A Modular, Catalytic Enantioselective Construction of Quaternary Carbon Stereocenters by Sequential Cross-Coupling Reactions

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I. General Information

^{1}H NMR spectra were recorded on either a Varian VNMRS-400 (400 MHz), Varian Gemini-500 (500 MHz), Varian Inova-500 (500 MHz), or Varian Gemini-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a Varian VNMRS-400 (100 MHz), Varian Gemini-500 (125 MHz), or Varian Gemini-600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). ^{11}B NMR spectra were recorded on a Varian Gemini-500 (160 MHz), or Varian Gemini-600 (192 MHz) spectrometer. ^{19}F NMR spectra were recorded on a Varian Gemini-500 (470 MHz) spectrometer. Infrared (IR) spectra were recorded on a Bruker alpha-P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter. High-resolution mass spectrometry (DART) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. GCMS was performed on an Agilent 7820A with ZB-5 column (30 m x 250 μm x 0.25 μm) and with an Agilent 5975 mass detector. The method used for GCMS was start at 50^{o}C for 4 minutes, then ramp to 250^{o}C at 20^{o}C, hold for 46 minutes.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography (TLC) was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm) and ceric ammonium molybdate (CAM) in ethanol.

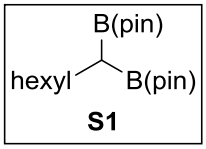
Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector with isopropanol, or methanol as the modifier.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and toluene were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after purging with N_2. Bis(pinacolato)diboron was generously donated by Allychem Co., Ltd. and used without further purification. Palladium (II) acetate and RuPhos were purchased from Strem Chemicals,

Inc. and used without further purification. Lithium 2,2,6,6-tetramethylpiperidide (LTMP) was purchased from Aldrich and used without purification. All other reagents were purchased from either Aldrich, Alfa Aesar or Acros and used without further purification.

II. Synthesis and Characterization of Geminal bis(Boronates)

Geminal bis(boronates) were prepared according to literature procedures.[1,2]

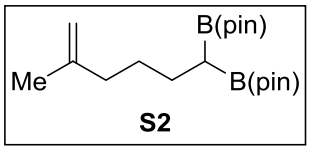


S1

2,2'-(Heptane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S1). Prepared according to a literature precedent with slight modification.[3] In an Ar-filled drybox, an oven-dried 50-mL round bottom flask with a magnetic stir bar was charged with lithium 2,2,6,6-tetramethylpiperidide (442 mg, 3.0 mmol). The flask was sealed with a rubber septum, and removed from the drybox. THF (10 mL) was added and the reaction was cooled to 0 °C. A solution of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane[1,3] (804 mg, 3.0 mmol) in THF (5 mL) was added *via* syringe and the mixture was allowed to stir at 0 °C for 5 minutes. Then 1-bromohexane (463 µL, 3.3 mmol) was added neat. The reaction mixture was allowed to warm to room temperature and stir for 4 hours. The reaction was diluted with Et_2O (10 mL), filtered through Celite with Et_2O (10 mL), and concentrated *in vacuo.* The crude mixture was purified by silica gel chromatography to afford clear, colorless oil (894 mg, 85% yield). R_f = 0.5 in 10% ethyl acetate/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.53 (q, *J* = 7.8 Hz, 2H), 1.30-1.20 (m, 32H), 0.86 (t, *J* = 6.6 Hz, 3H), 0.71 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 82.96, 32.67, 31.89, 29.42, 25.81, 24.97, 24.64, 22.73, 14.21. ^{11}B NMR (192 MHz, $CDCl_3$) δ 31.50. IR (neat) ν_{max} 2977 (m), 2924 (m), 2859 (w), 1466 (w), 1354 (m),

[1] Sun, C.; Potter, B.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 6534.
[2] Potter, B.; Szymaniak, A. A.; Edelstein, E. K.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 17918.
[3] Matteson, D. S.; Moody, R. J. *Organometallics*, **1982**, *1*, 20.

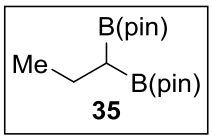
1308 (s), 1268 (s), 1214 (w), 1140 (s), 969 (m), 850 (m) cm^{-1}. HRMS (DART) calc. for $C_{19}H_{39}B_2O_4$ $[M+H]^+$ 353.3034, found 353.3041.



S2

2,2'-(5-Methylhex-5-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S2). Prepared according to a literature precedent with slight modification.[3] In an Ar-filled drybox, an oven-dried 50-mL round bottom flask with a magnetic stir bar was charged with lithium 2,2,6,6-tetramethylpiperidide (353 mg, 2.4 mmol). The flask was sealed with a rubber septum, and removed from the drybox. THF (8 mL) was added and the reaction was cooled to 0 °C. A solution of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane[1,3] (638 mg, 2.4 mmol) in THF (4 mL) was added *via* syringe and the mixture was allowed to stir at 0 °C for 5 minutes. Then 4-methylpent-4-en-1-yl 4-methylbenzenesulfonate[4] (666 mg, 2.6 mmol) was added as a solution in THF (2 mL). The reaction mixture was allowed to warm to room temperature and stir for 4 hours. The reaction was diluted with Et_2O (10 mL), filtered through Celite with Et_2O (10 mL), and concentrated *in vacuo.* The crude mixture was purified by silica gel chromatography (5% ethyl acetate/hexanes) to afford clear, colorless oil (560 mg, 67% yield). R_f = 0.5 in 10% ethyl acetate/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.63 (s, 2H), 1.97 (t, J = 7.2 Hz, 2H), 1.67 (s, 3H), 1.53 (q, J = 7.8 Hz, 2H), 1.44-1.37 (m, 2H), 1.21 (s, 12H), 1.20 (s, 12H), 0.72 (t, J = 7.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.37, 109.53, 83.01, 38.01, 30.68, 25.56, 24.97, 24.63, 22.51. ^{11}B NMR (192 MHz, $CDCl_3$) δ 31.30. IR (neat) ν_{max} 2977 (m), 2924 (m), 2860 (w), 1459 (w), 1359 (m), 1308 (s), 1265 (m), 1138 (s), 969 (m), 849 (m) cm^{-1}. HRMS (DART) calc. for $C_{19}H_{37}B_2O_4$ $[M+H]^+$ 351.2878, found 351.2881.

[4] Larock, R. C.; Yang, H.; Weinreb, S. M.; Herr, R. J. *J. Org. Chem.* **1994**, *59*, 4172.

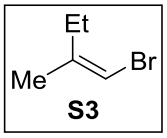


35

2,2'-(Propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (35). Prepared according to a literature precedent with slight modification.[5] A 250-mL round bottom flask with a magnetic stir bar was charged with 4-methyl-N'-propylidenebenzenesulfonohydrazide[5] (2.3 g, 10 mmol) and NaH (480 mg, 12 mmol, 60% wt in oil) and purged with N_2. Toluene (40 mL) was added followed by a vigorous evolution of hydrogen. The reaction was stirred at room temperature for 1 hour. Bis(pinacolato)diboron (1.9 g, 7.0 mmol) was added as a solution in toluene (20 mL) *via* syringe. The reaction was sealed and heated to 105ºC for 12 hours. After cooling to room temperature, Et_2O (30 mL) and water (30 mL) were added and vigorously stirred for 10 minutes. The reaction was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted with Et_2O (2 x 20 mL). The organic layers were combined, washed with brine (20 mL), dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by silica gel chromatography (7% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil (1.8 g, 81% yield). R_f = 0.4 in 10% ethyl acetate/hexanes on TLC. The spectral data matched those reported in the literature.[6]

III. Synthesis and Characterization of Alkenyl Halides

Alkenyl bromides were prepared according to literature procedures.[2]

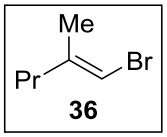


S3

(Z)-1-Bromo-2-methylbut-1-ene (S3). Prepared according to a literature precedent with slight modification.[7] In an Ar-filled drybox, to an oven-dried 2-neck 250-mL round bottom flask equipped with a magnetic stirbar was charged with Cp_2ZrCl_2 (643 mg, 2.2 mmol). The flask was sealed with rubber septa and removed from the drybox. Under a constant pressure of N_2, one septum was replaced a Dewar condenser. CH_2Cl_2 (48 mL) was added to the reaction vessel followed cautiously by triethylaluminum (30 mL, 30 mmol, 1 M in hexanes) *via* syringe. The reaction was cooled to -23ºC and water (270 µL, 15 mmol) was added dropwise with vigorous stirring. After stirring for 10 minutes, the Dewar condenser was cooled to -78 ºC and propyne (670 µL, 10 mmol) was added dropwise *via* the

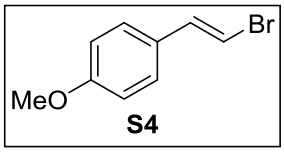
[5] Li, H.; Shangguan, X.; Zhang, Z.; Huang, S.; Zhang, Y.; Wang, J. *Org. Lett*. **2014**, *16*, 448.
[6] Endo, K.; Hirokami, M.; Shibata, T. *J. Org. Chem*. **2010**, *75*, 3469.
[7] Lim, S.; Wipf, P. *Angew. Chem. Int. Ed. Engl*. **1993**, *32*, 1068.

condenser. The reaction was stirred for an additional 10 minutes at -23°C before adding NBS (5.3 g, 30 mmol) as a solid. The reaction was allowed to warm to room temperature and stirred under N_2 for 12 hours. The reaction was cooled to 0°C and carefully quenched with a saturated solution of K_2CO_3 (3 mL). After stirring for 10 minutes, excess $Na_2SO_{4(s)}$ was added. The mixture was filtered through a short pad of silica and concentrated *in vacuo*. The crude mixture was purified on silica gel (pentane, stain in CAM) to afford a clear, colorless oil (538 mg, 36% yield). R_f = 0.9 in pentane on TLC. The spectral data matched those reported in the literature.[8]



36

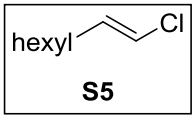
(*E*)-1-bromo-2-methylpent-1-ene (36). Prepared according to a literature precedent with slight modification.[7] In an Ar-filled drybox, an oven-dried 100-mL round bottom flask with a magnetic stir bar was charged with Cp_2ZrCl_2 (640 mg, 2.2 mmol). The flask was removed from the drybox and CH_2Cl_2 (15 mL) was added followed cautiously by trimethylaluminum (2.9 mL, 30 mmol) *via* syringe. The reaction was cooled to -23°C and water (270 µL, 15 mmol) was added dropwise with vigorous stirring. After stirring for 10 minutes, pentyne (990 µL,10 mmol) was added in a solution of CH_2Cl_2 (5 mL). The reaction was stirred for an additional 10 minutes at -23°C before adding NBS (5.3 g, 30 mmol) as a solid. The reaction was allowed to warm to room temperature and stirred under N_2 for 12 hours. The reaction was cooled to 0°C and carefully quenched with a saturated solution of K_2CO_3 (3 mL). After stirring for 10 minutes, excess $Na_2SO_{4(s)}$ was added. The mixture was filtered through a short pad of silica and concentrated *in vacuo*. The crude mixture was purified by silica gel chromatography (pentane, stain in $KMnO_4$) to afford a clear, colorless oil (1.03 g, 63% yield). R_f = 0.9 in pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.88 (s, 1H), 2.08 (t, J = 7.2 Hz, 2H), 1.78 (s, 3H), 1.50-1.42 (m, 2H), 0.88 (t, J = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.92, 101.09, 40.48, 20.78, 19.08, 13.65. GCMS: T_R 5.72; MS: 164, 162, 135, 133, 122, 120, 83, 55 (basepeak).



S4

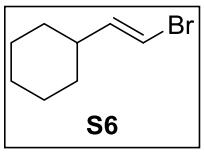
(*E*)-1-(2-Bromovinyl)-4-methoxybenzene (S4). Prepared according to a literature precedent.[9]

[8] Normant, J. F.; Chuit, C.; Cahiez, G.; Villiera, J. *Synthesis*, **1974**, 803.
[9] Müller, D.; Alexakis, A. *Org. Lett*. **2012**, *14*, 1842.



S5

(*E*)-1-Chlorooct-1-ene (S5). To an oven-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N_2 was added octyne (740 μL, 5.0 mmol). DIBAL-H (5.5 mL, 5.5 mmol, 1.0 M in hexanes) was added *via* syringe and the reaction was stirred for 15 minutes at room temperature before heating to 50°C for 5 hours. The reaction was cooled to room temperature and Et_2O (3 mL) was added. The reaction was further cooled to -78°C and NCS (1.34 g, 10.0 mmol) was added as a solid. Upon warming to room temperature, the reaction was stirred for 16 hours. To quench, the reaction was poured into a mixture of 6M HCl (15 mL), pentane (30 mL), and ice. The layers were separated in a separatory funnel, and the aqueous layer was extracted with pentane (3 x 20 mL). The organic layers were combined and washed successively with 1M NaOH (10 mL) and a saturated solution of $Na_2S_2O_3$ (10 mL). The organic layer was dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The crude mixture was purified by silica gel chromatography (pentane, stain in $KMnO_4$) to afford a clear, colorless oil (429 mg, 59% yield). R_f = 0.9 in pentane on TLC. The spectral data matched those reported in the literature.[10]



S6

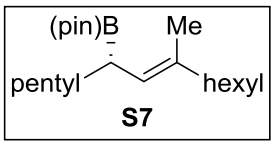
(*E*)-(2-Bromovinyl)cyclohexane (S6). Prepared according to a literature precedent with slight modification.[11] To an oven-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N_2 was added ethynylcyclohexane (683 μL, 5.0 mmol). DIBAL-H (5.5 mL, 5.5 mmol, 1.0 M in hexanes) was added *via* syringe and the reaction was stirred for 15 minutes at room temperature before heating to 50°C for 5 hours. The reaction was cooled to room temperature and Et_2O (3 mL) was added. The reaction was further cooled to -78°C and NBS (1.78 g, 10.0 mmol) was added as a solid. Upon warming to room temperature, the reaction was stirred for 16 hours. To quench, the reaction was poured into a mixture of 6M HCl (15 mL), pentane (30 mL), and ice. The layers were separated in a separatory funnel, and the aqueous layer was extracted with pentane (3 x 20 mL). The organic layers were combined and washed successively with 1M NaOH (10 mL) and a saturated solution of $Na_2S_2O_3$ (10 mL). The organic layer was dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The crude mixture was purified by silica gel chromatography (pentane,

[10] Brown, H. C.; Hamaoka, T.; Ravindran, N.; Subrahmanyam, C.; Somayaji, V.; Bhat, N. G. *J. Org. Chem*. **1989**, *54*, 6075.
[11] Hanessian, S.; Tehim, A.; Chen, P. *J. Org. Chem*. **1993**, *58*, 7768.

stain in $KMnO_4$) to afford a clear, colorless oil (846 mg, 89% yield). R_f = 0.9 in pentane on TLC. The spectral data matched those reported in the literature.[12]

IV. Synthesis and Characterization of Allyl Boronates

Allyl boronates were prepared according to a literature procedure.[2]



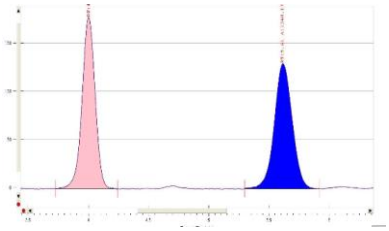
(*S*,*E*)-4,4,5,5-Tetramethyl-2-(8-methyltetradec-7-en-6-yl)-1,3,2-dioxaborolane (S7). Prepared according to a literature precedent.[2] The crude mixture was purified by silica gel chromatography (15% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (68% yield). R_f = 0.6 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.01 (d, J = 9.6 Hz, 1H), 1.98-1.90 (m, 3H), 1.57 (s, 3H), 1.53-1.47 (m, 1H), 1.37-1.18 (m, 27H), 0.89-0.84 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.51, 125.59, 82.92, 39.96, 32.08, 31.98, 31.68, 29.09, 28.93, 28.19, 24.85, 24.68, 22.85, 22.76, 16.38, 14.28, 14.21. ^{11}B NMR (192 MHz, $CDCl_3$) δ 30.58. IR (neat) ν_{max} 2956 (m), 2924 (s), 2855 (m), 1459 (w), 1370 (s), 1316 (s), 1215 (w), 1143 (s), 968 (w), 849 (w) cm^{-1}. HRMS (DART) calc. for $C_{21}H_{42}BO_2$ $[M+H]^+$ 337.3278, found 337.3274. $[\alpha]^{20}_D$: +15.8 (c = 0.963, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary homoallylic alcohol upon allylation with PhCHO.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 2% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

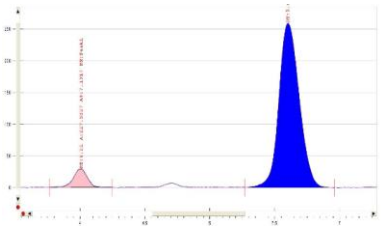


Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.0574	1343.2611	4	177.9711	0.0063
2	49.9426	1340.1797	5.61	129.6618	0.0088
Total:	100	2683.4408			

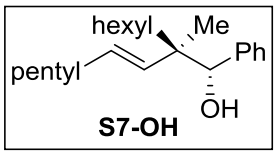
[12] Kuang, C.; Senboku, H.; Tokuda, M. *Tetrahedron*, **2002**, *58*, 1491.

Reaction Product

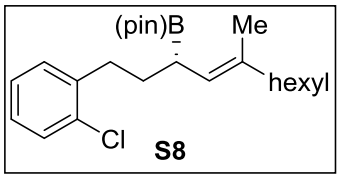


Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	7.1917	217.5807	4.01	28.9493	0.0061
2	92.8083	2807.8653	5.6	258.7188	0.0086
Total:	100	3025.446			



(1*R*,2*R*,*E*)-2-Hexyl-2-methyl-1-phenylnon-3-en-1-ol (S7-OH). Prepared according to a literature precedent.[2] The crude allylation mixture was purified by silica gel chromatography (30% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil. R_f = 0.5 in 60% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.24 (m, 5H), 5.47 (dt, J = 16.2, 6.6 Hz, 1H), 5.40 (d, J = 15.6 Hz, 1H), 4.37 (d, J = 1.8 Hz, 1H), 2.12-2.07 (m, 3H), 1.42-1.12 (m, 16H), 0.91 (t, J = 6.0 Hz, 3H), 0.88-0.84 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.80, 135.75, 132.28, 128.29, 127.53, 127.41, 80.41, 45.32, 38.28, 33.10, 32.07, 31.58, 30.27, 29.48, 24.26, 22.81, 22.68, 17.14, 14.22. IR (neat) ν_{max} 3459 (br), 3029 (m), 2955 (s), 2925 (w), 2855 (m), 1454 (w), 1377 (w), 1024 (w), 982 (w), 746 (w), 701 (s) cm^{-1}. HRMS (DART) calc. for $C_{22}H_{35}$ $[M+H-H_2O]^+$ 299.2739, found 299.2729. $[\alpha]^{20}_D$: +31.4 (c = 0.625, $CHCl_3$, *l* =50 mm).



(*S*,*E*)-2-(1-(2-Chlorophenyl)-5-methylundec-4-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S8). Prepared according to a literature precedent.[2] The crude mixture was purified by silica gel chromatography (20% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (57% yield). R_f = 0.6 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, J = 7.8, 1.2 Hz, 1H), 7.19 (dd, J = 6.6, 1.2 Hz, 1H), 7.15 (dt, J = 7.8, 1.2 Hz, 1H), 7.10 (dt, 7.2, 1.8 Hz, 1H), 5.10 (d, J = 9.6 Hz, 1H), 2.79 (ddd, J = 13.2, 10.8, 5.4 Hz, 1H), 2.63 (ddd, J = 13.2, 10.2, 5.4 Hz, 1H), 2.04-1.98 (m, 3H), 1.84 (ddt, J = 12.6, 11.4, 6.6 Hz, 1H), 1.67 (ddt, J = 13.2, 10.2, 4.2 Hz, 1H), 1.60 (s, 3H), 1.39 (p, J = 7.2 Hz, 2H), 1.31-1.20 (m, 18H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.57, 135.48, 134.05, 130.59, 129.47, 127.14, 126.71, 124.83, 83.09, 40.00, 33.35, 31.99, 31.70, 28.98, 28.22, 24.91, 24.69, 22.84, 16.51, 14.28. ^{11}B NMR (192 MHz, $CDCl_3$) δ 30.71. IR (neat) ν_{max} 3063 (w), 2976 (w), 2954 (w), 2926 (m), 2857 (m), 1473 (w), 1443 (w), 1370 (m), 1318 (s), 1268 (w), 1142 (s), 1052 (w), 968 (w),

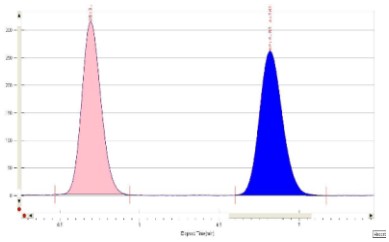
847 (w), 750 (m) cm^{-1}. HRMS (DART) calc. for $C_{24}H_{39}BClO_2$ $[M+H]^+$ 405.2732, found 405.2741. $[\alpha]^{20}_D$: +5.05 (c = 0.967, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol upon oxidation.

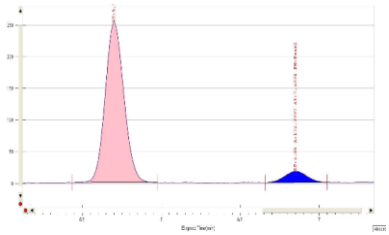
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 10% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

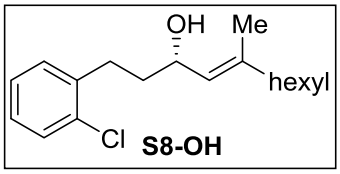


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.9815	2609.8667	5.69	313.4595	0.0099
2	50.0185	2611.7971	6.82	261.6207	0.0119
Total:	100	5221.6638			

Reaction Product

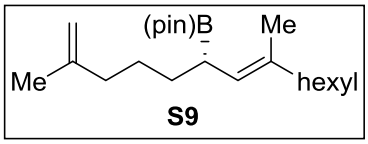


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	92.3006	2073.9236	5.7	252.4993	0.0081
2	7.6994	172.9997	6.85	17.8703	0.0097
Total:	100	2246.9233			



(*S*,*E*)-1-(2-Chlorophenyl)-5-methylundec-4-en-3-ol (S8-OH). Prepared according to a literature precedent.[2] The crude oxidation mixture was purified by silica gel chromatography (60% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil. R_f = 0.2 in 75% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, J = 7.2, 1.2 Hz, 1H), 7.23 (dd, J = 7.2, 1.2 Hz, 1H), 7.18 (dt, J = 7.2, 1.2 Hz, 1H), 7.13 (dt, J = 7.8, 1.8 Hz, 1H), 5.23 (dd, J = 9.0, 1.2 Hz, 1H), 4.42 (7.31-7.25 (m, 2H), 7.24-7.15 (m, 3H), 5.22 (d, *J* = 8.5 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 1H), 2.67 (m, 2H), 2.00 (t, *J* = 7.5 Hz, 2H), 1.93 (ddt, *J* = 13.5, 9.5, 6.5 Hz, 1H), 1.76 (ddt, *J* = 13.5, 10.0, 6.5 Hz, 1H), 1.64 (s, 3H), 1.45-1.24 (m, 9H), 0.89 (t, *J* = 5.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.84, 139.77, 134.09, 130.44, 129.60, 127.44, 127.40, 126.88, 68.40, 39.73, 37.60, 31.89, 29.86, 29.09, 27.83, 22.76, 16.74, 14.25. IR (neat) ν_{max} 3333 (br), 3059 (w), 2955 (m), 2926 (s), 2855 (m), 1474 (w), 1443 (m), 1370 (w), 1052 (m), 1025 (w),

749 (s) cm^{-1}. HRMS (DART) calc. for $C_{18}H_{26}Cl$ $[M+H-H_2O]^+$ 277.1723, found 277.1719. $[\alpha]^{20}_D$: -22.8 (c = 0.700, $CHCl_3$, *l* =50 mm).



S9

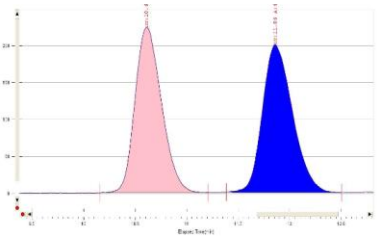
(*S*,*E*)-2-(2,8-Dimethyltetradeca-1,7-dien-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S9). Prepared according to a literature precedent.[2] The crude mixture was purified by silica gel chromatography (25% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (83% yield). R_f = 0.3 in 30% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.01 (d, J = 9.6 Hz, 1H), 4.66 (s, 1H), 4.65 (s, 1H), 2.02-1.92 (m, 5H), 1.69 (s, 3H), 1.58 (s, 3H), 1.55-1.42 (m, 2H), 1.40-1.30 (m, 4H), 1.29-1.18 (m, 18H), 0.87 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.35, 134.71, 125.36, 109.69, 82.96, 39.97, 38.05, 31.98, 31.37, 28.93, 28.19, 27.42, 24.86, 24.69, 22.84, 22.51, 16.40, 14.28. ^{11}B NMR (192 MHz, $CDCl_3$) δ 32.62. IR (neat) ν_{max} 2977 (w), 2957 (w), 2926 (s), 2855 (w), 1457 (w), 1370 (s), 1316 (s), 1143 (s), 968 (w), 884 (m) cm^{-1}. HRMS (DART) calc. for $C_{22}H_{42}BO_2$ $[M+H]^+$ 349.3278, found 349.3270. $[\alpha]^{20}_D$: +15.8 (c = 1.10, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary homoallylic alcohol upon allylation with PhCHO.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 4% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

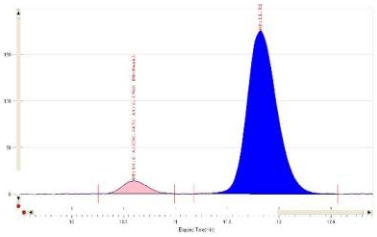
Racemic



Peak Info

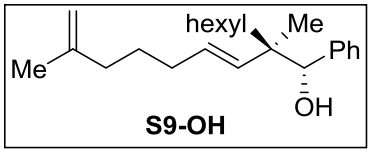
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.6533	4000.0783	10.61	223.5944	0.017
2	50.3467	4055.9414	11.86	200.1265	0.019
Total:	100	8056.0197			

Reaction Product

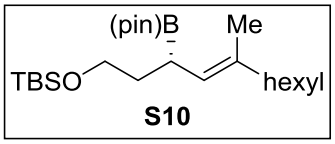


Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	6.1968	230.6491	10.6	13.9548	0.0166
2	93.8032	3491.4029	11.82	174.9157	0.0185
Total:	100	3722.052			



(1*R*,2*R*,*E*)-2-Hexyl-2,8-dimethyl-1-phenylnona-3,8-dien-1-ol (S9-OH). Prepared according to a literature precedent.[2] The crude allylation mixture was purified by silica gel chromatography (30% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil. R_f = 0.3 in 60% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.23 (m, 5H), 5.49-5.40 (m, 2H), 4.72 (s, 1H), 4.69 (s, 1H), 4.38 (s, 1H), 2.15-2.00 (m, 5H), 1.73 (s, 3H), 1.58-1.51 (m, 2H), 1.40-1.34 (m, 1H), 1.31-1.13 (m, 9H), 0.90-0.83 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.95, 140.81, 136.09, 131.77, 128.29, 127.53, 127.43, 110.05, 80.45, 45.30, 38.24, 37.44, 32.73, 32.06, 30.26, 27.74, 24.28, 22.80, 22.56, 17.22, 14.21. IR (neat) ν_{max} 3456 (br), 3027 (w), 2977 (m), 2928 (s), 2856 (m), 1453 (m), 1375 (w), 1037 (w), 1024 (w), 886 (m), 747 (m), 702 (s) cm^{-1}. HRMS (DART) calc. for $C_{23}H_{35}$ $[M+H-H_2O]^+$ 311.2739, found 311.2744. $[\alpha]^{20}_D$: +29.6 (c = 1.16, $CHCl_3$, *l* =50 mm).



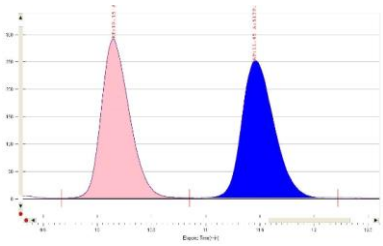
(*S*,*E*)-tert-Butyldimethyl((5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-en-1-yl)oxy)silane (S10). Prepared according to a literature precedent.[2] The crude mixture was purified by silica gel chromatography (75% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil (54% yield). R_f = 0.4 in 80% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.99 (d, J = 9.6 Hz, 1H), 3.60-3.50 (m, 2H), 2.04 (q, J = 9.6 Hz, 1H), 1.95 (t, J = 7.8 Hz, 2H), 1.79-1.72 (m, 1H), 1.59-1.53 (m, 4H), 1.35 (p, J = 7.8 Hz, 2H), 1.31-1.18 (m, 18H), 0.90-0.85 (m, 12H), 0.22 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.25, 124.68, 82.99, 62.80, 39.96, 34.57, 31.98, 28.95, 28.18, 26.16, 24.86, 24.66, 22.82, 18.52, 16.41, 14.28, -5.11, -5.14. ^{11}B NMR (192 MHz, $CDCl_3$) δ 32.62. IR (neat) ν_{max} 2955 (m), 2927 (s), 2856 (m), 1464 (w), 1370 (m), 1316 (s), 1253 (m), 1143 (s), 1097 (s), 835 (s), 774 (s) cm^{-1}. HRMS (DART) calc. for $C_{24}H_{50}BO_3Si$ $[M+H]^+$ 425.3622, found 425.3636. $[\alpha]^{20}_D$: +22.1 (c = 0.852, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary homoallylic alcohol upon allylation with PhCHO.

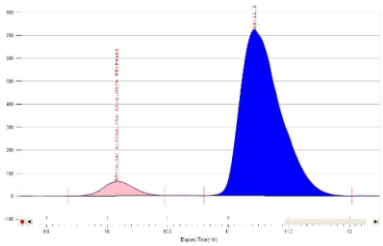
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 4% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

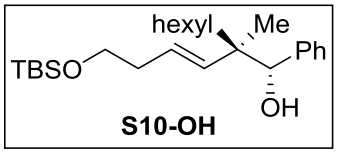


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.2099	5222.661	10.15	290.8857	0.0149
2	49.7901	5179.001	11.45	250.6197	0.0169
Total:	100	10401.662			

Reaction Product

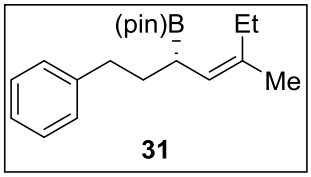


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	6.0574	1066.056	10.08	61.478	0.0134
2	93.9426	16533.1976	11.22	722.5205	0.0149
Total:	100	17599.2536			



S10-OH

(1*R*,2*R*)-2-((*E*)-4-((tert-Butyldimethylsilyl)oxy)but-1-en-1-yl)-2-methyl-1-phenyloctan-1-ol (S10-OH). Prepared according to a literature precedent.[2] The crude allylation mixture was purified by silica gel chromatography (3% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. R_f = 0.2 in 5% ethyl acetate/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.23 (m, 5H), 5.50-5.42 (m, 2H), 4.36 (d, J = 1.8 Hz, 1H), 3.70-3.63 (m, 2H), 2.36-2.28 (m, 2H), 2.18 (d, J = 1.8 Hz, 1H), 1.40-1.33 (m, 1H), 1.30-1.13 (m, 9H), 0.91 (s, 9H), 0.89-0.84 (m, 6H), 0.07 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.77, 138.04, 128.50, 128.29, 127.52, 127.40, 80.20, 63.16, 45.49, 38.19, 36.76, 32.05, 30.27, 26.14, 24.30, 22.82, 18.55, 17.04, 14.22, -5.08, -5.10. IR (neat) ν_{max} 3452 (br), 3029 (w), 2954 (m), 2928 (s), 2856 (m), 1454 (w), 1379 (w), 1254 (m), 1097 (s), 834 (s), 775 (s), 701 (s) cm^{-1}. HRMS (DART) calc. for $C_{25}H_{43}OSi$ $[M+H-H_2O]^+$ 387.3083, found 387.3100. $[\alpha]^{20}_D$: +31.4 (c = 0.945, $CHCl_3$, *l* =50 mm).



31

(*S*,*Z*)-2-(1-(2-Chlorophenyl)-5-methylundec-4-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (31). Prepared according to a literature precedent.[2] The crude mixture was purified by silica gel chromatography (20% CH_2Cl_2/pentane, stain in CAM) to afford a clear,

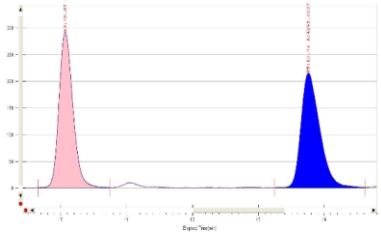
colorless oil (80% yield). R_f = 0.3 in 20% CH_2Cl_2/pentane on TLC. The spectral data matched those reported in the literature.[13] $[\alpha]^{20}_D$: +1.87 (c = 1.42, $CHCl_3$, *l* =50 mm). Lit. for (S)-enantiomer: $[\alpha]^{20}_D$: +4.8 (c = 1.65, $CHCl_3$, *l* =50 mm).[13]

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol upon oxidation.

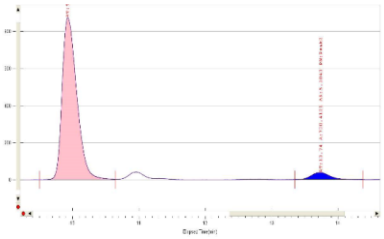
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 4% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

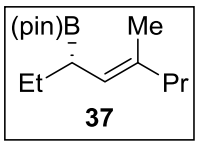


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.1961	4279.2372	10.07	291.4759	0.0101
2	49.8039	4245.8037	13.76	214.4542	0.0138
Total:	100	8525.0409			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	94.8157	13358.5764	9.93	874.4155	0.0095
2	5.1843	730.4121	13.74	37.826	0.0132
Total:	100	14088.9885			



37

(*S*,*E*)-4,4,5,5-Tetramethyl-2-(5-methyloct-4-en-3-yl)-1,3,2-dioxaborolane (37). Prepared according to a literature precedent with slight modification.[2] A 2-dram vial with a magnetic stir bar was charged with **L1·PdCl₂** (10.2 mg, 0.012 mmol).[2] The vial was sealed with rubber septum, and purged with N_2 for 10 minutes. A solution of 2,2'-(propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **35** (186 mg, 0.60 mmol) in dioxane (1.0 mL) and (*E*)-1-bromo-2-methylpent-1-ene **36** (65.2 mg, 0.40 mmol) in dioxane (1.0 mL) were added sequentially *via* syringe. The reaction was stirred and 8M $KOH_{(aq)}$[14] (230 µL, 1.80 mmol) was added *via* syringe. The reaction was stirred under an atmosphere of N_2 at room temperature for 18 hours. The reaction was diluted with Et_2O (3 mL) and filtered through a plug

[13] Chen, J. L.-Y.; Aggarwal, V. K. *Angew. Chem. Int. Ed*. **2014**, *53*, 10992.
[14] $KOH_{(aq.)}$ was sparged with N_2 for 30 min at room temperature before use.

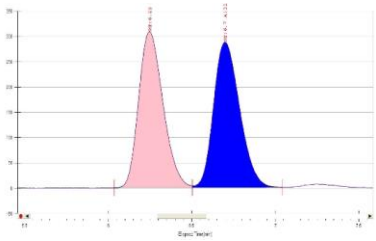
of Celite with additional Et_2O (25 mL). The filtrate was concentrated *in vacuo*. The crude mixture was purified by silica gel chromatography (20% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (77.9 mg, 77% yield). R_f = 0.6 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.02 (d, J = 10.2 Hz, 1H), 1.95 (t, J = 7.8 Hz, 2H), 1.86 (d, J = 7.2 Hz, 1H), 1.59-1.51 (m, 4H), 1.42-1.33 (m, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 0.88 (t, J = 7.8 Hz, 3H), 0.83 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.49, 125.56, 82.93, 42.09, 24.85, 24.68, 21.28, 16.32, 13.95, 13.68. ^{11}B NMR (192 MHz, $CDCl_3$) δ 30.48. IR (neat) ν_{max} 2977 (w), 2957 (m), 2929 (w), 2870 (w), 1460 (w), 1369 (m), 1353 (s), 1313 (s), 1264 (m), 1142 (s), 967 (m), 827 (w) cm^{-1}. HRMS (DART) calc. for $C_{15}H_{30}BO_2$ $[M+H]^+$ 253.2339, found 253.2337. $[\alpha]^{20}_D$: +31.3 (c = 0.880, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary homoallylic alcohol upon allylation with PhCHO.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 3% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic



Peak Info

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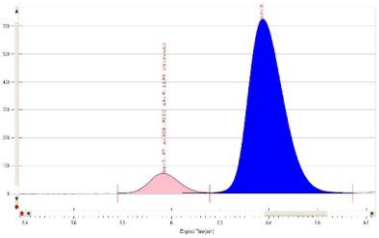
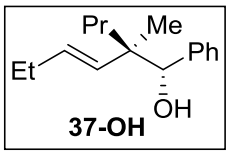
Total:	100	6223.2714			

Reaction Product



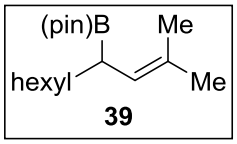
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	9.1194	628.9205	5.97	72.4993	0.0069
2	90.8806	6267.5735	6.37	624.5861	0.0074
Total:	100	6896.494			

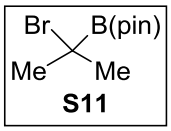


(1*R*,2*R*,*E*)-2-Methyl-1-phenyl-2-propylhex-3-en-1-ol (37-OH). Prepared according to a literature precedent.[2] The crude allylation mixture was purified by silica gel chromatography (40% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil. R_f = 0.3 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ

7.27-7.20 (m, 5H), 5.48 (dt, J = 15.6, 6.0 Hz, 1H), 5.37 (d, J = 15.6 Hz, 1H), 4.34 (d, J = 1.8 Hz, 1H), 2.11-2.03 (m, 3H), 1.33-1.27 (m, 1H), 1.19-1.12 (m, 3H), 0.98 (t, J = 7.8 Hz, 3H), 0.83-0.80 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.77, 134.76, 133.67, 128.31, 127.52, 127.42, 80.40, 45.23, 40.57, 26.17, 17.47, 17.14, 14.97, 14.27. IR (neat) ν_{max} 3458 (br), 3027 (w), 2958 (s), 2931 (m), 2871 (m), 1453 (m), 1378 (m), 1023 (m), 980 (m), 913 (w), 745 (m), 702 (s) cm^{-1}. HRMS (DART) calc. for $C_{16}H_{23}$ $[M+H-H_2O]^+$ 215.1800, found 215.1808. $[\alpha]^{20}_D$: +64.8 (c = 0.150, $CHCl_3$, *l* =50 mm).



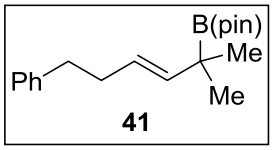
4,4,5,5-Tetramethyl-2-(2-methyldec-2-en-4-yl)-1,3,2-dioxaborolane (39). Prepared according to a literature precedent with racemic **L1·PdCl$_2$**.[2] The crude mixture was purified by silica gel chromatography (25% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (71% yield). R_f = 0.5 in 25% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.03 (d, J = 9.6 Hz, 1H), 1.92 (q, J = 8.4 Hz, 1H), 1.69 (s, 3H), 1.59 (s, 3H), 1.53-1.47 (m, 1H), 1.36-1.20 (m, 21H), 0.87 (t, J = 6.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 130.58, 125.66, 82.96, 31.99, 31.81, 29.56, 29.36, 25.98, 24.86, 24.68, 22.79, 18.28, 14.23. ^{11}B NMR (192 MHz, $CDCl_3$) δ 30.63. IR (neat) ν_{max} 2977 (w), 2960 (w), 2923 (m), 2854 (w), 1458 (w), 1370 (m), 1314 (s), 1143 (s), 968 (w), 837 (w) cm^{-1}. HRMS (DART) calc. for $C_{17}H_{34}BO_2$ $[M+H]^+$ 281.2652, found 281.2668.



2-(2-Bromopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S11). Prepared according to a literature precedent with slight modification.[15] A 50-mL round bottom flask with a magnetic stir bar and equipped with a $NaHCO_{3(aq)}$ scrubber under N_2, was charged with CCl_4 (6 mL) *via* syringe. Then 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (419 µL, (2.2 mmol) was added *via* syringe, followed by bromine (103 µL, 2.0 mmol) *via* syringe. The reaction was stirred at room temperature under N_2 for 3 hours. The stir bar was removed and the reaction was concentrated *in vacuo* to afford the title compound as a brown oil (98%, 487 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.77 (s, 6H), 1.28 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 84.34, 30.40, 24.53. ^{11}B NMR (192 MHz, $CDCl_3$) δ 28.72. IR (neat) ν_{max}

[15] Matteson, D. S.; Fernando, D. *Journal of Organometallic Chemistry*, **2003**, *680*, 100.

2981 (w), 2955 (m), 1464 (m), 1385 (m), 1363 (s), 1329 (s), 1168 (m), 1140 (s), 1088 (m), 968 (w), 856 (m) cm^{-1}. HRMS (DART) calc. for $C_9H_{19}BBrO_2$ $[M+H]^+$ 249.0662, found 249.0651.



(*E*)-4,4,5,5-Tetramethyl-2-(2-methyldec-3-en-2-yl)-1,3,2-dioxaborolane (41). An oven-dried 25-mL round bottom flask with a magnetic stir bar under N_2 was charged with THF (6 mL) *via* syringe. Then (*E*)-1-bromooct-1-ene[16] (115 mg, 0.6 mmol) was added as a solution in THF (2 mL). The reaction was cooled to -78ºC and *t*BuLi (706 µL, 1.7M in pentane, 1.2 mmol) was added dropwise. The reaction was stirred for 5 minutes at -78ºC and 2-(2-bromopropan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **S11** (165 mg (0.66 mmol) was added as a solution in THF (2 mL). The reaction was stirred for 5 minutes at -78ºC before warming to room temperature and stirring continued for an additional 1 hour. The reaction was quenched with the addition of water (5 mL) and poured into a separatory funnel with Et_2O (20 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 10 mL). The organic layers were combined, dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The crude mixture was purified by silica gel chromatography (20% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (85.7 mg, 51% yield). R_f = 0.5 in 25% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (d, *J* = 15.5 Hz, 1H), 5.28 (dt, *J* = 16.0, 6.5 Hz, 1H), 1.98 (q, *J* = 6.0 Hz, 2H), 1.33-1.19 (m, 20H), 1.02 (s, 6H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.24, 126.56, 83.12, 33.02, 31.92, 29.92, 28.87, 24.69, 24.44, 22.81, 14.25. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.73. IR (neat) ν_{max} 2976 (w), 2956 (w), 2924 (m), 2857 (w), 1469 (m), 1385 (m), 1371 (s), 1341 (s), 1308 (s), 1133 (s), 968 (m), 852 (m) cm^{-1}. HRMS (DART) calc. for $C_{17}H_{34}BO_2$ $[M+H]^+$ 281.2652, found 281.2662.

V. Procedures for Stereospecific Cross-Coupling

Method A (for commercial, liquid electrophiles). A 2-dram vial with a magnetic stir bar was charged with allylic boronate (0.10 mmol). The vial was sealed with rubber septum, and purged with N_2 for 10 minutes. Dioxane (500 µL) was added and the reaction stirred. Then a solution of $Pd(OAc)_2$ in dioxane (100 µL, 0.0020 mmol, 0.02M) and RuPhos in dioxane (100 µL, 0.0040 mmol, 0.04M) were added sequentially *via* syringe. Then aryl or alkenyl halide (0.30

[16] Posner, G. H.; Tang, P. *J. Org. Chem.* **1978**, *43*, 4131.

mmol) and 8M $KOH_{(aq)}$[14] (56 μL, 0.45 mmol) were added sequentially *via* syringe. The reaction was heated to either 50°C (alkenyl electrophiles) or 60°C (aryl electrophiles) under an atmosphere of N_2 for 14 hours. The reaction was cooled to room temperature, diluted with Et_2O (2 mL), and filtered through a plug of silica with additional Et_2O (5 mL). The filtrate was concentrated *in vacuo* and purified by silica gel chromatography to afford the desired compound.

Method B (for solid electrophiles). A 2-dram vial with a magnetic stir bar was charged with allylic boronate (0.10 mmol) and aryl or alkenyl halide (0.30 mmol). The vial was sealed with rubber septum, and purged with N_2 for 10 minutes. Dioxane (500 μL) was added and the reaction stirred. Then a solution of $Pd(OAc)_2$ in dioxane (100 μL, 0.0020 mmol, 0.02M) and RuPhos in dioxane (100 μL, 0.0040 mmol, 0.04M) were added sequentially *via* syringe. Then 8M $KOH_{(aq)}$[14] (56 μL, 0.45 mmol) was added *via* syringe. The reaction was heated to either 50°C (alkenyl electrophiles) or 60°C (aryl electrophiles) under an atmosphere of N_2 for 14 hours. The reaction was cooled to room temperature, diluted with Et_2O (2 mL), and filtered through a plug of silica with additional Et_2O (5 mL). The filtrate was concentrated *in vacuo* and purified by silica gel chromatography to afford the desired compound.

Method C (for liquid electrophiles). A 2-dram vial with a magnetic stir bar was charged with allylic boronate (0.10 mmol). The vial was sealed with rubber septum, and purged with N_2 for 10 minutes. Dioxane (400 μL) was added and the reaction stirred. Then a solution of $Pd(OAc)_2$ in dioxane (100 μL, 0.0020 mmol, 0.02M) and RuPhos in dioxane (100 μL, 0.0040 mmol, 0.04M) were added sequentially *via* syringe. Then aryl or alkenyl halide (0.30 mmol) was added as a solution in dioxane (100 μL) followed by 8M $KOH_{(aq)}$[14] (56 μL, 0.45 mmol) *via* syringe. The reaction was heated to either 50°C (alkenyl electrophiles) or 60°C (aryl electrophiles) under an atmosphere of N_2 for 14 hours. The reaction was cooled to room temperature, diluted with Et_2O (2 mL), and filtered through a plug of silica with additional Et_2O (5 mL). The filtrate was concentrated *in vacuo* and purified by silica gel chromatography to afford the desired compound.

Method D (one-pot procedure from geminal bis(boronates)). A 2-dram vial with a magnetic stir bar was charged with **L1·PdCl₂**[2] (0.9 mg, 0.0010 mmol) and 1,1-diborylalkane (0.15 mmol). The vial was sealed with rubber septum, and purged with N_2 for 10 minutes. Dioxane (250 μL) was added and the reaction stirred for 5 minutes. Then a solution of vinyl bromide in dioxane (250 μL, 0.10 mmol, 0.4M) and 8M $KOH_{(aq)}$[14] (56 μL, 0.45 mmol) were added sequentially *via* syringe. The reaction was stirred under an atmosphere of N_2 at room temperature for 18 hours.

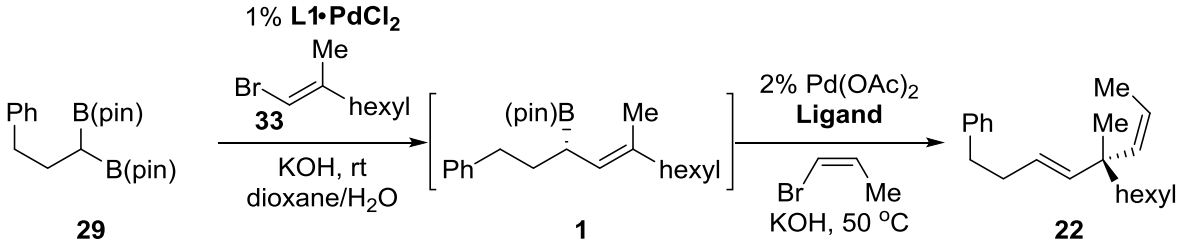
Then a solution of $Pd(OAc)_2$ in dioxane (100 μL, 0.0020 mmol, 0.02M) and RuPhos in dioxane (100 μL, 0.0040 mmol, 0.04M) were added sequentially *via* syringe. Then aryl or alkenyl halide (0.30 mmol) was added as a solution in dioxane (100 μL) followed by 8M $KOH_{(aq)}$[14] (56 μL, 0.45 mmol) *via* syringe. The reaction was heated to either 50°C (alkenyl electrophiles) or 60°C (aryl electrophiles) under an atmosphere of N_2 for 14 hours. The reaction was cooled to room temperature, diluted with Et_2O (2 mL), and filtered through a plug of silica with additional Et_2O (5 mL). The filtrate was concentrated *in vacuo* and purified by silica gel chromatography to afford the desired compound.

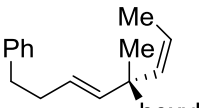
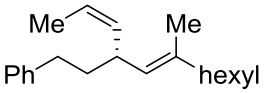
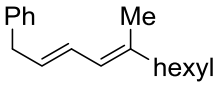
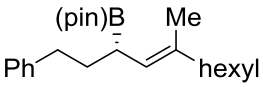
Method E (for chloropyridine·HCl salts electrophiles). A 2-dram vial with a magnetic stir bar was charged with allylic boronate (0.10 mmol) and chloropyridine·HCl salt (0.30 mmol). The vial was sealed with rubber septum, and purged with N_2 for 10 minutes. Dioxane (500 μL) was added and the reaction stirred. Then a solution of $Pd(OAc)_2$ in dioxane (100 μL, 0.0020 mmol, 0.02M) and RuPhos in dioxane (100 μL, 0.0040 mmol, 0.04M) were added sequentially *via* syringe. Then 8M $KOH_{(aq)}$[14] (94 μL, 0.75 mmol) was added *via* syringe. The reaction was heated to 60°C under an atmosphere of N_2 for 14 hours. The reaction was cooled to room temperature, diluted with Et_2O (2 mL), and filtered through a plug of silica with additional Et_2O (5 mL). The filtrate was concentrated *in vacuo* and purified by silica gel chromatography to afford the desired compound.

VI. Ligand Optimization

The following ligands were investigated for the stereospecific allyl-aryl cross-coupling utilizing ***Method D***.

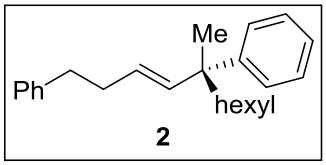
Table S1: Ligand Optimization



Ligand (%)	 **22** (%)	 α (%)	 **β-Hydride Elimination** (%)	 **1** (%)
RuPhos (4%)	80	<5	<5	<5
SPhos (4%)	65	<10	<10	<5
tBu·XPhos (4%)	<10	<10	17	12
dppf (2.2%)	<10	<10	<10	10

[a]Yield was determined by ^{1}H-NMR in comparison to 1,1,2,2-tetrachloroethane as an internal standard.

VII. Characterization of Reaction Products and Analysis of Stereochemistry



(*R*,*E*)-(5-Methylundec-3-ene-1,5-diyl)dibenzene (2). The reaction was performed according to the *Representative Procedure (Method A)* with chlorobenzene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (29.6 mg, 93% yield). R_f = 0.2 in hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.16 (m, 10H), 5.63 (d, J = 15.6 Hz, 1H), 5.46 (dt, J = 15.0, 6.0 Hz, 1H), 2.75 (t, J = 7.2 Hz, 2H), 2.42 (q, J = 6.6 Hz, 2H), 1.73 (td, J = 13.2, 5.4 Hz, 1H), 1.66 (td, J = 12.6, 4.8 Hz, 1H), 1.33 (s, 3H), 1.31-1.21 (m, 6H), 1.18-1.04 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.67, 142.16, 139.52, 128.73, 128.39, 128.05, 126.76, 126.53, 125.84, 125.59, 43.60, 41.87, 36.28, 34.80, 31.94, 30.21, 25.94,

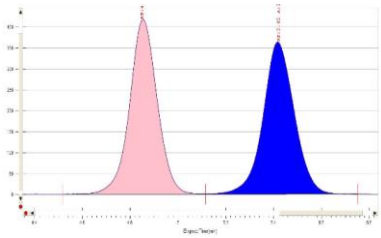
24.61, 22.84, 14.24. IR (neat) ν_{max} 3085 (w), 3062 (w), 3026 (w), 2957 (m), 2926 (s), 2854 (m), 1495 (w), 1445 (w), 1375 (w), 976 (w), 763 (w), 698 (s) cm^{-1}. HRMS (DART) calc. for $C_{24}H_{33}$ $[M+H]^+$ 321.2582, found 321.2592. $[\alpha]^{20}_D$: -0.831 (c = 0.927, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

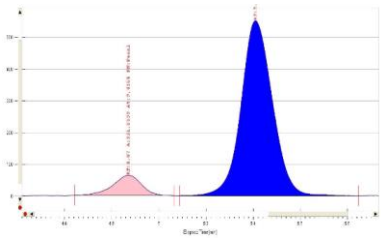
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 5% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

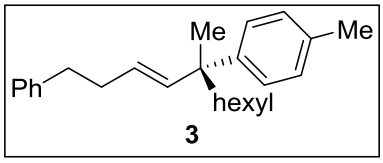


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.4648	3353.8049	4.85	417.7803	0.0076
2	49.5352	3292.027	5.42	363.5387	0.0085
Total:	100	6645.8319			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	9.4504	531.8539	4.87	63.6616	0.0077
2	90.5496	5096.0035	5.41	551.3769	0.0086
Total:	100	5627.8574			



3

(*R*,*E*)-1-Methyl-4-(5-methyl-1-phenylundec-3-en-5-yl)benzene (3). The reaction was performed according to the *Representative Procedure (Method B)* with 1-bromo-4-methylbenzene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (28.1 mg, 84% yield). R_f = 0.1 in pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.23-7.19 (m, 3H), 7.13 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 5.61 (d, J = 15.6 Hz, 1H), 5.44 (dt, J = 15.0, 6.6 Hz, 1H), 2.74 (t, J = 7.2 Hz, 2H), 2.41 (q, J = 6.6 Hz, 2H), 2.34 (s, 3H), 1.71 (td, J = 13.2, 4.8 Hz, 1H), 1.64 (td, J = 12.6, 4.8 Hz, 1H), 1.33-1.21 (m, 9H), 1.18-1.04 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.69, 142.20, 140.12, 134.99, 128.78, 128.73, 128.38, 126.64, 126.33, 125.83, 43.24, 41.87, 36.30, 34.81, 31.95, 30.24, 25.98, 24.64, 22.85, 21.02, 14.25. IR (neat) ν_{max} 3110 (w), 3062 (w),

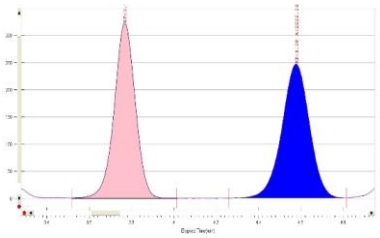
3025 (w), 2956 (m), 2928 (s), 2855 (m), 1603 (w), 1512 (m), 1454 (m), 975 (m), 816 (s), 745 (m), 698 (s) cm^{-1}. HRMS (DART) calc. for $C_{25}H_{35}$ $[M+H]^+$ 335.2739, found 335.2748. $[\alpha]^{20}_D$: -5.72 (c = 0.355, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

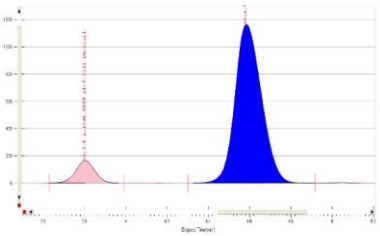
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 7% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

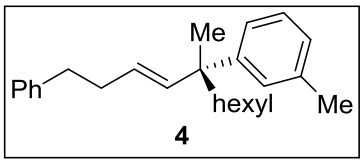


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.0076	2223.0389	3.77	322.3998	0.0037
2	49.9924	2222.3604	4.58	246.3777	0.0045
Total:	100	4445.3993			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	9.3161	1068.2039	3.8	163.9179	0.0032
2	90.6839	10398.0686	4.58	1164.522	0.0039
Total:	100	11466.2725			



4

(*R*,*E*)-1-Methyl-3-(5-methyl-1-phenylundec-3-en-5-yl)benzene (4). The reaction was performed according to the *Representative Procedure (Method A)* with 1-bromo-3-methylbenzene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (28.5 mg, 85% yield). R_f = 0.1 in pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.22-7.16 (m, 4H), 7.09 (s, 1H), 7.05 (d, J = 7.8 Hz, 1H), 7.00 (d, J = 7.2 Hz, 1H), 5.63 (d, J = 15.0 Hz, 1H), 5.45 (dt, J = 15.6, 6.6 Hz, 1H), 2.74 (t, J = 7.2 Hz, 2H), 2.42 (q, J = 6.6 Hz, 2H), 2.35 (s, 3H), 1.72 (td, J = 12.6, 4.2 Hz, 1H), 1.65 (td, J = 13.2, 4.8 Hz, 1H), 1.32 (s, 3H), 1.30-1.21 (m, 6H), 1.18-1.03 (m, 2H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.69, 142.20, 140.01, 137.42, 128.71, 128.38, 127.93, 127.45, 126.40, 126.37, 125.85, 123.83, 43.47, 41.87, 36.31, 34.78, 31.93, 30.21, 25.88, 24.61, 22.85, 21.85, 14.25. IR (neat) ν_{max} 3084 (w), 3061 (w), 3026 (w), 2956 (m), 2927 (s), 2855 (m), 1604 (m), 1495 (m), 1453 (m), 1374 (w),

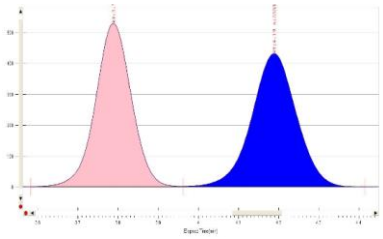
974 (m), 783 (m), 745 (m), 697 (s) cm^{-1}. HRMS (DART) calc. for $C_{25}H_{35}$ $[M+H]^+$ 335.2739, found 335.2742. $[\alpha]^{20}_D$: -2.44 (c = 0.633, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 5% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

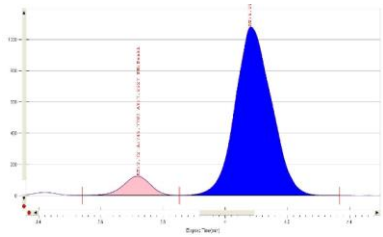
Racemic



Peak Info

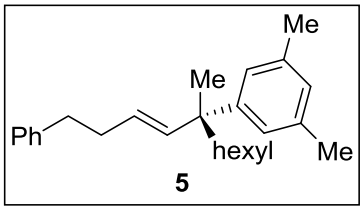
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.6127	3282.195	3.79	529.4354	0.0033
2	50.3873	3333.4376	4.19	431.4743	0.0037
Total:	100	6615.6326			

Reaction Product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	7.8527	745.7787	3.72	123.0209	0.0044
2	92.1473	8751.3287	4.08	1077.8912	0.0048
Total:	100	9497.1074			



5

(*R*,*E*)-1,3-Dimethyl-5-(5-methyl-1-phenylundec-3-en-5-yl)benzene (5). The reaction was performed according to the *Representative Procedure (Method A)* with 1-bromo-3,5-dimethylbenzene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (33.5 mg, 96% yield). R_f = 0.2 in hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.21-7.16 (m, 3H), 6.87 (s, 2H), 6.81 (s, 1H), 5.61 (d, J = 15.6 Hz, 1H), 5.43 (dt, J = 15.6, 6.0 Hz, 1H), 2.72 (t, J = 7.8 Hz, 2H), 2.40 (q, J = 7.8 Hz, 2H), 2.30 (s, 6H), 1.69 (td, J = 13.2, 5.4 Hz, 1H), 1.62 (td, J = 12.6, 4.8 Hz, 1H), 1.31-1.22 (m, 9H), 1.17-1.01 (m, 2H), 0.87 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.78, 142.23, 140.05, 137.32, 128.69, 128.37, 127.33, 126.28, 125.86, 124.55, 43.36, 41.87, 36.34, 34.76, 31.93, 30.23, 25.85, 24.62, 22.85, 21.72, 14.26. IR (neat) ν_{max} 3026 (w), 2956 (m), 2927 (s), 2855 (m), 1601 (m), 1496 (w), 1454 (m), 974 (m), 847 (m), 745 (m), 697 (s) cm^{-1}.

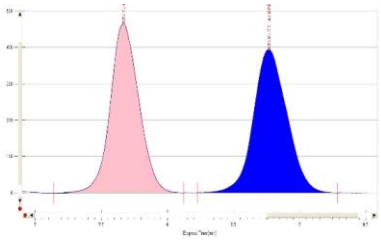
HRMS (DART) calc. for $C_{26}H_{37}$ $[M+H]^+$ 349.2900, found 349.2890. $[\alpha]^{20}_D$: -2.48 (c = 1.13, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 1% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

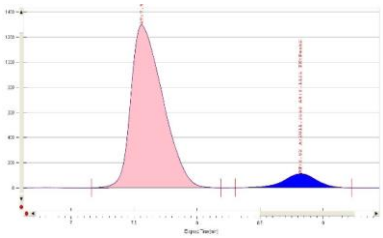
Racemic



Peak Info

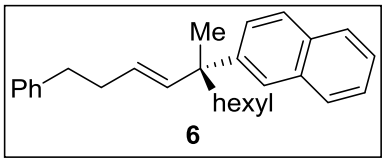
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.0904	6972.1479	7.67	464.7446	0.0117
2	49.9096	6946.9923	8.77	393.8707	0.0133
Total:	100	13919.1402			

Reaction Product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	91.8899	22788.8101	7.56	1299.8321	0.0109
2	8.1101	2011.3066	8.82	111.4696	0.0128
Total:	100	24800.1167			



6

(*R*,*E*)-2-(5-Methyl-1-phenylundec-3-en-5-yl)naphthalene (6). The reaction was performed according to the *Representative Procedure (Method B)* with 2-bromonaphthalene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (32.6 mg, 88% yield). R_f = 0.1 in pentane on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 1H), 7.68 (s, 1H), 7.49-7.39 (m, 3H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 3H), 5.72 (d, J = 16.0 Hz, 1H), 5.50 (dt, J = 13.5, 6.0 Hz, 1H), 2.76 (t, J = 7.5 Hz, 2H), 2.44 (q, J = 8.0 Hz, 2H), 1.85 (td, J = 13.0, 5.0 Hz, 1H), 1.76 (td, J = 13.0, 4.5 Hz, 1H), 1.44 (s, 3H), 1.30-1.14 (m, 7H), 1.12-1.04 (m, 1H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.01, 142.15, 139.99, 133.47, 131.89, 128.73, 128.40, 128.09, 127.51, 127.47, 126.92, 126.11, 125.88, 125.80, 125.39, 124.67, 43.78, 41.74, 36.29, 34.79, 31.93, 30.23, 25.87, 24.65, 22.84, 14.22. IR (neat) ν_{max} 3111 (w), 3083 (m), 3025 (m), 2955 (s), 2928 (s), 2855 (s), 1631 (w), 1600 (m), 1496 (m), 1454 (s), 1375 (m), 1029 (m), 974 (w), 816 (m), 745 (s), 698 (s) cm^{-1}. HRMS

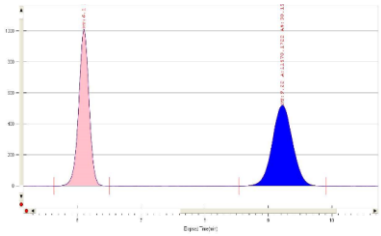
(DART) calc. for $C_{28}H_{35}$ $[M+H]^+$ 371.2739, found 371.2740. The optical rotation was too low to be accurately measured.

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 15% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

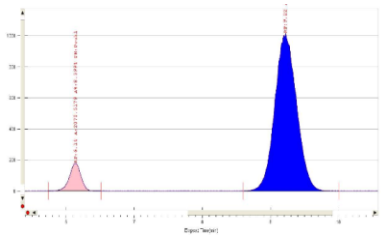
Racemic



Peak Info

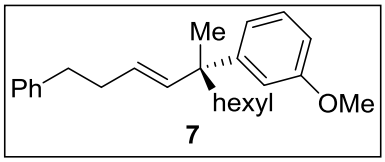
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.842	11397.9119	6.1	1010.8219	0.0056
2	50.158	11470.1722	9.22	520.5545	0.0084
Total:	100	22868.0841			

Reaction Product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	8.3994	2070.5179	6.14	177.8656	0.0059
2	91.6006	22580.2119	9.22	1014.3772	0.0089
Total:	100	24650.7298			



7

(*R*,*E*)-1-Methoxy-3-(5-methyl-1-phenylundec-3-en-5-yl)benzene (7). The reaction was performed according to the *Representative Procedure (Method A)* with 1-chloro-3-methoxybenzene. The crude mixture was purified by silica gel chromatography (15% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (32.9 mg, 94% yield). R_f = 0.3 in 20% CH_2Cl_2/pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.22-7.19 (m, 4H), 6.87-6.82 (m, 2H), 6.73 (dd, J = 7.8, 1.8 Hz, 1H), 5.63 (d, J = 15.6 Hz, 1H), 5.46 (dt, J = 15.6, 6.6 Hz, 1H), 3.81 (s, 3H), 2.73 (t, J = 7.8 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 1.71 (td, J = 13.2, 4.8 Hz, 1H), 1.64 (td, J = 13.2, 4.2 Hz, 1H), 1.32 (s, 3H), 1.29-1.20 (m, 6H), 1.18-1.03 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.45, 150.55, 142.18, 139.77, 128.93, 128.69, 128.38, 126.61, 125.85, 119.38, 113.42, 110.18, 55.26, 43.66, 41.87, 36.33, 34.79, 31.93, 30.21, 25.87, 24.60, 22.85, 14.24. IR (neat) ν_{max} 3062 (w), 3027 (w), 2929 (s), 2855 (m), 1602 (m), 1582 (m), 1486 (m), 1454 (m), 1432 (m), 1290 (m), 1251 (m), 1050 (m), 976 (w), 699 (s) cm^{-1}. HRMS

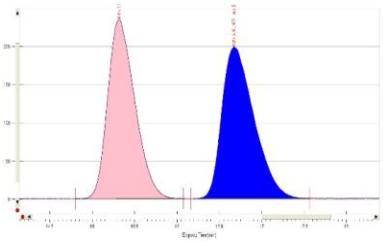
(DART) calc. for $C_{25}H_{35}O$ $[M+H]^+$ 351.2688, found 351.2693. $[\alpha]^{20}_D$: -0.617 (c = 1.06, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

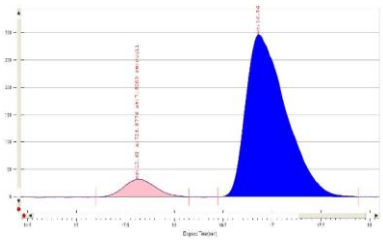
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 4% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

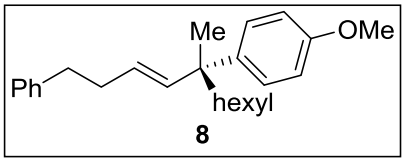


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.9733	5227.541	15.32	234.9481	0.0197
2	50.0267	5233.1251	16.67	198.9441	0.0215
Total:	100	10460.6661			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	7.9203	724.8776	15.62	31.9434	0.0165
2	92.0797	8427.2421	16.86	297.3786	0.0179
Total:	100	9152.1197			



8

(*R*,*E*)-1-Methoxy-4-(5-methyl-1-phenylundec-3-en-5-yl)benzene (8). The reaction was performed according to the *Representative Procedure (Method A)* with 1-chloro-4-methoxybenzene. The crude mixture was purified by silica gel chromatography (15% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (32.2 mg, 92% yield). R_f = 0.3 in 20% CH_2Cl_2/pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.23-7.19 (m, 3H), 7.14 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 5.60 (d, J = 15.6 Hz, 1H), 5.43 (dt, J = 15.0, 6.0 Hz, 1H), 3.81 (s, 3H), 2.74 (t, J = 7.2 Hz, 2H), 2.41 (q, J = 7.2 Hz, 2H), 1.69 (td, J = 13.2, 4.8 Hz, 1H), 1.62 (td, J = 12.6, 4.2 Hz, 1H), 1.33-1.19 (m, 9H), 1.16-1.03 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.47, 142.18, 140.77, 140.24, 128.73, 128.38, 127.73, 126.26, 125.83, 113.36, 55.31, 42.95, 41.96, 36.29, 34.78, 31.95, 30.22, 26.08, 24.63, 22.85, 14.25. IR (neat) ν_{max} 3062 (w), 3027 (w), 2955 (m), 2928 (s), 2854 (m), 1607 (w), 1510 (s), 1454 (m), 1247

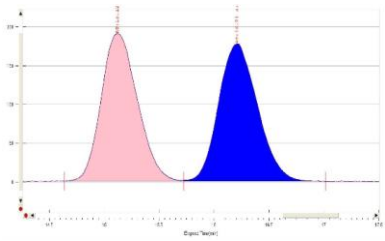
(s), 1180 (m), 1035 (m), 975 (m), 828 (m), 745 (m), 698 (s) cm^{-1}. HRMS (DART) calc. for $C_{25}H_{35}O$ $[M+H]^+$ 351.2688, found 351.2690. $[\alpha]^{20}_D$: -1.25 (c = 0.937, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

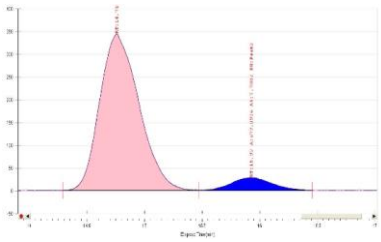
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 3% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

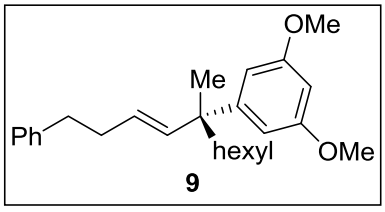


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.9201	4356.6994	15.12	190.5845	0.0144
2	50.0799	4370.6533	16.21	177.8941	0.0155
Total:	100	8727.3527			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	92.2918	8130.9139	14.76	343.9009	0.0153
2	7.7082	679.0936	15.93	28.0038	0.0165
Total:	100	8810.0075			



9

(*R*,*E*)-1,3-Dimethoxy-5-(5-methyl-1-phenylundec-3-en-5-yl)benzene (9). The reaction was performed according to the *Representative Procedure (Method B)* with 1-bromo-3,5-dimethoxybenzene. The crude mixture was purified by silica gel chromatography (25% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (36.2 mg, 95% yield). R_f = 0.3 in 30% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.21-7.16 (m, 3H), 6.47 (d, J = 2.0 Hz, 2H), 6.31 (t, J = 2.0 Hz, 1H), 5.62 (d, J = 15.5 Hz, 1H), 5.46 (dt, J = 15.5, 6.5 Hz, 1H), 3.79 (s, 6H), 2.72 (t, J = 7.5 Hz, 2H), 2.39 (q, J = 7.0 Hz, 2H), 1.69 (td, J = 13.5, 5.0 Hz, 1H), 1.62 (td, J = 12.5, 5.0 Hz, 1H), 1.33-1.20 (m, 2H), 1.18-1.01 (m, 2H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.54, 151.44, 142.17, 139.63, 128.64, 128.37, 126.66, 125.86, 105.54, 97.03, 55.35, 43.85, 41.84, 36.37, 34.77, 31.92, 30.20, 25.80, 24.57, 22.84, 14.22. IR (neat) ν_{max} 3026 (w), 2996 (w), 2928 (m), 2855 (w), 1593 (s), 1454

(m), 1421 (m), 1203 (s), 1152 (s), 1065 (m), 831 (w), 746 (w), 698 (s) cm^{-1}. HRMS (DART) calc. for $C_{26}H_{37}O_2$ $[M+H]^+$ 381.2794, found 381.2803. $[\alpha]^{20}_D$: +1.84 (c = 1.37, $CHCl_3$, *l* =50 mm).

Millimole Scale Procedure

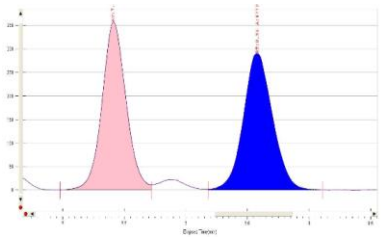
A 50-mL round bottom flask a magnetic stir bar was charged with allylic boronate **1** (741 mg, 2.00 mmol) and 1-bromo-3,5-dimethoxybenzene (868 mg, 4.00 mmol). The flask was sealed with rubber septum, and purged with N_2 for 10 minutes. Dioxane (10 mL) was added and the reaction stirred. Then a solution of $Pd(OAc)_2$ in dioxane (2.00 mL, 0.0400 mmol, 0.02M) and RuPhos in dioxane (2.00 mL, 0.0800 mmol, 0.04M) were added sequentially *via* syringe. Then 8M $KOH_{(aq)}$[14] (1.13 mL, 9.00 mmol) was added *via* syringe. The reaction was heated to 60°C under an atmosphere of N_2 for 14 hours. The reaction was cooled to room temperature, diluted with Et_2O (20 mL), and filtered through a plug of silica with additional Et_2O (30 mL). The filtrate was concentrated *in vacuo* and purified by silica gel chromatography to afford the desired compound. The crude material was purified by silica gel chromatography (25% CH_2Cl_2/pentane to 40% CH_2Cl_2/pentane, stain in CAM) to afford the title compound as a clear, colorless oil (691 mg, 91% yield). The spectral data matched those above.

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 3% ^{i}PrOH, 100 bar, 35 °C)-analysis of the reaction product.

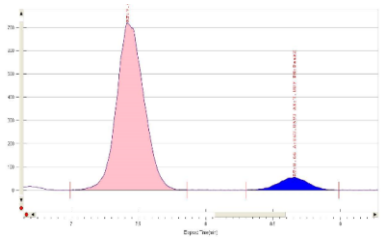
Racemic



Peak Info

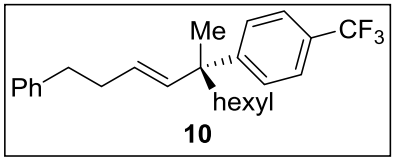
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.247	4826.6231	7.41	357.4494	0.0094
2	49.753	4779.1796	8.58	289.9541	0.0109
Total:	100	9605.8027			

Reaction Product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	92.191	10188.982	7.42	719.4295	0.0074
2	7.809	863.0593	8.66	55.9533	0.0086
Total:	100	11052.0413			



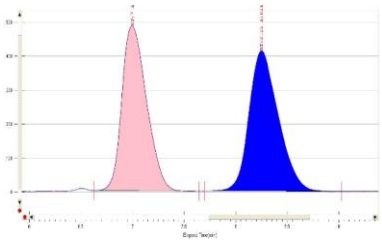
(*R*,*E*)-1-(5-Methyl-1-phenylundec-3-en-5-yl)-4-(trifluoromethyl)benzene (10). The reaction was performed according to the *Representative Procedure (Method A)* with 1-bromo-4-(trifluoromethyl)benzene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (37.0 mg, 95% yield). R_f = 0.2 in hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, J = 7.8 Hz, 2H), 7.32-7.27 (m, 4H), 7.23-7.17 (m, 3H), 5.57 (d, J = 16.2 Hz, 1H), 5.45 (dt, J = 15.6, 7.2 Hz, 1H), 2.74 (t, J = 6.6 Hz, 2H), 2.43 (q, J = 7.2 Hz, 2H), 1.72 (td, J = 13.2, 4.2 Hz, 1H), 1.66 (td, J = 13.2, 4.8 Hz, 1H), 1.33 (s, 3H), 1.31-1.20 (m, 6H), 1.16-0.99 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.82, 141.95, 139.16, 128.75, 128.43, 127.88 (q, J = 32.3 Hz), 127.38, 127.14, 125.93, 124.96 (q, J = 3.5 Hz), 43.87, 41.76, 36.11, 34.70, 31.89, 30.13, 25.90, 24.54, 22.82, 14.21. ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.28. IR (neat) ν_{max} 3027 (w), 2957 (w), 2929 (m), 2856 (w), 1454 (w), 1325 (s), 1163 (m), 1121 (s), 1069 (m), 1015 (m), 840 (m), 745 (m), 698 (m) cm^{-1}. HRMS (DART) calc. for $C_{25}H_{32}F_3$ $[M+H]^+$ 389.2456, found 389.2467. $[\alpha]^{20}_D$: -0.487 (c = 1.17, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 2% ^{i}PrOH, 100 bar, 35 °C)-analysis of the reaction product.

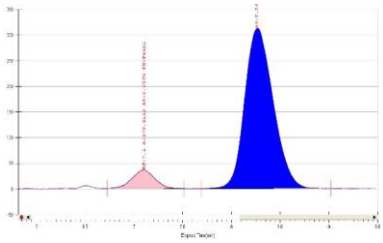
Racemic



Peak Info

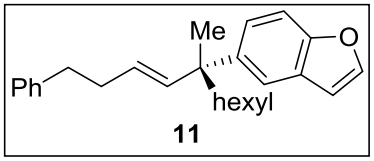
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.6577	8036.5811	7	485.6504	0.0138
2	50.3423	8147.364	8.25	412.7889	0.0162
Total:	100	16183.9451			

Reaction Product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	8.3596	578.6163	7.1	35.9994	0.0118
2	91.6404	6342.9329	8.26	312.6478	0.0137
Total:	100	6921.5492			



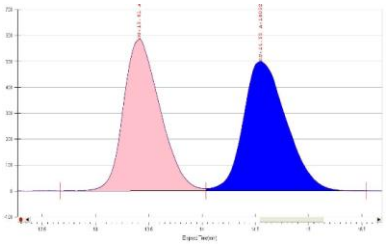
(*R*,*E*)-5-(5-Methyl-1-phenylundec-3-en-5-yl)benzofuran (11). The reaction was performed according to the *Representative Procedure (Method A)* with 5-bromobenzofuran. The crude mixture was purified by silica gel chromatography (10% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (30.0 mg, 83% yield). R_f = 0.4 in 10% CH_2Cl_2/pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 2.4 Hz, 1H), 7.45 (d, J = 1.8 Hz, 1H), 7.40 (d, J = 9.0 Hz, 1H), 7.32-7.29 (m, 2H), 7.24-7.16 (m, 4H), 6.74 (d, J = 3.0 Hz, 1H), 5.67 (d, J = 15.6 Hz, 1H), 5.47 (dt, J = 15.6, 6.6 Hz, 1H), 2.76 (t, J = 7.2 Hz, 2H), 2.44 (q, J = 7.2 Hz, 2H), 1.78 (td, J = 13.2, 5.4 Hz, 1H), 1.71 (td, J = 13.2, 4.8 Hz, 1H), 1.38 (s, 3H), 1.30-1.21 (m, 6H), 1.19-1.03 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.35, 145.01, 143.24, 142.16, 140.43, 128.75, 128.39, 127.12, 126.35, 125.86, 123.65, 118.92, 110.70, 106.90, 43.58, 42.25, 36.26, 34.76, 31.95, 30.23, 26.50, 24.68, 22.84, 14.24. IR (neat) ν_{max} 3085 (w), 3063 (w), 3025 (m), 2956 (s), 2927 (s), 2854 (s), 1603 (w), 1538 (w), 1466 (s), 1374 (m), 1329 (m), 1258 (m), 1134 (s), 1080 (s), 1031 (s), 975 (s), 811 (m), 736 (s), 698 (s) cm^{-1}. HRMS (DART) calc. for $C_{26}H_{33}O$ $[M+H]^+$ 361.2531, found 361.2538. $[\alpha]^{20}_D$: -1.28 (c = 0.827, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 7% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

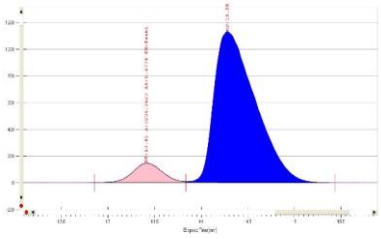
Racemic



Peak Info

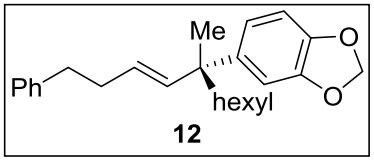
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.8376	13961.3588	13.41	585.2548	0.0129
2	50.1624	14052.3539	14.55	499.86	0.014
Total:	100	28013.7127			

Reaction Product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	8.4774	3234.3623	13.41	145.9792	0.0155
2	91.5226	34918.4995	14.28	1133.3254	0.0165
Total:	100	38152.8618			



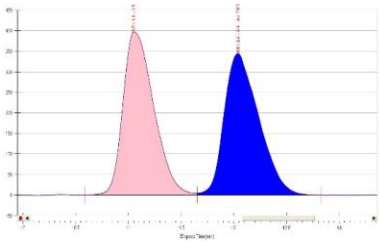
(*R*,*E*)-5-(5-Methyl-1-phenylundec-3-en-5-yl)benzo[d][1,3]dioxole (12). The reaction was performed according to the *Representative Procedure (Method A)* with 5-chlorobenzo[*d*][1,3]dioxole. The crude mixture was purified by silica gel chromatography (10% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (27.7 mg, 76% yield). R_f = 0.2 in 10% CH_2Cl_2/pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.22-7.16 (m, 3H), 6.77 (d, J = 1.8 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.66 (dd, J = 8.4, 1.8 Hz, 1H), 5.93 (s, 2H), 5.56 (d, J = 16.2 Hz, 1H), 5.43 (dt, J = 15.6, 6.0 Hz, 1H), 2.73 (t, J = 7.2 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 1.66 (td, J = 13.8, 4.8 Hz, 1H), 1.60 (td, J = 13.2, 4.8 Hz, 1H), 1.31-1.20 (m, 9H), 1.18-1.01 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.47, 145.31, 142.84, 142.11, 140.04, 128.71, 128.39, 126.44, 125.88, 119.57, 107.68, 107.67, 100.86, 43.49, 42.04, 36.25, 34.76, 31.95, 30.20, 26.21, 24.60, 22.84, 14.23. IR (neat) ν_{max} 3085 (w), 3062 (w), 3025 (w), 2955 (m), 2927 (s), 2855 (m), 1502 (m), 1485 (s), 1431 (m), 1375 (w), 1343 (w), 1234 (s), 1113 (w), 1040 (s), 976 (w), 917 (m), 810 (m), 746 (m), 727 (m), 698 (s) cm^{-1}. HRMS (DART) calc. for $C_{25}H_{32}O_2$ $[M+H]^+$ 364.2402, found 364.2411. The optical rotation was too low to be accurately measured.

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 3% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

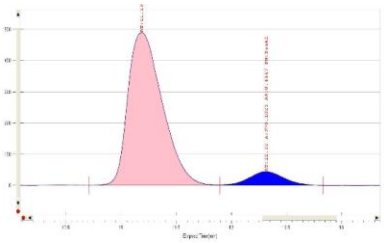
Racemic



Peak Info

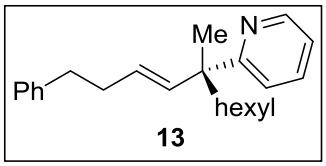
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.534	8049.1565	11.05	396.3532	0.0103
2	49.466	7879.0315	12.04	344.6257	0.0112
Total:	100	15928.188			

Reaction Product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	91.5553	10604.371	11.19	488.871	0.0137
2	8.4447	978.1025	12.32	44.9023	0.0151
Total:	100	11582.4735			



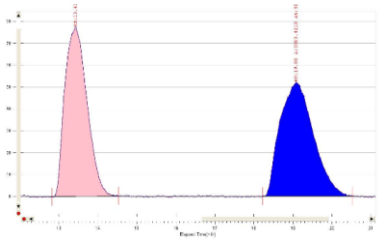
(*R*,*E*)-2-(5-Methyl-1-phenylundec-3-en-5-yl)pyridine (13). The reaction was performed according to the *Representative Procedure (Method E)* with 2-chloropyridine hydrochloride. The crude mixture was purified by silica gel chromatography (55% CH_2Cl_2/hexanes, stain in $KMnO_4$) to afford a clear, colorless oil (15.0 mg, 47% yield). R_f = 0.4 in CH_2Cl_2 on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, J = 4.2 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.19-7.15 (m, 2H), 7.10-7.06 (m, 3H), 6.99 (d, J = 7.8 Hz, 1H), 6.95 (dd, J = 7.2, 4.8 Hz, 1H), 5.63 (d, J = 15.6 Hz, 1H), 5.37 (dt, J = 15.6, 7.2 Hz, 1H), 2.62 (t, J = 7.2 Hz, 2H), 2.31 (q, J = 7.2 Hz, 2H), 1.74 (td, J = 13.2, 4.8 Hz, 1H), 1.62 (td, J = 13.2, 4.8 Hz, 1H), 1.28 (s, 3H), 1.20-1.09 (m, 6H), 1.02-0.89 (m, 2H), 0.75 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.46, 148.76, 142.15, 138.98, 136.02, 128.73, 128.38, 127.20, 125.82, 121.28, 120.73, 46.24, 41.38, 36.19, 34.81, 31.93, 30.12, 24.57, 24.42, 22.81, 14.22. IR (neat) ν_{max} 3062 (w), 3026 (w), 2955 (s), 2927 (s), 2855 (s), 1587 (m), 1569 (w), 1468 (m), 1429 (m), 978 (w), 746 (s), 698 (s) cm^{-1}. HRMS (DART) calc. for $C_{23}H_{32}N$ $[M+H]^+$ 322.2535, found 322.2538. $[\alpha]^{20}_D$: -9.55 (c = 0.610, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (AD-H, Chiraldex, 5 mL/min, 4% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

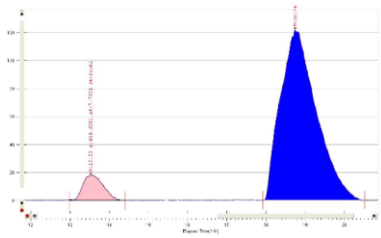
Racemic



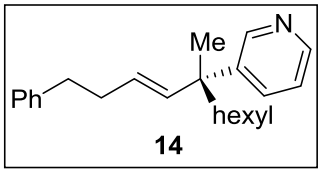
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.8584	3066.0064	13.43	77.6095	0.0195
2	50.1416	3083.4218	19.08	52.2345	0.0277
Total:	100	6149.4282			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	7.7331	646.6301	13.53	18.1347	0.019
2	92.2669	7715.2478	18.74	121.9619	0.0263
Total:	100	8361.8779			



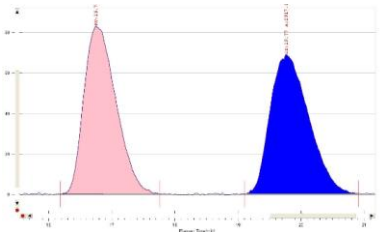
(*R,E*)-3-(5-Methyl-1-phenylundec-3-en-5-yl)pyridine (14). The reaction was performed according to the *Representative Procedure (Method E)* with 3-chloropyridine hydrochloride. The crude mixture was purified by silica gel chromatography (8% ethyl acetate/hexanes, stain in $KMnO_4$) to afford a clear, colorless oil (27.8 mg, 87% yield). R_f = 0.2 in 20% ethyl acetate/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.41 (d, J = 4.8 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.30-7.12 (m, 6H), 5.57 (d, J = 16.2 Hz, 1H), 5.43 (dt, J = 15.6, 6.0 Hz, 1H), 2.71 (t, J = 7.8 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 1.71 (td, J = 14.4, 5.4 Hz, 1H), 1.65 (td, J = 12.6, 4.8 Hz, 1H), 1.33 (s, 3H), 1.31-1.16 (m, 6H), 1.14-1.00 (m, 2H), 0.86 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.77, 147.00, 143.64, 141.90, 138.83, 134.43, 128.68, 128.40, 127.60, 125.90, 122.97, 42.46, 41.61, 36.10, 34.67, 31.86, 30.05, 25.69, 24.47, 22.77, 14.19. IR (neat) ν_{max} 3059 (w), 3026 (w), 2955 (m), 2928 (s), 2855 (m), 1466 (m), 1414 (w), 1021 (w), 976 (w), 745 (m), 715 (s), 699 (s) cm^{-1}. HRMS (DART) calc. for $C_{23}H_{32}N$ $[M+H]^+$ 322.2535, found 322.2548. $[\alpha]^{20}_D$: -2.18 (c = 1.20, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding primary alcohol upon ozonolysis and reduction.

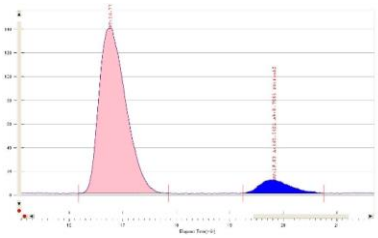
Chiral SFC (AD-H, Chiraldex, 5 mL/min, 4% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

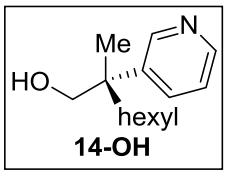


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.1263	2932.752	16.75	83.0098	0.0209
2	49.8737	2917.9776	19.77	68.8913	0.0247
Total:	100	5850.7296			

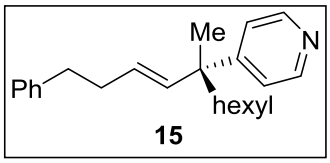
Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	91.2956	4882.8264	16.77	139.6424	0.0252
2	8.7044	465.5421	19.83	11.5186	0.0298
Total:	100	5348.3685			



(*S*)-2-Methyl-2-(pyridin-3-yl)octan-1-ol (14-OH). Prepared according to a literature precedent.[2] The crude mixture was purified by silica gel chromatography (25% ethyl acetate/pentane, stain in $KMnO_4$) to afford a clear, colorless oil. R_f = 0.3 in 40% ethyl acetate/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.47 (d, J = 5.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.45 (dd, J = 8.4, 6.0 Hz, 1H), 3.75 (d, J = 10.2 Hz, 1H), 3.60 (d, J = 10.8 Hz, 1H), 1.77 (td, J = 13.8, 4.8 Hz, 1H), 1.59 (td, J = 12.6, 4.8 Hz, 1H), 1.37 (s, 3H), 1.28-1.14 (m, 8H), 0.97-0.90 (m, 1H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.64, 145.07, 137.87, 124.72, 71.18, 42.71, 38.21, 31.73, 29.92, 23.83, 22.70, 21.44, 14.15. IR (neat) ν_{max} 3502 (br), 2927 (s), 28.57 (m), 2368 (s), 2312 (m), 2274 (w), 1486 (m), 1430 (m), 1378 (s), 1168 (s), 1040 (s), 811 (m), 724 (s) cm^{-1}. HRMS (DART) calc. for $C_{14}H_{24}NO$ $[M+H]^+$ 222.1858, found 222.1854. $[\alpha]^{20}_D$: -6.28 (c = 0.165, $CHCl_3$, *l* =50 mm).



(*R*,*E*)-4-(5-Methyl-1-phenylundec-3-en-5-yl)pyridine (15). The reaction was performed according to the *Representative Procedure (Method E)* with 4-chloropyridine hydrochloride. The crude mixture was purified by silica gel chromatography (20% ethyl acetate/hexanes, stain in $KMnO_4$) to afford a clear, colorless oil (26.4 mg, 82% yield). R_f = 0.4 in 40% ethyl acetate/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, J = 6.0 Hz, 2H), 7.29-7.25 (m, 2H), 7.21-7.15 (m, 3H), 7.06 (d, J = 6.6 Hz, 2H), 5.52 (d, J = 16.2 Hz, 1H), 5.43 (dt, J = 15.0, 6.0 Hz, 1H), 2.72 (t, J = 7.8 Hz, 2H), 2.41 (q, J = 7.2 Hz, 2H), 1.70-1.57 (m, 2H), 1.29 (s, 3H), 1.27-1.16 (m, 6H), 1.12-0.98 (m, 1H), 0.86 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.63, 149.66, 141.82, 138.27, 128.71, 128.42, 127.89, 125.93, 122.11, 43.55, 41.30, 36.01, 34.63, 31.83, 30.04, 25.22, 24.42, 22.76, 14.18. IR (neat) ν_{max} 3062 (w), 3025 (w), 2954 (m), 2928 (s), 2855 (m), 1594 (s), 1495 (m), 1454

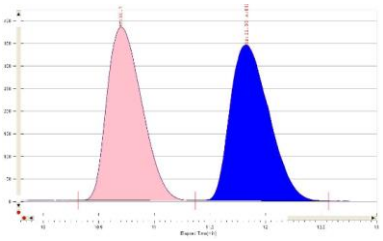
(m), 1409 (m), 975 (w), 821 (m), 745 (m), 698 (s) cm^{-1}. HRMS (DART) calc. for $C_{23}H_{32}N$ $[M+H]^+$ 322.2535, found 322.2546. $[\alpha]^{20}_D$: -5.24 (c = 1.03, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding primary alcohol upon ozonolysis and reduction.

Chiral SFC (AD-H, Chiraldex, 3 mL/min, 10% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

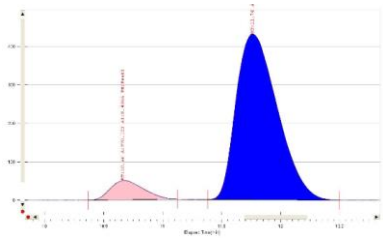
Racemic



Peak Info

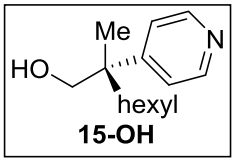
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.8193	8365.336	10.7	383.2732	0.0124
2	50.1807	8426.0365	11.83	345.2802	0.0137
Total:	100	16791.3725			

Reaction Product

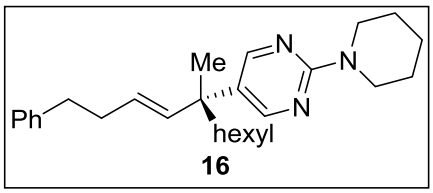


Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	8.4866	970.123	10.66	50.0986	0.0176
2	91.5134	10461.1754	11.76	431.3181	0.0194
Total:	100	11431.2984			



(*S*)-2-Methyl-2-(pyridin-4-yl)octan-1-ol (15-OH). Prepared according to a literature precedent.[2] The crude mixture was purified by silica gel chromatography (20% ethyl acetate/pentane, stain in $KMnO_4$) to afford a clear, colorless oil. R_f = 0.3 in 40% ethyl acetate/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, J = 6.6 Hz, 2H), 7.45 (d, J = 6.6 Hz, 2H), 3.76 (d, J = 10.2 Hz, 1H), 3.61 (d, J = 10.8 Hz, 1H), 1.74 (td, J = 13.2, 4.2 Hz, 1H), 1.57 (td, J = 13.2, 4.2 Hz, 1H), 1.36 (s, 3H), 1.29-1.11 (m, 8H), 0.93-0.87 (m, 1H), 0.85 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.89, 147.14, 123.97, 71.01, 44.18, 38.14, 31.69, 29.93, 23.84, 22.69, 21.21, 14.13. IR (neat) ν_{max} 3474 (br), 2953 (m), 2927 (s), 2857 (m), 2367 (s), 2313 (m), 2277 (m), 1628 (m), 1465 (w), 1433 (m), 1170 (s), 1067 (m), 1038 (m), 834 (m) cm^{-1}. HRMS (DART) calc. for $C_{14}H_{23}NO$ $[M+H]^+$ 222.1858, found 222.1858. $[\alpha]^{20}_D$: -6.83 (c = 0.420, $CHCl_3$, *l* =50 mm).



16

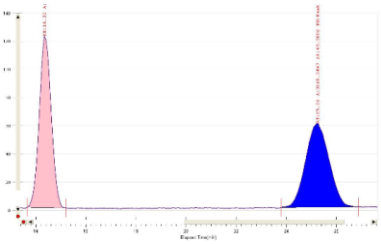
(*R*,*E*)-5-(5-Methyl-1-phenylundec-3-en-5-yl)-2-(piperidin-1-yl)pyrimidine (16). The reaction was performed according to the *Representative Procedure (Method B)* with 5-bromo-2-(piperidin-1-yl)pyrimidine. The crude mixture was purified by silica gel chromatography (1.5% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil (32.7 mg, 81% yield). R_f = 0.3 in 5% ethyl acetate/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 2H), 7.29-7.25 (m, 2H), 7.20-7.15 (m, 3H), 5.52 (d, J = 15.6 Hz, 1H), 5.41 (dt, J = 16.2, 6.0 Hz, 1H), 3.78-3.75 (m, 4H), 2.68 (t, J = 7.2 Hz, 2H), 2.35 (q, J = 7.2 Hz, 2H), 1.80-1.54 (m, 8H), 1.42-1.04 (m, 11H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.51, 156.57, 141.98, 138.94, 128.61, 128.38, 127.84, 127.37, 125.90, 44.98, 41.41, 40.36, 36.24, 34.72, 31.92, 30.08, 25.87, 25.55, 25.02, 24.48, 22.81, 14.21. IR (neat) ν_{max} 3025 (w), 2928 (m), 2852 (m), 1595 (s), 1495 (s), 1444 (m), 1365 (m), 1271 (m), 1256 (w), 947 (w), 798 (w), 698 (m) cm^{-1}. HRMS (DART) calc. for $C_{27}H_{40}N_3$ $[M+H]^+$ 406.3222, found 406.3228. $[\alpha]^{20}_D$: -3.80 (c = 1.00, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 8% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

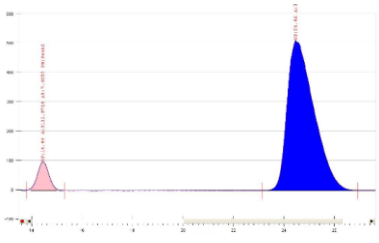
Racemic



Peak Info

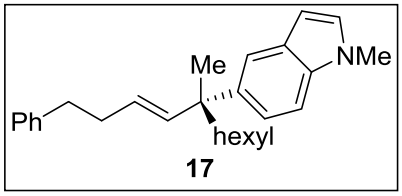
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.9114	4003.586	14.35	121.3137	0.0154
2	49.0886	3860.2447	25.26	59.4093	0.0272
Total:	100	7863.8307			

Reaction Product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	7.6055	3111.8714	14.44	98.2552	0.0215
2	92.3945	37804.4203	24.46	513.0743	0.0364
Total:	100	40916.2917			



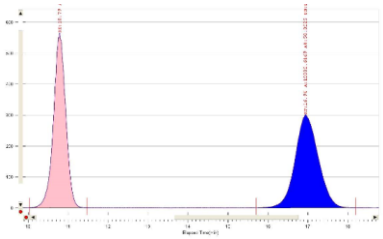
(*R*,*E*)-1-Methyl-5-(5-methyl-1-phenylundec-3-en-5-yl)-1H-indole (17). The reaction was performed according to the *Representative Procedure (Method B)* with 5-bromo-1-methyl-1H-indole. The crude mixture was purified by silica gel chromatography (3% CH_2Cl_2/hexanes to 10% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil (26.0 mg, 70% yield). R_f = 0.2 in 10% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.32-7.28 (m, 2H), 7.26-7.20 (m, 4H), 7.16 (m, 1H), 7.03 (d, J = 3.0 Hz, 1H), 6.46 (d, J = 3.0 Hz, 1H), 5.71 (d, J = 15.0 Hz, 1H), 5.47 (dt, J = 15.6, 7.2 Hz, 1H), 3.78 (s, 3H), 2.75 (t, J = 7.8 Hz, 2H), 2.43 (q, J = 7.2 Hz, 2H), 1.81 (td, J = 13.2, 4.8 Hz, 1H), 1.73 (td, J = 13.2, 4.8 Hz, 1H), 1.40 (s, 3H), 1.32-1.06 (m, 8H), 0.88 (t, J = 6.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.34, 140.97, 139.53, 135.12, 128.81, 128.74, 128.38, 128.32, 125.83, 125.81, 121.25, 118.42, 108.68, 101.05, 43.45, 42.25, 36.39, 34.87, 32.94, 31.98, 30.31, 26.49, 24.75, 22.87, 14.25. IR (neat) ν_{max} 3025 (w), 2955 (m), 2928 (s), 2854 (m), 1514 (w), 1489 (m), 1454 (m), 1335 (w), 1248 (m), 975 (w), 798 (m), 718 (s), 698 (s) cm^{-1}. HRMS (DART) calc. for $C_{27}H_{36}N$ $[M+H]^+$ 374.2848, found 374.2833. $[\alpha]^{20}_D$: -3.54 (c = 0.800, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 15% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

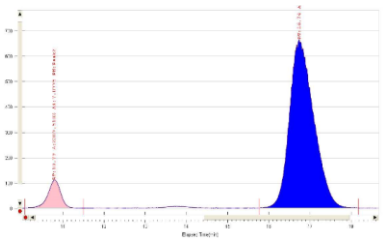
Racemic



Peak Info

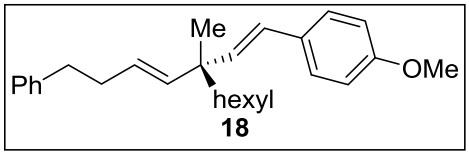
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.9775	11991.8319	10.79	564.9365	0.0103
2	50.0225	12002.6469	16.94	300.7842	0.0161
Total:	100	23994.4788			

Reaction Product



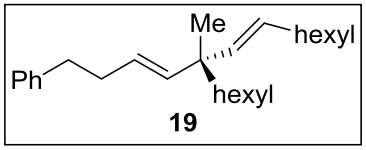
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	7.8775	2307.5102	10.79	109.3813	0.0181
2	92.1225	26984.9788	16.74	662.4339	0.0281
Total:	100	29292.489			



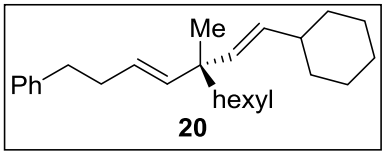
18

1-Methoxy-4-((*R*,*E*)-3-methyl-3-((*E*)-4-phenylbut-1-en-1-yl)non-1-en-1-yl)benzene (18). The reaction was performed according to the *Representative Procedure (Method B)* with **S4**. The crude mixture was purified by silica gel chromatography (10% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (32.2 mg, 80% yield). R_f = 0.3 in 20% CH_2Cl_2/pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.27 (m, 4H), 7.22-7.18 (m, 3H), 6.86 (d, J = 8.4 Hz, 2H), 6.20 (d, J = 16.2 Hz, 1H), 6.05 (d, J = 16.8 Hz, 1H), 5.51-5.39 (m, 2H), 3.82 (s, 3H), 2.71 (t, J = 7.8 Hz, 2H), 2.38 (q, J = 7.2 Hz, 2H), 1.46-1.38 (m, 2H), 1.36-1.19 (m, 8H), 1.15 (s, 3H), 0.90 (t, J = 5.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.80, 142.22, 138.91, 137.14, 131.02, 128.69, 128.35, 127.27, 126.81, 125.99, 125.83, 114.03, 55.44, 42.03, 41.76, 36.35, 34.83, 32.01, 30.26, 24.55, 24.25, 22.85, 14.26. IR (neat) ν_{max} 3085 (w), 3063 (w), 3027 (w), 2955 (m), 2927 (s), 2855 (m), 1607 (w), 1510 (s), 1441 (m), 1278 (w), 1246 (s), 1174 (m), 1037 (m), 971 (m), 851 (w), 817 (w), 746 (w), 698 (w) cm^{-1}. HRMS (DART) calc. for $C_{27}H_{37}O$ $[M+H]^+$ 377.2844, found 377.2828. The optical rotation was too low to be accurately measured. The enantiomers were not able to be separated with chiral chromatography techniques.



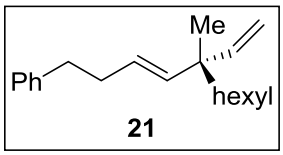
19

((*S*,3*E*,6*E*)-5-Hexyl-5-methyltrideca-3,6-dien-1-yl)benzene (19). The reaction was performed according to the *Representative Procedure (Method C)* with **S5**. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (31.2 mg, 88% yield). R_f = 0.6 in pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.20-7.16 (m, 3H), 5.41-5.31 (m, 3H), 5.25 (dt, J = 15.6, 6.6 Hz, 1H), 2.69 (t, 7.8 Hz, 2H), 2.34 (q, J = 6.6 Hz, 2H), 2.00 (q, J = 6.0 Hz, 2H), 1.40-1.13 (m, 18H), 1.02 (s, 3H), 0.92-0.88 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.33, 139.57, 138.53, 128.69, 128.33, 127.27, 126.08, 125.79, 42.05, 41.33, 36.44, 34.83, 32.97, 32.05, 31.90, 30.29, 29.82, 28.97, 24.49, 24.38, 22.87, 22.83, 14.27. IR (neat) ν_{max} 3086 (w), 3026 (m), 2956 (s), 2925 (s), 2854 (s), 1496 (m), 1454 (s), 1376 (m), 1342 (w), 1030 (w), 972 (s), 744 (s), 697 (s) cm^{-1}. HRMS (DART) calc. for $C_{26}H_{43}$ $[M+H]^+$ 355.3365, found 355.3367. The optical rotation was too low to be accurately measured. The enantiomers were not able to be separated with chiral chromatography techniques.



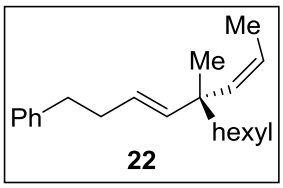
20

((*R*,*E*)-5-((*E*)-2-Cyclohexylvinyl)-5-methylundec-3-en-1-yl)benzene (20). The reaction was performed according to the *Representative Procedure (Method C)* with **S6**. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (29.6 mg, 90% yield). R_f = 0.7 in pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.20-7.16 (m, 3H), 5.43-5.28 (m, 3H), 5.21 (dd, J = 15.6, 6.0 Hz, 1H), 2.69 (t, J = 7.8 Hz, 2H), 2.34 (q, J = 6.6 Hz, 2H), 1.95-1.87 (m, 1H), 1.76-1.62 (m, 6H), 1.33-1.02 (m, 14H), 1.01 (s, 3H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.34, 139.68, 135.94, 133.18, 128.70, 128.32, 126.04, 125.79, 42.03, 41.09, 41.07, 36.45, 34.81, 33.59, 32.04, 30.28, 26.43, 26.33, 24.44, 24.38, 22.87, 14.28. IR (neat) ν_{max} 3086 (w), 3062 (w), 3026 (m), 2955 (m), 2923 (s), 2851 (s), 1496 (m), 1450 (s), 1374 (w), 1030 (w), 972 (s), 892 (w), 744 (m), 697 (s) cm^{-1}. HRMS (DART) calc. for $C_{26}H_{41}$ $[M+H]^+$ 353.3208, found 353.3220. The optical rotation was too low to be accurately measured. The enantiomers were not able to be separated with chiral chromatography techniques.



21

(*S*,*E*)-(5-Methyl-5-vinylundec-3-en-1-yl)benzene (21). The reaction was performed according to the *Representative Procedure (Method A)* utilizing vinyl bromide as a solution in THF (1M). The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (20.5 mg, 76% yield). R_f = 0.5 in pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.20-7.16 (m, 3H), 5.78 (dd, J = 18.0, 11.4 Hz, 1H), 5.42-5.35 (m, 2H), 4.94 (dd, J = 10.2, 1.8 Hz, 1H), 4.89 (dd, J = 17.4, 1.8 Hz, 1H), 2.69 (t, J = 7.8 Hz, 2H), 2.37-2.32 (m, 2H), 1.35-1.20 (m, 10H), 1.04 (s, 3H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.94, 142.25, 138.60, 128.67, 128.35, 126.74, 125.82, 111.17, 42.27, 41.53, 36.38, 34.84, 32.01, 30.23, 24.41, 23.58, 22.85, 14.27. IR (neat) ν_{max} 3105 (w), 3063 (w), 3026 (w), 2957 (m), 2927 (s), 2856 (m), 1604 (w), 1496 (w), 1454 (m), 1371 (w), 1030 (w), 972 (m), 910 (s), 744 (m), 697 (s) cm^{-1}. HRMS (DART) calc. for $C_{20}H_{31}$ $[M+H]^+$ 271.2426, found 271.2434. The optical rotation was too low to be accurately measured. The enantiomers were not able to be separated with chiral chromatography techniques.



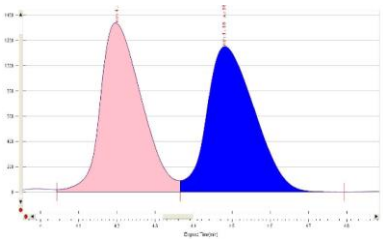
((*S*,*E*)-5-Methyl-5-((*Z*)-prop-1-en-1-yl)undec-3-en-1-yl)benzene (22). The reaction was performed according to the *Representative Procedure (Method A)* with (*Z*)-1-bromoprop-1-ene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (26.8 mg, 94% yield). R_f = 0.3 in pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.21-7.15 (m, 3H), 5.51 (d, J = 16.2 Hz, 1H), 5.45-5.34 (m, 2H), 5.29 (d, J = 12.0 Hz, 1H), 2.70 (t, J = 7.2 Hz, 2H), 2.37 (q, J = 7.2 Hz, 2H), 1.60 (d, J = 6.6 Hz, 3H), 1.42-1.18 (m, 10H), 1.12 (s, 3H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.34, 139.33, 138.25, 128.63, 128.36, 125.81, 125.58, 124.67, 43.50, 41.34, 36.37, 34.79, 32.04, 30.26, 25.95, 24.45, 22.86, 14.64, 14.27. IR (neat) ν_{max} 3086 (w), 3063 (w), 3025 (m), 3009 (m), 2956 (s), 2927 (s), 2855 (s), 1585 (w), 1496 (m), 1454 (s), 1375 (m), 1077 (w), 1030 (w), 974 (s), 904 (w), 744 (s), 697 (s) cm^{-1}. HRMS (DART) calc. for $C_{21}H_{33}$ $[M+H]^+$ 285.2582, found 285.2595. The optical rotation was too low to be accurately measured.

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 2.5 mL/min, 1% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

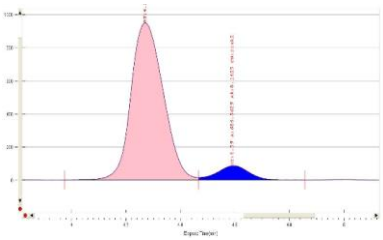
Racemic



Peak Info

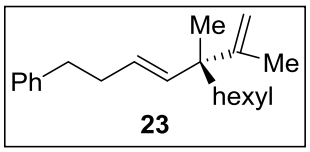
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.0763	9927.261	4.2	1337.6305	0.0038
2	49.9237	9897.0031	4.48	1152.0239	0.0041
Total:	100	19824.2641			

Reaction Product

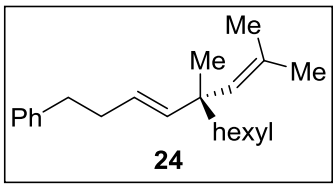


Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	91.8575	7745.2763	4.27	948.1861	0.0052
2	8.1425	686.5629	4.59	85.5053	0.0056
Total:	100	8431.8392			



(*R*,*E*)-(5-Methyl-5-(prop-1-en-2-yl)undec-3-en-1-yl)benzene (23). The reaction was performed according to the *Representative Procedure (Method A)* with 2-chloroprop-1-ene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (25.0 mg, 88% yield). R_f = 0.4 in pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.20-7.16 (m, 3H), 5.40-5.36 (m, 2H), 4.76 (t, J = 1.8 Hz, 1H), 4.70 (d, J = 1.2 Hz, 1H), 2.69 (t, J = 7.2 Hz, 2H), 2.37-2.32 (m, 2H), 1.63 (d, J = 1.2 Hz, 3H), 1.48 (ddd, J = 17.4, 12.6, 5.4 Hz, 1H), 1.36-1.22 (m, 7H), 1.17-1.06 (m, 5H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.32, 142.25, 139.25, 128.66, 128.35, 126.40, 125.82, 110.24, 44.61, 38.77, 36.39, 34.81, 32.03, 30.30, 24.40, 23.68, 22.88, 19.92, 14.26. IR (neat) ν_{max} 3086 (w), 3063 (w), 3027 (w), 2956 (s), 2928 (s), 2856 (s), 1635 (m), 1496 (m), 1453 (s), 1373 (m), 1077 (w), 1030 (w), 974 (s), 890 (s), 745 (s), 697 (s) cm^{-1}. HRMS (DART) calc. for $C_{21}H_{33}$ $[M+H]^+$ 285.2582, found 285.2580. The optical rotation was too low to be accurately measured. The enantiomers were not able to be separated with chiral chromatography techniques.



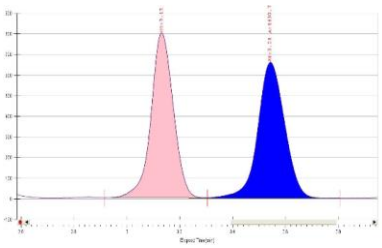
(*R*,*E*)-(5-Methyl-5-(2-methylprop-1-en-1-yl)undec-3-en-1-yl)benzene (24). The reaction was performed according to the *Representative Procedure (Method A)* with 1-bromo-2-methylprop-1-ene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (27.4 mg, 92% yield). R_f = 0.4 in pentane on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.21-7.16 (m, 3H), 5.47 (d, J = 16.2 Hz, 1H), 5.36 (dt, J = 15.6, 6.6 Hz, 1H), 5.11 (s, 1H), 2.69 (t, J = 7.2 Hz, 2H), 2.36 (q, J = 6.6 Hz, 2H), 1.69 (s, 3H), 1.58 (s, 3H), 1.41-1.16 (m, 10H), 1.09 (s, 3H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.40, 139.73, 132.51, 132.47, 128.63, 128.35, 125.79, 125.40, 43.96, 40.56, 36.44, 34.78, 32.06, 30.31, 27.68, 26.06, 24.43, 22.88, 19.20, 14.28 IR (neat) ν_{max} 3084 (w), 3062 (w), 3026 (w), 2957 (s), 2926 (s), 2855 (s), 1604 (w), 1496 (m), 1453 (s), 1373 (m), 1117 (w), 1030 (w), 975 (s), 823 (w), 744 (s), 697 (s) cm^{-1}. HRMS (DART) calc. for $C_{22}H_{34}$ $[M+H]^+$ 298.2661, found 298.2656. The optical rotation was too low to be accurately measured.

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

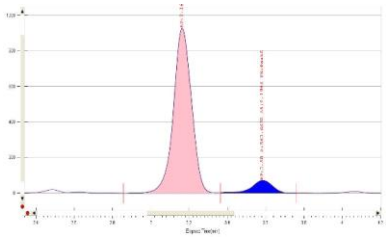
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 1% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

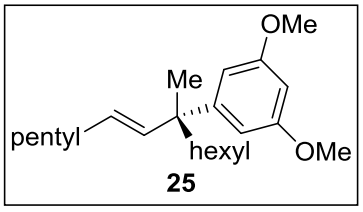


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.2456	4676.4912	3.13	800.8214	0.004
2	49.7544	4630.7692	3.54	658.3299	0.0045
Total:	100	9307.2604			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	91.8054	6090.7841	3.16	928.4353	0.0029
2	8.1946	543.6692	3.58	71.1944	0.0033
Total:	100	6634.4533			



25

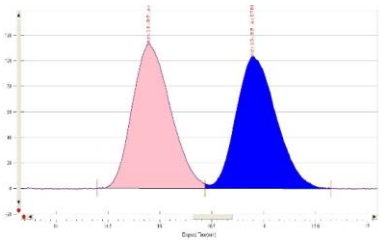
(*R*,*E*)-1,3-Dimethoxy-5-(7-methyltetradec-8-en-7-yl)benzene (25). The reaction was performed according to the *Representative Procedure (Method B)* with 1-bromo-3,5-dimethoxybenzene. The crude mixture was purified by silica gel chromatography (15% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (30.2 mg, 87% yield). R_f = 0.2 in 20% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.49 (d, J = 2.4 Hz, 2H), 6.30 (t, J = 2.4 Hz, 1H), 5.58 (d, J = 15.0 Hz, 1H), 5.42 (dt, J = 15.6, 6.6 Hz, 1H), 3.78 (s, 6H), 2.06 (q, J = 7.2 Hz, 2H), 1.71 (td, J = 13.8, 4.8 Hz, 1H), 1.63 (td, J = 13.2, 4.2 Hz, 1H), 1.39 (p, J = 7.2 Hz, 2H), 1.34-1.07 (m, 17H), 0.89 (t, J = 7.2 Hz, 3H), 0.86 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.51, 151.76, 138.77, 127.74, 105.49, 97.08, 55.34, 43.86, 41.87, 32.94, 31.95, 31.59, 30.22, 29.55, 25.90, 24.65, 22.83, 22.71, 14.22. IR (neat) ν_{max} 3015 (w), 2955 (m), 2927 (s), 2855 (m), 1595 (s), 1456 (m), 1421 (m), 1308 (w), 1204 (m), 1154 (s), 1067 (w), 976 (w), 831 (w), 699 (w) cm^{-1}. HRMS (DART) calc. for $C_{23}H_{39}O_2$ $[M+H]^+$ 347.2950, found 347.2966. $[\alpha]^{20}_D$: -2.31 (c = 0.940, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

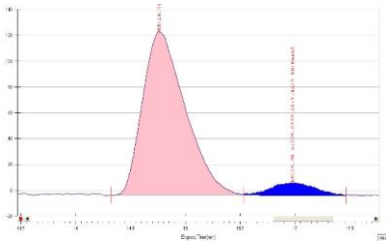
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 0% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

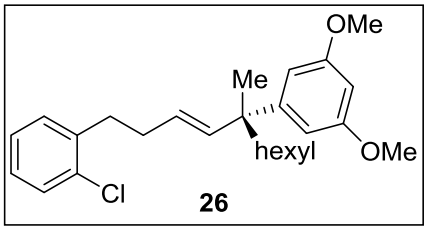


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.857	2885.3135	14.89	113.2751	0.0231
2	49.143	2788.0709	15.89	103.4318	0.0246
Total:	100	5673.3844			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	92.5383	3421.3798	14.76	126.8963	0.0266
2	7.4617	275.8799	15.98	9.809	0.0288
Total:	100	3697.2597			



26

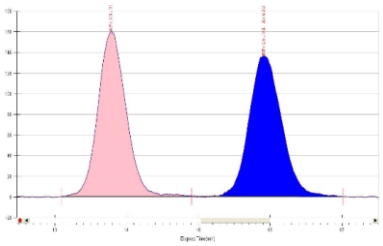
(*R*,*E*)-1-(1-(2-Chlorophenyl)-5-methylundec-3-en-5-yl)-3,5-dimethoxybenzene (26). The reaction was performed according to the *Representative Procedure (Method B)* with 1-bromo-3,5-dimethoxybenzene. The crude mixture was purified by silica gel chromatography (25% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (33.2 mg, 80% yield). R_f = 0.2 in 30% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.4, 1.8 Hz, 1H), 7.22-7.15 (m, 2H), 7.13 (dt, J = 7.8, 2.4 Hz, 1H), 6.46 (d, J = 2.4 Hz, 2H), 6.31 (t, J = 2.4 Hz, 1H), 5.61 (d, J = 16.2 Hz, 1H), 5.47 (dt, J = 15.6, 6.6 Hz, 1H), 3.79 (s, 6H), 2.84 (t, J = 6.6 Hz, 2H), 2.40 (q, J = 7.2 Hz, 2H), 1.69 (td, J = 13.2, 5.4 Hz, 1H), 1.62 (td, J = 12.6, 4.8 Hz, 1H), 1.32-1.20 (m, 9H), 1.17-1.02 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.53, 151.38, 139.94, 139.62, 134.09, 130.68, 129.53, 127.37, 126.75, 126.25, 105.49, 97.05, 55.35, 43.85, 41.81, 33.95, 33.03, 31.92, 30.19, 25.77, 24.56, 22.84, 14.24. IR (neat) ν_{max} 3065 (w), 2995 (w), 2953 (m), 2928 (s), 2855 (w), 1593 (s), 1454 (m), 1421 (m), 1289 (w), 1203 (s), 1152 (s), 1050 (m), 974 (w), 831 (w), 749 (s), 699 (m) cm^{-1}. HRMS (DART) calc. for $C_{26}H_{36}ClO_2$ $[M+H]^+$ 415.2404, found 415.2411. $[\alpha]^{20}_D$: -0.566 (c = 0.960, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

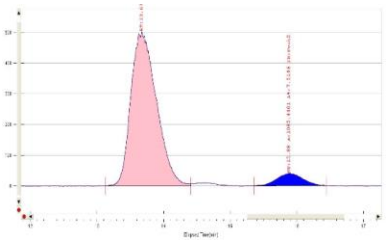
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 1% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

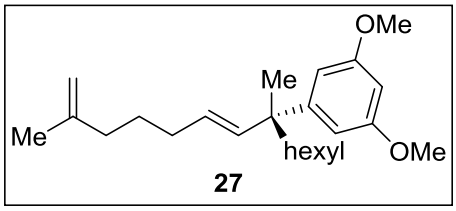


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.0682	4320.7061	13.78	159.6868	0.0185
2	49.9318	4308.9317	15.91	136.3174	0.0214
Total:	100	8629.6378			

Reaction Product

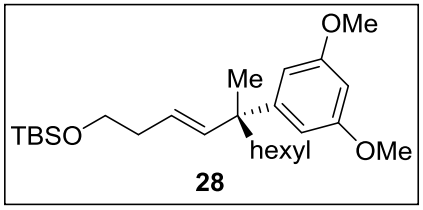


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	92.4854	13358.9284	13.67	501.2386	0.0154
2	7.5146	1085.4401	15.88	40.5207	0.0178
Total:	100	14444.3685			



27

(*R*,*E*)-1-(7,13-Dimethyltetradeca-8,13-dien-7-yl)-3,5-dimethoxybenzene (27). The reaction was performed according to the *Representative Procedure (Method B)* with 1-bromo-3,5-dimethoxybenzene. The crude mixture was purified by silica gel chromatography (15% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (34.1 mg, 95% yield). R_f = 0.2 in 20% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.49 (d, J = 2.4 Hz, 2H), 6.30 (t, J = 2.4 Hz, 1H), 5.60 (d, J = 15.6 Hz, 1H), 5.42 (dt, J = 15.6, 6.6 Hz, 1H), 4.71 (s, 1H), 4.67 (s, 1H), 3.79 (s, 6H), 2.10-2.01 (m, 4H), 1.75-1.67 (m, 4H), 1.64 (td, J = 12.0, 4.8 Hz, 1H), 1.54 (p, J = 7.2 Hz, 2H), 1.32 (s, 3H), 1.30-1.08 (m, 8H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.52, 151.62, 146.09, 139.24, 127.31, 109.95, 105.50, 97.07, 55.34, 43.87, 41.85, 37.44, 32.57, 31.94, 30.21, 27.81, 25.85, 24.64, 22.83, 22.56, 14.22. IR (neat) ν_{max} 2929 (m), 2856 (w), 1594 (s), 1455 (m), 1422 (m), 1204 (s), 1153 (s), 1066 (w) cm^{-1}. HRMS (DART) calc. for $C_{24}H_{39}O_2$ $[M+H]^+$ 359.2950, found 359.2965. $[\alpha]^{20}_D$: -2.18 (c = 1.14, $CHCl_3$, *l* =50 mm). The enantiomers were not able to be separated with chiral chromatography techniques.



28

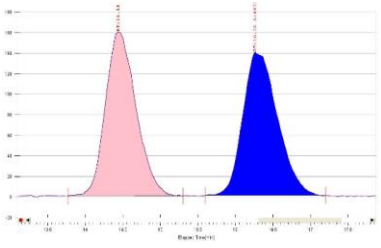
(*R*,*E*)-tert-Butyl((5-(3,5-dimethoxyphenyl)-5-methylundec-3-en-1-yl)oxy)dimethylsilane (28). The reaction was performed according to the *Representative Procedure (Method B)* with 1-bromo-3,5-dimethoxybenzene. The crude mixture was purified by silica gel chromatography (45% CH_2Cl_2/pentane, stain in CAM) to afford a clear, colorless oil (41.2 mg, 95% yield). R_f = 0.2 in 30% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.47 (d, J = 2.4 Hz, 2H), 6.30 (d, J = 2.4 Hz, 1H), 5.66 (d, J = 15.6 Hz, 1H), 5.43 (dt, J = 15.6, 6.6 Hz, 1H), 3.78 (s, 6H), 3.65 (t, J = 7.2 Hz, 2H), 2.28 (q, J = 7.2 Hz, 2H), 1.71 (td, J = 13.2, 4.8 Hz, 1H), 1.63 (td, J = 13.2, 4.2 Hz, 1H), 1.31 (s, 3H), 1.30-1.06 (m, 8H), 0.90 (s, 9H), 0.859 (t, J = 6.6 Hz, 3H), 0.06 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.52, 151.34, 140.86, 123.85, 105.50, 97.02, 63.56, 55.32, 43.95, 41.78, 36.67, 31.91, 30.18, 26.10, 26.08, 25.69, 24.58, 22.83, 18.50, 14.22, -5.11. IR (neat) ν_{max} 2953 (m), 2929 (s), 2856 (m), 1595 (s), 1458 (m), 1422 (w), 1254 (w), 1204 (m), 1154 (s), 1099 (s), 833 (s), 775 (m) cm^{-1}. HRMS (DART) calc. for $C_{26}H_{47}O_3Si$ $[M+H]^+$ 435.3295, found 435.3310. $[\alpha]^{20}_D$: -0.704 (c = 0.812, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding primary alcohol after silyl deprotection.

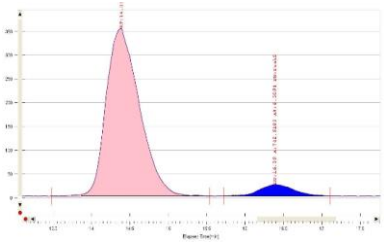
Chiral SFC (OD-H, Chiraldex, 5.0 mL/min, 3% ^{i}PrOH, 100 bar, 35 °C)-analysis of the reaction product.

Racemic

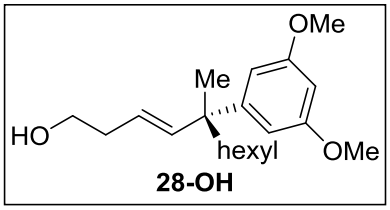


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.3526	4537.3759	14.44	159.7837	0.0246
2	49.6474	4473.8345	16.26	139.6059	0.0277
Total:	100	9011.2104			

Reaction Product

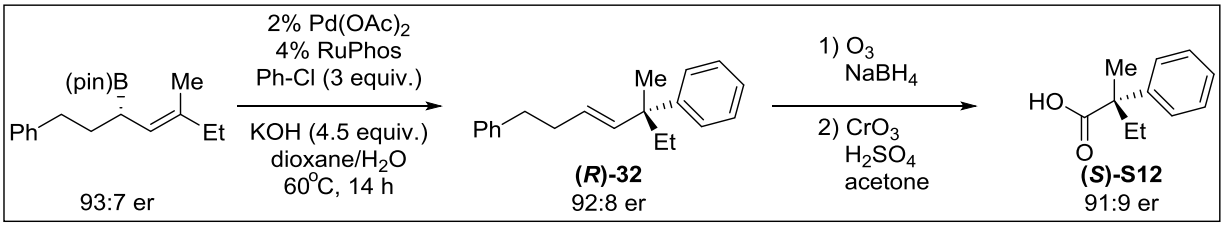


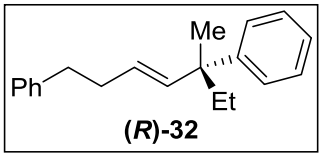
Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	93.4906	10670.0377	14.39	353.2563	0.0265
2	6.5094	742.9183	16.39	24.3383	0.0302
Total:	100	11412.956			



(*R*,*E*)-5-(3,5-Dimethoxyphenyl)-5-methylundec-3-en-1-ol (28-OH). A 2-dram vial with a magnetic stir bar was charged with **28** and purged with N_2. THF (1 mL) was added followed by TBAF (10 equiv., 1M in THF). The reaction was stirred under N_2 at room temperature for 4h. The reaction was quenched with H_2O (2 mL) and poured into a separatory funnel with Et_2O (5 mL).The layers were separated and the aqueous layer was extracted with Et_2O (2 x 5 mL). The organic layers were combined, dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The crude mixture was purified by silica gel chromatography (20% ethyl acetate/pentane, stain in CAM) to afford a clear, colorless oil. R_f = 0.3 in 30% ethyl acetate/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.47 (d, J = 2.5 Hz, 2H), 6.30 (t, J = 2.5 Hz, 1H), 5.73 (d, J = 15.5 Hz, 1H), 5.40 (dt, J = 15.5, 6.5 Hz, 1H), 3.78 (s, 6H), 3.66 (t, J = 6.0 Hz, 2H), 2.33 (q, J = 6.5 Hz, 2H), 1.73 (td, J = 11.5, 5.5 Hz, 1H), 1.64 (td, J = 12.5, 5.0 Hz, 1H), 1.33 (s, 3H), 1.31-1.04 (m, 9H), 0.86 (t, J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.61, 151.02, 142.71, 123.08, 105.46, 97.15, 62.40, 55.36, 44.07, 41.77, 36.39, 31.90, 30.15, 25.58, 24.63, 22.81, 14.20. IR (neat) ν_{max} 3406 (br), 2954 (m), 2930 (m), 2857 (w), 1595 (s), 1456 (m), 1422 (m), 1204 (m), 1154 (s), 1046 (m) cm^{-1}. HRMS (DART) calc. for $C_{20}H_{33}O_3$ $[M+H]^+$ 321.2430, found 321.2435. $[\alpha]^{20}_D$: -2.20 (c = 0.955, $CHCl_3$, *l* =50 mm).

VIII. Structure Proof for Stereospecific Cross-Coupling





(*R*,*E*)-(5-Methylhept-3-ene-1,5-diyl)dibenzene ((*R*)-32). The reaction was performed according to the *Representative Procedure (Method A)* with (*S*,*E*)-4,4,5,5-tetramethyl-2-(5-methyl-1-phenylhept-4-en-3-yl)-1,3,2-dioxaborolane[2] and chlorobenzene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (23.5 mg, 89% yield). R_f = 0.3 in pentane on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.14 (m, 10H), 5.62 (d, *J* = 15.5 Hz,

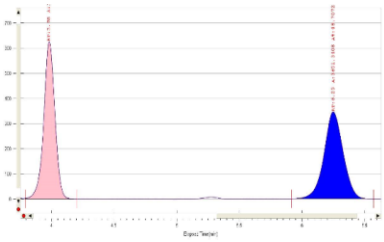
1H), 5.47 (dt, *J* = 16.0, 6.5 Hz, 1H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.42 (q, *J* = 7.5 Hz, 2H), 1.83-1.68 (m, 2H), 1.32 (s, 3H), 0.74 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.36, 142.15, 139.66, 128.73, 128.39, 128.05, 126.87, 126.78, 125.84, 125.63, 43.84, 36.30, 34.82, 34.05, 25.30, 9.12. IR (neat) ν_{max} 3085 (w), 3059 (w), 3025 (w), 2965 (m), 2924 (m), 2877 (w), 1494 (m), 1453 (m), 974 (m), 788 (m), 760 (m), 696 (s) cm^{-1}. HRMS (DART) calc. for $C_{20}H_{28}N$ $[M+NH_4]^+$ 282.2222, found 282.2213. The optical rotation was too low to be accurately measured.

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

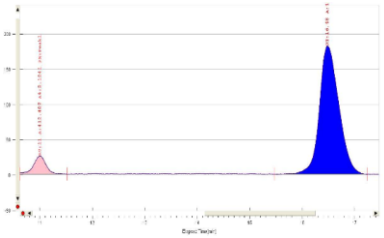
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 3% ^{i}PrOH, 100 bar, 35 °C)-analysis of the reaction product.

Racemic

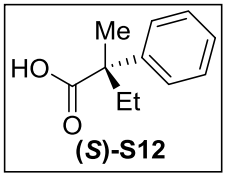


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	51.2928	3845.1741	3.98	624.3186	0.0038
2	48.7072	3651.3408	6.25	345.5808	0.006
Total:	100	7496.5149			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	8.1241	412.489	11	25.4065	0.0119
2	91.8759	4664.8353	16.48	181.4752	0.0178
Total:	100	5077.3243			



(*S*)-2-Methyl-2-phenylbutanoic acid ((*S*)-S12). A 4-dram vial was charged with (*R*)-**32** (23.5 mg, 0.089 mmol), CH_2Cl_2 (2 mL), and MeOH (2 mL). The reaction was stirred and cooled to -78°C. A stream of O_3 was bubbled into the reaction for approximately 3 minutes as the color changed from bright yellow to red/brown. $NaBH_4$ (76 mg, 2.0 mmol) was added as a solid. The reaction stirred at -78°C for 5 minutes before warming to room temperature and further stirring for 12 hours. H_2O (2 mL) was added and the reaction was poured into a separatory funnel with ethyl acetate (10 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, dried over $Na_2SO_{4(s)}$, filtered and concentrated *in vacuo*. The

crude material was purified by silica gel chromatography (10% ethyl acetate/hexanes) to afford the corresponding primary alcohol as a clear, colorless oil (10.5 mg, 72% yield). R_f = 0.2 in 10% ethyl acetate/hexanes on TLC. A scintillation vial was charged with the primary alcohol (10.5 mg, 0.07 mmol), diluted with acetone (4 mL), and cooled to 0°C. Jones reagent (70 µL, 0.14 mmol, 2M in $H_2SO_{4(aq)}$) was added *via* syringe. The reaction was stirred at 0°C under air for 15 minutes. H_2O (2 mL) was added and the reaction was poured into a separatory funnel with ethyl acetate (10 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The organic layers were combined, dried over $Na_2SO_{4(s)}$, filtered and concentrated *in vacuo*. The crude material was purified by silica gel chromatography (20% ethyl acetate/pentane) to afford to afford a white solid (5.8 mg, 46% yield). R_f = 0.5 in 20% ethyl acetate/pentane on TLC. The spectral data matched those reported in the literature.[17] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.32 (m, 4H), 7.28-7.24 (m, 1H), 2.14-1.96 (m, 2H), 1.57 (s, 3H), 0.86 (t, J = 6.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.66, 143.00, 128.53, 127.01, 126.41, 50.52, 31.77, 21.87, 9.19. HRMS (DART) calc. for $C_{20}H_{28}N$ $[M+H]^+$ 179.1072, found 179.1071. m.p.: 81-82°C. $[\alpha]^{20}_D$: +29.9 (c = 0.220, C_6H_6, *l* = 50 mm). The absolute stereochemistry was assigned by comparing the optical rotation with a reported value in the literature for (*R*)-**S12**, $[\alpha]^{20}_D$: -32.6 (c = 0.3, C_6H_6).[18]

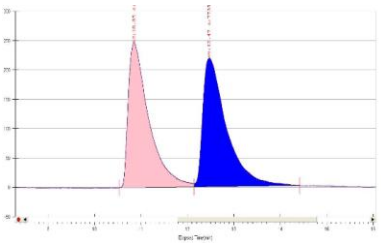
Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 1% ^{i}PrOH, 100 bar, 35 °C)-analysis of the reaction product.

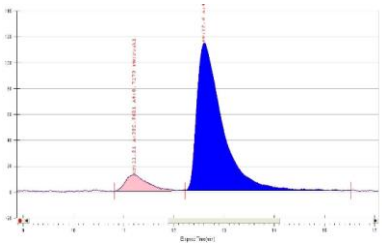
[17] Zhu, Q.; Lu, Y. *Chem. Commun*. **2010**, *46*, 2235.
[18] Ruano, J. L. G.; Martin-Castro, A. M.; Tato, F.; Torrente, E.; Poveda, A. M. *Chem. Eur. J.* **2010**, *16*, 6317.

Racemic



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.6067	7615.2217	10.85	246.2401	0.0121
2	50.3933	7735.9696	12.47	218.9199	0.0139
Total:	100	15351.1913			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	8.7173	382.9621	11.21	12.5195	0.0136
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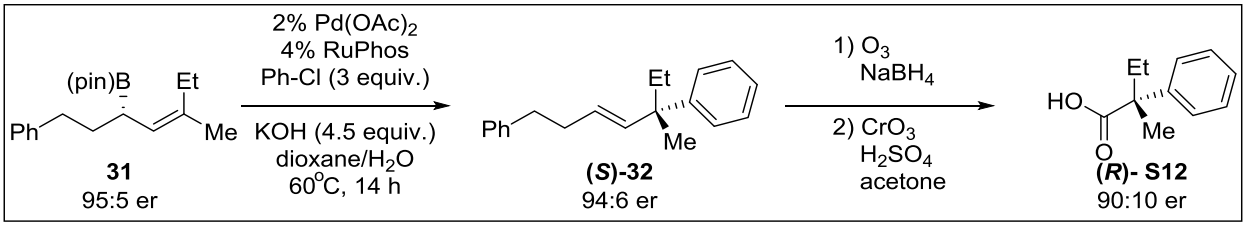
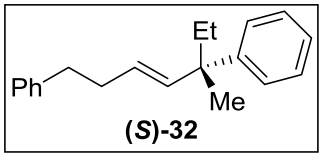
Total:	100	4393.1346			





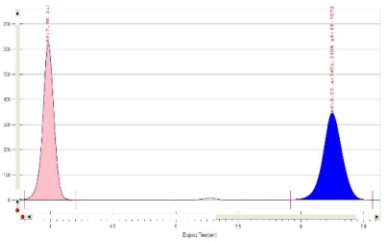
(*S*,*E*)-(5-Methylhept-3-ene-1,5-diyl)dibenzene ((*S*)-32). The reaction was performed according to the *Representative Procedure (Method A)* with (*S*,*Z*)-2-(1-(2-Chlorophenyl)-5-methylundec-4-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**31)** and chlorobenzene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (20.4 mg, 77% yield). R_f = 0.3 in pentane on TLC. The spectral data matched **(*R*)-32**. The optical rotation was too low to be accurately measured.

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

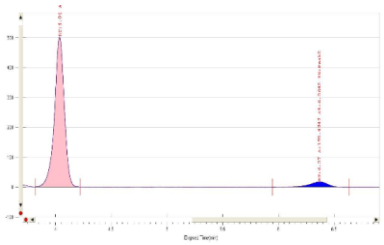
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 1% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

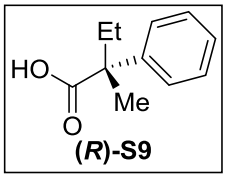


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	51.2928	3845.1741	3.98	624.3186	0.0038
2	48.7072	3651.3408	6.25	345.5808	0.006
Total:	100	7496.5149			

Reaction Product



Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	93.9358	3074.7133	4.04	502.7725	0.0038
2	6.0642	198.4949	6.37	17.8699	0.006
Total:	100	3273.2082			



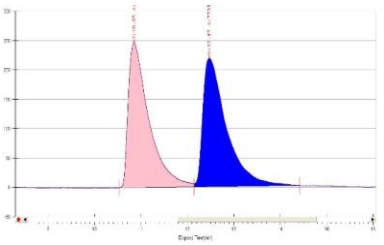
(*R*)-2-Methyl-2-phenylbutanoic acid ((*R*)-S12). The reaction was performed analogously to (*S*)-**S12** with (*S*)-**32** with comparable yields. The spectral data matched (*S*)-**S12**. (*R*)-**S12**: $[\alpha]^{20}_{D}$: -30.0 (c = 0.100, C_6H_6, *l* = 50 mm). The absolute stereochemistry was assigned by comparing the optical rotation with a reported value in the literature for (*R*)-**S12**, $[\alpha]^{20}_{D}$: -32.6 (c = 0.3, C_6H_6).[18]

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis.

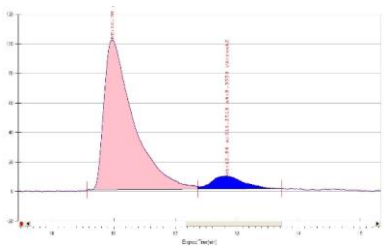
Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 1% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic



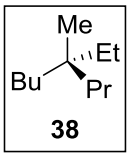
Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.6067	7615.2217	10.85	246.2401	0.0121
2	50.3933	7735.9696	12.47	218.9199	0.0139
Total:	100	15351.1913			

Reaction Product



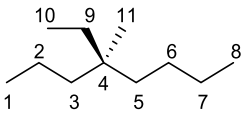
Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	91.4446	3358.8779	10.98	101.4288	0.0129
2	8.5554	314.2514	12.84	9.0364	0.0151
Total:	100	3673.1293			

IX. Synthesis and Characterization of (R)-4-Ethyl-4-methyloctane (38)



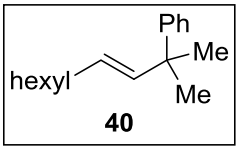
38

(*R*)-4-Ethyl-4-methyloctane (38). A 2-dram vial with magnetic stir bar was charged with (*S*,*E*)-4,4,5,5-tetramethyl-2-(5-methyloct-4-en-3-yl)-1,3,2-dioxaborolane (**38**) (50.4 mg, 0.20 mmol). The vial was sealed with rubber septum, and purged with N_2 for 10 minutes. Dioxane (1 mL) was added and the reaction stirred. Then a solution of $Pd(OAc)_2$ in dioxane (200 μL, 0.0040 mmol, 0.02M) and RuPhos in dioxane (200 μL, 0.0080 mmol, 0.04M) were added sequentially *via* syringe. Then vinyl bromide (600 μL, 0.60 mmol, 1.0M) and 8M $KOH_{(aq)}$[13] (113 μL, 0.90 mmol) were added sequentially *via* syringe. The reaction was heated to 50°C under an atmosphere of N_2 for 14 hours. The reaction was cooled to room temperature, 10%wt. Pd/C (20 mg, 0.02 mmol), and EtOH (2 mL) were added. The reaction was equipped with a balloon of H_2 and purged. The reaction stirred at room temperature for 12 hours. The reaction was filtered through Celite with pentane (10 mL) into a separatory funnel containing H_2O (10 mL). The layers were separated and the organic washed with H_2O (2 x 5 mL). The organic layer was dried over $Na_2SO_{4(s)}$, filtered, and carefully concentrated on the rotovap to afford a colorless liquid. The crude ^{1}H-NMR indicated incomplete hydrogenation. The crude material was dissolved in EtOH (2 mL) and 10%wt. Pd/C (20 mg, 0.02 mmol) was added. The reaction was equipped with a balloon of H_2 and purged. The reaction stirred at room temperature for 12 hours. The reaction was filtered through Celite with pentane (10 mL) into a separatory funnel containing H_2O (10 mL). The layers were separated and the organic washed with H_2O (2 x 5 mL). The organic layer was dried over $Na_2SO_{4(s)}$, filtered, and carefully concentrated on the rotovap. Cyclohexane (6.1 mg) was added as a ^{13}C-NMR internal standard which indicated a 72% yield. Filtration through a short plug of silica gave characterizable material that contained 1 equivalent of pentane. Attempts to further remove pentane were resulted in great loss of the title compound. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30-1.10 (m, 12H), 0.92-0.84 (m, 12H), 0.77 (s, 3H), 0.76 (t, J = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.74, 38.84, 35.04, 31.73, 25.93, 24.72, 23.88, 16.86, 15.27, 14.36, 8.12. GCMS: T_R 7.42; MS: 156, 127, 113, 99, 85, 71, 57 (basepeak).



Carbon Atom	^{13}C-NMR shift (ppm) ($CDCl_3$: 77.00 ppm)	Fujita and co-workers[19]
10	7.96	7.99
8	14.20	14.23
1	15.11	15.13
2	16.70	16.71
7	23.72	23.74
11	24.56	24.58
6	25.77	25.79
9	31.57	31.58
4	34.88	34.89
5	38.68	38.69
3	41.58	41.59

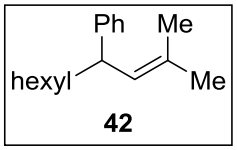
X. Characterization of Compounds in Mechanistic Studies



(*E*)-(2-Methyldec-3-en-2-yl)benzene (40). The reaction was performed according to the *Representative Procedure (Method A)* with 4,4,5,5-tetramethyl-2-(2-methyldec-2-en-4-yl)-1,3,2-dioxaborolane (**39**) and chlorobenzene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (18.0 mg, 78% yield). R_f = 0.7 in hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.32-7.28 (m, 2H), 7.20-7.16 (m, 1H), 5.63 (d, *J* = 16.0 Hz, 1H), 5.44 (dt, *J* = 15.5, 6.5 Hz, 1H), 2.05 (q, *J* = 6.5 Hz, 2H), 1.42-1.36 (m, 8H), 1.35-1.24 (m, 8H), 0.90 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.71, 140.05, 128.13, 126.80, 126.31, 125.71, 40.42, 32.80, 31.88, 29.77, 29.13, 29.00, 22.81, 14.24. IR (neat) ν_{max} 3021 (w),

[19] Fujita, T.; Obata, K.; Kuwahara, S.; Miura, N.; Nakahashi, A.; Monde, K.; Decatur, J.; Harada, N. *Tetrahedron Lett*. **2007**, *48*, 4219.

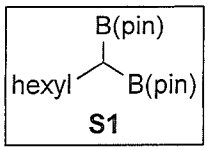
2961 (m), 2924 (s), 2854 (m), 1493 (w), 1465 (w), 1445 (w), 974 (m), 762 (s), 698 (s) cm^{-1}. HRMS (DART) calc. for $C_{17}H_{26}$ $[M]^+$ 230.2035, found 230.2042.



42

(2-Methyldec-2-en-4-yl)benzene (42). The reaction was performed according to the *Representative Procedure (Method A)* with (*E*)-4,4,5,5-tetramethyl-2-(2-methyldec-3-en-2-yl)-1,3,2-dioxaborolane (**41**) and chlorobenzene. The crude mixture was purified by silica gel chromatography (pentane, stain in CAM) to afford a clear, colorless oil (17.9 mg, 78% yield). R_f = 0.7 in pentane on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.21-7.14 (m, 3H), 5.27 (d, *J* = 9.0 Hz, 1H), 3.44 (q, *J* = 8.5 Hz, 1H), 1.71 (s, 3H), 1.66 (s, 3H), 1.65-1.54 (m, 2H), 1.32-1.15 (m, 8H), 0.88 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.67, 131.23, 129.35, 128.47, 127.45, 125.79, 44.51, 37.49, 31.99, 29.49, 27.71, 26.05, 22.81, 18.27, 14.23. IR (neat) ν_{max} 3026 (w), 2957 (m), 2924 (s), 2854 (m), 1493 (w), 1451 (w), 1376 (w), 755 (m), 697 (s) cm^{-1}. HRMS (DART) calc. for $C_{22}H_{34}$ $[M+NH_4]^+$ 248.2378, found 248.2387.

^{1}H and ^{13}C NMR Spectral Data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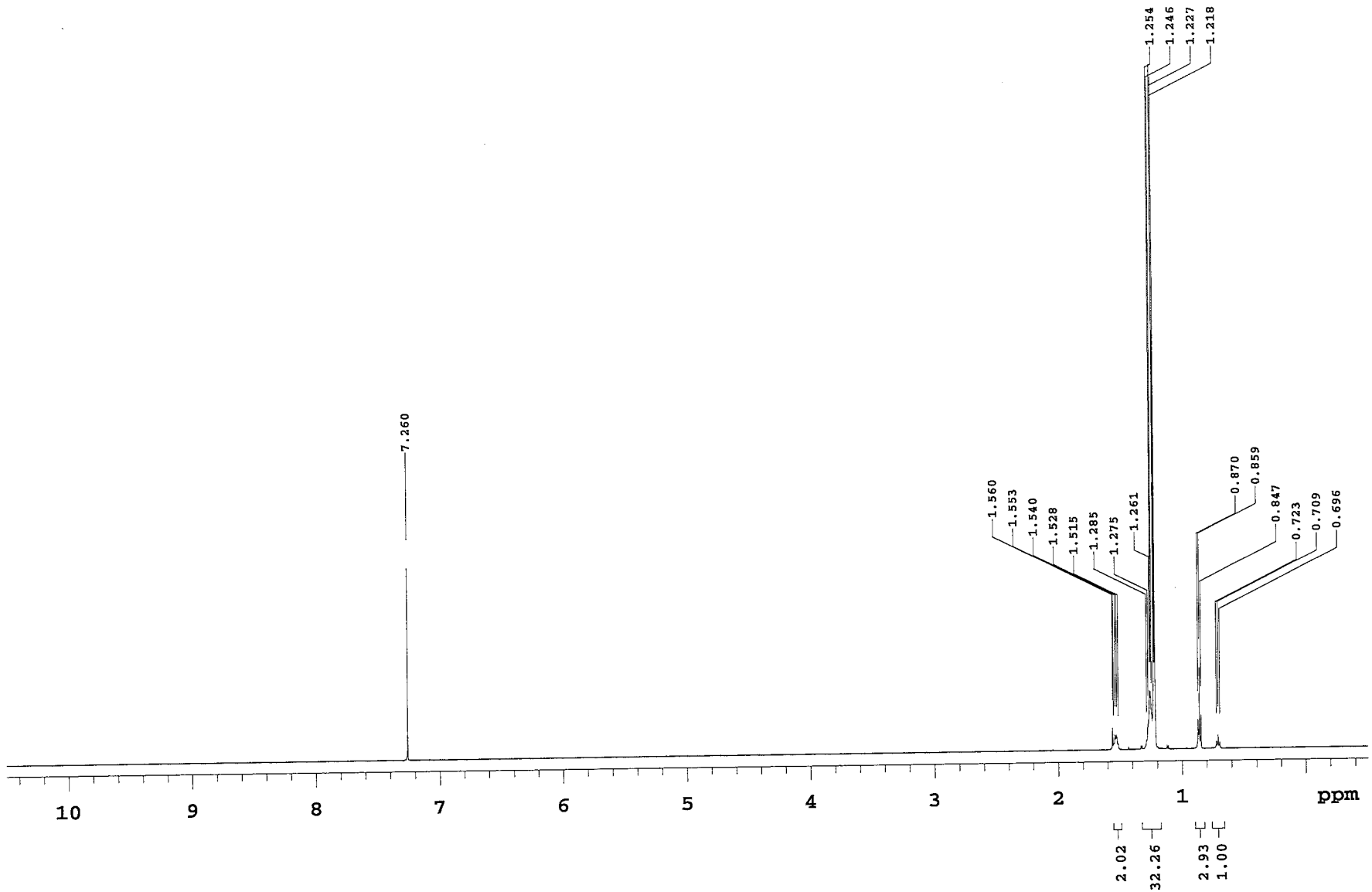
hexyl
B(pin)

S1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1.540
1.528
1.515
1.285
1.275
1.261
1.254
1.246
1.227
1.218
0.870
0.859
0.847
0.723
0.709
0.696
10
9
8
7
6
5
4
3
2
1
ppm
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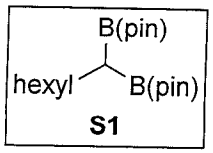
1.00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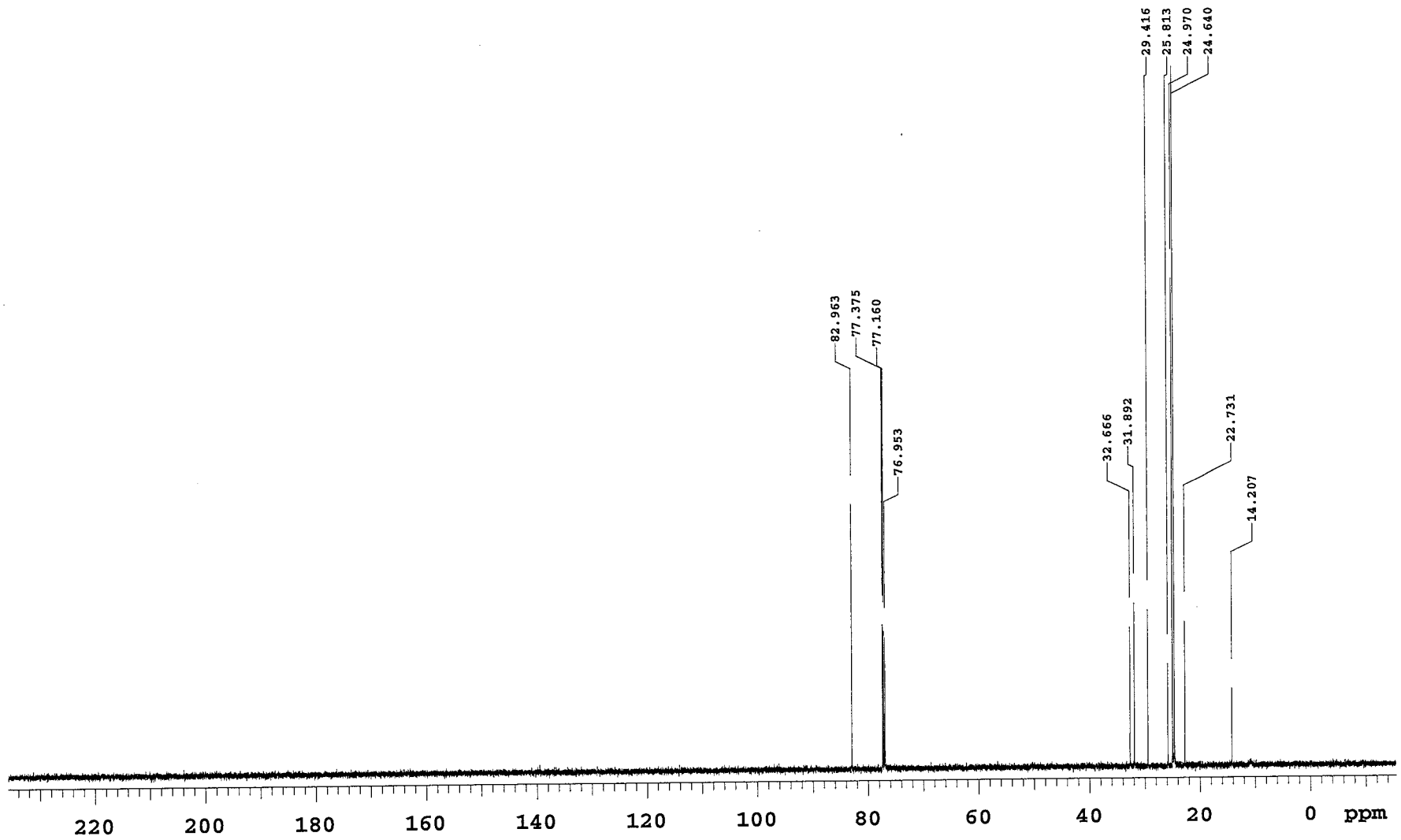
hexyl
B(pin)

S1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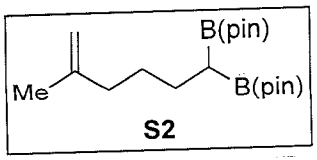
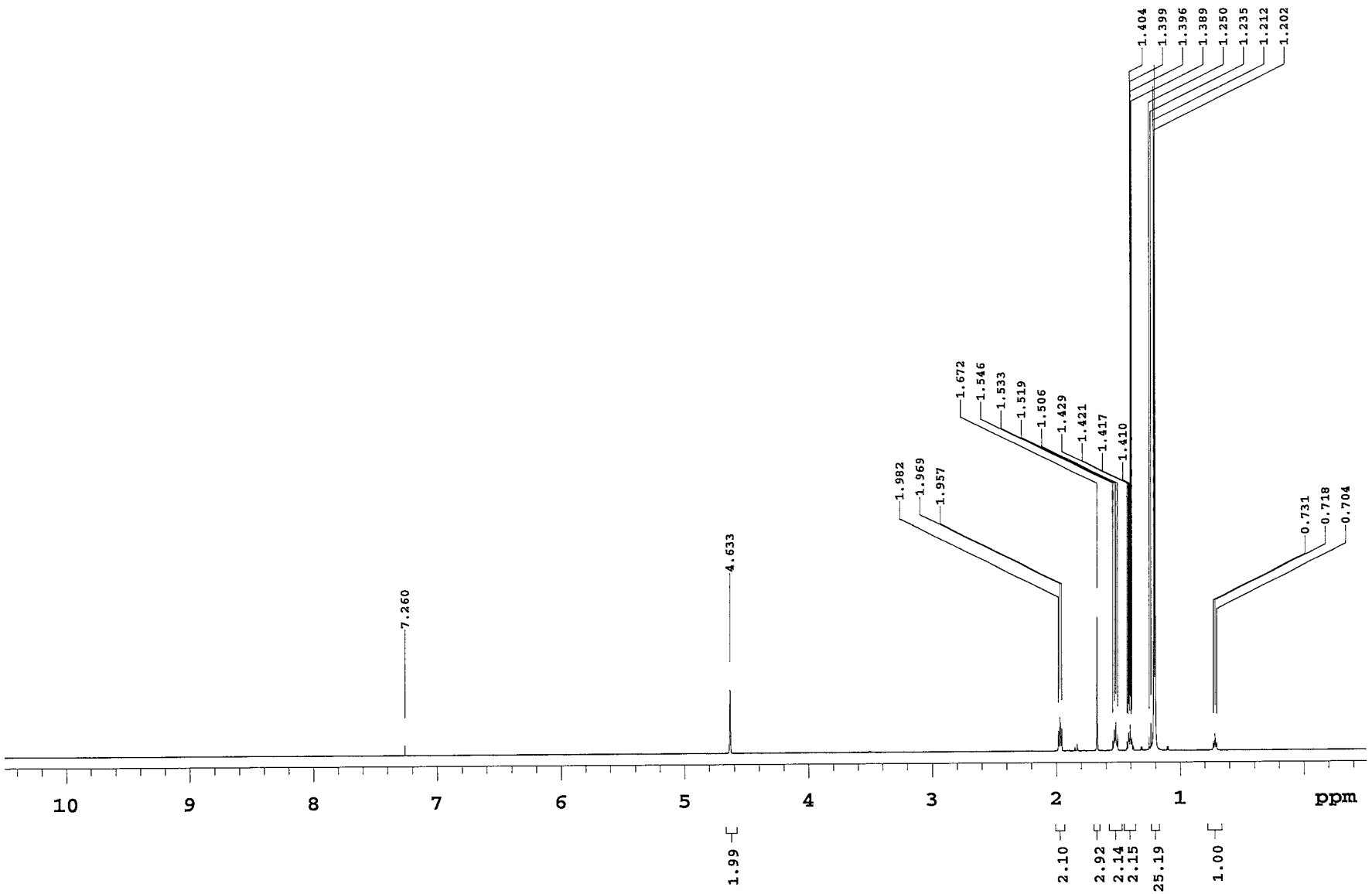
76.953
32.666
31.892
29.416
25.813
24.970
24.640
22.731
14.207
220
200
180
160
140
120
100
80
60
40
20
0
ppm


B(pin)
Me
B(pin)

S2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1.202
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1.533
1.519
1.506
1.429
1.421
1.417
1.410
1.982
1.969
1.957
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0.718
0.704
7.260
4.633
10
9
8
7
6
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4
3
2
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2.92
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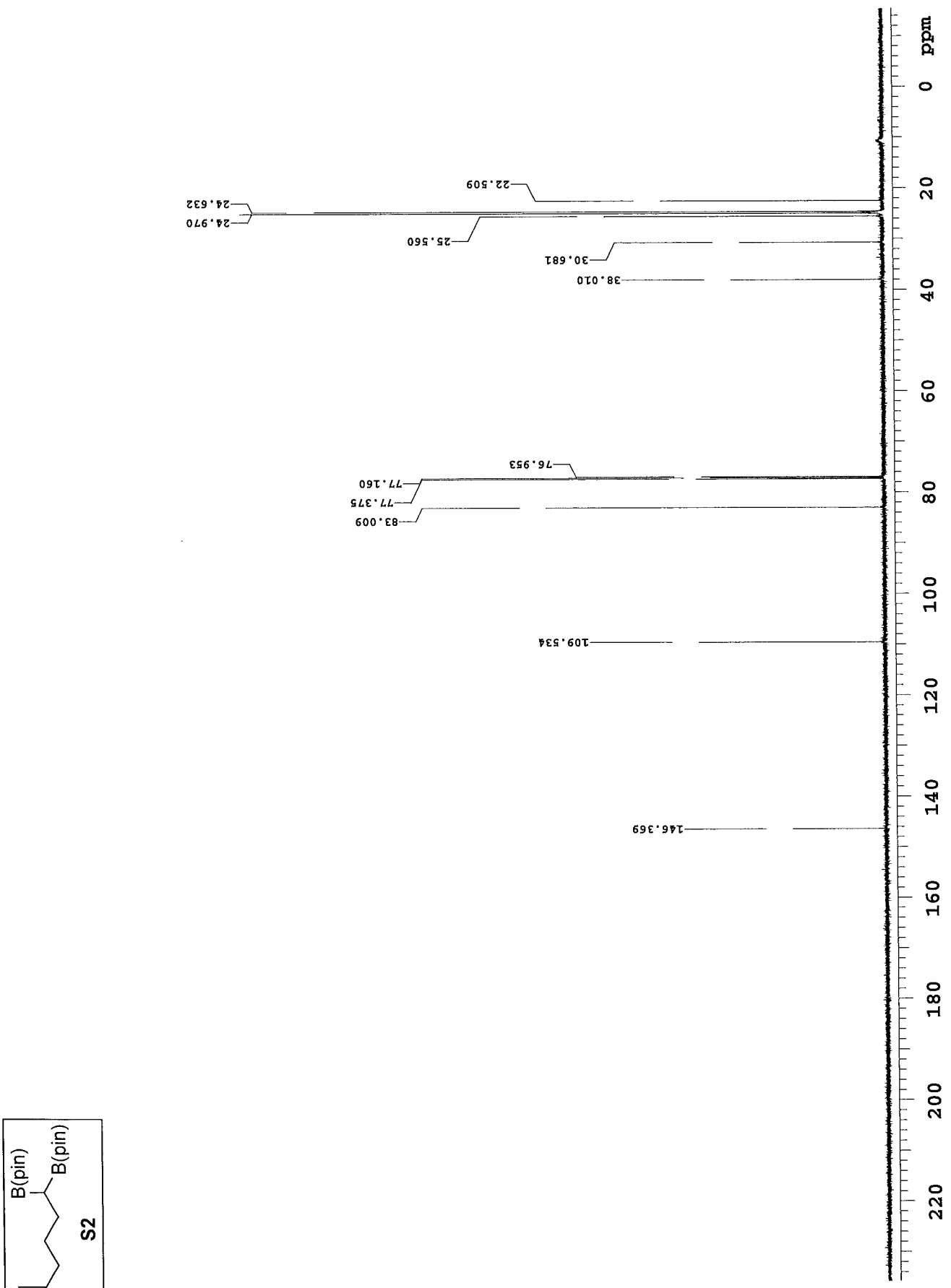
25.19
1.00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B(pin)
Me
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77.160
76.953
38.010
30.681
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24.632
22.509
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20
40
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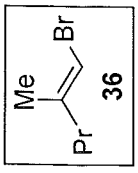
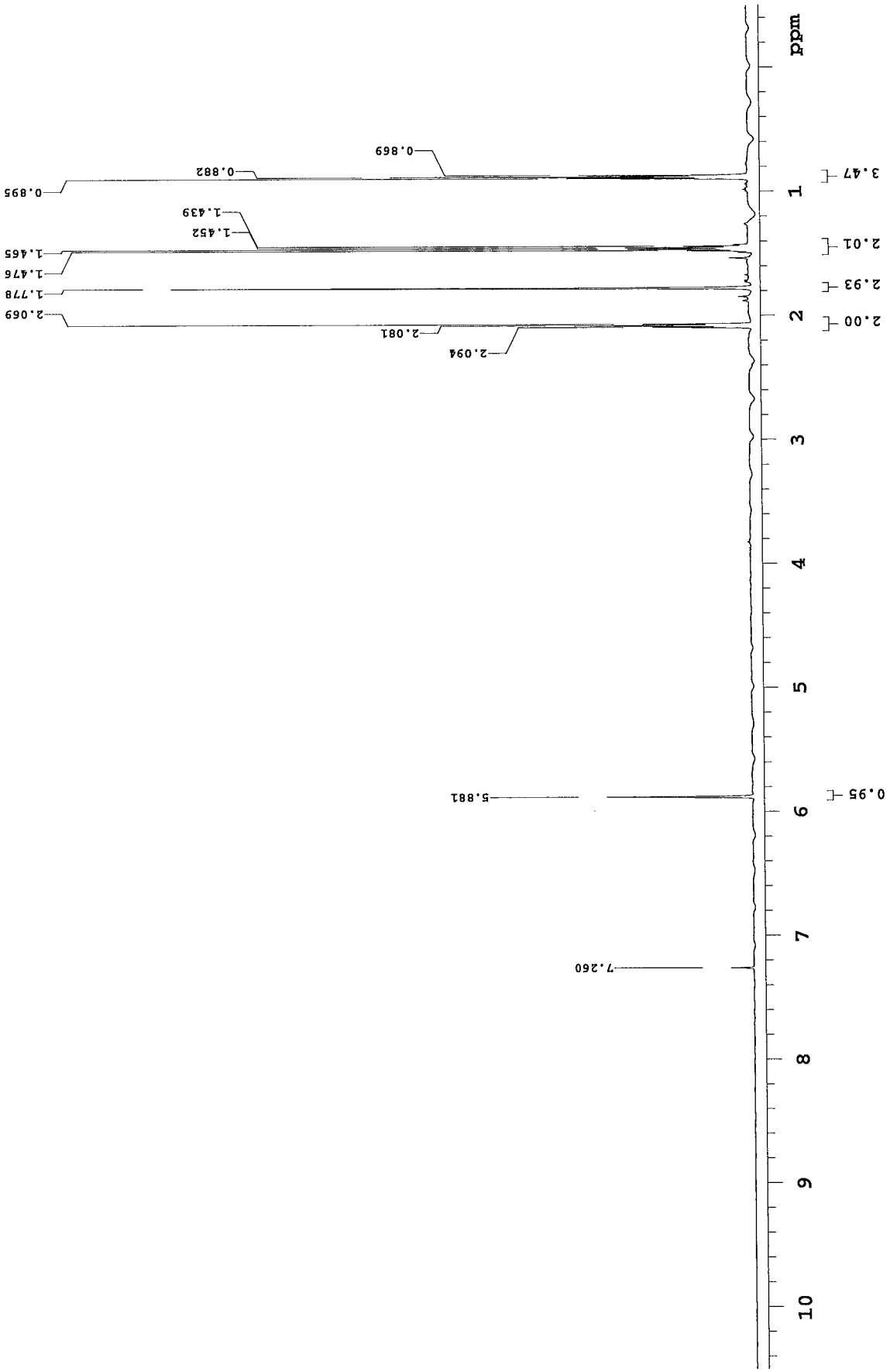
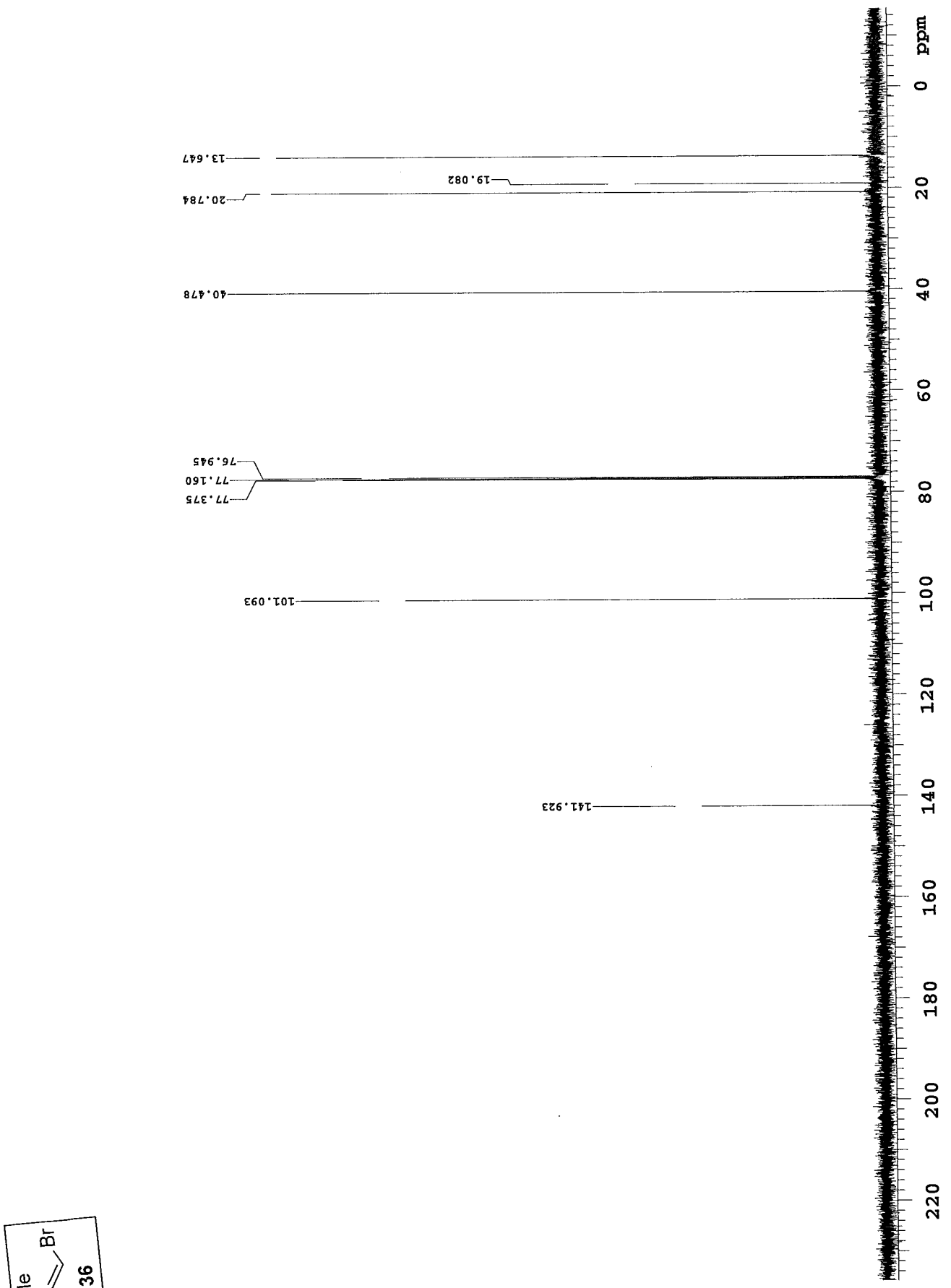
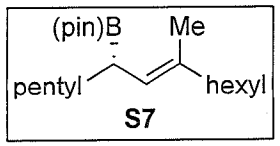
80
100
120
140
160
180
200
220
ppm


Me
Br
Pr
36

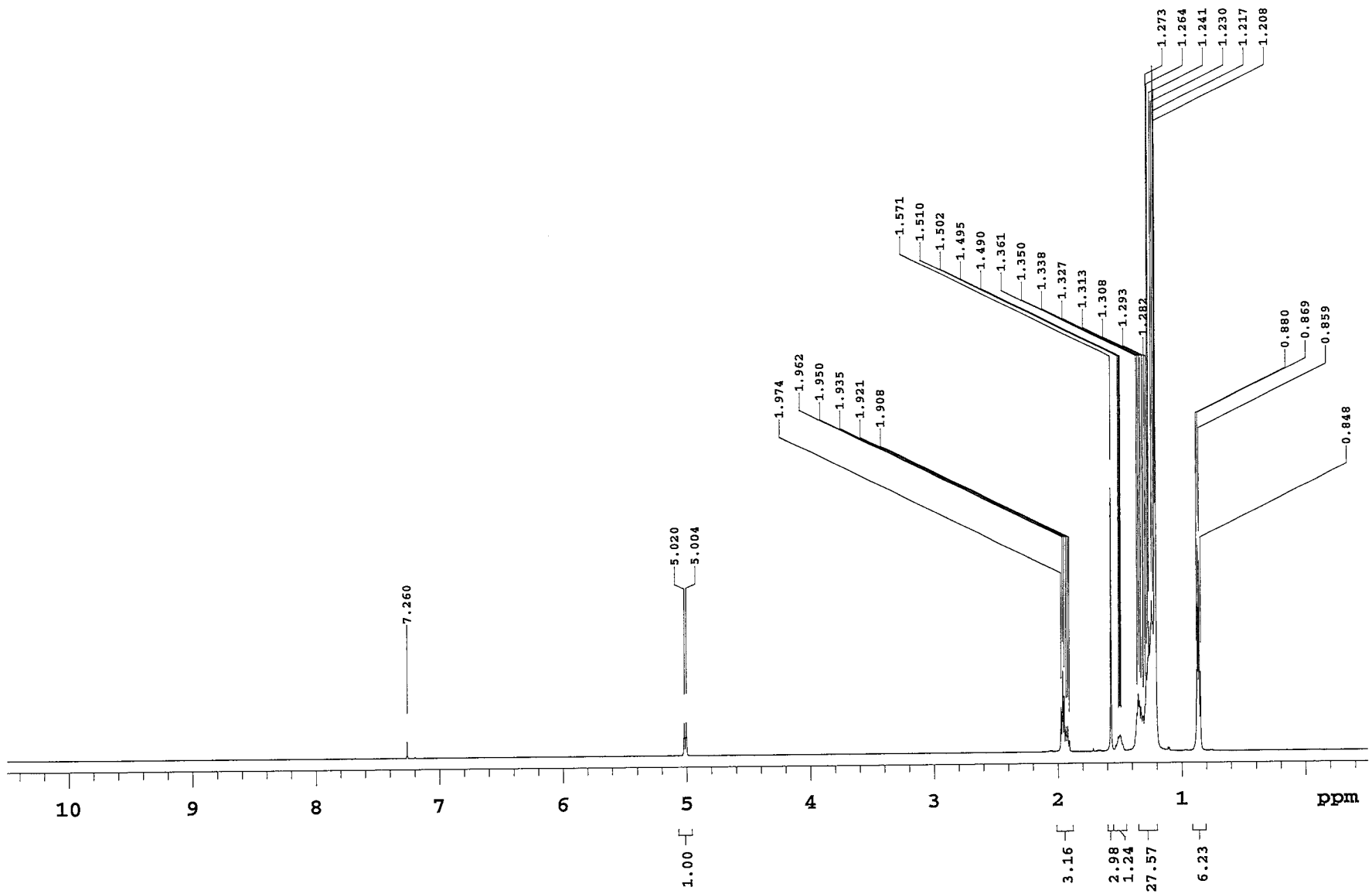

ppm
10
9
8
7
6
5
4
3
2
1
0.95
2.00
2.93
2.01
3.47
7.260
5.881
2.094
2.081
2.069
1.778
1.476
1.465
1.452
1.439
0.895
0.882
0.869


13.647
19.082
20.784
40.478
76.945
77.160
77.375
101.093
141.923
0
20
40
60
80
100
120
140
160
180
200
220
ppm

Me
Br
Pr
36


(pin)B
Me
pentyl
hexyl

S7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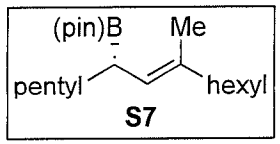
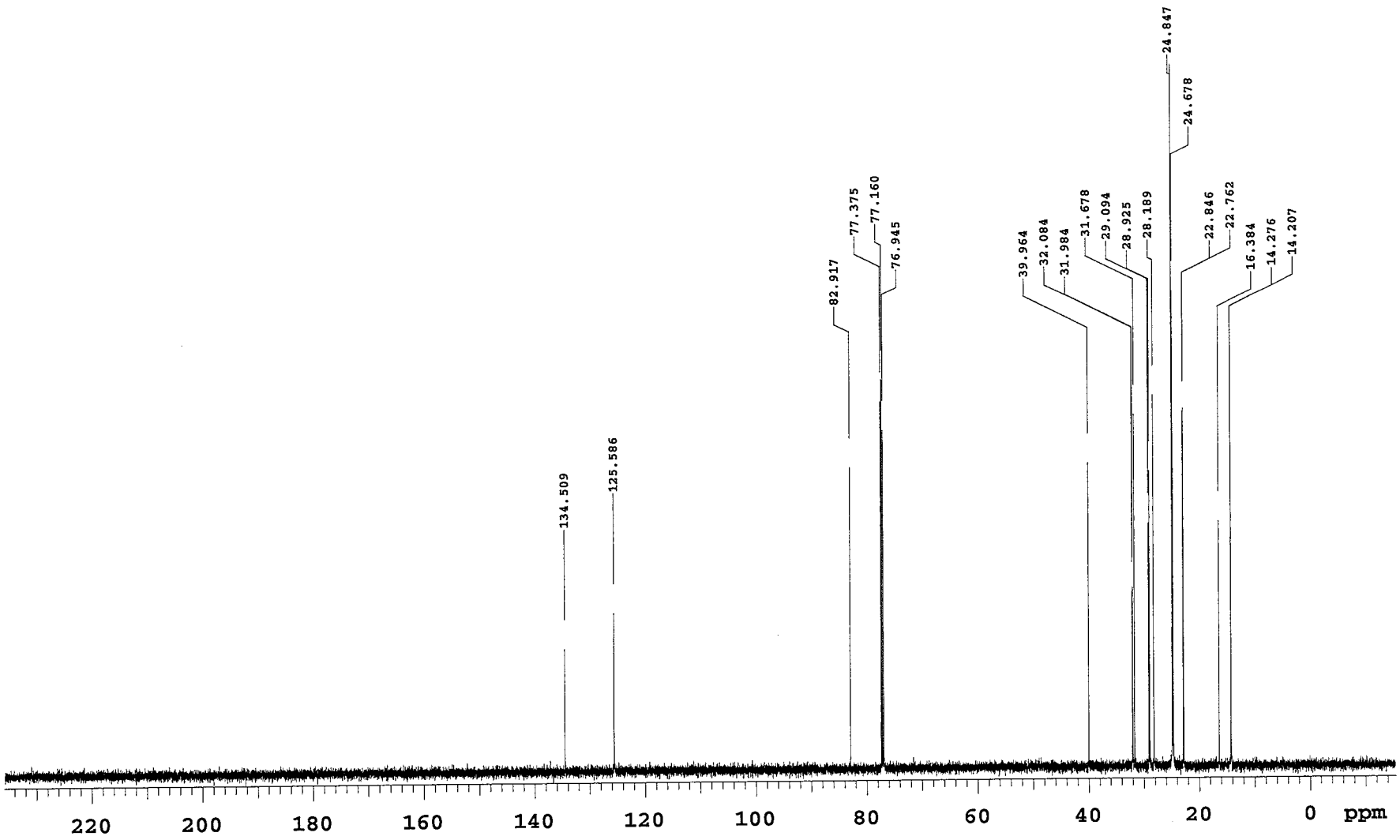
5.020
5.004
1.974
1.962
1.950
1.935
1.921
1.908
1.571
1.510
1.502
1.495
1.490
1.361
1.350
1.338
1.327
1.313
1.308
1.293
1.282
1.273
1.264
1.241
1.230
1.217
1.208
0.880
0.869
0.859
0.848
10
9
8
7
6
5
4
3
2
1
ppm
1.00
3.16
2.98
1.24
27.57
6.23


(pin)B
Me
pentyl
hexyl

S7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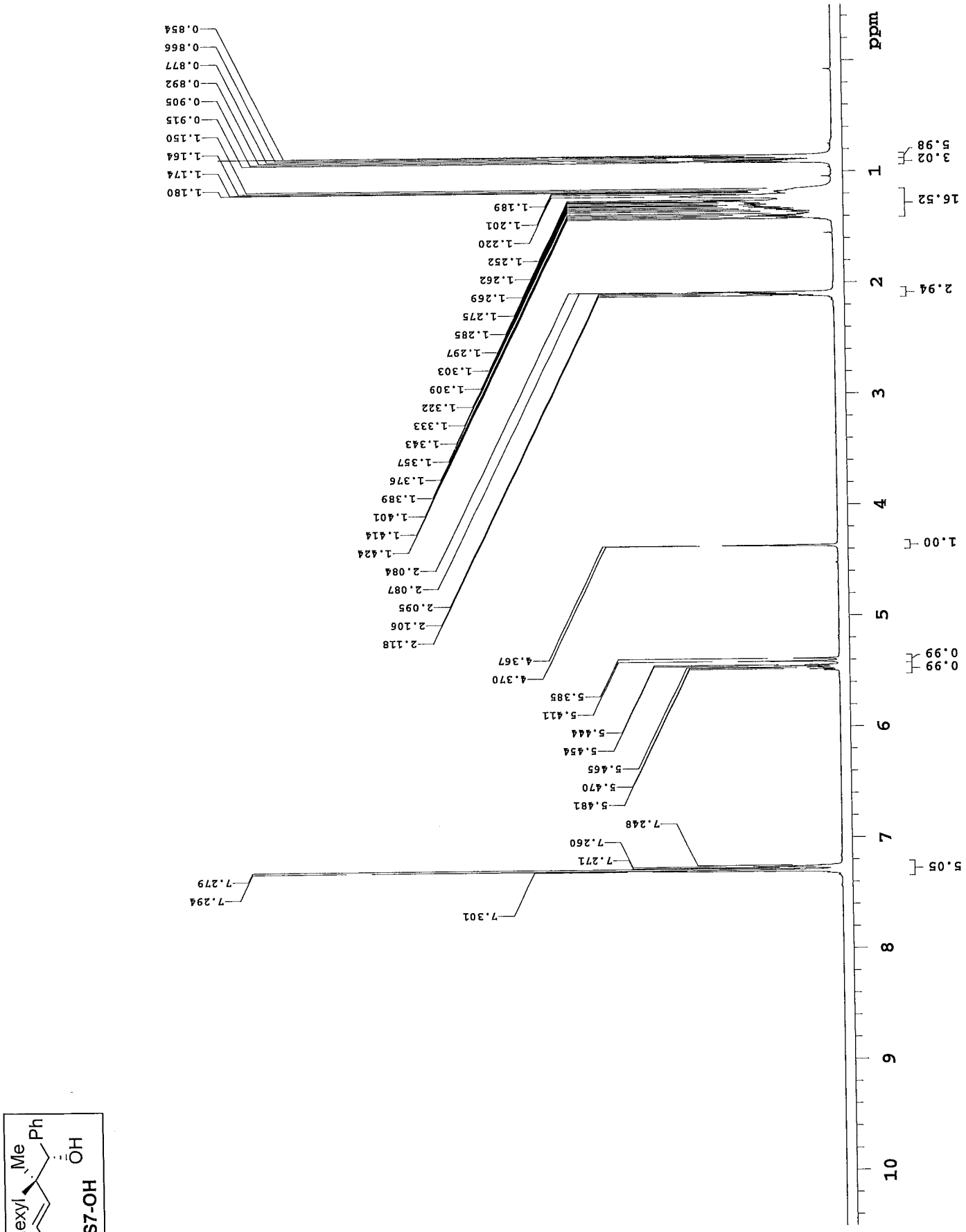
125.586
82.917
77.375
77.160
76.945
39.964
32.084
31.984
31.678
29.094
28.925
28.189
24.847
24.678
22.846
22.762
16.384
14.276
14.207
220
200
180
160
140
120
100
80
60
40
20
0
ppm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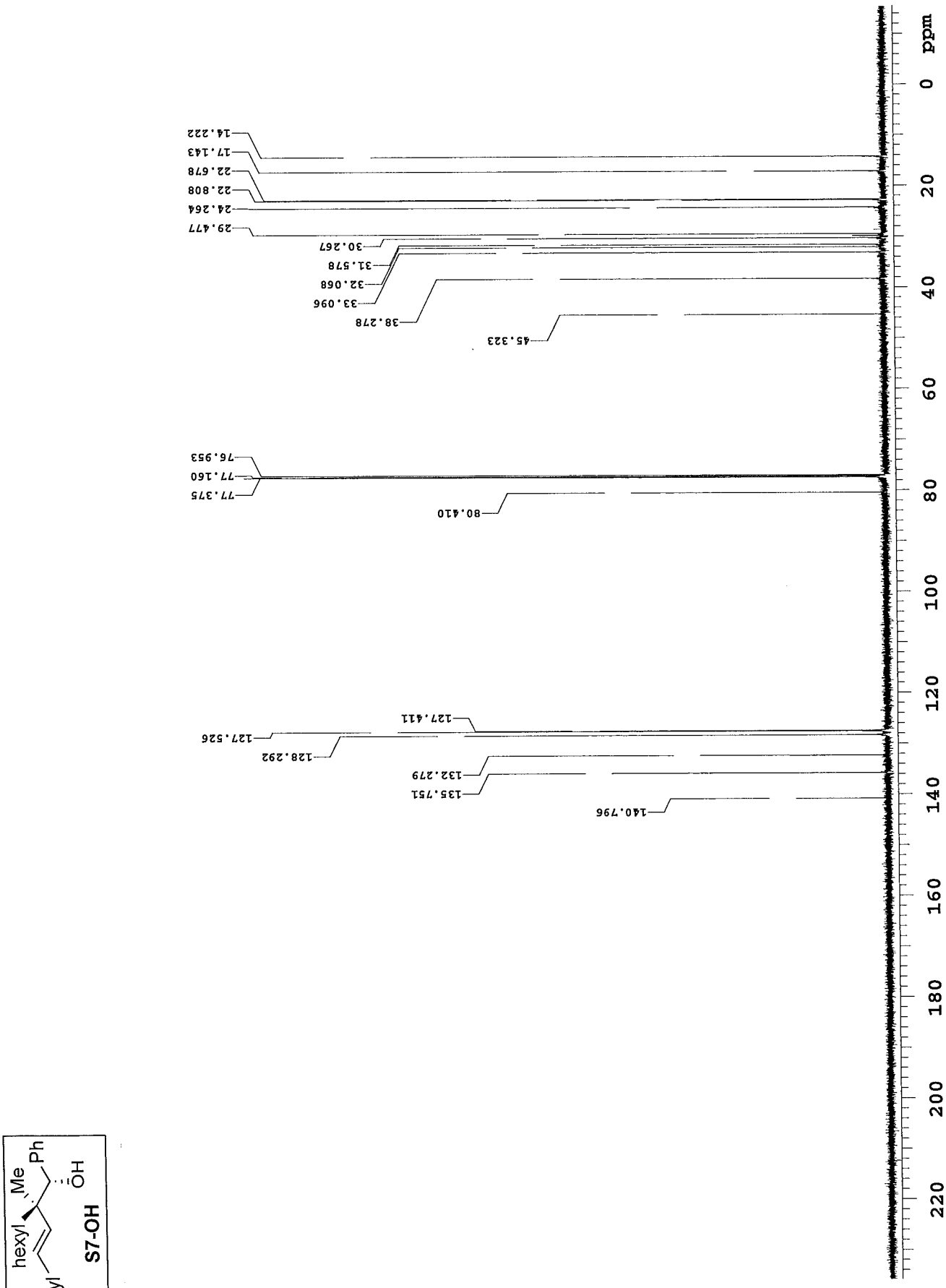
0.866
0.877
0.892
0.905
0.915
1.150
1.164
1.174
1.180
1.189
1.201
1.220
1.252
1.262
1.269
1.275
1.285
1.297
1.303
1.309
1.322
1.333
1.343
1.357
1.376
1.389
1.401
1.414
1.424
2.084
2.087
2.095
2.106
2.118
4.367
4.370
5.385
5.411
5.444
5.454
5.465
5.470
5.481
7.248
7.260
7.271
7.279
7.294
7.301
ppm
1
2
3
4
5
6
7
8
9
10
5.98
3.02
16.52
2.94
1.00
0.99
0.99
5.05

hexyl
Me
Ph
OH
pentyl
S7-OH


hexyl
Me
Ph
OH
pentyl
S7-OH
14.222
17.143
22.678
22.808
24.264
29.477
30.267
31.578
32.068
33.096
38.278
45.323
76.953
77.160
77.375
80.410
127.411
127.526
128.292
132.279
135.751
140.796
0
20
40
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80
100
120
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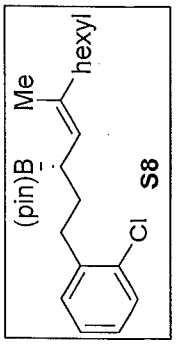
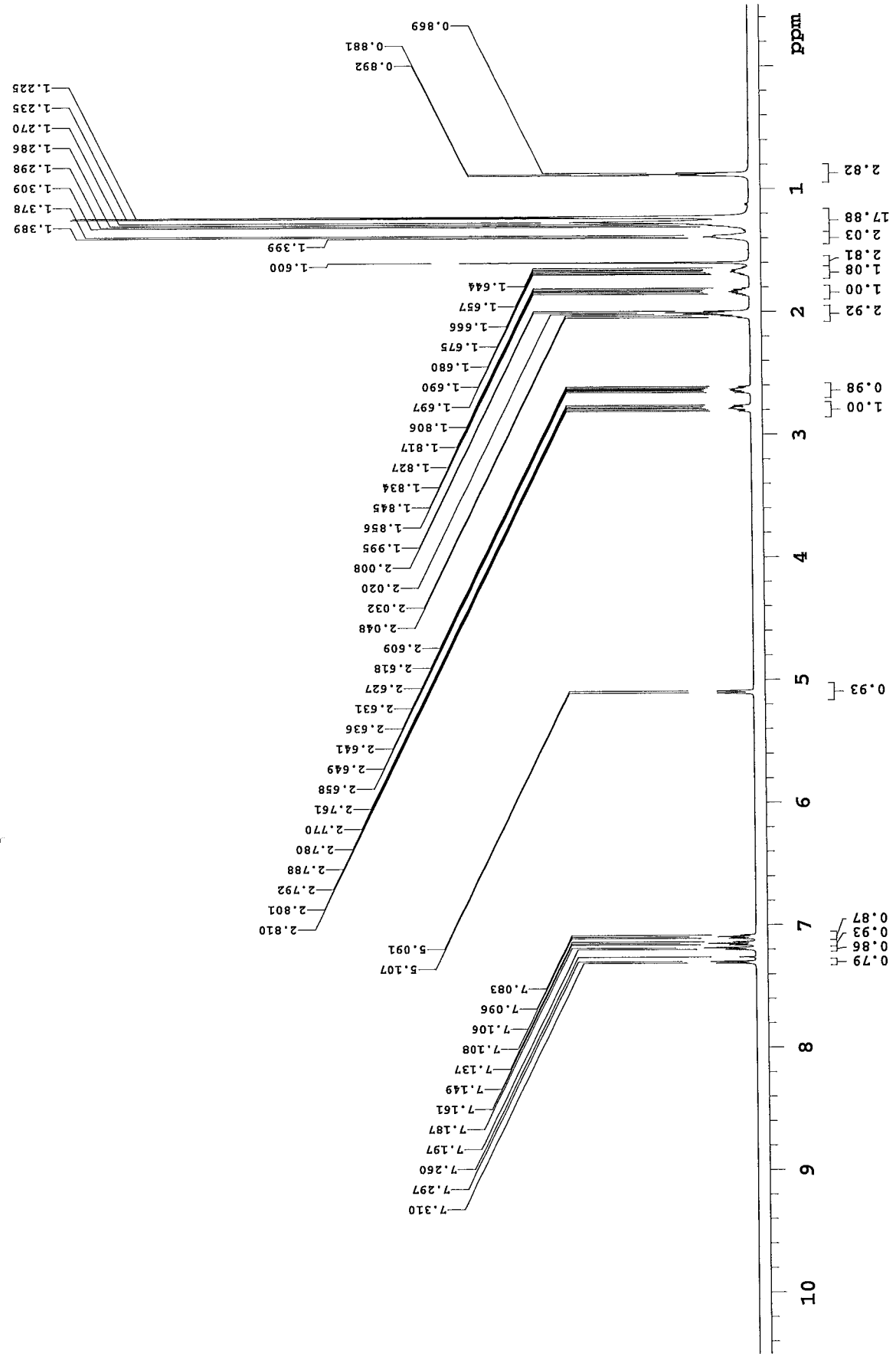
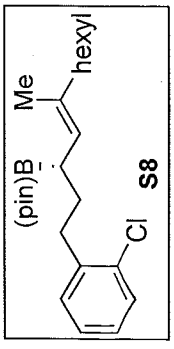
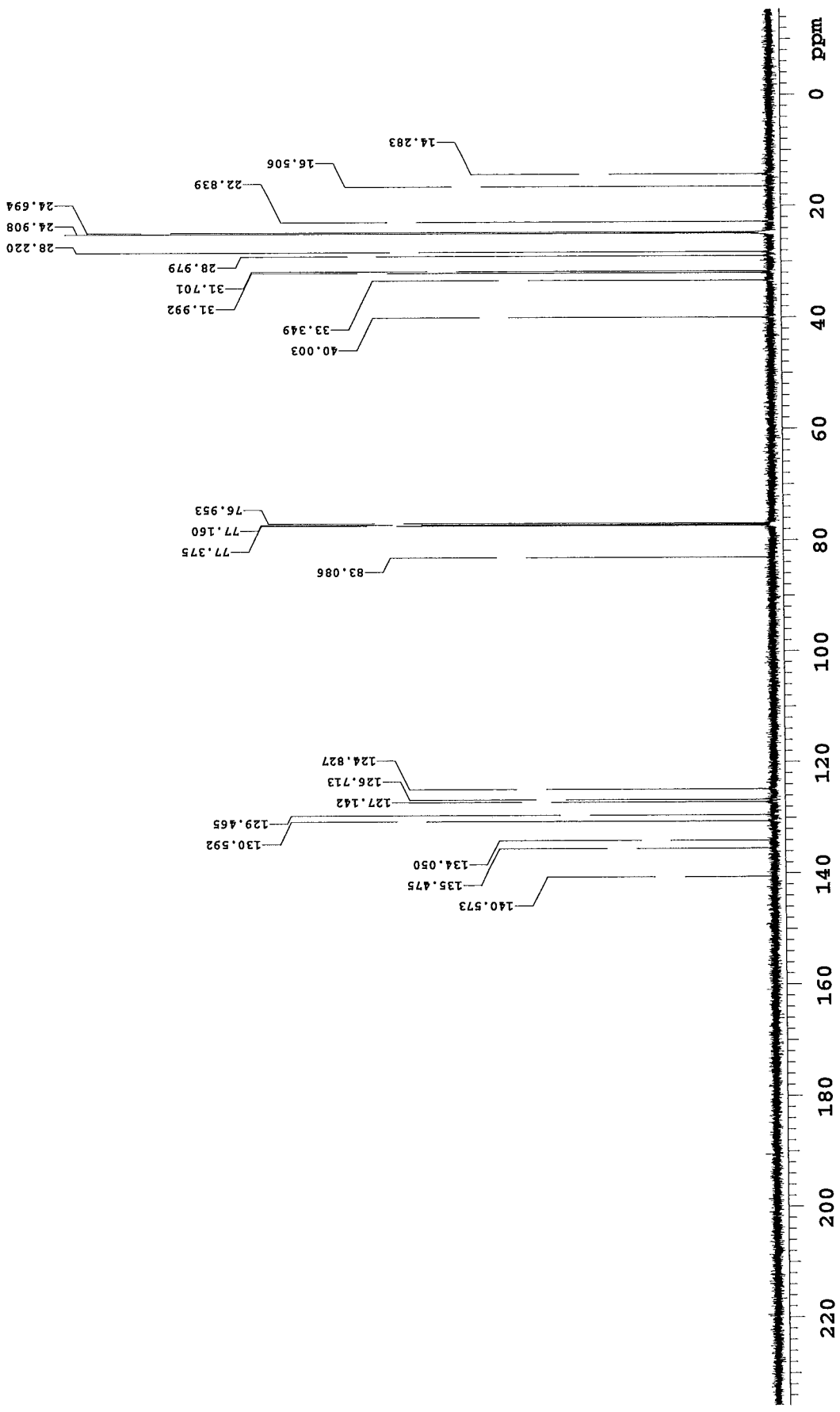
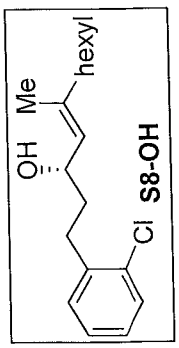
160
180
200
220
ppm

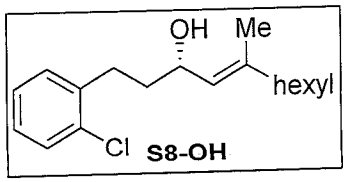

(pin)B
Me
hexyl
Cl
S8

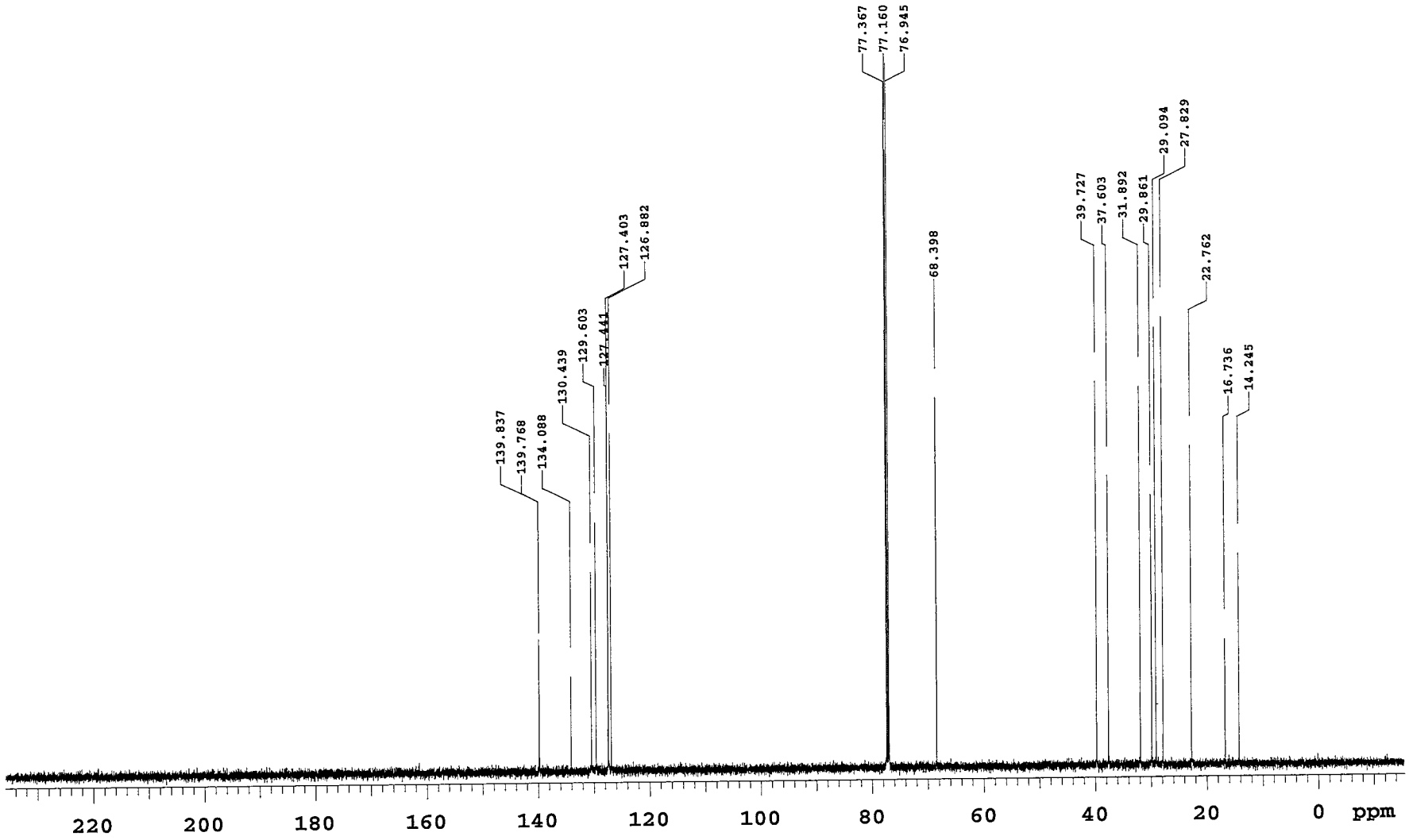

ppm
1
2
3
4
5
6
7
8
9
10
2.82
17.88
2.03
2.81
1.08
1.00
2.92
0.98
1.00
0.93
0.79
0.86
0.93
0.87
0.869
0.881
0.892
1.225
1.235
1.270
1.286
1.298
1.309
1.378
1.389
1.399
1.600
1.644
1.657
1.666
1.675
1.680
1.690
1.697
1.806
1.817
1.827
1.834
1.845
1.856
1.995
2.008
2.020
2.032
2.048
2.609
2.618
2.627
2.631
2.636
2.641
2.649
2.658
2.761
2.770
2.780
2.788
2.792
2.801
2.810
5.091
5.107
7.083
7.096
7.106
7.108
7.137
7.149
7.161
7.187
7.197
7.260
7.297
7.310


(pin)B
Me
hexyl
Cl
S8


14.283
16.506
22.839
24.694
24.908
28.220
28.979
31.701
31.992
33.349
40.003
76.953
77.160
77.375
83.086
124.827
126.713
127.142
129.465
130.592
134.050
135.475
140.573
0
20
40
60
80
100
120
140
160
180
200
220
ppm


OH
Me
hexyl
Cl
S8-OH


OH
Me
hexyl
Cl
S8-OH


77.367
77.160
76.945
68.398
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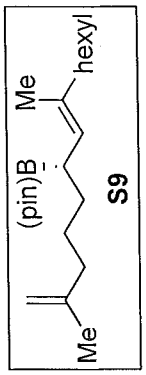
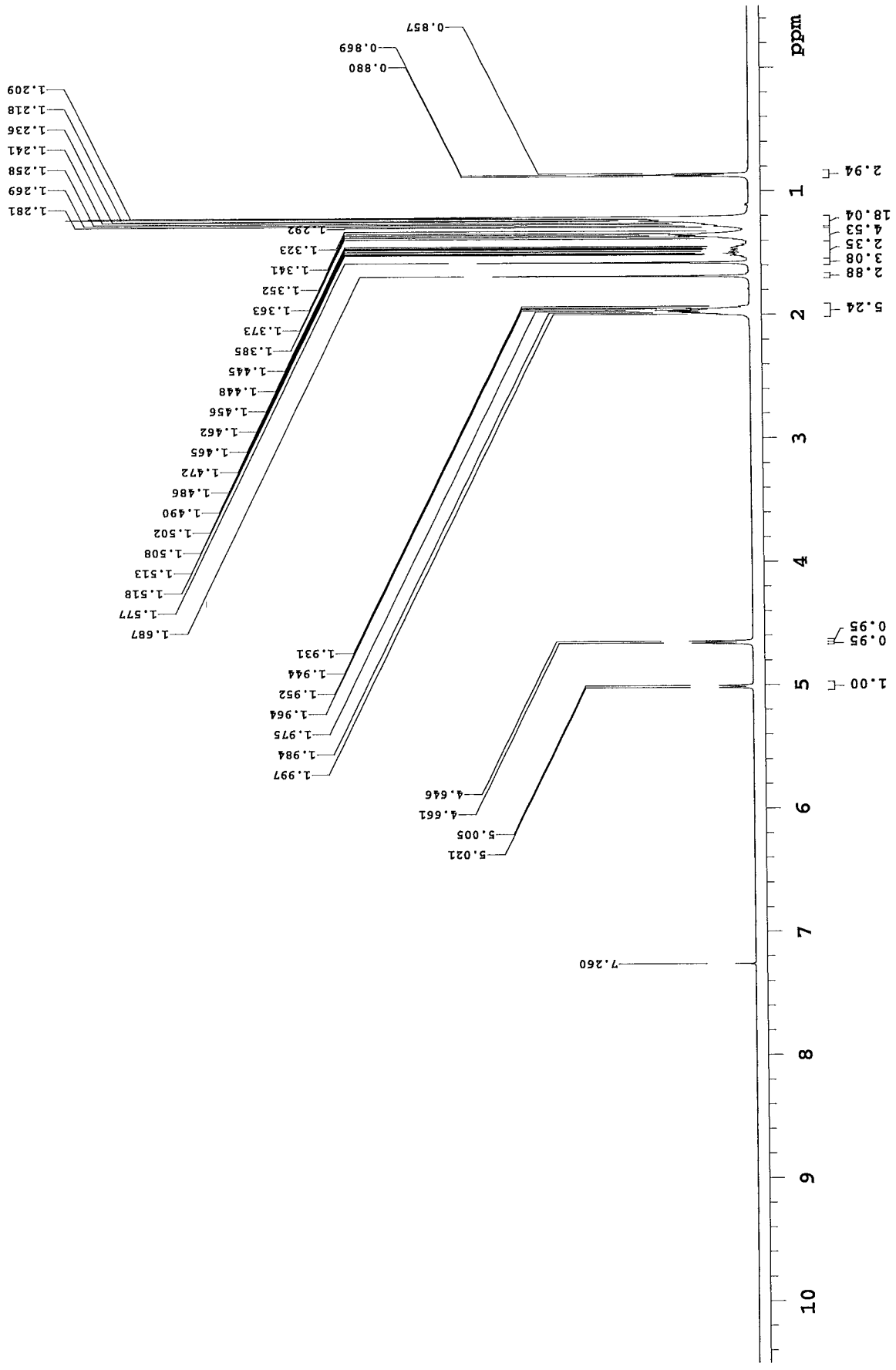
37.603
31.892
29.861
29.094
27.829
22.762
16.736
14.245
139.837
139.768
134.088
130.439
129.603
127.441
127.403
126.882
220
200
180
160
140
120
100
80
60
40
20
0
ppm


(pin)B
Me
hexyl
Me
S9


ppm
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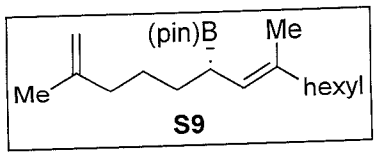
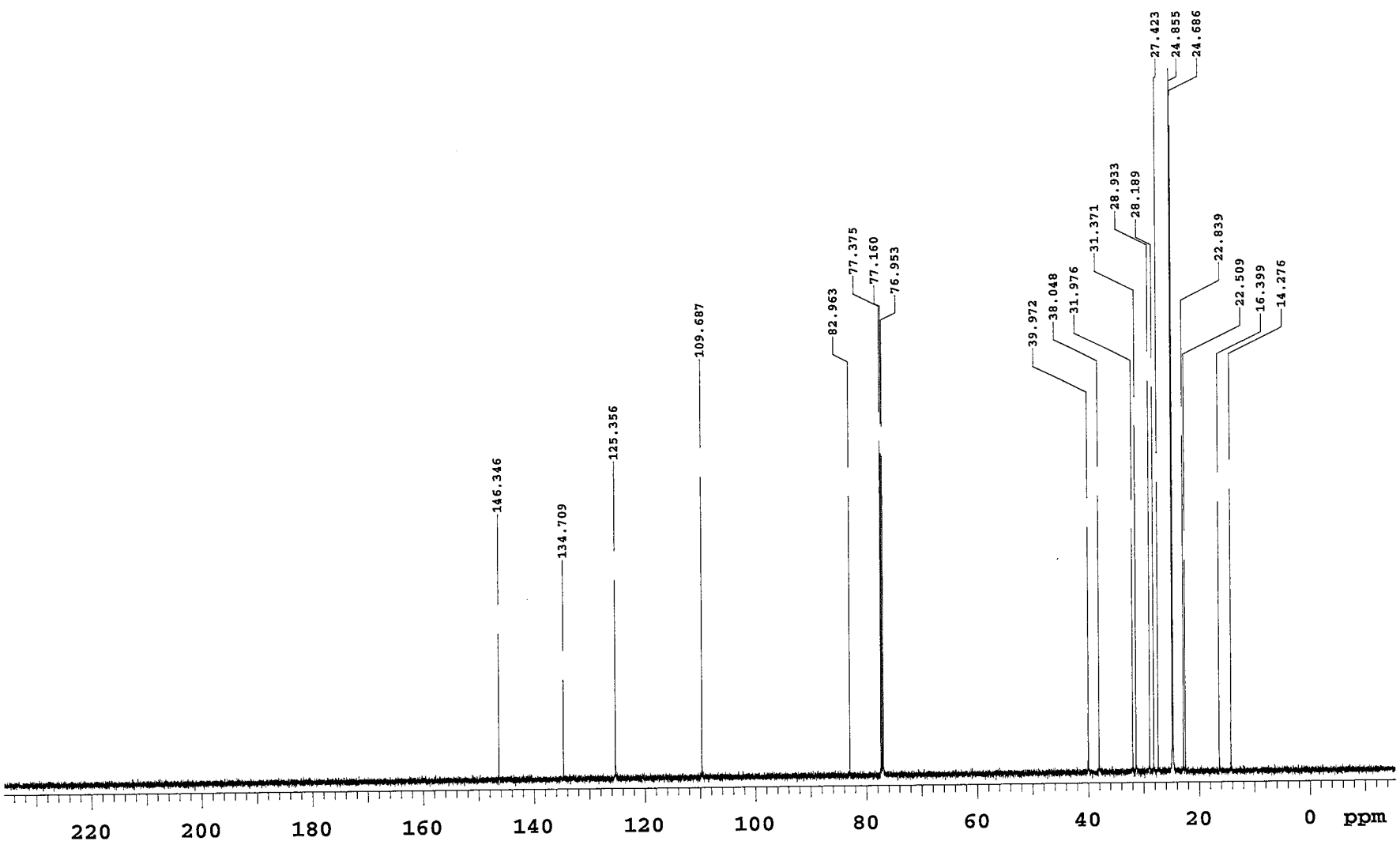
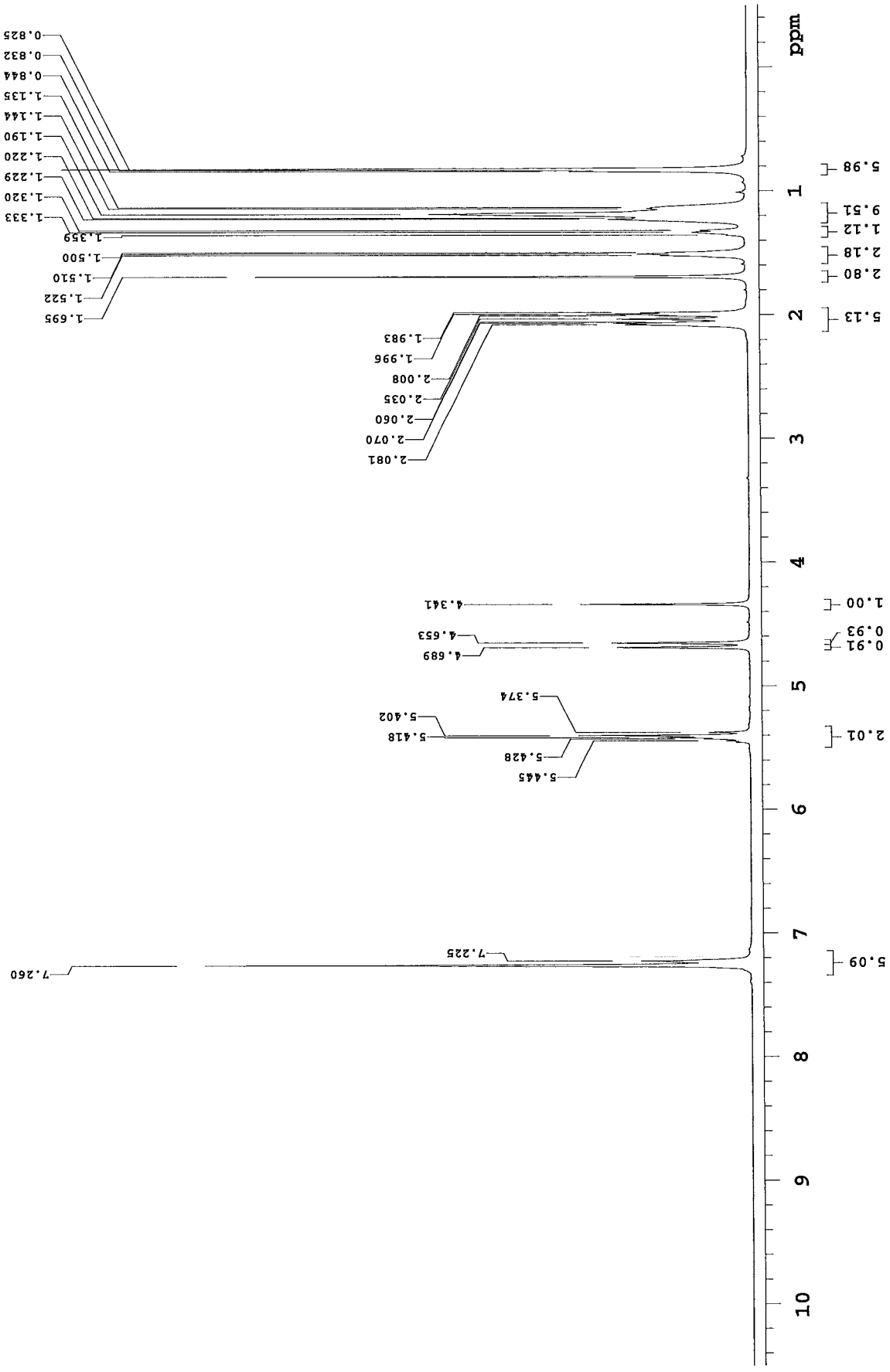
0.869
0.880
1.209
1.218
1.236
1.241
1.258
1.269
1.281
1.292
1.323
1.341
1.352
1.363
1.373
1.385
1.445
1.448
1.456
1.462
1.465
1.472
1.486
1.490
1.502
1.508
1.513
1.518
1.577
1.687
1.931
1.944
1.952
1.964
1.975
1.984
1.997
4.646
4.661
5.005
5.021
7.260
0.95
0.95
1.00
5.24
2.88
3.08
2.35
4.53
18.04
2.94


(pin)B
Me
Me
hexyl

S9


146.346
134.709
125.356
109.687
82.963
77.375
77.160
76.953
39.972
38.048
31.976
31.371
28.933
28.189
27.423
24.855
24.686
22.839
22.509
16.399
14.276
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Me
Ph
OH
hexyl
Me
S9-OH


7.260
7.225
5.445
5.428
5.418
5.402
5.374
4.689
4.653
4.341
2.081
2.070
2.060
2.035
2.008
1.996
1.983
1.695
1.522
1.510
1.500
1.359
1.333
1.320
1.229
1.220
1.190
1.144
1.135
0.844
0.832
0.825
ppm
1
2
3
4
5
6
7
8
9
10
5.98
9.51
1.12
2.18
2.80
5.13
1.00
0.91
0.93
2.01
5.09

Me
Ph
hexyl
OH
Me
S9-OH

145.947
140.811
136.089
131.773
128.285
127.533
127.426
110.047
80.449
77.375
77.160
76.953
45.300
38.240
37.442
32.728
32.061
30.259
27.737
24.280
22.800
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17.219
14.214
ppm
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60
80
100
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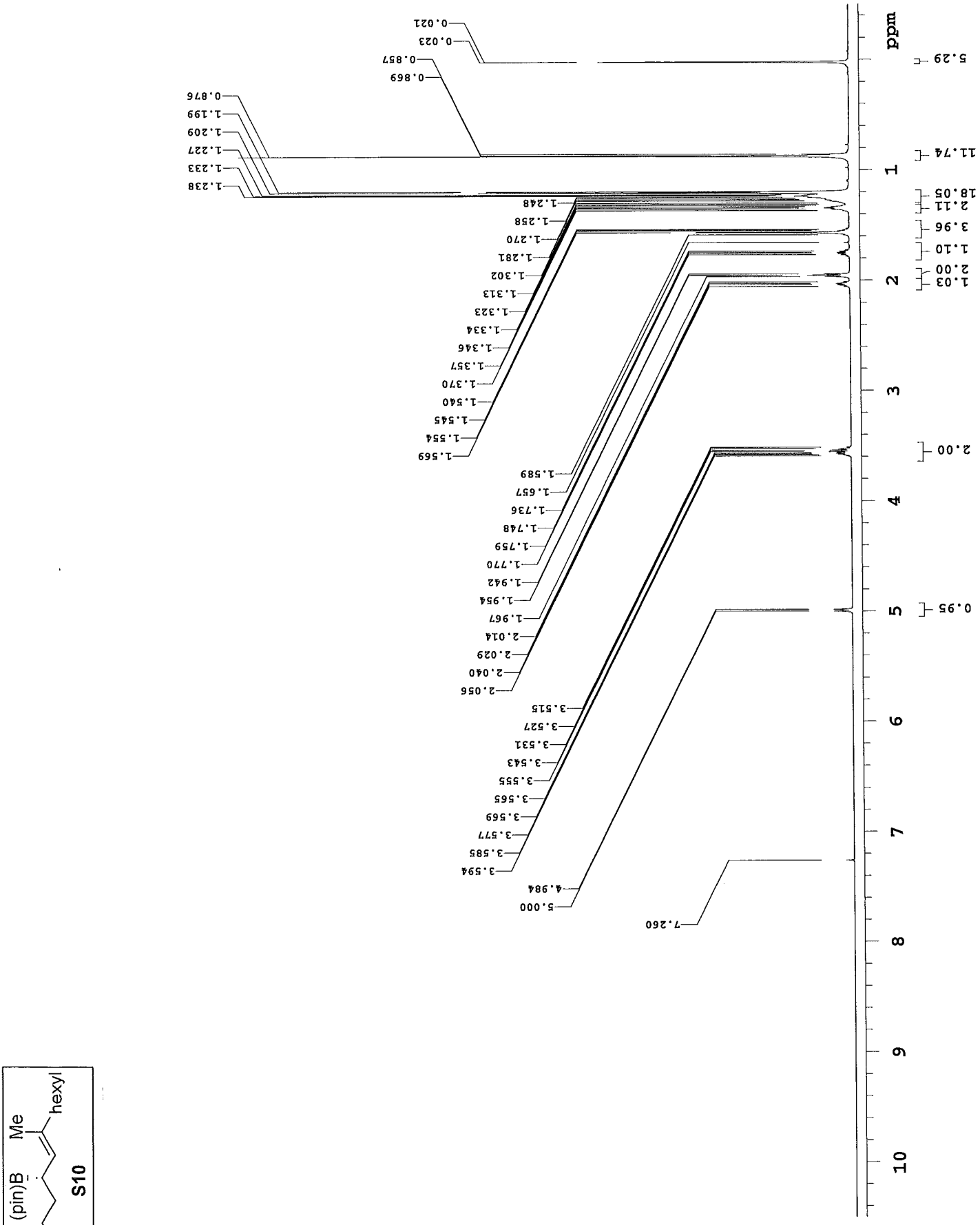
140
160
180
200
220


(pin)B
Me
hexyl
TBSO
S10
ppm
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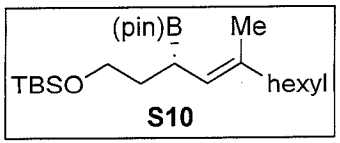
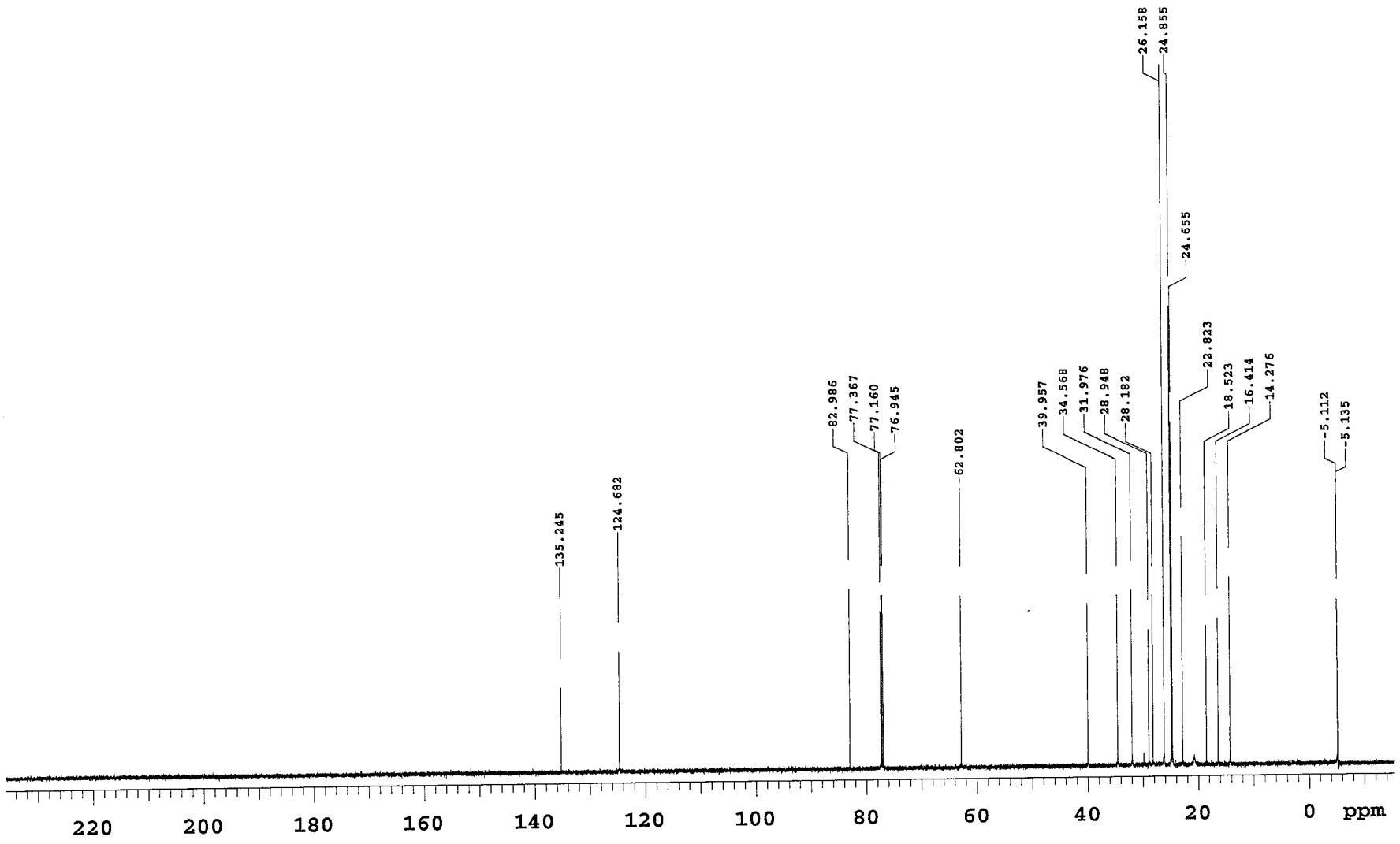
0.023
0.857
0.869
0.876
1.199
1.209
1.227
1.233
1.238
1.248
1.258
1.270
1.281
1.302
1.313
1.323
1.334
1.346
1.357
1.370
1.540
1.545
1.554
1.569
1.589
1.657
1.736
1.748
1.759
1.770
1.942
1.954
1.967
2.014
2.029
2.040
2.056
3.515
3.527
3.531
3.543
3.555
3.565
3.569
3.577
3.585
3.594
4.984
5.000
7.260
5.29
11.74
18.05
2.11
3.96
1.10
2.00
1.03
2.00
0.95


(pin)B
Me
TBSO
hexyl

S10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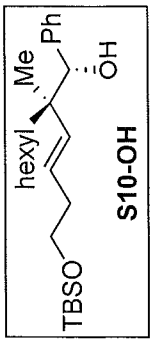
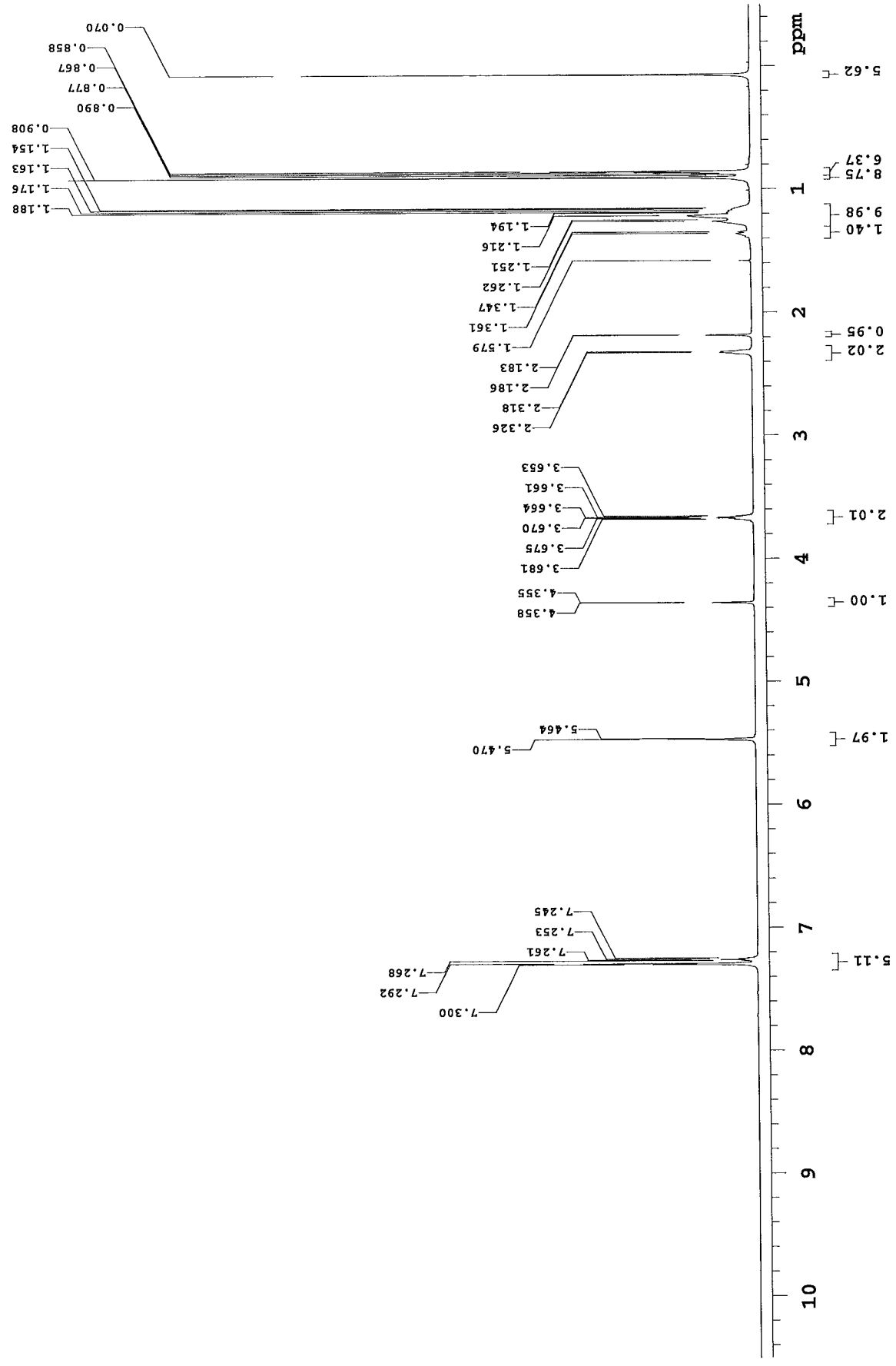
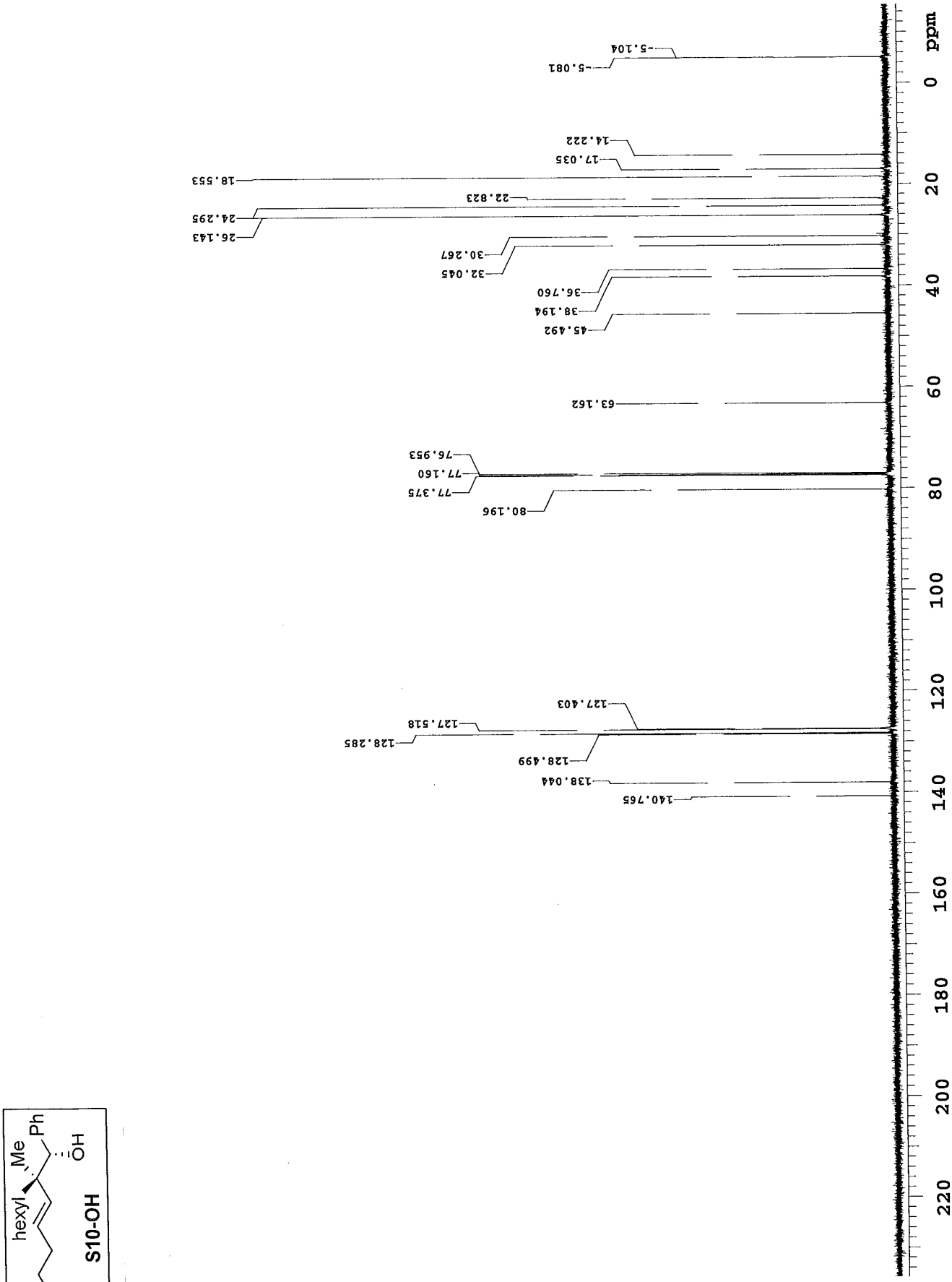
24.855
24.655
22.823
18.523
16.414
14.276
-5.112
-5.135
82.986
77.367
77.160
76.945
62.802
39.957
34.568
31.976
28.948
28.182
135.245
124.682
220
200
180
160
140
120
100
80
60
40
20
0
ppm


TBSO
hexyl
Me
Ph
OH
S10-OH


ppm
10
9
8
7
6
5
4
3
2
1
7.300
7.292
7.268
7.261
7.253
7.245
5.470
5.464
4.358
4.355
3.681
3.675
3.670
3.664
3.661
3.653
2.326
2.318
2.186
2.183
1.579
1.361
1.347
1.262
1.251
1.216
1.194
1.188
1.176
1.163
1.154
0.908
0.890
0.877
0.867
0.858
0.070
5.11
1.97
1.00
2.01
2.02
0.95
1.40
9.98
8.75
6.37
5.62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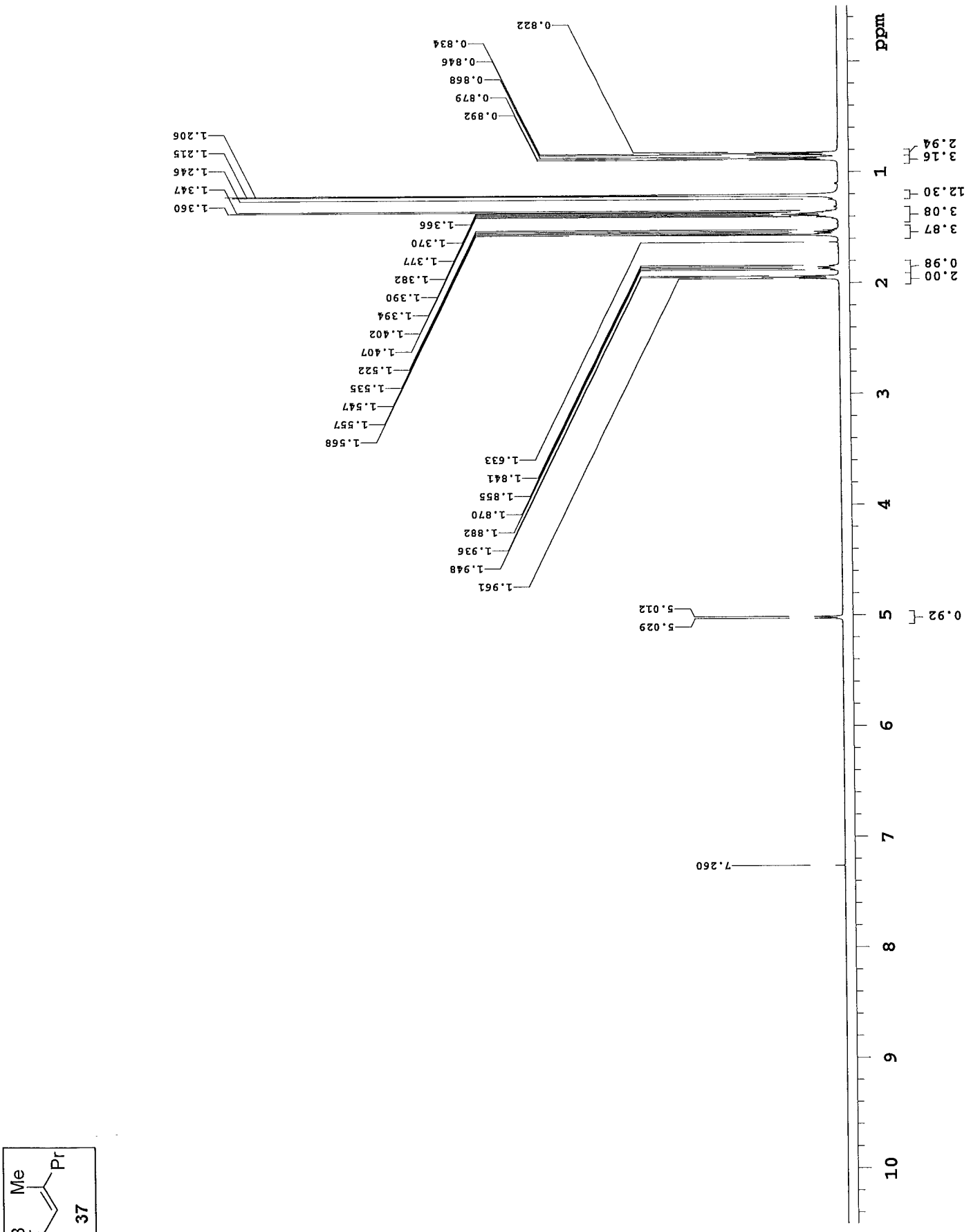
-5.081
14.222
17.035
18.553
22.823
24.295
26.143
30.267
32.045
36.760
38.194
45.492
63.162
76.953
77.160
77.375
80.196
127.403
127.518
128.285
128.499
138.044
140.765
ppm
0
20
40
60
80
100
120
140
160
180
200
220
TBSO
hexyl
Me
Ph
OH
S10-OH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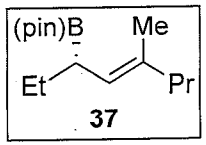
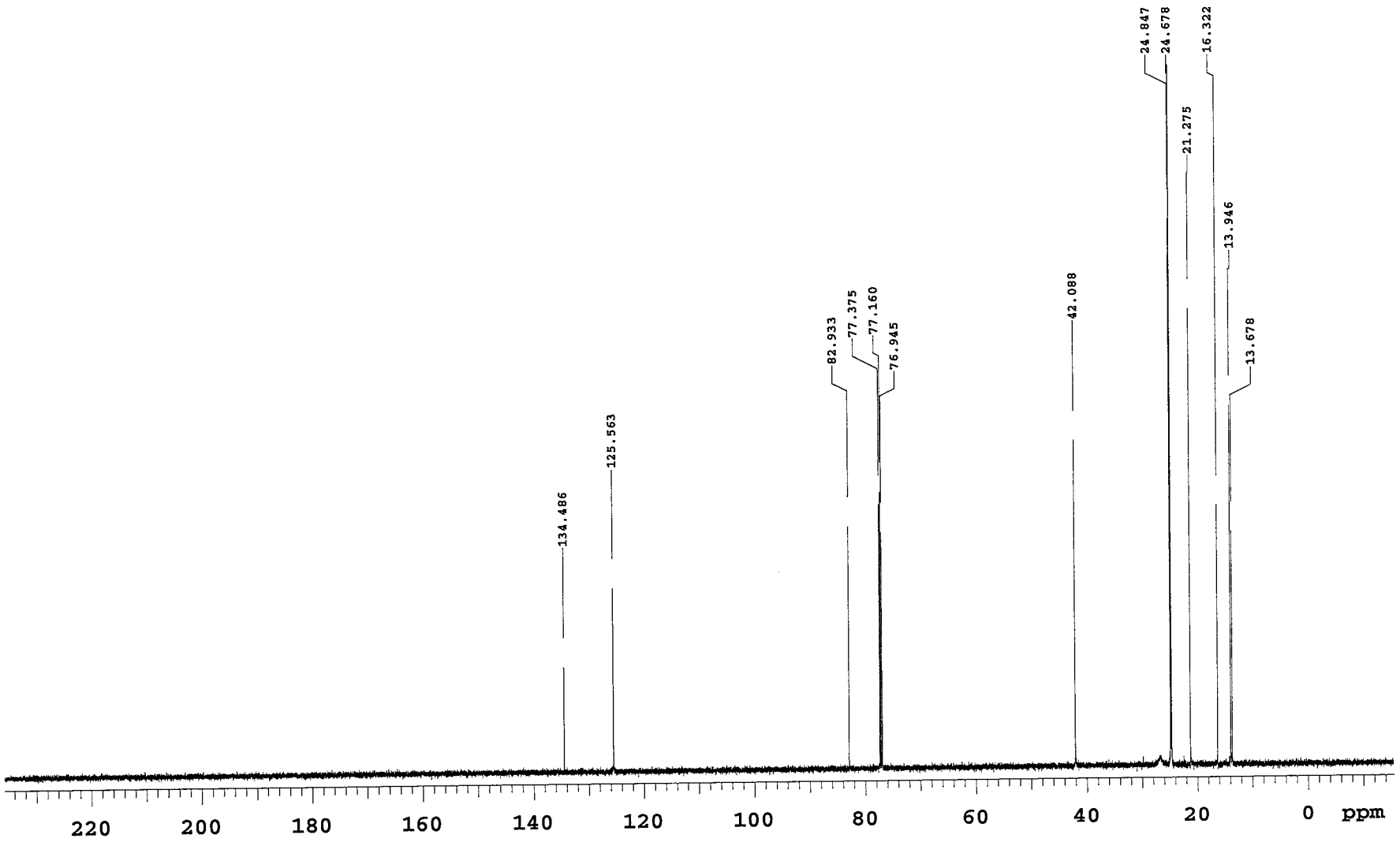
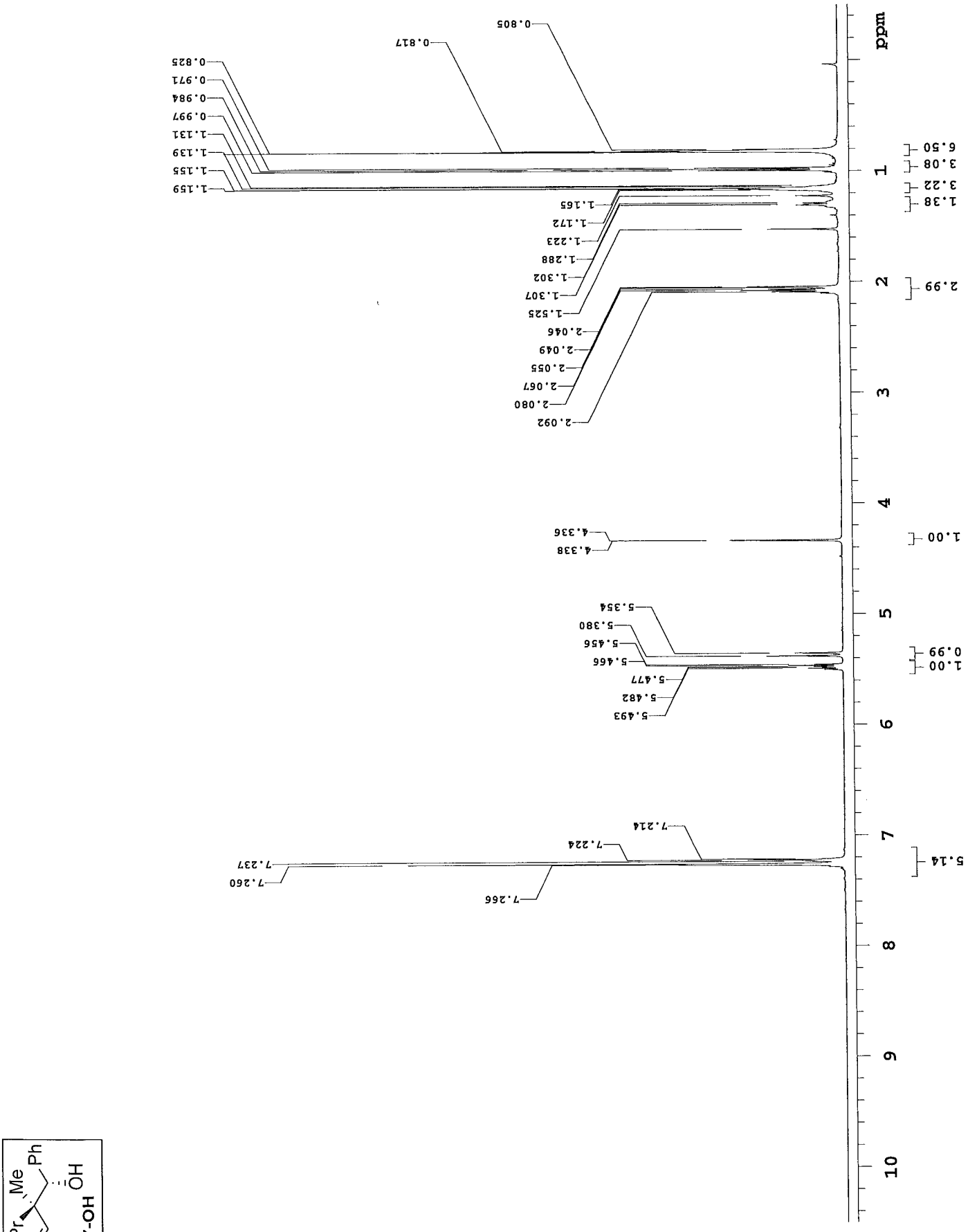
0.834
0.846
0.868
0.879
0.892
1.206
1.215
1.246
1.347
1.360
1.366
1.370
1.377
1.382
1.390
1.394
1.402
1.407
1.522
1.535
1.547
1.557
1.568
1.633
1.841
1.855
1.870
1.882
1.936
1.948
1.961
5.012
5.029
7.260
ppm
0.92
2.00
0.98
3.87
3.08
12.30
3.16
2.94
(pin)B
Me
Pr
Et
37


(pin)B
Me
Et
Pr
37


24.847
24.678
16.322
21.275
13.946
13.678
42.088
82.933
77.375
77.160
76.945
125.563
134.486
220
200
180
160
140
120
100
80
60
40
20
0
ppm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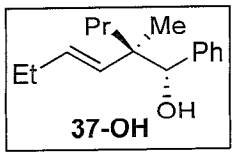
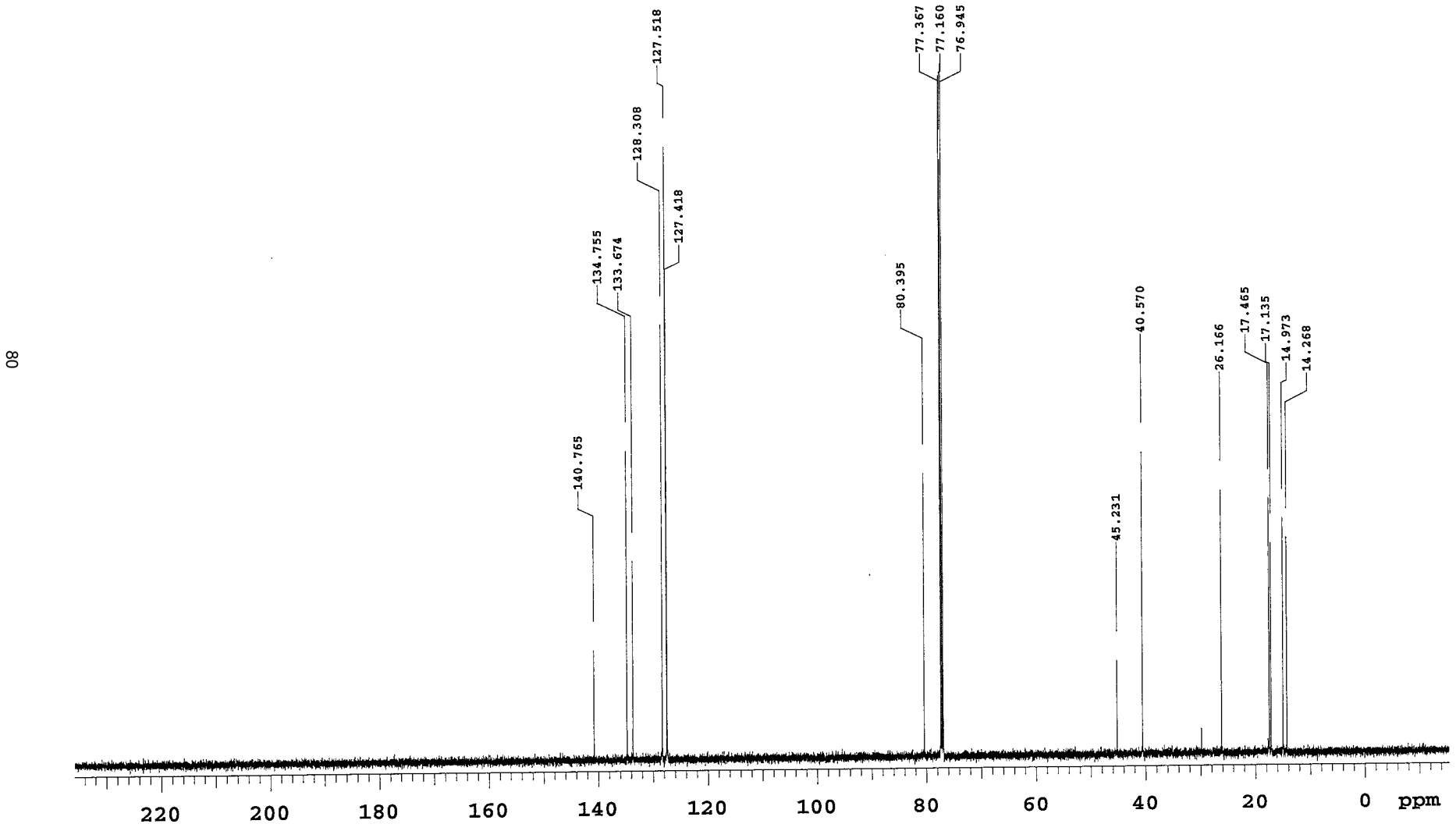
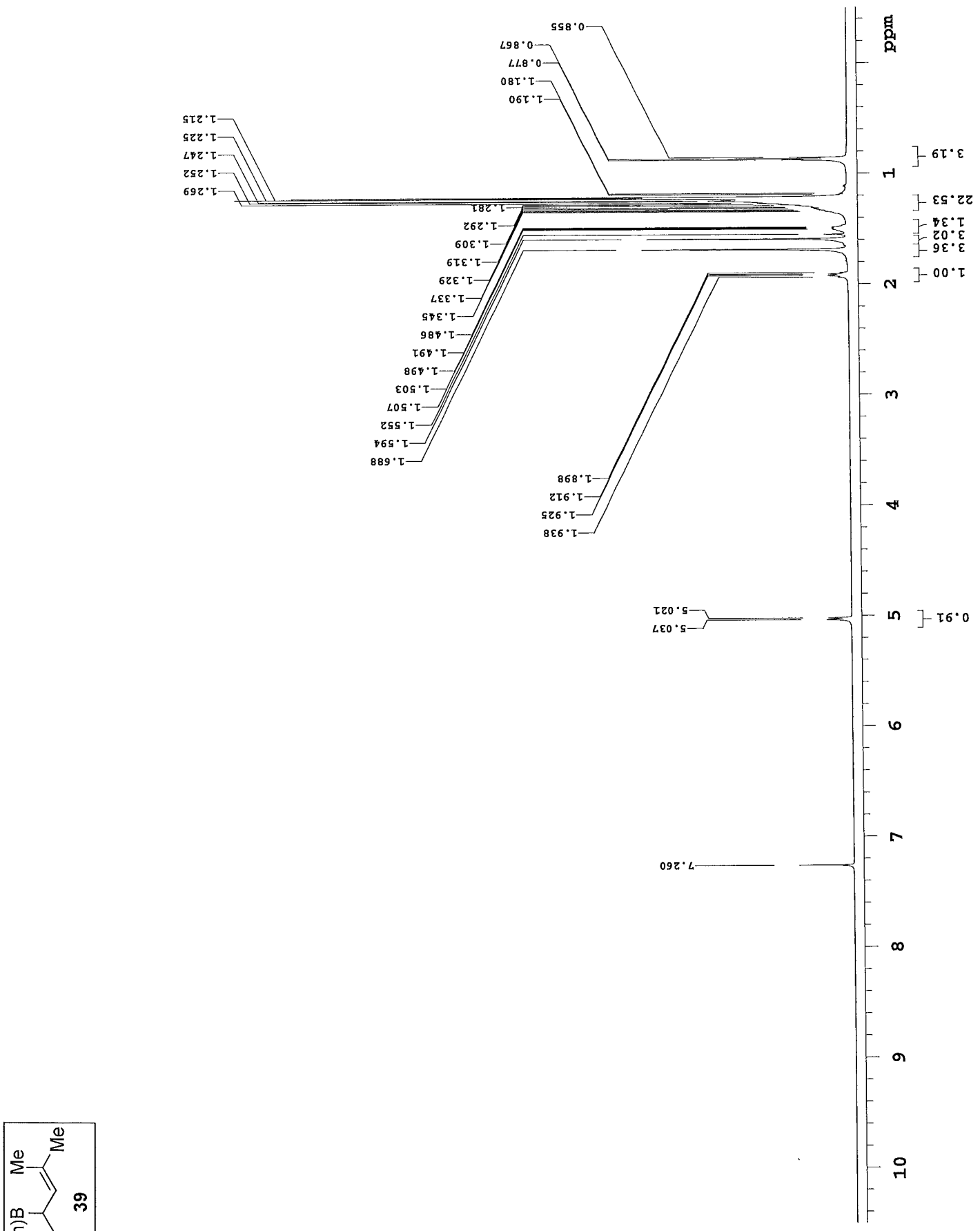
0.817
0.825
0.971
0.984
0.997
1.131
1.139
1.155
1.159
1.165
1.172
1.223
1.288
1.302
1.307
1.525
2.046
2.049
2.055
2.067
2.080
2.092
4.336
4.338
5.354
5.380
5.456
5.466
5.477
5.482
5.493
7.214
7.224
7.237
7.260
7.266
ppm
6.50
3.08
3.22
1.38
2.99
1.00
1.00
0.99
5.14

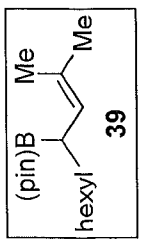
Pr
Me
Ph
OH
Et
37-OH

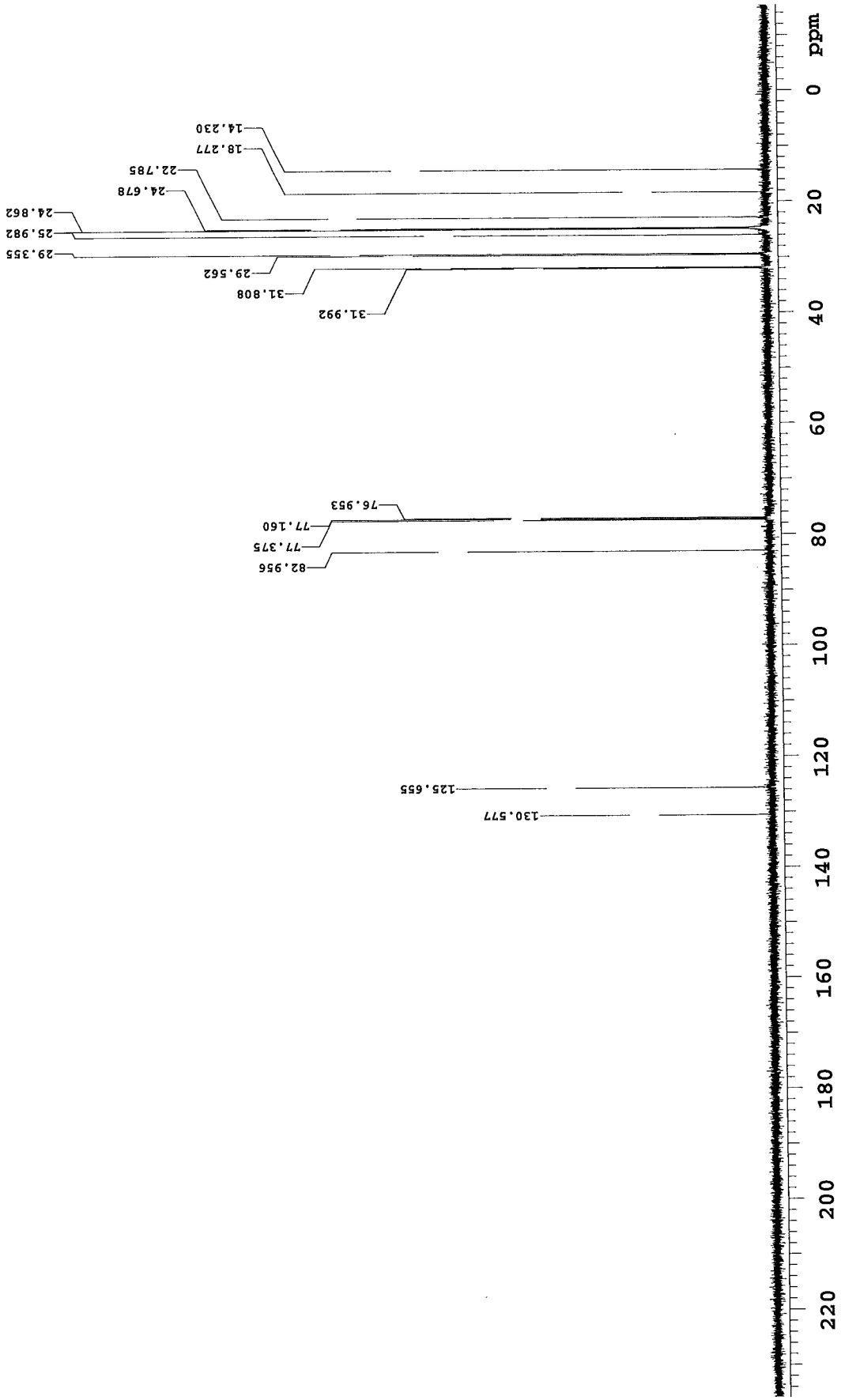

Pr
Me
Ph
Et
OH
37-OH

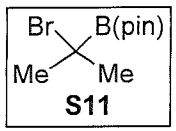

140.765
134.755
133.674
128.308
127.518
127.418
80.395
77.367
77.160
76.945
45.231
40.570
26.166
17.465
17.135
14.973
14.268
220
200
180
160
140
120
100
80
60
40
20
0
ppm


ppm
1
2
3
4
5
6
7
8
9
10
3.19
22.53
1.34
3.02
3.36
1.00
0.91
7.260
5.037
5.021
1.938
1.925
1.912
1.898
1.688
1.594
1.552
1.507
1.503
1.498
1.491
1.486
1.345
1.337
1.329
1.319
1.309
1.292
1.281
1.269
1.252
1.247
1.225
1.215
1.190
1.180
0.877
0.867
0.855

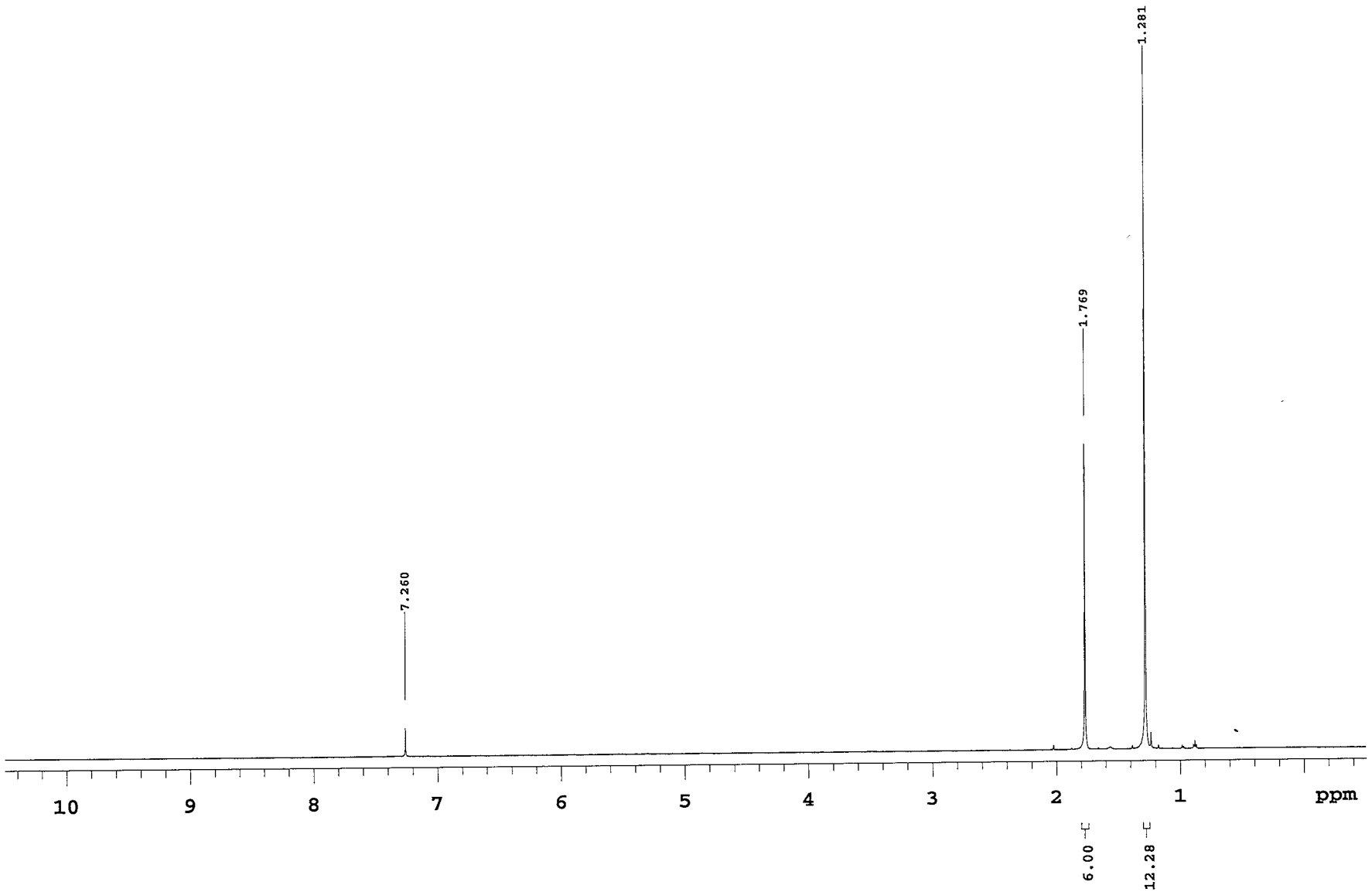
(pin)B
Me
Me
hexyl
39

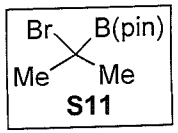

(pin)B
Me
Me
hexyl
39


14.230
18.277
22.785
24.678
24.862
25.982
29.355
29.562
31.808
31.992
76.953
77.160
77.375
82.956
125.655
130.577
0
20
40
60
80
100
120
140
160
180
200
220
ppm

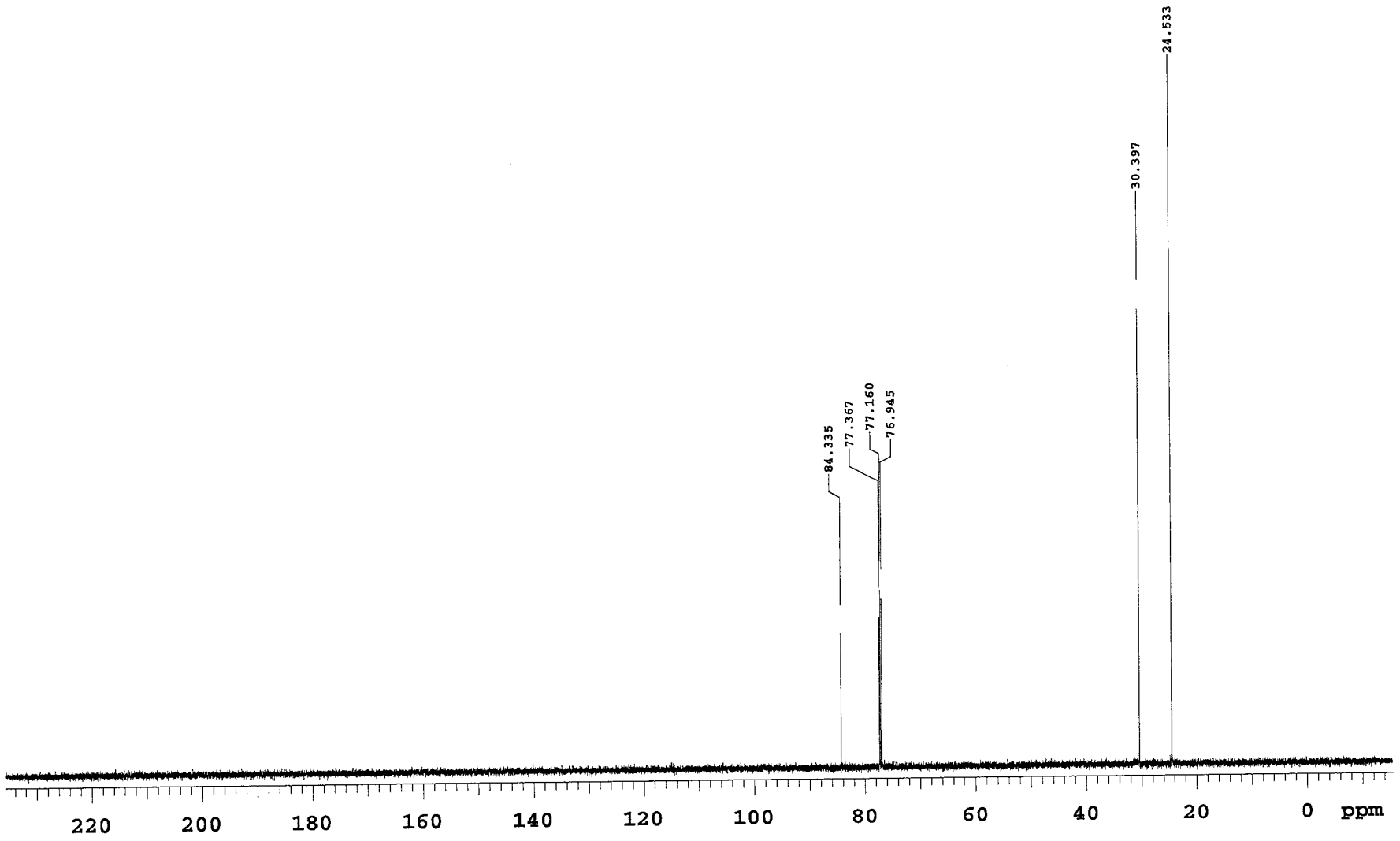


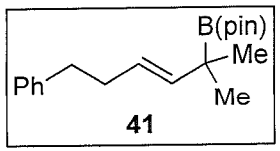
S11



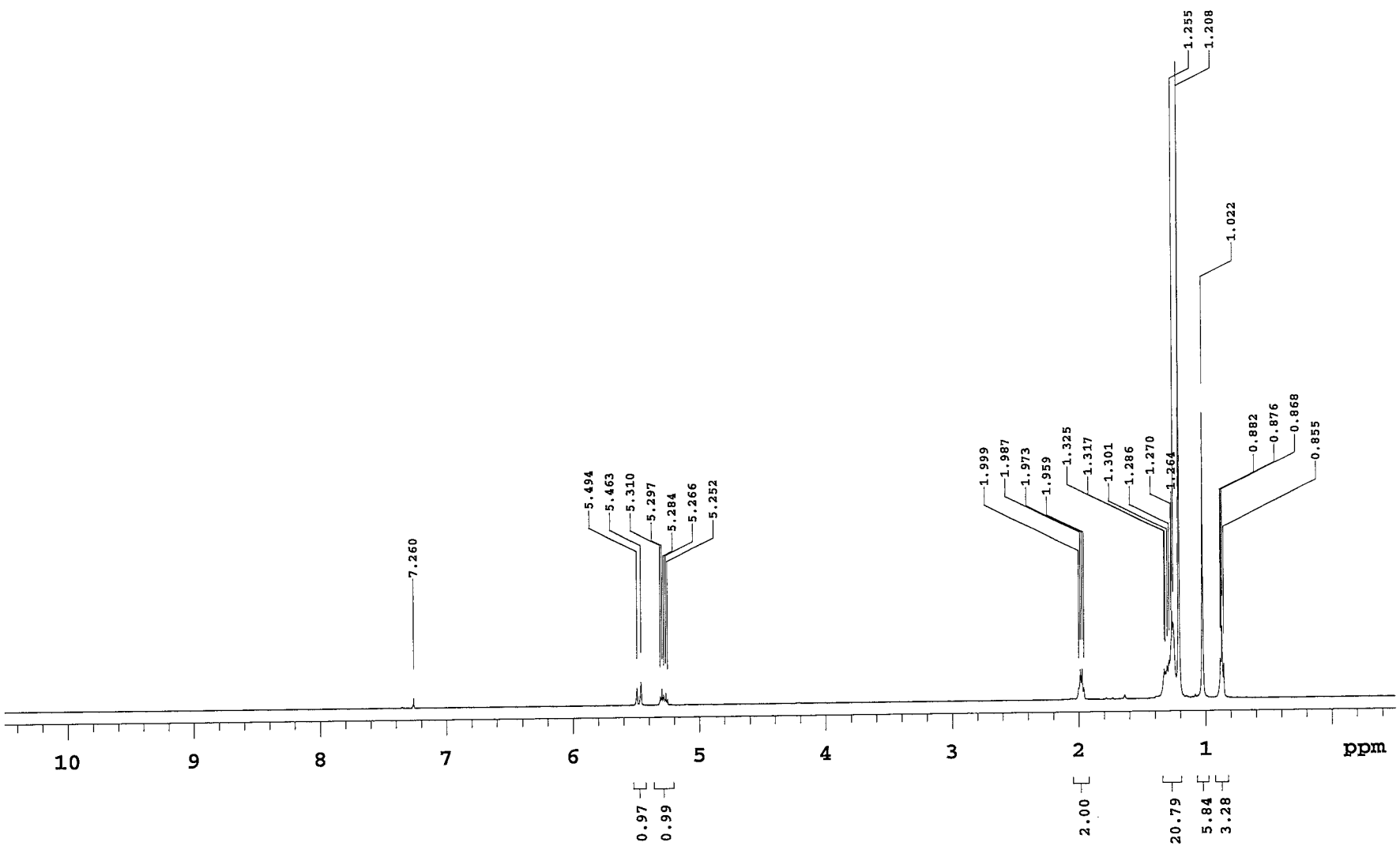

Br
B(pin)
Me
Me

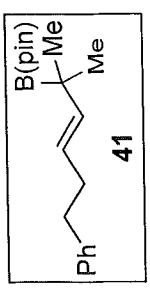
S11

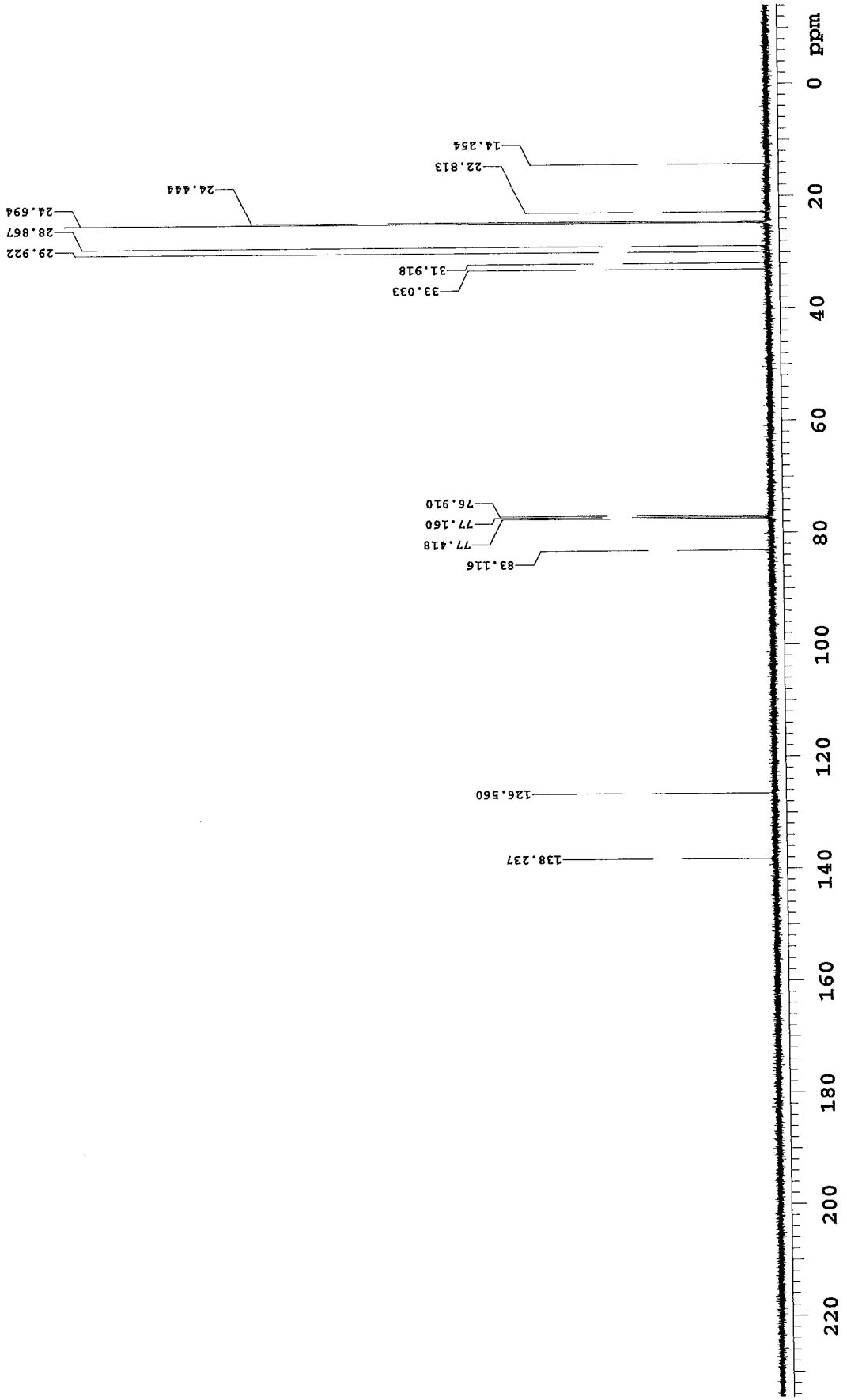

24.533
30.397
84.335
77.367
77.160
76.945
220
200
180
160
140
120
100
80
60
40
20
0
ppm

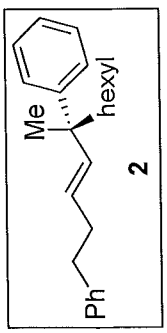

B(pin)
Me
Ph
Me

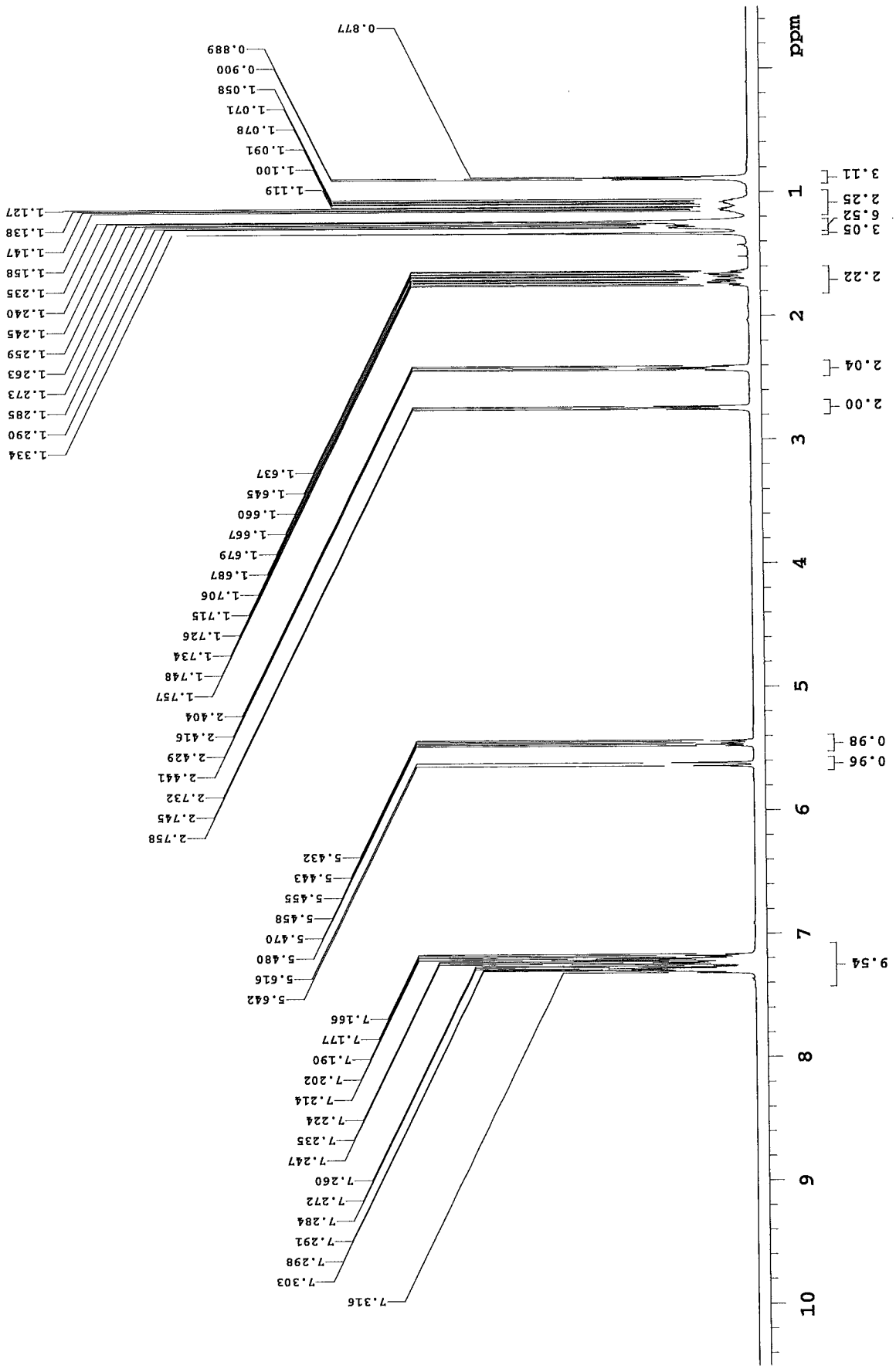
41

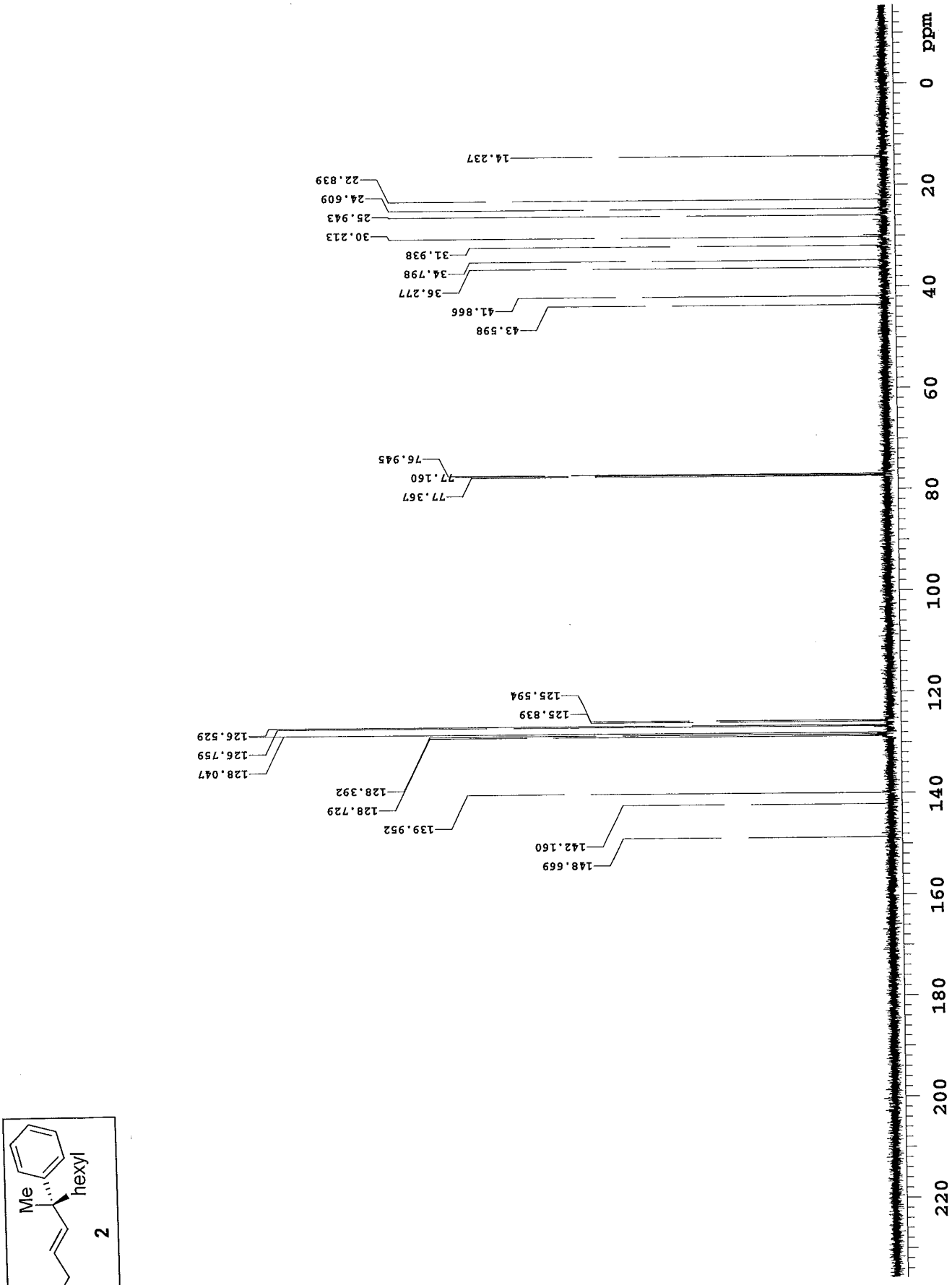

7.260
5.494
5.463
5.310
5.297
5.284
5.266
5.252
1.999
1.987
1.973
1.959
1.325
1.317
1.301
1.286
1.270
1.264
1.255
1.208
1.022
0.882
0.876
0.868
0.855
10
9
8
7
6
5
4
3
2
1
ppm
0.97
0.99
2.00
20.79
5.84
3.28

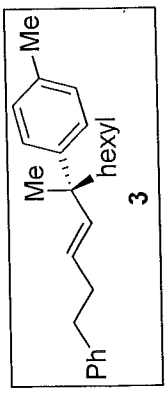

B(pin)
Me
Me
Ph
41

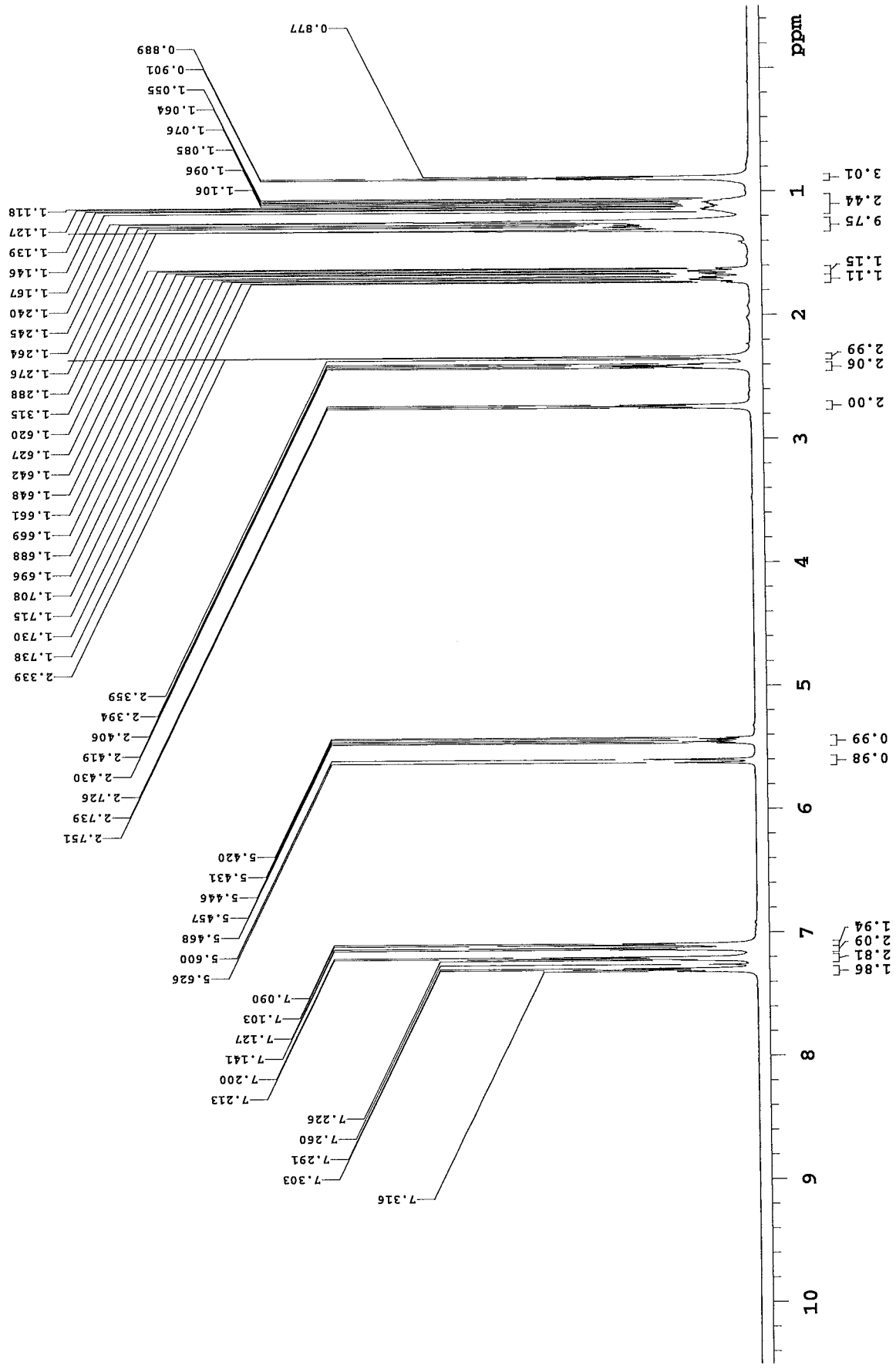

14.254
22.813
24.444
24.694
28.867
29.922
31.918
33.033
76.910
77.160
77.418
83.116
126.560
138.237
0
20
40
60
80
100
120
140
160
180
200
220
ppm

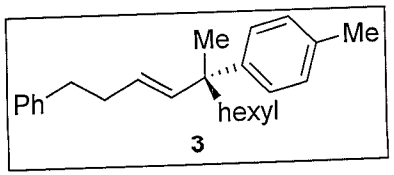

Me
hexyl
Ph
2

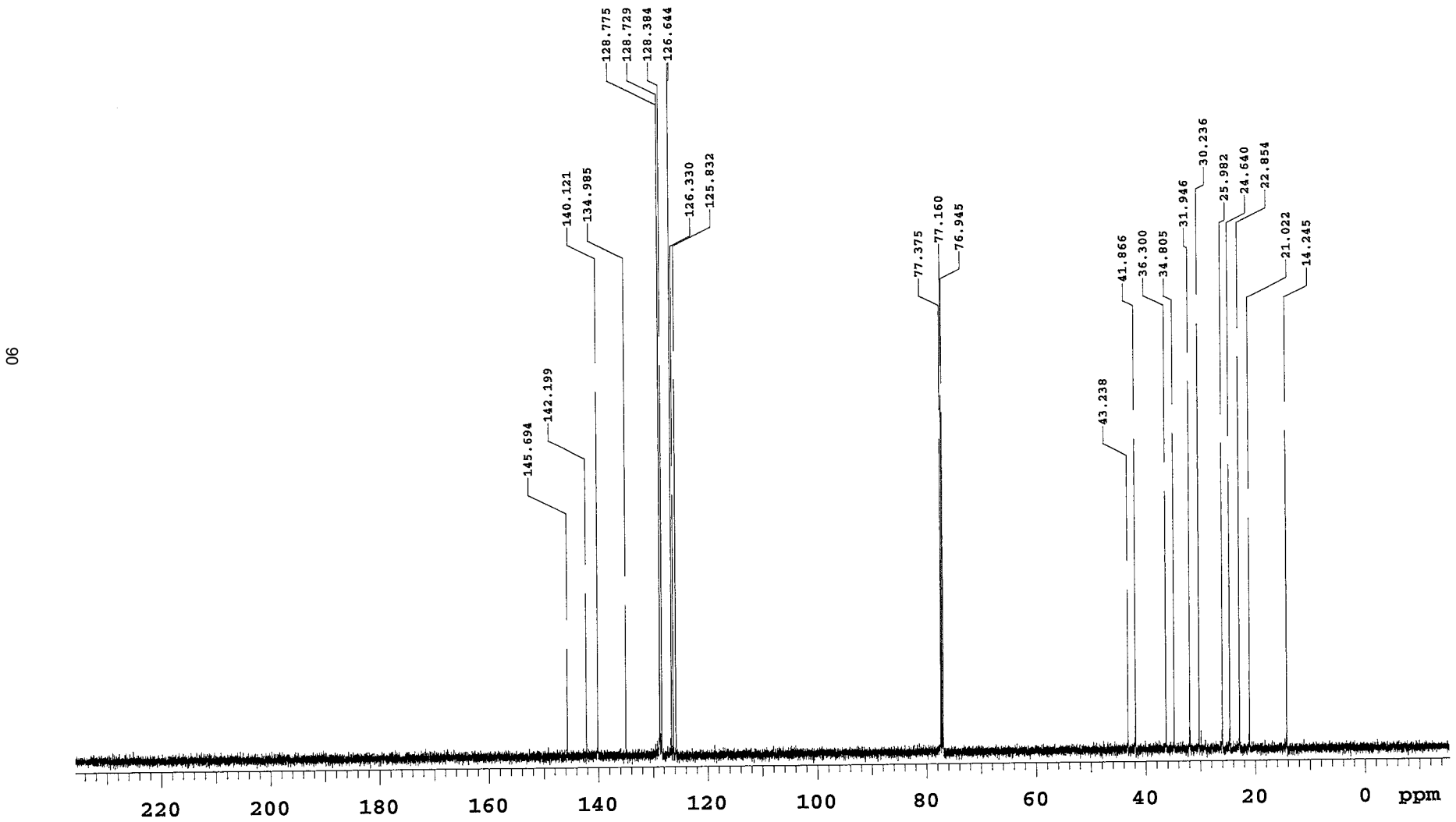

ppm
0.877
0.889
0.900
1.058
1.071
1.078
1.091
1.100
1.119
1.127
1.138
1.147
1.158
1.235
1.240
1.245
1.259
1.263
1.273
1.285
1.290
1.334
1.637
1.645
1.660
1.667
1.679
1.687
1.706
1.715
1.726
1.734
1.748
1.757
2.404
2.416
2.429
2.441
2.732
2.745
2.758
5.432
5.443
5.455
5.458
5.470
5.480
5.616
5.642
7.166
7.177
7.190
7.202
7.214
7.224
7.235
7.247
7.260
7.272
7.284
7.291
7.298
7.303
7.316
3.11
2.25
6.52
3.05
2.22
2.04
2.00
0.98
0.96
9.54


148.669
142.160
139.952
128.729
128.392
128.047
126.759
126.529
125.839
125.594
77.367
77.160
76.945
43.598
41.866
36.277
34.798
31.938
30.213
25.943
24.609
22.839
14.237
0 ppm
20
40
60
80
100
120
140
160
180
200
220
Me
hexyl
Ph
2

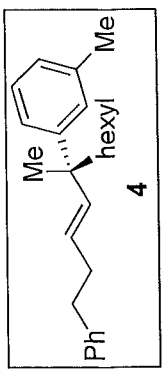

Me
Me
hexyl
3
Ph

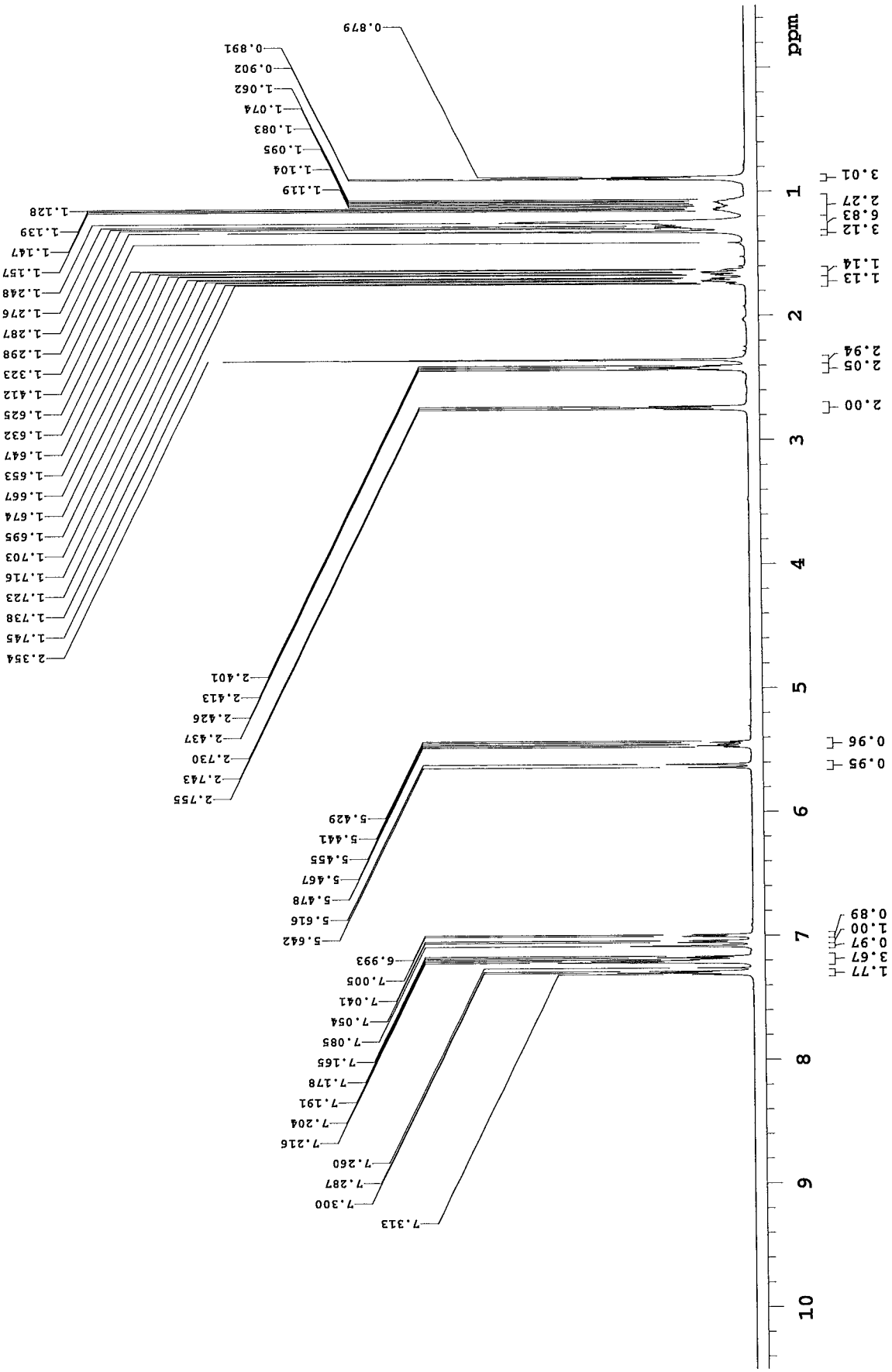

ppm
1 2 3 4 5 6 7 8 9 10
3.01
2.44
9.75
1.11
1.15
2.06
2.99
2.00
0.98
0.99
1.86
2.81
2.09
1.94
0.877
0.889
0.901
1.055
1.064
1.076
1.085
1.096
1.106
1.118
1.127
1.139
1.146
1.167
1.240
1.245
1.264
1.276
1.288
1.315
1.620
1.627
1.642
1.648
1.661
1.669
1.688
1.696
1.708
1.715
1.730
1.738
2.339
2.359
2.394
2.406
2.419
2.430
2.726
2.739
2.751
5.420
5.431
5.446
5.457
5.468
5.600
5.626
7.090
7.103
7.127
7.141
7.200
7.213
7.226
7.260
7.291
7.303
7.316

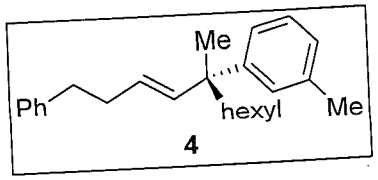

Me
Me
Ph
hexyl
3

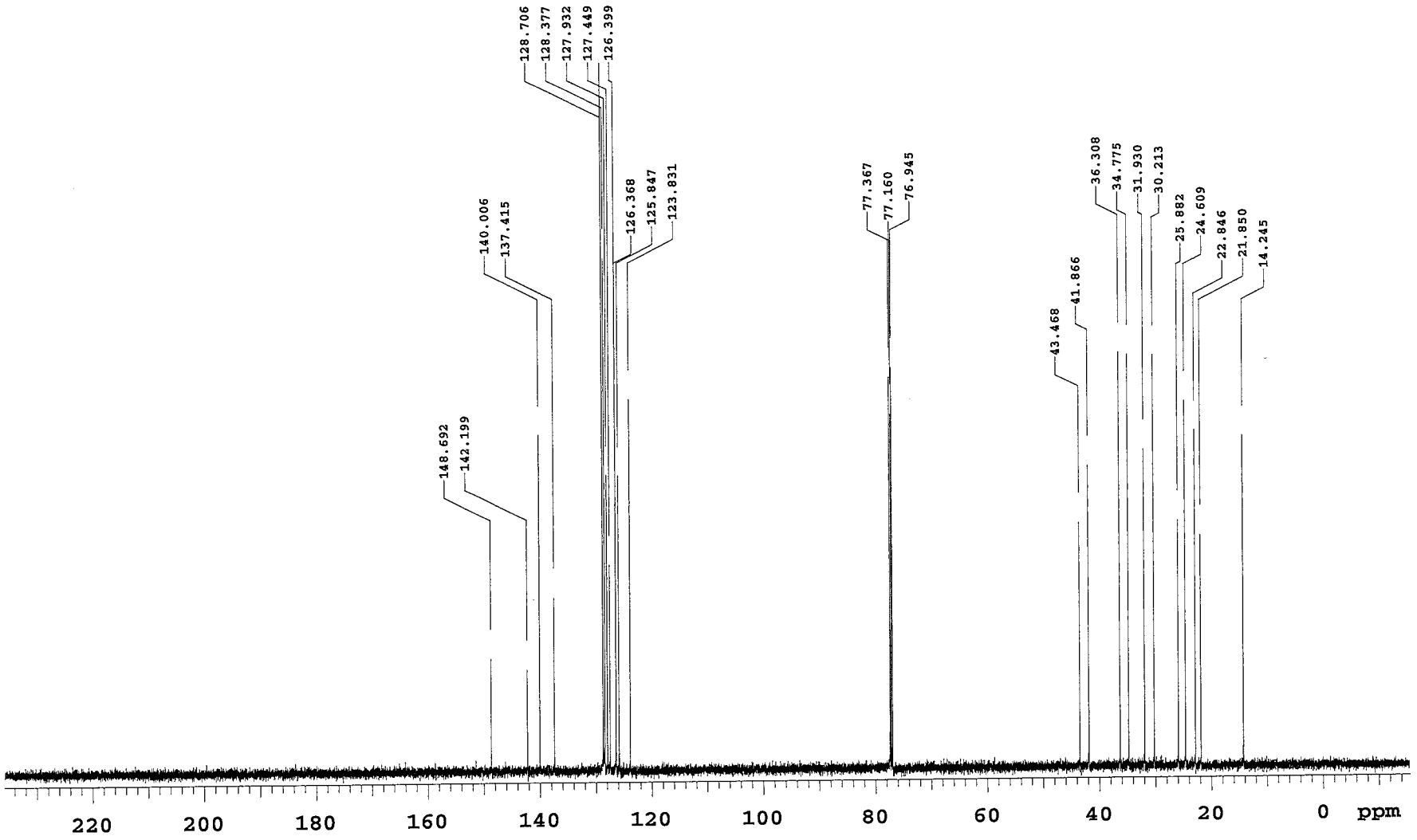

145.694
142.199
140.121
134.985
128.775
128.729
128.384
126.644
126.330
125.832
77.375
77.160
76.945
43.238
41.866
36.300
34.805
31.946
30.236
25.982
24.640
22.854
21.022
14.245
220
200
180
160
140
120
100
80
60
40
20
0
ppm

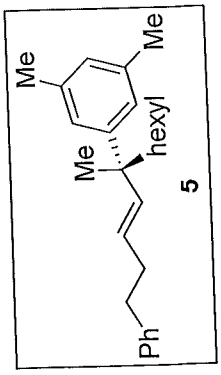
90

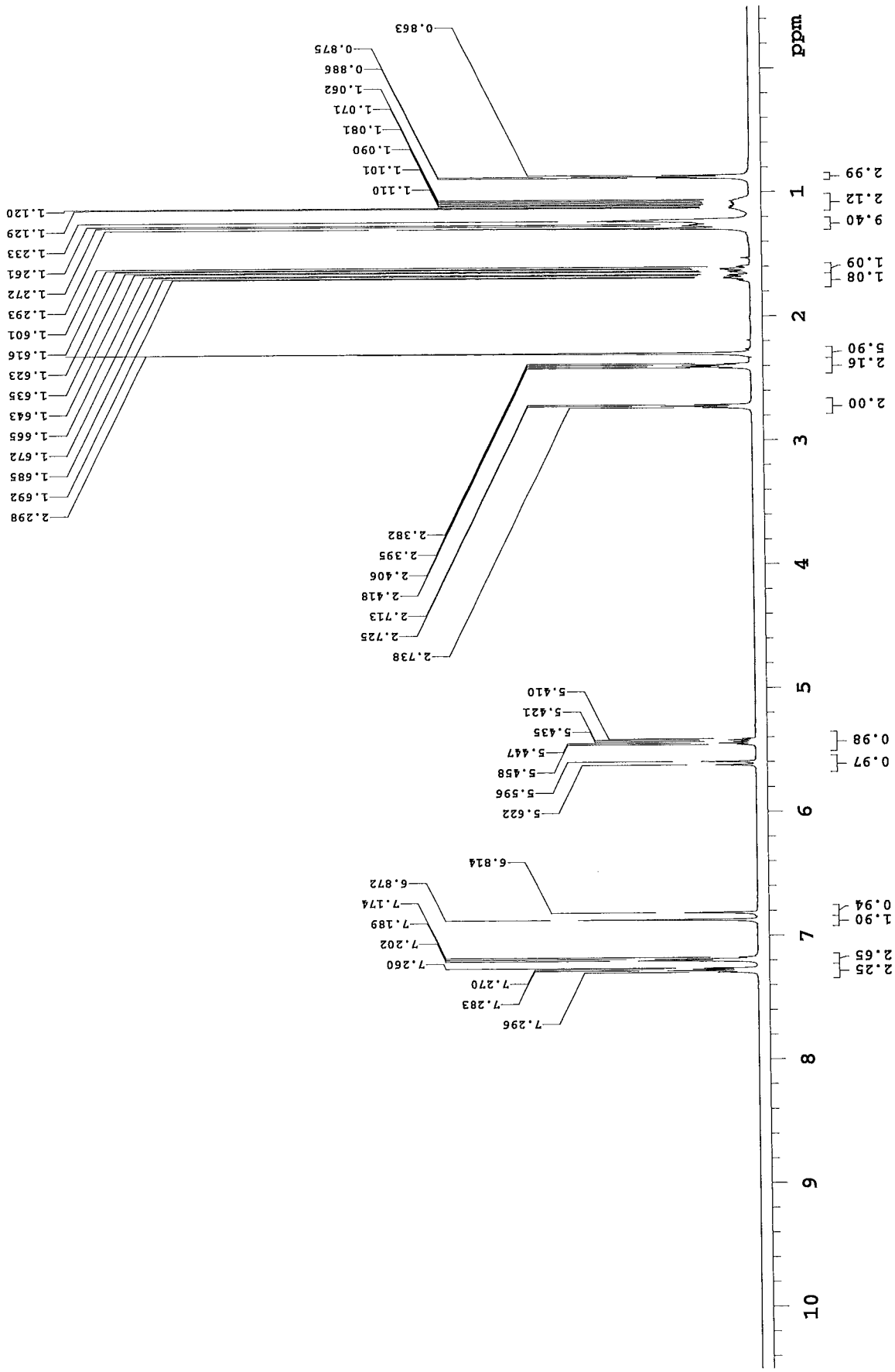

Me
Me
hexyl
4
Ph

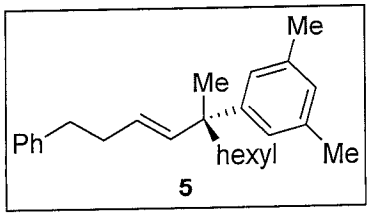

ppm
1
2
3
4
5
6
7
8
9
10
3.01
2.27
6.83
3.12
1.13
1.14
2.05
2.94
2.00
0.95
0.96
1.77
3.67
0.97
1.00
0.89
0.879
0.891
0.902
1.062
1.074
1.083
1.095
1.104
1.119
1.128
1.139
1.147
1.157
1.248
1.276
1.287
1.298
1.323
1.412
1.625
1.632
1.647
1.653
1.667
1.674
1.695
1.703
1.716
1.723
1.738
1.745
2.354
2.401
2.413
2.426
2.437
2.730
2.743
2.755
5.429
5.441
5.455
5.467
5.478
5.616
5.642
6.993
7.005
7.041
7.054
7.085
7.165
7.178
7.191
7.204
7.216
7.260
7.287
7.300
7.313

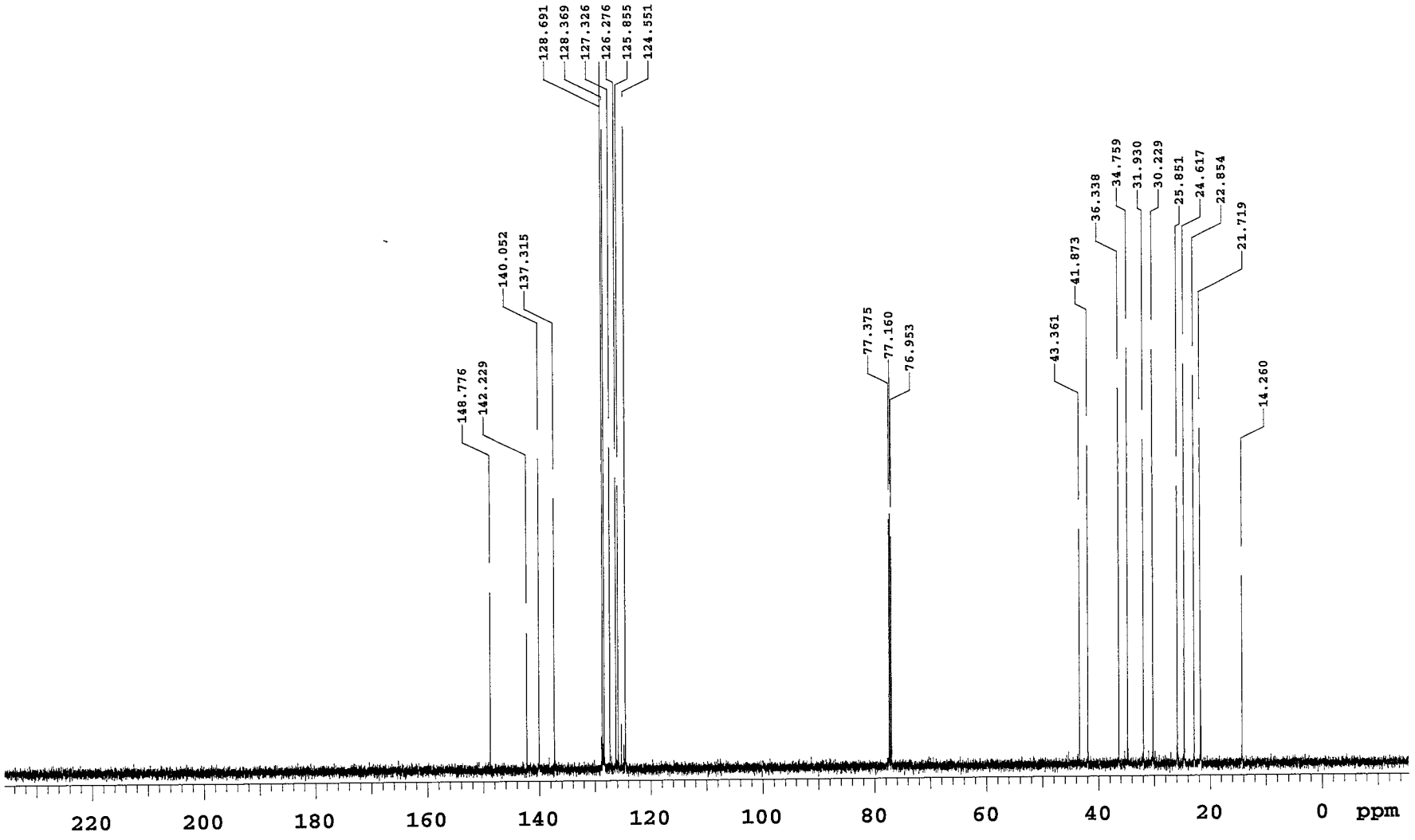

Me
Ph
hexyl
Me
4

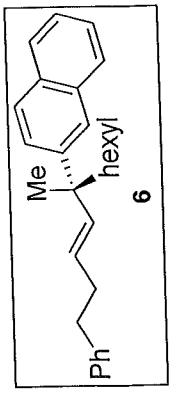

128.706
128.377
127.932
127.449
126.399
126.368
125.847
123.831
140.006
137.415
148.692
142.199
77.367
77.160
76.945
36.308
34.775
31.930
30.213
25.882
24.609
22.846
21.850
14.245
43.468
41.866
220
200
180
160
140
120
100
80
60
40
20
0
ppm

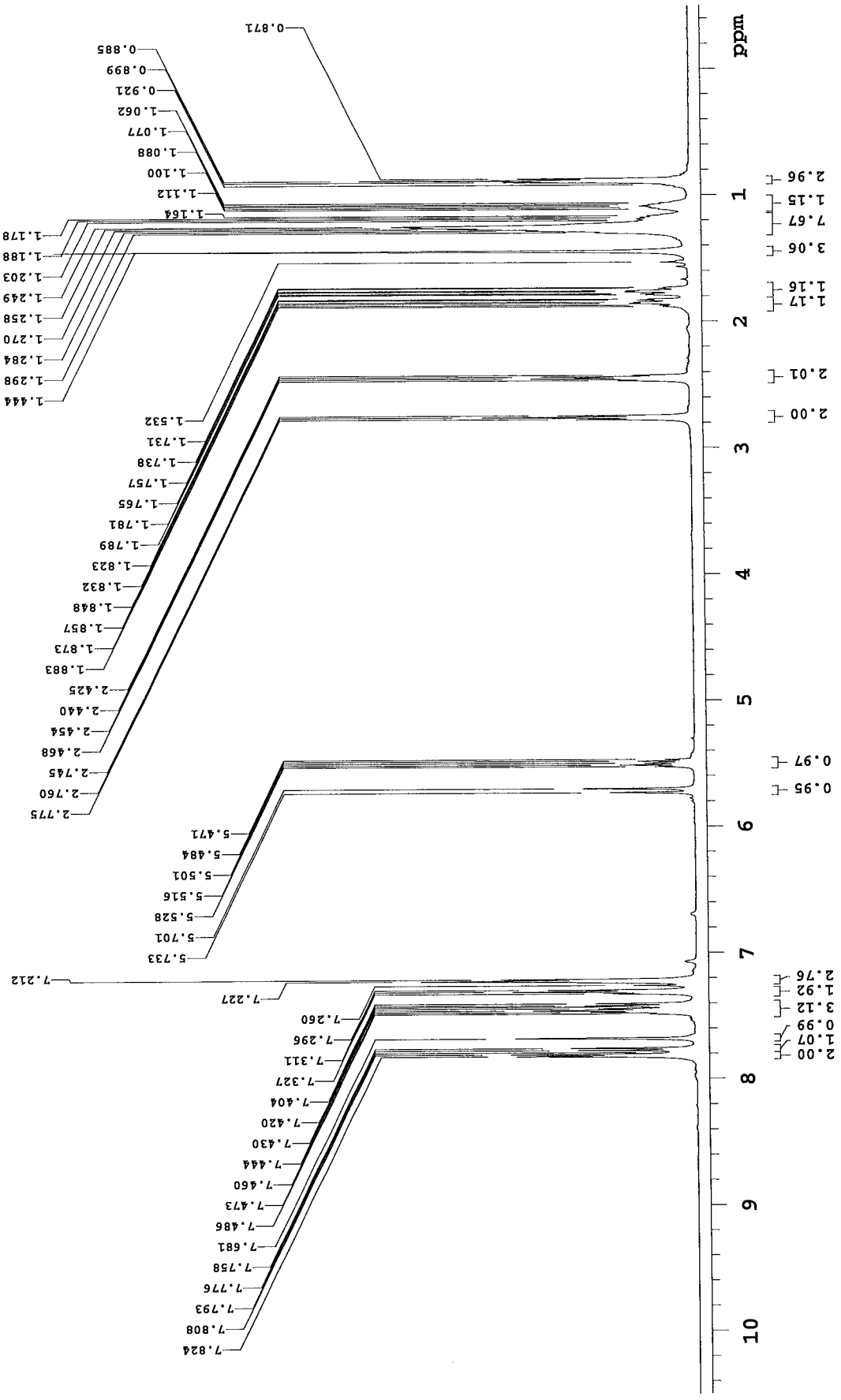

Me
Me
Me
hexyl
5
Ph

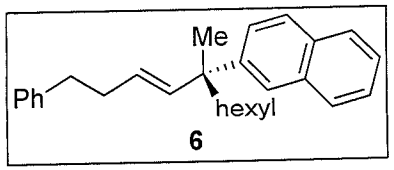

ppm
10
9
8
7
6
5
4
3
2
1
0.863
0.875
0.886
1.062
1.071
1.081
1.090
1.101
1.110
1.120
1.129
1.233
1.261
1.272
1.293
1.601
1.616
1.623
1.635
1.643
1.665
1.672
1.685
1.692
2.298
2.382
2.395
2.406
2.418
2.713
2.725
2.738
5.410
5.421
5.435
5.447
5.458
5.596
5.622
6.814
6.872
7.174
7.189
7.202
7.260
7.270
7.283
7.296
2.99
2.12
9.40
1.08
1.09
2.16
5.90
2.00
0.98
0.97
2.25
2.65
1.90
0.94

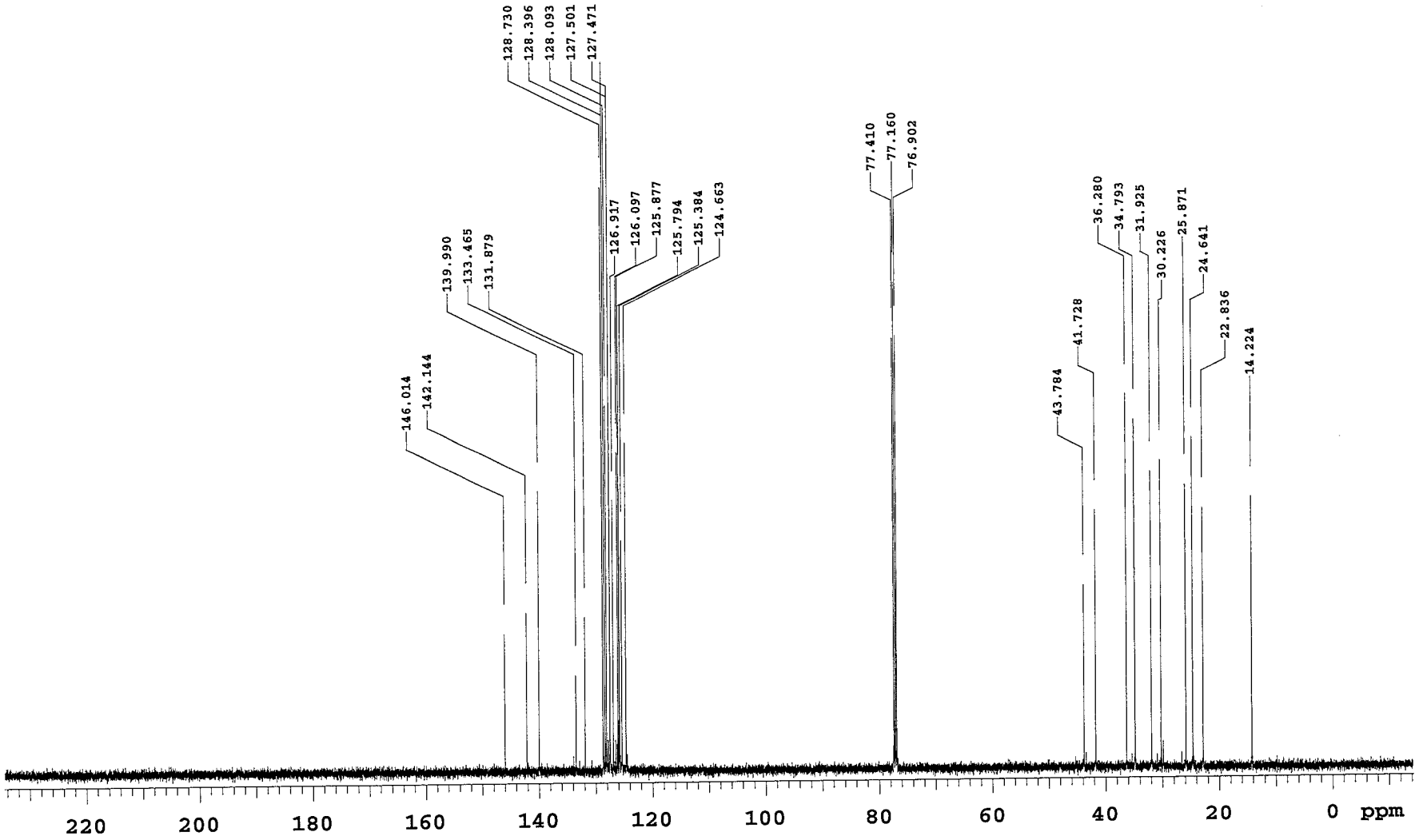

Me
Me
Ph
hexyl
Me
5

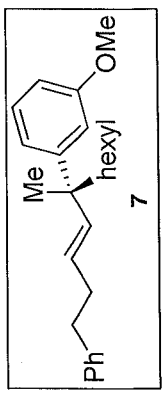

128.691
128.369
127.326
126.276
125.855
124.551
140.052
137.315
148.776
142.229
77.375
77.160
76.953
43.361
41.873
36.338
34.759
31.930
30.229
25.851
24.617
22.854
21.719
14.260
220
200
180
160
140
120
100
80
60
40
20
0
ppm

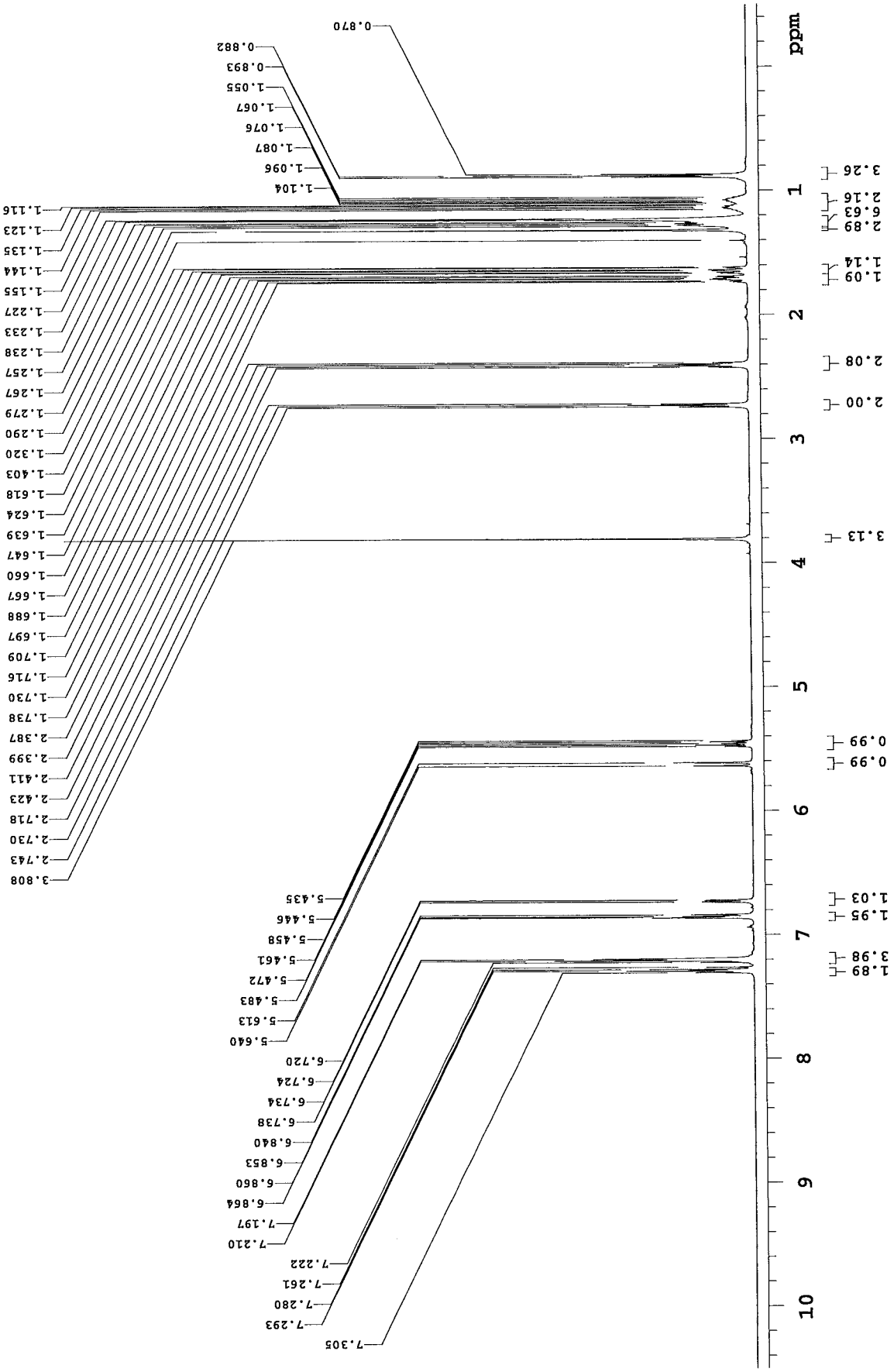

Me
hexyl
Ph
6

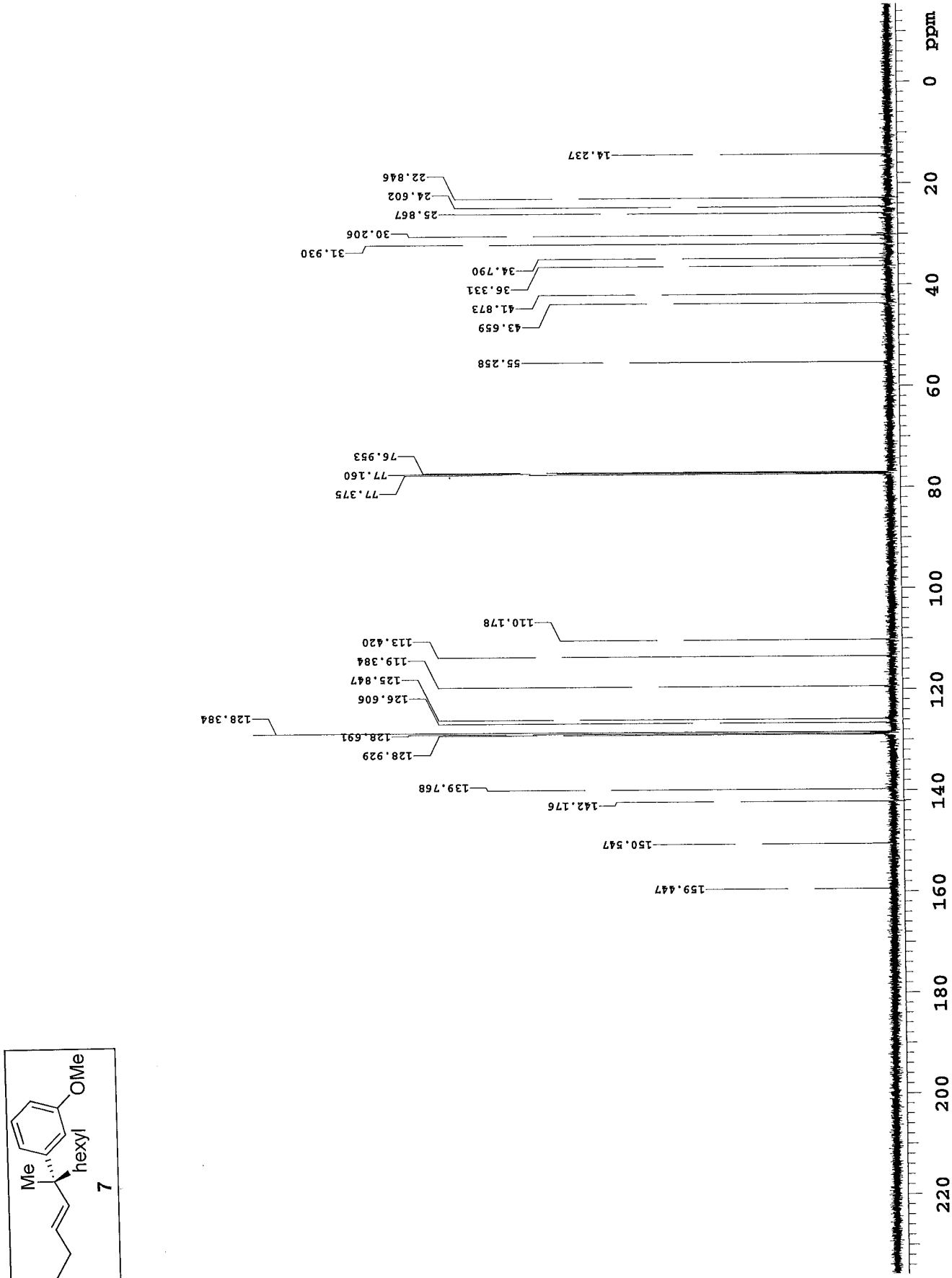

ppm
1
2
3
4
5
6
7
8
9
10
2.96
1.15
7.67
3.06
1.17
1.16
2.01
2.00
0.97
0.95
2.00
1.07
0.99
3.12
1.92
2.76
0.871
0.885
0.899
0.921
1.062
1.077
1.088
1.100
1.112
1.164
1.178
1.188
1.203
1.249
1.258
1.270
1.284
1.298
1.444
1.532
1.731
1.738
1.757
1.765
1.781
1.789
1.823
1.832
1.848
1.857
1.873
1.883
2.425
2.440
2.454
2.468
2.745
2.760
2.775
5.471
5.484
5.501
5.516
5.528
5.701
5.733
7.212
7.227
7.260
7.296
7.311
7.327
7.404
7.420
7.430
7.444
7.460
7.473
7.486
7.681
7.758
7.776
7.793
7.808
7.824


Me
Ph
hexyl
6


128.730
128.396
128.093
127.501
127.471
126.917
126.097
125.877
125.794
125.384
124.663
139.990
133.465
131.879
146.014
142.144
77.410
77.160
76.902
36.280
34.793
31.925
30.226
25.871
24.641
22.836
14.224
43.784
41.728
220
200
180
160
140
120
100
80
60
40
20
0
ppm


OMe
Me
hexyl
Ph
7


ppm
1
2
3
4
5
6
7
8
9
10
3.26
2.16
6.63
2.89
1.09
1.14
2.08
2.00
3.13
0.99
0.99
1.03
1.95
1.89
3.98
0.870
0.882
0.893
1.055
1.067
1.076
1.087
1.096
1.104
1.116
1.123
1.135
1.144
1.155
1.227
1.233
1.238
1.257
1.267
1.279
1.290
1.320
1.403
1.618
1.624
1.639
1.647
1.660
1.667
1.688
1.697
1.709
1.716
1.730
1.738
2.387
2.399
2.411
2.423
2.718
2.730
2.743
3.808
5.435
5.446
5.458
5.461
5.472
5.483
5.613
5.640
6.720
6.724
6.734
6.738
6.840
6.853
6.860
6.864
7.197
7.210
7.222
7.261
7.280
7.293
7.305


159.447
150.547
142.176
139.768
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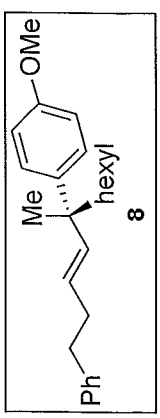
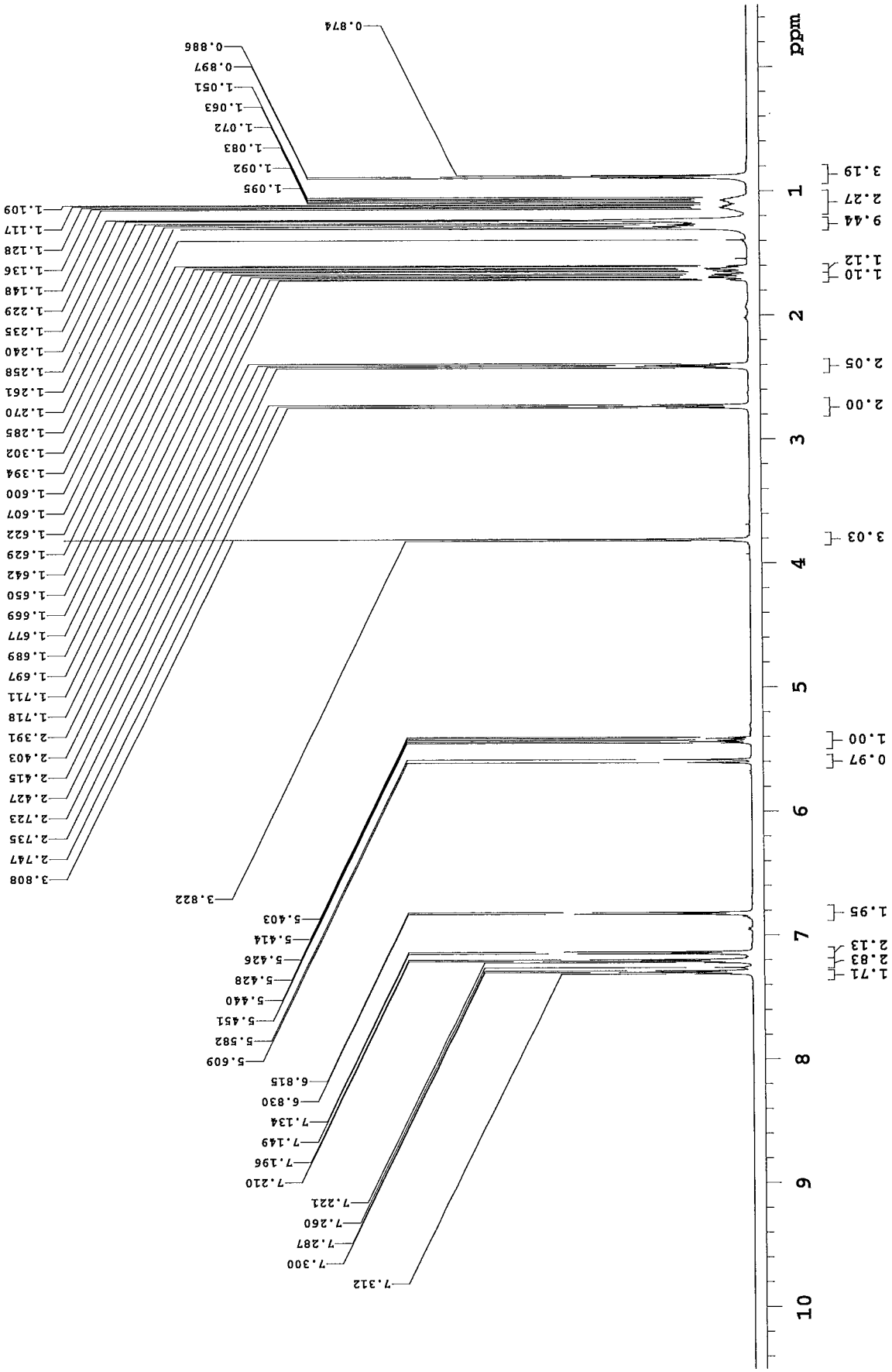
128.691
128.384
126.606
125.847
119.384
113.420
110.178
77.375
77.160
76.953
55.258
43.659
41.873
36.331
34.790
31.930
30.206
25.867
24.602
22.846
14.237
ppm
0
20
40
60
80
100
120
140
160
180
200
220

OMe
Me
hexyl
Ph
7


OMe
Me
hexyl
Ph
8


ppm
1 2 3 4 5 6 7 8 9 10
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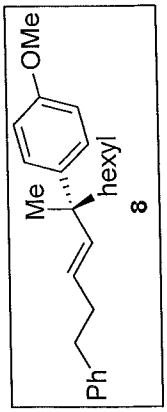
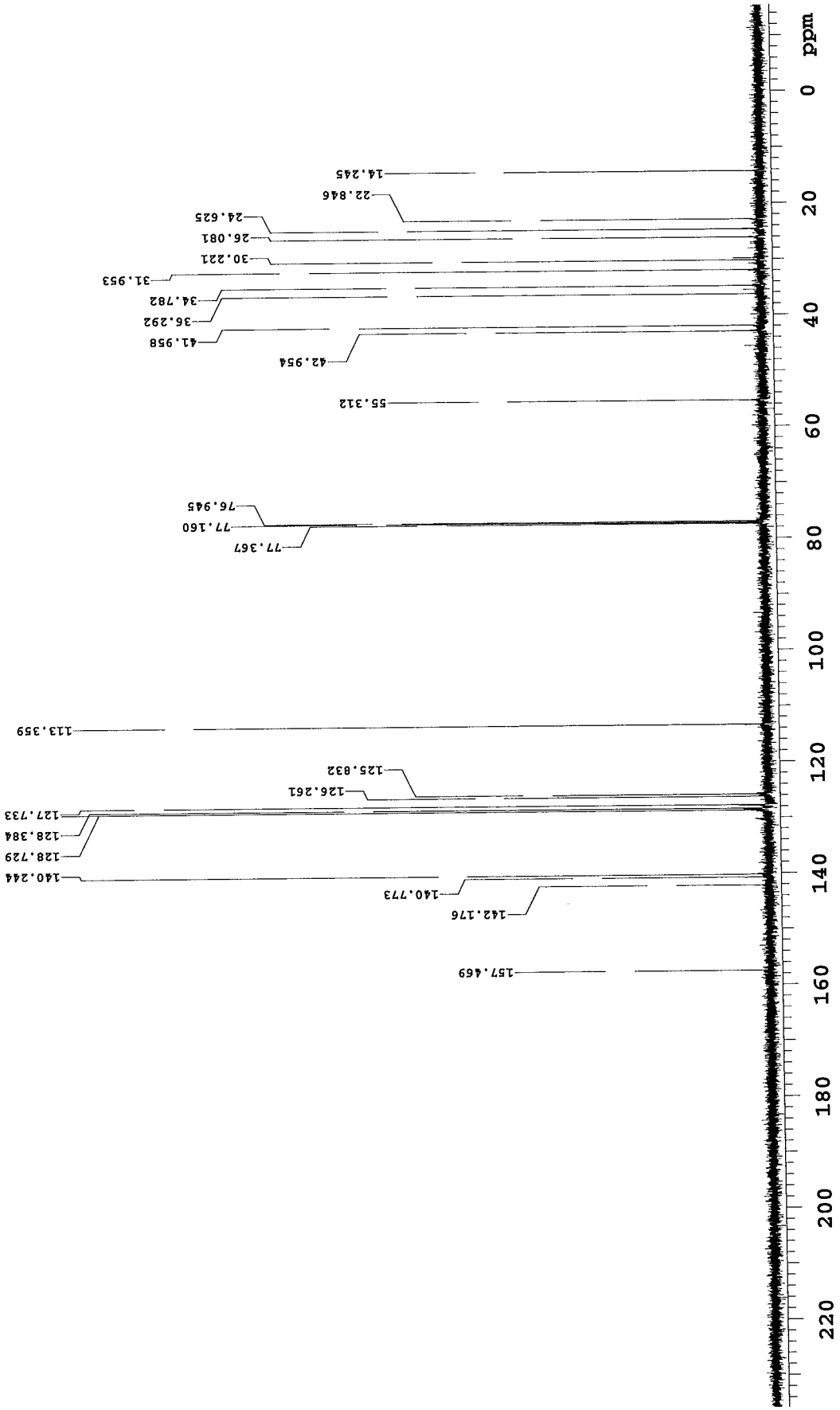
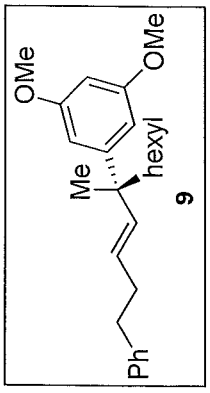
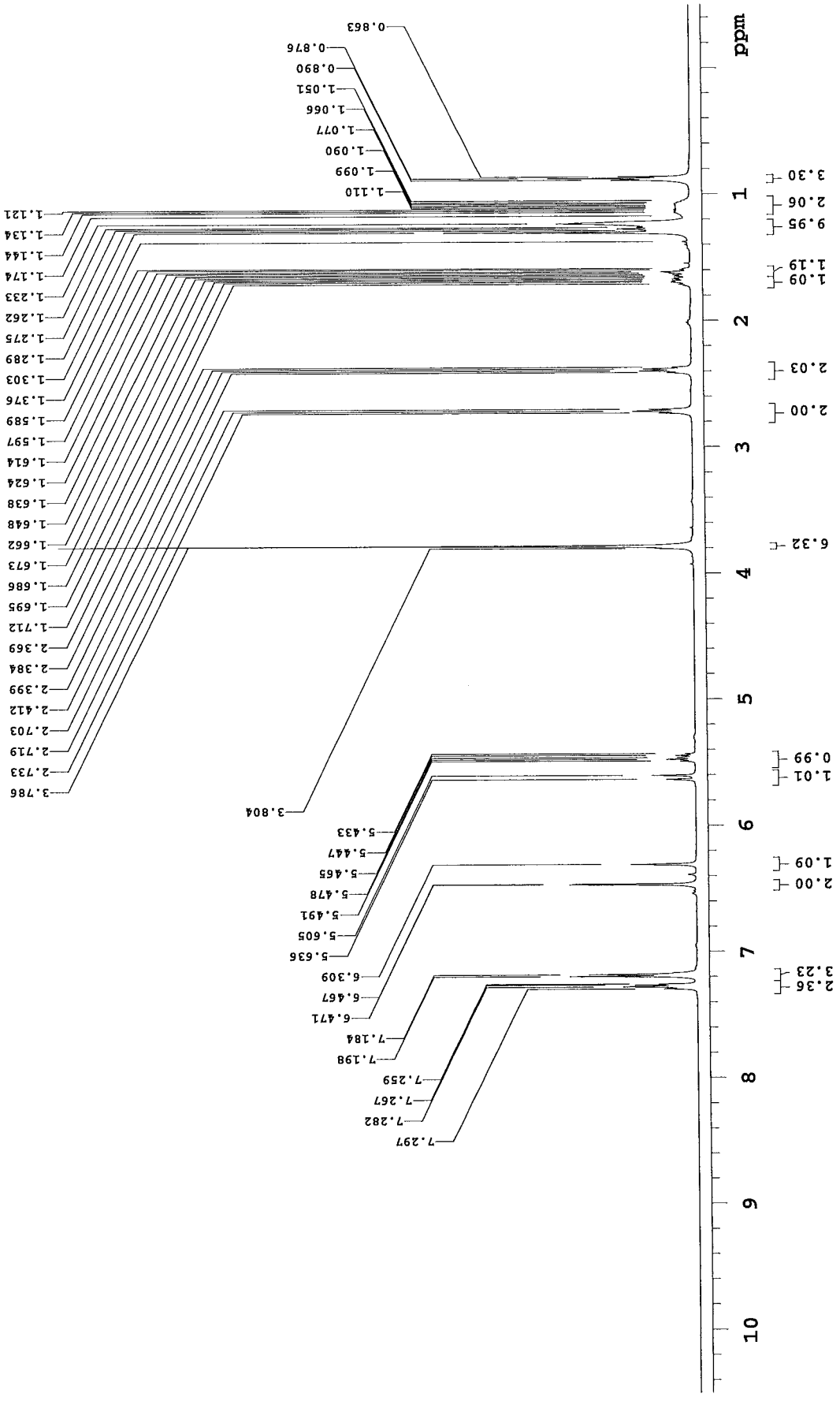
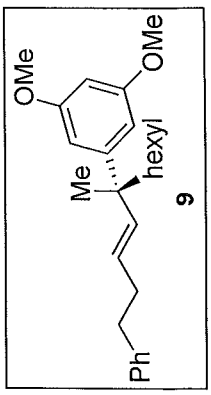
2.27
9.44
1.10
1.12
2.05
2.00
3.03
0.97
1.00
1.95
1.71
2.83
2.13
0.874
0.886
0.897
1.051
1.063
1.072
1.083
1.092
1.095
1.109
1.117
1.128
1.136
1.148
1.229
1.235
1.240
1.258
1.261
1.270
1.285
1.302
1.394
1.600
1.607
1.622
1.629
1.642
1.650
1.669
1.677
1.689
1.697
1.711
1.718
2.391
2.403
2.415
2.427
2.723
2.735
2.747
3.808
3.822
5.403
5.414
5.426
5.428
5.440
5.451
5.582
5.609
6.815
6.830
7.134
7.149
7.196
7.210
7.221
7.260
7.287
7.300
7.312

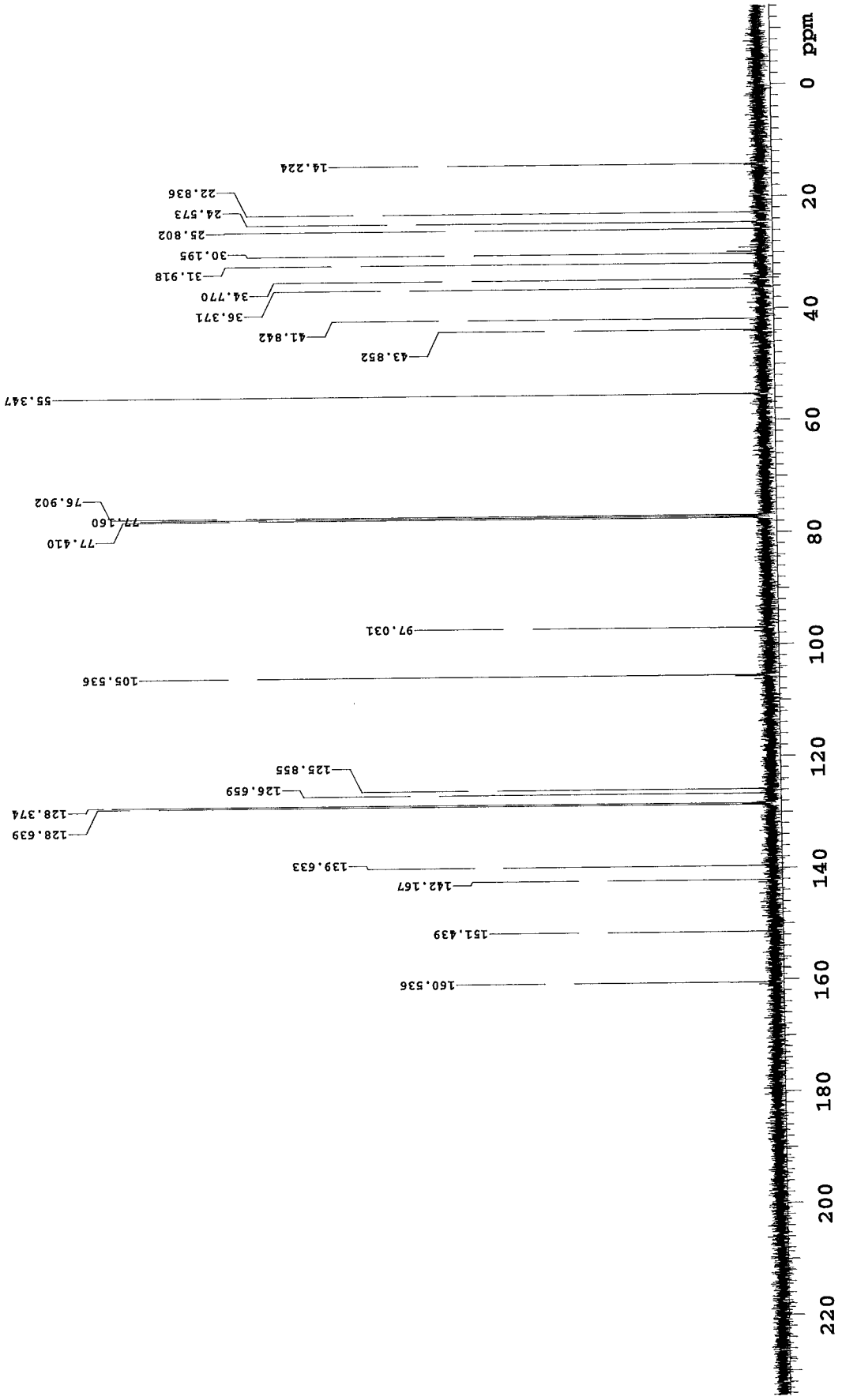

OMe
Me
hexyl
Ph
8

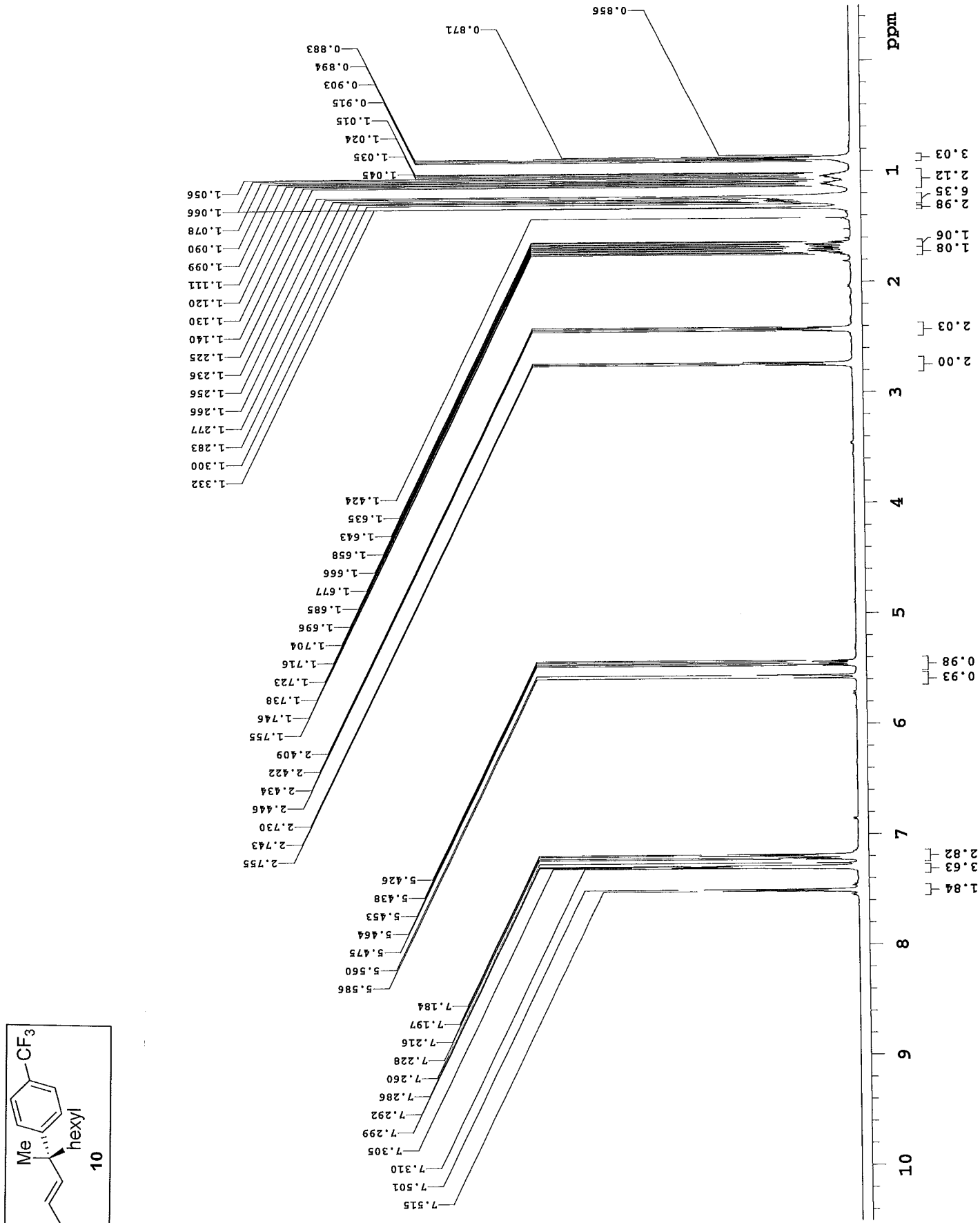

157.469
142.176
140.773
140.244
128.729
128.384
127.733
126.261
125.832
113.359
77.367
77.160
76.945
55.312
42.954
41.958
36.292
34.782
31.953
30.221
26.081
24.625
22.846
14.245
0 ppm
20
40
60
80
100
120
140
160
180
200
220

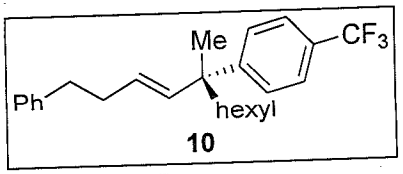

OMe
OMe
Me
hexyl
Ph
9


ppm
1
2
3
4
5
6
7
8
9
10
3.30
2.06
9.95
1.09
1.19
2.03
2.00
6.32
1.01
0.99
2.00
1.09
2.36
3.23
0.863
0.876
0.890
1.051
1.066
1.077
1.090
1.099
1.110
1.121
1.134
1.144
1.174
1.233
1.262
1.275
1.289
1.303
1.376
1.589
1.597
1.614
1.624
1.638
1.648
1.662
1.673
1.686
1.695
1.712
2.369
2.384
2.399
2.412
2.703
2.719
2.733
3.786
3.804
5.433
5.447
5.465
5.478
5.491
5.605
5.636
6.309
6.467
6.471
7.184
7.198
7.259
7.267
7.282
7.297

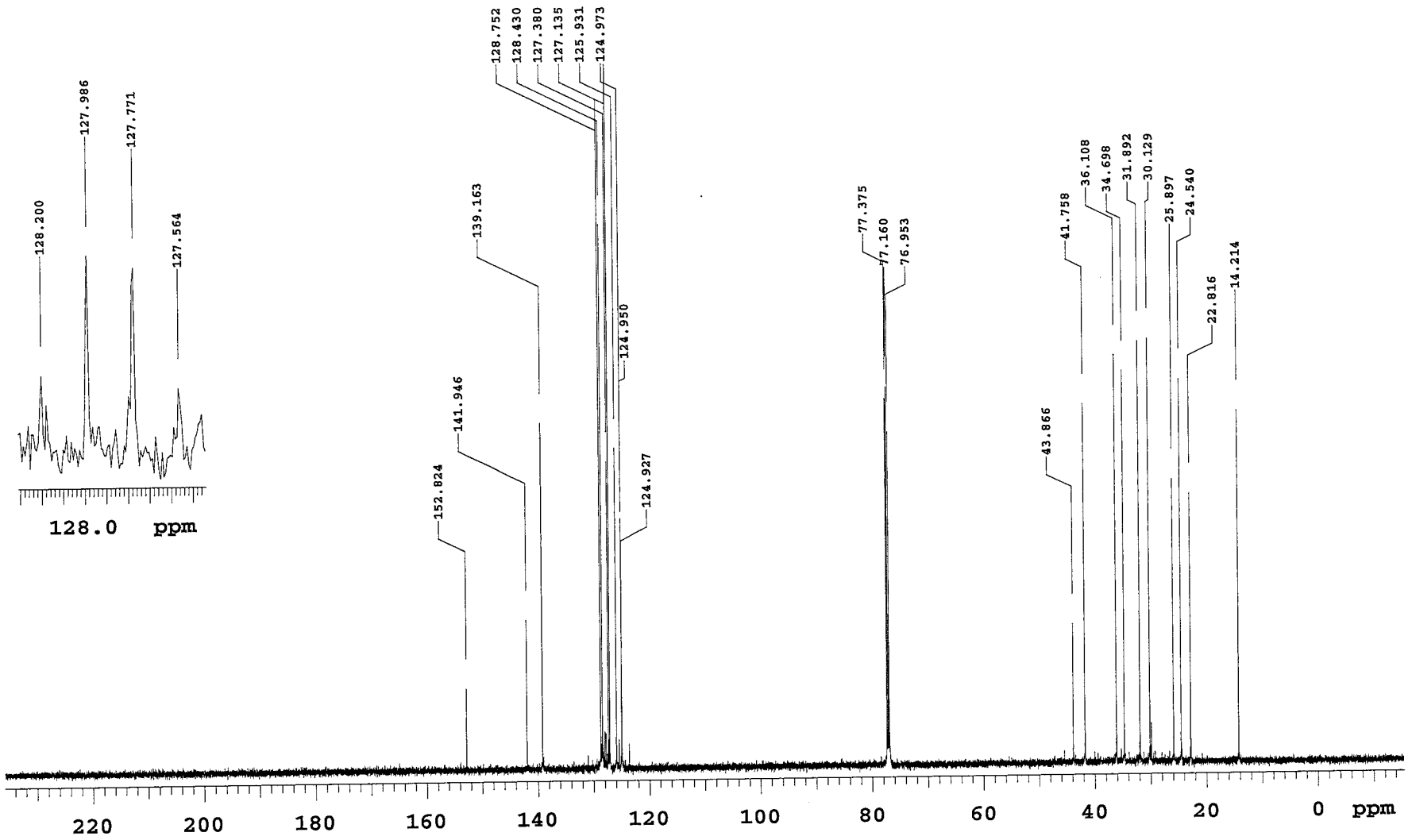

OMe
OMe
Me
hexyl
Ph
9

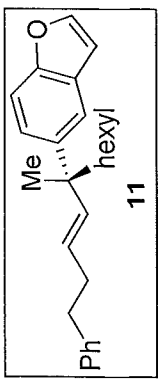

14.224
22.836
24.573
25.802
30.195
31.918
34.770
36.371
41.842
43.852
55.347
76.902
77.160
77.410
97.031
105.536
125.855
126.659
128.374
128.639
139.633
142.167
151.439
160.536
0
20
40
60
80
100
120
140
160
180
200
220
ppm

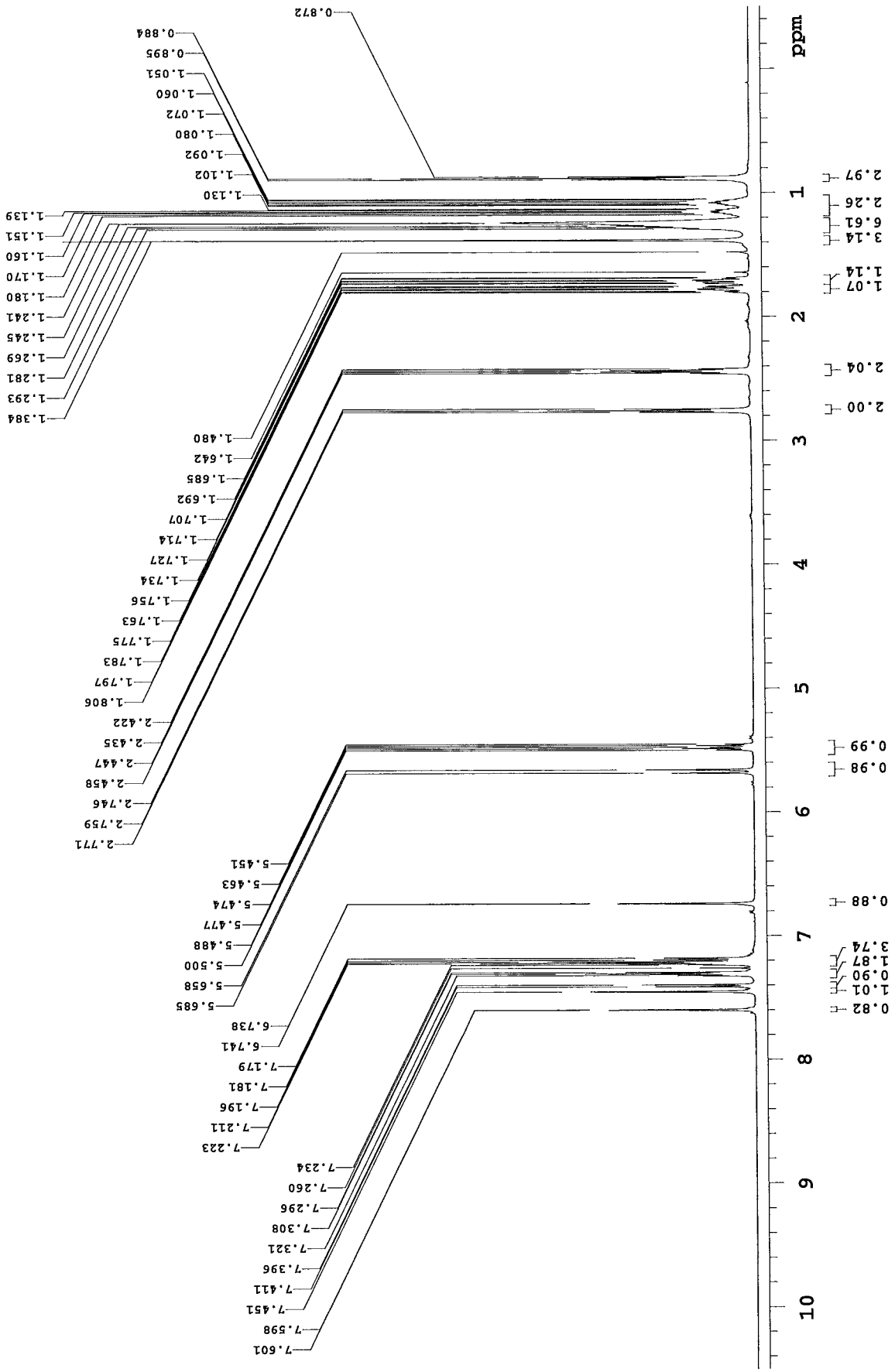

0.856
0.871
0.883
0.894
0.903
0.915
1.015
1.024
1.035
1.045
1.056
1.066
1.078
1.090
1.099
1.111
1.120
1.130
1.140
1.225
1.236
1.256
1.266
1.277
1.283
1.300
1.332
1.424
1.635
1.643
1.658
1.666
1.677
1.685
1.696
1.704
1.716
1.723
1.738
1.746
1.755
2.409
2.422
2.434
2.446
2.730
2.743
2.755
5.426
5.438
5.453
5.464
5.475
5.560
5.586
7.184
7.197
7.216
7.228
7.260
7.286
7.292
7.299
7.305
7.310
7.501
7.515
ppm
1
2
3
4
5
6
7
8
9
10
3.03
2.12
6.35
2.98
1.06
1.08
2.03
2.00
0.98
0.93
1.84
3.63
2.82
Me
CF3
hexyl
Ph
10

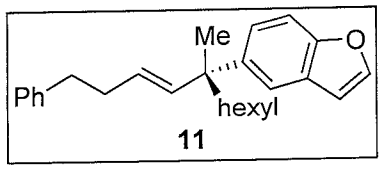

Me
CF3
Ph
hexyl

10

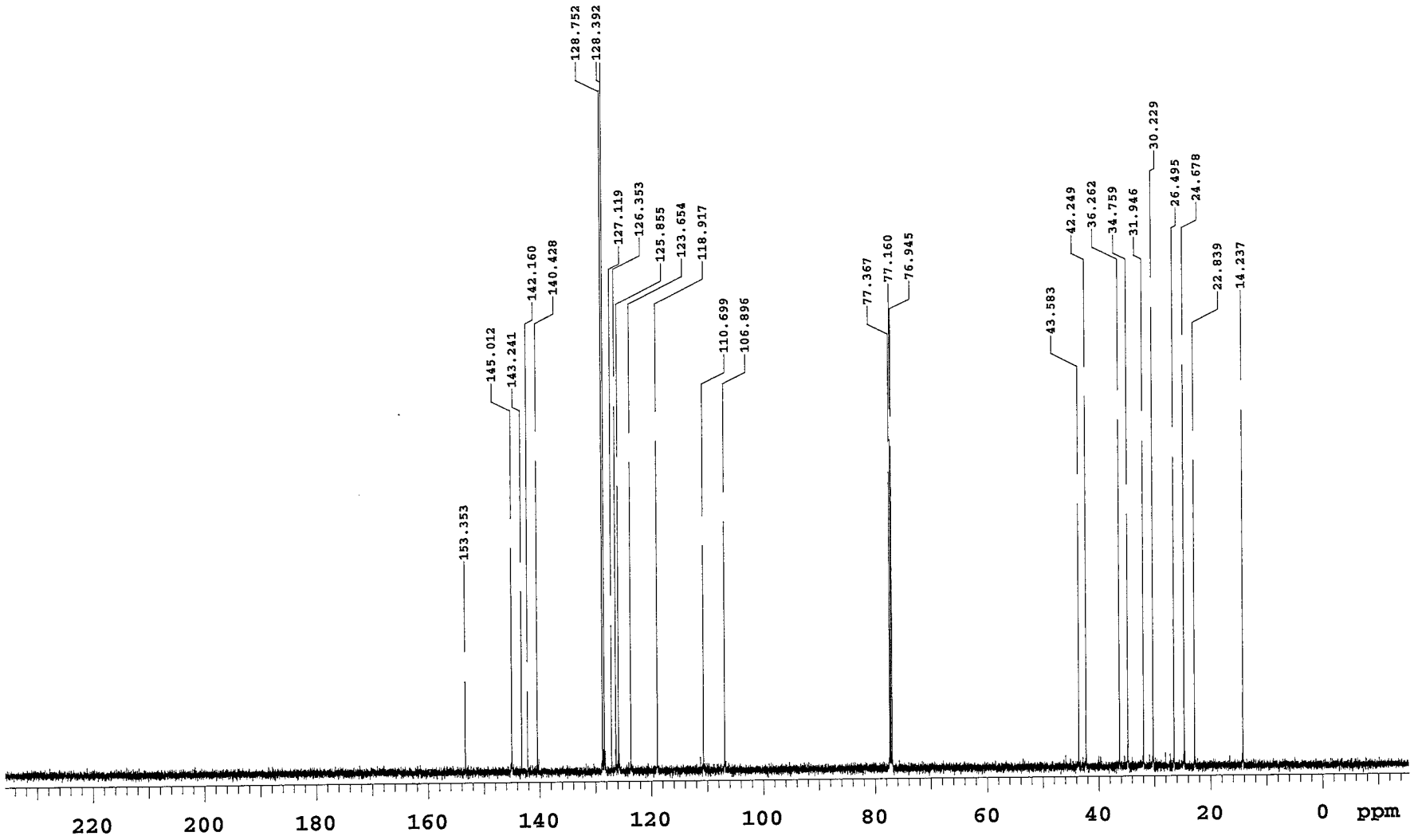

128.200
127.986
127.771
127.564
128.0 ppm
128.752
128.430
127.380
127.135
125.931
124.973
139.163
124.950
124.927
152.824
141.946
77.375
77.160
76.953
43.866
41.758
36.108
34.698
31.892
30.129
25.897
24.540
22.816
14.214
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
Me
hexyl
11
Ph


ppm
1
2
3
4
5
6
7
8
9
10
2.97
2.26
6.61
3.14
1.07
1.14
2.04
2.00
0.99
0.98
0.88
3.74
1.87
0.90
1.01
0.82
0.872
0.884
0.895
1.051
1.060
1.072
1.080
1.092
1.102
1.130
1.139
1.151
1.160
1.170
1.180
1.241
1.245
1.269
1.281
1.293
1.384
1.480
1.642
1.685
1.692
1.707
1.714
1.727
1.734
1.756
1.763
1.775
1.783
1.797
1.806
2.422
2.435
2.447
2.458
2.746
2.759
2.771
5.451
5.463
5.474
5.477
5.488
5.500
5.658
5.685
6.738
6.741
7.179
7.181
7.196
7.211
7.223
7.234
7.260
7.296
7.308
7.321
7.396
7.411
7.451
7.598
7.601


Me
O
Ph
hexyl

11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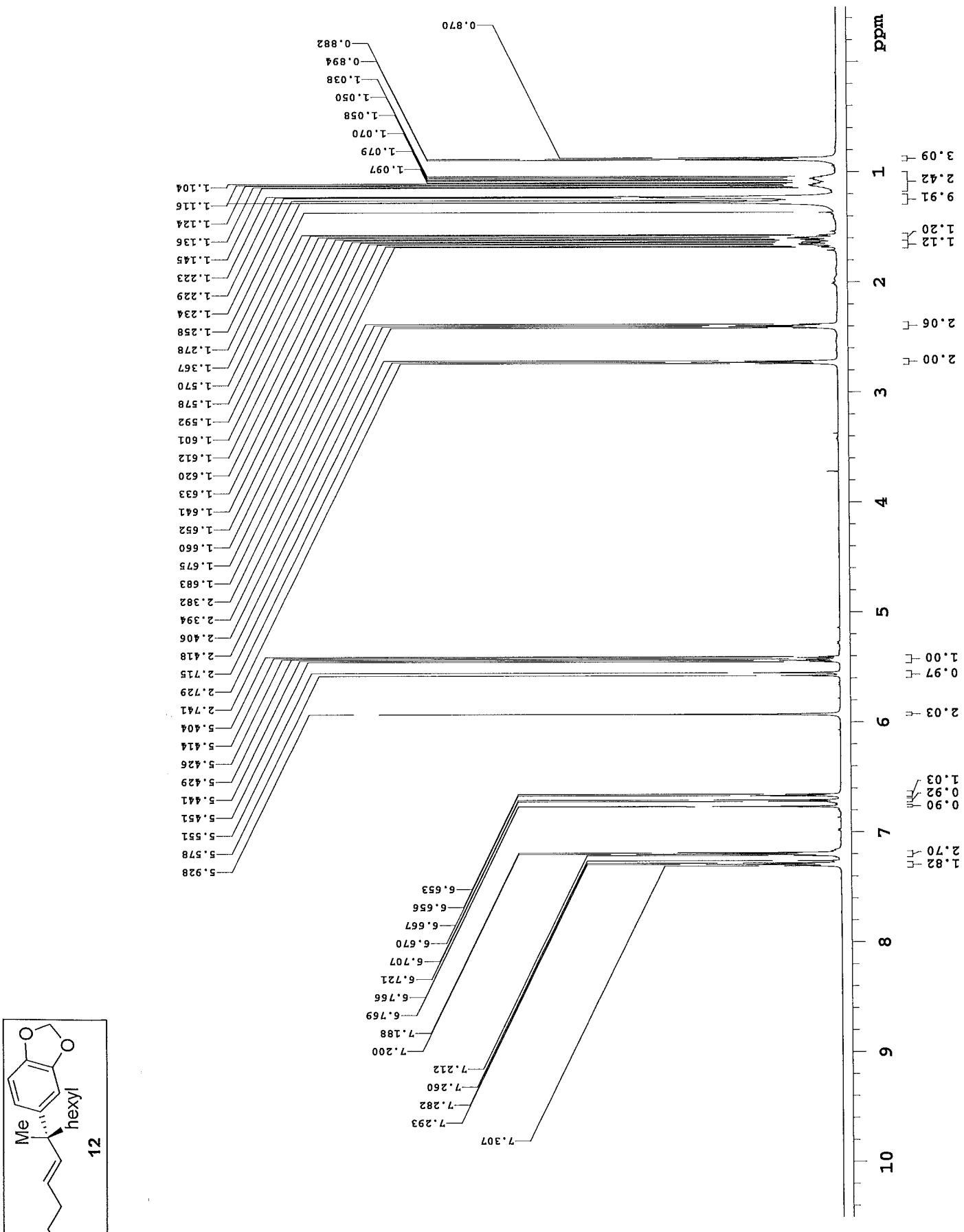
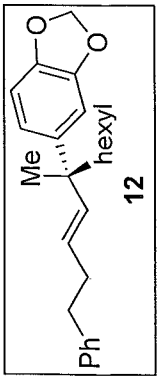
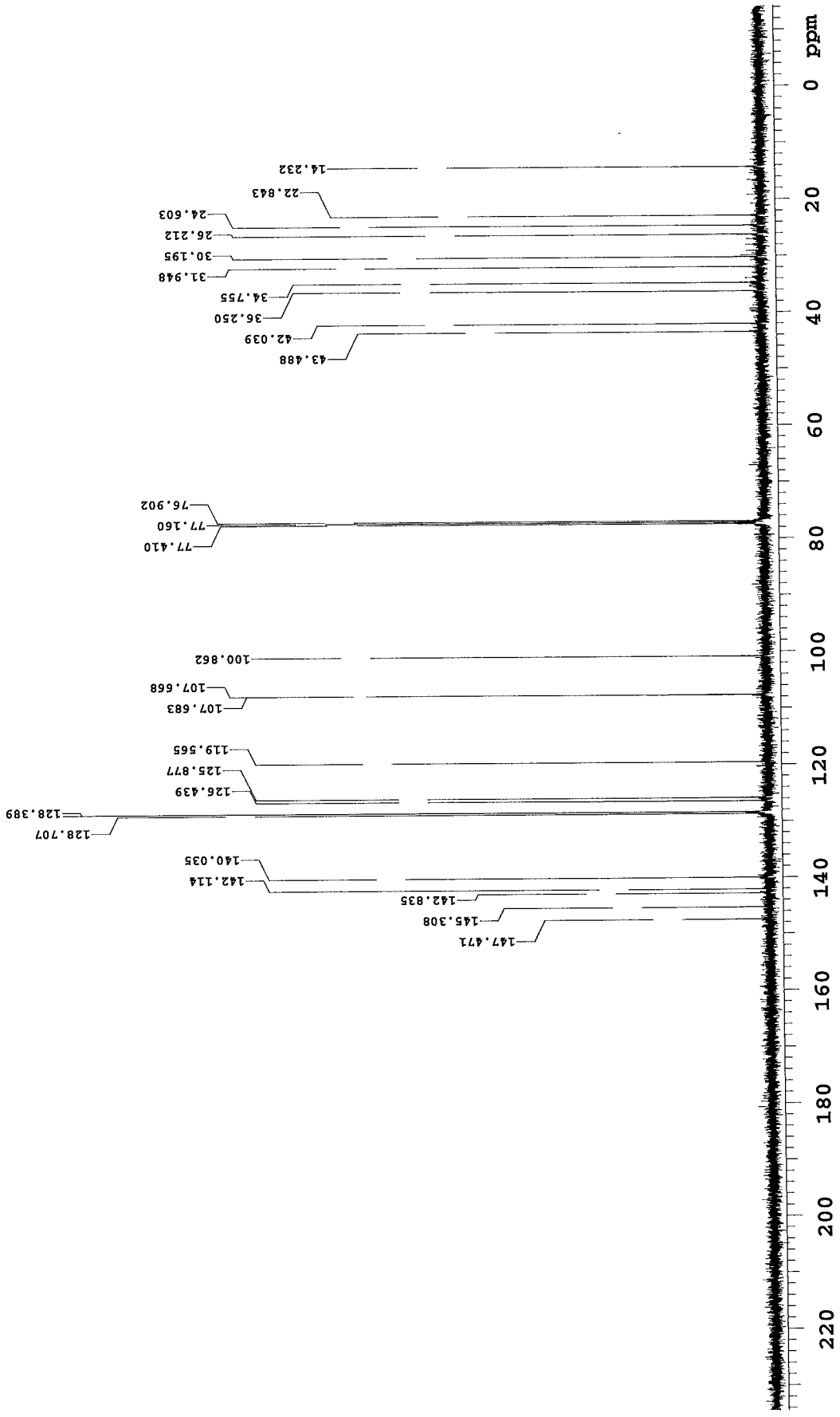
143.241
142.160
140.428
128.752
128.392
127.119
126.353
125.855
123.654
118.917
110.699
106.896
77.367
77.160
76.945
43.583
42.249
36.262
34.759
31.946
30.229
26.495
24.678
22.839
14.237
220
200
180
160
140
120
100
80
60
40
20
0
ppm


0.870
0.882
0.894
1.038
1.050
1.058
1.070
1.079
1.097
1.104
1.116
1.124
1.136
1.145
1.223
1.229
1.234
1.258
1.278
1.367
1.570
1.578
1.592
1.601
1.612
1.620
1.633
1.641
1.652
1.660
1.675
1.683
2.382
2.394
2.406
2.418
2.715
2.729
2.741
5.404
5.414
5.426
5.429
5.441
5.451
5.551
5.578
5.928
6.653
6.656
6.667
6.670
6.707
6.721
6.766
6.769
7.188
7.200
7.212
7.260
7.282
7.293
7.307
ppm
1
2
3
4
5
6
7
8
9
10
3.09
2.42
9.91
1.12
1.20
2.06
2.00
1.00
0.97
2.03
0.90
0.92
1.03
1.82
2.70
Me
hexyl
Ph
12


Me
hexyl
12
Ph


147.471
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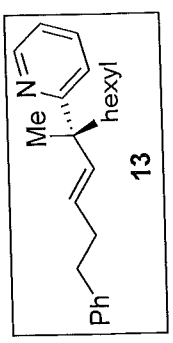
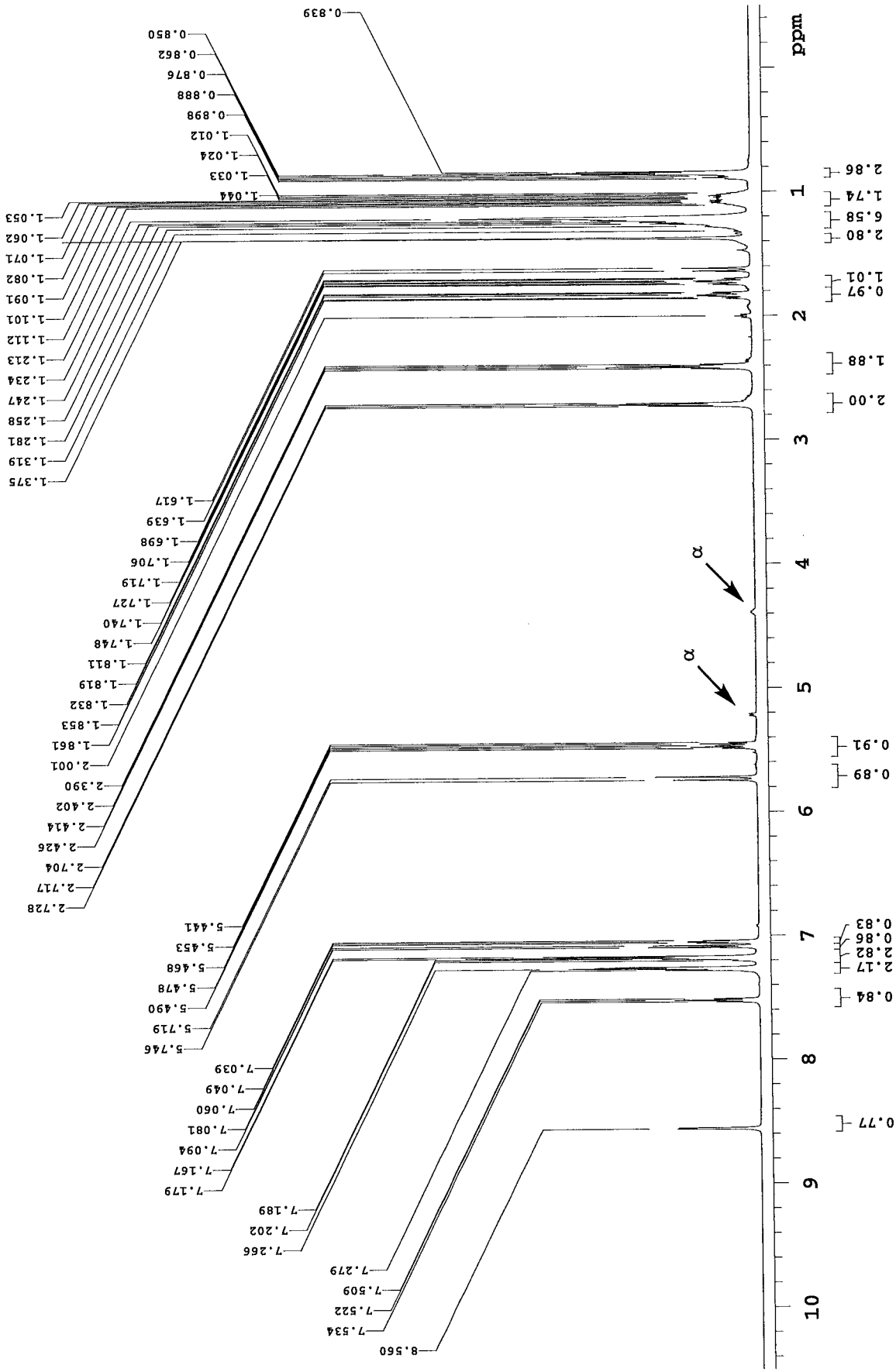
142.835
142.114
140.035
128.707
128.389
126.439
125.877
119.565
107.668
107.683
100.862
77.410
77.160
76.902
43.488
42.039
36.250
34.755
31.948
30.195
26.212
24.603
22.843
14.232
0 ppm
20
40
60
80
100
120
140
160
180
200
220


Me
N
hexyl
Ph
13


ppm
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α
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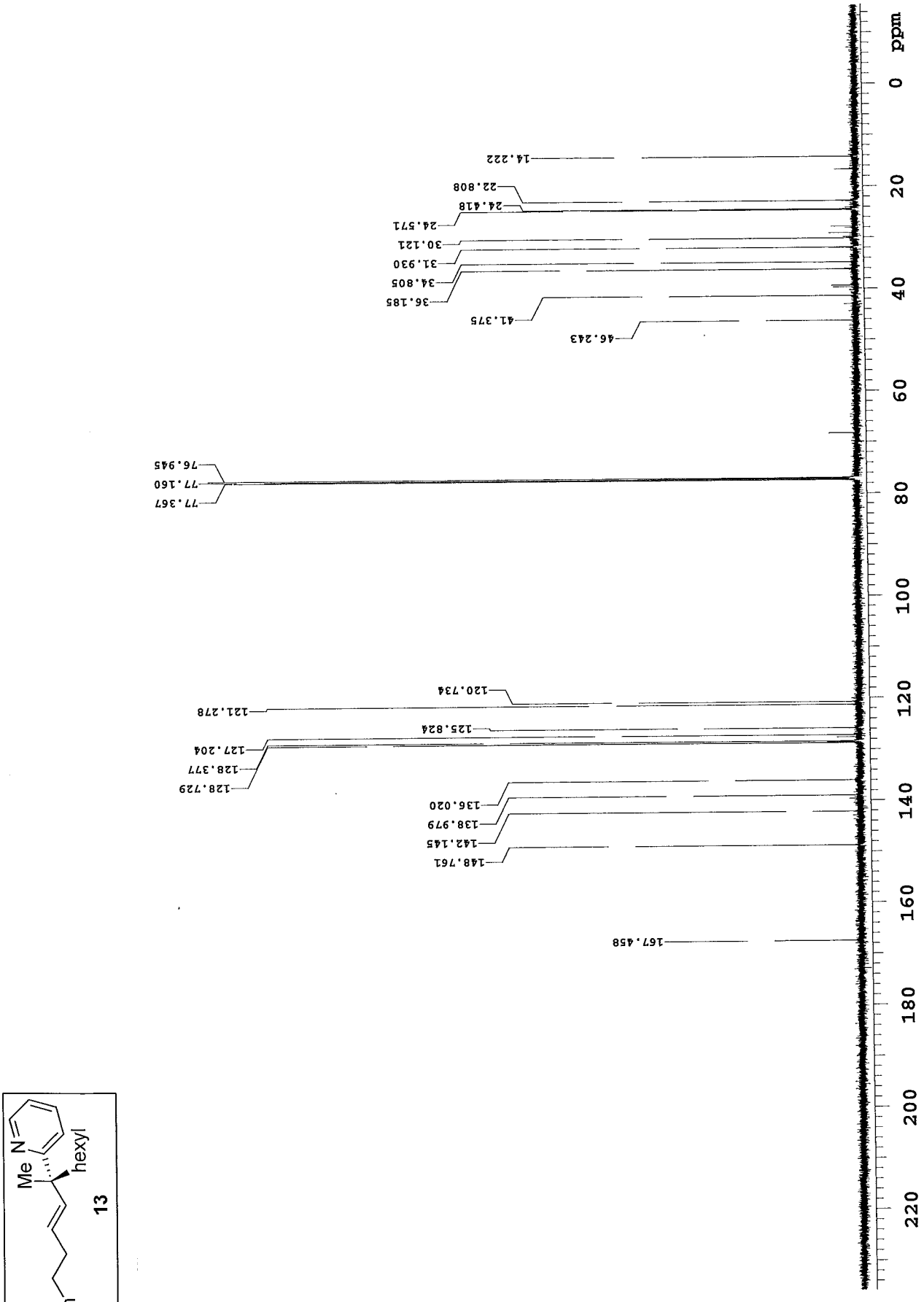
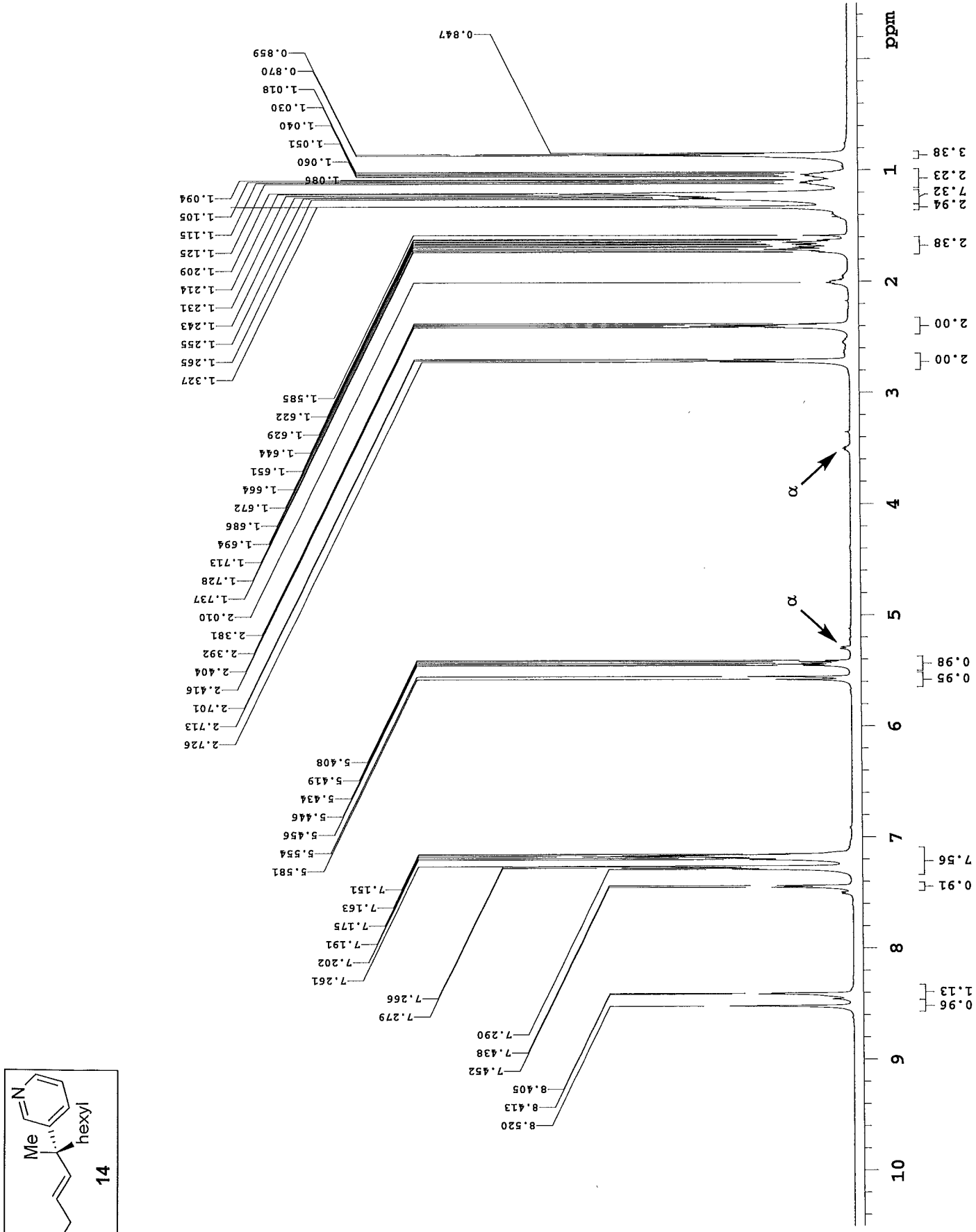
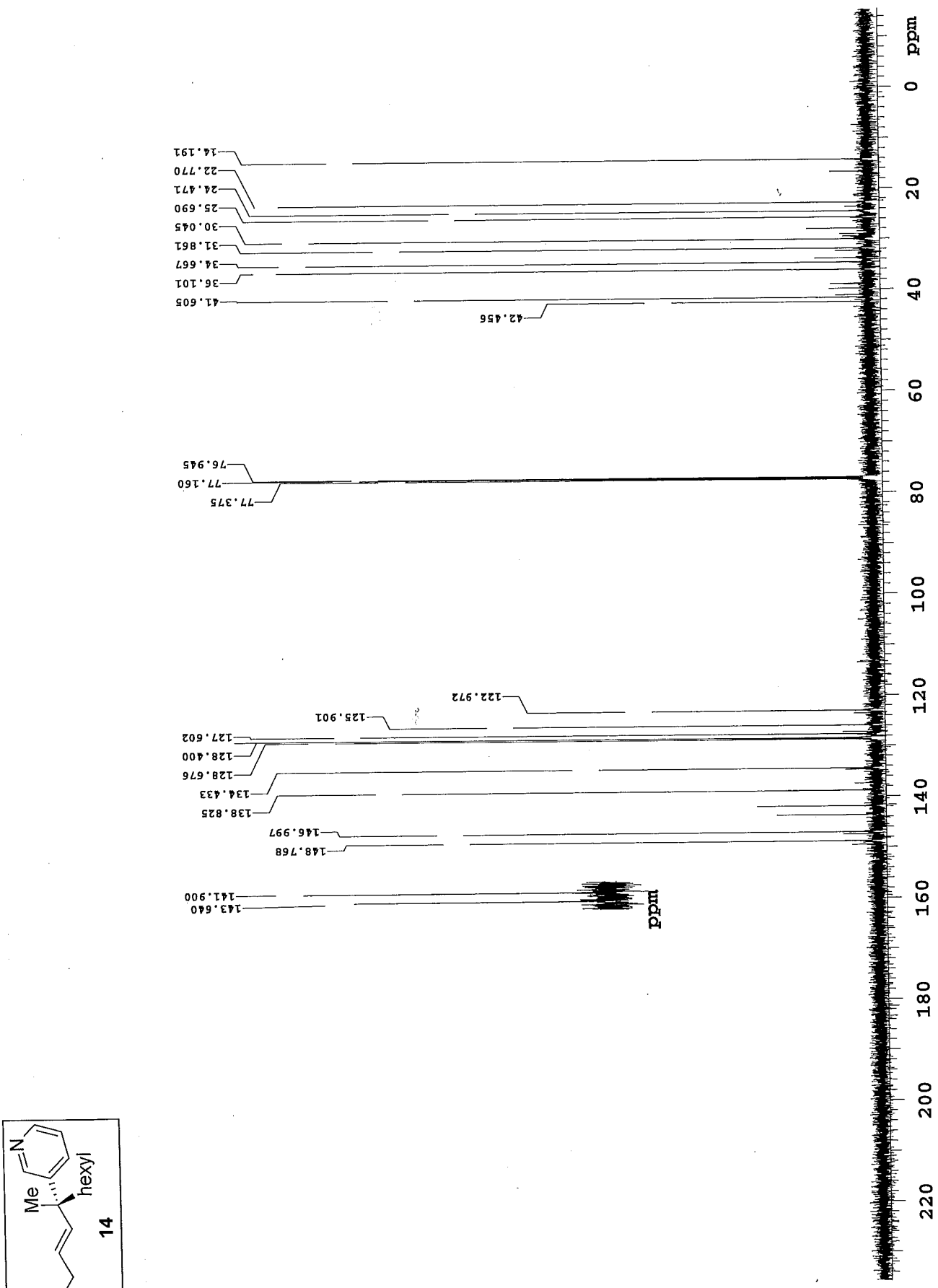
0.862
0.876
0.888
0.898
1.012
1.024
1.033
1.044
1.053
1.062
1.071
1.082
1.091
1.101
1.112
1.213
1.234
1.247
1.258
1.281
1.319
1.375
1.617
1.639
1.698
1.706
1.719
1.727
1.740
1.748
1.811
1.819
1.832
1.853
1.861
2.001
2.390
2.402
2.414
2.426
2.704
2.717
2.728
5.441
5.453
5.468
5.478
5.490
5.719
5.746
7.039
7.049
7.060
7.081
7.094
7.167
7.179
7.189
7.202
7.266
7.279
7.509
7.522
7.534
8.560
0.77
0.84
2.17
2.82
0.86
0.83
0.89
0.91
2.00
1.88
0.97
1.01
2.80
6.58
1.74
2.86


14.222
22.808
24.418
24.571
30.121
31.930
34.805
36.185
41.375
46.243
76.945
77.160
77.367
120.734
121.278
125.824
127.204
128.377
128.729
136.020
138.979
142.145
148.761
167.458
0 ppm
20
40
60
80
100
120
140
160
180
200
220
Me
N
hexyl
Ph
13


0.847
0.859
0.870
1.018
1.030
1.040
1.051
1.060
1.086
1.094
1.105
1.115
1.125
1.209
1.214
1.231
1.243
1.255
1.265
1.327
1.585
1.622
1.629
1.644
1.651
1.664
1.672
1.686
1.694
1.713
1.728
1.737
2.010
2.381
2.392
2.404
2.416
2.701
2.713
2.726
5.408
5.419
5.434
5.446
5.456
5.554
5.581
7.151
7.163
7.175
7.191
7.202
7.261
7.266
7.279
7.290
7.438
7.452
8.405
8.413
8.520
α
α
ppm
1
2
3
4
5
6
7
8
9
10
3.38
2.23
7.32
2.94
2.38
2.00
2.00
0.98
0.95
7.56
0.91
1.13
0.96

N
Me
hexyl
Ph
14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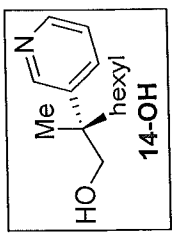
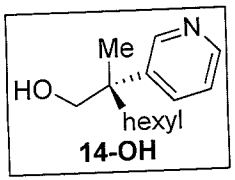
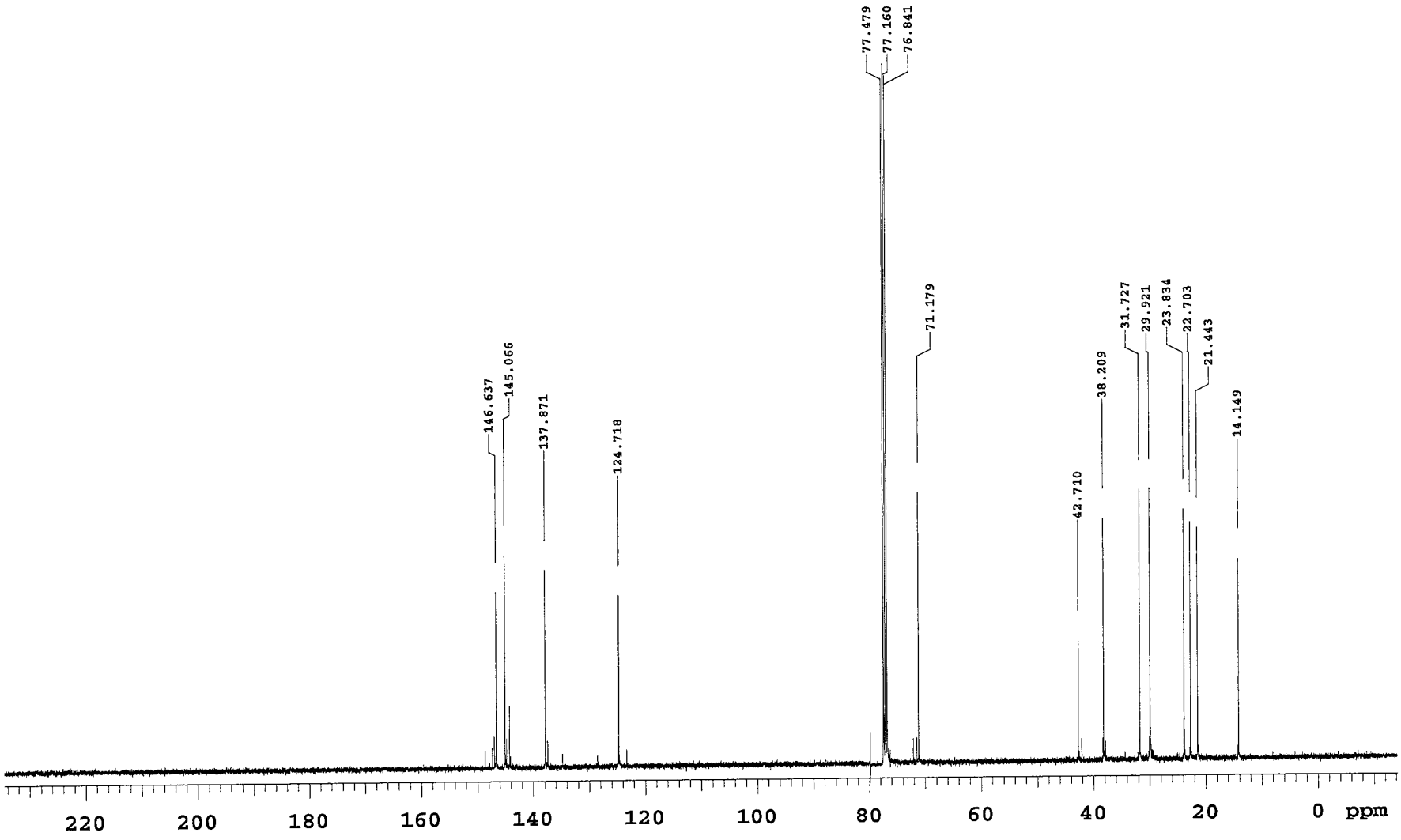
24.471
25.690
30.045
31.861
34.667
36.101
41.605
42.456
76.945
77.160
77.375
122.972
125.901
127.602
128.400
128.676
134.433
138.825
146.997
148.768
141.900
143.640
ppm
0
20
40
60
80
100
120
140
160
180
200
220
ppm
N
Me
hexyl
Ph
14


N
Me
hexyl
HO
14-OH


Me
HO
N
hexyl

14-OH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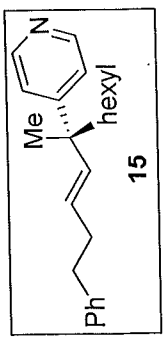
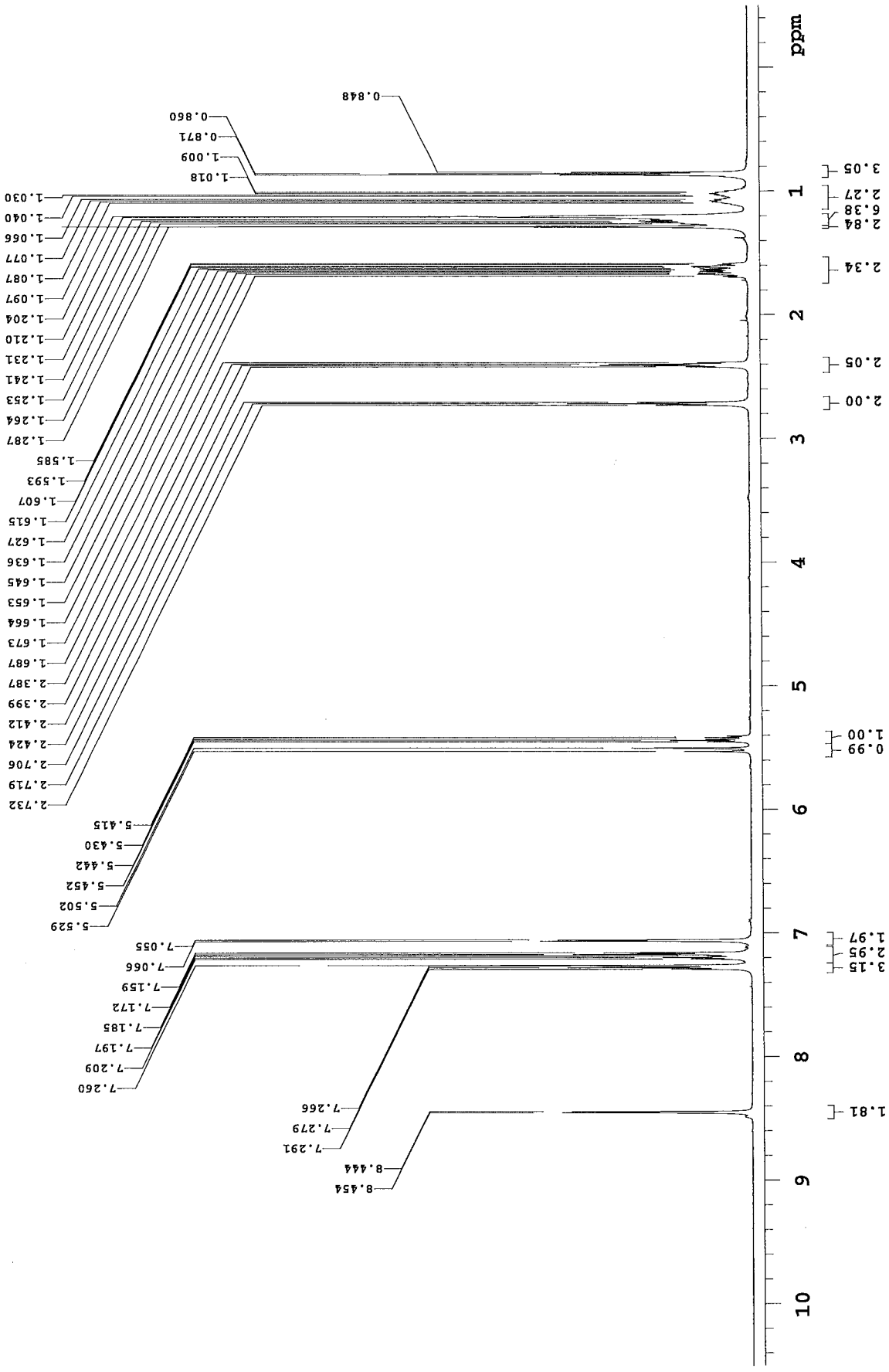
77.160
76.841
146.637
145.066
137.871
124.718
71.179
42.710
38.209
31.727
29.921
23.834
22.703
21.443
14.149
220
200
180
160
140
120
100
80
60
40
20
0
ppm


N
Me
hexyl
Ph
15


ppm
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0.860
0.871
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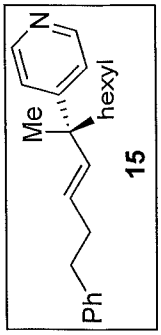
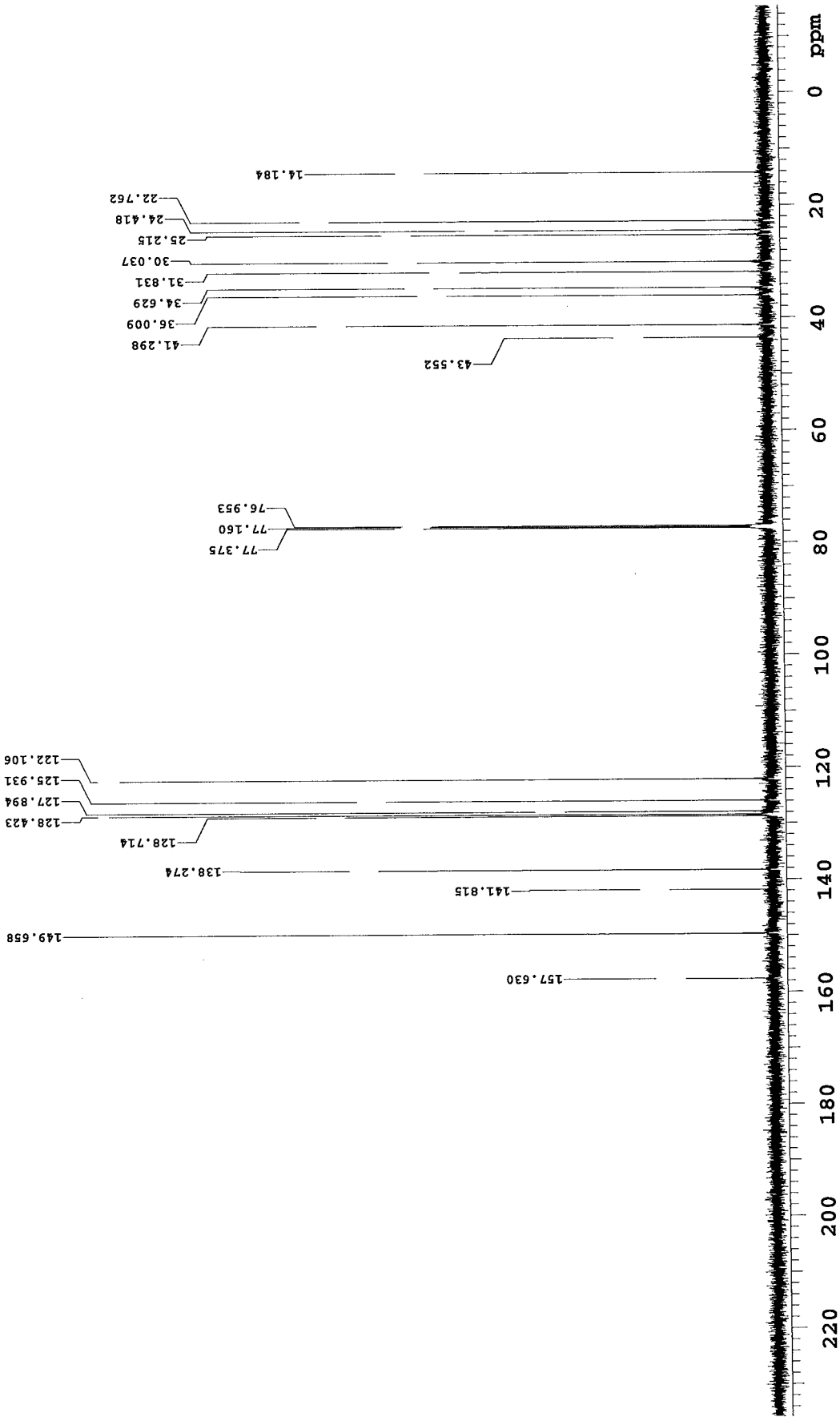
1.018
1.030
1.040
1.056
1.077
1.087
1.097
1.204
1.210
1.231
1.241
1.253
1.264
1.287
1.585
1.593
1.607
1.615
1.627
1.636
1.645
1.653
1.664
1.673
1.687
2.387
2.399
2.412
2.424
2.706
2.719
2.732
5.415
5.430
5.442
5.452
5.502
5.529
7.055
7.066
7.159
7.172
7.185
7.197
7.209
7.260
7.266
7.279
7.291
8.444
8.454
3.05
2.27
6.38
2.84
2.34
2.05
2.00
1.00
0.99
1.97
2.95
3.15
1.81


N
Me
hexyl
Ph
15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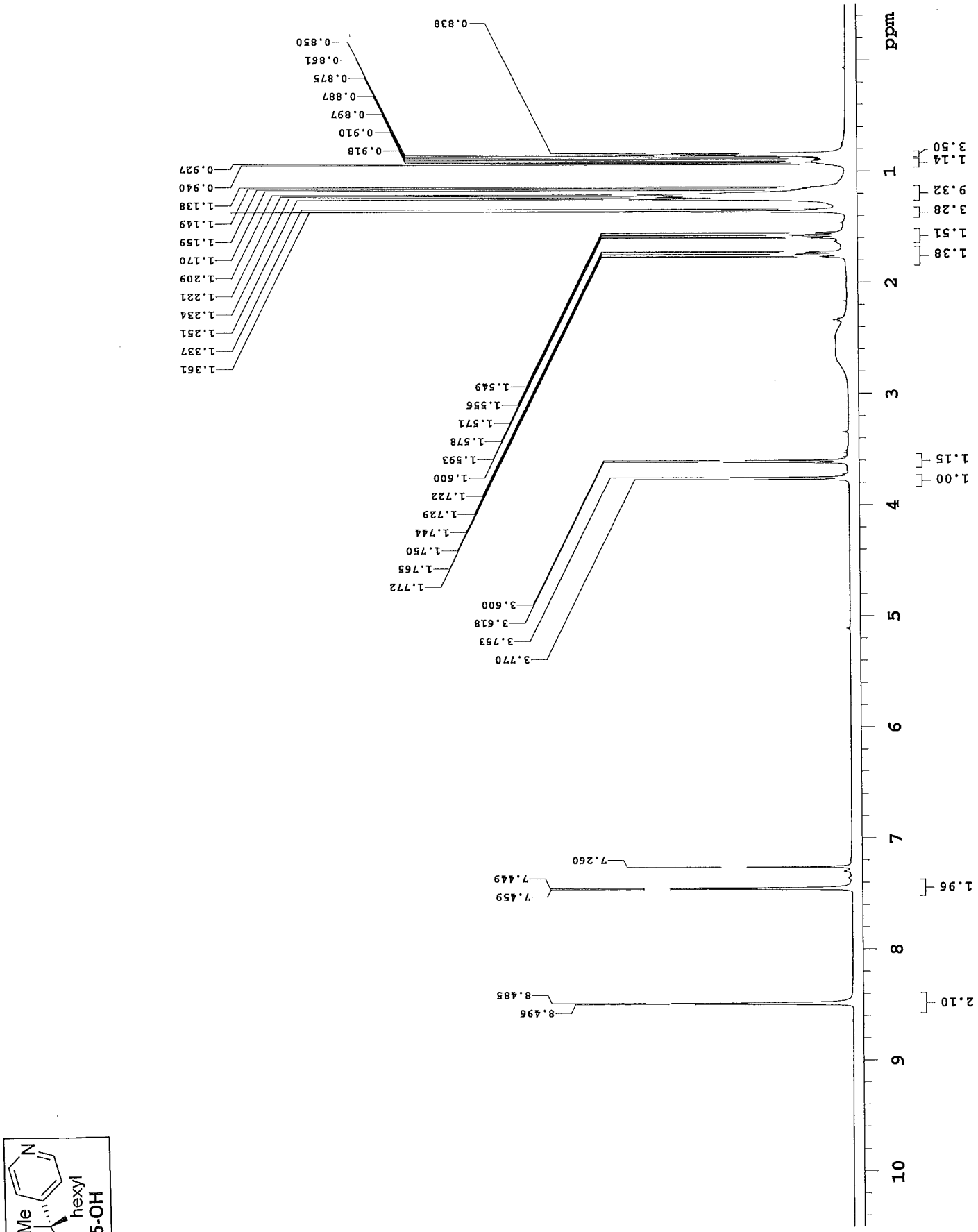
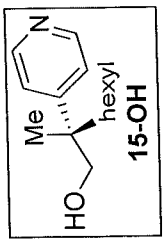
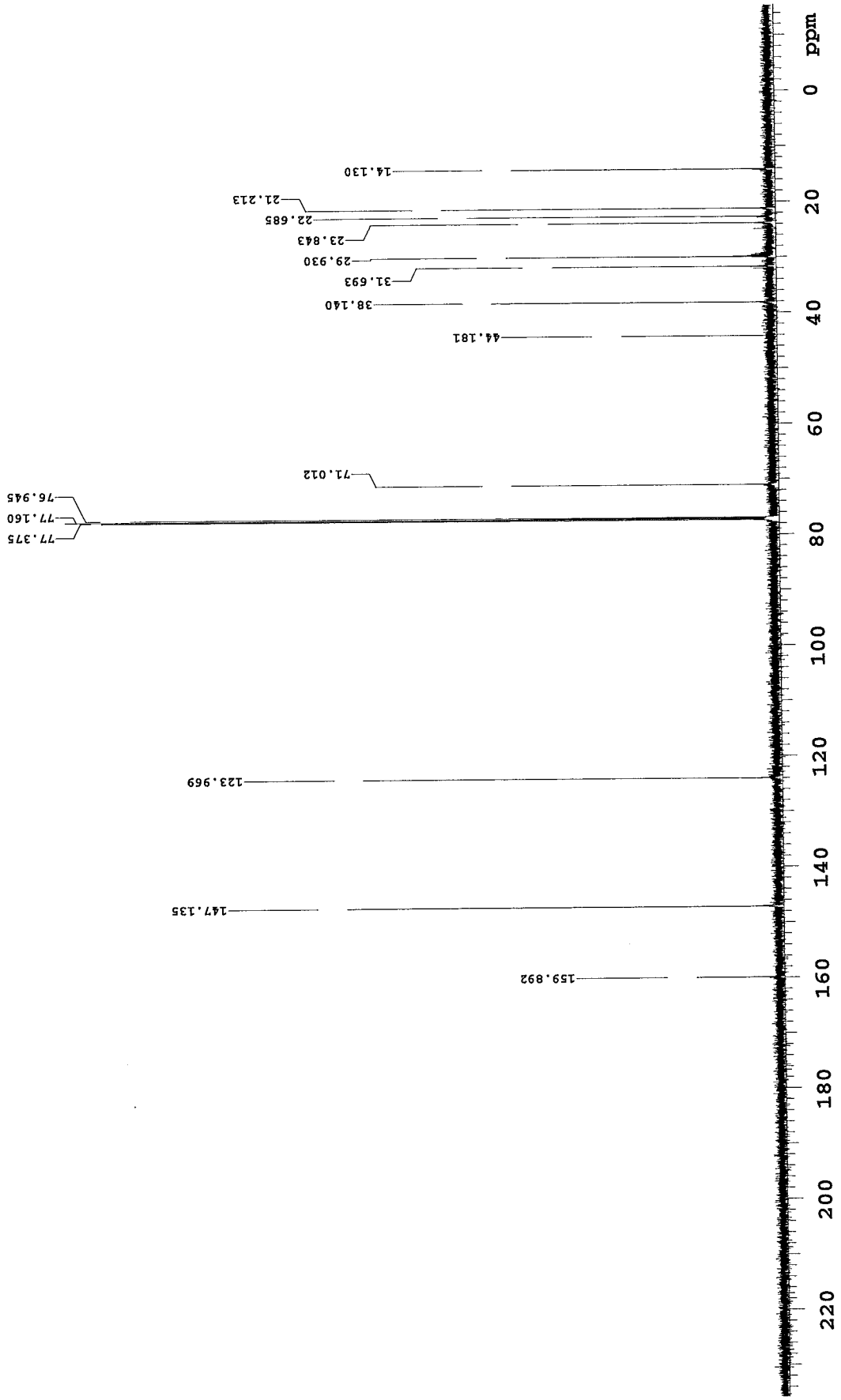
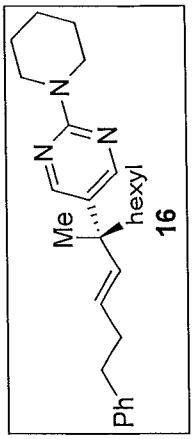
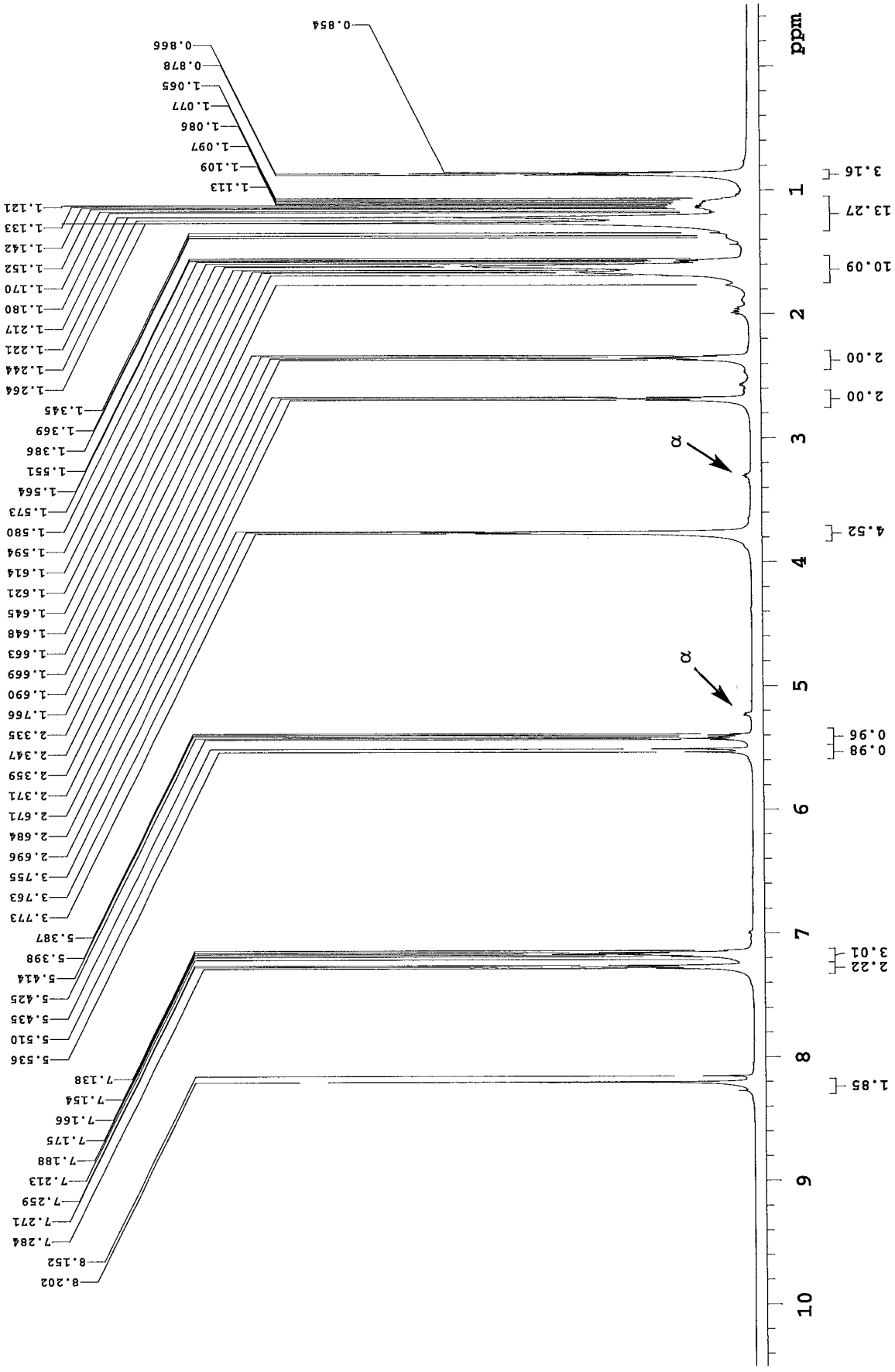
24.418
25.215
30.037
31.831
34.629
36.009
41.298
43.552
76.953
77.160
77.375
122.106
125.931
127.894
128.423
128.714
138.274
141.815
149.658
157.630
0
20
40
60
80
100
120
140
160
180
200
220
ppm

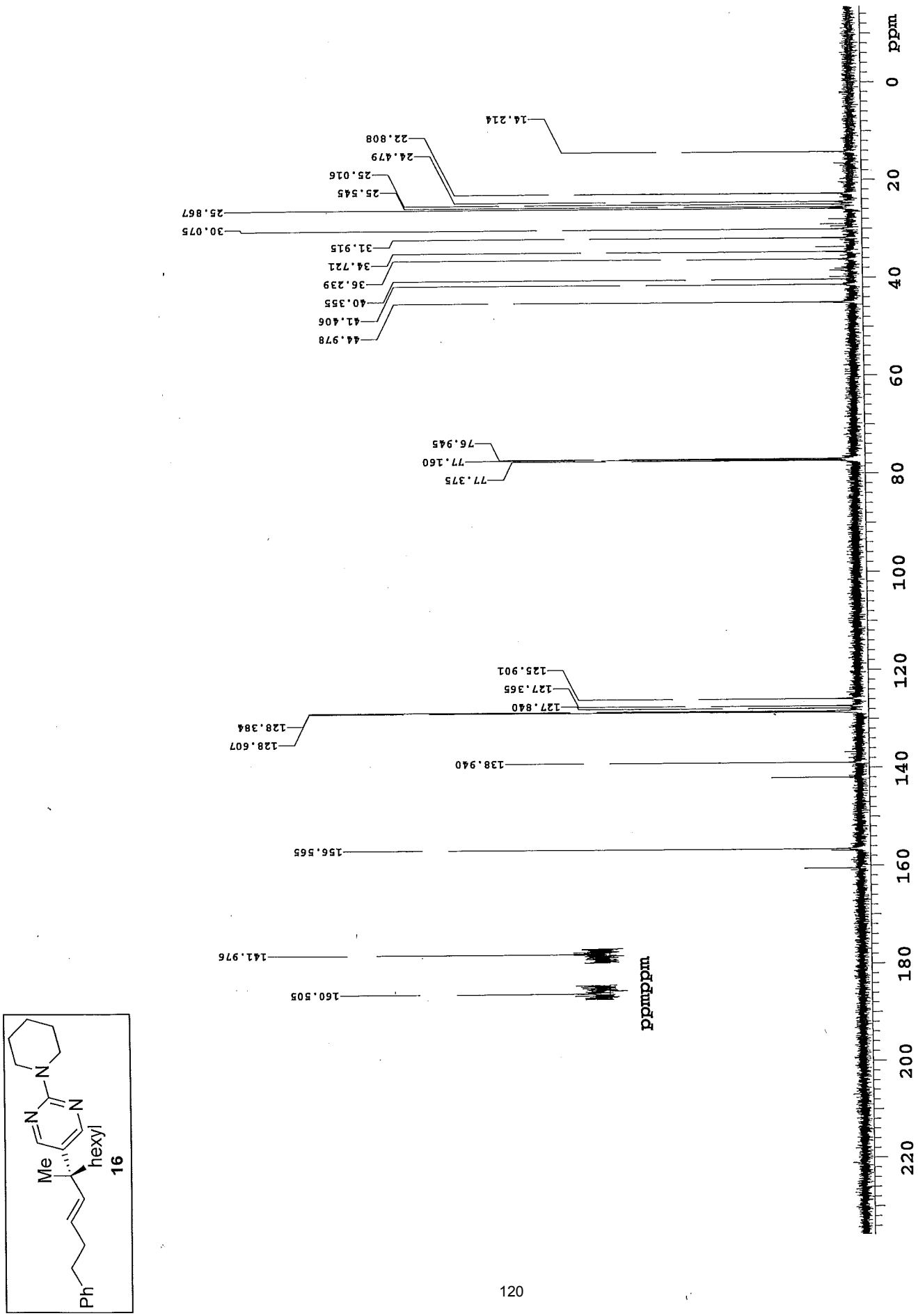

ppm
1 2 3 4 5 6 7 8 9 10
2.10
1.96
1.00
1.15
1.38
1.51
3.28
9.32
1.14
3.50
8.496
8.485
7.459
7.449
7.260
3.770
3.753
3.618
3.600
1.772
1.765
1.750
1.744
1.729
1.722
1.600
1.593
1.578
1.571
1.556
1.549
1.361
1.337
1.251
1.234
1.221
1.209
1.170
1.159
1.149
1.138
0.940
0.927
0.918
0.910
0.897
0.887
0.875
0.861
0.850
0.838
N
Me
hexyl
15-OH
HO

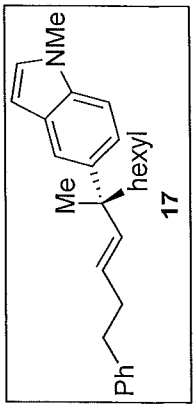

N
Me
hexyl
HO
15-OH

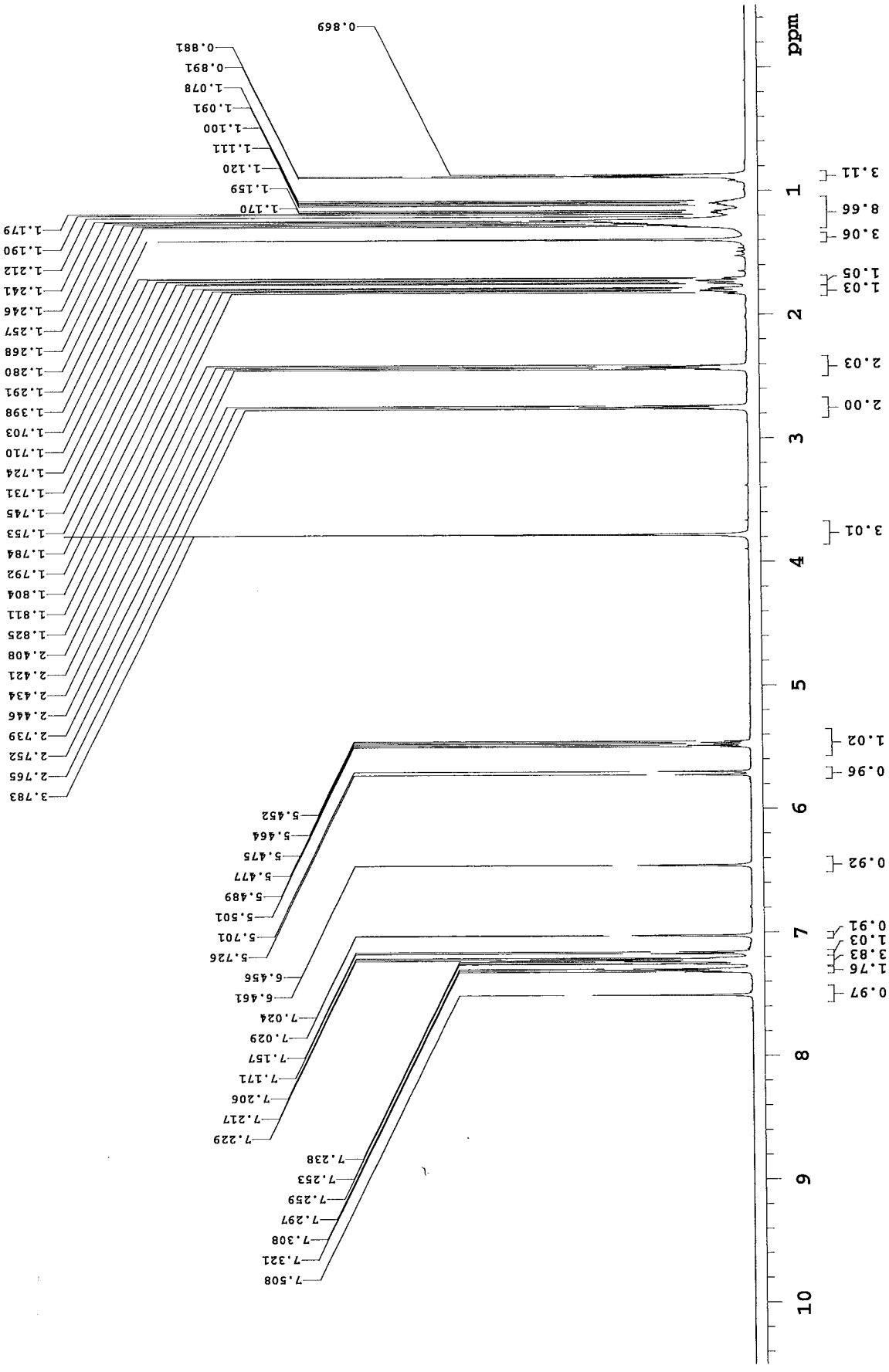

14.130
21.213
22.685
23.843
29.930
31.693
38.140
44.181
71.012
76.945
77.160
77.375
123.969
147.135
159.892
0
20
40
60
80
100
120
140
160
180
200
220
ppm

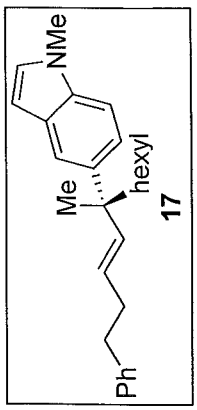

Me
hexyl
Ph
16

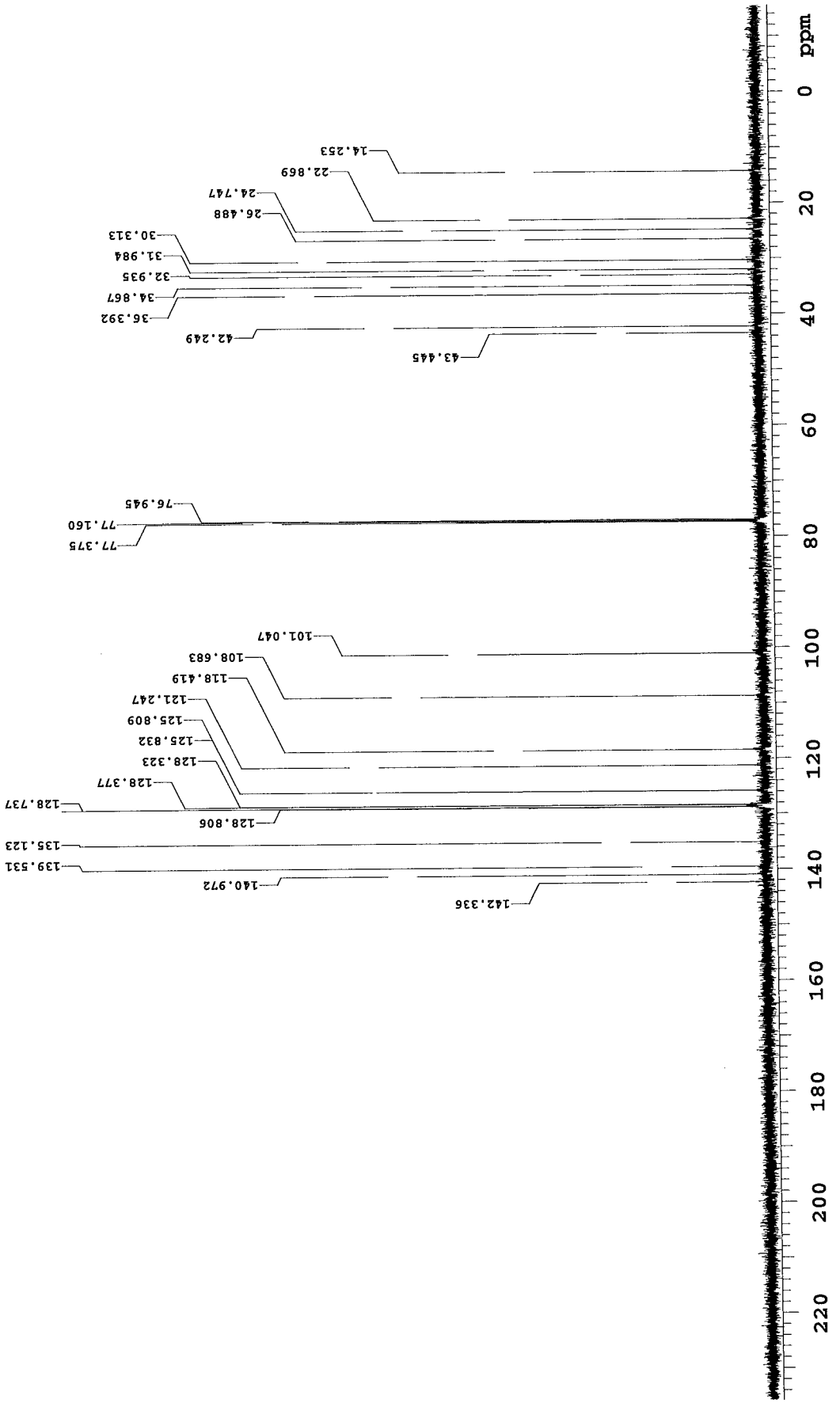

ppm
α
α
3.16
13.27
10.09
2.00
2.00
4.52
0.98
0.96
2.22
3.01
1.85
0.854
0.866
0.878
1.065
1.077
1.086
1.097
1.109
1.113
1.121
1.133
1.142
1.152
1.170
1.180
1.217
1.221
1.244
1.264
1.345
1.369
1.386
1.551
1.564
1.573
1.580
1.594
1.614
1.621
1.645
1.648
1.663
1.669
1.690
1.766
2.335
2.347
2.359
2.371
2.671
2.684
2.696
3.755
3.763
3.773
5.387
5.398
5.414
5.425
5.435
5.510
5.536
7.138
7.154
7.166
7.175
7.188
7.213
7.259
7.271
7.284
8.152
8.202

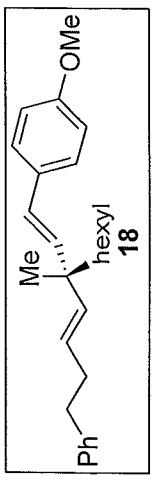

14.214
22.808
24.479
25.016
25.545
25.867
30.075
31.915
34.721
36.239
40.355
41.406
44.978
76.945
77.160
77.375
125.901
127.365
127.840
128.384
128.607
138.940
156.565
141.976
160.505
ppm
0
20
40
60
80
100
120
140
160
180
200
220
Me
hexyl
Ph
16

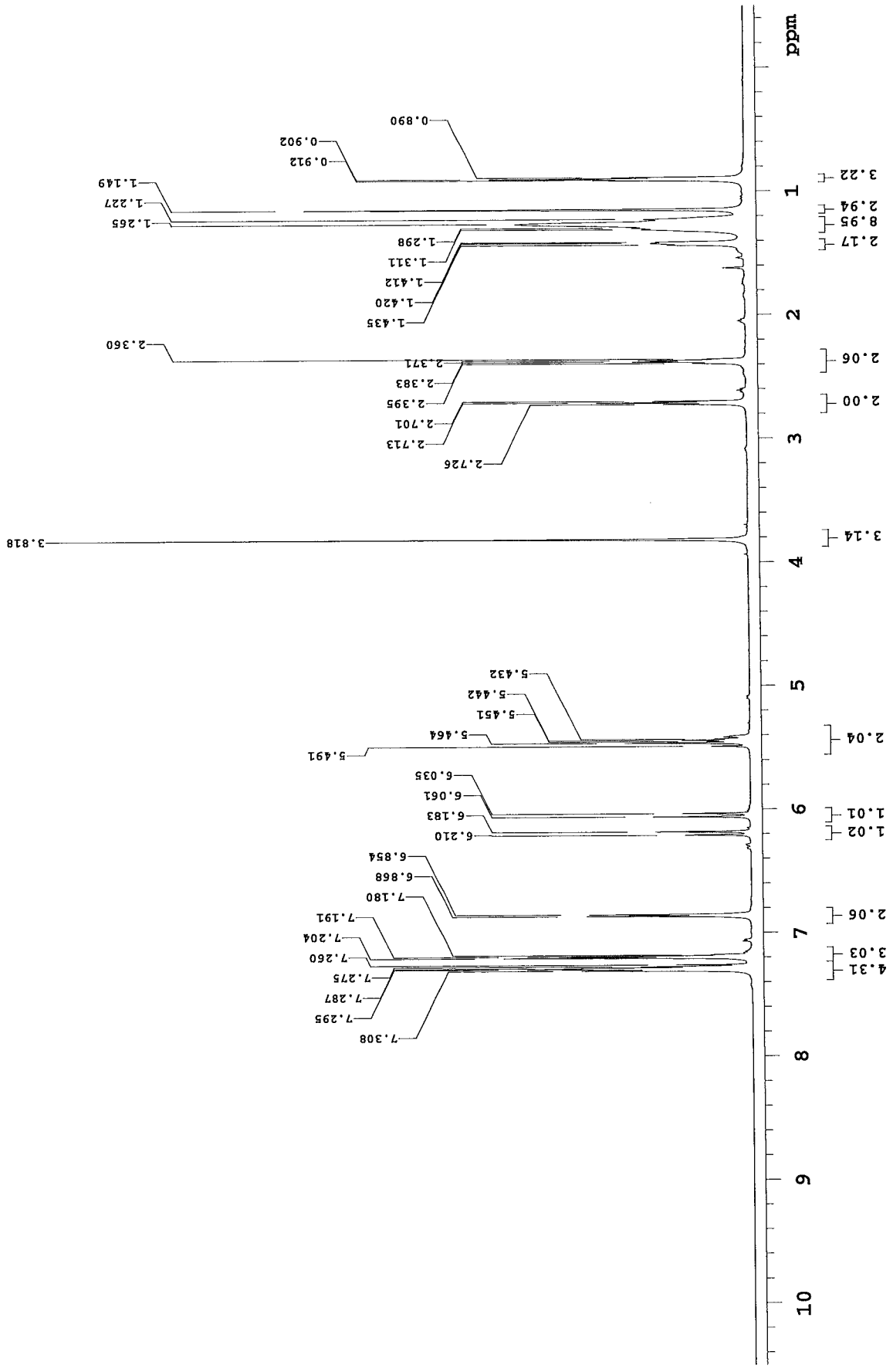

NMe
Me
hexyl
Ph
17


ppm
1
2
3
4
5
6
7
8
9
10
3.11
8.66
3.06
1.03
1.05
2.03
2.00
3.01
1.02
0.96
0.92
0.97
1.76
3.83
1.03
0.91
0.869
0.881
0.891
1.078
1.091
1.100
1.111
1.120
1.159
1.170
1.179
1.190
1.212
1.241
1.246
1.257
1.268
1.280
1.291
1.398
1.703
1.710
1.724
1.731
1.745
1.753
1.784
1.792
1.804
1.811
1.825
2.408
2.421
2.434
2.446
2.739
2.752
2.765
3.783
5.452
5.464
5.475
5.477
5.489
5.501
5.701
5.726
6.456
6.461
7.024
7.029
7.157
7.171
7.206
7.217
7.229
7.238
7.253
7.259
7.297
7.308
7.321
7.508


NMe
Me
hexyl
Ph
17


14.253
22.869
24.747
26.488
30.313
31.984
32.935
34.867
36.392
42.249
43.445
76.945
77.160
77.375
101.047
108.683
118.419
121.247
125.809
125.832
128.323
128.377
128.737
128.806
135.123
139.531
140.972
142.336
0
20
40
60
80
100
120
140
160
180
200
220
ppm


OMe
Me
hexyl
18
Ph


ppm
1
2
3
4
5
6
7
8
9
10
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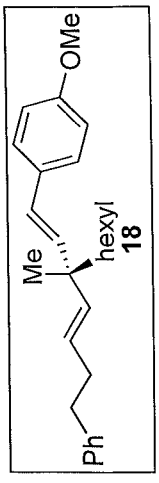
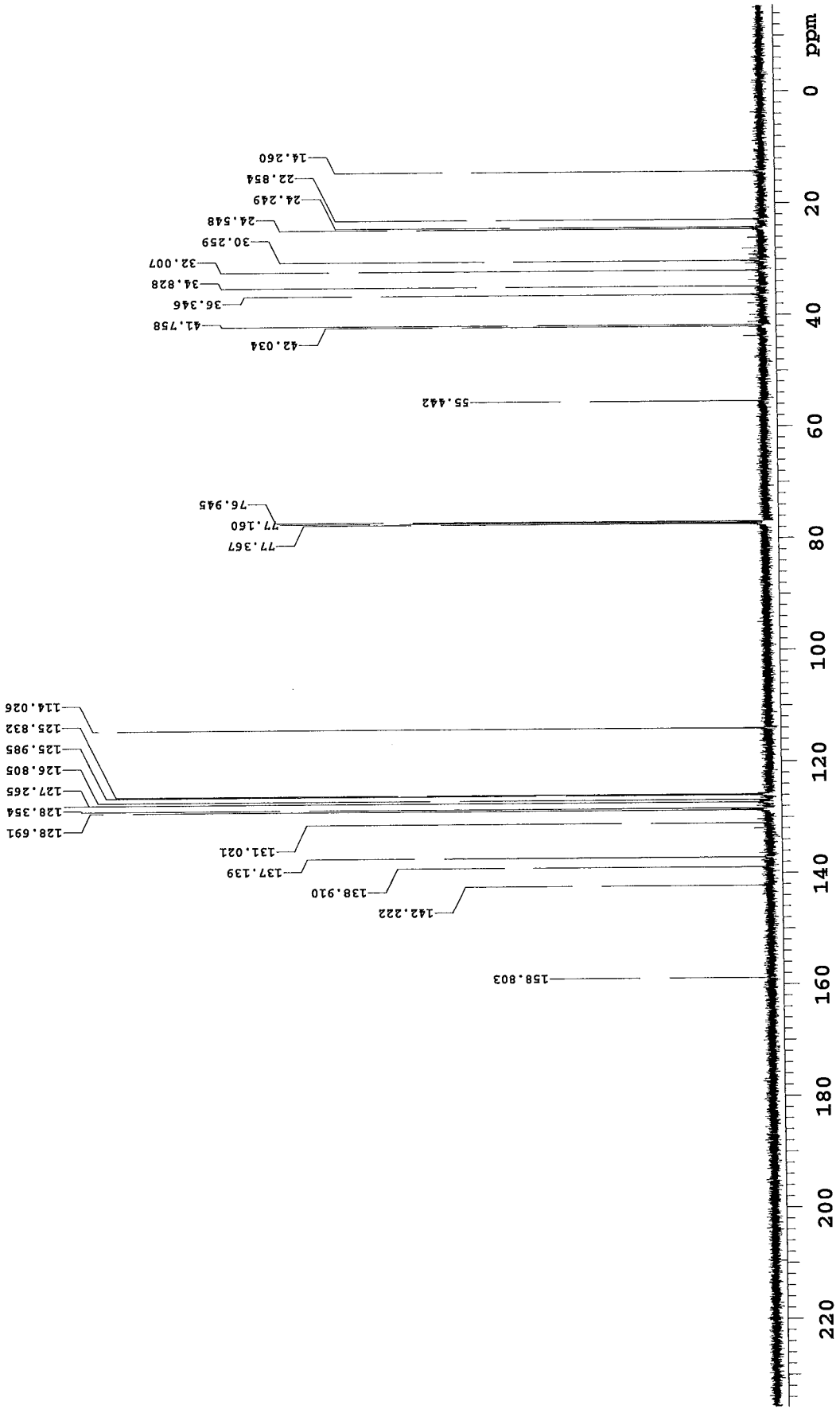
0.902
0.912
1.149
1.227
1.265
1.298
1.311
1.412
1.420
1.435
2.360
2.371
2.383
2.395
2.701
2.713
2.726
3.818
5.432
5.442
5.451
5.464
5.491
6.035
6.061
6.183
6.210
6.854
6.868
7.180
7.191
7.204
7.260
7.275
7.287
7.295
7.308
3.22
2.94
8.95
2.17
2.06
2.00
3.14
2.04
1.01
1.02
2.06
3.03
4.31


OMe
Me
hexyl
18
Ph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138.910
137.139
131.021
128.691
128.354
127.265
126.805
125.985
125.832
114.026
77.367
77.160
76.945
55.442
42.034
41.758
36.346
34.828
32.007
30.259
24.548
24.249
22.854
14.260
ppm
0
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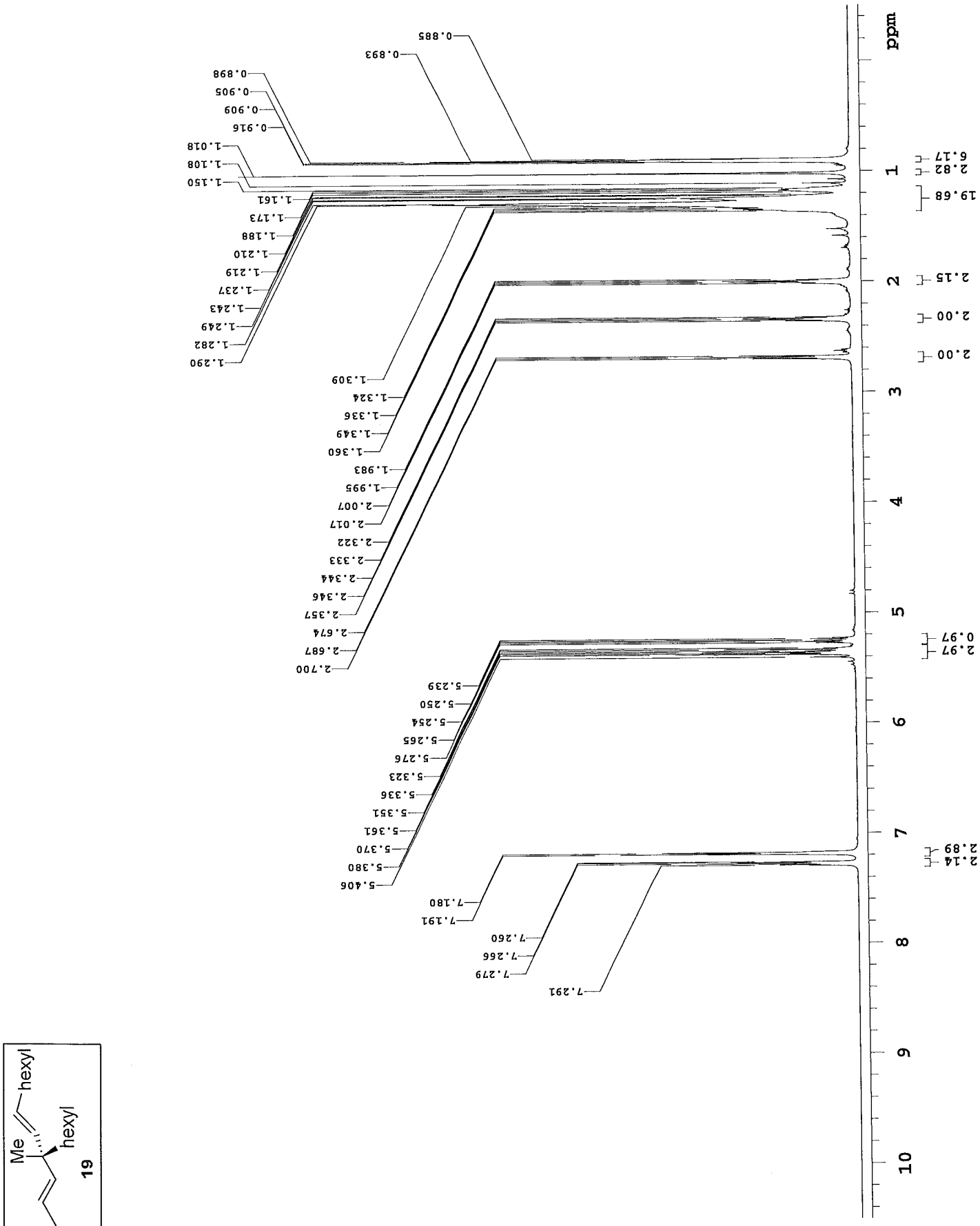
40
60
80
100
120
140
160
180
200
220


Me
hexyl
hexyl
Ph
19
ppm
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0.898
0.905
0.909
0.916
1.018
1.108
1.150
1.161
1.173
1.188
1.210
1.219
1.237
1.243
1.249
1.282
1.290
1.309
1.324
1.336
1.349
1.360
1.983
1.995
2.007
2.017
2.322
2.333
2.344
2.346
2.357
2.674
2.687
2.700
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5.250
5.254
5.265
5.276
5.323
5.336
5.351
5.361
5.370
5.380
5.406
7.180
7.191
7.260
7.266
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7.291
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2.00
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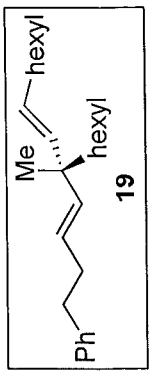
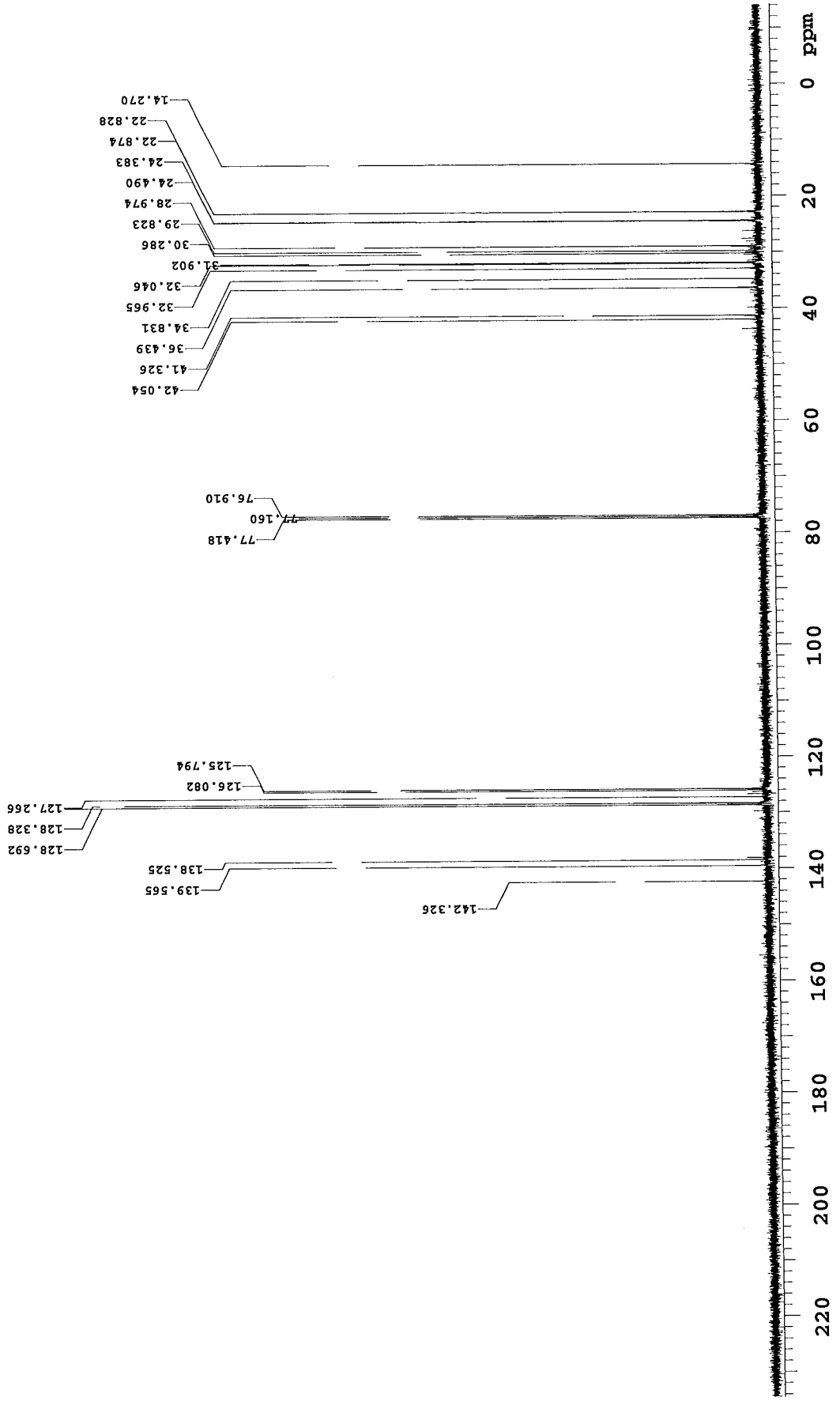
2.14


Me
hexyl
hexyl
Ph
19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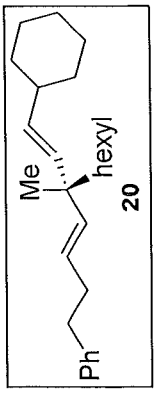
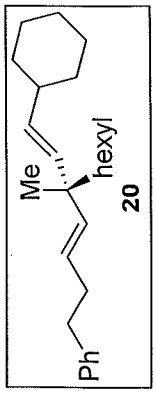
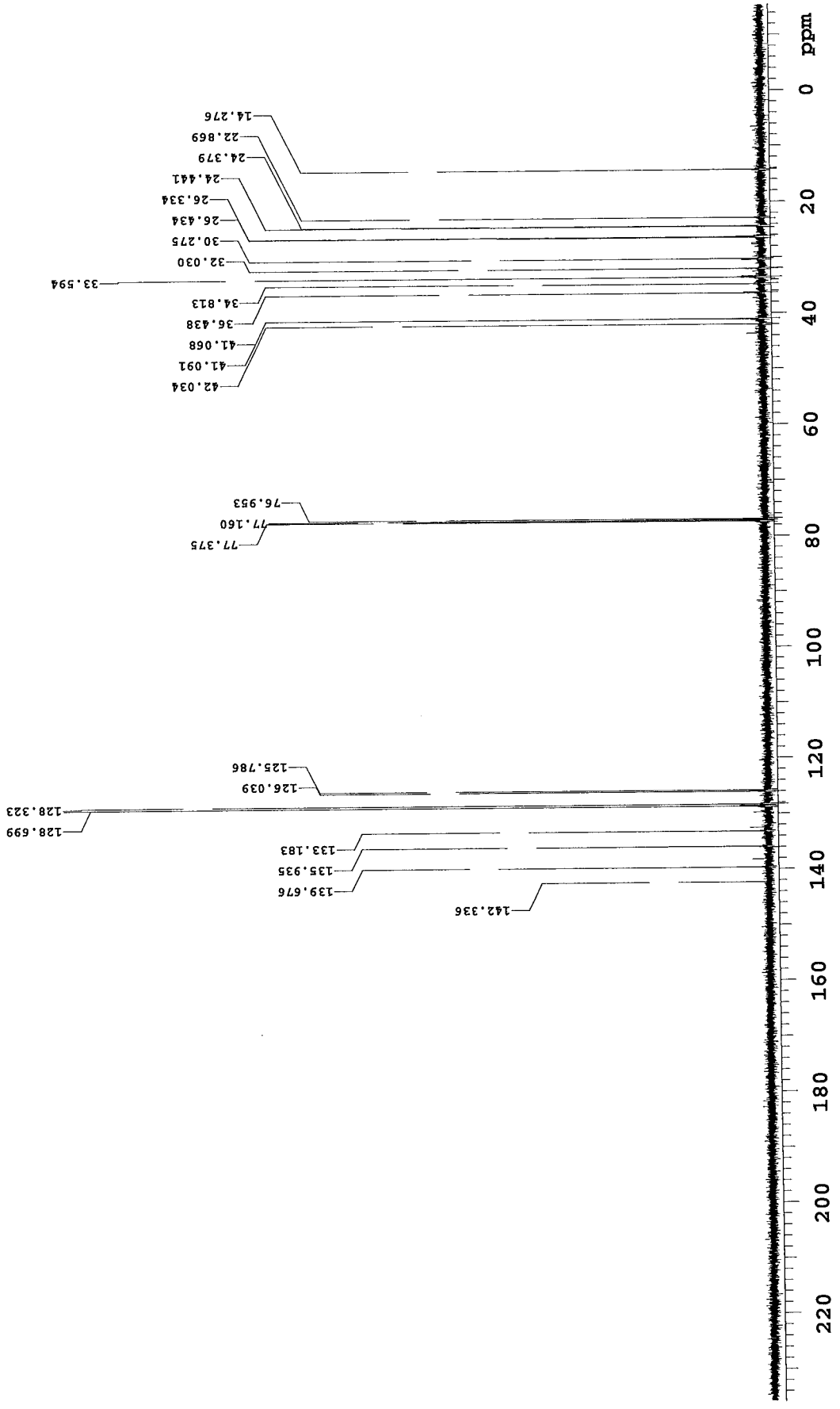
128.692
128.328
127.266
126.082
125.794
77.418
77.160
76.910
42.054
41.326
36.439
34.831
32.965
32.046
31.902
30.286
29.823
28.974
24.490
24.383
22.874
22.828
14.270
0 ppm
20
40
60
80
100
120
140
160
180
200
220


Me
hexyl
Ph
20


Me
hexyl
Ph

20


14.276
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26.434
30.275
32.030
33.594
34.813
36.438
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41.091
42.034
76.953
77.160
77.375
125.786
126.039
128.323
128.699
133.183
135.935
139.676
142.336
0 ppm
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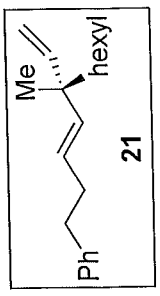
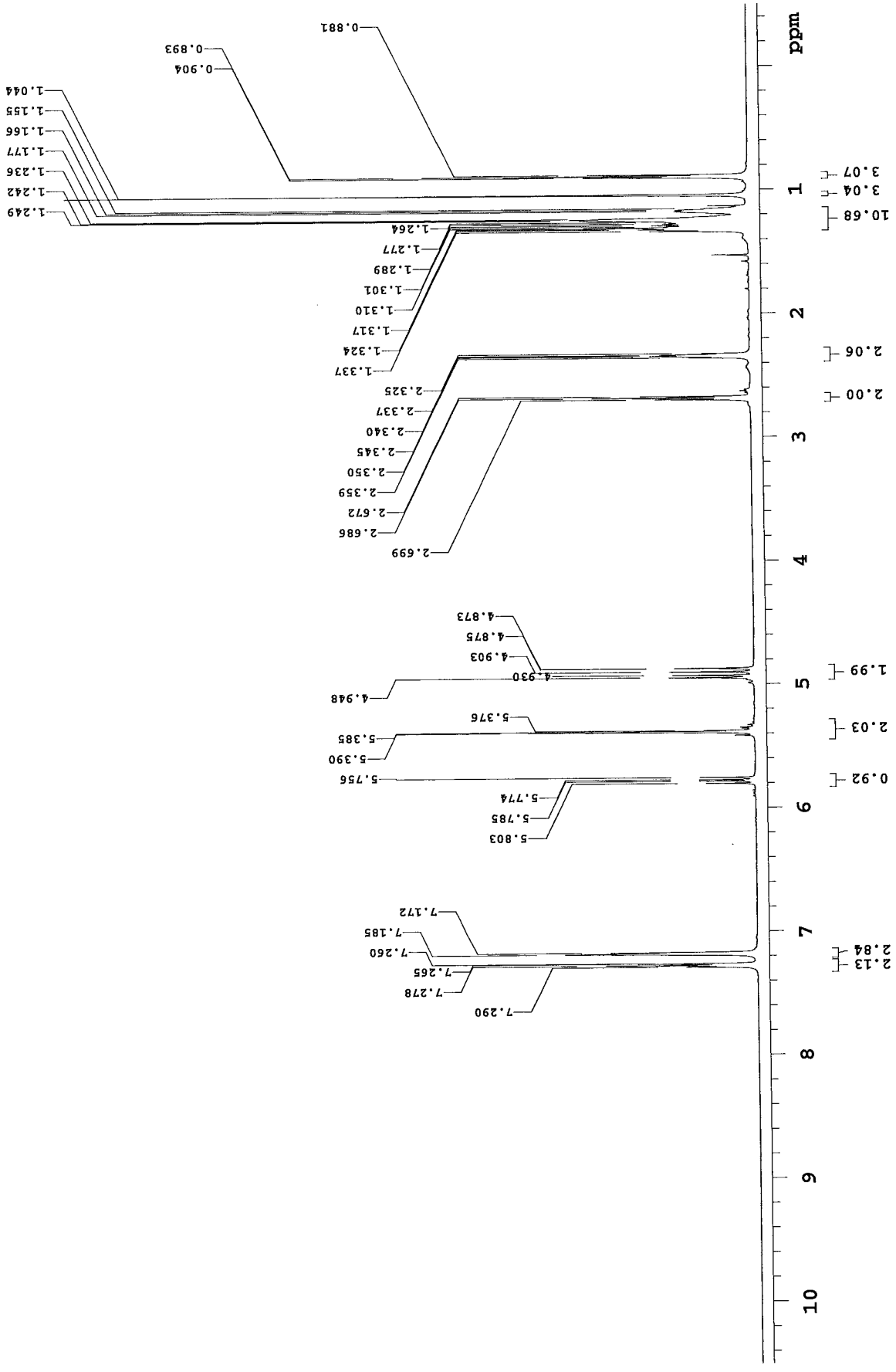
40
60
80
100
120
140
160
180
200
220


Me
hexyl
Ph
21


ppm
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2
3
4
5
6
7
8
9
10
3.07
3.04
10.68
2.06
2.00
1.99
2.03
0.92
2.13
2.84
0.881
0.904
0.893
1.044
1.155
1.166
1.177
1.236
1.242
1.249
1.264
1.277
1.289
1.301
1.310
1.317
1.324
1.337
2.325
2.337
2.340
2.345
2.350
2.359
2.672
2.686
2.699
4.873
4.875
4.903
4.930
4.948
5.376
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5.774
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7.185
7.260
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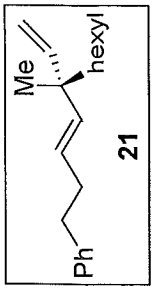
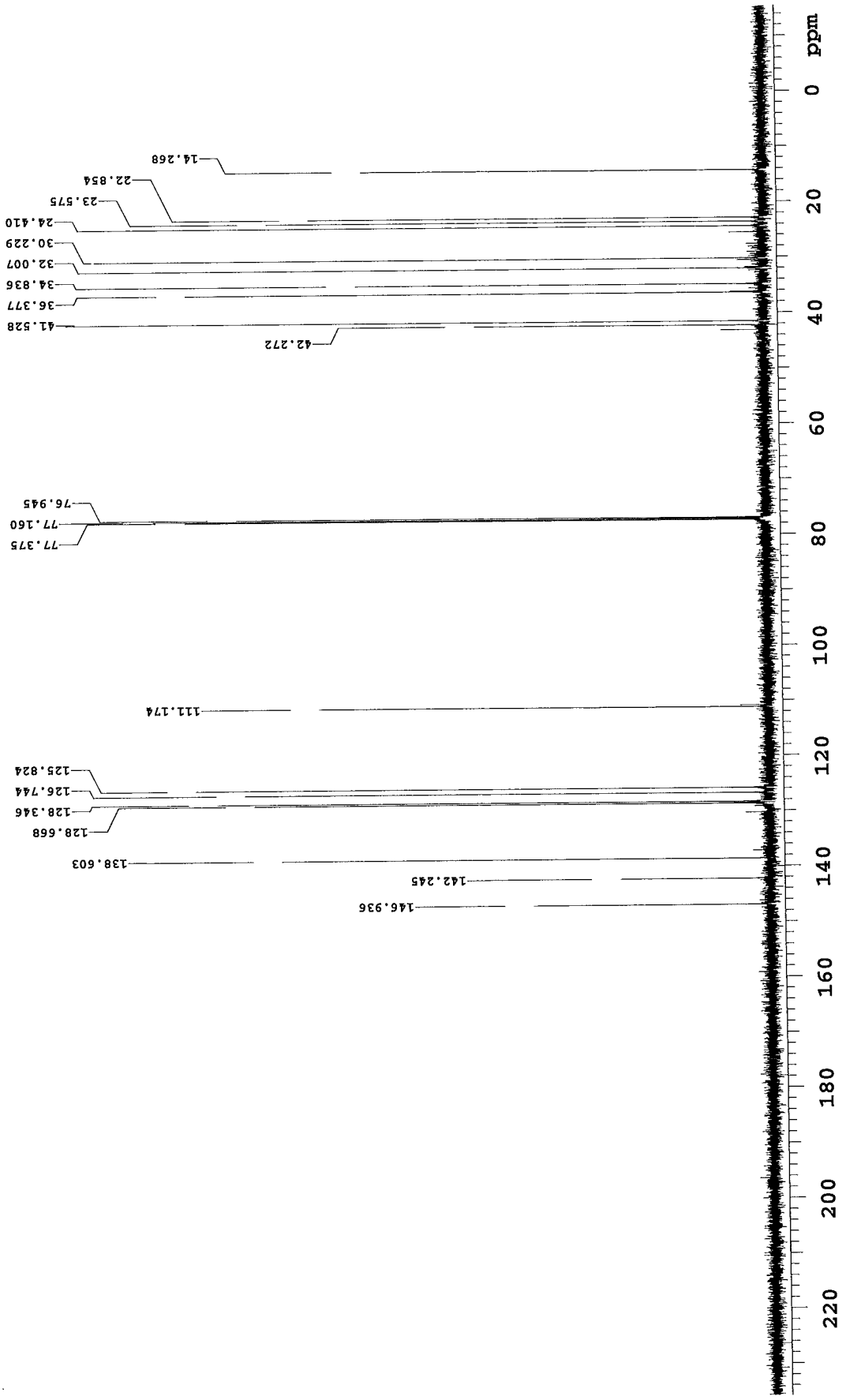
7.278
7.290


Me
hexyl
Ph
21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24.410
30.229
32.007
34.836
36.377
41.528
42.272
76.945
77.160
77.375
111.174
125.824
126.744
128.346
128.668
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142.245
146.936
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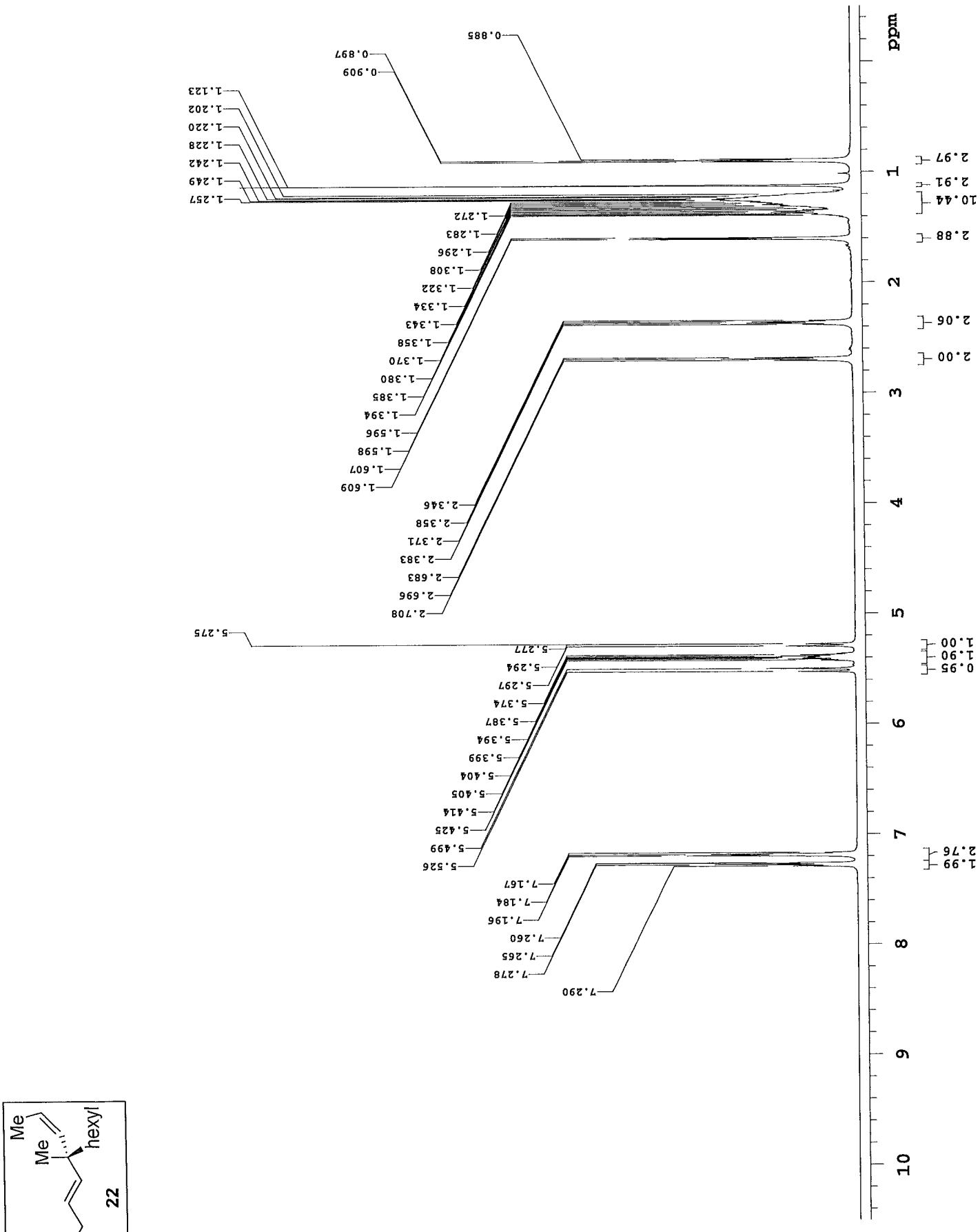
40
60
80
100
120
140
160
180
200
220
ppm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0.909
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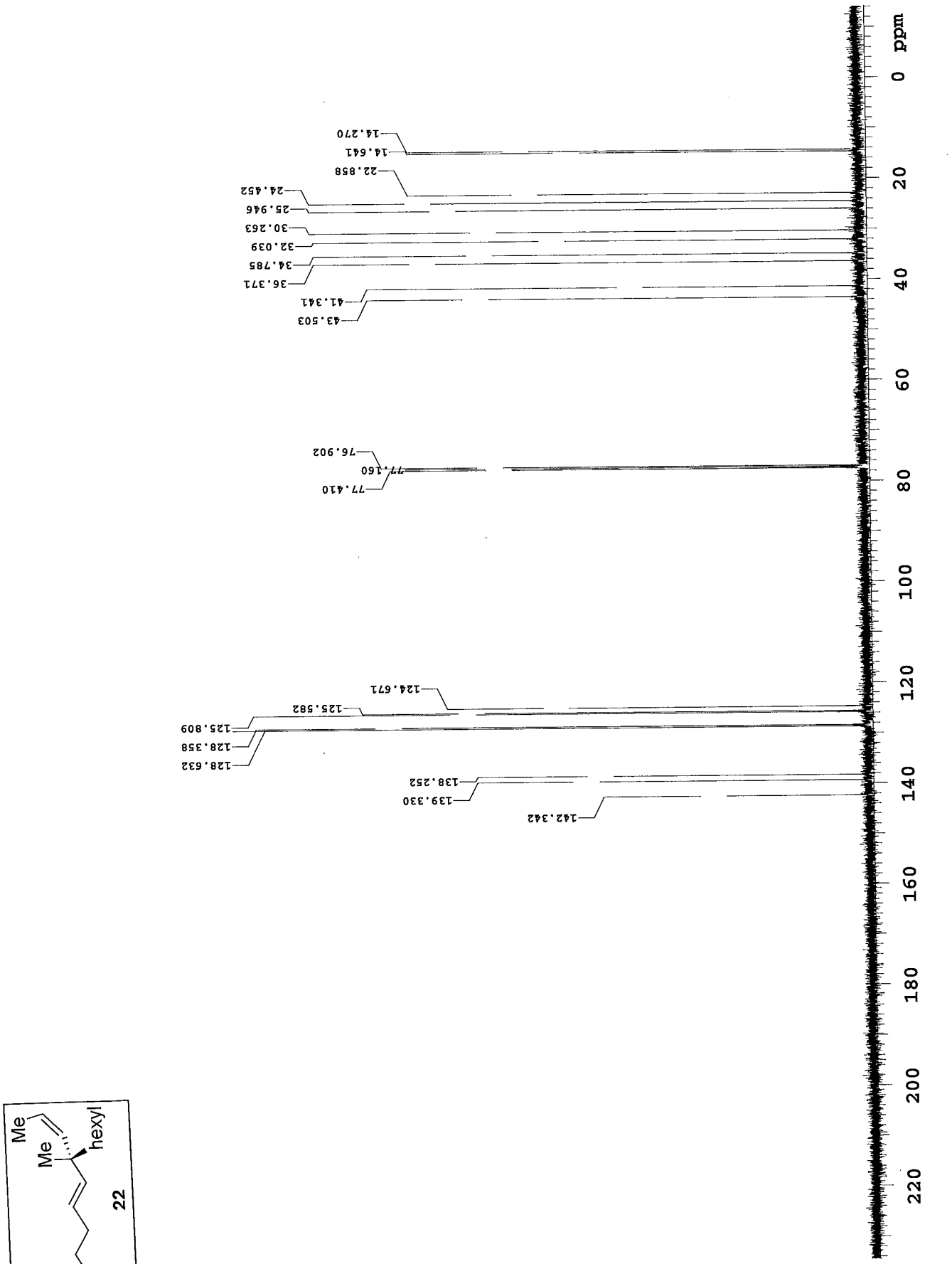
1.202
1.220
1.228
1.242
1.249
1.257
1.272
1.283
1.296
1.308
1.322
1.334
1.343
1.358
1.370
1.380
1.385
1.394
1.596
1.598
1.607
1.609
2.346
2.358
2.371
2.383
2.683
2.696
2.708
5.275
5.277
5.294
5.297
5.374
5.387
5.394
5.399
5.404
5.405
5.414
5.425
5.499
5.526
7.167
7.184
7.196
7.260
7.265
7.278
7.290
ppm
1
2
3
4
5
6
7
8
9
10
2.97
2.91
10.44
2.88
2.06
2.00
1.00
1.90
0.95
1.99
2.76

Me
Me
hexyl
Ph
22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138.252
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128.358
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125.582
124.671
77.410
77.160
76.902
43.503
41.341
36.371
34.785
32.039
30.263
25.946
24.452
22.858
14.641
14.270
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20
40
60
80
100
120
140
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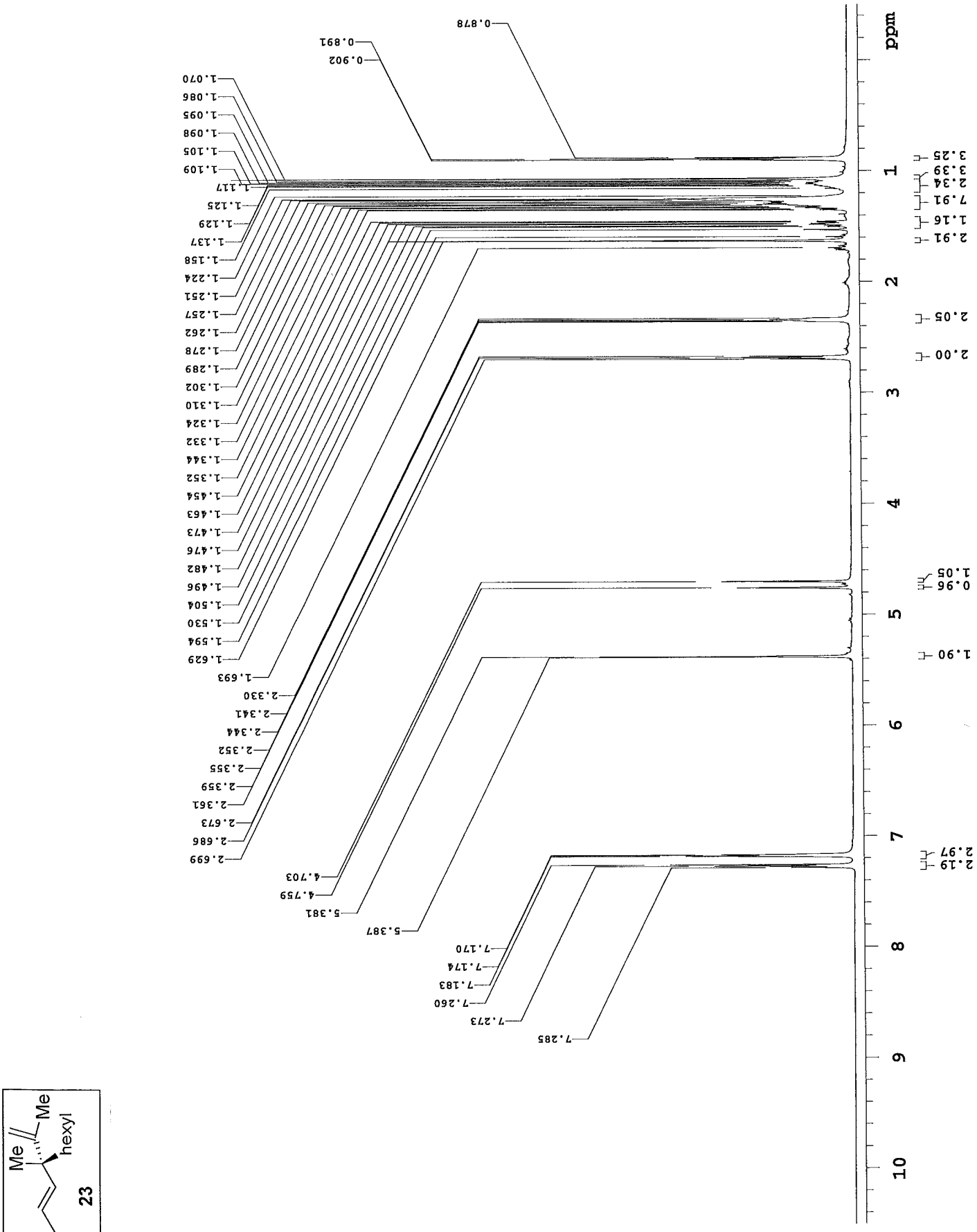
180
200
220

Me
Me
hexyl
Ph
22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1.125
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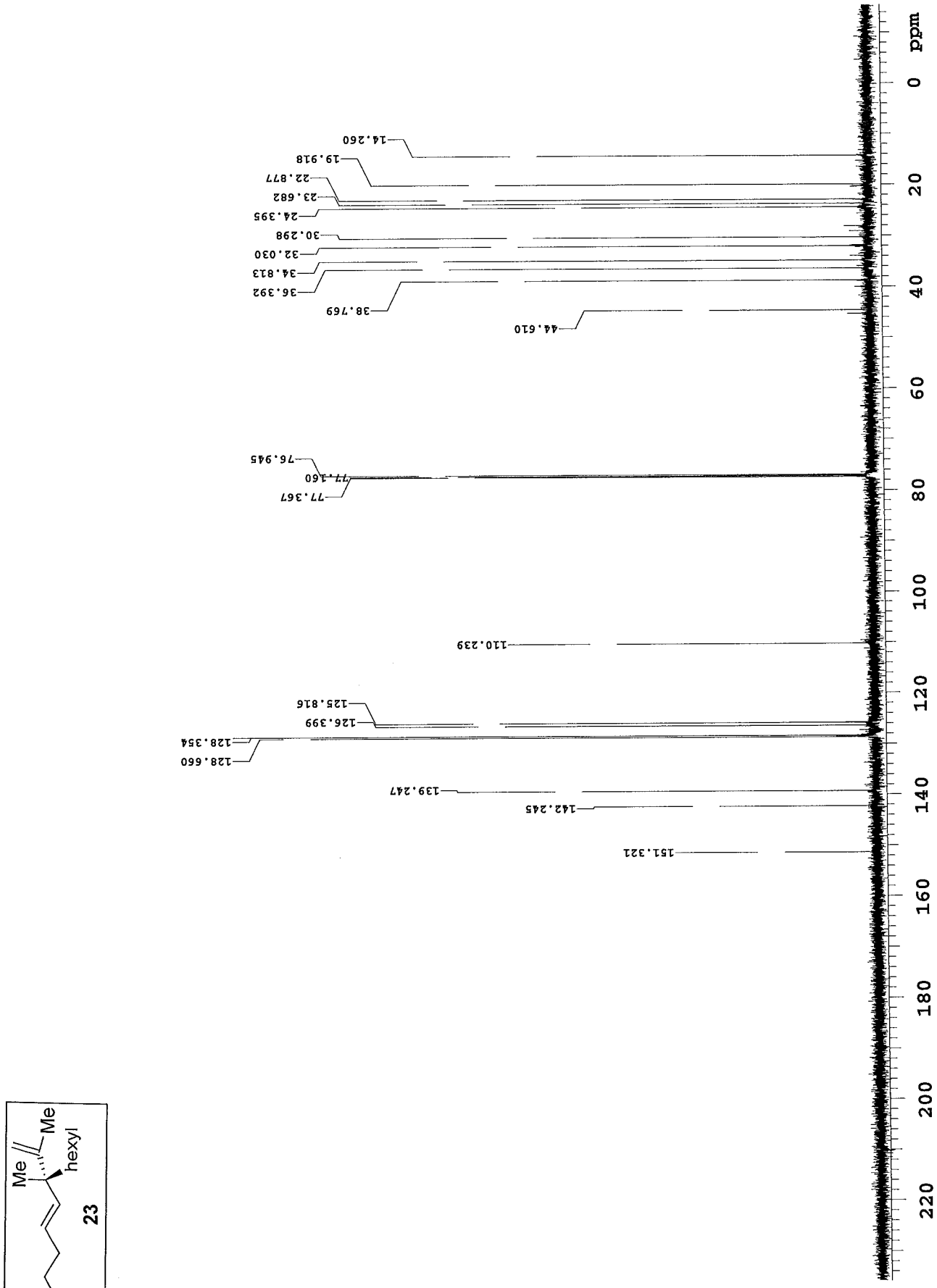
1.137
1.158
1.224
1.251
1.257
1.262
1.278
1.289
1.302
1.310
1.324
1.332
1.344
1.352
1.454
1.463
1.473
1.476
1.482
1.496
1.504
1.530
1.594
1.629
1.693
2.330
2.341
2.344
2.352
2.355
2.359
2.361
2.673
2.686
2.699
4.703
4.759
5.381
5.387
7.170
7.174
7.183
7.260
7.273
7.285
ppm
1
2
3
4
5
6
7
8
9
10
3.25
3.39
2.34
7.91
1.16
2.91
2.05
2.00
0.96
1.05
1.90
2.19
2.97

Me
Me
hexyl
23
Ph


Me
Me
hexyl
Ph
23
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139.247
128.660
128.354
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125.816
110.239
77.367
77.160
76.945
44.610
38.769
36.392
34.813
32.030
30.298
24.395
23.682
22.877
19.918
14.260
0 ppm
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40
60
80
100
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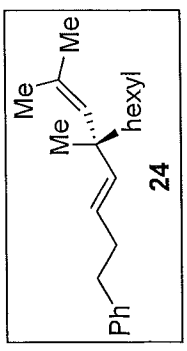
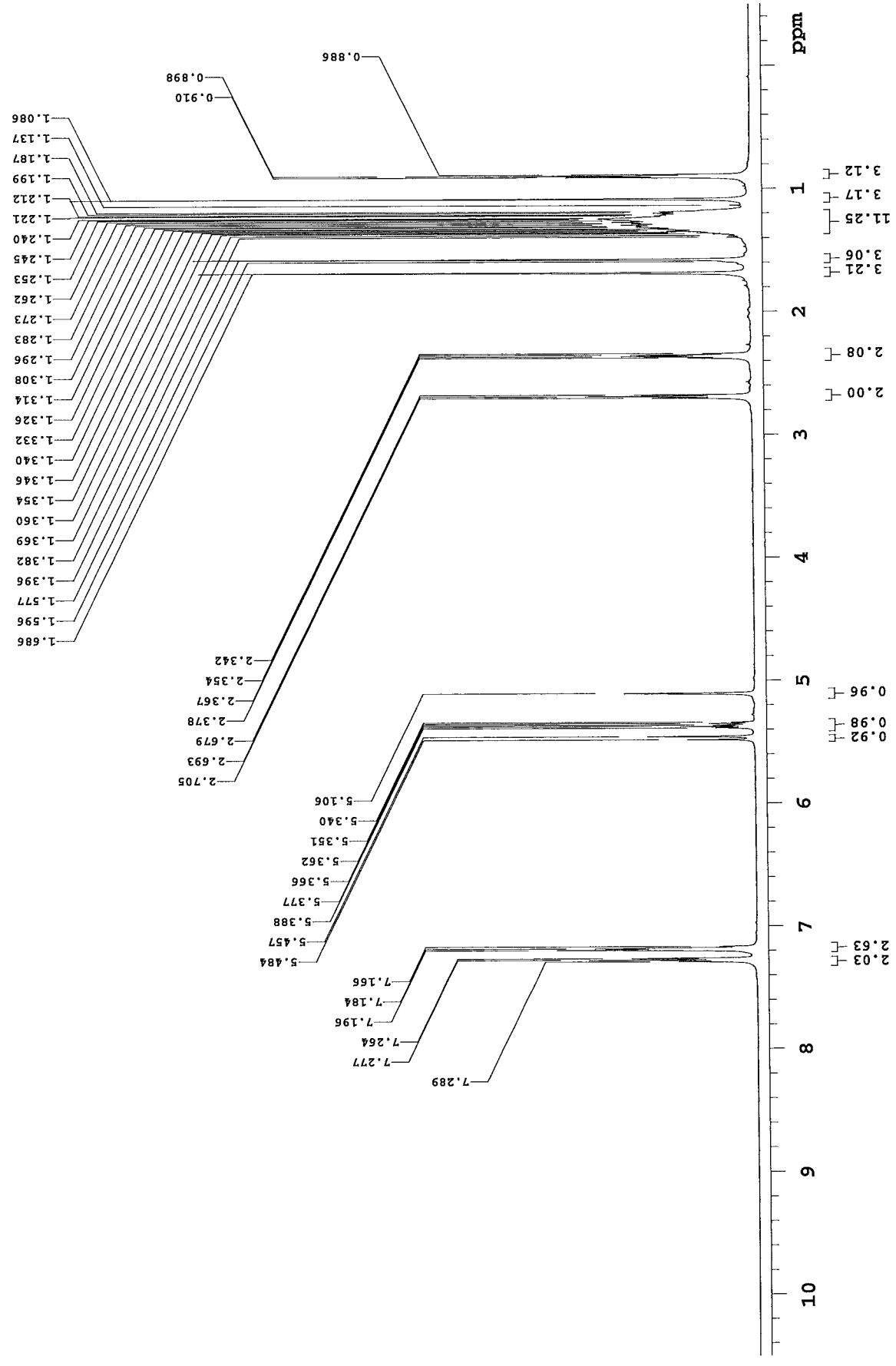
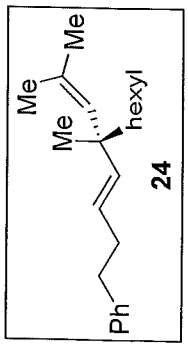
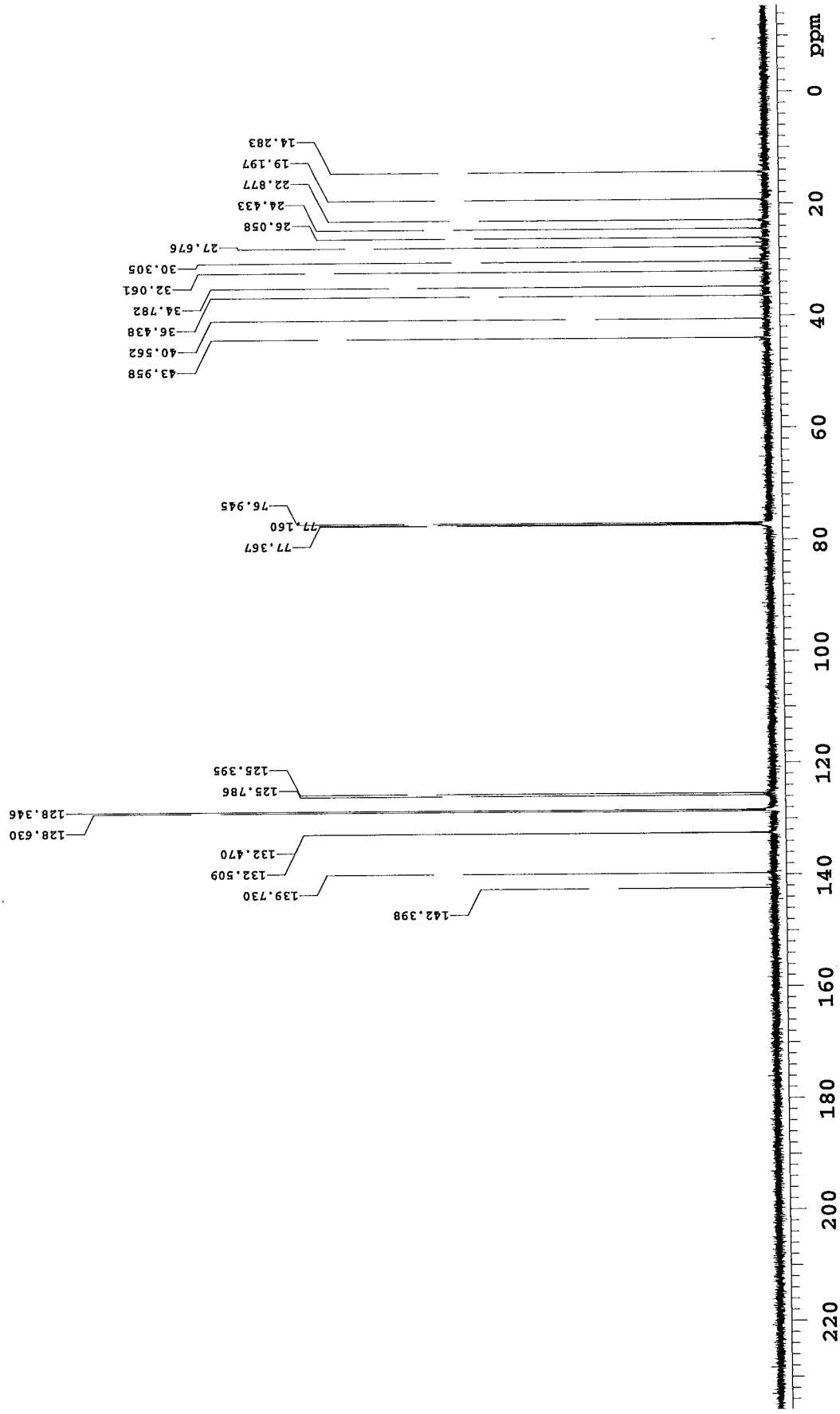
160
180
200
220


Me
Me
Me
hexyl
Ph
24


ppm
1
2
3
4
5
6
7
8
9
10
3.12
3.17
11.25
3.06
3.21
2.08
2.00
0.96
0.92
0.98
2.03
2.63
0.886
0.898
0.910
1.086
1.137
1.187
1.199
1.212
1.221
1.240
1.245
1.253
1.262
1.273
1.283
1.296
1.308
1.314
1.326
1.332
1.340
1.346
1.354
1.360
1.369
1.382
1.396
1.577
1.596
1.686
2.342
2.354
2.367
2.378
2.679
2.693
2.705
5.106
5.340
5.351
5.362
5.366
5.377
5.388
5.457
5.484
7.166
7.184
7.196
7.264
7.277
7.289


Me
Me
Me
hexyl
Ph
24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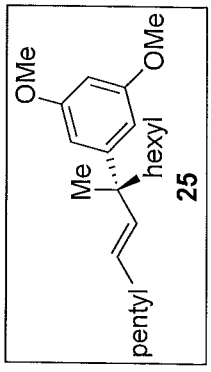
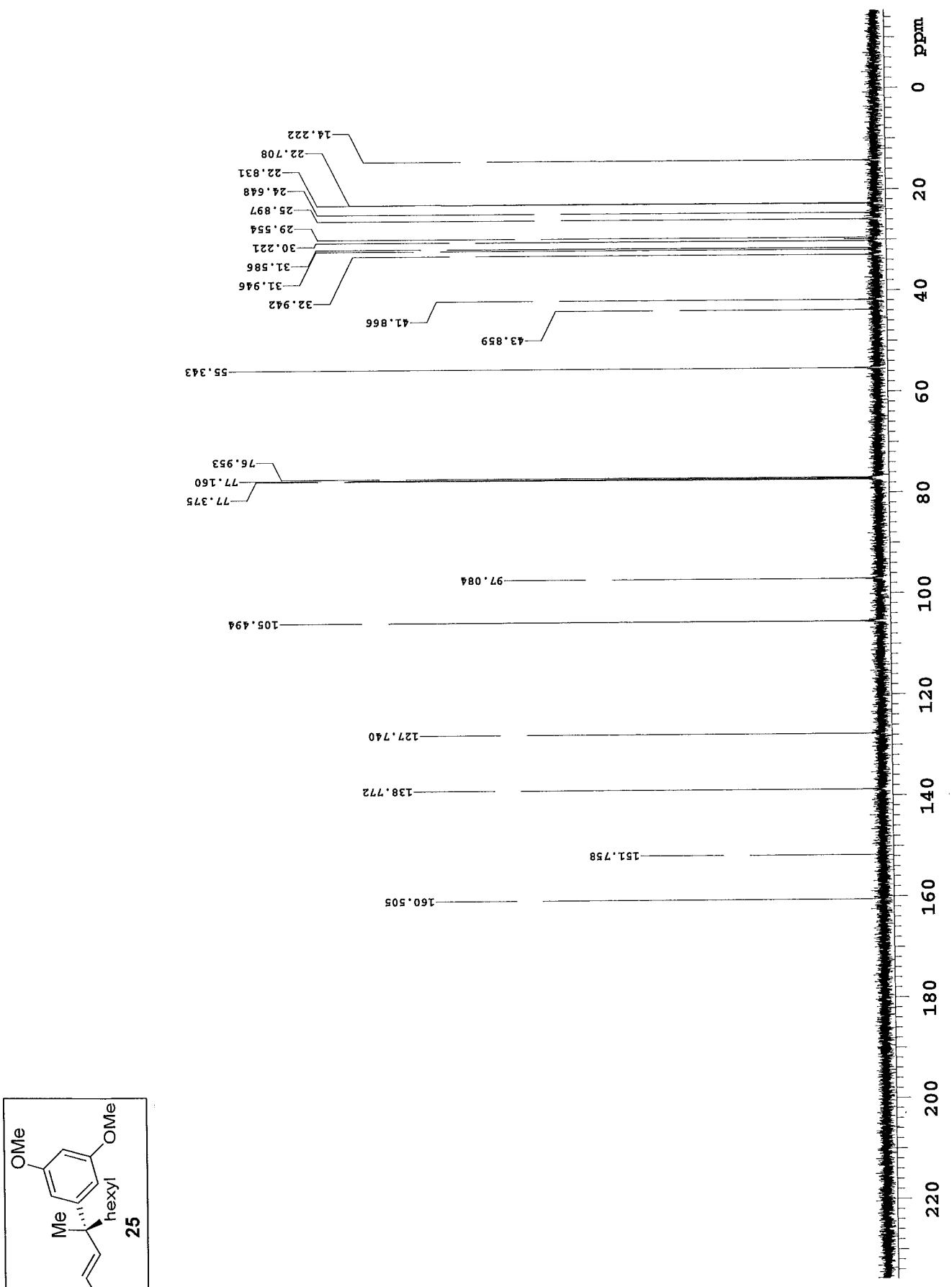
139.730
132.509
132.470
128.630
128.346
125.786
125.395
77.367
77.160
76.945
43.958
40.562
36.438
34.782
32.061
30.305
27.676
26.058
24.433
22.877
19.197
14.283
0 ppm
20
40
60
80
100
120
140
160
180
200
220


OMe
OMe
Me
hexyl
pentyl
25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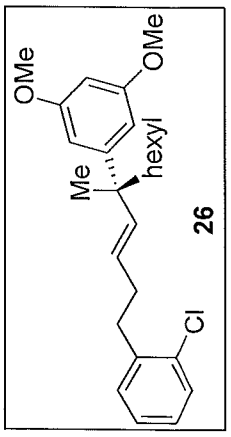
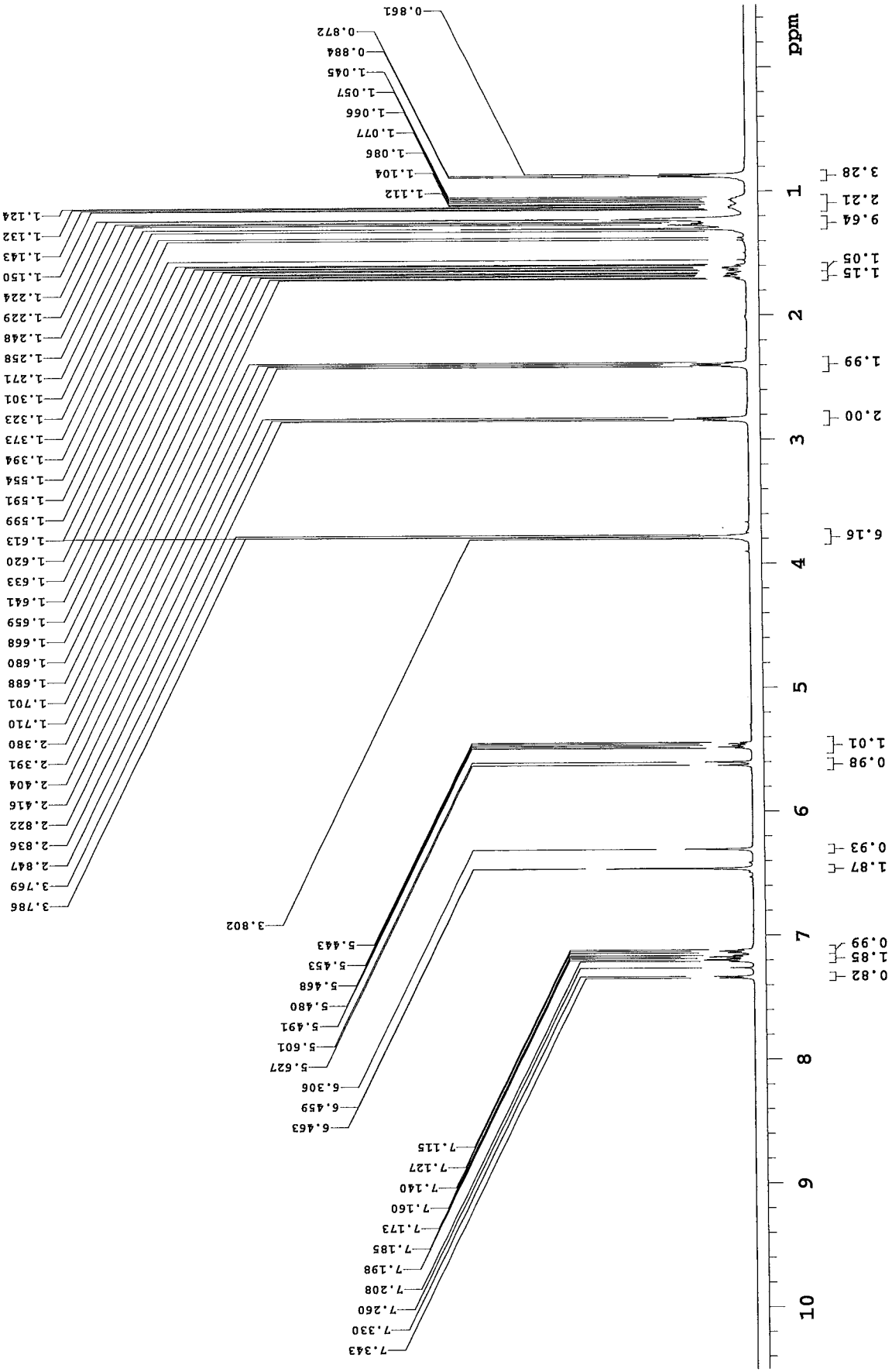
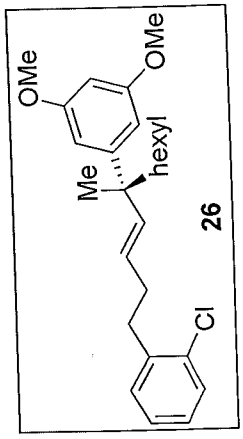
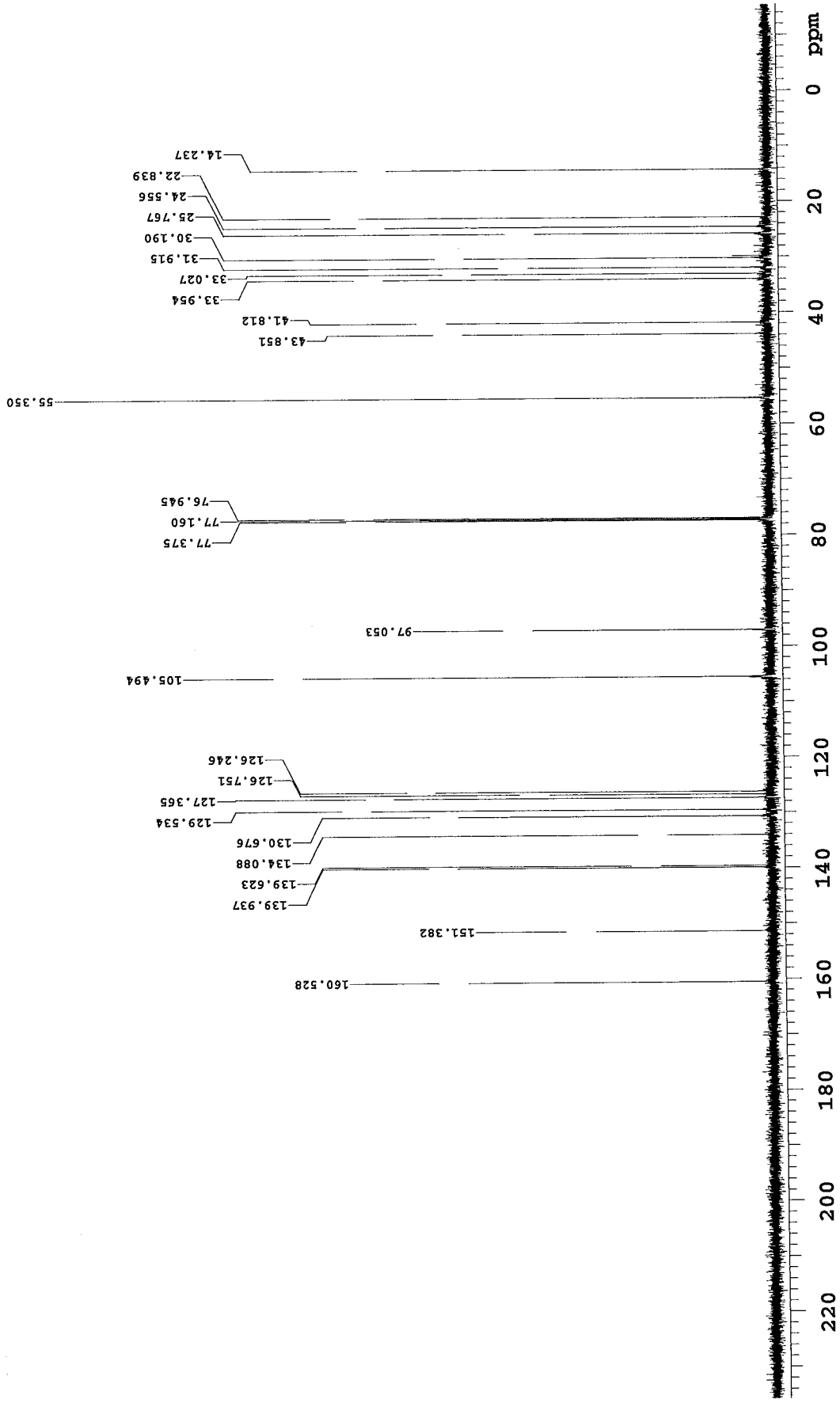
22.831
24.648
25.897
29.554
30.221
31.586
31.946
32.942
41.866
43.859
55.343
76.953
77.160
77.375
97.084
105.494
127.740
138.772
151.758
160.505
0
20
40
60
80
100
120
140
160
180
200
220
ppm
OMe
OMe
Me
hexyl
pentyl
25


OMe
OMe
Me
hexyl
Cl
26


ppm
1
2
3
4
5
6
7
8
9
10
3.28
2.21
9.64
1.15
1.05
1.99
2.00
6.16
1.01
0.98
0.93
1.87
0.99
1.85
0.82
0.861
0.872
0.884
1.045
1.057
1.066
1.077
1.086
1.104
1.112
1.124
1.132
1.143
1.150
1.224
1.229
1.248
1.258
1.271
1.301
1.323
1.373
1.394
1.554
1.591
1.599
1.613
1.620
1.633
1.641
1.659
1.668
1.680
1.688
1.701
1.710
2.380
2.391
2.404
2.416
2.822
2.836
2.847
3.769
3.786
3.802
5.443
5.453
5.468
5.480
5.491
5.501
5.627
6.306
6.459
6.463
7.115
7.127
7.140
7.160
7.173
7.185
7.198
7.208
7.260
7.330
7.343


OMe
OMe
Me
hexyl
Cl
26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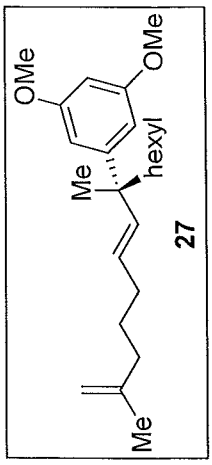
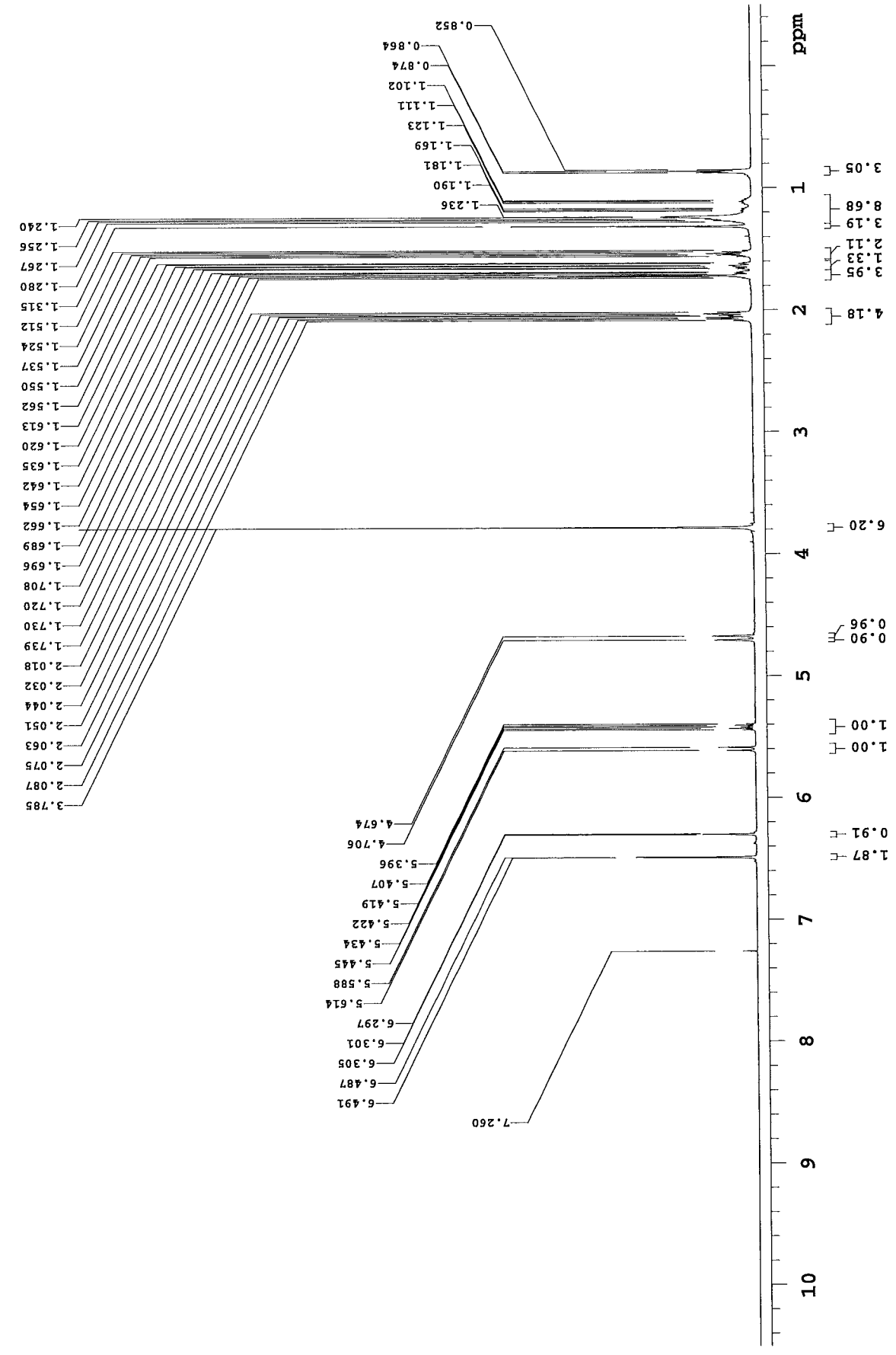
25.767
30.190
31.915
33.027
33.954
41.812
43.851
55.350
76.945
77.160
77.375
97.053
105.494
126.246
126.751
127.365
129.534
130.676
134.088
139.623
139.937
151.382
160.528
0 ppm
20
40
60
80
100
120
140
160
180
200
220


OMe
OMe
hexyl
Me
Me
27


ppm
1
2
3
4
5
6
7
8
9
10
3.05
8.68
3.19
2.11
1.33
3.95
4.18
6.20
0.90
0.96
1.00
1.00
0.91
1.87
0.852
0.864
0.874
1.102
1.111
1.123
1.169
1.181
1.190
1.236
1.240
1.256
1.267
1.280
1.315
1.512
1.524
1.537
1.550
1.562
1.613
1.620
1.635
1.642
1.654
1.662
1.689
1.696
1.708
1.720
1.730
1.739
2.018
2.032
2.044
2.051
2.063
2.075
2.087
3.785
4.674
4.706
5.396
5.407
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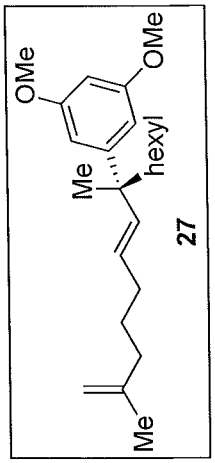
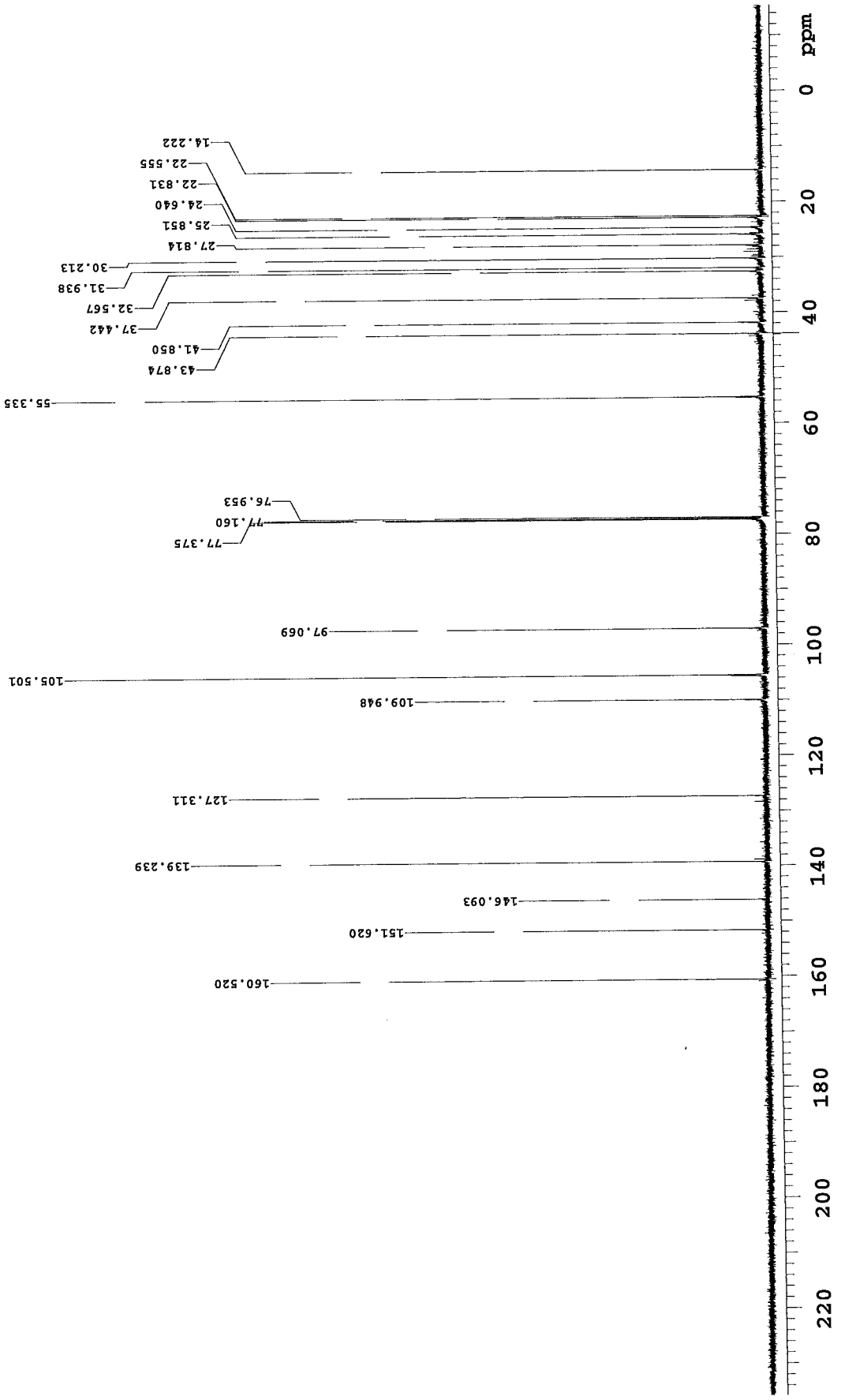
5.422
5.434
5.445
5.588
5.614
6.297
6.301
6.305
6.487
6.491
7.260


OMe
OMe
Me
hexyl
Me
27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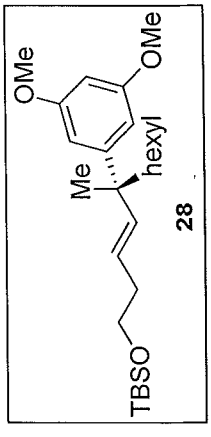
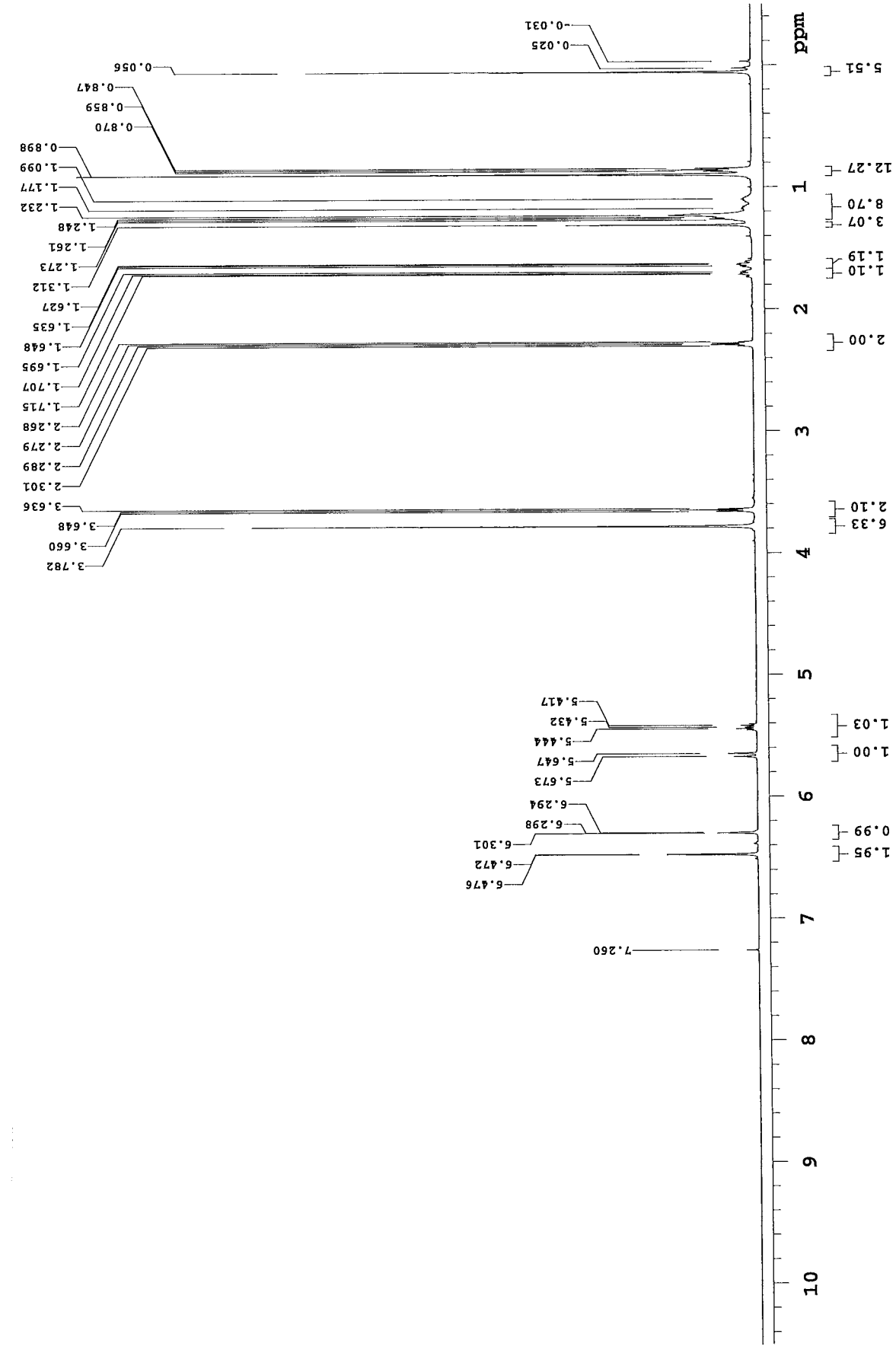
139.239
127.311
109.948
105.501
97.069
77.375
77.160
76.953
55.335
43.874
41.850
37.442
32.567
31.938
30.213
27.814
25.851
24.640
22.831
22.555
14.222
0 ppm
20
40
60
80
100
120
140
160
180
200
220


OMe
OMe
Me
hexyl
TBSO
28


ppm
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9
8
7
6
5
4
3
2
1
0
5.51
12.27
8.70
3.07
1.10
1.19
2.00
6.33
2.10
1.03
1.00
0.99
1.95
7.260
6.476
6.472
6.301
6.298
6.294
5.673
5.647
5.444
5.432
5.417
3.782
3.660
3.648
3.636
2.301
2.289
2.279
2.268
1.715
1.707
1.695
1.648
1.635
1.627
1.312
1.273
1.261
1.248
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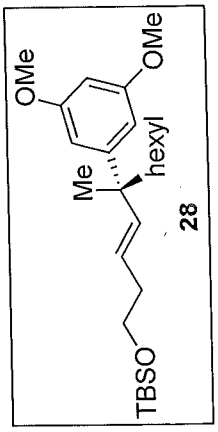
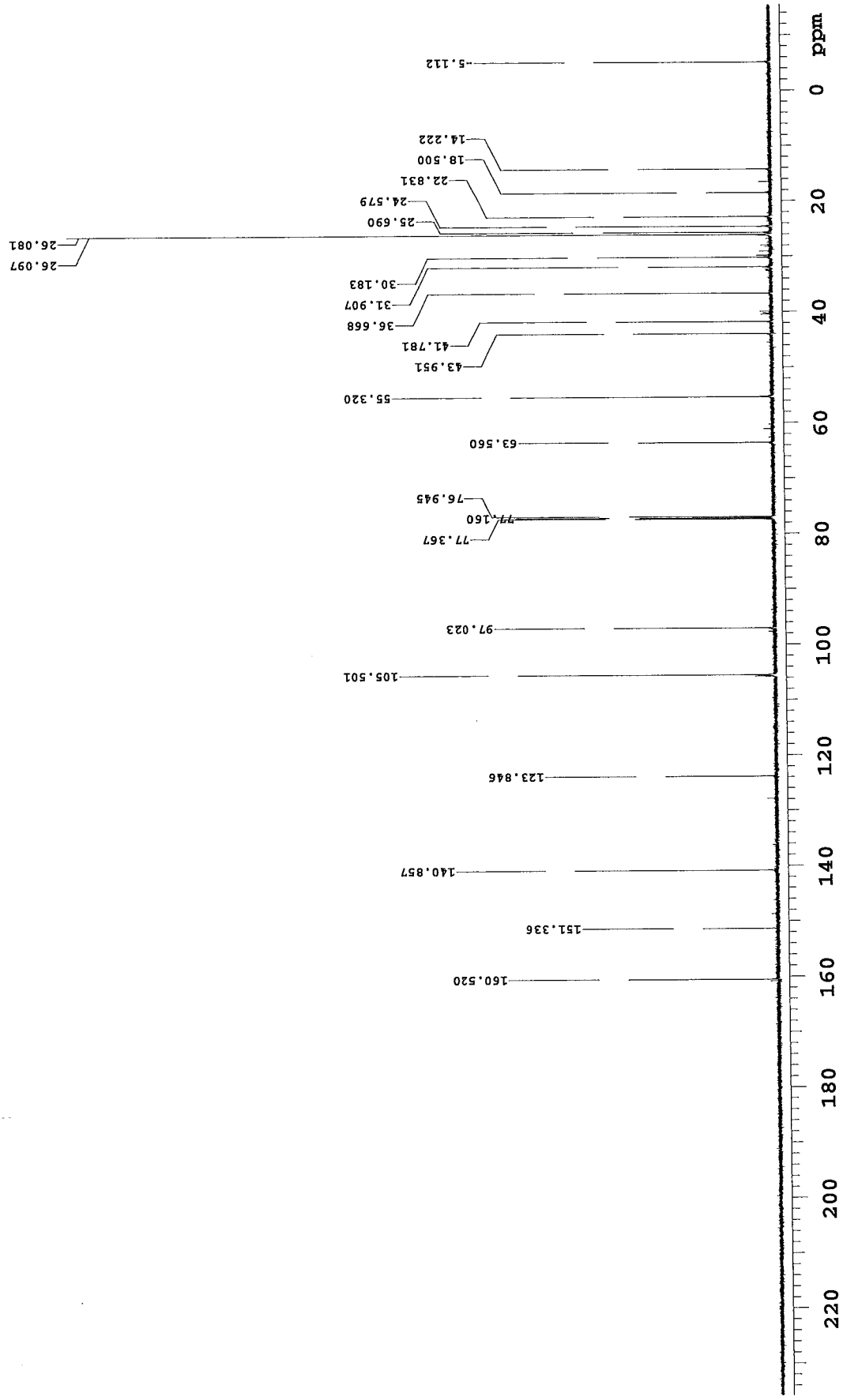
1.177
1.099
0.898
0.870
0.859
0.847
0.056
0.025
-0.031


OMe
OMe
Me
hexyl
TBSO
28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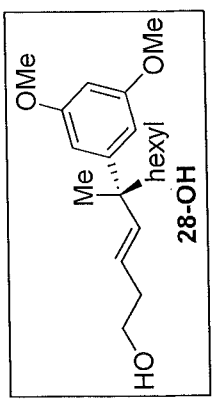
24.579
25.690
26.081
26.097
30.183
31.907
36.668
41.781
43.951
55.320
63.560
76.945
77.160
77.367
97.023
105.501
123.846
140.857
151.336
160.520
0
20
40
60
80
100
120
140
160
180
200
220
ppm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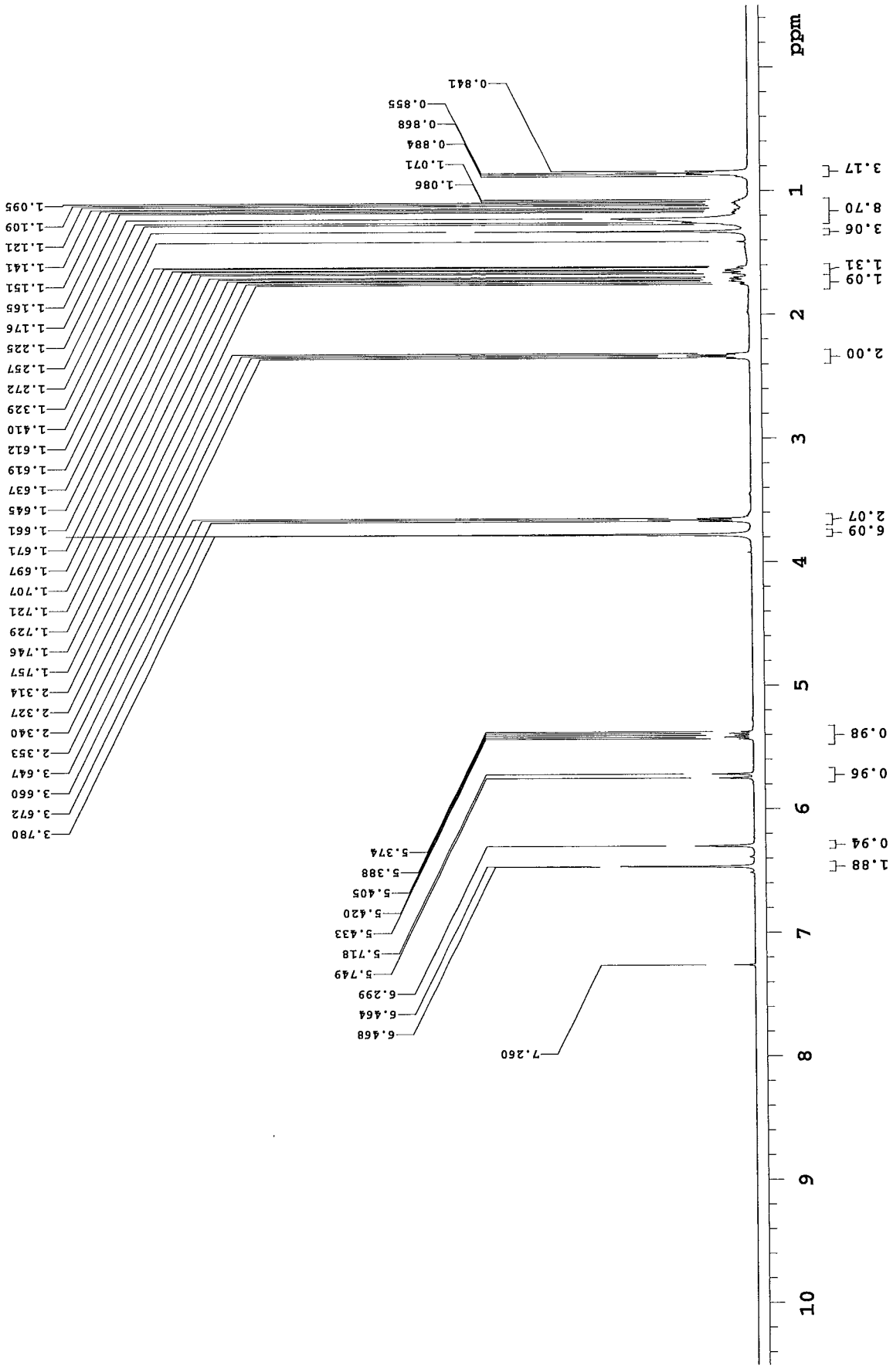
OMe
Me
hexyl
HO
28-OH


ppm
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3
4
5
6
7
8
9
10
3.17
8.70
3.06
1.09
1.31
2.00
6.09
2.07
0.98
0.96
0.94
1.88
0.841
0.855
0.868
0.884
1.071
1.086
1.095
1.109
1.121
1.141
1.151
1.165
1.176
1.225
1.257
1.272
1.329
1.410
1.612
1.619
1.637
1.645
1.661
1.671
1.697
1.707
1.721
1.729
1.746
1.757
2.314
2.327
2.340
2.353
3.647
3.660
3.672
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5.374
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5.405
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5.433
5.718
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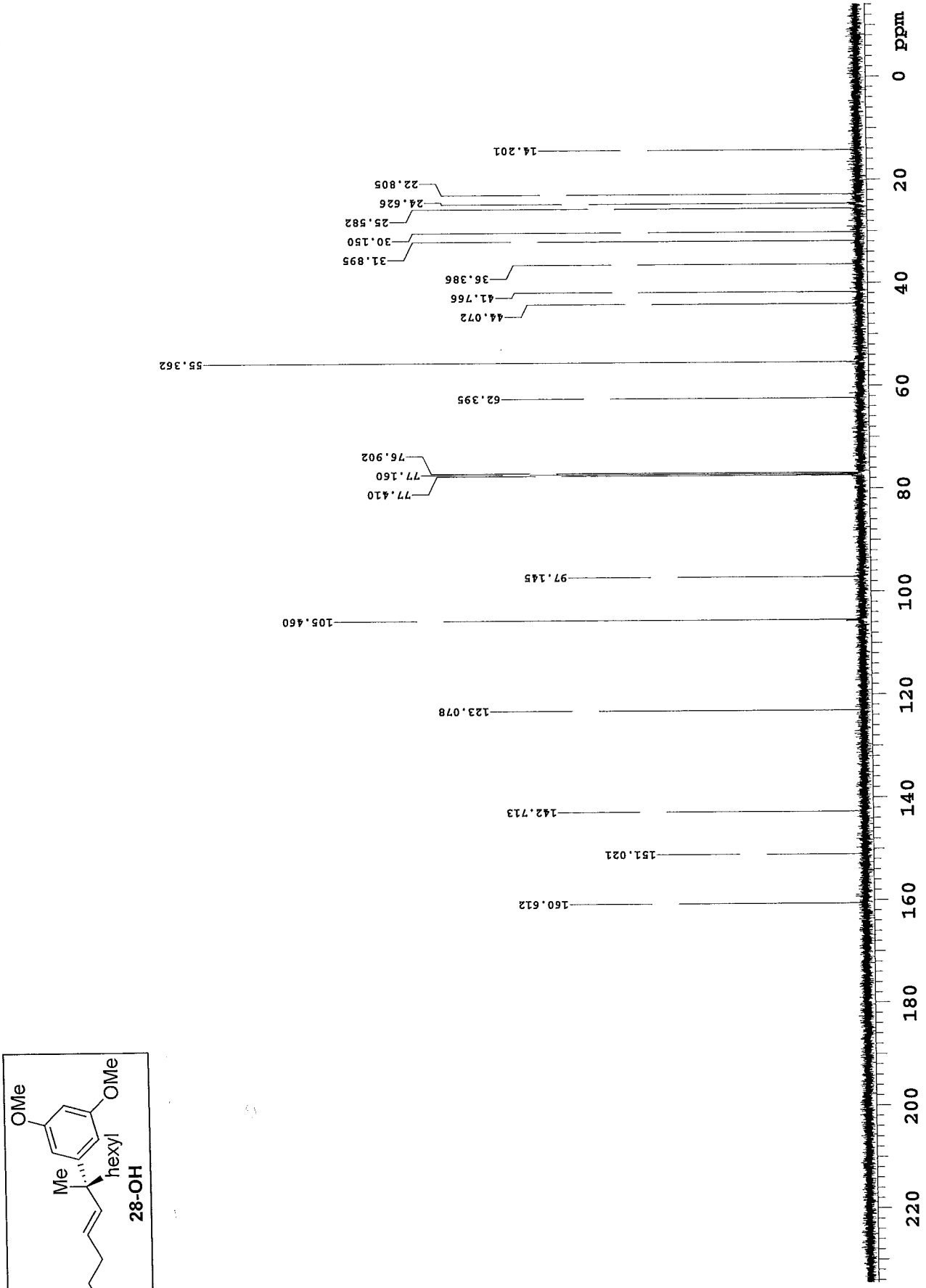
6.464
6.468
7.260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41.766
44.072
55.362
62.395
76.902
77.160
77.410
97.145
105.460
123.078
142.713
151.021
160.612
0 ppm
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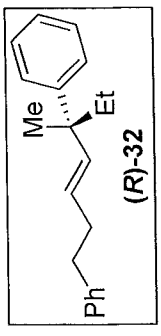
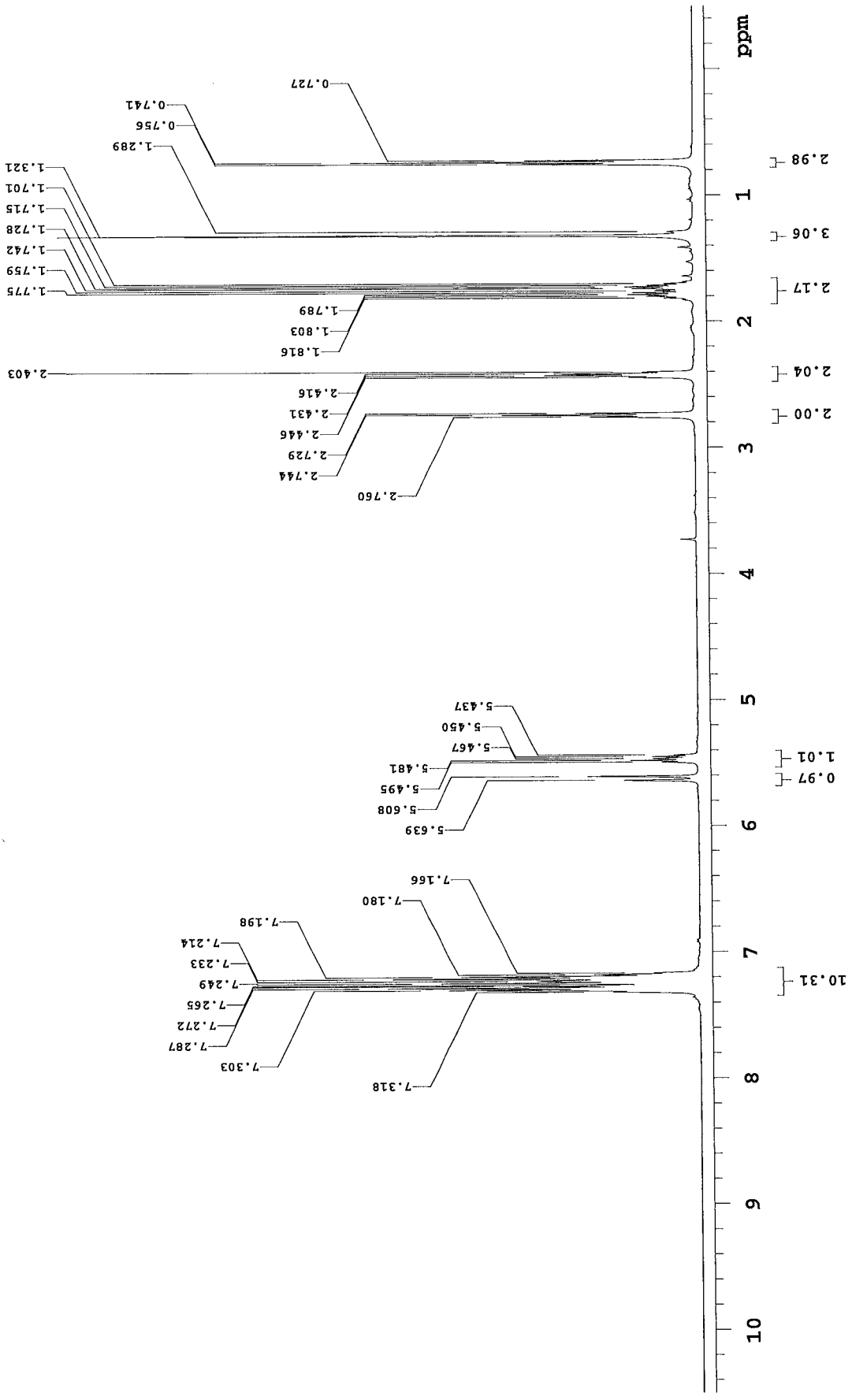
60
80
100
120
140
160
180
200
220
OMe
OMe
Me
hexyl
HO
28-OH


Me
Et
Ph
(R)-32


ppm
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2.04
2.00
2.17
3.06
2.98
7.318
7.303
7.287
7.272
7.265
7.249
7.233
7.214
7.198
7.180
7.166
5.639
5.608
5.495
5.481
5.467
5.450
5.437
2.760
2.744
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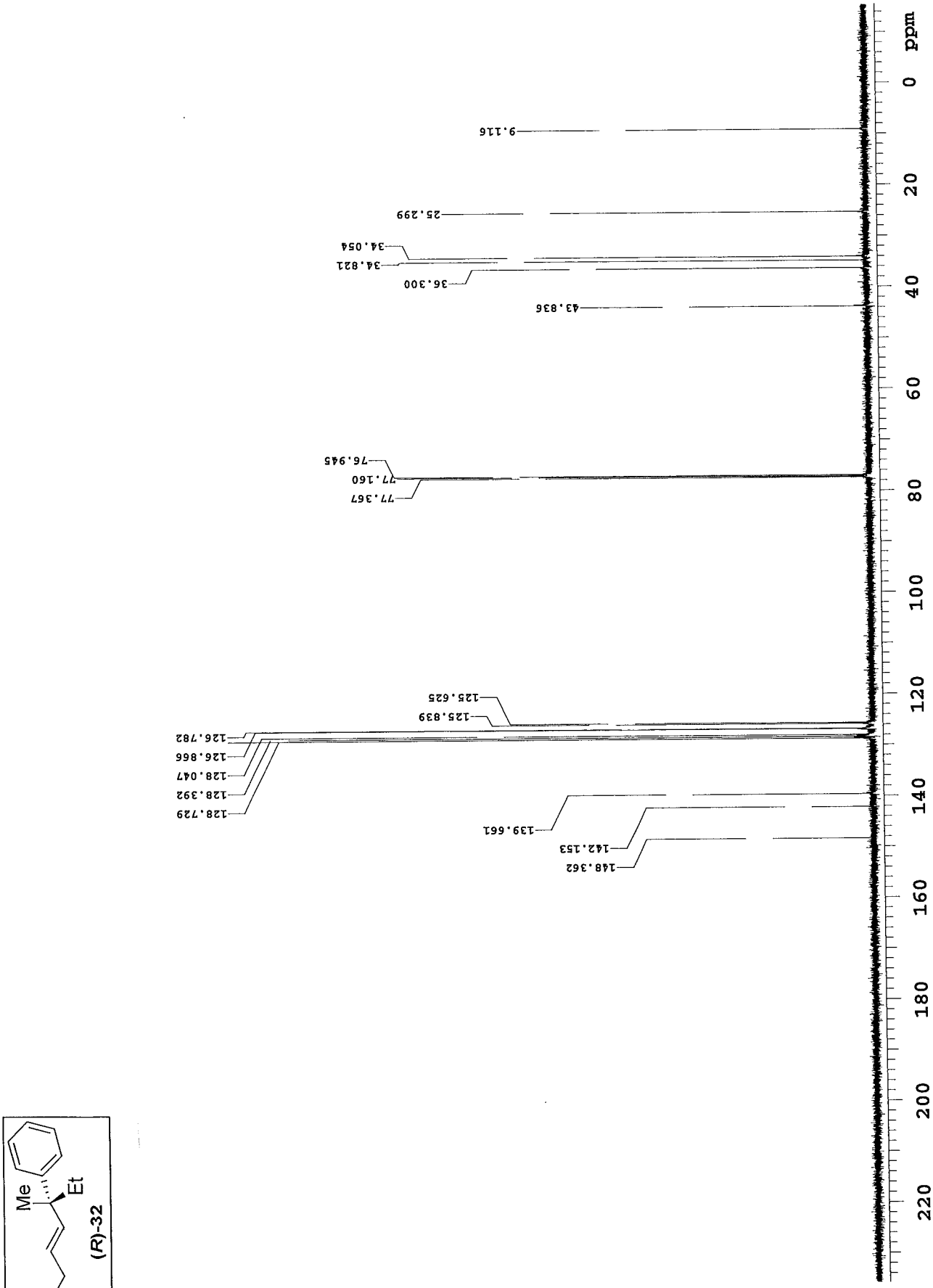
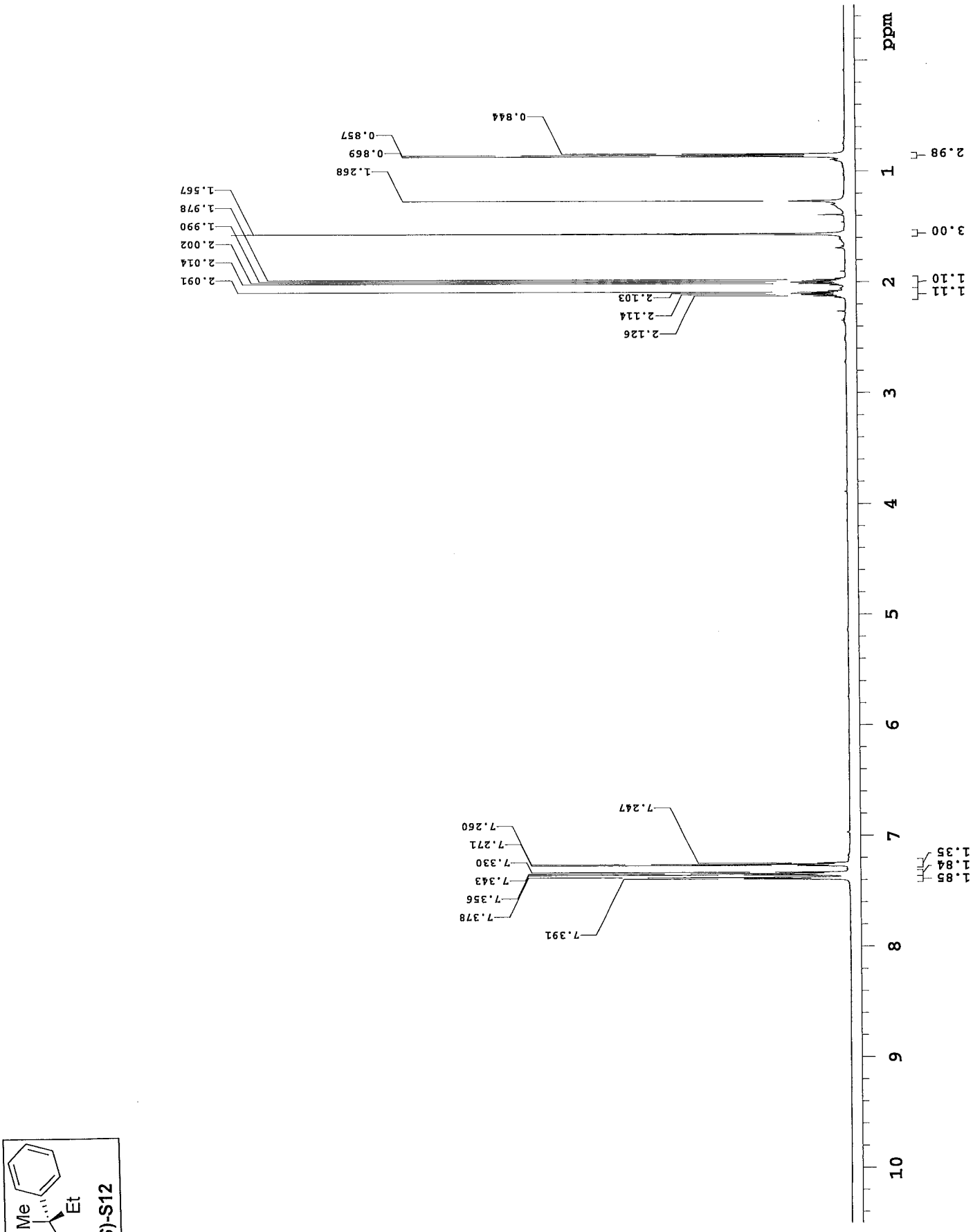
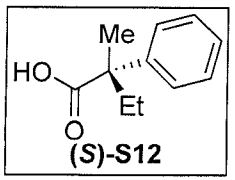
2.431
2.416
2.403
1.816
1.803
1.789
1.775
1.759
1.742
1.728
1.715
1.701
1.321
1.289
0.756
0.741
0.727


9.116
25.299
34.054
34.821
36.300
43.836
76.945
77.160
77.367
125.625
125.839
126.782
126.866
128.047
128.392
128.729
139.661
142.153
148.362
ppm
0
20
40
60
80
100
120
140
160
180
200
220

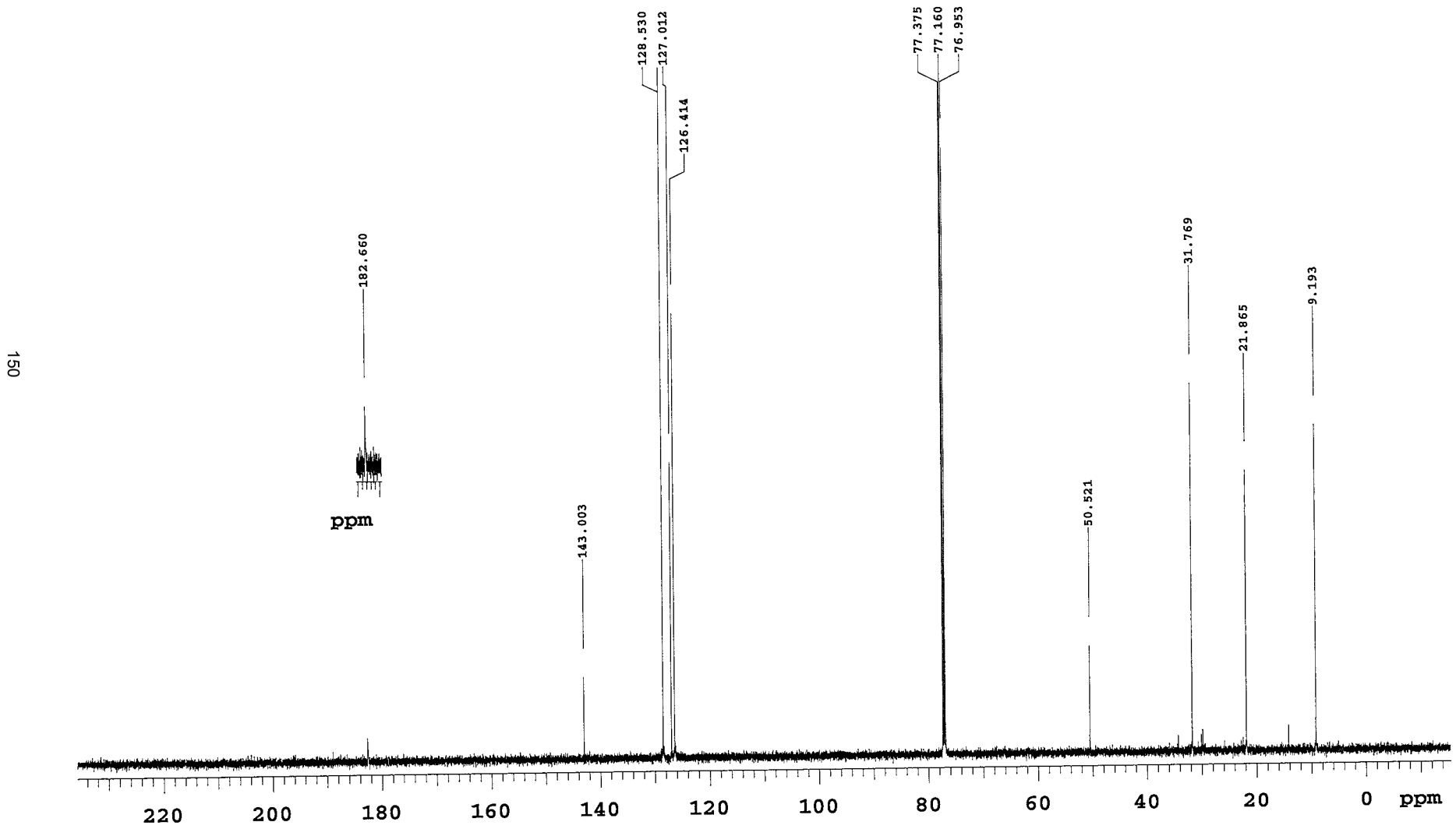
Me
Et
Ph
(R)-32

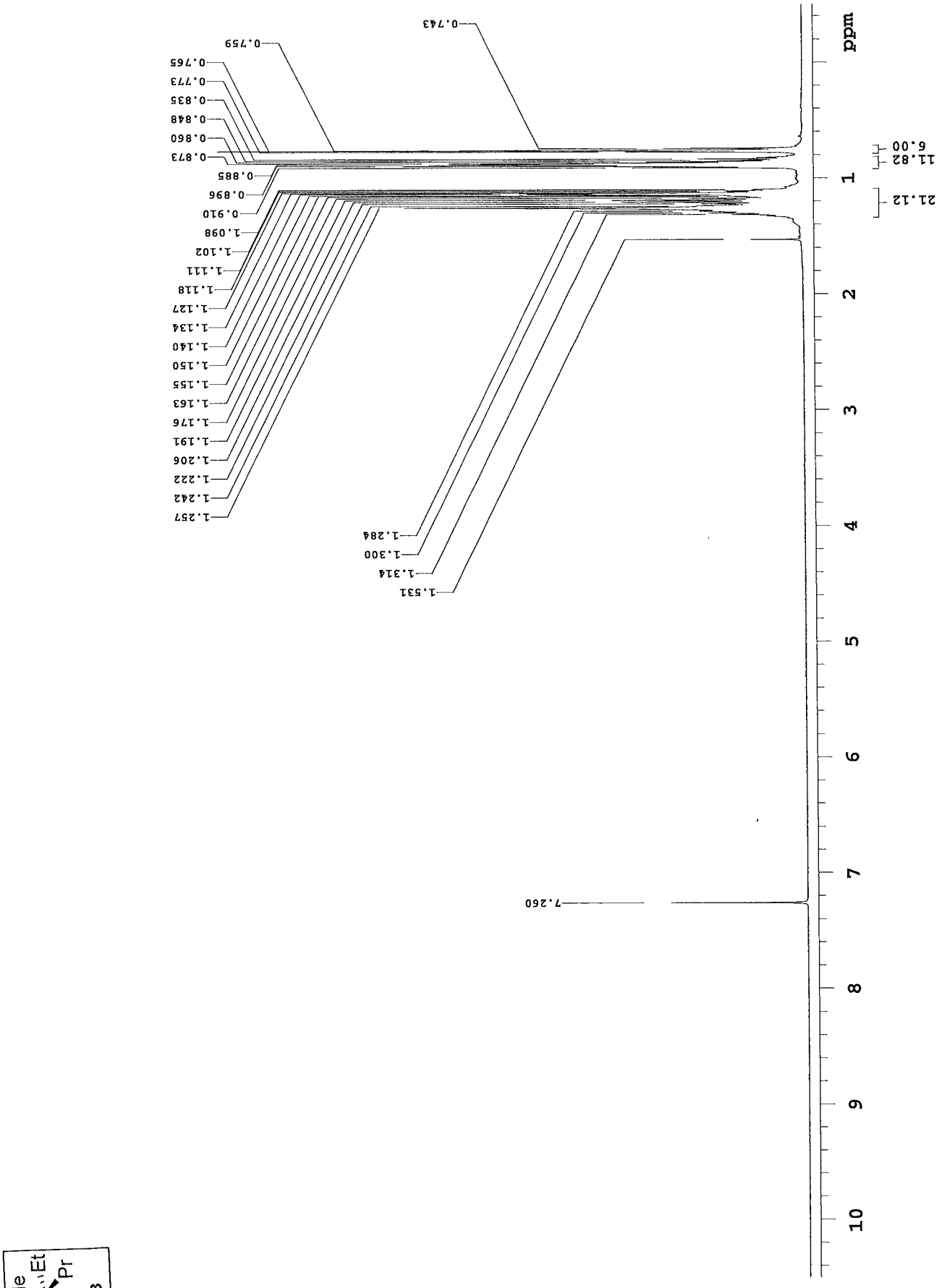

0.844
0.857
0.869
1.268
1.567
1.978
1.990
2.002
2.014
2.091
2.103
2.114
2.126
7.247
7.260
7.271
7.330
7.343
7.356
7.378
7.391
ppm
2.98
3.00
1.10
1.11
1.35
1.84
1.85

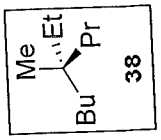
Me
Et
HO
O
(S)-S12

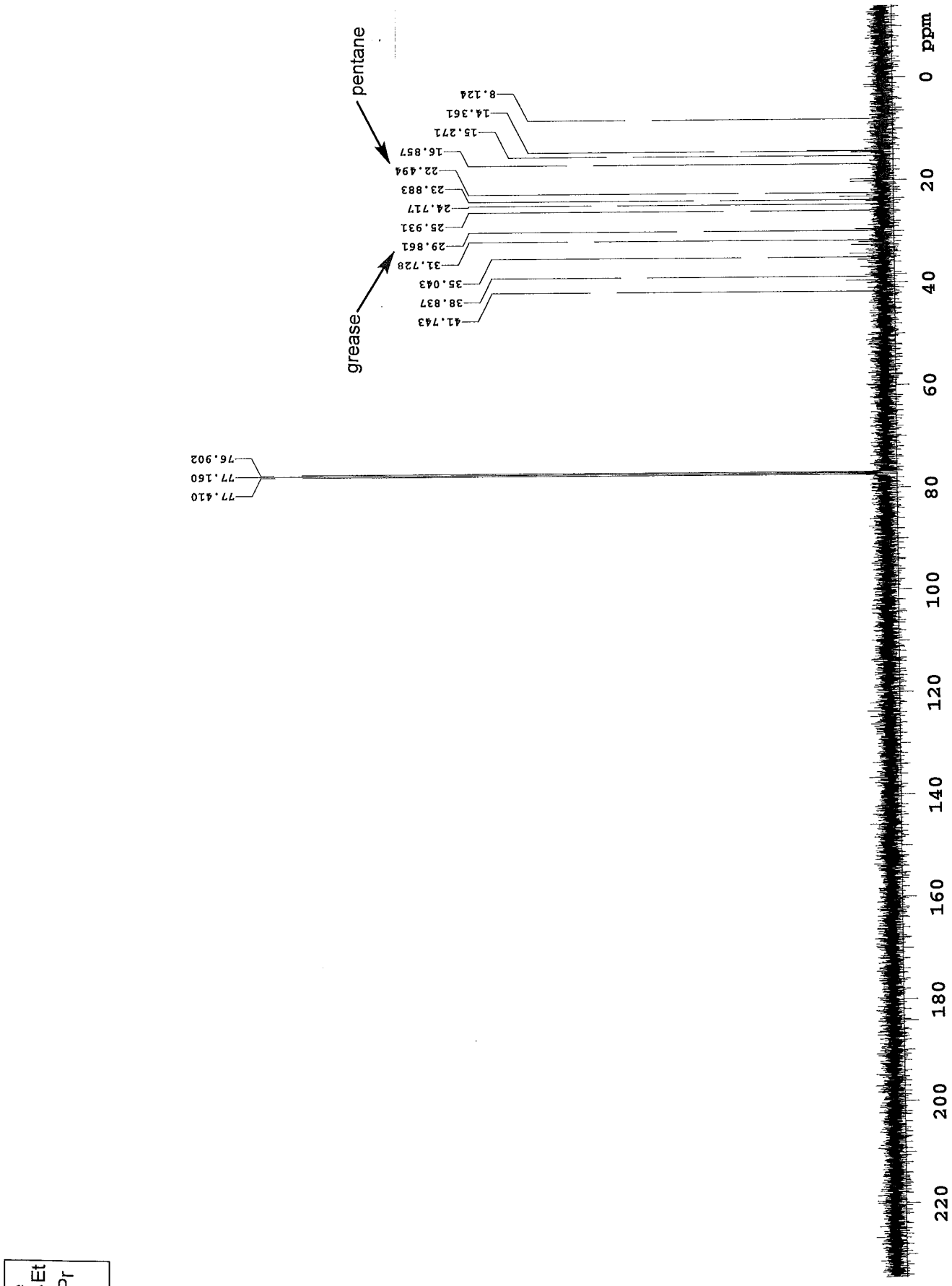

Me
HO
Et
O

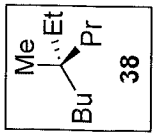
(*S*)-S12

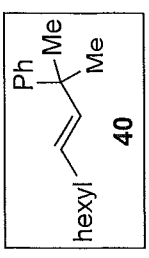

182.660
143.003
128.530
127.012
126.414
77.375
77.160
76.953
50.521
31.769
21.865
9.193
ppm
220
200
180
160
140
120
100
80
60
40
20
0
ppm

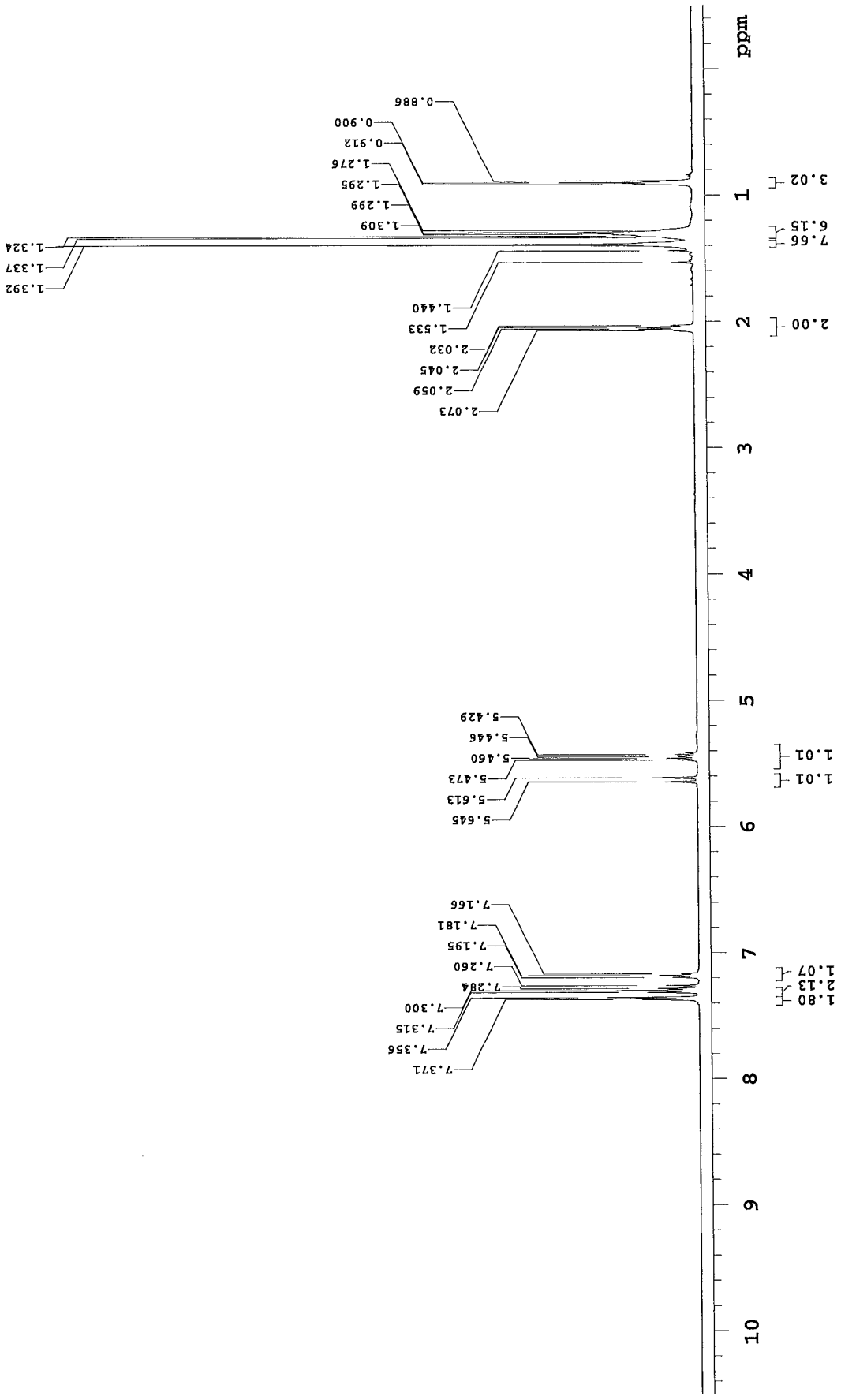

ppm
10
9
8
7
6
5
4
3
2
1
7.260
1.531
1.314
1.300
1.284
1.257
1.242
1.222
1.206
1.191
1.176
1.163
1.155
1.150
1.140
1.134
1.127
1.118
1.111
1.102
1.098
0.910
0.896
0.885
0.873
0.860
0.848
0.835
0.773
0.765
0.759
0.743
21.12
11.82
6.00

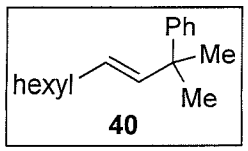

Me
Et
Pr
Bu
38


pentane
grease
8.124
14.361
15.271
16.857
22.494
23.883
24.717
25.931
29.861
31.728
35.043
38.837
41.743
76.902
77.160
77.410
0 ppm
20
40
60
80
100
120
140
160
180
200
220

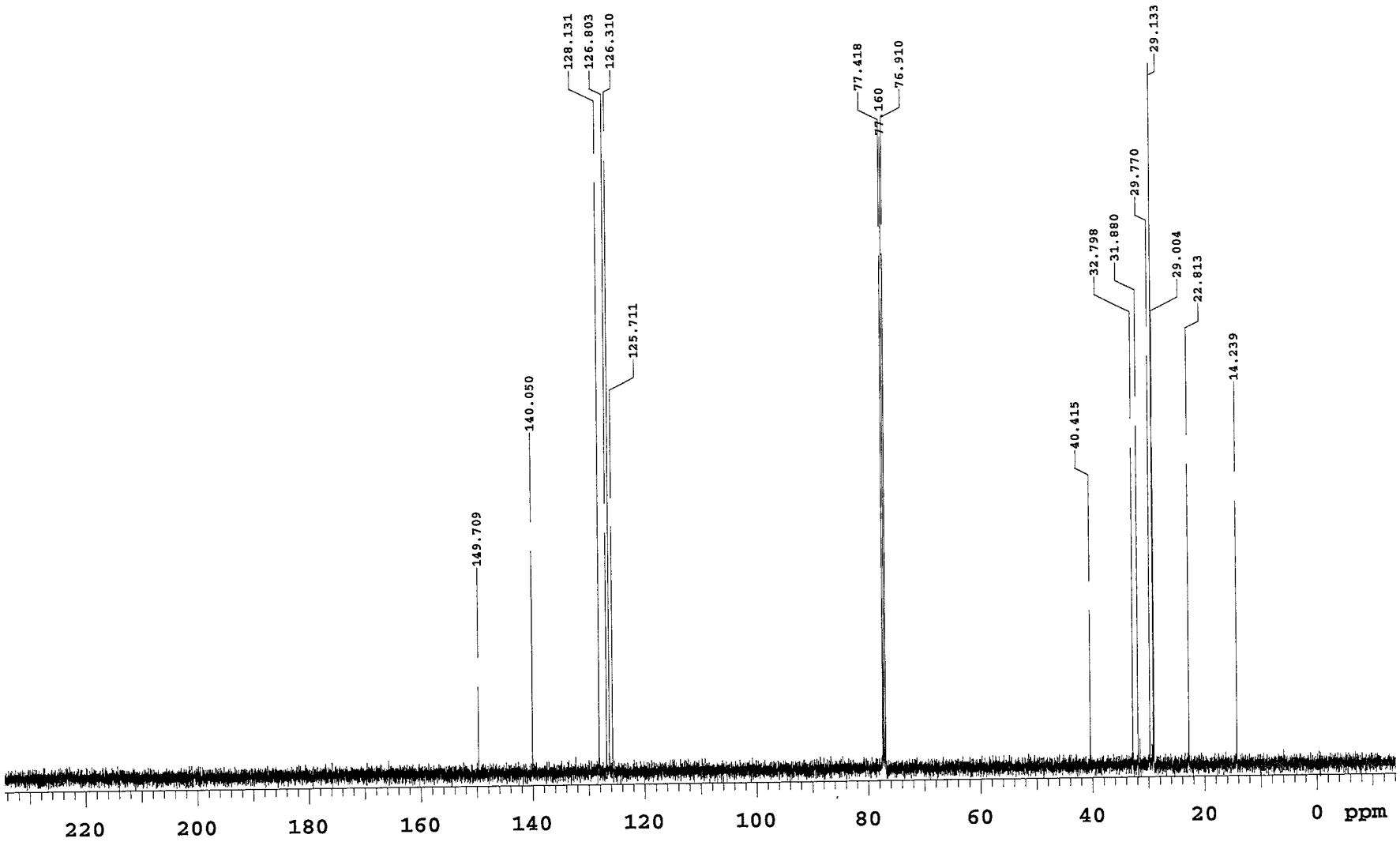

Me
Et
Pr
Bu
38

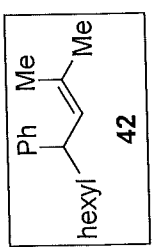

Ph
Me
Me
hexyl
40

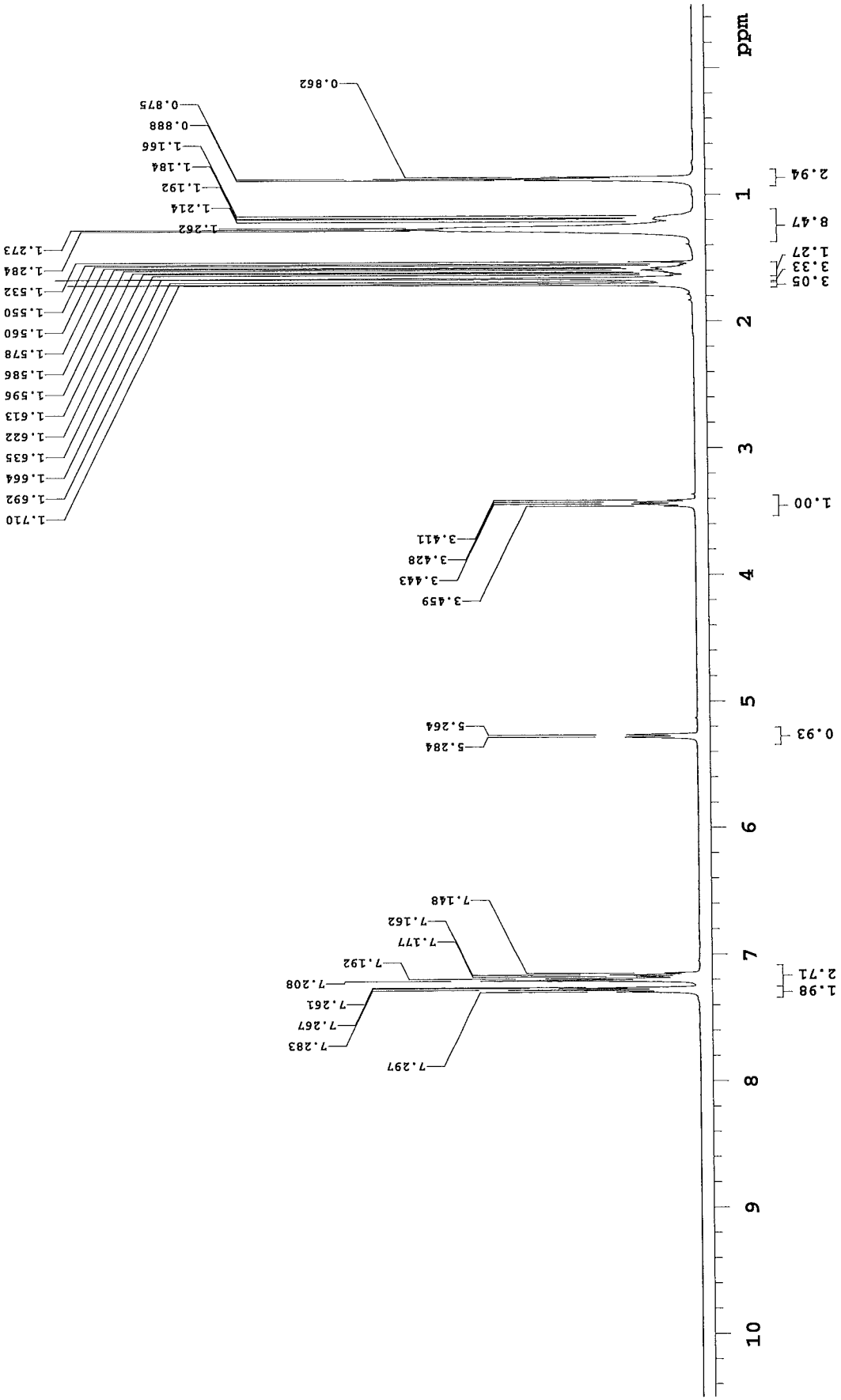

ppm
1
2
3
4
5
6
7
8
9
10
3.02
6.15
7.66
2.00
1.01
1.01
1.07
2.13
1.80
0.886
0.900
0.912
1.276
1.295
1.299
1.309
1.324
1.337
1.392
1.440
1.533
2.032
2.045
2.059
2.073
5.429
5.446
5.460
5.473
5.613
5.645
7.166
7.181
7.195
7.260
7.284
7.300
7.315
7.356
7.371

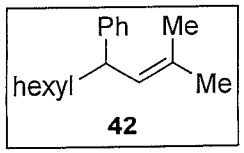

Ph
Me
hexyl
Me

40

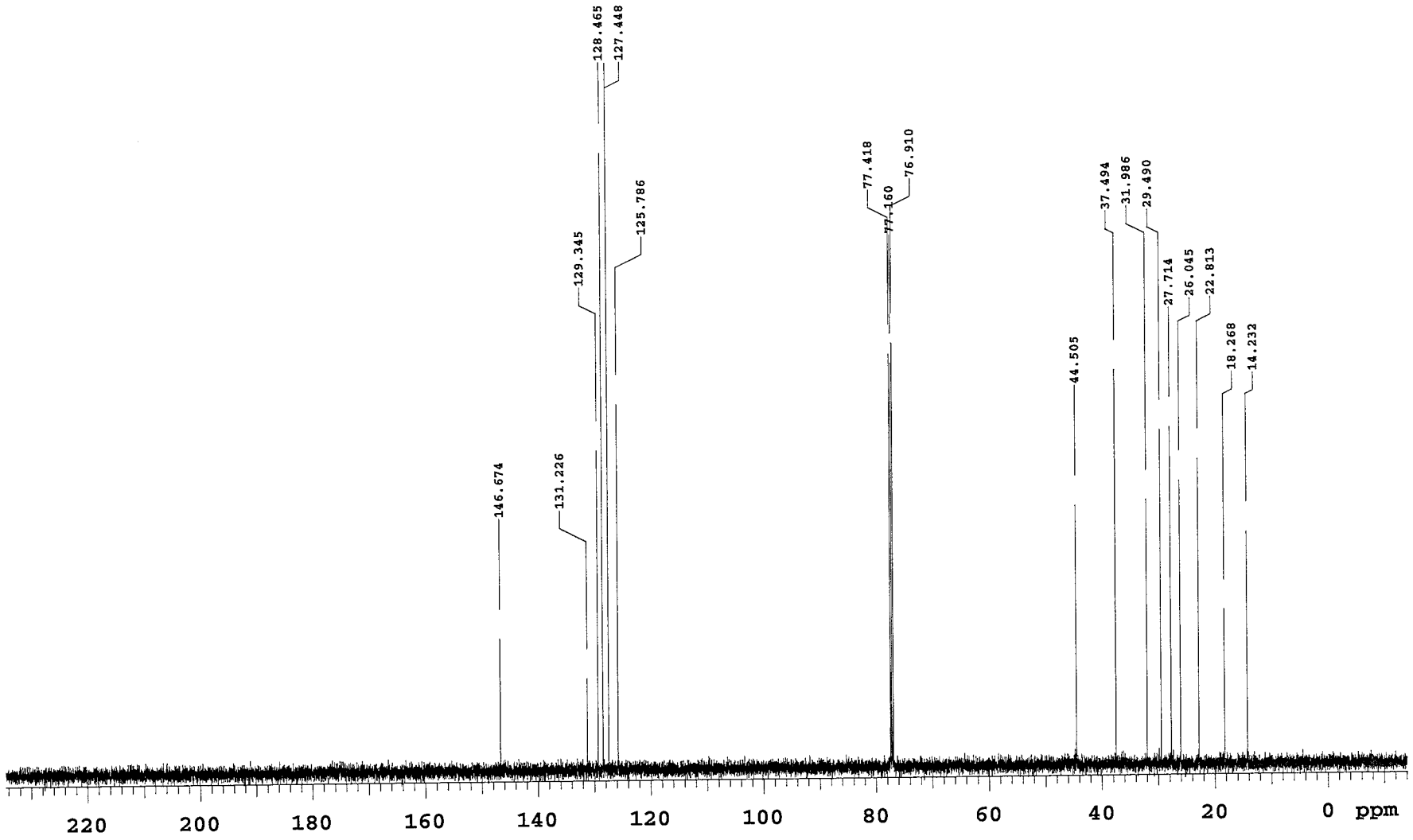

128.131
126.803
126.310
125.711
149.709
140.050
77.418
77.160
76.910
40.415
32.798
31.880
29.770
29.133
29.004
22.813
14.239
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
Me
Me
hexyl
42


ppm
1
2
3
4
5
6
7
8
9
10
2.94
8.47
1.27
3.33
3.05
1.00
0.93
2.71
1.98
0.862
0.875
0.888
1.166
1.184
1.192
1.214
1.262
1.273
1.284
1.532
1.550
1.560
1.578
1.586
1.596
1.613
1.622
1.635
1.664
1.692
1.710
3.411
3.428
3.443
3.459
5.264
5.284
7.148
7.162
7.177
7.192
7.208
7.261
7.267
7.283
7.297


Ph
Me
hexyl
Me

42


128.465
127.448
129.345
125.786
77.418
77.160
76.910
37.494
31.986
29.490
27.714
26.045
22.813
18.268
14.232
44.505
146.674
131.226
220
200
180
160
140
120
100
80
60
40
20
0
ppm