Supplementary Information

Carbocations from Dibenz[a,j]anthracene and Dibenz[a,h]anthracene, their Methylated Derivatives, and Oxidized Metabolites; A Stable Ion and DFT Study.

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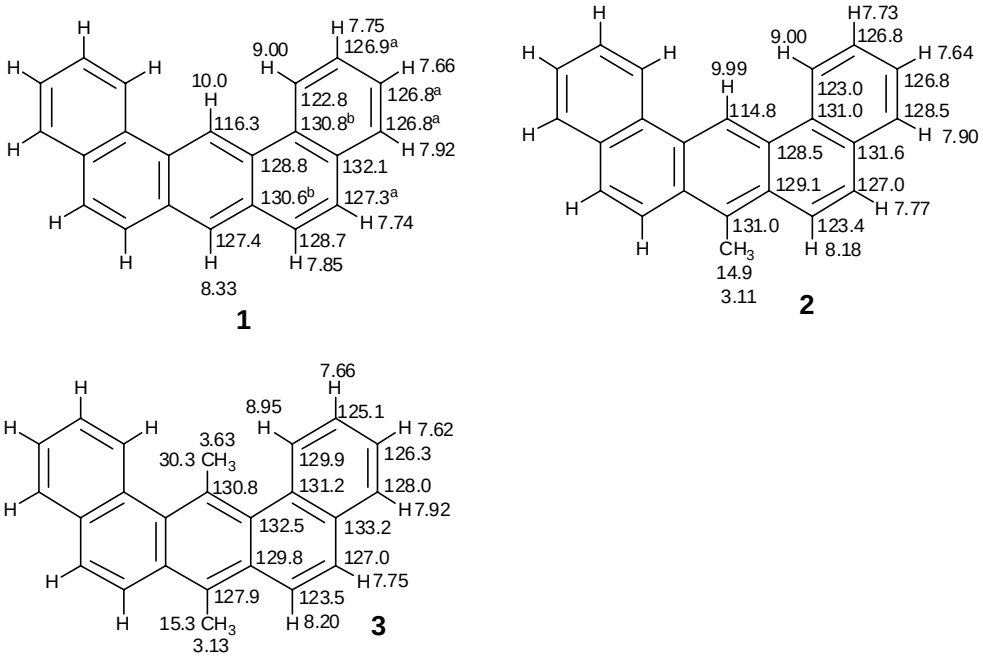


Chart S1. ^{1}H and ^{13}C NMR assignments for dibenz[*a*,*j*]anthracenes **1**, **2**, and **3** (a and b denote interchangeable assignments).

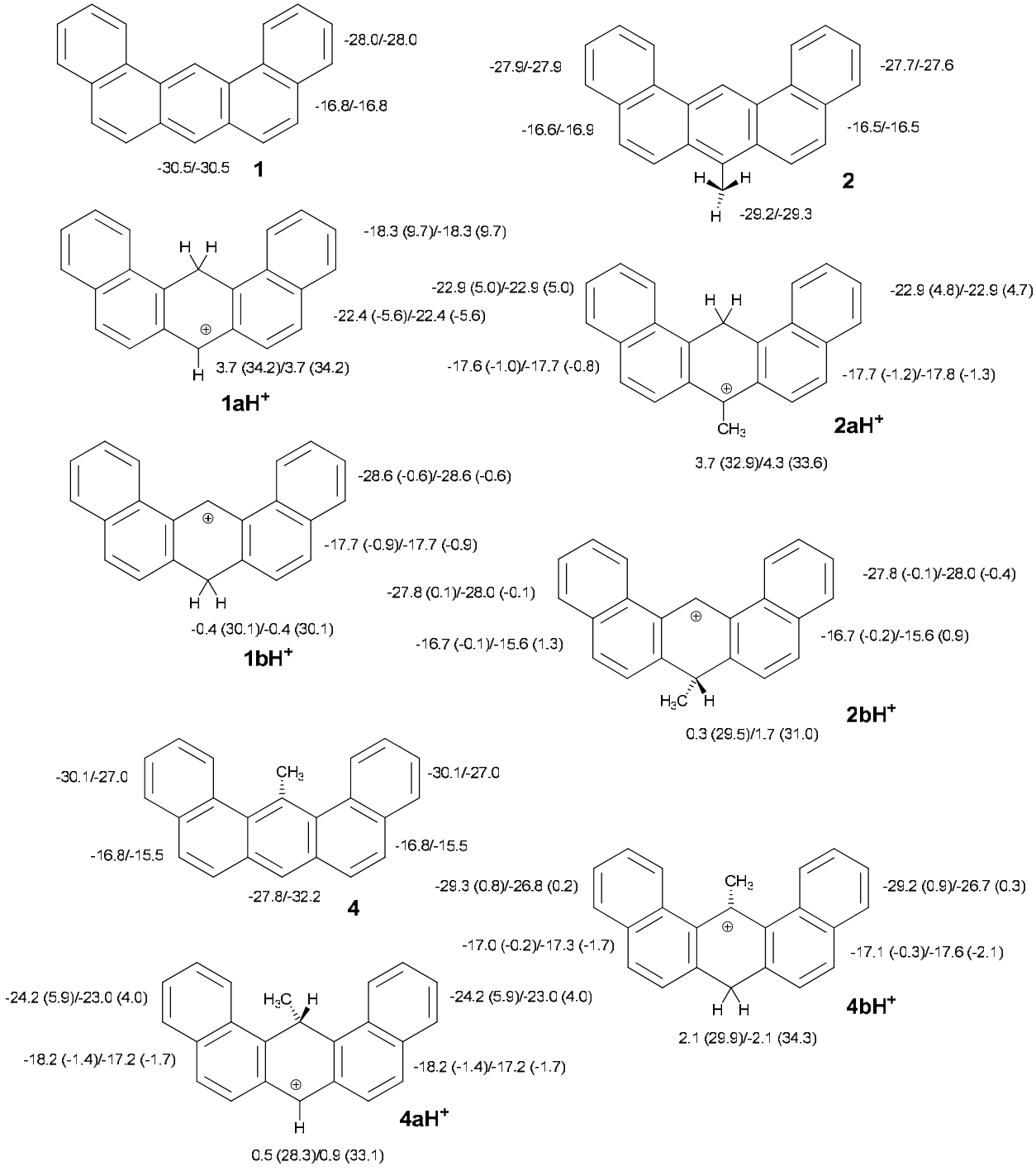


Chart S2. NICS(1)zz above/below molecules (ΔNICS(1)zz) by B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) for dibenz[a,j]anthracenes and their Carbocations.

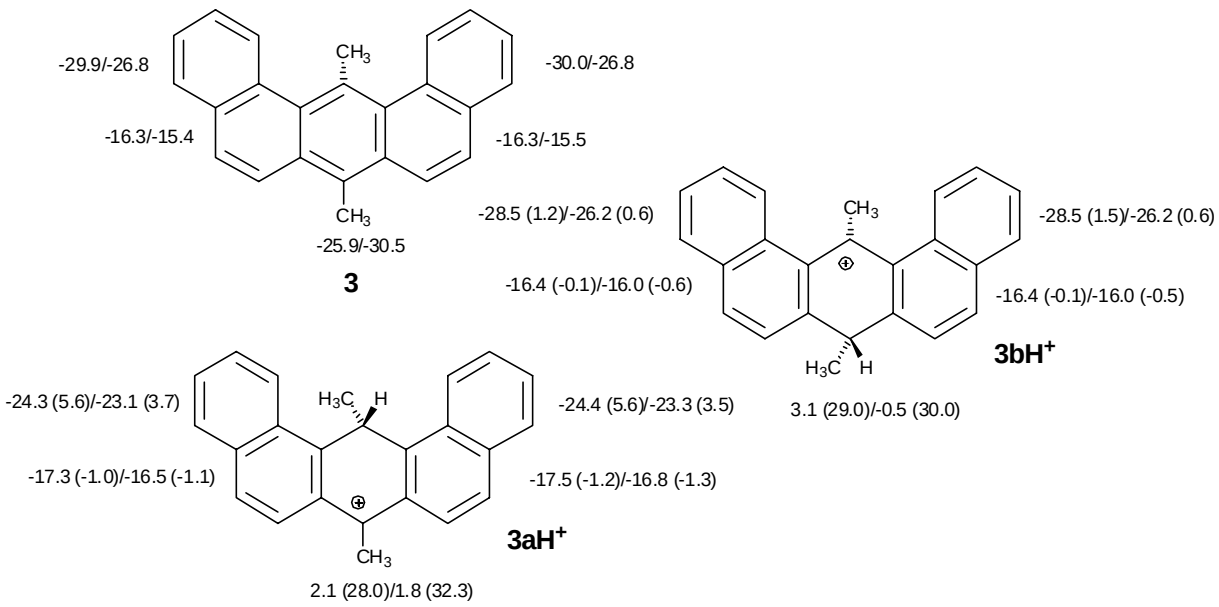


Chart S2 (continued).

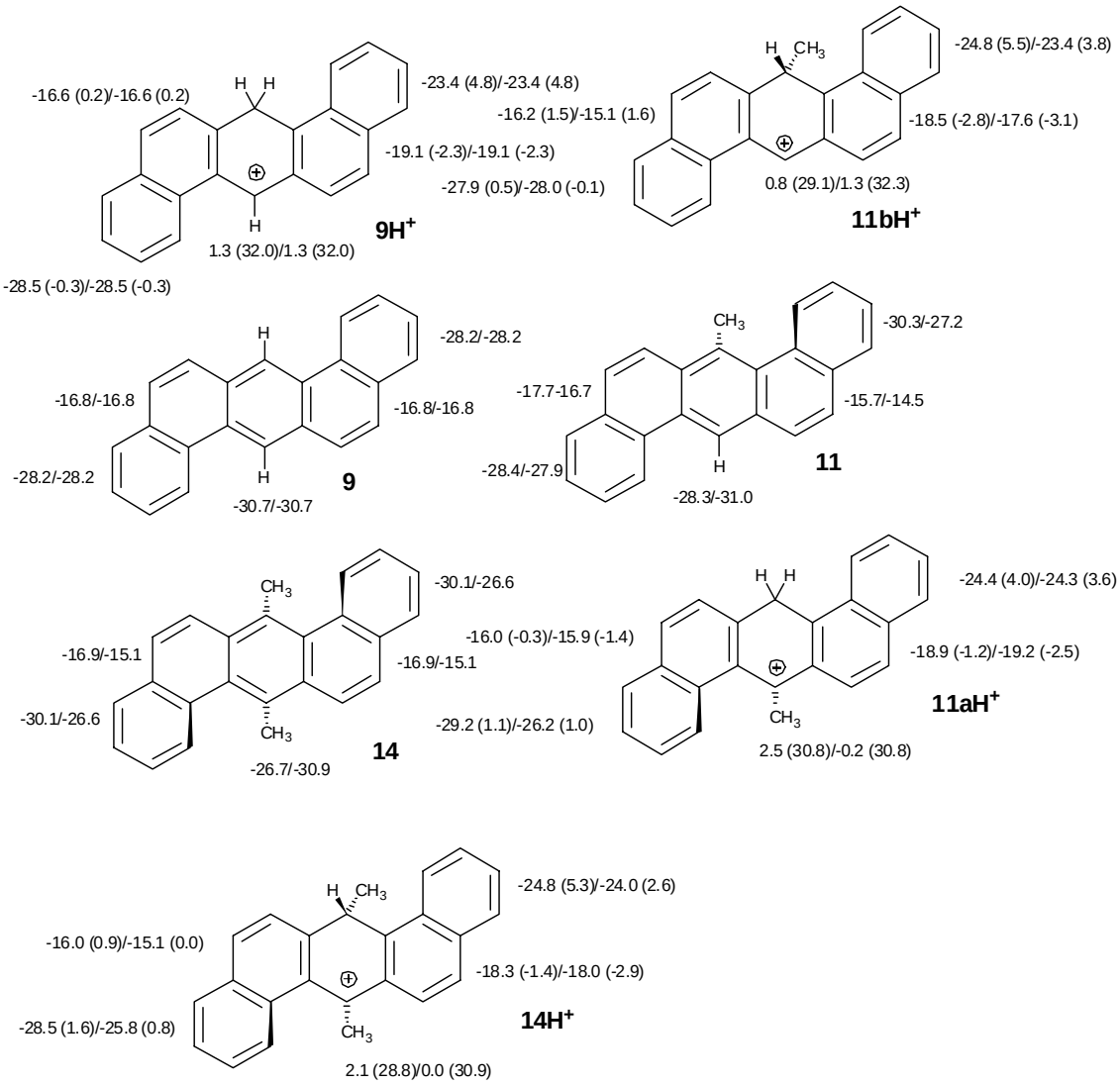
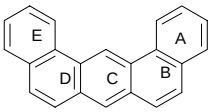
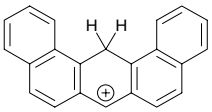
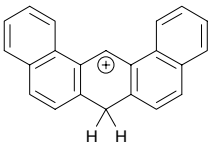
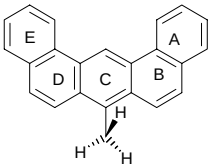
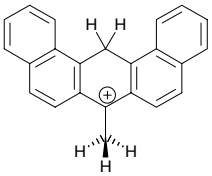
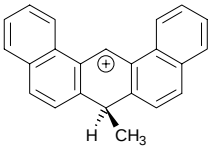
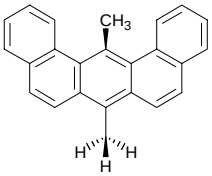
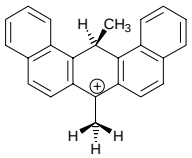
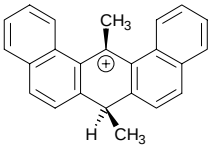


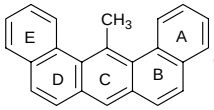
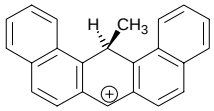
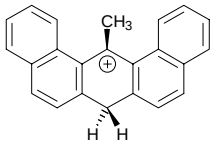
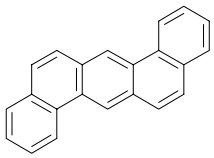
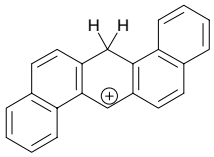
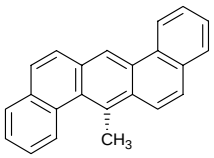
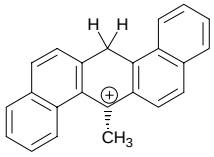
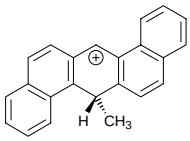
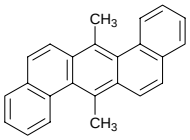
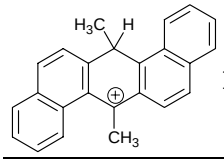
Chart S3. NICS(1)$_{zz}$ above/below molecules (ΔNICS(1)$_{zz}$) by B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) for dibenz[*a*,*h*]anthracenes and their Carbocations.

Table S1. Energy (E), Zero Point Energy (ZPE), Gibbs Free Energy (G), and Relative Gibbs Free Energy (ΔG) of the Optimized Structures for the DBAs and their Protonated Carbocations by B3LYP/6-31G(d).

Structures	Symmetry	E, hartree	ZPE, hartree	G, hartree	ΔG, kcal/mol[a]
 **1**	C_1	-846.826251	0.288555	-846.579650	(0)
 **1aH$^+$**	C_1	-847.1860834	0.300648	-846.927737	-218.4
 **1bH$^+$**	C_1	-847.1878926	0.300410	-846.930577	-220.2
 **2**	C_1	-886.1362597	0.316559	-885.864564	(0)
 **2aH$^+$**	C_1	-886.5015434	0.328667	-886.218374	-222.0
 **2bH$^+$**	C_1	-886.5008274	0.329291	-886.215800	-220.4
 **3**	C_1	-925.4268624	0.345485	-925.126957	(0)
 **3aH$^+$**	C_1	-925.813171	0.357662	-925.501159	-234.8
 **3bH$^+$**	C_1	-925.7992484	0.357720	-925.486601	-225.7

[a] Gibbs free energies relative to those of the corresponding neutral PAHs.

Table S1 (continued).

Structures	Symmetry	E, hartree	ZPE, hartree	G, hartree	ΔG, kcal/mol[a]
 **4**	C_1	-886.1183201	0.317504	-885.843481	(0)
 **4bH$^+$**	C_1	-886.4971396	0.329585	-886.210965	-230.6
 **4aH$^+$**	C_1	-886.4862237	0.328962	-886.200952	-224.3
 **9**	C_1	-846.8266086	0.288517	-846.580094	(0)
 **9H$^+$**	C_1	-847.1874248	0.300520	-846.929677	-219.4
 **11**	C_1	-886.127868	0.317176	-885.853734	(0)
 **11aH$^+$**	C_1	-886.4950068	0.328970	-886.209731	-223.4
 **11bH$^+$**	C_1	-886.4994067	0.329476	-886.213679	-225.9
 **14**	C_1	-925.4296662	0.345714	-925.127940	(0)
 **14H$^+$**	C_1	-925.8073439	0.357799	-925.494377	-229.9

[a] Gibbs free energies relative to those of the corresponding neutral PAHs.

Table S2. Angle between rings (°) from Optimized Geometries by B3LYP/6-31G(d)

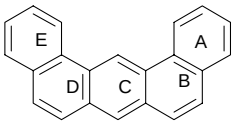
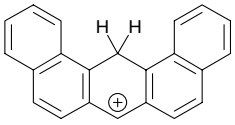
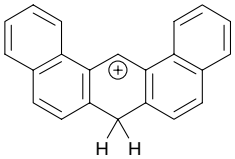
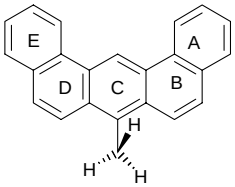
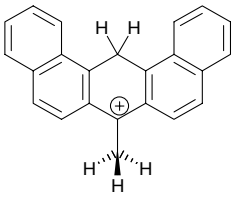
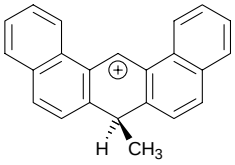
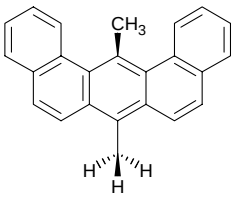
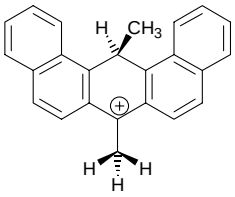
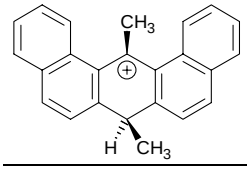
Structures	AB	AC	AD	AE	BC	BD	BE	CD	CE	DE
 **1**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
 **1aH$^+$**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
 **1bH$^+$**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
 **2**	0.3	1.2	2.0	1.8	1.2	2.2	2.1	1.5	1.6	0.4
 **2aH$^+$**	0.7	3.1	5.7	5.4	3.1	6.0	5.7	3.2	3.2	0.7
 **2bH$^+$**	0.8	5.8	9.1	8.9	5.5	9.2	9.1	5.5	5.8	0.8
 **3**	9.3	16.3	10.9	5.1	7.5	6.2	10.9	7.5	16.3	7.5
 **3aH$^+$**	0.2	7.8	14.7	14.7	7.7	14.6	14.7	7.7	7.8	0.2
 **3bH$^+$**	5.8	9.3	11.8	10.2	5.5	10.4	11.8	5.5	9.3	5.8

Table S2 (continued).

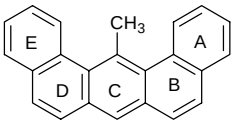
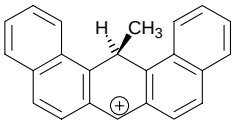
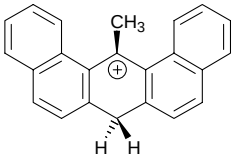
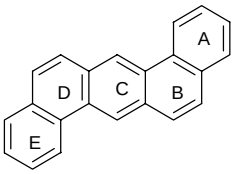
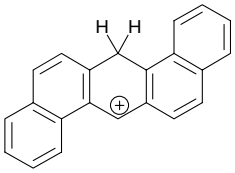
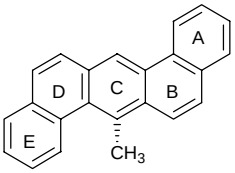
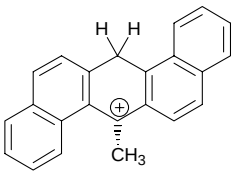
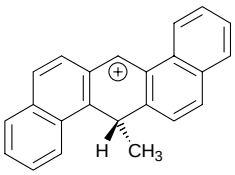
Structures	AB	AC	AD	AE	BC	BD	BE	CD	CE	DE
 **4**	8.3	13.5	8.8	2.5	5.3	3.1	8.8	5.3	13.5	8.3
 **4bH$^+$**	0.9	6.6	9.5	9.7	5.8	9.2	9.5	5.8	6.6	0.9
 **4aH$^+$**	6.6	11.3	7.1	2.6	9.8	2.3	7.1	4.8	11.3	8.6
 **9**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
 **9H$^+$**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
 **11**	0.8	3.3	11.3	20.6	2.8	10.5	19.8	8.5	17.8	9.4
 **11aH$^+$**	0.8	4.9	11.6	19.5	5.2	12.2	20.2	9.4	17.5	8.1
 **11bH$^+$**	0.7	6.4	9.7	9.9	6.1	9.7	10.1	5.8	6.7	1.1

Table S2 (continued).

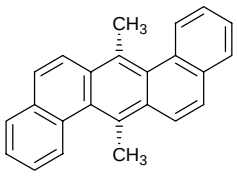
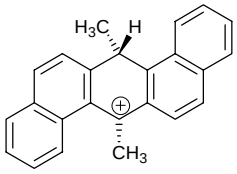
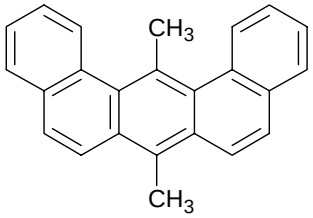
Structures	AB	AC	AD	AE	BC	BD	BE	CD	CE	DE	
 **14**	9.4	20.3	31.2	40.6	10.9	21.9	31.2	10.9	20.3		9.4
 **14H$^+$**	0.4	10.0	16.5	22.1	9.7	16.2	21.9	7.0	13.8	7.3	

Table S3. Angle between Rings (^{o}) of 7,14-Dimethyldibenz[*a*,*j*]anthracene **3** by X-ray Analysis and via B3LYP/6-31G(d) Calculations

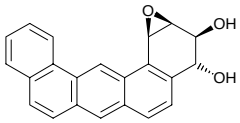
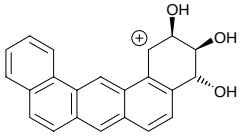
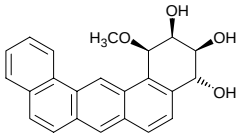
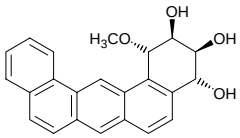
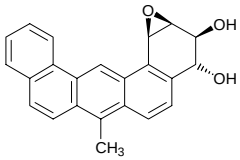
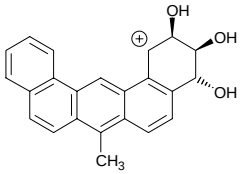
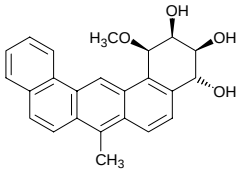
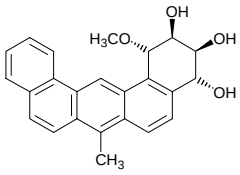


3

Method	AB	AC	AD	AE	BC	BD	BE	CD	CE	DE
X-ray[a]	5.2	8.5	11.6	5.3	13.2	16.1	9.2	3.4	4.4	6.9
B3LYP/6-31G(d)	16.3	10.9	5.1	7.5	6.2	10.9	7.5	16.3	7.5	9.3

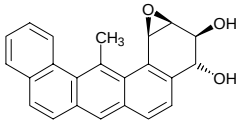
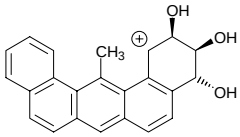
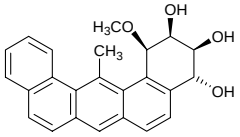
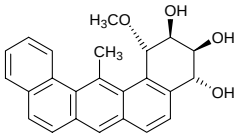
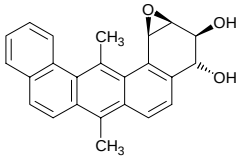
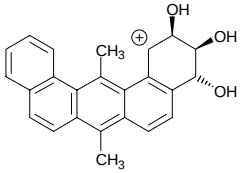
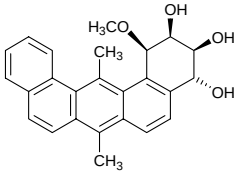
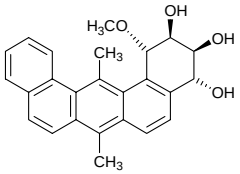
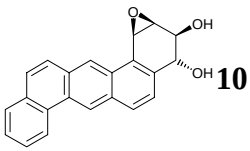
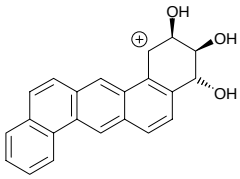
[a] Carrell, C. J.; Carrell, H. L.; Glusker, J. P.; Abu-Shaqara, E.; Cortez, C.; Harvey, R. G. *Carcinogenesis* **1994**, *15*, 2931.

Table S4. Energy (E), Zero Point Energy (ZPE), Gibbs Free Energy (G), and Relative Gibbs Free Energy (ΔG) of the Optimized Structures for Diol-epoxides (DEs), their Bay-region Carbocations and Quenching, by B3LYP/6-31G(d)

Structures	Symmetry	E, hartree	ZPE, hartree	G, hartree	ΔG, kcal/mol[a]
 **5**	C_1	-1073.6263036	0.325280	-1073.346930	(0)
 **5$^+$**	C_1	-1074.0079233	0.336892	-1073.718086	-232.9
 **5a**	C_1	-1189.3823009	0.381755	-1189.050361	(0)
 **5b**	C_1	-1189.3786045	0.381093	-1189.047941	1.5
 **6**	C_1	-1112.9368286	0.353355	-1112.632101	(0)
 **6$^+$**	C_1	-1113.3215975	0.365068	-1113.005524	-234.3
 **6a**	C_1	-1228. 692682	0.409827	-1228.335572	(0)
 **6b**	C_1	-1228.6891034	0.409188	-1228.333033	1.6

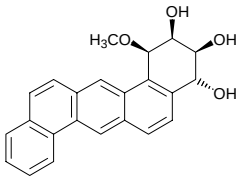
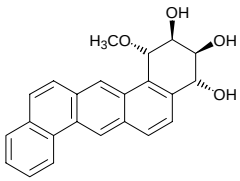
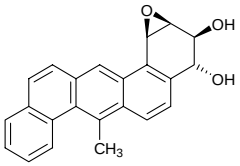
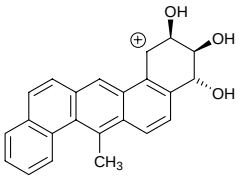
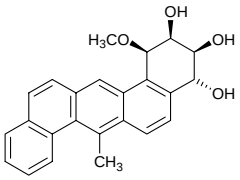
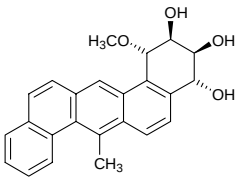
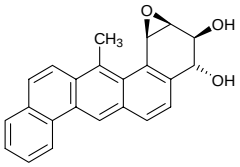
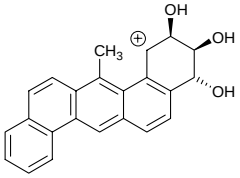
[a] Gibbs free energies for bay-region carbocations relative to epoxides.

Table S4 (continued).

Structures	Symmetry	E, hartree	ZPE, hartree	G, hartree	ΔG, kcal/mol[a]
 **7**	C_1	-1112.9197449	0.354045	-1112.612390	(0)
 **7$^+$**	C_1	-1113.30 65581	0.365816	-1112.988410	-236.0
 **7a**	C_1	-1228.66889	0.410330	-1228.308611	(0)
 **7b**	C_1	-1228.6675398	0.409851	-1228.308368	0.2
 **8**	C_1	-1152.2288762	0.382173	-1151.895690	(0)
 **8$^+$**	C_1	-1152.6187755	0.393941	-1152.274443	-237.7
 **8a**	C_1	-1267.9778575	0.438431	-1267.591857	(0)
 **8b**	C_1	-1267.9767372	0.437978	-1267.591742	0.1
 **10**	C_1	-1073.6267107	0.325247	-1073.347476	(0)
 **10$^+$**	C_1	-1074.0101389	0.337032	-1073.720065	-233.8

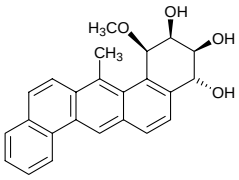
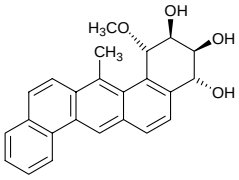
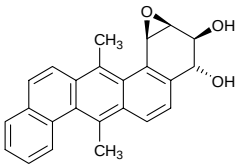
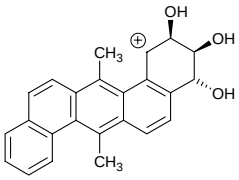
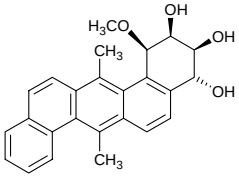
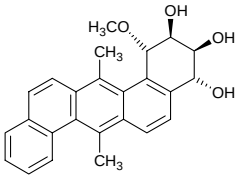
[a] Gibbs free energies for bay-region carbocations relative to epoxides.

Table S4 (continued).

Structures	Symmetry	E, hartree	ZPE, hartree	G, hartree	ΔG, kcal/mol[a]
 **10a**	C_1	-1189.3827531	0.381725	-1189.050950	(0)
 **10b**	C_1	-1189.3776089	0.381400	-1189.046614	2.7
 **12**	C_1	-1112.9288375	0.353907	-1112.621952	(0)
 **12$^+$**	C_1	-1113.3147837	0.365587	-1112.997179	-235.5
 **12a**	C_1	-1228.6845447	0.410458	-1228.324903	(0)
 **12b**	C_1	-1228.680705	0.409953	-1228.321869	1.9
 **13**	C_1	-1112.9290445	0.353851	-1112.622164	(0)
 **13$^+$**	C_1	-1113.3189847	0.365612	-1113.001388	-238.0

[a] Gibbs free energies for bay-region carbocations relative to epoxides.

Table S4 (continued).

Structures	Symmetry	E, hartree	ZPE, hartree	G, hartree	ΔG, kcal/mol[a]
 **13a**	C_1	-1228.6778643	0.410346	-1228.318824	(0)
 **13b**	C_1	-1228.6757757	0.410322	-1228.316331	1.6
 **15**	C_1	-1152.2278743	0.382315	-1151.893455	(0)
 **15$^+$**	C_1	-1152.6235248	0.394041	-1152.278537	-241.6
 **15a**	C_1	-1267.9808545	0.438586	-1267.594807	(0)
 **15b**	C_1	-1267.9783169	0.437969	-1267.592805	1.3

[a] Gibbs free energies for bay-region carbocations relative to epoxides.

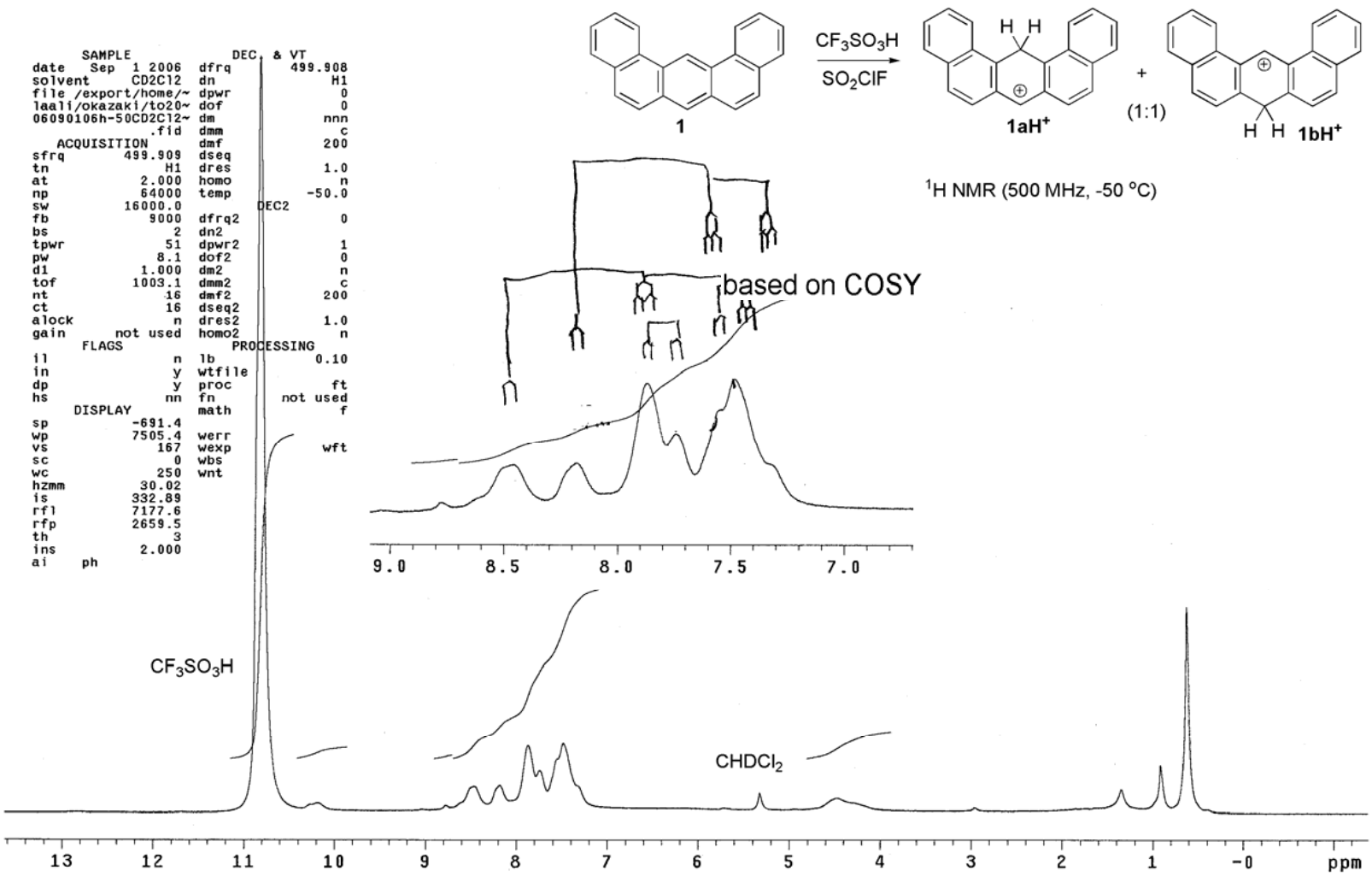


Figure S1. ^{1}H NMR spectrum for carbocations **1aH**$^{+}$ and **1bH**$^{+}$ derived from dibenz[*a*,*j*]anthracene **1** in CF_3SO_3H/SO_2ClF at -50 °C.

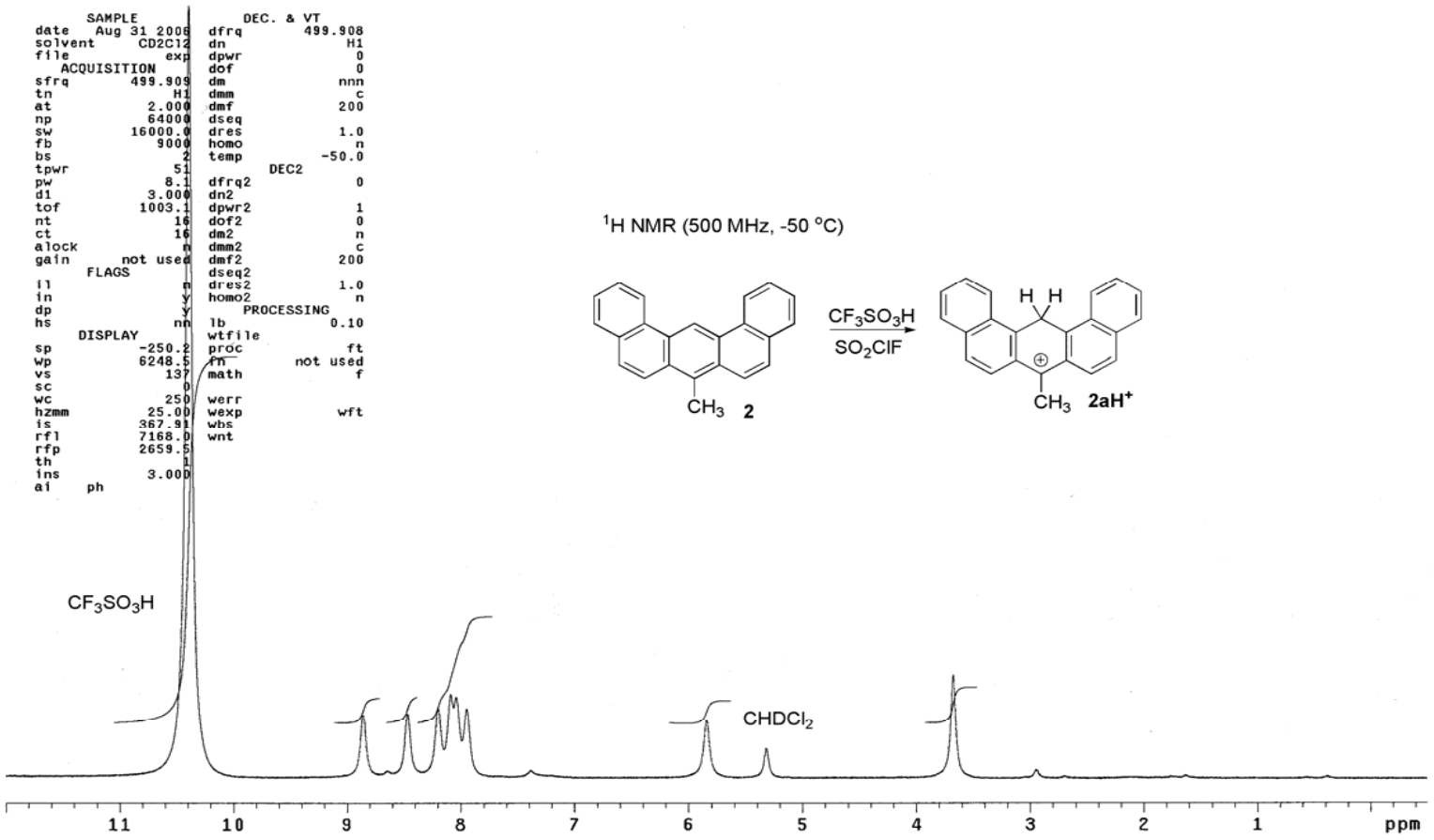


Figure S2. ^{1}H NMR spectrum for carbocation **2aH**$^{+}$ derived from 7-methyldibenz[*a*,*j*]anthracene **2** in CF_3SO_3H/SO_2ClF at -50 ^{o}C.

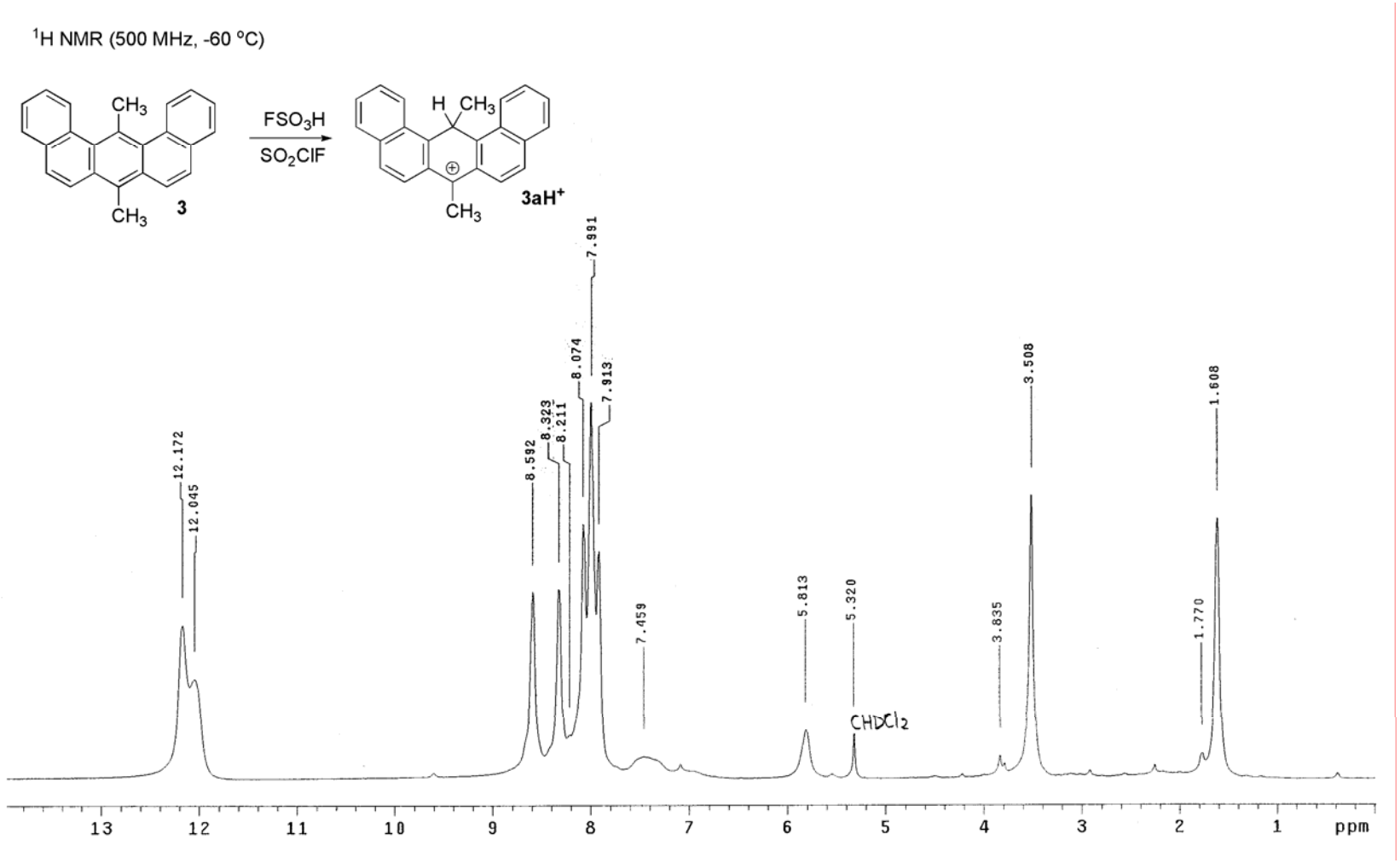


Figure S3. ^{1}H NMR spectrum for carbocation **3aH**$^{+}$ derived from 7,12-dimethyldibenz[*a*,*j*]anthracene **3** in FSO_3H/SO_2ClF at -60 ^{o}C.

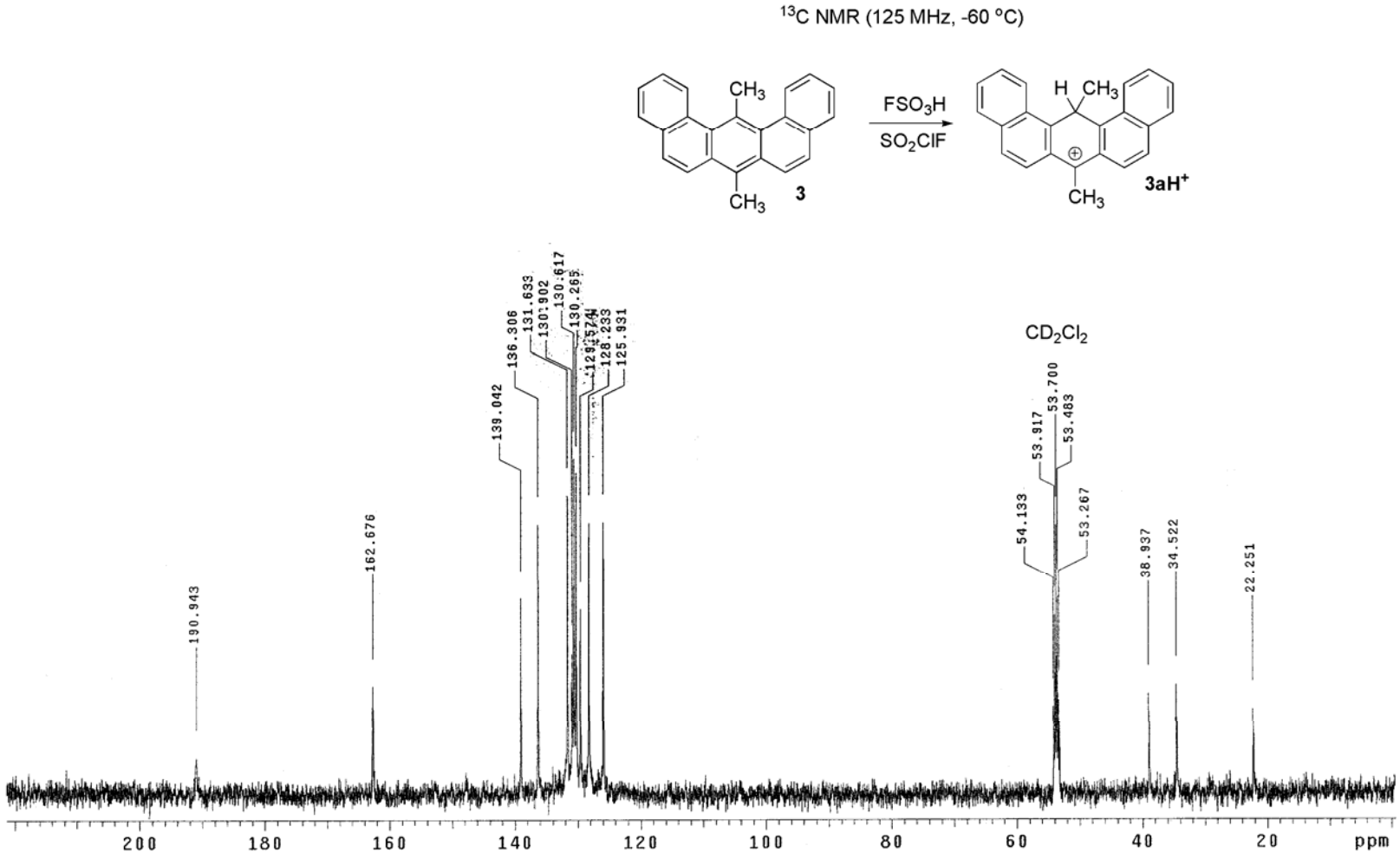


Figure S4. ^{13}C NMR spectrum for carbocation **3aH$^+$** derived from 7,12-dimethyldibenz[*a*,*j*]anthracene **3** in FSO_3H/SO_2ClF at -60 ^{o}C.