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Synthesis of Dihydropyrano[3,2-*c*]pyrazoles via Double Bond Migration and Ring-Closing Metathesis

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Received: 25 December 2018; Accepted: 11 January 2019; Published: 15 January 2019

Abstract: Three types of pyrazole-fused heterobicycles, i.e., 1,5-, 1,7-, and 2,5-dihydropyrano[3,2-*c*] pyrazoles, were synthesized from 4-allyloxy-1*H*-pyrazoles. A sequence of the Claisen rearrangement of 4-allyloxy-1*H*-pyrazoles, ruthenium-hydride-catalyzed double bond migration, *O*-allylation, and ring-closing metathesis was employed in this study.

Keywords: dihydropyrano[3,2-*c*]pyrazole; synthesis; double bond migration; ruthenium hydride catalyst; ring-closing metathesis

1. Introduction

The synthesis of substituted or functionalized pyrazoles has been studied extensively thus far because they show or are expected to show important and diverse bioactivities [1,2]. Celecoxib, a non-steroidal anti-inflammatory drug (NSAID), is a representative pyrazole-containing compound, which acts through selective cyclooxygenase (COX)-2 inhibition. Whereas the late-stage construction of a pyrazole ring through some cycloadditions of already-substituted components is the basis for most syntheses of substituted pyrazoles [3,4], direct functionalization of pyrazoles has not been investigated satisfactorily to date. As investigations on it seem rare, we have been interested in and studied the direct functionalization of pyrazoles through coupling reactions of halogenated analogues derived from commercially available pyrazole [5–8]. In addition, pyrazole-fused heterocycles have recently been synthesized for reasons similar to those described above or because of characteristic activities not seen in monocyclic substituted pyrazoles [9]. Many pyrazole-fused heterocyclic compounds possess unique and important biological activities [10]. Some examples of pyrano[2,3-*c*]pyrazoles [11–14], pyrano[3,2-*c*]pyrazoles [15,16], and furo[3,2-*c*]pyrazoles [17,18] are presented in Figure 1.

The Claisen rearrangement followed by ring-closing metathesis (RCM) is an effective sequence for constructing various polycyclic systems [19,20]. On the basis of our previous work on the synthesis of withasomnines [21,22], we recently reported the synthesis of dihydrooxepino[3,2-*c*]pyrazoles (**4** and its isomers) via a combination of the Claisen rearrangement of 4-allyloxy-1*H*-pyrazoles (**1a–d**), *O*-allylation of Claisen rearrangement product **2** into **3**, and subsequent RCM of **3** [23]. This realized the construction of pyrazole-containing 5,7-bicyclic system **4**, shown in Scheme 1.

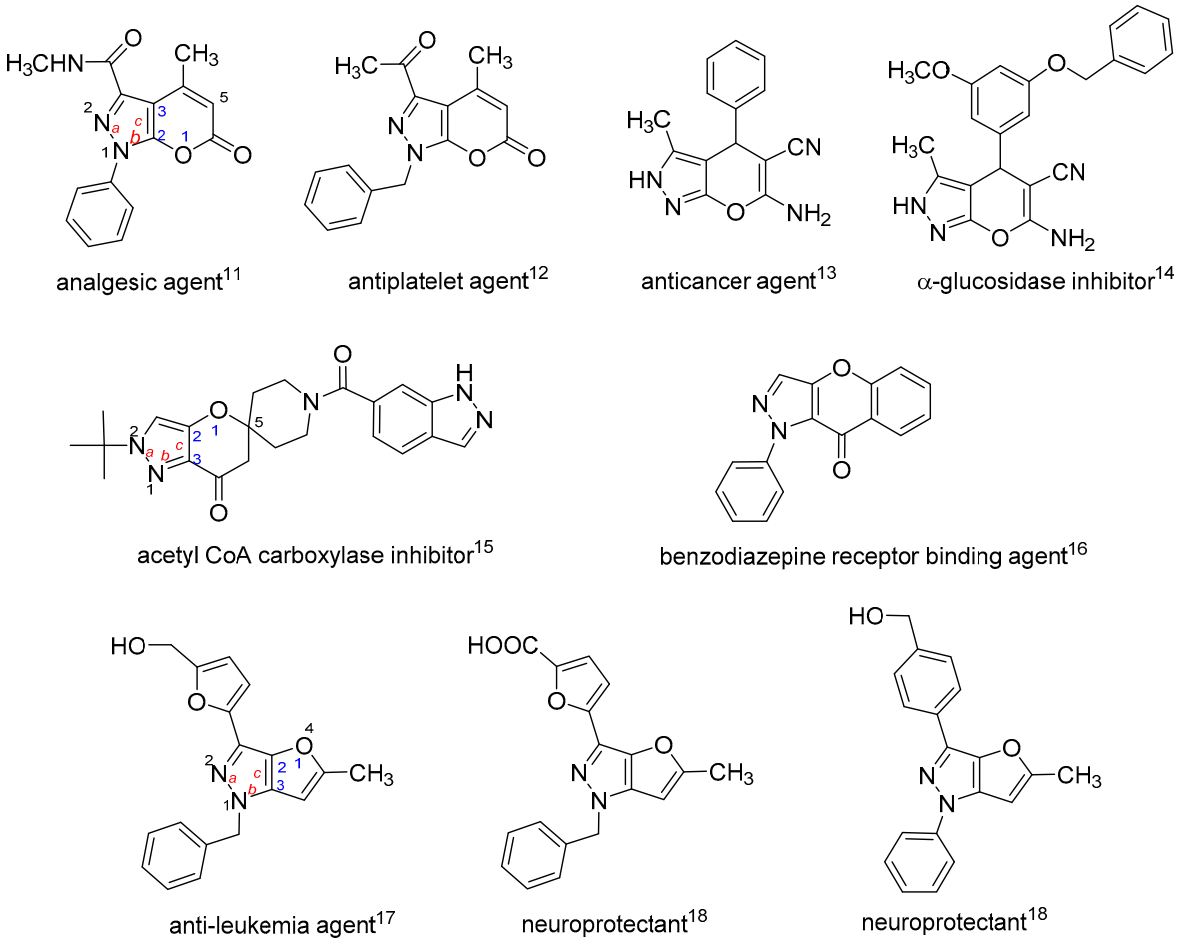
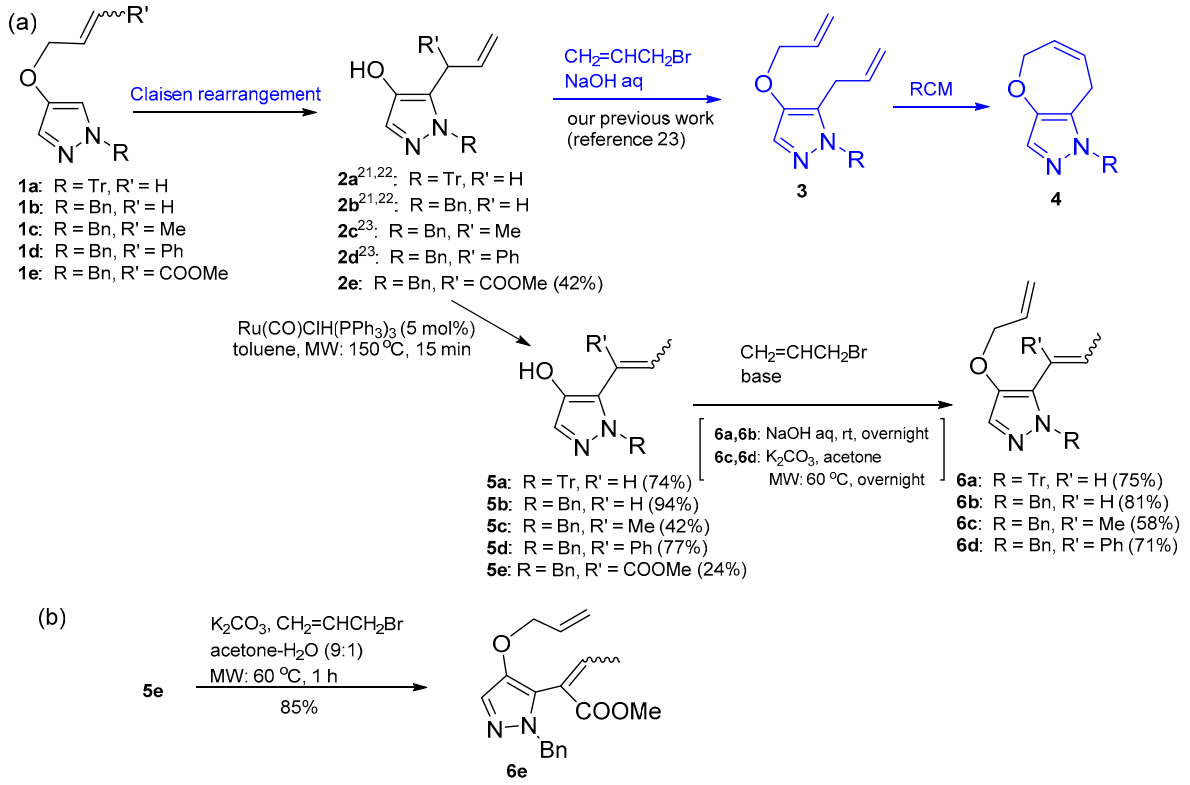


Figure 1. Examples of bioactive pyrano[2,3-*c*]pyrazoles, pyrano[3,2-*c*]pyrazoles, and furo[3,2-*c*]pyrazoles.

After the migration of the double bond in the side chain of intermediate **2** in Scheme 1, expected product **5** can be *O*-allylated to **6**. The subsequent RCM of **6** may provide a pyrazole-containing 5,6-bicyclic system, i.e., a dihydropyrano[3,2-*c*]pyrazole. These are expected to show various types of activities. There have been many reports of syntheses of pyrano[2,3-*c*]pyrazoles [10–14], but very few for pyrano[3,2-*c*]pyrazoles [15,16,24,25]. In addition, the development of a new synthetic method for furo[3,2-*c*]pyrazoles, which are extremely important as mentioned above, seems possible if both double bond migration and dehydrohalogenation occur on a 5-allyl-4-(2-haloethyl)oxy-1*H*-1-tritylpyrazole. Described herein is a new and selective synthesis of three types of dihydropyrano[3,2-*c*]pyrazoles, namely **7**, **8**, and **20**, with pyrazole-fused heterocyclic skeletons from **1** via the combination of Claisen rearrangements and RCM, along with efforts toward furo[3,2-*c*]pyrazoles (**17**).



Scheme 1. Preparation of 5-allyl-4-allyloxy-1*H*-pyrazoles (**6**) from 4-allyloxy-1*H*-pyrazoles (**2**).

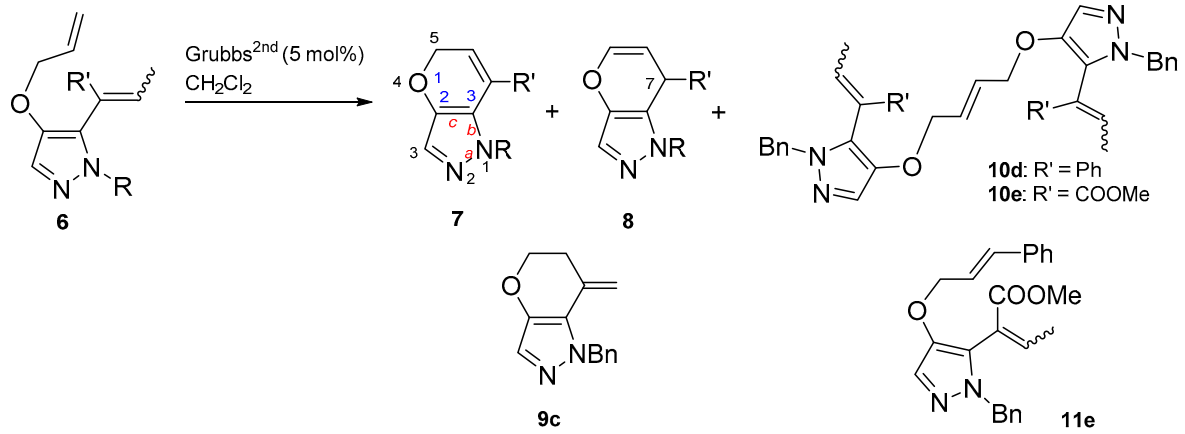
2. Results

2.1. Synthesis of 1,5-*Dihydropyrano[3,2-c]pyrazoles*

Our initial efforts in the synthesis of 1,5-dihydropyrano[3,2-*c*]pyrazoles (**7**) are presented in Scheme 1 and Table 1. In our earlier efforts for double bond migration for the conversion of **2a** to **5a** with potassium tert-butoxide (*t*-BuOK) as a base, every trial under microwave (MW) irradiation in a different solvent (tetrahydrofuran (THF), EtOH, MeCN, acetone, 1,2-dimethoxyethane (DME), toluene, THF-toluene) failed to give the desired product **5a** [20,26]. Alternatively, carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) [(RuClH(CO)(PPh_3)$_3$] was applied to the double bond migration for the conversion of **2** to **5**, as shown in Scheme 1 [27]. MW irradiation of the reaction mixture of **2** and 5 mol% of the ruthenium hydride catalyst in toluene gave the desired product **5**, whereas the same reaction at room temperature (rt) did not occur. Starting compounds **2a**–**d** are known compounds [21–23], and 1-benzyl-4-hydroxy-5-((1-methoxycarbonyl)-2-propen-1-yl)-1H-pyrazole (**2e**) is the Claisen rearrangement product of **1e**, which was newly prepared from 1-benzyl-4-iodo-1H-pyrazole for this work and already contained a small part of **5e** (see Experimental section).

Then, the C4-hydroxyl groups in 4-hydroxy-5-(1-propenyl)-1H-pyrazoles **5a** and **5b** were treated with aqueous NaOH followed by alkenyl halides in order to prepare the RCM substrates **6a** and **6b**. Conversion of **5c** and **5d**, which have a substituent, to **6c** and **6d** using the same condition took a long time with poor yields. So, alternative transformation of **5c** and **5d** to **6c** and **6d** was carried out using K_2CO_3 in acetone under MW irradiation, respectively. The reactions proceeded smoothly and the chemical yields of **6c** and **6d** are presented in Scheme 1a. In a separate experiment, compound **2e**, which already contains a small part of **5e** as noted above, was transformed directly to **6e** through treatment with K_2CO_3 and allyl bromide in acetone under MW irradiation in 63% yield, since the yield from **2e** to **5e** was not satisfactory. The yield of the MW-aided transformation of **2e** to **6e** was improved to 85% by applying acetone-water (9:1) as the solvent system (Scheme 1b).

Table 1. Ring-closing metathesis (RCM) of 5-allyl-4-allyloxy-1*H*-pyrazoles.



Entry	Substrate	R	R′	Temp. (°C)	Time (min)	Product Yield (%)		
1	**6a**	Tr	H	rt	5	**7a** (89) [e]		
2	**6a**			rt	30	**7a** (92)		
3	**6a**			rt	60	**7a** (83)		
4	**6a**			rt	120	**7a** (44)		
5	**6a**			80 (MW)	3	**7a** (87)		
6	**6a**			100 (MW)	0.5	**7a** (71)		
7	**6a**			140 (MW)	10	**7a** (65)		
8	**6b**	Bn	H	rt	30	**7b** (96)		
9	**6b**			80 (MW)	3	**7b** (91)		
10	**6b**			140 (MW)	10	**7b** (75)	**8b** (15)	
11 [a]	**6c**	Bn	Me	rt	overnight	**7c** (10)		
12	**6c**			140 (MW)	60	**7c** (24)		**9c** (45)
13	**6d**	Bn	Ph	rt	overnight	-	-	-
14	**6d**			140 (MW)	60	-	-	**10d** (30)
15 [b]	**6e**	Bn	COOMe	rt	overnight	-	-	-
16 [c]	**6e**			80 (MW)	60	**7e** (2)		**10e** (29)
17 [d]	**6e**			100 (MW)	60	**7e** (7)		**10e** (30)
18	**6e**			140 (MW)	60	**7e** (15)		

a. 60% of starting material **6c** was recovered. b. 50% of **6e** was recovered. c. Undesired **11e** (2%) was obtained during the recovery of **6e** (21%). d. **11e** was obtained (4%). e. A small amount of **6a** was detected in the NMR spectrum and was inseparable from **7a**.

RCM substrates **6** were treated with 5 mol% Grubbs′ second-generation catalyst (Grubbs^{2nd}) in CH_2Cl_2. The results of the RCM reactions are summarized in Table 1. With substrate **6a**, reaction at rt afforded the desired RCM product **7a** within 30 min (entry 2). A shorter reaction time also led to **7a**, but with an inseparable trace amount of **6a** (entry 1). In contrast, extended reaction times led to reduced product yields (entries 3 and 4). The MW-aided reaction was also examined in an attempt to reduce the reaction time (entries 5–7). In these trials, only **7a** was formed and double bond migration product **8a** could not be detected [23]. Moreover, higher temperatures above 100 °C reduced the reaction yield (entry 7). The optimal reaction conditions in entries 2 and 5 for substrate **6a** were applied to the RCM of **6b** and gave similar results producing **7b** (entries 8 and 9, respectively). The MW reaction of **6b** at a higher temperature of 140 °C led to partial double bond migration to produce **8b** (entry 10). When the substrate had an R′ substituent, different results were obtained, as shown by the following entries. Substrates **6d** and **6e** did not react at rt (entries 13 and 15, respectively).

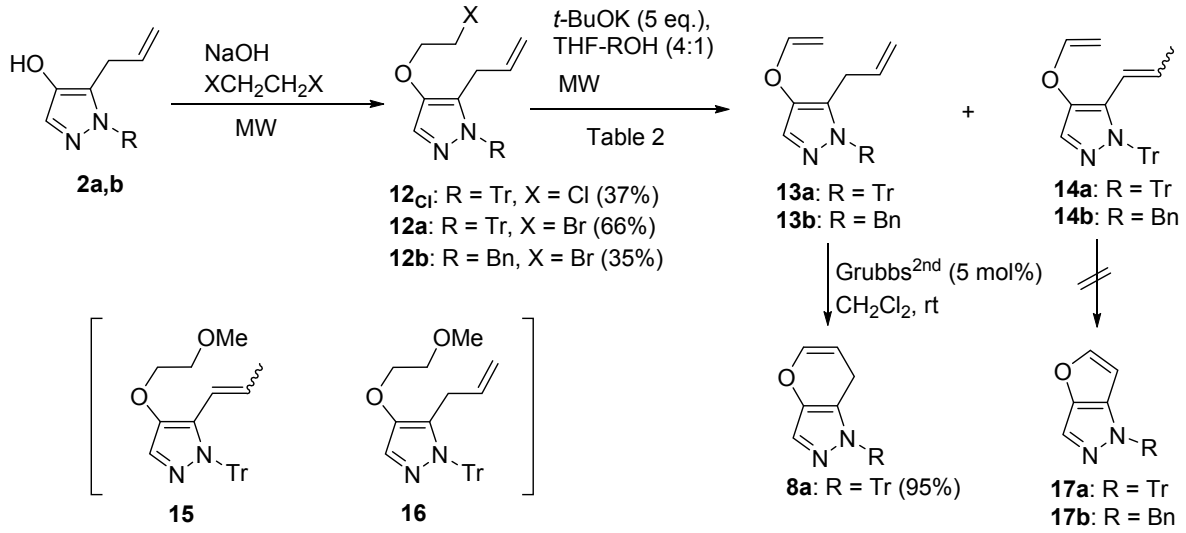
The MW-aided reaction (140 °C) of **6c** afforded RCM product **7c** as a minor product (24%) and **9c** (45%) with an exomethylene moiety as the major product (entry 12). The structure of **9c** was determined through the heteronuclear single quantum coherence (HSQC) correlations between a carbon signal at δ 107.2 ppm and two proton signals at δ 4.78 and 4.96 ppm. Generally, endo-cyclic alkene is considered to be more stable than the corresponding exo-alkene. But in this case, **7c** is thought

to be less stable than exo-diene **9c** due to the strain caused by 6-membered endo-diene structure in the thermodynamic condition.

However, the same MW conditions applied to substrate **6d** did not result in **7d**, but dimeric **10d** formed through intermolecular metathesis in 30% yield (entry 14). Mass spectrometry (MS) revealed that compound **10d** had an m/z of 632 (M^+), which corresponds to $C_{42}H_{42}N_4O_2$. The ^1H nuclear magnetic resonance (NMR) spectrum of **10d** suggested the presence of a $=CHCH_3$ moiety through the signals at δ 6.29 (q, J = 7.1 Hz) and 1.51 ppm (d, J = 7.1 Hz) in a 1:3 integral ratio and the lack of an exomethylene from the starting **6d**. These data suggest that the intermolecular metathesis product **10d** formed by expelling an ethylene molecule [339 (**6d**) × 2 − 28 (CH_2=CH_2) = 632 ((M^+) for **10d**)]. The presence of a bulky R′ substituent may lead to serious repulsion in the transition state for RCM. When the substrate had a methoxycarbonyl group as R′, the results were confusing. The MW reaction of **6e** at 140 °C gave a complex mixture and only **7e** was isolated in 15% yield (entry 18). The MW reactions of **6e** at lower temperatures (80 and 100 °C) gave **10e** in similar yields (29% and 30%, respectively) with **7e** as a minor product (entries 16 and 17). In both of these entries, **11e**, which is a metathesis product of **6e** and the Grubbs catalyst, was also isolated as a minor product. The structure of **11e** was confirmed through detailed NMR analysis and an M^+ peak at m/z 388.1785 ($C_{24}H_{24}N_2O_3$) in the high-resolution MS (HRMS) spectrum. However, our attention was focused on increasing the yields of **7e** and decreasing the yields of **10e** by increasing the reaction temperature (entries 16–18). Then, we hypothesized that **10e** transforms into **7e**; **10e** may be the initial product at lower reaction temperatures. Therefore, the MW reaction of pure **10e** with Grubbs^{2nd} at 140 °C was examined independently in an attempt to observe the formation of **7e** as the major product in the reaction mixture.

2.2. *Synthesis of* 1,7-*Dihydropyrano*[3,2-*c*]*pyrazoles*

We attempted to expand this methodology to the syntheses of different types of pyrazole-fused heterobicycles, i.e., 1,7-dihydropyrano[3,2-*c*]pyrazoles (**8**) and furo[3,2-*c*] pyrazoles (**17**), as illustrated in Scheme 2. In order to realize this, 4-*O*-vinylation was required. First, the 4-hydroxyl group of **2a** was treated with 1,2-dichloroethane to obtain a pyrazole with a 2-chloroethoxy group at C4, $\mathbf{12_{Cl}}$. However, dehydrochlorination of $\mathbf{12_{Cl}}$ did not occur under basic conditions. Then, 2-bromoethylation of the 4-hydroxyl group was examined, aimed at improving the leaving ability. Desired 5-allyl-4-(2-bromoethyl)oxy-1*H*-1-tritylpyrazole (**12a**) was smoothly prepared through the MW-aided reaction of **2a**. The examination of the dehydrobromination of **12a** is summarized in Table 2. Whereas treatment of **12a** with *t*-BuOK in toluene resulted in no reaction (entry 1), application of THF-MeOH (4:1) led to the desired dehydrobromination (entries 2–5). The MW reaction at 100 °C for 30 min afforded only double bond migration product (*E*/*Z*)-5-allyl-4-vinyloxy-1*H*-1-tritylpyrazole (**13a**) but in 14% yield (entry 2). Increasing the reaction time to 60 min resulted in an inseparable mixture of **13a** and 5-(1-propenyl)-4-vinyloxy-1*H*-1-tritylpyrazole (**14a**) in 19% combined yield (entry 3). A higher temperature of 130 °C resulted in only **14a** in 30% yield (entry 4). A similar MW reaction at 80 °C produced **13a** in a similar yield (entry 5). In these trials (entries 2–5), the chemical yields of desired **13a** and **14a** were not satisfactory. Close inspection of entries 4 and 5 led us to isolate and elucidate the structures of side product **15** (28% yield), which should have formed via S_N2 attack by a methoxide on **12a**, and **16** (17% yield) (see footnotes of Table 2). To improve the chemical yields, inhibition of the S_N2 attack on **12a** by a nucleophile formed from the solvent under basic conditions was required. Hence, *t*-BuOH was applied instead of MeOH as a co-solvent. Although the MW reaction at 80 °C afforded only a trace amount of desired product **13a** (entry 6), the same reaction at 130 °C afforded only **13a** in 87% yield (entry 7). Inspired by the result in entry 4, the MW reaction was attempted at a higher temperature of 180 °C and afforded **14a** selectively in 67% yield (entry 8). Treatment of the *N*-benzyl derivative **12b** with *t*-BuOK at 130 °C resulted in only **14b** (72%) (entry 9). Then, the dehydrobromination of **12b** was examined at a lower temperature (entry 10), but resulted in an inseparable mixture of **12b** and **14b**.



Scheme 2. Challenges in the syntheses of 1,7-dihydropyrano[3,2-*c*]pyrazoles (**8**) and furo[3,2-*c*]pyrazoles (**19**).

Table 2. Potassium *t*-butoxide promoted dehydrohalogenation of **12**.

Entry	Substrate	Solvent	Time (min)	Temp. (°C)	Product Yield (%)	
1	**12a**	THF	30	100	No reaction	
2	**12a**	THF:MeOH (4:1)	30	100	**13a** (14)	**14a** (0)
3	**12a**	THF:MeOH (4:1)	60	100	**13a** + **14a** (19) [a]	
4 [b]	**12a**	THF:MeOH (4:1)	60	130	**13a** (0)	**14a** (30)
5 [c]	**12a**	THF:MeOH (4:1)	60	80	**13a** (27)	**14a** (0)
6	**12a**	THF:*t*-BuOH (4:1)	60	80	**13a** (trace)	**14a** (0)
7	**12a**	THF:*t*-BuOH (4:1)	60	130	**13a** (87)	**14a** (0)
8	**12a**	THF:*t*-BuOH (4:1)	60	180	**13a** (0)	**14a** (67)
9	**12b**	THF:*t*-BuOH (4:1)	60	130	**13b** (0)	**14b** (72)
10 [d]	**12b**	THF:*t*-BuOH (4:1)	60	80	**13b** (0)	**14b** (31) [e]

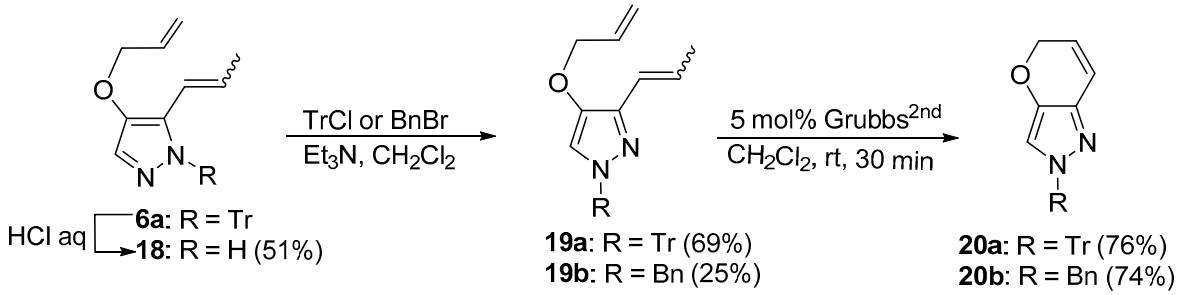
a. Combined yield of **13a** and **14a**. b. Formation of side product **15** (28%) was observed. c. Formation of side product **16** (17%) was observed. d. An inseparable mixture of **12b** and **14b** was obtained. e. Combined yields of (*E*)-**14b** (25%) and (*Z*)-**14b** (6%) calculated from the ^{1}H NMR spectrum with unreacted **12b** (6%).

The RCM of prepared substrates **13a**, **14a**, and **14b** were examined. Treatment of **13a** with Grubbs^{2nd} (5 mol%) at rt gave the desired product **8a** in 95% yield. However, the corresponding reactions of **14a** and **14b** did not afford the desired products **17a** and **17b**, even with MW assistance. Further examinations of **14a** with alternative catalysts, such as the Grubbs^{1st}, Hoveyda-Grubbs, and Schrock catalysts, also did not lead to **17a**. Our synthesis of **17** will be continued in a future study.

2.3. Synthesis of 2,5-Dihydropyrano[3,2-c]pyrazoles

The synthesis of 2,5-dihydropyrano[3,2-*c*]pyrazoles (**20**) was examined and the results are summarized in Scheme 3. For this purpose, selective preparation of 3-alkenyl-4-allyloxy-1*H*-pyrazoles **19** is required since 3-allyl-4-hydroxy-1*H*-1-tritylpyrazole is a minor Claisen rearrangement product of **1a**, and the corresponding 3-allyl-1-benzyl-4-hydroxy-1*H*-pyrazole could not be obtained by heating **1b** [21,22]. Hence, an alternative method of preparing **19** via a deprotection-reprotection sequence was examined. 4-Allyloxy-5-(1-propenyl)-1*H*-1-tritylpyrazole (**6a**) was deprotected with aqueous HCl to give **18**, which was then treated with trityl chloride or benzyl bromide under basic conditions. An *E*/*Z* mixture of 4-allyloxy-3-(1-propenyl)-1*H*-1-tritylpyrazole (**19a**) was obtained exclusively owing to the steric repulsion between the propenyl group on the pyrazole ring and an introduced bulky trityl group. However, *N*-benzylation of **18** afforded a mixture of **19b** and **6b** in a ca. 4:1 ratio in 60% combined yield, and separation gave pure **19b** in 25% yield. The obtained substrates **19a** and **19b** were

independently treated with 5 mol% Grubbs^{2nd} at rt to afford the desired RCM products **20a** and **20b**, respectively, in good yields.



Scheme 3. Synthesis of 2,5-dihydropyrano[3,2-*c*]pyrazoles (**20**).

3. Conclusions

We synthesized 1,5-, 1,7-, and 2,5-dihydropyrano[3,2-*c*]pyrazoles (**7**, **8**, and **20**) from 5-allyl-4-hydroxy-1*H*-1-tritylpyrazoles via a combination of the Claisen rearrangement, ruthenium-hydride-catalyzed double bond isomerization, *O*-alkenylation, and RCM. In the synthesis of 1,5-dihydropyrano[3,2-*c*]pyrazoles **7**, the presence of a substituent on the 5-alkenyl group inhibited smooth RCM through steric hindrance. In these cases, MW-aided reactions were effective, but gave various products. Towards the selective synthesis of 1,7-dihydro-1-tritylpyrano[3,2-*c*]pyrazole **8a**, temperature-dependent selective dehydrobromination was effective for preparing the RCM substrate **13b**. For the synthesis of 2,5-dihydropyrano[3,2-*c*]pyrazoles **20**, a deprotection-reprotection sequence was applied to obtain the RCM substrate **19**.

4. Materials and Methods

Infrared (IR) spectra were obtained using a Perkin Elmer 1720X FT-IR spectrometer (Perkin Elmer, Wattham, MA, USA). HRMS was performed using a JEOL JMS-700 (2) mass spectrometer (JEOL, Tokyo, Japan). NMR spectra were recorded at 27 °C using Agilent 300, 400-MR-DD2, and 600-DD2 spectrometers in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard. Liquid column chromatography was conducted using silica gel BW127ZH (Fuji Silysia Chemical Ltd., Tokyo, Japn). Analytical and preparative thin layer chromatography (TLC) analyses were performed using pre-coated Merck glass plates (silica gel 60 F_{254}), and the compounds were visualized by dipping the plates in an ethanol solution of phosphomolybdic acid followed by heating (Merk & Co., Inc., Darmstadt, Germany). MW-assisted reactions were carried out using a Biotage Initiator® (Basel, Switzerland). Anhydrous CH_2CH_2 was purchased from Wako Pure Chemical Industries (Osaka, Japan).

*4.1. Synthesis of (E)-Methyl 4-((1-Benzyl-1H-pyrazol-4-yl)oxy)but-2-enoate (***1e***)*

To 1-benzyl-4-formyl-1*H*-pyrazole (200 mg, 1.07 mmol) in CH_2Cl_2 (5 mL) was added 70% *meta*-chloroperoxybenzoic acid (397.6 mg, 1.61 mmol) at 0 °C. After it was stirred overnight at room temperature, the mixture was quenched by adding aqueous $NaHCO_3$ and then extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and evaporated to give a crude residue. The crude material was dissolved in *t*-BuOH-CH_2Cl_2 (5 mL/5 mL) at 40 °C, and then potassium *tert*-butoxide (428.6 mg, 3.82 mmol) was added to the solution. After it was stirred overnight at 40 °C, the mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The separated organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure to afford a crude residue, which was purified using silica gel column chromatography (eluent: EtOAc:hexane = 1:3) to afford (*E*/*Z*)-**1e** (128.1 mg, 44%): oil; IR (film) υ_{max} 1724 (C=O), 1574 (C=C), 1437 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.74 (3H, s, -COO*Me*), 4.52 (2H, dd, *J* = 4.1, 1.9 Hz, -OC*H*$_2$CH=CH-), 6.13 (1H, br d, *J* = 15.9 Hz, -COC*H*=CH-), 6.99 (1H, dt, *J* = 15.9, 4.1 Hz, -CH_2CH=C*H*-), 7.05 (1H, d, *J* = 0.6 Hz, pyrazole-H), 7.18 (2H, br d, *J* = 8.0 Hz, Bn-H), 7.30–7.35 (4H, m, Bn-H, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

51.6, 56.6, 70.0, 115.1, 121.4, 127.2, 127.5, 128.0, 128.7, 136.3, 142.5, 145.2, 166.4; high-resolution electron ionization mass spectrometry (HREIMS) m/z calcd. for $C_{15}H_{16}N_2O_3$ (M^+) 272.1161, found 272.1163.

*(*E*)-Methyl 4-((1-trityl-1*H*-pyrazol-4-yl)oxy)but-2-enoate (**1f**) was synthesized in a similar manner as **1e**, but it was not rearranged under the thermal condition described below. **1f**: colorless crystals (CH_2Cl_2); mp 155–158 °C; IR (film) υ_{max} 1725 (C=O), 1572 (C=C), 1492 (C=C), 1442 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.76 (3H, s, -COO*Me*), 4.53 (2H, dd, *J* = 4.1, 2.0 Hz, -OCH_2CH=CH-), 5.20 (2H, s, ArCH_2Ph), 6.14 (1H, dt, *J* = 15.9, 1.9 Hz, -COCH=CH-), 7.00 (1H, dt, *J* = 15.9, 4.1 Hz, -CH_2CH=CH-), 7.05 (1H, s, pyrazole-H), 7.13–7.18 (6H, m, Tr-H), 7.30–7.35 (9H, m, Tr-H), 7.42 (1H, s, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.7, 70.0, 78.7, 118.4, 121.5, 127.68, 127.71, 127.9, 130.1, 142.5, 143.0, 143.8, 166.4; HREIMS m/z calcd. for $C_{27}H_{24}N_2O_3$ (M^+) 424.1786, found 424.1779.

*4.2. Synthesis of Methyl 2-(1-Benzyl-4-hydroxy-1H-pyrazol-5-yl)but-3-enoate (**2e**)*

A sealed microwave vial containing a solution of **1e** (128.1 mg, 0.47 mmol) in 1,2-dimethoxyethane (DME) (2 mL) was heated under microwave irradiation at 200 °C for 30 min. After it had cooled, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The separated organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure to afford a crude residue, which was purified using silica gel column chromatography (eluent: EtOAc:hexane = 1:1) to afford **2e** with a small amount of the isomer, **5e** (53.9 mg, 42%).

2e (major) and **5e** (minor) in ca. 2:1 ratio: oil; IR (film) υ_{max} 1716 (C=O), 1497 (C=C), 1435 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.65 (1H, d, *J* = 7.3 Hz, =CHCH_3 of **5e**), 3.64 (1H, s, -COO*Me* of **5e**), 3.68 (2H, s, -COO*Me* of **2e**), 4.37 (0.7H, br d, *J* = 7.0 Hz, ArC*H*(COOMe)CH=), 4.93 (0.7H, dd, *J* = 17.0, 1.5 Hz, -CH=C*H*H), 5.01 (0.6H, s, ArCH_2Ph), 5.12 (0.7H, dd, *J* = 10.3, 1.5 Hz, -CH=CH*H* of **2e**), 5.19 (0.7H, br d, *J* = 16.1 Hz, ArC*H*HPh of **2e**), 5.25 (0.7H, br d, *J* = 16.1 Hz, ArCH*H*Ph of **2e**), 5.86 (1H, ddd, *J* = 17.0, 10.3, 6.5 Hz, -CH(COOMe)C*H*=CH_2 of **2e**), 6.83 (0.6H, br s, -OH of **2e**), 7.03–7.05 (2H, m, Ph-H), 7.19–7.31 (3H, m, Ph-H; 0.3H, m, overlapped, =C*H*CH_3 of **5e**), 7.30 (1H, br s, pyrazole-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 15.8 (**5e**), 46.4, 52.3 (**5e**), 53.2, 54.4 (**5e**), 54.6, 118.7, 120.6, 122.4 (**5e**), 122.9 (**5e**), 126.6, 127.2 (**5e**), 127.6 (**5e**), 127.9, 128.2 (**5e**), 128.40 (**5e**), 128.44, 129.1, 130.7, 136.9 (**5e**), 139.8 (**5e**), 140.9, 147.0, 166.5 (**5e**), 173.2; HREIMS m/z calcd. for $C_{15}H_{16}N_2O_3$ (M^+) 272.1161, found 272.1162.

4.3. Double Bond Migration of 5-Allyl-4-hydroxy-1H-pyrazoles (Scheme 1)

General procedure: To a toluene solution (10 mL) of 5-allyl-4-hydroxy-1-trityl-1*H*-pyrazole (**2a**) (0.434 g, 1.19 mmol) in a microwave vial (5–20 mL), $RuClH(CO)(PPh_3)_3$ (56.6 mg, 0.059 mmol) was added. The reaction vial was sealed and then heated at 150 °C for 15 min under microwave irradiation. The cooled reaction mixture was evaporated to give a crude residue, which was purified using column chromatography (eluent: hexane:EtOAc = 1:1) to afford 4-hydroxy-5-(1-propenyl)-1-trityl-1*H*-pyrazole (**5a**) (0.323 g, 74% yield) as an *E*/*Z* mixture.

**Pure starting material gave the desired product as described above, but a small contamination inhibited the isomerization. In that case, a toluene-MeOH (9:1) solvent system was effective for isolating the desired product.

5a: oil; IR (film) υ_{max} 3268 (-OH), 1597 (C=C), 1494 (C=C), 1446 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.43 (3H, dd, *J* = 6.5, 1.2 Hz, =CHCH_3), 5.17 (1H, dd, *J* = 11.4, 1.4 Hz, ArC*H*=CH-), 5.23 (1H, dq, *J* = 11.4, 6.6 Hz, -CH=C*H*CH_3), 7.09–7.34 (16H, m, Tr-H, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 78.8, 118.3, 126.2, 127.3, 127.4, 127.6, 127.8, 129.6, 130.0, 130.1, 130.28, 130.34, 142.6; HREIMS m/z calcd. for $C_{25}H_{22}N_2O$ (M^+) 366.1732, found 366.1731.

(*E*/*Z*)-1-Benzyl-4-hydroxy-5-(1-propenyl)-1*H*-pyrazole (**5b**): *E*/*Z* mixture in ca. 5:1 ratio (X)**;** oil; IR (film) υ_{max} 3031 (-OH), 1589 (C=C), 1496 (C=C), 1454 (C=C) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.72 (0.5H, dd, *J* = 6.8, 1.5 Hz, -CH=CHCH_3 of (*E*)-isomer), 1.83 (2.5H, dd, *J* = 6.8, 1.8 Hz, -CH=CHCH_3 of (*Z*)-isomer), 5.15 (0.3H, s, -NCH_2Ph of (*Z*)-isomer), 5.24 (1.5H, s, -NCH_2Ph of (*E*)-isomer), 5.93 (0.15H, dq, *J* = 10.1, 6.8 Hz, -CH=C*H*CH_3 of (*Z*)-isomer), 5.99 (0.15H, dq, *J* = 10.1, 1.5 Hz, ArC*H*=CHCH_3 of

(*Z*)-isomer), 6.15 (0.85H, dq, *J* = 16.1, 1.5 Hz, ArC*H*=CHCH$_3$ of (*E*)-isomer), 6.38 (0.85H, dq, *J* = 16.1, 6.8 Hz, -CH=C*H*CH$_3$ of (*E*)-isomer), 7.06–7.09 (6H, m, Tr-H), 7.16 (1H, s, pyrazole-H), 7.22–7.31 (9H, m, Tr-H); ^{13}C NMR of (*E*)-isomer (150 MHz, CDCl$_3$): δ 19.2, 53.7, 116.7, 126.6, 127.6, 127.9, 128.7, 130.3, 137.1, 138.9 (two carbon signals were deduced to have overlapped); (*Z*)-isomer: δ 15.4, 54.0, 115.4, 126.8, 126.9, 127.9, 128.6, 133.4, 137.0, 138.4 (two carbon signals were deduced to have overlapped); HREIMS *m*/*z* calcd. for $C_{13}H_{14}N_2O$ (M^+) 214.1106, found 214.1104.

(*E*/*Z*)-1-Benzyl-4-hydroxy-5-(1-(1-methyl)propen-1-yl)-1*H*-pyrazole (**5c**): *E*/*Z* ratio = ca. 1:1; oil; IR (film) υ_{max} 3063 (OH), 1563 (C=C), 1497 (C=C), 1456 (C=C) cm^{-1}; ^{1}H NMR of *E*/*Z* mixture (400 MHz, CDCl$_3$): δ 1.41 (1.6H, dd, *J* = 6.9, 1.5 Hz, -CH=CHC*H*$_3$), 1.73 (1.4H, dd, *J* = 6.8, 1.2 Hz, -CH=CHC*H*$_3$), 1.79 (3H, br s, C$_q$CH$_3$), 4.30 (0.47H, br s, -OH), 4.43 (0.53H, br s, -OH), 5.08 (0.9H, s, -NC*H*$_2$Ph), 5.15 (1.1H, s, -NC*H*$_2$Ph), 5.57 (0.47H, qq, *J* = 6.8, 1.6 Hz, -CCH=C*H*CH$_3$), 5.78 (0.53H, qq, *J* = 6.9, 1.6 Hz, -CCH$_3$=C*H*CH$_3$), 7.03 (0.94H, br d, *J* = 6.7 Hz, Ph-H), 7.07 (1.06H, br d, *J* = 6.7 Hz, Ph-H), 7.06–7.09 (6H, m, Ph-H), 7.16–7.36 (3H, m, Ph-H), 7.21 (1H, s, pyrazole-H); ^{13}C NMR of *E*/*Z* mixture (100 MHz, CDCl$_3$): δ 14.0, 15.0, 16.2, 32.0, 53.9, 54.1, 124.2, 124.6, 126.8, 127.2, 127.4, 127.5, 127.91, 127.94, 128.46, 128.49, 128.6, 129.8, 130.0, 132.6, 137.3, 137.6, 137.8; HREIMS *m*/*z* calcd. for $C_{14}H_{16}N_2O$ (M^+) 228.1263, found 228.1260.

(*E*/*Z*)-1-Benzyl-4-hydroxy-5-(1-(1-phenyl)propenyl)-1*H*-pyrazole (**5d**): isomer ratio = ca. 5:1; oil; IR (film) υ_{max} 3031 (OH), 1573 (C=C), 1496 (C=C) cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$): δ 1.55 (2.5H, d, *J* = 7.0 Hz, =CHC*H*$_3$), 1.85 (0.5H, d, *J* = 7.3 Hz, =CHC*H*$_3$), 4.61 (1H, br s, *J* = 14.8 Hz, -NC*H*HPh), 4.95 (1H, br s, *J* = 15.3 Hz, -NCH*H*Ph), 5.94 (0.16H, q, *J* = 7.2 Hz, C$_q$=C*H*CH$_3$), 6.31 (0.84H, br q, *J* = 7.0 Hz, C$_q$=C*H*CH$_3$), 6.87–6.90 (0.66H, m, Ph-H), 6.93–6.96 (1.34H, m, Ph-H), 7.06–7.34 (4H, m, Ph-H), 7.32 (1H, s, pyrazole-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.7, 54.3, 126.2, 127.0, 127.38, 127.45, 127.6, 128.3, 128.4, 128.6, 128.9, 129.3, 131.1, 136.9, 139.9 (minor isomer: 15.4, 54.0, 126.4, 127.68, 127.8); HREIMS *m*/*z* calcd. for $C_{19}H_{18}N_2O$ (M^+) 290.1419, found 290.1417.

(*E*/*Z*)-1-Benzyl-4-hydroxy-5-(1-(1-methoxycarbonyl)propenyl)-1*H*-pyrazole (**5e**): *E*/*Z* mixture in ca. 13:1 ratio; oil; IR (film) υ_{max} 3090 (OH), 1716 (C=O), 1507 (C=C), 1436 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.72 (2.6H, d, *J* = 7.3 Hz, -CH=CHC*H*$_3$ of major isomer), 1.83 (0.4H, d, *J* = 7.2 Hz, -CH=CHC*H*$_3$ of minor isomer), 3.66 (2.6H, s, -OC*H*$_3$ of major isomer), 3.71 (0.4H, s, -OC*H*$_3$ of minor isomer), 4.73 (1H, s, -OH), 5.06 (1.86H, s, -NC*H*$_2$Ph of major isomer), 5.17 (0.14H, s, -NC*H*$_2$Ph of minor isomer), 7.04 (2H, br d, *J* = 6.6 Hz, Ph-H), 7.19–7.30 (4H, m, Ph-H, =C*H*CH$_3$), 7.33 (1H, s, pyrazole-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 15.8, 52.3, 54.5, 122.2, 122.9, 127.3, 127.6, 128.1, 128.4, 136.7, 140.0, 147.5, 166.5; HREIMS *m*/*z* calcd. for $C_{15}H_{16}N_2O_3$ (M^+) 272.1161, found 272.1160.

4.4. O-Allylation of 1-Protected 5- or 3-Allyl-4-allyloxy-1H-pyrazoles (Scheme 1)

General procedure: To a solution of an *E*/*Z* mixture of 4-hydroxy-5-(1-propenyl)-1*H*-1-tritylpyrazole (**5a**) (0.410 g, 1.12 mmol) in acetone (2 mL), 20% aqueous NaOH (1 mL) and allyl bromide (142 μL, 1.68 mmol) were added. The reaction mixture was stirred for 1 h and then quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude residue was purified with column chromatography (eluent: hexane:EtOAc = 3:1) to afford 4-allyloxy-5-(1-propenyl)-1*H*-1-tritylpyrazole (**6a**) (*E*/*Z* mixture in ca. 3:1 ratio, 0.334 g, 73% yield).

(*E*)-**6a**: mp 152–155 °C; IR (KBr) υ_{max} 1567 (C=C), 1491 (C=C), 1446 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.40 (3H, dd, *J* = 6.7, 1.5 Hz, C*H*$_3$CH=), 4.50 (2H, dt, *J* = 5.3, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 5.26 (1H, dq, *J* = 15.8, 1.4 Hz, -CH$_2$CH=C*H*H), 5.37 (1H, dq, *J* = 17.2, 1.5 Hz, -CH$_2$CH=C*H*H), 5.46 (1H, dq, *J* = 15.8, 1.4 Hz, ArC*H*=CHCH$_3$), 6.04 (1H, ddt, *J* = 17.2, 10.5, 5.3 Hz, -OCH$_2$C*H*=CH$_2$), 6.14 (1H, dq, *J* = 15.8, 6.7 Hz, ArCH=C*H*CH$_3$), 7.07–7.16 (6H, m, Tr-H), 7.24–7.39 (9H, m, Tr-H), 7.32 (1H, s, pyrazole-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 18.9, 72.0, 79.0, 117.5, 120.0, 124.7, 127.3, 127.4, 127.6, 128.5, 130.3, 133.5, 142.9, 143.5; HREIMS *m*/*z* calcd. for $C_{28}H_{26}N_2O$ (M^+) 406.2055, found 406.2047.

(*Z*)-**6a**: mp 82–86 °C; IR (KBr) υ_{max} 1567 (C=C), 1491 (C=C), 1446 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.42 (3H, d, *J* = 5.1 Hz, C*H*$_3$CH=), 4.47 (2H, dt, *J* = 5.5, 1.6 Hz, -OC*H*$_2$CH=CH$_2$), 5.16–5.20

(2H, m), 5.22 (1H, dq, *J* = 10.6, 1.4 Hz, -CH_2CH=C*H*H), 5.34 (1H, dq, *J* = 17.2, 1.5 Hz, -CH_2CH=C*H*H), 6.00 (1H, ddt, *J* = 17.2, 10.6, 5.6 Hz, -OCH_2C*H*=CH_2), 7.03–7.17 (6H, m, Tr-H), 7.21–7.32 (9H, m, Tr-H), 7.37 (1H, s, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.4, 72.0, 78.9, 117.4, 117.9, 124.9, 127.2, 127.3, 127.9, 129.8, 130.1, 133.7, 142.6, 142.9; HREIMS *m*/*z* calcd. for $C_{28}H_{26}N_2O$ (M^+) 406.2046, found 406.2050.

(*E*/*Z*)-4-Allyloxy-1-benzyl-5-(1-propenyl)-1*H*-pyrazole (**6b**) (an inseparable *E*/*Z* mixture in a ca. 8:2 ratio, 0.334 g, 73% yield): oil; IR (film) υ_{max} 1566 (C=C), 1495 (C=C), 1452 (C=C) cm^{-1}; HREIMS *m*/*z* calcd. for $C_{16}H_{18}N_2O$ (M^+) 254.1419, found 254.1421. (*E*)-isomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.82 (3H, d, *J* = 6.7, 1.8 Hz, C*H*$_3$CH=), 4.50 (2H, dt, *J* = 5.4, 1.4 Hz, -OC*H*$_2$CH=CH_2), 5.26 (1H, dq, *J* = 10.6, 1.4 Hz, -CH_2CH=C*H*H), 5.28 (2H, s, NC*H*$_2$Ph), 5.39 (1H, ddd, *J* = 17.3, 3.2, 1.8 Hz, -CH_2CH=CH*H*), 6.05 (1H, ddt, *J* = 17.3, 10.6, 5.4 Hz, -OCH_2C*H*=CH_2), 6.16 (1H, br d, *J* = 15.8 Hz, ArC*H*=CHCH_3), 6.46 (1H, dq, *J* = 15.8, 6.7 Hz, -CH=C*H*CH_3), 7.07 (2H, br d, *J* = 7.6 Hz, Ph-H), 7.24 (1H, br t, *J* = 7.6 Hz, Ph-H), 7.26 (1H, s, pyrazole-H), 7.30 (2H, br t, *J* = 7.6 Hz, Ph-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.3, 53.9, 72.2, 116.6, 117.5, 125.8, 126.5, 126.8, 127.5, 128.6, 128.7, 129.6, 133.5, 137.2; (*Z*)-isomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.72 (3H, dd, *J* = 6.8, 1.8 Hz, C*H*$_3$CH=), 4.46 (2H, dt, *J* = 5.6, 1.5 Hz, -OC*H*$_2$CH=CH_2), 5.18 (2H, s, NC*H*$_2$Ph), 5.24 (1H, dq, *J* = 10.5, 1.5 Hz, -CH_2CH=C*H*H), 5.36 (1H, dq, *J* = 17.1, 1.5 Hz, -CH_2CH=CH*H*), 5.91 (1H, dq, *J* = 11.2, 6.8 Hz, -CH=C*H*CH_3), 6.01 (1H, ddt, *J* = 17.1, 10.5, 5.6 Hz, -OCH_2C*H*=CH_2), 6.01 (1H, br d, *J* = 11.2 Hz, ArC*H*=CHCH_3, overlapped), 7.07 (2H, br d, *J* = 7.6 Hz, Ph-H), 7.24 (1H, br t, *J* = 7.6 Hz, Ph-H), 7.28 (1H, s, pyrazole-H), 7.30 (2H, br t, *J* = 7.6 Hz, Ph-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 15.7, 53.9, 72.4, 115.4, 117.4, 126.59, 126.64, 127.5, 133.2, 137.1, 142.7 (three signals should be overlapped with signals of the (*E*)-isomer).

(*E*/*Z*)-4-Allyloxy-1-benzyl-5-(1-(1-methyl)propenyl)-1*H*-pyrazole (**6c**): isomer ratio = ca. 1:1; oil; IR (film) υ_{max} 1562 (C=C), 1496 (C=C), 1455 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (1.6H, dd, *J* = 6.7, 1.4 Hz, C*H*$_3$CH=), 1.72 (1.4H, dd, *J* = 6.9, 1.2 Hz, C*H*$_3$CH=), 4.414 (1.06H, d, *J* = 5.5 Hz, -OC*H*$_2$CH=), 4.417 (0.94H, d, *J* = 5.5 Hz, -OC*H*$_2$CH=), 5.08 (0.94H, s, NC*H*$_2$Ph), 5.19 (1.06H, s, NC*H*$_2$Ph), 5.19–5.36 (2H, m, =CH_2), 5.54 (0.44H, qq, *J* = 6.9, 1.6 Hz, -C(CH_3)*H*=CH_3), 5.75 (0.56H, qq, *J* = 6.8, 1.6 Hz, -C(CH_3)*H*=CH_3), 5.92–6.04 (1H, m, -CH_2C*H*=CH_2), 7.02 (0.94H, br d, *J* = 7.3 Hz, Ph-H), 7.07 (1.06H, br d, *J* = 7.2 Hz, Ph-H), 7.18–7.29 (3H, m, Ph-H), 7.29 (1H, s, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 15.2, 16.0, 23.1, 53.7, 54.0, 72.8, 117.45, 117.54, 125.0, 126.77, 126.86, 127.21, 127.3, 127.5, 128.46, 128.49, 129.0, 129.2, 129.5, 133.2, 133.7, 133.8, 137.3, 137.8, 141.6, 141.7; HREIMS *m*/*z* calcd. for $C_{17}H_{20}N_2O$ (M^+) 268.1576, found 268.1575.

(*E*/*Z*)-4-Allyloxy-1-benzyl-5-(1-(1-phenyl)propenyl)-1*H*-pyrazole (**6d**): isomer ratio = ca. 7:1; oil; IR (film) υ_{max} 1556 (C=C), 1500 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55 (2.7H, d, *J* = 6.9 Hz, C*H*$_3$CH=), 1.85 (0.3H, d, *J* = 7.3 Hz, C*H*$_3$CH=), 4.38 (0.25H, br d, *J* = 5.5 Hz, -OC*H*$_2$CH=), 4.44 (1.75H, br d, *J* = 3.9 Hz, -OC*H*$_2$CH=CH_2), 4.64 (1H, br d, *J* = 14.9 Hz, NC*H*HPh), 4.94 (1H, br d, *J* = 14.8 Hz, NCH*H*Ph), 5.19 (1H, dd, *J* = 10.5, 1.3 Hz, -CH_2CH=C*H*H), 5.29 (1H, dq, *J* = 17.2, 1.6 Hz, -CH_2CH=CH*H*), 5.89–6.99 (1H, m, -OCH_2C*H*=CH_2 overlaps with 0.12H, m, =C*H*CH_3), 6.31 (0.88H, q, *J* = 7.0 Hz, =C*H*CH_3), 6.89–6.90 (2H, m, Ph-H), 7.08–7.49 (8H, m, Ph-H), 7.39 (1H, s, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8, 54.3, 72.7, 117.5, 126.2, 127.0, 127.1, 127.4, 128.27, 128.33, 128.5, 129.2, 129.3, 131.2, 133.7, 137.0, 139.7, 143.3; HREIMS *m*/*z* calcd. for $C_{22}H_{22}N_2O$ (M^+) 330.1732, found 330.1729.

Synthesis of (*E*/*Z*)-4-allyloxy-1-benzyl-5-(1-(1-methoxycarbonyl)propenyl)-1*H*-pyrazole (**6e**) from **2e**: To an acetone solution (4.5 mL) of **2e** with a small amount of **5e** (121.8 mg, 0.45 mmol) in a microwave vial were added K_2CO_3 (61.8 mg, 0.45 mmol) in water (0.5 mL) and allyl bromide (0.04 mL, 0.45 mmol). After the reaction vial was sealed, the mixture was heated under microwave irradiation at 60 °C for 1 h. After it had cooled, the reaction was quenched by adding aqueous NH_4Cl. Then, the reaction mixture was extracted with EtOAc three times. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and then evaporated to give a crude residue, which was purified using column chromatography (eluent: hexane:EtOAc = 2:1) to give pure **6e** (117.1 mg, 84%).

6e (isomer ratio = ca. 13:1): oil; IR (film) υ_{max} 1717 (C=O), 1500 (C=C) cm^{-1}; ^1H NMR: δ 1.54 (2.6H, d, *J* = 7.2 Hz, C*H*$_3$CH= of major isomer), 2.12 (0.4H, d, *J* = 7.2 Hz, C*H*$_3$CH= of minor isomer), 3.52 (0.4H, s, -OC*H*$_3$ of minor isomer), 3.60 (2.6H, s, -OC*H*$_3$ of major isomer), 4.92 (0.93H, br d, *J* = 15.3 Hz, NCH*H*Ph of major isomer), 5.01 (0.14H, s, NC*H*$_2$Ph of minor isomer), 5.03 (0.93H, br d, *J* = 15.3 Hz, NC*H*HPh of major isomer), 5.11 (0.93H, dq, *J* = 10.6, 1.4 Hz, -CH$_2$CH=C*H*H of major isomer), 5.14 (0.07H, dq, *J* = 10.6, 1.5 Hz, -CH$_2$CH=C*H*H of minor isomer), 5.22 (0.93H, dq, *J* = 17.5, 1.6 Hz, -CH$_2$CH=CH*H* of major isomer), 5.23 (1H, dq, *J* = 17.4, 1.6 Hz, -CH$_2$CH=CH*H* of minor isomer), 5.87–5.93 (1H, m, -OCH$_2$C*H*=CH$_2$), 6.46 (0.07H, q, *J* = 7.3 Hz, -C$_q$=C*H*CH$_3$ of minor isomer), 7.06 (2H, br d, *J* = 6.6 Hz, Ph-H), 7.17–7.30 (3H, m, Ph-H), 7.20 (0.07H, q, *J* = 7.2 Hz, -C$_q$=C*H*CH$_3$ of major isomer), 7.32 (1H, s, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7, 52.0, 54.6, 72.5, 117.6, 122.0, 123.2, 126.4, 127.4, 127.6, 128.4, 133.4, 136.7, 143.2, 147.9, 165.9 (minor isomer: 16.2, 51.5, 54.1, 72.8, 121.5, 123.1, 126.6, 127.5, 136.9, 147.7); HREIMS *m*/*z* calcd. for $C_{18}H_{20}N_2O_3$ (M^+) 312.1474, found 312.1467.

4.5. Ring-Closing Metathesis of 6 to 1H-1,5-Dihydropyrano[3,2-c]pyrazoles **7** *(Table 1)*

General procedure (Table 1, entry 3): To a solution of **6a** (21.8 mg, 0.054 mmol) in CH_2Cl_2 (2 mL) was added Grubbs^{2nd} (1.7 mg, 2.7 mmol) at rt. The reaction mixture was stirred at rt for 1 h, and then the solvent was removed under reduced pressure, affording a crude residue, which was purified using silica gel column chromatography (eluent: EtOAc:hexane = 1:3) to afford **7a** (16.2 mg, 83%).

*General procedure for MW-aided reaction (Table 1, entry 5): To a solution of **6a** (16.4 mg, 0.04 mmol) in CH_2Cl_2 (2 mL) was added Grubbs^{2nd} (2.3 mg, 2.0 mmol) in a microwave vial. The reaction mixture was heated under microwave irradiation at 80 °C for 3 min. After the reaction mixture had cooled, the solvent was removed under reduced pressure, affording a crude residue, which was purified using silica gel column chromatography (eluent: EtOAc:hexane = 1:4) to afford **7a** (12.8 mg, 87%).

1,5-Dihydro-1-tritylpyrano[3,2-*c*]pyrazole (**7a**): oil; IR (film) υ_{max} 1677 (C=C), 1581 (C=C), 1493 (C=C), 1447 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.64 (2H, dd, *J* = 3.8, 1.8 Hz, -OC*H*$_2$CH=CH-), 5.15 (1H, dt, *J* = 10.2, 3.7 Hz, -OCH$_2$C*H*=CH-), 5.28 (1H, dtd, *J* = 10.2, 1.8, 0.8 Hz, -OCH$_2$CH=C*H*-), 7.08–7.17 (6H, m, Tr-H), 7.18 (1H, d, *J* = 0.8 Hz, pyrazole-H), 7.23–7.32 (9H, m, Tr-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 66.9, 78.0, 117.7, 118.6, 124.3, 127.55, 127.57, 130.1, 141.4, 142.7; HREIMS *m*/*z* calcd. for $C_{25}H_{20}N_2O$ (M^+) 364.1575, found 364.1585.

1-Benzyl-1,5-dihydropyrano[3,2-*c*]pyrazole (**7b**): oil; IR (film) υ_{max} 1566 (C=C), 1495 (C=C), 1452 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.75 (2H, dd, *J* = 3.9, 1.8 Hz, -OC*H*$_2$CH=), 5.21 (2H, s, ArC*H*$_2$Ph), 5.53 (1H, dt, *J* = 10.0, 3.9 Hz, -OCH$_2$C*H*=CH-), 6.34 (1H, br d, *J* = 10.0 Hz, -OCH$_2$CH=C*H*-), 7.10 (1H, d, *J* = 0.8 Hz, pyrazole-H), 7.10–7.14 (2H, d, *J* = 6.6 Hz, Ph-H), 7.26–7.32 (3H, m, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.0, 67.2, 115.5, 119.7, 124.5, 127.1, 127.9, 128.8, 136.6, 140.9; HREIMS *m*/*z* calcd. for $C_{13}H_{12}N_2O$ (M^+) 212.0950, found 212.0949.

1-Benzyl-1,5-dihydro-7-methylpyrano[3,2-*c*]pyrazole (**7c**): oil; IR (film) υ_{max} 1732 (C=O), 1541 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.96 (3H, br s, C$_q$C*H*$_3$), 4.64 (2H, dq, *J* = 3.3, 1.6 Hz, -OC*H*$_2$C*H*=), 5.23–5.26 (1H, m, -OCH$_2$C*H*=), 5.39 (2H, s, NC*H*$_2$Ph), 7.01 (2H, br d, *J* = 7.0 Hz, Ph-H), 7.17 (1H, s, pyrazole-H), 7.24–7.32 (3H, m, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.1, 55.3, 67.6, 116.5, 124.7, 126.0, 127.6, 127.3, 128.7, 137.7, 141.4; HREIMS *m*/*z* calcd. for $C_{15}H_{14}N_2O_3$ (M^+) 270.1004, found 270.1003.

1-Benzyl-1,5-dihydro-7-methoxycarbonylpyrano[3,2-*c*]pyrazole (**7e**): oil; IR (film) υ_{max} 1732 (C=O), 1541 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.76 (3H, s, -COOC*H*$_3$), 4.72 (2H, d, *J* = 4.5 Hz, -OC*H*$_2$CH=), 5.57 (2H, s, ArC*H*$_2$Ph), 6.45 (1H, t, *J* = 4.5 Hz, -OCH$_2$C*H*=C$_q$), 6.33 (1H, br d, *J* = 10.0 Hz, -OCH$_2$CH=C*H*-), 7.04 (2H, br d, *J* = 6.5 Hz, Ph-H), 7.23 (1H, *s*, pyrazole-H), 7.23–7.31 (3H, m, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.3, 56.4, 66.9, 124.0, 124.7, 127.0, 127.4, 128.4, 128.7, 137.5, 142.4, 163.8; HREIMS *m*/*z* calcd. for $C_{15}H_{14}N_2O_3$ (M^+) 270.1004, found 270.1003.

1-Benzyl-1,7-dihydropyrano[3,2-*c*]pyrazole (**8b**): oil; IR (film) υ_{max} 1607 (C=C), 1586 (C=C), 1557 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.23 (2H, dd, *J* = 3.3, 2.0 Hz, ArC*H*$_2$CH=), 4.77 (1H,

dt, *J* = 6.3, 3.4 Hz, -CH_2CH=CH-), 5.17 (2H, s, *Ar*CH_2Ph), 6.42 (1H, dt, *J* = 6.2, 2.0 Hz, =CH=C*H*O-), 7.06–7.20 (2H, m, Ph-H), 7.22–7.33 (4H, m, Ph-H, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 53.8, 97.1, 125.1, 126.4, 127.0, 127.9, 128.8, 129.0, 136.6, 141.3; HREIMS *m*/*z* calcd. for $C_{13}H_{12}N_2O$ (M^+) 212.0950, found 212.0947.

1-Benzyl-1,7-dihydro-7-methylenepyrano[3,2-*c*]pyrazole (**9c**): oil; IR (film) υ_{max} 1644 (C=C), 1556 (C=C), 1401 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (2H, br t, *J* = 5.6 Hz, -$OCH_2CH_2C_q$), 4.17 (2H, t, *J* = 5.7 Hz, -OCH_2CH_2-), 4.78 (1H, br s, C_qCH*H*), 4.96 (1H, br s, C_qCH*H*), 5.43 (2H, s, NCH_2Ph), 7.02 (2H, d, *J* = 7.0 Hz, Ph-H), 7.22–7.32 (4H, m, Ph-H, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.2, 55.4, 68.3, 107.2, 124.0, 125.3, 126.2, 127.5, 128.7, 129.7, 136.9, 142.6; HREIMS *m*/*z* calcd. for $C_{14}H_{14}N_2O$ (M^+) 226.1106, found 226.1102.

1,4-Bis((1-benzyl-5-(1-phenylprop-1-en-1-yl)-1*H*-pyrazol-4-yl)oxy)but-2-ene (**10d**): oil; IR (film) υ_{max} 1569 (C=C), 1496 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (6H, d, *J* = 7.1 Hz, =CHCH_3), 4.40 (4H, br s, -OCH_2CH=), 4.62 (2H, br d, *J* = 14.8 Hz, *Ar*C*H*HPh), 4.92 (2H, br d, *J* = 14.4 Hz, *Ar*CH*H*Ph), 5.82–5.84 (2H, m, -OCH_2CH=), 6.29 (2H, q, *J* = 7.1 Hz, =*CH*CH_3), 6.92–6.95 (4H, m, Ph-H), 7.06–7.25 (6H, m, Ph-H), 7.35 (2H, s, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8, 54.3, 71.6, 126.1, 127.1, 127.35, 127.42, 128.3, 128.7, 129.1, 129.2, 131.2, 137.0, 140.0, 143.2 (three carbon signals overlapped); HREIMS *m*/*z* calcd. for $C_{42}H_{40}N_4O_2$ (M^+) 632.3151, found 632.3145.

1,4-Bis((1-benzyl-5-(1-(methoxycarbonyl)prop-1-en-1-yl)-1*H*-pyrazol-4-yl)oxy)but-2-ene (**10e**): oil; IR (film) υ_{max} 1722 (C=O), 1712 (C=O), 1642 (C=C), 1573 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54 (5.4H, d, *J* = 7.0 Hz, =CHCH_3 of major isomer), 2.14 (0.6H, d, *J* = 7.2 Hz, =CHCH_3 of minor isomer), 3.61 (0.6H, s, -OCH_3 of minor isomer), 3.62 (5.4H, s, =CHCH_3 of major isomer), 4.42 (3.6H, br s, -OCH_2CH= of major isomer), 4.48 (0.4H, br s, -OCH_2CH= of minor isomer), 5.08 (1.8H, br d, *J* = 13.3 Hz, ArC*H*HPh of major isomer), 5.11 (0.4H, s, ArCH_2Ph of minor isomer), 5.12 (1.8H, br d, *J* = 13.3 Hz, ArCH*H*Ph of major isomer), 5.77 (3.6H, br t, *J* = 3.7 Hz, -OCH_2CH= of minor isomer), 5.88 (0.4H, br t, *J* = 3.7 Hz, -OCH_2CH= of major isomer), 6.28 (0.2H, q, *J* = 7.5 Hz, =*CH*CH_3 of minor isomer), 7.08 (4H, d, *J* = 6.8 Hz, Ph-H), 7.20–7.32 (7.8H, m, Ph-H, =*CH*CH_3 of major isomer), 7.33 (2H, s, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.7, 52.1, 54.6, 71.5, 122.1, 123.2, 126.4, 127.4, 127.6, 128.4, 128.5, 136.7, 147.9, 165.9; HREIMS *m*/*z* calcd. for $C_{34}H_{36}N_4O_6$ (M^+) 596.2635, found 596.2634.

Methyl 2-(1-benzyl-4-(cinnamyloxy)-1*H*-pyrazol-5-yl)but-2-enoate (**11e**): oil; IR (film) υ_{max} 1716 (C=O), 1644 (C=C), 1574 (C=C) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.58 (3H, d, *J* = 7.3 Hz, =CHCH_3), 3.58 (3H, s, -$COOCH_3$), 4.58 (2H, d, *J* = 6.2 Hz, -OCH_2CH=), 5.02 (1H, br d, *J* = 15.2 Hz, ArC*H*HPh), 5.12 (1H, br d, *J* = 15.2 Hz, ArCH*H*Ph), 6.30 (1H, dt, *J* = 15.9, 6.2 Hz, -OCH_2CH=CH-), 6.62 (1H, d, *J* = 15.9 Hz, -CH=C*H*Ph), 7.09 (2H, d, *J* = 7.3 Hz, Ph-H), 7.20–7.38 (8H, m, Ph-H), 7.30 (1H, q, *J* = 7.3 Hz, -C_q=*CH*CH_3), 7.40 (1H, s, pyrazole-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 15.8, 52.0, 54.7, 72.7, 122.2, 123.6, 124.7, 126.6, 126.9, 127.4, 127.6, 127.9, 128.4, 128.6, 133.1, 136.4, 136.7, 143.2, 147.9, 165.9; HREIMS *m*/*z* calcd. for $C_{24}H_{24}N_2O_3$ (M^+) 388.1787, found 388.1785.

*4.6. Synthesis of 5-Allyl-4-(2-haloethoxy)-1H-pyrazoles (***12***) (Scheme 2)*

General procedure: To a solution of **2a** (50.8 mg, 0.14 mmol) in acetone (2 mL) in a microwave vial were added 1,2-dibromoethane (0.05 mL, 0.56 mmol), 20% aqueous NaOH (0.11 mL, 0.56 mmol), and a catalytic amount of tetrabutylammonium bromide. The sealed reaction vial was MW irradiated at 140 °C for 30 min. After it had cooled, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The separated organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure to afford a crude residue. The residue was purified using silica gel column chromatography (eluent: EtOAc:hexane = 1:3) to afford **12a** (42.9 mg, 65%) as an oil.

5-Allyl-4-(2-bromoethoxy)-1*H*-1-tritylpyrazole (**12a**): pale yellow crystals (CH_2Cl_2); mp 135–140 °C; IR (film) υ_{max} 1581 (C=C), 1491 (C=C), 1446 (C=C) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.85 (2H, dt, *J* = 6.5, 1.2 Hz, ArCH_2CH=CH_2), 3.56 (2H, t, *J* = 6.2 Hz, -OCH_2CH_2CBr), 4.20 (2H, t, *J* = 6.2 Hz, -OCH_2CH_2Br), 4.63 (1H, dq, *J* = 17.0, 1.6 Hz, -CH=CH*H*), 4.66 (1H, dq, *J* = 10.0, 1.4 Hz, -CH=CH*H*), 4.97 (1H, ddt, *J* = 17.0, 10.0, 6.5 Hz, -CH_2CH=CH_2), 7.10–7.13 (6H, m, Tr-H), 7.25–7.30

(9H, m, Tr-H), 7.33 (1H, s, pyrazole-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.4, 31.2, 71.6, 78.7, 115.9, 125.6, 127.4, 127.6, 129.9, 130.1, 132.4, 142.8, 143.6; HREIMS *m*/*z* calcd. for $C_{27}H_{25}BrN_2O$ (M^+) 472.1151, found 472.1149.

5-Allyl-1-benzyl-4-(2-bromoethoxy)-1*H*-pyrazole (**12b**): oil; IR (film) υ_{max} 1583 (C=C), 1496 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.29 (2H, dd, *J* = 4.7, 1.7 Hz, ArCH_2CH=), 3.56 (2H, br t, *J* = 6.2 Hz, -OCH$_2$CH_2Br), 4.20 (2H, br t, *J* = 6.2 Hz, -OCH_2CH$_2$Br), 5.00 (1H, dd, *J* = 7.0, 1.4 Hz, -CH=CH*H*), 5.07 (1H, dd, *J* = 10.2, 1.4 Hz, -CH=CH*H*), 5.73–5.83 (1H, m, -CH$_2$C*H*=CH$_2$), 7.06 (2H, br d, *J* = 8.1 Hz, Bn-H), 7.25–7.33 (4H, m, Ph-H, pyrazole-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.1, 29.5, 53.9, 72.4, 116.5, 126.7, 127.2, 127.7, 127.8, 128.7, 133.6, 136.9, 141.6; HREIMS *m*/*z* calcd. for $C_{15}H_{17}BrN_2O$ (M^+) 320.0524, found 320.0520.

5-Allyl-4-(2-chloroethoxy)-1*H*-1-tritylpyrazole (**12$_{Cl}$**): white powder (CH_2Cl_2); mp 120–125 °C; IR (KBr) υ_{max} 1580 (C=C), 1493 (C=C), 1446 (C=C) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.85 (2H, br d, *J* = 7.6 Hz, ArCH_2CH=), 3.72 (2H, t, *J* = 5.7 Hz, -OCH$_2$CH_2Cl), 4.14 (2H, t, *J* = 5.7 Hz, -OCH_2CH$_2$CCl), 4.63 (1H, dq, *J* = 17.0, 1.6 Hz, -CH=CH*H*), 4.66 (1H, dq, *J* = 10.0, 1.4 Hz, -CH=CH*H*), 4.97 (1H, ddt, *J* = 17.0, 10.0, 6.7 Hz, -CH$_2$C*H*=CH$_2$), 7.10–7.14 (6H, m, Tr-H), 7.24–7.31 (9H, m, Tr-H), 7.34 (1H, s, pyrazole-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.2, 42.1, 71.7, 78.6, 115.8, 125.5, 127.3, 127.6, 129.9, 130.0, 132.4, 142.8, 143.7; HREIMS *m*/*z* calcd. for $C_{27}H_{25}ClN_2O$ (M^+) 428.1655, found 428.1654. *MW conditions: 160 °C, 30 min.

4.7. Reaction of **12** *with Potassium Tert-Butoxide (Table 2, Scheme 2)*

General procedure (Table 2, entry 7): To a solution of **12a** (28.8 mg, 0.05 mmol) in anhydrous THF:*t*-BuOH (2 mL:0.5 mL) in a microwave vial was added potassium *tert*-butoxide (28.8 mg, 0.26 mmol). The sealed reaction vial was MW irradiated at 130 °C for 1 h. After it had cooled, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The separated organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure to afford a crude residue. The residue was purified using silica gel column chromatography (eluent: EtOAc:hexane = 1:3) to afford **13a** (20.8 mg, 87%).

5-Allyl-1-trityl-1*H*-4-vinyloxypyrazole (**13a**): white powder (CH_2Cl_2); mp 75–80 °C; IR (KBr) υ_{max} 1639 (C=C), 1624 (C=C), 1566 (C=C) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.81 (2H, ddd, *J* = 6.8, 1.5, 1.2 Hz, ArCH_2CH=CH$_2$), 4.23 (1H, dd, *J* = 5.4, 1.8 Hz, -OCH=C*H*H), 4.50 (1H, dd, *J* = 13.8, 2.1 Hz, -OCH$_2$=CH*H*), 4.62 (1H, dq, *J* = 16.7, 1.5 Hz, -CH$_2$CH=C*H*H), 4.68 (1H, dq, *J* = 10.9, 1.5 Hz, -CH$_2$CH=CH*H*), 4.99 (1H, ddt, *J* = 16.5, 10.9, 2.1 Hz, -CH$_2$C*H*=CH$_2$), 6.53 (1H, dd, *J* = 13.8, 6.5 Hz, -OC*H*=CH$_2$), 7.12–7.14 (6H, m, Tr-H), 7.25–7.31 (9H, m, Tr-H), 7.40 (1H, s, pyrazole-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 31.1, 77.8, 91.3, 116.1, 127.4, 127.6, 128.3, 130.0, 131.7, 131.9, 140.4, 142.3, 150.7; HREIMS *m*/*z* calcd. for $C_{27}H_{24}N_2O$ (M^+) 392.1888, found 392.1880.

5-(1-Propenyl)-1-trityl-1*H*-4-vinyloxypyrazole (**14a**): white powder (CH_2Cl_2); mp 133–135 °C; IR (KBr) υ_{max} 1639 (C=C), 1560 (C=C), 1492 (C=C) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.39 (3H, dd, *J* = 6.8, 1.8 Hz, -CH=CHCH_3), 4.29 (1H, dd, *J* = 6.2, 2.0 Hz, -OCH=C*H*H), 4.59 (1H, dd, *J* = 13.8, 2.0 Hz, -OCH=CH*H*), 5.39 (1H, br dq, *J* = 15.8, 0.8 Hz, -C*H*=CHCH$_3$), 5.98 (1H, dq, *J* = 15.8, 6.8 Hz, -CH=C*H*CH$_3$), 6.56 (1H, dd, *J* = 13.8, 6.2 Hz, -OC*H*=CH$_2$), 7.11–7.15 (6H, m, Tr-H), 7.26–7.32 (9H, m, Tr-H), 7.38 (1H, br s, pyrazole-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 18.8, 79.8, 92.3, 119.1, 127.38, 127.44, 128.0, 129.1, 130.3, 131.2, 139.5, 142.7, 150.4; HREIMS *m*/*z* calcd. for $C_{27}H_{24}N_2O$ (M^+) 392.1889, found 392.1887.

(*E*/*Z*)-1-Benzyl-5-(1-propenyl)-1*H*-4-vinyloxypyrazole (**14b**): *E*/*Z* ratio = ca. 5:1; oil; IR (film) υ_{max} 1642 (C=C), 1562 (C=C), 1493 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68 (0.5H, d, *J* = 6.3 Hz, =CHCH_3 of (*Z*)-isomer), 1.82 (2.5H, dd, *J* = 6.6, 1.6 Hz, =CHCH_3 of (*E*)-isomer), 4.22 (0.17H, dd, *J* = 6.3, 2.0 Hz, -CH=C*H*H of (*Z*)-isomer), 4.29 (0.83H, dd, *J* = 6.3, 2.0 Hz, -CH=C*H*H of (*E*)-isomer), 4.57 (0.17H, dd, *J* = 13.7, 2.0 Hz, -CH=CH*H* of (*Z*)-isomer), 4.59 (0.83H, dd, *J* = 13.7, 2.0 Hz, -CH=CH*H* of (*E*)-isomer), 5.93 (0.17H, dq, *J* = 11.0, 6.5 Hz, -CH=C*H*CH$_3$ of (*Z*)-isomer), 5.98 (0.17H, br d, *J* = 11.0 Hz, Ar*CH*=CHCH$_3$ of (*Z*)-isomer), 6.11 (0.83H, br dq, *J* = 16.0, 1.6 Hz, Ar*CH*=CHCH$_3$ of (*E*)-isomer), 6.34

(0.83H, dq, *J* = 15.8, 6.8 Hz, -CH=C*H*CH_3 of (*E*)-isomer), 6.49 (0.17H, dd, *J* = 13.7, 6.3 Hz, -OC*H*=CH_2 of (*Z*)-isomer), 6.55 (0.83H, dd, *J* = 13.7, 6.3 Hz, -OC*H*=CH_2 of (*E*)-isomer), 7.07 (2H, br d, *J* = 7.0 Hz, Ph-H), 7.23–7.37 (3H, m, Ph-H), 7.33 (1H, br s, pyrazole-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 16.0 (minor), 19.3, 53.4 (minor), 54.0, 91.9 (minor), 92.3, 114.7 (minor), 115.9, 126.5, 126.9, 127.7, 128.7, 128.8, 129.0 (minor), 131.5, 134.2 (minor), 136.9, 138.5 (minor), 150.4 (minor), 150.5; HREIMS *m*/*z* calcd. for $C_{15}H_{16}N_2O$ (M^+) 240.1263, found 240.1256.

(*E*/*Z*)-4-(2-Methoxy)ethoxy-3-(1-propenyl)-2*H*-2-tritylpyrazole (**15**): oil; IR (film) υ_{max} 1492 (C=C), 1446 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (3H, d, *J* = 6.7 Hz, =CHCH_3), 3.65 (0.5H, br t, *J* = 4.1 Hz, -OC$H_2$$CH_2$Br), 3.7 (1.5H, br t, *J* = 4.1 Hz, -CH_2CH_2Br), 4.07 (0.5H, br t, *J* = 3.9 Hz, -CH_2CH_2Br), 3.70 (1.5H, br t, *J* = 4.1 Hz, -OC$H_2$$CH_2$Br), 5.44 (1H, br d, *J* = 15.8 Hz, (*E*)-ArC*H*=CH-), 6.09–6.18 (1H, m, -CH=C*H*CH_3), 7.11–7.20 (6H, m, Tr-H), 7.24–7.29 (9H, m, Tr-H), 7.32 (1H, s, pyrazole-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 18.9, 59.2, 70.6, 71.3, 79.0, 119.9, 124.8, 127.3, 127.4, 127.6, 130.1, 130.4, 142.9, 143.7; HREIMS *m*/*z* calcd. for $C_{28}H_{28}N_2O_2$ (M^+) 424.2151, found 424.2157.

4-(2-Methoxy)ethoxy-3-(2-propenyl)-2*H*-2-tritylpyrazole (**16**): oil; IR (film) υ_{max} 1580 (C=C), 1447 (C=C) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.84 (2H, br d, *J* = 6.5 Hz, ArCH_2CH=), 3.41 (3H, s, -OCH_3), 3.66 (1H, br t, *J* = 5.0 Hz, -OC$H_2$$CH_2$O-), 4.05 (2H, br t, *J* = 5.0 Hz, -OCH_2CH_2O-), 4.60 (1H, dq, *J* = 17.0, 1.7 Hz, -CH=C*H*H), 4.64 (1H, dq, *J* = 10.5, 1.5 Hz, -CH=CH*H*), 7.10–7.13 (6H, m, Tr-H), 7.23–7.33 (9H, m, Tr-H), 7.34 (1H, s, pyrazole-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 31.2, 59.2, 71.2, 71.4, 78.5, 115.6, 125.5, 127.3, 127.6, 127.9, 130.1, 132.6, 143.0, 144.4; HREIMS *m*/*z* calcd. for $C_{28}H_{28}N_2O_2$ (M^+) 424.2151, found 424.2157.

4.8. RCM of **13a** *and* **14a** *and* **14b**

The RCM reactions of **13a** and **14a** and **14b** in Scheme 2 were carried out as described above.

1,7-Dihydro-1-tritylpyrano[3,2-*c*]pyrazole (**8a**): oil; IR (film) υ_{max} 1583 (C=C), 1493 (C=C), 1446 (C=C) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.27 (2H, dd, *J* = 3.5, 2.0 Hz, ArCH_2CH=CH-), 4.49 (1H, dt, *J* = 6.5, 3.5 Hz, -OCH=C*H*CH_2-), 6.33 (1H, dt, *J* = 6.4, 2.0 Hz, -OC*H*=CHCH_2-), 7.12–7.15 (6H, m, Tr-H), 7.26–7.32 (9H, m, Tr-H), 7.32 (1H, s, pyrazole-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 22.5, 29.7, 78.6, 98.2, 124.3, 127.6, 127.6, 127.9, 130.4, 140.3, 142.6; HREIMS *m*/*z* calcd. for $C_{25}H_{20}N_2O$ (M^+) 364.1575, found 364.1576.

4.9. Acid-Catalyzed Hydrolysis of **6a** *(Scheme 3)*

To a solution of **6a** (121.5 mg, 0.30 mmol) in acetone (10 mL) was added 1 N aqueous HCl (0.6 mL). The reaction mixture was warmed under reflux for 90 min with stirring. After the reaction mixture had cooled, it was treated with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The separated organic layer was dried over $MgSO_4$, filtered, and condensed under reduced pressure to give a crude residue, which was purified using silica gel column chromatography (eluent: EtOAc:hexane = 1:2) to afford (*Z*)-**18** (9.1 mg, 20%) and (*E*)-**18** (14.2 mg, 31%).

(*E*)-4-Allyloxy-5-(1-propenyl)-1*H*-pyrazole ((*E*)-**18**): oil; IR (film) υ_{max} 1568 (C=C), 1516 (C=C) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.89 (3H, br d, *J* = 6.0 Hz, CH_3CH=), 4.60 (2H, dt, *J* = 5.5, 1.5 Hz, -OCH_2CH=CH_2), 4.46 (1H, dq, *J* = 10.0, 1.5 Hz, -CH=C*H*H), 5.40 (1H, dq, *J* = 17.3, 1.5 Hz, -CH=CH*H*), 6.04 (1H, ddt, *J* = 17.3, 10.5, 5.5 Hz, -OCH_2C*H*=CH_2), 6.34 (1H, d, *J* = 16.7 Hz, ArC*H*=CH-), 6.35–6.41 (1H, m, -CH=C*H*CH_3), 7.22 (1H, s, pyrazole-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 18.9, 72.7, 117.7, 118.7, 127.6, 133.4, 142.0; HREIMS *m*/*z* calcd. for $C_9H_{12}N_2O$ (M^+) 164.0950, found 164.0950.

(*Z*)-4-Allyloxy-5-(1-propenyl)-1*H*-pyrazole ((*Z*)-**18**): oil; IR (film) υ_{max} 1570 (C=C), 1524 (C=C), 1450 (C=C) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.98 (3H, dd, *J* = 7.0, 1.8 Hz, CH_3CH=), 3.49 (3H, s, -OCH_3), 4.45 (2H, dt, *J* = 5.2, 1.5 Hz, -OCH_2CH=CH_2), 5.27 (1H, dq, *J* = 10.6, 1.5 Hz, -CH=C*H*H), 5.38 (1H, dq, *J* = 17.0, 1.5 Hz, -CH=CH*H*), 5.82 (1H, dq, *J* = 11.4, 7.0 Hz, -CH=C*H*CH_3), 6.03 (1H, ddt, *J* = 17.3, 10.6, 5.3 Hz, -OCH_2C*H*=CH_2), 6.27 (1H, dq, *J* = 11.5, 1.5 Hz, ArC*H*=CHCH_3), 7.27 (1H, s, pyrazole-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 69.1, 69.3, 117.7, 118.7, 127.6, 133.4, 142.0; HREIMS *m*/*z* calcd. for $C_9H_{12}N_2O$ (M^+) 164.0950, found 164.0949.

4.10. Reprotection of **18** *(Scheme 3)*

General procedure: To a stereo mixture of (*E*/*Z*)-**18** (15.9 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) were added TrCl (43.0 mg, 0.15 mmol) and Et_3N (0.022 mL, 0.15 mmol) at 0 °C. The reaction mixture was stirred at rt overnight, and then quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and condensed under reduced pressure to give a crude residue, which was purified using silica gel column chromatography (eluent: EtOAc:hexane = 1:4) to afford **19a** (28.9 mg, 68%) as an oil.

(*E*/*Z*)-4-Allyloxy-3-(1-propenyl)-1*H*-1-tritylpyrazole (**19a**): oil; IR (film) υ_{max} 1560 (C=C), 1491 (C=C), 1445 (C=C) cm^{-1}; ^1H NMR of (*E*)-isomer (600 MHz, $CDCl_3$): δ 1.90 (3H, dd, *J* = 7.1, 1.8 Hz, C*H*$_3$CH=CH-), 4.27 (2H, dt, *J* = 5.6, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 5.20 (1H, ddd, *J* = 10.6, 3.2, 1.5 Hz, -CH$_2$CH=CH*H*), 5.28 (1H, ddd, *J* = 17.0, 3.2, 1.8 Hz, -CH$_2$CH=C*H*H), 5.75 (1H, dq, *J* = 11.5, 7.1 Hz, -CH=C*H*CH$_3$), 5.95 (1H, ddt, *J* = 17.3, 10.7, 5.6 Hz, -OCH$_2$C*H*=CH$_2$), 6.29 (1H, dq, *J* = 11.5, 1.5 Hz, ArC*H*=CHCH$_3$), 6.84 (1H, s, pyrazole-H), 7.14–7.18 (6H, m, Tr-H), 7.26–7.30 (9H, m, Tr-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (14.2), 15.6, (60.4), 72.9, 78.6, (117.4), 117.6, 117.7, 127.4, 127.5, (127.6), 127.9, 130.4, 133.3, (138.6), (142.0), 143.4, signals in parentheses correspond to some of those of the (*Z*)-isomer; HREIMS *m*/*z* calcd. for $C_{28}H_{26}N_2O$ (M^+) 406.2045, found 406.2040.

(*E*)-4-Allyloxy-1-benzyl-3-(1-propenyl)-1*H*-pyrazole (**19b**): oil; IR (film) υ_{max} 1566 (C=C), 1496 (C=C), 1445 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.87 (3H, dd, *J* = 6.3, 1.2 Hz, C*H*$_3$CH=CH-), 4.35 (2H, dt, *J* = 5.4, 1.5 Hz, -OC*H*$_2$CH=CH$_2$), 5.16 (2H, s, ArC*H*$_2$Ph), 5.24 (1H, dq, *J* = 10.5, 1.5 Hz, -CH$_2$CH=CH*H*), 5.36 (1H, dq, *J* = 17.2, 1.6 Hz, -CH$_2$CH=C*H*H), 6.00 (1H, ddt, *J* = 17.2, 10.5, 5.4 Hz, -OCH$_2$C*H*=CH$_2$), 6.40 (1H, br d, *J* = 16.3 Hz, ArC*H*=CHCH$_3$), 6.53 (1H, dq, *J* = 16.3, 6.3 Hz, ArCH=C*H*CH$_3$), 6.92 (1H, s, pyrazole-H), 7.18 (2H, br d, *J* = 8.0 Hz, Ph-H), 7.26–7.35 (3H, m, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 56.5, 72.6, 114.7, 117.6, 121.4, 127.4, 127.9, 128.7, 133.2, 136.8, 138.4, 143.1; HREIMS *m*/*z* calcd. for $C_{16}H_{18}N_2O$ (M^+) 254.1419, found 254.1416.

4.11. RCM of **19**

The RCM reactions of **19** were carried out in a similar manner to that described above to afford **20**.

2,5-Dihydro-2-tritylpyrano[3,2-*c*]pyrazole (**20a**): oil; IR (film) υ_{max} 1492 (C=C), 1447 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.76 (2H, dd, *J* = 2.9, 1.9 Hz, -OC*H*$_2$CH=CH-), 5.72 (1H, dt, *J* = 10.2, 3.5 Hz, -OCH$_2$C*H*=CH-), 6.62 (1H, br d, *J* = 10.0 Hz, -OCH$_2$CH=C*H*Ar), 6.80 (1H, s, pyrazole-H), 7.18–7.20 (6H, m, Tr-H), 7.28–7.31 (9H, m, Tr-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 67.2, 78.0, 116.5, 120.1, 122.7, 126.5, 127.6, 127.7, 137.5, 139.1, 143.3; HREIMS *m*/*z* calcd. for $C_{25}H_{20}N_2O$ (M^+) 364.1575, found 364.1584.

2-Benzyl-2,5-dihydropyrano[3,2-*c*]pyrazole (**20b**): oil; IR (film) υ_{max} 1660 (C=C), 1576 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.77 (2H, dd, *J* = 3.5, 1.9 Hz, -OC*H*$_2$CH=CH-), 5.73 (1H, dt, *J* = 10.0, 3.5 Hz, -OCH$_2$C*H*=CH-), 6.63 (1H, dt, *J* = 10.0, 1.9 Hz, -OCH$_2$CH=C*H*Ar), 6.84 (1H, s, pyrazole-H), 7.18–7.20 (2H, br d, *J* = 6.5 Hz, Ph-H), 7.27–7.36 (3H, m, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.4, 67.2, 113.3, 119.5, 122.3, 127.5, 128.0, 128.8, 136.6, 137.2, 140.5; HREIMS *m*/*z* calcd. for $C_{13}H_{12}N_2O$ (M^+) 212.0949, found 212.0950.

Author Contributions: Y.U. and K.S. conceived and designed the experiments; K.S., A.K., Y.T., and Y.U. performed the experiments; Y.U., H.Y., and S.H. wrote the paper.

Funding: This research received no external funding.

Acknowledgments: The authors are grateful to K. Minoura and M. Fujitake for NMR and MS measurements, respectively. Y. Suzuki, R. Nakamura, K. Hashimoto, and H. Matsukawa of our laboratory group are also appreciated for their experimental assistance. We would like to thank Editage (www.editage.jp) for English language editing.

Conflicts of Interest: The authors declare no conflicts of interest.

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Sample Availability: Samples of the compounds are not available from the authors.