**Supporting information**

# Transannular π-π interactions in Janusenes and in related rigid systems with cofacial aromatic rings; gauging aromaticity in the hydrocarbons and in model carbocations; a DFT study .

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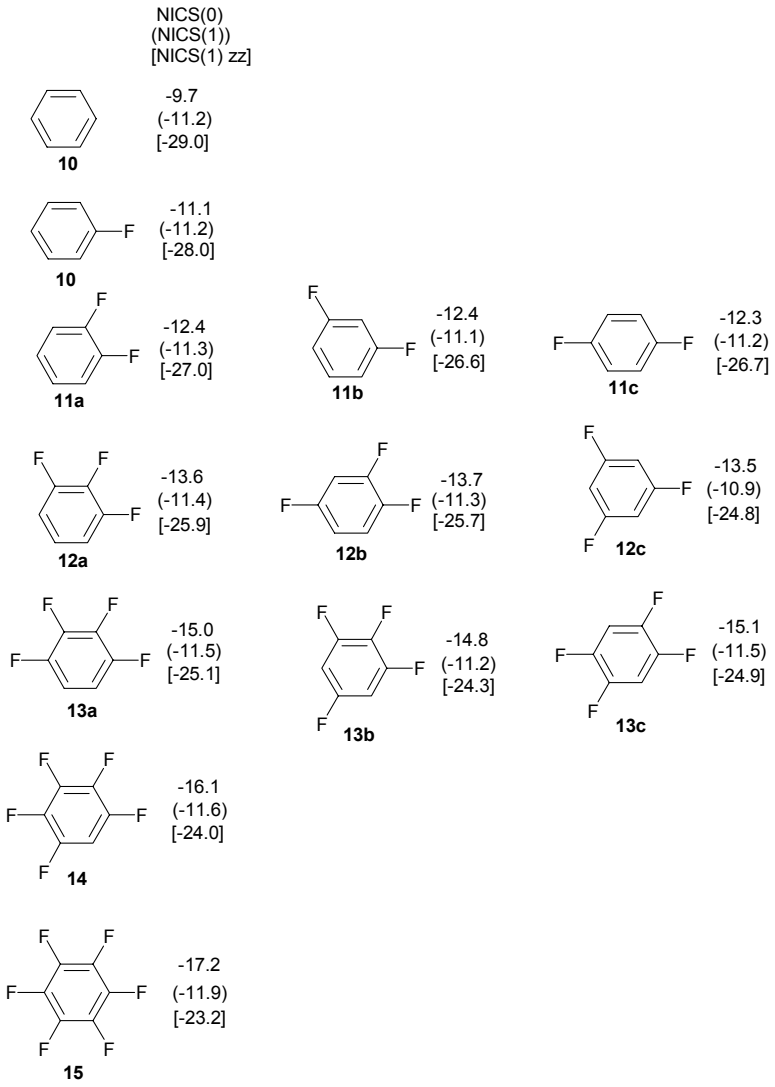



**Fig. S1.** NICS(0), (NICS(1) in parentheses) and [NICS(1)$_{zz}$ in brackets] for benzene (**9**) and fluorinated benzenes (**10-15**) by B3LYP/6-31G(d).

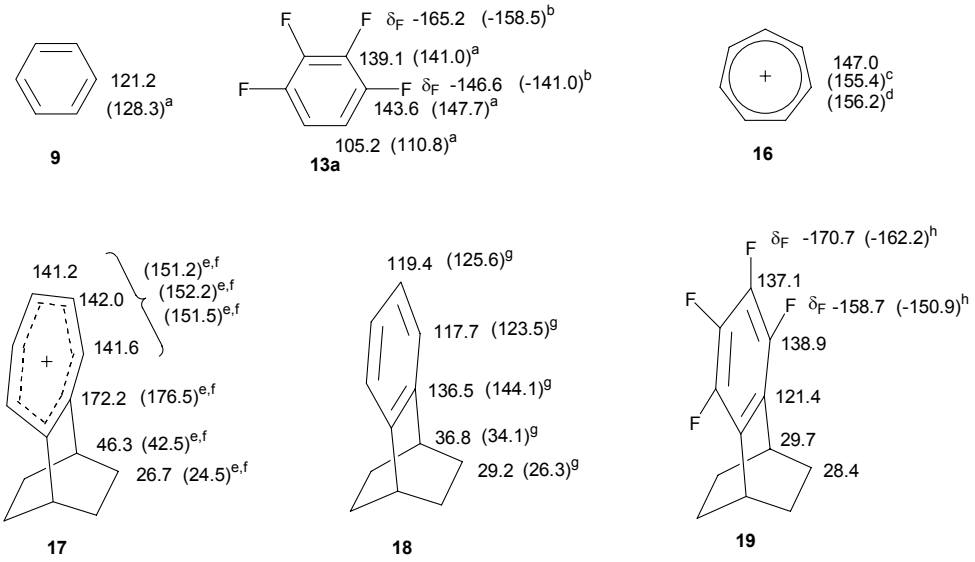



**Figure S2.** GIAO-derived NMR data for benzene (**9**),[a] 1,2,3,4-tetrafluorobenzene (**13a**),[a,b] tropylium ion (**16**),[c,d] bicyclo[2.2.2]octenotropylium ion (**17**),[e,f] bicyclo[2.2.2]octenobenzene (**18**),[g] and tetrafluorobicyclo[2.2.2]octenobenzene (**19**)[h] by B3LYP/6-31G(d) (Experimental $\delta^{13}C$ and $\delta^{19}F$ in parentheses).


[a] In $CDCl_3$: The Aldrich/ACD Library of FT-NMR Spectra Standard, Aldrich Chemical Co., Inc. 1998.

[b] G. A. Olah and Y. K. Mo, *J . Org. Chem.*, 1973, **38**, 3212.

[c] Tetrafluoroborate salts: H. Spieseche and W. G. Schneider, *Tetrahedron Lett.*, 1961, 468

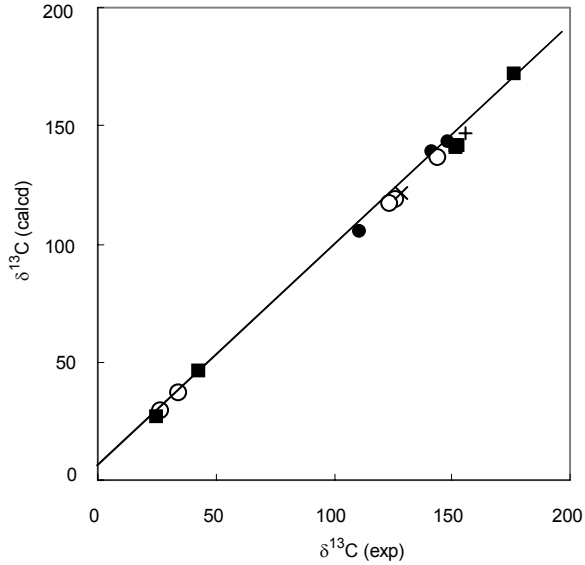
[d] Perchlorate in $CD_3CN$: K. Takeuchi, Y. Yokomichi, Y. Kubota and K. Okamoto, *Tetrahedron*, 1980, **36**, 2939.

[e] Perchlorate salts in $CD_3CN$: K. Komatsu, H. Akamatsu, S. Aonuma, Y. Jinbu, N. Maekawa and K. Takeuchi, *Tetrahedron*, 1991, **47**, 6951.

[f] Tetrafluoroborate salts: T. Nakazawa, Y. Niimoto, K. Kubo and I. Murata, *Angew. Chem.*, 1980, **92**, 566.

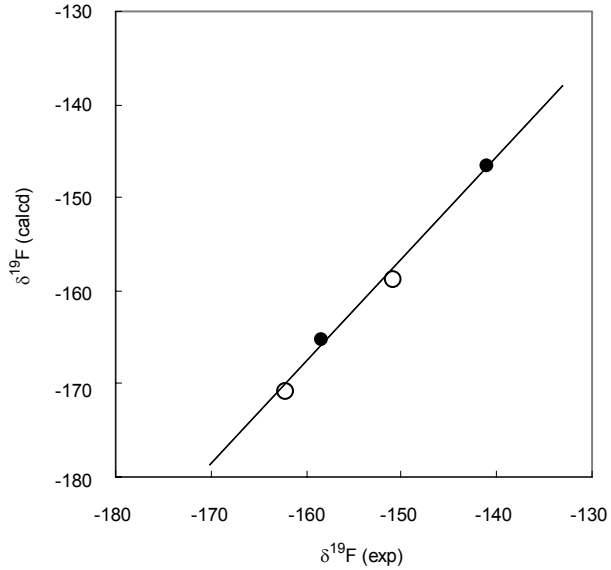
[g] In $CDCl_3$: K. Kitahonoki, K. Sakurawi, K. Tori and M. Uneyama, *Tetrahedron Lett.*, 1976, 263.

[h] G. M. Brooke, R. S. Matthews and A. C. Young, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1411.




$\delta^{13}C$ (calcd) = 0.92 × $\delta^{13}C$ (exp) + 5.0  $R^2$ = 0.9973

**Figure S3.** Plot of GIAO-derived $\delta^{13}C$ by B3LYP/6-31G(d) against experimental $\delta^{13}C$ for benzene (**9**: ×), 1,2,3,4-tetrafluorobenzene (**13a**: ●), tropylium ion (**16**: +), bicyclo[2.2.2]octenotropylium ion (**17**: ■) and bicyclo[2.2.2]octenobenzene (**18**: ○).




$\delta^{19}F$ (calcd) = 1.10 × $\delta^{19}F$ (exp) + 8.7  $R^2$ = 0.9937

**Figure S4.** Plot of GIAO-derived $\delta^{19}F$ by B3LYP/6-31G(d) against experimental $\delta^{19}F$ for 1,2,3,4-tetrafluorobenzene (**13a**: ●) and tetrafluorobicyclo[2.2.2]octenobenzene (**19**: ○).

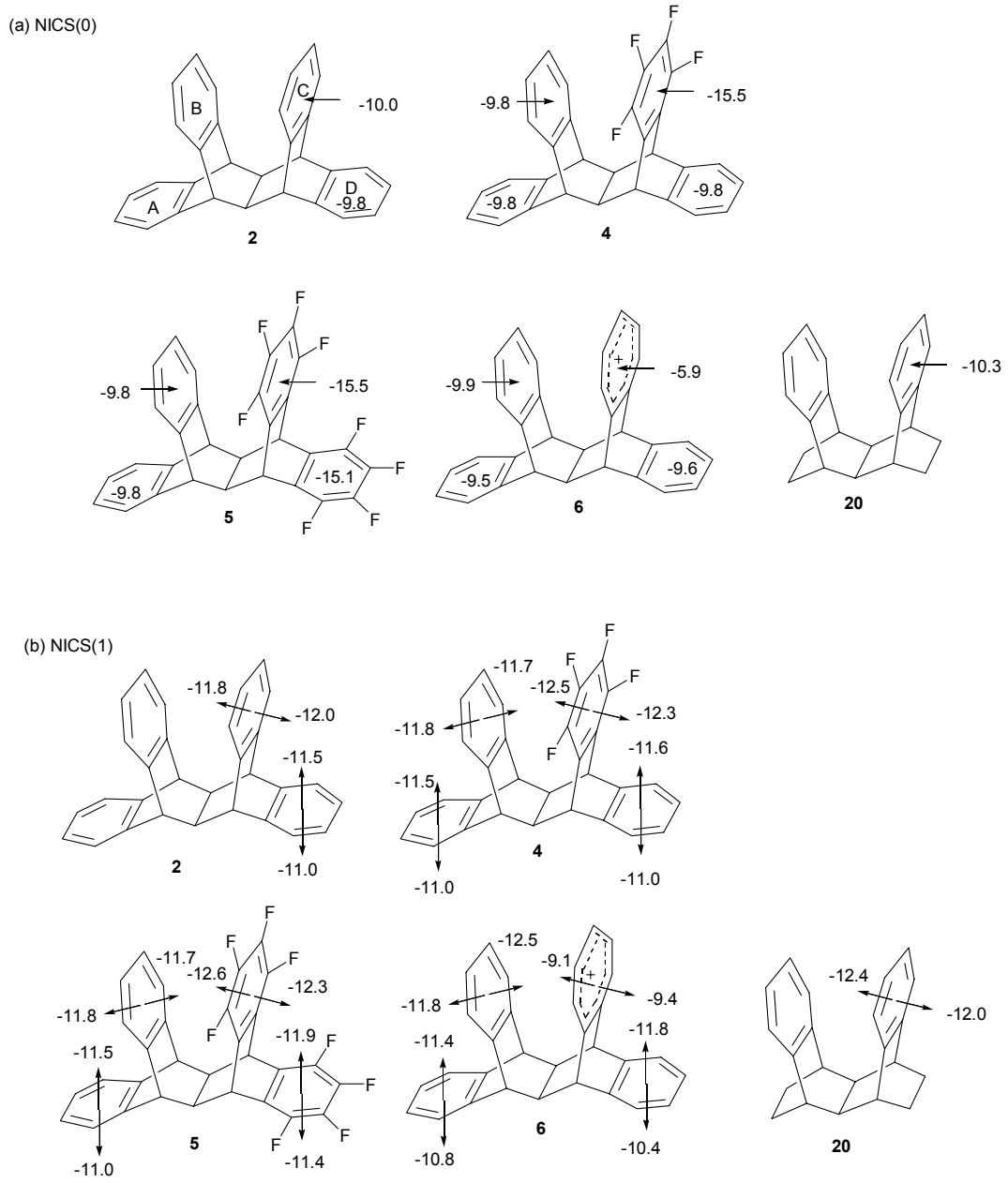
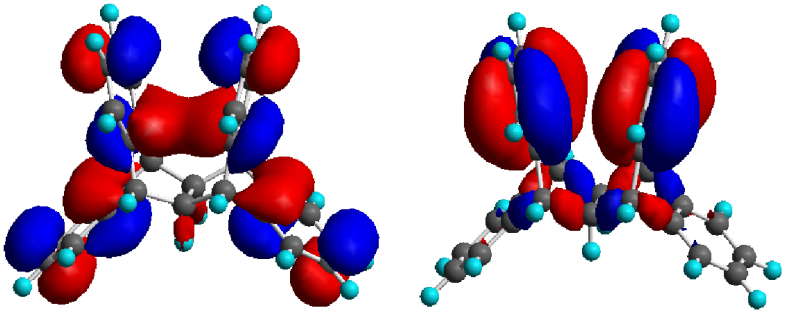
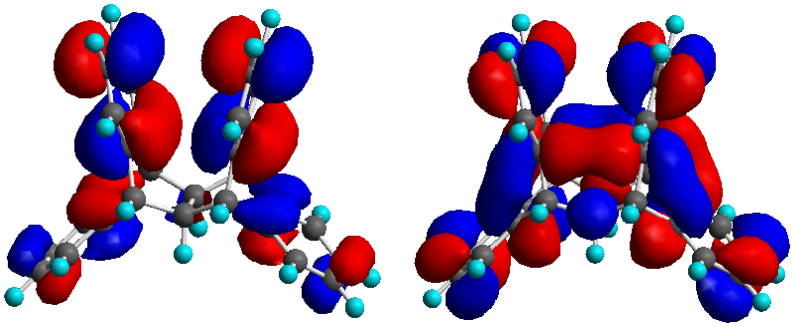



**Figure S5.** (a) NICS(0) and (b) NICS(1) for janusene (**2**), fluorinated janusenes (**4** and **5**), tropiliojanusene (**6**) and *syn*-sesquibenzobicyclo[2.2.2]octane (**20**) by B3LYP/6-31G(d).



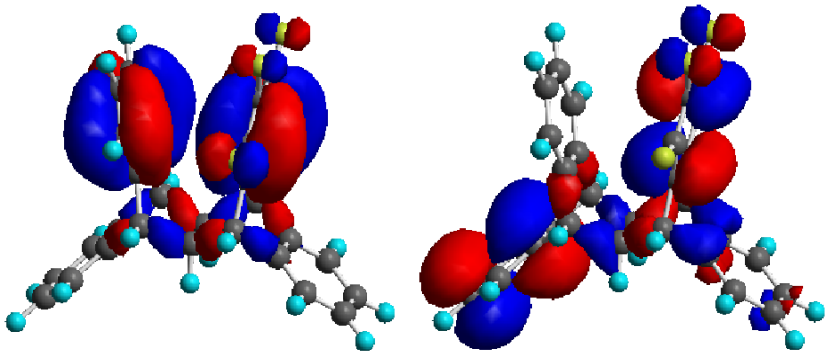
HOMO-2 HOMO-1

**2**



HOMO LUMO

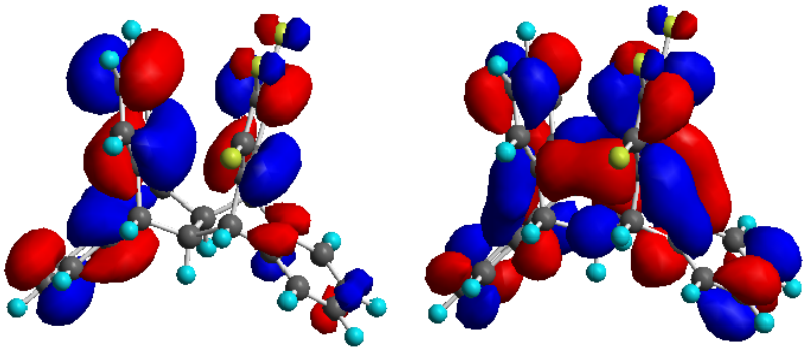
**2**



HOMO-2 HOMO-1

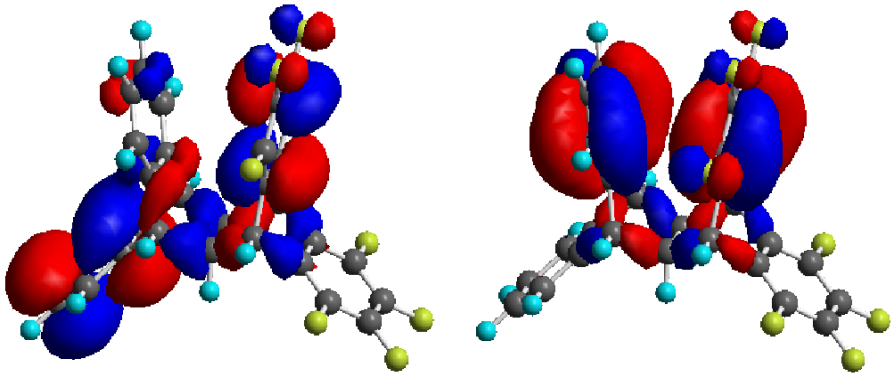
**4**

**Figure S6.** Drawings of HOMO-2, HOMO-1, HOMO and LUMO for **2** and **4**-**6**.



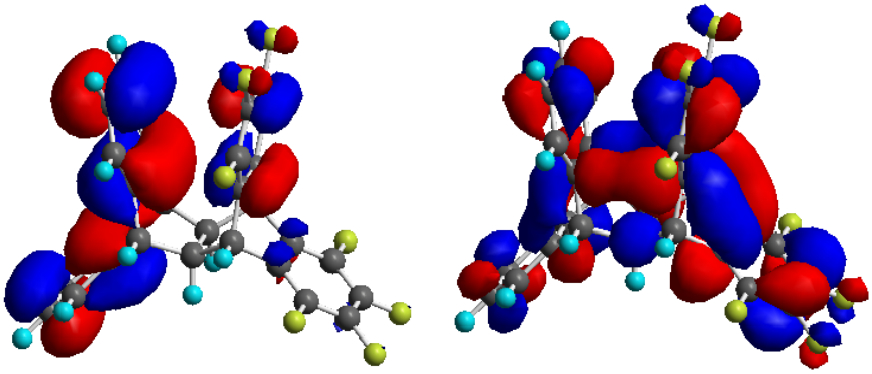
HOMO LUMO

**4**



HOMO-2 HOMO-1

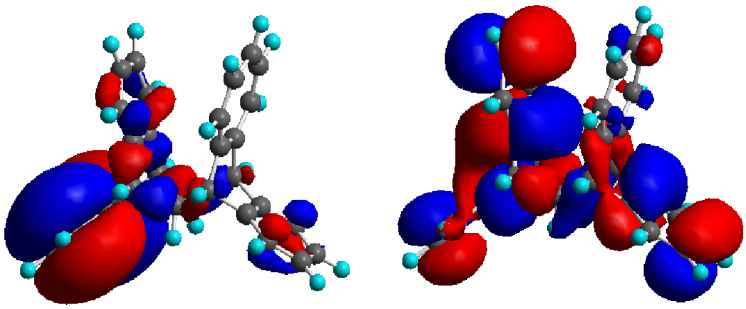
**5**



HOMO LUMO

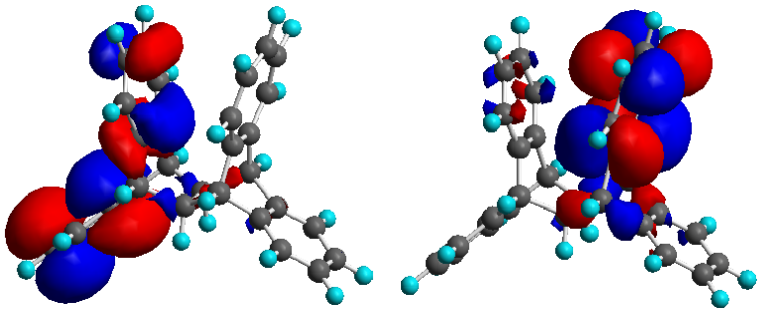
**5**

**Figure S6 (continued).**



HOMO-2 HOMO-1

**6**



HOMO LUMO

**6**

**Figure S6 (continued).**

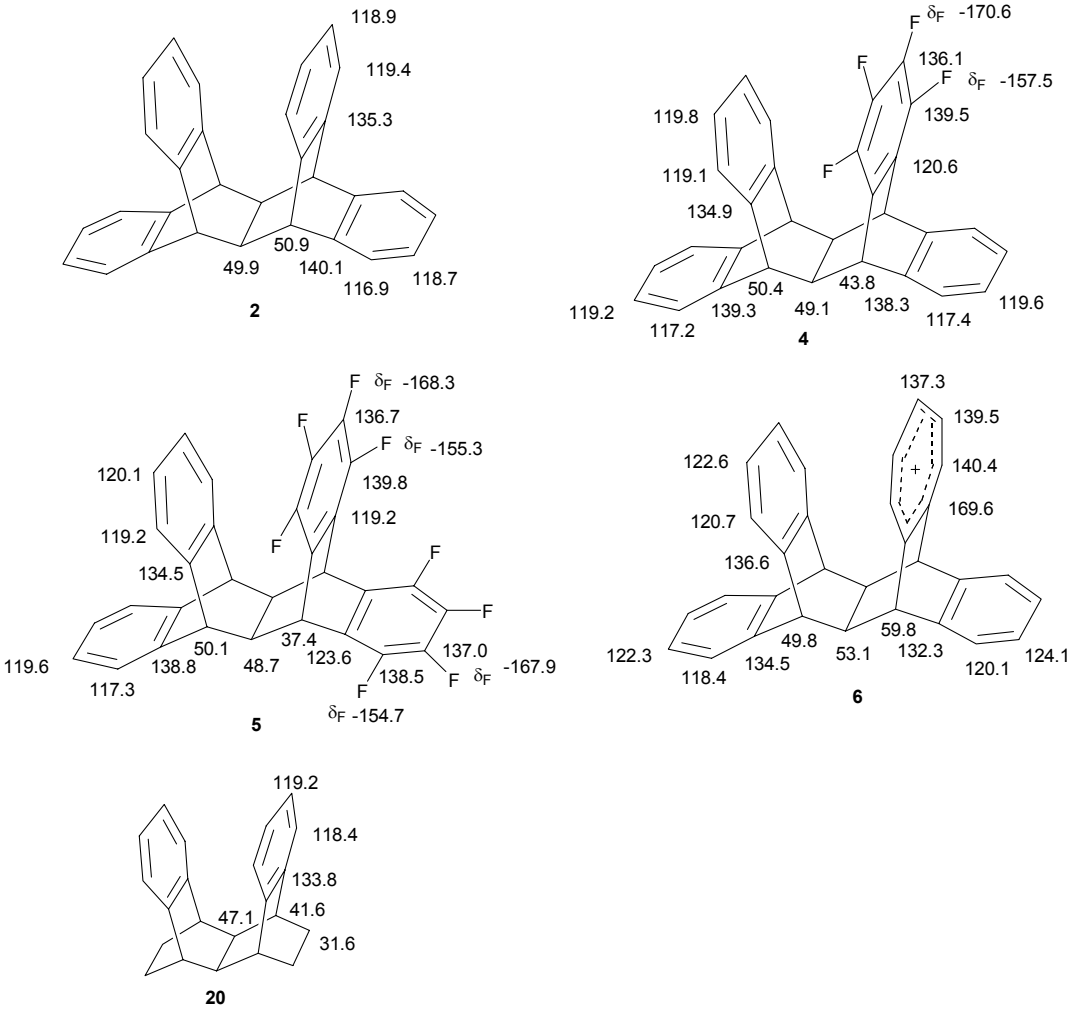
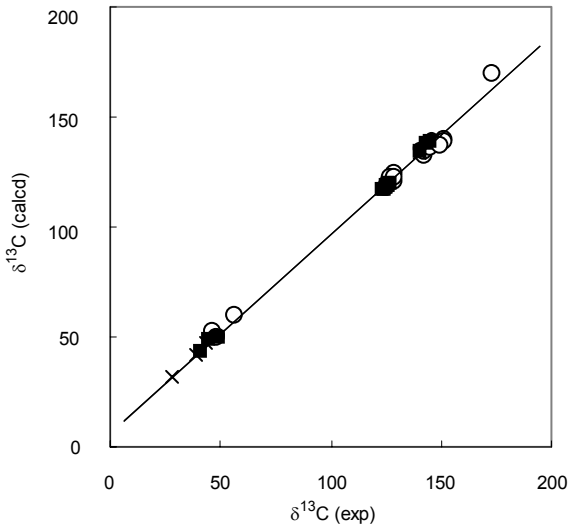
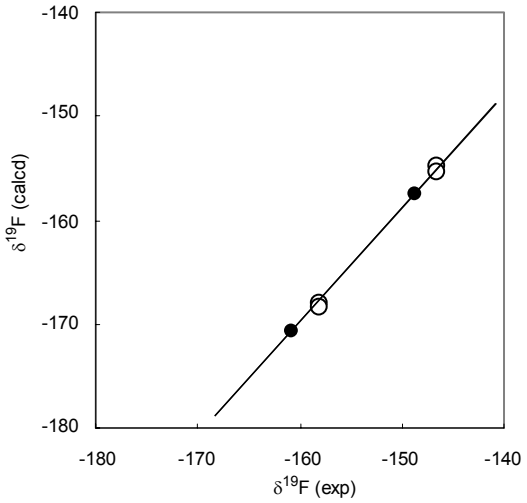



**Figure S7.** GIAO-derived NMR data for janusene (**2**), tetrafluorojanusene (**4**), octafluorojanusene (**5**), tropiliojanusene (**6**) and *syn*-sesquibenzobicyclo[2.2.2]octane (**20**) by B3LYP/6-31G(d). Experimental NMR data; **2**: $\delta^{13}$C (in $CDCl_3$) 145.6, 140.4, 125.6, 125.5, 125.3, 123.8, 49.1, 45.1, J. M. Mcintosh and R. K. Leavitt, *J. Org. Chem.*, 1984, **49**, 3407; **4**: $\delta^{13}$C (in $CDCl_3$) 144.81, 143.21, 140.12, 126.36, 126.01, 125.83, 124.70, 123.59, 123.21, 48.51, 44.27, 40.90, $\delta^{19}$F (in $CDC1_3$) -148.87--148.64, -161.12--160.72, R. Filler and G. L. Cantrell, *J. Fluorine Chem.*, 1987, **36**, 407; **5**: $\delta^{19}$F NMR (in $CDCl_3$) -146.94--146.39, -158.23; $\delta^{13}$C (in $CDCl_3$) 144.27, 139.68, 126.26, 126.12, 124.78, 48.04, 43.36, 33.55, R. Filler and G. L. Cantrell, *J. Fluorine Chem.*, 1987, **36**, 407; **6**: $\delta^{13}$C (in $CD_3CN$) 172.8, 151.1, 151.0, 149.1, 145.1, 141.9, 141.8, 128.8, 128.5, 128.1, 127.0, 126.2, 124.6, 56.1, 48.1, 46.6, K. Komatsu, K. Takahashi and K. Okamoto, *Tetrahedron Lett.*, 1979, 4747; **20**: $\delta^{13}$C (in $CDCl_3$) 140.63. 125.35, 124.73, 43.60, 39.33, 27.87, W. Grimme, H. T. Kaemmerling, J. Lex, R. Gleiter, J. Heinze and M.Dietrich, *Angew. Chem., Int. Ed.,* 1991, **30**, 205.




$\delta^{13}C$ (calcd) = 0.89 × $\delta^{13}C$ (exp) + 7.8  $R^2$ = 0.9972

**Figure S8.** Plot of GIAO-derived $\delta^{13}C$ by B3LYP/6-31G(d) against experimental $\delta^{13}C$ for janusene (**2**: ●), tetrafluorojanusene (**4**: ■), tropiliojanusene (**6**: ○) and *syn*-sesquibenzobicyclo[2.2.2]octane (**20**: ×) by B3LYP/6-31G(d).




$\delta^{19}F$ (calcd) = 1.11 × $\delta^{19}F$ (exp) + 8.5  $R^2$ = 0.9984

**Figure S9.** Plot of GIAO-derived $\delta^{19}F$ by B3LYP/6-31G(d) against experimental $\delta^{19}F$ for tetrafluorojanusene (**4**: ■) and octafluorojansuene (**5**: ○).

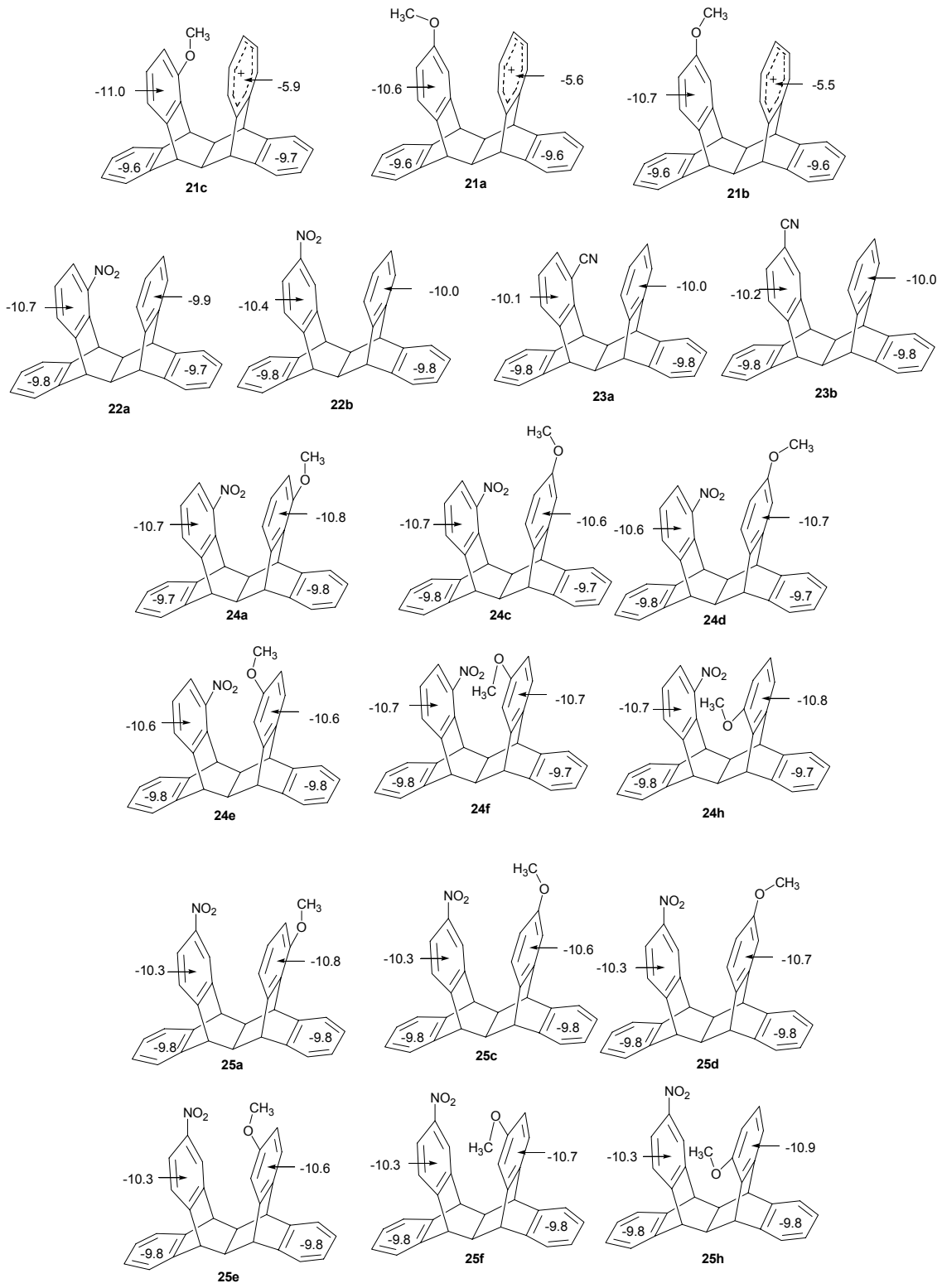



**Figure S10.** NICS(0) for **21-25** by B3LYP/6-31G(d).

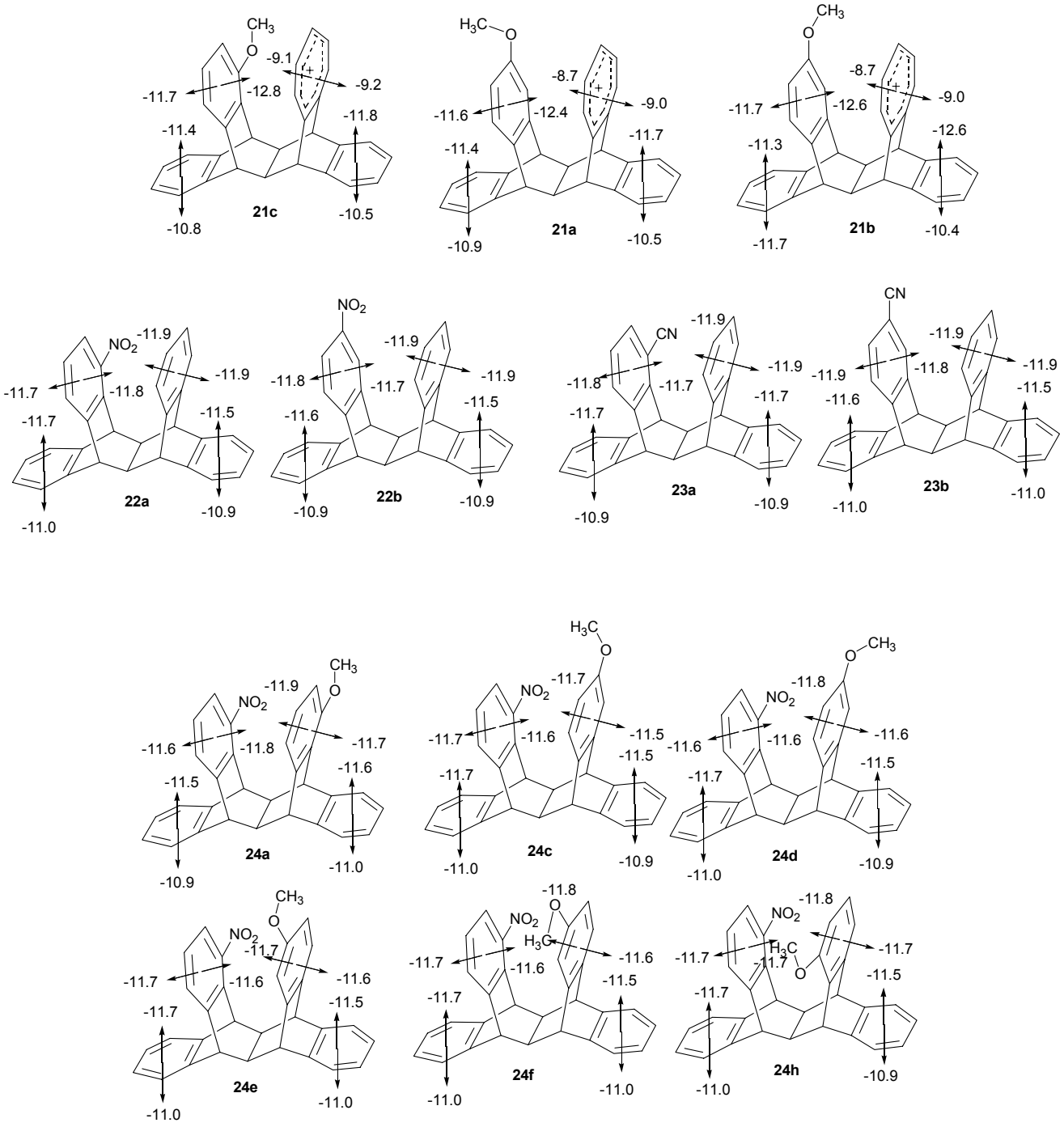



**Figure S11.** NICS(1) for **21-25** by B3LYP/6-31G(d)

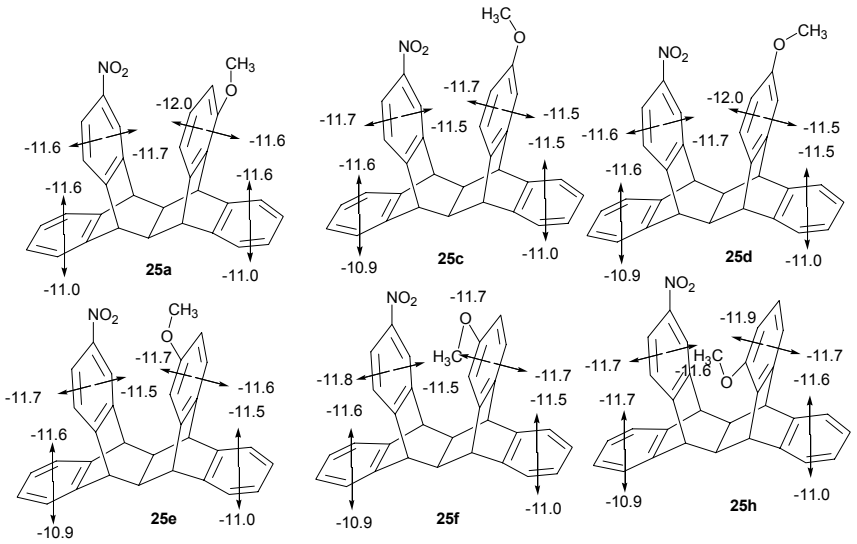



**Figure S11 (continued).**

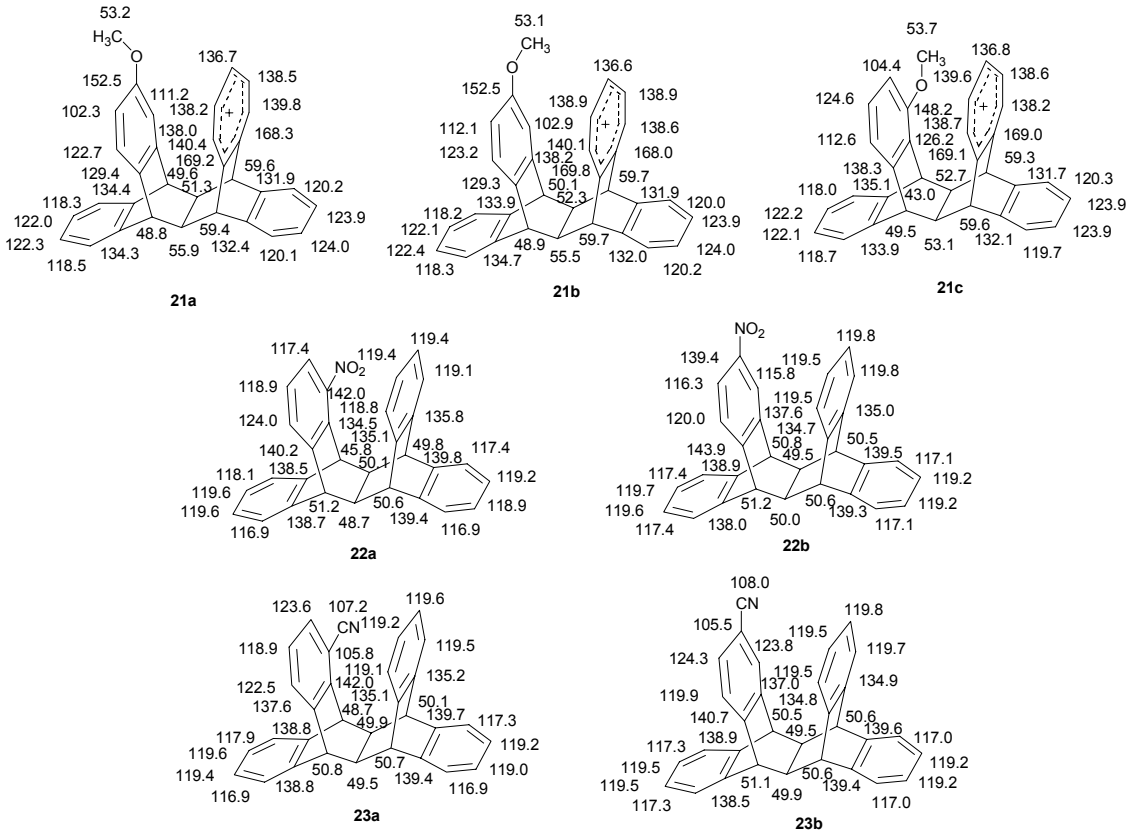



**Figure S12.** GIAO derived $^{13}$C NMR chemical shifts for **21**-**25** by B3LYP/6-31G(d).

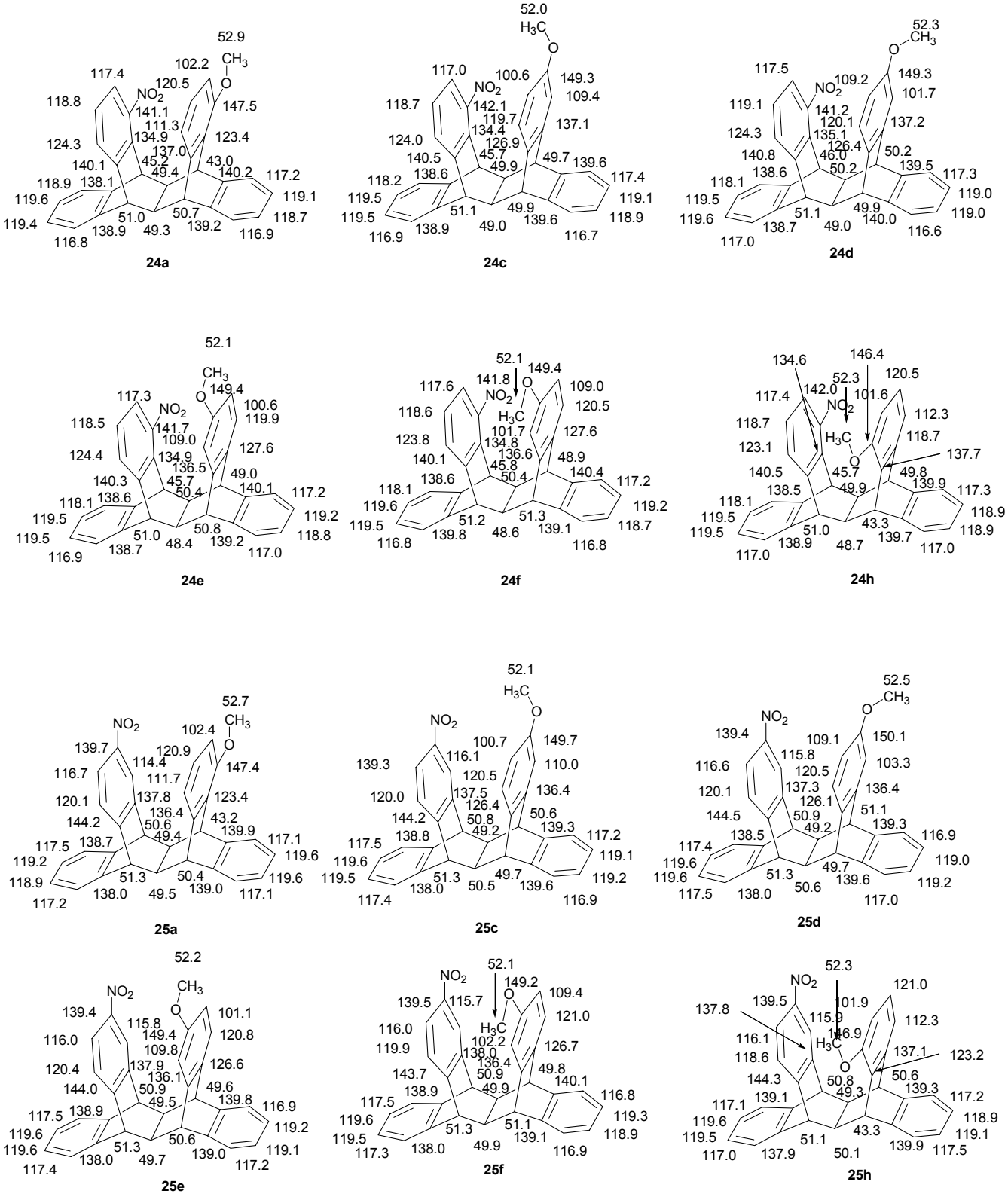



**Figure S12 (continued).**

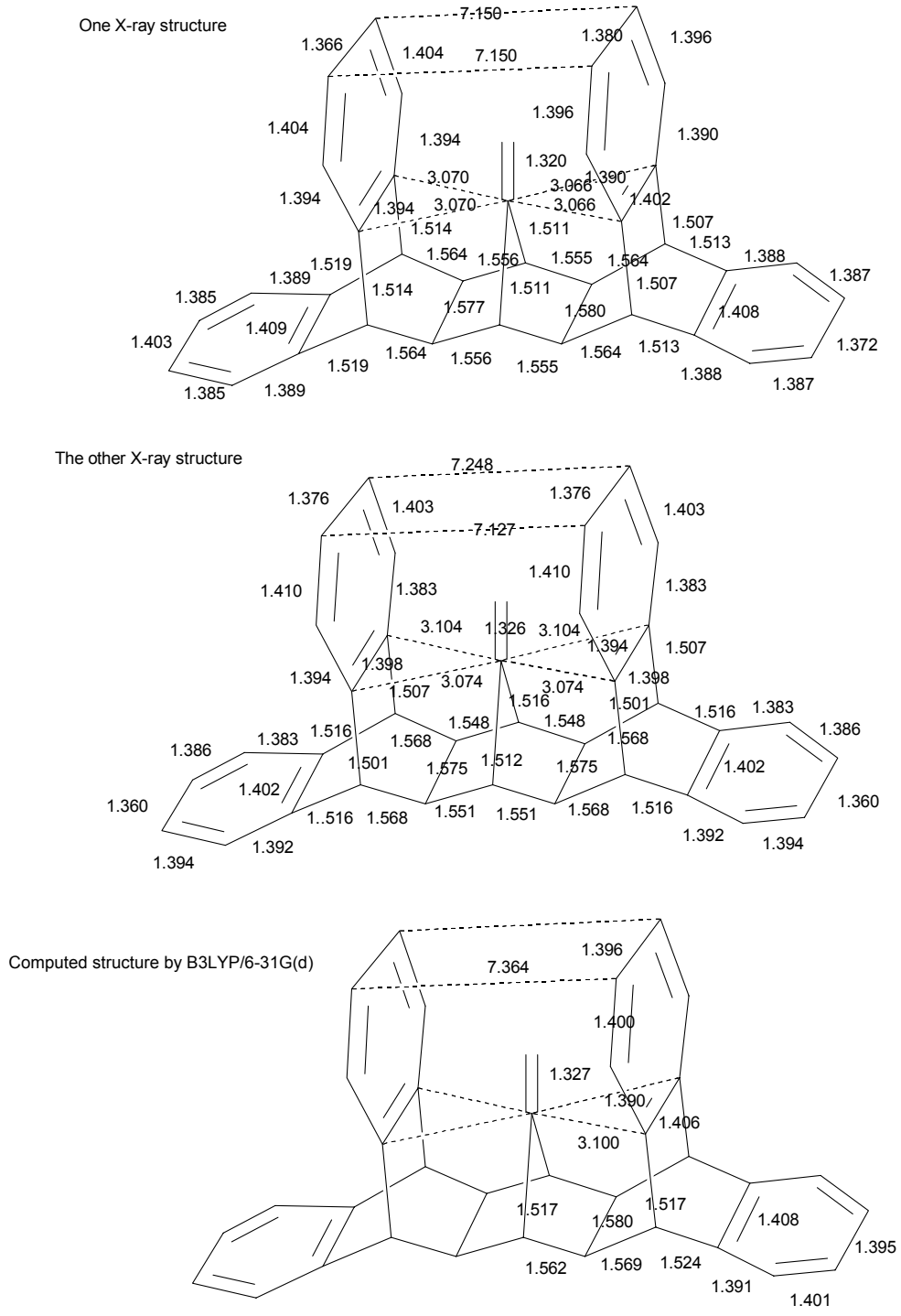



**Figure S13.** Bond lengths, Å, of two X-ray structures for **8** in reference 24 and computed structures by B3LYP/6-31G(d).

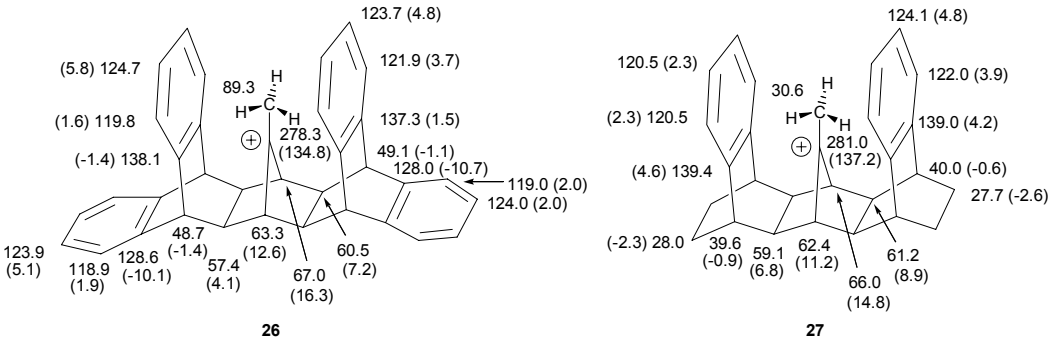



**Figure S14.** GIAO derived $^{13}C$ NMR data for **26** and **27** (relative δ $^{13}C$ to those of parent hydrocarbon in parentheses).

**Table S1.** Electronic Energies (E), Zero Point Energies (ZPE), Gibbs Free Energies (G) and Relative Gibbs Free Energies (ΔG) for Optimized Structures of **9-15** by B3LYP/6-31G(d)

| Compd | Molecular point group | E, hartree | ZPE, hartree | G, hartree | ΔG, kcal/mol |
|---|---|---|---|---|---|
| **9** | $D_{6h}$ | -232.2486611 | 0.100745 | -232.173032 | |
| **10** | $C_{2v}$ | -331.4822992 | 0.092602 | -331.417863 | |
| **11a** | $C_{2v}$ | -430.7086894 | 0.084434 | -430.653735 | 4.0[a] |
| **11b** | $C_{2v}$ | -430.7149935 | 0.084437 | -430.660030 | (0)[a] |
| **11c** | $D_{2h}$ | -430.7138727 | 0.084368 | -430.658327 | 1.1[a] |
| **12a** | $C_{2v}$ | -529.9341808 | 0.076201 | -529.888753 | 7.8[b] |
| **12b** | $C_s$ | -529.9395316 | 0.076179 | -529.894768 | 4.0[b] |
| **12c** | $C_{2v}$ | -529.9465657 | 0.076197 | -529.901107 | (0)[b] |
| **13a** | $C_{2v}$ | -629.1580885 | 0.067917 | -629.122216 | 3.7[c] |
| **13b** | $C_{2v}$ | -629.1640899 | 0.067930 | -629.128182 | (0)[c] |
| **13c** | $D_{2h}$ | -629.1634303 | 0.067924 | -629.126873 | 0.8[c] |
| **14** | $C_{2v}$ | -728.3810288 | 0.059656 | -728.354670 | |
| **15** | $D_{6h}$ | -827.5969386 | 0.051333 | -827.578501 | |

[a] Gibbs free energy relative to **11b**.

[b] Gibbs free energy relative to **12c**.

[c] Gibbs free energy relative to **13b**.

**Table S2.** Electronic Energies (E), Zero Point Energies (ZPE), Gibbs Free Energies (G) and Relative Gibbs Free Energies (ΔG) for Optimized Structures of **2**-**6**, **8**, **8a**, **16**-**20**, **26** and **27** by B3LYP/6-31G(d)

| Compd | Molecular point group | E, hartree | ZPE, hartree | G, hartree | ΔG, kcal/mol |
|---|---|---|---|---|---|
| **2** | $C_{2v}$ | -1156.4603804 | 0.430397 | -1156.076799 | |
| **4** | $C_s$ | -1553.3732834 | 0.397718 | -1553.027816 | |
| **5** | $C_s$ | -1950.2812209 | 0.364529 | -1949.974030 | |
| **6** | $C_s$ | -1194.9216571 | 0.448968 | -1194.522018 | |
| **16** | $D_{7h}$ | -270.6785399 | 0.119474 | -270.585616 | |
| **17** | $C_{2v}$ | -504.1720394 | 0.249817 | -503.956767 | |
| **18** | $C_{2v}$ | -465.72139 | 0.231130 | -465.523187 | |
| **19** | $C_{2v}$ | -862.6322714 | 0.198398 | -862.471645 | |
| **20** | $C_{2v}$ | -851.6087357 | 0.384569 | -851.265371 | |
| **8** | $C_{2v}$ | -1388.6812626 | 0.535505 | -1388.197197 | (0)[a] |
| **26** | $C_s$ | -1389.0583156 | 0.546934 | -1388.563626 | -229.9[a] |
| **8a** | $C_{2v}$ | -1083.8279705 | 0.489728 | -1083.383934 | (0)[b] |
| **27** | $C_s$ | -1084.2052438 | 0.501207 | -1083.750622 | -230.1[b] |

[a] Gibbs free energy relative to **8**.

[b] Gibbs free energy relative to **8a**.

**Table S3.** Energy (E) for HOMO and LUMO of JAN (**2**), $F_4$-JAN (**4**), $F_8$-JAN (**5**), trop-JAN (**6**), Bicyclo[2.2.2]octenobenzene (**18**) and *syn*-Sesquibenzobicyclo[2.2.2]octane (**20**) and Their Energy Gaps (ΔE) by B3LYP/6-31G(d)

| Compound | E for HOMO, hartree | E for LUMO, hartree | ΔE, eV |
|---|---|---|---|
| **2** | -0.21274 | -0.01841 | 5.3 |
| **4** | -0.22380 | -0.03154 | 5.2 |
| **5** | -0.23171 | -0.04439 | 5.1 |
| **6** | -0.31874 | -0.23402 | 2.3 |
| **18** | -0.22827 | 0.00992 | 6.5 |
| **20** | -0.21102 | 0.00334 | 5.8 |

**Table S4.** Electronic Energies (E), Zero Point Energies (ZPE), Gibbs Free Energies (G) and Relative Gibbs Free Energies (ΔG) for Optimized Structures of **21a-25h** by B3LYP/6-31G(d)

| Compd | Molecular point group | E, hartree | ZPE, hartree | G, hartree | ΔG, kcal/mol |
|---|---|---|---|---|---|
| **21a** | $C_1$ | -1309.4466648 | 0.481705 | -1309.017350 | 0.3[a] |
| **21b** | $C_1$ | -1309.4457965 | 0.481573 | -1309.016859 | 0.6[a] |
| **21c** | $C_1$ | -1309.4474037 | 0.481746 | -1309.017893 | (0)[a] |
| **21d** | Structural optimization of **21d** gave **21c.** | | | | |
| **22a** | $C_1$ | -1360.9616697 | 0.433275 | -1360.579266 | 2.7[b] |
| **22b** | $C_1$ | -1360.9651303 | 0.433139 | -1360.583521 | (0)[b] |
| **23a** | $C_1$ | -1248.7065741 | 0.428999 | -1248.327651 | (0)[c] |
| **23b** | $C_1$ | -1248.7062109 | 0.429042 | -1248.327231 | 0.3[c] |
| **24a** | $C_1$ | -1475.4846974 | 0.466209 | -1475.072323 | 0.9[d] |
| **24b** | Structural optimization of **24b** gave **24a.** | | | | |
| **24c** | $C_1$ | -1475.4837836 | 0.465965 | -1475.072130 | 1.0[d] |
| **24d** | $C_1$ | -1475.4843786 | 0.465857 | -1475.073711 | (0)[d] |
| **24e** | $C_1$ | -1475.4843287 | 0.465965 | -1475.072677 | 0.6[d] |
| **24f** | $C_1$ | -1475.483632 | 0.465982 | -1475.072019 | 1.1[d] |
| **24g** | Structural optimization of **24g** gave **24h.** | | | | |
| **24h** | $C_1$ | -1475.4844169 | 0.466086 | -1475.072588 | 0.7[d] |
| **25a** | $C_1$ | -1475.489565 | 0.466049 | -1475.077614 | (0)[e] |
| **25b** | Structural optimization of **25b** gave **25a.** | | | | |
| **25c** | $C_1$ | -1475.4876775 | 0.465747 | -1475.077409 | 0.1[e] |
| **25d** | $C_1$ | -1475.4883792 | 0.465973 | -1475.076607 | 0.6[e] |
| **25e** | $C_1$ | -1475.487996 | 0.465678 | -1475.077477 | 0.1[e] |
| **25f** | $C_1$ | -1475.4868664 | 0.465802 | -1475.075955 | 1.0[e] |
| **25g** | Structural optimization of **25g** gave **25h.** | | | | |
| **25h** | $C_1$ | -1475.4882657 | 0.465964 | -1475.077263 | 0.2[e] |

[a] Gibbs free energy relative to **21c**.

[b] Gibbs free energy relative to **22b**.

[c] Gibbs free energy relative to **23a**.

[d] Gibbs free energy relative to **24d**.

[e] Gibbs free energy relative to **25a**.

**Table S5.** Electronic Energies (E), Zero Point Energies (ZPE), Gibbs Free Energies (G) and Relative Gibbs Free Energies (ΔG) for Optimized Structures of **8**, **26** and **28-35** by B3LYP/6-31G(d)

| Compd | Molecular point group | E, hartree | ZPE, hartree | G, hartree | ΔG, kcal/mol |
|---|---|---|---|---|---|
| **28** | $C_s$ | -850.3655306 | 0.358852 | -850.048268 | (0) [a] |
| **29** | $C_1$ | -850.7290848 | 0.369972 | -850.402285 | -222.1[a] |
| **30**[b] | $C_1$ | -850.7136452 | 0.370215 | -850.383853 | -210.6[a] |
| **31** | $C_1$ | -850.7352613 | 0.371456 | -850.405241 | -224.0[a] |
| **32** | $C_1$ | -850.3781002 | 0.359065 | -850.060095 | -7.4[a] |
| **8** | $C_{2v}$ | -1388.6812626 | 0.535505 | -1388.197197 | (0)[c] |
| **26** | $C_s$ | -1389.0583156 | 0.546934 | -1388.563626 | -229.9[c] |
| **33**[b] | $C_1$ | -1389.016498 | 0.546898 | -1388.520577 | -202.9[c] |
| **34** | $C_1$ | -1389.026278 | 0.547241 | -1388.531353 | -209.7 [c] |
| **35** | $C_1$ | -1388.6702878 | 0.535424 | -1388.186639 | 6.6 [c] |

[a] Gibbs free energy relative to **28**. [b] Number of imaginary frequencies is 1. [c] Gibbs free energy relative to **8**.