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Gold-Catalyzed Tandem [3,3]-Propargyl Ester Rearrangement Leading to (*E*)-1*H*-Inden-1-ones

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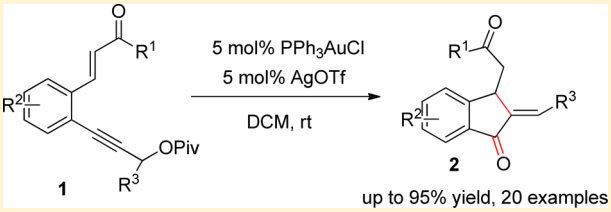
Supporting Information

ABSTRACT: An efficient method for the synthesis of (*E*)-1*H*-inden-1-ones using gold-catalyzed tandem [3,3]-propargyl ester rearrangement followed by Michael addition under mild reaction conditions has been developed. The resulting products are important frameworks found in numerous natural products and pharmaceutically active compounds, as well as being valuable intermediates in organic synthesis.



INTRODUCTION

Gold-catalyzed rearrangement reactions of propargylic esters offer a highly efficient synthetic strategy for their synthetic utility in a wide variety of fascinating transformations.[1,2] Accordingly, this field has drawn much attention from the synthetic community. In recent years, tremendous efforts have been made toward the rearrangement reactions and much progress has already been achieved, with a number of natural products and complex molecules being constructed.[3] Specifically, early works by the Fürstner group and other groups showed that propargyl esters could undergo a gold-catalyzed [2,3]-rearrangement following a 1,2-acyl migration to give alkenyl gold carbenoids of type **A**[1] (Scheme 1).[4] Subsequently, Zhang group found that propargyl esters could also undergo [3,3]-rearrangements through either consecutive 1,2-acyl migrations or a 1,3-acyl migration to give the α-vinyl gold oxocarbenium intermediate **B**[2] via allene **B**[1] (Scheme 1).[5] The equilibrium reversible interconversion between **B**[1] and **B**[2] is largely determined by the steric and electronic nature of the substituents.[6] It is worth noting that many interesting and important rearrangement reactions have been reported utilizing the interception of the intermediates **B**[1] and **B**[2] with various nucleophiles and electrophiles.[6b,7]

In 2012, the Cran group reported an interesting Au-catalyzed [3,3]-sigmatropic rearrangement of propargylic esters to form unsaturated carbocycles and exocyclic enones (Scheme 2).[8] However, to the best of our knowledge, utilizing this efficient protocol to build 1*H*-inden-1-ones has not yet been studied. The indane core, and specifically the indanone subunit, is a common skeleton in both natural products and synthetic drugs.[9−11]

Over the years, several palladium-catalyzed strategies have been reported for synthesizing 1*H*-inden-1-ones (Scheme 3).[12] Pioneering work by the Chiusoli group showed that bifunctional aromatic compounds with terminal alkynes and carbon monoxide under palladium catalyst could give 1*H*-inden-1-ones (Scheme 3, eq 1).[12a] Recently, Buchwald and co-workers have developed an efficient intramolecular palladium-catalyzed synthesis of enantiomeric 1*H*-inden-1-ones (Scheme 3, eq 2).[12b] Subsequently, Li et al. found that arynes with allyl carbonates and carbon monoxide via palladium-catalyzed cyclocarbonylation reactions could give two types of 1*H*-inden-1-ones, which depended on both substrates and ligands (Scheme 3, eq 3).[12c] Great achievements have been made with respect to palladium-catalyzed strategies. However, due to the importance of the core, alternative methods for the construction of 1*H*-inden-1-ones are indeed desirable.

As part of our continuing interest in gold-catalyzed chemistry,[13] we herein synthesized the propargyl pivolate **1a**, with the expectation that it would undergo rearrangement and cyclization to efficiently constructing the 1*H*-inden-1-one **2a** under mild conditions. The results obtained with various catalysts are summarized in Table 1.

RESULTS AND DISCUSSION

Initially, we found that no reaction occurred even after 24 h when AuCl, $AuCl_3$, and PPh_3AuCl were employed alone in nitromethane at room temperature, respectively (Table 1, entries 1−3). Surprisingly, when we chose 5 mol % of PPh_3AuCl/AgOTf in nitromethane at room temperature, the expected tandem [3,3]-propargyl ester rearrangement indeed occurred to give **2a** in 67% yield after only 15 min (Table 1, entry 4). The structure of compound **2a** was identified unambiguously by X-ray diffraction (Figure 1). Then, the effect of solvents was also tested, and we found that a 56% yield of **2a** was obtained in DCE and a 86% yield of **2a** was achieved in DCM, remarkably (Table 1, entries 5 and 6). To improve the reaction efficiency, other catalyst systems were then investigated subsequently in DCM. A similar result was obtained when **A**/AgOTf was employed as catalyst (Table 1, entry 7). The use of IPrAuCl/AgOTf and **B**/AgOTf resulted in complete consumption of the starting material, but the isolated yields were much lower at 67% and 74%, respectively (Table 1,

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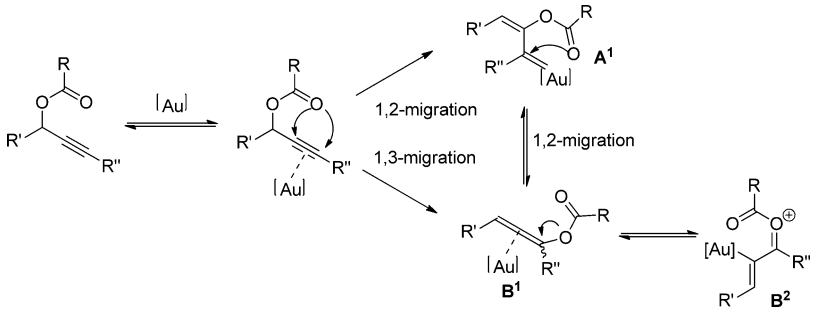
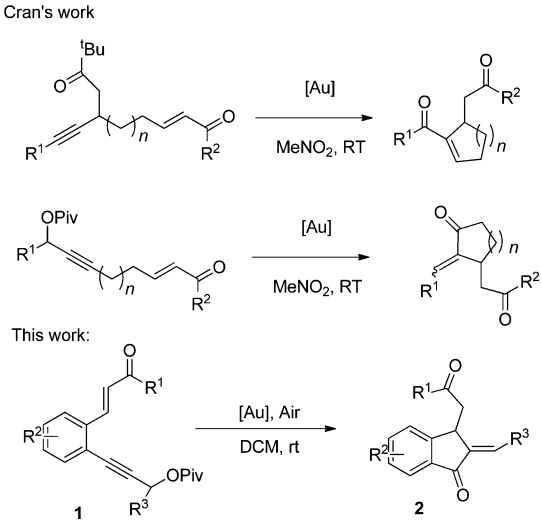
Scheme 1. Proposed Gold-Catalyzed Propargyl Ester Rearrangements



Scheme 2. Gold-Catalyzed [3,3]-Sigmatropic Rearrangement Reactions



Scheme 3. Palladium-Catalyzed Methods for Synthesis of 1*H*-Inden-1-ones

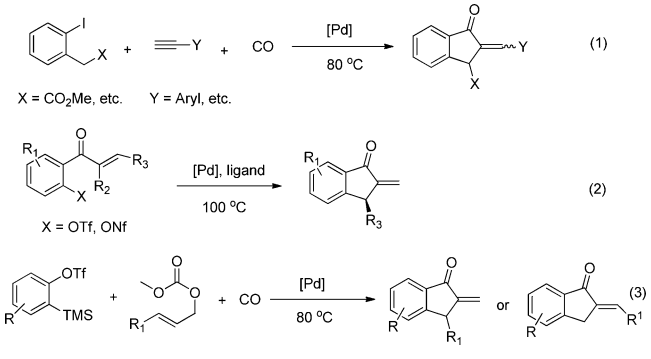
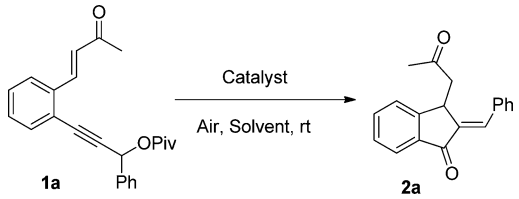
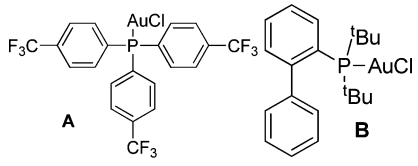


Table 1. Optimization Studies on the [3,3]-Rearrangement of 1a[a]



entry	catalyst	solvent	time	yield (%)[b,c]
1	AuCl	$MeNO_2$	24 h	NR
2	$AuCl_3$	$MeNO_2$	24 h	NR
3	PPh_3AuCl	$MeNO_2$	24 h	NR
4	$PPh_3AuCl/AgOTf$	$MeNO_2$	15 min	67
5	$PPh_3AuCl/AgOTf$	DCE	15 min	56
6	$PPh_3AuCl/AgOTf$	DCM	15 min	86
7	**A**/AgOTf	DCM	30 min	82
8	IPrAuCl/AgOTf	DCM	10 min	67
9	**B**/AgOTf	DCM	30 min	74
10	$PPh_3AuCl/AgNTf_2$	DCM	20 min	59
11	$PPh_3AuCl/AgSbF_6$	DCM	30 min	24
12	$PPh_3AuCl/AgOCOCF_3$	DCM	24 h	NR
13	AgOTf	DCM	24 h	NR
14	*p*-TsOH	DCM	24 h	NR
15	$PPh_3AuCl/AgOTf$	DCM	15 min	NR

[a]Reaction conditions: substrate **1a** (0.2 mmol), solvent (3 mL), in air at room temperature; entries 1–3 and entry 13, 5 mol % of the catalyst; entries 4–12, [Au] (5 mol %), [Ag] (5 mol %); entry 14, 20 mol % of *p*-TsOH; entry 15, 5 mol % PPh_3AuCl/5 mol % AgOTf and Celite filtration; reaction monitored by TLC. Abbreviations: DCM, dichloromethane; DCE, 1,2-dichloroethane; IPr, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.



[b]Isolated yield. [c]*E*:*Z* > 10:1, ratio determined using ^1H NMR spectroscopy. The stereochemistry was confirmed by X-ray diffraction.

entries 8 and 9). Somewhat surprisingly, a change of the counterion to $AgNTf_2$ and $AgSbF_6$ under the same conditions of entry 6 resulted in much lower yields of 59% and 24%, respectively (Table 1, entries 10 and 11). In addition, the use of $PPh_3AuCl/AgOCOCF_3$ gave no reaction (Table 1, entry 12). Furthermore, AgOTf was found to be inactive as a catalyst (Table 1, entry 13), and *p*-TsOH also could not catalyze the reaction (Table 1, entry 14). Subsequently, in order to figure out the silver effects in gold catalysis, we placed **1a** in a solution containing 5 mol % of PPh_3AuCl/5 mol % of AgOTf in DCM; this mixture was then stirred at room temperature for 10 min and filtered through Celite to remove AgCl. We found that no reaction occurred after 15 min. This result clearly demonstrated that the addition of AgOTf not only served as a scavenger for chloride but also influenced the gold cation reactivity (Table 1, entry 15).[13b,14]

Finally, in an attempt to optimize the yield of the product **2a**, we further studied the influence of the leaving group on the substrate, but no better results were observed (Scheme 4). By the series of detailed investigations mentioned above, the reaction conditions were eventually optimized as in Table 1,

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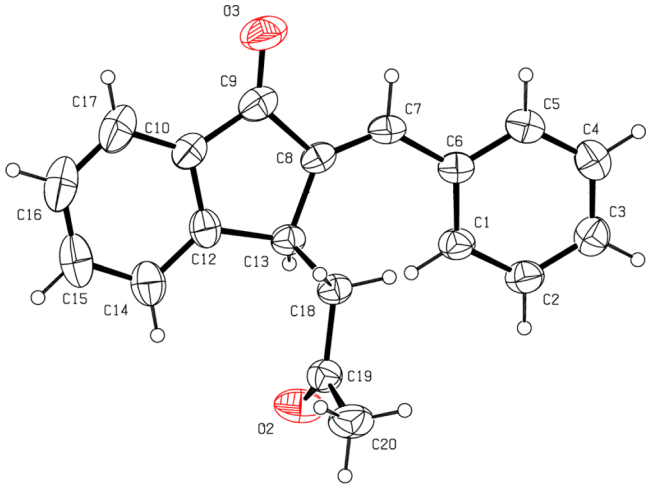
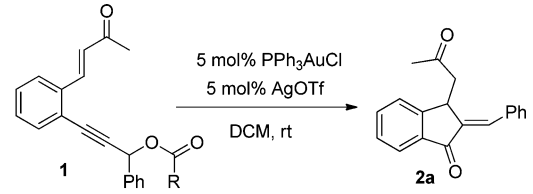


Figure 1. Structure of **2a**.

Scheme 4. Study of the Influence of the Leaving Group in the Substrate



entry 6: 1.0 equiv of **1a** and 5 mol % of $PPh_3AuCl/AgOTf$ in the presence of 3 mL of DCM at room temperature.

With the optimized conditions in hand, the scope of the gold-catalyzed [3,3]-sigmatropic rearrangement of propargylic esters was investigated with a variety of substrates **1** (Table 2).

The reactions of substrates **1b,e** bearing an electron-withdrawing or an electron-donating ortho substituent aromatic R^3 group produced the corresponding rearrangement products **2b,e** in excellent yields (entries 2 and 5). However, compounds **1c,d** and **1f,g** with an electron-withdrawing or an electron-donating meta or para substituent aromatic R^3 group only gave the desired inden-1-ones in moderate yields (entries 3 and 4 and entries 6 and 7). Subsequently, we designed compound **1h** having two methyl groups of aromatic R^3, which proceeded to give the desired cyclization product **2h** in a yield of 60% (entry 8). The reactions also worked well with the compounds **1i−k** with an aliphatic group at R^3, which proceeded to give the desired cyclization products **2i−k** in good yields of 85%, 73%, and 76%, respectively (entries 9−11). We also determined that the substrates **1l−n** with trisubstituted propargyl esters gave the corresponding products in good yield. However, the reactions must be run with a 10 mol % catalyst loading of $PPh_3AuCl/AgOTf$ (entries 12−14). We further tested the effect of substituents at R^1. Similarly, substrates **1o−q** underwent the cyclization smoothly to give the corresponding rearrangement products, but only in lower yields (entries 15−17). Furthermore, to expand the scope of this reaction, we also investigated the effect of the substituent at R^2. To our delight, **1s,t** gave the corresponding products in good yields (entries 19 and 20), but **1r** only gave the desired product in a yield of 47% (entry 18). We considered that the failure to obtain a good yield of **1r** may be the result of the steric effect of the substituent at R^2.

From the study of substrate scope, we noticed that products **2** were mainly the *E* stereoisomer. To explain this phenomenon, we believe that the cis relationship between R^3 and Au in **D** is more stable than the relationship where R^3 is cis to the oxocarbenium group, due to the reduced steric crowding as a consequence of the long Au−C(sp^2) bond (Scheme 5).[7h]

On the basis of the above observations and other previous works,[4,8] we propose the plausible mechanism given in Scheme 5 for this gold-catalyzed [3,3]-sigmatropic rearrangement of propargylic ester cyclization. We envisioned the following: (i) the alkyne moiety of substrates **1** after coordination to the gold catalyst eventually undergoes the known [3,3]-sigmatropic rearrangement described in Scheme 1, thus delivering **C**; (ii) **D** interconverts reversibly with **C**; (iii) intermediate **D** is primed for Michael addition, thus delivering intermediate **E**; (iv) intermediate **E** through hydrolysis gives the product **2**.

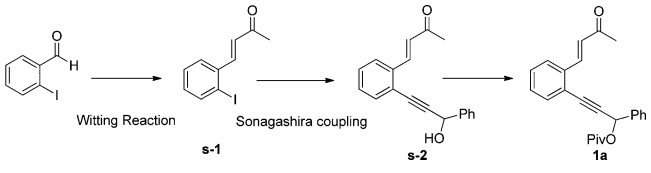
CONCLUSION

In conclusion, we have demonstrated a concise strategy for the synthesis of (*E*)-1*H*-inden-1-ones, utilizing a gold-catalyzed tandem [3,3]-propargyl ester rearrangement followed by Michael addition. This transformation is efficient and proceeds under extremely mild reaction conditions. Furthermore, the inden-1-ones are important frameworks found in numerous natural products and pharmaceutically active compounds, as well as being valuable intermediates in organic synthesis.[11] Further studies on gold-catalyzed rearrangement reactions are in progress in our laboratory.

EXPERIMENTAL SECTION

General Remarks. Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded at 400 MHz in $CDCl_3$, and ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), and m (multiplet). IR spectra were recorded on a FT-IR spectrometer, and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All products were further characterized by high-resolution MS (the instrument is a Maxis 4G, and the source type is ESI); their ^1H NMR and ^{13}C NMR spectra are provided in the Supporting Information. The room temperature was 23−25 °C. Commercially available reagents and solvents were used without further purification unless otherwise indicated. DCM was dried over calcium hydride.

Starting Materials..[8,15] *General Procedure for the Preparation of 1a.* To a 0.2 M solution of 2-iodobenzaldehyde in DCM was added 2 equiv of Wittig reagent,[15b] and the reaction mixture was stirred for 12 h or until completion, as indicated by TLC. Reduction in vacuo and purification by column chromatography yielded the desired **s-1** as a light yellow solid.



To a triethylamine solution (25 mL) of **s-1** (2.72 g, 10 mmol) were added $Pd(PPh_3)Cl_2$ (140 mg, 0.2 mmol) and CuI (75 mg, 0.4 mmol) at room temperature, and the mixture was stirred for 15 min under argon before addition of 1-phenylprop-2-yn-1-ol (1.45 g, 11 mmol). The resulting mixture was stirred for 4 h at 50 °C under argon. Then,

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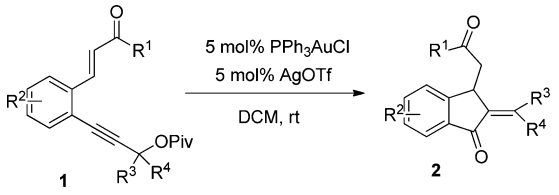
Table 2. Study of Substrate Scope[a]



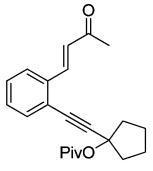
entry	substrate	time	products/ yield (%)[b]	E/Z[c]
1	R^1 = Me, R^2 = R^4 = H , R^3 = Ph (**1a**)	15min	**2a**/86	16:1
2	R^1 = Me, R^2 = R^4 = H, R^3 = *o*-Cl-C_6H_4 (**1b**)	30min	**2b**/95	9:1
3	R^1 = Me, R^2 = R^4 = H, R^3 = *m*-Cl-C_6H_4 (**1c**)	30min	**2c**/71	16:1
4	R^1 = Me, R^2 = R^4 = H, R^3 = *p*-Cl-C_6H_4 (**1d**)	80min	**2d**/65	>20:1
5	R^1 = Me, R^2 = R^4 = H, R^3 = *o*-Me-C_6H_4 (**1e**)	2h	**2e**/85	>20:1
6	R^1 = Me, R^2 = R^4 = H, R^3 = *p*-Me-C_6H_4 (**1f**)	15min	**2f**/68	13:1
7	R^1 = Me, R^2 = R^4 = H, R^3 = *m*-OMe-C_6H_4 (**1g**)	55min	**2g**/50	8:1
8	R^1 = Me, R^3 = 3,4-dimethylphenyl, R^2 = R^4 = H (**1h**)	2h	**2h**/60	7:1
9	R^1 = Me, R^2 = R^4 = H, R^3 = Me (**1i**)	40min	**2i**/85	>20:1
10	R^1 = Me, R^2 = R^4 = H, R^3 = *n*-propyl (**1j**)	1h	**2j**/73	>20:1
11	R^1 = Me, R^2 = R^4 = H, R^3 = *n*-hexyl (**1k**)	12h	**2k**/76	>20:1
12[d]	R^1 = R^3 = R^4 = Me, R^2 = H (**1l**)	12h	**2l**/93	-
13[d]	R^1 = Me, R^2 = H, R^3 = Ph, R^4 = ethyl (**1m**)	12h	**2m**/90	-
14[d]	 (**1n**)	12h	**2n**/84	-
15	R^1 = R^3 = Ph, R^2 = R^4 = H (**1o**)	30min	**2o**/55	8:1
16	R^1 = *p*-Cl-C_6H_4, R^2 = R^4 = H, R^3 = Ph (**1p**)	15min	**2p**/45	>20:1
17	R^1 = *p*-Me-C_6H_4, R^2 = R^4 = H, R^3 = Ph (**1q**)	25min	**2q**/62	>20:1

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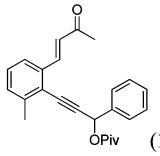
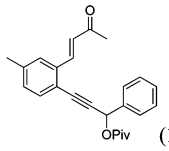
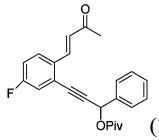
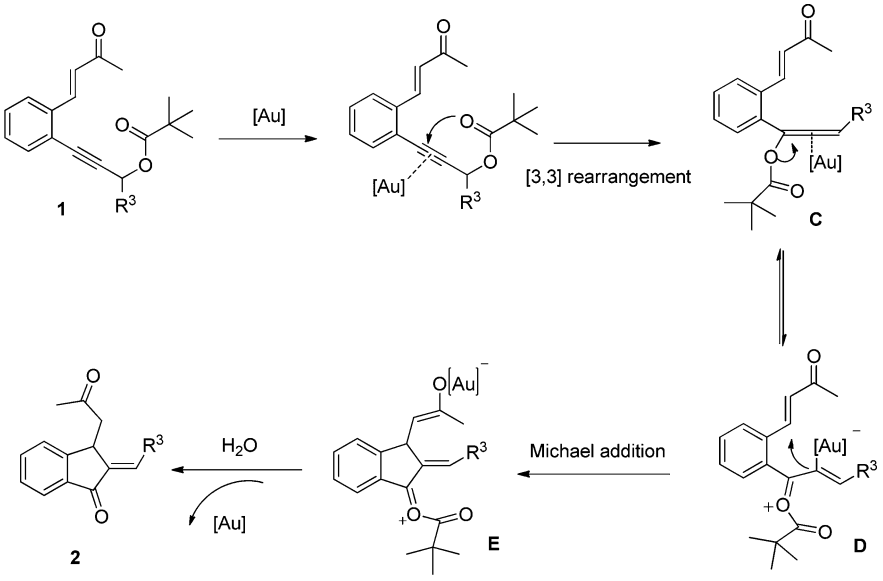
Table 2. continued

entry	substrate	time	products/ yield (%)[b]	E/Z[c]
18	 (**1r**)	10min	**2r**/47	6:1
19	 (**1s**)	15min	**2s**/83	4:1
20	 (**1t**)	12h	**2t**/76	>20:1

[a]All reactions were run under the following conditions unless otherwise indicated: 0.2 mmol of **1** with 5 mol % of $PPh_3AuCl/AgOTf$ in 3 mL of DCM at room temperature. [b]Isolated yield. [c]Ratio determined using ^1H NMR spectroscopy. Stereochemistry confirmed by X-ray diffraction of **2a,d,f,o**. [d]The reaction was run under 0.2 mmol of **1** with 10 mol % of $PPh_3AuCl/AgOTf$ in 3 mL of DCM at room temperature.

Scheme 5. Proposed Mechanism for the Formation of 2



the solvent was added with a saturated NH_4Cl solution and extracted with ethyl acetate, and the extracts were washed with a saturated NaCl solution, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 20/1) to give compound **s-2** (2.62 g, 9.5 mmol, 95%) as a yellow solid.

To a stirred solution of **s-2** and Et_3N (1.10 equiv) in DCM (0.4 M) were added pivaloyl chloride (1.05 equiv) and DMAP (0.05−0.10 equiv). The reaction progress was monitored by TLC. Upon consumption of the starting material, the reaction mixture was poured into water (10 mL). The aqueous and organic layers were separated, and the aqueous layer was extracted with DCM (2 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to give compound **1a**.

Typical Procedure for the Preparation of Product ***2a.*** To a solution of **1a** (0.20 mmol) in DCM (3.0 mL) was added 5 mol % of $PPh_3AuCl/AgOTf$. The resulting mixture was stirred at room temperature. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica gel to afford the corresponding 1*H*-inden-1-one **2a**.

Characterization Data of ***1a−t, 1aa,*** *and* ***1ab.*** *(E)-3-(2-(3-Oxobut-1-en-1-yl)phenyl)-1-phenylprop-2-yn-1-yl pivalate* ***(1a):*** eluent petroleum ether/ethyl acetate (20/1); yield 2.73 mmol (91%), light yellow liquid; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 16.4 Hz, 1H), 7.65−7.63 (m, 1H), 7.61−7.59 (m, 2H), 7.54−7.52 (m, 1H), 7.45−7.34 (m, 5H), 6.69 (t, J = 8 Hz, 2H), 2.32 (s, 3H), 1.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.9, 177.2, 141.2, 137.2, 136.3, 133.2, 129.9, 129.3, 129.2, 128.9, 128.8, 127.3, 126.0, 123.1,

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92.2, 84.2, 65.9, 38.8, 27.0, 26.6; IR (neat, cm^{-1}) 3432, 2928, 2362, 1732, 1670, 1613, 1539, 1454, 1363, 1255, 1138, 1010, 904, 758, 692.

*(E)-1-(2-Chlorophenyl)-3-(2-(3-oxobut-1-en-1-yl)phenyl)prop-2-yn-1-yl pivalate (**1b**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.79 mmol (93%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 16.4 Hz, 1H), 7.82 (dd, J = 7.2 Hz, J = 2 Hz, 1H), 7.65−7.63 (m, 1H), 7.54−7.52 (m, 1H), 7.43 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.39−7.31 (m, 4H), 7.00 (s, 1H), 6.69 (d, J = 16.8 Hz, 1H), 2.35 (s, 3H), 1.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.7, 176.8, 141.0, 136.4, 134.7, 133.2, 133.2, 130.1, 129.9, 129.8, 129.3, 129.2, 128.9, 127.2, 125.9, 122.9, 90.9, 84.3, 63.3, 38.9, 27.0, 26.6; IR (neat, cm^{-1}): 2971, 2918, 2849, 2362, 1734, 1671, 1481, 1362, 1257, 1139, 1041, 976, 877, 758, 692.

*(E)-1-(3-Chlorophenyl)-3-(2-(3-oxobut-1-en-1-yl)phenyl)prop-2-yn-1-yl pivalate (**1c**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.76 mmol (92%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, J = 16.4 Hz, 1H), 7.66−7.63 (m, 1H), 7.58 (s, 1H), 7.54−7.52 (m, 1H), 7.49−7.47 (m, 1H), 7.40−7.32 (m, 4H), 6.70 (d, J = 16.4 Hz, 1H), 6.65 (s, 1H), 2.35 (s, 3H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.6, 177.0, 140.9, 139.1, 136.3, 134.6, 133.2, 130.1, 129.8, 129.3, 129.0, 127.3, 126.0, 125.4, 122.7, 91.3, 84.6, 65.1, 38.8, 26.9, 26.6; IR (neat, cm^{-1}) 3379, 2975, 2920, 2870, 2335, 1736, 1672, 1616, 1477, 1362, 1255, 1136, 976, 760, 686, 534.

*(E)-1-(4-Chlorophenyl)-3-(2-(3-oxobut-1-en-1-yl)phenyl)prop-2-yn-1-yl pivalate (**1d**):* eluent petroleum ether/ethyl acetate (20/1); yield 3 mmol (95%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, J = 16.4 Hz, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.55−7.51 (m, 3H), 7.41−7.32 (m, 3H), 6.71 (d, J = 16.4 Hz, 1H), 6.65 (s, 1H), 2.34 (s, 3H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.5, 177.0, 140.8, 136.3, 135.7, 134.8, 133.2, 129.8, 129.3, 129.1, 129.0, 128.7, 126.0, 122.8, 91.5, 84.5, 65.2, 38.8, 26.9, 26.8; IR (neat, cm^{-1}) 3434, 2972, 2874, 2362, 1734, 1671, 1614, 1483, 1401, 1361, 1257, 1137, 1091, 1011, 822, 759, 677.

*(E)-3-(2-(3-Oxobut-1-en-1-yl)phenyl)-1-(o-tolyl)prop-2-yn-1-yl pivalate (**1e**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.88 mmol (96%), light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 16.4 Hz, 1H), 7.67−7.62 (m, 2H), 7.52−7.50 (m, 1H), 7.37−7.21 (m, 5H), 6.78 (s, 1H), 6.67 (d, J = 16.4 Hz, 1H), 2.50 (s, 3H), 2.30 (s, 3H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.8, 177.1, 141.2, 136.3, 136.1, 135.2, 133.2, 130.9, 129.8, 129.3, 129.1, 128.9, 127.6, 126.3, 125.9, 123.2, 91.9, 84.0, 64.1, 38.9, 27.0, 26.5, 19.1; IR (neat, cm^{-1}) 3389, 2968, 2362, 1733, 1671, 1614, 1477, 1390, 1257, 1139, 1030, 906, 758, 673.

*(E)-3-(2-(3-Oxobut-1-en-1-yl)phenyl)-1-(p-tolyl)prop-2-yn-1-yl pivalate (**1f**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.61 mmol (87%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 16.8 Hz, 1H), 7.64−7.62 (m, 1H), 7.53−7.48 (m, 3H), 7.37−7.31 (m, 2H), 7.22 (d, J = 8 Hz, 2H), 6.71−6.66 (m, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.7, 177.1, 141.1, 138.7, 136.2, 134.2, 133.1, 129.8, 129.4, 129.2, 129.1, 127.2, 125.9, 123.1, 92.3, 83.9, 65.7, 38.7, 26.9, 26.5, 21.1; IR (neat, cm^{-1}) 3432, 2975, 2929, 2859, 2362, 1732, 1672, 1615, 1478, 1362, 1255, 1140, 1024, 978, 922, 815, 759.

*(E)-1-(3-Methoxyphenyl)-3-(2-(3-oxobut-1-en-1-yl)phenyl)prop-2-yn-1-yl pivalate (**1g**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.58 mmol (86%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 16.8 Hz, 1H), 7.65−7.63 (m, 1H), 7.54−7.51 (m, 1H), 7.38−7.32 (m, 3H), 7.19−7.12 (m, 2H), 6.91 (dd, J = 8 Hz, J = 2 Hz, 1H), 6.71−6.66 (m, 2H), 3.83 (s, 3H), 2.32 (s, 3H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.9, 177.1, 159.8, 141.2, 138.7, 136.3, 133.2, 129.8, 129.3, 129.2, 125.9, 123.0, 119.4, 114.0, 113.0, 92.0, 84.1, 65.7, 55.2, 38.8, 27.0, 26.5; IR (neat, cm^{-1}) 3433, 2970, 2874, 2362, 1733, 1671, 1607, 1483, 1362, 1318, 1258, 1140, 1043, 976, 873, 759, 692.

*(E)-1-(3,4-Dimethylphenyl)-3-(2-(3-oxobut-1-en-1-yl)phenyl)-prop-2-yn-1-yl pivalate (**1h**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.55 mmol (85%), light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 16.8 Hz, 1H), 7.64−7.62 (m, 1H), 7.53−7.51 (m, 1H), 7.36−7.32 (m, 4H), 7.17 (d, J = 8 Hz, 1H), 6.68 (d, J = 16.8 Hz, 1H), 6.62 (s, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.8, 177.2, 141.3, 137.4, 137.0, 136.3, 134.7, 133.1, 130.0, 129.8, 129.2, 129.1, 128.5, 125.9, 124.7, 123.2, 92.5, 83.7, 65.8, 38.8, 27.0, 26.4, 19.8, 19.5; IR (neat, cm^{-1}) 3072, 2973, 2870, 1733, 1672, 1610, 1478, 1362, 1254, 1141, 1029, 977, 881, 757, 649.

*(E)-4-(2-(3-Oxobut-1-en-1-yl)phenyl)but-3-yn-2-yl pivalate (**1i**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.25 mmol (75%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, J = 16.4 Hz, 1H), 7.65−7.63 (m, 1H), 7.50 (dd, J = 6.8 Hz, J = 1.6 Hz, 1H), 7.37−7.29 (m, 2H), 6.72 (d, J = 16.4 Hz, 1H), 5.72−5.67 (m, 1H), 2.44 (s, 3H), 1.63 (d, J = 6.8 Hz, 3H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.7, 177.2, 141.1, 136.0, 133.0, 129.8, 129.0, 125.9, 123.2, 93.9, 81.7, 60.4, 38.6, 26.9, 26.7, 21.1; IR (neat, cm^{-1}) 3434, 2977, 2875, 2362, 1731, 1672, 1614, 1478, 1454, 1363, 1284, 1254, 1151, 1080, 1030, 980, 856, 759.

*(E)-1-(2-(3-Oxobut-1-en-1-yl)phenyl)hex-1-yn-3-yl pivalate (**1j**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.46 mmol (82%), light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, J = 16.8 Hz, 1H), 7.65−7.63 (m, 1H), 7.50−7.48 (m, 1H), 7.37−7.32 (m, 2H), 6.71 (d, J = 16.4 Hz, 1H), 5.61 (t, J = 6.8 Hz, 1H), 2.44 (s, 3H), 1.93−1.87 (m, 2H), 1.63−1.54 (m, 2H), 1.24 (s, 9H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.7, 177.4, 141.3, 136.1, 133.2, 129.8, 129.1, 128.9, 125.9, 123.4, 93.2, 82.3, 64.1, 38.8, 36.7, 27.0, 26.7, 18.5, 13.7; IR (neat, cm^{-1}) 3446, 2964, 2873, 1731, 1673, 1616, 1476, 1362, 1254, 1151, 1110, 979, 759.

*(E)-1-(2-(3-Oxobut-1-en-1-yl)phenyl)non-1-yn-3-yl pivalate (**1k**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.34 mmol (78%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, J = 16.4 Hz, 1H), 7.65−7.63 (m, 1H), 7.50−7.48 (m, 1H), 7.37−7.31 (m, 2H), 6.71 (d, J = 16.4 Hz, 1H), 5.59 (t, J = 6.8 Hz, 1H), 2.44 (s, 3H), 1.94−1.88 (m, 2H), 1.57−1.50 (m, 2H), 1.40−1.31 (m, 6H), 1.24 (s, 9H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.8, 177.4, 141.3, 136.1, 133.2, 129.8, 129.2, 128.9, 125.9, 123.4, 93.3, 82.3, 64.3, 38.8, 34.7, 31.6, 28.8, 27.0, 26.7, 25.1, 22.5, 14.0; IR (neat, cm^{-1}) 3414, 2928, 2861, 1729, 1674, 1564, 1468, 1364, 1251, 1152, 1070, 981.

*(E)-2-Methyl-4-(2-(3-oxobut-1-en-1-yl)phenyl)but-3-yn-2-yl pivalate (**1l**):* eluent petroleum ether/ethyl acetate (20/1); yield 1.2 mmol (40%), light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, J = 16.4 Hz, 1H), 7.64 (dd, J = 6.4 Hz, J = 2.8 Hz, 1H), 7.49−7.47 (m, 1H), 7.35−7.30 (m, 2H), 6.70 (d, J = 16.4 Hz, 1H), 2.51 (s, 3H), 1.78 (s, 6H), 1.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.5, 176.6, 141.8, 136.3, 133.1, 129.7, 129.2, 128.7, 125.8, 123.7, 96.5, 81.2, 71.5, 39.0, 28.9, 27.0, 26.6; IR (neat, cm^{-1}) 3390, 2978, 2874, 2363, 1732, 1672, 1616, 1477, 1363, 1286, 1254, 1172, 1121, 1028, 982, 871, 759, 672.

*(E)-1-(2-(3-Oxobut-1-en-1-yl)phenyl)-3-phenylpent-1-yn-3-yl pivalate (**1m**):* eluent petroleum ether/ethyl acetate (20/1); yield 1.05 mmol (35%), light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, j = 16.8 Hz, 1H), 7.63 (dd, J = 6 Hz, J = 2.8 Hz, 1H), 7.46−7.44 (m, 1H), 7.37−7.28 (m, 7H), 6.67 (d, J = 16.4 Hz, 1H), 3.37−3.24 (m, 2H), 2.41 (s, 3H), 1.78 (s, 3H), 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.6, 176.6, 141.8, 136.4, 135.6, 133.0, 131.0, 129.7, 129.4, 128.8, 127.9, 127.0, 125.9, 123.6, 95.5, 83.5, 74.5, 47.4, 39.2, 27.1, 26.5, 26.4; IR (neat, cm^{-1}) 3447, 2966, 2866, 1732, 1670, 1618, 1469, 1367, 1256, 1146, 1080, 980, 756, 701.

*(E)-1-((2-(3-Oxobut-1-en-1-yl)phenyl)ethynyl)cyclopentyl pivalate (**1n**):* eluent petroleum ether/ethyl acetate (20/1); yield 1.14 mmol (38%), light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, j = 16.8 Hz, 1H), 7.64−7.62 (m, 1H), 7.48−7.46 (m, 1H), 7.33−7.30 (m, 2H), 6.70 (d, J = 16.4 Hz, 1H), 2.50 (s, 3H), 2.36−2.21 (m, 4H), 1.84−1.80 (m, 4H), 1.20 (s, 9H) ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.5, 176.8, 141.9, 136.3, 133.1, 129.7, 129.2, 128.7, 125.9, 123.9, 96.0, 81.8, 80.3, 40.4, 39.0, 36.4, 33.5, 27.1, 26.7, 23.4; IR (neat, cm^{-1}) 3447, 2962, 2872, 1732, 1672, 1615, 1476, 1361, 1254, 1145, 978, 758, 676.

*(E)-3-(2-(3-Oxo-3-phenylprop-1-en-1-yl)phenyl)-1-phenylprop-2-yn-1-yl pivalate (**1o**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.1 mmol (70%), light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, J = 16 Hz, 1H), 8.00−7.97 (m, 2H), 7.73−7.71 (m, 1H), 7.60−7.53 (m, 5H), 7.47−7.44 (m, 2H), 7.41−7.32 (m, 5H),

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6.72 (s, 1H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.6, 177.1, 142.2, 138.1, 137.1, 136.7, 133.5, 132.7, 129.7, 129.0, 128.8, 128.7, 128.6, 127.4, 126.7, 124.6, 123.2, 92.1, 84.5, 65.8, 38.8, 27.0; IR (neat, cm^{-1}) 3428, 3062, 2971, 2924, 2873, 2361, 2229, 1969, 1733, 1665, 1604, 1479, 1402, 1324, 1274, 1214, 1139, 1017, 936, 757, 694.

*(E)-3-(2-(3-(4-Chlorophenyl)-3-oxoprop-1-en-1-yl)phenyl)-1-phenylprop-2-yn-1-yl pivalate (**1p**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.04 mmol (68%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.17 (d, J = 16 Hz, 1H), 7.91 (d, J = 8.8 Hz, 2H), 7.71−7.69 (m, 1H), 7.58−7.51 (m, 4H), 7.42−7.32 (m, 7H), 6.71 (s, 1H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.4, 177.1, 142.7, 139.1, 137.0, 136.5, 136.4, 133.6, 130.0, 129.9, 129.1, 128.9, 128.8, 128.7, 127.4, 126.9, 124.1, 123.2, 92.2, 84.5, 65.8, 38.8, 27.0; IR (neat, cm^{-1}) 3430, 3065, 2972, 2920, 2870, 1732, 1664, 1599, 1480, 1397, 1323, 1274, 1212, 1139, 1094, 1016, 938, 830, 758, 699.

*(E)-3-(2-(3-Oxo-3-(p-tolyl)prop-1-en-1-yl)phenyl)-1-phenylprop-2-yn-1-yl pivalate (**1q**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.22 mmol (74%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, J = 16 Hz, 1H), 7.90 (d, J = 8 Hz, 2H), 7.71 (d, J = 7.2 Hz, 1H), 7.59−7.52 (m, 4H), 7.41−7.30 (m, 5H), 7.25 (d, J = 8 Hz, 2H), 6.72 (s, 1H), 2.41 (s, 3H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.1, 177.1, 143.5, 141.8, 137.1, 136.8, 135.5, 133.5, 129.6, 129.3, 129.0, 128.7, 128.7, 127.4, 126.7, 124.7, 123.1, 92.0, 84.6, 65.8, 38.8, 26.9, 21.6; IR (neat, cm^{-1}) 3397, 3068, 2972, 2928, 2874, 2362, 1732, 1659, 1605, 1466, 1394, 1325, 1275, 1213, 1138, 1021, 908, 759, 700.

*(E)-3-(2-Methyl-6-(3-oxobut-1-en-1-yl)phenyl)-1-phenylprop-2-yn-1-yl pivalate (**1r**):* eluent petroleum ether/ethyl acetate (20/1); yield 1.95 mmol (65%), light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, J = 16.4 Hz, 1H), 7.61 (d, J = 6.8 Hz, 2H), 7.48−7.38 (m, 4H), 7.25−7.24 (m, 2H), 6.72 (s, 1H), 6.63 (d, j = 16.4 Hz, 1H), 2.44 (s, 3H), 2.30 (s, 3H), 1.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.8, 177.1, 141.8, 141.8, 137.2, 136.5, 131.0, 129.2, 128.8, 128.7, 128.6, 127.2, 123.3, 96.7, 83.0, 66.0, 38.8, 27.0, 26.5, 21.0; IR (neat, cm^{-1}) 3462, 2974, 2928, 2878, 2362, 1734, 1672, 1643, 1456, 1360, 1268, 1139, 1004, 934, 778, 700.

*(E)-3-(4-Methyl-2-(3-oxobut-1-en-1-yl)phenyl)-1-phenylprop-2-yn-1-yl pivalate (**1s**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.7 mmol (90%), light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 16.4 Hz, 1H), 7.59 (d, J = 7.2 Hz, 2H), 7.44−7.37 (m, 5H), 7.15 (d, J = 7.6 Hz, 1H), 6.70−6.66 (m, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 1.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.8, 177.2, 141.3, 139.4, 137.4, 136.2, 133.1, 130.9, 129.1, 128.8, 128.7, 127.3, 126.6, 120.3, 91.4, 84.4, 66.0, 38.8, 29.7, 27.0, 26.6, 21.5; IR (neat, cm^{-1}) 3404, 2923, 2857, 2361, 1732, 1670, 1461, 1371, 1261, 1139, 1075, 1023, 938, 824, 659.

*(E)-3-(5-Fluoro-2-(3-oxobut-1-en-1-yl)phenyl)-1-phenylprop-2-yn-1-yl pivalate (**1t**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.61 mmol (87%), light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, J = 16.8 Hz, 1H), 7.64−7.67 (m, 3H), 7.45−7.38 (m, 3H), 7.23−7.20 (m, 1H), 7.10−7.15 (m, 1H), 6.68 (s, 1H), 6.63 (d, J = 16.4 Hz, 1H), 2.30 (s, 3H), 1.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.5, 177.1, 164.3, 161.8, 139.9, 136.9, 132.8, 132.8, 129.0, 128.9, 128.1, 128.0, 127.2, 125.0, 119.8, 119.6, 117.1, 116.9, 93.2, 83.1, 83.0, 65.7, 38.9, 27.0, 26.7; IR (neat, cm^{-1}) 3443, 3068, 2972, 2917, 2862, 1734, 1672, 1602, 1482, 1361, 1260, 1137, 1025, 976, 699.

*(E)-3-(2-(3-Oxobut-1-en-1-yl)phenyl)-1-phenylprop-2-yn-1-yl acetate (**1aa**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.61 mmol (87%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 16.4 Hz, 1H), 7.65−7.62 (m, 3H), 7.55−7.53 (m, 1H), 7.46−7.44 (m, 3H), 7.42−7.32 (m, 2H), 6.72−6.78 (m, 2H), 2.31 (s, 3H), 2.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.7, 169.7, 141.1, 136.8, 136.3, 133.1, 129.8, 129.2, 129.1, 128.8, 127.6, 125.9, 122.9, 91.8, 84.4, 66.1, 26.6, 21.0; IR (neat, cm^{-1}) 3063, 2928, 2229, 1740, 1671, 1611, 1595, 1541, 1494, 1454, 1429, 1367, 1253, 1223, 1044, 976, 955, 834, 731, 547.

*(E)-3-(2-(3-Oxobut-1-en-1-yl)phenyl)-1-phenylprop-2-yn-1-yl propionate (**1ab**):* eluent petroleum ether/ethyl acetate (20/1); yield 2.7 mmol (90%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 16.4 Hz, 1H), 7.65−7.61 (m, 3H), 7.55−7.52 (m, 1H), 7.45−7.43 (m, 3H), 7.41−7.32 (m, 2H), 6.73−6.67 (m, 2H), 2.51−2.36 (m, 2H), 2.31 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.8, 173.2, 141.1, 136.9, 136.3, 133.1, 129.8, 129.2, 129.2, 129.0, 128.8, 127.6, 125.9, 122.9, 92.0, 84.3, 65.9, 27.5, 26.6, 8.9; IR (neat, cm^{-1}) 3304, 3033, 2942, 2228, 1743, 1693, 1671, 1611, 1494, 1477, 1421, 1360, 1314, 1254, 1166, 1079, 1018, 914, 824, 759, 731, 699, 633, 546, 460.

*Characterization Data of **2a**−**t**. (E)-2-Benzylidene-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one (**2a**):* eluent petroleum ether/ethyl acetate (10/1); yield (86%), E/Z (16/1) white solid, mp 89−91 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, J = 7.6 Hz, 1H), 7.67 (s, 1H), 7.59 (t, J = 8 Hz, 3H), 7.50 (d, J = 7.6 Hz, 1H), 7.46−7.37 (m, 4H), 5.03 (d, J = 9.6 Hz, 1H), 3.03−2.98 (m, 1H), 2.57 (dd, J = 18.4 Hz, J = 9.6 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.2, 193.6, 154.3, 138.9, 136.9, 135.1, 134.3, 133.5, 130.7, 129.7, 129.0, 128.1, 125.7, 124.3, 47.1, 36.4, 30.4; IR (neat, cm^{-1}) 3390, 3064, 2915, 2350, 1703, 1627, 1460, 1411, 1334, 1288, 1240, 1202, 1158, 1091, 1042, 973, 755, 694, 558; HRMS (ESI) calcd for $C_{19}H_{17}O_2$ $[M + H]^+$ 277.1226, found 277.1223.

*(E)-2-(2-Chlorobenzylidene)-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one (**2b**):* eluent petroleum ether/ethyl acetate (10/1); yield (95%), E/Z (9/1) light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 2 Hz, 1H), 7.90 (d, J = 9.6 Hz, 1H), 7.62−7.55 (m, 2H), 7.49−7.42 (m, 3H), 7.34−7.31 (m, 2H), 4.97 (d, J = 8.8 Hz, 1H), 2.76 (dd, J = 18.4 Hz, J = 2 Hz, 1H), 2.55 (dd, J = 18.4 Hz, J = 9.2 Hz, 1H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.6, 192.9, 154.0, 141.0, 136.9, 135.6, 135.3, 132.9, 130.4, 130.1, 130.1, 129.8, 128.1, 127.0, 125.6, 124.3, 47.1, 35.9, 30.2; IR (neat, cm^{-1}) 3397, 3266, 3067, 2921, 2847, 2356, 1704, 1631, 1466, 1433, 1362, 1287, 1240, 1159, 1093, 1046, 973, 752, 664; HRMS (ESI) calcd for $C_{19}H_{16}ClO_2$ $[M + H]^+$ 311.0838, found 311.0833.

*(E)-2-(3-Chlorobenzylidene)-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one (**2c**):* eluent petroleum ether/ethyl acetate (10/1); yield (71%), E/Z (16/1) white solid, mp 60−62 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, J = 7.6 Hz, 1H), 7.63−7.61 (m, 2H), 7.59−7.43 (m, 4H), 7.38−7.37 (m, 2H), 5.01 (d, J = 9.6 Hz, 1H), 2.97 (dd, J = 18.4 Hz, J = 1.6 Hz, 1H), 2.60 (dd, J = 18.4 Hz, J = 9.6 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.7, 193.3, 154.2, 140.3, 136.7, 136.2, 135.4, 135.0, 131.8, 130.5, 130.2, 129.6, 128.4, 128.2, 125.7, 124.4, 47.1, 36.3, 30.3; IR (neat, cm^{-1}) 3400, 2923, 2854, 2353, 1705, 1628, 1467, 1418, 1363, 1287, 1203, 1157, 1090, 1037, 979, 751, 676; HRMS (ESI) calcd for $C_{19}H_{16}ClO_2$ $[M + H]^+$ 311.0838, found 311.0833.

*(E)-2-(4-Chlorobenzylidene)-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one (**2d**):* eluent petroleum ether/ethyl acetate (10/1); yield (65%), E/Z (>20/1) white solid, mp 112−114 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, J = 7.6 Hz, 1H), 7.61−7.58 (m, 2H), 7.53−7.41 (m, 7H), 5.01 (d, J = 9.6 Hz, 1H), 2.95 (dd, J = 18.4 Hz, J = 1.6 Hz, 1H), 2.60 (dd, J = 18.4 Hz, 9.6 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.0, 193.4, 154.1, 139.4, 136.8, 135.8, 135.3, 132.8, 132.0, 131.8, 129.3, 128.2, 125.7, 124.4; IR (neat, cm^{-1}) 3411, 3068, 2919, 2854, 2337, 1703, 1627, 1482, 1410, 1335, 1287, 1240, 1202, 1090, 1047, 827, 753, 642; HRMS (ESI) calcd for $C_{19}H_{16}ClO_2$ $[M + H]^+$ 311.0838, found 311.0833.

*(E)-2-(2-Methylbenzylidene)-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one (**2e**):* eluent petroleum ether/ethyl acetate (10/1); yield (85%), E/Z (>20/1) light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92−7.90 (m, 2H), 7.61−7.57 (m, 1H), 7.49−7.41 (m, 3H), 7.29−7.23 (m, 3H), 4.95 (d, J = 9.2 Hz, 1H), 2.79 (dd, J = 18.4 Hz, J = 2 Hz, 1H), 2.50 (dd, J = 18.4 Hz, J = 9.2 Hz, 1H), 2.44 (s, 3H), 1.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.9, 193.3, 154.3, 139.5, 138.6, 137.1, 135.1, 133.4, 132.0, 130.6, 129.4, 128.5, 127.9, 126.2, 125.6, 124.3, 46.8, 36.1, 30.2, 20.0; IR (neat, cm^{-1}) 3395, 3064, 2921, 2847, 1703, 1625, 1469, 1363, 1289, 1212, 1158, 1092, 1044, 978, 750, 662; HRMS (ESI) calcd for $C_{20}H_{19}O_2$ $[M + H]^+$ 291.1385, found 291.1380.

*(E)-2-(4-Methylbenzylidene)-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one (**2f**):* eluent petroleum ether/ethyl acetate (10/1); yield (68%), E/Z (13/1) white solid, mp 132−134 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 1.2 Hz, 1H), 7.60−7.57 (m, 1H), 7.51−7.41 (m, 4H), 7.25 (d, J = 8 Hz, 2H), 5.01 (d, J =

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9.6 Hz, 1H), 3.03 (dd, J = 18.4 Hz, J = 1.6 Hz, 1H), 2.56 (dd, J = 18.4 Hz, J = 9.6 Hz, 1H), 2.40 (s, 3H), 2.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.3, 193.7, 154.2, 140.3, 137.9, 137.0, 135.0, 133.6, 131.5, 130.8, 129.8, 128.0, 125.7, 124.2, 47.0, 36.4, 30.4, 21.4; IR (neat, cm^{-1}) 3431, 2920, 2856, 1700, 1616, 1511, 1462, 1410, 1361, 1288, 1195, 1157, 1092, 1028, 972, 818, 745, 697; HRMS (ESI) calcd for $C_{20}H_{19}O_2$ $[M + H]^+$ 291.1385, found 291.1380.

(E)-2-(3-Methoxybenzylidene)-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one ***(2g):*** eluent petroleum ether/ethyl acetate (10/1); yield (50%), E/Z (8/1) light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, J = 8 Hz, 1H), 7.65 (d, J = 2 Hz, 1H), 7.61−7.57 (m, 1H), 7.50−7.42 (m, 2H), 7.35 (t, J = 8 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.10 (s, 1H), 6.95 (dd, J = 8 Hz, J = 2 Hz, 1H), 5.04 (d, J = 10 Hz, 1H) 3.83 (s, 3H), 3.03 (dd, J = 18.4 Hz, J = 10 Hz, 1H), 2.58 (dd, J = 18.4 Hz, J = 9.6 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.2, 193.6, 159.9, 154.3, 139.0, 136.9, 135.6, 135.2, 133.5, 129.9, 128.1, 125.7, 124.3, 123.2, 116.2, 115.1, 55.3, 47.2, 36.4, 30.5; IR (neat, cm^{-1}) 3412, 2923, 2850, 2338, 1702, 1622, 1584, 1462, 1329, 1263, 1161, 1091, 1043, 915, 739; HRMS (ESI) calcd for $C_{20}H_{19}O_3$ $[M + H]^+$ 307.1332, found 307.1329.

(E)-2-(3,4-Dimethylbenzylidene)-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one ***(2h):*** eluent petroleum ether/ethyl acetate (10/1); yield (60%), E/Z (7/1) white solid, mp 110−112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, J = 7.2 Hz, 1H), 7.63 (d, J = 1.2 Hz, 1H), 7.58 (d, J = 6.8 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.37−7.32 (m, 2H), 7.20 (d, J = 8 Hz, 1H), 5.03 (d, J = 9.6 Hz, 1H), 3.08−3.04 (m, 1H), 2.56 (dd, J = 18.4 Hz, J = 9.6 Hz, 1H), 2.30 (s, 3H), 2.30 (s, 3H), 2.12 (s. 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.4, 193.7, 154.4, 139.1, 137.8, 137.4, 137.1, 135.0, 133.8, 132.3, 131.9, 130.3, 128.4, 128.0, 125.6, 124.2, 47.1, 36.5, 30.4, 19.8, 19.8, 19.8; IR (neat, cm^{-1}) 3411, 2921, 2843, 2303, 1700, 1617, 1502, 1460, 1290, 1226, 1159, 1091, 1023, 917, 810, 744, 660; HRMS (ESI) calcd for $C_{21}H_{21}O_2$ $[M + H]^+$ 305.1549, found 305.1536.

(E)-2-Ethylidene-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one ***(2i):*** eluent petroleum ether/ethyl acetate (10/1); yield (85%), E/Z (>20/1) light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, J = 7.6 Hz, 1H), 7.58−7.54 (m, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 6.94−6.89 (m, 1H), 4.52 (d, J = 9.2 Hz, 1H), 3.03 (dd, J = 18 Hz, J = 2.8 Hz, 1H), 2.73 (dd, J = 18 Hz, J = 9.2 Hz, 1H), 2.17 (s, 3H), 1.96 (d, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.6, 192.6, 153.6, 141.2, 137.4, 134.9, 132.8, 127.9, 125.8, 124.2, 48.7, 35.6, 30.5, 14.9; IR (neat, cm^{-1}) 3411, 3010, 2917, 1707, 1649, 1605, 1462, 1364, 1287, 1241, 1204, 1158, 1094, 902, 752, 698; HRMS (ESI) calcd for $C_{14}H_{15}O_2$ $[M + H]^+$ 215.1069, found 215.1067.

(E)-2-Butylidene-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one ***(2j):*** eluent petroleum ether/ethyl acetate (10/1); yield (73%), E/Z (>20/1) light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, J = 8 Hz, 1H), 7.58−7.54 (m, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 6.84−6.80 (m, 1H), 4.51 (d, J = 9.6 Hz, 1H), 3.01 (dd, J = 18.4 Hz, J = 3.2 Hz, 1H), 2.73 (dd, J = 18.4 Hz, J = 9.6 Hz, 1H), 2.32−2.22 (m, 2H), 2.16 (s, 3H), 1.62−1.53 (m, 2H), 0.99 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.6, 192.9, 153.7, 140.2, 138.0, 137.5, 134.9, 127.9, 125.9, 124.2, 49.2, 35.8, 31.2, 30.6, 21.9, 13.9; IR (neat, cm^{-1}) 3369, 2963, 2870, 2707, 1707, 1648, 1609, 1458, 1371, 1290, 1238, 1158, 1040, 747; HRMS (ESI) calcd for $C_{16}H_{19}O_2$ $[M + H]^+$ 243.1384, found 243.1380.

(E)-2-Heptylidene-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one ***(2k):*** eluent petroleum ether/ethyl acetate (10/1); yield (76%), E/Z (>20/1) light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, J = 7.6 Hz, 1H), 7.58−7.46 (m, 2H), 7.40 (t, J = 7.6 Hz, 1H), 6.84−6.81 (m, 1H), 4.50 (d, J = 9.2 Hz, 1H), 3.00 (dd, J = 18 Hz, J = 3.2 Hz, 1H), 2.73 (dd, J = 18 Hz, J = 9.2 Hz, 1H), 2.36−2.25 (m, 2H), 2.16 (s, 3H), 1.57−1.50 (m, 2H), 1.31−1.29 (m, 5H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.6, 192.9, 153.7, 140.1, 138.3, 137.6, 134.9, 128.0, 125.9, 124.2, 49.2, 35.9, 31.6, 30.6, 29.3, 29.1, 28.6, 22.5, 14.0; IR (neat, cm^{-1}) 3396, 3076, 2925, 2858, 1708, 1649, 1608, 1462, 1361, 1289, 1244, 1157, 1095, 805, 748, 697; HRMS (ESI) calcd for $C_{19}H_{25}O_2$ $[M + H]^+$ 285.1858, found 285.1849.

3-(2-Oxopropyl)-2-(propan-2-ylidene)-2,3-dihydro-1H-inden-1-one ***(2l):*** eluent petroleum ether/ethyl acetate (10/1); yield (93%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, J = 7.6 Hz, 1H), 7.56−7.47 (m, 2H), 7.43−7.35 (m, 2H), 4.49 (d, J = 9.6 Hz, 1H), 2.98 (dd, J = 18 Hz, J = 2.4hz, 1H), 2.65 (dd, J = 18 Hz, 10 Hz, 1H), 2.41 (s, 3H), 2.14 (s, 3H), 1.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.0, 193.6, 152.4, 148.8, 138.8, 134.7, 134.2, 134.0, 132.0, 129.3, 129.1, 127.7, 125.5, 123.8, 49.5, 37.5, 30.6, 24.1, 20.6; IR (neat, cm^{-1}) 3399, 2917, 1691, 1630, 1461, 1370, 1291, 1250, 1156, 1027, 753, 665; HRMS (ESI) calcd for $C_{15}H_{17}O_2$ $[M + H]^+$ 229.1225, found 229.1223.

(E)-3-(2-Oxopropyl)-2-(1-phenylpropylidene)-2,3-dihydro-1H-inden-1-one ***(2m):*** eluent petroleum ether/ethyl acetate (10/1); yield (90%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.45−7.38 (m, 2H), 7.27−7.26 (m, 4H), 7.20 (t, J = 4 Hz, 1H), 4.53−4.47 (m, 2H), 4.19 (d, J = 13.2 Hz, 1H), 2.95 (dd, J = 18 Hz, 2.4 Hz, 1H), 2.67 (dd, J = 18 Hz, J = 9.6 Hz, 1H), 2.11 (s, 3H), 1.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.8, 193.4, 152.4, 150.4, 139.3, 138.7, 135.5, 134.5, 129.0, 128.4, 127.8, 126.2, 125.6, 124.0, 49.4, 38.5, 37.8, 30.6, 21.4; IR (neat, cm^{-1}) 3403, 3080, 3025, 2919, 2862, 1689, 1627, 1459, 1365, 1289, 1249, 1156, 1090, 1027, 969, 749, 700; HRMS (ESI) calcd for $C_{21}H_{21}O_2$ $[M + H]^+$ 305.1534, found 305.1536.

2-Cyclopentylidene-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one ***(2n):*** eluent petroleum ether/ethyl acetate (10/1); yield (84%), light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, J = 7.6 Hz, 1H), 7.54−7.50 (m, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 4.37 (d, J = 9.2 Hz, 1H), 3.10−2.94 (m, 3H), 2.67 (dd, J = 18 Hz, J = 9.6 Hz, 1H), 2.48−2.46 (m, 2H), 2.14 (s, 3H), 1.88−1.81 (m, 2H), 1.78−1.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.2, 193.2, 160.6, 153.0, 138.7, 134.0, 131.5, 127.7, 125.6, 123.7, 48.1, 37.9, 33.7, 33.0, 30.6, 26.3, 25.5; IR (neat, cm^{-1}) 3370, 2927, 2773, 2641, 2493, 1695, 1636, 1542, 1460, 1371, 1301, 1161, 1059, 722, 660, 540; HRMS (ESI) calcd for $C_{17}H_{19}O_2$ $[M + H]^+$ 255.1382, found 255.1380.

(E)-2-Benzylidene-3-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-inden-1-one ***(2o):*** eluent petroleum ether/ethyl acetate (10/1); yield (55%), E/Z (8/1) white solid, mp 106−108 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, J = 7.6 Hz, 1H), 7.85−7.83 (m, 2H), 7.74 (d, J = 1.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 6.8 Hz, 3H), 7.42−7.33 (m, 6H), 5.31 (d, J = 9.6 Hz, 1H), 3.45 (dd, J = 18.4 Hz, J = 2 Hz, 1H), 3.21 (dd, J = 18.4 Hz, J = 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.7, 193.8, 154.4, 139.1, 136.9, 136.5, 135.1, 134.3, 133.6, 133.4, 130.8, 129.7, 129.0, 128.6, 128.1, 126.0, 124.3, 42.4, 36.7; IR (neat, cm^{-1}) 3359, 2923, 2854, 2291, 1691, 1627, 1455, 1337, 1287, 1248, 1210, 1088, 1033, 752, 689; HRMS (ESI) calcd for $C_{24}H_{19}O_2$ $[M + Na]^+$ 361.1212, found 361.1199.

(E)-2-benzylidene-3-(2-(4-chlorophenyl)-2-oxoethyl)-2,3-dihydro-1H-inden-1-one ***(2p):*** petroleum ether/ethyl acetate (10/1); yield (45%), E/Z (>20/1) white solid, mp 62−64 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, J = 7.6 Hz, 1H) 7.85−7.83 (m, 2H), 7.74 (d, J = 1.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.54−7.51 (m, 3H), 7.42−7.33 (m, 6H), 5.31 (d, J = 9.6 Hz, 1H), 3.45 (dd, J = 18.4 Hz, J = 2 Hz, 1H), 3.21 (dd, J = 18.4 Hz, J = 10 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.5, 193.6, 154.2, 140.0, 138.9, 137.0, 135.1, 134.8, 134.3, 133.8, 130.7, 129.8, 129.5, 129.0, 129.0, 128.1, 125.9, 124.3, 42.3, 36.7, 27.0; IR (neat, cm^{-1}) 3441, 3334, 3071, 2920, 2858, 2784, 1692, 1624, 1596, 1459, 1400, 1338, 1286, 1249, 1209, 1093, 984, 803, 756, 694; HRMS (ESI) calcd for $C_{24}H_{18}ClO_2$ $[M + H]^+$ 373.1007, found 373.0995.

(E)-2-Benzylidene-3-(2-oxo-2-(p-tolyl)ethyl)-2,3-dihydro-1H-inden-1-one ***(2q):*** eluent petroleum ether/ethyl acetate (10/1); yield (62%), E/Z (>20/1) light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8 Hz, 3H), 7.64 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 3.6 Hz, 2H), 7.41−7.31 (m, 4H), 7.19 (d, J = 8 Hz, 2H), 5.29 (d, J = 9.6 Hz, 1H), 3.42 (dd, J = 18.4 Hz, J = 2 Hz, 1H), 3.18 (dd, J = 18.4 Hz, J = 9.6 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.2, 193.8, 154.5, 144.3, 139.2, 136.9, 135.1, 134.3, 134.1, 133.6, 130.8, 129.7, 129.3, 129.0, 128.2, 128.0, 126.0, 124.2, 42.2, 36.7, 27.0, 21.6; IR (neat, cm^{-1}) 3338, 3192, 3060, 2923, 2275, 1690, 1618, 1459, 1409, 1338, 1288, 1251, 1181, 1094, 972, 803, 758, 696; HRMS (ESI) calcd for $C_{25}H_{21}O_2$ $[M + H]^+$ 353.1540, found 353.1536.

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*(E)-2-Benzylidene-7-methyl-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one (**2r**):* eluent petroleum ether/ethyl acetate (10/1); yield (47%), *E*/*Z* (6/1) white solid, mp 72−74 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60−7.56 (m, 3H), 7.45−7.37 (m, 4H), 7.30−7.26 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 4.99 (d, *J* = 9.6 Hz, 1H), 2.99−2.94 (m, 1H), 2.74 (s, 3H), 2.56 (dd, *J* = 18.8 Hz, *J* = 9.6 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.2, 194.5, 155.0, 139.4, 134.6, 134.4, 134.3, 132.6, 130.8, 130.6, 129.9, 129.5, 128.9, 127.9, 122.8, 47.3, 35.9, 30.4, 18.6; IR (neat, cm^{-1}) 3409, 3146, 3021, 2921, 2850, 2637, 1695, 1627, 1594, 1445, 1198, 1158, 1046, 785, 659; HRMS (ESI) calcd for $C_{26}H_{19}INO$ $[M + H]^+$ 488.0501, found 488.0511.

*(E)-2-Benzylidene-5-methyl-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one (**2s**):* eluent petroleum ether/ethyl acetate (10/1); yield (83%), *E*/*Z* (4/1) light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 8 Hz, 1H), 7.64 (d, *J* = 1.6 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.45−7.37 (m, 3H), 7.28−7.23 (m, 2H), 4.98 (d, *J* = 9.6 Hz, 1H), 3.01−2.96 (m, 1H), 2.56 (dd, *J* = 18.4 Hz, *J* = 9.6 Hz, 1H), 2.44 (s, 3H), 2.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.2, 193.1, 154.8, 146.5, 139.3, 134.4, 133.0, 130.6, 129.5, 129.3, 128.9, 127.9, 125.9, 124.1, 47.2, 36.1, 30.3, 22.3; IR (neat, cm^{-1}) 3395, 2923, 2858, 1700, 1618, 1447, 1327, 1278, 1206, 1153, 1106, 1036, 970, 766, 697, 552; HRMS (ESI) calcd for $C_{20}H_{19}O_2$ $[M + H]^+$ 291.1385, found 291.1380.

*(E)-2-Benzylidene-6-fluoro-3-(2-oxopropyl)-2,3-dihydro-1H-inden-1-one (**2t**):* eluent petroleum ether/ethyl acetate (10/1); yield (76%), *E*/*Z* (>20/1) light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 1.6 Hz, 1H), 7.57−7.40 (m, 7H), 7.32−7.27 (m, 1H), 4.99 (d, *J* = 9.2 Hz, 1H), 3.02 (dd, *J* = 18.8 Hz, *J* = 1.6 Hz, 1H), 2.54 (dd, *J* = 18.8 Hz, *J* = 10 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.1, 192.6, 163.9, 161.4, 149.7, 138.9, 138.8, 134.1, 130.7, 129.9, 129.0, 127.5, 127.4, 122.7, 122.4, 110.2, 110.0, 47.1, 35.9, 30.3; IR (neat, cm^{-1}) 3387, 3060, 2921, 2862, 1704, 1624, 1482, 1441, 1360, 1268, 1163, 1103, 1038, 741, 696, 555; HRMS (ESI) calcd for $C_{19}H_{16}FO_2$ $[M + H]^+$ 295.1139, found 295.1129.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^{1}H NMR and ^{13}C NMR spectra for all compounds and CIF files giving crystal data for **2a,d,f,o**. 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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