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PAPER

First example of a heterobimetallic 'Pd–Sn' catalyst for direct activation of alcohol: efficient allylation, benzylation and propargylation of arenes, heteroarenes, active methylenes and allyl-Si nucleophiles†

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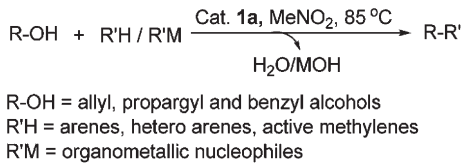
Arenes, heteroarenes, 1,3-dicarbonyls and organosilicon nucleophiles undergo highly efficient alkylation with allylic, propargylic and benzylic alcohols in the presence of a new 'Pd–Sn' bimetallic catalyst in nitromethane; water being the sole byproduct. The plausible mechanism of alkylation and the intermediacy of ether has been enumerated.

Introduction

Nucleophilic substitution of π-activated electrophiles such as halides, acetates, sulfonates, carbonates and their surrogates is one of the major tools for C–C bond formation.[1] But such electrophiles are mostly prepared from the corresponding alcohols. Therefore, the direct coupling of an alcohol with a nucleophile would be an attractive process as it obviates the preparation of a reactive electrophile, and only water would be the byproduct of the alkylation reaction.[2] We report here a heterobimetallic catalyst [Pd(COD)Cl–$SnCl_3$] **1a** (Scheme 1, Fig. 1) which is insensitive to water and is capable of directly activating an alcohol (ROH). Once activated, the alcohol smoothly couples with a nucleophile (R′H) such as an arene, hetero arene, active methylene compound or an organometallic nucleophile (R′M) to give the desired product (R–R′).



Scheme 1 Alkylation strategy in this work.

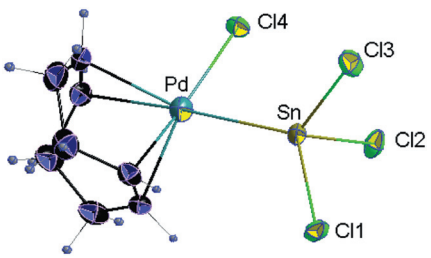


Fig. 1 Molecular structure of **1a**, 30% probability thermal ellipsoids.

Results and discussion

In the course of our continuing effort to exploit the organic reactivity of a reagent combination involving transition metal and tin as the partners,[3] we became attracted to the immense potential of heterobimetallic catalysis.[4] Irrespective of the type, a heterobimetallic catalyst offers superior results in terms of efficiency and selectivity relative to the individuals. Incorporation of two metals in a single scaffold also results in selective substrate binding, dual and synergistic activation, and higher efficiency toward coupling. A relatively soft bimetallic scaffold could be generated by the insertion reaction of a main group (possibly Si, Sn, In) halide or surrogate across a low-valent late transition metal partner.[5] Indeed the insertion reaction of $SnCl_2$ across a low-valent late transition metal complex, namely 'Pd–Cl', generates the corresponding stanna-metal motif **1a–1d** with excellent yield in CH_2Cl_2–acetone medium at room temperature (Scheme 2).[6] The structure of **1a** has been unambiguously established by X-ray crystal structure analysis (Fig. 1).

In view of the importance of metal-catalyzed activation of alcohols[1b,c,7] and our own enthusiasm,[4d–g] we became interested to test whether this heterobimetallic motif is amenable toward coupling with nucleophiles. In this regard, one may note that a few transition metal salts,[7a–e] Lewis acids[7f–l] and Brønsted acids[8] are known to catalyze these reactions. In certain cases, extra

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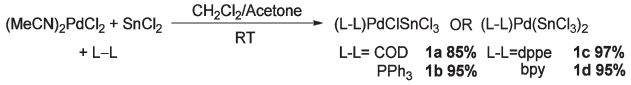
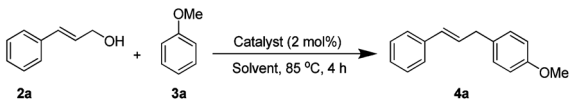


Scheme 2 Preparation of complexes.

Table 1 Catalyst screening[a]



Entry	Catalyst	Solvent	Yield of **4a** (%)
1	—	$MeNO_2$	Trace
2	$SnCl_2$	$MeNO_2$	34
3	$SnCl_4$	$MeNO_2$	32
4	$PdCl_2$	$MeNO_2$	12
5	$PdCl_2$(COD)	$MeNO_2$	7
6[b]	PdCl(COD)–$SnCl_3$ (**1a**)	$MeNO_2$	74
7	PdCl(COD)–$SnCl_3$ (**1a**)	DCE	62
8	PdCl(COD)–$SnCl_3$ (**1a**)	MeCN	6
9	PdCl(COD)–$SnCl_3$ (**1a**)	Toluene	5
10	$PdCl(PPh_3)_2$–$SnCl_3$ (**1b**)	$MeNO_2$	20
11	$Pd(dppe)(SnCl_3)_2$ (**1c**)	$MeNO_2$	26
12	$Pd(bpy)(SnCl_3)_2$ (**1d**)	$MeNO_2$	41
13	$[Pd(PPh_3)_2(MeCN)_2]^{2+}[BF_4]^{2-}$	$MeNO_2$	21

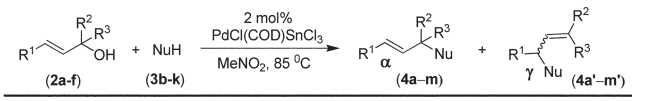
[a] A mixture of cinnamyl alcohol **2a** (1 mmol), anisole **3a** (2 mmol), and catalyst (2 mol%) in 2 mL of solvent was stirred at 85 °C for 4 h. Then the crude mixture was subjected to ^{1}H NMR analysis to determine the yield of **4a** using triphenyl methane as external standard. [b] With 1.5 mol % loading 62% yield of **4a** was obtained.

additives are added or the reaction conditions are harsh. In our case, the 'Pd–Sn' catalyst [Pd(COD)Cl–$SnCl_3$] **1a** turned out to be highly efficient in promoting the direct coupling of π-activated 1°, 2°, and 3° alcohols with a large spectrum of carbon nucleophiles. Moreover, **1a** is very selective, mild, stable, and easy to handle giving smooth transformations (discussed later).

For model studies cinnamyl alcohol **2a** and anisole **3a** were selected as the starting materials, the desired coupling product being 1-cinnamyl-4-methoxybenzene **4a**. The catalytic efficiency of the 'Pd–Sn' heterobimetallic catalyst [Pd(COD)Cl–$SnCl_3$] **1a** was satisfactory at 2 mol% loading in nitromethane as the solvent and only the *para* isomer **4a** was obtained in 74% yield (Table 1, entry 6). In contrast, [Pd(COD)Cl_2] is individually inactive, while $SnCl_2$ is poorly active. The reaction proceeds with catalytic $SnCl_4$ but with very poor TOF. Similarly, other bimetallic 'Pd–Sn' catalysts such as $Pd(PPh_3)_2Cl$–$SnCl_3$, $Pd(dppe)(SnCl_3)_2$ and $Pd(bpy)(SnCl_3)_2$ were inefficient. The suggestion that catalysis could be triggered *via* concomitant HCl (which in turn may originate *via* partial hydrolysis of the catalyst **1a**) was clearly ruled out since a control experiment with the model reaction partners in presence of 100 mol% aq. HCl in nitromethane at 85 °C for 4 h yielded **4a** in only 25% yield. Even $PdCl_2$ and cationic Pd(II) species showed very low efficiency.[9]

Attracted by the direct cinnamylation of anisole **3a**, we studied the coupling of various allylic alcohols with activated arenes or heteroarenes. Indeed the allylation of arenes and heteroarenes was smooth irrespective of whether a primary or a

Table 2 Pd–Sn catalyzed allylation of various nucleophiles (NuH)[a]



Entry	Allyl alcohol	NuH	Time (h)	Yield (%)	α:γ
1	2a	3a	4	74	100:0 (**4a**)
2	2b	3b	12	60	0:100 (**4b′**)
3[b]	2c	3c	3	82	NA[c] (**4c**, **4c′**)
4	2a	3d	6	60	66:34 (**4d**:**4d′**)
5	2d	3d	0.5	81	85:15 (**4e**:**4e′**)
6	2e	3d	0.5	92	48:52 (**4f**:**4f′**)
7[d]	2a	3e	6	70	100:0 (**4g**)
8	2e	3f	4	71	53:47 (**4h**:**4h′**)
9	2b	3g	12	70	0:100 (**4i′**)
10	2f	3h	1	73	NA[c] (**4j**, **4j′**)
11	2c	3i	10	77	NA[c] (**4k**, **4k′**)
12	2f	3j	2	92	NA[c] (**4l**, **4l′**)
13	2d	3k	2	78	75:25 (**4m**, **4m′**)

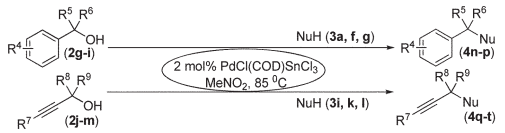
[a] Alcohol (1 mmol) and nucleophile (2 mmol). [b] Only 2-alkylated product is obtained. [c] Not applicable. [d] The regioisomers corresponding to 5- and 3-positions in thiophene ring are obtained in a ratio of 83 : 17.

secondary allyl alcohol has been used (Table 2, entries 2–8). On aspects of regioselectivity, the change of product distribution (*α versus γ*) was observed upon increasing methyl substitution at the allylic position of the allyl alcohol (entries 5 and 6). The reaction of indole **3f** with alcohol **2e** afforded the *C*-alkylated product; no *N*-alkylated product was obtained (entry 8). As expected, the secondary allyl alcohols were more reactive as compared to primary ones.

We further extended the coupling reaction of allyl alcohols with substituted 1,3-dicarbonyls (entries 9–11), and organometallic nucleophiles (entries 12, 13), which led to equally efficient carbon–carbon bond formation. Noticeably, allyltributyltin did not serve as a nucleophile to produce the coupling product while with vinyl silane, instead of the desired product, the reduced product (*E*)-1,3-di(*p*-tolyl)prop-2-ene **5** was obtained corresponding to the allyl alcohol **2f** in 40% yield (ESI, S-2†).

We also tested the activity of the catalyst **1a** in other alkylation reactions using benzyl and propargyl alcohols under similar reaction conditions; the results have been extremely gratifying. As shown in Table 3, the alkylation efficiency depended on the nucleophilic partner. For benzylation reactions, the possible intermediacy of styrene[10] was ruled out, as we failed to detect any styrene intermediate in the reaction mixture even at ambient

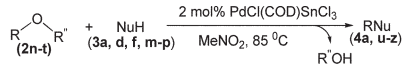
Table 3 Benzylation and propargylation of various nucleophiles (NuH)[a]



Entry	Alcohol	NuH	Product	Time (h)	Yield (%)
1	2g	3g	4n	12	55
2	2h	3f	4o	1	88
3[b]	2i	3a	4p	12	50
4[c]	2j	3a	4q	1	75
5	2k	3k	4r	2	71
6	2l	3i	4s	6	60
7[d]	2m	3l	4t	6	72

[a] Alcohol (1 mmol) and nucleophile (2 mmol). [b] 5% of catalyst was used, o/p ratio 38 : 62. [c] 15% eliminated product. [d] 5 mmol NuH was used.

Table 4 Allylation, benzylation and propargylation of various nucleophiles (NuH) with ethers as alkylating agents[a]



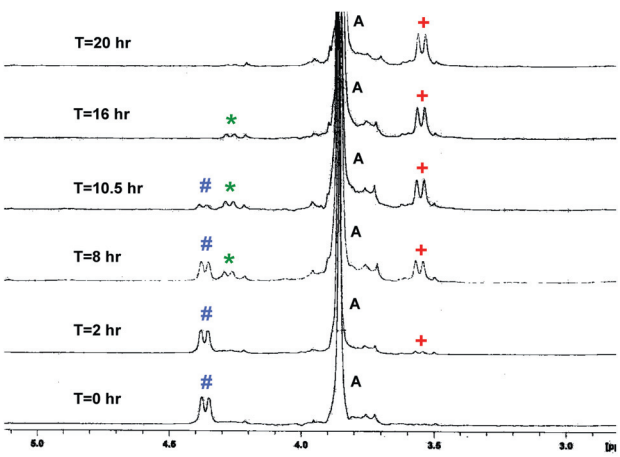
Entry	Ether	NuH	Product	Time (h)	Yield (%)
1	2n	3a	4a	4	55
2	2o	3d	4u	4	90
3	2p	3m	4v	4	80
4	2q	3n	4w	10	60
5	2r	3o	4x	6	62
6	2s	3p	4y	10	70
7	2t	3f	4z	6	51

[a] Ether (1 mmol) and nucleophile (2 mmol).

temperature. Moreover, in a separate experiment, when styrene was used as an alkylating agent with anisole as the arene partner, the desired benzylation product was not formed.

Next, we extended the scope of the reaction by successfully employing symmetrical and unsymmetrical π-activated ethers as the alkylating partner in the allylation, benzylation and propargylation reactions (Table 4). The affinity of Sn(IV) towards the hard oxygen centre is well known in literature.[11] In line with this, we believe that in the initial stage of the cycle, the alcohol could be activated by the oxophilic 'Pd–Sn' catalyst **1a**.[4g,12] Lewis acids are known promoters for conversion of alcohols to symmetric ethers.[13] To obtain an insight into the reaction pathway, we followed the reaction of cinnamyl alcohol **2a** with anisole **3a** in presence of catalyst **1a** (10 mol%) in deuterated chloroform at 60 °C by continuous ^{1}H-NMR monitoring of the reaction mixture (Fig. 2). Intially (after 2 h) only the coupling product **4a** was obtained along with unreacted **2a**. Then symmetrical dicinnamyl ether **2n** started to generate in the reaction medium. With time, both the alcohol **2a** and dicinnamyl ether **2n** were consumed to give the desired alkylated product **4a**. This indicates that both the reaction pathways, with and without the intermediacy of ether, are operating simultaneously. It may be noted that when dicinnamyl ether **2n** was used as an alkylating agent with anisole **3a** as the nucleophile, **4a** was obtained in lower yield (55%, Table 4) as compared to the corresponding reaction with alcohol **2a** as the alkylating agent (74%).

In an effort to ascertain the role of the two metal centers in the catalyst, *in situ* ^{13}C NMR studies of a 1 : 1 mixture of benzyl alcohol **2i** and **1a** were carried out in $CDCl_3$ at room temperature. A downfield shift of benzylic carbon was observed which



= Allylic 2H of cinnamyl alcohol, * = Allylic 4H of dicinnamyl ether, + = Allylic 2H of alkylated product **4a**, **A** = 3H(OMe) of anisole

Fig. 2 ^{1}H NMR study for the ether intermediate.

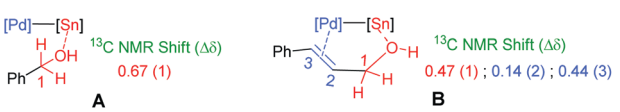


Fig. 3 Substrate catalyst interaction.

suggested hard–hard interaction between the hydroxy group and the Lewis acidic Sn centre (**A**, Fig. 3). On the other hand, ^{13}C NMR monitoring of a mixture of cinnamyl alchol **2a** and **1a**

showed a downfield shift of the double bond and allylic CH_2 carbon, implying a dual activation of allyl alcohol by the catalyst **1a** (**B**, Fig. 3).[14]

Conclusions

We have presented a novel homogeneous heterobimetallic 'Pd–Sn' catalyst **1a** for the direct alkylation of various carbon nucleophiles with a wide variety of π-activated alcohols. As the catalyst is air and water stable, highly efficient, of wide applicability and above all is palladium based, we believe that it will be well exploited by synthetic chemists. Further work is now underway in our laboratory to broaden the scope of the new catalyst and to better understand its mechanism.

Experimental

General methods

Pre-coated silica gel $60F_{254}$ was used for thin layer chromatography and silica gel 60–120 mesh was used for column chromatography. $PdCl_2$, 1,5-cyclooctadiene, PPh_3, nitromethane and other reagents were of acceptable purity, and were purified when necessary following standard laboratory protocol. Dry $SnCl_2$ was prepared from commercially available $SnCl_2{\cdot}2H_2O$. ^1H (200, 400 MHz) and ^{13}C (54.6, 100 MHz) NMR spectra were recorded on a Brucker-AC 200 MHz spectrometer and a Brucker-Avance II 400 MHz Spectrometer. ^1H chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, dd = double doublet, m = multiplet), coupling constant (Hz). ^{13}C chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.0 ppm). ^{31}P chemical shifts are recorded in ppm from H_3PO_4. FT-IR (4000–500 cm^{-1}; using KBr pellet) spectra were obtained using a Thermo Nicolet FTIR Spectrometer (NEXUS-870). Single-crystal X-ray diffraction analysis was carried out on an Enraf Nonius Turbo CAD4 diffractometer at 298 K. UV-visible spectra were recorded at 293 K on Shimadzu UV-1601 UV-VIS Spectrometer. Elemental analyses were performed on Perkin Elmer Instruments 2400 Series II CHNS/O Analyzer.

Syntheses and characterization of 'Pd–Sn' complexes[6]

[Pd(COD)Cl($SnCl_3$)] (**1a**): 1,5-Cyclooctadiene (55.1 mg, 0.51 mmol) was dissolved in dry CH_2Cl_2 (10 mL) by stirring with a magnetic stirrer and a solution of $SnCl_2$ (95 mg, 0.5 mmol) in 0.5 mL of Me_2CO was added, giving a milky suspension. Then solid $PdCl_2(MeCN)_2$ (130 mg, 0.5 mmol) was added to this suspension and stirring was continued for 10 min. Freshly distilled petroleum ether (30 ml) was added to the mixture and stirring continued was for another 10 min. The precipitate was separated by filtration, washed with petroleum ether and dried in vacuum to give **1a** as a yellow solid (yield 85%.)

^1H NMR (200 MHz, $CDCl_3$): δ 6.31 (br, s, 4H), 2.89–2.95 (m, 4H), 2.50–2.62 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.6, 30.9. DEPT 135: 116.6 (=CH), 30.9 (CH_2). UV-VIS (DCE): (λ_{max}, nm): 325, 390 Anal. Calcd for $C_8H_{12}Cl_4PdSn$: C, 20.22; H, 2.55. Found: C, 20.31; H, 2.48.

[PdCl(PPh_3)$_2$$SnCl_3$] (**1b**) was prepared following the above procedure by taking 2 eq. of triphenyl phosphine ligand with respect to $SnCl_2$.

Yellow solid. Yield 95%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68–7.73 (m, 12H), 7.36–7.49 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.0, 134.98, 134.92, 130.4, 128.1, 128.0, 127.9. ^{31}P NMR ($CDCl_3$ + DCM): δ 27.32. Anal. Calcd for $C_{36}H_{30}Cl_4P_2PdSn$: C, 48.50; H, 3.39. Found: C, 48.27; H, 3.28.

Similarly, **[Pd(dppe)($SnCl_3$)$_2$]** (**1c**) and **[Pd(bpy)($SnCl_3$)$_2$]** (**1d**) were prepared by taking 2 eq. of $SnCl_2$ with respect to the ligand (dppe/bpy) or $PdCl_2(MeCN)_2$.

[Pd(dppe)($SnCl_3$)$_2$] (**1c**): Brown solid, Yield 97%. Anal. Calcd for $C_{26}H_{24}Cl_6P_2PdSn_2$: C, 32.7; H, 2.53. Found: C, 32.58; H, 2.61.

[Pd(bpy)($SnCl_3$)$_2$] (**1d**): Red-brown solid, Yield 95%. Anal. Calcd for $C_{10}H_8Cl_6N_2PdSn_2$: C, 16.86; H, 1.13; N 3.93. Found: C, 16.69; H, 1.21; N, 3.79.

General procedure for the catalytic *C*-alkylation of alcohol

A mixture of alcohol (1 mmol), nucleophile (2 mmol), and [Pd(COD)Cl($SnCl_3$)] (2 mol%) in 2 mL of nitromethane was stirred at 85 °C. Following completion (*vide* TLC) the reaction mixture was evaporated and the mixture was subjected to column chromatography to give rise to the *C*-alkylated product.

Product data

The spectral data of **4a**,[15] **4c**,[7h] **4d**,[13a] **4d′**,[13a] **4e**,[16] **4e′**,[16] **4g**,[13a] **4i**,[17] **4m**,[18] **4m′**,[18] **4n**,[19] **4p**,[7i] **4q**,[4g] **4r**,[4g] **4s**,[20] **4u**,[21] **4w**,[9,21] **4x**,[22] **4y**[9] and **5**[23] were in an excellent agreement with the reported data. The spectral data for the products **4b′**, **4f**, **4f′**, **4h**, **4h′**, **4j**, **4k**, **4l**, **4o**, **4t**, **4v** and **4z** are shown below.

(*E*)-1-Cinnamyl-2,3,4,5,6-pentamethylbenzene (4b′). White solid. ^1H NMR (200 MHz, $CDCl_3$): δ 7.26–7.45 (m, 5H), 6.39–6.55 (m, 2H), 3.72 (d, 2H, J = 4.0 Hz), 2.39 (s, 9H), 2.37 (s, 6H). ^{13}C NMR (54.6 MHz, $CDCl_3$): δ 137.9, 133.5, 133.1, 132.6, 132.5, 130.1, 128.6, 128.5, 127.0, 126.1, 34.1, 17.1, 17.0, 16.7. DEPT 135: 130.1, 128.6, 128.5, 127.0, 126.1, 34.1, 17.1, 17.0, 16.7. IR (KBr, cm^{-1}): 2924, 1636, 1456, 965, 733, 693. ESI-MS for $C_{20}H_{24}$ [M], $[M + H]^+$ = 265.27. Anal. Calcd ($C_{20}H_{24}$): C, 90.85; H, 9.15. Found: C, 90.93; H, 9.21.

(*E*)-2-Methyl-5-(2-methyl-4-phenylbut-3-en-2-yl)furan (4f) and 2-methyl-5-(3-methyl-1-phenylbut-2-enyl)furan (4f′). The two diastereomers could not be separated and their ratio was determined by ^1H NMR analysis; **4f** : **4f′** = 63 : 37.

Colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ 7.18–7.41 (m, 5H **4f** + 5H **4f′**), 6.44 (d, 1H **4f**, J = 16.2 Hz), 6.33 (d, 1H **4f**, J = 16.0 Hz), 5.89–5.98 (m, 2H **4f** + 2H **4f′**), 5.57 (d, 1H **4f′**, J = 9.4 Hz), 4.86 (d, 1H **4f′**, J = 9.4 Hz), 2.29 (s, 3H **4f**), 2.26 (s, 3H **4f′**), 1.79 (s, 3H **4f′**), 1.76 (s, 3H **4f′**), 1.48 (s, 6H **4f**).

^{13}C NMR (100 MHz, $CDCl_3$; major + minor isomers): δ 159.6, 155.4, 150.9, 150.6, 143.2, 137.7, 137.6, 132.9, 128.4, 128.3, 127.7, 126.9, 126.4, 126.23, 126.21, 124.8, 106.4, 105.8,

105.6, 104.0, 43.9, 38.1, 26.8, 25.8, 18.0, 13.6. IR (KBr, cm^{-1}): 2922, 2853, 1559, 1494, 1454, 1260, 1021, 780, 697. ESI-MS for $C_{16}H_{18}O$ [M], $[M + K]^+$ = 265.25. Anal. Calcd ($C_{16}H_{18}O$): C, 84.91; H, 8.02. Found: C, 84.97; H, 8.11.

(*E*)-3-(2-Methyl-4-phenylbut-3-en-2-yl)-1*H*-indole (4h) and 3-(3-methyl-1-phenylbut-2-enyl)-1*H*-indole (4h′). The two diastereomers could not be separated and their ratio was determined by ^{1}H NMR analysis; **4h** : **4h′** = 53 : 47.

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H **4h** + 1H **4h′**), 7.73 (d, 1H **4h**, J = 8.0 Hz), 7.14–7.37 (m, 7H **4h** + 8H **4h′**), 6.98–7.06 (m, 2H **4h** + 1H **4h′**), 6.92 (s, 1H **4h′**), 6.55 (d, 1H **4h**, J = 16.0 Hz), 6.44 (d, 1H **4h**, J = 16.0 Hz), 5.67 (d, 1H **4h′**, J = 9.6 Hz), 5.11 (s, 1H **4h′**, J = 9.6 Hz), 1.79 (s, 6H **4h′**), 1.63 (s, 6H **4h**).

^{13}C NMR (100 MHz, $CDCl_3$; major + minor isomers): δ 145.2, 140.1, 138.0, 137.1, 136.8, 131.6, 128.6, 128.4, 128.1, 127.7, 127.0, 126.8, 126.3, 126.2, 126.1, 126.0, 124.1, 122.2, 122.0, 121.7, 121.5, 120.3, 120.0, 119.8, 119.3, 119.1, 111.3, 111.2, 41.8, 37.2, 28.7, 25.9, 18.2. DEPT 135: 140.1, 128.6, 128.1, 127.7, 127.0, 126.3, 126.2, 126.1, 126.0, 122.2, 122.0, 121.7, 121.5, 120.3, 120.0, 119.3, 119.1, 111.3, 111.2, 41.8, 28.7, 25.9, 18.2. IR (KBr, cm^{-1}): 3420, 1634, 1456, 747, 698. ESI-MS for $C_{19}H_{19}N$ [M], $[M + H]^+$ = 262.21. Anal. Calcd ($C_{19}H_{19}N$): C, 87.31; H, 7.33; N, 5.36. Found C, 87.42; H, 7.21, N, 5.44.

(*E*)-3-(1,3-Dip-tolylallyl)-4-hydroxy-2*H*-chromen-2-one (4j). White solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.78–7.83 (dd, 1H, J = 8.0, 1.4 Hz), 7.49–7.58 (m, 1H), 7.04–7.38 (m, 10H), 6.73 (dd, 1H, J = 16.0, 6.2 Hz), 6.51 (d, 1H, J = 16.0 Hz), 5.43 (d, 1H, J = 6.2 Hz), 2.35 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (54.6 MHz, $CDCl_3$): δ 164.2, 161.8, 153.7, 138.9, 138.3, 137.6, 134.5, 133.0, 130.9, 130.3, 129.0, 128.5, 128.2, 127.5, 124.9, 124.1, 117.5, 117.0, 107.7, 44.7, 22.2, 22.0. IR (KBr, cm^{-1}): 3421, 1608, 1386, 1195, 1162, 758. ESI-MS for $C_{26}H_{22}O_3$ [M], $[M + Na]^+$ = 405.71. Anal. Calcd ($C_{26}H_{22}O_3$): C, 81.65; H, 5.80. Found: C, 81.76; H, 5.74.

(*E*)-3-(1,3-Bis(4-bromophenyl)allyl)-3-methylpentane-2,4-dione (4k). White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.41 (m, 4H), 7.13–7.16 (m, 4H), 6.29–6.39 (m, 2H), 4.60 (d, 1H, J = 6.8 Hz), 2.13 (s, 3H), 1.95 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.1, 205.4, 138.5, 135.6, 132.4, 131.7, 131.5, 131.4, 128.1, 127.9, 121.6, 121.2, 71.3, 50.9, 27.9, 27.4, 16.0. DEPT 135: 132.4, 131.7, 131.5, 131.4, 128.1, 127.9, 50.9, 27.9, 27.4, 16.0. IR (KBr, cm^{-1}): 1720, 1690, 1484, 1355, 1206, 1068, 1008, 806. ESI-MS for $C_{21}H_{20}Br_2O_2$ [M], $[M + Na]^+$ = 487.20. Anal. Calcd ($C_{21}H_{20}Br_2O_2$): C, 54.34; H, 4.34. Found: C, 54.41; H, 4.29.

(*E*)-4,4′-(Hexa-1,5-diene-1,3-diyl)bis(methylbenzene) (4l). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, 2H, J = 8.0 Hz), 7.21–7.26 (m, 4H), 7.16 (d, 2H, J = 8.0 Hz), 6.34–6.46 (m, 2H), 5.79–5.90 (m, 1H), 5.13 (d, 1H, J = 17.2 Hz), 5.06 (d, 1H, J = 10.0 Hz), 3.53–3.58 (m, 1H), 2.63 (t, 2H, J = 6.4 Hz), 2.40 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 136.8, 136.7, 135.8, 134.7, 132.7, 129.4, 129.2, 129.1, 127.6, 126.1, 116.2, 48.5, 40.3, 21.2, 21.0. DEPT 135: 136.7, 132.7, 129.4, 129.2, 129.1, 127.6, 126.1, 116.2, 48.5, 40.3, 21.2, 21.0. IR (KBr, cm^{-1}): 3020, 2921, 2859, 1512, 1441, 966, 812, 798. ESI-MS for $C_{20}H_{22}$ [M], $[M + Na]^+$ = 284.90. Anal. Calcd ($C_{20}H_{22}$): C, 91.55; H, 8.45. Found: C, 91.39; H, 8.51.

3-(1-(Thiophen-2-yl)ethyl)-1*H*-indole (4o). Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.56 (d, 1H, J = 7.8 Hz), 7.36 (d, 1H, J = 8.2 Hz), 6.92–7.26 (m, 6H), 4.69 (q, 1H, J = 7.0 Hz), 1.84 (d, 3H, J = 7.0 Hz). ^{13}C NMR (54.6 MHz, $CDCl_3$): δ 151.4, 136.6, 126.5, 124.2, 123.4, 123.1, 122.1, 121.4, 121.0, 119.6, 119.4, 111.2, 32.4, 23.5. IR (KBr, cm^{-1}): 3416, 1636, 1456, 1337, 1224, 1096, 1010, 742, 697. ESI-MS for $C_{14}H_{13}NS$ [M], $[M + K]^+$ = 265.96. Anal. Calcd ($C_{14}H_{13}NS$): C, 73.97; H, 5.76; N, 6.16. Found C, 73.86; H, 5.79, N, 6.21.

2-(1-(4-Chlorophenyl)-3-phenylprop-2-ynyl)thiophene (4t). Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.46–7.57 (m, 4H), 7.29–7.39 (m, 5H), 7.25 (dd, 1H, J = 5.0, 1.2 Hz), 6.96–7.06 (m, 2H), 5.45 (s, 1H). ^{13}C NMR (54.6 MHz, $CDCl_3$): δ 145.2, 139.8, 133.3, 131.8, 129.1, 128.9, 128.4, 126.9, 125.3, 125.1, 123.0, 89.0, 84.8, 38.6. IR (KBr, cm^{-1}): 3063, 1488, 1090, 1014, 826, 755, 690. ESI-MS for $C_{19}H_{13}ClS$ [M], $[M + K]^+$ = 347.12. Anal. Calcd ($C_{19}H_{13}ClS$): 73.89; H, 4.24. Found C, 73.67; H, 4.36.

(*E*)-2-(4-(4-Chlorophenyl)but-3-en-2-yl)-3,5-dimethylphenol (4v). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.44 (m, 4H), 6.65 (s, 2H), 6.53–6.56 (m, 2H), 5.35 (s, 1H), 4.03–4.06 (m, 1H), 2.37 (s, 3H), 2.27 (s, 3H), 1.53 (d, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 137.2, 136.7, 135.5, 134.6, 132.9, 128.7, 128.2, 127.4, 125.5, 124.0, 115.6, 35.2, 20.8, 20.4, 17.4. DEPT 135: 134.6, 128.7, 128.2, 127.4, 124.0, 115.6, 35.2, 20.8, 20.4, 17.4. IR (KBr, cm^{-1}): 3481, 2924, 1490, 1457, 1282, 1090, 1011, 968, 839, 809. ESI-MS for $C_{18}H_{19}ClO$ [M], $[M + K]^+$ = 325.05. Anal. Calcd ($C_{18}H_{19}ClO$): 75.38; H, 6.68. Found C, 75.49; H, 6.61.

3-(3-Phenyl-1-*p*-tolylprop-2-ynyl)-1*H*-indole (4z). Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.64 (d, 1H, J = 7.8 Hz), 7.42–7.50 (m, 4H), 7.23–7.38 (m, 4H), 7.19–7.05 (m, 5H), 5.45 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (54.6 MHz, $CDCl_3$): δ 139.3, 137.7, 137.3, 132.6, 130.2, 129.1, 128.8, 127.1, 126.9, 124.8, 123.5, 123.2, 120.6, 120.5, 118.1, 112.2, 91.8, 84.1, 36.1, 22.0. IR (KBr, cm^{-1}): 3219, 2923, 2852, 1457, 742. ESI-MS for $C_{24}H_{19}N$ [M], $[M + H]^+$ = 322.29. Anal. Calcd ($C_{24}H_{19}N$): C, 89.68; H, 5.96; N, 4.36. Found C, 89.87; H, 5.89; N, 4.52.

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