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Efficient Hydration of Alkynes through Acid Assisted Brønsted Acid Catalysis

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Supporting Information

1. General

¹H and ¹³C NMR spectra were recorded at 500 MHz and 126 MHz (or 400 MHz and 101 MHz) respectively using CDCl₃ as a solvent. The chemical shifts are reported in δ (ppm) values (¹H and ¹³C NMR relative to CHCl₃, δ 7.26 ppm for ¹H NMR and δ 77.0 ppm for ¹³C NMR and CFCl₃ (δ 0 ppm for ¹⁹F NMR), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants (*J*), are reported in Hertz (Hz). All reagents and solvents were employed without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 aluminum sheets. All reagents were purchased from Aldrich or Alfa Aesar and used as received without any further purification. A commercial microwave reactor (CEM, model Discovery) was used.

2. General procedure

Preparation of Ga(OTf)₃ stock solution in HOAc (0.05 M)

In a glass vial with a screw cap, $Ga(OTf)_3$ (129.5 mg) was dissolved in HOAc (5 mL).

General procedure for hydration of alkynes 1

Method A: To a mixture of alkyne **1** (1.25 mmol), H_2O (1.25 mmol, 1 equiv) in HOAc (0.45 mL), $Ga(OTf)_3$ stock solution (50 µl) was added. The mixture was stirred in an oil bath at 100 °C for 1 - 20 h and then cooled down to room temperature. The yield was determined by analysis of the ¹H NMR spectrum of the crude product mixture.

Method B: To a mixture of alkyne **1** (1.25 mmol), H₂O (1.25 mmol, 1 equiv) in HOAc (0.25 mL), Ga(OTf)₃ stock solution (250 μ l) was added. The mixture was stirred in a microwave reactor at 100 °C for 1 h and then cooled down to room temperature. The yield was determined by analysis of the ¹H NMR spectrum of the crude product mixture.

3. ¹H NMR spectrums of hydration product 2

All of the hydration products (ketones 2): 2a (98-86-2), 2b (100-06-1), 2c (403-42-9), 2d (577-16-2), 2e (111-13-7), 2f (589-63-9), 2g (451-40-1), 2h (93-55-0), 2i (932-66-1), 2k (123-76-2), 2l (932-66-1), 2m (14371-10-9), 2n (1009-61-6) are commercial available. Their spectroscopic data agrees well with the standard spectrums. Some of the ¹H NMR spectrums of products which were simply isolated through extraction between H_2O/Et_2O are as following.

Acetophenone (2a)



¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 2.60 (s, 3H).

4-Methoxyacetophenone (2b)



¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 2.55 (s, 3H).

4-Fluoroacetophenone (2c)



¹H NMR (400 MHz, CDCl₃) δ 7.97 (m, 2H), 7.12 (m, 2H), 2.58 (s, 3H).

2-Methylacetophenone (2d)



¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 7.7 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.26 (m, 2H), 2.58 (s, 3H), 2.53 (s, 3H).

2-octanone (2e)

¹H NMR (400 MHz, CDCl₃) δ 2.39 (t, J = 7.5 Hz, 2H), 2.11 (s, 3H), 1.56 – 1.50 (m, 2H), 1.30 – 1.20 (m, 6H), 0.85 (t, J = 6.5 Hz, 3H).

4-octanone (2f)



¹H NMR (400 MHz, CDCl₃) δ 2.37 (dd, J = 12.7, 7.3 Hz, 4H), 1.64 – 1.47 (m, 4H), 1.30 (dd, J = 15.0, 7.5 Hz, 2H), 0.90 (td, J = 7.3, 2.5 Hz, 6H).

1,2-diphenylethanone (2g)



¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.97 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 – 7.21 (m, 5H), 4.29 (s, 2H).

Propiophenone (2h)



¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.86 (m, 2H), 7.53 (m, 1H), 7.46 – 7.41 (m, 2H), 2.99 (q, J = 7.3 Hz, 2H), 1.21 (t, J = 7.3 Hz, 3H).

1-Acetylcyclohexene (2i)



¹H NMR (400 MHz, CDCl₃) δ 6.98 – 6.82 (m, 1H), 2.26 (s, 3H), 2.25 – 2.21 (m, 2H), 2.20 – 2.17 (m, 2H), 1.68 – 1.52 (m, 4H).

4-oxopentanoic acid (2k)



¹H NMR (400 MHz, CDCl₃) δ 2.74 (t, J = 6.4 Hz, 2H), 2.62 (t, J = 6.4 Hz, 2H), 2.19 (s, 3H).

Cinnamaldehyde (2m)



¹H NMR (400 MHz, CDCl₃) δ 9.68 (d, J = 7.7 Hz, 1H), 7.57-7.54 (m, 2H), 7.48 (d, J = 16.0 Hz, 1H), 7.44 – 7.39 (m, 3H), 6.73 (dd, J = 15.9, 7.7 Hz, 1H).

1,4-Diacetylbenzene (2n)



 1 H NMR (400 MHz, CDCl₃) δ 8.00 (s, 4H), 2.62 (s, 6H).





