REVISED 9/8

Supporting Information

General Remarks: Reactions were performed under a nitrogen atmosphere unless otherwise specified. Tetrahydrofuran was distilled on sodium benzophenone ketyl, dichloromethane, diisopropylamine, triethylamine, NMP from calcium hydride, methanol from magnesium. Anhydrous DMF was purchased from Aldrich Chemicals co. in SureSeal bottles and used as such. All other reagents were purchased from Aldrich Chemicals co. and used with no further purification unless otherwise specified. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ and are referenced in ppm with respect to the residual signals of the solvent, using the standard abbreviations. Infrared spectra were recorded as films and are given in cm^{-1}, MS and HRMS spectra were recorded using electronic ionisation (EI).

Trans dienophile series

(*E*)-Methyl 2-methoxycarbonyl-5-methyl-8-(tetrahydropyran-2-yloxy)-oct-5-enoate (**2**)

A solution of silyl ether **1** (2.24 g, 6.82 mmol) in 40 ml anhydrous THF at 0°C was treated with TBAF (8.2 ml of a 1 M solution in THF, 8.2 mmol). After 4 h at r.t., the mixture was evaporated on silica gel and the product purified on a short silica gel pad (ethyl acetate:hexanes 20:80 to 50:50), to yield 1.42 g of the desired alcohol as a clear oil (97%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.26 (t, 1H, 5.6 Hz); 4.68 (dd, 1H, 2.9 Hz, 4.2 Hz); 3.90-3.76 (m, 1H); 3.75-3.58 (m, 3H); 3.54-3.38 (m, 2H); 2.37 (q, 2H, 7.2 Hz); 2.25 (t, 2H, 5.6 Hz); 1.85-1.48 (m, 10H).

The resulting alcohol (1.42 g, 6.62 mmol) was solubilized into methylene chloride, and to the solution was added triethylamine (2.1 ml, 15.4 mmol) and DMAP (98 mg, 0.8 mmol). The mixture was cooled down to 0°C, and methanesulfonyl chloride (0.900 ml, 11.6 mmol) was added. The mixture was stirred at r.t. overnight, poured into a saturated solution of ammonium chloride and extracted with methylene chloride three times. The combined organic layers were dried on magnesium sulphate and the solvent removed *in vacuo*. The product was purified on a silica gel pad (ethyl acetate:hexanes 20:80 to 50:50), to give 1.84 of the desired mesylate as a colorless oil (93%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.27 (t, 1H, 5.6 Hz); 4.55 (m, 1H); 4.28 (t, 2H, 6.9 Hz); 3.87-3.79 (m, 1H); 3.76-3.64 (m, 1H); 3.55-3.47 (m, 1H); 3.46-3.33 (m, 1H); 2.96 (s, 3H); 2.41 (t, 2H, 6.9 Hz); 2.33 (q, 2H, 5.6 Hz); 1.87-1.48 (m, 9H).

To a suspension of sodium hydride (480 mg of a 60% dispersion, washed with pentane, 12.0 mmol) in 30 ml dry THF and 30 ml dry DMF at 0°C, was added dimethyl malonate (1.44 ml, 12.6 mmol). After stirring for 40 min at r.t., it was cooled down to 0°C and a solution of the previously synthesized mesylate (1.84 g, 6.3 mmol) in 5 ml dry THF (+ 3 ml rinse) was added *via canula*, followed by potassium iodide (116 mg, 0.7 mmol). The mixture was stirred overnight at 80°C, cooled down to r.t., poured into a saturated ammonium chloride solution and extracted three times with a 1:1 mixture of ether and hexane. The combined organic layers were washed with brine and dried over magnesium sulphate, and the solvent removed *in vacuo*. The product was purified on a silica gel pad (ethyl acetate:hexanes 0:100 to 30:70) to give 1.86 g of the desired malonate **2** as a clear oil (90%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.15 (t, 1H, 7.0 Hz); 4.58 (dd, 1H, 2.8 Hz, 4.1 Hz); 3.86 (m, 1H); 3.76-3.65 (m, 1H); 3.72 (s, 6H); 3.53-3.45 (m ,1H); 3.40-3.31 (m, 2H); 2.29 (q, 2H, 7.3 Hz); 2.05-1.99 (m, 4H); 1.85-1.48 (m, 9H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 169.89; 135.30; 122.01; 98.75; 67.02; 62.29; 52.44; 50.84; 37.08; 30.69; 28.62; 26.93; 25.45; 19.59.
IR (film) ν 2948; 2869; 1742; 1440.
HRMS (EI) $C_{17}H_{28}O_6$ theoretical: 328.1886; experimental: 328.1891 ±0.0010.

Methyl (*E*, *E*)-12-iodo-6-methyl-2,9,9-tris(methoxycarbonyl)-dodeca-5,11-dienoate (**3**)

To a suspension of sodium hydride (185 mg of a 60% dispersion, washed with pentane, 4.64 mmol) in 10 ml dry THF and 10 ml dry DMF cooled down to 0°C, was added malonate **2** (800 mg, 2.44 mmol) in 3 ml dry THF (+ 2 ml rinse), and the mixture was stirred at r.t. for 40 min. It was cooled down to 0°C, then stannane **4a** (1.78 g, 4.88 mmol) was added dropwise, followed by tetrabutylammonium iodide (111 mg, 0.3 mmol). The mixture was stirred at r.t. overnight, then poured into a saturated ammonium chloride solution, and extracted three times with a 1:1 mixture of ether and hexanes. The combined organic layers were washed with brine, dried on magnesium sulphate and the solvent was removed *in vacuo*. The product was purified by flash chromatography (ethyl acetate:hexanes 0:100 to 10:90) to give 1.1 g of the desired stannane as a colorless oil (69%).
^{1}H NMR (300 MHz, CDCl$_3$) δ 6.03 (d, 1H, 18.1 Hz); 5.72 (dt, 1H, 18.1 Hz, 6.5 Hz); 5.12 (t, 1H, 6.0 Hz); 4.58 (t, 1H, 5.5 Hz); 3.89-3.81 (m, 1H); 3.71-3.60 (m, 1H); 3.69 (s, 6H); 3.51-3.45 (m, 1H); 3.40-3.31 (m, 1H); 2.71 (dd, 1H, 0.9 Hz, 6.5 Hz); 2.31 (q, 2H, 7.1 Hz); 1.98-1.77 (m, 4H); 1.70-1.19 (m, 21 H); 0.97-0.79 (m, 15H).

To the stannane (1.0 g, 1.52 mmol) in solution in dry methylene chloride (15 ml) was added iodine until a pink color persisted (about 390 mg, 1.5 mmol). The solution was washed with a 10% solution of sodium thiosulfate, the aqueous layer extracted twice with methylene chloride, the combined organic layers were dried on magnesium sulphate and the solvent was removed *in vacuo*. The product was purified by flash chromatography (ethyl acetate:hexanes 0:100 to 10:90) to give 790 mg of the vinylic iodide as a colorless oil (97%).
^{1}H NMR (300 MHz, CDCl$_3$) δ 6.37 (dt, 1H, 7.2 Hz, 15.2 Hz); 6.17 (d, 1H, 15.2 Hz); 5.13 (t, 1H, 5.9 Hz); 4.61-4.56 (m, 1H); 3.88-3.77 (m, 1H); 3.75-3.65 (m, 1H); 3.69 (s, 6H); 3.55-3.39 (m, 1H); 3.37-3.30 (m, 1H); 2.65 (dd, 2H, 0.9 Hz, 7.5 Hz); 2.27 (q, 2H, 6.8 Hz); 1.97-1.43 (m, 13H).

To a solution of vinylic iodide (730 mg, 1.4 mmol) in dry methanol (15 ml) was added *p*-toluenesulfonic acid (48 mg, 0.28 mmol). After stirring for 2 h at r.t., a saturated solution of sodium bicarbonate was added, and the aqueous layer was extracted three times with ethyl acetate, the organic layers were dried on magnesium sulphate and the solvent was removed *in vacuo*. The product was purified by flash chromatography (ethyl acetate:hexanes 15:85 to 40:60) to give the desired alcohol (460 mg) as a clear oil (80%).
^{1}H NMR (300 MHz, CDCl$_3$) δ 6.36 (dt, 1H, 7.5 Hz, 15.0 Hz); 6.17 (d, 1H, 15.0 Hz); 5.14 (t, 1H, 5.8 Hz); 3.70 (s, 6H); 3.59 (q, 2H, 6.8 Hz); 2.60 (dd, 2H, 0.9 Hz, 7.6 Hz); 2.24 (q, 2H, 7.5 Hz); 2.05-1.81 (m, 4H); 1.62 (s, 3H).

To a solution of the alcohol (460 mg, 1.12 mmol) in dry methylene chloride (10 ml) at 0°C, was added triethylamine (0.312 ml, 2.24 mmol) and DMAP (14 mg, 0.11 mmol) followed by methanesulfonyl chloride (0.130 ml, 1.68 mmol). The mixture was stirred overnight at r.t., quenched with a saturated solution of ammonium chloride, and the aqueous layer was extracted three times with methylene chloride. The combined organic layers were dried with magnesium sulphate and the solvent was removed *in vacuo*. The product was

purified on a silica gel pad (ethyl acetate:hexanes 20:80) to give 470 mg of the mesylate as a colorless oil (86%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.37 (dt, 1H, 7.6 Hz, 14.7 Hz); 6.15 (d, 1H, 14.7 Hz); 5.09 (t, 1H, 5.9 Hz); 4.18 (t, 2H, 7.5 Hz); 3.72 (s, 6H); 2.99 (s, 3H); 2.61 (dd, 2H, 1.0 Hz, 7.6 Hz); 2.45 (q, 2H, 7.5 Hz); 2.01-1.79 (m, 4H); 1.62 (s, 3H).

To a suspension of sodium hydride (77 mg of a 60% dispersion in oil, washed with pentane, 1.92 mmol) in a mixture of dry THF (3 ml) and dry DMF (3 ml) was added dimethyl malonate at 0°C. The mixture was stirred at r.t. for 40 min, cooled down to 0°C and a solution of the previously synthesized mesylate (470 mg, 0.96 mmol) in 1 ml THF (+ 1 ml rinse) was addwd *via canula*, followed by tetrabutylammonium iodide (37 mg, 0.1 mmol). The mixture was stirred at 80°C overnight, cooled down to r.t., and poured in a saturated solution of ammonium chloride. The aqueous layer was extracted three times with a 1:1 mixture of ether and hexanes, the combined organic layers were washed with brine and dried on magnesium sulphate, then the solvent was removed *in vacuo*. The product was purified by flash chromatography (ethyl acetate:hexanes 20:80) to give the desired malonate **3** as a colorless oil (480 mg, 94%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.39 (dt, 1H, 7.7 Hz, 14.3 Hz); 6.15 (d, 1H, 14.3 Hz); 5.08 (t, 1H, 5.9 Hz); 3.72 (s, 6H); 3.71 (s, 6H); 3.35 (t, 1H, 7.2 Hz); 2.61 (dd, 2H, 1.0 Hz, 7.7 Hz); 2.05-1.78 (m, 8H); 1.56 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.08; 169.83; 140.33; 135.64; 123.41; 121.12; 78.54; 57.00; 52.56; 50.96; 39.31; 33.94; 31.44; 28.68; 25.55; 15.95.
IR (film) ν 2954; 1733; 1606; 1436.
HRMS (EI) $C_{19}H_{26}IO_7$ (M-OCH_3) theoretical: 493.0723; experimental: 493.0727 ±0.0015.

Representative procedure for the synthesis of trienes **5a**, **5b**:

(*E*,*E*,*E*)-14-iodo-8-methyl-4,4,11,11-tetrakis(methoxycarbonyl)-1-tributylstannyltetradeca-1,7,13-triene (**5a**).

To a solution of malonate **3** (100 mg, 0.19 mmol) in a mixture of dry THF (1 ml) and dry DMF (1 ml) at 0°C, was added sodium hydride (15 mg of a 60% dispersion in oil, 0.38 mmol). The mixture was stirred at r.t. for 40 min, cooled down to 0°C then stannane **4a** (139 mg, 0.38 mmol) was added dropwise, followed by tetrabutylammonium iodide (8 mg, 0.02 mmol). The mixture was stirred at r.t. overnight, poured into a saturated ammonium chloride solution and extracted three times with a 1:1 mixture of ether and hexanes. The combined organic layers were washed with brine, dried on magnesium sulphate and the solvent was removed *in vacuo*. The product was purified by flash chromatography (ethyl acetate:hexanes 5:95) to give the desired triene **5a** (138 mg) as a colorless oil (85%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.37 (dt, 1H, 7.7 Hz, 14.3 Hz); 6.14 (d, 1H, 14.3 Hz); 6.03 (d, 1H, 18.7 Hz); 5.73 (dt, 1H, 6.8 Hz, 18.7 Hz); 5.08 (m, 1H); 3.71 (s, 6H); 3.70 (s, 6H); 2.74 (d, 2H, 6.8 Hz); 2.61 (d, 2H, 7.7 Hz); 2.0-1.80 (m, 9H); 1.70-1.20 (m, 14H); 0.96-0.82 (m, 15H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.67; 171.08; 142.30; 140.34; 134.62; 133.74; 123.97; 120.21; 78.49; 57.46; 57.03; 52.52; 52.24; 41.13; 39.30; 33.84; 32.30; 31.39; 29.03; 27.22; 22.68; 13.68; 9.43.
IR (film) ν 2954; 2926; 1736; 1603; 1436.
HRMS $C_{31}H_{50}IO_8Sn$ (M-C_4H_9) theoretical 797.1572; experimental 797.1563 ±0.0024.

(*1Z,7E,13E*)-14-iodo-8-methyl-4,4,11,11-tetrakis(methoxycarbonyl)-1-tributylstannyltetradeca-1,7,13-triene (**5b**).

Stannane **4b** (139 mg, 0.38 mmol) was used as the electrophile. Triene **5b** was obtained as a colorless oil (104 mg, 64%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.43-6.28 (m, 2H); 6.14 (d, 1H, 14.4 Hz); 5.95 (d, 1H, 12.7 Hz); 5.08 (m, 1H); 3.71 (s, 6H); 3.70 (s, 6H); 2.67-2.60 (m, 4H); 1.97-1.77 (m, 8H); 1.61-1.44 (m, 9H); 1.36-1.24 (m, 6H); 0.95-.086 (m, 15H).
^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 171.68; 171.09; 141.97; 140.34; 134.77; 132.62; 123.89; 120.61; 78.50; 57.19; 57.03; 52.52; 52.29; 39.60; 39.30; 33.82; 33.08; 31.40; 29.13; 27.28; 22.87; 13.67; 10.13.
IR (film) ν 2955; 2927; 1735; 1458; 1437.
HRMS $C_{31}H_{50}IO_8Sn$ ($M-C_4H_9$) theoretical 797.1572; experimental 797.1586 ±0.0024.

Cis dienophile series

(*5Z,11E*)-Methyl 6-methyl-12-tributylstannyl-2,9,9-tris(methoxycarbonyl)deca-5,11-dienoate (**8**).

To a suspension of sodium hydride (840 mg of a 60% dispersion in oil, washed with pentane, 21 mmol) in 50 ml dry THF and 50 ml dry DMF at 0°C was added malonate **6** (3.94 g, 11 mmol) in 10 ml dry THF (+ 5 ml rinse). The mixture was stirred at r.t. for 40 min, then cooled down to 0°C and stannane **4a** (8.0 g, 22 mmol) was added dropwise, followed by tetrabutylammonium iodide (406 mg, 1.1 mmol). The mixture was stirred at r.t. overnight, poured into a saturated ammonium chloride solution, extracted three times with a 1:1 mixture of ether and hexanes. The combined organic layers were washed with brine, dried on magnesium sulphate and the solvent was removed *in vacuo*. The product was purified by flash chromatography (ethyl acetate:hexanes 4:96) to give 5.29 g of stannane **7** as a clear oil (70%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (d, 1H, 18.3 Hz); 5.72 (dt, 1H, 5.8 Hz, 18.3 Hz); 5.12 (t, 1H, 5.9 Hz); 3.69 (s, 6H); 3.64 (t, 1H, 6.0 hz); 2.73 (dd, 0.9 Hz, 5.9 Hz); 2.12 (q,2H, 6.0 Hz); 1.90 (s, 4H); 1.65 (s, 3H); 1.51-1.38 (m, 6H); 1.35-1.23 (m, 6H); 0.95-0.79 (m, 15H).

To a solution of stannane **7** (4.4 g, 6.4 mmol) in dry THF (60 ml) at –10°C was added TBAF (7.7 ml of a 1 M solution, 7.7 mmol). The mixture was stirred at 0°C for 5 h, then evaporated on silica gel and purified by flash chromatography to give 2.9 g of the desired alcohol as a clear oil (79%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.06 (d, 1H, 18.5 Hz); 6.72 (dt, 1H, 5.9 Hz, 18.5 Hz); 5.12 (t, 1H, 5.8 Hz); 3.70 (s, 6H); 3.65 (t, 2H, 5.9 Hz); 2.78 (dd, 1H, 0.9 Hz, 5.9 Hz); 2.21 (q, 2H, 6.5 Hz); 1.97 (s, 4H); 1.71 (s, 3H); 1.65-1.25 (m, 12H); 1.0-0.78 (m, 15H).

The previous alcohol (2.9 g, 5.1 mmol) was dissolved in methylene chloride at 0°C, and triethylamine (1.42 ml, 10.2 mmol) was added, followed by DMAP (62 mg, 0.51 mmol) and methanesulfonyl chloride (0.59 ml, 7.6 mmol). The mixture was stirred at r.t. overnight, poured into a saturated solution of ammonium chloride, and the aqueous layer was extracted three times with methylene chloride. The combined organic layers were washed with brine, dried on magnesium sulphate and the solvent was removed *in vacuo*. The product was purified by flash chromatography to give 2.93 g of the desired mesylate (90%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (d, 1H, 18.3 Hz); 5.80 (dt, 1H, 5.9 Hz, 18.3 Hz); 5.09 (t, 1H, 5.9 Hz); 4.16 (t, 1H, 6.9 hz); 3.70 (s, 6H); 2.98 (s, 3H); 2.72 (dd, 2H, 1.0 Hz, 5.9 Hz);

2.38 (q, 2H, 6.5 Hz); 1.90 (s, 4H); 1.66 (s, 3H); 1.55-1.40 (m, 6H); 1.39-1.22 (m, 6H); 0.98-0.80 (m, 15H).

To a suspension of sodium hydride (365 mg of a 60% dispersion in oil, washed with pentane, 9.12 mmol) in 20 ml dry THF and 20 ml dry DMF at 0°C was added dimethyl malonate (1.0 ml, 9.12 mmol). The mixture was stirred at 0°C for 40 min, then cooled down to 0°C and the previously synthesized mesylate (2.93 g, 4.56 mmol) in 5 ml dry THF (+ 3 ml rinse) was added *via canula*, followed by tetrabutylammonium iodide (185 mg, 0.5 mmol). The mixture was stirred at 80°C overnight, then cooled down to r.t. It was poured into a saturated solution of ammonium chloride. Then extracted three times with a 1:1 mixture of ether and hexanes. The combined organic layers were washed with brine, dried on magnesium sulphate and the solvents removed *in vacuo*. The product was purified by flash chromatography (ethyl acetate:hexanes 0:100 to 10:90) to give 2.73 g of malonate **8** (87%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (d, 1H, 19.4 Hz); 5.76 (dt, 1H, 19.4 Hz, 6.9 Hz); 5.03 (m, 1H); 3.72 (s, 6H); 3.71 (s, 6H); 3.33 (t, 1H, 6.7 Hz); 2.72 (d, 2H, 6.8 Hz); 2.05-1.78 (m, 8H); 1.64 (s, 3H); 1.59-1.41 (m, 6H); 1.39-1.23 (m, 6H); 0.98-0.79 (m, 15H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.55; 169.80; 142.27; 142.22; 136.17; 133.86; 123.69; 57.45; 52.41; 52.24; 50.81; 41.05; 30.81; 29.02; 28.85; 27.23; 26.37; 25.20; 23.21; 13.64; 9.40.
IR (film) ν 2927; 2853; 1734; 1599; 1437.
HRMS (EI) $C_{28}H_{47}O_8Sn$ (M-C_4H_9) theoretical: 631.2293; experimental: 631.2301 ±0.0019.

Representative procedure for the synthesis of trienes **5c-5f**:

(1E,7Z,13E)-14-iodo-7-methyl-4,4,11,11-tetrakis(methoxycarbonyl)-1-tributylstannyltetradeca-1,7,13-triene (**5c**).

To a solution of malonate **8** (200 mg, 0.31 mmol) in a mixture of dry THF (1 ml) and dry DMF (1 ml) at 0°C, was added sodium hydride (25 mg of a 60% dispersion in oil, washed with pentane, 0.62 mmol). The mixture was stirred at r.t. for 40 min, cooled down to 0°C then iodide **4c** (182 mg, 0.62 mmol) was added dropwise. The mixture was shielded from light with aluminum foil and stirred at r.t. overnight, poured into a saturated ammonium chloride solution and extracted three times with a 1:1 mixture of ether and hexanes. The combined organic layers were washed with brine, dried on magnesium sulphate and the solvent was removed *in vacuo*. The product was purified by flash chromatography (ethyl acetate:hexanes 4:96) to give the desired triene **5c** (150 mg) as a colorless oil (57%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (dt, 1H, 7.7 Hz, 14.3 Hz); 6.17 (d, 1H, 14.3 Hz); 6.03 (d, 1H, 18.8 Hz); 5.74 (dt, 1H, 6.8 Hz, 18.8 Hz); 5.03 (m, 1H); 3.71 (s, 12H); 2.73 (dd, 2H, 0.9 Hz, 6.8 Hz); 2.62 (dd, 2H, 0.9 Hz, 7.6 Hz); 1.91-1.81 (m, 8H); 1.64 (s, 3H); 1.51-1.41 (m, 6H); 1.34-1.22 (m, 6H); 0.90-0.79 (m, 15H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.57; 171.05; 142.23; 140.38; 135.34; 133.90; 124.04; 78.62; 52.51; 52.27; 41.30; 39.35; 32.87; 30.95; 29.04; 27.24; 26.40; 23.16; 22.37; 13.66; 9.42.
IR (film) ν 2955, 2928, 1735, 1437.
HRMS (EI) $C_{31}H_{50}IO_8Sn$ (M-C_4H_9) theoretical: 797.1572, experimental: 797.1563 ±0.0024.

(1E,7Z,13E)-7,13-dimethyl-14-iodo-4,4,11,11-tetrakis(methoxycarbonyl)-1-tributylstannyltetradeca-1,7,13-triene (**5d**)

Bromide **4d** (162 mg, 0.62 mmol) was used as the electrophile, to give triene **5d** (165 mg) as a colorless oil (59%).

^1H NMR (300 MHz, $CDCl_3$) δ 6.07 (s, 1H); 6.03 (d, 1H, 17.1 Hz); 5.75 (dt, 1H, 6.8 Hz, 18.7 Hz); 5.02 (m, 1H); 3.71 (d, 12H); 2.89 (s, 2H); 2.73 (d, 2H, 6.8 Hz); 1.86-1.80 (m, 8H); 1.75 (d, 3H, 0.9 Hz); 1.59 (s, 3H); 1.52-1.42 (m, 6H); 1.34-1.22 (m, 6H); 0.90-0.82 (m, 15H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.58; 171.41; 143.00; 142.24; 135.25; 133.89; 124.10; 80.06; 57.46; 56.97; 52.46; 56.97; 52.46; 52.26; 42.14; 41.31; 32.91; 31.56; 90.95; 29.04; 27.24; 26.42; 22.53; 13.66; 9.42.
IR (film) ν 2955, 2924, 2853, 1732, 1600, 1436.
HRMS (EI) $C_{32}H_{52}IO_8Sn$ ($M-C_4H_9$) theoretical: 811.17298, experimental:811.1735 0.0024.

(*1E*,*7Z*,*13Z*)-14-iodo-7-methyl-4,4,11,11-tetrakis(methoxycarbonyl)-1-tributylstannyltetradeca-1,7,13-triene (**5e**)

Iodide **4e** (137 mg, 0.47 mmol) was used as the electrophile, to give triene **5e** (175 mg) as a colorless oil (66%).
^1H NMR (300 MHz, $CDCl_3$) δ 6.37 (d, 1H, 7.6 Hz); 6.12-6.01 (m, 2H); 7.74 (dt, 1H, 6.9 Hz, 18.7 Hz); 5.05 (m, 1H); 3.73 (s, 6H); 3.72 (s, 6H); 2.77-2.72 (m, 4H); 1.89-1.84 (m, 8H); 1.65 (s, 3H); 1.52-1.42 (m, 6H); 1.34-1.22 (m, 6H); 0.90-0.82 (m, 15H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.57; 171.26; 142.28; 135.59; 135.28; 133.87; 124.13; 85.69; 57.47; 56.69; 52.54; 52.29; 41.21; 38.09; 33.11; 30.85; 29.04; 27.25; 26.41; 23.15; 22.63; 13.67; 9.43.
IR (film) ν 2955, 2851, 1733, 1599, 1436.
HRMS (EI) $C_{31}H_{50}IO_8Sn$ ($M-C_4H_9$) theoretical: 797.1572; experimental: 797.1563 ±0.0024.

(*1E*,*7Z*,*13Z*)-7,13-dimethyl-14-iodo-4,4,11,11-tetrakis(methoxycarbonyl)-1-tributylstannyltetradeca-1,7,13-triene (**5f**)

Bromide **4f** (123 mg, 0.47 mmol) was used as the electrophile, to give a 5:1 mixture of triene **5f** and starting diene **8** (170 mg), which proved to be extremely difficult to separate (54% yield). After three iterative chromatographies using ether:hexanes 5:95 to 10:90), 40 mg of triene **5f** was obtained, almost completely separated from diene **8** (~20:1 ratio from ^1H NMR analysis) and was used as such for coupling.
^1H NMR (300 MHz, $CDCl_3$) δ 6.10 (d, 1H, 18.7 Hz); 5.75 (dt, 1H, 6.8 Hz, 18.7 Hz); 5.05 (m, 1H); 3.73 (s, 6H); 3.72 (s, 6H); 2.97 (s, 2H); 2.73 (dd, 2H, 1 Hz, 6.9 Hz); 1.93-1.86 (m, 8H); 1.78 (d, 3H, 1.4 Hz); 1.65 (s, 3H); 1.53-1.41 (m, 6H); 1.35-1.22 (s, 6H); 0.90-0.82 (m, 15H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.60; 143.17; 142.30; 135.10; 133.85; 124.37; 122.97; 79.37; 57.49; 56.82; 52.46; 52.30; 41.84; 41.19; 33.61; 30.82; 29.09; 29.05; 27.26; 26.44; 23.14; 13.69; 9.42.
IR (film) ν 2952; 2925; 2852; 1737; 1599; 1441.
HRMS (EI) $C_{32}H_{52}IO_8Sn$ ($M-C_4H_9$) theoretical: 811.1729; experimental: 811.1744 ±0.0024.

Representative procedure for Stille macrocyclizations:

Triene (38 mg, 0.044 mmol) and triphenylarsine (13 mg, 0.044 mmol) were combined in a flask equipped with a reflux condenser. Dry THF (11 ml) and dry DMF (11 ml) were added, followed by diisopropylethylamine (0.008 ml, 0.044 mmol). The mixture was degassed three times (vacuum then argon), then $Pd_2(dba)_3$ (2 mg, 0.0022 mmol, 5%) was added, and the mixture was degassed once more. The flask was shielded from light with aluminum foil and immersed in an oil bath at 90°C under Ar and stirred at that temperature for 24 h. It was then cooled down to r.t., water (5 ml) was added, and the mixture was extracted three times with 15 ml of a 1:1 mixture of hexanes and ether. The combined organic layers were washed with brine (5 ml), dried on magnesium sulphate and the solvents removed *in vacuo*. The macrocycle was purified by silica gel flash chromatography (ether: hexanes 10:90 to 20:80).

Macrocyclization on triene **5a**: a mixture of *trans-anti-cis* and *cis-anti-trans* tricycles **10a** and **10b** (14 mg, 73%) was obtained in a ratio of 2:1 as a clear oil. The direct obtention of a tricycle is in agreement with previously reported observations (ref. 13, main text). Spectroscopic data were identical to those reported (ref. 13).

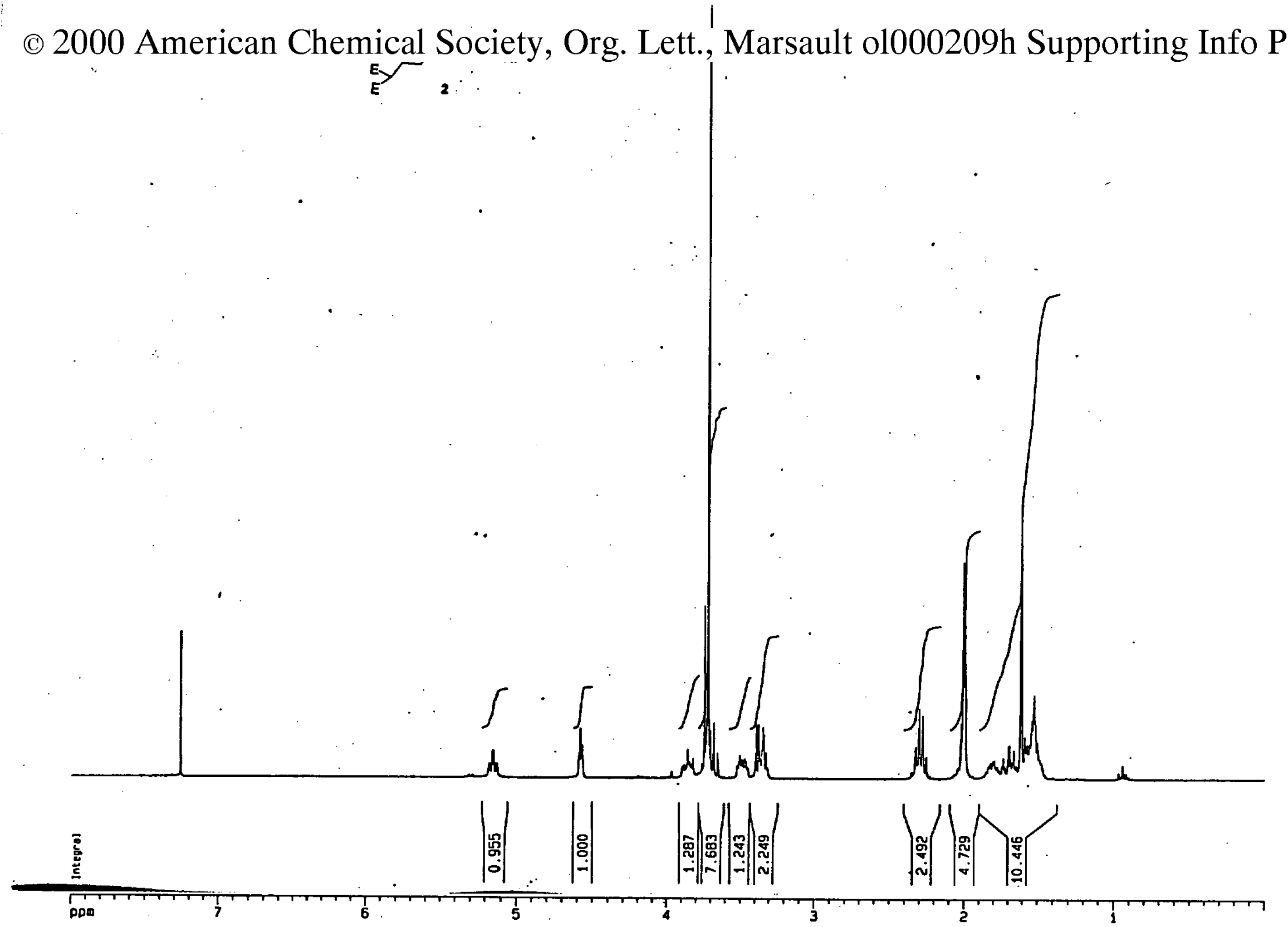
Macrocyclization on triene **5b**: macrocycle *trans-cis-trans* **11** (12 mg, 63%) was obtained as a white solid, m.p. 153-155°C (ref. 13, main text, m.p. 154-156°C). Spectroscopic data were identical to those reported (ref. 13).

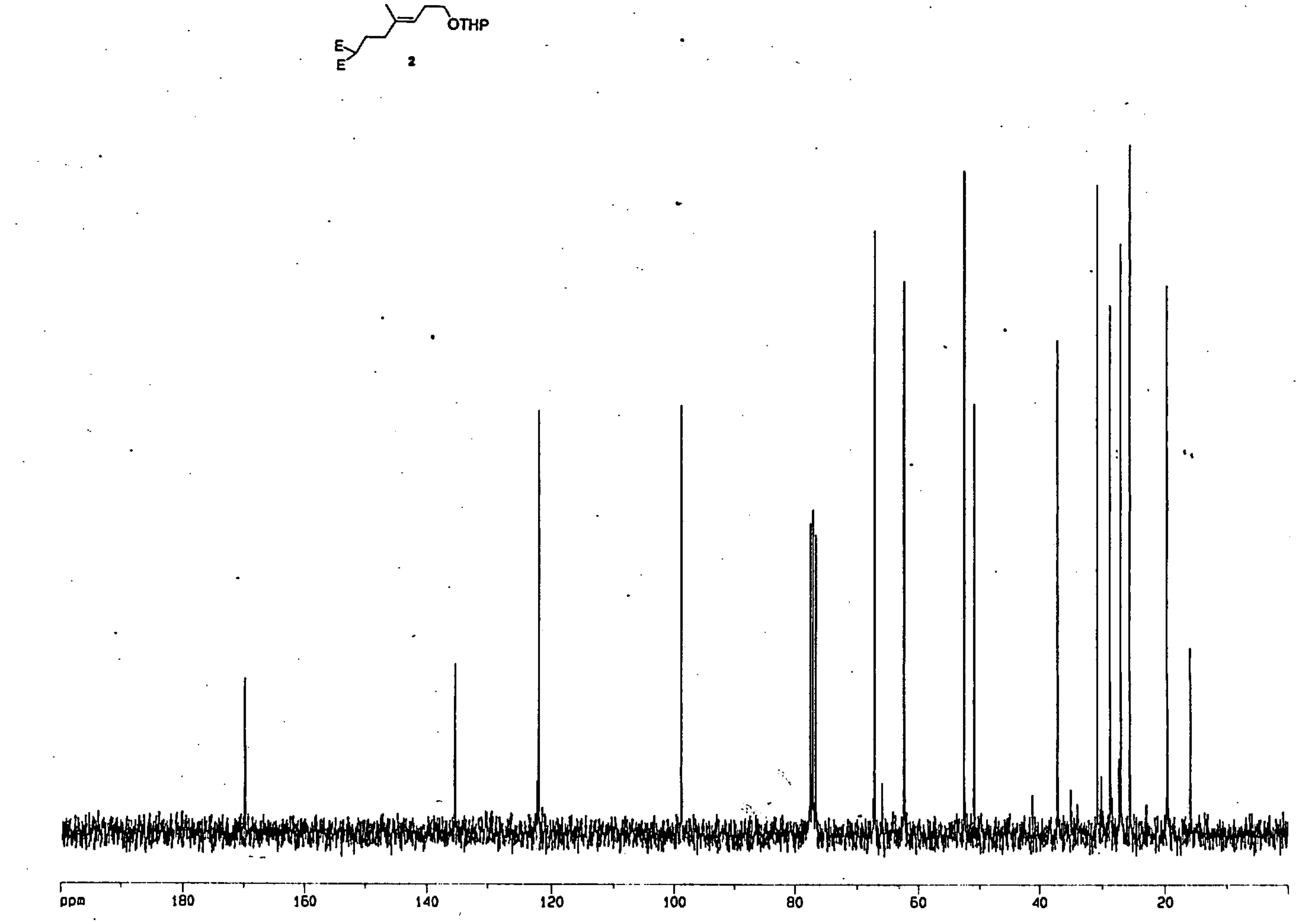
Macrocyclization on triene **5c**: tricycle *trans-syn-trans* **12** was directly obtained (17 mg, 89%) as a white solid, m.p. 113-115°C (ref. 13, main text, m.p. 116-118°C). Spectroscopic data were identical to those reported (ref.13).

Macrocyclization on triene **5d**: macrocycle *trans-trans(Me)-cis* **13** was obtained (16 mg, 81%) as a white solid, m.p. 156-157°C (ref. 17, main text, m.p. 115-117°C). Spectroscopic data were identical to those reported (ref.17).

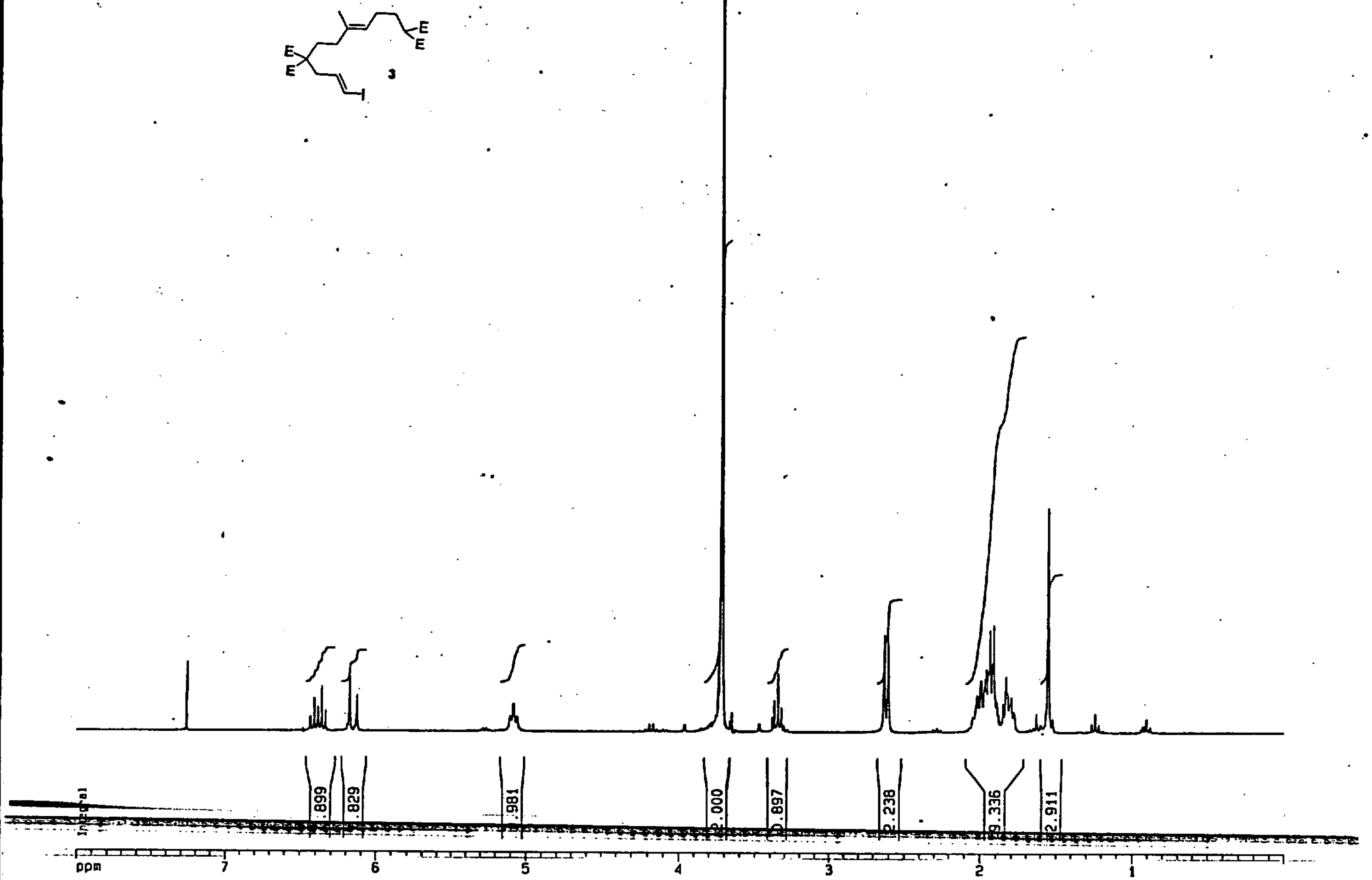
Macrocyclization on triene **5e**: macrocycle trans-cic-cis **14** was obtained (18 mg, 94%) as a white solid, m.p. 219-222°C (ref. 16, main text m.p. 224-225°C). Spectroscopic data were identical to those reported (ref. 16).

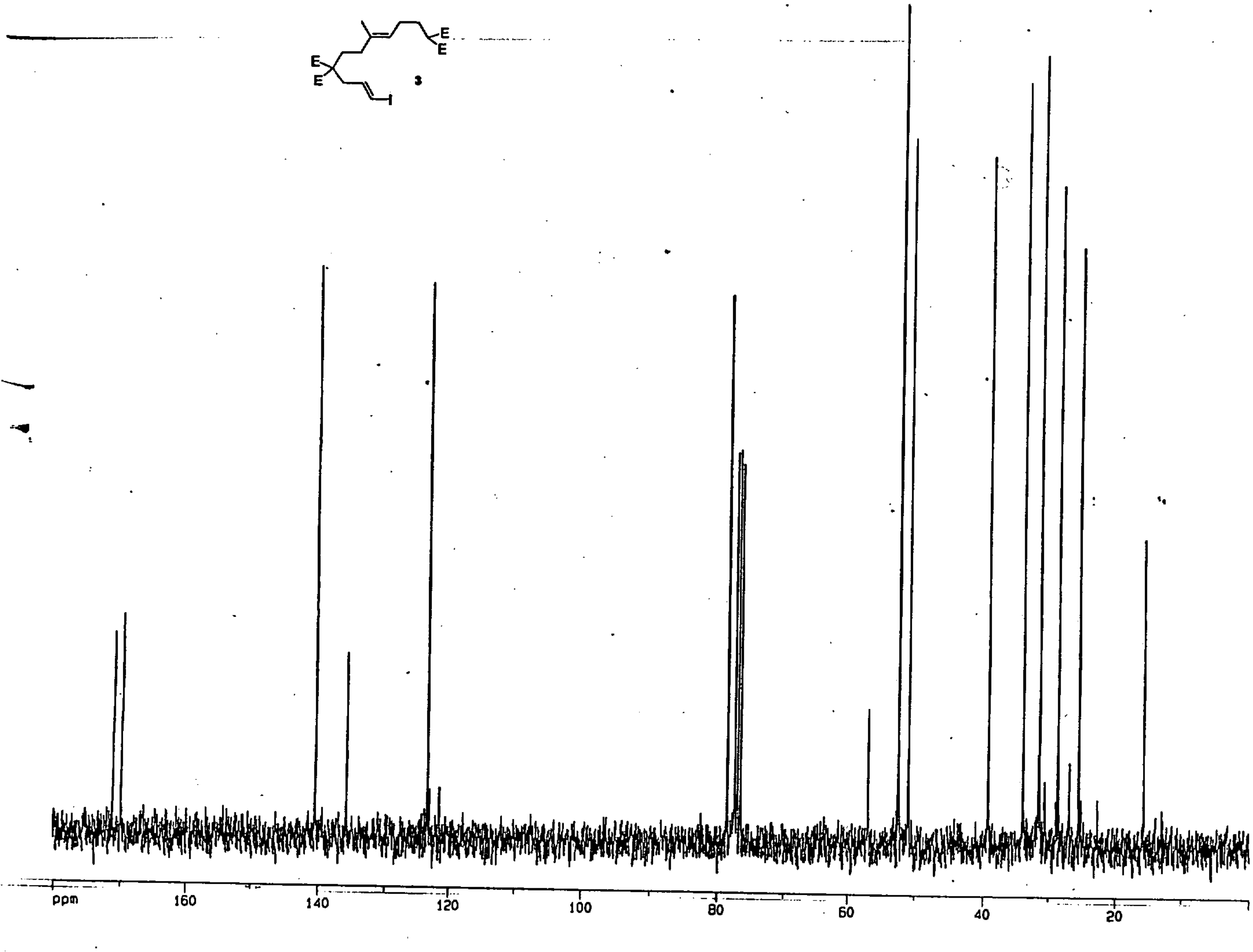
Macrocyclization on triene **5f**: macrocycle *trans-cis(Me)-cis* **15** was obtained as a white solid, m.p. 177-178°C (ref. 17, main text, m.p. 178-181°C). Analytical data were identical to those reported (ref. 17).

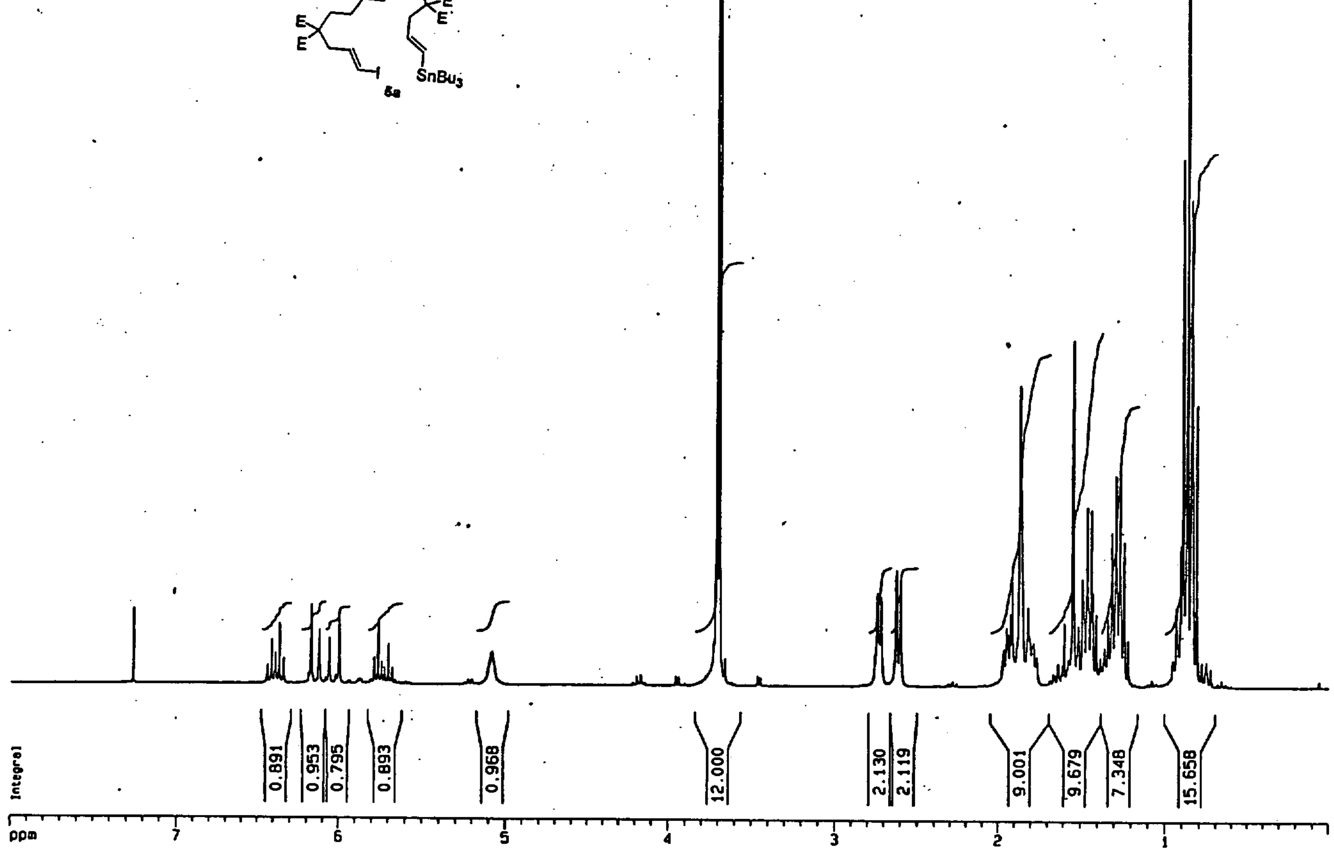

E
E
2
0.955
1.000
1.287
7.683
1.243
2.249
2.492
4.729
10.446
Integral
ppm
7
6
5
4
3
2
1

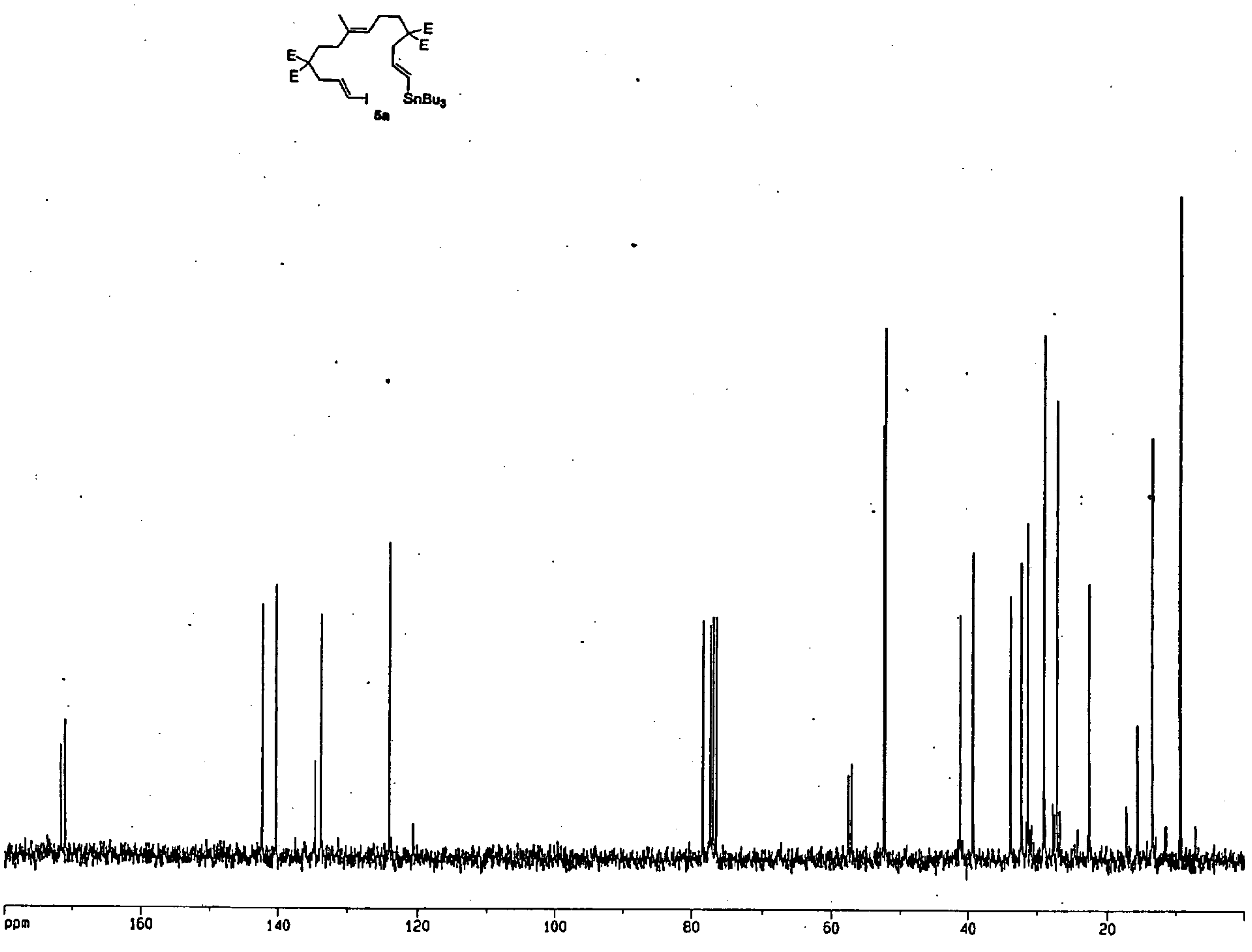

OTHP
E
E
2
ppm
180
160
140
120
100
80
60
40
20

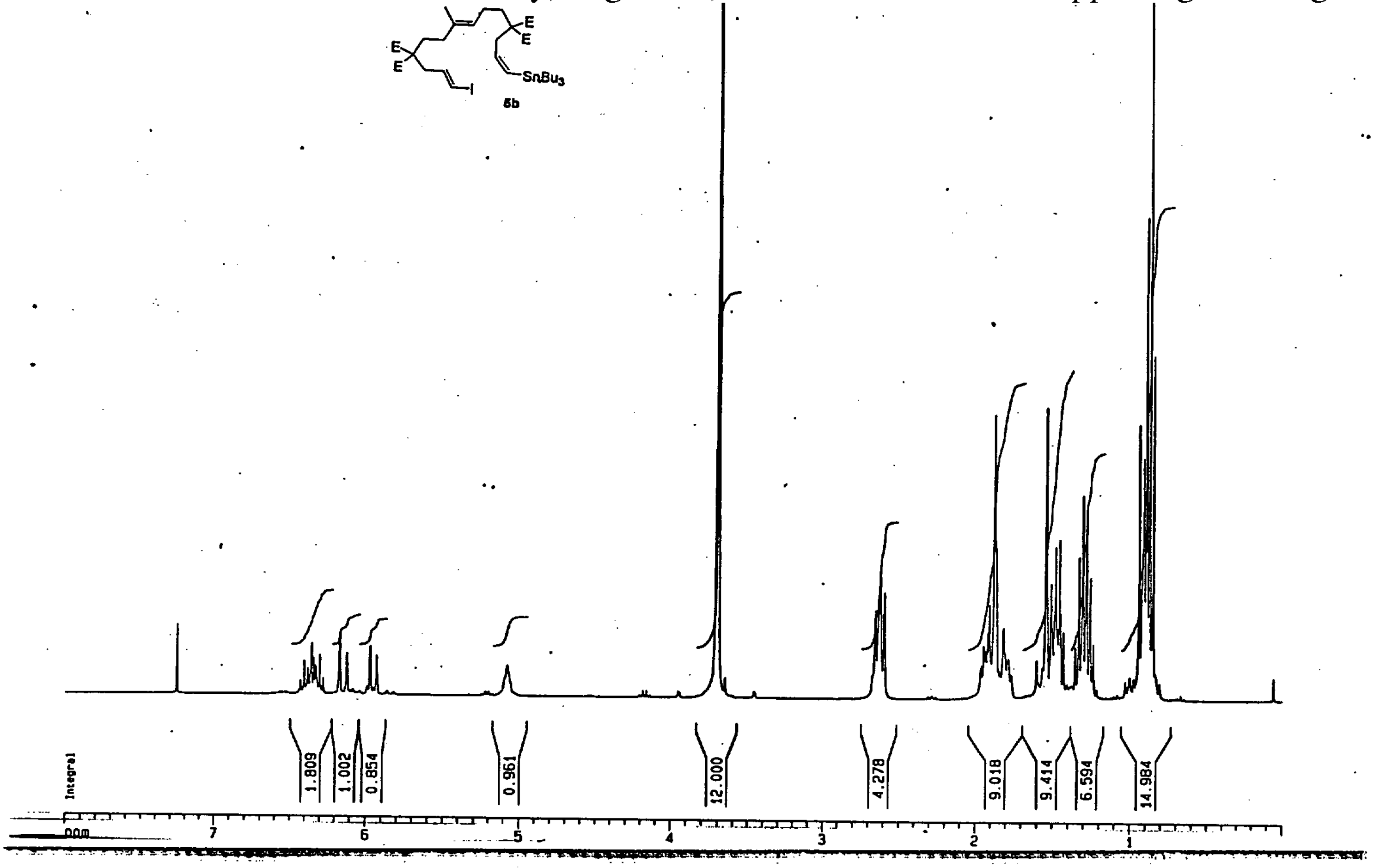
9

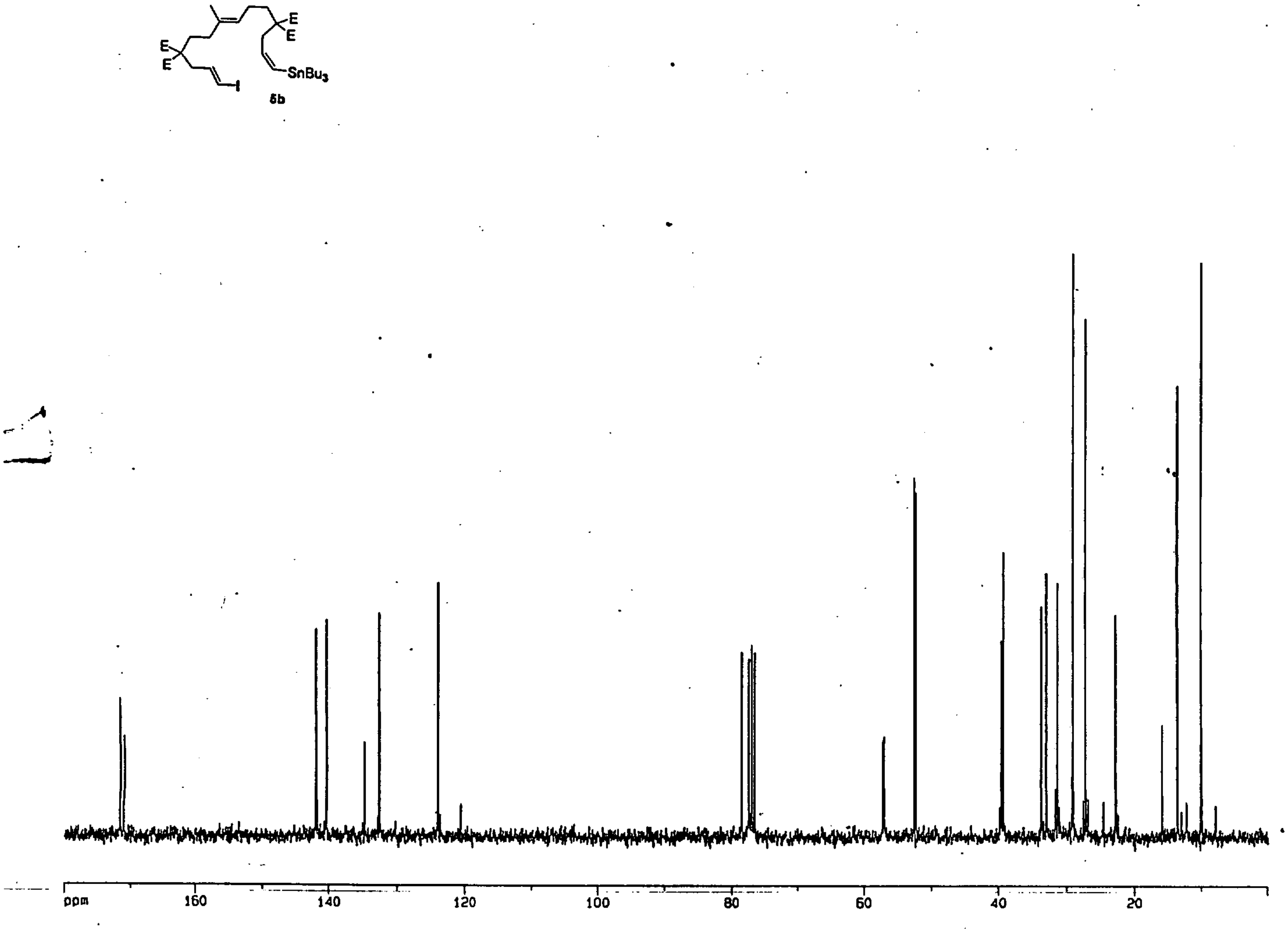

E
E
E
E
I
3
Integral
.899
.829
.981
2.000
0.897
2.238
9.336
2.911
ppm
7
6
5
4
3
2
1

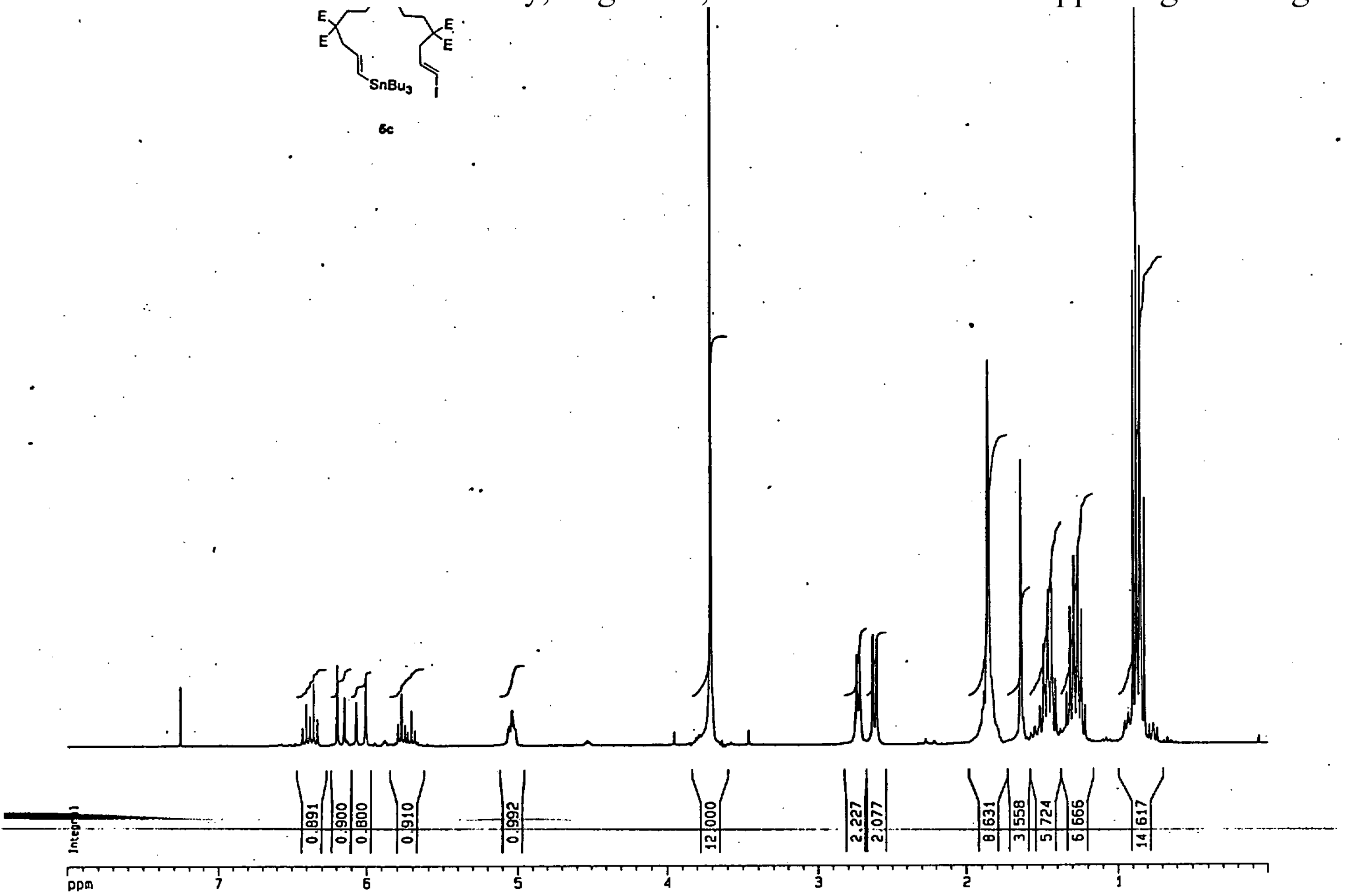

E
E
E
E
I
3
ppm
160
140
120
100
80
60
40
20

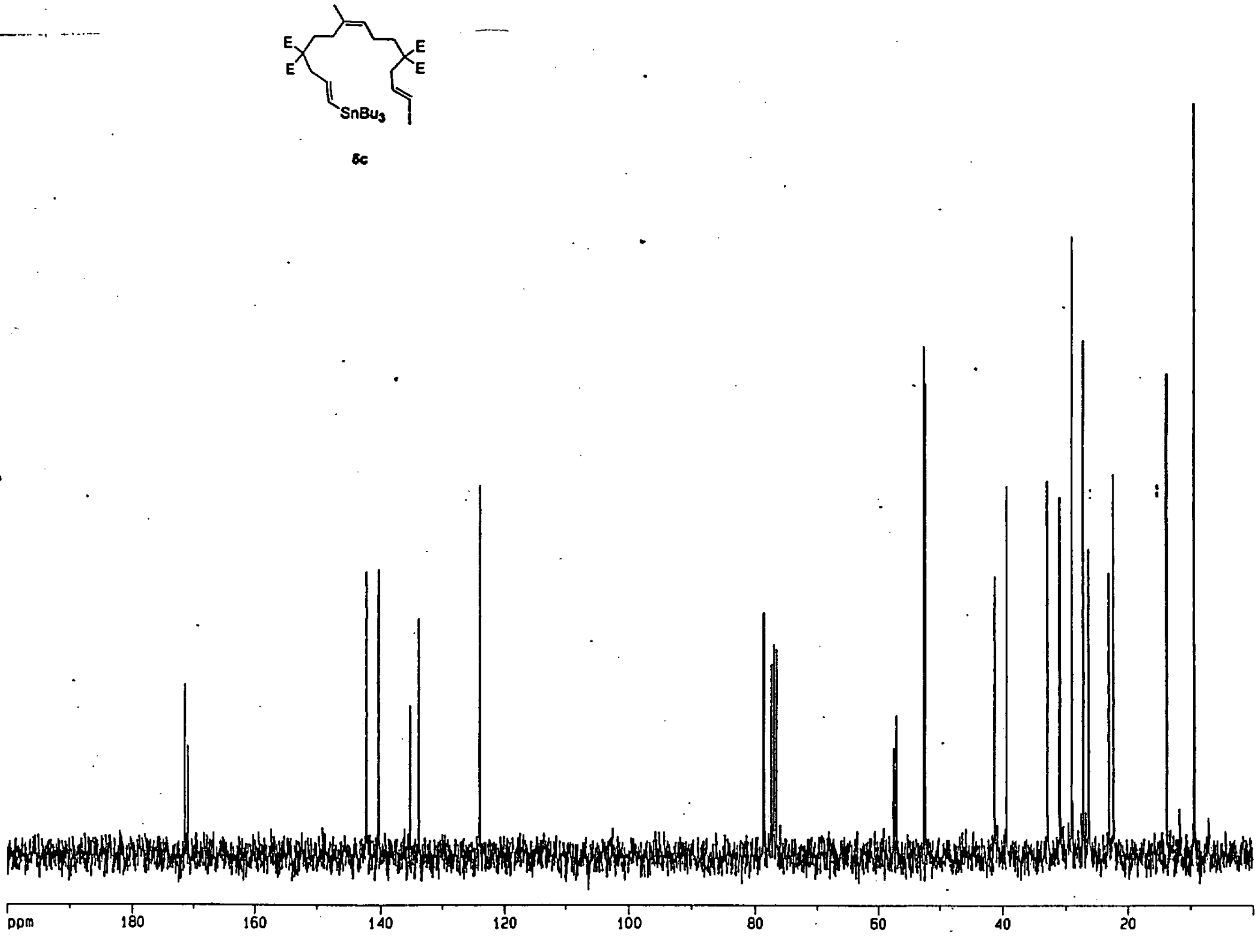

E
E
I
SnBu3
E
E
8a
Integral
0.891
0.953
0.795
0.893
0.968
12.000
2.130
2.119
9.001
9.679
7.348
15.658
ppm
7
6
5
4
3
2
1

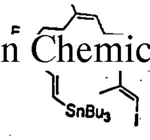

E
E
E
E
I
SnBu3
8a
ppm
160
140
120
100
80
60
40
20


E
E
E
E
SnBu$_3$
I
5b
Integral
1.809
1.002
0.854
0.961
12.000
4.278
9.018
9.414
6.594
14.984
ppm
7
6
5
4
3
2
1

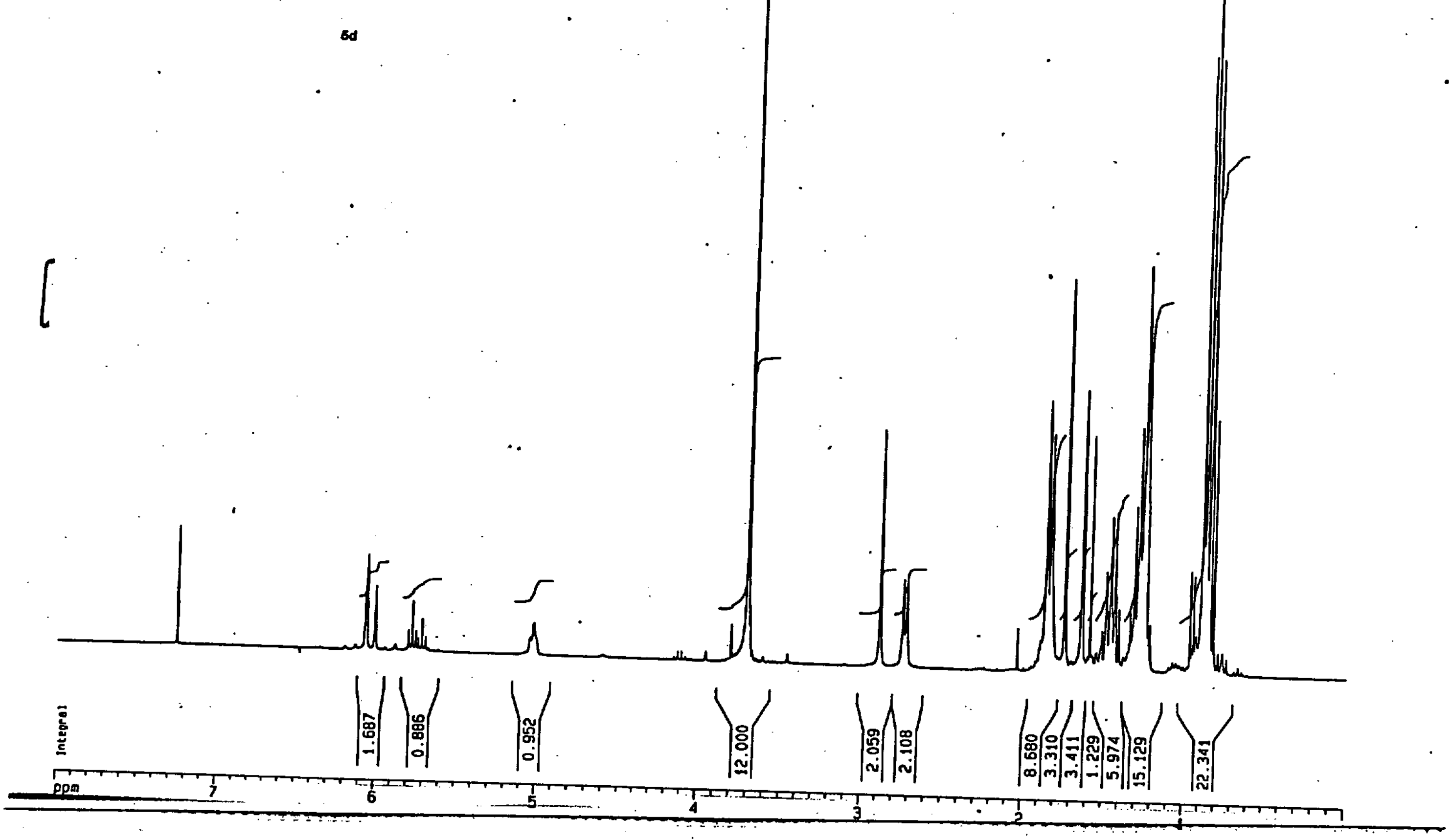

E
E
E
E
SnBu$_3$
I
5b
ppm
160
140
120
100
80
60
40
20

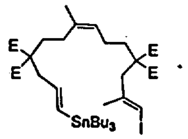

E
E
E
E
SnBu3
I
6c
0.891
0.900
0.800
0.910
0.992
12.000
2.227
2.077
8.631
3.558
5.724
6.666
14.617
Integral
ppm
7
6
5
4
3
2
1


E
E
E
E
SnBu3
I
6c
ppm
180
160
140
120
100
80
60
40
20

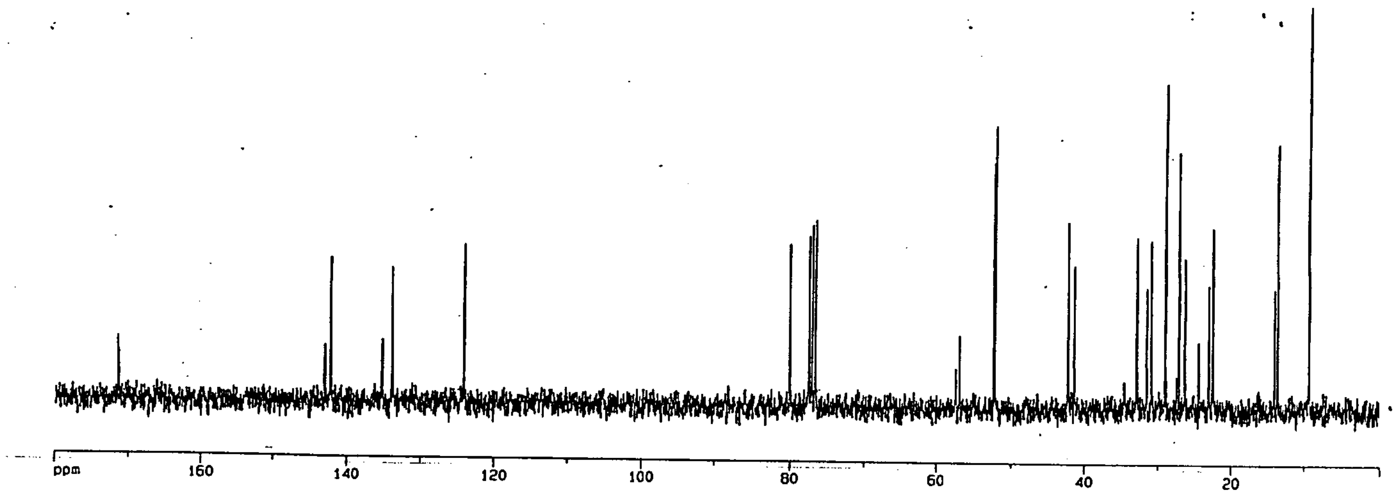

SnBu3
I

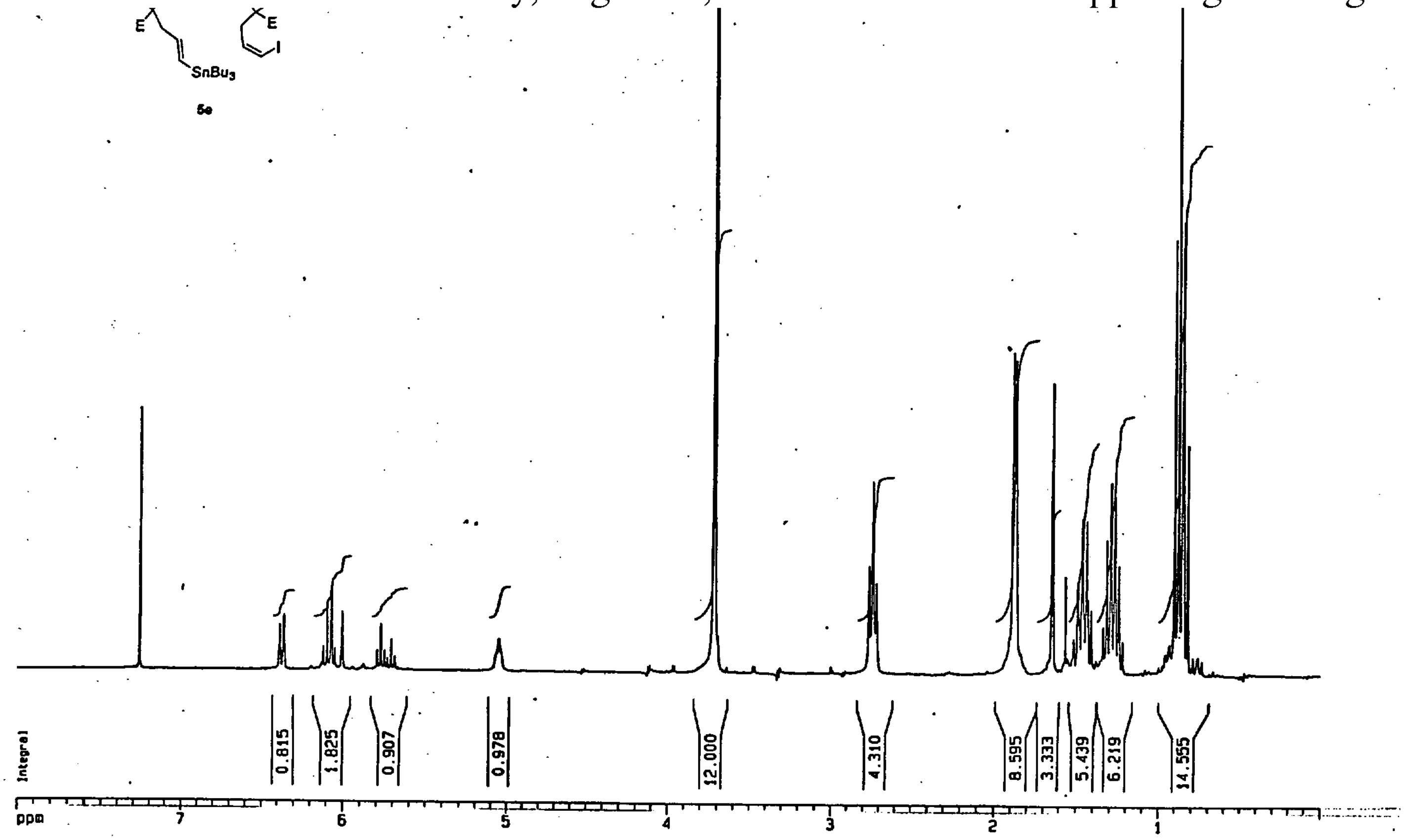
5d

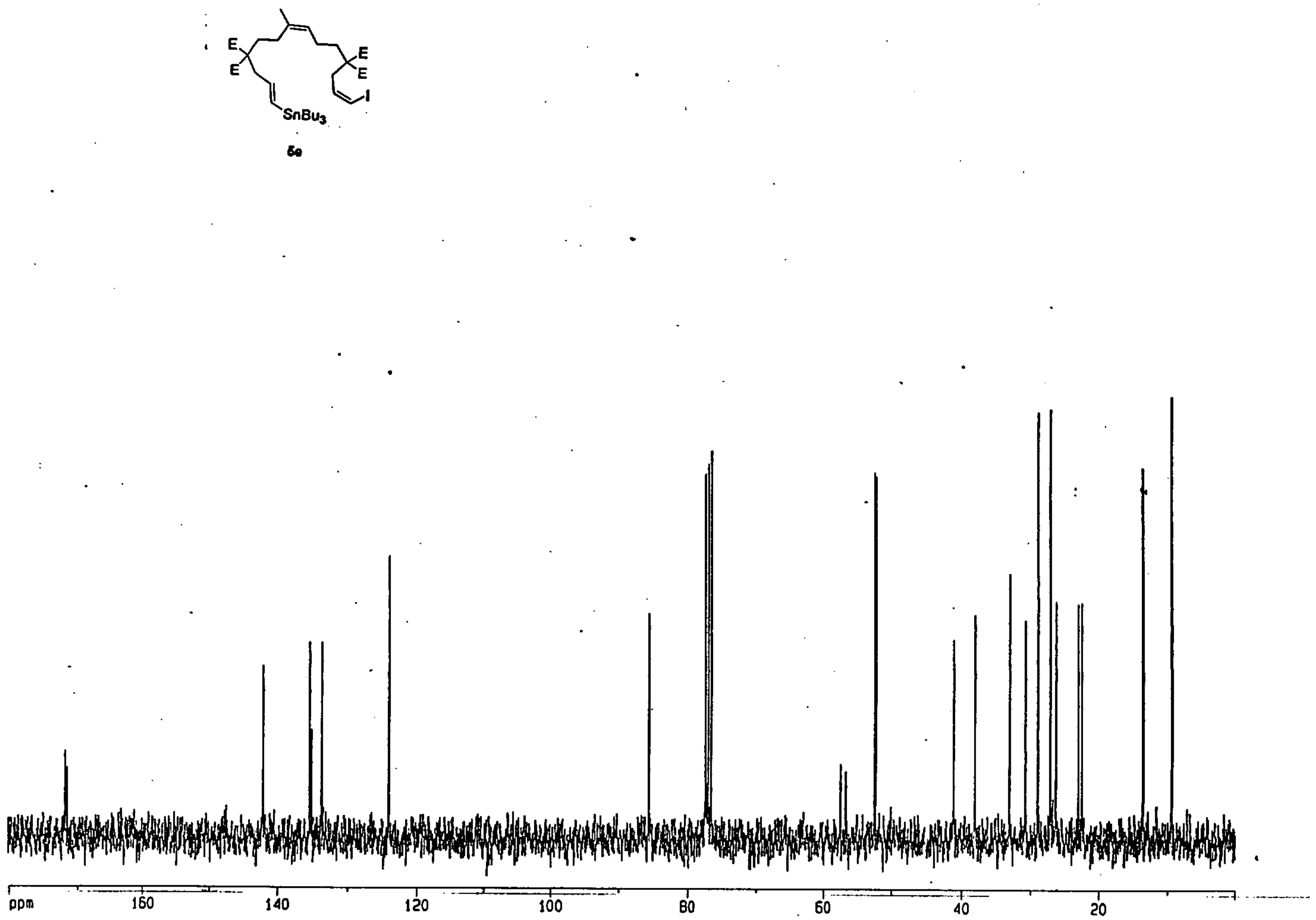

1.687
0.886
0.952
12.000
2.059
2.108
8.680
3.310
3.411
1.229
5.974
15.129
22.341
Integral
ppm
7
6
5
4
3
2
1

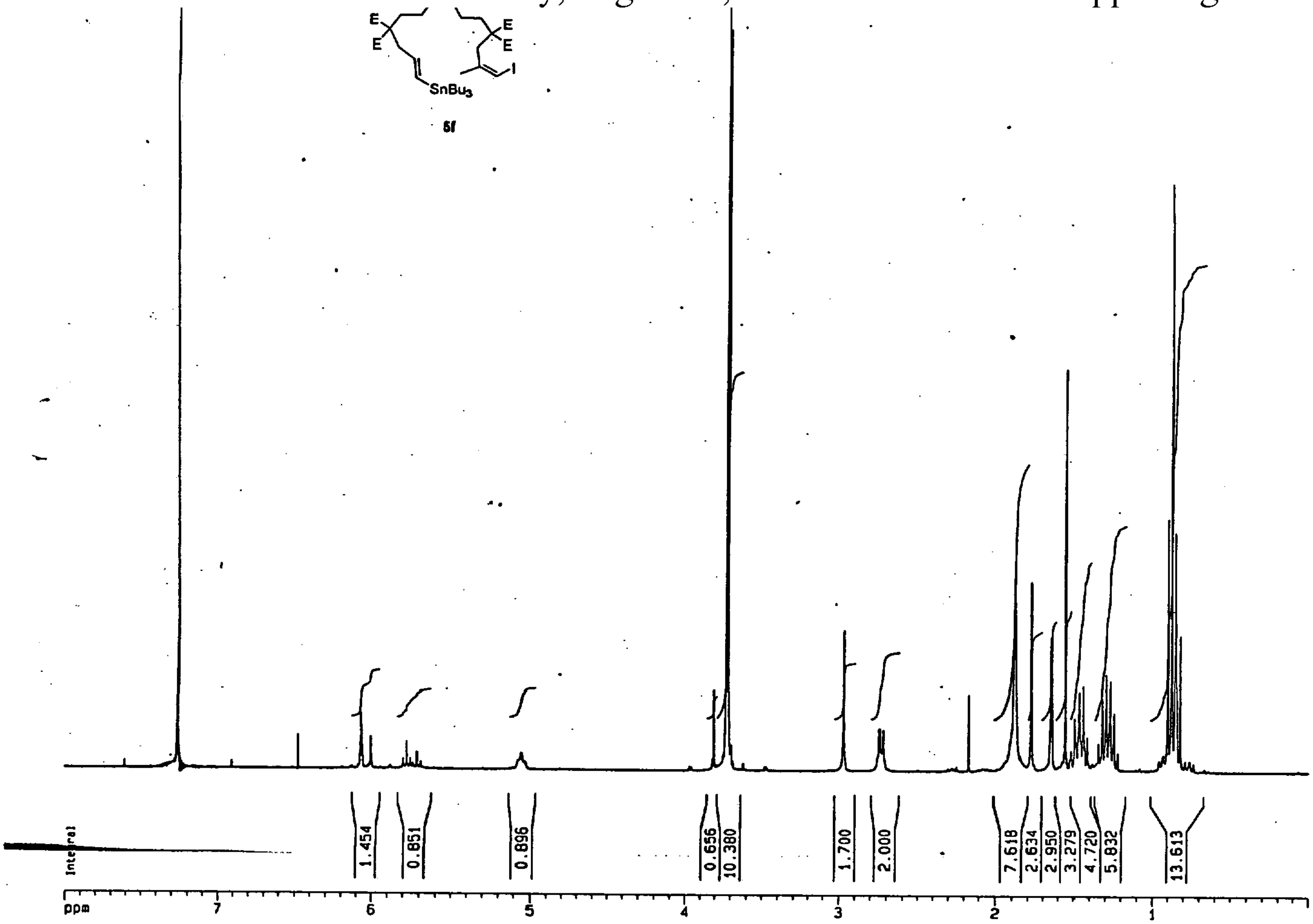

E
E
E
E
SnBu3
I

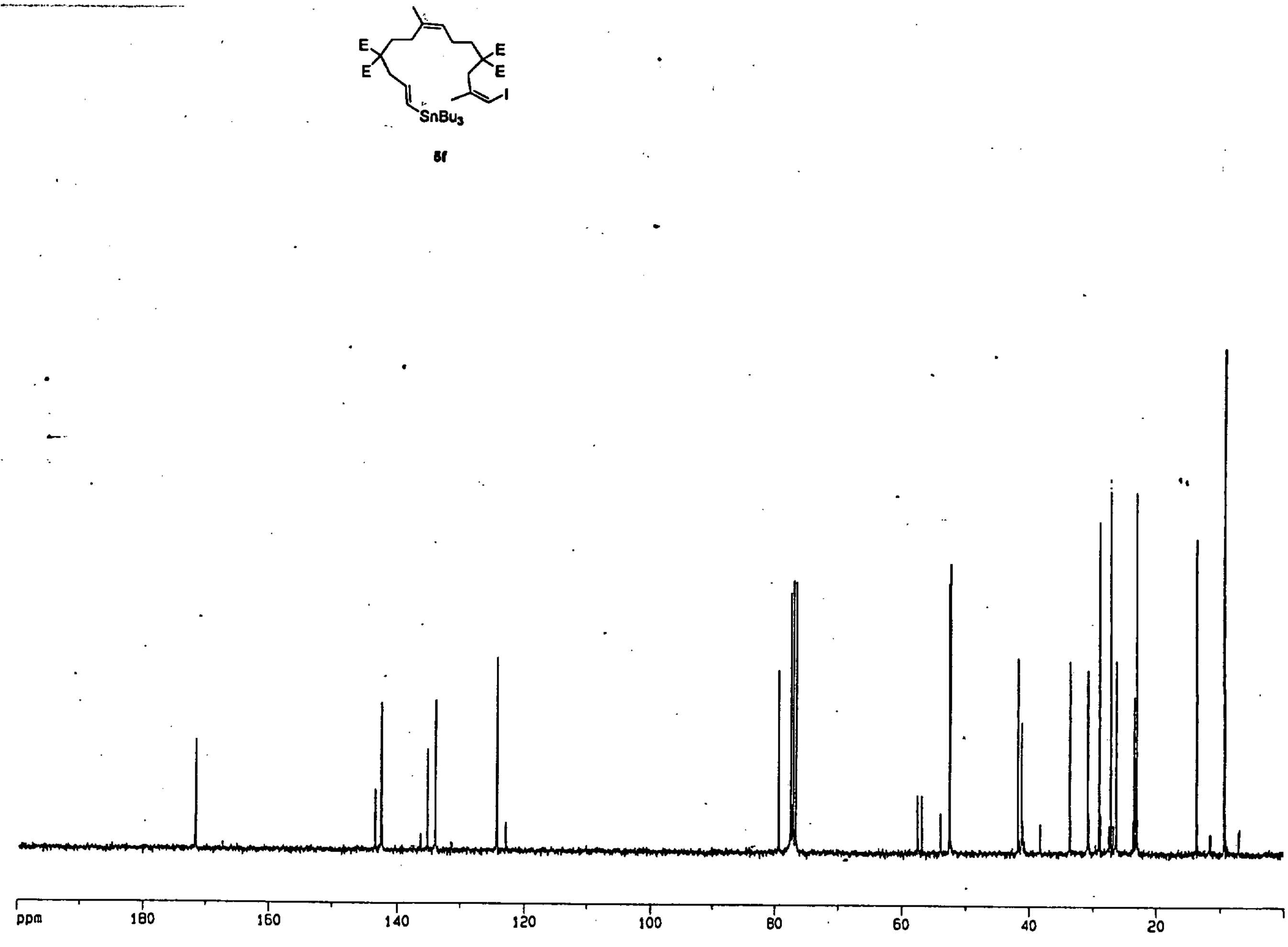
5d

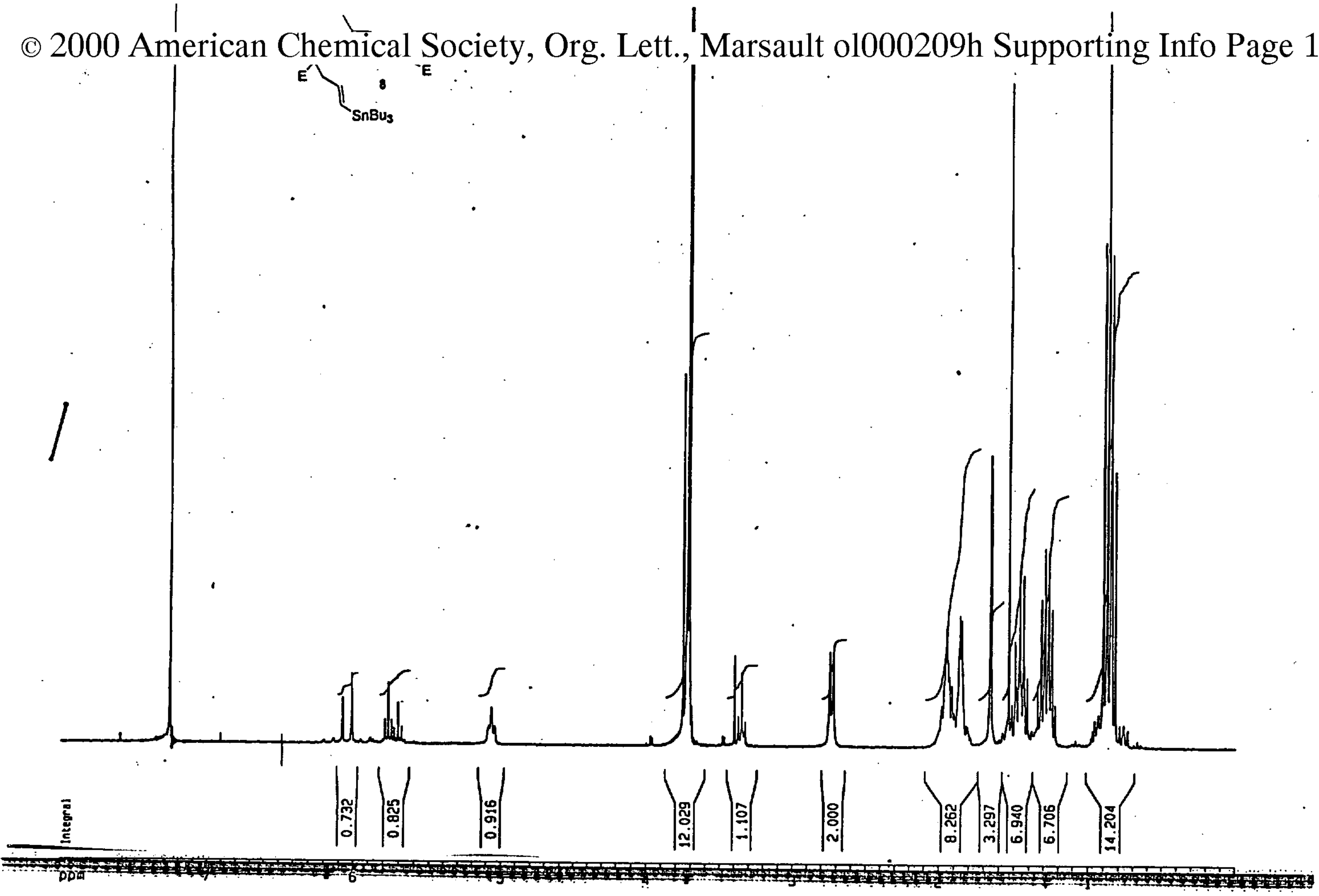

ppm
160
140
120
100
80
60
40
20

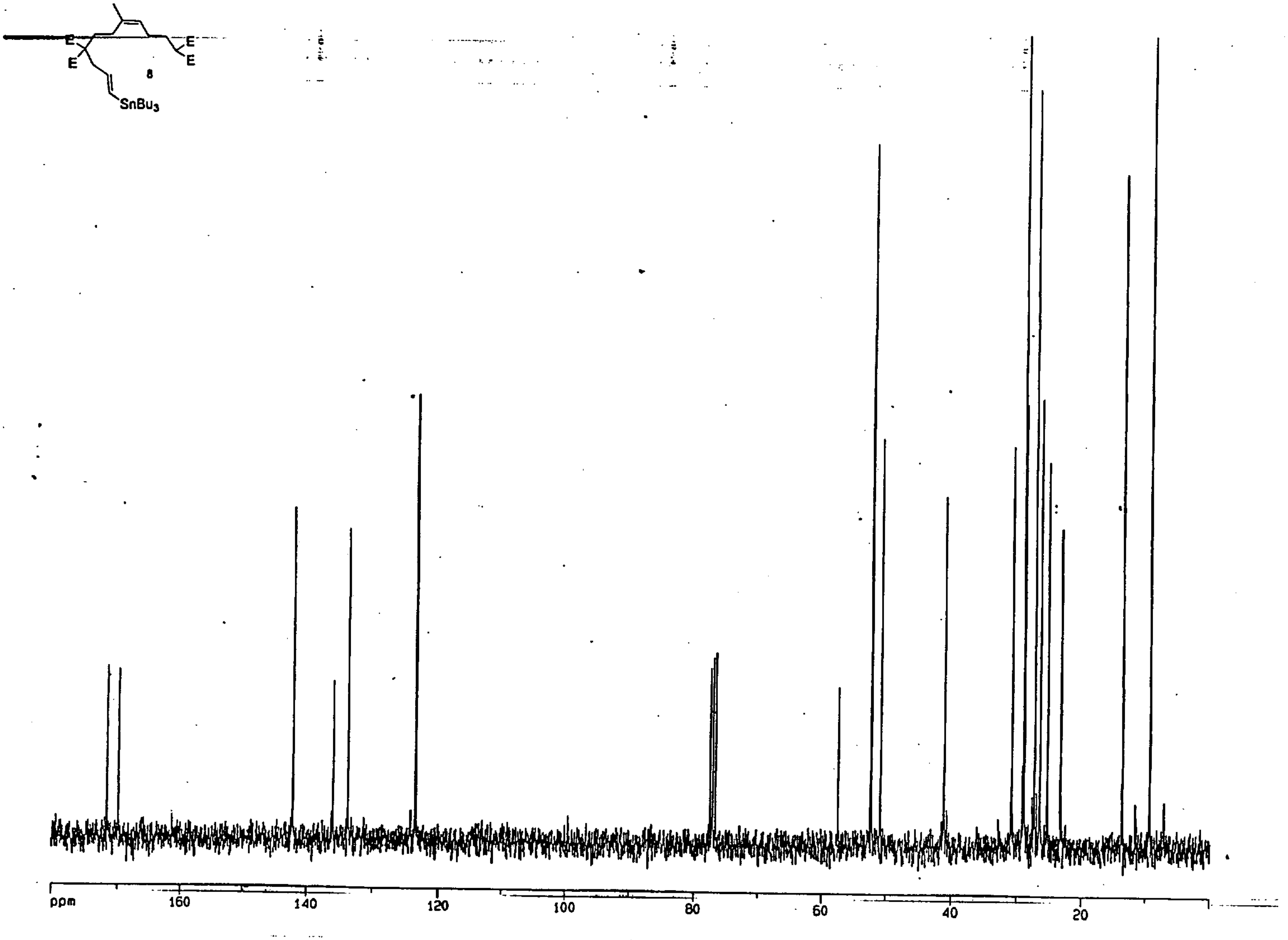

E
E
SnBu3
I
5e
Integral
0.815
1.825
0.907
0.978
12.000
4.310
8.595
3.333
5.439
6.219
14.555
ppm
7
6
5
4
3
2
1

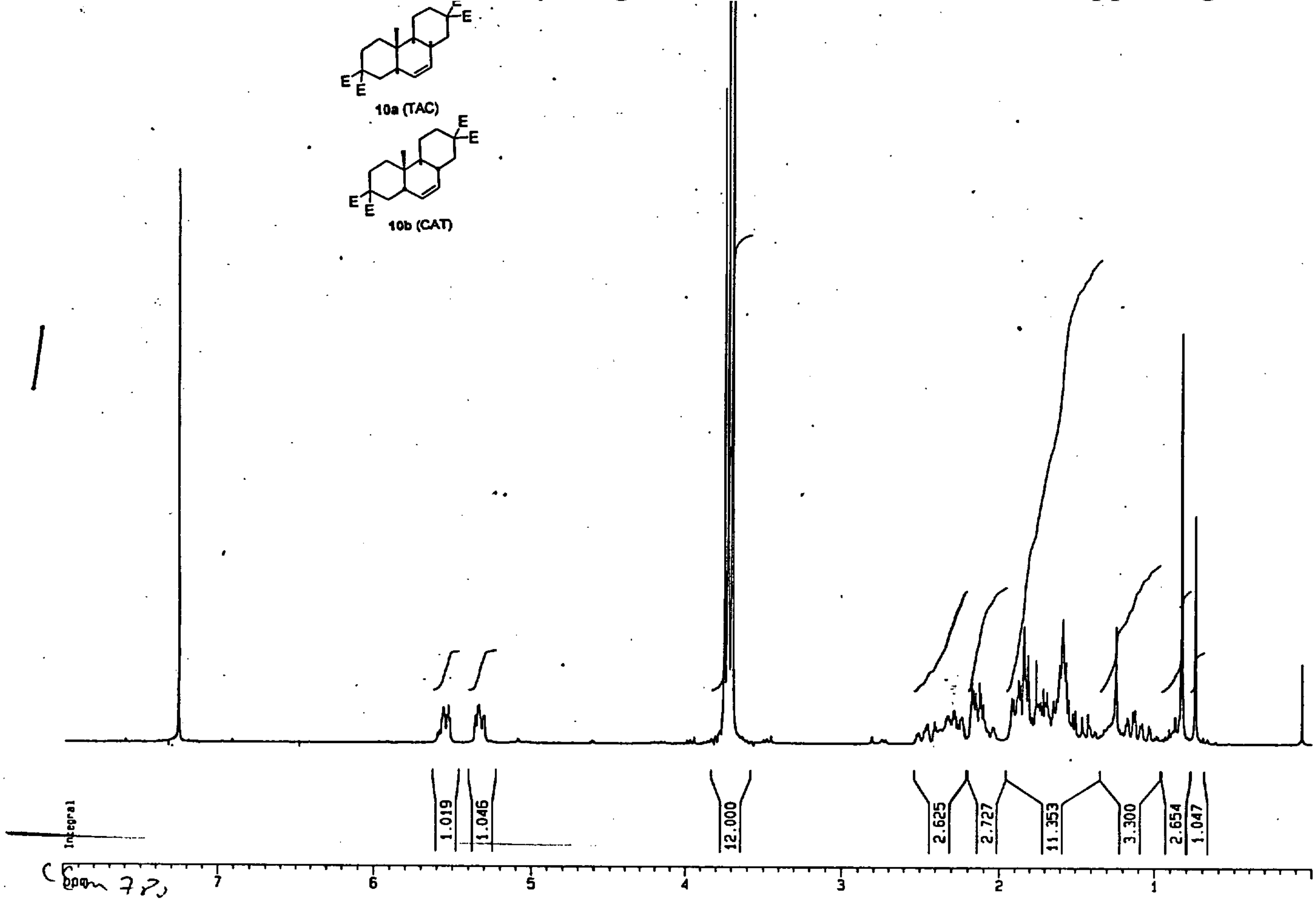

E
E
E
E
SnBu3
I
5e
ppm
160
140
120
100
80
60
40
20


E
E
E
E
SnBu3
I
5f
Integral
1.454
0.851
0.896
0.656
10.380
1.700
2.000
7.618
2.634
2.950
3.279
4.720
5.832
13.613
ppm
7
6
5
4
3
2
1

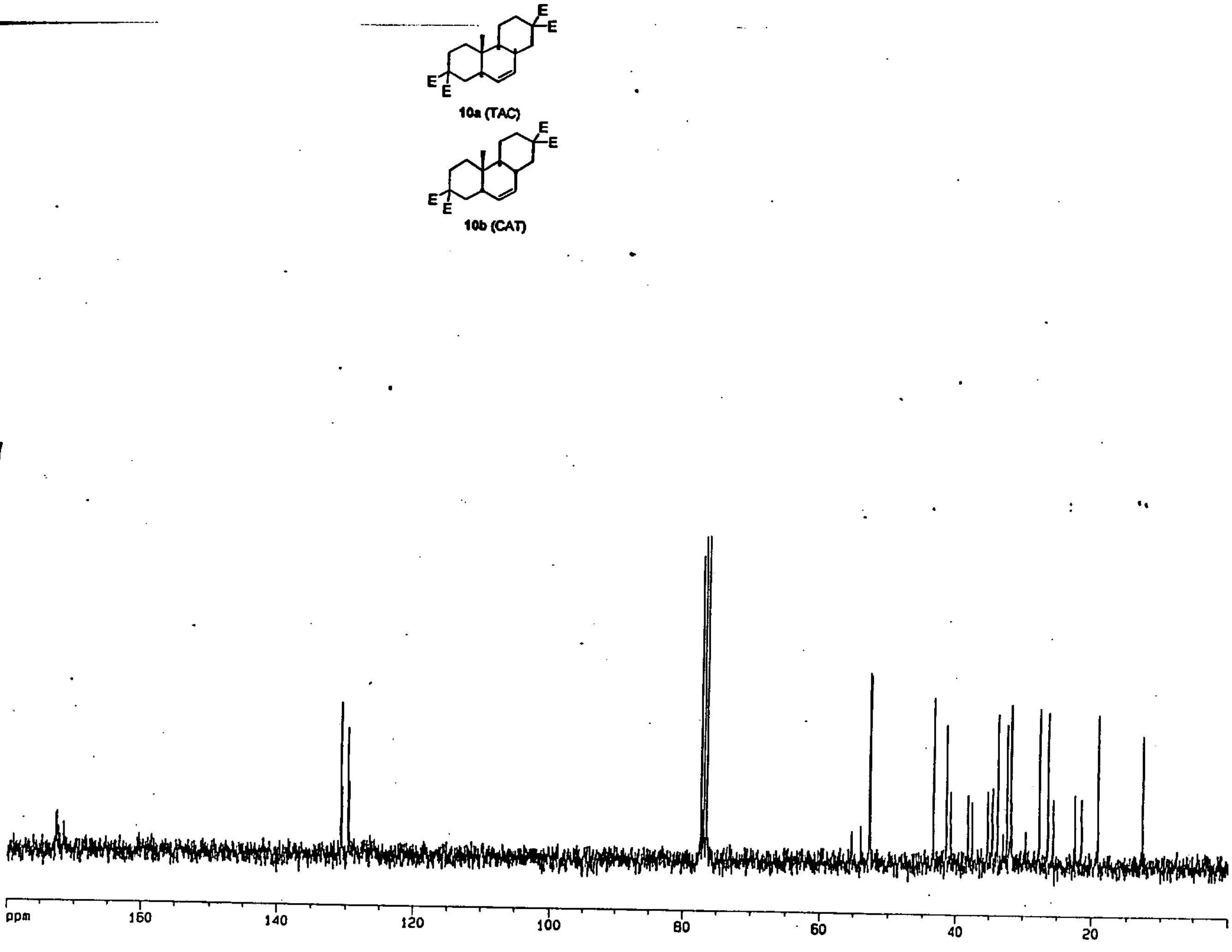

E
E
E
E
I
SnBu3
5f
ppm
180
160
140
120
100
80
60
40
20


E
E
8
SnBu3
0.732
0.825
0.916
12.029
1.107
2.000
8.262
3.297
6.940
6.706
14.204
Integral
ppm
6
5
4
3
2
1

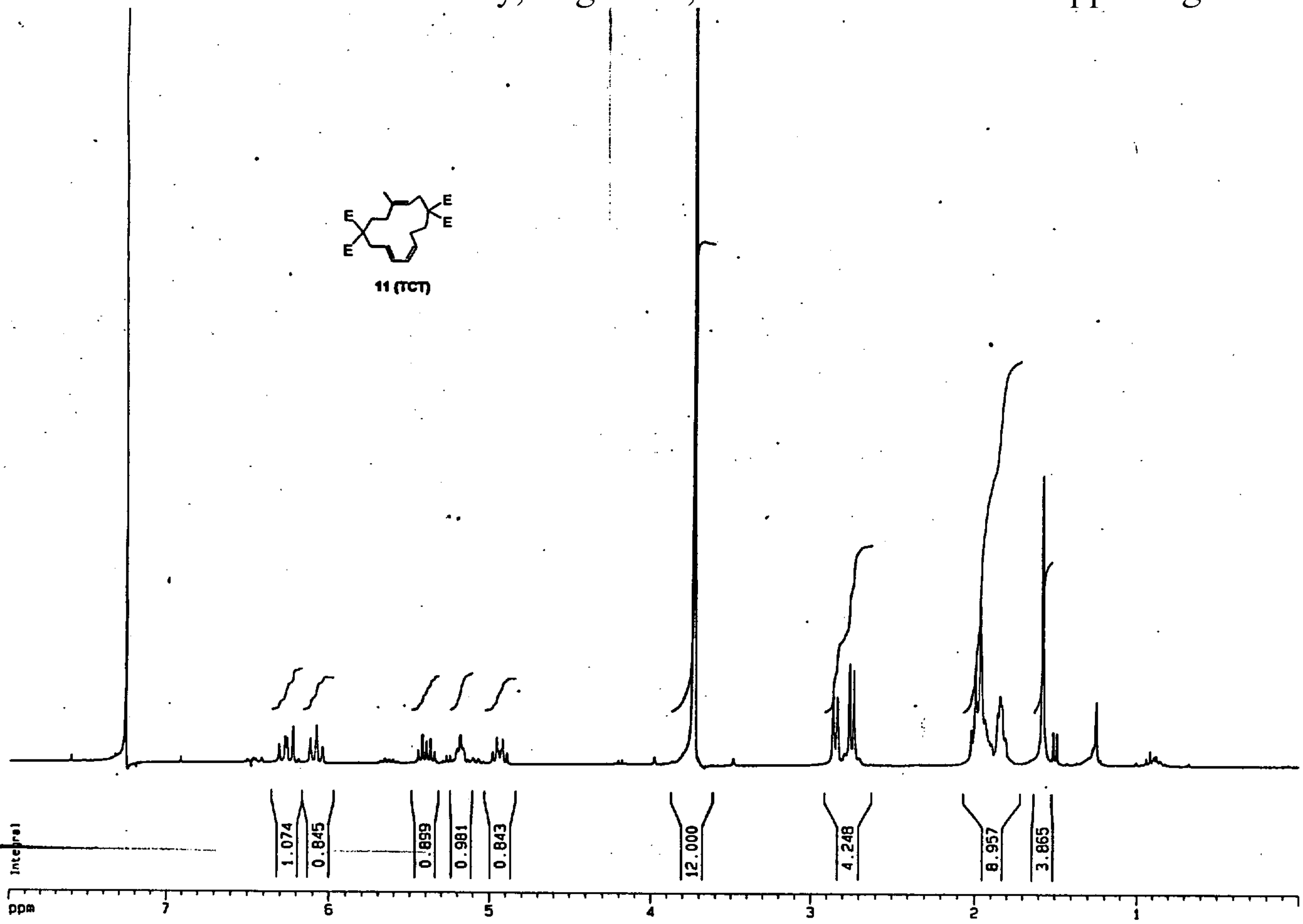

E
E
E
E
8
SnBu3
ppm
160
140
120
100
80
60
40
20

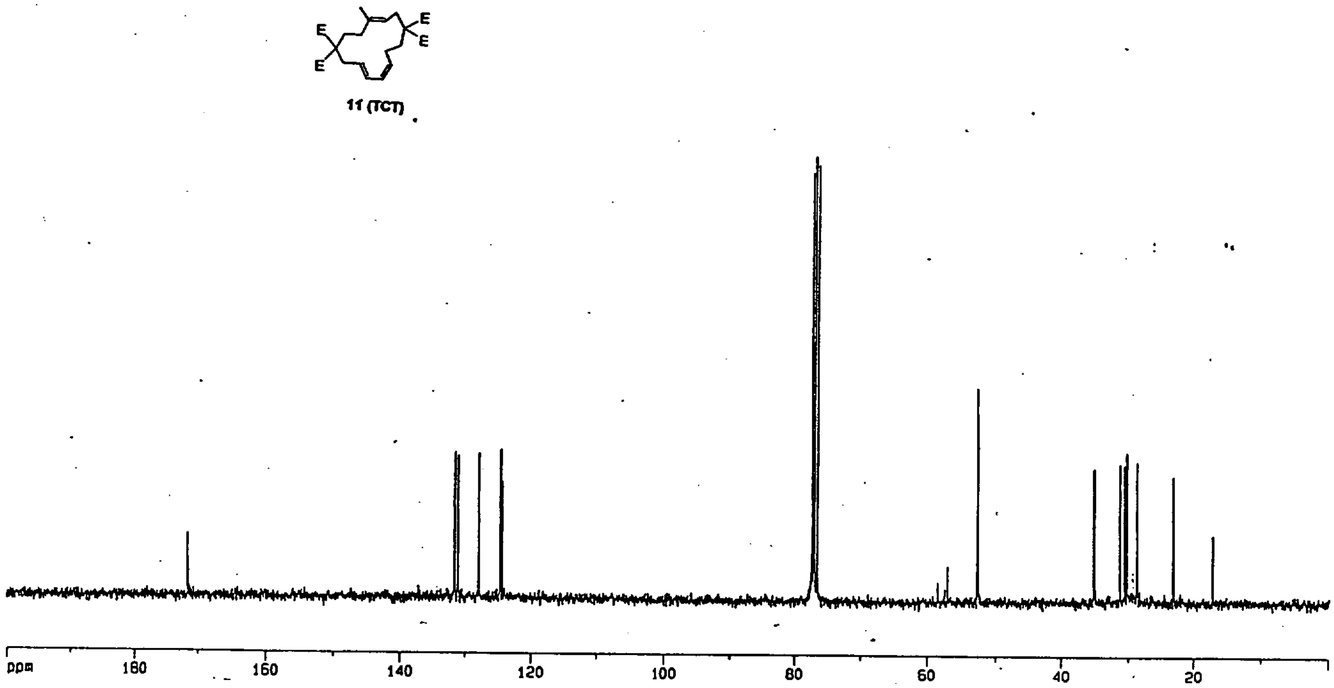


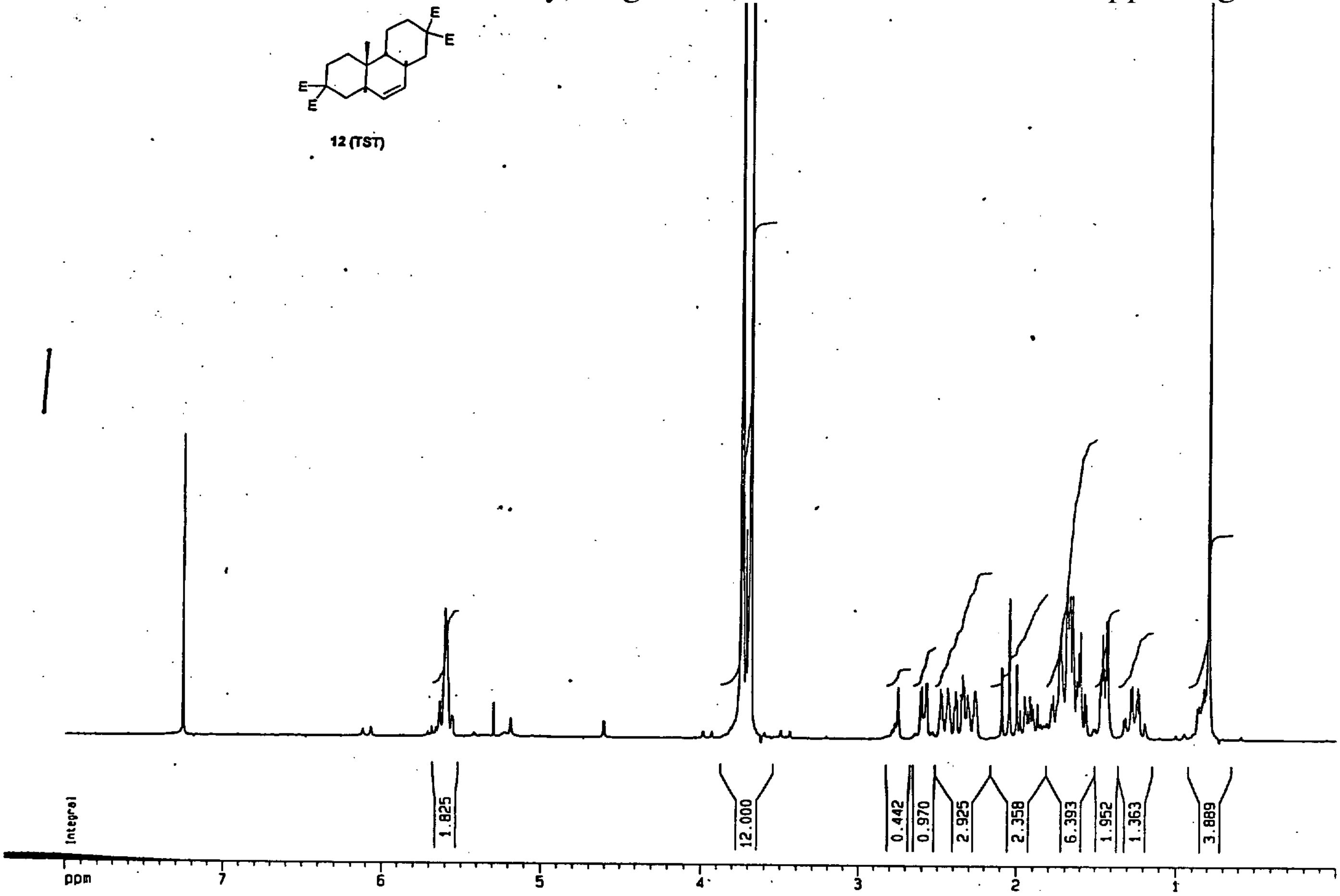
E
E
E
10a (TAC)
E
E
E
E
10b (CAT)
1.019
1.046
12.000
2.625
2.727
11.353
3.300
2.654
1.047
Integral
C6D6 ppm 7.2
7
6
5
4
3
2
1

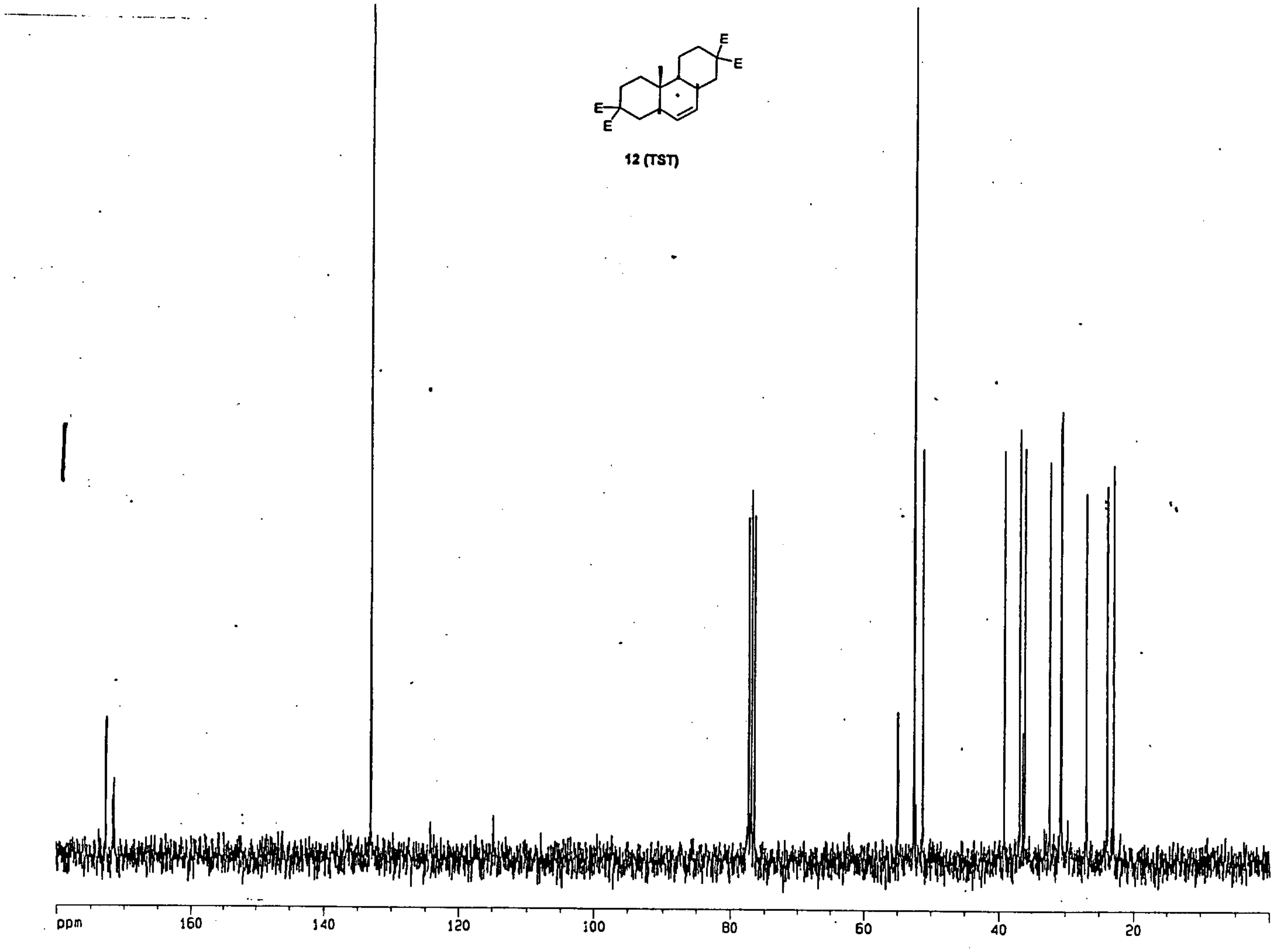


E
E
E
E
10a (TAC)
E
E
E
E
10b (CAT)
ppm
160
140
120
100
80
60
40
20

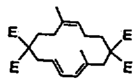

E
E
E
E
11 (TCT)
Integral
1.074
0.845
0.899
0.981
0.843
12.000
4.248
8.957
3.865
ppm
7
6
5
4
3
2
1


E
E
E
E
11 (TCT)
ppm
180
160
140
120
100
80
60
40
20

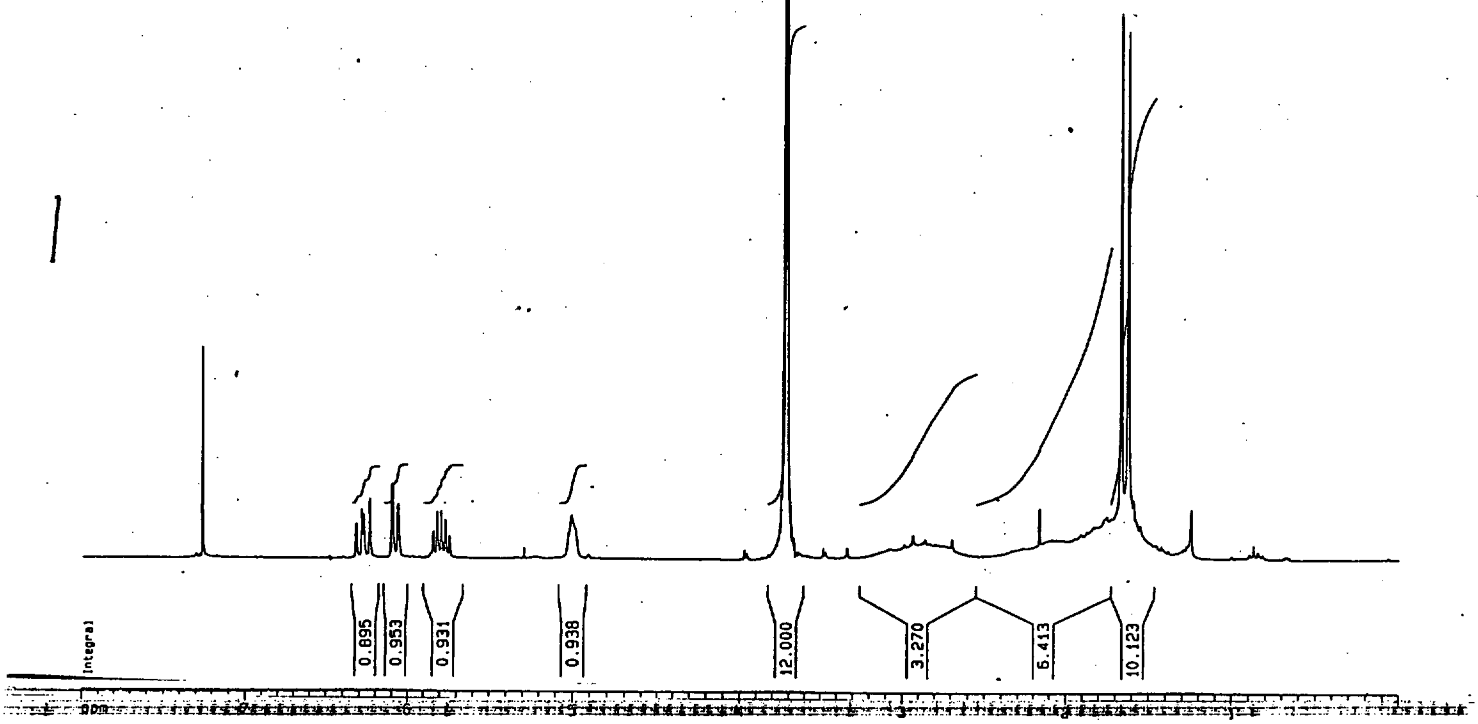

E
E
E
E
12 (TST)
Integral
1.825
12.000
0.442
0.970
2.925
2.358
6.393
1.952
1.363
3.889
ppm
7
6
5
4
3
2
1

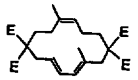

E
E
E
E
12 (TST)
ppm
160
140
120
100
80
60
40
20

2D

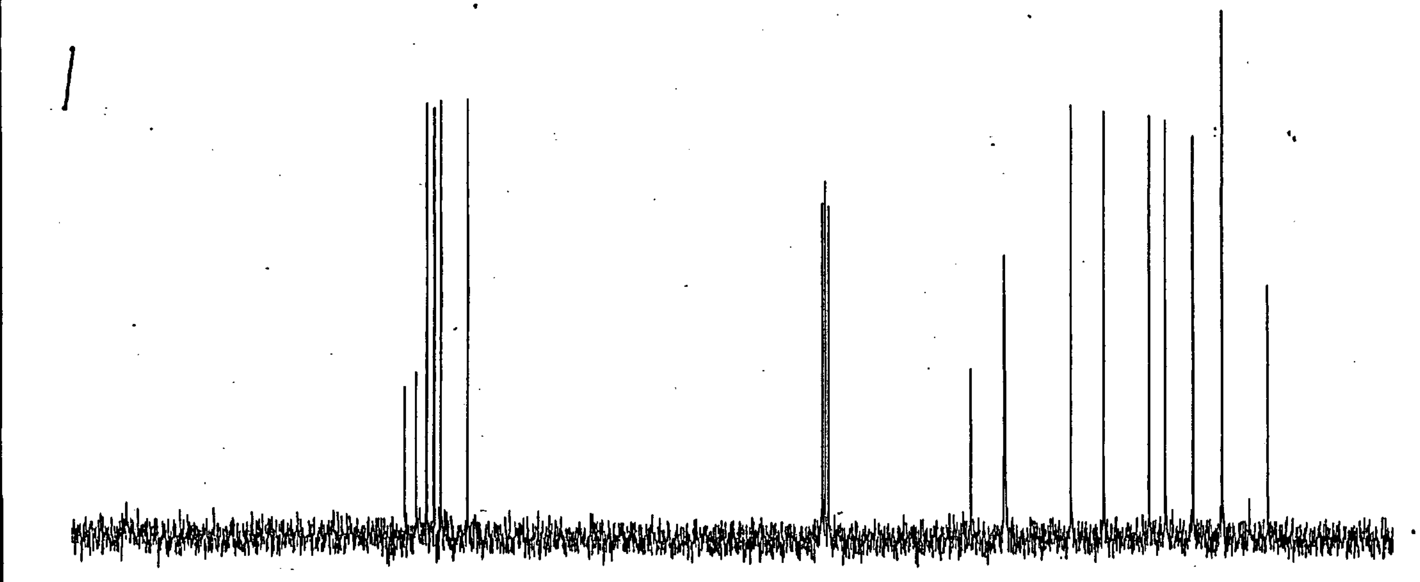


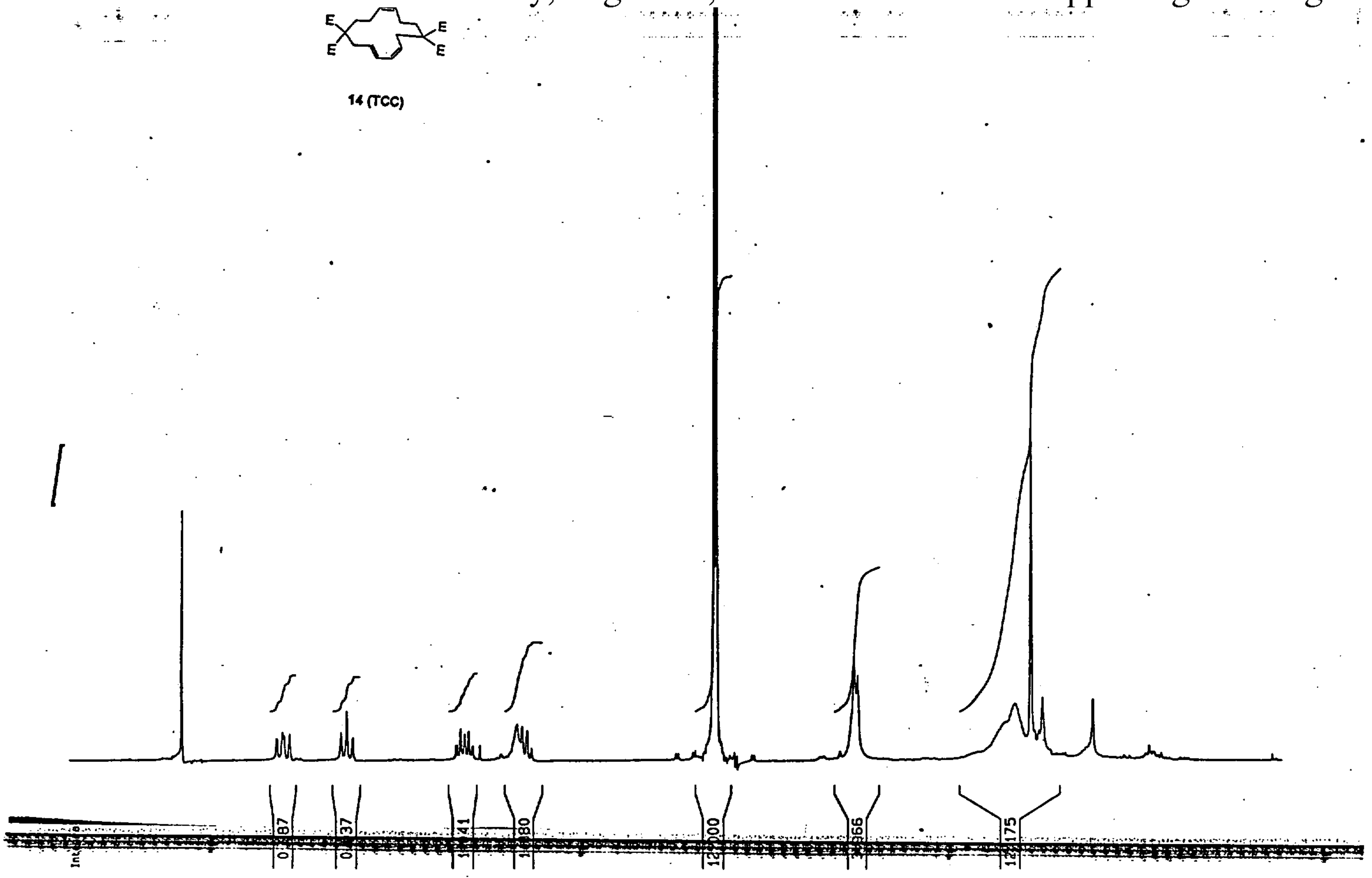
13 (TT^{Me}C)



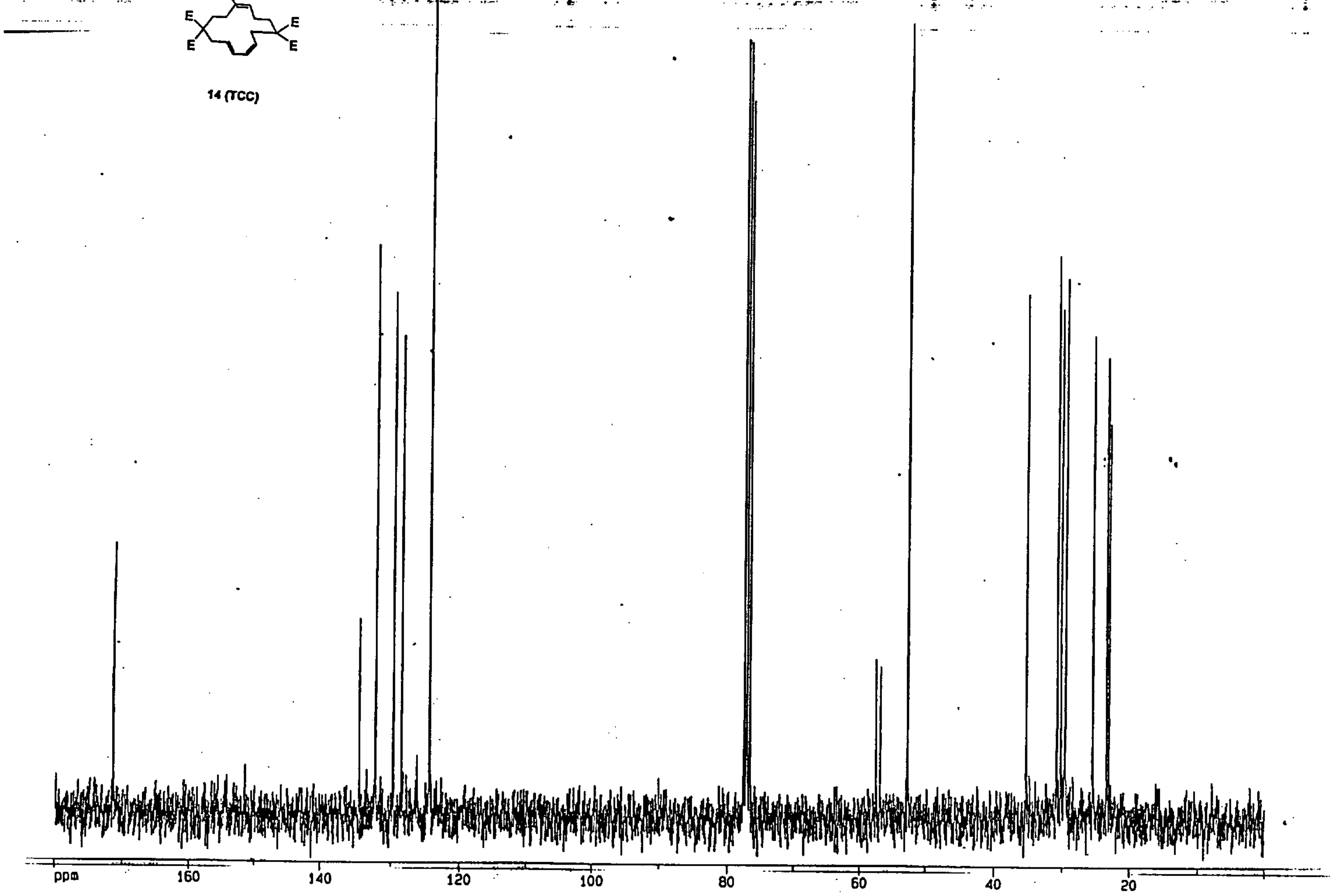


13 (TT^{Me}C)

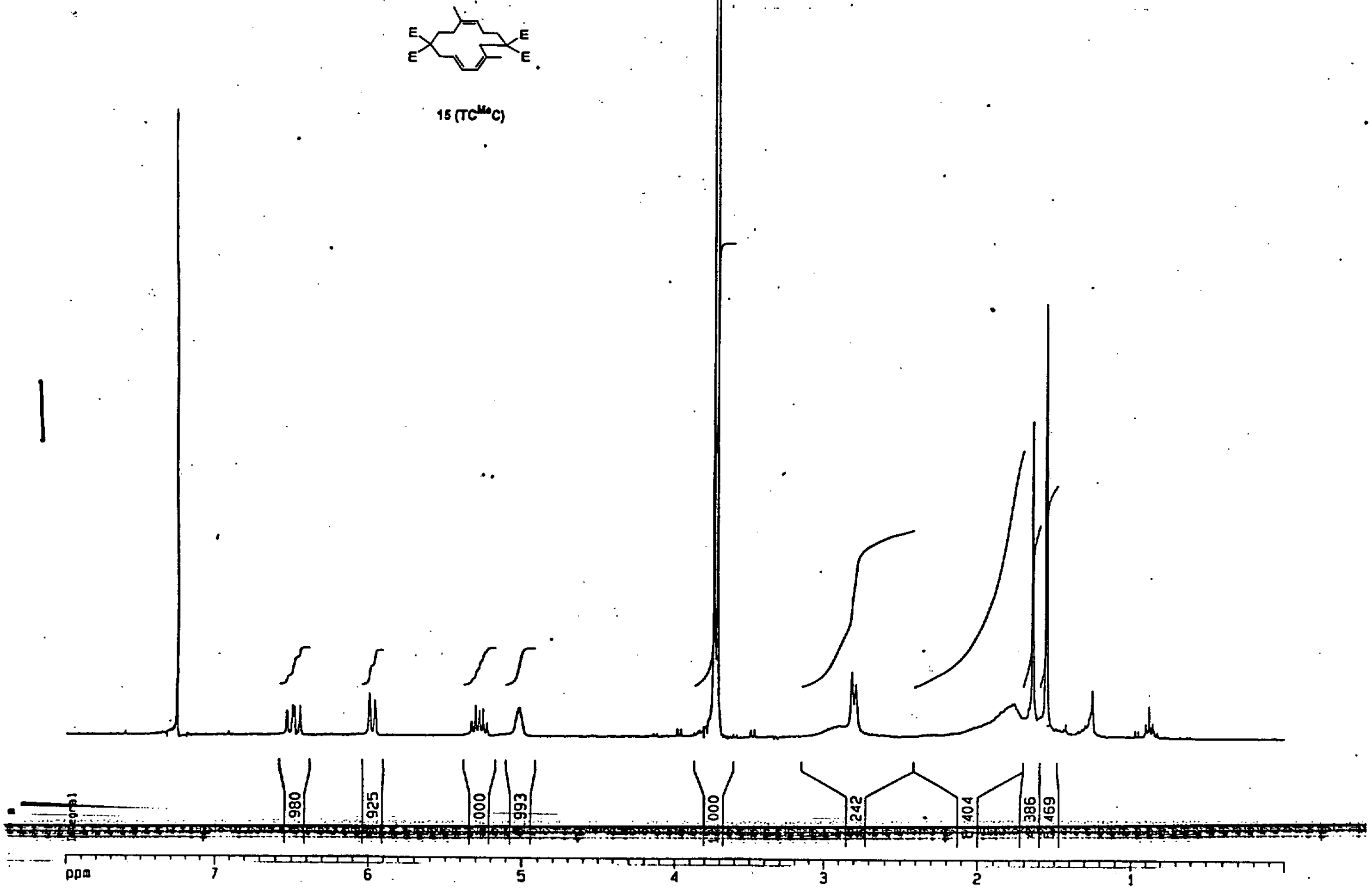


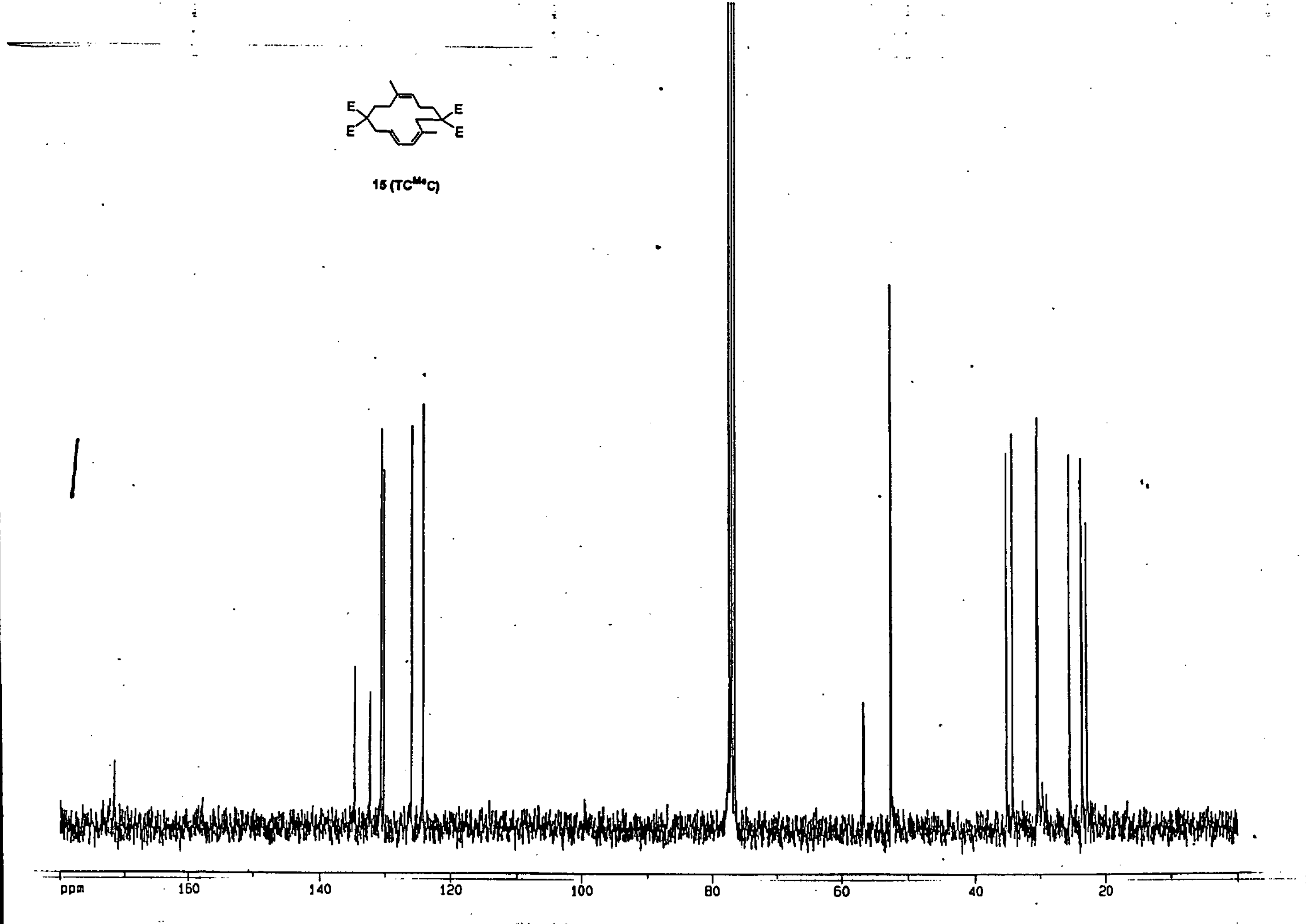


14 (TCC)



14 (TCC)


15 (TC^{Me}C)


15 (TC^{Me}C)