

Thiyl Radical Mediated Racemization of Non Activated Aliphatic Amines

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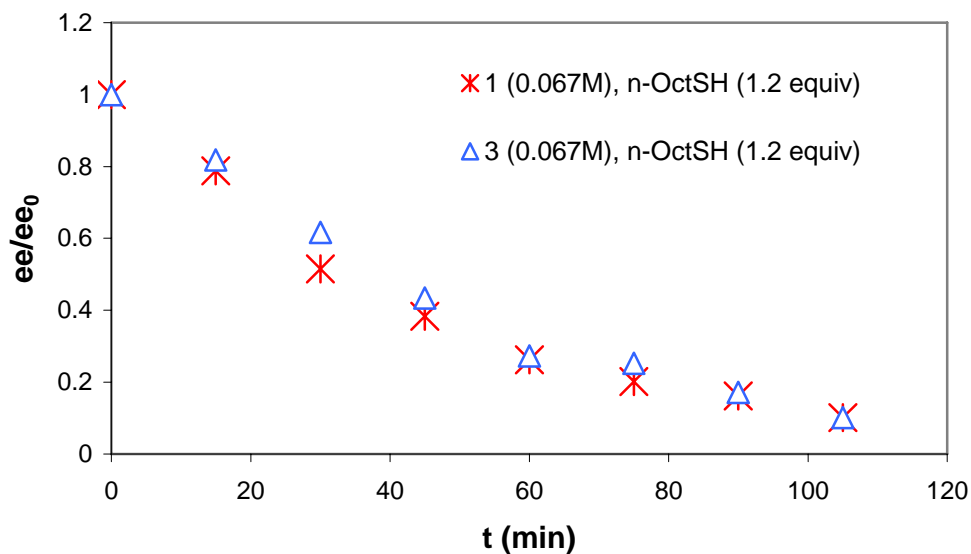
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SUPPORTING INFORMATION

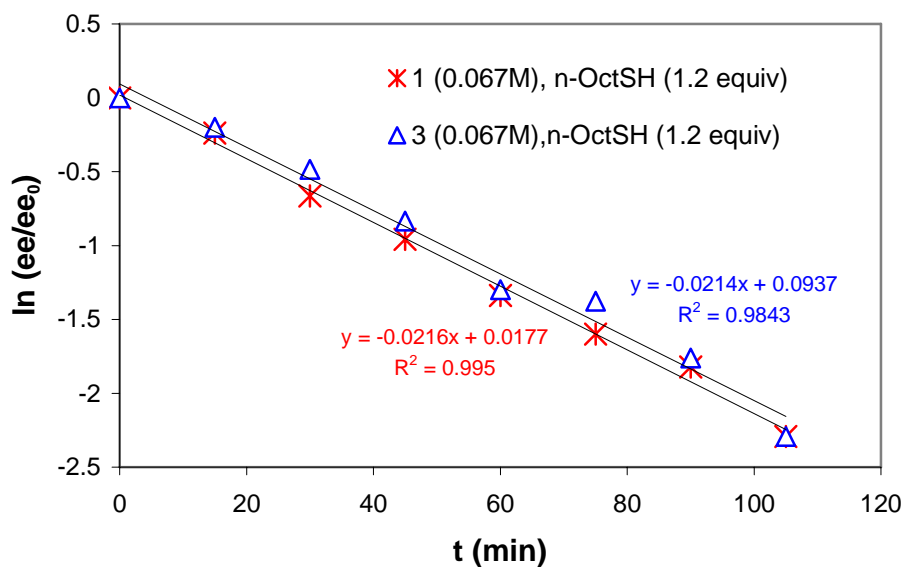
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Plots for the variation of ee/ee_0 versus time for the racemization of amines **1** and **3** in the presence of 1.2 equiv of *n*-OctSH



Plots for the variation of $\ln(ee/ee_0)$ versus time for amines **1** and **3**



In the presence of 1.2 equiv of thiol, the racemization rate constants was estimated from the slopes by the equation $-2kt = \ln(ee/ee_0)$, where $2k$ is the racemization constant. This equation is adapted from the usual expression for a reversible, first-order reaction where the equilibrium constant K is 1. The rate constant for the racemization process would be very close to $3.5 \times 10^{-4} \text{ s}^{-1}$.

Experimental Section

General: All reactions were carried out under argon atmosphere. Solvents were degassed before use. The ^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively. Chemical shifts (δ) are reported in ppm and coupling constants (J) given in Hz. Enantiomeric excesses (ee) were determined by analytical chiral HPLC. The solvents for chiral chromatography (n -hexane, 2-PrOH, EtOH) were HPLC grade. They were degassed and filtered on a 0.45 μm membrane before use. The chiral HPLC analyses were performed on Chiralcel OD-H (250*4.6mm), a cellulose tris-(3,5-dimethylphenylcarbamate) chiral stationary phase with UV and polarimetric detection. The retention times t_R in minutes for each enantiomer, the retention factors $k = (t_R - t_0)/t_0$ where t_0 is the retention time for an unretained peak determined by injection of tri-*tert*iobutyl-benzene, the enantioselectivity factor $\alpha = k_2/k_1$ and the resolution R_s are given to characterize the chiral separations. The sign given by the on-line polarimeter is the sign of the enantiomer in the mobile phase used for the chiral HPLC analysis.¹ Detailed chromatographic conditions are reported hereafter. The enantiomeric excess of the primary amine was determined, after derivatization in trifluoroacetamide with 1.5 equiv of *N*-methyl-bis-trifluoroacetamide, by gas chromatography (GC) analysis on a chromatograph fitted with a Lipodex D column with flame ionization detector (FID), using the derivatized racemic compound as reference. Compound **1** and **4** were prepared according to a literature procedure.² All other commercially available compounds (**9**, **10** and thiols) were used without further purification.

(S)-2-Amino-4-phenylbutane (1): $ee=94\%$. Chiral HPLC conditions for the racemic mixture: Chiralcel OD-H, Hexane/Isopropanol (90/10), 1 mL/min. Detector: UV (254 nm) and polarimeter. t_R (R , -) = 8.00, t_R (S , +) = 10.33, k (R , -) = 1.58, k (S , +) = 2.33, $\alpha = 1.48$, $R_s = 1.66$. Amine **1** was analyzed by GC (after derivatization in 2,2,2-trifluoro-*N*-(4-phenylbutan-2-yl)acetamide) under the following conditions for the racemic mixture: Lipodex D column, injector 250°C, program: 25 min./140°C then 5°C/min from 140 to 180°C. Detector: FID. t_R (R) = 18.3, t_R (S) = 19.3, k (R) = 8.16, k (S) = 8.67, $\alpha = 1.06$. In order to set up analytical conditions, an authentic sample of 2,2,2-trifluoro-*N*-(4-phenylbutan-2-

yl)acetamide was prepared as follows: trifluoroacetic anhydride (189 μ L, 1.34 mmol) was added at 0°C to a solution of 2-amino-4-phenylbutane (100 mg, 0.67 mmol) and triethylamine (187 μ L, 1.34 mmol) in CH₂Cl₂ (5 ml). The solution was stirred for 0.5 h at room temperature. The solvent was removed in vacuo and the crude material was diluted with Et₂O, washed with HCl (0.1N), brine and dried under Na₂SO₄. After concentration, the crude material was subjected to flash column chromatography on silica gel (5/95 AcOEt/pentane) to give 2,2,2-trifluoro-*N*-(4-phenylbutan-2-yl)acetamide (111 mg, 0.45 mmol, 68%). ¹H NMR (CDCl₃, 300 MHz): δ 7.11-7.44 (m, 5H), 6.11 (s large, NH), 4.10 (pseudo sept, *J* = 6.8, 1H), 2.66-2.71 (m, 2H), 1.85-1.93 (m, 2H), 1.28 (d, *J* = 6.6, 3H). ¹³C NMR (CDCl₃, 75 MHz) : δ 20.7 (CH₃), 32.6 (CH₂), 38.2 (CH₂), 46.8 (CH), 116.3 (q, *J* = 288, CF₃), 126.6 (CH), 128.7 (CH), 129.0 (CH), 141.25 (C), 157.0 (q, *J* = 37, CO). ¹⁹F NMR (CDCl₃, 282 MHz): -76.45.

Ethyl 3-((*S*)-(+)-4-phenylbutan-2-ylamino)propanoate (2): To a solution of (*S*)-(+)-2-amine-4-phenylbutane (**1**) (250 mg, 1.67 mmol) in EtOH (7.5 ml) was added ethyl acrylate (273 μ L, 2.51 mmol). The solution was stirred for 18 h at room temperature. The solvent was removed in vacuo and the crude material was subjected to flash column chromatography on silica gel (5/95 triethylamine/pentane) to give **2** (349 mg, 1.40 mmol, 84%). *ee*=94%. Chiral HPLC conditions for the racemic mixture: Chiralcel OD-H, Hexane/Isopropanol (99/1), 1 mL/min. Detector: UV (254 nm) and polarimeter. *t_R* (*R*, -) = 13.23, *t_R* (*S*, +) = 14.42, *k* (*R*, -) = 3.27, *k* (*S*, +) = 3.65, α = 1.12, *R_s* = 0.97. ¹H NMR (CDCl₃, 300 MHz): δ 7.18-7.35 (m, 5H), 4.16 (q, *J* = 7.2, 2H), 2.90 (m, 2H), 2.60-2.75 (m, 3H), 2.50 (t, *J* = 6.5, 2H), 1.55-1.87 (m, 2H), 1.46 (broad s, NH), 1.30 (t, *J* = 7.2, 3H), 1.11 (d, *J* = 6.2, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ 14.6 (CH₃), 20.7 (CH₃), 32.6 (CH₂), 35.4 (CH₂), 39.1 (CH₂), 42.7 (CH₂), 52.8 (CH), 60.8 (CH₂), 126.1 (CH), 128.7 (CH), 128.8 (CH), 142.8 (C), 173.3 (CO). **Anal.** Calcd for C₁₅H₂₃NO₂: C, 72.25; H, 9.30; N, 5.62. Found C, 71.95; H, 9.42; N, 5.67.

(*S*)-(+)-Ethyl 3-[(2-ethoxycarbonyl-ethyl)-(4-phenylbutan-2-yl)-amino]-propanoate (3): To a solution of **1** (1.5g, 10 mmol) in EtOH (25 ml) was added ethyl acrylate (1.5g, 15 mmol). The solution was stirred 18 h at room temperature. Then the mixture was warmed at 60°C for 72 h with addition

of ethyl acrylate every 24 h (3 times 2g, 20 mmol). The solvent was removed in vacuo and the crude material was subjected to flash column chromatography on silica gel (10/90 AcOEt/pentane) to give **3** (2.78g, 8 mmol, 80%). *ee*=94%. Chiral HPLC conditions for the racemic mixture: Chiralcel OD-H, Hexane/Isopropanol (99/1), 1 mL/min. Detector: UV (254 nm) and polarimeter. t_R (*S*, +) = 10.24, t_R (*R*, -) = 11.18, k (*S*, +) = 2.30, k (*R*, -) = 2.61, α = 1.13, R_s = 1.30. ^1H NMR (CDCl_3 , 300 MHz): δ 7.10-7.31 (m, 5H), 4.12 (q, J = 7.1, 4H), 2.82 (dt, J = 13.2 et 7.6, 2H), 2.45-2.73 (m, 5H), 2.40 (m, 3H), 1.65-1.85 (m, 1H), 1.45-1.62 (m, 2H), 1.25 (t, J = 7.1, 6H), 0.96 (d, J = 6.6, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 14.5 (CH_3), 14.6 (CH_3), 33.6 (CH_2), 35.1 (CH_2), 36.4 (CH_2), 46.1 (CH_2), 55.3 (CH), 60.6 (CH_2), 126.0 (CH), 128.7 (CH), 128.8 (CH), 143.2 (C), 173.2 (CO). Anal. Calcd for $\text{C}_{20}\text{H}_{31}\text{NO}_4$: C, 68.74; H, 8.94; N, 4.01. Found C, 68.86; H, 9.13; N, 4.08.

(*R*)-*N*-(4-Phenylbutan-2-yl) acetamide (4): *ee*= 86%. Chiral HPLC conditions for the racemic mixture: Chiralcel OD-H, Hexane/Isopropanol (90/10), 1 mL/min. Detector: UV (254 nm) and polarimeter. t_R (*R*, +) = 5.42, t_R (*S*, -) = 6.12, k (*R*, +) = 0.75, k (*S*, -) = 0.97, α = 1.30, R_s = 1.89.

(*S*)-2-amino-octane (9): **9** was analyzed (after derivatization in 2,2,2-trifluoro-*N*-(octan-2-yl)acetamide) by GC under the following conditions for the racemic mixture: Lipodex D column, injector 250°C, program: 10 min./110°C then 3°C/min from 110 to 160°C and 23 min./160°C. Detector: FID. t_R (*R*) = 10.13, t_R (*S*) = 10.67, k (*R*) = 4.06, k (*S*) = 4.33, α = 1.07. In order to set up analytical conditions, an authentic sample of 2,2,2-trifluoro-*N*-(octan-2-yl)acetamide³ was prepared as follows: trifluoroacetic anhydride (328 μL , 2.32 mmol) was added at -40°C to a solution of 2-amino-octane (200 mg, 1.55 mmol) and triethylamine (335 μL , 2.40 mmol) in CH_2Cl_2 (10 ml). The solution was stirred for 18 h at room temperature. The solvent was removed in vacuo and the crude material was diluted with Et_2O , washed with HCl (0.1N), brine and dried under Na_2SO_4 . After concentration, the crude material was subjected to flash column chromatography on silica gel (3/97 AcOEt/pentane) to give 2,2,2-trifluoro-*N*-(octan-2-yl)acetamide (280 mg, 1.24 mmol, 80%). ^1H NMR(CDCl_3 , 300 MHz) : δ 6.02 (s large, NH), 3.94-4.10 (m, 1H), 1.44-1.57 (m, 2H), 1.24-1.39 (m, 8H), 1.21 (d, J = 6.6, 3H), 0.88 (t, J =

6.7, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 14.3 (CH_3), 20.5 (CH_3), 22.9 (CH_2), 26.2 (CH_2), 29.3 (CH_2), 32.0 (CH_2), 36.6 (CH_2), 46.9 (CH), 116.3 (q, $J = 288$, CF_3), 157.0 (q, $J = 37$, CO). ^{19}F NMR (CDCl_3 , 282 MHz): -76.56.

(R)-1-cyclohexylethylamine (10): **10** was analyzed (after derivatization in 2,2,2-trifluoro-*N*-(1-cyclohexylethyl)acetamide) by GC under the following conditions for the racemic mixture: Lipodex D column, injector 250°C, program: 16 min./110°C then 3°C/min from 110 to 180°C and 20 min./180°C. Detector: FID. t_R (*R*) = 14.34, t_R (*S*) = 14.96, k (*R*) = 5.83, k (*S*) = 6.12, $\alpha = 1.05$. In order to set up analytical conditions, an authentic sample of 2,2,2-trifluoro-*N*-(1-cyclohexylethyl)acetamide was prepared as follows: trifluoroacetic anhydride (240 μL , 1.7 mmol) was added at -40°C to a solution of 1-cyclohexylethylamine (150 mg, 1.27 mmol) and triethylamine (266 μL , 1.9 mmol) in CH_2Cl_2 (10 ml). The solution was stirred for 18 h at room temperature. The solvent was removed in vacuo and the crude material was diluted with Et_2O , washed with HCl (0.1N), brine, and dried under Na_2SO_4 . After concentration, the crude material was subjected to flash column chromatography on silica gel (3/97 AcOEt/pentane) to give 2,2,2-trifluoro-*N*-(1-cyclohexylethyl)acetamide (230 mg, 1.03 mmol, 81%). ^1H NMR (CDCl_3 , 300 MHz): δ 6.31 (s large, NH), 3.94-4.10 (dq, $J = 15.4$ et 6.8, 1H), 1.61-1.82 (m, 5H), 1.32-1.50 (m, 1H), 1.09-1.31 (m, 3H), 1.17 (superimposed d, $J = 6.8$, 3H), 0.87-1.08 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 18.0 (CH_3), 26.6 (2* CH_2), 26.8 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 43.2 (CH), 51.41 (CH), 116.6 (q, $J = 288$, CF_3), 157.3 (q, $J = 36$, CO).

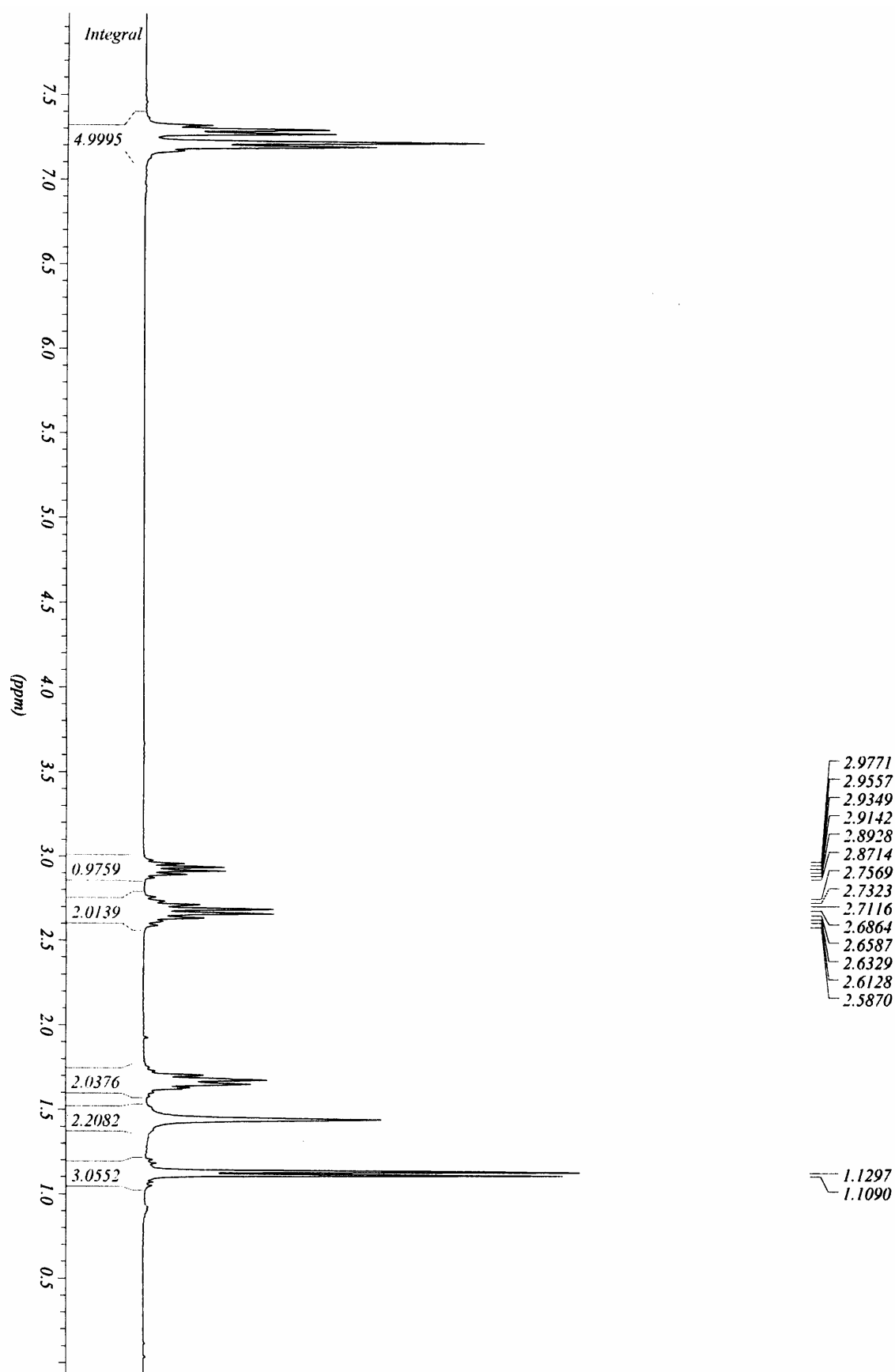
6-Methylhept-5-en-2-amine (rac-11): To a solution of 6-methylhept-5-en-2-one (2.52 g, 40 mmol), ammonium acetate (18g, 0.234 mol) in ethanol (120 ml) was added portion-wise sodium cyanoborohydride (3g, 48 mmol) at room temperature. The mixture was heated for 6h at 50°C. When TLC showed the completion of the reaction, water was added (10 ml) and the solution was stirred for 2h at RT. After evaporation, the residue was diluted with HCl (1 N) and extracted with Et_2O (2x). The aqueous phase was basified with sodium hydroxide and extracted with Et_2O (3x). After drying (Na_2SO_4) and concentration, the crude product was purified by distillation (70°C, 0.5 mmHg) leading to **11**

(2.84g, 22 mmol, 56%). ^1H NMR (CDCl_3 , 300 MHz): δ 5.09 (br t, $J = 7.00$, 1H), 3.98 (sext, $J = 6.4$, 1H), 2.00 (br q, $J = 6.6$, 2H), 1.69 (s, 3H), 1.60 (s, 3H), 1.56 (br s, 2H), 1.34 (m, 2H), 1.04 (d, $J = 6.4$, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 18.0 (CH_3), 24.2 (CH_3), 25.4 (CH_2), 26.1 (CH_3), 40.5 (CH_2), 47.0 (CH), 124.6 ($=\text{CH}$), 131.9 ($\text{C}=\text{}$).

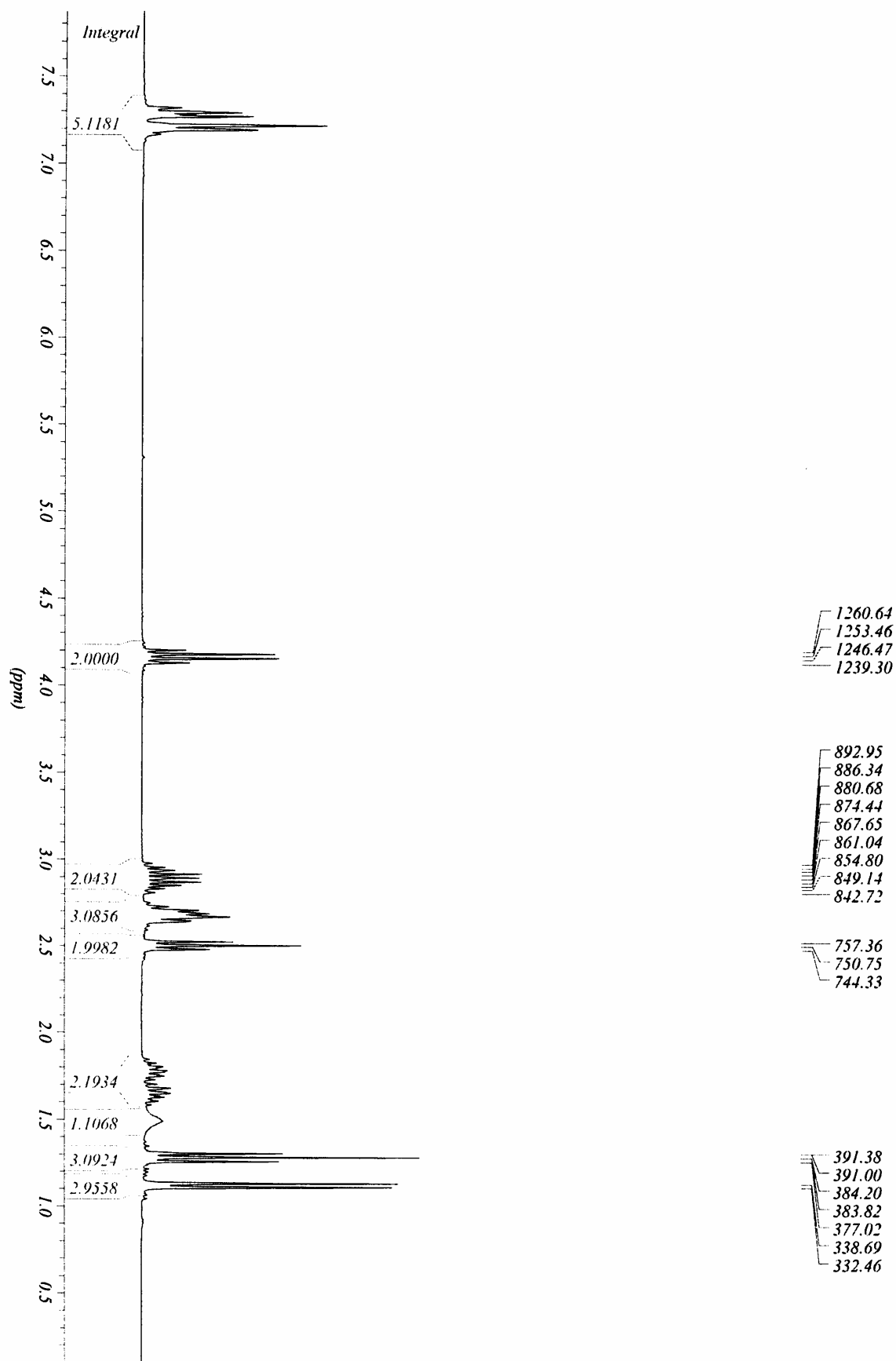
(S)-6-Methylhept-5-en-2-amine (11): A solution of 6-Methylhept-5-en-2-amine (127 mg, 1 mmol) and *Candida antarctica* lipase B (CAL-B, Novozym 435) (100 mg) in AcOEt (5 ml) was heated for 23h at 50°C. When GC showed the completion of the reaction, the organic phase was washed 3 times with HCl (1 N). The aqueous phase was basified with sodium hydroxide and extracted with Et_2O (3x). After drying (Na_2SO_4) and concentration, the crude product was purified by distillation (70°C, 0.5 mmHg) leading to (S)-11 (60 mg, 0.47 mmol, 47%, ee 99%). The ee was determined by GC (after derivatization in 2,2,2-trifluoro-N-((S)-6-methylhept-5-en-2-yl)acetamide) under the following conditions used for the racemic mixture: Lipodex D column, injector 250°C, program: 20 min./100°C then 5°C/min from 100 to 180°C and 20 min./180°C. Detector: FID. t_R (R) = 15.72, t_R (S) = 16.85, k (R) = 6.36, k (S) = 6.90, α = 1.08.

General procedure for the racemization experiments: A 0.06M solution of amine (100 mg) and thiol (1.2 equiv or 0.2 equiv) in benzene was refluxed for 2 h (stoichiometric condition) or 7 h (catalytic condition) in the presence of AIBN (whenever the reaction time was superior to 2 h, the overall quantity of 20 mol% of AIBN, was divided in three equal portions that were added successively each 2 hours). After concentration, the residue was diluted with HCl (1M) and the solution was washed with Et_2O . The aqueous phase was basified with saturated sodium carbonate and extracted with Et_2O . The pure amine was isolated after drying on MgSO_4 and concentration.

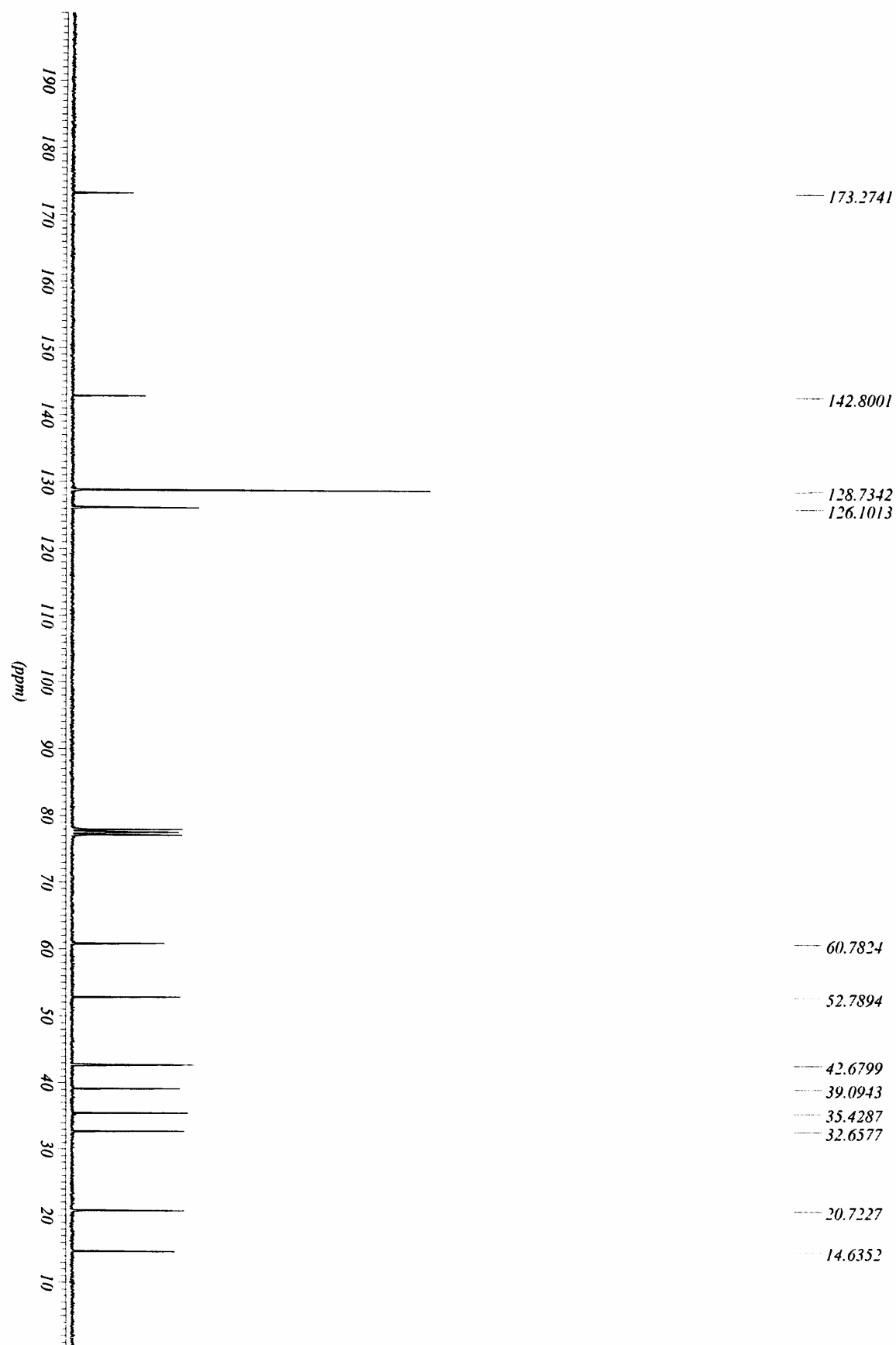
(S)-2-Amino-4-phenylbutane (1): ^1H NMR



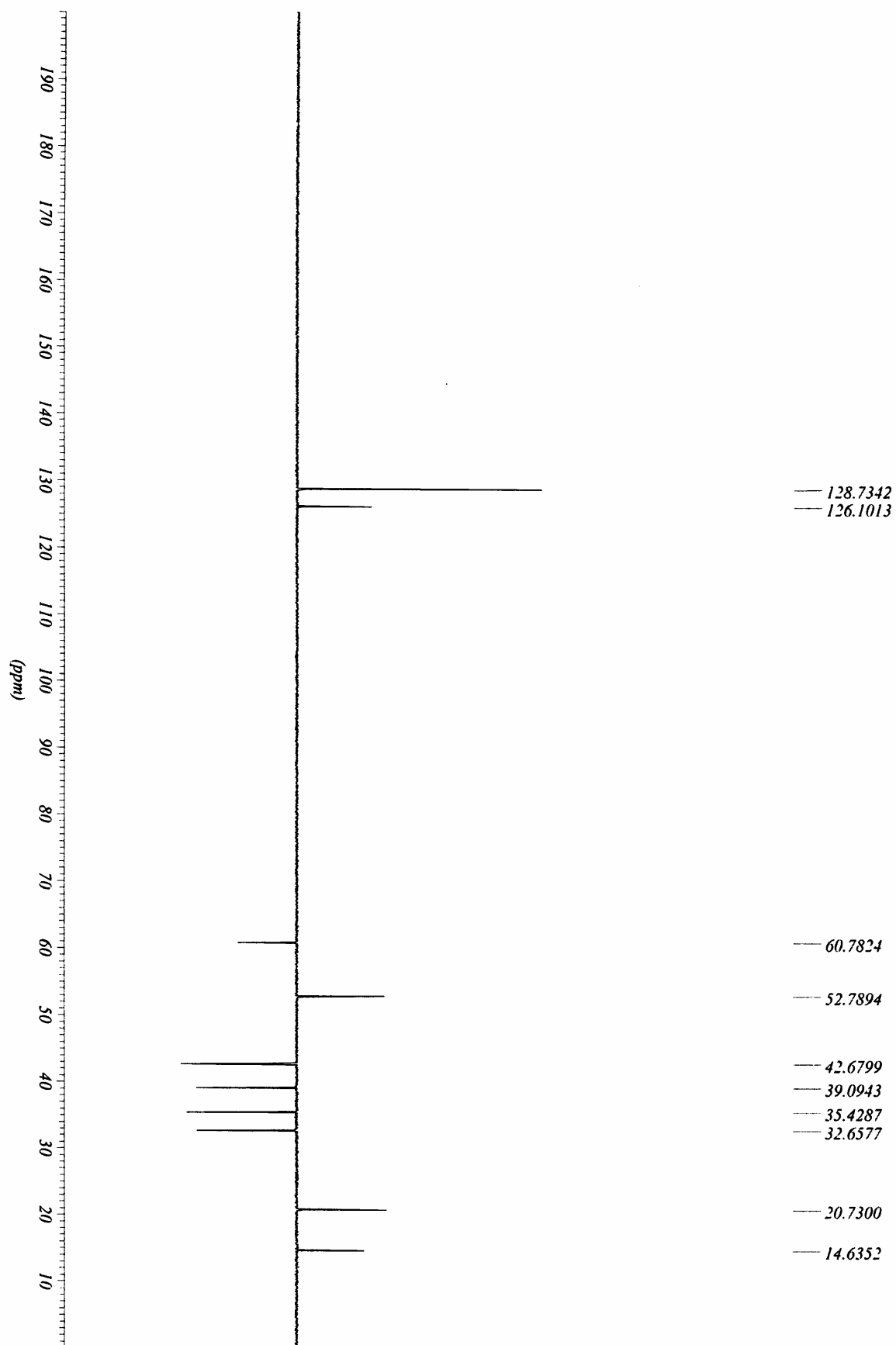
Ethyl 3-((S)-(+)-4-phenylbutan-2-ylamino)propanoate (2): ^1H NMR



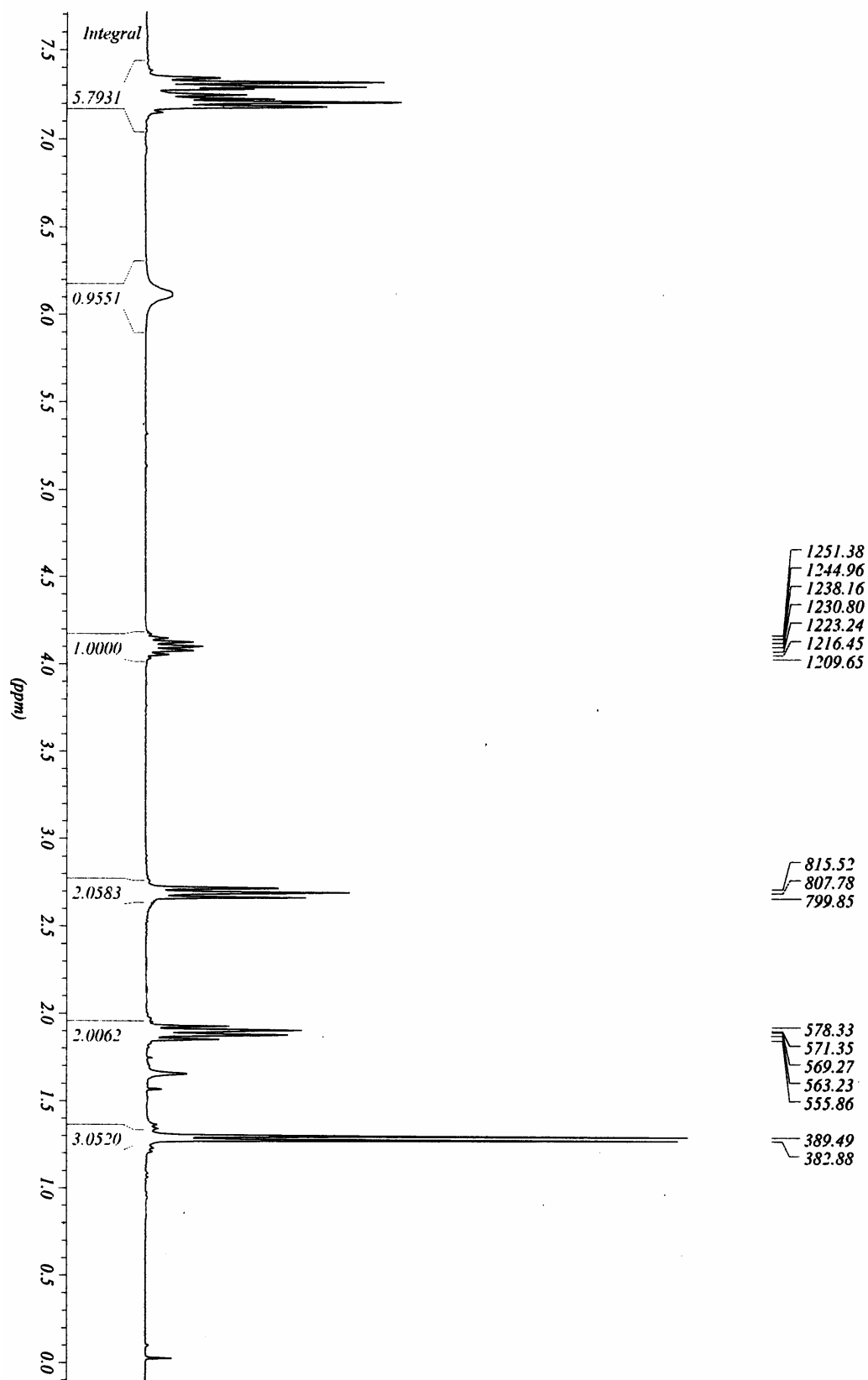
Ethyl 3-((S)-(+)-4-phenylbutan-2-ylamino)propanoate (2): ^{13}C NMR



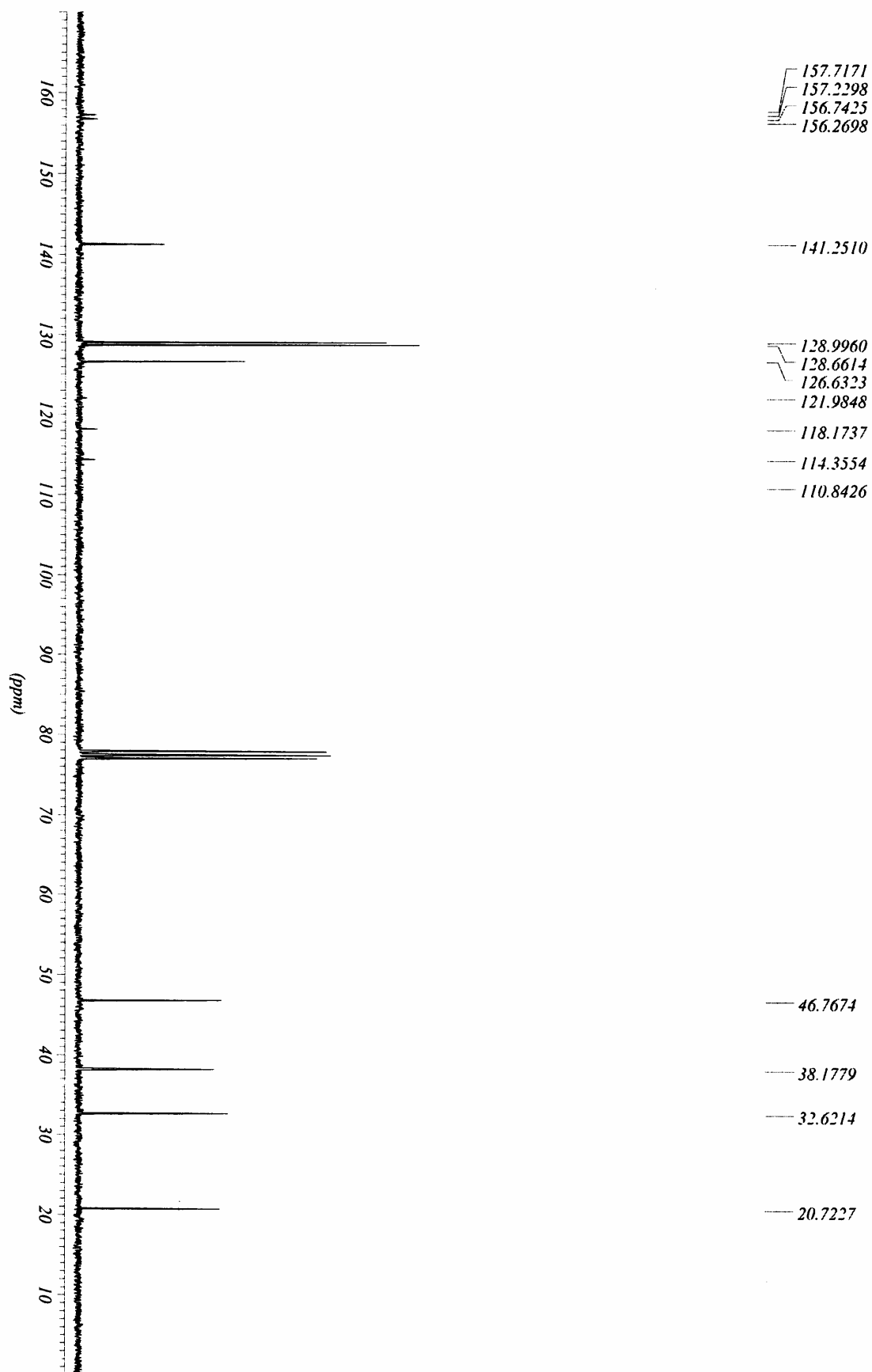
Ethyl 3-((S)-(+)-4-phenylbutan-2-ylamino)propanoate (2): DEPT 135



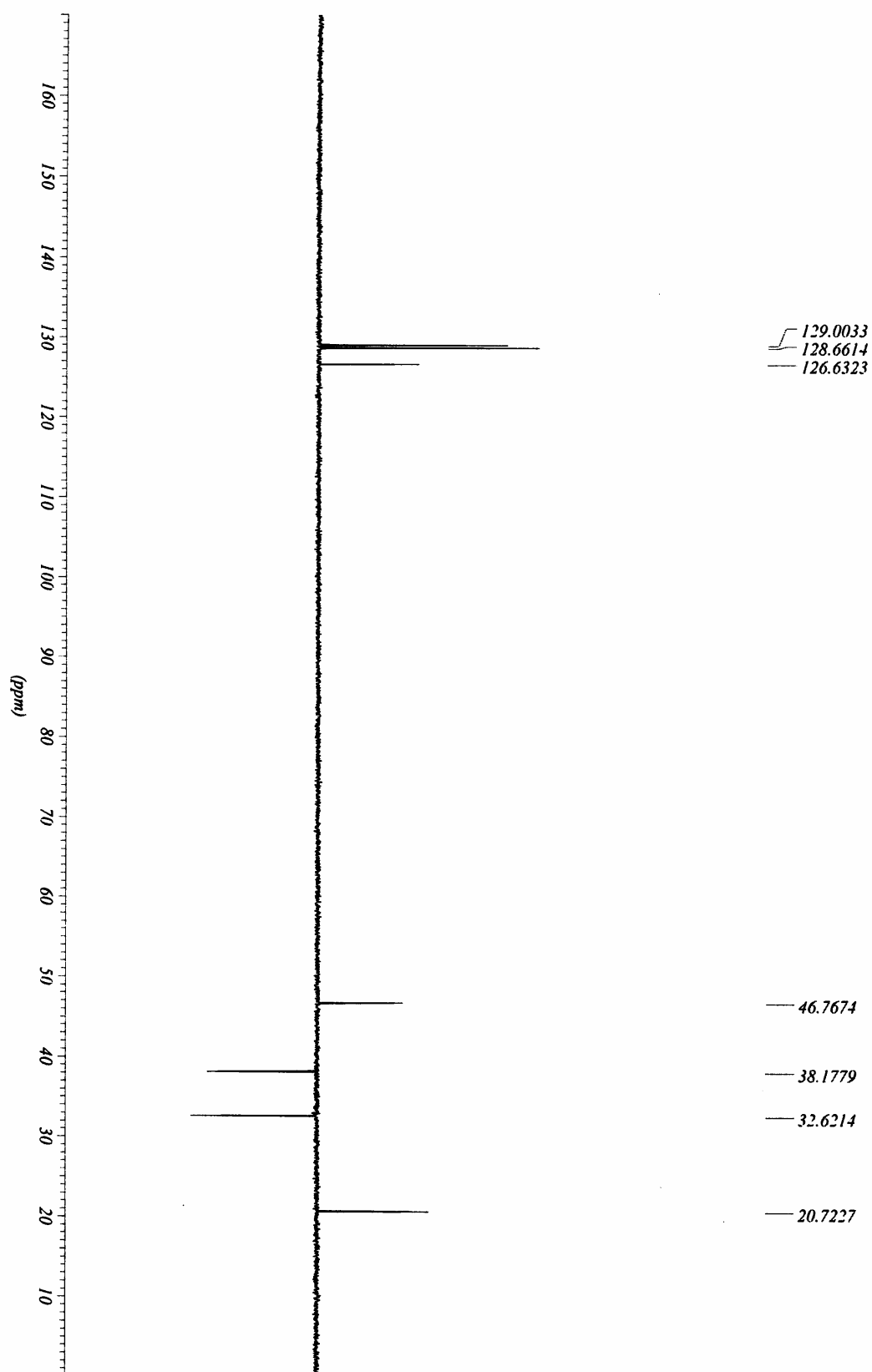
2,2,2-trifluoro-*N*-(4-phenylbutan-2-yl)acetamide: ^1H NMR



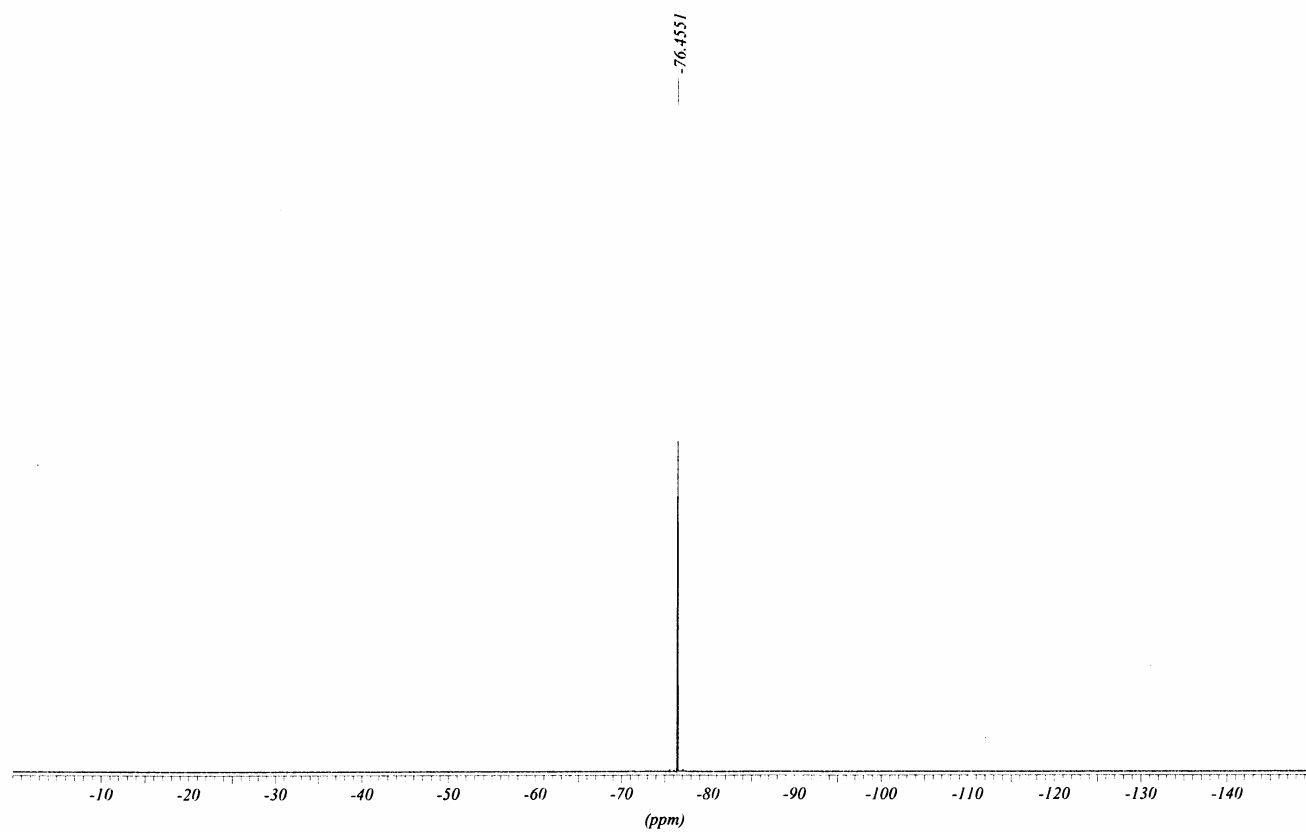
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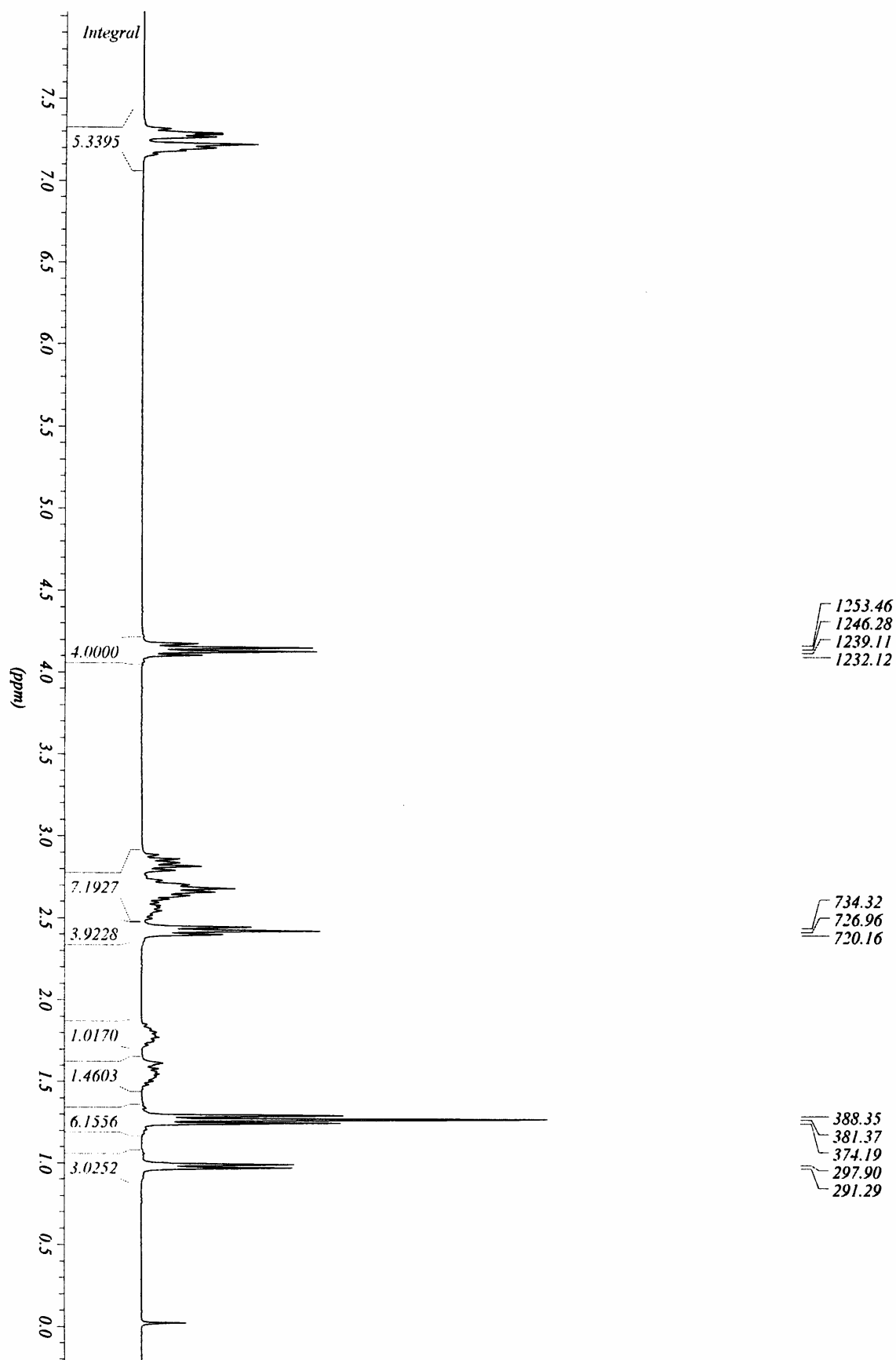
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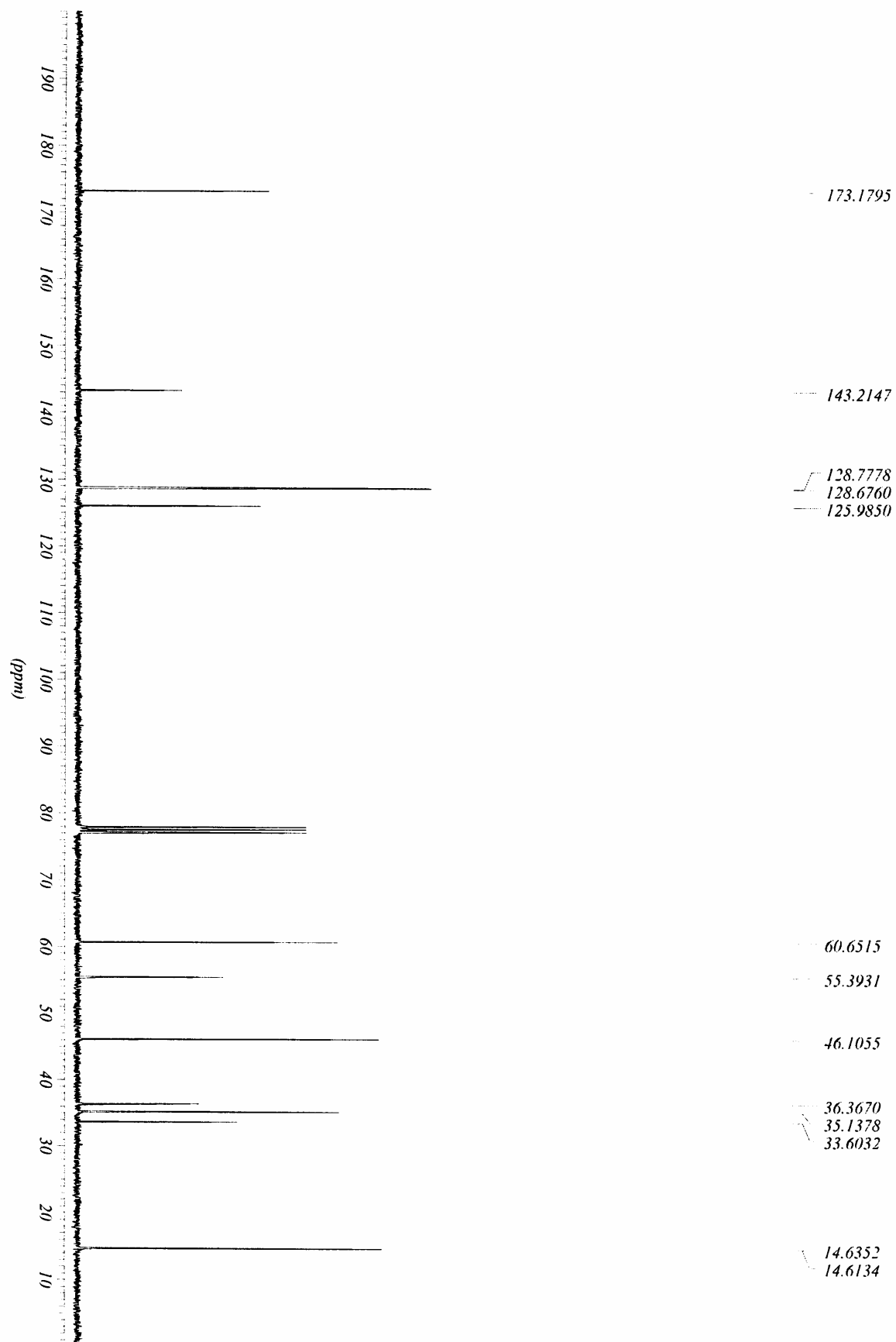
2,2,2-trifluoro-*N*-(4-phenylbutan-2-yl)acetamide: ^{19}F NMR



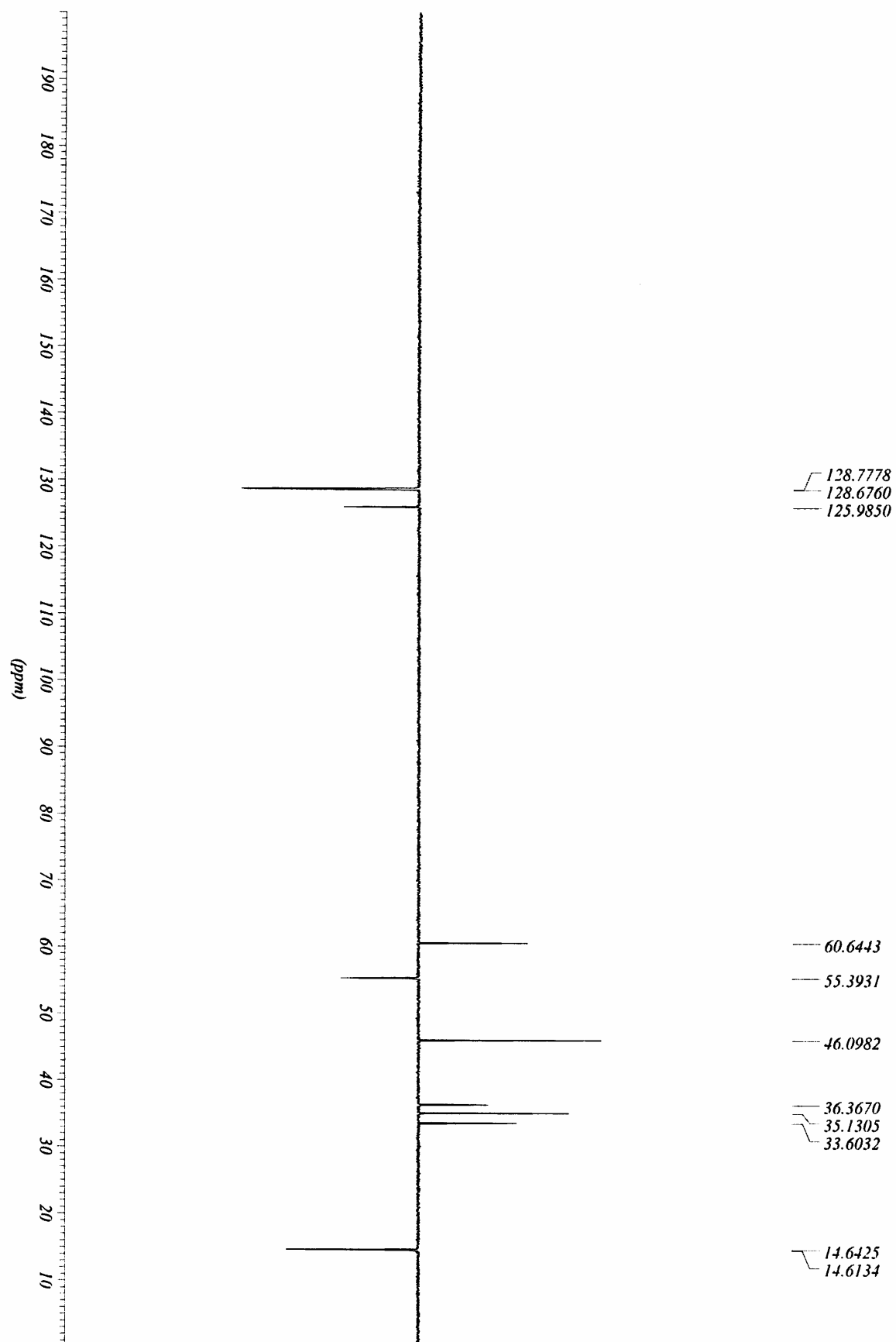
(S)-(+)-Ethyl 3-[(2-ethoxycarbonyl-ethyl)-(4-phenylbutan-2-yl)-amino]-propanoate (3): ^1H NMR



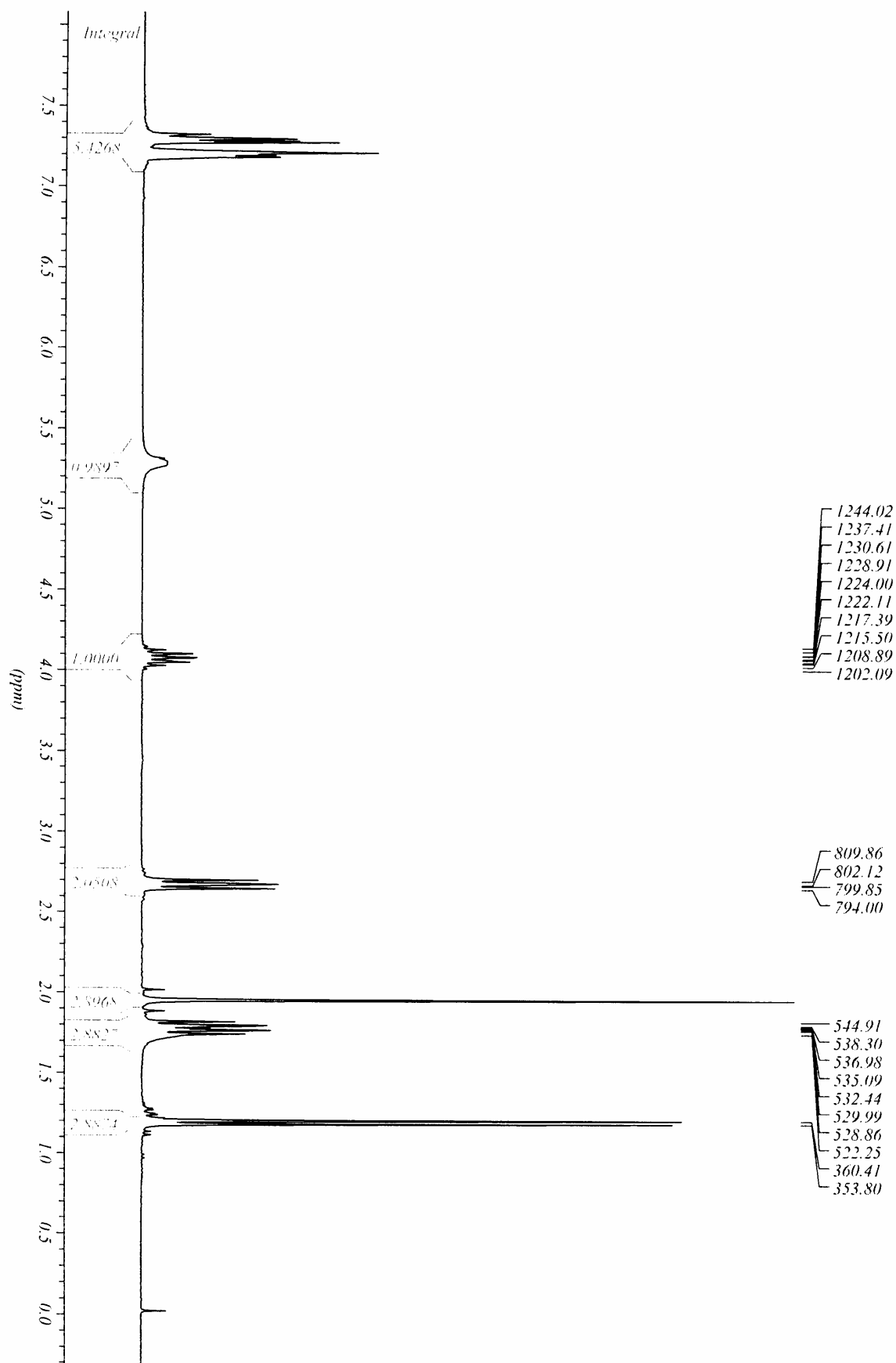
(S)-(+)-Ethyl 3-[(2-ethoxycarbonyl-ethyl)-(4-phenylbutan-2-yl)-amino]-propanoate (**3**): ^{13}C NMR



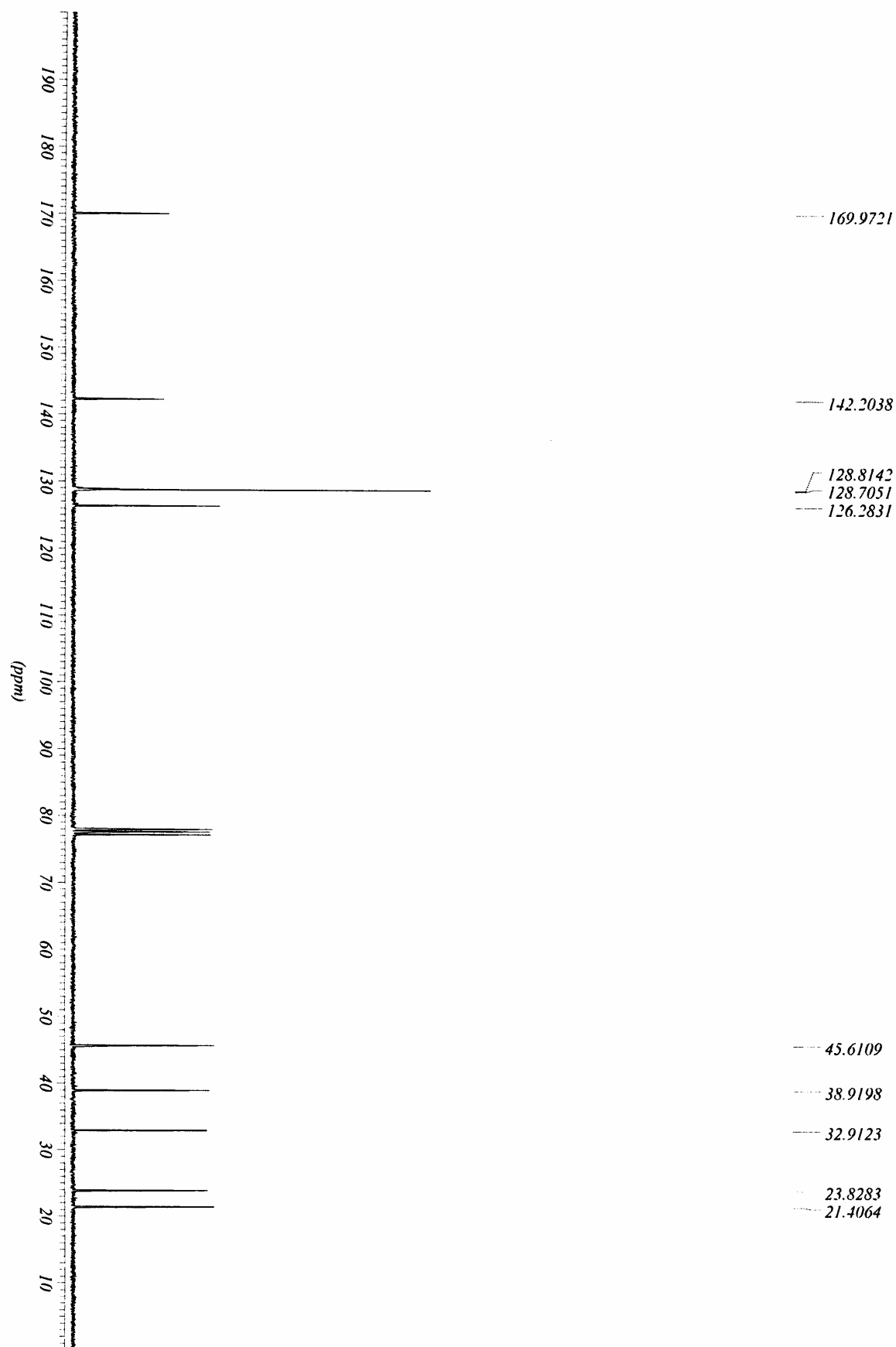
(S)-(+)-Ethyl 3-[(2-ethoxycarbonyl-ethyl)-(4-phenylbutan-2-yl)-amino]-propanoate (**3**): DEPT 135



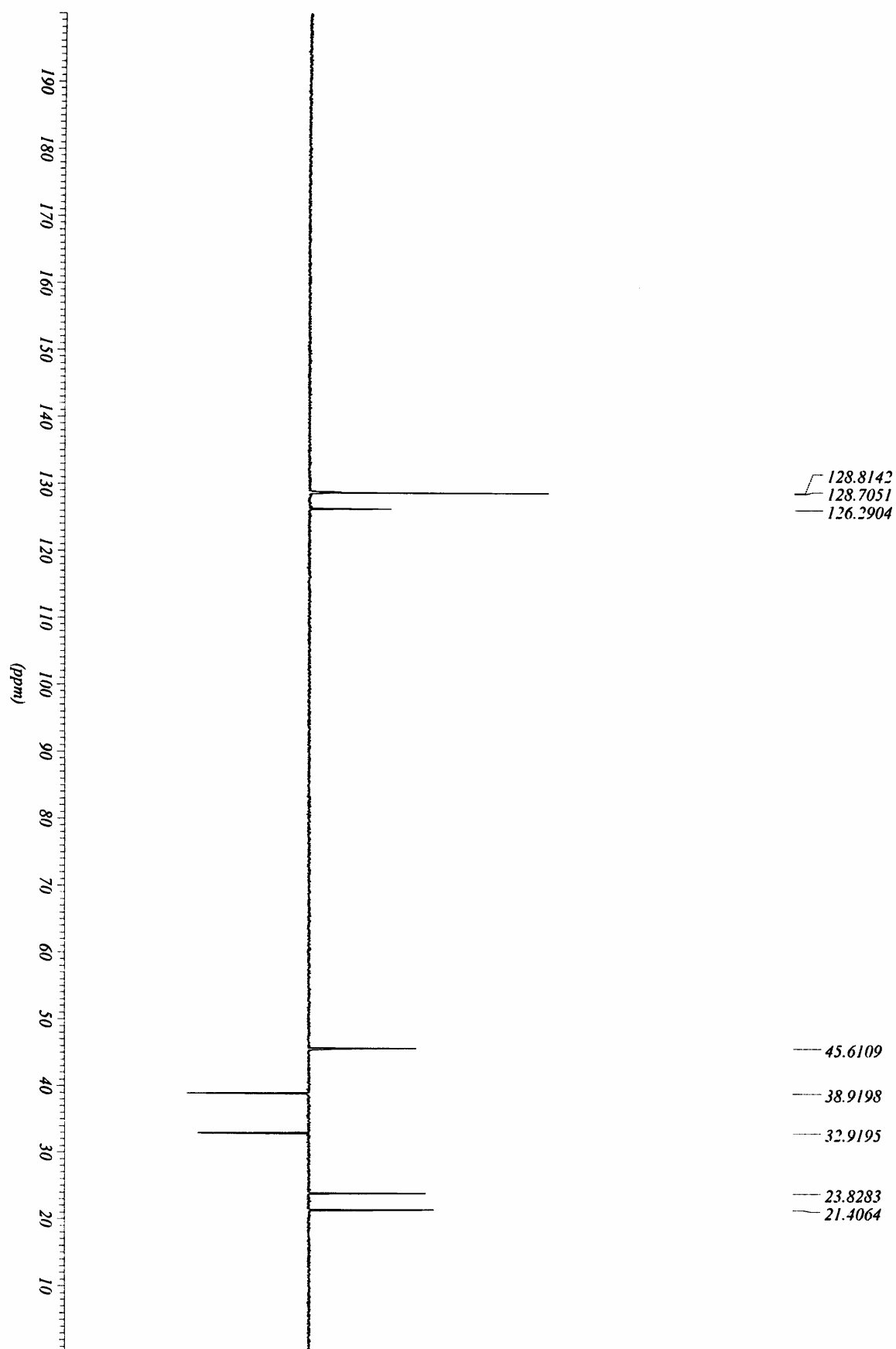
(R)- N-(4-Phenylbutan-2-yl) acetamide (4): ^1H NMR



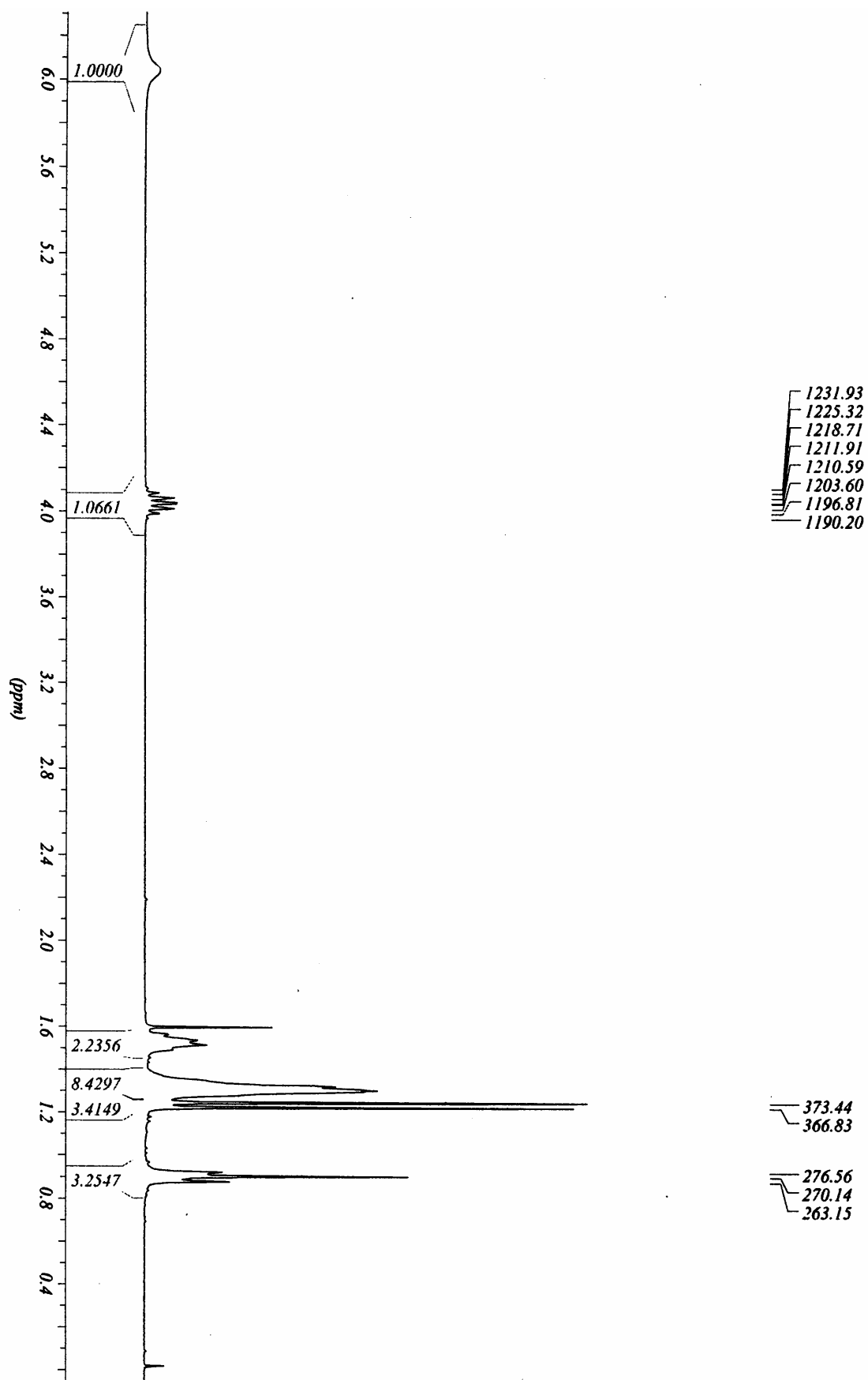
(R)- N-(4-Phenylbutan-2-yl) acetamide (4): ^{13}C NMR



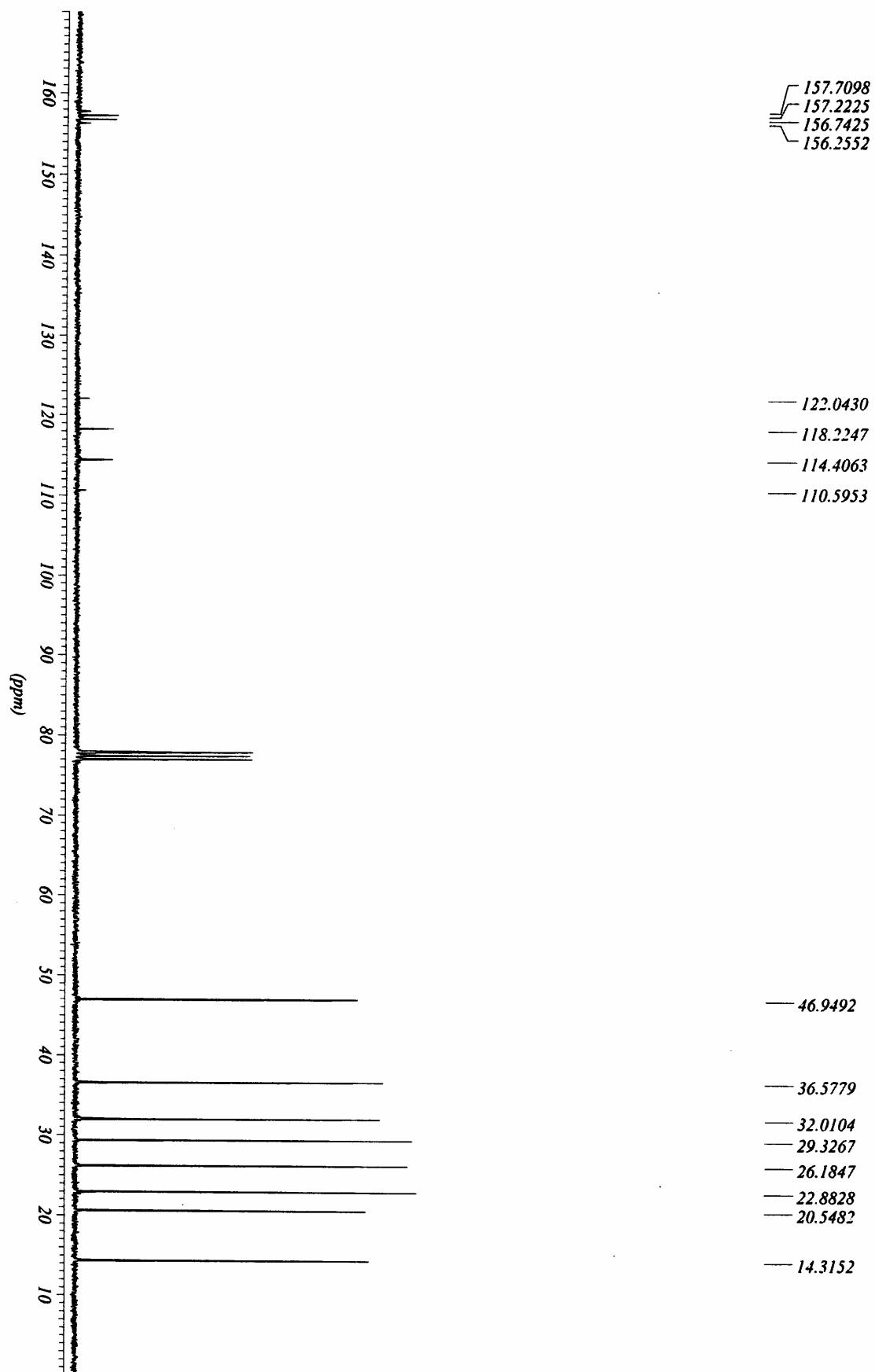
(R)- N-(4-Phenylbutan-2-yl) acetamide (4): DEPT 135



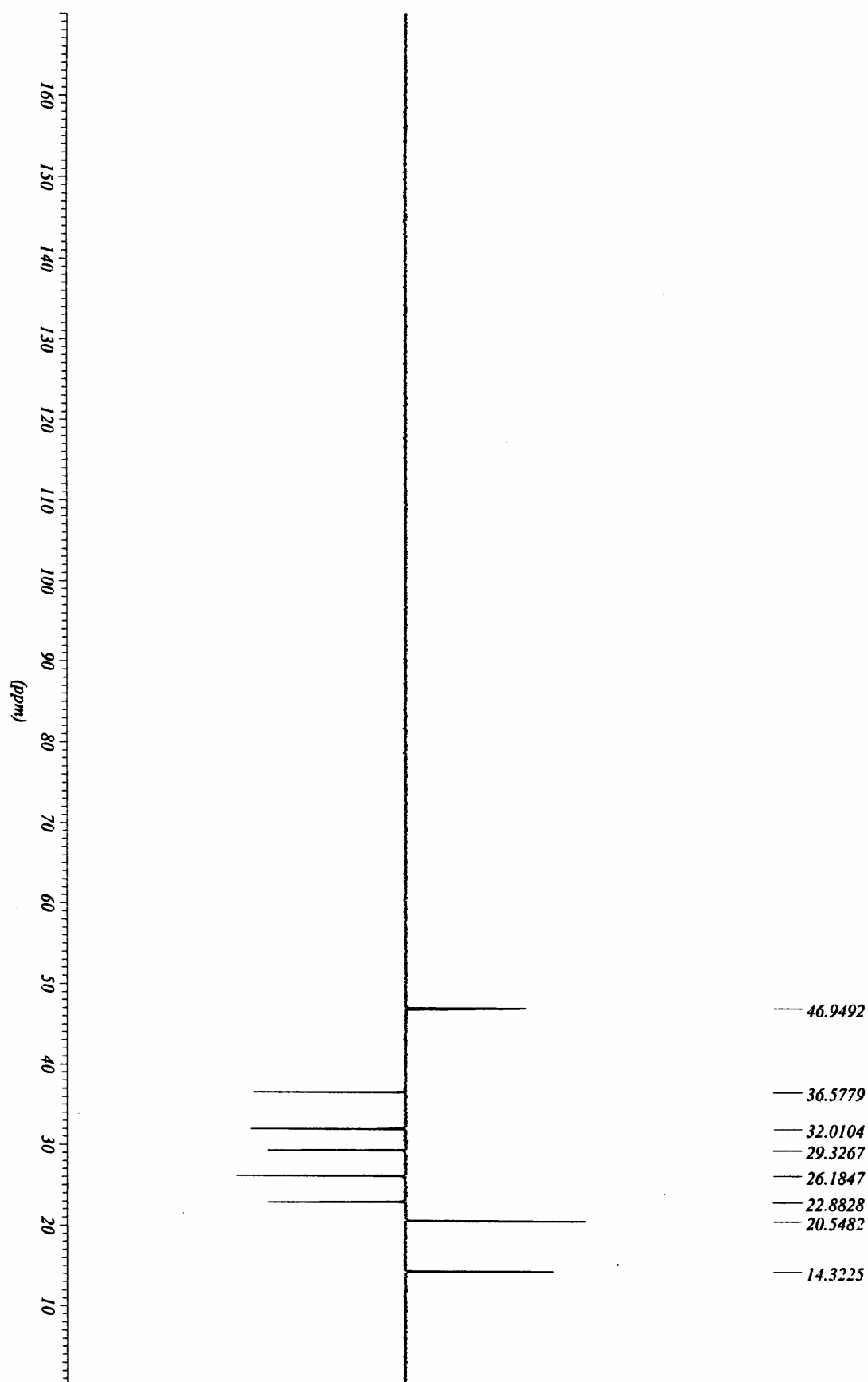
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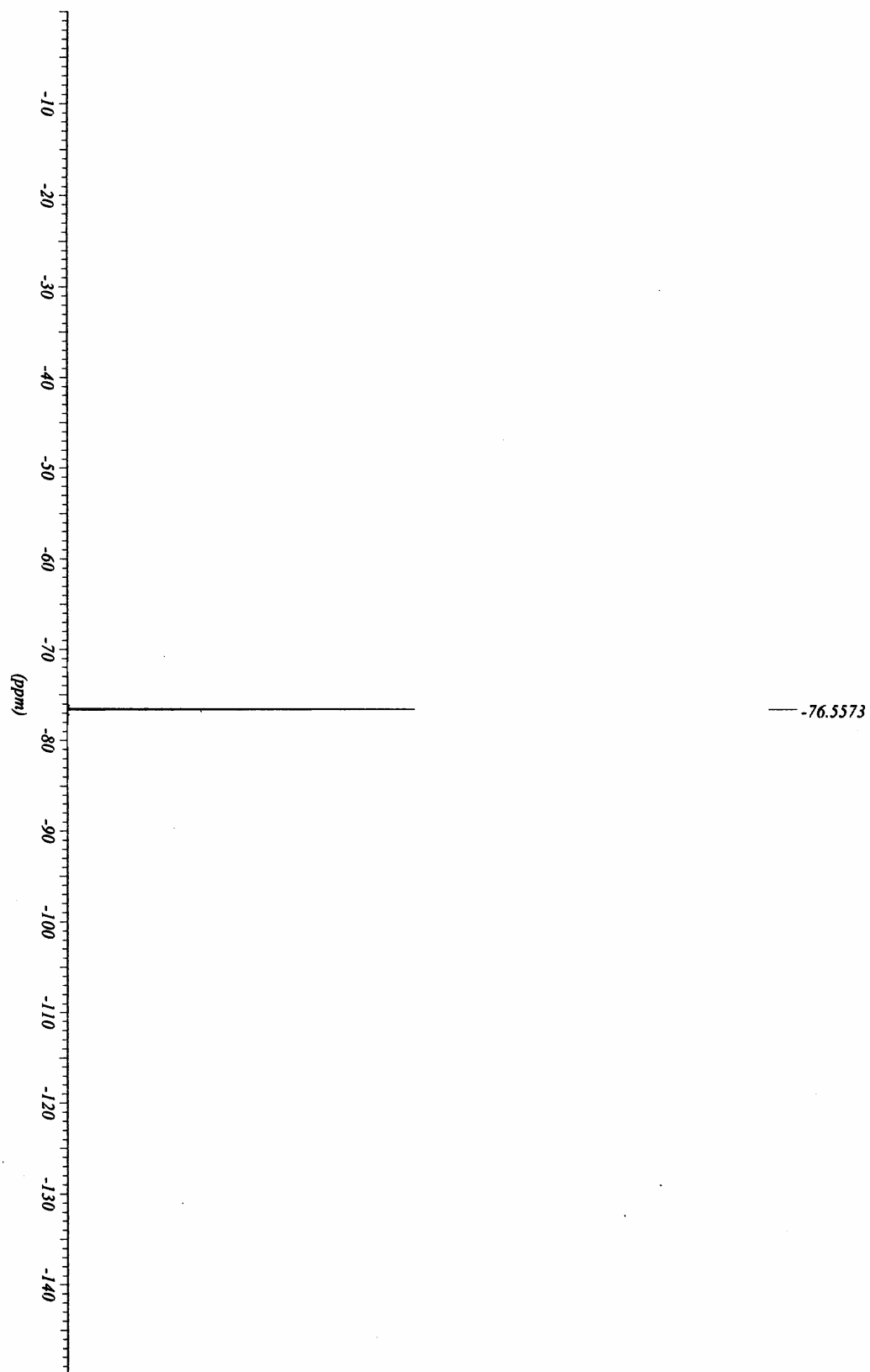
2,2,2-trifluoro-*N*-(octan-2-yl)acetamide: ^{13}C NMR



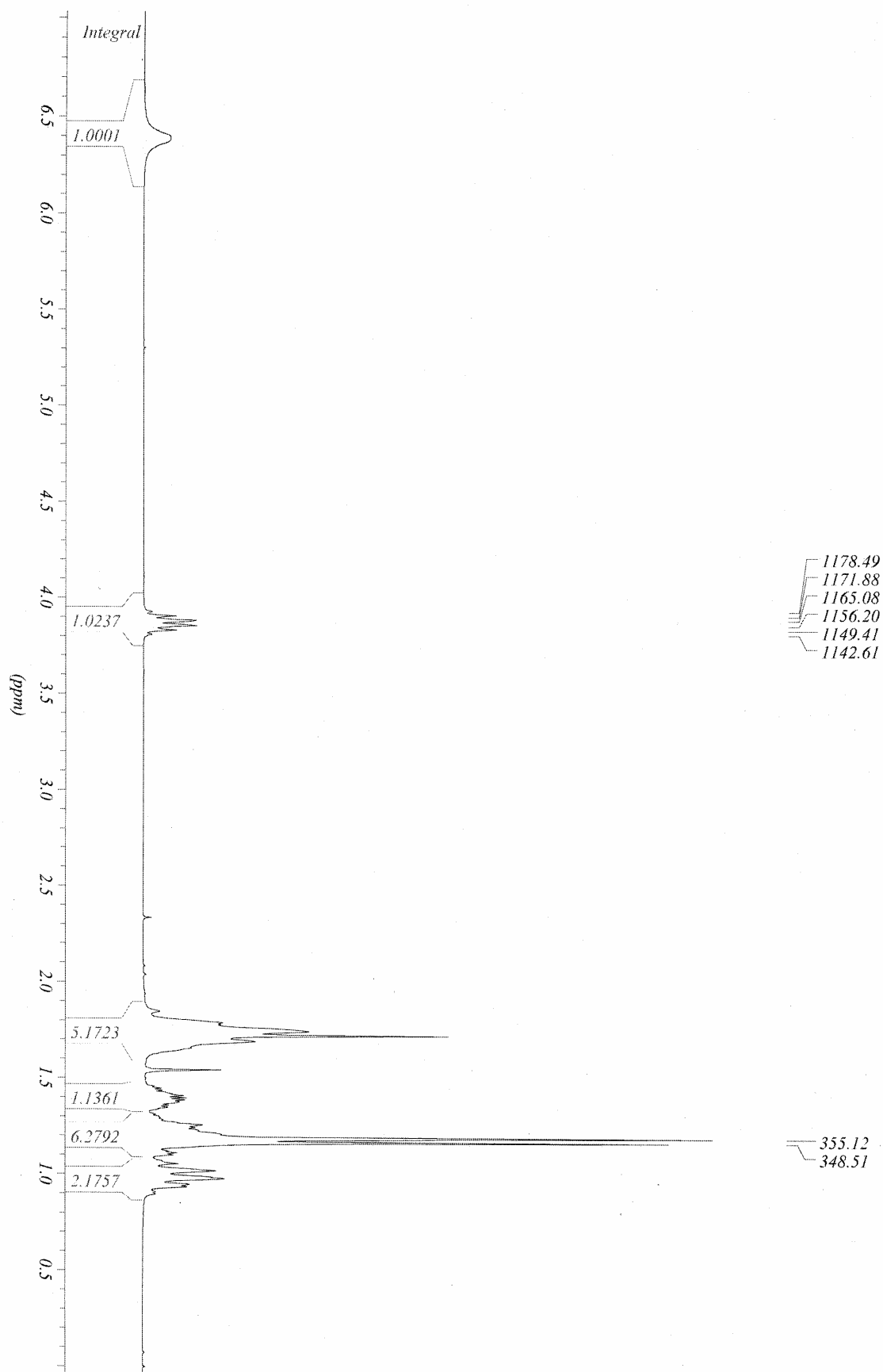
2,2,2-trifluoro-*N*-(octan-2-yl)acetamide: DEPT



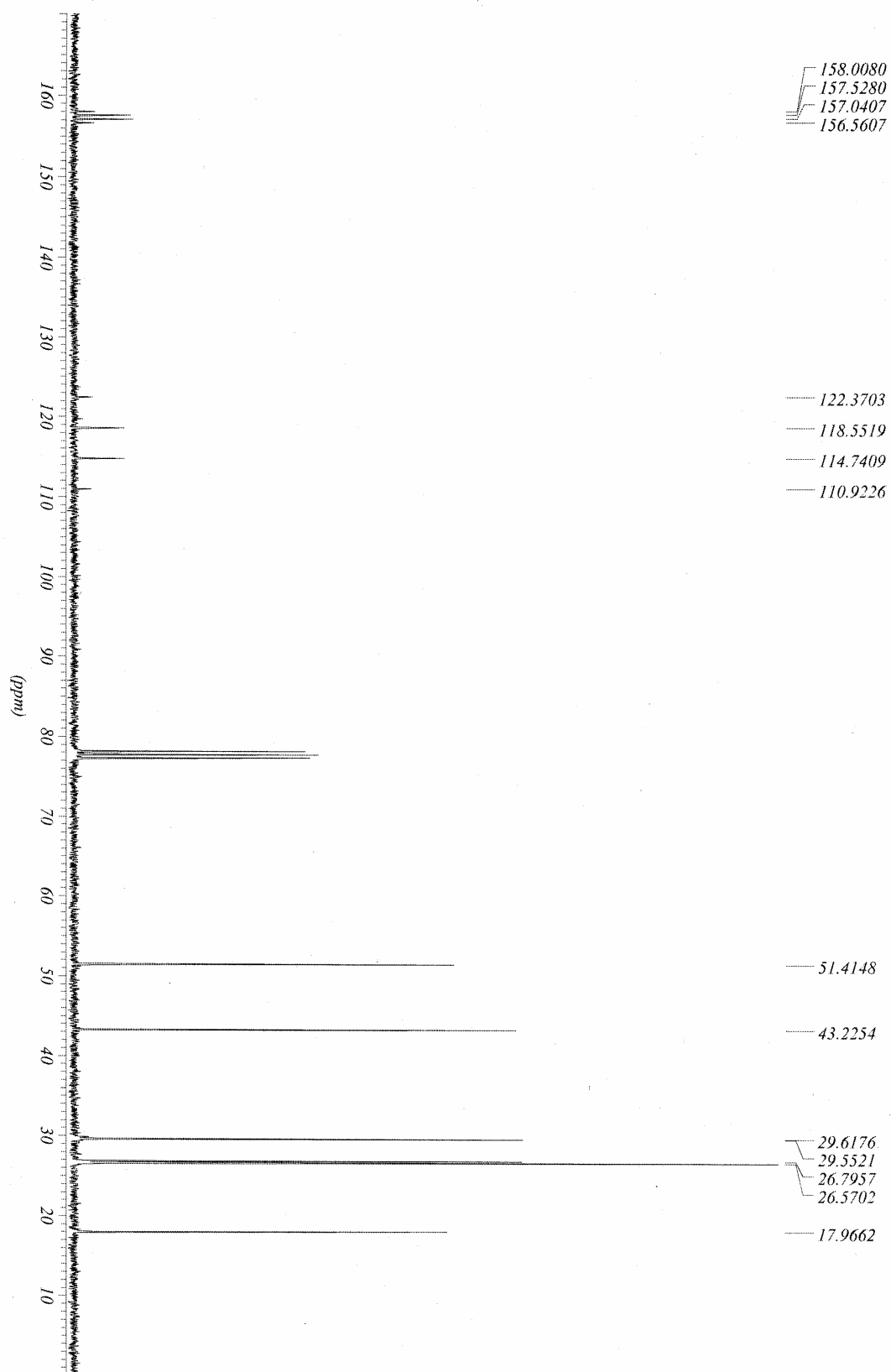
2,2,2-trifluoro-*N*-(octan-2-yl)acetamide: ^{19}F NMR



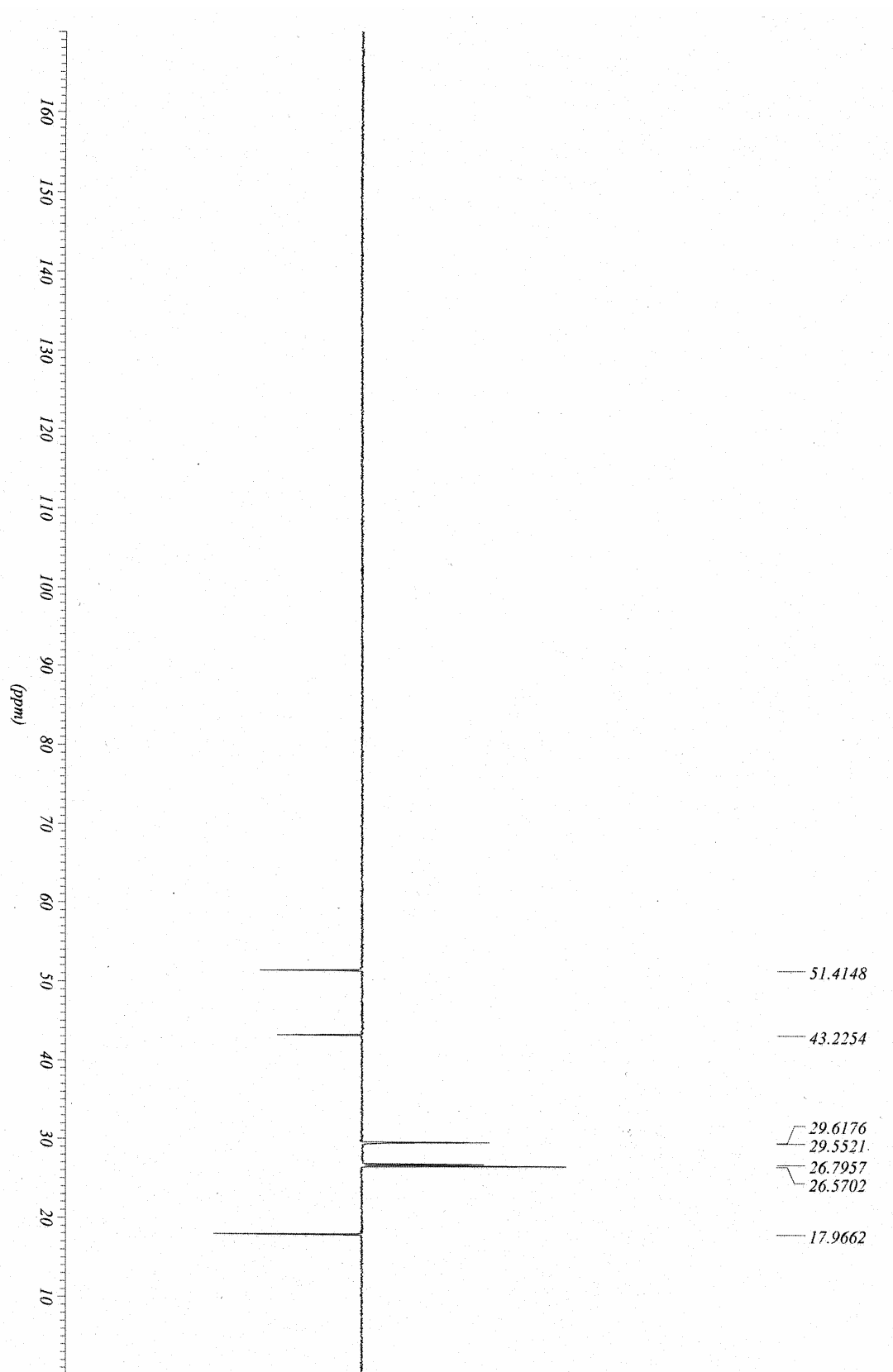
2,2,2-trifluoro-*N*-(1-cyclohexylethyl)acetamide : ^1H NMR



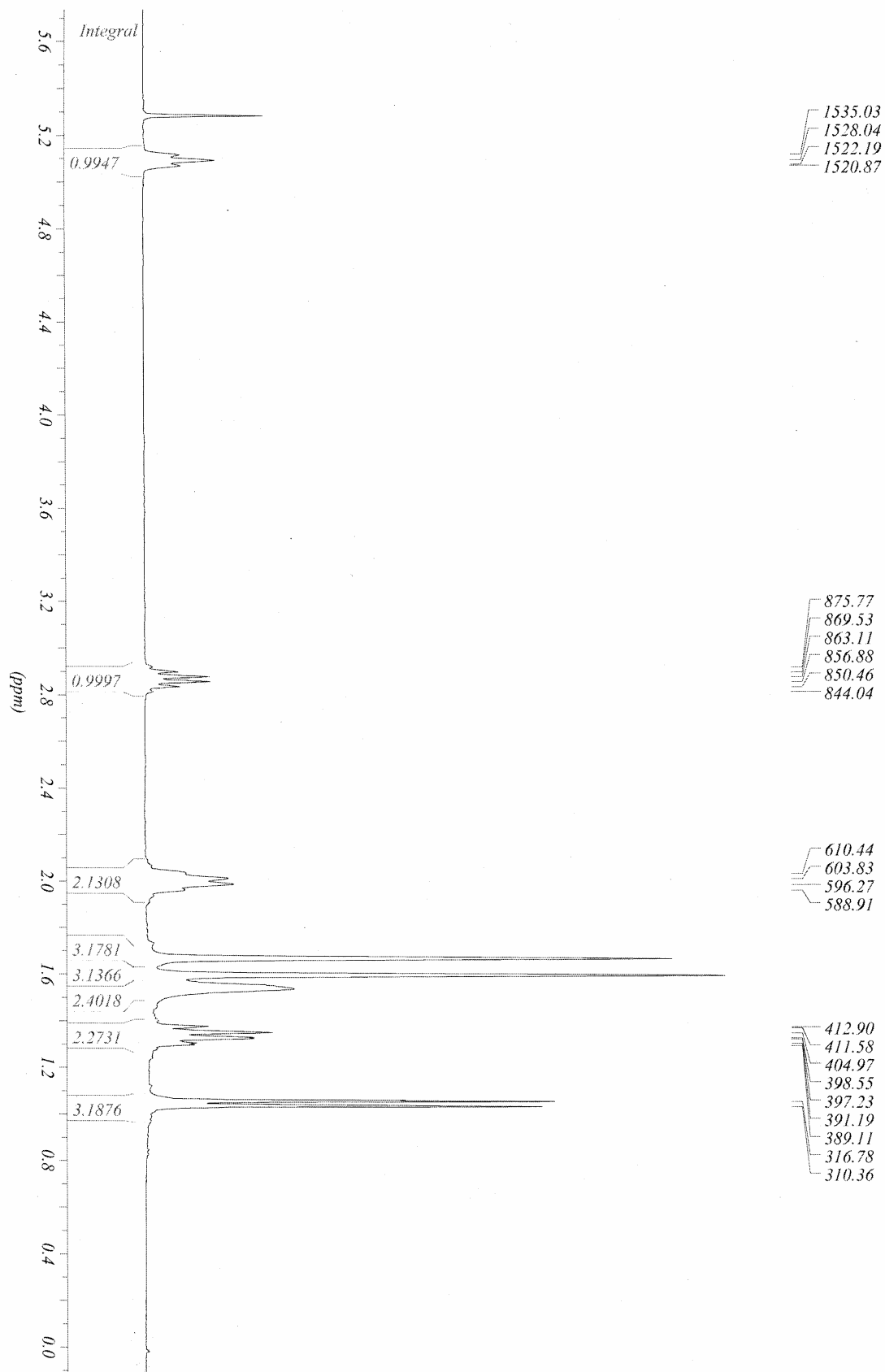
2,2,2-trifluoro-*N*-(1-cyclohexylethyl)acetamide: ^{13}C NMR



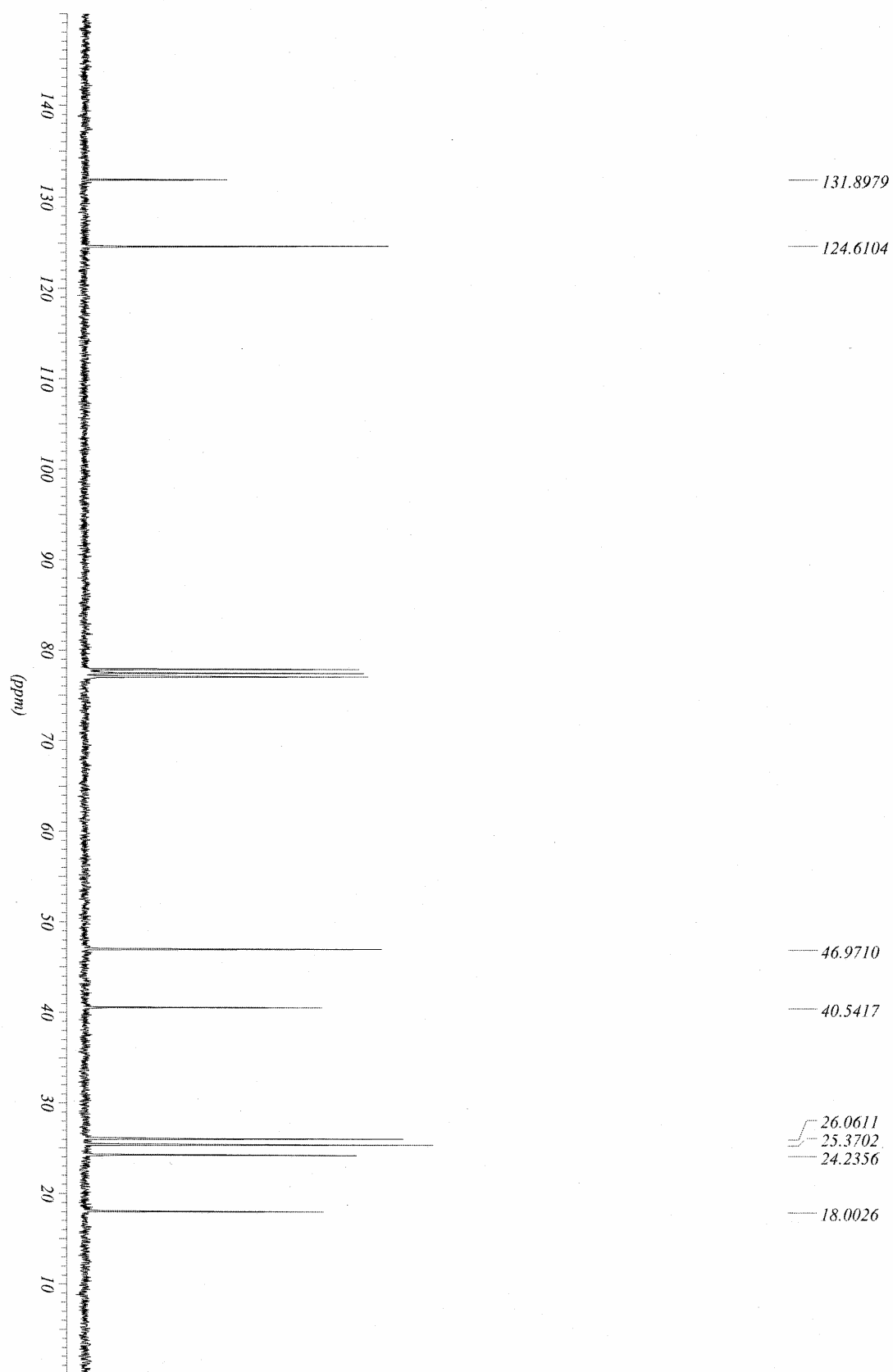
2,2,2-trifluoro-*N*-(1-cyclohexylethyl)acetamide: DEPT



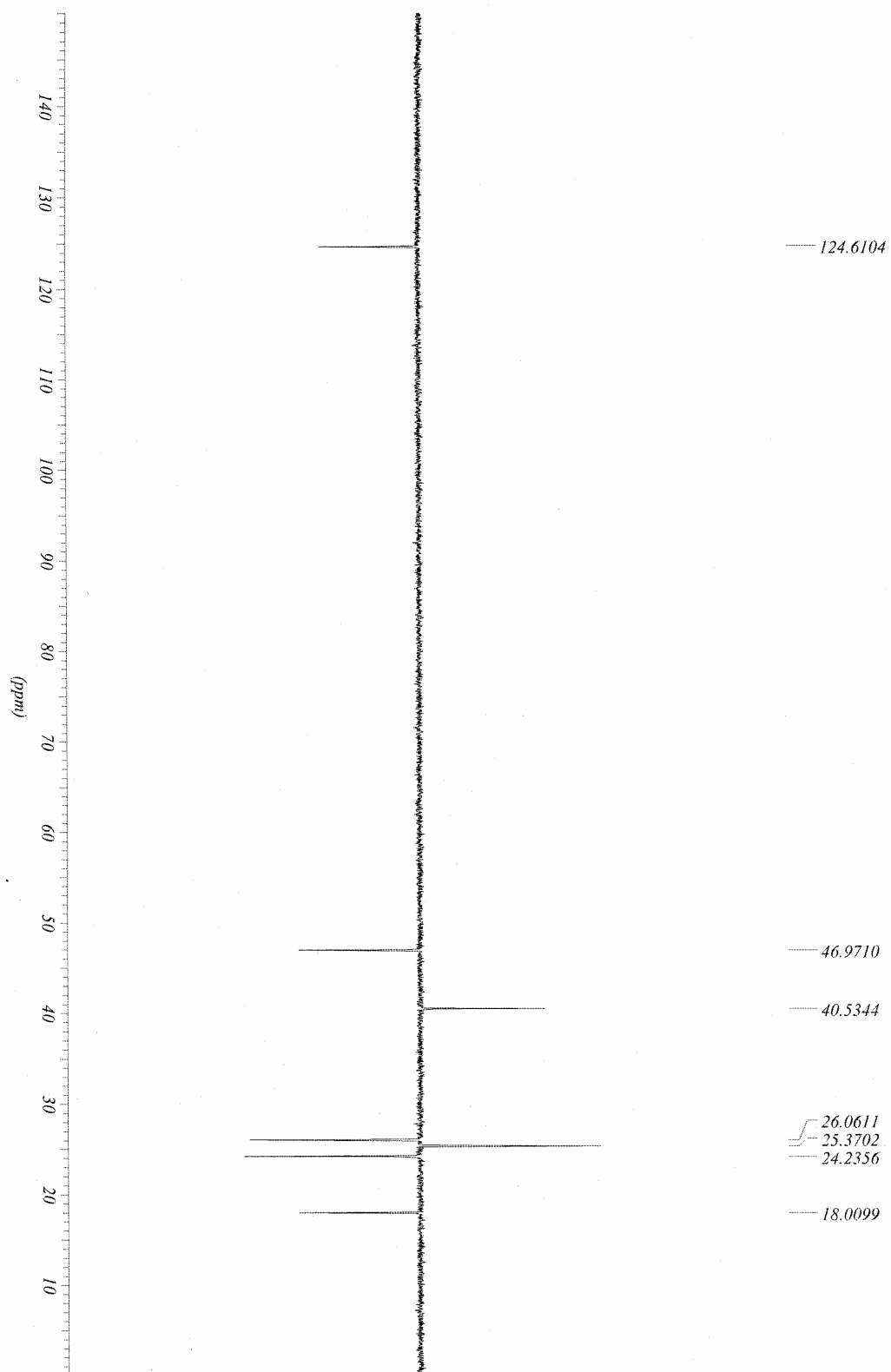
(S)-6-Methylhept-5-en-2-amine (11): ^1H NMR



(S)-6-Methylhept-5-en-2-amine (11): ^{13}C NMR



(S)-6-Methylhept-5-en-2-amine (11): DEPT



Computational details.

All the calculations were performed with the Gaussian-03 molecular orbital package.⁴ Geometry optimizations were carried out without constraints at the UB3LYP/6-31G(d) level of theory. Vibrational frequencies were calculated at the UB3LYP/6-31G(d) level to determine the nature of the located stationary points. The spin contamination was low for all radical species (maximum value for $\langle S^2 \rangle = 0.772$). In all cases vibrational frequencies were scaled by a factor of 0.9804 in considering the zero-point energy.⁵ The BDE values at 298 K were calculated by standard statistical thermodynamic methods using the above mentioned frequencies. The single point energies were then calculated at the UB3P86/6-311++G(d,p) level of theory. In order to obtain more accurate results, some BDEs were calculated using G3B3 and G3B3(MP2) composite methods.^{5,6} Natural bond orbital interactions were calculated using NBO 3.1⁷ method included in the Gaussian-03 package.

UB3P86/6-311++G(d,p) computed total energies, $\langle S^2 \rangle$ for radical species, and UB3LYP/6-31G(d) ZPE and cartesian coordinates for **5**, **6**, **7**, **8**; **BuSH**, **MeO₂CCH₂SH**. G3B3 enthalpies at 298K and cartesian coordinates for **5**, **6**, **7**; **BuSH**, **MeO₂CCH₂SH**

5:

E(B3P86/6-311++G(d,p)) = -175.165964 au.
ZPE = 312.71 kJ.mol⁻¹

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.472015
H	0.961005	0.000000	-0.341691
H	-0.418086	-0.865294	-0.341689
H	0.543982	-0.866894	1.894064
C	0.695836	1.272006	1.962674
C	-1.448039	-0.073285	1.962675
H	-1.492044	-0.071276	3.057641
H	-2.019317	0.782056	1.585069
H	-1.939049	-0.989628	1.610868
H	0.713195	1.312492	3.057641
H	0.174118	2.158457	1.585090
H	1.734518	1.315570	1.610841

6:

E(B3P86/6-311++G(d,p)) = -214.625288 au.
ZPE = 385.88 kJ.mol⁻¹

N	0.000000	0.000000	0.000000
---	----------	----------	----------

C	0.000000	0.000000	1.469013
H	0.968355	0.000000	-0.315789
H	0.296055	-0.993611	1.864891
C	1.019890	1.030964	1.960898
C	-1.399502	0.319184	2.008275
H	-1.391059	0.344515	3.103975
H	-1.732642	1.295179	1.637343
H	-2.137509	-0.430127	1.702825
H	1.048614	1.061329	3.055385
H	0.759851	2.029738	1.591934
H	2.031156	0.790633	1.607760
C	-0.681574	-1.136934	-0.610935
H	-0.497989	-1.127581	-1.690432
H	-0.364751	-2.121406	-0.215647
H	-1.763820	-1.055161	-0.465332

7:

E(B3P86/6-311++G(d,p)) = -254.083912 au.
 ZPE = 458.70 kJ.mol⁻¹

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.477377
H	1.047033	0.000000	1.850516
C	-0.697634	1.250975	2.033790
C	-0.697649	-1.251022	2.033728
H	-0.784622	-1.174316	3.122694
H	-1.706355	-1.341159	1.613638
H	-0.150987	-2.173270	1.817922
H	-0.785435	1.173765	3.122652
H	-1.706036	1.341633	1.613060
H	-0.150460	2.173108	1.818775
C	0.628459	-1.191206	-0.563571
H	0.620941	-1.117159	-1.655966
H	1.681219	-1.325330	-0.241227
H	0.072505	-2.091764	-0.293699
C	0.626844	1.191963	-0.563784
H	0.069937	2.091815	-0.293541
H	1.679614	1.327297	-0.241985
H	0.618834	1.117920	-1.656177

8:

E(B3P86/6-311++G(d,p)) = -403.654071 au.
 ZPE = 424.94 kJ.mol⁻¹

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.466587
H	0.892556	0.000000	-0.475539
H	-0.972729	-0.394277	1.774500
C	1.095472	-0.950306	1.958648
C	0.160597	1.414558	2.043088
H	0.120316	1.394523	3.138597
H	1.122503	1.850295	1.745932
H	-0.639798	2.067935	1.682834
H	1.096367	-0.999246	3.052463
H	2.088598	-0.603097	1.643566
H	0.945048	-1.960881	1.565562
C	-1.037743	0.350424	-0.815661
O	-0.952622	0.492929	-2.022762
O	-2.195100	0.497733	-0.111266
C	-3.340442	0.809944	-0.913437
H	-4.168434	0.911688	-0.210156
H	-3.187834	1.742603	-1.462965
H	-3.544038	0.008310	-1.628732

BuSH:

E(B3P86/6-311++G(d,p)) = -557.639104 au.
 ZPE = 341.75 kJ.mol⁻¹

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.533337
H	1.020454	0.000000	-0.397717
H	-0.512351	-0.884703	-0.395593
H	-0.512378	0.884673	-0.395617
C	-1.415415	-0.000738	2.129861
H	0.548529	-0.878647	1.899335
H	0.547699	0.879176	1.899332
C	-1.403613	0.000629	3.660292
H	-1.964819	0.878876	1.769235
H	-1.963101	-0.882021	1.770638
H	-0.884492	-0.885895	4.036767
H	-0.890055	0.891061	4.035144
S	-3.139265	-0.004089	4.299275
H	-2.831268	0.002234	5.612204

MeO₂CCH₂SH:

E(B3P86/6-311++G(d,p)) = -667.697565 au.
 ZPE = 232.86 kJ.mol⁻¹

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.211778
O	1.112925	0.000000	-0.758053
C	2.353210	0.016864	-0.027996
H	3.136951	0.013887	-0.785568
H	2.417386	0.915103	0.591327
H	2.431548	-0.865089	0.612906
C	-1.253970	-0.005779	-0.853992
H	-1.849758	-0.887110	-0.601264
H	-1.004106	-0.033907	-1.915319
S	-2.256446	1.516186	-0.593870
H	-2.350473	1.378792	0.746066

5:

G3B3 enthalpy at 298K = -174.30736 au.

N	-0.880126	1.056462	-0.260072
C	-0.159943	-0.091236	0.315215
H	-1.861308	0.812070	-0.393627
H	-0.872921	1.831531	0.402874
H	-0.594322	-0.422474	1.278098
C	-0.245039	-1.264719	-0.663882
C	1.291435	0.320140	0.574454
H	1.864839	-0.510855	1.000535
H	1.768278	0.635060	-0.360426
H	1.344854	1.158759	1.280436
H	0.284379	-2.141069	-0.273217
H	0.196298	-0.986457	-1.627390
H	-1.287929	-1.556912	-0.841501

6:

G3B3 enthalpy at 298K = -213.56704 au.

N	-0.208182	0.930579	-0.290431
C	0.231859	-0.292247	0.394449
H	-0.037193	1.719417	0.330803
H	1.339613	-0.351830	0.425452
C	-0.283188	-0.260986	1.836240
C	-0.282109	-1.536349	-0.339944
H	0.025274	-2.446621	0.187495

H	-1.376464	-1.515740	-0.395635
H	0.108715	-1.600634	-1.360995
H	0.024794	-1.159785	2.381177
H	-1.377721	-0.204811	1.848384
H	0.107998	0.608650	2.380145
C	0.460828	1.193816	-1.560682
H	0.179269	2.191092	-1.914618
H	1.565749	1.145001	-1.509900
H	0.132899	0.475800	-2.319668

7:

G3B3 enthalpy at 298K = -252.82876 au.

N	-0.668003	-0.000370	-0.322247
C	0.668358	0.000098	0.307659
H	1.452302	0.000396	-0.480340
C	0.873762	1.251131	1.175964
C	0.874601	-1.250866	1.175903
H	1.822515	-1.173830	1.718876
H	0.064560	-1.341309	1.909213
H	0.912804	-2.173090	0.589389
H	1.821284	1.174251	1.719639
H	0.063208	1.341483	1.908731
H	0.912236	2.173289	0.589361
C	-0.909397	-1.191648	-1.131032
H	-1.900755	-1.117948	-1.589991
H	-0.168910	-1.325489	-1.945871
H	-0.902002	-2.092216	-0.513097
C	-0.911137	1.191521	-1.129616
H	-0.904459	2.091363	-0.510625
H	-0.171235	1.327137	-1.944691
H	-1.902648	1.117130	-1.588133

BuSH:

G3B3 enthalpy at 298K = -556.31137 au.

C	1.490988	0.000127	-2.648853
C	1.491570	0.000958	-1.116659
H	2.511844	0.000760	-3.047011
H	0.978779	-0.885402	-3.044201
H	0.977297	0.884361	-3.045169
C	0.076065	-0.000110	-0.521357
H	2.040989	-0.877180	-0.749359
H	2.039302	0.880554	-0.750319
C	0.088240	0.000990	1.008728
H	-0.474043	0.879399	-0.882197
H	-0.472148	-0.881303	-0.880994
H	0.607716	-0.885774	1.385781
H	0.605057	0.889845	1.384499
S	-1.647300	-0.001115	1.646026
H	-1.339176	0.000798	2.961405

MeO₂CCH₂SH:

G3B3 enthalpy at 298K = -666.24175 au.

C	0.316841	-0.441285	0.230197
O	0.313788	-0.425137	1.441865
O	1.431670	-0.453501	-0.524953
C	2.670142	-0.429266	0.207968
H	3.455782	-0.443827	-0.547499
H	2.734495	0.477023	0.815433
H	2.745160	-1.302748	0.860759
C	-0.934983	-0.456062	-0.626829
H	-1.533108	-1.332813	-0.363901
H	-0.682500	-0.498804	-1.687049

S	-1.935166	1.071136	-0.389556
H	-2.032834	0.951789	0.951847

Radical species

5:

E(B3P86/6-311++G(d,p)) = -174.494596 au. $\langle S^2 \rangle = 0.7536$
 ZPE = 276.46 kJ.mol⁻¹

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.412561
H	0.933683	0.000000	-0.402168
H	-0.540949	-0.761011	-0.402168
C	0.969993	0.942899	2.056008
C	-1.330509	-0.244318	2.056008
H	-1.215943	-0.428492	3.130157
H	-2.024232	0.610448	1.943705
H	-1.836056	-1.118935	1.622057
H	1.053730	0.742816	3.130157
H	0.675228	2.003554	1.943704
H	1.975761	0.848225	1.622057

6:

E(B3P86/6-311++G(d,p)) = -213.953997 au. $\langle S^2 \rangle = 0.7536$
 ZPE = 349.91 kJ.mol⁻¹

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.408302
H	0.944006	0.000000	-0.373422
C	1.097038	0.809542	2.034072
C	-1.326890	-0.068198	2.104077
H	-1.178632	-0.172741	3.184413
H	-1.939137	0.841522	1.948702
H	-1.935765	-0.919201	1.774766
H	1.196624	0.572979	3.099476
H	0.926112	1.900363	1.958967
H	2.069364	0.609710	1.561014
C	-0.866595	-0.912566	-0.733641
H	-0.673091	-0.799249	-1.804646
H	-0.724513	-1.973015	-0.463377
H	-1.917006	-0.658245	-0.560663

7:

E(B3P86/6-311++G(d,p)) = -253.412719 au. $\langle S^2 \rangle = 0.7538$
 ZPE = 422.99 kJ.mol⁻¹

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.412694
C	1.335057	0.000000	2.104906
C	-1.147524	0.682463	2.104746
H	-1.016881	0.616600	3.189303
H	-1.227618	1.758144	1.855459
H	-2.121989	0.233382	1.873360
H	1.188971	0.010476	3.189444
H	1.953889	0.883448	1.855472
H	1.942957	-0.884226	1.873851
C	-1.285504	-0.115044	-0.676280
H	-1.144034	0.069404	-1.746112
H	-1.746326	-1.112959	-0.558948
H	-1.987432	0.631878	-0.300517
C	1.045916	-0.756069	-0.676430
H	2.031096	-0.472969	-0.300865
H	0.931828	-1.849306	-0.559064
H	1.018442	-0.525246	-1.746263

8:

E(B3P86/6-311++G(d,p)) = -402.976335 au. <S²>=0.7546
ZPE = 388.00 kJ.mol⁻¹

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.407415
H	0.906518	0.000000	-0.450640
C	1.370477	0.096061	2.006935
C	-1.183498	0.502323	2.175296
H	-0.993655	0.389860	3.247507
H	-1.375700	1.573811	1.985885
H	-2.104090	-0.031135	1.928407
H	1.351183	-0.208784	3.058320
H	1.780843	1.123029	1.979362
H	2.090029	-0.551811	1.488793
C	-0.992841	-0.156158	-0.940396
O	-0.767734	-0.170264	-2.139708
O	-2.225002	-0.287951	-0.393858
C	-3.283892	-0.431810	-1.350968
H	-4.196126	-0.523814	-0.760023
H	-3.336882	0.442947	-2.004482
H	-3.132418	-1.323984	-1.964005

BuS:

E(B3P86/6-311++G(d,p)) = -556.975949 au. <S²>=0.7529
ZPE = 315.38 kJ.mol⁻¹

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.532231
H	1.020983	0.000000	-0.397750
H	-0.512982	-0.884855	-0.395758
H	-0.512979	0.884858	-0.395756
C	-1.415284	0.000068	2.128063
H	0.549834	-0.878556	1.898921
H	0.549906	0.878509	1.898921
C	-1.405850	0.000020	3.658542
H	-1.968846	0.878443	1.771501
H	-1.968945	-0.878225	1.771455
H	-0.865944	-0.873364	4.053185
H	-0.865747	0.873260	4.053237
S	-3.039135	0.000178	4.460249

MeO₂CCH₂S:

E(B3P86/6-311++G(d,p)) = -667.032083 au. <S²>=0.7530
ZPE = 207.13 kJ.mol⁻¹

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.210514
O	1.110203	0.000000	-0.763257
C	2.353149	0.054539	-0.040841
H	3.133401	0.041058	-0.801913
H	2.408514	0.971321	0.551785
H	2.447226	-0.807519	0.624591
C	-1.249169	0.019558	-0.859803
H	-2.090383	-0.378402	-0.283601
H	-1.119758	-0.603823	-1.753126
S	-1.687797	1.689201	-1.438663

5:

G3B3 enthalpy at 298K = -173.66284 au.

N	0.682560	-1.115008	0.504687
C	0.052862	0.105173	0.173074
H	1.691552	-1.034215	0.599100
H	0.299201	-1.551722	1.338844
C	0.729514	0.909121	-0.894530
C	-1.442626	0.101784	0.259510
H	-1.839486	1.120604	0.186370
H	-1.917010	-0.491686	-0.545003
H	-1.792590	-0.322451	1.211559
H	0.303545	1.917123	-0.952206
H	0.631827	0.455661	-1.899179
H	1.806538	1.015269	-0.700629

6:

G3B3 enthalpy at 298K = -212.92241 au.

N	0.219252	-0.957456	0.090856
C	-0.286155	0.295457	-0.306744
H	-0.001904	-1.681151	-0.585862
C	-1.614982	0.242523	-1.000901
C	0.021625	1.477752	0.563221
H	-0.332562	2.397385	0.084826
H	-0.469347	1.419550	1.554250
H	1.095811	1.599920	0.749170
H	-1.832727	1.194287	-1.498593
H	-2.455498	0.038108	-0.310616
H	-1.640340	-0.543366	-1.769582
C	1.588094	-1.076365	0.574720
H	1.802855	-2.131100	0.771561
H	2.343481	-0.692166	-0.132080
H	1.703977	-0.535478	1.519164

7:

G3B3 enthalpy at 298K = -252.18358 au.

N	0.144438	0.661889	-0.175561
C	-0.216663	-0.651565	0.198806
C	-0.299798	-0.954019	1.669569
C	-1.132233	-1.407298	-0.724288
H	-1.336772	-2.399744	-0.310906
H	-2.111336	-0.910834	-0.867567
H	-0.708541	-1.560208	-1.725237
H	-0.597383	-1.996919	1.816112
H	-1.044400	-0.329788	2.200186
H	0.654565	-0.818267	2.194495
C	0.337909	0.931693	-1.594322
H	0.443461	2.011415	-1.741417
H	1.237753	0.440317	-2.007588
H	-0.527657	0.600975	-2.171568
C	1.119847	1.357622	0.653696
H	0.820097	1.335219	1.703183
H	2.135956	0.929541	0.574776
H	1.168814	2.406470	0.343699

BuS:

G3B3 enthalpy at 298K = -555.67610 au.

C	1.429500	-0.000088	-2.644478
C	1.430472	-0.000158	-1.112247
H	2.450231	-0.000169	-3.042876
H	0.916180	-0.884874	-3.039951
H	0.916356	0.884838	-3.039868
C	0.015565	0.000020	-0.515517
H	1.980453	-0.878784	-0.745946

H	1.980696	0.878281	-0.745866
C	0.025971	-0.000099	1.014955
H	-0.538136	0.878464	-0.871687
H	-0.538406	-0.878203	-0.871814
H	0.566042	-0.873554	1.409216
H	0.566410	0.873069	1.409347
S	-1.606805	0.000180	1.817698

MeO₂CCH₂S[•]:

G3B3 enthalpy at 298K = -665.60469 au.

C	0.126492	-0.488104	0.478035
O	0.130536	-0.496775	1.688512
O	1.234121	-0.476437	-0.288862
C	2.479152	-0.420136	0.429821
H	3.256921	-0.423809	-0.333900
H	2.531398	0.492673	1.028830
H	2.580243	-1.286400	1.088730
C	-1.125631	-0.469361	-0.377477
H	-1.962691	-0.876130	0.198626
H	-0.995743	-1.085595	-1.275677
S	-1.575467	1.201910	-0.942880

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