



Gold-catalyzed cyclization of 1-alkynyl cyclopropyl *tert*-butyl carbonate to construct multifunctionalized vinyl cyclopropane derivatives

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ABSTRACT

A convenient new method was developed to prepare two types of vinyl cyclopropane derivatives through gold-catalyzed cyclization of 1-alkynyl cyclopropyl *tert*-butyl carbonates **2**. Different from the previous reported 5-*exo-dig* route, the 6-*endo-dig* addition is the preferred pathway to provide six-membered cyclized carbonates. Two factors, including stereoelectronic effect and steric effect might affect the regioselectivity. Therefore, low steric aliphatic substrates afforded only six-membered isomers. The synthetic utility of compound **3** was also explored to afford a series of β -carbonyl cyclopropanol derivatives.

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1. Introduction

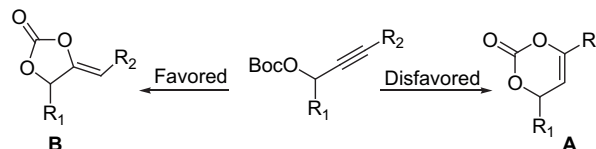
Vinyl cyclopropane species are found as the important structural elements in a wide range of bioactive natural, non-natural compounds.^{1,2} With a unique combination of a reactive double bond and an unstable three-membered ring in one molecule, these species can be employed as C5 or C3 building blocks in many metal-catalyzed inter- or intramolecular (5+2,³ 3+2,⁴ 4+1)⁵ cycloaddition reactions to construct cyclopentene or cycloheptene derivatives of various structural characteristics and functionalities.⁶

Methods for the preparation of vinyl cyclopropane derivatives are very limited. The reported results generally proceed via two similar transformations, including addition of carbene to the conjugated diene⁷ or the reaction of α -vinyl carbenoid with an isolated olefin.⁸ However, the synthetic utilities of these transformations often suffered from the tedious preparation of the diene or carbene reactants, and from the difficulties to introduce structural or functional diversity. Therefore, developing new approaches to construct these important synthetic entities would greatly broaden their application in organic synthesis.

Gold (I) complexes have emerged as an efficient and mild catalyst for the transformation of substrates possessing alkyne or alkene functionality into a range of useful structural motifs. As part of a program directed toward the development of new gold-catalyzed

reactions, we want to report herein a convenient new method to prepare multifunctionalized vinyl cyclopropane derivatives via gold-catalyzed cyclization of 1-alkynyl cyclopropyl *tert*-butyl carbonates.

In previous reports, most of the metal-catalyzed cyclization of propargylic carbonates, as indicated in Scheme 1, are favored to proceed in an intramolecular 5-*exo-dig* process to afford five-membered ring products **B**.⁹ For example: Gagosz group has reported that Au(I)-catalyzed 5-*exo-dig* cyclization of propargylic *tert*-butyl carbonates to give five-membered 4-alkylidene-1,3-dioxolan-2-ones even from an internal alkyne.¹⁰ Whereas in this paper, gold-catalyzed reaction of 1-alkynyl cyclopropyl *tert*-butyl carbonates **2** mainly provided six-membered isomers **3** (A type products, Scheme 1) via a 6-*endo-dig* route. The unusual regioselectivity might be owing to the special stereoelectronic effect in the cyclopropane-containing system.



Scheme 1. Metal-catalyzed cyclization of propargylic carbonates.

The starting 1-alkynyl cyclopropyl *tert*-butyl carbonate **2** can be readily prepared from the reaction of 1-alkynyl cyclopropanol with *tert*-butoxyl carbonate in CH_2Cl_2 .¹¹ Subsequent gold-catalyzed

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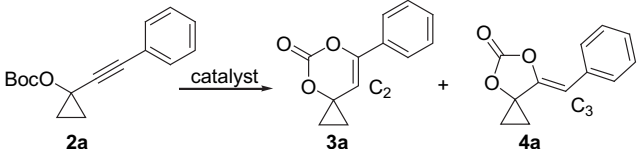
cyclization of compound **2** afforded two types of vinyl cyclopropane derivatives. The structure of the minor product **4a** was identified to be a five-membered spiro-cyclopropyl alkylidene-1,3-dioxolan-2-one derivative by X-ray crystallography.¹² The structure of **3a** was then determined to be a six-membered isomer.

A range of five- or six-membered carbonate bearing vinyl cyclopropanes were then prepared. Synthetic utility of major products **3** was also explored to provide cyclopropane-containing β -hydroxy ketone derivatives **5**.¹³ These compounds represent a useful source to prepare cyclopentanone and other elaborated structures.¹⁴

2. Results and discussions

In the preliminary studies, the reaction of 1-phenyl alkynyl cyclopropyl *tert*-butyl carbonate **2a** was chosen as the model system to investigate the reaction condition. As shown in Table 1, when 0.5 mmol **2a** was treated with 2 mol% equivalent of AuPPh₃Cl/AgBF₄ in CH₂Cl₂ at rt for 50 h, two cyclized products **3a** and **4a** were obtained in a total yield of 76% (3a/4a=1.5/1).

Table 1
Reaction optimization of gold-catalyzed cyclization of 1-phenyl ethynyl cyclopropyl *tert*-butyl carbonate **2a**^a



	Catalyst	T (h)	Sol/temp	Yield (%) ^b (ratio 3a/4a) ^c
1	AuPPh ₃ Cl/AgBF ₄	50	DCM/rt	76 (1.5/1)
2	AuPPh ₃ Cl/AgSbF ₆	15	DCM/rt	65 (1.9/1)
3	AuPPh ₃ Cl/AgPF ₆	48	DCM/rt	0
4	Au(PPh ₃)NTf ₂	72	DCM/rt	11 (2.6/1)
5	AuPPh ₃ Cl/AgOTf	2	DCM/rt	88 (2.4/1)
6	AuPPh ₃ Cl/AgOTf	2	DCE/rt	78 (1.8/1)
7	AuPPh ₃ Cl/AgOTf	40	THF/rt	60 (1.6/1)
8	AuPPh ₃ Cl/AgOTf	38	Toluene/rt	50 (2.6/1)
9	AuPPh ₃ Cl/AgOTf	40	CH ₃ CN/rt	0
10	AuPPh ₃ Cl/AgOTf	20	Et ₂ O/rt	Trace
11	AuCl ₃	30	DCM/rt	0
12	PtCl ₂	48	DCM/rt	0
13	AgOTf	48	DCM/rt	0
14	Cu(OTf) ₂	48	DCM/rt	0

^a All reactions were carried out at 0.5 mmol scale, using 2 mol% of gold catalyst in 2 mL solvent at rt.

^b Separated yield.

^c The ratio 3a/4a was based on the separated yields.

The ¹H and ¹³C NMR spectra data for compound **3a** and **4a** are very similar. Only one obvious difference exists between the chemical shift of **3a**'s hydrogen at C2 position (5.52 ppm, **3a**) and that of **4a**'s C3 hydrogen (5.15 ppm, **4a**). The structure of **4a** was then identified to be 7-benzylidene-4,6-oxa-5-carbonyl-spiro[2,4]-heptane by X-ray crystallography (Fig. 1). Then, the structure of **3a** can be deduced to be 7-phenyl-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene.

A series of experiments were performed to optimize this reaction. Different silver salts were tested, it was found that AuPPh₃Cl/AgPF₆ and Au(PPh₃)NTf₂ have low activities (entries 3 and 4, Table 1). With AuPPh₃Cl/AgPF₆ as catalyst, the desired product was obtained in 65% yield with 3a/4a=1.9/1 (entry 2, Table 1). The best catalyst, as shown in Table 1, was proved to be AuPPh₃Cl/AgOTf (entry 5, Table 1), which provide **3a** and **4a** in 88% with a ratio of 2.4/1. Several solvents were also screened. CH₃CN and Et₂O were found to be ineffective (entries 9 and 10, Table 1). When DCE, THF, and toluene were used as the solvent, the reaction

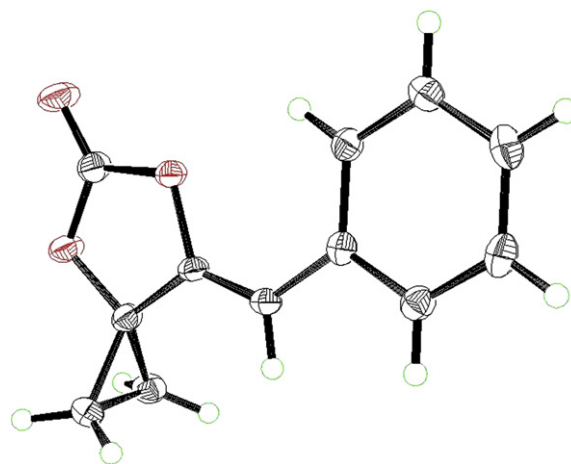


Figure 1. The X-ray diffraction structure of compound **4a**.

yields were lower than that in DCM (entries 6–8, Table 1). AuCl₃ and other non-gold catalysts, such as PtCl₂, AgOTf, and Cu(OTf)₂ were then investigated. These catalysts were proved to be inferior to the Au(I) complexes and afforded no product (entries 11–14, Table 1). The optimal reaction condition was then determined to be 2 mol% of AuPPh₃Cl/AgOTf in CH₂Cl₂ at rt.

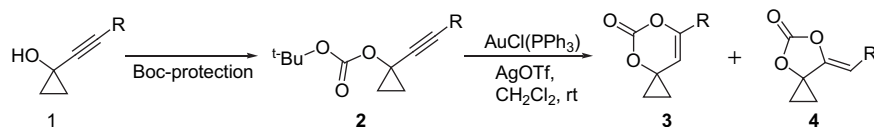
With the optimized condition in hand, we explored the scope and the limitation of this reaction. As shown in Table 2, a range of 1-alkynyl cyclopropyl *tert*-butyl carbonates were prepared through the reaction of the corresponding 1-alkynyl cyclopropanols with *tert*-butyl carbonate.

Compound **2** were then treated with AuPPh₃Cl/AgOTf to prepare vinyl cyclopropane derivatives **3** and **4**. Both aromatic and aliphatic alkynyl substrates exhibited good reactivities. Two types of vinyl cyclopropane derivatives were readily obtained in moderate to good yields. Aryl alkynyl cyclopropyl *tert*-butyl carbonates bearing electron-donating groups, such as methyl, ethyl, *n*-butyl, and methoxy substitutes (Table 2, entries 2–5), displayed relative high reactivities and gave higher conversion. While other aryl alkynyl substrates with electron-withdrawing chloro or fluoro groups had relative low reactivities (Table 2, entries 6–9). Aliphatic alkynyl substrates also worked effectively in this reaction (Table 2, entries 10 and 11), which nevertheless, only gave the six-membered cyclization products.

The regioselectivity for the aromatic alkynyl substrates ranged from 1.5/1 to 6/1. Electron rich substrates seem to have a better selectivity for the formation of the major isomers (Table 2, entries 2–5), as compared with the lower 3/4 ratio obtained in their electron deficient counterparts (Table 2, entries 6–9). The highest ratio was obtained in substrate **2g** (Table 2, entry 5), which has an electron-donating *p*-methoxy substitutes on the phenyl group. However, the aliphatic substrates only gave the single major products.

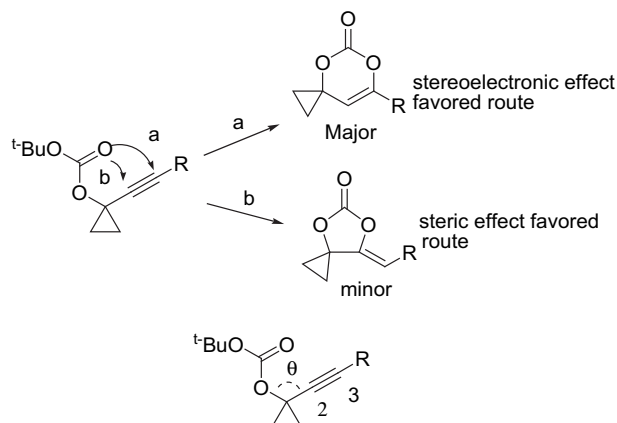
We assumed that the regioselectivity might be affected by two factors. The first is the stereoelectronic effect. In substrate **2**, angle θ for C2–C1–O is larger than the normal bond angle in an sp³ hybridized carbon (109.5°), because of the existence of a small, strained bond angle in cyclopropane (Scheme 2). Therefore, S_N2 addition of the carbonate oxygen onto the gold activated triple bond is favored to proceed through a 6-*endo-dig* route (Scheme 2, route a). However, high steric aromatic group would affect the attack of the carbonyl oxygen, and favored the 5-*exo-dig* pathway to construct minor five-membered isomer (Scheme 2, route b). Aliphatic substrates, which have no high steric aromatic group, would therefore give only the major products.

The quench step of the gold-catalyzed cyclization reaction was then investigated (Scheme 3). When 3 equiv of D₂O was added into

Table 2Gold-catalyzed cyclization of compound **2** to afford **3** and **4**^a

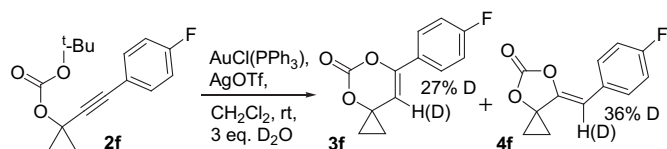
Entry	Compound 2 /yield (%) ^b	Products 3	Product 4	Yield (%) ^b (ratio a/b) ^c
1				84% (2.4/1)
2				85% (3/1)
3				87% (5/1)
4				86% (2.3/1)
5				81% (6/1)
6				58% (1.6/1)
7				72% (1.6/1)
8				77% (2/1)
9				69% (1.5/1)
10			ND	80%
11			ND	56%

^a Unless noted, all reactions were carried out at 0.5 mmol scale, using 2 mol % of AuPPh₃Cl/AgOTf in 2 mL CH₂Cl₂ at rt.^b Separated yield.^c The ratio **3/4** was based on the separated yields.



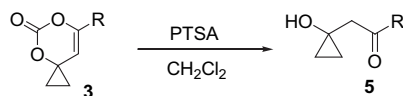
Scheme 2. A working mechanism for the regioselectivity.

the reaction mixture of compound **2a**, it was found that 27% deuterium was incorporated into C2 position of compound **3a**, and 36% deuterium into C3 position of compound **4a**.¹⁵



Scheme 3. Experiment to trap the reaction with D₂O.

Table 3
Preparation of β -hydroxy ketone derivatives **5**^a



	3a	Product	Yield (%) ^b
1			91
4			85
2			88
3			95
5			83

^a Unless noted, all reactions were carried out at 0.3 mmol scale, using a catalytic amount of *p*-toluene sulfonic acid in 2 mL CH₂Cl₂ at rt.

^b Separated yield.

As shown in Table 3, when enol carbonate **3b** was treated with a catalytic amount of *p*-toluene sulfonic acid in CH₂Cl₂ at rt, a new compound, cyclopropane-containing β -hydroxy ketone **5b**, was obtained in a high yield, in which the cyclic carbonate was removed. Using the same method, five β -hydroxy ketone derivatives were then synthesized (Table 3).

3. Conclusion

In conclusion, we have developed a convenient new method to prepare two types of vinyl cyclopropane derivatives through gold-catalyzed cyclization of 1-alkynyl cyclopropyl *tert*-butyl carbonates **2**. Different from the previous results to give five-membered products via a 5-*exo-dig* route, cyclization of compound **2** preferred to take a 6-*endo-dig* pathway to provide six-membered carbonates. Two factors, including stereoelectronic effect and steric effect might affect the regioselectivity. Low steric aliphatic substrates afforded only six-membered vinyl cyclopropane products. The synthetic utilities of compound **3** were also explored to afford a series of cyclopropyl β -hydroxy ketone derivatives.

4. Experimental section

4.1. Typical general procedure for the preparation of Boc-protected cyclopropanol **2a**

To a solution of 316 mg (2 mmol) of 1-alkynyl cyclopropanol **1** and 872 mg (4 mmol) di-*tert*-butyl-dicarbonate in 20 mL of dichloromethane were added aqueous sodium hydroxide (2 N,

2 mL, 4 mmol), tetrabutylammonium chloride (138 mg, 0.5 mmol), and then 4-dimethylaminopyridine (24.4 mg, 0.2 mmol) at 0 °C. After 30 min, the reaction mixture was extracted with dichloromethane. The combined organic phase was dried over MgSO₄ and concentrated with a rotary evaporator. The crude product was purified via flash chromatography over silica gel with 50/1 PE/EtOAc as eluting solvent. Compound **2a** was then obtained in 62% as a colorless liquid.

4.1.1. tert-Butyl 1-(phenylethynyl)cyclopropyl carbonate 2a. Obtained as colorless oil in 62% yield ($R_f=0.2$, PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 1.30 (s, 4H), 1.51 (s, 9H), 7.26–7.29 (m, 3H), 7.41–7.43 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 16.4, 27.7, 50.4, 82.9, 83.0, 87.5, 122.6, 128.2, 128.3, 131.9, 152.5.

4.1.2. tert-Butyl 1-((4-ethylphenyl)ethynyl)cyclopropyl carbonate 2b. Obtained as a yellow solid in 70% yield ($R_f=0.2$, PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 1.21 (t, $J=7.6$ Hz, 3H), 1.30 (s, 4H), 1.51 (s, 9H), 2.62 (q, $J=7.6$ Hz, 2H), 7.13 (d, $J=8.0$ Hz, 2H), 7.37 (d, $J=8.4$ Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 15.4, 16.4, 27.7, 28.8, 50.5, 82.8, 83.2, 86.7, 119.7, 127.7, 131.9, 144.8, 152.5. MS (m/z , rel intensity): 286 (M^+ , 2), 187 (14), 186 (100), 171 (40), 169 (33), 157 (65), 129 (25), 57 (67).

4.1.3. tert-Butyl 1-(p-tolylethynyl)cyclopropyl carbonate 2c. Obtained as a yellow solid in 76% yield ($R_f=0.2$, PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 1.23 (s, 4H), 1.45–1.47 (m, 9H), 2.26 (s, 3H), 7.02–7.04 (m, 2H), 7.24–7.28 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 16.3, 21.3, 27.3, 50.3, 83.0, 84.9, 86.7, 119.5, 128.9, 131.7, 138.3, 146.7, 152.4. MS (m/z , rel intensity): 272 (M^+ , 2), 172 (75), 155 (49), 143 (65), 129 (38), 57 (100).

4.1.4. tert-Butyl 1-((4-butylphenyl)ethynyl)cyclopropyl carbonate 2d. Obtained as a yellow solid in 65% yield ($R_f=0.2$, PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, $J=7.6$ Hz, 3H), 1.28–1.51 (m, 17H), 2.57 (t, $J=8.0$ Hz, 2H), 7.08 (d, $J=8.0$ Hz, 2H), 7.33 (d, $J=8.4$ Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 16.4, 22.2, 27.7, 33.4, 35.5, 50.4, 82.8, 83.1, 86.7, 119.7, 128.3, 131.8, 143.4, 152.5. MS (m/z , rel intensity): 314 (M^+ , 2), 215 (18), 214 (92), 171 (100), 142 (15), 57 (62).

4.1.5. tert-Butyl 1-((4-methoxyphenyl)ethynyl)cyclopropyl carbonate 2e. Obtained as a white solid in 71% yield ($R_f=0.2$, PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 1.28 (d, $J=1.6$ Hz, 4H), 1.50 (s, 9H), 3.77 (s, 3H), 6.80 (d, $J=8.8$ Hz, 2H), 7.36 (d, $J=8.8$ Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 16.4, 27.7, 50.5, 55.2, 82.8, 82.9, 85.9, 113.8, 114.6, 133.4, 152.5, 159.7.

4.1.6. tert-Butyl 1-((4-fluorophenyl)ethynyl)cyclopropyl carbonate 2f. Obtained as a white solid in 65% yield ($R_f=0.2$, PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 1.17 (s, 4H), 1.37–1.39 (m, 9H), 6.86 (t, $J=8.4$ Hz, 2H), 7.25–7.29 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 16.2, 27.5, 50.1, 81.8, 82.6, 87.1, 115.4 (d, $J=22.0$ Hz), 118.5 (d, $J=3.5$ Hz), 133.7 (d, $J=8.0$ Hz), 152.4, 162.4 (d, $J=248.2$ Hz). MS (m/z , rel intensity): 276 (M^+ , 1), 176 (49), 159 (51), 147 (47), 133 (28), 57 (100).

4.1.7. tert-Butyl 1-((3-chlorophenyl)ethynyl)cyclopropyl carbonate 2g. Obtained as a white solid in 72% yield ($R_f=0.2$, PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 1.08 (s, 4H), 1.27–1.29 (m, 9H), 6.99–7.07 (m, 3H), 7.15 (t, $J=1.6$ Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 16.3, 27.5, 49.9, 81.4, 82.6, 84.8, 124.2, 128.5, 131.4, 133.8, 152.3. MS (m/z , rel intensity): 292 (M^+ , 2), 194 (13), 192 (35), 175 (38), 163 (28), 129 (21), 57 (100).

4.1.8. tert-Butyl 1-((2,4-difluorophenyl)ethynyl)cyclopropyl carbonate 2h. Obtained as a white solid in 85% yield ($R_f=0.2$,

PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 1.34 (s, 4H), 1.53 (s, 9H), 6.80–6.86 (m, 2H), 7.38–7.44 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 16.5, 27.7, 50.3, 75.5, 83.1, 92.5, 104.2 (t, $J=25.2$ Hz), 107.7, 111.4 (d, $J=25.1$ Hz), 134.5 (d, $J=9.5$ Hz), 152.4, 161.7 (dd, $J=52.5$, 12.2 Hz), 164.2 (dd, $J=55.0$, 11.9 Hz). MS (m/z , rel intensity): 294 (M^+ , 2), 195 (14), 194 (100), 177 (82), 165 (53), 151 (32), 129 (25), 57 (77).

4.1.9. tert-Butyl 1-((3-fluorophenyl)ethynyl)cyclopropyl carbonate 2i. Obtained as colorless oil in 60% yield ($R_f=0.2$, PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 1.32 (s, 4H), 1.52 (s, 9H), 6.98–7.03 (m, 1H), 7.10–7.12 (m, 1H), 7.18–7.28 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 16.4, 27.7, 50.2, 81.8, 83.0, 88.5, 115.6 (d, $J=21.0$ Hz), 118.5 (d, $J=22.7$ Hz), 124.4 (d, $J=9.5$ Hz), 127.6, 129.7 (d, $J=8.5$ Hz), 152.5, 162.2 (d, $J=244.9$ Hz). MS (m/z , rel intensity): 276 (M^+ , 2), 176 (86), 159 (78), 147 (60), 133 (32), 57 (100).

4.1.10. tert-Butyl 1-(hex-1-ynyl)cyclopropyl carbonate 2j. Obtained as colorless oil in 78% yield ($R_f=0.2$, PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, $J=7.2$ Hz, 3H), 1.13 (dd, $J=14.6$, 3.6 Hz, 4H), 1.36–1.49 (m, 13H), 2.20 (t, $J=6.8$ Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 13.6, 15.8, 18.5, 21.8, 27.7, 30.5, 50.5, 78.2, 82.6, 84.0, 152.5. MS (m/z , rel intensity): 238 (M^+ , 1), 138 (18), 109 (22), 96 (20), 57 (100).

4.1.11. tert-Butyl 1-(4-phenylbut-1-ynyl)cyclopropyl carbonate 2k. Obtained as colorless oil in 82% yield ($R_f=0.2$, PE/AcOEt=50/1). ¹H NMR (400 MHz, CDCl₃) δ 1.09–1.13 (m, 2H), 1.16–1.20 (m, 2H), 1.51 (s, 9H), 2.50 (t, $J=7.56$ Hz, 2H), 2.82 (t, $J=7.56$ Hz, 2H), 7.19–7.22 (m, 3H), 7.27–7.31 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 15.9, 21.2, 27.7, 34.9, 50.3, 79.1, 82.6, 85.1, 126.2, 128.3, 128.5, 140.6, 152.6. MS (m/z , rel intensity): 286 (M^+ , 2), 186 (14), 185 (29), 157 (23), 154 (14), 91 (65), 57 (100).

4.2. Typical procedure for the preparation of compounds 3 and 4

To a solution of 30 mg compound **2a** in 2 mL dichloromethane was added 2% AuCl(PPh₃)/AgOTf at rt. After stirred for 2 h under N₂, the reaction mixture was extracted with EtOAc. The organic phase was combined, dried over MgSO₄, and evaporated in vacuo. Crude product purified by flash chromatography over silica gel gave the desired cyclic carbonates **3a** and **4a** readily in 26% and 62% yields, respectively.

4.2.1. 7-Phenyl-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3a. ¹H NMR (400 MHz, CDCl₃) δ 0.97–1.01 (m, 2H), 1.41–1.44 (m, 2H), 5.52 (s, 1H), 7.39–7.41 (m, 3H), 7.58–7.61 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 14.38, 62.97, 100.95, 127.42, 128.25, 128.68, 132.27, 148.77. MS (m/z , rel intensity): 202 (M^+ , 100), 130 (38), 129 (94), 118 (78), 102 (65), 90 (62). HRMS (EI) calcd for C₁₂H₁₀O₃ [M]⁺: 202.0630, found: 202.0625.

4.2.2. 7-Benzylidene-4,6-oxa-5-carbonyl-spiro[2,4]-heptane 4a. IR (neat) 1815, 1703, 1242, 1231, 1047, 918 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.20–1.25 (m, 2H), 1.64–1.68 (m, 2H), 5.15 (s, 1H), 7.24–7.26 (m, 1H), 7.35 (t, $J=7.2$ Hz, 2H), 7.51 (d, $J=7.6$ Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 14.40, 66.18, 97.63, 127.42, 128.25, 128.68, 132.27, 151.62. MS (m/z , rel intensity): 202 (M^+ , 100), 130 (38), 129 (95), 118 (75), 115 (45), 102 (62), 90 (58), 89 (30). HRMS (EI) calcd for C₁₂H₁₀O₃ [M]⁺: 202.0630, found: 202.0625.

4.2.3. 7-(4-Ethylphenyl)-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3b. ¹H NMR (400 MHz, CDCl₃) δ 0.98–1.01 (m, 2H), 1.26 (t, $J=7.6$ Hz, 3H), 1.41–1.45 (m, 2H), 2.69 (q, $J=7.6$ Hz, 2H), 5.50 (s, 1H), 7.25 (d, $J=8.4$ Hz, 2H), 7.53 (d, $J=8.4$ Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 14.4, 15.4, 28.7, 62.9, 100.9, 124.2, 127.6, 128.2, 146.2, 147.1, 148.8.

MS (*m/z*, rel intensity): 230 (M^+ , 52), 201 (98), 157 (48), 143 (42), 131 (52), 129 (88), 115 (37). HRMS (EI) calcd for $C_{14}H_{14}O_3$ [M] $^+$: 230.0943, found: 230.0944.

4.2.4. 7-(4-Ethylbenzylidene)-4,6-oxa-5-carbonyl-spiro[2,4]-heptane 4b. IR (neat) 3007, 2963, 2929, 2870, 1829, 1809, 1703, 1514, 1249, 1229, 1194, 1045, 1015, 864, 760 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.21–1.28 (m, 5H), 1.65–1.69 (m, 2H), 2.66 (q, $J=7.6$ Hz, 2H), 5.17 (s, 1H), 7.20 (d, $J=8.0$ Hz, 2H), 7.46 (d, $J=8.0$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 15.5, 28.6, 66.2, 97.6, 128.2, 128.3, 129.7, 143.7, 146.2, 151.6. MS (*m/z*, rel intensity): 230 (M^+ , 58), 201 (98), 157 (56), 143 (40), 131 (50), 129 (87), 115 (36). HRMS (EI) calcd for $C_{14}H_{14}O_3$ [M] $^+$: 230.0943, found: 230.0941.

4.2.5. 7-(4-Methylphenyl)-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3c. 1H NMR (400 MHz, $CDCl_3$) δ 0.97–1.01 (m, 2H), 1.41–1.44 (m, 2H), 2.40 (s, 3H), 5.49 (s, 1H), 7.22 (d, $J=8.2$ Hz, 2H), 7.50 (d, $J=8.2$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 21.3, 62.9, 100.9, 124.1, 127.4, 129.4, 139.9, 147.0, 148.8. MS (*m/z*, rel intensity): 216 (M^+ , 100), 201 (33), 143 (34), 132 (42), 129 (96), 115 (52), 104 (35). HRMS (EI) calcd for $C_{13}H_{12}O_3$ [M] $^+$: 216.0786, found: 216.0779.

4.2.6. 7-(4-Methylbenzylidene)-4,6-oxa-5-carbonyl-spiro[2,4]-heptane 4c. IR (neat) 3456, 1809, 1703, 1694, 1514, 1362, 1249, 1229, 1194, 1047, 1020, 939, 864 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.20–1.24 (m, 2H), 1.65–1.69 (m, 2H), 2.37 (s, 3H), 5.15 (s, 1H), 7.17 (d, $J=8.1$ Hz, 2H), 7.43 (d, $J=8.1$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 21.3, 66.2, 97.6, 128.2, 129.4, 137.3, 146.2, 151.6. MS (*m/z*, rel intensity): 216 (M^+ , 93), 201 (31), 143 (35), 132 (44), 129 (100), 115 (55), 104 (38). HRMS (EI) calcd for $C_{13}H_{12}O_3$ [M] $^+$: 216.0786, found: 216.0788.

4.2.7. 7-(4-Butylphenyl)-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3d. 1H NMR (400 MHz, $CDCl_3$) δ 0.97–1.01 (m, 5H), 1.34–1.45 (m, 4H), 1.58–1.66 (m, 2H), 2.65 (t, $J=7.6$ Hz, 2H), 5.50 (s, 1H), 7.23 (d, $J=8.4$ Hz, 2H), 7.52 (d, $J=8.4$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.4, 22.3, 33.4, 35.5, 62.9, 100.9, 124.2, 127.6, 128.8, 144.9, 147.1, 148.8. MS (*m/z*, rel intensity): 258 (M^+ , 39), 202 (10), 201 (100), 157 (32), 143 (34), 131 (47), 129 (52), 115 (22). HRMS (EI) calcd for $C_{16}H_{18}O_3$ [M] $^+$: 258.1256, found: 258.1252.

4.2.8. 7-(4-Butylbenzylidene)-4,6-oxa-5-carbonyl-spiro[2,4]-heptane 4d. IR (neat) 2957, 2926, 1829, 1809, 1701, 1249, 1229, 1194, 1047, 1020 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, $J=7.4$ Hz, 3H), 1.19–1.23 (m, 2H), 1.33–1.39 (m, 2H), 1.56–1.68 (m, 4H), 2.61 (t, $J=7.6$ Hz, 2H), 5.15 (s, 1H), 7.17 (d, $J=8.2$ Hz, 2H), 7.44 (d, $J=8.2$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.4, 22.4, 33.5, 35.4, 66.2, 97.6, 128.2, 128.8, 129.6, 142.4, 146.2, 151.6. MS (*m/z*, rel intensity): 258 (M^+ , 41), 202 (11), 201 (97), 157 (31), 143 (33), 131 (48), 129 (52), 115 (21). HRMS (EI) calcd for $C_{16}H_{18}O_3$ [M] $^+$: 258.1256, found: 258.1251.

4.2.9. 7-(4-Methoxyphenyl)-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3e. 1H NMR (400 MHz, $CDCl_3$) δ 0.95–0.99 (m, 2H), 1.38–1.42 (m, 2H), 3.85 (s, 3H), 5.40 (s, 1H), 6.92 (d, $J=8.9$ Hz, 2H), 7.53 (d, $J=8.9$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 55.4, 63.0, 99.8, 114.1, 122.8, 125.8, 147.1, 148.6, 160.7. MS (*m/z*, rel intensity): 232 (M^+ , 100), 159 (50), 145 (65), 120 (24), 117 (30). HRMS (EI) calcd for $C_{13}H_{12}O_4$ [M] $^+$: 232.0736, found: 232.0727.

4.2.10. 7-(4-Methoxybenzylidene)-4,6-oxa-5-carbonyl-spiro[2,4]-heptane 4e. IR (neat) 3003, 2931, 2839, 1834, 1815, 1707, 1599, 1512, 1296, 1246, 1186, 1180, 1047, 1018, 843 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.18–1.23 (m, 2H), 1.63–1.67 (m, 2H), 3.84 (s, 3H), 5.13 (s, 1H), 6.90 (d, $J=8.8$ Hz, 2H), 7.47 (d, $J=8.8$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 55.3, 66.2, 97.3, 114.1, 124.9, 129.6, 145.2,

151.6, 158.8. MS (*m/z*, rel intensity): 232 (M^+ , 89), 160 (40), 159 (86), 145 (100), 120 (48), 117 (63), 91 (42), 89 (48), 77 (41), 51 (37). HRMS (EI) calcd for $C_{13}H_{12}O_4$ [M] $^+$: 232.0736, found: 232.0738.

4.2.11. 7-(4-Fluorophenyl)-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3f. 1H NMR (400 MHz, $CDCl_3$) δ 0.98–1.02 (m, 2H), 1.41–1.45 (m, 2H), 5.49 (s, 1H), 7.10 (t, $J=8.6$ Hz, 2H), 7.57–7.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 62.9, 101.6, 115.8 (d, $J=21.5$ Hz), 126.3 (d, $J=8.3$ Hz), 146.7, 147.8, 163.4 (d, $J=248.8$ Hz). MS (*m/z*, rel intensity): 220 (M^+ , 95), 148 (45), 147 (100), 136 (94), 133 (48), 120 (74), 108 (95), 107 (39). HRMS (EI) calcd for $C_{12}H_9O_3F$ [M] $^+$: 220.0536, found: 220.0538.

4.2.12. 7-(4-Fluorobenzylidene)-4,6-oxa-5-carbonyl-spiro[2,4]-heptane 4f. IR (neat) 1834, 1815, 1703, 1591, 1508, 1366, 1252, 1231, 1192, 1047, 1015, 864, 831 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.21–1.25 (m, 2H), 1.67–1.71 (m, 2H), 5.15 (s, 1H), 7.06 (t, $J=8.8$ Hz, 2H), 7.49–7.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 66.1, 96.6, 115.6 (d, $J=21.5$ Hz), 128.5, 129.9 (d, $J=7.5$ Hz), 146.7, 151.3, 161.8 (d, $J=246.4$ Hz). MS (*m/z*, rel intensity): 220 (M^+ , 100), 148 (46), 147 (100), 136 (94), 133 (48), 120 (73), 108 (94), 107 (38). HRMS (EI) calcd for $C_{12}H_9O_3F$ [M] $^+$: 220.0536, found: 220.0527.

4.2.13. 7-(3-Chlorophenyl)-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3g. 1H NMR (400 MHz, $CDCl_3$) δ 1.01–1.05 (m, 2H), 1.44–1.48 (m, 2H), 5.59 (s, 1H), 7.35–7.37 (m, 2H), 7.48–7.51 (m, 1H), 7.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 62.9, 103.2, 122.3, 124.4, 129.7, 130.0, 131.9, 134.9, 146.4, 147.3. MS (*m/z*, rel intensity): 236 (M^+ , 58), 201 (72), 152 (82), 136 (49), 129 (100), 124 (35), 89 (41). HRMS (EI) calcd for $C_{12}H_9O_3Cl$ [M] $^+$: 236.0240, found: 236.0243.

4.2.14. 7-(3-Chlorobenzylidene)-4,6-oxa-5-carbonyl-spiro[2,4]-heptane 4g. IR (neat) 3447, 1815, 1638, 1629, 1595, 1049, 1015 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.23–1.27 (m, 2H), 1.69–1.72 (m, 2H), 5.12 (s, 1H), 7.22–7.31 (m, 2H), 7.40 (d, $J=7.6$ Hz, 1H), 7.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 66.2, 96.4, 126.3, 127.4, 128.0, 129.9, 134.1, 134.5, 148.3, 151.1. MS (*m/z*, rel intensity): 236 (M^+ , 28), 201 (33), 154 (22), 152 (73), 136 (46), 129 (100), 124 (47), 89 (81), 63 (26), 39 (22). HRMS (EI) calcd for $C_{12}H_9O_3Cl$ [M] $^+$: 236.0240, found: 236.0243.

4.2.15. 7-(2,4-Difluorophenyl)-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3h. 1H NMR (400 MHz, $CDCl_3$) δ 0.99–1.04 (m, 2H), 1.42–1.46 (m, 2H), 5.77 (s, 1H), 6.86–6.99 (m, 2H), 7.71–7.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 62.8, 104.8 (t, $J=26.0$ Hz), 107.4 (d, $J=14.8$ Hz), 111.8 (dd, $J=21.3$, 3.3 Hz), 128.1 (dd, $J=9.6$, 3.1 Hz), 142.3 (d, $J=4.9$ Hz), 146.6, 158.9 (d, $J=11.7$ Hz), 161.6 (dd, $J=41.6$, 12.2 Hz), 164.3 (d, $J=12.2$ Hz). MS (*m/z*, rel intensity): 238 (M^+ , 50), 166 (28), 165 (58), 154 (94), 138 (62), 126 (100), 125 (26). HRMS (EI) calcd for $C_{12}H_8O_3F_2$ [M] $^+$: 238.0442, found: 238.0420.

4.2.16. 7-(2,4-Difluorobenzylidene)-4,6-oxa-5-carbonyl-spiro[2,4]-heptane 4h. IR (neat) 3447, 1811, 1695, 1611, 1587, 1501, 1429, 1359, 1242, 1221, 1144, 1049, 1020, 970 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.26–1.30 (m, 2H), 1.69–1.74 (m, 2H), 5.38 (s, 1H), 6.80–6.85 (m, 1H), 6.91–6.96 (m, 1H), 7.89–7.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 66.4, 88.2 (d, $J=7.1$ Hz), 103.7 (t, $J=25.6$ Hz), 111.7 (dd, $J=21.2$, 3.7 Hz), 130.2 (dd, $J=9.3$, 3.7 Hz), 148.2, 151.1, 158.1 (d, $J=14.3$ Hz), 160.5 (dd, $J=12.4$, 7.4 Hz), 163.1 (d, $J=12.4$ Hz). MS (*m/z*, rel intensity): 238 (M^+ , 68), 166 (37), 165 (68), 154 (94), 138 (67), 126 (100), 125 (30). HRMS (EI) calcd for $C_{12}H_8O_3F_2$ [M] $^+$: 238.0442, found: 238.0445.

4.2.17. 7-(3-Fluorophenyl)-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3i. IR (neat) 1689, 1585, 1481, 1443, 1270, 1242, 1172, 1019 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.01–1.03 (m, 2H), 1.44–1.47 (m, 2H), 5.59

(s, 1H), 6.93–6.97 (m, 1H), 7.25–7.36 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.6, 62.9, 103.2, 112.3 (d, $J=21.2$ Hz), 112.8 (d, $J=22.7$ Hz), 123.0 (d, $J=2.3$ Hz), 128.8, 130.0 (d, $J=8.2$ Hz), 131.3 (d, $J=8.3$ Hz), 147.8, 161.2 (d, $J=246.4$ Hz). MS (m/z , rel intensity): 220 (M^+ , 100), 148 (28), 147 (56), 136 (65), 133 (24), 120 (39), 108 (44). HRMS (EI) calcd for $\text{C}_{12}\text{H}_9\text{O}_3\text{F}$ [$\text{M}]^+$: 220.0536, found: 220.0534.

4.2.18. 7-(3-Fluorobenzylidene)-4,6-oxa-5-carbonyl-spiro[2,4]-heptane 4i. IR (neat) 3447, 2924, 1815, 1749, 1692, 1610, 1587, 1442, 1280, 1244, 1197, 1152, 1049, 1024 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 1.21–1.25 (m, 2H), 1.67–1.70 (m, 2H), 5.13 (s, 1H), 6.92–6.96 (m, 1H), 7.23–7.33 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.6, 66.2, 96.6, 114.3 (d, $J=21.2$ Hz), 114.8 (d, $J=22.8$ Hz), 124.0 (d, $J=2.3$ Hz), 130.1 (d, $J=8.3$ Hz), 134.3 (d, $J=8.3$ Hz), 148.2, 151.1, 162.9 (d, $J=244.0$ Hz). MS (m/z , rel intensity): 220 (M^+ , 100), 148 (25), 147 (52), 136 (65), 133 (27), 120 (38), 108 (45). HRMS (EI) calcd for $\text{C}_{12}\text{H}_9\text{O}_3\text{F}$ [$\text{M}]^+$: 220.0536, found: 220.0532.

4.2.19. 7-Butyl-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3j. IR (neat) 3466, 2959, 2931, 2872, 1782, 1713, 1265, 1184, 1136, 1103, 1047, 966, 941 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.79–0.81 (m, 2H), 0.91 (t, $J=7.3$ Hz, 3H), 1.24–1.28 (m, 2H), 1.31–1.40 (m, 2H), 1.48–1.55 (m, 2H), 2.18 (t, $J=7.4$ Hz, 2H), 4.77 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 21.9, 27.8, 31.3, 62.5, 101.7, 147.3, 151.9. MS (m/z , rel intensity): 182 (M^+ , 40), 85 (100), 81 (17), 57 (51), 56 (26), 41 (16). HRMS (EI) calcd for $\text{C}_{10}\text{H}_{14}\text{O}_3$ [$\text{M}]^+$: 182.0943, found: 182.0942.

4.2.20. 7-Phenethyl-4,6-oxa-5-carbonyl-spiro[2,5]-7-octene 3k. IR (neat) 3501, 3026, 2929, 1778, 1715, 1603, 1497, 1454, 1373, 1261, 1186, 1128, 1053, 1029 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.79–0.81 (m, 2H), 1.27–1.29 (m, 2H), 2.53 (t, $J=8.1$ Hz, 2H), 2.90 (t, $J=8.1$ Hz, 2H), 4.76 (s, 1H), 7.20–7.26 (m, 3H), 7.28–7.35 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 32.1, 33.6, 62.5, 102.8, 126.4, 128.4, 128.6, 140.1, 147.2, 150.7. MS (m/z , rel intensity): 230 (M^+ , 19), 186 (12), 105 (44), 91 (100). HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3$ [$\text{M}]^+$: 230.0943, found: 230.0944.

4.3. Typical procedure for the preparation of compound 5

To a solution of 20 mg compound **3d** in 5 mL dichloromethane was added 1 mg *p*-toluene sulfonic acid at rt. After stirring for 3 h, the organic solvent was evaporated in vacuo. The combined organic phase purified by flash chromatography on silica gel gave the desired products **5d** in 91% yields.

4.3.1. 1-(4-Ethylphenyl)-2-(1-hydroxycyclopropyl)ethanone 5b. IR (neat) 3447, 2967, 2934, 1672, 1607, 1460, 1414, 1373, 1285, 1267, 1240, 1219, 1182, 1009 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.50–0.53 (m, 2H), 0.93–0.96 (m, 2H), 1.28 (t, $J=7.6$ Hz, 3H), 2.73 (q, $J=7.6$ Hz, 2H), 3.26 (s, 2H), 4.02 (s, 1H), 7.32 (d, $J=8.2$ Hz, 2H), 7.89 (d, $J=8.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 12.9, 15.2, 28.9, 45.9, 52.2, 128.2, 131.7, 134.3, 150.7, 200.6. MS (m/z , rel intensity): 204 (M^+ , 2), 175 (8), 148 (7), 134 (8), 133 (100), 105 (10). HRMS (EI) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$ [$\text{M}]^+$: 204.1150, found: 204.1151.

4.3.2. 2-(1-Hydroxycyclopropyl)-1-*p*-tolylethanone 5c. IR (neat) 3447, 1672, 1607, 1285, 1221, 1207, 1182, 1011 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.48–0.51 (m, 2H), 0.91–0.94 (m, 2H), 2.42 (s, 3H), 3.23 (s, 2H), 3.99 (s, 1H), 7.27 (d, $J=8.2$ Hz, 2H), 7.84 (d, $J=8.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 12.9, 21.7, 45.8, 52.2, 128.2, 129.4, 134.1, 144.6, 200.5. MS (m/z , rel intensity): 190 (M^+ , 3), 161 (9), 134 (10), 119 (100), 91 (23). HRMS (EI) calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$ [$\text{M}]^+$: 190.0994, found: 190.0995.

4.3.3. 1-(4-Butylphenyl)-2-(1-hydroxycyclopropyl)ethanone 5d. IR (neat) 3502, 3005, 2957, 2929, 2860, 1672, 1606, 1462, 1413, 1219,

1182, 1008 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.50–0.53 (m, 2H), 0.93–0.97 (m, 5H), 1.35–1.41 (m, 2H), 1.59–1.66 (m, 2H), 2.69 (t, $J=7.8$ Hz, 2H), 3.25 (s, 2H), 4.03 (s, 1H), 7.29 (d, $J=8.2$ Hz, 2H), 7.88 (d, $J=8.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 12.9, 13.9, 22.3, 33.2, 35.7, 45.8, 52.2, 128.2, 128.8, 134.3, 149.5, 200.6. MS (m/z , rel intensity): 232 (M^+ , 5), 203 (7), 176 (8), 162 (10), 161 (100), 133 (18), 91 (8). HRMS (EI) calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$ [$\text{M}]^+$: 232.1463, found: 232.1466.

4.3.4. 2-(1-Hydroxycyclopropyl)-1-(4-methoxyphenyl)ethanone 5e. IR (neat) 3466, 1665, 1601, 1574, 1510, 1261, 1219, 1171, 1113, 1015 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.47–0.50 (m, 2H), 0.90–0.92 (m, 2H), 3.20 (s, 2H), 3.87 (s, 3H), 6.94 (d, $J=8.8$ Hz, 2H), 7.91 (d, $J=8.8$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 12.9, 45.5, 52.3, 55.5, 113.9, 129.7, 130.4, 163.9, 199.4. MS (m/z , rel intensity): 206 (M^+ , 2), 177 (10), 150 (9), 135 (100), 133 (10), 107 (7), 77 (8). HRMS (EI) calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$ [$\text{M}]^+$: 206.0943, found: 206.0944.

4.3.5. 1-(3-Fluorophenyl)-2-(1-hydroxycyclopropyl)ethanone 5i. IR (neat) 3447, 1680, 1587, 1487, 1445, 1269, 1246, 1192, 1169, 1153 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 0.49–0.52 (m, 2H), 0.91–0.94 (m, 2H), 2.42 (s, 3H), 3.22 (s, 2H), 3.81 (s, 1H), 7.26–7.31 (m, 1H), 7.43–7.48 (m, 1H), 7.62 (d, $J=9.2$ Hz, 1H), 7.70 (d, $J=7.7$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 12.9, 46.4, 52.0, 114.7 (d, $J=22.2$ Hz), 120.6 (d, $J=21.3$ Hz), 123.8 (d, $J=2.7$ Hz), 130.4 (d, $J=7.5$ Hz), 138.6 (d, $J=5.9$ Hz), 162.9 (d, $J=246.9$ Hz), 199.4. MS (m/z , rel intensity): 194 (M^+ , 2), 166 (7), 165 (10), 138 (18), 123 (100), 96 (10), 95 (33). HRMS (EI) calcd for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{F}$ [$\text{M}]^+$: 194.0743, found: 194.0744.

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Supplementary data

Experimental details and NMR spectra are available as Supplementary data. Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.10.087.

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