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前 言

中国化学会第十九届全国金属有机化学学术讨论会于2016年10月28~31日在浙江大学紫金港校区体育馆成功举行。本届会议由中国化学会主办,浙江大学化学系、浙江省化学会和中国科学院上海有机化学研究所金属有机化学国家重点实验室共同承办,并得到国家自然科学基金委与浙江省科协的资助。本届会议云集了我国金属有机化学界的著名专家学者以及广大研究生约1500人,其中包括8位院士、25位国家杰青等著名专家学者,另外,还邀请了美国、香港以及新加坡的著名化学家。与会代表围绕金属有机化学研究的前沿科学问题展开热烈交流,展示最新研究成果、展望学科未来,极大地促进了我国金属有机化学研究的进一步发展。

本届会议共收到会议论文549篇,参会代表们围绕金属有机化学研究的前沿科学问题,以大会报告、邀请报告、口头报告和墙报展等进行了形式多样、丰富多彩的交流。会议共安排了5个大会报告、1个黄耀曾金属有机化学终身成就奖获奖报告、2个黄耀曾金属有机化学奖获奖报告、25个邀请报告、24个口头报告以及317个墙报展。会议的成功举办,也获得中国化学会的赞誉,并授予本次会议承办单位“优秀学术交流组织奖”。本届会议还得到了国家自然科学基金委员会、浙江省科协和26家相关领域企业和公司的赞助与支持,在此表示衷心地感谢!

为了支持我国金属有机化学的发展,集中展示我国金属有机化学研究的最新成果,《有机化学》编辑部于2017年5月出版一期“金属有机化学专辑”。该专辑共录用稿件29篇,其中综述与进展8篇,研究论文14篇,研究简报6篇,研究通讯1篇。感谢《有机化学》编辑部对本专辑按时出版所付出的辛劳!萨恩化学技术(上海)有限公司、苏州欣家园化学科技有限公司、江苏欣诺科催化剂有限公司、三泰科技(常州)有限公司对本专辑印刷出版提供了大力支持,在此也深表感谢!

中国化学会第十九届全国金属有机
化学学术讨论会组委会主席

《有机化学》主编

钯/对甲苯磺酸催化烯丙基苯异构化合成 β -甲基苯乙烯衍生物的方法研究

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摘要 发展了简便、高效地烯丙基苯异构化制备 β -甲基苯乙烯的合成方法。通过对不同的酸、溶剂和催化剂的考察,确定了最优反应条件: 三氟乙酸钯和对甲苯磺酸为催化剂、二氯甲烷为溶剂、空气条件下室温反应 12 h。在最优条件下对底物适用范围进行考察,含有给电子基和吸电子基的烯丙基苯均可以有效地得到 β -甲基苯乙烯产物,反应收率在 65%~90%之间。根据氘代实验的结果对反应机理进行了推测。

关键词 异构化; 烯丙基苯; β -甲基苯乙烯; 钯催化

Facile Synthesis of β -Methylstyrenes via Pd/TsOH-Catalyzed Isomerization of Allylbenzenes

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Abstract Convenient and efficient protocol for isomerization of allylbenzenes into corresponding β -methylstyrenes has been developed. Different acids, solvents and catalysts have been investigated. Pd(TFA)₂ and TsOH·H₂O as catalysts in dichloromethane at room temperature under air for 12 h were selected as standard conditions for exploring the substrate scope. Allylbenzenes containing electron-donating groups and electron-withdrawing groups were working under the optimized condition, and β -methylstyrene products were obtained in the yields of 65%~90%. The reaction mechanism was proposed according to the deuterated experiment.

Keywords isomerization; allylbenzene; β -methylstyrene; palladium-catalyzed

β -Methylstyrenes motif is a basic skeleton in a wide range of biologically important antibiotics, bacterial enzyme inhibitors^[1] and pharmaceutical products.^[2] These vinylarenes have been synthesized by a number of methods.^[3] Ranging from famous Heck-type cross coupling,^[4,5] new protocols with Fe,^[6] Ni catalyzed cross-coupling reactions,^[7] cross-coupling reactions of aryllithium, arylmagnesium and arylmanganese compounds with vinyl partners,^[8] as well as the arylation of propyne involving a vinylborane cross-coupling/oxidation protocol under strongly basic conditions,^[9] are famous methods for preparation of β -methylstyrenes.

Isomerization of the double bond of allylbenzenes is considered as an important handle for the synthesis of β -methylstyrenes.^[10] This area was investigated by researchers in past by using strong bases (KF/Al₂O₃ and K₂CO₃)^[11] or transition metal complexes (Ti^[12] and Fe^[13]

and soft Lewis acid derivatives of Rh,^[14] Ru,^[15] Ir,^[16] Pt^[17] and Ni^[18]). A variety of Pd based catalytic systems had been developed for selective double bond isomerization.^[19] Although a large number of methods in isomerization have been successful, there are still some limitations which need to be addressed: (1) High loading of the strong base or transition-metal catalyst were used; (2) The reactions normally proceeded in harsh conditions, especially at high temperature, and the protic solvents were needed in the reaction; (3) No catalytic system can realize "one size fits all". For example, Pd(MeCN)₂Cl₂ has been used as efficient catalyst in isomerization reaction, however the substrates containing OMe group or OH group were needed. These issues may limit its application in organic synthesis.

Herein, in this study we present a convenient ligand free, acid mediated palladium catalyzed reaction for isomerization of allylbenzenes into 2-alkenes (*E*) at room tempera-

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ture in non-protonic solvent for a wide range of substrates (electron-donating groups and electron-withdrawing groups) (Eq. 1). Acid was crucial in the current procedure for isomerization: (1) Acid enhanced the electrophilicity of palladium catalyst. Electron-withdrawing group reduced the nucleophilicity of double bond, so we wanted to improve the activity of catalyst with the help of acid. (2) Acid was used as a handbarrow for 1,3-H shift. 1,3-H shift in the allylic structure was difficult, especially not at high temperature. Carbonyl group in the acid could abstract H via hydrogen-bonding interaction, we wanted to realize the isomerization with the help of acid.

This work: Ligand-free Pd/TsOH-Catalyzed isomerization

1 Results and discussion

In our initial studies, the isomerization of allylbenzene (**1a**) was selected as a model reaction to optimize the reaction conditions, and the results are summarized in Table 1. Initially we screened different reaction conditions to find the suitable acid, solvent and catalyst for our reaction.

Table 1 Reaction conditions screening^a

Entry	Catalyst/mol%	Additive (mol%)	Solvent	Yield ^b /%
1	Pd(TFA) ₂ (5)	TsOH•H ₂ O (100)	DCM	80
2	Pd(TFA) ₂ (5)	Ph-COOH (100)	DCM	NR ^c
3	Pd(TFA) ₂ (5)	CH ₃ COOH (100)	DCM	54
4	Pd(TFA) ₂ (5)	CF ₃ COOH (100)	DCM	75
5	Pd(TFA) ₂ (5)	TsOH•H ₂ O (10)	DCM	80
6	Pd(TFA) ₂ (5)	TsOH•H ₂ O (5)	DCM	56
7	Pd(TFA) ₂ (2.5)	TsOH•H ₂ O (10)	DCM	80
8	Pd(TFA) ₂ (2.5)	TsOH•H ₂ O (5)	DCM	52
9	Pd(TFA) ₂ (1)	TsOH•H ₂ O (10)	DCM	35
10	Pd(OAc) ₂ (2.5)	TsOH•H ₂ O (10)	DCM	70
11	PdCl ₂ (2.5)	TsOH•H ₂ O (10)	DCM	50
12	None	TsOH•H ₂ O (100)	DCM	NR ^c
13	Pd(TFA) ₂ (2.5)	None	DCM	NR ^c
14	Pd(TFA) ₂ (2.5)	TsOH•H ₂ O (10)	THF	57
15	Pd(TFA) ₂ (2.5)	TsOH•H ₂ O (10)	CH ₃ CN	63
16	Pd(TFA) ₂ (2.5)	TsOH•H ₂ O (10)	Acetone	67

^a Allylbenzene (**1a**, 0.3 mmol, 35.4 mg), catalyst in solvent (2.0 mL) at 30 °C under air for 12 h. ^b Isolated yield. ^c No reaction; the starting material **1a** was almost completely recovered.

The product **2a** was obtained in 80% when reaction of substrate **1a** was run in the presence of 5 mol% of Pd(TFA)₂ as a catalyst and one equivalent of *p*-toluene-

sulfonic acid in dichloromethane (DCM) for 12 h at 30 °C (Entry 1). The reaction failed to proceed when TsOH•H₂O was replaced by benzoic acid (Entry 2). The product **2a** was obtained in the low yield of 54% and 75% when in the presence of 5 mol% of catalyst Pd(TFA)₂ acetic acid and trifluoroacetic acid were used respectively (Entries 3~4). From the data obtained it is suggested that strong acids are working better in this reaction. The product **2a** was obtained in yield of 80% when the loading of *p*-toluene-sulfonic acid was decreased to 10 mol% in DCM as solvent under air at 30 °C (Entry 5). Further decrease of acid loading to 5 mol% resulted in lower yield of product **2a** in 56% (Entry 6). Product **2a** was obtained in as high as 80% yield when we further reduced the catalyst loading to 2.5 mol% in presence catalytic amount of *p*-toluenesulfonic acid (10 mol%) in DCM as solvent (Entry 7). However, in presence of 2.5 mol% catalyst when *p*-toluenesulfonic acid was reduced to 5 mol% using DCM as solvent, the yield of **2a** decreased to 52% (Entry 8). Depression in the yield of **2a** was also observed when the catalyst loading was reduced to 1 mol% (Entry 9). To enhance the yield of product **2a**, Pd(OAc)₂ and PdCl₂ were tested as alternative catalysts, but compared to Pd(TFA)₂, they produced 70% and 50% yields, respectively (Entries 10~11).

The reaction failed to proceed and starting material was completely recovered when blank reaction without catalyst was conducted (Entry 12). No product was obtained when reaction in presence of catalyst without acid was conducted as well (Entry 13). We also observed that solvents such as THF, acetonitrile, and acetone produced product **2a** in comparatively less yields 57%~67% as compared to DCM (Entries 14~16). Therefore, Pd(TFA)₂ (2.5 mol%) and TsOH•H₂O (10 mol%) as catalysts in DCM at 30 °C under air for 12 h were selected as standard conditions for exploring the substrate scope.

With the optimized conditions in hand we extended the scope of catalytic isomerization of terminal alkenes into internal alkenes. To our delight, the reaction successfully isomerized allylbenzene substrates into only *E* isomers in all products. The simple allylbenzene **1a** produced product **2a** in high yields (80%) in standard conditions. It was observed that electron-donating group (methyl) at *para*, *ortho* and *meta* position of allylbenzene did not hinder the reaction and produced the desired products **2b**~**2d** in high yields (80%~85%). Even *ortho*-dimethyl substituted substrate was successfully transformed to product **2e** in high yield (85%). Substrates **1f**~**1h** bearing bulky groups (ethyl, *n*-propyl and *tert*-butyl) at *para* position of allylbenzene when tested in standard conditions produced **2f**~**2h** in high yields (86%~90%). Besides the aliphatic substituents, phenyl and hydroxyl groups containing substrates **1i** and **1j** produced desired products in fair yields of 65% and 80%, respectively. Not only the substrates bearing electron donating groups but also the substrates having electron withdrawing groups at *para* position were equally tolerated in this reaction. Due to the

Table 2 Substrate scope

Entry ^a	Substrate 1	Product 2	Time/h	Yield ^b /%	Entry ^a	Substrate 1	Product 2	Time/h	Yield ^b /%
1			12	80	10			12	80
2			12	85	11			60	72
3			12	82	12			60	81
4			12	82	13			24	70
5			12	85	14			24	80
6			12	86	15			60	65
7			12	86	16			72	69
8			12	90	17			72	0
9			24	65					

^a Allylbenzene (**1a**, 0.3 mmol, 35.4 mg), Pd(TFA)₂ (2.48 mg, 2.5 mol%), TsOH·H₂O (5.7 mg, 10 mol%) in DCM (2.0 mL) at 30 °C under air for 12 h. ^b Isolated yield.

electronic effects, substrates **1k** and **1l** required double loading of the catalyst (5 mol%), additive TsOH·H₂O (20

mol%), as well as longer duration to produce products **2k** and **2l** in yields of 65%, 72% and 81%, respectively. To

our delight, our reaction offered versatility in wide range of substrates when allylated naphthalenes **1m**, **1n**, as well as heterocyclic compounds **1o**, **1p** were isomerized to their corresponding products **2m**~**2p** in yields of 65%~80%. However, *tert*-butyl 3-allyl-1*H*-indole-1-carboxylate (**1q**) unfortunately failed to produce the desired product under optimized conditions.

When tested under standard conditions, 1-allyl-4-methoxybenzene (**1r**) underwent head to tail dimerization^[20] producing product **2r** in 50% yield instead of the desired isomerized product (Eq. 2). It is suggested that double bond isomerization happened. Dimerization may be due to the high activity of reaction intermediate.

In order to gain mechanistic insights of reaction, when reaction of **1a** was conducted in presence of $\text{Pd}(\text{TFA})_2$ and deuterated trifluoroacetic acid in DCM under air, no deuterated product was observed (Eq. 3). It indicates that unfortunately acid is not acting as a hydride source in catalytic cycle, however it plays a key role in reaction.

Thus in the light of the deuterated experiments and published literatures, it was proposed that $\text{Pd}(\text{TFA})_2$ in the presence of *p*-toluenesulfonic acid formed cationic palladium species.^[21] Then cationic palladium coordinated with the η^2 carbon of double bond of allylbenzene. The TsOH through hydrogen bonding linked to the carbonyl center of palladium species as well as sequester the α -hydrogen to afford intermediate A. Meanwhile, intermediate A went through inversion of η^2 to η^3 palladium complex^[23] transferring α -hydrogen to the terminal end via hydrogen bonding of acid to afford a more stable isomer. Subsequently proton was transferred to terminal carbon of allyl moiety completing the catalytic cycle to produce β -methylstyrene **2a** and regenerating the cationic palladium species as well as the acid.

2 Conclusions

An efficient protocol for isomerization of allylbenzenes into *E* isomers of 2-alkenes is developed by using $\text{Pd}(\text{TFA})_2$ and *p*-toluenesulfonic acid ($\text{TsOH}\cdot\text{H}_2\text{O}$) as catalyst, dichloromethane as solvent in air at room tempera-

Scheme 1 Proposed mechanism.

ture, respectively. The reaction tolerated wide range of functional groups and proceeded smoothly under mild conditions to produce the corresponding products in satisfactory to high yields. The wide availability of reactants, mild reaction conditions, and simple experimental process could make the present methodology considerably useful in organic chemistry.

3 Experimental section

3.1 General

Thin layer chromatography (TLC) was carried out on SiO_2 (silica gel 60 F254, Merck). Solvents were obtained commercially and used after distillation. ^1H NMR and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C) or a Bruker Avance II-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C); CDCl_3 with internal standard TMS was used as a solvent. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on a GC-TOF mass spectrometer.

3.2 Procedure for synthesis of products **2a**~**2p** and **2r**

A mixture of compound **1a** (35.4 mg, 0.3 mmol), $\text{Pd}(\text{TFA})_2$ (2.48 mg, 2.5 mol%) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (5.7 mg, 10 mol%) was added to dichloromethane (2 mL) in air, and the reaction mixture was allowed to stir at 30 °C for 12 h. The reaction progress was monitored by TLC. After the starting materials were completely consumed, the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether) to afford product **2a** in 80% yield (28.3 mg).

(*E*)-Prop-1-en-1-ylbenzene (**2a**)^[22a]: Colorless oil (28.3 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.33~7.28 (m, 5H), 6.39 (d, $J=16.0$ Hz, 1H), 6.28~6.19 (m, 1H), 1.87 (d, $J=6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 137.9, 131.0, 128.4, 126.7, 125.8, 125.7, 18.5.

(*E*)-1-Methyl-4-(prop-1-en-1-yl)benzene (**2b**)^[22b]: Co-

lorless oil (33.6 mg, 85% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.21 (d, $J=7.6$ Hz, 2H), 7.08 (d, $J=8.0$ Hz, 2H), 6.36 (d, $J=15.6$ Hz, 1H), 6.21~6.14 (m, 1H), 2.31 (s, 3H), 1.86 (d, $J=6.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 136.3, 135.1, 130.8, 129.1, 125.7, 124.6, 21.1, 18.4.

(*E*)-1-Methyl-2-(prop-1-en-1-yl)benzene (**2c**)^[22b]: Colorless oil (32.5 mg, 82% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.38 (d, $J=6.8$ Hz, 1H), 7.13~7.11 (m, 3H), 6.56 (d, $J=15.6$ Hz, 1H), 6.14~6.05 (m, 1H), 2.32 (s, 3H), 1.90 (d, $J=1.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 137.0, 134.8, 130.1, 128.8, 126.9, 126.7, 126.0, 125.4, 19.8, 18.8.

(*E*)-1-Methyl-3-(prop-1-en-1-yl)benzene (**2d**)^[22b]: Colorless oil (32.5 mg, 82% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.19~7.11 (m, 3H), 6.99 (d, $J=6.8$ Hz, 1H), 6.36 (d, $J=16.0$ Hz, 1H), 6.24~6.18 (m, 1H), 2.32 (s, 3H), 1.86 (d, $J=6.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 137.9, 131.0, 128.4, 127.5, 126.6, 125.5, 122.9, 21.4, 18.5.

(*E*)-1,3-Dimethyl-5-(prop-1-en-1-yl)benzene (**2e**)^[22c]: Colorless oil (37.3 mg, 85% yield). ^1H NMR (400 MHz, CDCl_3) δ : 6.94 (s, 2H), 6.83 (s, 1H), 6.33 (d, $J=16.8$ Hz, 1H), 6.22~6.17 (m, 1H), 2.31 (s, 6H), 1.85 (d, $J=6.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 137.8, 131.1, 128.4, 125.2, 123.7, 21.2, 18.5.

(*E*)-1-Ethyl-4-(prop-1-en-1-yl)benzene (**2f**)^[22g]: Colorless oil (37.6 mg, 86% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.24 (d, $J=7.6$ Hz, 2H), 7.11 (d, $J=8.0$ Hz, 2H), 6.37 (d, $J=15.6$ Hz, 1H), 6.22~6.15 (m, 1H), 2.61 (q, $J=15.2$, 7.6 Hz, 2H), 1.86 (d, $J=6.8$ Hz, 3H), 1.21 (t, $J=7.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 142.8, 135.4, 130.8, 127.9, 125.7, 124.7, 28.5, 18.4, 15.5.

(*E*)-1-(Prop-1-en-1-yl)-4-propylbenzene (**2g**): Colorless oil (41.3 mg, 86% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.23 (d, $J=7.6$ Hz, 2H), 7.08 (d, $J=7.6$ Hz, 2H), 6.36 (d, $J=15.6$ Hz, 1H), 6.20~6.15 (m, 1H), 2.54 (t, $J=15.6$, 7.6 Hz, 2H), 1.85 (d, $J=6.8$ Hz, 3H), 1.62 (q, $J=15.2$, 7.6 Hz, 2H), 0.92 (t, $J=14.8$, 7.6 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 141.2, 135.4, 130.8, 128.5, 125.6, 124.6, 37.7, 24.5, 18.4, 13.8. IR (KBr) ν : 2959, 2930, 2871, 1699, 1609, 1512, 1456, 1377, 1269, 1076, 962, 825, 415 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{16}$: 160.1252, found 160.1254.

(*E*)-1-(*tert*-Butyl)-4-(prop-1-en-1-yl)benzene (**2h**)^[22d]: Colorless oil (47.0 mg, 90% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.31~7.24 (m, 4H), 6.39~6.35 (m, 1H), 6.22~6.15 (m, 1H), 1.85 (dd, $J=6.8$, 1.6 Hz, 3H), 1.30 (s, 9H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 149.7, 135.2, 130.7, 125.5, 125.4, 124.8, 34.5, 31.3, 18.5.

(*E*)-4-(Prop-1-en-1-yl)-1,1'-biphenyl (**2i**)^[22d]: Colorless oil (37.9 mg, 65% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.61 (s, 2H), 7.55 (d, $J=8.4$ Hz, 2H), 7.45~7.41 (m, 5H), 6.46 (d, $J=15.6$ Hz, 1H), 6.34~6.28 (m, 1H), 1.93 (dd, $J=6.4$, 1.6 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 140.8, 139.5, 137.0, 130.6, 128.7, 127.2, 127.1, 126.9, 126.2, 125.9, 18.6.

(*E*)-2-(Prop-1-en-1-yl)phenol (**2j**)^[22b]: Colorless oil (32.2 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.29

(d, $J=7.6$ Hz, 1H), 7.09 (t, $J=12.8$, 7.6 Hz, 1H), 6.87 (t, $J=10.8$, 7.2 Hz, 1H), 6.79 (d, $J=8.0$ Hz, 1H), 6.59 (d, $J=16.0$ Hz, 1H), 6.22~6.21 (m, 1H), 4.96 (s, 1H), 1.91 (d, $J=6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 152.4, 128.5, 128.1, 127.5, 125.4, 125.2, 121.0, 115.8, 19.1.

(*E*)-4-Chloro-2-methyl-1-(prop-1-en-1-yl)benzene (**2k**)^[22d]: Colorless oil (35.9 mg, 72% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.29 (d, $J=8.8$ Hz, 1H), 7.08 (d, $J=6.8$ Hz, 2H), 6.49 (d, $J=15.6$ Hz, 1H), 6.10~6.04 (m, 1H), 2.28 (s, 3H), 1.88 (d, $J=6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 136.5, 135.5, 132.0, 129.8, 127.8, 127.6, 126.6, 126.0, 19.6, 18.8.

(*E*)-4-(Prop-1-en-1-yl)benzonitrile (**2l**)^[22c]: Colorless oil (34.8 mg, 81% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.55 (d, $J=8.0$ Hz, 2H), 7.38 (d, $J=8.0$ Hz, 2H), 6.39 (d, $J=3.6$ Hz, 2H), 1.92 (d, $J=4.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 142.3, 132.3, 130.2, 129.7, 126.2, 119.1, 109.9, 18.6.

(*E*)-1-(Prop-1-en-1-yl)naphthalene (**2m**)^[22b]: Colorless oil (35.3 mg, 70% yield). ^1H NMR (400 MHz, CDCl_3) δ : 8.11 (s, 1H), 7.81 (s, 1H), 7.72 (d, $J=8.0$ Hz, 1H), 7.53~7.47 (m, 4H), 7.42 (d, $J=8.0$ Hz, 1H), 6.26~6.19 (m, 1H), 1.99 (d, $J=6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 135.7, 133.6, 131.1, 128.9, 128.4, 128.2, 127.2, 125.8, 125.7, 125.6, 123.9, 123.5, 19.0.

(*E*)-2-(Prop-1-en-1-yl)naphthalene (**2n**)^[22d]: Colorless oil (40.3 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.74 (t, $J=9.2$ Hz, 3H), 7.63 (s, 1H), 7.53 (s, 1H), 7.40~7.39 (m, 2H), 6.55 (d, $J=15.6$ Hz, 1H), 6.51~6.31 (m, 1H), 1.91 (dd, $J=8.0$, 6.4 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 135.4, 133.7, 132.6, 131.2, 128.1, 127.8, 127.6, 126.2, 126.1, 125.4, 125.2, 123.5, 18.6.

(*E*)-2-(Prop-1-en-1-yl)benzo[b]thiophene (**2o**)^[22f]: White solid (34.0 mg, 65% yield). m.p. 49 °C (lit.^[22f] m.p. 48~49 °C); ^1H NMR (400 MHz, CDCl_3) δ : 7.71 (d, $J=8.0$ Hz, 1H), 7.63 (d, $J=8.0$ Hz, 1H), 7.26 (t, $J=12.0$, 7.2 Hz, 2H), 7.02 (s, 1H), 6.61 (d, $J=15.6$ Hz, 1H), 6.21~6.12 (m, 1H), 1.90 (d, $J=6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 143.1, 138.5, 128.6, 125.0, 124.3, 124.2, 123.1, 122.1, 120.9, 18.4.

(*E*)-2-(Prop-1-en-1-yl)benzofuran (**2p**): Colorless oil (32.7 mg, 69% yield). ^1H NMR (400 MHz, CDCl_3) δ : 7.50~7.46 (m, 1H), 7.41 (d, $J=8.2$ Hz, 1H), 7.24~7.19 (m, 1H), 7.16 (d, $J=7.5$ Hz, 1H), 6.49 (dd, $J=15.7$, 6.8 Hz, 1H), 6.45 (s, 1H), 6.34 (d, $J=15.7$ Hz, 1H), 1.93 (dd, $J=6.8$, 4.1 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.2, 154.6, 128.6, 123.9, 122.6, 120.6, 120.0, 110.7, 102.4, 18.5; IR (KBr) ν : 3306, 2962, 1658, 1555, 1452, 1253, 1194, 985, 925, 781, 745, 436 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{10}\text{O}$: 158.0732, found 158.0736.

(*E*)-4,4'-(2-Methylpent-1-ene-1,3-diyl)bis(methoxybenzene) (**2r**)^[22h]: White solid (44.4 mg, 50% yield). m.p. 40~40.5 °C (lit.^[22i] m.p. 39~40 °C); ^1H NMR (400 MHz, CDCl_3) δ : 7.18~7.16 (m, 4H), 6.86~6.82 (m, 4H), 6.40 (s, 1H), 3.79 (s, 6H), 3.26~3.22 (m, 1H), 1.82~1.69 (m, 2H), 1.64 (s, 3H), 0.90 (t, $J=14.4$, 7.2 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 157.8, 139.8, 135.9, 131.1, 130.1,

128.8, 124.5, 113.5, 55.8, 55.2, 25.4, 15.7, 12.6.

Supporting Information ^1H NMR and ^{13}C NMR spectra of products **2a**~**2p** and **2r**. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn>.

References

- [1] (a) Gillis, E. P.; Burke, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 6716.
(b) Gross, P. J.; Brase, S. *Chem. Eur. J.* **2010**, *16*, 12660.
(c) Gross, P. J.; Furche, F.; Nieger, M.; Brase, S. *Chem. Commun.* **2010**, *46*, 9215.
(d) Kwon, Y.-J.; Sohn, M.-J.; Zheng, C.-J.; Kim, W.-G. *Org. Lett.* **2007**, *9*, 2449.
- [2] (a) Kabalka, G. W.; Wu, Z.; Ju, Y. *Tetrahedron Lett.* **2003**, *44*, 1187.
(b) Lantaño, B.; Aguirre, J. M.; Ugliarolo, E. A.; Benegas, M. L.; Moltrasio, G. Y. *Tetrahedron* **2008**, *64*, 4090.
(c) Mondal, P.; Thander, L.; Chattopadhyay, S. K. *Tetrahedron Lett.* **2012**, *53*, 1328.
(d) Seijas, J. A.; Vázquez-Tato, M. P.; Entenza, C.; Montserrat Martínez, M.; Ónega, M. G.; Veiga, S. *Tetrahedron Lett.* **1998**, *39*, 5073.
- [3] (a) Catellani, M.; Frignani, F.; Rangoni, A. *Angew. Chem., Int. Ed.* **1997**, *36*, 119.
(b) Goßßen, L. J.; Paetzold, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 1095.
- [4] Jeffery, T. *Tetrahedron Lett.* **2000**, *41*, 8445.
- [5] Peyroux, E.; Berthiol, F.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2004**, 1075.
- [6] (a) Mayer, M.; Czaplik, W. M.; Jacobi von Wangelin, A. *Adv. Synth. Catal.* **2010**, *352*, 2147.
(b) Akiyama, F.; Miyazaki, H.; Kaneda, K.; Teranishi, S.; Fujiwara, Y.; Abe, M.; Taniguchi, H. *J. Org. Chem.* **1980**, *45*, 2359.
- [7] (a) Miller, J.; Dankwardt, J.; Penney, J. *Synthesis* **2003**, *2003*, 1643.
(b) Rollin, Y.; Meyer, G.; Troupel, M.; Fauvarque, J.-F.; Perichon, J. *J. Chem. Soc., Chem. Commun.* **1983**, 793.
- [8] (a) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U.; Bhat, N. G.; Prasad, J. V. N. V. *J. Org. Chem.* **1988**, *53*, 239.
(b) Cahiez, G.; Avedissian, H. *Synthesis* **1998**, 1199.
(c) Kondo, H.; Kageyama, A.; Yamaguchi, Y.; Haga, M.-A.; Kirchner, K.; Nagashima, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1927.
(d) Nagaki, A.; Moriwaki, Y.; Haraki, S.; Kenmoku, A.; Takabayashi, N.; Hayashi, A.; Yoshida, J. *Chem. Asian J.* **2012**, *7*, 1061.
- [9] Colberg, J. C.; Rane, A.; Vaquer, J.; Soderquist, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 6065.
- [10] Hassam, M.; Tahir, A.; Arnot, G. E.; Green, I. R.; Van Otterlo, W. A. *L. Chem. Rev.* **2015**, *115*, 5462.
- [11] (a) Luu, T. X.; Lam, T. T.; Le, T. N.; Duus, F. *Molecules* **2009**, *14*, 3411.
(b) Waldman, S. R.; Monte, A. P.; Bracey, A.; Nichols, D. E. *Tetrahedron Lett.* **1996**, *37*, 7889.
- [12] Lee, H. S.; Lee, G. Y. *Bull. Korean Chem. Soc.* **2005**, *26*, 461.
- [13] (a) Reddy, M. R.; Periasamy, M. *J. Organomet. Chem.* **1995**, *491*, 263.
(b) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248.
- [14] Setty-Fichman, M.; Sasson, Y.; Blum, J. *J. Mol. Catal. A: Chem.* **1997**, *126*, 27.
- [15] (a) Donohoe, T. J.; O'Riordan, T. J.; Rosa, C. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 1014.
(b) Sharma, S. K.; Srivastava, V. K.; Jasra, R. V. *J. Mol. Catal. A: Chem.* **2006**, *245*, 200.
- [16] (a) Biswas, S.; Huang, Z.; Choliy, Y.; Wang, D. Y.; Brookhart, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 13276.
(b) Chianese, A. R.; Shaner, S. E.; Tendler, J. A.; Pudalov, D. M.; Shopov, D. Y.; Kim, D.; Rogers, S. L.; Mo, A. *Organometallics* **2012**, *31*, 7359.
(c) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1976**, 716.
(d) Ge'ard, H. I.; Eisenstein, O.; Lee, D.-H.; Chen, J.; Crabtree, R. H. *New J. Chem.* **2001**, *25*, 1121.
- [17] Scarso, A.; Colladon, M.; Sgarbossa, P.; Santo, C.; Michelin, R. A.; Strukul, G. *Organometallics* **2010**, *29*, 1487.
- [18] (a) Bricout, H.; Mortreux, A.; Monflier, E. *J. Organomet. Chem.* **1998**, *553*, 469.
(b) Jinesh, C. M.; Antonyraj, C. A.; Kannan, S. *Catal. Today* **2009**, *141*, 176.
(c) Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 2994.
- [19] (a) Sui-Seng, C.; Groux, L. F.; Zargarian, D. *Organometallics* **2006**, *25*, 571.
(b) Lim, H. J.; Smith, C. R.; RajanBabu, T. V. *J. Org. Chem.* **2009**, *74*, 4565.
(c) Kim, I. S.; Dong, G. R.; Jung, Y. H. *J. Org. Chem.* **2007**, *72*, 5424.
(d) Jennerjahn, R.; Piras, I.; Jackstell, R.; Franke, R.; Wiese, K. D.; Beller, M. *Chem. Eur. J.* **2009**, *15*, 6383.
(e) Fan, J.; Wan, C.; Wang, Q.; Gao, L.; Zheng, X.; Wang, Z. *Org. Biomol. Chem.* **2009**, *7*, 3168.
- [20] (a) Myagmarsuren, G.; Tkach, V. S.; Shmidt, F. K.; Mohamad, M.; Suslov, D. S. *J. Mol. Catal. A: Chem.* **2005**, *235*, 154.
(b) Gandeepan, P.; Cheng, C. H. *J. Am. Chem. Soc.* **2012**, *134*, 5738.
(c) Ma, H.; Sun, Q.; Li, W.; Wang, J.; Zhang, Z.; Yang, Y.; Lei, Z. *Tetrahedron Lett.* **2011**, *52*, 1569.
- [21] (a) Jia, C. *Science* **2000**, *287*, 1992.
(b) Wang, Y. F.; Gao, Y. R.; Mao, S.; Zhang, Y. L.; Guo, D. D.; Yan, Z. L.; Guo, S. H.; Wang, Y. Q. *Org. Lett.* **2014**, *16*, 1610.
(c) Bedford, R. B.; Haddow, M. F.; Mitchell, C. J.; Webster, R. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 5524.
- [22] (a) Gauthier, D.; Lindhardt, A. T.; Olsen, E. P.; Overgaard, J.; Skrydstrup, T. *J. Am. Chem. Soc.* **2010**, *132*, 7998.
(b) Wu, Q.; Wang, L.; Jin, R.; Kang, C.; Bian, Z.; Du, Z.; Ma, X.; Guo, H.; Goa, L. *Eur. J. Org. Chem.* **2016**, 5415.
(c) Shu, L.; Shi, Y. *Tetrahedron Letters*, **2004**, *45*, 8115.
(d) Hakim siddiqi, S. M. A.; Touchy, A. S.; Kon, K.; Shimizu, K.-C. *Chem. Eur. J.* **2016**, *22*, 6111.
(e) Simonetti, S. O.; Largh, E. L.; Kaufman, T. S. *Org. Biomol. Chem.* **2014**, *12*, 3735.
(f) Xie, W.; Chang, X. *Angew. Chem., Int. Ed.* **2016**, *55*, 1876.
(g) Nishioka, Y.; Uchida, T.; Katsuki, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 1739.
(h) Fornes, V.; Garcia, H.; Marti, V.; Fernandez, L. *Tetrahedron* **1998**, *54*, 3827.
(i) Baker, W.; Flemons, G. F. *J. Chem. Soc.* **1948**, 1984.
- [23] (a) Albéniz, A. C.; Epsinet, P.; Lin, Y.-S. *Organometallics* **1995**, *14*, 2977.
(b) Trost, M. B.; Zhang, T.; Sieber, J. D. *Chem. Sci.* **2010**, *1*, 427.

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