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Saucy-Marbet Rearrangements of Alkynyl Halides in the Synthesis of Highly Enantiomerically Enriched Allenyl Halides

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Abstract

A stereospecific Saucy-Marbet rearrangement of alkynyl halides is described here. These rearrangements provide an entry to highly enantiomerically enriched allenyl bromides and chlorides through excellent chirality transfer and the reservation of optical integrity of alkynyl halides.

Allenes are among the most powerful building blocks in organic synthesis.[1,2] Recently, both Trost[3] and we[4] communicated copper(I)-catalyzed amidations of allenyl halides **2** en route to an atom-economical synthesis of allenamides **4** [Scheme 1], a class of heteroatom-substituted allenes that have attracted much attention from the synthetic community.[1,2,5–8] Specifically in our work,[4] the cross-coupling is completely stereospecific when employing enantiomerically enriched allenyl halides **2-*P*** and **2-*M*** [Scheme 1].

However, we were met with the challenge of preparing optically pure allenyl halides. With the exception of diastereosel ective examples,[9,10] for axially chiral allenyl halides such as **2**, the level of enantiomeric enrichment was at best modest even when employing known conditions starting from mesylation of optically pure propargyl alcohols *(R)*-**1** and (S)-**1**.[1,2,11,12] Our interest[13] in both the Saucy-Marbet rearrangement for the synthesis of chiral allenes[9,14–16] and reactivities of alkynyl halides such as **5**[17,18] prompted us to explore the synthesis of en antiomerically pure allenyl halides **7** by uniting the two concepts.[19] We communicate here the concept of employing a stereospecific Saucy-Marbet rearrangement of alkynyl halides in the synthesis of highly enantiomerically enriched allenyl halides.

Conditions for the proposed rearrangement could be readily established using racemic alkynyl halides as shown in Table 1 Alkynyl iodide **8** was not as effective as alkynyl bromide **9** [entry 1 versus 2], and an acid catalyst such as AcOH was critical [entries 3–6] and so was the optimal temperature of 100 °C [entry 5 versus 6]. With these conditions in hand, enantiomerically pure alkynyl bromides *(R)*- and *(S)*-**9**[20] were prepared from their respective chiral propargyl alcohol *(R)*- and *(S)*-**12** using $AgNO_3$ and NBS [Scheme 2]. Subsequent Saucy-Marbet rearrangements led to the respective allenyl bromides **11-*P*** and **11-*M*** in good yields over two steps. Given the ability of [3,3]-sigmatropic rearrangements to conserve and transfer chirality, these reactions should be highly stereoselective through intermediates *(R)*- and *(S)*-**13**, leading to **11-*P*** and **11-*M*** with high levels of enantiomeric purity. Representative examples of these

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rearrangements of allenyl halides are shown in Figure 1 in which both allenyl bromides and chlorides could be accessed.

To unambiguously confirm that these rearrangements indeed gave allenyl halides possessing high levels of enantiomeric purity, in the absence of a conclusive chiral HPLC analysis, we attained enantiomeric ratios by examining ratios of the respective diast ereomeric derivatives. Reduction of allenyl bromide **11-*P*** using DIBAL and subsequent esterification of the resulting alcohol using Cbz-protected *L*-proline led to homo-allenyl ester **18-*P*** in 44% overall yield with a diastereomeri c ratio of ≥ 95:5, thereby reflecting a high degree of optical purity of **11-*P*** [Scheme 3]. Likewise, allenyl bromide **14-*P*** could be transformed into homo-allenyl ester **19-*P*** using *(S)*-2-(6-methoxynaphthalen-2-yl)-propanoic acid [or naproxen].

Overall, with the exception of **14-*P*** and **14-*M*** [see **19-*M*** for the *dr*], all other allenyl halides are of high enantiomeric purity. Currently, we are not certain as to the source of erosion during the rearrangement of alkynyl bromides *(R)*- and *(S)*-**15**. Nevertheless, this new protocol allows better preservation and transference of the optical integrity from chiral propargyl alcohols to allenyl halides. It is also noteworthy that the concept that we have established here is not limited to commercially available optically pure propargyl alcohols. Asymmetric protocols such as asymmetric reductions of acetylenic ketones[21] and acetylene c additions to aldehydes [22] should in principle provide practical access to a diverse array of allenyl halides [Figure 2].

In addition to their usage in amidative cross-couplings for the synthesis of allenamides, allenyl halides are well known as highly useful synthons in organic transformations.[23] To showcase one of the possible transformations with these enantiomerically pure allenyl halides, we investigated the propargyl trichlorosilane addition to benzyaldehyde employing known conditions[24] and allenyl bromides **11-*P*** and **11-*M*** [Scheme 4]. The respective addition products, allenols **22**-*[P,S]* and **22**-*[M,R]*, were isolated in good yields and high diastereoesel ectivity.

The stereochemistry of the benzylic carbon was assigned using Mosher's ester anaylsis.[25] The high degree of diastereosel ectivity suggests excellent chirality transfer from allenyl bromides **11-*P*** and **11-*M***. This chirality transfer lilely proceed through allenyl copper intermediates **23-P** and **23-*M*** and also *(S)* and *(R)*-propargyl tricholorosilanes shown in the Zimmermann-Traxler transition states [TS-*S* and TS-*R*] for the ensuing addition.[24] Stereochemical assignments of **22**-*[P,S]* and **22**-*[M,R]* also imply a *syn*-facial transmetallation of copper intermediates **23-*P*** and **23-*M*** with $HSiCl_3$ as shown in **24**.

We have described here the concept of employing a stereospecific Saucy-Marbet rearrangement of alkynyl halides in the synthesis of highly enantiomerically enriched allenyl bromides and chlorides. Further applications employing these allenyl halides are underway.

Acknowledgments

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20. **General Procedure for the Synthesis and Rearrangement of Alkynyl Halides**. *Alkynyl Bromides*. A solution of a respective propargyl alcohol [1.0 equiv] and $AgNO_3$ [20 mol %] in acetone [1.0 *M*] was stirred at rt for 25 min. After which, NBS [1.1 equiv] was added. The reaction was stirred at rt for overnight before filtrated through a small pad of Celite™. The filtrate was concentrated and the crude bromo-propargyl alcohol was used for the next step without further purification.*Alkynyl Chlorides*. A solution of a respective propargyl alcohol [1.0 equiv] in THF [0.2 *M*] was added *n*-BuLi

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(1.6 M in hexane) [2.2 equiv] at −78 °C, and after 10 min, NCS [2.2 equiv] was added into the mixture. The reaction mixture was stirred at −78 °C for 1h, and the ice bath was removed to allow the mixture to warm up to rt. After The reaction was stirred at r.t. for 10 min. The mixture was then diluted with H_2O [20 mL] and extracted with CH_2Cl_2 [150 mL]. The organic layer was dried [$MgSO_4$]. The solution was distilled under reduced pressure. The crude chloro-propargyl alcohol was used for the next step without further purification.*Rearrangement*. To a solution of an alkynyl halide prepared above in anhyd toluene [0.2 *M*] were added triethyl orthoacetate [2.0 equiv] and acetic acid [5 mol %], and the reaction mixture was heated for 18 h at 100 °C in a sealed tube. The solvent was removed under reduced pressure, and the crude residue was purified using flash silica gel column chromatography [gradient eluent: 0–10% ether in pentane] to provide allenyl bromide as yellow oil.**For characterizations, see: 11-*P:*** [56.8 mg, 55% yield]. R_f = 0.57 [25% EtOAc in hexanes]; $[\alpha]_D^{20}$ = 82.0 (c 0.64 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, 3 H, *J* = 7.2 Hz), 1.77 (d, 3 H, *J* = 7.2 Hz), 3.41 (d, 2 H, *J* = 2.0 Hz), 4.18 (q, 2 H, *J* = 7.2 Hz), 5.33 (qt, 1 H, *J* = 7.2, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.3, 43.9, 61.3, 83.3, 94.6, 169.2, 202.1; IR (thin film) cm^{-1} 2981w, 1734s, 1156w, 1033w; mass spectrum (ESI): m/e (% relative intensity) 241.2 (100) $(M + Na)^+$, 243.2 (83) $(M + 2 + Na)^+$. **11-*M:*** [51.2 mg, 51% yield]. R_f = 0.57 [25% EtOAc in hexanes]; $[\alpha]_D^{20}$ = − 83.0 (c 0.53 in CH_2Cl_2); 1H NMR (500 MHz, $CDCl_3$) δ 1.26 (t, 3 H, *J* = 7.5 Hz), 1.78 (d, 3 H, *J* = 7.0 Hz), 3.41 (d, 2 H, *J* = 2.0 Hz), 4.17 (q, 2 H, *J* = 7.5 Hz) , 5.33 (qt, 1 H, *J* = 7.5, 2.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 14.6, 44.1, 61.5, 83.3, 94.7, 169.3, 202.1; IR (thin film) cm^{-1} 2981w, 1939s, 1167s, 1032w; mass spectrum (ESI): m/e (% relative intensity) 241.2 (100) $(M + Na)^+$, 243.2 (83) $(M + 2 + Na)^+$.**14-*P:*** [22.1 mg, 40% yield]. R_f = 0.68 [33% EtOAc in hexanes]; $[\alpha]_D^{20}$ = 85.0 (c 0.43 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (t, 3 H, *J* = 7.5 Hz), 3.57 (dq, 2 H, *J* = 2.0, 16.5 Hz), 4.21 (q, 2 H, *J* = 7.0 Hz), 6.29 (t, 1 H, *J* = 2.0 Hz), 7.25–7.41 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 44.1, 61.7, 86.6, 101.4, 128.4, 128.9, 129.1, 132.3, 169.0, 202.4; IR (thin film) cm^{-1} 2981w, 1734s, 1235m, 1178s, 1027m; mass spectrum (ESI): m/e (% relative intensity) 303.3 (75) $(M + Na)^+$, 305.3 (72) $(M + 2 + Na)^+$. **14-*M:*** [24.3 mg, 42% yield]. R_f = 0.68 [33% EtOAc in hexanes]; $[\alpha]_D^{20}$ = − 123.0 (c 0.63 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (t, 3 H, *J* = 7.5 Hz), 3.56 (dq, 2 H, *J* = 2.5, 16.5 Hz), 4.21 (q, 2 H, *J* = 7.5 Hz), 6.29 (t, 1 H, *J* = 2.0 Hz), 7.26–7.41 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 44.1, 61.7, 86.6, 101.4, 128.4, 128.9, 129.1, 132.3, 169.0, 202.4; IR (thin film) cm^{-1} 1737s, 1220s, 1014m; mass spectrum (ESI): m/e (% relative intensity) 303.3 (100) $(M + Na)^+$; 305.3 (100) $(M + 2 + Na)^+$.**16-*P:*** [28.7 mg, 52% yield]. R_f = 0.67 [33% EtOAc in hexanes]; $[\alpha]_D^{20}$ = 127.0 (c 0.96 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89–0.92 (m, 3 H), 1.26–1.33 (m, 7 H), 1.46–1.48 (m, 2 H), 2.13 (dq, 2 H, *J* = 3.0, 7.5 Hz), 3.44 (d, 2 H, *J* = 2.5 Hz), 4.20 (q, 2 H, *J* = 7.0 Hz), 5.37–5.42 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.1, 22.3, 27.8, 28.4, 31.1, 43.9, 61.1, 83.7, 99.6, 168.9, 201.0; IR (thin film) cm^{-1} 2928m, 1735s, 1157m, 1032m; mass spectrum (ESI): m/e (% relative intensity) 297.3 (100) $(M + Na)^+$, 299.3 (99) $(M + 2 + Na)^+$. **16-*M***: [24.9 mg, 48% yield]. R_f = 0.67 [33% EtOAc in hexanes]; $[\alpha]_D^{20}$ = − 106.0 (c 0.81 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81–0.91 (m, 3 H), 1.20–1.29 (m, 7 H), 1.36–1.44 (m, 2 H), 2.06 (dq, 2 H, *J* = 3.0, 7.5 Hz) , 3.36 (s, 2 H), 4.13 (q, 2 H, *J* = 7.5 Hz), 5.31–5.35 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.1, 22.4, 27.8, 28.4, 31.1, 43.9, 61.1, 83.8, 99.6, 168.8, 201.1; IR (thin film) cm^{-1} 2927m, 1734s, 1156m, 1031m; mass spectrum (ESI): m/e (% relative intensity) 297 (100) $(M + Na)^+$, 299.3 (98) $(M + 2 + Na)^+$.**17-*P:*** [25.5 mg, 46% yield]. R_f = 0.65 [10% MTBE in hexanes]; $[\alpha]_D^{20}$ = 20.9 (c 2.5 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88–0.91 (m, 3 H), 1.23–1.36 (m, 7 H), 1.42–1.50 (m, 2 H), 2.11 (q, 2 H, *J* = 7.5 Hz), 3.32 (d, 2 H, *J* = 2.0 Hz), 4.19 (q, 2 H, *J* = 7.2 Hz), 5.60–5.63 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 14.4, 22.7, 28.1, 29.2, 31.4, 42.9, 61.4, 98.3, 101.2, 169.2, 201.0; IR (thin film) cm^{-1} 2929m, 2369s, 1734m, 1158w; mass spectrum (ESI): m/e (% relative intensity) 253.4 (90) $(M + Na)^+$. **17-*M:*** [9.3 mg, 46% yield]. R_f = 0.65 [10% MTBE in hexanes]; $[\alpha]_D^{20}$ = − 18.5 (c 1.90 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88–0.92 (m, 3 H), 1.25–1.40 (m, 7 H), 1.42–1.50 (m, 2 H), 2.12 (q, 2 H, *J* =7.2 Hz), 3.33 (d, 2 H, *J* = 1.8 Hz), 4.20 (q, 2 H, *J* = 6.9 Hz), 5.59–5.67 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.1, 22.4, 27.8, 28.9, 31.2, 42.6, 61.2, 98.0, 100.9, 168.9, 200.8; IR (thin film) cme^{-1} 2929m, 2364s, 1734m, 1158w; mass spectrum (ESI): m/e (% relative intensity) 253.4 (18) $(M + Na)^+$.**General Procedure of DIBAL-H Reduction and Esterification.** A solution of a respective allenyl bromide [or chloride] in toluene [0.2 *M*] was cooled to 0 °C followed the addition of DIBAL-H [2.2 equiv]. The reaction mixture was stirred for 2 h at 0 °C before it was quenched by MeOH and diluted by EtOAc. A sat aq K/Na-tartrate solution was then added and the mixture was stirred for another 2–4 h until it was separated as two clear layers. The aqueous layer

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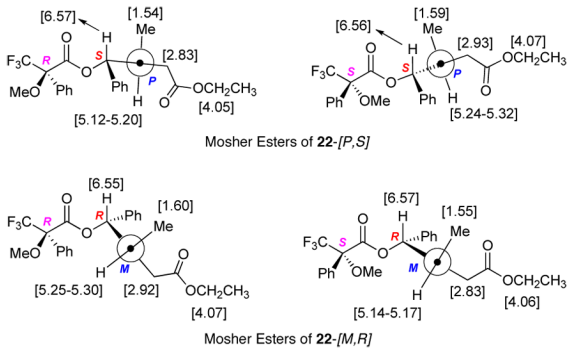
was extracted twice with EtOAc [equal volume] after separation. The combined organic extracts were concentrated under reduced pressure, and the crude alcohol was used for the next step without further purification.To a solution of the above crude alcohol, carboxylic acid [1.5 equiv], and DMAP [0.1 equiv] in CH_2Cl_2 [0.2 *M*] was added a solution of DCC [1.5 equiv] in CH_2Cl_2 [0.6 *M*] at 0 °C. After which, the reaction was allowed to warm to rt and stirred overnight before filtrated through a small pad of Celite™. The filtrate was concentrated under reduced pressure, and the crude residue was purified using flash silica gel column chromatography [gradient eluent: 0–10% EtOAc in hexanes] to provide the corresponding ester.**For selected characterizations, see: 18-*P:*** [9.10 mg, 44% yield]. R_f = 0.57 [50% EtOAc in hexanes]; $[\alpha]_D^{20}$ = − 4.40 (c 3.15 in CH_2Cl_2); "&" indicates rotamers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.76 (t, 3 H, *J* = 7.5 Hz), 1.90–2.02 (m, 3 H), 2.19-2.02 (m, 1 H), 2.56–2.59 (m, 1 H), 2.70–2.74 (m, 1 H), 3.46–3.56 (m, 1 H), 3.59–3.65 (m, 1 H), 4.01–4.16 (m, 1 H), 4.23–4.31 (m, 1 H), 4.36 & 4.40 (dd, 1 H, *J* = 4.0, 9.0 Hz), 5.07–5.19 (m, 2 H), 6.26-5.33 (m, 1 H), 7.29–7.37 (m, 5 H); IR (thin film) cm^{-1} 2953w, 1698s, 1417m, 1350w, 1166m, 1116w, 1058w; mass spectrum (ESI): m/e (% relative intensity) 430.5 (100) $(M + Na)^+$, 432.5 (98) $(M + 2 + Na)^+$. **18-*M:*** [8.50 mg, 42% yield]. R_f = 0.57 [50% EtOAc in hexanes]; $[\alpha]_D^{20}$ = − 63.0 (c 8.65 in CH_2Cl_2); "&" indicates rotamers. ^{1}H NMR (500 MHz, Toluene-d_8) δ 1.38 (dd, 3 H, *J* = 7.5, 33.0 Hz), 1.46–1.62 (m, 3 H), 2.05–2.10 (m, 1 H), 2.26-2.10 (m, 1 H), 2.41–2.44 (m, 1 H), 3.05–3.07 & 3.23–3.28 (m, 1 H), 3.32–3.37 & 3.45–3.52 (m, 1 H), 3.94 (t, 1 H, *J* = 6.0 Hz), 4.04 (t, 1 H, *J* = 6.0 Hz), 4.08–4.11 & 4.27–4.30 (m, 1 H), 4.92–5.14 (m, 3 H), 6.98–7.19 (m, 5 H); IR (thin film) cm^{-1} 2955m, 1698s, 1417m, 1350m, 1167s, 1116w, 1085; mass spectrum (ESI): m/e (% relative intensity) 430.5 (100) $(M + Na)^+$, 432.5 (98) $(M + 2 + Na)^+$.**21-*P***: [19.0 mg, 80% yield]. R_f = 0.10 [20% EtOAc in hexanes]; $[\alpha]_D^{20}$ = 38.0 (c 0.56 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 7.0 Hz), 1.20–1.39 (m, 6 H), 1.57 (d, 3 H, *J* = 7.5 Hz), 1.97 (dt, 2 H, *J* = 7.5, 14.0 Hz), 2.56–2.65 (m, 2 H), 3.85 (q, 1 H, *J* = 8.0 Hz), 3.91 (s, 3 H), 4.17–4.28 (m, 2 H), 5.32–5.37 (m, 1 H), 7.10–7.16 (m, 2 H), 7.38–7.42 (m, 1 H), 7.65–7.72 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 18.9, 22.7, 28.3, 29.3, 31.4, 36.0, 45.7, 55.6, 62.0, 101.2, 101.4, 105.8, 119.2, 126.2, 126.5, 127.4, 129.2, 129.5, 134.0, 135.8, 157.9, 174.7, 199.7; IR (thin film) cm^{-1} 2928w, 1734s, 1154m, 1032w; mass spectrum (ESI): m/e (% relative intensity) 423.6 (100) $(M + Na)^+$, 425.6 (29) $(M + 2 + Na)^+$. **21-*M:*** [24.0 mg, 83% yield]. R_f = 0.10 [20% EtOAc in hexanes]; $[\alpha]_D^{20}$ = − 1.50 (c 0.55 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 7.5 Hz), 1.20–1.34 (m, 6 H), 1.29–1.31 (m, 2 H), 1.57 (d, 3 H, *J* = 7.5 Hz), 1.93 (q, 2 H, *J* = 7.0 Hz) , 2.60 (dt, 2 H, *J* = 2.5, 6.5 Hz), 3.85 (q, 1 H, *J* = 7.5 Hz), 3.92 (s, 3 H), 4.17–4.27 (m, 2 H), 5.23–5.29 (m, 1 H), 7.10–7.16 (m, 2 H), 7.39–7.42 (m, 1 H), 7.65–7.73 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 18.8, 22.7, 28.3, 29.3, 31.4, 36.0, 45.7, 55.6, 62.0, 101.2, 101.4 105.8, 119.3, 126.2, 126.5, 127.4, 129.2, 129.5, 134.0, 135.9, 157.9, 174.7, 199.6; IR (thin film) cm^{-1} 2930w, 1733s, 1233w, 1174w, 1033w; mass spectrum (ESI): m/e (% relative intensity) 423.6 (100) $(M + Na)^+$, 425.6 (29) $(M + 2 + Na)^+$.**General Procedure for Addition of Allenyl Bromides 11-P to Benzaldehyde**. To a stirred solution of allenyl bromide **11-*P*** [1.0 equiv] in THF [0.5 *M*] were added CuCl [0.10 equiv], $HSiCl_3$ [2.0 equiv] and $^iPr_2NEt$ [2.0 equiv], successively at rt. The mixture was stirred at 40 °C for 6 h. After which, DMF-CH_3CN [0.5 *M*, 1:1 v/v] was added and the mixture was cooled to 0 °C. Then benzaldehyde [1.0 equiv] was added and the mixture was remained at 0 °C for 18 h before quenched with cold H_2O and extracted with ether. The extract was washed with sat aq NaCl, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified using flash silica gel column chromatography [gradient eluent: 0–50% EtOAc in hexanes] to provide the allenylic alcohol.**For characterizations, see: 22-*[P,S]***: [7.10 mg, 57% yield]. R_f = 0.23 [20% EtOAc in hexanes]; $[\alpha]_D^{20}$ = − 21.0 (c 1.05 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, 3 H, *J* = 7.2 Hz), 1.69 (d, 3 H, *J* = 7.2 Hz), 2.91 (dq, 2 H, *J* = 2.0, 16.4Hz), 3.20–3.22 (m, 1H), 4.10 (q, 2 H, *J* = 7.2 Hz), 5.28–5.30 (m, 1 H), 5.31–5.37 (m, 1 H), 7.24–7.39 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 14.5, 35.5, 61.3, 74.6, 90.0, 101.2, 126.6, 127.8, 128.4, 142.1, 172.7, 203.4; IR (thin film) cm^{-1} 2981w, 1733m, 1716s, 1156m, 1025m; mass spectrum (MALDI): m/e (% relative intensity) 269 (100) $(M + Na)^+$; *m/e* calcd for $C_{15}H_{18}O_3Na^+$ 269.1148, found 269.1152. **22-*[M,R]***: [4.40 mg, 51% yield]. R_f = 0.23 [20% EtOAc in hexanes]; $[\alpha]_D^{20}$ = 18.8 (c 1.85 in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, 3 H, *J* = 6.8 Hz), 1.69 (d, 3 H, *J* = 6.8 Hz), 2.91 (dq, 2 H, *J* = 2.0, 16.4 Hz), 3.18–3.22 (m, 1H), 4.11 (q, 2 H, *J* = 7.2 Hz), 5.28–5.30 (m, 1 H), 5.31–5.40 (m, 1 H), 7.24–7.39 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 14.5, 35.5, 61.3, 74.6, 90.0, 101.2, 126.6, 127.8, 128.4, 142.1, 172.7, 203.4; IR (thin film) cm^{-1} 2982w, 1733m, 1716m, 1157w, 1025m; mass spectrum (MALDI): m/e (% relative intensity) 269 (100) $(M + Na)^+$; *m/e* calcd for $C_{15}H_{18}O_3Na^+$ 269.1148, found 269.1148.

21. For leading references on such asymmetric reductions, see:(a) Bach J, Berenguer R, Garcia J, Loscertales T, Vilarrasa J. J. Org. Chem 1996;61:9021. [PubMed: 11667889] (b) Helal CJ, Magriotis PA, Corey EJ. J. Am. Chem. Soc 1996;118:10938. (c) Matsumura K, Hashiguchi S, Ikariya T, Noyori R. J. Am. Chem. Soc 1997;119:8738. (d) Parker KA, Ledeboer MW. J. Org. Chem 1996;61:3214. [PubMed: 11667191]
22. For reviews on asymmetric additions of acetylenes to carbonyl systems, see:(a) Pu L, Yu H-B. Chem. Rev 2001;101:757. [PubMed: 11712502] (b) Pu L. Tetrahedron 2003;59:9873. (c) Walsh PJ. Acc. Chem. Res 2003;36:739. [PubMed: 14567707]
23. For a review, see:(a) Marshall, JA.; Gung, BW.; Grachan, ML. Modern Allene Chemistry. Krause, N.; Hashmi, ASK., editors. Vol. Vol 1. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; 2004. p. 493-592. (b) Marshall JA. Chem. Rev 1996;96:31. [PubMed: 11848743]
24. For leading references on allenyl silane chemistry employing $HSiCl_3$ and CuCl, see:(a) Kobayashi S, Nisho K. J. Am. Chem. Soc 1995;117:6392. (b) Kobayashi S, Nishio K. J. Org. Chem 1994;59:6620. (c) Becker DA, Danheiser RL. J. Am. Chem. Soc 1989;111:389. (d) Calas R. J. Organomet. Chem 1980;200:11. (e) Marshall JA, Adams ND. J. Org. Chem 1997;62:8976.
25. Respective proton chemical shifts are in the brackets.



Mosher Esters of **22**-*[P,S]*

Mosher Esters of **22**-*[M,R]*

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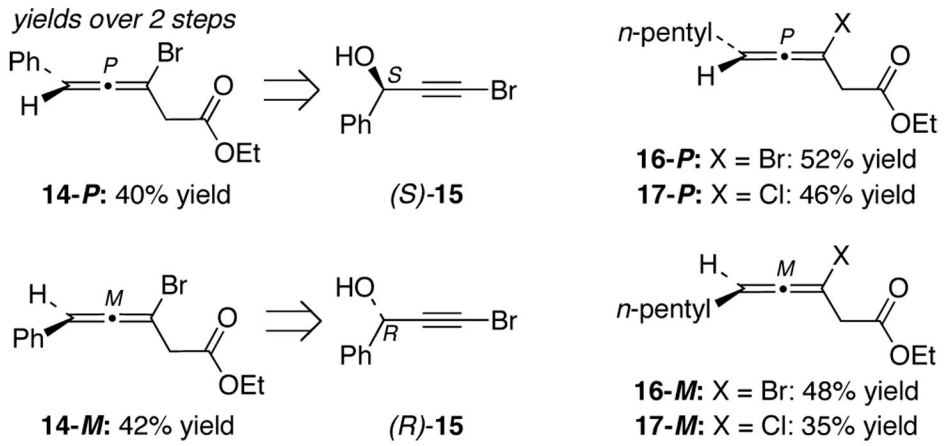

Figure 1.
Highly Enantiomerically Pure Allenyl Halides.

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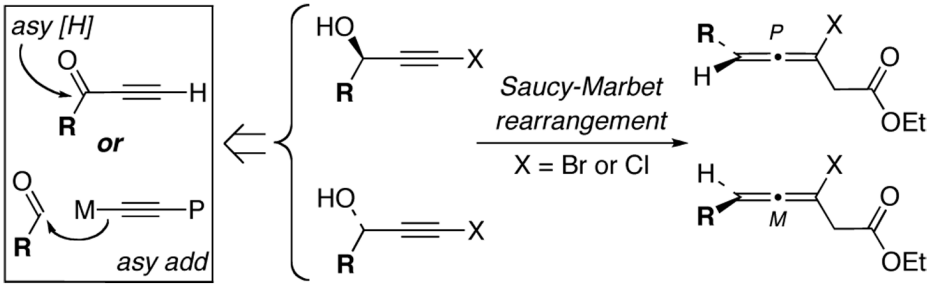

Figure 2.
A Concept of Accesing Chiral Allenyl Halides.

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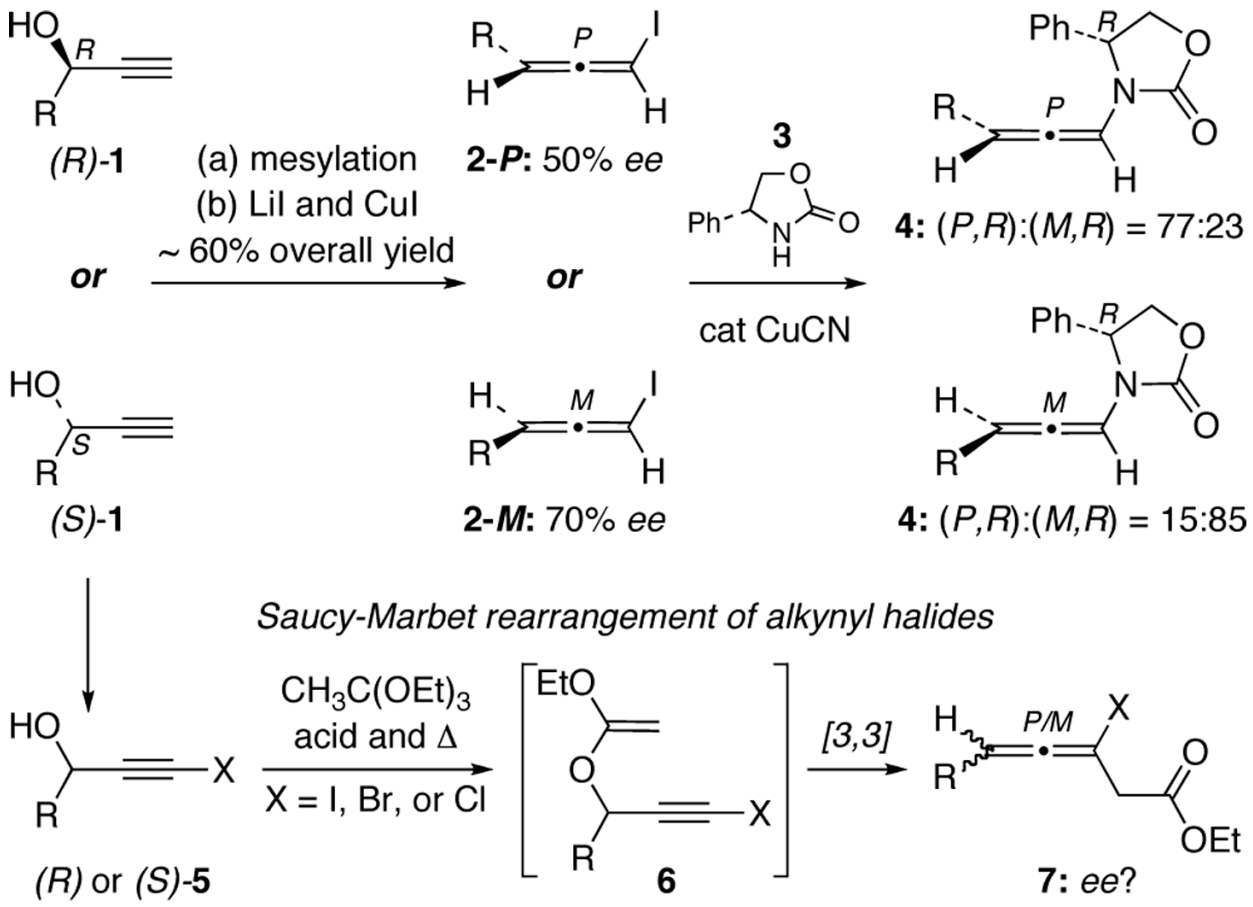

Scheme 1.
Access to Optically-Enriched Allenyl Halide

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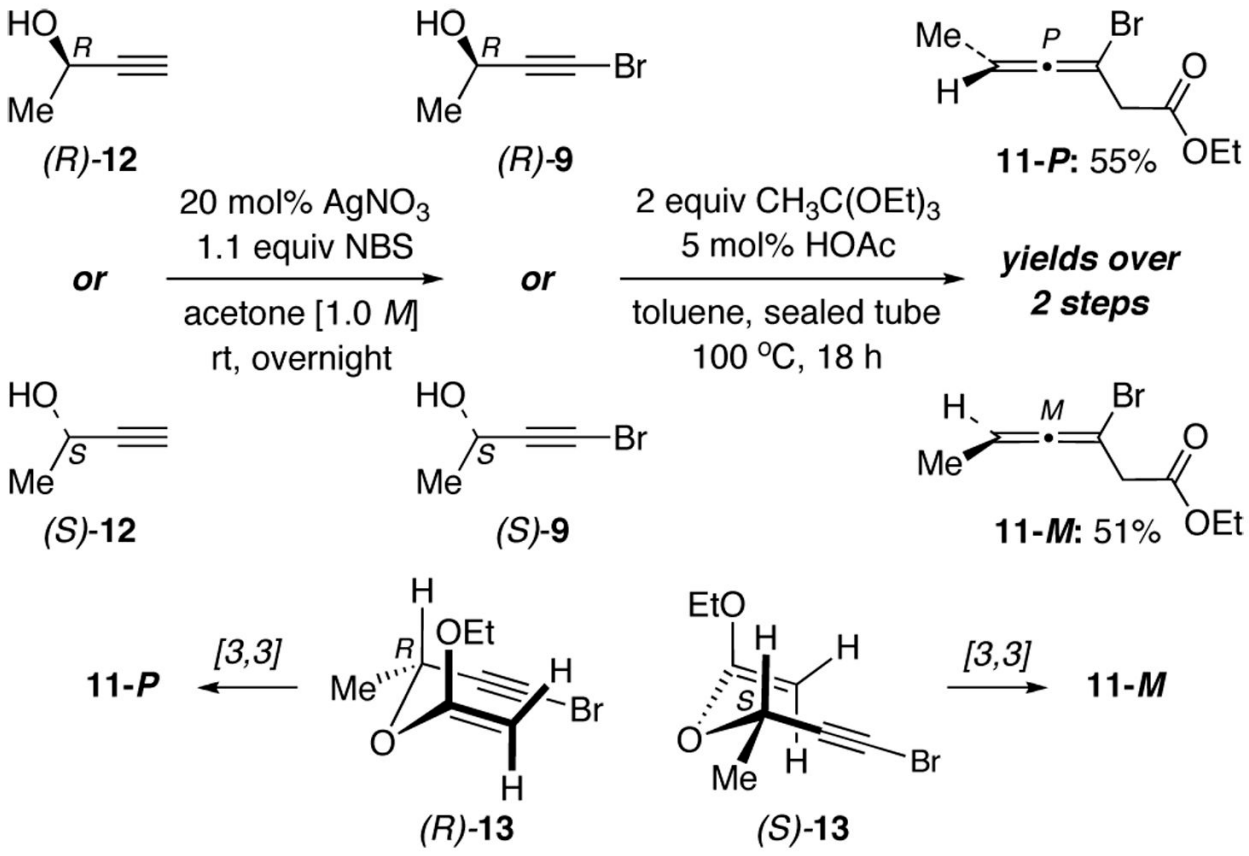

Scheme 2.
Stereospecific Saucy-Marbet Rearrangements.

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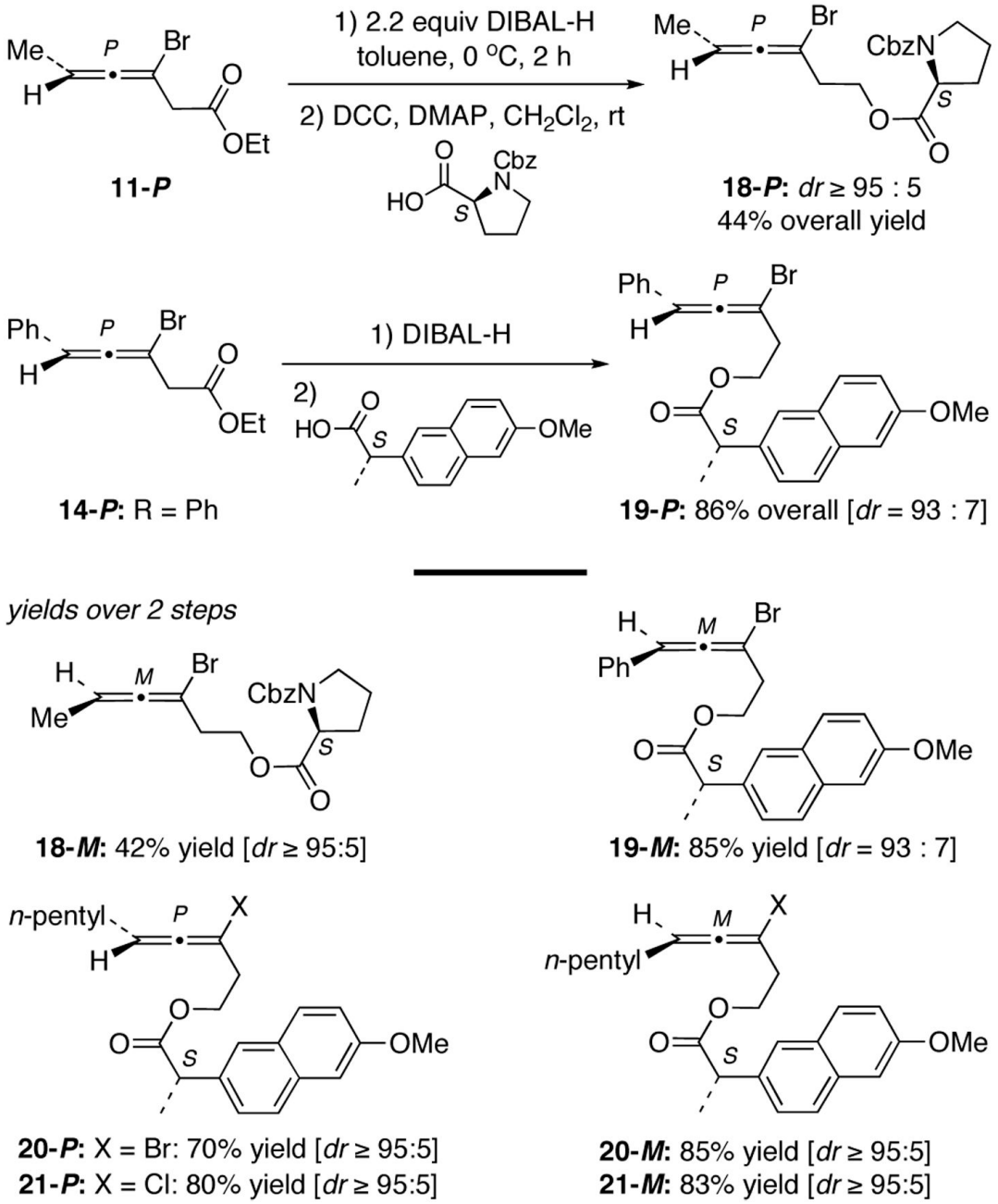

Scheme 3.
Determination of Enantiomeric Purity.

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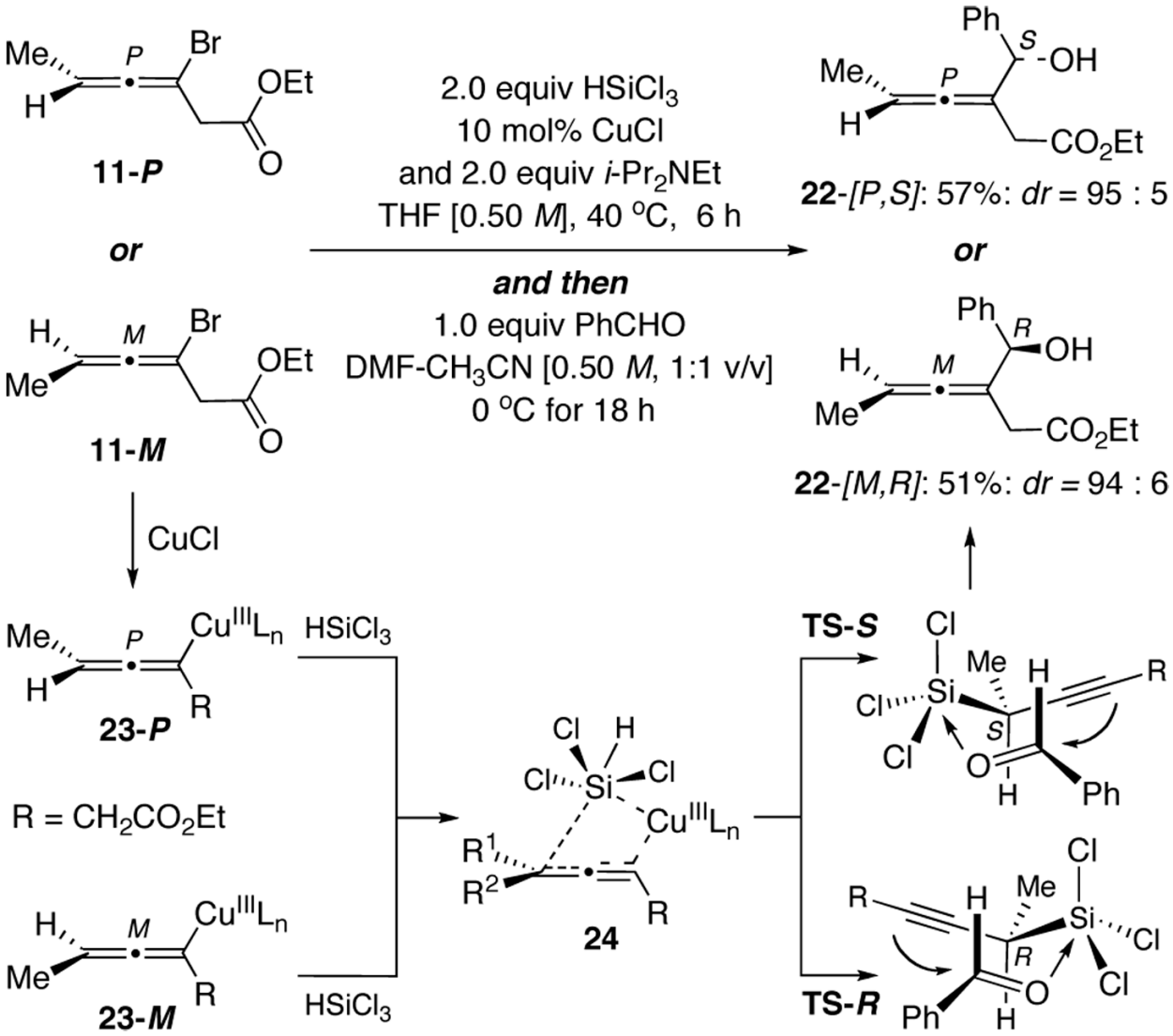

Scheme 4.
Chirality Transfer via Propargyl Trichlorosilane Addition.

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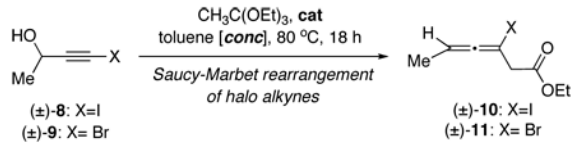
Table 1

Alkynyl Halides in Saucy-Marbet Rearrangements.



entry	halides	$CH_3C(OEt)_3$	*conc* [*M*]	cat [mol%]	allenes	yield [%][a]
1	(±)-**8**	solvent[b]	-	none	(±)-**10**	trace + sm[c]
2	(±)-**9**	solvent[b]	-	none	(±)-**11**	10% + 85% sm
3	(±)-**9**	2.0 equiv	0.10	*p*-TsOH [10]	(±)-**11**	20% + 56%
4	(±)-**9**	2.0 equiv	0.10	$EtCO_2H$ [10]	(±)-**11**	20% + 56% sm
5	(±)-**9**	2.0 equiv	0.10	AcOH [10]	(±)-**11**	24% + 54% sm
6	(±)-**9**	2.0 equiv	0.10	AcOH [10]	(±)-**11**	95%[d]