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Platinum-Catalyzed Tandem Cycloisomerization Reaction of Benzoendiynyl Esters: Regioselective Long-Range 1,5-Acyl Migration

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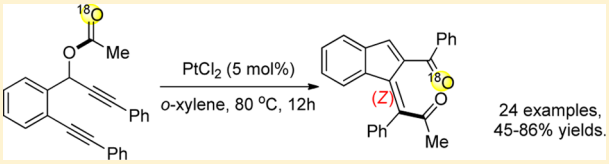
Supporting Information

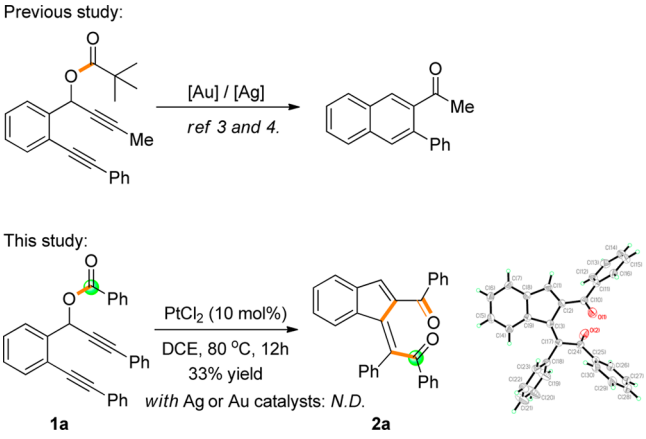
ABSTRACT: A Pt^{II}-catalyzed intramolecular chemo- and regioselective pentannulation/long-range 1,5-acyl migration reaction is described. This cascade cycloisomerization protocol produces a wide variety of benzofulvene diketones in good to excellent yields with exclusively the *Z* configuration of the exocyclic double bond of the final product. The ^{18}O isotope experiment together with ^{13}C NMR, HRMS, and HMBC analyses confirmed an interesting long-range acyl rearrangement process in this transformation.



During the past few decades, transition-metal-catalyzed electrophilic cycloisomerization reactions involving chain rearrangement of unsaturated π-conjugated propargylic esters have aroused considerable attention[1,2] because these types of rearrangements have proved to be highly efficient strategies for the cascade synthesis of complex aromatic molecules. For instances, in 2006, Toste[3] and Oh[4] reported the Au-catalyzed [3,3] sigmatropic rearrangement/6-*endo*-*dig* cyclization reaction of 1,6-diynyl esters to give naphthyl ketones. The key intermediate in the reaction was realized as a carboxyallene species that was formed through 3,3-acyloxy migration of the propargyl esters. Liu and co-workers established an elegant strategy for Au-catalyzed cyclizations of 1,6-diynyl carbonates leading to benzo[*b*]fluorenes by arylation of oxocarbenium ion intermediates and subsequent decarboxylative etherification.[5] Malacria and co-workers disclosed that the 5-*exo*-*dig* cyclization of the carboxyallene species is favored in the case of substrates bearing a monosubstituted terminal alkyne moiety, and the resulting acyl group in the oxonium ion can be electrophilically trapped by the remote C−Au bond to produce exclusive *E* stereochemistry of the double bond in the final products.[6]

Our group recently reported novel Ag-catalyzed electrophilic cyclization reactions of *N*-halosuccinimide (NXS) with 1,6-diynols or 1,3,5-triynols, which generated various aromatic scaffolds through halonium-mediated intramolecular 6-*endo*-*dig* cyclization and the subsequent rearrangement sequences.[7] The success of these transformations prompted us to envision that a strong electrophilic species such as acylium cation might also be workable in the metal-catalyzed tandem cycloisomerization reactions, which should open up interesting extensions for the rapid creation of cyclic aromatic compounds and the further related mechanistic studies. With these considerations in mind, we recently accidentally found that compound **2a** could be formed in 33% yield in the $PtCl_2$-catalyzed intramolecular cyclization reaction of acylated 1,6-diynol **1a** (Scheme 1). The structure of compound **2a** was identified unambiguously by X-ray diffraction analysis as a formal 1,5-acyl migration product

Scheme 1. Examination of Au/Ag- and Pt-Catalyzed Cycloisomerization Reactions of 1,6-Diynyl Esters



with a *Z*-configured 1-methylene-1-benzofulvene diketone core structural motif.[8] It is worth noting that no desired product **2a** but only Toste's 2-naphthyl ketone[3] was detected when various Ag or Au catalysts were applied instead of $PtCl_2$ in the reaction of **1a**. This unexpected result attracted our interest, since to the best of our knowledge no formal example of a Pt-catalyzed cycloisomerization/long-range acyl migration reaction has been reported.[9,10]

Fulvene derivatives rank among the most important classes of conjugated olefins in synthetic chemistry and materials science because of their versatility to be applied as anti-inflammatory agents[11] or as building blocks for the preparation of metallocene catalysts or fullerenes.[12] The traditional reliable method for the preparation of π-conjugated fulvenes is the condensation reaction of cyclopentadiene with carbonyl

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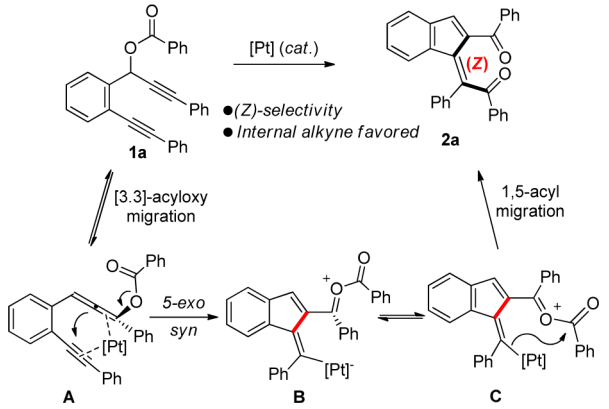
compounds.[13] Recent elegant examples using a 5-*exo*-*dig* radical cyclization strategy[14] or metal-mediated procedures[15] have been well-established. In 2012, the groups of Zhang and Hashmi independently reported gold-catalyzed benzofulvene formation reactions of enyne systems.[16] 1,6-Diynyl esters that undergo long-range 1,*n*-acyl migration reactions have also been proven to be powerful reagents for the synthesis of fulvene derivatives, as described by Malacria and co-workers.[6]

However, the divergent reactivities of platinum and gold catalysts have often been recognized by means of a sharp contrast in the carbon chain reorganization reactions of propargylic esters.[17,18] Therefore, unlike Malacria's work on the Au-catalyzed one-step preparation of *E*-configured fulvene *δ*-diketones from monosubstituted terminal diynes (hepta-1,6-diyn-3-yl esters),[6] we report herein a novel Pt-triggered pentannulation and cycloisomerization reaction of endiynyl esters containing internal alkynes to prepare exclusively *Z*-configured benzofulvene diketone derivatives (Scheme 2). The

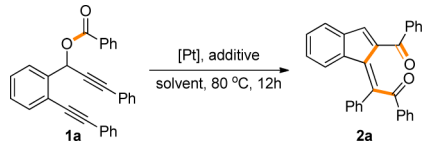
Scheme 2. Possible Mechanism for the Platinum-Catalyzed Pentannulation/Long-Range 1,5-Acyl Migration Reaction



results can be rationalized in terms of the known Pt-catalyzed [3,3] sigmatropic rearrangement of propargylic esters **1a** to give reactive carboxyallene species **A**.[17b,19] The platinum cation in **A** can coordinate to both the alkyne bond and the alkene bond to form a chelate complex,[20] and the subsequent 5-*exo*-*dig*-favored *syn* nucleophilic attack of the allenic moiety to the platinum-coordinated triple bond may afford pentannulated complex **B** along with its carbon−carbon *σ*-bond rotation isomer **C**. The resulting zwitterion intermediate **C** may undergo an intramolecular 1,5-acyl migration to give the final *Z*-configured product **2a**. To our knowledge, such a Pt-catalyzed long-range 1,5-migration mode is rare.[21]

We sought to explore the reaction conditions by using 1,6-diynol benzoate **1a** as a model substrate (Table 1).[22] We were pleased to find that with $PtCl_2$ as the catalyst, a preliminary screening of the solvent effect revealed that less polar solvents such as toluene and PhCl can efficiently promote the reaction, and further screening of the solvent proved *o*-xylene to be the optimal choice, as it delivered **2a** in 73% yield (entries 1−4). Fortunately, an improved yield of 79% was observed when 5 mol % $PtCl_2$ was used as the catalyst (entries 5−7). Other platinum salts, such as $Pt(acac)_2$, $Pt(COD)Br_2$, $PtCl_4$, and $PtPh_4$ were also examined in the reaction (entries 8−11). The blank experiment clearly demonstrated the necessity of the platinum catalyst (entry 12). Different types of additives were evaluated. No improvement in the yield of compound **2a** was

Table 1. Optimization of the Reaction Conditions[a]



entry	[Pt] (mol %)	additive	solvent	yield (%)
1	$PtCl_2$ (10)	–	DCE	33
2	$PtCl_2$ (10)	–	toluene	58
3	$PtCl_2$ (10)	–	PhCl	59
4	$PtCl_2$ (10)	–	*o*-xylene	73
5	$PtCl_2$ (5)	–	*o*-xylene	79
6	$PtCl_2$ (2.5)	–	*o*-xylene	65
7	$PtCl_2$ (1.0)	–	*o*-xylene	58[b]
8	$Pt(acac)_2$ (5)	–	*o*-xylene	49
9	$Pt(COD)Br_2$ (5)	–	*o*-xylene	43
10	$PtCl_4$ (5)	–	*o*-xylene	27
11	$PtPh_4$ (5)	–	*o*-xylene	trace
12	–	–	*o*-xylene	0
13	$PtCl_2$ (5)	dppp (10 mol %)	*o*-xylene	53
14	$PtCl_2$ (5)	CO (1 atm)	*o*-xylene	74
15	$PtCl_2$ (5)	O_2 (1 atm)	*o*-xylene	64
16	$PtCl_2$ (5)	H_2O (1.0 equiv)	*o*-xylene	37
17	$PtCl_2$ (5)	4 Å MS	*o*-xylene	71

[a]Reactions were carried out with **1a** (0.3 mmol) in the presence of a catalyst in 3.0 mL of solvent at 80 °C for 12 h. [b]The reaction time was 24 h.

observed when various phosphine ligands were employed (entry 13). Meanwhile, carbon monoxide, which is known to be involved in the catalyst-activation process in many documented platinum-catalyzed cyclization reactions,[17b,19,23] did not show any obvious positive effect (entry 14). On the other hand, a decreased yield was obtained when the reaction was carried out under aerobic conditions (entry 15).[24] While the reaction was retarded when 1.0 equiv of water was present,[20a,25] no promotion was observed when activated 4 Å MS was employed in the reaction (entries 16 and 17). Impressively, this reaction seemed to be sensitive to moisture but not very sensitive to aerobic conditions. More importantly, the reaction is easily handled and requires only the catalyst and solvent to facilitate the expected transformation.

Having defined the optimal reaction conditions, we investigated the scope of the transformation (Scheme 3). The reactivity of substrates **1** with various R^1 in the migratory acyl group were first examined. When R_1 was a substituted phenyl group, common phenyl substituents, including methyl (**2b**, **2c**), methoxy (**2d**), chloride (**2e**, **2f**), and nitro (**2g**), were compatible in the present catalytic reaction, implying that the obtained products **2** are suitable for further incorporation into larger systems. When R^1 in the migratory acyl group was an aromatic *β*-naphthyl group, the desired benzofulvene **2h** was obtained in 50% yield. The presence of a *π*-conjugated vinyl moiety at the R^1 position in compounds **1** was found to have less influence on the course of the acyl migration, affording the expected products **2i** and **2j** in moderate yields. With regard to migratory groups with a saturated alkyl group in the R^1 position, we were pleased to find that the methyl (**2k**), ethyl (**2l**), benzyl (**2m**), and cyclohexyl (**2n**) groups were all tolerated in the cascade reaction, affording the corresponding products in good yields. A scaled-up reaction of substrate **1k** (2.5 mmol scale) was conducted without difficulty to produce

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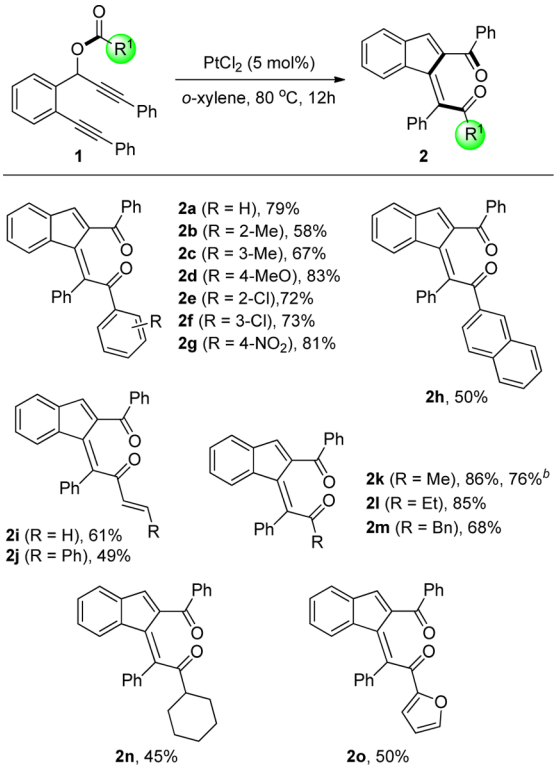
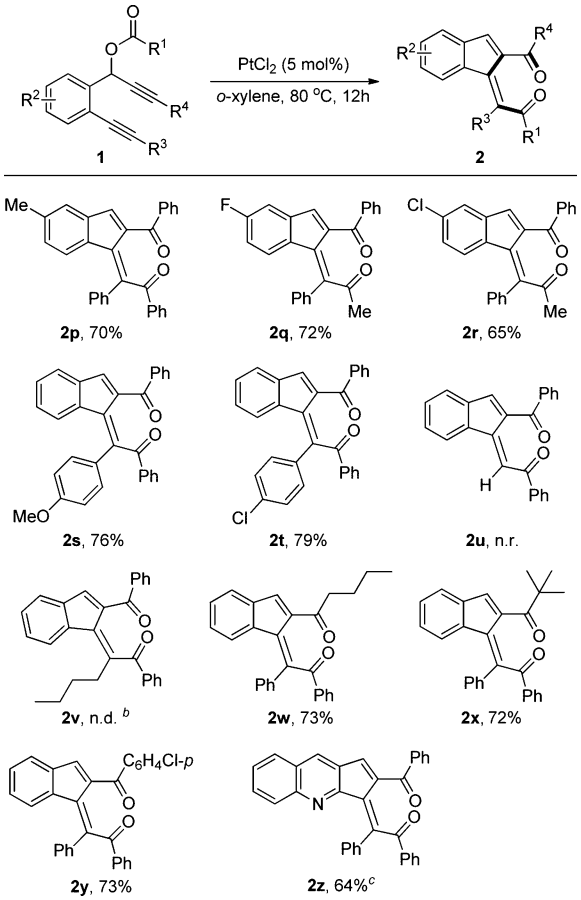
Scheme 3. Scope of the Acyl Group in the $PtCl_2$-Catalyzed Long-Range Acyl Migration Reaction[a]



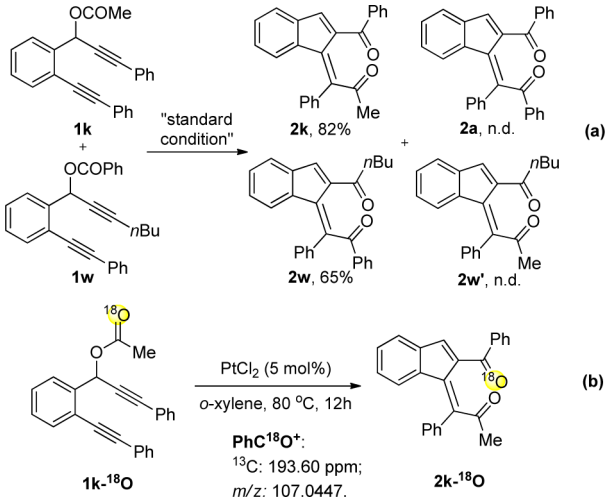
[a]Reactions were carried out with **1** (0.3 mmol) in the presence of $PtCl_2$ catalyst (5 mol %) in 3.0 mL of *o*-xylene as the solvent at 80 °C for 12 h. [b]2.5 mmol scale.

Scheme 4. Scope of the Substituents in Substrates 1[a]



[a]Reaction conditions: compound **1** (0.3 mmol), $PtCl_2$ (0.015 mmol), *o*-xylene (3.0 mL), N_2, 80 °C, 10–12 h. [b]The starting material **1v** was consumed, but no desired product was found. [c]With $PtCl_2$ (10 mol %), CO atmosphere (1 atm), 100 °C, 24 h.

Scheme 5. Crossover and ^{18}O Isotope Experiments



the desired product **2k** in 76% yield. A heterocycle such as furan also noticeably migrated in the reaction, as it worked pleasingly to afford the desired product **2o** in serviceable yield.

The effects of the substituents at the R^2, R^3, and R^4 positions in substrate **1** were examined as well (Scheme 4). The results showed that substrates **1** bearing electron-donating or electron-withdrawing groups have less influence on the reaction outcome. For example, the electron-donating methyl substituent and the electron-deficient 5-fluoro and 5-chloro substituents at the R^2 position were tolerated in the Pt-catalyzed pentannulation/1,5-acyl migration reaction, which proceeded smoothly to give the expected compounds **2p**–**r** in acceptable yields. In the case of substituents attached to a triple bond (R^3 or R^4), good yields were observed for aromatic moieties substituted with a methoxy (**2s**) or chloride (**2t**, **2y**) group. However, poor reactions were observed when terminal hydrogen (**2u**) or an aliphatic group (**2v**) was attached at the R^3 position. In a sharp contrast, aliphatic groups at the R^4 position were nicely tolerated, providing the alkylated products **2w** and **2x** in good yields. For the quinoline-based diynol benzoate **1z**, the expected product **2z** was successfully isolated in 26% yield under the standard conditions. Interestingly, when a carbon monoxide balloon was used instead of an inert atmosphere[23] and the catalyst loading was increased to 10 mol % and the temperature to 100 °C, the reaction proceeded smoothly to give a 64% yield of compound **2z**.

To gain further insights into the reaction mechanism, a crossover experiment using a 1:1 mixture of **1k** and **1w** was performed under the standard conditions (Scheme 5a). The products **2k** and **2w** were isolated from the reaction in 82% and 65% yield, respectively, while no crossover products **2a** and **2w′** could be detected. This result indicated that the $PtCl_2$-catalyzed pentanuulation/formal 1,5-acyl migration reaction is an intramolecular pathway and that no elimination of the acyloxy group occurs during the migration process. In addition, to understand the origins of the two carbonyl oxygen atoms, we synthesized

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the ^{18}O-labeled acetate **1k-^{18}O** according to the literature method[26] and subjected it to the optimized reaction conditions (Scheme 5b). The ^{18}O atom existed in the product **2k-^{18}O** as detected by ^{13}C NMR, HMBC, and HRMS, and the fragmentation peak clearly demonstrated it to be located in the phenyl carbonyl moiety (^{13}C NMR: 193.64 and 193.60 ppm; PhC^{18}O$^+$: *m*/*z* 107.0447).[22] These results support our hypothesis of the reaction mechanism outlined in Scheme 2.

In conclusion, we have developed a novel $PtCl_2$-catalyzed sequential pentannulation/long-range 1,5-acyl migration reaction of propargylic diynyl esters that affords a wide variety of benzofulvene diketones in good to high yields along with excellent functional group tolerance. In contrast to the previous gold-catalyzed [1,5] sigmatropic acyl migration reaction using terminal alkynes as the active substrates, we discovered herein that internal alkynes can be used for the platinum-catalyzed long-range 1,5-acyl migration process, thus affording exclusively *Z*-configured benzofulvene derivatives in a chemo- and regiocontrolled manner. The reactivity mode and mechanistic aspects of the current reaction represent a considerable extension of the metal-catalyzed long-range acyl migration transformation, and the reaction offers a potentially useful addition to the synthetic applications of complex benzofulvene ring systems.

EXPERIMENTAL SECTION

General Information for the Reagents. Unless otherwise noted, reagents were purchased from commercial suppliers and were used as received. All solvents were dried and distilled according to standard procedures before use. Reactions were conducted using standard Schlenk techniques on a vacuum line. Analytical thin-layer chromatography (TLC) was performed using glass plates precoated with a 0.25 mm layer of 230−400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Flash column chromatography was performed using silica gel (60 Å pore size, 32−63 μm, standard grade). Organic solutions were concentrated on rotary evaporators at ∼20 Torr (house vacuum) at 25−35 °C. NMR spectra were recorded in parts per million from internal standard tetramethylsilane (TMS) on the δ scale. High-resolution mass spectrometry (HRMS) analysis was performed by electrospray ionization (ESI-micrOTOF).

General Procedure for the Preparation of Substrates 1. All of the substrates **1** were prepared using a procedure similar to that for compound **1a**.

*a. Synthesis of 2-(Phenylethynyl)benzaldehyde (**1a_1**).* To a solution of 2-bromobenzaldehyde (1.86 g, 10.0 mmol) and phenylacetylene (1.22 g, 12.0 mmol) in Et_3N (40 mL) were added $PdCl_2(PPh_3)_2$ (140 mg, 2 mol %) and CuI (20 mg, 1 mol %). The resulting mixture was heated to 50 °C under an atmosphere of N_2. The reaction was monitored by TLC to establish completion. When the 2-bromobenzaldehyde starting material was consumed, the mixture was allowed to cool to room temperature, and the solvent was removed on a rotary evaporator under reduced pressure. The residue was diluted with 40 mL of petroleum ether, and the resulting mixture was concentrated again to remove the polar solvent. The resulting residue was purified by silica gel column chromatography using petroleum ether/EtOAc (20:1 v/v) to afford 1.94 g (94% yield) of 2-(2-phenylethynyl)benzaldehyde (**1a_1**) as a yellow oil with spectral properties identical to those previously reported.[27]

*b. Synthesis of 1,6-Diynol **1a_2**.*[28] Phenylacetylene (0.67 mL, 6 mmol) was weighed and dissolved in anhydrous THF (30 mL) in an oven-dried flask under a nitrogen atmosphere, and the solution was cooled to −78 °C. Then *n*BuLi (1.0 M in hexane, 7 mmol) was slowly added, and the mixture was stirred for further 30 min. Next, **1a_1** (1.03 g, 5 mmol) was added, and the reaction mixture was stirred for 30 min at −78 °C under N_2 and then allowed to warm to room temperature overnight. The reaction mixture was quenched with saturated aqueous ammonium chloride (10 mL) and extracted with CH_2Cl_2 (15 mL × 3). The organic layers were combined, dried over sodium sulfate, and concentrated on a rotary evaporator. The resultant oil was purified by flash column chromatography on silica gel to afford the desired product **1a_2** in 76% yield.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol (**1a_2**).*[7a] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.57−7.54 (m, 3H), 7.45−7.42 (m, 2H), 7.39 (m, 1H), 7.35−7.32 (m, 4H), 7.29−7.23 (m, 3H), 6.16 (d, *J* = 5.6 Hz, 1H), 2.92 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.3, 132.5, 131.7, 131.4, 128.9, 128.7, 128.5, 128.3, 128.2, 126.7, 122.9, 122.5, 121.4, 95.0, 88.3, 86.6, 86.4, 63.6.

*c. Synthesis of 1,6-Diynol Benzoate **1a**.*[29] To an ice-cold stirred solution of 1,6-diynol **1a_2** (1.54 g, 5 mmol), *N*,*N*-dimethylpyridin-4-amine (DMAP) (31 mg, 0.25 mmol), and TEA (2.1 mL, 15 mmol) in DCM (20 mL) was added benzoyl chloride (840 mg, 6 mmol) dropwise slowly over a period of 15 min. Then the ice-cold bath was removed, and the resulting suspension was stirred at room temperature for 2−4 h. The reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with CH_2Cl_2 (15 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated. The resultant residue was purified via silica gel column chromatography to afford the desired product **1a** in 90% yield.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl Benzoate (**1a**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.00 Hz, 2H), 7.96 (d, *J* = 8.00 Hz, 1H), 7.59 (d, *J* = 8.00 Hz, 1H), 7.50−7.46 (m, 5H), 7.41−7.37 (m, 5H), 7.27 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 138.4, 133.1, 132.5, 132.0, 131.7, 129.9, 129.9, 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 128.3, 128.2, 123.0, 122.9, 122.2, 95.3, 87.5, 86.4, 85.4, 65.2.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl 4-Methoxybenzoate (**1d**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.00 Hz, 2H), 7.94 (d, *J* = 8.00 Hz, 1H), 7.59 (d, *J* = 8.00 Hz, 1H), 7.53−7.46 (m, 4H), 7.42−7.37 (m, 3H), 7.29−7.26 (m, 6H), 6.86−6.83 (m, 2H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 163.5, 132.5, 132.0, 132.0, 131.8, 131.7, 128.8, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 122.9, 113.6, 95.2, 87.2, 86.4, 85.5, 64.9, 55.4.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl 2-Chlorobenzoate (**1e**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.00 Hz, 1H), 7.84 (d, *J* = 8.00 Hz, 1H), 7.61−7.57 (m, 3H), 7.50−7.48 (m, 2H), 7.42−7.37 (m, 4H), 7.32−7.28 (m, 7H), 7.21−7.17 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 137.9, 134.1, 132.7, 132.5, 132.0, 131.8, 131.6, 131.0, 129.1, 128.8, 128.7, 128.6, 128.3, 128.3, 126.5, 123.0, 122.8, 122.2, 95.4, 87.8, 86.3, 85.0, 65.7.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl 3-Chlorobenzoate (**1f**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.97 (d, *J* = 8.00 Hz, 1H), 7.91 (d, *J* = 8.00 Hz, 1H), 7.59 (d, *J* = 8.00 Hz, 1H), 7.52−7.45 (m, 5H), 7.41−7.35 (m, 3H), 7.27−7.22 (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 134.6, 133.2, 132.7, 132.6, 132.0, 131.8, 131.6, 129.9, 129.8, 129.2, 129.0, 128.8, 128.7, 128.7, 128.4, 128.4, 128.1, 123.1, 122.8, 122.1, 95.6, 88.0, 86.4, 85.1, 65.8.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl 2-Naphthoate (**1h**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.08 (d, *J* = 8.00 Hz, 1H), 8.00 (d, *J* = 8.00 Hz, 1H), 7.84−7.79 (m, 3H), 7.62−7.61 (m, 1H), 7.54−7.46 (m, 8H), 7.36 (d, *J* = 8.00 Hz, 1H), 7.28−7.27 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 138.5, 135.6, 132.6, 132.4, 132.0, 131.7, 131.5, 129.4, 129.0, 128.8, 128.6, 128.5, 128.3, 128.3, 128.1, 127.7, 127.1, 126.6, 125.4, 123.0, 122.9, 122.3, 95.4, 87.5, 86.4, 85.4, 65.4.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl Acetate (**1k**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.00 Hz, 1H), 7.58−7.57 (m, 3H), 7.49−7.47 (m, 2H), 7.39−7.27 (m, 8H), 7.20 (s, 1H), 2.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7, 138.2, 132.4, 132.0, 131.7, 129.0, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 122.9, 122.9, 122.2, 95.2, 87.3, 86.3, 85.3, 64.5, 21.0.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl Propionate (**1l**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.00 Hz, 1H), 7.60−7.55 (m, 3H), 7.48−7.45 (m, 2H), 7.38−7.35 (m, 1H), 7.32−7.23 (m, 8H), 2.34 (q, ^1J = 8.0 Hz, ^2J = 12 Hz, 2H), 1.10−1.06 (t, *J* = 8.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1, 138.4, 132.5, 132.0, 131.8, 129.0, 128.9, 128.7, 128.5, 128.4, 128.1, 123.0, 122.9, 122.3, 95.3, 87.4, 86.5, 85.5, 64.5, 27.6, 9.1.

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*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl Cyclohexanecarboxylate (**1n**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.00 Hz, 1H), 7.47−7.43 (m, 3H), 7.34−7.32 (m, 2H), 7.25−7.18 (m, 8H), 7.08 (m, 1H), 2.20−2.15 (m, 1H), 1.61−1.44 (m, 4H), 1.36−1.27 (m, 4H), 1.15−1.04 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 138.5, 132.4, 131.9, 131.8, 128.8, 128.7, 128.6, 128.5, 128.3, 128.3, 128.0, 122.9, 122.3, 95.2, 87.1, 86.4, 85.5, 64.2, 42.9, 28.8, 25.7, 25.3.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl Furan-2-carboxylate (**1o**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.00 Hz, 1H), 7.57−7.53 (m, 3H), 7.45−7.32 (m, 6H), 7.27−7.23 (m, 5H), 7.15 (s, 1H), 6.39−6.33 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 146.8, 144.2, 132.5, 132.0, 131.8, 129.2, 129.0, 128.8, 128.8, 128.7, 128.4, 128.4, 123.0, 122.8, 122.1, 118.9, 112.0, 95.6, 87.9, 86.3, 85.1, 65.1.

*1-(5-Fluoro-2-(phenylethynyl)phenyl)-3-phenylprop-2-yn-1-yl Acetate (**1q**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51−7.43 (m, 3H), 7.38 (d, J = 8.00 Hz, 2H), 7.25−7.16 (m, 6H), 7.04 (s, 1H), 6.69−6.94 (m, 2H), 2.02 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 162.4 (^1J = 249 Hz), 140.8, 134.2 (^3J = 8.0 Hz), 132.0, 131.6, 129.0, 128.6, 128.4, 122.7, 121.9, 118.8, 118.8, 116.2 (^2J = 22 Hz), 115.4 (^2J = 24 Hz), 94.8, 87.6, 85.2, 84.6, 64.0, 20.8.

*1-(2-(Phenylethynyl)phenyl)hept-2-yn-1-yl Benzoate (**1w**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.00 Hz, 2H), 7.92 (d, J = 8.00 Hz, 1H), 7.55 (d, J = 8.00 Hz, 1H), 7.51−7.49 (m, 2H), 7.40−7.35 (m, 2H), 7.30−7.22 (m, 7H), 2.26−2.23 (t, J = 8.00 Hz, 2H), 1.49−1.46 (m, 2H), 1.37−1.35 (m, 2H), 0.85−0.81 (t, J = 8.00 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 139.0, 133.1, 132.5, 131.8, 131.7, 130.1, 129.9, 128.9, 128.6, 128.5, 128.4, 128.1, 123.0, 95.3, 88.9, 86.6, 76.6, 65.2, 30.6, 22.0, 18.7, 13.6.

*3-Phenyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl 4-Chlorobenzoate (**1y**).* **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.00 Hz, 2H), 7.52−7.47 (m, 6H), 7.39−7.33 (m, 4H), 7.29−7.27 (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2, 140.2, 134.6, 133.6, 133.3, 132.0, 131.7, 130.0, 129.6, 129.2, 129.0, 128.7, 128.4, 128.4, 128.3, 122.5, 121.9, 121.4, 96.3, 87.9, 85.4, 84.6, 64.6.

General Procedure for the Platinum-Catalyzed Intramolecular Pentannulation and 1,5-Acyl Migration Reaction of Diynol Benzoates 1. An oven-dried 10 mL Schlenk tube was charged with diynol benzoate **1** (0.3 mmol, 1.0 equiv) and $PtCl_2$ (4.0 mg, 0.015 mmol) in anhydrous *o*-xylene (3.0 mL) under an atmosphere of N_2. The mixture was sealed with a screw cap and stirred at 80 °C for about 10 h until the starting material **1** was consumed, as monitored by TLC. The reaction mixture was quenched with saturated NaCl solution (3.0 mL), stirred for an additional 10 min, and then extracted with CH_2Cl_2 (3.0 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude residue was purified by flash column chromatography (EtOAc/petroleum ether 1:10) to give the desired product **2**.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-1,2-diphenylethanone (**2a**).* Yield 98 mg, 79%; light-yellow solid; mp 101−102 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.00 Hz, 2H), 7.74 (d, J = 8.00 Hz, 2H), 7.51−7.49 (m, 3H), 7.42−7.33 (m, 7H), 7.30−7.21 (m, 3H), 7.19 (s, 1H), 7.01−6.97 (m, 1H), 6.67 (d, J = 8.00 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.5, 193.0, 146.7, 142.3, 140.9, 139.5, 138.9, 138.1, 137.3, 137.1, 136.9, 132.6, 132.2, 130.0, 129.6, 129.5, 129.3, 129.1, 128.9, 128.1, 128.0, 124.8, 123.4; **HRMS** (ESI) calcd for $C_{30}H_{20}O_2$ $[M + Na]^+$ 435.1361, found 435.1383.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-2-phenyl-1-(o-tolyl)-ethanone (**2b**).* Yield 75 mg, 58%; light-yellow solid; mp 180−181 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86−7.84 (m, 1H), 7.74 (d, J = 8.00 Hz, 2H), 7.52−7.46 (m, 3H), 7.41−7.30 (m, 6H), 7.24−7.20 (m, 1H), 7.14−7.11 (m, 3H), 6.99−6.95 (m, 1H), 6.91−6.89 (m, 1H), 6.57 (d, J = 8.00 Hz, 1H), 2.41 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 192.7, 147.2, 141.4, 141.4, 141.0, 140.1, 139.8, 139.6, 137.6, 137.3, 137.2, 136.8, 132.6, 132.4, 131.5, 131.4, 129.5, 129.4, 128.9, 128.0, 127.8, 124.9, 124.8, 123.2, 20.9; **HRMS** (ESI) calcd for $C_{31}H_{22}O_2$ $[M + Na]^+$ 449.1512, found 449.1524.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-2-phenyl-1-(m-tolyl)-ethanone (**2c**).* Yield 86 mg, 67%; light-yellow solid; mp 150−151 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.00 Hz, 2H), 7.65 (d, J = 8.00 Hz, 2H), 7.53−7.49 (m, 3H), 7.44−7.32 (m, 6H), 7.25−7.21 (m, 1H), 7.17−7.12 (m, 3H), 7.01−6.98 (m, 1H), 6.66 (d, J = 8.00 Hz, 1H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 193.0, 146.7, 141.9, 140.9, 139.5, 138.8, 138.0, 137.8, 137.3, 137.1, 137.0, 133.4, 132.5, 130.4, 129.6, 129.4, 129.0, 128.8, 128.0, 127.9, 127.9, 127.8, 124.8, 123.3, 21.2; **HRMS** (ESI) calcd for $C_{31}H_{22}O_2$ $[M + Na]^+$ 449.1512, found 449.1489.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-1-(4-methoxyphenyl)-2-phenylethanone (**2d**).* Yield 110 mg, 83%; light-yellow solid; mp 180−181 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.00 Hz, 2H), 7.77 (d, J = 8.00 Hz, 2H), 7.53−7.49 (m, 2H), 7.43−7.36 (m, 5H), 7.32 (d, J = 8.00 Hz, 1H), 7.25−7.20 (m, 2H), 7.15 (s, 1H), 7.00−6.96 (m, 1H), 7.74 (d, J = 8.00 Hz, 2H), 6.69 (d, J = 8.00 Hz, 1H), 3.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.3, 192.9, 163.0, 147.0, 141.5, 140.9, 139.7, 138.7, 138.0, 139.7, 137.2, 137.0, 132.5, 130.5, 129.7, 129.4, 129.0, 128.8, 128.0, 127.8, 124.7, 123.2, 113.5, 55.3; **HRMS** (ESI) calcd for $C_{31}H_{22}O_3$ $[M + Na]^+$ 465.1461, found 465.1445.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-1-(2-chlorophenyl)-2-phenylethanone (**2e**).* Yield 96 mg, 72%; light-yellow solid; mp 201−202 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92−7.88 (m, 3H), 7.57−7.54 (m, 1H), 7.46−7.42 (m, 4H), 7.37−7.35 (m, 3H), 7.32 (d, J = 8.00 Hz, 1H), 7.26−7.19 (m, 5H), 6.98−6.94 (m, 1H), 6.59 (d, J = 8.00 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.6, 193.4, 146.3, 142.9, 141.2, 140.8, 139.8, 138.3, 137.2, 136.9, 136.0, 133.0, 132.7, 132.0, 131.9, 130.5, 129.8, 129.7, 129.3, 129.2, 128.9, 128.2, 128.0, 126.0, 124.9, 123.4; **HRMS** (ESI) calcd for $C_{30}H_{19}ClO_2$ $[M + Na]^+$ 469.0966, found 469.0974.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-1-(3-chlorophenyl)-2-phenylethanone (**2f**).* Yield 97 mg, 73%; light-yellow solid; mp 192−193 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81−7.74 (m, 4H), 7.53−7.49 (m, 3H), 7.44−7.39 (m, 5H), 7.34 (d, J = 8.00 Hz, 1H), 7.30 (d, J = 8.00 Hz, 1H), 7.26−7.21 (m, 3H), 7.02−6.98 (m, 1H), 6.66 (d, J = 8.00 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1, 193.1, 145.8, 143.0, 141.0, 139.3, 139.1, 138.8, 138.0, 137.0, 136.4, 134.3, 132.7, 132.4, 130.0, 129.9, 129.7, 129.6, 129.5, 129.3, 129.2, 129.1, 128.4, 128.2, 124.8, 123.5; **HRMS** (ESI) calcd for $C_{30}H_{19}ClO_2$ $[M + Na]^+$ 469.0966, found 469.0952.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-1-(4-nitrophenyl)-2-phenylethanone (**2g**).* Yield 111 mg, 81%; yellow solid; mp 199−200 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.00 Hz, 2H), 8.01 (d, J = 8.00 Hz, 2H), 7.78 (d, J = 8.00 Hz, 2H), 7.53−7.48 (m, 3H), 7.43−7.39 (m, 5H), 7.34 (d, J = 8.00 Hz, 1H), 7.28 (s, 1H), 7.23 (d, J = 8.00 Hz, 1H), 7.03−6.99 (m, 1H), 6.72 (d, J = 8.00 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.7, 193.3, 149.5, 145.5, 144.1, 142.0, 141.0, 139.7, 138.7, 138.1, 136.9, 135.7, 132.9, 131.0, 129.7, 129.6, 129.5, 129.4, 128.5, 128.3, 124.8, 123.8, 123.4; **HRMS** (ESI) calcd for $C_{30}H_{19}NO_4$ $[M + Na]^+$ 480.1206, found 480.1203.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-1-(naphthalen-2-yl)-2-phenylethanone (**2h**).* Yield 69 mg, 50%; yellow solid; mp 100−101 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.94−7.91 (m, 1H), 7.82 (d, J = 8.00 Hz, 1H), 7.70−7.66 (m, 3H), 7.59 (d, J = 8.00 Hz, 2H), 7.48−7.33 (m, 8H), 7.26−7.21 (m, 3H), 7.17 (s, 1H), 7.03−6.99 (m, 1H), 6.72 (d, J = 8.00 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.5, 193.0, 146.6, 142.0, 141.9, 141.0, 139.5, 139.2, 137.7, 137.1, 137.0, 135.0, 132.5, 132.3, 132.2, 129.6, 129.5, 129.1, 129.0, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 126.4, 125.6, 124.8, 123.4; **HRMS** (ESI) calcd for $C_{34}H_{22}O_2$ $[M + Na]^+$ 485.1512, found 485.1538.

*(Z)-1-(2-Benzoyl-1H-inden-1-ylidene)-1-phenylbut-3-en-2-one (**2i**).* Yield 85 mg, 61%; light-yellow solid; mp 78−79 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.00 Hz, 2H), 7.57 (d, J = 8.00 Hz, 1H), 7.52−7.46 (m, 7H), 7.30 (d, J = 8.00 Hz, 1H), 7.25−7.18 (m, 2H), 6.96 (d, J = 8.00 Hz, 1H), 6.56 (d, J = 8.00 Hz, 1H), 6.48−6.41 (m, 1H), 6.19−6.14 (m, 1H), 5.70−5.67 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9, 193.2, 146.5, 142.7, 141.1, 139.7, 139.0, 138.4, 137.1, 136.0, 135.5, 132.8, 129.9, 129.7, 129.6, 129.4, 129.3, 129.1, 128.4, 128.0, 124.8, 123.3; **HRMS** (ESI) calcd for $C_{26}H_{18}O_2$ $[M + Na]^+$ 385.1199, found 385.1173.

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*(1Z,3E)-1-(2-Benzoyl-1H-inden-1-ylidene)-1,4-diphenylbut-3-en-2-one (**2j**).* Yield 64 mg, 49%; light-yellow solid; mp 86−87 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.00 Hz, 2H), 7.54−7.47 (m, 6H), 7.44−7.40 (m, 2H), 7.36−7.34 (m, 2H), 7.31−7.27 (m, 4H), 7.23−7.19 (m, 3H), 6.97−6.94 (m, 1H), 6.72 (d, J = 16.00 Hz, 1H), 6.56 (d, J = 8.00 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.5, 193.0, 146.9, 143.9, 141.9, 141.2, 140.2, 139.4, 138.3, 137.1, 136.3, 134.6, 132.7, 130.4, 129.7, 129.7, 129.4, 129.3, 129.0, 128.6, 128.5, 128.2, 127.8, 125.8, 124.8, 123.2; **HRMS** (ESI) calcd for $C_{32}H_{22}O_2$ [M + Na]$^+$ 461.1512, found 461.1498.

*(Z)-1-(2-Benzoyl-1H-inden-1-ylidene)-1-phenylpropan-2-one (**2k**).* Yield 90 mg, 86%; light-yellow solid; mp 66−67 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.00 Hz, 2H), 7.61−7.48 (m, 8H), 7.29 (d, J = 8.00 Hz, 1H), 7.21−7.17 (m, 2H), 6.95−6.91 (m, 1H), 6.42 (d, J = 8.00 Hz, 1H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.3, 193.7, 148.3, 142.6, 141.1, 139.7, 138.3, 137.2, 137.0, 136.1, 132.8, 129.7, 129.4, 129.0, 128.9, 128.4, 127.9, 124.7, 123.3, 29.5; **HRMS** (ESI) calcd for $C_{25}H_{18}O_2$ [M + Na]$^+$ 373.1199, found 373.1188.

*(Z)-1-(2-Benzoyl-1H-inden-1-ylidene)-1-phenylbutan-2-one (**2l**).* Yield 93 mg, 85%; light-yellow solid; mp 67−68 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.00 Hz, 2H), 7.61−7.57 (m, 1H), 7.51−7.45 (m, 7H), 7.29 (d, J = 8.00 Hz, 1H), 7.19−7.16 (m, 2H), 6.94−6.90 (m, 1H), 6.40 (d, J = 8.00 Hz, 1H), 2.62−2.57 (m, 2H), 0.99−0.95 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.2, 193.5, 148.5, 142.1, 141.1, 139.8, 138.3, 137.1, 137.1, 136.5, 132.8, 129.7, 129.3, 129.2, 129.0, 128.7, 128.3, 127.8, 124.6, 123.2, 35.2, 7.4; **HRMS** (ESI) calcd for $C_{26}H_{20}O_2$ [M + Na]$^+$ 387.1361, found 387.1370.

*(Z)-1-(2-Benzoyl-1H-inden-1-ylidene)-1,3-diphenylpropan-2-one (**2m**).* Yield 87 mg, 68%; yellow solid; mp 101−102 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.00 Hz, 2H), 7.61−7.57 (m, 1H), 7.50−7.48 (m, 5H), 7.39−7.37 (m, 2H), 7.29 (d, J = 8.00 Hz, 1H), 7.21−7.13 (m, 5H), 7.02−7.00 (m, 2H), 6.94−6.91 (m, 1H), 6.45 (d, J = 8.00 Hz, 1H), 3.95 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.5, 193.5, 148.3, 142.4, 141.1, 139.6, 138.2, 137.6, 137.1, 135.8, 134.2, 132.8, 129.9, 129.8, 129.3, 129.3, 128.9, 128.8, 128.4, 128.0, 127.9, 126.4, 124.7, 123.3, 48.2; **HRMS** (ESI) calcd for $C_{31}H_{22}O_2$ [M + Na]$^+$ 449.1517, found 449.1528.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-1-cyclohexyl-2-phenylethanone (**2n**).* Yield 56 mg, 45%; yellow solid; mp 102−103 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.00 Hz, 2H), 7.60−7.57 (m, 1H), 7.53−7.44 (m, 7H), 7.27−7.25 (m, 1H), 7.18−7.12 (m, 2H), 6.91−6.87 (m, 1H), 6.23 (d, J = 8.00 Hz, 1H), 2.46−2.39 (m, 1H), 1.86−1.82 (m, 2H), 1.68−1.65 (m, 2H), 1.34−1.30 (m, 2H), 1.13−0.96 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.5, 193.1, 147.4, 141.3, 141.0, 140.2, 139.4, 138.3, 137.2, 137.0, 132.8, 129.7, 129.2, 129.1, 128.8, 128.3, 127.6, 124.9, 123.0, 49.4, 28.0, 25.8, 25.8; **HRMS** (ESI) calcd for $C_{30}H_{26}O_2$ [M + Na]$^+$ 441.1830, found 441.1846.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-1-(furan-2-yl)-2-phenylethanone (**2o**).* Yield 60 mg, 50%; yellow solid; mp 149−150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.00 Hz, 2H), 7.58−7.51 (m, 3H), 7.48−7.40 (m, 6H), 7.30−7.32 (m, 1H), 7.23−7.20 (m, 2H), 6.99−6.95 (m, 1H), 6.85 (d, J = 4.00 Hz, 1H), 6.82 (d, J = 8.00 Hz, 1H), 6.35−6.34 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.9, 182.8, 153.3, 146.8, 146.7, 145.0, 142.5, 141.0, 139.6, 139.6, 138.1, 137.1, 136.7, 132.7, 129.7, 129.4, 129.1, 128.2, 128.0, 124.8, 123.3, 119.9, 112.2; **HRMS** (ESI) calcd for $C_{28}H_{18}O_3$ [M + Na]$^+$ 425.1154, found 425.1172.

*(Z)-2-(2-Benzoyl-5-methyl-1H-inden-1-ylidene)-1,2-diphenylethanone (**2p**).* Yield 89 mg, 70%; yellow solid; mp 135−136 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.00 Hz, 2H), 7.74 (d, J = 8.00 Hz, 2H), 7.52−7.48 (m, 3H), 7.41−7.32 (m, 6H), 7.28−7.25 (m, 2H), 7.14 (s, 2H), 6.80 (d, J = 8.00 Hz, 1H), 6.54 (d, J = 8.00 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.6, 193.0, 145.6, 142.4, 141.2, 139.7, 139.1, 139.0, 138.1, 137.4, 137.0, 134.5, 132.5, 132.4, 130.1, 129.8, 129.5, 129.5, 129.0, 128.8, 128.0, 128.0, 124.5, 124.0, 21.3; **HRMS** (ESI) calcd for $C_{31}H_{22}O_2$ [M + Na]$^+$ 449.1517, found 449.1539.

*(Z)-1-(2-Benzoyl-5-fluoro-1H-inden-1-ylidene)-1-phenylpropan-2-one (**2q**).* Yield 79 mg, 72%; yellow solid; mp 67−68 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.00 Hz, 2H), 7.60 (d, J = 8.00 Hz, 1H), 7.54−7.48 (m, 5H), 7.46−7.43 (m, 2H), 7.27−7.26 (m, 1H), 7.13 (s, 1H), 6.89 (d, J = 8.00 Hz, 1H), 6.32 (d, J = 8.00 Hz, 1H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.1, 193.4, 163.2 (d, ^1J = 247 Hz), 149.0, 148.3, 142.6, 138.0, 137.9, 135.8, 135.7, 135.2, 134.7, 129.7, 129.5, 129.0, 128.4, 125.5, 123.5, 110.3 (d, ^2J = 22 Hz), 110.2 (d, ^2J = 23 Hz), 29.4; **HRMS** (ESI) calcd for $C_{25}H_{17}FO_2$ [M + Na]$^+$ 391.1105, found 391.1114.

*(Z)-1-(2-Benzoyl-5-chloro-1H-inden-1-ylidene)-1-phenylpropan-2-one (**2r**).* Yield 75 mg, 65%; yellow solid; mp 80−81 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.00 Hz, 2H), 7.60 (d, J = 8.00 Hz, 1H), 7.54−7.48 (m, 5H), 7.47−7.44 (m, 2H), 7.13 (s, 1H), 6.70−6.97 (m, 1H), 6.64−6.59 (m, 1H), 6.37−6.34 (m, 1H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.1, 193.4, 149.0, 142.6, 141.0, 140.5, 137.9, 136.1, 135.7, 135.2, 134.7, 133.1, 129.7, 129.6, 129.5, 128.9, 128.4, 127.5, 125.5, 29.4; **HRMS** (ESI) calcd for $C_{25}H_{17}ClO_2$ [M + Na]$^+$ 407.0809, found 407.0780.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-2-(4-methoxyphenyl)-1-phenylethanone (**2s**).* Yield 101 mg, 76%; yellow solid; mp 181−182 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.00 Hz, 2H), 7.76 (d, J = 8.00 Hz, 2H), 7.52−7.49 (m, 1H), 7.44−7.33 (m, 6H), 7.30−7.22 (m, 3H), 7.18 (s, 1H), 7.05−7.01 (m, 1H), 6.93 (d, J = 8.00 Hz, 2H), 6.88 (d, J = 8.00 Hz, 1H), 3.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.0, 193.2, 160.3, 146.7, 141.9, 140.9, 139.6, 138.8, 138.2, 137.5, 137.2, 132.5, 132.4, 131.3, 130.2, 129.6, 129.1, 128.8, 128.1, 127.9, 124.6, 123.3, 114.5, 55.3; **HRMS** (ESI) calcd for $C_{31}H_{22}O_3$ [M + Na]$^+$ 465.1461, found 465.1463.

*(Z)-2-(2-Benzoyl-1H-inden-1-ylidene)-2-(4-chlorophenyl)-1-phenylethanone (**2t**).* Yield 106 mg, 79%; yellow solid; mp 197−198 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.00 Hz, 2H), 7.74 (d, J = 8.00 Hz, 2H), 7.53−7.46 (m, 6H), 7.40−7.34 (m, 3H), 7.31−7.25 (m, 3H), 7.20 (s, 1H), 7.07 (m, 1H), 6.74 (d, J = 8.00 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.2, 192.8, 145.0, 142.5, 141.0, 139.4, 139.4, 138.0, 137.2, 136.8, 135.4, 135.3, 132.7, 132.6, 131.0, 130.1, 129.5, 129.4, 129.2, 128.2, 128.1, 128.1, 124.7, 123.5; **HRMS** (ESI) calcd for $C_{30}H_{19}ClO_2$ [M + Na]$^+$ 469.0966, found 469.0974.

*(Z)-1-(1-(2-Oxo-1,2-diphenylethylidene)-1H-inden-2-yl)pentan-1-one (**2w**).* Yield 86 mg, 73%; yellow solid; mp 133−134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.00 Hz, 2H), 7.53 (s, 1H), 7.46−7.42 (m, 3H), 7.39−7.35 (m, 6H), 7.24−7.20 (m, 1H), 6.98−6.94 (m, 1H), 6.49 (d, J = 8.00 Hz, 1H), 2.64−2.60 (m, 2H), 1.48−1.40 (m, 2H), 1.24−1.19 (m, 2H), 0.87−0.83 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.0, 194.4, 147.4, 140.9, 140.6, 139.5, 137.6, 137.3, 137.1, 136.6, 132.4, 129.9, 129.3, 129.0, 129.0, 128.6, 128.2, 124.8, 123.4, 40.3, 26.5, 22.3, 13.8; **HRMS** (ESI) calcd for $C_{28}H_{24}O_2$ [M + Na]$^+$ 415.1669, found 415.1692.

*(Z)-2,2-Dimethyl-1-(1-(2-oxo-1,2-diphenylethylidene)-1H-inden-2-yl)propan-1-one (**2x**).* Yield 85 mg, 72%; light-yellow solid; mp 167−168 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.2 Hz, 2H), 7.49−7.46 (m, 2H), 7.43 (d, J = 7.8 Hz, 1H), 7.35−7.39 (m, 4H), 7.30−7.34 (m, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.91 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 1.21(s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.5, 195.8, 146.6, 141.5, 139.7, 139.1, 137.1, 136.8, 135.8, 135.4, 132.8, 130.2, 129.5, 129.1, 128.8, 128.2, 127.2, 124.6, 122.8, 44.1, 27.6; **HRMS** (ESI) calcd for $C_{28}H_{25}O_2$ [M + H] $^+$ 393.1855, found 393.1861.

*(Z)-2-(2-(4-Chlorobenzoyl)-1H-inden-1-ylidene)-1,2-diphenylethanone (**2y**).* Yield 97 mg, 73%; yellow solid; mp 169−170 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.00 Hz, 2H), 7.70 (d, J = 8.00 Hz, 2H), 7.52−7.50 (m, 2H), 7.43−7.41 (m, 3H), 7.36−7.33 (m, 3H), 7.30−7.24 (s, 3H), 7.17 (s, 1H), 7.03−6.98 (m, 2H), 6.69 (d, J = 8.00 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.5, 191.7, 146.8, 141.9, 140.8, 139.2, 139.0, 139.0, 137.3, 137.0, 136.8, 136.4, 132.6, 130.9, 130.1, 129.5, 129.1, 129.1, 129.0, 128.4, 128.1, 124.8, 123.4; **HRMS** (ESI) calcd for $C_{30}H_{19}ClO_2$ [M + Na]$^+$ 469.0966, found 469.0952.

General Procedure for the Preparation of Compound 2z Using a CO Balloon. An oven-dried 10 mL Schlenk tube was charged with quinoline-based 1,6-diynol benzoate **1z** (138.9 mg, 0.3 mmol) and $PtCl_2$ (8.0 mg, 0.03 mmol) in anhydrous *o*-xylene (3.0 mL) under

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a carbon monoxide atmosphere (1 atm balloon). The mixture was sealed with a screw cap and stirred at 100 °C for about 24 h until the starting material **1z** was consumed, as monitored by TLC. The reaction mixture was quenched with saturated NaCl solution (3.0 mL), stirred for an additional 10 min, and then extracted with CH_2Cl_2 (3.0 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude residue was purified by flash column chromatography (EtOAc/petroleum ether 1:6) to give the desired product **2z** (88.9 mg, 64% yield) as a light-yellow solid.

*(E)-2-(2-Benzoyl-3H-cyclopenta[b]quinolin-3-ylidene)-1,2-diphenylethanone (**2z**).* Yield 89 mg, 64%; light-yellow solid; mp 95−96 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01−8.00 (m, 1H), 7.98−7.95 (m, 1H), 7.79−7.76 (m, 2H), 7.70 (d, J = 8.00 Hz, 1H), 7.60−7.54 (m, 2H), 7.50−7.31 (m, 8H), 7.25−7.16 (m, 4H), 7.09 (d, J = 8.00 Hz, 1H), 6.97 (d, J = 8.00 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.1, 193.9, 156.5, 147.0, 146.3, 143.1, 137.8, 137.1, 137.0, 135.9, 134.9, 132.7, 131.2, 131.1, 130.3, 129.9, 129.7, 129.6, 129.2, 128.9, 128.4, 128.2, 127.9, 127.5, 127.4, 126.6, 126.0; **HRMS** (ESI) calcd for $C_{33}H_{21}NO_2$ $[M + H]^+$ 464.1651, found 464.1675.

Scaled-Up Preparation of Compound 2k. An oven-dried 100 mL Schlenk tube was charged with diynol acetate **1k** (870 mg, 2.5 mmol) and $PtCl_2$ (33 mg, 0.125 mmol) in anhydrous *o*-xylene (25 mL) under an atmosphere of N_2. The mixture was sealed with a screw cap and stirred at 80 °C for 12 h until the disappearance of the starting material **1k**, as monitored by TLC. The reaction mixture was quenched with saturated NaCl solution (20 mL), stirred for an additional 10 min, and then extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude residue was purified by flash column chromatography (EtOAc/petroleum ether 1:10) to give 670 mg (76% yield) of the desired product **2k** as a light-yellow solid.

Crossover Experiment Using Equimolar Amounts of 1k and 1w. An oven-dried 10 mL Schlenk tube was charged with compound **1k** (105 mg, 0.3 mmol), compound **1w** (117.6 mg, 0.3 mmol), and $PtCl_2$ (4.0 mg, 0.015 mmol) in anhydrous *o*-xylene (3.0 mL) under N_2. The resulting mixture was sealed with a screw cap and stirred at 80 °C for about 12 h until the two starting materials were consumed, as monitored by TLC. The reaction mixture was quenched with saturated NaCl solution (4.0 mL), stirred for an additional 10 min, and then extracted with CH_2Cl_2 (4.0 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude residue was purified by flash column chromatography to give the desired products **2k** (86.1 mg, 82% yield) and **2w** (76.5 mg, 65% yield). It is noteworthy that no crossover products **2a** and **2w′** were detected by TLC and GC−MS analysis.

Synthesis of ^{18}O-Labeled Compound 1k-^{18}O.[26] Acetyl chloride (471 mg, 0.34 mL, 6.0 mmol) was placed in an oven-dried 10 mL Schlenk tube under nitrogen. The flask was then cooled to −20 °C, and 0.12 mL of $H_2{}^{18}O$ was added dropwise via syringe. The flask was warmed to 0 °C. After 30 min at room temperature, the flask was recooled to 0 °C, and 277.0 mg (0.17 mL) of PCl_3 was added. The mixture was allowed to warm to room temperature and stand for 1 h, after which 2.0 mL of anhydrous CH_2Cl_2 was added. The top layer was taken up and added to a solution of 1,6-diynol **1a_2** (924 mg, 3.0 mmol), Et_3N, and DMAP in anhydrous CH_2Cl_2. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 10:1) to give ^{18}O-labeled acetyl propargyl ester **1k-^{18}O** as a light-yellow solid.

The ^{18}O content of **1k-^{18}O** was 62.2% as determined by HRMS (ESI). There were two carbonyl group peaks observed in the **^{13}C NMR** spectrum for the carbon attached with an ester moiety (169.65 and 169.61 ppm); the upfield one was assigned as the carbon substituted with the ^{18}O atom.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.00 Hz, 1H), 7.60−7.57 (m, 3H), 7.49 (d, J = 8.00 Hz, 2H), 7.42−7.30 (m, 8H), 7.18 (s, 1H), 2.11 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.65, 169.61, 138.2, 132.4, 131.9, 131.7, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 122.9, 95.1, 87.3, 86.2, 85.2, 64.5, 20.9; **HRMS** (ESI) calcd for $C_{25}H_{18}O_2$ $[M + Na]^+$ 375.1247, found 375.1228.

Synthesis of ^{18}O-Labeled Compound 2k-^{18}O. An oven-dried 10 mL Schlenk tube was charged with the ^{18}O-labeled substrate **1k-^{18}O** (105.6 mg, 0.3 mmol) and $PtCl_2$ (4.0 mg, 0.015 mmol) in anhydrous *o*-xylene (3.0 mL) under an atmosphere of N_2. The mixture was sealed with a screw cap and stirred at 80 °C for about 10 h until the starting material was consumed, as monitored by TLC. The reaction mixture was quenched with saturated NaCl solution (3.0 mL), stirred for an additional 10 min, and then extracted with CH_2Cl_2 (3.0 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude residue was purified by flash column chromatography (EtOAc/petroleum ether 1:10) to give 97.6 mg (79% yield) of the desired product **2k-^{18}O** as a light-yellow solid.

The ^{18}O content of **2k-^{18}O** was 56.7% as determined by HRMS (ESI). There were three carbonyl group peaks observed in **^{13}C NMR** spectrum (203.20, 193.64, and 193.60 ppm). The peak located at 203.20 ppm was assigned as the carbon in the acetyl group; the other two peaks were assigned as the carbons in the benzoyl groups, the upfield one being due to the carbon substituted with the ^{18}O atom.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.00 Hz, 2H), 7.61 (d, J = 8.00 Hz, 1H), 7.55−7.52 (m, 3H), 7.50−7.46 (m, 3H), 7.32−7.29 (m, 2H), 7.22−7.17 (m, 2H), 6.95−6.90 (m, 1H), 6.42 (d, J = 8.00 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.20, 193.64, 193.60, 148.3, 142.4, 141.1, 139.7, 138.3, 137.2, 137.0, 136.1, 132.8, 129.9, 129.7, 129.4, 129.3, 129.0, 128.8, 128.3, 127.8, 127.7, 124.7, 123.2, 29.4; **HRMS** (ESI) calcd for $C_{25}H_{18}O_2$ $[M + Na]^+$ 375.1247, found 375.1199; **HRMS** (ESI) calcd for $PhC^{18}O$ $[M]^+$ 107.0383, found 107.0447.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of all new products and the X-ray crystallographic data (CIF) for compound **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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