

methylene-9-norbornanone.⁷ The *exo*-5,6-trimethylene-9-norbornanone (4) was quantitatively separated from the *exo*-5,6-trimethylene-8-norbornanone (8) by bisulfite addition.⁷ After workup,⁷ the *exo*-5,6-trimethylene-9-norbornanone (4) was obtained in 27% yield [bp 102–104 °C (15 mm)], and the *exo*-5,6-trimethylene-8-norbornanone was obtained in 40% yield [bp 102–104 °C (15 mm)]. These ketones gave satisfactory analytical data (C, $\pm 0.3\%$; H, $\pm 0.2\%$). The ¹³C NMR data were in accordance with the assigned structures.

Precursors. 9-Aryl-*exo*-5,6-trimethylene-9-norbornanols (9) and 9-aryl-*endo*-5,6-trimethylene-9-norbornanols (10) were prepared by addition of the corresponding ketone to the Grignard reagent prepared from the corresponding substituted bromo- or iodobenzenes. The physical constant data for these precursors are summarized in Table IV. All of these compounds gave ¹³C NMR data in accordance with the assigned structures. Satisfactory elemental analyses were obtained for all of the new compounds ($\pm 0.3\%$ for C, H, Cl, and F).

Carbocations. The ions were prepared by slow addition of the appropriate precursor to a solution of FSO₃H/SbF₅ (1:1 M)/SO₂ClF cooled to -78 °C with rapid vortex mixing. The "magic acid", SbF₅/FSO₃H (1:1 M), concentration in the solution was 3 M. The concentration of the ion based on the alcohol added was ~ 0.5 M. Transfer of the solutions under nitrogen to an 8-mm NMR tube was achieved via a cooled double-ended syringe, as described previously.¹⁸

NMR Spectra. ¹³C NMR spectra were recorded at -80 °C on a Varian CFT-20 spectrometer with 8-mm tubes containing a concentric 3-mm (o.d.) capillary tube of acetone-*d*₆ and Me₄Si, 8192 data points, a spectral width of 6500 Hz, and a pulse angle of 45°. Chemical shifts are in parts per million downfield from external Me₄Si.

Registry No. 1 (Z = *p*-OCH₃), 77826-81-4; 1 (Z = *p*-CH₃), 77826-82-5; 1 (Z = *p*-F), 77826-83-6; 1 (Z = *p*-Cl), 77826-84-7; 1 (Z = H), 77826-85-8; 1 (Z = *m*-Cl), 77845-74-0; 1 (Z = *m*-CF₃), 77826-86-9; 1 (Z = 3,5-Cl₂), 77826-87-0; 1 (Z = *p*-CF₃), 77826-88-1; 1 (Z = 3,5-(CF₃)₂), 77845-75-1; 2 (Z = *p*-OCH₃), 77826-72-3; 2 (Z = *p*-CH₃), 77826-73-4; 2 (Z = *p*-F), 77826-74-5; 2 (Z = *p*-Cl), 77845-63-7; 2 (Z = H), 77826-75-6; 2 (Z = *m*-F), 77845-76-2; 2 (Z = *m*-CF₃), 77826-77-8; 2 (Z = 3,5-Cl₂), 77826-78-9; 2 (Z = *p*-CF₃), 77826-79-0; 3, 19138-60-4; 4, 77845-77-3; 9 (Z = *p*-OCH₃), 77845-78-4; 9 (Z = *p*-CH₃), 77845-79-5; 9 (Z = *p*-F), 77845-80-8; 9 (Z = *p*-Cl), 77845-81-9; 9 (Z = H), 77845-82-0; 9 (Z = *m*-Cl), 77845-83-1; 9 (Z = *m*-CF₃), 77845-84-2; 9 (Z = 3,5-Cl₂), 77845-85-3; 9 (Z = *p*-CF₃), 77845-86-4; 9 (Z = 3,5-(CF₃)₂), 77845-87-5; 10 (Z = *p*-OCH₃), 77845-88-6; 10 (Z = *p*-CH₃), 77845-89-7; 10 (Z = *p*-F), 77845-90-0; 10 (Z = *p*-Cl), 77845-91-1; 10 (Z = Ph), 27409-21-8; 10 (Z = *m*-F), 77845-92-2; 10 (Z = *m*-CF₃), 77845-93-3; 10 (Z = 3,5-Cl₂), 77845-94-4; 10 (Z = *p*-CF₃), 77845-95-5; 10 (Z = 3,5-(CF₃)₂), 77845-96-6.

(18) Kelly, D. P.; Brown, H. C. *Aust. J. Chem.* 1976, 29, 957.

Structural Effects in Solvolytic Reactions. 38. Carbon-13 Nuclear Magnetic Resonance Studies of Carbocations. 6.¹ Effect of Increasing Electron Demand on the Chemical Shifts of the α -Carbon Atoms in Substituted Aryldialkyl Carbocations. Correlation of the Data with a New Set of Substituent Constants, $\sigma^{\alpha C^+}$

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With increasing electron demand, the ¹³C NMR shifts of the α -carbons, the carbon atoms adjacent to the cationic center (C⁺), undergo significant downfield shifts. However, the substituent chemical shifts, $\Delta\delta^{C^+}$, for the α -carbon atoms (CH₃) of substituted *tert*-cumyl cations are not correlated either by the σ^+ or the σ^{C^+} constants. Plots of $\Delta\delta^{C^+}$ against σ^+ and of $\Delta\delta^{C^+}$ against σ^{C^+} reveal that the points for the para derivatives deviate systematically from the lines defined by the data for the meta derivatives. These deviations indicate that a new set of para substituent constants, one intermediate in value between the σ_p^+ and $\sigma_p^{C^+}$ constants, is needed to correlate satisfactorily the α -carbon chemical shifts for the para derivatives. Accordingly, such a set of substituent constants, $\sigma^{\alpha C^+}$, was estimated by using the slope (-4.1) of the line defined by a plot of $\Delta\delta^{C^+}$ for the meta derivatives vs. σ_m^+ to satisfy the Hammett-type equation $\Delta\delta^{C^+} = \rho^{\alpha C^+} \sigma^{\alpha C^+}$. The utility of these new $\sigma^{\alpha C^+}$ constants to correlate chemical shift data for the α positions of substituted benzylic cations was tested with the data for ten different systems. Indeed, very good correlations were observed when the chemical shifts for these systems are plotted against these $\sigma^{\alpha C^+}$ values: 2-aryl-2-butyl, $r = 0.997$, $\rho(\text{CH}_2)^{\alpha C^+} = -4.1$, $r = 0.998$, $\rho(\text{CH}_3)^{\alpha C^+} = -4.0$; 3-aryl-3-pentyl, $r = 0.999$, $\rho^{\alpha C^+} = -3.9$; 4-aryl-4-heptyl, $r = 0.994$, $\rho^{\alpha C^+} = -3.6$; 1-aryl-1-cyclopentyl, $r = 0.999$, $\rho^{\alpha C^+} = -4.9$; 1-aryl-1-cyclohexyl, $r = 0.998$, $\rho^{\alpha C^+} = -4.9$; 1-aryl-1-cycloheptyl, $r = 0.999$, $\rho^{\alpha C^+} = -4.7$; 9-aryl-*exo*-5,6-trimethylene-9-norbornyl, $r = 0.999$, $\rho^{C^+} = -4.1$; 9-aryl-*endo*-5,6-trimethylene-9-norbornyl, $r = 0.998$, $\rho^{\alpha C^+} = -4.4$; 2-aryl-2-adamantyl, $r = 0.993$, $\rho^{\alpha C^+} = -5.9$. The trend in the $\rho^{\alpha C^+}$ values in these cations is discussed.

Although isolated attempts to correlate the α -carbon shifts in substituted benzylic cations against σ^+ constants have been reported,^{3,4} no systematic examination has been made to test the practicality and validity of such correlations.

Recently we undertook a systematic investigation of the effect of increasing electron demand on the ¹³C NMR shifts of arylalkyl carbocations. We established that new enhanced substituent constants are needed to correlate the chemical shifts of the cationic center in these cations.⁵ We determined these σ^{C^+} constants as follows. The data for the meta derivatives were correlated satisfactorily by σ_m^+ . The para derivatives deviated seriously, indicating much greater resonance interactions with the cationic center than

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(3) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* 1977, 99, 5683.

(4) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* 1978, 31, 1209.

(5) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* 1980, 77, 6956.

Table II. Substituent Constants^{a,b}

substituent (Z)	σ_m	σ_m^+	$\sigma_m^{C^+}$	$\sigma_m^{\alpha C^+}$	σ_p	σ_p^+	$\sigma_p^{C^+}$	$\sigma_p^{\alpha C^+}$
OCH ₃	0.115	0.047			-0.268	-0.778	-2.02	-1.29
CH ₃	-0.069	-0.066	-0.13	-0.15	-0.170	-0.311	-0.67	-0.49
isopropyl		-0.060	-0.14	-0.07	-0.151	-0.280		
F	0.337	0.352	0.35	0.29	0.062	-0.073	-0.40	-0.24
Cl	0.373	0.399	0.36	0.34	0.227	0.114	-0.24	-0.07
Br	0.391	0.405	0.33	0.29	0.232	0.150	-0.19	-0.10
CF ₃	0.42	0.52	0.56	0.51	0.54	0.612	0.79	0.71
3,5-Cl ₂	0.746	0.798	0.66	0.66				
3,5-(CF ₃) ₂	0.84	1.04	1.03	1.07				

^a σ and σ^+ values are taken from ref 11. ^b σ^{C^+} values are taken from ref 5.

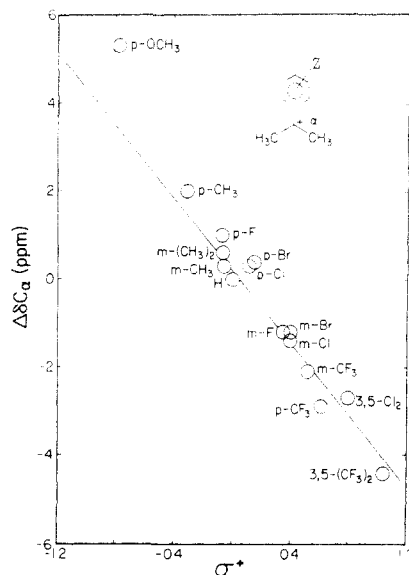


Figure 2. Plot of $\Delta\delta^{C\alpha}$ values against σ^+ for substituted *tert*-cumyl cations. The correlation line is defined by the data for the meta derivatives and the parent unsubstituted *tert*-cumyl cation.

discussion, the α -carbon shifts for these ions are summarized in Table I.

$\sigma^{\alpha C^+}$ Constants. Recently, we proposed a new set of $\sigma^{\alpha C^+}$ substituent constants to correlate the chemical shifts of the cationic carbon centers in aryldialkyl carbocations.⁵ We first attempted to correlate the α -carbon shifts in substituted *tert*-cumyl cations with these σ^{C^+} constants. A plot of the $\Delta\delta^{C\alpha}$ values for the *tert*-cumyl cations against σ^{C^+} constants gives only a fair correlation, providing a slope of -3.1 and a correlation coefficient of 0.987. More importantly, all of the para points, with the exception of that for *p*-CF₃, deviate systematically, lying below the correlation line for the meta derivatives (Figure 1). This systematic deviation suggested a need for para substituent constants with less negative values than those of the $\sigma_p^{C^+}$ set.

Since the σ_p^+ constants are less negative, it seemed possible that those values might correlate the $\Delta\delta^{C\alpha}$ shifts. However, a plot of the $\Delta\delta^{C\alpha}$ values against the σ^+ constants reveals only a fair correlation, providing a slope of -5.0 and correlation coefficient of 0.982. Here the para points also deviate systematically, lying above the correlation line defined by the meta derivatives (Figure 2). In this case the nature of the deviation suggests the need for para substituent constants with more negative values than those of the σ_p^+ set.

These considerations made it clear that a set of substituent constants with values lying between those of the σ_p^+ and $\sigma_p^{C^+}$ sets was needed to correlate the $\Delta\delta^{C\alpha}$ data for the para derivatives. Consequently, we decided to develop a new set of such constants, $\sigma^{\alpha C^+}$, and to test their utility for the correlation of the α -¹³C shifts in these carbocations.

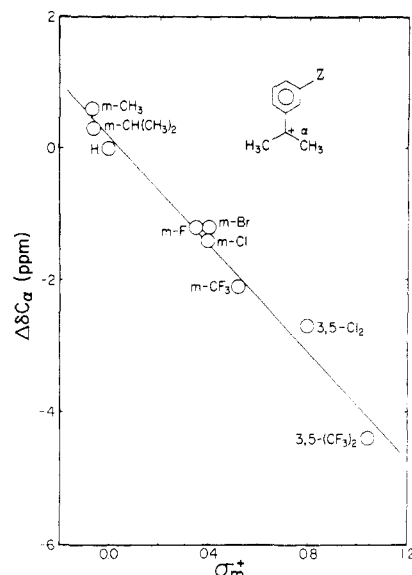


Figure 3. Plot of $\Delta\delta^{C\alpha}$ values against σ_m^+ constants for the meta-substituted *tert*-cumyl cations.

We followed the usual procedure. We plotted the $\Delta\delta^{C\alpha}$ shifts for the meta-substituted *tert*-cumyl cations against the σ_m^+ values (Figure 3). Least-squares treatment of the plot provided a slope of -4.1 with a correlation coefficient of 0.989. This slope was then used with the Hammett-type equation $\Delta\delta^{C\alpha} = \rho^{\alpha C^+} \sigma^{\alpha C^+}$, $\Delta\delta^{C\alpha} = \delta^{C\alpha} (Z = H) - \delta^{C\alpha} (Z \neq H)$ to calculate the new substituent constants. These new constants are designated as $\sigma^{\alpha C^+}$ to indicate their origin in the α -carbon chemical shifts for substituted benzylic carbocations. These new $\sigma^{\alpha C^+}$ values are listed in Table II, together with the σ^{C^+} , σ^+ , and σ constants.

$\Delta\delta^{C\alpha}-\sigma^{\alpha C^+}$ Plots. To test the validity and utility of these new $\sigma^{\alpha C^+}$ constants, we examined their ability to correlate the α -carbon shifts in the cations of nine representative structural systems (2-10).

Plots of the $\Delta\delta^{C\alpha}$ values against the $\sigma^{\alpha C^+}$ constants for the acyclic ions 2-4 are shown in Figure 4. The 2-aryl-2-butyl (2) system gives a $\rho^{\alpha C^+}$ value of -4.1 with a correlation coefficient *r* of 0.997 for the α -CH₂ carbon and a $\rho^{\alpha C^+}$ value of -4.0 with *r* of 0.998 for the α' -CH₃ carbon. The $\Delta\delta^{C\alpha}$ values for the other acyclic ions 3 and 4 are also nicely correlated with the $\sigma^{\alpha C^+}$ constants: 3, *r* = 0.999, $\rho^{\alpha C^+}$ = -3.9; 4, *r* = 0.994, $\rho^{\alpha C^+}$ = -3.6.

Plots of the $\Delta\delta^{C\alpha}$ values against the $\sigma^{\alpha C^+}$ values for the alicyclic systems, 5 and 6, are shown in Figure 5. The 1-aryl-1-cyclopentyl (5) system gives a $\rho^{\alpha C^+}$ of -4.9 with an *r* of 0.999. The 1-aryl-1-cyclohexyl (6) system gives a $\rho^{\alpha C^+}$ of -4.9 with an *r* of 0.998. Finally, the 1-aryl-1-cycloheptyl (7) system yields a $\rho^{\alpha C^+}$ of -4.7 with an *r* of 0.999.

Similar plots for the $\Delta\delta^{C\alpha}$ values against the $\sigma^{\alpha C^+}$ values for the polycyclic ions, 8-10, are shown in Figure 6. The 9-aryl-*exo*-5,6-trimethylene-9-norbornyl (8) system gives

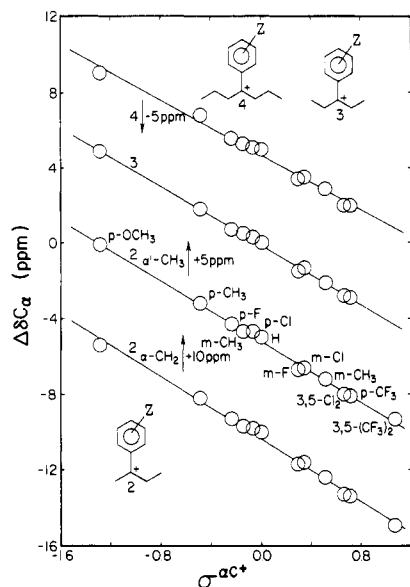


Figure 4. $\Delta\delta^{C\alpha}-\sigma^{C^+}$ plots for the following: 2- α -CH₂, 2-aryl-2-butyl cations (α -CH₂); 2- α' -CH₃, 2-aryl-2-butyl cations (α' -CH₃); 3 = 3-aryl-3-pentyl cations; 4 = 4-aryl-4-heptyl cations.

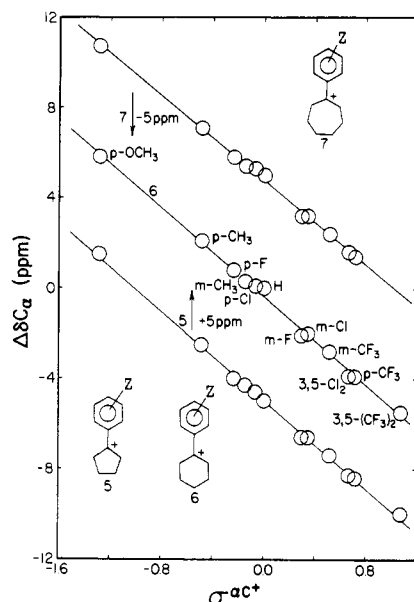


Figure 5. $\Delta\delta^{C\alpha}-\sigma^{C^+}$ plots for the following: 5, 1-aryl-1-cyclopentyl cations; 6, 1-aryl-1-cyclohexyl cations; 7, 1-aryl-1-cycloheptyl cations.

a ρ^{C^+} of -4.1 and an r of 0.999. The 9-aryl-*endo*-5,6-trimethylene-9-norbornyl (9) system yields a ρ^{C^+} of -4.4 and an r of 0.998. The 2-aryl-2-adamantyl (10) system yields a ρ^{C^+} of -5.9 and an r of 0.993.

For convenience, these correlation parameters are summarized in Table III. However, it should be noted that these correlations are less precise compared to those achieved for the $\Delta\delta^{C^+}$ values against the σ^{C^+} constants.⁵⁻⁹ This may be the result of a larger experimental uncertainty associated with the determination of the α -carbon shifts, which vary much less with electron demand, and is approximately one-fourth the magnitude of those realized for the cationic carbon.

Comparison of the ρ^{C^+} Values. The acyclic systems, 1-4, have ρ^{C^+} values in the range of -3.6 to -4.1. The alicyclic systems, 5-7, have ρ^{C^+} values in the range of -4.6 to -4.9. The 9-aryl-*exo*-5,6-trimethylene-9-norbornyl system (8) and 9-aryl-*endo*-5,6-trimethylene-9-norbornyl systems (9) have ρ^{C^+} values -4.1 and -4.4, respectively,

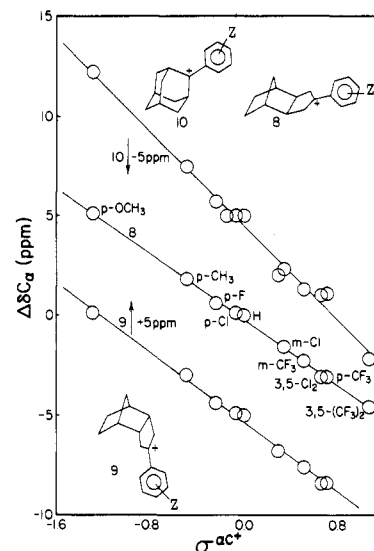


Figure 6. $\Delta\delta^{C\alpha}-\sigma^{C^+}$ plots for the following: 9, 9-aryl-*endo*-5,6-trimethylene-9-norbornyl cations; 8, 9-aryl-*exo*-trimethylene-9-norbornyl cations; 10, 2-aryl-2-adamantyl cations.

Table III. Correlation Parameters for the $\sigma^{C^+}-\Delta\delta^{C\alpha}$ Plots

system	r	slope, ρ^{C^+}	standard deviation	
			ρ^{C^+}	$\Delta\delta^{C\alpha}$
2 (α -CH ₂)	0.997	-4.1	0.11	0.20
2 (α' -CH ₃)	0.998	-4.0	0.08	0.15
3	0.999	-3.9	0.07	0.11
4	0.994	-3.6	0.13	0.22
5	0.999	-4.9	0.06	0.12
6	0.998	-4.9	0.09	0.18
7	0.999	-4.7	0.08	0.13
8	0.999	-4.1	0.06	0.10
9	0.998	-4.4	0.11	0.18
10	0.993	-5.9	0.22	0.42

slightly less negative compared to the value of -4.9 for the 1-aryl-1-cyclopentyl (5) system.

The ρ^{C^+} value of -5.9 for the 2-aryl-2-adamantyl system (10) is considerably more negative than the ρ^{C^+} values for all of these ions. This could be accounted for on the basis of the rigid adamantyl structure where the α -carbon orbitals are fixed in only one orientation. The results indicate that this orientation of the α -carbon orbitals may favor better hyperconjugation with the C⁺ carbon.

Correlation of the β -Carbon Shifts. Delocalization of charge through the carbon skeleton (inductive and hyperconjugative effects) is not expected to occur past the α -carbon to any great extent. This is substantiated by the behavior of the β -carbon atoms in most of these cases. Generally, the β -carbon shifts are affected either to a much lesser extent or not at all by increasing electron demand at the cationic center.⁵⁻⁹ However, in two cases, the β -carbon atoms undergo significant downfield shifts with increasing electron demand at the cationic center. For example, in the case of the 1-aryl-1-cyclohexyl system, the β -carbon atom undergoes a downfield shift of 13.5 ppm from *p*-OCH₃ to 3,5-(CF₃)₂.⁸ The corresponding downfield shift is 8.7 ppm for the 2-aryl-2-adamantyl system.⁷ A possible explanation is the favorable orientation of the C^β orbitals, favoring hyperconjugation through the C^β-C^α-C⁺ chain in these systems. Indeed, the C^β shifts for the 2-aryl-2-adamantyl system are nicely correlated with the C^β carbon shifts of the 1-aryl-1-cyclohexyl system (Figure 7, slope = 0.64 and r = 0.999). This suggests that the downfield shifts with increasing electron demand in both 1-aryl-1-cyclohexyl and 2-aryl-2-adamantyl systems probably have the same origin.

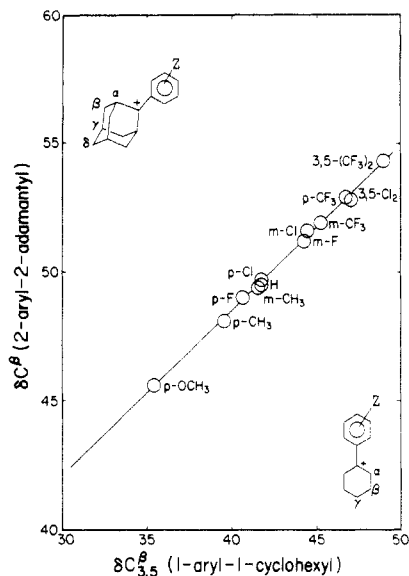


Figure 7. Plot of the C^β carbon shifts of the 1-aryl-1-cyclohexyl cations against the C^β carbon shifts of 2-aryl-2-adamantyl cations.

Conclusions

This program was initiated to test the conclusions of Olah³ and Farnum¹⁰ that certain peculiarities in the C^+ and $\alpha-C^+$ shifts of the substituted 2-aryl-2-norbornyl cations with the more electron-demanding substituents reveal the onset of σ bridging. We first undertook to lay the foundation for a quantitative treatment of C^+ and $\alpha-C^+$ shifts in cations of unambiguous characteristics (1-10). We are now in position to analyze critically the behavior of the 2-aryl-2-norbornyl cations, as well as other carbocations for which nonclassical structures have been proposed.¹² We hope to publish soon the results of that analysis.

(12) Brown, H. C. "The Nonclassical Ion Problem"; Plenum: New York, 1977.

Registry No. 1 ($Z = p\text{-OCH}_3$), 22666-71-3; 1 ($Z = p\text{-CH}_3$), 20605-66-7; 1 ($Z = p\text{-F}$), 25807-60-7; 1 ($Z = p\text{-Cl}$), 41912-29-2; 1 ($Z = p\text{-Br}$), 67595-62-4; 1 ($Z = m\text{-isopropyl}$), 77826-64-3; 1 ($Z = m\text{-CH}_3$), 20605-65-6; 1 ($Z = H$), 17637-68-2; 1 ($Z = m\text{-F}$), 25807-61-8; 1 ($Z = m\text{-Cl}$), 77826-65-4; 1 ($Z = m\text{-Br}$), 77826-66-5; 1 ($Z = m\text{-CF}_3$), 77826-67-6; 1 ($Z = 3,5\text{-Cl}_2$), 77826-68-7; 1 ($Z = p\text{-CF}_3$), 22666-73-5; 1 ($Z = 3,5\text{-(CF}_3)_2$), 67595-63-5; 2 ($Z = p\text{-OCH}_3$), 35144-43-5; 2 ($Z = p\text{-CH}_3$), 14290-14-3; 2 ($Z = p\text{-F}$), 51804-44-5; 2 ($Z = p\text{-Cl}$), 76499-76-8; 2 ($Z = m\text{-CH}_3$), 76499-77-9; 2 ($Z = H$), 14290-13-2; 2 ($Z = m\text{-F}$), 76499-78-0; 2 ($Z = m\text{-Cl}$), 76499-79-1; 2 ($Z = m\text{-CF}_3$), 76499-80-4; 2 ($Z = 3,5\text{-Cl}_2$), 76499-81-5; 2 ($Z = p\text{-CF}_3$), 36043-26-2; 2 ($Z = 3,5\text{-(CF}_3)_2$), 76499-82-6; 3 ($Z = p\text{-OCH}_3$), 76481-14-6; 3 ($Z = p\text{-CH}_3$), 76481-15-7; 3 ($Z = p\text{-F}$), 51804-43-4; 3 ($Z = p\text{-Cl}$), 76481-16-8; 3 ($Z = m\text{-CH}_3$), 76481-17-9; 3 ($Z = H$), 76481-18-0; 3 ($Z = m\text{-F}$), 76481-19-1; 3 ($Z = m\text{-Cl}$), 76481-20-4; 3 ($Z = m\text{-CF}_3$), 76481-21-5; 3 ($Z = 3,5\text{-Cl}_2$), 76481-22-6; 3 ($Z = p\text{-CF}_3$), 76481-23-7; 4 ($Z = p\text{-OCH}_3$), 76499-83-7; 4 ($Z = p\text{-CH}_3$), 76499-84-8; 4 ($Z = p\text{-F}$), 76499-85-9; 4 ($Z = p\text{-Cl}$), 76499-86-0; 4 ($Z = m\text{-CH}_3$), 76499-87-1; 4 ($Z = H$), 76499-88-2; 4 ($Z = m\text{-F}$), 76499-89-3; 4 ($Z = m\text{-Cl}$), 76499-90-6; 4 ($Z = m\text{-CF}_3$), 76499-91-7; 4 ($Z = 3,5\text{-Cl}_2$), 76499-92-8; 4 ($Z = p\text{-CF}_3$), 76499-93-9; 5 ($Z = p\text{-OCH}_3$), 67275-39-2; 5 ($Z = p\text{-CH}_3$), 67275-41-6; 5 ($Z = p\text{-F}$), 51804-49-0; 5 ($Z = p\text{-Cl}$), 67275-42-7; 5 ($Z = m\text{-CH}_3$), 77826-69-8; 5 ($Z = H$), 25845-31-2; 5 ($Z = m\text{-F}$), 67275-44-9; 5 ($Z = m\text{-Cl}$), 67275-45-0; 5 ($Z = m\text{-CF}_3$), 77826-70-1; 5 ($Z = 3,5\text{-Cl}_2$), 77826-71-2; 5 ($Z = p\text{-CF}_3$), 67275-46-1; 5 ($Z = 3,5\text{-(CF}_3)_2$), 67275-47-2; 6 ($Z = p\text{-OCH}_3$), 67275-48-3; 6 ($Z = p\text{-CH}_3$), 67275-49-4; 6 ($Z = p\text{-F}$), 51804-48-9; 6 ($Z = p\text{-Cl}$), 67275-51-8; 6 ($Z = m\text{-CH}_3$), 77826-16-5; 6 ($Z = H$), 25779-82-2; 6 ($Z = m\text{-F}$), 67275-53-0; 6 ($Z = m\text{-Cl}$), 77826-17-6; 6 ($Z = m\text{-CF}_3$), 77826-18-7; 6 ($Z = 3,5\text{-Cl}_2$), 77826-19-8; 6 ($Z = p\text{-CF}_3$), 67275-55-2; 6 ($Z = 3,5\text{-(CF}_3)_2$), 67275-56-3; 7 ($Z = p\text{-OCH}_3$), 77826-20-1; 7 ($Z = p\text{-CH}_3$), 77826-21-2; 7 ($Z = p\text{-F}$), 57502-89-3; 7 ($Z = p\text{-Cl}$), 77826-22-3; 7 ($Z = m\text{-CH}_3$), 77826-23-4; 7 ($Z = H$), 51348-25-5; 7 ($Z = m\text{-F}$), 77826-24-5; 7 ($Z = m\text{-Cl}$), 77826-25-6; 7 ($Z = m\text{-CF}_3$), 77826-26-7; 7 ($Z = 3,5\text{-Cl}_2$), 77826-27-8; 7 ($Z = p\text{-CF}_3$), 77826-28-9; 8 ($Z = p\text{-OCH}_3$), 77826-72-3; 8 ($Z = p\text{-CH}_3$), 77826-73-4; 8 ($Z = p\text{-F}$), 77826-74-5; 8 ($Z = p\text{-Cl}$), 77845-63-7; 8 ($Z = H$), 77826-75-6; 8 ($Z = m\text{-Cl}$), 77826-76-7; 8 ($Z = m\text{-CF}_3$), 77826-77-8; 8 ($Z = 3,5\text{-Cl}_2$), 77826-78-9; 8 ($Z = p\text{-CF}_3$), 77826-79-0; 8 ($Z = 3,5\text{-(CF}_3)_2$), 77826-80-3; 9 ($Z = p\text{-OCH}_3$), 77826-81-4; 9 ($Z = p\text{-CH}_3$), 77826-82-5; 9 ($Z = p\text{-F}$), 77826-83-6; 9 ($Z = p\text{-Cl}$), 77826-84-7; 9 ($Z = H$), 77826-85-8; 9 ($Z = m\text{-F}$), 77846-64-1; 9 ($Z = m\text{-CF}_3$), 77826-86-9; 9 ($Z = 3,5\text{-Cl}_2$), 77826-87-0; 9 ($Z = p\text{-CF}_3$), 77826-88-1; 10 ($Z = p\text{-OCH}_3$), 76481-24-8; 10 ($Z = p\text{-CH}_3$), 76481-25-9; 10 ($Z = p\text{-F}$), 51804-53-6; 10 ($Z = p\text{-Cl}$), 76481-26-0; 10 ($Z = m\text{-CH}_3$), 76481-27-1; 10 ($Z = H$), 52873-73-1; 10 ($Z = m\text{-F}$), 76481-28-2; 10 ($Z = m\text{-Cl}$), 76481-29-3; 10 ($Z = m\text{-CF}_3$), 76481-30-6; 10 ($Z = 3,5\text{-Cl}_2$), 76481-31-7; 10 ($Z = p\text{-CF}_3$), 76481-32-8; 10 ($Z = 3,5\text{-(CF}_3)_2$), 76481-33-9.