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Catalytic hydroarylation of alkynes with arenes in the presence of FeCl3 and AgOTf

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1. Introduction

Catalytic functionalization of C–H bonds forming new C–C bonds is one of the significant subjects in organic synthesis [1]. Such direct functionalization of C–H bonds does not require any pre-functionalization of the C–H bonds transforming into reactive C–halogen bonds, and consequently it reduces reaction steps to furnish highly efficient synthetic processes.

Hydroarylation of alkynes is a highly efficient reaction with high atom economy, and it provides aromatic alkenes through a direct introduction of a double bond into an aromatic C—H bond [2]. Noble and rare metals have been used so far as the catalysts for the hydroarylation of alkynes [3]. The hydroarylation reactions of alkynes proceed through aromatic C—H activation or through alkyne activation. The previous studies on the hydroarylation reactions through the activation of alkynes prove that soft catalysts with a high Lewis acidity such as Pd, Pt, Au, and In are essential. However, these metals are rare, expensive, and not economical. If such noble metal catalysts could be replaced by abundant and economical metals, the hydroarylation reactions of alkynes would be a more valuable method for synthesis of aromatic alkenes.

Iron is a cheap, readily available, non-toxic and environmentally friendly transition metal, and shows increasing and promising catalytic ability in many organic syntheses [4]. Until now, however, little attention has been paid to iron as a catalyst for hydroarylation

ABSTRACT

Hydroarylation of propiolic acids with various arenes in TFA proceeded efficiently in the presence of FeCl₃/AgOTf catalyst system. In the case of electron-rich arenes, the iron-catalyzed hydroarylation gave cinnamic acids in moderate to high yields. The hydroarylation of phenylacetylene was observed but the catalyst was not effective under the same conditions.

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reactions of alkynes [5]. Recently, Lu et al. reported the hydroarylation reaction of aryl-substituted alkynes with simple and substituted arenes in the presence of FeCl₃ in nitromethane without using any additives under mild conditions [5b]. Arylsubstituted alkynes undergo the hydroarylation with electron-rich arenes to afford 1,1-diarylalkenes. In the hydroarylation reaction of an electron-deficient propiolic acid, it is necessary to increase a cationic property of FeCl₃ because the hydroarylation reaction is considered to proceed through electrophilic aromatic substitution. Thus, we decided to use FeCl₃ activated with silver triflate (AgOTf) and found that hydroarylation of propiolic acid with arenes proceeded efficiently under a FeCl₃/AgOTf catalytic system [6]. Very recently, Takaki et al have demonstrated that Fe(OTf)₃ catalyzes intramolecular hydroarylation of aryl-substituted alkynes [7]. Herein we report the hydroarylation reaction of alkynes with arenes with the aid of the FeCl₃/AgOTf catalytic system.

2. Results and discussion

2.1. Iron-catalyzed hydroarylation of propiolic acids

As we have found that trifluoroacetic acid (TFA) is a good solvent for hydroarylation reactions [3l-r], a mixed solvent of TFA and 1,2dichloroethane (DCE) is a good choice of the solvent even in the iron-catalyzed hydroarylation of propiolic acids. First, we optimized the reaction conditions concerning the hydroarylation of propiolic acid (**2a**) with mesitylene (**1a**), where 3-(2,4,6-trimethylphenyl)propenoic acid (**3a**) was the hydroarylation product. For



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Table 1

Hydroarylation of **2a** with **1a** in the presence of iron catalysts.^a



Entry	Catalyst	mol%	Yield (%) ^b	E/Z^{c}
1	FeCl ₃	20	62	71/29
2	FeCl ₃ /AgOTf	20/60	99	66/34
3	FeCl ₃ /AgOTf	10/30	38	66/34
4	FeCl ₃ /AgOTf	20/20	46	72/28
5 ^d	FeCl ₃ /AgOTf	20/60	100	55/45
6 ^e	FeCl ₃ /AgOTf	20/60	88	58/42
7 ^f	FeCl ₃ /AgOTf	20/60	0	-
8	FeCl ₃ ·6H ₂ O	20	15	10/90
9	FeCl ₃ ·6H ₂ O/AgOTf	10/30	12	16/84
10	FeCl ₃ ·6H ₂ O/AgOTf	20/20	22	11/89
11	FeCl ₃ ·6H ₂ O/AgOTf	20/60	32	14/86
12 ^g	FeCl ₃ ·6H ₂ O/AgOTf	20/60	3	12/88
13	AgOTf	20	52	20/80
14 ^h	-	-	0	-

 $^a\,$ Reaction conditions: Fe catalyst, AgOTf, 1a (4 mmol), 2a (2 mmol), TFA (0.5 mL) and DCE (0.5 mL) at 60 $^\circ C$ for 15 h.

^b Isolated yield.

^c Determined by ¹H NMR.

^d Only TFA (1 mL) was used as solvent.

^e TFA (0.5 mL) and nitromethane (0.5 mL) were used as solvent.

^f Only nitromethane (1 mL) was used as solvent.

^g Molecular sieves 4A (0.126 g) was added.

^h In the absence of FeCl₃ and AgOTf.

the iron catalyst, FeCl₃, FeCl₃· $6H_2O$, FeCl₃/AgOTf and FeCl₃· $6H_2O$ / AgOTf were examined. The results are given in Table 1.

Even in the presence of FeCl₃ only, the hydroarylation reaction proceeded to afford 3a in 62% yield (entry 1). Addition of 3 equivalents of AgOTf significantly improved the hydroarylation reaction, which proceeded almost quantitatively to give 3a in 99% yield (entry 2). However, a lower loading of the catalyst or AgOTf resulted in poor yields of **3a** (entries 3 and 4). Use of TFA as solvent was effective for the hydroarylation to give **3a** quantitatively (entry 5). This result indicates that the use of TFA as the solvent is also essential for the present iron-catalyzed hydroarylation. Interestingly, the hydroarylation catalyzed by FeCl₃/AgOTf provides a mixture of E- and Z-cinnamic acids 3a with a slightly excess of the *E* isomer. This behavior is different from that of the hydroarylation reaction with Pd or Pt catalyst, in which thermodynamically unstable Z isomer 3 is formed predominantly [31-r]. Replacement of DCE by nitromethane as the co-solvent decreased the product yield to 88% (entry 6). When the reaction was conducted only in nitromethane, no hydroarylation products were formed (entry 7). This result differs from that reported by Lu et al. [5b]. We also examined the reaction with FeCl₃·6H₂O catalyst. However, it was found that FeCl₃·6H₂O catalyst was not effective under the present conditions even in the presence of AgOTf (entries 8-11). The addition of molecular sieves retarded the reaction (entry 12). The hydroarylation took place in the presence of AgOTf (20 mol%) but the yield of 3a was 52% (entry 13). Since the reactions without any catalysts do not take place (entry 14), an iron is considered to be an actual catalyst for hydroarylation.

A different selectivity of *E* and *Z* isomers was observed between the reactions with $FeCl_3$ and $FeCl_3 \cdot 6H_2O$. As the result was thought to be attributable to the degree of the isomerization, the isomerization of *Z*-**3a** was examined under the hydroarylation conditions. Scheme 1 indicates that the isomerization proceeds under the hydroarylation conditions.



Scheme 1. Isomerization of Z-3a under the reaction conditions.

With the optimized reaction conditions in hand, we examined the scope of this hydroarylation with various arenes. The results are given in Table 2. For electron-rich arenes such as pentamethylbenzene (1b) and 2,4,6-trimethylphenol (1f) the hydroarylation proceeded well (entries 1, 2, 7, 8), but for moderately activated or inactivated arenes the reaction gave low yields of the hydroarylation products 3 (entries 3-6, 9). In the reaction of phenylpropiolic acid (2b), the hydroarylation reaction proceeded as well to give 3,3-diarylpropenoic acids **3h**–**3j** when electron-rich arenes were employed (entries 10-12). Interestingly, the hydroarylation of **2b** gave the single isomer. We estimated the chemical shift of the vinylic proton according to the literature [8]. The calculation of the chemical shift concerning the vinylic proton of the products **3h–3j** indicates 6.67 ppm for the Z isomer and 6.34 ppm for the *E* isomer. The observed chemical shift ranges from 6.60 to 6.68 ppm. Therefore, the configuration of these products **3h–3i** arising from the double bond is considered to be Z. We also found that E/Z isomerization occurred when Z-3a was treated under the same conditions using FeCl₃/AgOTf. Accordingly, a stable Z isomer is considered to be formed after the isomerization. The hydroarylation of phenylpropiolic acid did not proceed in the absence of FeCl₃/AgOTf catalyst (entry 13). The same reaction with FeCl₃ catalyst only gave **3h** in 28% yield (entry 14). The combined FeCl₃/AgOTf catalyst is good for this reaction.

On the other hand, the reaction with methoxy-substituted benzenes showed a different behavior from that with the above aromatic substrates **1**, as shown in Table 3. In the reaction of **2a** with anisole (**1h**), two anisole molecules added to the triple bond of **2a** to give 3,3-bis(4-methoxyphenyl)propionic acid (**4a**) in 22% yield. This double hydroarylation of propiolic acid has been also observed in the palladium-catalyzed hydroarylation [3q]. Similarly, the reactions with 4-methoxytoluene (**1i**) and 1,4-dimethoxybenzene (**1j**) proceeded smoothly to give the corresponding double addition products **4b** and **4c** in 58 and 76% yields, respectively.

Furthermore, the hydroarylation of ethyl propiolate (**5**) with mesitylene (**1a**) was conducted under the same conditions, as shown in Scheme 2. Although the hydroarylation reaction proceeded efficiently, cinnamic acid **3a** was obtained as a major product, together with ethyl cinnamate **6**. It is interesting that hydrolysis of ethyl ester **6** takes place under the conditions using FeCl₃/AgOTf catalyst because the same hydroarylation reaction using PtCl₂/AgOTf or K₂PtCl₄/AgOTf catalyst does not cause the hydrolysis [3n,3o].

In the FeCl₃/AgOTf-catalyzed hydroarylation reaction of propiolic acid, there exist the following characteristic results to consider the reaction mechanism. (1) The hydroarylation reaction catalyzed by FeCl₃/AgOTf in TFA provided a mixture of (*E*)- and (*Z*)-cinnamic acids **3**. This is strongly contrasts with the reaction catalyzed by palladium and platinum compounds where the (*Z*)-cinnamic acids are formed selectively [3l-3r]. (2) In the present reaction, isomerization of *cis*- to *trans*-cinnamic acids is not important because the hydroarylation with FeCl₃·6H₂O under the similar conditions gives (*Z*)-cinnamic acid **3a** as the major isomer. (3) Activated, electron-rich arenes show high reactivity.

 Table 2
 FeCl₃/AgOTf-catalyzed hydroarylation of 2 with various arenes 1.^a

		FeCl ₃ (20 mol%) AgOTf (60 mol%)	R
Ar-H +	RCO ₂ H	TFA, DCE	Ar CO ₂ H
1	2	60 °C, 15 h	3

Entry	Arene 1	2 R	TFA (mL)	DCE (mL)	Product 3	Yield (%) ^b	E/Z ^c
1	H 1b	Н	1	2	CO ₂ H 3b	92	70/30
2	1b	Н	1	0	3b	78	58/42
3	H lc	н	0.5	0.5	CO ₂ H ^{3c}	34	69/31
4	H ^{1d}	Н	0.5	0.5	CO ₂ H 3d	7	68/32
5 ^d	1d	Н	1	1	3d	11	69/31
6	H le	Н	1	0.5	Generation Se	9	63/37
7	H If	Н	0.5	0.5	OH 3f	48	70/30
8	1f	Н	0.5	1	3f	59	66/34
9	H lg Br	Н	0.5	0.5	Br CO ₂ H 3g	17	72/28
10	la	Ph	0.5	0.5	Ph 3h CO ₂ H	41	Ζ
11	1b	Ph	0.5	0.5	Ph 3i CO ₂ H	55	Ζ
12	1c	Ph	0.5	0.5	Ph 3j CO ₂ H	74	Ζ

(continued on next page)

Table 2 (continued)

Entry	Arene 1	2 R	TFA (mL)	DCE (mL)	Product 3	Yield (%) ^b	E/Z ^c
13 ^e	1a	Ph	0.5	0.5	3h	0	_
14 ^f	1a	Ph	0.5	0.5	3h	28	Ζ

^a Reaction conditions: FeCl₃ (0.4 mmol), AgOTf (1.2 mmol), **1** (4 mmol), **2** (2 mmol), TFA and DCE at 60 °C for 15 h except for entries 10 and 12 where the reaction time was 4 h.

^c Determined by ¹H NMR.

^d At refluxing temperature.

^e In the absence of FeCl3 and AgOTf.

^f In the presence of AgOTf (0.4 mmol).

A proposed mechanism is shown in Scheme 3. First, FeCl₃ reacts with AgOTf to generate a highly cationic, reactive Fe(OTf)₃, which interacts with propiolic acid to form a vinyl cation. Since a primary open vinyl cation is very unstable and the formation is not possible [9], Fe(OTf)₃ should coordinate with the oxygen atom of the carbonyl and activate the propiolic acid. Formation of a bridged vinyl cation is possible but it may be ruled out by judging from the formation of the *E* and *Z* isomers of cinnamic acids. The resulting vinyl cation undergoes electrophilic aromatic substitution with an electron-rich arene and finally generates a product by protonation. At the same time, regeneration of Fe(OTf)₃ is concomitant and completes the catalytic cycle. In the cases of methoxybenzenes, the cinnamic acids produced in the first hydroarylation further undergo second hydroarylation to give 3,3-diarylpropionic acids because such cinnamic acids are electron-rich compounds [10].

2.2. Hydroarylation of phenylacetylene in the presence of \mbox{FeCl}_3 and \mbox{AgOTf}

As it is reported that hydroarylation of arylacetylenes proceeds in nitromethane in the presence of Fe catalysts [5,7], the hydroarylation of phenylacetylene as the arylacetylenes was examined under our reaction conditions using 10 mol% FeCl₃/3AgOTf catalyst.

Table 3

Double hydroarylation of 2a catalyzed by FeCl₃/AgOTf.^a

The results are given in Table 4. The reaction of phenylacetylene (**7**) with mesitylene (**1a**) using a FeCl₃/AgOTf catalyst system in a mixed solvent of TFA and CH₂Cl₂ at 30 °C for 60 h afforded 1-phenyl-1-(2,4,6-trimethylphenyl)ethene (**8a**) in 86% yield (entry 1). The reaction of electron-rich arenes such as pentamethylbenzene (**1b**), 1,2,4,5-tetramethylbenzene (**1c**), 1,4-dimethylbenzene (**1d**) and 1-bromo-2,4,6-trimethylbenzene (**1g**) afforded 1-aryl-1-phenyl-ethenes **8** in good to high yields (entries 2–4, 6).Benzene (**1e**) showed a low reactivity with **6** to afford the hydroarylation product **8e** only in 18% yield (entry 5).

When the present reaction was compared with the similar reaction without Fe catalysts [11], the results were almost same as those in the reaction in TFA without Fe catalysts. The FeCl₃/AgOTf catalyst did not increase the yields of hydroarylation products **8** under the present conditions using TFA as the solvent.

3. Conclusion

In conclusion, we have demonstrated that iron-catalyzed hydroarylation of propiolic acids with various arenes in TFA. The reaction proceeded efficiently in the presence of FeCl₃/AgOTf catalytic system. Especially, in the case of electron-rich arenes, the iron-catalyzed hydroarylation proceeded well and gave cinnamic





^a Reaction conditions: FeCl₃ (0.4 mmol), AgOTf (1.2 mmol), 1 (4 mmol), 2a (2 mmol), TFA (0.5 mL) and DCE (0.5 mL) at 60 °C for 15 h.

^b Isolated yield.



Scheme 2. Hydroarylation of 5 with 1a.

acids in moderate to high yields. Even FeCl₃ only is capable of catalyzing the hydroarylation reaction, but the addition of AgOTf enhances the reactivity. However, it has been found that the same hydroarylation of phenylacetylene under the present conditions does not require Fe catalysts.

4. Experimental

All solvents and starting materials were used during the research works as received without further purification unless otherwise indicated. ¹H and ¹³C NMR were recorded on a JEOL JNM-AL 300 FT-NMR spectrometer (TMS as an internal standard). Melting points were measured with a YANACO micro melting point apparatus and are uncorrected. Elemental analysis was performed by the Service Center of the Elemental Analysis of Organic Compounds, Faculty of Science, Kyushu University, Japan.

4.1. General procedure for FeCl₃/AgOTf-catalyzed hydroarylation of propiolic acids

After a mixture of FeCl₃ (0.4 mmol) and AgOTf (1.2 mmol) in TFA and DCE was stirred at room temperature for 10 min, arene **1** (4 mmol) and propiolic acid **2** (2 mmol) were added and then the mixture was stirred at 60 °C for 15 h. The reaction mixture was poured into water (20 mL), neutralized with NaHCO₃, and extracted with ether (20 mL × 3). The ethereal layer was washed with 2 M NaOH (10 mL × 3). The aqueous layer was washed with ether, acidified with HCl (ca. 36%) and extracted with CH₂Cl₂ (20 mL × 3). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give cinnamic acids **3** as solids.

4.1.1. 3-(2,4,6-Trimethylphenyl)propenoic acid (3a) [30]

A mixture of *E* and *Z* isomers, white solid; ¹H NMR (300 MHz, CDCl₃) δ 2.18 (s, Me), 2.28 (s, Me), 2.29 (s, Me), 2.35 (s, Me), 6.08 (d, *J* = 16.2 Hz, vinyl-H), 6.12 (d, *J* = 12.0 Hz, vinyl-H), 6.86 (s, ArH), 6.91 (s, ArH), 7.15 (d, *J* = 16.2 Hz, vinyl-H), 7.96 (d, *J* = 12.0 Hz, vinyl-H), 11.20 (brs, CO₂H); ¹³C NMR (75 MHz, CDCl₃) δ 20.00, 20.89, 122.07, 127.89, 131.99, 134.44, 136.92, 146.28, 171.10.



Scheme 3. A proposed mechanism.

4.1.2. 3-(Pentamethylphenyl)propenoic acid (3b) [30]

A mixture of *E* and *Z* isomers; white solid; ¹H NMR (300 MHz, CDCl₃) δ 2.14 (s, Me), 2.16 (s, Me), 2.20 (s, Me), 2.23 (s, Me), 2.26 (s, Me), 5.91 (d, *J* = 16.2 Hz, vinyl-H), 6.17(d, *J* = 11.7 Hz, vinyl-H), 7.26 (d, *J* = 11.7 Hz, vinyl-H), 8.02 (d, *J* = 16.2 Hz, vinyl-H), 8.51 (brs, CO₂H); ¹³C NMR (75 MHz, CDCl₃) δ 16.35, 16.76, 17.62, 121.72, 129.87, 132.22, 132.38, 134.51, 148.28, 170.19.

4.1.3. 3-(2,3,5,6-Tetramethylphenyl)propenoic acid (3c) [3o]

A mixture of *E* and *Z* isomers; white solid; ¹H NMR (300 MHz, CDCl₃) δ 2.09 (s, Me), 2.17 (s, Me), 2.22 (s, Me), 2.23 (s, Me), 5.92 (d, *J* = 16.5 Hz, vinyl-H), 6.17 (d, *J* = 12.0 Hz, vinyl-H), 6.92 (s, ArH), 6.96 (s, ArH), 7.20 (d, *J* = 12.3 Hz, vinyl-H), 7.96 (d, *J* = 16.5 Hz, vinyl-H), 9.94 (brs, CO₂H); ¹³C NMR (75 MHz, CDCl₃) δ 16.52, 19.90, 121.89, 130.36, 130.98, 133.39, 134.04, 147.81, 169.95.

4.1.4. 3-(2,5-Dimethylphenyl)propenoic acid (3d) [30]

A mixture of *E* and *Z* isomers; white solid; ¹H NMR (300 MHz, CDCl₃) δ 2.21 (s, Me), 2.22 (s, Me), 2.28 (s, Me), 2.33 (s, Me), 6.00 (d, *J* = 12.3 Hz, vinyl-H), 6.33 (d, *J* = 15.9 Hz, vinyl-H), 7.01–7.05 (m, 2H, ArH), 7.08 (s, ArH), 7.13 (s, ArH), 7.21 (d, *J* = 12.3 Hz, vinyl-H), 8.03 (d, *J* = 15.9 Hz, vinyl-H), 10.30 (brs, CO₂H); ¹³C NMR (75 MHz, CDCl₃) δ 19.34, 20.83, 119.69, 129.33, 129.57, 129.66, 132.75, 134.16, 134.72, 146.07, 171.20.

4.1.5. Cinnamic acid (3e) [3o]

A mixture of *E* and *Z* isomers; white solid; ¹H NMR (300 MHz, CDCl₃) δ 5.95 (d, *J* = 12.6 Hz, vinyl-H), 6.43 (d, *J* = 15.9 Hz, vinyl-H), 7.05 (d, *J* = 12.6 Hz, vinyl-H), 7.32–7.36 (m, ArH), 7.57–7.60 (m, ArH), 7.77 (d, *J* = 15.6 Hz, vinyl-H), 11.32 (brs, CO₂H); ¹³C NMR (75 MHz, CDCl₃) δ 118.66, 128.06, 129.36, 129.94, 134.32, 145.90, 171.67.

4.1.6. 3-(3-Hydroxy-2,4,6-trimethylphenyl)propenoic acid (3f)

A mixture of *E* and *Z* isomers; white solid; ¹H NMR (300 MHz, CDCl₃) δ 2.10 (s, Me), 2.20 (s, Me), 2.23 (s, Me), 4.93 (s, OH), 5.99 (d, *J* = 16.2 Hz, vinyl-H), 6.15 (d, *J* = 12.0 Hz, vinyl-H), 6.80 (s, ArH), 6.84 (s, ArH), 7.11 (d, *J* = 12.0 Hz, vinyl-H), 7.89 (d, *J* = 16.2 Hz, vinyl-H), 9.79 (brs, CO₂H); ¹³C NMR (75 MHz, CDCl₃) δ 13.02, 15.86, 19.54, 120.40, 122.21, 122.96, 126.31, 129.37, 133.55, 146.04, 149.84. 169.95. The structure was further confirmed by converting to the known ethyl ester, ethyl 3-(3-hydroxy-2,4,6-trimethylphenyl)propenoate [3q].

4.1.7. 3-(3-Bromo-2,4,6-trimethylphenyl)propenoic acid (**3g**) [30]

A mixture of *E* and *Z* isomers; white solid; ¹H NMR (300 MHz, CDCl₃) δ 2.10 (s, Me), 2.21 (s, Me), 2.28 (s, Me), 2.36 (s, Me), 2.49 (s, Me), 2.57 (s, Me), 5.92 (d, *J* = 16.5 Hz, vinyl-H), 6.11 (d, *J* = 12.3 Hz, vinyl-H), 6.91 (s, ArH), 6.96 (s, ArH), 7.10 (d, *J* = 12.0 Hz, vinyl-H), 7.84 (d, *J* = 16.2 Hz, vinyl-H), 10.77 (brs, CO₂H); ¹³C NMR (75 MHz, CDCl₃) δ 19.92, 21.26, 23.95, 122.47, 125.13, 129.43, 133.14, 133.81, 134.28, 137.27, 146.05, 170.54.

4.1.8. (2Z)-3-Phenyl-3-(2,4,6-trimethylphenyl)propenoic acid (**3h**) [3n]

Colorless crystals; mp 195–197 °C (AcOEt/Hexane); ¹H NMR (300 MHz, CDCl₃) δ 2.03 (s, 6H, Me), 2.32 (s, 3H, Me), 6.60 (s, 1H, vinyl-H), 6.90 (s, 2H, ArH), 7.31–7.34 (m, 5H, ArH); ¹³C NMR

Table 4

Hydroarylation of 7 with 1 in the presence of FeCl₃/AgOTf catalyst.^a



Entry	Arene	Time (h)	Product	Yield (%) ^b	Yield (%) without Fe catalysts ^c
1	1a	24	8a	86	71
2 ^d	16	30	8b	77	93
3	1c	24	Sc Sc	80	75
4	1d	24	8d	50	63
5	1e	60	8e	18	9
6	1g	56	8g Br	62	69

^a Reaction conditions: 7 (1.0 mmol), 1 (5.0 mmol), FeCl₃ (0.10 mmol), AgOTf (0.30 mmol), TFA (1.0 mL), CH₂Cl₂ (3.0 mL) at 30 °C.

^b Isolated yield based on 7.

^c Reference [11].

^d CH₂Cl₂ (6.0 mL) was used instead of 3.0 mL.

(75 MHz, CDCl₃) δ 19.71, 21.12, 116.90, 127.18, 128.26, 128.73, 129.86, 134.36, 134.76, 137.19, 138.17, 157.03, 169.16.

4.1.9. (2Z)-3-(Pentamethylphenyl)-3-phenylpropenoic acid (**3i**) [3n]

Colorless crystals; mp 236–238 °C (AcOEt/Hexane); ¹H NMR (300 MHz, CDCl₃) δ 2.04 (s, 6H, Me), 2.23 (s, 6H, Me), 2.29 (s, 3H, Me), 6.68 (s, 1H, vinyl-H), 7.31–7.34 (m, 5H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 16.54, 16.93, 17.54, 117.11, 127.28, 128.78, 129.88, 130.60, 133.16, 133.45, 135.46, 138.39, 157.66, 166.99.

4.1.10. (2Z)-3-Phenyl-3-(2,3,5,6-tetramethylphenyl)propenoic acid (**3***j*) [12]

Colorless crystals; mp 203–206 °C (AcOEt/Hexane); ¹H NMR (300 MHz, CDCl₃) δ 1.98 (s, 6H, Me), 2.25 (s, 6H, Me), 6.67 (s, 1H,

vinyl-H), 7.02 (s, 1H, ArH), 7.31–7.35 (m, 5H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 16.30, 19.99, 116.93, 127.23, 128.69, 129.77, 130.64, 131.15, 133.60, 137.04, 138.45, 157.98, 169.46.

4.1.11. 3,3-Bis(4-methoxyphenyl)propionic acid (4a) [3q,13]

Colorless crystals; mp 125–126 °C (EtOH/hexane); ¹H NMR (300 MHz, CDCl₃) δ 3.01 (d, *J* = 7.5 Hz, 2H, CH₂), 3.75 (s, 6H, OMe), 4.42 (t, *J* = 7.5 Hz, 1H, CH), 6.80 (d, *J* = 8.7 Hz, 2H, ArH), 7.11 (d, *J* = 8.7 Hz, 2H, ArH), 8.71 (brs, 1H, CO₂H); ¹³C NMR (75 MHz, CDCl₃) δ 40.72, 45.10, 55.20, 113.99, 128.47, 135.78, 158.17, 177.94.

4.1.12. 3,3-Bis(2-methoxy-5-methylphenyl)propionic acid (4b) [6]

Colorless crystals; mp 158–159 °C (EtOH/hexane); ¹H NMR (300 MHz, CDCl₃) δ 2.22 (s, 6H, Me), 3.00 (d, *J* = 7.8 Hz, 2H, CH₂), 3.70 (s, 6H, OMe), 5.12 (t, *J* = 7.8 Hz, 1H, CH), 6.71 (d, *J* = 8.1 Hz, 2H,

ArH), 6.89 (s, 2H, ArH), 6.95 (d, J = 8.1 Hz, 2H, ArH), 9.83 (brs, 1H, CO₂H); ¹³C NMR (75 MHz, CDCl₃) δ 20.71, 34.65, 38.50, 55.60, 110.80, 127.65, 129.05, 129.28, 130.95, 155.07, 178.60.

4.1.13. 3,3-Bis(2,5-dimethoxyphenyl)propionic acid (4c) [3q]

Colorless crystals; mp 111–112 °C (EtOH/hexane); ¹H NMR (300 MHz, CDCl₃) δ 3.00 (d, *J* = 7.8 Hz, 2H, CH₂), 3.70 (s, 12H, OMe), 5.10 (t, *J* = 7.8 Hz, 1H, CH), 6.66–6.76 (m, 6H, ArH), 8.96 (brs, 1H, CO₂H); ¹³C NMR (75 MHz, CDCl₃) δ 35.27 38.19, 55.59, 56.17, 111.32, 111.96, 115.30, 132.33, 151.53, 153.42, 178.12.

4.1.14. Ethyl 3-(2,4,6-trimethylphenyl)propenoate (6) [3q]

Colorless liquid; ¹H NMR (300 MHz, CDCl₃) δ 1.10 (t, J = 7.0 Hz, Me), 1.34 (t, J = 7.0 Hz, Me), 2.28 (s, Me), 2.33 (s, Me), 4.02 (d, J = 7.0 Hz, CH₂), 4.26 (d, J = 7.0 Hz, CH₂), 6.02 (d, J = 16.2 Hz, vinyl-H), 6.09 (d, J = 11.7 Hz, vinyl-H), 6.82 (s, ArH), 6.89 (s, ArH), 7.01 (d, J = 11.7 Hz, vinyl-H), 7.81 (d, J = 16.2 Hz, vinyl-H).

4.2. General procedure for hydroarylation of phenylacetylene in the presence of FeCl₃ and AgOTf

A mixture of FeCl₃ (0.10 mmol), AgOTf (0.30 mmol), TFA (1.0 mL), and CH₂Cl₂ (1.0 mL) was stirred for about 15 min at room temperature. An arene (5.0 mmol), a phenylacetylene (1.0 mmol) and CH₂Cl₂ (2.0 mL) were then added into the catalysts mixture and stirred at 30 °C until the completion of the reaction. The reaction mixture was dissolved in 20 mL of dichloromethane and passed through a short path silica gel (2.0 g) column to remove the insoluble catalysts. The column was washed with dichloromethane. Collected dichloromethane solution was washed with 5% aqueous NaHCO₃ solution to remove TFA and dried over anhydrous Na₂SO₄. Finally, dichloromethane was removed under reduced pressure. Individual pure compounds were isolated from the reaction mixture by column chromatography on silica gel.

4.2.1. 1-Phenyl-1-(2,4,6-trimethylphenyl)ethane (8a) [11]

Colorless liquid; ¹H NMR (300 MHz, CDCl₃) δ 2.11(s, 6H, Me), 2.31 (s, 3H, Me), 5.09 (d, J = 1.2 Hz, 1H, vinyl-H), 5.95 (d, J = 1.2 Hz, 1H, vinyl-H), 6.90 (s, 2H, ArH), 7.27–7.20 (m, 5H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 20.06, 21.02, 114.45, 125.82, 127.51, 128.11, 128.39, 136.08, 136.38, 138.17, 139.55, 146.91.

4.2.2. 1-(Pentamethyphenyl)-1-phenylethene (8b) [11]

White crystals; mp 71.4–72.7 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.10 (s, 6H, Me), 2.24 (s, 6H, Me), 2.29 (s, 3H, Me), 5.06 (d, J = 1.2 Hz, 1H, vinyl-H), 5.97 (d, J = 1.5 Hz, 1H, vinyl-H), 7.29–7.23 (m, 5H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 16.55, 16.75, 17.83, 114.27, 126.01, 127.41, 128.35, 131.56, 132.33, 133.70, 138.72, 140.03, 148.66.

4.2.3. 1-Phenyl-(2,3,5,6-tetramethylphenyl)ethene (8c) [11]

White Crystals; mp 67.8–68.9 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.96 (s, 6H, Me), 2.16 (s, 6H, Me), 4.97 (d, J = 1.5 Hz, 1H, vinyl-H), 5.89 (d, J = 1.5 Hz, 1H, vinyl-H), 6.88 (s, 1H, ArH), 7.19–7.11 (m, 5H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 16.63 20.12, 114.16, 125.94, 127.47, 128.36, 130.29, 131.96, 133.51, 139.77, 141.08, 148.05.

4.2.4. 1-(2,5-Dimethylphenyl)-1-phenylethene (8d) [11]

Colorless liquid; ¹H NMR (300 MHz, CDCl₃) δ 2.01 (s, 3H, Me), 2.33 (s, 3H, Me), 5.18 (d, J = 1.2 Hz, 1H, vinyl-H), 5.75 (d, J = 1.2 Hz, 1H, vinyl-H), 7.03 (m, 1H, ArH), 7.06 (m, 2H, ArH), 7.28–7.22 (m, 5H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 19.57, 20.89, 114.61, 126.48,

127.49, 128.16, 128.28, 129.94, 130.65, 132.92, 135.02, 140.67, 141.46, 149.58.

4.2.5. 1,1-Diphenylethene (8e) [11]

Colorless liquid; ¹H NMR (300 MHz, CDCl₃) δ 5.46 (s, 2H, vinyl-H), 7.35–7.30 (m, 10H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 114.24, 127.69, 128.15, 128.26, 141.50, 150.08.

4.2.6. 1-(3-Bromo-2,4,6-trimethylphenyl)-1-phenylethene(8g) [11]

Colorless liquid; ¹H NMR (300 MHz, CDCl₃) δ 2.07 (s, 3H, Me), 2.27 (s, 3H, Me), 2.42 (s, 3H, Me), 5.07 (d, J = 1.5 Hz, 1H, vinyl-H), 5.97 (d, J = 1.5 Hz, 1H, vinyl-H), 7.00 (s, 1H, ArH), 7.30–7.24 (m, H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ 19.91, 21.41, 23.94, 114.80, 125.45, 125.81, 127.78, 128.50, 129.61, 134.91, 136.13, 136.82, 138.97, 139.97, 147.07.

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