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$C(sp^3)$–$C(sp^3)$ Bond Breaking in Methylenecyclopropanes Involving a Au^I/Au^{III} Catalytic Cycle

Di-Han Zhang,[a] Lun-Zhi Dai,[a] and Min Shi*[a]

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Gold(I) can catalyze the diacetoxylation of methylenecyclopropanes to produce the corresponding diacetoxylated products in moderate to good yields in acetic acid in the presence of iodosobenzene diacetate via C–C bond breaking under mild condition.

Introduction

Gold salts and complexes have emerged in the past few years as powerful catalysts for electrophilic activation of carbon-carbon multiple bonds toward a variety of nucleophiles.[1] Generally, this type of reaction relies on the interaction of the gold catalysts with the π-bonds of alkenes, alkynes, and allenes. Recently, an unprecedented gold-catalyzed oxidative cross-coupling of propargylic acetates and arylboronic acid has been developed from Au^I and Au^{III} catalytic cycles in the presence of oxidants such as Selectfluor, leading to a one-step synthesis of α-arylenones.[2] This interesting finding opens up a new perspective field for the gold-catalyzed organic reactions.

The introduction of strained small-ring systems as molecular building blocks has drawn increasing attention because the relief of ring strain can provide a potent thermodynamic driving force. Due to their inherent ring strains, interesting preparative aspects and the applications specific to these ring compounds have been developed. Since the first example of gold-catalyzed transformation of cyclopropane was reported by Thomas in 1976,[3] the gold-catalyzed reactions using strained small rings have increased rapidly. Such systems include cyclopropane, cyclopropene, oxirane and aziridine and others. Previously, we reported the diacetoxylation of methylenecyclopropanes (MCPs)[4] via a Pd^{II}/Pd^{IV} catalytic cycle under mild conditions.[4l] In this paper, we wish to report a novel C–C bond breaking reaction of MCPs of type **1**, a kind of highly strained small rings, catalyzed by gold in the presence of oxidant such as iodosobenzene diacetate [$PhI(OAc)_2$], leading to diacetoxylation of methylenecyclopropanes under mild conditions.

[a] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China
Fax: +86-21-64166128
E-mail: Mshi@mail.sioc.ac.cn

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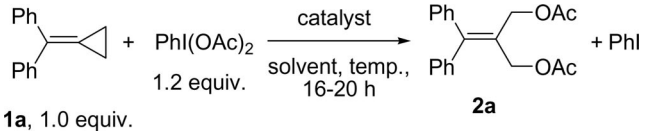
Results and Discussion

Initial studies using (diphenylmethylene)cyclopropane (**1a**) as the substrate were aimed at determining the reaction outcomes and subsequently optimizing the reaction conditions (0.2 mmol). The results of these experiments are summarized in Table 1. We found that the diacetoxylated product **2a** was obtained in 62% yield using $(Ph_3P)AuCl$ as the catalyst (5 mol-%) in the presence of $PhI(OAc)_2$ (1.2 equiv.) in acetic acid (HOAc) at 80 °C (Table 1, entry 1). Using $NaAuCl_4{\cdot}2H_2O$ or $AuCl_3$ as the catalyst afforded **2a** in 50% and 65% yield, respectively under identical conditions (Table 1, entries 2 and 3). In the presence of $(Me_3P)AuCl$ or (IPr)AuCl, **2a** could be also obtained in 67% and 64% yield, respectively (Table 1, entries 4 and 5). Adding silver salts did not improve the reaction outcomes (Table 1, entries 6–9). Further examination of solvent and temperature effects revealed that using $(Me_3P)AuCl$ (5 mol-%) as the catalyst produced **2a** in 76% yield in HOAc at 60 °C in the presence of $PhI(OAc)_2$ (1.2 equiv.) (Table 1, entry 18), which serves as the optimal conditions for the diacetoxylation of **1a** and other organic solvents such as CH_2Cl_2, CH_3CN, tetrahydrofuran (THF), toluene, methanol and 1,2-dichloroethane (DCE) or Ac_2O did not facilitate the formation of **2a** (Table 1, entries 10–16 and 17–20). Moreover, adding $PhI(OAc)_2$ (2.2 equiv.) into the reaction system afforded **2a** in 77% yield at 60 °C in HOAc in the presence of $(Me_3P)AuCl$ (5 mol-%), indicating that the yield could not receive an evident improvement even using large excess amount of $PhI(OAc)_2$ (Table 1, entry 21). The control experiments have also indicated that no reaction occurs in the absence of gold catalyst or iodosobenzene diacetate.

With these optimal conditions in hand, we next examined a variety of MCPs **1** in this reaction and the results of these experiments are shown in Table 2. As can be seen from Table 2, as for various diarylmethylenecyclopropanes in which both R^1 and R^2 are aromatic groups, the corresponding diacetoxylated products **2b**–**2k** could be obtained in 40–83% yields within 16 h under the standard condi-

Table 1. Optimization of the reaction conditions.



1a, 1.0 equiv. **2a**

Entry[a]	Catalyst	Solvent	*T* [°C]	Yield [%][b], **2a**
1	$(Ph_3P)AuCl$	HOAc	80	62
2	$NaAuCl_4{\cdot}2H_2O$	HOAc	80	50
3	$AuCl_3$	HOAc	80	65
4	$(Me_3P)AuCl$	HOAc	80	67
5	(IPr)AuCl	HOAc	80	64
6[c]	$(Me_3P)AuCl/AgOAc$	HOAc	80	64
7[c]	$(Me_3P)AuCl/AgOTf$	HOAc	80	26
8[c]	$(Me_3P)AuCl/AgBF_4$	HOAc	80	56
9[c]	$(Me_3P)AuCl/AgSbF_6$	HOAc	80	complex
10	$(Me_3P)AuCl$	CH_2Cl_2	reflux	complex
11	$(Me_3P)AuCl$	CH_3CN	80	complex
12	$(Me_3P)AuCl$	THF	reflux	complex
13	$(Me_3P)AuCl$	toluene	80	complex
14	$(Me_3P)AuCl$	MeOH	reflux	complex
15	$(Me_3P)AuCl$	DCE	80	trace
16	$(Me_3P)AuCl$	Ac_2O	80	complex
17	$(Me_3P)AuCl$	HOAc	70	68
18	$(Me_3P)AuCl$	***HOAc***	***60***	***76***
19	$(Me_3P)AuCl$	HOAc	50	72
20	$(Me_3P)AuCl$	HOAc	40	71
21[d]	$(Me_3P)AuCl$	HOAc	60	77

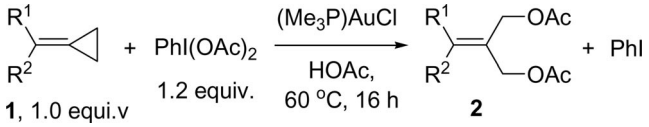
[a] All reactions were carried out using **1** (0.2 mmol), $PhI(OAc)_2$ (1.2 equiv.) in the presence of catalyst (5 mol-%) in various solvents (1.0 mL) otherwise specified. [b] Isolated yield. [c] 10 mol-% of Ag salt was added. [d] $PhI(OAc)_2$ (2.2 equiv.) was added.

tions. The electronic properties of the substituents on their benzene rings significantly influenced the reaction outcomes (Table 2, entries 1–10). For MCPs having electron-withdrawing groups on the benzene rings, the products **2** could be obtained in good to high yields (Table 2, entries 2, 3 and 7). Furthermore, as for unsymmetrical MCPs **1l**–**1o**, in which R^1 is an aromatic group and R^2 is a hydrogen atom, the reactions also proceeded smoothly to give the corresponding diacetoxylated products **2l**–**2o** in 54–99% yields under the standard conditions (Table 2, entries 11–14). Only in the cases of aliphatic MCP **1p** and unsymmetrical MCP **1q** in which R^1 is an aromatic group and R^2 is a methyl group, complex product mixtures were formed under the standard conditions (Table 2, entries 15 and 16). The product structures of **2a**–**2o** were determined by NMR spectroscopic data, MS, and HRMS (see Supporting Information).

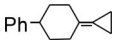
On the other hand, in the case of MCPs **1r** and **1s**, in which both R^1 and R^2 are aromatic rings with electron-donating groups, the reaction produced the corresponding intramolecular rearrangement products **3a** in 91% yield and **3b** as two isomeric mixtures in 51% yield, respectively, rather than the diacetoxylated products under the standard conditions, presumably due to the easier 1,2-migration of electron-rich aromatic rings (Scheme 1).[5]

To verify the active catalytic species, several ^{31}P NMR measurements were conducted to detect the real active catalytic species. The ^{31}P NMR spectrum of a sample of (Ph_3P)-

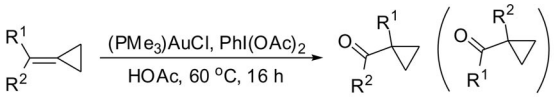
Table 2. $(Me_3P)AuCl$-catalyzed diacetoxylation of various MCPs **1** under the optimized conditions.



1, 1.0 equi.v **2**

Entry[a]	**1**, R^1/R^2	Yield [%][b], **2**
1	**1b**, $4\text{-}CH_3C_6H_4/4\text{-}CH_3C_6H_4$	**2b**, 65
2	**1c**, $4\text{-}FC_6H_4/4\text{-}FC_6H_4$	**2c**, 85
3	**1d**, $4\text{-}ClC_6H_4/4\text{-}ClC_6H_4$	**2d**, 80
4	**1e**, $4\text{-}BrC_6H_4/4\text{-}BrC_6H_4$	**2e**, 74
5	**1f**, $3\text{-}CF_3C_6H_4/4\text{-}CH_3C_6H_4$	**2f**, 76
6	**1g**, $2,4\text{-}F_2C_6H_3/4\text{-}CH_3C_6H_4$	**2g**, 51
7	**1h**, $4\text{-}ClC_6H_4/4\text{-}CH_3C_6H_4$	**2h**, 78
8	**1i**, $4\text{-}BrC_6H_4/4\text{-}CH_3C_6H_4$	**2i**, 57
9	**1j**, $2,5\text{-}(CH_3)_2C_6H_3/C_6H_5$	**2j**, 40
10	**1k**, $4\text{-}CH_3C_6H_4/C_6H_5$	**2k**, 46
11	**1l**, $4\text{-}CH_3OC_6H_4/H$	**2l**, 54
12	**1m**, $2\text{-}CH_3OC_6H_4/H$	**2m**, 77
13	**1n**, $2,4\text{-}(CH_3O)_2C_6H_3/H$	**2n**, 92
14	**1o**, $3,4,5\text{-}(CH_3O)_3C_6H_2/H$	**2o**, 99
15	**1p**, 	**2p**, complex
16	**1q**, C_6H_5/CH_3	**2q**, complex

[a] All reactions were carried out using **1** (0.2 mmol), $PhI(OAc)_2$ (1.2 equiv.) in the presence of $(Me_3P)AuCl$ (5 mol-%) in HOAc (1.0 mL) at 60 °C for 16 h. [b] Isolated yield.



1r: $R^1 = R^2 = 4\text{-}CH_3OC_6H_4$
1s: $R^1 = 4\text{-}CH_3OC_6H_4$, $R^2 = 4\text{-}CH_3C_6H_4$

3a: 91 yield
3b: 51 yield (two isomers, 11:1)

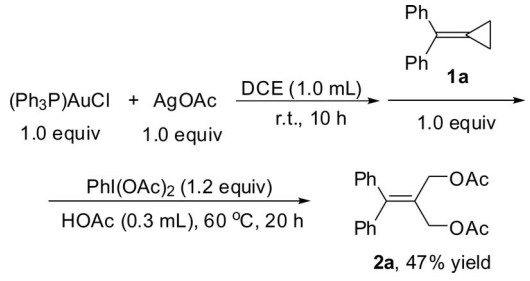
Scheme 1. Intramolecular rearrangement of MCPs **1r** and **1s** under the standard conditions.

AuCl showed a sharp signal at δ = 33.1 ppm in $CDCl_3$ (see Figure S1 in the Supporting Information). Further examination of the ^{31}P NMR spectrum revealed that upon heating $(Ph_3P)AuCl$ in HOAc at 80 °C for 10 h did not alter the catalyst since the signal of $(Ph_3P)AuCl$ was observed at δ = 32.8 ppm in $CDCl_3$ (see Figure S2 in the Supporting Information). Interestingly, if measuring the ^{31}P NMR spectrum of $(Ph_3P)AuCl$ under the standard reaction conditions [in HOAc with $PhI(OAc)_2$ and MCP **1** at 60 °C for 2 h and 10 h], the ^{31}P NMR spectrum showed a new signal at δ = 33.7 ppm and 33.8 ppm in $CDCl_3$, suggesting that (Ph_3P)-AuCl has been changed during the reaction (see Figure S3 and Figure S4 in the Supporting Information).[6]

The MALDI-MS spectrum obtained from the crude reaction mixture of $(Ph_3P)AuCl$ (5 mol-%) with 1a (0.1 mmol) and $PhI(OAc)_2$ (1.2 equiv.) in HOAc under the standard conditions after a short period showed a cluster at *m*/*z* 518.0, which might be attributed to the gold species $[(C_6H_5)_3PAu(OAc)]^+$ (see Supporting Information). Moreover, using $[(4\text{-}FC_6H_4)_3]PAuCl$ instead of $(Ph_3P)AuCl$ under the same reaction conditions, a similar cluster at *m*/*z* 572.0 was observed, which was attributed to the corresponding

gold species $[(4\text{-}FC_6H_4)_3PAu(OAc)]^+$ (see Supporting Information). This result further suggests that a $(R_3P)AuOAc$ species exists in this catalytic reaction system.

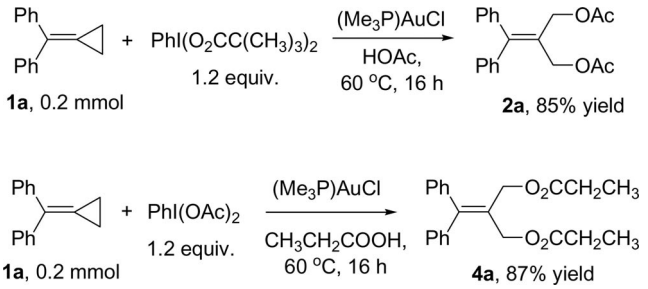
Another stoichiometric experiment using a LAuOAc species, which was generated from Ph_3PAuCl and AgOAc, as the catalyst was carried out to further verify the active species (Scheme 2). It was found that in the absence of $PhI(OAc)_2$ or HOAc, no reaction occurred in DCE and adding 1.2 equiv. of $PhI(OAc)_2$ and 0.3 mL of HOAc into the reaction system afforded **2a** in 47% yield at 60 °C if using **1a** as substrate (Scheme 2). These results suggest that the acetoxylated Au^I species might be the real active species in this reaction and $PhI(OAc)_2$ as well as HOAc are essential in this interesting transformation.



Scheme 2. $(Ph_3P)AuOAc$-catalyzed diacetoxylation of MCP **1a**.

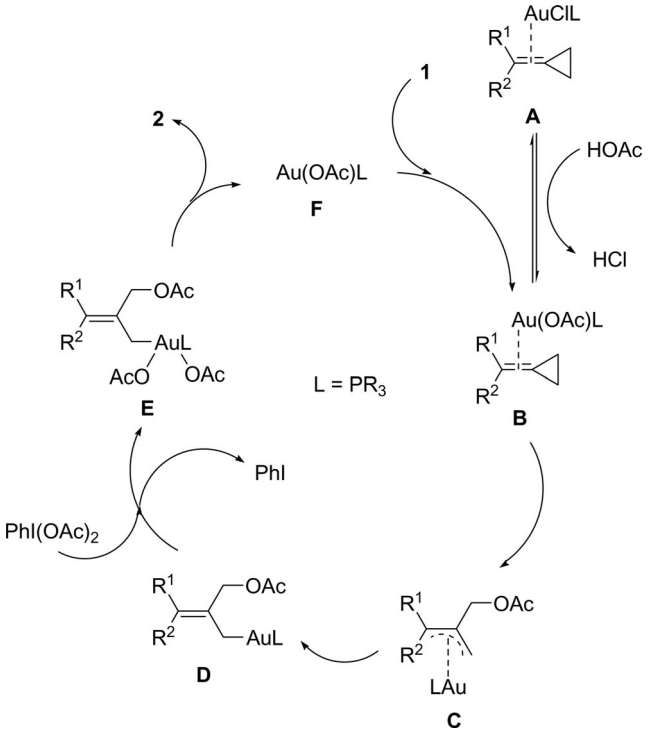
On the other hand, to determine the coordination pattern of Au^I with MCP **1**, ^{13}C NMR spectroscopic measurements were conducted to verify whether Au^I complex coordinates to the double bond or the cyclopropane. The ^{13}C NMR spectrum of **1a** showed olefinic carbon signals at δ = 129.943 and 124.345 ppm as well as cyclopropyl carbon signal at δ = 3.540 ppm in $CDCl_3$, respectively (see Figure S5 in the Supporting Information). Interestingly, if measuring the ^{13}C NMR spectrum of the mixture of **1a** (0.1 mmol) with $(Ph_3P)AuCl$ (0.1 mmol) and AgOAc (0.1 mmol) in $CDCl_3$ at room temperature after 20 h, the ^{13}C NMR spectrum showed olefinic carbon signals at δ = 129.812 and 124.302 ppm as well as cyclopropyl carbon signal at δ = 3.463 ppm, respectively, indicating a relatively obvious upfield shift with $\Delta\delta$ = 0.131 ppm at the olefinic carbon. These results may indicate that Au^I such as $(Ph_3P)AuOAc$ can be potentially coordinated by olefinic moiety in MCPs, although the observed chemical shift differences are small.

Moreover, as shown in Scheme 3, we found that if using iodosobenzene dipivalate to replace $PhI(OAc)_2$ in this reaction using **1a** as substrate, **2a** could still be produced in 85% yield under the standard conditions, suggesting that the carboxylate moiety of iodosobenzene dicarboxylate is exchangeable with the employed carboxylic acid solvent and acetic acid is involved in the initial stage of this reaction.[7] Utilizing $PhI(OAc)_2$ in propionic acid (CH_3CH_2COOH) provided dipropionyloxylated product **4a** in 87% yield (Scheme 3). We also confirmed that **2a** could not be transformed into **4a** in propionic acid under the standard conditions.



Scheme 3. Control experiments of MCP **1a** with iodosobenzene dicarboxylates under the standard conditions.

A plausible mechanism for the formation of these diacetoxylated derivatives **2** is tentatively outlined in Scheme 4 on the basis of above spectroscopic data and the control experiments. Au^I complex first coordinates to methylenecyclopropane **1** to give intermediate **A**.[2] There might be an equilibrium between the intermediate **A** and intermediate **B** in HOAc at 60 °C,[1s] in which intermediate **B** is attacked by AcO^- from LAuOAc to afford intermediate **C**. The intermediate **C** generates intermediate **D** via allylic rearrangement, which undergoes oxidative addition with $PhI(OAc)_2$ to provide Au^{III} intermediate **E**.[8] The reductive elimination of intermediate **E** produces diacetoxylated product **2** and generates Au^I species **F** [LAuOAc]. The Au^I complex **F** then coordinates to methylenecyclopropane **1** to give intermediate **B** again, which produces intermediate **C** via ring-opening process with AcO^- and completes the catalytic cycle.



Scheme 4. A plausible reaction mechanism.

In summary, we have reported in this paper an interesting gold-catalyzed diacetoxylation of methylenecyclopropanes in moderate to good yields in the presence of iodosobenz-

ene diacetate via C–C bond breaking under mild conditions. The reaction is considered to proceed via a Au^{I}/Au^{III} catalytic cycle. Clarification of the reaction mechanism and further application of this chemistry are in progress.

Experimental Section

General Remarks: Melting points were determined on a digital melting point apparatus. ^1H and ^{13}C NMR spectra were recorded at 300 (400) and 75 (100) MHz, respectively. Mass and HRMS spectra were recorded by EI method. The employed solvents were dry up by the standard procedures. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

General Procedure for the Reaction of MCPs Under the Standard Reaction Conditions: Under ambient atmosphere, methylenecypropanes 1 (MCPs) (0.20 mmol, 1.0 equiv.), $PhI(OAc)_2$ (0.24 mmol, 1.2 equiv.), $(Me_3P)AuCl$ (0.01 mmol, 5 mol-%), and HOAc (1.00 mL) were added into an Schlenk tube. The reaction mixture was stirred at 60 °C until the reaction completed. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products 2 in moderate to good yields.

Compound 2a: Yield 49 mg, 76%. This is a known compound. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.08 (s, 6 H, CH_3), 4.69 (s, 4 H, CH_2), 7.14–7.16 (m, 4 H, Ar), 7.26–7.35 (m, 6 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.9, 62.8, 127.2, 127.8, 128.2, 129.2, 140.3, 148.8, 170.7 ppm.

Compound 2b: Yield 46 mg, 65%. This is a known compound. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.08 (s, 6 H, CH_3), 2.33 (s, 6 H, CH_3), 4.69 (s, 4 H, CH_2), 7.02 (d, J = 8.4 Hz, 4 H, Ar), 7.11 (d, J = 8.4 Hz, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.9, 21.2, 63.1, 126.4, 128.8, 129.2, 137.60, 137.65, 149.0, 170.8 ppm.

Compound 2c: Yield 61 mg, 85%. This is a known compound. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.08 (s, 6 H, CH_3), 4.66 (s, 4 H, CH_2), 7.00–7.05 (m, 4 H, Ar), 7.09–7.13 (m, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.8, 62.7, 115.3 (d, J = 21.3 Hz), 127.9, 131.0 (d, J = 7.6 Hz), 136.12, 136.15, 146.7, 162.4 (d, J = 246.5 Hz), 170.6 ppm.

Compound 2d: Yield 63 mg, 80%. This is a known compound. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.08 (s, 6 H, CH_3), 4.66 (s, 4 H, CH_2), 7.07 (d, J = 8.8 Hz, 4 H, Ar), 7.30 (d, J = 8.8 Hz, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.8, 62.6, 128.6, 130.6, 134.2, 138.3, 146.3, 170.6 ppm.

Compound 2e: Yield 72 mg, 74%. A colorless oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 2926, 1743, 1487, 1378, 1235, 1071, 1024, 1011, 971, 824, 727 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.08 (s, 6 H, CH_3), 4.65 (s, 4 H, CH_2), 7.01 (d, J = 8.8 Hz, 4 H, Ar), 7.46 (d, J = 8.8 Hz, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.8, 62.5, 122.4, 128.6, 130.8, 131.5, 138.7, 146.2, 170.5 ppm. MS (EI): m/z (%) = 482 (0.60) [M^+ + 2], 480 (0.29) [M^+], 364 (6.56), 362 (13.50), 301 (12.44), 299 (12.80), 283 (31.94), 281 (31.27), 272 (10.80), 270 (11.60), 203 (17.73), 202 (12.28), 189 (10.56), 101 (3.51), 43 (100.00). HRMS (EI) Calcd. for $C_{20}H_{18}O_4Br_2$ (M^+): 479.9572; found 479.9576.

Compound 2f: Yield 63 mg, 76%. A light yellow oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 3025, 2927, 1744, 1379, 1336, 1300, 1239, 1128, 1023, 806, 706 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.08 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 4.60 (s, 2 H, CH_2), 4.71 (s, 2 H, CH_2), 7.02 (d, J = 8.0 Hz, 2 H, Ar), 7.14 (d, J = 8.0 Hz, 2 H, Ar), 7.32 (d, J = 7.6 Hz, 1 H, Ar), 7.44 (dd, J = 7.6, J = 8.0 Hz, 1 H, Ar), 7.48 (s, 1 H, Ar), 7.55 (d, J = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.7, 20.8, 21.1, 62.6, 63.0, 123.9 (q, J = 270.8 Hz), 124.6 (q, J = 3.8 Hz), 125.9 (q, J = 3.8 Hz), 128.3, 128.7, 129.1, 130.6 (q, J = 32.6 Hz), 132.5, 136.6, 138.2, 141.3, 147.7, 170.6, 170.7 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz, CF_3COOH): δ = –62.65 (s) ppm. MS (EI): m/z (%) = 406 (1.47) [M^+], 304 (10.78), 289 (31.75), 286 (100.00), 271 (18.19), 259 (5.00), 235 (5.11), 217 (12.03), 203 (7.58), 183 (10.46), 159 (3.62), 129 (5.66), 115 (3.62), 105 (5.20), 91 (3.37), 77 (1.68), 43 (39.70). HRMS (EI) Calcd. for $C_{22}H_{21}O_4F_3$ (M^+): 406.1392; found 406.1407.

Compound 2g: Yield 38 mg, 51%. A colorless oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 2925, 1743, 1501, 1378, 1234, 1140, 1024, 969, 817, 513 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.04 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 4.60 (s, 2 H, CH_2), 4.73 (s, 2 H, CH_2), 6.79–6.88 (m, 2 H, Ar), 7.04 (d, J = 8.0 Hz, 2 H, Ar), 7.12 (q, J = 8.0 Hz, 3 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.76, 20.86, 21.1, 62.2, 62.7, 104.2 (t, J = 25.8 Hz), 111.4 (dd, J = 3.1, J = 20.5 Hz), 124.2 (d, J = 19.8 Hz), 128.7, 129.0, 130.1, 131.8 (dd, J = 5.3, J = 9.1 Hz), 136.2, 138.0, 140.6, 159.4 (dd, J = 12.9, J = 248.1 Hz), 162.6 (dd, J = 12.1, J = 248.8 Hz), 170.64, 170.66 ppm. ^{19}F NMR ($CDCl_3$, 376 MHz, CF_3COOH): δ = –109.88 to –109.79 (m), –109.67 to –109.60 (m) ppm. MS (EI): m/z (%) = 374 (1.51) [M^+], 314 (4.19), 272 (9.62), 257 (39.69), 254 (100.00), 239 (31.32), 227 (8.60), 201 (5.14), 151 (13.22), 127 (8.45), 115 (3.53), 105 (8.39), 91 (3.53), 77 (1.86), 43 (41.82). HRMS (EI) Calcd. for $C_{21}H_{20}O_4F_2$ (M^+): 374.1330; found 374.1327.

Compound 2h: Yield 57 mg, 78%. A colorless oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 3025, 2925, 1743, 1488, 1378, 1361, 1236, 1091, 1016, 970, 819, 513 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.08 (s, 6 H, CH_3), 2.34 (s, 3 H, CH_3), 4.66 (s, 2 H, CH_2), 4.68 (s, 2 H, CH_2), 7.00 (d, J = 7.8 Hz, 2 H, Ar), 7.07–7.14 (m, 4 H, Ar), 7.29 (d, J = 7.8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 20.9, 21.2, 62.8, 62.9, 127.4, 128.4, 129.0, 129.1, 130.6, 133.8, 137.0, 138.0, 138.9, 147.6, 170.7 ppm. MS (EI): m/z (%) = 372 (0.25) [M^+], 252 (10.43), 217 (24.15), 203 (6.13), 189 (3.55), 149 (3.84), 129 (5.05), 115 (4.63), 105 (4.68), 84 (6.75), 71 (8.99), 57 (12.38), 43 (100.00). HRMS (EI) Calcd. for $C_{21}H_{21}O_4Cl$ (M^+): 372.1128; found 372.1126.

Compound 2i: Yield 47 mg, 57%. A light yellow oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 2925, 2855, 1743, 1485, 1378, 1236, 1023, 1011, 970, 820, 508 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.08 (s, 6 H, CH_3), 2.33 (s, 3 H, CH_3), 4.66 (s, 2 H, CH_2), 4.68 (s, 2 H, CH_2), 7.00 (t, J = 8.8 Hz, 4 H, Ar), 7.12 (d, J = 8.0 Hz, 2 H, Ar), 7.44 (d, J = 8.0 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.8, 21.1, 62.7, 62.9, 122.0, 127.5, 129.0, 129.1, 130.9, 131.3, 136.9, 137.9, 139.4, 147.6, 170.6, 170.7 ppm. MS (EI): m/z (%) = 418 (1.73) [M^+ + 2], 416 (1.79) [M^+], 316 (4.85), 315 (5.69), 298 (35.74), 296 (35.26), 283 (8.84), 235 (19.27), 217 (100.00), 206 (45.86), 203 (27.71), 191 (14.52), 189 (14.96), 178 (7.72), 165 (5.86), 129 (4.69), 115 (6.08), 105 (5.67), 91 (3.82), 43 (46.07). HRMS (EI) Calcd. for $C_{21}H_{21}O_4Br$ (M^+): 416.0623; found 416.0630.

Compound 2j: Yield 28 mg, 40%. This is a known compound. ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.03 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 4.50 (d, J = 12.0 Hz, 1 H, CH_2), 4.56 (d, J = 12.0 Hz, 1 H, CH_2), 4.77 (d, J = 12.4 Hz, 1 H, CH_2), 4.81 (d, J = 12.4 Hz, 1 H, CH_2), 6.95 (s, 1 H, Ar), 6.98–7.05 (m, 2 H, Ar), 7.16–7.19 (m, 2 H, Ar), 7.24–7.31 (m, 3 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 19.2, 20.8,

20.9, 62.3, 63.0, 127.7, 128.1, 128.6, 129.0, 129.6, 130.3, 132.4, 135.0, 139.1, 139.6, 147.8, 170.76, 170.82 ppm.

Compound 2k: Yield 31 mg, 46%. This is a known compound. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.077 (s, 3 H, CH_3), 2.083 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 4.69 (s, 2 H, CH_2), 4.71 (s, 2 H, CH_2), 7.03 (d, J = 8.1 Hz, 2 H, Ar), 7.11–7.16 (m, 4 H, Ar), 7.26–7.32 (m, 3 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 20.9, 21.1, 62.96, 62.99, 126.8, 127.7, 128.1, 128.8, 129.1, 129.2, 137.4, 137.6, 140.5, 148.9, 170.8 ppm.

Compound 2l: Yield 30 mg, 54%. A green oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 2934, 2839, 1736, 1608, 1512, 1371, 1235, 1178, 1026, 834, 506 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.10 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 3.82 (s, 3 H, OCH_3), 4.74 (d, J = 0.8 Hz, 2 H, CH_2), 4.80 (s, 2 H, CH_2), 6.79 (s, 1 H, CH), 6.89 (d, J = 8.8 Hz, 2 H, Ar), 7.20 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.88, 20.94, 55.2, 60.8, 66.7, 113.8, 127.7, 129.2, 130.1, 134.4, 159.3, 170.7, 170.8 ppm. MS (EI): *m*/*z* (%) = 278 (2.02) [M$^+$], 176 (4.67), 175 (6.02), 147 (14.82), 131 (3.40), 115 (8.20), 103 (5.62), 91 (5.99), 77 (5.40), 58 (10.18), 43 (100.00). HRMS (EI) Calcd. For $C_{15}H_{18}O_5$ (M$^+$): 278.1154; found 278.1152.

Compound 2m: Yield 43 mg, 77%. A colorless oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 2936, 1743, 1602, 1493, 1464, 1372, 1288, 1230, 1028, 757, 513 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.01 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 4.53 (d, J = 12.8 Hz, 1 H, CH_2), 4.59 (d, J = 12.8 Hz, 1 H, CH_2), 5.26 (d, J = 17.2 Hz, 2 H, CH_2), 6.72 (s, 1 H, CH), 6.88 (dd, J = 8.0, J = 1.2 Hz, 1 H, Ar), 6.93–6.97 (m, 1 H, Ar), 7.26–7.30 (m, 1 H, Ar), 7.33 (dd, J = 7.6, J = 1.6 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.7, 21.0, 55.5, 64.2, 69.5, 110.7, 114.9, 120.5, 126.3, 127.3, 129.3, 141.9, 156.6, 169.6, 170.5 ppm. MS (EI): *m*/*z* (%) = 278 (0.24) [M$^+$], 176 (5.35), 175 (3.21), 159 (5.91), 158 (4.58), 144 (12.65), 135 (8.62), 131 (5.09), 116 (7.86), 115 (7.14), 91 (6.35), 77 (8.11), 58 (6.67), 43 (100.00). HRMS (EI) Calcd. For $C_{15}H_{18}O_5$ (M$^+$): 278.1154; found 278.1155.

Compound 2n: Yield 56 mg, 92%. A yellow oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 2942, 1740, 1609, 1504, 1464, 1370, 1233, 1028, 963, 834, 522 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.08 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3), 3.81 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 4.76 (s, 4 H, CH_2), 6.45–6.49 (m, 2 H, Ar), 6.86 (s, 1 H, CH), 7.10 (d, J = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 20.9, 21.0, 55.35, 55.40, 61.2, 66.7, 98.4, 104.0, 117.0, 129.2, 130.2, 130.6, 158.4, 161.0, 170.8, 170.9 ppm. MS (EI): *m*/*z* (%) = 308 (6.18) [M$^+$], 239 (3.19), 205 (13.44), 189 (24.93), 188 (26.33), 177 (22.97), 155 (5.74), 141 (7.97), 127 (14.46), 113 (17.56), 99 (20.31), 85 (48.15), 71 (73.07), 57 (94.75), 43 (100.00). HRMS (EI) Calcd. For $C_{16}H_{20}O_6$ (M$^+$): 308.1260; found 308.1255.

Compound 2o: Yield 68 mg, 99%. A colorless oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 2940, 1743, 1592, 1506, 1461, 1422, 1372, 1227, 1128, 1027, 926, 513 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.04 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 3.86 (s, 6 H, OCH_3), 4.45 (d, J = 13.5 Hz, 1 H, CH), 4.60 (d, J = 13.5 Hz, 1 H, CH), 5.34 (s, 2 H, CH_2), 6.25 (s, 1 H, CH), 6.57 (s, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 20.7, 21.1, 56.0, 60.7, 64.0, 75.3, 104.4, 115.2, 133.0, 137.9, 141.8, 153.2, 169.6, 170.5 ppm. MS (EI): *m*/*z* (%) = 338 (0.46) [M$^+$], 219 (2.80), 205 (7.06), 188 (1.98), 115 (2.41), 91 (3.02), 77 (3.94), 57 (4.61), 43 (100.00). HRMS (EI) Calcd. For $C_{17}H_{22}O_7$ (M$^+$): 338.1366; found 338.1367.

Compound 3a: Yield 51 mg, 91%. A light yellow oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 3005, 2957, 2837, 1666, 1602, 1513, 1306, 1257, 1166, 1031, 989, 838, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.25 (dd, J = 4.0, J = 6.8 Hz, 2 H, CH_2), 1.57 (dd, J = 4.0, J = 6.8 Hz, 2 H, CH_2), 3.74 (s, 3 H, CH_3), 3.78 (s, 3 H, CH_3), 6.75–6.79 (m, 4 H, Ar), 7.14 (dd, J = 2.0, J = 6.8 Hz, 2 H, Ar), 7.79 (dd, J = 2.4, J = 6.8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 15.5, 34.0, 55.15, 55.26, 113.2, 114.4, 128.8, 129.5, 131.8, 133.4, 158.1, 162.5, 198.6 ppm. MS (EI): *m*/*z* (%) = 283 (21.07) [M$^+$ + 1], 282 (100.00) [M$^+$], 267 (9.12), 147 (19.94), 135 (84.52), 115 (8.15), 92 (10.32), 84 (8.00), 77 (16.61). HRMS (EI) Calcd. for $C_{18}H_{18}O_3$ (M$^+$): 282.1256; found 282.1258.

Compounds 3b and 3b′ (3.00:0.25 mixture of the two isomers): Yield 27 mg, 51%. A colorless oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 3004, 2955, 2836, 1671, 1608, 1514, 1278, 1175, 1032, 992, 828, 560 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.26 (**3b** and **3b′**, dd, J = 4.0, J = 6.8 Hz, 2.17 H, CH_2), 1.56 (**3b** or **3b′**, dd, J = 4.0, J = 6.8 Hz, 0.17 H, CH_2), 1.60 (4b′ or 4b, dd, J = 4.0, J = 6.8 Hz, 2 H, CH_2), 2.26 (**3b** or **3b′**, s, 0.25 H, CH_3), 2.29 (**3b′** or **3b**, s, 3 H, CH_3), 3.73 (**3b** or **3b′**, s, 3 H, OCH_3), 3.76 (**3b′** or **3b**, s, 0.25 H, OCH_3), 6.74–6.78 (**3b** and **3b′**, m, 2.17 H, Ar), 7.05–7.15 (**3b** and **3b′**, m, 4.33 H, Ar), 7.66–7.69 (**3b** or **3b′**,m, 2 H, Ar), 7.79–7.83 (**3b′** or **3b**, m, 0.17 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 15.5, 15.8, 21.5, 34.3, 55.1, 113.2, 113.9, 127.3, 127.4, 128.6, 129.0, 129.3, 129.6, 130.2, 131.9, 133.2, 134.3, 137.4, 142.5, 158.1, 200.0 ppm. MS (EI): *m*/*z* (%) = 267 (20.99) [M$^+$ + 1], 266 (100.00) [M$^+$], 251 (8.94), 147 (34.96), 119 (48.42), 115 (11.03), 91 (33.30), 77 (5.75), 65 (9.92). HRMS (EI) Calcd. for $C_{18}H_{18}O_2$ (M$^+$): 266.1307; found 266.1306.

Compound 4a: Yield 61 mg, 87%. A white solid. Mp: 91–93 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 2968, 1738, 1462, 1173, 1004, 774, 709, 507 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.15 (t, J = 7.6 Hz, 6 H, CH_3), 2.36 (q, J = 7.6 Hz, 4 H, CH_2), 4.70 (s, 4 H, CH_2), 7.15 (d, J = 6.4 Hz, 4 H, Ar), 7.26–7.32 (m, 6 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 9.1, 27.5, 62.8, 127.5, 127.8, 128.1, 129.2, 140.4, 148.5, 174.1 ppm. MS (EI): *m*/*z* (%) = 352 (0.52) [M$^+$], 278 (0.95), 221 (11.27), 204 (100.00), 193 (12.48), 178 (9.58), 165 (6.56), 115 (14.60), 91 (4.58), 57 (21.76). HRMS (EI) Calcd. for $C_{22}H_{24}O_4$ (M$^+$): 352.1675; found 352.1671.

Supporting Information (see also the footnote on the first page of this article): ^{1}H NMR and ^{13}C NMR spectroscopic and analytic data of the compounds **2**, **3** and **4a** are included.

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$$PhI(O_2CCH_3)_2 + 2\,R'CO_2H \xrightarrow[-\,CH_3COOH]{C_6H_5Cl} PhI(O_2CR')_2$$

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