Synthesis of Functionalized Cyclopentene Derivatives through Gold-Catalyzed Reaction of Stabilized Vinyldiazo Compounds and Styrenes

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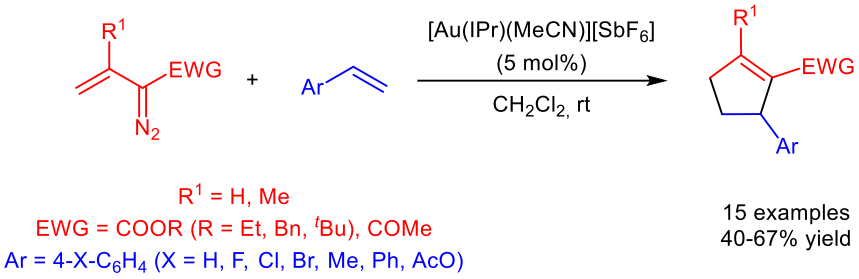

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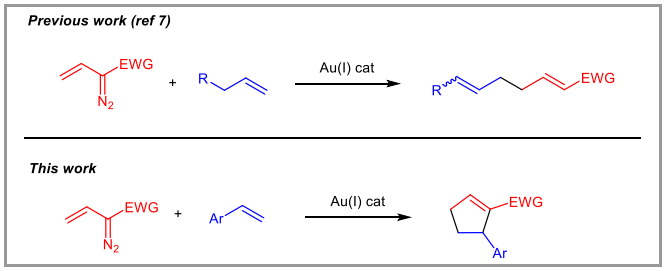
Abstract The reaction of alkenyldiazo compounds with styrene derivatives in the presence of [Au(IPr)(MeCN)][SbF_6] provided cyclopentene derivatives resulting from a formal [3+2] cycloaddition reaction as major products. This reaction outcome stand in marked contrast with that previously observed for other olefinic derivatives. From a mechanistic point of view, this process would involve the initial generation of a highly electrophilic alkenylgold carbene intermediate, which would be subsequently involved in a stepwise carbocationic process.

Key words gold, cyclopentenes, diazo compounds, styrene derivatives, [3+2] carbocycloaddition

In the last years, gold catalysis has had a tremendous impact in organic synthesis.[1] Probably, the most salient feature of gold complexes is their ability to bind to unsaturated organic substrates, mainly alkynes and allenes.[2] The so generated electrophilic organometallic species are prone to undergo different transformations, most commonly initiated by a nucleophilic attack. A plethora of synthetic applications have been developed on the basis of this conceptually simple reactivity pattern.

Although more recently developed, the gold-catalyzed decomposition of diazocompounds has also gained substantial interest as it represents a convenient tool for accessing reactivity patterns previously unattainable using other metal complexes.[3,4] This extraordinary impetus of gold catalysis has been also of particular benefit to the chemistry of vinyldiazo compounds, a subclass of diazo reagents with manifold applications in organic synthesis through metal catalyzed transformations.[5,6] In this regard, some years ago our group reported the gold-catalyzed reactions of stabilized vinyl diazocompounds and unsaturated hydrocarbons.[7] In particular, we found that reaction of vinyldiazo compounds with an array of unbiased alkenes provided dienoates resulting from the regioselective coupling of the Csp^2(alkene) and the Cγ(vinyldiazo) atoms (Scheme 1). This reaction is believed to proceed by means of a gold carbene intermediate with an enhanced reactivity at the conjugated position (vinylogous reactivity). This reactivity pattern is in great contrast with that observed not only for rhodium carbenoids generated from vinyl diazocompounds,[8] but also for other common precursors of alkenylgold carbenes, such as cyclopropenes and propargylic esters for which a formal [2+1] cycloaddition reaction with formation of cyclopropane derivatives is the preferred pathway (carbenic reactivity).[9]

In the context of our ongoing interest in the development of new transition metal-catalyzed transformations of vinyldiazo compounds,[10] we herein report their gold-catalyzed reaction with styrene derivatives that results in most cases in the regioselective formation of functionalized cyclopentene derivatives arising from a formal [3+2] carbocycloaddition reaction.[11]



Scheme 1. Divergent reactivity in gold-catalyzed reactions of vinyldiazo compounds with alkenes.

This study was carried out using vinyl diazocompounds **1a-g** and styrene derivatives **2a-i** outlined in Figure 1.

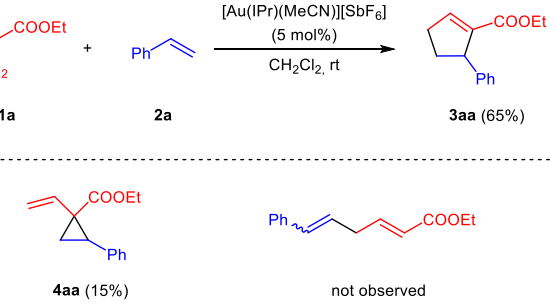
1a (R^1 = R^2 = H; EWG = COOEt)
1b (R^1 = R^2 = H; EWG = COOBn)
1c (R^1 = R^2 = H; EWG = COO^{t}Bu)
1d (R^1 = Me; R^2 = H; EWG = COOEt)
1e (R^1 = Me; R^2 = H; EWG = COMe)
1f (R^1 = H; R^2 = EWG = COOEt)
1g (R^1 = H; R^2 = Cl; EWG = COOEt)

2a (Ar = Ph)
2b (Ar = *p*-ClC_6H_4)
2c (Ar = *p*-BrC_6H_4)
2d (Ar = *p*-FC_6H_4)
2e (Ar = *p*-MeC_6H_4)
2f (Ar = *p*-PhC_6H_4)
2g (Ar = *p*-$AcOC_6H_4$)
2h (Ar = *p*-$CH_3OC_6H_4$)
2i (Ar = 2,4,6-$Me_3C_6H_2$)

Figure 1. Starting materials used in this work.

For our initial studies, ethyl 2-diazo-but-3-enoate (**1a**) and styrene (**2a**) were chosen as the model substrates. According to our previous research,[7] [Au(IPr)(MeCN)][SbF_6] was initially selected as the catalyst. Thus, stirring a solution of vinyldiazo acetate **1a**, styrene (**2a**) and 5 mol% of [Au(IPr)(MeCN)][SbF_6] in dichloromethane at room temperature resulted in the formation of a reaction mixture from which ethyl 5-phenylcyclopent-1-ene-1-carboxylate (**3aa**) was isolated after column chromatography in 65% along with minor amounts (15%) of cyclopropane derivative **4aa** (Scheme 2). In contrast with our previous investigations involving unbiased alkenes, no open-chain diene derivatives were isolated in this reaction. Other gold catalysts showed similar or inferior results in terms of chemical yield and selectivity.

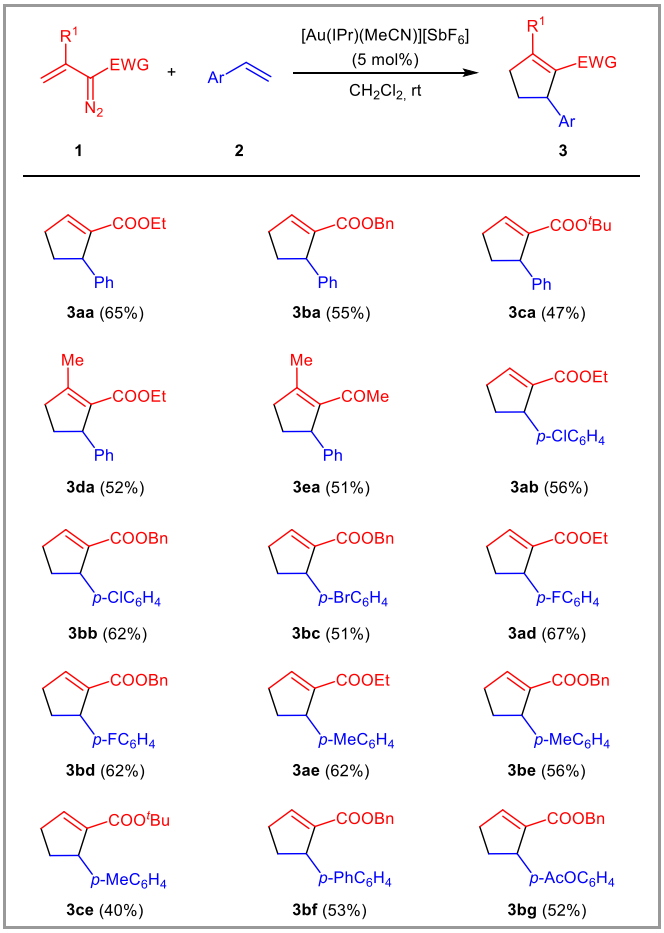
The structure of compound **3aa** was ascertained by NMR spectroscopic methods. Moreover, the spectroscopic data match those previously reported in the literature.[12]



Scheme 2. Gold-catalyzed reaction of vinyldiazo compound **1a** and styrene (**2a**): Initial finding.

Once demonstrated the divergent behavior of styrene with respect to other alkenes, next we investigated the scope of this gold-catalyzed [3+2] cycloaddition reaction (Scheme 3). First, we found that the nature of the ester substituent seemed to exert little effect in the reaction outcome. Indeed, reaction of benzyl 2-diazobut-3-enoate (**1b**; R = H; EWG = COOBn) and styrene (**2a**) afforded the corresponding cyclopentene derivative **3ba** in 55% isolated yield. Similarly, the reaction of *tert*-butyl substituted vinyldiazo compound (**1c**; R = H; EWG = COO^{t}Bu) provided the expected cyclopentene **3ca**, albeit in lower yield (47%). As in the model reaction, cyclopropane derivatives resulting from a competitive [2+1] cycloaddition reaction were formed in low yields and were easily separated from the [3+2] cycloadducts by column chromatography. Unless otherwise stated, no attempts were made to characterize these cyclopropane derivatives.

A vinyldiazo compound bearing an alkyl group at the C3 atom (diazo compound **1d**; R = Me; EWG = COOEt) was also amenable to this cyclization affording the corresponding cyclopentene derivative **3da** in moderate isolated yield (52%). A nearly identical result was obtained with an acetyl-stabilized diazo compound (**1e**; R = Me; EWG = COMe) as demonstrated by the formation of cyclopentene derivative **3ea** in moderate yield (51%).



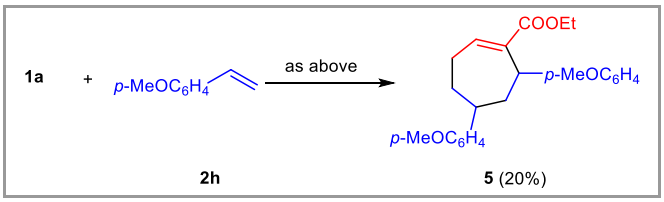
Scheme 3. Gold-catalyzed [3+2] cycloaddition reaction of vinyldiazo compounds **1** and styrene derivatives **2**. Reaction conditions: **1** (0.2 mmol), **2** (0.8 mmol), [Au(IPr)(MeCN)][SbF_6] (5 mol%), CH_2Cl_2, rt. The reported yields are those of the products isolated after column chromatography.

Regarding the alkene component, an array of substituted styrene derivatives are suitable substrates in this [3+2] cyclization reaction. For example, as shown in Scheme 3, styrene derivatives **2b-d** bearing halogens at the *para*-position of the aryl group were perfectly compatible with this protocol affording the corresponding cycloadducts in moderate isolated yields (51-67%).

Styrene derivatives **2e** and **2f** with alkyl and aryl groups installed at *para* position were also suitable substrates in this gold-catalyzed [3+2] cycloaddition reaction affording the expected cyclopentene derivatives in moderate yields (40-62%). Likewise, an electron donating acetoxy group posed no

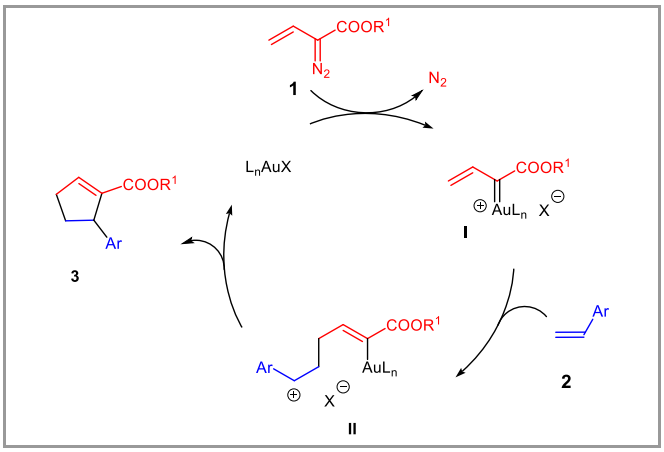
problems delivering the expected cyclopentene **3bg** in an acceptable yield (52%).

Notably, the use of a styrene derivative with a strong donor group, namely 1-methoxy-4-vinylbenzene (**2h**), provided an unexpected result (Scheme 4). Thus, reaction of ethyl 2-diazo-but-3-enoate (**1a**) with **2h**, under otherwise similar conditions (5 mol% of the gold catalyst, CH_2Cl_2, room temperature), afforded a complex mixture of products. The cycloheptene derivative **5** resulting from a formal [3+2+2] cyclization reaction was isolated from this mixture in 20% yield.



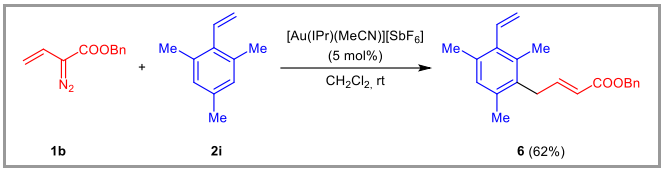
Scheme 4. Gold-catalyzed [3+2+2] cycloaddition reaction of vinyldiazo compounds **1a** and styrene derivative **2h**.

On the basis of the respective literature precedents on gold-catalyzed transformations of vinyldiazo compounds, a mechanistic rationale for the formation of cyclopentene derivatives **3** is depicted in Scheme 5. Indeed, initial decomposition of the vinyldiazo compound would generate the gold carbene intermediate **I**. It is well-documented that these intermediates display an enhanced vinylogous reactivity. Consequently, regioselective nucleophilic attack of the styrene derivative **2** to the vinylogous position would form carbocationic intermediate **II**. The complete regioselectivity of this step would rely on the formation of the most stable carbocationic intermediate. Finally, intermediate **II** would undergo a cyclization reaction to produce the corresponding cyclopentene derivative **3** with regeneration of the gold(I) complex, thus closing the catalytic cycle.[13]



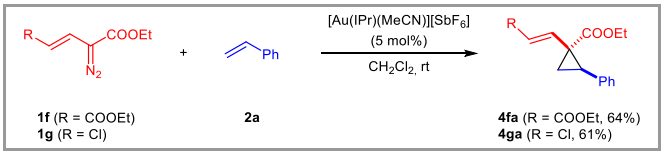
Scheme 5. Proposed mechanism for the formation of cyclopentene derivatives **3**.

In the course of our study, we found that some substrates failed to provide the corresponding cyclopentene derivatives. For example, it was observed that steric factors can exert an important impact on the reaction outcome as demonstrated the reaction of vinyldiazo compound **1b** and the sterically encumbered styrene derivative **2i** (Scheme 6). Indeed, under otherwise identical conditions, this reaction did not deliver the expected [3+2] cycloadduct. Instead, γ-aryl-substituted 2-butenoate **6** was isolated as single *E*-isomer in 62% isolated yield.[14]



Scheme 6. Gold-catalyzed reaction of vinyldiazo compound **1b** and styrene derivative **2i**.

A divergent reaction outcome was also observed for some β-substituted vinyldiazo derivatives. For example, the reaction of vinyldiazo compounds **1f** and **1g** with styrene (**2a**) under the optimized reaction conditions resulted in the formation of vinyl-substituted cyclopropane derivatives **4fa** and **4ga** in 64 and 61% yield, respectively (Scheme 7). Apparently, the structure of the diazo compound seems to favor a competitive [2+1] cycloaddition reaction.[15]



Scheme 7. Gold-catalyzed cyclopropanation reaction of β-substituted vinyldiazo compounds **1f,g** and styrene.

In conclusion, a catalytic methodology for the synthesis of cyclopentene carboxylic acid derivatives from stabilized vinyldiazo compounds and styrene derivatives has been developed. Notably, the reaction course differs significantly from that observed using unbiased alkenes as the olefinic partner. Although both processes are thought to occur by initial generation of an electrophilic vinylgold carbene intermediate, in the present one the subsequently formed carbocationic intermediate would evolve through a cyclization reaction leading to products resulting from a formal [3+2] cyclization reaction, an unusual pathway in reaction of vinyldiazo compounds and styrene derivatives. Nevertheless, the reaction was found to be sensible to the structure of both components and some competitive reaction pathways have been identified.

All reactions were carried out under nitrogen using standard Schlenck techniques. Dichloromethane was distilled from CaH_2. The solvents used in column chromatography, hexane and ethyl acetate, were obtained from commercial suppliers and used without further purification. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator. Flash column chromatography was carried out on silica gel (230-240 mesh). ^1H NMR (300, 400 MHz) and ^{13}C NMR (75.5 and 100 MHz) spectra were recorded at room temperature in $CDCl_3$ on a Bruker DPX-300, or Bruker AVANCE-300 MHz and 400 MHz instruments. Chemical shifts are given in ppm relative to TMS (^1H, 0.0 ppm) or $CDCl_3$ (^{13}C, 77.0 ppm). 2D NMR experiments were recorded on a Bruker AVANCE-400 MHz. High-resolution mass spectra were determined on a VG Autospec M mass spectrometer. Vinyldiazo compounds **1** were prepared according to well-known procedures previously described in

the literature.[16] All other reagents used in this work were of the best commercial grade available and used without further purification.

General Procedure for the Synthesis of Cyclopentene Derivatives 3

$[Au(IPr)(CH_3CN)]SbF_6$ (8.6 mg, 0.01 mmol, 5 mol%) was added to a solution of vinyldiazo compound **1** (0.2 mmol) and styrene derivative **2** (0.8 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4-12 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel; hexanes/ethyl acetate 40:1) to afford the [3+2] cycloadducts **3** along with cyclopropane derivatives **4**.

Ethyl 5-phenylcyclopent-1-ene-1-carboxylate (3aa)

Yield: 28.1 mg (65%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31-7.17 (m, 5H), 7.00 (dd, *J* = 3.9 and 2.1 Hz, 1H), 4.19-4.01 (m, 3H), 2.74-2.50 (m, 3H), 2.00-1.90 (m, 1H), 1.14 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 165.2 (C), 145.7 (C), 144.9 (CH), 140.0 (C), 128.7 (CH), 127.5 (CH), 126.5 (CH), 60.4 (CH_2), 50.6 (CH), 34.5 (CH_2), 32.6 (CH_2), 14.5 (CH_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{14}H_{16}O_2$: 216.1150; found: 216.1152.

The spectroscopic data of compound **3aa** match those previously reported in the literature.[12]

Benzyl 5-phenylcyclopent-1-ene-1-carboxylate (3ba)

Yield: 30.6 mg (55%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.39-7.10 (m, 11H), 5.17 (d, *J* = 12.9 Hz, 1H), 5.01 (d, *J* = 12.9 Hz, 1H), 4.23-4.20 (m, 1H), 2.78-2.50 (m, 3H), 2.02-1.92 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.6 (C), 145.6 (CH), 145.3 (C), 139.2 (C), 136.1 (C), 128.5 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 127.1 (CH), 126.3 (CH), 65.8 (CH_2), 50.2 (CH), 34,2 (CH_2), 32.3 (CH_2).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{19}H_{18}O_2$: 278.1307; found: 278.1302.

***tert*-Butyl 5-phenylcyclopent-1-ene-1-carboxylate (3ca)**

Yield: 23.0 mg (47%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.32-7.26 (m, 2H), 7.22-7.17 (m, 3H), 6.94-6.93 (m, 1H), 4.12-4.07 (m, 1H), 2.71-2.46 (m, 3H), 1.96-1.90 (m, 1H), 1.33 (s, 9H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.4 (C), 145.7 (C), 143.9 (CH), 141.2 (C), 128.2 (CH), 127.1 (CH), 126.0 (CH), 80.1 (C), 50.5 (CH), 34.3 (CH_2), 32.0 (CH_2), 27.9 (CH_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{16}H_{20}O_2$: 244.1458; found: 244.1460.

Ethyl 2-methyl-5-phenylcyclopent-1-ene-1-carboxylate (3da)

Yield: 24.0 mg (52%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30-7.15 (m, 5H), 4.21-4.17 (m, 1H), 4.09-3.94 (m, 2H), 2.76-2.63 (m, 1H), 2.56-2.37 (m, 2H), 2.23 (s, 3H), 1.83-1.73 (m, 1H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 165.9 (C), 156.4 (C), 146.3 (C), 130.8 (C), 128.2 (CH), 127.0 (CH), 125.9 (CH), 59.5 (CH_2), 52.3 (CH), 39.5 (CH_2), 32.4 (CH_2), 16.4 (CH_3), 14.0 (CH_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{15}H_{18}O_2$: 230.1301; found: 230.1304.

1-(2-Methyl-5-phenylcyclopent-1-en-1-yl)ethan-1-one (3ea)

Yield: 20.4 mg (51%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33-7.14 (m, 5H), 4.26-4.21 (m, 1H), 2.67-2.62 (m, 1H), 2.53-2.36 (m, 2H), 2.21 (s, 3H), 1.96 (s, 3H), 1.80-1.68 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 199.2 (C), 155.3 (C), 145.7 (C), 138.8 (C), 128.7 (CH), 127.0 (CH), 126.4 (CH), 53.0 (CH), 39.3 (CH_2), 33.3 (CH_2), 30.2 (CH_3), 16.8 (CH_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{14}H_{16}O$: 200.1196; found: 200.1199.

Ethyl 5-(4-chlorophenyl)cyclopent-1-ene-1-carboxylate (3ab)

Yield: 28.1 mg (56%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.26-7.23 (m, 2H), 7.14-7.10 (m, 2H), 7.00 (dd, *J* = 3.9 and 2.4 Hz, 1H), 4.16-4.01 (m, 3H), 2.74-2.46 (m, 3H), 1.94-1.85 (m, 1H), 1.16 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.6 (C), 144.9 (CH), 143.9 (C), 139.3 (C), 131.8 (C), 128.5 (CH), 128.4 (CH), 60.1 (CH_2), 49.6 (CH), 34.0 (CH_2), 32.2 (CH_2), 14.1 (CH_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{14}H_{15}ClO_2$: 250.0761; found: 250.0759.

Benzyl 5-(4-chlorophenyl)cyclopent-1-ene-1-carboxylate (3bb)

Yield: 38.8 mg (62%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.66-7.43 (m, 10H), 5.51 (d, *J* = 12.6 Hz, 1H), 5.33 (d, *J* = 12.6 Hz, 1H), 4.52-4.48 (m, 1H), 3.09-2.84 (m, 3H), 2.29-2.21 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.4 (C), 145.9 (CH), 143.8 (C), 138.9 (C), 136.0 (C), 131.9 (C), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 65.9 (CH_2), 49.7 (CH), 34.1 (CH_2), 32.3 (CH_2).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{19}H_{17}ClO_2$: 312.0917; found: 312.0914.

Benzyl 5-(4-bromophenyl)cyclopent-1-ene-1-carboxylate (3bc)

Yield: 36.4 mg (51%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40-7.31 (m, 5H), 7.14-7.05 (m, 5H), 5.18 (d, *J* = 12.6 Hz, 1H), 4.99 (d, *J* = 12.6 Hz, 1H), 4.17-4.14 (m, 1H), 2.77-2.49 (m, 3H), 1.95-1.89 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.4 (C), 145.9 (CH), 144.3 (C), 138.8 (C), 136.0 (C), 131.5 (CH), 128.9 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 120.0 (C), 65.9 (CH_2), 49.7 (CH), 34.0 (CH_2), 32.3 (CH_2).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{19}H_{17}BrO_2$: 356.0412; found: 356.0409.

Ethyl 5-(4-fluorophenyl)cyclopent-1-ene-1-carboxylate (3ad)

Yield: 31.4 mg (67%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.14-7.11 (m, 2H), 6.99-6.93 (m, 3H), 4.14-4.00 (m, 3H), 2.72-2.62 (m, 1H), 2.59-2.47 (m, 2H), 1.92-1.86 (m, 1H), 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.6 (C), 162.0 (C, J_{CF} = 247.5 Hz), 144.6 (CH), 141.3 (C), 139.6 (C), 128.4 (CH, J_{CF} = 7.0 Hz), 115.1 (CH, J_{CF} = 21.0 Hz), 60.1 (CH_2), 49.5 (CH), 34.0 (CH_2), 32.1 (CH_2), 14.1 (CH_3).

^{19}F-NMR ($CDCl_3$, 282 MHz): -117.4.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{14}H_{15}FO_2$: 234.1056; found: 234.1057.

Benzyl 5-(4-fluorophenyl)cyclopent-1-ene-1-carboxylate (3bd)

Yield: 36.7 mg (62%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28-7.12 (m, 3H), 7.09-6.95 (m, 7H), 5.17 (d, *J* = 12.6 Hz, 1H), 5.00 (d, *J* = 12.6 Hz, 1H), 4.20-4.17 (m, 1H), 2.77-2.49 (m, 3H), 1.96-1.93 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.5 (C), 161.5 (C, J_{CF} = 242.1 Hz), 145.6 (CH), 140.9 (C), 139.1 (C), 136.0 (C), 128.5, 128.4, 128.0, 127.8, 115.2 (C, J_{CF} = 21.1 Hz), 65.8 (CH_2), 49.5 (CH), 34.1 (CH_2), 32.2 (CH_2).

^{19}F-NMR ($CDCl_3$, 282 MHz): -117.3.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{19}H_{17}FO_2$: 296.1213; found: 296.1211.

Ethyl 5-(*p*-tolyl)cyclopent-1-ene-1-carboxylate (3ae)

Yield: 28.6 mg (62%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.10-7.05 (m, 4H), 6.96 (dd, *J* = 4.0 and 2.0 Hz, 1H), 4.13-4.02 (m, 3H), 2.72-2.63 (m, 1H), 2.57-2.47 (m, 2H), 2.31 (s, 3H), 1.95-1.88 (m, 1H), 1.15 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.8 (C), 144.2 (CH), 142.3 (C), 139.7 (C), 135.6 (C), 129.1 (CH), 126.9 (CH), 60.0 (CH_2), 49.7 (CH), 34.1 (CH_2), 32.2 (CH_2), 21.0 (CH_3), 14.1 (CH_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{15}H_{18}O_2$: 230.1301; found: 230.1304.

Benzyl 5-(*p*-tolyl)cyclopent-1-ene-1-carboxylate (3be)

Yield: 32.7 mg (56%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31-7.28 (m, 3H), 7.16-7.07 (m, 7H), 5.18 (d, *J* = 12.7 Hz, 1H), 5.01 (d, *J* = 12.7 Hz, 1H), 4.19-4.16 (m, 1H), 2.77-2.51 (m, 3H), 2.37 (s, 3H), 1.99-1.90 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.7 (C), 145.3 (CH), 142.2 (C), 139.4 (C), 136.2 (C), 135.7 (C), 129.2 (CH), 128.3 (CH), 127.8 (CH), 127.7 (CH), 127.0 (CH), 65.7 (CH_3), 49.8 (CH), 34.3 (CH_2), 32.3 (CH_2), 21.1 (CH_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{20}H_{20}O_2$: 292.1458; found: 292.1461.

***tert*-Butyl 5-(*p*-tolyl)cyclopent-1-ene-1-carboxylate (3ce)**

Yield: 20.7 mg (40%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.12-7.03 (m, 4H), 6.92-6.91 (m, 1H), 4.07-4.05 (m, 1H), 2.69-2.44 (m, 3H), 2.34 (s, 3H), 1.94-1.80 (m, 1H), 1.32 (s, 9H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.4 (C), 143.5 (CH), 142.6 (C), 141.3, 135.4 (C), 128.9 (CH), 127.0 (CH), 80.0 (C), 50.0 (CH), 34.4 (CH_2), 32.0 (CH_2), 27.9 (CH_3), 21.0 (CH_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{17}H_{22}O_2$: 258.1614; found: 258.1618.

Benzyl 5-([1,1'-biphenyl]-4-yl)cyclopent-1-ene-1-carboxylate (3bf)

Yield: 37.6 mg (53%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.63-7.24 (m, 12H), 7.14-7.10 (m, 3H), 5.19 (d, *J* = 12.6 Hz, 1H), 5.00 (d, *J* = 12.6 Hz, 1H), 4.26-4.22 (m, 1H), 2.65-2.55 (m, 3H), 2.02-1.99 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.6 (C), 145.7 (CH), 144.4 (C), 141.1 (C), 139.1 (C), 136.1 (C), 128.7 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 127.5 (CH), 127.2 (CH), 127.0 (CH), 65.8 (CH_2), 49.9 (CH), 34.2 (CH_2), 32.3 (CH_2).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{25}H_{22}O_2$: 354.1620; found: 354.1621.

Benzyl 5-(4-acetoxyphenyl)cyclopent-1-ene-1-carboxylate (3bg)

Yield: 35.0 mg (52%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30-7.00 (m, 10H), 5.16 (d, *J* = 12.6 Hz, 1H), 5.01 (d, *J* = 12.6 Hz, 1H), 4.21-4.18 (m, 1H), 2.77-2.47 (m, 3H), 2.32 (s, 3H), 2.00-1.95 (m, 1H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.6 (C), 164.5 (C), 149.1 (C), 145.7 (CH), 142.7 (C), 139.1 (C), 136.0 (C), 128.4 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 121.4 (CH), 65.9 (CH_2), 49.6 (CH), 34.0 (CH_2), 32.2 (CH_2), 21.2 (CH_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{21}H_{20}O_4$: 336.1362; found: 336.1360.

Synthesis of Cycloheptene Derivative 5

[Au(IPr)(CH_3CN)]SbF_6 (8.6 mg, 0.01 mmol, 5 mol%) was added to a solution of vinyldiazo compound **1a** (28.0 mg, 0.2 mmol) and styrene derivative **2h** (107.3 mg, 0.8 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel; hexanes/ethyl acetate 40:1) to afford the [3+2+2] cycloadduct **5**.

Yield: 15.2 mg (20%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): 7.23-7.20 (m, 2H), 7.16-7.13 (m, 2H), 6.87-6.83 (m, 4H), 5.93 (s, 1H), 4.69 (dd, *J* = 11.1 and 6.9 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 2.85-2.74 (m, 2H), 2.47-2.39 (m, 1H), 2.20-1.87 (m, 4H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz): 165.9 (C), 162.5 (C), 157.9 (C), 157.8 (C), 138.8 (C), 136.5 (C), 128.0 (CH), 127.7 (CH), 117.3 (CH), 113.8 (CH), 113.7 (CH), 59.7 (CH_2), 55.3 (CH_3), 55.2 (CH_3), 44.0 (CH), 39.7 (CH_2), 39.0 (CH), 33.0 (CH_2), 32.4 (CH_2), 14.2 (CH_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{24}H_{28}O_4$: 380.1988; found: 380.1984.

Synthesis of γ-aryl-substituted 2-butenoate 6

[Au(IPr)(CH_3CN)]SbF_6 (8.6 mg, 0.01 mmol, 5 mol%) was added to a solution of vinyldiazo compound **1b** (40.4 mg, 0.2 mmol) and styrene derivative **2i** (117.0 mg, 0.8 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel; hexanes/ethyl acetate 40:1) to afford γ-aryl-substituted 2-butenoate **6**.

Yield: 39.7 mg (62%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): 7.42-7.38 (m, 5H), 7.21 (dt, *J* = 15.6 and 5.6 Hz, 1H), 6.95 (s, 1H), 6.72 (dd, *J* = 17.9 and 11.4 Hz, 1H), 5.69 (dt, *J* = 15.6 and 2.0 Hz, 1H), 5.58 (dd, *J* = 11.4 and 2.1 Hz, 1H), 5.23-5.19 (overlapped s and dd, 3H), 3.60 (dd, *J* = 5.6 and 1.8 Hz, 2H), 2.32 (s, 3H), 2.28 (s, 3H)., 2.26 (s, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz): 166.5 (C), 147.4 (CH), 136.7 (C), 136.0 (CH), 135.1 (C), 134.4 (C), 134.2 (C), 131.6 (C), 128.8 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 121.1 (CH), 119.5 (CH_2), 66.2 (CH_2), 32.6 (CH_2), 20.8 (CH_3), 20.0 (CH_3), 16.9 (CH_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{22}H_{24}O_2$: 320.1776; found: 320.1772.

Synthesis of Vinylcyclopropane Derivatives 4fa and 4ga

[Au(IPr)(CH_3CN)]SbF_6 (8.6 mg, 0.01 mmol, 5 mol%) was added to a solution of the corresponding vinyldiazo compound (0.2 mmol) and styrene (**2a**) (83.3 mg, 0.8 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred at room temperature until the disappearance of the starting diazo compound (monitored by TLC: 4-12 h). The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (silica gel; hexanes/ethyl acetate 20:1) to afford cyclopropane derivatives **4fa** and **4ga** along with several unidentified products.

Cyclopropane 4fa

Yield: 36.9 mg (64%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): 7.29-6.91 (m, 5H), 6.93 (d, *J* = 15.9 Hz, 1H), 5.65 (d, *J* = 15.9 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.23 (dd, *J* = 9.2 and 8.0 Hz, 1H), 2.12 (dd, *J* = 9.2 and 5.0 Hz, 1H), 1.78 (dd, *J* = 8.0 and 5.0 Hz, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz): 172.1 (C), 166.1 (C), 142.4 (CH), 134.4 (C), 129.5 (CH), 128.3 (CH), 127.3 (CH), 121.7 (CH), 61.6 (CH_2), 60.2 (CH_2), 37.5 (CH), 32.4 (C), 20.2 (CH_2), 14.23 (CH_3), 14.15 (CH_3).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{17}H_{20}O_4$: 288.1362; found: 288.1359.

The spectroscopic data of cyclopropane derivative **4fa** match those previously reported in the literature.[17]

Cyclopropane 4ga

Yield: 30.6 mg (61%); colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): 7.34-7.26 (m, 3H), 7.15-7.12 (m, 2H), 6.01 (d, *J* = 13.5 Hz, 1H), 5.83 (d, *J* = 13.5 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.99 (dd, *J* = 9.3 and 7.2 Hz, 1H), 1.98 (dd, *J* = 9.3 and 5.1 Hz, 1H), 1.64 (dd, *J* = 7.2 and 5.1 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 75 MHz): 172.5 (C), 135.0 (C), 129.1 (CH), 128.2 (CH), 128.0 (CH), 127.1 (CH), 121.2 (CH), 61.5 (CH_2), 34.1 (CH), 31.7 (C), 18.6 (CH_2), 14.2 (CH_3).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{14}H_{15}ClO_2$: 250.0761; found: 250.0764.

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Supporting Information

Is there **Supporting Information** to be published? YES.

Primary Data

Is there **Primary Data** to be associated with this manuscript? NO.

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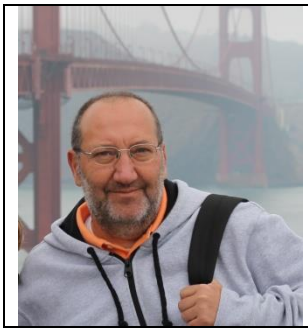
Biosketches

Enol López was born in 1991 in Gijón (Spain). He studied Chemistry at the Universidad de Oviedo (2009-2013). In 2014, he obtained his master degree with a work on gold-catalyzed C-H bond functionalization of metalocenes. He is currently pursuing PhD studies under the supervision of Dr. Luis A. López. His work mainly focuses on the development of new metal-catalyzed reactions involving diazo compounds. He recently was bestowed with the 2017 RSEQ-Lilly Award for PhD students.

Giacomo Lonzi was born in Siena, Italy, in 1983. He studied at the University of Siena where he obtained his Degree in Pharmaceutical Chemistry and Technology in 2007. Then, he joined the group of Prof. J. Barluenga at the Universidad de Oviedo where he received his PhD in Chemistry in 2013 with a thesis on the development of new synthetic applications of vinyldiazo compounds. Since then, he has worked in the pharmaceutical sector.



Luis A. López studied chemistry at the Universidad de Oviedo, where he also earned his PhD in 1990 working in the field of heterocyclic chemistry under the supervision of Prof. J. Barluenga and Prof. M. Tomás. Then, as an Alexander von Humboldt postdoctoral fellowship, he carried out research on group 4 organometallic chemistry at the Organisch-Chemisches Institut der Universität Münster with Prof. G. Erker. In 1993, he took a position as a Research Associate at the Universidad de Oviedo, where he was promoted to Associate Professor in 2000. His research interests include the metal-catalyzed transformations of diazo compounds, the C-H bond functionalization of metallocene derivatives and the development of sustainable synthetic methodologies.