Hetero [4+2] Cycloadditions of (Trialkylsilyl)vinylketenes. Synthesis of α,β-Unsaturated δ-Valerolactones and –Lactams

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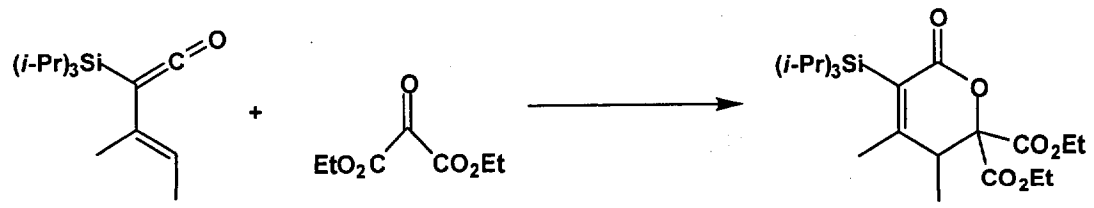
Supporting Information

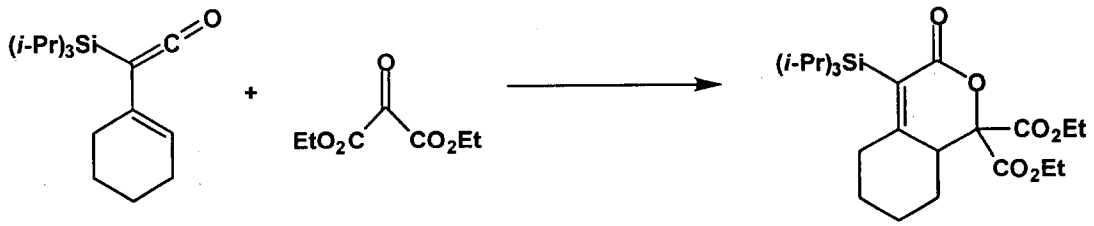
General Procedures. All reactions were performed in flame-dried glassware under a positive pressure of nitrogen or argon with magnetic stirring (except for reactions carried out in sealed tubes). Sensitive liquids and solutions were transferred via syringe or cannula and were introduced into reaction vessels through rubber septa. Reaction product solutions were concentrated using a Büchi rotary evaporator at ca. 20 mmHg. Column chromatography was performed on EM Science silica gel 60 (35-75 μm).

Materials. Commercial grade reagents and solvents were used without further purification except as indicated below. Acetonitrile and dichloromethane were distilled from calcium hydride. Ketenes **1**, **2**, and **3**, and cyclobutenone **5** were prepared as described by us previously.[1] *N*-(Trimethylsilyl)benzaldimine (**11**) was prepared using the procedure of Hart.[2] *N*-(Trimethylsilyl)cinnamaldimine (**12**) was prepared as described by Colvin.[3] *N*-(Trimethylsilyl)benzophenone imine (**13**) was prepared according to the procedure of Rochow.[4] *N*-(Trimethylsilyl)pivaldimine (**14**) was prepared as described previously.[2] *N*-Methyl benzaldimine (**24**) was synthesized using the literature procedure.[5] (Triisopropylsilyl)ketene (**27**) was synthesized as described previously.[6]

Instrumentation. ^{1}H NMR spectra were recorded on Varian XL-300 (300 MHz), Varian Unity 300 (300 MHz), Varian Mercury 300 (300 MHz), and Varian Inova 500 (500 MHz) spectrometers using $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on Varian Unity 300 (75 MHz) and Varian Inova 500 (125 MHz) spectrometers using $CDCl_3$ as solvent. ^{1}H NMR chemical shifts and ^{13}C NMR shifts are expressed in parts per million (δ) relative to $CDCl_3$. Infrared spectra were obtained on a Perkin-Elmer 1320 grating spectrophotometer.



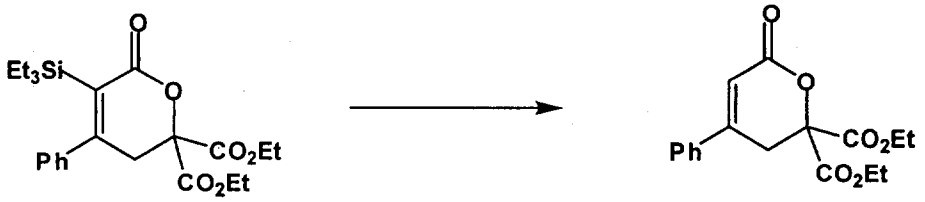
3,4-Dimethyl-6-oxo-5-(triisopropylsilyl)-3,6-dihydropyran-2,2-dicarboxylic acid diethyl ester (7). A 10-mL, two-necked, pear-shaped flask equipped with a glass stopper and a reflux condenser fitted with a rubber septum and an argon inlet needle was charged with ketene **1** (0.121 g, 0.479 mmol), diethyl ketomalonate (0.110 mL, 0.719 mmol), and 0.4 mL of acetonitrile. The reaction mixture was heated at reflux for 15 min and then cooled and concentrated at reduced pressure to give 0.280 g of a yellow liquid. Column chromatography on 14 g of silica gel (elution with 5% EtOAc-hexane) provided 0.191 g (94%) of lactone **7** as a white solid, mp 69-70 °C: IR (CH_2Cl_2): 2930, 2860, and 1715 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.21-4.36 (m, 3H), 4.04-4.36 (m, 1H), 3.21 (q, J = 7.2 Hz, 1H), 2.12 (s, 3H), 1.47 (sept, J = 7.5 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.13 (d, J = 7.0 Hz, 3H), 1.05 (d, J = 7.5 Hz, 9H), and 1.04 (d, J = 7.5 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 166.6, 164.4, 163.7, 122.0, 85.0, 62.7, 62.5, 41.5, 23.3, 19.0, 14.0, 13.7, 12.9, and 12.4. Anal. Calcd for $C_{22}H_{38}O_6Si$: C, 61.93; H, 8.98. Found: C, 62.12; H, 9.05.



3-Oxo-3,5,6,7,8,8a-hexahydro-isochromene-1,1-dicarboxylic acid diethyl ester (8). A flame-dried, threaded Pyrex tube (13 mm O.D., 10 mm I.D.) was charged with ketene **3** (0.208 g, 0.679 mmol), diethyl ketomalonate (0.155 mL, 1.02 mmol), and 0.7 mL of acetonitrile. The tube was tightly sealed with a teflon cap and the reaction mixture was heated at reflux for 2 h and then cooled and concentrated at reduced pressure to give 0.461 g of an yellow-orange oil. Column chromatography on 10 g of silica gel (elution with 5% EtOAc-hexane) provided 0.250 g (77%) of lactone **8** as a white solid, mp 79-80 °C: IR ($CDCl_3$) 2930, 2850, 1740 and 1710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.24-4.38 (m, 3H), 4.05-4.14 (m, 1H), 3.26 (dd, J = 12.0, 3.3 Hz, 1H), 2.74-2.78 (m, 1H), 2.35 (dt, J = 12.3, 4.6 Hz, 1H), 2.08-2.12 (m, 1H), 1.82-1.91 (m, 2H), 1.54-1.67 (m, 3H), 1.46 (sept, J = 7.3 Hz, 3H), 1.32 (t, J =

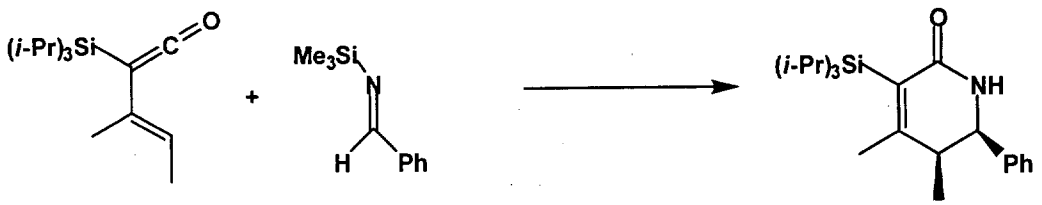
7.3 Hz, 3H), 1.25 (t, J = 7.3 Hz, 3H), and 1.05 (d, J = 7.3 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$): 174.1, 167.9, 165.7, 164.6, 122.0, 85.0, 63.9, 63.4, 46.8, 37.4, 31.0, 30.5, 26.2, 19.8, 14.8, 14.5, and 13.0.

6-Oxo-4-phenyl-5-(triethylsilyl)-3,6-dihydropyran-2,2-dicarboxylic acid diethyl ester (9). A flame-dried, threaded Pyrex tube (13 mm O.D., 10 mm I.D.) was charged with cyclobutenone **5** (0.115 g, 0.445 mmol), diethyl ketomalonate (0.10 mL, 0.67 mmol), and 0.4 mL of acetonitrile. The tube was tightly sealed with a teflon cap and the reaction mixture was heated at reflux for 15 h and then cooled and concentrated at reduced pressure to afford 0.250 g of a yellow oil. Column chromatography on 12 g of silica gel (elution with 10% EtOAc-hexane) provided 0.176 g (92%) of the lactone **9** as a white solid, mp 63 °C: IR (film) 2960, 2880, 1735, and 1575 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.33 (m, 3H), 7.18-7.21 (m, 2H), 4.27-4.37 (m, 4H), 3.21 (s, 2H), 1.26 (t, J = 7.3 Hz, 6H), 0.71 (t, J = 7.9 Hz, 9H), and 0.34 (q, J = 7.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 164.6, 163.4, 139.9, 129.9, 129.5, 128.2, 127.7, 82.8, 63.1, 38.1, 13.9, 7.4 and 4.2. Anal. Calcd for $C_{23}H_{32}O_6Si$: C, 63.86; H, 7.46. Found: C, 63.78; H, 7.31.



6-Oxo-4-phenyl-3,6-dihydropyran-2,2-dicarboxylic acid diethyl ester (10). A flame-dried, threaded Pyrex tube (13 mm O.D., 10 mm I.D.) was charged with a solution of silyl lactone **9** (0.065 g, 0.151 mmol) in 0.75 mL of CH_2Cl_2 and methanesulfonic acid (0.049 mL, 0.756 mmol) was then added rapidly dropwise. The tube was tightly sealed with a teflon cap and heated at reflux for 15 h. The reaction mixture was cooled, diluted with 10 mL of CH_2Cl_2, and washed with 10 mL of saturated $NaHCO_3$ solution, 10 mL of water, 10 mL of 10% aqueous HCl solution, and 10 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to afford 0.060 g of a brown oil. Column chromatography on 14 g of silica gel (elution with 20-50% EtOAc-hexane) provided 0.048 g (100%) of

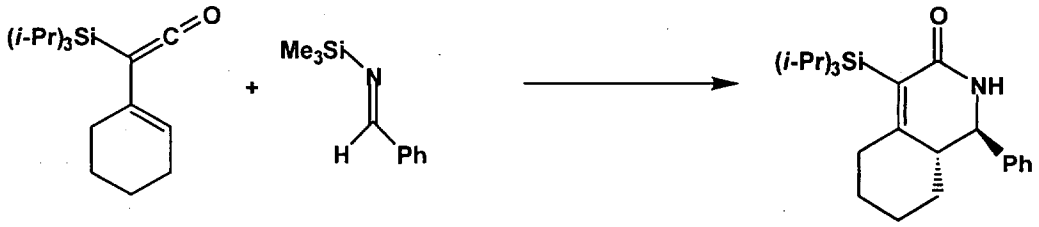
the lactone **10** as a white solid, mp 68.5 °C: IR (film) 2950, 2900, 1705, 1435, and 1360 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45-7.55 (m, 5H), 6.33 (s, 1H), 4.31 (q, J = 7.1 Hz, 4H), 3.48 (s, 2H), and 1.29 (t, J = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 165.9, 161.9, 152.3, 135.2, 131.0, 129.0, 126.1, 114.4, 82.9, 63.2, 31.1, and 13.8. Anal. Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.25; H, 5.88.



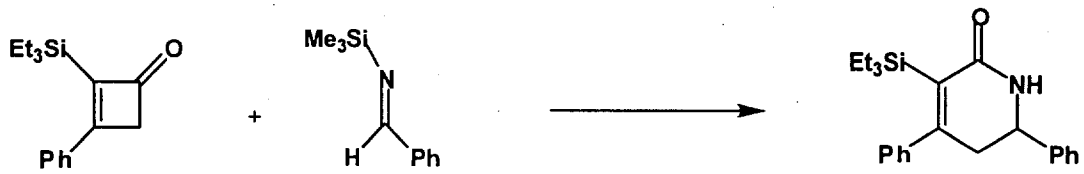
***cis*-4,5-Dimethyl-6-phenyl-3-(triisopropylsilyl)-5,6-dihydro-1*H*-pyridin-2-one (15).** A 10-mL, two-necked, pear-shaped flask equipped with a glass stopper and reflux condenser fitted with a rubber septum and argon inlet needle was charged with ketene **1** (0.134 g, 0.531 mmol), imine **11** (0.147 g, 0.829 mmol), and 0.5 mL of acetonitrile. The tube was tightly sealed with a teflon cap and the reaction mixture was heated at reflux for 1.5 h and then cooled and concentrated at reduced pressure to afford 0.272 g of a yellow oil. Column chromatography on 27 g of silica gel (elution with 5% EtOAc-hexane) provided 0.151 g (79%) of lactam **15** as a white solid, mp 197-199 °C: IR ($CDCl_3$) 3400, 2930, 2850, and 1625 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28-7.42 (m, 5H), 5.51 (br s, 1H), 4.77 (d, J = 3.6 Hz, 1H), 2.16-2.23 (m, 1H), 2.10 (s, 3H), 1.53 (sept, J = 7.3 Hz, 3H), 1.12 (d, J = 5.7 Hz, 9H), 1.10 (d, J = 5.7 Hz, 9H), and 0.82 (d, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 165.9, 138.4, 128.5, 127.6, 126.6, 126.4, 58.1, 45.0, 23.0, 19.3, 13.0, and 11.0. Anal. Calcd for $C_{22}H_{35}NOSi$: C, 73.89; H, 9.86; N, 3.92. Found: C, 73.80; H, 9.88; N, 3.84.

***cis*-4,5-Dimethyl-6-phenyl-3-(triethylsilyl)- 5,6-dihydro-1*H*-pyridin-2-one (16).** A 5-mL, pear-shaped flask equipped with a reflux condenser fitted with a rubber septum and argon inlet needle was charged with ketene **2** (0.160 g, 0.761 mmol) and imine **11** (0.202 g, 1.14 mmol). The reaction mixture was stirred at room temperature for 2 h, and the resulting yellow oil was purified by column chromatography on 10 g of silica gel (elution with 0-10% EtOAc-hexane) to provide 0.182 g

(76%) of lactam **16** as a white solid, mp 155 °C: IR (CH_2Cl_2) 2930, 2850, and 1630 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28-7.41 (m, 5H), 5.56 (br s, 1H), 4.79 (d, J = 4.0 Hz, 1H), 2.20-2.23 (m, 1H), 2.08 (s, 3H), 0.97 (t, J = 7.8 Hz, 9H), and 0.78-0.90 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 167.5, 139.4, 129.3, 128.5, 127.3, 127.1, 58.9, 44.9, 22.8, 11.7, 8.5, and 5.8.

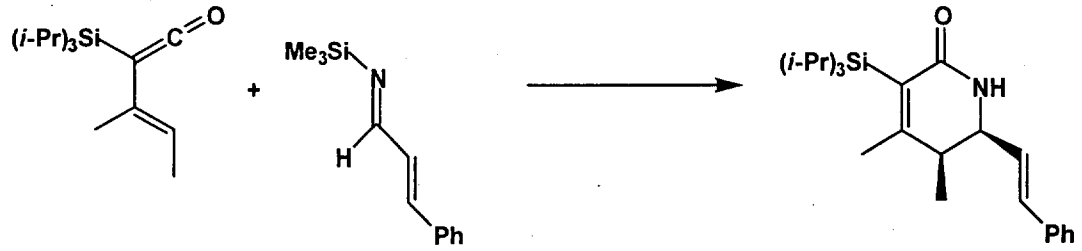


***trans*-1-Phenyl-4-(triisopropylsilyl)-1,5,6,7,8,8a-hexahydro-2*H*-isoquinolin-3-one (17).** A flame-dried, threaded Pyrex tube (13 mm O.D., 10 mm I.D.) was charged with ketene **3** (0.208 g, 0.679 mmol), imine **11** (0.184 g, 1.04 mmol), and 0.7 mL of acetonitrile. The tube was tightly sealed with a teflon cap and the reaction mixture was heated at reflux for 25 h and then cooled and concentrated at reduced pressure to afford 0.403 g of a yellow oil. Column chromatography on 14 g of silica gel (elution with 10% EtOAc-hexane) provided 0.256 g (91%) of lactam **17** as a white solid, mp 211-212 °C: IR ($CDCl_3$) 3400, 2930, 2850, and 1625 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.41 (m, 5H), 5.43 (br s, 1H), 4.79 (d, J = 5.2Hz, 1H), 2.82 (d, J = 11.6 Hz, 1H), 2.23-2.29 (m, 2H), 1.99-2.02 (m, 1H), 1.72-1.75 (m, 1H), 1.52 (sept, J = 7.4 Hz, 3H), 1.25-1.48 (m, 4H), 1.12 (d, J = 7.5 Hz, 9H), and 1.11 (d, J = 7.5 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 138.5, 128.5, 127.7, 126.7, 123.7, 57.3, 49.2, 36.9, 30.9, 28.2, 25.9, 19.3, and 12.6. Anal. Calcd for $C_{24}H_{37}NOSi$: C, 75.14; H, 9.72; N, 3.65. Found: C, 75.10; H, 10.01; N, 3.66.

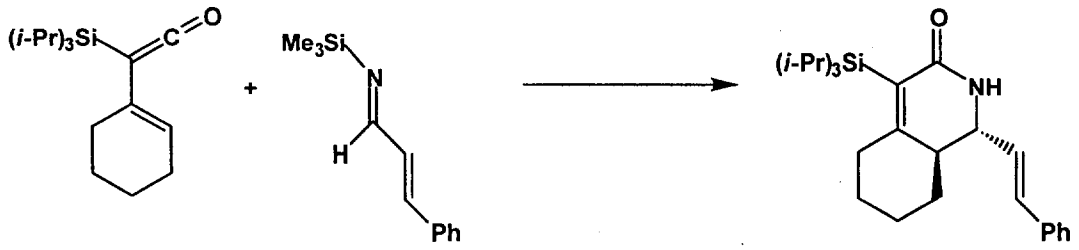


4,6-Diphenyl-3-(triethylsilyl)- 5,6-dihydro-1*H*-pyridin-2-one (18). A 10-mL, two-necked, pear-shaped flask equipped with a glass stopper and a reflux condenser fitted with a rubber septum and argon inlet needle was charged with cyclobutenone **5** (0.134 g, 0.518 mmol), imine **11** (0.133 g, 0.778 mmol), and 0.5 mL of acetonitrile. The reaction mixture was heated at reflux for 45 min and then cooled and concentrated at reduced pressure to afford 0.259 g of a yellow oil. Column chromatography on 25 g

of silica gel (elution with 5-20% EtOAc-hexane) provided 0.157 g (84%) of lactam **18** as a white solid, mp 130-131 °C: IR (film) 3400, 2940, 2860, and 1630 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.29-7.41 (m, 8H), 7.12-7.18 (m, 2H), 5.72 (s, 1H), 4.74 (dq, J = 5.1, 1.6 Hz, 1H), 2.70-2.89 (m, 2H), 0.81 (t, J = 7.6 Hz, 9H), and 0.43 (q, J = 7.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 162.7, 142.8, 141.6, 134.4, 129.6, 129.1, 128.9, 128.7, 128.5, 127.3, 56.0, 43.7, 8.5, and 5.2. Anal. Calcd for $C_{23}H_{29}NOSi$: C, 75.98; H, 8.04; N, 3.85. Found: C, 75.76; H, 7.99; N, 3.77.

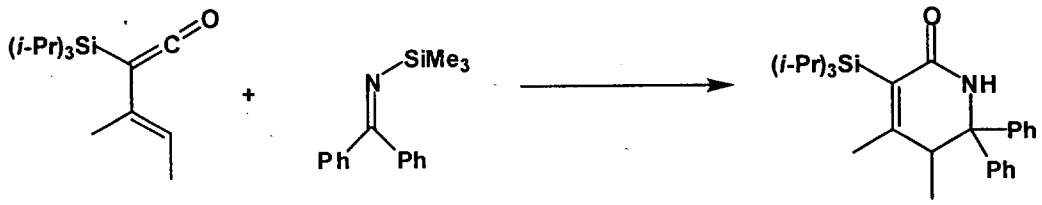


***cis*-4,5-Dimethyl-6-styryl-3-(triisopropylsilyl)-5,6-dihydro-1*H*-pyridin-2-one (19).** A 10-mL, pear-shaped flask equipped with a rubber septum and argon inlet needle was charged with ketene **1** (0.165 g, 0.654 mmol) and imine **12** (0.135 g, 0.654 mmol). The reaction mixture was stirred at room temperature for 15 min and then transferred to a round-bottomed flask with 5 mL of CH_2Cl_2 and concentrated at reduced pressure to provide 0.321 g of an orange oil. Column chromatography on 12 g of silica gel (elution with 0-10% EtOAc-hexane) gave 0.196 g (78%) of lactam **19** as a pale yellow oily solid: IR (film) 3160, 3040, 2900, 1625, and 1455 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24-7.40 (m, 5H), 6.62 (d, J = 15.8 Hz, 1H), 6.16 (dd, J = 16.0, 7.8 Hz, 1H), 5.84 (br s, 1H), 4.26 (dd, J = 7.7, 3.9 Hz, 1H), 2.17-2.20 (m, 1H), 2.06 (s, 3H), 1.50 (sept, J = 7.5 Hz, 3H), 1.09 (d, J = 7.5 Hz, 9H), 1.07 (d, J = 7.5 Hz, 9H), and 1.07 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 166.9, 136.9, 133.6, 129.4, 128.7, 127.5, 127.2, 126.8, 56.8, 44.1, 23.6, 20.0, 13.5, and 11.7.

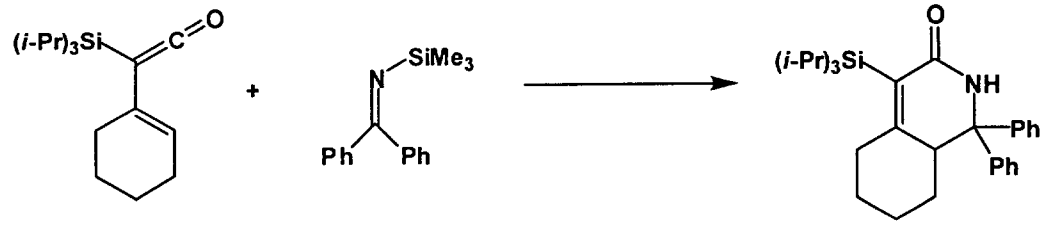


***trans*-1-Styryl-4-(triisopropylsilyl)-1,5,6,7,8,8a-hexahydro-2*H*-isoquinolin-3-one (20).** A flame-dried, 5-mL flask equipped with a rubber septum and argon inlet needle was charged with ketene **3** (0.199 g, 0.649 mmol) and imine **12** (0.133 g, 0.649 mmol). The reaction mixture was stirred at room

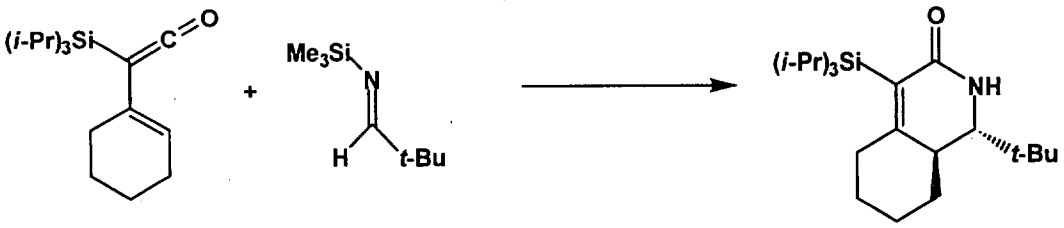
temperature for 10 min and then transferred to a round-bottomed flask with 5 mL of CH_2Cl_2 and concentrated at reduced pressure to afford 0.384 g of a yellow-orange liquid. Column chromatography on 12 g of silica gel (elution with 0-50% EtOAc-hexane) provided 0.209 g (73%) of lactam **20** as a white solid, mp 162-163 °C: IR (film) 3400, 2930, 2860, and 1625 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28-7.38 (m, 5H), 6.57 (d, J = 15.8 Hz, 1H), 6.20 (dd, J = 8.1, 15.8 Hz, 1H), 5.37 (br s, 1H), 4.19-4.23 (m, 1H), 2.77-2.81 (m, 1H), 2.33-2.36 (m, 1H), 2.20-2.22 (m, 1H), 1.96-2.00 (m, 1H), 1.80-1.88 (m, 2H), 1.50 (m, 6H), and 1.09 (d, J = 7.5 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 169.2, 136.2, 132.6, 128.7, 128.0, 126.5, 126.4, 124.6, 55.5, 46.8, 36.3, 29.3, 28.0, 25.5, 19.4, and 12.7. Anal. Calcd for $C_{26}H_{39}NO$: C, 76.23; H, 9.60; N, 3.42. Found: C, 75.97; H, 9.84; N, 3.57.



4,5-Dimethyl-6,6-diphenyl-3-(triisopropylsilyl)-5,6-dihydro-1*H*-pyridin-2-one (21). A flame-dried, threaded Pyrex tube (13 mm O.D., 10 mm I.D.) was charged with ketene **1** (0.153 g, 0.606 mmol), imine **13** (0.233 g, 0.909 mmol), and 0.6 mL of acetonitrile. The tube was tightly sealed with a teflon cap and the reaction mixture was heated at reflux for 45 min and then cooled and concentrated at reduced pressure to afford an orange oil. Column chromatography on 10 g of silica gel (elution with 0-10% EtOAc-hexane) provided 0.208 g (79%) of lactam **21** as a white solid, mp 182 °C: IR ($CDCl_3$) 2930, 2850, and 1620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.11-7.37 (m, 11 H), 3.09 (q, J = 6.9 Hz, 1H), 2.13 (s, 3H), 1.36 (sept, J = 7.5 Hz, 3H), 0.94 (d, J = 6.9 Hz, 3H), 0.85 (d, J = 7.3 Hz, 9H), and 0.82 (d, J = 7.5 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 165.5, 146.6, 142.6, 128.4, 128.0, 127.4, 126.9, 126.5, 126.4, 125.8, 65.0, 46.5, 23.7, 19.0, 14.0, and 12.5. Anal. Calcd for $C_{28}H_{39}NOSi$: C, 77.54; H, 9.06; N, 3.23. Found: C, 77.87; H, 9.17; N, 3.32.

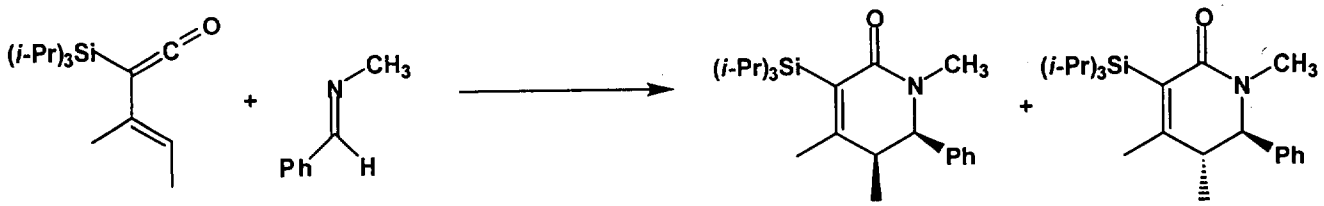


1,1-Diphenyl-4-(triisopropylsilyl)-1,5,6,7,8,8a-hexahydro-2*H*-isoquinolin-3-one (22). A flame-dried, threaded Pyrex tube (13 mm O.D., 10 mm I.D.) was charged with ketene **3** (0.208 g, 0.679 mmol), imine **13** (0.150 g, 0.489 mmol), and 0.5 mL of acetonitrile. The tube was tightly sealed with a teflon cap and then heated at reflux for 24 h. The reaction mixture was cooled to room temperature and concentrated at reduced pressure to give 0.342 g of a yellow-orange oil. Column chromatography on 10 g of silica gel (elution with 10% EtOAc-hexane) provided 0.149 g (66%) of lactam **22** as a white solid, mp 237-237.5 °C: IR (film) 3040, 2930, 2850, and 1630 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.14-7.30 (m, 10 H), 7.03 (br s, 1H), 2.99 (dd, J = 2.4, 9.1 Hz, 1H), 2.84 (dd, J = 3.1, 11.6 Hz, 1H), 2.36-2.42 (m, 1H), 2.04-2.09 (m, 1H), 1.75-1.78 (m, 1H), 1.41-1.54 (m, 3H), 1.33 (sept, J = 7.3 Hz, 3H), 1.13 (d, J = 12.8 Hz, 1H), 0.87 (d, J = 7.3 Hz, 9H), and 0.80 (d, J = 7.3 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.3, 146.9, 143.2, 128.3, 127.9, 127.3, 126.9, 126.6, 126.4, 125.3, 64.3, 51.1, 37.3, 31.5, 31.2, 26.5, 19.0, and 12.5. Anal. Calcd for $C_{30}H_{41}NOSi$: C, 78.38; H, 9.01; N, 3.05. Found: C, 78.44; H, 9.41; N, 3.03.

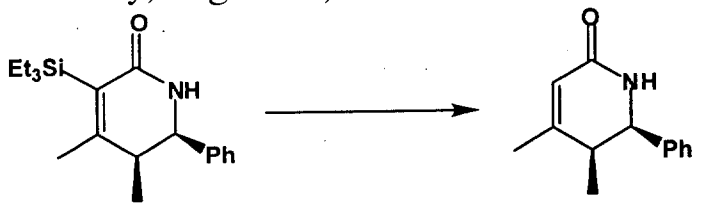


***trans*-1-(1,1-Dimethylethyl)-4-(triisopropylsilyl)-1,5,6,7,8,8a-hexahydro-2*H*-isoquinolin-3-one (23).** A flame-dried, threaded Pyrex tube (13 mm O.D., 10 mm I.D.) was charged with ketene **3** (0.162 g, 0.529 mmol), imine **14** (0.165 g, 1.06 mmol), and 0.5 mL of acetonitrile. The tube was tightly sealed with a teflon cap and heated at reflux for 4 h and then at 110 °C for 65 h. The reaction mixture was cooled to room temperature, additional imine (0.093 g, 0.53 mmol) was added, and the mixture was heated at 110-130 °C for 23 h. The resulting mixture was cooled to room temperature and concentrated to give 0.307 g of a yellowish liquid which was filtered through Celite with the aid of CH_2Cl_2 and then concentrated at reduced pressure to afford 0.187 g of a pale yellow solid. This material was washed

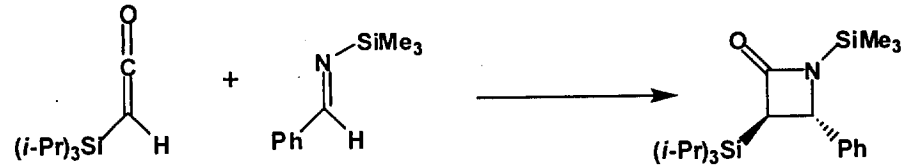
with heptane to furnish 0.115 g (56%) of lactam **23** as a white solid, mp 235-237 °C: IR (CH_2Cl_2) 2950, 2850, and 1630 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.19 (br s, 1H), 3.21 (d, J = 4.1 Hz, 1H), 2.70-2.75 (m, 1H), 2.20-2.28 (m, 2H), 1.99-2.02 (m, 2H), 1.79-1.82 (m, 1H), 1.47 (m, 6H), 1.07 (d, J = 7.1 Hz, 18H), and 1.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 170.4, 124.0, 60.7, 47.2, 37.2, 32.5, 30.8, 28.6, 27.3, 26.0, 19.3, and 12.6. Anal. Calcd for $C_{22}H_{41}NOSi$: C, 72.66; H, 11.36; N, 3.85. Found: C, 72.59; H, 11.65; N, 3.78.



***trans*-6-Phenyl-3-(triisopropylsilyl)-1,4,5-trimethyl-5,6-dihydro-1*H*-pyridin-2-one (25a) and *cis*-6-Phenyl-3-(triisopropylsilyl)-1,4,5-trimethyl-5,6-dihydro-1*H*-pyridin-2-one (25b).** A flame-dried, threaded Pyrex tube (13 mm O.D., 10 mm I.D.) was charged with a solution of ketene **1** (0.069 g, 0.273 mmol), 0.3 mL of acetonitrile, and imine **24** (0.050 g, 0.410 mmol). The tube was tightly sealed with a threaded teflon cap and heated at 120 °C for 42 h. The reaction mixture was cooled and concentrated at reduced pressure to give 0.120 g of an orange oil. Column chromatography on 12 g of silica gel (elution with 5% EtOAc-hexane) afforded 0.072 g (71%) of lactams **25a** and **25b** as a pale yellow oil. Both isomers: IR (neat) 2940, 2850, and 1615 cm^{-1}; major isomer (**25a**): ^1H NMR (300 MHz, $CDCl_3$) δ 7.19-7.29 (m, 5H), 4.32 (d, J = 6.1 Hz, 1H), 2.90 (m, obscured by the s at 2.89, 1H), 2.89 (s, 3H), 1.92 (s, 3H), 1.45-1.57 (m, 3H), 1.06 (d, J = 7.4 Hz, 18H), and 0.92 (d, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 160.4, 137.2, 129.0, 128.0, 127.8, 126.1, 66.2, 40.6, 33.5, 21.7, 19.4, 19.3, and 13.1. Minor isomer (**25b**): ^1H NMR (300 MHz, $CDCl_3$) δ 7.19-7.29 (m, 5H), 4.19 (s, 1H), 3.03 (s, 3H), 2.35 (q, J = 7.0 Hz, 1H), 1.79 (s, 3H), 1.54 (sept, J = 7.4 Hz, 3H), 1.30 (d, J = 7.0 Hz, 3H), and 1.00 (d, J = 7.4 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 160.9, 140.3, 128.6, 128.2, 127.4, 127.2, 66.7, 45.4, 35.1, 23.5, 19.2, 14.0, and 12.9.



4,5-Dimethyl-6-phenyl-5,6-dihydro-1*H*-pyridin-2-one (26). A flame-dried, 25-mL, round-bottomed flask equipped with a reflux condenser fitted with a rubber septum and argon inlet needle was charged with a solution of silyl lactam **16** (0.075 g, 0.238 mmol) in 1.2 mL of CH_2Cl_2. Methanesulfonic acid (0.077 mL, 1.19 mmol) was added and the reaction mixture was heated at reflux for 6 h. The resulting mixture was cooled, diluted with 10 mL of CH_2Cl_2, and washed with 10 mL of saturated $NaHCO_3$ solution, 10 mL of water, 10 mL of 10% aqueous HCl solution, 10 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to afford 0.087 g of an oily yellow solid. Column chromatography on 8 g of silica gel (elution with 20-100% EtOAc-hexane) furnished 0.040g (83%) of lactam **26** as a white solid, mp 170.5 °C: IR (CH_2Cl_2) 3980, 2950, 1655, and 1615 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.42 (m, 5H), 5.76 (s, 1H), 5.46 (br s, 1H), 4.90 (d, J = 4.6 Hz, 1H), 2.27-2.32 (m, 1H), 2.00 (s, 3H), and 0.80 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 159.4, 139.2, 129.5, 128.8, 127.2, 119.6, 59.9, 41.4, 22.5, and 12.2.



***N*-(Trimethylsilyl)-4-phenyl-3-(triisopropylsilyl)-azetidin-2-one (28).** A flame-dried, threaded Pyrex tube (13 mm O.D., 10 mm I.D.) was charged with (triisopropylsilyl)ketene **27** (0.063 g, 0.318 mmol) and imine **11** (0.057 g, 0.321 mmol). The tube was tightly sealed with a threaded teflon cap and heated at 70 °C for 20 h and then at 140 °C for 3 h. The reaction mixture was cooled and the resulting orange oil was purified by column chromatography on 10 g of silica gel (elution with 0-20% EtOAc-hexane) to afford 0.085g (71%) of lactam **28** as a pale yellow oil: IR (film) 2930, 2850, 2230, 1710, and 1450 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29-7.40 (m, 5H), 4.47 (d, J = 3.1 Hz, 1H), 3.00 (d, J = 3.1 Hz, 1H), 1.26 (sept, J = 7.0 Hz, 3H), 1.09 (d, J = 7.3 Hz, 9H), 1.05 (d, J = 7.6 Hz, 9H), and 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 143.0, 129.3, 128.7, 127.2, 54.6, 52.1, 19.4, 11.1, and –0.4.

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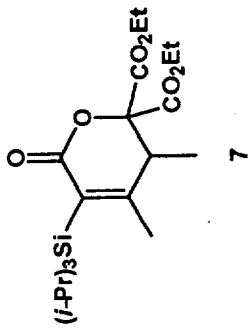

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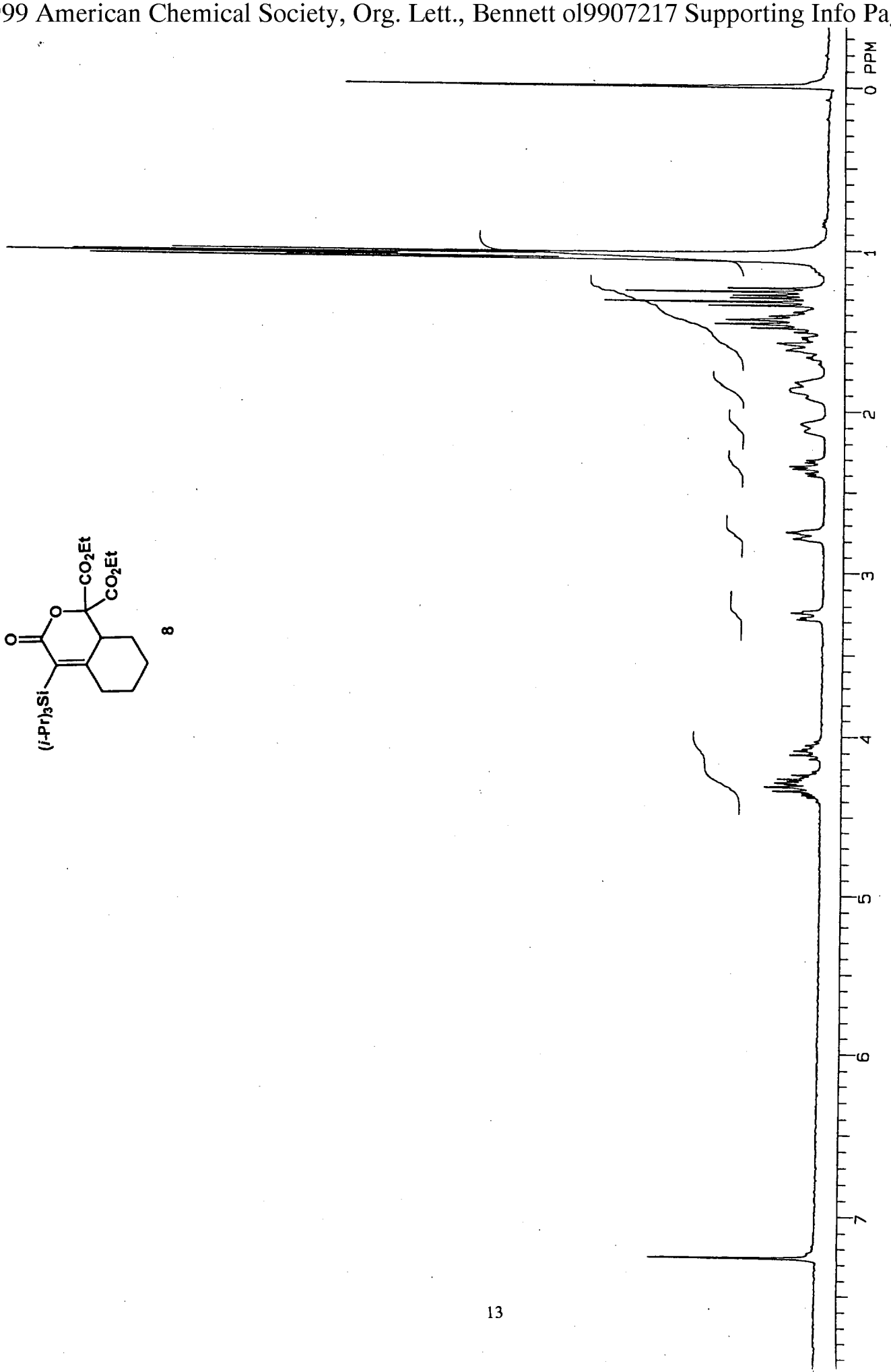

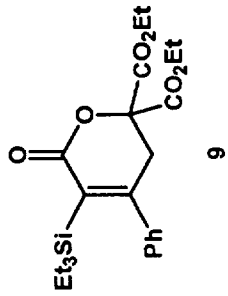

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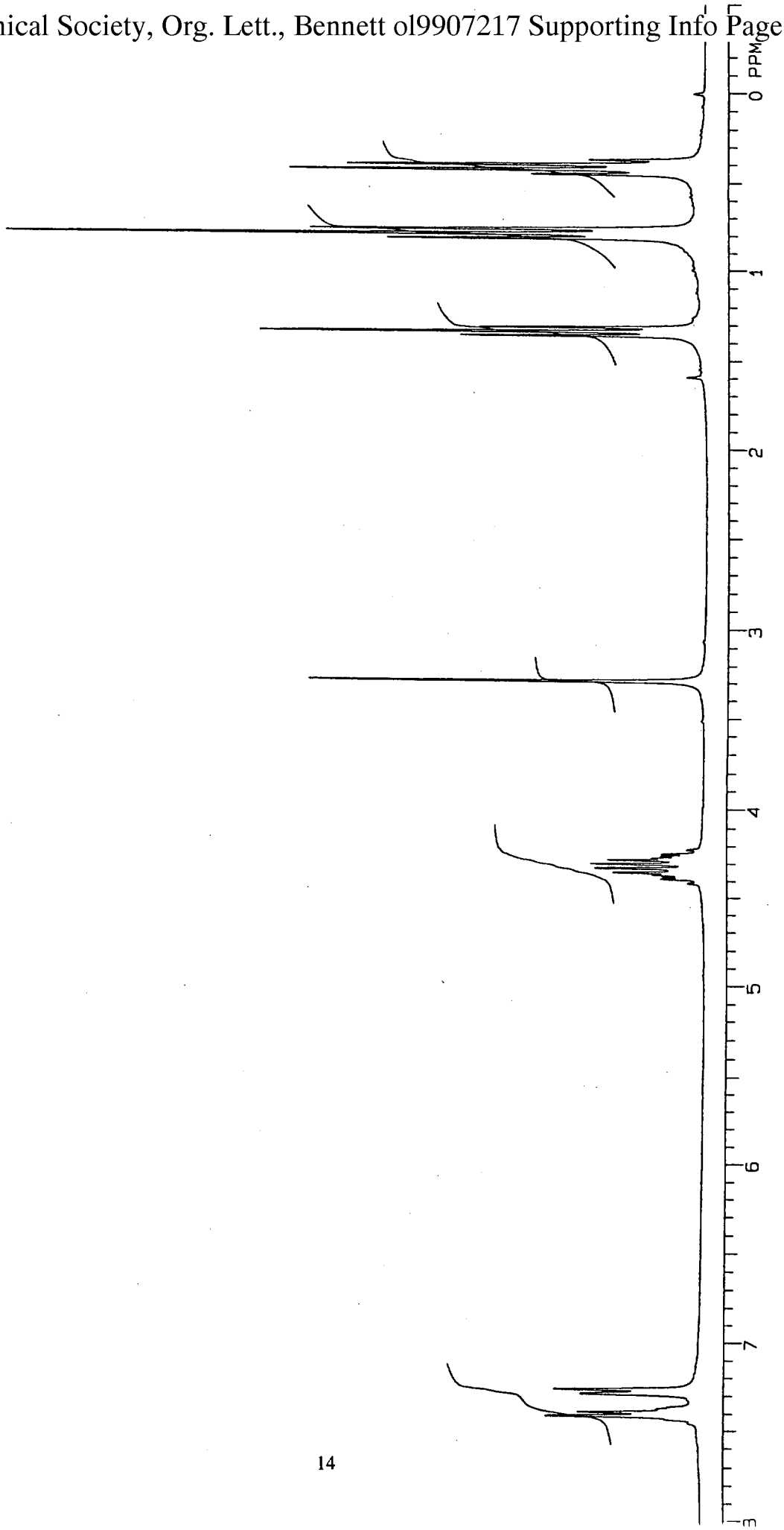

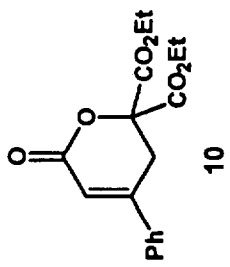

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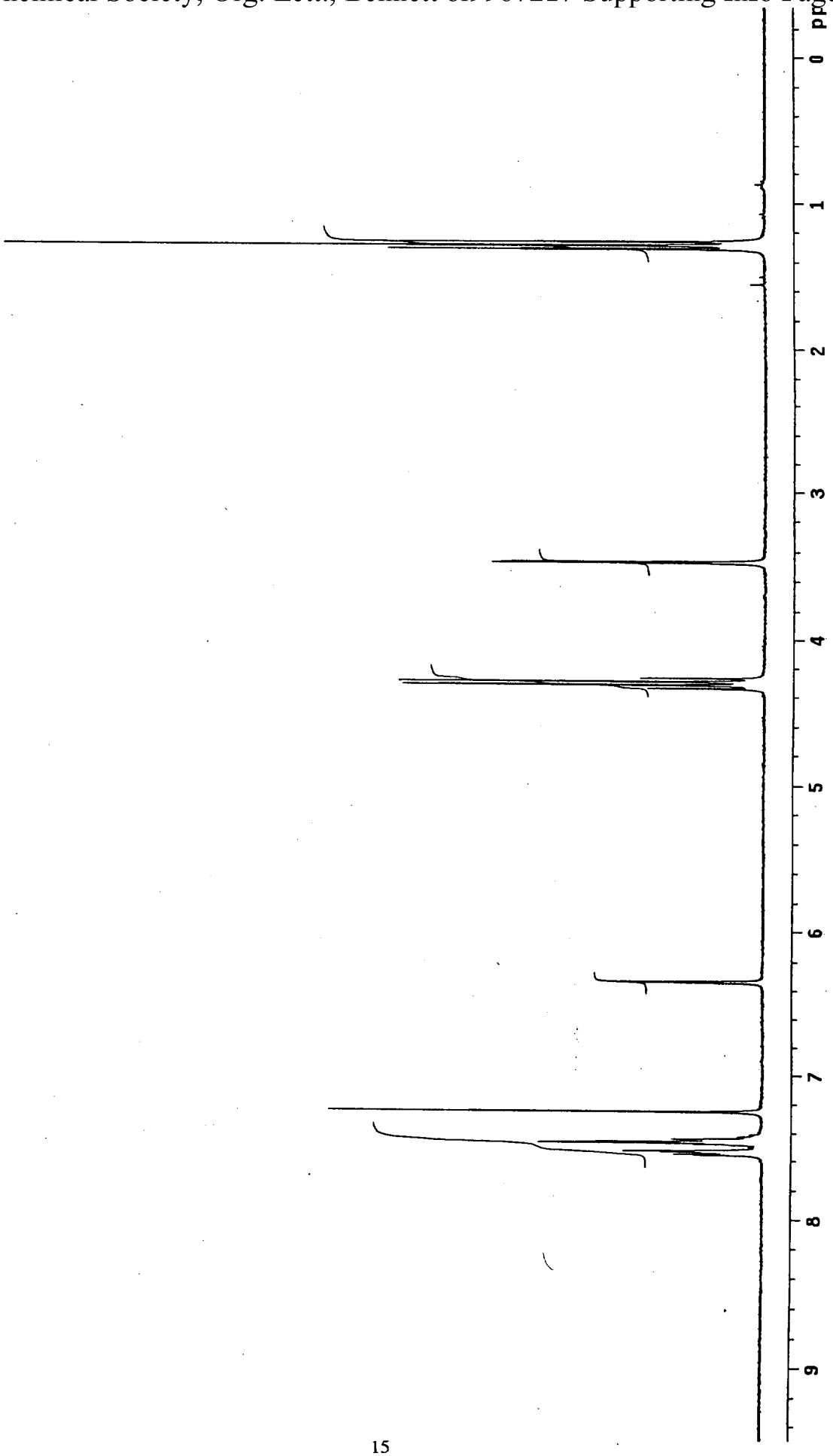

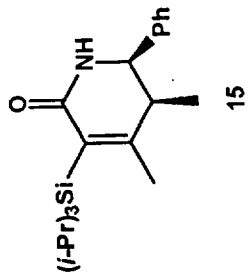

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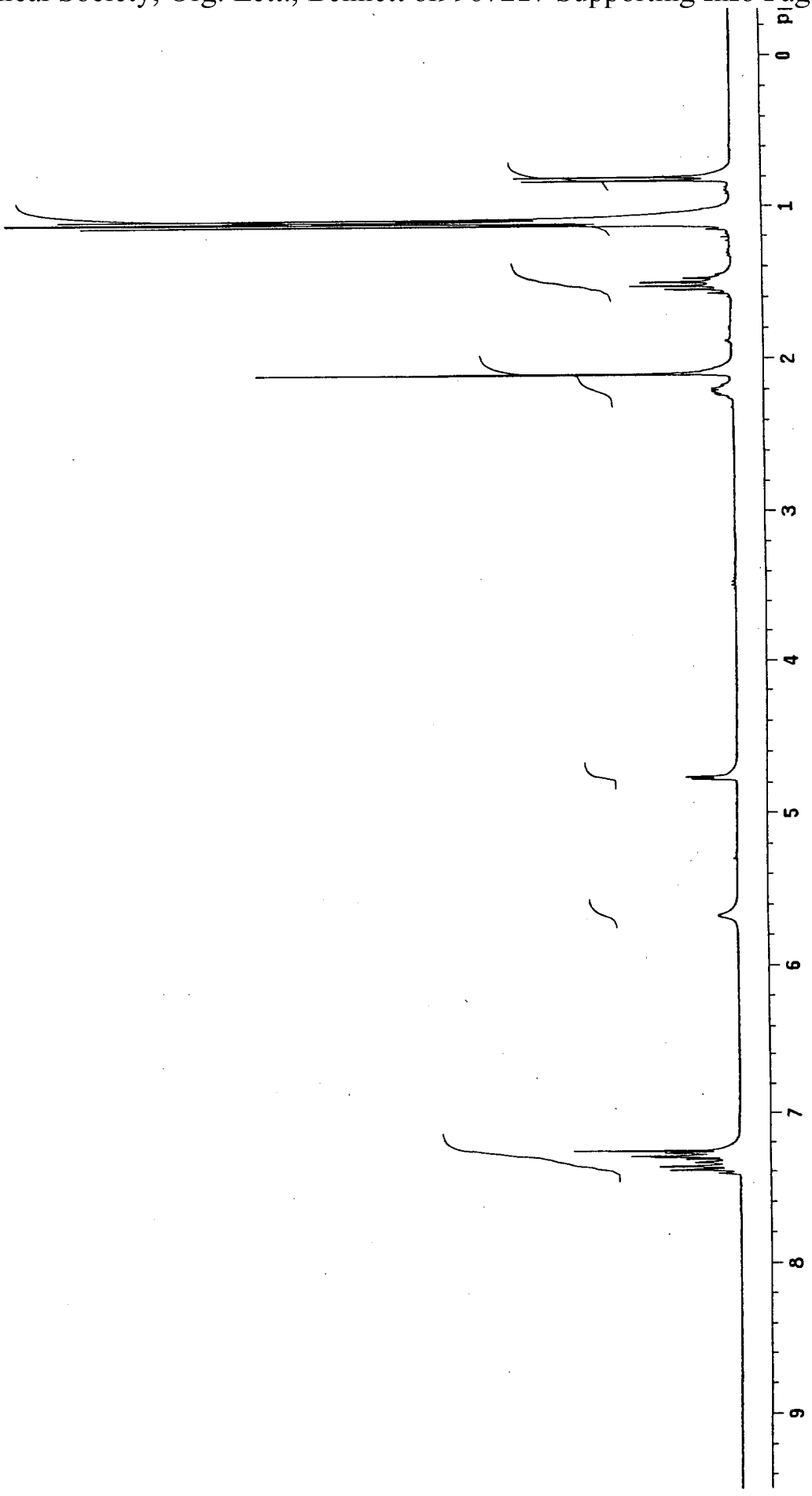

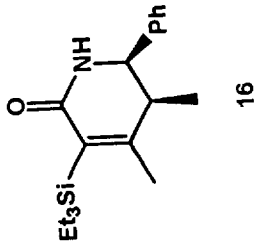

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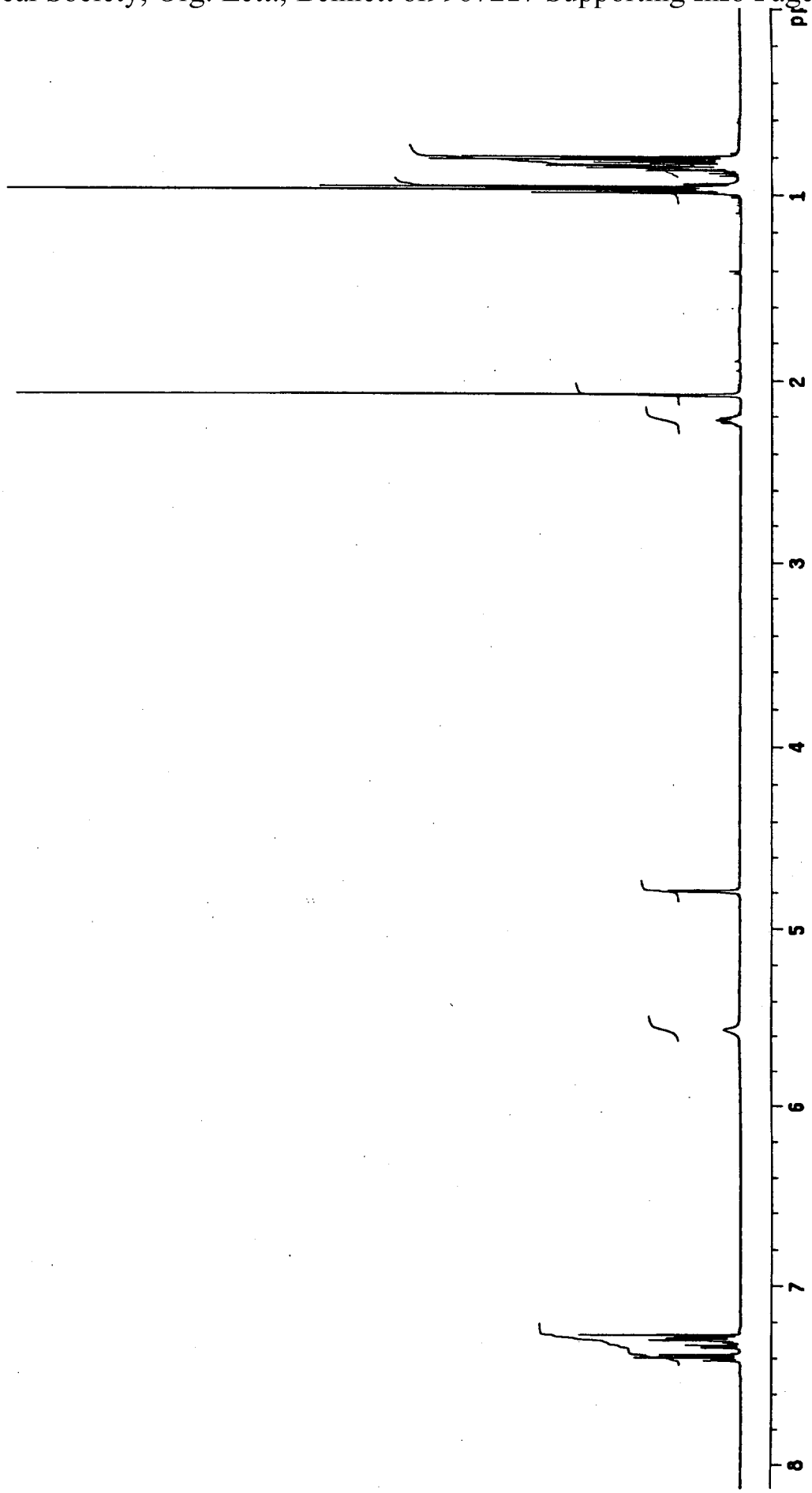

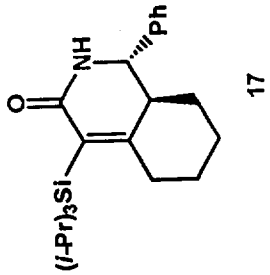

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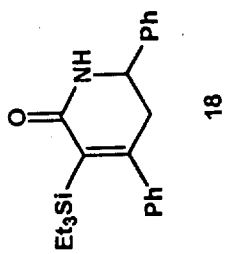

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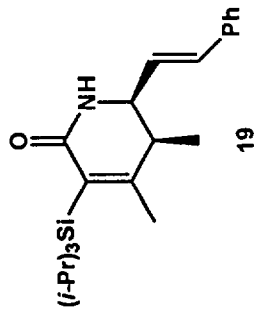

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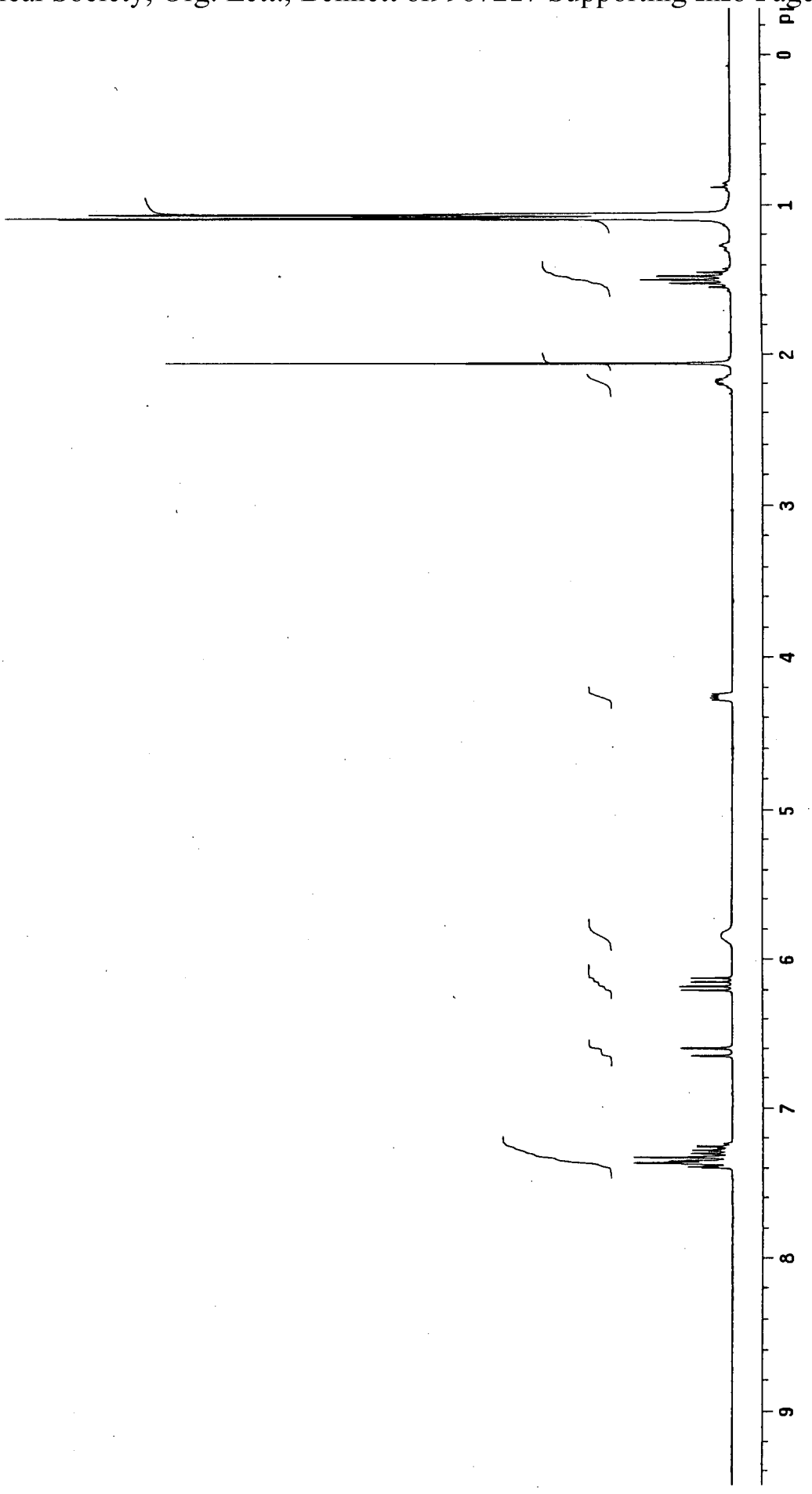

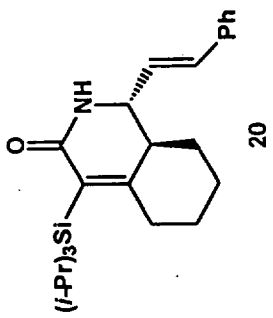

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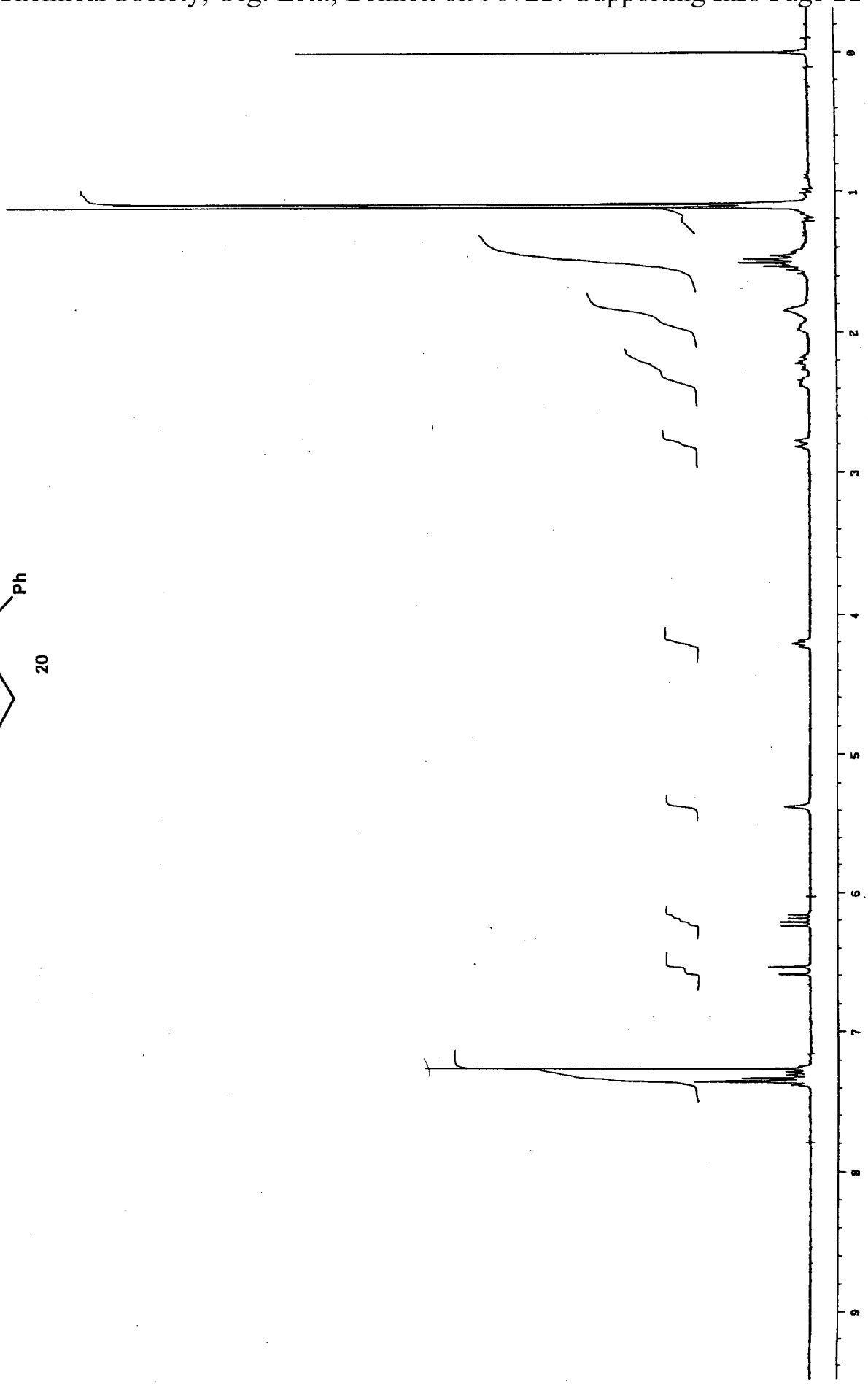

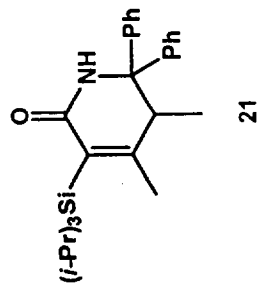

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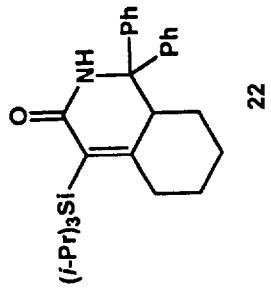

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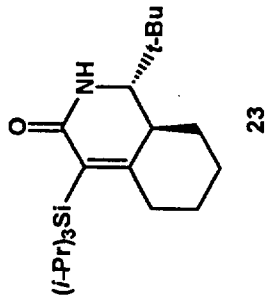

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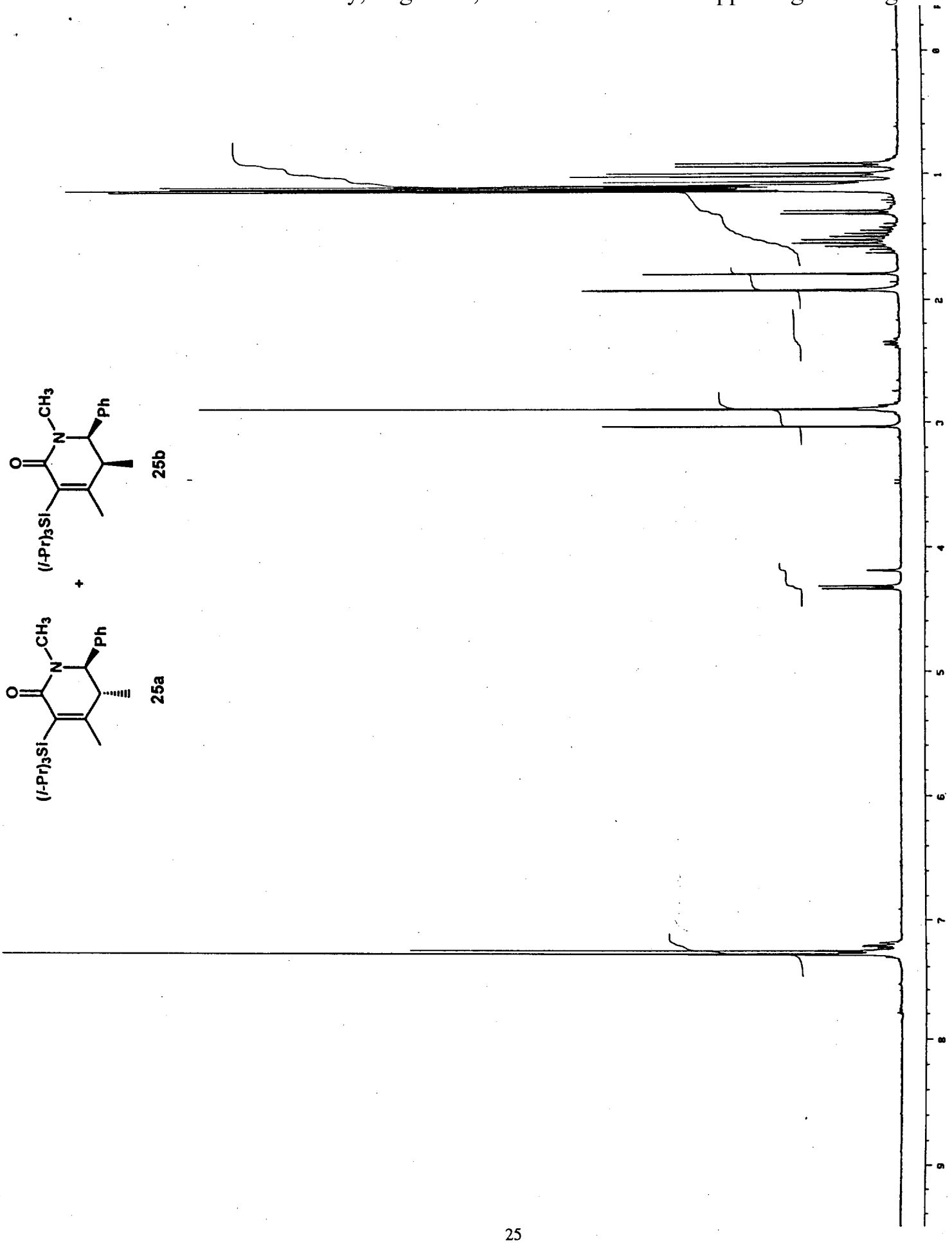

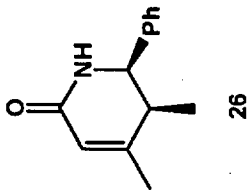

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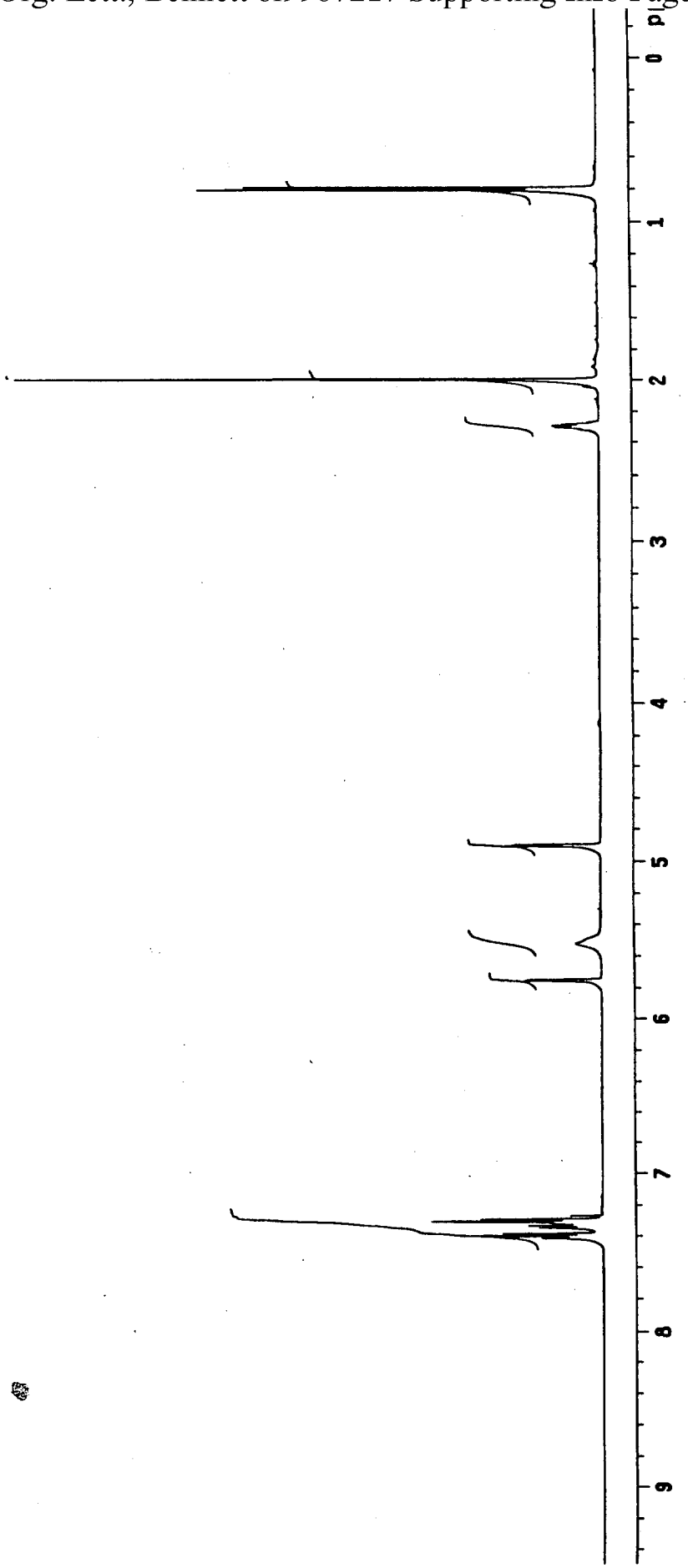

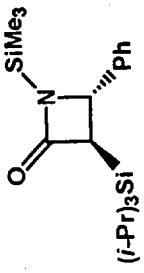

28