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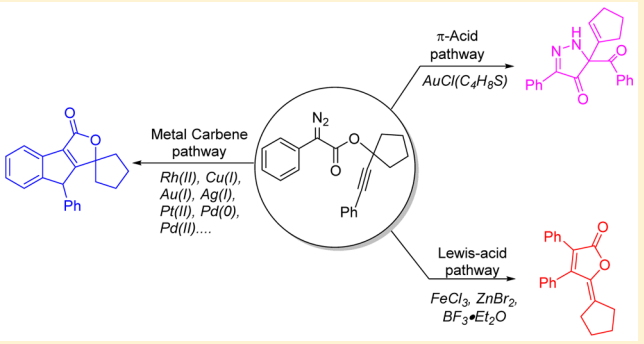
Diverse Pathways in Catalytic Reactions of Propargyl Aryldiazoacetates: Selectivity between Three Reaction Sites

Huang Qiu, Yifan Deng, Kostiantyn O. Marichev, and Michael P. Doyle*

Department of Chemistry, The University of Texas at San Antonio, San Antonio, Texas 78249, United States

Supporting Information

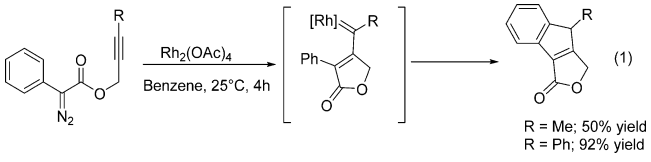
ABSTRACT: Three catalyst-dependent divergent reaction pathways for reactions of propargyl aryldiazoacetates are disclosed. Transition metal catalysts including those of rhodium(II), palladium(0 and II), silver(I), mercury(II), copper(I and II), platinum(II), and cationic gold(I) are effective for reactions that proceed through dinitrogen extrusion, carbene/alkyne metathesis, and aromatic substitution to form fused indeno-furanones, and use of tetrakis(acetonitrile)copper(I) provides indeno-furanones in the highest product yields. A Lewis acid catalyzed pathway that forms furan-2-ones is uncovered with $FeCl_3$, $ZnBr_2$, and $BF_3{\cdot}Et_2O$ as catalysts that proceed through activation of the aryldiazoacetate ester for arylpropargyl cation dissociation followed by recombination through cation addition to the diazo carbon. Neutral gold catalysts selectively activate the triple bond of propargyl aryldiazoacetates, resulting in the formation of allenic aryldiazoesters that further undergo uncatalyzed rearrangement.



INTRODUCTION

Domino reactions in which two or more sequential bond-forming events occur inter- or intramolecularly under the same reaction conditions are efficient and economical processes for the synthesis of organic compounds.[1] The development of these processes has advanced dramatically over the past two decades due to their catalytic applications that rapidly build molecular complexity.[2−4] Comprehensive reviews have highlighted catalytic metal carbene reactions as providing effective pathways for domino processes, and dirhodium(II) catalysts have been used almost exclusively for these transformations.[4,5] However, few actual investigations have reported the outcome of reactions with catalysts other than those of dirhodium(II),[6] so little is known about the comparative effectiveness of catalysts for domino reactions of diazo compounds.

An example of the intramolecular domino reaction of propargyl phenyldiazoesters that produced an indene-fused lactone in high yield upon treatment with a catalytic amount of $Rh_2(OAc)_4$ was reported in 2000 (eq 1).[7] This process was



reported to take place by initial rhodium-catalyzed dinitrogen extrusion to form a metal carbene that then undergoes carbene/alkyne metathesis and subsequent aromatic substitution to form fused indeno-furanones. This pattern of reaction (dinitrogen extrusion−carbene/alkyne metathesis−subsequent metal carbene reaction) is characteristic of a wide diversity of catalytic reactions that take place with propargyl-substituted diazocarbonyl compounds.[4,5,8] However, π-bond acceptor catalysts do not follow the same pathway and, instead, activate the carbon−carbon triple bond for subsequent reactions:[9] 1,3-acyloxy migration of the propargyl ester is the initial step,[10] and allenic diazoesters are the reaction intermediates.[11] Highly Lewis acidic catalysts can promote C−O bond cleavage reactions that produce propargyl cations in an S_N1/E1-like pathway for subsequent reactions.[12] Our intent in this investigation is to assess the relative reactivity of propargyl diazoacetates toward the three reaction pathways determined by association of the catalyst at the diazo carbon, the ester, or the carbon−carbon triple bond. Catalyst dependence of product yields in the domino process that produces fused indeno-furanones provides a comparative assessment of reactions that proceed through metal carbene formation in competition with activation of the ester for propargyl cation dissociation.

This investigation proceeded with the expectation that three reaction pathways are possible for reactions of propargyl diazoacetates: (A) the σ-bond acceptor catalyst reacts at the diazo functionality to displace dinitrogen and form a metal carbene that undergoes a cascade transformation which is

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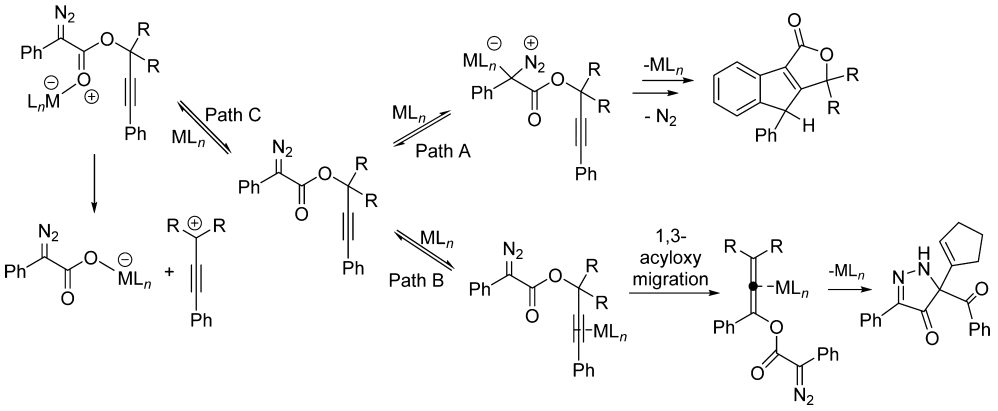
Scheme 1. Three Catalyst-Dependent Reaction Pathways of Propargyl Aryldiazoacetates



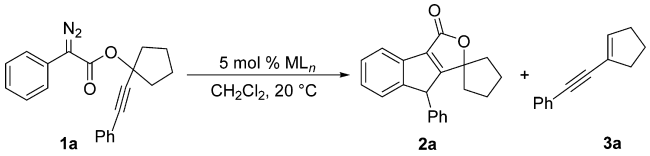
completed by electrophilic substitution into the aromatic ring of the original aryldiazoacetate;[7] (B) the π-bond acceptor catalyst activates the internal carbon−carbon triple bond of propargyl esters and undergoes 1,3-acyloxy migration to produce an allenic intermediate[13] that continues to a pyrazoline product via dipolar cycloaddition;[14] and (C) Lewis acid association at the ester carbonyl group activates the diazoacetate as a leaving group to promote nucleophilic substitution or elimination reactions of the propargyl group (Scheme 1).

RESULTS AND DISCUSSION

Assessments of reactions of transition metal catalysts with phenylpropargyl phenyldiazoacetate **1a** were performed using 1−5 mol % of catalyst. Reactions were followed to completion by TLC (thin-layer chromatography), and isolated product yields were determined by mass. With 1 mol % of $Rh_2(OAc)_4$ the indene-fused product **2a** from the domino transformation was formed in 76% isolated yield (Table 1, entry 1). The more Lewis acidic catalyst $Rh_2(TFA)_4$ gave an improved yield of **2a** without observable formation of the enyne elimination product **3a** (Table 1, entry 2). The commonly used palladium catalysts[15] produced **2a** as the dominant product, but the catalytic activity of these catalysts was much lower than that of $Rh_2(OAc)_4$, and enyne elimination to form **3a** was a competing process. With the silver(I) catalyst ($AgSbF_6$) the domino product **2a** was obtained in moderate yield together with elimination product **3a**. Three cationic gold(I) catalysts, Au(JohnPhos)(MeCN)SbF_6, Au(PPh_3)Cl/$AgSbF_6$, and $IPrAuBF_4$, previously reported as effective catalysts in reactions of donor/acceptor diazoacetates,[16] gave **1a** along with measurable amounts of **3a**. Platinum(II) catalysts gave the domino product **2a** in moderate yield, and the elimination product **3a** was a major byproduct. With Lewis acidic catalysts such as $Hg(OTf)_2$ and $HgCl_2$ that have been reported to form metal carbene intermediates,[17] elimination product **3a** was dominant, but the product of the apparent carbene cascade process was also observed. Although $Cu(OTf)_2$ gave both **2a** and **3a** in similar isolated yields, surprisingly, both Cu(MeCN)$_4BF_4$ and Cu(MeCN)$_4PF_6$ gave **2a** exclusively, and Cu(MeCN)$_4PF_6$ gave the highest yield of domino product **2a** among all the catalysts that were employed.

Since the use of Cu(MeCN)$_4PF_6$ exhibited high efficiency and excellent selectivity in the formation of **2a**, we examined this catalyst to assess its scope with propargyl aryldiazoacetates **1b**−**1l**, and these results are reported in Table 2. Reactions with **1b** and **1c** that have electron-donating substituents gave higher yields compared to that with **1a**; however, reactions with propargyl aryldiazoacetates whose aryl groups have electron-withdrawing groups also produced elimination product **3** in relative amounts proportional to the electron-withdrawing ability of the substituent. Propargyl substrates with 1,1-dimethyl

Table 1. Catalysts Screening for Reactions of Phenylpropargyl Phenyldiazoacetate 1a



entry[a]	catalyst	reaction time (h)	conversion of **1a** (%)[b]	yield of **2a** (%)[c]	yield of **3a** (%)[c]
1[d]	$Rh_2(OAc)_4$	6	>95	76	<5
2[d]	$Rh_2(TFA)_4$	3	>95	83	<5
3	$Pd(OAc)_2$	48	>95	71	10
4	$Pd(acac)_2$	48	>95	65	23
5	$Pd(cod)Cl_2$	48	>95	67	24
6	$Pd(dba)_2$	48	>95	69	20
7	$PdCl_2(PhCN)_2$	48	>95	76	11
8	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	48	>95	65	15
9	$AgSbF_6$	1	>95	65	30
10	Au(JohnPhos)(MeCN)SbF_6	10	>95	86	4
11	AuCl(PPh_3)/$AgSbF_6$	12	>95	83	8
12	$IPrAuBF_4$	10	>95	50	16
13[e]	$PtCl_2$	12	>95	60	35
14[e]	$[PtCl_2(C_2H_4)]_2$	12	>95	52	38
15	$Hg(OTf)_2$	48	>95	10	80
16	$HgCl_2$	48	>95	15	76
17	$Cu(OTf)_2$	6	>95	40	50
18	Cu(MeCN)$_4BF_4$	1	>95	92	<5
19	Cu(MeCN)$_4PF_6$	1	>95	94	<5

[a]Reactions were carried out at 20 °C on a 0.20 mmol scale: a solution of **1a** in 2.0 mL of CH_2Cl_2 was added dropwise to a solution of catalyst (5 mol %) in 2.0 mL of CH_2Cl_2 under a nitrogen atmosphere within 10 min, and the resulting reaction mixture was stirred for the stated reaction time. [b]The conversion of **1a** was determined by ^1H NMR spectroscopy using 2,4,6-trimethoxybenzaldehyde as an internal standard. [c]The yields of **2a** and **3a** were isolated yields after chromatography. [d]Catalyst loading was 1 mol %; TFA = trifluoroacetate, OTf = trifluoromethanesulfonate. [e]Reactions were carried out at 84 °C, and $ClCH_2CH_2Cl$ was used as the solvent.

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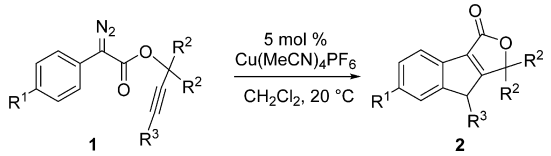
Table 2. Substrate Scope with the $Cu(MeCN)_4PF_6$ Catalyzed Domino Reaction of Propargyl Aryldiazoacetates



1 2

entry[a]	1 and 2	R^1	R^2	R^3	yield of 2 (%)[b]
1	**b**	OMe	$-(CH_2)_4-$	Ph	98
2	**c**	Me	$-(CH_2)_4-$	Ph	95
3	**d**	Br	$-(CH_2)_4-$	Ph	86 (6)[c]
4	**e**	Cl	$-(CH_2)_4-$	Ph	78 (12)[c]
5	**f**	NO_2	$-(CH_2)_4-$	Ph	15 (65)[c]
6	**g**	H	Me	Ph	90
7	**h**	H	$-(CH_2)_3-$	Ph	90
8	**i**	H	$-(CH_2)_5-$	Ph	80
9	**j**	H	$-(CH_2)_4-$	cyclopropyl	85
10	**k**	H	$-(CH_2)_4-$	$SiMe_3$	52[d]

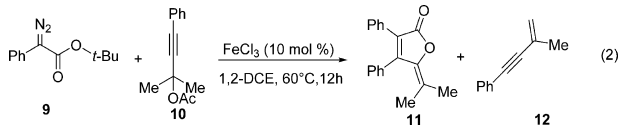
[a]Reactions were performed at 20 °C on a 0.20 mmol scale: a solution of **1** in 2.0 mL of CH_2Cl_2 was added dropwise to a 5 mol % solution of $Cu(MeCN)_4PF_6$ in 2.0 mL of CH_2Cl_2 under a nitrogen atmosphere within 10 min, and the resulting reaction mixture was stirred for another 1 h. [b]Isolated yield of domino product **2a**. [c]Isolated yield of elimination product **3a** in parentheses. [d]Product without the TMS group was obtained; reaction time was 3 h.

as well as carbocycles that included cyclohexyl and cyclobutyl **1g–i** underwent the domino process to form **2g–i** exclusively and in good yields. Substrate **1j**, which was derived from cyclopropylacetylene, produced **2j** in 85% yield under the same reaction conditions, but lower yields were obtained with the TMS analog after a reaction time of 3 h. Reactions of **1a** using chiral catalysts, including chiral dirhodium carboxylates such as $Rh_2(S\text{-PTTL})_4$,[18] $Rh_2(S\text{-NTTL})_4$, $Rh_2(S\text{-PTA})_4$, $Rh_2(S\text{-PTV})_4$, $Rh_2(S\text{-PTIL})_4$, $Rh_2(S\text{-DOSP})_4$, $Rh_2(4S\text{-MEPY})_4$, and $Cu(CH_3CN)_4PF_6$ with chiral BOX ligands,[19] gave only racemic **2a** and **3a**.

The mechanism of these domino reactions is consistent with previous reports for reactions catalyzed by rhodium acetate.[20] The copper(I) complex reacts with phenyldiazoacetate **1a** to produce metal carbene intermediate **4**, which undergoes a carbene/alkyne metathesis or cyclopropenation/spontaneous ring opening process to form the second cyclic vinyl carbene intermediate **5**,[21] followed by intramolecular electrophilic aromatic substitution to **6** then through **7** to indene product **2a** (Scheme 2).

Catalysis of some diazo compounds by iron[22] and zinc[23] complexes have been reported to occur through metal carbene intermediates, but the domino reaction that produces **2a** did not occur with representative zinc and iron compounds. Instead, the elimination product **3a** was dominant, and an unexpected product **8a** was also obtained (Table 3). Lewis acids such as $Sc(OTf)_3$, $In(OTf)_3$, and $Zn(OTf)_2$ failed to give furan-2-one **8a**, but $BF_3{\cdot}Et_2O$ formed **8a** in 20% yield at either 60 or 20 °C. However, the formation of elimination product **3a** was always dominant with these Lewis acids.

The plausible mechanism for the Lewis acid catalyzed rearrangement (Scheme 3) involves coordination of the Lewis acid with the carbonyl oxygen to release the propargyl cation whose allenyl cationic form combines with the Lewis acid bound diazoacetate. The resulting diazonium salt then undergoes intramolecular cyclization to form the furan-2-one product **8**. A control experiment was conducted using propargyl acetate **10** with *tert*-butyl phenyldiazoacetate (eq 2); the

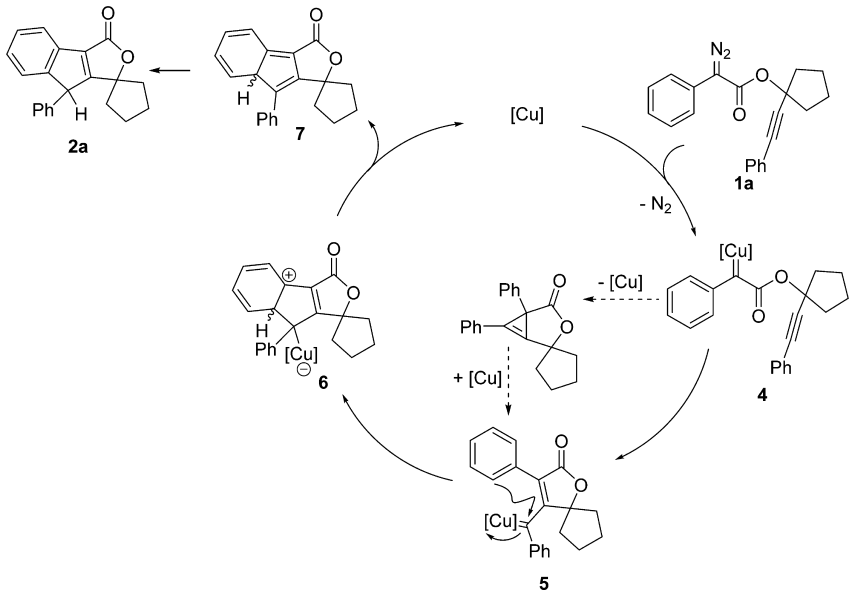


9 10 11 12

analogous rearrangement product **11** was obtained in 17% isolated yield together with the major elimination product **12** (70% yield) with catalysis by $FeCl_3$ at 60 °C, and the same outcome was obtained with $BF_3{\cdot}Et_2O$ at room temperature.[24]

The reactivity of diazo compounds toward gold catalysts is of increasing interest, but there are few indicators of their relative

Scheme 2. Postulated Copper-Catalyzed Reaction Pathway



2a 7 1a 6 4 5

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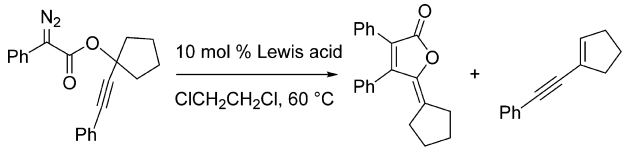
Table 3. Lewis Acid Catalyzed Reactions of Phenylpropargyl Phenyldiazoacetate 1a

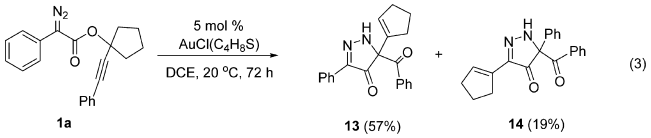


1a 8a 3a

entry[a]	Lewis acid	reaction time (h)	reaction temp (°C)	yield of **8a** (%)[b]	yield of **3a** (%)[b]
1	$FeCl_3$	12	60	21	75
2	$FeCl_3$	24	20	3	45
3	$FeCl_3$	6	80	15	75
4	$Zn(OTf)_2$	24	60	<1	80
5	$ZnBr_2$	24	60	4	90
6	$ZnBr_2$[c]	12	60	17	75
7	$Sc(OTf)_3$	10	60	<1	80
8	$In(OTf)_3$	10	60	<1	95
9	$BF_3{\cdot}Et_2O$	1	60	20	80
10	$BF_3{\cdot}Et_2O$	12	20	20	65

[a]Reactions were performed at 60 °C on a 0.20 mmol scale: a solution of **1a** in 2.0 mL of $ClCH_2CH_2Cl$ was added to a solution of of catalyst (10 mol %) in 2.0 mL of $ClCH_2CH_2Cl$ under a nitrogen atmosphere, and the resulting reaction mixture was stirred for the stated reaction time. The conversion of **1a**, determined by ^1H NMR spectroscopy using 2,4,6-trimethoxybenzaldehyde as an internal standard, was >95%. [b]Isolated yield. [c]1.0 equiv of $ZnBr_2$ was used.

preference in molecular systems that contain both diazo and alkyne functional groups.[25] During the screening of neutral gold(I) chloride complexes with propargyl phenyldiazoacetate **1a**, we found that the carbene/alkyne domino product **2** was not observed under catalysis by $AuCl(C_4H_8S)$ and neither was elimination product **3**; but, instead, isomeric 1*H*-pyrazoline **13** and its acyl transfer product **14** were obtained in good combined yields (eq 3).[14] The previously reported mechanism



1a 13 (57%) 14 (19%) (3)

involves formation of the allene intermediate, which undergoes a complex transformation not catalyzed by gold. In that subsequent transformation the terminal nitrogen of the diazo functional group adds at the central carbon of the allene to initiate a sequence of bond forming reactions resulting in the production of 1*H*-pyrazolines.[14]

CONCLUSION

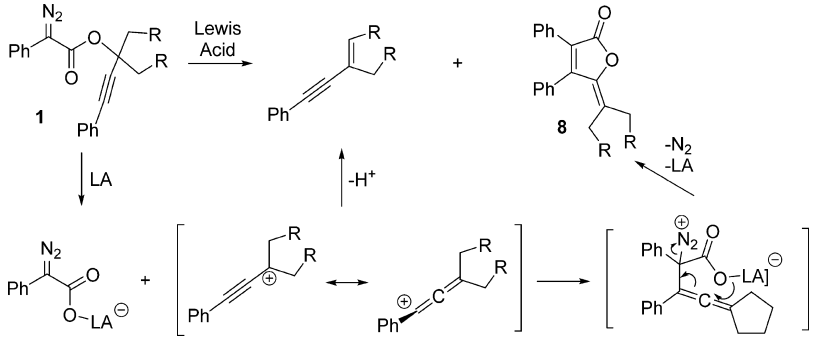
We have disclosed that propargyl aryldiazoesters are converted exclusively into three structurally different products as a function of catalysts. The domino reactions of propargyl aryldiazoacetates are highly suggestive of sequential metal carbene processes that in this study occur not only with transition metal catalysts that are well-known to form metal carbene intermediates from aryldiazoacetates[26] but also with mercury(II) catalysts that are less well-known to form metal carbene intermediates. Transition metal complexes that include rhodium(II), palladium(0 and II), silver(I), mercury(II), platinum(II), copper(I and II), and cationic gold(I) complexes are effective in the catalytic domino reactions of propargyl aryldiazoesters. $Cu(MeCN)_4PF_6$ has been demonstrated as a superior catalyst in the domino reaction for the formation of indene derivatives **2**. Because the same Lewis acid characteristics that are essential for transition metal electrophilic addition to the diazo carbon promote the propargyl cation dissociation and elimination to **3a** or recombination that forms furanone **8a**, results obtained from this study show the limitations of transition metal complex Lewis acidity for the generation of metal carbene intermediates. Lastly, neutral gold(I) catalysts exhibit a unique catalytic reactivity, selectively activating the carbon−carbon triple bond and retaining the diazo functional group in the final products.[14]

EXPERIMENTAL SECTION

General Information. Unless noted all reactions were carried out under an inert atmosphere of nitrogen in oven-dried glassware with magnetic stirring using freshly distilled solvents. All solvents were purified and dried using standard methods. Thin layer chromatography (TLC) plates were performed on precoated analytical silica gel 60 F_{254} plates. High resolution mass spectra (HRMS) were performed on a microTOF−ESI mass spectrometer using CsI as the standard. Accurate masses were reported for the molecular ion $[M + Cs]^+$, $[M + Na]^+$, or $[M + H]^+$. Melting points were determined on a device and were uncorrected. Flash chromatography was performed with silica gel. IR spectra were recorded using an FT-IR spectrometer. All NMR spectra were recorded on 500, 400, and 300 MHz (^1H NMR) and 75, 100, and 126 MHz (^{13}C NMR). Chemical shifts are reported in ppm with the solvent signals as reference (in $CDCl_3$ as solvent), and coupling constants (J) are given in hertz (Hz). The peak information is described as br = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = complex multiplet of magnetically nonequivalent protons.

Materials. $Rh_2(OAc)_4$, $Rh_2(TFA)_4$, $Pd(OAc)_2$, $Pd(acac)_2$, $Pd(cod)Cl_2$, $Pd(dba)_2$, $PdCl_2(PhCN)_2$, $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, $AgSbF_6$,

Scheme 3. Lewis Acid Catalyzed Elimination and Rearrangement



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Au(JohnPhos)(MeCN)SbF_6, AuCl(PPh_3), IPrAuBF_4, AuCl(C_4H_8S), $PtCl_2$, [$PtCl_2(C_2H_4)$]$_2$, Hg(OTf)$_2$, $HgCl_2$, Cu(MeCN)$_4$BF_4, Cu(OTf)$_2$, Cu(MeCN)$_4$PF_6, $FeCl_3$, Zn(OTf)$_2$, $ZnBr_2$, In(OTf)$_3$, Sc(OTf)$_3$, and BF_3·Et_2O were purchased from commercial suppliers and directly used without further purification. Rh$_2$(*S*-PTTL)$_4$, Rh$_2$(*S*-NTTL)$_4$, Rh$_2$(*S*-PTA)$_4$, Rh$_2$(*S*-PTV)$_4$, Rh$_2$(*S*-PTIL)$_4$, Rh$_2$(*S*-DOSP)$_4$, and Rh$_2$(4*S*-MEPY)$_4$ were prepared according to literature procedures.[18,19,27] Propargyl aryldiazoacetates,[12,25] *tert*-butyl phenyldiazoacetate,[28] and propargyl acetate[29] were prepared according to the literature procedures. Other chemicals were obtained from commercial sources and used without further purification.

General procedures for the preparation of propargyl diazoacetates **1** from corresponding alkynes, ketones, and arylacetic acids and characterization data of compounds **1a**–**i** have been reported previously.[12,25]

*1-(Cyclopropylethynyl)cyclopentyl 2-Diazo-2-phenylacetate (**1j**).* 0.69 g, 47% yield from the corresponding alkyne. Yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–7.45 (comp, 2H), 7.40–7.33 (comp, 2H), 7.20–7.13 (comp, 1H), 2.36–2.23 (comp, 2H), 2.18–2.05 (comp, 2H), 1.80–1.70 (comp, 4H), 1.32–1.22 (comp, 1H), 0.80–0.72 (comp, 2H), 0.69 (dt, J = 8.2, 4.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 128.8, 125.7, 125.6, 123.8, 88.9, 82.3, 77.4, 77.00, 76.6, 75.4, 40.8, 23.3, 8.4, −0.4. IR (neat) 2076, 1702, 1597, 1497, 1242, 1141 cm^{-1}. HRMS (ESI) m/z calcd for $C_{18}H_{18}N_2O_2Na$ [M + Na]$^+$ 317.1266; found 317.1274.

*1-((Trimethylsilyl)ethynyl)cyclopentyl 2-Diazo-2-phenylacetate (**1k**).* 0.98 g, 60% yield from the corresponding alkyne. Yellow solid, mp 131–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–7.47 (comp, 2H), 7.41–7.35 (comp, 2H), 7.22–7.14 (m, 1H), 2.36–2.27 (comp, 2H), 2.23–2.15 (comp, 2H), 1.82–1.70 (comp, 4H), 0.17 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 128.8, 125.7, 125.6, 123.9, 89.6, 81.9, 40.8, 23.4, −0.1. IR (neat) 2088, 1704, 1250, 1151, 903, 723 cm^{-1}. HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2SiO_2Na$ [M + Na]$^+$ 349.1348; found 349.1352.

Transition Metal-Catalyzed Domino Reactions of Phenylpropargyl Phenyldiazoacetate 1a at Room Temperature. *This procedure is suitable for the catalysts including Rh$_2$(OAc)$_4$, Rh$_2$(TFA)$_4$, Pd(OAc)$_2$, Pd(acac)$_2$, Pd(cod)Cl$_2$, Pd(dba)$_2$, PdCl$_2$(PhCN)$_2$, [Pd(η^3-C_3H_5)Cl]$_2$, AgSbF_6, Au(JohnPhos)(MeCN)SbF_6, IPrAuBF_4, AuCl(PPh$_3$)/AgSbF_6, Hg(OTf)$_2$, $HgCl_2$, Cu(MeCN)$_4$BF_4, Cu(OTf)$_2$, Cu(MeCN)$_4$PF_6.* To a flame-dried 10 mL Schlenk flask charged with a magnetic stirring bar, a transition metal catalyst (0.010 or 0.002 mmol) and 2.0 mL of DCM were added under a nitrogen atmosphere. 1-(Phenylethynyl)cyclopentyl 2-diazo-2-phenylacetate **1a** (0.20 mmol, 66.0 mg) dissolved in 2.0 mL of DCM was added into the flask via a syringe pump over 10 min under a flow of nitrogen. The resulting mixture was stirred at room temperature and monitored periodically by TLC. Upon consumption of **1a** (1–48 h), the reaction mixture was purified by column chromatography (100:1 to 10:1 gradient of hexanes/ethyl acetate as eluents) to afford pure 8′-phenylspiro[cyclopentane-1,1′-indeno[1,2-*c*]furan]-3′(8′*H*)-one (**2a**) and (cyclopent-1-en-1-ylethynyl)benzene (**3a**).[12] [Note: *the AuCl(PPh$_3$)/AgSbF_6 catalyst was prepared in situ from AuCl(PPh$_3$) and AgSbF_6 according to a previously reported procedure.*[30]]

Platinum(II)-Catalyzed Domino Reactions of Phenylpropargyl Phenyldiazoacetate 1a in Refluxing DCE. *This procedure is suitable for the catalysts including [PtCl$_2$(C$_2$H$_4$)]$_2$, PtCl$_2$.* To a flame-dried 10 mL Schlenk flask charged with a magnetic stirring bar, a platinum catalyst (0.010 mmol) and 2.0 mL of DCE were added under a nitrogen atmosphere. The solution was heated to reflux. 1-(Phenylethynyl)cyclopentyl 2-diazo-2-phenylacetate (**1a**) (0.20 mmol, 66.0 mg) dissolved in 2.0 mL of DCE was added into the flask was added in one portion into the solution under a flow of nitrogen. The resulting mixture was stirred under refluxing temperature and monitored periodically by TLC. Upon consumption of **1a** (1–48 h), the reaction mixture was purified by column chromatography (100:1 to 10:1 gradient of hexanes: ethyl acetate as eluents) to afford pure 8′-phenylspiro[cyclopentane-1,1′-indeno[1,2-*c*]furan]-3′(8′*H*)-one (**2a**) and (cyclopent-1-en-1-ylethynyl)benzene (**3a**).

General Procedure for Copper-Catalyzed Domino Cascade Reaction of Propargyl Aryldiazoacetates 1. To a flame-dried 10 mL Schlenk flask charged with a magnetic stirring bar, CuPF_6(MeCN)$_4$ (0.010 mmol) and 2.0 mL of DCM were added under a nitrogen atmosphere. Propargyl aryldiazoacetates **1** (0.20 mmol) dissolved in 2.0 mL of DCM were added into the flask via a syringe pump over 10 min under a flow of nitrogen. The resulting mixture was stirred for 1–3 h at room temperature (20 °C). The reaction mixture was purified by column chromatography (100:1 to 10:1 gradient of hexanes/ethyl acetate as eluents) to afford pure domino cascade reaction product **2** and **3**.

*5′-Methoxy-8′-phenylspiro(cyclopentane-1,1′-indeno[1,2-c]furan)-3′(8′H)-one (**2b**).* 65.1 mg, 98% yield. White solid, mp 152–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.3 Hz, 1H), 7.22–7.20 (comp, 3H), 6.98–6.96 (comp, 2H), 6.81–6.78 (m, 1H), 6.70–6.69 (m, 1H), 4.65 (s, 1H), 3.66 (s, 3H), 1.98–1.94 (comp, 2H), 1.88–1.86 (m, 1H), 1.78–1.74 (m, 1H), 1.71–1.66 (m, 1H),1.59–1.54 (m, 1H), 1.47–1.40 (m, 1H), 1.20–1.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 176.9, 166.5, 159.2, 153.9, 136.1, 135.6, 129.0, 128.1, 127.8, 127.0, 121.3, 112.6, 111.8, 95.4, 55.4, 52.4, 38.3, 36.7, 24.3. IR (neat) 1754, 1451, 1284, 1232, 706 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{20}O_3Na$ [M + Na]$^+$ 355.1305; found 355.1309.

*5′-Methyl-8′-phenylspiro[cyclopentane-1,1′-indeno[1,2-c]furan]-3′[8′H]-one (**2c**).* 60.0 mg, 95% yield. White solid, mp 98–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.4 Hz, 1H), 7.24–7.18 (comp, 3H), 7.09 (d, J = 8.4 Hz, 1H), 6.98–6.95 (comp, 3H), 4.66 (s, 1H), 2.24 (s, 3H), 1.99–1.96 (comp, 2H), 1.93–1.86 (m, 1H), 1.82–1.75 (m, 1H), 1.73–1.64 (m, 1H), 1.63–1.56 (m, 4H), 1.50–1.41 (m, 1H), 1.21–1.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 166.6, 152.3, 136.9, 136.2, 136.0, 131.5, 129.1, 128.4, 128.1, 127.8, 125.8, 120.5, 95.4, 52.3, 38.4, 36.7, 24.3, 21.5. IR (neat) 1753, 1449, 1232, 843 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{20}O_2Na$ [M + Na]$^+$ 339.1361; found 339.1371.

*5′-Bromo-8′-phenylspiro(cyclopentane-1,1′-indeno[1,2-c]furan)-3′[8′H]-one (**2d**).* 65.4 mg, 86% yield. White solid, mp 143–144 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.34–7.32 (m, 1H), 7.33–7.29 (comp, 3H), 7.08–6.99 (comp, 2H), 4.77 (s, 1H), 2.10–2.04 (comp, 2H), 2.01–1.93 (m, 1H), 1.90–1.83 (m, 1H), 1.79–1.73 (m, 1H), 1.70–1.65 (m, 1H), 1.55–1.51 (m, 1H), 1.29–1.22 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 165.9, 153.8, 135.4, 134.9, 133.2, 130.9, 129.3, 128.4, 128.2, 128.0, 122.0, 121.0, 95.4, 52.4, 38.4, 36.7, 24.4, 24.3. IR (neat) 1745, 1463, 1273, 880 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{17}O_2BrNa$ [M + Na]$^+$ 403.0310; found 403.0306.

*5′-Chloro-8′-phenylspiro[cyclopentane-1,1′-indeno[1,2-c]furan]-3′(8′H)-one (**2e**).* 52.4 mg, 78% yield. White solid, mp 101–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 1H), 7.29–7.24 (comp, 4H), 7.19–7.12 (m, 1H), 6.98–6.96 (comp, 2H), 4.70 (s, 1H), 2.02–1.97 (comp, 2H), 1.93–1.87 (m, 1H), 1.83–1.77 (m, 1H), 1.72–1.67 (m, 1H), 1.64–1.57 (m, 1H), 1.51–1.45 (m, 1H), 1.23–1.15 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 179.1, 166.0, 153.6, 135.5, 135.0, 133.0, 132.8, 129.3, 128.2, 128.1, 125.6, 121.7, 95.5, 52.5, 38.5, 36.8, 24.5, 24.4. IR (neat) 1755, 1449, 1428, 1066, 707, 673 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{17}O_2ClNa$ [M + Na]$^+$ 359.0815; found 359.0821.

*5′-Nitro-8′-phenylspiro[cyclopentane-1,1′-indeno[1,2-c]furan]-3′(8′H)-one (**2f**).* 10.4 mg, 15% yield. White solid, mp 162–163 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34–8.30 (m, 1H), 8.09–8.06 (m, 1H), 7.87–7.82 (m, 1H), 7.36–7.32 (m, 3H), 7.05 (s, 2H), 4.90 (s, 1H), 2.15–2.07 (m, 2H), 2.03–1.98 (m, 1H), 1.92–1.87 (m, 1H), 1.84–1.78 (m, 1H), 1.75–1.71 (m, 1H), 1.59–1.56 (m, 1H), 1.33–1.29 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.5, 165.3, 153.0, 147.0, 140.4, 135.2, 133.7, 129.6, 128.7, 128.0, 124.3, 121.1, 120.4, 95.8, 52.9, 38.6, 36.9, 24.5, 24.5. IR (neat) 1745, 1559, 1306, 1031, cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{17}NO_4Na$ [M + Na]$^+$ 370.1055; found 370.1047.

*2-Methyl-4-phenylbut-3-yn-2-yl 2-diazo-2-phenylacetate (**2g**).* 49.7 mg, 90% yield. White solid, mp 88–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 1H), 7.32–7.28 (m, 1H), 7.24–7.14 (comp, 5H), 6.98–6.96 (comp, 2H), 4.70 (s, 1H), 1.54 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 166.2, 151.6, 135.6, 135.1, 134.3, 129.1, 128.2, 127.9, 127.8, 127.0, 121.1, 85.4, 52.5, 26.4, 25.7. IR (neat) 1741, 1450, 1314, 944, 742, 706 cm^{-1}; HRMS

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(ESI) m/z calcd for $C_{19}H_{16}O_2Na$ $[M + Na]^+$ 299.1043; found 299.1050.

8′-Phenylspiro[cyclohexane-1,1′-indeno[1,2-c]furan]-3′(8′H)-one (2i). 50.1 mg, 80% yield. White solid, mp 175−176 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.4 Hz, 1H), 7.39−7.35 (m, 1H), 7.33−7.29 (comp, 3H), 7.24 (d, J = 7.4 Hz, 1H), 7.21 (d, J = 7.4 Hz, 1H), 7.07−7.03 (comp, 2H), 4.76 (s, 1H), 1.85−1.77 (comp, 3H), 1.75−1.46 (comp, 3H), 1.43−1.39 (comp, 2H), 1.19−1.08 (m, 1H), 1.06−0.97 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.0, 166.6, 151.8, 135.7, 135.2, 134.2, 129.0, 128.2, 127.8, 127.7, 126.9, 125.0, 121.0, 87.4, 52.7, 35.7, 34.7, 24.3, 22.1, 21.7. IR (neat) 1754, 1449, 1429, 1031, 991, 707 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{20}O_2Na$ $[M + Na]^+$ 339.1361; found 339.1364.

8′-Cyclopropylspiro[cyclopentane-1,1′-indeno[1,2-c]furan]-3′[8′H]-one (2j). 42.6 mg, 80% yield. White solid, mp 135−136 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 7.4 Hz, 1H), 7.63 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 2.89 (d, J = 9.6 Hz, 1H), 2.57−2.47 (m, 1H), 2.17−1.89 (comp, 7H), 0.93−0.83 (m, 1H), 0.81−0.69 (comp, 3H), 0.46 (td, J = 9.6, 5.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2, 150.7, 135.8, 134.1, 127.7, 126.5, 124.4, 120.8, 95.6, 51.8, 38.8, 36.8, 25.1, 24.9, 11.8, 4.8, 4.3. IR (neat) 1755, 1450, 994, 753 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{18}O_2Na$ $[M + Na]^+$ 289.1024; found 289.1026.

Lewis Acid Catalyzed Reactions of PhenylPropargyl Phenyldiazoester. *This procedure is suitable for the catalysts including $FeCl_3$, $Zn(OTf)_2$, $ZnBr_2$, $In(OTf)_3$, $Sc(OTf)_3$, $BF_3{\cdot}Et_2O$.* To a flame-dried 10 mL Schlenk flask charged with a magnetic stir bar. A Lewis acid (0.020 mmol) and 2.0 mL of DCE were added under a nitrogen atmosphere. 1-(Phenylethynyl)cyclopentyl 2-diazo-2-phenylacetate **1a** (0.20 mmol) dissolved in 2.0 mL of DCE was added in one portion into the solution under the flow of nitrogen. The resulting mixture was stirred for 12 h at 60 °C; the crude product was purified by column chromatography (100:1 to 10:1 gradient of hexanes/ethyl acetate as eluents) to afford pure **3a** in 70% yield as a colorless oil and **8a**[30] in 20% yield as a white solid. *5-Cyclopentylidene-3,4-diphenylfuran-2[5H]-one (8a)*: 12.1 mg, 20% yield. White solid, mp 93−94 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.42 (comp, 3H), 7.41−7.37 (comp, 2H), 7.29−7.25 (comp, 2H), 7.25−7.19 (comp, 3H), 2.77 (t, J = 6.9 Hz, 2H), 1.87 (t, J = 7.2 Hz, 2H), 1.71−1.63 (comp, 2H), 1.62−1.56 (comp, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 149.0, 141.5, 136.3, 132.8, 129.8, 129.0, 128.9, 128.4, 128.2, 128.1, 125.7, 32.5, 30.5, 27.3, 25.3. IR (neat) 1452, 1428, 1233, 1066, 706 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{18}O_2Na$ $[M + Na]^+$ 325.1199; found 325.1191.

Procedure for $FeCl_3$-Catalyzed Reaction of *tert*-Butyl 2-Diazo-2-phenylacetate and 2-Methyl-4-phenylbut-3-yn-2-yl Acetate. To a flame-dried 10 mL Schlenk flask charged with a magnetic stirring bar. $FeCl_3$ (0.020 mmol) and 2.0 mL of DCE were added under a a nitrogen atmosphere. *tert*-Butyl 2-diazo-2-phenylacetate (0.20 mmol) and 2-methyl-4-phenylbut-3-yn-2-yl acetate (0.20 mmol) dissolved in 2.0 mL of DCE were added in one portion into the solution under the flow of nitrogen. The resulting mixture was stirred for 12 h at 60 °C; the reaction mixture was purified by column chromatography (100:1 to 10:1 gradient of hexanes/ethyl acetate as eluents) to afford pure **12**[31] (70% yield) as a colorless oil and **11** (17% yield) as a white solid. *3,4-Diphenyl-5-(propan-2-ylidene)furan-2[5H]-one (11)*: 9.4 mg, 17% yield. White solid, mp 87−88 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45−7.40 (comp, 3H), 7.35−7.31 (comp, 2H), 7.29−7.26 (comp, 2H), 7.23−7.18 (comp, 3H), 2.10 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 148.8, 144.0, 133.3, 129.7, 129.0, 129.0, 128.9, 128.5, 128.2, 128.0, 127.2, 125.6, 21.2, 19.2. IR (neat) 1449, 1429, 1154, 1032, 943, 880, 772 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{16}O_2Na$ $[M + Na]^+$ 299.1043; found 299.1040.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02770.

^{1}H and ^{13}C NMR spectra of all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: michael.doyle@utsa.edu.

ORCID

Michael P. Doyle: 0000-0003-1386-3780

Notes

The authors declare no competing financial interest.

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