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**Kinetics of the Solvolyses of Benzhydryl Derivatives:
Basis for the Construction of a Comprehensive Nucleofugality Scale**

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CAUTION: One or more of the chloro-substituted benzhydryl compounds caused severe irritations of the skin, and have to be handled with extreme care.

Substituted Benzhydrols

General Procedure A (GP A). In a dried, nitrogen-flushed three-necked round-bottom flask, equipped with a reflux condenser, and two dropping funnels, Mg, which was activated with iodine at 75 °C, was suspended in THF (distilled from Na). A solution of the bromobenzene derivative in THF was carefully added to the Mg, to keep the solution under reflux. After the reaction was complete, a solution of the benzaldehyde derivative in THF was added. After stirring at room temperature for 2 h, the solution was poured on 0.5 M NH₄Cl-solution (150 mL) and extracted with Et₂O (3 × 100 mL). The combined organic phases were washed with water (100 mL), dried with MgSO₄, and filtered. Evaporation of the solvent in the vacuum gave the crude product. In some cases the benzhydrols were contaminated by the corresponding benzophenones. To remove the by-product, the product mixture was treated with sodium borohydride in ethanol for 12 h at ambient temperature. The solution was then hydrolyzed with a 0.02 M HCl and extracted with CH₂Cl₂ (5 × 50 mL). Again the solution was dried and filtered. The evaporation of the solvent in vacuo gave the crude benzhydrol.

3-Chlorobenzhydrol^[S1] (GP A) was obtained from Mg (3.74 g, 154 mmol), bromobenzene (22.9 g, 146 mmol), and 3-chloro-benzaldehyde (20.5 g, 146 mmol). The reduction was carried out with NaBH₄ (2.27 g, 60.0 mmol) in EtOH (200 mL). The crude product was distilled in the vacuum (118-120 °C/3.6 × 10⁻⁵ mbar) to give a colorless oil (27.5 g, 86 %) which solidified after several hours; mp 37-39 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.23 (br. s, 1 H, OH), 5.71 (s, 1 H, CHOH), 7.15–7.32 (m, 9 H, Ar); ¹³C NMR (75.5 MHz, CDCl₃): δ = 75.7 (d, CHOH), 124.6 (d), 126.6 (d), 127.6 (d), 127.9 (d), 128.7 (d), 129.7 (d), 134.4 (s), 143.2 (s), 145.7 (s); NMR data are in accord with the data previously published.^[S2]

3,4'-Dichlorobenzhydrol^[S3] (GP A) was obtained from Mg (2.68 g, 110 mmol), 1-bromo-4-chlorobenzene (19.2 g, 100 mmol), and 3-chloro-benzaldehyde (14.1 g, 100 mmol). The crude product was distilled in the vacuum (200-204 °C/1.0 × 10⁻² mbar) to give a colorless oil (17.8 g, 70 %). ¹H NMR (300 MHz, CDCl₃): δ = 2.96 (br. s, 1 H, OH), 5.61 (s, 1 H, CHOH), 7.10–7.26 (m, 8 H, Ar); ¹³C NMR (75.5 MHz, CDCl₃): δ = 74.8 (d, CHOH), 124.5 (d), 126.4 (d), 127.8 (d), 128.7 (d), 129.8 (d), 133.5 (s), 134.4 (s), 141.4 (s), 145.2 (s).

3,3'-Dichlorobenzhydrol^[S3] (GP A) was obtained from Mg (1.34 g, 55.1 mmol), 1-bromo-3-chlorobenzene (9.57 g, 50.0 mmol), and 3-chloro-benzaldehyde (7.03 g, 50.0 mmol). The reduction was carried out with NaBH₄ (0.76 g, 20.1 mmol) in EtOH (80 mL). The crude product was distilled in the vacuum (147-149 °C/2.3 × 10⁻⁵ mbar) to give a colorless oil (10.1 g, 80 %). ¹H NMR (300 MHz, CDCl₃): δ = 2.41 (br. s, 1 H, OH), 5.73 (s, 1 H, CHOH), 7.18–7.36 (m, 8 H, Ar); ¹³C NMR (75.5 MHz, CDCl₃): δ = 75.0 (d, CHOH), 124.6 (d), 126.6 (d), 127.7 (d), 129.9 (d), 134.5 (s), 145.1 (s).

3,3',5'-Trichlorobenzhydrol (GP A) was obtained from Mg (2.67 g, 110 mmol), 1-bromo-3,5-dichlorobenzene (23.1 g, 102 mmol), and 3-chloro-benzaldehyde (14.1 g, 100 mmol). The crude

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product was distilled in the vacuum (175-180 °C/ 2.1×10^{-5} mbar) to give a pale yellow oil (25.1 g, 87 %). ^1H NMR (300 MHz, CDCl_3): δ = 2.48 (br. s, 1 H, OH), 5.68 (s, 1 H, CHOH), 7.19–7.26 (m, 7 H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3): δ = 74.6 (d, CHOH), 124.6 (d), 124.9 (d), 126.6 (d), 127.9 (d), 128.4 (d), 130.1 (d), 134.7 (s), 135.2 (s), 144.4 (s), 146.3 (s).

3,3',5,5'-Tetrachlorobenzhydrol. In a dried, nitrogen-flushed three-necked round-bottom flask, equipped with a reflux condenser, and two dropping funnels, Mg (1.18 g, 48.6 mmol, activated with I_2 at 75 °C) was suspended in THF (distilled from Na). A solution of 1-bromo-3,5-dichloro-benzene (9.94 g, 44.0 mmol) in THF (20 mL) was slowly added to the Mg suspension, to keep the solution under reflux. After the reaction was complete, a solution of the ethylformiate (1.32 g, 17.8 mmol) in THF (20 mL) was added. After stirring for 2 h at room temperature, the solution was poured on a 0.5 M NH_4Cl solution (100 mL) and extracted with Et_2O (50 mL) and CH_2Cl_2 (3×75 mL). The combined organic phases were dried (MgSO_4), filtered, and the solvent was evaporated in the vacuum. Crystallization of the crude product from cold CH_2Cl_2 gave a colorless solid (2.00 g, 35 %); mp 131 °C. ^1H NMR (300 MHz, CDCl_3): δ = 2.40 (d, $^3J = 2$ Hz, 1 H, OH), 5.68 (d, $^3J = 2$ Hz, 1 H, CHOH), 7.23–7.30 (m, 6 H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3): δ = 74.1 (d, CHOH), 124.9 (d), 128.3 (d), 135.4 (s), 145.7 (s). Elemental analysis calcd (%) for $\text{C}_{13}\text{H}_8\text{Cl}_4\text{O}$ (322.02): C 48.49, H 2.50, Cl 44.04; found C 48.22, H 2.74, Cl 43.77.

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Substituted Benzhydryl Chlorides

General Procedure B (GP B).^[S4, S5, S6] The benzhydryl derivative was dissolved in either CH₂Cl₂ or benzene/petroleum in presence of anhydrous CaCl₂ and treated with a stream of dry hydrogen chloride gas. The conversion was monitored by either GC or TLC. After completion, the solvent and HCl were distilled off in the vacuum. Benzhydryl chloride was purified by distillation (b.p. 145-146 °C / 3-5mm). Solvolytic kinetic measurements of the samples before and after distillation in several solvents gave identical rate constants within the experimental error. Other liquid chlorides were used for the kinetic measurement without further purification^[S4] since the NMR spectra proved the absence of detectable impurities. The crude chlorides were either washed with small amounts of petroleum or crystallized from light petroleum/hexane.

General Procedure C (GP C). The substituted benzhydryl was dissolved in CH₂Cl₂ at 0 °C. Over a dropping funnel, a solution of SOCl₂ in CH₂Cl₂ was added to the well stirred solution. After 2 h, the solvent was evaporated in the vacuum and removing of the remaining SOCl₂ (60 °C/0.01 mbar) furnished the crude product.

4,4'-Dichlorobenzhydryl chloride (GP B). ¹H NMR (600 MHz, CDCl₃): δ = 6.08 (s, 1H, Ar₂CH), 7.34 (s, 8H, ArH). ¹³C NMR (150 MHz, CDCl₃): δ = 62.1 (Ar₂CH), 128.5, 133.7, 138.7 (Ar)

4-Chlorobenzhydryl chloride (GP B). ¹H NMR (300 MHz, CDCl₃): δ = 6.13 (s, 1H, Ar₂CH), 7.32-7.45 (m, 9H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 63.4 (Ar₂CH), 127.7-129.2, 134.0, 139.7, 140.6 (Ar)

Benzhydryl chloride (GP B). ¹H NMR (600 MHz, CDCl₃): δ = 6.20 (s, 1H, Ar₂CH), 7.30-7.49 (m, 10H, ArH).

4-Fluorobenzhydryl chloride (GP B). ¹H NMR (600 MHz, CDCl₃): δ = 6.11 (s, 1H, Ar₂CH), 7.02 (t, 2H, *J*_{HHF} = 17.3 Hz, ArH), 7.28-7.40 (m, 7H, ArH).

4-Methylbenzhydryl chloride (GP B). ¹H NMR (300 MHz, CDCl₃): δ = 2.32 (s, 3H, ArCH₃), 6.11 (s, 1H, Ar₂CH), 7.14 (d, 2H, *J* = 8 Hz, ArH), 7.27-7.42 (m, 7H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 21.0 (ArCH₃), 64.1 (Ar₂CH), 127.6-129.1, 137.8, 138.1, 141.0 (Ar)

4,4'-Dimethylbenzhydryl chloride (GP B). ¹H NMR (300 MHz, CDCl₃): δ = 2.32 (s, 6H, ArCH₃), 6.09 (s, 1H, Ar₂CH), 7.13 (d, 4H, *J* = 8 Hz, ArH), 7.29 (d, 4H, *J* = 8.2 Hz, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 21.0 (ArCH₃), 64.2 (Ar₂CH), 127.5, 129.1, 137.7, 138.2 (Ar)

4-Phenoxybenzhydryl chloride (GP B). ¹H NMR (300 MHz, CDCl₃): δ = 6.12 (s, 1H, Ar₂CH), 6.92-7.44 (m, 14H, ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 63.8, (Ar₂CH), 118.3, 119.1, 123.5, 127.6-129.7, 135.6, 140.8, (Ar) 156.5, 157.1 (-H₄C₅C-O-CC₃H₅).

4-Methoxybenzhydryl chloride (GP B). ¹H NMR (300 MHz, CDCl₃): δ = 3.76 (s, 3H, Ar-OCH₃), 6.11 (s, 1H, Ar₂CH), 6.86 (d, 2H, *J* = 9 Hz, ArH), 7.24-7.42 (m, 7H, ArH). ¹³C NMR (75 MHz,

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CDCl_3): $\delta = 55.1$ (Ar-O- CH_3), 64.1 (Ar $_2$ CH), 113.7, 127.5-129.0, 133.2, 141.1 (Ar), 159.2 (- $\text{H}_4\text{C}_5\text{C}-\text{OCH}_3$).

3-Chlorobenzhydryl chloride^[S7] (*GP C*) was obtained from a solution of the 3-chlorobenzhydryl (9.46 g, 43.3 mmol) in CH_2Cl_2 (75 mL) and a solution of SOCl_2 (7.14 g, 60.0 mmol) in CH_2Cl_2 (10 mL). The crude product was distilled in the vacuum (118-120 °C/ 2.0×10^{-5} mbar) to give a colorless oil (8.84 g, 86 %). ^1H NMR (300 MHz, CDCl_3): $\delta = 6.06$ (s, 1 H, CHCl), 7.25–7.41 (m, 9 H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 63.3$ (d, CHCl), 125.9 (d), 127.7 (2d), 127.9 (d), 128.2 (d), 128.3 (d), 128.7 (2d), 129.8 (d), 134.4 (s), 140.4 (s), 143.0 (s). Elemental analysis calcd. (%) for $\text{C}_{13}\text{H}_{10}\text{Cl}_2$ (237.13): C 65.85, H 4.25, Cl 29.90; found C 66.32, H 4.56, Cl 28.87.

3,4'-Dichlorobenzhydryl chloride^[S4] (*GP C*) was obtained from a solution of the 3,4'-dichlorobenzhydryl (2.55 g, 10.1 mmol) in 25 mL CH_2Cl_2 and a solution of SOCl_2 (4.76 g, 40.0 mmol) in CH_2Cl_2 (10 mL). The crude product was distilled in the vacuum (115-120 °C/ 2.0×10^{-5} mbar) to give a colorless oil (2.50 g, 91 %). ^1H NMR (300 MHz, CDCl_3): $\delta = 6.02$ (s, 1 H, CHCl), 7.24–7.38 (m, 8 H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 62.4$ (d, CHCl), 125.8 (d), 127.8 (d), 128.4 (d), 128.9 (d), 129.1 (d), 129.9 (d), 134.3 (s), 134.6 (s), 138.9 (s), 142.5 (s).

3,3'-Dichlorobenzhydryl chloride (*GP C*) was obtained from a solution of the 3,3'-dichlorobenzhydryl (11.9 g, 47.0 mmol) in CH_2Cl_2 (75 mL) and a solution of SOCl_2 (14.5 g, 122 mmol) in CH_2Cl_2 (25 mL). The crude product was purified by chromatography (silica gel, pentane/ $\text{Et}_2\text{O} = 100:1$, $R_f = 0.67$) and gave a colorless oil (8.53 g, 67 %). ^1H NMR (300 MHz, CDCl_3): $\delta = 5.99$ (s, 1 H, CHCl), 7.24–7.39 (m, 8 H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 62.3$ (d, CHCl), 125.8 (d), 127.8 (d), 128.5 (d), 129.9 (d), 134.6 (s), 142.3 (s).

3,3',5'-Trichlorobenzhydryl chloride (*GP C*) was obtained from a solution of the 3,3',5'-trichlorobenzhydryl (4.38 g, 15.2 mmol) in CH_2Cl_2 (25 mL) and a solution of SOCl_2 (18.9 g, 159 mmol) in CH_2Cl_2 (20 mL). The crude product was distilled in the vacuum (140-145 °C/ 2.3×10^{-5} mbar) to give a colorless oil (3.69 g, 79 %). ^1H NMR (300 MHz, CDCl_3): $\delta = 5.94$ (s, 1 H, CHCl), 7.24–7.37 (m, 7 H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 61.6$ (d, CHCl), 125.8 (d), 126.2 (d), 127.8 (d), 128.6 (d), 128.9 (d), 130.1 (d), 134.8 (s), 135.3 (s), 141.6 (s), 143.6 (s). Elemental analysis calcd (%) for $\text{C}_{13}\text{H}_8\text{Cl}_4$ (306.02): C 51.02, H 2.64, Cl 46.34; found C 51.15, H 2.70, Cl 45.81.

3,3',5,5'-Tetrachlorobenzhydryl chloride (*GP C*) was obtained from a solution of the 3,3',5,5'-tetrachlorobenzhydryl (1.09 g, 3.38 mmol) in CH_2Cl_2 (20 mL), and a solution of SOCl_2 (2.38 g, 20.0 mmol) in CH_2Cl_2 (10 mL). After heating for 6 h, the solution was washed with ice/water (2×15 mL), dried (MgSO_4), and filtered. After evaporating the solvent, crystallization from Et_2O gave the product as a pale red solid (0.73 g, 63 %). ^1H NMR (300 MHz, CDCl_3): $\delta = 5.89$ (s, 1 H, CHCl), 7.25 (d, $J = 1.8$ Hz, 4 H), 7.33 (t, $J = 1.8$ Hz, 2 H); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 60.8$ (d, CHCl), 126.2 (d), 128.9 (d), 135.5 (s), 142.3 (s).

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Synthesis of Substituted Benzhydryl Bromides

General Procedure D (GP D). A solution of the benzhydryl derivative in dry CH_2Cl_2 was treated by a stream of dry hydrogen bromide gas in a presence of anhydrous Na_2SO_4 . The conversion was monitored by either GC or TLC. After completion of the conversion, the solvent and the excess of the hydrogen bromide were removed under vacuum. Crude benzhydryl bromides were crystallized from either light petroleum or hexane. The liquid benzhydryl bromides were used without further purification since the NMR spectra proved the absence of detectable impurities.

General Procedure E (GP E). The substituted benzhydryl was dissolved in CH_2Cl_2 at 0 °C. Over a dropping funnel a solution of PBr_3 in CH_2Cl_2 , was added to the well stirred solution. The solvent was evaporated in the vacuum, and removing of the remaining PBr_3 (60 °C/0.01 mbar) gave the crude product.

4,4'-Dichlorobenzhydryl bromide (GP D). ^1H NMR (300 MHz, CDCl_3): δ = 6.20 (s, 1H, Ar_2CH), 7.29-7.37 (m, 8H, ArH). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 53.0 (Ar_2CH), 128.7, 129.6, 134.1, 139.0 (Ar)

4-Chlorobenzhydryl bromide (GP D). ^1H NMR (300 MHz, CDCl_3): δ = 6.23 (s, 1H, Ar_2CH), 7.22-7.44 (m, 9H, ArH). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 54.1 (Ar_2CH), 128.2-129.7, 133.8, 139.5, 140.4 (Ar).

Benzhydryl bromide (GP D). ^1H NMR (300 MHz, CDCl_3): δ = 6.28 (s, 1H, Ar_2CH), 7.23-7.47 (m, 10H, ArH). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 55.3 (Ar_2CH), 128.3, 140.9 (Ar)

4-Fluorobenzhydryl bromide (GP D). ^1H NMR (300 MHz, CDCl_3): δ = 6.26 (s, 1H, Ar_2CH), 7.00 (t, 2H, J_{HHF} = 17.3 Hz, ArH), 7.25-7.51 (m, 7H, ArH). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 54.3 (Ar_2CH), 115.3, 128.2, 136.9, 140.7 (Ar), 161.8 (d, J_{CF} = 248 Hz, $-\text{H}_4\text{C}_5\text{C}-\text{F}$)

4-Methylbenzhydryl bromide (GP D). ^1H NMR (300 MHz, CDCl_3): δ = 2.32 (s, 3H, Me), 6.27 (s, 1H, Ar_2CH), 7.13 (d, 2H, J = 8 Hz, ArH), 7.20-7.47 (m, 7H, ArH). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 21.0 (Me), 55.4 (Ar_2CH), 128.3, 129.1, 137.8, 138.1, 141.0 (Ar)

4,4'-Dimethylbenzhydryl bromide (GP D). ^1H NMR (300 MHz, CDCl_3): δ = 2.39 (s, 6H, 2 × Me), 6.32 (s, 1H, Ar_2CH), 7.15-7.41 (m, 8H, ArH).

3-Chlorobenzhydryl bromide^[S8] (GP E) was obtained from a solution of the 3-chlorobenzhydryl (4.66 g, 21.3 mmol) in CH_2Cl_2 (60 mL) and a solution of PBr_3 (6.77 g, 25.0 mmol) in CH_2Cl_2 (15 mL). After 46 h at room temp., the solution was poured on ice/water (40 mL), extracted with CH_2Cl_2 (2 × 30 mL), dried (MgSO_4), filtered, and the solvent was evaporated. The product remained as a colorless oil (5.80 g, 97 %). ^1H NMR (300 MHz, CDCl_3): δ = 6.17 (s, 1 H, CHBr), 7.19–7.44 (m, 9 H, Ar); ^{13}C NMR (75.5 MHz, CDCl_3): δ = 53.9 (d, CHBr), 126.6 (d), 128.2 (d), 128.3 (d), 128.5 (d), 128.6 (d),

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129.7 (d), 134.3 (s), 140.3 (s), 143.0 (s). Elemental analysis calcd (%) for $C_{13}H_{10}BrCl$ (281.58): C 55.45, H 3.58; found C 55.24, H 3.60.

3,4'-Dichlorobenzhydryl bromide (*GP E*) was obtained from a solution of the 3,4'-dichlorobenzhydryl (3.62 g, 14.3 mmol) in CH_2Cl_2 (30 mL) and a solution of PBr_3 (4.20 g, 15.5 mmol) in CH_2Cl_2 (15 mL). After 8 h at room temp., the solvent was evaporated. The crude product was distilled in the vacuum (158–162 °C/ 3.1×10^{-5} mbar) to give a colorless oil (3.17 g, 70 %). 1H NMR (300 MHz, $CDCl_3$): δ = 6.15 (s, 1 H, *CHBr*), 7.25–7.42 (m, 8 H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 52.8 (d, *CHBr*), 126.5 (d), 128.4 (d), 128.5 (d), 128.9 (d), 129.7 (d), 129.9 (d), 134.3 (s), 134.5 (s), 139.0 (s), 142.5 (s). Elemental analysis calcd (%) for $C_{13}H_9BrCl_2$ (316.03): C 49.41, H 2.87; found C 49.64, H 2.43.

3,3'-Dichlorobenzhydryl bromide (*GP E*) was obtained from a solution of the 3,3'-dichlorobenzhydryl (5.08 g, 20.1 mmol) in CH_2Cl_2 (50 mL) and a solution of PBr_3 (2.20 mL, 23.4 mmol) in CH_2Cl_2 (20 mL). After 2 h at room temp., the solution was poured into brine/ice, dried, and filtered. After the solvent was evaporated, the product remained as a colorless oil (6.02 g, 95 %). 1H NMR (300 MHz, $CDCl_3$): δ = 6.12 (s, 1 H, *CHBr*), 7.26–7.42 (m, 8 H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 52.6 (d, *CHBr*), 126.5 (d), 128.50 (d), 128.52 (d), 129.9 (d), 134.6 (s), 142.3 (s). Elemental analysis calcd (%) for $C_{13}H_9BrCl_2$ (316.03): C 49.41, H 2.87; found C 49.66, H 2.89.

3,3',5'-Trichlorobenzhydryl bromide (*GP E*) was obtained from a solution of the 3,3',5'-trichlorobenzhydryl (4.06 g, 14.1 mmol) in CH_2Cl_2 (25 mL) and a solution of PBr_3 (3.86 g, 14.3 mmol) in CH_2Cl_2 (20 mL). The crude product was distilled in the vacuum (198–202 °C/ 5×10^{-6} mbar) to give a colorless oil (3.08 g, 62 %). 1H NMR (300 MHz, $CDCl_3$): δ = 6.05 (s, 1 H, *CHBr*), 7.25–7.40 (m, 7 H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 51.5 (d, *CHBr*), 126.5 (d), 126.9 (d), 127.4 (d), 128.4 (d), 128.5 (d), 128.8 (d), 130.1 (s), 134.8 (s), 135.3 (s), 141.6 (s), 143.6 (s). Elemental analysis calcd (%) for $C_{13}H_8BrCl_3$ (350.47): C 44.55, H 2.30; found C 44.77, H 2.55.

3,3',5,5'-Tetrachlorobenzhydryl bromide (*GP E*) was obtained from a solution of the 3,3',5,5'-tetrachlorobenzhydryl (0.91 g, 2.8 mmol) in CH_2Cl_2 (20 mL) and a solution of PBr_3 (0.92 g, 3.40 mmol) in CH_2Cl_2 (10 mL). After heating for 6 h, the solution was washed with ice/water (2×15 mL), dried ($MgSO_4$), and filtered. After evaporating the solvent, crystallization from Et_2O delivered the product as a white solid (0.89 g, 83 %); mp 101–102 °C. 1H NMR (300 MHz, $CDCl_3$): δ = 5.91 (s, 1 H, *CHBr*), 7.18–7.25 (m, 6 H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 50.4 (d, *CHBr*), 126.8 (d), 128.8 (d), 135.5 (s), 142.9 (s). Elemental analysis calcd (%) for $C_{13}H_7BrCl_4$ (384.92): C 40.57, H 1.83; found C 40.58, H 1.74.

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Substituted Benzhydryl *p*-Tosylates

General Procedure F (GP F).^[S9] Under an atmosphere of dry N₂, silver *p*-tolylsulfonate (AgOTs, 1.40 g, 5.02 mmol) was added to a well stirred solution of the substituted benzhydryl chloride (for preparation, see below) in Et₂O (20 mL). After several hours of heating, the reaction-mixture was filtered. Partial removal of the solvent led to the precipitation of the product.

3-Chlorobenzhydryl *p*-tosylate (GP F) was obtained from 3-chlorobenzhydryl chloride (0.24 g, 1.01 mmol) in Et₂O (20 mL) and AgOTs. Filtration and removal of the solvent gave a solid crude product. Crystallization from Et₂O gave a colorless solid (0.14 g, 37 %). ¹H NMR (200 MHz, C₆D₆): δ = 1.81 (s, 3 H, CH₃), 6.55 (s, 1 H, CHOTs), 6.59–7.20 (m, 11 H, Ar), 7.59 (d, ³J = 8.2 Hz, 2 H, 3,5-CH-Tol).

3,4'-Dichlorobenzhydryl *p*-tosylate (GP F) was obtained from 3,4'-dichlorobenzhydryl chloride (0.34 g, 1.25 mmol) and AgOTs. After filtration and removal of the solvent, the crude product precipitated. Crystallization from Et₂O to yield a colorless solid (0.17 g, 30 %). ¹H NMR (200 MHz, C₆D₆): δ = 1.89 (s, 3 H, CH₃), 6.46 (s, 1 H, CHOTs), 6.61–7.27 (m, 10 H, Ar), 7.62 (d, ³J = 8.1 Hz, 2 H, 3,5-CH-Tol).

3,3'-Dichlorobenzhydryl *p*-tosylate (GP F) was obtained from 3,3'-dichlorobenzhydryl chloride (0.26 g, 0.96 mmol) and AgOTs. After filtration and removal of the solvent, the crude product precipitated. The product was crystallized from Et₂O to yield a colorless solid (0.14 g, 36 %). ¹H NMR (300 MHz, C₆D₆): δ = 1.90 (s, 3 H, CH₃), 6.43 (s, 1 H, Ar₂CH), 6.61–7.37 (m, 10 H, Ar), 7.62 (d, ³J = 8.1 Hz, 2 H, 3,5-CH-Tol).

3,3',5'-Trichlorobenzhydryl *p*-tosylate. At –78 °C, n-BuLi (8.0 mL of a 1.6 M solution in hexane) was slowly added to a solution of 3,3',5'-trichlorobenzhydryl chloride (3.70 g, 12.9 mmol) in THF (40 mL, dried over Na). After 10 min, a solution of *p*-tosyl chloride (2.45 g, 12.9 mmol) in THF (15 mL) was added. After the reaction mixture had warmed to room temp., the solvent was evaporated, the precipitated LiCl was filtered off, and the crude product was recrystallized from Et₂O to give colorless crystals (2.23 g, 39 %). ¹H NMR (600 MHz, CDCl₃): δ = 2.39 (s, 3 H, CH₃), 6.33 (s, 1 H, CHOTs), 7.03–7.24 (m, 7 H, Ar), 7.60 (d, ³J = 8.1 Hz, 2 H, 3,5-CH-Tol); ¹³C NMR (150.8 MHz, CDCl₃): δ = 21.6 (q, CH₃), 81.8 (s, CHOTs), 125.3 (d), 125.5 (d), 127.2 (d), 127.8 (d), 128.7 (d), 129.1 (d), 129.6 (d), 130.0 (d), 133.5 (s), 134.7 (s), 135.3 (s), 138.9 (s), 140.9 (s), 145.2 (s). Elemental analysis calcd (%) for C₂₀H₁₅Cl₃O₃S (441.76): C 54.38, H 3.42; found C 53.90, H 3.64.

3,3',5,5'-Tetrachlorobenzhydryl *p*-tosylate (GP F) was obtained from 3,3',5,5'-tetrachlorobenzhydryl chloride (0.34 g, 1.00 mmol) and silver tosylate (1.40 g, 5.02 mmol). After filtration and removal of the solvent, the crude product precipitated. Crystallization from Et₂O yielded a white solid (0.34 g, 71 %). ¹H NMR (300 MHz, C₆D₆): δ = 1.90 (s, 3 H, CH₃), 6.19 (s, 1 H, CHOTs), 6.64 (d, ³J = 8.1 Hz, 2 H, 2,6-CH), 6.93 (s, 5 H, Ar), 7.05 (s, 1 H, Ar), 7.53 (d, ³J = 8.1 Hz, 2 H, 3,5-CH-Tol); ¹³C NMR (75.5 MHz, C₆D₆): δ = 21.1 (q, CH₃), 80.8 (s, CHOTs), 125.1 (d), 125.6 (d), 129.2 (d), 129.6 (d), 135.7 (s), 140.9 (s), 144.9 (s), 146.4 (s).

Substituted Benzhydryl Trifluoroacetates

Trifluoroacetates were prepared according to the procedure by Bunton and Hadwick^[S10] with some adjustments.

Benzhydryl trifluoroacetate. A dry diethyl ether solution (30 mL) of benzhydrol (2.00 g, 10.9 mmol) and trifluoroacetic anhydride (3.30 g, 15.7 mmol) was stirred under Ar atmosphere and cooling with an ice bath for 24 h. Then the reaction mixture was left at ambient temperature for 2 h. The solution was vigorously washed with aqueous NaHCO₃. After drying and evaporating the solvent under vacuum, 2.30 g (5.85 mmol, 54%) of a pale yellow oil remained. According to the NMR spectra the product did not contain the free acid, the parent alcohol nor any other detectable impurity. Conductivity measurements proved the absence of acid impurities. Distillation under reduced pressure (7 Torr) failed because of decomposition of the trifluoroacetate (lit.^(S6): bp 93 °C / 2.5 Torr). ¹H NMR (300 MHz, CDCl₃): δ = 7.05 (s, 1H, Ar₂CH), 7.41 (s, 10H, ArH). ¹³C NMR (75.5 MHz, CDCl₃): δ = 81.0 (Ar₂CH), 127.1, 128.8, 137.9 (Ar).

4-Fluorobenzhydryl trifluoroacetate was obtained from 4-fluorobenzhydrol (2.00 g, 9.90 mmol) and trifluoroacetic anhydride (2.70 g, 12.9 mmol) by following the procedure used for preparation of benzhydryl trifluoroacetate: 2.10 g (5.11 mmol, 52%). ¹H NMR (300 MHz, CDCl₃): δ = 6.97 (s, 1H, Ar₂CH), 7.05 (t, 2H, *J*_{H,F} = 17.2 Hz, ArH), 7.23-7.41 (m, 7H, ArH).

4-Methylbenzhydryl trifluoroacetate was obtained from 4-methylbenzhydrol (1.50 g, 7.58 mmol) and trifluoroacetic anhydride (1.70 g, 8.10 mmol) by following the procedure used for preparation of benzhydryl trifluoroacetate: 1.40 g (3.44 mmol, 45%). ¹H NMR (300 MHz, CDCl₃): δ = 2.34 (s, 3H, Me), 6.97 (s, 1H, Ar₂CH), 7.11–7.38 (m, 9H, ArH). ¹³C NMR (75.5 MHz, CDCl₃): δ = 21.0 (ArCH₃), 80.9 (Ar₂CH), 126.8, 127.0, 128.7, 129.4, 134.8, 137.9, 138.7 (Ar)

4,4'-Dimethylbenzhydryl trifluoroacetate was obtained from 4,4'-dimethylbenzhydrol (2.00 g, 9.43mmol), and trifluoroacetic anhydride (2.00 g, 9.53 mmol) by following the procedure used for preparation of benzhydryl trifluoroacetate. After removal of the solvent under reduced pressure, the crude product was washed with small amounts of hexane: 1.38 g (5.73 mmol, 61%). ¹H NMR (300 MHz, CDCl₃): δ = 2.30 (s, 6H, 2 × Me), 6.94 (s, 1H, Ar₂CH), 7.16 (d, 4H, *J* = 8 Hz, ArH), 7.24 (d, 4H, *J* = 8 Hz, ArH). ¹³C NMR (75.5 MHz, CDCl₃): δ = 21.0 (Me), 80.9 (Ar₂CH), 126.9, 129.3, 134.9, 138.5 (Ar)

4-Methoxybenzhydryl trifluoroacetate. 4-Methoxybenzhydryl trifluoroacetate was obtained from 4-methoxybenzhydrol and trifluoroacetic anhydride dissolved in CH₂Cl₂. This ester was not isolated because it decomposed during removal of the solvent. It was stable, however, in CH₂Cl₂ even after washing with aqueous NaHCO₃. For the kinetic measurements, samples were taken directly from the CH₂Cl₂ solution after washing with NaHCO₃ and drying with Na₂SO₄. Conductivity of the kinetic solutions after injection of the sample proved the absence of acid impurities, and kinetic curves for the both 90% aqueous acetone, and 100% ethanol followed first-order kinetics.

Substituted Benzhydryl 3,5-Dinitrobenzoates

The procedures described below are the variants of the approach used by Rappoport and coworkers for the synthesis of benzhydryl 3,5-dinitrobenzoate.^[S11]

4,4'-Dimethoxybenzhydryl 3,5-dinitrobenzoate. A solution of 4,4'-dimethoxybenzhydrol (1.50 g, 6.15 mmol), 3,5-nitrobenzoyl chloride (1.64 g, 7.11 mmol), and pyridine (1.17 g, 14.80 mmol) in benzene (100 mL) was stirred under Ar atmosphere at ambient temperature for 15 h. Precipitated pyridinium chloride was removed by filtration. The excess of pyridine was removed by 5% hydrochloric acid, after which the benzene solution was successively washed with aqueous NaHCO₃ and water. The solution was dried, benzene was evaporated in the vacuum, and the remaining residue was recrystallized from light petroleum to give 1.65 g (3.47 mmol, 56%) of pale yellow crystals. ¹H NMR (300 MHz, CDCl₃): δ = 3.84 (s, 6H, OMe), 6.87-6.96 (m, 4H, ArH), 7.18 (s, 1H, Ar₂CH), 7.27-7.40 (m, 4H, ArH), 9.22 (s, 3H, (O₂N)₂-ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 55.2 (OMe), 79.2 (Ar₂CH), 114.0 (Ar), 122.9 (Ar-NO₂), 128.6 (Ar), 129.3, 131.0 (Ar-NO₂), 134.0 (Ar), 148.6 (Ar-NO₂), 159.6 (Ar), 161.7 (C=O).

4-Methoxy-4'-phenoxybenzhydryl 3,5-dinitrobenzoate. A solution of 4-methoxy-4'-phenoxybenzhydrol (1.30 g, 4.22 mmol), 3,5-nitrobenzoyl chloride (1.20 g, 5.21 mmol), and pyridine (0.90 g, 11.4 mmol) in benzene (100 mL) was stirred under Ar atmosphere at ambient temperature for 15 h. Precipitated pyridinium chloride was removed by filtration. The excess of pyridine was removed by 5% hydrochloric acid, after which the benzene solution was successively washed with aqueous NaHCO₃ and water. The solution was dried, benzene was evaporated in the vacuum, and the remaining residue was recrystallized from diethyl ether to yield 1.20 g (2.23 mmol, 53%) of pale yellow crystals. ¹H NMR (300 MHz, CDCl₃): δ = 3.81 (s, 3H, OMe), 6.85-7.43 (m, 14H, ArH + Ar₂CH + Ar-OC₆H₅), 9.20 (s, 3H, (O₂N)₂-ArH). ¹³C NMR (150 MHz, CDCl₃): δ = 55.2 (ArOCH₃), 79.0 (Ar₂CH), 114.1, 118.5, 119.2, 122.4 (Ar), 123.7 (Ar-NO₂), 128.6, 129.3 (Ar), 129.7, 130.8 (Ar-NO₂), 133.5, 134.0 (Ar), 148.6 (Ar-NO₂), 156.5, 157.6, 159.7 (Ar), 161.7 (C=O).

4-Methoxy-4'-methylbenzhydryl 3,5-dinitrobenzoate. A solution of 4-methoxy-4'-methylbenzhydrol (1.30 g, 5.70 mmol), 3,5-nitrobenzoyl chloride (1.80 g, 7.81 mmol), and pyridine (1.20 g, 15.19 mmol) in benzene (100 mL) was stirred under Ar atmosphere at ambient temperature for 15 h. Precipitated pyridinium chloride was removed by filtration. The excess of pyridine was removed by 5% hydrochloric acid, after which the benzene solution was successively washed with aqueous NaHCO₃ and water. The solution was dried, benzene was evaporated in the vacuum, and the remaining residue was recrystallized from diethyl ether yielding 1.20 g (2.95 mmol, 52%) of pale yellow crystals. ¹H NMR (300 MHz, CDCl₃): δ = 2.38 (s, 3H, Me), 3.82 (s, 3H, OMe), 6.93 (d, 2H, *J* = 9 Hz, ArH), 7.17 (s, 1H, Ar₂CH), 7.21-7.39 (m, 6H, ArH + Ar₂CH), 9.22 (s, 3H, (O₂N)₂-ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 21.2 (Me), 55.3 (OMe), 79.4 (Ar₂CH), 114.1 (Ar), 122.5 (Ar-NO₂),

127.0, 128.9 (Ar), 129.5 (Ar, Ar-NO₂), 131.1 (Ar-NO₂), 134.1, 136.1, 138.4 (Ar), 148.7 (Ar-NO₂), 159.7 (Ar), 161.8 (C=O).

4-Methoxybenzhydryl 3,5-dinitrobenzoate. A solution of 4-methoxybenzhydryl (1.00 g, 4.67 mmol), 3,5-nitrobenzoyl chloride (1.43 g, 6.20 mmol), and pyridine (1.13 g, 14.3 mmol) in dry CH₂Cl₂ (80 mL) was stirred under Ar atmosphere at ambient temperature for 15 h. The excess of pyridine was removed by 5% hydrochloric acid, after which the organic solution was washed with aqueous NaHCO₃ and water. The solution was dried, CH₂Cl₂ was distilled off under vacuum. Pale green crystals (0.60 g, 1.35 mmol, 30%) appeared after removing diethyl ether in vacuum. Recrystallization failed from all common organic solvents. According to NMR, impurities were not presented in the product. ¹H NMR (600 MHz, CDCl₃): δ = 3.80 (s, 3H, OMe), 6.91 (d, 2H, *J* = 8.8 Hz, ArH), 7.18 (s, 1H, Ar₂CH), 7.35-7.44 (m, 7H, ArH), 9.20 (s, 3H, (O₂N)₂-ArH). ¹³C NMR (75.5 MHz, CDCl₃): δ = 55.2 (OMe), 79.3(Ar₂CH), 114.1 (Ar), 122.4 (Ar-NO₂), 126.8, 128.3, 128.7, 128.9(Ar), 129.4, 130.8 (Ar-NO₂), 133.9, 138.9 (Ar), 148.6 (Ar-NO₂), 159.7 (Ar), 161.6 (C=O).

4,4'-Dimethylbenzhydryl 3,5-dinitrobenzoate. A solution of 4,4'-dimethylbenzhydryl (1.50 g, 7.08 mmol), 3,5-nitrobenzoyl chloride (2.00 g, 8.68 mmol), and pyridine (1.34 g, 17.0 mmol) in benzene (50 mL) was stirred under Ar atmosphere at ambient temperature for 15 h. Precipitated pyridinium chloride was removed by filtration. The excess of pyridine was removed by 5% hydrochloric acid, after which the benzene solution was successively washed with aqueous NaHCO₃ and water. The solution was dried, benzene was evaporated in the vacuum, and the remaining residue was recrystallized from light petroleum yielding 2.20 g (4.98 mmol, 70%) of pale yellow crystals. ¹H NMR (600 MHz, CDCl₃): δ = 2.35 (s, 6H, Me), 7.14 (s, 1H, Ar₂CH), 7.19 (d, 4H, *J* = 8 Hz, ArH), 7.32 (d, 4H, *J* = 8 Hz, ArH), 9.20 (s, 3H, (O₂N)₂-ArH). ¹³C NMR (75.5 MHz, CDCl₃): δ = 21.0 (Me), 79.5 (Ar₂CH), 122.3 (Ar-NO₂), 127.0 (Ar), 129.3 (Ar, Ar-NO₂), 134.0 (Ar-NO₂), 136.0, 138.3 (Ar), 148.6 (Ar-NO₂), 161.6(C=O).

Substituted Benzhydryl 4-Nitrobenzoates

The procedures described below are the variants of the approach used by Fox and Kohnstam for the synthesis of benzhydryl 4-nitrobenzoate.^[S12]

4,4'-Dimethoxybenzhydryl 4-nitrobenzoate. A solution of 4,4'-dimethoxybenzhydrol (1.00 g, 4.10 mmol), 4-nitrobenzoyl chloride (0.82 g, 4.42 mmol), and pyridine (0.72 g, 9.11 mmol) in dry benzene (20 mL) was heated under reflux for 30 min. After cooling (3 h), the crude pyridinium chloride was removed by filtration while the excess of pyridine was removed by 5% hydrochloric acid. The benzene solution was successively washed with aqueous NaHCO₃ and water. After drying, and removal of benzene in the vacuum, the resulting residue was recrystallized from light petroleum yielding 0.86 g (2.00 mmol, 49 %) of pale green-yellow crystals. ¹H NMR (300 MHz, CDCl₃): δ = 3.79 (s, 6H, Ar-OCH₃), 6.83–6.91 (m, 4H, ArH), 7.08 (s, 1H, Ar₂CH), 7.23–7.35 (m, 4H, ArH), 8.27 (s, 4H, O₂N-ArH). ¹³C NMR (150 MHz, CDCl₃): δ = 55.2 (ArOCH₃), 77.9 (Ar₂CH), 113.9 (Ar), 123.4 (Ar-NO₂), 128.4 (Ar), 130.7, 131.8 (Ar-NO₂), 134.7 (Ar), 150.5 (Ar-NO₂), 159.3 (Ar), 163.7 (C=O).

4-Methoxy-4'-phenoxybenzhydryl 4-nitrobenzoate. A solution of 4-methoxy-4'-phenoxybenzhydrol (1.50 g, 4.87 mmol), 4-nitrobenzoyl chloride (0.92 g, 4.96 mmol), and pyridine (0.60 g, 7.59 mmol) in benzene (100 mL) was stirred under an argon atmosphere at room temperature for 48 h. Precipitated pyridinium chloride was removed from the solution several times by filtration. The excess of pyridine was removed by 5% hydrochloric acid, after which the benzene solution was washed with aqueous NaHCO₃ and water. The solution was dried, benzene was removed in the vacuum, and the remaining residue was recrystallized from dry diethyl ether to afford 0.60 g (1.31 mmol, 27%) of pale green-yellow crystals. ¹H NMR (600 MHz, CDCl₃): δ = 3.76 (s, 3H, OMe), 6.87–7.34 (m, 14H, ArH + Ar₂CH + Ar-OC₆H₅), 8.25 (s, 4H, O₂N-ArH). ¹³C NMR (150 MHz, CDCl₃): δ = 54.8 (OMe), 77.4 (Ar₂CH), 113.6, 118.1, 118.8, (Ar), 123.1 (Ar-NO₂), 128.1, 129.3 (Ar), 130.4, 131.2 (Ar-NO₂), 133.9, 135.2 (Ar), 150.2 (Ar-NO₂), 156.9, 159.1 (Ar), 163.3 (C=O).

4-Methoxy-4'-methylbenzhydryl 4-nitrobenzoate. A solution of 4-methoxy-4'-methylbenzhydrol (2.60 g, 11.4 mmol), 4-nitrobenzoyl chloride (2.30 g, 12.4 mmol), and pyridine (1.30g, 16.5 mmol) in benzene (120 mL) was stirred at room temperature for 20 h. During the reaction, precipitated pyridinium chloride was removed from the solution several times by filtration. The excess of pyridine was removed by 5% hydrochloric acid, after which the benzene solution was washed with aqueous NaHCO₃, and water. The solution was dried, benzene was removed under vacuum, and the remaining residue was recrystallized from light petroleum affording 3.10 g (8.20 mmol, 72%) of pale green-yellow crystals. ¹H NMR (600 MHz, CDCl₃): δ = 2.30 (s, 3H, Me), 3.75 (s, 3H, OMe), 6.85 (d, 2H, *J* = 8.7 Hz, ArH), 7.04 (s, 1H, Ar₂CH), 7.14 (d, 2H, *J* = 7.9 Hz, ArH), 7.26 (d, 2H, *J* = 8 Hz, ArH), 7.31 (d, 2H, *J* = 8.6 Hz, ArH), 8.24 (s, 4H, O₂N-ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 20.7 (Me), 54.8 (OMe), 77.8(Ar₂CH), 113.6 (Ar), 123.1 (Ar-NO₂), 126.5, 128.2, 128.8 (Ar), 130.4, 131.4 (Ar-NO₂), 135.3, 136.4, 137.5 (Ar), 150.1 (Ar-NO₂), 159.0 (Ar), 163.3 (C=O).

4-Methoxybenzhydryl 4-nitrobenzoate was prepared in 56% yield (0.95g, 2.61 mmol) from 4-methoxybenzhydrol (1 g, 4.67 mmol), 4-nitrobenzoyl chloride (0.87 g, 4.69 mmol), and pyridine (0.74g, 9.37 mmol) by the same procedure used for 4,4'-dimethoxybenzhydryl 4-nitrobenzoate. ¹H NMR (300 MHz, CDCl₃): δ = 3.79 (s, 3H, OMe), 6.90 (d, 2H, *J* = 8 Hz, ArH), 7.11 (s, 1H, Ar₂CH), 7.25-7.43 (m, 7H, ArH), 8.29 (s, 4H, O₂N-ArH). ¹³C NMR (75 MHz, CDCl₃): δ = 55.2 (OMe), 78.2(Ar₂CH), 113.9 (Ar), 123.5 (Ar-NO₂), 126.8, 128.0, 128.7 (Ar), 130.7, 131.6 (Ar-NO₂), 135.6, 139.7 (Ar), 150.5 (Ar-NO₂), 159.5 (Ar), 163.7 (C=O).

Kinetics of Solvolysis Reactions

Solvolysis rates of benzhydrylium derivatives (Tables 1 and S1) were monitored by following the increase of the conductivity of the reaction mixtures (conductimeters: WTW LF530 or Tacussel CD 810, Pt electrode: WTW LTA 1/NS).^[S13] Freshly prepared solvents (30 mL) were thermostated (± 0.1 °C) at the given temperature for 5 min prior to adding the substrate. Typically, 20 to 70 mg of substrate was dissolved in 100-150 μL of CH_2Cl_2 and injected into the solvent, and the conductance (G) was recorded at given time intervals.

The first order rate constants k (s^{-1}) were obtained by least squares fitting of the conductance data to a single-exponential equation $G_t = G_0 \exp(-kt) + C$. Each rate constant was averaged from at least three kinetic runs.

Most solvolyses were performed at 25 °C. Slower kinetics were followed at three or more different higher temperatures, and the rate constants were extrapolated to 25 °C. Faster kinetics were followed at lower temperatures.

Calibrations showed linear relationships between conductance and the concentrations of liberated HCl, HBr, TsOH. In the case of 4-nitrobenzoate, 3,5-dinitrobenzoate, and trifluoroacetate appropriate base, which ionized liberated acid well enough to give linear response between conductance and concentration of the ions, was added to the kinetic mixture. 2,6-Lutidine was employed for ionizing trifluoroacetic acid in 90A10W, 80A20W, E, 80E20W, and 3,5-dinitrobenzoic acid in 80E20W. Triethylamine was employed for ionizing 4-nitrobenzoic acid in 80E. Proton sponge [= 1,8-bis-(dimethylamino)-naphthalene] was used for ionizing 3,5-dinitrobenzoic acid in 90A10W, 80A20W, and E. Measuring the standard chlorides from the literature showed that the solvent ionizing power was not affected by added base.

Solvents were purified and dried according to the standard procedures.

Table S1. Solvolysis rate constants k_s of X,Y-substituted benzhydryl derivatives in different solvents^[a] (25 °C).

solvent	leaving group	X, Y substituents	k_s [s ⁻¹]	used in correl.	ref. short cuts ^[b]
90A10W	TsO	H	3.01×10^{-1}	☑	–
		3-Cl, 4'-Cl	2.60×10^{-3}	☑	–
		3-Cl, 3'-Cl	2.05×10^{-4}	☑	–
90A10W	Br	4-Me, 4'-Me	6.24×10^{-2}	☑	–
		4-OPh	6.86×10^{-2}	☑	–
		4-Me	4.08×10^{-3}	☑	–
			6.28×10^{-4}	☒	[Kee62]
		4-F	3.60×10^{-4}	☑	–
		H	1.87×10^{-4}	☑	–
			1.88×10^{-4}	☒	[Liu97]
			1.8×10^{-4}	☒	[Swa53]
			1.64×10^{-4}	☒	[Kee62]
	4-Cl	6.45×10^{-5}	☑	–	
90A10W	Cl	4-Me, 4'-Me	1.83×10^{-3}	☑	–
			1.43×10^{-3}	☒	[Ber68]
		4-Me	1.11×10^{-4}	☑	–
			1.15×10^{-4}	☒	[Ber64]
			1.12×10^{-4}	☒	[Ber68]
			9.47×10^{-5}	☒	[Liu98]
			9.46×10^{-5}	☒	[Ing40b]
		4-F	9.78×10^{-6}	☑	–
		H	5.07×10^{-6}	☑	[Ber68]
			5.54×10^{-6}	☒	[Ber64]
	4.60×10^{-6}	☒	[Ing40b]		
	4.40×10^{-6}	☒	[Liu98]		
90A10W	CF ₃ CO ₂	4-OMe	1.44×10^{-2}	☑	–
		4-Me, 4'-Me	7.97×10^{-4}	☑	–
		4-Me	4.95×10^{-5}	☑	–
90A10W	DNB	4-OMe, 4'-OMe	9.42×10^{-4} ^[c]	☑	–
		4-OMe, 4'-OPh	1.01×10^{-4} ^[c]	☑	–
		4-OMe, 4'-Me	2.87×10^{-5} ^[c]	☑	–
80A20W	TsO	3-Cl, 4'-Cl	1.41×10^{-2}	☑	–
		3-Cl, 3'-Cl	1.07×10^{-3}	☑	–
		3,5-(Cl) ₂ , 3'-Cl	4.05×10^{-5}	☑	–
80A20W	Br	4-OPh	2.59×10^{-1}	☑	[Min72]
		4-Me	4.54×10^{-2}	☑	–
			4.81×10^{-2}	☒	[Min72]
		3,5-(Me) ₂	8.99×10^{-3}	☑	[Min73]
		4-OPh, 4'-NO ₂	5.19×10^{-3}	☑	[Liu02]
		4-F	3.71×10^{-3}	☑	–
			5.21×10^{-3}	☒	[Min72]
		3-Me	4.08×10^{-3}	☑	[Min72]

Table S1 (continued).

solvent	leaving group	X, Y substituents	k_s [s ⁻¹]	used in correl.	ref. short cuts ^[b]			
80A20W	Br	H	2.03×10^{-3}	☑	–			
			2.00×10^{-3}	☒	[Min72]			
			1.91×10^{-3}	☒	[Liu97]			
			1.53×10^{-3}	☒	[Ing52]			
		4-Cl	6.81×10^{-4}	☑	–			
			6.74×10^{-4}	☒	[Min72]			
			4-Br	4.60×10^{-4}	☑	[Min72]		
			4-Cl, 4'-Cl	2.72×10^{-4}	☑	–		
			3-Cl	4.42×10^{-5}	☑	[Min72]		
			4-NO ₂	3.33×10^{-6}	☑	[Kee64]		
80A20W	Cl	4-Me, 4'-Me	2.79×10^{-2}	☑	–			
			4-OPh	2.64×10^{-2}	☑	–		
			4-Me	1.76×10^{-3}	☑	–		
		4-Me	1.64×10^{-3}	☒	[Liu98]			
			1.60×10^{-3}	☒	[Ing40b], [Arn50]			
			1.57×10^{-3}	☒	[Sch60], [Har73]			
			1.56×10^{-3}	☒	[Ing40a]			
			3,5-(Me) ₂	2.25×10^{-4}	☑	[Sch60]		
			4-OPh, 4'-NO ₂	2.05×10^{-4}	☑	[Liu02]		
			4-F	1.34×10^{-4}	☑	–		
			3-Me	1.22×10^{-4}	☑	[Sch60], [Ber58]		
			H	6.82×10^{-5}	☑	–		
				7.37×10^{-5}	☒	[Str64]		
		7.30×10^{-5}		☒	[Min72]			
		7.28×10^{-5}		☒	[Ing40a]			
		7.27×10^{-5}		☒	[Kee64]			
		7.24×10^{-5}		☒	[Ing40b], [Ber58]			
		7.23×10^{-5}		☒	[Arn50]			
		7.17×10^{-5}		☒	[Liu98]			
		7.00×10^{-5}		☒	[Ing52]			
		6.74×10^{-5}		☒	[Koh63]			
		4-Cl	6.07×10^{-5}	☒	[Ber68]			
			2.31×10^{-5}	☑	[Sch71]			
			1.93×10^{-5}	☒	[Ber68]			
			4-Br	1.66×10^{-5}	☑	[Ber68]		
			4-Cl, 4'-Cl	8.40×10^{-6}	☑	[Ber68]		
			1.45×10^{-5}	☒	[Har73]			
			3-Cl	1.20×10^{-6}	☑	[Liu98]		
			80A20W	CF ₃ CO ₂	4-Me, 4'-Me	3.77×10^{-3}	☑	–
						4-Me	2.85×10^{-4}	☑
4-F	3.24×10^{-5}				☑	–		
H	2.04×10^{-5}	☑			[Min72]			
80A20W	DNB	4-OMe, 4'-OMe			2.99×10^{-3} [c]	☑	–	
		4-OMe, 4'-OPh	3.34×10^{-4} [c]	☑	–			
		4-OMe, 4'-Me	1.08×10^{-4} [c]	☑	–			
		4-OMe	1.85×10^{-5} [c]	☑	–			
		H	4.39×10^{-10}	☑	[Min72]			

Table S1 (continued).

solvent	leaving group	X, Y substituents	k_s [s^{-1}]	used in correl.	ref. short cuts ^[b]
ethanol	TsO	3-Cl	5.57×10^{-2}	☑	–
		3-Cl, 4'-Cl	2.83×10^{-2}	☑	–
		3-Cl, 3'-Cl	1.83×10^{-3}	☑	–
		3,5-(Cl) ₂ , 3'-Cl	9.65×10^{-5}	☑	–
		3,5-(Cl) ₂ , 3',5'-(Cl) ₂	5.81×10^{-6}	☑	–
ethanol	Br	4-Me	2.95×10^{-2}	☑	–
		4-OPh, 4'-NO ₂	3.55×10^{-3}	☑	[Liu02]
		4-F	2.38×10^{-3}	☑	–
		H	1.34×10^{-3}	☑	–
			1.24×10^{-3}	☒	[Win72]
			1.23×10^{-3}	☒	[Dvo89]
			1.20×10^{-3}	☒	[Liu97]
		4-Cl	5.00×10^{-4}	☑	–
		4-Cl, 4'-Cl	2.10×10^{-4}	☑	–
		3-Cl, 4'-Cl	1.58×10^{-5}	☑	–
ethanol	Cl	4-OMe, 4'-OMe	5.72×10^1	☑	[Sch88]
		4-OMe, 4'-OPh	1.52×10^1	☑	[Sch88]
		4-OMe, 4'-Me	5.14	☑	[Sch88]
		4-OMe	5.00×10^{-1}	☑	[Sch88]
			3.30×10^{-1}	☒	[Nis67a]
		4-Me, 4'-Me	2.17×10^{-2}	☑	–
			2.02×10^{-2}	☒	[Sch88]
			1.83×10^{-2}	☒	[Nor28c]
			1.70×10^{-2}	☒	[Nis67b]
		4-OPh	2.22×10^{-2}	☑	[Sch88]
			1.41×10^{-2}	☒	[Nor28c]
		4-Me	1.54×10^{-3}	☑	–
			1.27×10^{-3}	☒	[Liu98]
			1.24×10^{-3}	☒	[Ing40a]
			1.23×10^{-3}	☒	[Nis67a]
			1.23×10^{-3}	☒	[Bad58]
			7.22×10^{-4}	☒	[Nor28b]
		3,5-(Me) ₂	2.25×10^{-4}	☑	[Nis67b]
			2.09×10^{-4}	☒	[Bad58]
		4-OPh, 4'-NO ₂	2.67×10^{-4}	☑	[Liu02]
		4-F	1.07×10^{-4}	☑	–
			9.30×10^{-5}	☒	[Nis67a]
		3-Me	1.12×10^{-4}	☑	[Nis67a]
			1.37×10^{-4}	☒	[Pac58]
			9.23×10^{-5}	☒	[Nor28c]
		H	5.54×10^{-5}	☑	–
			5.75×10^{-5}	☒	[War27]
			5.72×10^{-5}	☒	[Ham37]
			5.42×10^{-5}	☒	[Liu98]
			5.41×10^{-5}	☒	[Win72]
	5.39×10^{-5}	☒	[Pac58]		
	5.37×10^{-5}	☒	[Bad58]		
	5.34×10^{-5}	☒	[Nis67a]		
	5.30×10^{-5}	☒	[Ing40a]		

Table S1 (continued).

solvent	leaving group	X, Y substituents	k_s [s^{-1}]	used in correl.	ref. short cuts ^[b]
ethanol	Cl	H	4.85×10^{-5}	☒	[Nor28a]
			4.43×10^{-5}	☒	[Nor28b]
		4-Cl	2.06×10^{-5}	☑	[Nis67a]
			1.78×10^{-5}	☒	[Nor28b]
		4-Br	1.61×10^{-5}	☑	[Nis67a]
			1.47×10^{-5}	☒	[Nor28c]
		4-Cl, 4'-Cl	8.07×10^{-6}	☑	[Nis67b]
			6.7×10^{-6}	☒	[Nor28b]
		3-Cl	1.25×10^{-6}	☑	[Nis67a]
			1.21×10^{-6}	☒	[Pac58]
			9.88×10^{-7}	☒	[Nor28c]
	3-Cl, 4'-Cl	5.03×10^{-7}	☑	[Nis67c]	
	4-NO ₂	4.24×10^{-8}	☑	[Nis67a]	
ethanol	CF ₃ CO ₂	4-OMe	2.86×10^{-2}	☑	–
		4-Me, 4'-Me	1.89×10^{-3}	☑	–
		4-Me	1.40×10^{-4}	☑	–
		4-F	1.84×10^{-5}	☑	–
		H	9.37×10^{-6}	☑	–
Ethanol	DNB	4-OMe, 4'-OMe	5.79×10^{-3} [c]	☑	–
		4-OMe, 4'-OPh	7.52×10^{-4} [c]	☑	–
		4-OMe, 4'-Me	1.88×10^{-4} [c]	☑	–
		4-OMe	3.22×10^{-5} [c]	☑	–
80E20W	TsO	3-Cl	6.54×10^{-1}	☑	–
		3-Cl, 4'-Cl	2.72×10^{-1}	☑	–
		3-Cl, 3'-Cl	1.59×10^{-2}	☑	–
		3,5-(Cl) ₂ , 3'-Cl	9.13×10^{-4}	☑	–
		3,5-(Cl) ₂ , 3',5'-(Cl) ₂	3.64×10^{-5}	☑	–
80E20W	Br	4-OPh, 4'-NO ₂	4.72×10^{-2}	☑	[Liu02]
		4-F	5.88×10^{-2}	☑	[Liu95]
			6.05×10^{-2}	☒	–
		H	3.04×10^{-2}	☑	[Liu95]
			3.44×10^{-2}	☒	–
		4-Cl	1.21×10^{-2}	☑	–
		4-Cl, 4'-Cl	4.81×10^{-3}	☑	–
		3-Cl	6.48×10^{-4}	☑	[Liu95]
		3-Cl, 4'-Cl	2.59×10^{-4}	☑	–
		4-NO ₂	2.63×10^{-5}	☑	[Liu95]
		3-Cl, 3'-Cl	8.99×10^{-6}	☑	–
3,5-(Cl) ₂ , 3'-Cl	3.84×10^{-7}	☑	–		
80E20W	Cl	4-Me	4.64×10^{-2}	☑	–
			4.20×10^{-2}	☒	[Liu98]
		3,5-(Me) ₂	5.84×10^{-3}	☑	[Sch60]
		4-OPh, 4'-NO ₂	4.26×10^{-3}	☑	[Liu02]
		4-F	3.67×10^{-3}	☑	–
		3-Me	3.40×10^{-3}	☑	[Sch60]

Table S1 (continued).

solvent	leaving group	X, Y substituents	k_s [s^{-1}]	used in correl.	ref. short cuts ^[b]
80E20W	Cl	H	2.04×10^{-3}	☑	–
			2.08×10^{-3}	☒	[Har81]
			1.95×10^{-3}	☒	[Liu98]
			1.94×10^{-3}	☒	[Sch60]
			1.72×10^{-3}	☒	[War27]
		4-Cl	7.29×10^{-4}	☑	–
			7.35×10^{-4}	☒	[Har81]
			2.86×10^{-4}	☑	–
		4-Cl, 4'-Cl	2.89×10^{-4}	☒	[Har81]
			3.56×10^{-5}	☑	[Liu98]
3-Cl	1.53×10^{-5}	☑	–		
	1.30×10^{-6}	☑	[Liu98]		
80E20W	CF ₃ CO ₂	4-Me, 4'-Me	2.30×10^{-2}	☑	–
			2.10×10^{-3}	☑	–
		4-Me	3.27×10^{-4}	☑	–
		H	1.55×10^{-4}	☑	–
80E20W	DNB	4-OMe, 4'-OMe	3.93×10^{-2}	☑	–
			5.59×10^{-3}	☑	–
		4-OMe, 4'-OPh	1.98×10^{-3}	☑	–
		4-OMe, 4'-Me	3.50×10^{-4}	☑	–
80E20W	PNB	4-OMe, 4'-OMe	2.65×10^{-3}	☑	–
			3.35×10^{-4}	☑	–
		4-OMe, 4'-OPh	1.11×10^{-4}	☑	–
		4-OMe, 4'-Me	2.38×10^{-5}	☑	–
		4-OMe	1.19×10^{-6}	☑	[Mcl82]
		H	4.50×10^{-9}	☑	[Ben91]
methanol	Br	4-OPh, 4'-NO ₂	4.74×10^{-2}	☑	[Liu02]
			2.92×10^{-2}	☑	[Liu95]
		H	1.76×10^{-2}	☑	[Liu95]
			1.58×10^{-2}	☒	[Dvo89]
		3-Cl	4.22×10^{-4}	☑	[Liu95]
		4-NO ₂	1.14×10^{-5}	☑	[Liu95]
methanol	Cl	4-Me	1.98×10^{-2}	☑	[Liu98]
			1.94×10^{-2}	☒	[Nis67a]
		3,5-(Me) ₂	3.87×10^{-3}	☑	[Nis67b]
		4-OPh, 4'-NO ₂	2.18×10^{-3}	☑	[Liu02]
		4-F	1.38×10^{-3}	☑	[Nis67a]
		3-Me	1.74×10^{-3}	☑	[Nis67a]
		H	8.33×10^{-4}	☑	[Win72]
			1.02×10^{-3}	☒	[Gri71]
			8.28×10^{-4}	☒	[Nis67a]
			8.15×10^{-4}	☒	[Alt52]
		4-Cl	8.10×10^{-4}	☒	[Liu98]
			2.97×10^{-4}	☑	[Nis67a]
			3.80×10^{-4}	☒	[Alt52]
			2.39×10^{-4}	☑	[Nis67a]

Table S1 (continued).

solvent	leaving group	X, Y substituents	k_s [s^{-1}]	used in correl.	ref. short cuts ^[b]
methanol	Cl	4-Cl, 4'-Cl	1.15×10^{-4}	☑	[Nis67b]
			1.05×10^{-4}	☒	[Alt52]
		3-Cl	1.93×10^{-5}	☑	[Liu98]
			2.03×10^{-5}	☒	[Nis67a]
			2.12×10^{-5}	☒	[Alt52]
		3-Cl, 4'-Cl	8.21×10^{-6}	☑	[Nis67c]
		4-NO ₂	5.50×10^{-7}	☑	[Alt52]
5.40×10^{-7}	☒	[Nis67a]			
TFE	TsO	3,5-(Cl) ₂ , 3'-Cl	4.36×10^{-2}	☑	–
		3,5-(Cl) ₂ , 3',5'-(Cl) ₂	1.07×10^{-3}	☑	–
TFE	Br	H	1.10	☑	–
		4-Cl, 4'-Cl	1.52×10^{-1}	☑	–
		3-Cl	6.62×10^{-2}	☑	–
			8.57×10^{-2}	☒	[Liu95]
		3-Cl, 4'-Cl	1.40×10^{-2}	☑	–
		4-NO ₂	2.89×10^{-4}	☒	[Liu95]
		3-Cl, 3'-Cl	6.70×10^{-4}	☑	–
		3,5-(Cl) ₂ , 3'-Cl	1.99×10^{-5}	☑	–
3,5-(Cl) ₂ , 3',5'-(Cl) ₂	3.41×10^{-7}	☑	–		
TFE	Cl	4-OPh, 4'-NO ₂	6.34×10^{-1}	☑	[Liu02]
		H	6.17×10^{-1}	☑	–
		4-Cl, 4'-Cl	6.40×10^{-2}	☑	–
		3-Cl	1.52×10^{-2}	☑	–
			1.47×10^{-2}	☒	[Liu98]
		3-Cl, 4'-Cl	4.85×10^{-3}	☑	–
		4-NO ₂	5.44×10^{-5}	☒	[Liu98]
		3-Cl, 3'-Cl	7.20×10^{-4}	☑	–
3,5-(Cl) ₂ , 3'-Cl	1.39×10^{-5}	☑	–		

^[a] Mixtures of solvents are given as (v/v), solvents: W = water, A = acetone, E = ethanol, M = methanol, T = trifluoroethanol. ^[b] This work if not mentioned otherwise; see Table S2 for references.

^[c] A part of the solvolysis rate constants for 3,5-dinitrobenzoates which were given in a preliminary report (B. Denegri, S. Minegishi, O. Kronja, H. Mayr, *Angew. Chem. Int. Ed.* **2004**, *43*, 2302–2305) have been reevaluated in this work.

Table S2. References used in Table S1.

ref. short cut	reference
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[Ben91]	T. W. Bentley, M. Christl, S. J. Norman, <i>J. Org. Chem.</i> 1991 , <i>56</i> , 6238–6240.
[Ber58]	E. Berliner, M. M. Chen, <i>J. Am. Chem. Soc.</i> 1958 , <i>80</i> , 343–347.
[Ber64]	L. Verbit, E. Berliner, <i>J. Am. Chem. Soc.</i> 1964 , <i>86</i> , 3307–3312.
[Ber68]	E. Berliner, M. Q. Malter, <i>J. Org. Chem.</i> 1968 , <i>33</i> , 2595–2596.
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[Ham37]	N. T. Farinacci, L. P. Hammett, <i>J. Am. Chem. Soc.</i> 1937 , <i>59</i> , 2542–2546.
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[Ing40b]	L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, N. A. Taher, <i>J. Chem. Soc.</i> 1940 , 979–1011.
[Ing52]	O.T. Benfey, E. D. Hughes, C. K. Ingold, <i>J. Chem. Soc.</i> 1952 , 2488–2493.
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[Liu97]	K.-T. Liu, C.-P. Chin, Y.-S. Lin, M.-L. Tsao, <i>J. Chem. Res. (S)</i> 1997 , 18–19.
[Liu98]	K.-T. Liu, Y.-S. Lin, M.-L. Tsao, <i>J. Phys. Org. Chem.</i> 1998 , <i>11</i> , 223–229.
[Liu02]	K.-T. Liu, C.-S. Chuang, B.-Y. Jin, <i>J. Phys. Org. Chem.</i> 2002 , <i>15</i> , 21–28.
[Mcl82]	D. J. McLennan, P. L. Martin, <i>J. Chem. Soc. Perkin Trans. 2</i> 1982 , 1091–1097.
[Min72]	J. Mindl, P. Pivoňka, M. Večeřa, <i>Collect. Czech. Chem. Commun.</i> 1972 , <i>37</i> , 3496–3505.
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Table S2 (continued).

ref. short cut	reference
[Nis67a]	S. Nishida, <i>J. Org. Chem.</i> 1967 , <i>32</i> , 2692–2695.
[Nis67b]	S. Nishida, <i>J. Org. Chem.</i> 1967 , <i>32</i> , 2695–2697.
[Nis67c]	S. Nishida, <i>J. Org. Chem.</i> 1967 , <i>32</i> , 2697–2701.
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[Nor28b]	J. F. Norris, C. Banta, <i>J. Am. Chem. Soc.</i> 1928 , <i>50</i> , 1804–1808.
[Nor28c]	J. F. Norris, J. T. Blake, <i>J. Am. Chem. Soc.</i> 1928 , <i>50</i> , 1808–1812.
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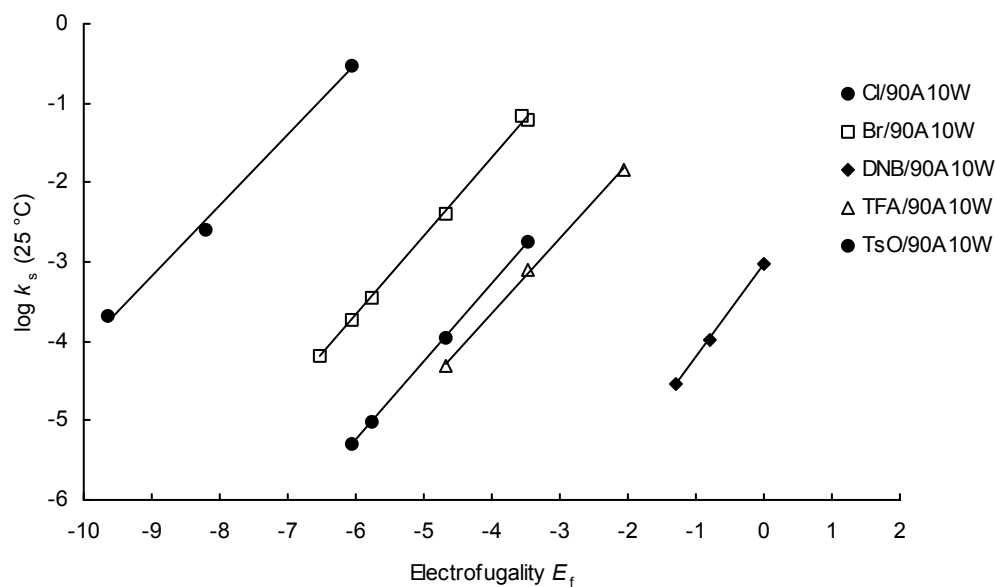


Figure S1. Plot of $\log k_s$ (25 °C) vs optimized E_f for solvolyses of the substituted benzhydrylium substrates in 90A10W.

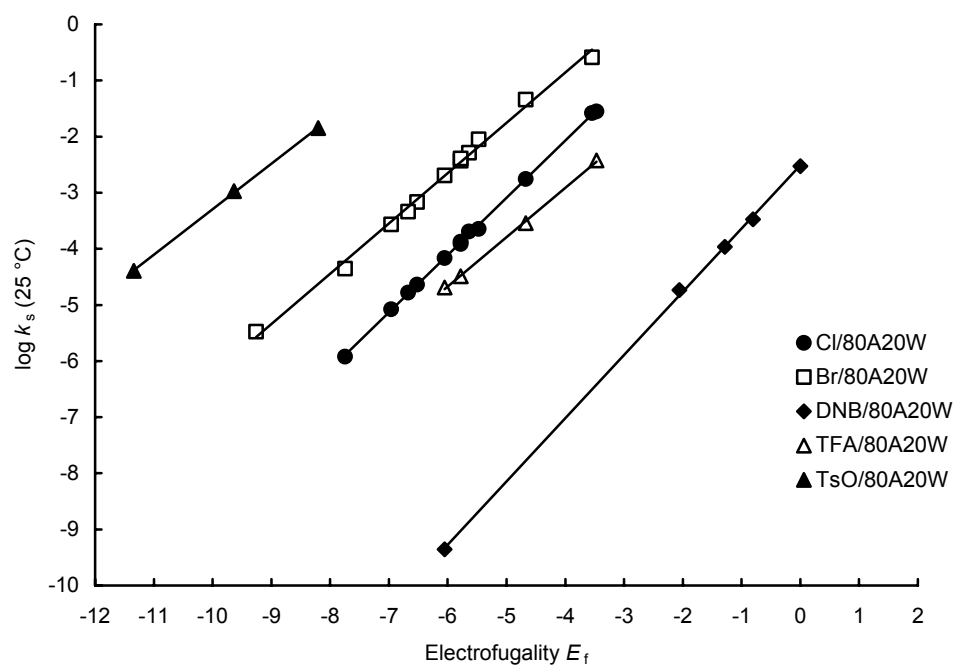


Figure S2. Plot of $\log k_s$ (25 °C) vs optimized E_f for solvolyses of the substituted benzhydrylium substrates in 80A20W.

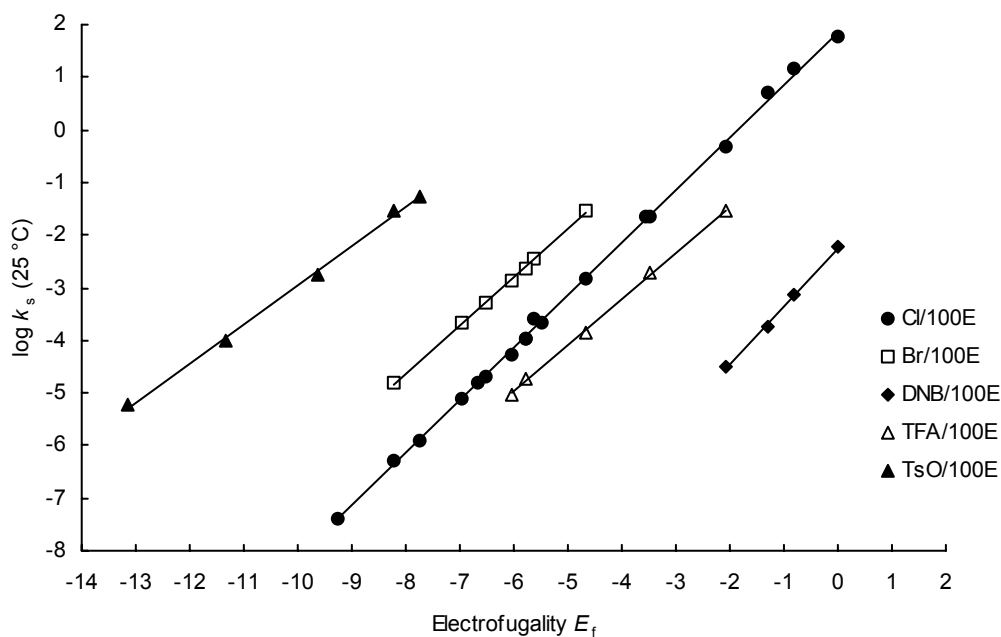


Figure S3. Plot of $\log k_s$ (25 °C) vs optimized E_f for ethanolyse of the substituted benzhydrylium substrates.

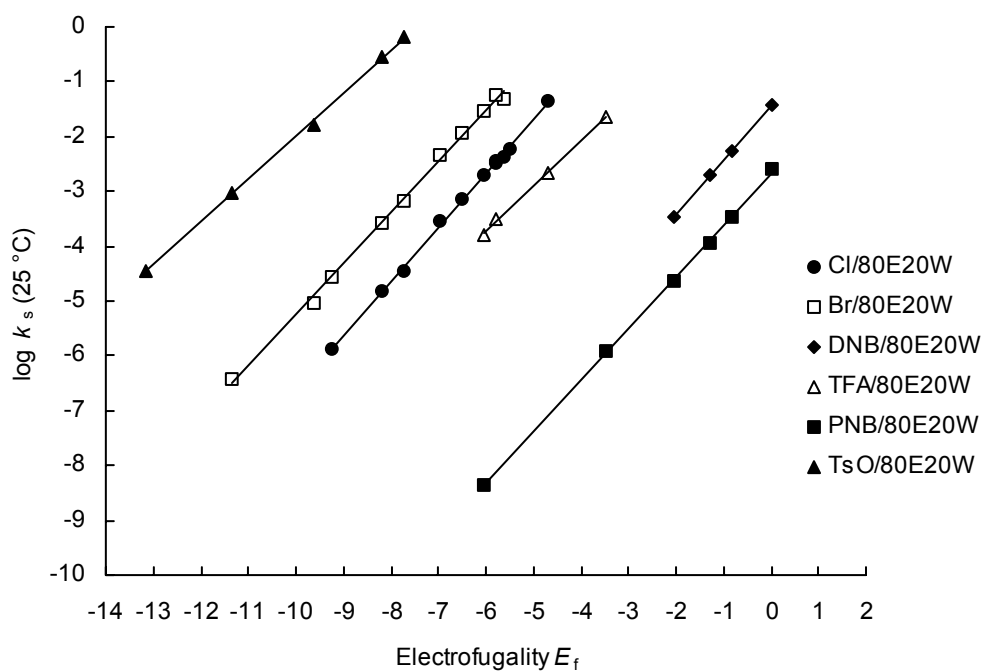


Figure S4. Plot of $\log k_s$ (25 °C) vs optimized E_f for solvolyses of the substituted benzhydrylium substrates in 80E20W.

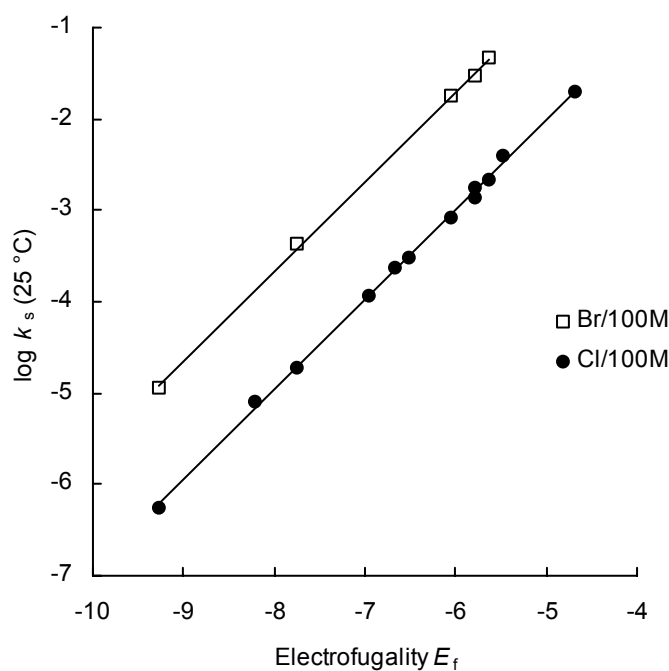


Figure S5. Plot of $\log k_s (25^\circ\text{C})$ vs optimized E_f for methanolyses of the substituted benzhydrylium substrates.

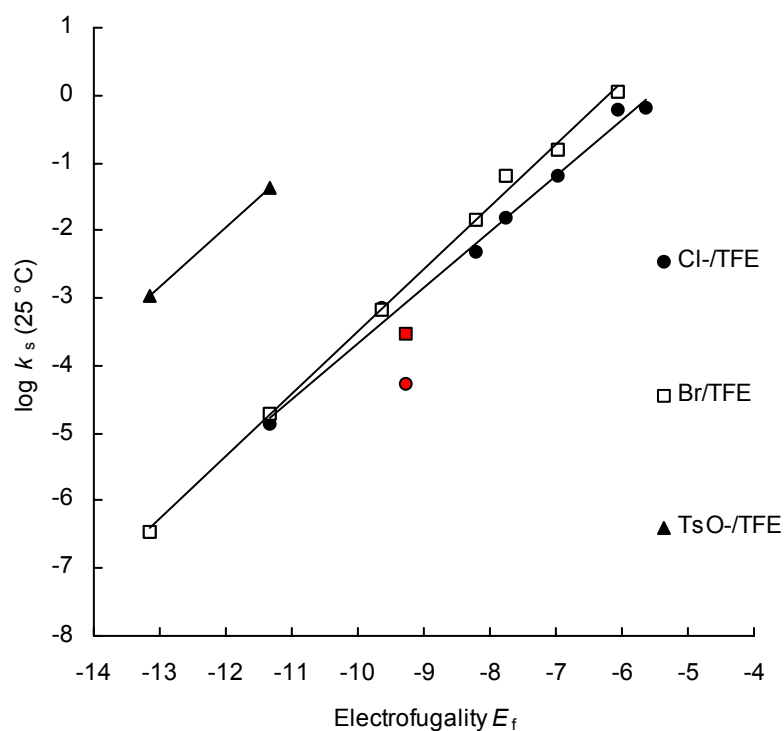


Figure S6. Plot of $\log k_s (25^\circ\text{C})$ vs optimized E_f for solvolyses of the substituted benzhydrylium substrates in trifluoroethanol. The solvolysis rate constants of 4-nitro benzhydryl chloride and bromide ($E_f = -9.26$) were excluded from the correlations.

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