Tetrasubstituted Allene Ethers; Synthesis and Use in Nazarov Reactions

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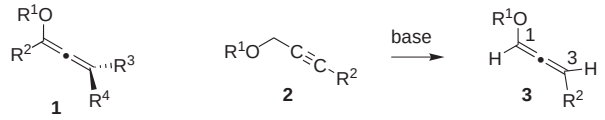
Abstract: A method for the synthesis of tetrasubstituted allene ethers is described, making use of a reverse Brook rearrangement in the key step. The allene products have been used in the Nazarov cyclization reaction.

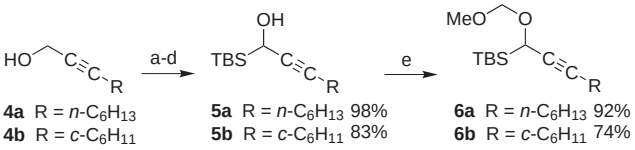
Key words: allenes, Nazarov reactions, ethers, rearrangements, alkynes, cyclizations

Allenes and other cumulenes are an attractive starting points for synthesis, in large part because of the high reactivity engendered by strain. In the case of allenes, the orthogonal π bonds also create an opportunity to exploit the axial chirality of unsymmetrically substituted cases.[1]Although many synthetic approaches to allenes have been described,[2,3] to date no completely general method has been reported for the preparation of fully substituted allene ethers (see **1**, Scheme 1).[4] Brandsma[5] and others[6] have demonstrated that exposure of propargyl ethers **2** to strong base results in isomerization to allenyl ethers **3**. In the case in which $R^2 \neq H$, the reaction often leads to an equilibrium mixture of propargyl and allene ethers.[7] It is possible to selectively deprotonate **3** at C1, and to trap the resulting allenyl nucleophile with electrophiles in a highly efficient process. If deprotonation at C1 in **3** is not possible, then deprotonation at C3 takes place upon exposure to alkyllithium base.[8] This process also leads to an allenyl nucleophile that can be trapped at C3 with electrophiles, resulting in a trisubstituted allenyl ether. In this communication we describe a more direct alternative process for the preparation of allenyl ethers, and also some examples of their use in the Nazarov reaction.[9]



Scheme 1

Our work makes use of the elegant reverse-Brook rearrangement that has been described by Ohfune and coworkers (Scheme 2).[10] Readily available propargyl alcohols **4a** and **4b** were converted to propargyl silanes **5a** and **5b** by sequential exposure to *n*-butyllithium, *tert*-butyldimethylsilyl chloride (TBSCl), followed by more *n*-butyllithium. Minor modifications to Ohfune's procedure were found to be crucial to the success of the process. The purity of the *n*-butyllithium was also important. Use of aged solutions of *n*-butyllithium, presumed to contain appreciable amounts of lithium hydroxide, resulted in erosion of the yield of rearranged product. Best yields were obtained when a freshly opened bottle of *n*-butyllithium solution in hexanes was used. After addition of the silyl chloride, the temperature of the solution was maintained at –20 °C for 40 minutes, rather than –45 °C for 2 hours, as described in Ohfune's procedure.[10] We found that the rearrangement in the case of **5a** and **5b** was very slow at –45 °C. The reaction was quenched with aq $NaHCO_3$ at –20 °C. These minor modifications of the published procedure led to reproducible high yields of **5a** and **5b**. Protection of the free hydroxyl group in **5a** and **5b** as the methoxymethyl derivative led to **6a** and **6b**.



Scheme 2 a) BuLi, THF, –78 °C; (b) TBSCl; (c) BuLi, –20 °C; (d) aq $NaHCO_3$; (e) $MeOCH_2Cl$, *i*-Pr_2NEt, CH_2Cl_2.

Exposure of **6a** and **6b** in THF solution at –78 °C to a small excess of *sec*-butyllithium, followed by an electrophile, led to the results that are summarized in Table 1. Product yields were good or excellent in all cases, and the reaction was successful with diverse electrophiles, including alkyl halides, ketones, amides and chlorosilanes. It was important to use *sec*-butyllithium as the base; *n*-butyllithium or *tert*-butyllithium led to mixtures of starting material and allene product. All products were moderately sensitive to acid, therefore reactions were quenched with aq $NaHCO_3$, and column chromatography on silica gel was performed with triethylamine (1%) in the eluent. By using these precautions, all allenes were stable to storage for several weeks at 0 °C.

The next goal was to determine whether the *tert*-butyldimethylsilyl group of the tetrasubstituted allenes could be exchanged for a proton. Treatment of tetrasubstituted allenyl ethers **8a** and **8b** with TBAF (1 equiv) and solid LiOH (1 equiv) in THF at room temperature led to the desired products **16a** and **16b** in 82% and 87% yield, respectively (Scheme 3). In the absence of LiOH, the desilylation reaction was extremely sluggish, and required ca. 8 equivalents TBAF to proceed to completion. In the

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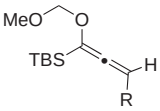
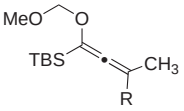
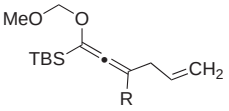
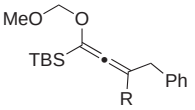
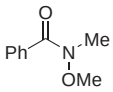
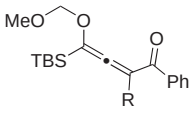
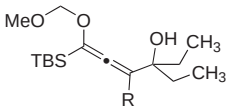
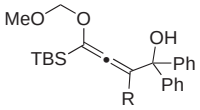
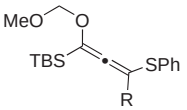
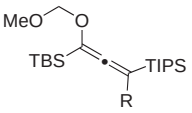
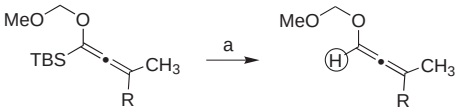
Table 1 Tetrasubstituted Allenyl Ethers

Electrophile	Product	Yield (%) R = *n*-C_6H_{13}	Yield (%) R = *c*-C_6H_{11}
EtOH		**7a** 85	**7b** 77
MeI		**8a** 96	**8b** 86
H_2C=CH–CH$_2$–Br			**9b** 85
$PhCH_2Br$		**10a** 98	
		**11a** 93	**11b** 54
3-pentanone		**12a** 61	**12b** 87
benzophenone		**13a** 76	**13b** 61
$PhSSO_2Ph$		**14a** 93	**14b** 97
TIPSCl		**15a** 95	**15b** 97

presence of 1 equivalent LiOH the reaction was complete within 2 hours at room temperature. At the end of 2 hours, the reaction mixture was completely homogeneous.

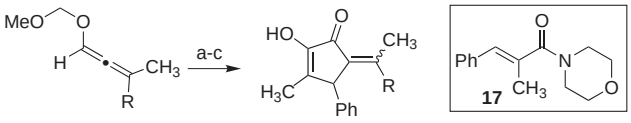


8a R = *n*-C_6H_{13}
8b R = *c*-C_6H_{11}

16a R = *n*-C_6H_{13} 82%
16b R = *c*-C_6H_{11} 87%

Scheme 3 (a) 1 equiv TBAF, 1 equiv LiOH (s), THF, r.t.

With a supply of allenyl ethers **16a** and **16b** in hand, we set out to examine them in each of the three broad categories of the cyclopentannelation reaction.[11] Depending upon the electrophile that is chosen to react with **16a** and **16b**, the cyclopentannelation leads either to an α-hydroxy-,[12] α-amino-,[13] or to an α-alkyl cyclopentenone.[14] Scheme 4 summarizes the results of the reactions of **16a** and **16b** with morpholino enamide **17**. Conversion of each allene to the α-lithio derivative, followed by addition of a solution of amide **17** presumably (*E*/*Z* ca. 1:2, 72% yield) and **18b** (*E*/*Z* ca. 1:5, 58% yield) took place when the reaction mixture was transferred via cannula into a solution of anhyd $FeCl_3$ in dichloromethane at room temperature. Quenching the reaction by transferring the solution into HCl in ethanol led to cyclic products **18a** and **18b**, but also resulted in hydrolysis of the excess allene ether. Chromatographic separation of the resulting enal from the desired product proved to be difficult; therefore $FeCl_3$ was the reagent of choice.

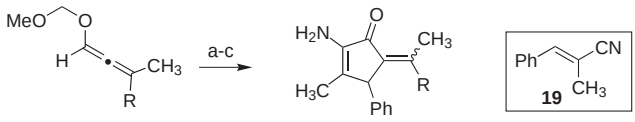


16a R = *n*-C_6H_{13}
16b R = *c*-C_6H_{11}

18a R = *n*-C_6H_{13} 72%
18b R = *c*-C_6H_{11} 58%

Scheme 4 (a) BuLi (1.8 equiv), THF, –78 °C; (b) **17** (1 equiv); (c) $FeCl_3$, CH_2Cl_2.

α-Aminocyclopentenones **20a** and **20b** were prepared in 68% (*E*–*Z* ca. 1:2) and 48% yield (*E*–*Z* ca. 1:5), respectively, in a similar way from α-methylcinnamonitrile **19** (Scheme 5). After quenching the reaction and inducing cyclization with $FeCl_3$ in diethyl ether, workup led to a solution of α-aminocyclopentenone product. Consistent with our earlier obsevations,[13] α-aminocyclopentenones **20a** and **20b** were labile, and underwent some decomposition during storage.



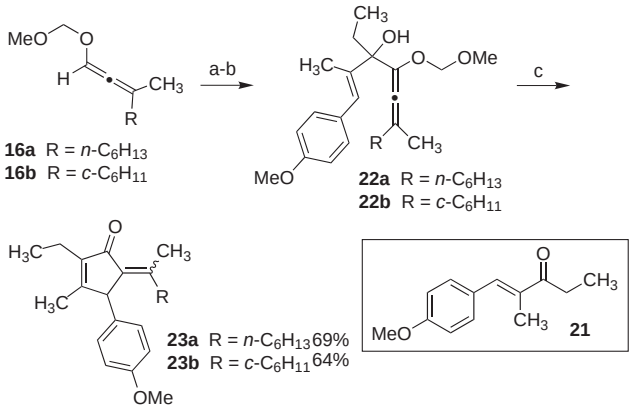
16a R = *n*-C_6H_{13}
16b R = *c*-C_6H_{11}

20a R = *n*-C_6H_{13} 64%
20b R = *c*-C_6H_{11} 53%

Scheme 5 (a) BuLi (1.8 equiv), THF, –78 °C; (b) **19** (1.0 equiv); (c) $FeCl_3$, Et_2O.

Scheme 5 summarizes the preparation of two α-alkyl cyclopentenones. In this case, the intermediate was tertiary alcohol **22**, which was isolated after workup and cyclized in a second step with $FeCl_3$ to give **23a** and **23b** in 69% yield (*E*–*Z* ca. 1:1) and 64% yield (*E*–*Z* ca. 1:5), respectively, for the two steps. For these reactions a small excess of allene was used so as to consume enone **21** completely. This was done because of the difficulty of separating excess **21** from the products. Whereas the chromatographic separation of *E* and *Z* isomers in the case of **18a**, **18b** and **20a** was straightforward by flash column chromatography on silica gel, in the case of **20b**, **23a** and **23b** this proved not to be possible.

An efficient general method for preparing tetrasubstituted allene ethers has been demonstrated. The products have



Scheme 6 (a) BuLi (1.05 equiv), THF, –78 °C; (b) **21** (0.5 equiv); (c) $FeCl_3$, CH_2Cl_2.

been shown to be useful in all three categories of the cyclopentannelation reaction. Cyclopentenones **18a**, **18b**, **20a**, **20b**, **23a** and **23b** are the first examples of cyclopentannelation products bearing a β,β-disubstituted exocyclic double bond. We anticipate that propargyl silanes **5** can be prepared asymmetrically, and further that conversion to the allene ether can be done with control of absolute stereochemistry. Chiral, non-racemic allene ethers are promising partners for a number of different annulation reactions.

^{1}H NMR and ^{13}CNMR spectra were recorded on either a Varian Mercury Plus 300 operating at 300 MHz or 75 MHz, respectively or on a Varian Unity Inova 500 operating at 500 MHz or 126 MHz, respectively. Infrared spectra were recorded on a Perkin-Elmer IR 1430 spectrometer. Electron impact mass spectra were recorded on a VG-70SE mass pectromter. TLC was performed on Sigma-Aldrich TLC plates, 250 μm, particle size 5–17 mm, pore size 60 A. Flash chromatography was performed on Natland International Corporation silica gel, 200–400 mesh. Anhdrous THF, Et_2O, CH_2Cl_2 were taken from a solvent purification system from Glass-Countour (www.glascounter.com). Et_3N and Hünig's base were distilled from CaH_2 and stored over KOH. Other reagents were used as received. All moisture sensitive reactions were performed under a static nitrogen or argon atmosphere in oven-fried or flame-dried glassware.

1-(*tert*-Butyldimethylsilanyl)non-2-yn-1-ol (5a)
To a solution of alkynol **4a** (6.0 g, 42.8 mmol) in THF (30 mL) at –78 °C was added BuLi (17.3 mL; 47.1 mmol; 2.7 M solution in hexane). The reaction mixture was warmed to 0 °C and allowed to stir for 30 min. After cooling to –78 °C, TBSCl (7.1 g, 68.5 mmol) in THF (3 mL) was added via cannula. After stirring for 2 h at r.t., the reaction mixture was cooled to –78 °C and BuLi (25.3 mL; 2.7 M solution in hexane) was added. The mixture was stirred for 40 min at –20 °C, and the reaction mixture was subsequently diluted with aq $NaHCO_3$ and Et_2O. The aq phase was extracted with Et_2O, the combined organic extracts dried ($MgSO_4$), and the solvent was removed in vacuo. Column chromatography (silica gel; 5% EtOAc–hexane) gave **5a**.

Yield: 10.7 g (41.9 mmol, 98%); yellow oil.

IR (film): 3420, 2940, 1690, 1460, 1250 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.20 (t, 1 H, *J* = 2.4 Hz, CH), 2.33 (td, 2 H, *J* = 6.9, 2.4 Hz, CH_2), 1.51–1.26 (m, 8 H, CH_2), 0.97 (s, 9 H, CH_3), 0.96–0.86 (m, 3 H, CH_3), 0.10 (s, 3 H, CH_3), 0.07 (s, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 89.0, 81.2, 55.2, 31.6, 29.1, 28.8, 27.1 (3 C), 22.8, 19.3, 17.2, 14.3, –7.7, –8.4.

MS (EI): *m*/*z* (%) = 73 (61), 75 (100), 197 (4), 211 (4), 254 (1).

HRMS: *m*/*z* calcd for $C_{15}H_{30}OSi$ [M$^+$]: 254.2066; found: 254.2052.

***tert*-Butyl-(1-methoxymethoxynon-2-ynyl)dimethylsilane (6a)**
To a solution of alkynol **5a** (7.2 g, 28.3 mmol) in CH_2Cl_2 (30 mL) was added Hünig's base (9.9 mL, 56.6 mmol). After cooling to 0 °C, chloromethyl methyl ether (3.7 mL, 48.7 mmol) was added and the mixture was allowed to stir at r.t. for 2 h. The reaction mixture was diluted with aq $NaHCO_3$ and Et_2O. The aq phase was extracted with Et_2O, the combined organic extracts dried ($MgSO_4$), and the solvent was removed in vacuo. Column chromatography (silica gel; 0.625% EtOAc–hexane) gave **6a**.

Yield: 7.8 g (44.8 mmol; 92%); pale yellow oil.

IR (film): 2950, 1460, 1250, 1140 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.99 (d, 1 H, *J* = 6.3 Hz, OCH_2O), 4.51 (d, 1 H, *J* = 6.3 Hz, OCH_2O), 4.18 (t, 1 H, *J* = 2.4 Hz, CH), 3.50 (s, 3 H, OCH_3), 2.21 (td, 2 H, *J* = 6.9, 2.4 Hz, CH_2), 1.58–1.23 (m, 8 H, CH_2), 0.99 (s, 9 H, CH_3), 0.98–0.88 (m, 3 H, CH_3), 0.09 (s, 3 H, CH_3), 0.08 (s, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 94.7, 93.1, 78.0, 57.6, 55.9, 31.6, 29.1, 28.8, 27.1 (3 C), 25.9, 22.8, 19.3, 17.3, –7.5, –8.0.

MS (EI): *m*/*z* (%) = 73 (100), 89 (29), 115 (13), 149 (5), 253 (14) 298 (1).

HRMS: *m*/*z* calcd for $C_{17}H_{34}O_2Si$ [M$^+$]: 298.2328; found: 298.2370.

***tert*-Butyl-(1-methoxymethoxy-3-methylnona-1,2-dienyl)dimethylsilane (8a)**
To a solution of methoxymethyl ether **6a** (2.5 g, 8.4 mmol) in THF (3 mL) was added *s*-BuLi (8.4 mL; 10.9 mmol; 1.3 M solution in hexane) at –78 °C. After stirring for 15 min, MeI (0.78 mL, 12.6 mmol) was added. The mixture was allowed to stir for an additional 15 min before dilution with aq $NaHCO_3$ and Et_2O. The aq phase was extracted with Et_2O, the combined organic extracts were dried ($MgSO_4$), and the solvent was removed in vacuo. Column chromatography (silica gel; 0.625% EtOAc–hexane) gave **8a**.

Yield: 2.5 g (8.0 mmol; 96%); pale yellow oil.

IR (film): 2980, 1960, 1465 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.77 (s, 2 H, OCH_2O), 3.37 (s, 3 H, OCH_3), 2.01–1.95 (m, 2 H, CH_2), 1.74 (s 3 H, CH_3), 1.48–1.18 (m, 8 H, CH_2), 0.94 (s, 9 H, CH_3), 0.91–0.85 (m, 3 H, CH_3), 0.04 (s, 3 H, CH_3), 0.03 (s, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.8, 126.8, 110.9, 94.7, 56.1, 35.0, 32.0, 27.9, 27.1 (3 C), 26.8, 22.8, 21.2, 17.1, 14.3, –6.1, –6.4.

MS (EI): *m*/*z* (%) = 218 (46), 230 (53), 243 (23), 268 (12), 312 (1).

HRMS: *m*/*z* calcd for $C_{18}H_{36}O_2Si$ [M$^+$]: 312.2485; found: 312.2477.

1-Methoxymethoxy-3-methylnona-1,2-diene (16a)
To a solution of allene ether **8a** (2.1 g, 6.7 mmol) in THF (10 mL) was added TBAF (2.1 g, 8.1 mmol) and LiOH (0.16 g, 6.7 mmol). After stirring at r.t. for 2 h, the reaction mixture was diluted with aq $NaHCO_3$ and Et_2O. The aq phase was extracted with Et_2O, the combined organic extracts were dried ($MgSO_4$), and the solvent was removed in vacuo. Column chromatography (silica gel; 0.625% EtOAc–hexane) gave **16a**.

Yield: 1.1 g (5.7 mmol; 82%); colorless oil.

IR (film): 2940, 1920, 1470, 1390 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.45 (m, 1 H, HC=C=C), 4.77 (s, 2 H, OCH_2O), 3.41 (s, 3 H, OCH_3), 2.02 (m, 2 H, CH_2), 1.79 (d, 3 H, *J* = 2.1 Hz, CH_3), 1.46–1.23 (m, 8 H, CH_2), 0.90–0.85 (m, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.0, 116.7, 116.0, 94.9, 56.1, 35.9, 32.0, 29.2, 27.6, 22.8, 21.6, 14.3.

MS (EI): *m*/*z* (%) = 68 (16), 81 (14), 128 (100), 142 (12), 198 (1).

HRMS: *m*/*z* calcd for $C_{12}H_{22}O_2$ [M^+]: 198.1620; found: 198.1615.

2-Hydroxy-3-methyl-5-(1-methylheptylidene)-4-phenylcyclopent-2-enone (18a)

To a solution of allene **16a** (200 mg, 1.01 mmol) in THF (5 mL) was added BuLi (0.45 mL; 1.21 mmol; 2.7 M solution in hexane) at –78 °C. After stirring for 1 h, morpholino enamide **17** (280 mg, 1.21 mmol) in THF (3 mL) was added via cannula. After stirring for 2 h, the reaction was transferred by cannula in to a solution of $FeCl_3$ (204 mg, (2.00 mmol) in Et_2O (10 mL). The reaction mixture was diluted with aq $NaHCO_3$ and Et_2O. The aq phase was extracted with Et_2O, the combined organic extracts were dried ($MgSO_4$), and the solvent was removed in vacuo. Column chromatography (silica gel; 5% EtOAc–hexane) gave **18a** as a ca. 1:2 mixture of *E* and *Z* isomers.

Yield: 216 mg (0.73 mmol; 72%); yellow oil.

Compound *Z*-18a

IR (film): 3250, 1690, 1640, 1400 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.06 (m, 5 H, ArH), 5.79 (s, 1 H, OH), 4.09 (s, 1 H, CH), 2.95–2.70 (m, 2 H, CH_2), 1.71 (d, 3 H, *J* = 1.2 Hz, CH_3), 1.58 (s, 3 H, CH_3), 1.43–1.25 (m, 8 H, CH_2), 0.91–0.85 (m, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.2, 163.3, 152.9, 150.5, 139.8, 138.4, 131.7, 128.2 (2 C), 127.1 (2 C), 50.2, 37.3, 31.8, 29.5, 26.8, 22.7, 18.5, 14.3, 11.6.

MS (EI): *m*/*z* (%) = 67 (15), 77 (15), 185 (45), 214 (6), 228 (19), 242 (37), 298 (72).

HRMS: *m*/*z* [M^+] calcd for $C_{20}H_{26}O_2$: 298.1933; found: 298.1952.

Compound *E*-18a

IR (film): 3300, 1680, 1400 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.08 (m, 5 H, ArH), 5.74 (s, 1 H, OH), 4.19 (s, 1 H, CH), 2.29 (s, 3 H, CH_3), 1.98–1.86 (m, 2 H, CH_2), 1.70 (d, 3 H, *J* = 0.9 Hz, CH_3), 1.28–0.93 (m, 8 H, CH_2), 0.84 (t, 3 H, *J* = 3.3 Hz, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.3, 168.2, 150.4, 141.2, 136.6, 131.9, 128.5, 128.0 (2 C), 126.8 (2 C), 50.4, 33.8, 31.9, 29.4, 28.6, 22.8, 21.7, 14.3, 11.7.

MS (EI): *m*/*z* (%) = 105 (65), 115 (29), 129 (26), 149 (21), 167 (13), 185 (54), 209 (14), 228 (100), 241 (28), 298 (69).

HRMS: *m*/*z* calcd for $C_{20}H_{26}O_2$ [M^+]: 298.1933; found: 298.1948.

2-Ethyl-4-(4-methoxyphenyl)-3-methyl-5-(1-methylheptylidene)cyclopent-2-enone (23a)

To a solution of allene **16a** (200 mg; 1.01 mmol) in THF (5 mL) was added BuLi (0.45 mL; 1.21 mmol; 2.7 M solution in hexane) at –78 °C. After stirring for 1 h, enone **21** (0.103 g, 0.50 mmol) in THF (3 mL) was added via cannula. After stirring for 2 h, the reaction was diluted with aq $NaHCO_3$ and Et_2O. The aq phase was extracted with Et_2O, the combined organic extracts dried ($MgSO_4$), and the solvent was removed in vacuo. To a solution of crude tertiary alcohol **22a** in CH_2Cl_2 (10 mL) was added $FeCl_3$ (82 mg, 0.50 mmol) at r.t. After stirring at r.t. for 20 min, the reaction mixture was diluted with aq $NaHCO_3$ and Et_2O. The aq phase was extracted with Et_2O, the combined organic extracts were dried ($MgSO_4$), and the solvent was removed in vacuo. Column chromatography (silica gel; 5% EtOAc–hexane) gave **23a** as a ca. 1:1 mixture of *E* and *Z* isomers.

Yield: 118 mg (0.35 mmol; 69%); yellow oil.

***E* + *Z*-23a**

IR (film): 2990, 1695, 1630 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.99 (d, 4 H, *J* = 8.7 Hz, ArH), 6.81 (d, 4 H, *J* = 8.7 Hz, ArH), 4.10 (s, 1 H, CH), 4.06 (s, 1 H, CH), 3.78 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH), 2.90 (m, 2 H, CH_2), 2.68 (m, 2 H, CH_2), 2.29 (m, 2 H, CH_2), 2.28 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 1.93 (m, 2 H, CH_2), 1.74 (s, 3 H, CH_3), 1.58 (s, 3 H, CH_3), 1.28–1.06 (m, 16 H, CH_2), 1.05 (m, 3 H, CH_3), 1.03 (m, 3 H, CH_3), 0.84 (m, 3 H, CH_3), 0.82 (m, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 69 (37), 91 (26), 101 (13), 115 (20), 135 (21), 147 (47), 175 (100), 204 (49), 270 (32), 340 (59).

HRMS: *m*/*z* calcd for $C_{23}H_{32}O_2$ [M^+]: 340.2402; found: 340.2416.

2-Amino-3-methyl-5-(1-methylheptylidene)-4-phenylcyclopent-2-enone (20a)

To a solution of allene **16a** (200 mg, 1.01 mmol) in THF (5 mL) was added BuLi (0.45 mL; 1.21 mmol; 2.7 M solution in hexane) –78 °C. After stirring for 1 h, α-methylcinnamonitrile (**19**) (144 mg, 0.14 mmol) was added via cannula. The reaction mixture was warmed to –40 °C and stirred for 1 h. The mixture was then transferred by cannula into a solution of $FeCl_3$ (204 mg, 2.00 mmol) in Et_2O (10 mL). The reaction mixture was diluted with aq $NaHCO_3$ and Et_2O. The aq phase was extracted with Et_2O, the combined organic extracts dried ($MgSO_4$), and the solvent was removed in vacuo. Column chromatography (silica gel; 5% EtOAc–hexane) gave *E*-**20a** and *Z*-**20a** (ca. 1:2).

Yield: 195 mg (0.65 mmol; 68% combined yield); orange oils.

Compound *E*-20a

IR (film): 3490, 3380, 1650, 1560 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.06 (m, 5 H, ArH), 4.11 (s, 1 H, CH), 2.28 (s, 3 H, CH_3), 1.94–1.89 (m, 2 H, CH_2), 1.63 (s, 3 H, CH_3), 1.28–0.87 (m, 8 H, CH_2), 0.82 (m, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.0, 151.2, 142.2, 142.1, 134.6, 133.0, 128.5, 127.9 (2 C), 126.4 (2 C), 51.5, 33.3, 31.8, 29.3, 28.4, 22.6, 21.6, 14.1, 12.3.

MS: *m*/*z* (%) = 185 (42), 241 (18), 255 (16), 297 (89).

HRMS: *m*/*z* calcd for $C_{20}H_{27}NO$ [M^+]: 297.2093; found: 297.2079.

Compound *Z*-20a

IR (film): 3490, 3380, 1650, 1560 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.01 (m, 5 H, ArH), 4.07 (s, 1 H, CH), 2.95–2.70 (m, 2 H, CH_2), 1.63 (d, 3 H, *J* = 1.2 Hz, CH_3), 1.56 (s, 3 H, CH_3), 1.50–1.27 (m, 8 H, CH_2), 0.87 (m, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.9, 150.3, 142.4, 142.3, 134.6, 132.8, 129.7, 128.4 (2 C), 126.5 (2 C), 51.2, 37.3, 31.6, 29.3, 26.6, 22.4, 14.7, 14.1, 12.3.

MS (EI): *m*/*z* (%) = 185 (67), 241 (34), 255 (8), 297 (92).

HRMS: *m*/*z* calcd for $C_{20}H_{27}NO$ [M^+]: 297.2093; found: 297.2083.

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