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Reestimation of the Taft's Substituent Constant of the Pentafluorophenyl Group

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Abstract: The Taft's substituent constant of the pentafluorophenyl group ($\sigma^*(C_6F_5)$) was reestimated to be 1.50 by correlation between IR spectral data ($\nu_{C=O}$) and σ^* constants for a series of esters (involving the pentafluorobenzyl group) of 3-phenylpropanoic acid and butanoic acid. The possibility of the disturbance of the correlation by the intramolecular $\pi-\pi$ interaction between C_6F_5 and C_6H_5 groups in pentafluorobenzyl 3-phenylpropanoate was excluded by ab initio and DFT calculations of the stable conformations and their carbonyl frequencies. The reestimated $\sigma^*(C_6F_5)$ value was used for calculation of the pK_a value of pentafluorobenzyl alcohol [14.5 (or 14.3)].

A pentafluorophenyl (C_6F_5) group is a distinctive and useful substituent in organic synthesis,[1] because of the $\pi-\pi$ stacking ability with an electron-rich aromatic ring[2] and of the enhanced electron-withdrawing property. For example, tris(pentafluorophenyl)borane highly accelerates the aldol-type reaction of ketene silyl acetal and aldehyde.[3,4] The increasing utilities of the C_6F_5 group for fine-tuning of the properties of advanced materials come to demand a precise index, i.e., the Taft's substituent constant σ^*, for the electron-withdrawing property.[5,6] A couple of Taft's constant values for the C_6F_5 group ($\sigma^*(C_6F_5)$) have been reported to be 1.1 by Chang et al.[7] and 1.96 by Brink,[8] although both of them involve the points in which reexamination is required in their estimation processes.[9] Both cases required the precise pK_a values of C_6F_5 group-containing alcohols or carboxylic acid; however, those were measured by potentiometric titrations under basic conditions. The method is unsuitable for the compounds containing a C_6F_5 group because of the high sensitivity at the 4-position toward oxy anions.[10] To avoid such experimental ambiguity, we here reestimated the $\sigma^*(C_6F_5)$ value by correlation between their IR spectral data ($\nu_{C=O}$) and σ^* constants using a series of esters, $Ph(CH_2)_2CO_2CH_2R$ (**1**) (method 1) and n-$C_3H_7CO_2CH_2R$ (**2**) (method 2), in which pentafluorobenzyl ($R = C_6F_5$) esters are involved.[11] The method should be more suitable for estimation of the σ^* value for substituents (R) sensitive to basic conditions. The $\sigma^*(C_6F_5)$ value (1.50) thus estimated was applied to give a reestimated pK_a value [14.5 (or 14.3)] for pentafluorobenzyl alcohol (**3**).

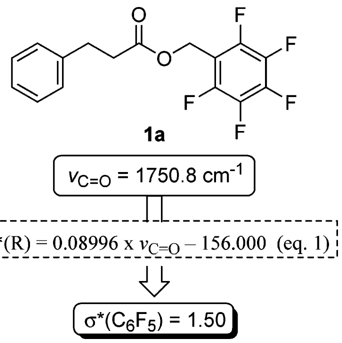

FIGURE 1. Estimation of the Taft's $\sigma^*(C_6F_5)$ value by using the carbonyl frequency of ester **1a**.

Results and Discussion. We first examined adapting the carbonyl frequency ($\nu_{C=O}$) of pentafluorobenzyl 3-phenylpropanoate[12] (**1a**) (Figure 1) to Cohen's equation derived by the correlation between $\nu_{C=O}$ and σ^* values (method 1).[11] The $\nu_{C=O}$ value of the prepared ester **1a** was measured in CCl_4 to show 1750.8 cm^{-1},[13] and its adaptation to Cohen's equation (eq 1, see Figure 1) gave the $\sigma^*(C_6F_5)$ value of 1.50 (Figure 1).

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[1] Chiral diol, amino alcohol, or diamine bearing pentafluorophenyl groups: (a) Sakai, T.; Kubo, K.; Kashino, S.; Uneyama, K. *Tetrahedron: Asymmetry* **1996**, *7*, 1883. (b) Sakai, T.; Takayama, T.; Ohkawa, T.; Yoshio, O.; Ema, T.; Utaka, M. *Tetrahedron Lett.* **1997**, *38*, 1987. (c) Sakai, T.; Miki, Y.; Tsuboi, M.; Takeuchi, H.; Ema, T.; Uneyama, K.; Utaka, M. *J. Org. Chem.* **2000**, *65*, 2740. (d) Korenaga, T.; Tanaka, H.; Ema, T.; Sakai, T. *J. Fluorine Chem.* **2003**, *122*, 201. (e) Sakai, T.; Korenaga, T.; Washio, N.; Nishio, Y.; Minami, S.; Ema, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1001.

[2] Review for interaction between the C_6F_5 group and aromatic rings: Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210.

[3] Review for applications of pentafluorophenylboranes: Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345.

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[6] More than 50 articles containing discussions using σ^* constants were published in 1999−2003. The articles published in 2003−2004 are shown here: (a) Babij, C.; Poë, A. J. *J. Phys. Org. Chem.* **2004**, *17*, 162. (b) El-Taher, S.; El-Azhary, A. A. *Int. J. Quantum Chem.* **2004**, *98*, 502. (c) Hamza, M. S. A.; Felluga, A.; Randaccio, L.; Tauzher, G.; Eldik, R. *Dalton Trans.* **2004**, 287. (d) Valentic, N. V.; Uscumlic, G. S.; Radojkovic-Velickovic, M. *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* **2003**, *42B*, 1137. (e) Lin, G.; Lai, C.; Liao, W.; Liao, P.; Chan, C. *J. Chin. Chem. Soc.* **2003**, *50*, 1259. (f) Drmanic, S. Z.; Jovanovic, B. Z.; Marinkovic, A. D.; Misic-Vukovic, M. M. *J. Serb. Chem. Soc.* **2003**, *68*, 515. (g) Cherkasov, A.; Sprous, D. G.; Chen, R. *J. Phys. Chem. A* **2003**, *107*, 9695.

[7] Chang, I. S.; Price, J. T.; Tomlinson, A. J.; Willis, C. J. *Can. J. Chem.* **1972**, *50*, 512.

[8] Brink, H. *Acta Pharm. Suec.* **1980**, *17*, 233.

[9] Chang's value ($\sigma^*(C_6F_5) = 1.1$) was proposed by adaptation of the pK_a values of a couple of alcohols containing a C_6F_5 group to the standard correlation equation between the pK_a values and the O−H frequency for nonfluorinated alcohols. However, the observed pK_a values for C_6F_5 group-containing alcohols were deviated from the standard correlation line, showing smaller pK_a values.[7] On the other hand, Brink's value ($\sigma^*(C_6F_5) = 1.96$) was derived from the pK_a value of C_6F_5COOH.[8] However, two different pK_a values (3.38[9a] or 1.75[9b]) had been reported independently, and the latter was used for estimation of the $\sigma^*(C_6F_5)$ value of 1.96:[8] (a) Chambers, R. D.; Drakesmith, F. G.; Musgrave, W. K. R. *J. Chem. Soc.* **1965**, 5045. (b) Ryan, M. T.; Berner, K. J. *Spectrochim. Acta, Part A* **1969**, *25*, 1155.

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[11] The method was established by Cohen et al., who reported the evaluation of the σ^* values for a series of substituents (R) by using an experimentally driven correlation equation between $\nu_{C=O}$ and $\sigma^*(R)$ values using $Ph(CH_2)_2CO_2CH_2R$: Takahashi, S.; Cohen, L. A.; Miller, H. K.; Peake, E. G. *J. Org. Chem.* **1971**, *36*, 1205.

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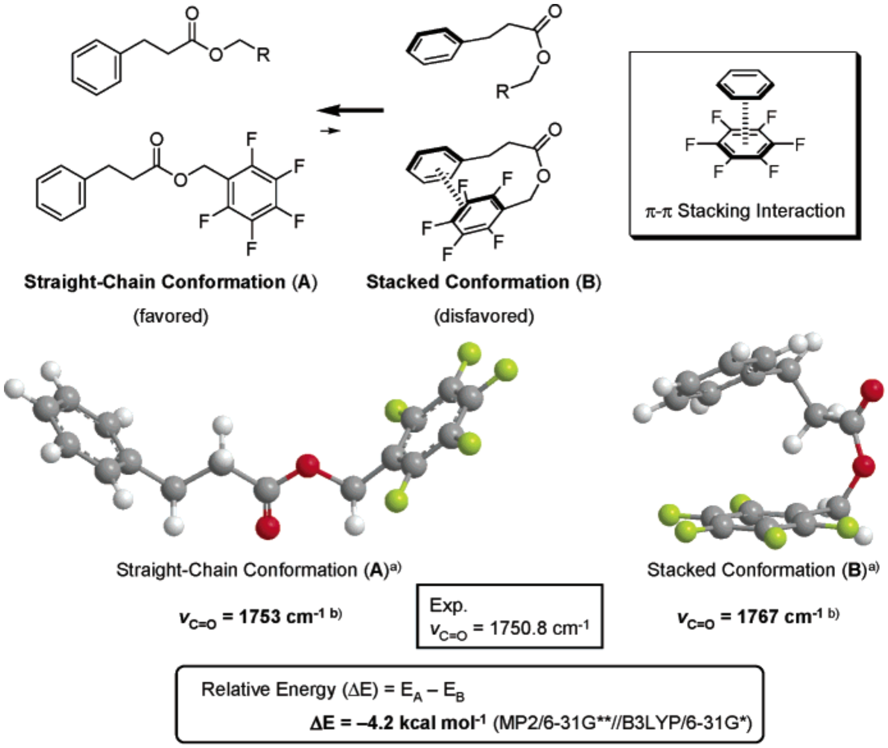
[13] The deviation is ±0.25 cm^{-1}.

10.1021/jo048939g CCC: $27.50



[a] Optimization at B3LYP/6-31G* level. [b] B3LYP/6-31G* level; Scaled by 0.9613.

FIGURE 2. Confirmation of possible conformations for ester **1a**.

Here, we should discuss the stability of the possible conformations **A** and **B** for ester **1a** (Figure 2), because conformation **B** may be stabilized by the intramolecular $\pi-\pi$ ($C_6F_5-C_6H_5$) interaction,[2,14] and it must exhibit an unsuitable $\nu_{C=O}$ for the correlation. We confirmed that conformation **A** is more stable than **B**[15] by ab initio and DFT calculations. The calculations of the optimized geometries of the ester **1a** were performed at the B3LYP/6-31G* level[16] using the Gaussian 03W.[17] The relative energy between **A** and **B** ($\Delta E = E_A - E_B$) was estimated to be -4.2 kcal mol^{-1} at the MP2/6-31G** level (Figure 2), which suggests a sufficient stability of conformation **A**. In addition, the carbonyl frequencies ($\nu_{C=O}$) of conformations **A** and **B** were calculated at the B3LYP/6-31G* level (Figure 2). After being scaled by 0.9613,[18] the $\nu_{C=O}$ of conformation **A** was estimated to be 1753 cm^{-1}, which was very close to the experimental value (1750.8 cm^{-1}). Thus, the abundance ratio of conformation **B** with $\nu_{C=O}$ (1767 cm^{-1}) is negligible.[19]

Then, we estimated the $\sigma^*(C_6F_5)$ value by using nonaromatic carboxylic acid esters (**2**), without the possibility of intramolecular $\pi-\pi$ interaction (method 2). The $\nu_{C=O}$ values of 12 kinds of esters[20] (**2a**−***l***) were measured (Table 1), and the correlation equation (eq 2) was derived by using the least-squares method.

$$\sigma^* = 0.094630\nu_{C=O} - 164.03 \qquad (r^2 = 0.993,\ \text{RMS error} = 0.07) \quad (2)$$

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[14] The interaction energy between C_6F_6 and C_6H_6 was estimated to be ca. -3.5 kcal mol^{-1}: (a) Williams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593. (b) West, A. P., Jr.; Mecozzi, S.; Dougherty, D. A. *J. Phys. Org. Chem.* **1997**, *10*, 347.

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[16] Frequency calculation performed on optimized structures at the same level produced no imaginary frequencies.

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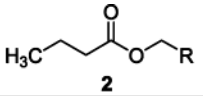
[18] Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

[19] To demonstrate the accuracy of the calculated $\nu_{C=O}$ value, the calculations of the $\nu_{C=O}$ of $Ph(CH_2)_2CO_2CH_2CF_3$ and $Ph(CH_2)_2CO_2CH_2CCl_3$ were carried out at the B3LYP/6-31G* level. After being scaled by 0.9613, the former was estimated to be 1761 cm^{-1} (experimental value 1763 cm^{-1}) and the later was estimated to be 1760 cm^{-1} (experimental value 1760 cm^{-1}).

[20] Ester **2c** is a new compound. Esters **2a**, **2b**, **2i**, **2k**, and **2l** were commercially available. **2d**: (a) Movsumzade, E. M.; Kulieva, D. A.; Mamedov, M. G.; Nasirov, Ya. F. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1985**, *28*, 12. **2e**: (b) Dominguez, E.; Carretero, J. C.; Fernandez-Mayoralas, A.; Conde, S. *Tetrahedron Lett.* **1991**, *32*, 5159. **2f**: (c) Sapozhkova, N. D.; Smirnova, N. P. *Metody Poluch. Khim. Reakt. Prep.* **1965**, *13*, 23. **2g**: (d) Zeinalov, B. K.; Nasirov, A. B.; Gadzhiev, T. P. *Azerb. Khim. Zh.* **1968**, *6*, 122. **2h**: (e) Pelter, A.; Colclough, E. *Tetrahedron* **1995**, *51*, 811. **2j**: (f) Tsujimoto, H. Japanese Kokai Tokkyo Koho JP 2004047183, 2004.

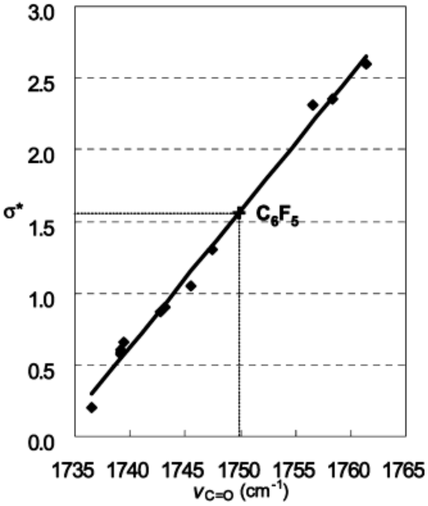
[21] The correlation coefficient for $Ph(CH_2)_2CO_2CH_2R$ was not described in ref 11. We calculated the correlation coefficient from their data by the least-squares method to give $r^2 = 0.997$ (RMS error = 0.05), which was slightly higher than that of $n\text{-}C_3H_7CO_2CH_2R$. Therefore, we selected the $\sigma^*(C_6F_5)$ value of 1.50 derived from eq 1.

TABLE 1. Carbonyl Frequencies of Butyric Acid Esters and σ^* Values



2

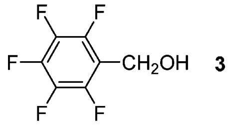
Ester	R	$\nu_{C=O}$ (cm^{-1})	σ^* [a)]
2a	CF_3	1761.4	2.60
2b	CCl_3	1758.4	2.35
2c	CBr_3	1756.5	2.31
2d	CH_2CN	1747.5	1.30
2e	CH_2Cl	1745.5	1.05
2f	CH_2I	1743.1	0.90
2g	CH_2OPh	1742.7	0.87
2h	CH_2OMe	1739.4	0.66
2i	Ph	1739.2	0.60
2j	CH_2OEt	1739.2	0.58
2k	$CH=CH_2$	1739.2	0.57
2l	CH_2Ph	1736.5	0.20
2m	**C_6F_5**	***1749.7***	***1.54*** [b)]



$\sigma^* = 0.094630 \times \nu_{C=O} - 164.03$

($r^2 = 0.993$, RMS error = 0.07)

[a] Reference 11. [b] Calculated by using eq 2.



3

p*K*a

$pKa = -1.44 \times \sigma^* + 16.67$ (eq. 3) **14.5**

$\sigma^*(C_6F_5) = 1.50$

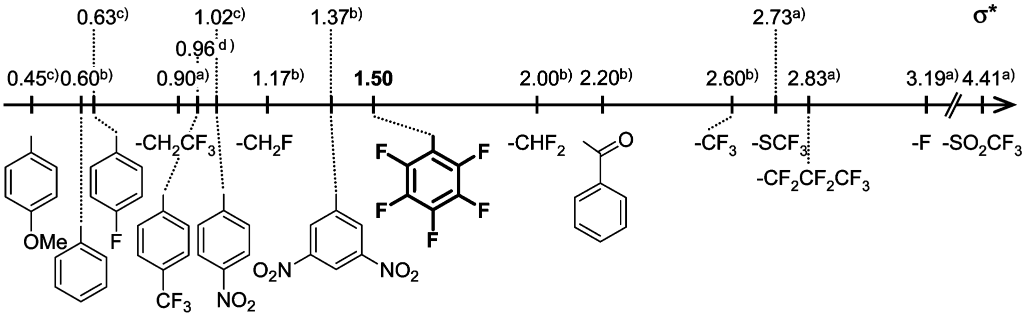
$pKa = -1.316 \times \sigma^* + 16.23$ (eq. 4) **14.3**

FIGURE 3. Estimation of the pK_a value for pentafluorobenzyl alcohol **3**.

Satisfactory correlation between the σ^*(R) and $\nu_{C=O}$ values for esters **2a**−***l*** was observed.[21] The $\sigma^*(C_6F_5)$ value was thus estimated to be 1.54 by adaptation of the measured $\nu_{C=O}$ value (1749.7 cm^{-1}) for ester **2m**[12] in CCl_4 to eq 2, and found that the value is consistent with that (1.50) determined by using ester **1a**. These results also suggest that influence of the intramolecular $\pi-\pi$ interaction in ester **1a** is negligible as was confirmed by the calculations. Consequently, we concluded that the $\sigma^*(C_6F_5)$ value is 1.50,[21] which is larger than Chang's value ($\sigma^*(C_6F_5)$ = 1.1) and smaller than Brink's value ($\sigma^*(C_6F_5)$ = 1.96).

Finally, we utilized the $\sigma^*(C_6F_5)$ value for estimation of the pK_a value of alcohol **3**. The $\sigma^*(C_6F_5)$ value (1.50) estimated above was adapted to the pKa−σ^*(R) correlation eqs 3[8] or 4[11] to give the pK_a values of 14.5 or 14.3 for **3**, respectively (Figure 3). These values must be more reliable as compared with the reported value (13.7) that was calculated by eq 3, using Brink's $\sigma^*(C_6F_5)$ value (1.96).[8]

In conclusion, Taft σ^* values were widely used in a variety of areas, for instance, kinetic or thermodynamic studies, designing of advanced materials, and so on.[6] Figure 4 shows the order of inductive effect for a series of fluorinated or aromatic substituents.[22] The pentafluorophenyl group is found to possess the moderate electron-withdrawing ability between 3,5-dinitrophenyl and difluoromethyl groups.



[a] Reference 22. [b] Reference 11. [c] Reference 8. [d] Reference 6a.

FIGURE 4. Taft's σ^* values for the fluorinated or aromatic compounds.

Experimental Section

Pentafluorobenzyl 3-Phenylpropanoate (1a).[12] To a solution of pentafluorobenzyl alcohol (0.59 g, 3.6 mmol) and pyridine (0.71 g, 9.0 mmol) in Et_2O (6.0 mL) was added 3-phenylpropanoyl chloride (0.51 g, 3.0 mmol) at 0 °C. After being stirred for 15 h, the mixture was acidified (pH <4) by 10% dilute HCl, and an organic layer was extracted with ether (3×4 mL) and treated in the usual manner. The product was purified by column chromatography (SiO_2, hexane/EtOAc (8:1)) to give **1a** (0.90 g, 2.7 mmol, 91% yield) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.94 (t, $J = 7.4$ Hz, 3H), 1.66 (m, 2H), 2.31 (t, $J = 7.4$ Hz, 2H), 5.19 (s, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -84.8 (m, 2F), -76.0 (t, $J = 21$ Hz, 1F), -65.4 (m, 2F); IR (CCl_4) 942, 1058, 1135, 1311, 1507, 1522, 1751, 2850, 2917, 3030 cm^{-1}.

2,2,2-Tribromoethyl Butyrate (2c). Ester **2c** was prepared from 2,2,2-tribromoethanol (1.0 g, 3.6 mmol), butyryl chloride (0.32 g, 3.0 mmol), and pyridine (0.71 g, 9.0 mmol) in 50% yield (0.54 g, 1.5 mmol) by the procedure described for ester **1a**. Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (t, $J = 7.5$ Hz, 3H), 1.76 (m, 2H), 2.47 (t, $J = 7.5$ Hz, 2H), 4.93 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.6, 18.1, 35.7, 36.0, 76.4, 171.2; IR (CCl_4) 1012, 1043, 1091, 1152, 1244, 1757, 2851, 2876, 2921, 2966 cm^{-1}. Anal. Calcd for $C_6H_9Br_3O_2$: C, 20.42; H, 2.57. Found: C, 20.23; H, 2.52.

2-Cyanoethyl Butyrate (2d).[20a] Ester **2d** was prepared from 2-cyanoethanol (0.60 g, 8.4 mmol), butyryl chloride (0.75 g, 7.0 mmol), and pyridine (1.7 g, 21 mmol) in 50% yield (0.49 g, 3.5 mmol). Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, $J = 7.4$ Hz, 3H), 1.68 (m, 2H), 2.35 (t, $J = 7.4$ Hz, 2H), 2.71 (t, $J = 6.4$ Hz, 2H), 4.29 (t, $J = 6.4$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.6, 17.1, 34.8, 57.8, 116.6, 171.9; IR (CCl_4) 1092, 1168, 1249, 1557, 1748, 2850, 2877, 2918, 2966 cm^{-1}.

2-Chloroethyl Butyrate (2e).[20b] Ester **2e** was prepared from 2-chloroethanol (0.58 g, 7.2 mmol), butyryl chloride (0.64 g, 6.0 mmol), and pyridine (1.4 g, 18 mmol) in 84% yield (0.76 g, 5.1 mmol). Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, $J = 7.4$ Hz, 3H), 1.68 (m, 2H), 2.34 (t, $J = 7.4$ Hz, 2H), 3.68 (t, $J = 6.0$ Hz, 2H), 4.34 (t, $J = 6.0$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.7, 17.7, 35.0, 41.1, 63.1, 171.9; IR (CCl_4) 1095, 1170, 1247, 1311, 1746, 2877, 2935, 2967 cm^{-1}.

2-Iodoethyl Butyrate (2f).[20c] Ester **2f** was prepared from 2-iodoethanol (0.83 g, 4.8 mmol), butyryl chloride (0.43 g, 4.0 mmol), and pyridine (0.95 g, 12 mmol) in 91% yield (0.88 g, 3.6 mmol). Brown oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, $J = 7.4$ Hz, 3H), 1.68 (m, 2H), 2.33 (t, $J = 7.4$ Hz, 2H), 3.30 (t, $J = 6.6$ Hz, 2H), 4.33 (t, $J = 6.6$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.6, 13.3, 17.7, 35.4, 63.8, 172.2; IR (CCl_4) 981, 1091, 1165, 1249, 1743, 2876, 2941, 2967 cm^{-1}.

2-Phenoxyethyl Butyrate (2g).[20d] Ester **2g** was prepared from 2-phenoxyethanol (0.83 g, 6.0 mmol), butyryl chloride (0.53 g, 5.0 mmol), and pyridine (1.2 g, 15 mmol) quantitatively (1.0 g, 5.0 mmol). Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, $J = 7.4$ Hz, 3H), 1.67 (m, 2H), 2.34 (t, $J = 7.4$ Hz, 2H), 4.17 (t, $J = 4.6$ Hz, 2H), 4.44 (t, $J = 4.6$ Hz, 2H), 6.89−7.0 (m, 3H), 7.26−7.33 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.9, 17.7, 35.1, 61.8, 65.1, 113.8, 120.3, 128.8, 157.9, 172.2; IR (CCl_4) 955, 1087, 1172, 1245, 1456, 1495, 1589, 1601, 1743, 2876, 2955, 2967 cm^{-1}.

2-Methoxyethyl Butyrate (2h).[20e] Ester **2h** was prepared from 2-methoxyethanol (0.73 g, 9.6 mmol), butyryl chloride (0.85 g, 8.0 mmol), and pyridine (2.1 g, 26 mmol) in 73% yield (0.85 g, 5.8 mmol). Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, $J = 7.4$ Hz, 3H), 1.67 (m, 2H), 2.33 (t, $J = 7.4$ Hz, 2H), 3.39 (s, 3H), 3.60 (t, $J = 4.8$ Hz, 2H), 4.23 (t, $J = 4.8$ Hz, 2H); IR (CCl_4) 1034, 1094, 1132, 1179, 1252, 1739, 2877, 2934, 2967 cm^{-1}.

2-Ethoxyethyl Butyrate (2j).[20f] Ester **2j** was prepared from 2-ethoxyethanol (0.65 g, 7.2 mmol), butyryl chloride (0.64 g, 6.0 mmol), and pyridine (1.4 g, 18 mmol) in 56% yield (0.54 g, 3.4 mmol). Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, $J = 7.6$ Hz, 3H), 1.22 (t, $J = 7.0$ Hz, 3H), 1.66 (m, 2H), 2.33 (t, $J = 7.6$ Hz, 2H), 3.54 (q, $J = 7.0$ Hz, 2H), 3.63 (t, $J = 4.6$ Hz, 2H), 4.23 (t, $J = 4.6$ Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.4, 14.9, 18.2, 35.8, 63.2, 66.3, 68.2, 173.3; IR (CCl_4) 1128, 1180, 1253, 1739, 2875, 2971 cm^{-1}.

Pentafluorobenzyl Butyrate (2m).[12] Ester **2m** was prepared from pentafluorobenzyl alcohol (0.71 g, 3.6 mmol), butyryl chloride (0.38 g, 3.6 mmol), and pyridine (0.85 g, 10.8 mmol) in 56% yield (0.54 g, 2.0 mmol). Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.94 (t, $J = 7.4$ Hz, 3H), 1.66 (m, 2H), 2.31 (t, $J = 7.4$ Hz, 2H), 5.19 (s, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -84.8 (m, 2F), -76.0 (t, $J = 21$ Hz, 1F), -65.4 (dd, $J = 6.8$, 21 Hz, 2F); IR (CCl_4) 943, 1058, 1134, 1163, 1312, 1507, 1522, 1750, 2876, 2934, 2968 cm^{-1}.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compound **2c** and Cartesian coordinates of **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Taft's σ^* data for several fluorine substituents: Brändström, A. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1855.