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FIRST SUCCESSFUL CORRELATION OF THE UV SPECTRA OF THREE KINDS OF STYRENES WITH SPIN-DELOCALIZATION SUBSTITUENT CONSTANTS $\sigma^{\cdot}$

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UV spectra of 17 *para*-Y-substituted styrenes, 8 *para*-Y-substituted α-methylstyrenes and 20 *para*-Y-substituted α,β,β-trifluorostyrenes were measured and correlated against spin-delocalization substituent constants ($\sigma^{\cdot}$) with confidence levels above 99·9%.

INTRODUCTION

Even though correlation analysis of UV data of aromatic compounds has remained a difficult task for many years and achievements are limited (see comments by Shorter[1]), the subject is still of interest to many chemists.[2] Of special interest to us is the substituent effect on the K-band of *para*-Y-substituted styrenes in which the substituent Y is directly conjugated with the double bond, and is thus expected to directly affect the π–π^* transition.[2a,2f,2g,3] We are particularly intrigued by the possibility of applying the spin-delocalization substituent constants $\sigma^{\cdot}$ [4] to the correlation of K-band data because the singlet excited state has two half-occupied molecular orbitals and may thus be diradicaloid in nature,[5] and because to our knowledge a successful correlation of UV data of simple benzenoid compounds with $\sigma^{\cdot}$ has never been reported.[2] Therefore, we prepared 17 *para*-Y-substituted styrenes (Y-STs), 8 *para*-Y-substituted α-methylstyrenes (Y-MSTs) and 20 *para*-Y-substituted α,β,β-trifluorostyrenes (Y-TFSs), and measured the K-band $\lambda_{\max}$ values of their UV absorption spectra, from which the corresponding wavenumbers ($\nu_{\max}$) were calculated. These $\lambda_{\max}$ values, together with their corresponding absorption coefficients (ε) and wave numbers ($\nu_{\max}$), are summarized in Table 1.

The wavenumbers ($\nu_{\max}$), which are direct measures of the excitation energy absorbed, were correlated against the polar parameter $\rho^X\sigma^X$ of equation (1), or against the spin-delocalization parameter $\rho^{\cdot}\sigma^{\cdot}$ of equation (2) or by the dual-parameter equation (3) ($\rho^X\sigma^X + \rho^{\cdot}\sigma^{\cdot}$). Representative Hammett-type unresolved polar substituent constants (σ^X) were used, i.e. σ_p,[6a] σ^+ [6a] and σ_{mb}.[6b] The most recent σ^X scale, σ_{mb}, is derived from a system (substituted α,β,β-trifluorostyrenes) in which the substituent interacts electronically with a double bond. It has already been successfully applied to spectral data and kinetic data based on a rigorous methodology for some styrene systems.[4d–4g] Similarly, representative spin-delocalization substituent constants, i.e. $\sigma_\alpha^{\cdot}$,[7a] $\sigma_C^{\cdot}$ [7b] and $\sigma_{JJ}^{\cdot}$ [4b] were used as $\sigma^{\cdot}$ values in equations (2) and (3). The $\sigma_{JJ}^{\cdot}$ scale is derived from ^{19}F NMR and dimerization-rate data at five different temperatures for substituted α,β,β-trifluorostyrenes, and is the most cross-checked and self-consistent $\sigma^{\cdot}$ scale now available. Recently, in conjunction with a σ^X, it has been very successfully applied to dual-parameter correlations [equation (3)].[4d–4g]

$$\nu_{\max} = \rho^X\sigma^X + C \qquad (1)$$

$$\nu_{\max} = \rho^{\cdot}\sigma^{\cdot} + C \qquad (2)$$

$$\nu_{\max} = \rho^X\sigma^X + \rho^{\cdot}\sigma^{\cdot} + C \qquad (3)$$

DISCUSSION

Results of correlation analysis by equations (1)–(3) are summarized in Tables 2, 3 and 4 for Y-STs, Y-MSTs and Y-TFSs, respectively. All Y-substituents are represented by the numbers given in bold in Table 1 and the identity of the substituents used in each entry is indicated by these numbers in the footnotes to Tables 2–4.

At this juncture, a caveat is in order. As a number of the σ values for some particular substituents are not available, it is not possible to use the same number (cf.

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Table 1. Wavenumbers (ν_{max}, cm^{-1}), λ_{max} (nm)[a] and ε_{max} values of Y-ST, Y-TFS and Y-MSTs

	Y-STs			Y-TFSs			Y-MSTs		
Y	ν_{max}	λ_{max}	$\varepsilon \times 10^{-4}$	ν_{max}	λ_{max}	$\varepsilon \times 10^{-4}$	ν_{max}	λ_{max}	$\varepsilon \times 10^{-4}$
F (**1**)	40650	246·0	1·35	42070	237·7	1·14	41288	242·2	1·02
H (**2**)	40453	247·2	1·49	41719	239·7	1·43	41237	242·5	1·04
Me(CO)O (**3**)	40161	249·0	1·62	41186	242·8	1·40			
$SiMe_3$ (**4**)	40000	250·0	1·30	40584	246·4	1·20			
Me (**5**)	39841	251·0	1·27	41152	243·0	1·92	40306	248·1	1·30
t-Bu (**6**)	39841	251·0	1·45	41152	243·0	1·52			
Cl (**7**)	39683	252·0	1·30	40519	246·8	1·90	40048	249·7	1·28
Br (**8**)	39277	254·6	1·56	40177	248·9	1·52			
$MeSO_2$ (**9**)	38911	257·0	2·01	39200	255·1	1·81			
OCH_3 (**10**)	38685	258·5	1·81	39984	250·1	1·99			
I (**11**)	38462	260·0	1·59						
MeSO (**12**)	38314	261·0	1·86	38432	260·2	1·88			
CO_2CH_3 (**13**)	38008	263·1	1·90	37736	265·0	2·0	37327	267·9	1·74
CN (**14**)	37951	263·5	2·25	38241	261·5	2·09			
COMe (**15**)	36430	274·5	1·53	36697	272·5	3·04	36010	277·7	1·55
SMe (**16**)	35461	282·0	1·36				36140	276·7	1·33
$N(CH_3)_2$ (**17**)	34014	294·0	2·01	30931	323·3	2·04			
CF_3 (**18**)				41305	242·1	1·50	40420	247·4	0·954
c-propanyl (**19**)				40000	250·0	1·37			
COOH (**20**)				38670	258·6	2·06			
$CONH_2$ (**21**)				38447	260·1	1·45			
Ph (**22**)				36969	270·5	2·47			

[a] Uncertainty: ±0·3 nm.

n column in the tables) of identical substituents for each entry. Further, it is well known that some complicating factors may affect the exact positions of the UV absorption peaks.[1] Therefore, in each table, exact comparison of the *r*, ψ and *F* values of entries with each other are unjustified. In other words, relatively small differences in the aforesaid values should not be taken seriously. On the other hand, we also note that the *r*, ψ and *F* values are still roughly comparable because most of the substituents used are the same in the different entries. In short, the results of our correlation analysis are meaningful.

In general, correlations with the *n* value (number of well distributed substituents) falling in the range *ca* 5–8 may be considered meaningful only when the *r* value is greater than 0·95 (cf. Ref. 8). However, the *r* value does not take into account the value of *n*. A more reliable criterion of the meaningfulness of a certain correlation is the confidence level (CL) based on the *F* values, which takes into account the value of *n* (see footnotes to the tables).[8,9] A CL of >99·9% (based on F_{001}) may be considered good and the corresponding correlation meaningful, even though the *r* (or *R*) value is smaller than 0·95.

Two interesting observations stand out from the results of the correlation analysis of our UV data: (1) none of the polar substituent constants σ^X ($\sigma^X = \sigma_p$, σ^+ and σ_{mb}, cf. Refs 4 and 6) can correlate the data by equation (1); and (2) good correlations have been obtained for all the three styrene systems by using the $\sigma^{\cdot}$ constants ($\sigma^{\cdot} = \sigma_{\alpha}^{\cdot}$, $\sigma_{C}^{\cdot}$ and $\sigma_{JJ}^{\cdot}$) according to equation (2), and correlation is not much improved by application of the dual-parameter equation (3).

For instance, inspection of Table 2 for the Y-STs immediately leads to two conspicuous observations which are not predicted by the conventional wisdom based on previous reports.[1,2] First, the data cannot be correlated with any of the polar substituent constants σ^X ($n = 14–17$) by equation (1). Second, the ν_{max} values can be correlated with any one of the three $\sigma^{\cdot}$ scales, i.e. $\sigma_{\alpha}^{\cdot}$, $\sigma_{C}^{\cdot}$ and $\sigma_{JJ}^{\cdot}$, all with *F* values which correspond to confidence levels greater than 99·9%.[9] Third, when the dual-parameter equation (3) is applied, most of the $\sigma^X + \sigma^{\cdot}$ combinations do not seem to improve the correlation significantly. For example, even though the $\sigma^+ + \sigma_{\alpha}^{\cdot}$ combination shows the best *R* and ψ values, the fact that its *n* value of eleven is the smallest among all $\sigma^{\cdot}$ and $\sigma^X + \sigma^{\cdot}$ entries ($n = 14–16$ in most cases) may be a cause for concern. In view of the above-mentioned arguments concerning the complicating factors, we prefer not to take this 'improvement' too seriously.

The correlation results for Y-MSTs (Table 3) are comparable to those for Y-STs, except that the *r* (or *R*) and ψ values look even better,especially for the $\sigma_p + \sigma_{\alpha}^{\cdot}$ pair. However, the number of substituents used is much smaller than those used for Y-STs and Y-TFSs. In fact, three entries in Table 3 ($\sigma^+ + \sigma_{JJ}^{\cdot}$, $\sigma^+ + \sigma_{\alpha}$ and $\sigma_p + \sigma_{C}^{\cdot}$) have confidence levels of >99·0% instead of >99·9%.

Table 2. Correlation results for Y-STs

σ^{X} or $\sigma^{\cdot}$ or $\sigma^{X}+\sigma^{\cdot}$	ρ^{X} $(\times 10^{-3})$	$\rho^{\cdot}$ $(\times 10^{-3})$	s^2 $(\times 10^{-3})$	r or R	ψ	F[a]	n
σ_{mb}	0·580		1·93	0·149	1·06	0·319	16[b]
σ^{+}	1·89		1·64	0·572	0·886	5·837	14[c]
σ_{p}	1·05		1·84	0·223	1·04	0·783	17[d]
$\sigma_{JJ}^{\cdot}$		−6·92	0·815	0·909	0·447	66·22	16[b]
$\sigma_{\alpha}^{\cdot}$		−6·24	0·575	0·933	0·388	80·86	14[e]
$\sigma_{C}^{\cdot}$		−7·28	0·705	0·933	0·389	80·72	14[f]
$\sigma_{mb}+\sigma_{JJ}^{\cdot}$	0·142	−6·89	0·843	0·909	0·462	31·03	16[b]
$\sigma_{mb}+10\sigma_{\alpha}^{\cdot}$	0·103	−6·31	0·598	0·934	0·404	37·31	14[e]
$\sigma_{mb}+\sigma_{C}^{\cdot}$	0·256	−7·15	0·724	0·935	0·399	38·46	14[f]
$\sigma^{+}+\sigma_{JJ}^{\cdot}$	0·168	−6·72	0·857	0·920	0·446	27·71	13[g]
$\sigma^{+}+10\sigma_{\alpha}^{\cdot}$	0·681	−6·63	0·438	0·967	0·300	57·19	11[h]
$\sigma^{+}+\sigma_{C}^{\cdot}$	0·453	−6·79	0·722	0·948	0·369	39·54	12[i]
$\sigma_{p}+\sigma_{JJ}^{\cdot}$	0·265	−6·84	0·838	0·910	0·459	31·41	16[b]
$\sigma_{p}+10\sigma_{\alpha}^{\cdot}$	−0·532	−6·06	0·571	0·940	0·386	41·56	14[e]
$\sigma_{p}+\sigma_{C}^{\cdot}$	−0·0873	−7·33	0·736	0·933	0·405	37·10	14[f]

[a] Critical F values: $F_{001}(15,1)=16{\cdot}59$, $F_{001}(14,1)=17{\cdot}14$, $F_{001}(12,1)=18{\cdot}64$, $F_{001}(13,2)=12{\cdot}31$, $F_{001}(11,2)=13{\cdot}81$, $F_{001}(10,2)=14{\cdot}91$, $F_{001}(9,2)=16{\cdot}39$, $F_{001}(8,2)=18{\cdot}49$.

[b] Substituents: **1–10, 12–17.**

[c] **1–8, 10, 11, 13, 14, 16, 17.**

[d] **1–17.**

[e] **1–7, 9, 10, 12–16.**

[f] **1, 2, 4–10, 12–14, 16, 17.**

[g] **1–8, 10, 13, 14, 16, 17.**

[h] **1–7, 10, 13, 14, 16.**

[i] **1, 2, 4–8, 10, 13, 14, 16, 17.**

Table 3. Correlation results for Y-MSTs

σ^{X} or $\sigma^{\cdot}$ or $\sigma^{X}+\sigma^{\cdot}$	ρ^{X} $(\times 10^{-3})$	$\rho^{\cdot}$ $(\times 10^{-3})$	s^2 $(\times 10^{-3})$	r or R	ψ	F[a]	n
σ_{mb}	−2·52		2·22	0·396	1·06	1·112	8[b]
σ^{+}	1·10		2·13	0·234	1·15	0·289	7[c]
σ_{p}	−2·93		2·26	0·353	1·08	0·852	8[b]
$\sigma_{JJ}^{\cdot}$		−8·57	0·678	0·960	0·325	69·92	8[b]
$\sigma_{\alpha}^{\cdot}$		−7·26	0·558	0·973	0·267	106·0	8[b]
$\sigma_{C}^{\cdot}$		−10·7	0·406	0·983	0·219	140·8	7[c]
$\sigma_{mb}+\sigma_{JJ}^{\cdot}$	−1·40	−8·19	0·473	0·984	0·227	75·35	8[b]
$\sigma_{mb}+10\sigma_{\alpha}^{\cdot}$	−1·06	−6·95	0·436	0·986	0·209	89·38	8[b]
$\sigma_{mb}+\sigma_{C}^{\cdot}$	0·365	−10·9	0·431	0·984	0·233	62·69	7[c]
$\sigma^{+}+\sigma_{JJ}^{\cdot}$	−1·29	−9·22	0·524	0·977	0·283	41·77	7[c]
$\sigma^{+}+10\sigma_{\alpha}^{\cdot}$	−0·895	−7·54	0·504	0·979	0·272	45·30	7[c]
$\sigma^{+}+\sigma_{C}^{\cdot}$	0·253	−10·6	0·435	0·984	0·235	61·44	7[c]
$\sigma_{p}+\sigma_{JJ}^{\cdot}$	−1·80	−8·29	0·480	0·983	0·230	73·40	8[b]
$\sigma_{p}+10\sigma_{\alpha}^{\cdot}$	−1·65	−7·02	0·324	0·992	0·155	163·9	8[b]
$\sigma_{p}+\sigma_{C}^{\cdot}$	0·134	−10·8	0·452	0·983	0·244	56·82	7[c]

[a] Critical F values: $F_{01}(4,2)=18{\cdot}00$, $F_{001}(6,1)=35{\cdot}51$, $F_{001}(5,1)=47{\cdot}18$, $F_{001}(5,2)=37{\cdot}12$, $F_{001}(4,2)=61{\cdot}25$.

[b] Substituents: **1, 2, 5, 7, 13, 15, 16, 18.**

[c] **1, 2, 5, 7, 13, 16, 18.**

Table 4. Correlation results for Y-TFSs

σ^X or $\sigma^{\cdot}$ or $\sigma^X + \sigma^{\cdot}$	ρ^X ($\times 10^{-3}$)	$\rho^{\cdot}$ ($\times 10^{-3}$)	s^2 ($\times 10^{-3}$)	r or R	ψ	F[a]	n
σ_{mb}	0·800		2·56	0·144	1·04	0·379	20[b]
σ^+	2·45		2·41	0·520	0·913	5·201	16[c]
σ_p	1·60		2·51	0·245	1·02	1·147	20[b]
$\sigma_{JJ}^{\cdot}$		−10·2	0·991	0·924	0·404	104·7	20[b]
$\sigma_{\alpha}^{\cdot}$		−7·21	0·778	0·893	0·486	47·19	14[d]
$\sigma_C^{\cdot}$		−11·2	0·793	0·959	0·304	159·2	16[e]
$\sigma_{mb} + \sigma_{JJ}^{\cdot}$	0·0541	−10·2	1·02	0·924	0·415	49·48	20[b]
$\sigma_{mb} + 10\sigma_{\alpha}^{\cdot}$	−0·981	−6·30	0·690	0·924	0·431	32·11	14[d]
$\sigma_{mb} + \sigma_C^{\cdot}$	0·163	−11·1	0·819	0·959	0·314	74·71	16[e]
$\sigma^+ + \sigma_{JJ}^{\cdot}$	−0·0472	−10·6	1·10	0·927	0·416	39·80	16[c]
$\sigma^+ + 10\sigma_{\alpha}^{\cdot}$	−0·603	−6·76	0·464	0·953	0·354	39·92	11[f]
$\sigma^+ + \sigma_C^{\cdot}$	0·422	−10·8	0·671	0·977	0·242	114·4	14[g]
$\sigma_p + \sigma_{JJ}^{\cdot}$	0·341	−10·1	1·01	0·925	0·412	50·50	20[b]
$\sigma_p + 10\sigma_{\alpha}^{\cdot}$	−1·85	−6·38	0·484	0·963	0·302	71·11	14[d]
$\sigma_p + \sigma_C^{\cdot}$	−0·140	−11·3	0·821	0·959	0·315	74·29	16[e]

[a] Critical F values: $F_{001}(18, 1) = 15{\cdot}38$, $F_{001}(14, 1) = 17{\cdot}14$, $F_{001}(12, 1) = 18{\cdot}64$, $F_{001}(17, 2) = 10{\cdot}66$, $F_{001}(13, 2) = 12{\cdot}31$, $F_{001}(11, 2) = 13{\cdot}81$, $F_{001}(8, 2) = 18{\cdot}49$.
[b] Substituents: **1–10, 12–15, 17–22.**
[c] **1–8, 10, 13, 14, 17–20, 22.**
[d] **1–7, 9, 10, 12–15, 18.**
[e] **1, 2, 4–10, 12–14, 17–19, 22.**
[f] **1–7, 10, 13, 14, 18.**
[g] **1, 2, 4–8, 10, 13, 14, 17–19, 22.**

For the Y-TFSs, the maximum number of substituents used is increased to 20 (for the $\sigma_{JJ}^{\cdot}$ entries). Again, with the exception of the first three σ^X entries in Table 4, all others have confidence levels greater than 99·9%. Evidently, as a whole the results are similar to those discussed previously for Y-STs and Y-MSTs. As an illustration, we chose to use correlations with the highest number of substituents for a comparison of the correlation results of equation (1) (σ_{mb}) with those of equation (2) ($\sigma_{JJ}^{\cdot}$), as shown in Figure 1. It clearly shows that there is no correlation of ν_{max} with the polar σ_{mb} scale (similar results were obtained with σ_p and σ^+), and that there is a good correlation with the spin-delocalization $\sigma_{JJ}^{\cdot}$ scale (similar results were obtained with $\sigma_{\alpha}^{\cdot}$ and $\sigma_C^{\cdot}$).

In conclusion, we propose that the ν_{max} values of the UV K-bands of styrenes are affected mainly by the spin-delocalization effect, although polar effects are probably not non-existent (most of the $|\rho^X/\rho^{\cdot}|$ values are small, cf. Refs 4e and 4f). Evidently, the negativity of all $\rho^{\cdot}$ values shows that the energy of the upper half-occupied orbital is lowered by the spin-delocalization effect of substituents. We hope that some theoreticians and spectroscopists will be interested in these results and provide theoretical interpretations.

EXPERIMENTAL

All UV spectra were taken at room temperature in 95% EtOH on a Perkin-Elmer Lambda 2 instrument with a wavelength accuracy of ±0·3 nm and a reproducibility of ±0·1 nm. ^{1}H NMR spectra were obtained at 60 MHz on a Varian EM-360A or at 90 MHz on a FX-90Q spectrometer with TMS as the external standard. Mass spectrometric data were measured on a Hewlett-Packard Model 5989A spectrometer. IR spectra were obtained on Bio-Rad FTS-45 spectrometer.

All the Y-substituted styrene substrates, i.e., *para*-Y-substituted styrenes (Y-STs), *para*-Y-substituted α,β,β-trifluorostyrenes (Y-TFSs) and *para*-Y-substituted α-methylstyrenes (Y-MSTs), are known compounds and were prepared according to the literature,[4b,4d,4e,10] as described below.

Some Y-STs were prepared according to the references cited, namely for Y = MeS, I, *t*-Bu,[10a–10c] for Y = MeSO, $MeSO_2$[10d] and for Y = AcO, NMe_2.[10e–10f] All the substrates mentioned were purified by column chromatography, and their identity was further confirmed by the following data: for Y = MeS,[10a–10c] ^{1}H NMR (90 MHz, $CDCl_3$), δ 7·36 (d, 2H, J = 8·9 Hz), 7·17 (d, 2H, J = 8·9 Hz), 6·66 (d-d, 1H, J = 11·5 Hz, 17·8 Hz), 5·69 (d, 1H, J = 17·8 Hz), 5·13 (d, 1H, J = 11·5 Hz), 2·46 (s, 3H); IR, 3072·5, 3017·6, 2965·3, 2866·9, 1596·8, 816·0 cm^{-1}. For Y = MeSO,[10d] ^{1}H NMR (90 MHz, $CDCl_3$), δ 7·62 (s, 4H), 6·78 (d-d, 1H, J = 11·5 Hz, 17·8 Hz), 5·88 (d, 1H, J = 17·8 Hz), 5·30 (d, 1H, J = 11·5 Hz), 2·72 (s, 3H); MS, *m/z* (relative intensity, %), 166 (62·3, M^+), 151 (100), 119 (21·2), 102 (13·0), 91 (14·5), 77 (31·8); IR, 2995·0, 1492·4, 1416·0, 1058·2, 838·8 cm^{-1}. For Y = $MeSO_2$,[10d]

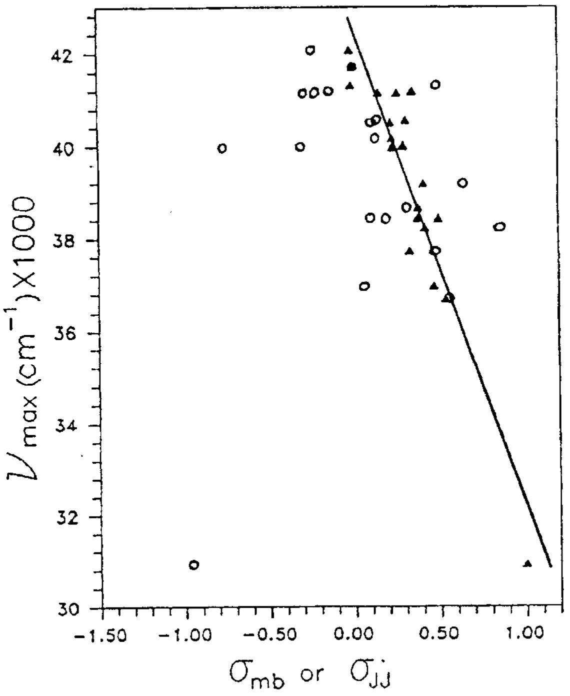

Figure 1. Plot of ν_{max} (cm^{-1}) vs σ_{mb} (O) or σ_{JJ} (▲)

^{1}H NMR (90 MHz, $CDCl_3$), δ 7·85 (d, 2H, J = 8·9 Hz), 7·65 (d, 2H, J = 8·9 Hz), 6·83 (d-d, 1H, J = 17·8 Hz, 11·5 Hz), 6·96 (d, 1H, J = 17·8 Hz), 5·41 (d, 1H, J = 11·5 Hz), 3·09 (s, 3H); MS, m/z (relative intensity, %), 182 (64·9, M^+), 167 (60·6), 119 (77·2), 103 (100), 77 (57·1); IR, 2926·0, 1594·0, 1302·2, 1144·2, 845·3 cm^{-1}. For Y = I,[10a–10c] MS, m/z (relative intensity, %), 230 (78·69, M^+), 217 (43·97), 206 (86·84), 204 (23·66), 202 (30·77), 191 (100), 127 (9·42), 104 (30·35), 89 (35·74); IR, 3082·9, 2961·7, 1583·4, 1481·9, 1454·7, 987·1, 910·4, 824·8 cm^{-1}. For Y = AcO,[10e–10f] ^{1}H NMR (90 MHz, $CDCl_3$), δ 7·35, 6·99 (AB, J = 8·2 Hz, 4H), 6·64 (d-d, J = 18·0 Hz, 11·6 Hz, 1H), 5·62 (d, J = 18·0 Hz, 1H), 5·17 (d, J = 11·6 Hz, 1H), 2·24 (s, 3H); MS, m/z (relative intensity, %), 162 (18·44, M^+), 120 (100), 91 (26·56); IR, 1758·4, 1601·5, 1504·3, 1203·0, 1188·9, 1163·3, 1011·7, 990·4, 907·2, 849·7 cm^{-1}. For Y = NMe_2,[10e–10f] MS, m/z (relative intensity, %), 147 (100, M^+), 131 (20·01), 130 (16·48), 103 (11·38); IR, 3083·0, 1608·2, 1518·9, 1443·5, 1349·4, 1221·6, 1185·3, 988·6, 885·2, 816·2 cm^{-1}. For Y = t-Bu,[10a–10c] MS, m/z (relative intensity, %), 160 (45·77, M^+), 145 (100), 129 (12·20), 117 (41·07), 105 (13·02); IR, 3085·2, 2960·6, 2869·4, 1604·8, 1512·2, 1479·4, 1462·1, 1398·1, 1268·6, 1199·5, 1126·1, 990·3, 904·9, 834·1 cm^{-1}.

Other substrates, i.e. all Y-TFSs, all Y-MSTs and some Y-STs (Y = F, $SiME_3$, Me, Cl, Br, OCH_3, CO_2CH_3, CN, COMe) were prepared in this laboratory and identified as reported previously, namely for Y-TFSs according to Ref. 4b and references cited therein, for Y-STs according to Ref. 4d and for Y-MSTs according to Ref. 4e.

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