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Synthesis of (*E*)-alkenes via hydroindation of C≡C in $InCl_3$–$NaBH_4$ system

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Abstract—In $InCl_3$–$NaBH_4$–MeCN system, terminal aryl alkynes could couple with aryl iodides and bromides to give disubstituted alkenes via hydroindation of C≡C. In the similar way, (*E*)-alkenylsilanes were synthesized via reduction of alkynylsilanes in tetrahydrofuran (THF) in high yields. The processes showed high regio- and stereoselectivity.

1. Introduction

During the past few decades, hydroboration and hydroalumination have proven reliable ways to reduce carbon–carbon multiple bonds to give alkenylmetals formed via hydrometalations of C≡C, which can then be utilized in various reactions.[1] But in these reactions expensive catalyst or high temperature is usually required. Although in the same group with boron and aluminum in the periodic table, the study of hydroindation is still limited compared to hydroboration and hydroalumination. However, since dichloroindium hydride (Cl_2InH) was generated firstly via combination of Indium(III) chloride and tributyltin hydride system,[2] Cl_2InH generated in situ has been applied to many organic reactions.[3–13] Especially, because of excellent properties, such as easy handling, mild conditions, and low toxicity, $InCl_3$–$NaBH_4$ system has attracted much interest.[3–7]

In the presence of a catalytic amount of triethylborane as a radical initiator, hydroindation of terminal alkynes with Cl_2InH generated in situ by a combination of $InCl_3$ and DIBAL-H gives (*Z*)-alkenylindiums, which couple with aryl iodides to form (*Z*)-alkenes smoothly.[12] However, up to now, coupling reaction of alkenylindium with halides to give (*E*)-alkenes in $InCl_3$–$NaBH_4$ system has not been reported.

In addition, it has been reported that alkynylsilanes were reduced via hydroboration and hydroalumination to form alkenylsilanes, which are important intermediates in organic synthesis.[13–15] But little attention was paid to hydroindation of alkynylsilanes. Recently, we have reported some facile hydroindations of alkyne in $InCl_3$–$NaBH_4$–MeCN system.[6,7] The good results stimulated us to further explore the reactivity of this system. We herein present a convenient and efficient method to synthesize (*E*)-alkenes under mild conditions via reduction of alkynylsilanes or coupling reactions of terminal alkynes with aryl iodides or bromides in an $InCl_3$–$NaBH_4$ system.

2. Results and discussion

2.1. Synthesis of (*E*)-alkenes via coupling reaction of terminal alkynes with aryl halides in $InCl_3$–$NaBH_4$–MeCN system

Initially, anhydrous $InCl_3$, $NaBH_4$, MeCN, phenyl acetylene, and iodobenzene were added in sequence in one-pot at −15 °C under nitrogen atmosphere. After the reaction was stirred overnight at room temperature, it was found that the only coupling product (*E*)-stilbene (**2a**) was obtained smoothly in 78% yield without **3a** and **4a** as byproducts (**2a**:**3a**:**4a**=100:0:0), showing high regio- and stereoselectivity. The product was determined by ^{1}H NMR (500 MHz) and MS. The *E* or *Z* stereochemistry in the double bond C=C of products was assigned on the basis of the value of ^{1}H NMR coupling constants between the olefinic protons and comparison of their ^{1}H NMR spectra with those previously reported.

Under the above reaction conditions, a variety of cross-coupling reactions of the different terminal alkynes and halides were examined. It was found that all the terminal aryl alkynes could couple with aryl iodides or bromides

Keywords: Hydroindation; Alkynes; (*E*)-Alkenes; (*E*)-Alkenylsilanes; $InCl_3$–$NaBH_4$ system.
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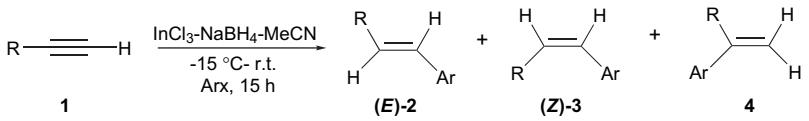
Table 1. The coupling reactions of terminal alkynes and halides in $InCl_3$–$NaBH_4$–MeCN system



Entry	R	Halides	**2**:**3**:**4**[a]	Yield (**2**+**3**%)[b]	Ref.
a	Ph	PhI	100:0:0	78	16
b	*p*-CH_3Ph	PhI	91:9:0	80	16
c	*p*-BrPh	PhI	95:5:0	72	16
d	*p*-CH_3OPh	PhI	94:6:0	73	16
e	*n*-Bu	PhI	—	—	—
f	$C_6H_{13}OCH_2$	PhI	—	—	—
g	Ph	*p*-ClC_6H_4I	95:5:0	77	17
h	*p*-CH_3Ph	*p*-ClC_6H_4I	91:9:0	74	18
i	*p*-BrPh	*p*-ClC_6H_4I	88:12:0	56	18
j	*p*-CH_3OPh	*p*-ClC_6H_4I	90:10:0	61	17
k	*n*-Bu	*p*-ClC_6H_4I	—	—	
l	$C_6H_{13}OCH_2$	*p*-ClC_6H_4I	—	—	
m	Ph	PhBr	92:8:0	72	16
n	*p*-CH_3Ph	PhBr	92:8:0	67	16
o	*p*-BrPh	PhBr	93:7:0	58	16
p	*p*-CH_3OPh	PhBr	88:12:0	62	16
q	*n*-Bu	PhBr	—	—	—
r	$C_6H_{13}OCH_2$	PhBr	—	—	—
s	Ph	PhCl	—	—	—
t	1-Cyclohexen-1-yl	PhI	92:8:0	68	6

[a] Determined by ^{1}H NMR.
[b] Isolated by terminal alkynes.

well. The regio-, stereoselectivity, and the yield were satisfactory. In all the reactions, no compound **4** was detected. On the other hand, aryl chloride failed to couple with aryl alkenylindium in $InCl_3$–$NaBH_4$–MeCN system (Table 1, entry **s**). We also attempted to apply this reaction to aliphatic alkynes and aliphatic bromides. But the results showed that no coupling product was obtained (Table 1, entries **e**–**f**, **k**–**l**, and **q**–**r**). It was interesting that the desired coupling product was obtained when (1-cyclohexen-1-yl) ethyne was used as the aliphatic terminal alkyne. It was considered that the conjugated structure in the compound (1-cyclohexen-1-yl)-ethyne stabilized the intermediate. All the results were summarized in Table 1.

2.2. Synthesis of (*E*)-alkenylsilanes via hydroindation of alkynylsilanes in $InCl_3$–$NaBH_4$–THF system

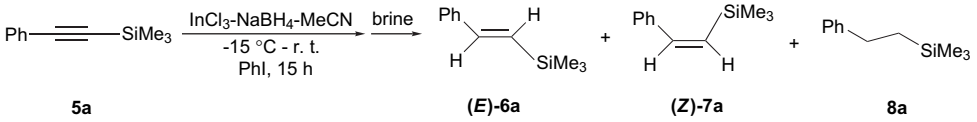
Considerable efforts have been devoted to develop the novel methods of forming vinylsilanes due to their versatile role as intermediates in organic synthesis.[19] Presently, there are no reports of vinylsilane synthesis via hydroindation of alkynylsilanes. So under the same conditions, the coupling of 2-phenylalkynylsilane and iodobenzene was also tested in the $InCl_3$–$NaBH_4$–MeCN system. Unexpectedly, the reaction worked poorly in this system, which was proved to be more excellent than others in many reactions. Only 2-phenylvinylsilanes (**6a**+**7a**) were obtained in only 2.5% conversion by GC–MS analysis even after stirring for 20 h. In order to improve the conversion, the reaction conditions were optimized involving solvent and the amount of $NaBH_4$. At first, various solvents instead of MeCN were tested under the conditions of entry 1 (Table 2). Attempts using solvents such as ethyl ether, CH_2Cl_2, toluene, and acetone all failed in which only a trace amount of the expected products were obtained (Table 2, entries 2–5). Interestingly, THF was found to be the best solvent in which the starting material could be consumed completely after carrying out this reaction for 3 h. But a large amount of over-reduced product (**8a**) was obtained (Table 2, entry 6). Thus, the ratio of $NaBH_4$ and phenylalkynylsilane was decreased to 1:1, and that led to high selectivity (**6a**/**7a**/**8a**=90:5:5) with 92% total yield (Table 2, entry 7). The products were determined by ^{1}H NMR and GC–MS. All the results were summarized in Table 2.

A variety of alkynylsilanes were examined (1 mmol) under the optimized reaction conditions [$InCl_3$ (1 mmol), $NaBH_4$ (1 mmol), THF (5 mL), −15 °C to rt, 2–4 h] (Table 2, entry 7; Scheme 2). It was found that all the arylalkynylsilanes could react well. Both stereoselectivities and yields were satisfactory. When the hydrogen atom, at the *para* position of benzene ring, was substituted by a methyl group (Table 3, entry **b**), the stereoselectivity decreased slightly, and more starting material was over-reduced than phenylalkynylsilane (Table 3, entry **a**). In contrast, the stereoselectivity and the yield were rather high when this hydrogen atom was substituted by an electron-withdrawing group such as F, Cl, and Br (Table 3, entries **c**–**e**). When R was C_4H_9 or C_5H_{11}, a mixture was obtained. About half of the starting material was over-reduced to **8f** or **8g** by GC–MS (Table 3, entries **f**–**g**). Diastereoisomeric excess (*E*/*Z*) determined by ^{1}H NMR was 3:1. Reduction of aliphatic alkynylsilanes to vinylsilanes is mostly difficult to control. All the results are summarized in Table 3.

2.3. Synthesis of (*E*)-2-phenylvinylphosphonate via hydroindation of phenylalkynylphosphonate in $InCl_3$–$NaBH_4$–MeCN system

Vinylphosphonates have been widely used as synthetic intermediates in organic chemistry[20] and investigated as biologically active compounds.[21] Recently, our group has afforded

Table 2. Study of the system in reduction of phenylalkynylsilane[a]

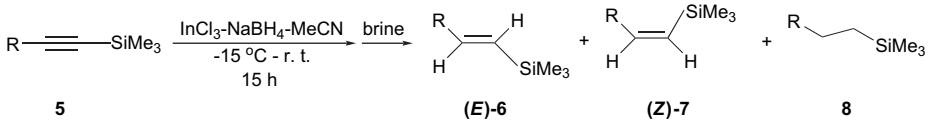


5a **(*E*)-6a** **(*Z*)-7a** **8a**

Entry	Solvent	**6a**:**7a**:**8a**[b,c]	Yield (**6a**+**7a**%)[b]
1	MeCN	—	2.5
2	Ethyl ether	—	—
3	CH_2Cl_2	—	Trace
4	Toluene	—	Trace
5	Acetone	—	Trace
6[d]	THF	56:7:37	61
7[e]	THF	90:5:5	92

[a] $InCl_3/NaBH_4$/phenylalkynylsilane = 1:2:1 and 20 h except that pointed out especially.
[b] Determined by GC–MS.
[c] Determined by ^1H NMR.
[d] 3 h.
[e] $InCl_3/NaBH_4$/phenylalkynylsilane = 1:1:1, 4 h.

Table 3. Synthesis of vinylsilanes in $InCl_3$–$NaBH_4$–THF system[a]



5 **(*E*)-6** **(*Z*)-7** **8**

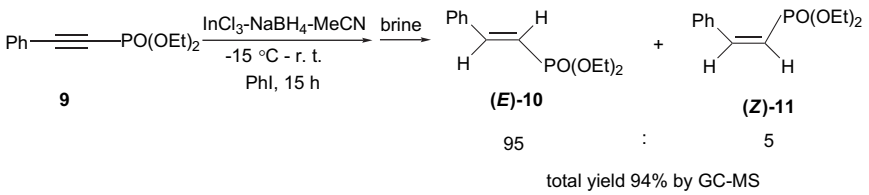
Entry	R	**6**:**7**:**8**[b,c]	Total Yield (**6**+**7**%)[b]
a	Ph	90:5:5	92
b	*p*-CH_3Ph	70:5:25	70
c	*p*-FPh	88:5:7	88
d	*p*-BrPh	95:2:3	94
e	*p*-ClPh	90:4:6	93
f	*n*-C_4H_9	3:1:4	Mixture
g	*n*-C_5H_{11}	3:1:3	Mixture

[a] Reaction conditions: $InCl_3$ (1 mmol), $NaBH_4$ (1 mmol), THF (5 mL), −15 °C to rt, 2∼4 h.
[b] Determined by GC–MS.
[c] Determined by ^1H NMR.

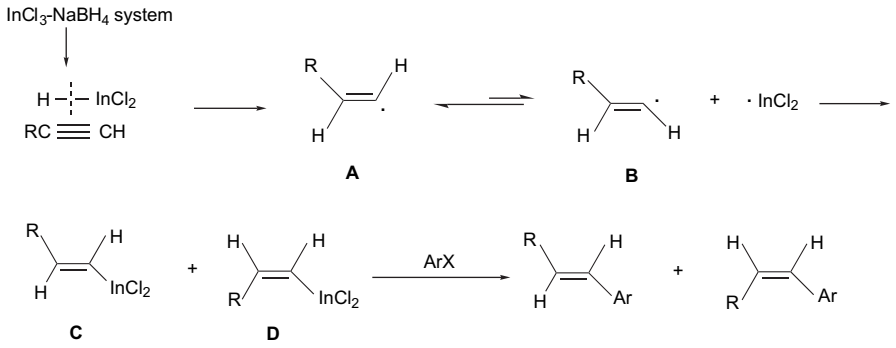
a convenient and efficient method to synthesize vinylphosphonates via hydroindation of 2-arylalkynylphosphonates in $InCl_3$–$NaBH_4$–MeCN system.[7] In the same way, the coupling reaction of phenylalkynylphosphonate and iodobenzene was tested. Only 2-phenylvinylphosphonates (**10**:**11**=95:5) were obtained in 94% yield without any desired coupling products (Scheme 1).

2.4. Proposed mechanism

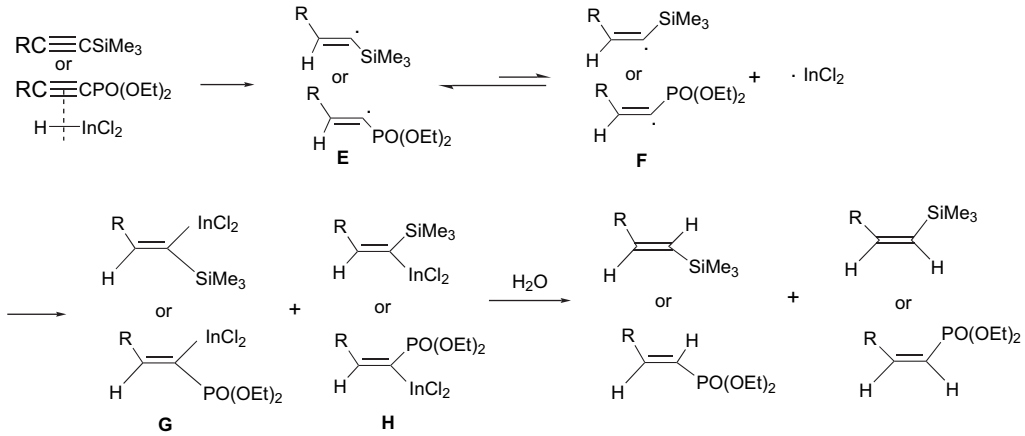
In accordance with previous reports, a similar mechanism is presently proposed (Schemes 2 and 3).[17,18] During the reaction *E*-configuration of the alkenyl radical (**A** or **E**) is more stable than *Z*-configuration (**B** or **F**). So hydroindation of alkynes gave (*E*)-alkenylindiums as major intermediate and (*Z*)-alkenylindiums as minor intermediate. At last, alkenylindiums (**C** and **D**) coupled with aryl iodides or bromides afforded alkenes. It was supposed that chlorobenzene was not active enough to couple with alkenylindiums. For alkynylphosphonates and alkynylsilanes, the intermediate **G** or **H** could not couple with iodobenzene to give the corresponding products because of steric hindrance. In our experiments, alkynylsilanes could be over-reduced. But in similar reaction system only alkenylphosphonates were obtained without any over-reduced products detected by GC–MS. The reasons have not been clarified. It may be explained that aliphatic alkenyl intermediates are not stable enough to couple with aryl halides in our experiments.



Scheme 1. Synthesis of (*E*)-2-phenylvinylphosphonate via hydroindation of phenylalkynylphosphonate in $InCl_3$–$NaBH_4$–MeCN system.



Scheme 2. Proposed mechanism of the coupling reaction of terminal alkynes with aryl halides in $InCl_3$–$NaBH_4$ system.



Scheme 3. Proposed mechanism of reduction of alkynylsilanes in $InCl_3$–$NaBH_4$ system.

3. Conclusion

$InCl_3$–$NaBH_4$ system was applied to the coupling reactions of the terminal aryl alkynes with aryl iodides or bromides in one-pot successfully. But in this system alkynylphosphonates and alkynylsilanes were only reduced to alkenylindiums, which could not couple with iodobenzene to synthesize trisubstituted alkenes. Moreover, it was found that $InCl_3$–$NaBH_4$–THF system is more active than $InCl_3$–$NaBH_4$–MeCN system in reduction of alkynylsilanes. Finally, many alkenylphosphonates and alkenylsilanes were obtained by hydrolyzation of alkenylindiums. An effective and simple approach to (*E*)-alkenes from alkynes was developed in the absence of expensive catalyst under the mild conditions.

4. Experimental

4.1. General

All the terminal alkynes and halides were purchased from J&K chemical Co., or other commercial suppliers and were used after appropriate purification (distillation). Alkynylsilane[22] and alkynylphosphonates[23] were prepared according to the literature. Acetonitrile was freshly distilled from phosphorus pentoxide before use. The ^{1}H NMR spectra were obtained with a Bruker AVANCE DRX-500 NMR spectrometer with TMS as an internal standard and $CDCl_3$ as solvent. GC–MS data were recorded by TRACE 2000 GC/MS (USA TRACE Company). Precoated thin-layer plates of silica gel 60 GF_{254} (Qingdao Haiyang Chemical Co. Ltd, Qingdao, China) were used for analytical purposed. The reactions were carried out in pre-dried (150 °C, 4 h) glassware under the atmosphere of dry nitrogen. All solvents and reagent were dried, deoxygenated, and redistilled before use.

4.2. General procedure for the cross-coupling reactions of terminal alkynes and halides in $InCl_3$–$NaBH_4$–MeCN system

After a mixture of $InCl_3$ (2.0 mmol) in dry MeCN (10 mL) and $NaBH_4$ (10 mmol) was stirred for 30 min at −15 °C under nitrogen, terminal alkyne (2 mmol) and aryl iodide or bromide (2 mmol) were added in sequence by syringe. The cooling bath was removed. The reaction mixture was warmed to room temperature, and stirred overnight. Saturated NH_4Cl solution (5 mL) was added to the reaction mixture to destroy excessive $NaBH_4$. The reaction mixture was stirred for another 10 min and then filtered. The filtrate was extracted with ether (20 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuum. Purification by silica gel column (petroleum ether bp 60–90 °C as eluent) could afford the corresponding products, which were identified by ^{1}H NMR and MS.

4.2.1. 1-[(*E*)-2-Phenylethenyl]benzene (2a). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.12 (2H, s), 7.25–7.28 (2H, m), 7.36 (4H, t, J=7.5 Hz), 7.52 (4H, d, J=7.5 Hz); MS, m/z 180 (M^+).

4.2.2. 1-Methyl-4-[(*E*)-2-phenylethenyl]benzene (2b). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.29 (3H, s), 7.00–7.45 (11H, m); MS, *m*/*z* 194 (M^+).

4.2.3. 1-Bromo-4-[(*E*)-2-phenylethenyl]benzene (2c). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.07–7.52 (11H, m); MS, *m*/*z* 258 (M^+).

4.2.4. 1-Methoxyl-4-[(*E*)-2-phenylethenyl]benzene (2d). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.90–7.48 (11H, m), 3.86 (3H, s); MS, *m*/*z* 210 (M^+).

4.2.5. 1-Chloro-4-[(*E*)-2-phenylethenyl]benzene (2g). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.06–7.51 (11H, m); MS, *m*/*z* 214 (M^+).

4.2.6. 1-[(*E*)-2-(4-Chlorophenyl)ethenyl]-4-methylbenzene (2h). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.96–7.48 (10H, m), 2.36 (3H, s); MS, *m*/*z* 228 (M^+).

4.2.7. 1-[(*E*)-2-(4-Chlorophenyl)ethenyl]-4-bromobenzene (2i). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.00–7.51 (10H, m); MS, *m*/*z* 292 (M^+).

4.2.8. 1-[(*E*)-2-(4-Chlorophenyl)ethenyl]-4-methoxylbenzene (2j). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.90–7.48 (10H, m), 3.84 (3H, s); MS, *m*/*z* 244 (M^+).

4.2.9. 1-[(*E*)-2-Phenylethenyl]cyclohexene (2t). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.65–2.26 (8H, m), 5.69 (1H, t, *J*=4.5 Hz), 6.43 (1H, d, *J*=16.5 Hz), 6.74 (1H, d, *J*=16.5 Hz), 7.13–7.31 (5H, m); MS, *m*/*z* 184 (M^+).

4.3. General procedure for the synthesis of (*E*)-vinylsilanes in $InCl_3$–$NaBH_4$ system

$InCl_3$ (1 mmol), dry solvent (5 mL), and $NaBH_4$ (1 mmol) were mixed at −15 °C under nitrogen. After the mixture was stirred for 30 min, alkynylsilanes (1 mmol) were added by syringe. The cooling bath was removed. The reaction mixture was warmed to room temperature, stirred for 2–4 h. Completion of the reaction was monitored by TLC. In order to destroy the excessive $NaBH_4$ saturated NH_4Cl solution (5 mL) was added to the reaction mixture. The reaction mixture was stirred for another 10 min and filtered. The filtrate was extracted with ethyl ether (10 mL×3). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuum. Purification by silica gel column chromatography (200–300 mesh), using petroleum ether (60–90 °C) as eluent could afford the corresponding products, which were identified by ^{1}H NMR and MS.

4.3.1. (*E*)-2-(Phenylethenyl)trimethylsilane (6a). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.18–7.43 (5H, m), 6.87 (1H, d, *J*=19.5 Hz), 6.48 (1H, d, *J*=19.5 Hz), 0.15 (9H, s); MS, *m*/*z* 176 (M^+).

4.3.2. (*E*)-2-(4-Methylphenylethenyl)trimethylsilane (6b). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.07–7.34 (4H, m), 6.81 (1H, d, *J*=19.2 Hz), 6.34 (1H, d, *J*=19.2 Hz), 2.59 (3H, s), 0.15 (9H, s); MS, *m*/*z* 190 (M^+).

4.3.3. (*E*)-2-(4-Fluorophenylethenyl)trimethylsilane (6c). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.00–7.39 (4H, m), 6.80 (1H, d, *J*=19.5 Hz), 6.35 (1H, d, *J*=19.5 Hz), 0.14 (9H, s); MS, *m*/*z* 194 (M^+).

4.3.4. (*E*)-2-(4-Chlorophenylethenyl)trimethylsilane (6d). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.10–7.34 (4H, m), 6.78 (1H, d, *J*=19.7 Hz), 6.42 (1H, d, *J*=19.7 Hz), 0.14 (9H, s); MS, *m*/*z* 210 (M^+).

4.3.5. (*E*)-2-(4-Bromophenylethenyl)trimethylsilane (6e). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.05–7.46 (4H, m), 6.78 (1H, d, *J*=19.3 Hz), 6.42 (1H, d, *J*=19.3 Hz), 0.14 (9H, s); MS, *m*/*z* 254 (M^+).

Acknowledgements

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