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Gold-Catalyzed Cycloisomerization of 1,6-Diyne Esters to 1*H*-Cyclopenta[*b*]naphthalenes, *cis*-Cyclopenten-2-yl *δ*-Diketones, and Bicyclo[3.2.0]hepta-1,5-dienes

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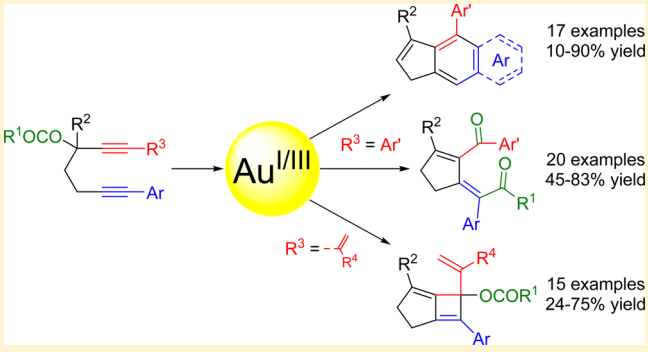
Supporting Information

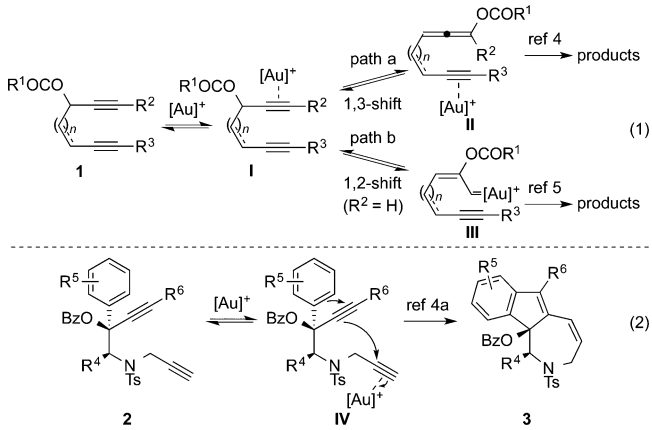
ABSTRACT: A synthetic method to chemoselectively prepare 1*H*-cyclopenta[*b*]naphthalenes, *cis*-cyclopenten-2-yl *δ*-diketones, and bicyclo[3.2.0]hepta-1,5-dienes efficiently by gold-catalyzed cycloisomerization of 1,6-diyne esters is described. These three product classes were accessed divergently by taking advantage of the electronic and steric differences between a phosphine and NHC (NHC = *N*-heterocyclic carbene) ligand in the respective gold(I) complexes and that of gold(III) complex combined with substrate substitution patterns and optimized reaction conditions. In the presence of $[PhCNAuIPr]^+SbF_6^-$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidine) as the catalyst, substrates with a pendant aryl group at the acetate alkynyl position were found to undergo preferential 1,3-acyloxy migration/5-*exo*-*dig* cyclization/Friedel−Crafts reaction to give 1*H*-cyclopenta[*b*]naphthalenes. In contrast, the analogous reactions with $PicAuCl_2$ (Pic =2-picolinate) were found to proceed by selective 1,3-acyloxy migration/5-*exo*-*dig* cyclization/1,5-acyl migration to afford *cis*-cyclopenten-2-yl *δ*-diketones. Changing the catalyst to $[MeCNAu(JohnPhos)]^+SbF_6^-$ (JohnPhos = (1,1′-biphenyl-2-yl)-di-*tert*-butylphosphine) and the acetate alkynyl position from an aryl to vinyl substituent in the starting ester led to 1,3-acyloxy migration/5-*exo*-*dig* cyclization/Prins-type [2 + 2]-cycloaddition to provide bicyclo[3.2.0]hepta-1,5-dienes.



INTRODUCTION

Gold-catalyzed 1,*n*-diyne cycloisomerizations have emerged as one of the most powerful synthetic strategies for the assembly of complex polycyclic scaffolds.[1−6] In particular, esters and carbonates of 1,*n*-diynes **1** have been employed in elegant syntheses to a variety of targets, as shown in Scheme 1.[4,5] Typically, these reactions were described to proceed with 1,3-acyloxy migration of the carboxylate group in gold-activated species **I** to give the allenyl intermediate **II** and subsequent products (Scheme 1, eq 1, path a).[4] Recently, we and others demonstrated two exceptions to this mode of reactivity. The first is the [2,3]-sigmatropic rearrangement of **I** to the putative gold carbenoid complex **III** (Scheme 1, eq 1, path b).[5] Further functionalization of this newly formed organometallic species by the remaining pendant group was then shown to give a variety of synthetically useful carbocyclic motifs. The second is the gold(I)-catalyzed concerted tandem 5-*endo*-*dig*/7-*endo*-*dig* cyclization of *syn*-1,7-diyne esters **2** to indeno[1,2-*c*]azepines **3** (Scheme 1, eq 2).[4a] In line with our present investigations in the field of gold-catalyzed alkyne cycloisomerizations,[6] we were interested in assessing 1,6-diyne esters **1** (Scheme 2). We postulated that these substrates would be prone to a 1,3-acyloxy

Scheme 1. Gold-Catalyzed Reaction Pathways of 1,*n*-Diyne Esters



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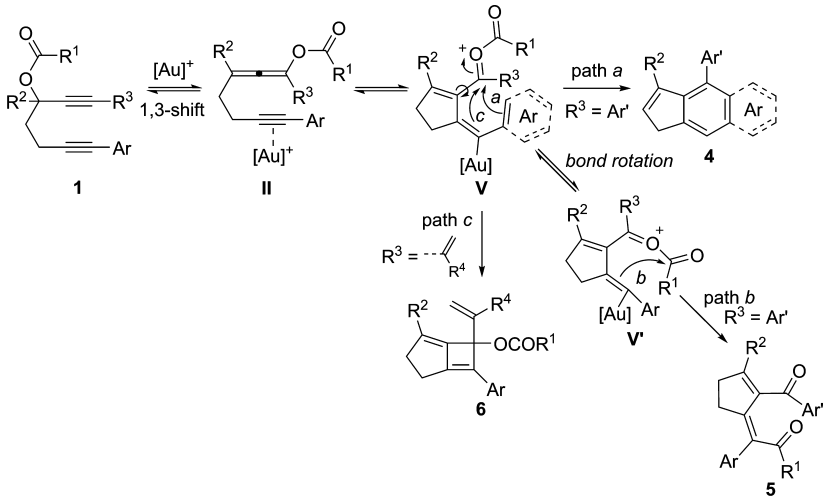
Scheme 2. Gold-Catalyzed Cycloisomerization of 1,6-Diyne Esters

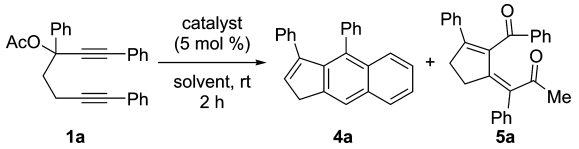


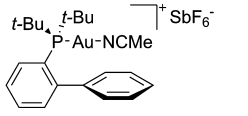
shift followed by activation of the remaining pendant substituted alkyne moiety by the metal catalyst. This may result in 5-*exo-dig* cyclization of the ensuing gold-coordinated species **II** to give the putative vinyl gold intermediate **V**. In doing so, we found that under NHC−gold(I) catalysis, an intramolecular Friedel−Crafts reaction involving trapping of the intermediate **V** gave 1*H*-cyclopenta[*b*]naphthalenes **4** (Scheme 2, path a).[7] On the other hand, *cis*-cyclopenten-2-yl *δ*-diketones **5** were formed selectively in the presence of a gold(III) catalyst (Scheme 2, path b).[8] In addition, when the acetate alkynyl substituent R^2 in the starting ester was changed to an isoprenyl moiety, reaction with a phosphine−gold(I) complex as the catalyst was discovered to result in Prins-type [2 + 2]-cycloaddition to give bicyclo[3.2.0]hepta-1,5-dienes **6** (Scheme 2, path c).[9,10] We report herein the development of this chemistry that provides an expedient and divergent approach to three different structural motifs under mild conditions at room temperature; the carbocyclic scaffolds of which may be found in a variety of bioactive molecules, functional materials, and their building blocks.[11−14]

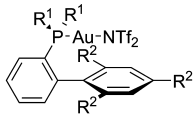
RESULTS AND DISCUSSION

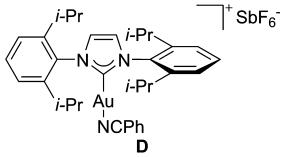
Our investigations commenced by establishing the reaction conditions for the gold-catalyzed cycloisomerization of 1,6-diyne ester **1a** (Table 1). This initially revealed that treatment of **1a** with 5 mol % of phosphine−gold(I) catalyst **A** in dichloromethane at room temperature for 2 h afforded the tricyclic 1*H*-cyclopenta[*b*]naphthalene **4a** in 64% yield (entry 1).[15] The structure of the aromatic carbocycle was determined by NMR spectroscopic measurements and X-ray crystallography.[16] Slightly lower product yields of 56 and 58% were obtained for the analogous reactions catalyzed by the triflimide-containing gold(I) complexes **B** and **C** (entries 2 and 3). Replacing the gold(I)−phosphine complex **A** with the NHC−Au(I) complex **D** proved slightly more efficacious, providing **4a** in 69% yield (entry 4). In contrast, control reactions catalyzed by either Ph_3PAuCl or $AgSbF_6$ were found to lead to the recovery of the substrate in the former and decomposition to a mixture of unidentifiable products in the latter (entries 8 and 11). Interestingly, further control experiments mediated by AuCl and $PtCl_2$ were found to lead to a change in product selectivity with the exclusive generation of the *cis*-cyclopenten-2-yl *δ*-diketone **5a** in 68 and 50% yield, respectively (entries 9

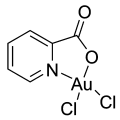
Table 1. Optimization of Reaction Conditions[a]











			yield (%)	
entry	catalyst	solvent	4a	5a
1	**A**	CH_2Cl_2	64	
2	**B**	CH_2Cl_2	58[b]	
3	**C**	CH_2Cl_2	56[b]	
4	**D**	CH_2Cl_2	69	
5	**D**	toluene	43[b]	
6	**D**	MeCN	62	
7[c]	**D**	THF	18[b]	
8[c]	Ph_3PAuCl	CH_2Cl_2	*d*	
9[c]	AuCl	CH_2Cl_2		68
10[c]	$PtCl_2$	CH_2Cl_2		50[b]
11	$AgSbF_6$	CH_2Cl_2	*e*	
12	**E**	CH_2Cl_2		83
13	**E**	toluene		73
14	**E**	MeCN		62
15[c]	**E**	THF		50[b]

[a]All reactions were performed on a 0.2 mmol scale with a catalyst/**1a** ratio of 1:20 at room temperature. [b]Complex mixture of unidentifiable decomposition adducts obtained in addition to the product. [c]Reaction time = 24 h. [d]No reaction based on ^{1}H NMR analysis of the crude mixture. [e]Decomposition observed based on ^{1}H NMR measurements and TLC analysis of the crude mixture.

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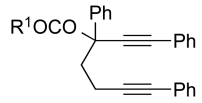
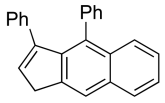
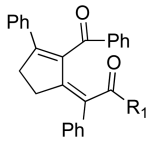
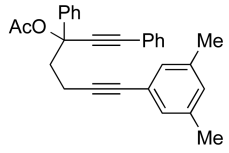
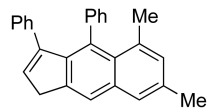
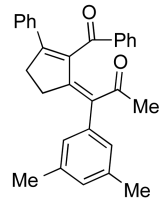
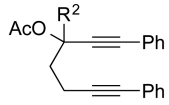
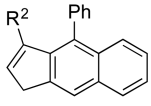
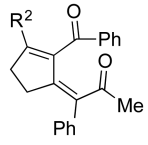
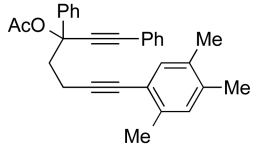
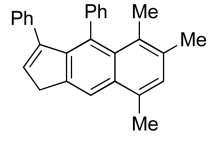
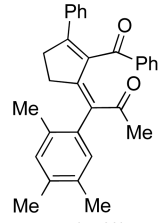
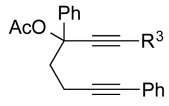
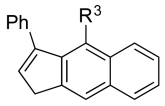
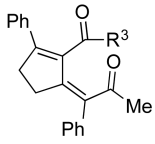
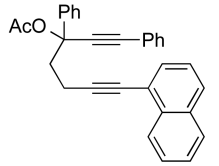
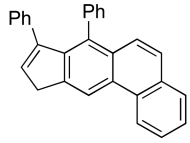
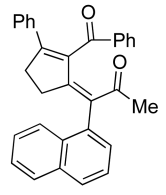
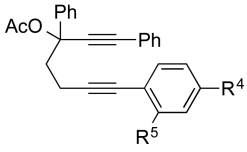
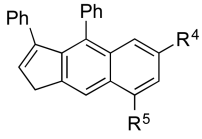
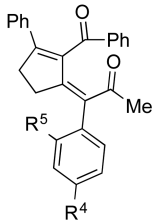
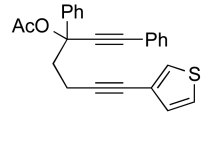
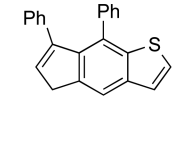
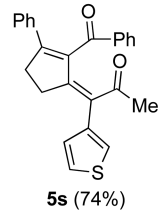
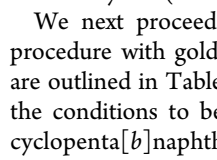
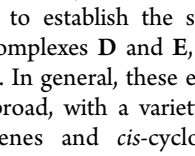
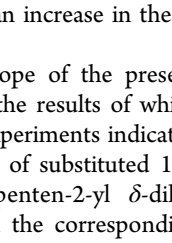
Table 2. Cycloisomerization of 1,6-Diyne Esters 1b−t Catalyzed by D and E[a]

substrate **1**	product **4**[b]	product **5**[c]	substrate **1**	product **4**[b]	product **5**[c]
					
1b: R^1 = Bn **1c**: R^1 = *t*-Bu **1d**: R^1 = cyclopropyl	**4a** (65%) **4a** (90%) **4a** (73%)	**5b** (68%) **5c** (-[d]) **5d** (67%)	**1p**	**4p** (53%)	**5p** (70%)
					
1e: R^2 = Me **1f**: R^2 = cyclopropyl **1g**: R^2 = 4-ClC_6H_4	**4e** (67%) **4f** (60%) **4g** (71%)	**5e** (23%) **5f** (50%) **5g** (50%)	**1q**	**4q** (42%)	**5q** (58%)
					
1h: R^3 = 4-FC_6H_4 **1i**: R^3 = 4-MeC_6H_4 **1j**: R^3 = 3-thiophenyl	**4h** (86%) **4i** (41%) **4j** (59%)	**5h** (78%) **5i** (71%) **5j** (59%)	**1r**	**4r** (57%)	**5r** (45%)
					
1k: R^4 = F, R^5 = H **1l**: R^4 = Br, R^5 = H **1m**: R^4 = *n*-Pent, R^5 = H **1n**: R^4 = Me, R^5 = H **1o**: R^4 = H, R^5 = Me	**4k** (65%) **4l** (81%) **4m** (57%) **4n** (68%) **4o** (81%)	**5k** (68%) **5l** (81%) **5m** (78%) **5n** (78%) **5o** (54%)	**1s**	**4s** (10%)	**5s** (74%)
					
			1t	**4t** (52%)	**5t** (71%)

[a]All reactions were performed on a 0.2 mmol scale with a catalyst/**1** ratio = 1:20 in dichloromethane at room temperature for 10 min−42 h. Values in parentheses denote product yield. [b]Reaction conducted with gold(I) catalyst **D**. [c]Reaction conducted with gold(III) catalyst **E**. [d]Substrate decomposition observed based on ^{1}H NMR measurements and TLC analysis of the crude reaction mixture.

and 10). The *Z*-stereochemistry and structure of the cyclopentene adduct was ascertained by NMR spectroscopic measurements and X-ray crystallographic analysis.[16,17] An increase in the yield of **5a** to 83% was subsequently achieved when the reaction was conducted with the gold(III) complex **E** as the catalyst (entry 12).

With gold(I) and gold(III) complexes **D** and **E** established as the optimal catalysts for the selective formation of **4a** and **5a**, the effect of the solvent was next assessed (entries 5−7 and 13−15). A comparable yield of 62% of **4a** was observed for the gold(I) complex **D**-catalyzed reaction with MeCN as the solvent (entry 6). However, the analogous reactions mediated by the same metal catalyst in toluene and THF proved less efficient, achieving product yields of 43 and 18% (entries 5 and 7). Likewise, the Au(III) complex **E**-mediated reactions in toluene, MeCN and THF did not lead to an increase in the *δ*-diketone yield (entries 13−15).

We next proceeded to establish the scope of the present procedure with gold complexes **D** and **E**, the results of which are outlined in Table 2. In general, these experiments indicated the conditions to be broad, with a variety of substituted 1*H*-cyclopenta[*b*]naphthalenes and *cis*-cyclopenten-2-yl *δ*-diketones furnished in yields up to 90% from the corresponding starting materials **1b−t**. Reactions of substrates possessing a benzoyl (**1b**) or cyclopropanecarbonyl (**1d**) moiety in place of an acetyl migrating group proceeded well to afford the corresponding products **4a**, **5b**, and **5d** in 65−73% yield. Introducing a 4-chlorophenyl substituent at the propargylic

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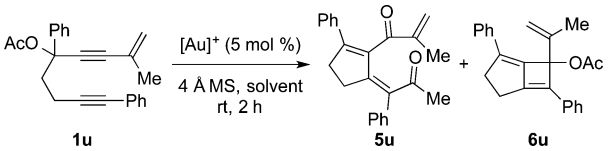
carbon center (**1g**) or replacing this aryl group with a cyclopropyl motif (**1f**) in the substrate also gave the corresponding targets **4f**, **5f**, **4g**, and **5g** in 50−71% yield. Variation of the acetate alkynyl position with a 4-fluorophenyl (**1h**), 4-methylphenyl (**1i**), or 3-thiophene-yl (**1j**) group did not significantly affect the course of the reaction in the presence of the gold(I) catalyst **D** or gold(III) complex **E**. A similar outcome was observed for starting actetates with a pendant 4-fluorophenyl (**1k**), 4-bromophenyl (**1l**), 4-*n*-pentylphenyl (**1m**), 4-methylphenyl (**1n**), 2-methylphenyl (**1o**), 3,5-dimethylphenyl (**1p**), or 2-thiophene-yl (**1t**) substituent at the alkynyl carbon center. In these transformations, the corresponding products **4h−p,t** and **5h−p,t** were obtained in yields of 41−86%. The structures of **4h**, **4j** and **5h** were also confirmed by X-ray crystallographic measurements.[16] Modification of the pendant alkynyl position of the substrate with bulkier 2,4,5-trimethylphenyl (**1q**) and 1-naphthalenyl (**1r**) substituents furnished the corresponding cycloadducts **4q**, **4r**, **5q**, and **5r** in 42−58% yield along with the structure of **4r** being determined by X-ray crystallography.[16] In contrast, exchanging the propargylic phenyl group with a methyl moiety at the R^2 position in the substrate, as in **1e**, was found to give mixed results. While the reaction of this starting ester in the presence of gold(I) catalyst **D** gave **4e** in 67% yield, the analogous transformation mediated by the gold(III) complex **E** afforded **5e** in 23% yield. Likewise, reactions of **1s** with a 3-thiophenyl group at the pendant alkynyl position gave **4s** and **5s** in contrasting respective yields of 10 and 74%. In our hands, reaction with the pivaloyl ester **1c** mediated by gold(I) catalyst **D** was the only instance that gave **4a** in 90% yield, but treatment with gold(III) complex **E** was met with substrate decomposition.

Intriguingly, the presence of an isoprenyl group in **1u** was observed to lead to a markedly different reaction outcome (Table 3). Treatment of this substrate with the gold(I) catalyst **A** in toluene at room temperature over 2 h led to the construction of the bicyclo[3.2.0]hepta-1,5-diene **6u** and the *cis*-cyclopenten-2-yl *δ*-diketone **5u** in 40 and 25% yield, respectively (Table 3, entry 1). The structure of **6u** was determined by NMR spectroscopic measurements and X-ray crystallography.[16] With this unexpected result, we extended our investigation so as to establish the optimal reaction conditions for this new pathway. When the reaction of **1u** with gold(I) complex **A** was repeated in the presence of 4 Å molecular sieves (MS), the yields of **6u** and **5u** were improved to 61 and 35% (entry 2). However, no improvement in product chemoselectivity or yield was obtained by employing the gold(I) phosphine complex **C**, NHC−gold(I) complex **D**, gold(III) complex **E**, or AuCl as the catalyst, and extending the reaction time from 2 to 24 h (entries 3−6). In each instance, the cycloadducts **6u** and **5u** were furnished in respective yields of 13−57 and 31−35%. Likewise, the analogous gold(I) complex **A**-catalyzed transformations in dichloromethane, benzene, *n*-hexane, cyclohexane or *n*-pentane instead of toulene as the reaction medium gave **6u** and **5u** in respective yields of 25−68 and 8−40% (entries 7−11). Using predried *n*-pentane as the solvent improved both product yield and chemoselectivity, with the cyclobutene **6u** and *δ*-diketone **5u** adducts furnished in 72 and 13% yield, respectively, after 24 h (entry 12).

Table 3. Optimization of Reaction Conditions[a]



1u 5u 6u

entry	catalyst	solvent	yield (%) 5u	yield (%) 6u
1[c]	**A**	toluene	25	40
2	**A**	toluene	35	61
3[d]	**C**	toluene	35	57
4[d]	**D**	toluene	31[b]	13
5	**E**	toluene	34	57
6[d]	AuCl	toluene	31	36
7	**A**	CH_2Cl_2	40	27
8	**A**	benzene	23[b]	25
9[d]	**A**	*n*-hexane	8	59
10[d]	**A**	cyclohexane	25	67
11[d]	**A**	*n*-pentane	16	68
12[d]	**A**	*n*-pentane[e]	13	72

[a]All reactions were performed on a 0.2 mmol scale with a catalyst/**1u** ratio of 1:20 and 4 Å MS (200 mg) at room temperature for 2 h. [b]Complex mixture of unidentifiable decomposition adducts obtained in addition to the product. [c]Reaction conducted without 4 Å MS. [d]Reaction time = 24 h. [e]Solvent dried over 4 Å MS prior to use.

With the optimal conditions established, we proceeded to investigate the substrate scope of this transformation (Table 4). Overall, these experiments showed that with Au(I) complex **A** as the catalyst, the reaction conditions proved to be broad and a variety of cyclobutene adducts could be afforded in up to 75% yield from the corresponding substrates **1v−α**, **1γ** and **1ε−λ**. Modification of the pendant alkynyl group with a variety of aryl substituents in the substrate had little impact of the efficiency of the reaction. The best results were obtained with 2-methylphenyl (**1θ**) and 2,4,5-trimethylphenyl (**1κ**) substituted starting materials providing their respective targets **6θ** and **6κ** in 75 and 72% yield, with the latter also allowing structure confirmation by X-ray crystallography.[16] The analogous reactions with 4-fluorophenyl- (**1ε**), 4-methylphenyl- (**1ζ**), 4-*n*-pentylphenyl- (**1η**), 3,5-dimethylphenyl- (**1ι**), and 2-thiophene-yl-substituted (**1λ**) derivatives afforded the corresponding cyclobutenes **6ε−η**, **6ι**, and **6λ** in 60−69% yield. Similarly, product yields of 68 and 63% were observed when the vinyl moiety was replaced with 2-heptenyl (**1γ**) or a methyl substituent was added to the propargylic phenyl ring in the substrate (**1z**). On the other hand, the analogous reactions with substrates containing the propargylic substituents 4-chlorophenyl (**1y**) and 1-naphthalenyl (**1α**) led to the formation of **6y** and **6α** in lower yields of 34 and 26%. Additionally, modification of the migratory acetyl group with a benzoyl (**1v**), pivaloyl (**1w**), and cyclopropylcarbonyl (**1x**) moiety was found to give the corresponding cyclobutene targets **6v−x** in lower yields of 24−48%. For cyclizations involving **1ζ** and **1θ−κ**, mixtures of both the cyclobutene and *δ*-diketone adduct were also obtained in ratios of 6:1 to 16:1 but the latter could not be isolated to a level of sufficient purity due to the scale of the reactions. Formation of the desired cyclobutene product was precluded for substrates with a pendant propargylic methyl moiety (**1β**) and a vinylogous phenyl substituent (**1δ**).

A tentative mechanism for the present Au(I)- and Au(III)-catalyzed 1*H*-cyclopenta[*b*]naphthalene **4**, *cis*-cyclopenten-2-yl *δ*-diketone **5** and bicyclo[3.2.0]hepta-1,5-diene **6** forming reactions is presented in Scheme 3. It is proposed that the reaction pathway may initially proceed by activation of the

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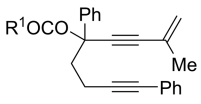
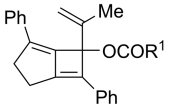
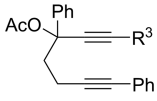
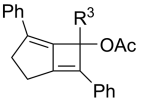
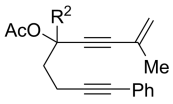
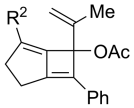
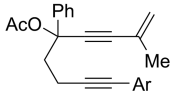
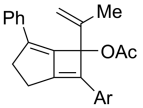
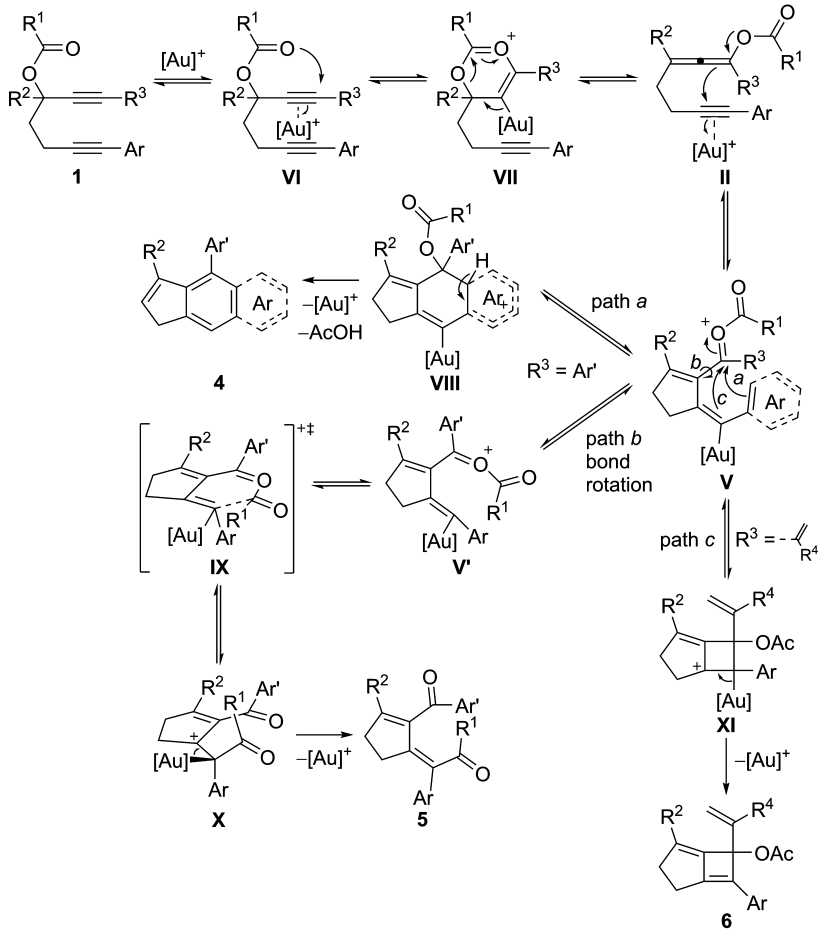
Table 4. Cycloisomerization of 1,6-Diyne Esters 1v–λ Catalyzed by A[a]

substrate **1**	product **6**	substrate **1**	product **6**
			
1v: R^1 = Bn **1w**: R^1 = *t*-Bu **1x**: R^1 = cyclopropyl	**6v** (48%) **6w** (24%) **6x** (31%)	**1γ**: R^3 = 2-heptenyl **1δ**: R^3 = 	**6γ** (68%) **6δ** (-[c])
			
1y: R^2 = 4-ClC_6H_4 **1z**: R^2 = 4-MeC_6H_4 **1α**: R^2 = 1-naphthalenyl **1β**: R^2 = Me	**6y** (34%) **6z** (63%) **6α** (26%) **6β** (-[b])	**1ε**: Ar = 4-FC_6H_4 **1ζ**: Ar = 4-MeC_6H_4 **1η**: Ar = 4-*n*-$PentC_6H_4$ **1θ**: Ar = 2-MeC_6H_4 **1ι**: Ar = 3,5-$Me_2C_6H_3$ **1κ**: Ar = 2,4,5-$Me_3C_6H_2$ **1λ**: Ar = 2-thiophenyl	**6ε** (68%) **6ζ** (69%)[d] **6η** (60%) **6θ** (75%)[e] **6ι** (60%)[f] **6κ** (72%)[g] **6λ** (69%)

[a]All reactions performed on a 0.2 mmol scale with an **A**/**1** ratio =1:20 in anhydrous *n*-pentane at room temperature for 12–30 h. Values in parentheses denote product yield. [b]Decomposed during purification by flash column chromatography on silica gel. [c]No reaction detected based on ^{1}H NMR analysis of the crude mixture. [d]Obtained as a mixture of **6ζ** + **5ζ** in a ratio = 8:1. [e]Obtained as a mixture of **6θ** + **5θ** in a ratio = 11:1. [f]Obtained as a mixture of **6ι** + **5ι** in a ratio = 6:1. [g]Obtained as a mixture of **6κ** + **5κ** in a ratio = 16:1.

Scheme 3. Proposed Mechanism for Gold(I)- and Gold(III)-Catalyzed Cycloisomerizations of 1,6-Diyne Esters



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acetate alkynyl moiety in the substrate by the group 11 metal catalyst to give the gold-coordinated complex **VI**. This may lead to 1,3-acyloxy migration and generation of the allene intermediate **II** via the 1,3-dioxin-1-ium species **VII**. Subsequent 5-*exo*-*dig* cyclization of this newly formed adduct involving anti addition of the allenic moiety to the C≡C bond in the ester would then provide the putative vinyl gold complex **V**. At this point, a divergence in the reactivity mode might occur depending on the nature of the gold catalyst and the substitution pattern of the substrate. In the presence of the Au(I) catalyst **D**, a Friedel−Crafts-type reaction involving attack of the pendant phenyl group to the oxocarbenium moiety in **V** may proceed in substrates where R^3 = Ar′ (Scheme 3, path a).[7] This could be due to unfavorable steric interactions between these two side-chains restricting the rate of rotation of the oxonium motif in the adduct. Protodeauration followed by rearomatization of the ensuing Wheland intermediate **VIII** would then deliver **4**. On the other hand, it is possible that the same steric interactions might be anticipated to be less so in the analogous intermediate generated from reaction of the substrate with the gold(III) complex **E**. As a result, rotation of the oxonium side chain in **V** can now take place more readily to give **V**′ and better orbital overlap between the HOMO of the vinyl gold bond and the LUMO of the carbonyl carbon center offered by this latter conformer (Scheme 3, path b).[8] In doing so, it is thought that the 1,5-acyl migration process, involving backside attack of the vinyl gold moiety to the carbonyl carbon center via the transition state **IX**, might now be favored. Deauration of the resulting organogold adduct **X** would then regenerate the gold(III) catalyst and give the *cis*-cyclopentene **5** with the geometry of the exocyclic C=C bond in the product being a consequence of the cyclization step. In contrast, it might be that there is a similar degree of restricted rate of rotation of the oxocarbenium side chain in adducts of **V** generated from reaction of substrates containing an isoprenyl group at R^3 with the Au(I) catalyst **A**. Moreover, the spatial volume occupied by the isoprenyl substituent may also be sufficient to hinder approach of the phenyl group to the oxonium moiety in the vinyl gold intermediate. Consequently, this may allow for the competitive Prins-type [2 + 2]-cyclization to proceed, involving attack of the oxocarbenium carbon center by the vinyl gold moiety in **V** (Scheme 3, path c).[9,10] Deauration of the resulting alkyl gold species **XI** would release the gold(I) catalyst and afford the bicyclic adduct **6**.

While the mechanistic premise put forward for the observed product chemoselectivities is speculative, it would be in good agreement with a number of experiments examined in this work. First is the gold(III) complex **E**-mediated reaction of **1c** leading to decomposition where, presumably, it could now be due to the presence of the bulky *t*-Bu ester group in the substrate restricting the rate of rotation of the oxonium side chain in **V** upon its formation. Likewise, the same type of unfavorable steric interactions in vinyl gold species **V** generated from substrates with a pendant alkynyl phenyl group possessing an *o*-substituent, as in **1o** (2-methylphenyl), **1q** (2,4,5-trimethylphenyl), and **1r** (1-naphthalenyl), would explain the lower product yields found for these reactions. The observed increase in selectivity in favor of the fused cyclobutene **6** in reactions catalyzed by Au(I) complex **A** with *n*-pentane as the solvent would also be consistent with the poor ability of nonpolar solvents to stabilize the cationic intermediate **V** sufficiently for bond rotation to occur.

CONCLUSION

In summary, we have described an efficient strategy for the synthesis of a variety of 1*H*-cyclopenta[*b*]naphthalenes, *cis*-cyclopenten-2-yl *δ*-diketones, and bicyclo[3.2.0]hepta-1,5-dienes by gold-catalyzed cycloisomerization of 1,6-diyne esters. The reaction conditions were shown to tolerate a broad substrate scope, providing products containing scaffolds of potential utility in medicinal chemistry and as functional materials. Our studies showed that effective and divergent chemoselectivity was possible by harnessing the inherent differences in electronic and steric properties of NHC−gold(I), phosphine−gold(I), and gold(III) complexes. Following an initial 1,3-acyloxy migration/5-*exo*-*dig* sequence, we demonstrated that phenyl or vinyl substituents at the acetate alkynyl position in the substrate enabled the respective formation of the 1*H*-cyclopenta[*b*]naphthalene and bicyclo[3.2.0]hepta-1,5-diene products. The latter, formed by a Prins-type [2 + 2]-cycloaddition, possessed a stable fused cyclobutene moiety. We also showed that the use of the more Lewis acidic gold(III) catalyst led to chemoselective formation of *cis*-cyclopenten-2-yl *δ*-diketones via 1,5-acyl migration following the 1,3-acyloxy migration/5-*exo*-*dig* cyclization pathway. Efforts to explore the scope and synthetic applications of the present reactions are in progress and will be reported in due course.

EXPERIMENTAL SECTION

General Considerations. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received while the 1,3,7-trisubstituted-1,6-diyn-3-ols used for starting material synthesis were prepared following literature procedures.[18] Gold(I) phosphine complexes **A**−**C** and gold(III) complex **E** were purchased from commercial sources and used as received, while NHC−gold(I) complex **D** was prepared following literature procedures.[15] Solvents were purified following standard literature procedures. Analytical thin-layer chromatography (TLC) was performed using precoated silica gel plates. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and a gradient solvent system (eluent: *n*-hexane/EtOAc/CH_2Cl_2). ^1H and proton-decoupled $^{13}C\{^1H\}$ NMR spectra were recorded on a 400 MHz spectrometer. 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), or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H, and coupling constants are reported as a *J* value in hertz. Infrared spectra were recorded on an FTIR spectrometer. Solid and liquid samples were examined as a thin film between NaCl salt plates. Low-resolution mass spectra were determined on a mass spectrometer and reported in units of mass to charge ratio (*m*/*z*). High-resolution mass spectra (HRMS) were obtained using an LC/HRMS TOF spectrometer using simultaneous electrospray (ESI).

General Procedures for the Preparation of 1,6-Diyne Esters. Method A: To a solution of the appropriate 1,3,7-trisubstituted 1,6-diyn-3-ol (1 mmol) in anhydrous THF (8 mL) was added LiHMDS (1.5 mL, 1.5 mmol, 1.0 M in THF) under an argon atmosphere at room temperature. The reaction was stirred for a further 20 min, R^3COCl (1.5 mmol) was added, and the reaction mixture was stirred at room temperature for 30 min. Upon completion (indicated by TLC), water was added (10 mL), and the solution was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc/CH_2Cl_2 = 50:1:1) to yield the title compound. Method B: To a solution of the appropriate 1,3,7-trisubstituted 1,6-diyn-3-ol (1 mmol) and DMAP (0.2 mmol) in CH_2Cl_2 (15 mL) were added Et_3N (0.557 mL, 4 mmol) and then acetic anhydride (0.378 mL, 4 mmol). The

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reaction mixture was stirred at room temperature for 15−24 h. Upon completion (indicated by TLC), the reaction mixture was quenched by addition of saturated $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with brine (15 mL), dried over $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: *n*-hexane/CH_2Cl_2/EtOAc = 100:5:3) to yield the title compound.

General Procedure for NHC−Gold(I) Complex D Catalyzed Cycloisomerization of 1,6-Diyne Esters 1a−t to 1*H*-Cyclopenta[*b*]naphthalene Derivatives 4. To a solution of 1,6-diyne ester **1** (0.2 mmol) in anhydrous CH_2Cl_2 (4 mL) was added NHC−gold(I) complex **D** (10 μmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 10 min to 42 h and monitored by TLC analysis until completion. The solution was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc/CH_2Cl_2 = 50:1:1) to give the title compound.

General Procedure for Gold(III) Complex E Catalyzed Cycloisomerization of 1,6-Diyne Esters 1 to *cis*-Cyclopenten-2-yl δ-diketone Derivatives 5. To a solution of the 1,6-diyne ester **1** (0.2 mmol) in anhydrous CH_2Cl_2 (4 mL) was added gold(III) complex **E** (10 μmol) under an argon atmosphere. The reaction mixture was stirred at room temperature for 10 min to 42 h and monitored by TLC analysis until completion. The solution was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc/CH_2Cl_2 = 10:1:1) to give the title compound.

General Procedure for Phosphine(I)−Gold Complex A Catalyzed Cycloisomerization of 1,6-Diyne Esters 1 to Bicyclo[3.2.0]hepta-1,5-diene Derivatives 6. To a solution of 1,6-diyne ester **1** (0.2 mmol) in anhydrous *n*-pentane (6 mL) were added phosphine−gold(I) complex **A** (10 μmol) and 4 Å MS (200 mg) under an argon atmosphere. The reaction mixture was stirred at room temperature for 12−30 h and monitored by TLC analysis until completion. The solution was filtered through Celite, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc/CH_2Cl_2 = 50:1:1) to give the title compound.

*1,3,7-Triphenylhepta-1,6-diyn-3-yl Acetate (**1a**).* Method B: wt 1.94 g; yield 80%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.15 (s, 3H), 2.40−2.46 (m, 1H), 2.62−2.70 (m, 2H), 2.79−2.85 (m, 1H), 7.30−7.32 (m, 3H), 7.34−7.46 (m, 8H), 7.60−7.63 (m, 2H), 7.67−7.70 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.4, 21.8, 43.7, 78.5, 81.0, 86.6, 89.0, 89.0, 122.3, 123.8, 125.3, 127.8, 128.2, 128.3, 128.4, 128.6, 128.9, 131.6, 132.1, 141.1, 168.4; IR (NaCl, neat) ν 3017, 2230, 1748, 1489, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{23}O_2$ (M^++H) 379.1698, found 379.1701.

*1,3,7-Triphenylhepta-1,6-diyn-3-yl Benzoate (**1b**).* Method A: wt 385 mg; yield 74%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.53−2.59 (m, 1H), 2.75−2.83 (m, 2H), 2.92−2.99 (m, 1H), 7.29−7.48 (m, 13H), 7.58−7.63 (m, 3H), 7.74−7.76 (m, 2H), 8.14−8.17 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.6, 44.0, 79.1, 81.1, 86.5, 89.2, 89.2, 122.3, 123.8, 125.3, 127.8, 128.2, 128.3, 128.4, 128.5, 128.6, 128.9, 129.8, 130.6, 131.6, 132.1, 133.1, 141.2, 163.9; IR (NaCl, neat) ν 3019, 2234, 1732, 1491, 1269 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{25}O_2$ (M^+ + H) 441.1855, found 441.1862.

*1,3,7-Triphenylhepta-1,6-diyn-3-yl Pivalate (**1c**).* Method A: wt 269 mg; yield 85%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.14 (s, 9H), 2.21−2.30 (m, 1H), 2.46−2.56 (m, 2H), 2.62−2.70 (m, 1H), 7.12−7.15 (m, 3H), 7.16−7.22 (m, 4H), 7.24−7.28 (m, 4H), 7.42−7.44 (m, 2H), 7.49−7.50 (d, 2H, *J* = 7.4 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.5, 27.1, 39.2, 43.9, 78.1, 81.0, 86.6, 88.7, 89.2, 122.4, 123.8, 125.2, 127.8, 128.1, 128.3, 128.4, 128.5, 128.8, 131.6, 132.1, 141.4, 175.3; IR (NaCl, neat) ν 3019, 2399, 1740, 1491, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{29}O_2$ (M^+ + H) 421.2168, found 421.2174.

*1,3,7-Triphenylhepta-1,6-diyn-3-yl Cyclopropanecarboxylate (**1d**).* Method A: wt 279 mg; yield 86%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88−0.91 (m, 2H), 0.99−1.02 (m, 1H), 1.07−1.09 (m, 1H), 1.71−1.75 (m, 1H), 2.39−2.45 (m, 1H), 2.63−2.70 (m, 2H), 2.76−2.88 (m, 1H), 7.29−7.33 (m, 3H), 7.35−7.45 (m, 8H), 7.58−7.61 (m, 2H), 7.66−7.68 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 8.4, 8.6, 13.6, 15.5, 43.8, 78.4, 81.0, 86.7, 88.9, 89.1, 122.4, 123.8, 125.2, 127.7, 128.1, 128.3, 128.4, 128.5, 128.8, 131.6, 132.1, 141.2, 172.0; IR (NaCl, neat) ν 3017, 2232, 1736, 1491, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}O_2$ (M^+ + H) 405.1855, found 405.1865.

*3-Methyl-1,7-diphenylhepta-1,6-diyn-3-yl Acetate (**1e**).* Method B: wt 280 mg; yield 88%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.84 (s, 3H), 2.07 (s, 3H), 2.20−2.27 (m, 1H), 2.36−2.44 (m, 1H), 2.71−2.75 (m, 2H), 7.27−7.33 (m, 6H), 7.40−7.42 (m, 2H), 7.45−7.48 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.1, 22.0, 26.6, 40.8, 74.8, 80.8, 85.8, 88.3, 89.3, 122.4, 123.8, 127.7, 128.2, 128.3, 128.5, 131.6, 131.9, 169.3; IR (NaCl, neat) ν 3017, 2234, 1740, 1489, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{21}O_2$ (M^+ + H) 317.1542, found 317.1547.

*3-Cyclopropyl-1,7-diphenylhepta-1,6-diyn-3-yl Acetate (**1f**).* Method B: wt 161 mg; yield 35%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.52−0.57 (m, 3H), 0.83−0.88 (m, 1H), 1.42−1.45 (m, 1H), 1.99 (s, 3H), 2.30−2.36 (m, 1H), 2.55−2.68 (m, 3H), 7.17−7.24 (m, 6H), 7.30−7.36 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 3.3, 3.3, 15.3, 17.9, 22.1, 39.3, 80.7, 81.6, 84.3, 87.3, 89.4, 122.1, 123.9, 127.6, 128.2, 128.3, 128.7, 131.5, 132.0, 169.3; IR (NaCl, neat) ν 3017, 2234, 1732, 1489, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}O_2$ (M^+ + H) 343.1698, found 343.1705.

*3-(4-Chlorophenyl)-1,7-diphenylhepta-1,6-diyn-3-yl Acetate (**1g**).* Method B: wt 227 mg; yield 74%; white solid; mp =99−100 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.97 (s, 3H), 2.18−2.27 (m, 1H), 2.41−2.51 (m, 2H), 2.59−2.68 (m, 1H), 7.13−7.16 (m, 3H), 7.20−7.25 (m, 7H), 7.42−7.46 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.4, 21.7, 43.4, 78.0, 81.2, 86.0, 88.7, 89.3, 122.0, 123.7, 126.9, 127.8, 128.3, 128.4, 128.7, 129.1, 131.6, 132.1, 134.0, 139.7, 168.3; IR (NaCl, neat) ν 3019, 2232, 1749, 1489, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{21}O_2ClNa$ (M^+ + Na) 435.1128, found 435.1129.

*1-(4-Fluorophenyl)-3,7-diphenylhepta-1,6-diyn-3-yl Acetate (**1h**).* Method B: wt 186 mg; yield 65%; yellow solid; mp = 96−97 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.09 (s, 3H), 2.32−2.38 (m, 1H), 2.53−2.58 (m, 2H), 2.68−2.73 (m, 1H), 6.70−7.04 (m, 2H), 7.23−7.25 (m, 3H), 7.28−7.39 (m, 5H), 7.50−7.54 (m, 2H), 7.58−7.60 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.4, 21.7, 43.5, 78.4, 81.0, 86.3, 87.9, 88.9, 115.5, 115.8, 118.3, 118.3, 123.7, 125.2, 127.7, 128.2, 128.2, 128.5, 131.5, 134.0, 134.1, 140.9, 161.6, 164.1, 168.4; IR (NaCl, neat) ν 3019, 2230, 1748, 1506, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{22}O_2F$ (M^+ + H) 397.1604, found 397.1605.

*3,7-Diphenyl-1-(p-tolyl)hepta-1,6-diyn-3-yl Acetate (**1i**).* Method B: wt 124 mg; yield 33%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.09 (s, 3H), 2.31−2.36 (m, 4H), 2.53−2.58 (m, 2H), 2.70−2.77 (m, 1H), 7.13−7.15 (d, 2H, *J* = 7.9 Hz), 7.24−7.26 (m, 3H), 7.28−7.39 (m, 5H), 7.43−7.45 (d, 2H, *J* = 8.1 Hz), 7.60−7.62 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.4, 21.5, 21.8, 43.6, 78.5, 80.8, 85.7, 89.0, 89.1, 119.2, 123.8, 125.3, 127.6, 128.0, 128.2, 128.5, 129.1, 131.5, 132.0, 139.0, 141.1, 168.3; IR (NaCl, neat) ν 3028, 2228, 1752, 1491, 1225 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}O_2$ (M^+ + H) 393.1855, found 393.1864.

*3,7-Diphenyl-1-(thiophene-3-yl)hepta-1,6-diyn-3-yl Acetate (**1j**).* Method B: wt 344 mg; yield 60%; brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.05 (s, 3H), 2.31−2.36 (m, 1H), 2.52−2.57 (m, 2H), 2.69−2.75 (m, 1H), 7.16−7.17 (m, 1H), 7.21−7.29 (m, 5H), 7.33−7.37 (m, 4H), 7.51−7.52 (m, 1H), 7.57−7.59 (d, 2H, *J* = 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.5, 21.8, 43.7, 78.6, 81.1, 84.2, 86.2, 89.1, 121.3, 123.8, 125.4, 125.6, 127.8, 128.2, 128.4, 128.6, 130.0, 130.2, 131.6, 141.1, 168.4; IR (NaCl, neat) ν 3107, 1748, 1491, 1221 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{21}O_2S$ (M^+ + H) 385.1262, found 385.1259.

*7-(4-Fluorophenyl)-1,3-diphenylhepta-1,6-diyn-3-yl Acetate (**1k**).* Method B: wt 518 mg; yield 87%; yellow solid; mp =75−76 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.15 (s, 3H), 2.39−2.45 (m, 1H), 2.58−2.69 (m, 2H), 2.77−2.83 (m, 1H), 6.98−7.02 (m, 2H), 7.34−7.40 (m, 6H), 7.42−7.46 (m, 2H), 7.60−7.63 (m, 2H), 7.68−7.70 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.4, 21.8, 43.6, 78.5, 80.0, 86.5,

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88.7, 89.0, 115.4, 115.6, 119.9, 122.3, 125.3, 128.2, 128.4, 128.6, 128.9, 132.1, 133.4, 133.4, 141.1, 160.9, 163.4, 168.3; IR (NaCl, neat) ν 3061, 2230, 1755, 1506, 1225 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{22}O_2F$ (M^+ + H) 397.1604, found 397.1605.

*7-(4-Bromophenyl)-1,3-diphenylhepta-1,6-diyn-3-yl Acetate (**1l**).* Method B: wt 296 mg; yield 70%; yellow solid; mp = 100−101 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.08 (s, 3H), 2.31−2.37 (m, 1H), 2.50−2.60 (m, 2H), 2.68−2.75 (m, 1H), 7.16−7.20 (m, 2H), 7.27−7.32 (m, 4H), 7.35−7.38 (m, 4H), 7.52−7.55 (m, 2H), 7.59−7.61 (d, 2H, J = 7.4 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.5, 21.8, 43.4, 78.5, 80.0, 86.5, 89.0, 90.4, 121.8, 122.2, 122.8, 125.3, 128.2, 128.4, 128.6, 128.9, 131.5, 132.1, 133.1, 141.0, 168.3; IR (NaCl, neat) ν 3061, 2230, 1748, 1487, 1225 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{18}Br$ (M^+ − OAc): 397.0592, found 397.0581.

*7-(4-Pentylphenyl)-1,3-diphenylhepta-1,6-diyn-3-yl Acetate (**1m**).* Method B: wt 262 mg; yield 54%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.76 (t, 3H, J = 6.8 Hz), 1.18−1.23 (m, 4H), 1.41−1.49 (m, 2H), 1.95 (s, 3H), 2.21−2.27 (m, 1H), 2.41−2.48 (m, 4H), 2.60−2.66 (m, 1H), 6.93−6.95 (d, 2H, J = 8.1 Hz), 7.15−7.20 (m, 6H), 7.23−7.27 (m, 2H), 7.41−7.44 (m, 2H), 7.49−7.51 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 14.2, 15.5, 21.8, 22.6, 31.0, 31.5, 35.9, 43.8, 78.5, 81.1, 86.6, 88.2, 89.0, 121.0, 122.3, 125.4, 128.2, 128.4, 128.6, 128.9, 131.5, 132.1, 141.2, 142.8, 168.3; IR (NaCl, neat) ν 2230, 1755, 1491, 1225 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{32}O_2Na$ (M^+ + Na) 471.2300, found 471.2296.

*1,3-Diphenyl-7-(p-tolyl)hepta-1,6-diyn-3-yl Acetate (**1n**).* Method B: wt 294 mg; yield 56%; yellow solid; mp = 108−109 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.16 (s, 3H), 2.38 (s, 3H), 2.42−2.47 (m, 1H), 2.61−2.71 (m, 2H), 2.80−2.87 (m, 1H), 7.13−7.15 (d, 2H, J = 8.0 Hz), 7.33−7.47 (m, 8H), 7.62−7.64 (m, 2H), 7.69−7.71 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.5, 21.5, 21.8, 43.8, 78.5, 81.1, 86.6, 88.2, 89.0, 120.8, 122.3, 125.4, 128.2, 128.6, 128.9, 129.1, 131.5, 132.1, 137.7, 141.1, 168.4; IR (NaCl, neat) ν 3017, 2230, 1749, 1491, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}O_2$ (M^+ + H) 393.1855, found 393.1850.

*1,3-Diphenyl-7-(o-tolyl)hepta-1,6-diyn-3-yl Acetate (**1o**).* Method B: wt 335 mg; yield 72%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.06 (s, 3H), 2.33−2.43 (m, 4H), 2.55−2.65 (m, 2H), 2.74−2.82 (m, 1H), 7.03−7.08 (m, 1H), 7.10−7.14 (m, 2H), 7.28−7.38 (m, 7H), 7.52−7.54 (m, 2H), 7.60−7.62 (d, 2H, J = 7.4 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.7, 20.9, 21.8, 43.9, 78.6, 80.0, 86.6, 89.0, 93.0, 122.3, 123.6, 125.4, 125.6, 127.8, 128.2, 128.4, 128.6, 128.9, 129.4, 131.9, 132.1, 140.0, 141.2, 168.4; IR (NaCl, neat) ν 3022, 2230, 1748, 1489, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}O_2$ (M^+ + H) 393.1855, found 393.1850.

*7-(3,5-Dimethylphenyl)-1,3-diphenylhepta-1,6-diyn-3-yl Acetate (**1p**).* Method B: wt 191 mg; yield 77%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.13 (s, 3H), 2.27 (s, 6H), 2.34−2.40 (m, 1H), 2.53−2.64 (m, 2H), 2.72−2.81 (m, 1H), 6.92 (s, 1H), 7.01 (s, 2H), 7.31−7.42 (m, 6H), 7.57−7.59 (m, 2H), 7.63−7.65 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.4, 21.1, 21.8, 43.7, 78.5, 81.2, 86.5, 88.2, 88.9, 122.3, 123.3, 125.3, 128.1, 128.3, 128.5, 128.8, 129.3, 129.6, 132.1, 137.7, 141.1, 168.3; IR (NaCl, neat) ν 3028, 2230, 1755, 1489, 1223 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{27}O_2$ (M^+ + H) 407.2011, found 407.2008.

*7-Mesityl-1,3-diphenylhepta-1,6-diyn-3-yl Acetate (**1q**).* Method B: wt 347 mg; yield 80%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.15 (s, 3H), 2.21 (s, 3H), 2.24 (s, 3H), 2.38 (s, 3H), 2.40−2.45 (m, 1H), 2.61−2.70 (m, 2H), 2.79−2.87 (m, 1H), 6.98 (s, 1H), 7.17 (s, 1H), 7.34−7.46 (m, 6H), 7.60−7.62 (m, 2H), 7.67−7.69 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.6, 19.1, 19.6, 20.1, 21.8, 44.0, 78.5, 80.0, 86.6, 88.9, 91.6, 120.7, 122.3, 125.3, 128.1, 128.4, 128.6, 128.9, 130.8, 132.1, 132.9, 133.6, 136.4, 137.2, 141.2, 168.4; IR (NaCl, neat) ν 3015, 2230, 1746, 1491, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{29}O_2$ (M^+ + H) 421.2168, found 421.2162.

*7-(Naphthalen-1-yl)-1,3-diphenylhepta-1,6-diyn-3-yl Acetate (**1r**).* Method B: wt 172 mg; yield 53%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.15 (s, 3H), 2.49−2.54 (m, 1H), 2.74−2.80 (m, 2H), 2.95−3.01 (m, 1H), 7.35−7.47 (m, 7H), 7.51−7.64 (m, 5H), 7.69−7.72 (m, 2H), 7.79−7.81 (d, 2H, J = 8.2 Hz), 7.84−7.86 (d, 2H, J = 7.7 Hz), 8.35−8.37 (d, 1H, J = 8.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.8, 21.8, 43.8, 78.6, 79.0, 86.5, 89.1, 94.0, 121.5, 122.3, 125.3, 125.3, 126.3, 126.3, 126.6, 128.2, 128.2, 128.3, 128.4, 128.6, 128.9, 130.1, 132.1, 133.2, 133.5, 141.1, 168.4; IR (NaCl, neat) ν 3057, 2230, 1751, 1491, 1227 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{21}$ (M^+ − OAc) 369.1643, found 369.1638.

*1,3-Diphenyl-7-(thiophene-3-yl)hepta-1,6-diyn-3-yl Acetate (**1s**).* Method B: wt 297 mg; yield 77%; yellow solid; mp =80−81 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.05 (s, 3H), 2.30−2.36 (m, 1H), 2.52−2.57 (m, 2H), 2.68−2.73 (m, 1H), 6.99−7.01 (m, 1H), 7.13−7.16 (m, 1H), 7.25−7.31 (m, 5H), 7.33−7.37 (m, 2H), 7.50−7.53 (m, 2H), 7.58−7.61 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.4, 21.8, 43.6, 76.2, 78.5, 86.6, 88.6, 89.0, 122.3, 122.8, 125.2, 125.4, 127.9, 128.2, 128.6, 129.0, 130.0, 132.1, 141.1, 168.4; IR (NaCl, neat) ν 3017, 2230, 1751, 1489, 1223 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{21}O_2S$ (M^+ + H) 385.1262, found 385.1261.

*1,3-Diphenyl-7-(thiophene-2-yl)hepta-1,6-diyn-3-yl Acetate (**1t**).* Method B: wt 381 mg; yield 76%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.14 (s, 3H), 2.40−2.46 (m, 1H), 2.63−2.74 (m, 2H), 2.83−2.92 (m, 1H), 7.16−7.23 (m, 2H), 7.37−7.40 (m, 4H), 7.42−7.45 (m, 3H), 7.59−7.62 (m, 2H), 7.67−7.69 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.7, 21.8, 43.5, 77.9, 78.5, 86.5, 89.0, 94.7, 122.2, 123.6, 125.3, 126.4, 128.2, 128.4, 128.6, 128.8, 128.9, 129.2, 132.1, 133.4, 135.7, 141.0, 168.3; IR (NaCl, neat) ν 3022, 2232, 1748, 1489, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{21}O_2S$ (M^+ + H) 385.1262, found 385.1257.

*2-Methyl-5,9-diphenylnona-1-en-3,8-diyn-5-yl Acetate (**1u**).* Method B: wt 803 mg; yield 81%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.96 (s, 3H), 2.05 (s, 3H), 2.24−2.30 (m, 1H), 2.42−2.53 (m, 2H), 2.63−2.69 (m, 1H), 5.30 (t, 1H, J = 1.6 Hz), 5.42 (d, 1H, J = 0.8 Hz), 7.21−7.29 (m, 4H), 7.32−7.36 (m, 4H), 7.52−7.54 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.3, 21.7, 23.4, 43.6, 78.3, 80.9, 85.4, 89.0, 90.1, 123.1, 123.8, 125.2, 126.1, 127.7, 128.1, 128.3, 128.5, 131.5, 141.1, 168.2; IR (NaCl, neat) ν 3019, 2222, 1748, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}O_2$ (M^+ + H) 343.1698, found 343.1703.

*2-Methyl-5,9-diphenylnona-1-en-3,8-diyn-5-yl Benzoate (**1v**).* Method A: wt 156 mg; yield 60%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.90 (s, 3H), 2.31−2.37 (m, 1H), 2.52−2.62 (m, 2H), 2.70−2.74 (m, 1H), 5.24 (t, 1H, J = 1.6 Hz), 5.37 (d, 1H, J = 0.8 Hz), 7.17−7.24 (m, 3H), 7.27−7.36 (m, 6H), 7.42−7.49 (m, 2H), 7.53−7.55 (m, 2H), 7.99−8.01 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.5, 23.4, 43.9, 79.0, 80.9, 85.4, 89.1, 90.4, 123.1, 123.7, 125.3, 126.1, 127.7, 128.1, 128.2, 128.4, 128.5, 128.9, 129.8, 129.8, 130.6, 131.6, 133.0, 141.1, 163.8; IR (NaCl, neat) ν 3019, 2224, 1730, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}O_2$ (M^+ + H) 405.1855, found 405.1843.

*2-Methyl-5,9-diphenylnona-1-en-3,8-diyn-5-yl Pivalate (**1w**).* Method A: wt 88 mg; yield 50%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (s, 9H), 1.96 (s, 3H), 2.24−2.29 (m, 1H), 2.47−2.56 (m, 2H), 2.67−2.72 (m, 1H), 5.30 (t, 1H, J = 1.6 Hz), 5.40 (d, 1H, J = 0.8 Hz), 7.25−7.30 (m, 4H), 7.33−7.37 (m, 4H), 7.52 (d, 2H, J = 7.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 15.4, 23.4, 27.0, 39.1, 43.8, 78.0, 80.9, 85.5, 89.1, 89.8, 122.8, 123.8, 125.1, 126.1, 127.7, 127.9, 128.2, 128.4, 131.5, 141.4, 175.2; IR (NaCl, neat) ν 3019, 1740, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{29}O_2$ (M^+ + H) 385.2168, found 385.2176.

*2-Methyl-5,9-diphenylnona-1-en-3,8-diyn-5-yl Cyclopropanecarboxylate (**1x**).* Method A: wt 150 mg; yield 51%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.74−0.77 (m, 2H), 0.82−0.86 (m, 1H), 0.92−0.96 (m, 1H), 1.56−1.60 (m, 1H), 1.88 (s, 3H), 2.17−2.23 (m, 1H), 2.40−2.44 (m, 2H), 2.57−2.63 (m, 1H), 5.23 (d, 1H, J = 1.4 Hz), 5.34 (s, 1H), 7.16−7.21 (m, 4H), 7.26−7.29 (m, 4H), 7.44−7.46 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 8.3, 8.4, 9.4, 13.5, 15.3, 23.4, 43.7, 78.2, 80.8, 85.6, 89.1, 90.0, 122.9, 123.8, 125.2, 126.1, 127.7, 127.9, 128.2, 128.4, 131.5, 141.2, 171.9; IR (NaCl, neat) ν 3019, 2222, 1740, 1159 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{25}O_2$ (M^+ + H) 369.1855, found 369.1853.

*5-(4-Chlorophenyl)-2-methyl-9-phenylnona-1-en-3,8-diyn-5-yl Acetate (**1y**).* Method B: wt 154 mg; yield 61%; yellow oil; ^{1}H NMR

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($CDCl_3$, 400 MHz) δ 1.96 (s, 3H), 2.06 (s, 3H), 2.21−2.29 (m, 1H), 2.43−2.51 (m, 2H), 2.60−2.69 (m, 1H), 5.33 (t, 1H, J = 1.2 Hz), 5.42 (s, 1H), 7.25−7.26 (m, 3H), 7.31−7.35 (m, 4H), 7.47−7.49 (d, 2H, J = 8.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.2, 21.7, 23.3, 43.3, 77.8, 81.0, 84.8, 88.7, 90.4, 123.3, 123.6, 125.9, 126.8, 127.7, 128.2, 128.6, 131.5, 134.0, 139.7, 168.2; IR (NaCl, neat) ν 3019, 2224, 1749, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}O_2Cl$ (M^+ + H) 377.1308, found 377.1312.

*2-Methyl-9-phenyl-5-(p-tolyl)nona-1-en-3,8-diyn-5-yl Acetate (**1z**).* Method B: wt 344 mg; yield 77%; yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.02 (s, 3H), 2.10 (s, 3H), 2.30−2.39 (m, 4H), 2.48−2.62 (m, 2H), 2.68−2.75 (m, 1H), 5.35−5.37 (m, 1H), 5.48 (t, 1H, J = 0.8 Hz), 7.20−7.22 (d, 2H, J = 8.0 Hz), 7.29−7.31 (m, 3H), 7.39−7.41 (m, 2H), 7.47−7.49 (d, 2H, J = 8.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.3, 21.1, 21.8, 23.4, 43.5, 78.3, 80.9, 85.7, 89.1, 90.0, 123.0, 123.8, 125.3, 126.1, 127.7, 128.3, 129.2, 131.6, 137.8, 138.1, 168.3; IR (NaCl, neat) ν 3019, 2224, 1748, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{25}O_2$ (M^+ + H) 357.1855, found 357.1865.

*2-Methyl-5-(naphthalen-1-yl)-9-phenylnona-1-en-3,8-diyn-5-yl Acetate (**1α**).* Method B: wt 131 mg; yield 60%; yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.99 (s, 3H), 2.05 (s, 3H), 2.51−2.55 (m, 1H), 2.59−2.66 (m, 1H), 2.76−2.82 (m, 1H), 2.92−2.96 (m, 1H), 5.33 (t, 1H, J = 1.6 Hz), 5.45 (d, 1H, J = 0.8 Hz), 7.21−7.23 (m, 3H), 7.28−7.31 (m, 2H), 7.43−7.51 (m, 3H), 7.78−7.80 (d, 1H, J = 8.2 Hz), 7.84−7.86 (m, 1H), 8.02−8.04 (m, 4H), 8.53−8.55 (d, 1H, J = 8.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.6, 21.4, 23.4, 40.8, 80.7, 80.9, 86.5, 89.1, 90.4, 123.1, 123.7, 124.8, 125.0, 125.4, 126.1, 126.1, 126.4, 127.7, 128.2, 129.4, 129.6, 129.7, 131.5, 134.9, 135.2, 168.2; IR (NaCl, neat) ν 3019, 2224, 1748, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}O_2$ (M^+ + H) 393.1855, found 393.1838.

*2,5-Dimethyl-9-phenylnona-1-en-3,8-diyn-5-yl Acetate (**1β**).* Method B: wt 126 mg; yield 70%; colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.75 (s, 3H), 1.89 (t, 3H, J = 1.2 Hz), 2.03 (s, 3H), 2.10−2.18 (m, 1H), 2.28−2.35 (m, 1H), 2.64 (t, 3H, J = 8.2 Hz), 5.23−5.24 (m, 1H), 5.31−5.32 (m, 1H), 7.26−7.29 (m, 3H), 7.37−7.40 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.0, 22.0, 23.3, 26.5, 40.7, 74.8, 80.7, 86.9, 87.3, 89.3, 122.5, 123.8, 126.1, 127.7, 128.2, 131.5, 169.2; IR (NaCl, neat) ν 3017, 1738, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{21}O_2$ (M^+ + H) 281.1542, found 281.1537.

*8-Methylene-1,5-diphenyltetradeca-1,6-diyn-5-yl Acetate (**1γ**).* Method B: wt 130 mg; yield 77%; yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.79−0.83 (m, 3H), 1.21−1.28 (m, 6H), 1.48−1.51 (m, 2H), 1.99 (s, 3H), 2.13−2.23 (m, 3H), 2.38−2.44 (m, 2H), 2.56−2.60 (m, 1H), 5.23 (d, 1H, J = 1.6 Hz), 5.36 (d, 1H, J = 1.8 Hz), 7.16−7.18 (m, 3H), 7.20−7.22 (m, 1H), 7.25−7.29 (m, 4H), 7.45−7.47 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 14.1, 15.3, 21.7, 22.6, 28.0, 28.6, 31.7, 37.1, 43.6, 78.4, 80.8, 86.1, 89.0, 89.4, 122.1, 123.8, 125.3, 127.6, 128.0, 128.2, 128.4, 131.1, 131.5, 141.1, 168.1; IR (NaCl, neat) ν 3019, 2222, 1751, 1219 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{33}O_2$ (M^+ + H) 413.2481, found 413.2484.

*2,5,9-Triphenylnona-1-en-3,8-diyn-5-yl Acetate (**1δ**).* Method B: wt 214 mg; yield 39%; yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.13 (s, 3H), 2.37−2.43 (m, 1H), 2.52−2.65 (m, 2H), 2.72−2.73 (m, 1H), 5.82 (s, 1H), 6.04 (s, 1H), 7.27−7.30 (m, 3H), 7.31−7.42 (m, 8H), 7.59−7.63 (m, 2H), 7.73−7.75 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.3, 21.7, 43.5, 78.4, 80.9, 87.9, 88.0, 88.9, 121.9, 123.7, 125.1, 125.3, 126.1, 127.7, 128.1, 128.2, 128.4, 128.5, 128.5, 129.9, 131.5, 136.9, 141.0, 168.3; IR (NaCl, neat) ν 3019, 2400, 1746, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}O_2$ (M^+ + H) 405.1855, found 405.1850.

*9-(4-Fluorophenyl)-2-methyl-5-phenylnona-1-en-3,8-diyn-5-yl Acetate (**1ε**).* Method B: wt 892 mg; yield 83%; white solid; mp = 83−84 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.00 (s, 3H), 2.09 (s, 3H), 2.23−2.29 (m, 1H), 2.41−2.53 (m, 2H), 2.61−2.67 (m, 1H), 5.32 (t, 1H, J = 1.6 Hz), 5.42 (s, 1H), 6.95 (t, 2H, J = 8.8 Hz), 7.29−7.38 (m, 5H), 7.52−7.54 (d, 2H, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.2, 21.7, 23.4, 43.5, 78.3, 79.8, 85.4, 88.6, 90.1, 115.3, 115.6, 119.8, 119.9, 123.1, 125.2, 126.0, 128.1, 128.5, 133.3, 133.4, 141.0, 160.9, 163.4, 168.2; IR (NaCl, neat) ν 3019, 1748, 1506, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}O_2F$ (M^+ + H) 361.1604, found 361.1612.

*2-Methyl-5-phenyl-9-(p-tolyl)nona-1-en-3,8-diyn-5-yl Acetate (**1ζ**).* Method B: wt 161 mg; yield 82%; yellow solid; mp = 113−114 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.96 (s, 3H), 2.06 (s, 3H), 2.22−2.30 (m, 4H), 2.41−2.53 (m, 2H), 2.62−2.71 (m, 1H), 5.31 (d, 1H, J = 1.4 Hz), 5.42 (s, 1H), 7.04−7.06 (d, 2H, J = 8.0 Hz), 7.22−7.29 (m, 3H), 7.33−7.37 (m, 2H), 7.52−7.54 (d, 2H, J = 7.4 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.3, 21.4, 21.7, 23.4, 43.7, 78.4, 80.9, 85.4, 88.2, 90.1, 120.7, 123.0, 125.2, 126.1, 128.0, 128.5, 129.0, 131.4, 137.7, 141.1, 168.3; IR (NaCl, neat) ν 3019, 2226, 1748, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{25}O_2$ (M^+ + H) 357.1855, found 357.1862.

*2-Methyl-9-(4-pentylphenyl)-5-phenylnona-1-en-3,8-diyn-5-yl Acetate (**1η**).* Method B: wt 110 mg; yield 74%; yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.79−0.82 (t, 3H, J = 6.8 Hz), 1.19−1.27 (m, 4H), 1.49−1.54 (m, 2H), 1.90 (s, 3H), 2.00 (s, 3H), 2.16−2.22 (m, 1H), 2.34−2.43 (m, 2H), 2.46−2.51 (m, 2H), 2.55−2.61 (m, 1H), 5.24 (s, 1H), 5.35 (s, 1H), 6.98−7.01 (d, 2H, J = 8.0 Hz), 7.17−7.23 (m, 3H), 7.27−7.30 (m, 2H), 7.45−7.47 (d, 2H, J = 7.3 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 14.0, 15.3, 21.7, 22.5, 23.3, 30.9, 31.4, 35.8, 43.6, 78.4, 80.9, 85.4, 88.1, 90.1, 120.9, 123.0, 125.2, 126.1, 128.0, 128.3, 128.4, 131.4, 141.1, 142.7, 168.2; IR (NaCl, neat) ν 3019, 2224, 1748, 1213 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{33}O_2$ (M^+ + H) 413.2481, found 413.2485.

*2-Methyl-5-phenyl-9-(o-tolyl)nona-1-en-3,8-diyn-5-yl Acetate (**1θ**).* Method B: wt 107 mg; yield 69%; yellow solid; mp =60−61 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.98 (s, 3H), 2.09 (s, 3H), 2.26−2.31 (m, 1H), 2.38 (s, 3H), 2.47−2.56 (m, 2H), 2.66−2.77 (m, 1H), 5.32 (s, 1H), 5.44 (s, 1H), 7.06−7.12 (m, 1H), 7.15−7.19 (m, 2H), 7.28−7.33 (m, 2H), 7.35−7.39 (m, 2H), 7.54−7.56 (d, 2H, J = 7.3 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.4, 20.7, 21.7, 23.4, 43.8, 78.4, 79.7, 85.4, 90.1, 92.9, 123.0, 123.5, 125.2, 125.4, 126.0, 127.6, 128.0, 128.5, 129.3, 131.8, 139.9, 141.1, 168.2; IR (NaCl, neat) ν 3019, 2224, 1748, 1219 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{25}O_2$ (M^+ + H) 357.1855, found 357.1855.

*9-(3,5-Dimethylphenyl)-2-methyl-5-phenylnona-1-en-3,8-diyn-5-yl Acetate (**1ι**).* Method B: wt 371 mg; yield 76%; yellow solid; mp =82−83 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.05 (s, 3H), 2.13 (s, 3H), 2.32−2.39 (m, 7H), 2.51−2.62 (m, 2H), 2.71−2.78 (m, 1H), 5.39 (t, 1H, J = 1.6 Hz), 5.51 (d, 1H, J = 0.7 Hz), 6.96 (s, 1H), 7.07 (s, 2H), 7.33−7.37 (m, 1H), 7.41−7.45 (m, 2H), 7.61−7.63 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.3, 21.1, 21.7, 23.4, 43.7, 77.6, 78.4, 81.2, 85.6, 88.2, 90.1, 123.1, 123.5, 125.3, 126.1, 128.1, 128.5, 129.3, 129.7, 137.8, 141.1, 168.2; IR (NaCl, neat) ν 2928, 2224, 1749, 1219 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{27}O_2$ (M^+ + H) 371.2011, found 371.2013.

*2-Methyl-5-phenyl-9-(2,4,5-trimethylphenyl)nona-1-en-3,8-diyn-5-yl Acetate (**1κ**).* Method B: wt 280 mg; yield 74%; yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.04 (s, 3H), 2.13 (s, 3H), 2.22 (s, 3H), 2.25 (s, 3H), 2.33−2.38 (m, 4H), 2.53−2.62 (m, 2H), 2.71−2.83 (m, 1H), 5.38 (t, 1H, J = 1.6 Hz), 5.50 (d, 1H, J = 0.8 Hz), 6.98 (s, 1H), 7.17 (s, 1H), 7.33−7.36 (m, 1H), 7.40−7.44 (m, 2H), 7.60−7.62 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.5, 19.1, 19.6, 20.1, 21.7, 23.4, 44.0, 78.4, 80.0, 85.6, 90.1, 91.6, 120.7, 123.0, 125.3, 126.1, 128.0, 128.5, 130.8, 132.9, 133.5, 136.3, 137.1, 141.2, 168.2; IR (NaCl, neat) ν 3017, 2224, 1748, 1219 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{29}O_2$ (M^+ + H) 385.2168, found 385.2166.

*2-Methyl-5-phenyl-9-(thiophene-2-yl)nona-1-en-3,8-diyn-5-yl Acetate (**1λ**).* Method B: wt 244 mg; yield 70%; yellow solid; mp = 73−74 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.01 (s, 3H), 2.10 (s, 3H), 2.27−2.32 (m, 1H), 2.49−2.59 (m, 2H), 2.68−2.76 (m, 1H), 5.36 (t, 1H, J = 1.6 Hz), 5.47 (d, 1H, J = 0.8 Hz), 6.93−6.95 (m, 1H), 7.11−7.12 (m, 1H), 7.17−7.18 (m, 1H), 7.30−7.34 (m, 1H), 7.38−7.41 (m, 2H), 7.56−7.59 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.6, 21.7, 23.4, 43.3, 74.1, 78.3, 85.4, 90.2, 93.1, 123.1, 123.9, 125.2, 126.0, 126.2, 126.8, 128.1, 128.5, 131.2, 141.0, 168.2; IR (NaCl, neat) ν 3017, 2222, 1749, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{21}O_2S$ (M^+ + H) 349.1262, found 349.1257.

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*3,4-Diphenyl-1H-cyclopenta[b]naphthalene (**4a**:).* wt 57.6 mg; yield 90%; yellow solid, mp = 218−219 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.68−3.69 (d, 2H, J = 1.2 Hz), 6.51 (t, 1H, J = 2.2 Hz), 6.84−6.86 (m, 2H), 6.90−6.94 (m, 2H), 6.98−7.09 (m, 6H), 7.31−7.35 (m, 1H), 7.43−7.47 (m, 1H), 7.65−7.67 (d, 1H, J = 7.9 Hz), 7.89−7.91 (d, 1H, J = 8.1 Hz), 7.98 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 37.0, 122.2, 125.0, 125.1, 125.8, 126.4, 126.5, 127.0, 127.2, 127.7, 128.1, 131.2, 131.9, 132.2, 132.3, 135.5, 137.2, 137.7, 139.9, 142.4, 147.3; HRMS (ESI) calcd for $C_{25}H_{19}$ (M^+ + H) 319.1487, found 319.1495.

*3-Methyl-4-phenyl-1H-cyclopenta[b]naphthalene (**4e**):* wt 34.8 mg; yield 67%; yellow solid, mp = 157−158 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.54 (t, 3H, J = 4.4 Hz), 3.47 (d, 2H, J = 0.8 Hz), 6.25 (d, 1H, J = 1.5 Hz), 7.29−7.33 (m, 1H), 7.37−7.41 (m, 3H), 7.43−7.48 (m, 4H), 7.85−7.88 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 16.5, 36.3, 121.8, 124.7, 124.9, 126.3, 127.2, 127.6, 131.1, 131.5, 132.5, 139.1, 141.5, 142.6; HRMS (ESI) calcd for $C_{20}H_{17}$ (M^+ + H) 257.1330, found 257.1326.

*3-Cyclopropyl-4-phenyl-1H-cyclopenta[b]naphthalene (**4f**):* wt 30.1 mg; yield 60%; yellow solid, mp = 134−135 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.26−0.31 (m, 2H), 0.38−0.42 (m, 2H), 0.87−0.90 (m, 1H), 3.46 (s, 2H), 6.13−6.14 (d, 1H, J = 1.4 Hz), 7.31−7.34 (m, 1H), 7.41−7.49 (m, 7H), 7.86−7.88 (d, 2H, J = 9.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 7.6, 11.5, 36.1, 121.8, 124.7, 124.9, 126.5, 127.0, 127.5, 127.5, 128.9, 131.1, 131.6, 131.7, 132.8, 139.5, 141.3, 142.8, 147.8; HRMS (ESI) calcd for $C_{22}H_{19}$ (M^+ + H) 283.1487, found 283.1497.

*3-(4-Chlorophenyl)-4-phenyl-1H-cyclopenta[b]naphthalene (**4g**):* wt 55.0 mg; yield 71%; yellow solid, mp = 168−169 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.68 (d, 2H, J = 1.1 Hz), 6.50 (t, 1H, J = 2.3 Hz), 6.76−6.78 (m, 2H), 6.88−6.90 (m, 2H), 7.00−7.02 (m, 2H), 7.05−7.09 (m, 2H), 7.15−7.19 (m, 1H), 7.33−7.37 (m, 1H), 7.44−7.48 (m, 1H), 7.66−7.69 (d, 1H, J = 8.6 Hz), 7.90−7.92 (d, 1H, J = 8.1 Hz), 7.98 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 37.1, 122.3, 125.1, 125.2, 126.4, 126.6, 127.2, 127.3, 127.7, 129.4, 131.3, 131.7, 132.0, 132.2, 135.7, 136.2, 137.2, 139.8, 142.1, 146.2; HRMS (ESI) calcd for $C_{25}H_{17}ClNa$ (M^++Na): 375.0916, found 375.0913.

*4-(4-Fluorophenyl)-3-phenyl-1H-cyclopenta[b]naphthalene (**4h**):* wt 58.0 mg; yield 86%; yellow solid, mp = 222−223 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.68 (d, 2H, J = 1.2 Hz), 6.52 (t, 1H, J = 2.3 Hz), 6.68−6.72 (m, 2H), 6.83−6.85 (m, 2H), 6.94−7.00 (m, 4H), 7.05−7.09 (m, 1H), 7.33−7.37 (m, 1H), 7.44−7.48 (m, 1H), 7.61−7.63 (d, 1H, J = 8.5 Hz), 7.90−7.92 (d, 1H, J = 8.1 Hz), 7.99 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 37.0, 113.9, 114.1, 122.3, 125.1, 125.2, 126.0, 126.1, 127.2, 127.8, 128.2, 131.9, 132.3, 132.6, 132.7, 135.6, 137.6, 140.4, 142.3, 147.1; HRMS (ESI) calcd for $C_{25}H_{18}F$ (M^+ + H) 337.1393, found 337.1401.

*3-Phenyl-4-(p-tolyl)-1H-cyclopenta[b]naphthalene (**4i**):* wt 13.3 mg; yield 41%; yellow solid, mp = 182−183 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.24 (s, 3H), 3.66 (d, 2H, J = 1.2 Hz), 6.49 (t, 1H, J = 2.3 Hz), 6.77−6.83 (m, 4H), 6.86−6.92 (m, 4H), 6.98−7.02 (m, 1H), 7.30−7.34 (m, 1H), 7.41−7.45 (m, 1H), 7.70−7.72 (d, 1H, J = 8.4 Hz), 7.87−7.89 (d, 1H, J = 8.1 Hz), 7.95 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 21.1, 37.0, 122.0, 124.9, 125.0, 125.3, 126.5, 126.9, 127.6, 127.8, 128.2, 131.0, 131.9, 132.3, 134.2, 135.3, 136.0, 137.8, 142.3, 147.4; HRMS (ESI) calcd for $C_{26}H_{21}$ (M^+ + H) 333.1643, found 333.1641.

*3-(3-Phenyl-1H-cyclopenta[b]naphthalen-4-yl)thiophene (**4j**):* wt 37.0 mg; yield 59%; yellow solid, mp = 219−220 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.67−3.68 (d, 2H, J = 1.0 Hz), 6.53 (t, 1H, J = 2.2 Hz), 6.76−6.77 (m, 1H), 6.81−6.83 (m, 1H), 6.93−6.96 (m, 2H), 7.02−7.12 (m, 4H), 7.35−7.39 (m, 1H), 7.44−7.48 (m, 1H), 7.74−7.76 (d, 1H, J = 8.5 Hz), 7.88−7.90 (d, 1H, J = 8.0 Hz), 7.97 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 37.0, 122.3, 123.9, 125.0, 125.1, 125.2, 125.9, 126.2, 126.9, 127.3, 127.7, 130.4, 131.9, 132.8, 135.8, 137.2, 137.7, 140.6, 142.3, 147.3; HRMS (ESI) calcd for $C_{23}H_{17}S$ (M^+ + H) 325.1051, found 325.1047.

*6-Fluoro-3,4-diphenyl-1H-cyclopenta[b]naphthalene (**4k**):* wt 43.0 mg; yield 65%; orange solid, mp = 130−131 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.65−3.66 (d, 2H, J = 1.3 Hz), 6.52 (t, 1H, J = 4.6 Hz), 6.81−6.84 (m, 2H), 6.88−6.92 (m, 2H), 6.96−7.06 (m, 6H), 7.18−7.28 (m, 2H), 7.84−7.87 (m, 1H), 7.94 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 36.9, 109.8, 110.0, 115.0, 115.2, 122.0, 125.9, 126.8, 127.1, 127.4, 128.1, 129.7, 129.8, 131.1, 136.2, 136.8, 137.4, 141.7, 147.2; HRMS (ESI) calcd for $C_{25}H_{18}F$ (M^+ + H) 337.1393, found 337.1402.

*6-Bromo-3,4-diphenyl-1H-cyclopenta[b]naphthalene (**4l**):* wt 62.0 mg; yield 81%; yellow solid, mp = 176−177 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.66 (d, 2H, J = 1.2 Hz), 6.54 (t, 1H, J = 2.2 Hz), 6.82−6.84 (m, 2H), 6.90−7.10 (m, 8H), 7.50−7.53 (m, 1H), 7.75−7.80 (m, 2H), 7.93 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 37.0, 119.4, 122.0, 125.9, 126.9, 127.1, 127.4, 128.1, 128.3, 128.5, 129.3, 130.3, 131.1, 131.5, 133.7, 136.3, 136.4, 137.3, 140.8, 142.9, 147.2; HRMS (ESI) calcd for $C_{25}H_{18}Br$ (M^+ + H) 397.0592, found 397.0583.

*6-Pentyl-3,4-diphenyl-1H-cyclopenta[b]naphthalene (**4m**):* wt 51.0 mg; yield 57%; yellow solid, mp = 83−84 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.76 (t, 3H, J = 6.8 Hz), 1.16−1.18 (m, 4H), 1.44−1.52 (m, 2H), 2.52 (t, 2H, J = 7.6 Hz), 3.55 (d, 2H, J = 1.2 Hz), 6.38 (t, 1H, J = 2.2 Hz), 6.73−6.75 (m, 2H), 6.80−6.84 (m, 2H), 6.87−6.98 (m, 6H), 7.20−7.22 (m, 1H), 7.32 (s, 1H), 7.71−7.73 (d, 1H, J = 8.3 Hz), 7.83 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.5, 31.2, 31.5, 36.3, 36.9, 121.9, 124.9, 125.7, 126.5, 127.0, 127.1, 127.6, 127.8, 127.9, 128.1, 128.4, 130.4, 131.3, 131.8, 132.4, 135.4, 137.4, 137.8, 139.7, 139.9, 141.5, 147.4; HRMS (ESI) calcd for $C_{30}H_{29}$ (M^+ + H) 389.2269, found 389.2265.

*6-Methyl-3,4-diphenyl-1H-cyclopenta[b]naphthalene (**4n**):* wt 45.3 mg; yield 68%; yellow solid, mp = 151−152 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 3.67 (d, 2H, J = 1.2 Hz), 6.49 (t, 1H, J = 2.3 Hz), 6.84−6.86 (m, 2H), 6.91−6.94 (m, 2H), 6.98−7.09 (m, 6H), 7.28−7.31 (m, 1H), 7.42 (d, 1H, J = 0.5 Hz), 7.80−7.82 (d, 1H, J = 8.3 Hz), 7.94 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 22.0, 36.9, 121.9, 125.3, 125.7, 126.5, 127.0, 127.2, 127.2, 127.6, 128.1, 130.2, 131.3, 131.7, 132.4, 134.6, 135.5, 137.4, 137.8, 140.0, 141.4, 147.4; HRMS (ESI) calcd for $C_{26}H_{21}$ (M^+ + H) 333.1643, found 333.1645.

*8-Methyl-3,4-diphenyl-1H-cyclopenta[b]naphthalene (**4o**):* wt 53.0 mg; yield 81%; yellow solid, mp = 207−208 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.78 (s, 3H), 3.70 (d, 2H, J = 1.2 Hz), 6.49 (t, 1H, J = 2.3 Hz), 6.82−6.84 (m, 2H), 6.89−6.92 (m, 2H), 6.95−7.03 (m, 6H), 7.19−7.24 (m, 1H), 7.28−7.29 (d, 1H, J = 6.8 Hz), 7.50−7.52 (d, 1H, J = 8.5 Hz), 8.16−8.17 (d, 1H, J = 0.7 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 20.0, 37.3, 118.4, 124.6, 125.0, 125.8, 125.9, 126.5, 127.0, 127.1, 128.1, 130.9, 131.3, 132.4, 132.7, 133.7, 135.4, 137.6, 137.7, 139.5, 142.3, 147.3; HRMS (ESI) calcd for $C_{26}H_{21}$ (M^+ + H) 333.1643, found 333.1638.

*5,7-Dimethyl-3,4-diphenyl-1H-cyclopenta[b]naphthalene (**4p**):* wt 38.0 mg; yield 53%; yellow solid, mp = 166−167 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.79 (s, 3H), 2.46 (s, 3H), 3.61−3.62 (d, 2H, J = 1.2 Hz), 6.37 (t, 1H, J = 2.3 Hz), 6.74−6.76 (m, 2H), 6.85−6.93 (m, 4H), 6.97−6.99 (m, 5H), 7.54 (s, 1H), 7.88 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 21.1, 25.1, 36.5, 122.9, 125.3, 126.2, 126.5, 126.5, 127.0, 128.4, 129.4, 131.6, 132.0, 132.8, 133.6, 134.2, 135.4, 136.0, 138.8, 140.2, 140.8, 141.2, 148.0; HRMS (ESI) calcd for $C_{27}H_{23}$ (M^+ + H) 347.1800, found 347.1792.

*5,6,8-Trimethyl-3,4-diphenyl-1H-cyclopenta[b]naphthalene (**4q**):* wt 12.2 mg; yield 42%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.64 (s, 3H), 2.29 (s, 3H), 2.72 (s, 3H), 3.64−3.65 (d, 2H, J = 1.2 Hz), 6.41 (t, 1H, J = 2.2 Hz), 6.70−6.72 (m, 2H), 6.82−7.00 (m, 8H), 7.16 (s, 1H), 8.11 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 19.9, 20.1, 21.5, 29.7, 36.7, 118.9, 125.2, 126.2, 126.6, 127.0, 128.0, 129.8, 130.8, 131.4, 131.6, 132.3, 132.9, 134.5, 136.0, 139.1, 140.3, 141.0, 147.9; HRMS (ESI) calcd for $C_{28}H_{25}$ (M^+ + H) 361.1956, found 361.1942.

*7,8-Diphenyl-10H-cyclopenta[b]phenanthrene (**4r**):* wt 39.0 mg; yield 57%; yellow solid, mp = 196−207 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.78 (s, 2H), 6.56 (t, 1H, J = 2.0 Hz), 6.87−7.11 (m, 10H), 7.57−7.64 (m, 3H), 7.67−7.70 (m, 1H), 7.86−7.88 (d, 1H, J = 7.8 Hz), 8.80−8.82 (d, 1H, J = 8.4 Hz), 8.91 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 37.7, 117.3, 122.9, 125.2, 125.8, 125.8, 126.2, 126.4, 126.6, 127.1, 127.2, 128.1, 128.3, 128.4, 130.2, 130.4, 131.3,

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131.6, 133.3, 135.3, 137.5, 137.6, 140.5, 143.2, 147.4; HRMS (ESI) calcd for $C_{29}H_{21}$ (M^+ + H) 369.1643, found 369.1639.

*7,8-Diphenyl-5H-indeno[5,6-b]thiophene (**4s**):* wt 7.0 mg; yield 10%; yellow solid, mp = 201−202 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.62 (d, 2H, J = 1.4 Hz), 6.50 (t, 1H, J = 2.2 Hz), 6.88−6.93 (m, 4H), 6.96−7.07 (m, 4H), 7.11−7.13 (m, 2H), 7.37−7.40 (m, 2H), 7.94 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 37.2, 117.9, 123.9, 126.0, 126.5, 127.0, 127.1, 127.5, 128.0, 129.6, 130.1, 134.3, 137.4, 137.4, 142.7; HRMS (ESI) calcd for $C_{23}H_{17}S$ (M^+ + H) 325.1051, found 325.1060.

*4,5-Diphenyl-7H-indeno[5,6-b]thiophene (**4t**):* wt 35.0 mg; yield 52%; yellow solid, mp = 182−183 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.72−3.73 (d, 2H, J = 1.1 Hz), 6.55 (t, 1H, J = 2.3 Hz), 6.81−6.83 (m, 2H), 6.89−6.93 (m, 2H), 6.96−7.02 (m, 5H), 7.18−7.22 (m, 1H), 7.52−7.57 (m, 2H), 8.45−8.46 (d, 1H, J = 0.7 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 37.3, 118.6, 124.6, 125.3, 125.7, 125.9, 126.8, 127.1, 127.2, 128.1, 129.1, 131.2, 131.7, 132.5, 133.8, 136.4, 136.9, 137.3, 140.6, 143.7, 147.1; HRMS (ESI) calcd for $C_{23}H_{17}S$ (M^+ + H) 325.1051, found 325.1058.

*(Z)-1-(2-Benzoyl-3-phenylcyclopent-2-en-1-ylidene)-1-phenylpropan-2-one (**5a**):* wt 36.0 mg; yield 83%; brown solid, mp = 139−140 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.83 (s, 3H), 2.78−2.80 (m, 2H), 2.97−3.00 (m, 2H), 7.11−7.13 (m, 3H), 7.17−7.19 (m, 2H), 7.25−7.29 (m, 4H), 7.34−7.37 (m, 2H), 7.40−7.44 (m, 2H), 7.82−7.84 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 29.5, 33.4, 34.9, 127.6, 127.8, 128.0, 128.1, 128.8, 129.0, 129.2, 129.2, 132.6, 135.8, 137.5, 139.0, 152.2, 195.3, 201.1; IR (NaCl, neat) ν 3015, 1668, 1653, 1580, 1356, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{23}O_2$ (M^+ + H) 379.1698, found 379.1703.

*(Z)-2-(2-Benzoyl-3-phenylcyclopent-2-en-1-ylidene)-1,2-diphenylethanone (**5b**):* wt 47.3 mg; yield 68%; yellow solid, mp = 173−174 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.08−3.10 (m, 2H), 3.13−3.16 (m, 2H), 7.08−7.09 (m, 3H), 7.13−7.20 (m, 7H), 7.25−7.32 (m, 6H), 7.63−7.69 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.9, 35.0, 127.3, 127.8, 127.9, 128.0, 128.6, 128.7, 128.9, 129.5, 129.9, 132.3, 132.8, 133.3, 135.8, 136.9, 137.4, 138.4, 138.6, 150.8, 155.7, 196.1, 196.5; IR (NaCl, neat) ν 3017, 1655, 1597, 1580, 1449, 1219 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{25}O_2$ (M^+ + H) 441.1855, found 441.1846.

*(Z)-2-(2-Benzoyl-3-phenylcyclopent-2-en-1-ylidene)-1-cyclopropyl-2-phenylethanone (**5d**):* wt 52.0 mg; yield 67%; yellow solid, mp = 109−110 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.57−0.61 (m, 2H), 0.80−0.84 (m, 2H), 1.60−1.66 (m, 1H), 2.88−2.91 (m, 2H), 2.97−3.01 (m, 2H), 7.09−7.15 (m, 5H), 7.25−7.27 (m, 2H), 7.32−7.41(m, 6H), 7.80−7.83 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 11.7, 21.0, 33.5, 35.0, 127.5, 127.8, 128.0, 128.7, 128.7, 129.1, 129.6, 132.5, 134.3, 136.0, 137.5, 138.6, 138.9, 151.2, 157.5, 194.7, 203.1; IR (NaCl, neat) ν 3017, 1659, 1597, 1582, 1379, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}O_2$ (M^+ + H) 405.1855, found 405.1858.

*(Z)-1-(2-Benzoyl-3-methylcyclopent-2-en-1-ylidene)-1-phenylpropan-2-one (**5e**):* wt 14.9 mg; yield 23%; brown solid, mp = 144−145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.65 (s, 3H), 1.83 (s, 3H), 2.54−2.58 (m, 2H), 2.59−2.60 (m, 2H), 7.20−7.22 (m, 2H), 7.30−7.33 (m, 1H), 7.38−7.41 (m, 2H), 7.45−7.49 (m, 2H), 7.51−7.55 (m, 1H), 7.92−7.94 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 17.4, 29.4, 32.8, 36.4, 127.4, 128.4, 128.9, 129.0, 129.3, 131.2, 132.6, 138.5, 138.9, 139.5, 154.3, 162.3, 193.7, 200.1; IR (NaCl, neat) ν 3013, 1670, 1597, 1580, 1356, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{21}O_2$ (M^+ + H) 317.1542, found 317.1534.

*(Z)-1-(2-Benzoyl-3-cyclopropylcyclopent-2-enylidene)-1-phenylpropan-2-one (**5f**):* wt 24.0 mg; yield 50%; yellow solid, mp = 142−143 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.77 (d, 4H, J = 6.6 Hz), 1.65 (s, 3H), 1.72−1.76 (m, 1H), 2.19−2.22 (m, 2H), 2.52−2.54 (m, 2H), 7.19−7.21 (m, 2H), 7.28−7.33 (m, 1H), 7.37−7.40 (m, 2H), 7.45−7.55 (m, 3H), 7.99−8.02 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 8.2, 13.7, 28.8, 29.4, 32.2, 127.4, 128.4, 128.9, 129.1, 129.4, 130.1, 132.5, 138.4, 138.6, 139.8, 154.5, 167.5, 193.8, 199.8; IR (NaCl, neat) ν 3013, 1670, 1647, 1597, 1541, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}O_2$ (M^+ + H) 343.1698, found 343.1693.

*(Z)-1-(2-Benzoyl-3-(4-chlorophenyl)cyclopent-2-enylidene)-1-phenylpropan-2-one (**5g**):* wt 47.3 mg; yield 50%; brown solid, mp = 165−166 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.81 (s, 3H), 2.77−2.80 (m, 2H), 2.94−2.96 (m, 2H), 7.08−7.14 (m, 4H), 7.26−7.36 (m, 5H), 7.40−7.44 (m, 3H), 7.82−7.84 (d, 2H, J = 7.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 29.5, 33.2, 34.8, 127.7, 128.2, 128.3, 129.0, 129.1, 129.1, 129.2, 132.8, 134.2, 134.7, 137.4, 138.9, 139.2, 151.9, 156.9, 195.0, 200.9; IR (NaCl, neat) ν 3019, 1663, 1597, 1580, 1354, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{22}O_2Cl$ (M^+ + H) 413.1308, found 413.1300.

*(Z)-1-(2-(4-Fluorobenzoyl)-3-phenylcyclopent-2-en-1-ylidene)-1-phenylpropan-2-one (**5h**):* wt 62.0 mg; yield 78%; brown solid, mp = 153−154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.88 (s, 3H), 2.77−2.80 (m, 2H), 2.97−3.00 (m, 2H), 6.92 (t, 2H, J = 8.7 Hz), 7.11−7.17 (m, 5H), 7.26−7.29 (m, 2H), 7.32−7.36 (m, 1H), 7.40−7.44 (m, 2H), 7.82−7.86 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 29.6, 33.5, 34.8, 115.1, 115.3, 127.7, 127.8, 128.1, 129.0, 129.0, 129.1, 131.7, 131.8, 133.7, 134.0, 134.1, 135.7, 138.4, 138.9, 152.1, 158.6, 164.0, 166.6, 193.9, 201.1; IR (NaCl, neat) ν 3015, 1663, 1653, 1595, 1219 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{22}O_2F$ (M^+ + H) 397.1604, found 397.1607.

*(Z)-1-(2-(4-Methylbenzoyl)-3-phenylcyclopent-2-en-1-ylidene)-1-phenylpropan-2-one (**5i**):* wt 39.0 mg; yield 71%; yellow solid, mp = 148−149 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.83 (s, 3H), 2.29 (s, 3H), 2.77−2.80 (m, 2H), 2.97−2.99 (m, 2H), 7.06−7.08 (d, 2H, J = 7.9 Hz), 7.12−7.14 (m, 3H), 7.19−7.21 (m, 2H), 7.26−7.34 (m, 4H), 7.39−7.43 (m, 2H), 7.72−7.75 (d, 2H, J = 8.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 21.7, 29.5, 33.3, 34.8, 127.6, 127.9, 128.0, 128.8, 128.9, 128.9, 129.1, 129.3, 133.8, 135.1, 135.9, 138.7, 139.0, 143.3, 152.0, 157.9, 195.1, 201.1; IR (NaCl, neat) ν 1655, 1603, 1572, 1491, 1354, 1265 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}O_2$ (M^+ + H) 393.1855, found 393.1847.

*(Z)-1-Phenyl-1-(3-phenyl-2-(thiophene-3-carbonyl)cyclopent-2-en-1-ylidene)propan-2-one (**5j**):* wt 55.3 mg; yield 59%; brown solid, mp = 128−129 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.90 (s, 3H), 2.77−2.79 (m, 2H), 2.96−2.99 (m, 2H), 7.10−7.12 (m, 1H), 7.16−7.24 (m, 5H), 7.25−7.29 (m, 2H), 7.31−7.35 (m, 1H), 7.39−7.43 (m, 3H), 7.79−7.80 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 29.6, 33.3, 34.9, 125.6, 127.5, 127.7, 127.8, 127.8, 128.1, 128.9, 129.0, 129.1, 133.5, 134.0, 135.9, 138.8, 139.4, 142.8, 151.3, 157.9, 189.1, 201.5; IR (NaCl, neat) ν 1647, 1636 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{21}O_2S$ (M^+ + H) 385.1229, found 385.1260.

*(Z)-1-(2-Benzoyl-3-phenylcyclopent-2-en-1-ylidene)-1-(4-fluorophenyl)propan-2-one (**5k**):* wt 53.1 mg; yield 68%; yellow solid, mp = 129−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.83 (s, 3H), 2.75−2.78 (m, 2H), 2.98−3.01 (m, 2H), 7.08−7.14 (m, 5H), 7.15−7.19 (m, 2H), 7.23−7.28 (m, 4H), 7.34−7.39 (m, 1H), 7.81−7.83 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 29.5, 33.4, 34.8, 115.9, 116.1, 127.8, 128.0, 128.1, 128.9, 129.2, 130.9, 130.9, 132.6, 132.6, 134.9, 134.9, 135.7, 137.5, 138.5, 152.7, 158.9, 161.0, 163.4, 195.2, 200.7; IR (NaCl, neat) ν 1653, 1647 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{22}O_2F$ (M^+ + H) 397.1592, found 397.1607.

*(Z)-1-(2-Benzoyl-3-phenylcyclopent-2-enylidene)-1-(4-bromophenyl)propan-2-one (**5l**):* wt 69.6 mg; yield 81%; yellow solid, mp = 153−154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.84 (s, 3H), 2.75−2.78 (m, 2H), 2.98−3.01 (m, 2H), 7.09−7.12 (m, 3H), 7.15−7.18 (m, 4H), 7.24−7.28 (m, 2H), 7.35−7.38 (m, 1H), 7.54−7.56 (m, 2H), 7.80−7.82 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 29.5, 33.4, 34.9, 121.8, 127.8, 128.1, 128.1, 129.0, 129.2, 130.9, 132.2, 132.4, 132.7, 135.6, 137.4, 137.9, 138.5, 152.8, 159.2, 195.2, 200.4; IR (NaCl, neat) ν 3015, 1667, 1549, 1356, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{22}O_2$ Br (M^+ + H) 457.0803, found 457.0813.

*(Z)-1-(2-Benzoyl-3-phenylcyclopent-2-en-1-ylidene)-1-(4-pentylphenyl)propan-2-one (**5m**):* wt 83.5 mg; yield 78%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, 3H, J = 7.0 Hz), 1.33−1.39 (m, 4H), 1.61−1.68 (m, 2H), 1.83 (s, 3H), 2.63 (t, 2H, J = 7.6 Hz), 2.79−2.82 (m, 2H), 2.96−2.99 (m, 2H), 7.09−7.12 (m, 3H), 7.15−7.27 (m, 8H), 7.34−7.37 (m, 1H), 7.82−7.84 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 14.1, 22.6, 29.5, 31.0, 31.6, 33.4, 34.9, 35.7, 127.8, 128.0, 128.0, 128.7, 128.9, 129.0, 129.2, 132.6, 133.9, 135.9, 136.0, 137.6, 138.7, 142.5, 151.7, 158.1, 195.4, 201.5; IR (NaCl, neat)

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ν 3017, 1667, 1582, 1449, 1356, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{33}O_2$ (M^+ + H) 449.2481, found 449.2486.

*(Z)-1-(2-Benzoyl-3-phenylcyclopent-2-en-1-ylidene)-1-(p-tolyl)-propan-2-one (**5n**):* wt 64.3 mg; yield 78%; brown solid, mp = 123−124 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.83 (s, 3H), 2.38 (s, 3H), 2.79−2.81 (m, 2H), 2.96−2.99 (m, 2H), 7.10−7.12 (m, 3H), 7.15−7.18 (m, 4H), 7.21−7.28 (m, 4H), 7.34−7.38 (m, 1H), 7.82−7.84 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.3, 29.5, 33.4, 34.9, 127.8, 128.0, 128.0, 128.7, 129.0, 129.2, 129.6, 132.6, 133.8, 135.9, 135.9, 137.4, 137.5, 138.7, 151.8, 158.3, 195.4, 201.5; IR (NaCl, neat) ν 3017, 1672, 1651, 1580, 1557, 1356, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}O_2$ (M^+ + H) 393.1855, found 393.1855.

*(Z)-1-(2-Benzoyl-3-phenylcyclopent-2-enylidene)-1-(o-tolyl)-propan-2-one (**5o**):* wt 41.0 mg; yield 54%; yellow solid, mp = 187−188 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.69 (s, 3H), 2.26 (m, 3H), 2.40−2.47 (m, 1H), 2.62−2.69 (m, 1H), 2.89−3.03 (m, 2H), 7.13−7.15 (m, 3H), 7.20−7.32 (m, 8H), 7.37−7.40 (m, 1H), 7.85−7.87 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 19.7, 29.0, 33.2, 34.7, 126.7, 127.9, 128.0, 128.1, 128.8, 129.1, 129.5, 130.7, 132.1, 132.4, 135.8, 136.4, 138.0, 139.0, 139.0, 154.2, 159.8, 194.4, 199.0; IR (NaCl, neat) ν 3019, 1667, 1356, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}O_2$ (M^+ + H) 393.1855, found 393.1855.

*(Z)-1-(2-Benzoyl-3-phenylcyclopent-2-enylidene)-1-(3,5-dimethylphenyl)propan-2-one (**5p**):* wt 56.5 mg; yield 70%; yellow solid, mp = 161−162 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.83 (s, 3H), 2.33 (s, 6H), 2.78−2.81 (m, 2H), 2.96−2.99 (m, 2H), 6.89 (s, 2H), 6.97 (s, 1H), 7.10−7.13 (m, 3H), 7.15−7.18 (m, 2H), 7.25−7.28 (m, 2H), 7.34−7.39 (m, 1H), 7.81−7.84 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.3, 29.5, 33.3, 34.9, 126.8, 127.7, 127.8, 128.0, 128.0, 128.3, 128.7, 129.0, 129.2, 132.5, 134.1, 135.9, 137.6, 138.4, 138.7, 138.8, 151.6, 158.2, 195.3, 201.4; IR (NaCl, neat) ν 3017, 1667, 1599, 1582, 1356, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{27}O_2$ (M^+ + H) 407.2011, found 407.2002.

*(Z)-1-(2-Benzoyl-3-phenylcyclopent-2-enylidene)-1-mesitylpropan-2-one (**5q**):* wt 53.2 mg; yield 58%; yellow solid, mp = 175−176 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.69 (s, 3H), 2.18 (s, 3H), 2.24 (s, 3H), 2.26 (s, 3H), 2.42−2.49 (m, 1H), 2.64−2.71 (m, 1H), 2.93−2.98 (m, 2H), 6.96 (s, 1H), 7.04 (s, 1H), 7.12−7.14 (m, 3H), 7.19−7.23 (m, 2H), 7.27−7.31 (m, 2H), 7.36−7.40 (m, 1H), 7.84−7.87 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 19.1, 19.3, 19.5, 28.9, 33.2, 34.7, 127.9, 128.0, 128.0, 128.8, 129.1, 130.5, 131.9, 132.3, 132.4, 133.4, 134.6, 135.8, 136.1, 136.3, 138.0, 139.0, 153.8, 159.4, 194.5, 199.5; IR (NaCl, neat) ν 3017, 1665, 1449, 1356, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{29}O_2$ (M^+ + H) 421.2168, found 421.2161.

*(Z)-1-(2-Benzoyl-3-phenylcyclopent-2-enylidene)-1-(naphthalen-1-yl)propan-2-one (**5r**):* wt 33.6 mg; yield 45%; yellow solid, mp = 144−145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.68 (s, 3H), 2.41−2.44 (m, 1H), 2.62−2.68 (m, 1H), 2.90−2.93 (m, 2H), 7.12−7.15 (m, 3H), 7.22−7.25 (m, 2H), 7.31−7.35 (m, 2H), 7.39−7.46 (m, 2H), 7.52−7.56 (m, 3H), 7.86−7.97 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 29.0, 33.1, 34.8, 125.0, 126.0, 126.3, 126.9, 127.2, 127.9, 128.1, 128.1, 128.3, 128.7, 128.9, 129.2, 130.8, 131.6, 132.5, 134.1, 135.7, 137.0, 137.9, 138.9, 155.3, 160.0, 194.7, 199.5; IR (NaCl, neat) ν 3017, 1663, 1655, 1358, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{25}O_2$ (M^+ + H) 429.1855, found 429.1863.

*(Z)-1-(2-Benzoyl-3-phenylcyclopent-2-enylidene)-1-(thiophene-3-yl)propan-2-one (**5s**):* wt 59.8 mg; yield 74%; brown solid, mp = 136−137 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.91 (s, 3H), 2.88−2.91 (m, 2H), 3.00−3.03 (m, 2H), 7.02−7.03 (m, 1H), 7.09−7.13 (m, 3H), 7.15−7.20 (3H), 7.23−7.27 (m, 2H), 7.34−7.39 (m, 2H), 7.80−7.82 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 29.4, 33.5, 34.9, 123.9, 126.0, 127.8, 128.0, 128.1, 128.2, 128.7, 128.8, 129.2, 132.7, 135.7, 137.4, 138.5, 138.6, 152.2, 158.3, 195.6, 201.4; IR (NaCl, neat) ν 3017, 1667, 1661, 1580, 1356, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{21}O_2S$ (M^+ + H) 385.1262, found 385.1270.

*(E)-1-(2-Benzoyl-3-phenylcyclopent-2-enylidene)-1-(thiophene-2-yl)propan-2-one (**5t**):* wt 57.4 mg; yield 71%; pink solid, mp = 185−186 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.71 (s, 3H), 2.60−2.63 (m, 2H), 2.89−2.96 (m, 1H), 3.00−3.07 (m, 1H), 7.13−7.15 (m, 3H), 7.21−7.25 (m, 2H), 7.29−7.34 (m, 4H), 7.37−7.41 (m, 1H), 7.49−7.51 (m, 1H), 7.87−7.89 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 28.9, 33.2, 34.8, 127.6, 127.9, 128.1, 128.1, 129.0, 129.1, 129.4, 129.7, 130.1, 131.3, 132.4, 134.1, 135.6, 138.0, 138.4, 138.9, 156.2, 161.4, 193.8, 197.3; IR (NaCl, neat) ν 3017, 1676, 1670, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{20}O_2SNa$ (M^++Na): 407.1082, found 407.1075.

*(Z)-2-Methyl-1-(5-(2-oxo-1-phenylpropylidene)-2-phenylcyclopent-1-en-1-yl)prop-2-en-1-one (**5u**):* wt 9.4 mg; yield 13%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.89 (s, 3H), 1.95 (s, 3H), 2.68−2.71 (m, 2H), 2.89−2.92 (m, 2H), 5.60 (s, 1H), 5.77 (s, 1H), 7.19−7.22 (m, 2H), 7.28−7.31 (m, 4H), 7.33−7.35 (m, 1H), 7.40−7.43 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 17.1, 29.8, 32.9, 34.5, 126.7, 127.6, 127.6, 128.2, 128.9, 129.0, 129.1, 133.4, 136.4, 139.1, 144.5, 152.0, 157.9, 197.4, 201.0; IR (NaCl, neat) ν 3017, 1674, 1670, 1217 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}O_2$ (M^+ + H) 343.1698, found 343.1692.

*4,7-Diphenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl Acetate (**6u**):* wt 50.0 mg; yield 72%; yellow solid, mp = 87−88 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.72 (s, 3H), 2.10 (s, 3H), 2.83−2.99 (m, 2H), 3.25−3.32 (m, 1H), 3.42−3.49 (m, 1H), 5.20 (t, 1H, J = 1.4 Hz), 5.46 (d, 1H, J = 0.4 Hz), 7.16−7.22 (m, 2H), 7.30−7.42 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 18.9, 21.6, 24.9, 38.9, 87.0, 112.9, 125.1, 126.8, 126.9, 127.7, 127.8, 128.2, 128.6, 133.3, 134.9, 136.8, 14 1.8, 147.2, 162.9, 168.7; IR (NaCl, neat) ν 3019, 1738, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}O_2$ (M^+ + H) 343.1698, found 343.1708.

*4,7-Diphenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl Benzoate (**6v**):* wt 38.0 mg; yield 48%; yellow solid, mp = 122−123 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.80 (s, 3H), 2.90−3.01 (m, 2H), 3.32−3.38 (m, 1H), 3.45−3.51 (m, 1H), 5.26 (t, 1H, J = 1.3 Hz), 5.65 (s, 1H), 7.16−7.20 (m, 2H), 7.29−7.34 (m, 4H), 7.40−7.45 (m, 6H), 7.51−7.55 (m, 1H), 8.07−8.09 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 19.0, 25.1, 38.9, 87.4, 113.2, 125.2, 126.8, 126.8, 127.5, 127.8, 128.3, 128.3, 128.6, 129.8, 130.9, 132.8, 133.4, 134.9, 136.9, 142.2, 147.5, 162.8, 164.1; IR (NaCl, neat) ν 3019, 1728, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}O_2$ (M^+ + H) 405.1855, found 405.1850.

*4,7-Diphenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl Pivalate (**6w**):* wt 18.0 mg; yield 24%; yellow solid, mp = 117−118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (s, 9H), 1.71 (s, 3H), 2.84−3.02 (m, 2H), 3.29−3.43 (m, 2H), 5.15 (t, 1H, J = 1.6 Hz), 5.60 (s, 1H), 7.14−7.19 (m, 2H), 7.28−7.35 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 19.0, 25.2, 27.4, 38.6, 39.7, 86.0, 112.8, 125.0, 126.6, 126.7, 127.1, 127.3, 127.8, 128.3, 128.5, 133.4, 135.1, 136.8, 142.7, 148.1, 161.6, 175.7; IR (NaCl, neat) ν 3019, 1736, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{29}O_2$ (M^+ + H) 385.2168, found 385.2177.

*4,7-Diphenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl Cyclopropanecarboxylate (**6x**):* wt 22.0 mg; yield 31%; yellow solid, mp = 119−120 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.78−0.82 (m, 2H), 0.94−0.96 (m, 2H), 1.65−1.70 (m, 4H), 2.87−2.94 (m, 2H), 3.26−3.33 (m, 1H), 3.38−3.45 (m, 1H), 5.17 (s, 1H), 5.50 (s, 1H), 7.15−7.20 (m, 2H), 7.30−7.33 (m, 4H), 7.36−7.39 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 8.3, 8.4, 13.5, 18.9, 25.0, 38.8, 86.7, 112.9, 125.1, 126.7, 127.5, 128.2, 128.5, 133.4, 134.9, 137.0, 142.1, 147.6, 162.5, 172.3; IR (NaCl, neat) ν 3019, 1734, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{19}$ (M^+−$OCOcC_3H_5$) 283.1487, found 283.1479.

*4-(4-Chlorophenyl)-7-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]-hepta-1(7),4-dien-6-yl Acetate (**6y**):* wt 17.4 mg; yield 34%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.63 (s, 3H), 2.02 (s, 3H), 2.76−2.90 (m, 2H), 3.13−3.19 (m, 1H), 3.32−3.39 (m, 1H), 5.13 (s, 1H), 5.34 (s, 1H), 7.10−7.14 (m, 1H), 7.18−7.30 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 18.8, 21.6, 24.9, 39.2, 87.1, 113.1, 125.2, 126.6, 127.0, 128.3, 128.6, 128.9, 132.5, 133.1, 133.3, 137.2, 137.9, 141.5, 147.6, 162.8, 168.8; IR (NaCl, neat) ν 3019, 1744, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}O_2Cl$ (M^+ + H) 377.1308, found 377.1317.

*7-Phenyl-6-(prop-1-en-2-yl)-4-(p-tolyl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl Acetate (**6z**):* wt 45.0 mg; yield 63%; yellow solid, mp = 77−78 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.73 (s, 3H), 2.10 (s, 3H), 2.35 (s, 3H), 2.83−2.98 (m, 2H), 3.23−3.30 (m, 1H), 3.42−3.48 (m, 1H), 5.20 (s, 1H), 5.44 (s, 1H), 7.14−7.20 (m, 3H), 7.31−7.39 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 18.9, 21.3, 21.6, 24.9, 39.0, 87.2, 112.8, 125.0, 126.6, 127.7, 127.9, 128.5, 128.9, 132.1, 133.5, 136.3,

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136.8, 141.9, 146.2, 163.1, 168.7; IR (NaCl, neat) ν 3019, 1742, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{25}O_2$ (M^+ + H) 357.1855, found 357.1858.

*4-(Naphthalen-1-yl)-7-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]-hepta-1(7),4-dien-6-yl Acetate (**6α**):* wt 20.0 mg; yield 26%; yellow solid, mp = 78−79 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.62 (s, 3H), 2.04 (s, 3H), 2.90−3.06 (m, 2H), 3.53−3.55 (m, 2H), 5.02 (t, 1H, J = 1.4 Hz), 5.31 (d, 1H, J = 0.4 Hz), 7.18−7.22 (m, 1H), 7.32−7.36 (m, 2H), 7.42−7.49 (m, 6H), 7.73−7.75 (d, 1H, J = 7.6 Hz), 7.82−7.85 (m, 1H), 8.20−8.22 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 19.0, 21.6, 24.9, 43.4, 87.9, 113.1, 125.3, 125.4, 125.4, 125.6, 126.1, 126.3, 126.8, 127.6, 128.3, 128.5, 131.4, 133.3, 133.7, 133.9, 136.5, 141.9, 149.0, 162.6, 168.5; IR (NaCl, neat) ν 3017, 1744, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}O_2$ (M^+ + H) 393.1855, found 393.1848.

*6-(Oct-1-en-2-yl)-4,7-diphenylbicyclo[3.2.0]hepta-1(7),4-dien-6-yl Acetate (**6γ**):* wt 50.0 mg; yield 68%; yellow solid, mp = 67−68 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.77 (t, 3H, J = 6.7 Hz), 1.06−1.17 (m, 6H), 1.34−1.43 (m, 2H), 1.97−2.03 (m, 2H), 2.10 (s, 3H), 2.89−2.95 (m, 2H), 3.27−3.33 (m, 1H), 3.42−3.45 (m, 1H), 5.22 (d, 1H, J = 1.0 Hz), 5.58 (s, 1H), 7.16−7.22 (m, 2H), 7.30−7.43 (m, 8H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 14.0, 21.7, 22.5, 25.0, 27.9, 29.0, 30.7, 31.6, 38.9, 87.4, 111.2, 125.2, 126.7, 126.8, 127.6, 127.7, 128.1, 128.5, 133.4, 134.9, 137.0, 145.9, 147.5, 163.1, 168.6; IR (NaCl, neat) ν 3017, 1746, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{33}O_2$ (M^+ + H) 413.2481, found 413.2475.

*7-(4-Fluorophenyl)-4-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]-hepta-1(7),4-dien-6-yl Acetate (**6ε**):* wt 43.0 mg; yield 68%; yellow solid, mp = 92−93 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.71 (s, 3H), 2.10 (s, 3H), 2.81−2.97 (m, 2H), 3.25−3.32 (m, 1H), 3.41−3.48 (m, 1H), 5.20 (s, 1H), 5.46 (s, 1H), 7.00−7.04 (m, 2H), 7.18−7.22 (m, 1H), 7.31−7.36 (m, 4H), 7.39−7.41 (d, 2H, J = 7.4 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 18.8, 21.6, 24.8, 38.9, 87.0, 113.1, 115.6, 115.8, 126.7, 126.8, 126.9, 127.6, 128.2, 129.8, 134.8, 135.8, 141.6, 146.9, 160.4, 162.2, 162.9, 168.6; IR (NaCl, neat) ν 3017, 1748, 1219 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}O_2F$ (M^+ + H) 361.1604, found 361.1596.

*4-Phenyl-6-(prop-1-en-2-yl)-7-(p-tolyl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl Acetate (**6ζ**):* wt 49.0 mg; yield 69%; yellow solid, mp = 144−145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.71 (s, 3H), 2.08 (s, 3H), 2.33 (s, 3H), 2.82−2.96 (m, 2H), 3.23−3.30 (m, 1H), 3.40−3.47 (m, 1H), 5.18 (t, 1H, J = 1.4 Hz), 5.44 (d, 1H, J = 0.6 Hz), 7.12−7.20 (m, 3H), 7.26−7.33 (m, 4H), 7.39−7.41 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 19.0, 21.5, 21.7, 24.9, 38.9, 87.1, 112.9, 125.2, 126.8, 127.1, 127.6, 128.2, 129.4, 130.7, 135.0, 136.8, 137.0, 141.9, 161.9, 168.7; IR (NaCl, neat) ν 3019, 1746, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{25}O_2$ (M^+ + H) 357.1855, found 357.1858.

*7-(4-Pentylphenyl)-4-phenyl-6-(prop-1-en-2-yl)bicyclo[3.2.0]-hepta-1(7),4-dien-6-yl Acetate (**6η**):* wt 51.0 mg; yield 60%; yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, 3H, J = 6.8 Hz), 1.33−1.36 (m, 4H), 1.58−1.66 (m, 2H), 1.73 (s, 3H), 2.10 (s, 3H), 2.59 (t, 2H, J = 7.6 Hz), 2.87−2.93 (m, 2H), 3.25−3.31 (m, 1H), 3.41−3.47 (m, 1H), 5.19 (t, 1H, J = 1.3 Hz), 5.46 (s, 1H), 7.14−7.21 (m, 3H), 7.29−7.34 (m, 4H), 7.41−7.43 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 14.0, 18.9, 21.6, 22.6, 24.9, 31.1, 31.5, 35.9, 38.9, 87.1, 112.8, 125.1, 126.7, 127.0, 127.6, 128.1, 128.7, 130.8, 135.0, 137.0, 141.8, 141.9, 147.3, 161.8, 168.6; IR (NaCl, neat) ν 3019, 1717, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{33}O_2$ (M^+ + H) 413.2481, found 413.2482.

*4-Phenyl-6-(prop-1-en-2-yl)-7-(o-tolyl)bicyclo[3.2.0]hepta-1(7),4-dien-6-yl Acetate (**6θ**):* wt 55.0 mg; yield 75%; yellow solid, mp = 91−92 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.72 (s, 3H), 2.10 (s, 3H), 2.50 (s, 3H), 2.93−3.08 (m, 2H), 3.24−3.30 (m, 1H), 3.40−3.46 (m, 1H), 5.22−5.23 (d, 1H, J = 1.2 Hz), 5.58 (s, 1H), 7.10−7.23 (m, 4H), 7.31−7.41 (m, 5H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 18.8, 21.6, 21.8, 28.0, 38.3, 86.7, 113.1, 125.8, 125.9, 126.8, 127.2, 127.5, 127.9, 128.2, 130.6, 132.2, 135.0, 135.1, 136.9, 142.2, 147.6, 163.4, 168.4; IR (NaCl, neat) ν 3019, 2399, 1746, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{25}O_2$ (M^+ + H) 357.1855, found 357.1858.

*7-(3,5-Dimethylphenyl)-4-phenyl-6-(prop-1-en-2-yl)bicyclo-[3.2.0]hepta-1(7),4-dien-6-yl Acetate (**6ι**):* wt 44.0 mg; yield 60%; yellow solid, mp = 129−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.73 (s, 3H), 2.11 (s, 3H), 2.32 (s, 6H), 2.84−2.99 (m, 2H), 3.25−3.32 (m, 1H), 3.42−3.49 (m, 1H), 5.20 (s, 1H), 5.48 (s, 1H), 6.85 (s, 1H), 7.00 (s, 2H), 7.20 (t, 1H, J = 7.3 Hz), 7.31−7.35 (m, 2H), 7.41−7.43 (d, 2H, J = 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 19.0, 21.4, 21.7, 25.0, 38.9, 87.1, 112.8, 122.9, 126.7, 127.4, 127.6, 128.1, 128.8, 133.3, 135.0, 137.1, 138.0, 141.9, 147.3, 162.5, 168.7; IR (NaCl, neat) ν 3019, 1744, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{27}O_2$ (M^+ + H) 371.2011, found 371.2010.

*4-Phenyl-6-(prop-1-en-2-yl)-7-(2,4,5-trimethylphenyl)bicyclo-[3.2.0]hepta-1(7),4-dien-6-yl Acetate (**6κ**):* wt 57.1 mg; yield 72%; yellow solid, mp = 158−159 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.72 (s, 3H), 2.10 (s, 3H), 2.22 (s, 3H), 2.23 (s, 3H), 2.43 (s, 3H), 2.91−3.05 (m, 2H), 3.21−3.28 (m, 1H), 3.38−3.45 (m, 1H), 5.22 (t, 1H, J = 1.4 Hz), 5.56 (d, 1H, J = 0.6 Hz), 6.94 (s, 1H), 7.18−7.21 (m, 2H), 7.31−7.39 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 18.9, 19.4, 19.5, 21.0, 21.8, 27.8, 38.3, 86.7, 112.9, 126.6, 127.0, 127.1, 127.4, 128.2, 129.9, 132.2, 132.6, 133.6, 135.1, 135.8, 137.0, 142.4, 147.8, 162.3, 168.4; IR (NaCl, neat) ν 3019, 1746, 1215 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{29}O_2$ (M^++ H): 385.2168, found 385.2177.

*4-Phenyl-6-(prop-1-en-2-yl)-7-(thiophene-2-yl)bicyclo[3.2.0]-hepta-1(7),4-dien-6-yl Acetate (**6λ**):* wt 51.0 mg; yield 69%; yellow solid, mp = 89−90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.68 (s, 3H), 2.02 (s, 3H), 2.68−2.81 (m, 2H), 3.16−3.22 (m, 1H), 3.30−3.37 (m, 1H), 5.10 (t, 1H, J = 1.4 Hz), 5.33 (s, 1H), 6.90−6.92 (m, 1H), 6.98−6.99 (d, 1H, J = 3.4 Hz), 7.09−7.16 (m, 2H), 7.22−7.26 (m, 2H), 7.32−7.35 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 19.0, 21.6, 24.7, 38.8, 87.7, 113.3, 123.6, 125.0, 126.9, 127.6, 127.8, 127.8, 128.2, 131.6, 134.8, 136.4, 141.3, 146.9, 160.8, 168.7; IR (NaCl, neat) ν 3019, 2359, 1748, 1219 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{21}O_2S$ (M^+ + H) 349.1262, found 349.1257.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C{^{1}H} NMR spectra for all starting materials and products, ORTEP drawings of **4a,h,j,r**, **5a,h**, **6u,κ**, and CIF files of these compounds. 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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(16) See Figures S90−S97 in the Supporting Information for ORTEP drawings of the crystal structures for **4a**,**h**,**j**,**r**, **5a**,**h**, and **6u**,**κ** reported in this work.

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