Iranian Journal of Organic Chemistry Vol. 6, No. 4 (2014) 1357-1363

BF_3 catalyzed hydroarylation reactions of arylsubstituted alkynes with different electron rich arenes

Md. Ataur Rahman[a]* and Tsugio Kitamura[b]

[a]*Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh.*
[b]*Department of Chemistry and Applied Chemistry, Graduate School of Science and Engineering, Saga University, Honjo-machi, Saga-840-8502, Japan.*

Received: September 2014; Revised: October 2014; Accepted: October 2014

Abstract: Hydroarylation reactions of aryl-substituted alkynes with arenes proceeded smoothly in the presence of BF_3 catalyst at 50°C and yielded aryl-substituted alkenes in moderate to high yields. Electron rich arenes gave high yields whereas the relatively less electron rich arenes gave moderate yields.

Keywords: Hydroarylation, Alkynes, Arenes, Arylalkenes**,** Catalyst, BF_3.

Introduction

Direct functionalization of simple arenes through the formation of new carbon-carbon bond has several advantages compared to conventional synthetic methods. In this direct carbon-carbon bond formation method aromatic C-H bond directly acts as a functional group and participates directly in the reaction. Transition metal-catalyzed hydroarylation reaction of alkynes is one of the attractive methods for the direct formation of carbon-carbon bond between arenes and alkynes and provides a direct synthesis of arylalkenes in one step from simple arenes. Friedel-Crafts reactions of aromatic compounds have been employed for the direct formation of new carbon-carbon bond, but these reactions require more than equimolar amount of a Lewis acid such as aluminium (III) chloride [1].

To date, different methods for the direct functionalization of arenes through the formation of new carbon-carbon bond between simple arenes and olefins have been developed, which were catalyzed by transition metals or Lewis acid metals [2]. There are some limitations of these developed methods, such as to carry out a transition metal-catalyzed hydroarylation reaction requires high temperature, strong acidic conditions and special cautions for handling the metal catalysts under inert atmosphere. In most cases transition metals alone cannot act as an efficient catalyst. An appropriate activating agent is required to improve the catalytic activity of the transition metals. Some transition metals and catalyst activating agents are very expensive that increase the reagent cost as well as the production cost. Therefore, it is desirable to seek an efficient, convenient, milder and inexpensive catalyst for the direct functionalization of aromatic compounds.

Literature survey shows that till now the use of BF_3 for the direct formation of carbon-carbon bond between arenes and alkynes through the hydroarylation reaction has not attracted the attention of chemists. Therefore, a more convenient, cheap and very simple direct carbon-carbon bond formation method between different electron rich arenes and arylsubstituted alkynes using the Lewis acid, BF_3 is reported.

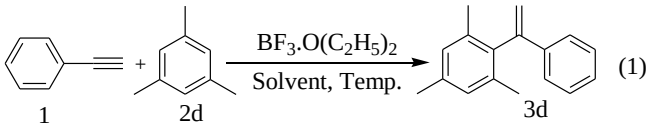
Results and discussion

Optimization of the reaction conditions:

Direct preparation of 1, 1-diarylalkenes was carried out from the corresponding arenes and alkynes using

*Corresponding author. Tel (PABX): 88-02-7791045-51, Ext.1278 (Res.), Fax: 88-02-7791052, E-mail: ataur_ju@yahoo.com

the Lewis acid BF_3 as a catalyst in the presence of dichloroethane solvent at 50°C. In the present study, to optimize the reaction conditions initially, the work was confined on the efficiency of the hydroarylation reaction of phenylacetylene **1** with mesitylene **2d** in the presence of BF_3 catalyst (Scheme **1**). The results are given in Table **1.**



(1)

Scheme 1: Hydroarylation reaction of phenylacetylene **1** with mesitylene **2d** in the presence of BF_3 catalyst under different reaction conditions.

Table 1: Hydroarylation reaction of phenylacetylene **1** with mesitylene **2d** in the presence of BF_3 catalyst under different reaction conditions.

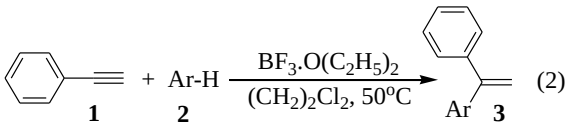
Entry	Arene 2d (mmol)	Temp.°C	Product **3d**	Yield(%)[a]
1	2d	30	3d	53[b]
2	2d	30	3d	55[c]
3	2d	30	3d	17[d]
4	2d	30	3d	52[e]
5	**2d**	**50**	**3d**	**57[f]**
6	2d	60	3d	54[g]
7	2d	50	–	–[h]
8	2d	50	3d	56[f,i]

Reaction conditions: Mesitylene 2d (5.0 mmol), phenylacetylene 1(1.0 mmol), $BF_3.(OC_2H_5)_2$ (1.0 mmol), CH_2Cl_2(2.0 mL) at 30°C for 24 hours.
[a]Isolated yield based on phenylacetylene 1.
[b]Molecular sieve 4A(0.2131g) was used.
[c]CH_2Cl_2 (0.5mL) was used and no molecular sieve was used.
[d]$BF_3.(OC_2H_5)_2$ (2.0 mmol) and molecular sieve 4A(0.2128g) were used.
[e]$BF_3.(OC_2H_5)_2$ (2.0 mmol), CH_2Cl_2(0.5 mL) were used and no molecular sieve was used.
[f]$(CH_2)_2Cl_2$ (0.5mL) at 50°C.
[g]$(CH_2)_2Cl_2$ (0.5mL) at 60°C.
[h]3-butyn-2-one (1.0 mmol), $(CH_2)_2Cl_2$ (0.5mL) at 50°C.
[i]H_2O (1.0 mmol) was used.

The reaction using BF_3 catalyst at 30°C for 24 hours in the presence of CH_2Cl_2 (2.0 mL) and molecular sieve afforded the hydroarylation product **3d** in 53% yield (Entry 1). When the reaction was carried out using less amount of CH_2Cl_2 (0.5 mL) in the absence of molecular sieve improved the yield of the hydroarylation product **3d** (Entry 2). Increasing the amount of BF_3 did not improve the yield (Entries 3, 4). When the reaction was carried out at 50°C then improved the yield but at 60°C decreased the yield (Entries 5, 6). No hydroarylation reaction occurred when the reaction was carried out with the alkyne, 3-butyn-2-one (Entry 7). When the reaction was carried out using equimolar amount of BF_3 and water then afforded 56% of the hydroarylation product **3d** (Entry 8). From the above screening results it was found that the entry 5 is the optimum condition for the reaction. Above experimental results also revealed that BF_3 under anhydrous or water free condition (Entries 1, 3) cannot act as an efficient catalyst. To improve the catalytic activity of BF_3 trace amount of water or atmospheric moisture is necessary (Entries 5, 8).

Scope of the hydroarylation reaction

Using the reaction conditions of Entry 5 the hydroarylation reaction of phenylacetylene **1** was further conducted with different electron rich arenes **2 (**Scheme **2)**. The results are given in Table **2.**



(2)

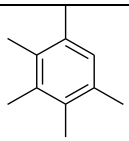
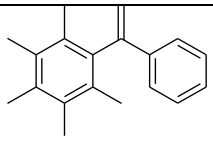
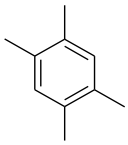
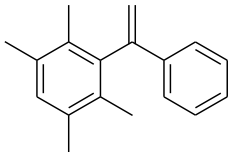
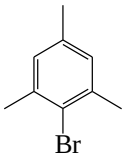
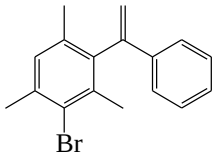
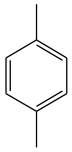
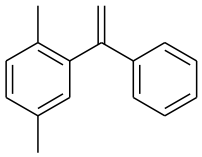
Scheme 2: Hydroarylation reaction of phenylacetylene **1** with different electron rich arenes **2** in the presence of $BF_3.O(C_2H_5)_2$ catalyst.

The hydroarylation reaction of electron rich arenes **2** such as pentamethylbenzene **2a**, 1,2,4,5-tetramethylbenzene **2b**, 1-bromo-2,4,6-trimethylbenzene **2c**, and 1,4-dimethylbenzene **2e** with phenylacetylene **1** afforded 1-aryl-1-phenylethenes **3** in moderate yields (Entries 1-4).

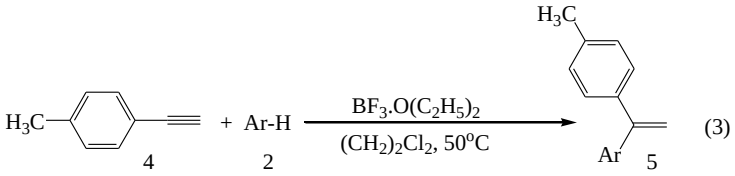
Next, the hydroarylation reactions of 4-methylphenylacetylene **4**, with different electron rich arenes **2** was carried out under the same reaction conditions (Scheme **3**) as that of the reaction of phenylacetylene **1** with different arenes **2**. The results are given in Table **3.** In the reaction of 4-methylphenylacetylene **4** with electron rich arenes **2a, 2b** and **2d** excellent yields of the hydroarylation products **5** were obtained (Entries 1-2, 4). However, the reaction with 1-bromo-2, 4, 6-trimethylbenzene **2c** and *p*-xylene **2e** resulted in a low yield of the hydroarylation products **5c** and **5e** (Entries 3, 5) respectively.

Again, the reaction of an electron withdrawing group containing alkyne, 4-fluorophenylacetylene **6** was examined with various electron rich arenes **2** under the above reaction conditions (Scheme **4**). The results of the reactions are shown in Table **4**. The reaction of electron rich arenes **2a-2d** gave the hydroarylation products **7** in moderate to low yields (Entries 1-5).

Table 2: Hydroarylation reaction of phenylacetylene **1** with different electron rich arenes **2** in the presence of $BF_3.O(C_2H_5)_2$ catalyst[a].

Entry	Arene 2	Time (h)	Product 3	Yield (%)[b]
1	 2a	24	 3a	55
2	 2b	24	 3b	51
3	 Br 2c	36	 Br 3c	32
4	 2e	24	 3e	39

[a]*Reaction conditions*: Arene 2(5.0 mmol), phenylacetylene 1 (1.0 mmol), $BF_3.O(C_2H_5)_2$ (1.0 mmol), $(CH_2)_2Cl_2$ (0.5mL) at 50°C.
[b]Isolated yield based on phenylacetylene 1.

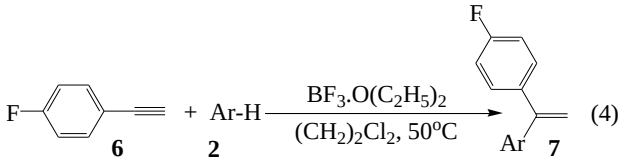


Scheme 3: Hydroarylation reaction of 4-methylphenylacetylene **4** with different electron rich arenes **2** in the presence of $BF_3.O(C_2H_5)_2$ catalyst.

Table 3: Hydroarylation reaction of 4-methylphenylacetylene **4** with different electron rich arenes **2** in the presence of $BF_3.O(C_2H_5)_2$ catalyst[a].

Entry	Arene 2	Time (h)	Product **5**	Yield (%)[b]
1	2a	24	5a	65
2	2b	24	5b	65
3	2c	36	5c	44
4	2d	24	5d	73
5	2e	24	5e	40

[a]*Reaction conditions*: Arene 2 (5.0 mmol), 4-methylphenylacetylene 4 (1.0 mmol), $BF_3.O(C_2H_5)_2$ (1.0 mmol), $(CH_2)_2Cl_2$ (0.5mL) at 50°C.
[b]Isolated yield based on 4-methylphenylacetylene 4.



Scheme 4: Hydroarylation reaction of 4-fluorophenylacetylene **6** with different electron rich arenes **2** in the presence of $BF_3.O(C_2H_5)_2$ catalyst.

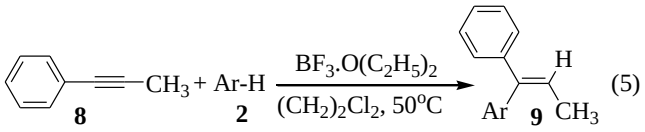
Finally, the hydroarylation reaction of internal alkyne 1-methyl-2-phenylacetylene **8** was examined with various electron rich arenes **2** under the above reaction conditions (Scheme **5**). The results of the reactions are shown in Table **5**. The reaction of 1-methyl-2-phenylacetylene **8** with pentamethylbenzene **2a,** 1, 2, 4, 5-tetramethylbenzene **2b**, 1-bromo-2, 4, 6-trimethylbenzene **2c**, and 1,4-dimethylbenzene **2e** afforded 1-aryl-1-phenylethenes **9** in moderate yields (Entries 1-3, 5). An excellent yield of the hydroarylation product **9d** was obtained when the

reaction was carried out with the electron rich arenes 1, 3, 5-trimethylbenzene **2d (**Entry 4**).**

Table 4: Hydroarylation reaction of 4-fluorophenylacetylene **6** with different electron rich arenes **2** in the presence of $BF_3.O(C_2H_5)_2$ catalyst[a].

Entry	Arene **2**	Time (h)	Product **7**	Yield (%)[b]
1	2a	24	7a	44
2	2b	24	7b	50
3	2c	36	7c	41
4	2d	24	7d	43

[a]*Reaction conditions*: Arene 2 (5.0 mmol), 4-fluorophenylacetylene 6 (1.0 mmol), $BF_3.O(C_2H_5)_2$ (1.0 mmol), $(CH_2)_2Cl_2$ (0.5mL) at 50°C.
[b]Isolated yield based on 4-fluorophenylacetylene 6.



8 **2** **9** (5)

Scheme 5: Hydroarylation reaction of internal alkyne **8** with different electron rich arenes **2** in the presence of $BF_3.O(C_2H_5)_2$ catalyst**.**

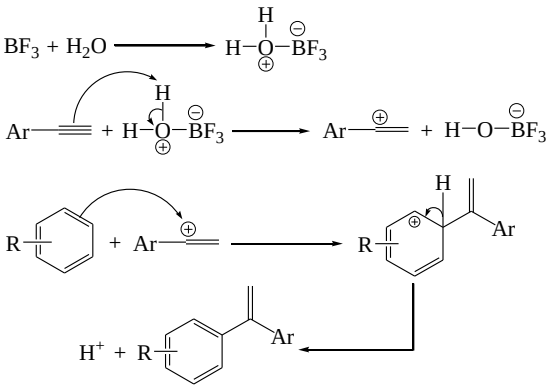
Table 5: Hydroarylation reaction of internal alkyne **8** with different electron rich arenes **2** in the presence of $BF_3.O(C_2H_5)_2$ catalyst[a].

Entry	Arene 2	Time (h)	Product **9**	Yield (%)[b]
1	2a	30	9a	35[c]
2	2b	30	9b	31
3	2c	36	9c	25[c]
4	2d	30	9d	70
5	2e	30	9e	56[c]

[a]*Reaction conditions*: Arene 2 (5.0 mmol), 1-methyl-2-phenylacetylene 8 (1.0 mmol), $BF_3.O(C_2H_5)_2$ (1.0 mmol), $(CH_2)_2Cl_2$ (0.5mL) at 50°C.
[b]Isolated yield based on 1-methyl-2-phenylacetylene 8.
[c]Mixture of *E*- and *Z*-isomer was formed.

Possible mechanism of the $BF_3.O(C_2H_5)_2$ catalyzed hydroarylation reaction [7]:

The hydroarylation reaction between arenes and arylsubstituted alkynes in the presence of $BF_3.O(C_2H_5)_2$ is considered to be a Friedel-Crafts type reaction (Scheme **6**). It has been observed that in BF_3 catalyzed hydroarylation reaction BF_3 directly does not act as a catalyst. First of all BF_3 rapidly reacts with atmospheric moisture / water and forms a hydrogen ion source $H_2O^+–BF_3^-$. An alkyne reacts with a hydrogen ion of the resulting hydrogen ion source, $H_2O^+–BF_3^-$ and forms arylvinyl cation. The resulting arylvinyl cation then undergoes electrophilic aromatic substitution reaction with an electron rich arene to give the desire hydroarylation product, 1, 1-diarylalkene.



Scheme 6: Mechanism of the $BF_3.O(C_2H_5)_2$ catalyzed hydroarylation of alkynes.

Conclusion

In summary, the author has demonstrated that the $BF_3.O(C_2H_5)_2$ catalyzed hydroarylation reaction of alkynes proceeds smoothly and efficiently when arylsubstituted alkynes and electron rich arenes are used. The simplicity of this procedure along with the mildness is practical as a synthetic tool of arylalkenes.

Experimental

*General***:**

All solvents and starting materials were used during the research works as received without further purification unless otherwise indicated. ^1H NMR and ^{13}C NMR were recorded on a JEOL JNM-Al-300FT-NMR spectrometer in $CDCl_3$ solution (TMS as an internal standard). Melting points of the pure compounds were recorded by thin disc method on a YANACO electrothermal melting point apparatus and are uncorrected.

General procedure for the hydroarylation of alkynes:

Required molar amount of $BF_3.O(C_2H_5)_2$(1.0 mmol), $(CH_2)_2Cl_2$ (0.5 mL), arene (5.0 mmol) and alkyne (1.0 mmol) were taken in a 25.0 mL quick-fit round bottom flask and stirred at 50°C temperature until the completion of the reaction. After the completion of the reaction the reaction mixture was poured into 20.0 mL of water. The aqueous reaction mixture was then extracted with dichloromethane (4 x 10.0 mL) and dried over anhydrous sodium sulfate. Finally, dichloromethane was removed under reduced pressure below 40°C**.** Individual pure compounds were isolated from the reaction mixture by column chromatography using silica gel as a stationary phase.

1-(Pentamethylphenyl)-1-phenylethene 3a [3]:

Yield: 0.1407g (55 %); white crystalline solid, Mp 70.0-71.6°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.31-7.24(m, 5H, Ar-H), 5.97(d, 1H, vinyl-H, *J* =1.5Hz), 5.07(d, 1H, vinyl-H, *J* =1.5Hz), 2.29(s, 3H, Me), 2.24(s, 6H, 2xMe), 2.10(s, 6H, 2xMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ =148.58, 139.98, 138.67, 133.72, 132.33, 131.56, 128.35, 127.41, 125.99, 114.31, 17.86, 16.79, 16.57.

1-Phenyl-(2, 3, 5, 6-tetramethylphenyl)ethene 3b [3]:

Yield: 0. 1338g (51%); white crystalline solid, Mp 66.9-68.0°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.29-7.23(m, 5H, Ar-H), 6.97(s, 1H, Ar-H), 5.98(d, 1H, vinyl-H, *J* =1.5Hz), 5.07(d, 1H, vinyl-H, *J* =1.5Hz), 2.25(s, 6H, 2xMe), 2.04(s, 6H, 2xMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ =147.99, 141.04, 139.72, 133.51, 131.96, 130.27, 128.36, 127.47, 125.91, 114.18, 20.16, 16.66.

1-(3-Bromo-2, 4, 6-trimethylphenyl)-1-phenylethene 3c [3]:

Yield: 0.0968g (32%); colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.32-7.24(m, 5H, Ar-H), 7.00(s, 1H, Ar-H), 5.98(d, 1H, vinyl-H, *J* =1.2Hz), 5.07(d, 1H, vinyl-H, *J* =1.2Hz), 2.42(s, 3H, Me), 2.27(s, 3H, Me), 2.07(s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ =147.01, 139.93, 138.92, 136.81, 136.12, 134.90, 129.59, 128.49, 127.77, 125.78, 125.44, 114.81, 23.97, 21.42, 19.93.

1-Phenyl-1-(2, 4, 6-trimethylphenyl)ethene 3d [3]:

Yield: 0.1305g (57%); colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.28-7.24(m, 5H, Ar-H), 6.91(s, 2H, Ar-H), 5.95(d, 1H, vinyl-H, *J* =1.5Hz), 5.09 (d, 1H, vinyl-H, *J* =1.5Hz), 2.32(s, 3H, Me), 2.11(s, 6H, 2xMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ =146.83, 139.51, 138.14, 136.39, 136.08, 128.38, 128.08, 127.51, 125.79, 114.48, 21.02, 20.07.

1-(2, 5-Dimethylphenyl)-1-phenylethene 3e [3]:

Yield: 0.0853g (39%); colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.29-7.24(m, 5H, Ar-H), 7.06(m, 2H, Ar-H), 7.04(m, 1H, Ar-H), 5.75(d, 1H, vinyl-H, *J* =1.5Hz), 5.18(d, 1H, vinyl-H, *J* =1.5Hz), 2.34(s, 3H, Me), 2.01(s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ =149.54, 141.43, 140.63, 135.01, 132.91, 130.65, 129.94, 128.28, 128.16, 127.48, 126.47, 114.62, 20.89, 19.59.

1-(4-Methylphenyl)-1-(pentamethylphenyl)ethene 5a [3]:

Yield: 0.1809g (65%); white crystalline solid, Mp 84.6-85.8°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.20(d, 2H, Ar-H, *J* = 8.1Hz), 7.09(d, 2H, Ar-H, *J* = 8.1 Hz), 5.93(d, 1H, vinyl-H, *J* =1.5 Hz), 5.00(d , 1H, vinyl-H, *J* =1.2 Hz), 2.32(s, 3H, Me), 2.29(s, 3H, Me), 2.23 (s, 6H, 2xMe), 2.09(s, 6H, 2xMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ =148.41, 138.87, 137.21, 137.18, 133.59, 132.28, 131.55, 129.07, 125.90, 113.31, 21.10, 17.83, 16.75, 16.54.

1-(4-Methylphenyl)-1-(2, 3, 5, 6-tetramethylphenyl) ethene 5b [3]:

Yield: 0.1688g (65%); white crystalline solid, Mp 113.8-115.3°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.18(d, 2H, Ar-H, *J* = 8.1 Hz), 7.09(d, 2H, Ar-H, *J* = 8.1 Hz), 6.96(s, 1H, Ar-H), 5.93(d, 1H, vinyl-H, *J* =1.2 Hz), 5.00(d, 1H, vinyl-H, *J* =1.2 Hz), 2.32(s, 3H, Me) , 2.24(s, 6H, 2xMe), 2.04(s, 6H, 2xMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ =147.82, 141.24, 137.28, 136.94, 133.46, 131.95, 130.19, 129.09, 125.84, 113.20, 21.10, 20.13, 16.62.

1-(3-Bromo-2, 4, 6-trimethylphenyl)-1-(4-methyl phenyl)ethene 5c [3]:

Yield: 0.1453g (44%); colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.16(d, 2H, Ar-H, *J* =8.4 Hz), 7.10(d, 2H, Ar-H, *J* =8.4 Hz), 6.99(s, 1H, Ar-H), 5.93(d, 1H, vinyl-H, *J* =1.2 Hz), 5.01(d, 1H, vinyl-H, *J* =1.2 Hz), 2.42(s, 3H, Me), 2.33(s, 3H, Me), 2.26(s, 3H,Me), 2.06(s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ =146.79, 140.11, 137.62, 136.68, 136.09, 136.07, 134.87, 129.55, 129.20, 125.68, 125.40, 113.81, 23.95, 21.39, 21.11, 19.89.

1-(4-Methylphenyl)-1-(2, 4, 6-trimethylphenyl)ethene 5d [3]:

Yield: 0.1824g (73%); colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.18(d, 2H, Ar-H, *J* = 8.1 Hz), 7.08(d, 2H, Ar-H, *J* = 8.1Hz), 6.90(s, 2H, Ar-H), 5.91(d, 1H, vinyl-H, *J* =1.2 Hz), 5.03(d, 1H, vinyl-H, *J* =1.2 Hz), 2.32(s, 6H, 2xMe), 2.11(s, 6H, 2xMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ =146.64, 138.33, 137.29, 136.67, 136.27, 136.07, 129.10, 128.05, 125.69, 113.48, 21.08, 21.02, 20.03.

1-(2, 5-Dimethylphenyl)-1-(4-methylphenyl)ethene 5e [3]:

Yield: 0.1025g (40%); colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.18-7.03(m, 7H, Ar-H), 5.71(d, 1H, vinyl-H, *J* = 1.5 Hz), 5.12(d, 1H, vinyl-H, *J* =1.5 Hz), 2.33 (s, 6H, 2xMe), 2.01(s, 3H, Me).

^{13}C NMR (75 MHz, $CDCl_3$): δ =149.30, 141.62, 137.79, 137.27, 134.96, 132.91, 130.60, 129.90, 128.99, 128.07, 126.36, 113.73, 21.11, 20.90, 19.58.

1-(4-Fluorophenyl)-1-(pentamethylphenyl)ethene7a [3]:

Yield: 0.1403g (44%); white crystalline solid, Mp 75.9-76.0°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.28[dd, 2H, Ar-H, *J* =7.8 (F-H) and 6.6Hz], 6.98[dd, 2H, Ar-H, *J* =8.7(F-H) and 9.0Hz], 5.90(d, 1H, vinyl-H, *J* =1.2Hz), 5.04(d, 1H, vinyl-H, *J* =1.2 Hz), 2.29(s, 3H, Me), 2.24(s, 6H, 2xMe), 2.09(s, 6H, 2xMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ =162.33(d, $^1J_{C-F}$ =245.4 Hz), 147.57, 138.45, 136.12(d, $^4J_{C-F}$ =3.08 Hz), 133.87, 132.44, 131.44, 127.64(d, $^3J_{C-F}$ =7.43Hz), 115.16(d, $^2J_{C-F}$ =21.0Hz), 113.98, 17.78, 16.76, 16.56.

1-(4-Fluorophenyl)-1-(2,3,5,6-tetramethyl phenyl) ethene 7b:

Yield: 0.1364g (50%); white crystalline solid, Mp 69.0-70.6°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.26-7.21(m, 2H, Ar-H), 6.98-6.92(m, 3H, Ar-H), 5.91(d, 1H, vinyl-H, *J* =0.9 Hz), 5.04(s, 1H, vinyl-H), 2.25(s, 6H, 2xMe), 2.03(s, 6H, 2xMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ =162.33(d, $^1J_{C-F}$ =244.73 Hz), 146.90, 140.77, 135.82(d, $^4J_{C-F}$ =3.08 Hz), 133.64, 131.86, 130.37, 127.55(d, $^3J_{C-F}$ =7.43Hz), 115.18(d, $^2J_{C-F}$ =21.08Hz), 113.90, 20.16, 16.60.

1-(3-Bromo-2, 4, 6-trimethylphenyl)-1-(4-fluorophenyl)ethene 7c.

Yield: 0.1357g (41%); colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.26-7.20(m, 2H, Ar-H), 7.00-6.93(m, 3H, Ar-H), 5.91(s, 1H, vinyl-H), 5.04(s, 1H, vinyl-H), 2.42(s, 3H, Me), 2.26(s, 3H, Me), 2.06(s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ =162.47(d, $^1J_{C-F}$ =245.4 Hz), 145.93, 139.65, 136.98, 136.03, 135.05(d, $^4J_{C-F}$ =3.75 Hz), 134.80, 129.67, 127.45(d, $^3J_{C-F}$ = 8.03Hz), 125.49, 115.36(d, $^2J_{C-F}$ =21.68Hz), 114.54(d, *J* =1.88 Hz), 23.97, 21.36, 19.87.

1-(4-Fluorophenyl)-1-(2,4,6-trimethylphenyl)ethene 7d:

Yield: 0.1091g (43%); colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.26-7.21(m, 2H, Ar-H), 6.98-6.92(m, 4H, Ar-H), 5.88(s, 1H, vinyl-H), 5.07(s, 1H, vinyl-H), 2.32(s, 3H, Me), 2.10(s, 6H, 2xMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ =162.38(d, $^1J_{C-F}$ =244.8Hz), 145.75, 137.87, 136.57, 136.00, 135.61(d, $^4J_{C-F}$ =3.08 Hz), 128.16, 127.42(d, $^3J_{C-F}$ =8.03 Hz), 115.22(d, $^2J_{C-F}$ =21.08Hz), 114.21(d, J_{C-F} =1.88 Hz), 21.02, 20.01.

1-(Pentamethylphenyl)-1-phenyl-2-methylethene 9a [4]:

Yield: 0.0989g (35%); colorless viscous liquid. Mixture of *E*- and *Z*-isomers (50:50). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.30-7.13(m, 10H, Ar-H), 6.40-6.33(q, 1H, vinyl-H), 5.63-5.56(q, 1H, vinyl-H), 2.28(s, 3H, Me), 2.25 (s, 3H, Me), 2.23(s, 6H, 2xMe), 2.21(s, 6H, 2xMe), 2.16(s, 6H, 2xMe), 2.04(s, 6H, 2xMe), 2.01-1.98(d, 3H, Me), 1.50-1.48(d, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ =141.80, 1.41.61, 141.32, 141.19, 139.88, 135.97, 133.38, 133.32, 132.27, 132.19, 131.81, 131.52, 129.17, 128. 22, 127.79, 126.42, 126.24, 125.91, 125.73, 123.22, 18.09, 17.14, 16.75, 16.61, 15.46, 15.12.

(*E*)*-1-(2, 3, 5, 6-tetramethylphenyl)-1-phenyl-2-methylethene 9b:*

Yield: 0.0816g (31%); white crystalline solid, Mp 84.5-85.8°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.31-7.16(m, 5H, Ar-H), 6.91(s, 1H, Ar-H), 5.63-5.56(q, 1H, vinyl-H), 2.22(s, 6H, 2xMe), 2.10(s, 6H, 2xMe), 2.02-1.99(d, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ =143.79, 140.57, 139.56, 133.46, 132.22, 130.00, 129.15, 127.78, 126.29, 125.89, 20.27, 16.92, 15.44.

1-(3-Bromo-2, 4, 6-trimethylphenyl)-1-phenyl-2-methylethene 9c [5]:

Yield: 0.0898g (25%); colorless viscous liquid. Mixture of *Z*- and *E*-isomers (86:14). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.38-7.14(m, 10H, Ar-H), 7.01 (s, 1H, Ar-H), 6.94(s, 1H, Ar-H), 6.42-6.35(q, 1H, vinyl-H), 5.65-5.57(q, 1H, vinyl-H), 2.42(s, 3H, Me), 2.38(s, 6H, 2xMe), 2.33(s, 6H, 2xMe), 2.22(s, 3H, Me), 2.10(s, 6H, 2xMe), 2.05(s, 3H, Me), 2.02-1.99(d, 3H, Me), 1.53-1.51(d, 3H, Me).

(*Z*)*-1-(2, 4, 6-trimethylphenyl)-1-phenyl-2-methyl ethene 9d* [2e]:

Yield: 0.1698g (70%); colorless viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.26-7.17(m, 5H, Ar-H), 6.92(s, 2H, Ar-H), 6.40-6.33(q, 1H, vinyl-H), 2.32(s, 3H, Me), 2.04(s, 6H, 2xMe), 1.54-1.52(d, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ =140.42, 139.82, 136.21, 136.18, 135.55, 128.28, 128.11, 126.56, 125.49, 123.30, 21.07, 19.69, 14.98.

1-(2, 5-Dimethylphenyl)-1-phenyl-2-methylethene 9e [6]:

Yield: 0.1497g (56%); colorless viscous liquid. Mixture of *E*-and *Z*-isomers (82:18). ^{1}H NMR (300 MHz, $CDCl_3$): δ =7.32-6.89(m, 16H, Ar-H), 6.31-

6.24(q, 1H, vinyl-H), 5.80-5.73(q, 1H, vinyl-H), 2.32(s, 3H, Me), 2.05(s, 3H, Me), 2.03(s, 3H, Me), 1.97(s, 3H, Me), 1.91-1.89(d, 3H, Me), 1.61-1.58(d, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ =143.88, 142.49, 141.53, 141.49, 140.05, 139.07, 135.01, 134.76, 133.35, 132.92, 130.88, 130.57,130.02, 129.86, 129.41, 128.16, 127.81, 127,79, 127.62, 126.54, 126.42, 126.05, 125.82, 123.55, 20.95, 20.87, 19.89, 18.99, 15.40, 15.35.

References

[1] a) Carey, F. A.; Sundberg, R. J. Advanced Organic Chemistry, Part B, 4th. Ed.; Kluwer Academic / Plenum Press: New York, **2001**, Chap. 11. (b) Smith, M. B.; March, J. March's Advanced Organic Chemistry, 6th. Ed.; Wiley-Interscience: New York, **2007**, Chap. 11.

[2] (a) Fujiwara, Y.; Kitamura, T. In Handbook of C-H transformations; Dyker, G., Ed.; Wiley- VCH: Weinheim, **2005**, 194. (b) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (c) Oyamada, J.; Kitamura, T. *Chem. Lett.* **2005**, *34***,** 1430. (d) Oyamada, J.; Kitamura, T. *Tetrahedron*, **2007**, *63*, 12754. (e) Reetz, M. T.; Sommer, K. Eur. *J. Org. Chem.* **2003**, 3485. (f) Nevado, C.; Echavarren, A. M. *Synthesis* **2005**, 167. (g) Shi, Z.; He, C. *J. Org. Chem.* **2004**, *69*, 3669. (h) Nakao, Y.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2008**, *130*, 2448. (i) Yoon, M.Y.; Kim, J. H.; Choi, D. S.; Shin, U. S.; Lee, J. Y.; Song, C. E. *Adv. Synth. Catal.* **2007**, *349*, 1725. (j) Li, R.; Wang, S. R.; Lu, W. *Org. Lett.* **2007**, *9*, 2219. (k) Biffis, A.; Tubaro, C.; Buscemi, G.; Basato, M. *Adv. Synth. Catal.* **2008**, *350*, 189. (l) Kakiuchi, F.; Chatnai, N. *Adv. Synth. Catal.* **2003**, *345*, 1077.

[3] Rahman, M. A.; Ogawa, O.; Oyamada, J.; Kitamura, T. *Synthesis* **2008**, 3755-3760.

[4] Biffis, A.; Gazzola, L.; Gobbo, P.; Buscemi, G.; Tubaro, C.; Basato, M. *Eur. J. Org. Chem.* **2009**, 3189.

[5] Viciu, M. S.; Stevens, E. W.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2004**, *23***,** 3752.

[6] Tsuchimoto, T.; Maeda, T.; Shirakawa, E.; Kawakami, Y. *Chem. Commun.* (Cambridge) **2000**, 1573.

[7] (a) Solomons, T. W. G; Fryhle, C. B.; Organic Chemistry, 7th Ed.; John Wiley and Sons, Inc.: New York, **2000**, 472. (b) Billmeyer, F. W. Jr; Text Book of Polymer Science; 3rd Ed.; Published by John Wiley & Sons (Asia) Pte. Ltd., Singapore; Reprint **2007**, 82-87.