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Azepine Synthesis from Alkyl Azide and Propargylic Ester via Gold Catalysis

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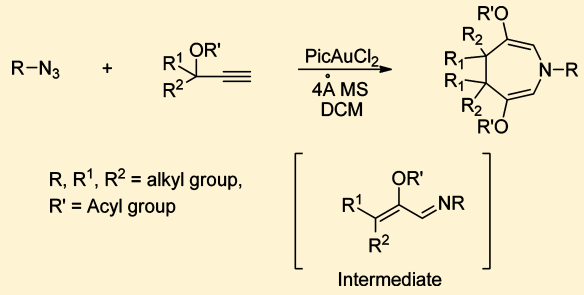
Supporting Information

ABSTRACT: An efficient new method was developed to synthesize multisubstituted 4, 5-dihydro-1*H*-azepine derivatives through the gold-catalyzed reaction of two molecules of propargylic esters with one molecule of alkyl azide. It was proposed that vinyl gold carbenoid, in situ generated from propargylic ester through gold-catalyzed 1, 2-rearrangement, was trapped by alkyl azide to give vinyl imine intermediate. These, in turn, could undergo a formal [4 + 3] cycloaddition with another molecule of vinyl gold carbenoid to afford the desired azepine product.



Azepine derivatives are important structural elements in many pharmacologically active compounds and have attracted considerable synthetic attention from organic chemists. Azepine rings can be prepared from intramolecular cyclization reactions through nucelophilic addition,[1] radical addition,[2] condensation reaction,[3] olefin metathesis[4] and pyrolysis,[5] or ring-expansion reactions through nitrogen transfer,[6] Beckman rearrangement,[7] and some related processes.[8] Despite these achievements, however, examples of azepine synthesis via intermolecular cycloaddition reaction are still very scarce.[9]

As shown in Scheme 1, vinyl gold or platinum carbenoid **A**, generated in situ from propargylic ester through gold-catalyzed 1, 2-rearrangement, has been reported to be an important synthetic intermediate.[10] Trapping intermediate A with alkene's double bonds,[11] sp^2 and sp^3 C–H bonds,[12,13] C–O bonds[14] and C–S bonds[15] led to the realization of a wide variety of carbene insertion reactions. Intermediate **A** can also engaged in β-elimination[16] and intramolecular annulation with neighboring alkenes,[17] pyridine,[18] or carbonyl groups.[19] Intermolecular cycloaddition with azomethine imines[20] and α,β-unsaturated imines[9b] is also documented.

It has been reported that trapping intermediate **A** by sulfoxide would give vinyl aldehyde.[21] We envisioned that a similar transformation of intermediate **A** with azide compound would provide vinyl imine **B**, which would further take a cycloaddition reaction with the second vinyl gold carbenoid unit **A** to give azepine product in a one-pot process (routes I and II, Scheme 1).

Constructing cyclic molecules from two or more acyclic precursors via tandem reaction is one of the most attractive strategies in organic synthesis.[22] We recently reported a diastereoselective cascade allylation/enyne cycloisomerization to construct densely functionalized oxygen hetereocycles from the reaction of the esters and the propargylic alcohols.[23] As a continuation of our efforts to develop the gold-catalyzed tandem reaction, we herein report an efficient new process to prepare polyfunctionalized 4,5-dihydro-1*H*-azepine derivatives from the reaction of propargylic esters with alkyl azides via gold catalysis.

The reaction of propargylic ester **1a** was chosen as the model system for our initial investigation. As shown in scheme 2, the reaction of **1a** with 2 mol equiv of phenyl azide **2** in the condition of 5% mol equiv of $AuCl_3$ gave no desired product.[24] However, when benzyl azide **3a** was used as the carbene trapper, azepine **5a** was obtained in 14% yield, together with the formation of vinyl aldehyde **4a**. Considering vinyl imine instability, 100 mg 4 Å MS was added to remove the moisture, which enhanced the yield of **5a** slightly (Scheme 2).

These preliminary results prompted us to further explore this reaction. As shown in Table 1, Au(I) catalysts exhibited poor activities. AuCl gave **5a** in 13% yield (Table 1, entry 2). Use of the phosphine or *N*-heterocyclic carbene ligands was also fruitless (Table 1, entries 3–5). Other Au(III) catalysts were then tested. $AuBr_3$ provided **5a** in 9% yield, while 2-benzylpyridine-ligated Au(III) catalyst **7** gave 15% yield (Table 1, entries 6 and 7).[25] $PicAuCl_2$ **6** performed best, affording **5a** in 25% yield (Table 1, entry 8). Increasing **1a**'s amount enhanced **5a**'s yield (Table 1, entry 9). Subsequent solvent screening proved DCM to be best reaction media (Table 1, entries 10–14). Under the conditions of 10% molar equiv of **6**, product **5a** was obtained in 54% yield (Table 1, entry 15). When catalyst **6** was added in two batches, **5a**'s yield was further improved to 68% yield (Table 1, entry 16).

Under the conditions from entry 16 in Table 1, the scope and limitations for this reaction were then explored. At first, we investigated the reaction of 2-methylbut-3-yn-2-yl benzoate **1a**

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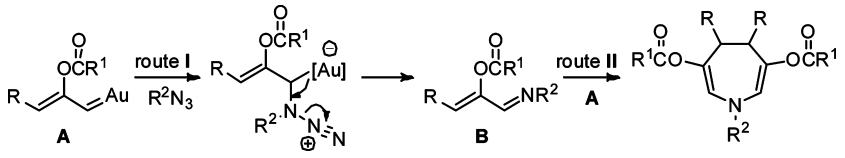
Scheme 1. Sequential Reactions of Gold Carbenoid A with Azide and Vinyl Imine



Scheme 2. Initial Exploration of 1a with Aryl and Alkyl Azide

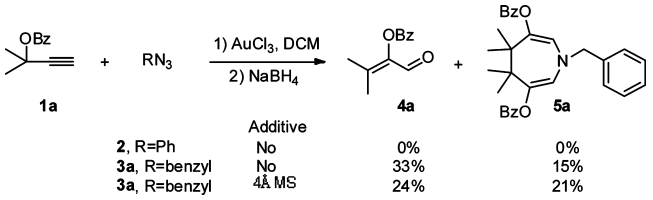
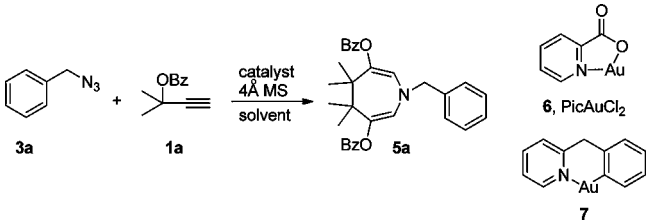


Table 1. Optimization of the Reaction of 1a with 3a[a]



	catalyst/loading (%)	ratio (3a/1a)	solution/time (h)	yield of 3a[b] (%)
1	$AuCl_3$/5	1/2.5	DCM/10	21
2	AuCl/5	1/2.5	DCM/11	13
3	$Ph_3PAuCl/AgSbF_6$/5	1/2.5	DCM/12	<5
4	IPrAuCl/$AgSbF_6$/5	1/2.5	DCM/9	0
5	SIPrAuCl/$AgSbF_6$/5	1/2.5	DCM/9	0
6	$AuBr_3$/5	1/2.5	DCM/10	9
7	7/5	1/2.5	DCM/10	15
8	$PicAuCl_2$/5	1/2.5	DCM/10	25
9	$PicAuCl_2$/5	1/5	DCM/10	37
10	$PicAuCl_2$/5	1/5	$MeNO_2$/8	23
11	$PicAuCl_2$/5	1/5	THF/8	12
12	$PicAuCl_2$/5	1/5	MeCN/8	trace
13	$PicAuCl_2$/5	1/5	$PhCH_3$/8	18
14	$PicAuCl_2$/5	1/5	DCE/10	35
15	$PicAuCl_2$/10	1/5	DCM/10	54
16[c]	$PicAuCl_2$/10	1/5	DCM/10	68

[a]Unless noted, all reactions were carried out at 0.1 mmol scale in 2 mL of solvent at rt with the addition of 100 mg of activated 4 Å MS. [b]Isolated yields. [c]10 mol % of catalyst **6** was added in two batches.

with a number of alkyl azides, including benyl azides with different substitution patterns. As shown in Table 2, substrates with electron-rich benzyl groups worked better than their electron-deficient analogues and gave higher reaction yields (**3a**,**b**,**f**, Table 2, entries 1, 2, and 6). ^{t}Butyl benzyl azide **3b** gave the best result. However, the reactions of electron-deficient substrates proceeded much faster than those of electron-rich analogues. Compounds **3d** and **3g** only took 5 h to give the corresponding products (Table 2, entries 4 and 7). Other alkyl azides, such as 2-naphthalene methyl azide **3h**, 2-phenyl ethyl azide **3i**, and methyl 2-azidoacetate **3j**, were also tested. The desired azepine products **5h**, **5i**, and **5j** were obtained in moderate yields (Table 2, entries 8−10).

A variety of bisubstituted propargylic esters **1a**−**g** (R^1, R^2 = alkyl group) were also investigated. A different acyl protection pattern was first studied. As compared with **1a**, pivalate and acetate substrates **1b** and **1c** gave relatively lower yields (Table 3, entries 2 and 3). Unsymmertic propargylic esters were then tested. The reaction of 3-methylpent-1-yn-3-ol benzoate **1d** afforded azepine **5n** in 48% yield with a high diastereoselectivity (*trans*/*cis* = 10/1, Table 3, entry 4). Similarly, the reactions of **1e** and **1f** also gave *trans*-**5o** and *trans*-**5p** as the major product in moderate yields (Table 3, entries 5 and 6). No desired product was obtained in the reaction of substrate **1g** and **3a**, possibly because of the increased steric hindrance. However, when electron-deficient *p*-fluorobenzyl azide **3d** was utilized as the reactant, the corresponding azpine **5r** was obtained in 16% yield (Table 3, entry 8). Monosubstituted propargylic ester (R^1 or R^2 = H, Table 3 reaction scheme) was also examined, but no desired product was obtained.

On the basis of the reaction sequence depicted in Scheme 1, employing two different vinyl gold carbenoids in routes I and II would provide an unsymmetric azepine product. As shown in Scheme 3, the reaction of benzyl azide **3a** (1.5 equiv) with 2-methylbut-3-yn-2-yl benzoate **1a** (1.0 equiv) and 3-methylhex-2-yn-3-yl benzoate **1f** (2.0 equiv) provided unsymmetric azepine adduct **8a** in 25% yield (Scheme 3). Similarly, in the reaction of **3a**, **1a**, and **1h**, **8b** was obtained in 18% yield (Scheme 3).

Vinyl aldehyde **4a** can be generated from the reaction of vinyl gold carbenoid with sulfoxide.[21] In the reaction of benzyl azide **3a** with **1a**, **4a** was generated as minor product through hydrolyzation of vinyl imine intermediate **B**. When 2 equiv of **3a** and 1 equiv of **1a** was treated with $PicAuCl_2$ at low temperature, **4a** was obtained as major product (scheme 4, eq 1). Further derivation of the azepine product **5b** was also performed. Hydrolyzation of **5k** with NaOH in a mixture of MeOH/THF afforded the azepane-3,6-dione product **9** in 80% yield (Scheme 4, eq 2).

In summary, we have developed an efficient new method to construct a series of densely functionalized 4,5-dihydro-1*H*-azepine products from the intermolecular reaction of alkyl azides with propargylic esters in which sequential reaction of vinyl gold carbenoids **A** with alkyl azides and vinyl imine intermediates **B** are involved.

EXPERIMENTAL SECTION

All reactions were run under an inert atmosphere (N_2) with flame-dried glassware using standard techniques for manipulating air-sensitive compounds. CH_2Cl_2 was obtained by fresh distilled over Calcium hydride. Commercial reagents were used as supplied or purified by standard techniques where necessary. Column chromatography was performed using 200−300 mesh silica with the proper solvent system according to TLC analysis using $KMnO_4$ stain and UV light to visualize the reaction components. Catalyst $PicAuCl_2$,[9b] alkyl azides,[9a] and propargylic esters[26] were synthesized according to the literature procedures.

Typical Procedure for the Gold-Catalyzed Carbocyclization of Propargylic Esters with Alkyl Azides. In a dry flask under

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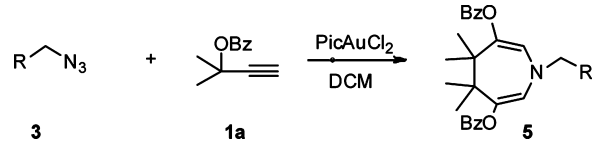
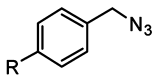
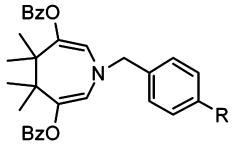
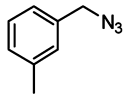
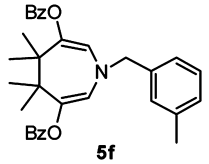
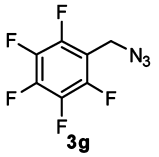
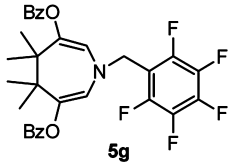
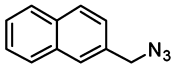
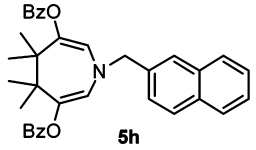
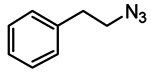
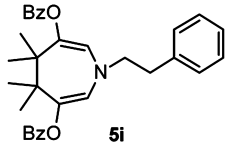
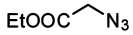
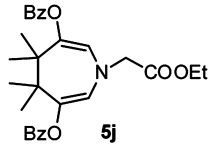
Table 2. Gold-Catalyzed Intermolecular Reaction of Propargylic Ester 1a with Alkyl Azides[a]



3 1a 5

entry	1	time	4	yield of 5 [c]
1	 **3a**, R = H	10	 **5a**, R = H	68
2	**3b**, R = ^{t}Bu	12	**5b**, R = ^{t}Bu	78
3	**3c**, R = Br	11	**5c**, R = Br	65
4	**3d**, R = F	5	**5d**, R = F	63
5	**3e**, R = NO_2	8	**5e**, R = NO_2	50
6	 **3f**	10	 **5f**	72
7	 **3g**	5	 **5g**	70
8	 **3h**	9	 **5h**	68
9	 **3i**	10	 **5i**	52
10	 **3j**	10	 **5j**	60

[a]Unless noted, all reactions were carried out on a 0.1 mmol scale (**1**/**3** = 5/1) in 2 mL of DCM at rt with the addition of 100 mg of activated 4 Å MS catalyzed by 10% molar equiv of $PicAuCl_2$ (added in two batches).

nitrogen equipped with a magnetic stir bar were sequentially added benzyl azide (~0.1 mmol, 1 equiv), propargyl esters (5 equiv), 100 mg of activated 4 Å MS, and CH_2Cl_2 (2 mL). $PicAuCl_2$ (0.1 equiv) was added in two portions at t = 0 and 4.5 h. The resulting mixture was stirred at room temperature and monitored periodically by TLC. Upon consumption of benzyl azide (8 − 20 h), the reaction mixture was directly subjected to silica gel chromatography (EA/PE) to give the desired azepine products.

1-Benzyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5a). Obtained as a yellow oil in 68% yield (32.7 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.6 Hz, 4H), 7.57 (t, J = 7.3 Hz, 2H), 7.45 (t, J = 7.6 Hz, 4H), 7.37−7.25 (m, 5H), 6.04 (s, 2H), 4.38 (s, 2H), 1.35 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ166.7, 137.9, 136.7, 133.1, 130.0, 129.9, 128.7, 128.4, 127.6, 127.2, 125.1, 61.0, 45.5, 26.8, 20.6; IR (neat) 2970, 2955, 1727, 1666, 1451, 1422, 1262, 1203, 1089, 1067, 1001, 705, 629 cm^{-1}; MS (m/z, rel intensity) 481 (M^+, 2), 391 (4), 390 (8), 377 (3), 376 (10), 294 (2), 287 (2), 122 (4), 106 (6), 105 (100), 91 (16), 77 (12), 51 (12); HRMS (EI) calcd for $C_{31}H_{31}NO_4$ $[M]^+$ 481.2253, found 481.2257.

1-(4-*tert*-Butylbenzyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5b). Obtained as a yellow oil in 78% yield (41.8 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.6 Hz, 4H), 7.57 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.6 Hz, 4H), 7.37 (d, J = 8.2 Hz, 2H), 7.26−7.24 (m, 2H), 6.04 (s, 2H), 4.36 (d, J = 1.5 Hz, 2H), 1.37 (s, 6H), 1.30 (s, 9H), 1.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.7, 150.4, 136.5, 134.9, 133.1, 130.0, 129.9, 128.4, 126.7, 125.6, 125.2, 60.6, 45.5, 34.5, 31.3, 26.8, 20.6; IR (neat) 2962, 2941, 1733, 1727, 1262, 1155, 1089, 1068, 1037, 707, 687 cm^{-1}; MS (m/z, rel intensity) 537 (M^+, 2), 390 (11), 350 (5), 161 (40), 147 (26), 132 (5), 106 (5), 105 (100), 77 (9); HRMS (EI) calcd for $C_{35}H_{39}NO_4$ $[M]^+$ 537.2879, found 537.2883.

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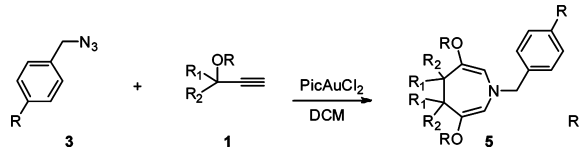
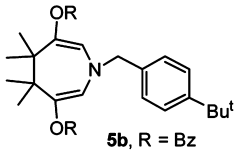
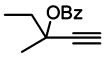
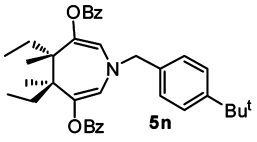
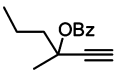
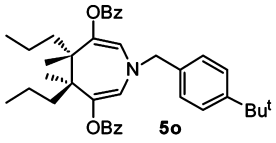
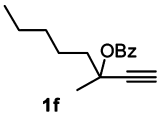
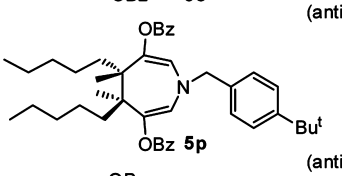
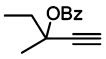
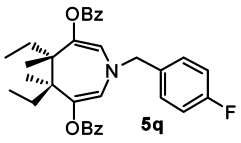
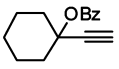
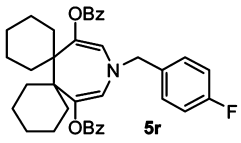
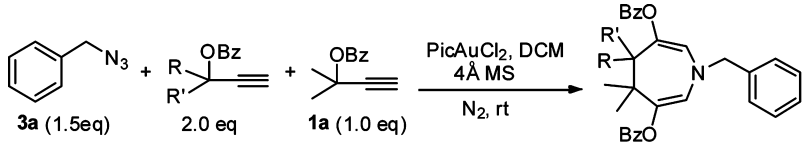
Table 3. Gold-Catalyzed Intermolecular Reaction of Substituted Benzyl Azides with Propargylic Alcohols[a,b]



entry	2	time	4	yield of 5
1	 **1a**, R = Bz	12	 **5b**, R = Bz	78
2	**1b**, R = Piv	16	**5k**, R = Piv	55
3	**1c**, R = Ac	15	**5m**, R = Ac	56
4	 **1d**	12	 **5n**	48 (anti / syn =10/1)
5	 **1e**	12	 **5o**	54 (anti / syn >20/1)[d]
6	 **1f**	20	 **5p**	40 (anti / syn >20/1)[d]
7[c]	 **1d**	9	 **5q**	32 (anti / syn = 20/1)
8[c]	 **1g**	20	 **5r**	16

[a]Unless noted, all reactions were carried out on a 0.1 mmol scale (**1**/**3** = 5/1) in 2 mL of DCM at rt with the addition of 100 mg of activated 4 Å MS catalyzed by 10% molar equiv of $PicAuCl_2$ (added in two batches). [b]The dr value was determined by ^1H NMR spectral data. [c]Substrate **3d** was employed. [d]No *syn*-product was detected.

Scheme 3. Reaction of 3a with Two Different Propargylic Esters



1f, R=Me, R'=^{n}Pr — **8a**, R=Me, R'=^{n}Pr, 25%

1h, R=H, R'=p-MeOPh — **8b**, R=H, R'=p-MeOPh, 18%

1-(4-Bromobenzyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5c). Obtained as a yellow oil in 65% yield (36.2 mg): ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.2 Hz, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.49–7.44 (m, 6H), 7.20 (d, J = 8.2 Hz, 2H), 6.00 (s, 2H), 4.31 (s, 2H), 1.34 (s, 6H), 1.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.6, 137.0, 136.9, 133.2, 131.8, 129.9, 128.9, 128.5, 124.9, 121.5, 60.4, 45.5, 26.8, 20.6; IR (neat) 2977, 2869, 1713, 1420, 1361, 1264, 1221, 1092, 1070, 1039, 713 cm^{-1}; MS (m/z, rel intensity) 391 (6), 390 (20), 186 (3), 184 (22), 182 (21), 170 (5), 168 (3), 156 (3), 106 (6), 105 (100), 77 (10); HRMS (EI) calcd for $C_{31}H_{30}BrNO_4$ $[M]^+$ 559.1358, found 559.1374.

1-(4-Fluorobenzyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5d). Obtained as a yellow oil in 63% yield (31.3 mg): ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.1 Hz, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.46 (t, J = 7.6 Hz, 4H), 7.27 (dd, J = 8.6, 5.4 Hz, 2H), 7.04 (t, J = 8.6 Hz, 2H), 6.02 (s, 2H), 4.34 (s, 2H),

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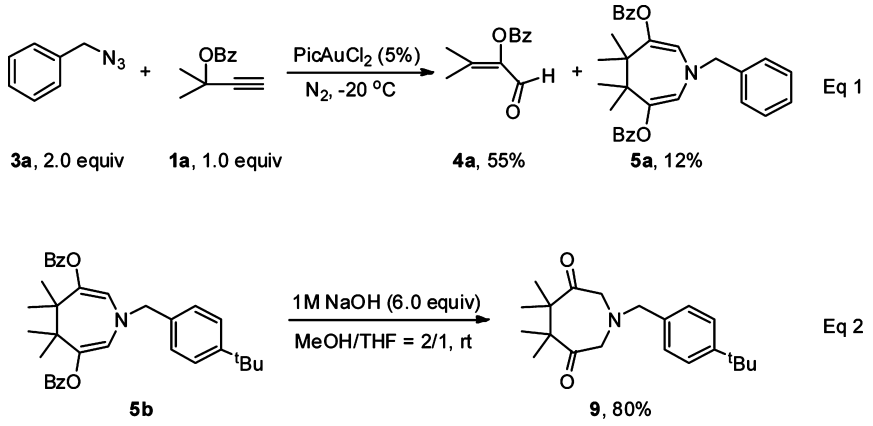
Scheme 4. Synthesis of Vinyl Aldehyde 4a and Further Derivation of Azepine 5k



1.31 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.6, 162.2 (d, J = 243.3 Hz), 136.8, 133.7, 133.2, 129.9, 128.8 (d, J = 8.1 Hz), 128.5, 124.9, 115.6 (d, J = 21.4 Hz), 60.3, 45.4, 26.7, 20.6; IR (neat) 2962, 2925, 1726, 1666, 1602, 1509, 1450, 1415, 1261, 1224, 1174, 1088, 1067, 1036, 1023, 824, 706 cm^{-1}; MS (m/z, rel intensity) 499 (M^+, 4), 395 (4), 394 (15), 390 (16), 268 (2), 138 (2), 123 (8), 109 (24), 105 (100), 77 (11); HRMS (EI) calcd for $C_{31}H_{30}FNO_4$ $[M]^+$ 499.2159, found 499.2163.

4,4,5,5-Tetramethyl-1-(4-nitrobenzyl)-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5e). Obtained as a yellow solid in 50% yield (26.3 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.7 Hz, 2H), 8.09 (d, J = 7.2 Hz, 4H), 7.61 (t, J = 7.4 Hz, 2H), 7.52 (d, J = 8.7 Hz, 2H), 7.47 (t, J = 7.5 Hz, 4H), 6.01 (s, 2H), 4.47 (s, 2H), 1.35 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ166.6, 147.5, 145.4, 137.4, 133.3, 129.9, 129.7, 128.5, 127.9, 124.8, 124.0, 60.3, 45.5, 26.7, 20.6; IR (neat) 2857, 1728, 1678, 1520, 1450, 1344, 1262, 1174, 1089, 1067, 1001, 800, 708 cm^{-1}; MS (m/z, rel intensity) 526 (M^+, 4), 422 (4), 421 (17), 390 (15), 141 (8), 106(10), 105 (100), 77 (11); HRMS (EI) calcd for $C_{31}H_{30}N_2O_6$ $[M]^+$ 526.2104, found 526.2101.

4,4,5,5-Tetramethyl-1-(3-methylbenzyl)-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5f). Obtained as a yellow oil in 72% yield (35.6 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 4H), 7.58 (t, J = 7.3 Hz, 2H), 7.47 (t, J = 7.7 Hz, 4H), 7.27–7.23 (m, 1H), 7.14–7.07 (m, 3H), 6.04 (s, 2H), 4.35 (s, 2H), 2.36 (s, 3H), 1.37 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.7, 138.3, 137.9, 136.5, 133.1, 130.0, 129.9, 128.6, 128.4, 128.3, 128.0, 125.2, 124.2, 61.0, 45.5, 26.8, 21.4, 20.7; IR (neat) 2965, 2945, 1727, 1666, 1601, 1450, 1419, 1261, 1175, 1156, 1067, 1037, 1001, 880, 707, 629 cm^{-1}; MS (m/z, rel intensity) 495 (M^+, 2), 404 (1), 391 (4), 390 (9), 308 (3), 286 (2), 122 (3), 119 (8), 106 (6), 105 (100), 91 (2), 77 (10), 51 (2); HRMS (EI) calcd for $C_{32}H_{33}NO_4$ $[M]^+$ 495.2410, found 495.2412.

4,4,5,5-Tetramethyl-1-((perfluorophenyl) methyl)-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5g). Obtained as a yellow solid in 70% yield (39.9 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.6 Hz, 4H), 7.60 (t, J = 7.3 Hz, 2H), 7.48 (t, J = 7.6 Hz, 4H), 6.06 (s, 2H), 4.47–4.38 (m, 2H), 1.25 (s, 6H), 1.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.3, 146.5 (m), 143.9 (m), 141.7 (m), 139.2 (m), 138.0, 133.2, 129.9, 128.5, 124.3, 120.0 (m), 111.6 (m), 47.9, 45.3, 26.4, 20.5; IR (neat) 2970, 2120, 1729, 1494, 1264, 1156, 1091, 1069, 1027, 709 cm^{-1}; MS (m/z, rel intensity) 571 (M^+, 2), 489 (3), 391 (4), 390 (14), 286 (3), 178 (8), 106 (7), 105 (100), 77 (13), 43 (3); HRMS (EI) calcd for $C_{31}H_{26}F_5NO_4$ $[M]^+$ 571.1782, found 571.1784.

4,4,5,5-Tetramethyl-1-(naphthalen-2-ylmethyl)-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5h). Obtained as a yellow oil in 68% yield (36.1 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.3 Hz, 4H), 7.85–7.80 (m, 3H), 7.76(s, 1H), 7.56 (t, J = 7.4 Hz, 2H), 7.47–7.43 (m, 7H), 6.10 (s, 2H), 4.53 (s, 2H), 1.38 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 136.7, 135.5, 133.3, 133.1, 132.9, 129.9, 128.6, 128.4, 127.9, 127.7, 126.1, 125.9, 125.2, 125.1, 61.2, 45.5, 26.8, 20.6; IR (neat) 2985, 2932, 1729, 1668, 1452, 1422, 1315, 1264, 1178, 1157, 1070, 1039, 1025, 882, 819, 755, 709, 632 cm^{-1}; MS (m/z, rel intensity) 531 (M^+, 9), 426 (15), 390 (31), 142 (8), 141 (100), 105 (30), 147 (66), 77 (6); HRMS (EI) calcd for $C_{35}H_{33}NO_4$ $[M]^+$ 531.2410, found 531.2412.

4,4,5,5-Tetramethyl-1-phenethyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5i). Obtained as a yellow oil in 52% yield (25.7 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 7.6 Hz, 4H), 7.59 (t, J = 7.3 Hz, 2H), 7.48 (t, J = 7.7 Hz, 4H), 7.28 (d, J = 7.8 Hz, 2H), 7.21–7.18 (m, 3H), 5.95 (s, 2H), 3.39 (t, J = 7.7 Hz, 2H), 2.94 (t, J = 7.8 Hz, 2H), 1.35 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.7, 138.2, 136.6, 133.1, 133.0, 129.9, 128.8, 128.5, 128.4, 126.4, 124.6, 59.5, 45.4, 37.1, 26.7, 20.6; IR (neat) 2975, 2850, 1729, 1262, 1090, 1068, 705, 668 cm^{-1}; MS (m/z, rel intensity) 495 (M^+, 10), 404 (15), 391 (17), 390 (100), 268 (3), 105 (57), 77 (7); HRMS (EI) calcd for $C_{32}H_{33}NO_4$ $[M]^+$ 495.2410, found 495.2408.

1-(2-Ethoxy-2-oxoethyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5j). Obtained as a yellow oil in 60% yield (28.6 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.3 Hz, 4H), 7.59 (t, J = 7.4 Hz, 2H), 7.47 (t, J = 7.7 Hz, 4H), 5.89 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 3.90 (q, J = 17.4 Hz, 2H), 1.42 (s, 6H), 1.29 (t, J = 7.1 Hz, 3H), 1.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ169.6, 166.5, 137.4, 133.2, 129.9, 128.5, 125.0, 61.4, 58.3, 45.4, 26.2, 20.6, 14.1; IR (neat) 2984, 2915, 1730, 1687, 1671, 1451, 1422, 1369, 1313, 1264, 1197, 1157, 1068, 1035, 1024, 709 cm^{-1}; MS (m/z, rel intensity) 477 (M^+, 4), 404 (2), 373 (6), 372 (30), 250 (2), 138(2), 123 (2), 106 (5), 105 (100), 77 (10); HRMS (EI) calcd for $C_{28}H_{31}NO_6$ $[M]^+$ 477.2151, found 477.2155.

1-(4-*tert*-butylbenzyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-azepine-3,6-diyl Bis(2,2-dimethylpropanoate) (5k). Obtained as a colorless oil in 55% yield (27.3 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 5.76 (s, 2H), 4.31 (s, 2H), 1.31 (s, 9H), 1.24 (s, 18H), 1.21 (s, 6H), 0.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ178.5, 150.2, 136.5, 135.3, 126.4, 125.6, 124.5, 60.4, 45.2, 38.9, 34.5, 31.3, 27.3, 26.5, 20.5; IR (neat) 2964, 2934, 1743, 1666, 1478, 1413, 1276, 1117, 1054, 894, 819 cm^{-1}; MS (m/z, rel intensity) 497 (M^+, 9), 413 (9), 412 (39), 351 (6), 350 (32), 266 (3), 248 (3), 148 (8), 147 (100), 132 (9), 119 (3), 117 (5), 105 (4), 57 (16), 41 (2); HRMS (EI) calcd for $C_{31}H_{47}NO_4$ $[M]^+$ 497.3505, found 497.3510.

1-(4-*tert*-Butylbenzyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-azepine-3,6-diyl Diacetate (5m). Obtained as a colorless oil in 56% yield (23.1 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 5.85 (s, 2H), 4.29 (d, J = 2.6 Hz, 2H), 2.10 (s, 6H), 1.30 (s, 9H), 1.19 (s, 6H), 1.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ171.0, 150.4, 136.1, 134.9, 126.6, 125.5, 124.8, 60.5, 45.0, 34.5, 31.3, 26.6, 20.7, 20.4; IR (neat) 2964, 2937, 1753, 1668, 1453, 1402, 1213, 1137, 1088, 1010, 898, 707 cm^{-1}; MS (m/z, rel intensity) 413 (M^+, 11), 371 (8), 370 (7), 328 (5), 312 (6), 266 (28), 224 (12), 187 (20), 164 (11), 161 (19), 147 (100), 132 (17), 131

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(14), 117 (16), 91 (9), 43 (20); HRMS (EI) calcd for $C_{25}H_{35}NO_4$ $[M]^+$ 413.2566, found 413.2567.

(4*R,5*R**)-1-(4-*tert*-Butylbenzyl)-4,5-diethyl-4,5-dimethyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5n).** Obtained as a colorless oil in 48% yield (27.1 mg, *anti/syn* = 10/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.3 Hz, 4H), 7.57 (t, J = 7.4 Hz, 2H), 7.46 (t, J = 7.8 Hz, 4H), 7.37 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 6.10 (s, 2H), 4.37 (s, 2H), 1.98 (dt, J = 20.8, 7.5 Hz, 2H), 1.61 (dt, J = 20.7, 7.4 Hz, 2H), 1.31 (s, 9H), 1.05 (s, 6H), 1.02 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.0, 150.4, 135.3, 133.9, 133.0, 130.2, 129.8, 128.4, 126.5, 125.6, 125.2, 61.3, 50.6, 34.5, 33.4, 31.3, 16.9, 9.4; IR (neat) 2962, 1728, 1666, 1451, 1259, 1174, 1149, 1089, 1067, 1000, 705, 618 cm^{-1}; MS (m/z, rel intensity) 565 (M^+, 7), 460 (13), 444 (3), 418 (20), 362 (3), 296 (2), 203 (3), 147 (38), 132 (9), 117 (7), 105 (100), 91 (2), 81 (4), 77 (17), 51 (3); HRMS (EI) calcd for $C_{37}H_{43}NO_4$ $[M]^+$ 565.3192, found 565.3195.

(4*R,5*R**)-1-(4-*tert*-Butylbenzyl)-4,5-dimethyl-4,5-dipropyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5o).** Obtained as a yellow oil in 54% yield (32.0 mg, only *anti*-isomer was detected by ^{1}H NMR): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.3 Hz, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.46 (t, J = 7.7 Hz, 4H), 7.37 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 6.11 (s, 2H), 4.41−4.32 (m, 2H), 1.88−1.83 (m, 2H), 1.59−1.38 (m, 6H), 1.31 (s, 9H), 1.08 (s, 6H), 0.93 (t, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ165.8, 150.4, 135.4, 134.3, 132.9, 130.4, 129.8, 128.4, 126.6, 125.6, 125.2, 61.5, 50.3, 43.2, 34.5, 31.3, 18.3, 17.7, 15.0; IR (neat) 2980, 1731, 1262, 1245, 1065, 1026, 833, 804, 737, 730, 619 cm^{-1}; MS (m/z, rel intensity) 593 (M^+, 8), 488 (20), 373 (6), 446 (9), 366 (8), 217(13), 147 (66), 132 (10), 105 (100), 95 (11), 77 (11); HRMS (EI) calcd for $C_{39}H_{47}NO_4$ $[M]^+$ 593.3505, found 593.3508.

(4*R,5*R**)-1-(4-*tert*-Butylbenzyl)-4,5-dimethyl-4,5-dipentyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5p).** Obtained as a yellow oil in 40% yield (26.0 mg, only *anti*-isomer was detected by ^{1}H NMR): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.3 Hz, 4H), 7.57 (t, J = 7.3 Hz, 2H), 7.46 (t, J = 7.7 Hz, 4H), 7.35 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.09 (s, 2H), 4.38 (s, 2H), 1.96−1.91 (m, 2H), 1.58−1.25 (m, 23H), 1.08 (s, 6H), 0.95−0.92 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ165.8, 150.3, 135.4, 133.9, 132.9, 130.3, 129.8, 128.4, 126.4, 125.5, 125.2, 61.4, 50.2, 40.9, 34.5, 32.8, 31.3, 24.7, 22.9, 17.7, 14.3; IR (neat) 2960, 2954, 1730, 1262, 1174, 1103, 1087, 1068, 1029, 705, 668, 639 cm^{-1}; MS (m/z, rel intensity) 649 (M^+, 10), 544 (25), 422 (10), 404 (11), 298 (7), 245 (9), 147 (57), 132 (8), 105 (100), 77 (8); HRMS (EI) calcd for $C_{43}H_{55}NO_4$ $[M]^+$ 649.4131, found 649.4135.

(4*R,5*R**)-4,5-Diethyl-1-(4-fluorobenzyl)-4,5-dimethyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5q).** Obtained as a yellow oil in 32% yield (16.9 mg, *anti/syn* = 20/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.46 (t, J = 7.7 Hz, 4H), 7.26 (dd, J = 8.3, 5.6 Hz, 2H), 7.04 (t, J = 8.5 Hz, 2H), 6.08 (s, 2H), 4.35 (s, 2H), 1.93 (dt, J = 20.8, 7.3 Hz, 2H), 1.60 (dt, J = 20.7, 7.2 Hz, 2H), 1.04 (s, 6H), 1.01 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ165.9, 162.2 (d, J = 244.0 Hz), 134.2, 134.0, 133.1, 130.1, 129.8, 128.6 (d, J = 8.1 Hz), 128.5, 124.9, 115.5 (d, J = 21.5 Hz), 60.9, 50.6, 33.3, 16.9, 9.4; IR (neat) 2877, 1720, 1280, 1130, 1100, 750 cm^{-1}; MS (m/z, rel intensity) 527 (M^+, 5), 422 (8), 418 (12), 376 (4), 300 (3), 109 (24), 105 (100), 77 (9); HRMS (EI) calcd for $C_{33}H_{34}FNO_4$ $[M]^+$ 527.2472, found 527.2479.

1-(4-Fluorobenzyl)-4,5-dicyclohexyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (5r). Obtained as a yellow oil in 16% yield (9.3 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.4 Hz, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.47 (t, J = 7.7 Hz, 4H), 7.29 (dd, J = 8.4, 5.5 Hz, 2H), 7.02 (t, J = 8.5 Hz, 2H), 6.18 (s, 2H), 4.36 (s, 2H), 1.95−1.93 (m, 2H), 1.85−1.82 (m, 2H), 1.61−1.26 (m, 14H), 1.10−1.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ165.9, 162.3 (d, J = 244.2 Hz), 135.3, 134.0, 133.0, 130.7, 129.9, 129.0 (d, J = 8.0 Hz), 128.5, 125.4, 115.5 (d, J = 21.4 Hz), 60.9, 51.9, 33.8, 29.1, 25.9, 24.7, 23.2; IR (neat) 2980, 2868, 1726, 1261, 1140, 1093, 1068, 701 cm^{-1}; MS (m/z, rel intensity) 579 (M^+, 3), 474 (5), 439 (4), 351 (17), 229 (16), 136 (10), 109 (48), 105 (100), 81(9), 77 (17); HRMS (EI) calcd for $C_{37}H_{38}FNO_4$ $[M]^+$ 579.2785, found 579.2793.

1-Benzyl-4,4,5-trimethyl-5-propyl-4,5-dihydro-1*H*-azepine-3,6-diyl Dibenzoate (8a). Obtained as a yellow oil in 25% yield (12.7 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 8.4 Hz, 2H), 7.58 (td, J = 7.2, 1.3 Hz, 2H), 7.46 (t, J = 7.1 Hz, 4H), 7.37−7.25 (m, 5H), 6.09 (s, 1H), 6.04−6.03 (m, 1H), 4.43−4.34 (m, 2H), 1.77−1.72 (m, 1H), 1.54−1.34 (m, 6H), 1.08 (s, 3H), 1.07 (s, 3H), 0.92 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ166.7, 165.9, 138.2, 135.9, 134.8, 133.1, 133.0, 130.2, 130.1, 129.9, 129.8, 128.7, 128.4, 127.6, 127.1, 127.0, 125.6, 124.7, 61.4, 49.3, 46.3, 42.4, 27.6, 20.9, 18.3, 17.5, 14.9; IR (neat) 2960, 2932, 1728, 1601, 1451, 1422, 1313, 1262, 1174, 1151, 1091, 1068, 1001, 707 cm^{-1}; MS (m/z, rel intensity) 446 (17), 432 (19), 324 (3), 320 (4), 217 (7), 106 (5), 105 (100), 95 (9), 91 (36), 77 (11), 67 (2); HRMS (EI) calcd for $C_{33}H_{35}NO_4$ $[M]^+$ 509.2566, found 509.2548.

1-Benzyl-5-(4-methoxyphenyl)-4,4-dimethyl-6-(pivaloyloxy)-4,5-dihydro-1*H*-azepin-3-yl Benzoate (8b). Obtained as a yellow oil in 18% yield (9.7 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.4 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.39−7.29 (m, 7H), 7.22 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 6.15 (s, 1H), 6.07 (s, 1H), 4.45 (s, 2H), 3.81 (s, 3H), 3.42 (s, 1H), 1.54 (s, 3H), 1.12 (s, 9H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ177.9, 166.2, 158.2, 137.9, 136.3, 135.4, 133.1, 131.2, 130.4, 129.8, 129.7, 128.8, 128.3, 127.7, 127.1, 125.3, 124.3, 113.1, 61.4, 59.0, 55.2, 41.4, 38.7, 29.9, 27.0, 25.7; IR (neat) 2973, 1732, 1510, 1452, 1265, 1246, 1059, 1025, 827, 706 cm^{-1}; MS (m/z, rel intensity) 539 (M^+, 20), 455 (19), 454 (100), 434 (5), 406 (4), 332 (8), 242 (3), 187 (3), 106 (4), 105 (52), 91 (41), 77 (8), 57 (15); HRMS (EI) calcd for $C_{34}H_{37}NO_5$ $[M]^+$ 539.2672, found 539.2668.

3-Methyl-1-oxobut-2-en-2-yl Benzoate (4a).[21] Obtained as a colorless oil in 55% yield (11.2 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.14 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 2.31 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ181.7, 164.2, 146.0, 142.8, 133.6, 130.2, 128.9, 128.5, 20.1, 18.0; IR (neat) 2950, 1734, 1678, 1654, 1451, 1374, 1250, 1120, 1064, 1024, 861, 708 cm^{-1}.

Procedure To Synthesize 9 from 5b. To a solution of azepine (40.0 mg, 0.074 mmol) in methanol/tetrahydrofuran (2/1, 1 mL) at 0 °C was added NaOH (1 M, 0.45 mL, 6 equiv). The resulting mixture was stirred at room temperature overnight. After consumption of the starting material, the reaction was diluted with brine and extracted with diethyl ether (3 × 2 mL). The combined organic extracts were dried over sodium sulfate, concentrated, and subjected to flash column chromatography on silica gel. The desired product was isolated as a white solid (19.6 mg, 80% yield).

1-(4-*tert*-Butylbenzyl)-4,4,5,5-tetramethylazepane-3,6-dione: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 3.68 (s, 2H), 3.39 (s, 4H), 1.31 (s, 9H), 1.16 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ211.0, 150.6, 133.9, 128.6, 125.4, 65.0, 62.8, 51.8, 34.5, 31.3, 20.7; IR (neat) 2963, 1696, 1117, 1023, 820, 720, 623 cm^{-1}; MS (m/z, rel intensity) 329 (M^+, 3), 301 (4), 273 (12), 189 (17), 188 (9), 174 (2), 148 (7), 147 (100), 132 (14), 126 (11), 117 (11), 105 (4), 91 (4), 42 (13); HRMS (EI) calcd for $C_{21}H_{31}NO_2$ $[M]^+$ 329.2355, found 329.2373.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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