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Facile Synthesis of 3-Amido-Dienynes via a Tandem α -Propargylation–Isomerization of Chiral Allenamides and their Applications in Diels-Alder Cycloadditions

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Abstract

A series of *de novo* 3-amido-dienynes was synthesized via tandem α -propargylation–isomerization of chiral allenamides with moderate *E/Z* ratio. Reactivities of *E*- and *Z*-isomers were examined.

Graphical abstract

Keywords

allenamide; tandem; 3-amido-dienyne; propargylation; Diels-Alder reaction

Recently, we developed a highly *E*-selective allenamide 1,3-H shift reaction under thermal or acid-promoted condition, which afforded an efficient route to access valuable 2-amidodiene building blocks.^{1,2} Furthermore, chiral 3-amidotrienes such as **2** could be prepared by the reactions starting from α -allyl-allenamides **1** (path a, scheme 1), which could be facily converted to cyclic 2-amidodienes **4** and further applied in various different transformations.^{1,3}

While much efforts have been dedicated to 3-amidotrienes, we were also interested in the reactivity and potential application of its structural sibling 3-amidodienynes, which could potentially be obtained following a similar α -propargylation–1,3-H shift sequence of allenamides (path b, scheme 1). Comparing to 3-amidotrienes, precedents of 3-amino- or 3-amido-dienynes are relative rare.^{4–7} An elegant example of 3-amidodienynes was reported

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

recently by Huang and coworker in which they developed an interesting route to 1-silyloxy-3-aminodienynes, and subsequently, applied these electronically enriched 3-aminodienynes in different ring-formation reactions.⁷ Herein, we wish to disclose our recent studies on the preparation of 3-amidodienynes and exploration of the reactivity of both *E*- and *Z*-isomers.

Given that 3-amidodienynes could be obtained *via* a 1,3-H-shift of the corresponding α -propargyl allenamides, we commenced our study through examining the propargylation of allenamides using **6a** bearing an *i*-Pr substituent on the oxazolidinone ring. To our surprise, under the standard alkylation conditions (*n*-BuLi, HMPA, propargyl bromide), in addition to the expected α -propargyl allenamide product **4a**, two new products were isolated from the reaction mixture. These two additional products turned to be the *E/Z* isomers of the desired 3-amidodienynes **5a** (entry 1, table 1). The direct formation of 3-amidodienynes could be promoted by base-promoted *in situ* 1,3-H-shift of α -propargyl allenamide in the presence of excess *n*-BuLi used for allenamide deprotonation, or even the α -deprotonated allenamide, although the exact mechanism remains unclear.⁸ Efforts to improve the conversion toward 3-amidodienyne formation, such as increasing the amount of *n*-BuLi and prolonged reaction time, proved to be fruitless.

Although this tandem propargylation–1,3-H-shift sequence afforded 3-amidodienynes in moderate *E/Z* ratios, we were satisfied with the efficiency that both isomers could be obtained in one-pot to set the stage for evaluation of their respective reactivities and potential applications. By employing the standard conditions, we examined tandem propargylation–1,3-H-shift reactions using combinations of different chiral allenamides and substituted propargyl bromides (entries 2–5, table 1). Generally, all these reactions proceeded smoothly in the standard conditions with different oxazolidinone auxiliaries. Interestingly, when either TMS (entry 2, table 1) or Ph (entry 5, table 1) substituted propargyl bromides was used, only 3-amidodienyne products were found in moderate yield with no α -propargyl allenamides isolated. This could be a result of enhanced activity of propargylic protons in the initial α -propargylated allenamide toward base-promoted 1,3-H-shift.

With these 3-amidodienynes in hand, their potential synthetic applications were investigated. We envisioned that these highly electron-rich *Z*-3-amidodienynes could serve as suitable diene components in a Diels-Alder cycloaddition reaction with the alkyne motif preserved as a useful handle for further transformations. Towards this goal, Diels-Alder reaction of **Z-5a** with methyl vinyl ketone (MVK) was explored. Considering the potential labile property of the substrate in the presence of Lewis acids, conventional thermal condition was selected for the Diels-Alder reaction and **Z-5a** was found to react smoothly with MVK at 130 °C in the presence of BHT (2,6-Di-*tert*-butyl-4-methylphenol) to afford the desired product **9a** in 56% yield with a diastereomeric ration of 8:1 (entry 1, table 2). Inspired by these results, the Diels-Alder reactions were further examined with other *Z*-3-amidodienynes (entries 2–6, table 2) under the standard thermal conditions. It was readily noticeable that the auxiliary employed played a key role in the reaction selectivity (entries 1,3, and 4). While **Z-5c** bearing a Bn substituted Evans auxiliary gave inferior selectivity comparing to **Z-5a** with an *i*-Pr substituent, the reaction with **Z-5d** incorporated with a Sibi auxiliary provided the

cycloaddition product as a single isomer.⁹ Similar selectivity results were also observed in our previous studies.^{3c}

While it would appear that these cycloadditions were compatible with variations on the alkyne motif (entries 2 and 5), the reaction with a terminal alkyne substrate gave relatively lower yield (entry 2). Other dienophiles such as **8b** and **8c** were also examined (entries 6 and 7). Dienophile **8b** with *p*-bromophenyl substitution was tolerant and it offered the desired product **9f** in good yield and selectivity under standard conditions. On the other hand, when **8c** with terminal phenyl substituent on the double bond (entry 7), the reaction became very sluggish even at higher temperature. The prolonged reaction time resulted in a messy reaction mixture with decomposition of the starting material, although the desired product was detected from the reaction mixture by mass spectrometry. This outcome suggests that the cycloaddition was quite sensitive to the β -substitutions of these enones. We also attempted the reaction with 2-cyclohexen-1-one (results not shown in the table), but no desired product was found with only slow decomposition of the starting material.

NOE experiment using cycloadduct **9f** confirmed its 1,3-*cis* relative stereochemistry, thereby suggesting an *endo*-selectivity for these cycloadditions. Furthermore, based on the mechanistic model from our previous studies using related amino-dienes, these Diels-Alder products would be assigned as *endo-II* cycloaddition products as shown in scheme 2.^{3c,d}

Having established a reliable Diels-Alder reaction of *Z*-3-amidodienynes established, we then focused on the reaction of *E*-3-amidodienynes. Given the similarity to 3-amidotrienes, these *E*-3-amidodienynes were postulated to be intrinsic candidates for electrocyclizations or similar transformations.¹⁰ Thus, we attempted to directly cyclize **E-5a** various conditions (Ti(OPr)₄, (JohnPhos)AuCl/AgSbF₆, PtCl₄ conventional heating, photo-activation conditions and so on), but none of these conditions led to desired products with decompositions being the case in most attempts (reaction a, scheme 3). When the direct cyclization failed to offer the desired product, a sequence of Pauson-Khand reaction-6 π -electrocyclization was envisioned and explored (reaction b, scheme 3).¹¹ Albeit in low yield (in 28% yield un-optimized), **E-5a** did react with norbornene to afford the desired Pauson-Khand product **11**. However, analysis selectivity was poor (roughly 1:1), which could be due to the long distance between the chiral auxiliary and the actual site of bond formation. Unfortunately, initial attempts at 6 π -electrocyclizations of **11** to give the octahydro-fluorenone derivative **12** proved to be challenging. Efforts are currently underway to achieve such synthetic design.

We have described here a tandem propargylation–1,3-H-shift sequence to access both *E*- and *Z*-isomer of chiral 3-amidodienynes. A series of 3-amidodienynes were synthesized with this method. An application of *Z*-3-amidodienynes in Diels-Alder cycloadditions gave *endo-II* products in good yields and excellent selectivity. Reactivity of the corresponding *E*-3-amidodienynes toward electrocyclization was also examined but was unsuccessful. Further efforts in developing synthetic applications of these *de novo* chiral 3-amido-dienynes will be reported in due courses.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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- General procedures for the propargylation/1,3-H-shift sequence of allenamides:** To a solution of allenamide **6a** (1.0 equiv) and HMPA (1.5 equiv) in THF (0.1 M) was added dropwise n-BuLi (2.5 M in Hexanes, 1.5 equiv) at -78°C . After stirring for 45 min, propargyl bromide **7a** (1.5 equiv) was added dropwise. The resulting solution was stirred at -78°C for 1 h and then at rt for overnight. The reaction mixture was quenched with sat. aq. NH_4Cl solution, extracted with EtOAc (3 times). The combined organic phases were washed with sat. aq. NaCl solution, dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure to afford a crude product which was purified via silica gel flash column chromatography [gradient eluent: EtOAc in hexane] to afford the desired products **4a** and **E/Z-5a**.
- Characterization of α -propargyl allenamide product 4 and 3-amidodienynes 54a** (77 mg, 34%), **E-5a** (34 mg, 15%) and **Z-5a** (59 mg, 26%) were obtained from allenamide **6a** (172 mg) according to the general procedure. **4a**: pale yellow oil; R_f = 0.45 (hexane:EtOAc = 2:1); $[\alpha]_{\text{D}}^{25}$ = 27.2 (c = 2.40, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 0.89 (d, J = 7.0 Hz, 3H), 0.93 (d, J = 7.0 Hz, 3H), 1.78 (t, J = 3.0 Hz, 3H), 2.16 (dq, J = 3.5, 7.0, 7.0 Hz, 1H), 3.35 (ABMN X_3 , J_{AM} =

$J_{BM} = J_{MX} = 2.5$ Hz, $J_{MN} = 18$ Hz, 1H), 3.45 (ABMNX₃, $J_{NX} = 2.5$ Hz, $J_{AN} = J_{BN} = 3.5$ Hz, $J_{MN} = 18$ Hz, 1H), 3.91 (ddd, $J = 3.5, 5.5, 9.0$ Hz, 1H), 4.12 (dd, $J = 6.0, 8.5$ Hz, 1H), 4.28 (dd, $J = 9.0, 9.0$ Hz, 1H), 5.19 (ABMN, $J_{AM} = 2.5$ Hz, $J_{AN} = 3.5$ Hz, $J_{AB} = 10.5$ Hz, 1H), 5.31 (ABMN, $J_{BM} = 2.5$ Hz, $J_{BN} = 3.5$ Hz, $J_{AB} = 10.5$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 3.7, 14.6, 17.9, 21.7, 28.2, 60.9, 63.3, 74.7, 78.2, 84.5, 105.5, 156.4, 204.4; IR (thin film) cm⁻¹ 3391brs, 2966w, 1748s, 1638w, 1452w, 1405m; HRMS (QTOF MS ESI) m/e calcd for C₁₃H₁₈NO₂ [M + H]⁺ 220.1332, found 220.1328. **E-5a**: pale yellow oil; R_f = 0.42 (hexane:EtOAc = 2:1); [α]_D²⁵ = 174.3 (c = 0.88, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 0.86 (d, $J = 6.8$ Hz, 3H), 0.88 (d, $J = 6.8$ Hz, 3H), 1.91 (dq, $J = 4.0, 6.8, 6.8$ Hz, 1H), 2.03 (d, $J = 2.4$ Hz, 3H), 4.01 (ddd, $J = 4.0, 5.6, 8.8$ Hz, 1H), 4.15 (dd, $J = 7.0, 9.2$ Hz, 1H), 4.35 (dd, $J = 8.8, 8.8$ Hz, 1H), 5.29–5.41 (m, 2H), 5.67 (s, 1H), 6.77 (dd, $J = 11.2, 17.6$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 4.96, 14.8, 18.0, 29.0, 61.2, 63.5, 75.3, 96.9, 111.8, 117.8, 129.7, 141.9, 156.8; IR (thin film) cm⁻¹ 3483brs, 2964w, 1747s, 1623w, 1576w, 1485w, 1402m; HRMS (QTOF MS ESI) m/e calcd for C₁₃H₁₈NO₂ [M + H]⁺ 220.1332, found 220.1329. **Z-5a**: pale yellow oil; R_f = 0.40 (hexane:EtOAc = 2:1); [α]_D²⁵ = -24.3 (c = 0.85, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 0.91 (d, $J = 7.0$ Hz, 3H), 0.97 (d, $J = 7.0$ Hz, 3H), 1.90–1.98 (m, 1H), 2.03 (d, $J = 2.5$ Hz, 3H), 4.19–4.21 (m, 1H), 4.35–4.41 (m, 2H), 5.25 (d, $J = 10.5$ Hz, 1H), 5.41 (d, $J = 17.5$ Hz, 1H), 5.69 (q, $J = 2.5$ Hz, 1H), 6.29 (dd, $J = 10.5, 17.5$ Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 5.1, 16.0, 18.7, 29.7, 61.2, 64.7, 75.9, 97.8, 110.7, 117.2, 133.2, 142.6, 156.2; IR (thin film) cm⁻¹ 3422brs, 2966w, 1749s, 1485w, 1406m; HRMS (QTOF MS ESI) m/e calcd for C₁₃H₁₈NO₂ [M + H]⁺ 220.1332, found 220.1330. **E-5b** (165 mg, 15%) and **Z-5b** (285 mg, 26%) were obtained from allenamide **6a** (912 mg) according to the general procedure. **E-5b**: pale yellow oil; R_f = 0.35 (hexane:EtOAc = 2:1); [α]_D²⁵ = 88.0 (c = 1.21, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 0.88 (d, $J = 7.0$ Hz, 3H), 0.89 (d, $J = 6.5$ Hz, 3H), 1.94 (dq, $J = 3.5, 7.0, 7.0$ Hz, 1H), 3.43 (d, $J = 2.5$ Hz, 3H), 4.06 (ddd, $J = 3.5, 5.0, 8.5$ Hz, 1H), 4.18 (dd, $J = 5.5, 9.0$ Hz, 1H), 4.37 (dd, $J = 8.5, 9.0$ Hz, 1H), 5.46 (d, $J = 11.0$ Hz, 1H), 5.51 (d, $J = 17.5$ Hz, 1H), 5.72 (s, 1H), 6.78 (dd, $J = 11.0, 17.5$ Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 14.7, 18.0, 29.0, 61.2, 63.5, 79.1, 87.3, 108.7, 119.7, 129.5, 144.7, 156.5; IR (thin film) cm⁻¹ 3303w, 3018w, 1748s, 1573w, 1485w, 1402m; HRMS (QTOF MS ESI) m/e calcd for C₁₂H₁₆NO₂ [M + H]⁺ 206.1176, found 206.1174. **Z-5b**: pale yellow oil; R_f = 0.31 (hexane:EtOAc = 2:1); [α]_D²⁵ = -5.6 (c = 1.62, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 0.91 (d, $J = 7.0$ Hz, 3H), 0.95 (d, $J = 6.5$ Hz, 3H), 1.95 (dq, $J = 4.0, 7.0, 7.0$ Hz, 1H), 3.46 (d, $J = 2.5$ Hz, 1H), 4.19 (dd, $J = 6.0, 8.5$ Hz, 1H), 4.40 (dd, $J = 8.5, 9.0$ Hz, 1H), 4.47 (ddd, $J = 4.0, 6.0, 8.5$ Hz, 1H), 5.34 (d, $J = 10.5$ Hz, 1H), 5.52 (d, $J = 17.0$ Hz, 1H), 5.69 (d, $J = 2.5$ Hz, 1H), 6.31 (dd, $J = 10.5, 17.0$ Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 16.0, 18.5, 29.6, 61.0, 64.7, 79.4, 88.2, 107.7, 119.0, 132.9, 145.3, 155.9; IR (thin film) cm⁻¹ 3301w, 3016w, 2970w, 1749s, 1585w, 1485w, 1406m; HRMS (QTOF MS ESI) m/e calcd for C₁₂H₁₆NO₂ [M + H]⁺ 206.1176, found 206.1174. **4c** (244 mg, 38%), **E-5c** (89 mg, 14%) and **Z-5c** (151 mg, 23%) were obtained from allenamide **6b** (518 mg) according to the general procedure. **4c**: pale yellow oil; R_f = 0.60 (hexane:EtOAc = 2:1); [α]_D²⁵ = 24.4 (c = 0.95, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.81 (t, $J = 2.5$ Hz, 3H), 2.71 (dd, $J = 9.0, 14.0$ Hz, 1H), 3.27 (dd, $J = 3.5, 14.0$ Hz, 1H), 3.42 (ABMNX₃, $J_{AM} = J_{BM} = J_{MX} = 2.5$ Hz, $J_{MN} = 18$ Hz, 1H), 3.48 (ABMNX₃, $J_{NX} = 2.5$ Hz, $J_{AN} = J_{BN} = 3.0$ Hz, $J_{MN} = 18$ Hz, 1H), 4.81 (dd, $J = 5.5, 8.0$ Hz, 1H), 4.14–4.20 (m, 1H), 4.23 (dd, $J = 8.0, 8.0$ Hz, 1H), 5.29 (ABMN, $J_{AM} = 1.5$ Hz, $J_{AN} = 3.0$ Hz, $J_{AB} = 10.5$ Hz, 1H), 5.40 (ABMN, $J_{BM} = 2.0$ Hz, $J_{BN} = 3.0$ Hz, $J_{AB} = 10.5$ Hz, 1H), 7.16–7.18 (m, 2H), 7.25–7.28 (m, 1H), 7.31–7.34 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 3.6, 21.8, 38.6, 58.2, 67.1, 74.6, 78.3, 85.0, 105.8, 127.3, 129.1, 129.3, 135.9, 155.8, 204.3; IR (thin film) cm⁻¹ 3369brs, 3027w, 2920w, 1749s, 1604w, 1497w, 1479w, 1453m, 1402m; HRMS (QTOF MS ESI) m/e calcd for C₁₇H₁₈NO₂ [M + H]⁺ 268.1332, found 268.1328. **E-5c**: pale yellow solid, mp 46–47 °C; R_f = 0.55 (hexane:EtOAc = 2:1); [α]_D²⁵ = 70.0 (c = 0.91, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 2.07 (d, $J = 2.5$ Hz, 3H); 2.59 (dd, $J = 10.0, 13.5$ Hz, 1H), 3.07 (dd, $J = 3.5, 13.5$ Hz, 1H), 4.11–4.15 (m, 1H), 4.22–4.30 (m, 2H), 5.41 (d, $J = 10.5$ Hz, 1H), 5.43 (d, $J = 17.5$ Hz, 1H), 5.74 (m, 1H), 6.88 (dd, $J = 11.0, 17.5$ Hz, 1H), 7.10–7.12 (m, 2H), 7.24–7.27 (m, 1H), 7.30–7.32 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 5.0, 39.0, 58.5, 67.3, 75.2, 97.2, 112.5, 117.9, 127.4, 129.1, 129.2, 135.5, 141.7, 156.3; IR (thin film) cm⁻¹ 3405brs, 3016w, 2918w, 1753s, 1624w, 1497w, 1479w, 1454w, 1403m; HRMS (QTOF MS ESI) m/e calcd for C₁₇H₁₈NO₂ [M + H]⁺ 268.1332, found 268.1327. **Z-5c**: pale yellow oil; R_f = 0.52 (hexane:EtOAc = 2:1); [α]_D²⁵ = -57.6 (c = 1.09, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 2.06 (d, $J = 2.5$ Hz, 3H), 2.67 (dd, $J = 10.5, 13.5$ Hz, 1H), 3.11 (dd, $J = 4.0, 13.5$ Hz, 1H), 4.18 (dd, $J = 7.0, 9.0$ Hz, 1H), 4.32 (dd, $J =$

8.5, 8.5 Hz, 1H), 4.63 (dddd, J = 4.0, 8.0, 9.0, 11.0 Hz, 1H), 5.29 (d, J = 10.5 Hz, 1H), 5.44 (d, J = 17.0 Hz, 1H), 5.77 (q, J = 2.0 Hz, 1H), 6.37 (dd, J = 10.5, 17.0 Hz, 1H), 7.14–7.15 (m, 2H), 7.24–7.27 (m, 1H), 7.30–7.33 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 5.2, 39.2, 58.1, 68.3, 75.8, 98.0, 111.8, 117.2, 127.3, 129.1, 129.2, 133.3, 135.9, 141.9, 155.8; IR (thin film) cm^{-1} 3406brs, 3017w, 1752s, 1498w, 1405m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$ 268.1332, found 268.1328. **4d** (142 mg, 41%), **E-5d** (40 mg, 12%) and **Z-5d** (66 mg, 19%) were obtained from allenamide **6c** (291 mg) according to the general procedure. **4d**: pale yellow oil; R_f = 0.45 (hexane:EtOAc = 2:1); $[\alpha]_D^{25}$ = -70.1 (c = 1.10, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 1.76 (t, J = 2.5 Hz, 3H), 3.05 (ABMNX₃, $J_{\text{AM}} = J_{\text{MX}} = 2.5$ Hz, $J_{\text{BM}} = 3.5$ Hz, $J_{\text{MN}} = 18.5$ Hz, 1H), 3.28 (ABMNX₃, $J_{\text{NX}} = J_{\text{AN}} = J_{\text{BN}} = 2.5$ Hz, $J_{\text{MN}} = 18.5$ Hz, 1H), 4.17 (dd, J = 5.0, 9.0 Hz, 1H), 4.40 (d, J = 9.0 Hz, 1H), 4.42 (d, J = 6.0 Hz, 1H), 4.77 (ddd, J = 5.0, 6.5, 11.5 Hz, 1H), 5.05 (ABMN, $J_{\text{AM}} = J_{\text{AN}} = 3.0$ Hz, $J_{\text{AB}} = 10.5$ Hz, 1H), 5.31 (ABMN, $J_{\text{BN}} = 3.0$ Hz, $J_{\text{BM}} = 3.5$ Hz, $J_{\text{AB}} = 10.5$ Hz, 1H), 7.19–7.20 (m, 4H), 7.23–7.26 (m, 2H), 7.29–7.34 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 3.7, 21.7, 53.5, 59.4, 65.8, 74.3, 78.5, 84.6, 105.5, 127.3, 127.6, 128.5, 128.9 (2 carbons), 129.0, 139.4, 140.7, 156.2, 205.2; IR (thin film) cm^{-1} 3397brs, 3017w, 2920w, 1750s, 1495w, 1452w, 1405m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$ 344.1645, found 344.1636. **E-5d**: yellow solid, mp 52–53 °C; R_f = 0.40 (hexane:EtOAc = 2:1); $[\alpha]_D^{25}$ = 1.5 (c = 0.72, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 1.96 (d, J = 2.5 Hz, 3H), 4.14 (d, J = 8.0 Hz, 1H), 4.20 (dd, J = 5.0, 9.0 Hz, 1H), 4.39 (dd, J = 9.0, 9.0 Hz, 1H), 4.93 (ddd, J = 5.0, 8.5, 8.5 Hz, 1H), 5.28 (d, J = 10.0 Hz, 1H), 5.30 (d, J = 17.5 Hz, 1H), 5.33 (m, 1H), 6.48 (dd, J = 11.0, 17.5 Hz, 1H), 7.15–7.32 (m, 10H); ^{13}C NMR (125 MHz, CDCl_3) δ 5.0, 55.6, 59.1, 66.3, 75.1, 96.7, 113.4, 116.9, 127.4, 127.7, 128.4 (2 carbons), 128.8, 129.3, 130.0, 139.8, 140.4, 141.6, 156.7; IR (thin film) cm^{-1} 3398brs, 3018w, 1751s, 1495w, 1453w, 1403m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$ 344.1645, found 344.1639. **Z-5d**: yellow solid, mp 54–55 °C; R_f = 0.38 (hexane:EtOAc = 2:1); $[\alpha]_D^{25}$ = -82.0 (c = 0.76, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 2.12 (d, J = 2.5 Hz, 3H), 4.11 (dd, J = 7.0, 9.0 Hz, 1H), 4.15 (d, J = 10.0 Hz, 1H), 4.35 (dd, J = 9.0 Hz, 9.0 Hz, 1H), 5.05 (d, J = 11.0 Hz, 5.25–5.30 (m, 2H), 5.41 (ddd, J = 7.0, 8.5, 10.0 Hz, 1H), 5.82 (dd, J = 10.5, 17.0 Hz, 1H), 7.14–7.31 (m, 10H); ^{13}C NMR (125 MHz, CDCl_3) δ 5.2, 56.7, 58.8, 67.5, 76.2, 97.6, 111.3, 116.6, 127.3, 127.6, 128.0, 128.3 (2 carbons), 129.3, 133.0, 140.5, 140.7, 143.1, 156.3; IR (thin film) cm^{-1} 3375brs, 3018w, 1753s, 1641w, 1494w, 1403m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$ 344.1645, found 344.1639. **E-5e** (37 mg, 13%) and **Z-5e** (63 mg, 22%) were obtained from allenamide **6c** (206 mg) according to the general procedure. **E-5e**: yellow solid, mp 57–58 °C; R_f = 0.40 (hexane:EtOAc = 2:1); $[\alpha]_D^{25}$ = 19.8 (c = 0.44, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 4.19 (d, J = 8.5 Hz, 1H), 4.22 (dd, J = 5.0, 9.0 Hz, 1H), 4.42 (dd, J = 9.0, 9.0 Hz, 1H), 4.99 (ddd, J = 5.0, 8.5, 8.5 Hz, 1H), 5.36 (d, J = 11.0 Hz, 1H), 5.41 (d, J = 17.5 Hz, 1H), 5.60 (s, 1H), 6.55 (dd, J = 11.0, 17.5 Hz, 1H), 7.17–7.20 (m, 3H), 7.23–7.28 (m, 6H), 7.31–7.34 (m, 4H), 7.37–7.39 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 55.7, 59.3, 66.4, 84.8, 99.4, 112.0, 118.0, 123.3, 127.5, 127.7, 128.4, 128.5 (2 carbons), 128.7, 128.9, 129.3, 130.1, 131.5, 139.7, 140.3, 142.3, 156.6; IR (thin film) cm^{-1} 3424brs, 3017w, 2920w, 1753s, 1599w, 1490w, 1453m, 1402m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{28}\text{H}_{24}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$ 406.1802, found 406.1794. **Z-5e**: yellow solid, mp 65–66 °C; R_f = 0.36 (hexane:EtOAc = 2:1); $[\alpha]_D^{25}$ = -100.4 (c = 0.53, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 4.15 (dd, J = 6.5, 9.0 Hz, 1H), 4.20 (d, J = 10.0 Hz, 1H), 4.40 (dd, J = 9.0, 9.0 Hz, 1H), 5.13 (d, J = 10.5 Hz, 1H), 5.37 (d, J = 17.0 Hz, 1H), 5.49–5.54 (m, 2H), 5.91 (dd, J = 10.5, 17.0 Hz, 1H), 7.16–7.21 (m, 4H), 7.24–7.29 (m, 6H), 7.38–7.40 (m, 3H), 7.47–7.50 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 56.8, 59.1, 67.5, 85.9, 100.4, 110.3, 117.4, 123.1, 127.4, 127.6, 128.0, 128.3, 128.4, 128.8, 129.2, 129.4, 131.7, 133.0, 140.4, 140.6, 144.0, 156.2; IR (thin film) cm^{-1} 3398brs, 3019w, 1753s, 1490w, 1403m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{28}\text{H}_{24}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$ 406.1802, found 406.1795.

14. **General procedures for the Diels-Alder reaction of Z-3-amidodienynes:** In a sealed tube, to a solution of diene **Z-5** (1.0 equiv) in toluene (3 mL) was added **8** (10.0 equiv) and BHT (2.0 equiv) at room temperature, and the reaction vessel was well sealed and heated to 130 °C overnight. After cooling to rt, the reaction mixture was concentrated under reduced pressure and the resulting crude residue was directly used for crude ^1H NMR analysis to determine isomer ratio. Then, the mixture was purified via silica gel flash column chromatography [gradient eluent: EtOAc in hexane] to afford the desired Diels-Alder product **9**.
15. **Characterization of the Diels-Alder products 9.9a** was obtained (15 mg, 58%) on a 20.0 mg scale reaction as a pale yellow oil according to the general procedure; R_f = 0.20 (hexane:EtOAc =

2:1); $[\alpha]_D^{25} = 182.7$ ($c = 0.33$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 0.89 (d, $J = 7.0$ Hz, 3H), 0.91 (d, $J = 7.0$ Hz, 3H), 1.62–1.68 (m, 1H), 1.73 (d, $J = 2.5$ Hz, 3H), 2.01–2.08 (m, 2H), 2.10–2.18 (m, 1H), 2.26 (s, 3H), 2.30–2.37 (m, 1H), 2.96 (ddd, $J = 3.0, 10.0, 10.0$ Hz, 1H), 3.57–3.60 (m, 1H), 4.06–4.13 (m, 2H), 4.29 (dd, $J = 8.5, 8.5$ Hz, 1H), 5.84 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 3.7, 14.9, 18.0, 23.3, 23.6, 29.1, 29.3 (2 carbons), 53.4, 59.1, 63.1, 78.3, 123.7, 130.8, 157.3, 209.6; IR (thin film) cm^{-1} 3404brs, 2963w, 2922w, 1746s, 1712m, 1670w, 1485w, 1411m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 290.1751, found 290.1750. **9b** was obtained (12 mg, 20%) on a 45.0 mg scale reaction as a pale yellow oil according to the general procedure; $R_f = 0.40$ (hexane:EtOAc = 1:1); $[\alpha]_D^{25} = 110.6$ ($c = 1.60$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 0.88 (d, $J = 7.0$ Hz, 3H), 0.91 (d, $J = 7.5$ Hz, 3H), 1.65–1.72 (m, 1H), 2.04–2.18 (m, 3H), 2.08 (d, $J = 3.0$ Hz, 1H), 2.26 (s, 3H), 2.31–2.38 (m, 1H), 3.00 (ddd, $J = 3.5, 7.0, 10.0$ Hz, 1H), 3.68–3.70 (m, 1H), 4.06–4.12 (m, 2H), 4.29 (dd, $J = 8.5, 8.5$ Hz, 1H), 5.85–5.87 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 1.2, 14.9, 18.0, 23.1, 23.4, 28.9, 29.0, 53.0, 59.0, 63.0, 70.8, 82.4, 124.1, 129.6, 157.1, 208.8; IR (thin film) cm^{-1} 3302brs, 2963w, 1746s, 1712m, 1671w, 1485w, 1411m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 276.1594, found 276.1594. **9c** was obtained (12 mg, 63%) on a 15.0 mg scale reaction as a pale yellow oil according to the general procedure; $R_f = 0.40$ (hexane:EtOAc = 1:1); $[\alpha]_D^{25} = 40.0$ ($c = 0.77$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 1.64–1.71 (m, 1H), 1.75 (d, $J = 2.0$ Hz, 3H), 2.02–2.16 (m, 2H), 2.26 (s, 3H), 2.28–2.35 (m, 1H), 2.70 (dd, $J = 4.0, 14.0$ Hz, 1H), 2.94 (ddd, $J = 3.5, 6.5, 9.0$ Hz, 1H), 3.19 (dd, $J = 4.5, 13.5$ Hz, 1H), 3.61–3.63 (m, 1H), 4.09 (dd, $J = 5.0, 8.5$ Hz, 1H), 4.28 (dd, $J = 8.5, 8.5$ Hz, 1H), 4.33–4.39 (m, 1H), 5.85 (ddd, $J = 2.0, 4.0, 4.0$ Hz, 1H), 7.16–7.21 (m, 2H), 7.24–2.27 (m, 1H), 7.31–7.34 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 3.8, 22.8, 23.3, 28.8, 29.3, 39.4, 53.3, 56.5, 67.0, 77.3, 78.5, 123.8, 127.3, 129.0, 129.5, 130.7, 136.2, 156.6, 209.2; IR (thin film) cm^{-1} 3417brs, 2921w, 2850w, 1750s, 1711m, 1671w, 1497w, 1480w, 1454w, 1407m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 338.1751, found 338.1749. **9d** was obtained (26 mg, 72%) on a 30.0 mg scale reaction as a yellow oil according to the general procedure; $R_f = 0.30$ (hexane:EtOAc = 1:1); $[\alpha]_D^{25} = 14.8$ ($c = 0.93$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 0.91 (dddd, $J = 5.5, 11.0, 11.0, 13.0$ Hz, 1H), 1.70–1.74 (m, 1H), 1.75 (d, $J = 2.5$ Hz, 3H), 1.78–1.85 (m, 1H), 2.062.15 (m, 1H), 2.19 (s, 3H), 2.72 (ddd, $J = 3.0, 9.0, 12.0$ Hz, 1H), 3.20–3.22 (m, 1H), 4.07 (dd, $J = 5.0, 9.0$ Hz, 1H), 4.25 (d, $J = 9.0$ Hz, 1H), 4.39 (dd, $J = 9.0$ Hz, 1H), 4.88 (ddd, $J = 5.0, 9.0, 9.0$ Hz, 1H), 5.57 (ddd, $J = 2.5, 2.5, 5.0$ Hz, 1H), 7.16–7.33 (m, 10H); ^{13}C NMR (125 MHz, CDCl_3) δ 3.7, 23.5, 23.9, 29.4, 29.7, 53.4, 56.3, 57.8, 66.6, 76.8, 78.7, 126.4, 127.3, 127.5, 128.3, 128.8, 128.9, 129.2, 130.6, 140.3, 141.2, 157.5, 209.5; IR (thin film) cm^{-1} 3403brs, 3061w, 3029w, 2921w, 1751s, 1711m, 1674w, 1600w, 1494w, 1477w, 1452w, 1408m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{27}\text{H}_{28}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 414.2064, found 414.2063. **9e** was obtained (17 mg, 61%) on a 24.0 mg scale reaction as a yellow solid according to the general procedure, mp 82–83 °C; $R_f = 0.35$ (hexane:EtOAc = 1:1); $[\alpha]_D^{25} = 50.8$ ($c = 0.87$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 0.92–1.00 (m, 1H), 1.74–1.79 (m, 1H), 1.831.88 (m, 1H), 2.11–2.19 (m, 1H), 2.24 (s, 3H), 2.85 (ddd, $J = 3.0, 9.0, 12.0$ Hz, 1H), 3.49–3.51 (m, 1H), 4.05 (dd, $J = 5.0, 9.0$ Hz, 1H), 4.25 (d, $J = 9.0$ Hz, 1H), 4.38 (dd, $J = 9.0, 9.0$ Hz, 1H), 4.94 (ddd, $J = 5.0, 9.0, 9.0$ Hz, 1H), 5.63 (ddd, $J = 2.5, 5.0, 5.0$ Hz, 1H), 7.18–7.33 (m, 13H), 7.36–7.38 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 23.5, 23.9, 29.6, 30.5, 53.0, 56.6, 57.9, 66.7, 83.2, 87.1, 122.8, 127.1, 127.4, 127.5, 128.2, 128.4, 128.5, 128.8, 128.9, 129.2, 130.1, 131.8, 140.3, 141.3, 157.6, 209.2; IR (thin film) cm^{-1} 3405brs, 3059w, 2923w, 1754s, 1713m, 1675w, 1599w, 1491w, 1452w, 1408m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{32}\text{H}_{30}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 476.2220, found 476.2220. **9f** was obtained (27 mg, 72%) on a 30.0 mg scale reaction as a yellow solid according to the general procedure, mp 82–83 °C; $R_f = 0.40$ (hexane:EtOAc = 2:1); $[\alpha]_D^{25} = 6.9$ ($c = 0.71$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 0.94 (ddd, $J = 5.5, 10.5, 10.5$ Hz, 1H), 1.65 (d, $J = 2.5$ Hz, 3H), 1.68–1.70 (m, 1H), 1.78–1.84 (m, 1H), 2.14–2.22 (m, 1H), 3.39–3.41 (m, 1H), 3.56 (ddd, $J = 2.5, 9.0, 12.0$ Hz, 1H), 4.07 (dd, $J = 4.5, 9.0$ Hz, 1H), 4.23 (d, $J = 9.5$ Hz, 1H), 4.40 (dd, $J = 9.0, 9.0$ Hz, 1H), 4.91 (ddd, $J = 4.5, 9.0, 9.0$ Hz, 1H), 5.61 (ddd, $J = 2.5, 2.5, 5.0$ Hz, 1H), 7.17–7.20 (m, 1H), 7.23–7.35 (m, 9H), 7.62 (d, $J = 8.5$ Hz, 2H), 7.81 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 3.7, 24.1, 25.0, 30.6, 48.0, 56.8, 57.9, 66.9, 76.6, 79.2, 126.9, 127.4, 127.5, 128.3, 128.7, 128.8, 129.0, 129.3, 130.2, 130.9, 132.2, 135.0, 140.5, 141.3, 157.7, 200.5; IR (thin film) cm^{-1} 3398brs, 2922w, 1752s, 1681m, 1585m, 1494w, 1452w, 1409m; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{32}\text{H}_{23}\text{BrNO}_3$ $[\text{M} + \text{H}]^+$ 554.1325, found 554.1329.

16. **Procedure of Pauson-Khand reaction:** To a solution of *E*-**5a** (44 mg, 0.2 mmol) in toluene (4.0 mL) was added $\text{Co}_2(\text{CO})_8$ (82 mg, 0.24 mmol) under Ar. The mixture was stirred at rt until the starting material was completely consumed as indicated by TLC (ca 3 h), then norbornene (56.5 mg, 0.6 mmol) and NMO (117 mg, 1.0 equiv) were added successively and the mixture was further stirred at 110 °C overnight. The reaction mixture was concentrated under reduced pressure to afford a crude mixture which was further purified via silica gel flash column chromatography [gradient eluent: EtOAc in hexane] to afford product **11** (19 mg, 28%) as a pale yellow oil. R_f = 0.40 (hexane:EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 0.89 (d, J = 7.0 Hz, 3H), 0.96 (d, J = 7.0 Hz, 3H), 1.00–1.01 (m, 1H), 1.02 (m, 1H), 1.25–1.36 (m, 2H), 1.57–1.64 (m, 1H), 1.67–1.74 (m, 1H), 1.99–2.07 (m, 1H), 2.05 (s, 3H), 2.24 (d, J = 5.5 Hz, 1H), 2.33 (dd, J = 4.0, 15.0 Hz, 1H), 2.44 (dd, J = 5.0, 5.0 Hz, 1H), 2.57 (d, J = 5.0 Hz, 1H), 4.04 (dddd, J = 2.0, 4.0, 5.5, 5.5 Hz, 1H), 4.19 (dd, J = 5.5, 8.5 Hz, 1H), 4.36 (dd, J = 9.0, 9.0 Hz, 1H), 5.28–5.34 (m, 2H), 6.05 (ddd, J = 6.0, 17.5, 19.5 Hz, 1H), 6.12 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.8/14.9, 18.1, 18.2, 28.7, 28.9, 29.3, 31.8, 38.0, 39.2, 53.5/53.8, 54.2/54.3, 60.9/61.0, 63.5/63.5, 117.2/117.3, 122.2, 129.9/130.0, 135.4, 138.8/138.9, 157.3, 175.7, 208.2/208.5; HRMS (QTOF MS ESI) m/e calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 359.2330, found 359.2334.
17. ORCID number of Z.-X. Ma: 0000-0002-9971-5158

Scheme 1.

3-amidodienes formation via 1,3-H-shift and the design to 3-amidodienynes

Scheme 2.

Structure assignment of the Diels-Alder reaction products

Scheme 3.
Reactions of *E*-3-amidodienynes

Table 1

Propargylation of allenamides^a

Entry	allenamide	Propargyl bromide	4/ E-5/ Z-5 (Yields %) ^b
1	6a (R = <i>i</i> -Pr)	7a (R ₁ = Me)	4a / E-5a / Z-5a (34/15/26)
2 ^c	6a (R = <i>i</i> -Pr)	7b (R ₁ = TMS)	4b / E-5b / Z-5b (0/15/26)
3	6b (R = Bn)	7a (R ₁ = Me)	4c / E-5c / Z-5c (38/14/23)
4	6c (R = CHPh ₂)	7a (R ₁ = Me)	4d / E-5d / Z-5d (41/12/19)
5	6c (R = CHPh ₂)	7c (R ₁ = Ph)	4e / E-5e / Z-5e (0/13/22)

^aReaction Conditions: *n*-BuLi (1.5 equiv.) was added to allenamide **6** (1.0 equiv) in HMPA (1.5 equiv) and THF (0.1 M) at -78 °C. Propargyl bromide **7** (1.5 equiv) was added 45 min later and the reaction was stirred at -78 °C for 1 h and then warmed to rt overnight.

^bIsolated yields in the bracket.

^cAll yields were overall yields of **E/Z-5b** (R¹ = H) after removal of TMS of the directly formed 3-amidodienynes products with TBAF since TMS protected 3-amidodienyne isomers were inseparable. TMS = trimethylsilyl.

Table 2

Diels-Alder reaction of 3-amidodienynes^a

Entry	Dieneyne	Dienophile	D-A Product ^b
1			
2			
3			
4			
5			
6 ^c			
7 ^c			- ^d

^aReaction Conditions: A solution of *Z*-3-amidodienyne (1 equiv), MVK (10 equiv) and BHT (2.0 equiv) in toluene (3 mL) in a sealed tube was heated at 130 °C overnight.

^bIsolated yields and ratios of *endo-II/endo-I* in the bracket.

^c 3 equiv. of dienophile was used.

^d The reaction was sluggish.

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