

## EXPERIMENTAL

All reagents were obtained from the Aldrich Chemical Co. (Milwaukee, WI) or Acros Organics (Pittsburgh, PA) unless stated otherwise. Et<sub>2</sub>O and THF were purified by passage through activated alumina columns under nitrogen. Moisture sensitive reactions were carried out in flame dried glassware under N<sub>2</sub>. 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). Elemental analysis was performed by Desert Analytics, Tucson AZ.

1,2-Bis(trimethylsilylethynyl)-benzene<sup>1</sup> and 1,2 diethynyl-benzene<sup>2</sup> were prepared according to the literature; spectral data matched accordingly.

**1,2-Bis(bromoethynyl) benzene.** To a solution of 1,2-bis(trimethylsilylethynyl) benzene ( 5.73 g, 21.2 mmol) in 100ml acetone was added N-bromosuccinamide (9.42 g, 52.9 mmol) and AgNO<sub>3</sub> ( 0.3 g, 1.77mmol). The suspension was stirred at 25°C for 10 h, after which the solvent was removed via rotary evaporation. The substrate was passed through a pad of silica gel with hexanes. The solvent was evaporated to yield 6.01 g (100 %) of dibromide as an unstable red oil that was subjected to cycloaromatization immediately.

**2,3-Dibromonaphthalene.** A solution of 1,2-Bis(bromoethynyl)benzene (0.5 g, 1.76 mmol) was deoxygenated under N<sub>2</sub> in 45 ml benzene for 1 h. 1,4-Cyclohexadiene (4.5 ml, 10% v/v) was added and the mixture was sealed under N<sub>2</sub> in a steel bomb, which was heated to 180°C for 2h (350 psi was the highest pressure reached). The benzene/cyclohexadiene mixture was recovered in vacuo, after which the residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> and passed through a pad of silica gel with 9:1 hexane/CH<sub>2</sub>Cl<sub>2</sub> as eluent, to remove any polymeric / oligomeric materials. The solvent was evaporated and the resulting solid recrystallized from heptane to yield 0.35 g (70%) of a light yellow solid, mp 137-139°C (lit 138-140°C<sup>4</sup>). <sup>1</sup>H NMR (200MHz, CDCl<sub>3</sub>) δ 7.92 (s, 2H), 7.51 (m, 2H), 7.30 (m, 2H); <sup>13</sup>C NMR (50MHz, CDCl<sub>3</sub>) δ 133.0, 132.2, 127.2, 126.8, 121.9. MS m/z (rel intensity) 286 (100, M<sup>+</sup>), 207(60, M-Br<sup>+</sup>). Anal. Calcd for C<sub>10</sub>H<sub>6</sub>Br<sub>2</sub>: C, 42.00; H, 2.11, found: C, 42.17; H, 2.01.

**2,3-Bis(trimethylsilylethynyl)naphthalene.** To a solution of trimethylsilyl acetylene (0.41 g, 4.2 mmol) in 5 ml THF cooled to -78 °C under N<sub>2</sub> was added BuLi (4.3 mmol, 1.74 ml, 2.46 M in hexanes). The mixture was allowed to warm to 25 °C and 5 mmol (5 ml, 1M solution in Et<sub>2</sub>O) ZnCl<sub>2</sub> was added quickly. After 15 min [1,1' bis(diphenylphosphino)-ferrocene]palladium(II)chloride (0.1 g, 2 mol %) and 2,3-dibromonaphthalene (0.2 g, 0.7 mmol) were added and the reaction heated to reflux. After 12 h, the reaction was 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 to afford 0.18 g (81%) of a yellow solid, mp 92-93 °C. FTIR (CCl<sub>4</sub>) 3055, 2959, 2151 cm<sup>-1</sup>. <sup>1</sup>H NMR (200MHz, CDCl<sub>3</sub>) δ 7.79 (s, 2 H), 7.42 (m, 2 H), 7.22 (m, 2 H), 0.13 (s, 18 H); <sup>13</sup>C NMR (50MHz, CDCl<sub>3</sub>) δ 132.50, 132.19, 127.48, 127.24, 122.07, 103.42, 97.71, 0.09; MS m/z (rel intensity) 320.3 (100, M<sup>+</sup>), 305.3 (60, M-Me), 217.2 (20). Anal. Calcd for C<sub>20</sub>H<sub>24</sub>Si<sub>2</sub>: C, 74.93; H, 7.54, found: C, 75.25; H, 7.34.

**2,3-Bis(bromoethynyl)naphthalene.** To a solution of 2,3-bis(trimethylsilylethynyl)naphthalene (0.36 g, 1.1 mmol) in 15 ml acetone was added N-bromosuccinimide (0.46 g, 2.52 mmol) and AgNO<sub>3</sub> (0.20 g, 1.2 mmol). The suspension was stirred at 25 °C for 10 h, after which the solvent was removed in vacuo. The substrate was taken up in hexanes, and passed through a pad of silica gel with hexanes. The solvent was evaporated to yield 0.36 g of an unstable red oil, which was used directly in the next step.

**2,3-Dibromoanthracene.** A solution of 2,3-bis(bromoethynyl)naphthalene (0.33g, 1 mmol) was deoxygenated by sparging under N<sub>2</sub> in 40 ml benzene for 1 h. 1,4-Cyclohexadiene (4 ml, 10% v/v) was added and the mixture was sealed under N<sub>2</sub> in a steel bomb, which was heated to 180 °C for 2h (300 psi was the highest pressure reached). The benzene/cyclohexadiene mixture was recovered in vacuo, after which the residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> and passed through a pad of silica gel with 9:1 hexane/CH<sub>2</sub>Cl<sub>2</sub> as eluent. The solvent was evaporated to yield 0.27g of a light sandy brown solid, which was used directly in the next step.

**2,3-Bis(trimethylsilylethynyl) anthracene.** To a solution of trimethylsilyl acetylene (0.35 g, 3.6 mmol) in 5 ml THF cooled to -78 °C under N<sub>2</sub> was added butyllithium (3.8 mmol, 1.54 ml, 2.46 M in hexanes), after which the reaction mixture was allowed to warm to 25 °C. ZnCl<sub>2</sub> (5 mmol, 1M solution in Et<sub>2</sub>O) was added, followed after 15 min by [1,1'-bis(diphenylphosphino)-ferrocene]palladium(II)chloride (0.1 g, 2 mol %) and the crude cycloaromatization product (2,3-dibromoanthracene) (0.2 g, 0.60 mmol), and the reaction was heated to reflux. After 12 h, the reaction was cooled and extracted into hexanes, washed with water, dried, and passed through a short pad of silica gel with hexanes. The crude oil was purified by silica gel chromatography with hexane eluent to afford 0.19g (86%) of canary yellow plates, mp 210-211°C. FTIR (CCl<sub>4</sub>) 2959, 2157 cm<sup>-1</sup>. <sup>1</sup>H NMR (200MHz, CDCl<sub>3</sub>) δ 8.02(s, 2 H), 7.92(s, 2 H), 7.69(m, 2 H), 7.20(m, 2 H), 0.11(s, 18 H); <sup>13</sup>C NMR (50MHz, CDCl<sub>3</sub>) δ 133.16, 132.43, 129.93, 128.26, 126.21, 126.14, 121.00, 103.60, 98.07, 0.11; MS m/z (rel intensity) 370.2 (100, M<sup>+</sup>), 355.1 (25, M-Me). Anal. Calcd for C<sub>24</sub>H<sub>26</sub>Si<sub>2</sub>: C, 77.77; H, 7.07, found: C, 77.59; H, 7.24.

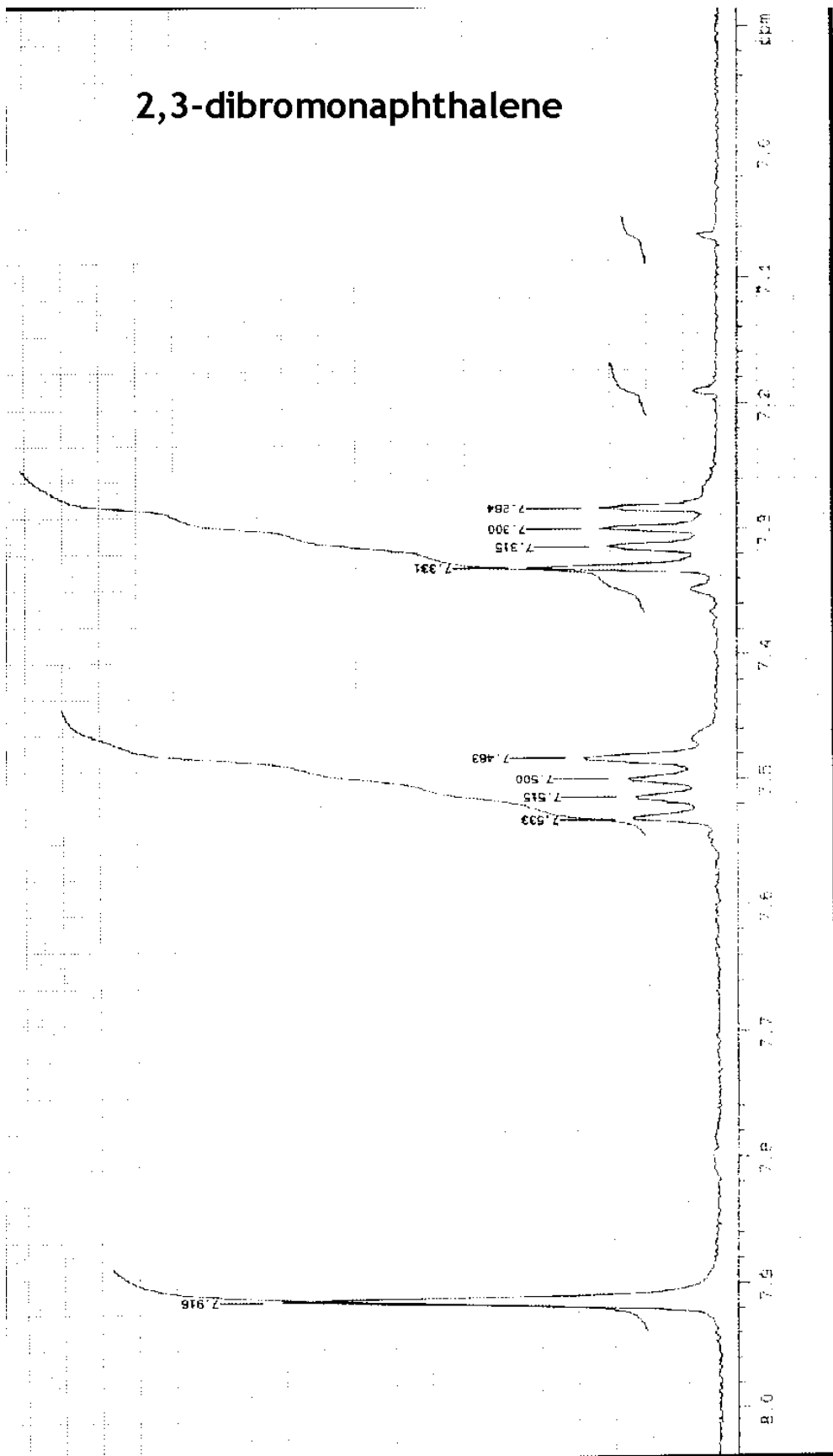
**Naphthacene.** To a solution of 2,3-Bis(trimethylsilylethynyl) anthracene (0.15 g, 0.45 mmol) in 2ml THF was added 5ml methanol, followed by NaH (0.02 g, 0.8 mmol). The suspension was allowed to stir for 2 h, after which it was poured into 500 ml H<sub>2</sub>O, extracted with 3 X 200 ml CH<sub>2</sub>Cl<sub>2</sub>, dried, and passed through a thin silica pad. Evaporation of solvent led to crude diethynyl anthracene. A solution of 60mg of this substance (0.27 mmol) in 40 ml benzene was deoxygenated under N<sub>2</sub> for 1 h. 1,4-Cyclohexadiene (4 ml, 10% v/v) was added and the mixture was sealed under N<sub>2</sub> in a steel bomb, which was heated to 160°C overnight (240 psi was the highest pressure reached). The benzene/cyclohexadiene mixture was recovered in vacuo, after which the residue was taken up in 1L of CH<sub>2</sub>Cl<sub>2</sub> and adsorbed onto silica gel by evaporation. The product was purified by silica gel chromatography with hexane eluent. The solvent was evaporated and the solid recrystallized from methylene chloride to yield 40mg (64%) of insoluble

orange plates, mp >300°C (lit 341°C<sup>4</sup>). <sup>1</sup>H NMR (200MHz, CDCl<sub>3</sub>) δ 7.40 (dd, 4H), 8.00 (dd, 4H), 8.67 (s, 4H). MS m/z (rel intensity) 228.1 (100%, M<sup>+</sup>), 114.0 (20%). Anal. Calcd for C<sub>18</sub>H<sub>12</sub>: C, 94.70; H, 5.29, found: C, 94.75; H, 5.24.

#### Literature Cited

1. Takahashi, S.; Kuroyama, Y.; Sonagashira, K.; Hagihara, N. *Synthesis*, **1980**, 627.
2. Semmelhack, M.F.; Neu, T.; Foubelo, F. *Tetrahedron Lett.*, **1992**, 3277.
3. Mallouli, A.; Lepage, Y. *Synthesis*, **1980**, 689.
4. Hart, H.; Luo, J. *J.Org. Chem.*, **1987**, 4833.

# 2,3-dibromonaphthalene

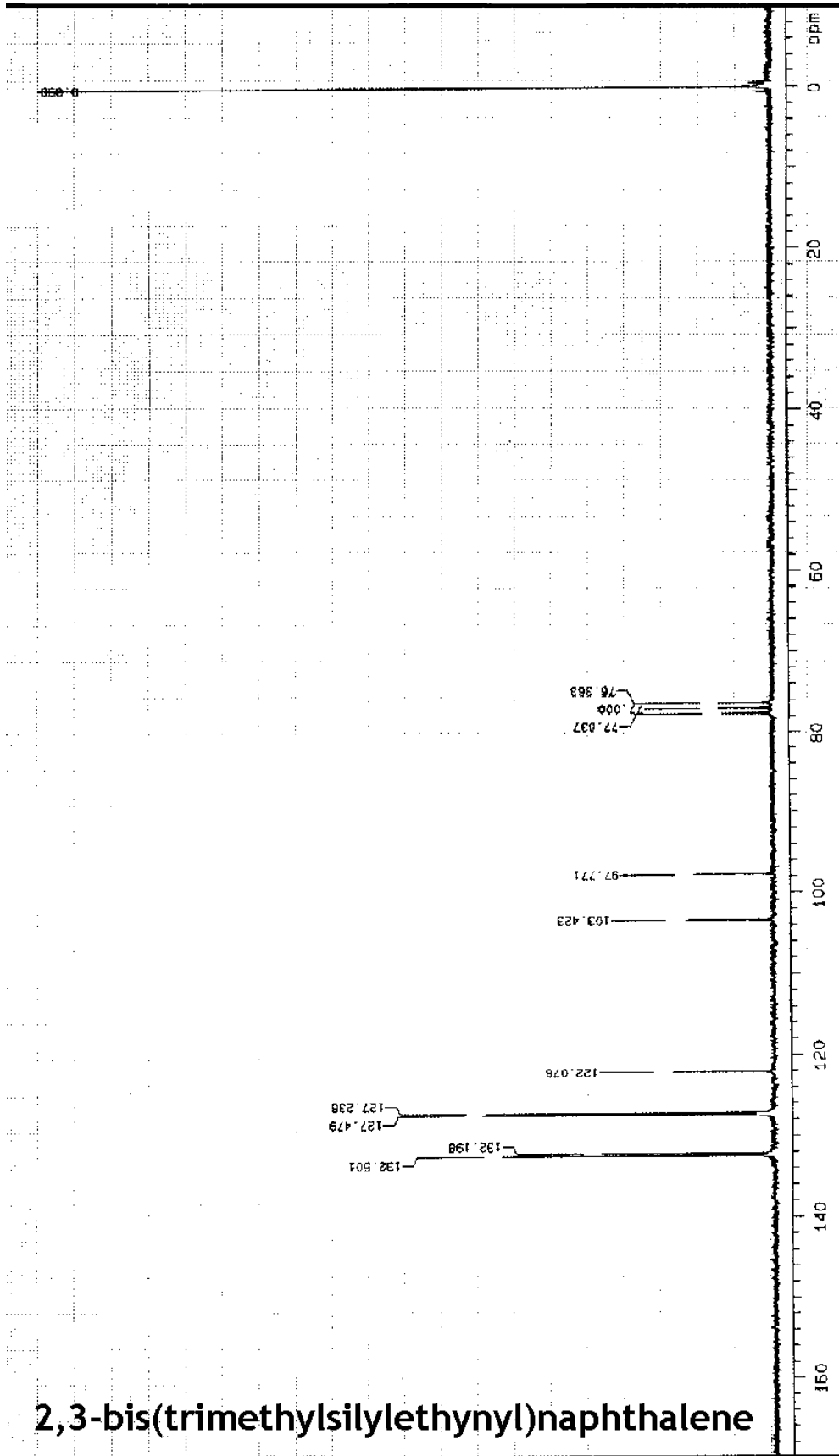


NAME		EXP. NO.		DATE	
NAME	199 9258	EXP. NO.	1023	DATE	0
CONC.	3000.3	INSTR.	200	PROG.	0
NO. OF	1.984	NO. OF	1375.4	NO. OF	0
NO. OF	1.0	NO. OF	00013	NO. OF	0
SAMPLE		EXPERIMENT		PLOT PROCESSING	
4H STANFORD PARAMETRS		IN NOT USED		IN NOT USED	
68MINI-C/H		DOT USED		DOT USED	
4/21/97 M.L.		230.4		1375.4	





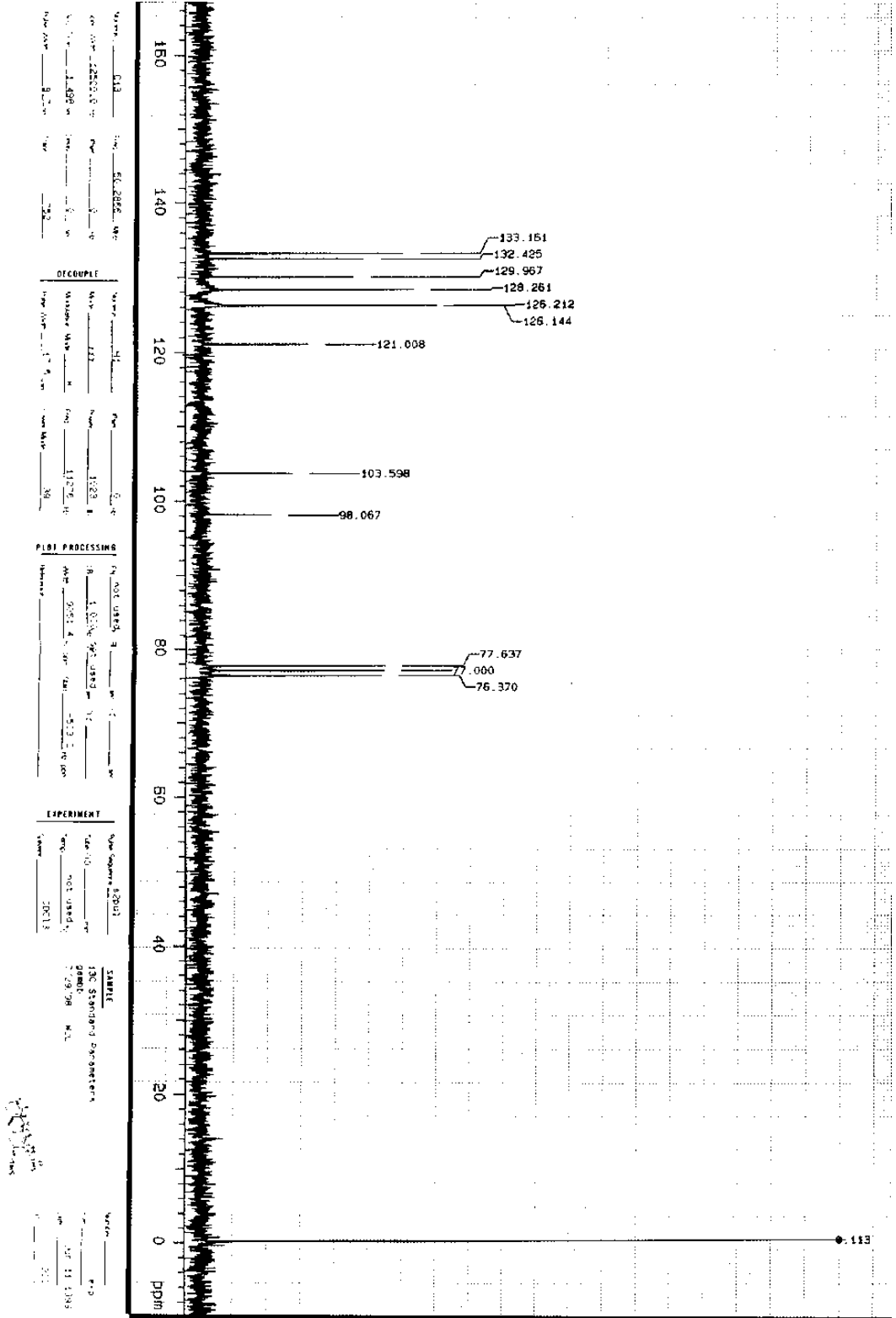
# 2,3-bis(trimethylsilylethynyl)naphthalene



RECORD		EXPERIMENT		SAMPLE	
NAME	C13	NAME	13C Standard Parameters	NAME	EXP
INSTRUM	12500.0 Hz	DATE	7/29/98	DATE	JUN 4 1998
PROBHD	1.498 mm	TIME	17:53	PROBHD	200
NUC1	13C	NUC2	13C	NUC3	
NUC3		NUC4		NUC5	
NUC6		NUC7		NUC8	
NUC9		NUC10		NUC11	
NUC12		NUC13		NUC14	
NUC15		NUC16		NUC17	
NUC18		NUC19		NUC20	
NUC21		NUC22		NUC23	
NUC24		NUC25		NUC26	
NUC27		NUC28		NUC29	
NUC30		NUC31		NUC32	
NUC33		NUC34		NUC35	
NUC36		NUC37		NUC38	
NUC39		NUC40		NUC41	
NUC42		NUC43		NUC44	
NUC45		NUC46		NUC47	
NUC48		NUC49		NUC50	
NUC51		NUC52		NUC53	
NUC54		NUC55		NUC56	
NUC57		NUC58		NUC59	
NUC60		NUC61		NUC62	
NUC63		NUC64		NUC65	
NUC66		NUC67		NUC68	
NUC69		NUC70		NUC71	
NUC72		NUC73		NUC74	
NUC75		NUC76		NUC77	
NUC78		NUC79		NUC80	
NUC81		NUC82		NUC83	
NUC84		NUC85		NUC86	
NUC87		NUC88		NUC89	
NUC90		NUC91		NUC92	
NUC93		NUC94		NUC95	
NUC96		NUC97		NUC98	
NUC99		NUC100		NUC101	
NUC102		NUC103		NUC104	
NUC105		NUC106		NUC107	
NUC108		NUC109		NUC110	
NUC111		NUC112		NUC113	
NUC114		NUC115		NUC116	
NUC117		NUC118		NUC119	
NUC120		NUC121		NUC122	
NUC123		NUC124		NUC125	
NUC126		NUC127		NUC128	
NUC129		NUC130		NUC131	
NUC132		NUC133		NUC134	
NUC135		NUC136		NUC137	
NUC138		NUC139		NUC140	
NUC141		NUC142		NUC143	
NUC144		NUC145		NUC146	
NUC147		NUC148		NUC149	
NUC150		NUC151		NUC152	
NUC153		NUC154		NUC155	
NUC156		NUC157		NUC158	
NUC159		NUC160		NUC161	
NUC162		NUC163		NUC164	
NUC165		NUC166		NUC167	
NUC168		NUC169		NUC170	
NUC171		NUC172		NUC173	
NUC174		NUC175		NUC176	
NUC177		NUC178		NUC179	
NUC180		NUC181		NUC182	
NUC183		NUC184		NUC185	
NUC186		NUC187		NUC188	
NUC189		NUC190		NUC191	
NUC192		NUC193		NUC194	
NUC195		NUC196		NUC197	
NUC198		NUC199		NUC200	







Name: 013  
 Exp: 502826  
 Date: 02/02/00  
 Time: 14:09  
 Operator: J.L.M.  
 Instrument: Bruker  
 P1: 1.0000  
 P2: 0.0000  
 P3: 0.0000  
 P4: 0.0000  
 P5: 0.0000  
 P6: 0.0000  
 P7: 0.0000  
 P8: 0.0000  
 P9: 0.0000  
 P10: 0.0000  
 P11: 0.0000  
 P12: 0.0000  
 P13: 0.0000  
 P14: 0.0000  
 P15: 0.0000  
 P16: 0.0000  
 P17: 0.0000  
 P18: 0.0000  
 P19: 0.0000  
 P20: 0.0000  
 P21: 0.0000  
 P22: 0.0000  
 P23: 0.0000  
 P24: 0.0000  
 P25: 0.0000  
 P26: 0.0000  
 P27: 0.0000  
 P28: 0.0000  
 P29: 0.0000  
 P30: 0.0000  
 P31: 0.0000  
 P32: 0.0000  
 P33: 0.0000  
 P34: 0.0000  
 P35: 0.0000  
 P36: 0.0000  
 P37: 0.0000  
 P38: 0.0000  
 P39: 0.0000  
 P40: 0.0000  
 P41: 0.0000  
 P42: 0.0000  
 P43: 0.0000  
 P44: 0.0000  
 P45: 0.0000  
 P46: 0.0000  
 P47: 0.0000  
 P48: 0.0000  
 P49: 0.0000  
 P50: 0.0000  
 P51: 0.0000  
 P52: 0.0000  
 P53: 0.0000  
 P54: 0.0000  
 P55: 0.0000  
 P56: 0.0000  
 P57: 0.0000  
 P58: 0.0000  
 P59: 0.0000  
 P60: 0.0000  
 P61: 0.0000  
 P62: 0.0000  
 P63: 0.0000  
 P64: 0.0000  
 P65: 0.0000  
 P66: 0.0000  
 P67: 0.0000  
 P68: 0.0000  
 P69: 0.0000  
 P70: 0.0000  
 P71: 0.0000  
 P72: 0.0000  
 P73: 0.0000  
 P74: 0.0000  
 P75: 0.0000  
 P76: 0.0000  
 P77: 0.0000  
 P78: 0.0000  
 P79: 0.0000  
 P80: 0.0000  
 P81: 0.0000  
 P82: 0.0000  
 P83: 0.0000  
 P84: 0.0000  
 P85: 0.0000  
 P86: 0.0000  
 P87: 0.0000  
 P88: 0.0000  
 P89: 0.0000  
 P90: 0.0000  
 P91: 0.0000  
 P92: 0.0000  
 P93: 0.0000  
 P94: 0.0000  
 P95: 0.0000  
 P96: 0.0000  
 P97: 0.0000  
 P98: 0.0000  
 P99: 0.0000  
 P100: 0.0000

2,3-bis(trimethylsilyylethynyl)anthracene