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Brønsted Acid Catalyzed Peterson Olefinations.

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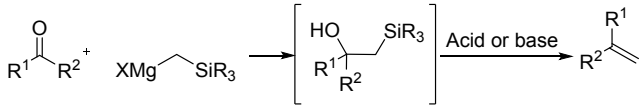
Supporting Information Placeholder

ABSTRACT: A mild and facile Peterson olefination has been developed employing low catalyst loading of the Brønsted acid $HNTf_2$. The reactions are typically performed at room temperature, with the reaction tolerant to a range of useful functionalities. Furthermore, we have extended this methodology to the synthesis of enynes.

Introduction

The Peterson olefination has enjoyed sustained interest from the synthetic community since its discovery in the late 1960's (Scheme 1).[1] This is unsurprising, given the large numbers of bioactive natural products that contain alkene functional groups.[2] In its simplest guise, the Peterson olefination, or silyl-Wittig, is the elimination of β-silyl alcohols, promoted by the β-silicon effect.[3].

Scheme 1. General Peterson Olefination

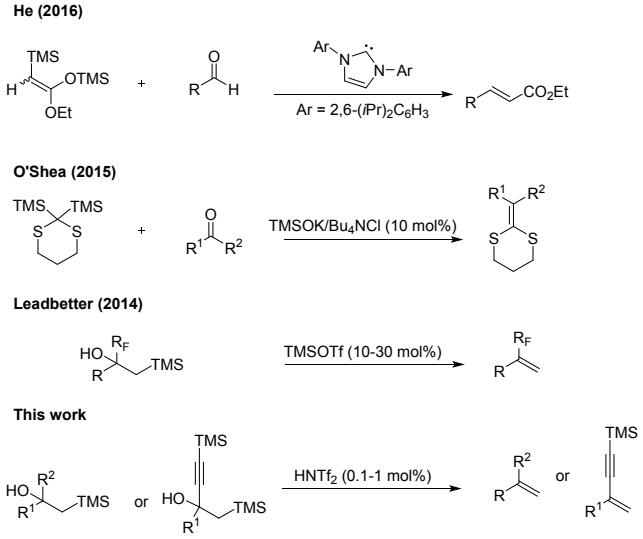


One key characteristic of the Peterson is that it can afford both *E* and *Z* isomers depending on the conditions employed.[4] Routinely employing super-stoichiometric quantities of strong acids or bases results in a facile elimination reaction, however due to the necessity of large quantities of reagents, functional group tolerance and utility in complex target synthesis remains an issue. Recent advances in rendering the Peterson olefination catalytic have resulted in a small number of strategies (Scheme 2),[5] however this area remains underexplored.

Brønsted acid catalysts have become a mainstay of modern synthetic chemistry, and have been successfully used in a wide range of applications.[6] BINOL-derived phosphoric acids and amides have shown great utility in the synthesis of complex scaffolds via numerous transformations,[7] as have urea[8] and thiourea derivatives.[9] These Brønsted acids have been shown to activate carbonyls, imines as well as olefins to form the corresponding salts or carbocations.[10] Furthermore, Brønsted acids have been shown to activate hydroxyl groups, but typically require much higher catalyst loadings.[11]

A potential solution is to use more acidic Brønsted acids, such as the readily available triflic acid, TfOH.[12] Although useful, its toxicity and difficulty in handling renders its use problematic. Nevertheless, the synthetic utility of super Brønsted acids has resulted in several alternatives being reported. Of these, triflimide $HNTf_2$, has shown promise.[13] Not only is it easier to handle (solid vs viscous oil) but it's pKa is a fold lower than TfOH (-12.3 vs -11.4 in DCE),[14] allowing for potentially milder activation conditions. We therefore envisaged that we could take advantage of this increased acidity, and develop a general catalytic Peterson olefination employing low catalyst loading.

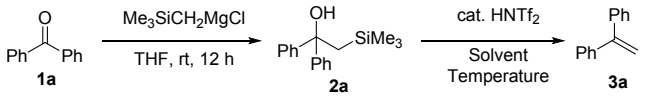
Scheme 2. Previously Reported Catalytic Peterson's



Results and Discussion

We began our investigation using crude **2a,** readily formed by the addition of $TMSCH_2MgCl$ to benzophenone (**1a**) followed by simple DCM workup, and 10 mol% $HNTf_2$ in refluxing DCM. To our delight, the reaction was complete within 15 minutes, affording the 1,1-disubstituted alkene in 90% yield. Reducing the catalyst loading to 1 mol% had little effect on the reaction, nor did running the reaction at room temperature. Further reducing the catalyst loading to 0.1 mol% produced **3a** in 89% yield after 15 minutes. Further attempts to increase the yield through varying the solvent were unsuccessful (Table 1). We also performed the reaction on 5.5 mmol scale, which resulted in effectively the same yield as the small scale reaction.

Table 1. Optimization Studies

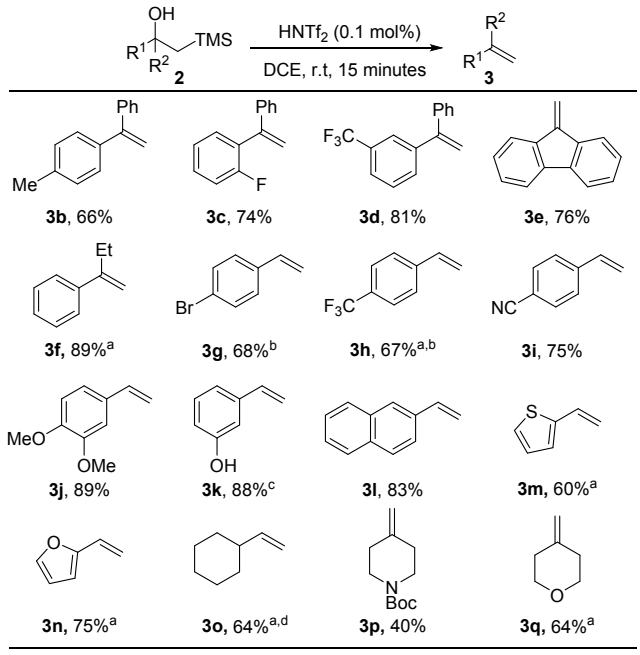


Entry	Cat. loading (mol %)	Solvent	Temp (°C)	Yield (%)[a]
1	10	DCM	40	90
2	1	DCM	40	87
3	1	DCM	rt	85
4	0.1	DCM	rt	88
5	0.1	1,2-DCE	rt	89 (88)[b]
6	0.1	MeCN	rt	88
7	0.1	Acetone	rt	60
8	-	1,2-DCE	rt	n.r

[a] Isolated Yields, [b] 5.5 mmol scale (starting from 1.0 g of **1a**)

With these conditions in hand, we probed the functional group tolerance of the reaction. We initially focused on the use of aldehydes and ketones to provide the corresponding styrenes. As shown, the reaction is tolerant to a range of both aromatic and alkyl substituents, providing the desired olefins in good yield after 15 minutes. Benzophenone derived products all reacted well (**3a-3d),** as did fluorenone (**3e**) and propionphenone (**3f**). Products derived from aldehydes were also synthesized via this methodology, with electron withdrawing groups such as bromide (**3g**) trifluromethyl (**3h**) and cyano (**3i**) providing the styrene in good yields. Electron donating groups also proved successful, giving the desired products (**3j-3l**) efficiently and in good yields. Heterocyclic groups are also well tolerated, with the corresponding thiophene and furan (**3m** and **3n**) derivatives being produced. Finally, this methodology can extend to cyclic alkyl (**3o**) and heteroalkyl (**3p** and **3q**) groups, providing the desired olefins in synthetically useful yields. Of particular note is the compatibility with carbamate protecting groups, which are well known to cause issues in traditional Peterson olefinations.

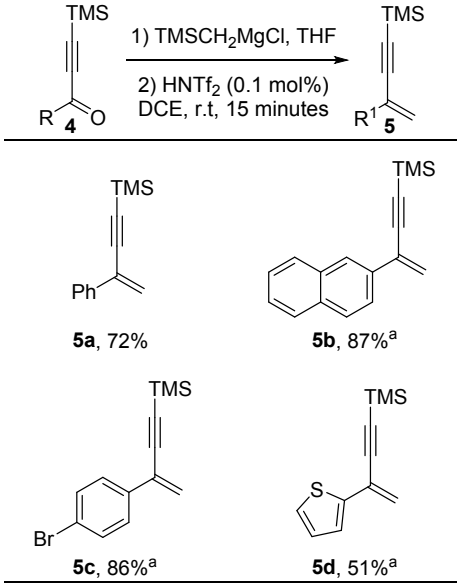
Scheme 3. Substrate Scope



[a] Reaction performed in $CDCl_3$ and the yield was determined through ^1H NMR spectroscopy of the reaction mixture using 1,3,5-trimethoxybenzene as an internal standard; [b] 1 mol% $HNTf_2$ used; [c] Reaction performed in MeCN; [d] 0.5 mol% $HNTf_2$ used

We then turned our attention to the use of readily available propargylic ketones to provide enynes following the Peterson olefination. As shown, the reaction proceeded smoothly, affording the desired enyne products in moderate to high yields (Scheme 4). This is one of very few examples of using the Peterson to produce these high value compounds,[15] and is, to the best of our knowledge, the only catalytic version of the Peterson to achieve this.

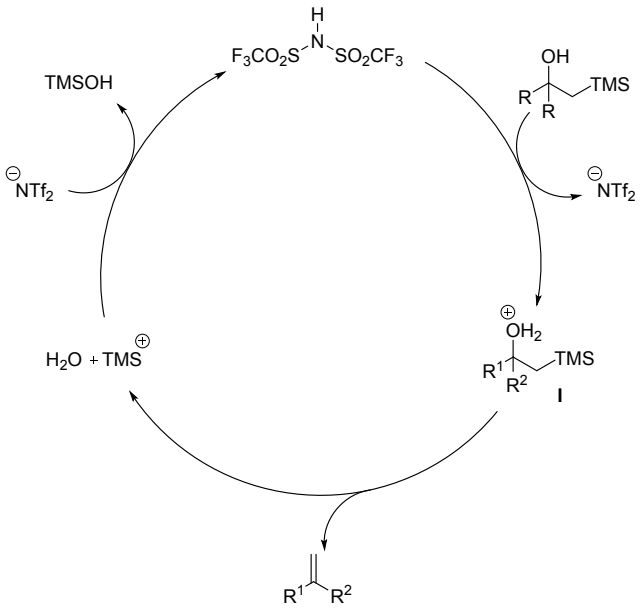
Scheme 4. Synthesis of Enynes



[a] Reaction performed in $CDCl_3$ and the yield was determined through ^1H NMR spectroscopy of the reaction mixture using 1,3,5-trimethoxybenzene as an internal standard

A proposed mechanism is shown below (Figure 1). Owing to the pKa differential between the catalyst and the alcohol, we envisage that a facile deprotonation event occurs. This results in intermediate **I**, which then undergoes elimination to form the desired product. The silylenium cation[16] is then trapped out with water to produce silanol, and the resultant proton generated via this process regenerates the catalyst.

Figure 1. Proposed Catalytic Cycle



In summary, we have developed a highly efficient, one pot catalytic Peterson olefination employing 0.1 mol% bistriflimide as catalyst. As shown, the reaction is tolerant of a range of functional groups, including groups unsuited to the traditional Peterson reaction (**3i, 3k** and **3p)**. We have also investigated the use of propargylic ketones in the reaction, affording a small library of enynes. Investigations towards its applicability in complex natural product synthesis is currently underway.

EXPERIMENTAL SECTION

Solvents and reagents

All solvents were purchased from commercial sources and used without purification (HPLC or analytical grade). Anhydrous solvent was obtained from a Pure Solv™ Solvent Purification System. Standard vacuum line techniques were used and glassware was oven dried prior to use. Organic solvents were dried during workup using anhydrous Na_2SO_4. All calcium catalyzed reactions where done without the need for anhydrous or air free conditions.

Purification and chromatography

Thin Layer Chromatography (TLC) was carried out using aluminum plates coated with 60 F254 silica gel. Plates were visualized using UV light (254 or 365 nm) or staining with 1% aq. $KMnO_4$. Normal-phase silica gel chromatography was carried out using either a Biotage Isolera One flash column chromatography system (LPLC) or traditional flash column chromatography using Geduran® Silica gel 60, 40–63 microns RE.

Characterization

Infrared spectroscopy was carried out with a Nicolet® 380 FT/IR – Fourier Transform Infrared Spectrometer. Only the most significant frequencies have been considered during the characterization and selected absorption maxima (νmax) recorded in wavenumbers (cm^{-1}). NMR spectra were recorded using a JEOL® ECS-400 MHz spectrometer using the deuterated solvent stated. Chemical shifts (δ) quoted in parts per million (ppm) and referenced to the residual solvent peak. Multiplicities are denoted as s- singlet, d- doublet, t- triplet, q- quartet and quin- quintet and derivatives thereof (br denotes a broad resonance peak). Coupling constants recorded as Hz and round to the nearest 0.1 Hz. High Resolution Mass Spectrometry (HRMS) was recorded using an Agilent Technologies® 6540 Ultra-High-Definition (UHD) AccurateMass equipped with a time of flight (Q-TOF) analyzer and the samples were ionized by ESI techniques and introduced through a high pressure oil chromatography (HPLC) model Agilent Technologies® 1260 Infinity Quaternary LC system.

Propargyl ketones **4a-d** were synthesized according to previously published procedures.[17]

General Procedure A: Synthesis of Alkenes. (Trimethylsilylmethyl)magnesium chloride (1.3 M solution in THF, 3.0 equiv.) was added dropwise to a stirred solution of aldehyde/ketone (1.0 equiv.) in THF (0.2 M) at 0 ºC under argon and then stirred at room temperature overnight. The reaction mixture was cooled to 0 ºC and quenched with a saturated aqueous solution of NH_4Cl (5 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL), dried (Na_2SO_4) and evaporated under reduced pressure to give the crude product, which was used without further purification. A stock solution of $HNTf_2$ in 1,2-DCE (0.01 M, 0.1-1.0 mol%) was added in one portion to a stirred solution of the crude product in 1,2-DCE (0.5 M) at room temperature, then stirred for 15 minutes. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography using an appropriate solvent system, as described for each individual procedure. *Note: stock solutions of trifluoromethanesulfonimide in 1,2-DCE were stored in the fridge to avoid decomposition*.

General Procedure B: NMR Reactions in the Synthesis of Alkenes. A stock solution of trifluoromethanesulfonimide in 1,2-DCE (0.01 M, 0.1-1.0 mol%) was added in one portion to a stirred solution of the crude product in $CDCl_3$ (0.5 M) at room temperature, then stirred for 15 minutes. An aliquot of the reaction mixture was removed (0.6 mL, 0.3 mmol of substrate), combined with 1,3,5-trimethoxybenzene and analyzed by ^1H NMR spectroscopy. The amount of alkene present was quantified using the following equation: $n_A = n_{IS} \times r_{A/IS}$, where n_A = mmol of analyte, n_{IS} = mmol of internal standard and $r_{A/IS}$ = ratio of analyte to internal standard (see supporting information for example calculation).

*1,1'-(ethene-1,1-diyl)dibenzene (**3a**)*. Using general procedure A, benzophenone (182 mg, 1.00 mmol) and $HNTf_2$ (0.1 mL, 0.1 mol%) provided alkene **3a** (161 mg, 0.89 mmol, 89%) as a colorless oil after purification by flash column chromatography (eluent: hexane).

R_f (hexane) = 0.38

^1H NMR (400 MHz, $CDCl_3$); δ 7.36–7.32 (m, 5H), 5.47 (s, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 150.2, 141.6, 128.4, 128.3, 127.9, 114.5.

Spectral data in accordance to previously published data.[18]

*1-Methyl-4-(1-phenylethenyl)benzene (**3b**)*. Using general procedure A, 4-methylbenzophenone (196 mg, 1.00 mmol) and $HNTf_2$ (0.1 mL, 0.1 mol%) provided alkene **3b** (133 mg, 0.68 mmol, 68%) as a colorless oil after purification by flash column chromatography (eluent: hexane).

R_f (hexane-EtOAc, 7:1) = 0.59

^1H NMR (400 MHz, $CDCl_3$); δ 7.36–7.31 (m, 5H), 7.25 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 5.44 (d, J = 1.2 Hz, 1H), 5.42 (d, J = 1.2 Hz, 1H), 2.38 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 150.0, 141.8, 138.7, 137.7, 129.0, 128.4, 128.29, 128.26, 127.8, 21.3.

Spectral data in accordance to previously published data.[19]

*1-Fluoro-2-(1-phenylethenyl)benzene (**3c**)*. Using general procedure A, 2-fluorobenzophenone (168 µL, 1.00 mmol) and $HNTf_2$ (0.1 mL, 0.1 mol%) provided alkene **3c** (147 mg, 0.74 mmol, 74%) as a colorless oil after purification by flash column chromatography (eluent: hexane).

R_f (hexane) = 0.26

^1H NMR (400 MHz, $CDCl_3$); δ 7.36–7.27 (m, 7H), 7.17–7.05 (m, 2H), 5.76 (d, J = 1.1 Hz, 1H), 5.43 (s, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 160.3 (d, J_F = 248.5 Hz), 144.3, 140.7, 131.7 (d, J_F = 3.4 Hz), 129.5 (d, J_F = 7.9 Hz), 129.3, 128.4, 127.9, 126.9, 124.1 (d, J_F = 3.6 Hz), 117.2 (d, J_F = 1.7 Hz), 115.9 (d, J_F = 22.2 Hz).

^{19}F (376 MHz, $CDCl_3$) δ -113.1

Spectral data in accordance to previously published data.[20]

*1-(1-Phenylethenyl)-3-(trifluoromethyl)benzene (**3d**)*. Using general procedure A, 3-(trifluoromethyl)benzophenone (249 mg, 1.00 mmol) and $HNTf_2$ (0.1 mL, 0.1 mol%) provided alkene **3d** (199 mg, 0.80 mmol, 81%) as a colorless oil after purification by flash column chromatography (eluent: hexane).

R_f (hexane) = 0.29

^1H NMR (400 MHz, $CDCl_3$); δ 7.62–7.43 (m, 4H), 7.38–7.30 (m, 5H), 5.55 (d, J = 0.6 Hz, 1H), 5.50 (d, J = 0.6 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 149.0, 142.4, 140.7, 131.7, 130.8 (q, J_F = 31.9 Hz), 128.8, 128.5, 128.3, 125.6, 125.1 (q, J_F = 3.5 Hz), 124.6 (q, J_F = 3.6 Hz), 122.9, 115.8.

^{19}F (376 MHz, $CDCl_3$) δ -62.5

Spectral data in accordance to previously published data.[21]

*9-Methylidene-9H-fluorene (**3e**)*. Using general procedure A, 9-fluorenone (181 mg, 1.00 mmol) and $HNTf_2$ (0.1 mL, 0.1 mol%) provided alkene **3e** (135 mg, 0.76 mmol, 76%) as a white solid after purification by flash column chromatography (eluent: hexane).
R_f (hexane) = 0.33
^{1}H NMR (400 MHz, $CDCl_3$); δ 7.76–7.10 (m, 4H), 7.41–7.30 (m, 4H), 6.09 (s, 2H).
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 143.5, 140.3, 138.2, 128.9, 127.2, 121.1, 119.9, 108.0.
Spectral data in accordance to previously published data.[20]

*(But-1-en-2-yl)benzene (**3f**)*. Using general procedure B, propiophenone (130 µL, 0.98 mmol), $HNTf_2$ (0.1 mL, 0.1 mol%) and 1,3,5-trimethoxybenzene (3.0 mg, 0.018 mmol) provided alkene **3f** (89% NMR yield).

*1-Bromo-4-ethenylbenzene (**3g**)*. Using general procedure A, 4-bromobenzaldehyde (187 mg, 1.01 mmol) and $HNTf_2$ (1.0 mL, 1.0 mol%) provided alkene **3g** (126 mg, 0.69 mmol, 68%) as a colorless oil after purification by flash column chromatography (eluent: hexane).
R_f (hexane) = 0.49
^{1}H NMR (400 MHz, $CDCl_3$); δ 7.48–7.43 (m, 2H), 7.30–7.27 (m, 2H), 6.67 (dd, J = 17.6, 11.0 Hz, 1H), 5.78–5.73 (m, 1H), 5.29 (d, J = 11.0 Hz, 1H).
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 136.6, 135.9, 131.8, 127.9, 121.7, 114.8.
Spectral data in accordance to previously published data.[22]

*1-Ethenyl-4-(trifluoromethyl)benzene (**3h**)*. Using general procedure B, 4-(trifluoromethyl)benzaldehyde (140 µL,1.03 mmol), $HNTf_2$ (1.0 mL, 1.0 mol%) and 1,3,5-trimethoxybenzene (4.0 mg, 0.024 mmol) provided alkene **3h** (67% NMR yield).
^{1}H NMR (400 MHz, $CDCl_3$); δ 7.57 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 5.84 (d, J = 17.6 Hz, 1H), 5.37 (d, J = 10.9 Hz, 1H).

*4-Ethenylbenzonitrile (**3i**)*. Using general procedure A, 4-cyanobenzaldehyde (131 mg, 1.00 mmol) and $HNTf_2$ (1.0 mL, 1.0 mol%) provided alkene **3i** (90 mg, 0.75 mmol, 75%) as a colorless oil after purification by flash column chromatography (eluent: hexane:Et_2O, 4:1).
R_f (hexane) = 0.13
^{1}H NMR (400 MHz, $CDCl_3$); δ 7.62–7.50 (m, 2H), 7.49–7.47 (m, 2H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 5.88 (d, J = 17.6 Hz, 1H), 5.45 (d, J = 10.9 Hz, 1H).
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 142.0, 135.5, 132.5, 126.9, 119.1, 117.9, 111.2.
Spectral data in accordance to previously published data.[23]

*4-Ethenyl-1,2-dimethoxybenzene (**3j**)*. Using general procedure A, 3,4-dimethoxybenzaldehyde (168 mg, 1.01 mmol) and $HNTf_2$ (0.1 mL, 0.1 mol%) provided alkene **3j** (147 mg, 0.90 mmol, 89%) as a colorless oil after purification by flash column chromatography (eluent: hexane:Et_2O, 4:1).
R_f (hexane-Et_2O, 4:1) = 0.26
^{1}H NMR (400 MHz, $CDCl_3$); δ 6.98–6.93 (m, 2H), 6.83 (d, J = 8.2 Hz, 1H), 6.66 (dd, J = 17.5, 11.0 Hz, 1H), 5.64–5.59 (m, 1H), 5.15 (dd, J = 11.0, 0.7 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H).
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 149.10, 149.08, 136.6, 130.8, 119.6, 112.0, 111.1, 108.6, 56.1, 55.9.
Spectral data in accordance to previously published data.[24]

*3-Ethenylphenol (**3k**)*. Using general procedure A, 3-hydroxybenzaldehyde (123 mg, 1.01 mmol) and $HNTf_2$ (0.1 mL, 0.1 mol%) provided alkene **3k** (108 mg, 0.89 mmol, 88%) as a colorless oil after purification by flash column chromatography (eluent: hexane:Et_2O, 4:1). *Note: the second step ($HNTf_2$ reaction) was performed in MeCN rather than 1,2-DCE due to solubility issues*.
R_f (hexane-Et_2O, 4:1) = 0.19
^{1}H NMR (400 MHz, $CDCl_3$); δ 7.21 (t, J = 7.9 Hz, 1H), 7.01–6.98 (m, 1H), 6.91–6.90 (m, 1H), 6.76–6.73 (m, 1H), 6.67 (dd, J = 17.4, 11.0 Hz, 1H), 5.73 (d, J = 17.4 Hz, 1H), 5.26 (d, J = 11.0 Hz, 1H), 5.06 (s, 1H).
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 155.8, 139.4, 136.6, 129.9, 119.3, 115.0, 114.5, 112.9.
Spectral data in accordance to previously published data.[25]

*2-Ethenylnaphthalene (**3l**)*. Using general procedure A, 2-naphthaldehyde (157 mg, 1.01 mmol) and $HNTf_2$ (0.1 mL, 0.1 mol%) provided alkene **3l** (129 mg, 0.84 mmol, 83%) as a white solid after purification by flash column chromatography (eluent: hexane).
R_f (hexane) = 0.42
^{1}H NMR (400 MHz, $CDCl_3$); δ 7.86–7.81 (m, 4H), 7.78 (s, 1H), 7.67 (dd, J = 8.6, 1.6 Hz, 1H), 7.51–7.44 (m, 2H), 6.91 (dd, J = 17.6, 10.9 Hz, 1H), 5.90 (d, J = 17.6 Hz, 1H), 5.37 (d, J = 10.9 Hz, 1H).
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 137.1, 135.1, 133.7, 133.3, 128.3, 128.2, 127.8, 126.5, 126.4, 126.0, 123.3, 114.3.
Spectral data in accordance to previously published data.[22]

*2-Ethenylthiophene (**3m**)*. Using general procedure B, 2-thiophenecarboxaldehyde (93 µL, 1.00 mmol), $HNTf_2$ (0.1 mL, 0.1 mol%) and 1,3,5-trimethoxybenzene (3.3 mg, 0.020 mmol) provided alkene **3m** (60% NMR yield).

*2-Ethenylfuran (**3n**)*. Using general procedure B, furfural (83 µL, 1.00 mmol), $HNTf_2$ (0.1 mL, 0.1 mol%) and 1,3,5-trimethoxybenzene (3.0 mg, 0.018 mmol) provided alkene **3n** (75% NMR yield).
^{1}H NMR (400 MHz, $CDCl_3$); δ 7.37–7.33 (m, 1H), 6.51 (dd, J = 17.6, 11.3 z, 1H), 6.37 (dd, J = 3.3, 1.8 Hz, 1H), 6.26 (d, J = 3.3 Hz, 1H), 5.66 (dd, J = 17.6, 1.2 Hz, 1H), 5.16 (dd, J = 11.3, 1.2 Hz, 1H).

*Ethenylcyclohexane (**3o**)*. Using general procedure B, cyclohexanecarboxaldehyde (120 µL, 0.99 mmol), $HNTf_2$ (0.5 mL, 0.5 mol%) and 1,3,5-trimethoxybenzene (3.1 mg, 0.018 mmol) provided alkene **3o** (64% NMR yield).

*tert-Butyl 4-methylidenepiperidine-1-carboxylate (**3p**)*. Using general procedure A, *N*-Boc-4-piperidone (298 mg, 1.50 mmol) and $HNTf_2$ (0.1 mL, 0.1 mol%) provided alkene **3p** (117 mg, 0.59 mmol, 40%) as a colorless oil after purification by flash column chromatography (eluent: hexane:EtOAc, 14:1).
R_f (hexane-EtOAc, 2:1) = 0.61
^{1}H NMR (400 MHz, $CDCl_3$); δ 4.74 (s, 2H), 3.43–3.39 (m, 4H), 2.19–2.16 (m, 4H), 1.46 (s, 9H).
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 154.9, 145.6, 109.2, 79.7, 45.5, 34.7, 28.6.
Spectral data in accordance to previously published data.[26]

*4-Methylideneoxane (**3q**)*. Using general procedure B, 4-oxotetrahydropyran (92 µL, 1.00 mmol), $HNTf_2$ (1.0 mL, 1.0 mol%) and 1,3,5-trimethoxybenzene (3.8 mg, 0.023 mmol) provided alkene **3q** (64% NMR yield).

*Trimethyl(3-phenylbut-3-en-1-yn-1-yl)silane (**5a**)*. Using general procedure A, ketone **4a** (67 mg, 0.33 mmol) and $HNTf_2$ (33 µL, 0.1 mol%) provided enyne **5a** (47 mg, 0.24 mmol, 72%) as a pale yellow oil after purification by flash column chromatography (eluent: hexane). *Note: crude and isolated samples of enynes **5** degraded regardless of storage temperature (See supporting information)*.

R_f (hexane-EtOAc, 2:1) = 0.63

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.66–7.63 (m, 2H), 7.38–7.31 (m, 3H), 5.94 (d, J = 0.8 Hz, 1H), 5.71 (s, 1H), 0.26 (s, 9H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 137.0, 130.7, 128.50, 128.45, 126.2, 121.6, 104.2, 96.0, 0.09.

Spectral data in accordance to previously published data.[27]

*Trimethyl[3-(naphthalen-2-yl)but-3-en-1-yn-1-yl]silane (**5b**)*. Using general procedure B, ketone **4b** (93 mg, 0.37 mmol), $HNTf_2$ (37 µL, 0.1 mol%) and 1,3,5-trimethoxybenzene (3.8 mg, 0.023 mmol) provided enyne **5b** (87% NMR yield).

*[3-(4-bromophenyl)but-3-en-1-yn-1-yl](trimethyl)silane (**5c**)*. Using general procedure B, ketone **4c** (142 mg, 0.51 mmol), $HNTf_2$ (50 µL, 0.1 mol%) and 1,3,5-trimethoxybenzene (3.9 mg, 0.023 mmol) provided enyne **5c** (86% NMR yield).

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.51–7.44 (m, 4H), 5.91– 5.89 (m, 1H), 5.71– 5.70 (m, 1H), 0.24 (s, 9H).

*Trimethyl[3-(thiophen-2-yl)but-3-en-1-yn-1-yl]silane (**5d**)*. Using general procedure B, ketone **4d** (104 mg, 0.50 mmol), $HNTf_2$ (50 µL, 0.1 mol%) and 1,3,5-trimethoxybenzene (2.1 mg, 0.013 mmol) provided enyne **5d** (51% NMR yield).ASSOCIATED CONTENT

Supporting Information

Copies of spectra and exemplar yield calculation.

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Notes

The authors declare no competing financial interests.

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