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Silver(I)-Catalyzed Reaction between Pyrazole and Propargyl Acetates: Stereoselective Synthesis of the Scorpionate Ligands (*E*)-Allyl-*gem*-dipyrazoles (ADPs)

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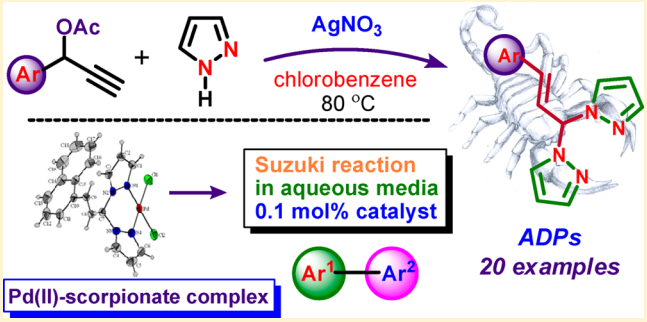
Supporting Information

ABSTRACT: The reaction between readily accessible pyrazole and propargyl acetates in the presence of Ag(I) catalyst yielded a new class of (*E*)-allyl-*gem*-dipyrazole scorpionate ligands: 1-aryl-2-*N*-pyrazolyl allyl acetates and 1,3-dipyrazolyl-3-arylpropene. The reaction showed broad substrate scope, and various functional and protecting groups were tolerated under the reaction conditions. The palladium(II) scorpionate complex could thus be easily prepared and successfully employed in Suzuki−Miyaura cross-couplings in water.



INTRODUCTION

Propargyl alcohols readily undergo nucleophilic substitution because of the presence of hydroxyl and alkyne functionalities and hence can be used for the facile construction of complex molecular frameworks.[1] The reaction between 1-substituted propargyl acetate and NH-heteroarenes allows for the formation of (1) propargyl heteroarenes through substitution of the hydroxyl group and its derivatives by the NH-heteroarene, (2) 1,2-disubstituted allyl acetates via hydroamination of the NH moiety with the alkyne, (3) 1,3-disubstituted allenes via attack of the heteroaryls at the terminal position of the alkyne, and (4) allyl-*gem*-diheteroaryl- and 1,3-diheteroaryl-substituted propenes through attack of the NH heteroarene on the in situ generated allene. Thus, various functionalized heteroarenes can be practically realized via a single-step reaction between propargyl acetates and NH-heteroarenes.[2] Recently, Shi's group demonstrated the synthesis of propargyl and allene triazoles by the iron-catalyzed regioselective attack of triazole on propargyl alcohols.[2b,c] The Au-catalyzed synthesis of functionalized allenes from propargyl alcohols and arenes has also been reported.[1o] Interestingly, *gem*-dipyrazolylalkanes were easily synthesized from the Ag-catalyzed regioselective attack of two pyrazoles at an aliphatic terminal alkyne carbon center.[2a] Our recent work in the development of novel reactions of propargyl alcohols inspired us to explore the Lewis acid catalyzed reaction between propargyl acetate and pyrazole.[3] We anticipated the formation of the rarely observed hydroamination compound 1-aryl-2-pyrazolyl allyl acetate (**3**, path I), 1-aryl-3-pyrazolyl allene (**A**, path II), and propargyl-*N*-pyrazole (**6**, path III) (Scheme 1). Furthermore, α-attack of pyrazole on the transiently formed allene pyrazole **A** could afford (*E*)-allyl-*gem*-dipyrazoles (**4**; ADPs), a new class of *scorpionate-type ligands*, whereas γ-attack of pyrazole could afford (*E*)-1,1′-(3-arylprop-1-ene-1,3-diyl)-bis(1*H*-pyrazole) (**5**).

Interestingly, the *gem*-dipyrazolyl derivatives exhibited analgesic and anti-inflammatory activities.[4] The two adjacent nitrogen atoms in **4** give strong chelation ability to the metal, and the complexes are useful in accomplishing various catalytic organic transformations.[5,6] Importantly, some of the Pt-coordinated complexes show anticancer activity.[7] We herein report the synthesis of novel ADPs (**4**), 1-aryl-2-*N*-pyrazolylallyl acetate (**3**), and 1,3-dipyrazolyl-3-arylpropene (**5**) from propargyl acetates and pyrazoles in the presence of $AgNO_3$.

RESULTS AND DISCUSSION

To start with, 1-phenylprop-2-ynyl acetate (**1a**) and pyrazole (**2**) were independently reacted in the presence of various Lewis acids at 80 °C for 24 h. The details of the optimization studies are shown in Table 1. The reaction between **1a** (1.0 equiv) and **2** (5.0 equiv) with 10 mol % AgOTf in chlorobenzene produced the (*E*)-allyl-*gem*-dipyrazole (ADP) **4a** in 41% yield, 1-phenyl-2-*N*-pyrazolyl allyl acetate (**3a**; 18%), and 1,3-dipyrazolyl-3-phenylpropene (**5a**; 20%) with incomplete consumption of **1a** (entry 1). Gratifyingly, **4a**, **3a**, **5a**, and unreacted **1a** were easily isolated through flash column chromatography in pure form. Incomplete conversion of **1a** and poor overall yield of the products **3a**−**5a** were noticed when $Cu(OTf)_2$, $In(OTf)_3$, and $CuNO_3{\cdot}H_2O$ were independently employed (entries 2−4). The use of Ph_3PAuCl or $AuCl_3$ catalyst was not satisfactory, giving a complex reaction profile with formation of a trace amount of **4a** (entries 5 and 6).

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Scheme 1. Reaction between Propargyl Acetate and Pyrazole

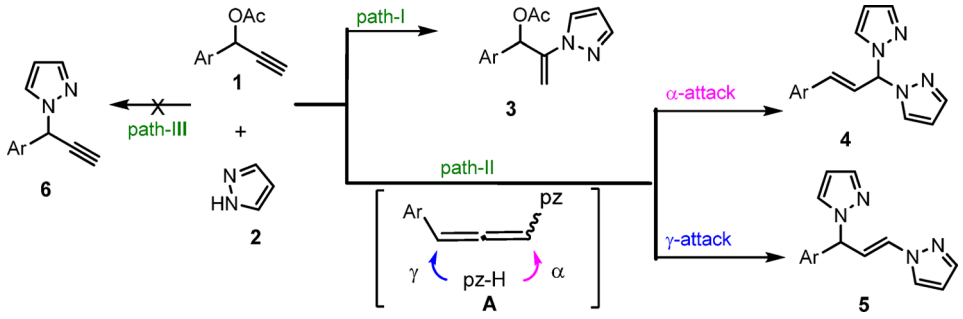
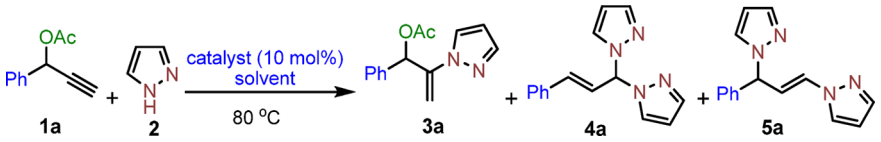


Table 1. Optimization of Reaction Conditions[a]



				yield (%)[b]		
entry	amt of **2** (equiv)	catalyst	solvent	**3a**	**4a**	**5a**
1	5.0	AgOTf	chlorobenzene	18	41	20
2	5.0	$Cu(OTf)_2$	chlorobenzene	<1	<5	<2
3	5.0	$In(OTf)_3$	chlorobenzene	<1	<6	<3
4	5.0	$CuNO_3{\cdot}H_2O$	chlorobenzene	<2	<8	<7
5	5.0	Ph_3PAuCl	chlorobenzene	n.d.	10	n.d.
6	5.0	$AuCl_3$	chlorobenzene	trace	<5	trace
7	**5.0**	**$AgNO_3$**	**chlorobenzene**	**21**	**58**	**11**
8	5.0	AgCl	chlorobenzene	<2	<9	<6
9	5.0	Ag_2CO_3	chlorobenzene	13	25	12
10	5.0	$AgBF_4$	chlorobenzene	17	35	18
11	5.0	$AgNO_3$	THF	18	36	16
12	5.0	$AgNO_3$	CH_3CN	10	37	29
13	5.0	$AgNO_3$	DMF	22	38	17
14	5.0	$AgNO_3$	DCE	08	20	12
15	2.0	$AgNO_3$	chlorobenzene	25	43	08
16	4.0	$AgNO_3$	chlorobenzene	21	55	10
17	6.0	$AgNO_3$	chlorobenzene	20	53	18
18	8.0	$AgNO_3$	chlorobenzene	21	51	19

[a]Reactions were carried out using **1a** (0.5 mmol) and catalyst (10 mol %) in solvent (0.5 mL) at 80 °C for 24 h. [b]Isolated yields. n.d. = not detected.

To our delight, reaction with $AgNO_3$ delivered an improved yield of **4a** (58%), though **3a** and **5a** were also isolated in 21% and 11% yields, respectively (Table 1, entry 7). A trace amount of products **3a**−**5a** were noted in GC-MS, when the reaction was conducted with AgCl (entry 8), whereas Ag_2CO_3 or $AgBF_4$ had only a moderate influence (entries 9 and 10). Of the various Ag salts examined, $AgNO_3$ was found to be effective (entry 7). It is worth mentioning that we did not observe even a trace of propargyl-*N*-pyrazole **6**.[2b] We next explored the effect of solvents. Incomplete conversion of **1a** with the formation of a moderate amount of **4a** was observed when polar aprotic solvents such as THF, CH_3CN, and DMF were used (entries 11−13). The reaction in DCE was poor (entry 14). The use of different amounts of pyrazole was further investigated. The loading of a lower amount of pyrazole, from 5.0 to 2.0 or 4.0 equiv, led to **4a** with slightly decreased yield (entries 15 and 16). An enhanced yield of **5a** was observed when 6.0/8.0 equiv of **2** was employed (entries 17 and 18). We therefore used 5.0 equiv of pyrazole in this transformation. However, the reaction of *O*-pivaloyl- or *O*-Boc-protected propargyl alcohols with pyrazole produced poor amounts of the ADPs.[8]

Reaction Scope. The optimized catalytic condition shown in entry 7 of Table 1 (10 mol % of $AgNO_3$ in chlorobenzene at 80 °C) was finally selected in screening the reaction among a series of propargyl acetates and pyrazole (**2**). The results are summarized in Table 2. The electron-neutral 1-phenylprop-2-ynyl acetate (**1a**) reacted with **2** to give **3a**−**5a** in overall good yields, with the isolation of 54% of **4a**. The F/Cl groups at the *para* position on the aryl moiety in **1b**,**c** reacted effectively with **2**, and the corresponding allyl acetates **3b**,**c** and dipyrazolyl-bearing compounds **4b**,**c** and **5b**,**c** were obtained in good overall yields.

The reaction of propargyl acetates having electron-donating methyl, methoxy, or phenoxy groups at the 4- and/or 3-position on the aryl ring with **2** gave the corresponding ADPs **4d**−**f** in 48%, 56%, and 63% yields, respectively. The free phenol −OH moiety did not affect the reaction outcome, and the corresponding phenol products **3g**−**5g** were isolated in 83% overall yield. Although annulation between phenols and

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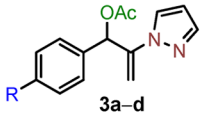
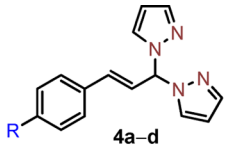
Table 2. $AgNO_3$-Catalyzed Reaction between Propargyl Acetates and Pyrazole (2)[a,b]



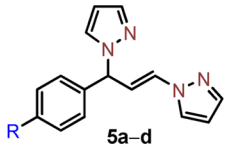
3a–d

R = H; **3a**, 25% R = Cl; **3c**, 19%
F; **3b**, 20% Me; **3d**, 22%



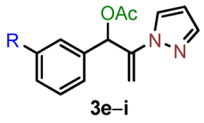
4a–d

R = H; **4a**, 54% R = Cl; **4c**, 54%
F; **4b**, 54% Me; **4d**,48%



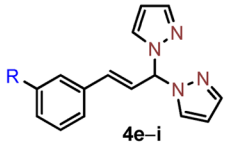
5a–d

R = H; **5a**, 9% R = Cl; **5c**, 6%
F; **5b**, 8% Me; **5d**, 14%



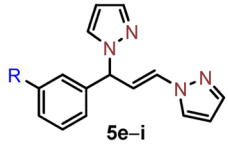
3e–i

R	R
MeO; **3e**, 24%	TBSO; **3h**, 21%
PhO; **3f**, 19%	MOMO; **3i**, 21%
HO; **3g**, 23%	AcO→OH; **3g**, 20%[c]



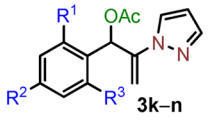
4e–i

R	R
MeO; **4e**, 56%	TBSO; **4h**, 49%
PhO; **4f**, 63%	MOMO; **4i**, 58%
HO; **4g**, 46%	AcO→OH; **4g**, 51%[c]



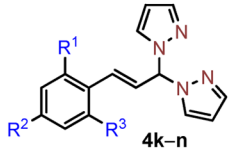
5e–i

R	R
MeO; **5e**, 6%	TBSO; **5h**, 10%
PhO; **5f**, 6%	MOMO; **5i**, trace
HO; **5g**, 14%	AcO→OH; **5g**, 11%[c]



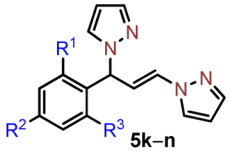
3k–n

R^1	R^2	R^3	
Me	H	H	**3k**, 27%
Br	H	H	**3l**, 20%
Cl	Cl	H	**3m**, 15%
Cl	H	Cl	**3n**, 12%



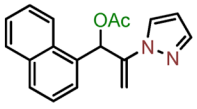
4k–n

R^1	R^2	R^3	
Me	H	H	**4k**, 38%
Br	H	H	**4l**, 50%
Cl	Cl	H	**4m**, 66%
Cl	H	Cl	**4n**, 51%

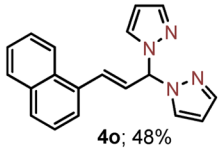


5k–n

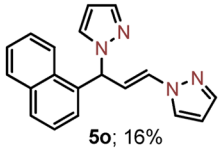
R^1	R^2	R^3	
Me	H	H	**5k**, 10%
Br	H	H	**5l**, trace
Cl	Cl	H	**5m**, trace
Cl	H	Cl	**5n**, trace



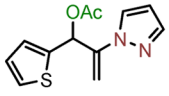
3o; 23%



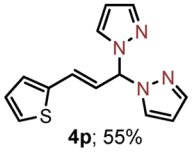
4o; 48%



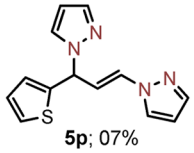
5o; 16%



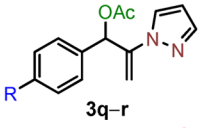
3p; 12%



4p; 55%

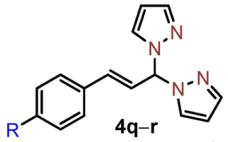


5p; 07%



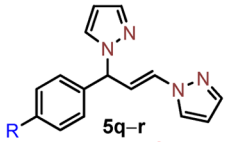
3q–r

R = OHC; **3q**, 19%; R =  ; **3r**, 20%



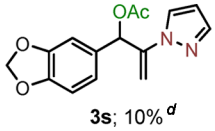
4q–r

R = OHC; **4q**, 54%; R =  ; **4r**, 43%

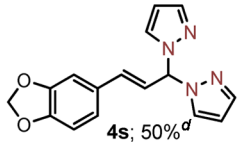


5q–r

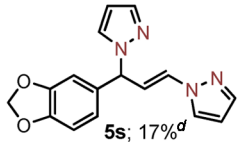
R = OHC; **5q**, trace; R =  ; **5r**, 14%



3s; 10%[d]



4s; 50%[d]



5s; 17%[d]

[a]Reactions were carried out using **1** (1.0 mmol), **2** (5.0 mmol), and $AgNO_3$ (10 mol %) in chlorobenzene (1.0 mL) at 80 °C for 24 h. [b]Isolated yield. [c]Deprotection of the acetyl group was observed. [d]Reaction continued for 53 h.

propargyl alcohols in the presence of a Lewis acid is known to furnish benzofurans,[9] not even a trace amount of benzofuran was observed by GC-MS analysis under the optimized reaction conditions. Gratifyingly, the hydroxyl protecting groups O-TBDMS and O-MOM survived during the reaction and the corresponding products **3h**–**5h** and **3i** and **4i** were obtained in good yields.

Since phenolic esters are more labile than esters obtained from alcohols,[10] we expect cleavage of the phenol-*O*-acetate group in this Ag-catalyzed transformation. As anticipated, the acyl group was cleaved under the reaction conditions to afford **3g**–**5g**. To investigate the effect of *ortho* substitution, *o*-methyl, *o*-bromo, and *o*,*p*-dichloro groups on the aryl moiety in the propargyl acetates were individually reacted with **2** and the corresponding products **3k**–**5k**, **3l** and **4l**, and **3m** and **4m**

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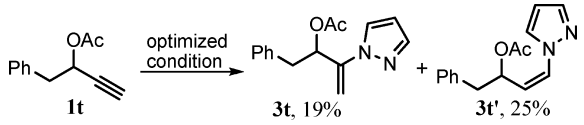
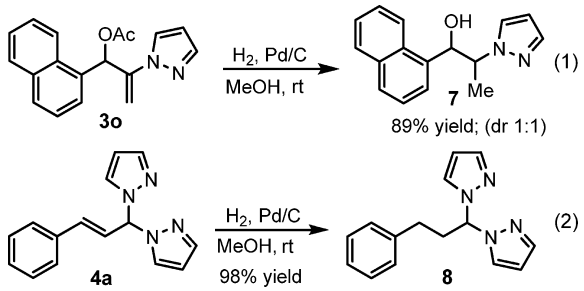
were isolated in 75%, 70% and 81% overall yields, respectively. Moreover, the reaction between the sterically demanding 1-(2,6-dichlorophenyl)-prop-2-ynyl acetate (**1n**) and **2** gave **3n** (12%) and **4n** (51%) in overall moderate amounts. X-ray crystallographic analysis unambiguously elucidated the structure of **4n**.[11] The 1-naphthyl-substituted ADP **4o** was obtained in 48% yield. The structures of **3o** and **5o** were confirmed on the basis of X-ray crystallographic analysis.[11] Generally, coordination of the S heteroatom to the Lewis acid has a negative impact on the reaction outcome.[12] However, the thienyl-2-substituted propargyl acetate **1p** reacted with **2** under the optimized conditions to afford **3p**−**5p**, albeit in relatively good isolated yields of 12%, 55%, and 7%, respectively. The formyl group did not affect the reaction, delivering **4q** and **3q** in 54% and 19% yields, respectively. The optimized conditions tolerate the labile 1,3-dioxolane protecting group, furnishing **3r**−**5r** in 77% overall yield. The electron-rich methylenedioxy-substituted propargyl acetate **1s** reacted sluggishly with **2**, delivering 10%, 50%, and 17% of **3s**−**5s**, respectively. However, the reaction of alkylpropargyl acetate with **2** gave the hydroamination products **3t** and **3t′** (Scheme 2).[2a]

Scheme 2. Reaction with Alkylpropargyl Acetate



With the isolation of the products **3** and ADPs **4**, the hydrogenation of the double bond in **3** and **4** was next investigated. For example, hydrogenation of 1-(naphthalen-1-yl)-2-(1*H*-pyrazol-1-yl)allyl acetate (**3o**) with Pd/C in the presence of an H_2 balloon in MeOH furnished a mixture of an equal amount of diastereomeric α-heteroarylated alcohol **7**, a key skeleton found in various azole-bearing antifungal agents[13] (Scheme 3, eq 1). Similarly, **4a** was hydrogenated under

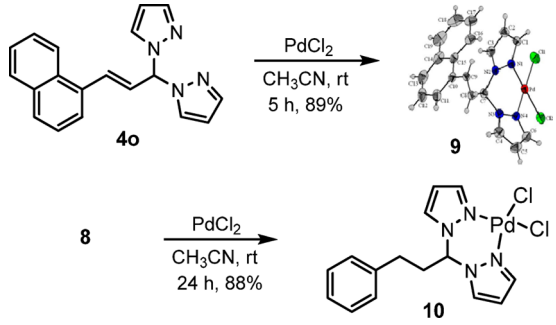
Scheme 3. Hydrogenation Reactions



identical conditions, producing the *gem*-dipyrazolyl alkane **8** in 98% yield (Scheme 3, eq 2). The *gem*-dipyrazolyl alkanes exhibit anti-inflammatory actions.[4]

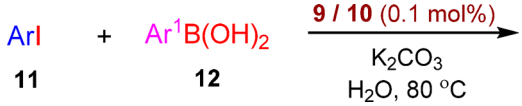
A wide array of the stereoselective scorpionate ligands (*E*)-allyl-*gem*-dipyrazoles (ADPs) have been prepared from propargyl acetates and pyrazole (Table 2). The presence of two adjacent N atoms in the ADPs provides strong chelation ability to the metal, allowing the formation of newly synthesized scorpionate ligands. We therefore envisioned examining the chelation ability of ADPs to the transition metal. Gratifyingly, the reaction of **4o**/**8** with $PdCl_2$ in CH_3CN at room temperature readily delivered the palladium complexes **9** and **10** as pale yellow solids in 89% and 88% yields, respectively (Scheme 4). The structure of **9** was confirmed on the basis of an X-ray crystallographic analysis.[11]

Scheme 4. Complexation with $PdCl_2$



To demonstrate the utility of the newly synthesized complex, we explored examining this scorpionate-ligand-bearing Pd complex **9**/**10** in the well-known Suzuki−Miyaura biaryl cross coupling (Table 3).[14] Gratifyingly, the electron-rich, electron-poor, sterically hindered, and heteroaryl iodides **11** were effectively coupled with $PhB(OH)_2$ (**12a**) under the influence of 0.1 mol % of catalyst **9** in aqueous K_2CO_3 at 80 °C (entries 1−4). Similarly, the reaction of substituted boronic acids **12b**−**d** with 4-methoxyiodobenzene (**11a**) afforded the desired biaryls in excellent yields (entries 5−7). Furthermore, 4-methoxybromobenzene (**11e**) successufully coupled with **12a** under the influence of catalyst **9** (entry 8), while the coupling of 4-methoxychlorobenzene (**11f**) with **12a** gave 8% of the desired biaryl (entry 9).

Table 3. Suzuki Coupling between Various Aryl Halides and Arylboronic Acids[a]



entry	Ar−X (**11**)	Ar^1−$B(OH)_2$ (**12**)	Ar−Ar^1 (**13**) yield (%)[b]
1	4-$MeOC_6H_4I$ (**11a**)	$PhB(OH)_2$ (**12a**)	97[c]
2	4-$F_3CC_6H_4I$ (**11b**)	**12a**	72[c]
3	2-MeC_6H_4I (**11c**)	**12a**	94[c]
4	2-thienyl-I (**11d**)	**12a**	80[c]
5	**11a**	4-$FC_6H_4B(OH)_2$ (**12b**)	95[c]
6	**11a**	3-$MeC_6H_4B(OH)_2$ (**12c**)	86[c]
7	**11a**	1-naphthyl-$B(OH)_2$ (**12d**)	96[c]
8	4-$MeOC_6H_4Br$ (**11e**)	**12a**	83[c]
9	4-$MeOC_6H_4Cl$ (**11f**)	**12a**	08[c]
10	**11a**	**12a**	96[d]
11	**11e**	**12a**	81[d]
12	**11f**	**12a**	trace[d]

[a]Reactions were carried out using **11** (3.0 mmol), **12** (6.0 mmol), catalyst **9**/**10** (0.1 mol %), and K_2CO_3 (6.0 mmol) in H_2O (10.0 mL) at 80 °C for 24 h. [b]Isolated yield. [c]Catalyst **9** was employed. [d]Catalyst **10** was used.

We next explored the catalytic activity of a scorpionate ligand having a reduced double bond and tethered phenyl group, Pd

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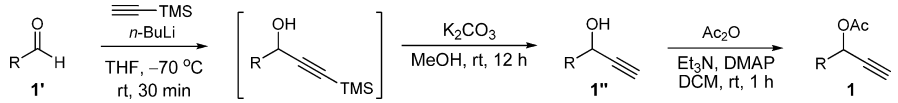
Scheme 5



complex **10**, in the Suzuki−Miyaura couplings (entries 10−12, Table 3). Gratifyingly, coupling of 4-methoxyiodo- and 4-methoxybromobenzene (**11a,e**) with **12a** successfully proceeded under the influence of catalyst **10**, delivering 96% and 81% of the biaryl, respectively (entries 10 and 11). A trace amount of the desired biaryl was detected in GC-MS when 4-methoxychlorobenzene (**11f**) reacted with **12a** in the presence of catalyst **10** (entry 12).

On the basis of precedence and our observations, a plausible reaction pathway is shown in Scheme 1.[1o,2,15] Markovnikov hydroamination of pyrazole to the Lewis acid activated triple bond of propargyl acetate provides the 1-aryl-2-pyrazolyl allyl acetate (path I).[15b] The attack of pyrazole at the terminal side of the alkyne in the propargyl acetate possibly generates the allene intermediate **A** with cleavage of the acetate moiety (path II).[21] Subsequently, addition of pyrazole at the α or γ position of the transiently formed allene delivers ADPs **4** (major) and 1,3-dipyrazolyl-3-aryl propenes **5** (minor). The coordination of pyrazole N and the β carbon of allene to the Ag(I) salt allows the formation of the intermediate **C**.[1j,22] The preferential attack of pyrazole at the intermediate **C** generates **4** as the major product. The lack of coordination of the aryl moiety to the Ag-activated allene is presumably responsible for the formation of the minor amount of **5**. Alternatively, hydroamination of pyrazole with **6** would lead to **5**. Unfortunately, we did not even observe a trace amount of **6** in this study, as the identical compounds of **6** are found to be unstable in the Lewis acid catalysts.[2b]

CONCLUSION

In conclusion, we have demonstrated an Ag-catalyzed reaction between propargyl acetate and pyrazole for the synthesis of novel ADPs. The reaction also affords 1,2-disubstituted allyl acetates **3** (10−25% yield) and 1,3-dipyrazolyl-3-aryl propenes **5** (6−17% yield), shows a broad substrate scope, and tolerates various O-bearing labile protecting groups. The $PdCl_2$-chelated complex of ADPs was successfully employed in Suzuki reactions for biaryl synthesis. Further investigation of the synthetic applications of ADP−metal complexes is currently underway.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all of the reagents and intermediates were obtained commercially and used without purification. Dichloromethane (DCM) and chlorobenzene were distilled over $CaCl_2$. THF was freshly distilled over sodium/benzophenone ketyl under dry nitrogen. Methanol was dried over magnesium cake. Analytical and spectral data of all those known compounds exactly match the reported values.

Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR, and ^{19}F NMR) were recorded on 400 MHz (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz; ^{19}F NMR, 376 MHz) and 500 MHz spectrometers (^{1}H NMR, 500 MHz; ^{13}C NMR, 126 MHz; ^{19}F NMR, 470 MHz) with the solvent resonance as internal standard (^{1}H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). In a few cases tetramethylsilane (TMS) at 0.00 ppm was used as the reference standard. IR spectra were recorded and reported in cm^{-1}. LC-MS spectra were obtained (EI positive/negative mode) with an ionization voltage of 70 eV; data are reported in the form of m/z (intensity relative to base peak 100). Elemental (C, H, N) analysis was carried out using an EA 1112 analyzer. Melting points were determined on an electro-thermal melting point apparatus and are uncorrected. X-ray data were collected at 298 K using graphite-monochromated Mo Kα radiation (0.71073 Å).

Preparation of 1″ from 1′: General Procedure GP-1 (Scheme 5). A solution of (trimethylsilyl)acetylene (1.2 equiv) in THF (50 mL) was stirred in a 100 mL oven-dried two-necked round-bottom flask under an argon atmosphere at −70 °C. *n*-Butyllithium (1.2 equiv, 1.60 M in THF) was introduced over 30 min at −70 °C. After an additional 1 h of stirring, a solution of the aldehyde (**1′**; 1.0 g, 1.0 equiv) in THF (5 mL) was added at −70 °C. The resulting mixture was stirred for 1 h and warmed to room temperature slowly, and the stirring was continued for 30 min. The reaction mixture was quenched with saturated NH_4Cl aqueous solution (20 mL) at 0 °C. The organic layer was separated; the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined extracts were washed with water (2 × 20 mL) and brine (25 mL) and dried over Na_2SO_4. The solvent was filtered and evaporated under the reduced pressure. The crude residue was subsequently used for the desilylation reaction.

Methanol (15 mL) and K_2CO_3 (2.5 equiv) were introduced to the crude residue obtained in the above reaction, and the heterogeneous mixture was stirred under an argon atmosphere at ambient temperature overnight. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (2 × 20 mL) and brine (10 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under vacuum. In most cases the crude residue was used for the acetylation reaction without purification, following the general procedure GP 2.

Synthesis of 1 from 1″ through Acylation of the −OH Moiety: General Procedure GP-2. To a solution of **1″** (1.0 equiv) and DMAP (0.1 equiv) in dichloromethane (15 mL) were added Et_3N (3 equiv) and acetic anhydride (1.3 equiv) under an argon atmosphere at an ambient temperature. The resulting reaction mixture was stirred for 1 h at an ambient temperature. Water (20 mL) was added to the reaction mixture. The organic layer was separated; the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined extracts were washed with water (2 × 20 mL) and brine (25 mL) and dried over Na_2SO_4. The solvent was filtered and evaporated under reduced pressure. The crude residue was purified using column chromatography on silica gel with hexane and ethyl acetate solvents as eluents.

Physical characterization data exactly match the reported values for the respective compounds **1a−h,k−q,s**,[3a] whereas data for **1i,j,r** are new.

*1-(3-(Methoxymethoxy)phenyl)prop-2-ynyl Acetate (**1i**).* Following the general procedures GP-1 and GP-2, the reaction of 3-(methoxymethoxy)benzaldehyde (**1′i**; 1.0 g, 6.02 mmol), (trimethylsilyl)acetylene (0.71 g, 7.22 mmol), and *n*-BuLi (4.6 mL, 1.6 M in THF, 7.22 mmol) followed by desilylation gave the crude product **1″i**. Acetylation of the −OH moiety of the crude **1″i** afforded 1-(3-(methoxymethoxy)phenyl)prop-2-ynyl acetate (**1i**; 775 mg) in overall 55% yield as a pale yellow liquid: R_f = 0.71 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 8.0 Hz, 1H), 7.21 (bt, J = 2.0 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.06 (ddd, J = 8.4, 2.4, 0.8 Hz, 1H), 6.42 (bd, J = 2.0 Hz, 1H), 5.20 (bs, 2H), 3.49 (s, 3H), 2.66 (bd, J = 2.0 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 157.3, 137.8, 129.7, 121.0, 116.6, 115.6, 94.3, 80.0, 75.4, 64.9, 55.9, 20.9; IR (neat) ν_{max} 3287, 2957, 2125, 1743, 1601, 1226, 696 cm^{-1}; MS (EI) m/z (%) 235 (M^+ + 1, 100), 220 (3). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.72; H, 6.15.

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*1-(3-Acetoxyphenyl)prop-2-ynyl Acetate (**1j**).* Following the general procedure GP-1 and GP-2, reaction of 3-((*tert*-butyldimethylsilyl)oxy)benzaldehyde (**1′j**; 1.0 g, 4.24 mmol), (trimethylsilyl)acetylene (498 mg, 5.07 mmol), and *n*-BuLi (3.2 mL, 1.6 M in THF, 5.08 mmol) gave the crude propargylic alcohol. Desilylation and acetylation of both −OH moieties afforded 1-(3-acetoxyphenyl)prop-2-ynyl acetate (**1j**; 462 mg) in 47% overall yield as a pale yellow oil: R_f = 0.11 (9/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.36 (m, 2H), 7.27 (s, 1H), 7.10 (bd, J = 2.8 Hz, 1H), 6.44 (s, 1H), 2.67 (bs, 1H), 2.28 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 169.1, 150.6, 137.8, 129.5, 124.9, 122.2, 120.8, 79.6, 75.6, 64.4, 20.9, 20.8; IR (neat) ν_{max} 3288, 2935, 1739, 1201, 1016, 800 cm^{-1}; MS (EI) m/z (%) 255 (M^+ + Na, 100), 232 (M^+, 4), 173 (8). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.35; H, 5.18.

*1-(4-(1,3-Dioxan-2-yl)phenyl)prop-2-ynyl Acetate (**1r**).* Following the general procedure GP-1 and GP-2, reaction of 4-(1,3-dioxan-2-yl)benzaldehyde (**1′r**; 1.0 g, 5.21 mmol), (trimethylsilyl)acetylene (0.61 g, 6.25 mmol), and *n*-BuLi (4.0 mL, 1.6 M in THF, 6.25 mmol) followed by desilylation gave the crude product **1″r**. Acetylation of the −OH moiety of the crude **1″r** afforded 1-(4-(1,3-dioxan-2-yl)phenyl)-prop-2-ynyl acetate (**1r**; 840 mg) in 62% overall yield as a colorless liquid: R_f = 0.69 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.49 (m, 4H), 6.45 (bd, J = 2.4 Hz, 1H), 5.51 (s, 1H), 4.27 (dd, J = 11.2, 5.2 Hz, 2H), 3.99 (td, J = 12.0, 2.4 Hz, 2H), 2.64 (bd, J = 2.0 Hz, 1H), 2.30−2.15 (m, 1H), 2.09 (s, 3H), 1.46 (dd, J = 13.6, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 139.5, 136.8, 127.5, 126.3, 100.9, 80.0, 75.4, 67.2, 64.9, 25.6, 20.9; IR (neat) ν_{max} 3287, 2966, 1741, 1377, 1016, 642 cm^{-1}; MS (EI) m/z (%) 261 (M^+ + 1, 100), 247 (5), 245 (5). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.06; H, 6.27.

Silver(I)-Catalyzed Reaction between Pyrazole (2) and Propargyl Acetates 1: General Procedure GP-3. Propargyl acetate **1** (1.0 mmol), pyrazole (5.0 mmol), and $AgNO_3$ (16.9 mg, 0.1 mmol) were placed in an oven-dried Schlenk flask under an argon atmosphere. Chlorobenzene (1.0 mL) was added to this mixture. The resulting solution was stirred at 80 °C for 24 h. Upon complete consumption of **1**, the crude reaction mixture was purified using column chromatography on silica gel with hexane and ethyl acetate solvents as eluents.

*(E)-1,1′-(3-Phenylprop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4a**):* colorless solid (135 mg, 54% yield); mp 94−95 °C; R_f = 0.30 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (bd, J = 2.4 Hz, 2H), 7.63 (bd, J = 1.6 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H), 7.36−7.27 (m, 3H), 7.23 (d, J = 6.4 Hz, 1H), 6.95 (dd, J = 15.6, 6.0 Hz, 1H), 6.60 (d, J = 16.0 Hz, 1H), 6.33 (bt, J = 1.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 135.5, 134.9, 128.6, 128.5, 128.4, 126.9, 122.4, 106.5, 76.0; IR (KBr) ν_{max} 3109, 1392, 1296, 970, 754, 628 cm^{-1}; MS (EI) m/z (%) 249 (M^+−1, 100), 229 (54), 211 (35), 171 (35), 134 (19), 113 (27). Anal. Calcd for $C_{15}H_{14}N_4$: C, 71.98; H, 5.64; N, 22.38. Found: C, 72.05; H, 5.71; N, 22.31.

*1-Phenyl-2-(1H-pyrazol-1-yl)allyl acetate (**3a**):* pale yellow oil (61 mg, 25% yield); R_f = 0.53 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 5.6, 2.4 Hz, 2H), 7.44 (dd, J = 8.0, 1.6 Hz, 2H), 7.37−7.29 (m, 3H), 7.12 (s, 1H), 6.27 (t, J = 2.0 Hz, 1H), 5.58 (bd, J = 0.8 Hz, 1H), 5.11 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 144.0, 140.5, 136.8, 128.5, 127.8, 127.2, 106.8, 103.3, 73.1, 21.0; IR (neat) ν_{max} 3474, 2932, 1745, 1226, 949, 752 cm^{-1}; MS (EI) m/z (%) 243 (M^+ + 1, 100), 159 (3), 137 (3), 81 (3). Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.75; H, 6.12; N, 11.15.

*(E)-1,1′-(3-Phenylprop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5a**):* yellow oil (23 mg, 9% yield); R_f = 0.23 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 4.8, 1.6 Hz, 2H), 7.56 (d, J = 2.4 Hz, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.41−7.27 (m, 5H), 6.85 (dd, J = 14.0, 0.8 Hz, 1H), 6.69 (dd, J = 14.0, 7.2 Hz, 1H), 6.36 (t, J = 2.0 Hz, 1H), 6.33 (t, J = 2.0 Hz, 1H), 6.22 (d, J = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 139.7, 138.8, 130.5, 128.9, 128.5, 128.34, 128.31, 127.3, 114.9, 107.4, 105.8, 65.1; IR (neat) ν_{max} 3433, 3113, 2924, 1680, 1394, 1091, 750 cm^{-1}; MS (EI) m/z (%) 249 (M^+ − 1, 100), 237 (14), 209 (4). Anal. Calcd for $C_{15}H_{14}N_4$: C, 71.98; H, 5.64; N, 22.38. Found: C, 71.86; H, 5.61; N, 22.45.

*(E)-1,1′-(3-(4-Fluorophenyl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4b**):* pale yellow solid (145 mg, 54% yield); mp 60−61 °C; R_f = 0.44 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (bd, J = 2.0 Hz, 2H), 7.59 (bd, J = 1.6 Hz, 2H), 7.34 (dd, J = 8.8, 5.6 Hz, 2H), 7.18 (d, J = 6.0, 1H), 6.97 (t, J = 8.8 Hz, 2H), 6.84 (dd, J = 16.0, 6.4 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 6.29 (t, J = 2.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, J = 250 Hz), 140.3, 134.2, 131.0, 128.6, 128.5, 122.2, 115.4 (d, J = 21.7 Hz), 106.5, 75.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.26 to −112.34 (m); IR (KBr) ν_{max} 3115, 2924, 1678, 1510, 1394, 1226, 752 cm^{-1}; MS (EI) m/z (%) 269 (M^+ + 1, 100), 186 (11), 137 (19), 91 (4). Anal. Calcd for $C_{15}H_{13}FN_4$: C, 67.15; H, 4.88; N, 20.88. Found: C, 67.22; H, 4.81; N, 20.75.

*1-(4-Fluorophenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3b**):* pale yellow semisolid (52 mg, 20% yield); R_f = 0.66 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 2.4 Hz, 1H), 7.56 (bd, J = 1.2 Hz, 1H), 7.46−7.37 (m, 2H), 7.09 (s, 1H), 7.00 (t, J = 8.8 Hz, 2H), 6.26 (bt, J = 2.0 Hz, 1H), 5.52 (s, 1H), 5.11 (s, 1H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 162.7 (d, J = 248 Hz), 144.2, 140.7, 132.9, 129.3 (d, J = 8.4 Hz), 127.8, 115.5 (d, J = 21.6 Hz) 107.0, 102.9, 72.4, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −113.07 to −113.14 (m); IR (neat) ν_{max} 3128, 1747, 1510, 1224, 752 cm^{-1}; MS (EI) m/z (%) 261 (M^+ + 1, 100), 233 (54), 219 (14), 201 (16), 113 (9). Anal. Calcd for $C_{14}H_{13}FN_2O_2$: C, 64.61; H, 5.03; N, 10.76. Found: C, 64.48; H, 5.10; N, 10.85.

*(E)-1,1′-(3-(4-Fluorophenyl)prop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5b**):* yellow oil (21 mg, 8% yield); R_f = 0.31 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (bd, J = 2.0 Hz, 1H), 7.61 (bd, J = 2.0 Hz, 1H), 7.56 (d, J = 2.4 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H), 7.26−7.17 (m, 2H), 7.10−7.03 (m, 2H), 6.82 (dd, J = 14.0, 0.8 Hz, 1H), 6.66 (dd, J = 14.0, 6.8 Hz, 1H), 6.37 (t, J = 2.0 Hz, 1H), 6.33 (t, J = 2.4 Hz, 1H), 6.19 (d, J = 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, J = 248 Hz), 141.5, 139.9, 134.7 (d, J = 3.2 Hz), 130.6, 129.1 (d, J = 8.5 Hz), 128.4 (2c), 115.8 (d, J = 21.9 Hz), 114.7, 107.5, 106.0, 64.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −113.53 to −113.60 (m); IR (neat) ν_{max} 2924, 1678, 1510, 1394, 1226, 752 cm^{-1}; MS (EI) m/z (%) 269 (M^+ + 1, 19), 201 (100), 113 (14). Anal. Calcd for $C_{15}H_{13}FN_4$: C, 67.15; H, 4.88; N, 20.88. Found: C, 67.06; H, 4.91; N, 20.95.

*(E)-1,1′-(3-(4-Chlorophenyl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4c**):* pale yellow solid (153 mg, 54% yield); mp 111−112 °C; R_f = 0.44 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (bd, J = 2.4 Hz, 2H), 7.59 (bd, J = 2.0 Hz, 2H), 7.28 (q, J = 8.4 Hz, 4H), 7.18 (dd, J = 6.0, 0.8 Hz, 1H), 6.89 (dd, J = 16.0, 6.0 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 6.30 (bt, J = 2.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 134.3, 134.1, 133.4, 128.7, 128.5, 128.1, 123.2, 106.6, 75.9; IR (KBr) ν_{max} 3099, 1390, 1089, 750 cm^{-1}; MS (EI) m/z (%) 286 (M^+ + 1, 100), 230 (21), 208 (4), 190 (6). Anal. Calcd for $C_{15}H_{13}ClN_4$: C, 63.27; H, 4.60; N, 19.68. Found: C, 63.41; H, 4.53; N, 19.58.

*1-(4-Chlorophenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3c**):* yellow oil (52 mg, 19% yield); R_f = 0.66 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 2.4 Hz, 1H), 7.57 (d, J = 1.6 Hz, 1H), 7.37 (dt, J = 8.8, 2.0 Hz, 2H), 7.29 (dt, J = 8.4, 2.0 Hz, 2H), 7.08 (s, 1H), 6.27 (bt, J = 2.4 Hz, 1H), 5.51 (bd, J = 1.2 Hz, 1H), 5.11 (s, 1H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 143.9, 140.6, 135.5, 134.4, 128.8, 128.7, 127.7, 107.0, 102.9, 72.4, 20.9; IR (neat) ν_{max} 3128, 2928, 1745, 1651, 1228, 752 cm^{-1}; MS (EI) m/z (%) 277 (M^+, 94), 249 (49), 217 (100), 183 (29), 149 (6). Anal. Calcd for $C_{14}H_{13}ClN_2O_2$: C, 60.77; H, 4.74; N, 10.12. Found: C, 60.61; H, 4.71; N, 10.18.

*(E)-1,1′-(3-(4-Chlorophenyl)prop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5c**):* yellow oil (17 mg, 6% yield); R_f = 0.31 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 1.6 Hz, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H), 7.34 (dt, J = 8.4, 2.0 Hz, 2H), 7.17 (dt, J = 8.4, 1.6 Hz, 2H), 6.83 (d, J = 14.4 Hz, 1H), 6.64 (dd, J = 14.0, 7.2 Hz, 1H), 6.36 (t, J = 2.0 Hz, 1H), 6.32 (t, J = 2.4 Hz, 1H), 6.17 (d, J = 6.8 Hz, 1H); ^{13}C

NMR (101 MHz, $CDCl_3$) δ 141.5, 140.6, 140.0, 137.4, 134.3, 130.8, 129.1, 128.6, 128.5, 114.4, 107.5, 106.0, 64.5; IR (neat) ν_{max} 3113, 2924, 1678, 1394, 1091, 752 cm^{-1}; MS (EI) m/z (%) 286 (M^+ + 1, 20), 285 (M^+, 40), 233 (40), 217 (100), 181 (40), 149 (35). Anal. Calcd for $C_{15}H_{13}ClN_4$: C, 63.27; H, 4.60; N, 19.68. Found: C, 63.35; H, 4.65; N, 19.55.

*(E)-1,1′-(3-p-Tolylprop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4d**):* pale yellow solid (127 mg, 48% yield); mp 79−80 °C; R_f = 0.44 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (bd, J = 2.4 Hz, 2H), 7.61 (bd, J = 2.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.19 (dd, J = 6.0, 1.2 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 6.88 (dd, J = 16.0, 6.4 Hz, 1H), 6.58 (d, J = 16.4 Hz, 1H), 6.31 (bt, J = 2.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 138.7, 135.6, 132.2, 129.3, 128.5, 126.9, 121.4, 106.5, 76.2, 21.1; IR (KBr) ν_{max} 2916, 1512, 1388, 972, 758 cm^{-1}; MS (EI) m/z (%) 265 (M^+ + 1, 100), 251 (11). Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.58; H, 6.15; N, 21.07.

*2-(1H-Pyrazol-1-yl)-1-p-tolylallyl acetate (**3d**):* pale yellow solid (56 mg, 22% yield); mp 60−61 °C; R_f = 0.62 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.56 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.04 (s, 1H), 6.26 (bt, J = 2.4 Hz, 1H), 5.58 (s, 1H), 5.10 (s, 1H), 2.32 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 144.1, 140.5, 138.4, 133.8, 129.2, 127.8, 127.3, 106.8, 103.1, 73.0, 21.1, 21.0; IR (KBr) ν_{max} 3026, 2924, 1745, 1228, 1028, 752 cm^{-1}; MS (EI) m/z (%) 257 (M^+ + 1, 100), 239 (8), 157 (16), 133 (16), 85 (8). Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.38; H, 6.21; N, 10.85.

*(E)-1,1′-(3-p-Tolylprop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5d**):* yellow oil (37 mg, 14% yield); R_f = 0.29 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (bd, J = 6.4 Hz, 2H), 7.53 (bd, J = 2.0 Hz, 1H), 7.45 (bd, J = 2.0 Hz, 1H), 7.16 (bd, J = 2.0 Hz, 4H), 6.82 (d, J = 14.0 Hz, 1H), 6.66 (dd, J = 14.0, 6.8 Hz, 1H), 6.32 (d, J = 17.2 Hz, 2H), 6.16 (d, J = 6.8 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 139.6, 138.1, 135.7, 130.3, 129.5, 128.4, 128.2, 127.2, 115.1, 107.3, 105.7, 64.8, 21.0; IR (neat) ν_{max} 3111, 2922, 1678, 1514, 1089, 754 cm^{-1}; MS (EI) m/z (%) 265 (M^+ + 1, 100), 197 (3), 147 (3). Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.85; H, 6.03; N, 21.28.

*(E)-1,1′-(3-(3-Methoxyphenyl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4e**):* pale yellow solid (157 mg, 56% yield); mp 97−98 °C; R_f = 0.24 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (bd, J = 2.4 Hz, 2H), 7.61 (bd, J = 1.6 Hz, 2H), 7.29−7.19 (m, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.99−6.90 (m, 2H), 6.85 (dd, J = 8.4, 2.0 Hz, 1H), 6.58 (d, J = 16.0 Hz, 1H), 6.32 (bt, J = 2.4 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 140.4, 136.3, 135.5, 129.5, 128.6, 122.7, 119.6, 114.5, 112.0, 106.5, 76.0, 55.1; IR (KBr) ν_{max} 3111, 2957, 1599, 1390, 1043, 754 cm^{-1}; MS (EI) m/z (%) 281 (M^+ + 1, 100), 265 (14), 163 (4), 137 (14). Anal. Calcd for $C_{16}H_{16}N_4O$: C, 68.55; H, 5.75; N, 19.99. Found: C, 68.47; H, 5.82; N, 19.85.

*1-(3-Methoxyphenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3e**):* colorless oil (65 mg, 24% yield); R_f = 0.43 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62−7.58 (m, 2H), 7.25 (t, J = 8.0 Hz, 1H), 7.08 (s, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.97 (bt, J = 2.0 Hz, 1H), 6.84 (ddd, J = 8.0, 2.4, 0.8 Hz, 1H), 6.27 (t, J = 2.0 Hz, 1H), 5.57 (d, J = 0.8 Hz, 1H), 5.11 (s, 1H), 3.78 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 159.6, 144.0, 140.5, 138.4, 129.5, 127.8, 119.4, 113.8, 112.9, 106.8, 103.4, 72.9, 55.1, 21.0; IR (neat) ν_{max} 3130, 2939, 1747, 1602, 1228, 1030, 754 cm^{-1}; MS (EI) m/z (%) 273 (M^+ + 1, 82), 245 (36), 229 (54), 213 (100), 145 (7), 102 (5). Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29. Found: C, 66.32; H, 5.86; N, 10.15.

*(E)-1,1′-(3-(3-Methoxyphenyl)prop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5e**):* yellow oil (17 mg, 6% yield); R_f = 0.14 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (bd, J = 1.2 Hz, 1H), 7.62 (bd, J = 1.6 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.51 (d, J = 2.0 Hz, 1H), 7.32−7.27 (m, 1H), 6.89−6.84 (m, 3H), 6.78 (bt, J = 1.6 Hz, 1H), 6.67 (dd, J = 11.2, 5.6 Hz, 1H), 6.37 (t, J = 1.6 Hz, 1H), 6.33 (t, J = 1.6 Hz, 1H), 6.18 (d, J = 5.6 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 141.3, 140.4, 139.7, 130.7, 129.9, 128.5, 128.3, 119.6, 114.8, 113.7, 113.2, 107.4, 105.9, 65.1, 55.3; IR (neat) ν_{max} 3117, 2932, 1678, 1601, 1261, 1043, 754 cm^{-1}; MS (EI) m/z (%) 281 (M^+ + 1, 100), 249 (8), 171 (4). Anal. Calcd for $C_{16}H_{16}N_4O$: C, 68.55; H, 5.75; N, 19.99. Found: C, 68.41; H, 5.71; N, 19.85.

*(E)-1,1′-(3-(3-Phenoxyphenyl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4f**):* pale yellow solid (215 mg, 63% yield); mp 75−76 °C; R_f = 0.35 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (bd, J = 2.8 Hz, 2H), 7.61 (bd, J = 1.2 Hz, 2H), 7.38−7.25 (m, 3H), 7.19 (dd, J = 12.8, 6.0 Hz, 2H), 7.14−7.08 (m, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 7.2 Hz, 1H), 6.91 (dd, J = 16.0, 6.0 Hz, 1H), 6.54 (d, J = 16.0 Hz, 1H), 6.31 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 156.8, 140.4, 136.8, 134.8, 129.8, 129.6, 128.5, 123.3, 123.2, 121.9, 119.1, 118.6, 117.2, 106.6, 75.9; IR (KBr) ν_{max} 3109, 1577, 1388, 1271, 750 cm^{-1}; MS (EI) m/z (%) 343 (M^+ + 1, 3), 275 (38), 243 (100), 242 (27), 207 (14), 130 (8). Anal. Calcd for $C_{21}H_{18}N_4O$: C, 73.67; H, 5.30; N, 16.36. Found: C, 73.57; H, 5.36; N, 16.25.

*1-(3-Phenoxyphenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3f**):* pale yellow oil (63 mg, 19% yield); R_f = 0.56 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 2.0 Hz, 1H), 7.60 (bd, J = 0.8 Hz, 1H), 7.38−7.33 (m, 2H), 7.30 (t, J = 6.4 Hz, 1H), 7.18 (d, J = 6.4 Hz, 1H), 7.15−7.09 (m, 3H), 6.98 (bt, J = 0.8 Hz, 1H), 6.97 (bt, J = 0.8 Hz, 1H), 6.96−6.92 (m, 1H), 6.30 (t, J = 1.6 Hz, 1H), 5.55 (bd, J = 0.8 Hz, 1H), 5.11 (s, 1H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 157.4, 156.9, 144.1, 140.6, 139.0, 129.9, 129.8, 127.9, 123.4, 122.1, 118.9, 118.7, 117.7, 106.9, 103.5, 72.8, 21.0; IR (neat) ν_{max} 3065, 2930, 1747, 1585, 1234, 1024, 754 cm^{-1}; MS (EI) m/z (%) 336 (M^+ + 2, 51), 335 (M^+ + 1, 100), 263 (11). Anal. Calcd for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38. Found: C, 71.68; H, 5.52; N, 8.31.

*(E)-1,1′-(3-(3-Phenoxyphenyl)prop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5f**):* yellow oil (21 mg, 6% yield); R_f = 0.20 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (bs, 1H), 7.60 (bd, J = 1.6 Hz, 1H), 7.56 (bd, J = 2.4 Hz, 1H), 7.51 (bd, J = 2.4 Hz, 1H), 7.37−7.28 (m, 3H), 7.11 (td, J = 7.6, 1.6 Hz, 1H), 7.01−6.86 (m, 6H), 6.64 (dd, J = 14.0, 7.2 Hz, 1H), 6.36 (bt, J = 2.4 Hz, 1H), 6.32 (bt, J = 2.4 Hz, 1H), 6.17 (d, J = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 156.7, 141.4, 141.0, 139.8, 130.8, 130.2, 129.8, 128.5, 128.3, 123.6, 121.8, 119.1, 118.2, 117.7, 114.5, 107.5, 105.9, 64.9; IR (neat) ν_{max} 2922, 1678, 1583, 1487, 1248, 752 cm^{-1}; MS (EI) m/z (%) 343 (M^+ + 1, 100), 209 (6), 135 (3). Anal. Calcd for $C_{21}H_{18}N_4O$: C, 73.67; H, 5.30; N, 16.36. Found: C, 73.56; H, 5.38; N, 16.21.

*(E)-3-(3,3-Bis(1H-pyrazol-1-yl)prop-1-enyl)phenol (**4g**):* light brown solid (122 mg, 46% yield); mp 100−101 °C; R_f = 0.34 (2/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (bd, J = 2.0 Hz, 2H), 7.61 (bd, J = 1.2 Hz, 2H), 7.12 (dd, J = 5.2, 0.8 Hz, 1H), 7.09 (d, J = 6.4 Hz, 1H), 6.86 (d, J = 6.4 Hz, 1H), 6.83−6.79 (m, 1H), 6.78 (d, J = 4.8 Hz, 1H), 6.77−6.73 (m, 1H), 6.43 (d, J = 12.8 Hz, 1H), 6.31 (t, J = 2.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 140.6, 136.4, 136.0, 129.8, 129.0, 122.2, 119.2, 116.3, 114.0, 106.8, 76.1; IR (KBr) ν_{max} 3142, 2729, 1595, 1392, 1089, 756 cm^{-1}; MS (EI) m/z (%) 268 (M^+ + 2, 100), 156 (14). Anal. Calcd for $C_{15}H_{14}N_4O$: C, 67.65; H, 5.30; N, 21.04. Found: C, 67.49; H, 5.26; N, 21.15.

*1-(3-Hydroxyphenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3g**):* brown oil (59 mg, 23% yield); R_f = 0.53 (2/1 hexane/EtOAc) [silica, UV and I_2]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (bd, J = 2.0 Hz, 1H), 7.58 (bd, J = 1.2 Hz, 1H), 7.18 (t, J = 6.0 Hz, 1H), 6.98 (s, 1H), 6.95 (d, J = 6.4 Hz, 1H), 6.88 (bt, J = 1.6 Hz, 1H), 6.79−6.74 (m, 1H), 6.27 (t, J = 1.6 Hz, 1H), 5.57 (bd, J = 0.8 Hz, 1H), 5.12 (s, 1H), 2.12 (s, 3H), 1.90−1.70 (bs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 156.1, 143.7, 140.6, 138.3, 129.8, 128.2, 119.2, 115.8, 114.3, 106.9, 104.4, 73.0, 21.0; IR (neat) ν_{max} 3333, 2926, 1747, 1593, 1228, 760 cm^{-1}; MS (EI) m/z (%) 260 (M^+ + 2, 100), 163 (6). Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 65.21; H, 5.41; N, 10.76.

(E)-3-(1,3-Bis(1H-pyrazol-1-yl)allyl)phenol (**5g**): brown oil (37 mg, 14% yield); R_f = 0.22 (2/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35−8.35 (bs, 1H), 7.61 (bd, J = 1.6 Hz, 1H), 7.54 (bd, J = 1.6 Hz, 1H), 7.51 (bd, J = 2.4 Hz, 1H), 7.49 (bd, J = 2.4 Hz, 1H), 7.09 (t, J = 8.0 Hz, 1H), 6.79 (d, J = 14.0 Hz, 1H), 6.66 (t, J = 8.0 Hz, 2H), 6.57 (dd, J = 14.0, 7.2 Hz, 1H), 6.48 (s, 1H), 6.34 (bt, J = 2.0 Hz, 1H), 6.28 (bt, J = 2.0 Hz, 1H), 6.07 (d, J = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 141.3, 139.8, 139.5, 130.8, 129.9, 129.0, 128.7, 118.4, 115.8, 114.6, 114.1, 107.5, 105.9, 64.8; IR (neat) ν_{max} 3146, 2928, 1678, 1601, 1282, 945, 653 cm^{-1}; MS (EI) m/z (%) 268 (M^+ + 2, 30), 267 (M^+ + 1, 100), 235 (81). Anal. Calcd for $C_{15}H_{14}N_4O$: C, 67.65; H, 5.30; N, 21.04. Found: C, 67.48; H, 5.21; N, 21.15.

(E)-1,1′-(3-(3-(tert-Butyldimethylsilyloxy)phenyl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4h**): colorless solid (186 mg, 49% yield); mp 62−63 °C; R_f = 0.53 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (bd, J = 2.4 Hz, 2H), 7.60 (bd, J = 1.6 Hz, 2H), 7.19 (t, J = 7.6 Hz, 2H), 7.03 (d, J = 7.6 Hz, 1H), 6.94−6.86 (m, 2H), 6.79 (dd, J = 8.0, 2.4 Hz, 1H), 6.54 (d, J = 15.6 Hz, 1H), 6.31 (bd, J = 1.6 Hz, 2H), 1.00 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 140.4, 136.4, 135.4, 129.4, 128.5, 122.5, 120.3, 120.1, 118.6, 106.5, 76.0, 25.5, 18.0, −4.5; IR (KBr) ν_{max} 3109, 1595, 1280, 966, 621 cm^{-1}; MS (EI) m/z (%) 381 (M^+ + 1, 100), 203 (3), 106 (6). Anal. Calcd for $C_{21}H_{28}N_4OSi$: C, 66.28; H, 7.42; N, 14.72. Found: C, 66.42; H, 7.35; N, 14.61.

1-(3-(tert-Butyldimethylsilyloxy)phenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3h**): pale yellow oil (78 mg, 21% yield); R_f = 0.70 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, J = 2.4 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.06−6.99 (m, 2H), 6.88 (bt, J = 2.4 Hz, 1H), 6.77 (ddd, J = 8.4, 2.4, 0.8 Hz, 1H), 6.26 (t, J = 2.4 Hz, 1H), 5.56 (bd, J = 0.8 Hz, 1H), 5.07 (s, 1H), 2.14 (s, 3H), 0.96 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 155.7, 144.0, 140.6, 138.3, 129.5, 127.9, 120.3, 120.1, 119.0, 106.8, 103.5, 72.9, 25.6, 21.0, 18.2, −4.5; IR (neat) ν_{max} 2957, 1751, 1602, 1226, 750 cm^{-1}; MS (EI) m/z (%) 373 (M^+ + 1, 100), 235 (9), 203 (9), 171 (3). Anal. Calcd for $C_{20}H_{28}N_2O_3Si$: C, 64.48; H, 7.58; N, 7.52. Found: C, 64.32; H, 7.63; N, 7.45.

(E)-1,1′-(3-(3-(tert-Butyldimethylsilyloxy)phenyl)prop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5h**): yellow oil (38 mg, 10% yield); R_f = 0.38 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (bd, J = 1.6 Hz, 1H), 7.60 (bd, J = 1.6 Hz, 1H), 7.54 (d, J = 2.4 Hz, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 6.87−6.82 (m, 2H), 6.82−6.78 (m, 1H), 6.68−6.61 (m, 2H), 6.35 (t, J = 2.0 Hz, 1H), 6.31 (t, J = 2.0 Hz, 1H), 6.15 (d, J = 6.8 Hz, 1H), 0.95 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 141.3, 140.3, 139.7, 130.6, 129.8, 128.5, 128.3, 120.1, 119.9, 118.9, 114.7, 107.4, 105.8, 64.9, 25.6, 18.1, −4.5; IR (neat) ν_{max} 2929, 1676, 1485, 1278, 748 cm^{-1}; MS (EI) m/z (%) 381 (M^+ + 1, 100), 201 (9), 145 (9), 105 (9). Anal. Calcd for $C_{21}H_{28}N_4OSi$: C, 66.28; H, 7.42; N, 14.72. Found: C, 66.32; H, 7.51; N, 14.86.

(E)-1,1′-(3-(3-(Methoxymethoxy)phenyl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4i**): pale yallow solid (180 mg, 58% yield); mp 57−58 °C; R_f = 0.23 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 2.4 Hz, 2H), 7.60 (bd, J = 1.6 Hz, 2H), 7.25 (t, J = 8.0 Hz, 1H), 7.17 (dd, J = 6.4, 1.6 Hz, 1H), 7.10 (bt, J = 2.4 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.98 (ddd, J = 8.0, 2.4, 0.8 Hz, 1H), 6.91 (dd, J = 15.6, 6.0 Hz, 1H), 6.56 (dd, J = 16.0, 0.8 Hz, 1H), 6.32 (t, J = 2.0 Hz, 2H), 5.17 (s, 2H), 3.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 140.5, 136.5, 135.4, 129.6, 128.6, 123.0, 120.8, 116.7, 114.6, 106.6, 94.3, 76.1, 55.9; IR (KBr) ν_{max} 2955, 1745, 1585, 1018, 756 cm^{-1}; MS (EI) m/z (%) 311 (M^+ + 1, 100), 269 (6), 227 (3). Anal. Calcd for $C_{17}H_{18}N_4O_2$: C, 65.79; H, 5.85; N, 18.05. Found: C, 65.58; H, 5.76; N, 18.21.

1-(3-(Methoxymethoxy)phenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3i**): yellow oil (63 mg, 21% yield); R_f = 0.41 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (bd, J = 2.4 Hz, 1H), 7.58 (bd, J = 1.6 Hz, 1H), 7.28−7.20 (m, 1H), 7.08 (bt, J = 2.0 Hz, 1H), 7.07−7.03 (m, 2H), 6.98 (ddd, J = 8.4, 2.4, 1.2 Hz, 1H), 6.26 (t, J = 2.0 Hz, 1H), 5.56 (bd, J = 1.2 Hz, 1H), 5.13 (s, 2H), 5.09 (s, 1H), 3.45 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 157.3, 143.9, 140.5, 138.4, 129.5, 127.8, 120.7, 116.0, 115.3, 106.8, 103.6, 94.4, 72.8, 55.9, 21.0; IR (neat) ν_{max} 2925, 1747, 1588, 1221, 767 cm^{-1}; MS (EI) m/z (%) 303 (M^+ + 1, 100), 282 (11), 215 (8), 79 (24). Anal. Calcd for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.42; H, 6.15; N, 9.31.

Following the general procedure GP-3, 1-(3-acetoxyphenyl)prop-2-ynyl acetate (**1j**; 232 mg, 1.0 mmol), pyrazole (**2**; 340 mg, 5.0 mmol), and $AgNO_3$ (16.9 mg, 0.1 mmol) in chlorobenzene (1.0 mL) were heated at 80 °C for 24 h. Finally, the crude mixture was purified by silica gel column chromatography with hexane/ethyl acetate (2/1) as eluent to afford the acetyl deprotected compounds **3g** (52 mg) in 20% yield as a brown oil, **4g** (135 mg) in 51% yield as a light brown solid, and **5g** (29 mg) in 11% yield as a brown oil.

(E)-1,1′-(3-o-Tolylprop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4k**): colorless solid (100 mg, 38% yield); mp 73−74 °C; R_f = 0.33 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 2.4 Hz, 2H), 7.62 (bd, J = 1.6 Hz, 2H), 7.53 (dd, J = 6.8, 2.4 Hz, 1H), 7.25−7.09 (m, 4H), 6.83 (bd, J = 2.8 Hz, 2H), 6.33 (t, J = 2.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 135.9, 134.0, 133.4, 130.3, 128.5, 126.1, 125.9, 123.6, 106.5, 76.2, 19.5; IR (KBr) ν_{max} 3109, 2986, 1510, 1392, 754 cm^{-1}; MS (EI) m/z (%) 265 (M^+ + 1, 100), 251 (12). Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.59; H, 6.18; N, 21.32.

2-(1H-Pyrazol-1-yl)-1-o-tolylallyl acetate (**3k**): yellow oil (69 mg, 27% yield); R_f = 0.57 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 2.4 Hz, 1H), 7.59 (bd, J = 1.6 Hz, 1H), 7.42 (dd, J = 6.8, 2.0 Hz, 1H), 7.27 (s, 1H), 7.24−7.16 (m, 3H), 6.31 (t, J = 2.0 Hz, 1H), 5.54 (s, 1H), 4.90 (s, 1H), 2.43 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 144.0, 140.5, 136.6, 135.0, 130.5, 128.4, 127.4, 126.6, 126.0, 106.8, 104.1, 70.1, 20.8, 19.0; IR (neat) ν_{max} 3128, 3024, 1745, 1232, 756 cm^{-1}; MS (EI) m/z (%) 257 (M^+ + 1, 90), 229 (34), 215 (21), 197 (100), 182 (5). Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.18; H, 6.21; N, 10.85.

(E)-1,1′-(3-o-Tolylprop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5k**): yellow oil (27 mg, 10% yield); R_f = 0.27 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (bd, J = 1.6 Hz, 1H), 7.60 (bd, J = 1.6 Hz, 1H), 7.51 (d, J = 2.4 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H), 7.29−7.18 (m, 3H), 7.17−7.08 (m, 1H), 6.66−6.62 (m, 2H), 6.42 (d, J = 4.8 Hz, 1H), 6.34 (t, J = 2.4 Hz, 1H), 6.29 (t, J = 2.0 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 139.7, 136.5, 136.3, 130.9, 130.1, 128.6, 128.5, 128.4, 127.2, 126.5, 114.8, 107.3, 105.7, 61.9, 19.0; IR (neat) ν_{max} 3024, 2924, 1678,1394, 960, 752 cm^{-1}; MS (EI) m/z (%) 265 (M^+ + 1, 100), 243 (4), 219 (12), 163 (12), 145 (8). Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.85; H, 6.04; N, 21.13.

(E)-1,1′-(3-(2-Bromophenyl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4l**): pale yellow solid (165 mg, 50% yield); mp 74−75 °C; R_f = 0.33 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (bd, J = 2.4 Hz, 2H), 7.60 (bd, J = 1.6 Hz, 2H), 7.57 (dd, J = 8.0, 1.6 Hz, 1H), 7.51 (dd, J = 8.0, 1.2 Hz, 1H), 7.26 (d, J = 4.4 Hz, 1H), 7.23 (d, J = 6.0 Hz, 1H), 7.10 (td, J = 7.6, 1.6 Hz, 1H), 7.00−6.84 (m, 2H), 6.31 (t, J = 2.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 134.9, 134.2, 132.8, 129.8, 128.6, 127.4, 127.3, 125.3, 123.9, 106.6, 75.7; IR (KBr) ν_{max} 3022, 2968, 1514, 1087, 968, 754 cm^{-1}; MS (EI) m/z (%) 331 (M^+ + 2, 78), 330 (M^+ + 1, 100), 264 (11), 262 (11). Anal. Calcd for $C_{15}H_{13}BrN_4$: C, 54.73; H, 3.98; N, 17.02. Found: C, 54.85; H, 3.91; N, 17.15.

1-(2-Bromophenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3l**): pale yellow semisolid (64 mg, 20% yield); R_f = 0.45 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 2.4 Hz, 1H), 7.60 (bs, 1H), 7.58 (d, J = 1.2 Hz, 1H), 7.48 (dd, J = 6.8, 1.6 Hz, 1H), 7.35−7.29 (m, 2H), 7.21 (td, J = 6.8, 1.6 Hz, 1H), 6.33 (t, J = 2.0 Hz, 1H), 5.65 (bd, J = 1.2 Hz, 1H), 4.82 (bt, J = 1.2 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 142.8, 140.7, 136.1, 133.1, 130.1, 128.4, 127.6, 127.2, 123.9, 107.0, 104.6, 72.3, 20.7; IR (neat) ν_{max} 3063, 2928, 1747, 1224, 756 cm^{-1}; MS (EI) m/z (%) 323 (M^+ + 2, 28), 321 (M^+, 28), 208 (17), 151 (100), 108 (34), 76 (38). Anal. Calcd for $C_{14}H_{13}BrN_2O_2$: C, 52.36; H, 4.08; N, 8.72. Found: C, 52.25; H, 4.12; N, 8.65.

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*(E)-1,1′-(3-(2,4-Dichlorophenyl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4m**):* colorless solid (210 mg, 66% yield); mp =107−108 °C; R_f = 0.54 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 2.4 Hz, 2H), 7.60 (bd, J = 1.6 Hz, 2H), 7.50 (dd, J = 8.4, 2.8 Hz, 1H), 7.33 (bt, J = 2.4 Hz, 1H), 7.22 (d, J = 3.2 Hz, 1H), 7.18 (dt, J = 8.4, 2.4 Hz, 1H), 6.94−6.91 (m, 2H), 6.31 (bt, J = 2.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 134.7, 134.0, 131.8, 130.5, 129.4, 128.6, 127.9, 127.2, 125.8, 106.7, 75.8; IR (KBr) ν_{max} 3109, 2962, 1585, 1388, 754 cm^{-1}; MS (EI) m/z (%) 320 (M^+ + 1, 8), 290 (13), 251 (100), 215 (21), 183 (11), 102 (8). Anal. Calcd for $C_{15}H_{12}Cl_2N_4$: C, 56.44; H, 3.79; N, 17.55. Found: C, 56.32; H, 3.83; N, 17.41.

*1-(2,4-Dichlorophenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3m**):* pale yellow solid (47 mg, 15% yield); mp 57−58 °C; R_f = 0.57 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 2.4 Hz, 1H), 7.58 (bd, J = 1.6 Hz, 1H), 7.41 (d, J = 11.2 Hz, 1H), 7.42 (s, 1H), 7.34 (s, 1H), 7.25 (dd, J = 8.4, 2.0 Hz, 1H), 6.32 (bt, J = 2.0 Hz, 1H), 5.60 (bd, J = 1.6 Hz, 1H), 4.88 (bt, J = 1.2 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 142.6, 140.8, 135.1, 134.6, 133.3, 129.7, 129.3, 127.34, 127.28, 107.2, 104.2, 69.6, 20.7; IR (KBr) ν_{max} 3128, 2932, 1751, 1222, 1026, 754 cm^{-1}; MS (EI) m/z (%) 313 (M^+ + 2, 67), 311 (M^+, 100), 289 (41), 253 (41), 251 (61), 216 (14), 102 (14). Anal. Calcd for $C_{14}H_{12}Cl_2N_2O_2$: C, 54.04; H, 3.89; N, 9.00. Found: C, 54.15; H, 3.81; N, 8.86.

*(E)-1,1′-(3-(2,6-Dichlorophenyl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4n**):* colorless solid (162 mg, 51% yield); mp 105−106 °C; R_f = 0.64 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.60 (s, 2H), 7.33−7.25 (m, 3H), 7.10 (t, J = 7.6 Hz, 1H), 6.96 (dd, J = 16.4, 4.4 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H), 6.32 (bd, J = 1.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 134.4, 132.5, 131.2, 129.4, 129.0, 128.8, 128.4, 106.6, 75.8; IR (KBr) ν_{max} 3109, 2962, 1582, 1388, 1041, 754 cm^{-1}; MS (EI) m/z (%) 320 (M^+ + 1, 37), 319 (M^+, 100), 146 (4), 110 (4). Anal. Calcd for $C_{15}H_{12}Cl_2N_4$: C, 56.44; H, 3.79; N, 17.55. Found: C, 56.51; H, 3.72; N, 17.41.

*1-(2,6-Dichlorophenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3n**):* colorless solid (37 mg, 12% yield); mp 86−87 °C; R_f = 0.57 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (bdd, J = 8.4, 1.6 Hz, 1H), 7.65 (bs, 1H), 7.60 (bd, J = 2.0 Hz, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 9.6 Hz, 1H), 6.34 (bt, J = 2.0 Hz, 1H), 5.74 (t, J = 8.8 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 141.6, 135.4, 134.7, 130.5, 129.5, 129.2, 128.0, 113.3, 106.9, 68.8, 20.9; IR (KBr) ν_{max} 2924, 1730, 1244, 761 cm^{-1}; MS (EI) m/z (%) 313 (M^+ + 2, 20), 311 (M^+, 35), 289 (17), 251 (100), 203 (100), 183 (41), 130 (17), 102 (100). Anal. Calcd for $C_{14}H_{12}Cl_2N_2O_2$: C, 54.04; H, 3.89; N, 9.00. Found: C, 53.95; H, 3.94; N, 9.12.

*(E)-1,1′-(3-(Naphthalen-1-yl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4o**):* colorless solid (144 mg, 48% yield); mp 85−86 °C; R_f = 0.38 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.94 (m, 1H), 7.89−7.81 (m, 2H), 7.75 (bd, J = 2.4 Hz, 2H), 7.72−7.65 (m, 3H), 7.54−7.44 (m, 3H), 7.35 (dd, J = 10.4, 4.4 Hz, 2H), 6.97 (dd, J = 16.0, 5.6 Hz, 1H), 6.37 (bt, J = 2.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 133.4, 132.9, 132.6, 130.9, 129.0, 128.6, 128.5, 126.3, 125.9, 125.6, 125.4, 124.4, 123.3, 106.7, 76.1; IR (KBr) ν_{max} 3117, 3057, 1512, 1390, 966, 754 cm^{-1}; MS (EI) m/z (%) 301 (M^+ + 1, 100), 287 (6), 255 (4). Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65. Found: C, 75.86; H, 5.31; N, 18.56.

*1-(Naphthalen-1-yl)-2-(1H-pyrazol-1-yl)allyl acetate (**3o**):* colorless solid (67 mg, 23% yield); mp 92−93 °C; R_f = 0.56 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 1H), 7.93 (s, 1H), 7.87 (dd, J = 11.6, 8.4 Hz, 2H), 7.71−7.64 (m, 2H), 7.62 (bd, J = 1.6 Hz, 1H), 7.59−7.49 (m, 2H), 6.47 (t, J = 7.6 Hz,. 1H), 6.31 (bt, J = 1.6 Hz,. 1H), 5.62 (bd, J = 1.2 Hz, 1H), 4.95 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 143.9, 140.7, 133.7, 132.4, 130.9, 129.4, 128.7, 127.4, 126.7, 125.9, 125.1, 123.4, 107.0, 104.6, 70.0, 20.9; IR (KBr) ν_{max} 3065, 2930, 1736, 1224, 773 cm^{-1}; MS (EI) m/z (%) 293 (M^+ + 1, 100). Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 74.05; H, 5.48; N, 9.51.

*(E)-1,1′-(3-(Naphthalen-1-yl)prop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5o**):* pale yellow solid (48 mg, 16% yield); mp 95−96 °C; R_f = 0.29 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.93 (m, 1H), 7.92−7.83 (m, 2H), 7.63 (d, J = 12.8 Hz, 2H), 7.53−7.41 (m, 5H), 7.33 (bd, J = 2.0 Hz, 1H), 7.02 (d, J = 5.6 Hz, 1H), 6.82 (dd, J = 14.0, 6.0 Hz, 1H), 6.63 (d, J = 14.0 Hz, 1H), 6.32 (bt, J = 2.0 Hz, 1H), 6.26 (bt, J = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 139.7, 133.9, 133.8, 130.9, 130.2, 129.5, 128.84, 128.77, 128.5, 126.9, 126.0, 125.7, 125.2, 122.9, 115.0, 107.2, 105.9, 61.7; IR (KBr) ν_{max} 3051, 2924, 1678, 1394, 958, 754 cm^{-1}; MS (EI) m/z (%) 301 (M^+ + 1, 100), 282 (11). Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65. Found: C, 75.85; H, 5.32; N, 18.71.

*(E)-1,1′-(3-(Thiophen-2-yl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4p**):* brown solid (141 mg, 55% yield); mp 63−64 °C; R_f = 0.35 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (bd, J = 2.4 Hz, 2H), 7.59 (bd, J = 1.6 Hz, 2H), 7.18 (dd, J = 11.2, 4.8 Hz, 2H), 6.99 (d, J = 3.6 Hz, 1H), 6.93 (t, J = 4.4 Hz, 1H), 6.69 (d, J = 5.2 Hz, 1H), 6.67 (s, 1H), 6.29 (bt, J = 2.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 139.6, 128.5, 128.4, 127.7, 127.3, 125.8, 121.4, 106.5, 75.6; IR (KBr) ν_{max} 3107, 1649, 1514, 1390, 1087, 960, 754 cm^{-1}; MS (EI) m/z (%) 257 (M^+ + 1, 100), 243 (3), 211 (30), 167 (16), 97 (6). Anal. Calcd for $C_{13}H_{12}N_4S$: C, 60.91; H, 4.72; N, 21.86. Found: C, 60.75; H, 4.81; N, 21.75.

*2-(1H-Pyrazol-1-yl)-1-(thiophen-2-yl)allyl acetate (**3p**):* brown oil (30 mg, 12% yield); R_f = 0.56 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (bd, J = 2.0 Hz, 1H), 7.61 (s, 1H), 7.34 (s, 1H), 7.27 (bd, J = 3.2 Hz, 1H), 7.09 (bd, J = 3.2 Hz, 1H), 6.93 (t, J = 4.0 Hz, 1H), 6.31 (bs, 1H), 5.57 (s, 1H), 5.27 (s, 1H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 143.8, 140.7, 139.9, 128.0, 127.3, 126.8, 126.3, 107.0, 102.9, 68.8, 21.0; IR (neat) ν_{max} 2926, 1747, 1653, 1224, 1024, 754 cm^{-1}; MS (EI) m/z (%) 247 (M^+−1, 100), 244 (54), 220 (30), 186 (6), 136 (3). Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87; N, 11.28. Found: C, 58.12; H, 4.81; N, 11.35.

*(E)-1,1′-(3-(Thiophen-2-yl)prop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5p**):* brown oil (18 mg, 7% yield); R_f = 0.20 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (bd, J = 1.6 Hz, 1H), 7.60 (bd, J = 1.6 Hz, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.32 (dd, J = 5.2, 1.2 Hz, 1H), 7.06 (bd, J = 3.6 Hz, 1H), 7.01 (dd, J = 5.2, 3.6 Hz, 1H), 6.92 (d, J = 13.6 Hz, 1H), 6.67 (dd, J = 14.0, 6.8 Hz, 1H), 6.43 (d, J = 7.2 Hz, 1H), 6.36 (bt, J = 2.0 Hz, 1H), 6.31 (bt, J = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 141.5, 139.8, 130.3, 128.5, 128.1, 127.0, 126.5, 126.3, 114.7, 107.5, 106.1, 60.7; IR (neat) ν_{max} 3107, 2924, 1678, 1520, 1394, 1089, 752 cm^{-1}; MS (EI) m/z (%) 257 (M^+ + 1, 100), 239 (6), 215 (6), 181 (9), 157 (12), 133 (12). Anal. Calcd for $C_{13}H_{12}N_4S$: C, 60.91; H, 4.72; N, 21.86. Found: C, 61.06; H, 4.68; N, 21.95.

*(E)-4-(3,3-Bis(1H-pyrazol-1-yl)prop-1-enyl)benzaldehyde (**4q**):* pale yellow solid (150 mg, 54% yield); mp 104−105 °C; R_f = 0.29 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 2.4 Hz, 2H), 7.61 (bd, J = 1.6 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.21 (dd, J = 5.6, 1.2 Hz, 1H), 7.06 (dd, J = 16.0, 6.0 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.34 (bd, J = 2.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 140.7, 140.5, 136.0, 134.0, 129.9, 128.6, 127.4, 126.1, 106.8, 75.7; IR (KBr) ν_{max} 2926, 1691, 1390, 1209, 1089, 765, 625 cm^{-1}; MS (EI) m/z (%) 279 (M^+ + 1, 100), 233 (3), 212 (5). Anal. Calcd for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found: C, 69.18; H, 5.15; N, 20.06.

*1-(4-Formylphenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3q**):* pale yellow oil (51 mg, 19% yield); R_f = 0.61 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.63−7.55 (m, 4H), 7.17 (s, 1H), 6.26 (bt, J = 2.0 Hz, 1H), 5.51 (bd, J = 1.2 Hz, 1H), 5.12 (s, 1H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 169.1, 143.6, 140.7, 136.2, 129.8, 127.8, 127.7, 107.1, 103.1, 72.5, 20.9; IR (neat) ν_{max} 2928, 1741, 1608, 1226, 1032, 758 cm^{-1}; MS (EI) m/z (%) 271 (M^+ + 1, 100), 240 (5). Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.48; H, 5.32; N, 10.25.

*(E)-1,1′-(3-(4-(1,3-Dioxan-2-yl)phenyl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4r**):* colorless solid (145 mg, 43% yield); mp 120−121 °C; R_f = 0.25 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (bd, J = 1.6 Hz, 2H), 7.59 (bs, 2H), 7.46 (bd, J = 6.8 Hz, 2H), 7.41 (bd, J = 6.4 Hz, 2H), 7.20 (dd, J = 5.2, 1.2 Hz, 1H), 6.91 (dd, J = 12.8, 4.8 Hz, 1H), 6.56 (d, J = 12.8 Hz, 1H), 6.29 (bd, J = 1.6 Hz, 2H), 5.47 (s, 1H), 4.23 (bdd, J = 8.8, 3.6 Hz, 2H), 3.94 (t, J = 10.0 Hz, 2H), 2.25−2.12 (m, 1H), 1.40 (bd, J = 10.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.0, 135.2, 135.0, 128.5, 126.7, 126.1, 122.7, 106.4, 100.8, 75.8, 67.0, 25.4; IR (KBr) ν_{max} 3101, 2962, 1392, 1105, 758 cm^{-1}; MS (EI) m/z (%) 337 (M^+ + 1, 100), 323 (3). Anal. Calcd for $C_{19}H_{20}N_4O_2$: C, 67.84; H, 5.99; N, 16.66. Found: C, 67.71; H, 5.91; N, 16.58.

*1-(4-(1,3-Dioxan-2-yl)phenyl)-2-(1H-pyrazol-1-yl)allyl acetate (**3r**):* colorless solid (66 mg, 20% yield); mp 119−120 °C; R_f = 0.44 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (bt, J = 2.0 Hz, 2H), 7.49−7.42 (m, 4H), 7.11 (s, 1H), 6.24 (t, J = 2.0 Hz, 1H), 5.56 (s, 1H), 5.48 (s, 1H), 5.09 (s, 1H), 4.25 (dd, J = 8.8, 4.0 Hz, 2H), 3.97 (td, J = 9.6, 1.6 Hz, 2H), 2.26−2.16 (m, 1H), 2.12 (s, 3H), 1.44 (d, J = 10.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 143.9, 140.5, 138.9, 137.4, 127.8, 127.2, 126.2, 106.8, 103.3, 101.0, 72.8, 67.3, 25.6, 20.9; IR (KBr) ν_{max} 3130, 2974, 1738, 1244, 763 cm^{-1}; MS (EI) m/z (%) 329 (M^+ + 1, 100), 223 (11), 121 (3). Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.72; H, 6.21; N, 8.65.

*(E)-1,1′-(3-(4-(1,3-Dioxan-2-yl)phenyl)prop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5r**):* pale yellow solid (47 mg, 14% yield); mp 105−106 °C; R_f = 0.17 (3/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (bd, J = 1.2 Hz, 1H), 7.59 (bd, J = 1.2 Hz, 1H), 7.53−7.48 (m, 3H), 7.43 (d, J = 1.6 Hz, 1H), 7.25 (d, J = 6.4 Hz, 2H), 6.77 (dd, J = 11.2, 0.4 Hz, 1H), 6.68 (dd, J = 11.2, 5.2 Hz, 1H), 6.34 (bt, J = 2.0 Hz, 1H), 6.29 (bt, J = 1.6 Hz, 1H), 6.23 (d, J = 5.6 Hz, 1H), 5.51 (s, 1H), 4.26 (dd, J = 8.4, 3.6 Hz, 2H), 3.99 (td, J = 10.0, 2.0 Hz, 2H), 2.28−2.16 (m, 1H), 1.45 (d, J = 10.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 139.6, 139.1, 138.9, 130.5, 128.5, 128.4, 127.2, 126.5, 114.8, 107.3, 105.8, 100.9, 67.3, 64.8, 25.6; IR (KBr) ν_{max} 3111, 2924, 1676, 1392, 1103, 748 cm^{-1}; MS (EI) m/z (%) 337 (M^+ + 1, 100), 323 (3). Anal. Calcd for $C_{19}H_{20}N_4O_2$: C, 67.84; H, 5.99; N, 16.66. Found: C, 67.92; H, 6.08; N, 16.75.

*(E)-1,1′-(3-(Benzo[d][1,3]dioxol-5-yl)prop-2-ene-1,1-diyl)bis(1H-pyrazole) (**4s**):* light brown solid (147 mg, 50% yield); mp 115−116 °C; R_f = 0.43 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (bd, J = 2.0 Hz, 2H), 7.59 (bd, J = 1.6 Hz, 2H), 7.13 (d, J = 6.0 Hz, 1H), 6.98 (bd, J = 1.2 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.78−6.70 (m, 2H), 6.50 (d, J = 16.0 Hz, 1H), 6.31 (bt, J = 2.0 Hz, 2H), 5.95 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 148.1, 140.4, 135.3, 129.5, 128.5, 122.3, 120.7, 108.3, 106.6, 106.1, 101.2, 76.3; IR (KBr) ν_{max} 3103, 2901, 1651, 1448, 1255, 1037, 761, 625 cm^{-1}; MS (EI) m/z (%) 294 (M^+, 24), 293 (M^+−1, 100). Anal. Calcd for $C_{16}H_{14}N_4O_2$: C, 65.30; H, 4.79; N, 19.04. Found: C, 65.21; H, 4.71; N, 19.15.

*1-(Benzo[d][1,3]dioxol-5-yl)-2-(1H-pyrazol-1-yl)allyl acetate (**3s**):* brown oil (29 mg, 10% yield); R_f = 0.64 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (bd, J = 2.8 Hz, 1H), 7.57 (bd, J = 1.6 Hz, 1H), 6.99 (s, 1H), 6.96−6.90 (m, 2H), 6.73 (d, J = 8.4 Hz, 1H), 6.26 (bt, J = 2.0 Hz, 1H), 5.92 (s, 2H), 5.53 (s, 1H), 5.12 (s, 1H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 147, 77, 147.76, 144.1, 140.5, 130.6, 127.7, 121.4, 108.2, 107.8, 106.8, 102.8, 101.2, 72.8, 21.0; IR (neat) ν_{max} 2924, 1743, 1228, 756, 696 cm^{-1}; MS (EI) m/z (%) 287 (M^+ + 1, 100), 269 (6), 241 (9), 229 (14), 197 (8). Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.85; H, 4.88; N, 9.65.

*(E)-1,1′-(3-(Benzo[d][1,3]dioxol-5-yl)prop-1-ene-1,3-diyl)bis(1H-pyrazole) (**5s**):* brown oil (50 mg, 17% yield); R_f = 0.18 (6/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (bd, J = 1.6 Hz, 1H), 7.60 (bd, J = 1.2 Hz, 1H), 7.56 (bd, J = 2.0 Hz, 1H), 7.48 (bd, J = 2.0 Hz, 1H), 6.83 (d, J = 11.6 Hz, 1H), 6.81−6.75 (m, 2H), 6.74 (bd, J = 1.2 Hz, 1H), 6.64 (dd, J = 11.2, 5.6 Hz, 1H), 6.36 (bt, J = 1.6 Hz, 1H), 6.31 (bt, J = 1.6 Hz, 1H), 6.12 (d, J = 5.6 Hz, 1H), 5.97−5.95 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.6, 141.3, 139.7, 132.6, 130.4, 128.4, 128.3, 120.9, 115.0, 108.4, 107.8, 107.4, 105.8, 101.3, 64.8; IR (neat) ν_{max} 2924, 1678, 1248, 1039, 754 cm^{-1}; MS (EI) m/z (%) 295 (M^+ + 1, 100), 252 (41), 204 (14). Anal. Calcd for $C_{16}H_{14}N_4O_2$: C, 65.30; H, 4.79; N, 19.04. Found: C, 65.48; H, 4.85; N, 18.89.

*1-Phenyl-3-(1H-pyrazol-1-yl)but-3-en-2-yl acetate (**3t**):* colorless oil (49 mg, 19% yield); R_f = 0.57 (19/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.67 (s, 1H), 7.48−7.12 (m, 5H), 6.38 (s, 1H), 6.22 (s, 1H), 5.33 (s, 1H), 4.95 (s, 1H), 3.23−3.13 (m, 1H), 3.06−2.90 (m, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 144.2, 140.8, 136.7, 129.5, 128.2, 127.8, 126.7, 107.0, 102.3, 39.6, 21.0; IR (neat) ν_{max} 3030, 2926, 1747, 1651, 1232, 1045, 754 cm^{-1}; MS (EI) m/z (%) 257 (M^+ + 1, 100), 199 (8), 167 (14), 139 (5). Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.18; H, 6.22; N, 10.88.

*(Z)-1-Phenyl-4-(1H-pyrazol-1-yl)but-3-en-2-yl acetate (**3t′**).* colorless oil (65 mg, 25% yield); R_f = 0.45 (19/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.50 (s, 1H), 7.36−7.18 (m, 5H), 6.74 (d, J = 9.6 Hz, 1H), 6.56 (s, 1H), 6.34 (s, 1H), 5.14 (t, J = 8.8 Hz, 1H), 3.24−3.15 (m, 1H), 3.05−2.98 (m, 1H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 141.4, 137.2, 130.3, 129.6, 128.1, 126.4, 125.7, 117.2, 106.6, 71.5, 40.4, 21.1; IR (neat) ν_{max} 3028, 2924, 1736, 1521, 1236, 738 cm^{-1}; MS (EI) m/z (%) 257 (M^+ + 1, 100), 223 (14), 211 (27), 167 (14), 97 (11), 91 (11). Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.35; H, 6.23; N, 10.99.

*1-(Naphthalen-1-yl)-2-(1H-pyrazol-1-yl)propan-1-ol (**7**):* pale yellow oil (45 mg, 89% yield); R_f = 0.61 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.59 (bd, J = 1.6 Hz, 2H), 7.57−7.47 (m, 4H), 7.32 (t, J = 8.0 Hz, 2H), 7.13−7.06 (m, 4H), 6.12 (t, J = 2.4 Hz, 2H), 4.77−4.67 (m, 2H), 3.70 (dd, J = 14.0, 7.2 Hz, 2H), 3.46 (dd, J = 13.6, 6.8 Hz, 2H), 1.62 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 134.0, 133.8, 131.8, 128.8, 127.8, 127.5, 127.4, 126.1, 125.5, 125.3, 123.4, 104.5, 58.6, 40.9, 20.6; IR (neat) ν_{max} 3059, 2934, 1745, 1396, 1045, 750, 623 cm^{-1}; MS (EI) m/z (%) 253 (M^+ + 1, 100), 207 (3), 184 (3), 168 (3). Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.28; H, 6.31; N, 11.25.

*1,1′-(3-Phenylpropane-1,1-diyl)bis(1H-pyrazole) (**8**):* colorless solid (99 mg, 98% yield); mp 69−70 °C; R_f = 0.35 (4/1 hexane/EtOAc) [silica, UV and I_2]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (bd, J = 2.4 Hz, 2H), 7.56 (bd, J = 1.6 Hz, 2H), 7.31 (bt, J = 7.6 Hz, 2H), 7.26−7.19 (m, 1H), 7.15 (bd, J = 1.6 Hz, 1H), 7.14 (s, 1H), 6.33 (t, J = 7.6 Hz, 1H), 6.28 (bt, J = 2.0 Hz, 2H), 2.95 (q, J = 7.2 Hz, 2H), 2.58 (t, J = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 139.6, 128.6, 128.5, 128.4, 126.4, 106.4, 74.5, 35.1, 31.1. IR (KBr) ν_{max} 3109, 2928, 1514, 1390, 1091, 752, 623 cm^{-1}; MS (EI) m/z (%) 253 (M^+ + 1, 100), 209 (3), 146 (3). Anal. Calcd for $C_{15}H_{16}N_4$: C, 71.40; H, 6.39; N, 22.21. Found: C, 71.56; H, 6.31; N, 22.15.

*Synthesis of Pd Complex **9** from **4o**:* pale yellow solid (127 mg, 89% yield); mp 275−276 °C dec; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.46 (bd, J = 2.4 Hz, 2H), 8.25 (bd, J = 4.0 Hz, 1H), 8.22 (d, J = 8.8 Hz, 1H), 8.08 (bd, J = 1.2 Hz, 2H), 8.03−7.89 (m, 3H), 7.67−7.45 (m, 4H), 7.10 (bs, 1H), 6.68 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.4, 135.3, 133.6, 132.1, 131.1, 130.0, 129.0, 127.3, 126.7, 126.2, 125.3, 124.2, 108.1, 73.8; IR (KBr) ν_{max} 3145, 3123, 2931, 1408, 1282, 1205, 1086, 947, 860, 783, 613 cm^{-1}. Anal. Calcd for $C_{19}H_{16}Cl_2N_4Pd$: C, 47.77; H, 3.38; N, 11.73. Found: C, 47.86; H, 3.32; N, 11.65.

*Synthesis of Pd Complex **10** from **8**:* pale yellow solid (150 mg, 88% yield); mp 254−256 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (s, 2H), 8.00 (s, 2H), 7.36−7.26 (m, 3H), 7.24−7.16 (m, 4H), 6.58 (s, 1H), 3.52 (bs, 2H), 2.35 (bs, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.3, 139.3, 135.5, 129.1, 128.6, 126.9, 107.7, 73.3, 39.3 (merged in DMSO-d_6 peaks), 30.6; IR (KBr) ν_{max} 3139, 3123, 3013, 2969, 2926, 1408, 1298, 1216, 1068, 772, 756, 695 cm^{-1}; HRMS calcd for $C_{15}H_{16}Cl_2N_4Pd$ [M + Na]$^+$ 450.9685, found 450.9685.

General Procedure for Suzuki−Miyaura Cross Coupling Reaction GP-4. A 25 mL Schlenk tube was charged with aryl halides

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(**11**; 1.0 equiv), arylboronic acids (**12**; 2.0 equiv), K_2CO_3 (2.0 equiv), and palladium complex **9**/**10** (0.1 mol %) in H_2O. The reaction mixture was stirred at 80 °C for 24 h. After the mixture was cooled to room temperature, it was diluted with water and extracted with EtOAc. The organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel. Analytical and spectral data of cross-coupled products **13** exactly match with the reported values. 4-Methoxybiphenyl (**13aa**):[16] 536 mg, 97% yield. 4-(Trifluoromethyl)-biphenyl (**13ba**):[17] 480 mg, 72% yield. 2-Methylbiphenyl (**13ca**):[18] 473 mg, 94% yield. 2-Phenylthiophene (**13da**):[16] 385 mg, 80% yield. 4-Fluoro-4′-methoxybiphenyl (**13ab**):[19] 577 mg, 95% yield. 4′-Methoxy-3-methylbiphenyl (**13ac**):[17] 511 mg, 86% yield. 1-(4-Methoxyphenyl)naphthalene (**13ad**):[20] 674 mg, 96% yield.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^1H and ^{13}C NMR spectra of new compounds and tables and CIF files giving crystallographic details of compounds **4n**, **3o**, **5o**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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(22) The activation of allene and pyrazole N by $AgNO_3$ would lead to the formation of major product **4**.