SUPPORTING INFORMATION

Organolanthanide-Catalyzed Intramolecular Hydroamination/Cyclization/Bicyclization of Sterically Encumbered Substrates. Scope, Selectivity, and Catalyst Thermal Stability for Amine-Tethered Unactivated 1,2-Disubstituted Alkenes.

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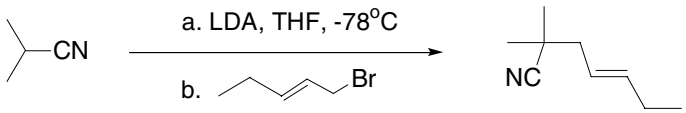
Materials and Methods. All manipulations of air-sensitive materials were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried Schlenk-type glassware on a dual-manifold Schlenk line or interfaced to a high-vacuum line (10^{-6} Torr), or in a nitrogen-filled Vacuum Atmospheres glovebox with a high capacity recirculator (< 1 ppm of O_2). Argon was purified by passage through a MnO oxygen-removal column[1] and a Davison 4Å molecular sieve column. All solvents were distilled before used under dry nitrogen over appropriate drying agents (sodium benzophenone ketyl, metal hydrides, Na/K alloy). Chloroform-*d* was obtained from commercial suppliers. Benzene-d_6, toluene-d_8, o-xylene-d_{10}, and cyclohexane-d_{12} used for NMR-scale reactions and thermolysis experiments were stored in vacuo over Na/K alloy in resealable bulbs, and were vacuum transferred immediately prior to use. All commercially available organic starting materials were used without further purification unless otherwise stated. All substrates were dried over CaH_2, next dried twice over freshly activated Davison 4Å molecular sieves, and then were degassed by freeze-pump-thaw methods. They were stored in vacuum-tight storage flasks. The organolanthanide precatalysts $Cp'_2LnCH(TMS)_2$ (**5**) (Ln = Y, Sm, La; Cp′= η^5-Me_5C_5),[2] $Me_2SiCp''_2SmCH(TMS)_2$ (**6**) (Cp″ = η^5-Me_4C_5),[3] (CGC)LnE(TMS)$_2$ (**7**) (CGC = [$Me_2Si(\eta^5$-$Me_4C_5)(^tBuN)$]; Ln = Sm, Y, Yb, Lu; E = N, CH),[4] $Me_2Si(OHF)(CpR^*)LnN(TMS)_2$ (**8**) (OHF = η^5-octahydrofluorenyl; Cp = η^5-C_5H_3; R* = (-)-menthyl; Ln = Sm, Y),[5] and $Me_2SiCp''(CpR^*)SmN(TMS)_2$ (**9**) (Cp″ = η^5-Me_4C_5; Cp = η^5-H_3C_5; R* = (-)-menthyl)[6] were prepared by published procedures. The substrate 2,2-dimethyl-hex-4-enylamine (**10**) [Registry No. 133885-74-2] was synthesized according to published procedures.[7]

Physical and Analytical Measurements. NMR spectra were recorded on either 300 MHz, 400 MHz, or 500 MHz for ^{1}H, and 75 MHz, 100 MHz, or 125 MHz for ^{13}C. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed

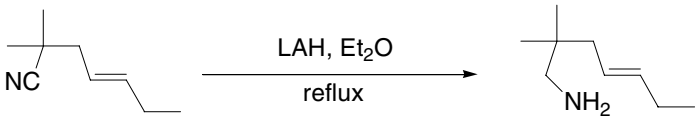
tubes. GCMS analyses were performed using a capillary column and an FID detector (5% Phenyl Methyl Siloxane, 30m x 250µm x 0.25µm). HPLC analyses were performed using a dual λ UV/VIS detector. HRMS studies were conducted on an instrument with 70 eV electron impact ionization or chemical ionization using CH_4 as a reagent gas. IR spectra were recorded using a Fourier transform spectrophotometer.

Synthesis of *trans*-2,2-Dimethyl-hept-4-enyl-amine (12)



12a

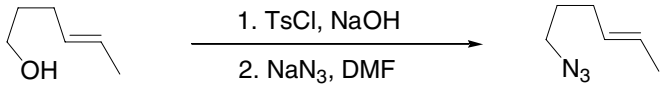
***trans*-2,2-Dimethyl-hept-4-enenitrile (12a).** Isobutyronitrile (7.9 mL, 86.9 mmol) in THF (30 mL) was added dropwise at –78 °C to a 2.0 M solution of LDA (48.3 mL, 95.6 mL) dissolved in heptane-THF-ethyl benzene (Aldrich). After stirring for 1 h at –78 °C and for 2 h at 0 °C, *trans*-1-bromo-2-pentene (11.9 mL, 9.6 mmol) in THF (15 mL) was added at 0 °C. The reaction mixture was stirred at room temperature for 20 h, after which the yellow solution was quenched with a saturated NH_4Cl solution, then water. The aqueous layer was next separated and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by vacuum distillation [bp 98 °C/20 mm Hg] yielding nitrile **12a** (9.28 g, 78%) as a colorless liquid with a metallic odor. ^{1}H NMR (400 MHz, C_6D_6): δ 5.37 (m, 2H), 1.87 (m, 2H), 1.79 (d, J = 4.8 Hz, 2H), 0.87 (t, J = 7.6 Hz, 3H), 0.84 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 137.9, 124.8, 123.6, 44.5, 32.9, 26.5, 26.4, 14.5; HRMS (*m/z*): calcd for $C_9H_{15}N$ (M^+), 137.12045; found, 137.12085; IR(thin film): ν_{max} = 3033 (=CH-), 2976, 2935, 2876, 2850, 2235 (-CN), 1461, 1369, 1199, 972 (=CH-) cm^{-1}.



12a **12**

***trans*-2,2-Dimethyl-hept-4-enylamine (12).** Unsaturated nitrile **12a** (9.28 g, 67.73 mmol) in ether (10 mL) was added dropwise with stirring to a suspension of $LiAlH_4$ (95%, 5.95g, 149 mmol) in dry ether (250 mL) at 0 ^oC. The reaction mixture was stirred at 0 ^oC for 10 min, and then brought to a reflux. After stirring for 2 h, the reaction mixture was cooled to 0 ^oC, and quenched by the sequential addition of water (6 mL), a 15% aqueous solution of NaOH (6 mL), and additional water (18 mL). The resulting white precipitate was filtered off and washed with ether. The filtrate was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Vacuum distillation [bp 64-66 ^oC/20 mmHg] of the residue yielded product amine **12** (6.9 g; 80% yield) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 5.38 (m, 2H), 2.37 (s, 2H), 1.96 (quintet, J = 7.6Hz, 2H), 1.83 (d, J = 6.8 Hz, 2H), 1.01 (brs, 2H), 0.92 (t, J = 7.6 Hz, 3H), 0.77 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 125.2, 52.8, 42.7, 35.2, 25.9, 24.9, 14.3; HRMS (*m/z*): calcd for $C_9H_{19}N$ (M^+), 141.15175; found, 141.15171; IR (thin film): ν_{max} = 3388 (-NH_2), 3312 (-NH_2), 3026 (=CH-), 2958, 2930, 2870, 1618, 1463, 1386, 1363, 1061, 969 (=CH-), 806 cm^{-1}.

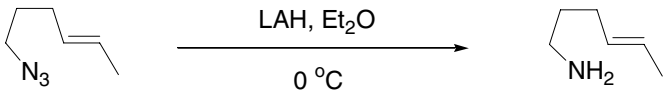
Synthesis of *trans*-Hex-4-enylamine (14)



14a

***trans*-6-Azido-hex-2-ene (14a).** *Trans*-hex-4-en-1-ol (25.0 g, 249 mmol) and TsCl (57.5 g, 301 mmol) were dissolved in ether (625 mL). With stirring, finely powdered KOH (167.9 g) was added in small portions at 0 ^oC over a period of 1 h. After stirring at 0 ^oC for an additional 1 h, the reaction mixture was poured into ice water with vigorous shaking. Two

layers separated, and the aqueous layer was extracted with ether. The organic layers were combined and dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo* to afford the corresponding tosylate as a yellow liquid. Without further purification, the crude tosylate was dissolved in DMF. Next, NaN_3 (37.0 g, 580 mmol) was added in one portion at room temperature. After stirring at 45 °C for 3 h, the white suspension was diluted with Et_2O (600 mL) and water (200 mL). The two layers were separated, and the aqueous layer was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Column chromatography of the residue on silica gel (100% pentane) afforded azide **14a** (26.2 g; 84% yield for 2 steps) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.54-5.38 (m, 2H), 3.29 (t, *J* = 7.0 Hz, 2H), 2.09 (q, *J* = 7.0 Hz, 2H), 1.68 (d, *J* = 7.0 Hz, 3H), 1.70-1.65 (m, 2H); ^{13}C NMR (125MHz, $CDCl_3$): δ 129.8, 126.5, 51.0, 29.8, 28.9, 18.1; HRMS (*m/z*): calcd for $C_6H_{11}N_3$ (M^+), 125.09530; found, 125.09501; Anal. Calcd. for $C_6H_{11}N_3$: C, 57.56; H, 8.86; N, 33.58. found: C, 57.42; H, 8.74; N, 33.50; IR (thin film): ν_{max} = 2938, 2856, 2096 (-N_3), 1451, 1348, 1280, 1255, 967 (=CH-) cm^{-1}.

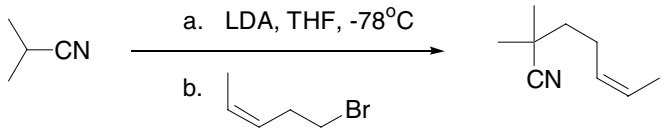


14a **14**

***trans*-Hex-4-enylamine[8] (14) [Registry No. 55108-01-5].** A suspension of $LiAlH_4$ (15.5 g, 387 mmol) in ether (700 mL) was stirred while a solution of azide **14a** (21.8 g, 174 mmol) in dry ether (50 mL) was added dropwise at 0 °C over a period of 10 min. After stirring at 0 °C for 30 min, the reaction mixture was quenched by the sequential addition of water (20 mL), a 15% aqueous solution of NaOH (20 mL), and water (60 mL). The white precipitate was filtered off and washed with ether. The filtrate was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Vacuum distillation [bp 54-56 °C/20 mm Hg] of the residue yielded amine **14** as a colorless liquid (13.2 g, 76% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 5.42-5.34

(m, 2H), 2.49 (t, J = 7.0 Hz, 2H), 1.97-1.94 (m, 2H), 1.59 (d, J = 3.5 Hz, 3H), 1.34 (quintet, J = 7.0 Hz, 2H), 0.508 (brs, 2H); ^{13}C NMR (125 MHz, C_6D_6): δ 132.0, 125.3, 42.4, 34.5, 30.7, 18.4; HRMS (*m/z*): calcd for $C_6H_{13}N$ (M^+), 99.10480; found, 99.10484; Anal. Calcd. for $C_6H_{13}N$: C, 72.66; H, 13.21; N, 14.12. found: C, 72.89; H, 13.18; N, 14.13; IR (thin film): ν_{max} = 3366 (-NH_2), 3291 (-NH_2), 3022 (=CH-), 2961, 2930, 2856, 1585, 1451,1439,1379, 1312, 966 (=CH-), 819 cm^{-1}.

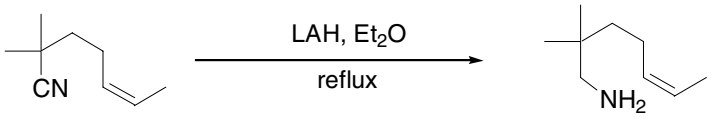
Synthesis of *cis*-2,2-Dimethyl-hept-5-enylamine (16)



16a

***cis*-2,2-Dimethyl-hept-5-enenitrile (16a).** With stirring, isobutyronitrile (20.2 mL, 219 mmol) in THF (35 mL) was added dropwise at –78 °C to a 2.0 M solution of LDA (120.5 mL, 241 mmol) dissolved in heptane-THF-ethyl benzene (Aldrich). After stirring for 1 h at –78 °C and for 2 h at 0 °C, *cis*-1-bromo-3-pentene (36.0 g, 241 mmol) in THF (30 mL) was added at 0 °C. The reaction mixture was stirred at room temperature for 12 h, after which time the yellow solution was quenched with a saturated NH_4Cl solution, then with water. The aqueous layer was separated and extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by vacuum distillation [bp 63-65 °C/5mm Hg] yielding nitrile **16a** (28.34g; 94% yield) as a colorless liquid with a metallic odor. ^{1}H NMR (400 MHz, C_6D_6): δ 5.43 (m, 1H), 5.25 (m, 1H), 2.07 (q, J = 7.6 Hz, 2H), 1.49 (d, J = 7.2Hz, 3H), 1.10 (m, 2H), 0.81 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ 129.4, 125.4, 124.8, 41.3, 32.7, 26.9, 23.8, 13.4; HRMS (*m/z*): calcd for $C_9H_{14}N$ (M-H^+), 136.11262; found, 136.11251; LRMS (relative abundance): [M^+] (3), [M-H^+] (14), 111 (8), 94 (14), 81 (11), 69 (91), 55 (50), 41 (100), 27 (45); IR (thin film): ν_{max} =

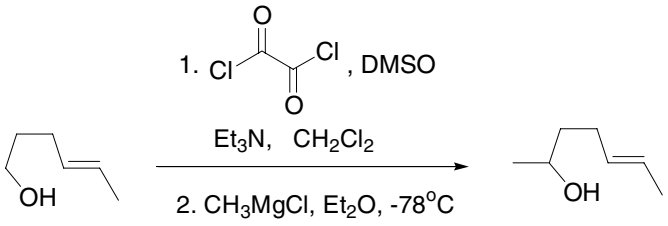
3016 (=CH-), 2976, 2935, 2860, 2233 (-CN), 1656, 1471, 1456, 1369, 1207, 722 (=CH-), 682 cm^{-1}.



16a **16**

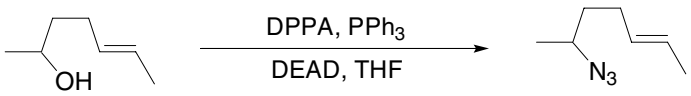
***cis*-2,2-Dimethyl-hept-5-enylamine (16).** With stirring, unsaturated nitrile **16a** (21.0 g, 153 mmol) in ether (50 mL) was added dropwise to a suspension of $LiAlH_4$ (95%, 13.5 g, 337 mmol) in dry ether (500 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min, and then brought to a reflux. After stirring for 1 h, the reaction mixture was cooled to 0 °C, and quenched by the sequential addition of water (13 mL), a 15% NaOH solution (13 mL), and water (39 mL). The resulting white precipitate was filtered off and washed with ether. The filtrate was then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Vacuum distillation [bp 63-65 °C/4.8 mm Hg] of the residue afforded product amine (16.9 g; 78% yield) **16** as a colorless liquid. ^{1}H NMR (400 MHz, C_6D_6): δ 5.46-5.41 (m, 2H), 2.28 (s, 2H), 1.97 (dt, J = 5.2 Hz, 8.4 Hz, 2H), 1.57 (d, J = 4.8 Hz, 3H), 1.21 (m, 2H), 0.75 (s, 6H), 0.61 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.0, 123.8, 53.2, 39.8, 25.1, 22.3, 13.1; HRMS (*m/z*): calcd for $C_9H_{19}N$ (M^+), 141.15175; found, 141.15162; IR (thin film): ν_{max} = 3389 (-NH_2), 3310 (-NH_2), 3012 (=CH-), 2954, 2866, 1655, 1618, 1471, 1402, 1387, 1363, 1063, 898, 814, 694 cm^{-1}.

Synthesis of *trans*-2-Amino-hept-5-ene (18)



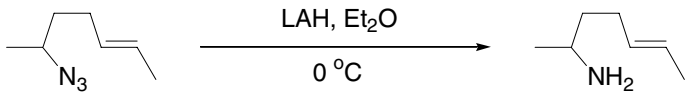
18a

***trans*-Hept-5-en-2-ol[9] (18a) [Registry No. 58927-83-6]**. Dimethyl sulfoxide (DMSO) (50.8 mL, 716 mmol) was added over a period of 20 min at –78 °C to a stirring 2 M solution of oxalyl chloride (179 mL, 358 mmol) dissolved in CH_2Cl_2 (179 mL). After the solution was stirred at –78 °C for an additional 10 min, *trans*-4-hexen-1-ol (36.3 mL, 298 mmol) dissolved in CH_2Cl_2 (150 mL) was next added dropwise. The reaction mixture was stirred at –78 °C for 30 min. Triethylamine (208 mL, 1490 mmol) was then added dropwise at –78 °C. The reaction mixture was stirred for an additional 30 min and then allowed to warm to room temperature. Water (400 mL) and CH_2Cl_2 (500 mL) were added and the resulting two layers were separated. The organic layer was washed with 10% aqueous HCl, then washed with brine. The organic layer was next dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo* to yield a pale yellow liquid. Without further purification, the crude aldehyde, *trans*-4-hexenal [Registry No. 25166-87-4][10], was dissolved in dry ether (800 mL) at –78 °C. A 3.0 M solution of MeMgCl (131 mL, 393 mmol) was added with stirring to the reaction mixture at –78 °C over a period of 30 min. The reaction mixture was next warmed to room temperature and stirred for an additional 1 h. The reaction mixture was then quenched with 10% HCl solution (50 mL) and extracted with ether. The combined ether extracts were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo*. Column chromatography on silica gel (EtOAc-pentane, 1:8) afforded pure alcohol **18a** (16.18 g; 44% yield): R_f = 0.41; ^{1}H NMR (400 MHz, C_6D_6): δ 5.39-5.41 (m, 2H), 3.55 (sextet, *J* = 6.4 Hz, 1H), 2.03 (m, 2H), 0.58 (d, *J* = 3.6 Hz, 3H), 1.40 (m, 1H), 1.31 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 132.0, 125.4, 67.6, 39.8, 29.7, 24.0; HRMS (*m/z*): calcd for $C_7H_{14}O$ (M^+), 114.10447; found, 114.10432.



18a **18b**

***trans*-6-Azido-hept-2-ene (18b).** *Trans*-hept-5-en-2-ol (**18a**) (15.4 g, 151 mmol), diphenylphosphoryl azide (DPPA; 66.9 mL, 301 mmol), and diethylazodicarboxylate (DEAD; 47.4 mL, 301 mmol) were added to a solution of PPh_3 (80.0 g, 301 mmol) in dry THF (1 L). The reaction mixture was stirred at room temperature for 1 h and then concentrated *via* rotary evaporation. The residue was then filtered through a plug of silica with pentane (300 mL). The filtrate was concentrated *in vacuo* and the residue purified by column chromatography on silica gel (100% pentane) to afford 4.2 g (20% yield) of the volatile azide **18b** as a light yellow liquid; $R_f = 0.51$; ^{1}H NMR (400 MHz, C_6D_6): δ 5.28 (m, 1H), 5.20 (m, 1H), 2.94 (sextet, J = 6.8 Hz, 1H), 1.84 (m, 2H), 1.52 (d, J = 6.0 Hz, 3H), 1.27 (m, 2H), 0.80 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 130.7, 126.2, 57.3, 36.7, 30.0, 19.8, 18.7; HRMS (*m/z*): calcd for $C_7H_{14}N_3$ ($M+H^+$), 140.1188; found, 140.1186.

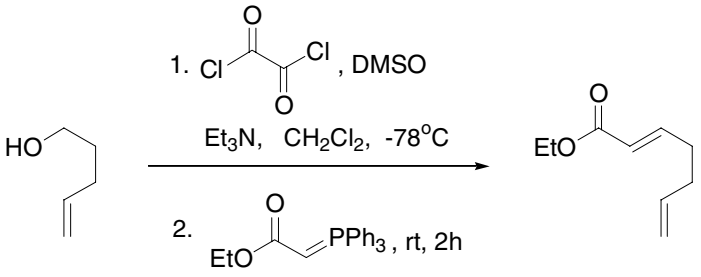


18a **18**

***trans*-2-Amino-hept-5-ene (18) [371255-23-1].** To a stirring suspension of $LiAlH_4$ (1.36 g, 34.2 mmol) in ether (200 mL) was added dropwise a solution of azide **18b** (2.38 g, 17.1 mmol) in dry ether (20 mL) at 0 °C over a period of 10 min. After stirring at 0 °C for 30 min, the reaction mixture was quenched by the sequential addition of water (4 mL), a 15% solution of NaOH (4 mL), and water (12 mL). The white precipitate was filtered off and washed with ether. The filtrate was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Vacuum distillation [bp 64-66 °C/20 mm Hg] of the residue yielded the amine **18** as a colorless liquid (760 mg; 39% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 5.40-5.37 (m, 2H), 2.66 (sextet, J =

6.5Hz, 1H), 1.97 (m, 2H), 1.59 (d, *J* = 3.5 Hz, 3H), 1.25 (m, 2H), 0.90 (d, *J* = 6.5Hz, 3H), 0.63 (brs, 2H); ^{13}C NMR (100 MHz, C_6D_6): δ 132.1, 125.1, 47.2, 40.9, 30.6, 25.0, 18.7; HRMS (*m/z*): calcd for $C_7H_{14}N$ ($M\text{-}H^+$), 112.1126; found, 112.1126. IR (thin film): ν_{max} = 3360 ($-NH_2$), 3280 ($-NH_2$), 3019 (=CH-), 2957, 2918, 2852, 1598, 1451, 1376, 1144, 966 (=CH-), 861, 819 cm^{-1}.

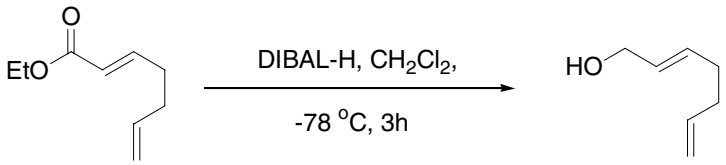
Synthesis of *trans*-2,2-Dimethyl-4,8-nonadieneylamine (20)



20a

(*E*)-Ethyl 2,6-heptadienoate[11] (20a) [Registry No. 95514-62-8]. Dimethyl sulfoxide (DMSO) (56 mL, 0.80 mol) in CH_2Cl_2 (60 mL) was added over a period of 20 min at –78 °C to a stirring 2 M solution of oxalyl chloride (200 mL, 0.4 mol) dissolved in CH_2Cl_2 (200 mL). After the solution was stirred at –78 °C for an additional 10 min, pent-4-en-1-ol (36.0 mL, 0.35 mol) dissolved in CH_2Cl_2 (350 mL) was next added dropwise. The reaction mixture was stirred at –78 °C for 30 min. Triethylamine (223 mL, 1.6 mol) was then added dropwise at –78 °C. The reaction mixture was stirred for an additional 30 min and then allowed to warm to room temperature. Next, (carbethoxymethylene)triphenylphosphorane[12] (183g, 0.53 mol) dissolved in CH_2Cl_2 (200 mL) was added dropwise at room temperature. After stirring 2 h at room temperature, the reaction mixture was quenched with water (400 mL) and the separated aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with 10% aqueous HCl, then washed with brine. The organic layer was next dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo* to yield a pale yellow liquid. The crude material was

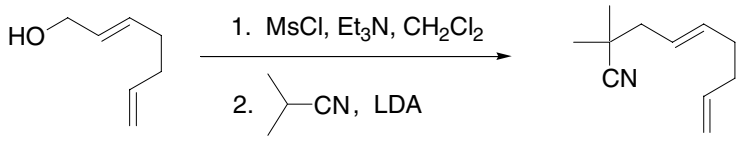
dissolved in pentane (300 mL), and the resulting precipitate was filtered off through a short plug of SiO_2. After removing the solvent, short column chromatography on silica gel (EtOAc-pentane, 1:19) afforded pure ester **20a** (52 g; 97% yield): R_f = 0.50; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.85 (dt, *J* = 15.5 Hz, *J* = 6.5 Hz, 1H), 5.73 (d, *J* = 15.5 Hz, 1H), 5.70 (m, 1H), 4.94 (d, *J* = 17 Hz, 1H), 4.90 (d, *J* = 9.5 Hz, 1H), 4.07 (q, *J* = 6.5 Hz, 2H), 2.20 (q, *J* = 6.5 Hz, 2H), 2.11 (q, *J* = 6.5 Hz, 2H), 1.17 (t, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.4, 137.3, 121.9, 115.7, 60.4, 32.2, 31.6, 27.1, 14.5; HRMS (*m/z*): calcd for $C_9H_{15}O_2$ ($M+H^+$), 115.1067; found, 115.1066; LRMS (relative abundance): [$M+H^+$] (100), [M^+] (45), 149 (12), 129 (6), 122 (7), 113 (10), 111 (13), 95 (25), 91 (28), 85 (46), 81 (49), 79 (59), 71 (61), 69 (96), 67 (73).



20a **20b**

***trans*-2,6-Heptadien-1-ol[11] (20b) [Registry No. 62019-06-1].** Diisobutylaluminum hydride (300 mL of a 1.0 M solution in hexane, 300 mmol) was added dropwise to a magnetically stirred solution of (*E*)-ethyl 2,6-heptadienoate (**20a**) (20g, 130 mmol) in CH_2Cl_2 (500 mL) at – 78 °C. The resulting mixture was stirred at –78 °C for 3h, then allowed to warm to 0 °C. Next, a 1.0 M aqueous solution of tartaric acid was added dropwise with stirring at 0 °C. After gas evolution ceased, the resulting mixtures was warmed to room temperature and stirred for 1h until two distinct layers were observed. The separated aqueous layer was extracted with CH_2Cl_2 and combined organic phases were washed with brine, then dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo* to yield a pale yellow liquid. Column chromatography on silica gel (EtOAc-hexane, 1:2) afforded pure alcohol **20b** (14.2 g; 97% yield): R_f = 0.45; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.80 (m, 1H), 5.70-5.64 (m, 2H),

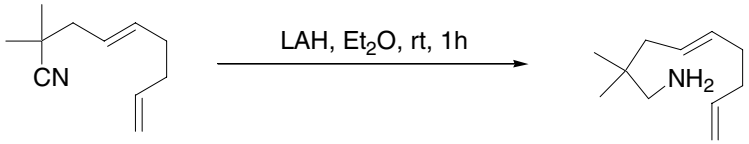
5.01 (d, J = 16.5 Hz, 1H), 4.96 (d, J = 9.5 Hz, 1H), 4.06 (d, J = 4.5 Hz, 2H), 2.14 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2, 132.4, 129.6, 115.0, 63.7, 33.4, 31.7; LRMS (relative abundance): [M^+] (7), [M-H^+] (75), 109 (14), 95 (42), 93 (50), 81 (80), 79 (44), 69 (17), 68 (32), 67 (100), 57 (45), 55 (57).



20b **20c**

***trans*-2,2-Dimethyl-4,8-nonadienenitrile (20c).** Methanesulfonyl chloride (10.3 mL, 134 mmol) was added dropwise to a stirring solution of **20b** and triethylamine (38 mL, 268 mmol) in CH_2Cl_2 (250 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2h and then was poured into a separatory funnel containing ice-cold 1.0 M HCl. The aqueous layer was separated and was extracted with CH_2Cl_2. The organic phases were combined, washed with saturated $NaHCO_3$, and dried over $MgSO_4$. After filtration, solvent was evaporated to give the crude mesylate. This material then dissolved in CH_2Cl_2 (25 mL) for the subsequent reaction. ^{n}BuLi (61 mL of a 1.6 M solution in hexane, 98 mmol) was added dropwise at –78 °C to a solution of diisopropylamine (13.7 mL, 98 mmol) dissolved in THF (500 mL). The resulting mixture was stirred at –78 °C for 30 min, and at 0 °C for 30 min. Isobutyronitrile (8 mL, 89 mmol) was then added dropwise to the reaction mixture at –78 °C. The resulting solution was stirred at –78 °C for 30 min, and at 0 °C for 30 min. the reaction mixture was cooled to –78 °C again, then the crude mesylate in CH_2Cl_2 was added dropwise at –78 °C. After stirring at –78 °C for 20 min, the resulting yellow solution was allowed to warm to room temperature and stirred for an additional 1h. The reaction mixture was then quenched with saturated ammonium chloride solution (100 mL), and extracted with ether. The combined ether extracts were washed with brine and dried over $MgSO_4$. After filtration, the

solvent was removed *in vacuo*. Column chromatography on silica gel (EtOAc-pentane, 1:19) afforded pure nitrile **20c** (3.6 g; 25% yield): R_f = 0.51; ^{1}H NMR (500 MHz, C_6D_6): δ 5.72 (m, 1H), 5.41-5.29 (m, 2H), 5.00 (d, *J* = 14.0 Hz, 1H), 4.98 (d, *J* = 8.0 Hz, 1H), 1.97 (qin, *J* = 6.0 Hz, 4H), 1.78 (d, *J* = 6.0 Hz, 2H), 0.86 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6): δ 138.6, 135.6, 125.0, 124.8, 115.4, 44.3, 34.2, 32.7, 32.4, 26.3; Anal. Calcd. for $C_{11}H_{17}N$: C, 80.93; H, 10.50; N, 8.58. found: C, 80.75; H, 10.33; N, 8.42; LRMS (relative abundance): [M+H$^+$] (46), 162 (10), 148 (6), 122 (11), 107 (11), 95 (100), 93 (16), 81 (13), 69 (31), 67 (49).

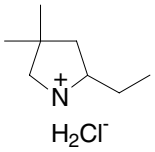


20c **20**

***trans*-2,2-Dimethyl-4,8-nonadieneylamine (20).** With stirring, unsaturated nitrile **20c** (2.31 g, 13.8 mmol) in ether (10 mL) was added dropwise to a suspension of $LiAlH_4$ (95%, 661 mg, 16.6 mmol) in dry ether (100 mL) at 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C for 10 min, and then warmed to room temperature. After stirring for 1 h, the reaction mixture was cooled to 0 ^{o}C, and quenched by the sequential addition of water (0.7 mL), a 15% aqueous NaOH solution (0.7 mL), and water (2.1 mL). The resulting white precipitate was filtered off and washed with ether. The filtrate was then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Vacuum distillation [bp 32-34 ^{o}C/3 mm Hg] of the residue afforded product amine **20** as a colorless liquid (2.1 g; 90% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 5.58 (m, 1H), 5.41-5.35 (m, 2H), 5.02 (d, *J* = 17.0 Hz, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 2.30 (s, 2H), 2.05 (m, 4H), 1.88 (d, *J* = 7.0 Hz, 2H) 0.78 (s, 6H), 0.60 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.9, 132.5, 128.1, 115.2, 53.1, 43.2, 35.6, 34.6, 32.8, 25.1; HRMS (*m/z*): calcd for $C_{11}H_{22}N$ (M+H$^+$), 168.1747; found, 168.1741; LRMS (relative abundance): [M+H$^+$] (100), 166 (6), 154 (17), 126 (12), 109 (7), 95 (19), 85 (13), 79 (16), 71 (16), 69 (26), 67 (20).

Typical Procedure for NMR-Scale Catalytic Reactions. In the nitrogen-filled glove box, the $Cp'_2LaCH(TMS)_2$ precatalyst (**5a**, 9.0 mg, 15.8 μmol) was weighed into an NMR tube equipped with a Teflon valve, and substrate **10** (41.2mg, 316 μmol) and *o*-xylene-d_{10} (0.7 mL) were added. The tube was then removed from the glove box. The catalyst : substrate ratio was confirmed to be 1:20.1 by ^{1}H NMR based on the quantitatively generated[19-23] internal $CH_2(TMS)_2$ standard. The tube was then brought to the desired reaction temperature (125 °C), and the ensuing catalytic reaction monitored by ^{1}H NMR. After 150 min, the reaction had proceeded to >95% conversion, as determined by ^{1}H NMR and GC-MS based on the $CH_2(TMS)_2$ internal standard. After reaction was complete, the reaction mixture was freeze-thaw degassed and the volatiles vacuum-transferred into a separate flask. The solvent was carefully removed on the rotary evaporator at 0 °C to give **11** as a slightly yellow liquid (36.7 mg, 90% yield).

Preparative-Scale Catalytic Reactions.

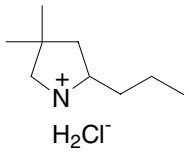


11-HCl

Synthesis of 2-Ethyl-4,4-Dimethylpyrrolidine[13] (11) hydrochloride [Registry No. 371255-30-0]. In the glove box, $(CGC)YbCH(TMS)_2$ (20 mg; 34 μmol) was loaded into a storage tube equipped with a magnetic stir bar and J. Young valve. At –78 °C, benzene (4 mL) was vacuum-transferred onto the catalyst, and 2,2-dimethyl-hex-4-enylamine **10** (128 mg; 1.0 mmol) was syringed in under Ar flush. The valve was then closed and the clear yellow solution stirred for 36 h at 125 °C behind a blast shield. The reaction mixture was next freeze-thaw degassed, and the volatiles were vacuum-transferred to a separate flask. A 1 M solution

of HCl (1.3 mL, 1.3 mmol) dissolved in ether was added dropwise with stirring to the volatiles at 0 °C. After stirring at 0 °C for 30 min, the solvent was removed *in vacuo*. Recrystallization from benzene-pentane afforded the HCl salt of amine **11** as a white crystalline solid (115 mg; 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.00 (brs, 1H), 9.38 (brs, 1H), 3.68 (m, 1H), 3.06-3.10 (m, 2H), 2.05 (m, 1H), 1.96 (d, *J* = 10 Hz, 1H), 1.81 (m, 1H), 1.57 (m, 1H), 1.22 (s, 3H), 1.19 (s, 3H), 1.06 (brs, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 61.6, 57.0, 45.7, 38.8, 27.7, 27.6, 27.0, 12.5; Anal. Calcd. for $C_8H_{18}ClN$: C, 58.70; H, 11.08; N, 8.56. found: C, 58.39; H, 10.97; N, 8.34

The free amine **11** obtained in the NMR scale experiments: ^{1}H NMR (500 MHz, C_6D_6): δ 2.88 (quintet, *J* = 7.0 Hz, 1H), 2.62 (d, *J* = 10 Hz, 1H), 2.47 (d, *J* = 10 Hz, 1H), 1.48 (dd, *J* = 12.5 Hz, 7.0 Hz, 1H), 1.40 (m, 1H), 1.32 (m, 1H), 1.21 (brs, 1H), 0.99 (s, 3H), 0.93 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6): δ 61.4, 61.1, 48.0, 39.5, 30.9, 29.2, 28.3, 12.2; HRMS (*m/z*): calcd for $C_8H_{17}N$ (M^+), 127.13610; found, 127.13619.

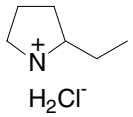


13-HCl

Synthesis of 4,4-Dimethyl-2-propylpyrrolidine (13) [Registry No. 371255-25-3] hydrochloride. In the glove box, the $Cp'_2LaCH(TMS)_2$ precatalyst (**5a**, 28.5 mg, 50 μmol), 2,2-dimethyl-hex-4-enylamine (**10**, 142 mg; 1.0 mmol), and benzene (4 mL) were loaded into a storage tube equipped with a magnetic stir bar and J. Young valve. The valve was then closed and the clear solution stirred for 16 h at 125 °C behind a blast shield. The reaction mixture was next freeze-thaw degassed and the volatiles were vacuum-transferred to a separate flask. A 1 M solution of HCl (1.3 mL, 1.3 mmol) dissolved in ether was added dropwise with stirring to the volatiles at 0 °C. After stirring at 0 °C for 30 min, the solvent

was removed *in vacuo*. Recrystallization from benzene-pentane afforded the HCl salt of amine **11** as a white crystalline solid (160 mg; 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.79 (brs, 1H), 9.15 (brs, 1H), 3.86 (m, 1H), 3.14 (m, 2H), 2.02-1.54 (m, 6H), 1.24 (s, 6H) 1.01 (brs, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 60.1, 57.7, 46.0, 38.7, 35.7, 28.0, 27.8, 20.9, 14.4; Anal. Calcd. for $C_9H_{20}ClN$: C, 60.83; H, 11.34; N, 7.88. found: C, 60.62; H, 11.62; N, 7.85; HRMS (*m/z*): calcd for $C_9H_{20}N$ (M^+-Cl), 142.1590; found, 142.1588. LRMS (relative abundance): [M^+-Cl+1] (12), [M^+-Cl] (100), 140(7), 98(14), 93(2), 61(3).

The free amine **13** obtained in the NMR scale experiments: ^{1}H NMR (500 MHz, C_7D_8): δ 2.93 (quintet, *J* = 6.5 Hz, 1H), 2.57 (d, *J* = 10.0 Hz, 1H), 2.44 (d, *J* = 10 Hz, 1H), 1.47 (dd, *J* = 12.0 Hz, 6.5 Hz, 1H), 1.33 (m, 2H), 1.24 (m, 2H), 1.14 (brs, 1H), 0.98 (s, 3H), 0.91 (s, 3H), 0.90 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, C_7D_8): δ 61.5, 59.5, 48.6, 40.6, 39.6, 29.4, 28.4, 21.4, 15.0; HRMS (*m/z*): calcd for $C_9H_{19}N$ (M^+), 141.15173; found, 141.15165. LRMS (relative abundance): [M^+] (2), [M-H^+] (2), 126 (5), 98 (100), 70 (16), 57 (15), 55 (11), 28 (50).

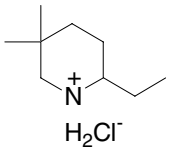


15-HCl

Synthesis of 2-Ethylpyrrolidine[14] (15) [Registry No. 1003-28-7] hydrochloride. In the glove box, the $Cp'_2LaCH(TMS)_2$ precatalyst (**5a**, 28.5 mg, 50 μmol), *trans*-hex-4-enylamine (**14**, 100 mg; 1.0 mmol), and benzene (4 mL) were loaded into a storage tube equipped with a magnetic stir bar and J. Young valve. The valve was then closed and the clear solution stirred for 36 h at 125 °C behind a blast shield. The reaction mixture was next freeze-thaw degassed and the volatiles were vacuum-transferred to a separate flask. A 1 M solution of HCl (1.3 mL, 1.3 mmol) dissolved in ether was added dropwise with stirring to the volatiles at 0 °C. After

stirring at 0 °C for 30 min, the solvent was removed *in vacuo*. Recrystallization from benzene-pentane afforded the HCl salt of amine **15** as a white crystalline solid (113 mg; 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (brs, 1H), 9.13 (brs, 1H), 3.37-3.32 (m, 2H), 3.23 (m, 1H), 2.09-1.89 (m, 4H), 1.73 (m, 1H) 1.60 (m, 1H), 0.99(t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.0, 44.6, 30.1, 25.5, 23.7, 11.6; Anal. Calcd. for $C_6H_{14}ClN$: C, 53.13; H, 10.40; N, 10.33. found: C, 52.70; H, 10.18; N, 9.88; HRMS (*m/z*): calcd for $C_6H_{13}N$ (M^+-HCl), 99.1048; found, 99.1043. LRMS (relative abundance): [M^+-HCl] (7), 98 (5), 91(3), 82(4), 77(3), 71(17), 68(9), 57(5), 56(14), 55(6).

The free amine **15** obtained in the NMR scale experiments: ^{1}H NMR (400 MHz, C_6D_6): δ 2.84 (ddd, *J* = 10.0 Hz, 7.6 Hz, 5.2 Hz, 1H), 2.72-2.61 (m, 2H), 1.63 (m, 1H), 1.54 (m, 1H), 1.47 (m, 1H), 1.38 (m, 1H), 1.29 (m, 1H), 1.06 (m, 1H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 61.5, 47.5, 32.4, 30.4, 26.4, 12.6; HRMS (*m/z*): calcd for $C_6H_{13}N$ $(M)^+$, 99.10480; found, 99.10495. LRMS (relative abundance): [M^+] (4), 84 (28), 75 (10), 71 (13), 70 (100), 68 (13), 56 (23), 54 (29), 52 (23), 42 (25), 40 (19), 38 (8), 28 (8).

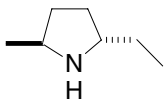


17-HCl

Synthesis of 2-Ethyl-5,5-dimethylpiperidine (17) hydrochloride [Registry No. 371255-31-1]. In the glove box, (CGC)YbCH(TMS)$_2$ (**7c**, 20 mg; 34 μmol) was loaded into a storage tube equipped with a magnetic stir bar and J. Young valve. At –78 °C, benzene (4 mL) was vacuum-transferred onto the catalyst and *cis*-2,2-dimethyl-hept-5-enylamine (**16**, 160 mg; 1.1 mmol) was syringed in under Ar flush. The valve was then closed and the clear yellow solution stirred for 5 d at 120 °C behind a blast shield. The reaction mixture was next freeze-thaw degassed and the volatiles were vacuum-transferred to a separate flask. A 1 M solution

of HCl (1.3 mL, 1.3 mmol) dissolved in ether was added dropwise with stirring to the volatiles at 0 °C. After stirring at 0 °C for 30 min, the solvent was removed *in vacuo*. Recrystallization from benzene-pentane gave the HCl salt of amine **17** as a white crystalline solid (166 mg; 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (brs, 1H), 8.82 (brs, 1H), 3.04 (d, *J* = 9.2 Hz, 1H), 2.82 (m, 1H), 2.67 (m, 1H), 2.13 (m, 1H), 1.87 (d, *J* = 12.4 Hz, 2H), 1.59-1.48 (m, 2H), 1.36 (t, *J* = 12.4 Hz, 1H) 1.23 (s, 3H), 1.04 (brs, 3H), 1.03 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6): δ 58.4, 54.3, 36.1, 29.6, 29.3, 26.3, 25.2, 24.7, 10.8; Anal. Calcd. for $C_9H_{20}ClN$: C, 72.66; H, 13.21; N, 14.12. found: C, 72.89; H, 13.18; N, 14.13

The free amine **17** obtained in the NMR-scale experiments: ^{1}H NMR (500 MHz, C_7D_8): δ 2.45 (d, *J* = 11.5 Hz, 1H), 2.29 (d, *J* = 11.5 Hz, 1H), 2.08 (m, 1H), 1.32 (m, 2H), 1.25 (quintet, *J* = 6.5 Hz, 2H), 1.13 (m, 2H), 0.99 (s, 3H), 0.84 (t, J = 6.5 Hz, 3H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, C_7D_8): δ 59.8, 59.4, 39.3, 30.8, 30.6, 30.0, 25.4, 24.7, 11.4; HRMS (*m/z*): calcd for $C_9H_{19}N$ (M^+), 141.15173; found, 141.15179. LRMS (relative abundance): [M^+] (2), [M-H^+] (2), 126 (7), 121(11), 112 (100), 100 (67), 98 (82), 70 (18), 56 (18), 41 (14), 28 (52).

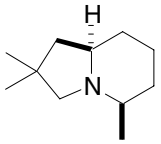


19 (±)

Synthesis of *trans*-2-Ethyl-5-methylpyrrolidine (19) [Registry No. 97478-53-0]. In the glove box, (CGC)YbCH(TMS)$_2$ (**7c**, 58 mg; 50 μmol), *trans*-2-amino-hept-5-ene **18** (113 mg; 1.0 mmol) and benzene (4 mL) were loaded into a storage tube equipped with a magnetic stir bar and J. Young valve. The valve was then closed and the clear solution stirred for 48 h at 125 °C behind a blast shield. The reaction mixture was next freeze-thaw degassed and the volatiles were vacuum-transferred to a separate flask. The solvent was removed *in vacuo*. Column chromatography on silica gel (hexane-methylene chloride-^{i}propylamine, 1:15:0.8)

afforded pure amine **19** (101 mg; 89% yield): R_f = 0.41; ^{1}H NMR (500 MHz, C_6D_6): δ 3.12 (sextet, *J* = 6.0 Hz, 1H), 2.94 (quintet, *J* = 6.5 Hz, 1H), 1.77 (m, 2H), 1.36 (td, *J* = 13.5 Hz, 6.5 Hz, 1H), 1.56 (m, 1H), 1.07 (m, 1H), 1.01 (d, *J* = 6.0 Hz, 3H), 0.90 (t, *J* = 7.0Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6): δ 60.3, 53.8, 35.4, 33.2, 31.0, 22.7, 12.2;

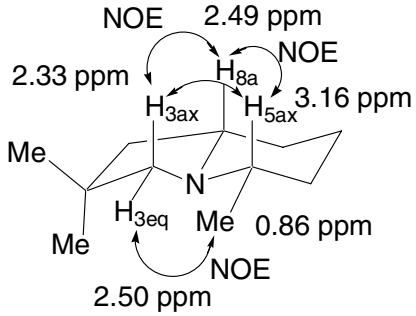
Free amine **19** was converted to the corresponding HCl salt of amine **19** using a 1 M ether solution of HCl (1.3 mL, 1.3 mmol), a white crystalline solid (121 mg; 81% yield for 2 steps). HRMS (*m/z*): calcd for $C_9H_{14}N$ ($M-Cl^-$), 114.1277; found, 114.1281; LRMS (relative abundance): [$M-Cl^-$] (100), 112 (12), 100 (5), 95 (5), 84 (26).



21 (±)

Synthesis of (±)-(5*R*, 8a*R*)-2,2,5-trimethyl-octahydroindolizine (21). In the glove box, (CGC)SmNH(TMS)$_2$ (**7a**, 58 mg; 50 μmol), 2,2-dimethylamino-nonadi-4,8-ene **20** (167 mg; 1.0 mmol), and benzene (2 mL) were loaded into a storage tube equipped with a magnetic stir bar and J. Young valve. The valve was then closed and the clear solution stirred for 2 days at 125 ^{o}C behind a blast shield. Et_2O (2.0 mL) was next added to the reaction mixture. The instantaneous precipitated catalyst was filtered off through a pad of Al_2O_3, and the pad then washed with Et_2O (2.0 mL). The solvent was removed *in vacuo*. Column chromatography on silica gel (ethyl acetate : methanol, 10:1) afforded pure amine **21** (99 mg; 59% yield) as a pale yellow liquid. The title compound was identified by GC/MS and NMR spectroscopic analysis including COSY and NOESY.[15] R_f = 0.47; ^{1}H NMR (500 MHz, C_6D_6): δ 3.16 (m, 1H), 2.50 (d, *J* = 8.5 Hz, 1H), 2.49 (m, 1H), 2.33 (d, *J* = 8.5 Hz, 2H), 1.87 (m, 1H), 1.62 (dm, J = 10 Hz, 1H), 1.52 (dd, *J* = 12 Hz, *J* = 6.5 Hz, 1H), 1.46-1.34 (m, 3H), 1.30-1.21 (m, 2H), 1.17 (s, 3H), 0.99 (s, 3H), 0.86 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6): δ 64.5, 54.5,

49.8, 48.1, 35.1, 32.5, 31.5, 31.4, 29.3, 19.6, 8.7; Anal. Calcd. for $C_{11}H_{21}N$: C, 78.97; H, 12.65; N, 8.37. found: C, 78.77; H, 12.36; N, 8.59. LRMS (relative abundance): [M^+] (14), [M-H^+] (14), 153.2 (15), 152.2 (100), 124.1 (20), 112.1 (45), 111.1 (27), 96.1 (20), 82.1 (13), 55.0 (17).



Catalyst Thermolysis Experiments. In the glove box, the precatalyst (ca. 2 mg) and a ferrocene internal standard (ca. 1 mg) were weighed into a NMR tube equipped with a Teflon valve. The tube was removed from the glove box, attached to the vacuum line, and C_6D_{12} or C_7D_8 (ca. 300-400 μL) was vacuum transferred in. The tube was sealed, brought to the desired temperature (120 ^oC), and the ensuing reaction monitored by ^1H NMR.

Determination of Enantiomeric Ratio and Optical Rotation of Products. In the nitrogen-filled glove box, the (*S*)-$Me_2Si(OHF)(CpR^*)YN(TMS)_2$ precatalyst (**5b**, 5.5 mg, 8 μmol) was weighed into an NMR tube equipped with a Teflon valve, and the substrate **16** (22.6mg, 160 μmol) and C_6D_6 (0.35 mL) were added. The tube was then removed from the glove box. The catalyst : substrate ratio was confirmed to be 1:20.1 by ^1H NMR based on the quantitatively generated internal $NH(TMS)_2$ standard. The tube was then brought to the desired reaction temperature (80 ^oC), and the ensuing catalytic reaction monitored by ^1H NMR. After 60 h, the reaction had proceeded to >95% conversion, as determined by ^1H NMR and GC-MS based on the $NH(TMS)_2$ internal standard. After reaction was complete, the reaction solution was separated from the catalyst residue by vacuum transfer. Anhydrous

methylenechloride (2 mL), triethylamine (66 μL, 480 μmol), and 1-naphthoylchloride (21 μL, 145 μmol) were added to the volatiles at 0 °C. After stirring 30 min at room temperature, H_2O (1 mL) and Et_2O were added. The aqueous phase extracted with Et_2O (2 x 1 mL). After column chromatograph (EtOAc: Hexane = 1: 2, R_f = 0.5), the enantioselectivity of the hydroamination reactions was assayed by chiral stationary phase HPLC analysis using a Regis (S,S)-Whelk O1 column (I.D.; 4.6mm, length; 25mm, particle size; 5mm) with a flow rate of 2.0 mL/min and hexane:^{i}PrOH (85:15) as eluent. The two enantiomers of N-1-naphthoyl derivatives[16] of racemic **11**, **13**, and **17** exhibited retention times of 9.1 min and 57.1 min, 9.0 min and 55.2 min, and 8.4 min and 47.0 min, respectively. The optical rotation values of the amines were determined by diluting the amines (1 mg) to a total volume of 1.0 mL C_6D_6, and measuring the optical rotation of the sample with a polarimeter.

Kinetic Studies of Hydroamination/Cyclization. In a typical experiment, an NMR sample was prepared as described above (see Typical NMR Catalytic Reaction), but maintained at –78 °C until kinetic measurements were begun. The sample tube was then inserted into the probe of the Inova-500 or Unity-400 spectrometer which had been previously set to the appropriate temperature (T ± 0.2 °C; checked with ethylene glycol temperature standard). Data were acquired using four scans per time interval with a long pulse delay (8 sec) to avoid signal saturation. The reaction kinetics were usually monitored from the intensity changes in the substrate olefinic resonances over three or more half-lives. The substrate concentration, C, was measured from the olefinic peak area, A_s, standardized to the area A_l of the free $EH(TMS)_2$ (E = N or CH) formed as turnover commences (Scheme 1 step *i*). The $EH(TMS)_2$ is present as a result of quantitative protonolytic ligand cleavage during catalyst generation. All data collected could be convincingly fit by least-squares to eq. (1) where C_o is the initial concentration of substrate ($C_o = A_{so}/A_{lo}$). The ratio of catalyst to substrate (E) was then accurately determined from the ratio of A_{so} and A_{lo}. The turnover

frequency (h^{-1}) was calculated from the least-squares determined slope (m) according to eq. (2).

$$C = mt + C_o \quad (1)$$

$$N_t\,(h^{-1}) = -(60\ \text{min}\ h^{-1}) \times m \quad (2)$$

Epimerization of $Me_2Si(OHF)[(-)\text{-menthylCp}]Y(NHR)(NH_2R)$. A 5 mm J. Young NMR tube was charged with 5.2 mg (7.6 μmol) of $Me_2Si(OHF)[(-)\text{-menthylCp}]YN(SiMe_3)_2$ in the glove box. Next, 12.5 μl (152 μmol) of *n*-propylamine (20 equiv.) and 0.35mL of *o*-xylene-d_{10} were added. The valve was then closed, and the tube was frozen at –78 °C. The sample was immediately inserted into the thermostated probe (80 °C ± 0.4 °C) of the Inova-500, and an initial spectrum was recorded. Protonolysis of the Ln-N bond of **8b** was complete within minutes, and the only solution species which was observed could be assigned to an (*S*)-$Me_2Si(OHF)[(-)\text{-menthylCp}]Y(NH^nPr)(NH_2{}^nPr)$ complex. The time evolution of the integrals of the cyclopentadienyl protons at 5.89 ppm (*R*) and 5.79 ppm (*S*) were monitored at 80 °C; the relative concentrations of the (*R*)-epimer and (*S*)-epimers were determined from the relative ratio areas of the integrals. The sample was then allowed to relax to equilibrium. The data were fit by linear least-squares analysis to the rate expression for the approach to equilibrium, eq 3. The plot of $\ln[(S_e - S_0)/(S_e - S)]$, where S and S_e are the mole fractions of S at time t, and at equilibrium, respectively, versus time, afforded $(k + k')$ from the line slope.[17] The forward (k) and reverse (k') constant for epimerization could be determined from the slope of the line and equilibrium expression, $K = k/k'$.

$$\ln[(S_e - S_0)/(S_e - S)] = (k + k')t \quad (3)$$

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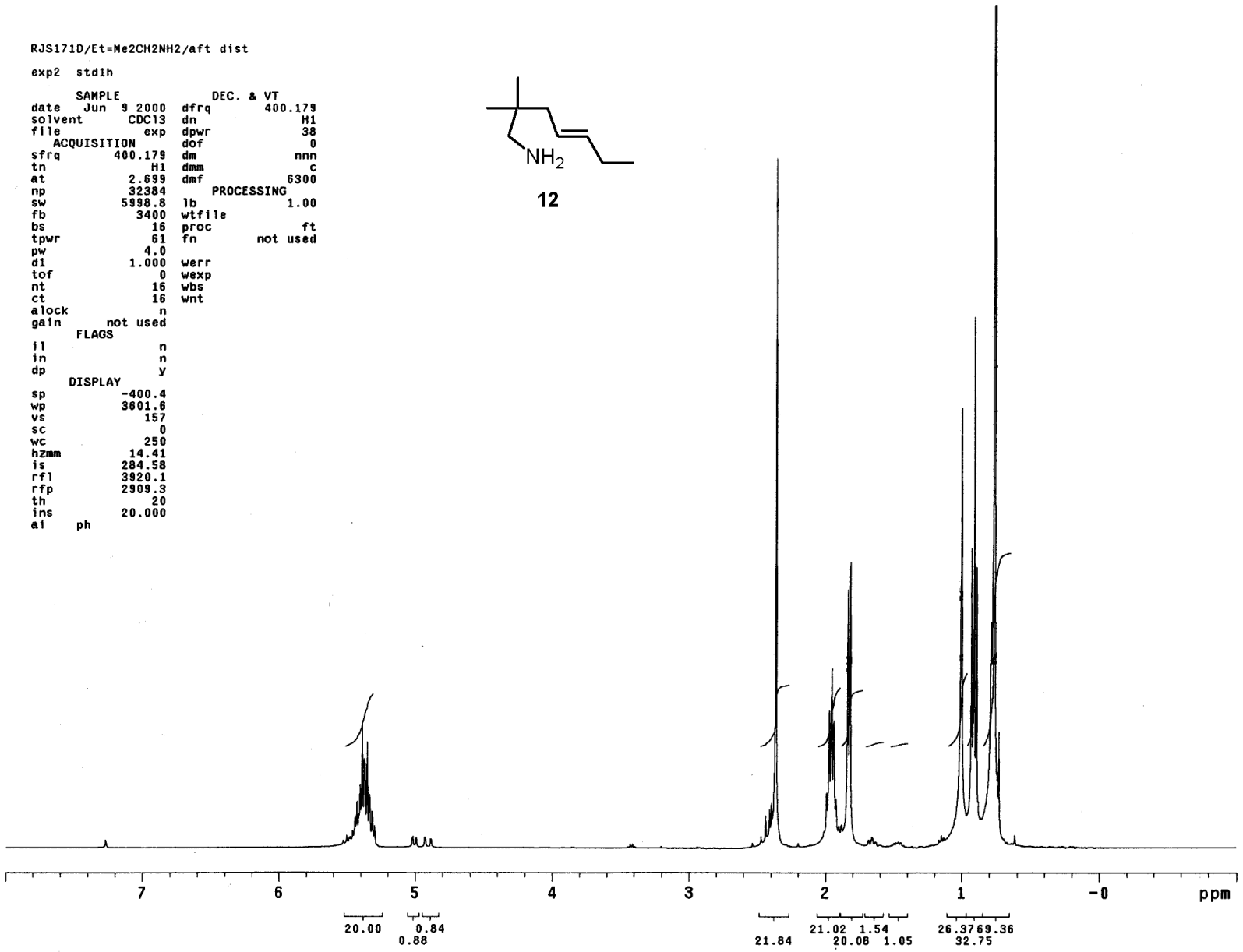
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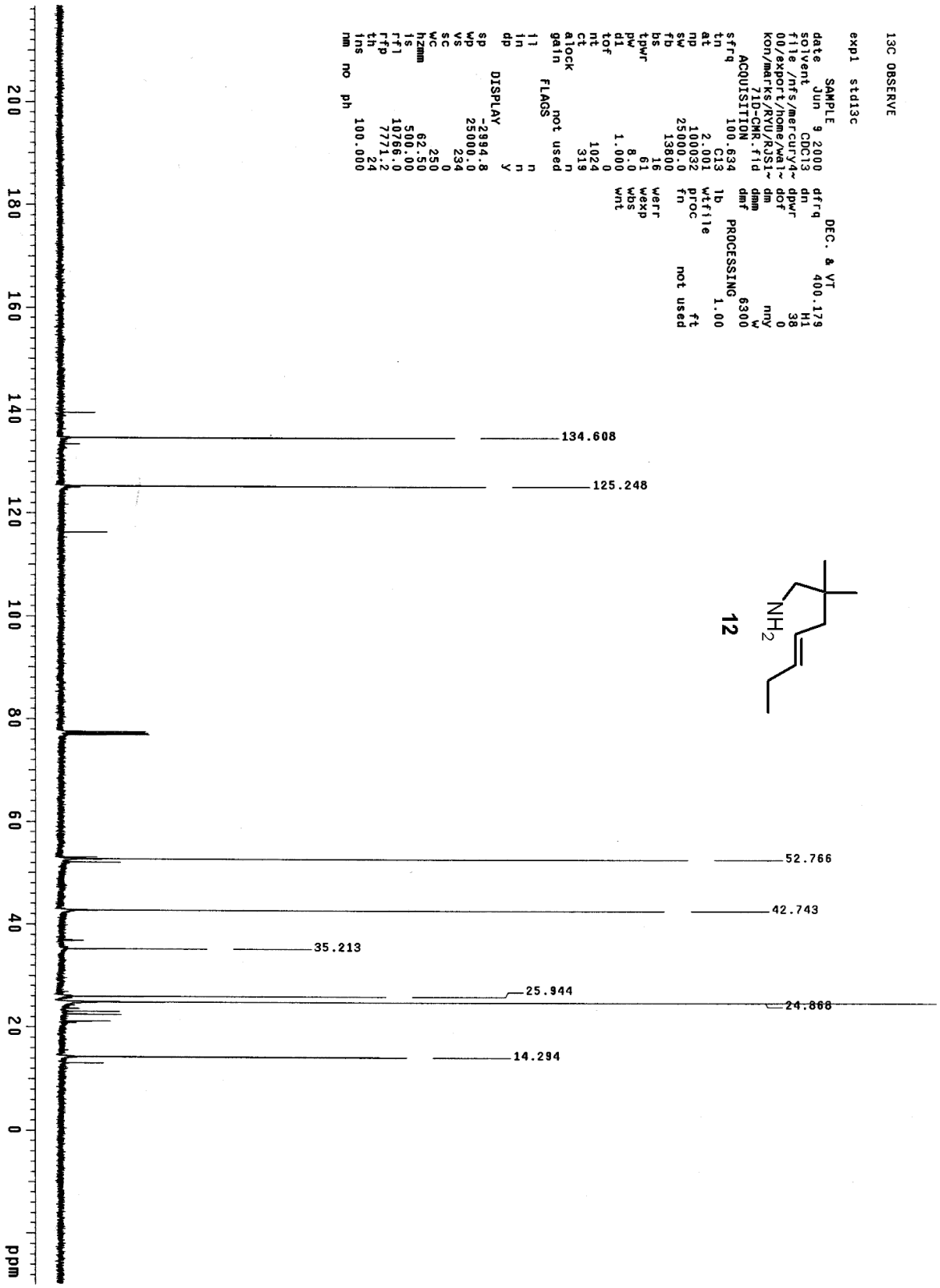
26.37
69.36
32.75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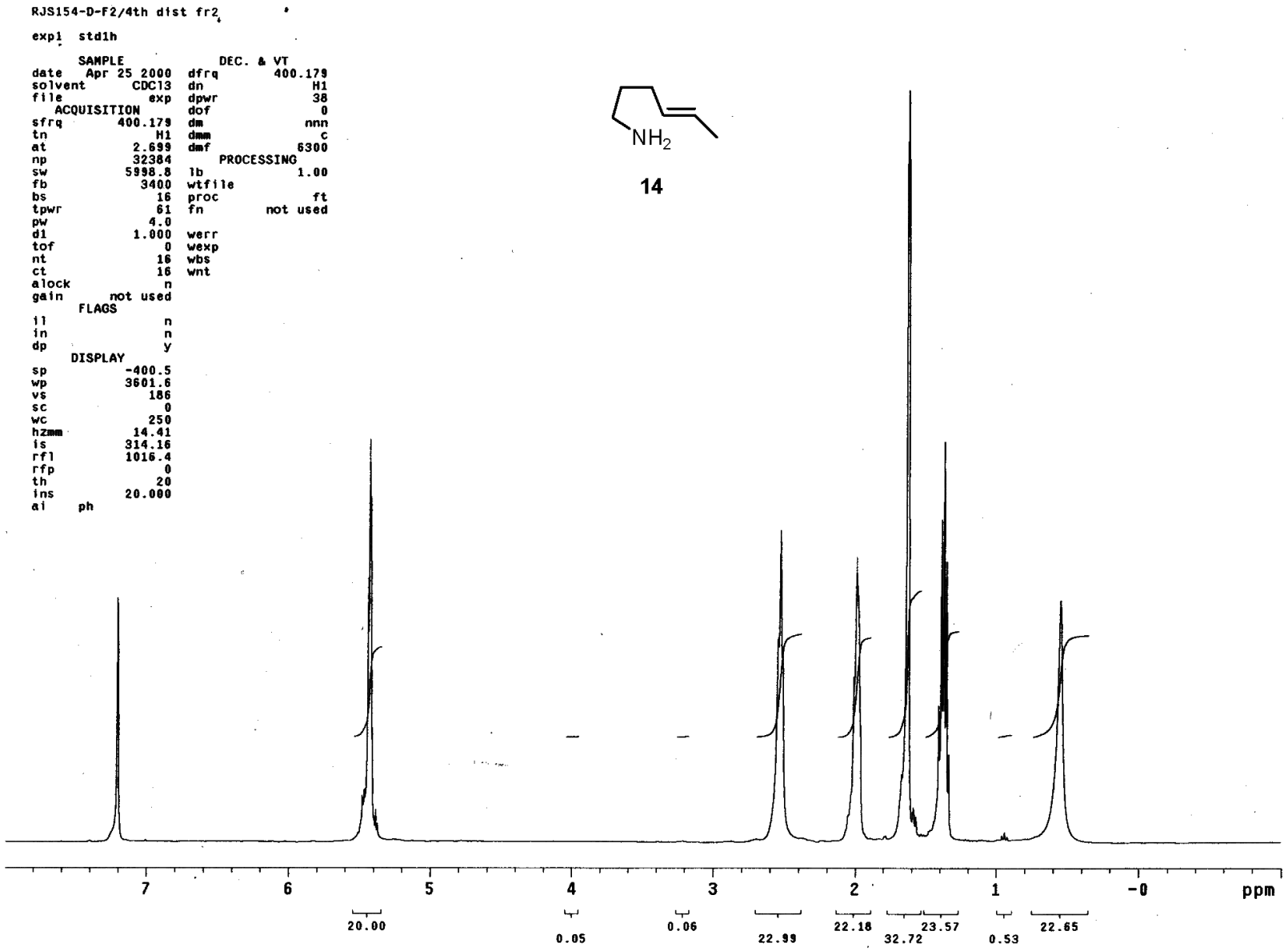
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wnt
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5
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3
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32.72
23.57
0.53
22.65

RJS174D1-F1/NH2-Me2-5-Hepten

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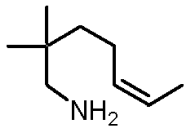

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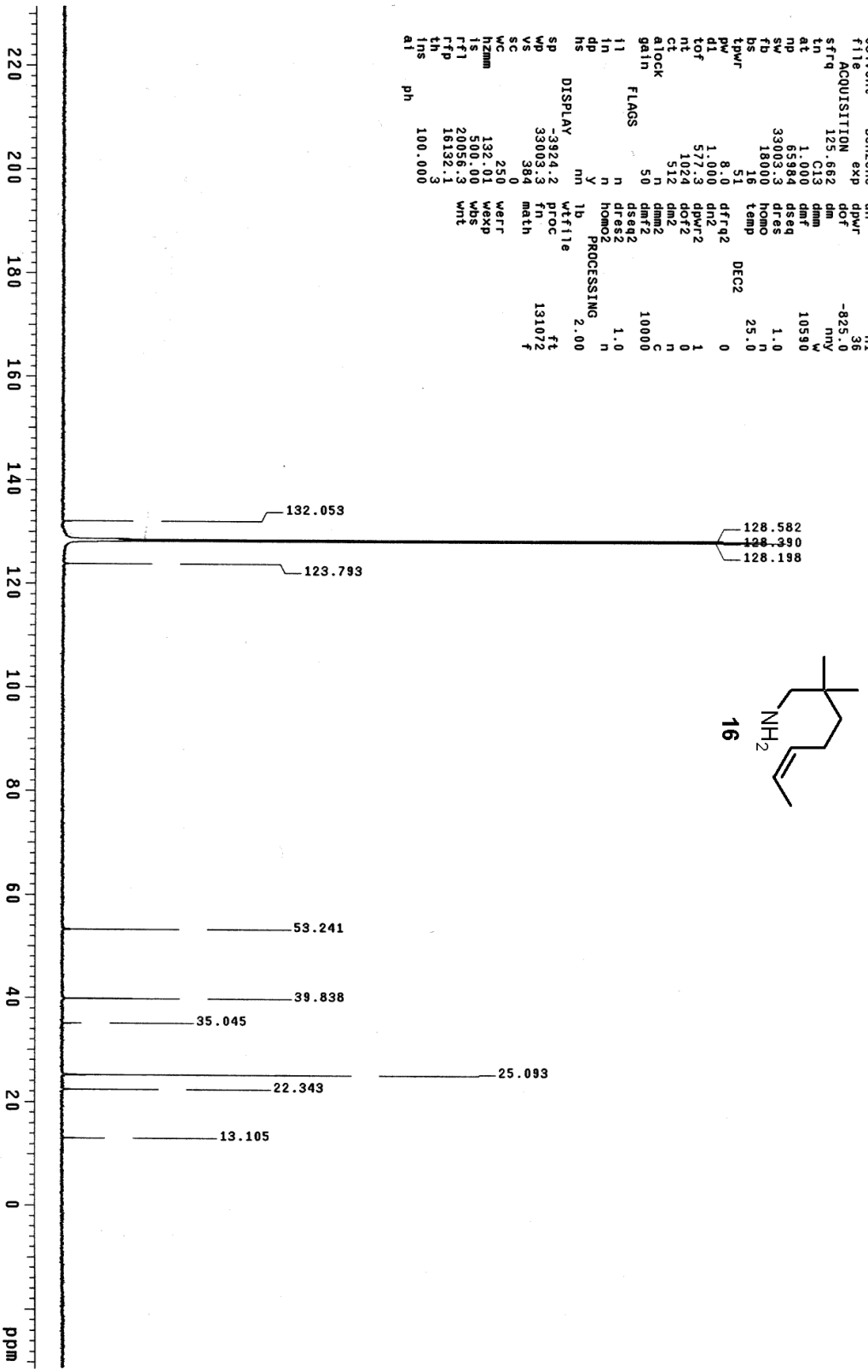
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20
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ppm

RJS150/CH3CH=CH-CH3NH2/aft dist

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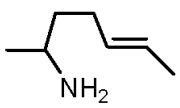

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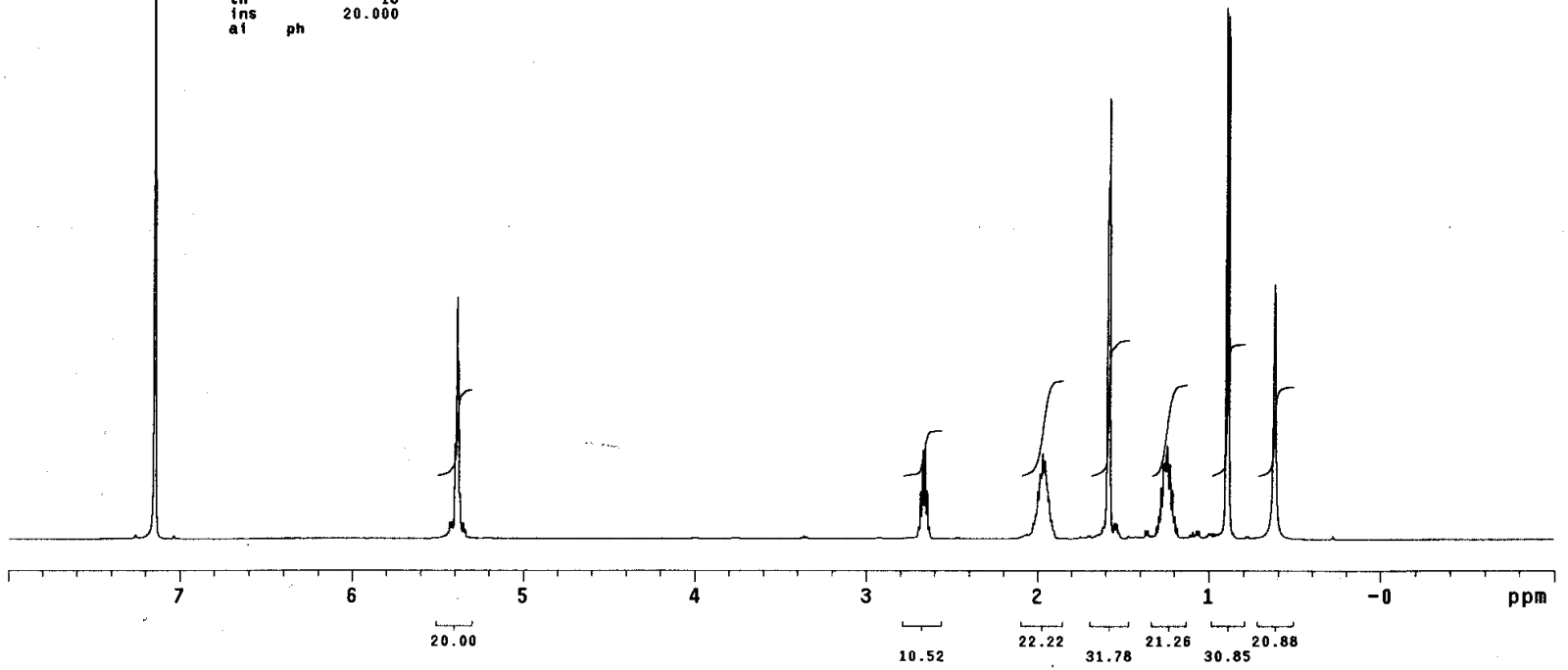

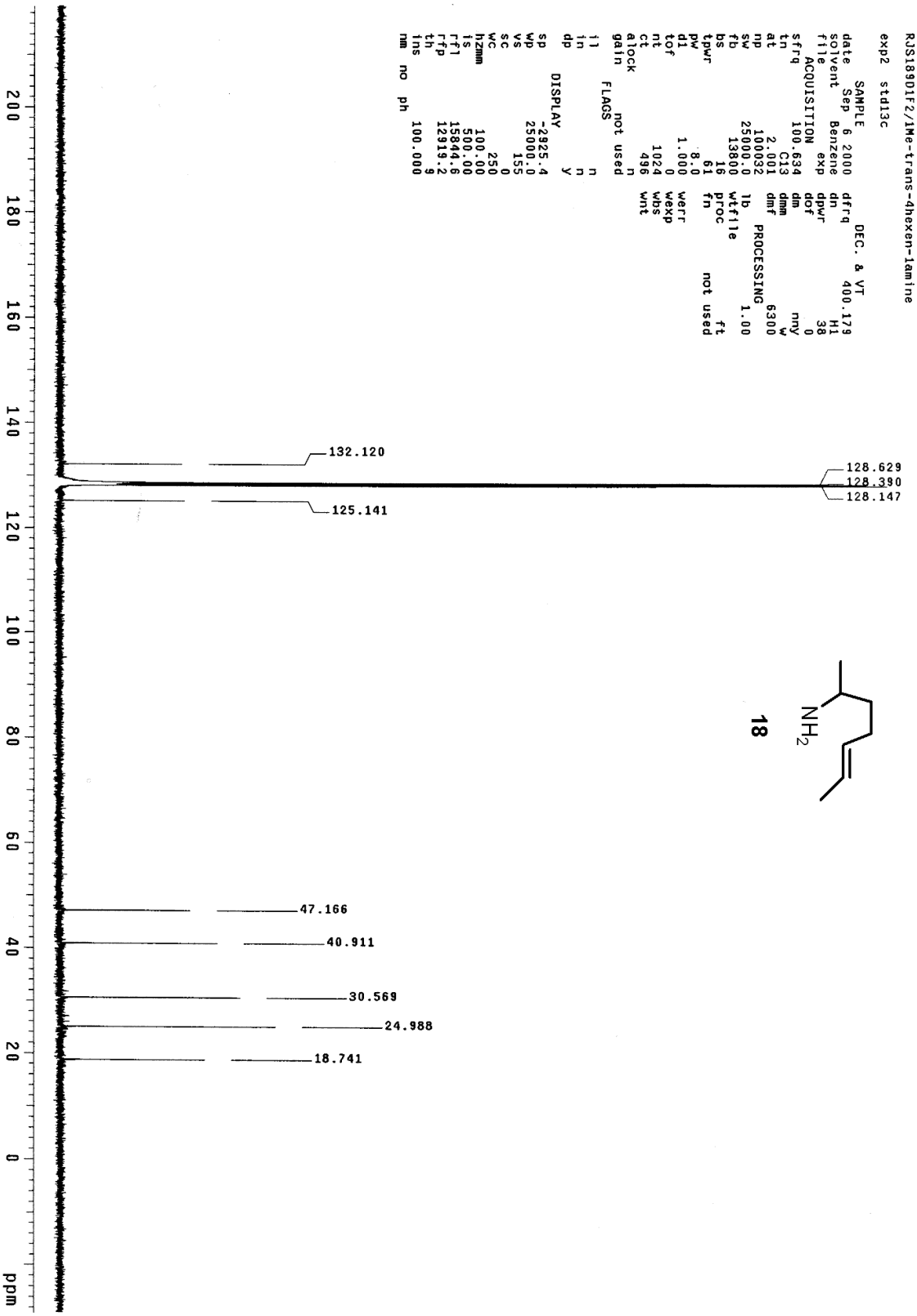
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NH2
18

RJS541C/2,2dimethylamininononadiene

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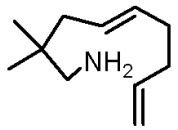

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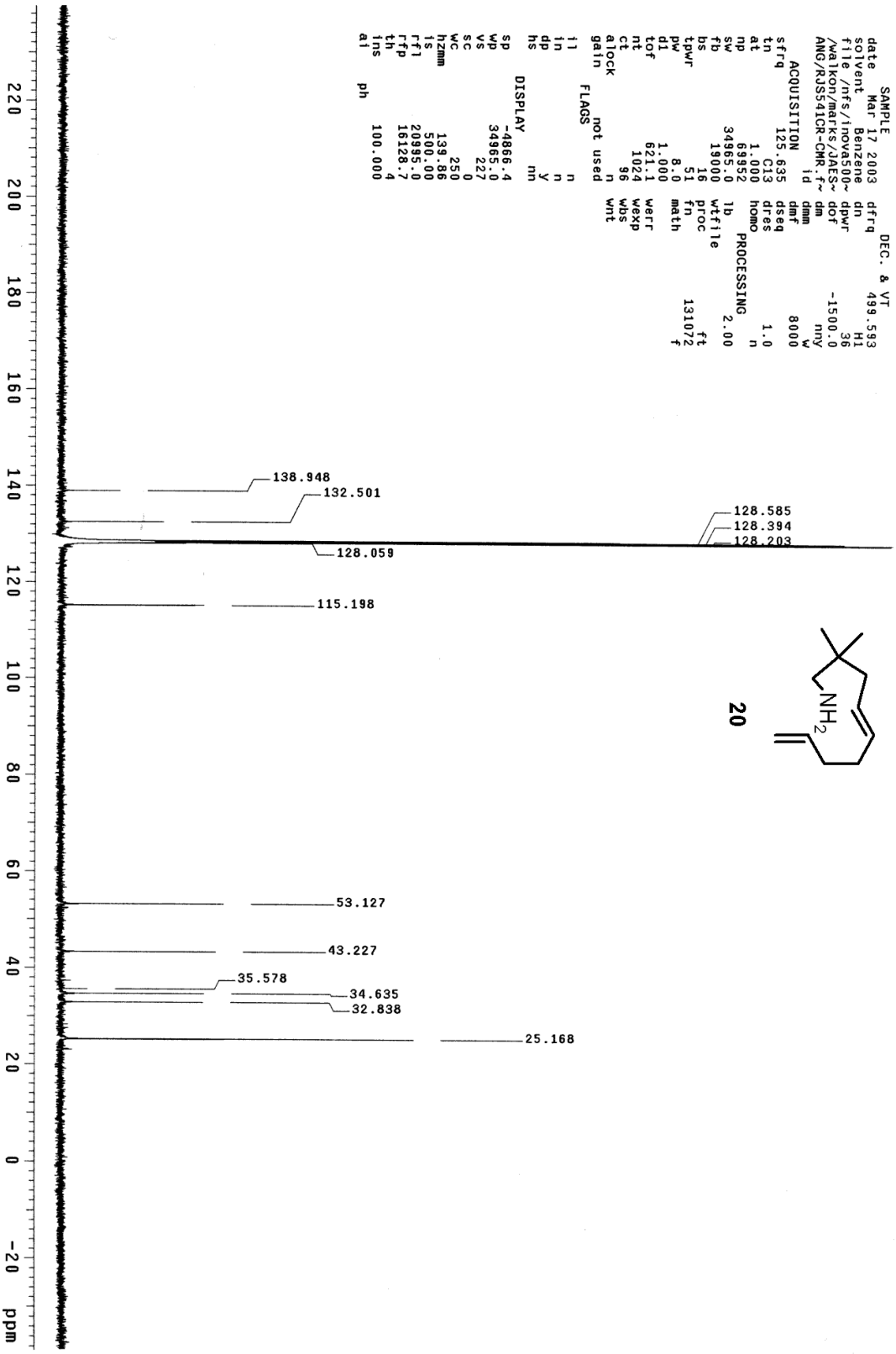
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40
20
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ppm

RJS261-salt/2ethyl4,4dimethylpyrrolidine
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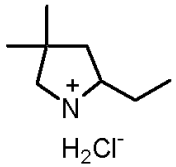
tof	-542.5	DISPLAY	
nt	32	sp	-0.0
ct	32	wp	5996.0
alock	n	vs	228
gain	not used	sc	0
FLAGS		wc	250
il	n	hzmm	23.98
in	n	is	454.07
dp	y	rfl	6673.2
hs	nn	rfp	3632.6
		th	2
		ins	10.000
		ai ph	



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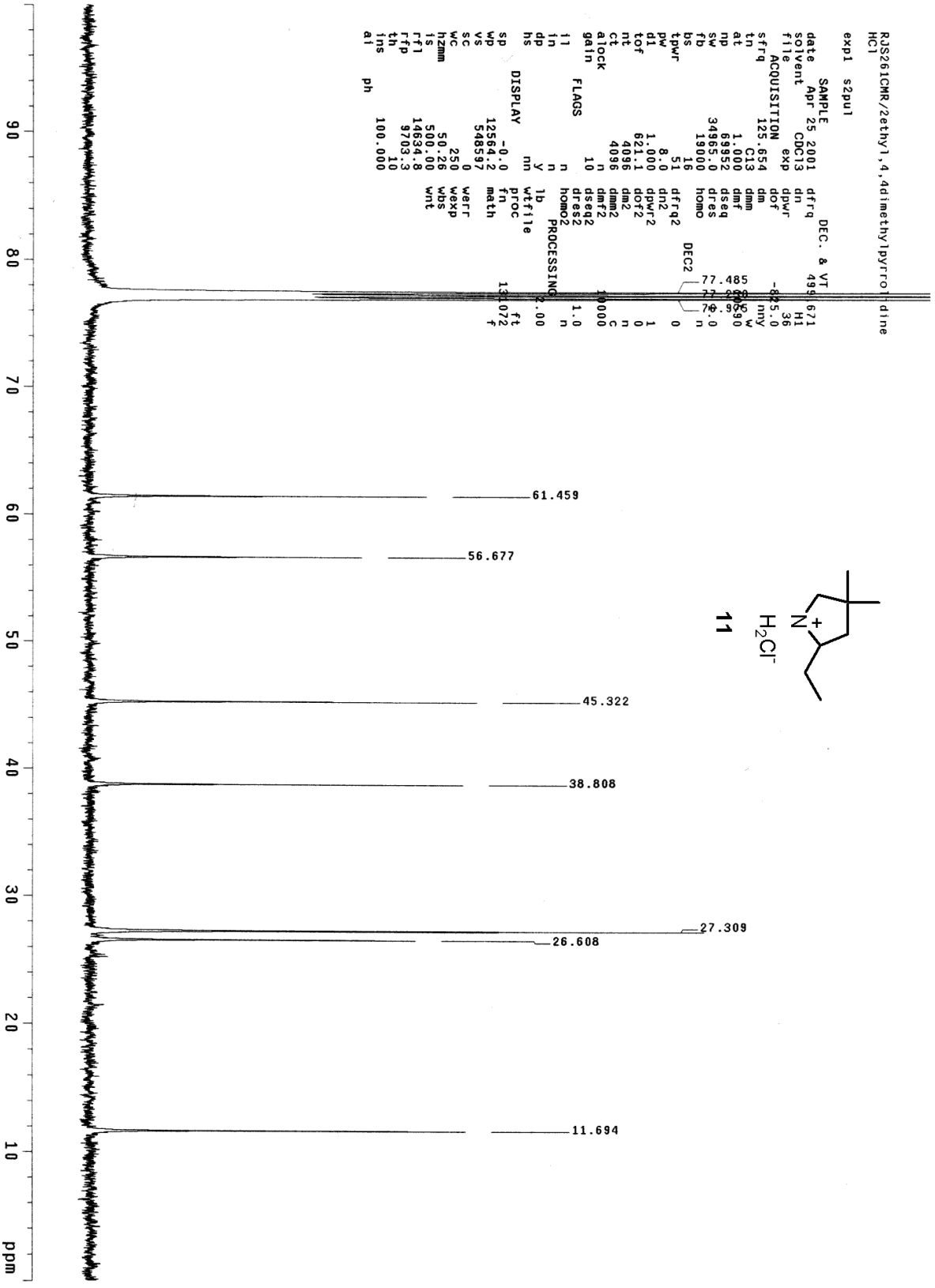
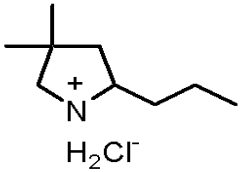

RJS261CMR/2ethyl,4,4dimethylpyrrolidine HCl
61.459
56.677
45.322
38.808
27.309
26.608
11.694
77.485
11
ppm

RJS463/4,4-dimethyl-2-propylpyrrolidineH
Cl salt

exp1 std1h

SAMPLE		DEC. & VT	
date	Jan 9 2003	dfrq	100.631
solvent	CDCl3	dn	C13
file	/nfs/mercury4~	dpwr	44
	00/export/home/wal~	dof	0
	kon/marks/RYU/RJS4~	dm	nnn
	63.fid	dmm	w
ACQUISITION		dmf	5000
sfrq	400.168	PROCESSING	
tn	H1	lb	1.00
at	0.998	wtfile	
np	9984	proc	ft
sw	5000.0	fn	not used
fb	not used		
bs	16	werr	
tpwr	60	wexp	
pw	4.0	wbs	
d1	1.000	wnt	
tof	0		
nt	16		
ct	16		
alock	n		
gain	20		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-400.5		
wp	4801.6		
vs	7708		
sc	0		
wc	187		
hzmm	25.65		
is	2625.93		
rfl	3416.6		
rfp	2909.2		
th	3		
ins	10.000		
ai	ph		



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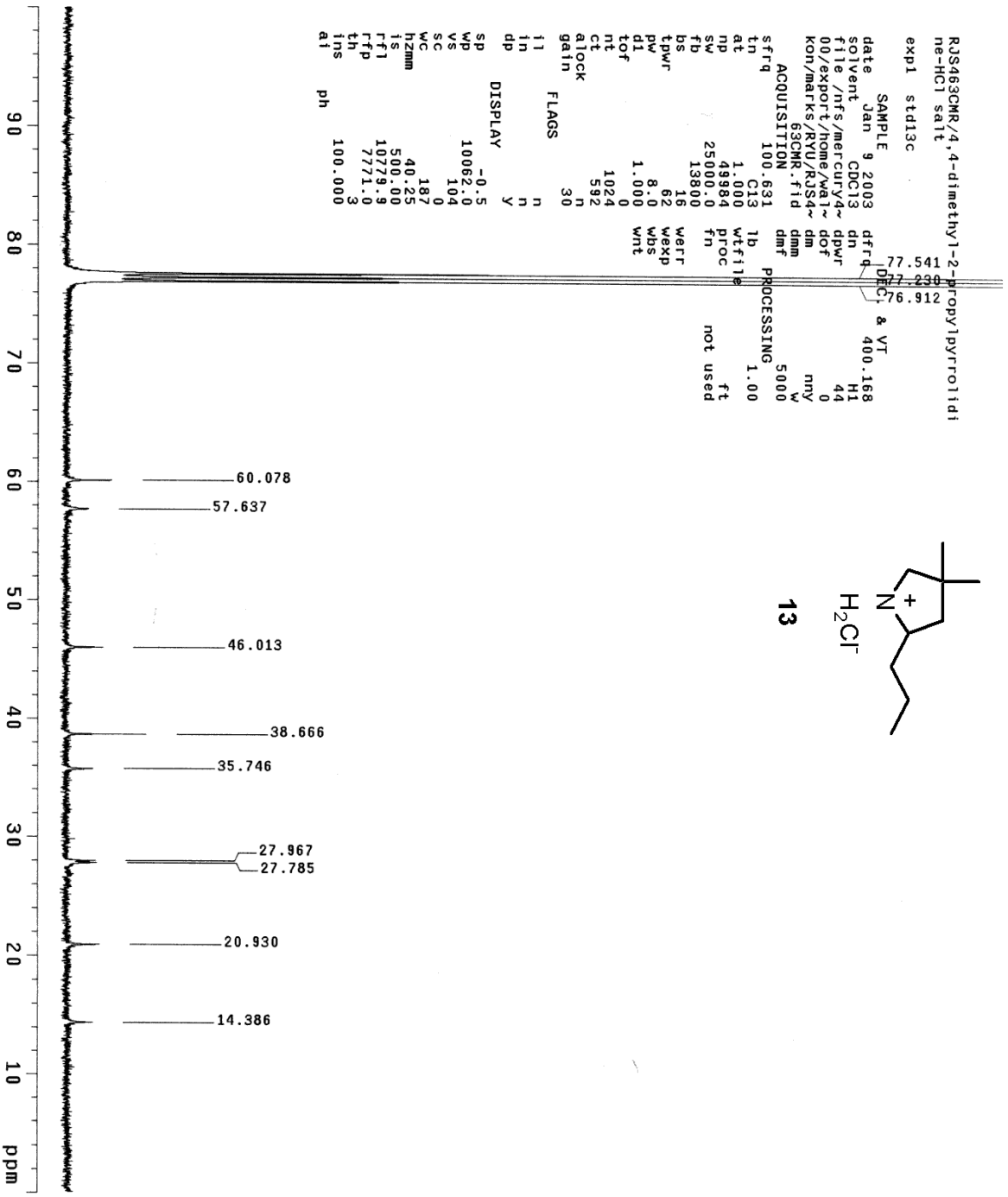
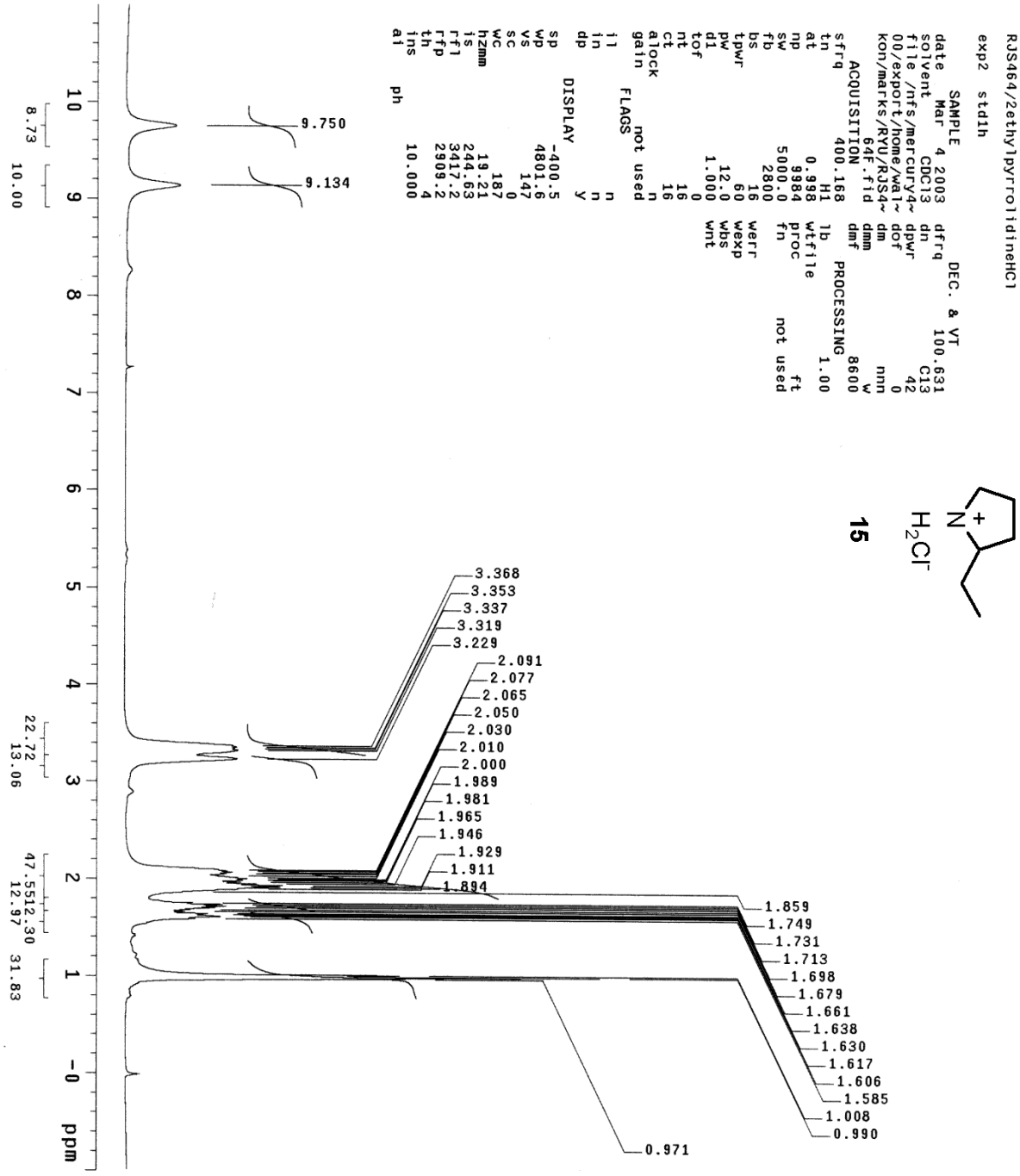

RJS463CMR/4,4-dimethyl-2-propylpyrrolidine-HCl salt
exp1 std13c
SAMPLE
date Jan 9 2003
solvent CDCl3
file /nfs/mercury4~/data/export/home/wal~/RJS4~/63CMR.fid
ACQUISITION
sfrq 100.631
tn C13
at 1.000
np 49984
sw 25000.0
fb 13800
bs 16
tpwr 62
pw 8.0
d1 1.000
tof 0
nt 1024
ct 592
alock n
gain 30
FLAGS
il n
in n
dp y
DISPLAY
sp -0.5
wp 10062.0
vs 104
sc 0
wc 187
hzmm 40.25
is 500.00
rfl 10779.9
rfp 7771.0
th 3
ins 100.000
ai ph
dfrq
dn
dpwr
dof
dm
dmm
dmf
PROCESSING
lb
wtfile
proc
fn
not used
DEC. & VT
400.168
H1
44
0
nny
w
5000
1.00
ft
77.541
77.230
76.912
60.078
57.637
46.013
38.666
35.746
27.967
27.785
20.930
14.386
90
80
70
60
50
40
30
20
10
ppm

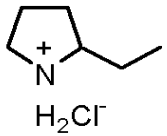
13


RJS464/2ethylpyrrolidineHCl
exp2 std1h
SAMPLE
date Mar 4 2003
solvent CDCl3
file /nfs/mercury4~/dpwr
00/export/home/wal~/dcf
kon/marks/RYU/RJS4~/dm
64F.fid dmm
ACQUISITION dmf
sfrq 400.168 PROCESSING
tn H1 lb
at 0.998 wtfile
np 9984 proc
sw 5000.0 fn
fb 2800
bs 16
tpwr 60
pw 12.0
d1 1.000
tof 0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -400.5
wp 4801.6
vs 147
sc 0
wc 187
hzmm 19.21
is 244.63
rfl 3417.2
rfp 2909.2
th 4
ins 10.000
ai ph
DEC. & VT
dfrq 100.631
dn C13
dpwr 42
dcf 0
dm nnn
dmm w
dmf 8600
lb 1.00
wtfile
proc ft
fn not used
wexp
wbs
wnt
15
9.750
9.134
3.368
3.353
3.337
3.319
3.229
2.091
2.077
2.065
2.050
2.030
2.010
2.000
1.989
1.981
1.965
1.946
1.929
1.911
1.894
1.859
1.749
1.731
1.713
1.698
1.679
1.661
1.638
1.630
1.617
1.606
1.585
1.008
0.990
0.971
8.73
10.00
22.72
13.06
47.55
12.30
12.97
31.83
10
9
8
7
6
5
4
3
2
1
-0
ppm

RJS464CMR/2ethylpyrrolidineHCl

exp2 std13c

SAMPLE		DEC. & VT	
date	Mar 4 2003	dfrq	400.168
solvent	CDCl3	dn	H1
file	/nfs/mercury4~	dpwr	42
	00/export/home/wal~	dof	0
	kon/marks/RYU/RJS4~	dm	nny
	64CMR.fid	dmm	w
ACQUISITION		dmf	8600
sfrq	100.631	PROCESSING	
tn	C13	lb	1.00
at	1.000	wtfile	
np	49984	proc	ft
sw	25000.0	fn	not used
fb	13800		
bs	16	werr	
tpwr	62	wexp	
pw	8.0	wbs	
d1	1.000	wnt	
tof	0		
nt	1024		
ct	96		
alock	n		
gain	30		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-0.5		
wp	15092.9		
vs	58		
sc	0		
wc	187		
hzmm	80.62		
is	500.00		
rfl	10771.5		
rfp	7771.0		
th	3		
ins	100.000		
ai no ph			



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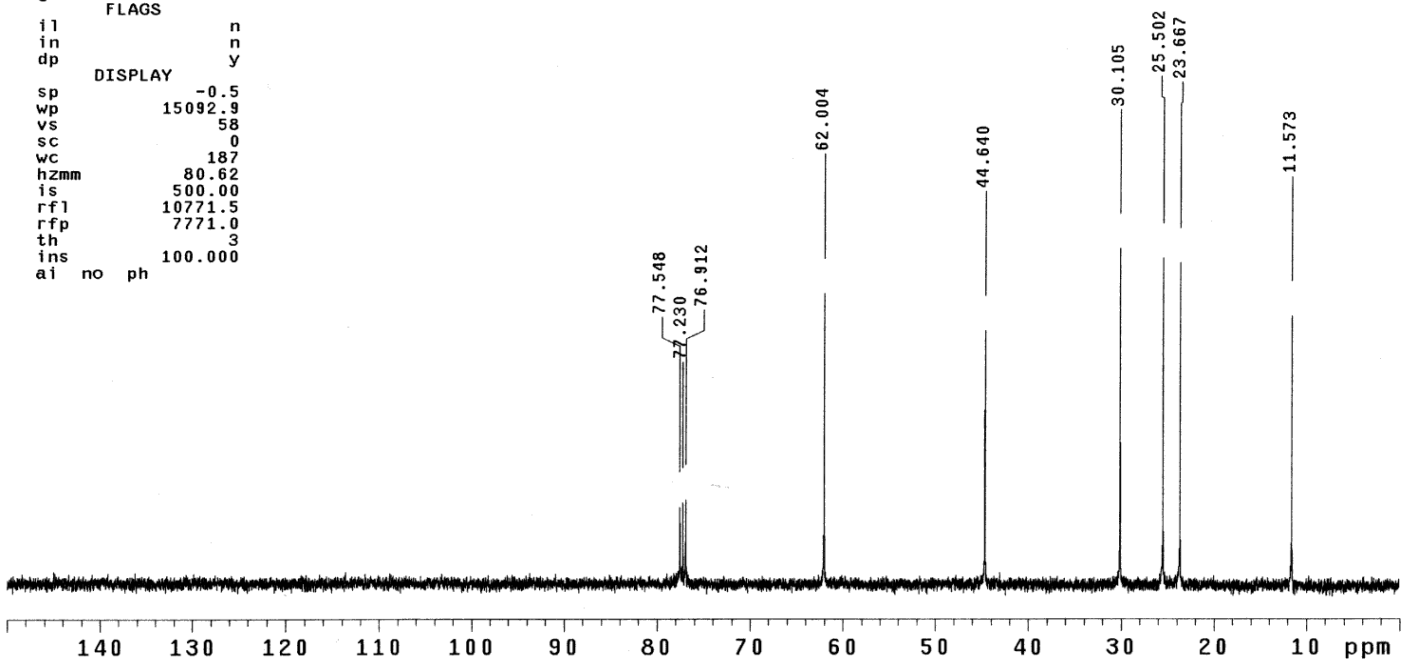
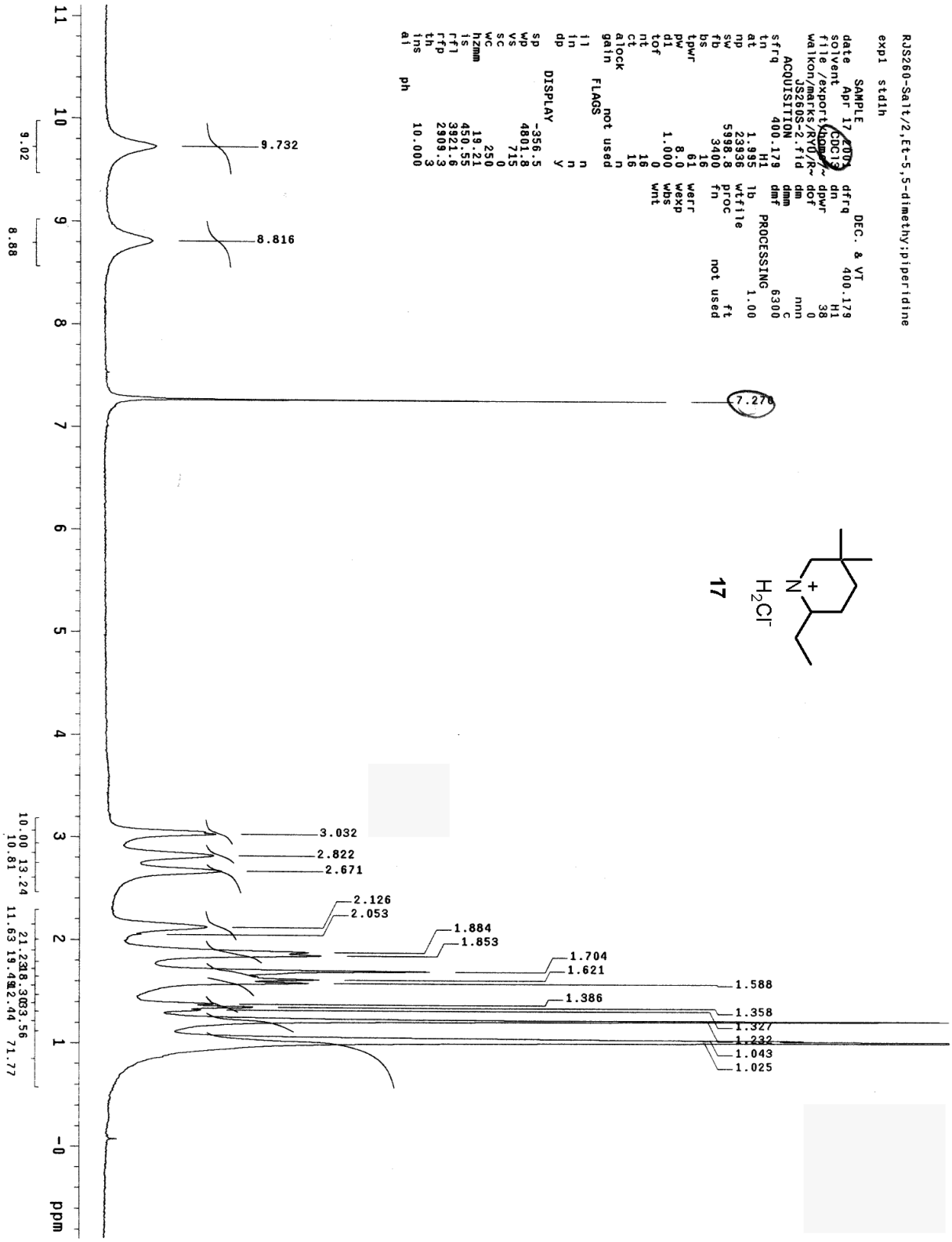
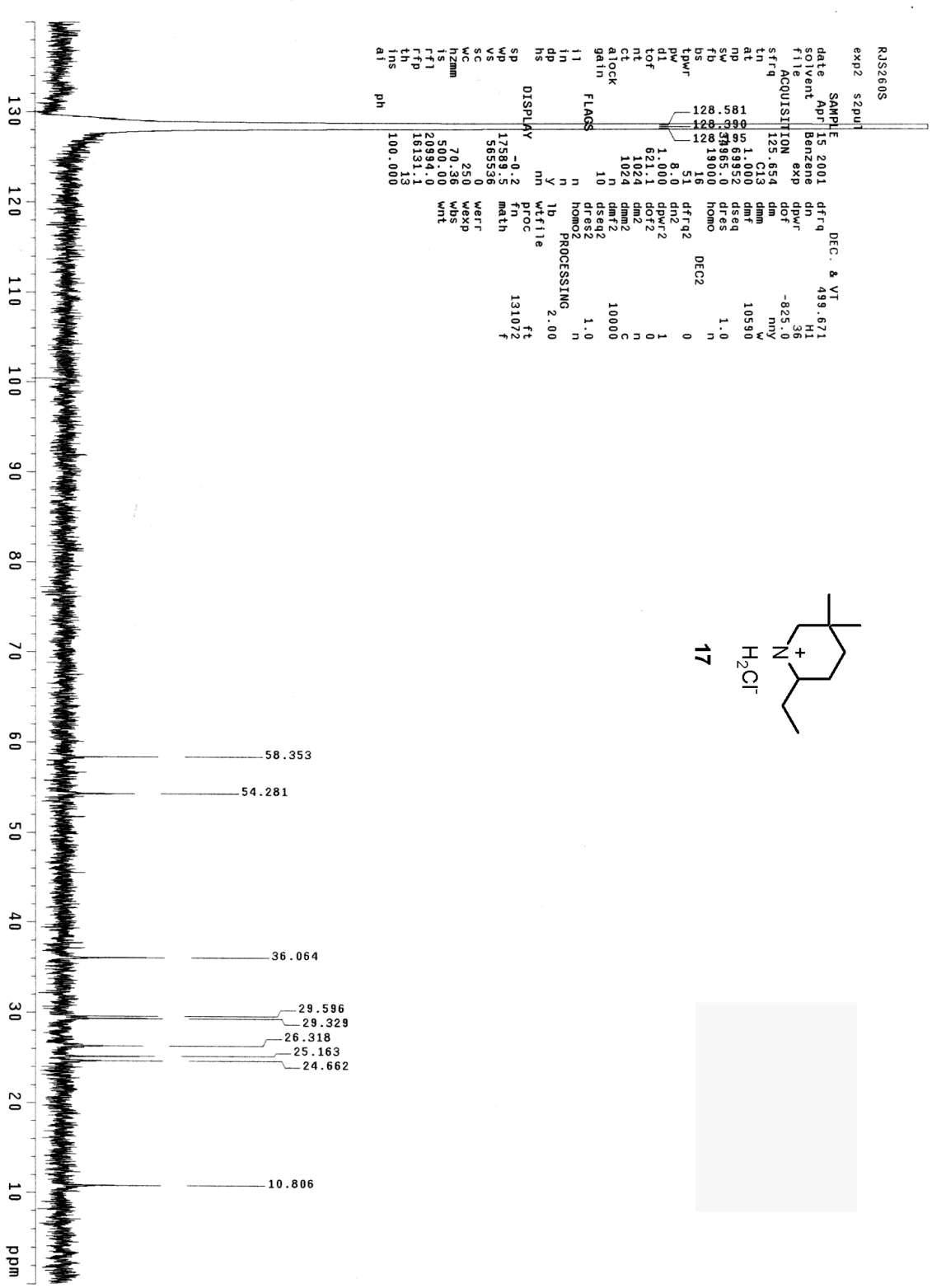
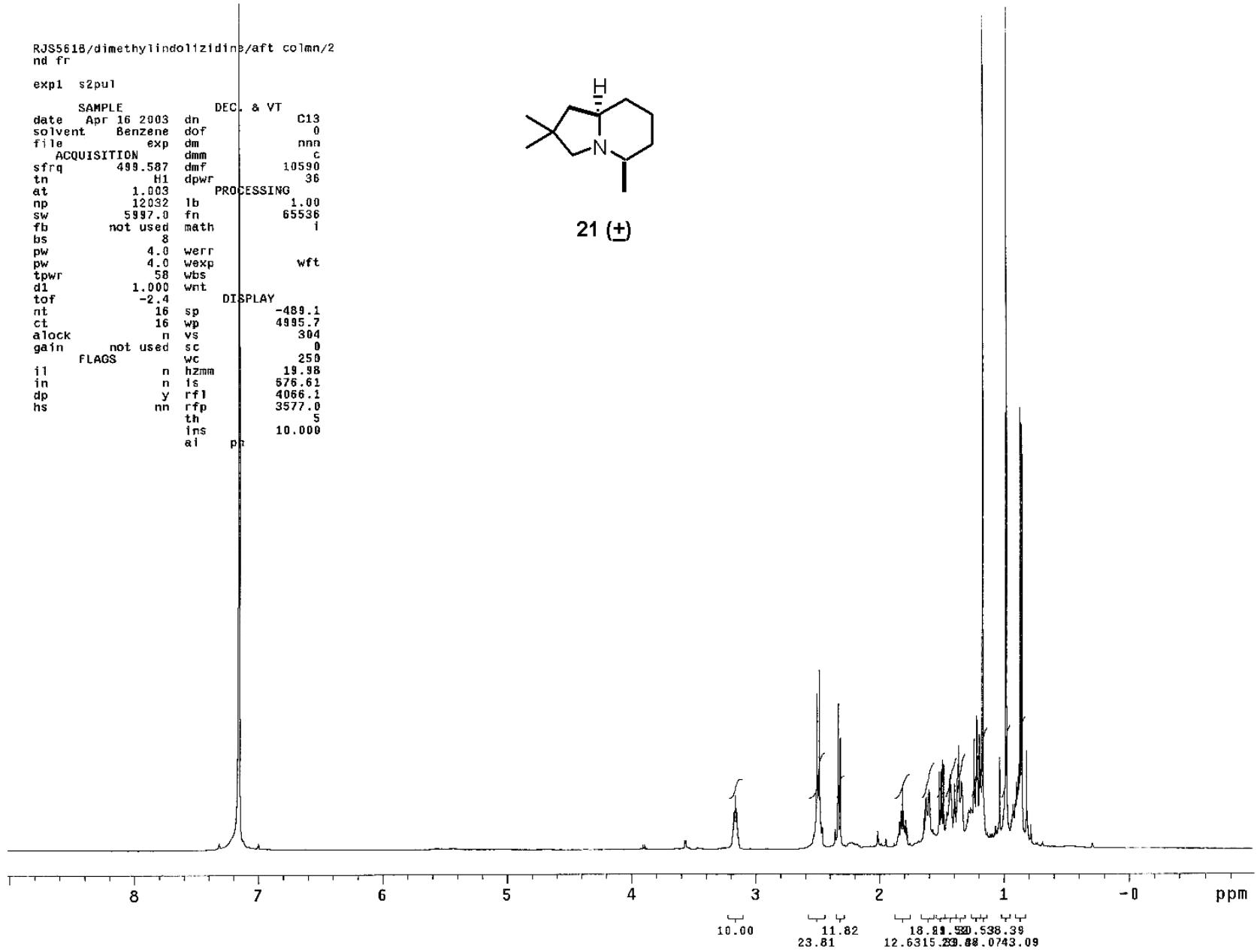


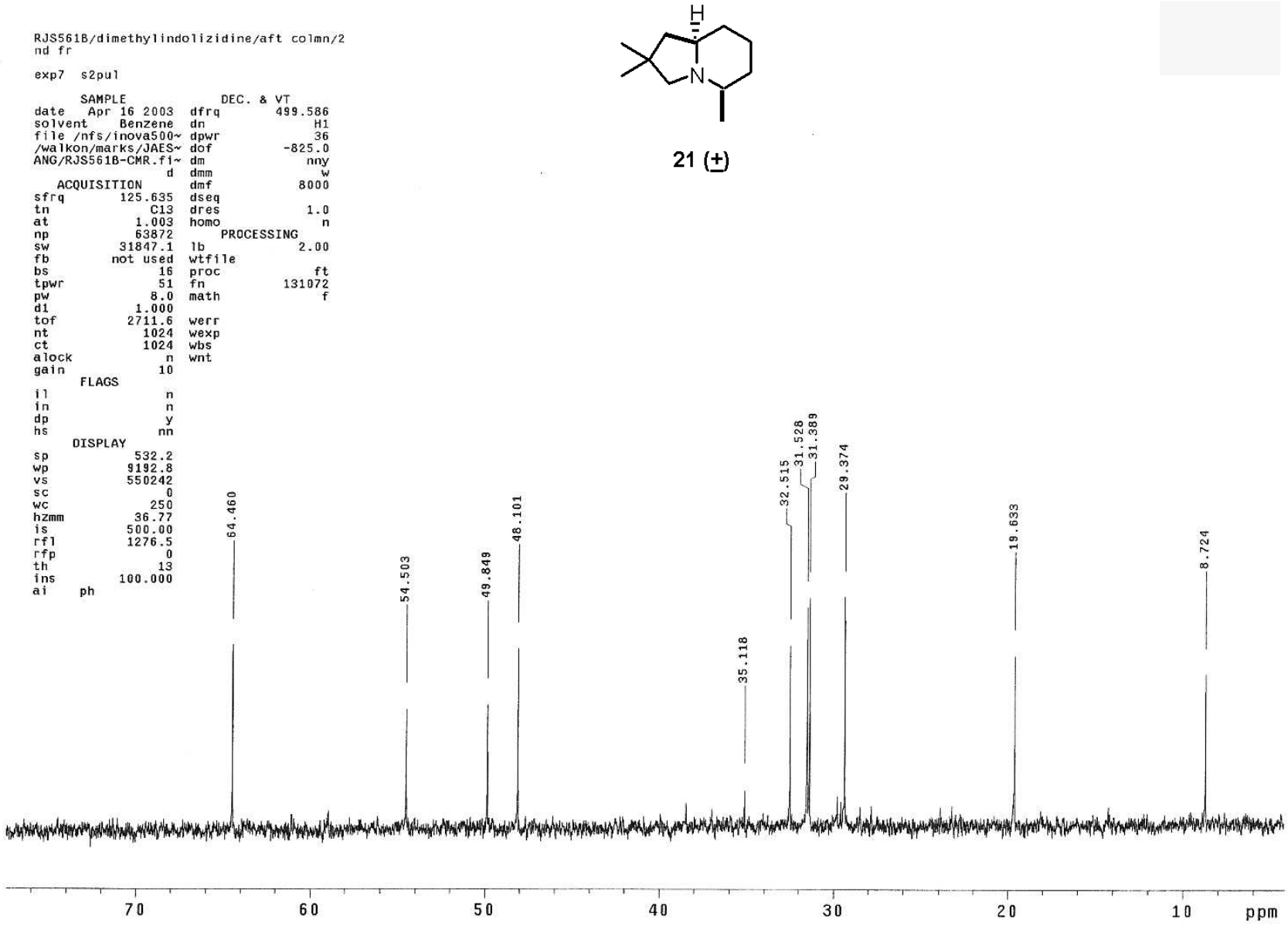

RJS260-Salt/2,Et-5,5-dimethylpiperidine
expl stdlh
SAMPLE
date Apr 17 2007
solvent CDCl3
file /export/home/~
walkon/marks/RYU/R~
JS260S-2.fid
ACQUISITION
sfrq 400.179 dmf 6300
tn H1 PROCESSING c
at 1.995 lb 1.00
np 23936 wtfile
sw 5998.8 proc not used
fb 3400 fn ft
bs 16
tpwr 61 werr
pw 8.0 wexp
d1 1.000 wbs
tof 0 wnt
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -356.5
wp 4801.8
vs 715
sc 0
wc 250
hzmm 19.21
is 450.55
rfl 3921.6
rfp 2909.3
th 3
ins 10.000
ai ph
DEC. & VT
dfrq 400.179
dn H1
dpwr 38
dof 0
dm nnn
dmm c
ft
not used
9.732
8.816
7.276
3.032
2.822
2.671
2.126
2.053
1.884
1.853
1.704
1.621
1.588
1.386
1.358
1.327
1.232
1.043
1.025
9.02
8.88
10.00 13.24
10.81
11.63 19.49 12.44 71.77
21.23 8.30 3.56
H2Cl
17
11 10 9 8 7 6 5 4 3 2 1 -0 ppm


RJS260S
exp2 s2pul
SAMPLE
date Apr 15 2001
solvent Benzene
file
ACQUISITION
sfrq 125.654
tn C13
at 1.000
np 69952
sw 19000
fb 16
bs 51
tpwr 56
pw 8.0
d1 1.000
tof 621.1
nt 1024
ct 1024
alock n
gain 10
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -0.2
wp 17589.5
vs 565536
sc 0
wc 250
hzmm 70.36
is 500.00
rfl 20994.0
rfp 16131.1
th 13
ins 100.000
ph
DEC. & VT
dfrq 499.671
dn H1
dpwr 36
dof -825.0
dm nny
dmm w
dmf 10590
dseq
dres 1.0
homo n
DEC2
dfrq2
dn2
dpwr2
dof2
dm2
dmf2 10000
dseq2 c
dres2 1.0
homo2 n
PROCESSING
lb 2.00
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
128.581
128.390
128.199
58.353
54.281
36.064
29.596
29.329
26.318
25.163
24.662
10.806
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

N
+
H2Cl⁻

17


RJS5618/dimethylindolizidine/aft colmn/2
nd fr
exp1 s2pul
SAMPLE
date Apr 16 2003
solvent Benzene
file exp
ACQUISITION
sfrq 499.587
tn H1
at 1.003
np 12032
sw 5997.0
fb not used
bs 8
pw 4.0
pw 4.0
tpwr 58
d1 1.000
tof -2.4
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DEC. & VT
dn C13
dof 0
dm nnn
dmm c
dmf 10590
dpwr 36
PROCESSING
lb 1.00
fn 65536
math i
werr
wexp wft
wbs
wnt
DISPLAY
sp -489.1
wp 4995.7
vs 304
sc 0
wc 250
hzmm 19.98
is 576.61
rfl 4066.1
rfp 3577.0
th 5
ins 10.000
ai pa
21 (±)
8
7
6
5
4
3
2
1
-0
ppm
10.00
11.82
23.81
18.81
20.53
8.39
12.63
15.29
8.07
43.09


RJS561B/dimethylindolizidine/aft colmn/2
nd fr
exp7 s2pul
SAMPLE
date Apr 16 2003
solvent Benzene
file /nfs/inova500~
/walkon/marks/JAES~
ANG/RJS561B-CMR.fi~
d
ACQUISITION
sfrq 125.635
tn C13
at 1.003
np 63872
sw 31847.1
fb not used
bs 16
tpwr 51
pw 8.0
d1 1.000
tof 2711.6
nt 1024
ct 1024
alock n
gain 10
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp 532.2
wp 9192.8
vs 550242
sc 0
wc 250
hzmm 36.77
is 500.00
rfl 1276.5
rfp 0
th 13
ins 100.000
ai ph
DEC. & VT
dfrq 499.586
dn H1
dpwr 36
dof -825.0
dm nny
dmm w
dmf 8000
dseq
dres 1.0
homo n
PROCESSING
lb 2.00
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
H
N
21 (±)
64.460
54.503
49.849
48.101
35.118
32.515
31.528
31.389
29.374
19.633
8.724
70
60
50
40
30
20
10
ppm