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[1,2]-Wittig Rearrangement of THP Acetal Compounds: Facile Synthesis of Aromatic Tertiary Alcohols

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Abstract: Several *sec*-aromatic THP acetal compounds have been found to be suitable substrates for the [1,2]-Wittig rearrangement in the absence of an external electrophile, which resulted in the generation of new carbon-carbon bond and the facile synthesis of aromatic tertiary alcohols. More interestingly, an unexpected effect of chlorotrimethylsilane on this [1,2]-Wittig rearrangement of *sec*-aromatic THP acetal compounds was found, in which two different products involving oxidative procedure were obtained due to the competitive [1,4]-Sigmatropic rearrangement versus [1,2]-Wittig rearrangement.

Keywords: Wittig rearrangement; acetal compound; alcohol; radical reaction; organosilicon

1. Introduction

Since the first example of Wittig rearrangement reported in 1942[1], past over half of century has witnessed extensive studies of this rearrangement, especially [2,3]-Wittig rearrangement, for organic synthesis and mechanistic processes.[2-7] The original Wittig rearrangement, which is now called '[1,2]-Wittig rearrangement', is the transformation of an α-lithiated ether into a lithium alkoxide by migration of a R group from the oxygen to the α-carbon atom. Despite potentially useful carbon-carbon bond forming reactions and many reports on mechanistic or stereochemical studies, [1,2]-Wittig rearrangement of synthetically useful levels has not so far been reported except for a few examples, mainly because of the rather low yields and the restricted range of substrates.[8-16]. The [1,2]-Wittig rearrangement is now widely recognized to proceed by a radical dissociation-recombination mechanism.[17-21] In the past decades, this rearrangement of substituted ethers with electron-withdrawing group, such as a ketone[22], ester[23], amide[24], imino[25-26], or imidazolium group[27], have been reported.

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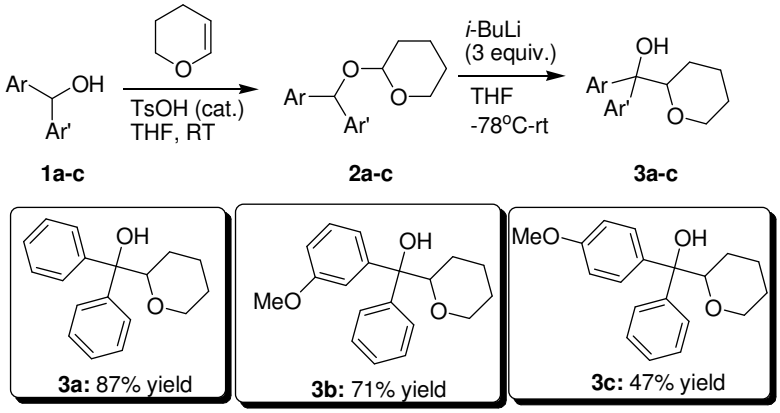
Although the [1,2]-Wittig rearrangement of allyl or benzyl acetals derived from *O*-glycosides have been examined by Nakai, Tomooka[11, 12], and Gärtner[28,29], the extension of [1,2]-Wittig rearrangement to broader type of acetal substrates is a challenge and highly desirable.[30] In general, the [1,2]-Wittig rearrangement of acetal systems usually suffers from rather low yields and a limited range of substrates.[31, 32]. For example, in 1994, Nakai et al.[33] have studied the [1,2]-Wittig rearrangement of tetrafuranyl ethers through the Sn/Li transmetalation-induced process. However, the reaction with *n*-BuLi gave the Wittig product in 0 or 16% yield according to different structure. Being interested in the tertiary alcohols produced by this reaction and in an effort to enhance the synthetic utility of the classic [1,2]-Wittig rearrangement, we started to investigate the Wittig rearrangement of THP acetyl compounds derived from the protection of alcohols with simple 3,4-dihydro-2*H*-pyran[34,35]. Thus, we would like to report herein the [1,2]-Wittig rearrangement of THP acetal systems generated from 3,4-dihydro-2*H*-pyran in order to have an access to aromatic tertiary alcohols with pyran moiety. Furthermore, in this paper we report a novel and unexpected side reaction involving [1,4]-Sigmatropic rearrangement versus [1,2]-Wittig rearrangement in the presence of chlorotrimethylsilane (TMSCl). The effect of TMSCl on the competitive reaction of [1,4]-Sigmatropic rearrangement versus [1,2]-Wittig rearrangement has been discussed on the basis of experimetal results.

2. Results and discussion

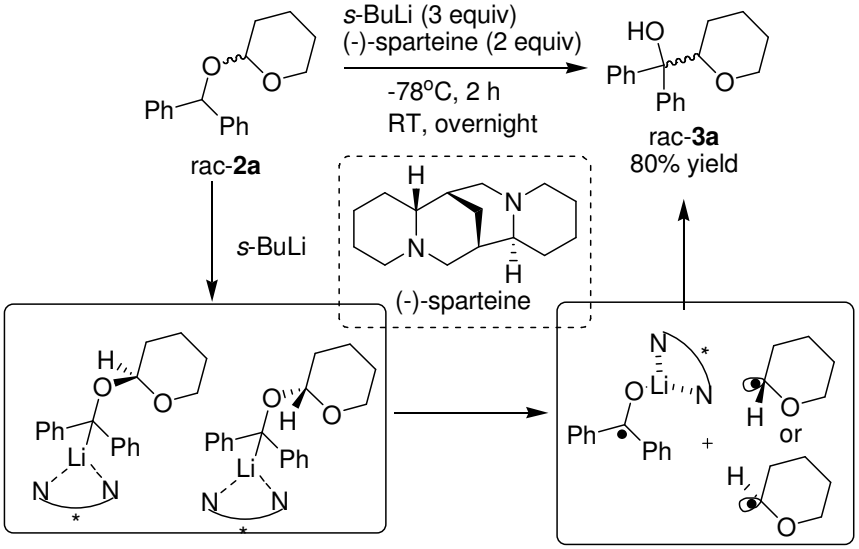
As a starting point for the development of the [1,2]-Wittig rearrangement of THP acetal compounds for the synthesis of tertiary alcohols, we initially studied rearrangement of the aromatic THP acetal compounds **2** generated from diarylmethanol and 3,4-dihydro-2*H*-pyran (Scheme 1).[36,37] As expected, the rearrangement of a substrate such as **2a** occurred smoothly after the treatment with *i*-butyllithium (2.0-3.0 equiv.) in tetrahydrofuran (THF) at -78°C-rt overnight and gave a tertiary alcohols **3a-c** containing pyran moiety, arising from selective [1,2]-Wittig rearrangement, in good yields. Although only three different substrates was shown to be effective in this [1,2]-Wittig rearrangement, these results certainly implied that aromatic THP acetal compounds **2** underwent deprotonation followed by a rearrangement step.



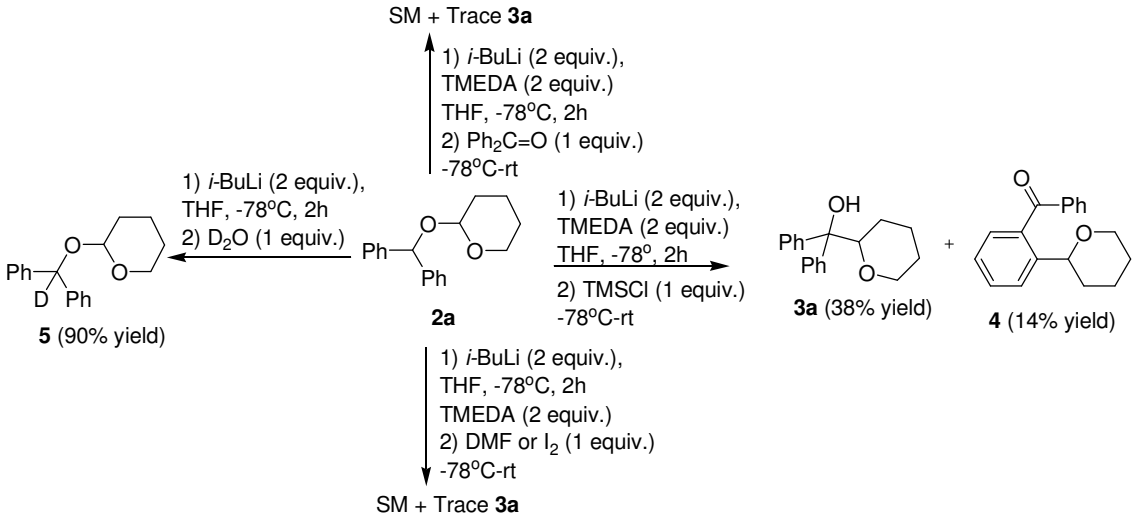
Scheme 1. Model [1,2]-Wittig rearrangement of the THP acetal compounds

To probe the effect of chiral stoichiometric ligand in the first step of deprotonation and subsequent rearrangement that could be considered with possible stereoselective induction or

asymmetric kinetic resolution, (-)-sparteine, an excellent chiral auxiliary for asymmetric lithiation-substition reaction[38-40], was used in the [1,2]-Wittig rearrangement of **2a**. However, racemic **3a** was generated and this model study revealed that there was no stereoselective activity in the lithiation in the presence of (-)-sparteine because the key step of rearrangement proceeded completely involving a radical dissociation/recombination process (Scheme 2).



Scheme 2. Chiral (-)-sparteine mediated [1,2]-Wittig rearrangement

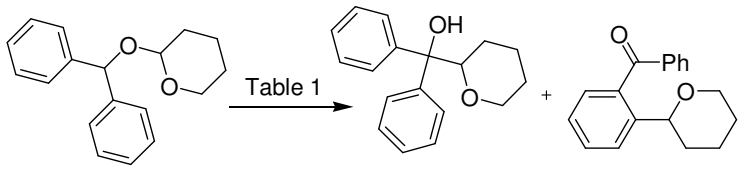


Scheme 3. The lithiation and subsequent possible substitution: the effect of electrophiles

Despite the fact that [1,2]-Wittig rearrangement of aromatic THP acetal compounds presents potential application in the synthesis of useful pyran derivatives, the presence of two oxygen-atom is an additional interesting parameter for the complexation of lithiated species because of its three possible reactive sites. However, to our knowledge, there was no report on the lithiation-substituion of

aromatic THP acetal compounds. Thus, the lithiation and subsequent possible substitution was carried out by using of 2.0 equiv of *i*-BuLi, 2.0 equiv of TMEDA (tetramethylethane-1,2-diamine), and substrate **2a**, at -78°C for 2 h, subsequent trapping with different electrophiles, such as TMSCl (chlorotrimethylsilane), iodine, DMF (N,N-dimethylformamide), and benzophenone (Scheme 3). Unfortunately, except the coupling reaction of TMSCl, no or only trace [1,2]-Wittig rearrangement product **3a** was obtained. The starting material **2a** was recovered in most cases. Interestingly, in the case of TMSCl used as additive, the major side product is not silicon-based derivative but a novel unexpected rearrangement product **4**. Although the yield of **4** is not good at present (14%), the studies and modification of reaction conditions is highly desired. Firstly, we wondered whether *ortho*-lithium of one aromatic ring would be a major contribution to the unexpected process. However, the deuterium labeling experiment showed only deuterated acetal compound **5** was isolated (Scheme 3). This revealed that the unexpected [1,4]-Sigmatropic rearrangement would be achieved from the partial silylation of lithiated intermediate.

Table 1. The Effect of TMSCl in the [1,2]-Wittig rearrangement of THP acetal compound[a]



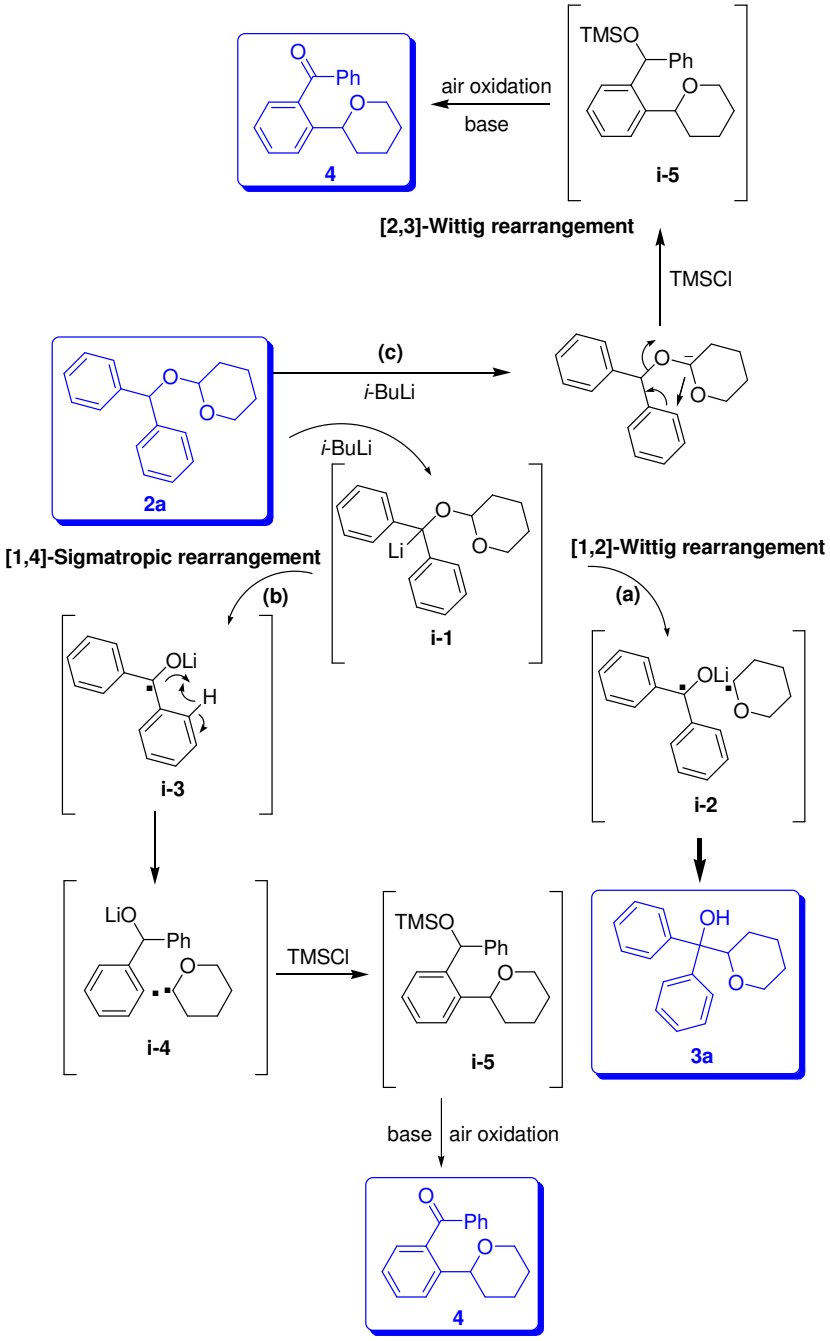
2a **3a** **4**

Entry	*i*-BuLi (equiv.)	TMEDA (equiv.)	Silane (x equiv.)	Time (h)	3a[b] (yield%)	4[b] (yield%)	3/4
1	3	2	0	20	87	0	-
2	2	2	(TMSCl)/1	20	38	14	2.7:1
3	3	2	(TMSCl)/1	20	81	8[c]	10:1
4	3	1	(TMSCl)/1	20	40	12[c]	3.3:1
5	3	0	(TMSCl)/1	20	64	22(15)[c]	2.9:1
6	4	2	(TMSCl)/2	22	79	4	20:1
7	3	3	(TMSCl)/1	20	70	5	14:1
8	1	1	(TMSCl)/1	20	-[d]	-	-
9	3	0	TBSCl/1	20	87	0	-
10	3	0	TBDPSCl/1	20	72	0	-

[a] The reaction was carried out at -78°C for 2 h and then stirred at room temperature.
[b] GC yields according to an internal standard.
[c] Isolated yields.
[d] No product was determined.

With these observations in hand, several experiments were performed in the presence of different amount of tetramethylethane-1,2-diamine (TMEDA) and chlorotrimethylsilane (TMSCl), *tert*-butyldimethylsilyl chloride (TBSCl), or *tert*-butyl diphenylchlorosilane (TBDPSCl), and the details for experimental parameters and results with regard to conversion, yield of product of [1,2]-Wittig rearrangement and as well as [1,4]-Sigmatropic rearrangement in all cases are presented in Table 1. As shown in Table 1, the addition of 1.0 equiv of TMSCl in the presence of 2.0 to 3.0 equiv with or without TMEDA resulted in better conversion (Entries 2-5) in accordance with product **4**, and up to 15% isolated yield could be obtained under suitable conditions (Entry 5). Interestingly, TBSCl and TBDPSCl resulted in no observation of any product of [1,4]-Sigmatropic rearrangement, it maybe due to the bulky group of these silanes. It is also worthy of note that the increase of the amount of *i*-BuLi from 3.0 to 6.0 equiv restrained the formation of side product.

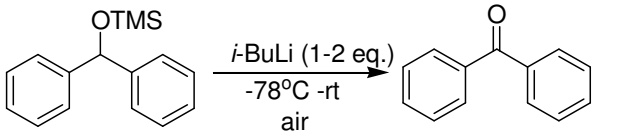
[1,2]-Wittig rearrangement of THP



Scheme 4. Proposed mechanism of competitive [1,4]-Sigmatropic rearrangement and Wittig rearrangement

With the competitive [1,2]-Wittig rearrangement and [1,4]-Sigmatropic rearrangement reaction in hand, a mechanistic discussion of these observations is extremely interesting based on above experimental results. The classic [1,2]-Wittig rearrangement for the formation of product **3** is easily acceptable and understandable with the process of radical dissociation and recombination via **2a**→***i-1***→***i-2***→**3a** (Scheme 4). Since we were not able to isolate neither the original carbanion nor the intermediate (***i-3-5***) deriving from the possible [1,4]-Sigmatropic rearrangement [41-43], it is not easy to determine the pathways followed by the system. However, the obtaining of product **4** and the

deuterium labeling experiment let us consider the possibility of **2a**→***i-3***→***i-4***→***i-5***→**4** in this process based on previous mechanistical studies [3,6,20]. In the last step of oxidation of lithium enolate, it is similarly to the oxidation of *sec*-aromatic alcohols could be promoted by strong base [44-45]. To gain support for the hypothesis of the silane-induced air oxidation, we made use of the model reaction of benzhydryloxytrimethylsilane with 1 equiv. of *i*-BuLi (Scheme 5). As expected, the desired product, benzophenone, was detected in this reaction, which supported that the mechanism of unexpected reaction to product **4** involving a oxidative procedure under basic conditions.



Scheme 5. Strong base promoted deprotection-oxidation of silyl ether.

3. Conclusion

In summary, the above results indicate that the [1,2]-Wittig rearrangement of *sec*-aromatic THP acetal compounds occurred smoothly in the presence of *i*-BuLi, which resulted in the facile synthesis of aromatic tertiary alcohols. In addition, we have shown an unexpected [1,4]-Sigmatropic rearrangement reaction was occurred to the finding of a novel side product based on a silicon-affected Wittig rearrangement. The effect of TMSCl on the competitive reaction of [1,4]-Sigmatropic rearrangement versus [1,2]-Wittig rearrangement has been investigated on the basis of experimetal results. Despite the yield of unexpected product is not good, some promising results that the silane-induced [1,4]-Sigmatropic rearrangement and air oxidation have been observed in the competitive [1,2]-Wittig rearrangement and [1,4]-Sigmatropic rearrangement in the presence of chlorotrimethylsilane (TMSCl). Further studies to widen the range of substrates amenable to this type of Wittig rearrangement are under investigation based on these findings and will be reported in due course.

4. Experimental

All reactions were performed in flame-dried and septum-sealed flasks under an atmosphere of argon. Solvents and reagents were transferred by means of syringes. THF was distilled from sodium. All reagents were used as purchased unless otherwise noted. *i*-BuLi was a commercial solution in hexanes (1.23 M) and used directly. Silica gel (200-300 mesh) was used for column chromatography. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 and 100 MHz, respectively on Advance (Brucker) 400 MHz Nuclear Magnetic Resonance Spectrometer, and were referenced to the internal solvent signals. IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer. EI and CI mass spectra were performed on a Trace DSQ GC/MS spectrometer. Data are reported in the form of (m/z). Compounds **2** were prepared by stirring a solution of the corresponding diarylmethanols and 3,4-Dihydro-2H-Pyran in THF catalyzed by TsOH and were simple known compounds [36, 37].

4.1.General procedure for the [1,2]-Wittig rearrangement reaction of THP Acetal compounds 2:

T he [1,2]-Wittig rearrangements were performed by stirring a solution of the acetal compounds **2** (5 mmol) in anhydrous THF (30 mL) at -78°C, followed by the addition of a solution of *i*-BuLi in hexane (1.23 M, 3.0 equiv) under N_2. The mixture was allowed to warm slowly to room temperature, then the mixture was stirred at room temperature overnight. After the reaction is completed, the

reaction was quenched with water and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude products were purified by column chromatography (silica gel: petroleum ether/EtOAc, 20/1) to afford the pure tertiary alcohols.

Diphenyl(tetrahydro-2*H*-pyran-2-yl)methanol 3a: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.64-1.45 (m, 5H), 1.85 (m, 1H), 3.24 (s, 1H), 3.61 (dt, 1H, J = 3.0 Hz, 8.0 Hz), 4.06 (m, 1H), 4.24 (m, 1H), 7.55-7.16 (m, 10H). ^{13}C NMR(100MHz, $CDCl_3$), δ = 23.4, 24.9, 25.9, 68.8, 79.2, 80.2, 125.8, 126.5, 126.8, 126.9, 127.97, 128.02, 143.9, 146.6. GC-MS, m/z (%):266 (1) [M+], 250 (2), 183 (81), 105 (66), 85 (100). IR (KBr): ν = 3494, 3086, 3057, 2946, 2856, 1598, 1491, 1470, 1449, 1306, 1267, 1201, 1186, 1088, 1063, 1044, 874 cm^{-1}.

(3-Methoxyphenyl)(phenyl)(tetrahydro-2*H*-pyran-2-yl)methanol 3b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61-1.41(m, 5H), 1.80 (m, 1H), 3.56 (m, 1H), 3.75 (s, 3H), 3.84 (d, 1H, J = 4 Hz), 4.02 (m,1H), 4.14 (m,1H), 7.52-6.67 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$), δ = 23.3, 24.9, 25.9, 55.2, 68.8, 79.2, 80.3, 111.8, 113.1, 119.1, 125.7, 126.6, 128.0, 128.9, 143.6, 148.2, 159.4. GC-MS, m/z (%): 298 (5) [M+], 213 (92), 135 (18), 105 (100), 85 (96). IR (KBr): ν = 3470, 2939, 2832, 1610, 1585, 1450, 1380, 1243, 1208, 1047, 772 cm^{-1}.

(4-Methoxyphenyl)(phenyl)(tetrahydro-2*H*-pyran-2-yl)methanol 3c: ^{1}H NMR(400 MHz, $CDCl_3$): δ = 1.59-1.37 (m, 5H), 1.82 (m, 1H), 3.15 (s, 1H), 3.57 (dt, 1H, J = 4.0 Hz, 12.0 Hz), 3.74 (s, 3H), 4.02 (m, 1H), 4.15 (m, 1H), 7.50-6.67 (m, 9H). ^{13}C NMR (100MHz, $CDCl_3$), δ = 23.4, 24.9, 25.9, 29.7, 55.2, 79.0, 80.32, 113.3, 126.7, 126.8, 127.0, 128.0, 136.2, 146.7, 158.2. GC-MS, m/z (%): 298 (1) [M+], 280 (6), 213 (100), 135 (20), 105 (33). IR (KBr): ν = 3489, 3057, 2930, 2854, 1610, 1511, 1464, 1446, 1247, 1170, 1089. 1064, 831 cm^{-1}.

4.2. General procedure for The Competitive [1,4]-Sigmatropic Rearrangement and Wittig Rearrangement in the presence of TMSCl:

The reaction were performed by stirring a solution of the acetal compound **2a** (5 mmol) in anhydrous THF (30 mL) at -78^{o}C, followed by the dropwise addition of a solution of *i*-BuLi in hexane (1.23 M, 3.0 equiv) under N_2. To the mixture was then added the TMSCl (5 mmol) subsequently. The solution was slowly allowed to warm to room temperature, and the mixture was stirred at room temperature overnight. After the reaction is completed, the reaction was quenched with water and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product were purified by column chromatography (silica gel: petroleum ether/EtOAc, 20/1) to afford the product **3** and **4** respectively.

Phenyl(2-(tetrahydro-2H-pyran-2yl)phenyl)methanone 4: ^{1}H NMR(400MHz, $CDCl_3$): δ = 1.71-1.60 (m, 4H); 1.89-1.98 (,m, 2H,), 4.19-3.61 (m, 2H), 4.42 (dd, 1H, J = 2.0 Hz, 10.8Hz), 7.80-7.46 (m, 9H). ^{13}C NMR(100MHz, $CDCl_3$), δ = 23.92, 25.78, 34.11, 68.99, 79.61, 125.62, 128.02, 128.26, 130.06, 130.17, 130.28, 132.34, 136.47, 137.77, 148.06, 196.58. GC-MS, m/z (%): 266 (13) [M+], 209 (9), 166 (61), 105 (100), 80 (53). IR (KBr): ν = 3057, 2930, 2853, 1664, 1609, 1584, 1511, 1493, 1329, 1211, 1089, 1047 cm^{-1}.

Acknowledgments

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