EXPERIMENTAL

All reagents were obtained from the Aldrich Chemical Co. (Milwaukee, WI) or Acros Organics (Pittsburgh, PA) unless stated otherwise. Diethyl ether and tetrahydrofuran were purified by passage through activated alumina columns under nitrogen. Moisture sensitive reactions were carried out in flame dried glassware under dry nitrogen. TLC was carried out on *MERCK Silica Gel 60* thin layer plates. Silica gel chromatography was performed on *Fisher Brand* silica gel (170-400 mesh). 2-Bromo-4-*tert*-butyl-6-iodo-aniline was prepared by literature methods.[1]

1-Bromo-5-*tert*-butyl-2,3-diiodo-benzene (4): To a solution of 2-Bromo-4-*tert*-butyl-6-iodo-aniline (7.08 g, 20.0 mmol) in 100 ml of acetic acid was added 20 mL of concentrated sulfuric acid, and the mixture allowed to stir at room temperature for 30 minutes. The solution was then cooled to 0° C, and a solution of sodium nitrite (1.5 g, 21.7 mmol) in 5 mL of water was added dropwise over 1 hour. The mixture was stirred for a further 30 minutes, and was then poured into a rapidly stirring mixture of potassium iodide (5 g, 30 mmol) and iodine (1.25 g, 5 mmol) in 50 mL of water. The frothy mixture was stirred rapidly for a further 24 hours. The mixture was then diluted with 250 mL of water and extracted three times with hexanes. The organic layer was then extracted twice each with saturated aqueous sodium thiosulfate, saturated sodium bicarbonate and water. Drying ($MgSO_4$) and evaporation led to the crude diiodide as a light-sensitive orange oil, which was used directly in the subsequent coupling reactions. Selected data for the diiodide: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.78 (d, J = 2.2 Hz, 1H), 7.56 (d, J = 2.2 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 154.6, 135.6, 129.4, 129.1, 111.1, 109.2, 34.5, 30.8 ppm; MS *m/z* 466 (M^+), 451 (M^+-Me)

1-Bromo-5-*tert*-butyl-2,3-bis(trimethylsilylethynyl)benzene (5). A solution of 1-Bromo-5-*tert*-butyl-2,3-diiodo-benzene (4.6 g, 10 mmol) in 15 mL of piperidine in a 25 mL screw-capped tube was deoxygenated under a vigorous flow of N_2 for 25 min. To this solution was then added sequentially bis(triphenylphosphine)palladium(II) chloride (70 mg, 1 mol%), copper(I) iodide (190 mg, 10 mol%), and trimethylsilyl acetylene (2.16 g, 2.2 equiv). The tube was then sealed, and heated at 60° C for 12 hours. The amine salts were then filtered away, and the clear solution evaporated to dryness. The dark residue was then taken up in hexanes, and passed through a thick pad of silica gel. Evaporation of the solvent led to the crude diethynyl compound, which was further purified by recrystallization from methanol to give 3.2 grams (80%) of pure compound as a colorless solid (mp 86-88 °C (methanol)); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.51 (d, J = 1.8 Hz, 1H), 7.39 (d, J = 1.8 Hz, 1H), 1.25 (s, 9H), 0.26 (s, 9H), 0.25 (s,9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.4, 129.7, 128.1, 127.0, 125.8, 124.7, 103.2, 103.0, 101.7, 98.6, 34.7, 30.8, -0.03, -0.06 ppm; IR (KBr) 3070, 2961, 2158, 1246, 886, 833 cm^{-1}; MS *m/z* 404 (M^+), 389 (M^+-Me); EI HRMS calcd for $C_{20}H_{29}BrSi_2$: 404.0991. Found: 404.0991.

1-Bromo-5-*tert*-butyl-2,3-di-hex-1-ynyl benzene (6). A solution of 1-Bromo-5-*tert*-butyl-2,3-diiodo-benzene (4.6 g, 10 mmol) in 15 mL of piperidine in a 25 mL screw-capped tube was deoxygenated under a vigorous flow of N_2 for 25 min. To this solution was then added sequentially bis(triphenylphosphine)palladium(II) chloride (70 mg, 1 mol%), copper(I) iodide (190 mg, 10 mol%), and trimethylsilyl acetylene (1.64 g, 2.0 equiv). The tube was then sealed, and heated at 85° C for 36 hours. The amine salts were then filtered away, and the clear solution evaporated to dryness. The dark residue was then taken up in hexanes, and passed through a thick pad of silica gel. Evaporation of the solvent led to the crude diethynyl compound, which was further purified by chromatography on silica gel (hexanes eluent) to give 1.5 grams (40%) of pure compound as a colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.46 (d, J = 1.8 Hz, 1H), 7.32 (d, J = 1.8 Hz, 1H), 2.50 (d, J = 6.8 Hz, 2H), 2.45 (d, J = 6.8Hz, 2H), 1.7-1.4 (m, 8H), 1.24 (s, 9H), 0.93 (t, J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 151.4, 128.8, 127.8, 127.7, 125.4, 125.2, 98.3, 94.2, 79.7, 78.6, 34.5, 30.8, 30.7, 30.6, 21.9 (two n-Bu peaks overlap), 19.4, 19.2, 13.6 (two n-Bu peaks overlap); IR (neat) 3066, 2957, 2931, 2862, 2228, 1455, 893, 734 cm^{-1}; EI HRMS calcd for $C_{22}H_{29}Br$: 372.1453. Found: 372.1439.

5,5'-Di-*tert*-butyl-2,3,2',3'-tetrakis(trimethylsilylethynyl)biphenyl (7). To a solution of 1-Bromo-5-*tert*-butyl-2,3-bis(trimethylsilylethynyl)benzene (1.6 g, 4 mmol) in 5 ml of THF cooled to -78 ^{o}C under N_2 was added n-BuLi (4.1 mmol,1.7 ml, 2.46 M in hexanes). After 20 minutes, solid iodine was added (0.55 g, 2.1 mmol) followed after 30 minutes by 3 mmol (3 ml, 1M solution in Et_2O) of $ZnCl_2$. As the solution warmed to room temperature, bis(triphenylphosphine) palladium(II)chloride (0.03 g, 1 mol %) was added, and after a further 2 hours the reaction mixture was heated to 60° C for 12 hours. The reaction was then cooled and extracted into hexanes, washed with water, dried, and passed through a short pad of silica gel with hexanes. The solvent was removed in vacuo, and the resulting oil chromatographed on silica gel to afford 1.18 g (81%) of a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.5 (d, J = 2.2 Hz, 2H), 7.3 (d, J = 2.2 Hz, 2H) 1.3 (s, 18H), 0.26 (s, 18H), 0.05 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.4, 143.7, 128.6, 127.9, 125.8, 122.3, 104.4, 102.6, 101.2, 97.3, 34.8, 31.0, 0.01, -0.1; IR (neat) 3057, 2950, 2899, 2868, 2146, 1726, 1383, 1244, 866 cm^{-1}; EI HRMS calcd for $C_{40}H_{58}Si_4$: 650.3616. Found: 650.3626.

5,5'-Di-*tert*-butyl-2',3'-di-hex-1-ynyl-2,3-bis(trimethylsilylethynyl)biphenyl (11). To a solution of 1-Bromo-5-*tert*-butyl-2,3-di-hex-1-ynyl benzene (0.75 g, 2 mmol) in 5 ml of THF cooled to -78 ^{o}C under N_2 was added n-BuLi (4.1 mmol,1.7 ml, 2.46 M in hexanes). After 20 minutes, 3 mmol (3 ml, 1M solution in Et_2O) of $ZnCl_2$ was added, and the solution was allowed to warm to room temperature. After stirring for 20 minutes at room temperature, 0.8 grams (2 mmol) of 1-Bromo-5-*tert*-butyl-2,3-bis(trimethylsilylethynyl)benzene and 0.015 g (1 mol%) of bis(triphenylphosphine) palladium(II)chloride were added sequentially, and the solution heated to 65° C for 72 hours. The reaction was then cooled and extracted into hexanes, washed with water, dried, and passed through a short pad of silica gel with hexanes. The solvent was removed in vacuo, and the resulting oil chromatographed on silica gel to yield 0.43 g (35%) of the desired biphenyl as a colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.43 (d, J = 2.2 Hz, 1H), 7.37 (d, J = 1.8 Hz, 2H), 7.28 (d, J = 2.0 Hz, 1H), 2.44 (t, J = 7 Hz, 2H), 2.17 (t, J = 7 Hz, 2H), 1.70-1.20 (m, 8H), 1.26 (s, 18H), 0.91 (t, J = 7 Hz, 3H), 0.80 (t, J = 7 Hz, 3H), 0.24 (s, 9H), 0.02 (, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.1, 149.1, 144.2, 142.8, 128.34, 128.30, 128.0, 126.9, 126.4, 125.8, 122.6, 122.1, 104.5, 102.6, 100.9, 97.0, 96.5, 92.8, 80.5, 78.8, 34.64, 34.57, 31.03, 30.92, 30.7 (n-Bu peaks overlap), 21.9, 21.7, 19.3 (n-Bu peaks overlap), 13.56, 13.51, -0.02, -0.15; IR (neat) 2959, 2871, 2154, 1589, 1429, 1248 cm^{-1}; MS *m/z* 618 (M^+), 575 (M^+-Pr); EI HRMS calcd for $C_{42}H_{58}Si_2$: 618.4077. Found: 618.4093.

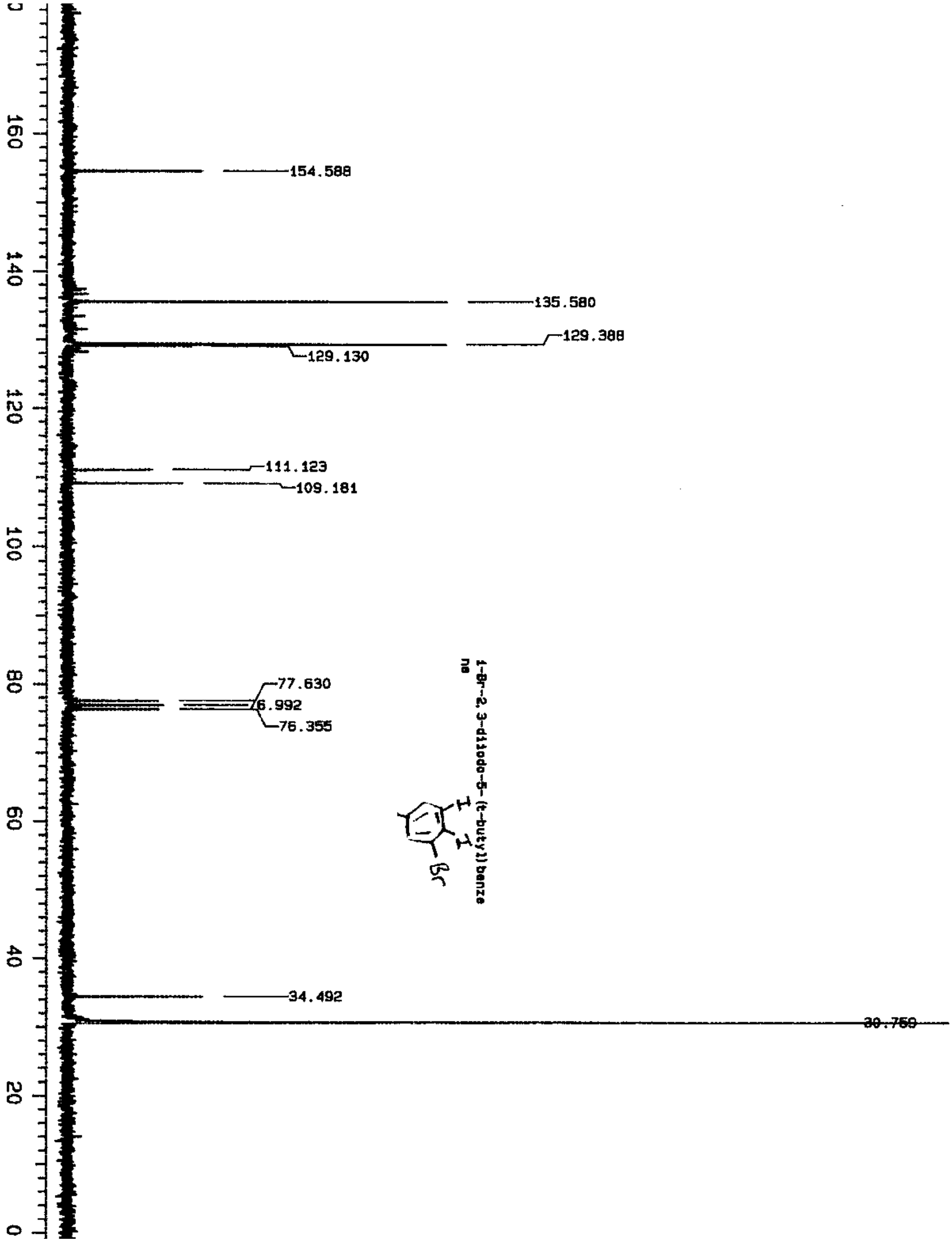
2,11-Di-*tert*-butyl-perylene (9) and 3,3'-Di-*tert*-butyl-[1,1']binaphthyl (10). Quantitative desilylation of 0.65 g (1 mmol) of 5,5'-Di-*tert*-butyl-2,3,2',3'-tetrakis(trimethylsilylethynyl)biphenyl was accomplished by stirring this compound in 5 mL methanol / 1 mL THF to which 0.1 g of NaH had been added for 30 minutes. The desilylated compound was extracted into hexanes, dried, evaporated and immediately taken up in 100 mL of benzene. This solution was then deoxygenated by sparging with dry nitrogen for 30 minutes. After this time, 10 mL of 1,4-cyclohexadiene was added, and the solution was sealed under a blanket of nitrogen in a steel bomb. After heating this compound to 180° C for 2 hours, the bomb was cooled, and the benzene/cyclohexadiene mixture was recovered in vacuo. The residue was chromatographed on reverse-phase silica gel (C-18, pentane eluent) to yield one major product and one minor product. The major product (0.425 g, 66%) was 2,11-Di-*tert*-butyl-perylene, a pale yellow amorphous solid: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.3 (d, J = 1.8 Hz, 2H), 8.1 (dd, J = 7.4 Hz, J = 1 Hz, 2H), 7.6 (d, J = 2 Hz, 4H), 7.5-7.4 (m, 2H), 1.5 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 148.9, 134.9, 131.1, 130.0, 128.4, 127.8, 126.5, 123.3, 119.5, 118.5, 34.8, 31.2; IR (neat) 3049, 2960, 2909, 2852, 1598, 1470, 1362 cm^{-1}; MS *m/z* 364 (M^+), 349 (M^+-CH_3); EI HRMS calcd for $C_{28}H_{28}$: 364.2191. Found: 364.2205.

The minor product (0.064 g, 10%) was 3,3'-Di-*tert*-butyl-[1,1']binaphthyl, a white solid (mp 170-172 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.95-7.90 (m, 4H), 7.6 (d, J = 2.2 Hz, 2H), 7.5-7.4 (m, 4H), 7.3-7.2 (m, 2H), 1.5 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 148.1, 138.4, 133.6, 131.3, 128.2, 127.0, 126.2, 125.8, 125.3, 122.8, 34.9, 31.2; IR (KBr) 3053, 2953, 2905, 2866, 1593, 1476, 1372, 1272, 881, 755 cm^{-1}; MS *m/z* 366 (M^+), 351 (M^+-CH_3); EI HRMS calcd for $C_{28}H_{30}$: 366.2348. Found: 366.2355.

3-*tert*-Butyl-1(5-*tert*-butyl-2,3-di-hex-1-ynylphenyl)naphthalene (13). Desilylation of 0.17 g (0.275 mmol) of 5,5'-Di-*tert*-butyl-2',3'-di-hex-1-ynyl-2,3-bis(trimethylsilyl- ethynyl)biphenyl was accomplished by stirring this compound in 5 mL methanol / 1 mL THF to which 0.1 g of NaH had been added for 30 minutes. The desilylated compound was extracted into hexanes, dried, evaporated and immediately taken up in 50 mL of benzene. This solution was then deoxygenated by sparging with dry nitrogen for 30 minutes. After this time, 5 mL of 1,4-cyclohexadiene was added, and the solution was sealed under a blanket of nitrogen in a steel bomb. After heating this compound to 170° C for 2 hours, the bomb was cooled, and the benzene/cyclohexadiene mixture was recovered in vacuo. The residue was chromatographed repeatedly on silica gel (pentane eluent) to yield the title compound as the only significant product (0.025 g of a colorless oil, 20%): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.86-7.74 (m, 2H), 7.60-7.26 (m, 6H), 2.5 (t, J = 6.6 Hz, 2H), 2.0 (t, J = 6.6 Hz, 2H), 1.65-1.23 (broad m, 5H), 1.4 (s, 9H), 1.3 (s, 9H), 1.1-0.7 (m, 6H), 0.6 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 149.6, 147.5, 143.1, 138.9, 133.5, 130.2, 128.0, 127.8, 127.3, 126.6, 125.9, 125.4, 125.0, 122.5, 96.8, 93.2, 80.4, 78.8, 34.8, 34.7, 31.2, 31.1, 30.9, 30.3, 22.0, 21.3, 19.4, 19.1, 13.7, 13.5 ; IR (neat) 2966, 2931, 2857, 2223, 1459 cm^{-1}; MS *m/z* 476 (M^+), 433 (M^+-C_3H_7); EI HRMS calcd for $C_{36}H_{44}$: 476.3443. Found: 476.3458.

Literature Cited

1. Höger, S.; Meckenstock, A.-D.; Pellen, H. *J. Org. Chem.* **1997**, *62*, 4556.



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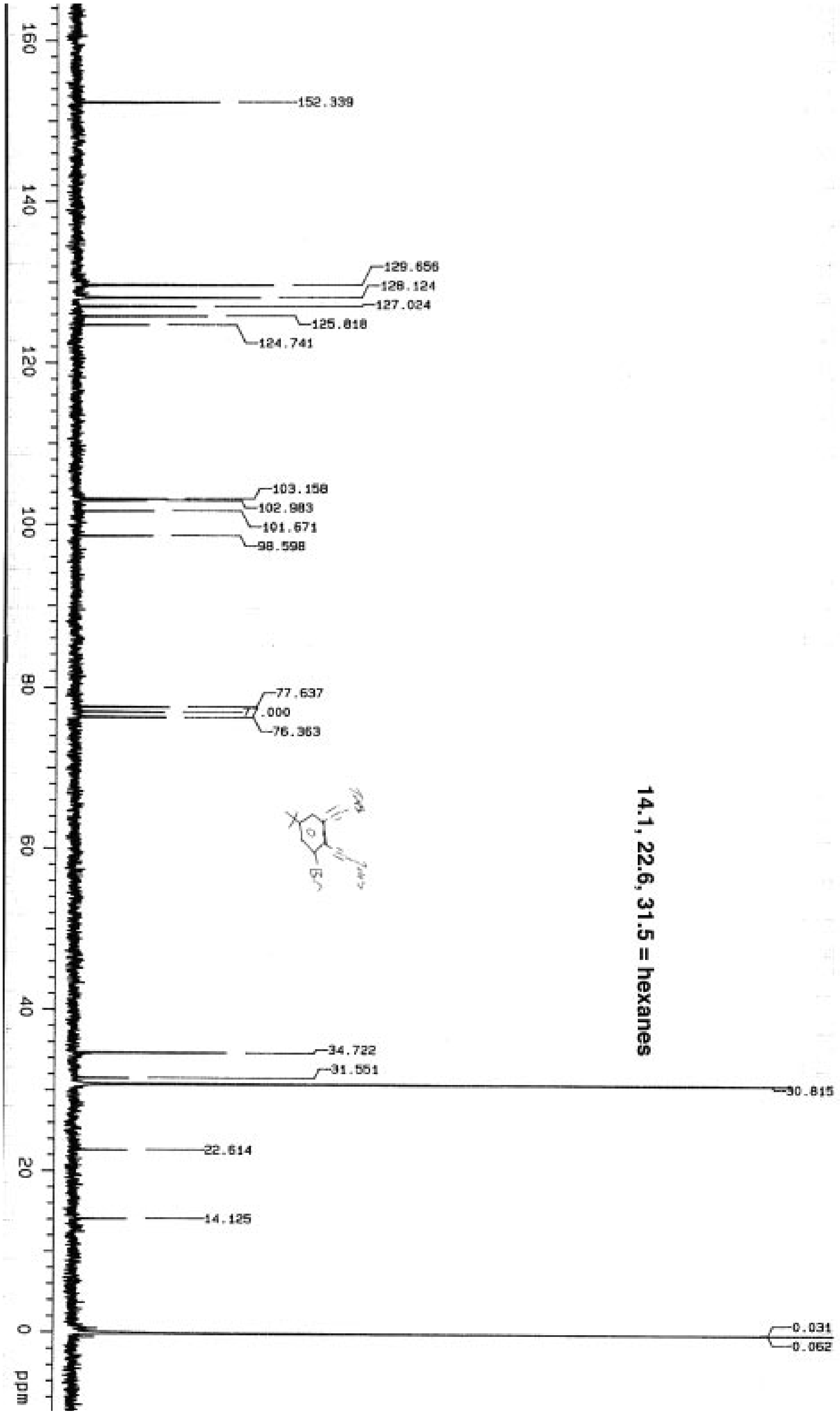

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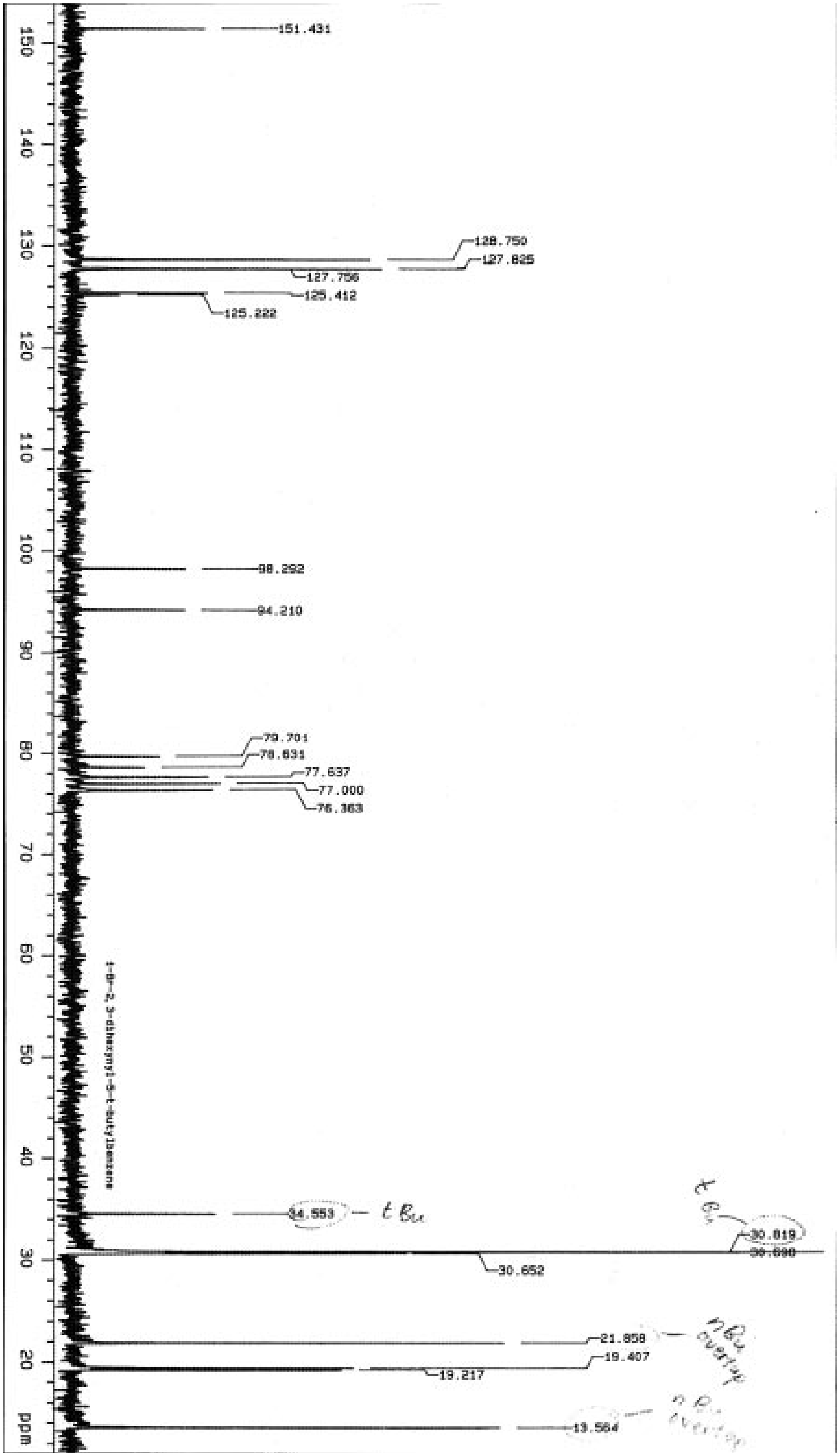
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34.553
t Bu
t Bu
30.819
30.690
30.652
21.858
19.407
19.217
n Bu overlap
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n Bu overlap
1-Br-2,3-dihexynyl-5-t-butylbenzene
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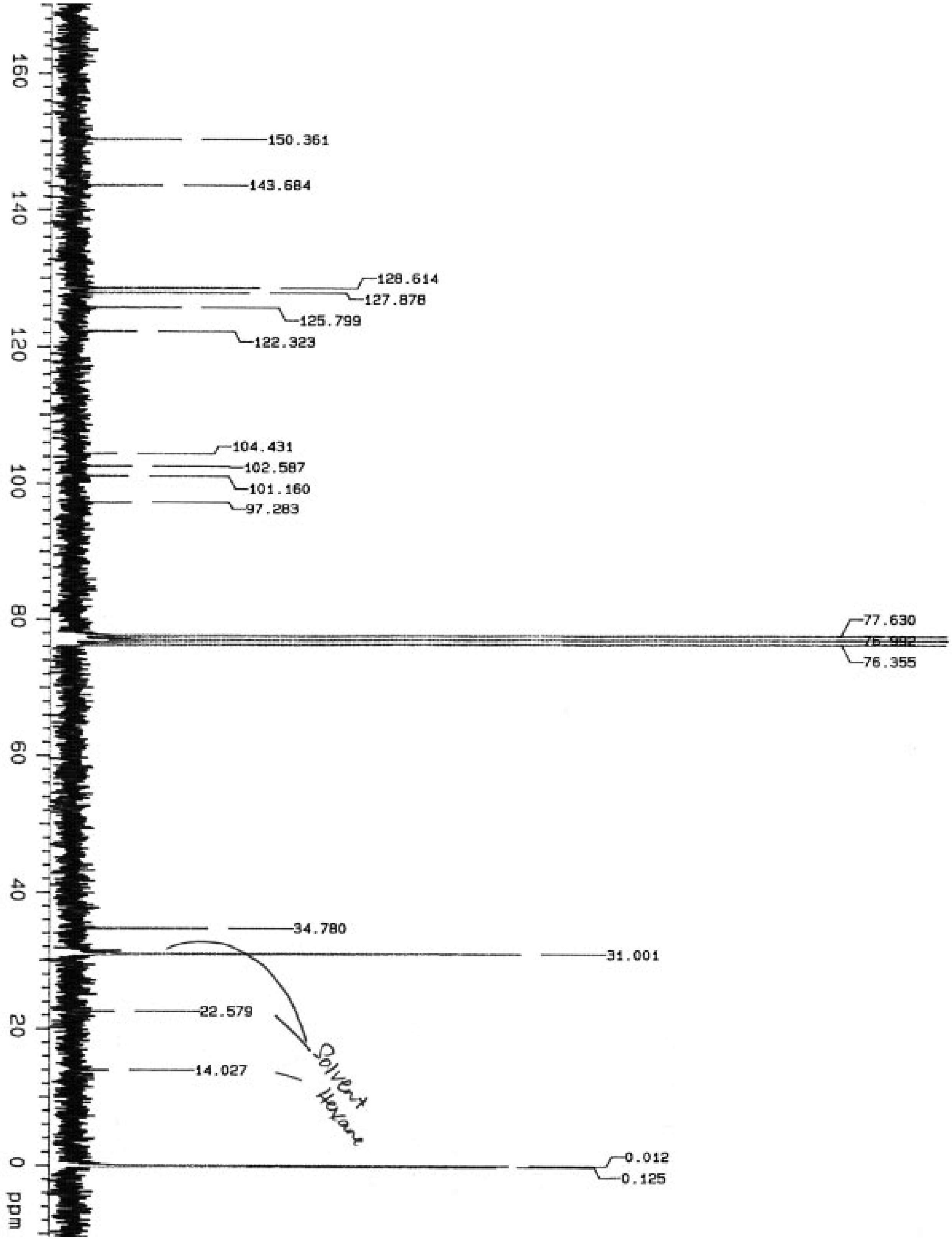

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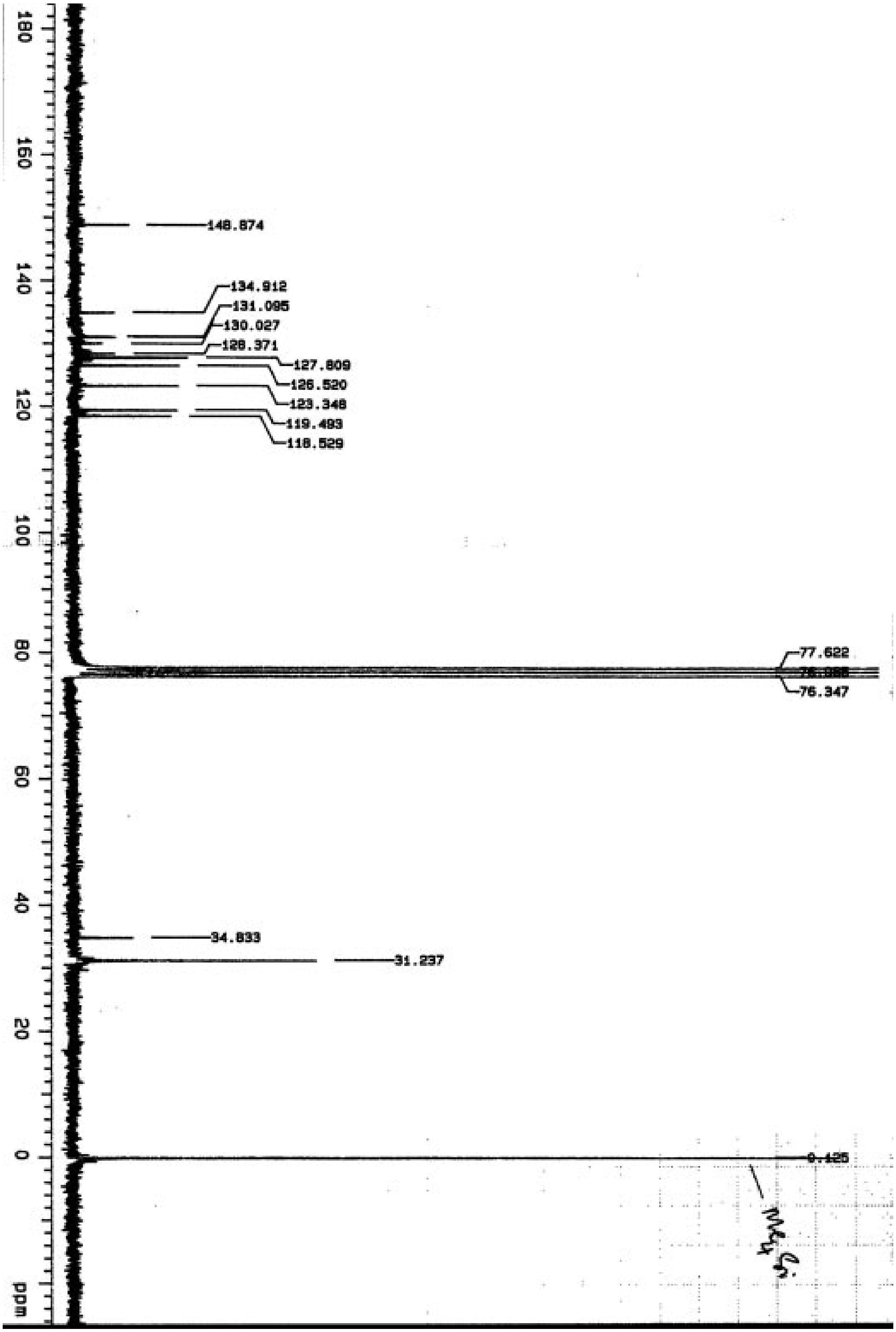
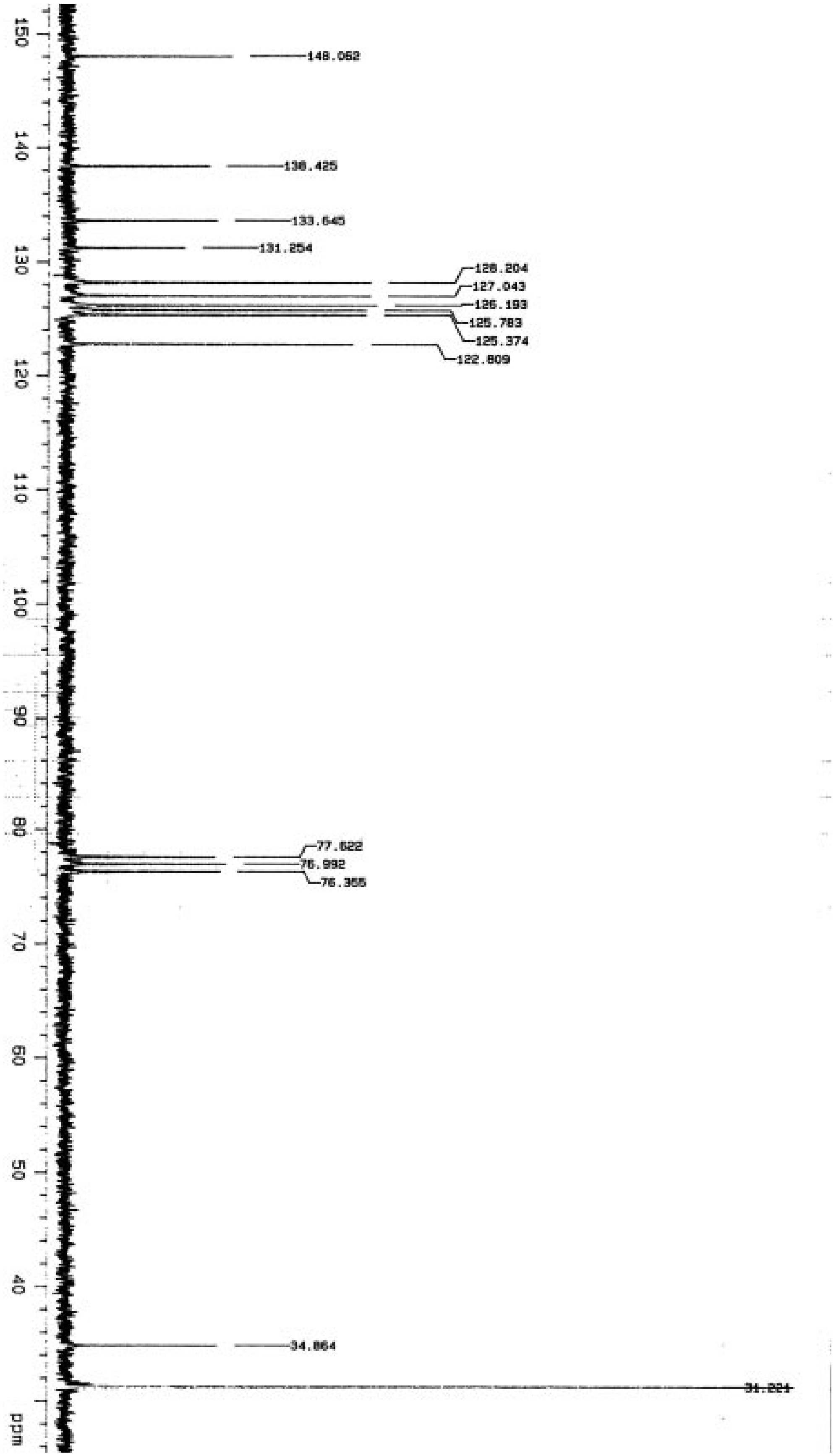
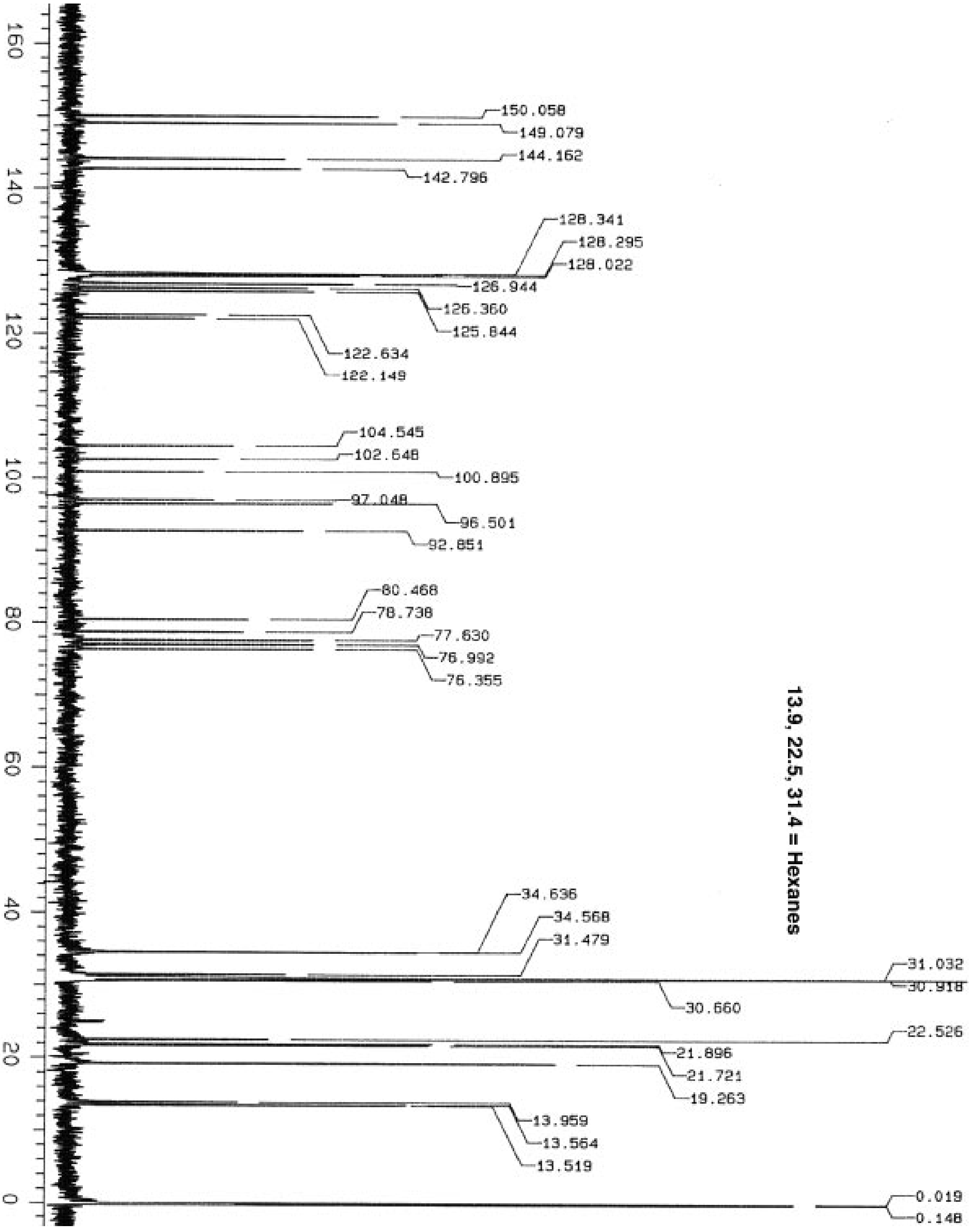


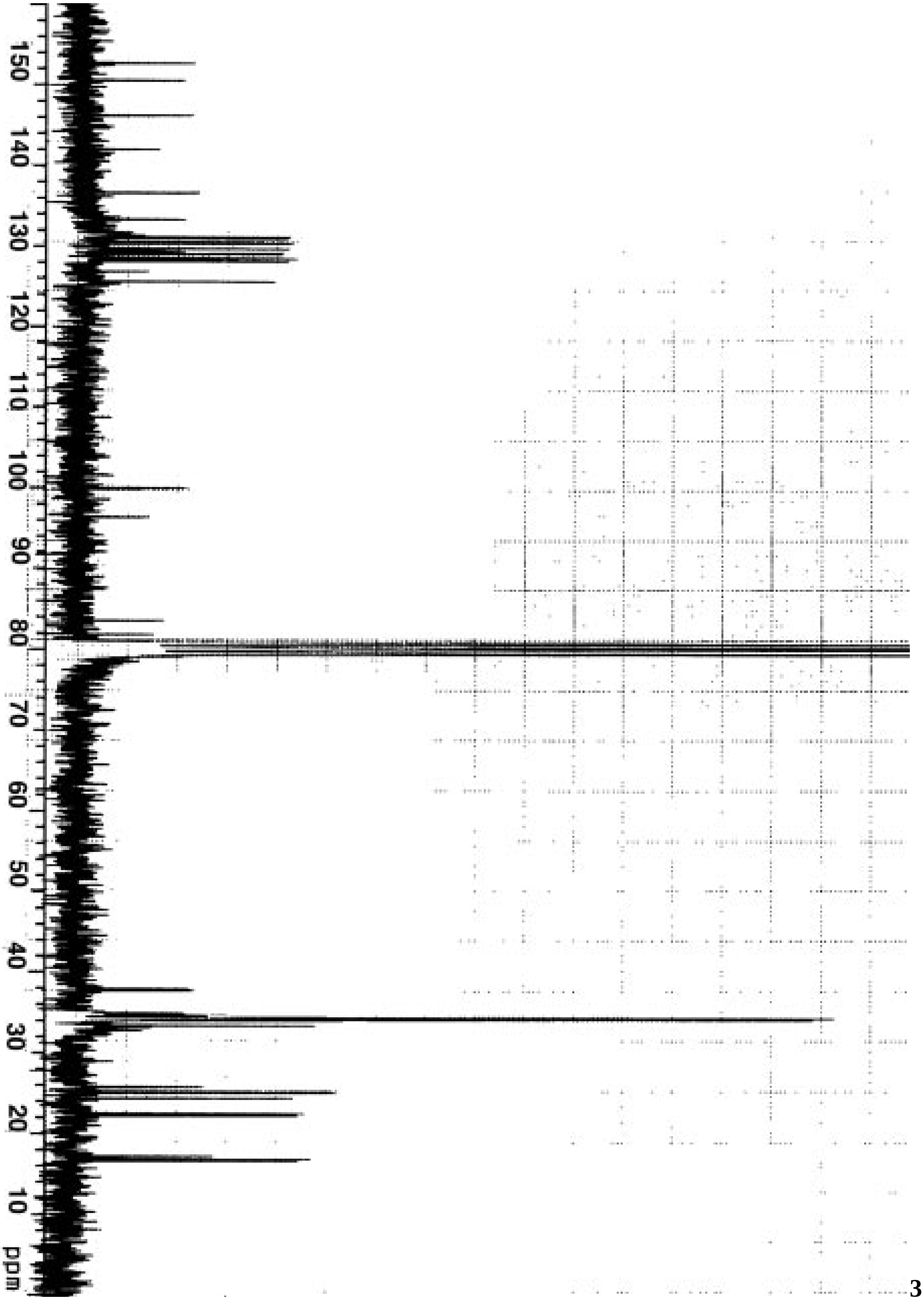
2,11-Di-*tert*-butyl-perylene (9)



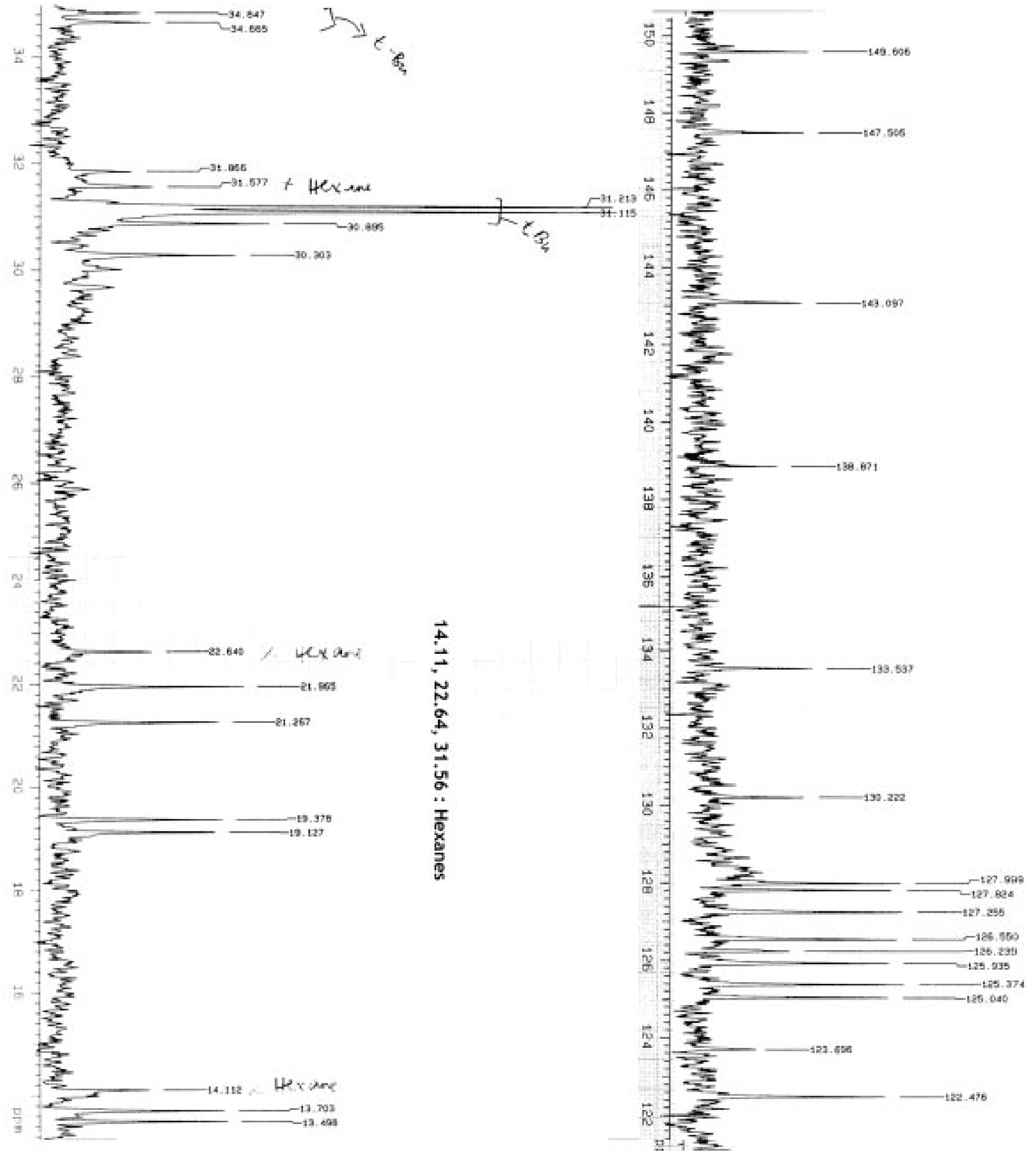
3,3'-Di-*tert*-butyl-[1,1']binaphthyl (10)



5,5'-Di-*tert*-butyl-2',3'-di-hex-1-ynyl-2,3-bis(trimethylsilylethynyl)biphenyl (11)



3-*tert*-Butyl-1(5-*tert*-butyl-2,3-di-hex-1-ynylphenyl)naphthalene (13)



3-*tert*-Butyl-1(5-*tert*-butyl-2,3-di-hex-1-ynylphenyl)naphthalene (13)