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Metal- and Acid-Free Methyl Triflate Catalyzed Meyer–Schuster Rearrangement

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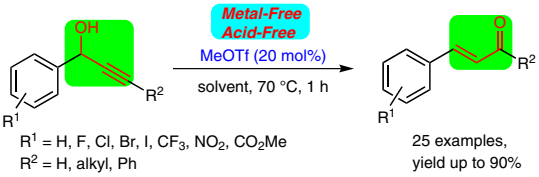

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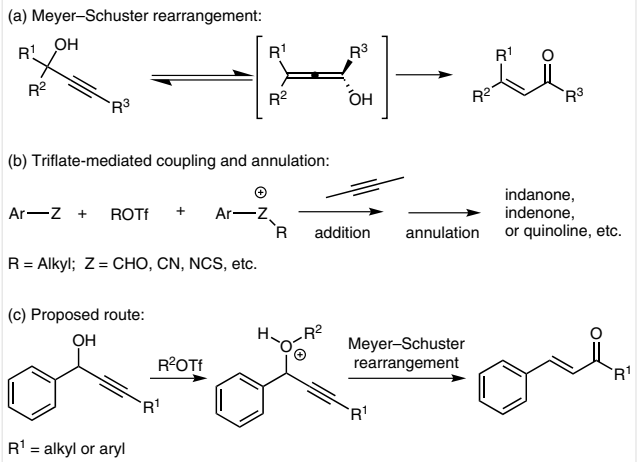
Abstract A novel metal- and acid-free preparation of synthetically useful α,β-unsaturated carbonyl compounds from propargyl alcohols has been realized. This Meyer–Schuster rearrangement process is effectively catalyzed by methyl triflate (20 mol%) to prepare a broad scope of conjugated *E*-enals and *E*-enones generally in good to excellent yields (up to 90%). This reaction procedure operates under mild conditions (70 °C), in air, with short reaction times (1 h). Moreover, a carbocation intermediate trapped by the solvent 2,2,2-trifluoroethanol was isolated during this transformation.

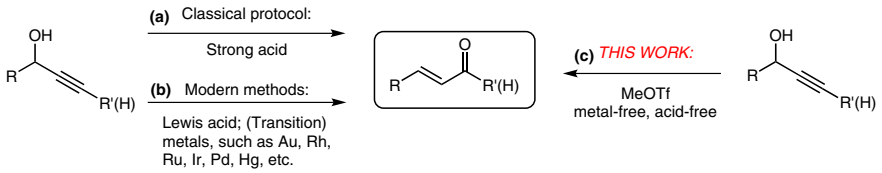
Key words Meyer–Schuster rearrangement, methyl triflate, propargyl alcohols, α,β-unsaturated carbonyl compounds, metal-free, acid-free

Compounds with conjugated enone and enal skeletons are valuable and versatile for the synthesis of pharmaceuticals, biological active natural products, perfumes, and agrochemicals.[1] Many methodologies have been revealed for synthesizing α,β-unsaturated carbonyl compounds.[2] However, these methods more or less suffer from multiple steps and poor atom economy.

The Meyer–Schuster rearrangement (Scheme 1 and Scheme 2 a),[3] first discovered by Meyer and Schuster in 1922, which involves the conversion of propargyl alcohols into enone-type structures, is attractive from the atom economy feature.[4] However, the scope of this reaction is severely limited due to the poor chemoselectivity and requirements of harsh reaction conditions, such as strong acid and high temperature (Scheme 1 a).[5] In recent years, various catalysts, such as transition metals and Lewis acids, have been utilized in this transformation (Scheme 1 b).[6] Nevertheless, there are some shortcomings, for example, costly and/or noxious catalysts, requirements of special preparation and handling, and long reaction times. This has left room for the development of new alternative catalytic systems.



Scheme 2 Design of the methyl triflate catalyzed Meyer–Schuster rearrangement



Scheme 1 Synthetic strategies for the Meyer–Schuster rearrangement

Recently, several triflate-mediated coupling reactions and annulations have been reported (Scheme 2 b),[7] in which alkyl triflates as an electrophile reacts with aldehyde or cyanide to give the oxonium or *N*-methylnitrilium ion, which reacts with alkyne to form highly reactive intermediates followed by formation of annulation products.

Inspired by these works, we envisioned that propargyl alcohol could undergo a related process when treated with triflates (Scheme 2 c). Herein, we report methyl triflate (MeOTf)-catalyzed Meyer–Schuster rearrangement of propargyl alcohols to afford α,β-unsaturated carbonyl compounds under metal-free, mild conditions (Scheme 1 c and Scheme 2 c).

To begin validating our hypothesis, 1-phenylprop-2-yn-1-ol (**1a**) was selected as the model substrate (Table 1) and treated with 20 mol% MeOTf in dichloroethane (DCE) at 70 °C under air for 1 hour. Surprisingly, the desired product, cinnamaldehyde (**2a**), was formed in 20% yield (Table 1, entry 6). Then, other solvents, such as acetonitrile, tetrahydrofuran, dimethyl sulfoxide, dimethylformamide, ethyl alcohol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoroisopropanol were screened (entries 2, 4–9). Among them, TFE was found to be the best one (entry 2). The addition of water decreased the yields (entries 10, 11). Next, varying amounts of the catalyst (entries 1–3) were tried; under 10 mol% MeOTf, propargyl alcohol was not fully transformed, and 20 mol% MeOTf turned out to be the best.

The effects of other triflates were investigated: EtOTf gave a moderate yield of 55% with a prolonged reaction time (Table 1, entry 12), whereas PhOTf had no catalytic ability on this transformation (entry 13). Increase or decrease of the reaction temperature had no positive effects on this reaction (entries 14 and 15). A control experiment was also conducted (entry 16). Therefore, propargyl alcohol **1a** (1 equiv) and MeOTf (0.2 equiv) in CF_3CH_2OH (0.5 mL) at 70 °C under air were chosen as the optimized reaction conditions (entry 2).

The scope of the substrates was examined next using the optimal reaction conditions (Scheme 3). First, the effects of other leaving groups at the propargylic position were evaluated by synthesizing the acetate and methyl ether analogues **1b** and **1c**. To our surprise, both precursors afforded enal **2a** in moderate yields (65% and 64%, respectively).

Next, the functional group compatibility was examined by utilizing various substituted propargyl alcohols **1d–l**. Substrates **1d–k**, without electron-donating groups (EDG) on the phenyl ring, gave the cinnamaldehydes in moderate to good yields. In addition, when (*E*)-1-phenylpent-1-en-4-yn-3-yl acetate (**1l**) was used in this reaction, a 35% yield of product (2*E*,4*E*)-5-phenylpenta-2,4-dienal (**2l**) was obtained.

When tertiary alcohols **1m–p**, with symmetric aryl groups, were used as substrate in this reaction system, 3,3-diarylacroleins were obtained in good to excellent yields with MeCN as solvent. However, the asymmetric tertiary alcohol **1q** afforded moderate yield of the product **2q** with an *E*/*Z* ratio of 1.7:1; whereas **2r** gave only 30% yield, due to the formation of a lot of by-products.

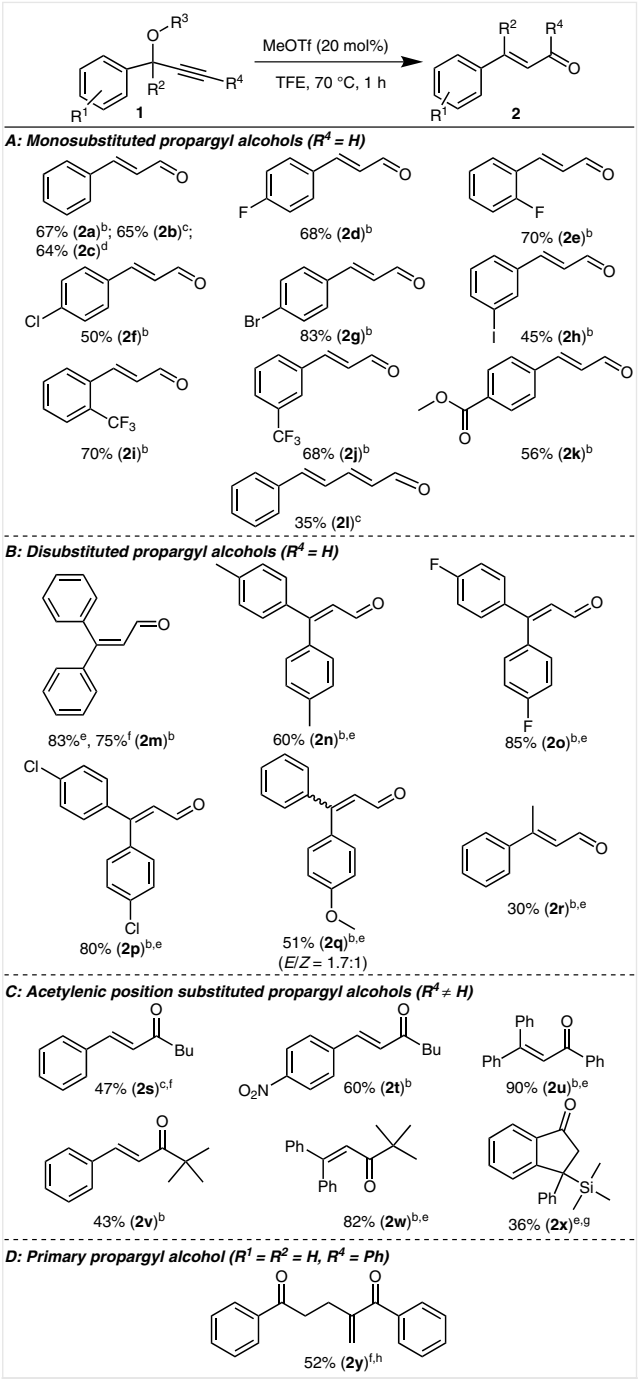
The influence of acetylenic substitution on the substrates **1s–x** was then studied. Moderate yields were obtained in the presence of butyl (**1s**, **1t**, **1v**, **1w**), and the acetate analogue gave better results when the reaction was performed in DCE (**1s**). Gratifyingly, **1v** and **1w** also gave good yields. Therefore, it is believed that the steric hindrance did not affect the reactivity remarkably. 1,3,3-Triphenylprop-2-en-1-one (**2u**) was produced in excellent yield, highlighting the efficiency of this synthetic methodology.

It should be noted that 3-phenyl-3-(trimethylsilyl)-2,3-dihydroinden-1-one (**2x**) was isolated when TMS-containing alkyne was used as the substrate. This outcome corresponds to the reported result.[6b] According to the proposed mechanism,[6b] the propargylic alcohol undergoes Meyer–Schuster rearrangement under MeOTf-catalyzed conditions. Then an intramolecular S_EAr reaction led to the formation of five-membered ring. Eventually, the product was obtained via two successive 1,2-shifts. The primary propargyl alcohol, 3-phenylprop-2-yn-1-ol (**1y**), afforded the dimeric diketone product **2y**,[6a] which was believed to have formed as a consequence of Michael addition of allenol in-

Table 1 Optimization of the Reaction Conditions for 1-Phenylprop-2-yn-1-ol (**1a**)[a]

Entry	Solvent	Catalyst (equiv)	Temp (°C)	Time (h)	Yield (%)[b]
1	TFE	MeOTf (0.3)	70	1	60
2	**TFE**	**MeOTf (0.2)**	**70**	**1**	**67**
3	TFE	MeOTf (0.1)	70	1	30
4	HFIP	MeOTf (0.2)	r.t.	1	trace
5	DMSO	MeOTf (0.2)	70	1	N.R.
6	DCE	MeOTf (0.2)	70	1	20
7	EtOH	MeOTf (0.2)	70	16	trace
8	MeCN	MeOTf (0.2)	70	6	23
9	DMF	MeOTf (0.2)	70	1	N.R.
10	TFE[c]	MeOTf (0.2)	70	1	15
11	TFE[d]	MeOTf (0.2)	70	12	35
12	TFE	EtOTf (0.2)	70	2	55
13	TFE	PhOTf (0.2)	70	1	N.R.
14	TFE	MeOTf (0.2)	80	1	45
15	TFE	MeOTf (0.2)	50	1	60
16	TFE	–	70	2	N.R.

[a] Reactions were carried out with 0.3 mmol of 1-phenylprop-2-yn-1-ol.
[b] Isolated yield; N.R. = no reaction.
[c] TFE/H_2O = 5:1.
[d] 1 equiv H_2O was added.

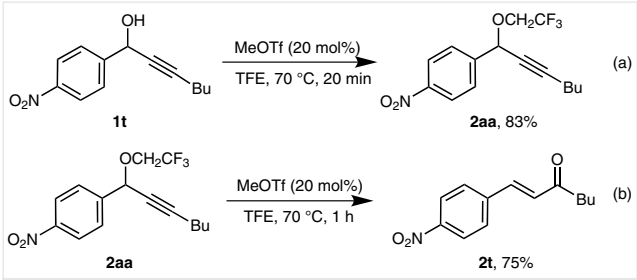


Scheme 3 Substrate scope.[a] *Reagents and conditions*: **1** (0.3 mmol) and MeOTf (0.06 mmol) in TFE (DCE, or MeCN), 70 °C, 1 h. [a] Isolated yields are shown. [b] R^3 = H. [c] R^3 = Ac. [d] R^3 = Me. [e] MeCN was used as solvent. [f] DCE was used as solvent. [g] **1w**: 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ol. [h] **1y**: 3-phenylprop-2-yn-1-ol.

termediate from Meyer–Schuster rearrangement of the primary propargyl alcohol. These two examples support the involvement of a Meyer–Schuster rearrangement pathway in this transformation.

In general, starting materials with different organic functional groups, including F (**1d**, **1e**, **1o**), Cl (**1f**, **1p**), Br (**1g**), I (**1h**), Me (**1n**), OMe (**1q**), CF_3 (**1i**, **1j**), ester (**1k**), NO_2 (**1t**), and styryl (**1l**) delivered the corresponding products in good yields, whereas the substrates possessing electron-withdrawing groups have higher yields than those with electron-donating groups. Tertiary alcohols and acetylenic substituted substrates also gave satisfactory results. Owing to the broad functional group and mild reaction conditions of this methodology, enormous potential for further functionalization of the rearrangement products is provided, particularly in complex natural product synthesis.

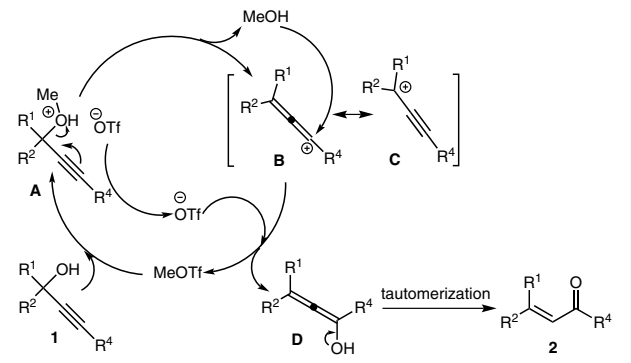
To gain more information for the mechanism of this transformation, more experiments were performed. Initially, **1t** was treated with MeOTf under the optimized conditions for 20 minutes. Intriguingly, **2aa** was isolated in 83% yield (Scheme 4 a), and the desired product **2t** was obtained in 75% yield (Scheme 4 b) when **2aa** transformed in the standard conditions. Undoubtedly, carbocation was formed as an intermediate during the reaction. It is noteworthy that although lots of additional reactions conducted in TFE have been proposed, the propensity of TFE to behave as a nucleophile has rarely been observed.[8]



Scheme 4 Control experiments

Based on the experimental results mentioned above, as well as reported literature,[7e,9] we propose a plausible mechanism (Scheme 5). First, MeOTf reacts with **1** to give the oxonium ion **A**, which produces trifluoromethanesulfonate ion and the highly active, tautomerizing carbocation intermediates **B** and **C**. Then the MeOH from **A** acts as a nucleophile to attack **B** producing **D**, which undergoes spontaneous isomerization to give product **2**, and with regeneration of MeOTf. In most cases, due to the highly activity of carbocation **B**, the trifluoroethoxylation products were not isolated, whereas when the carbocation produced from **1** was vulnerable to TFE's attack, trifluoroethoxylation species **2aa** formed, which further supports this carbocation reaction mechanism.

In summary, we have described a novel method of MeOTf-catalyzed transformation that enables the formation of conjugated *E*-enones and -enals from easily accessible propargyl alcohols. To the best of our knowledge, this is the first MeOTf-catalyzed Meyer–Schuster rearrangement.

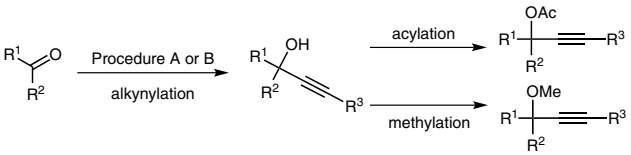


Scheme 5 A plausible reaction mechanism

This process occurs under mild conditions and does not require the addition of acid or metal. Furthermore, our study gained an insight into the mechanistic aspects of this transformation and led to the proposal of carbocation intermediate generated in situ from propargyl alcohols.

Solvents and reagents were purchased from Alfa Aesar, Sigma-Aldrich, TCI, and J & K chemical companies, and used without further purification, unless otherwise indicated. The products were purified by flash column chromatography by using gradient elution (PE and EtOAc) of the Still protocol. ^{1}H, ^{13}C, and ^{19}F NMR were recorded on a Bruker Avance 400 spectrometer at ambient temperature. All signals were recorded in δ units, parts per million (ppm) with the internal reference of 7.26 ppm or 77.0 ppm for $CDCl_3$ as the reference. Multiplicity data are reported using standard abbreviations. Coupling constants (*J*) are given in hertz (Hz). High-resolution mass spectra (HRMS) were performed on a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method. IR spectra were obtained with a PerkinElmer Spectrum One FTIR Spectrometer. These Compounds have been previously described in the literature: **2a–e**,[10] **2f**,[11] **2g**,[12] **2h**,[13] **2i**,[14] **2j**,[10] **2k**,[15] **2l**,[16] **2m–p**,[17] **2q**,[16] **2r**,[18] **2s**,[19] **2t**,[20] **2u**,[21] **2v**,[22] **2w**,[22] **2x**,[23] **2y**.[24]

Propargylic Alcohols, and Their Acetate and Methyl Ether Analogues; General Procedure (Scheme 6)



Scheme 6 Synthesis of propargylic alcohols, and their acetate and methyl ether analogues

Alkynylation[19,25]

1,1-Di(*p*-tolyl)prop-2-yn-1-ol (1n);[25] Typical Procedure

Procedure A: In a 50 mL oven-dried round-bottomed flask were placed di(*p*-tolyl) ketone (630 mg, 3 mmol, 1 equiv) and anhyd THF (15 mL) under N_2. Ethynylmagnesium bromide (0.5 M in THF, 775 mg, 6 mmol, 2 equiv) was added to the solution at 0 °C and the reaction was allowed to warm up to r.t. After stirring for 3–4 h, the reaction was quenched with sat. aq NH_4Cl (5 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine, dried (anhyd $MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (silica gel) with PE/EtOAc as eluent to give the propargylic alcohol **1n**[25] as a yellow oil; yield: 602 mg (85%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.56 – 7.50 (m, 4 H), 7.18 (d, *J* = 8.0 Hz, 4 H), 2.89 (s, 1 H), 2.83 (s, 1 H), 2.37 (s, 6 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 141.76, 137.59, 129.00, 125.92, 86.70, 75.24, 74.07, 21.12.

1-Phenylhept-2-yn-1-ol;[19] Typical Procedure

Procedure B: In an oven-dried round-bottomed flask, hex-1-yne (320 mg, 3.9 mmol, 1.3 equiv) and *n*-BuLi 1.6 M (3.6 mmol, 1.2 equiv) were added to THF (15 mL) and stirred for 20 min under N_2 at –78 °C. To the reaction mixture, benzaldehyde (318 mg, 3 mmol, 1 equiv) was added and the mixture was stirred for 20 min. The reaction was then allowed to warm up to r.t. and quenched with sat. aq NH_4Cl (5 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine, dried (anhyd $MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (silica gel) with PE/EtOAc as eluent to give 1-phenylhept-2-yn-1-ol[19] as a solid; yield: 741 mg (87%); mp 80–82 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78–7.29 (m, 15 H), 2.96 (s, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 145.03, 131.82, 128.73, 128.37, 128.36, 127.78, 126.10, 122.44, 91.73, 87.28, 74.88.

Acylation[19]

1-Phenylhept-2-ynyl Acetate (1s);[19] Typical Procedure

1-Phenylhept-2-yn-1-ol (188 mg, 1 mmol, 1 equiv), anhyd CH_2Cl_2 (5 mL), 4-(dimethylamino)pyridine (36 mg, 0.3 mmol, 0.3 equiv), Et_3N (404 mg, 4 mmol, 4 equiv), and Ac_2O (204 mg, 2 mmol, 2 equiv) were added to a round-bottomed flask. The reaction mixture was stirred at r.t. for 10 min. The reaction was then quenched with sat. aq NH_4Cl (5 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine, dried (anhyd $MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (silica gel) with PE/EtOAc as eluent to give **1s**[19] as a colorless oil; yield: 269 mg (88%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.55 (dd, *J* = 7.7, 1.4 Hz, 2 H), 7.44–7.34 (m, 3 H), 6.49 (d, *J* = 1.8 Hz, 1 H), 2.30 (td, *J* = 7.1, 2.0 Hz, 2 H), 2.12 (s, 3 H), 1.60–1.51 (m, 2 H), 1.44 (tt, *J* = 14.1, 7.0 Hz, 2 H), 0.94 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 169.91, 137.71, 128.73, 128.56, 127.72, 88.38, 76.69, 66.08, 30.50, 21.98, 21.20, 18.56, 13.59.

Methylation[25]

1-(1-Methoxyprop-2-ynyl)benzene (1c)[25]

To a round-bottomed flask were added anhyd THF (15 mL) and NaH (60% dispersion in paraffin oil, 60 mg, 1.5 mmol, 1.5 equiv) under N_2. 1-Phenylprop-2-yn-1-ol (132 mg, 1 mmol, 1 equiv) was added to the solution at 0 °C and the mixture was stirred for 30 min. MeI (284 mg, 2 mmol, 2 equiv) was added to the solution and the mixture was warmed up to r.t. for 4 h. The reaction was then quenched with sat. aq NH_4Cl (5 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine, dried

(anhyd $MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography (silica gel) with PE/EtOAc as eluent to give **1c**[25] as a colorless oil; yield: 133 mg (91%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.58–7.52 (m, 2 H), 7.40 (tdd, *J* = 6.9, 4.6, 2.2 Hz, 3 H), 5.13 (d, *J* = 2.0 Hz, 1 H), 3.48 (s, 3 H), 2.69 (d, *J* = 2.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 137.97, 128.58, 128.55, 127.35, 81.29, 75.79, 72.81, 55.94.

Methyl Triflate Catalyzed Meyer–Schuster Rearrangement; Cinnamaldehyde (2a); Typical Procedure

To a 25 mL round-bottomed flask were added 1-phenylprop-2-yn-1-ol (**1a**; 40 mg, 0.3 mmol), TFE (0.5 mL), and MeOTf (6 μL, 0.06 mmol, 0.2 equiv). Then the flask was immersed in a 70 °C preheated oil bath and the mixture was stirred for 1 h. After completion, the solution was removed and the residue was subject to flash chromatography (silica gel) with PE/EtOAc as eluent to afford the desired rearrangement product **2a**[10] as a colorless oil; yield: 27 mg (67%).

Cinnamaldehyde (2a, 2b, 2c)[10] (Scheme 3)

Colorless oil; yield: **2a** 27 mg (67%); **2b** 26 mg (65%); **2c** 25 mg (64%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.74 (d, *J* = 7.7 Hz, 1 H), 7.60 (dd, *J* = 6.7, 2.8 Hz, 2 H), 7.51 (d, *J* = 16.0 Hz, 1 H), 7.46 (dd, *J* = 5.0, 1.8 Hz, 3 H), 6.75 (dd, *J* = 16.0, 7.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 193.72, 152.79, 134.04, 131.30, 129.13, 128.64, 128.52.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_9O^+$: 133.0648; found: 133.0654.

(*E*)-3-(4-Fluorophenyl)acrylaldehyde (2d)[10]

Yellow oil; yield: 31 mg (68%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.72 (d, *J* = 7.6 Hz, 1 H), 7.63–7.56 (m, 2 H), 7.47 (d, *J* = 16.0 Hz, 1 H), 7.16 (t, *J* = 8.6 Hz, 2 H), 6.68 (dd, *J* = 16.0, 7.6 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 193.45, 164.47 (d, *J* = 253.1 Hz), 151.32, 130.51 (d, *J* = 8.7 Hz), 130.33 (d, *J* = 3.4 Hz), 128.39 (d, *J* = 2.2 Hz), 116.39 (d, *J* = 22.1 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_8FO^+$: 151.0554; found: 151.0556.

(*E*)-3-(2-Fluorophenyl)acrylaldehyde (2e)[10]

Yellow oil; yield: 32 mg (70%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.75 (d, *J* = 7.7 Hz, 1 H), 7.69 (d, *J* = 16.2 Hz, 1 H), 7.62 (td, *J* = 7.7, 1.4 Hz, 1 H), 7.49–7.42 (m, 1 H), 7.24 (t, *J* = 7.6 Hz, 1 H), 7.20–7.13 (m, 1 H), 6.82 (dd, *J* = 16.2, 7.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 193.82, 161.22 (d, *J* = 254.8 Hz), 144.79 (d, *J* = 3.6 Hz), 132.88 (d, *J* = 8.9 Hz), 130.54 (d, *J* = 5.3 Hz), 128.79 (d, *J* = 2.5 Hz), 124.70 (d, *J* = 3.6 Hz), 122.17 (d, *J* = 11.6 Hz), 116.36 (d, *J* = 21.7 Hz).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_9H_7FONa^+$: 173.0373; found: 173.0376.

(*E*)-3-(4-Chlorophenyl)acrylaldehyde (2f)[11]

Light yellow solid; yield: 25 mg (50%); mp 59–60 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.73 (d, *J* = 7.6 Hz, 1 H), 7.55–7.51 (m, 2 H), 7.49–7.41 (m, 3 H), 6.72 (dd, *J* = 16.0, 7.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.42, 151.10, 137.30, 132.49, 129.63, 129.46, 128.96.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_8ClO^+$: 167.0102; found: 167.0104.

(*E*)-3-(4-Bromophenyl)acrylaldehyde (2g)[12]

Pale yellow solid; yield: 53 mg (83%); mp 78–79 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.73 (d, *J* = 7.6 Hz, 1 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.44 (dd, *J* = 12.3, 5.3 Hz, 3 H), 6.72 (dd, *J* = 16.0, 7.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.37, 151.11, 132.92, 132.42, 129.80, 129.04, 125.70.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_9H_7BrONa^+$: 232.9572; found: 232.9569.

(*E*)-3-(3-Iodophenyl)acrylaldehyde (2h)[13]

Yellow solid; yield: 35 mg (45%); mp 34–35 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.73 (d, *J* = 7.6 Hz, 1 H), 7.92–7.95 (m, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.56 (d, *J* = 7.8 Hz, 1 H), 7.40 (d, *J* = 16.0 Hz, 1 H), 7.20 (t, *J* = 7.8 Hz, 1 H), 6.72 (dd, *J* = 16.0, 7.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.22, 150.59, 139.92, 137.25, 136.13, 130.71, 129.58, 127.46, 94.83.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_8IO^+$: 258.9614; found: 258.9621.

(*E*)-3-[2-(Trifluoromethyl)phenyl]acrylaldehyde (2i)[14]

Yellow solid; yield: 42 mg (70%); mp 43–44 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (d, *J* = 7.6 Hz, 1 H), 7.91 (dd, *J* = 15.8, 1.8 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 2 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 6.73 (dd, *J* = 15.8, 7.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.33, 147.51 (q, *J* = 2.1 Hz), 132.69 (q, *J* = 1.4 Hz), 132.05, 131.78, 130.50, 128.93 (q, *J* = 30.6 Hz), 128.03, 126.41 (q, *J* = 5.6 Hz), 123.89 (q, *J* = 274.0 Hz).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_7F_3ONa^+$: 223.0341; found: 223.0335.

(*E*)-3-[3-(Trifluoromethyl)phenyl]acrylaldehyde (2j)[10]

Yellow oil; yield: 41 mg (68%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.78 (d, *J* = 7.5 Hz, 1 H), 7.85–7.70 (m, 3 H), 7.62 (d, *J* = 7.8 Hz, 1 H), 7.54 (d, *J* = 16.0 Hz, 1 H), 6.80 (dd, *J* = 16.0, 7.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 193.13, 150.38, 134.78, 131.49 (q, *J* = 32.8 Hz), 131.19, 130.04, 129.72, 127.58 (q, *J* = 3.5 Hz), 125.17 (q, *J* = 3.8 Hz), 123.65 (q, *J* = 272.4 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_8F_3O^+$: 201.0522; found: 201.0516.

(*E*)-Methyl 4-(3-Oxoprop-1-enyl)benzoate (2k)[15]

White solid; yield: 32 mg (56%); mp 103–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.77 (d, *J* = 7.6 Hz, 1 H), 8.12 (d, *J* = 8.3 Hz, 2 H), 7.66 (d, *J* = 8.3 Hz, 2 H), 7.53 (d, *J* = 16.0 Hz, 1 H), 6.81 (dd, *J* = 16.0, 7.6 Hz, 1 H), 3.97 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.31, 166.26, 150.86, 138.08, 132.22, 130.39, 130.27, 128.31, 52.41.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{10}O_3Na^+$: 213.0522; found: 213.0531.

(2*E*,4*E*)-5-Phenylpenta-2,4-dienal (2l)[16]

Yellow oil; yield: 17 mg (56%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.66 (d, *J* = 8.0 Hz, 1 H), 7.56–7.51 (m, 2 H), 7.44–7.37 (m, 3 H), 7.35–7.31 (m, 1 H), 7.06–7.02 (m, 2 H), 6.30 (dd, *J* = 15.0, 8.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 193.65, 152.11, 142.48, 135.60, 131.65, 129.72, 128.97, 127.56, 126.21.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{10}ONa^+$: 181.0629; found: 181.0632.

3,3-Diphenylacrylaldehyde (2m)[17]

Yellow oil; yield: 52 mg (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.56 (d, *J* = 8.0 Hz, 1 H), 7.54–7.44 (m, 4 H), 7.41–7.38 (m, 4 H), 7.35–7.32 (m, 2 H), 6.63 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.61, 162.33, 139.74, 136.70, 130.78, 130.54, 129.50, 128.72, 128.66, 128.38, 127.31.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{12}ONa^+$: 231.0780; found: 231.0782.

3,3-Di(*p*-tolyl)acrylaldehyde (2n)[17]

Yellow oil; yield: 42 mg (60%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.54 (d, *J* = 8.0 Hz, 1 H), 7.30–7.26 (m, 4 H), 7.24–7.19 (m, 4 H), 6.58 (d, *J* = 8.0 Hz, 1 H), 2.46 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 193.78, 162.59, 140.97, 139.64, 137.14, 133.92, 130.85, 129.33, 128.99, 128.78, 126.46, 21.40, 21.39.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{16}ONa^+$: 259.1093; found: 259.1089.

3,3-Bis(4-fluorophenyl)acrylaldehyde (2o)[17]

Yellow oil; yield: 62 mg (85%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.52 (d, *J* = 7.9 Hz, 1 H), 7.38–7.29 (m, 4 H), 7.22–7.15 (m, 2 H), 7.13–7.07 (m, 2 H), 6.56 (d, *J* = 7.9 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 192.89, 164.24 (d, *J* = 252.4 Hz), 163.55 (d, *J* = 250.6 Hz), 159.85, 135.74 (d, *J* = 3.2 Hz), 132.61 (d, *J* = 8.4 Hz), 132.46 (d, *J* = 3.5 Hz), 130.68 (d, *J* = 8.6 Hz), 127.36, 115.90 (d, *J* = 21.8 Hz), 115.73 (d, *J* = 21.8 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}F_2O^+$: 245.0772; found: 245.0770.

3,3-Bis(4-chlorophenyl)acrylaldehyde (2p)[17]

Yellow oil; yield: 66 mg (80%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.53 (d, *J* = 7.9 Hz, 1 H), 7.49–7.44 (m, 2 H), 7.40–7.36 (m, 2 H), 7.32–7.24 (m, 4 H), 6.58 (d, *J* = 7.9 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 192.69, 159.42, 137.79, 136.99, 136.06, 134.62, 131.99, 129.88, 129.08, 128.91, 127.72.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{11}Cl_2O^+$: 277.0181; found: 277.0173.

3-(4-Methoxyphenyl)-3-phenylacrylaldehyde (2q)[16]

Yellow oil; yield: 36 mg (51%) (*E*/*Z* =1.7:1).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.59 (d, *J* = 8.0 Hz, 1 H, *Z*-CHC*H*O), 9.48 (d, *J* = 8.1 Hz, 1 H, *E*-CHC*H*O), 7.51–7.27 (m, 14 H, *Z*/*E*-ArH), 6.99 (d, *J* = 8.7 Hz, 2 H, *Z*-ArH), 6.92 (d, *J* = 8.9 Hz, 2 H, *E*-ArH), 6.59 (d, *J* = 8.1 Hz, 1 H, *E*-C*H*CHO), 6.56 (d, *J* = 7.9 Hz, 1 H, *Z*-C*H*CHO), 3.91 (s, 3 H, *Z*-OCH_3), 3.87 (s, 3 H, *E*-OCH_3).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 193.67, 193.60, 162.32, 162.03, 161.70, 160.86, 140.29, 138.18, 136.91, 132.57, 131.89, 130.69, 130.44, 130.33 , 129.34, 128.97, 128.57, 128.30, 127.05, 125.60, 114.06, 113.75, 55.45, 55.43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{14}O_2Na^+$: 261.0886; found: 261.0882.

(*E*)-3-Phenylbut-2-enal (2r)[18]

Yellow oil; yield: 13 mg (30%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.22 (d, *J* = 7.9 Hz, 1 H), 7.60–7.56 (m, 2 H), 7.45 (dd, *J* = 4.2, 2.3 Hz, 3 H), 6.45 – 6.40 (m, 1 H), 2.61 (s, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 191.30, 157.68, 140.56, 130.11, 128.77, 127.30, 126.28, 16.42.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{10}ONa^+$: 169.0624; found: 169.0616.

(*E*)-1-Phenylhept-1-en-3-one (2s)[19]

Colorless oil; yield: 27 mg (47%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ =7.61–7.58 (m, 2 H), 7.58–7.55 (m, 1 H), 7.45–7.40 (m, 3 H), 6.77 (d, *J* = 16.2 Hz, 1 H), 2.70 (t, *J* = 7.5 Hz, 2 H), 1.70 (dt, *J* = 15.3, 7.6 Hz, 2 H), 1.42 (dd, *J* = 15.0, 7.5 Hz, 2 H), 0.97 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 200.70, 142.31, 134.61, 130.38, 128.94, 128.25, 126.28, 40.70, 26.51, 22.48, 13.94.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{16}ONa^+$: 211.1093; found: 211.1089.

(*E*)-1-(4-Nitrophenyl)hept-1-en-3-one (2t)[20]

Yellow solid; yield: 42 mg (60%); mp 60–61 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.28 (d, *J* = 8.7 Hz, 2 H), 7.72 (d, *J* = 8.7 Hz, 2 H), 7.59 (d, *J* = 16.2 Hz, 1 H), 6.87 (d, *J* = 16.2 Hz, 1 H), 2.72 (t, *J* = 7.4 Hz, 2 H), 1.76–1.66 (m, 2 H), 1.42 (dd, *J* = 15.0, 7.5 Hz, 2 H), 0.97 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 199.85, 148.53, 140.88, 139.09, 129.57, 128.79, 124.20, 41.30, 26.19, 22.40, 13.91.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{15}NO_3Na^+$: 256.0944; found: 256.0942.

1,3,3-Triphenylprop-2-en-1-one (2u)[21]

Yellow oil; yield: 76 mg (90%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.97–7.91 (m, 2 H), 7.51 (t, *J* = 7.4 Hz, 1 H), 7.44–7.38 (m, 7 H), 7.32–7.28 (m, 3 H), 7.22 (dd, *J* = 6.5, 3.2 Hz, 2 H), 7.15 (s, 1 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 2192.74, 154.77, 141.39, 139.03 138.25, 132.70, 129.77, 129.38 128.77, 128.62, 128.47, 128.40, 128.39, 128.08, 124.05.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{21}H_{17}O^+$: 285.1274; found: 285.1282.

(*E*)-4,4-Dimethyl-1-phenylpent-1-en-3-one (2v)[22]

Yellow oil; yield: 24 mg (43%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.71 (d, *J* = 15.6 Hz, 1 H), 7.63–7.59 (m, 2 H), 7.43–7.40 (m, 3 H), 7.16 (d, *J* = 15.6 Hz, 1 H), 1.26 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 204.30, 142.92, 134.96, 130.22, 128.88, 128.31, 120.74, 43.29, 26.34.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{16}ONa^+$: 211.1093; found: 211.1083.

4,4-Dimethyl-1,1-diphenylpent-1-en-3-one (2w)[22]

Colorless oil; yield: 65 mg (82%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.38 (dd, *J* = 3.9, 2.6 Hz, 5 H), 7.36 (d, *J* = 2.0 Hz, 1 H), 7.34–7.32 (m, 1 H), 7.32–7.30 (m, 1 H), 7.20–7.16 (m, 2 H), 6.94 (s, 1 H), 1.24 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 205.46, 154.60, 141.81, 139.45, 129.21, 129.07, 128.40, 128.38, 128.00, 121.59, 44.14, 26.63.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{20}ONa^+$: 287.1406; found: 287.1405.

3-Phenyl-3-(trimethylsilyl)-2,3-dihydroinden-1-one (2x)[23]

Orange oil; yield: 30 mg (36%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86–7.82 (m, 1 H), 7.73–7.67 (m, 2 H), 7.42 (m, 1 H), 7.39–7.35 (m, 2 H), 7.35–7.30 (m, 2 H), 7.23–7.18 (m, 1 H), 3.28 (d, *J* = 19.6 Hz, 1 H), 3.03 (d, *J* = 19.6 Hz, 1 H), –0.01 (s, 9 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 205.65, 159.11, 144.54, 136.61, 134.30, 128.44, 127.71, 126.87, 126.71, 125.58, 124.20, 49.83, 42.99, –2.74.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{20}OSiNa^+$: 303.1176; found: 303.1177.

2-Methylene-1,5-diphenylpentane-1,5-dione (2y)[24]

Colorless oil; yield: 41 mg (52%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.01 (d, *J* = 7.6 Hz, 2 H), 7.76 (d, *J* = 7.6 Hz, 2 H), 7.57 (s, 2 H), 7.47 (d, *J* = 9.8 Hz, 4 H), 5.99 (s, 1 H), 5.71 (s, 1 H), 3.27 (t, *J* = 7.3 Hz, 2 H), 2.95 (t, *J* = 7.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 199.27, 198.14, 146.81, 137.79, 136.80, 133.11, 132.24, 129.50, 128.63, 128.22, 128.11, 127.26, 37.25, 27.41.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}O_2^+$: 265.1223; found: 265.1224.

1-Nitro-4-[1-(2,2,2-trifluoroethoxy)hept-2-ynyl]benzene (2aa)

To a 25 mL round-bottomed flask were added into 1-(4-nitrophenyl)hept-2-yn-1-ol (70 mg, 0.3 mmol), TFE 0.5 mL, and MeOTf (6 μL, 0.06 mmol, 0.2 equiv.). Then the flask was immersed in a 70 °C preheated oil bath and the mixture was stirred for 20 min. After completion of the reaction, the solution was concentrated and the residue was subjected to flash chromatography on silica gel with PE/EtOAc as eluent to afford the desired rearrangement product **2aa** as a light yellow oil; yield: 0.078 g (83%).

IR (film): 3433, 2958, 2938, 2874, 2225, 1609, 1527, 1494, 1458, 1431, 1352, 1279, 1165, 1109, 971, 854 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.29–8.25 (m, 2 H), 7.75–7.71 (m, 2 H), 5.49 (s, 1 H), 4.05 (qd, *J* = 8.6, 2.0 Hz, 2 H), 2.35 (td, *J* = 7.1, 2.0 Hz, 2 H), 1.60–1.54 (m, 2 H), 1.51–1.40 (m, 2 H), 0.96 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 148.00, 144.64, 128.12, 123.85 (q, $J_{C,F}$ = 278.6 Hz). 123.76, 91.91, 74.75, 71.55, 64.95 (q, $J_{C,F}$ = 34.8 Hz), 30.42, 22.00, 18.47, 13.54.

^{19}F NMR ($CDCl_3$, 376 MHz): δ = –73.54.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{16}F_3NO_3Na^+$: 338.0974; found: 338.0968.

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Supporting Information

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