

New Approach to the Stereoselective Synthesis of Metallated Dienes via an Isomerization-Elimination Sequence

Nicka Chinkov, Swapan Majumdar and Ilan Marek*

Department of Chemistry and Institute of Catalysis Science and Technology

Technion-Israel Institute of Technology.

Technion City 32000 Haifa Israel

Supporting Information

Detailed reaction procedure and analytical data

General

All reactions involving air- and moisture- sensitive compounds were carried out under argon atmosphere, using flamed flask and dry, oxygen-free solvents. Diethyl ether and tetrahydrofuran were distilled under argon from sodium benzophenone ketyl. HMPA was distilled under vacuum from CaH_2 . Allyl bromide, allyl chloride and methallyl chloride were distilled under argon from K_2CO_3 . $n\text{-BuLi}$ was commercially obtained from Aldrich and titrated under argon atmosphere by 1M 2 isobutanol solution in toluene, using 1,10-phenantroline as an indicator. All NMR spectra were recorded at room temperature with a Bruker-AM-200 and Bruker-AM-400 instruments. Chemical shifts are referenced to the residual proton or carbon resonance of the deuterated solvent and are reported relative to $\text{Si}(\text{CH}_3)_4$.

1-Methoxy-2-pentyl-(Z)1,4-pentadiene **3Z**

To an ethereal solution (100 ml) of dibutyl cuprate reagent, prepared from CuI (4.26 g, 25 mmol) and $n\text{BuLi}$ (36.76 ml, 50 mmol, 1.36M solution in hexane) was added dropwise at -50°C , methoxyallene (2.8 g, 40 mmol) in 20 ml of Et_2O . The mixture was stirred at -40°C for 30 min, while the formation of the alkenyl cuprate reagent was confirmed by GC analysis. The reaction mixture was cooled down to -65°C , and allyl bromide (10.15 ml, 120 mmol) in THF (20 ml) was slowly added. After the addition, the temperature was allowed to reach -40°C and was maintained at this temperature for 1h. Hydrolysis was carried out by a saturated aqueous solution of $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}=2:1$. The mixture was then stirred 1h and then filtered through a pad of Celite, on a sintered glass funnel (the salts were washed several times with ether). The aqueous phase was extracted with ether (5×50 ml), the combined organic extracts and filtrates were washed with a saturated solution of NH_4Cl (until the blue color vanished), brine and dried over K_2CO_3 . Filtration and concentration under reduced pressure afforded an orange crude oil, which was then distilled on Kugel-Rohr ($130^\circ\text{C}/30\text{ mmHg}$) to yield 6 g (89%) of **3Z**. ^1H NMR (200 MHz, CDCl_3) δ 0.85 (t, $J=6.97\text{Hz}$, 3H), 1.15-1.39 (m, 6H), 1.83 (t, $J=7.43\text{Hz}$, 2H), 2.76 (d, $J=6.58\text{Hz}$, 2H), 3.51 (s, 3H), 4.91-5.05 (m, 2H), 5.64-5.81 (m, 1H), 5.77 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 13.9, 22., 27.7, 31.3, 31., 31.6, 59.1, 114.5, 116.2, 136.6, 142.3.

1-Methoxy-2-pentyl-(E)1,4-pentadiene 3E

The reaction was carried out according to the procedure described above, but in THF instead of Et₂O: CuI (457.1 mg, 2.4 mmol), nBuLi (194 ml, 2.4 mmol), THF (15 ml), methoxyallene (140 mg, 2 mmol) in THF (5 ml), allyl bromide (0.3 ml, 3.5 mmole) in THF (2 ml). Purification by chromatography on silica gel (Hexane/EtOAc=90:1) yielded 0.2 g (60%) of **3E**. ¹H NMR (200 MHz, CDCl₃) δ 0.87 (t, *J*=6.88Hz, 3H), 1.15-1.41 (m, 6H), 2.01 (t, *J*=7.78Hz, 2H), 2.57 (d, *J*=6.65Hz, 2H), 3.51 (s, 3H), 4.94-5.06 (m, 2H), 5.65-5.79 (m, 1H), 5.74 (s, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 13.9, 22.5, 27.7, 31.3, 31.5, 31.6, 59.1, 114.5, 116.2, 136.6, 142.3.

1-Methoxy-2-pentyl-(Z)1,5-hexadiene 4

The reaction was carried out according to the procedure described for **3Z**: nBuLi (5.37 ml 7mmol), CuI (666.54 mg, 3.5 mmol) in Et₂O (25 ml), methoxyallene (465.5 mg, 6.65 mmol). Then, freshly distilled HMPA (1.22 ml, 7 mmol) in THF (8 ml) followed by 4-iodo-but-1-ene (1.27 g, 7 mmol) in THF (5 ml) were dropwise added at -30°C. The mixture was allowed to reach room temperature and stirred for 3h at +20°C, then hydrolyzed at -20°C with 3N HCl (16.8 ml). After classical treatment, the crude was purified by chromatography on basic alumina (Hexane/EtOAc=100:1) to yield 0.8 g (66%) of **4** as pale yellow oil. ¹H NMR (200 MHz, CDCl₃) δ 0.86 (t, *J*=6.79Hz, 3H), 1.24-1.39 (m, 6H), 1.83 (t, *J*=7.27Hz, 2H), 2.10 (s, 2H), 2.11 (s, 2H), 3.501 (s, 3H), 4.88-5.03 (m, 2H), 5.79-5.84 (m, 1H), 5.74 (s, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 14.2, 22.8, 26.6, 28.1, 31.6, 31.7, 32.2, 59.4, 114.1, 118.2, 139.2, 142.5.

1-Methoxy-2-pentyl-(Z)1,6-heptadiene 5

The reaction was carried out according to the procedure described for **3Z**: nBuLi (3.86 ml, 5.26 mmol), CuI (500.85 mg, 2.63 mmol) in Et₂O (18 ml), methoxyallene (350 mg, 5 mmol). Then, freshly distilled HMPA (0.92 ml, 5.26 mmol) in THF (5 ml) followed by 5-iodo-pent-1-ene (1.03 g, 5.26 mmol) in THF (5 ml) and triethylphosphite (1.35 ml, 7.89 mmol) were dropwise added at -30°C. The mixture was allowed to reach room temperature and stirred for 17h at +20°C, then hydrolyzed at -20°C with 5N HCl. After classical treatment, the crude was purified by chromatography on silica gel (Hexane/EtOAc=100:1) to yield 790 mg (80%) of **5**. ¹H NMR (200 MHz, CDCl₃) δ 0.86 (t, *J*=6.94Hz, 3H), 1.15-1.34 (m, 6H), 1.42 (q, *J*=7.89Hz, 2H), 1.82 (t, *J*=7.23Hz, 2H), 1.96-2.07 (m, 2H), 3.49 (s, 3H), 4.89-5.02 (m, 2H), 5.73 (s, 1H), 5.75-5.89 (s, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 14.2, 22.5, 26.4, 27.1, 27.9, 31.4, 31.5, 33.7, 59.2, 114.1, 118.4, 139.1, 142.1.

1-Methoxy-2-(7-octene)-E(1)-heptene 6

The reaction was carried out according to the procedure described for **3Z**: nBuLi (3.87 ml, 5.23 mmol), CuI (498 mg, 2.6 mmol) in Et₂O (12 ml), methoxyallene (347 mg, 5 mmol), freshly distilled HMPA (1.83 ml, 10.46 mmol) in THF (5 ml), 8-iodo-oct-1-ene (0.88 ml, 5.23 mmol) in THF (5 ml) and triethylphosphite (1.34 ml, 7.85 mmol) were dropwise added at -30°C. The mixture was allowed to reach room temperature and stirred for 1 h at +20°C, then hydrolyzed at -20°C with 5N HCl. After classical treatment, the crude was purified by chromatography on silica gel (Hexane/EtOAc=100:1) to yield 786 mg (66%) of **6**. ¹H NMR (200 MHz, CDCl₃) δ 0.86 (t, *J*=7.04Hz, 3H), 1.27 (m, 14H), 1.81 (t, *J*=7.17Hz, 2H), 1.96-2.07 (m, 4H), 3.49 (s, 3H), 4.87-5.00 (m, 2H), 5.71 (s, 1H),

5.71-5.86 (m, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 22.5, 26.7, 27.7, 27.9, 28.9, 29.0, 29.4, 31.4, 31.6, 33.8, 59.2, 114.1, 118.9, 139.3, 141.9.

1-Methoxy-2-pentyl-Z(1,4)-trans-hexadiene 7.

The reaction was carried out according to the procedure described for **3Z**: CuI (2.23 g, 12 mmol), *n*BuLi (19.5 ml, 24 mmol), Et_2O (50 ml), methoxyallene (700 mg, 10 mmol) in Et_2O (8 ml), crotylbromide (3.1 ml, 3.0 mmol) in Et_2O (8 ml). The reaction was complete within 1h 40 min. Purification by chromatography on silica gel (Hexane/ EtOAc =100:1) gives 1.045 g of pure **7** and 66 mg of the isomeric 1-methoxy-3-methyl-2-pentyl-Z(1,4)-pentadiene (the balance being the mixture of the two products) ^1H NMR (200 MHz, CDCl_3) δ 0.85 (t, J =7.15Hz, 3H), 1.17-1.38 (m, 6H), 1.6 (d, J =4.81, 3H), 1.82 (t, J =7.36Hz, 2H), 2.68 (d, J =5.18Hz, 2H), 3.51 (s, 3H), 5.26-5.48 (m, 2H), 5.73 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 22.5, 27.7, 30.3, 31.2, 31.5, 31.8, 59.2, 115.0, 125.2, 138.2, 141.9.

1-Pentyl-2-methoxy-Z(1,4)-pentadiene 8

The reaction was carried out according to the procedure described for **3Z**: *n*BuLi (1.71 ml, 2.4 mmol), CuI (228.5 mg, 1.2 mmol) in Et_2O (10 ml) on methoxyhexa-1,2,5-triene (110mg, 1 mmol) in Et_2O (5 ml). The reaction was stirred over 1 h at -20°C . Purification by column chromatography on basic alumina (hexane as eluent) afforded 118 mg (70%) of **8** (Z/E ratio equal 10:1). ^1H NMR (200 MHz, CDCl_3) δ 0.86 (t, J =6.63Hz, 3H), 1.24-1.42 (m, 6H), 1.93 (m, 2H), 2.85 (d, J =6.1 Hz, 2H), 3.46 (s, 3H), 4.39 (t, J =7.34Hz, 1H), 5.02 (m, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 22.5, 26.4, 30.6, 31.4, 34.9, 54.1, 97.6, 115.3, 136.0, 156.9.

1-iodo-(1,1)-bisdeutero-hex-3-trans-ene

A 150-ml dry 4-necked flask under Ar, equipped with mechanical stirrer and reflux condenser was loaded with ethyl *trans*-3-hexenoate (4.25 ml, 0.026 mol) and dry Et_2O (60 ml). Then LiAlD_4 powder (900 mg, 0.0214 mol) was added in portions, keeping the temperature of the reaction mixture at -5°C . After the addition, the reaction mixture is heated under reflux for 1h. The reaction was quenched by 1ml of aqueous solution of saturated Na_2SO_4 at 0°C . After 2h of stirring, the white precipitate was filtered off, washed several times with ether and the combined ethereal phases were removed under vacuum (30 mmHg). The crude (1,1)-bisdeutero-hex-3-trans-ene-1-ol (84.3%) was without further purification, transformed into the corresponding mesylate in the step (b). ^1H NMR (200 MHz, CDCl_3) δ 0.95 (t, J =7.46Hz, 3H), 2.00 (m, 2H), 2.20 (d, J =6.68Hz, 2H), 5.26-5.40 (m, 1H), 5.50-5.64 (m, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 13.06, 24.9, 35.7, 60.1(q), 124.7, 135.73.

(b) Mesityl chloride (2.08 ml, 0.027 mol) was added dropwise at 0°C to the mixture of E-(1,1)-bisdeutero-hex-3-ene-1-ol (2.3 g, 0.022 mol) and Et_3N (4.65 ml, 3.3 mol) in dichloromethane (50 ml). The reaction was allowed then to reach the ambient temperature, and stirred for 45 min. When the reaction was complete (followed by TLC, 20% ethyl acetate-hexane), ice water was added and the separated aqueous layer was washed several times with dichloromethane. The combined organic extracts were successively washed with an aqueous solution of HCl 1M, brine, then dried over MgSO_4 and concentrated, to afford 4.02 g (100% yield) of the crude *E*-methanesulfonic acid (1,1)-bisdeutero-hex-3-enyl ester.

(c) To the crude *E*-methanesulfonic acid (1,1)-bisdeutero-hex-3-enyl ester (4 g, 0.022 mol), NaI (5.32 g, 0.035 mol) and acetone (22 ml). The reaction was over within 3h, as indicated by TLC analysis. Distillation of the crude residue by means of Kügel-Rohr apparatus (80-95 °C/30 mmHg) afforded the title product in 76% yield (3.58 g). ¹H NMR (200 MHz, CDCl₃) δ 0.95 (t, *J*=7.44Hz, 3H), 1.91-2.05 (m, 2H), 2.48 (d, *J*=6.47Hz, 2H), 5.31 (dt, *J*=6.59Hz, 15.54Hz, 1H), 5.38 (dt, *J*=6.39Hz, 15.46Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 5.6 (q), 13.9, 25.7, 36.9, 127.5, 135.5.

1-Methoxy-(3,3)-bisdeutero-2-pentyl-Z(1,5)-octadiene 18

The reaction was carried out according to the procedure described for **3Z**: *n*BuLi (5.37 ml, 7mmol), CuI (666.54 mg, 3.5 mmol) in Et₂O (25 ml), methoxyallene (465.5 mg, 6.65 mmole) in Et₂O (10 ml), freshly distilled HMPA (1.22 ml, 7 mmol) in THF (8 ml), 1-iodo-(1,1)-bisdeutero-hex-3-*trans*-ene (1.48 g, 7 mmol) in THF (5 ml) were dropwise added at -30 °C. The mixture was allowed to reach room temperature and stirred overnight at +20°C, then hydrolyzed at -20°C with 5N HCl (12 ml). After classical treatment, the crude was purified by chromatography on basic alumina (hexane) to yield 294 mg of **18**. ¹H NMR (200 MHz, CDCl₃) δ 0.89-1.00 (m, 6H), 1.17-1.38 (m, 6H), 1.82 (t, *J*=7.36Hz, 2H), 1.9-2.05 (m, 4H), 3.51 (s, 3H), 5.35-5.45 (m, 2H), 5.69 (s, 1H).

General Procedure for the isomerization-elimination sequence mediated by zirconocene 1

A solution of *n*-butyllithium in hexane (2.4 eq) was added dropwise to a stirred solution of bis(cyclopentadienyl)zirconiumdichloride (1.2 eq) in dry THF at -78°C under inert atmosphere. The temperature was slowly allowed to reach -50°C and the substrate (1 eq), diluted in 5 ml THF, was added dropwise, keeping the temperature below -50°C. When the addition was finished, the cooling bath was removed and the reaction mixture was warmed as fast as possible to room temperature (the delay in warming the reaction mixture may cause the formation of side products). It was then heated to +50°C for 15 min, and the metallated diene is ready for further use, or, alternatively, can be hydrolyzed by 1N HCl, after cooling down to room temperature. The layers were separated and the aqueous phase was extracted 5 times with ether. The combined organic extracts were washed successively with sodium bicarbonate saturated solution, brine and dried over MgSO₄. The obtained residue is finally purified by column chromatography on silica gel.

2-Pentyl-1,3-*trans*-pentadiene 10

The previously described procedure was carried out on **3Z**; (168 mg, 1mmol) in THF (5 ml), Cp₂ZrCl₂ (350.6 mg, 1.2 mmol) in THF (15 ml) and *n*BuLi (1.8 ml, 2.4 mmol). The purification of the crude residue afforded the desired diene in 80% of yield. ¹H NMR (200 MHz, CDCl₃) δ 0.87 (m, 3H), 1.22-1.49 (m, 6H), 1.73 (d, *J*=6.08Hz, 3H), 2.15 (t, *J*=7.96Hz, 2H), 4.80 (s, 1H), 4.83 (s, 1H), 5.71 (dq, *J*=6.58, 15.72Hz, 1H), 6.01 (d, *J*=15.77Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 13.3, 17.5, 21.9, 27.4, 31.2, 31.6, 111.9, 123.9, 132.8, 145.9. Anal. Calcd for C₁₀H₁₈: C, 86.87; H, 13.12 Found: C, 87.10 H, 13.67

1-Iodo-2-pentyl-(Z,E)1,3-pentadiene 11

The previously described procedure was carried out on **3Z**; (295 mg, 1.75 mmol) in THF (5 ml), Cp₂ZrCl₂ (614 mg, 2.01 mmol) in THF (15 ml) and *n*BuLi (1.7 ml, 4.2 mmole). Iodinolysis (1.1 g, 4.4 mmol) in THF was carried out at -40°C. After

classical work-up, crude **11** was obtained as reddish oil. Due to the high sensitivity to light, heat and acidic conditions, **11** was quickly purified by florisil (pentane as an eluent) to afford **11** in 75% of yield. ^1H NMR (200 MHz, C_6D_6) δ 0.81 (m, 3H), 1.02-1.21 (m, 6H), 1.47 (dd, $J=1.19$, 6.64Hz, 3H), 2.01 (t, $J=7.78$ Hz, 2H), 5.5-5.71 (m, 1H), 5.75 (s, 1H), 6.42 (d, $J=15.8$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 18.5, 22.6, 28.4, 31.5, 35.0, 76.7, 129.8, 132.3, 145.9.

5-Pentyl-(Z,E)-1,4,6-octatriene **12**

The previously described procedure was carried out on **3Z**; (168 mg, 1 mmol) in THF (5 ml), Cp_2ZrCl_2 (350.64 mg, 1.2 mmol) in THF (17 ml) and $n\text{BuLi}$ (1.17 ml, 2.4 mmol). When the formation of the dienyl zirconium derivative **9** was complete and confirmed by GC analysis, freshly distilled allyl chloride (0.12 ml, 1.5 mmol), CuCl (9.9 mg, 0.1 mmol) and LiCl (85 mg, 2 mmol) were added at 0°C . The solution was then heated to $+60^\circ\text{C}$ and stirred at this temperature for 1 h. Quenching the reaction by addition of an aqueous mixture of $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ (2:1) was done at room temperature and the solution was worked-up as usual. Further purification by column chromatography on silica gel (hexane) afforded the expected **12** as a unique isomer in 70 % yield. ^1H NMR (200 MHz, CDCl_3) δ 0.87 (t, $J=6.78$ Hz, 3H), 1.24-1.52 (m, 6H), 1.76 (d, $J=6.744$ Hz, 3H), 2.14 (t, $J=7.92$ Hz, 2H), 2.88 (t, $J=6.83$ Hz, 2H), 4.93-5.05 (m, 2H), 5.21 (t, $J=7.5$ Hz, 1H), 5.62-5.84 (m, 2H), 6.24 (d, $J=15.7$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 18.6, 22.5, 28.7, 31.6, 31.9, 34.2, 114.5, 124.0, 125.1, 127.4, 134.6, 137.3.

5-pentyl-1-4Z-6E-nonatriene **13**

The previously described procedure was carried out on **4** (182 mg, 1 mmol) in THF (5 ml), Cp_2ZrCl_2 (350.6 mg, 1.2 mmol) in THF (17 ml) and $n\text{BuLi}$ (1.65 ml, 2.4 mmol). When the formation of dienyl zirconium derivative was complete and confirmed by GC analysis, freshly distilled allyl chloride (0.12 ml, 1.5 mmol), CuCl (9.9 mg, 0.1 mmol) and LiCl (85 mg, 2 mmol) were added at 0°C . The solution was heated then to $+60^\circ\text{C}$ and stirred at this temperature for 2 h. After classical treatment and further purification by column chromatography on silica gel (hexane), **13** was isolated as a unique isomer in 68% yield. ^1H NMR (200 MHz, CDCl_3) δ 0.87 (t, $J=6.7$ Hz, 3H), 1.01 (t, $J=7.46$ Hz, 3H), 1.24-1.50 (m, 6H), 2.05-2.18 (m, 2H), 2.88 (t, $J=6.73$ Hz, 2H), 4.92-5.07 (m, 2H), 5.23 (t, $J=7.48$ Hz, 1H), 5.65-5.82 (m, 2H), 6.22 (d, $J=15.7$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 13.8, 14.0, 22.5, 26.3, 28.6, 31.6, 31.9, 34.2, 114.5, 124.3, 125.0, 132.3, 137.3, 137.5.

5-Pentyl-1-4Z-6E-decatriene **14**

The previously described procedure was carried out on **5** (98 mg, 0.5 mmol) in THF (3 ml), Cp_2ZrCl_2 (306.81 mg, 1 mmol) in THF (15 ml) and $n\text{BuLi}$ (1.38 ml, 2 mmol). When the formation of dienyl zirconium derivative was complete and confirmed by GC analysis, freshly distilled allyl chloride (0.17 ml, 2.1 mmol), CuCl (9.9 mg, 0.1 mmol) and LiCl (110.2 mg, 2.6 mmol) were added at 0°C . The solution was heated then to $+60^\circ\text{C}$ and stirred at this temperature for 2 h. After classical treatment and further purification by column chromatography on silica gel (hexane) pure **14** was isolated in 65% yield. ^1H NMR (200 MHz, CDCl_3) δ 0.83-0.92 (m, 6H), 1.23-1.52 (m, 8H), 2.03-2.18 (m, 4H), 2.88 (t, $J=6.86$ Hz, 2H), 4.93-5.05 (m, 2H), 5.22 (t, $J=7.48$ Hz, 1H), 5.61-5.9 (m, 2H), 6.21(d, $J=15.7$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 14.3, 22.5, 22.7, 28.6, 31.6, 31.8, 34.2, 35.4, 114.5, 124.2, 126.1, 130.6, 137.3, 137.5.

2-Pentyl-1-3E-decadiene 15

The previously described procedure was carried out on **6** (131 mg, 0.55 mmol) in THF (3 ml), Cp_2ZrCl_2 (208.6 mg, 0.71 mmol) in THF (13 ml) and *n*BuLi (0.89 ml, 1.43 mmol). Purification by column chromatography on silica gel (hexane) yielded 63% of the desired product **15**. ^1H NMR (200 MHz, CDCl_3) δ 0.84-0.87 (m, 6H), 1.23-1.48 (m, 14H), 2.01-2.19 (m, 4H), 4.81 (s, 1H), 4.84 (s, 1H), 5.67 (dt, $J=6.78$, 15.75Hz, 1H), 5.98 (d, $J=15.8$ Hz, 1H); ^{13}C NMR (200 MHz, CDCl_3) δ 14.0, 22.5, 22.6, 28.0, 28.9, 29.4, 29.7, 31.7, 31.8, 32.3, 32.8, 112.7, 130.1, 132.0, 146.6.

2E-4Z-decadiene 17

The previously described procedure was carried out on **8** (100 mg, 0.59 mmol) in THF (3ml), Cp_2ZrCl_2 (208.6 mg, 0.714 mmol) in THF (15 ml) and *n*BuLi (1.02 ml, 1.4 mmol). Purification by column chromatography on silica gel (hexane) yielded **17** in 75% yield. ^1H NMR (200 MHz, CDCl_3) δ 0.81-0.90 (m, 3H), 1.25-1.38 (m, 6H), 1.76 (d, $J=6.44$ Hz, 3H), 2.13 (m, 2H), 5.28 (dt, $J=7.43$ Hz, 1H), 5.65 (m, 1H), 5.93 (t, $J=10.75$ Hz, 1H), 6.28 (m, 1H); ^{13}C NMR (200 MHz, CDCl_3) δ 14.09, 22.56, 22.7, 27.66, 29.37, 31.5, 31.95. Anal. Calcd for $\text{C}_{10}\text{H}_{18}$: C, 86.87; H, 13.12 Found: C, 87.02 H, 13.56

2-pentyl-3,5-bisdeutero-1,3-trans-octadiene 19

The previously described procedure was carried out on **18** (105 mg, 0.49 mmol) in THF (5 ml), Cp_2ZrCl_2 (434.2 mg, 1.48 mmol) in THF (20 ml) and *n*BuLi (2.2 ml, 2.9 mmol). Purification by column chromatography on silica gel (hexane) yielded 62% of the desired **19**. An unidentified side product was formed as well. ^1H NMR (200 MHz, CDCl_3) δ 0.86 (m, 6H), 1.23-1.49 (m, 10H), 1.93-2.06 (m, 1H), 2.15 (t, $J=7.88$ Hz, 2H), 4.82 (s, 1H), 4.84 (s, 1H), 5.62, (d, $J=6.4$ Hz, 1H); ^{13}C NMR (200 MHz, CDCl_3) δ 13.9, 14.0, 22.1, 22.7, 28.0, 29.7, 31.5, 31.8, 32.2 (t), 112.7, 129.9, 130.6(t), 146.5.

(Nona-1,3-diene-3-sulfonyl)-benzene 21a

A solution of *n*BuLi (11.8 ml, 17.7 mmol, 1.50M in hexane) was slowly added to the stirred solution of allylphenyl sulfone (3.0g, 16.5 mmol) in THF (20ml) at -78°C . After being stirred at -78°C for 30 min, a solution of valeraldehyde (1.80g, 16.9 mmol) in THF (5ml) was added and stirred for 1h at that temperature. Then, acetic anhydride (7.5 ml) was added and warmed up to room temperature for 2h, followed by addition of a solution of KOH (10g, 178 mmol) in water (10ml). The reaction mixture was stirred for an additional 2h. The mixture was then diluted with water (50ml) and dichloromethane (50 ml). After classical treatment, the crude was purified by chromatography on silica gel [eluent: hexane-ethyl acetate(1:9)] to give the title compound **21a** as a mixture of two geometric isomers trans/cis 85/15 in 72% yield. ^1H NMR (CDCl_3 , 200 MHz) (major) δ 7.80 – 7.73 (m, 2H), 7.56 – 7.37 (m, 3H), 6.96 (t, $J = 7.6$ Hz, 1H), 6.26 – 6.11 (dd, $J = 17.7$, 11.5 Hz, 1H), 5.45 (d, $J = 17.9$ Hz, 1H), 5.32 (d, $J = 11.6$ Hz, 1H), 2.30 – 2.02 (m, 2H), 1.46 – 1.19 (m, 6H), 0.81 (bs, 3H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 143.41, 142.92, 140.05, 132.84, 128.73, 127.64, 125.40, 122.84, 31.19, 28.37, 28.06, 22.14, 13.70.

(1-Cyclohexyl-buta-1,3-diene-2-sulfonyl)-benzene 21b

The previously described procedure was carried out for the preparation of **21b** with cyclohexane carboxaldehyde; Combined yield 70%

21b (E): ^1H NMR (CDCl_3 , 200 MHz) δ 7.75 – 7.71 (d, J = 8.0 Hz, 2H), 7.53 – 7.36 (m, 3H), 6.79 (d, J = 10 Hz, 1H), 6.26–6.12 (dd, J = 17.7, 11.6 Hz, 1H), 5.47 (d, J = 17.3 Hz, 1H), 5.29 (d, J = 11.6 Hz, 1H), 2.41 – 2.36 (m, 1H), 1.65 – 1.60 (m, 4H), 1.17 (bs, 6H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 147.83, 140.13, 137.60, 132.87, 128.79, 127.65, 125.48, 122.60, 37.50, 31.80, 25.50, 25.10

21b (Z): ^1H NMR (CDCl_3 , 200 MHz) δ 7.81 (d, J = 7.0 Hz, 2H), 7.58 – 7.29 (m, 3H), 6.49 – 6.35 (dd, J = 17.0, 10.8 Hz, 1H), 6.06 (d, J = 10.8 Hz, 1H), 5.35 (d, J = 17.0 Hz, 1H), 5.10 (d, J = 10.9 Hz, 1H), 3.31 – 3.25 (m, 1H), 1.76 – 1.61 (m, 4H), 1.30 – 0.89 (m, 6H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 148.05, 141.68, 138.42, 133.12, 131.71, 128.88, 127.04, 118.15, 37.49, 32.39, 25.91, 25.43.

(1-Benzyl-buta-1,3-diene-2-sulfonyl)- benzene **21c**

21c (E): White solid, 89%. ^1H NMR (CDCl_3 , 200 MHz) δ 7.88 – 7.45 (m, 2H), 7.57 – 7.33 (m, 8H), 6.43 – 6.28 (dd, J = 18.3, 11.6 Hz, 1H), 5.88 (d, J = 18.2 Hz, 1H), 5.44 (d, J = 11.7 Hz, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ 139.93, 138.60, 138.20, 133.25, 133.08, 130.35, 129.92, 128.88, 128.58, 128.05, 126.40, 123.85.

General Experimental Procedure for the preparation of **24a-c**

A solution of *n*butyllithium in hexane (3.4 mmol) was added slowly to a solution of bis(cyclopentadienyl)zirconium dichloride (1.7 mmol) in dry THF (10ml) at -78°C . The solution was stirred for 30 min at -78°C and the vinylsulfone **21a-c** (1 mmol) was added at -78°C . The reaction mixture was allowed to warm to room temperature very rapidly and stirred for 2h for **21c** and overnight for **21a-b**. Then, the reaction mixture was quenched by a 1M HCl aqueous solution and diluted with ether (10ml). The layer was separated; the aqueous layer was extracted with ether (3 x 5ml). The combined organic layers were washed with aqueous NaHCO_3 (3x10ml), brine (3x10ml) and evaporated under vacuum to afford a crude residue, which was purified by column chromatography on silica gel using hexane as eluent.

Nona-1,3Z-diene **24a**

52 %; ^1H NMR (200 MHz, CDCl_3) δ 6.72–6.53 (dt, J = 16.8, 10.5 Hz, 1H), 5.97 (t, J = 10.9 Hz, 1H), 5.50 – 5.37 (m, 1H), 5.14 (d, J = 16.8 Hz, 1H), 5.05 (d, J = 10.2 Hz, 1H), 2.21 – 2.07 (m, 2H), 1.43 – 1.23 (m, 6H), 0.89 – 0.83 (m, 3H). ^{13}C NMR (50 MHz, CDCl_3) δ 133.10, 132.39, 129.13, 116.63, 31.45, 29.30, 27.72, 22.53, 14.02. Anal. Calcd for $\text{C}_{10}\text{H}_{10}$: C, 92.25; H, 7.77 Found: C, 92.73 H, 7.95

Buta-1,3Z-dienyl-cyclohexane **24b**

Yield: 71%; ^1H NMR (200 MHz, CDCl_3) δ 6.72–6.53 (m, 1H), 5.879 (t, J = 10.9 Hz, 1H), 5.28 (t, J = 9.8 Hz, 1H), 5.15 (d, J = 16.8 Hz, 1H), 5.04 (d, J = 9.3 Hz, 1H), 2.45 (m, 1H), 1.60 (m, 4H), 1.16 (m, 6H). ^{13}C NMR (50 MHz, CDCl_3) δ 138.9, 132.6, 127.3, 115.1, 36.8, 33.2, 26.0, 25.8. Anal. Calcd for $\text{C}_{10}\text{H}_{16}$: C, 88.15; H, 11.84 Found: C, 88.62 H, 12.24

Buta-1,3Z-dienyl-benzene **24c**

Yield 73%; ^1H NMR (200 MHz, CDCl_3) δ 7.41–7.17 (m, 5H), 6.97 (dt, J = 16.8, 11.4 Hz, 1H), 6.45 (d, J = 11.5 Hz, 1H), 6.25 (t, J = 11.4 Hz, 1H), 5.36 (d, J = 16.7 Hz, 1H), 5.22 (d, J = 10.1 Hz, 1H). ^{13}C NMR (50 MHz, CDCl_3) δ 137.36, 133.21, 130.79, 130.42, 129.01, 128.22, 127.04, 119.61.

Transmetallation of vinyl zirconocene **23aZr** into **23aCu**. Isomerization of Metallated Dienes.

After the formation of vinyl zirconocene **23aZr**, anhydrous CuCl (1.8 mmol) and LiCl (3.6 mmol) were added to the reaction mixture and heated at 45⁰C for 1hr. Then, a mixture of 25% NH₃ and saturated aqueous solution of NH₄Cl (1:1) was added and stirred for 2h. The mixture was then filtered through celite and washed with ether (50ml). After classical treatment, the crude product obtained was purified by column chromatography on silica gel with hexane as eluent to give the corresponding trans diene exclusively.

Buta-1,3E-dienyl-benzene **24c**

Yield 73%; ¹H NMR (200 MHz, CDCl₃) δ 7.41-7.17 (m, 5H), 6.97 (dt, *J* = 16.8, 11.4 Hz, 1H), 6.45 (d, *J* = 11.5 Hz, 1H), 6.25 (t, *J* = 11.4 Hz, 1H), 5.36 (d, *J* = 16.7 Hz, 1H), 5.22 (d, *J* = 10.1 Hz, 1H). ¹³C NMR (50 MHz, CDCl₃) δ 137.36, 133.21, 130.79, 130.42, 129.01, 128.22, 127.04, 119.61.

Reaction of **23cCu** with allyl chloride

Preparation of E-(2-vinyl-penta-1,4-dienyl)-benzene **29**

When the transmetalation step was over as described above, the reaction mixture was cool down to 0⁰C and then freshly distilled allyl chloride (5 mmol, 3 fold excess) was added followed by heating at 45⁰C for 1h. The reaction mixture was then hydrolyzed with aqueous. NH₄Cl and 25 % NH₃ solution (1:1). The mixture was filtered off through a celite pad on a sintered glass funnel, and after classical treatment, the residue was purified by column chromatography on silica gel (eluent hexane) to give the title product in 76% yield. ¹H NMR (200 MHz, CDCl₃) δ 7.37 (m, 5H), 6.62 (s, 1H), 6.55 – 6.41 (dd, *J* = 17.4, 10.7 Hz, 1H), 6.10 (m, 1H), 5.29 (d, *J* = 17.4 Hz, 1H), 5.15 – 5.07 (m, 3H), 3.22 – 3.18 (m, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 140.36, 137.45, 137.26, 135.95, 132.80, 128.77, 128.18, 126.94, 115.87, 113.70, 31.30. Anal. Calcd for C₁₃H₁₄: C, 91.70; H, 8.28 Found: C, 91.45 H, 8.66

Preparation of cis-3-bromo-4-phenyl-1,3-butadiene **25**¹

When the transmetalation step was over as described above, the reaction mixture was cool down to 0⁰C and then NBS (1.7 mmol, 1.7 eq.) was added. After classical treatment, the residue was purified by column chromatography on silica gel (eluent hexane) to give the title product in 61% yield. ¹H NMR (200 MHz, CDCl₃) δ 7.70 (d, *J* = 6.9 Hz, 2H), 7.41 – 7.25 (m, 3H), 6.97 (s, 1H), 6.56 – 6.43 (dd, *J* = 16.2, 10.4 Hz, 1H), 5.72 (d, *J* = 16.2 Hz, 1H), 5.33 (d, *J* = 10.3 Hz, 1H). ¹³C NMR (50 MHz, CDCl₃) δ 137.11, 135.57, 132.31, 129.55, 128.27, 128.15, 123.92, 119.02.

Preparation of 3E-(1-benzylidene-allyl)-cyclohexanone **30**

A premixed solution of cyclohexenone (0.18 ml, 1.8 mmol) and TMSCl (0.3 ml, 2 mmol) was added to the mixture in THF at 0⁰C. After 30 min, the cool bath was removed and the reaction mixture was stirred overnight at room temperature. After usual work-up, the purification by column chromatography on silica gel afforded **30** in 59% yield. ¹H NMR (200 MHz, CDCl₃) δ 7.35-7.13 (m, 5H), 6.64 (s, 1H), 6.50 –

6.36 (dd, $J = 17.2, 10.9$ Hz, 1H), 5.56 – 5.47 (dd, $J = 17.4, 1.3$ Hz, 1H), 5.18 – 5.13 (dd, $J = 10.8, 1.1$ Hz, 1H), 3.24 – 3.12 (m, 1H), 2.53 (t, $J = 14.0$ Hz, 1H), 2.35 – 2.24 (m, 3H), 2.11 – 2.01 (m, 1H), 1.84–1.78 (m, 2H), 1.68 – 1.62 (m, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 210.75, 142.19, 137.09, 136.02, 128.62, 128.36, 127.28, 126.92, 115.86, 46.33, 41.13, 39.20, 30.03, 25.37. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}$: C, 84.91; H, 8.01 Found: C, 85.23 H, 8.44

Preparation of trans-(hept-6-en-2-one)-benzene 28

Yield: 75%; ^1H NMR, (200 MHz, CDCl_3) δ 7.36 – 7.20 (m, 5H), 6.50 (s, 1H), 6.46 – 6.32 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.24 (d, $J = 17.6$ Hz, 1H), 5.12 (d, $J = 10.8$ Hz, 1H), 2.77 – 2.57 (m, 4H), 2.11 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 207.81, 140.05, 138.97, 137.77, 132.14, 128.54, 128.35, 126.92, 113.00, 42.67, 29.74, 20.66. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: C, 83.95; H, 8.05 Found: C, 84.22 H, 8.62

Pd-Catalyzed Cross-Coupling Reactions

Preparation of cis-(2-vinyl-oct-1-en-3-ynyl)-benzene 26

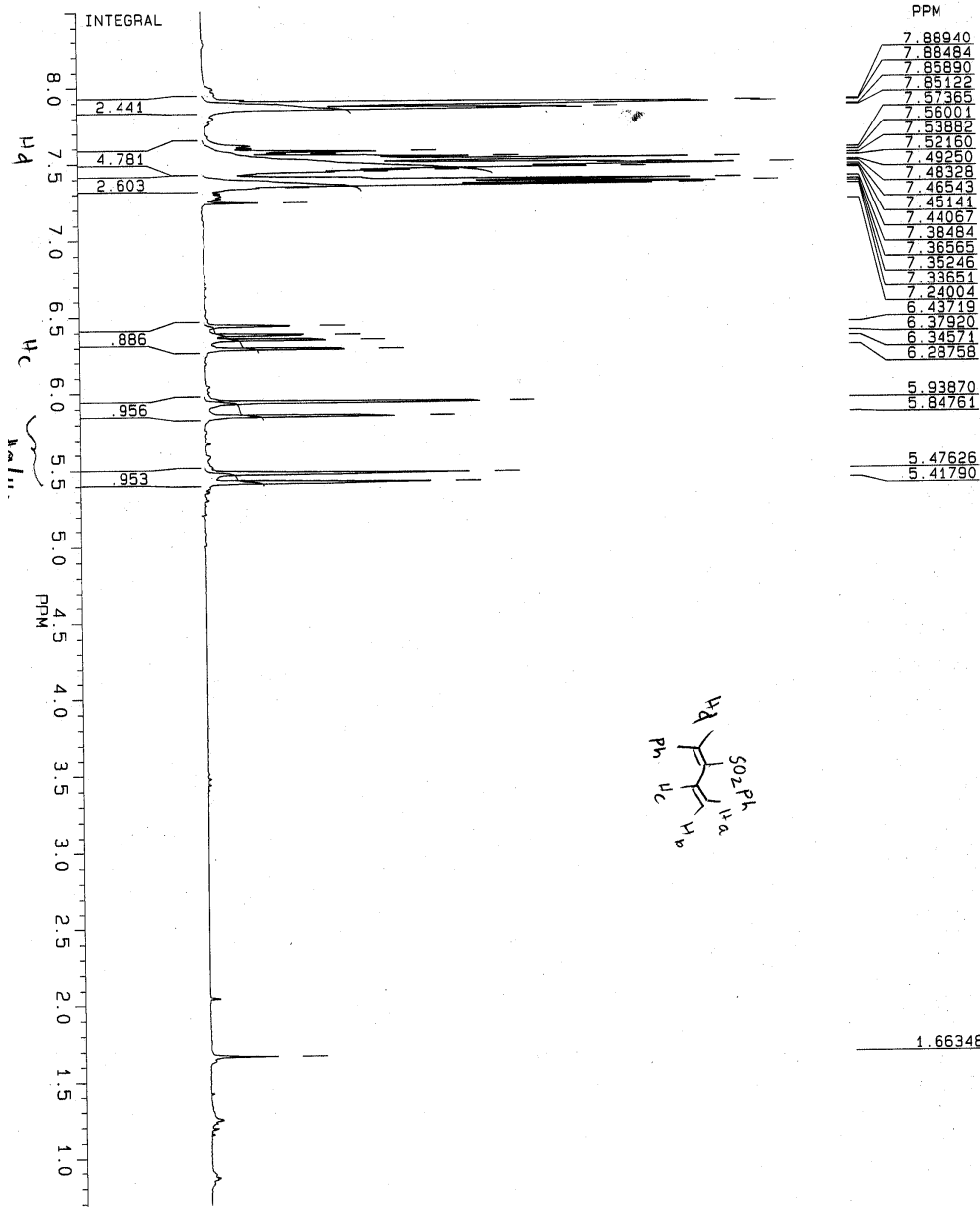
When the transmetalation step was over as described above, the reaction mixture was cool down to room temperature and $\text{Pd}(\text{PPh}_3)_4$ (10%) and 1-iodohexyne (1mmol) was added. The mixture was heated to reflux at 68°C for 4hrs. Then, after hydrolysis and classical treatment, the crude was purified by chromatography on silica gel (eluent hexane) to afford the desired product in 61% yield. ^1H NMR (200 MHz, CDCl_3) δ 7.44–6.87 (m, 10H), 6.78 – 6.64 (dd, $J = 17.2, 10.4$ Hz, 1H), 6.56 (s, 1H), 5.13 (d, $J = 10.4$ Hz, 1H), 4.83 (d, $J = 17.3$ Hz, 1H), 2.83 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 142.17, 142.03, 137.10, 134.00, 132.51, 131.60, 131.31, 130.30, 128.17, 127.06, 116.50, 21.23.

Preparation of cis-(2-vinyl-oct-1-en-3-tolyl)-benzene 27²

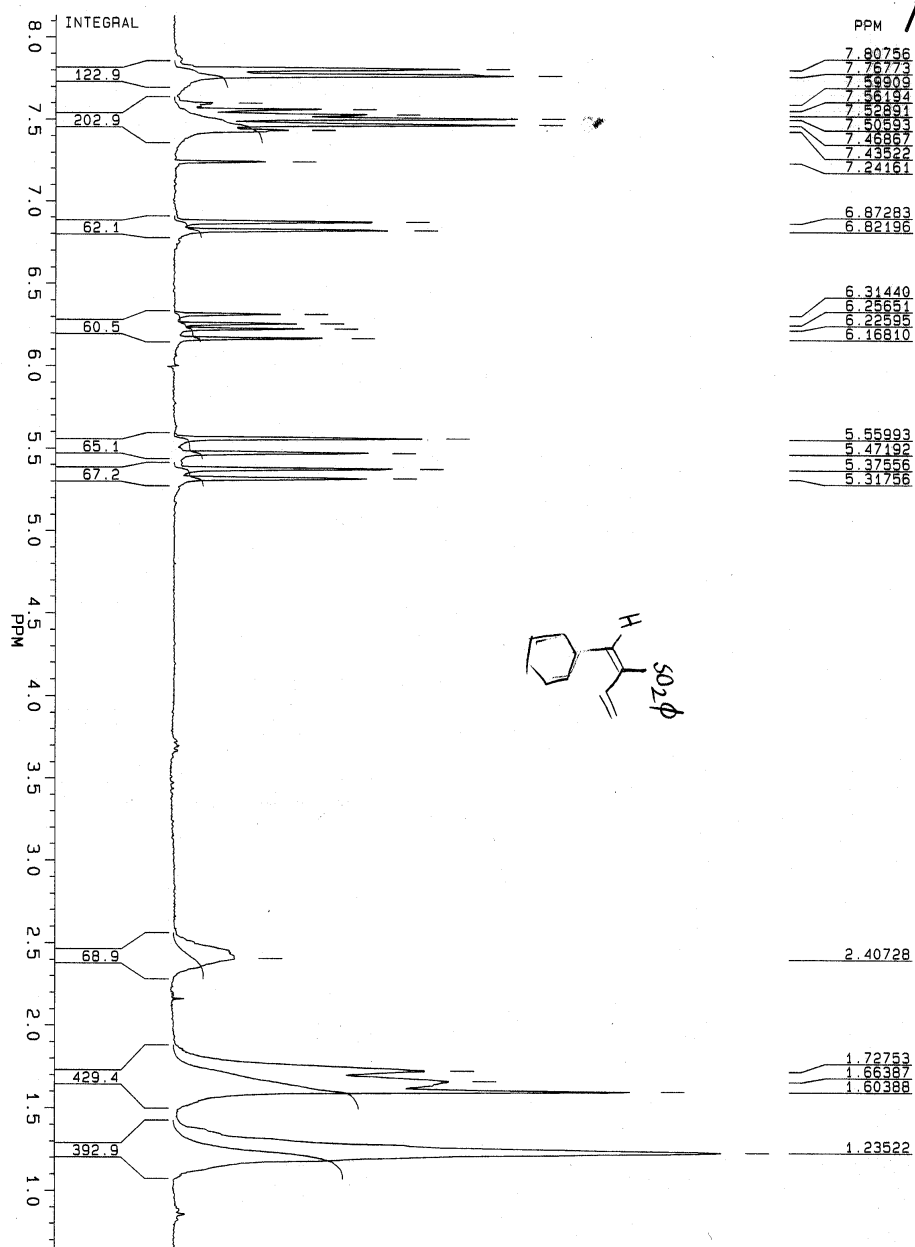
The same experimental procedure was used with piodotoluene and 27 was obtained in 59% yield. ^1H NMR (200 MHz, CDCl_3) δ 7.89 (d, $J = 7.0$ Hz, 1H), 7.38–7.18 (m, 4H), 6.62 (s, 1H), 6.55 – 6.41 (dd, $J = 16.9, 10.1$ Hz, 1H), 5.71 (d, $J = 17.4$ Hz, 1H), 5.24 (d, $J = 10.0$ Hz, 1H), 2.51 (t, $J = 6.8$ Hz, 2H), 1.70 – 1.42 (m, 4H), 0.95 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 141.81, 138.73, 136.22, 128.90, 128.12, 128.03, 121.71, 119.04, 115.96, 30.69, 22.08, 19.48, 13.60.

References

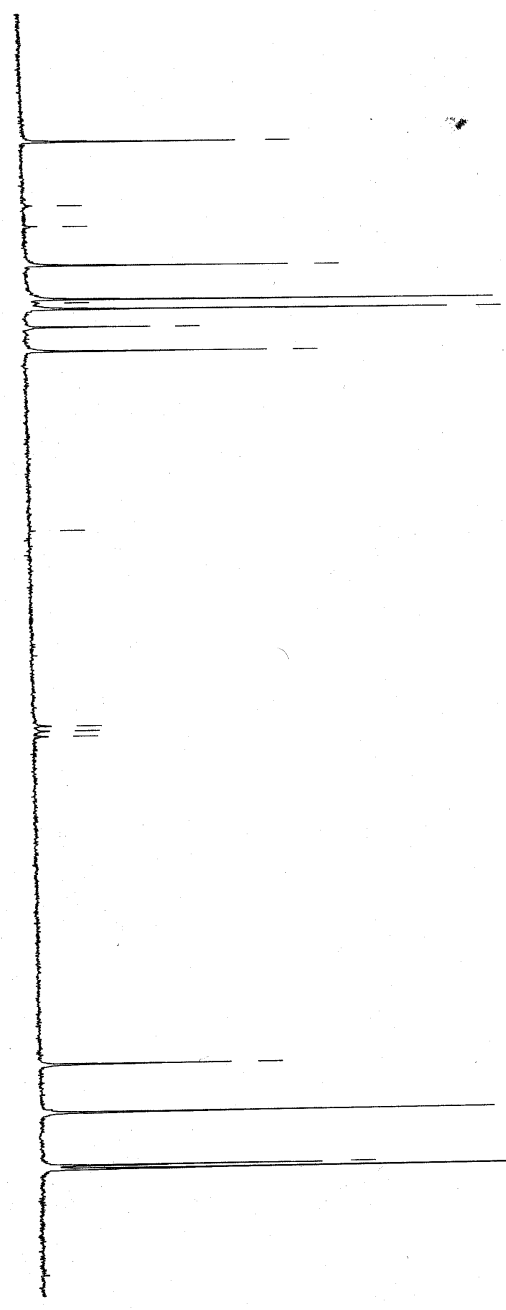
- (1) Krijnen, Erik, S.; Zuihof, H.; Lodder G. *J. Org. Chem.* **1994**, 59, 8139
- (2) Leach, Andrew G.; Houk, K. N. *J. Org. Chem.* **2001**, 66, 5192



SM03/089-PURE



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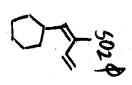
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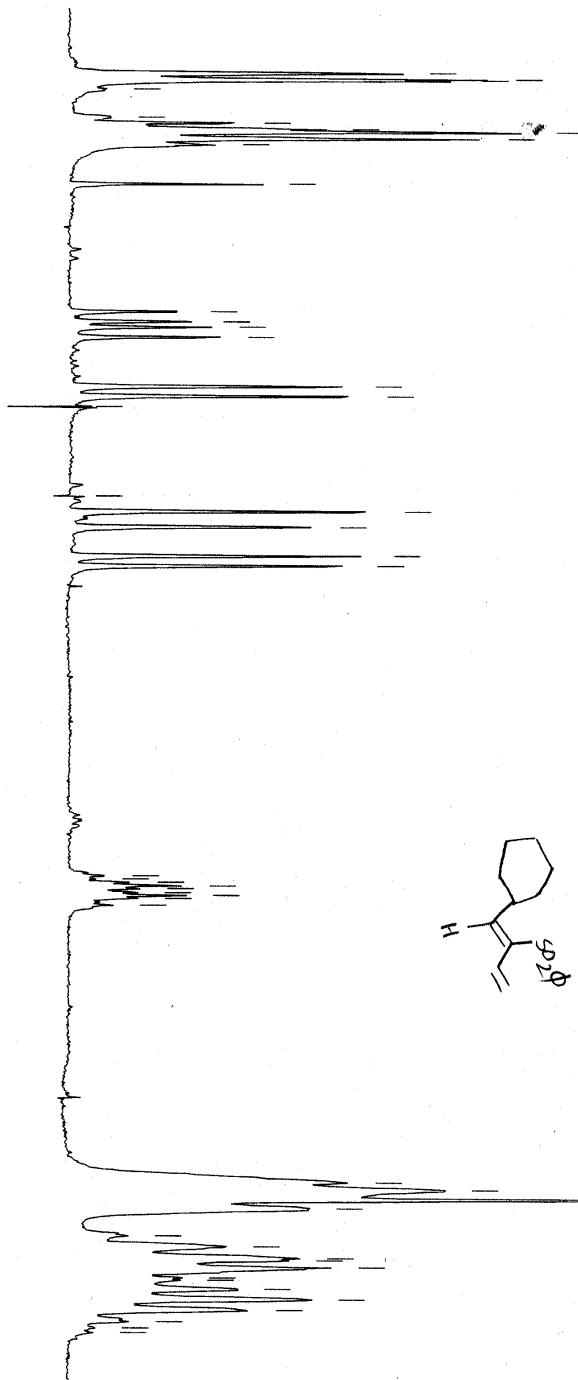


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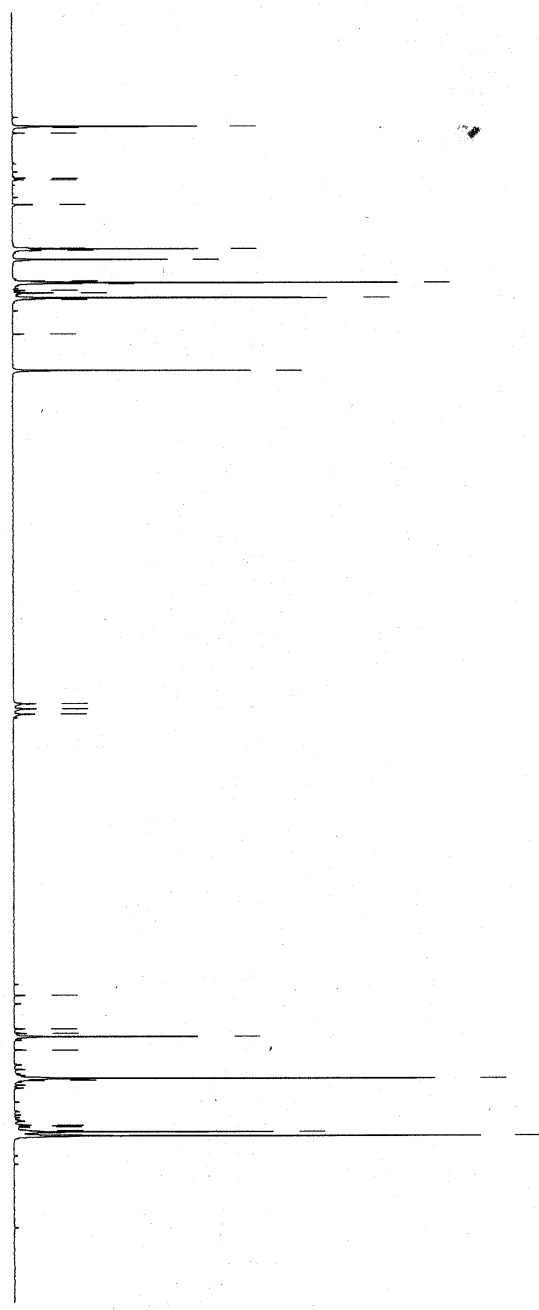
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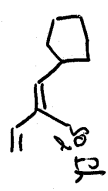
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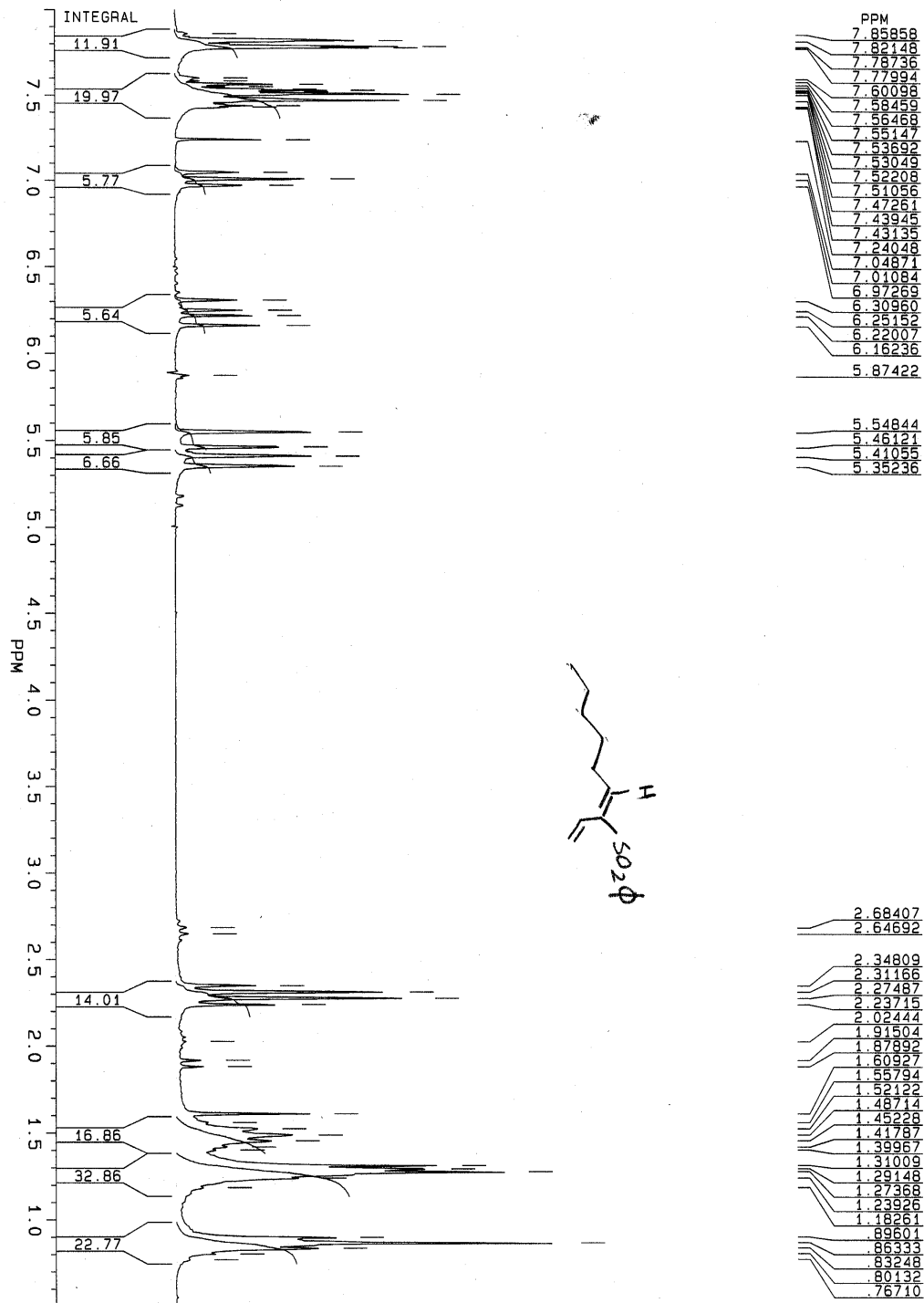
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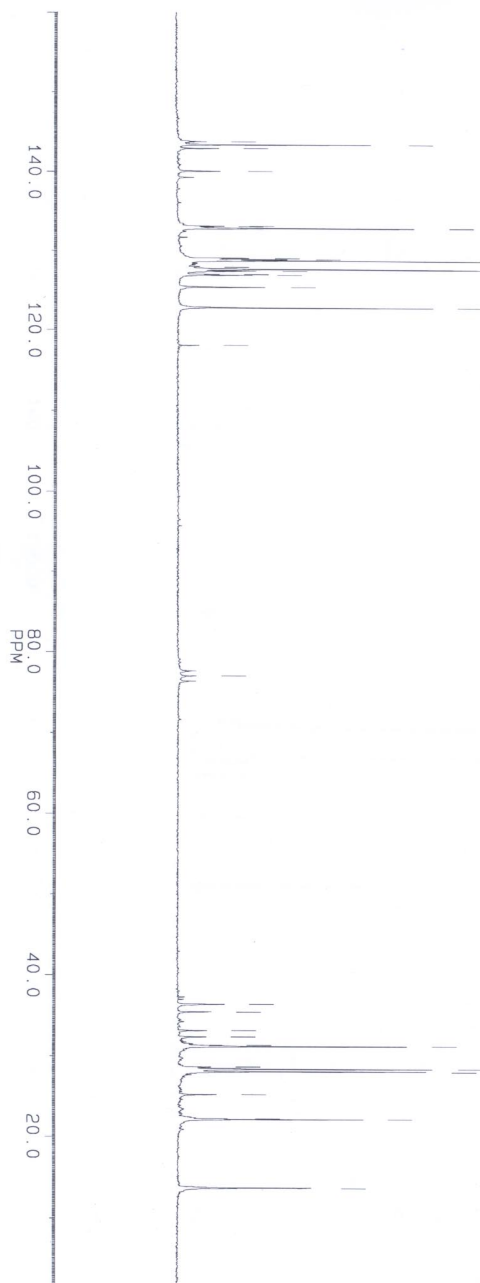
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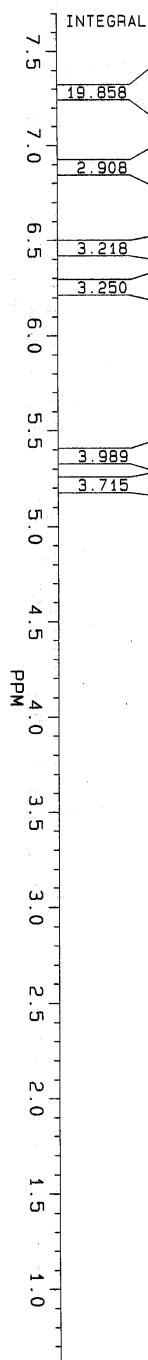
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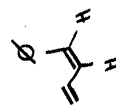
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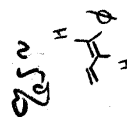
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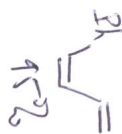
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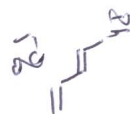
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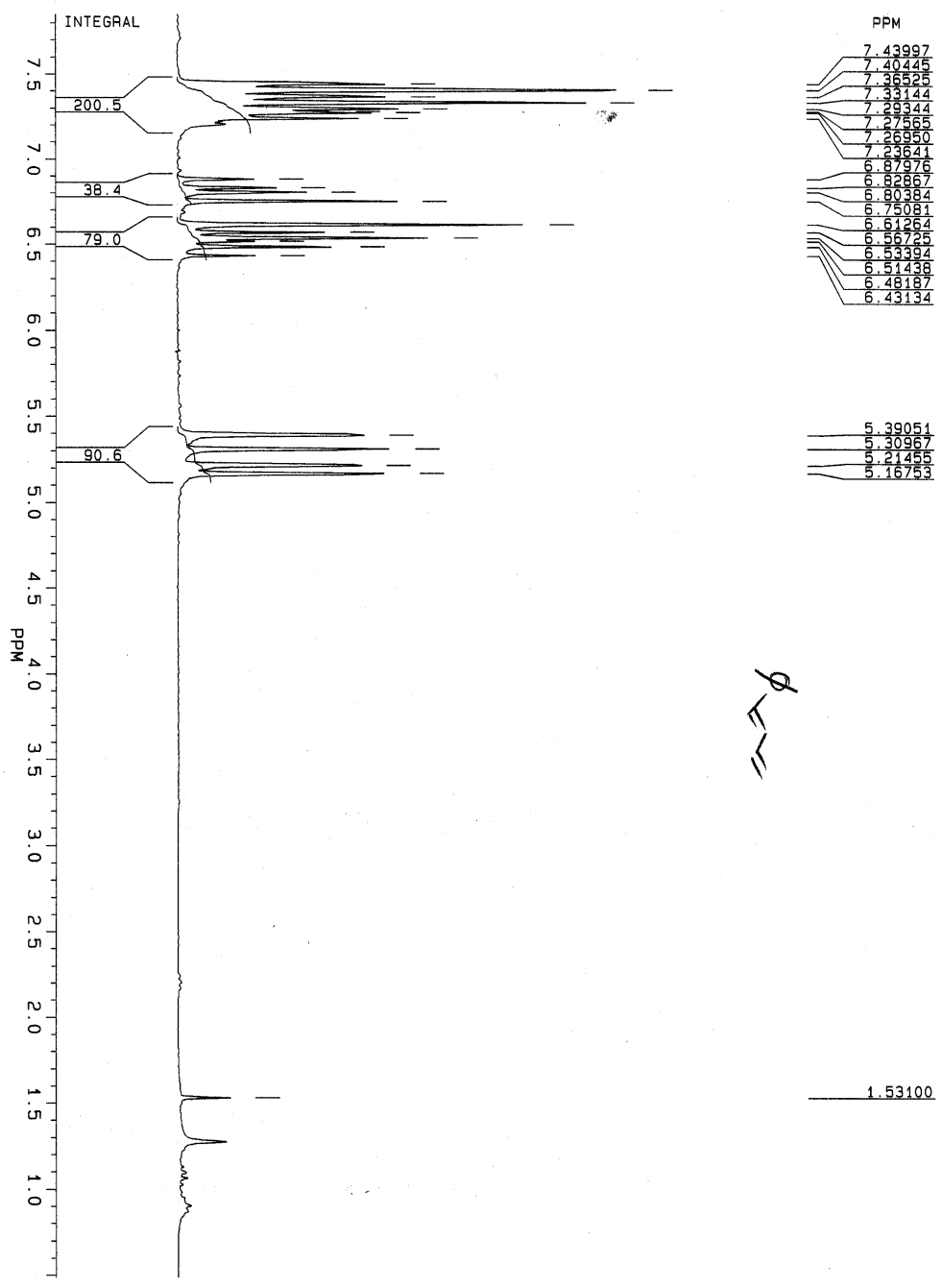
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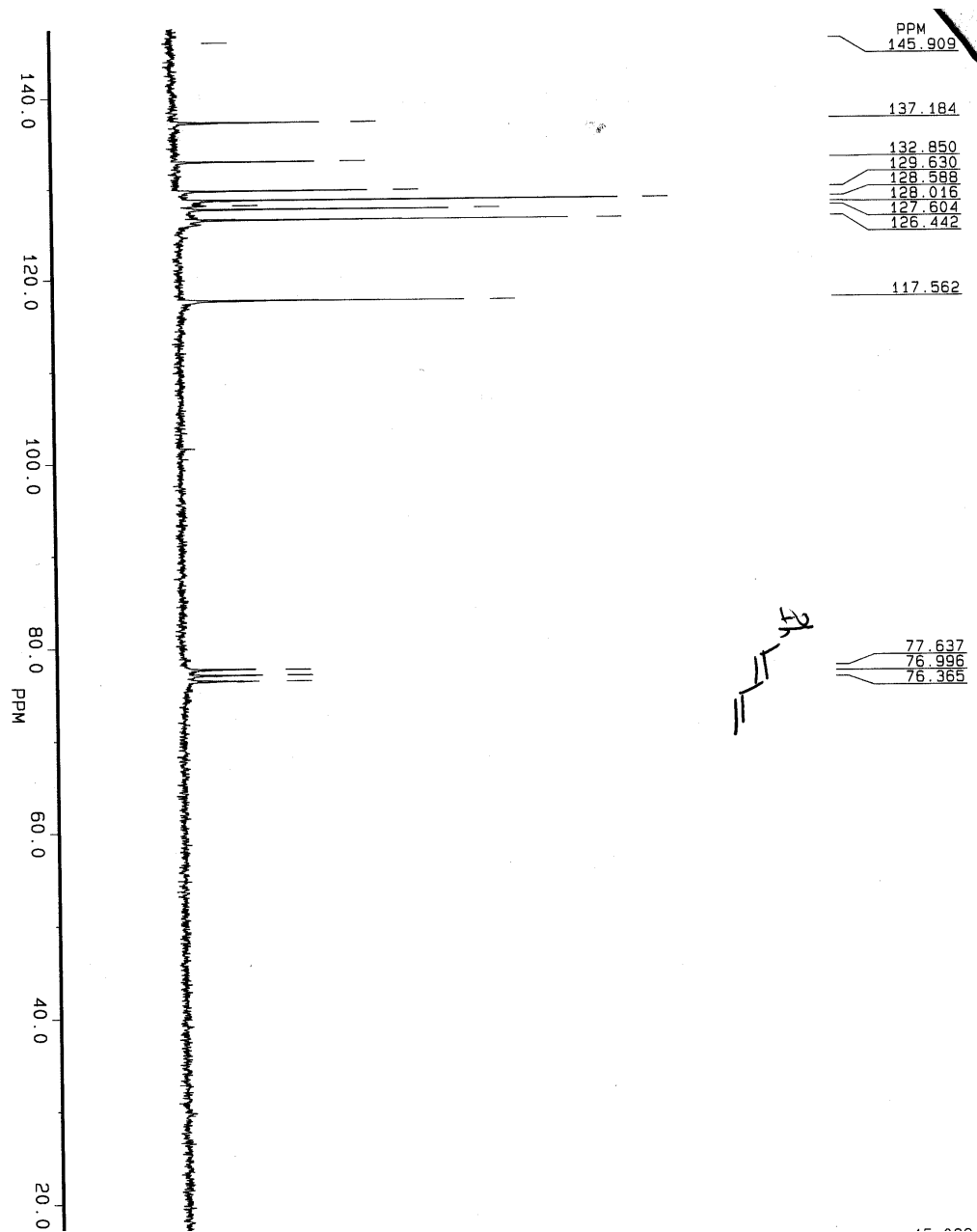
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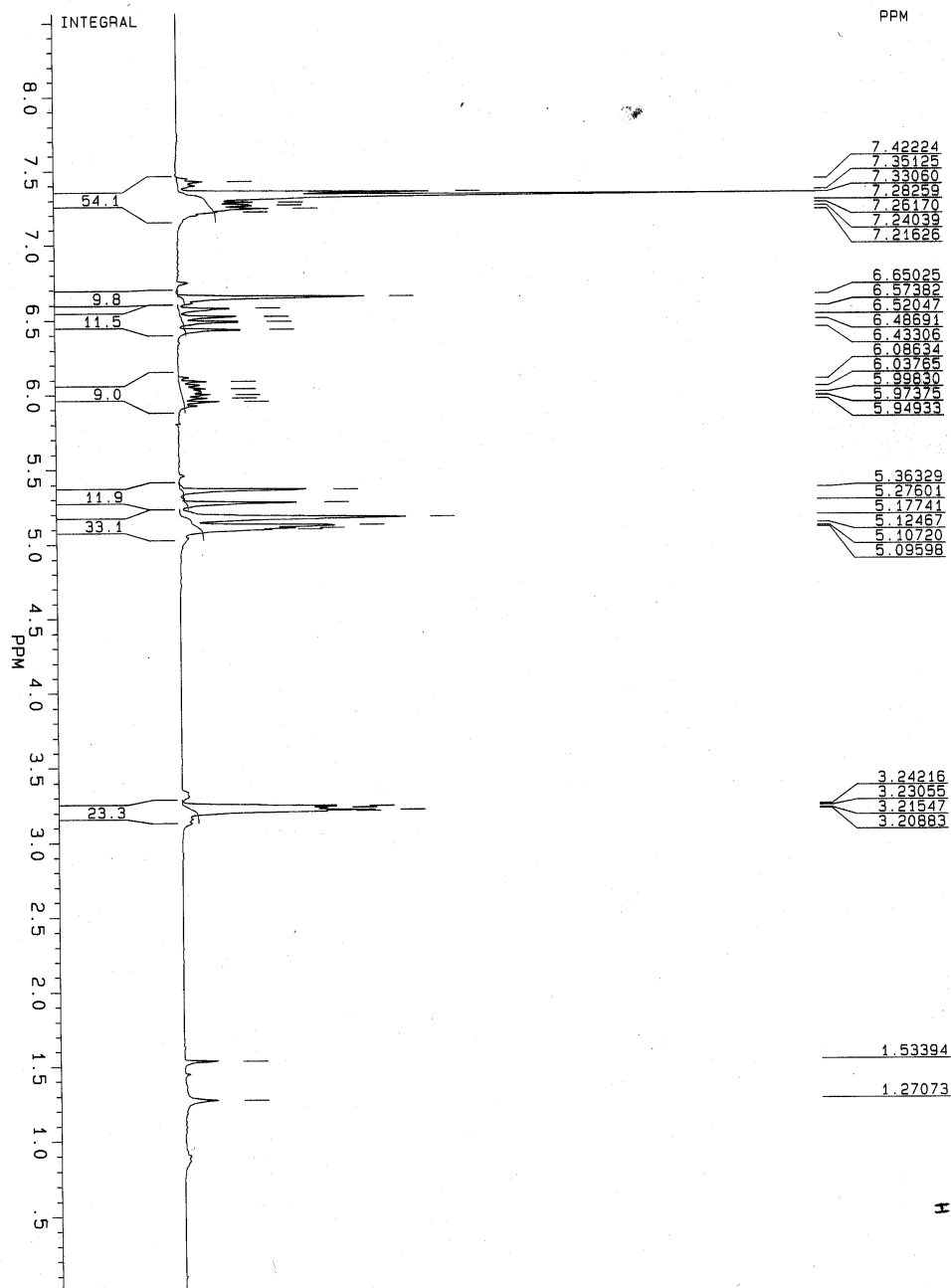
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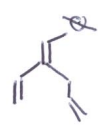


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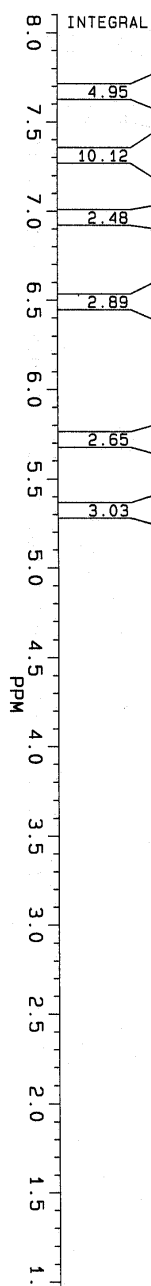






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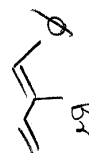
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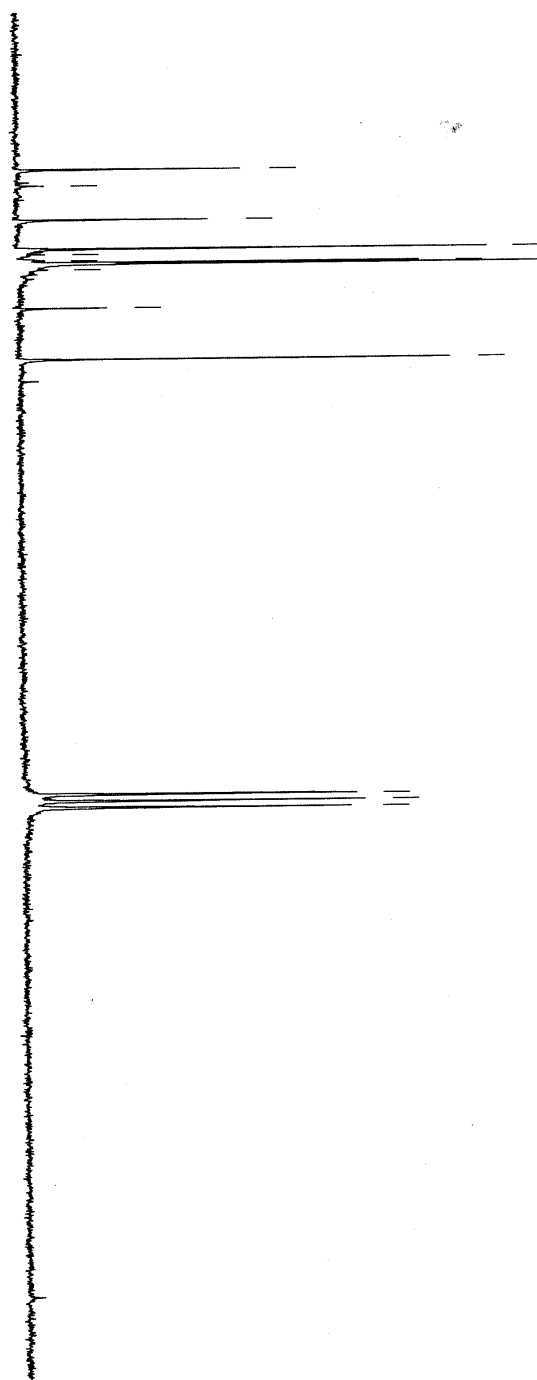
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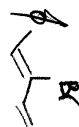
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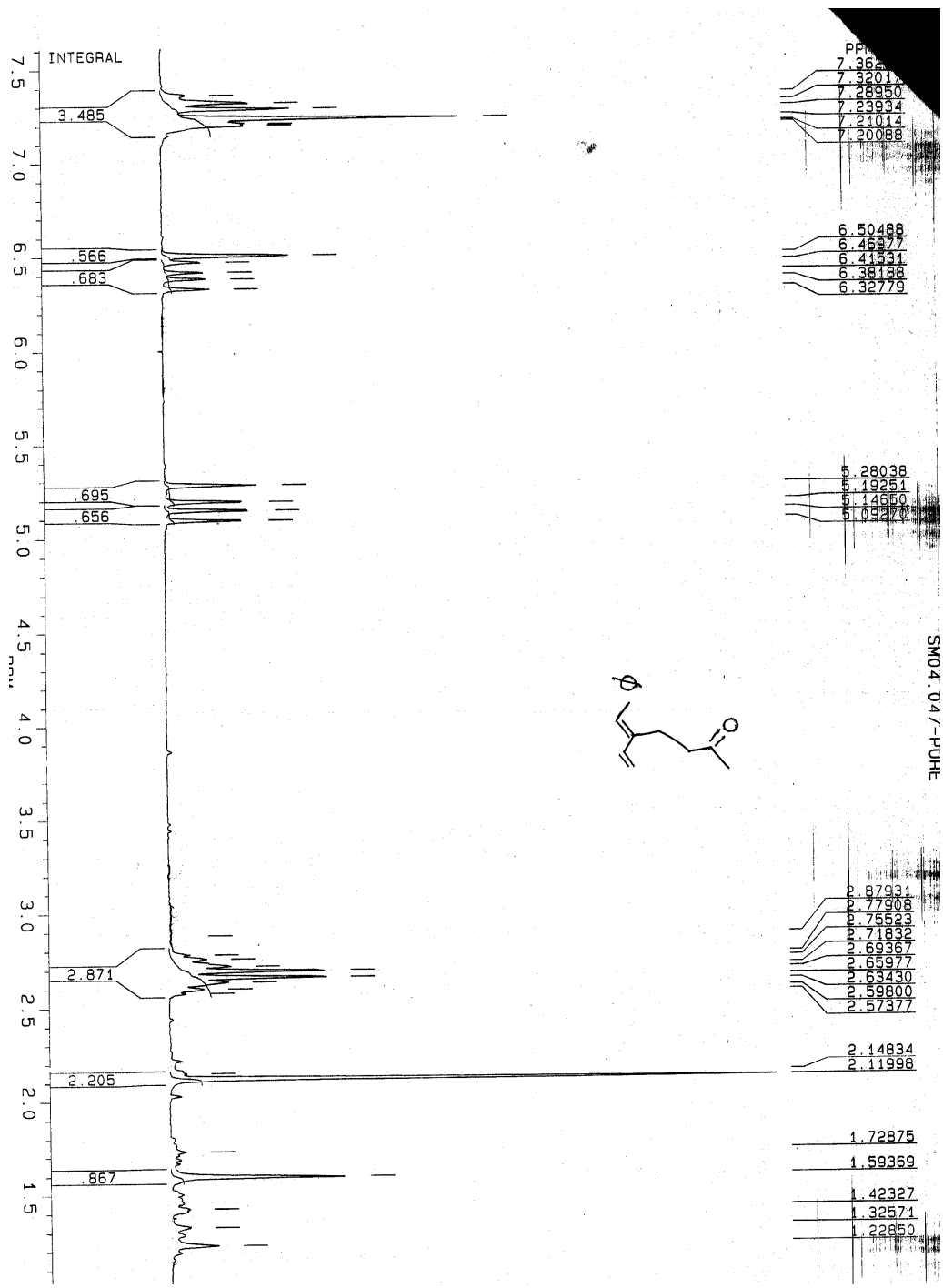


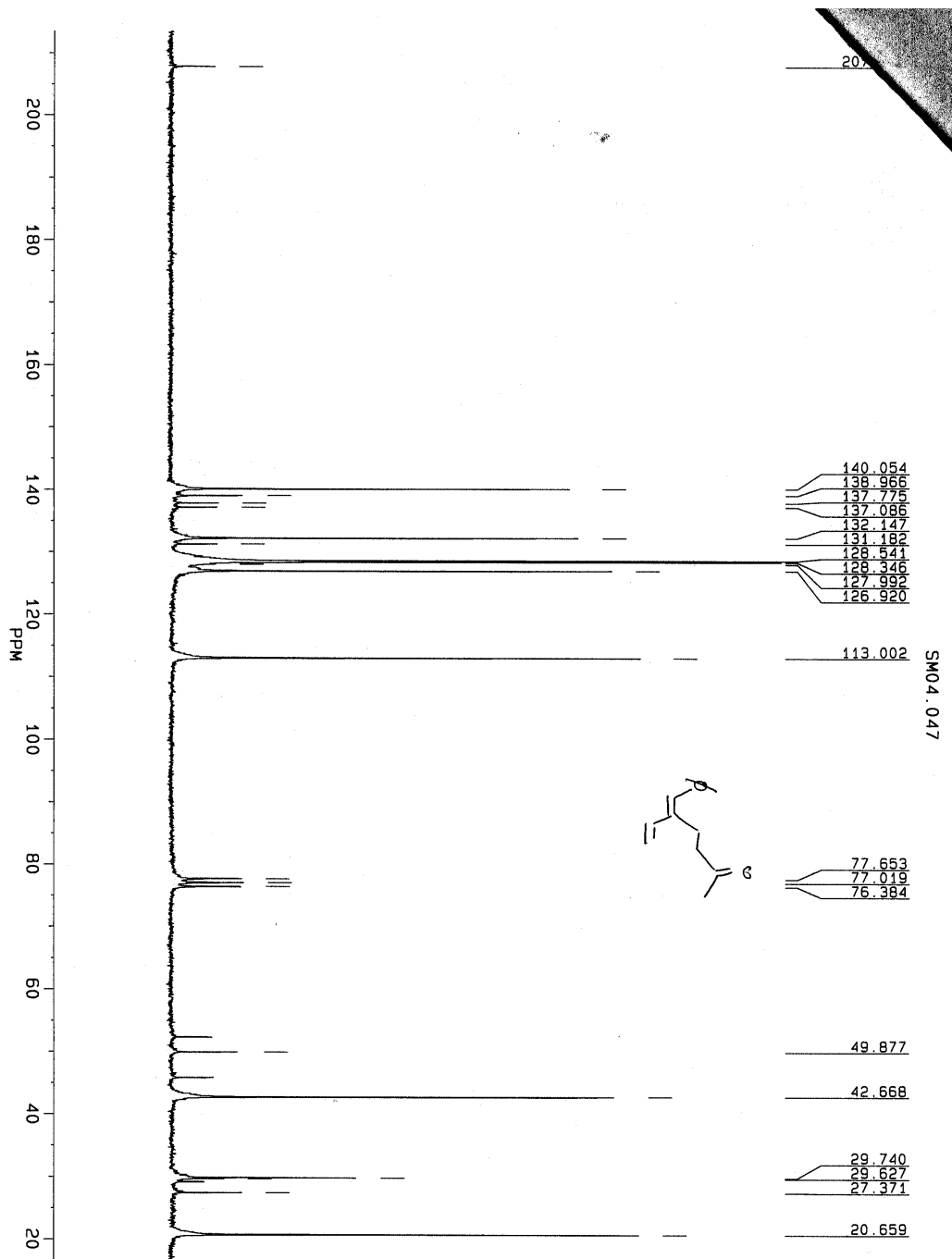
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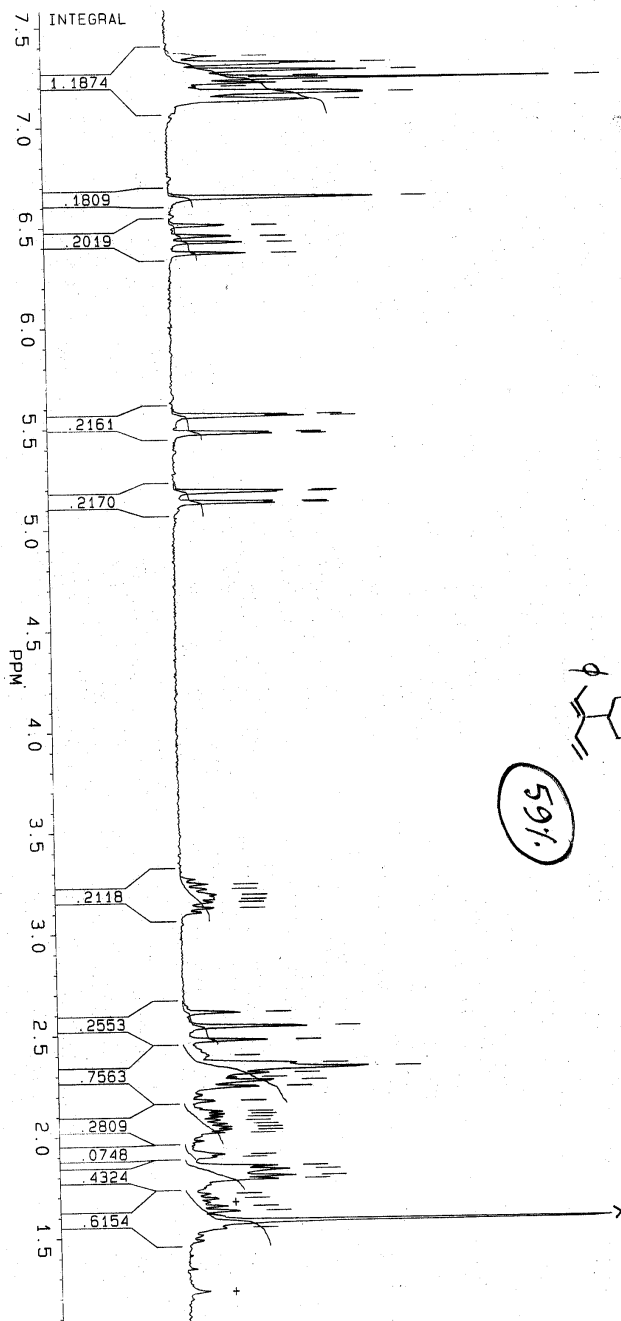
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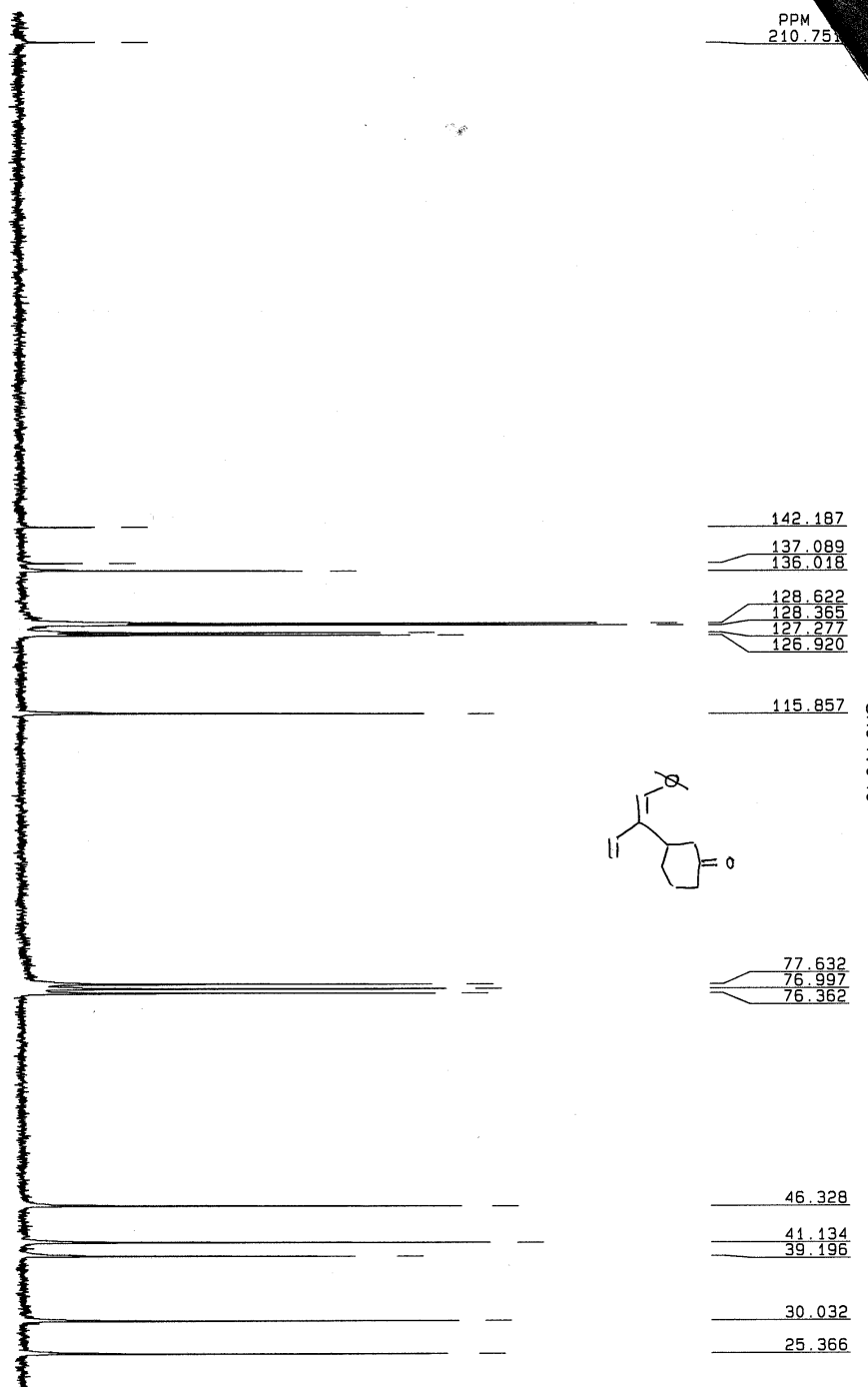




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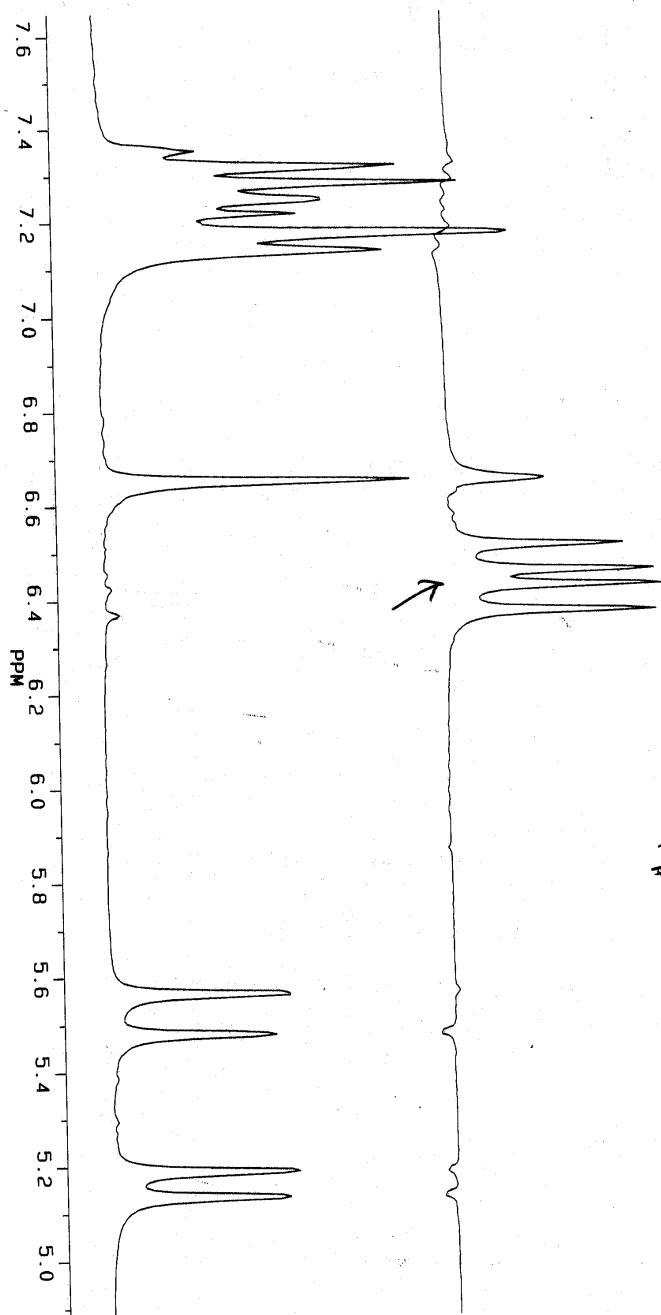
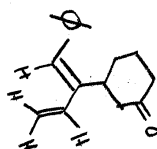
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2.30399
2.28399
2.26399
2.24399
2.22399
2.20399
2.18399
2.16399
2.14399
2.12399
2.10399
2.08399
2.06399
2.04399
2.02399
2.00399
1.98399
1.96399
1.94399
1.92399
1.90399
1.88399
1.86399
1.84399
1.82399
1.80399
1.78399
1.76399
1.74399
1.72399
1.70399
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1.66399
1.64399
1.62399
1.60399
1.58399
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1.54399
1.52399
1.50399

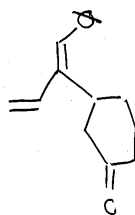
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180
160
140
120
100
80
60
40



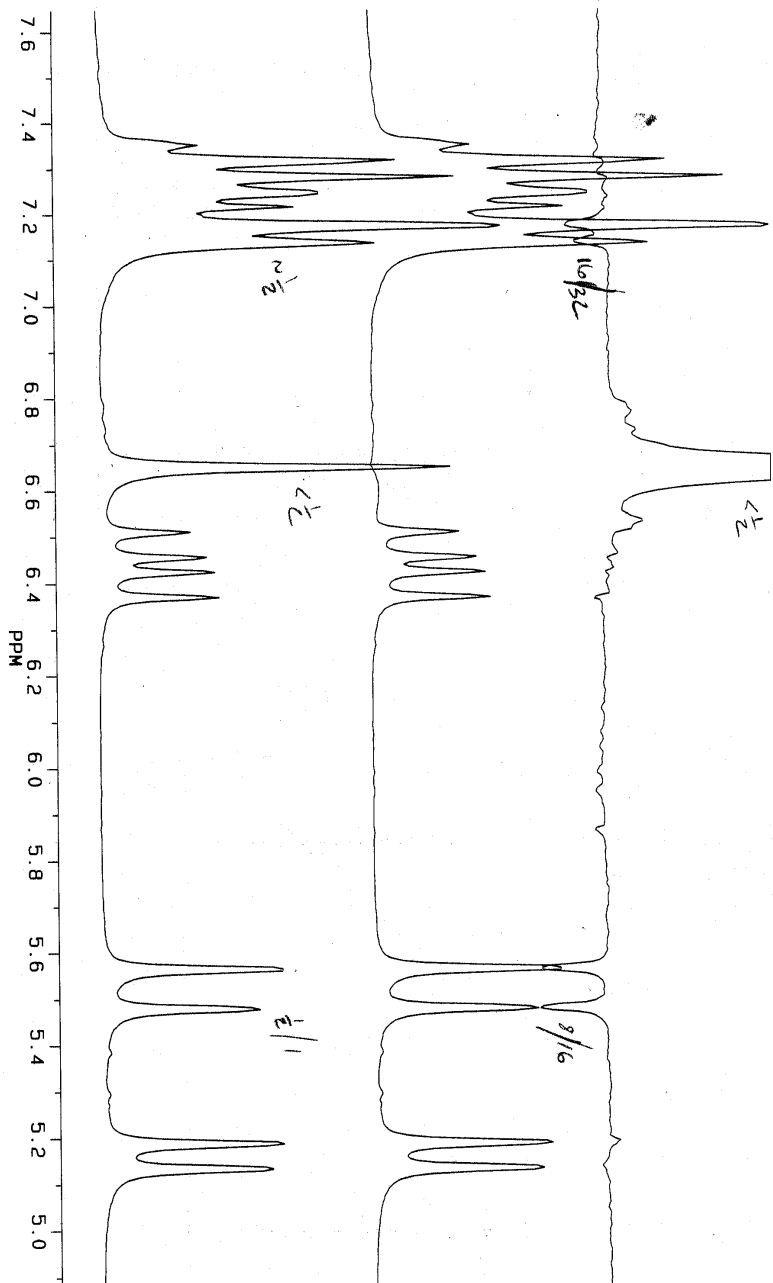
No 51

CDCL₃





SM04.040 200°OLD* 1D NOE S3=53L



INTEGRAL

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6.5

6.0

5.5

5.0

4.5

4.0

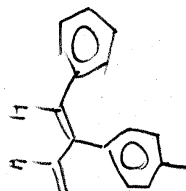
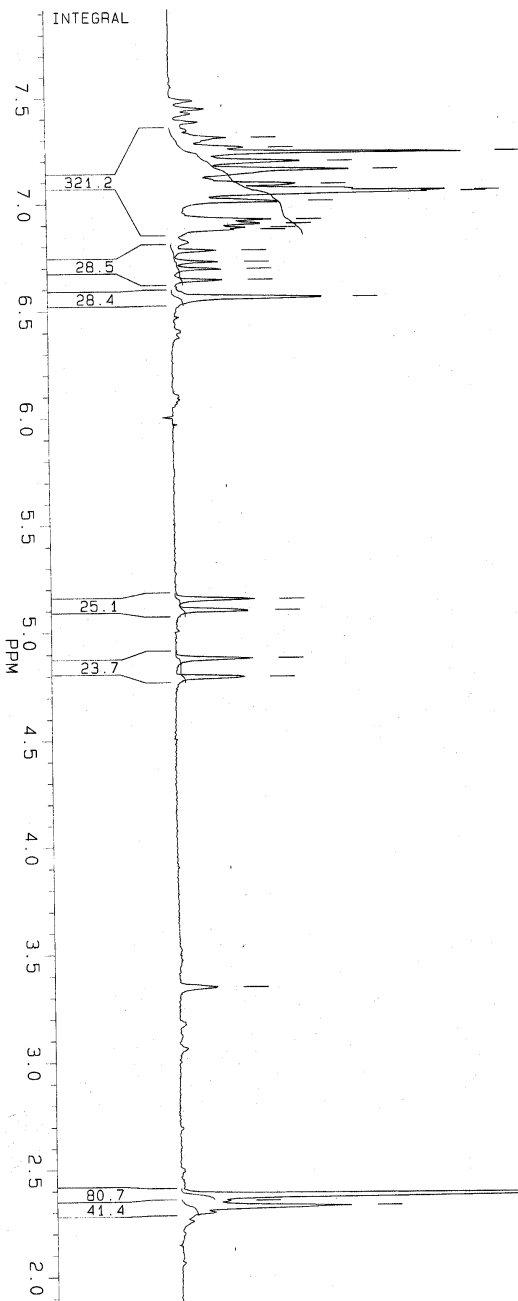
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3.0

2.5

2.0

PPM



PPM

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7.19634
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7.08944
7.05618
7.05097
7.00969
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6.88000
6.87500
6.87000
6.77920
6.72685
6.69339
6.64164
6.56164

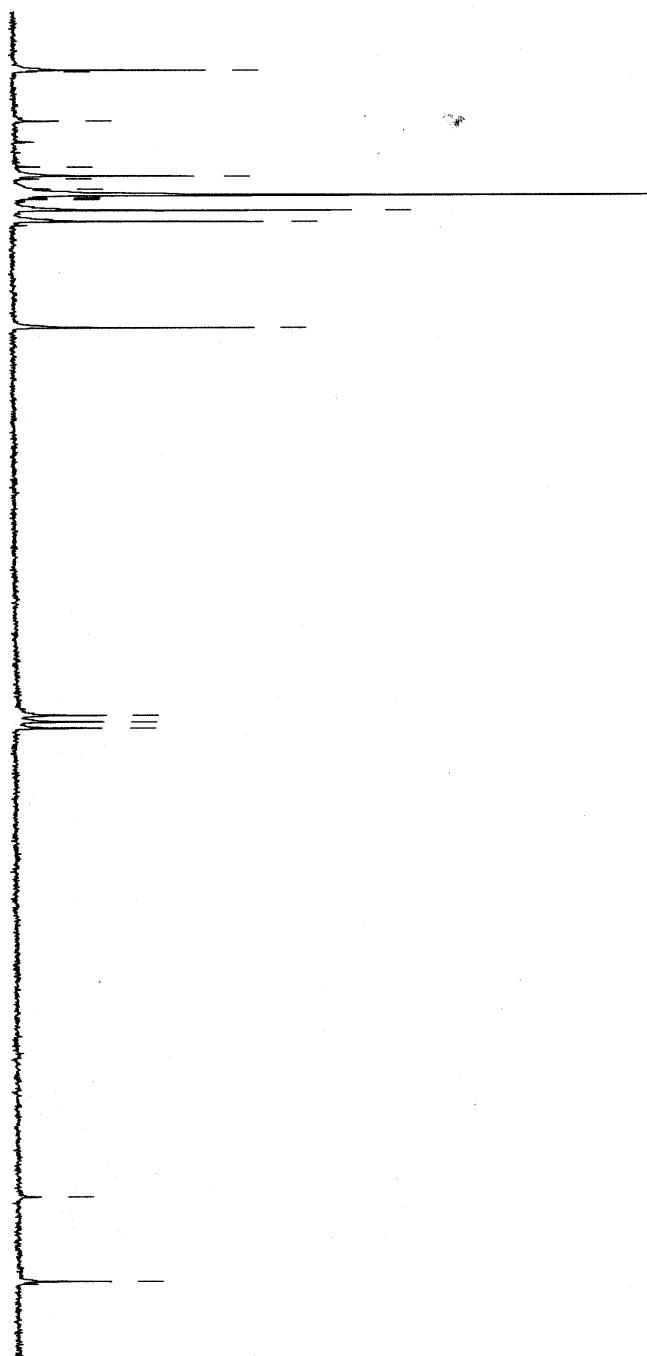
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4.87804
4.79243

3.34647

2.37798
2.35222
2.32642

SM04.051

140
130
120
110
100
90
80
70
60
50
40
30
20
PPM



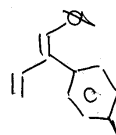
PPM

142.172
142.028
137.093
132.515
131.605
131.310
130.307
129.704
129.432
129.285
128.159
127.058

116.505

77.902
77.268
76.633

SMU4_U21



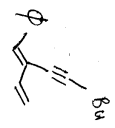
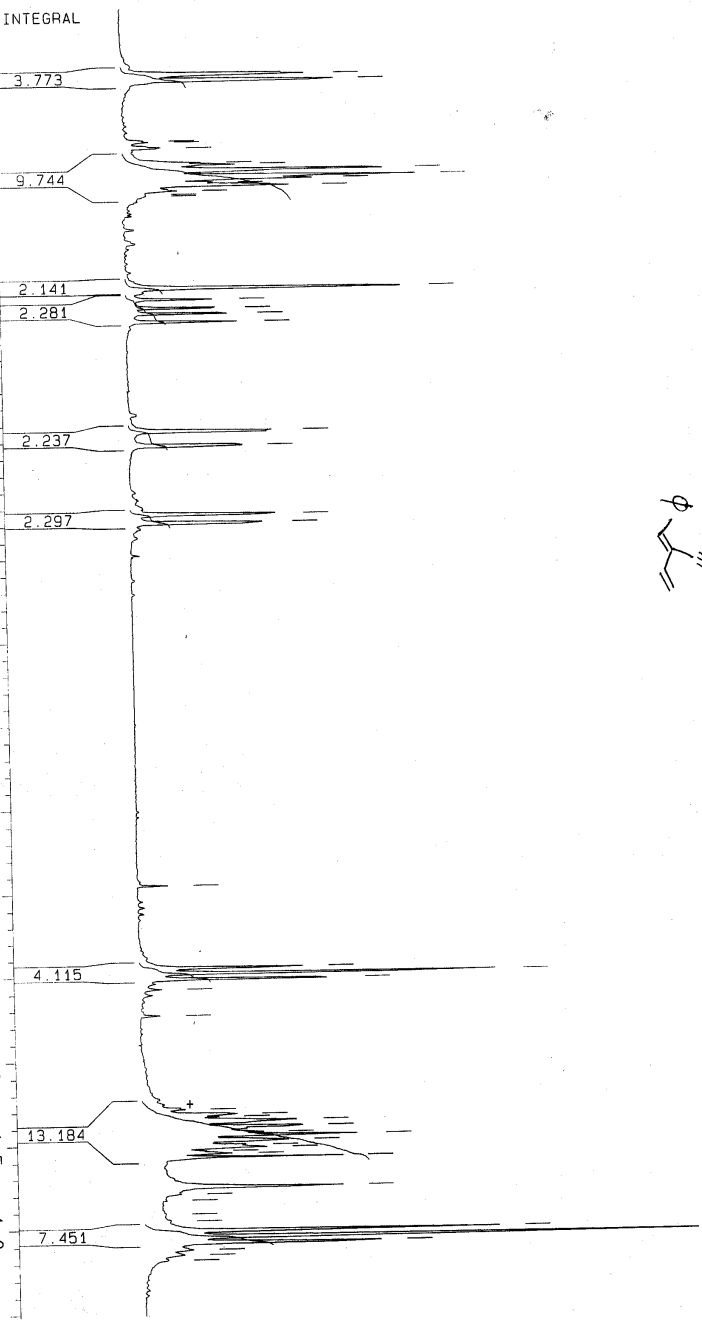
29.966

21.560

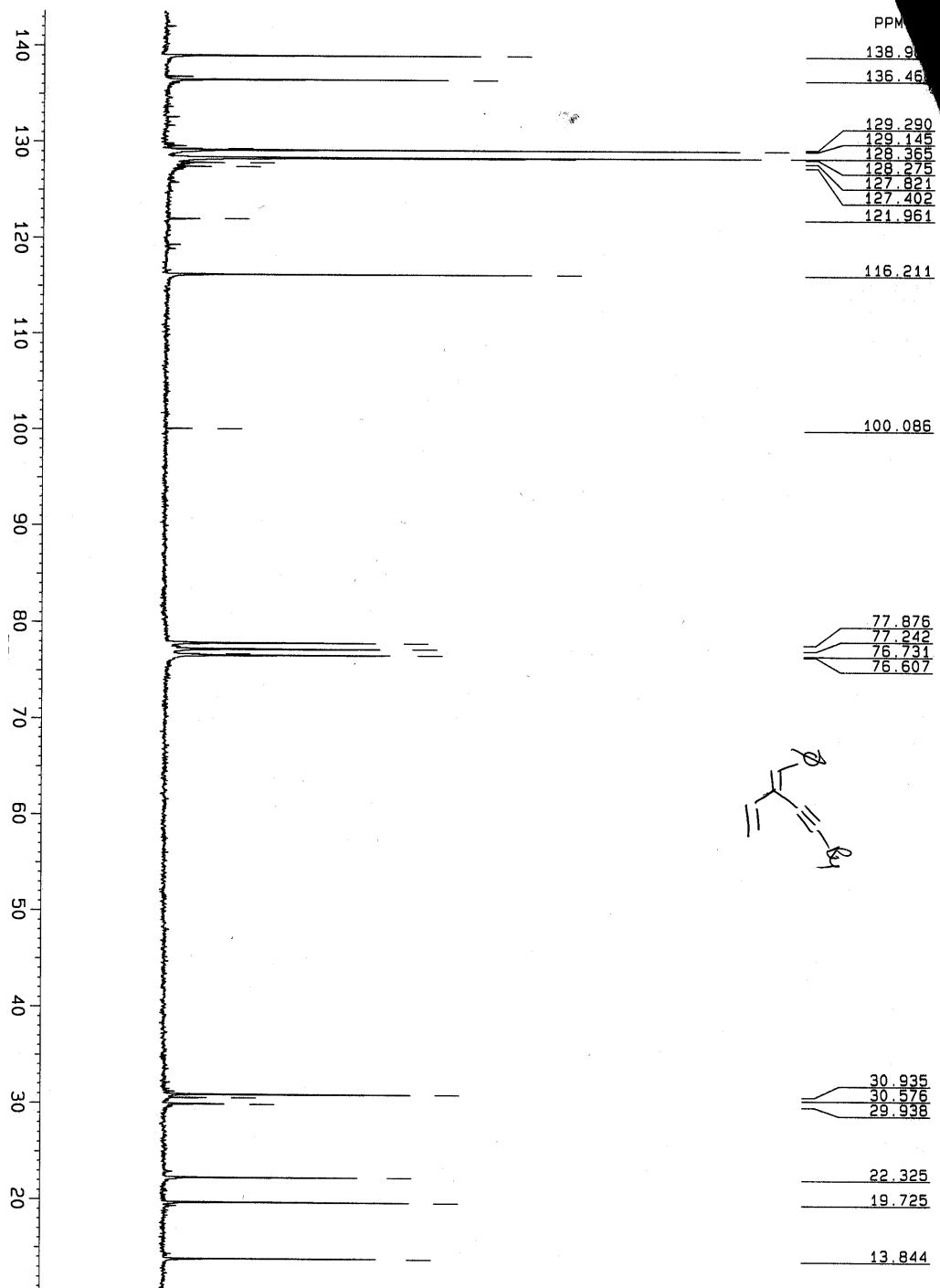
INTEGRAL

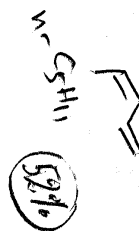
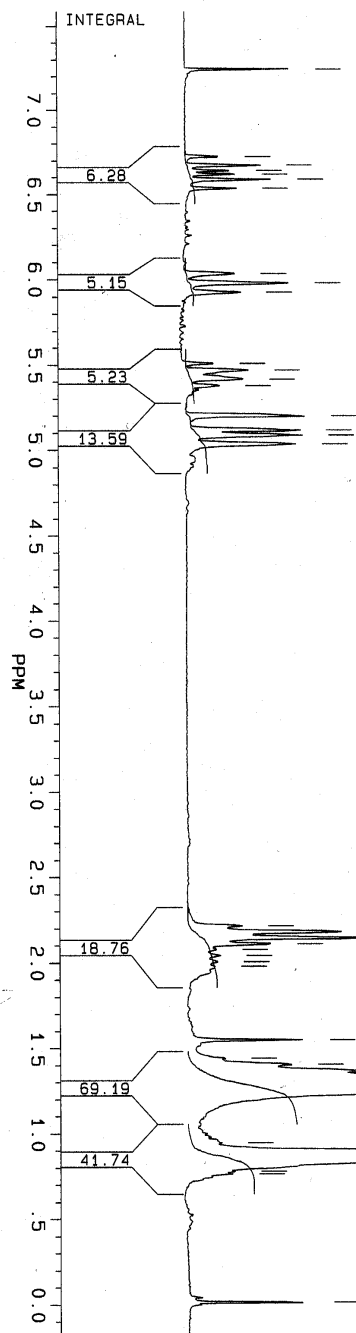
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

ppm



7.913
7.878
7.512
7.506
7.471
7.380
7.369
7.369
7.298
7.283
7.260
7.241
7.211
7.190
7.182
6.622
6.554
6.503
6.469
6.419
5.761
5.673
5.263
5.213
3.045
2.550
2.517
2.482
2.422
2.266
1.709
1.679
1.663
1.641
1.606
1.572
1.552
1.521
1.495
1.481
1.458
1.444
1.428
1.412
1.396
1.380
1.364
1.348
1.332
1.316
1.300
1.284
1.268
1.252
1.236
1.220
1.204
1.188
1.172
1.156
1.140
1.124
1.108
1.092
1.076
1.060
1.044
1.028
1.012
0.996
0.980
0.964
0.948
0.932
0.916
0.900
0.884
0.868
0.852
0.836
0.820
0.804
0.788
0.772
0.756
0.740
0.724
0.708
0.692
0.676
0.660
0.644
0.628
0.612
0.596
0.580
0.564
0.548
0.532
0.516
0.500
0.484
0.468
0.452
0.436
0.420
0.404
0.388
0.372
0.356
0.340
0.324
0.308
0.292
0.276
0.260
0.244
0.228
0.212
0.196
0.180
0.164
0.148
0.132
0.116
0.100
0.084
0.068
0.052
0.036
0.020
0.004





PPM

7.24346

6.72362

6.67124

6.63981

6.61888

6.58746

6.53446

6.03426

5.97957

5.92517

5.50771

5.46946

5.41556

5.37744

5.19934

5.11524

5.08687

5.03606

2.21471

2.18080

2.14585

2.11021

2.07807

2.04152

2.00598

1.97758

1.94795

1.91952

1.89094

1.86602

1.83194

1.80524

1.78659

1.76645

1.73790

1.71524

1.69458

1.67038

1.64721

1.62661

1.60358

01331

10.9310.88

SM04/076-CISDIENE ?

70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
PPM



PPM

57.6005
56.8887
53.6256

41.1351

2.6870
2.1497
1.5160
0.8789

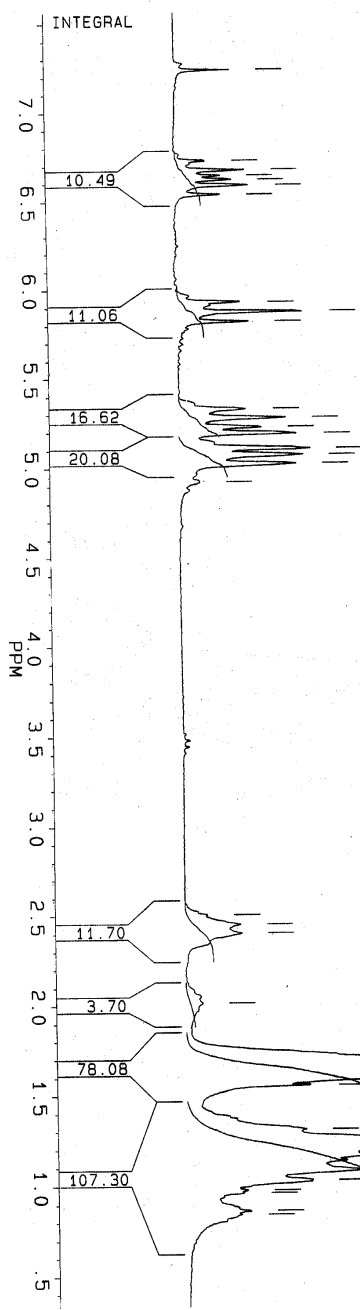


SM04/076

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-47.7743

-52.9586

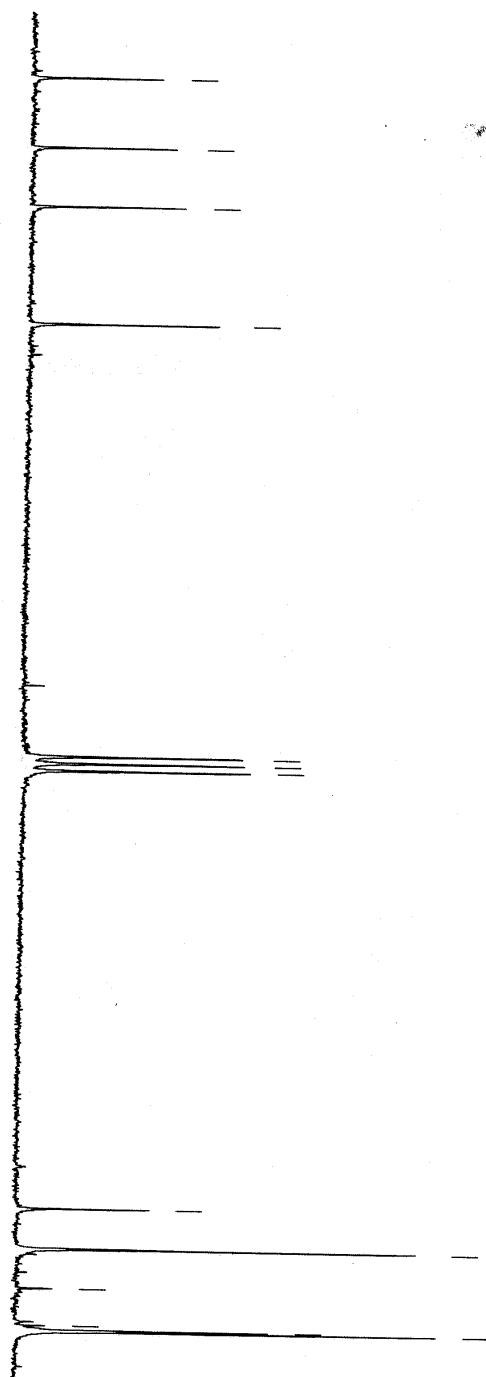
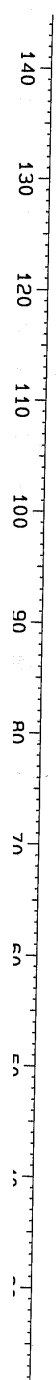
-60.3750
-61.4646



PPM

7.23964
6.72716
6.67467
6.64307
6.62202
6.59001
6.53739
5.93076
5.87623
5.82155
5.32956
5.28056
5.22845
5.19167
5.10765
5.07340
5.02347
4.92157
2.50367
2.45176
2.40157
2.01257
1.66221
1.60973
1.59253
1.55360
1.30689
1.23252
1.20314
1.16447
1.13482
1.07979
1.02705
0.97342
0.95933
0.95933
0.94169

SM04.039-PURE



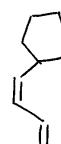
PPM

138.904

132.570

127.235

116.638



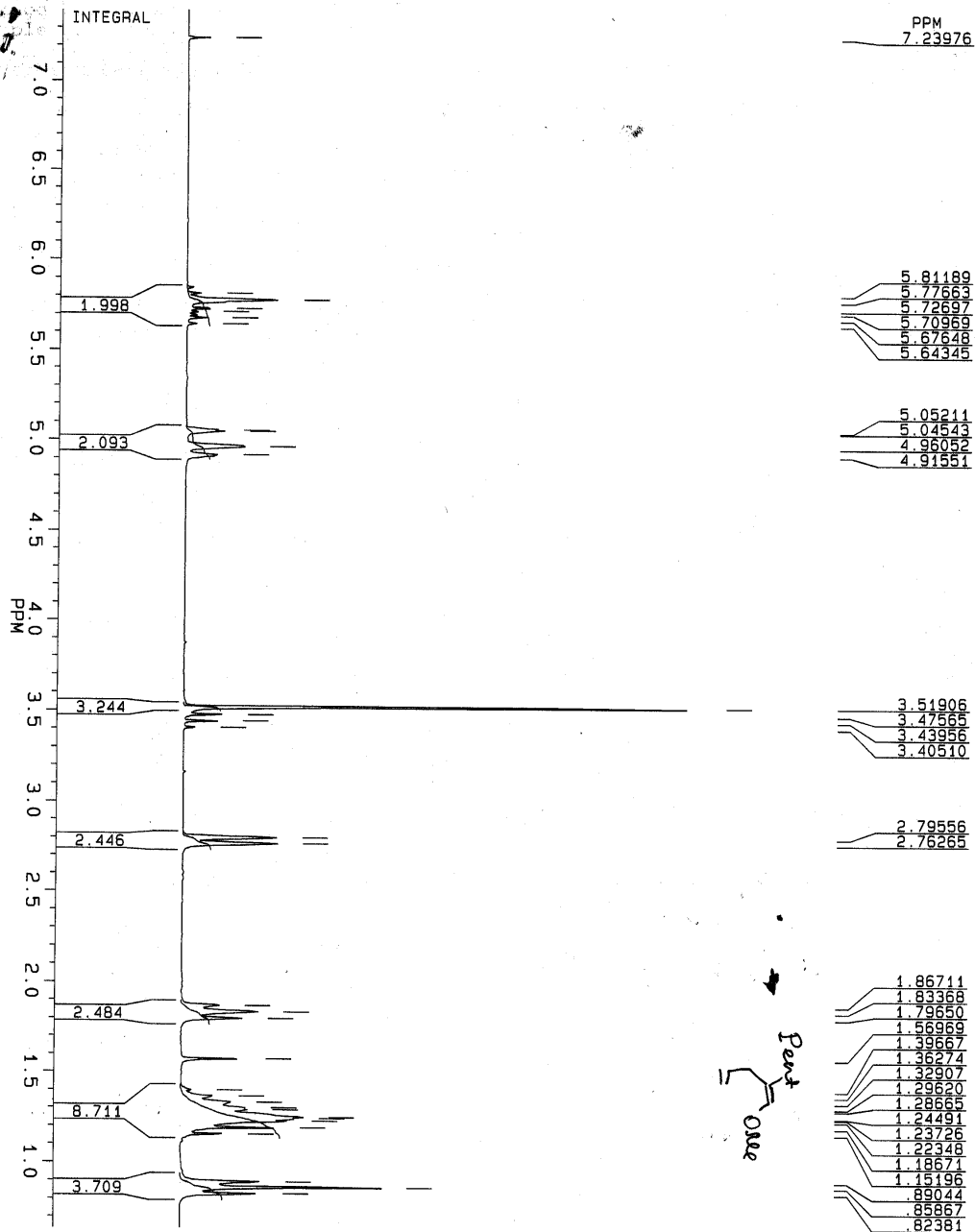
SM04.039

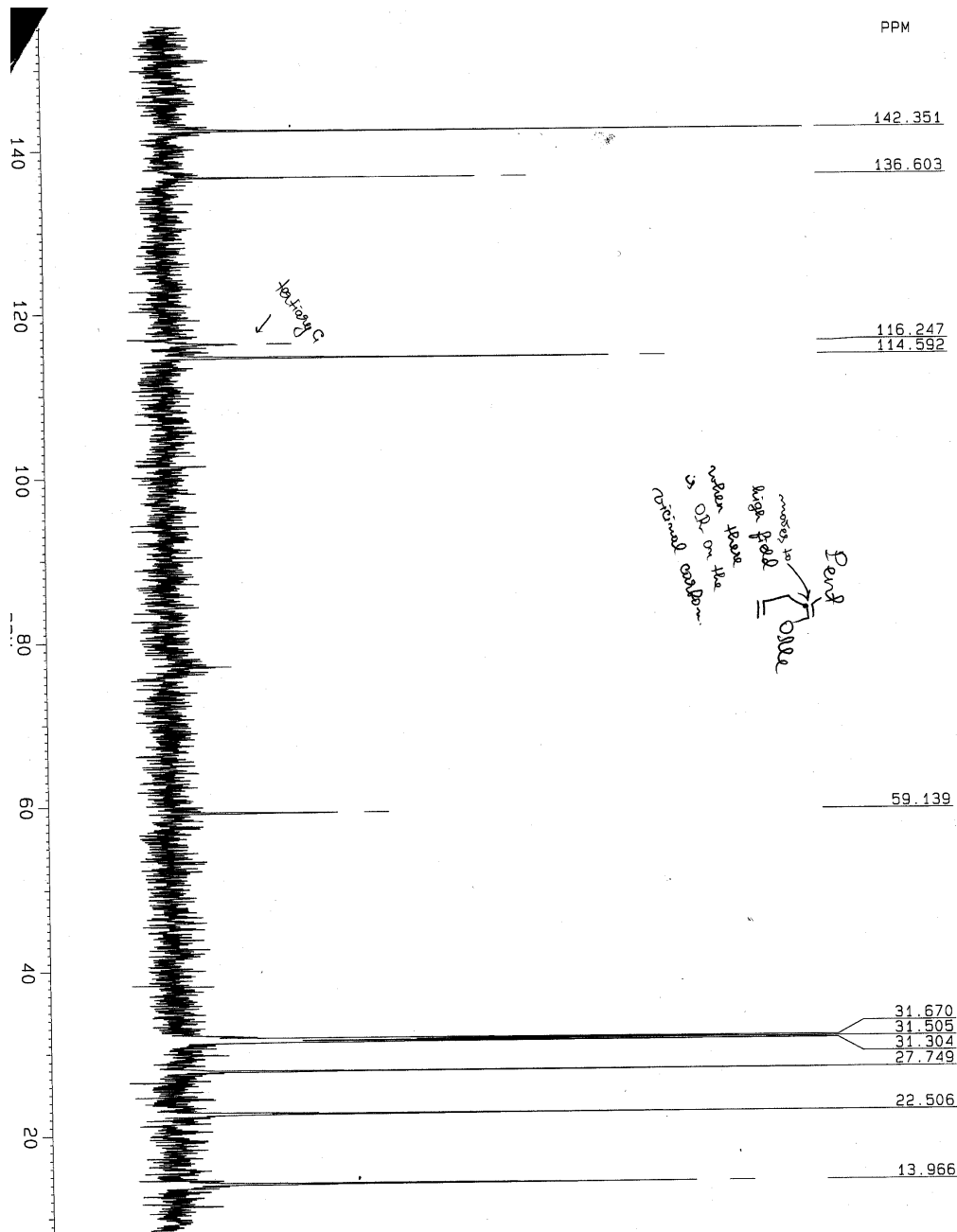
77.628
76.994
76.360

36.827

33.214

29.694
28.370
28.062
27.833





INTEGRAL

7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

PPM

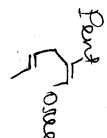
PPM
7.23837

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5.43799
5.40999
5.38580
5.36911
5.34345
5.29408
5.26519
4.92442
4.91695

3.51254
3.47690

2.80226
2.76900
2.71546
2.68955

1.85299
1.81977
1.78297
1.63294
1.60685
1.55110
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14:1

