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Synthesis of sterically congested bicyclic tetrahydrofurans via Pd-catalyzed cyclization

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Abstract—Prins-type cyclization followed by palladium-catalyzed cyclization provided sterically congested bi- or tricyclic tetrahydrofurans, which are very stereoselective as well. *cis*-2,5-Disubstituted tetrahydrofurans obtained from Prins-type cyclization have an allenyl group and a functional group such as alcohol, carboxylic acid, and aryl halide. The tetrahydrofurans bearing an allene group underwent palladium-catalyzed cyclization to give sterically congested bi- or tricyclic tetrahydrofurans.

1. Introduction

Substituted and fused cyclic tetrahydrofurans are commonly observed structural units in many bioactive natural products, resulting in the development of several synthetic approaches to these natural products over the past several decades.[1] The synthetic methods to fused bi- or tricyclic tetrahydrofurans have been developed using many strategies, such as radical cyclization reaction,[2] Grubb's ring closing methathesis,[1b] intramolecular C-glycosidation,[1g] Pd-catalyzed hydroxylation, carbonylation and lactonization of ene-diols,[3] radical reaction of methylthioethers,[4] and thermal benzannulation of 1,3,5-metallahexatrienes.[5] There are bi- or polycyclic tetrahydrofurans, incorporating quaternary centers at the ring junctions (Fig. 1).[1d,6] Those sterically congested tetrahydrofurans are relatively hard to synthesize. The synthetic schemes are relatively long, sometimes with low stereoselectivity.[7] Therefore, there is no straightforward method to synthesize sterically congested polycyclic tetrahydrofurans.

In our previous study, we reported highly stereoselective synthesis of 2,5-disubstituted 3-vinylidene tetrahydrofurans via Prins-type cyclization.[8,9] The tetrahydrofurans with vinylidene (allene) moieties are good substrates of palladium-catalyzed reactions.[10] According to the nucleophiles after activation of allenes by palladium, various functional groups can be introduced. In addition, the allene moieties could generate quaternary centers at the ring junctions via palladium-catalyzed cyclization. We envisaged that this strategy, successive Prins-type cyclization and palladium-catalyzed cyclization, could be a new method to synthesize sterically congested bicyclic tetrahydrofurans. Therefore, we report herein the stereoselective synthesis of sterically congested bi- or tricyclic tetrahydrofurans via Prins-type cyclization followed by palladium-mediated cyclization.

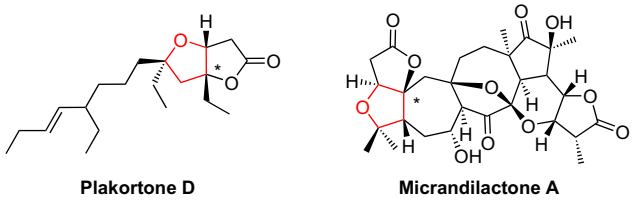

Figure 1.

2. Results and discussion

Recently, we reported a novel methodology for the stereoselective synthesis of cis-disubstituted tetrahydrofurans bearing vinylidene (allene) group at 3-position via Prins-type cyclization. This highly stereoselective synthetic method provided a useful intermediate for further derivatization. As shown in Scheme 1, we believed that various

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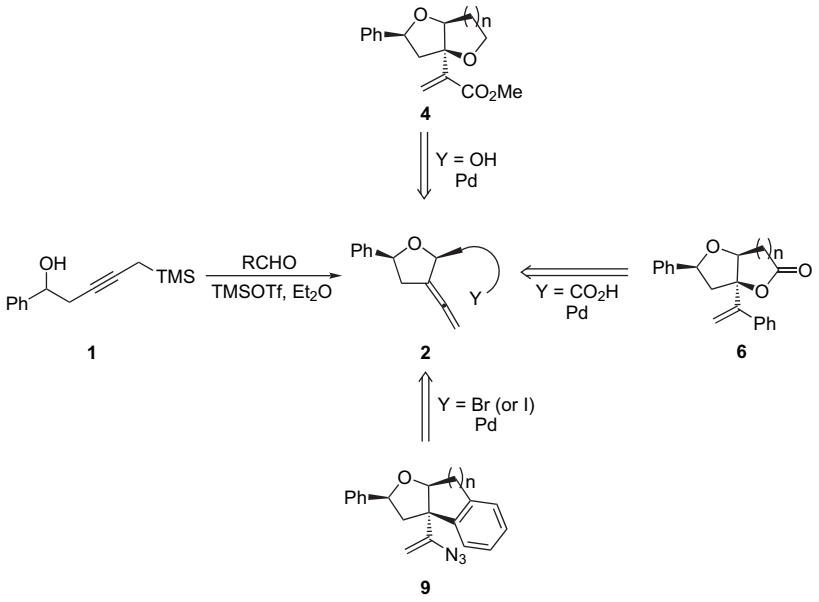


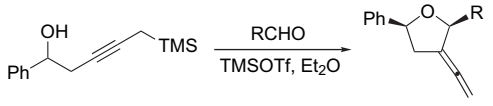
Scheme 1.

tetrahydrofurans **2** obtained via our Prins-type cyclization could be converted to sterically congested bi- or tricyclic tetrahydrofurans via palladium-catalyzed cyclization.[11]

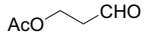
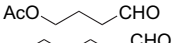
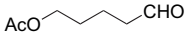
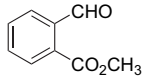
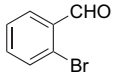
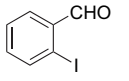
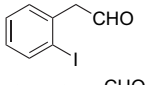
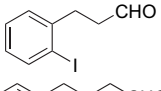
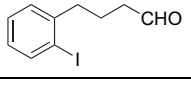
2.1. Preparation of the substrates 2

The substrates **2** for the palladium-catalyzed cyclization were prepared by our Prins-type cyclization previously reported.[8] Prins-type cyclization of the alcohol **1** and various aldehydes in the presence of TMSOTf gave intermediate oxocarbenium ions, which were cyclized with trimethylsilylmethylalkyne moiety to afford the tetrahydrofurans **2** (Table 1). All products **2** were obtained in 58–93% yields and had only cis-relationship between the 2- and 5-positions. The aldehydes possess functional groups such as alcohols, carboxylic esters, and aryl halide in order to carry out the next palladium-catalyzed cyclization.

Table 1. Prins-type cyclization of the substrate **1** and various aldehydes



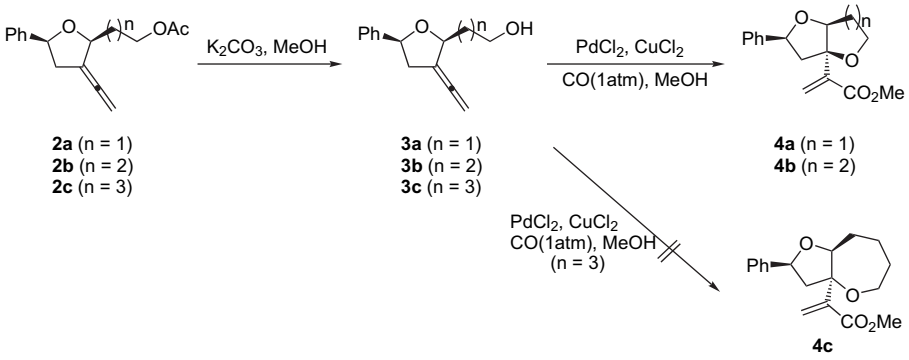
1 **2**

Entry	RCHO	Product	Yield[a] (%)
1		**2a**	78
2		**2b**	82
3		**2c**	86
4		**2d**	58
5		**2e**	91
6		**2f**	93
7		**2g**	82
8		**2h**	78
9		**2i**	77

[a] Isolated yields.

2.2. Alkoxypalladation followed by methoxycarbonylation

Allenes are good substrates of palladium-catalyzed reactions. The nucleopalladation of allenes by Pd(II) catalysts generates vinylpalladium complexes, which can be quenched by insertion of alkenes,[12] carbon monoxide,[13] and so on. Intermolecular alkoxypalladation/methoxycarbonylations[13a,b] and intramolecular aminopalladation/methoxycarbonylations[13c] of allenes have been reported. In this study, after deprotection, the substrates **2a**–**2c** with allene moiety underwent intramolecular alkoxypalladation, followed by methoxycarbonylation through insertion of carbon monoxide, to afford sterically congested bicyclic tetrahydrofurans **4a** and **4b** (Scheme 2). The allenyl esters **2a**, **2b**, and **2c** were hydrolyzed under basic conditions to afford the alcohols **3a**, **3b**, and **3c** in 90%, 89%, and 93% yields, respectively. The alcohols **3a** and **3b** were treated with a catalytic amount of $PdCl_2$ in the presence of $CuCl_2$ and carbon monoxide in methanol to give bicyclic tetrahydrofurans **4a** and **4b** in 98% and 31% yields, respectively. The alcohols **3a** and **3b** underwent palladium(II)-catalyzed intramolecular alkoxypalladation to give the vinylpalladium complexes, which were quenched by insertion of carbon monoxide to give bicyclic tetrahydrofurans **4a** and **4b**. In the case of the alcohol **3c**, no desired seven-membered ring compound **4c** was obtained and the alcohol **3c** was decomposed. The stereochemistry was determined by an NOE experiment of the bicyclic tetrahydrofuran **4b**.



Scheme 2.

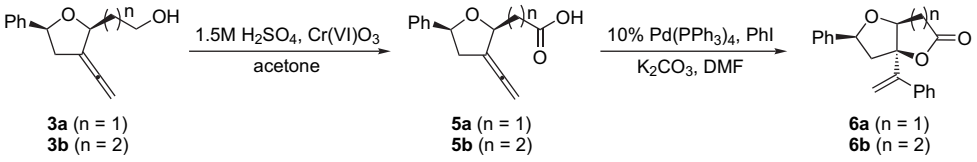
2.3. Palladium-catalyzed lactonization

The palladium-catalyzed cyclization reaction has received much attention as an efficient method for the preparation of oxygen- and nitrogen-containing heterocycles.[14] Walkup et al. have reported that γ-hydroxyallenes or hexa-4,5-dienoic acid reacted with arylpalladium(II) halides generated in situ from palladium(0) and aryl halides to form cyclized tetrahydrofurans or butyrolactones via sequential cyclization–coupling reaction.[15] We were interested in synthetic approaches to sterically congested bicyclic lactones via palladium-catalyzed cyclization of allenyl tetrahydrofurans with carboxylic acid moiety from the substrates **2** (Scheme 3). The deacetylated alcohols **3a** and **3b** were oxidized with 1.5 M sulfuric acid and $Cr(VI)O_3$ in acetone and converted to the carboxylic acid derivatives **5a** and **5b** in 55% and 62% yields, respectively. The acid derivatives **5a** and **5b** were treated with tetrakis(triphenylphosphine)palladium(0), iodobenzene, and potassium carbonate in DMF, as reported by Gallagher,[16] to accomplish the palladium-catalyzed lactonization. The allenes of the acid derivatives **5a** and **5b** reacted with phenylpalladium(II) iodide generated in situ from palladium(0) and iodobenzene to give π-allylpalladium intermediates,[17] which were attacked by the intramolecular nucleophile, the carboxylate moiety to afford the sterically congested bicyclic lactones **6a** and **6b** in 32% and 20% yields, respectively. To synthesize the fused seven-membered lactone, the compound **3c** was oxidized and treated under palladium-catalyzed conditions, but no desired product was obtained.

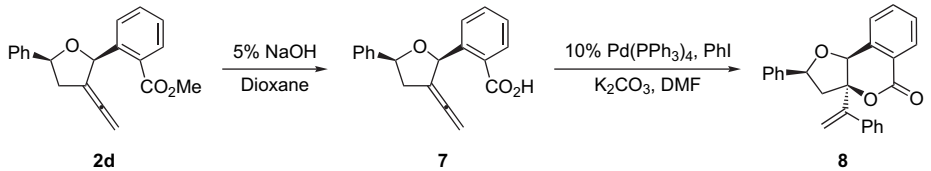
In addition, we tried palladium-catalyzed lactonization with the acid derivative **7** obtained from the compound **2d** by saponification (Scheme 4). The compound **2d** was hydrolyzed under basic conditions to afford the acid derivative **7** in 56% yield. The compound **7** underwent palladium-catalyzed lactonization under the same conditions as used in Scheme 3 to give the sterically congested tricyclic lactone **8** in 51% yield. The fused tricyclic lactone moiety is an important heterocycle in bioactive natural product.[18]

2.4. Intramolecular palladium-catalyzed azidation

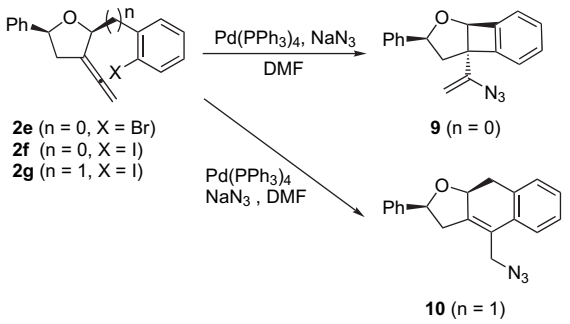
Among the compounds **2**, the compounds **2e**–**2i** bearing aryl halides could undergo intramolecular palladium-catalyzed reaction without additional aryl halides as in Scheme 4. On the other hand, additional nucleophiles were necessary like azide anion. The compounds **2e** and **2f** were treated with $Pd(PPh_3)_4$ and NaN_3 in DMF to give the congested tricyclic tetrahydrofuran **9** possessing a four-membered ring (Scheme 5). The aryl halide within the compounds **2e** and **2f** reacted with $Pd(PPh_3)_4$ to form the arylpalladium halides, which were added to the alkene to give the vinylpalladium intermediate, followed by the azide nucleophilic attack to afford the desired product **9** in 59% and 73% yields, respectively. The stereochemistry of the compound **9** was determined by the NOE experiment. The compound **2g** was also treated with $Pd(PPh_3)_4$ and NaN_3 in DMF to undergo a different palladium-catalyzed cyclization from those of the compounds **2e** and **2f**. The arylpalladium iodide from the



Scheme 3.



Scheme 4.



Scheme 5.

compound **2g** underwent insertion into the center carbon of the allene moiety to give a π-allylpalladium intermediate possibly due to the steric reason. The π-allylpalladium intermediate was attacked by the azide nucleophile to give the product **10** in 74% yield. The compounds **2h** and **2i** were treated with $Pd(PPh_3)_4$, but no desired product was obtained.

2.5. Mechanism

The compounds **2**, obtained by Prins-type cyclization, underwent intramolecular palladium-catalyzed cyclization by palladium(II) or palladium(0) species to give sterically congested bi- or tricyclic tetrahydrofuran derivatives. Various compounds bearing alcohol, carboxylic acid or aryl halide underwent palladium-catalyzed cyclization via different mechanisms. The compounds **3a** and **3b** with alcohol underwent alkoxypalladation followed by insertion of carbon monoxide with palladium(II) species (Fig. 2a). Alkoxypalladation of the allenes in the compounds **3a** and **3b** would give the vinylpalladium intermediate.[10,15] For the palladium-catalyzed lactonization of compounds **5a** and **5b**, arylpalladium halide was added to the center carbon of allenes in compounds **5a** and **5b**, resulting in the formation of π-allylpalladium intermediates (Fig. 2b).[17] The π-allylpalladium intermediates were attacked by the intramolecular nucleophile, carboxylate to afford the desired products. The compounds **2f** and **2g** underwent palladium-catalyzed cyclization via different palladium intermediates, plausibly due to

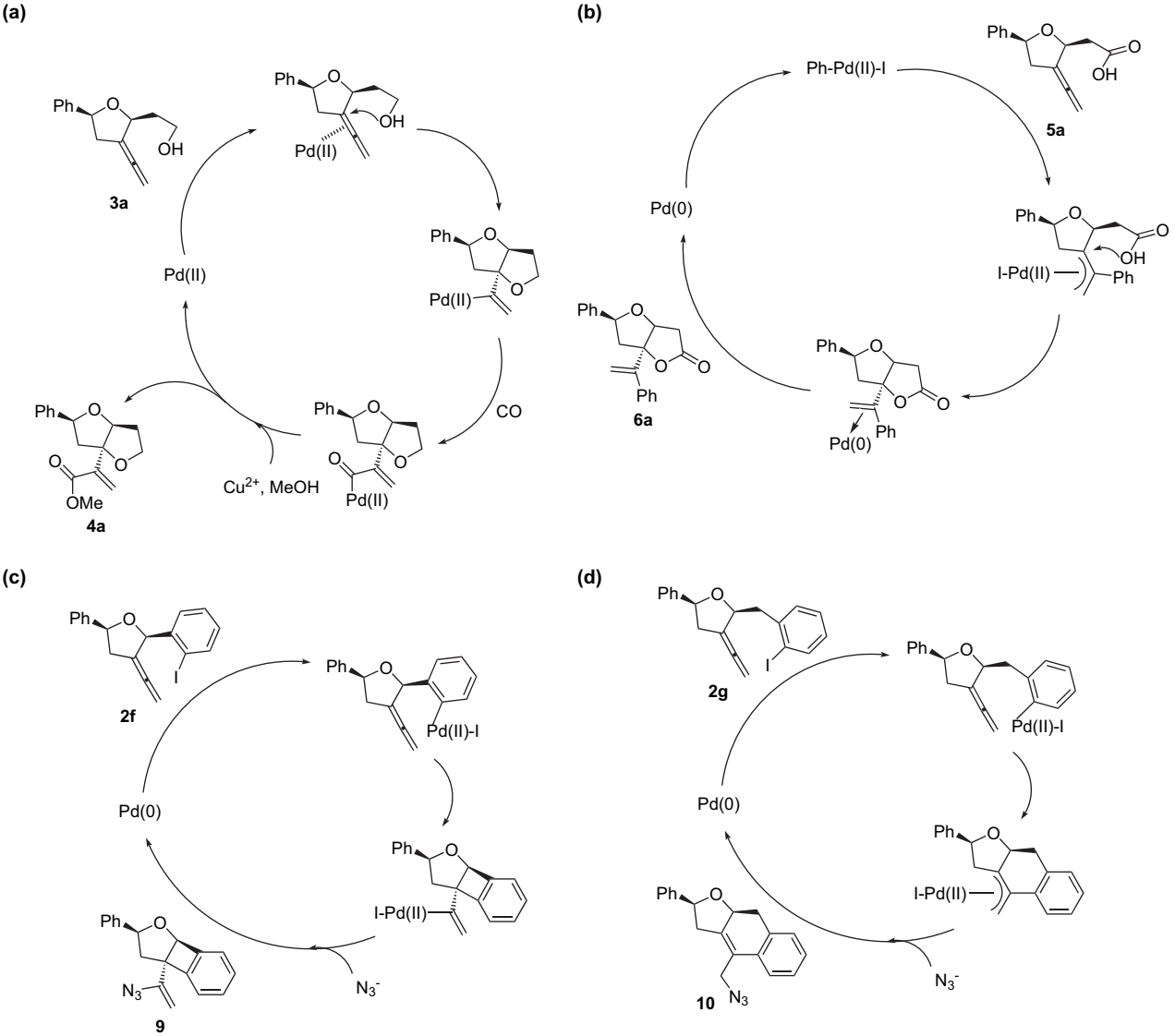


Figure 2. Proposed mechanism of palladium-catalyzed cyclization.

the steric reason (Fig. 2c and d). Oxidative addition of palladium(0) to the aryl halide of compound **2f** gave arylpalladium halide, which underwent 4-*exo-trig* cyclization to generate the vinylpalladium intermediate. On the other hand, the arylpalladium halide from the compound **2g** underwent 6-*endo-trig* cyclization to form π-allylpalladium intermediate. From the results of palladium cyclization of compounds **2f** and **2g**, the 4-*exo-trig* cyclization is preferred to the 5-*endo-trig* cyclization and 6-*endo-trig* cyclization to 5-*exo-trig* cyclization. *exo-trig* Cyclization resulted in formation of the vinylpalladium intermediate (Fig. 2c) and *endo-trig* cyclization provided the π-allylpalladium intermediate (Fig. 2d).

3. Conclusions

Previously obtained *cis*-2,5-disubstituted tetrahydrofurans having an allenyl group via Prins-type cyclization are good substrates for palladium-catalyzed reactions. The tetrahydrofurans with an allenyl group could be converted to various sterically congested bi- or tricyclic tetrahydrofurans via palladium-catalyzed cyclization. Prins-type cyclization followed by palladium-catalyzed cyclization provides a very good methodology for the synthesis of various sterically congested bi- or tricyclic tetrahydrofurans, which are very stereoselective as well. The sterically congested bi- or tricyclic ring system can be useful as key intermediates for the synthesis of natural products.

4. Experimental

4.1. General methods

All the commercially available reagents used were obtained from Aldrich, Fluka, Sigma, and Lancaster and generally used without further purification. Analytical thin layer chromatography was carried out with precoated silica gel glass plates (Merck Silica gel $60F_{254}$, layer thickness 0.25 mm). Flash column chromatography was conducted with silica gel grade 230–400 mesh (Merck Silica gel 60, particle size 0.040–0.063 mm). ^{1}H NMR spectra were obtained on a Brucker Avance 300 MHz and a Gemini Varian 600 MHz spectrometer. Chemical shifts were reported in parts per million. The data were reported as follows: chemical shift, number of protons, multiplicity (s=singlet, d=doublet, q=quartet, dd=doublet of doublet, m=multiplet, br=broadened), and coupling constants. ^{13}C NMR spectra were recorded on a Brucker Avance 75 MHz and a Gemini Varian 250 MHz spectrometer. Mass spectra were obtained by EI (70 eV) on a Hewlett Packard 5890. HRMS data were obtained on a VG70-VSEQ (VG ANALYTICAL, UK) mass spectrometer.

4.2. General procedure for the preparation of allenyl tetrahydrofuran derivatives 2

To a stirred solution of 1-phenyl-5-trimethylsilanyl-pent-3-yn-1-ol **1** (1.08 mmol) and aldehyde (1.08 mmol) in diethyl ether (10 mL) was added TMSOTf (1.25 mmol) under N_2 gas atmosphere at −78 °C. The reaction mixture was warmed to room temperature for 3 h slowly and stirred for 30 min at room temperature. After completion of reaction, the reaction mixture was diluted with ethyl acetate and H_2O, and extracted with ethyl acetate (10 mL×3). The collected organic solution was washed with brine, dried over $MgSO_4$, evaporated, and purified by silica gel flash chromatography (*n*-hexane/ethyl acetate=10:1) to afford tetrahydrofuran **2**.

4.2.1. Acetic acid 2-(5-phenyl-3-vinylidene-tetrahydrofuran-2-yl)-ethyl ester (2a). According to the general procedure for the preparation of allenyl tetrahydrofuran derivatives **2**, the product **2a** was obtained in 78% yield as viscous pale brown oil: FTIR (film, cm^{-1}) ν 3063, 3032, 2962, 2926, 1967, 1739, 1603, 1495, 1452, 1367, 1240, 1043; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.30 (m, 5H), 4.96–4.91 (m, 3H), 4.71 (s, 1H), 4.40–4.29 (m, 2H), 3.10–3.01 (m, 1H), 2.73–2.63 (m, 1H), 2.22–2.03 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 171.3, 141.10, 128.7, 128.0, 126.2, 103.8, 81.0, 79.5, 76.6, 61.69, 39.9, 33.7, 21.3; HRMS (CI) calcd for $C_{16}H_{19}O_3$, 259.1334 [M+H]$^+$; found, 259.1335 [M+H]$^+$.

4.2.2. Acetic acid 3-(5-phenyl-3-vinylidene-tetrahydrofuran-2-yl)-propyl ester (2b). According to the general procedure for the preparation of allenyl tetrahydrofuran derivatives **2**, the product **2b** was obtained in 82% yield as viscous pale brown oil: FTIR (film, cm^{-1}) ν 2958, 1966, 1736, 1602, 1450, 1367, 1243, 1174, 1043; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.30 (m, 5H), 4.94–4.89 (m, 3H), 4.64 (s, 1H), 4.20–4.14 (m, 2H), 3.09–3.00 (m, 1H), 2.72–2.59 (m, 1H), 2.09 (s, 1H), 1.98–1.75 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 171.5, 141.2, 128.7, 128.0, 126.3, 104.0, 80.9, 79.2, 64.8, 40.2, 31.0, 24.7, 21.2; HRMS (CI) calcd for $C_{17}H_{19}O_3$, 271.1334 [M−H]$^+$; found, 271.1332 [M−H]$^+$.

4.2.3. Acetic acid 4-(5-phenyl-3-vinylidene-tetrahydrofuran-2-yl)-butyl ester (2c). According to the general procedure for the preparation of allenyl tetrahydrofuran derivatives **2**, the product **2c** was obtained in 86% yield as viscous pale brown oil: FTIR (film, cm^{-1}) ν 2958, 1966, 1735, 1603, 1451, 1391, 1367, 1244, 1165, 1403; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.30 (m, 5H), 4.94–4.89 (m, 3H), 4.63–4.60 (m, 1H), 4.15–4.11 (m, 2H), 3.08–2.99 (m, 1H), 2.71–2.60 (m, 1H), 2.09 (s, 3H), 1.89–1.60 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 171.5, 141.3, 128.6, 128.0, 127.1, 126.3, 104.2, 80.9, 79.5, 79.0, 64.7, 40.2, 34.3, 28.8, 22.1, 21.2; HRMS (CI) calcd for $C_{18}H_{23}O_3$, 287.1647 [M+H]$^+$; found, 287.1648 [M+H]$^+$.

4.2.4. 2-(5-Phenyl-3-vinylidene-tetrahydrofuran-2-yl)-benzoic acid methyl ester (2d). According to the general procedure for the preparation of allenyl tetrahydrofuran derivatives **2**, the product **2d** was obtained in 58% yield as viscous brown oil: FTIR (film, cm^{-1}) ν 2953, 1958, 1725, 1596, 1489, 1435, 1283, 1127, 1077; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, 2H, J=5.1 Hz), 7.62–7.55 (m, 3H), 7.47–7.30 (m, 4H), 6.63 (t, 1H, J=4.5 Hz), 5.16 (dd, 1H, J=11.4, 7.5 Hz), 4.88–4.80 (m, 1H), 4.70–4.62 (m, 1H), 3.92 (s, 3H), 3.25–3.16 (m, 1H), 2.92–2.81 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.8, 168.1, 142.3, 141.1, 132.5, 130.5, 128.8, 128.1, 127.4, 127.2, 126.5, 104.8, 80.8, 79.3, 77.7, 52.2, 40.1, 31.8, 22.9, 14.4; HRMS

(CI) calcd for $C_{20}H_{18}O_3$, 306.1256 $[M]^+$; found, 306.1255 $[M]^+$.

4.2.5. (2-Bromophenyl)-5-phenyl-3-vinylidene-tetrahydrofuran (2e). According to the general procedure for the preparation of allenyl tetrahydrofuran derivatives **2**, the product **2e** was obtained in 91% yield as white solid: mp 61–64 °C; FTIR (film, cm^{-1}) ν 3064, 3032, 2863, 1968, 1605, 1568, 1494, 1469, 1439, 1379, 1342, 1314, 1264, 1203, 1158, 1111, 1054, 1023; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58–7.06 (m, 9H), 5.92 (s, 1H), 5.04 (dd, 1H, J=9.9, 6.0 Hz), 4.83–4.75 (m, 1H), 4.67–4.60 (m, 1H), 3.16–3.07 (m, 1H), 2.87–2.76 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.7, 140.9, 140.0, 132.9, 129.5, 129.1, 128.8, 127.8, 127.0, 126.5, 123.4, 104.2, 81.1, 80.6, 79.8, 40.2; HRMS (CI) calcd for $C_{18}H_{16}BrO$, 327.0385 $[M+H]^+$; found, 327.0385 $[M+H]^+$. Anal. Calcd for $C_{18}H_{15}BrO\cdot 0.1C_6H_{14}$: C, 66.52; H, 4.92. Found: C, 66.62; H, 4.60.

4.2.6. (2-Iodophenyl)-5-phenyl-3-vinylidene-tetrahydrofuran (2f). According to the general procedure for the preparation of allenyl tetrahydrofuran derivatives **2**, the product **2f** was obtained in 93% yield as pale brown solid: mp 88–90 °C; FTIR (film, cm^{-1}) ν 3062, 3032, 2863, 1967, 1605, 1586, 1563, 1494, 1463, 1435, 1379, 1341, 1261, 1203, 1159, 1107, 1052, 1039, 1011; ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 1H, J=7.8 Hz), 7.51–7.17 (m, 7H), 6.94–6.89 (m, 1H), 5.75 (t, 1H, J=3.9 Hz), 5.02 (dd, 1H, J=10.5, 6.6 Hz), 4.81–4.73 (m, 1H), 4.65–4.57 (m, 1H), 3.16–3.06 (m, 1H), 2.84–2.74 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.7, 143.0, 140.9, 139.5, 129.8, 128.8, 128.6, 128.2, 126.4, 104.3, 98.8, 84.9, 81.0, 80.2, 77.7, 77.3, 76.8; HRMS (CI) calcd for $C_{18}H_{16}IO$, 375.0246 $[M+H]^+$; found, 375.0246 $[M+H]^+$. Anal. Calcd for $C_{18}H_{15}IO$: C, 57.77; H, 4.04. Found: C, 58.09; H, 4.01.

4.2.7. 2-(2-Iodobenzyl)-5-phenyl-3-vinylidene-tetrahydrofuran (2g). According to the general procedure for the preparation of allenyl tetrahydrofuran derivatives **2**, the product **2g** was obtained in 82% yield as viscous pale brown oil: FTIR (film, cm^{-1}) ν 3061, 2921, 2853, 1966, 1561, 1495, 1466, 1434, 1331, 1082, 1013; ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, 1H, J=6.6 Hz), 7.48–7.29 (m, 7H), 6.98–6.93 (m, 1H), 4.99–4.87 (m, 1H), 3.33–3.18 (m, 1H), 3.11–3.01 (m, 1H), 2.76–2.66 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 141.4, 139.6, 131.4, 128.6, 128.4, 128.3, 127.9, 126.3, 103.7, 101.5, 81.2, 79.4, 79.1, 46.1, 40.1; HRMS (CI) calcd for $C_{19}H_{17}IO$, 388.0324 $[M]^+$; found, 388.0324 $[M]^+$.

4.2.8. 2-[2-(2-Iodophenyl)-ethyl]-5-phenyl-3-vinylidene-tetrahydrofuran (2h). According to the general procedure for the preparation of allenyl tetrahydrofuran derivatives **2**, the product **2h** was obtained in 78% yield as viscous pale brown oil: FTIR (film, cm^{-1}) ν 3058, 2926, 1962, 1718, 1670, 1595, 1436, 1379, 1163, 1119, 1092, 1062, 1010; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, 1H, J=8.4 Hz), 7.40–7.19 (m, 7H), 7.19–6.80 (m, 1H), 4.91–4.84 (m, 1H), 4.61 (t, 1H, J=4.5 Hz), 3.02–2.90 (m, 3H), 2.68–2.57 (m, 1H), 2.04–2.57 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.7, 145.1, 141.4, 139.7, 129.8, 128.7, 128.6, 128.0, 127.9, 126.3, 104.0, 100.8, 81.0, 79.4, 78.9, 40.4, 36.8, 35.2; HRMS (CI) calcd for $C_{20}H_{20}IO$, 403.0559 $[M+H]^+$; found, 403.0560 $[M+H]^+$.

4.2.9. 2-[3-(2-Iodophenyl)-propyl]-5-phenyl-3-vinylidene-tetrahydrofuran (2i). According to the general procedure for the preparation of allenyl tetrahydrofuran derivatives **2**, the product **2i** was obtained in 77% yield as viscous pale brown oil: FTIR (film, cm^{-1}) ν 3058, 2929, 2861, 1965, 1721, 1598, 1492, 1455, 1435, 1268, 1221, 1157, 1116, 1010; ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, 1H, J=7.8 Hz), 7.47–7.26 (m, 7H), 6.96–6.90 (m, 1H), 4.97–4.92 (m, 3H), 4.69 (s, 1H), 3.10–3.02 (m, 1H), 2.87–2.82 (m, 2H), 2.75–2.64 (m, 1H), 1.99–1.84 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.7, 145.2, 141.4, 139.7, 129.6, 128.7, 128.5, 128.0, 127.9, 126.3, 80.9, 79.6, 79.1, 41.1, 40.3, 34.2, 26.0; HRMS (CI) calcd for $C_{21}H_{21}IO$, 416.0637 $[M]^+$; found, 416.0635 $[M]^+$.

4.3. General procedure for the preparation of the alcohols 3

To a stirred solution of allenyl tetrahydrofuran ester (0.43 mmol) in methanol (5 mL) were added K_2CO_3 (0.83 mmol) and H_2O (1 mL) at room temperature. After stirring for 4 h, the reaction mixture was diluted with ethyl acetate and H_2O, and extracted with ethyl acetate (5 mL×3). The collected organic solution was washed with brine, dried over $MgSO_4$, evaporated, and purified by silica gel column chromatography (*n*-hexane/ethyl acetate=4:1) to afford alcohol **3**.

4.3.1. 2-(5-Phenyl-3-vinylidene-tetrahydrofuran-2-yl)-ethanol (3a). According to the general procedure for the preparation of the alcohols **3**, the product **3a** was obtained in 90% yield as pale yellow oil: FTIR (film, cm^{-1}) ν 2957, 2926, 2856, 1968, 1727, 1655, 1638, 1571, 1458, 1379, 1285, 1123, 1073; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.29 (m, 5H), 4.96–4.91 (m, 3H), 4.79 (t, 1H, J=3.3 Hz), 3.99–3.85 (m, 2H), 3.11–3.02 (m, 1H), 2.75–2.66 (m, 1H), 2.45 (s, 1H), 2.16–1.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.5, 140.7, 128.8, 128.2, 127.1, 126.3, 103.9, 81.4, 79.6, 79.5, 61.1, 39.8, 36.5.

4.3.2. 3-(5-Phenyl-3-vinylidene-tetrahydrofuran-2-yl)-propan-1-ol (3b). According to the general procedure for the preparation of the alcohols **3**, the product **3b** was obtained in 89% yield as colorless oil: FTIR (film, cm^{-1}) ν 2925, 2867, 1967, 1719, 1671, 1595, 1494, 1450, 1376, 1232, 1160, 1048; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43–7.30 (m, 5H), 4.97–4.91 (m, 3H), 4.65 (br s, 1H), 3.78–3.72 (m, 2H), 3.10–3.01 (m, 1H), 2.75–2.64 (m, 1H), 2.23 (s, 1H), 2.10–1.78 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.7, 142.9, 140.9, 133.4, 128.7, 128.1, 127.1, 126.3, 104.1, 81.0, 79.8, 79.3, 63.2, 40.0, 31.5, 29.3, 25.3.

4.3.3. 4-(5-Phenyl-3-vinylidene-tetrahydrofuran-2-yl)-butan-1-ol (3c). According to the general procedure for the preparation of the alcohols **3**, the product **3c** was obtained in 93% yield as pale brown oil: FTIR (film, cm^{-1}) ν 2932, 2869, 1966, 1722, 1601, 1492, 1452, 1370, 1268, 1171, 1070; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41–7.21 (m, 5H), 4.91–4.86 (m, 2H), 4.59 (br s, 1H), 3.69 (t, 2H,

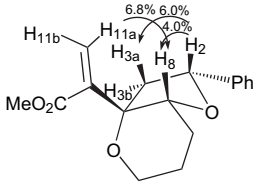
J=6.6 Hz), 3.04–2.97 (m, 1H), 2.70–2.62 (m, 1H), 1.85–1.65 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 141.0, 128.4, 127.7, 126.1, 104.0, 80.6, 79.4, 78.7, 76.5, 62.9, 40.0, 34.2, 32.7, 21.6.

4.4. General procedure for the preparation of bicyclic tetrahydrofuran derivatives 4

Allenyl tetrahydrofuran alcohol **3** (0.18 mmol) was dissolved in MeOH (2.0 mL) and the solution was saturated with CO gas (1 atm). $PdCl_2$ (0.014 mmol) and $CuCl_2$ (0.54 mmol) were added to the reaction mixture. After stirring for 4 h, the reaction mixture was diluted with ethyl acetate and H_2O, and extracted with ethyl acetate (5 mL×3). The collected organic solution was washed with brine, dried over $MgSO_4$, evaporated, and purified by silica gel column chromatography (*n*-hexane/ethyl acetate=25:1) to afford bicyclic tetrahydrofuran **4**.

4.4.1. 2-(2-Phenyl-tetrahydrofuro[3,2-*b*]furan-3a-yl)-acrylic acid methyl ester (4a). According to the general procedure for the preparation of bicyclic tetrahydrofuran derivatives **4**, the product **4a** was obtained in 95% yield as white solid: mp 41–43 °C; FTIR (film, cm^{-1}) ν 2947, 2876, 1719, 1623, 1494, 1438, 1327, 1227, 1191, 1145, 1091, 1061; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.29 (m, 5H), 6.39 (d, 1H, J=1.5 Hz), 6.19 (s, 1H), 5.35 (dd, 1H, J=8.7, 6.6 Hz), 4.75 (d, 1H, J=3.6 Hz), 4.33–4.25 (m, 1H), 4.16–4.10 (m, 1H), 3.86 (s, 3H), 2.83 (dd, 1H, J=13.2, 7.2 Hz), 2.64–2.16 (m, 2H), 1.94–1.87 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 142.9, 141.8, 141.1, 128.7, 127.9, 126.9, 126.6, 94.1, 87.3, 82.6, 67.6, 52.1, 49.1, 31.9; HRMS (CI) calcd for $C_{16}H_{19}O_4$, 275.1283 [M+H]$^+$; found, 275.1283 [M+H]$^+$. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.20; H, 6.67.

4.4.2. 2-(2-Phenyl-hexahydrofuro[3,2-*b*]pyran-3a-yl)-acrylic acid methyl ester (4b). According to the general procedure for the preparation of bicyclic tetrahydrofuran derivatives **4**, the product **4b** was obtained in 31% yield as viscous pale yellow oil: FTIR (film, cm^{-1}) ν 2952, 2873, 1725, 1621, 1562, 1492, 1439, 1313, 1269, 1201, 1148, 1101, 1046; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, 2H, J=7.2 Hz), 7.41–7.27 (m, 3H), 6.34 (s, 1H), 5.91 (s, 1H), 5.06 (dd, 1H, J=9.3, 6.0 Hz), 4.39 (t, 1H, J=2.7 Hz), 3.89–3.77 (m, 1H), 3.81 (s, 3H), 3.63–3.54 (m, 1H), 2.85 (dd, 1H, J=14.4, 9.9 Hz), 2.33–2.14 (m, 3H), 1.82–1.72 (m, 1H), 1.41–1.35 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 143.1, 140.0, 128.6, 127.7, 127.2, 126.7, 82.3, 79.3, 76.8, 63.3, 52.2, 50.9, 30.5, 24.0, 20.4; HRMS (CI) calcd for $C_{17}H_{20}O_4$, 288.1361 [M]$^+$; found, 288.1362 [M]$^+$.



Results of NOE experiment of compound ***4b***

4.5. General procedure for the preparation of carboxylic acid derivatives 5

Chromium(VI) oxide (1.59 mmol) was dissolved in 1.5 M H_2SO_4 and then, a solution of alcohol (0.46 mmol) in acetone (3 mL) was added to the reaction mixture slowly at 0 °C. After stirring for 3 h at 0 °C, the solvent was removed under reduced pressure and the resulting residue was basified with 1 N NaOH. Then, the aqueous layer was acidified with 1 M H_2SO_4 and the resulting solution was extracted with ethyl acetate (3 mL×3). The collected organic solution was washed with brine, dried over $MgSO_4$, evaporated, and dried in vacuo to give acid **5**.

4.5.1. (5-Phenyl-3-vinylidene-tetrahydrofuran-2-yl)-acetic acid (5a). According to the general procedure for the preparation of carboxylic acid derivatives **5**, the product **5a** was obtained in 55% yield as viscous pale brown oil: FTIR (film, cm^{-1}) ν 2864, 1968, 1711, 1429, 1288, 1178, 1026; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.17 (m, 5H), 4.91–4.83 (m, 4H), 3.01–2.92 (m, 1H), 2.74–2.70 (m, 2H), 2.67–2.56 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 177.1, 140.7, 134.0, 130.4, 128.9, 128.8, 128.7, 128.2, 126.4, 125.9, 103.3, 81.4, 80.2, 75.7, 39.9, 39.6.

4.5.2. 3-(5-Phenyl-3-vinylidene-tetrahydrofuran-2-yl)-propionic acid (5b). According to the general procedure for the preparation of carboxylic acid derivatives **5**, the product **5b** was obtained in 62% yield as viscous pale yellow oil: FTIR (film, cm^{-1}) ν 2926, 2854, 1967, 1734, 1654, 1559, 1496, 1452, 1377, 1257, 1166, 1056; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.30 (m, 5H), 4.94 (s, 3H), 4.69 (s, 1H), 3.08–3.03 (m, 1H), 2.85–2.65 (m, 3H), 2.22–2.09 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 180.1, 140.9, 130.4, 128.9, 128.7, 128.1, 126.3, 126.00, 103.4, 81.0, 79.5, 78.4, 40.1, 30.1, 29.2.

4.6. General procedure for the preparation of bicyclic lactone derivatives 6

To a solution of allenyl tetrahydrofuran carboxylic acid (0.12 mmol), $Pd(PPh_3)_4$ (0.012 mmol), and K_2CO_3 (0.61 mmol) in 3 mL of DMF were added PhI (0.61 mmol) and the reaction mixture was stirred for 4 h at 85 °C. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and H_2O, and extracted with ethyl acetate (5 mL×3). The collected organic solution was washed with brine, dried over $MgSO_4$, evaporated, and purified by silica gel column chromatography (*n*-hexane/ethyl acetate=15:1) to afford bicyclic lactone **6a**.

4.6.1. 5-Phenyl-6a-(1-phenyl-vinyl)-tetrahydrofuro[3,2-*b*]-furan-2-one (6a). According to the general procedure for the preparation of bicyclic lactone derivatives **6**, the product **6a** was obtained in 32% yield as viscous pale yellow oil: FTIR (film, cm^{-1}) ν 2926, 1784, 1493, 1449, 1401, 1263, 1177, 1067; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.28 (m, 10H), 5.57 (d, 1H, J=5.4 Hz), 5.37 (d, 1H, J=5.4 Hz), 4.97–4.90 (m, 1H), 4.80 (t, 1H, J=4.8 Hz), 2.96–2.68 (m, 3H), 2.58–2.49 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 147.0, 139.8, 138.8, 128.6, 128.5, 128.4, 128.2, 126.1, 116.4, 96.2, 81.7, 81.4, 77.2,

45.9, 35.8; HRMS (CI) calcd for $C_{20}H_{19}O_3$, 307.1334 $[M+H]^+$; found, 307.1336 $[M+H]^+$.

4.6.2. 2-Phenyl-3a-(1-phenyl-vinyl)-hexahydrofuro[3,2-*b*]-pyran-5-one (6b). According to the general procedure for the preparation of bicyclic lactone derivatives **6**, the product **6b** was obtained in 20% yield as dark brown solid: mp 84–88 °C; FTIR (film, cm^{-1}) ν 2926, 1740, 1496, 1444, 1384, 1319, 1251, 1202, 1176, 1078, 1042; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.28 (m, 10H), 5.63 (s, 1H), 5.33 (s, 1H), 4.90 (t, 1H, J=7.5 Hz), 4.33 (t, 1H, J=3.3 Hz), 3.04 (m, 1H, J=6.0 Hz), 2.85–2.73 (m, 1H), 2.59–2.43 (m, 2H), 2.31–2.21 (m, 1H), 2.17–2.09 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 148.4, 140.7, 139.6, 130.3, 129.1, 128.9, 128.6, 128.3, 128.2, 126.5, 117.7, 93.1, 79.2, 76.0, 48.0, 25.2, 21.6; HRMS (CI) calcd for $C_{21}H_{20}O_3$, 320.1412 $[M]^+$; found, 320.1411 $[M]^+$. Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.88; H, 6.30.

4.7. 2-(5-Phenyl-3-vinylidene-tetrahydrofuran-2-yl)-benzoic acid (7)

A solution of 2-(5-phenyl-3-vinylidene-tetrahydrofuran-2-yl)-benzoic acid methyl ester (43 mg, 0.14 mmol) and 5% NaOH (2 mL) in 3 mL of 1,4-dioxane was stirred for 3 h at 85 °C. After completion of the reaction, the solvent was removed under reduced pressure and the resulting residue was diluted with ethyl acetate and H_2O, and extracted with ethyl acetate (5 mL×3). The collected organic solution was washed with brine, dried over $MgSO_4$, evaporated, and dried in vacuo to give acid **7** (23 mg, 0.079 mmol) in 56% yield as pale yellow solid: mp 183–185 °C; FTIR (film, cm^{-1}) ν 2922, 2884, 1685, 1569, 1447, 1404, 1352, 1269, 1181, 1158, 1047; ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (q, 1H, J=1.2 Hz), 7.98 (d, 1H, J=7.8 Hz), 7.69–7.64 (m, 1H), 7.58–7.35 (m, 6H), 6.69 (d, 1H, J=3.9 Hz), 5.19 (dd, 1H, J=10.2, 6.0 Hz), 4.89–4.81 (m, 1H), 4.74–4.66 (m, 1H), 3.27–3.19 (m, 1H), 2.94–2.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.9, 173.1, 142.9, 140.9, 133.4, 131.5, 128.8, 128.2, 127.7, 127.6, 127.4, 126.5, 104.6, 80.9, 79.8, 78.0, 40.0. Anal. Calcd for $C_{19}H_{16}IO_3 \cdot 1.5H_2O$: C, 71.46; H, 6.00. Found: C, 71.11; H, 5.69.

4.8. 2-Phenyl-3a-(1-phenyl-vinyl)-hexahydrofuro-[3,2-*b*]pyran-5-one (8)

To a solution of 2-(5-phenyl-3-vinylidene-tetrahydrofuran-2-yl)-benzoic acid (23 mg, 0.08 mmol), $Pd(PPh_3)_4$ (8.9 mg, 0.008 mmol), and K_2CO_3 (53 mg, 0.39 mmol) in 2 mL of DMF was added PhI (43 μL, 0.39 mmol) and the reaction mixture was stirred for 4 h at 85 °C. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and H_2O, and extracted with ethyl acetate (5 mL×3). The collected organic solution was washed with brine, dried over $MgSO_4$, evaporated, and purified by silica gel column chromatography (*n*-hexane/ethyl acetate=12:1) to afford bicyclic lactone **8** (15 mg, 0.041 mmol) in 51% yield as pale yellow solid: mp 126–130 °C; FTIR (film, cm^{-1}) ν 2923, 2855, 1722, 1605, 1492, 1460, 1361, 1288, 1243, 1218, 1122, 1092, 1027; ^1H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, 1H, J=7.8 Hz), 7.75–7.52 (m, 3H), 7.41–7.19 (m, 10H), 5.45 (s, 1H), 5.18 (s, 1H), 5.14 (dd, 1H, J=9.9, 6.0 Hz), 5.02 (s, 1H), 3.05 (dd, 1H, J=16.2, 9.0 Hz), 2.73 (dd, 1H, J=14.4, 5.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 147.3, 141.0, 139.5, 134.9, 134.5, 130.7, 130.6, 129.6, 129.4, 128.8, 128.5, 128.3, 128.2, 127.7, 126.8, 125.7, 125.0, 118.4, 92.1, 80.0, 77.4, 47.3, 30.5, 29.9; HRMS (CI) calcd for $C_{25}H_{20}O_3$, 368.1412 $[M]^+$; found, 368.1414 $[M]^+$. Anal. Calcd for $C_{25}H_{20}O_3 \cdot 1.0H_2O \cdot 0.75CHCl_3$: C, 64.98; H, 4.82. Found: C, 65.27; H, 5.13.

4.9. General procedure for the preparation of fused tricyclic tetrahydrofuran derivatives 9 and 10

To a solution of allenyl halophenyl tetrahydrofuran (0.37 mmol) and $Pd(PPh_3)_4$ (0.037 mmol) in 5 mL of DMF was added NaN_3 (0.55 mmol) and the reaction mixture was stirred for 4 h at 85 °C. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and H_2O, and extracted with ethyl acetate (1 mL×3). The collected organic solution was washed with brine, dried over $MgSO_4$, evaporated, and purified by silica gel column chromatography (*n*-hexane/ethyl acetate=30:1) to afford tricyclic compounds.

4.9.1. 3a-(1-Azido-vinyl)-2-phenyl-2,3,3a,7b-tetrahydro-1-oxa-cyclopenta[3,4]-cyclobuta[1,2]benzene (9). According to the general procedure for the preparation of fused tricyclic tetrahydrofuran derivatives, the product **9** was obtained in 59% yield from compound **2e** and also obtained in 73% yield from compound **2f** as viscous dark brown oil: FTIR (film, cm^{-1}) ν 2958, 929, 2874, 2099, 1725, 1655, 1603, 1579, 1459, 1379, 1286, 1201, 1121, 1069, 1018; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64–7.59 (m, 2H), 7.49–7.46 (m, 2H), 7.34–7.30 (m, 5H), 5.85 (s, 1H), 5.54 (s, 1H), 5.44 (s, 1H), 5.36 (dd, 1H, J=10.8, 4.2 Hz), 2.60 (dd, 1H, J=13.2, 5.1 Hz), 2.11–1.99 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9, 141.6, 140.1, 137.9, 130.4, 129.8, 128.6, 128.2, 127.0, 126.4, 121.8, 107.2, 90.1, 83.4, 79.3, 47.8, 25.4; HRMS (CI) calcd for $C_{18}H_{15}N_3O$, 289.1215 $[M]^+$; found, 289.1222 $[M]^+$.

4.9.2. 4-(Azidomethyl)-2-phenyl-2,3,9,9a-tetrahydro-naphtho[2,3-*b*]furan (10). According to the general procedure for the preparation of fused tricyclic tetrahydrofuran derivatives, the product **10** was obtained in 74% yield as viscous dark brown oil: FTIR (film, cm^{-1}) ν 3031, 2942, 2098, 1634, 1488, 1452, 1335, 1244, 1094, 1068, 1031; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51–7.20 (m, 11H), 5.11 (dd, 1H, J=8.7, 6.6 Hz), 4.82–4.75 (m, 1H), 4.32 (d, 1H, J=13.8 Hz), 4.13 (d, 1H, J=13.8 Hz), 3.34–3.22 (m, 2H), 3.07 (t, 1H, J=14.2 Hz), 2.89–2.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 141.4, 134.0, 133.7, 129.2, 128.8, 128.2, 127.6, 127.4, 127.1, 126.3, 125.9, 123.3, 121.9, 80.8, 78.4, 49.8, 38.2, 35.3; HRMS (CI) calcd for $C_{19}H_{17}N_3O$, 303.1372 $[M]^+$; found, 303.1365 $[M]^+$.

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