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FeX_3-Promoted Intermolecular Addition of Benzylic Alcohols to Aromatic Alkynes: A Mild and Efficient Strategy for the Synthesis of Alkenyl Halides

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Keywords: Alkenes / Alkynes / Alcohols / Iron / Synthetic methods / Halides

A convenient, effective, mild and simple strategy has been developed for the synthesis of alkenyl halides by the intermolecular addition of benzylic alcohols to aromatic alkynes. The reactions were carried out in the presence of iron(III) bromide or chloride in 1,2-dibromoethane without additives in air at room temperature. Alkenyl bromides and chlorides were obtained with high regio- and stereoselectivity (*E*/*Z* up to 99:1) in good-to-excellent yields in 0.5–1 h under mild reaction conditions.

Introduction

Lewis acid promoted carbon–carbon bond-forming reactions by the addition of carbonium ions to alkenes have been extensively explored in the past.[1] However, compared with alkenes, the use of alkynes as electron-rich substrates attacked by carbonium ions has been limited.[2] In addition, most of these transformations are catalysed by anhydrous zinc(II) chloride and bromide.[2c,2d] Clearly, these methods have significant drawbacks, such as the difficulty in handling the moisture-sensitive catalyst, the need for anhydrous conditions and long reaction times. Thus, the development of more convenient and effective Lewis acid mediators for the addition of electrophiles to alkynes is desirable.

Iron is one of the most abundant metals on the earth and consequently one of the most inexpensive and environmentally friendly ones. Iron salts as effective, alternative and promising transition-metal catalysts have received much attention because of their unique properties.[3] Over the past few years, iron-catalysed oxidation,[4] hydrogenation,[5] hydrosilylation,[6] rearrangement,[7] Michael addition[8] and Mannich reactions[9] have been intensively investigated. In addition, iron-catalysed C–S,[10] C–N,[11] C–O[12] and C–C bond-forming reactions (such as Sonogashira, Heck, Negishi, Kumada, and Suzuki reactions) have recently been developed.[13] However, Buchwald and Bolm recently found that the actual catalyst for the above C–N (–S, –O) bond-forming reactions is a catalytic amount of Cu^{II} and not Fe^{III}.[14] It is assumed that the reported reactions with $FeCl_3$ may in certain cases be significantly affected by trace quantities of other metals, particularly copper. However, we are certain that it is desirable to expand the application scope of iron salts in organic transformations due to their unique properties and significant advantages for both the academic and industrial community. Herein we wish to report an efficient and mild iron-promoted intermolecular addition of benzylic alcohols to aromatic alkynes, which generates the corresponding alkenyl halides in high yields.

The relative stabilities of benzylic, allylic and propargylic carbonium ions are well documented and have been the subject of numerous theoretical and experimental studies.[15] Yet, the availability of these cations has not resulted in their general use as synthetic intermediates due to the strong acidic conditions required to generate them.[16] The direct utilization of benzylic alcohols as electrophiles would be quite useful as they would be more atom-economic and environmentally friendly and are commercially available.[17] To the best of our knowledge, there is only one report, by Kabalka et al., of the reactions of benzylic alcohols with aromatic alkynes in the presence of *n*BuLi and BCl_3, which gives (*E*)-alkenyl chlorides as the major products.[18] It would be desirable to develop a protocol for the direct addition of benzylic alcohols to alkynes mediated by a milder Lewis acid. During our ongoing efforts devoted to iron-mediated organic reactions, we have developed an effective and mild FeX_3-promoted strategy for the synthesis of alkenyl halides by the addition of benzylic alcohols to aromatic alkynes. The reactions were carried out in the presence of iron(III) bromide or chloride in 1,2-dibromoethane without any additives in air and generated alkenyl bromides or chlorides in high yields and with high regio- and stereoselectivity at room temperature within 1 h with the *E* isomers as the major products (*E*/*Z* up to 99:1; Scheme 1).

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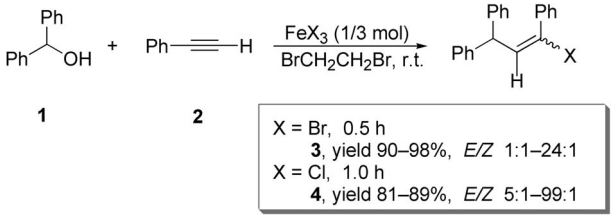
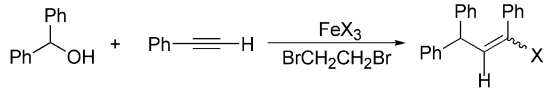


Scheme 1.

Results and Discussion

To optimize the reaction conditions and identify the best iron species, solvent and reaction temperature, diphenylmethanol and phenylacetylene were chosen as model substrates, and the results are summarized in Table 1. When 33.33 mol-% of $FeBr_3$ or $FeCl_3$ was used as the promoter at room temperature in 1,2-dichloroethane, the desired alkenyl bromide (**3a**) and chloride (**4a**) were obtained in 73 and 55% yields, respectively (Table 1, Entries 1 and 2). Interestingly, **4a** was isolated in only 30% yield when $FeCl_3{\cdot}6H_2O$ was used instead of $FeCl_3$, which showed that $FeCl_3$ is a far better Lewis acid (Table 1, Entry 3). However, $FeCl_2$ did not promote this addition reaction and the starting materials were recovered (Table 1, Entry 4).

Table 1. Optimization of the reaction conditions for the addition of diphenylmethanol to phenylacetylene.[a]



Entry	Fe salt	Solvent	Product	Yield [%][b]
1	$FeCl_3$	$ClCH_2CH_2Cl$	**4a**	55
2	$FeBr_3$	$ClCH_2CH_2Cl$	**3a**	73
3	$FeCl_3{\cdot}6H_2O$	$ClCH_2CH_2Cl$	**4a**	30
4	$FeCl_2$	$ClCH_2CH_2Cl$	–	0
5	$FeCl_3$	$BrCH_2CH_2Br$	**4a**	85
6	$FeBr_3$	$BrCH_2CH_2Br$	**3a**	98
7	$FeBr_3$	toluene	**3a**	15
8	$FeBr_3$	1,4-dioxane	**3a**	10
9	$FeBr_3$	DMSO	–	0
10	$FeBr_3$	DMF	–	0
11	$FeBr_3$	C_2H_5OH	–	0
12	$FeBr_3$	CH_3NO_2	–	0 (18)[c]
13	$FeBr_3$	CH_3CN	–	0 (13)[c]
14[d]	$FeBr_3$	$BrCH_2CH_2Br$	**3a**	98
15[e]	$FeBr_3$	$BrCH_2CH_2Br$	**3a**	99
16[f]	$FeBr_3$	$BrCH_2CH_2Br$	**3a**	61
17[g]	$FeBr_3$	$BrCH_2CH_2Br$	**3a**	29

[a] Reaction conditions: diphenylmethanol (1.0 equiv.), phenylacetylene (1.1 equiv.), Fe salt (0.3333 equiv.) and solvent (1.0 mL equiv.$^{-1}$), 25 °C, 1 h. [b] Isolated yield of the *E*/*Z* mixture. [c] Yield of 1,3,3-triphenylpropan-1-one. [d] At 50 °C. [e] At 75 °C. [f] In the presence of 0.2 equiv. $FeBr_3$. [g] In the presence of 0.1 equiv. $FeBr_3$.

Further investigation of the solvent effect indicated that the nature of the reaction media significantly affects the reaction (Table 1). 1,2-Dibromoethane was found to be an excellent solvent for the addition of diphenylmethanol to phenylacetylene, giving a quantitative yield of **3a** in the presence of 33.33 mol-% $FeBr_3$ at room temperature in 1 h (Table 1, entry 6). The use of 1,2-dibromoethane afforded **4a** in good yield with $FeCl_3$ as the promoter, although the yield of **4a** was slightly lower than that of **3a** (Table 1, Entry 5 vs. 6). In other classic solvents, such as toluene and 1,4-dioxane, the yields of the desired addition products were dramatically lowered (Table 1, Entries 7 and 8). Unfortunately, the desired product was not isolated when the reaction was carried out in DMSO, DMF, C_2H_5OH, CH_3NO_2 or CH_3CN (Table 1, Entries 7–13). Interestingly, 1,3,3-triphenylpropan-1-one was isolated in yields of 10–20% when the reaction of diphenylmethanol and phenylacetylene was carried out in CH_3NO_2 or CH_3CN in the presence of $FeBr_3$ (Table 1, Entries 12 and 13).[19] The effect of temperature on the reaction was also surveyed, and the results show that the yield of **3a** was not improved when the reaction temperature was increased to 50 or 75 °C (Table 1, Entries 14 and 15).

With respect to the iron salt loading, 33.33 mol-% of $FeBr_3$ or $FeCl_3$ was found to be optimal. When 20 or 10 mol-% of $FeBr_3$ was used, the desired product **3a** was isolated in 61 and 29% yields, respectively (Table 1, Entries 16 and 17). In this reaction, $FeBr_3$ and $FeCl_3$ act as both Lewis acid promoter and the source of halide ions.

To examine the scope of the reaction, different types of benzylic alcohols were prepared according to the literature or purchased commercially and subjected to the previously optimized reaction conditions. The results are outlined in Table 2. Initially, phenylacetylene was used as the model substrate, and a variety of benzylic alcohols were examined in the presence of $FeBr_3$. As can be seen from Table 2, secondary benzylic alcohols were often much more reactive than primary ones (Table 2, Entries 1–7 and 11–14 vs. 8–10) and gave the desired addition products in excellent yields with an *E*/*Z* ratio in the range of 4:1 to 14:1 (Table 2, Entries 1–7). Secondary benzylic alcohols with either electron-donating or -withdrawing groups attached to the benzene ring smoothly underwent the addition reaction and generated the corresponding products in high yields (Table 2, Entries 2–5). Moreover, steric effects were not obvious (Table 2, Entry 3). However, when other secondary or tertiary alcohols, such as *tert*-butyl alcohol, 2-propanol or cyclohexanol, were treated with phenylacetylene, the desired addition products were not obtained.

Various alkynes were investigated as substrates in the reaction with diphenylmethanol under the standard reaction conditions (Table 2). Aromatic terminal alkynes with either electron-donating or -withdrawing functional groups, such as methyl, fluoro, bromo and chloro groups, reacted with diphenylmethanol in the presence of $FeBr_3$ to afford the corresponding alkenyl bromides in good yields and stereoselectivities (Table 2, Entries 11–14). A 1,2-disubstituted ethyne, 1,2-diphenylethyne, also underwent the reaction with diphenylmethanol to produce the desired product in a moderate yield and with a very high *E*/*Z* ratio (25:1, Table 2, Entry 15). However, aliphatic terminal alkynes,

Table 2. $FeBr_3$-promoted addition of benzylic alcohols to alkynes.[a]

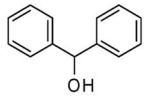
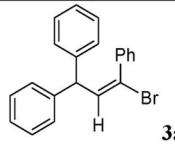
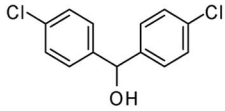
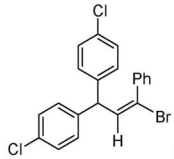
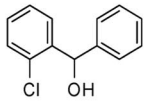
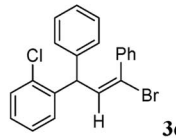
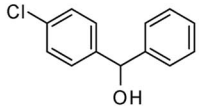
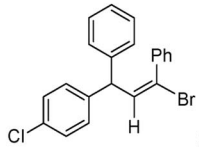
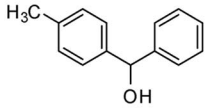
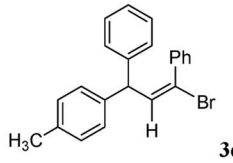
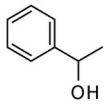
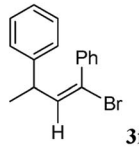
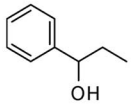
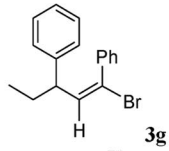
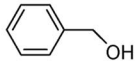
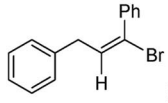
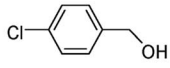
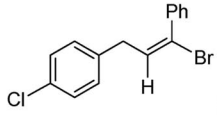
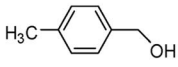
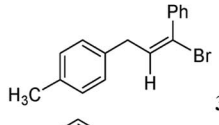
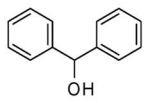
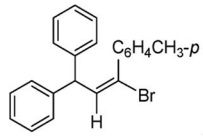
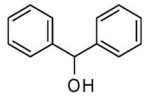
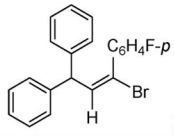
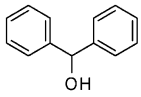
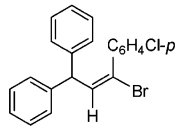
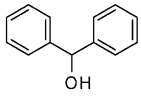
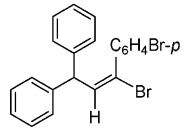
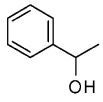
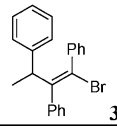
Entry	Alcohol	Alkyne	Main product	Yield [%][b] (*E*/*Z*)
1		PhC≡CH	 **3a**	98 (7:1)
2		PhC≡CH	 **3b**	96 (6:1)
3		PhC≡CH	 **3c**	90 (14:1)
4		PhC≡CH	 **3d**	95 (6:1)
5		PhC≡CH	 **3e**	97 (5:1)
6		PhC≡CH	 **3f**	98 (5:1)
7		PhC≡CH	 **3g**	95 (4:1)
8		PhC≡CH	 **3h**	57 (8:1)
9		PhC≡CH	 **3i**	55 (2:1)
10		PhC≡CH	 **3j**	62 (2:1)
11		*p*-$CH_3C_6H_4C$≡CH	 **3k**	98 (1:1)
12		*p*-FC_6H_4C≡CH	 **3l**	99 (4:1)

Table 2. *(Continued)*

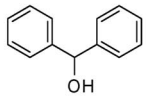
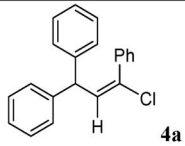
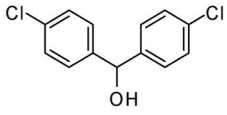
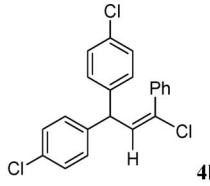
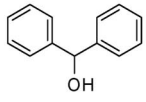
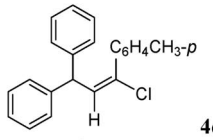
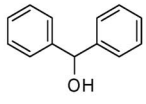
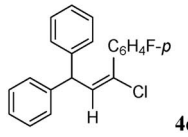
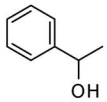
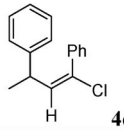
Entry	Alcohol	Alkyne	Main product	Yield [%][b] (*E*/*Z*)
13		*p*-ClC$_6$H$_4$C≡CH	 **3m**	99 (24:1)
14		*p*-BrC$_6$H$_4$C≡CH	 **3n**	97 (6:1)
15		PhC≡CPh	 **3o**	62 (25:1)

[a] Reaction conditions: alcohol (1 equiv.), alkyne (1.1 equiv.), $FeBr_3$ (>98%, 0.3333 equiv.) and 1,2-dibromoethane (1.0 mL equiv.$^{-1}$) at room temperature (25 °C) for 0.5 h. [b] Isolated yield of the *E*/*Z* mixture; the *E*/*Z* ratio was determined by ^{1}H NMR spectroscopy.

such as 1-octyne and 1-decyne, were inactive in this reaction.

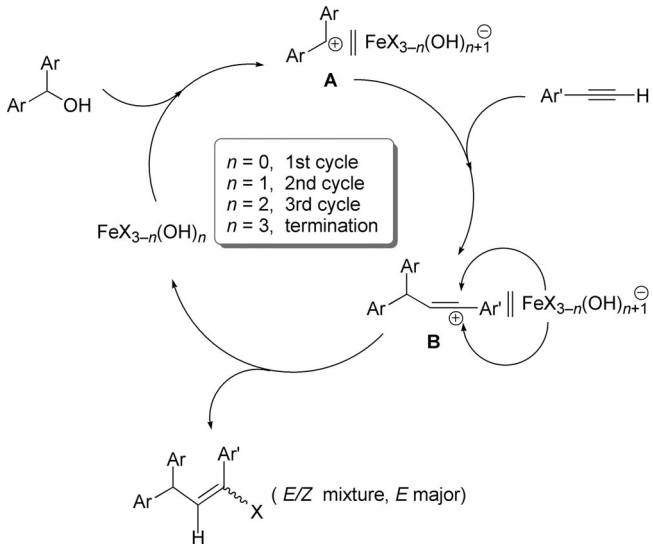
To synthesize different kinds of alkenyl chlorides, the reactions of a variety of alcohols and alkynes were examined in the presence of $FeCl_3$ under the above reaction conditions. The results in Table 3 show that secondary benzylic alcohols and terminal aromatic alkynes are good substrates for the addition reaction, and 81–89% yields of the desired alkenyl chlorides were obtained in 1 h with an *E*/*Z* ratio in the range of 5:1 to 99:1 (Table 3, Entries 1–5). The results also revealed that the electronic characteristics of general electron-donating (such as CH_3) or -withdrawing groups (such as F, Cl) attached to the benzene ring of the benzylic alcohols or aromatic alkynes were relatively insensitive to the reaction conditions (Table 3, Entries 1–5). However, when primary benzylic alcohols and aliphatic terminal alkynes served as the starting materials, poor yields of the corresponding products were observed.

Table 3. $FeCl_3$-promoted addition of benzyl alcohols to alkynes.[a]

Entry	Alcohol	Alkyne	Main product	Yield [%][b] (*E*/*Z*)
1		PhC≡CH	 **4a**	85 (24:1)
2		PhC≡CH	 **4b**	84 (5:1)
3		*p*-CH$_3$C$_6$H$_4$C≡CH	 **4c**	89 (23:1)
4		*p*-FC$_6$H$_4$C≡CH	 **4d**	88 (99:1)
5		PhC≡CH	 **4e**	81 (7:1)

[a] Reaction conditions: benzylic alcohol (1.0 equiv.), arylalkyne (1.1 equiv.), $FeCl_3$ (>99.99%, 0.3333 equiv.) and 1,2-dibromoethane (1.0 mL equiv.$^{-1}$) at room temperature (25 °C) for 1 h. [b] Isolated yield of the *E*/*Z* mixture; the *E*/*Z* ratio was determined by ^{1}H NMR spectroscopy.

A possible mechanism for the FeX_3-promoted addition of benzylic alcohol to aromatic alkyne is shown in Scheme 2. Benzyl alcohol is activated by the Lewis acid, $FeBr_3$ or $FeCl_3$, to form a carbocation intermediate **A** and $Fe(OH)X_3^-$ as an ion-pair in the first cycle. The carbocation **A** attacks the electron-rich aromatic alkyne with excellent regioselectivity to generate vinyl cation **B**. The sp-hybridized vinyl cation **B** can be attacked by X^- in $Fe(OH)X_3^-$ to give an *E*/*Z* mixture of the alkenyl halide with good stereoselectivity (*E* isomer as the major product) and $Fe(OH)X_2$, which is used to activate the benzyl alcohol in the second cycle, until it is finally transformed into $Fe(OH)_3$ without activity. It is clear that FeX_3 (X = Br or Cl) acts as both Lewis acid promoter and the source of halide ions. To lower the FeX_3 loading, the reaction of diphenylmethanol and phenylacetylene was examined in the presence of 10 mol-% of $FeCl_3$ with aq. NaCl (2 equiv.), aq. HCl (2 equiv.) or tetrabutylammonium chloride (2 equiv.) as additive to provide chloride ions as nucleophiles to attack the vinyl cation **B**. However, the yield of the desired product **4a** was not improved in comparison with the reaction without additive, even with a prolonged reaction time (10 h). Meanwhile, the reaction of diphenylmethanol with phenylacetylene in the presence of a copper salt or oxide, such as $CuCl_2$, CuBr, CuI or Cu_2O (0.50 equiv.), in $BrCH_2CH_2Br$ was examined. However, the desired product was not observed.



Scheme 2. Possible mechanism for the FeX_3-promoted addition of benzylic alcohol to aromatic alkyne.

Conclusions

We have successfully developed a convenient, effective and mild strategy for the synthesis of alkenyl bromides and chlorides by the intermolecular addition of benzylic alcohols to aromatic alkynes. The reactions were carried out in the presence of $FeBr_3$ or $FeCl_3$ (33.33 mol-%) in 1,2-dibromoethane without any additive in air and generated the desired products in good to excellent yields at room temperature in 0.5–1 h with high regio- and stereoselectivities (*E*/*Z* ratio up to 99:1). In addition, the reaction may expand the scope of iron salts as a versatile tool in organic synthesis. Further investigations of the application of this kind of iron salt in asymmetric organic reactions are underway in our laboratory.

Experimental Section

General: All reactions were carried out in air. All reagents were purchased from commercial suppliers and used after further purification. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance NMR spectrometer (400 or 100 MHz, respectively) with $CDCl_3$ as solvent. Chemical shifts are given in ppm relative to tetramethylsilane as the internal standard. High-resolution mass spectrometry data were collected with a Waters micromass GCT premier instrument.

General Procedure for the FeX_3-Promoted Intermolecular Addition of Benzylic Alcohols to Aromatic Alkynes: A reaction tube equipped with a magnetic stirring bar was charged with the benzylic alcohol (1.0 mmol), arylalkyne (1.1 mmol), $FeBr_3$ or $FeCl_3$ (0.3333 mmol) and 1,2-dibromoethane (1.0 mL). The reaction vessel was placed in the open air at room temperature (25 °C). After stirring the mixture at this temperature for 0.5–1 h, it was diluted with dichloromethane. The resulting solution was directly filtered through a pad of silica gel by using a sintered-glass funnel and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether) to give the desired alkenyl bromide or chloride as product.

(*E*)-3a:[2a] ^1H NMR (400 MHz, $CDCl_3$): δ = 7.20–7.13 (m, 10 H), 7.08 (d, *J* = 6.8 Hz, 2 H), 6.99 (d, *J* = 6.0 Hz, 3 H), 6.60–6.56 (m, 1 H), 4.61 (d, *J* = 10.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9, 138.3, 135.5, 128.7, 128.6, 128.3, 128.1, 127.7, 126.6, 121.2, 51.6 ppm.

(*E*)-3b: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.14 (m, 10 H), 7.00 (d, *J* = 8.4 Hz, 3 H), 6.56 (d, *J* = 10.8 Hz, 1 H), 4.64 (d, *J* = 10.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 138.0, 134.3, 132.7, 129.4, 128.9, 128.5, 127.7, 122.2, 50.4 ppm. HRMS (ESI): calcd. for $C_{21}H_{15}BrCl_2$ $[M]^+$ 415.9734; found 415.9731.

(*E*)-3c: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.17 (m, 11 H), 7.14–7.09 (m, 3 H), 6.65 (d, *J* = 10.8 Hz, 1 H), 5.20 (d, *J* = 10.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.1, 140.5, 138.1, 134.1, 133.8, 129.9, 129.7, 128.8, 128.7, 128.6, 128.2, 128.0, 127.9, 127.1, 126.6, 122.6, 48.3 ppm. HRMS (ESI): calcd. for $C_{21}H_{16}BrCl$ $[M]^+$ 382.0124; found 382.0120.

(*E*)-3d: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.08 (m, 11 H), 7.08–7.00 (m, 3 H), 6.62 (d, *J* = 10.8 Hz, 1 H), 4.67 (d, *J* = 10.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 141.5, 138.1, 134.9, 132.4, 129.4, 128.8, 128.7, 128.6, 128.4, 128.0, 126.8, 121.7, 51.0 ppm. HRMS (ESI): calcd. for $C_{21}H_{16}BrCl$ $[M]^+$ 382.0124; found 382.0130.

(*E*)-3e: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.01 (m, 14 H), 6.67 (d, *J* = 10.4 Hz, 1 H), 4.68 (d, *J* = 10.8 Hz, 1 H), 2.92 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 140.0, 139.7, 138.3, 136.2, 135.6, 129.3, 128.8, 128.7, 128.6, 128.3, 128.1, 126.5, 121.0, 51.2, 21.0 ppm. HRMS (ESI): calcd. for $C_{22}H_{19}Br$ $[M]^+$ 362.0670; found 362.0668.

(*E*)-3f:[2a] ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.24 (m, 7 H), 7.18–7.11 (m, 3 H), 6.34 (d, *J* = 10.4 Hz, 1 H), 3.52–3.47 (m, 1 H),

1.30 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 138.7, 138.4, 128.7, 128.6, 128.5, 128.3, 126.7, 126.4, 119.8, 40.7, 22.0 ppm.

(*E*)-3g: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.34 (m, 7 H), 7.28–7.16 (m, 3 H), 6.44 (d, J = 10.8 Hz, 1 H), 3.28 (q, J = 7.2, 10.8 Hz, 1 H), 1.79–1.71 (m, 2 H), 0.87 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 138.8, 137.4, 128.8, 128.6, 128.4, 128.2, 127.2, 126.4, 120.4, 48.3, 29.7, 11.9 ppm. HRMS (ESI): calcd. for $C_{17}H_{17}Br$ $[M]^+$ 300.0514; found 300.0512.

(*E*)-3h:[2a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.13 (m, 10 H), 6.38 (t, J = 7.2 Hz, 1 H), 3.73 (d, J = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 139.1, 130.2, 128.6, 128.5, 128.2, 127.6, 126.4, 126.2, 38.8 ppm.

(*E*)-3i: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.18 (m, 8 H), 7.06–7.04 (m, 1 H), 6.35–6.30 (m, 1 H), 3.68 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 137.5, 132.2, 129.8, 129.5, 128.9, 128.7, 128.3, 127.6, 121.9, 38.1 ppm. HRMS (ESI): calcd. for $C_{15}H_{12}BrCl$ $[M]^+$ 305.9811; found 305.9808.

(*E*)-3j: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.28 (m, 5 H), 7.17–7.01 (m, 4 H), 6.39–6.34 (m, 1 H), 3.32 (d, J = 8.0 Hz, 2 H), 2.31 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 136.0, 135.9, 132.7, 129.3, 129.0, 128.3, 128.1, 127.6, 121.1, 36.3, 21.0 ppm. HRMS (ESI): calcd. for $C_{16}H_{15}Br$ $[M]^+$ 286.0357; found 286.0353.

(*E*)-3k:[18b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.32 (m, 1 H), 7.14–7.07 (m, 9 H), 7.00–6.98 (m, 4 H), 6.56–6.50 (m, 1 H), 4.62 (d, J = 10.4 Hz, 1 H), 2.19 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 138.6, 135.4, 135.1, 129.0, 128.6, 128.5, 128.1, 126.6, 121.5, 51.6, 21.1 ppm.

(*E*)-3l: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20–7.07 (m, 9 H), 7.00–6.98 (m, 3 H), 6.90–6.83 (m, 2 H), 6.59 (d, J = 10.8 Hz, 1 H), 4.56 (d, J = 10.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8, 161.3, 142.8, 135.9, 134.4, 134.3, 130.7, 130.6, 128.7, 128.3, 126.7, 124.9, 120.0, 115.5, 115.3, 51.7 ppm. HRMS (ESI): calcd. for $C_{21}H_{16}BrF$ $[M]^+$ 366.0419; found 366.0419.

(*E*)-3m: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.21 (m, 10 H), 7.09 (d, J = 8.0 Hz, 4 H), 6.69 (d, J = 10.8 Hz, 1 H), 4.66 (d, J = 10.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 136.7, 136.2, 134.7, 130.1, 128.7, 128.6, 128.0, 126.7, 119.8, 51.7 ppm. HRMS (ESI): calcd. for $C_{21}H_{16}BrCl$ $[M]^+$ 382.0124; found 382.0117.

(*E*)-3n: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.39 (m, 2 H), 7.30–7.17 (m, 9 H), 7.11–7.09 (m, 3 H), 6.70 (d, J = 10.8 Hz, 1 H), 4.66 (d, J = 10.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 137.2, 136.2, 131.6, 130.4, 128.7, 128.0, 126.7, 123.0, 119.8, 51.7 ppm. HRMS (ESI): calcd. for $C_{21}H_{16}Br_2$ $[M]^+$ 425.9617; found 425.9618.

(*E*)-3o:[2a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.50 (m, 1 H), 7.36–7.16 (m, 14 H), 4.03 (q, J = 7.6, 7.6 Hz, 1 H), 1.30 (d, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 147.7, 144.9, 138.4, 135.6, 129.5, 129.4, 128.5, 128.0, 127.2, 126.6, 125.1, 122.8, 120.4, 45.9, 16.6 ppm.

(*E*)-4a:[18b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.22 (m, 5 H), 7.19–7.16 (m, 4 H), 7.11–7.08 (m, 2 H), 7.01 (d, J = 7.6 Hz, 4 H), 6.36 (d, J = 10.8 Hz, 1 H), 4.69 (d, J = 10.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 136.8, 131.5, 131.4, 128.9, 128.6, 128.3, 128.3, 128.1, 126.6, 50.7 ppm.

(*E*)-4b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.21 (m, 5 H), 7.15 (d, J = 8.4 Hz, 4 H), 7.04 (d, J = 8.4 Hz, 1 H), 6.90 (d, J = 8.0 Hz, 3 H), 6.22 (d, J = 10.0 Hz, 1 H), 4.61 (d, J = 11.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 140.9, 136.5, 132.7, 132.4, 129.4, 128.9, 128.5, 128.4, 126.6, 49.5 ppm. HRMS (ESI): calcd. for $C_{21}H_{15}Cl_3$ $[M]^+$ 372.0239; found 372.0245.

(*E*)-4c:[18b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.20 (m, 8 H), 7.17–7.12 (m, 6 H), 6.41 (d, J = 11.2 Hz, 1 H), 4.79 (d, J = 11.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4, 138.9, 134.0, 131.6, 131.0, 129.0, 128.6, 128.5, 128.2, 126.6, 50.7, 21.3 ppm.

(*E*)-4d: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.21 (m, 6 H), 7.15–7.11 (m, 2 H), 7.03 (d, J = 7.6 Hz, 4 H), 6.94 (t, J = 8.8 Hz, 2 H), 6.37 (d, J = 11.2 Hz, 1 H), 4.64 (d, J = 10.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 161.5, 143.1, 132.9, 131.7, 130.6, 130.5, 130.4, 128.7, 128.1, 126.7, 115.5, 115.3, 50.8 ppm. HRMS (ESI): calcd. for $C_{21}H_{16}ClF$ $[M]^+$ 322.0925; found 322.0930.

(*E*)-4e:[2a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.18 (m, 7 H), 7.09–7.05 (m, 3 H), 6.03 (d, J = 10.8 Hz, 1 H), 3.50–3.46 (m, 1 H), 1.25 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9, 137.2, 134.2, 130.1, 128.6, 128.3, 127.0, 126.7, 126.5, 126.4, 39.6, 22.4 ppm.

Acknowledgments

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