Supporting Information
for the manuscript entitled

Reactions of Enamines with Selectfluor: A Straightforward Route to
Difluorinated Carbonyl Compounds

Weimin Peng and Jean'ne M. Shreeve

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, USA

jshreeve@uidaho.edu

Table of Contents

S2. General Methods and Experimental Section; Analytical and Spectral Data for **2g**, **4c**,
4d, **5c**, **5d**

S4. ¹H NMR spectrum of **2c**

S5. ¹H NMR spectra of **2d** and **2e**

S6. ¹H NMR spectra of **2f** and **4a**

S7. ¹H NMR spectra of **4b** and **4e**

S8. ¹H NMR spectra of **5b** and **6e**

S9. References

General Methods.

^1H , ^{13}C and ^{19}F NMR spectra were recorded on a 300 MHz spectrometer operating at 300.13, 75.48, 282.5 MHz, respectively. Chemical shifts were reported relative to Me_4Si or CFCl_3 . Deuterated chloroform was the solvent unless otherwise specified. GC/MS spectra were determined using an appropriate instrument. IR spectra were recorded using NaCl plates for neat liquids and KBr pellets for solids. Melting points are uncorrected. Elemental analyses were performed commercially.

Experimental Section

Enamines **1a**¹ and **1b**² were prepared according to literature procedures. Enamines **1c** and **1e** were obtained by Michael addition reactions of pyrrolidine with ethyl β -chlorocinnamate and β -chloroenone, respectively, followed by chloride elimination.³ Enamines **1d**, **1f**, **1g** and **1h** were synthesized by addition of pyrrolidine or morphine to the corresponding acetylenic ketone.⁴

Analytical data for **4c**, **4d**, **5c**.

Enamine **4c** from 4-nitroacetophenone (10 min reflux): **1-morpholino-1-(4-nitrophenyl)ethene**. Brown solid. ^1H NMR δ 8.21 (d, $J = 7.0$ Hz, 2H), 7.66 (d, $J = 7.0$ Hz, 2H), 4.50 (s, 1H), 4.40 (s, 1H), 3.80 (t, $J = 4.8$ Hz, 4H), 2.84 (t, $J = 4.8$ Hz, 4H).

Enamine **4d** from 4-ethoxycarbonylacetophenone (25 min reflux): **1-morpholino-1-(4-ethoxycarbonylphenyl)ethene**. Pale yellow oil. ^1H NMR δ 8.03 (d, $J = 6.3$ Hz, 2H), 7.55 (d, $J = 6.3$ Hz, 2H), 4.43 (s, 1H), 4.40 (q, $J = 7.1$ Hz, 2H), 4.30 (s, 1H), 3.79 (t, $J = 4.7$ Hz, 4H), 2.84 (t, $J = 4.7$ Hz, 4H), 1.42 (q, $J = 7.1$ Hz, 2H).

5c: 2, 2-Difluoro-1-(4-nitrophenyl)-ethanone (contaminated by 5% of the hydrated form). Yellow solid (mp 44-46 °C, *n*-hexane/AcOEt/CH₂Cl₂ (3/1/1), *R_f* 0.2). ¹H NMR δ 8.40 (d, *J* = 6.9 Hz, 2H), 8.27 (d, *J* = 6.9 Hz, 2H), 6.30 (t, *J* = 53.2 Hz, 1H). ¹⁹F NMR δ 121.5 (d, *J* = 53.2 Hz). ¹³C NMR δ 187.3 (t, *J* = 26.7 Hz), 152.0, 136.6 (t, *J* = 2.0 Hz), 131.6 (t, *J* = 2.5 Hz), 124.9, 111.9 (t, *J* = 254.0 Hz). GC-MS (EI) 201 (M⁺), 185, 155, 150, 127, 120, 104, 92, 76, 64, 50, 38. IR (KBr) 3117, 2984, 1940, 1716, 1604, 1531, 1350, 1234, 1184, 1128, 1077, 983, 887, 856, 829, 750, 715, 680, 632, 551, 533, 499 cm⁻¹. Anal. Calcd for C₈H₅F₂NO₃: C, 47.77; H, 2.51; N, 6.96. Found: C, 47.50; H, 2.67; N, 6.73.

NMR spectra supporting the syntheses of the known compounds.

- 1 Leonard N. J.; Adamcik, J. A. *J. Am. Chem. Soc.* **1959**, *81*, 595-602.
2. McMurry, J. E. *Org. Syn.* **1973**, *53*, 59-62.
3. Kashima, C.; Tajima, T.; Higuchi, C.; Omote, Y. *J. Heterocyclic Chem.* **1984**, *21*, 345-347.
- 4 (a) Fouli, F. A.; Beshay, A. D. *Indian J. Chem.* **1980**, *19B*, 410-412. (b) Truce, W. E.; Brady, D. G. *J. Am. Chem. Soc.* **1966**, *31*, 3543-3550. (c) Chowdhury, C.; Kundu, N. G. *Tetrahedron*, **1999**, *55*, 7.11-7016.