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Supporting Information

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Iridium-Catalyzed Synthesis of Primary Allylic Amines From Allylic Alcohols: Sulfamic Acid as Ammonia Equivalent

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All reactions were performed in oven dried glass ware under argon. For the reactions, solvents were purified by distillation and dried by passage over two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; Macherey und Nagel; activated under a flow of N_2 at 300º over night; solvent drying system) under an argon atmosphere (H_2O content < 30 ppm, *Karl-Fischer* titration). For flash chromatography technical grade solvents were used, which were distilled prior to use.

For all allylic amination reactions absolute *N*,*N*-Dimethylformamide (puriss., > 99.5% (GC) stored over molecular sieves) received from Fluka was employed. Sulfamic acid was obtained from Fluka (puriss. p.a. (>99.3%, lot number: 1097230). $[IrCl(cyclooctene)_2]_2$ was prepared according to literature procedures from $IrCl_3$.[1] Ligands **L1** was used as received from Strem Chemicals, ligand **L2** was synthesized according to the literature.[2] All allylic alcohols were prepared by the reaction of the corresponding aldehyde with vinyl magnesium bromide. Commercially available chemicals were used as received unless noted otherwise. Deuterated solvents were obtained from Armar Chemicals, Döttingen, Switzerland in the indicated purity grade.

Chromatographic purification of the ligands was performed as flash chromatography using Brunschwig silica 32-63, 60Å, using hexanes/toluene as eluent with 0.5 bar pressure. Chromatographic purification of the allylic amines was performed using alumina Woelm N, Akt. 1 using dichloromethane/methanol as eluent.

TLC was performed on Merck silica gel 60 F_{254} TLC glass plates and visualized with UV light or permanganate stain.

Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected.

^{1}H-NMR spectra were recorded on a VARIAN Mercury 300 MHz or a Gemini 300 MHz spectrometer in the indicated deuterated solvent. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration, interpretation).

^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a VARIAN Mercury 75 MHz spectrometer in the indicated deuterated solvent.

^{19}F-NMR spectra were recorded with ^{1}H-decoupling on a VARIAN Mercury 282 MHz spectrometer in the indicated deuterated solvent.

^{31}P-NMR spectra were recorded with ^{1}H-decoupling on a VARIAN Mercury 121 MHz spectrometer in the indicated deuterated solvent.

Infrared spectra were recorded neat on a Varian 800 FT-IR Scimilar Series spectrophotometer.

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[1] R. H. Crabtree, J. M. Quirk, *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 407.

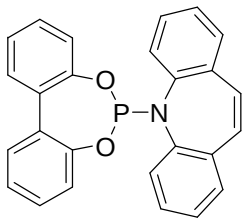
[2] B. Bartels, C. Garcia-Yebra, F. Rominger, G. Helmchen, *Eur. J. Inorg. Chem.* **2002**, 2569.

Optical rotations were measured on a JASCO DIP-1000 digital polarimeter in 10 cm, 2 mL cells, the concentration in g/100 mL and the solvent is given in parentheses.
HPLC analyses were carried out on a Merck Hitachi D-7000 system with Daicel columns in hexane/isopropanol mixtures. The absolute configurations were assigned by comparison of the $[a]_D$ values of known compounds.
High resolution mass spectrometric measurements were performed by the mass spectrometry service of the Laboratorium für Organische Chemie at the ETH Zürich on an Ion Spec Ultima MALDI-FT-ICR MS using the DHB-tl (2,5-Dihydroxybenzoic acid-two layers) method at 4.7 Tesla. EI measurements were performed on a VG Tribrid spectrometer, 70 eV. ESI measurements were performed on a TSQ 7000.
Elemental analysis was performed by the Mikroelementaranalytisches Laboratorium der ETH Zürich.

General Procedure 1: Synthesis of the Phosphoramidites L3-L5

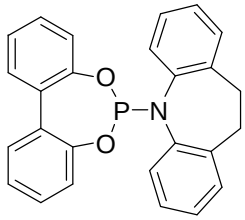
A Schlenk flask under argon was charged with the diol (1 equiv). PCl_3 (15 equiv) and a catalytic amount of *N*-methylpyrrolidone (0.03 equiv) were added and the reaction mixture was heated at 50 °C during 30 min. The initially heterogeneous mixture turned into a brownish homogenous solution. After cooling to 23 °C, the excess PCl_3 was evaporated in vacuo, 1 mL toluene was added to azeotropically remove remaining PCl_3. The resulting phosphorchloridite (air-and moisture-sensitive!) was redissolved in 25 mL THF.
In a separate Schlenk flask under argon, the amine (1.2 equiv) dissolved in 25 mL THF was deprotonated at -78 °C by the slow addition of *n*-BuLi (1.1 equiv, 1.6M solution in hexanes). The resulting deep blue solution was continued to stir at -78 °C for 1 hour before the phosphorchloridite solution was slowly transferred via cannula. The resulting mixture was stirred at -78°C, then warmed to 23°C and continued to stir during 8 h. After completion of the reaction, as determined by TLC, the solvents were evaporated in vacuo. Purification of the residue by flash chromatography on silica gel using hexanes/toluene as eluent afforded the desired product as a white foam.

(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']diphenyl-4-en)-dibenzo[*b,f*]azepine L3



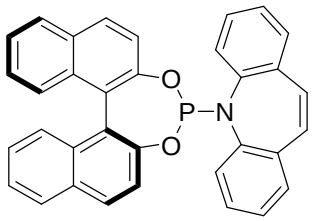
Prepared according to General Procedure 1 using 2.23 g (12.0 mmol) 2,2'-biphenol. Yield: 1.35 g (3.31 mmol, 28%) (off-white powder). Keep under inert atmosphere for long-term storage. mp 159 °C; IR (neat) ν 3062, 3025, 1486, 1434, 1196, 1095, 984, 890, 848, 759, 746; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35-7.38 (m, 2H), 7.22-7.27 (m, 4H), 7.10-7.20 (m, 8H), 6.98-7.08 (m, 2H), 6.96 (s, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 150.6, 142.4, 135.8, 131.3, 130.4, 130.3, 129.4, 128.9, 128.8, 128.7, 126.4, 124.2, 121.9; ^{31}P-NMR (121 MHz, $CDCl_3$) 137.9; HR-MALDI-MS *m/z* calcd for $C_{26}H_{18}NO_2P$ $[M+H]^+$ 408.1148, found 408.1149.

(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']diphenyl-4-en)-10,11-dihydro-dibenzo-[*b,f*]azepine L4



Prepared according to General Procedure 1 using 834 mg (4.48 mmol) 2,2'-biphenol. Yield: 568 mg (1.39 mmol, 31%) (off-white powder). Keep under inert atmosphere for long-term storage. mp 145 °C; IR (neat) ν 3061, 3029, 1486, 1436, 1184, 1094, 990, 880, 842, 699; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.43-7.6.94 (m, 16H), 3.77-3.61 (m, 2H), 3.01-2.93 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 150.5, 142.3, 136.8, 130.2, 130.0, 129.9, 128.8, 127.9, 126.5, 126.2, 124.2, 121.2 , 31.6; ^{31}P-NMR (121 MHz, $CDCl_3$) 136.4; HR-MALDI-MS *m/z* calcd for $C_{26}H_{20}NO_2P$ $[M+H]^+$ 410.1304 found 410.1303.

(S)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)-dibenzo-[*b,f*]-azepine L5



Prepared according to General Procedure 1 using 300 mg (1.05 mmol) *(S)*-BINOL. Yield: 239 mg (0.47 mmol, 45%) (off-white powder). Keep under inert atmosphere for long-term storage. mp 246 °C; $[\alpha]_D^{25}$ +313.6 (*c* 1.07, $CHCl_3$); IR (neat) ν 3057, 3023, 1590, 1484, 1236, 1201, 1070, 979, 938, 800, 767; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.60 (dd, *J* = 8.8, 0.7 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1 H), 7.38-7.31 (m, 2H), 7.23-7.13 (m, 2H), 7.19-7.13 (m, 6H), 7.11-7.07 (m, 1H), 6.96 (d, *J* = 11.6 Hz, 1H), 6.92-6.87 (m, 2H), 6.84 (dd, *J* = 8.8, 0.5 Hz, 1H), 6.53-6.49 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$)
δ 149.9, 149.9, 148.7, 143.0, 142.8, 142.5, 135.4, 135.2, 132.8, 132.1, 131.5, 131.4, 131.3, 130.2, 130.1, 129.1, 129.0, 128.9, 128.8, 128.5, 128.4, 128.3, 128.3, 127.8, 126.8, 126.7, 126.1, 126.0, 1 25.6, 124.8, 124.2, 122.1, 121.5, 121.1; ^{31}P-NMR (121 MHz, $CDCl_3$) 138.0; HR-MALDI-MS *m/z* calcd for $C_{34}H_{22}NO_2P$ $[M+H]^+$ 508.1461, found 508.1463.

Substrate, Solvent, Ligand Screening

Representative Procedure: A Schlenk flask under argon was charged with $[\{Ir(cod)Cl\}_2]$ (10.1 mg, 15 μmol, 3 mol %) and the corresponding ligand (30 μmol, 6 mol %). 2 mL (0.25 M) solvent were added and the reaction mixture was stirred at 23 °C for 15 min. The allylic carbonate resp. alcohol (0.50 mmol, 1 equiv) was added via syringe followed by the addition of solid sulfamic acid (49 mg, 0.50 mmol, 1 equiv). The resulting reaction mixture was stirred at 23 °C for 24

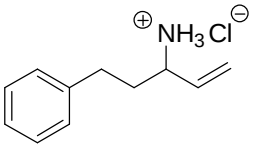
hours. Conversion was checked by disappearance of the starting material on TLC and/or by measuring ^{1}H-NMR of an aliquot taken from the reaction mixture. In cases, in which the conversion was above 50%, triethylamine (202 mg, 2.00 mmol, 4 equiv) and freshly distilled benzoylchloride (141 mg, 1.00 mmol, 2 equiv) were added to the reaction mixture and stirring was continued during 4 hours at 23 °C. Subsequently, the reaction mixture was partitioned between 10 mL CH_2Cl_2 and 10 mL H_2O. The aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude allylic benzamide. Purification of the residue by flash chromatography on silica gel using hexanes/EtOAc as eluent afforded the desired benzamide.

General Procedure 2: Iridium-Catalyzed Allylic Amination with Sulfamic Acid

Representative Procedure: A Schlenk flask under argon was charged with [{Ir(cod)Cl}$_2$] (10 mg, 15 μmol, 1.5 mol %) and ligand (3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']diphenyl-4-en)-dibenzo[*b,f*]azepine **L3** (12 mg, 30 μmol, 3 mol %). 2 mL *N*,*N*-dimethylformamide were added and the reaction mixture was stirred at 23 °C for 15 min. The allylic alcohol (1.00 mmol, 1 equiv) was added via syringe followed by the addition of solid sulfamic acid (97 mg, 1.00 mmol, 1 equiv). The resulting reaction mixture was heated to 50°C. After completion of the reaction (usually 6-7 h), as determined by TLC, the solvent was evaporated at high vacuum. The resulting brown residue was dissolved in 10 mL CH_2Cl_2 and 10 ml sat. aqueous $NaHCO_3$ solution and stirred for 10 min. The aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude allylic amine. The ratio of regioisomers was determined by ^{1}H NMR analysis of the unpurified sample. Purification of the residue by flash chromatography on basic or neutral alumina using CH_2Cl_2/MeOH as eluent afforded the desired amine. As some amines proved to be unstable and/or volatile, they were precipitated by addition of 2M HCl in Et_2O and stored as their hydrochloride salts.

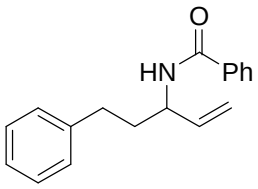
Substrates:

5-Phenylpent-1-en-3-amine hydrochloride (table 1, entry 1)



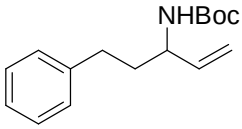
Prepared according to general procedure 2. Off-white solid. Yield: 162 mg (0.82 mmol, 82%); mp 168 °C; IR (neat) ν 2882 (br), 2045, 1601, 1511, 1453, 988, 936, 765, 745; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.67 (br. s, 3H), 7.31-7.19 (m, 5H), 5.93 (ddd, *J* = 17.3, 10.5, 7.7 Hz, 1H), 5.47 (d, *J* = 17.3 Hz, 1H), 5.36 (d, *J* = 10.5 Hz), 3.74 (br. s, 1H), 2.82-2.64 (m, 2H), 2.32-2.04 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 139.8, 132.9, 128.4, 128.3, 126.2, 121.2, 54.1, 34.7, 31.4; HR-ESI-MS *m/z* calcd for $C_{11}H_{13}$ $[M\text{-}NH_3]^+$ 145.1012, found 145.1012. Combustion Analysis: Anal. calcd for $C_{11}H_{16}NCl$: C, 66.83; H, 8.16; N, 7.08 found C, 66.54; H, 8.09; N, 6.81.

N-(5-phenylpent-1-en-3-yl)-benzamide (table 1, entry 2)



A Schlenk flask under argon was charged with [{Ir(cod)Cl}$_2$] (10 mg, 15 μmol, 3 mol %) and ligand (3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']diphenyl-4-en)-dibenzo[*b,f*]azepine **L3** (12 mg, 30 μmol, 6 mol %). 2 mL *N*,*N*-dimethylformamide were added and the reaction mixture was stirred at 23 °C for 15 min. 5-phenylpent-1-en-3-ol **3** (81 mg, 0.50 mmol, 1 equiv) was added via syringe followed by the addition of solid sulfamic acid (49 mg, 0.50 mmol, 1 equiv). The resulting reaction mixture was heated to 50°C. Conversion was checked by disappearance of the starting material on TLC and/or by measuring ^{1}H-NMR of an aliquot taken from the reaction mixture. After completion of the reaction (usually 3-4 h), triethylamine (202 mg, 2.00 mmol, 4 equiv) and freshly distilled benzoylchloride (141 mg, 1.00 mmol, 2 equiv) were added to the reaction mixture and stirring was continued during 4 hours at 23 °C. Subsequently, the reaction mixture was partitioned between 10 mL CH_2Cl_2 and 10 mL H_2O. The aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude allylic benzamide. Purification of the residue by flash chromatography on silica gel using hexanes/EtOAc as eluent afforded *N*-(5-phenylpent-1-en-3-yl)-benzamide (97 mg, 0.37 mmol, 73%) as an off-white solid.
mp 131 °C; IR (neat) ν 3326, 2946, 2979, 2862, 1633, 1526, 1487, 1334, 1292, 920, 748, 698; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.71-7.68 (m, 2H), 7.52-7.37 (m, 3H), 7.31-7.17 (m, 5H), 6.11 (d, *J* = 8.2 Hz, 1H), 5.90 (ddd, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.24 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.18 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.76 (br. quintet, 1H), 2.75 (t, *J* = 2.9 Hz, 2H), 2.10-1.90 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 166.7, 141.5, 138.0, 134.5, 131.4, 128.5, 128.4, 128.4, 126.8, 126.0, 115.4, 51.6, 36.3, 32.1; HR-MALDI-MS *m/z* calcd for $C_{18}H_{19}NO$ $[M+H]^+$ 266.1539, found 266.1538.

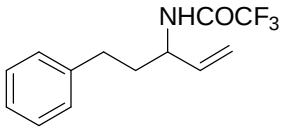
tert-Butyl 5-phenylpent-1-en-3-ylcarbamate (table 1, entry 3)



A Schlenk flask under argon was charged with [{Ir(cod)Cl}$_2$] (10 mg, 15 μmol, 3 mol %) and ligand (3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']diphenyl-4-en)-dibenzo[*b,f*]azepine **L3** (12 mg, 30 μmol, 6 mol %). 2 mL *N*,*N*-dimethylformamide were added and the reaction mixture was stirred at 23 °C for 15 min. 5-phenylpent-1-en-3-ol **3** (81 mg, 0.50 mmol, 1 equiv) was added via syringe followed by the addition of solid sulfamic acid (49 mg, 0.50 mmol, 1 equiv). The resulting reaction mixture was heated to 50°C. Conversion was checked by disappearance of the starting material on TLC and/or by measuring ^{1}H-NMR of an aliquot taken from the reaction mixture. After completion of the reaction (usually 3-4 h), the reaction mixture was carefully concentrated and cooled to 23 °C. The resulting brownish oil was redissolved in 3 mL CH_2Cl_2 and at 0 °C, 202 mg (1.00 mmol, 2 equiv) Boc_2O and a catalytic amount (ca. 10 mg) of the phase

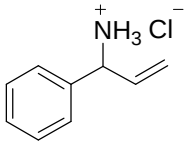
transfer reagent *n*-Bu_4NHSO_4 was added. At 0 °C, the reaction mixture was treated with 3 mL of a 0.5 M aqueous NaOH solution and warmed to 23 °C during 6 hours. Subsequently, the reaction mixture was partitioned between 10 mL CH_2Cl_2 and 10 mL H_2O. The aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude Boc-protected amine. Purification of the residue by flash chromatography on silica gel using hexanes/EtOAc as eluent afforded *tert*-Butyl 5-phenylpent-1-en-3-ylcarbamate (93 mg, 0.36 mmol, 71%) as an off-white solid.
mp 53 °C; IR (neat) ν 3364, 3028, 2979, 2945, 1681, 1517, 1330, 1243, 1172, 1045, 1030, 926, 752, 701; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.17-7.31 (m, 5H), 5.79 (ddd, *J* = 16.5, 10.3, 5.6 Hz, 1H), 5.10-5.21 (m, 2H), 4.49 (br. S, 1H), 4.16 (br. S, 1H), 2.62-2.96 (m, 2H), 1.78-1.89 (m, 2H), 1.46 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 155.2, 141.5, 138.6, 128.3, 128.2, 125.8, 114.6, 79.3, 52.6, 37.0, 32.2, 28.6; HR-ESI-MS *m/z* calcd for $C_{16}H_{23}NO_2Na$ $[MNa]^+$ 284.1621, found 284.1623.

2,2,2-Trifluoro-*N*-(5-phenylpent-1-en-3-yl)-acetamide (table 1, entry 4)



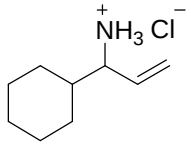
A Schlenk flask under argon was charged with [{Ir(cod)Cl}$_2$] (10 mg, 15 μmol, 3 mol %) and ligand (3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']diphenyl-4-en)-dibenzo[*b,f*]azepine **L3** (12 mg, 30 μmol, 6 mol %). 2 mL *N,N*-dimethylformamide were added and the reaction mixture was stirred at 23 °C for 15 min. 5-phenylpent-1-en-3-ol **3** (81 mg, 0.50 mmol, 1 equiv) was added via syringe followed by the addition of solid sulfamic acid (49 mg, 0.50 mmol, 1 equiv). The resulting reaction mixture was heated to 50°C. Conversion was checked by disappearance of the starting material on TLC and/or by measuring ^{1}H-NMR of an aliquot taken from the reaction mixture. After completion of the reaction (usually 3-4 h), the reaction mixture was carefully concentrated and cooled to 23 °C. The resulting brownish oil was redissolved in 2 mL CH_2Cl_2 and at 0 °C, 315 mg trifluoroacetic anhydride (1.50 mmol, 3 equiv) and 276 mg solid, anhydrous K_2CO_3 (2.00 mmol, 4 equiv) were added. The reaction mixture was continued to stir during 8 hours at 23 °C. Subsequently, it was partitioned between 10 mL CH_2Cl_2 and 10 mL H_2O. The aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude trifluoroacetamide. Purification of the residue by flash chromatography on silica gel using hexanes/EtOAc as eluent afforded 2,2,2-trifluoro-*N*-(5-phenylpent-1-en-3-yl)-acetamide (91 mg, 0.36 mmol, 71%) as a yellow oil.
IR (neat) ν 3293, 3088, 2928, 1698, 1554, 1206, 1181, 1154, 747, 724, 698; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.13-7.99 (m, 5H), 6.14 (br. s, 1H), 5.79 (ddd, *J* = 17.0, 10.7, 6.0 Hz, 1H), 5.19-5.25 (m, 2H), 4.46-4.55 (br. quintet, 1H), 2.67 (t, *J* = 7.8 Hz, 2H), 1.89-2.01 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 156.5 (q, *J* = 36.9 Hz), 140.6, 135.9, 128.6, 128.3, 126.3, 117.0, 115.8 (q, *J* = 288.3 Hz), 52.1, 35.7, 31.9; ^{19}F-NMR (282 MHz, $CDCl_3$) -75.7; HR-ESI-MS *m/z* calcd for $C_{13}H_{14}NOF_3Na$ $[MNa]^+$ 280.0919, found 280.0919.

1-Phenylprop-2-en-1-amine hydrochloride (table 1, entry 5)



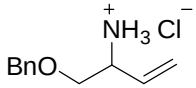
Prepared according to general procedure 2. Off-white solid. Yield: 132 mg (0.78 mmol, 78%); ^{1}H-NMR (300 MHz, CD_3OD) δ 7.43-7.57 (m, 5H), 6.19 (ddd, *J* = 17.3, 10.6, 6.5 Hz, 1H), 5.51 (dd, *J* = 10.6, 1.0 Hz, 1H), 5.44 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.04 (d, *J* = 6.5, 1H), 4.55 (br. s, 3H).
For other spectroscopic data see: A. Zwierzak, A. Napieraj, *Synthesis*, **1999**, 930-934.

1-Cyclohexylprop-2-en-1-amine hydrochloride (table 1, entry 6)



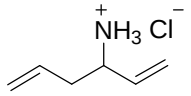
Prepared according to general procedure 2. White flakes. Yield: 132 mg (0.75 mmol, 75%); mp 231 °C; IR (neat) ν 3274, 2921, 2851, 1629, 1600, 1510, 1447, 993, 933, 918, 687; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.54 (br. s, 3H), 5.91-5.79 (ddd, *J* = 17.3, 9.6, 6.9 Hz, 1H), 5.42 (d, *J* = 17.3 Hz, 1H), 5.37 (d, *J* = 9.6 Hz, 1H); 3.51-3.46 (m, 1H), 1.89-1.61 (m, 6H), 1.45-1.03 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 131.9, 121.0, 59.5, 40.3, 29.1, 28.1, 25.6; HR-ESI-MS *m/z* calcd for $C_{11}H_{13}$ $[MH\text{-}NH_3]^+$ 145.1012, found 145.1012.

1-(Benzyloxy)but-3-en-2-amine hydrochloride (table 1, entry 7)



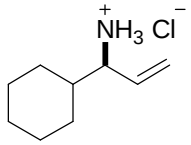
Prepared according to general procedure 2. White powder. Yield: 152 mg (0.71 mmol, 71%); ^{1}H-NMR (300 MHz, CD_3OD) δ 7.39-7.26 (m, 5H), 5.88 (m, 1H), 5.41 (d, *J* = 17.4 Hz, 1H), 5.37 (d, *J* = 11.2 Hz, 1H), 4.59 (s, 2H), 3.87 (m, 1H), 3.64 (dd, *J* = 10.1, 3.9 Hz), 1H), 3.49 (dd, *J* = 10.1, 7.8 Hz, 1H).
For other spectroscopic data see: B. M. Trost, R. C. Bunt, R. C. Lemoine, T. L. Calkins, *J. Am. Chem. Soc.* **2000**, *122*, 5968-5976.

Hexa-1,5-dien-3-amine hydrochloride (table 1, entry 8)

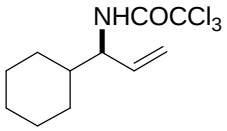


Prepared according to general procedure 2. Off-white solid. Yield: 101 mg (0.75 mmol, 75%); ^{1}H-NMR (300 MHz, D_2O) δ 5.64-5.86 (m, 2H), 5.14-5.34 (m, 4H), 3.81 (q, *J* = 6.7 Hz, 1H), 2.31-2.46 (m, 2H).
For other spectroscopic data see: D. B. Grotjahn, X: Zhang, *J. Mol. Cat. A: Chemical* **1997**, *116*, 99-107.

Enantioselective Example (Equation 3)



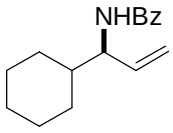
A Schlenk flask under argon was charged with [{$IrCl_2(coe)_2$}$_2$] (13.1 mg, 15 μmol, 3 mol %) and ligand (S)-(+)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)-dibenzo-[*b*,*f*]-azepine **L5** (16.2 mg, 30 μmol, 6 mol %). 2 mL *N*,*N*-dimethylformamide were added and the reaction mixture was stirred at 23 °C for 15 min. Racemic 1-cyclohexylprop-2-en-1-ol (70 mg, 0.50 mmol, 1 equiv) was added via syringe followed by the addition of solid sulfamic acid (49 mg, 0.50 mmol, 1 equiv). The resulting reaction mixture was stirred at 23°C for 24 hours. After completion of the reaction, as determined by TLC, the solvent was carefully evaporated at high vacuum. The resulting brown residue was dissolved in 10 mL CH_2Cl_2 and 10 mL saturated aqueous $NaHCO_3$ solution and stirred for 10 min. The aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude allylic amine. The ratio of regioisomers was determined by ^{1}H NMR analysis of the unpurified sample. Purification of the residue by flash chromatography on neutral alumina using CH_2Cl_2/MeOH as eluent afforded the desired amine which was immediately treated with 2M HCl in diethylether. The corresponding hydrochloride salt precipitated as a white solid in 70 % yield (61 mg, 0.35 mmol).



To determine the absolute configuration, 50 mg (0.28 mmol, 1 equiv) of the amine hydrochloride were suspended in 1 mL Et_2O and treated with 0.5 mL (10 equiv) 6 M KOH. After stirring at 23 °C for 30 min, the mixture was partitioned between Et_2O and H_2O. The aqueous phase was extracted three times with Et_2O. The combined organic layers were washed with brine and dried over $MgSO_4$. The mixture was carefully (!) concentrated under reduced pressure to obtain a brownish oil that was immediately dissolved in 2 mL CH_2Cl_2 and treated with 115 mg (1.14 mmol, 4 equiv) triethylamine and 103 mg (0.57 mmol, 2 equiv) freshly distilled trichloroacetyl chloride. After 3 h stirring at 23 °C, the reaction mixture was partitioned between CH_2Cl_2 and H_2O. The aqueous phase was extracted three times with CH_2Cl_2. The combined organic layers were washed with brine and dried over $MgSO_4$. Concentration of the mixture under reduced pressure yielded in a brownish residue that was subjected to chromatography on silica gel (30:1 hexanes/EtOAc) to obtain 36 mg (0.13 mmol, 45%) 2,2,2-trichloro-*N*-(1-cyclohexylallyl)-acetamide as a colorless solid. The optical rotation was measured: $[\alpha]_D^{25}$ -26.5 (*c* 0.45, $CHCl_3$); Comparison to the literature $[\alpha]_D^{25}$ +30.7 (*c* 0.42, $CHCl_3$) (C. E. Anderson, L. E. Overman *J. Am. Chem. Soc.* **2003**, *125*, 12412-12413). allowed to establish the absolute configuration for the product as: *(S)*-2,2,2-Trichloro-*N*-(1-cyclohexylallyl)acetamide.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.58 (br s, 1 H), 5.79 (ddd, *J* = 17.1, 10.5, 6.0 Hz, 1H), 5.19-5.25 (m, 2H), 4.27 (dd, *J* = 14.8, 6.2 Hz, 1H), 1.65-1.81 (m, 5H), 1.51-1.60 (m, 1H), 0.95-1.30 (m, 5H).

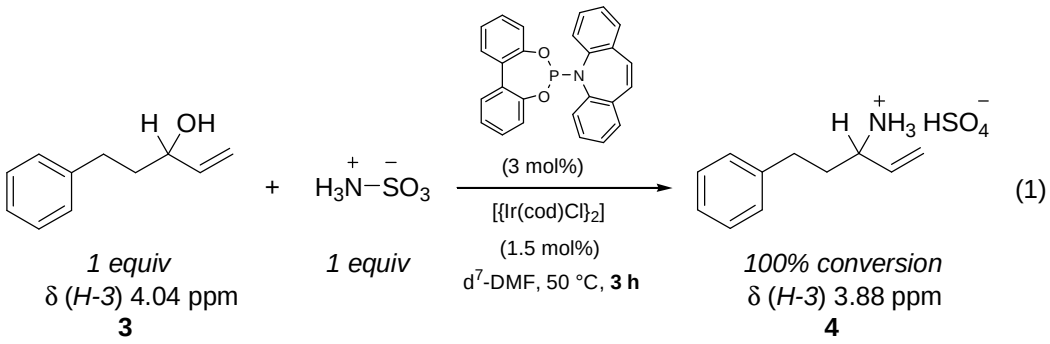
For other spectroscopic data see: C. E. Anderson, L. E. Overman *J. Am. Chem. Soc.* **2003**, *125*, 12412-12413.



For determination of the enantioselectivity, the allylic amination procedure described above was repeated but it differed in the workup: Thus, the resulting amine was directly protected by the addition of triethylamine (202 mg, 2.00 mmol, 4 equiv) and freshly distilled benzoylchloride (141 mg, 1.00 mmol, 2 equiv). The mixture was stirred at 23 °C for 3 hours, then partitioned between CH_2Cl_2 and H_2O. The aqueous phase was extracted three times with CH_2Cl_2. The combined organic layers were washed with brine and dried over $MgSO_4$. Concentration of the solvents under reduced pressure and purification of the residue by silica gel chromatography yielded a white solid.
$[\alpha]_D^{25}$ -35.1 (*c* 0.53, $CHCl_3$); *N*-(1-cyclohexylallyl)-benzamide was obtained (67 mg, 0.28 mmol, 55% yield) after chromatographical purification in 70% ee as determined by HPLC analysis (Chiralcel OD-H, 95:5 hexanes/i-PrOH, flow: 1 mL/min, 220 nm), t_r 22.6 (minor) t_r 27.4 (minor).
When the hydrochloride salt obtained from the allylic amination was triturated with Et_2O, enantioselectivity could be upgraded to 93% ee. Enantioselectivity was determined after derivatisation to the corresponding benzamide in an analogous way.
For other spectroscopic data see: A. Lee, J. A. Ellman, *Org. Lett.* **2001**, *3*, 3707-3709.

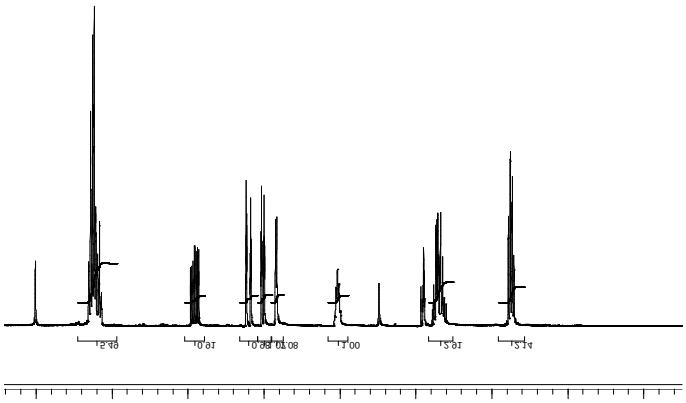
Detailed description of the spectroscopic experiments (Figure 2).

A) Iridium-catalyzed allylic amination using 1 equivalent sulfamic acid

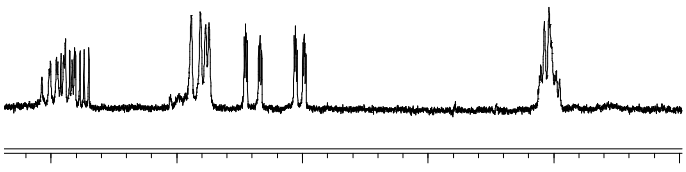


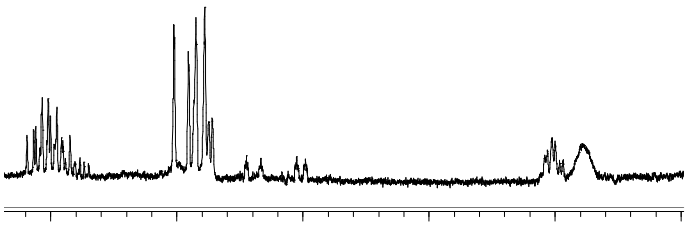
A Schlenk flask under argon was charged with [{Ir(cod)Cl}$_2$] (10 mg, 15 μmol, 1.5 mol %) and ligand (3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']diphenyl-4-en)-dibenzo[*b*,*f*]azepine **L3** (12 mg, 30 μmol, 3 mol %). 1.5 mL d^7-*N*,*N*-dimethylformamide were added and the reaction mixture was stirred at 23 °C for 15 min. 5-Phenylpent-1-en-3-ol **3** (81 mg, 0.50 mmol, 1 equiv) was added via syringe followed by the addition of solid sulfamic acid (49 mg, 0.50 mmol, 1 equiv). The resulting reaction mixture was heated to 50°C. At regular intervals, aliquots à 100 μL were taken from the reaction mixture and ^{1}H-NMR spectra were measured. In the spectra the relevant range (δ 6.49-3.21 ppm) is depicted.

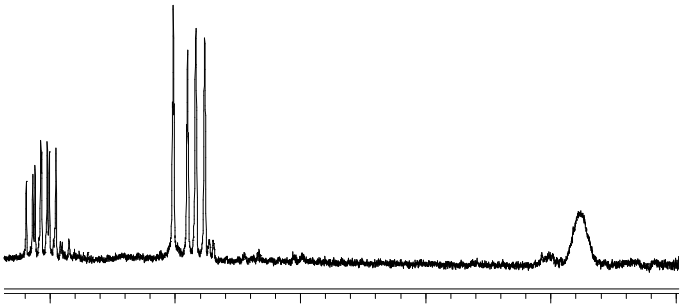
5-Phenylpent-1-en-3-ol **3**:
^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.32-7.17 (m, 5H), 5.92 (ddd, *J* = 17.4, 10.4, 6.1 Hz, 1H), 5.26 (d, *J* = 17.4 Hz, 1H), 5.15 (d, *J* = 10.4 Hz, 1H), 4.14 (br quintet, *J* = 5.9 Hz, 1H), 2.81-2.64 (m, 2H), 1.86 (q, *J* = 7.5 Hz, 2H), 1.49 (d, *J* = 4.0 Hz, 1H).
B. M. Trost, R. J. Kulawiec, *J. Am. Chem. Soc.* **1993**, *115*, 2027-2036.

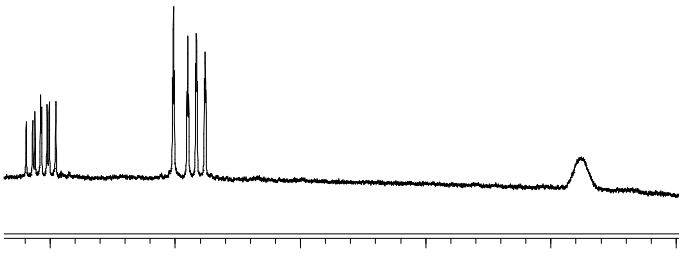


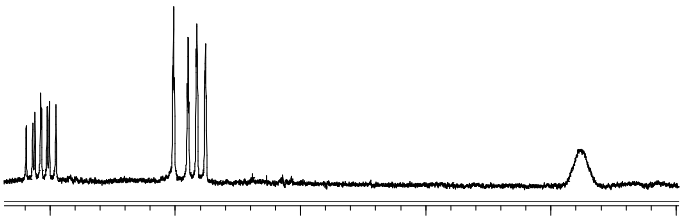
^{1}H-NMR (d^7-DMF, 300 MHz) δ 7.31-7.14 (m, 5H), 5.91 (ddd, *J* = 17.4, 10.4, 5.6 Hz, 1H), 5.20 (d, *J* = 17.4 Hz, 1H), 5.02 (d, *J* = 10.4 Hz), 4.83 (d, *J* = 4.7 Hz), 4.04 (br. quintet, *J* = 5.6 Hz, 1H), 2.78-2.60 (m, 2H), 1.78-1.71 (m, 2H).



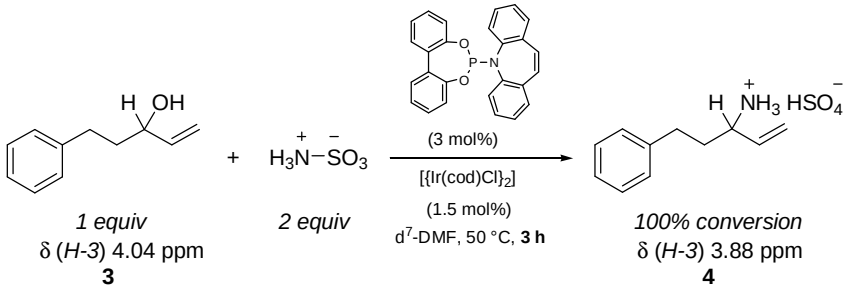




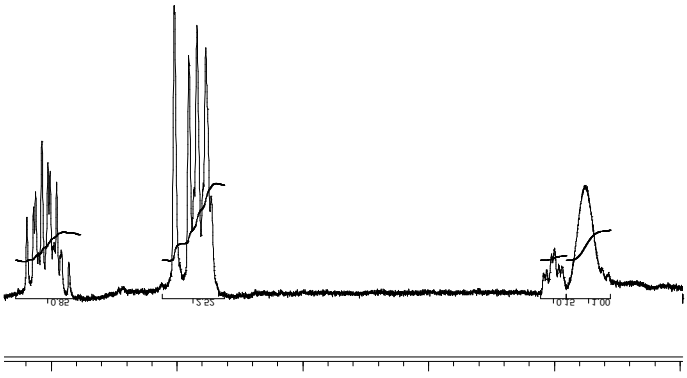


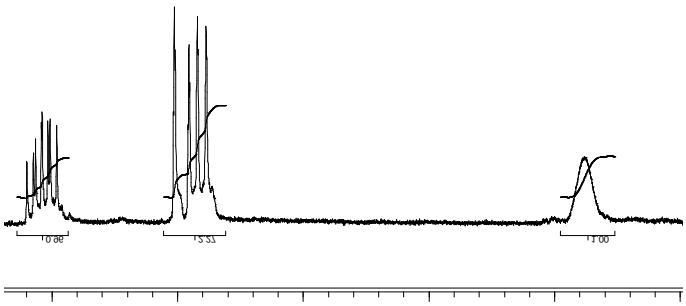


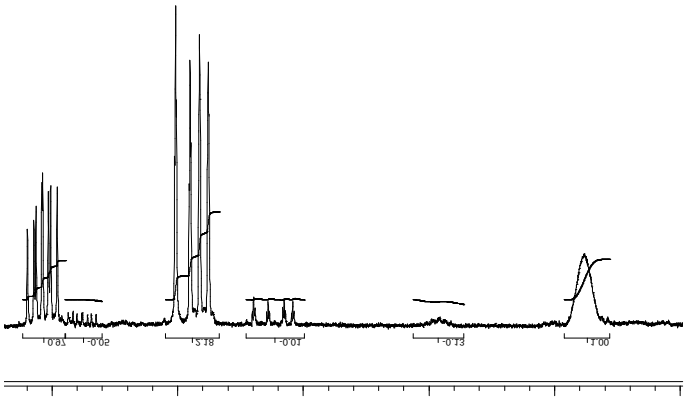
B) Iridium-catalyzed allylic amination using 2 equivalents sulfamic acid

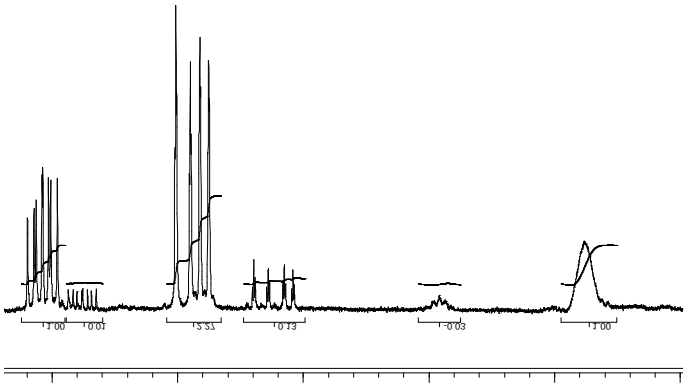


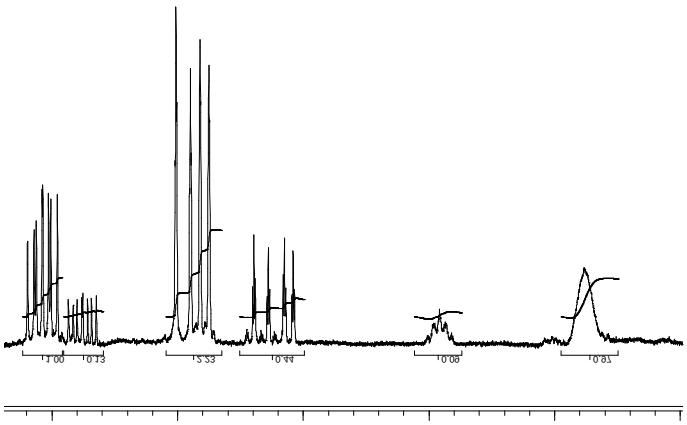
A Schlenk flask under argon was charged with [{Ir(cod)Cl}$_2$] (10 mg, 15 µmol, 1.5 mol %) and ligand (3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']diphenyl-4-en)-dibenzo[*b*,*f*]azepine **L3** (12 mg, 30 µmol, 3 mol %). 1.5 ml d^7-*N*,*N*-dimethylformamide were added and the reaction mixture was stirred at 23 °C for 15 min. 5-Phenylpent-1-en-3-ol **3** (81 mg, 0.50 mmol, 1 equiv) was added via syringe followed by the addition of solid sulfamic acid (97 mg, 1.00 mmol, 2 equiv). The resulting reaction mixture was heated to 50°C. At regular intervals, aliquots à 100 µL were taken from the reaction mixture and ^{1}H-NMR spectra were measured. In the spectra the relevant range (δ 6.49-3.21 ppm) is depicted.

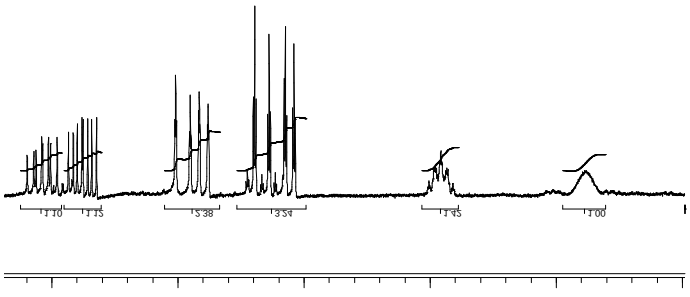




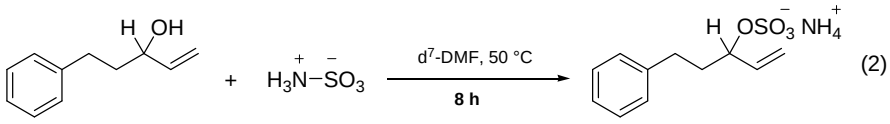








C) Sulfation of alcohol 3 using 2 equivalents sulfamic acid

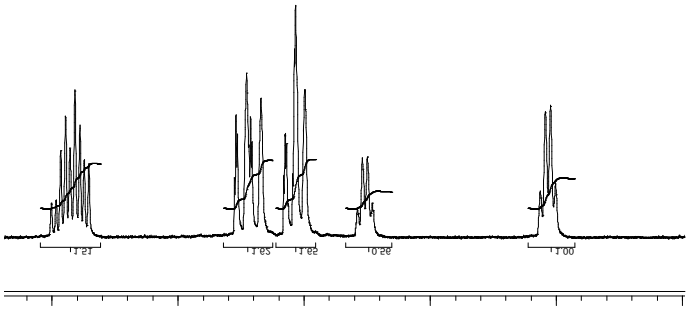


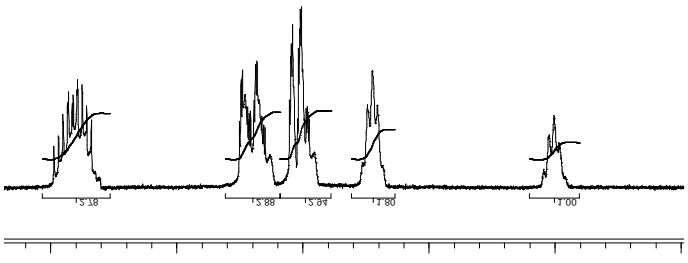
1 equiv
δ (*H-3*) 4.04 ppm
3

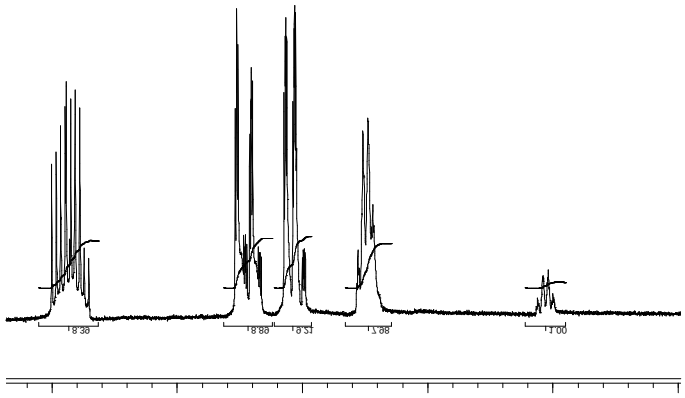
2 equiv

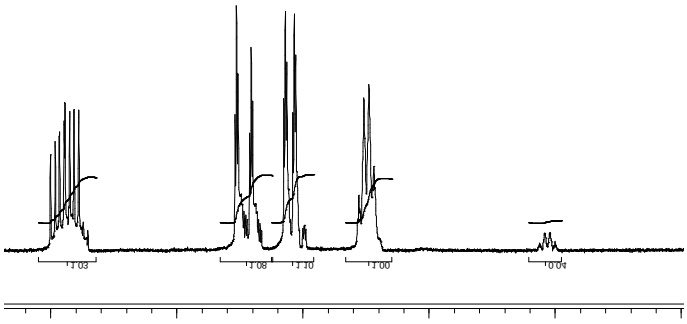
100% conversion
δ (*H-3*) 4.72 ppm
5

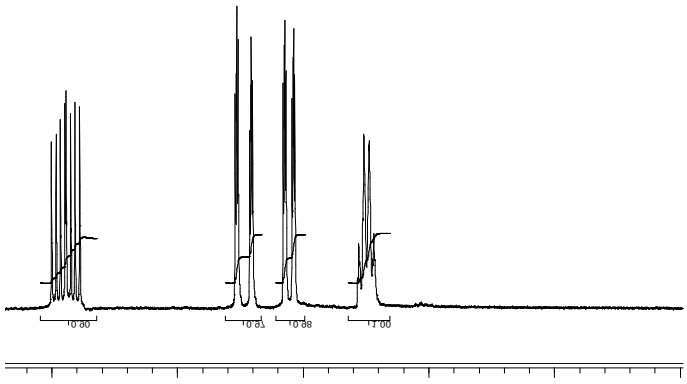
A Schlenk flask under argon was charged with 5-Phenylpent-1-en-3-ol **3** (81 mg, 0.50 mmol, 1 equiv). 0.7 mL d^7-*N*,*N*-dimethylformamide were added followed by the addition of solid sulfamic acid (97 mg, 1.00 mmol, 2 equiv). The resulting homogenous reaction mixture was heated to 50 °C. At regular intervals, aliquots à 100 µL were taken from the reaction mixture and ^{1}H-NMR spectra were measured. In the spectra the relevant range (δ 6.49-3.21 ppm) is depicted.



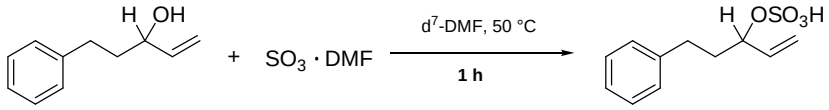








D) Sulfation of alcohol 3 using 2 equivalents SO_3-DMF

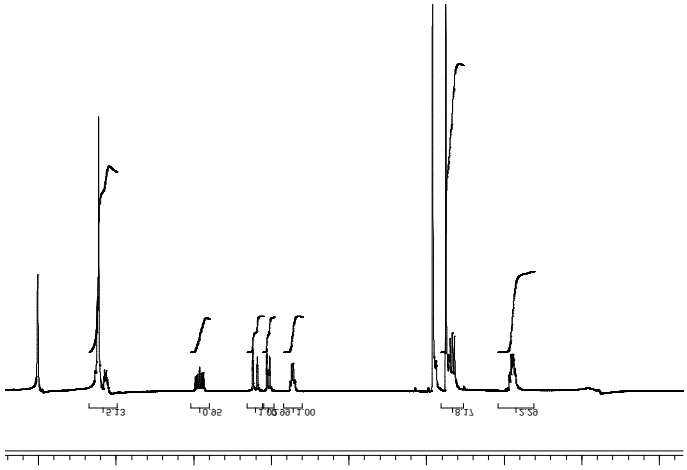


1 equiv
δ (*H-3*) 4.04 ppm
3

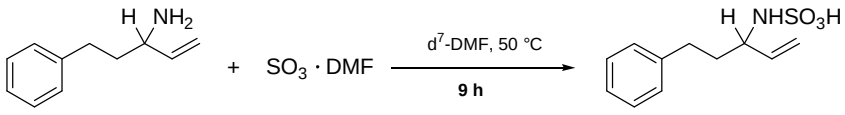
2 equiv

100% conversion
δ (*H-3*) 4.72 ppm
5

A Schlenk flask under argon was charged with 5-Phenylpent-1-en-3-ol **3** (81 mg, 0.50 mmol, 1 equiv). 0.7 mL d^7-*N*,*N*-dimethylformamide were added followed by the addition of solid SO_3-DMF (153 mg, 1.00 mmol, 1 equiv). The resulting homogenous reaction mixture was heated to 50°C. After one hour reaction time, an aliquot à 100 µl was taken from the reaction mixture and a ^{1}H-NMR spectrum was measured.



E) Sulfamation of the amine 4 with 2 equiv SO_3-DMF (figure XX, equation 4)

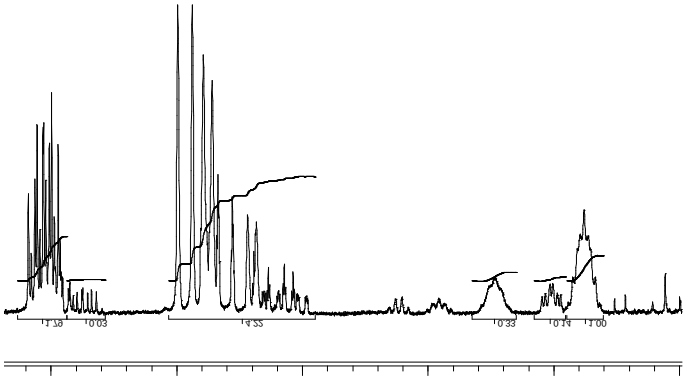


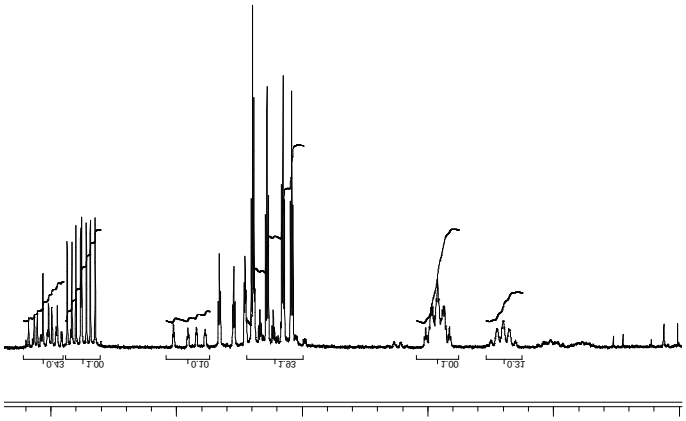
1 equiv
δ (*H-3*) 3.88 ppm
4

2 equiv

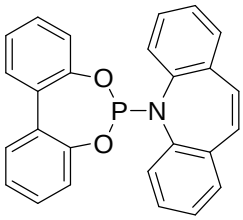
δ (*H-3*) 4.46 ppm
6

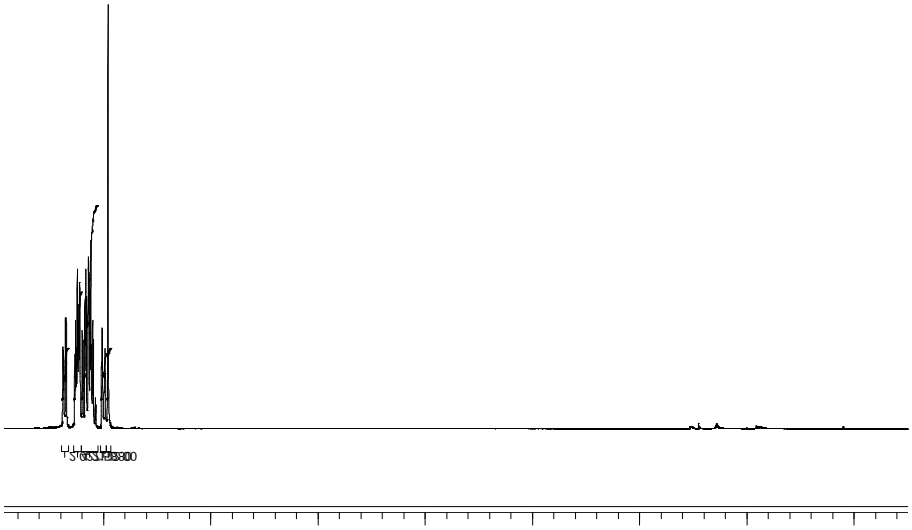
A Schlenk flask under argon was charged with 5-Phenylpent-1-en-3-ol **3** (81 mg, 1.00 mmol, 1 equiv). 0.7 ml d^7-*N*,*N*-dimethylformamide were added followed by the addition of solid SO_3-DMF (153 mg, 0.50 mmol, 1 equiv). The resulting homogenous reaction mixture was heated to 50°C. At regular intervals, aliquots à 100 µL were taken from the reaction mixture and ^{1}H-NMR spectra were measured. In the spectra the relevant range (δ 6.49-3.21 ppm) is depicted. The analysis was complicated due to the formation of various side products.

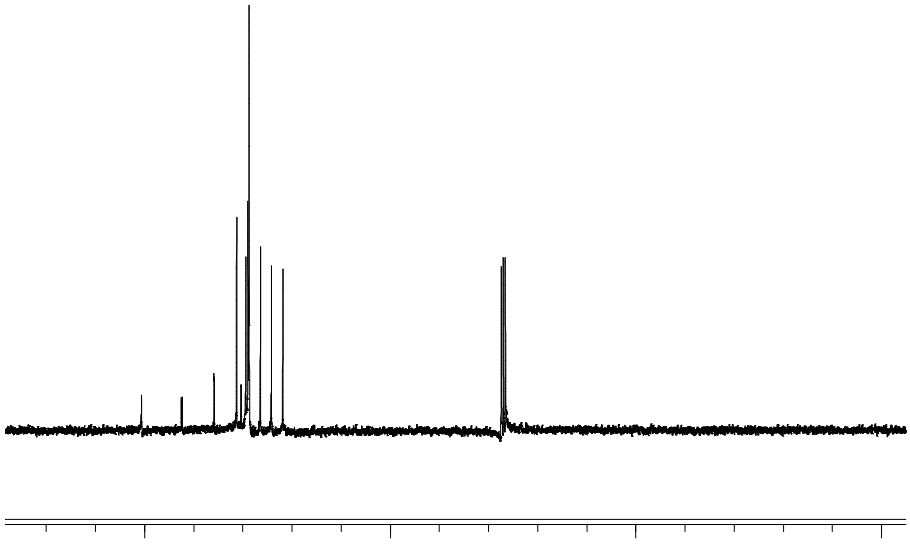


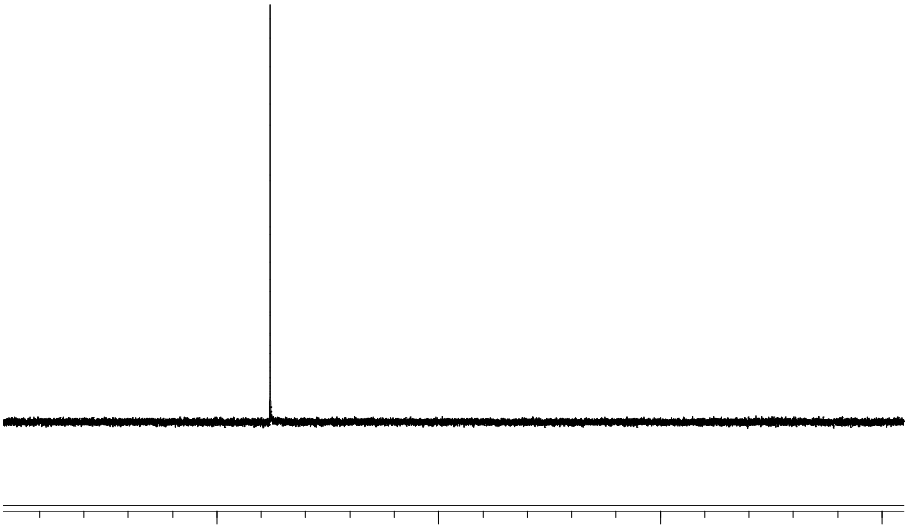


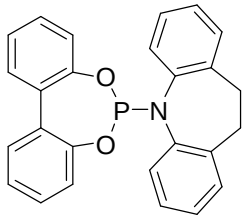
NMR spectra of new compounds










O
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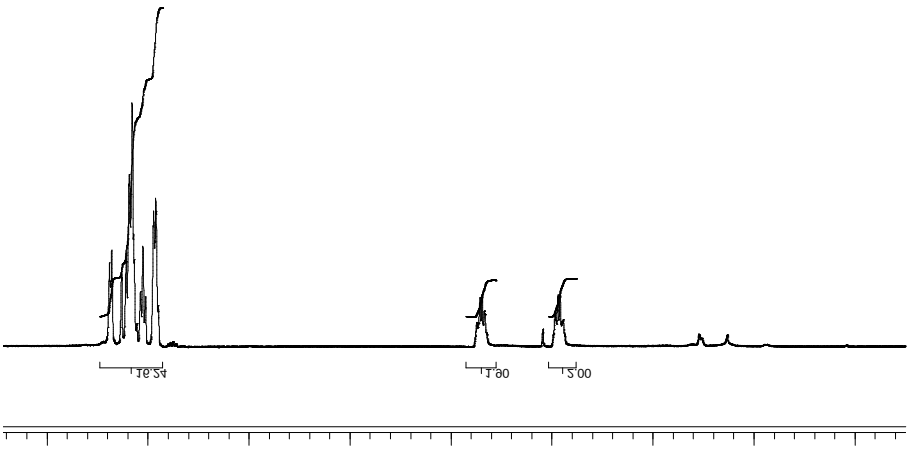

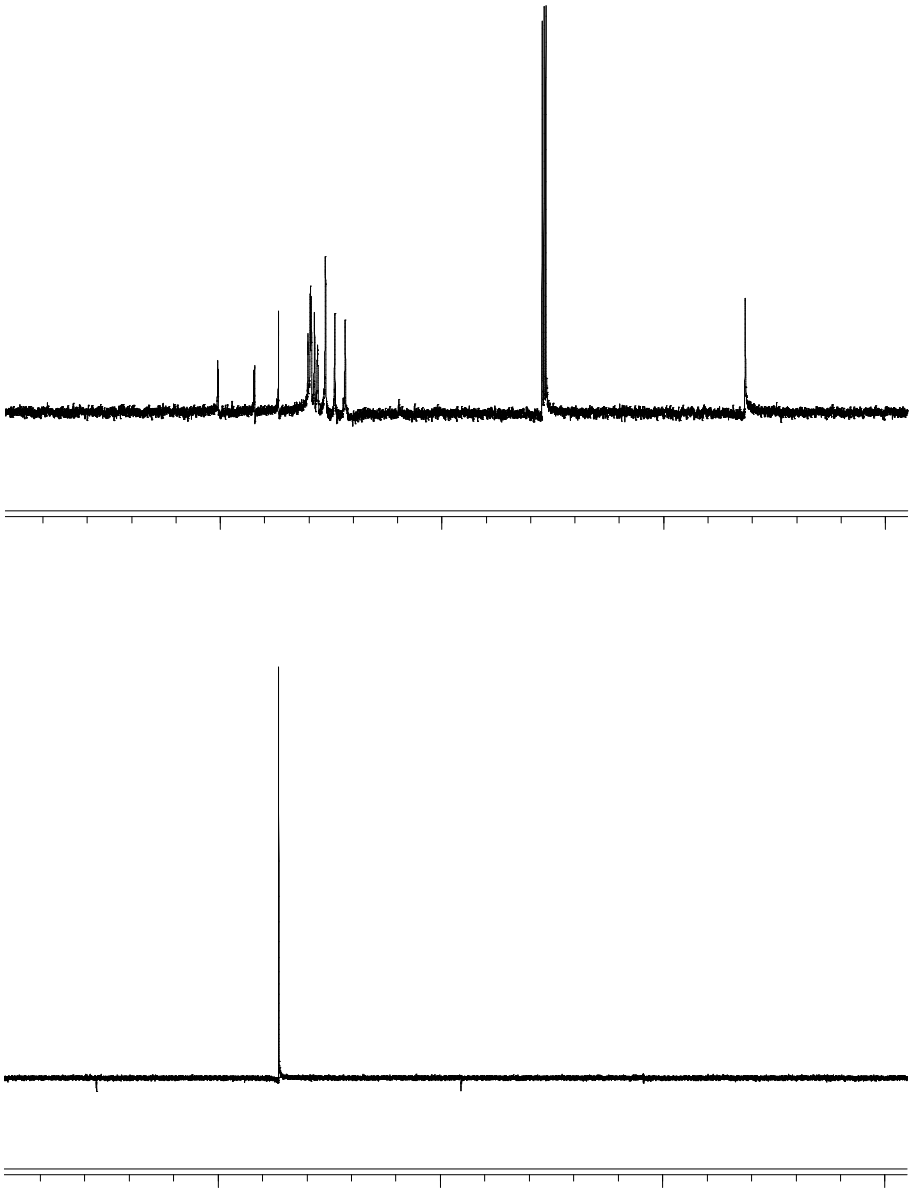

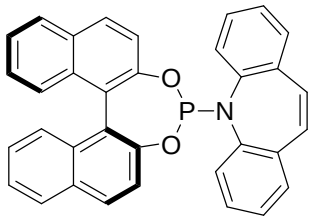
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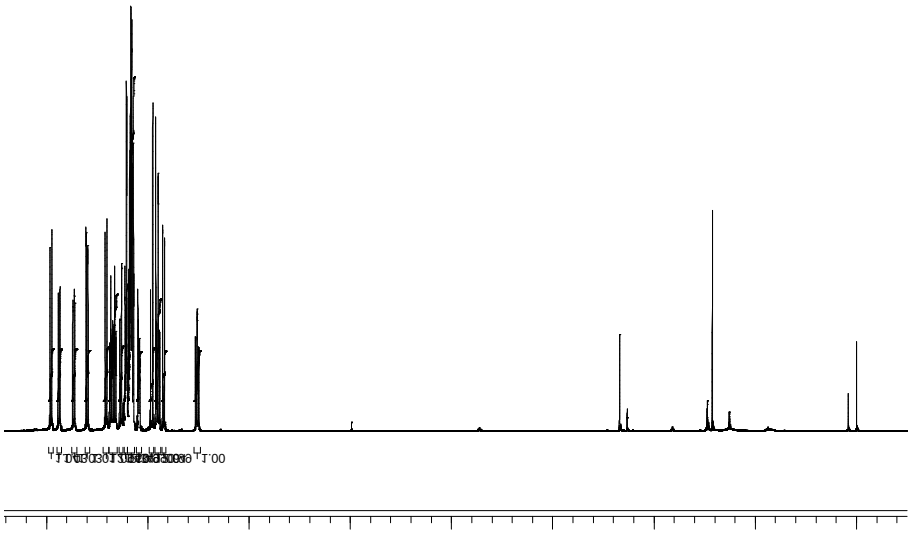
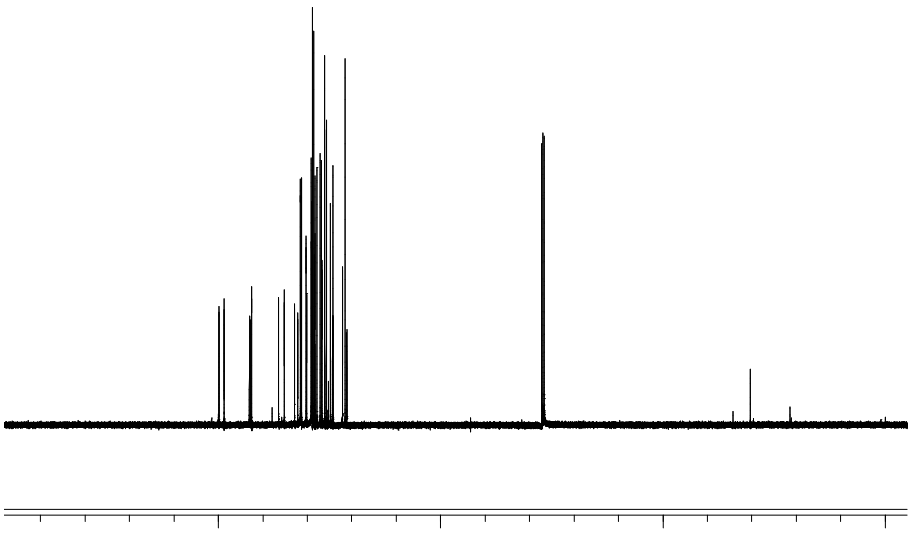
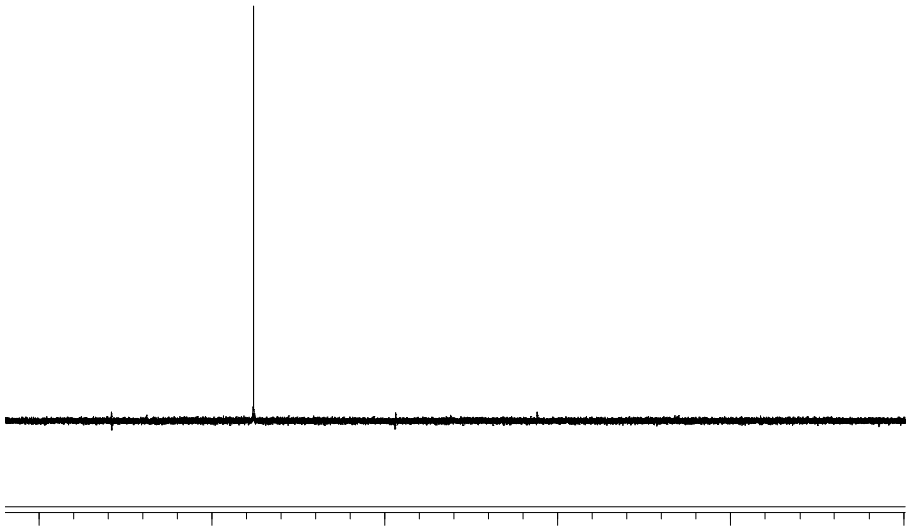
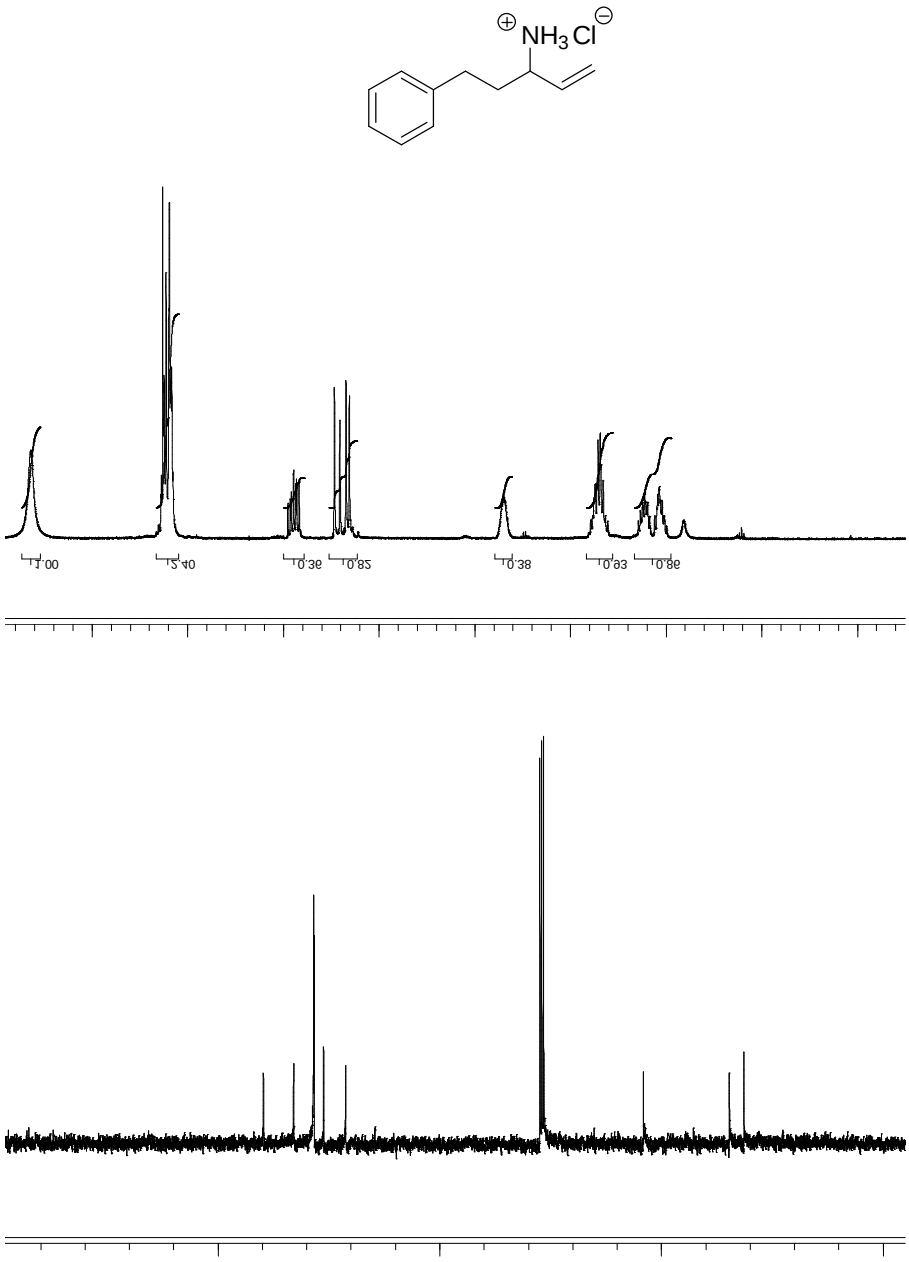
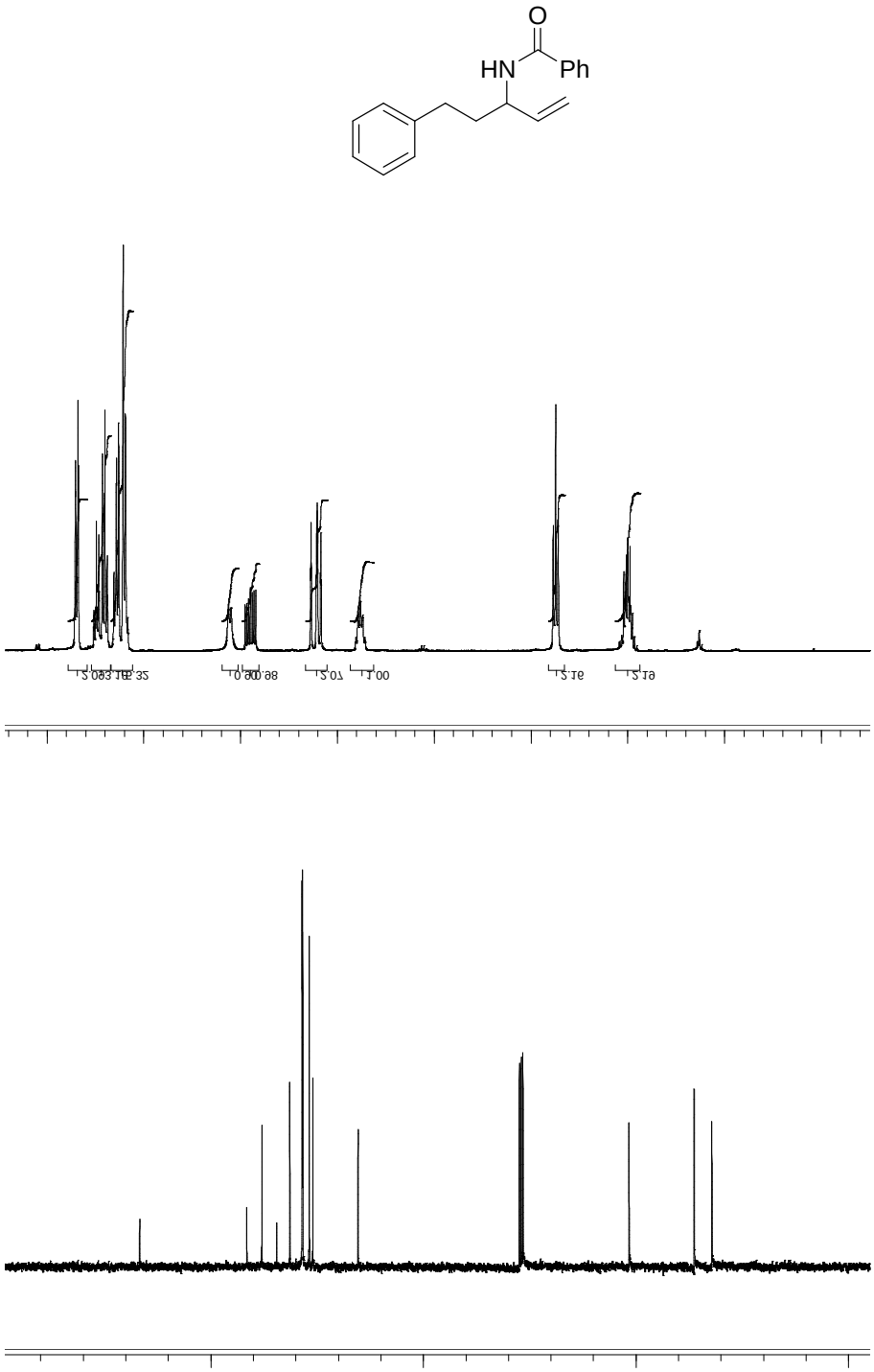
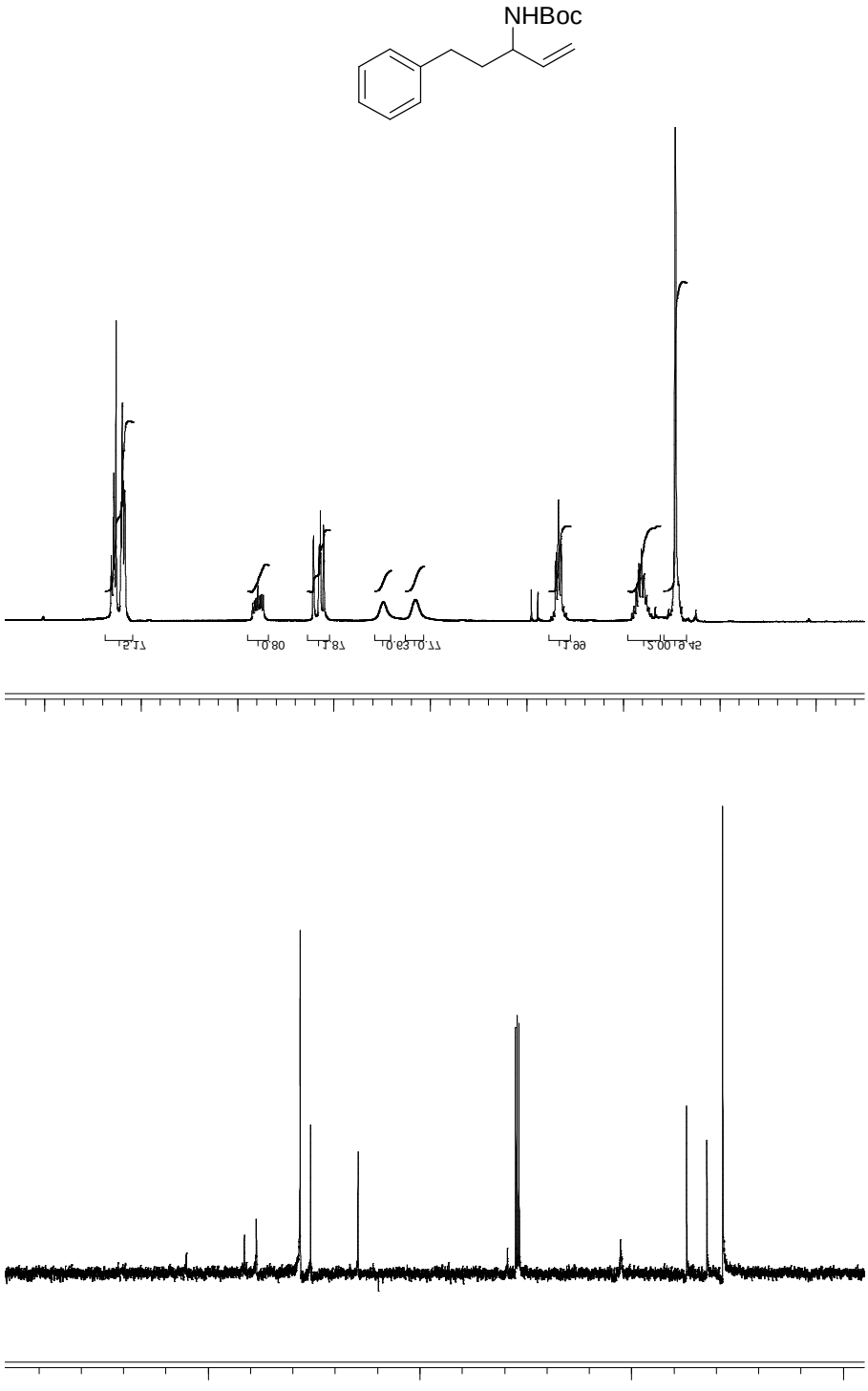


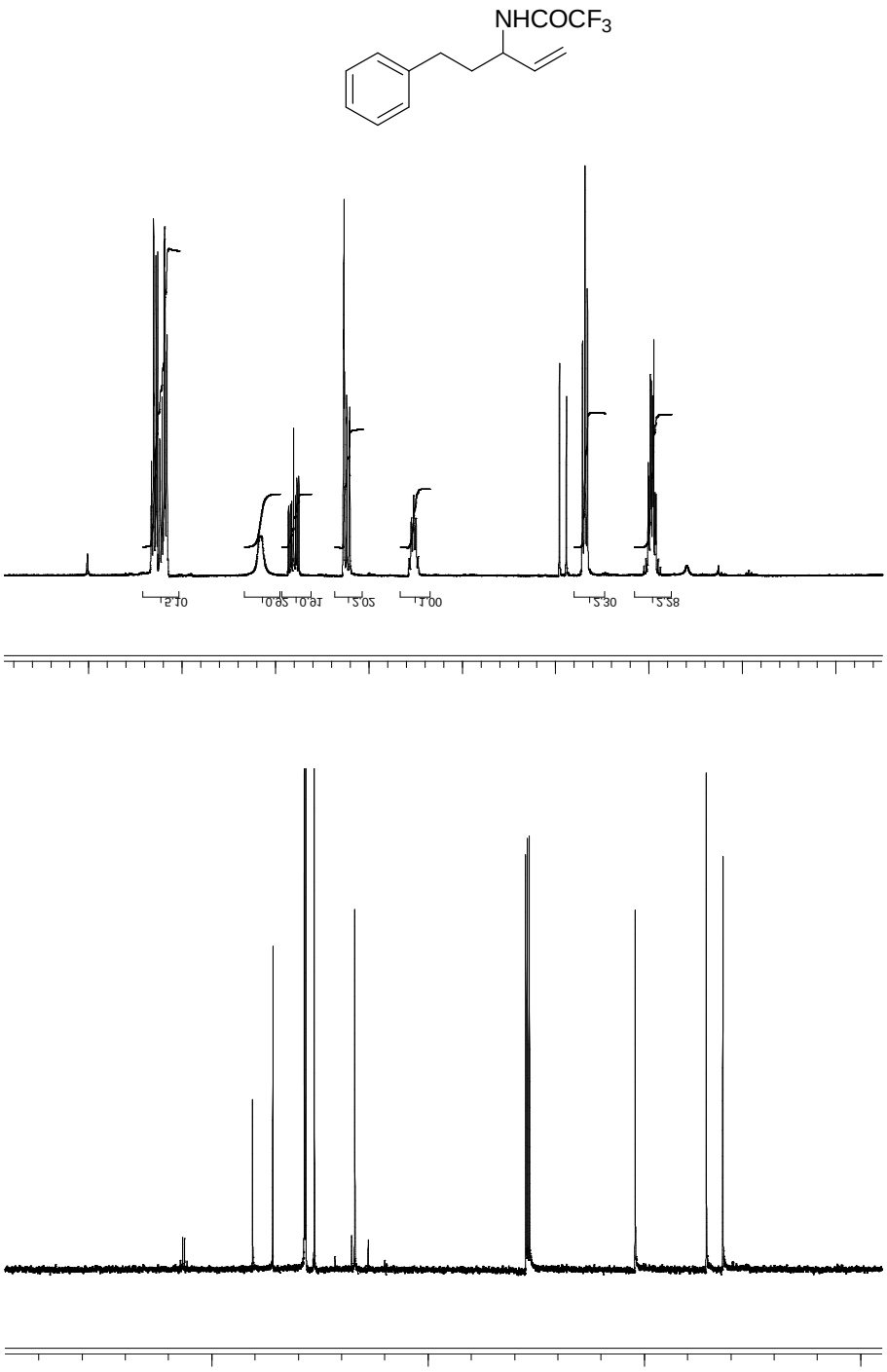


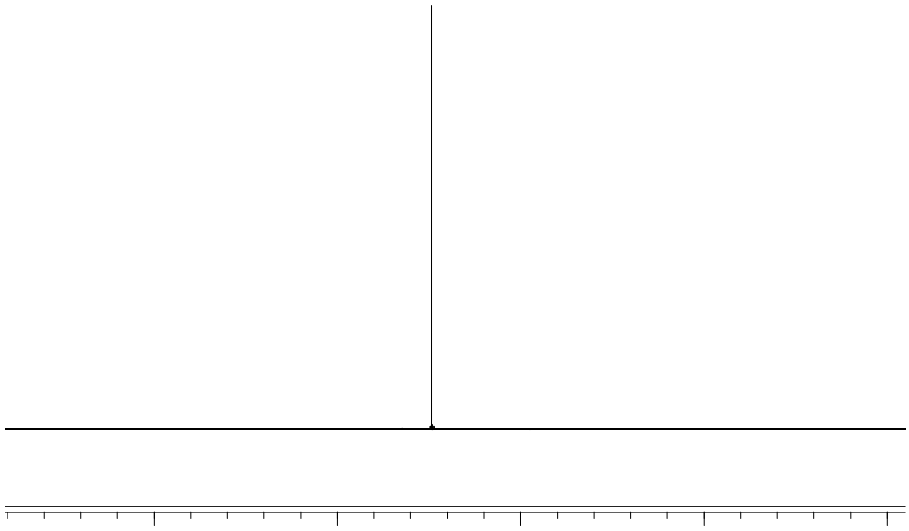


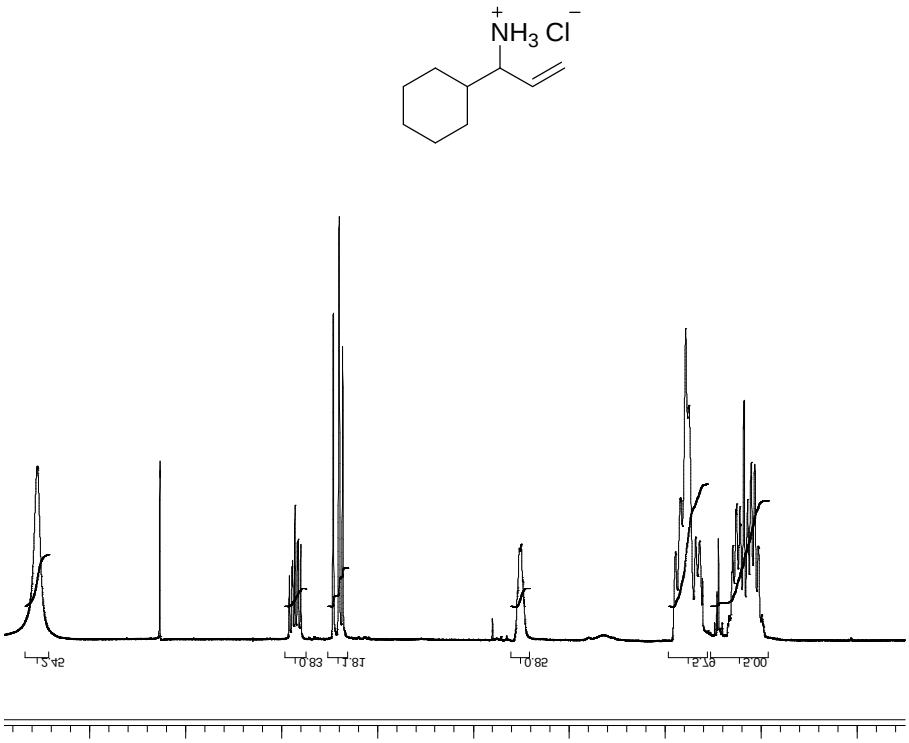

NH3 Cl

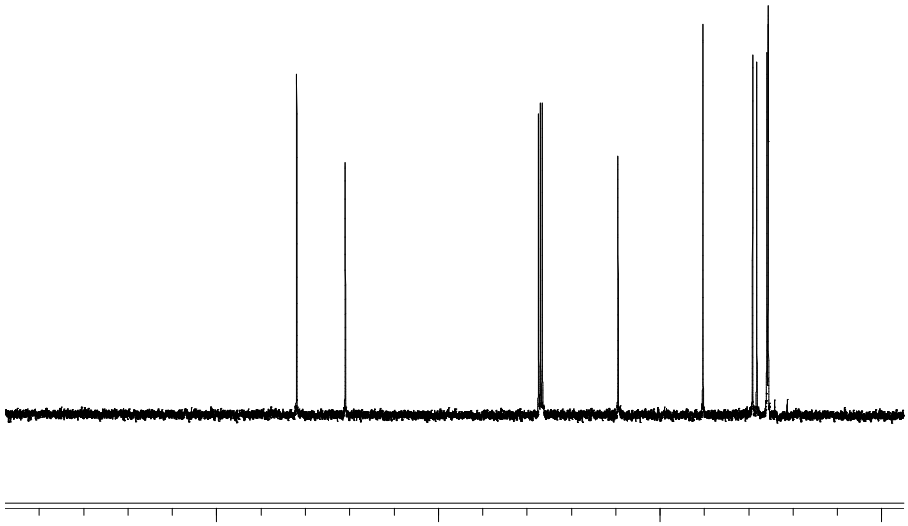

O
HN
Ph


NHBoc


NHCOCF3




+
NH3 Cl−



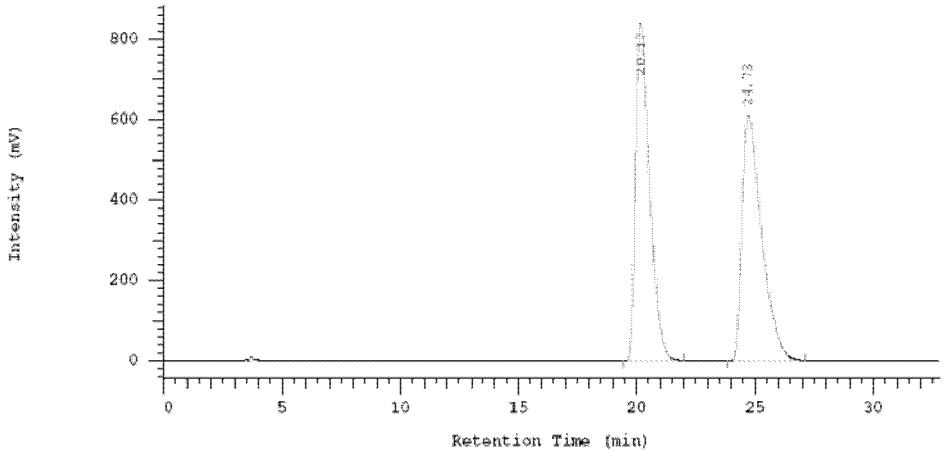
D-7000 HPLC System Manager Report

Analyzed: 08/15/06 03:55 PM
Reported: 01/07/07 07:49 PM
Processed: 08/15/06 04:29 PM

Data Path: C:\WIN32APP\HSM\Christian D\DATA\0690\
Processing Method: LS_F

System(acquisition): emcgroup
Series:0690
Application: Christian D
Vial Number: 1
Sample Name: CD1163
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: He:iP95:5 1ml/min 220nm ODH

Chrom Type: HPLC Channel : 1



Acquisition Method: LS_F
Column Type: Siehe vorschrift
Developed by:
Pump A Type: L-7100
Solvent A: Hexan
Solvent B: iPrOH
Method Description:

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Conc 1	BC
1	20.17	34929660	49.933	BB
2	24.73	35022816	50.067	BB
		69952476	100.000	

Peak rejection level: 0

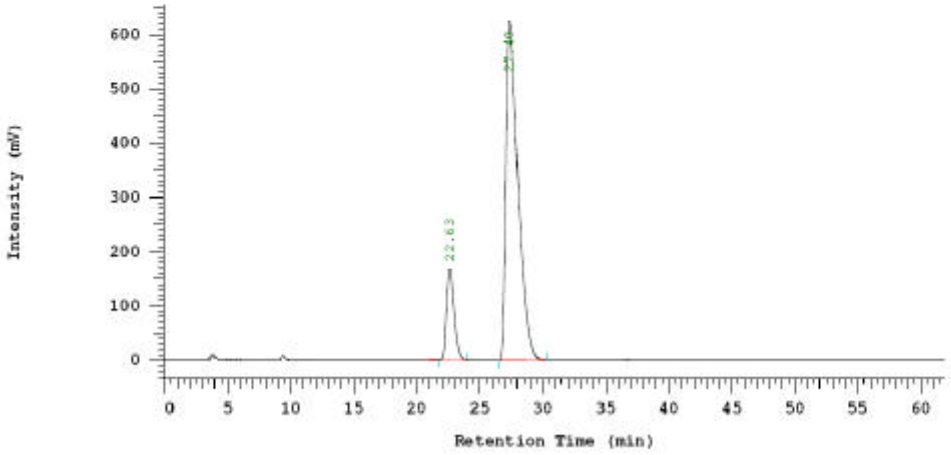
D-7000 HPLC System Manager Report

Analyzed: 08/15/06 11:09 AM
Reported: 01/07/07 07:50 PM
Processed: 08/15/06 12:13 PM

Data Path: C:\WIN32APP\HSM\Christian D\DATA\0689\
Processing Method: LS_F

System(acquisition): emcgroup
Series:0689
Application: Christian D
Vial Number: 1
Sample Name: CD1163
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: He:iP95:5 1ml/min 220nm ODH

Chrom Type: HPLC Channel : 1



Acquisition Method: LS_F
Column Type: Siehe vorschrift
Developed by:
Pump A Type: L-7100
Solvent A: Hexan
Solvent B: iPrOH
Method Description:

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Conc 1	BC
1	22.63	7119092	15.026	VB
2	27.40	40260454	84.974	BB
		47379546	100.000	

Peak rejection level: 0

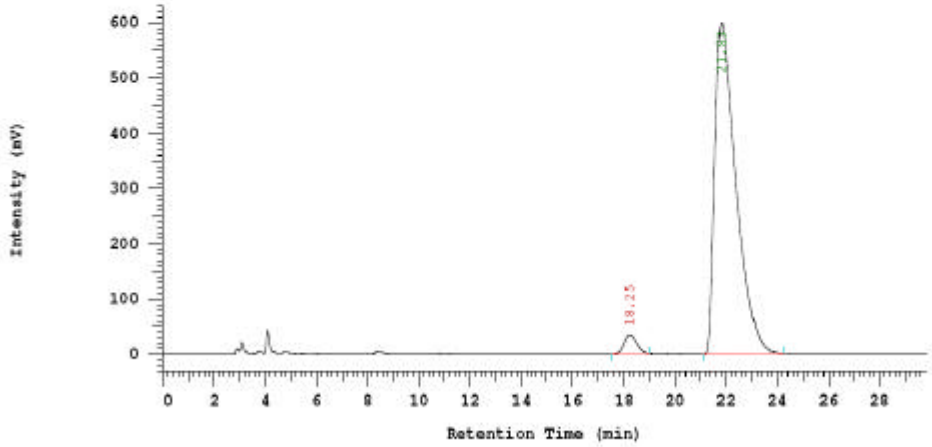
D-7000 HPLC System Manager Report

Analyzed: 01/11/07 11:15 PM
Reported: 01/12/07 01:44 PM
Processed: 01/11/07 11:47 PM

Data Path: C:\WIN32APP\HSM\Christian D\DATA\0725\
Processing Method: LS_F

System(acquisition): emcgroup
Series:0725
Application: Christian D
Vial Number: 1
Sample Name: CD1304
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 20.0 ul
Sample Description: H:iPr 99:1 0.8ml/min 230nm

Chrom Type: HPLC Channel : 1



Acquisition Method: LS_F
Column Type: Siehe vorschrift
Developed by:
Pump A Type: L-7100
Solvent A: Hexan
Solvent B: iPrOH
Method Description:

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Conc 1	BC
1	18.25	1238459	3.509	MC
2	21.83	34053910	96.491	BB
		35292369	100.000	

Peak rejection level: 0