Supporting Information
For
FeCl₃-Catalyzed Alkenylation of Simple
Arenes with Aryl-Substituted Alkynes

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General Information:

Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. The purchased reagents are listed as follows:

Arenes:

Mesitylene, *p*-Xylene, *p*-Xylene- d_{10} , Pentamethylbenzene, Naphthalene, 1,4-Dimethoxybenzene.

Alkynes:

Phenylacetylene, Diphenylacetylene, 1-Phenyl-1-propyne, 3-Ethynylanisole, 4-Ethynylanisole, 1-Ethynyl-2,4,5-trimethylbenzene, 1-Ethynyl-4-pentylbenzene, 1-Chloro-4-ethynylbenzene, Ethyl phenylpropiolate.

Solvents:

Nitromethane, Nitromethane- d_3 , Methanol, Ethanol, 1,4-Dioxane, Acetic acid, Acetonitrile, Dichloromethane, Chloroform, 1,2-Dichloroethane, Ethyl acetate, Nitrobenzene.

Catalysts:

$FeCl_3$, $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $BiCl_3$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $Pd(OAc)_2$, $PdCl_2$, $PtCl_2$, $AgOAc$.

Others:

Hexachloroethane, Benzoic acid, Petroleum ether, Hexane, Phenylpropiolic acid, *N,N'*-Dicyclohexyl-carbodiimide, 4-Dimethylaminopyridine, 4-*tert*-Butylphenol.

All new compounds were determined by 1H NMR, ^{13}C NMR, and HRMS. Previously reported compounds were characterized *via* 1H NMR and mp and compared to literature values.

Instrumentation:

- 1H NMR spectra and ^{13}C NMR spectra were recorded on a Varian 400MHz NMR system in $CDCl_3$ solvent with TMS internal standard unless otherwise specified.
- TLC was run on 2cm $\times$ 5cm silica plate. Column chromatography was run on silica gel (300-400 mesh).
- Some GC analyses were performed on a GC112A Gas-Chromatograph. Other GC analyses were performed on a GC9160 Gas-Chromatograph. The capillary column used is AT-FFAP (Column ID: 0.32 mm, Length: 32 m, Film Thickness: 0.33 μm).
- EIMS and HRMS were performed at the Shanghai Institute of Organic Chemistry, Chinese Academic of Science.
- Melting points were measured with X-4 Microscopic Melting-point Detector and are uncorrected.

Procedure:

General Preparation of Intermolecular Alkenylation Products:

In a flame dried flask (10 mL), FeCl_3 (16.2 mg, 0.1mmol), nitromethane (0.5 mL), arene (3.0 mmol) and alkyne (1.0 mmol) were mixed and stirred at room temperature. The reaction propagation was monitored by TLC and GC analysis (hexachloroethane or benzoic acid as internal standard). After 5-6 hours, the reaction mixture was diluted by CH_2Cl_2 and filtered. Then the solvent was evaporated. Reaction products were isolated by flash column chromatography (the content of gradient elution was listed in the following table, **Table S-1**). The products were characterized by their physical constants and spectral analysis.

Table S-1 Reaction's Condition and the Content of Gradient Elution

Entry	Alkyne	Arene	FeCl_3 [mmol]	Time [h]	Temp. [°C]	Product	Gradient Elution
1			0.1	5	r.t.	3a	Petroleum ether
2			0.1	5	r.t.	3i	Petroleum ether
3			0.1	5	r.t.	3j	Petroleum ether
4			0.1	6	r.t.	3k	Petroleum ether
5			0.1	6	r.t.	3l	Petroleum ether
6			0.1	6	r.t.	3m	Petroleum ether
7			0.1	5	60	3g	Petroleum ether
8			0.2	38	80	3h	Petroleum ether / $\text{CH}_2\text{Cl}_2 = 2:1$
9			0.1	20	80	3n	Petroleum ether / $\text{CH}_2\text{Cl}_2 = 10:1$
10			0.1	5	60	3f	Hexane / Ethyl acetate = 50 :1
11			0.1	6	60	3c	Petroleum ether

12			0.1	5	r.t.	3d	Petroleum ether
13			0.1	5	60	3b	Petroleum ether
14			0.1	12	40	3e	Petroleum ether
15			0.2	17	80	3o	Petroleum ether

Preparation of Iodomesitylene:

In a flame dried flask (10 mL), mesitylene (601.0 mg, 5 mmol), I_2 (634.5 mg, 2.5 mmol), BNP (60.5 mg, 0.125 mmol), BiCl_3 (39.0 mg, 0.125 mmol) and MeCN (5.0 mL) were mixed and stirred at room temperature for 6 hours. The reaction propagation was monitored by TLC and GC analysis. Then the reaction mixture was desorbed by dichloromethane (3×10 mL). The organic extracts were successively washed with aq. $\text{Na}_2\text{S}_2\text{O}_3$ solution, dried over anhydrous MgSO_4 and then evaporated under reduced pressure. The crude product was purified by column chromatography over silica to yield 968.0 mg (3.95 mmol, 79%) of the product.¹

Preparation of 4'-*tert*-Butylphenyl phenylpropiolate:

To a solution of 4-*tert*-butylphenol (1.52 g, 10.0 mmol) and phenylpropionic acid (0.43 g, 2.9 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added a combined solution of DCC (1.50 g, 4.5 mmol) and DMAP (9.3 mg, 0.08 mmol) in CH_2Cl_2 (5 mL) over a period of 1 hour. The reaction was stirred for 5 hours. The reaction mixture was diluted by CH_2Cl_2 and filtered. Following evaporation of the solvents, the crude product was purified by silica gel chromatography (Petroleum ether / CH_2Cl_2 = 1:1) to yield 513.1 mg (1.84 mmol, 63%) of the product.²

Cyclization of 4'-*tert*-Butylphenyl phenylpropiolate:

In a flame dried flask (10 mL), we dissolved 4'-*tert*-butylphenyl phenylpropiolate (138.6 mg, 0.5 mmol) in nitromethane (1.0 mL) containing FeCl₃ (16.2 mg, 0.1 mmol) and stirred the mixture at 80 °C. The reaction propagation was monitored by TLC. After 72 hours, the reaction mixture was diluted by CH₂Cl₂ and filtered. Then the solvent was evaporated. Reaction products were isolated by flash column chromatography (gradient elution was petroleum ether / ethyl acetate = 15:1) to yield 76.6 mg (isolated yield: 53%).

Screening the Reaction Conditions:

An Example on Alkenylation Reaction of Mesitylene by Phenylacetylene:

Table S-2 The effects of the Catalysts ^a

Entry	Catalyst [mmol]	Time [h]	Yield [%]	Convsn [%]
1	FeCl ₃	5	86	>99
2	FeCl ₂ ·4H ₂ O	5	0	0
3	Fe(NO ₃) ₃ ·9H ₂ O	24	0	0
4	BiCl ₃	5	0	0
5	CuCl ₂ ·2H ₂ O	24	0	0
6	ZnCl ₂	24	7	-
7	CoCl ₂ ·6H ₂ O	24	0	Trace
8	NiCl ₂ ·6H ₂ O	24	0	Trace
9 ^b	Pd(OAc) ₂	5	0	>99
10 ^b	PdCl ₂	5	0	>99
11 ^b	PtCl ₂	5	0	0
12	AgOAc	5	0	0
13	HCl	5	0	0
14	None	5	0	0

^a **1a** (1.0 mmol), **2a** (3.0 mmol), cat. 10 mol %, CH₃NO₂ (0.5 mL), rt. Yield was determined by GC analysis (Benzoic acid as internal standard). ^b cat. 5 mol %.

Table S-3 The effect of the Solvents ^a

Entry	Solvent [mmol]	Yield [%]	Convsn [%]
1	CH ₃ NO ₂	86	>99
2	CH ₃ OH	0	0
3	C ₂ H ₅ OH	0	0
4	1,4-Dioxane	0	0
5	HOAc	6	14
6	CHCl ₃	12	26
7	CH ₂ Cl ₂	23	36
8	ClCH ₂ CH ₂ Cl	30	60
9	PhNO ₂	41	75
10	CH ₃ CN	3	6
11	CH ₃ COOC ₂ H ₅	4	8
12	CH ₃ COCH ₃	Trace	Trace
13	None	10	24

^a **1a**(1.0 mmol), **2a**(3.0 mmol), FeCl₃ 10 mol %, CH₃NO₂ (0.5 mL), rt, 5 h. Yield was determined by GC analysis (Benzoic acid as internal standard).

Table S-4 The effects of Concentrations of FeCl₃ ^a

Entry	FeCl ₃ [mmol]	Temp. [°C]	Time [h]	Yield [%]	Convsn [%]
1	0.05	r.t.	5	35	43
2	0.05	60	3	61	79
3	0.05	60	4	74	>99
4	0.10	r.t.	5	86	>99
5	0.10	60	2	88	>99

^a **1a**(1.0 mmol), **2a**(3.0 mmol), CH₃NO₂ (0.5 mL).Yield was determined by GC analysis (Benzoic acid as internal standard).

Table S-4 The effects of Concentrations of Arene ^a

Entry	Mesitylene [mmol]	Sel. [%]	Yield [%]	Convsn [%]
1	1.0	64	64	>99
2	2.0	70	70	>99
3	3.0	86	86	>99
4	6.0	85	85	>99

^a **1a**(1.0 mmol), FeCl₃ 10 mol %, CH₃NO₂ (0.5 mL), rt, 5 h. Yield was determined by GC analysis (Benzoic acid as internal standard).

Table S-5 The effects of Concentrations of Solvent ^a

Entry	CH ₃ NO ₂ [mmol]	Sel. [%]	Yield [%]	Conv'n [%]
1	0.2	40	14	35
2	1.0	58	33	58
3	5.0	72	72	>99
4	10.0	86	86	>99
5	20.0	74	74	>99
6	40.0	72	21	29

^a **1a**(1.0 mmol), **2a**(3.0 mmol), FeCl₃ 10 mol %, rt, 5 h. Yield was determined by GC analysis (Benzoic acid as internal standard).

An Example on Alkenylation Reaction of *p*-Xylene with Phenylacetylene:

Table S-6 The effects of Reaction Temperature ^a

Entry	Temp. [°C]	Time [h]	Sel. [%]	Yield [%]	Conv'n [%]
1	80	4	71	71	>99
2	60	5	84	76	94
3	60	6	84	84	>99
4	r.t.	7	86	66	77

^a **1a**(1.0 mmol), **2c**(3.0 mmol), FeCl₃ 10 mol %, CH₃NO₂ (0.5 mL). Yield was determined by GC analysis (Benzoic acid as internal standard).

Mechanistic Study of the Alkenylation Reaction:

To examine the resource of protons in this reaction, we dissolved phenylacetylene (102.2 mg, 1.0 mmol) in *p*-xylene-d₁₀ (349.0 mg, 3.0 mmol) containing nitromethane (0.5 mL), FeCl₃ (16.2 mg, 0.1 mmol) and stirred the mixture at 60 °C. The reaction propagation was monitored by GC analysis. After 6 hours, the reaction mixture was diluted by CH₂Cl₂ and filtered. Then the solvent was evaporated.

Reaction products were isolated by flash column chromatography (gradient elution was petroleum ether) to yield 138.0 mg (isolated yield: 42%). Finally, we analyze the reaction production by ^1H NMR spectroscopy and found that the ratio of the three isomers is 1.3:1.1:1.0.

^1H NMR (400 MHz, CDCl_3 , δ): 7.28-7.22 (m, 5H), 5.73 (s, 1H), 5.17 (s, 1H).

^1H NMR (400 MHz, CDCl_3 , δ): 7.28-7.22 (m, 5H), 5.75 (d, $J = 1.6$ Hz, 1H), 5.18 (d, $J = 1.6$ Hz, 1H).

To determine whether CH_3NO_2 could provide protons in this reaction, we dissolved phenylacetylene (102.2 mg, 1.0 mmol) in *p*-xylene (310.0 mg, 3.0 mmol) containing CD_3NO_2 (0.5 mL), FeCl_3 (16.2 mg, 0.1 mmol) and stirred the mixture at 60°C . After 6 hours, the reaction mixture was diluted by CH_2Cl_2 and filtered. Then the solvent was evaporated. Reaction products were isolated by flash column chromatography (gradient elution was petroleum ether) to yield 44.0 mg (isolated yield: 21%). Finally, we found that there is any deuterated product in this reaction.

^1H NMR (400 MHz, CDCl_3 , δ): 7.28-7.22 (m, 5H), 7.07-7.06 (d, $J = 2.0$ Hz, 2H), 7.04 (s, 1H), 5.75 (d, $J = 1.6$ Hz, 1H), 5.18 (d, $J = 1.6$ Hz, 1H), 2.33 (s, 3H), 2.01 (s, 3H).

In a flame dried flask (10 mL), we dissolved phenylacetylene (102.2 mg, 1.0 mmol) in *p*-xylene- d_{10} (176.0 mg, 1.5 mmol) and *p*-xylene (160.0 mg, 1.5 mmol) containing nitromethane (0.5 mL), $FeCl_3$ (16.2 mg, 0.1 mmol) and stirred the mixture at $60^\circ C$. The reaction propagation was monitored by GC analysis. After 6 hours, the reaction mixture was diluted by CH_2Cl_2 and filtered. Then the solvent was evaporated. Reaction products were isolated by flash column chromatography (gradient elution was petroleum ether) to yield 60.7 mg (isolated yield: 28%). Finally, we analyze the reaction production by 1H NMR spectroscopy and found that the ratio of the product from the *p*-xylene- d_{10} and *p*-xylene is 1:1 (KIE = 1.00).

1H NMR (400 MHz, $CDCl_3$, δ): 7.28-7.22 (m, 5H), 5.75-5.73 (m, 1H), 5.18-5.17 (m, 1H).

1H NMR (400 MHz, $CDCl_3$, δ): 7.28-7.22 (m, 5H), 7.07-7.06 (d, $J = 2.0$ Hz, 2H), 7.04 (s, 1H), 5.75-5.73 (m, 1H), 5.18-5.17 (m, 1H), 2.33 (s, 3H), 2.01 (s, 6H).

In order to eliminate the effects caused by the concentration of fluctuation, we also used **1a** to react with **2c-d₁₀** and **2c** respectively in the presence of 3 mol % FeCl₃ at room temperature and used GC analysis to monitor the reaction process meanwhile. Finally, we found the ratio of the initial rates of the two reactions is $K_{\text{H}}/K_{\text{D}} = 0.98$.

Further more, to probe the mechanism, we also mixed FeCl₃ (16.2 mg, 0.1 mmol) with mesitylene (120.2 mg, 1.0 mmol) containing nitromethane (0.5 mL) and stirred

the mixture at room temperature for 2 hours. Then the mixture was analyzed by ^1H NMR spectroscopy and no disappearance of the aromatic proton signal was found in the ^1H NMR spectrum. This result suggests that the first step of metalation may happen on the alkyne substrates.

Mesitylene (2a)³: Colorless oil liquid.

^1H NMR (400 MHz, CDCl_3 , δ): 6.81 (s, 3H), 2.28 (s, 9H).

CH_3NO_2

Nitromethane (solvent)⁴: Colorless oil liquid.

^1H NMR (400 MHz, CDCl_3 , δ): 4.36 (s, 3H).

In addition, we mixed FeCl_3 (9.0 mg, 0.05 mmol) with xylene- d_{10} (61.2 mg, 0.5 mmol) containing nitromethane (0.25 mL) and H_2O (0.5 mmol) and stirred the mixture at room temperature for 48 hours. Then the mixture was analyzed by ^1H NMR spectroscopy and no D-H exchange signal was found between the arene-d and the H_2O in the ^1H NMR spectrum.

CH₃NO₂

Nitromethane (solvent) ⁴: Colorless oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 4.34 (s, 3H).

Characterization of the products:

1-Mesityl-1-phenylethene (3a)⁵: Colorless oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 7.28-7.21 (m, 5H), 6.91 (s, 2H), 5.96 (d, J = 1.2 Hz, 1H), 5.10 (d, J = 1.6 Hz, 1H), 2.32 (s, 3H), 2.11 (s, 6H).

1-Pentamethylphenyl-1-phenylethylene (3b)⁶: White crystals.

¹H NMR (400 MHz, CDCl₃, δ): 7.31-7.22 (m, 5H), 5.97 (d, J = 1.6 Hz, 1H), 5.06 (d, J = 2.0 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 6H), 2.10 (s, 6H).
mp 75-77 °C (lit.⁶ mp 66-67 °C)

1-(2,5-Dimethylphenyl)-1-phenylethylene (3c)⁷: Colorless oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 7.28-7.22 (m, 5H), 7.07-7.06 (d, J = 2.0 Hz, 2H), 7.04 (s, 1H), 5.75 (d, J = 1.6 Hz, 1H), 5.18 (d, J = 1.6 Hz, 1H), 2.33 (s, 3H), 2.01 (s, 3H).

1-(1-Phenyl-vinyl)-naphthalene (3d)⁸: White crystals.

¹H NMR (400 MHz, CDCl₃, δ): 7.87-7.84 (m, 2H), 7.77-7.75 (m, 1H), 7.51-7.40 (m, 3H), 7.34-7.30 (m, 3H), 7.29-7.24 (m, 3H), 5.98 (d, J = 1.6 Hz, 1H), 5.39 (d, J = 1.6 Hz, 1H).
mp 60-61 °C (lit.⁹ mp 59-61 °C)

Iodomesitylene (2e)¹: White crystals.

¹H NMR (400 MHz, CDCl₃, δ): 6.89 (s, 2H), 2.43 (s, 6H), 2.24 (s, 3H).

mp: 30-31 °C. (lit. ¹ mp 30-31 °C)

1-(3-Iodo-mesityl)-1-phenylethene (3e): New compound. Colorless oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 7.32-7.24 (m, 5H), 7.03 (s, 1H), 5.97 (s, 1H), 5.07 (s, 1H), 2.50 (s, 3H), 2.37 (s, 3H), 2.09 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ): 147.3, 140.7, 139.5, 138.9, 138.8, 135.9, 128.7, 128.5, 127.8, 125.8, 114.7, 106.3, 29.9, 27.5, 19.9.

EIMS (m/z): M.⁺ 348 (17), 206 (100), 191 (18), 207 (17), 333 (16), 89 (12), 51 (11), 77 (10).

HRMS (m/z): Calc for C₁₇H₁₇ I, 348.0375; found, 348.0386.

(Z)- and (E)-1-(2,5-Dimethoxyphenyl)-1-phenyl-1-propene (Z- and E-3f)¹⁰: Slight yellow oil liquid as an inseparable *Z,E*-mixture (*Z:E* = 85 :15).

EIMS (m/z): M.⁺ 254 (100), 115 (45), 91 (30), 225 (30), 165 (26), 152 (23), 103 (22), 77 (20).

HRMS (m/z): Calc for C₁₇H₁₈O₂, 254.1307; found, 254.1315.

Due to the difficulty in isolating the two isomers, the ratio between two isomers was based on the analysis of ChemDraw Ultra 10.0.

(Z)-1-(2,5-Dimethoxyphenyl)-1-phenyl-1-propene:

¹H NMR (400 MHz, CDCl₃, δ): 7.31-7.15 (m, 5H), 6.89 (s, 1H), 6.86-6.85 (m, 1H), 6.67-6.66 (m, 1H), 6.29 (q, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 3.65 (s, 3H), 1.67 (d, *J* = 7.2 Hz, 3H).

(E)-1-(2,5-Dimethoxyphenyl)-1-phenyl-1-propene:

¹H NMR (400 MHz, CDCl₃, δ): 7.31-7.15 (m, 5H), 6.91 (s, 1H), 6.84-6.83 (m, 1H), 6.76-6.75 (m, 1H), 5.96 (q, *J* = 6.8 Hz, 1H), 3.76 (s, 3H), 3.50 (s, 3H), 1.85 (d, *J* = 6.8 Hz, 3H).

(Z)-1-Mesityl-1-phenyl-1-propene (Z-3g)⁵: Colorless oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 7.25-7.15 (m, 5H), 6.92 (s, 2H), 6.37 (q, *J* = 6.8 Hz, 1H), 2.32 (s, 3H), 2.04 (s, 6H), 1.53 (d, *J* = 6.8 Hz, 3H).

(E)-1-Mesityl-1-phenyl-1-propene (E-3g)⁵: Colorless oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 7.25-7.15 (m, 5H), 6.86 (s, 2H), 5.63 (q, *J* = 7.2 Hz, 1H), 2.28 (s, 3H), 2.15 (s, 6H), 1.98 (d, *J* = 7.2 Hz, 3H).

(Z)-2-Ethyl 3-Mesitylcinnamate (Z-3h)⁶: Slight yellow oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 7.37-7.27 (m, 5H), 6.91 (s, 2H), 6.62 (s, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.03 (s, 6H), 1.11 (t, *J* = 7.2 Hz, 3H).

(E)-2-Ethyl 3-Mesitylcinnamate (E-3h): Slight yellow oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 7.37-7.27 (m, 5H), 6.88 (s, 2H), 5.89 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 2.18 (s, 6H), 1.20 (t, *J* = 7.2 Hz, 3H).

1-Mesityl-1-(4-methoxyphenyl)ethene (3i)⁵: Slight yellow oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 7.23-7.20 (m, 2H), 6.91 (s, 2H), 6.83-6.79 (m, 2H), 5.85 (d, *J* = 1.6 Hz, 1H), 4.98 (d, *J* = 1.6 Hz, 1H), 3.80 (s, 3H), 2.33 (s, 3H), 2.12 (s, 6H).

1-Mesityl-1-(3-methoxyphenyl)ethene (3j): New compound. Colorless oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 7.22-7.19 (m, 1H), 6.92 (s, 2H), 6.88-6.80 (m, 3H), 5.97 (d, *J* = 1.2 Hz, 1H), 5.12 (d, *J* = 2.0 Hz, 1H), 3.79 (s, 3H), 2.33 (s, 3H), 2.13 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, δ): 159.6, 146.7, 141.1, 138.0, 136.3, 136.0, 129.3, 128.0, 118.5, 114.8, 112.4, 111.8, 55.1, 21.0, 20.1.

EIMS (*m/z*): M⁺ 252 (91), 237 (100), 222 (67), 206 (47), 221 (45), 179 (27), 236 (27), 178 (20).

HRMS (*m/z*): Calc for C₁₈H₂₀O, 252.1514; found, 252.1526.

1-(4-Chlorophenyl)-1-mesitylethene (3k)⁵: Colorless oil liquid.

¹H NMR (400 MHz, CDCl₃, δ): 7.25-7.20 (m, 4H), 6.93 (s, 2H), 5.95 (s, 1H), 5.12 (s, 1H), 2.33 (s, 3H), 2.10 (s, 6H).

1-Mesityl-1-(4-pentylphenyl)ethene (3l): New Compound. Slight yellow oil liquid.

^1H NMR (400 MHz, CDCl_3 , δ): 7.27 (d, $J = 7.6$ Hz, 2H), 7.16 (d, $J = 7.6$ Hz, 2H), 6.99 (s, 2H), 6.00 (s, 1H), 5.12 (s, 1H), 2.65 (m, 2H), 2.40 (s, 3H), 2.20 (s, 6H), 1.72-1.66 (m, 2H), 1.42-1.39 (m, 4H), 0.98 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 146.7, 142.4, 138.4, 136.9, 136.2, 136.1, 128.4, 128.0, 125.7, 113.5, 35.6, 31.5, 31.1, 22.5, 21.0, 20.1, 14.0.

EIMS (m/z): M^+ 292 (20), 221 (100), 206 (61), 277 (25), 207 (23), 205 (22), 222 (19), 41 (13).

HRMS (m/z): Calc for $\text{C}_{22}\text{H}_{28}$, 292.2191; found, 292.2194.

1-Mesityl-1-(2,4,5-trimethylphenyl)ethene (3m): New compound. White crystals.

^1H NMR (400 MHz, CDCl_3 , δ): 7.04 (s, 1H), 6.94 (s, 2H), 6.78 (s, 1H), 5.62 (d, $J = 2.4$ Hz, 1H), 5.36 (d, $J = 1.6$ Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H), 2.23 (s, 6H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 146.4, 140.4, 138.1, 136.3, 136.2, 135.4, 133.8, 132.9, 132.8, 130.1, 128.6, 119.7, 21.3, 20.91, 20.86, 19.60, 19.55.

EIMS (m/z): M^+ 264 (31), 234 (100), 249 (86), 221 (44), 206 (27), 235 (24), 250 (20), 219 (16).

HRMS (m/z): Calc for $\text{C}_{20}\text{H}_{24}$, 264.1878; found, 264.1874.

mp 64-66 °C

(Z)- and (E)-1-Mesityl-1,2-diphenylethene (Z- and E-3n)⁵: Colorless oil liquid as an inseparable Z,E-mixture (Z:E = 40 :60).

EIMS (m/z): M^+ 298 (22), 178 (100), 179 (55), 91 (50), 180 (31), 76 (30), 82 (28), 192 (20).

HRMS (m/z): Calc for C₂₃H₂₂, 298.1722; found, 298.1721.

Due to the difficulty in isolating the two isomers, the ratio between two isomers was based on the analysis of ChemDraw Ultra 10.0.

(E)-1-Mesityl-1,2-diphenylethene:

¹H NMR (400 MHz, CDCl₃, δ): 7.36-7.01 (m, 10H), 6.90 (s, 2H), 6.51 (s, 1H), 2.30 (s, 3H), 2.24 (s, 6H).

(Z)-1-Mesityl-1,2-diphenylethene:

¹H NMR (400 MHz, CDCl₃, δ): 7.36-7.01 (m, 9H), 6.97-6.94 (m, 2H), 6.92 (s, 2H), 2.34 (s, 3H), 2.00 (s, 6H).

Triphenylethene (3o)¹¹: White Crystals.

¹H NMR (400 MHz, CDCl₃, δ): 7.35-7.01 (m, 15H), 6.96 (s, 1H).
mp 70-72 °C (lit.¹² mp 73-74 °C)

4'-tert-Butylphenyl phenylpropiolate (2h)¹²: White crystals.

¹H NMR (400 MHz, CDCl₃, δ): 7.63-7.61 (m, 2H), 7.50-7.42 (m, 5H), 7.12-7.10 (m, 2H), 1.33 (s, 9H).

¹³C NMR (100 MHz, CDCl₃, δ): 152.6, 149.2, 147.7, 133.1, 131.0, 128.6, 126.5, 120.7, 119.2, 88.5, 80.3, 34.5, 31.4.

mp 91-93 °C

4-Phenyl-6-tert-butylcoumarin (3p)¹²: Slight yellow crystals.

¹H NMR (400 MHz, CDCl₃, δ): 7.63-7.61 (m, 1H), 7.56-7.54 (m, 3H), 7.49-7.47 (m, 3H), 7.36 (d, *J* = 8.8 Hz, 1H), 6.37 (s, 1H), 1.27 (s, 9H).

mp 105-108 °C (lit.¹² mp 108-109 °C)

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NMR Spectrum:

Figure S-1 ^1H NMR of 1-Mesityl-1-phenylethene (3a):

Figure S-2 ^1H NMR of 1-Pentamethylphenyl-1-phenylethylene (3b):

Figure S-3 ^1H NMR of 1-(2,5-Dimethylphenyl)-1-phenylethylene (3c):

Figure S-4 ^1H NMR of 1-(1-Phenyl-vinyl)-naphthalene (3d):

Figure S-5 ^1H NMR of Iodomesitylene (2e):

Figure S-6 ^1H NMR of 1-(3-Iodo-mesityl)-1-phenylethene (3e):

Chemical structure: CC1=C(C)C(=C(C=C1)C=C(C2=CC=CC=C2)C)C3=CC=CC=C3

¹³C NMR peaks (ppm): 147.259, 140.676, 139.500, 138.923, 138.822, 135.921, 128.713, 128.484, 127.753, 125.757, 114.736, 106.250, 77.308, 76.578, 76.070, 29.900, 27.492, 19.887.

Chemical structure: COc1cc(OC)cc(C=Cc2ccccc2)cc1

¹H NMR spectrum (CDCl₃) showing peaks and integration values:

- 7.309, 7.291, 7.276, 7.265, 7.255, 7.237, 7.227, 7.206, 7.200, 7.188, 7.176, 7.165, 7.155, 7.145, 7.135, 7.125, 7.115, 7.105, 7.095, 7.085, 7.075, 7.065, 7.055, 7.045, 7.035, 7.025, 7.015, 7.005, 6.995, 6.985, 6.975, 6.965, 6.955, 6.945, 6.935, 6.925, 6.915, 6.905, 6.895, 6.885, 6.875, 6.865, 6.855, 6.845, 6.835, 6.825, 6.815, 6.805, 6.795, 6.785, 6.775, 6.765, 6.755, 6.745, 6.735, 6.725, 6.715, 6.705, 6.695, 6.685, 6.675, 6.665, 6.655, 6.645, 6.635, 6.625, 6.615, 6.605, 6.595, 6.585, 6.575, 6.565, 6.555, 6.545, 6.535, 6.525, 6.515, 6.505, 6.495, 6.485, 6.475, 6.465, 6.455, 6.445, 6.435, 6.425, 6.415, 6.405, 6.395, 6.385, 6.375, 6.365, 6.355, 6.345, 6.335, 6.325, 6.315, 6.305, 6.295, 6.285, 6.275, 6.265, 6.255, 6.245, 6.235, 6.225, 6.215, 6.205, 6.195, 6.185, 6.175, 6.165, 6.155, 6.145, 6.135, 6.125, 6.115, 6.105, 6.095, 6.085, 6.075, 6.065, 6.055, 6.045, 6.035, 6.025, 6.015, 6.005, 5.995, 5.985, 5.975, 5.965, 5.955, 5.945, 5.935, 5.925, 5.915, 5.905, 5.895, 5.885, 5.875, 5.865, 5.855, 5.845, 5.835, 5.825, 5.815, 5.805, 5.795, 5.785, 5.775, 5.765, 5.755, 5.745, 5.735, 5.725, 5.715, 5.705, 5.695, 5.685, 5.675, 5.665, 5.655, 5.645, 5.635, 5.625, 5.615, 5.605, 5.595, 5.585, 5.575, 5.565, 5.555, 5.545, 5.535, 5.525, 5.515, 5.505, 5.495, 5.485, 5.475, 5.465, 5.455, 5.445, 5.435, 5.425, 5.415, 5.405, 5.395, 5.385, 5.375, 5.365, 5.355, 5.345, 5.335, 5.325, 5.315, 5.305, 5.295, 5.285, 5.275, 5.265, 5.255, 5.245, 5.235, 5.225, 5.215, 5.205, 5.195, 5.185, 5.175, 5.165, 5.155, 5.145, 5.135, 5.125, 5.115, 5.105, 5.095, 5.085, 5.075, 5.065, 5.055, 5.045, 5.035, 5.025, 5.015, 5.005, 4.995, 4.985, 4.975, 4.965, 4.955, 4.945, 4.935, 4.925, 4.915, 4.905, 4.895, 4.885, 4.875, 4.865, 4.855, 4.845, 4.835, 4.825, 4.815, 4.805, 4.795, 4.785, 4.775, 4.765, 4.755, 4.745, 4.735, 4.725, 4.715, 4.705, 4.695, 4.685, 4.675, 4.665, 4.655, 4.645, 4.635, 4.625, 4.615, 4.605, 4.595, 4.585, 4.575, 4.565, 4.555, 4.545, 4.535, 4.525, 4.515, 4.505, 4.495, 4.485, 4.475, 4.465, 4.455, 4.445, 4.435, 4.425, 4.415, 4.405, 4.395, 4.385, 4.375, 4.365, 4.355, 4.345, 4.335, 4.325, 4.315, 4.305, 4.295, 4.285, 4.275, 4.265, 4.255, 4.245, 4.235, 4.225, 4.215, 4.205, 4.195, 4.185, 4.175, 4.165, 4.155, 4.145, 4.135, 4.125, 4.115, 4.105, 4.095, 4.085, 4.075, 4.065, 4.055, 4.045, 4.035, 4.025, 4.015, 4.005, 3.995, 3.985, 3.975, 3.965, 3.955, 3.945, 3.935, 3.925, 3.915, 3.905, 3.895, 3.885, 3.875, 3.865, 3.855, 3.845, 3.835, 3.825, 3.815, 3.805, 3.795, 3.785, 3.775, 3.765, 3.755, 3.745, 3.735, 3.725, 3.715, 3.705, 3.695, 3.685, 3.675, 3.665, 3.655, 3.645, 3.635, 3.625, 3.615, 3.605, 3.595, 3.585, 3.575, 3.565, 3.555, 3.545, 3.535, 3.525, 3.515, 3.505, 3.495, 3.485, 3.475, 3.465, 3.455, 3.445, 3.435, 3.425, 3.415, 3.405, 3.395, 3.385, 3.375, 3.365, 3.355, 3.345, 3.335, 3.325, 3.315, 3.305, 3.295, 3.285, 3.275, 3.265, 3.255, 3.245, 3.235, 3.225, 3.215, 3.205, 3.195, 3.185, 3.175, 3.165, 3.155, 3.145, 3.135, 3.125, 3.115, 3.105, 3.095, 3.085, 3.075, 3.065, 3.055, 3.045, 3.035, 3.025, 3.015, 3.005, 2.995, 2.985, 2.975, 2.965, 2.955, 2.945, 2.935, 2.925, 2.915, 2.905, 2.895, 2.885, 2.875, 2.865, 2.855, 2.845, 2.835, 2.825, 2.815, 2.805, 2.795, 2.785, 2.775, 2.765, 2.755, 2.745, 2.735, 2.725, 2.715, 2.705, 2.695, 2.685, 2.675, 2.665, 2.655, 2.645, 2.635, 2.625, 2.615, 2.605, 2.595, 2.585, 2.575, 2.565, 2.555, 2.545, 2.535, 2.525, 2.515, 2.505, 2.495, 2.485, 2.475, 2.465, 2.455, 2.445, 2.435, 2.425, 2.415, 2.405, 2.395, 2.385, 2.375, 2.365, 2.355, 2.345, 2.335, 2.325, 2.315, 2.305, 2.295, 2.285, 2.275, 2.265, 2.255, 2.245, 2.235, 2.225, 2.215, 2.205, 2.195, 2.185, 2.175, 2.165, 2.155, 2.145, 2.135, 2.125, 2.115, 2.105, 2.095, 2.085, 2.075, 2.065, 2.055, 2.045, 2.035, 2.025, 2.015, 2.005, 1.995, 1.985, 1.975, 1.965, 1.955, 1.945, 1.935, 1.925, 1.915, 1.905, 1.895, 1.885, 1.875, 1.865, 1.855, 1.845, 1.835, 1.825,

Figure S-9 ^1H NMR of (Z)- and (E)-1-Mesityl-1-phenyl-1-propene (Z- and E-3g):

Figure S-10 ^1H NMR of (Z)- 1-Mesityl-1-phenyl-1-propene (Z- 3g):

Figure S-11 ^1H NMR of (Z)- and (E)-2-Ethyl 3-Mesitylcinnamate (Z- and E-3h):

Figure S-12 ^1H NMR of (Z)- 2-Ethyl 3-Mesitylcinnamate (Z- 3h):

Figure S-13 ^1H NMR of 1-Mesityl-1-(4-methoxyphenyl)ethene (3i):

Figure S-14 ^1H NMR of 1-Mesityl-1-(3-methoxyphenyl)ethene (3j):

Figure S-15 ^{13}C NMR of 1-Mesityl-1-(3-methoxyphenyl)ethene (3j):

Figure S-16 ^1H NMR of 1-(4-Chlorophenyl)-1-mesitylethene (3k):

Figure S-17 ^1H NMR of 1-Mesityl-1-(4-pentylphenyl)ethene (3I):

Figure S-18 ^{13}C NMR of 1-Mesityl-1-(4-pentylphenyl)ethene (3I):

Figure S-19 ^1H NMR of 1-Mesityl-1-(2,4,5-trimethylphenyl)ethene (3m):

Figure S-20 ^{13}C NMR of 1-Mesityl-1-(2,4,5-trimethylphenyl)ethene (3m):

Figure S-21 ^1H NMR of (Z)- and (E)-1-Mesityl-1,2-diphenylethene (Z- and E-3n):

Figure S-22 ^1H NMR of Triphenylethene (3o):

Figure S-23 ^1H NMR of 4'-*tert*-Butylphenyl phenylpropiolate (2h):

Figure S-24 ^{13}C NMR of 4'-*tert*-Butylphenyl phenylpropiolate (2h):

Figure S-25 ^1H NMR of 4-Phenyl-6-*tert*-butylcoumarin (3p):