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Supporting Information

Enantio- and Diastereoselective Michael Addition Reactions of Unmodified Aldehydes and Ketones with Nitroolefins Catalyzed by a Pyrrolidine Sulfonamide

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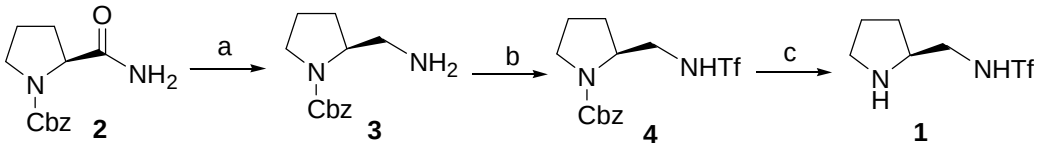
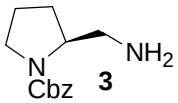
General. Unless specified, all reactions were performed under aerobic atmosphere. Commercial, HPLC grade solvents used directly for reactions without further purification. HPLC grade EtOAc and hexanes were used for column chromatography. Anhydrous THF was obtained from distillation of Na and benzophenone. Column chromatography was performed with silica gel (230-400 mesh size). TLC plates with F_{254} indicator were used for monitoring reactions. The combined organic layers were dried over $MgSO_4$. Solvents were evaporated under reduced pressure. All yields given refer to as isolated yields. ^1H NMR was recorded on a 500 MHz and ^{13}C on a 125 MHz spectrometer. HRMS experiment was performed on a high resolution magnetic sector spectrometer. Tetramethylsilane (TMS) was used as a reference for ^1H NMR experiments. Data for ^1H are reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Data for ^{13}C NMR are reported as ppm.

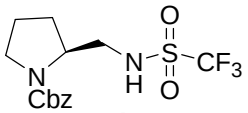
Procedures for preparation of pyrrolidine trifluoromethanesulfonamide organocatalyst 1.[a]



[a] Reagents and conditions: (a) BH_3, THF, reflux, 7 h, 74%; (b) Tf_2O, TEA, CH_2Cl_2, 4.5 h, 76%; (c) 10% Pd/C, H_2, MeOH, 3 h, 93%.

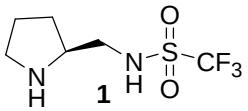


(S)-2-Aminomethyl-1-*N*-Cbz-pyrrolidine (3). To a solution of (*S*)-2-carbamoyl-1-*N*-Cbz-pyrrolidine **2** (0.5 g, 2 mmol) in THF (10 mL) was added borane BH_3 (12 mL, 12 mmol, 1.0 M THF solution) slowly at 0 °C under N_2. The resulting solution was heated to reflux for 7 h, then cooled to 0 °C, followed by slow addition of 4.5 mL of 12 *N* HCl to destroy the B-N complex. The mixture was heated to reflux for 6 h, cooled to RT, then was neutralized to pH 8 by a 1*N* NaOH aqueous solution. After THF and water were removed under reduced pressure, the crude product was purified by flash silica gel column chromatography (1/10 = MeOH/CH_2Cl_2) to afford a clear, slightly yellow oil in 74% yield (348 mg). $[\alpha]^{25}_D$ = -15.4 (*c* = 1.0, $CHCl_3$); ^1H NMR(500MHz, $CDCl_3$): d 7.31-7.37 (m, 5H); 5.12 (t, 2H); 3.94, 3.83(brs, 1H); 3.38-3.49 (m, 2H); 2.67-2.95(m, 2H); 1.77-2.00 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): d 156.4, 136.8, 128.7, 128.2, 128.1, 67.3, 59.0, 47.2, 45.2, 29.4, 24.0.



4

(*S*)-2-(trifluoro methane sulfonylamino methyl)-1-*N*-Cbz-pyrrolidine (4). To a solution of (*S*)-2-aminomethyl-1-*N*-Cbz-pyrrolidine **3** (2.0 g, 8.55 mmol) and TEA (1.43 mL, 10.3 mmol) in 40 mL of CaH_2 dried CH_2Cl_2 was added trifluoromethanesulfonic anhydride (1.6 mL, 9.4 mmol) dropwisely by a syringe pump over 1 h at 0 °C under N_2. The resulting solution was stirred for 4.5 h at rt, then diluted with 80 mL of CH_2Cl_2 and washed with 50 mL of 1*N* HCl aqueous solution. The organic layer was dried over $MgSO_4$, and concentrated *in vacuo*. Flash chromatography (Ethyl Acetate/Hexane = 1/7) afforded a colorless oil in 76% yield (2.38 g, 6.50 mmol). $[\alpha]^{25}_D$ = -27.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): d 7.68 (s, 1H), 7.10-7.39 (m, 5H), 5.15 (q, 2H), 3.98-4.09 (m, 1H), 3.24-3.57 (m, 4H), 2.12 (m, 1H), 1.88 (m, 2H), 1.67 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): d 157.7, 136.2, 128.8, 128.6, 128.5, 128.3, 68.0, 58.1, 49.9, 47.5, 30.0, 24.1. HRMS (FAB) calcd for $C_{14}H_{18}F_3N_2O_4S$ (M + 1) m/z 367.0939, found 367.0928.

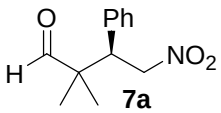


1

(*S*)-2-(trifluoro methane sulfonylamino methyl)-pyrrolidine (1). A solution of (*S*)-2-(trifluoromethane sulfonylamino methyl)-1-*N*-Cbz-pyrrolidine **4** (0.794 g, 2.17 mmol) in 15 mL of MeOH was hydrogenated in the presence of 10% Pd/C (0.16 g) with a H_2 balloon at rt for 5 h. The catalyst was filtered through a pad of celite and washed with 2 × 20 mL of MeOH. The filtrate was concentrated *in vacuo* to give a white solid (>95% purity) in 93% yield (0.469 g, 2.02 mmol). The product was recrystallized in MeOH to give a crystal, which was used for catalyzing reactions. $[\alpha]^{25}_D$ = + 10.5 (c 1.0, CH_3OH); ^{1}H NMR (500MHz, CD_3OD): d = 3.47 (m, 1H), 3.08-3.28 (m, 4H), 1.86-2.02 (m, 3H), 1.61-1.68 (m, 1H); ^{13}C NMR (125 MHz, CD_3OD): d = 123.5 (q, *J* = 325 Hz), 122.2, 63.7, 46.4, 28.5, 24.7. HRMS (FAB) calcd for $C_6H_{12}F_3N_2O_2S$ (M + 1) *m/z* 233.0572, found 233.0580.

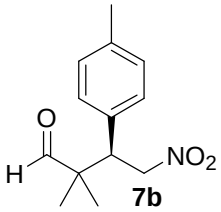
Typical procedure A for Michael addition reaction of aldehydes: To a vial containing *iso*-butyraldehyde (0.20 mL, 2.19 mmol), and 1.0 mL of dry isopropyl alcohol was added catalyst pyrrolidine sulfonamide **1** (10 mg, 0.044 mmol) at 0 °C. The mixture was vigorously stirred for 15 min, and then *trans*-β–nitrostyrene (33 mg, 0.219 mmol) was added. After 4.5 d stirring, TLC analysis indicated completion of the reaction. After reaction mixture was concentrated under reduced pressure, the resulting residue was then purified by silica gel chromatography (ethyl acetate/hexane = 1/30 to 1/5)

and fractions were collected and concentrated *in vacuo* to provide a clear oil (41 mg, 0.186 mmol, 85%). Relative and absolute configurations of the product were determined by comparison with the known ^{1}H NMR, ^{13}C NMR and optical rotation values.



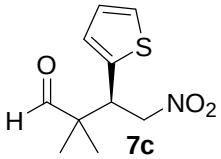
7a

(*R*)-2,2-Dimethyl-4-nitro-3-phenylbutanal (7a)[1] (Table 2, entry 1): The title compound was prepared according to the typical procedure, as described above in 85% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 10/90, flow rate 0.5 mL/min, ? = 254 nm): t_{minor} = 22.2 min, t_{major} = 23.0 min, ee = 90%; $[\alpha]^{25}_{D}$ = +18.6 (*c* = 1.0 in $CHCl_3$).



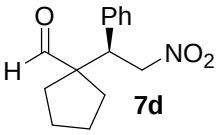
7b

(*R*)-2,2-Dimethyl-4-nitro-3-*p*-tolylbutanal (7b) (Table 2, entry 2): The title compound was prepared according to the typical procedure, as described above in 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): d = 9.53 (s, 1H), 7.13 (d, ^{3}J(H, H) = 8.0 Hz, 2H), 7.07 (d, ^{3}J(H, H) = 8.0 Hz, 2H), 4.82 (dd, ^{3}J(H, H) = 12.5 Hz, ^{2}J(H, H) = 11.5 Hz, 1H), 4.67 (dd, ^{3}J(H, H) = 13.0 Hz, ^{2}J(H, H) = 4.0 Hz, 1H), 3.74 (dd, ^{3}J(H, H) = 11.5 Hz, ^{2}J(H, H) = 4.0 Hz, 1H), 2.32 (s, 3H), 1.13 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 204.6, 138.1, 132.4, 129.6, 129.1, 76.6, 48.4, 21.8, 21.2, 19.1; HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 15.1 min, t_{major} = 10.4 min, ee = 90%; $[\alpha]^{25}_{D}$ = +25.4 (*c* = 0.5 in $CHCl_3$); HRMS (EI) calcd for $C_{13}H_{17}NO_3 + Na^+$ 235.1202, obsd 235.1203.



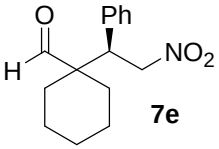
7c

(*R*)-2,2-Dimethyl-4-nitro-3-(thiophen-2-yl)butanal (7c) (Table 2, entry 3): The title compound was prepared according to the typical procedure, as described above in 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d = 9.54 (s, 1H), 7.26-6.92 (m, 3H), 4.73-4.67 (m, 2H), 4.14 (dd, ^{3}J(H, H) = 10.8 Hz, ^{2}J(H, H) = 4.0 Hz, 1H), 1.21 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 192.8, 138.1, 129.6, 129.2, 125.2, 59.9, 30.9, 25.7, 24.2; HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 19.8 min, t_{major} = 11.4 min, ee = 89%; $[\alpha]^{25}_{D}$ = +54.1 (*c* = 1.0 in $CHCl_3$); HRMS (EI) calcd for $C_{10}H_{13}NO_3S + Na^+$ 250.0508, obsd 250.0516.



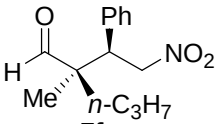
7d

1-((*R*)-2-Nitro-1-phenylethyl)cyclopentanecarbaldehyde (7d)[2] (Table 2, entry 4): The title compound was prepared according to the typical procedure, as described above in 89% yield. HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 14.6 min, t_{major} = 10.5 min, ee = 93%; $[\alpha]^{25}_{D}$ = -7.2 (*c* = 3.8 in $CHCl_3$).



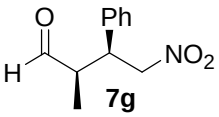
7e

1-((R)-2-Nitro-1-phenylethyl)cyclohexanecarbaldehyde (7e)[1] (Table 2, entry 5): The title compound was prepared according to the typical procedure, as described above in 42% yield. HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 19.2 min, t_{major} = 9.6 min, ee = 64%; $[\alpha]^{25}_{D}$ = -3.1 (*c* = 1.0 in $CHCl_3$).



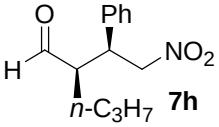
7f

(2*R*, 3*R*)-2-Ethyl-2-methyl-4-nitro-3-phenylbutanal (7f)[1] (Table 2, entry 6): The title compound was prepared according the typical procedure, as described above in 71% yield. HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 10/90, flow rate 1.0 mL/min, ? = 254 nm): (major isomer) t_{minor} = 17.7 min, t_{major} = 13.7 min, ee =60%; (minor isomer): t_{minor} = 25.1 min, t_{major} = 16.0 min, ee =65%, dr = 1.3:1; $[\alpha]^{25}_{D}$ = +12.1 (*c* = 0.7 in $CHCl_3$).



7g

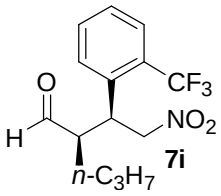
(2*R*, 3*S*)-2-Methyl-4-nitro-3-phenylbutanal (7g)[3] (Table 2, entry 7): The title compound was prepared according to the typical procedure, as described above in 77% yield. HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 237 nm): t_{minor} = 14.9 min, t_{major} = 19.7 min, ee = 97%, dr = 12:1; $[\alpha]^{25}_{D}$ = +45.3 (*c* = 1.1 in $CHCl_3$).



7h

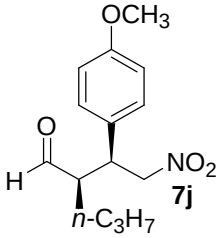
(*R*)-2-[(*S*)-2-Nitro-1-phenylethyl]pentanal (7h)[2] (Table 2, entry 8): The title compound was prepared according to the typical procedure, as described above in 99% yield. HPLC (Chiralcel OD-H,

i-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 10.9 min, t_{major} = 12.9 min, ee = 97%, dr = 50:1; $[\alpha]^{25}_{D}$ (major) = +51.2 (*c* = 0.5 in $CHCl_3$).



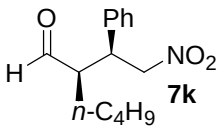
7i

(*R*)-2-[(*S*)-1-(2-(Trifluoromethyl)phenyl)-2-nitroethyl]pentanal (7i) (Table 2, entry 9): The title compound was prepared according to the typical procedure, as described above in 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d = 9.76 (d, ^3J(H, H) = 3.0 Hz, 1H), 7.73 (d, ^3J(H, H) = 8.0 Hz, 1H), 7.59 (t, ^3J(H, H) = 7.5 Hz, 1H), 7.45 (t, ^3J(H, H) = 8.0 Hz, 1H), 7.37 (d, ^3J(H, H) = 7.5 Hz, 1H), 4.80 (dd, ^3J(H, H) = 13.0 Hz, ^2J(H, H) = 7.5 Hz, 1H), 4.66 (dd, ^3J(H, H) = 13.0 Hz, ^2J(H, H) = 5.0 Hz, 1H), 4.17-4.14 (m, 1H), 2.95-2.93 (m, 1H), 1.60-1.20 (m, 4H), 0.81 (t, ^3J(H, H) = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 203.0, 136.3, 132.6, 129.4 (q), 128.0, 126.9, 125.1, 123.0, 77.8, 54.0, 38.6, 30.3, 20.1, 13.9; HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 8.6 min, t_{major} = 10.1 min, ee = 94%, dr = 22:1; $[\alpha]^{25}_{D}$ (major) = +31.4 (*c* = 1.0 in $CHCl_3$); HRMS (EI) calcd for $C_{13}H_{16}F_3NO_3$ + Na^+ 326.0974, obsd 326.0958.



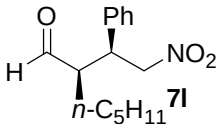
7j

(*S*)-2-[(*R*)-1-(4-Methoxyphenyl)-2-nitroethyl]pentanal (7j) (Table 2, entry 10): The title compound was prepared according to the typical procedure, as described above in 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d = 9.69 (d, ^3J(H, H) = 3.0 Hz, 1H), 7.08 (d, ^3J(H, H) = 8.5 Hz, 2H), 6.86 (d, ^3J(H, H) = 8.5 Hz, 2H) 4.66 (dd, ^3J(H, H) = 13.0 Hz, ^2J(H, H) = 5.0 Hz, 1H), 4.60 (dd, ^3J(H, H) = 13.0, ^2J(H, H) = 10.0 Hz, 1H), 3.78 (s, 3H), 3.75-3.71 (m, 1H), 2.66-2.65 (m, 1H), 1.49-1.29 (m, 4H), 0.80 (t, ^3J(H, H) = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 203.6, 159.4, 129.2, 128.7, 114.7, 78.8, 55.4, 54.1, 42.6, 29.6, 20.0, 14.1; HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 10/90, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 18.4 min, t_{major} = 21.5 min, ee = 99%, dr = 20:1; $[\alpha]^{25}_{D}$ (major) = +41.7 (*c* = 2.0 in $CHCl_3$); HRMS (EI) calcd for $C_{14}H_{19}NO_4$ + Na^+ 265.1309, obsd 265.1310.



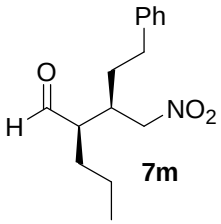
7k

(*R*)-2-[(*S*)-2-Nitro-1-phenylethyl]hexanal (7k)[3] **(**Table 2, entry 11**)**: The title compound was prepared according to the typical procedure, as described above in 94% yield. HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 10.4 min, t_{major} = 11.8 min, ee = 99%, dr = 30:1; $[\alpha]^{25}_{D}$ (major) = +52.4 (*c* = 0.5 in $CHCl_3$), ref [3].$[\alpha]^{25}_{D}$ (major) = +33.4 (*c* = 1.4 in $CHCl_3$).



7l

(*R*)-2-[(*S*)-2-Nitro-1-phenylethyl]heptanal (7l) (Table 2, entry 12): The title compound was prepared according to the typical procedure, as described above in 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d = 9.70 (d, ^3J(H, H) = 3.0 Hz, 1H), 7.36-7.17 (m, 5H), 4.73-4.62 (m, 2H), 3.80-3.75 (m, 1H), 2.72-2.67 (m, 1H), 1.53-1.08 (m, 8H), 0.80 (t, ^3J(H, H) = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 203.4, 137.0, 129.3, 128.4, 128.2, 78.7, 54.1, 43.4, 31.8, 27.5, 26.3, 22.4, 14.0; HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 9.7 min, t_{major} = 11.0 min, ee = 97%, dr = 50:1; $[\alpha]^{25}_{D}$ (major) = +59.0 (*c* = 2.0 in $CHCl_3$); HRMS (EI) calcd for $C_{15}H_{21}NO_3$ + Na^+ 263.1516, obsd 263.1528.

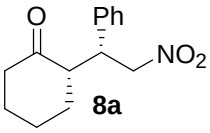


7m

(*R*)-2-((*R*)-1-Nitro-4-phenylbutan-2-yl)pentanal (7m) (Table 2, entry 13): The title compound was prepared according to the typical procedure, as described above in 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d = 9.67 (s, 1H), 7.40-7.02 (m, 5H), 4.53 (dd, ^3J(H, H) = 12.0 Hz, ^3J(H, H) = 5.0 Hz, 1H), 4.46 (dd, ^3J(H, H) = 12.0 Hz, ^2J(H, H) = 6.5 Hz, 1H), 2.73-2.67 (m, 3H), 2.65-3.45 (m, 1H), 1.80-1.60 (m, 3H), 1.49-1.20 (m, 4H), 0.90 (t, ^3J(H, H) = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 202.9, 140.4, 128.6, 128.1, 126.3, 52.0, 36.5, 33.0, 30.9, 27.5, 20.7, 14.0; HPLC (Chiralcel OD-H, *i*-Propanol/Hexane = 8/92, flow rate 0.5 mL/min, ? = 254 nm): t_{minor} = 44.2 min, t_{major} = 40.5 min, ee = 22%, dr = 50:1; $[\alpha]^{25}_{D}$ (major) = +5.7 (*c* = 0.5 in $CHCl_3$); HRMS (EI) calcd for $C_{15}H_{21}NO_3$ + Na^+ 263.1516, obsd 263.1528.

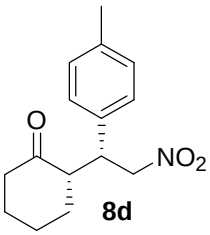
Typical procedure B for Michael addition reaction of ketones (Tables 3 and 4): To a vial containing cyclohexanone (0.23 mL, 2.19 mmol), and 1.0 mL of dry isopropyl alcohol was added

catalyst pyrrolidine sulfonamide **1** (10 mg, 0.044 mmol) at 0°C. The mixture was vigorously stirred for 15 min, and then *trans-b*–nitrostyrene (33 mg, 0.219 mmol) was added. After 10 h stirring, TLC analysis indicated completion of the reaction. After reaction mixture was concentrated under reduced pressure, the resulting residue was then purified by silica gel chromatography (ethyl acetate/hexane = 1/30 to 1/5) and fractions were collected and concentrated *in vacuo* to provide a white solid (52 mg, 0.210 mmol, 96%). Relative and absolute configurations of the product were determined by comparison with the known ^{1}H NMR, ^{13}C NMR and optical rotation values.



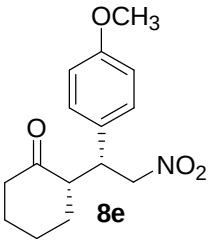
8a

(*S*)-2-[(*R*)-2-Nitro-1-phenylethyl]cyclohexanone (8a)[4](Table 3, entry 1): The title compound was prepared according to the typical procedure, as described above in 96% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 25/75, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 7.9 min, t_{major} = 12.2 min, ee = 97%, dr = 50:1; $[\alpha]^{25}_{D}$ (major) = -17.3 (*c* = 2.0 in $CHCl_3$).



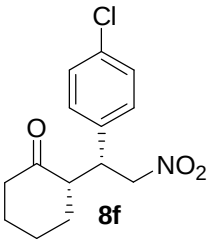
8d

(*S*)-2-((*R*)-2-Nitro-1-p-tolylethyl)cyclohexanone (8d)[9] (Table 3, entry 4): The title compound was prepared according to the typical procedure, as described above in 84% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 25/75, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 6.2 min, t_{major} = 11.2 min, ee = 97%, dr = 50:1; $[\alpha]^{25}_{D}$ (major) = -21.6 (*c* = 1.5 in $CHCl_3$).



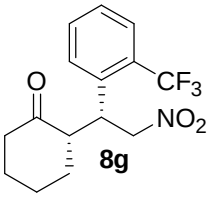
8e

(*S*)-2-((*R*)-1-(4-Methoxyphenyl)-2-nitroethyl)cyclohexanone (8e)[8] (Table 3, entry 5): The title compound was prepared according to the typical procedure, as described above in 92% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 25/75, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 14.5 min, t_{major} = 20.0 min, ee = 98%, dr = 50:1; $[\alpha]^{25}_{D}$ (major) = -27.6 (*c* = 0.9 in $CHCl_3$).



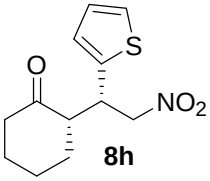
8f

(*S*)-2-((*R*)-1-(4-Chlorophenyl)-2-nitroethyl)cyclohexanone (8f)[9] (Table 3, entry 6): The title compound was prepared according to the typical procedure, as described above in 83% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 25/75, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 8.5 min, t_{major} = 13.8 min, ee = 99%, dr = 50:1; $[\alpha]^{25}_{D}$ (major) = -20.8 (*c* = 0.9 in $CHCl_3$).



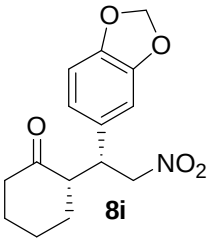
8g

(*S*)-2-((*R*)-1-(2-(Trifluoromethyl)phenyl)-2-nitroethyl)cyclohexanone (8g)[10] (Table 3, entry 7): The title compound was prepared according to the typical procedure, as described above in 70% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 10/90, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 9.5 min, t_{major} = 11.2 min, ee = 88%, dr = 50:1; $[\alpha]^{25}_{D}$ (major) = -13.3 (*c* = 0.6 in $CHCl_3$).



8h

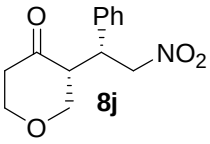
(*S*)-2-((*S*)-2-Nitro-1-(thiophen-2-yl)ethyl)cyclohexanone (8h)[8] (Table 3, entry 8): The title compound was prepared according to the typical procedure, as described above in 79% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 25/75, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 10.3 min, t_{major} = 13.9 min, ee = 86%, dr = 30:1; $[\alpha]^{25}_{D}$ (major) = -22.5 (*c* = 1.2 in $CHCl_3$).



8i

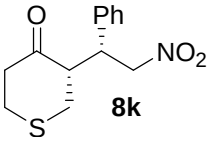
(*S*)-2-((*R*)-1-(Benzo[d][1,3]dioxol-6-yl)-2-nitroethyl)cyclohexanone (8i)[11] (Table 3, entry 9): The title compound was prepared according to the typical procedure, as described above in 91% yield.

HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 25/75, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 25.1 min, t_{major} = 32.6 min, ee = 98%, dr = 50:1; $[\alpha]^{25}_D$ (major) = -17.1 (*c* = 1.0 in $CHCl_3$).



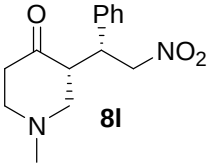
8j

(*R*)-Tetrahydro-3-((*R*)-2-nitro-1-phenylethyl)pyran-4-one (8j) (Table 3, entry 10): The title compound was prepared according to the typical procedure, as described above in 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d = 7.36-7.24 (m, 3H), 7.22-7.15 (m, 3H), 4.93 (dd, ^3J(H, H) = 12.5 Hz, ^2J(H, H) = 5.0 Hz, 1H), 4.64 (dd, ^3J(H, H) = 12.5 Hz, ^2J(H, H) = 10.0 Hz, 1H), 4.18-4.04 (m, 1H), 3.88-3.73 (m, 2H), 3.69 (dd, ^3J(H, H) = 11.5 Hz, ^2J(H, H) = 5.5 Hz, 1H), 3.27 (dd, ^3J(H, H) = 11.5 Hz, ^2J(H, H) = 9.0 Hz, 1H), 2.92-2.84 (m, 1H), 2.73-2.61 (m, 1H), 2.60-2.53 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 207.3, 136.2, 129.2, 128.4, 127.9, 78.7, 71.5, 68.9, 53.2, 42.9, 41.3; HPLC (Chiralpak AD, *i*-Propanol/Hexane = 15/85, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 13.3 min, t_{major} = 23.7 min, ee = 98%, dr = 50:1; $[\alpha]^{25}_D$ (major) = -27.5 (*c* = 0.8 in $CHCl_3$); HRMS (EI) calcd for $C_{13}H_{15}NO_4 + Na^+$ 272.2625, obsd 272.2610.



8k

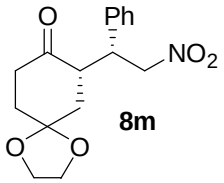
(*S*)-Tetrahydro-3-((*R*)-2-nitro-1-phenylethyl)thiopyran-4-one (8k)[8] (Table 3, entry 11): The title compound was prepared according to the typical procedure, as described above in 95% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 50/50, flow rate 0.5 mL/min, ? = 254 nm): t_{minor} = 18.6 min, t_{major} = 23.9 min, ee = 97%, dr = 30:1; $[\alpha]^{25}_D$ (major) = -9.2 (*c* = 1.0 in $CHCl_3$); $[\alpha]^{25}_D$ (major) = -22.0 (*c* = 0.8 in $CHCl_3$).



8l

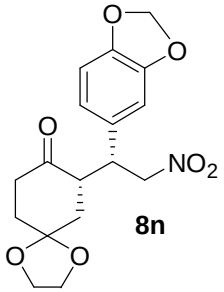
(*R*)-1-Methyl-3-((*R*)-2-nitro-1-phenylethyl)piperidin-4-one (8l) (Table 3, entry 12): The title compound was prepared according to the typical procedure, as described above in 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d = 7.36-7.15 (m, 5H), 4.92 (dd, ^3J(H, H) = 12.5 Hz, ^2J(H, H) = 4.5 Hz, 1H), 4.62 (dd, ^3J(H, H) = 12.5 Hz, ^2J(H, H) = 10.5 Hz, 1H), 3.91-3.82 (m, 1H), 2.98-2.86 (m, 2H), 2.72-2.61 (m, 1H), 2.57-2.46 (m, 3H), 2.23 (s, 3H), 2.04 (dd, ^3J(H, H) = 11.0 Hz, ^2J(H, H) = 10.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 209.4, 137.0, 129.1, 128.1, 78.8, 59.8, 56.2, 51.5, 45.0, 42.4, 41.4; HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 20/80, flow rate 0.8 mL/min, ? = 254 nm): t_{minor} = 14.8 min,

t_{major} = 16.3 min, ee = 96%, dr = 50:1; $[\alpha]^{25}_D$ (major) = -20.7 (*c* = 0.8 in $CHCl_3$); HRMS (EI) calcd for $C_{14}H_{18}N_2O_3 + Na^+$ 285.1209, obsd 285.1222.



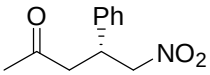
8m

(*S*)-2-[(*R*)-2-Nitro-1-phenylethyl]-4-[1,3-dioxolane]-cyclohexanone (8m) (Table 3, entry 13): The title compound was prepared according to the typical procedure, as described above in 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d 7.36-7.10 (m, 5H), 4.93 (dd, ^3J(H, H) = 12.5 Hz, ^2J(H, H) = 4.5 Hz, 1H), 4.61 (dd, ^3J(H, H) = 12.5 Hz, ^2J(H, H) = 10.0 Hz, 1H), 4.01-3.75 (m, 5H), 3.10-2.98 (m, 1H), 2.75-2.63 (m, 1H), 2.46 (dt, ^3J(H, H) = 13.5 Hz, ^2J(H, H) = 4.5 Hz, 1H), 2.08-2.00 (m, 1H), 2.00-1.91 (m, 1H), 1.71-1.63 (m, 1H), 1.59-1.51 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 201.3, 137.2, 128.9, 128.2, 127.8, 107.0, 78.9, 64.7, 64.5, 48.1, 43.4, 39.2, 38.5, 35.0; HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 40/60, flow rate 0.8 mL/min, ? = 254 nm): t_{minor} = 9.3 min, t_{major} = 14.3 min, ee = 95%, dr = 50:1; $[\alpha]^{25}_D$ (major) = -16.5 (*c* = 1.0 in $CHCl_3$); HRMS (EI) calcd for $C_{16}H_{19}NO_5 + Na^+$ 328.1155, obsd 328.1137.



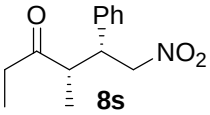
8n

(*S*)-2-((*R*)-1-(Benzo[d][1,3]dioxol-6-yl)-2-nitroethyl)-4-[1,3-dioxolane]-cyclohexanone (8n) (Table 3, entry 14): The title compound was prepared according to the typical procedure, as described above in 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d = 6.72-6.56 (m, 5H), 5.90 (d, ^3J(H, H) = 3.5 Hz, 2H), 4.86 (dd, ^3J(H, H) = 12.5 Hz, ^2J(H, H) = 4.5 Hz, 1H), 4.50 (dd, ^3J(H, H) = 12.0 Hz, ^2J(H, H) = 10.0 Hz, 1H), 3.96-3.80 (m, 4H), 3.75-3.66 (m, 1H), 2.98-2.90 (m, 1H), 2.69-2.60 (m, 1H), 2.46-2.37 (m, 1H), 2.05-1.96 (m, 1H), 1.96-1.86 (m, 1H), 1.74-1.66 (m, 1H), 1.54(t, *J* = 14.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 210.3, 148.1, 147.1, 130.8, 121.6, 108.6, 108.2, 107.0, 101.0, 78.9, 64.7, 64.5, 48.2, 43.2, 39.3, 38.5, 34.9; HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 40/60, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 17.4 min, t_{major} = 23.1 min, ee = 99%, dr = 50:1; $[\alpha]^{25}_D$ (major) = -4.0 (*c* = 0.5 in $CHCl_3$); HRMS (EI) calcd for $C_{17}H_{19}NO_7 + Na^+$ 372.1054, obsd 372.1059.



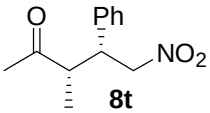
8r

(*R*)-5-Nitro-4-phenylpentan-2-one (8r)[5] (Table 4, entry 1): The title compound was prepared according to the typical procedure, as described above in 96% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 15.8 min, t_{major} = 20.9 min, ee =55%; $[\alpha]^{25}_{D}$ (major) = -8.3 (*c* = 0.4 in $CHCl_3$).



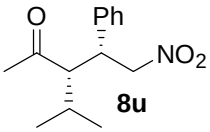
8s

(4*S*, 5*R*)-4-methyl-6-nitro-5-phenylhexan-3-one (8s)[7] (Table 4, entry 2): The title compound was prepared according to the typical procedure, as described above in 85% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 7.3 min, t_{major} = 9.4 min, ee =93%, dr = 50:1; $[\alpha]^{25}_{D}$ (major) = -32.5 (*c* = 0.8 in $CHCl_3$).



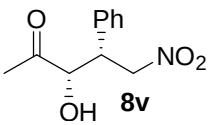
8t

(3*S*, 4*R*)-3-Methyl-5-nitro-4-phenylpentan-2-one (8t)[4] (Table 4, entry 3): The title compound was prepared according to the typical procedure, as described above in 47% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 10/90, flow rate 1.0 mL/min, ? = 254 nm): (major isomer) t_{minor} = 11.9 min, t_{major} = 15.1 min, ee =55%; (minor isomer): t_{minor} = 16.2 min, t_{major} = 20.9 min, ee =55%, dr = 1.1:1.



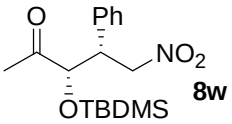
8u

(*S*)-4-Methyl-3-((*R*)-2-nitro-1-phenylethyl)pentan-2-one (8u) (Table 4, entry 4): The title compound was prepared according to the typical procedure, as described above in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d = 7.34-7.15 (m, 5H), 4.67 (dd, ^3J(H, H) = 12.5 Hz, ^2J(H, H) = 7.0 Hz, 1H), 4.59 (dd, ^3J(H, H) = 12.0 Hz, ^2J(H, H) = 7.5 Hz, 1H), 4.05-3.96 (m, 1H), 2.90-2.77 (m, 2H), 2.27-2.14 (m, 2H), 2.11-2.01 (m, 1H), 0.84 (d, ^3J(H, H) = 1.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 207.4, 139.0, 129.0, 127.8, 127.4, 79.5, 52.3, 45.8, 39.1, 24.5, 22.4, 22.3; HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 10/90, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 9.5 min, t_{major} = 13.3 min, ee =77%, dr = 50:1; $[\alpha]^{25}_{D}$ (major) = -6.5 (*c* = 1.0 in $CHCl_3$); HRMS (EI) calcd for $C_{14}H_{19}NO_3 + Na^+$ 249.1359, obsd 249.1349.



8v

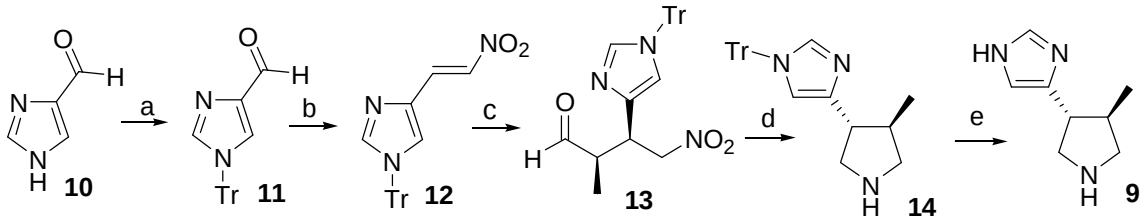
(3*S*, 4*R*)-3-Hydroxy-5-nitro-4-phenylpentan-2-one (8v)[6] (Table 4, entry 5): The title compound was prepared according to the typical procedure, as described above in 46% yield. HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 10/90, flow rate 1.0 mL/min, ? = 254 nm): (major isomer) t_{minor} = 24.1 min, t_{major} = 63.5 min, ee = 46%; (minor isomer): t_{minor} = 25.9 min, t_{major} = 31.8 min, ee = 7%; dr = 3:1.



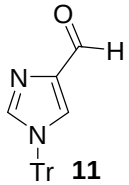
8w

(3*S*, 4*R*)-3-*tert*-Butyldimethylsilaneoxy-5-nitro-4-phenylpentan-2-one (8w) (Table 4, entry 6): The title compound was prepared according to the typical procedure, as described above in 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$): d = 7.35-7.20 (m, 5H), 4.83-4.72 (m, 1H), 4.72-4.62 (m, 1H), 4.35-4.28 (m, 1H), 3.86-3.79 (m, 1H), 1.74 (s, 3H), 0.94 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): d = 210.4, 134.7, 129.0, 128.7, 128.3, 79.1, 76.3, 47.2, 26.3, 25.7, 18.0, -4.9, -5.5; HPLC (Chiralpak AS-H, *i*-Propanol/Hexane = 20/80, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 6.9 min, t_{major} = 11.5 min, ee =86%, dr = 14:1; $[\alpha]^{25}_D$ (major) = -11.8 (*c* = 0.5 in $CHCl_3$); HRMS (EI) calcd for $C_{17}H_{27}NO_4Si + Na^+$ 360.1601, obsd 360.1587.

Procedures for total synthesis of Sch 50971 (9).



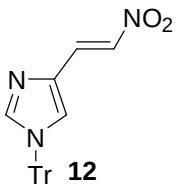
Conditions: (a) TrCl, TEA, CH_2Cl_2, RT, 95%; (b) CH_3NO_2, Piperidine, CH_3COOH, RT, 79%; (c) Propionaldehyde, *i*PrOH/CH_2Cl_2, 20 mol% catalyst, 0ºC, 78%; (d) 20% $Pd(OH)_2$, MeOH, 45 Psi, RT, 65%; (e) 95% CF_3COOH, 3h, 91%.



11

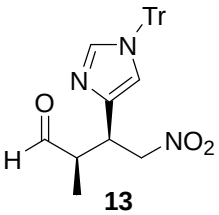
1-(1,1-Diphenylethyl)-1H-imidazole-4-carbaldehyde (11):[12] To a solution of 1*H*-imidazole-4-carbaldehyde **10** (0.5 g, 5.2 mmol) and triethylamine (0.87 mL, 6.3 mmol) in 15 mL of dichloromethane was added chlorotriphenylmethane (1.73g, 6.3 mmol) at room temperature and the reaction mixture was stirred for 14 h. After reaction mixture was concentrated under reduced pressure,

the resulting residue was then purified by silica gel chromatography (ethyl acetate/hexane = 1/10 to 1/2) and fractions were collected and concentrated *in vacuo* to provide a white solid (1.67 g, 95%).



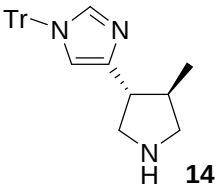
12

4-((*E*)-2-Nitrovinyl)-1-(1,1-diphenylethyl)-1H-imidazole (12):[12] To a solution of 1-(1,1-diphenylethyl)-1H-imidazole-4-carbaldehyde (**11**) (0.2 g, 0.59 mmol) in 3 mL of nitromethane was added 1 drop of piperidine and 1 drop of acetic acid at room temperature and the reaction mixture was stirred for 8 h. After reaction mixture was concentrated under reduced pressure, the resulting residue was then purified by silica gel chromatography (ethyl acetate/hexane = 1/10 to 1/3) and fractions were collected and concentrated *in vacuo* to afford a pale solid (178 mg, 79%).



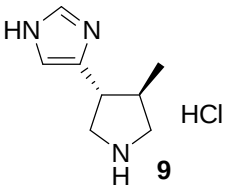
13

(2*R*, 3*R*)-2-Methyl-4-nitro-3-(1-trityl-1H-imidazol-4-yl)butanal (13): To a solution of 4-((*E*)-2-nitrovinyl)-1-(1,1-diphenylethyl)-1H-imidazole (**12**) (38 mg, 0.1 mmol) and propionaldehyde (73 μL, 1.0 mmol) in 0.5 ml of dichloromethane and 0.5 mL of isopropanol was added catalyst **I** (4 mg, 0.02 mmol) at 0 °C and the reaction mixture was stirred for 24 h. After reaction mixture was concentrated under reduced pressure, the resulting residue was then purified by silica gel chromatography (ethyl acetate/hexane = 1/10 to 1/3) and fractions were collected and concentrated *in vacuo* to afford a white solid (34 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 9.72 (s, 1H), 7.39 (s, 1H), 7.36-7.30 (m, 9H), 7.11-7.06 (m, 6H), 6.63 (s, 1H), 4.80 (dd, ^{3}J(H, H) = 12.0, 8.5 Hz, 1H), 4.72 (dd, ^{3}J(H, H) = 12.0 Hz, 5.5 Hz, 1H), 3.88 (dd, ^{3}J(H, H) = 15.0 Hz, 7.5 Hz, 1H), 2.87-2.78 (m, 1H), 1.05 (d, ^{3}J(H, H) = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.5, 142.1, 139.1, 136.5, 129.6, 128.1, 128.0, 75.4, 47.4, 37.5, 11.1; HRMS (EI) calcd for $C_8H_{10}N_3O_3 + Na^+$ 219.0620, obsd 219.0626; HPLC (Chiralpak AD, *i*-Propanol/Hexane = 10/90, flow rate 1.0 mL/min, ? = 254 nm): t_{minor} = 28.3 min, t_{major} = 22.1 min, ee = 99%, dr = 12:1 (after further silica gel column purification, dr was improve ed to 20:1; $[\alpha]^{25}_{D}$ (major) = +44.4 (*c*=0.8 in $CHCl_3$).



14

4-((3*R*, 4*R*)-4-Methylpyrrolidin-3-yl)-1-trityl-1H-imidazole (14):[13] To a solution of (2*R*, 3*R*)-2-methyl-4-nitro-3-(1-trityl-1H-imidazol-4-yl)butanal (**13**) (70 mg, 0.16 mmol) in 10 mL of methanol was added 20% $Pd(OH)_2$ (21 mg, 30%) and the reaction mixture was reductively cyclized at 45 psi for 96 h. After reaction mixture was concentrated under reduced pressure, the resulting residue was then purified by silica gel chromatography (methanol/dichloromethane = 1/5) and fractions were collected and concentrated *in vacuo* to afford a clear solid (41 mg, 65%).



9

4-((3*R*, 4*R*)-4-Methylpyrrolidin-3-yl)-1H-imidazole (9) (Sch 50971):[13] 5 ml of 95% CF_3COOH was added to 4-((3*R*, 4*R*)-4-methylpyrrolidin-3-yl)-1-trityl-1H-imidazole (**14**) (70 mg, 0.18 mmol) and the reaction mixture was stirred for 96 h. After reaction mixture was concentrated under reduced pressure, *1N* HCl (4 mL) was added to the reaction mixture and products were extracted with Et_2O (3 × 10 mL). The aqueous phase was concentrated under reduced pressure to afford a white solid (22 mg, 91%). $[\alpha]^{25}_D$ (major) = +36.1 (*c* = 0.6 in MeOH), lit.[13] $[\alpha]^{25}_D$ (major) = +43.5 (*c*= 0.34 in MeOH).

I. Stationary point geometries for the Michael addition reaction of propanal to *trans*-β-nitrostyrene catalyzed by organocatalyst (*S*)-pyrrolidine sulfonamide 1.

A: Reactant Complex (RC) (*si* face)

O .000000000000 .000000000000 .000000000000

N .000000000000 .000000000000 2.860979760000

H .219178305514 .000000000000 1.858759828331

C .427578016949 1.124341139423 3.698571529115

C .069720346894 2.482760865078 3.066734360946

H .462423290012 2.494718820307 2.036008089859

N -1.361103550787 2.794433589891 3.077817816396

C .700192784948 3.628659491035 3.886842263306

C -2.262644108406 2.167933957903 2.232067954422

C -1.647544462566 4.101621371705 3.665157121967

C -.279032606236 4.796748005507 3.712472384226

H -2.369443788101 4.641261288081 3.039440535051

H -2.089778289504 4.007531681348 4.669321448932

H -.205087197465 5.540062932902 4.512436752535

H -.089796582271 5.307317118031 2.760839517035

H .755573967473 3.339113975220 4.944764477619

H 1.716537960151 3.857354176722 3.552930543350

C -1.377577159835 .228917566345 -2.329663484974

C -.309679151108 1.003665965353 -2.057377000855

N .329586634393 .916787478392 -.776681111553

H -.069019362255 1.030555261534 4.666880411443

H 1.514208855735 1.079443001254 3.855630277457

S -.679630322641 -1.365828954254 3.419812507165

O -1.356077709609 -2.032037479065 2.302519889577

H .144544766244 1.758720056473 -2.682927432297

O -1.334240979342 -1.117627653704 4.698627363804

C .769404866767 -2.476740423760 3.818765418638

F 1.560821075135 -1.857029353019 4.705712274674

F .343089345065 -3.627745200997 4.336686097886

F 1.472243149968 -2.721931036376 2.709193647897

C -2.144278424340 .204941278065 -3.566077088495

C -1.836897057317 .992888488621 -4.694034569123

C -3.250726645097 -.665722388189 -3.625356901189

C -2.614602995523 .910681615158 -5.842185169458

H -.986984532214 1.668851187944 -4.671246188341

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H -3.484654310317 -1.272530106492 -2.754661767272

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O 1.183534759138 1.766577154253 -.507827579751

C -3.578270217893 2.424774533746 2.105890708669

H -4.056207090045 3.171093325649 2.737468801201

H -1.819012732513 1.382797541205 1.625363464891

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H -2.322113555036 -1.691889757275 .593534054071

C -4.458305476781 1.693932395635 1.129844418128

H -5.307030206205 1.206133141771 1.632299862616

H -4.891963274498 2.365609795178 .373922715380

H -3.895616184353 .919757447407 .594075729296

H -1.728597298046 -.434467365348 -1.539864745430

B: Transition State (TS) (*si* face)

O .000000000000 .000000000000 .000000000000

N .000000000000 .000000000000 2.787591550000

H .254942783947 .000000000000 1.783159113752

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H -.424791082480 2.199359544509 1.575183179179

N -2.381331433945 1.551558784501 1.227563391576

C -1.881930323525 3.314288605954 2.710435607936

C -2.632132899611 .299213333003 .863933646255

C -3.179364411184 2.713330201870 .763344056917

C -2.546737097067 3.922635283730 1.468819493149

H -3.148316883379 2.799973562803 -.323787888582

H -4.222715251690 2.556490236304 1.065372035228

H -3.288364030743 4.690278060069 1.704807563858

H -1.783739759459 4.371973750152 .824713941214

H -2.620140433545 3.125630630588 3.501283520999

H -1.090857374510 3.944899935991 3.124771529400

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H -1.863806913905 .501116087936 3.669807194313

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S .469565498543 -1.271949028014 3.691155678045

O .934656239712 -2.341739742478 2.805247223625

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O -.497918527178 -1.496072406419 4.762191143566

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F 1.713773922638 .459204156532 5.234216650965

F 2.473260034747 -1.579388923019 5.381183882347

F 2.949742316005 -.362315399909 3.639913036771

C -2.942525521085 .103305441872 -2.972766098068

C -3.594549110503 1.271101381178 -3.403504435929

C -3.111913522197 -1.069428745399 -3.725942281576

C -4.377514877117 1.269421691649 -4.555435228122

H -3.490486591739 2.190033146083 -2.831449559781

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H -2.611959084334 -1.981173541672 -3.409836895903

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H -5.141914520694 .095687932868 -6.197811762101

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H -3.237798158857 -2.186562278732 .022647839533

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C: RC (*re* face)

O .000000000000 .000000000000 .000000000000

N .000000000000 .000000000000 2.848297230000

H .204443575597 .000000000000 1.840429198367

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C 4.079072774830 -1.345325384747 3.431648737327

H 3.905982531601 -3.005046122799 2.006458717631

H 3.795397312277 -1.406763973394 1.244750970793

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O -2.227515584606 .955760715213 2.182055383469

H 1.461949175206 .717234702172 -2.768327093783

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F -3.609986411211 -1.481387571635 3.414486234618

F -2.208303757635 -1.954014895345 1.813698631093

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H .678142721027 1.059524488637 -4.905149408207

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H -3.252803195079 .751490648606 -3.166717837116

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H -.328201797290 1.519164793470 -7.107300941939

H -4.265309679677 1.215559959683 -5.392906993050

H -2.798325108968 1.599875147375 -7.363183469961

H -1.463500179726 .428065793324 -1.771867801868

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C 1.633282214107 -3.402919261752 .387200820887

H 2.639929717446 -3.281956753126 -.007299032386

C .681241584233 -4.239951250749 -.420891483756

H -.304198545544 -4.295374571887 .057027552669

H .532871028271 -3.836690051106 -1.433543578484

H 1.043211466749 -5.270598176641 -.547454382734

H .263352675124 -2.903181095277 1.904323744843

H -2.926373079156 -.746656174360 -.236380950224

O -3.215280157475 .135371698986 -.516083933717

H -2.962079021171 .682415748228 .249108919660

D: TS (*re* face)

O .000000000000 .000000000000 .000000000000

N .000000000000 .000000000000 2.712895610000

H .281425001716 .000000000000 1.714977904921

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N -2.873151412910 .174935640711 1.628938651137

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C -4.078212031413 -.549285607868 1.168569733967

C -4.114562868894 -1.785941025211 2.064587430256

H -4.962274427734 .087641813429 1.322567022797

H -4.000050218932 -.783200098394 .108031049661

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H -5.117857343111 -2.213880915860 2.139328344656

H -3.217521086111 -2.033875356445 4.065746737156

H -4.380673527830 -.710615013406 3.934493842009

C -1.944153456452 .694201906893 -1.706646042114

C -1.714151911796 -.652485898160 -1.337474711420

N -.741364547495 -.961592247925 -.437400506662

H -1.015065799379 -1.771423816973 2.364285399760

H -.913067944602 -1.305101203157 4.073496994278

S 1.117268486352 .564523717564 3.758290400473

O 2.219457945520 1.109353065631 2.963109197200

H -2.302708597614 -1.496059735704 -1.666788879136

O 1.319797018627 -.339959597414 4.887313365640

C .281947386506 2.054839701037 4.519588107382

F -.829798673286 1.664012381115 5.172367090862

F 1.108023935794 2.636758064806 5.386060763856

F -.066446515245 2.936100784021 3.578622703865

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C -4.029205848126 .265428368091 -3.083370621802

C -2.438740743369 1.919065020132 -3.826324741587

C -4.815322028206 .516603365053 -4.205225083468

H -4.356198116613 -.476712133543 -2.359151516531

C -3.224012249849 2.170101728734 -4.952068848468

H -1.505552848486 2.458605741875 -3.688034719202

C -4.415243833398 1.470615501441 -5.145041457968

H -5.742880268029 -.031501585524 -4.346961250385

H -2.902223698778 2.912057591304 -5.677612943211

H -5.029559651425 1.666403620486 -6.019445347123

H -1.064831414818 1.328851142175 -1.658025418778
O -.586720786967 -2.134998238168 -.023597141307
C -2.861165216469 1.775650308153 -.205345359545
H -3.874204121571 1.484550517373 -.477361639700
C -2.504094656900 3.219200232223 -.511963074869
H -1.469458760189 3.435618594276 -.225075695389
H -2.628008225506 3.435421422735 -1.577943981103
H -3.157852431579 3.912437214419 .033180978308
H -1.546620723509 1.739235959039 1.510198534834
H .650851359943 1.840957307341 .151059964720
O .710044931148 2.674151537169 .649456703937
H 1.409877982179 2.502527387097 1.301155468837

II. Stationary point geometries for the Michael addition reaction of 3-pentanone to *trans*-b-nitrostyrene catalyzed by organocatalyst (*S*)-pyrrolidine sulfonamide 1.

A: RC (*si* face)

O .000000000000 .000000000000 .000000000000
N .000000000000 .000000000000 2.899705660000
H .131161264243 .000000000000 1.881583567799
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C 1.866229773084 1.584724096013 3.314134352806
H 2.028875814359 1.535081695577 2.222192356724
N 1.150300334868 2.811137206632 3.700858095551
C 3.239420057309 1.733177017172 4.019804876054
C -.113784285740 3.116261267263 3.053424623706
C 2.155913822349 3.880843068553 3.664124384064
C 3.373578469068 3.243355284005 4.346899719478
H 2.404509421651 4.179551493780 2.628602210948
H 1.783340759557 4.771119798279 4.180709798520
H 3.327350076492 3.403688197422 5.428365261335
H 4.315048292565 3.671300428598 3.988790520446
H 3.268864057739 1.134221916282 4.937059293895

H 4.043195383236 1.370172127582 3.371914155986
C -.979419725482 .764342860646 -2.418797781813
C .323001265394 .898142939080 -2.104372502312
N .774647515440 .584841869240 -.777438636290
H .819496317855 .396077788739 4.780829704784
H 1.883907157847 -.535230745876 3.701075014660
S -1.291507615825 -.850982029264 3.399374199433
O -2.304693297394 -.801377347000 2.340265228784
H 1.125009281372 1.274118997628 -2.723541625218
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C -.736069719466 -2.637787548443 3.435613069335
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F -1.731553650160 -3.428271440446 3.833526304998
F -.333935266363 -3.008795663573 2.215928181083
C -1.602934665465 1.058649981124 -3.700691765396
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C -3.002234436176 .918325138290 -3.788349250552
C -1.554126050871 1.728292689261 -6.035157952594
H .192610010881 1.574987225650 -4.801823945862
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H -3.461811925367 1.791753874944 -7.041802523581
O 1.925406926931 .919408705926 -.479158928122
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H -2.242369308736 3.956617330475 1.486095793037

H -1.650957075363 .435815790593 -1.626346917821

C -1.272224436370 3.214487748684 4.020178537417

H -1.383439416287 2.239699048943 4.514355040253

H -2.207880945866 3.395664004953 3.481177219493

C -1.084161773953 4.291985156798 5.100625841606

H -1.023316173222 5.293891528827 4.658850032560

H -1.923667519459 4.283736152884 5.804965661979

H -.165803726427 4.109745990065 5.667625384278

H -1.190438852708 4.280853991568 .102766017714

B: TS (*si* face)

O .000000000000 .000000000000 .000000000000

N .000000000000 .000000000000 2.759246560000

H .247440941127 .000000000000 1.749195751693

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H -.403587003057 2.172191983250 1.551917943635

N -2.370655782244 1.705925021939 1.035937251693

C -1.827532568706 3.310199105641 2.682957161486

C -2.832090873078 .553655191693 .505322903391

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H -1.362190600293 4.544327207638 .974613762589

H -2.677395370204 3.139490552334 3.356803871096

H -1.035725384215 3.806847318789 3.250463179925

C -1.763271115297 .403290912363 -2.040157753821

C -.767897146111 1.342176844955 -1.676549777567

N .062025065480 1.129555353231 -.622657955085

H -1.920233344020 .452884061778 3.570614893555

H -.616325467386 1.536013687830 4.040072324595

S .214340445328 -1.437918389861 3.513329873543

O .670356000204 -2.424013443751 2.532228535318

H -.637227689735 2.304712453533 -2.149580667731

O -.899125721878 -1.697193067972 4.426649483159

C 1.684527676204 -1.100695874722 4.614216309677

F 1.399257380495 -.063883423171 5.414903544080

F 1.939896312741 -2.175390407718 5.360284258262

F 2.754134029393 -.804431967137 3.878111788567

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H -2.664064824612 2.682214039891 -3.313760846602

C -3.078887874040 -.510577842028 -5.469904766694

H -2.244456168617 -1.573045947037 -3.791777772166

C -3.462241256277 .730134654112 -5.980471302832

H -3.608032662388 2.846387328179 -5.585426013156

H -3.193622282758 -1.407988709572 -6.071598008591

H -3.880125108783 .804760993909 -6.980569494703

O .848433942541 2.027327419943 -.228524150895

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H -3.720947501711 1.542182386868 -1.167676635055

H -.380916014246 -3.036219233779 .491188805380

O -.671218934527 -2.732216127732 -.384931194644

H -.249449956623 -1.855303821245 -.447454440749

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H -4.601871657219 -.409289668204 -2.299441747652

H -3.943076796969 -1.532891449420 -1.109317248072

H -1.565519819805 -.622655848455 -1.746365077439

C -2.778431005592 -.749370365428 1.264245898122

H -1.905235525326 -.797756682696 1.899452749247

H -2.651101544743 -1.572098608142 .557671170991

C -4.039695267856 -.959632596563 2.128644565721

H -4.950604007468 -1.026299172946 1.526305107441

H -3.938538656752 -1.890257209618 2.695850397696

H -4.173314068036 -.142812029642 2.847420589838

H -5.314227961509 -.495305755699 -.690556251487

C: RC (*re* face)

O .000000000000 .000000000000 .000000000000

N .000000000000 .000000000000 2.912647380000

H .164225045157 .000000000000 1.898885309179

C .270479516377 1.258807006149 3.627363046359

C 1.762832464800 1.427975778355 3.997450884860

H 2.037870022003 .626826431678 4.689249662118

N 2.674997719025 1.449592472707 2.855212489326

C 2.000195994635 2.821958364960 4.608917829724

C 3.117439845323 .320040971773 2.147244749337

C 2.676349845409 2.778545583444 2.246704956469

C 2.218375219284 3.733167789366 3.378913629648

H 3.685734972799 3.000530840757 1.878350010278

H 1.994505165935 2.844874599433 1.384687999125

H 1.290136382631 4.241147581330 3.097977903867

H 2.959440179723 4.512324190221 3.579598837655

H 1.172217698301 3.155796455815 5.243571159073

H 2.901870472835 2.788026854190 5.228589260468

C -1.642418787148 -.110673854963 -2.182235441921

C -1.195461687439 1.056286775978 -1.679802263462

N -.449453050163 1.069073527324 -.454476062959

H -.062736084377 2.088114287786 2.993510248570

H -.337004120425 1.272442234804 4.536020743432

S -1.206906628881 -1.016304936043 3.349967713955

O -1.746247106921 -1.654985917256 2.145446848233

H -1.381114647305 2.055458583904 -2.047548913060

O -2.070038022816 -.417927784390 4.364209340683

C -.288433614851 -2.372491279536 4.244895752239

F .438454740996 -1.839484327153 5.237608660396

F -1.158434465932 -3.242593879064 4.755911711280

F .530281063641 -3.008181617529 3.401901531264

C -2.439922714126 -.298724139638 -3.383998366820

C -2.798545053749 .745828250849 -4.260199083067

C -2.867299494794 -1.609423157359 -3.676450249446

C -3.562857175415 .483588932204 -5.390240752359

H -2.474661753258 1.762755143829 -4.057751062774

C -3.634472606984 -1.867355637287 -4.809785759676

H -2.589374975227 -2.413331538622 -2.999641614287

C -3.983392829898 -.822917910686 -5.667730084174

H -3.833252080887 1.295081965717 -6.059886187306

H -3.959236768445 -2.881539865600 -5.023472630661

H -4.581020179778 -1.022316982859 -6.552984423199

H -1.414657973163 -1.017513119238 -1.619651150704

O -.296917938333 2.163276069857 .099779252405

C 3.388643068234 .388503877521 .822747720483

H 3.150195758350 1.312685318805 .302977639705

C 4.017380494961 -.661851176000 -.050957124775

H 4.263610553734 -1.584605205265 .481287142965

H 3.351896472248 -.931940134585 -.883624496899

C 3.400527598967 -.904917695724 2.997799934562

H 2.514623334451 -1.175441928390 3.580927660270

H 3.586834043919 -1.760802322770 2.344964829021

C 4.598828751896 -.717876639879 3.944633877690

H 4.768868663650 -1.621664819291 4.541288558602

H 5.512090830309 -.506490019323 3.377516273650

H 4.438917122497 .118403484331 4.633616555606

H 4.948712791515 -.295584005372 -.507434728879

O -1.161012896440 -2.843090941014 -.528934058526

H -.254824456732 -2.504689152764 -.458618362191

H -1.551249717809 -2.559175231614 .317508644524

D: TS (*re* face)

O .000000000000 .000000000000 .000000000000

N .000000000000 .000000000000 2.750594490000

H .314701950122 .000000000000 1.764336149475

C -1.175262261394 -.812374165079 3.057869174684

C -2.517623127341 -.076818089347 2.829304170198

H -2.439689121140 .925338803648 3.250657677025

N -2.926637722611 .015481648042 1.390375089995

C -3.689692062894 -.858307099714 3.450850316928

C -2.666023892303 1.044307252861 .558867516986

C -3.950677161402 -1.016662876621 1.074009046989

C -4.079994222911 -1.852884421240 2.350598761447

H -4.896144134533 -.509725071383 .837412396761

H -3.652102388595 -1.606937214008 .207880901017

H -3.385515172158 -2.699217959516 2.329277856660

H -5.090113525090 -2.254108241784 2.470058661408

H -3.412421561239 -1.338520281462 4.393113367245

H -4.521535448073 -.174146118220 3.655893917554

C -1.848742358716 -.084297783528 -1.948439339453

C -1.391714817190 -1.245578304668 -1.292579201424

N -.450800600599 -1.165702351540 -.308678209263

H -1.117631154562 -1.722129407047 2.451920925315

H -1.120079137280 -1.103988439125 4.110192328241

S 1.117497986577 .426589270426 3.860135522605

O 2.383014163277 .675128890742 3.169049943669

H -1.751407867396 -2.246004260898 -1.483620253481

O 1.017064813260 -.408054630986 5.055392782984

C .528036021995 2.107441477971 4.431745578365

F -.738198176728 2.002657206367 4.881748887827

F 1.302343087699 2.546416875131 5.422389761150

F .550374806310 2.985868150827 3.427647714212

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C -3.648464036998 -1.226178610354 -3.313920063086

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C -4.339336519148 -1.397920842915 -4.511104839365

H -3.904509865798 -1.843427172986 -2.456332001661

C -3.022820099483 .353214157429 -5.523527934135

H -1.547472651013 1.273596139236 -4.254341554173

C -4.028051613981 -.609277865394 -5.621985292621

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H -2.771591134301 .970545522193 -6.381626273711

H -4.567128603124 -.743940884095 -6.555550965447

H -1.138525484585 .736960820589 -1.963152509452

O -.063908544303 -2.192813042332 .295017928150

C -3.185804651483 1.041437580151 -.766353514450

H -4.018761987954 .365875130656 -.936348311338

C -3.318440101068 2.342441797638 -1.534502624452

H -2.384847028720 2.913770478733 -1.562874339345

H -3.612056630140 2.138702710738 -2.567472922608

C -1.844895308680 2.209132198746 1.065002388460

H -1.093927340658 1.871695862087 1.774397136232

H -1.272966782176 2.628100528779 .235297661981

C -2.709090464062 3.311658295603 1.711471719637

H -2.055908016227 4.107981222753 2.081944117745

H -3.415611651288 3.754657788938 1.003044444229

H -3.286979590244 2.932319848658 2.562592923274

H -4.088707039484 2.994737037943 -1.103611142561

O 1.642712163346 2.246805174893 .638559239501

H 1.404792154227 1.446891140312 .141292274553

H 2.207033434369 1.908369113649 1.352852337584

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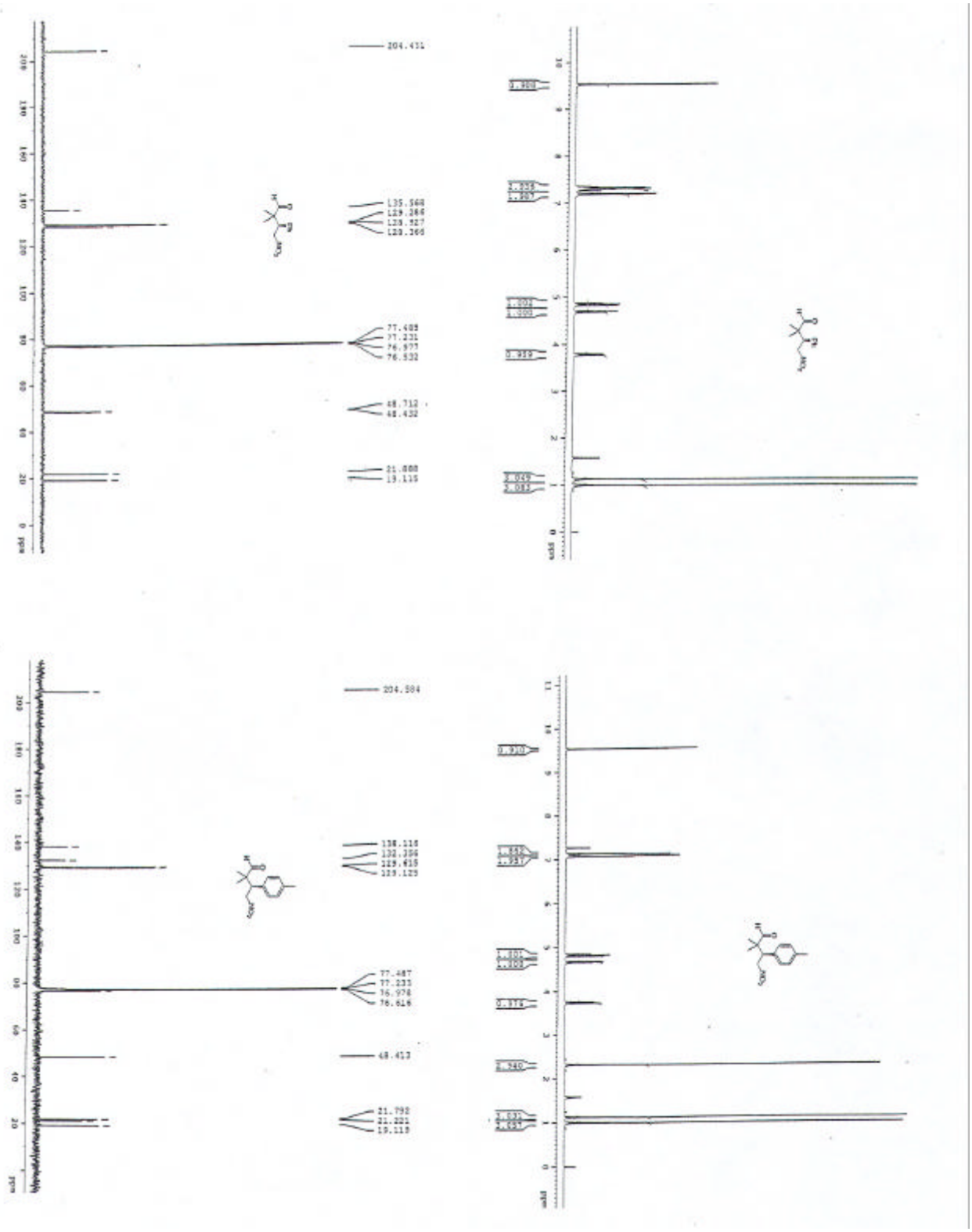

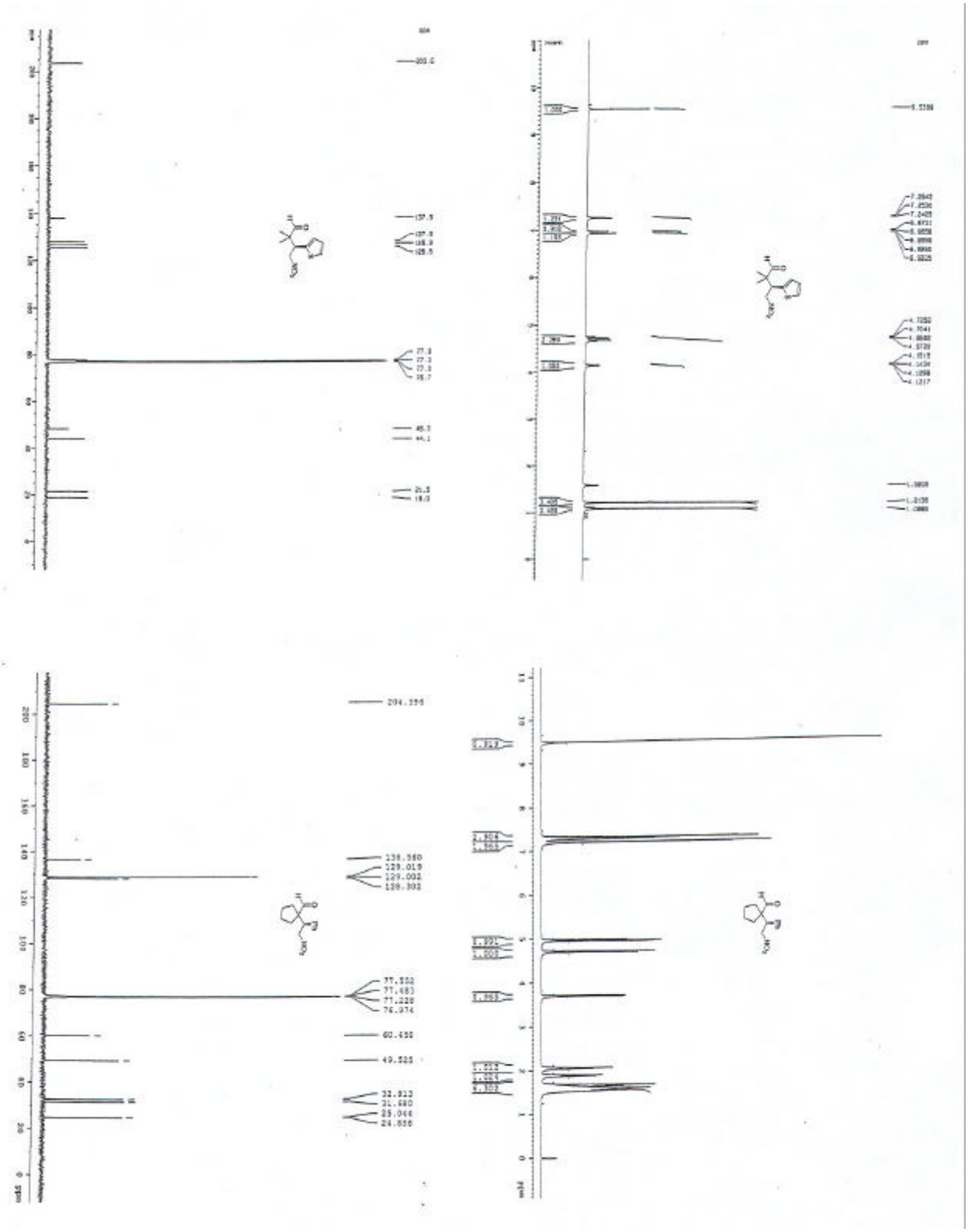

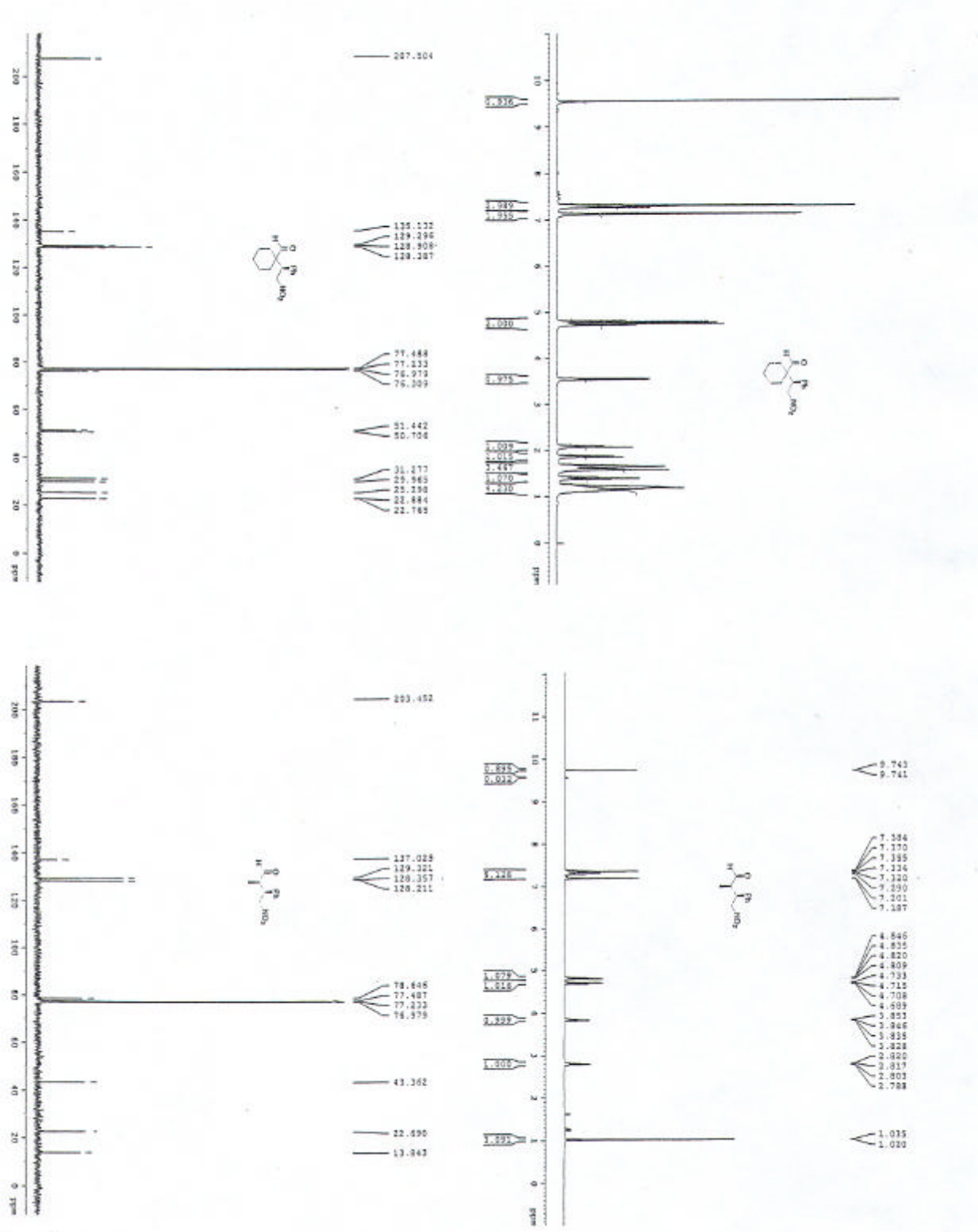

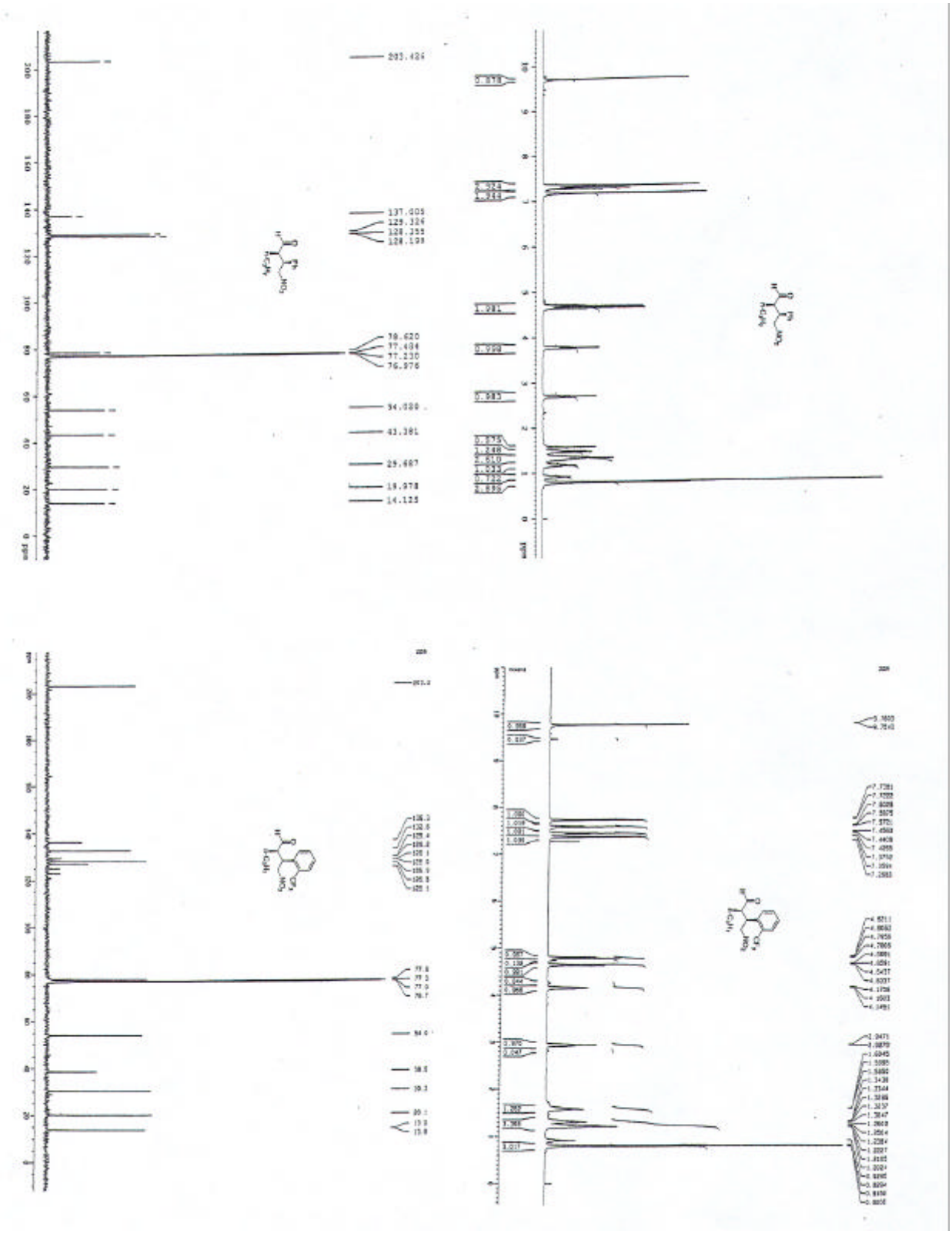

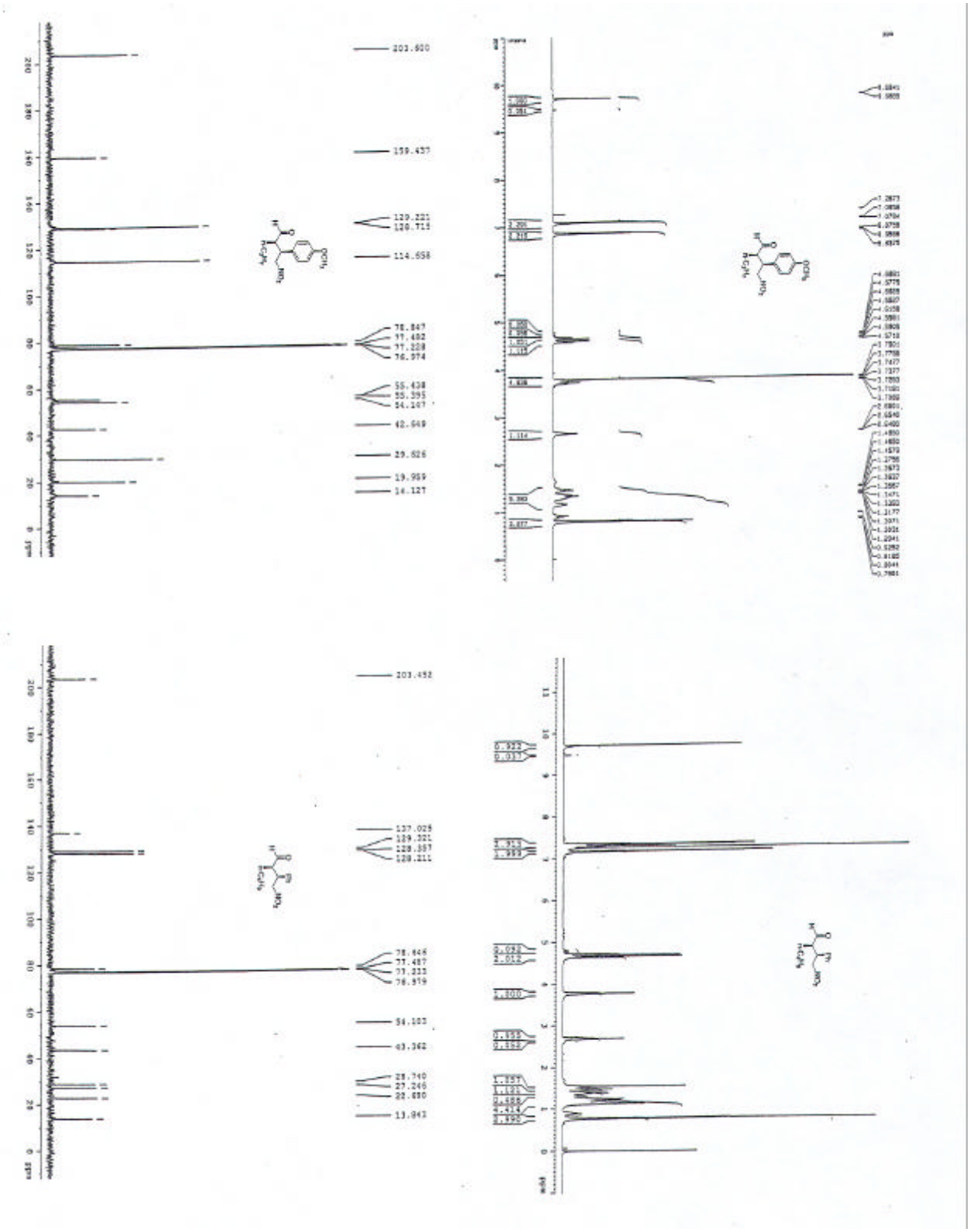

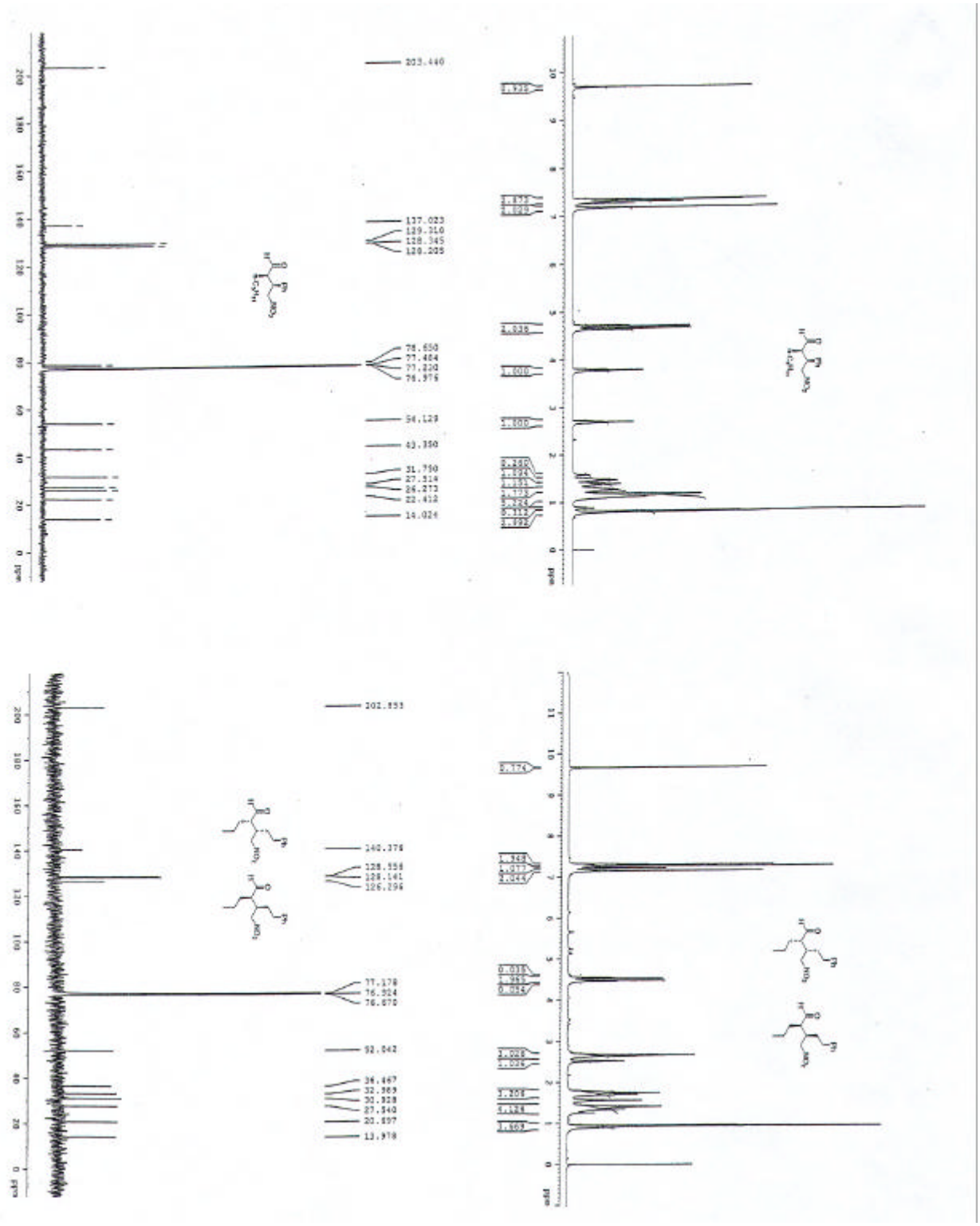

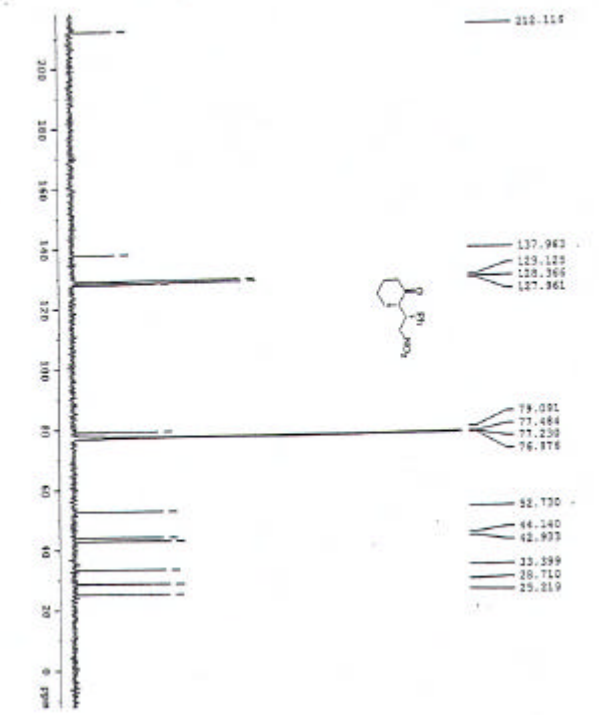

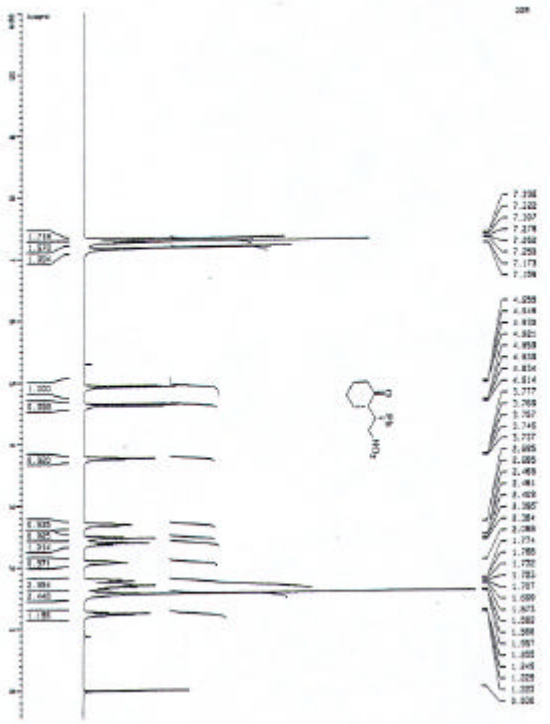

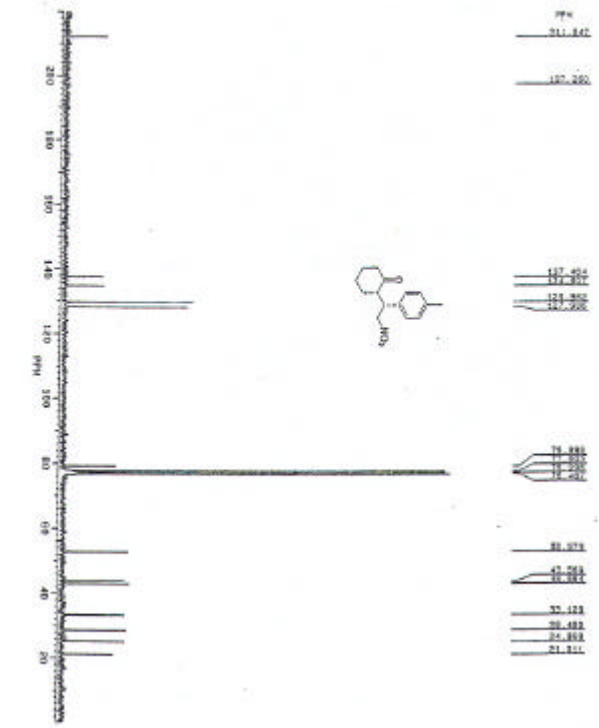

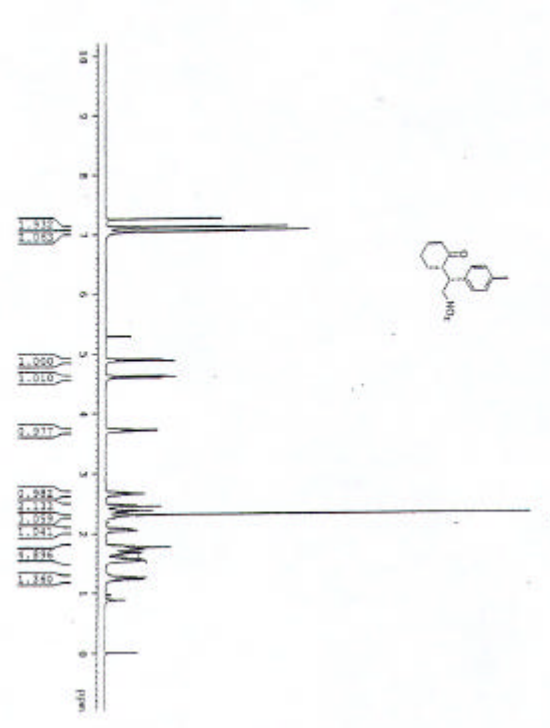

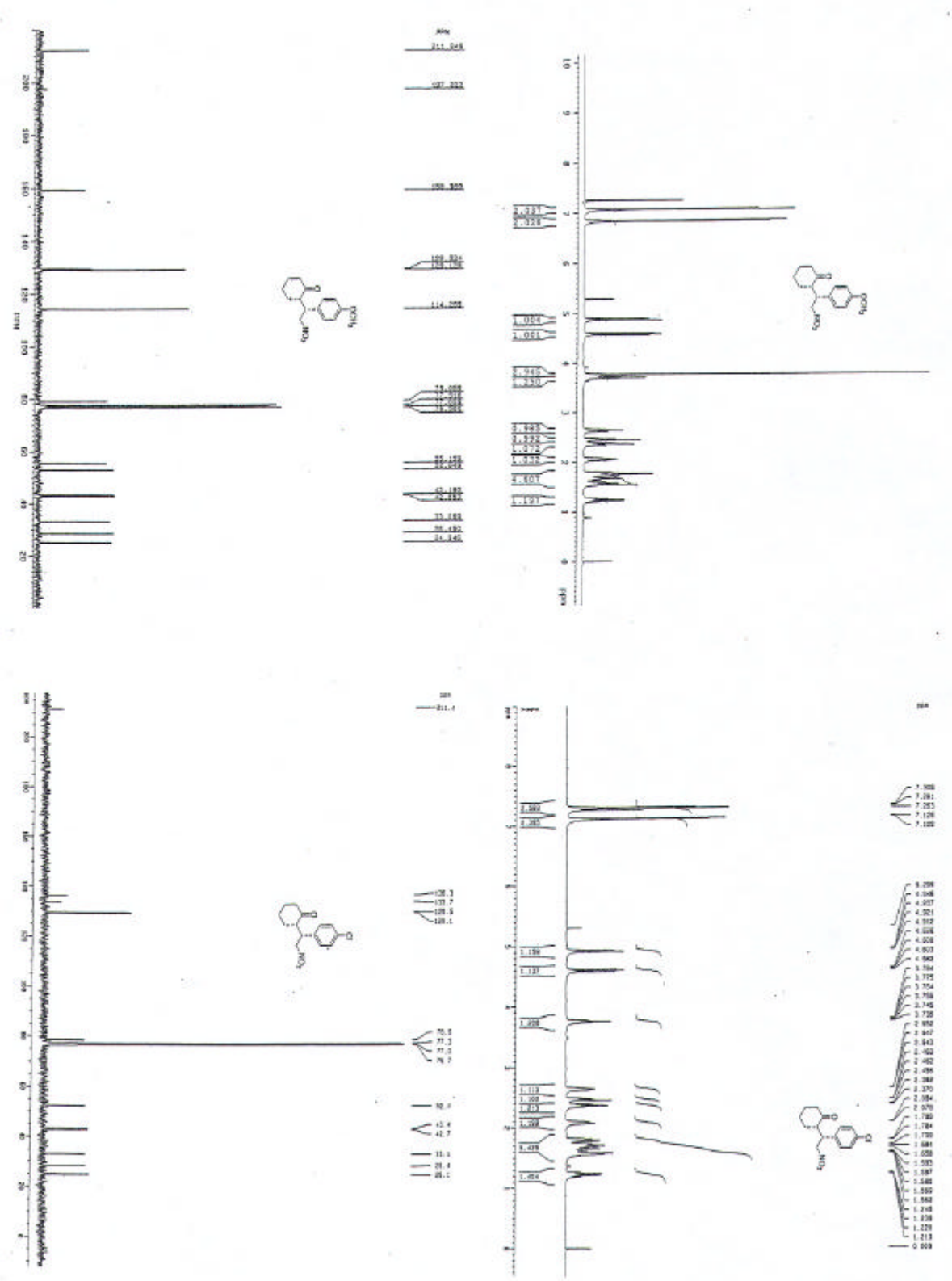

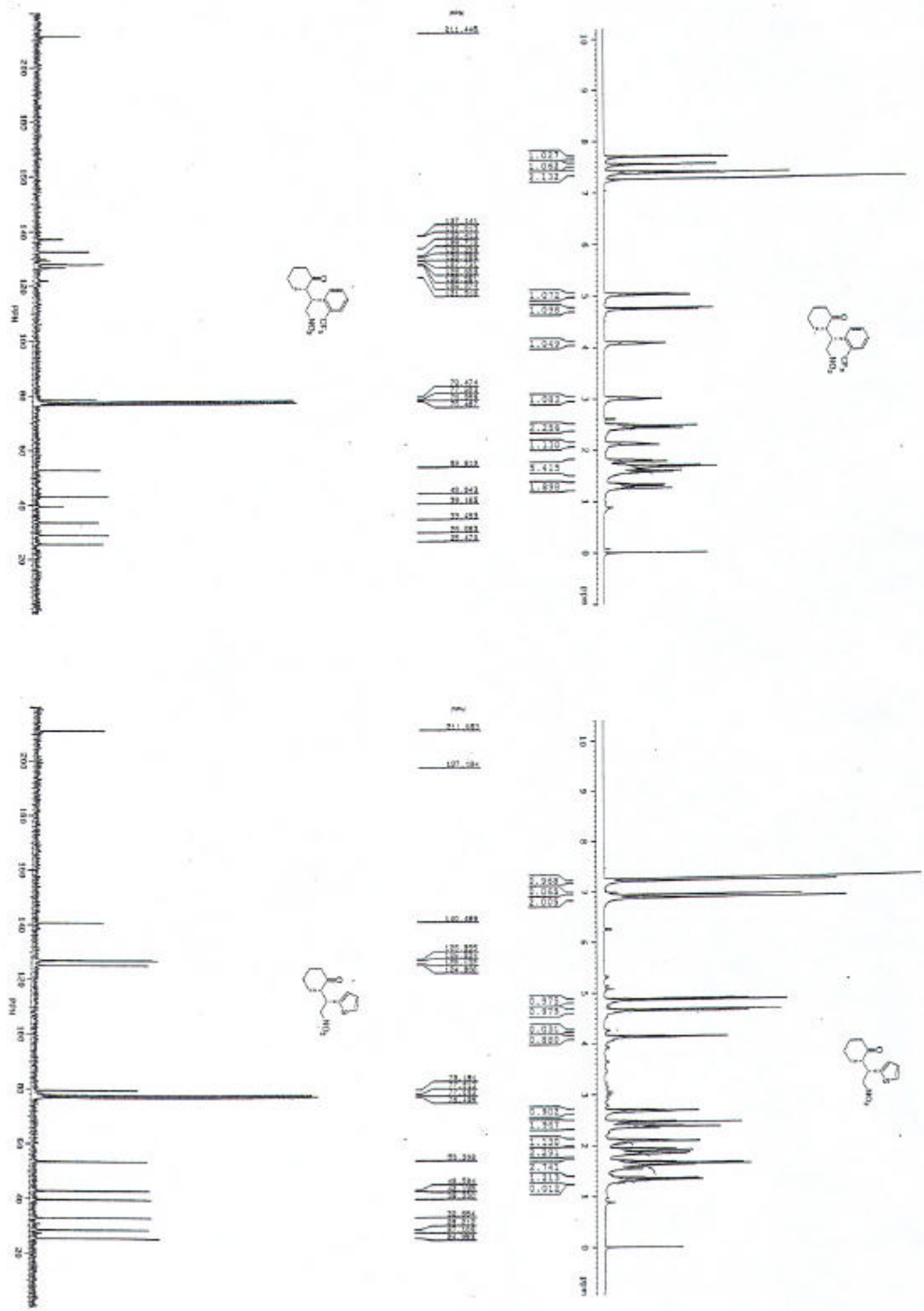

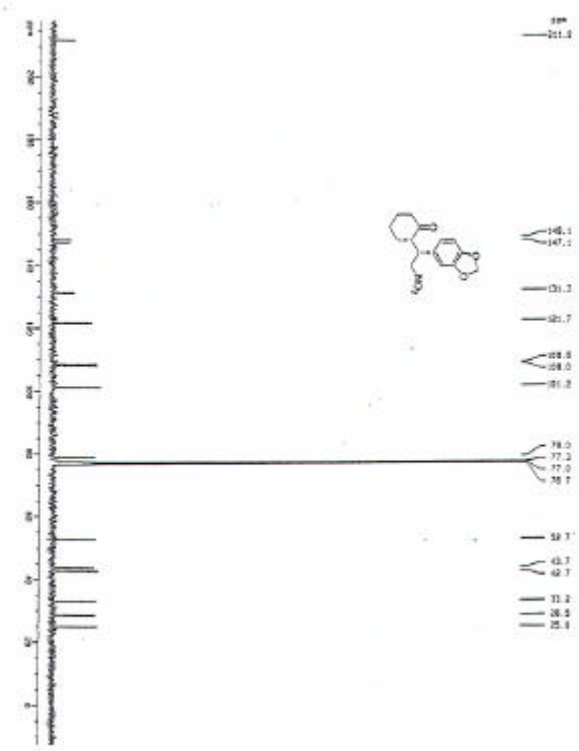

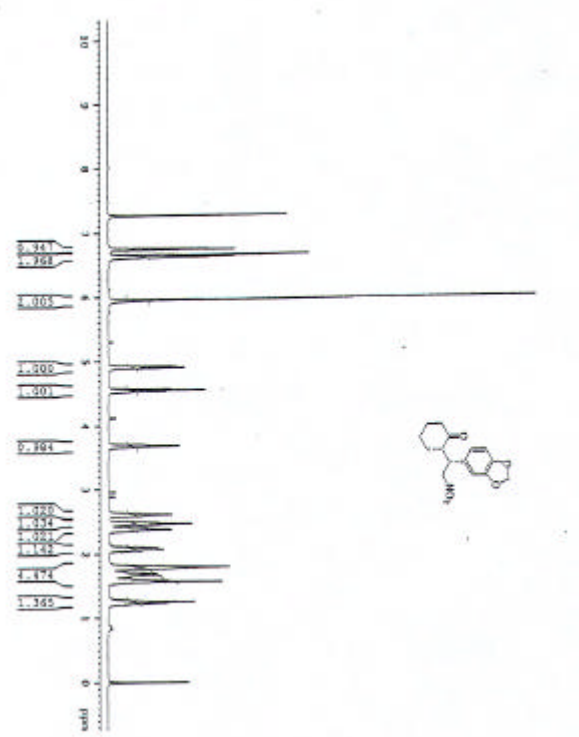

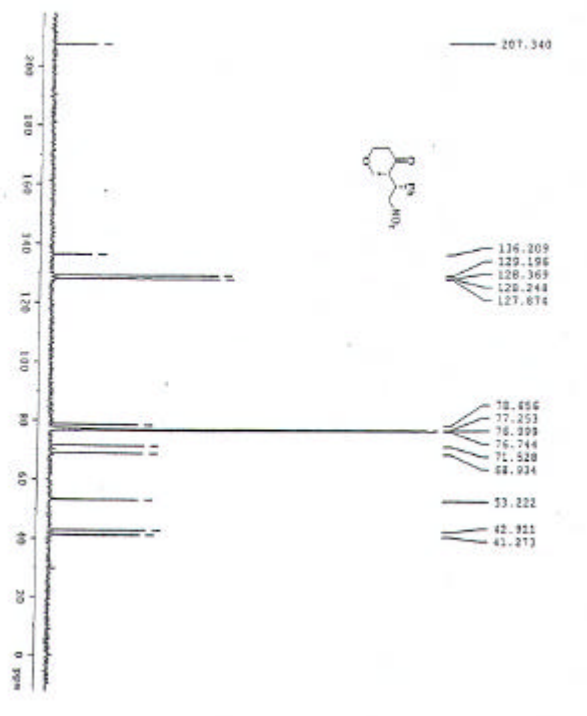

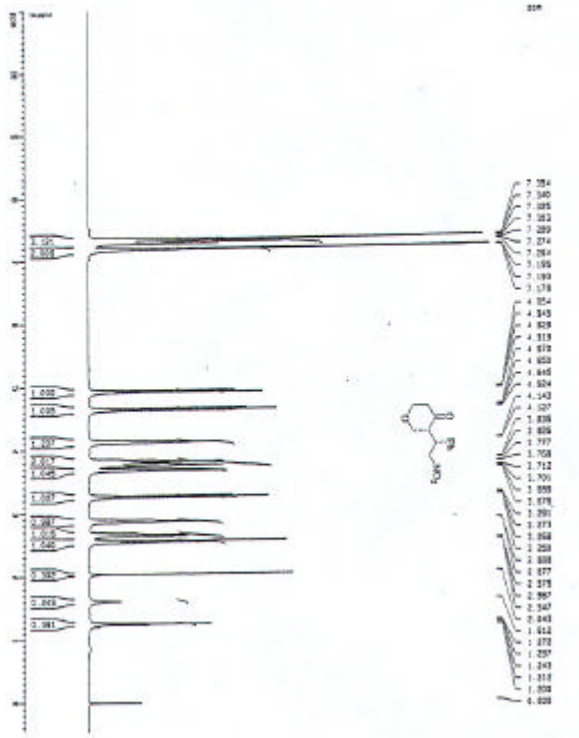

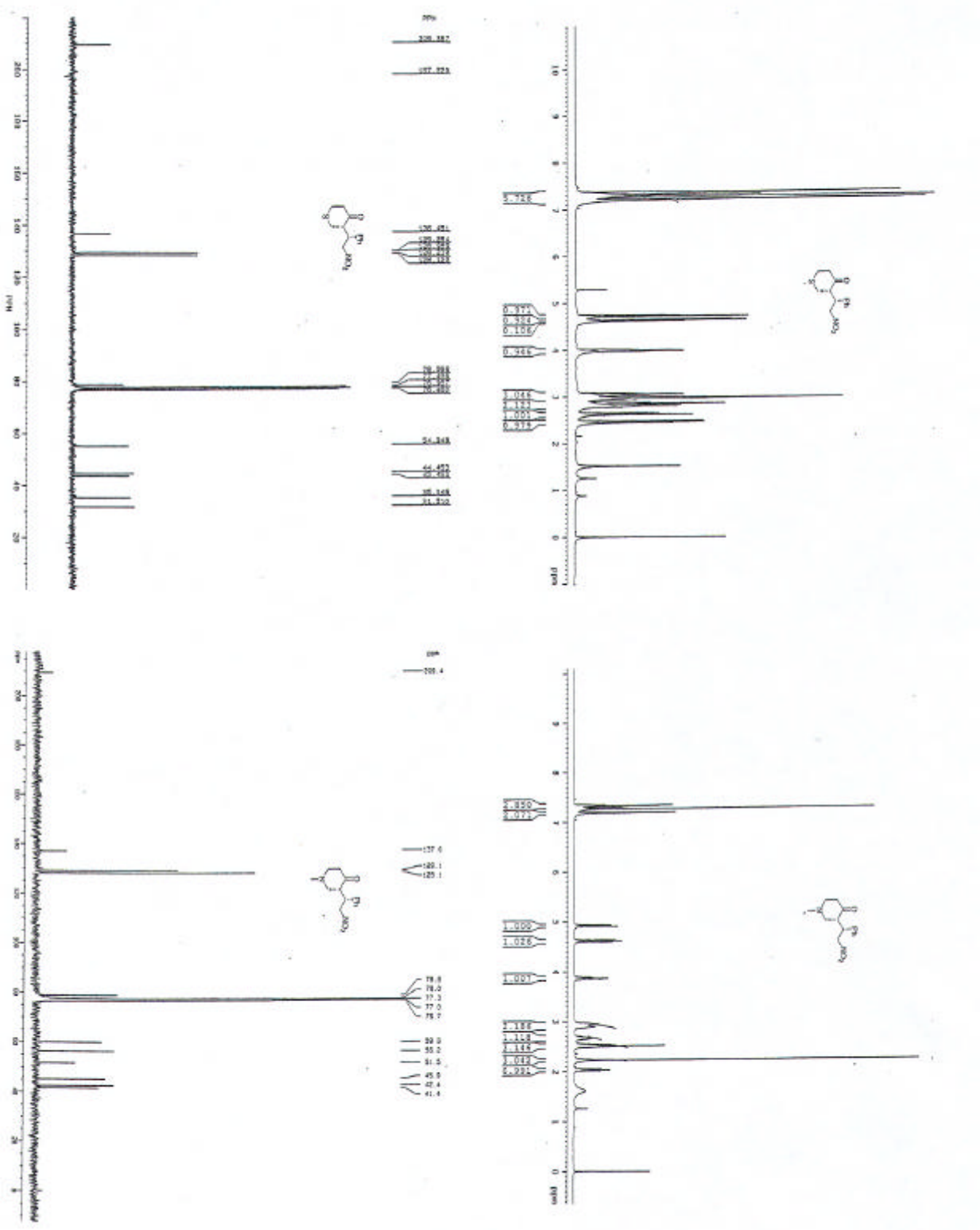

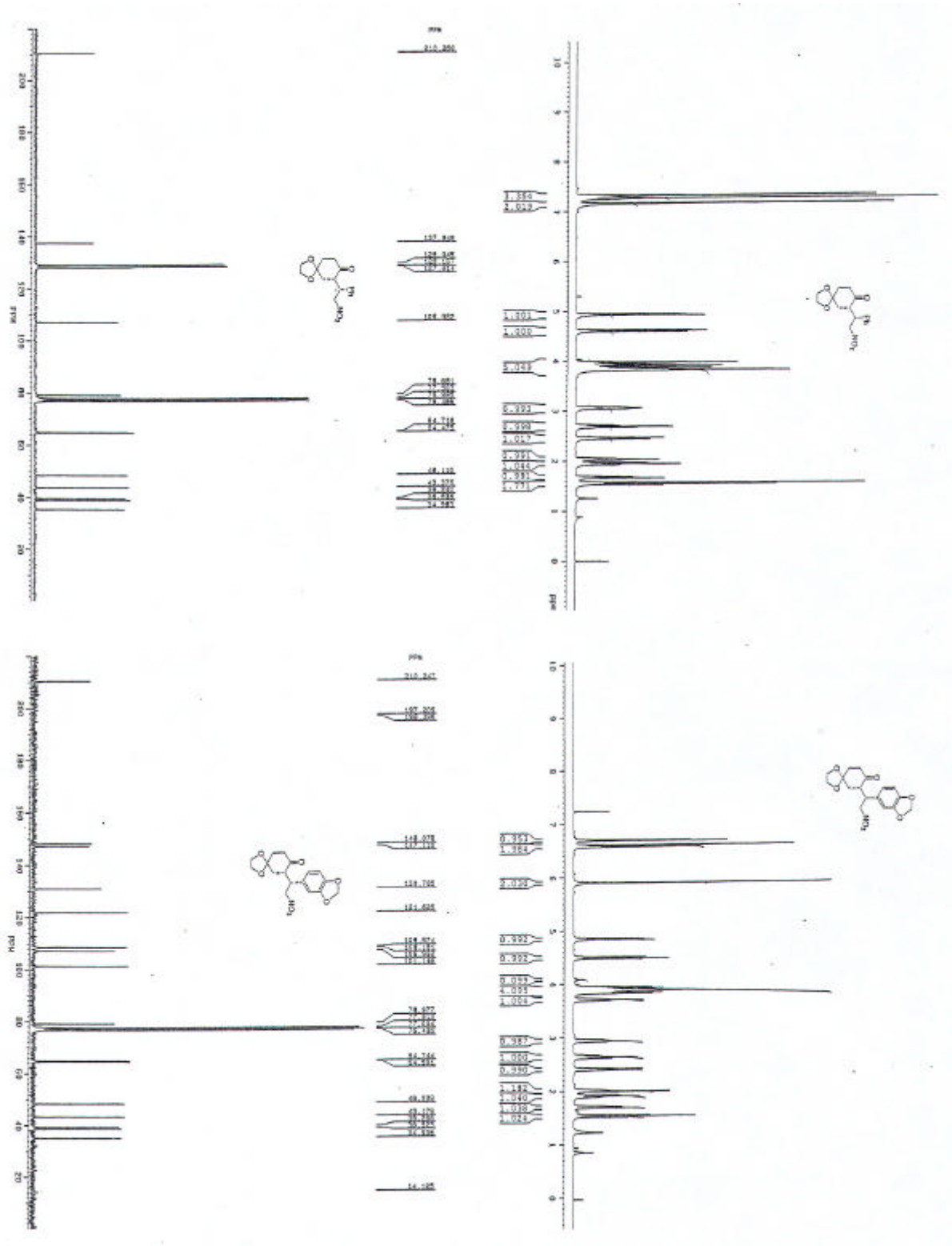

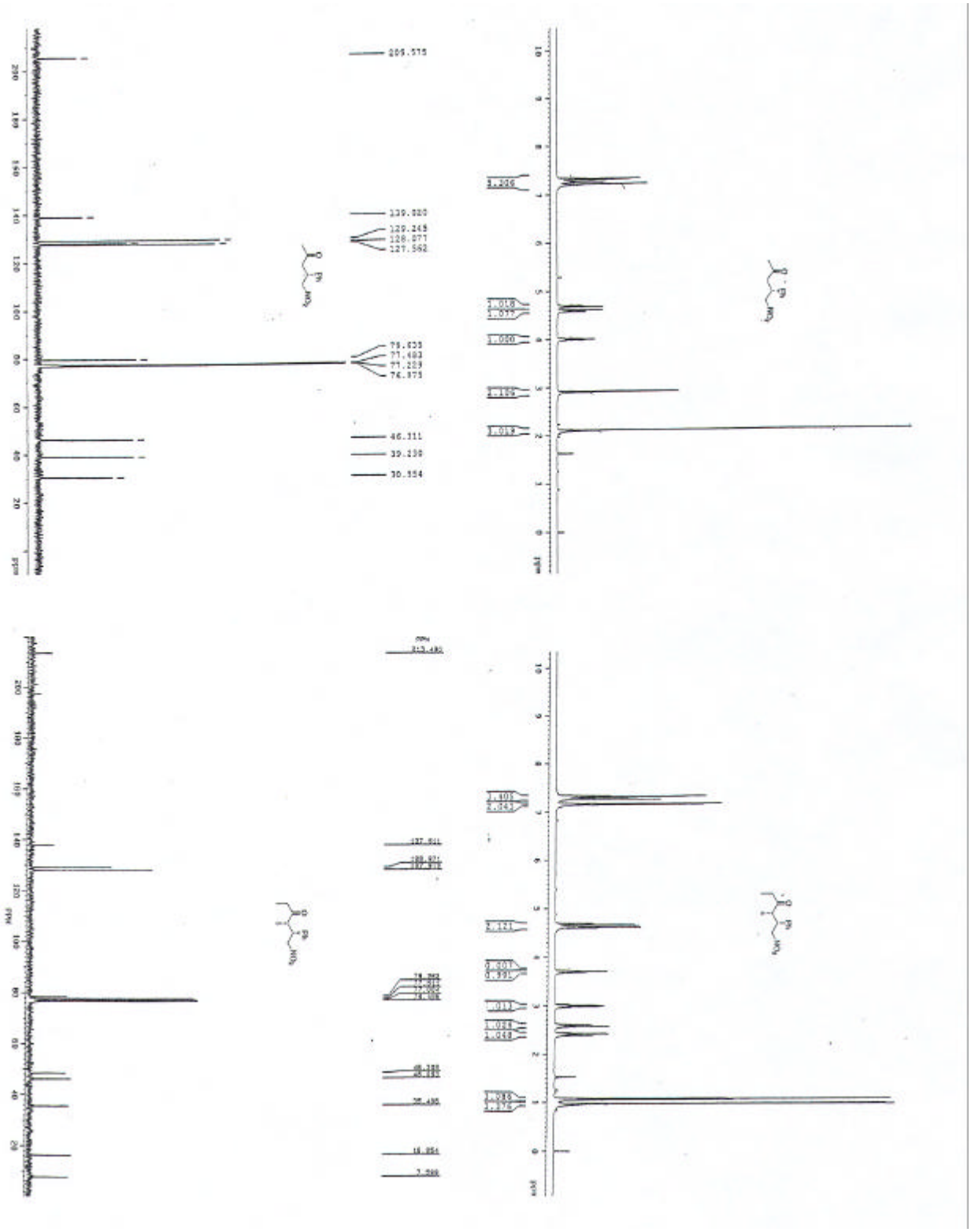

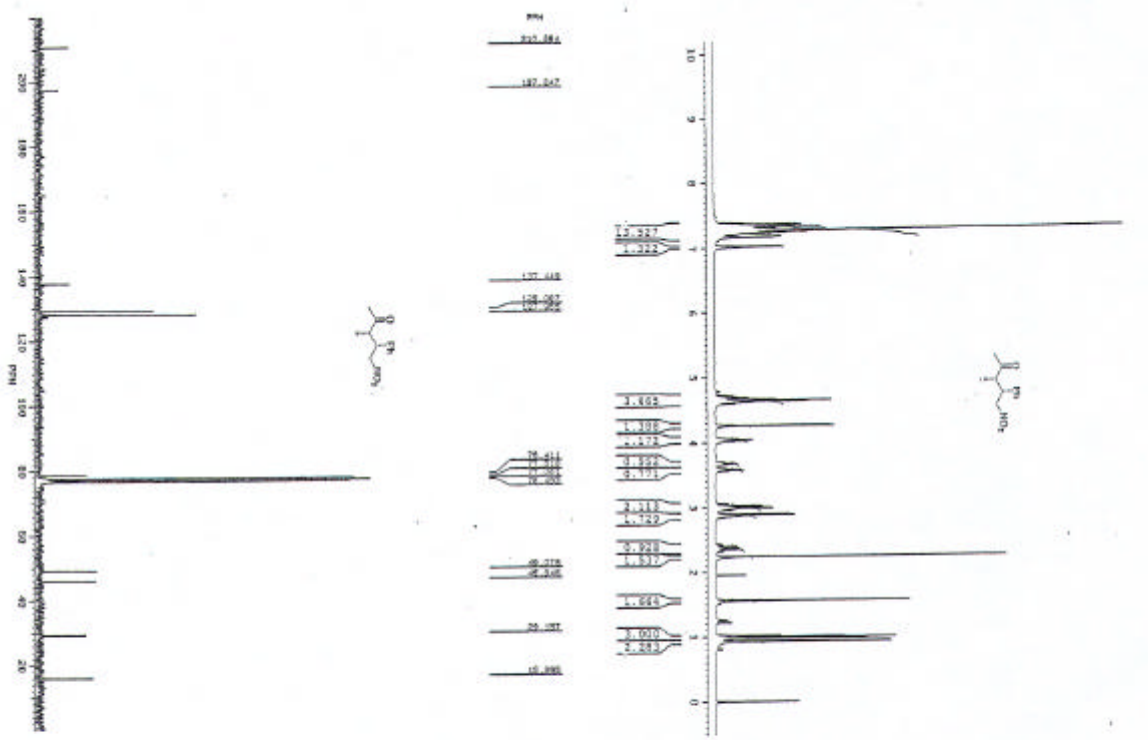

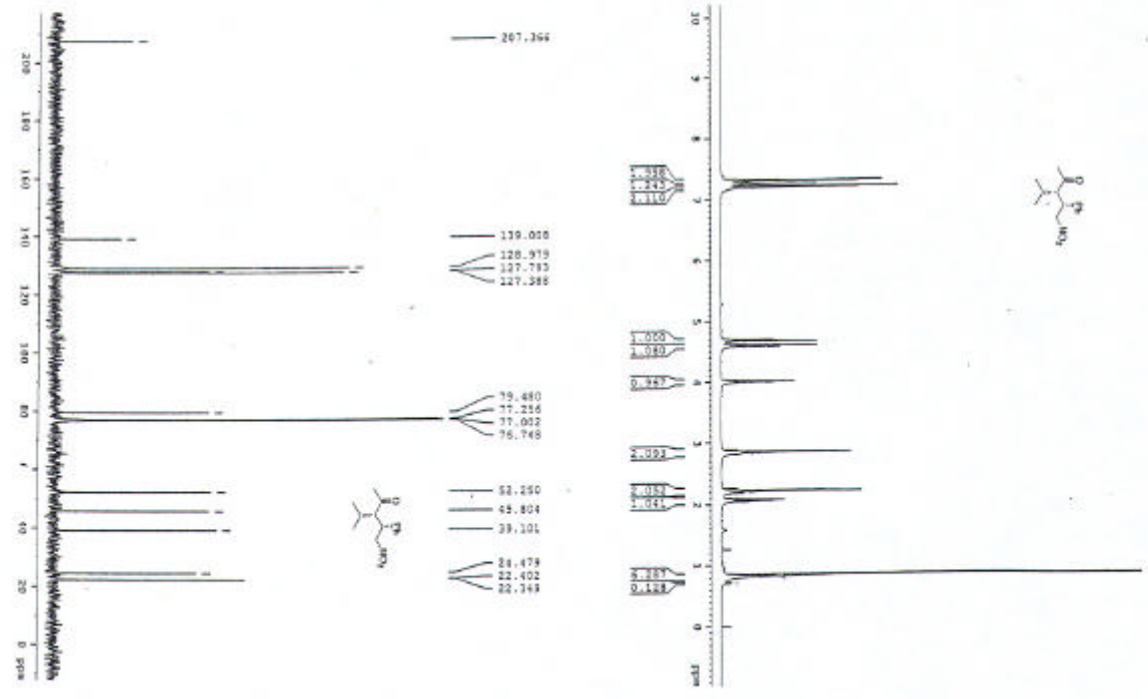

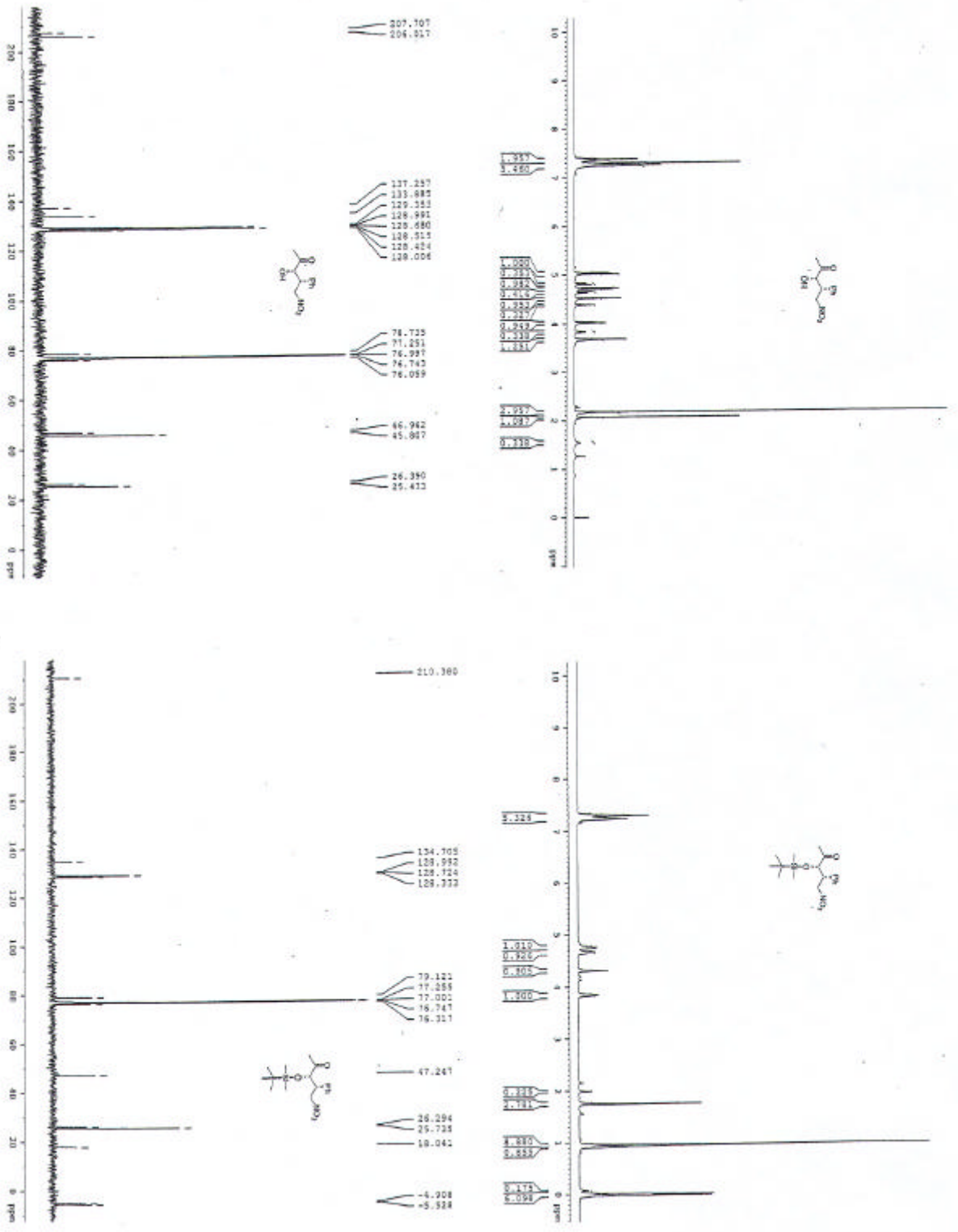

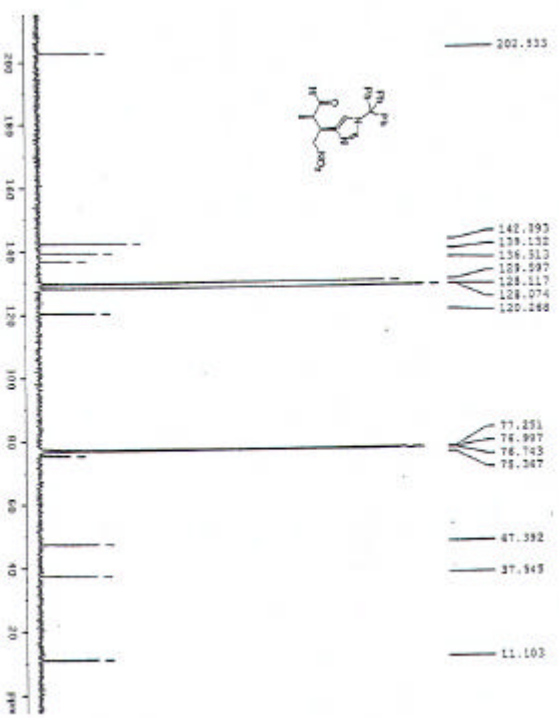
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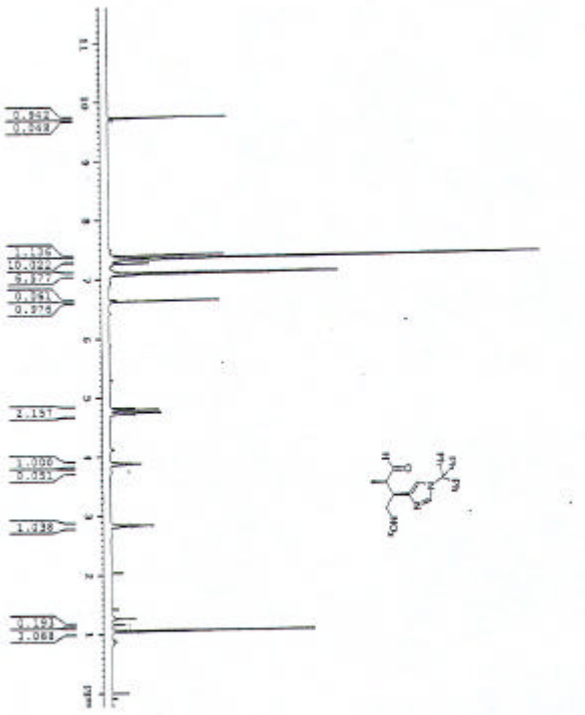
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