*Supporting Information***Organocatalysis with a Fluorous Tag: Asymmetric Reduction of Imines with Trichlorosilane Catalyzed by Amino Acid-Derived Formamides**

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General Methods. Melting points were determined on a Kofler block and are uncorrected. Optical rotations were recorded in CHCl₃ at 25 °C unless otherwise indicated, with an error of $\leq \pm 0.1$. The $[\alpha]_D$ values are given in 10⁻¹ deg cm³ g⁻¹. The NMR spectra were recorded in CDCl₃, ¹H at 400 MHz and ¹³C at 100.6 MHz, with chloroform-*d*₁ (δ 7.26, ¹H; δ 77.0, ¹³C) as internal standard unless otherwise indicated; ¹⁹F spectra were recorded at 376.5 MHz in CDCl₃ using CFCl₃ (δ 0) as a standard. Various 2D-techniques and DEPT experiments were used to establish the structures and to assign the signals. The IR spectra were recorded for KBr discs or for a thin film between NaCl plates. The mass spectra (EI and/or CI) were measured on a dual sector mass spectrometer using direct inlet and the lowest temperature enabling evaporation. All reactions were performed under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware, twice evacuated and filled with inert gas. Solvents and solutions were transferred by syringe-septum and cannula techniques. All solvents for the reactions were of reagent grade and were dried and distilled under nitrogen immediately before use as follows: toluene from sodium/benzophenone, dichloromethane from calcium hydride, triethylamine from calcium hydride. Petroleum ether refers to the fraction boiling in the range of 60-80 °C. Yields are given for isolated products showing one spot on a TLC plate and no impurities detectable in the NMR spectrum. The identity of the products prepared by different methods was checked by comparison of their NMR, IR, and MS data and by the TLC behavior. The chiral HPLC methods were calibrated with the corresponding racemates. Nitrophenol **9c**^{S1} and 2,6-diisopropyl-4-nitroaniline **6**^{S2} were prepared according to the literature. Imines **1b-e**,^{S3} **1i**,^{S4} and **1k**^{S5} are known compounds and were prepared following the literature procedures.

References and Notes

- S1 For the synthesis of **9c**, see: Helfenbein, J.; Lartigue, C.; Noirault, E.; Azim, E.; Legailliard, J.; Galmier, M. J.; and Madelmont, J. C. *J. Med. Chem.* **2002**, *45*, 5806.
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- S3 (a) Malkov, A. V.; Mariani, A.; MacDougall, K. N.; Kočovský, P. *Org. Lett.* **2004**, *6*, 2253.
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- S5 Ackland, M. J.; Danks, T. N.; Howells, M. E. *J. Chem. Soc., Perkin Trans. 1* **1998**, 813.

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CH₂Cl₂

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12c

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12c

S 34

12d

13a

S 36

13a

S 37

13b

S 38

S 39

13c

S 40

13c

S 41

13d

S 42

13d

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16b

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