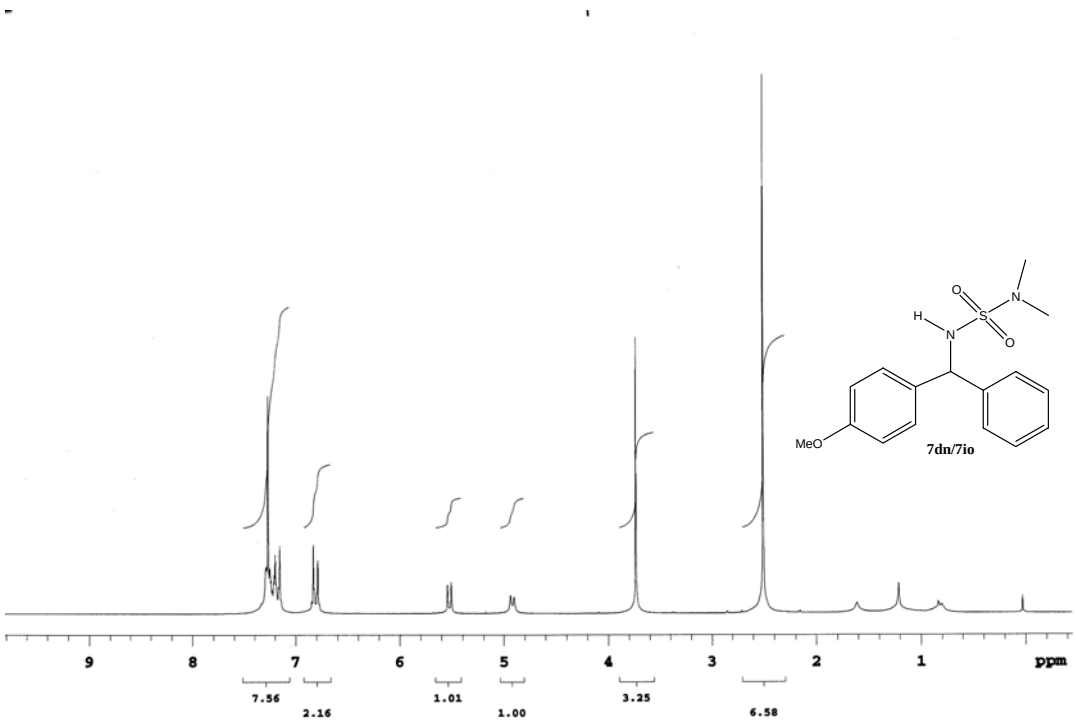
6.32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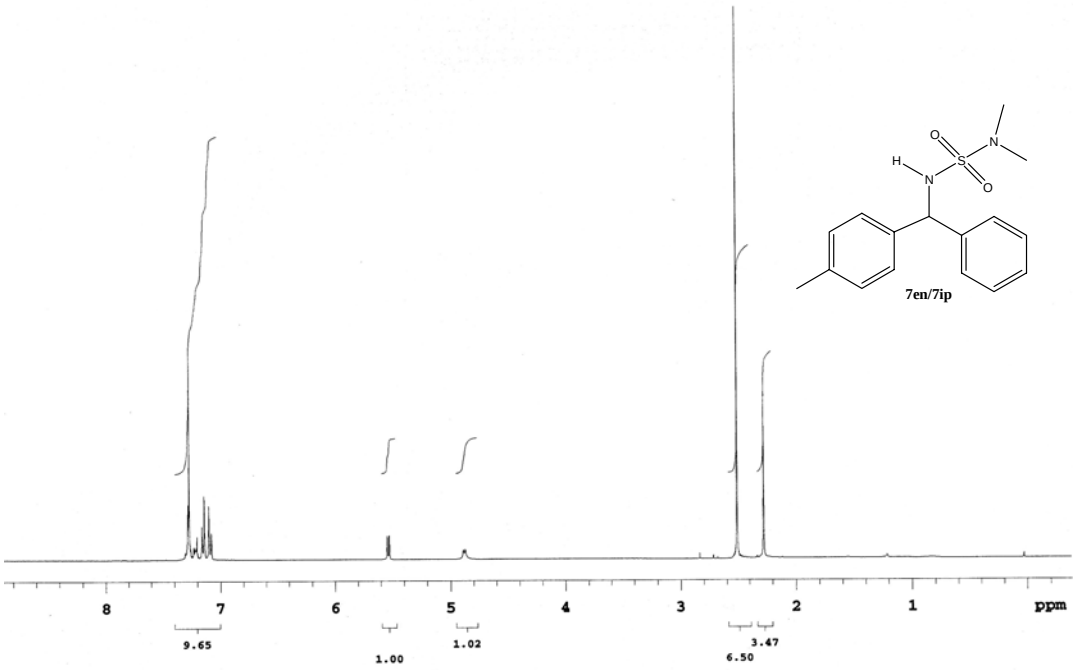
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6
5
4
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1.02
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3.47

O
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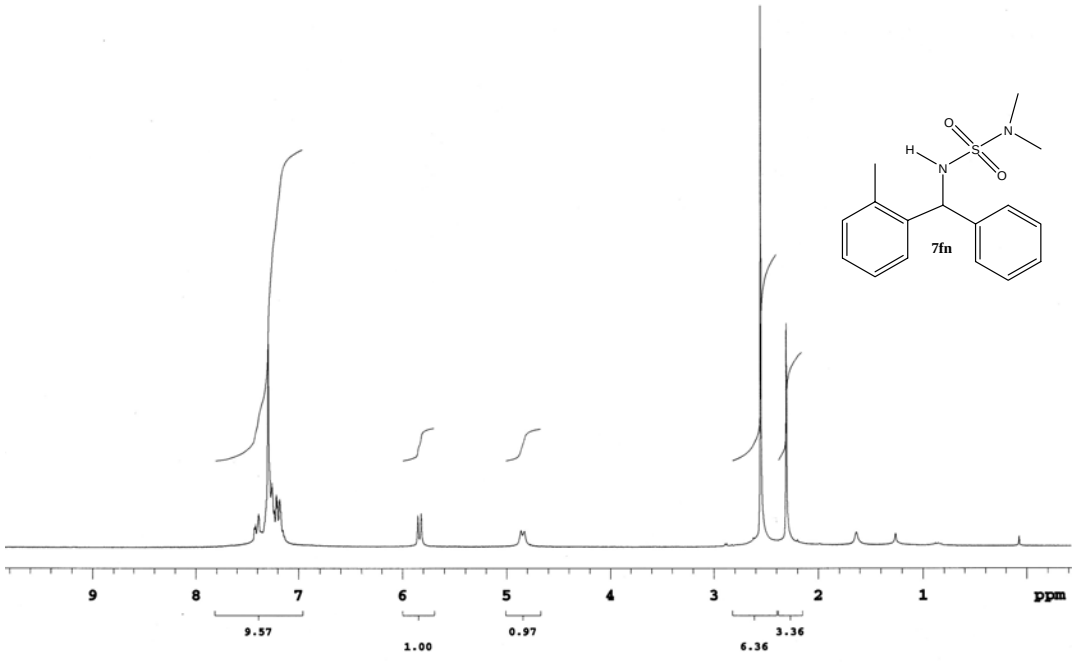
H
S
N
O

7en/7ip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7
6
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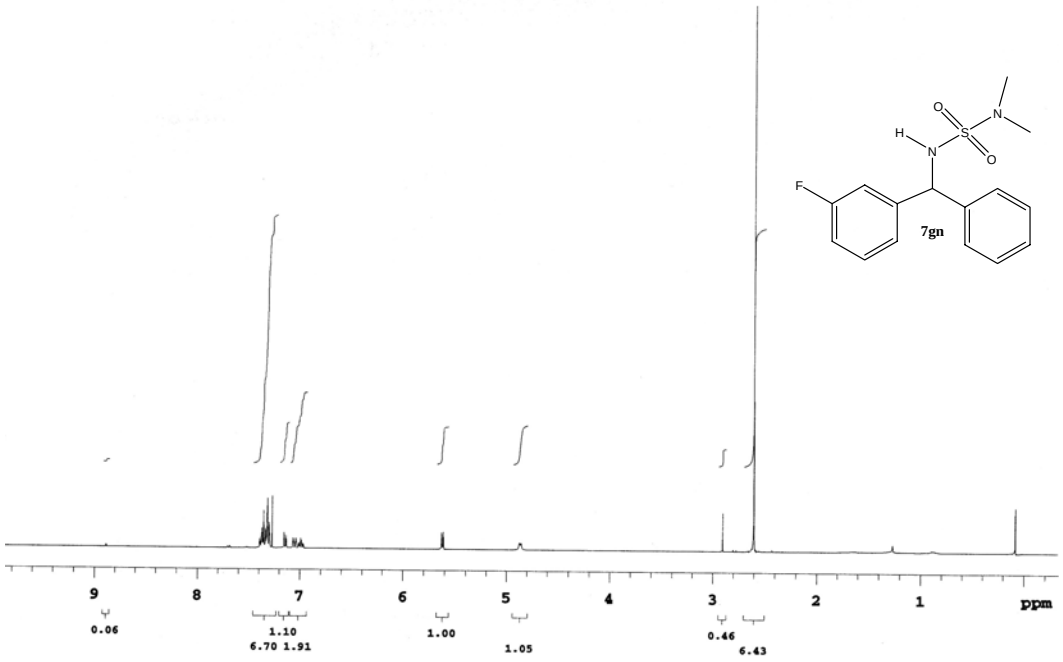
6.36
3.36

O
N
H
S
N
O

7fn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8
7
6
5
4
3
2
1
ppm
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1.10
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1.00
1.05
0.46
6.43

O
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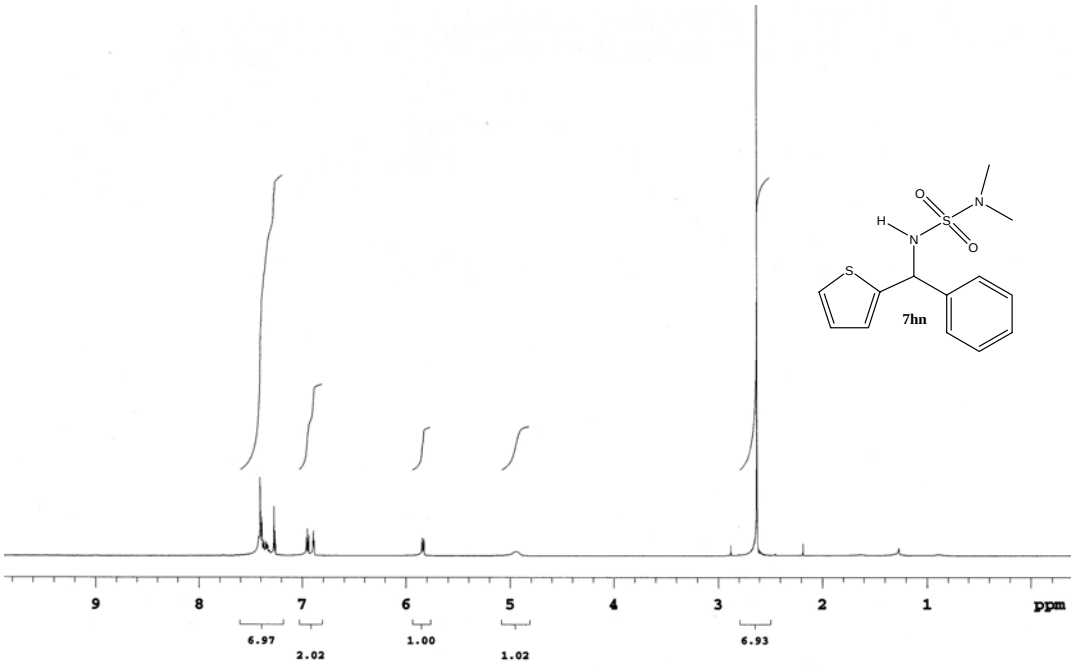
H
S
N
O
F

7gn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6
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4
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ppm
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2.02
1.00
1.02
6.93

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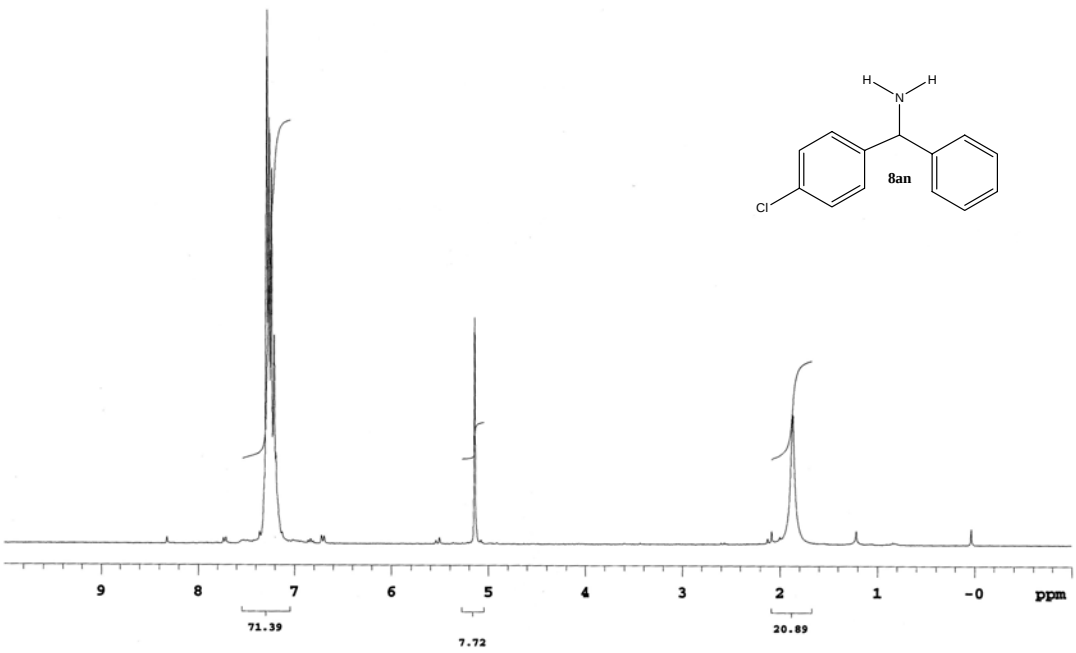
H
S
N
O
S

7hn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H
Cl
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6
5
4
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2
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-0
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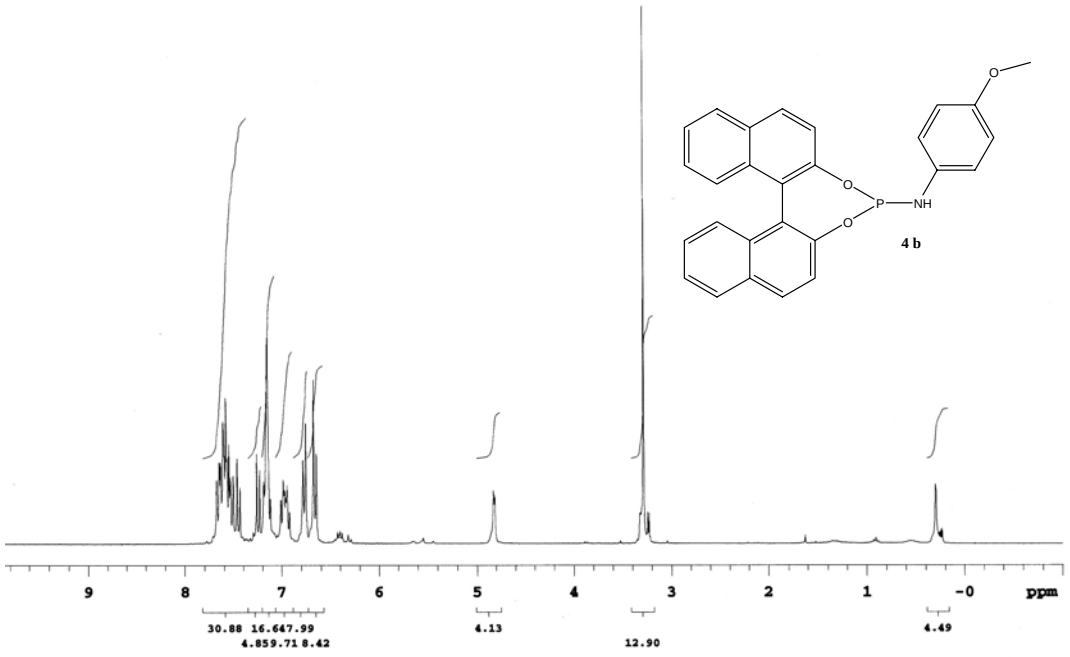
20.89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P
NH
O
4 b
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7
6
5
4
3
2
1
-0
ppm
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4.859.71 8.42
4.13
12.90
4.49