A Novel, Selective, and Efficient Route to Carotenoids and Related Natural Products *via* Zr-Catalyzed Carboalumination and Pd- and Zn-Catalyzed Cross Coupling

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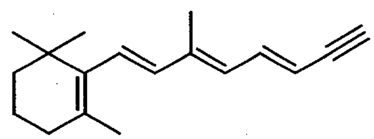
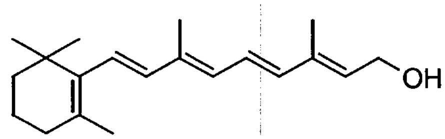
Supplementary Data.

General. All reactions were carried out under dry Ar atmosphere, unless otherwise indicated. THF was freshly distilled from sodium/benzophenone. Dichloroethane and DMF was freshly distilled from CaH_2. $ZnBr_2$ and $ZnCl_2$ were flame-dried *in vacuo* (1 mmHg). The other commercially available reagents were used directly, unless otherwise indicated. Reactions were monitored by GLC and TLC analysis of reaction aliquots. GLC and NMR yields were determined by using hydrocarbons and dibromomethane, respectively, as internal standards. Flash chromatography was carried out on 230-400 mesh silica gel 60 or neutral alumina. GLC analysis was performed on an HP 6890 Gas Chromatograph using HP-5 capillary column (30 m×0.32 mm, 0.5 μm film). ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 (200 MHz) or a Varian Inova-300 (300MHz) spectrometer. IR spectra were recorded on Perkin-Elmer Spectrum 2000 FTIR spectrometer. Isomeric purity of the compounds reported herein was determined from the ^1H and ^{13}C NMR spectra.

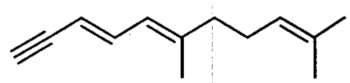
(*E*)-1-Bromo-4-trimethylsilyl-1-buten-3-yne. To a solution of (trimethylsilyl)acetylene (2.8 mL, 20 mmol) in THF (30 mL) was added *via* a syringe MeMgBr (8 mL of 3M ether solution; 24 mmol). The reaction mixture was stirred at room temperature for 3 h, and a solution of anhydrous $ZnBr_2$ (5.85 g, 26 mmol) in THF (10 mL) was added at 0°C. The mixture was stirred at 0°C for 30min and added *via* cannula to a solution of (*E*)-1-bromo-2-iodoethylene (5.12 g, 22 mmol) and $Pd(PPh_3)_4$ (0.46g, 0.02 equiv) in THF (15 ml). The resultant mixture was stirred at room temperature for 10h, quenched with aqueous NH_4Cl, and extracted with pentane. The pentane fraction was washed with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and distilled to afford 3.29g (81% yield) of the title compound (≥ 99% *E* by ^{13}C NMR spectroscopy) as a colorless liquid: bp 72-74°C(15 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9H), 6.21(d, J=14.1Hz, 1H), 6.75(d, J=14.1Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -0.325(3H), 97.33, 100.91, 117.61, 119.97; IR(neat) 3075, 2168, 2111, 1696, 1577, 1252, 1199, 1062, 845 cm^{-1}.



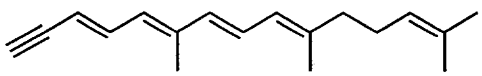
1-((*E*,*E*,*E*)-3-Methyl-1,3,5-octatrien-7-ynyl)-2,6,6-trimethyl-1-cyclohexene. An oven-dried, round-bottomed flask was charged with Cp_2ZrCl_2 (0.584 g, 2 mmol). To this were added sequentially at 0°C 1,2-dichloroethane (10 mL), Me_3Al (0.38 mL, 4 mmol) and (*E*)-1-(buten-3-ynyl)-2,6,6-trimethyl-1-cyclohexene (0.348 g, 2 mmol). The reaction mixture was stirred at room temperature for 4 h, at which point carboalumination was complete, as determined by GLC. The dichloroethane and excess Me_3Al were removed by evaporation at 50°C *in vacuo*, and dry THF (4mL) was added. In another flask, $Pd_2(dba)_3$ (46 mg, 0.05 mmol) was dissolved in DMF (6 mL) to which TFP (46 mg, 0.2 mmol) was added at 0°C. After 10 min, a clear pale green solution thus obtained was treated with (*E*)-1-bromo-4-trimethylsilyl-1-buten-3-yne (426 mg, 2.1 mmol). After 5 additional minutes, the alkenylalane obtained above was transferred *via* cannula to this solution at 0 °C, which was followed by addition of $ZnCl_2$ (272 mg, 2 mmol) in THF (1 mL), and the cross coupling reaction was followed by GLC analysis. After stirring at room temperature for 6 h, the reaction mixture was quenched with water, extracted with pentane, dried over $MgSO_4$, concentrated, and examined by GLC, ^{1}H and ^{13}C NMR spectroscopy using mesitylene as an internal standard. The cross coupling product of ≥99% stereoisomeric purity was formed in 76% NMR yield along with 1-trimethylsilyl-3-penten-1-yne, 1-(2,6,6-trimethyl-1-cyclohexenyl)-3-methyl-1,3-butadiene, 1-(2,6,6-trimethyl-1-cyclohexenyl)-3-methyl-1,3-pentadiene, and 1,8-bis(trimethylsilyl)-3,5-octadien-1,7-diyne formed in 20%, 5%, 9% and 7% yields, respectively. The crude product was passed through a short (15 cm) silica gel column using pentane as an eluent. After the pentane was evaporated, 10 mL of methanol was added to the residue, which was then treated with K_2CO_3 (276 mg, 2 mmol). After stirring for 3h at room temperature, the reaction mixture was quenched with water, extracted with pentane, washed with aqueous NH_4Cl and brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatograghy (silica gel, pentane) afforded 336 mg (70%, ≥99% isomerically pure by ^{13}C NMR spectroscopy) of the title compound as a red oil: ^1H NMR ($CDCl_3$) δ 1.04(s, 6H), 1.48(m. 2H), 1.62(m, 2H), 1.72(s, 3H), 1.96(s, 3H), 2.03(m, 2H), 3.10(d, J=2.4Hz, 1H), 5.57(dd, J=2.4 and 15.5Hz, 1H), 6.10(m, 2H), 6.28(d, J=15.8Hz, 1H), 7.07(dd, J=11.7 and 15.5Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.25, 19.74, 22.23, 29.44(2C), 33.58, 34.74, 40.08, 80.49, 84.45, 109.31, 129.02, 129.41, 130.39, 137.49, 138.13, 139.54, 140.35; IR(neat) 3312, 2906, 2827, 2095, 1593, 1444, 1360, 965, 637 cm^{-1}; HRMS calculated for $C_{18}H_{24}$: 240.1878; found 240.1887.



Vitamin A. To a slurry of Cp_2ZrCl_2 (234 mg, 0.8 mmol) in 4 mL of 1,2-dichloroethane was added Me_3Al (0.15 mL, 1.6 mmol) at room temperature. To the lemon yellow solution thus obtained was added dropwise 1-((*E*,*E*,*E*)-3-methyl-1,3,5-octatrien-7-ynyl)-2,6,6-trimethyl-1-cyclohexene (192 mg, 0.8 mmol) in 2 mL of 1,2-dichloroethane at 0 °C. After the mixture was stirred for 20 h at room temperature, volatile compounds were evaporated at reduced pressure (maximum 50 °C, 0.3 mmHg). The organic compounds were extracted with *n*-hexane, and the extract was transferred into another flask *via* cannula. To this was added *n*-BuLi (0.32 mL, 2.5 M in hexanes, 0.8 mmol). THF (4 ml) was added to dissolve the precipitate, and the resultant solution was added to a suspension of paraformaldehyde (72 mg, 2.4 mmol) in THF (4 mL). The reaction mixture was stirred for 5 h, quenched with H_2O, and extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and concentrated. Column chromatography (neutral alumina, 85:15 EtOAc-hexane) afforded 153mg of vitamin A (67% yield, $\geq$ 99% isomerically pure by ^{13}C NMR spectroscopy): ^1H NMR (CD_2Cl_2) δ 1.03(s, 6H), 1.47(m, 2H), 1.62(m, 2H), 1.71(s, 3H), 1.86(s, 3H), 1.96(s, 3H), 2.01(m, 2H), 4.28(d, *J*=6.9Hz, 2H), 5.68(t, *J*=6.9Hz, 1H), 6.14(m, 3H), 6.30(d, *J*=15.1Hz, 1H), 6.64(dd, *J*=11.1 and 15.1 Hz, 1H); ^{13}C NMR(CD_2Cl_2) δ 12.71, 12.79, 19.63, 21.81, 29.05(2C), 33.38, 34.52, 39.97, 59.66, 125.42, 127.13, 129.60, 130.43, 130.93, 136.46, 136.68, 136.92, 137.99, 138.14; IR(neat) 3400, 3040, 1722, 1341, 1274, 1080, 973cm^{-1}. The ^1H and ^{13}C NMR spectral data are in good agreement with those of an authentic sample obtained from Aldrich Chemical Company.

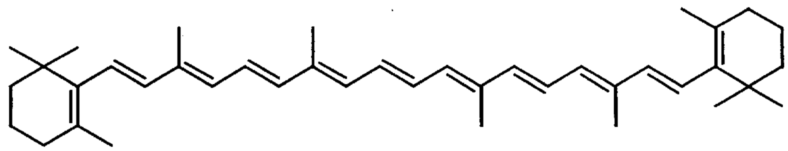


6,10-Dimethyl-3*E*,5*E*,9-undecatrien-1-yne. The Zr-catalyzed carboalumination and Pd- and Zn- catalyzed cross coupling were performed as in the preparation of 1-((*E*,*E*,*E*)-3-methyl-1,3,5-octatrien-7-ynyl)-2,6,6-trimethyl-1-cyclohexene by using the following reagents in the amounts indicated in paratheses: Cp_2ZrCl_2 (438 mg, 1.5 mmol), Me_3Al (0.29 mL, 3 mmol), $ClCH_2CH_2Cl$ (8 ml), 6-methyl-5-hepten-1-yne(162 mg, 1.5 mmol), $Pd_2(dba)_3$ (34 mg, 0.0375 mmol), TFP (35 mg, 0.15 mmol), DMF (8 mL), (*E*)-1-bromo-4-trimethylsilyl-1-buten-3-yne(325 mg, 1.6 mmol), $ZnCl_2$ (204 mg, 1.5 mmol). Examination of the crude product by GLC and ^1H and ^{13}C NMR spectroscopy indicated that the desired cross-coupling product of $\geq$99% stereoisomeric purity was formed in 86% yield along with 1-trimethylsilyl-3-penten-1-yne and 2,6-dimethyl-1,5-heptadiene formed in 17% and 8% yields, respectively. Its deprotection utilized MeOH (8 mL) and K_2CO_3 (207 mg, 1.5 mmol), and afforded 196mg (75%, $\geq$99% stereoisomerically pure by ^{13}C NMR spectroscopy) of the title compound as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 1.61(s, 3H), 1.69(s, 3H), 1.74(s, 3H), 2.10(s, 4H), 2.99(d, J=2.2Hz, 1H), 5.08(t, J=1.4Hz, 1H), 5.46(dd, J=2.2 and 15.5 Hz, 1H), 5.90(d, J=11.2Hz, 1H), 6.92(dd, J=11.2 and 15.5Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.47, 18.15, 26.15, 26.91, 40.51, 79.13, 84.23, 107.74, 124.13, 124.66, 132.36, 140.49, 143.78; IR(neat) 3308, 2968, 2095, 1636, 1446, 1377, 1217, 953, 759, 640cm^{-1}; HRMS calculated for $C_{13}H_{18}$: 174.1409; found 174.1400.

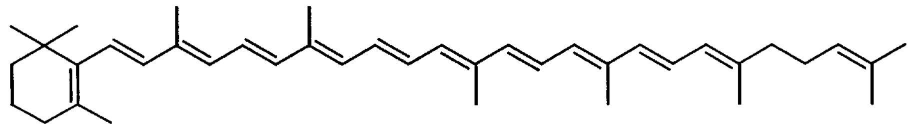


6,10,14-Trimethyl-3*E*,5*E*,7*E*,9*E*,13-pentadecapentaen-1-yne. The Zr-catalyzed carboalumination and Pd- and Zn- catalyzed cross coupling were performed as in the preparation of 1-((*E*,*E*,*E*)-3-methyl-1,3,5-octatrien-7-ynyl)-2,6,6-trimethyl-1-cyclohexene by using the following reagents in the amounts indicated in paratheses: Cp_2ZrCl_2 (584 mg, 2 mmol), Me_3Al (0.38 mL, 4 mmol), $ClCH_2CH_2Cl$ (10 ml), 6,10-dimethyl-3*E*,5*E*,9-undecatrien-1-yne (348 mg, 2 mmol), $Pd_2(dba)_3$ (46 mg, 0.05 mmol), TFP (46 mg, 0.2 mmol), DMF (7 mL), (*E*)-1-bromo-4-trimethylsilyl-1-buten-3-yne (426 mg, 2.1 mmol), $ZnCl_2$ (272 mg, 2 mmol). Examination of the crude product by GLC, ^{1}H and ^{13}C NMR spectroscopy indicated that the desired cross-coupling product of ≥99% stereoisomeric purity by ^{13}C NMR spectroscopy was formed in 82% yield along with 1-trimethylsilyl-3-penten-1-yne and 2,6,10-trimethyl-1, 3*E*,5*E*, 9-undecatetraene formed in 19% and 12% yields, respectively. Its deprotection utilized MeOH (12 mL) and K_2CO_3 (276 mg, 2 mmol). Examination of the crude product by ^{1}H NMR indicated the formation of the title compound in 76% yield. Column chromatography (silica gel, pentane) afford 331 mg (69%, ≥99% stereoisomerically pure by ^{13}C NMR spectroscopy) of the title compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.63(s, 3H), 1.71(s, 3H), 1.84(s, 3H), 1.96(s, 3H), 2.14(d, J=3.0Hz, 4H), 3.12(d, J=2.2Hz, 1H), 5.12(m, 1H), 5.57(dd, J=2.2 and 15.4Hz, 1H), 5.96(d, J=11.0Hz, 1H), 6.11(d, J=11.7Hz, 1H), 6.20(d, J=15.0 Hz, 1H), 6.59(dd, J=11.0 and 15.0Hz, 1H), 7.05(dd, J=11.7 and 15.4Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.81, 16.93, 17.64, 25.64, 26.56, 40.16, 80.18, 83.99, 108.76, 123.81, 125.41, 126.27, 128.95, 131.67, 134.38, 139.14, 139.78, 140.75; IR(neat)

3308, 2959, 1682, 1456, 1266, 961, 759, 741 cm^{-1}; HRMS calculated for $C_{18}H_{24}$: 240.1878; found 240.1871.



β-Carotene. To a slurry of Cp_2ZrCl_2 (207 mg, 0.71 mmol) in 4 mL of 1,2-dichloroethane was added Me_3Al (0.13 mL, 1.42 mmol) at room temperature. To the lemon yellow solution thus obtained was added dropwise 1-((*E*,*E*,*E*)-3-methyl-1,3,5-octatrien-7-ynyl)-2,6,6-trimethyl-1-cyclohexene (170 mg, 0.71 mmol) in 2 mL of 1,2-dichloroethane at 0 °C. After the mixture was stirred for 20 h at room temperature, volatile compounds were evaporated at reduced pressure(maximum 50 °C, 0.3 mmHg), and dry THF (2 mL) was added. In another flask, $Pd_2(dba)_3$ (16 mg, 0.018 mmol) was dissolved in DMF (3 mL) to which TFP (16 mg, 0.071 mmol) was added at 0°C. After 10 min, a clear pale green solution thus obtained was treated with (*E*)-1-bromo-2-iodoethylene (84 mg, 0.36 mmol). After 5 additional minutes, the alkenylalane obtained above was transferred *via* cannula to this solution at 0 °C, which was followed by addition of $ZnCl_2$ (96 mg, 0.71 mmol) in THF (0.5 mL). After stirring at room temperature for 5 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (neutral alumina, pentane) afforded 129 mg of β-carotene (68% yield, $\geq$ 99% isomerically pure by ^{13}C NMR spectroscopy) as a red solid: ^1H NMR ($CDCl_3$) δ 1.09(s, 12H), 1.54(m, 4H), 1.68(m, 4H), 1.78(s, 6H), 2.03(s, 12H), 2.08(m, 4H), 6.67-6.72(m, 4H), 6.18-6.44(m, 10H); ^{13}C NMR($CDCl_3$) δ 13.02, 13.08, 19.54, 22.03, 29.25(2C), 33.39, 34.55, 39.93, 125.31, 126.92, 129.64, 130.26, 131.12, 132.69, 136.28, 136.74, 137.51, 138.04, 138.19; IR(neat) 3030, 2915, 2850, 1724, 1455, 1376, 971, 832, 725 cm^{-1}. The ^1H and ^{13}C NMR spectral data are in good agreement with those of an authentic sample obtained from Aldrich Chemical Company.



γ-**Carotene**. To a slurry of Cp_2ZrCl_2 (350 mg, 1.2 mmol) in 5 mL of 1,2-dichloroethane was added Me_3Al (0.23 mL, 2.4 mmol) at room temperature. To the lemon yellow solution thus obtained was added dropwise 1-((*E*,*E*,*E*)-3-methyl-1,3,5-octatrien-7-ynyl)-2,6,6-trimethyl-1-cyclohexene (288 mg, 1.2 mmol) in 2 mL of 1,2-dichloroethane at 0 °C. After the mixture was stirred for 20 h at room temperature, volatile compounds were evaporated at reduced pressure (maximum 50°C, 0.3 mmHg), and dry THF (3 mL) was added. The THF solution was then added *via* cannula to a solution of (*E*)-1-bromo-2-iodoethylene (308 mg, 1.32 mmol) and $Pd(PPh_3)_4$ (69 mg, 0.05 equiv) in DMF (7 mL) at 0 °C, which was followed by addition of $ZnCl_2$ (96 mg, 0.71 mmol) in THF (0.5 mL). After stirring at room temperature for 2 h, the reaction mixture was quenched with water, extracted with pentane, washed with brine, dried over $MgSO_4$, and concentrated. The crude product was passed through a short (10 cm) neutral alumina column using pentane as an eluent, and kept as a solution in dry THF (2 mL) to minimize its decomposition before the next cross coupling.

To a slurry of Cp_2ZrCl_2 (292 mg, 1 mmol) in 4 mL of 1,2-dichloroethane was added Me_3Al (0.19 mL, 2 mmol) at room temperature. To the lemon yellow solution thus obtained was added dropwise 6,10,14-trimethyl-3*E*,5*E*,7*E*,9*E*,13-pentadecapentaen-1-yne (240 mg, 1 mmol) in 2 mL of 1,2-dichloroethane at 0 °C. After the mixture was stirred for 12 h at room temperature, volatile compounds were evaporated at reduced pressure (maximum 50 °C, 0.3 mmHg), and dry THF (3 mL) was added. In another flask, $Pd_2(dba)_3$ (23 mg, 0.025 mmol) was dissolved in DMF (3 mL) to which TFP (23mg, 0.1 mmol) was added at 0°C. After 10 min, a clear pale green solution thus obtained was treated with 1-((*E*,*E*,*E*,*E*,*E*)-3,7-dimethyl-10-bromo-1,3,5,7,9-decapentaenyl)-2,6,6-trimethyl-1-cyclohexene in THF obtained above. After 5 additional minutes, the alkenylalane obtained above was transferred *via* cannula to this solution at 0°C, which was followed by addition of $ZnCl_2$ (136 mg, 1 mmol) in THF (0.8 mL). After stirring at room temperature for 5 h, the reaction mixture was quenched with water, extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (neutral alumina, pentane) afford 284mg of γ-carotene (53% yield, ≥ 99% isomerically pure by ^{13}C spectroscopy) as a red solid: ^1H NMR (CD_2Cl_2) δ 1.04(s, 6H), 1.44-1.54(m, 2H), 1.63(s, 3H), 1.58-1.65(m, 2H), 1.69(s, 3H), 1.72(s, 3H), 1.82(s,3H), 1.98(s, 12H), 2.00-2.08(m, 2H), 2.13(s, 4H), 5.04-5.19(m, 1H), 5.96(d, *J*=11.0Hz, 1H), 6.11-6.40(m, 9H), 6.52(dd, *J*=11.0 and 14.9Hz, 1H), 6.62-6.73(m, 4H); ^{13}C NMR(CD_2Cl_2) δ 12.72, 12.78, 12.81, 12.87, 16.89, 17.64, 19.53, 21.73, 25.64, 26.92, 28.97(2C), 33.34, 34.44, 39.93, 40.44, 124.18, 125.23, 125.46(2C), 125.95, 127.03, 129.64, 130.29, 130.35, 131.05, 131.69, 131.93, 132.64, 132.82, 135.45, 136.37, 136.54, 136.88, 136.91, 137.36, 137.52, 137.99, 138.13, 139.90; IR(neat) 3123, 2926, 2303, 2197, 1750, 1717, 1559, 1395, 993, 954, 828, 711, 679cm^{-1}. HRMS calculated for $C_{40}H_{56}$: M^{+}+1, 537.4460; found 537.4448.

A Highly Selective and Efficient Route to Carotenoi...

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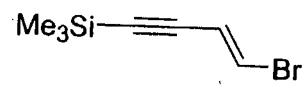
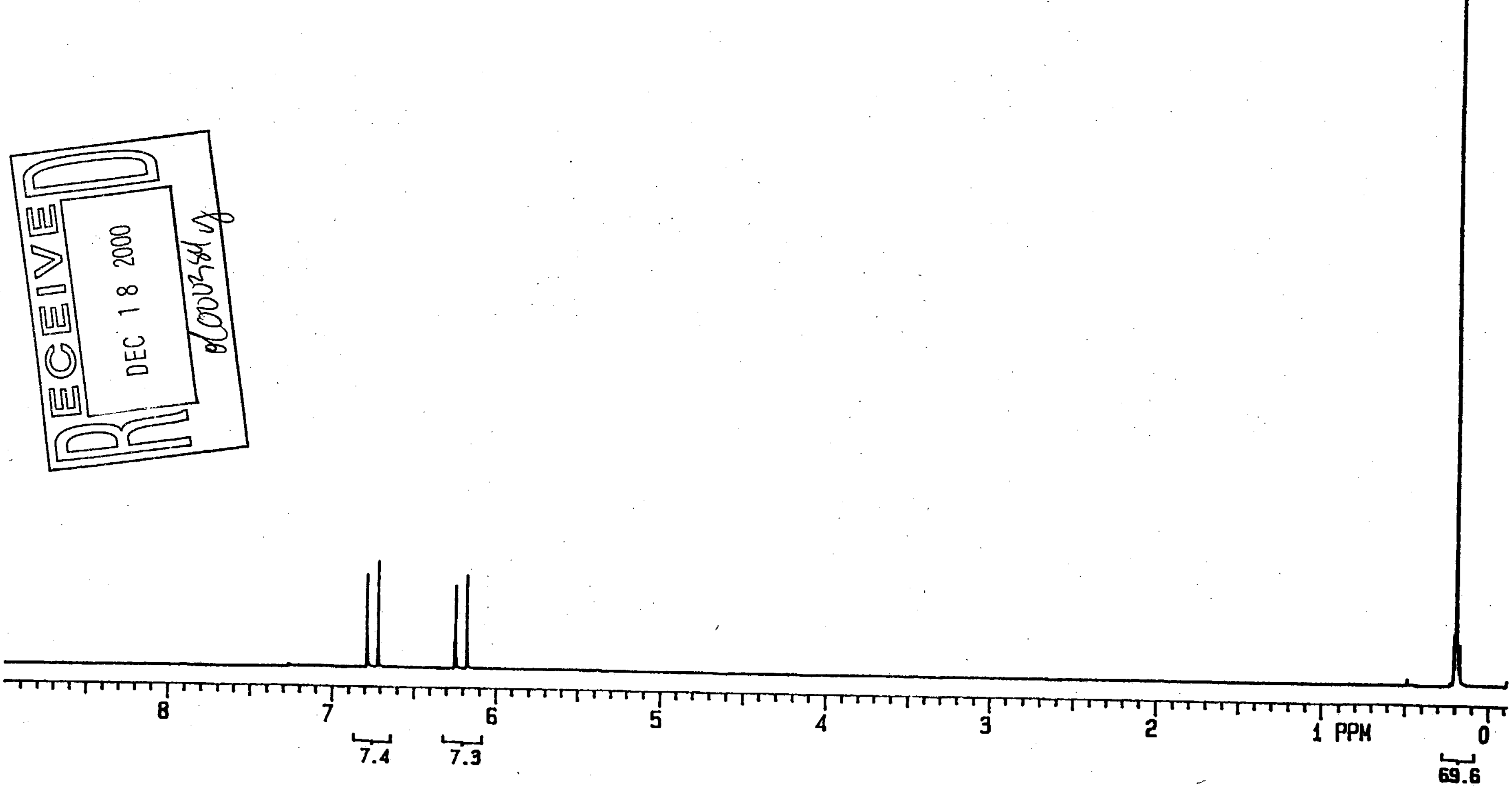
GEMINI-200 1H SENSITIVITY
SPECTRAL LINES FOR TH= 18.65
RFL= 426.7 RFP= 0

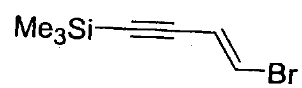
INDEX	FREQ	PPM	INTENSITY
01	1356.61	6.784	24.866
02	1342.41	6.713	29.373
03	1249.16	6.247	23.643
04	1235.04	6.176	25.119
05	37.63	0.188	488.809



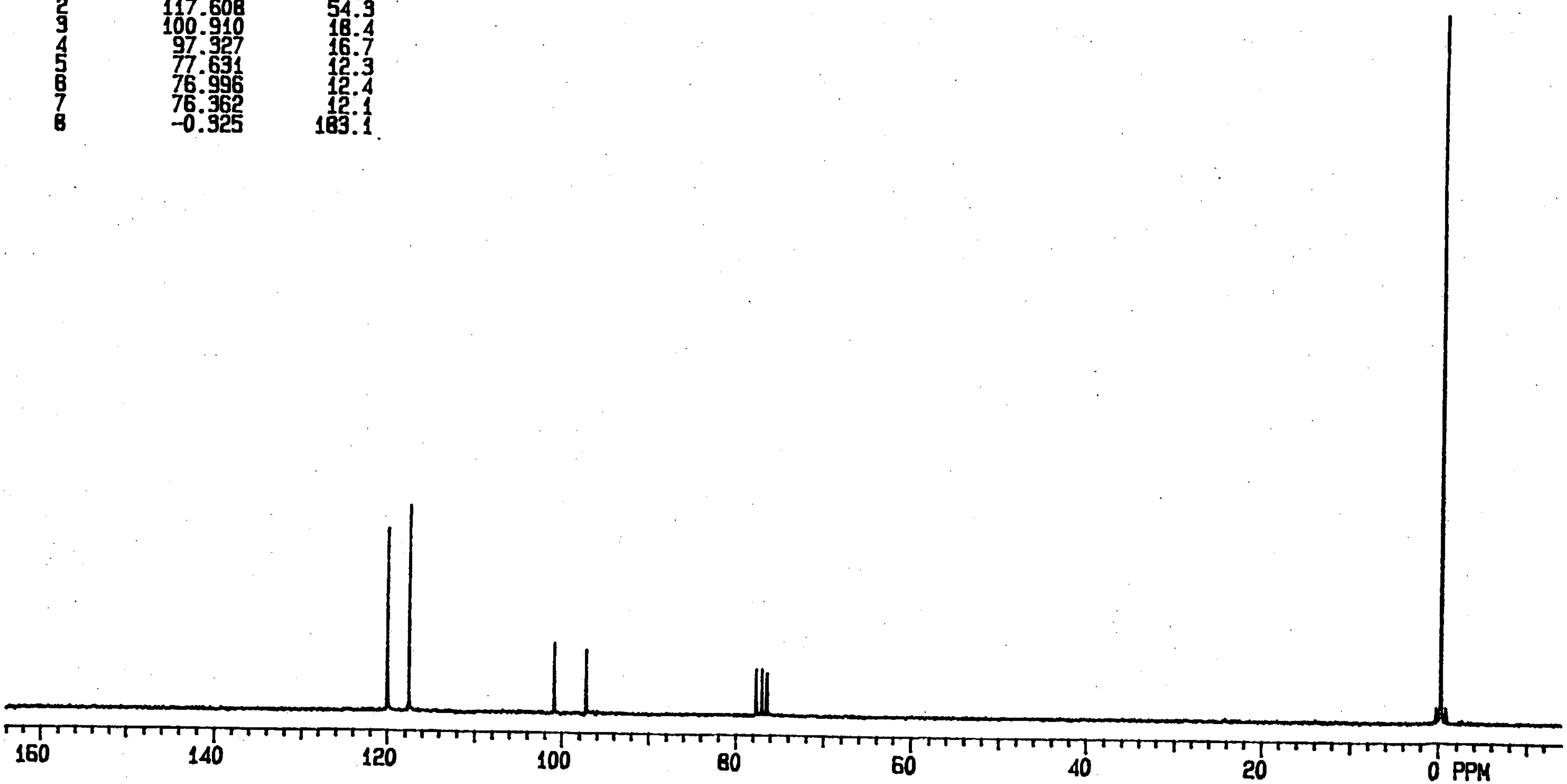


A Highly Selective and Efficient Route to Carotenoi

Fanxing Zeng and Ei-ichi Negishi*



INDEX	FREQUENCY (PPM)	HEIGHT
1	119.970	53.0
2	117.608	54.3
3	100.910	18.4
4	97.327	16.7
5	77.631	12.3
6	76.996	12.4
7	76.362	12.1
8	-0.325	183.1



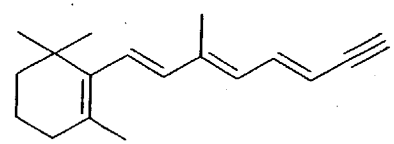
2

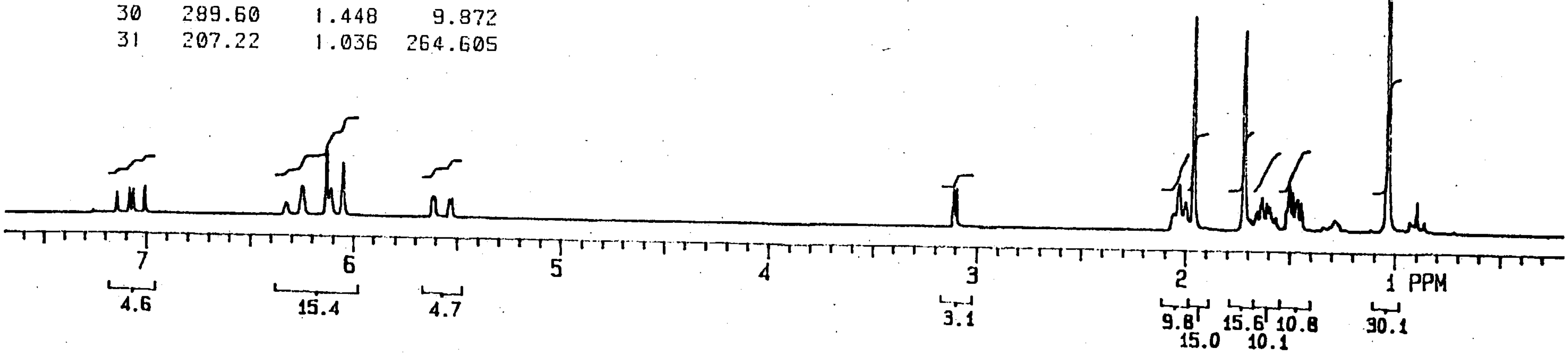
A Highly Selective and Efficient Route to Carotenoids

Fanxing Zeng and Ei-ichi Negishi*

RFL= 428.7 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	1428.77	7.145	7.086
02	1417.05	7.086	8.380
03	1413.30	7.067	8.062
04	1401.66	7.009	8.964
05	1249.29	6.247	10.081
06	1226.21	6.132	23.315
07	1222.55	6.113	9.408
08	1210.25	6.052	18.444
09	1123.28	5.617	7.184
10	1121.00	5.606	7.298
11	1107.82	5.540	6.564
12	1105.41	5.528	6.665
13	621.62	3.109	12.731
14	619.26	3.097	13.099
15	411.86	2.060	5.940
16	406.08	2.031	15.837
17	399.85	2.000	9.693
18	391.79	1.959	72.599
19	343.08	1.716	68.346
20	331.80	1.659	7.210
21	328.26	1.642	9.188
22	326.43	1.632	11.647
23	322.16	1.611	9.810
24	320.08	1.601	8.635
25	317.89	1.590	7.890
26	300.67	1.504	16.221
27	298.55	1.493	13.977
28	295.38	1.477	10.091
29	292.77	1.464	11.404
30	289.60	1.448	9.872
31	207.22	1.036	264.605



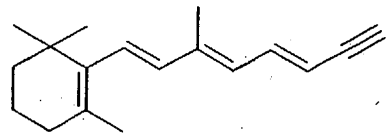


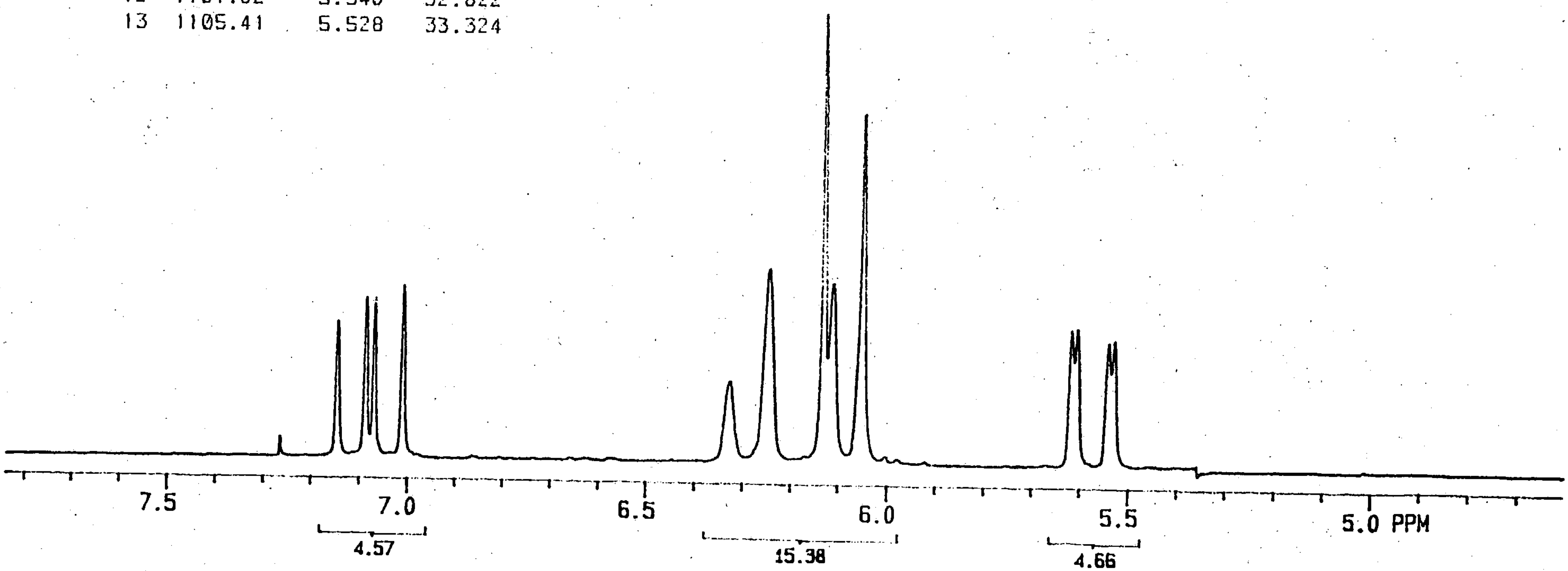
3

Fanxing Zeng and Ei-ichi Negishi*

GEMINI-200 1H SENSITIVITY
SPECTRAL LINES FOR TH= 18.42
RFL= 428.7 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	1428.77	7.145	35.428
02	1417.05	7.086	41.901
03	1413.30	7.067	40.312
04	1401.66	7.009	44.821
05	1265.04	6.326	21.355
06	1249.29	6.247	50.405
07	1226.21	6.132	116.573
08	1222.55	6.113	47.041
09	1210.25	6.052	92.222
10	1123.28	5.617	35.919
11	1121.00	5.606	36.492
12	1107.82	5.540	32.822
13	1105.41	5.528	33.324

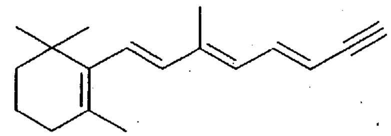


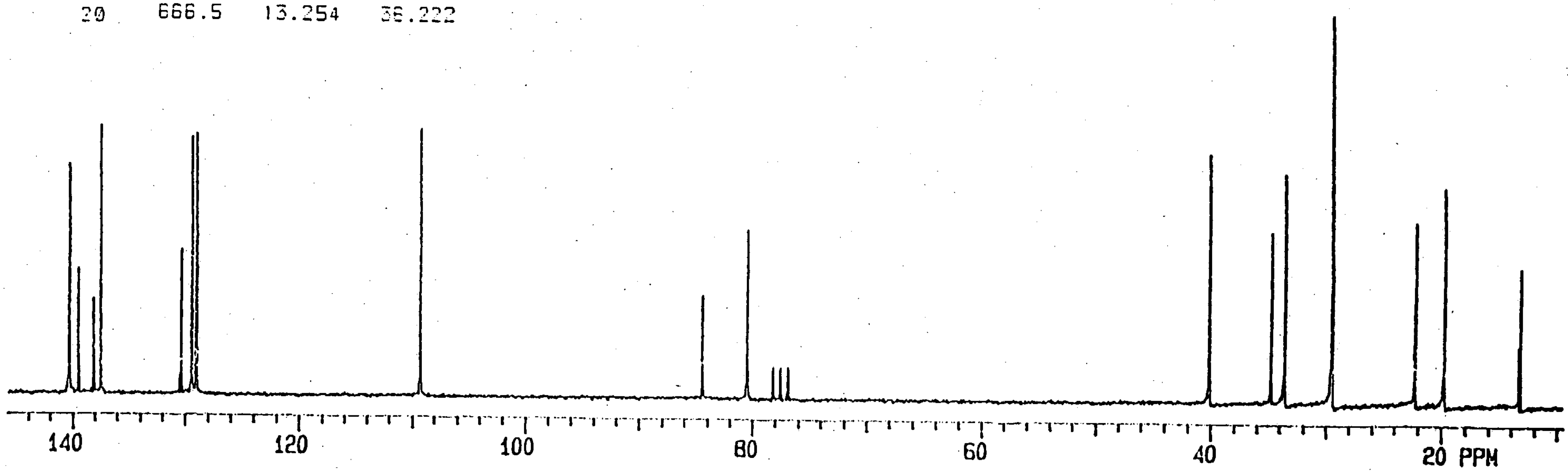


Fanxing Zeng and Ei-ichi Negishi*

GEMINI-200 1H SENSITIVITY
SPECTRAL LINES FOR TH= 7.02
RFL= -393.3 RFP= 0

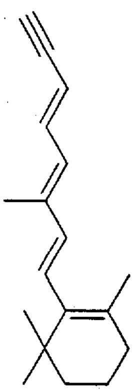
INDEX	FREQ	PPM	INTENSITY
01	7058.2	140.352	65.533
02	7017.3	139.538	32.993
03	6946.3	138.126	35.003
04	6914.2	137.488	70.957
05	6557.1	130.388	38.225
06	6508.1	129.412	58.442
07	6488.3	129.019	71.033
08	5496.9	109.306	70.807
09	4247.1	84.454	26.842
10	4047.8	80.489	45.242
11	3931.9	78.184	8.332
12	3899.9	77.547	9.447
13	3867.9	76.913	9.328
14	2015.8	40.084	67.729
15	1746.9	34.736	45.882
16	1688.6	33.577	65.556
17	1480.7	29.444	120.720
18	1117.9	22.230	49.763
19	992.6	19.738	58.668
20	666.5	13.254	36.222

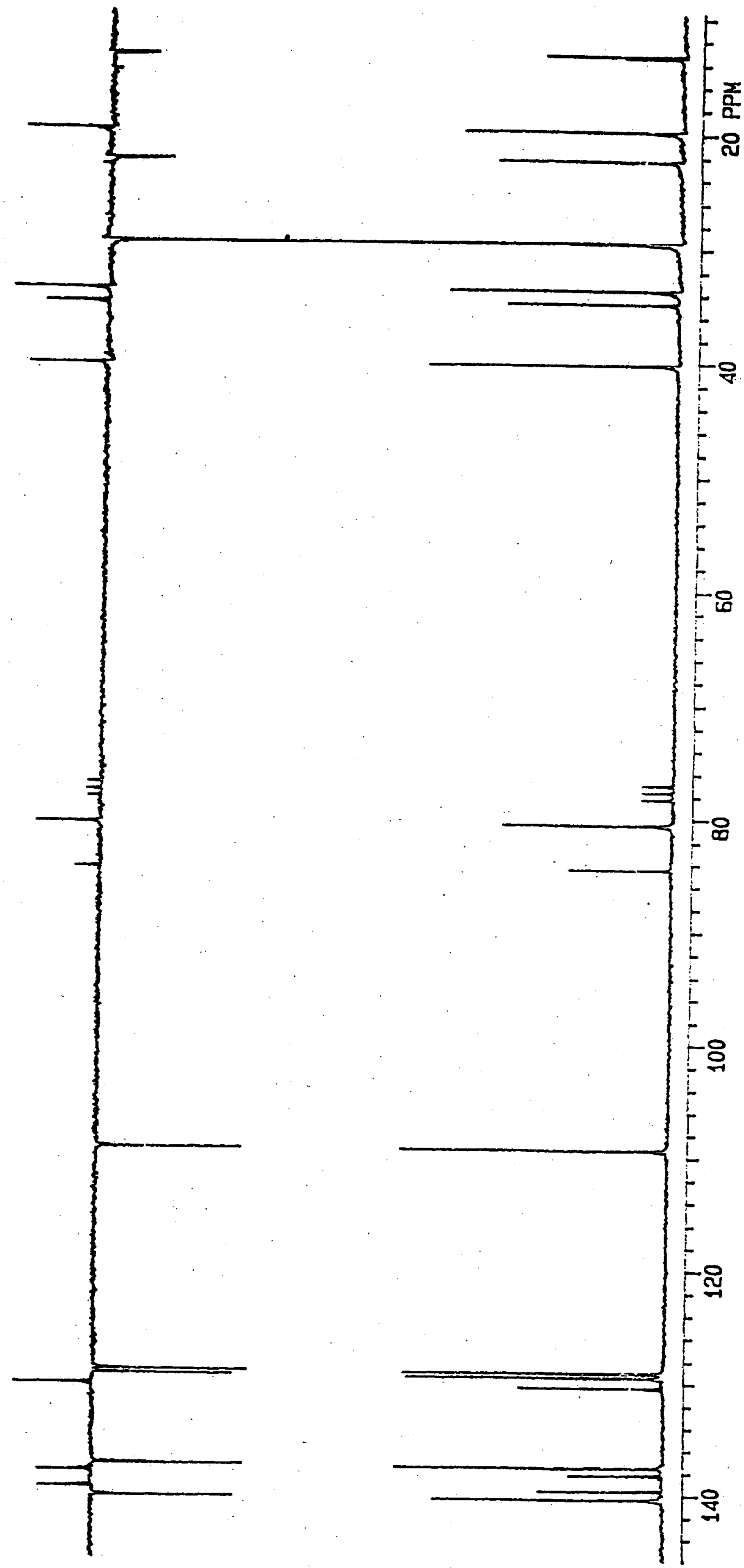




A Highly Selective and Efficient Route to Carotenoids

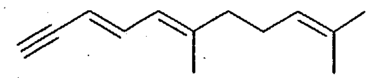
Fanxing Zeng and Ei-ichi Negishi*

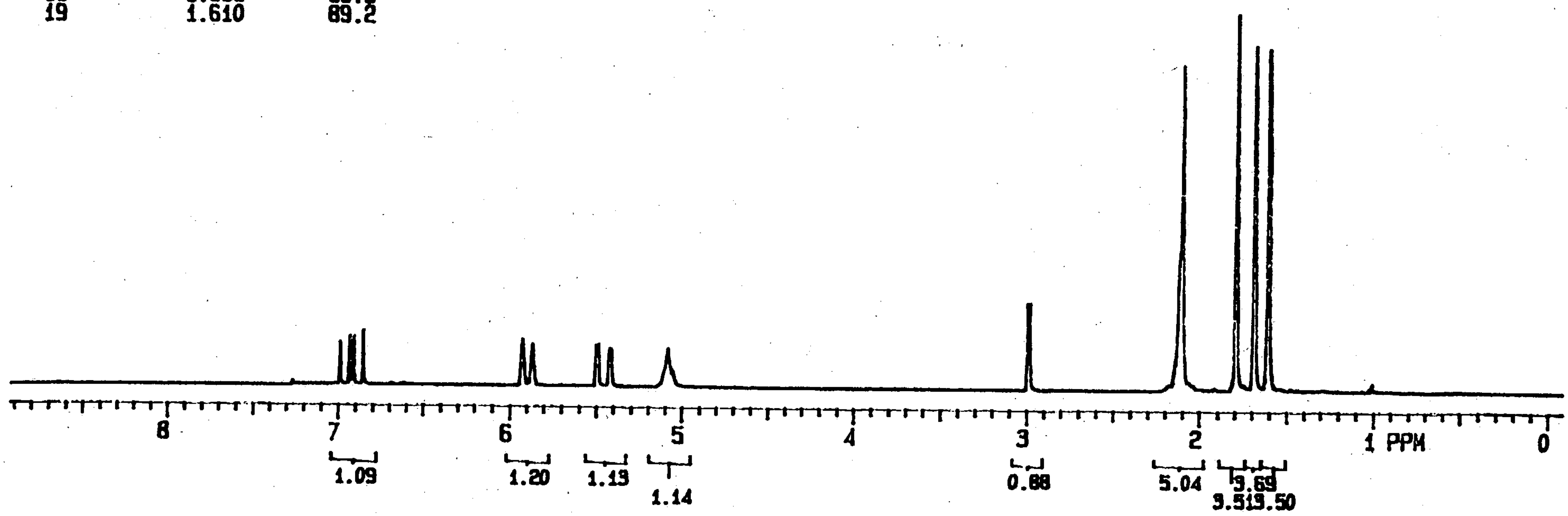




Fanxing Zeng and Ei-ichi Negishi*

INDEX	FREQUENCY (PPM)	HEIGHT
1	6.990	11.4
2	6.934	13.1
3	6.912	13.0
4	6.855	14.2
5	5.927	12.4
6	5.871	11.3
7	5.502	11.2
8	5.491	11.5
9	5.425	10.3
10	5.414	10.1
11	5.084	10.6
12	5.077	9.4
13	2.996	22.7
14	2.985	22.9
15	2.104	85.1
16	1.797	98.3
17	1.791	97.5
18	1.688	89.9
19	1.610	89.2

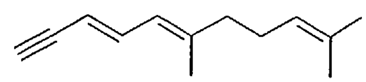


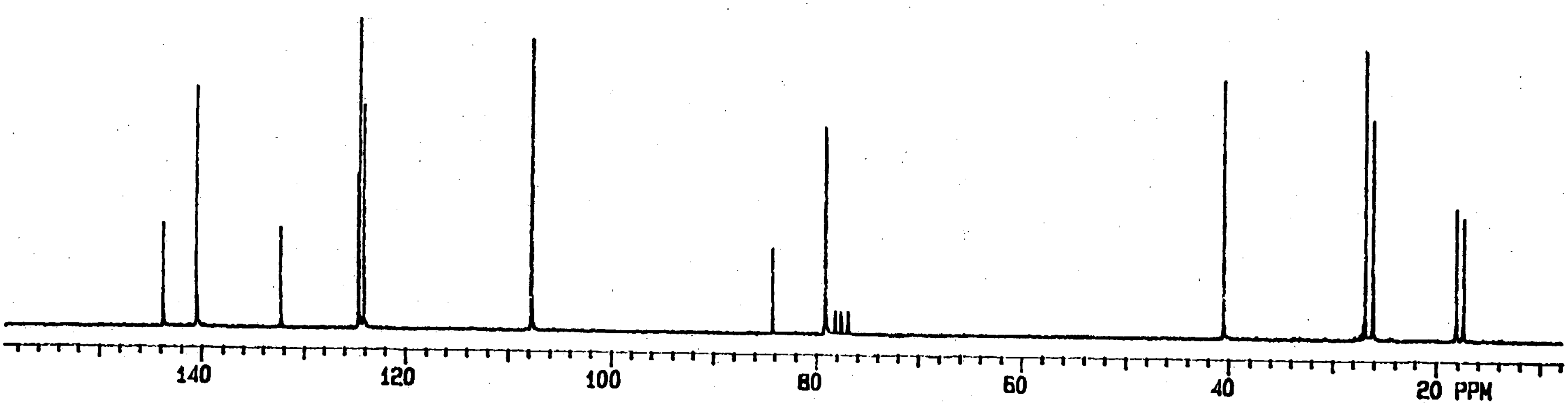


Fanxing Zeng and Ei-ichi Negishi*

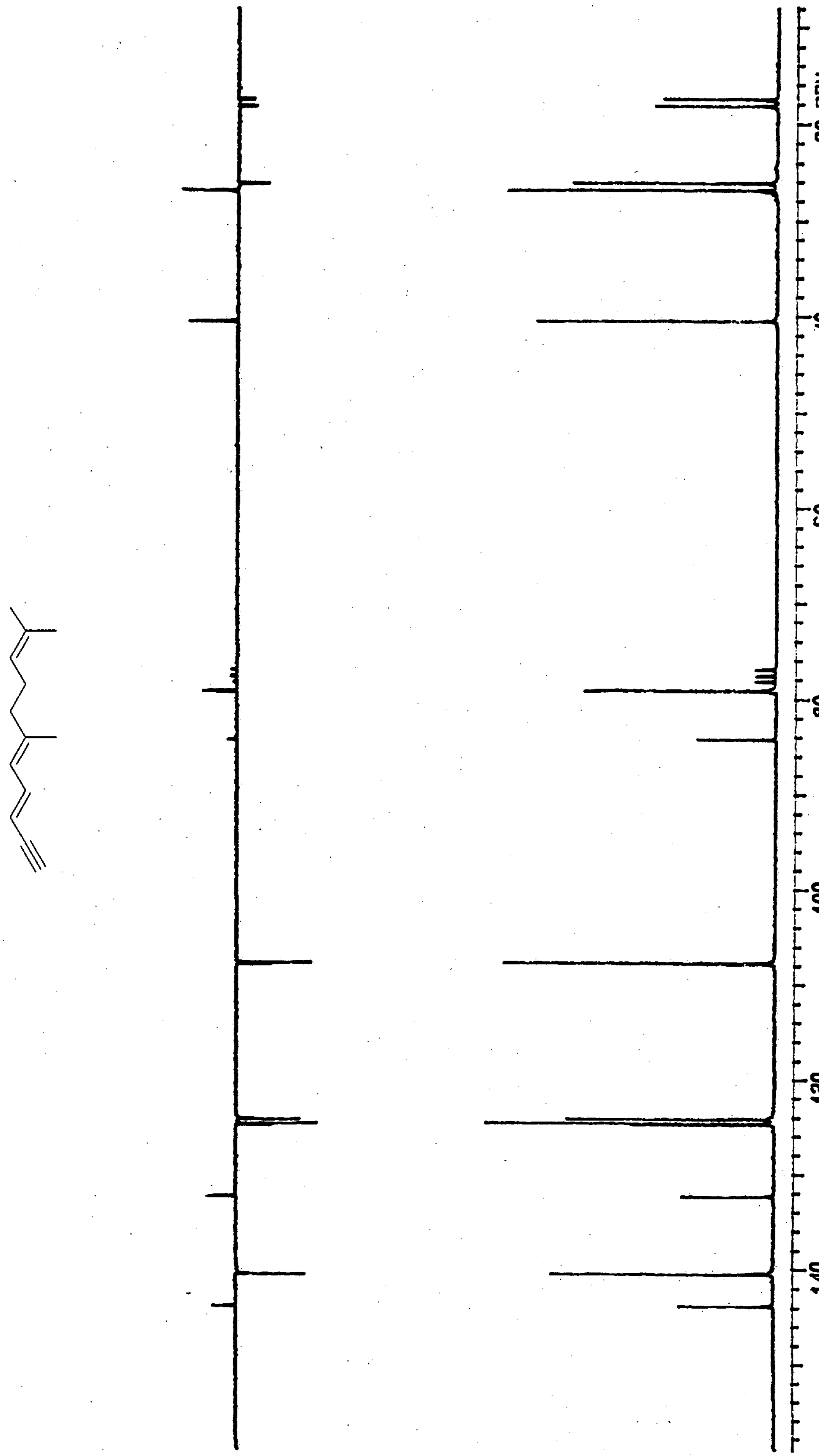
GEMINI-200 1H SENSITIVITY
SPECTRAL LINES FOR TH= 5.31
RFL= -393.3 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	7230.8	143.784	28.250
02	7065.4	140.495	69.490
03	6656.4	132.362	26.632
04	6268.9	124.657	81.556
05	6242.2	124.126	64.010
06	5418.1	107.739	76.627
07	4236.0	84.233	22.817
08	3979.6	79.134	54.305
09	3933.7	78.222	6.047
10	3901.7	77.586	6.238
11	3869.9	76.952	6.178
12	2037.3	40.511	75.056
13	1353.1	26.906	76.673
14	1315.2	26.153	60.009
15	912.8	18.151	35.112
16	878.4	17.466	34.040





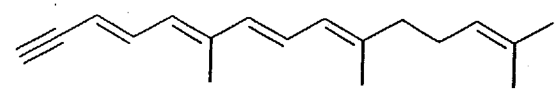
Fanxing Zeng and Ei-ichi Negishi*

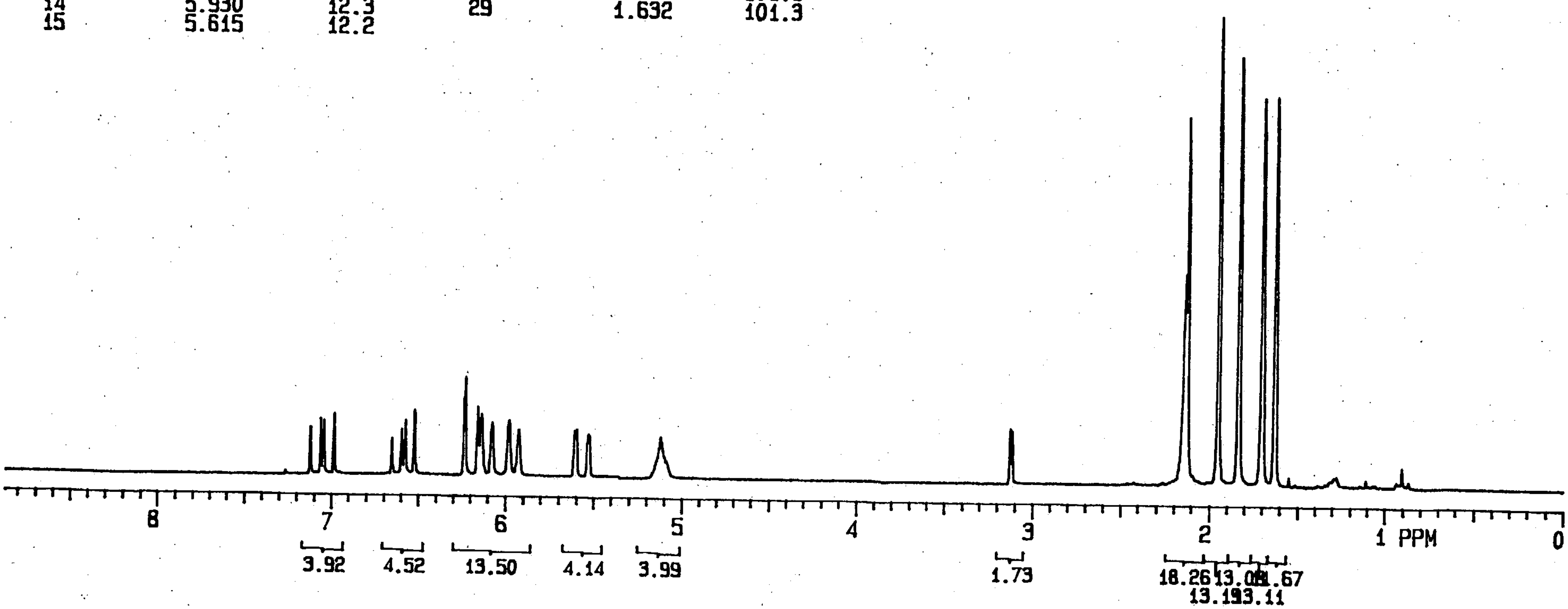


Fanxing Zeng and Ei-ichi Negishi*

INDEX	FREQUENCY (PPM)	HEIGHT
1	7.124	12.5
2	7.066	14.7
3	7.047	14.4
4	6.989	15.8
5	6.654	9.6
6	6.599	12.0
7	6.579	14.5
8	6.524	17.1
9	6.234	25.8
10	6.159	18.0
11	6.137	16.1
12	6.079	14.0
13	5.983	14.6
14	5.930	12.3
15	5.615	12.2

INDEX	FREQUENCY (PPM)	HEIGHT
16	5.604	12.4
17	5.538	11.1
18	5.527	11.2
19	5.126	10.2
20	5.119	11.0
21	5.113	9.5
22	3.130	14.1
23	3.118	13.7
24	2.144	51.3
25	2.129	95.7
26	1.956	121.5
27	1.837	112.0
28	1.705	101.1
29	1.632	101.3

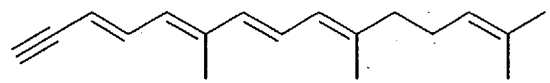


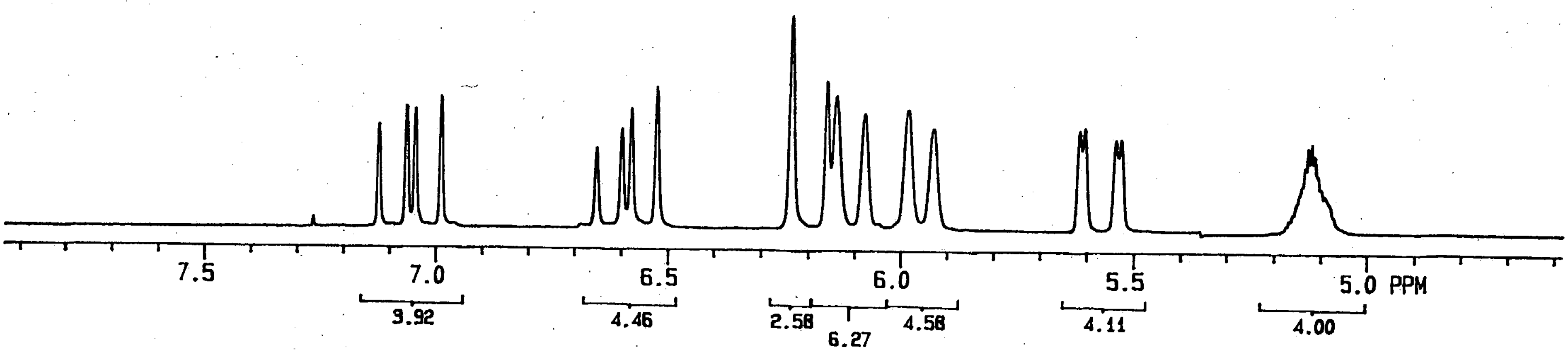


A Highly Selective and Efficient Route to Carotenoids

Fanxing Zeng and Ei-ichi Negishi*

INDEX	FREQUENCY (PPM)	HEIGHT
1	7.124	26.9
2	7.066	31.6
3	7.047	31.0
4	6.989	34.1
5	6.654	20.8
6	6.599	25.9
7	6.579	31.2
8	6.524	37.0
9	6.234	55.7
10	6.159	38.9
11	6.137	34.8
12	6.079	30.2
13	5.983	31.4
14	5.930	26.4
15	5.615	26.2
16	5.604	26.8
17	5.538	23.9
18	5.527	24.1
19	5.133	17.4
20	5.126	22.1
21	5.119	23.8
22	5.113	20.6

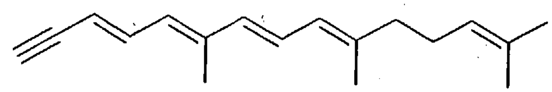


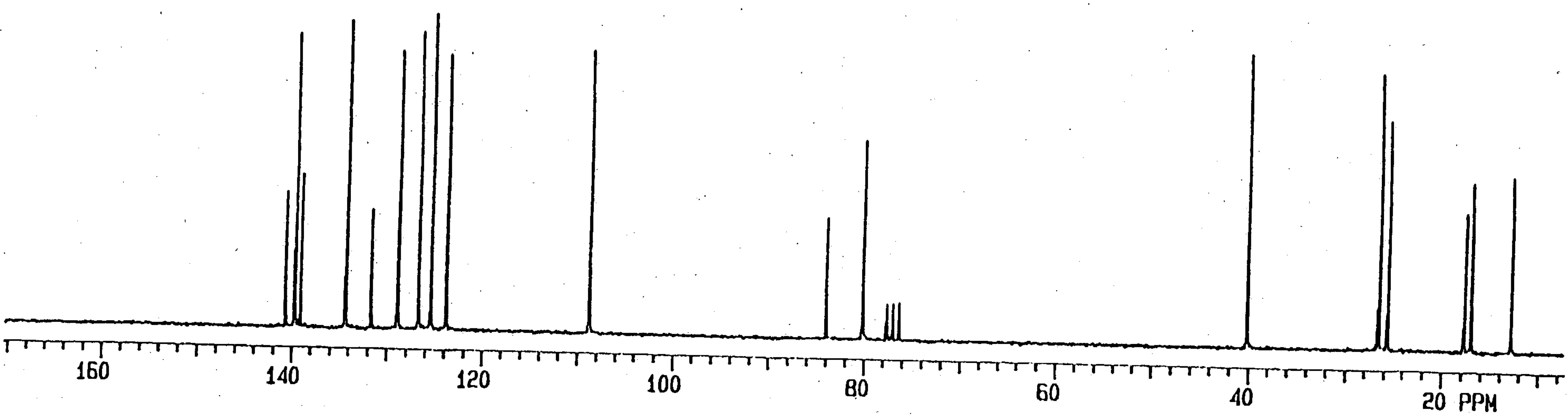


Fanxing Zeng and Ei-ichi Negishi*

GEMINI-200 1H SENSITIVITY
SPECTRAL LINES FOR TH= 7.90
RFL= 3507.6 RFP= 3672.3

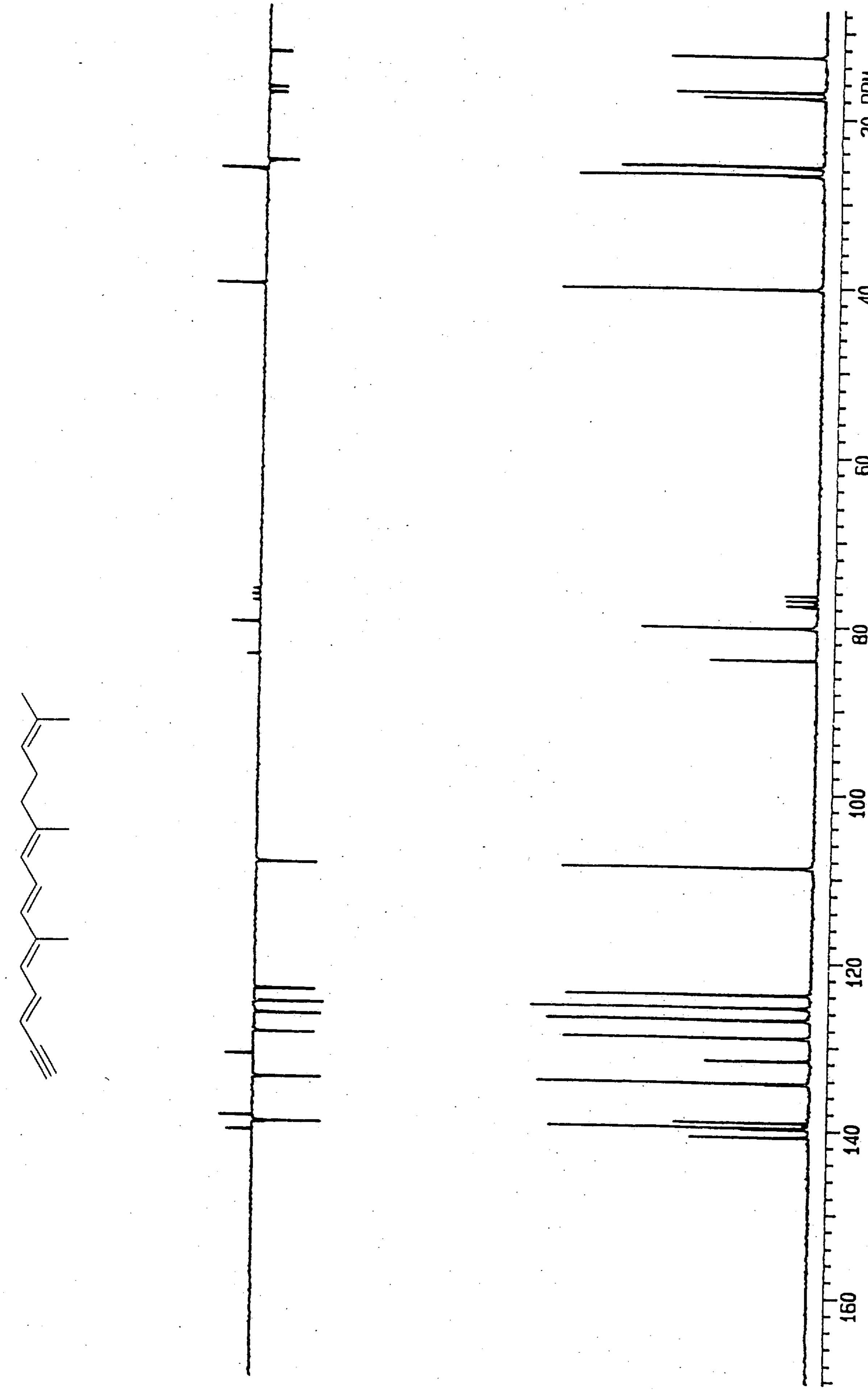
INDEX	FREQ	PPM	INTENSITY
01	7076.0	140.745	39.465
02	7029.3	139.777	77.893
03	6997.1	139.137	41.412
04	6756.1	134.364	62.410
05	6621.9	131.675	32.190
06	6485.0	128.954	80.445
07	6375.0	126.766	79.360
08	6306.7	125.409	83.496
09	6226.2	123.807	73.501
10	5469.3	106.757	77.626
11	4224.1	83.995	33.431
12	4032.4	80.184	54.269
13	3904.6	77.642	9.405
14	3872.6	77.006	9.969
15	3840.7	76.372	9.849
16	2019.7	40.162	79.294
17	1335.8	26.563	75.870
18	1289.4	25.639	64.226
19	887.2	17.641	39.241
20	851.2	16.926	45.994
21	644.4	12.813	47.542





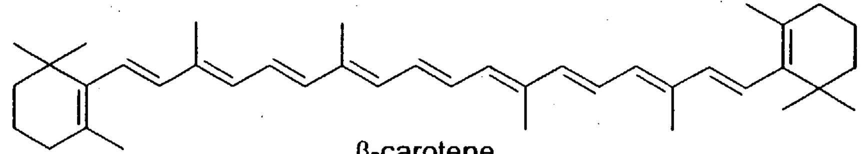
12

Fanxing Zeng and Ei-ichi Negishi*

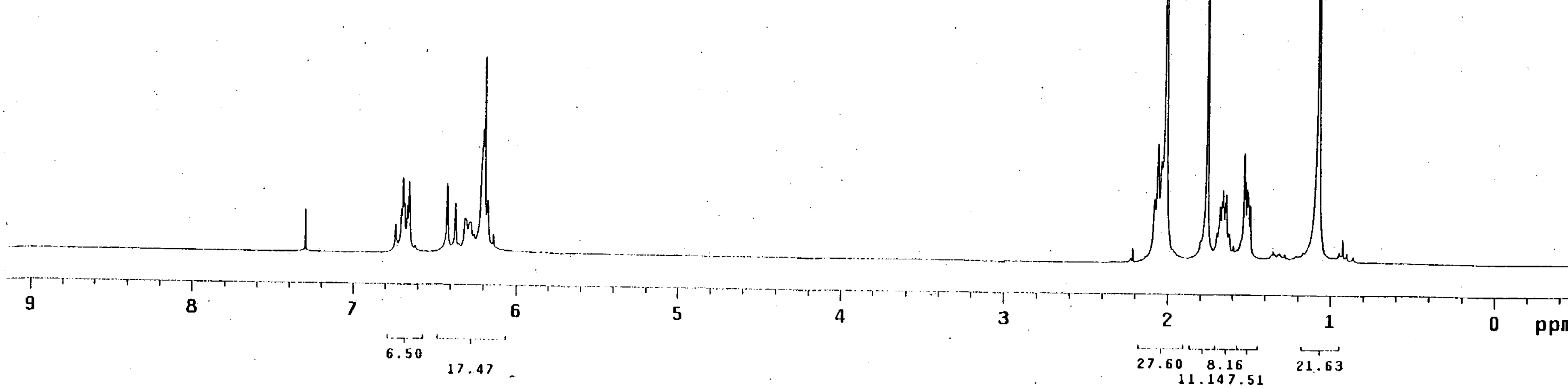


Fanxing Zeng and Ei-ichi Negishi*

INDEX	FREQUENCY	PPM	HEIGHT
1	2009.528	6.699	7.1
2	2006.781	6.690	11.9
3	2004.034	6.681	7.8
4	1998.846	6.664	7.6
5	1995.947	6.654	11.4
6	1925.755	6.420	11.0
7	1910.800	6.370	8.0
8	1860.140	6.201	19.8
9	1857.393	6.192	31.3
10	1852.357	6.175	8.6
11	625.361	2.085	10.1
12	619.562	2.065	18.9
13	613.001	2.044	16.1
14	604.761	2.016	120.0
15	528.770	1.763	62.6
16	504.355	1.681	9.1
17	500.998	1.670	9.8
18	498.709	1.663	11.7
19	494.894	1.650	9.7
20	492.605	1.642	11.0
21	459.035	1.530	17.6
22	456.746	1.523	13.1
23	453.236	1.511	11.8
24	450.795	1.503	10.7
25	447.590	1.492	9.4
26	322.465	1.075	200.0

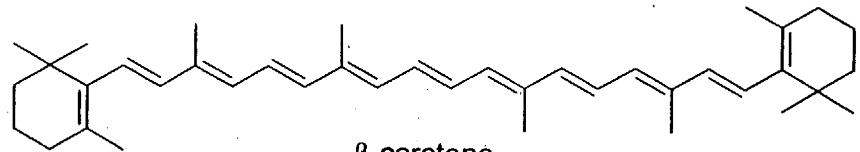


β-carotene

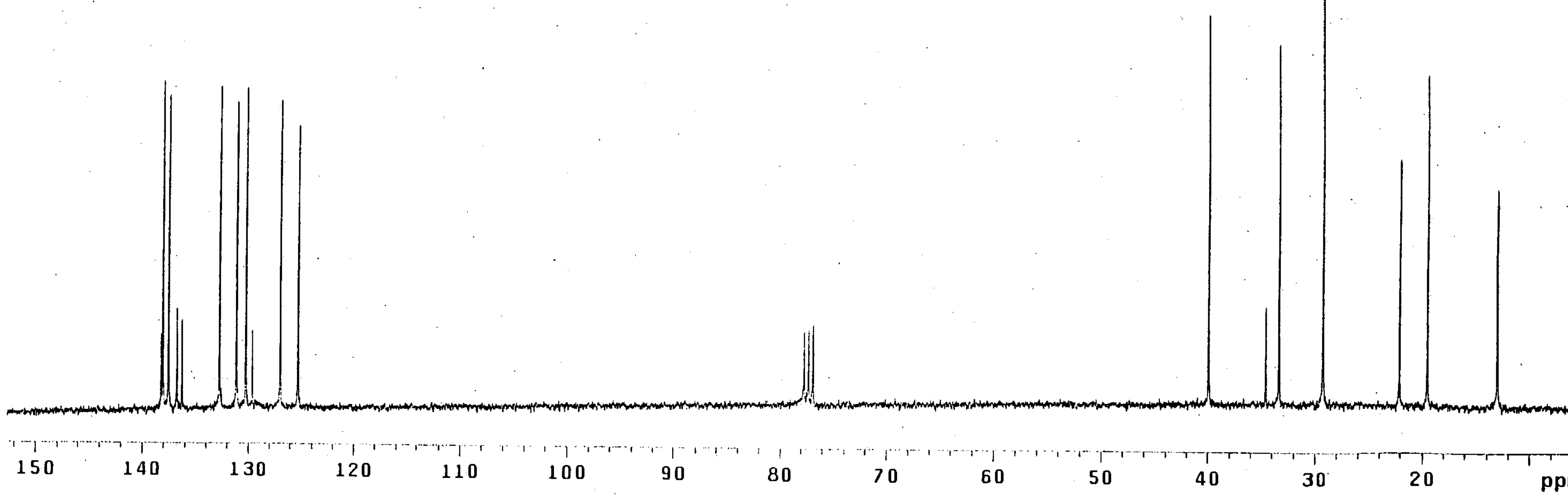


Fanxing Zeng and Ei-ichi Negishi*

INDEX	FREQUENCY	PPM	HEIGHT
1	10423.234	138.193	12.4
2	10411.651	138.040	52.5
3	10371.363	137.506	50.3
4	10313.448	136.738	16.4
5	10279.203	136.284	14.6
6	10008.263	132.692	51.8
7	9889.412	131.116	49.4
8	9824.951	130.261	51.7
9	9778.115	129.640	13.1
10	9573.148	126.923	49.7
11	9451.275	125.307	45.6
12	5860.062	77.694	13.7
13	5827.832	77.267	13.9
14	5796.105	76.846	14.7
15	3011.668	39.929	64.5
16	2605.762	34.548	18.0
17	2518.135	33.386	59.8
18	2205.899	29.246	127.4
19	1661.501	22.029	41.7
20	1473.656	19.538	55.2
21	986.669	13.081	37.1
22	982.137	13.021	35.6

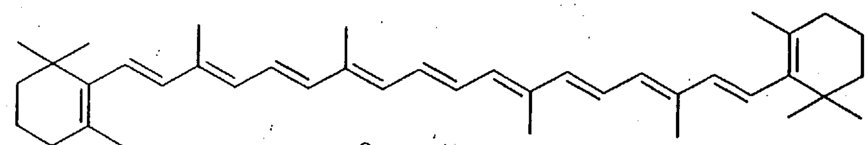


β-carotene

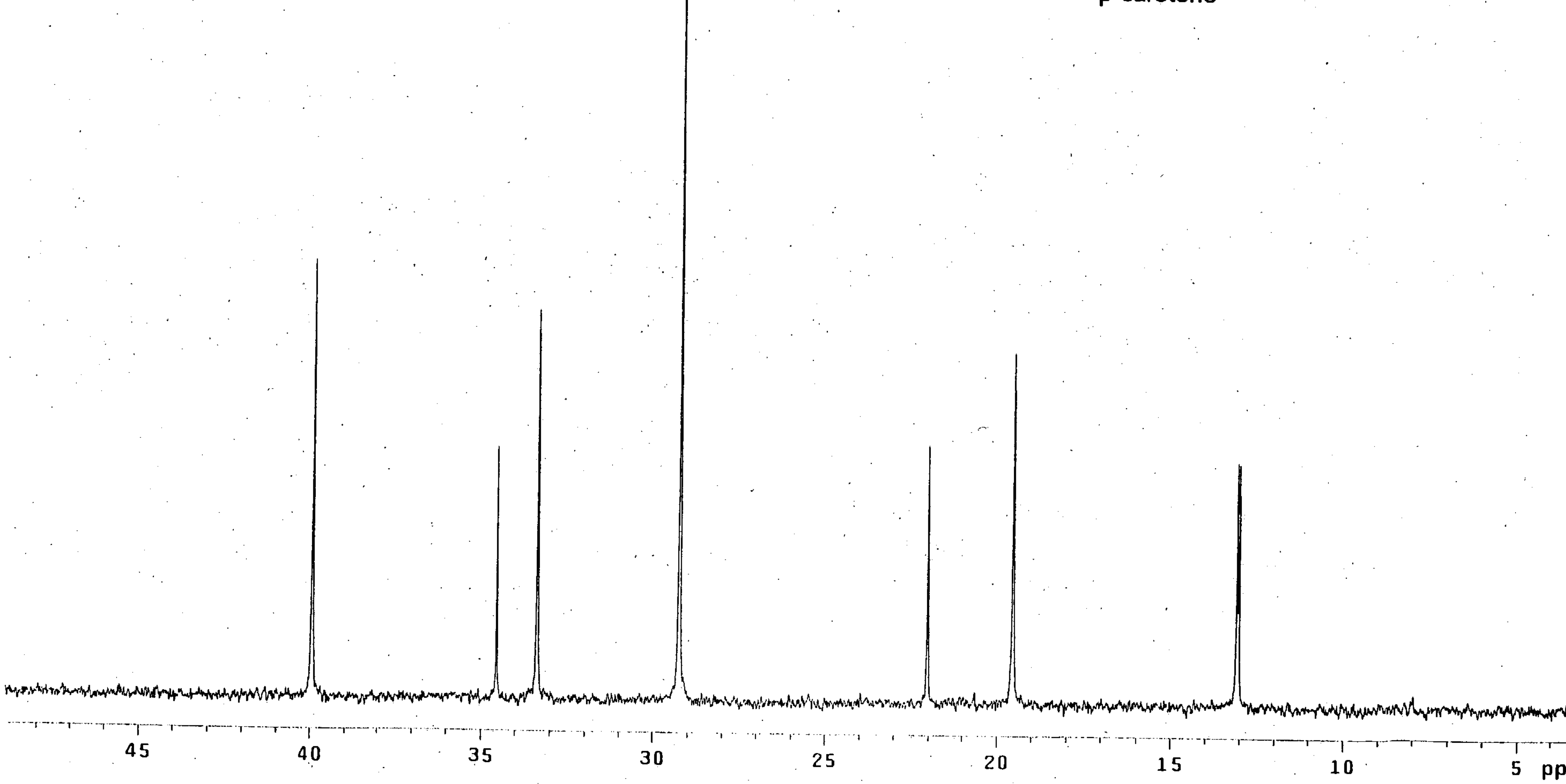


Fanxing Zeng and Ei-ichi Negishi*

INDEX	FREQUENCY	PPM	HEIGHT
1	3012.172	39.936	69.4
2	2605.762	34.548	40.2
3	2518.135	33.386	61.9
4	2205.899	29.246	133.5
5	1661.501	22.029	41.2
6	1474.160	19.545	55.8
7	986.669	13.081	38.9
8	982.641	13.028	38.7



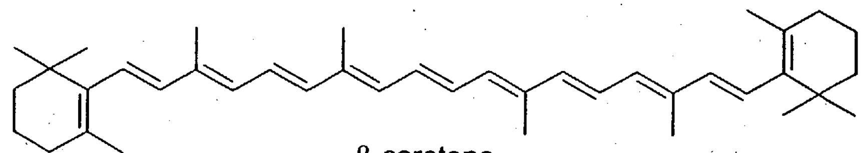
β-carotene



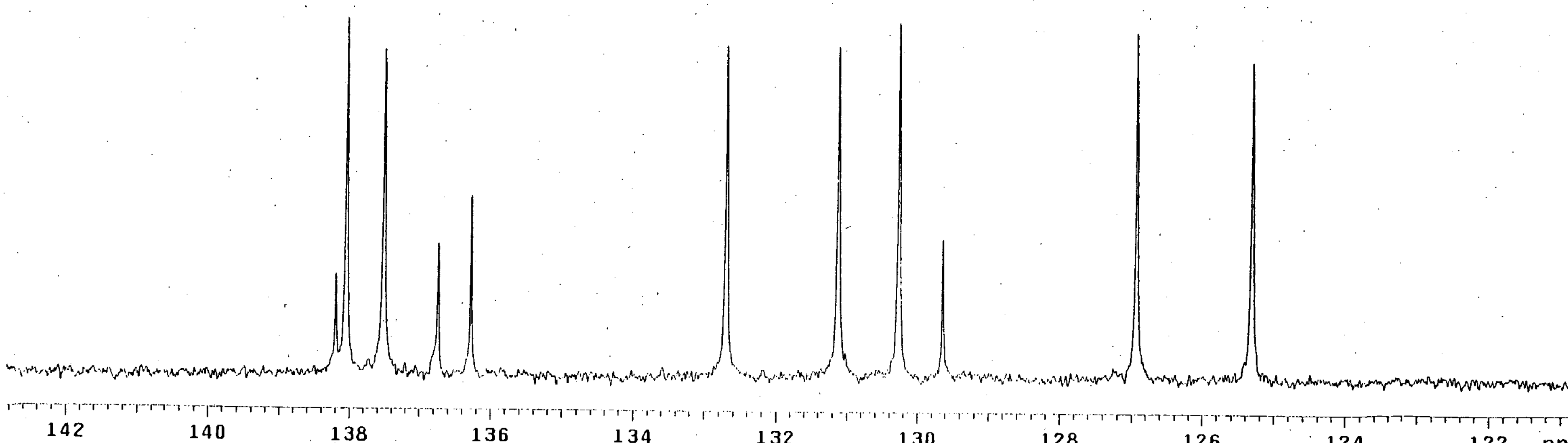
16

Fanxing Zeng and Ei-ichi Negishi*

INDEX	FREQUENCY	PPM	HEIGHT
1	10423.738	138.200	16.5
2	10412.155	138.047	57.2
3	10371.867	137.512	52.3
4	10313.448	136.738	21.4
5	10278.699	136.277	29.0
6	10008.767	132.698	53.2
7	9889.412	131.116	53.1
8	9824.951	130.261	57.0
9	9777.612	129.634	22.6
10	9573.148	126.923	55.6
11	9451.275	125.307	51.1

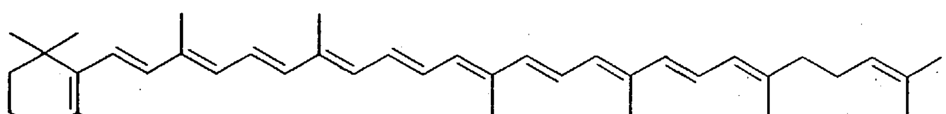


β-carotene

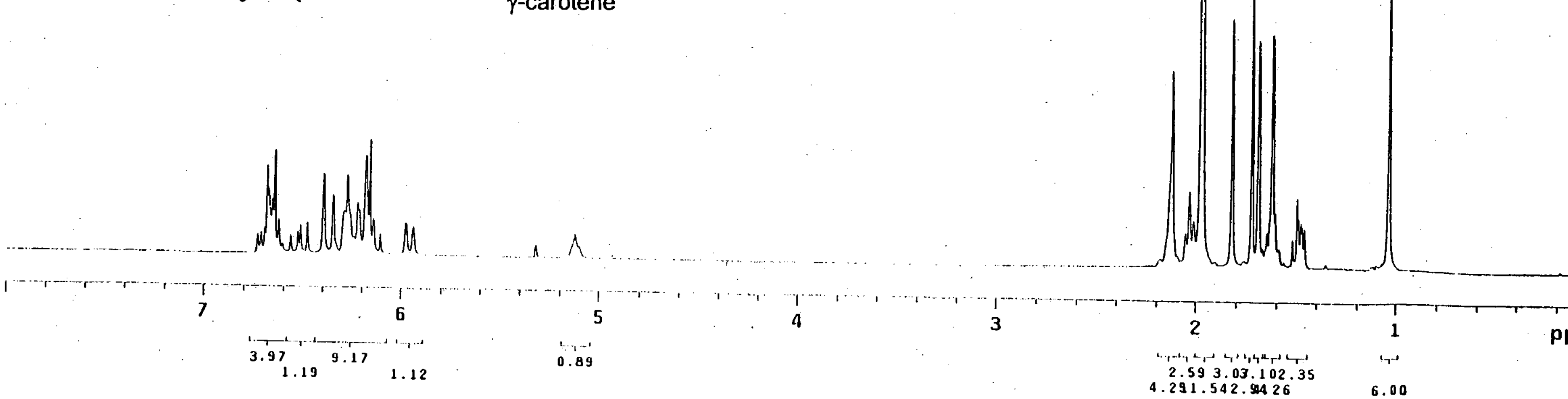


Fanxing Zeng and Ei-ichi Negishi*

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2018.929	6.731	13.2	31	1533.532	5.112	10.3
2	2013.436	6.712	14.4	32	1531.396	5.105	8.3
3	2007.484	6.692	17.8	33	1529.717	5.100	8.0
4	2003.822	6.680	58.7	34	637.356	2.125	132.5
5	2001.381	6.672	43.1	35	629.116	2.097	8.4
6	1998.787	6.664	29.7	36	615.993	2.054	23.5
7	1995.887	6.654	36.6	37	610.042	2.034	51.6
8	1992.988	6.644	69.5	38	603.786	2.013	31.9
9	1987.037	6.624	22.9	39	593.714	1.979	461.5
10	1968.878	6.564	13.0	40	546.869	1.823	166.5
11	1958.044	6.528	15.4	41	516.960	1.723	191.3
12	1953.924	6.514	19.3	42	507.194	1.691	153.1
13	1942.938	6.477	21.3	43	500.480	1.668	14.3
14	1918.676	6.396	53.9	44	496.971	1.657	13.1
15	1903.721	6.347	39.4	45	494.224	1.648	24.7
16	1886.021	6.288	28.9	46	487.815	1.626	156.7
17	1881.596	6.273	53.1	47	482.474	1.608	38.1
18	1871.524	6.239	12.0	48	478.507	1.595	13.9
19	1866.336	6.222	34.5	49	476.371	1.588	14.3
20	1854.587	6.183	67.0	50	456.839	1.523	20.3
21	1848.788	6.163	77.3	51	449.820	1.500	47.8
22	1843.142	6.145	23.7	52	447.531	1.492	34.0
23	1832.613	6.110	14.3	53	443.716	1.479	31.9
24	1792.787	5.977	21.9	54	441.580	1.472	28.7
25	1781.800	5.940	19.5	55	438.223	1.461	27.2
26	1595.790	5.320	8.6	56	311.723	1.039	596.1
27	1594.722	5.316	8.4				
28	1537.805	5.127	14.0				
29	1536.431	5.122	16.3				
30	1535.058	5.118	14.3				



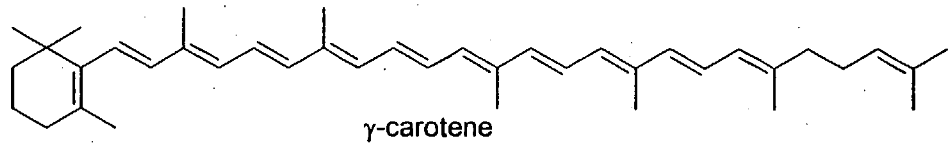
γ-carotene



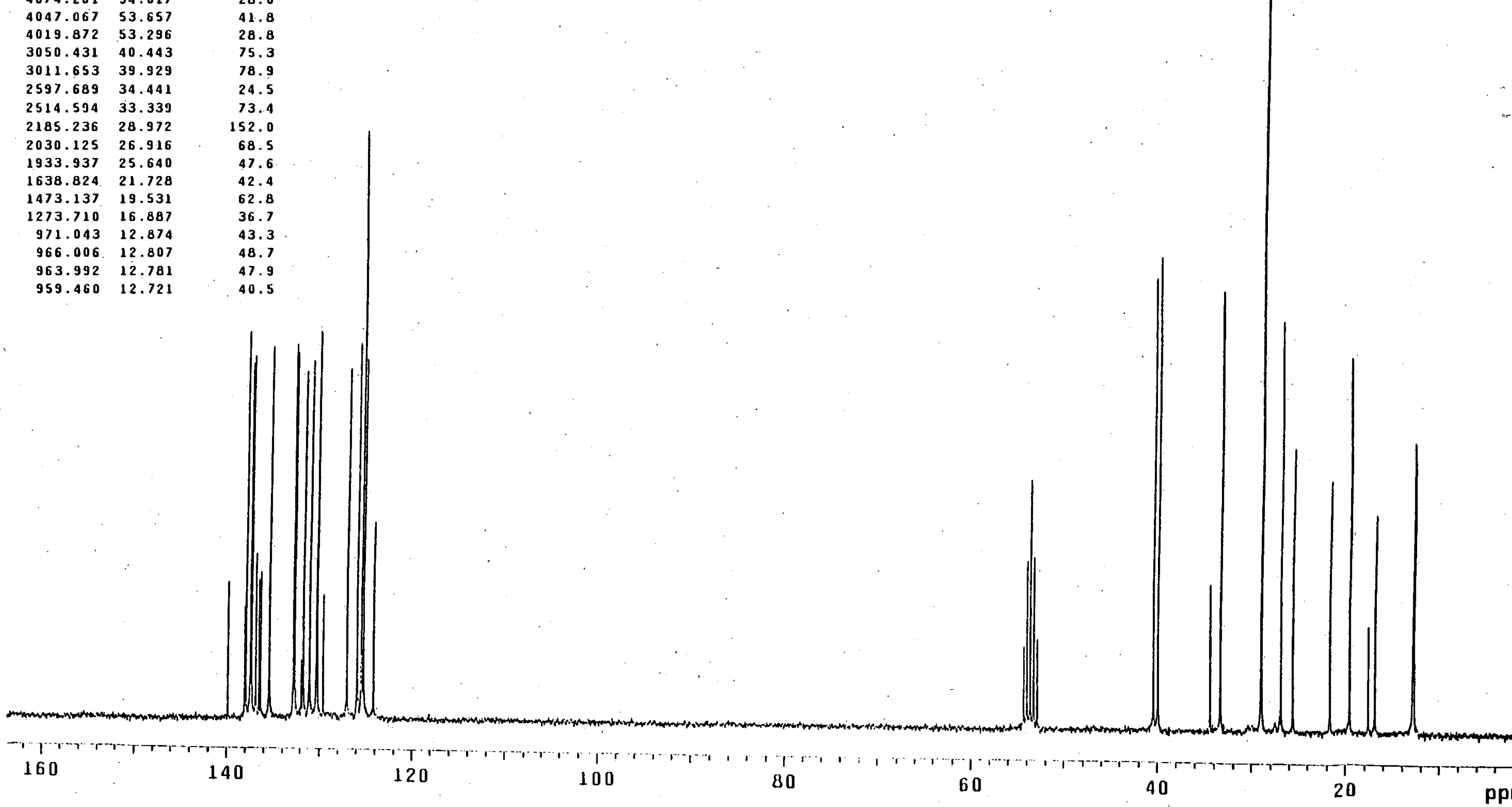
Highly Selective and Efficient Route to Carotenoids.

Fanxing Zeng and Ei-ichi Negishi*

1	[illegible]	[illegible]	[illegible]
2	10407.607	137.986	64.1
3	10372.355	137.519	59.0
4	10360.268	137.358	60.1
5	10326.527	136.911	26.9
6	10324.009	136.878	27.3
7	10298.829	136.544	22.8
8	10285.735	136.370	24.2
9	10216.741	135.455	61.7
10	10017.817	132.818	62.2
11	10004.219	132.638	60.9
12	9932.707	131.690	57.9
13	9884.361	131.049	59.6
14	9831.986	130.354	64.4
15	9826.950	130.288	63.8
16	9778.100	129.640	20.4
17	9581.190	127.029	58.4
18	9499.606	125.948	62.6
19	9462.843	125.460	97.8
20	9445.720	125.233	60.0
21	9366.151	124.178	32.9
22	4074.261	54.017	28.0
23	4047.067	53.657	41.8
24	4019.872	53.296	28.8
25	3050.431	40.443	75.3
26	3011.653	39.929	78.9
27	2597.689	34.441	24.5
28	2514.594	33.339	73.4
29	2185.236	28.972	152.0
30	2030.125	26.916	68.5
31	1933.937	25.640	47.6
32	1638.824	21.728	42.4
33	1473.137	19.531	62.8
34	1273.710	16.887	36.7
35	971.043	12.874	43.3
36	966.006	12.807	48.7
37	963.992	12.781	47.9
38	959.460	12.721	40.5



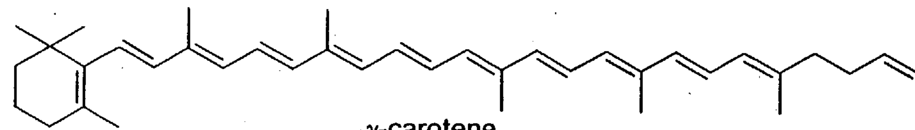
γ-carotene



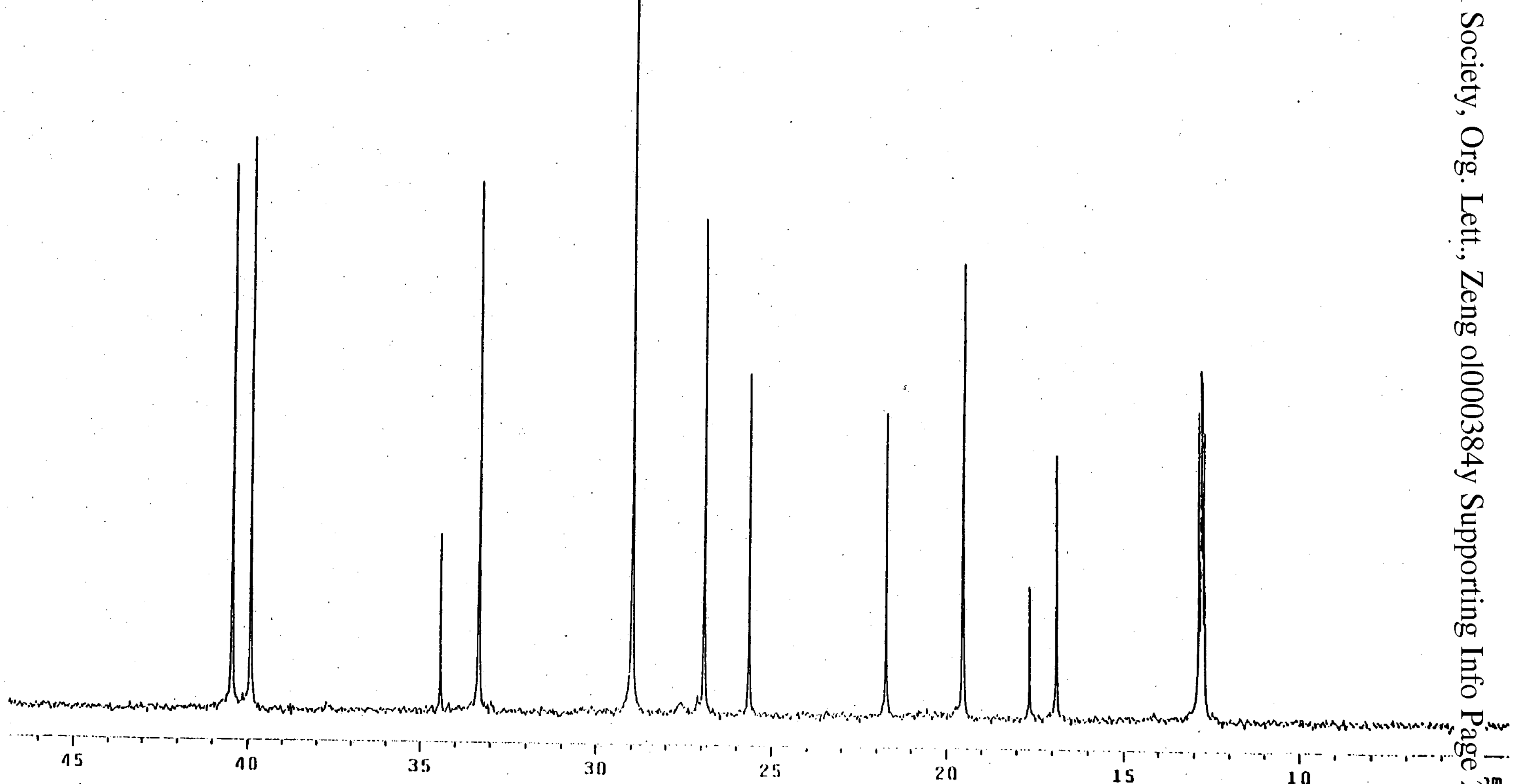
19

Fanxing Zeng and Ei-ichi Negishi*

INDEX	FREQUENCY	PPM	HEIGHT
1	3050.431	40.443	93.8
2	3011.653	39.929	98.2
3	2597.689	34.441	30.5
4	2514.594	33.339	91.4
5	2185.236	28.972	189.3
6	2030.125	26.916	85.3
7	1933.937	25.640	59.2
8	1638.824	21.728	52.8
9	1473.137	19.531	78.2
10	1330.113	17.635	22.1
11	1273.710	16.887	45.7
12	971.043	12.874	53.9
13	966.006	12.807	60.7
14	963.992	12.781	59.6
15	959.460	12.721	50.4



γ-carotene



20

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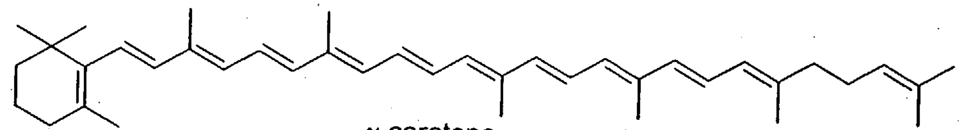
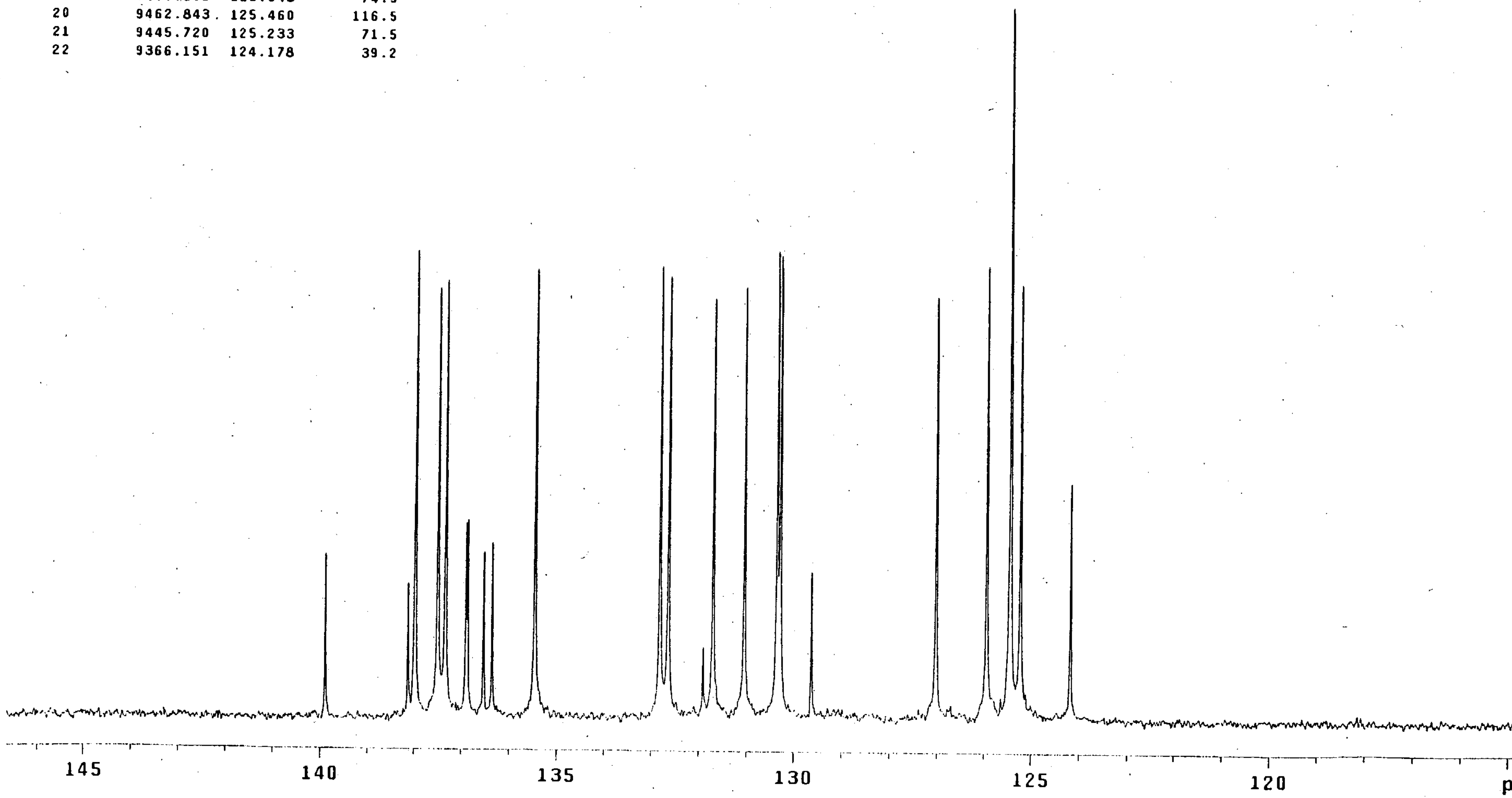
INDEX	FREQUENCY	PPM	HEIGHT
1	10551.639	139.896	26.6
2	10418.687	138.133	21.9
3	10407.607	137.986	76.3
4	10372.355	137.519	70.3
5	10360.268	137.358	71.6
6	10326.527	136.911	32.0
7	10324.009	136.878	32.4
8	10298.829	136.544	27.2
9	10285.735	136.370	28.8
10	10216.741	135.455	73.5
11	10017.817	132.818	74.1
12	10004.219	132.638	72.4
13	9932.707	131.690	68.9
14	9884.361	131.049	71.0
15	9831.986	130.354	76.6
16	9826.950	130.288	75.9
17	9778.100	129.640	24.3
18	9581.190	127.029	69.5
19	9499.606	125.948	74.5
20	9462.843	125.460	116.5
21	9445.720	125.233	71.5
22	9366.151	124.178	39.2



γ-carotene



21

 22

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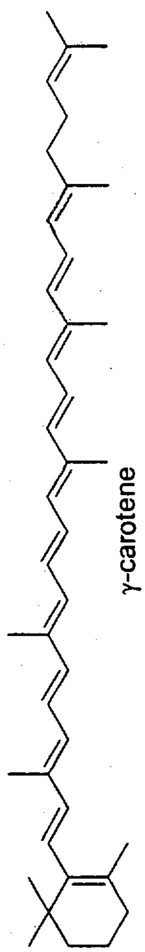
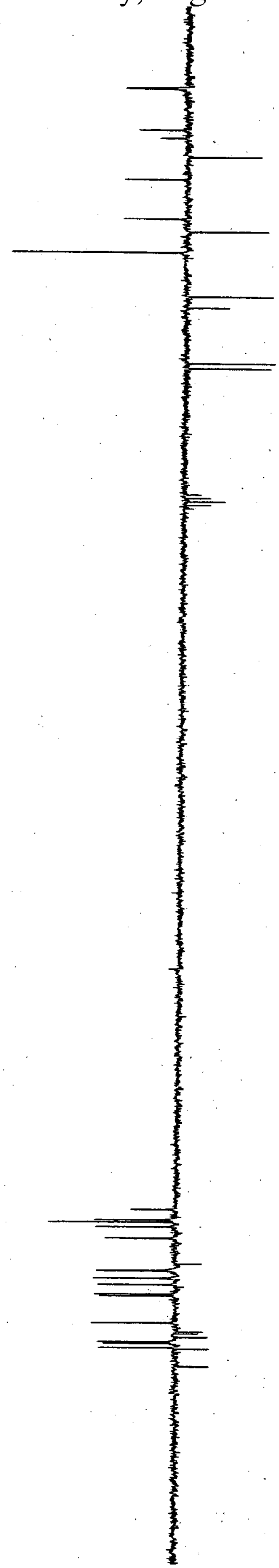
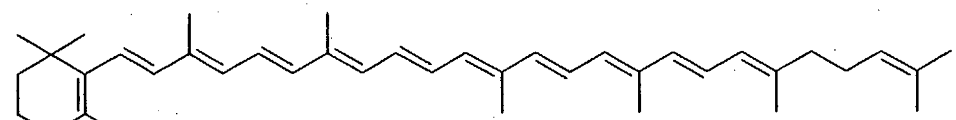


γ-carotene

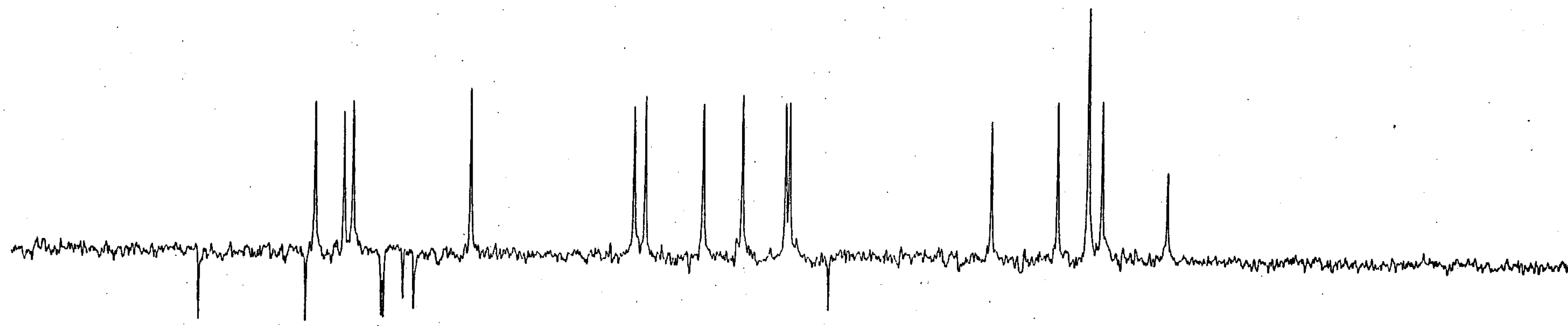


A Highly Selective and Efficient Route to Carotenoid

Fanxing Zeng and Ei-ichi Negishi*



γ-carotene



23

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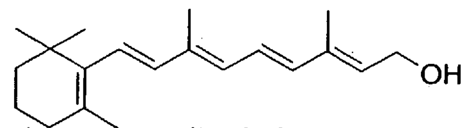
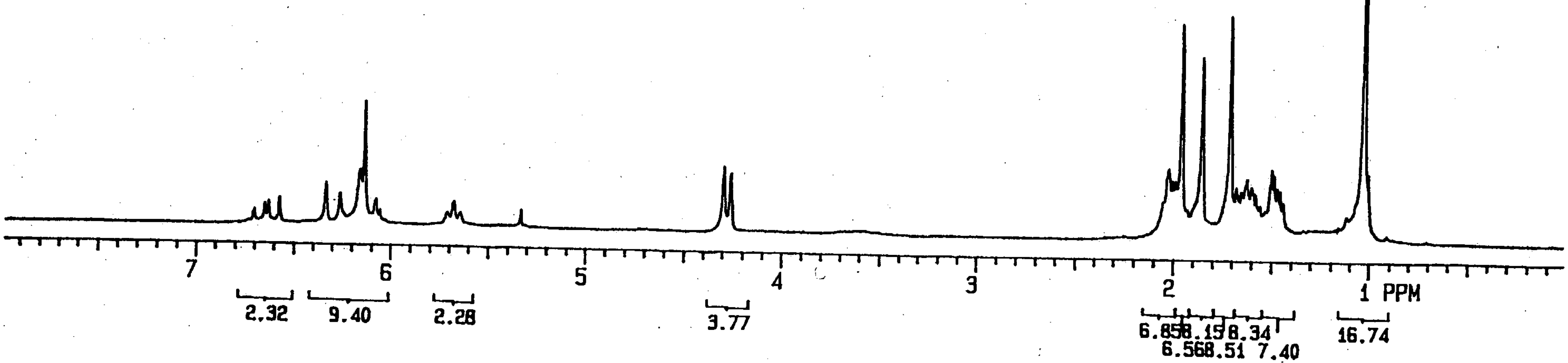
GEMINI-200 1H SENSITIVITY
SPECTRAL LINES FOR TH= 34.62
RFL= 434.3 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	1232.33	6.162	39.945
02	1227.49	6.138	89.849
03	858.71	4.294	46.883
04	851.75	4.259	42.172
05	404.88	2.025	50.456
06	401.46	2.008	42.780
07	398.65	1.993	41.716
08	392.42	1.962	154.391
09	371.83	1.859	132.391
10	342.28	1.712	161.519
11	341.51	1.708	144.808
12	336.09	1.681	37.836
13	330.52	1.653	35.051
14	325.11	1.626	44.416
15	320.71	1.604	38.522
16	318.88	1.595	36.668
17	299.67	1.499	51.735
18	297.55	1.488	46.505
19	294.34	1.472	37.789
20	291.69	1.459	35.856
21	205.25	1.026	556.090
22	201.14	1.006	49.065



vitamin A

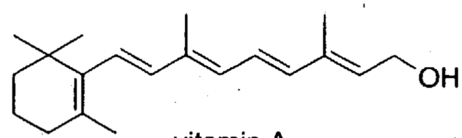


A Highly Selective and Efficient Route to Carotenoids....

Fanxing Zeng and Ei-ichi Negishi*

SPECTRUM 00

INDEX	FREQ	PPM	INTENSITY
01	6947.2	138.145	14.362
02	6939.6	137.994	47.734
03	6885.6	136.920	16.987
04	6873.8	136.685	45.935
05	6862.6	136.461	18.884
06	6584.5	130.933	46.183
07	6559.4	130.433	45.933
08	6517.6	129.602	20.118
09	6393.0	127.125	45.412
10	6307.5	125.423	43.414
11	3000.1	59.657	43.664
12	2759.9	54.881	26.259
13	2732.7	54.340	52.910
14	2705.6	53.800	81.344
15	2678.3	53.257	52.346
16	2651.0	52.715	27.032
17	2010.1	39.971	51.561
18	1736.0	34.521	23.968
19	1678.7	33.380	48.574
20	1461.1	29.054	100.507
21	1096.8	21.811	44.428
22	987.3	19.632	50.670
23	643.4	12.795	35.389
24	639.5	12.716	30.396



vitamin A