Selected Paper

Palladium-Catalyzed Carboacylation of Alkenes by Using Acylchromates as Acyl Donors

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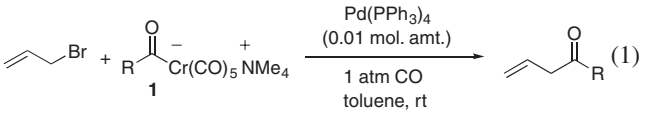
Palladium-catalyzed arylacylation of alkenes proceeds by employing acylchromates as acyl donors. When active alkenes such as norbornene and methoxyallene are treated with an aryl iodide, an acylchromate, and a catalytic amount of $Pd(OAc)_2/2P(o\text{-}Tol)_3$, arylacylation of these alkenes proceeds at room temperature. From aryl iodides having an intramolecular alkene moiety, cyclization–acylation products are obtained via intramolecular arylpalladation followed by acylation with acylchromates.

Acyl transition metal complexes play a key role as intermediates of transition metal-catalyzed ketone synthesis.[1] There are three main routes to generate acyl transition metal intermediates. One is the oxidative addition of acyl compounds, such as acyl halides,[2] acid anhydrides,[3] esters,[4] aldehydes,[5] and acyl metals,[6] to low valent transition metals. The second one is the carbonylation of alkylmetals with carbon monoxide.[7] The last method is the metal exchange between acylmetals and transition metal complexes. The former two routes have been widely applied in the catalytic ketone synthesis, whereas the last route is not common because few suitable acylation reagents have been developed. Although some kinds of acylmetals, such as acylstannanes,[8] acylirons[9] and acylzirconiums,[10] are used in palladium(0)-catalyzed preparation of simple ketones, these acylmetals are unstable in the air or not so reactive, so heating is required for the transmetalation step. Particularly, acylsilane has attracted attention as a stable acyl donor and two types of acylation reactions were developed recently, although these processes need heating.[11]

We have been interested in the use of acyl complexes of the group VI metals as acylation reagents, especially acylchromium compounds.[12] Acyl complexes of Group VI metals are often isolated as air-stable solids and are commonly used as the precursors of Fischer-type carbene complexes.[13] We have found that the transmetalation between palladium(II) complexes and acylchromates smoothly proceeds in the Pd(0)-catalyzed preparation of aryl and allyl ketones from aryl and allyl halides (Eq. 1).[12a]



(1)

Arylacylation of unsaturated compounds is recognized as a convenient way to synthesize various ketones, as exemplified by the rhodium-catalyzed arylacylation of norbornene with tetraphenylborate and acid anhydrides.[3a] In this reaction acid anhydride acts as acyl donor to generate a key acylrhodium intermediate through oxidative addition. As a communication, we have briefly reported a palladium-catalyzed arylacylation of norbornene by using acylchromates as acyl donors.[14] In this paper are explained the details of this palladium-catalyzed arylacylation of several alkenes including intramolecular reactions.

Results and Discussion

Palladium-Catalyzed Arylacylation of Norbornene. The palladium-catalyzed arylacylation of norbornene was investigated with phenyl iodide and tetramethylammonium *p*-methoxybenzoylchromate **1a** in the presence of a catalytic amount of palladium complexes. Several palladium precatalysts such as $Pd(PPh_3)_4$ and $Pd(dba)_2$ were examined. Finally, combinations of $Pd(OAc)_2$ and phosphines gave higher yield of the arylacylation product; these results are summarized in Table 1 (Eq. 2).

Table 1. Effect of Solvent and Ligand for Arylacylation of Norbornene with Acylchromate **1a** and PhI[a)]

Entry	Solvent	Ligand	Yield/%	
			3ad	**4ad**
1	toluene	PPh_3	71	16
2	benzene	PPh_3	54	18
3	CH_2Cl_2	PPh_3	38	45
4	THF	PPh_3	31	43
5	CH_3CN	PPh_3	14	42
6	toluene	$P(o\text{-}Tol)_3$	94	—
7	toluene	$P(C_6H_4\text{–}p\text{-}OMe)_3$	82	18
8	toluene	$P(C_6H_4\text{–}p\text{-}CF_3)_3$	80	14
9	toluene	$P(C_6H_4\text{–}3,5\text{-}(CF_3)_2)_3$	83	9
10	toluene	PCy_3	75	3
11	toluene	$Pt\text{-}Bu_3$	5	87
12	hexane	PPh_3	63	17

a) Molar ratio PhI:Norbornene:**1a**:$Pd(OAc)_2$:Ligand = 5:5:1:0.05:0.1.

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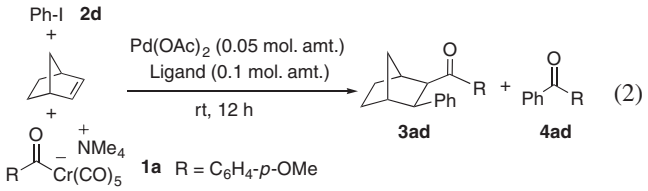


(2)

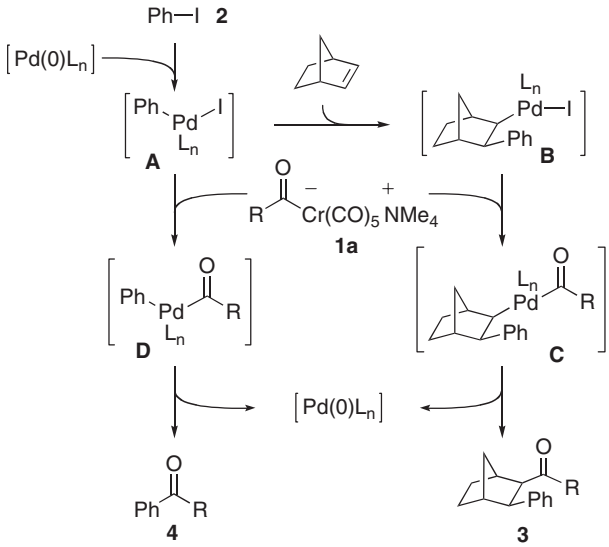
The reaction in toluene with 0.05 molar amount of $Pd(OAc)_2/2PPh_3$ gave the desired arylacylated norbornene **3ad** in 71% yield along with *p*-methoxyphenyl phenyl ketone (**4ad**), the coupling product between phenyl iodide and acylchromate **1a** in 16% yield (entry 1). A plausible mechanism is shown in Scheme 1. Norbornene reacts with phenylpalladium(II) iodide **A**, generated by oxidative addition of phenyl iodide to Pd(0), to give 3-phenylbicyclo[2.2.1]hept-2-ylpalladium(II) intermediate **B**. A transmetalation between acylchromate **1** and **B** and a successive reductive elimination affords arylacylation product **3**. Aryl ketone **4** is formed by a reductive elimination from acyl(aryl)palladium(II) intermediate **D**, which is formed by acylation of **A** with acylchromate **1** without the insertion of norbornene.

The ratio of arylacylation product **3ad** and *p*-methoxyphenyl phenyl ketone (**4ad**) greatly depended on the solvents, and the yield of arylacylation product **3ad** was increased along with the decrease of the polarity of solvents (entries 1–5). Acylchromate **1a** dissolved completely in polar solvents, while significant amounts of **1a** remained undissolved in nonpolar solvents at the beginning of the reaction. Due to the low concentration of acylchromate **1a** in nonpolar solvents, the insertion of norbornene to arylpalladium(II) intermediate **A** is preferred over the transmetalation between **A** and acylchromate **1a** (Scheme 1).

The use of a bulky triarylphosphine, tri-*o*-tolylphosphine was found to give the arylacylation product **3ad** in 94% yield without the formation of *p*-methoxyphenyl phenyl ketone (**4ad**) (entry 6). In all the reactions, the arylacylation product **3ad** was obtained stereoselectively as the *exo-cis* adduct.

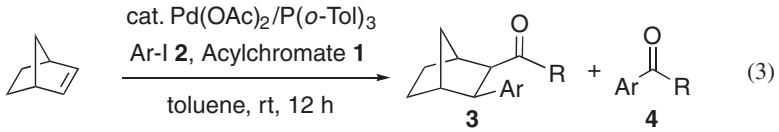
The scope of this arylacylation of norbornene was examined with various combinations of acylchromates and aryl iodides under the above optimized conditions (reaction 3, Table 2).

In most of the cases, arylacylation products **3** were obtained in high yields. Not only aroylchromates **1a–f** (entries 1–7) but



Scheme 1. Formation of arylacylation product **3** and aryl ketone **4**.

Table 2. Investigation of Acylchromates **1** and Aryl Iodides **2** in Arylacylation of Norbornene[a)]



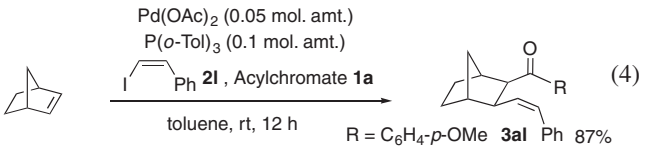
(3)

Entry	Acylchromate **1**		Ar–I **2**		Yield/%			
	R		Ar		**3**		**4**	
1	*p*-$MeOC_6H_4$	**1a**	Ph	**2d**	**3ad**	94	**4ad**	—
2	*o*-$MeOC_6H_4$	**1b**	Ph	**2d**	**3bd**	90	**4bd**	—
3	*p*-MeC_6H_4	**1c**	Ph	**2d**	**3cd**	90	**4cd**	10
4	Ph	**1d**	Ph	**2d**	**3dd**	39	**4dd**	47
5[b)]	Ph	**1d**	Ph	**2d**	**3dd**	79	**4dd**	8
6	*p*-$CF_3C_6H_4$	**1e**	Ph	**2d**	**3ed**	83	**4ed**	—
7	2-Furyl	**1f**	Ph	**2d**	**3fd**	84	**4fd**	<18
8	*n*-Bu	**1g**	Ph	**2d**	**3gd**	38	**4gd**	20
9[b)]	*n*-Bu	**1h**	Ph	**2d**	**3gd**	78	**4gd**	8
10	*t*-Bu	**1i**	Ph	**2d**	**3hd**	71	**4hd**	<13
11	Me	**1a**	Ph	**2d**	**3id**	98	**4id**	—
12	*p*-$MeOC_6H_4$	**1a**	*p*-$MeOC_6H_4$	**2a**	**3aa**	95	**4aa**	5
13	*p*-$MeOC_6H_4$	**1a**	*o*-$MeOC_6H_4$	**2b**	**3ab**	96	**4ab**	4
14	*p*-$MeOC_6H_4$	**1a**	*p*-MeC_6H_4	**2c**	**3ac**	89	**4ac**	8
15	*p*-$MeOC_6H_4$	**1a**	*p*-$O_2NC_6H_4$	**2j**	**3aj**	84	**4aj**	—
16	*p*-$MeOC_6H_4$	**1a**	*p*-$MeCOC_6H_4$	**2k**	**3ak**	85	**4ak**	—

a) Molar ratio ArI **2**:Norbornene:**1**:$Pd(OAc)_2$:P(*o*-Tol)$_3$ = 5:5:1:0.05:0.1. b) Reactions were performed in hexane.

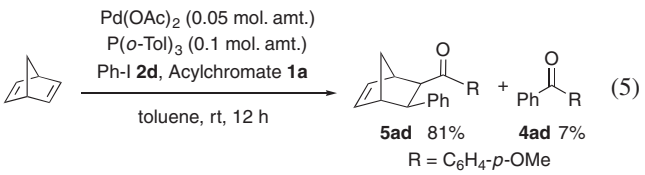
also alkanoylchromates **1g–i** (entries 8–11) were available for this palladium-catalyzed reaction. For the reaction of acylchromates, such as benzoylchromate **1d** and pentanoylchromate **1g**, the use of hexane improved the yields of the desired products **3** due to the low solubilities in hexane (entries 4, 5, 8, and 9). This reaction proceeded smoothly regardless of the substituents on aryl iodides (entries 12–16).

Vinyl iodide could be employed in the catalytic vinylacylation of norbornene. From (*Z*)-1-iodo-2-phenylethene (**2l**), *p*-methoxyphenyl 3-(*Z*)-2-phenylethenylbicyclo[2.2.1]hept-2-yl ketone (**3al**) was obtained in 87% yield with retention of the *Z* configuration of the styrene moiety (Eq. 4).



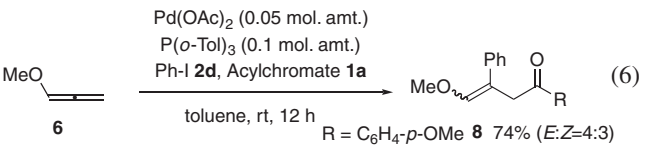
(4)

Norbornadiene reacted with acylchromate **1a** and phenyl iodide under the same conditions, giving the desired arylacylation product **5ad** in 81% yield (Eq. 5). Non-activated alkenes such as cyclopentene, styrene, and 1-octene, however, were found to be inert toward the palladium-catalyzed arylacylation, and only aryl ketones **4** were obtained.



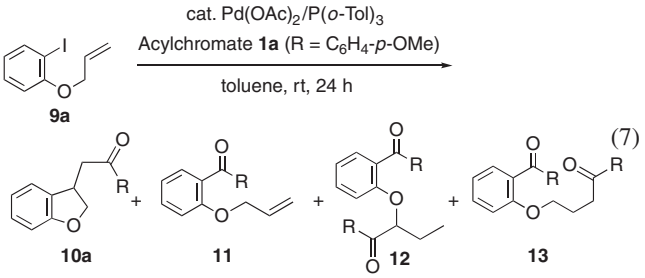
(5)

As allene derivatives are highly reactive toward carbometalation,[15] methoxyallene (**6**)[16] reacted with phenyl iodide and *p*-methoxybenzoylchromate **1a** in the presence of a catalytic amount of $Pd(OAc)_2/2P(o\text{-}Tol)_3$. 2,3-Arylacylation product **8** was obtained as an *E*/*Z* mixture in 74% yield (Eq. 6).



(6)

Preparation of Acylated Benzofuran and Indole Derivatives. Then we investigated the intra- and intermolecular arylacylation by using aryl iodides having an alkene moiety at an appropriate position, expecting that intramolecular arylpalladation might proceed even by employing non-activated alkenes due to the entropic advantage. The results of the palladium-catalyzed arylacylation of allyl *o*-iodophenyl ether (**9a**) with acylchromate **1a** are summarized in Table 3 (Eq. 7).



(7)

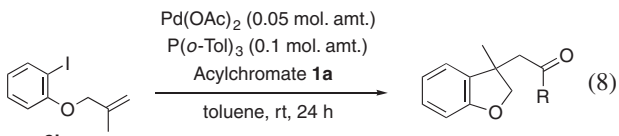
When allyl *o*-iodophenyl ether (**9a**) was treated with acylchromate **1a** in the presence of 0.05 molar amount of $Pd(OAc)_2$ and 0.1 molar amount of $P(o\text{-}Tol)_3$ in toluene at room temperature for 1 h, the cyclized acylation product 3-(*p*-methoxybenzoyl)methyl-2,3-dihydrobenzofuran (**10a**) was obtained in 45% yield with by-products such as ketones **11**, **12**, and **13** (entry 1). It was considered that diacylated compounds **12** and **13** were produced via isomerization and/or hydroacylation of the allyl part by the action of the palladium(II) hydride, which was undesirably generated via intramolecular Heck reaction of allyl *o*-iodophenyl ether. In fact, the reaction under ethene atmosphere gave 1-*p*-methoxyphenylpropan-1-one in 22% yield based on the acylchromate complex used, which means hydroacylation of ethene proceeded by palladium(II) hydride generated by the undesired Heck reaction (entry 2).[17] The yield of acylated dihydrobenzofuran **10a** was increased up to about 80% when the reaction was carried out by the use of an excess amount of allyl *o*-iodophenyl ether (**9a**), and an equimolar amount of $P(o\text{-}Tol)_3$ (entries 5 and 6).

Table 3. Preparation of 3-Acylmethyl-2,3-dihydrobenzofuran **10a**[a)]

Entry	**9a**[b)]	$P(o\text{-}Tol)_3$[b)]	Products		
			10a/%	**11**/%	**12** + **13**/%
1[c)]	1	0.1	45	6	4
2[d,e)]	1	0.1	72	—	8
3	1	0.2	55	—	23
4	1	1	58	—	8
5	5	1	77	3	12
6[f)]	5	1	82	—	8

a) Molar ratio **1a**:$Pd(OAc)_2$ = 1:0.05. Yields are based on **1a**. b) Molar amounts based on **1a**. c) The reaction was quenched after 1 h stirring. d) The reaction was carried out under an ethene atmosphere. e) 1-*p*-Methoxyphenylpropan-1-one was obtained in 22% yield. f) Bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$) was used instead of $Pd(OAc)_2$.

Then we tried the reaction of *o*-iodophenyl 2-methyl-2-propenyl ether **9b**, which has no β-hydrogen participating in the Heck reaction. As expected, the desired aryl acylated dihydrobenzofuran **10b** was obtained in 86% yield with an equimolar amount of the substrate **9b** (Eq. 8). In addition, *o*-iodophenyl ether **9c** having an allene part reacted with **1a** to give acylated benzofuran **10c** in 96% yield, although 5 molar amounts of **9c** was necessary (Eq. 9).



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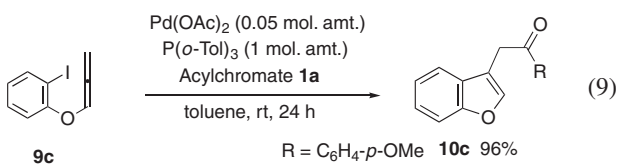
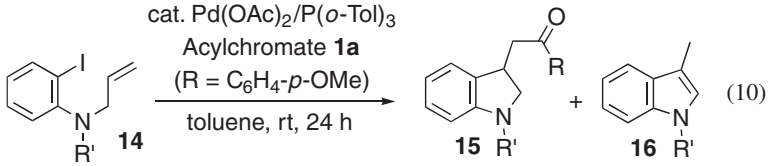


(9)

This intramolecular arylacylation was nicely applied to prepare indoline derivatives as summarized in Table 4 (reaction 10).

Table 4. Preparation of 3-Acylmethylindoline **15**[a)]

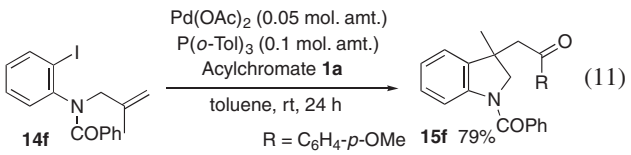


Entry	Substrate[b)]			P(*o*-Tol)$_3$[b)]	Products			
	14	R′			**15**/%		**16**/%	
1	**14a**	COPh	1	0.1	**15a**	58	**16a**	32
2			1	1		73		—
3[c)]			1	0.1		70		21
4	**14b**	CO_2Bn	1	0.1	**15b**	55	**16b**	29
5			5	1		80		—
6	**14c**	Ts	1	0.1	**15c**	63	**16c**	19
7[d)]	**14d**	allyl	1	0.1	**15d**	63	**16d**	18
8			2	1		84		3
9	**14e**	CH_2Ph	1	0.1	**15e**	66	**16e**	24
10			5	0.1		92		—

a) Molar ratio Acylchromate **1a**:Pd(OAc)$_2$ = 1:0.05. Yields are based on **1a**. b) Numbers show molar amounts based on **1a**. c) An equimolar amount of 2-methyl-2-butene was added. d) Reactions were carried out under 1 atm of ethene.

When *N*-allyl-*N*-*o*-iodophenylbenzamide **14a** was treated with acylchromate **1a** in the presence of 0.05 molar amount of Pd(OAc)$_2$ and 0.1 molar amount of P(*o*-Tol)$_3$ in toluene at room temperature for 24 h, the desired 3-acylmethylindoline **15a** was obtained in 58% yield besides 32% yield of a Heck-type product, 3-methylindole **16a** (entry 1). *N*-Allyl-2-iodoanilines **14b–e**, which have an amino protecting group such as CO_2Bn (entries 5–8), CO_2t-Bu (entry 9), tosyl (entry 10), allyl (entries 11–14), or benzyl (entries 15–17), gave acylated indoline **15b–e** in moderate to high yields. In all cases, the use of an equimolar amount of P(*o*-Tol)$_3$ suppressed the formation of Heck-type by-product, 3-methylindole **16**,[18] and increased the yields of 3-acylmethylindolines **15** (entries 2, 7, 8, 13, 14, and 16).

From the reaction of acylchromate **1a** and *N*-2-methyl-2-propenyl-*N*-*o*-iodophenylbenzamide **14f**, which has no β-hydrogen for the Heck-type reaction, 3-acylmethyl-3-methylindoline **15f** was obtained in 79% (Eq. 11).



Conclusion

Palladium-catalyzed arylacylation of alkenes was developed by employing acylchromates as acyl donors. Treatment of reactive alkenes such as norbornene and a 1,2-propadienyl ether with acylchromate complexes and a catalytic amount of Pd(OAc)$_2$/2P(*o*-Tol)$_3$ gave arylacylation products in good yields. Application of this catalytic arylacylation provides a preparative method of benzofuran and indoline derivatives.

Experimental

General. ^{1}H NMR (500 MHz) spectra in $CDCl_3$ were recorded on Bruker AM500 and Bruker DRX500 spectrometers using $CHCl_3$ as an internal standard ($\delta = 7.24$). ^{13}C NMR (125 MHz) spectra in $CDCl_3$ were measured with Bruker AM 500 and Bruker DRX500 spectrometers using $CDCl_3$ as an internal standard ($\delta = 77.0$). IR spectra were recorded on a Horiba FT 300-S spectrophotometer. High-resolution mass spectra were obtained with a JEOL JMS-SX102A mass spectrometer. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo.

Benzene and toluene was distilled from $CaCl_2$, and dried over Molecular Sieves 4A. Dichloromethane was distilled from P_2O_5, then from CaH_2, and dried over Molecular Sieves 4A. Acetonitrile was dried over CaH_2 and distilled from P_2O_5, then from CaH_2, and dried over Molecular Sieves 4A. Tetrahydrofuran (THF) was purchased in anhydrous form from Kanto Chemical Co., Inc. Hexane was distilled. Silica gel column chromatography was carried out with Merck Art 7734 and Kanto 60N. Preparative TLC was performed on silica gel (Wakogel B-5F).

Acylchromate complexes **1a–i**,[13] (*Z*)-1-iodo-2-phenylethene,[19] and methoxyallene[15] were prepared according to the literature procedure. Norbornene, norbornadiene, phosphine ligands, and aryl iodides **2a–d**, **2j**, and **2k** were purified by distillation or recrystallization before to use. Pd(OAc)$_2$ and Pd(dba)$_2$ were purchased from Wako Pure Chemical Industries, Ltd. and Tokyo Kasei Kogyo Co., Ltd., respectively and used as they arrived. *o*-Iodophenyl ethers **9a**,[20] **9b**,[21] **9c**,[22] and *o*-iodoaniline derivatives **14**[23,24] were prepared according to literature methods.

All the reactions were carried out under argon atmosphere.

General Procedure of Arylacylation of Alkenes. To a mixture of Pd(OAc)$_2$ (3.7 mg, 0.016 mmol), P(*o*-Tol)$_3$ (9.9 mg, 0.033 mmol), and acylchromate complex **1** (0.33 mmol) in toluene (1 mL) was added a toluene (1 mL) solution of alkene (1.6 mmol)

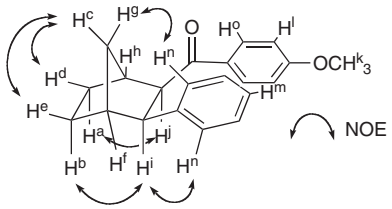


Fig. 1.

and aryl iodide (1.6 mmol). The reaction mixture was stirred at room temperature for 24 h, filtered through celite, and then solvent was removed under reduced pressure. The crude material was purified by preparative TLC (hexane/AcOEt = 3/1 or benzene/$CHCl_3$ = 3/2), to give arylacylation product.

Physical properties of products are as follows. Relative configuration of the compounds **3** having a norbornane structure was estimated as *exo-cis* adduct ((2*R**,3*S**)-bicyclo[2.2.1]heptane structure) according to the NOESY analysis of **3ad** (Fig. 1). All of the ketones **4** are commercially available.

***p*-Methoxyphenyl (2*R**,3*S**)-3-*p*-Methoxyphenylbicyclo[2.2.1]hept-2-yl Ketone (3aa):** White solid; mp 94–95 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34–1.46 (3H, m), 1.64–1.70 (2H, m), 2.35 (1H, s), 2.49 (1H, d, J = 10.1 Hz), 2.64 (1H, s), 3.23 (1H, d, J = 10.1 Hz), 3.61 (3H, s), 3.73 (1H, d, J = 10.1 Hz), 3.78 (3H, s), 6.48 (2H, d, J = 8.7 Hz), 6.70 (2H, d, J = 8.8 Hz), 6.80 (2H, d, J = 8.7 Hz), 7.57 (2H, d, J = 8.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.0, 31.0, 37.2, 39.1, 43.6, 53.2, 55.0, 55.2, 55.7, 112.9, 128.2, 129.2, 130.2, 131.5, 134.1, 157.3, 162.5, 200.2; IR (ZnSe): 1171, 1230, 1512, 1599, 1668 cm^{-1}; Anal. Found: C, 78.47; H, 7.21%. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19%.

***p*-Methoxyphenyl (2*R**,3*S**)-3-*o*-Methoxyphenylbicyclo[2.2.1]hept-2-yl Ketone (3ab):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.41 (1H, d, J = 10.1 Hz), 1.46 (2H, d, J = 6.4 Hz), 1.66–1.74 (2H, m), 2.46–2.48 (2H, m), 2.55 (1H, s), 3.30 (3H, s), 3.49 (1H, d, J = 9.4 Hz), 3.80 (3H, s), 3.90 (1H, d, J = 9.4 Hz), 6.40 (1H, d, J = 8.1 Hz), 6.77 (2H, d, J = 8.8 Hz), 6.84 (1H, dd, J = 7.5, 8.1 Hz), 7.00 (1H, dd, J = 7.5, 7.6 Hz), 7.27 (1H, d, J = 7.6 Hz), 7.67 (2H, d, J = 8.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.5, 30.9, 36.9, 40.4, 41.2, 45.6, 53.8, 54.2, 55.3, 108.8, 112.8, 120.1, 126.6, 126.9, 130.0, 130.7, 131.7, 155.9, 162.4, 199.9; IR (ZnSe): 1171, 1215, 1240, 1601, 1670 cm^{-1}; Anal. Found: C, 78.39; H, 7.29%. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19%.

(2*R,3*S**)-3-*p*-Tolylbicyclo[2.2.1]hept-2-yl *p*-Methoxyphenyl Ketone (3ac):** White solid; mp 92–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34–1.36 (3H, m), 1.65–1.72 (2H, m), 2.11 (3H, s), 2.38 (1H, s), 2.45 (1H, d, J = 10.1 Hz), 2.64 (1H, s), 3.25 (1H, d, J = 10.1 Hz), 3.74 (1H, d, J = 10.1 Hz), 3.77 (3H, s), 6.70 (2H, d, J = 8.8 Hz), 6.75 (2H, d, J = 7.9 Hz), 6.85 (2H, d, J = 7.9 Hz), 7.58 (2H, d, J = 8.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 29.1, 31.0, 37.3, 39.3, 43.5, 53.7, 55.2, 55.7, 112.9, 128.1, 128.2, 130.2, 131.6, 135.0, 138.8, 200.1; IR (ZnSe): 813, 840, 1029, 1170, 1230, 1259, 1417, 1455, 1509, 1600, 1668, 2871, 2954 cm^{-1}; Anal. Found: C, 82.22; H, 7.69%. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55%.

***p*-Methoxyphenyl (2*R**,3*S**)-3-Phenylbicyclo[2.2.1]hept-2-yl Ketone (3ad):**[3a] White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36–1.39 (1H, m, H^a), 1.41–1.49 (2H, m, H^b and H^c), 1.64–1.73 (2H, m, H^d and H^e), 2.38–2.42 (1H, m, H^f), 2.44–2.48 (1H, m, H^g), 2.64–2.68 (1H, m, H^h), 3.24–3.29 (1H, m, J = 10.0 Hz, H^i), 3.74–3.78 (1H, m, J = 10.0 Hz, H^j), 3.76 (3H, s, H^k), 6.68 (2H, d, J = 8.9 Hz, H^l), 6.89–6.91 (1H, m, H^m), 6.92–6.97 (4H, m, H^n), 7.55 (2H, d, J = 8.9 Hz, H^o); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.0, 31.1, 37.4, 39.3, 43.5, 54.0, 55.3, 55.7, 113.0, 125.8, 127.6, 128.3, 130.2, 131.5, 141.9, 162.6, 196.8; IR (ZnSe): 700, 836, 1029, 1230, 1257, 1455, 1508, 1602, 1662, 2871, 2954 cm^{-1}.

(2*R,3*S**)-3-*p*-Methoxyphenylbicyclo[2.2.1]hept-2-yl *p*-Nitrophenyl Ketone (3aj):** White solid; mp 135–136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39–1.51 (3H, m), 1.69–1.74 (2H, m), 2.09–2.43 (2H, m), 2.66 (1H, s), 3.33 (1H, d, J = 10.1 Hz), 3.77 (3H, s), 3.84 (1H, d, J = 10.1 Hz), 6.71 (2H, d, J = 9.3 Hz), 7.11 (2H, d, J = 8.8 Hz), 7.56 (2H, d, J = 9.8 Hz), 7.80 (2H, d, J = 9.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.0, 30.9, 37.2, 39.8, 43.0, 53.5, 55.4, 55.4, 113.4, 112.7, 129.0, 130.2, 131.0, 145.9, 150.1, 163.1, 199.1; IR (ZnSe): 1028, 1171, 1228, 1259, 1342, 1510, 1597, 1666 cm^{-1}; Anal. Found: C, 71.48; H, 6.00; N, 4.00%. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99%.

(2*R,3*S**)-3-*p*-Acetylphenylbicyclo[2.2.1]hept-2-yl *p*-Methoxyphenyl Ketone (3ak):** White solid; mp 121 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38–1.48 (3H, m), 1.66–1.70 (2H, m), 2.40–2.45 (2H, m), 2.42 (3H, s), 2.62–2.65 (1H, m), 3.30 (1H, d, J = 10.3 Hz), 3.75 (3H, s), 3.82 (1H, d, J = 10.3 Hz), 6.65–6.70 (2H, m), 7.03–7.06 (2H, m), 7.53–7.56 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.4, 29.0, 31.0, 37.2, 39.6, 43.1, 53.8, 55.3, 55.5, 113.2, 127.7, 128.4, 130.2, 131.2, 134.7, 147.9, 162.9, 197.7, 199.5; IR (ZnSe): 1168, 1215, 1228, 1259, 1599, 1674 cm^{-1}; Anal. Found: C, 79.07; H, 7.07%. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94%.

***o*-Methoxyphenyl (2*R**,3*S**)-3-Phenylbicyclo[2.2.1]hept-2-yl Ketone (3bd):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60–1.70 (3H, m), 1.94 (2H, d, J = 7.6 Hz), 2.67 (2H, m), 2.95 (1H, s), 3.44 (1H, d, J = 10.0 Hz), 4.09 (3H, s), 4.23 (1H, d, J = 10.0 Hz), 6.92 (2H, t, J = 7.3 Hz), 6.98–7.06 (5H, m), 7.45–7.50 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.0, 31.1, 37.5, 39.9, 42.9, 53.3, 55.3, 60.5, 110.8, 120.2, 125.6, 127.6, 128.3, 130.1, 130.2, 132.2, 142.5, 157.4, 203.8; IR (ZnSe): 696, 752, 1020, 1240, 1282, 1597, 1662 cm^{-1}; HR-FABMS: Found: m/z 307.1690. Calcd for $C_{21}H_{22}O_2$ + H: M + H, 307.1694.

***p*-Tolyl (2*R**,3*S**)-3-Phenylbicyclo[2.2.1]hept-2-yl Ketone (3cd):** White solid; mp 120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35–1.49 (3H, m), 1.65–1.72 (2H, m), 2.28 (3H, s), 2.41 (1H, s), 2.46 (1H, d, J = 10.3 Hz), 2.66 (1H, s), 3.78–3.81 (1H, m), 4.09–4.12 (1H, m), 6.86–6.94 (5H, m), 6.98–7.02 (2H, m), 7.44–7.47 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 29.0, 31.1, 37.4, 39.3, 43.4, 53.9, 55.9, 125.7, 127.6, 128.1, 128.3, 128.5, 135.9, 141.8, 142.6, 201.3; IR (ZnSe): 700, 1230, 1606, 1672 cm^{-1}; Anal. Found: C, 86.61; H, 7.83%. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64%.

Phenyl (2*R,3*S**)-3-Phenylbicyclo[2.2.1]hept-2-yl Ketone (3dd):**[3a] White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40–1.48 (3H, m), 1.65–1.75 (2H, m), 2.44 (1H, s), 2.44–2.47 (1H, m), 2.70 (1H, s), 3.29 (1H, d, J = 10.0 Hz), 3.84 (1H, d, J = 10.0 Hz), 6.90–6.94 (5H, m), 7.18–7.25 (2H, m), 7.32–7.35 (1H, m), 7.52–7.55 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.0, 31.1, 37.4, 39.1, 43.5, 53.9, 56.2, 125.8, 127.6, 127.9, 128.0, 128.4, 132.0, 138.4, 141.8, 201.7; IR (ZnSe): 1214, 1226, 1448, 1676 cm^{-1}.

Phenyl (2*R,3*S**)-3-*p*-(Trifluoromethyl)phenylbicyclo[2.2.1]hept-2-yl Ketone (3ed):** White solid; mp 124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39–1.54 (3H, m), 1.69–1.74 (2H, m), 2.40–2.44 (2H, m), 2.72 (1H, s), 3.27 (1H, d, J = 10.3

Hz), 3.81 (1H, d, $J = 10.3$ Hz), 6.87–6.91 (5H, m), 7.45 (2H, d, $J = 8.1$ Hz), 7.56 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.7, 31.1, 37.4, 38.8, 43.6, 53.7, 56.8, 123.5 (q, $J_{CF} = 270.9$ Hz), 124.8 (q, $J_{CF} = 3.6$ Hz), 126.0, 127.7, 128.1, 128.3, 133.1 (q, $J_{CF} = 32.3$ Hz), 141.1, 141.4, 200.9; IR (ZnSe): 771, 1066, 1110, 1118, 1174, 1326, 1670 cm^{-1}; Anal. Found: C, 73.28; H, 5.70%. Calcd for $C_{21}H_{19}F_3O$: C, 73.24; H, 5.56%.

2-Furyl (2*R,3*S**)-3-Phenylbicyclo[2.2.1]hept-2-yl Ketone (3fd):** White solid; mp 81 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36–1.50 (3H, m), 1.64–1.71 (2H, m), 2.41–2.45 (1H, m), 2.44 (1H, s), 2.63 (1H, s), 3.32 (1H, d, $J = 10.3$ Hz), 3.69 (1H, d, $J = 10.3$ Hz), 6.27–6.29 (2H, m), 6.71–6.73 (1H, m), 6.94–7.01 (5H, m), 7.36–7.38 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.9, 31.1, 37.7, 38.8, 42.8, 53.6, 56.2, 112.0, 115.7, 125.8, 127.6, 127.9, 141.5, 144.9, 153.5, 190.6; IR (ZnSe): 700, 754, 840, 1012, 1247, 1467, 1567, 1670, 2871, 2954 cm^{-1}; Anal. Found: C, 80.96; H, 6.96%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

Butyl (2*R,3*S**)-3-Phenylbicyclo[2.2.1]hept-2-yl Ketone (3gd):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.65 (3H, t, $J = 7.4$ Hz), 0.67–0.78 (1H, m), 0.85–0.95 (2H, m), 1.11–1.19 (1H, m), 1.20–1.26 (1H, m), 1.30–1.40 (2H, m), 1.55–1.63 (2H, m), 1.65–1.75 (1H, m), 1.84–1.94 (1H, m), 2.26–2.30 (1H, m), 2.34 (1H, s), 2.50 (1H, s), 2.96 (1H, d, $J = 10.2$ Hz), 3.14 (1H, d, $J = 10.2$ Hz), 7.09–7.22 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 22.0, 25.1, 28.6, 31.3, 37.3, 38.6, 43.4, 44.1, 52.8, 61.5, 128.1, 128.3, 128.4, 128.5, 211.7; IR (ZnSe): 1456, 1705, 2929, 2954 cm^{-1}; Anal. Found: C, 84.19; H, 9.21%. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.44%.

***t*-Butyl (2*R**,3*S**)-3-Phenylbicyclo[2.2.1]hept-2-yl Ketone (3hd):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (9H, s), 1.26–1.40 (3H, m), 1.56–1.69 (2H, m), 2.25–2.29 (1H, m), 2.36–2.39 (1H, m), 2.50–2.56 (1H, m), 3.06 (1H, d, $J = 9.5$ Hz), 3.36 (1H, d, $J = 9.5$ Hz), 6.70–7.21 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.0, 29.4, 31.1, 36.7, 42.0, 42.6, 44.3, 53.9, 54.6, 125.9, 127.8, 128.6, 142.9, 216.1; IR (ZnSe): 1074, 1215, 1365, 1454, 1477, 1698, 2952 cm^{-1}; Anal. Found: C, 84.50; H, 9.61%. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.44%.

Methyl (2*R,3*S**)-3-Phenylbicyclo[2.2.1]hept-2-yl Ketone (3id):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19–1.26 (1H, m), 1.32–1.43 (2H, m), 1.49 (3H, s), 1.57–1.67 (2H, m), 2.20–2.24 (1H, m), 2.35–2.37 (1H, m), 2.52–2.56 (1H, m), 2.98 (1H, d, $J = 10.3$ Hz), 3.19 (1H, d, $J = 10.3$ Hz), 7.16–7.26 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 31.1, 31.2, 37.1, 38.4, 43.5, 52.6, 62.5, 126.4, 128.2, 128.4, 142.3, 209.9; IR (ZnSe): 1169, 1215, 1228, 1259, 1599, 1674 cm^{-1}; Anal. Found: C, 83.85; H, 8.51%. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47%.

***p*-Methoxyphenyl (2*R**,3*S**)-3-(*Z*)-Styrylbicyclo[2.2.1]hept-2-yl Ketone (3al):** White solid; mp 123–124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24–1.43 (3H, m), 1.59–1.70 (2H, m), 2.00–2.05 (1H, m), 2.15–2.17 (1H, m), 2.61–2.63 (1H, m), 2.85 (1H, dd, $J = 9.4$, 10.0 Hz), 3.48 (1H, d, $J = 9.4$ Hz), 3.77 (3H, s), 5.77 (1H, dd, $J = 10.0$, 15.6 Hz), 6.11 (1H, d, $J = 15.6$ Hz), 6.79 (2H, d, $J = 8.8$ Hz), 6.97–6.99 (2H, m), 7.04–7.09 (2H, m), 7.10–7.14 (1H, m), 7.82 (2H, d, $J = 8.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.1, 29.4, 35.7, 39.1, 43.7, 52.0, 54.2, 55.3, 113.4, 126.0, 126.8, 128.2, 130.5, 130.5, 131.0, 131.1, 137.5, 162.9, 199.9; IR (ZnSe): 694, 742, 1025, 1112, 1230, 1259, 1417, 1455, 1509, 1600, 1668, 2871, 2952 cm^{-1}; Anal. Found: C, 82.89; H, 7.38%. Calcd for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28%.

Bis(4-methoxyphenyl) Ketone (4aa):[25] Colorless crystal; mp 123–124 °C ($CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (6H, s), 6.92–6.96 (4H, m), 7.75–7.79 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 113.4, 130.7, 132.2, 162.8, 194.5; IR (ZnSe): 1022, 1165, 1253, 1317, 1602, 1643 cm^{-1}.

2-Methoxyphenyl 4-Methoxyphenyl Ketone (4ab):[26] Colorless crystal; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.74 (3H, s), 3.86 (3H, s), 6.89–6.92 (2H, m), 6.97–7.01 (1H, m), 7.01–7.05 (1H, m), 7.30–7.33 (1H, m), 7.42–7.47 (1H, m), 7.79–7.82 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 55.6, 111.4, 113.4, 120.4, 129.2, 130.4, 130.6, 131.4, 132.3, 157.0, 163.5, 195.0; IR (ZnSe): 906, 926, 1024, 1147, 1252, 1597, 1653 cm^{-1}.

4-Methoxyphenyl *p*-Tolyl Ketone (4ac):[27] Colorless crystal; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.45 (3H, s), 3.95 (3H, s), 6.95 (2H, d, $J = 8.8$ Hz), 7.27 (2H, d, $J = 8.0$ Hz), 7.67 (2H, d, $J = 8.0$ Hz), 7.81 (2H, d, $J = 8.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 55.4, 113.4, 128.8, 130.0, 130.4, 132.4, 135.4, 142.6, 163.0, 195.3; IR (ZnSe): 757, 1171, 1255, 1597, 1645 cm^{-1}.

4-Methoxyphenyl Phenyl Ketone (4ad):[28] Colorless crystal; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (3H, s), 6.95 (2H, d, $J = 8.9$ Hz), 7.42–7.47 (2H, m), 7.52–7.57 (1H, m), 7.71–7.75 (2H, m), 7.83 (2H, d, $J = 8.9$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.5, 113.5, 128.2, 129.7, 130.1, 131.9, 132.5, 138.2, 163.2, 195.6; IR (ZnSe): 700, 1147, 1171, 1253, 1281, 1597, 1651 cm^{-1}.

4-Methylphenyl Phenyl Ketone (4cd):[29] Colorless crystal; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (3H, s), 7.25–7.30 (2H, m), 7.45–7.49 (2H, m), 7.55–7.60 (1H, m), 7.70–7.73 (2H, m), 7.77–7.80 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 128.2, 128.9, 129.9, 130.3, 132.1, 134.8, 137.9, 143.2, 196.5; IR (ZnSe): 1147, 1255, 1597, 1653 cm^{-1}.

Benzophenone (4dd):[30] Colorless crystal; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.51 (4H, m), 7.54–7.60 (2H, m), 7.77–7.81 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.3, 130.3, 132.4, 137.6, 196.8; IR (ZnSe): 698, 1276, 1657 cm^{-1}.

2-Furyl Phenyl Ketone (4fd):[31] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57–6.59 (1H, m), 7.21–7.24 (1H, m), 7.45–7.50 (2H, m), 7.55–7.61 (1H, m), 7.69–7.70 (1H, m), 7.94–7.97 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 112.2, 120.6, 128.4, 129.2, 132.5, 137.2, 147.1, 152.2, 182.5; IR (ZnSe): 870, 1294, 1389, 1461, 1644 cm^{-1}.

1-Phenylpentan-1-one (4gd):[32] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (3H, t, $J = 7.4$ Hz), 1.40 (2H, tq, $J = 7.4$, 7.4 Hz), 1.70 (2H, tt, $J = 7.4$, 7.4 Hz), 2.95 (2H, t, $J = 7.4$ Hz), 7.40–7.46 (2H, m), 7.50–7.54 (1H, m), 7.92–7.95 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 22.5, 26.5, 38.3, 128.0, 128.5, 132.9, 137.1, 200.6; IR (KBr): 690, 1448, 1684, 2931, 2958 cm^{-1}.

2,2-Dimethyl-1-phenylpropan-1-one (4hd):[33] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (9H, s), 7.35–7.40 (2H, m), 7.42–7.46 (1H, m), 7.65–7.70 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 44.2, 127.8, 128.0, 130.8, 138.6, 209.3; IR (ZnSe): 906, 960, 1174, 1192, 1673 cm^{-1}.

***p*-Methoxyphenyl (2*R**,3*S**)-3-Phenylbicyclo[2.2.1]hept-5-en-2-yl Ketone (5ad):** White solid; mp 120–121 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.68 (1H, d, $J = 8.9$ Hz), 2.53 (1H, d, $J = 8.9$ Hz), 2.93 (1H, s), 3.14 (1H, s), 3.20 (1H, d, $J = 10.1$ Hz), 3.62 (1H, d, $J = 10.1$ Hz), 3.77 (3H, s), 6.32–6.34 (1H, m), 6.45–6.48 (1H, m), 6.68–6.72 (2H, m), 6.90–6.98 (5H, m), 7.54–7.58 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.1, 46.1, 48.7, 49.9, 49.9, 55.3, 113.0, 125.9, 127.7, 128.4, 130.2, 131.6, 138.5, 140.8, 141.0, 162.7, 201.5 cm^{-1}; IR (ZnSe): 1171, 1213, 1255, 1599, 1670 cm^{-1}; Anal. Found: C, 82.84; H, 6.71%. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62%.

4-Methoxy-1-*p*-methoxyphenyl-3-phenylbut-3-en-1-one (8):

This compound was obtained as a mixture of E/Z isomers (4:3). Colorless oil; (*E*)-**8** ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.71 (3H, s), 3.85 (3H, s), 4.10 (2H, s), 6.53 (1H, s), 6.88–6.91 (2H, m), 7.12–7.16 (1H, m), 7.22–7.25 (4H, m), 7.97–8.00 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.9, 55.4, 60.1, 113.4, 113.6, 125.5, 126.2, 128.4, 130.0, 130.5, 138.9, 146.9, 163.3, 196.3; (*Z*)-**8** ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.67 (3H, s), 3.84 (3H, s), 3.87 (2H, s), 6.14 (1H, s), 6.88–6.91 (2H, m), 7.12–7.16 (1H, m), 7.22–7.28 (2H, m), 7.45–7.47 (2H, m), 7.92–7.96 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.0, 55.5, 60.4, 110.2, 113.7, 126.3, 127.8, 128.0, 129.8, 130.6, 137.2, 147.5, 163.4, 196.8; IR (ZnSe): 694, 1140, 1167, 1205, 1257, 1508, 1574, 1597, 1676 cm^{-1}; Anal. Found: C, 76.29; H, 6.47%. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43%.

General Procedure for Preparation of Acylated Benzofurans and Indoles by Catalytic Intra- and Intermolecular Arylacylation. To a mixture of $Pd(OAc)_2$ (3.7 mg, 0.016 mmol), P(*o*-Tol)$_3$ (0.033–0.33 mmol), and acylchromate complex (0.33 mmol) in toluene (1 mL) was added a solution of aryl iodide **9** or **14** (0.33–1.6 mmol) in toluene (1 mL). The reaction mixture was stirred for 24 h and filtered through celite, then the solvent was removed under reduced pressure. The crude product was purified on preparative TLC (hexane/AcOEt = 3/1). By-products **11**, **12**, and **13** were obtained as a mixture of other products and were not isolated as pure forms. Spectral data of the starting materials and products are as follows.

Allyl *o*-Iodophenyl Ether (9a):[20] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.58 (2H, d, J = 4.8 Hz), 5.30 (1H, dd, J = 1.4, 10.5 Hz), 5.51 (1H, dd, J = 1.4, 17.3 Hz), 6.04 (1H, ddt, J = 4.8, 10.5, 17.3 Hz), 6.68–6.71 (1H, m), 6.79 (1H, d, J = 8.2 Hz), 7.24–7.28 (1H, m), 7.76 (1H, dd, J = 1.4, 7.8 Hz); ^{13}C NMR (500 MHz, $CDCl_3$) δ 69.6, 86.6, 112.4, 117.6, 122.6, 129.3, 132.5, 139.5, 157.0; IR (ZnSe): 744, 906, 1016, 1246, 1275, 1469, 1579 cm^{-1}.

***o*-Iodophenyl 2-Methyl-2-propenyl Ether (9b):**[21] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.85 (3H, s), 4.46 (2H, s), 5.00 (1H, s), 5.18 (1H, s), 6.68 (1H, dd, J = 7.5, 7.5 Hz), 6.78 (1H, d, J = 8.1 Hz), 7.25 (1H, dd, J = 7.5, 8.1 Hz), 7.75 (1H, d, J = 7.5 Hz); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 19.5, 72.5, 86.5, 112.2, 112.9, 122.5, 129.3, 139.4, 140.2, 157.1; IR (ZnSe): 744, 902, 1016, 1244, 1439, 1469, 1581 cm^{-1}.

***o*-Iodophenyl 1,2-Propadienyl Ether (9c):**[22] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.36–5.45 (2H, m), 6.78–6.82 (2H, m), 7.05–7.08 (1H, m), 7.24–7.30 (1H, m), 7.75–7.79 (1H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 87.2, 90.4, 116.7, 118.3, 124.7, 129.3, 139.6, 156.2, 202.3; IR (ZnSe): 748, 912, 993, 1018, 1149, 1232, 1336, 1437, 1466, 1579 cm^{-1}.

3-(*p*-Methoxybenzoyl)methyl-2,3-dihydrobenzofuran (10a): White solid; mp 129–130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.21 (1H, dd, J = 9.7, 17.8 Hz), 3.47 (1H, dd, J = 4.4, 17.8 Hz), 3.86 (3H, s), 4.04 (1H, dddd, J = 4.4, 6.3, 9.1, 9.7 Hz), 4.18 (1H, dd, J = 6.3, 9.3 Hz), 4.86 (1H, dd, J = 9.1, 9.3 Hz), 6.80 (1H, d, J = 7.8 Hz), 6.84 (1H, dd, J = 7.5, 7.5 Hz), 6.92 (2H, d, J = 8.8 Hz), 7.13 (1H, dd, J = 7.5, 7.8 Hz), 7.18 (1H, d, J = 7.5 Hz), 7.92 (2H, d, J = 8.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.5, 44.1, 55.5, 77.4, 109.7, 113.8, 120.4, 124.3, 128.5, 129.6, 129.9, 130.3, 159.9, 163.7, 196.8; IR (ZnSe): 1169, 1221, 1261, 1483, 1599, 1674 cm^{-1}; Anal. Found: C, 76.26; H, 6.08%. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%.

3-(*p*-Methoxybenzoyl)methyl-3-methyl-2,3-dihydrobenzofuran (10b): White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (3H, s), 3.17 (1H, d, J = 18.3 Hz), 3.52 (1H, d, J = 18.3 Hz), 3.85 (3H, s), 4.52 (1H, d, J = 9.3 Hz), 4.56 (1H, d, J = 9.3 Hz), 6.80 (1H, d, J = 7.9 Hz), 6.87–6.91 (3H, m), 7.11–7.15 (2H, m), 7.90 (2H, d, J = 8.9 Hz); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 25.3, 43.8, 47.4, 55.5, 82.8, 109.8, 113.7, 120.5, 122.8, 128.4, 130.2, 130.3, 135.4, 159.0, 163.5, 196.5; IR (ZnSe): 580, 752, 833, 970, 1016, 1167, 1261, 1479, 1599, 1674 cm^{-1}; HR-FABMS: Found: m/z 283.1334. Calcd for $C_{18}H_{18}O_3$ + H: M + H, 283.1335.

3-(*p*-Methoxybenzoyl)methylbenzofuran (10c): White solid; mp 91–92 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (3H, s), 4.18 (2H, s), 6.81–6.84 (2H, m), 7.12 (1H, dd, J = 7.5, 7.5 Hz), 7.18 (1H, dd, J = 7.5, 7.5 Hz), 7.35 (1H, d, J = 7.5 Hz), 7.42 (1H, d, J = 7.5 Hz), 7.50 (1H, s), 7.90–7.93 (2H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 33.5, 55.5, 111.5, 113.9, 113.9, 119.7, 122.6, 124.4, 127.9, 129.3, 130.8, 142.9, 155.1, 163.7, 194.8; IR (ZnSe): 746, 1093, 1169, 1217, 1259, 1452, 1599, 1681 cm^{-1}; Anal. Found: C, 76.47; H, 5.41%. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%.

***o*-Allyloxyphenyl *p*-Methoxyphenyl Ketone (11):** Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.87 (3H, s), 4.35 (2H, d, J = 9.5 Hz), 5.06 (2H, m), 5.45–5.48 (1H, m), 6.85–7.07 (4H, m), 7.10 (1H, m), 7.54 (1H, m), 7.87 (2H, d, J = 8.9 Hz).

2-[2-(*p*-Methoxybenzoyl)phenoxy]-1-(*p*-methoxyphenyl)butan-1-one (12): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (3H, t, J = 13.7 Hz), 1.84 (2H, dq, J = 12.0, 13.7 Hz), 3.82 (3H, s), 3.86 (3H, s), 5.02 (1H, t, J = 12.0 Hz), 6.72 (1H, d, J = 14.5 Hz), 6.82 (2H, d, J = 15.5 Hz), 6.89–7.23 (4H, m), 7.24–7.30 (1H, m), 7.85 (2H, d, J = 15.5 Hz), 7.97 (2H, d, J = 15.5 Hz).

4-[2-(*p*-Methoxybenzoyl)phenoxymethyl]-1-(*p*-methoxyphenyl)butan-1-one (13): Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.95 (2H, tt, J = 5.9, 7.3 Hz), 2.68 (2H, t, J = 7.3 Hz), 3.74 (3H, s), 3.85 (3H, s), 4.02 (2H, t, J = 5.9 Hz), 6.80–6.85 (4H, m), 6.94–7.04 (2H, m), 7.31 (1H, t, J = 8.2 Hz), 7.41 (1H, t, J = 8.2 Hz), 7.62–7.71 (4H, m).

1-*p*-Methoxyphenylpropan-1-one:[34] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (3H, t, J = 7.3 Hz), 2.96 (2H, q, J = 7.3 Hz), 3.87 (3H, s), 6.93 (2H, d, J = 8.8 Hz), 7.96 (2H, d, J = 8.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.4, 31.4, 55.4, 113.6, 130.2, 134.9, 163.3, 199.5.

***N*-Allyl-*N*-*o*-iodophenylbenzamide (14a):**[35] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (1H, dd, J = 7.7, 14.5 Hz), 4.98 (1H, dd, J = 4.9, 14.5 Hz), 5.09–5.15 (2H, m), 5.97–6.15 (1H, m), 6.87 (1H, dd, J = 7.5, 7.5 Hz), 6.99 (1H, d, J = 7.8 Hz), 7.11–7.21 (4H, m), 7.35 (2H, d, J = 7.5 Hz), 7.77 (1H, d, J = 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3, 100.1, 118.9, 127.6, 128.3, 128.8, 129.1, 129.7, 131.8, 132.4, 135.7, 140.1, 144.8, 170.2; IR (ZnSe): 714, 912, 1304, 1377, 1469, 1643 cm^{-1}.

Benzyl *N*-Allyl-*N*-(*o*-iodophenyl)carbamate (14b):[24] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80 (1H, dd, J = 7.2, 15.0 Hz), 4.58 (1H, dd, J = 5.6, 15.0 Hz), 5.08–5.29 (4H, m), 5.90–5.99 (1H, m), 6.70 (1H, dd, J = 7.2, 7.2 Hz), 7.15–7.44 (7H, m), 7.88 (1H, d, J = 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.7, 67.3, 100.4, 118.4, 127.4, 127.7, 128.2, 128.9, 129.1, 130.0, 132.9, 136.4, 139.5, 143.4, 154.7; IR (ZnSe): 725, 1011, 1147, 1215, 1296, 1396, 1471, 1701 cm^{-1}.

***N*-Allyl-*N*-(2-iodophenyl)-*p*-toluenesulfonamide (14c):** Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (3H, s), 4.09 (1H, dd, J = 7.1, 14.5 Hz), 4.20 (1H, dd, J = 7.1, 14.5 Hz), 4.97 (1H, d, J = 17.1 Hz), 5.02 (1H, d, J = 10.0 Hz), 5.85 (1H, ddt, J = 7.1, 10.0, 17.1 Hz), 6.90 (1H, dd, J = 1.2, 7.8 Hz), 7.01 (1H, dd, J = 7.8, 7.8 Hz), 7.24–7.30 (1H, m), 7.29 (2H, d, J = 8.1 Hz), 7.66 (1H, d, J = 8.1 Hz), 7.89 (1H, d, J = 7.8 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 54.5, 103.2, 119.6, 128.1, 128.6, 129.5, 129.8, 130.7, 132.2, 136.2, 140.2, 141.0, 143.7; IR (ZnSe): 544, 570, 652, 714, 742, 854, 1090, 1161, 1346, 1466 cm^{-1}; Anal. Found: C, 46.35; H, 3.93; N, 3.32%. Calcd for $C_{16}H_{16}INO_2S$: C, 46.50; H, 3.90; N, 3.39%.

Diallyl(*o*-iodophenyl)amine (14d):[24] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.62 (4H, d, $J = 6.2$ Hz), 5.11 (2H, dd, $J = 1.4$, 9.7 Hz), 5.17 (2H, dd, $J = 1.4$, 17.3 Hz), 5.83 (2H, ddt, $J = 6.2$, 9.7, 17.3 Hz), 6.77 (1H, dd, $J = 1.1$, 7.8 Hz), 7.02 (1H, dd, $J = 1.1$, 7.8 Hz), 7.27 (1H, dd, $J = 1.1$, 7.8 Hz), 7.85 (1H, dd, $J = 1.1$, 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.1, 100.3, 117.7, 124.1, 125.6, 128.4, 134.8, 139.9, 151.7; IR (ZnSe): 644, 723, 758, 918, 991, 1012, 1213, 1415, 1466 cm^{-1}.

Allyl(benzyl)*o*-iodophenylamine (14e):[24] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.57 (2H, d, $J = 6.4$ Hz), 4.18 (2H, s), 5.11–5.12 (1H, m), 5.13–5.15 (1H, m), 5.82–5.89 (1H, m), 6.77 (1H, dt, $J = 1.4$, 7.6 Hz), 7.00 (1H, dd, $J = 1.4$, 8.0 Hz), 7.19–7.29 (4H, m), 7.37 (2H, d, $J = 7.4$ Hz), 7.86 (1H, dd, $J = 1.4$, 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.1, 56.9, 100.1, 118.1, 124.3, 125.7, 126.9, 128.1, 128.5, 128.8, 134.4, 138.1, 140.0, 151.7; IR (ZnSe): 696, 721, 758, 918, 1012, 1209, 1468, 1577 cm^{-1}.

***N*-(*o*-Iodophenyl)-*N*-(2-methylprop-2-enyl)benzamide (14f):**[24] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.86 (3H, s), 3.60 (1H, d, $J = 15.0$ Hz), 4.79 (1H, s), 4.88 (1H, s), 5.17 (1H, d, $J =$ 15.0 Hz), 6.86 (1H, dd, $J = 7.8$ Hz), 7.09–7.14 (3H, m), 7.16–7.20 (2H, m), 7.35 (2H, d, $J = 8.0$ Hz), 7.74 (1H, d, $J = 7.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 54.6, 99.9, 114.0, 127.5, 128.2, 128.6, 129.1, 129.6, 131.4, 136.0, 140.1, 140.4, 144.9, 170.3; IR (ZnSe): 613, 715, 902, 1018, 1290, 1373, 1468, 1577, 1643 cm^{-1}.

1-Benzoyl-3-(*p*-methoxybenzoylmethyl)indoline (15a): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.18 (1H, dd, $J = 9.4$, 17.7 Hz), 3.43 (1H, dd, $J = 4.3$, 17.7 Hz), 3.62–3.72 (1H, m), 3.84 (3H, s), 3.93–4.02 (1H, m), 4.39–4.46 (1H, m), 6.85–6.87 (5H, m), 6.90 (2H, d, $J = 8.5$ Hz), 7.21 (1H, d, $J = 7.5$ Hz), 7.39–7.42 (2H, m), 7.52 (1H, d, $J = 7.5$ Hz), 7.89 (2H, d, $J =$ 8.5 Hz); IR (ZnSe): 1149, 1257, 1321, 1597, 1653 cm^{-1}; Anal. Found: C, 77.75; H, 5.85; N, 3.61%. Calcd for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77%.

1-Benzoyloxycarbonyl-3-(*p*-methoxybenzoylmethyl)indoline (15b): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.19 (1H, dd, $J = 9.9$, 17.6 Hz), 3.42 (1H, d, $J = 17.6$ Hz), 3.66–3.70 (1H, m), 3.85 (3H, s), 3.94–3.99 (1H, m), 4.37–4.41 (1H, m), 5.17–5.25 (2H, m), 6.91 (2H, d, $J = 8.8$ Hz), 6.94–6.98 (1H, m), 7.17 (1H, d, $J = 7.4$ Hz), 7.22–7.24 (1H, m), 7.30–7.42 (6H, m), 7.94 (2H, d, $J = 8.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.2, 44.7, 54.3, 55.4, 66.9, 113.3, 113.8, 114.9, 122.7, 123.8, 127.5, 128.1, 128.5, 129.6, 130.3, 132.2, 133.7, 136.2, 163.7, 171.1, 196.6; HR-FABMS: Found: m/z 402.1700. Calcd for $C_{25}H_{23}NO_4$ + H: M + H, 402.1706.

3-(*p*-Methoxybenzoylmethyl)-1-(*p*-tolylsulfonyl)indoline (15c): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (3H, s), 2.67 (1H, dd, $J = 9.6$, 18.2 Hz), 3.08 (1H, dd, $J = 4.4$, 18.2 Hz), 3.61 (1H, dd, $J = 5.0$, 11.2 Hz), 3.69 (1H, dddd, $J = 4.4$, 5.0, 9.6, 9.9 Hz), 3.83 (3H, s), 4.15 (1H, dd, $J = 9.9$, 11.2 Hz), 6.88 (2H, d, $J = 8.8$ Hz), 6.96–6.99 (1H, m), 7.07 (1H, d, $J = 7.4$ Hz), 7.15 (2H, d, $J = 8.2$ Hz), 7.19–7.24 (1H, m), 7.62 (2H, d, $J = 8.2$ Hz), 7.66 (1H, d, $J = 8.1$ Hz), 7.76 (2H, d, $J = 8.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 35.5, 44.1, 55.4, 56.0, 113.7, 115.2, 123.9, 124.5, 127.2, 128.2, 129.3, 129.6, 130.1, 133.8, 134.8, 141.7, 144.0, 163.6, 196.1; IR (ZnSe): 1165, 1257, 1352, 1599, 1672 cm^{-1}; HR-FABMS: Found: m/z 422.1425. Calcd for $C_{24}H_{23}NO_4$ + H: M + H, 422.1427.

1-Allyl-3-(*p*-methoxybenzoylmethyl)indoline (15d): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.03 (1H, dd, $J = 6.4$, 9.3 Hz), 3.21 (1H, dd, $J = 9.3$, 17.4 Hz), 3.38 (1H, dd, $J = 4.8$, 12.4 Hz), 3.66–3.70 (3H, m), 3.82–3.85 (4H, m), 5.16 (1H, dd, $J = 1.4$, 9.9 Hz), 5.25 (1H, dd, $J = 1.4$, 17.2 Hz), 5.84–5.91 (1H, m), 6.50 (1H, d, $J = 7.3$ Hz), 6.67 (1H, dd, $J = 7.3$, 7.3 Hz), 6.92 (2H, d, $J = 8.8$ Hz), 7.07–7.10 (2H, m), 7.95 (2H, d, $J = 8.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 43.2, 51.5, 55.3, 59.3, 60.2, 107.3, 113.6, 117.3, 117.5, 123.7, 127.7, 129.9, 130.2, 132.8, 133.8, 151.7, 163.4, 197.3; IR (ZnSe): 746, 1165, 1255, 1597, 1672, 2837 cm^{-1}; HR-FABMS: Found: m/z 308.1679. Calcd for $C_{20}H_{22}NO_2$ + H: M + H, 308.1651.

1-Benzyl-3-(*p*-methoxybenzoylmethyl)indoline (15e): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.99–3.02 (1H, m), 3.20 (1H, dd, $J = 9.3$, 17.4 Hz), 3.39 (1H, dd, $J = 4.5$, 17.4 Hz), 3.66–3.69 (1H, m), 3.84–3.88 (4H, m), 4.21 (1H, d, $J = 14.9$ Hz), 4.28 (1H, d, $J = 14.9$ Hz), 6.53 (1H, d, $J = 7.8$ Hz), 6.68 (1H, dd, $J = 7.3$, 7.3 Hz), 6.91 (2H, d, $J = 8.8$ Hz), 7.09–7.11 (2H, m), 7.23–7.39 (5H, m), 7.93 (2H, d, $J = 8.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 36.2, 43.4, 53.1, 55.4, 59.9, 107.1, 113.7, 117.6, 123.8, 127.1, 127.8, 127.9, 128.5, 130.0, 130.3, 132.6, 138.2, 152.2, 163.5, 197.4; IR (ZnSe): 731, 746, 1167, 1217, 1255, 1599, 1672 cm^{-1}; HR-FABMS: Found: m/z 358.1785. Calcd for $C_{24}H_{23}NO_2$ + H: M + H, 358.1808.

1-Benzoyl-3-(*p*-methoxybenzoylmethyl)-3-methylindoline (15f): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (3H, s), 3.14 (1H, d, $J = 16.7$ Hz), 3.39 (1H, d, $J = 16.7$ Hz), 3.83 (3H, s), 4.01–4.03 (1H, m), 4.18–4.20 (1H, m), 6.86 (2H, d, $J = 8.7$ Hz), 7.19 (2H, d, $J = 7.6$ Hz), 7.40–7.46 (5H, m), 7.53 (2H, d, $J = 7.2$ Hz), 7.82 (2H, d, $J = 8.7$ Hz); HR-FABMS: Found: m/z 386.1736. Calcd for $C_{25}H_{23}NO_2$ + H: M + H, 386.1757.

1-Benzoyl-3-methylindole (16a):[36] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (3H, s), 7.04 (1H, s), 7.32–7.39 (2H, m), 7.49–7.59 (4H, m), 7.70 (2H, d, $J = 7.7$ Hz), 8.37 (1H, d, $J =$ 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.7, 116.5, 117.9, 118.9, 123.7, 124.4, 125.0, 128.5, 129.0, 131.6, 131.8, 134.9, 136.3, 168.4; IR (ZnSe): 746, 904, 1215, 1261, 1348, 1450, 1680 cm^{-1}.

1-Benzoyloxycarbonyl-3-methylindole (16b): Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (3H, s), 5.42 (2H, s), 7.24–7.50 (10H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.6, 68.4, 115.1, 117.3, 118.9, 122.3, 122.7, 124.5, 128.4, 128.6, 128.7, 131.4, 135.3, 150.8; IR (ZnSe): 696, 754, 908, 1026, 1084, 1238, 1350, 1396, 1452, 1724 cm^{-1}; Anal. Found: C, 76.72; H, 5.78; N, 5.20%. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28%.

3-Methyl-1-(*p*-tolylsulfonyl)indole (16c):[37] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (3H, s), 2.32 (3H, s), 7.18–7.23 (3H, m), 7.30 (2H, s), 7.44 (1H, d, $J = 7.2$ Hz), 7.74 (2H, d, $J = 7.2$ Hz), 7.98 (1H, d, $J = 7.7$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.7, 21.5, 113.6, 118.6, 119.3, 122.9, 123.0, 124.5, 126.7, 129.7, 131.8, 135.2, 135.4, 144.6; IR (ZnSe): 667, 744, 1119, 1171, 1367, 1446 cm^{-1}.

1-Allyl-3-methylindole (16d):[23] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (3H, s), 4.66 (2H, d, $J = 5.4$ Hz), 5.08 (1H, dd, $J = 1.2$, 17.1 Hz), 5.17 (1H, dd, $J = 1.2$, 10.3 Hz), 5.98 (1H, ddt, $J = 5.4$, 10.3, 17.1 Hz), 6.86 (1H, s), 7.09–7.11 (1H, m), 7.17–7.19 (1H, m), 7.27 (1H, d, $J = 8.1$ Hz), 7.57 (1H, d, $J =$ 7.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.6, 48.5, 109.3, 110.5, 117.0, 118.6, 119.0, 121.4, 125.4, 128.8, 133.8, 136.3; IR (ZnSe): 737, 1188, 1329, 1466, 2916 cm^{-1}.

1-Benzyl-3-methylindole (16e):[38] Colorless oil; ^{1}H NMR

(500 MHz, $CDCl_3$) δ 2.33 (3H, s), 5.24 (2H, s), 6.88 (1H, s), 7.09–7.12 (3H, m), 7.16 (1H, dd, $J = 7.0$, 7.0 Hz), 7.23–7.28 (4H, m), 7.58 (1H, d, $J = 7.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.6, 49.7, 109.4, 110.8, 118.7, 119.0, 121.6, 125.8, 126.8, 127.4, 128.7, 128.9, 136.6, 137.9; IR (ZnSe): 737, 1452, 1466, 2916 cm^{-1}.

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