Supplementary Information

Ammonium Catalyzed Cyclitive Additions: Evidence for a Cation-π Interaction with Alkynes

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Cyclization rate data $(t_{1/2})$ in various solvents via NMR (Table 1)

The reactions reported in Table 1 were performed in a small oven dried round bottom flask to which was added a Teflon coated magnetic stirrer along with the alkyne **1** (50 mg) under Argon gas. To the flask was also added solvent (0.1 M in alkyne substrate) followed by TBAB (1.0 eq). Each reaction was allowed to proceed for a given time followed by quenching with saturate aqueous NH₄Cl and extraction three times using a separatory funnel with ether. The organic extractions were collected, dried over Na₂SO₄, and then filtered through a cotton plug. The solvent was then removed under vacuum and the resulting crude was analyzed by ¹H NMR in MeCN-*d*₃.

The peaks of comparison were the two rotameric peaks of the alkyne found at 2.89 and 2.75 ppm and the doublet of the vinyl proton from the cyclized product located at 5.21 ppm (see sample spectrum on page S2). Once the spectrum was obtained, the mentioned peaks were integrated always maintaining the alkynyl proton at an integrated value of 1. Using a simple mathematical calculation, the % conversion was then analyzed:

% conversion =
$$\frac{x}{x+1} \times 100$$

Where x = the integrated value of the vinyl proton's doublet when the integration value of the alkynyl proton is set to 1.



Data used to generate $t_{1/2}$ values reported in Table 1

DBU with TBAB MeCN:

Reaction time (minutes)	% conversion
120	33
180	44
240	58

DBU without TBAB in MeCN:

Reaction time (minutes)	% conversion
120	12
390	35
1470	70

NaOPh with TBAB in MeCN:

Reaction time (minutes)	% conversion
35	34
45	44
55	52

NaOPh without TBAB in MeCN:

Reaction time (minutes)	% conversion
1140	52

NaOPh with TEAB in MeCN:

Reaction time (minutes)	% conversion
40	40
52	48
60	54

NaOPh with TPAB in MeCN:

Reaction time (minutes)	% conversion
40	39
50	48
62	58

NaOPh with TOAB in MeCN:

Reaction time (minutes)	% conversion
40	45
50	54
60	64

NaOPh with TBAB in THF:

Reaction time (minutes)	% conversion
17	17
30	45
60	79

NaOPh without TBAB in THF:

Reaction time (minutes)	% conversion
450	12
1350	28
2070	32

NaOPh with TBAB in Pyridine:

Reaction time (minutes)	% conversion
20	14
60	36
260	78

NaOPh without TBAB in Pyridine:

Reaction time (minutes)	% conversion
60	14.5
260	45
385	50

NaOPh with TBAB in DMF:

Reaction time (minutes)	% conversion
1	49
5	98
30	100

NaOPh without TBAB in DMF:

Reaction time (minutes)	% conversion
30	41
60	46
140	100

General procedure for Raman study

Solutions of each alkyne with TBAB at various concentration ratios were prepared in DCM unless otherwise stated. For the solutions with TBAB:alkyne molar ratios of 0:1, 0.25:1, 0.5:1, 0.75:1, and 1:1 the concentration of the alkyne was initially 100 μ M. For the 5:1 solution, the concentration of the alkyne was initially 20 μ M. Each solution was vortexed vigorously before 10 μ L of solution was pipetted onto a glass microscope slide. Raman spectra were collected immediately within the solution droplet before it had dried using an XploRA ONE Raman microscope (Horiba Scientific, Edison, NJ) with 12 mW, 532 nm laser excitation, 10x microscope objective, 1800 g/mm grating, 200 μ m slit width, 500 μ m confocal hole diameter, and 1-5 min accumulation time per spectrum. All spectra were manually baseline corrected and calibrated against the standard Raman band of silicon (520.7 cm⁻¹).

Raman data (Table 2)



Entry 1. Raman titration of **1** with added TBAB. The inset peaks correspond to the alkyne C=C stretch and the arrow indicates the trend in peak change accompanying increasing TBAB:**1** molar ratios: 0:1 (pure **1**), 0.25:1, 0.5:1, 1:1, and 5:1 (red curve).



Entry 2. Raman titration of **3** with added TBAB. The peak corresponds to the alkyne C=C stretch and the arrow indicates the trend in peak change accompanying increasing TBAB:**3** molar ratios: 0:1 (pure **3**), 0.25:1, 0.5:1, 1:1, and 5:1 (red curve).



Entry 3. Raman spectrum of **4** in the C=C stretching region in the absence (black curve) and presence (red curve) of 5 mole equivalents of TBAB. Peaks are normalized to the same arbitrary intensity.



Entry 4. Raman spectrum of **5** in the C=C stretching region in the absence (black curve) and presence (red curve) of 5 mole equivalents of TBAB. Peaks are normalized to the same arbitrary intensity.



Entry 5. Raman spectrum of **6** in the C=C stretching region in the absence (black curve) and presence (red curve) of 5 mole equivalents of TBAB. Peaks are normalized to the same arbitrary intensity.



Entry 6. Raman spectrum of **7** in the C=C stretching region in the absence (black curve) and presence (red curve) of 5 mole equivalents of TBAB. Peaks are normalized to the same arbitrary intensity.



Entry 7. Raman spectrum of **3** in the C=C stretching region in the absence (black curve) and presence (red curve) of 5 mole equivalents of KBr.



Entry 8. Raman spectrum of **1** in the C=C stretching region in the absence (black curve) and presence (red curve) of 5 mole equivalents of TBAB in DMF solvent. Peaks are normalized to the same arbitrary intensity.



Entry 9. Raman spectrum of **1** in the C=C stretching region in the absence (black curve) and presence (red curve) of 5 mole equivalents of TBAB in THF solvent. Peaks are normalized to the same arbitrary intensity.



Entry 10. Raman spectrum of **1** in the C=C stretching region in the absence (black curve) and presence (red curve) of 5 mole equivalents of TPAB. Peaks are normalized to the same arbitrary intensity.