Synthesis and Properties of 9-Alkyl and 9-Aryl Cyclopenta[*a*]phenalenes

Kevin M. Shea, Katherine L. Lee, and Rick L. Danheiser*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

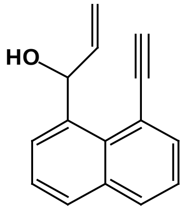
danheisr@mit.edu

Supporting Information

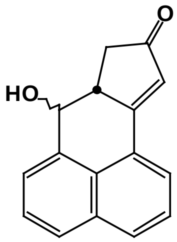
General Procedures. All reactions were performed in flame-dried glassware under a positive pressure of nitrogen or argon with magnetic stirring. Sensitive liquids and solutions were transferred via syringe or cannula and were introduced into reaction vessels through rubber septa. Reaction product solutions were concentrated using a Büchi rotary evaporator at ca. 20 mmHg. Column chromatography was performed on EM Science silica gel 60 (35-75 μm) or Silicycle silica gel 60.

Materials. Commercial grade reagents and solvents were used without further purification except as indicated below. Acetonitrile, benzene, dichloromethane, pyridine, pyrrolidine, and triethylamine were distilled from calcium hydride. Diethyl ether and tetrahydrofuran were distilled from benzophenone ketyl or dianion. Acrolein was distilled immediately prior to use. Acetic anhydride was distilled from quinoline. Cerium(III) chloride was dried by heating at 110 °C under vacuum overnight. Copper(I) iodide was continuously extracted with THF for 18 h.[1] Dichlorobis(triphenylphosphine)palladium was prepared according to the procedure of Heck and was recrystallized from chloroform.[2] Triphenylphosphine was recrystallized from hexane. 1,8-Diiodonaphthalene (**6**) was prepared as described by House.[3] 8-Iodo-1-naphthaldehyde[4] was prepared using a modification of the procedure of Katz.[5]

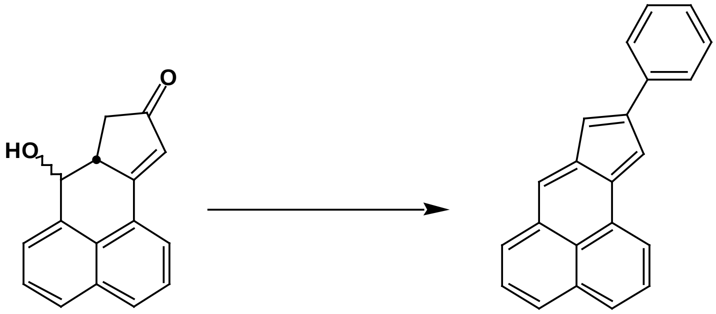
Instrumentation. ^{1}H NMR spectra were recorded on Varian XL-300 (300 MHz), Varian Unity 300 (300 MHz), and Varian Inova 500 (500 MHz) spectrometers. ^{13}C NMR spectra were recorded on Varian Unity 300 (75 MHz) and Varian Inova 500 (125 MHz) spectrometers. ^{1}H NMR chemical shifts and ^{13}C NMR shifts are expressed in parts per million (δ) relative to $CDCl_3$. Infrared spectra were obtained on a Perkin-Elmer 1320 grating or a Perkin-Elmer 1600 series FTIR spectrophotometer. Elemental analyses were performed by E&R Microanalytical Laboratory, Inc. of Parsippany, New Jersey.



1-(1-Hydroxy-2-propenyl)-8-ethynylnaphthalene (8). Gold solid, mp 46.5-47.0 °C: IR (thin film): 3560, 3400 (br), 3300, 3060, 3020, 2930, 2670, 2250, 2090, 1940, 1860, 1830, 1760, 1620, 1600, 1580, 1500, 1410 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 1 H), 7.86 (d, *J* = 7.3 Hz, 1 H), 7.81-7.78 (m, 2 H), 7.50 (t, *J* = 7.8 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 7.23 (br s, 1 H), 6.31 (ddd, *J* = 17.3, 10.7, 4.2 Hz, 1 H), 5.49 (d, *J* = 17.1 Hz, 1 H), 5.30 (d, *J* = 10.7 Hz, 1 H), 3.52 (s, 1 H), 2.65 (d, *J* = 4.4 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 139.5, 136.3, 134.6, 131.2, 130.3, 129.5, 127.0, 126.0, 124.6, 116.6, 114.1, 85.6, 81.9, 69.0. Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.80. Found: C, 86.51; H, 5.95.



(7S*, 7aR*)-Cyclopenta[*a*]phenalen-9(7aH,8H)-one-7-ol (9a) and (7R*, 7aR*)-Cyclopenta[*a*]phenalen-9(7a,8H)-one-7-ol (9b). Yellow solid, mp 142-143 °C. Slow recrystallization from chloroform provided a pure sample of the major isomer **9a**: IR (CH_2Cl_2): 3560, 3360 (br), 2870, 1670, 1595, 1490, 1360 cm^{-1}; for isomer **9a**, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1 H), 7.89-7.84 (m, 3 H), 7.64-7.55 (m, 2 H), 6.63 (d, *J* = 2.8 Hz, 1 H), 4.86 (dd, *J* = 11.5, 7.6 Hz, 1 H), 3.6-2.4 (br s or d, *J* = 7.6 Hz, 1 H), 3.36-3.30 (m, 1 H), 2.95 (dd, *J* = 18.5, 6.3 Hz, 1 H), 2.64 (dd, *J* = 19.2, 2.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.1, 172.8, 137.6, 133.7, 131.7, 128.1, 127.6, 126.6, 125.9, 125.6, 124.4, 123.2, 74.0, 47.1, 40.4; for isomer **9b**, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1 H), 7.85-7.75 (m, 2 H), 7.58-7.50 (m, 3 H), 6.59 (d, *J* = 2.0 Hz, 1 H), 5.08 (dd, *J* = 11.5, 7.6 Hz, 1 H), 3.51-3.47 (m, 1 H), 2.92 (dd, *J* = 18.3, 2.9 Hz, 1 H), 2.66 (dd, *J* = 18.2, 6.8 Hz, 1 H), 2.1-1.8 (br s or d, *J* = 7.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.9, 171.2, 135.4, 133.3, 128.9, 127.4, 127.3, 127.2, 127.1, 126.5, 125.5, 124.8, 69.7, 44.6, 37.1. For isomers **9a** and **9b**, Anal. Calcd for $C_{16}H_{12}O_2$:C, 81.34; H, 5.12. Found: C, 81.32; H, 5.09.



General Procedure for the Synthesis of Cyclopenta[*a*]phenalene Derivatives from Enone 9. 9-Phenylcyclopenta[*a*]phenalene (12). A 25-mL, one-necked, round-bottomed flask equipped with a rubber septum and argon inlet needle was charged with cerium(III) chloride (0.258 g, 1.05 mmol) and 6 mL of THF. The resulting white suspension was stirred vigorously at room temperature for 2 h and then cooled at -78 °C while phenyllithium (0.567 mL of a 1.80

M solution in cyclohexane-diethyl ether, 1.02 mmol) was added dropwise via syringe over ca. 2 min. The resulting yellow suspension was stirred at -78 °C for 2 h and then a solution of enone **9** (0.060 g, 0.255 mmol) in 6 mL of THF was added dropwise via cannula over 15 min. The resulting brown suspension was stirred at -78 °C for 1.5 h, diluted with 3 mL of saturated $NaHCO_3$ solution, and then allowed to warm to room temperature and diluted with 50 mL of diethyl ether. The organic phase was separated and washed with two 50-mL portions of water, and the combined aqueous phases were back-extracted with two 50-mL portions of diethyl ether. The combined organic phases were then washed with 50 mL of brine, and the resulting yellow solution of diol was stirred over ca. 25 g of $MgSO_4$ for 20 min at room temperature. This produced a dark brown solution that was filtered and concentrated to yield a dark brown solid which was purified by column chromatography on 5 g of alumina (elution with 5% ethyl acetate-hexanes) to afford 0.016 g (23%) of **12** as a dark brown powder, mp 118-122 °C: IR ($CHCl_3$): 3015, 1633, 1598, 1498 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) δ 8.41 (d, *J* = 7.2 Hz, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 7.94 (d, *J* = 8.1 Hz, 1 H), 7.90 (d, *J* = 7.0 Hz, 1 H), 7.85 (d, *J* = 8.1 Hz, 2 H), 7.81 (s, 1 H), 7.73 (dd, *J* = 8.1, 7.2 Hz, 1 H), 7.70 (s, 1 H), 7.65 (dd, *J* = 8.4, 7.0 Hz, 1 H), 7.47 (appar t, *J* = 7.7 Hz, 2 H), 7.36 (appar t, *J* = 7.3 Hz, 1 H), 6.99 (s, 1 H); ^{13}C NMR (125 MHz, acetone-d_6) δ 148.6, 145.4, 137.6, 134.4, 134.3, 134.0, 133.8, 132.8, 132.2, 130.6, 130.1, 129.6, 129.3, 129.2, 128.5, 127.8, 126.8, 124.6, 121.1, 115.1; UV-Vis max ($CHCl_3$): 460 (ε = 3642), 438 (3801), 380 (2009) nm; MS-EI: *m/z* (%): 278 (100) [M^+].

Figure 1. Partial ^{1}H NMR Spectrum (500 MHz, CD_3CN) of 9-Phenylcyclopenta[*a*]phenalene

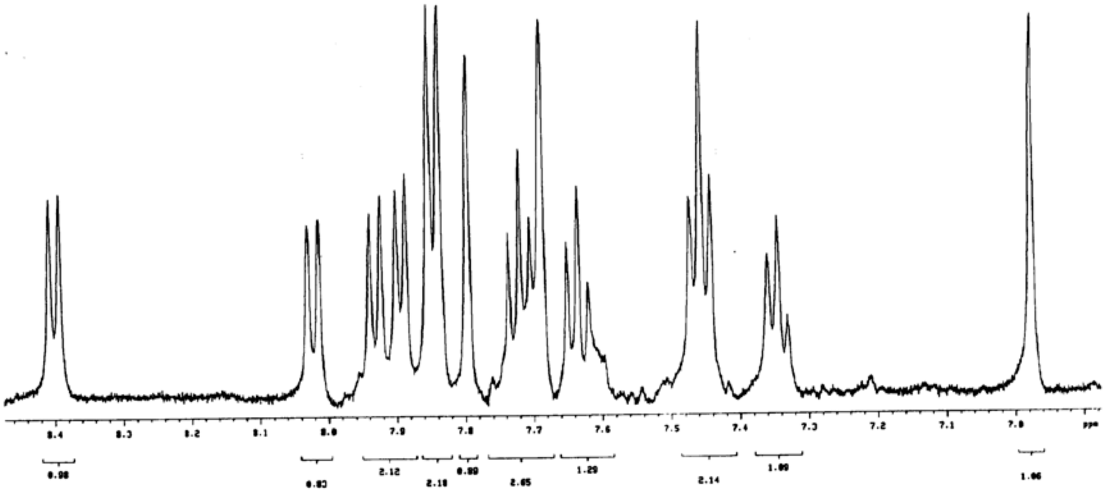


Figure 2. TOCSY Spectrum (500 MHz, CD_3CN) of 9-Phenylcyclopenta[*a*]phenalene

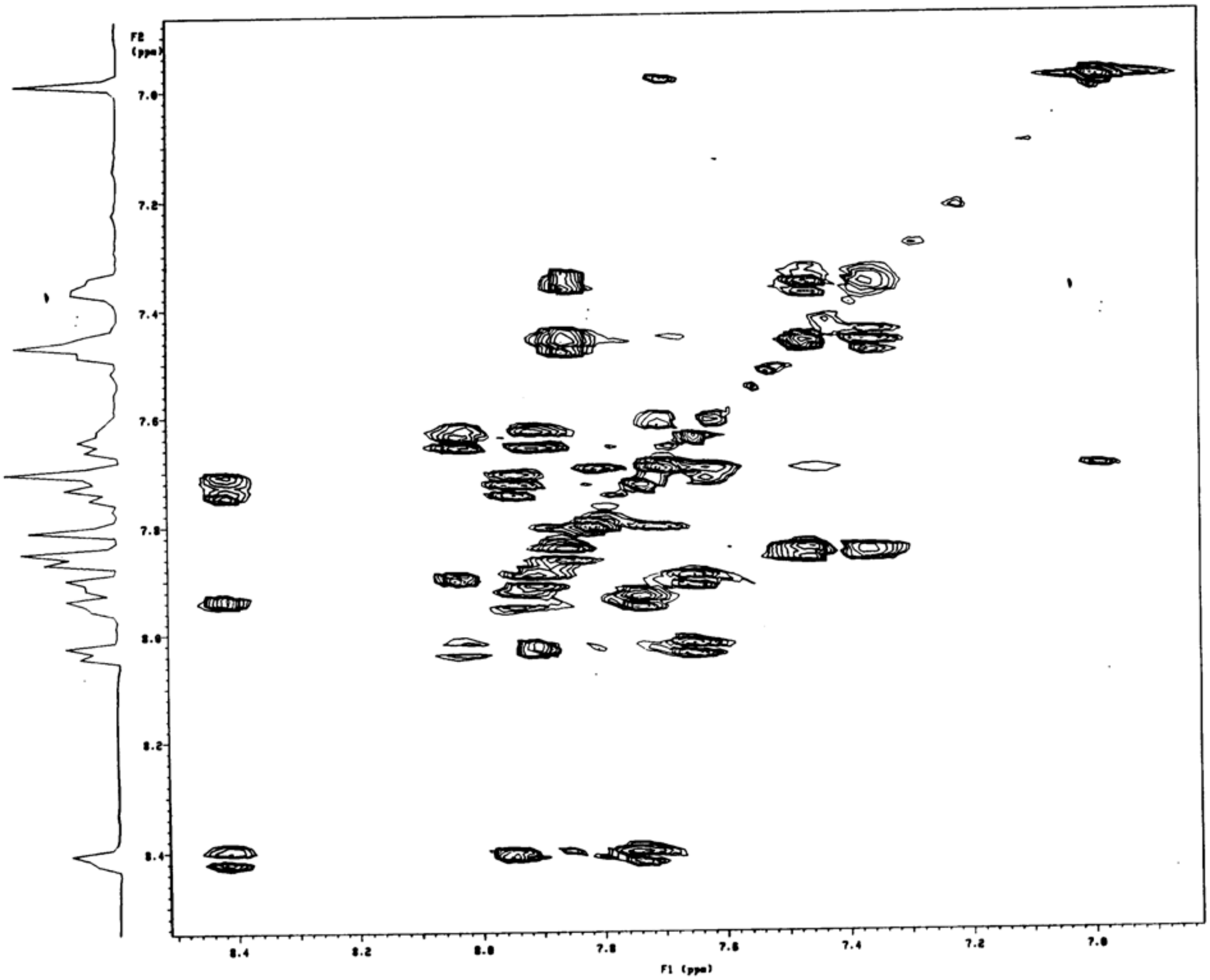


Figure 3. HMQC Spectrum (500 MHz, CD_3CN) of 9-Phenylcyclopenta[*a*]phenalene

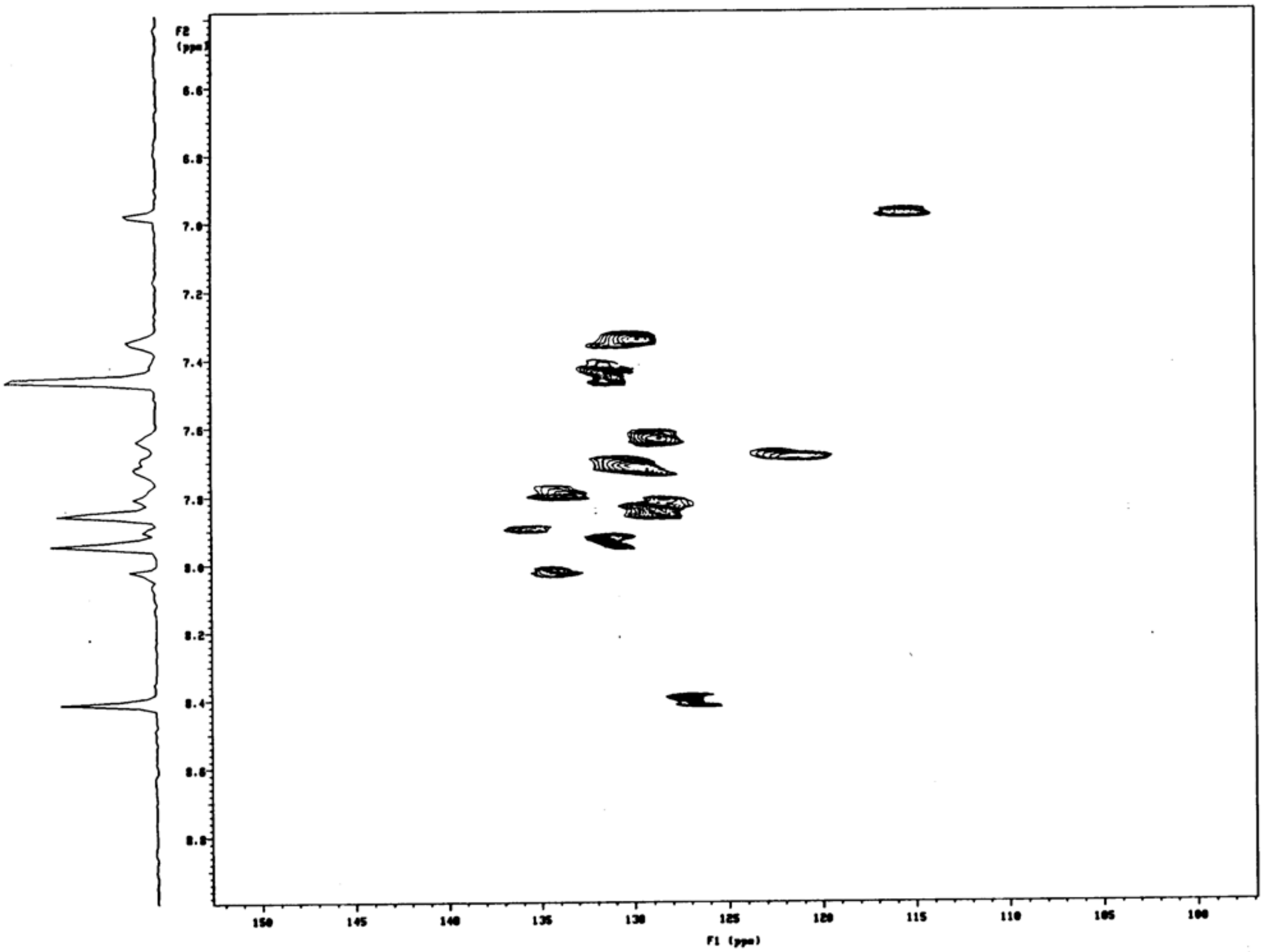
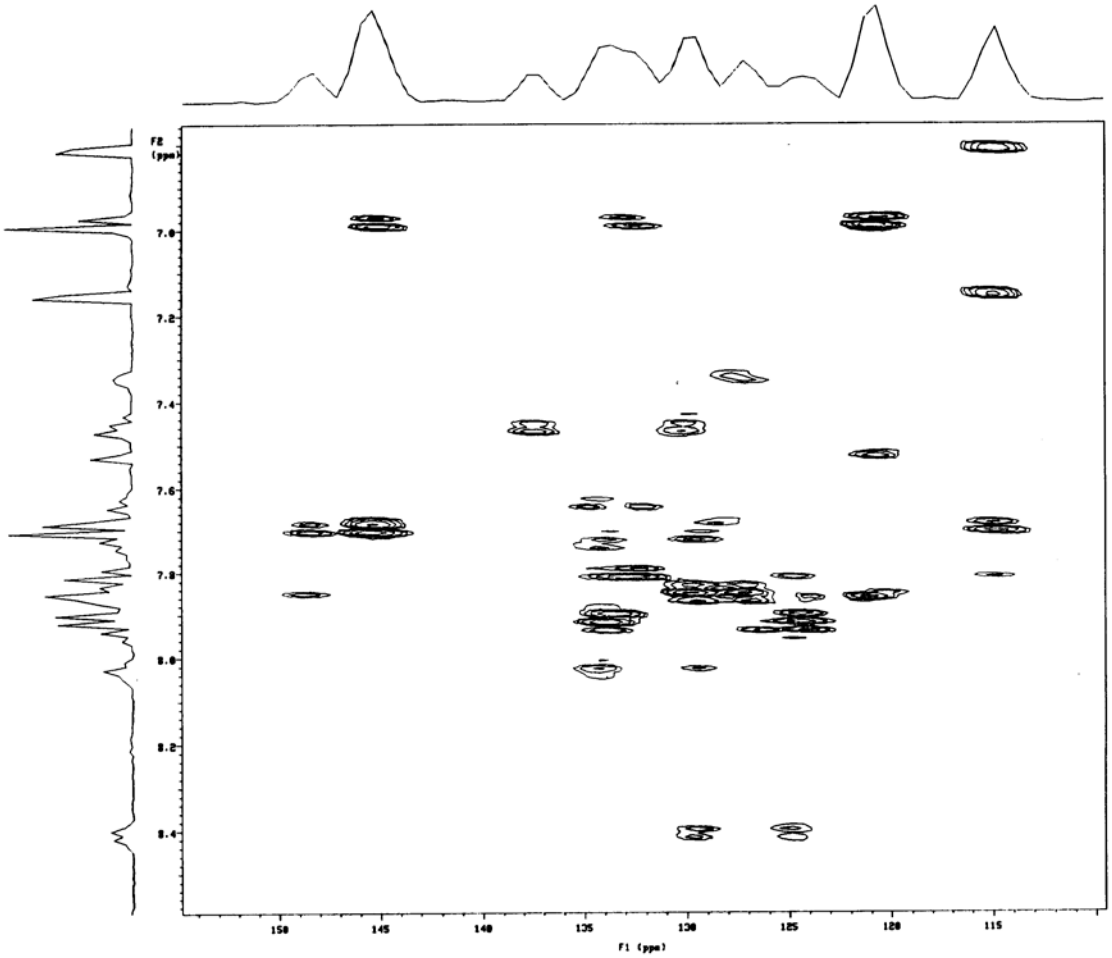
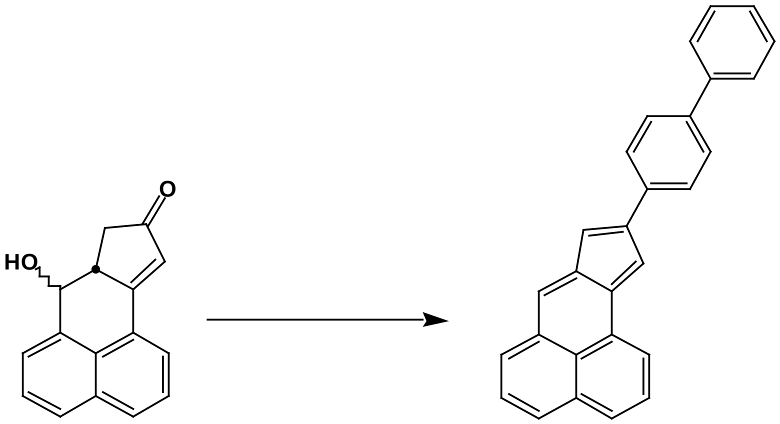
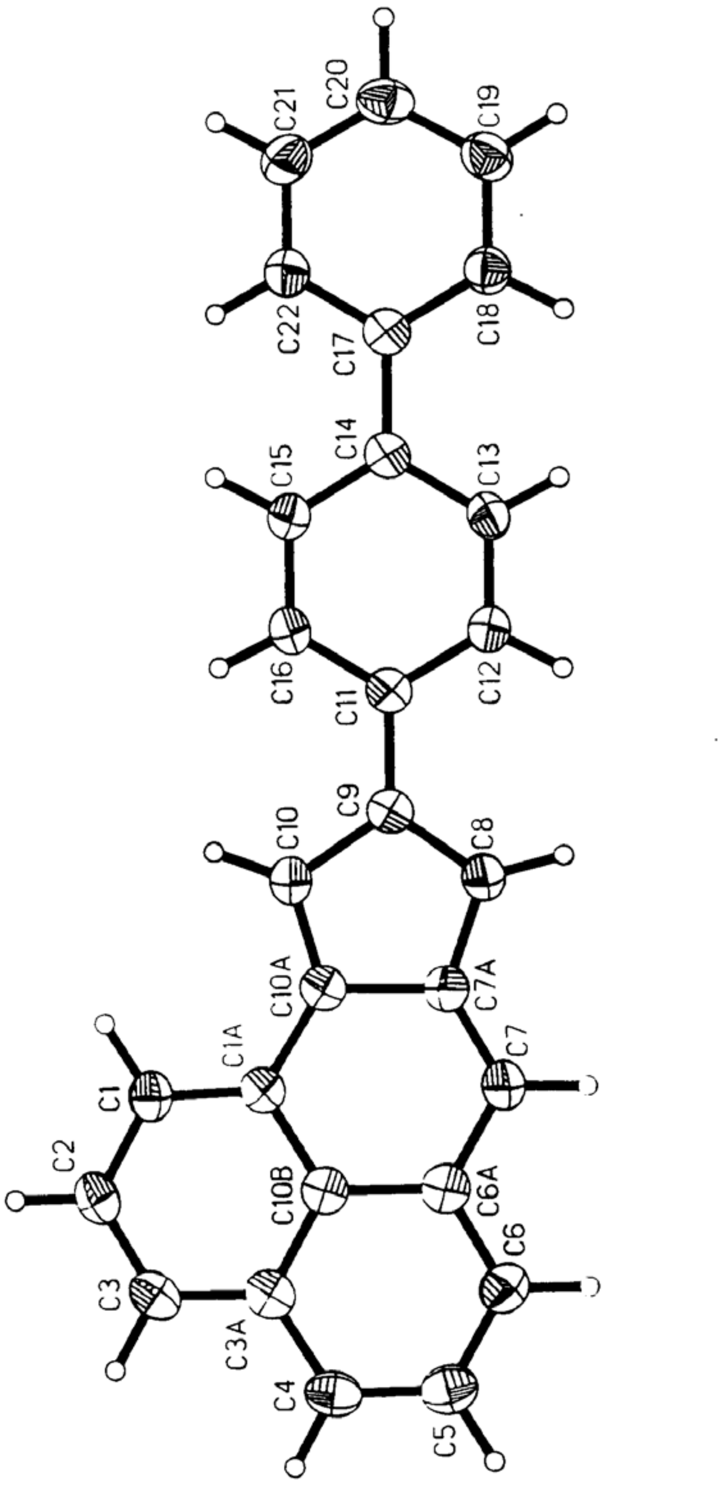


Figure 4. HMBC Spectrum (500 MHz, CD_3CN) of 9-Phenylcyclopenta[*a*]phenalene





9-(4-Biphenyl)cyclopenta[*a*]phenalene (13). Reaction of cerium(III) chloride (0.585 g, 2.38 mmol), 4-lithiobiphenyl[6] (0.546 g, 2.34 mmol), and enone **9** (0.090 g, 0.390 mmol) in 24 mL of 3:1 THF-diethyl ether according to the general procedure provided a black solid which was purified by column chromatography on 5 g of alumina (elution with benzene) to afford 0.083 g (60%) of **13** as a dark green solid, mp 209-211 °C (dec.): IR (KBr): 3025, 1630, 1472, 1355 cm^{-1}; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.36 (d, *J* = 7.6 Hz, 1 H), 7.96 (d, *J* = 7.6 Hz, 1 H), 7.91-7.87 (m, 2 H), 7.82 (d, *J* = 7.0 Hz, 1 H), 7.77-7.66 (m, 7 H), 7.62-7.59 (m, 2 H), 7.49-7.46 (m, 2 H), 7.39-7.35 (m, 1 H), 6.98 (d, *J* = 1.2 Hz, 1 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ 146.9, 141.1, 140.8, 135.4, 133.3, 132.8, 132.6, 131.7, 130.5, 129.4, 128.7, 128.0, 127.9, 127.8, 127.5, 127.4, 127.3, 127.2, 127.0, 125.4, 124.3, 120.7, 119.7, 114.0; UV-Vis max ($CHCl_3$): 446 (ε = 16000), 312 (28000), 277 (35000), 238 (43000) nm; MS-EI: *m/z* (%): 354 (100) [M^+].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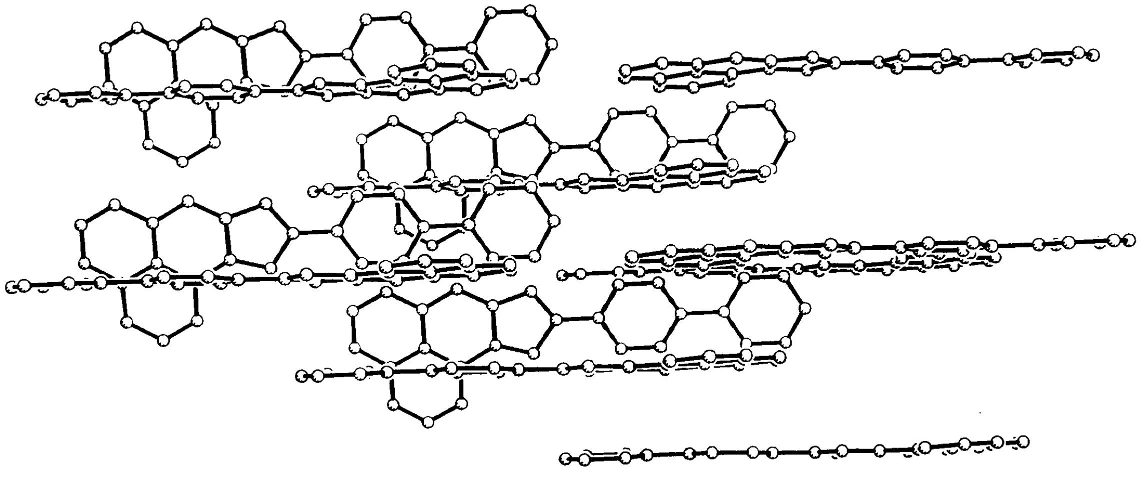


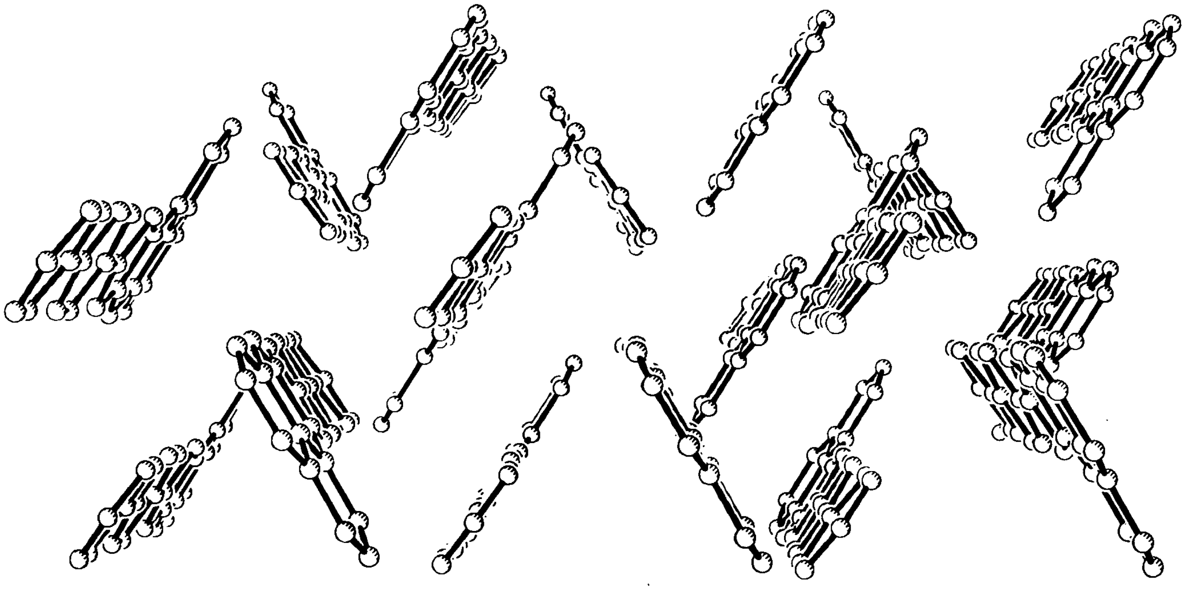


Table 1. Crystal data and structure refinement for 1.

Identification code	sad
Empirical formula	C28 H18
Formula weight	354.42
Temperature	188(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 10.060(2) A alpha = 90 deg. b = 7.841(2) A beta = 93.74(2) deg. c = 22.693(6) A gamma = 90 deg.
Volume, Z	1786.2(8) A^3, 4
Density (calculated)	1.318 Mg/m^3
Absorption coefficient	0.075 mm^-1
F(000)	744
Crystal size	0.43 x 0.4 x 0.04 mm
Theta range for data collection	1.80 to 28.20 deg.
Limiting indices	-13<=h<=12, -10<=k<=9, -30<=l<=25
Reflections collected	10066
Independent reflections	4035 [R(int) = 0.0424]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4035 / 0 / 326
Goodness-of-fit on F^2	1.000
Observed reflections [I>2sigma(I)]	2413
Final R indices [I>2sigma(I)]	R1 = 0.0536, wR2 = 0.1025
R indices (all data)	R1 = 0.1076, wR2 = 0.1185
Extinction coefficient	0.0074(11)
Largest diff. peak and hole	0.243 and -0.182 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	6197(2)	2305(2)	216(1)	33(1)
C(1A)	5678(2)	3221(2)	671(1)	29(1)
C(2)	5415(2)	1909(2)	-300(1)	37(1)
C(3)	4111(2)	2414(2)	-369(1)	36(1)
C(3A)	3525(2)	3338(2)	83(1)	33(1)
C(4)	2181(2)	3901(2)	23(1)	39(1)
C(5)	1649(2)	4816(3)	465(1)	43(1)
C(6)	2409(2)	5202(2)	983(1)	38(1)
C(6A)	3730(2)	4697(2)	1065(1)	33(1)
C(7)	4524(2)	5161(2)	1591(1)	34(1)
C(7A)	5832(2)	4725(2)	1660(1)	31(1)
C(8)	6838(2)	5060(2)	2124(1)	34(1)
C(9)	8007(2)	4347(2)	1971(1)	29(1)
C(10)	7765(2)	3523(2)	1392(1)	31(1)
C(10B)	4315(2)	3736(2)	610(1)	29(1)
C(10A)	6455(2)	3736(2)	1204(1)	29(1)
C(11)	9299(2)	4385(2)	2314(1)	29(1)
C(12)	9454(2)	5213(2)	2860(1)	36(1)
C(13)	10664(2)	5256(2)	3183(1)	36(1)
C(14)	11801(2)	4470(2)	2984(1)	28(1)
C(15)	11643(2)	3654(2)	2437(1)	35(1)
C(16)	10428(2)	3607(2)	2114(1)	35(1)
C(17)	13099(2)	4487(2)	3341(1)	29(1)
C(18)	13262(2)	5387(2)	3872(1)	35(1)
C(19)	14464(2)	5380(2)	4208(1)	40(1)
C(20)	15537(2)	4473(2)	4022(1)	40(1)
C(21)	15407(2)	3578(3)	3498(1)	42(1)
C(22)	14205(2)	3587(2)	3162(1)	38(1)

Table 3. Bond lengths [A] and angles [deg] for 1.

C(1)-C(1A)	1.388(2)
C(1)-C(2)	1.402(2)
C(1A)-C(10B)	1.428(2)
C(1A)-C(10A)	1.453(2)
C(2)-C(3)	1.370(3)
C(3)-C(3A)	1.416(2)
C(3A)-C(4)	1.419(2)
C(3A)-C(10B)	1.427(2)
C(4)-C(5)	1.370(3)
C(5)-C(6)	1.392(3)
C(6)-C(6A)	1.388(2)
C(6A)-C(10B)	1.435(2)
C(6A)-C(7)	1.439(2)
C(7)-C(7A)	1.359(2)
C(7A)-C(8)	1.437(2)
C(7A)-C(10A)	1.465(2)
C(8)-C(9)	1.368(2)
C(9)-C(10)	1.470(2)
C(9)-C(11)	1.471(2)
C(10)-C(10A)	1.369(2)
C(11)-C(16)	1.391(2)
C(11)-C(12)	1.398(2)
C(12)-C(13)	1.379(2)
C(13)-C(14)	1.400(2)
C(14)-C(15)	1.396(2)
C(14)-C(17)	1.491(2)
C(15)-C(16)	1.385(2)
C(17)-C(18)	1.396(2)
C(17)-C(22)	1.400(2)
C(18)-C(19)	1.386(3)
C(19)-C(20)	1.381(3)
C(20)-C(21)	1.379(3)
C(21)-C(22)	1.387(3)
C(1A)-C(1)-C(2)	121.2(2)
C(1)-C(1A)-C(10B)	118.6(2)
C(1)-C(1A)-C(10A)	123.7(2)
C(10B)-C(1A)-C(10A)	117.6(2)
C(3)-C(2)-C(1)	120.9(2)
C(2)-C(3)-C(3A)	120.3(2)
C(3)-C(3A)-C(4)	121.9(2)
C(3)-C(3A)-C(10B)	119.0(2)
C(4)-C(3A)-C(10B)	119.1(2)
C(5)-C(4)-C(3A)	120.5(2)
C(4)-C(5)-C(6)	120.8(2)
C(6A)-C(6)-C(5)	121.3(2)
C(6)-C(6A)-C(10B)	119.1(2)
C(6)-C(6A)-C(7)	121.0(2)
C(10B)-C(6A)-C(7)	119.9(2)
C(7A)-C(7)-C(6A)	120.8(2)
C(7)-C(7A)-C(8)	131.9(2)
C(7)-C(7A)-C(10A)	120.5(2)
C(8)-C(7A)-C(10A)	107.6(2)
C(9)-C(8)-C(7A)	108.3(2)
C(8)-C(9)-C(10)	108.2(2)
C(8)-C(9)-C(11)	127.0(2)
C(10)-C(9)-C(11)	124.8(2)
C(10A)-C(10)-C(9)	108.9(2)
C(3A)-C(10B)-C(1A)	119.9(2)
C(3A)-C(10B)-C(6A)	119.1(2)
C(1A)-C(10B)-C(6A)	121.0(2)
C(10)-C(10A)-C(1A)	132.8(2)

C(10)-C(10A)-C(7A)	106.99(14)
C(1A)-C(10A)-C(7A)	120.2(2)
C(16)-C(11)-C(12)	116.6(2)
C(16)-C(11)-C(9)	121.9(2)
C(12)-C(11)-C(9)	121.5(2)
C(13)-C(12)-C(11)	121.7(2)
C(12)-C(13)-C(14)	122.0(2)
C(15)-C(14)-C(13)	116.1(2)
C(15)-C(14)-C(17)	122.1(2)
C(13)-C(14)-C(17)	121.7(2)
C(16)-C(15)-C(14)	121.9(2)
C(15)-C(16)-C(11)	121.8(2)
C(18)-C(17)-C(22)	117.0(2)
C(18)-C(17)-C(14)	121.5(2)
C(22)-C(17)-C(14)	121.5(2)
C(19)-C(18)-C(17)	121.4(2)
C(20)-C(19)-C(18)	120.4(2)
C(21)-C(20)-C(19)	119.5(2)
C(20)-C(21)-C(22)	120.1(2)
C(21)-C(22)-C(17)	121.6(2)

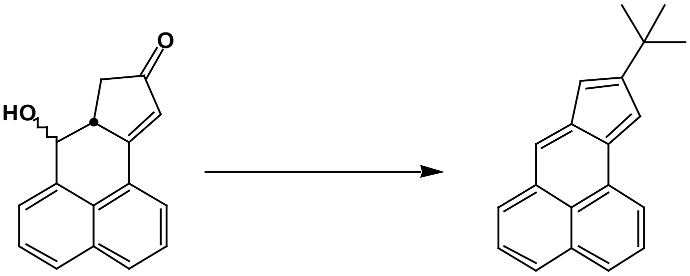
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 1.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	39(1)	27(1)	35(1)	0(1)	6(1)	0(1)
C(1A)	33(1)	23(1)	29(1)	4(1)	2(1)	-2(1)
C(2)	46(1)	33(1)	31(1)	-4(1)	3(1)	-2(1)
C(3)	43(1)	32(1)	33(1)	2(1)	-2(1)	-8(1)
C(3A)	37(1)	27(1)	34(1)	5(1)	3(1)	-7(1)
C(4)	34(1)	40(1)	41(1)	3(1)	-5(1)	-7(1)
C(5)	34(1)	47(1)	48(1)	1(1)	0(1)	-1(1)
C(6)	34(1)	39(1)	43(1)	0(1)	5(1)	1(1)
C(6A)	36(1)	29(1)	35(1)	4(1)	5(1)	-3(1)
C(7)	38(1)	34(1)	31(1)	-2(1)	6(1)	1(1)
C(7A)	32(1)	31(1)	31(1)	1(1)	4(1)	-1(1)
C(8)	34(1)	36(1)	31(1)	-4(1)	4(1)	1(1)
C(9)	30(1)	27(1)	29(1)	2(1)	2(1)	-2(1)
C(10)	35(1)	29(1)	30(1)	-1(1)	6(1)	2(1)
C(10B)	32(1)	23(1)	32(1)	5(1)	5(1)	-5(1)
C(10A)	33(1)	26(1)	29(1)	4(1)	2(1)	-1(1)
C(11)	32(1)	26(1)	29(1)	2(1)	2(1)	-2(1)
C(12)	34(1)	39(1)	34(1)	-6(1)	2(1)	6(1)
C(13)	39(1)	39(1)	29(1)	-7(1)	-1(1)	6(1)
C(14)	33(1)	24(1)	26(1)	3(1)	3(1)	-2(1)
C(15)	31(1)	41(1)	35(1)	-6(1)	5(1)	1(1)
C(16)	36(1)	39(1)	31(1)	-8(1)	3(1)	1(1)
C(17)	33(1)	26(1)	29(1)	5(1)	3(1)	-2(1)
C(18)	37(1)	36(1)	31(1)	-1(1)	0(1)	4(1)
C(19)	44(1)	39(1)	36(1)	-2(1)	-6(1)	3(1)
C(20)	38(1)	36(1)	44(1)	4(1)	-8(1)	1(1)
C(21)	35(1)	42(1)	50(1)	-2(1)	2(1)	7(1)
C(22)	37(1)	40(1)	37(1)	-6(1)	2(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

	x	y	z	U(eq)
H(1)	7197(18)	1940(20)	248(6)	36(5)
H(2)	5807(17)	1251(22)	-623(7)	43(5)
H(3)	3571(16)	2195(20)	-760(7)	37(5)
H(4)	1636(17)	3655(21)	-349(7)	40(5)
H(5)	686(19)	5211(23)	416(8)	55(6)
H(6)	2028(16)	5936(21)	1297(7)	37(5)
H(7)	4109(17)	5858(22)	1901(7)	45(5)
H(8)	6683(17)	5738(22)	2485(7)	41(5)
H(10)	8456(16)	2886(20)	1183(7)	32(4)
H(12)	8686(18)	5800(22)	3022(7)	43(5)
H(13)	10722(17)	5832(22)	3560(8)	43(5)
H(15)	12428(18)	3074(22)	2264(7)	44(5)
H(16)	10392(15)	3005(20)	1737(7)	32(5)
H(18)	12492(18)	6070(22)	4020(7)	44(5)
H(19)	14577(17)	6040(22)	4569(7)	41(5)
H(20)	16431(18)	4492(20)	4260(7)	36(5)
H(21)	16160(19)	2931(25)	3352(8)	55(6)
H(22)	14122(17)	2892(23)	2785(8)	50(5)



9-*t*-Butylcyclopenta[*a*]phenalene (14). Reaction of cerium(III) chloride (0.786 g, 3.19 mmol), *t*-butyllithium (1.84 mL of a 1.70 M solution in pentane, 3.13 mmol), and enone **9** (0.125 g, 0.531 mmol) in a total of 30 mL of THF according to the general procedure provided a black solid which was purified by column chromatography on 15 g of alumina (elution with 5% diethyl ether-pentane) to afford 0.019 g (14%) of **14** as a dark brown solid, mp 100-103 °C; for spectral data, see page S23.

Figure 5. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 9-*t*-Butylcyclopenta[*a*]phenalene

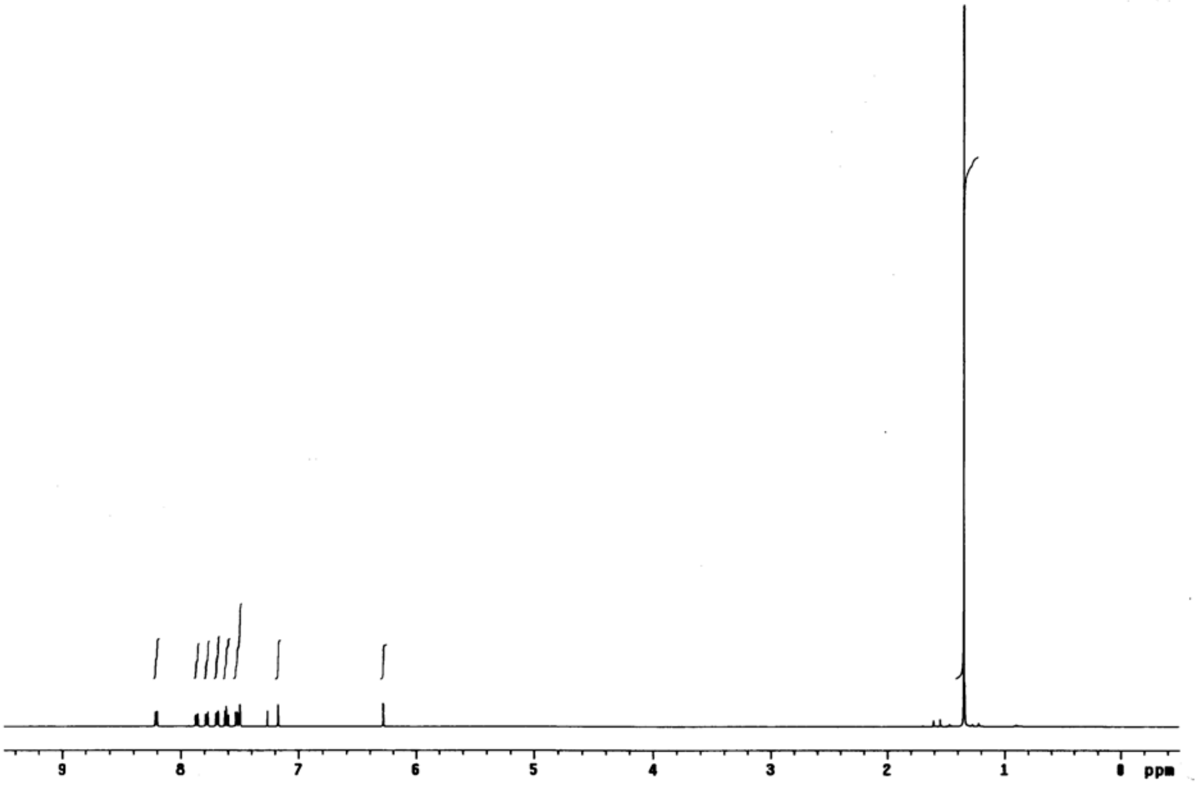


Figure 6. Partial ^{1}H NMR Spectrum (500 MHz, acetone-d_6) of 9-*t*-Butylcyclopenta[*a*]phenalene

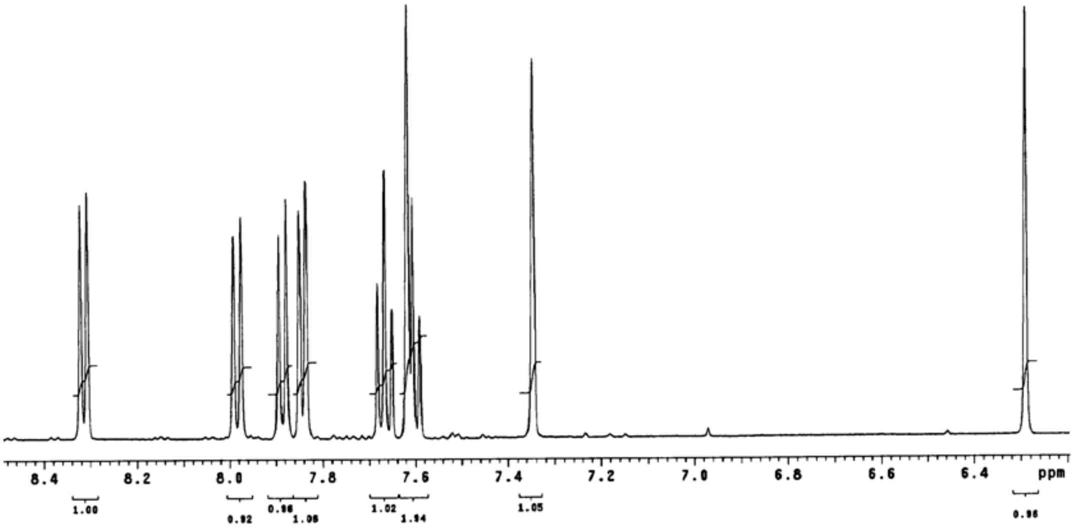


Figure 7. Partial TOCSY Spectrum (500 MHz, acetone-d_6) of 9-*t*-Butylcyclopenta[*a*]phenalene

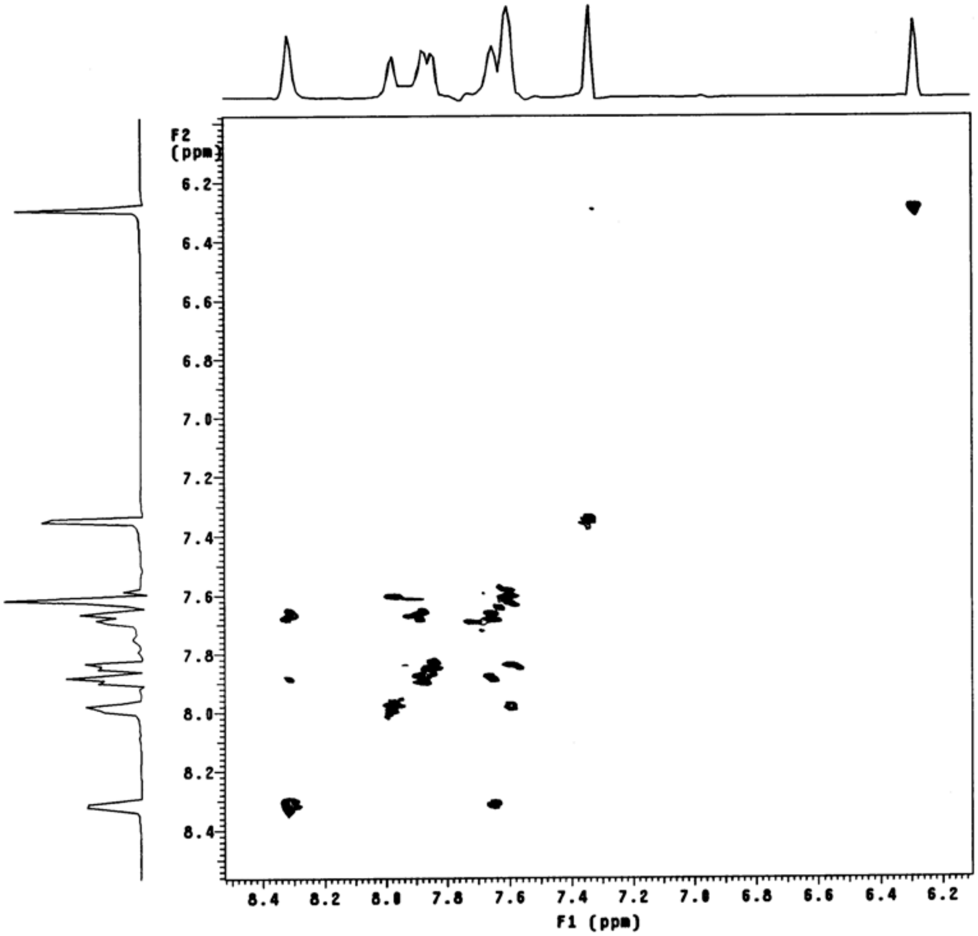


Figure 8. Partial HMQC Spectrum (500 MHz, acetone-d_6) of 9-*t*-Butylcyclopenta[*a*]phenalene[7]

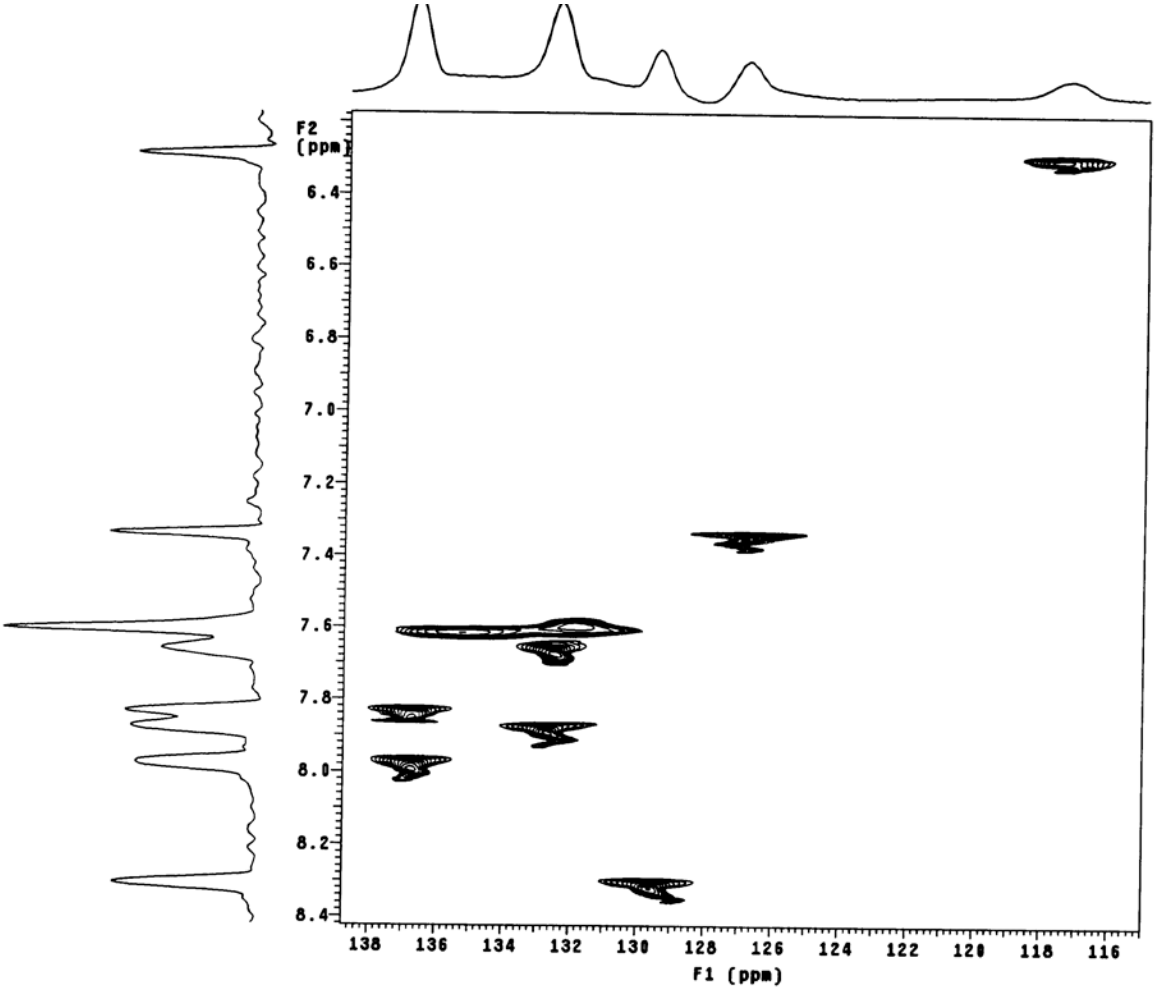


Figure 9. HMBC Spectrum (500 MHz, acetone-d_6) of 9-*t*-Butylcyclopenta[*a*]phenalene

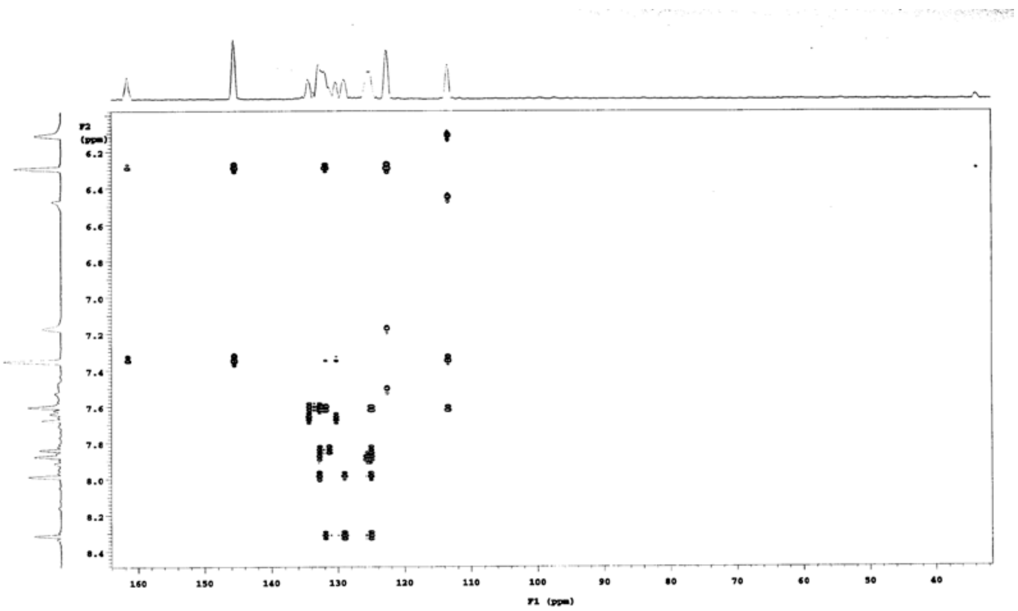
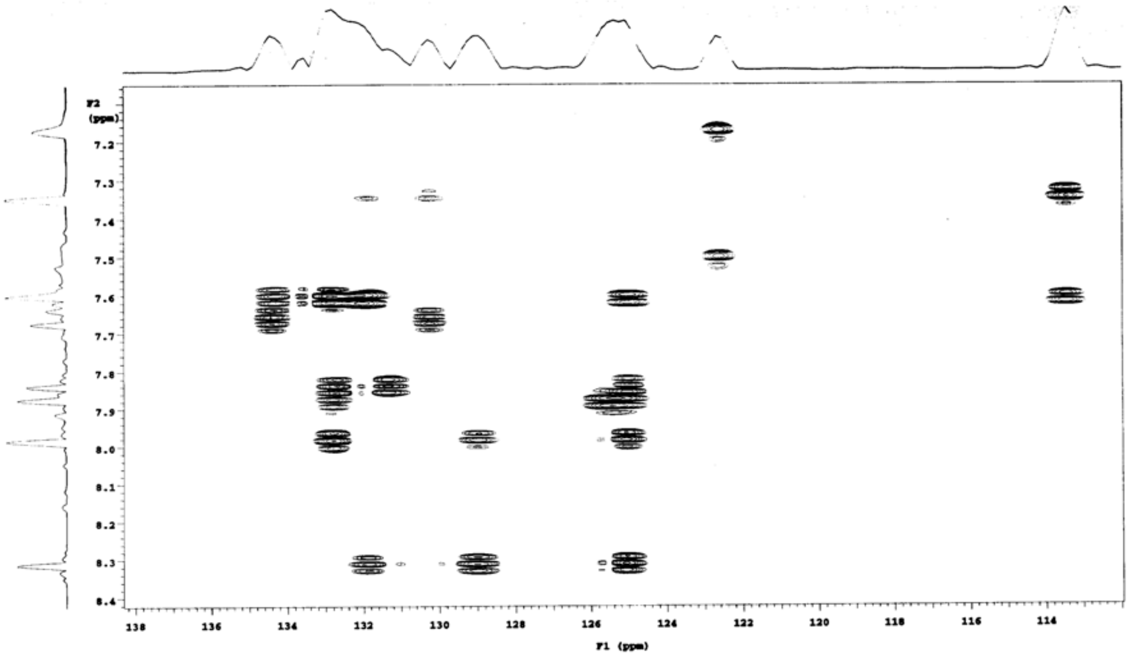
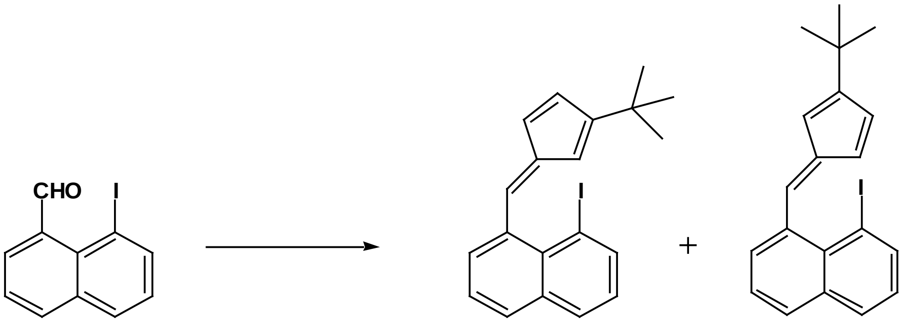
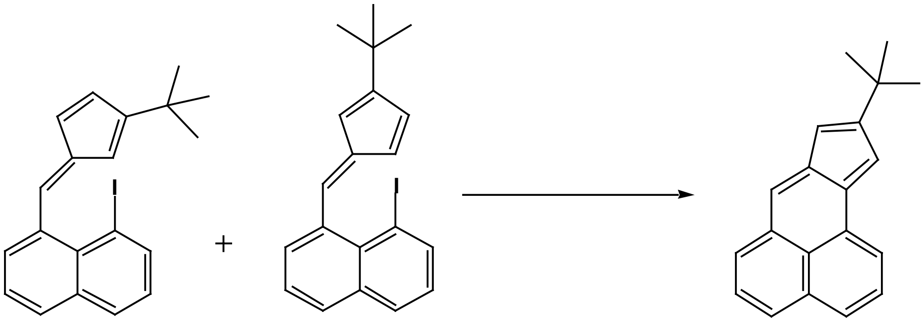


Figure 10. HMBC Spectrum (500 MHz, acetone-d_6) of 9-*t*-Butylcyclopenta[*a*]phenalene, close-up





1-(8-Iodonaphthyl)-4-*t*-butylfulvene (16) and 1-(8-Iodonaphthyl)-5-*t*-butylfulvene (17). Orange oil: IR ($CHCl_3$): 3059, 3005, 2963, 2901, 2867, 1619, 1553, 1462, 1363 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1 H), 8.42 (s, 1 H), 8.27 (d, *J* = 7.3 Hz, 2 H), 7.88-7.81 (m, 4 H), 7.56 (dt, *J* = 7.2, 1.1 Hz, 1 H), 7.51-7.44 (m, 3 H), 7.12 (t, *J* = 7.8 Hz, 2 H), 6.69-6.66 (m, 2 H), 6.48 (dd, *J* = 5.3, 2.0 Hz, 1 H), 6.42 (dd, *J* = 5.2, 2.4 Hz, 1 H), 6.11 (t, *J* = 2.0 Hz, 1 H), 6.07 (br t, *J* = 1.8 Hz, 1 H), 1.30 (s, 9 H), 1.24 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 157.9, 144.4, 144.3, 141.7, 141.6, 137.5, 137.4, 135.8, 135.6, 135.5, 134.3, 134.0, 133.9, 133.0, 132.9, 131.9, 130.6, 130.1, 130.0, 127.1, 126.9, 125.7, 125.6, 122.8, 116.8, 112.8, 92.5, 92.4, 32.8, 32.5, 29.9, 29.8.



9-*t*-Butylcyclopenta[*a*]phenalene (14). A 50-mL, one-necked, round-bottomed flask equipped with a rubber septum and an argon inlet needle was charged with 19 mL of acetonitrile and a mixture of iodofulvenes **16** and **17** (0.341 g, 0.883 mmol). Palladium acetate (0.020 g, 0.088 mmol), triphenylphosphine (0.046 g, 0.177 mmol), and potassium carbonate (0.244 g, 1.77 mmol) were added and the rubber septum was removed and replaced with a reflux condenser fitted with an argon inlet adapter. The reaction mixture was heated at reflux for 4 h, and the dark brown mixture was allowed to cool to room temperature and then filtered through Celite with the aid of 100 mL of dichloromethane. The dark brown filtrate was concentrated to yield 0.321 g of a brown solid that was purified by column chromatography on silica gel (elution with pentane) to afford 0.103 g (45%) of **14** as a brown solid, mp 100-103 °C: IR ($CHCl_3$): 3053, 2963, 1633, 1422, 1379, 1272 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 7.3 Hz, 1 H), 7.87 (d, J = 7.6 Hz, 1 H), 7.78 (d, J = 7.9 Hz, 1 H), 7.70 (d, J = 6.7 Hz, 1 H), 7.62 (t, J = 7.8 Hz, 1 H), 7.52 (dd, J = 8.1, 7.2 Hz, 1 H), 7.50 (d, J = 1.2 Hz, 1 H), 7.17 (br s, 1 H), 6.28 (d, J = 1.2 Hz, 1 H), 1.34 (s, 9 H); ^1H NMR (500 MHz, acetone-d_6) δ 8.31 (d, J = 7.3 Hz, 1 H), 7.98 (d, J = 8.3 Hz, 1 H), 7.88 (d, J = 7.8 Hz, 1 H), 7.84 (d, J = 6.8 Hz, 1 H), 7.66 (appar t, J = 7.8 Hz, 1 H), 7.62 (d, J = 1.0 Hz, 1 H), 7.60 (appar t, J = 7.3 Hz, 1 H), 7.34 (s, 1 H), 6.28 (d, J = 1.0 Hz, 1 H), 1.31 (s, 9 H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.6, 145.0, 133.6, 132.2, 131.7, 131.6, 130.5, 129.8, 128.0, 127.6, 126.7, 125.0, 124.7, 121.8, 113.1, 33.2, 30.6; ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 144.0, 132.9, 131.5, 131.4, 130.8, 130.3, 128.9, 127.7, 127.3, 126.4, 124.4, 121.1, 112.1, 33.0, 30.2; UV-Vis max ($CHCl_3$): 311 (ε = 6911) nm. Anal. Calcd for $C_{20}H_{18}$: C, 92.96; H, 7.04. Found: C, 93.26; H, 7.22.

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[1] Taylor, R. J. K. *Organocopper Reagents: A Practical Approach*; Oxford University Press: Oxford, 1994; pp 39-40.

[2] Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985; p 18.

[3] House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003.

[4] Bailey, R.J.; Card, P.J.; Shechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6096.

[5] Katz, H. E. *Organometallics* **1986**, *5*, 2308.

[6] Diorazio, L. J.; Widdowson, D. A.; Clough, J. M. *Tetrahedron* **1992**, *48*, 8073.

[7] Due to a referencing error, the ^{13}C NMR chemical shifts appear 4 ppm higher than their actual values.