# A Facile Synthesis of Tetraarylethenes via Cross McMurry Coupling between Diaryl Ketones

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**Abstract:** The one-pot, cross McMurry coupling between two different diaryl ketones gave structurally varied tetraarylethenes in 59– 80% isolated yields. This synthetic protocol is more convenient and effective compared to previously reported procedures

**Key words:** cross McMurry reaction, tetraphenylethene, diaryl ketone, McMurry reaction, low-valent titanium

Tetraphenylethene and its ring-substituted analogues display several interesting photophysical and redox properties by virtue of the fact that they contain both aromatic and olefinic centers.<sup>1</sup> They enjoy widespread, or potential, use in various reactions such as reduction, oxidation, and photocyclization;<sup>2</sup> in materials science they are used as columnar liquid crystals<sup>3</sup> or molecular switches.<sup>4</sup> Recently tetrakis(2-hydroxyphenyl)ethene and its derivatives were investigated as an alternative to the calix[4]arene ligand system.<sup>5</sup> Noteworthy is the report that tetra(4-bromophenyl)ethene forms chiral inclusion crystals with achiral guests such as acetone and benzene, which provides a new strategy for the preparation of chiral crystals.<sup>6</sup> Although there is an extensive need for such molecules, the reported procedures are mainly limited to the preparation of symmetrical tetraarylethenes via homocoupling reactions of diaryldiazomethanes,5,7 diaryldichloromethanes,8 diaryl thioketones,9 and diaryl ketones.3,4a,10 The synthesis of unsymmetrically substituted analogues is generally achieved using palladium- or nickel-catalyzed cross-coupling reactions.<sup>11</sup>

We report herein a novel synthetic protocol for the preparation of tetraarylethenes, especially for unsymmetrically substituted analogues, using cross McMurry coupling between two different diaryl ketones. Because the reagents are readily available and the operations are simple, this synthesis proves to be more convenient and effective compared to those previously reported.

Although the preparation of tetraarylethenes via the McMurry homocoupling of diaryl ketones has been documented,<sup>3,4a,10</sup> the synthesis by the cross coupling of two different diaryl ketones still remains a challenge. This results from the general belief that the cross McMurry coupling between two different carbonyl compounds will generate a roughly statistical mixture of the possible prod-

ucts.<sup>12</sup> So far the few successful cross McMurry reactions are mainly limited to: (a) two carbonyl compounds with significant molecular mass difference;<sup>13</sup> and (b) diaryl ketones with aryl or alkyl ketones or aldehydes.<sup>13,14</sup>

Initially we studied the cross McMurry coupling of diphenyl ketone (benzophenone, **1a**) with 4-methylphenyl phenyl ketone (**1b**) and bis[4-(morpholin-4-yl)phenyl] ketone (**1c**) (Table 1, entries 1, 2). The reactions were performed with the titanium(IV) chloride/zinc/pyridine system under standard conditions,<sup>15</sup> and the ketones were charged in equimolar amounts. It was observed that the coupling of **1a** with **1b** (Table 1, entry 1) resulted in a roughly statistical, inseparable, mixture of three possible products **2a**, **2b**, and **3b**. By contrast, the coupling of **1a** with **1c** (Table 1, entry 2) resulted in selective cross coupling to give **2c** in 56% isolated yield. We postulate that the strong affinity of the morpholin-4-yl group to the low-valent titanium surface played an important role with regards to moderating selectivity.

This is exemplified by comparing two cross-coupling reactions: **1a** with **1b** (Table 1, entry 1) and **1a** with 4-(morpholin-4-ylmethyl)phenyl phenyl ketone (**1d**) (Table 1, entry 3). Obviously apart from a morpholin-4-yl group, the reduction potential or electronic density of the carbonyl moiety of **1d** and **1b** appears quite similar. Optimization of the reaction parameters (mole ratio of **1a** to **1b–d**, source and number of equivalents of the low-valent-titanium reagent, temperature) was then performed on the coupling of **1a** with **1c**. The results are summarized in Table 1, entries 4–16.

It was observed that an excess of 1c relative to 1a improved the yields of the cross coupling slightly (Table 1, entries 4, 5). We found that the homocoupling of 1c (to give 3c) went more slowly than that of 1a (to give 2a). Using **1c** in excess slowed the entire reaction significantly, alternatively using an excess of **1a** resulted in an obvious increase in the yield of its cross-coupling product (Table 1, compare entries 4, 5 vs entries 6, 7). The influence of the amount of low-valent-titanium reagent indicated that 4-8 equivalents of titanium were sufficient for selective cross coupling. However, when the number of equivalents of the low-valent-titanium reagent was raised to 15:1, the mixed coupling gave a roughly statistical mixture of three products (Table 1, entries 8–11). Lowering the reaction temperature decelerated the coupling reaction, but did not enhance the selectivity of the cross coupling (Table 1, entries 12, 13). Two other types of low-

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Table 1 Cross McMurry Coupling of Diphenyl Ketone (1a) with Diaryl Ketones 1b-d and Optimization of the Reaction Conditions



**1−3 b**: Ar<sup>1</sup> = Ph, Ar<sup>2</sup> = 4-Tol

**c**  $Ar^1 = Ar^2 = 4$ -(morpholin-4-yl)phenyl

**d**  $Ar^1 = Ph$ ,  $Ar^2 = 4$ -(morpholin-4-ylmethyl)phenyl

Entry	Ketone	[Ti] <sup>a</sup> (equiv)	Mole ratio <sup>b</sup>	Products 2,3	Products 2 and 3, yield (%)			
					2a	2b-d	3b-d	
1	1b	A (5)	1:1	b	28°	44 <sup>c</sup>	28 <sup>c</sup>	
2	1c	<b>A</b> (5)	1:1	c	17	56	17	
3	1d	<b>A</b> (5)	1:1	d	14	61	9	
4 <sup>d</sup>	1c	<b>A</b> (5)	1:1.2	c	13	62	12	
5 <sup>d</sup>	1c	<b>A</b> (5)	1:1.5	c	6	64.5	12	
6	1c	<b>A</b> (5)	1.2:1	c	13	73	8	
7	1c	<b>A</b> (5)	1.5:1	c	13	71	6	
8	1c	<b>A</b> (2)	1.2:1	c	16	64	11	
9	1c	<b>A</b> (4)	1.2:1	c	14	70	8	
10	1c	<b>A</b> (8)	1.2:1	c	8	72	9	
11	1c	<b>A</b> (15)	1.2:1	c	28	36	27	
12 <sup>e</sup>	1c	<b>A</b> (5)	1.2:1	c	14	59	12	
13 <sup>f</sup>	1c	<b>A</b> (5)	1.2:1	c	13	62	11	
14 <sup>g</sup>	1c	<b>B</b> (5)	1.2:1	c	19	56	16	
15 <sup>h</sup>	1c	<b>B</b> (5)	1.2:1	c	20	51	19	
16	1c	<b>C</b> (15)	1.2:1	-	70	-	-	

<sup>a</sup> Low-valent-titanium reagent: **A**, TiCl<sub>4</sub>, Zn, py, THF; **B**, TiCl<sub>4</sub>, Zn, KCl, THF; **C**, Ti powder, TMSCl, THF; unless otherwise stated, reflux, 30 h. <sup>b</sup> Mole ratio of **1a** to **1b–d**.

<sup>c</sup> The yields were determined by GC analysis.

<sup>d</sup> The coupling was complete in ca. 45 h.

<sup>e</sup> Conditions: r.t., 67 h.

 $^{\rm f}$  Conditions: 40–45 °C, 50 h.

g Conditions: r.t., 17 h.

<sup>h</sup> Conditions: reflux, 7 h.

valent-titanium reagent<sup>10b,16</sup> were also tested in the cross coupling. It was found that the coupling using a titanium(IV) chloride/zinc/potassium chloride system occurred faster with lower yields of the cross-coupling product **2b** than those using the titanium(IV) chloride/zinc/pyridine system (Table 1, entries 14, 15). In our hands, only the homocoupling of **1a** to give **2a** occurred using the titanium powder/chlorotrimethylsilane system. (Table 1, entry 16).

Under the optimized reaction conditions a variety of tetraarylethenes **5** were conveniently prepared in 59-80%isolated yields through the cross coupling of two different diaryl ketones **1** and **4**. The results are summarized in Table 2. It was observed that a series of substituents containing nitrogen or oxygen atom(s) could enhance the selectivity of the cross coupling. The position of these substituents on aromatic rings did not affect the outcome of the cross coupling substantially (Table 2, entries 1–3, 7, 8, 10, 11). Diaryl ketones with these cross-coupling-enhancing-substituents could also cross couple with 3-bromophenyl or 4-tolyl ketones selectively (Table 2, entries 5, 9, 12). It should be noted that although lacking such substituents, 4-fluorophenyl 2-furyl ketone (**4m**) still coupled selectively with diphenyl ketone (**1a**) (Table 2, entry

 Table 2
 Preparations of Tetraarylethenes via the Cross McMurry Coupling of Two Different Diaryl Ketones<sup>a</sup>



1a: Ar<sup>1</sup> = Ar<sup>2</sup> = Ph **1c**:  $Ar^1 = Ar^2 = 4$ -(morpholin-4-yl)phenyl **1e**:  $Ar^1 = Ar^2 = 4 - HOC_6H_4$ **1f**:  $Ar^1 = Ph$ ,  $Ar^2 = 4 - H_2NC_6H_4$ 

Entry	Product	Ar <sup>1</sup>	Ar <sup>2</sup>	Ar <sup>3</sup>	Ar <sup>4</sup>	Yield (%)
1	5a	Ph	Ph	Ph	$4-HOC_6H_4$	66
2	5b	Ph	Ph	Ph	$3-HOC_6H_4$	62
3 <sup>b</sup>	5c	Ph	Ph	Ph	$2-HOC_6H_4$	64
4	5d	Ph	Ph	$4-HOC_6H_4$	$4-HOC_6H_4$	69
5	5e	$4-HOC_6H_4$	$4-HOC_6H_4$	Ph	$4-BrC_6H_4$	69
6	5f	Ph	Ph	4-MeOC <sub>6</sub> H <sub>4</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	59
7	5g	Ph	Ph	Ph	4-(morpholin-4-yl)- phenyl	62
8	5h	Ph	Ph	Ph	2-(morpholin-4-yl)- phenyl	61
9	5i	4-(morpholin-4-yl)- phenyl	4-(morpholin-4-yl)- phenyl	Ph	4-BrC <sub>6</sub> H <sub>4</sub>	77
10	5j	Ph	Ph	Ph	$4-H_2NC_6H_4$	80
11	5k	Ph	Ph	Ph	$2-H_2NC_6H_4$	72
12	51	Ph	$2-H_2NC_6H_4$	4-Tol	4-Tol	76
13	5m	Ph	Ph	$4-FC_6H_4$	2-furyl	70
14	5n	Ph	Ph	4-(morpholin-4-yl)- phenyl	2-thienyl	65

<sup>a</sup> The ketones were charged with the mole ratios of 1.2 to 1 (1 to 4); 5 equiv of low-valent-titanium reagent were used, reflux, 20–30 h. <sup>b</sup> The coupling was performed using low-valent-titanium reagent (2 equiv), reflux.

13). In contrast, the selective cross coupling of 2-thienyl ketone was achieved in the presence of a morpholin-4-yl group (Table 2, entry 14).

During research into the photophysical properties of tetraarylethenes, we needed a series of tetraarylethene-based building blocks, such as 1-(4-bromophenyl)-1,2,2-triphenylethene and 1-[4-(chloromethyl)phenyl]-1,2,2-triphenylethene (6), which can be easily linked to a target molecule. These compounds can be conveniently prepared by means of the above-mentioned synthetic protocol. For example, 1-(4-bromophenyl)-1,2,2-triphenylethene was prepared in two steps in 61% total yield by cross McMurry coupling of 1 with 4j to give 5j (Table 2, entry 10); (b) diazotization of 5j followed by bromination gave the desired product. In contrast, its reported preparation was as a side product in only 5% yield.<sup>17</sup> 1-[4-(Chloromethyl)phenyl]-1,2,2-triphenylethene (6) was first synthesized as illustrated in Scheme 1.



Scheme 1 Synthesis of 1-[4-(chloromethyl)phenyl]-1,2,2-triphenylethene. Reagents and conditions: (a) TiCl<sub>4</sub>, Zn, py, THF, reflux, 30 h, 61%; (b) ClCO<sub>2</sub>Et, MeCN, reflux, 7 h, 87%.

In conclusion, we report a novel synthetic approach to tetraarylethenes. Its advantages over previously reported procedures are: (a) the reagents are readily available; (b) the two different diaryl ketones are charged in nearly equimolar amounts (1.2:1); (c) the operations are simple and performed in one flask; and (d) the yields are acceptable. Importantly, we also provide a new procedure for cross McMurry coupling. The investigation of the mechanism of these selective cross-coupling reactions and the general cross McMurry coupling between two different carbonyl compounds are under way in our laboratory.

Melting points were obtained on a RY-1 microscopical instrument and were uncorrected. NMR spectra were recorded with an Advance 500 Bruker (500 MHz) spectrometer. Elemental analyses were performed with an Elementar Vario EL analyzer. IR spectra were recorded with a Vaatar 360 FT-IR spectrophotometer. MS spectra were recorded on a Trace MS 2000 spectrometer. GC was performed with a Varian CP-3800 gas chromatography analyzer. All reagents and solvents used for the McMurry reactions were freshly dried before use. Zinc powder was freshly activated by aq 1% HCl, washed with distilled H<sub>2</sub>O, abs EtOH, and Et<sub>2</sub>O, and then dried under vacuum. All glassware was oven dried (120 °C) and cooled under a stream of argon gas.

#### Diaryl Ketones 2b-d and 5a-n; General Procedure

Under an argon atmosphere, a 4-necked flask equipped with a magnetic stirrer was charged with Zn powder (1.6 g, 24 mmol) and THF (40 mL). The mixture was cooled to -5 °C to 0 °C, and TiCl<sub>4</sub> (1.3 mL, 12 mmol) was added slowly by syringe with the temperature maintained under 10 °C. The suspended mixture was warmed to r.t. and stirred for 0.5 h, then heated to reflux for 2.5 h. The mixture was again cooled to -5 °C to 0 °C, charged with pyridine (0.5 mL, 6 mmol), and stirred for 10 min. The soln of two diaryl ketones [in 1:1.5 to 1.2:1 mole ratio (as illustrated in Tables 1 and 2)], 2.4 mmol (or as illustrated in Tables 1 and 2)] in THF (15 mL) was added slowly. When the addition was complete, the mixture was heated to reflux until the carbonyl compounds were consumed (monitored by TLC). The reaction was quenched by addition of 10% aq K<sub>2</sub>CO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The products were isolated and purified by flash chromatography.

#### **1,1-Bis(4-morpholin-4-ylphenyl)-2,2-diphenylethene (2c)** Yellow solid; mp 205.1–206.2 °C.

IR (KBr): 3044.5, 2954.4, 1606.5, 1513.3, 1230.6, 1122.9, 925.5, 701.7  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.14 (br s, 8 H), 3.86 (br s, 8 H), 6.91 (s, 4 H), 6.95 (m, 4 H), 7.04–7.05 (m, 4 H), 7.07–7.14 (m, 6 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 48.9, 66.9, 114.3, 125.9, 127.6, 131.4, 132.4, 135.5, 138.6, 140.3, 144.6, 149.3.

MS (EI): m/z (%) = 503 (M<sup>+</sup>, 100), 444 (36), 386 (26), 252 (30), 165 (17).

Anal. Calcd for  $C_{34}H_{34}N_2O_2{:}$  C, 81.24; H, 6.82; N, 5.57. Found: C, 80.93; H, 7.24; N, 5.58.

**1-[4-(Morpholin-4-ylmethyl)phenyl]-1,2,2-triphenylethene (2d)** Colorless solid; yield: 61%; mp 152.1–153.0 °C.

IR (KBr): 2922.4, 2852.7, 1597.7, 1491.6, 1443.2, 1116.9, 696.5 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.42 (s, 4 H), 3.45 (s, 2 H), 3.73 (s, 4 H), 6.99–7.12 (m, 19 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 53.5, 63.2, 66.9, 126.3, 126.4, 127.6, 128.5, 131.2, 131.3, 135.6, 140.7, 140.9, 142.7, 143.6, 143.7, 143.8.

MS (EI): m/z (%) = 431 (M<sup>+</sup>, 75), 345 (45), 252 (26), 86 (41), 49 (100).

Anal. Calcd for  $C_{31}H_{19}N$ : C, 86.27; H, 6.77; N, 3.25. Found: C, 85.99; H, 6.77; N, 3.25.

# 1-(4-Hydroxyphenyl)-1,2,2-triphenylethene (5a)<sup>18</sup>

Colorless solid; yield: 66%; mp 215–216 °C (Lit.<sup>18</sup> 215–217 °C); Analytical data were identical with those reported.

#### **1-(3-Hydroxyphenyl)-1,2,2-triphenylethene (5b)** Colorless solid; yield: 62%; mp 228.9–229.5 °C.

IR (KBr): 3519.9, 3050.5, 3017.1, 1591.7, 1441.9, 1180.3, 745.4, 699.4, 639.5 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.47 (br, 1 H), 6.52 (s, 1 H), 6.60–6.65 (m, 2 H), 6.99 (m, 1 H), 7.03–7.08 (m, 6 H), 7.11–7.13 (m, 9 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 113.6, 118.1, 124.1, 126.5, 126.5, 127.7, 128.8, 131.1, 131.2, 131.3, 140.4, 141.2, 143.5, 143.6, 145.3, 154.9. MS (EI): *m/z* (%) = 348 (M<sup>+</sup>, 100), 333 (9), 270 (17), 252 (27), 165 (23).

Anal. Calcd for  $C_{26}H_{20}O$ : C, 89.62; H, 5.79. Found: C, 89.33; H, 5.72.

# 1-(2-Hydroxyphenyl)-1,2,2-triphenylethene (5c)

Colorless solid; yield: 64%; mp 201.4–202.7 °C.

IR (KBr): 3527.3, 3014.8, 1589.8, 1488.6, 1442.4, 1176.7, 873, 749.8, 699.2, 624.8 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 5.09 (br, 1 H), 6.75–6.78 (m, 2 H), 7.01 (d, J = 8.5 Hz, 1 H), 7.04–7.12 (m, 6 H), 7.14–7.18 (m, 10 H).

MS (EI): m/z (%) = 348 (M<sup>+</sup>, 97), 270 (57), 165 (100), 105 (62), 77 (56).

Anal. Calcd for  $C_{26}H_{20}O$ : C, 89.62; H, 5.79. Found: C, 89.79, H, 5.56.

### **1,1-Bis(4-hydroxyphenyl)-2,2-diphenylethene (5d)** Colorless solid; yield: 69%; mp 222.9–223.7 °C.

IR (KBr): 3404.2, 1608.2, 1508.4, 1442.8, 1254.9, 1170.7, 834.6, 765.8, 700.6, 592.4, 570.0  $\rm cm^{-1}$ .

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.58 (s, 2 H), 6.59 (d, *J* = 8.44 Hz, 4 H), 6.92 (d, *J* = 8.43 Hz. 4 H), 7.04 (d, *J* = 7.32 Hz, 4 H), 7.12 (t, *J* = 7.03 Hz, 6 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 114.4, 125.9, 127.6, 131.1, 132.4, 134.9, 144.6, 156.1.

MS (EI): m/z (%) = 364 (M<sup>+</sup>, 100), 270 (15), 165 (14).

Anal. Calcd for  $C_{26}H_{20}O_2$ : C, 85.69; H, 5.53. Found: C, 85.39; H, 5.80.

# 1-(4-Bromophenyl)-2,2-bis(4-hydroxyphenyl)-1-phenylethene (5e)

Colorless solid; yield: 69%; mp 234.5-235.0 °C.

IR (KBr): 3316.3, 3019.1, 1605.5, 1591.6, 1506.5, 1237.9, 838.35, 703.0  $\rm cm^{-1}.$ 

 $^1\text{H}$  NMR (CDCl\_3):  $\delta=4.64$  (br, 2 H), 6.59–6.78 (m, 4 H), 6.78 (m, 1 H), 6.89–6.92 (m, 5 H), 7.05–7.25 (m, 7 H).

MS (EI): m/z (%) = 444 (M<sup>+</sup>, 100), 364 (32), 252 (10), 165 (26), 107 (40).

Anal. Calcd for  $C_{26}H_{19}BrO_2$ : C, 70.44; H, 4.32. Found: C, 70.12; H, 4.61.

# 1-(4-Methoxyphenyl)-1,2,2-triphenylethene (5f)

Colorless solid; yield: 59%; mp 140–141.5 °C (Lit.<sup>19</sup> 139–141 °C); Analytical data (IR, <sup>1</sup>H NMR) were identical with those reported.

# 1-(4-Morpholin-4-ylphenyl)-1,2,2-triphenylethene (5g)

Yellow solid; yield: 62%; mp 177.4–178.8 °C.

IR (KBr): 2931.1, 2857.0, 1599.6, 1519.3, 1448.4 1231.6, 1113.3, 926.5, 771.0 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.24 (br s, 4 H), 4.00 (br s, 4 H), 6.83–7.49 (m, 19 H).

 $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  = 48.8, 66.9, 114.3, 126.2, 126.3, 127.6, 127.7, 131.4, 131.5, 132.3, 135.1, 139.7, 140.6, 144.1, 144.17, 144.23, 149.4.

MS (EI): m/z (%) = 417 (M<sup>+</sup>, 100), 359 (52), 252 (48).

Anal. Calcd for  $C_{30}H_{27}NO$ : C, 86.30; H, 6.52; N, 3.35. Found: C, 86.59; H, 6.76; N, 3.35.

# **1-(2-Morpholin-4-ylphenyl)-1,2,2-triphenylethene (5h)** Colorless solid; yield: 61%; mp 173.5–174.7 °C.

IR (KBr): 3074.1, 3029.6, 2851.9, 1597.2, 1490.1, 1448.6, 1112.6, 921.0, 746.1, 736.6, 697.8  $\rm cm^{-1}$ .

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.58 (br s, 4 H), 3.80 (br s, 4 H), 6.98–7.23 (m, 19 H).

MS (EI): m/z (%) = 417 (M<sup>+</sup>, 100), 359 (52), 252 (98), 165 (98), 152 (46).

Anal. Calcd for  $C_{30}H_{27}NO$ : C, 86.30; H, 6.52; N, 3.35. Found: C, 86.01; H, 6.82; N, 3.18.

# 1-(4-Bromophenyl)-2,2-bis(2-morpholin-4-ylphenyl)-1-phenylethene (5i)

Yellow solid; yield: 77%; mp 236.1-237.9 °C.

IR (KBr): 3030.0, 2962.1, 2852.7, 1602.8, 1512.0, 1230.4, 1118.5, 923.3, 696.9  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.23 (m, 8 H), 3.96 (m, 8 H), 6.89 (m, 3 H), 6.91 (m, 3 H), 6.97–7.01 (m, 3 H), 7.12 (m, 5 H), 7.23–7.25 (m, 3 H).

MS (EI): *m*/*z* (%) = 580 (M<sup>+</sup>, 100), 524 (15), 502 (25), 252 (41), 165 (35), 105 (21).

Anal. Calcd for  $C_{34}H_{33}BrN_2O_2:$  C, 70.22; H, 4.82; N, 5.72. Found: C, 69.91; H, 5.81; N, 4.73.

### **1-(4-Aminophenyl)-1,2,2-triphenylethene (5j)** Yellow solid; yield: 80%; mp 202.1–203.4 °C.

IR (KBr): 3203.3, 1597.3, 1492.0, 1443.3, 1071.6, 694.4 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.57 (br s, 2 H), 6.69 (m, 2 H), 6.91 (d, J = 7.8 Hz, 2 H), 7.04 (m, 7 H), 7.16 (m, 8 H).

MS (EI): *m*/*z* (%) = 347 (M<sup>+</sup>, 100), 270 (31), 252 (37), 239 (17), 84 (32).

Anal. Calcd for  $C_{26}H_{21}N$ : C, 89.88; H, 6.09; N, 4.03. Found: C, 89.84; H, 6.06; N, 4.38.

### 1-(2-Aminophenyl)-1,2,2-triphenylethene (5k)

Yellow solid; yield: 72%; mp 208.1–209.1 °C.

IR (KBr): 3441.6, 3367.0, 3047.4, 3016.2, 1611.9, 1489.3, 1297.7, 749.7, 699.9 cm $^{-1}$ .

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 6.58-6.62$  (m, 2 H), 6.95 (d, J = 1.5 Hz, 1 H), 6.97 (d, J = 1.5 Hz, 1 H), 7.09–7.11 (m, 12 H), 7.16–7.17 (m, 3 H). MS (EI): m/z (%) = 347 (M<sup>+</sup>, 100), 270 (93), 80 (57), 65 (86), 152 (47). Anal. Calcd for  $C_{26}H_{21}N$ : C, 89.88; H, 6.09; N, 4.03. Found: C, 89.75; H, 5.75; N, 3.93.

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# 1-(4-Aminophenyl)-2,2-bis(4-methylphenyl)-1-phenylethene (5l)

Yellow solid; yield: 76%; mp 173.3-173.9 °C.

IR (KBr): 3447.8, 3368.3, 3020.7, 2916.1, 1619.0, 1514.0, 1283.1, 818.1, 758.6, 702.8  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.26 (s, 3 H), 2.29 (s, 3 H), 3.71 (br, 2 H), 6.45 (d, *J* = 8 Hz, 2 H), 6.82 (d, *J* = 10 Hz, 2 H), 6.89 (s, 4 H), 6.95 (s, 4 H), 7.06 (d, *J* = 10 Hz, 2 H), 7.11 (m, 3 H).

 $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  = 21.1, 21.2, 114.4, 126.0, 127.5, 128.2, 128.3, 131.2, 131.3, 131.4, 132.4, 134.5, 135.6, 139.2, 139.9, 141.4, 141.5, 144.5, 144.6.

MS (EI): m/z (%) = 375 (M<sup>+</sup>, 100), 360 (14), 267 (26), 252 (22), 180 (29).

Anal. Calcd for  $C_{28}H_{25}N$ : C, 89.56; H, 6.71; N, 3.73. Found: C, 89.77; H, 6.42; N, 3.98.

#### **1-(4-Fluorophenyl)-1-(2-furyl)-2,2-diphenylethene (5m)** Colorless solid; yield: 70%; mp 147.9–149.1 °C.

IR (KBr): 1597.8, 1505.9, 1490.8, 1442.6, 1213.5, 1157.3, 1020.0, 844.8, 812.0, 766.3, 743.0, 703.3, 595.5 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 5.71 (d, *J* = 3.3 Hz, 1 H), 5.84 (d, *J* = 3.2 Hz, 1 H), 6.27 (dd, *J*<sub>1</sub> = 3.1 Hz, *J*<sub>2</sub> = 1.4 Hz, 1 H), 6.88–7.27 (m, 14 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 110.9, 112.1, 114.8, 115.0, 126.6, 126.9, 127.6, 127.7, 127.9, 130.1, 131.1, 131.8, 132.8, 132.9, 141.5, 142.0, 142.7, 143.8, 161.3.

MS (EI): m/z (%) = 340 (M<sup>+</sup>, 36), 233 (37), 21 (41), 84 (86), 49 (100).

Anal. Calcd for  $C_{24}H_{17}FO$ : C, 84.68; H, 5.03. Found: C, 84.41; H, 5.23.

# 1-(4-Morpholin-4-ylphenyl)-2,2-diphenyl-1-(2-thienyl)ethene (5n)

Yellow solid; yield: 65%; mp 150.5-151.2 °C.

IR (KBr): 2955.8, 2857.0, 2814.0, 1604.9, 1558.4, 1508.3, 1449.7, 1231.3, 1121.1, 929.5, 855.5, 767.6, 700.5  $\rm cm^{-1}.$ 

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.15 (t, *J* = 4.8 Hz, 4 H), 3.86 (t, *J* = 4.6 Hz, 4 H), 6.61 (s, 1 H), 6.69 (s, 2 H), 6.71 (s, 1 H), 7.06–7.24 (m, 13 H).

 $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta$  = 48.8, 66.8, 114.3, 125.9, 126.0, 126.1, 126.8, 127.6, 128.1, 129.4, 130.9, 131.0, 132.2, 133.4, 134.5, 140.2, 143.6, 144.1, 146.9, 149.8.

MS (EI): m/z (%) = 423 (M<sup>+</sup>, 13), 258 (19), 165 (100), 77 (79).

Anal. Calcd for  $C_{28}H_{25}NOS$ : C, 79.40; H, 5.95; N, 3.31. Found: C, 79.48; H, 6.23; N, 3.05;

# 1-(4-Bromophenyl)-1,2,2-triphenylethene

1-(4-Aminophenyl)-1,2,2-triphenylethene (**5j**) was diazotized and brominated according to a published procedure.<sup>20</sup> The product was purified by flash chromatography (petroleum ether). Colorless solid; yield: 76%; mp 160.5–161.5 °C (Lit.<sup>17</sup> 160–161 °C); analytical data were in agreement with the structure.

# 1-[4-(Chloromethyl)phenyl]-1,2,2-triphenylethene (6)

Under an argon atmosphere, ethyl chloroformate (0.74 g, 6.8 mmol) was added to a soln of **2d** (1.5 g, 3.4 mmol) in anhyd MeCN (15 mL). The mixture was refluxed with magnetic stirring for 7 h and then it was evaporated under vacuum and the residue was taken up in  $CH_2Cl_2$  (30 mL). The soln was washed by 2% aq HCl (2 × 20 mL) and brine (2 × 20 mL) and dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed to give the crude product. Flash chromatography (petro-

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leum ether) gave the pure product as a colorless solid; yield: 87%; mp 178.6–179.2 °C.

IR (KBr): 3024.9, 2925.2, 1607.9, 1513.4, 1235.5, 1010.4, 699.6  $\rm cm^{-l}.$ 

<sup>1</sup>H NMR(CDCl<sub>3</sub>):  $\delta$  = 4.53 (s, 2 H), 7.05–7.17 (m, 19 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 46.1, 126.5, 126.6, 127.6, 127.7, 127.8, 127.9, 128.1, 128.5, 128.7, 128.9, 129.3, 131.3, 131.6, 135.4, 140.3, 141.5, 143.5, 143.6, 143.9.

MS (EI): *m/z* (%) = 380 (M<sup>+</sup>, 100), 345 (71), 252 (42), 167 (43), 84 (72), 49 (74).

Anal. Calcd for  $C_{27}H_{21}Cl: C$ , 85.14; H, 5.56. Found: C, 84.83; H, 5.42.

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