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Synthesis of Di- and Triarylmethanes through Palladium-Catalyzed Reductive Coupling of *N*-Tosylhydrazones and Aryl Bromides

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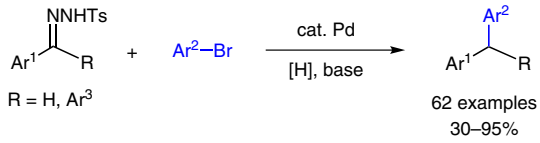

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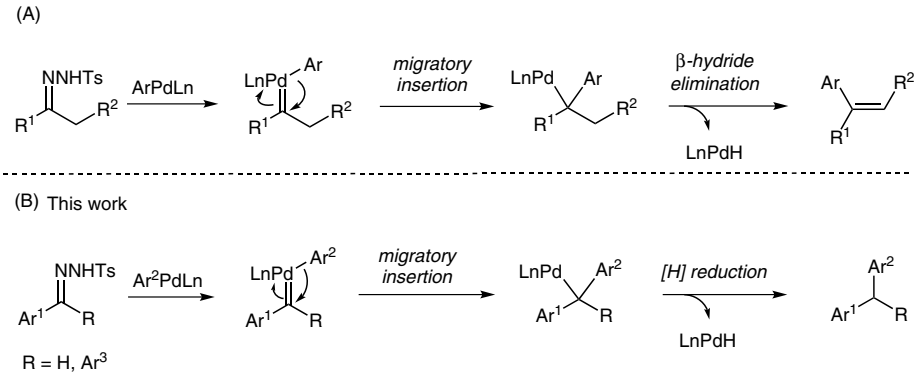
Abstract A palladium-catalyzed reductive coupling between *N*-tosylhydrazones and aryl bromides has been developed. The reaction provides an efficient method for the synthesis of diarylmethanes and triarylmethanes via the formation of C(sp^2)–C(sp^3) single bonds. This new methodology for the synthesis of diarylmethanes and triarylmethanes is featured by the ready availability of the starting materials, mild reaction conditions, and the tolerance of wide range of functional groups. The reaction follows a pathway including palladium carbene formation, migratory insertion, and reduction of the alkylpalladium(II) intermediate.

Key words *N*-tosylhydrazone, cross-coupling, carbene, palladium, diarylmethane, triarylmethane

Di- and triarylmethanes are important motifs, which widely exist in natural products, pharmaceutically related compounds, and supramolecular structures.[1,2] In view of their importance in various fields, the development of synthetic methods that can rapidly access di- and triarylmethanes from readily available starting materials has attracted significant attention.[3] The traditional methods to access di- and triarylmethanes are Friedel–Crafts alkylations and their variants, which form a C–C bond by introducing an alkyl group into an aromatic ring.[4] These methods, although widely used, are generally found difficult to be applied for the synthesis of di- and triarylmethanes bearing electron-withdrawing groups or *meta*-substituents. Recently, the method based on transition-metal-catalyzed cross-coupling reactions has emerged as efficient and practical tools for the synthesis of di- and triarylmethanes.[5] For example, Watson developed a nickel-catalyzed cross coupling of benzylic ammonium triflates with arylboronic acids to give diarylmethanes.[5c] Bedford reported an iron(I)-catalyzed Negishi cross-coupling reaction with arylzinc reagents for the synthesis of a series of structurally diverse diarylmethanes.[5d]

Among the transition-metal-catalyzed cross-coupling reactions, palladium-catalyzed reactions have been proven powerful for the synthesis of di- and triarylmethanes.[6] For the synthesis of diarylmethanes, Sarkar developed an Hiyama coupling of benzylic halides with aryltrialkoxysilanes using palladium catalysts.[6b] McLaughlin reported a Suzuki–Miyaura cross-coupling reaction between benzylic phosphates and arylboronic acids to access diarylmethanes.[6e] In contrast, the methods for the synthesis of triarylmethanes are less developed.[7] Walsh provided an approach to triarylmethanes by the coupling of diarylmethanes and aryl bromides by transforming the benzylic C–H bonds into the C–C bonds.[7c] Kuwano and co-workers presented a coupling between diarylmethyl carbonates and arylboronic acids.[7f] More recently, Hirano and Miura reported a Pd-catalyzed coupling of oxazoles with diarylmethyl carbonates or pivalates to afford triarylmethanes in good yields.[7a] Although many efforts have been devoted to this area, it is still highly desirable to develop novel and efficient coupling reactions for the synthesis of di- and triarylmethanes.

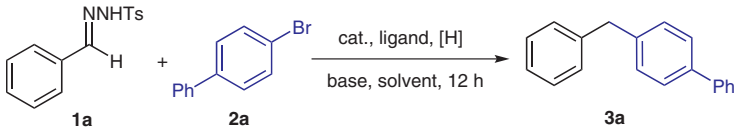
N-Tosylhydrazones are commonly used substrates in organic synthesis and they can be readily accessed by condensation of carbonyl compounds with *N*-tosylhydrazide. Recently, *N*-tosylhydrazones have been proven as a new type of cross-coupling partners in Pd-catalyzed reactions.[8] In these reactions, *N*-tosylhydrazones are first converted to non-stabilized diazo compounds in situ with base through Bamfod–Stevens reaction.[9] Then dinitrogen extrusion occurs to form Pd carbene intermediates, which undergo migratory insertion leading to the formation of C–C single bond.[8,10] Recently, Pd-catalyzed cross-coupling reactions of *N*-tosylhydrazones with benzyl halides, terminal alkynes, and boronic acids have been well established.[11] In these re-



Scheme 1 Pd-Catalyzed cross-coupling of *N*-tosylhydrazones

actions, the regeneration of Pd catalyst was achieved via β-hydrogen elimination of palladium species that are generated from Pd carbene migratory insertion, leading to the formation of C=C double bond. Thus, the *N*-tosylhydrazones can be considered as vinylmetallic reagent equivalents in these cases (Scheme 1 A). In 2013, we communicated a palladium-catalyzed reductive cross coupling of *N*-tosylhydrazones, in which the *N*-tosylhydrazones can be considered as alkylmetallic reagent precursors. The reaction is a novel and efficient approach toward triarylmethanes (Scheme 1

Table 1 Condition Optimization for the Pd-Catalyzed Reductive Cross-Coupling Reaction[a]



1a **2a** **3a**

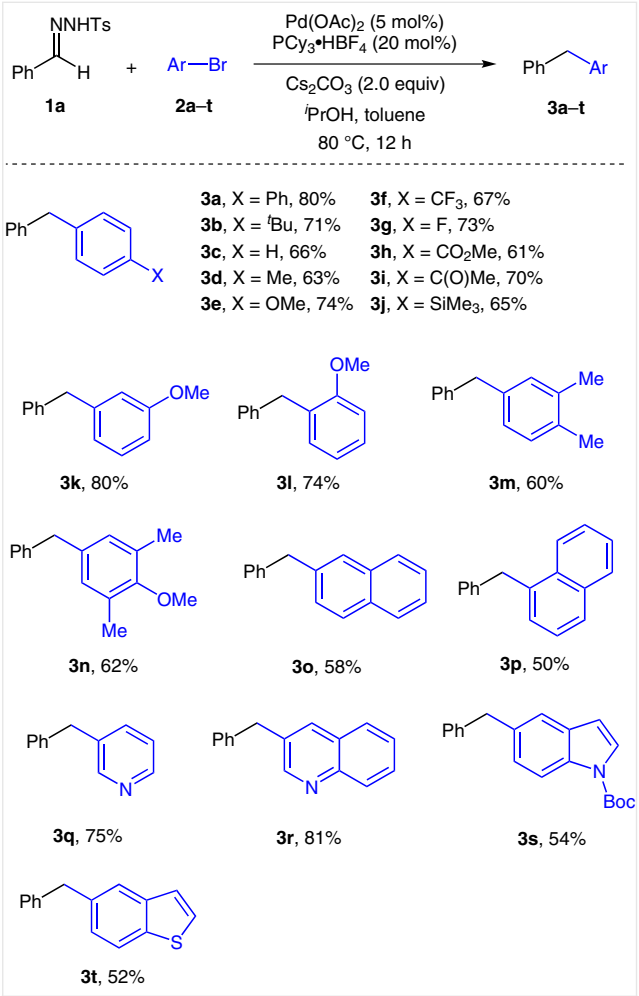
Entry	Cat. (mol%)	Ligand (mol%)	[H]	Base	Solvent	Temp (°C)	Yield (%)[b]
1	$Pd(PPh_3)_4$ (5)	none	HCO_2NH_4	K_2CO_3	DCE	90	trace
2	$Pd(PPh_3)_4$ (5)	none	HCO_2NH_4	Cs_2CO_3	DCE	90	<5
3	$Pd(PPh_3)_4$ (5)	none	HCO_2NH_4	*t*-BuOLi	DCE	90	0
4	$Pd(PPh_3)_4$ (5)	none	Et_3SiH	Cs_2CO_3	DCE	90	trace
5	$Pd(PPh_3)_4$ (5)	none	*i*-PrOH	Cs_2CO_3	DCE	90	<10
6	$Pd(OAc)_2$ (5)	P(2-furyl)$_3$ (15)	HCO_2NH_4	Cs_2CO_3	DCE	90	trace
7	$Pd(OAc)_2$ (5)	Xphos (15)	HCO_2NH_4	Cs_2CO_3	DCE	90	trace
8	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (15)	HCO_2NH_4	Cs_2CO_3	DCE	90	<10
9	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (15)	*i*-PrOH	Cs_2CO_3	toluene	80	23
10	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (15)	*i*-PrOH	Cs_2CO_3	1,4-dioxane	80	0
11	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (15)	*i*-PrOH	Cs_2CO_3	MeCN	80	trace
12[c]	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (15)	*i*-PrOH	Cs_2CO_3	toluene	80	50
13[d]	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (15)	*i*-PrOH	Cs_2CO_3	toluene	80	57
14[d]	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (15)	*i*-PrOH	Cs_2CO_3	toluene	70	40
15[d]	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (15)	*i*-PrOH	Cs_2CO_3	toluene	80	54
16[e]	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (15)	*i*-PrOH	Cs_2CO_3	toluene	80	51
17[f]	$Pd(OAc)_2$ (5)	$PCy_3{\cdot}HBF_4$ (15)	*i*-PrOH	Cs_2CO_3	toluene	80	74
18[f]	**$Pd(OAc)_2$ (5)**	**$PCy_3{\cdot}HBF_4$ (20)**	***i*-PrOH**	**Cs_2CO_3**	**toluene**	**80**	**80**

[a] Unless otherwise noted, the reaction was carried out with **1a** (0.30 mmol), **2a** (0.30 mmol), [H] (0.3 mmol), and base (2.0 equiv) in solvent (3 mL) for 12 h.
[b] Yields refer to the isolated products.
[c] Toluene (2.5 mL), *i*-PrOH (0.5 mL).
[d] Toluene (2.7 mL), *i*-PrOH (0.3 mL).
[e] Toluene (2.7 mL), *i*-PrOH (0.3 mL), **1a**/**2a** = 1.5:1.
[f] Toluene (2.7 mL), *i*-PrOH (0.3 mL), **1a**/**2a** = 1.2:1.

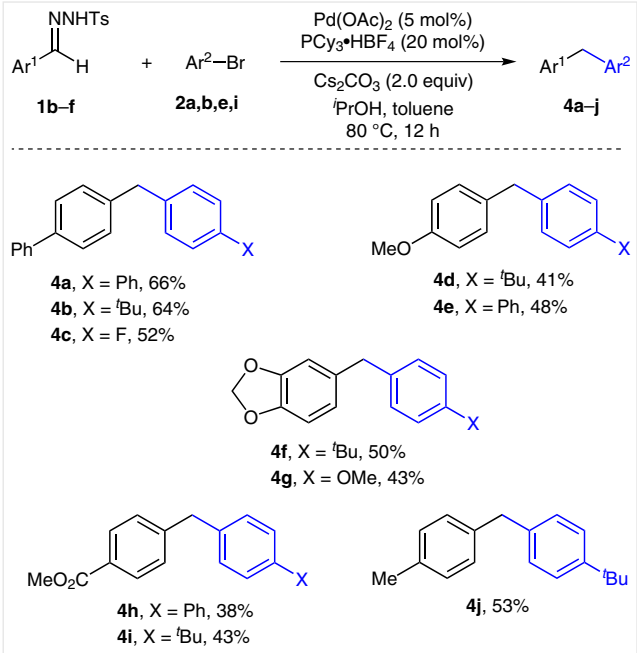
B, R = Ar[3]).[12] As a continuation of our interest in carbene-coupling reactions, we have further extended the substrate scope of this reaction and developed an efficient access toward diarylmethanes (Scheme 1 B, R = H). Herein we report the details of this methodology.

At the outset, we chose benzaldehyde *N*-tosylhydrazone **1a** and 4-bromo-1,1′-biphenyl (**2a**) as the substrates to optimize the reductive coupling reaction (Table 1). Initially, it was observed that with Cs_2CO_3 as the base the expected coupling product **3a** could be isolated, albeit in only low yield (Table 1, entry 2). With Cs_2CO_3 as the base and DCE as the solvent, the effect of phosphine ligands and reducing agents were then examined, but the reactions did not gave satisfactory results (entries 6–8). Next, the effect of solvent was investigated (entries 9–11), toluene was found to afford an improved result (entry 9). It was noted that the direct reduction of **2a** to biphenyl was the major side reaction. Further optimization of the reaction conditions revealed that the reaction yields could be significantly improved by raising the equivalent of reducing agent *i*-PrOH (entries 12 and 13). Furthermore, the temperature was found not significantly affect the reaction (entries 14 and 15). Finally, the reaction could be further improved by increasing the loading of ligand and the substrate ratio of **1a** to **2a** (entries 16–18). The optimized reaction conditions are shown in entry 18, under which the coupling product **3a** could be obtained in 80% yield.

With the optimized conditions in hand, the scope of the reaction we first explored with benzaldehyde *N*-tosylhydrazone and a variety of aryl bromides (Scheme 2). The reactions occurred smoothly with electron-donating and electron-withdrawing substituted aryl bromides to afford the corresponding diarylmethanes in moderate to good yields, and that *ortho*-, *para*- and *meta*-substituted substrates could also provide satisfactory results (**3a**–**n**). Notably, the reaction exhibited good tolerance to various functional groups including carbonyl, methoxycarbonyl, and trimethylsilyl (**3h**–**j**). Aryl bromides containing fused ring gave the coupling products in diminished yields (**3o**,**p**). In



Scheme 2 Substrate scope of aryl bromides for the synthesis of diarylmethanes. All reactions were carried out with **1a** (0.36 mmol), **2a–t** (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol), $PCy_3{\cdot}HBF_4$ (0.060 mmol), Cs_2CO_3 (0.60 mmol), and *i*-PrOH (0.3 mmol) in toluene (2.7 mL) at 80 °C for 12 h. Yields refer to the isolated products by silica gel column chromatography.

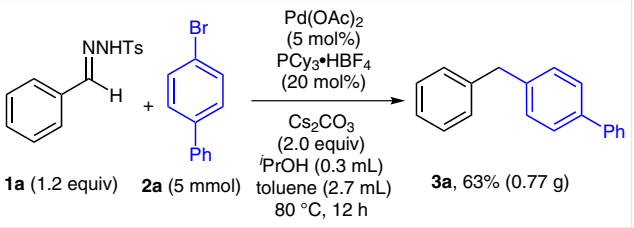


Scheme 3 Substrate scope of *N*-tosylhydrazones for the synthesis of diarylmethanes. All the reactions were carried out with **1b–f** (0.36 mmol), **2a**,**b**,**e**,**i** (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol), $PCy_3{\cdot}HBF_4$ (0.060 mmol), Cs_2CO_3 (0.60 mmol), and *i*-PrOH (0.3 mmol) in toluene (2.7 mL) at 80 °C for 12 h. Yields refer to the isolated products by silica gel column chromatography.

addition, the scope of substrates was extended to heteroaromatic bromides and the corresponding products were obtained in moderate to good yields (**3q–t**).

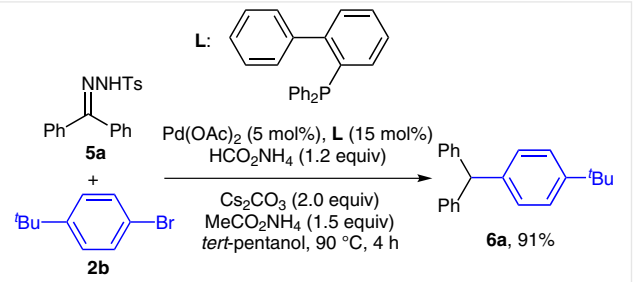
Next, the reaction was examined with a series of *N*-tosylhydrazones **1b–f** as the substrates to react with aryl bromides **2a**, **2b**, **2e**, and **2i**. As shown in Scheme 3, it was observed that the reaction could tolerate a variety of functional groups in the *N*-tosylhydrazones. The substrates bearing both electron-donating and electron-withdrawing substituents on the aromatic ring could afford the corresponding products in moderately high yields.

In order to demonstrate the practical application of this reductive coupling method, the standard reaction was scaled up and was carried out for gram-scale preparation. As show in Scheme 4, the reaction gave the desired product **3a** in good yield.



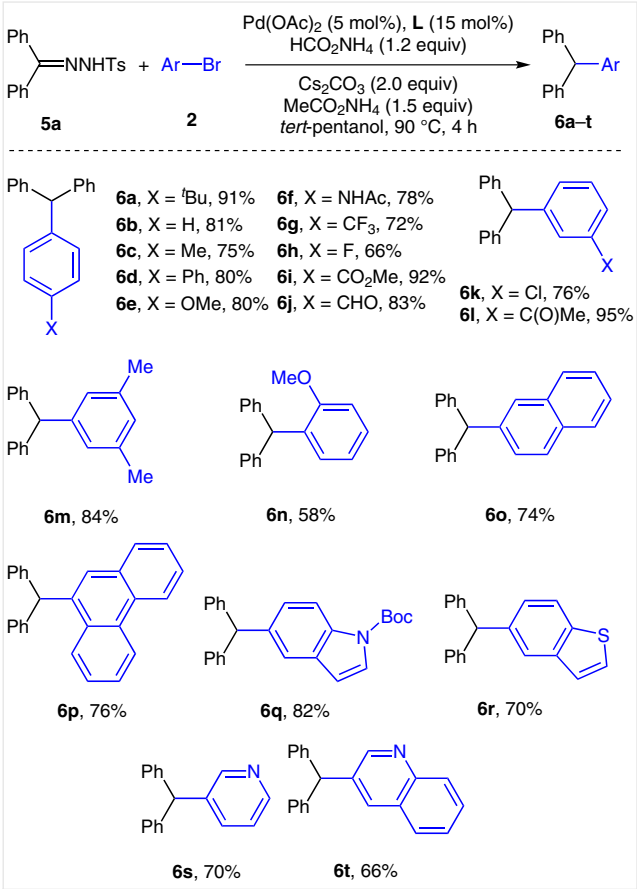
Scheme 4 Gram-scale preparation of **3a**

Furthermore, we proceeded to extend the reductive cross-coupling method for the synthesis of triarylmethanes. *N*-Tosylhydrazone **5a** and aryl bromide **2b** were employed as the substrates to optimize the reaction. However, under the above optimized reaction conditions, the reaction only afforded a trace amount of the coupling product **6a**. Thus, a series of experiments were carried out to improve the yields. Finally, it was concluded that under the reaction conditions described in Scheme 5, the desired coupling product could be isolated in 91% yield.[13] It should be noted that this part of the study has been previously published in a preliminary communication.[12]



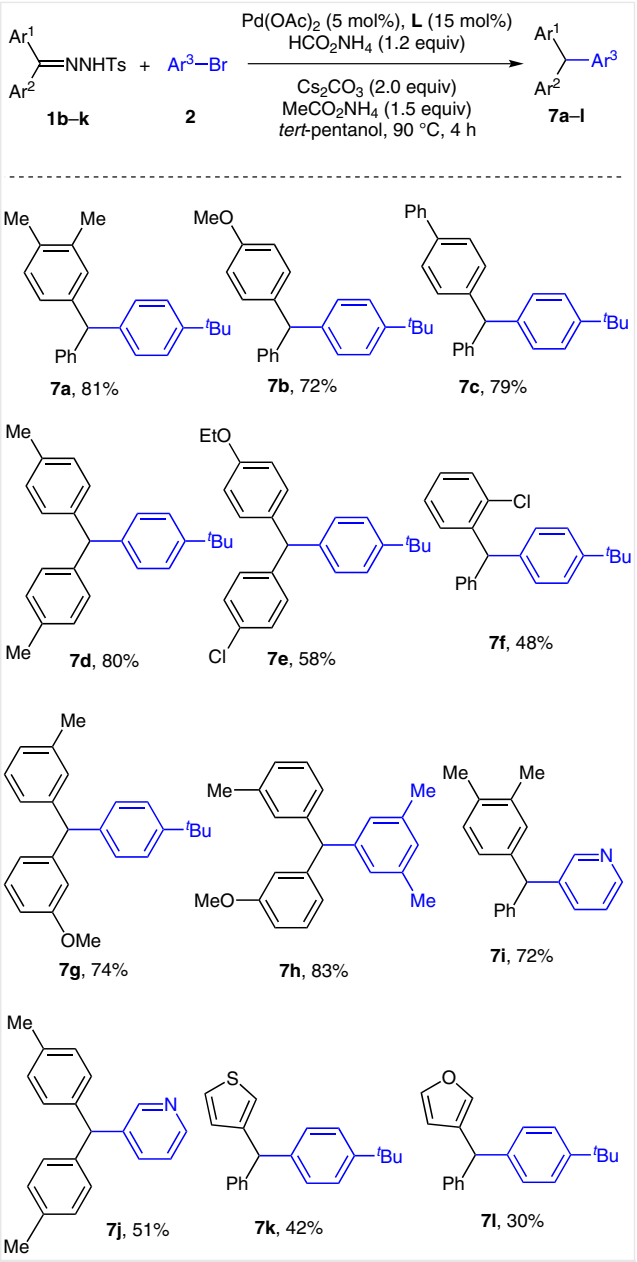
Scheme 5 Optimized conditions for the preparation of triarylmethane **6a**

With the optimized reaction conditions, benzophenone *N*-tosylhydrazone **5a** and a series of aryl bromides were used as the substrates to examine the scope of this reaction. As shown in Scheme 6, the reductive coupling reactions provided the corresponding triarylmethanes in moderate to excellent yields. The aryl bromides with both electron-rich and electron-deficient substituents were effective, and that the substituents on the *para*- or *meta*-position could afford the products in 66–95% yield (**6a–m**). However, an *ortho* substituent gave slightly lower yield (**6n**). Notably, the aryl bromides containing fused ring were also suitable substrates for this reaction (**6o**,**p**). In addition, the heteroaryl bromides could be tolerated under the given reaction conditions (**6q–t**).



Scheme 6 Substrate scope of aryl bromides for the synthesis of triarylmethanes. Reactions were carried out with **5a** (0.36 mmol), **2** (0.3 mmol), in the presence of $Pd(OAc)_2$ (5 mol%), **L** (15 mol%), HCO_2NH_4 (0.36 mmol), $MeCO_2NH_4$ (0.45 mmol), and Cs_2CO_3 (0.6 mmol) in *tert*-pentyl alcohol (3.0 mL) at 90 °C for 4 h. Yields refer to isolated products by silica gel column chromatography.

Finally, the reductive coupling reactions with a range of diarylmethanone *N*-tosylhydrazones as the substrate were explored, affording the corresponding triarylmethanes in moderate to good yields (Scheme 7). It was worth noting that the product **7h** could not be obtained through the traditional Friedel–Crafts reactions. Moreover, the diarylmethanone *N*-tosylhydrazones containing heterocyclic moieties



Scheme 7 Substrate scope of *N*-tosylhydrazones for the synthesis of triarylmethanes. Reactions were carried out with **1** (0.36 mmol), **2** (0.3 mmol), in the presence of $Pd(OAc)_2$ (5 mol%), **L** (15 mol%), HCO_2NH_4 (0.36 mmol), $MeCO_2NH_4$ (0.45 mmol), and Cs_2CO_3 (0.6 mmol) in *tert*-pentyl alcohol (3.0 mL) at 90 °C for 4 h. All the yields refer to isolated products by silica gel column chromatography.

were also found as suitable substrates in the reactions (**7i–l**).

Based on our understanding of the palladium-catalyzed coupling reaction of *N*-tosylhydrazones,[8] we propose a possible mechanism as shown in Scheme 8. First, Pd(0)L **A** is oxidized to Pd(II) species **B** by aryl bromides. Then treatment of *N*-tosylhydrazone with base generates diazo substrate **D** in situ, followed by the formation of Pd carbene intermediate **E**. Migratory insertion of Pd carbene **E** affords species **F**, followed by hydrogen transfer from *i*-PrOH or HCO_2NH_4 to give the palladium-hydride complex **G**. Finally, the product **P** is produced through the reductive elimination of the intermediate **G**, with simultaneous regeneration of Pd(0) catalyst. In this transformation, the major by-product **C** is generated by the direct reduction of the intermediate **B**. In the case of triarylmethane synthesis, the side reaction can be minimized by adding ammonium acetate as the additive.[13]

In summary, we have developed a novel reaction for the synthesis of di- and triarylmethanes through Pd-catalyzed reductive coupling of *N*-tosylhydrazones with aryl halides. This reaction utilized *N*-tosylhydrazones as the alkyl metallic reagent equivalents to form the C–C single bonds. The reaction tolerates various functional groups. The reaction with substrates containing heterocyclic moiety also proceeded well. It is thus expected that the reaction may find applications in the synthesis of related compounds.

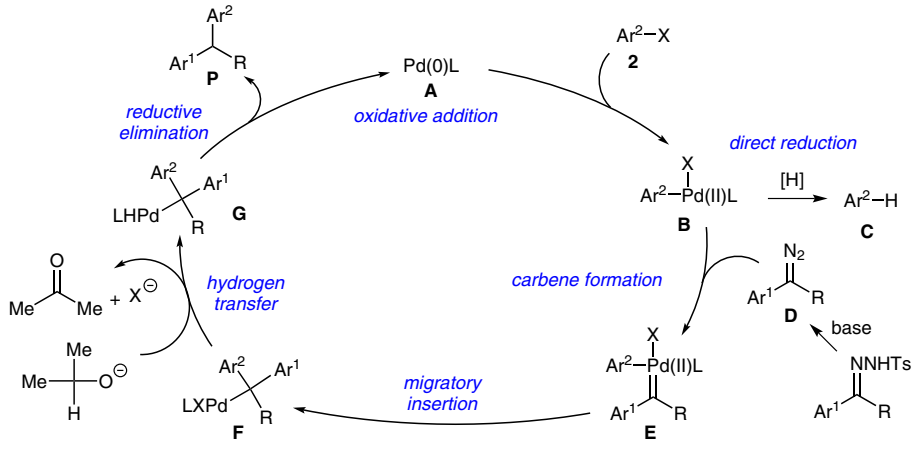
All the palladium-catalyzed reactions were performed under argon atmosphere in a flame-dried reaction flask. All solvents were distilled under N_2 atmosphere prior to use. 1,4-Dioxane and toluene were dried over Na with benzophenone-ketyl intermediate as indicator, and *tert*-pentyl alcohol, DCE, MeCN were dried over CaH_2. *i*-PrOH was dried over anhyd Na_2SO_4. HCO_2NH_4 and $MeCO_2NH_4$ were used after drying under vacuum at r.t. for 24 h. For chromatography, 200–300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm using TMS as an internal standard. IR spectra were recorded with a Nicolet 5MX-S IR spectrometer. LRMS were recorde on an Agilent 5975C inert 350 EI mass spectrometer. HRMS data were recorded on a Bruker Apex IV FTMS by ESI or GCT CA127 Micronass UK by EI.

Aromatic Aldehyde *N*-Tosylhydrazones 1a–f; Benzaldehyde *N*-Tosylhydrazone 1a; Typical Procedure 1

To a solution of benzaldehyde (3.18 g, 30 mmol) in MeOH (25 mL) was added $TsNHNH_2$ (5.58 g, 30 mmol). The resulting mixture was heated to 60 °C and stirred for 5 h. After completion of the reaction, the mixture was cooled to r.t., the precipitate was collected by filtration, and washed with PE. The precipitate was dried in a desiccator under vacuum to afford the pure product **1a** (6.98 g, 85%). The yields for other tosylhydrazones **1b–f** were about 73–88%. The reactions were usually carried out overnight and were monitored by TLC.

Diarylmethanone *N*-Tosylhydrazones 5a–k; Benzophenone *N*-Tosylhydrazone 5a; Typical Procedure 2

To a solution of benzophenone (7.28 g, 40 mmol) in EtOH (30 mL) were added $TsNHNH_2$ (7.44 g, 40 mmol) and $TsOH{\cdot}H_2O$ (76 mg, 0.4 mmol, 1 mol%). The resulting mixture was refluxed for 5 h. After completion of the reaction, the mixture was cooled to r.t., the precipitate was collected by filtration, and washed with PE. The precipitate was dried in a desiccator under vacuum to afford the pure product **5a** (13.12 g, 94%). The yields for other tosylhydrazones **5b–k** were about 75–95%. The reactions were usually carried out overnight and were monitored by TLC.



Scheme 8 Proposed reaction mechanism

Palladium-Catalyzed Reductive Coupling Reaction for the Synthesis of Diarylmethanes; 4-Benzyl-1,1′-biphenyl (3a); Typical Procedure 3

Under an argon atmosphere, $Pd(OAc)_2$ (3.3 mg, 0.015 mmol, 5 mol%), $PCy_3{\cdot}HBF_4$ (22.1 mg, 0.06 mmol, 20 mol%), benzaldehyde *N*-tosylhydrazone **1a** (99 mg, 0.36 mmol), 4-bromo-1,1′-biphenyl (**2a**; 70 mg, 0.3 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) were successively added to a flame-dried 25 mL Schlenk flask. The reaction flask was degassed three times with argon. Then anhyd toluene (2.7 mL) and *i*-PrOH (0.3 mL) were added with a syringe. Note that the aryl bromide in oil form was added to the reaction flask prior to *i*-PrOH. The reaction was heated at 80 °C with stirring for about 12 h, then it was cooled to r.t., and filtered through a short pad of neutral alumina with EtOAc (25 mL) as eluent. Solvent was then removed in vacuo to leave a crude mixture, which was purified by silica gel column chromatography (eluent: PE) to give **3a**[3d] as a white solid (59 mg, 80%); mp 84–85 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.55 (m, 2 H), 7.52–7.49 (m, 2 H), 7.43–7.38 (m, 2 H), 7.33–7.19 (m, 8 H), 4.00 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.9, 140.2, 139.0, 129.2, 128.9, 128.6, 128.4, 127.1, 127.0, 126.9, 126.1, 41.5.

Benzyl-4-(*tert*-butyl)benzene (3b)[6c]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (47 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.25 (m, 4 H), 7.21–7.18 (m, 3 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 3.94 (s, 2 H), 1.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 141.2, 138.0, 128.9, 128.5, 128.4, 125.9, 125.3, 41.4, 34.3, 31.3.

Diphenylmethane (3c)[3d]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (33 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.28 (m, 4 H), 7.19–7.16 (m, 6 H), 3.96 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 128.9, 128.4, 126.0, 41.9.

1-Benzyl-4-methylbenzene (3d)[3d]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (34 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.24 (m, 2 H), 7.19–7.15 (m, 3 H), 7.11–7.05 (m, 4 H), 3.92 (s, 2 H), 2.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 138.0, 135.5, 129.1, 128.8, 128.7, 128.4, 125.9, 41.4, 20.9.

1-Benzyl-4-methoxybenzene (3e)[3d]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 100:1), the product was isolated as a colorless oil (44 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.17 (m, 2 H), 7.12–7.07 (m, 3 H), 7.02 (d, *J* = 8.4 Hz, 2 H), 6.74 (d, *J* = 8.4 Hz, 2 H), 3.82 (s, 2 H), 3.68 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 141.5, 133.2, 129.8, 128.7, 128.3, 125.9, 113.8, 55.2, 40.9.

1-Benzyl-4-(trifluoromethyl)benzene (3f)[3d]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (47 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.0 Hz, 2 H), 7.32–7.27 (m, 4 H), 7.24–7.15 (m, 3 H), 4.02 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1, 139.9, 129.1, 128.9, 128.6, 128.4 (q, *J* = 32.1 Hz), 126.4, 125.3 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 271.6 Hz), 41.6.

1-Benzyl-4-fluorobenzene (3g)[3d]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (41 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.26 (m, 2 H), 7.22–7.10 (m, 5 H), 6.97–6.93 (m, 2 H), 3.94 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4 (d, *J* = 242.6 Hz), 140.9, 136.7 (d, *J* = 3.0 Hz), 130.2 (d, *J* = 7.8 Hz), 128.8, 128.5, 126.1, 115.1 (d, *J* = 21.1 Hz), 41.0.

Methyl 4-Benzylbenzoate (3h)[6f]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 50:1), the product was isolated as a yellow oil (41 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.2 Hz, 2 H), 7.31–7.20 (m, 5 H), 7.16 (d, *J* = 7.6 Hz, 2 H), 4.01 (s, 2 H), 3.88 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 146.4, 140.0, 129.7, 128.9, 128.5, 128.0, 126.3, 51.9, 41.8.

1-(4-Benzylphenyl)ethanone (3i)[6d]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 30:1), the product was isolated as a colorless oil (44 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.4 Hz, 2 H), 7.31–7.16 (m, 7 H), 4.02 (s, 2 H), 2.56 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 146.7, 139.9, 135.2, 129.0, 128.8, 128.5, 126.3, 41.8, 26.5.

(4-Benzylphenyl)trimethylsilane (3j)[6c]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (47 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.6 Hz, 2 H), 7.30–7.25 (m, 2 H), 7.21–7.16 (m, 5 H), 3.96 (s, 2 H), 0.24 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.7, 140.9, 137.7, 133.5, 128.9, 128.4, 128.3, 126.0, 41.9, -1.0.

1-Benzyl-3-methoxybenzene (3k)[6b]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 100:1), the product was isolated as a colorless oil (47 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.25 (m, 2 H), 7.23–7.17 (m, 4 H), 6.78 (d, *J* = 7.2 Hz, 1 H), 6.75–6.72 (m, 2 H), 3.94 (s, 2 H), 3.75 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 142.6, 140.8, 129.3, 128.8, 128.4, 126.0, 121.3, 114.7, 111.2, 55.0, 41.9.

1-Benzyl-2-methoxybenzene (3l)[5c]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 100:1), the product was isolated as a colorless oil (44 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.16 (m, 6 H), 7.06 (d, *J* = 6.8 Hz, 1 H), 6.89–6.84 (m, 2 H), 3.97 (s, 2 H), 3.80 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 141.0, 130.2, 129.6, 128.9, 128.2, 127.3, 125.7, 120.4, 110.3, 55.3, 35.8.

4-Benzyl-1,2-dimethylbenzene (3m)[3c]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (35 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.24 (m, 2 H), 7.21–7.17 (m, 3 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 6.95 (s, 1 H), 6.91 (d, *J* = 7.6 Hz, 1 H), 3.90 (s, 2 H), 2.21 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 138.5, 136.5, 134.1, 130.2, 129.6, 128.8, 128.3, 126.2, 125.9, 41.5, 19.7, 19.2.

5-Benzyl-2-methoxy-1,3-dimethylbenzene (3n)[14]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 100:1), the product was isolated as a colorless oil (42 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.17 (m, 2 H), 7.12–7.09 (m, 3 H), 6.74 (s, 2 H), 3.77 (s, 2 H), 3.60 (s, 3 H), 2.15 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 141.4, 136.3, 130.6, 129.1, 128.8, 128.3, 125.9, 59.6, 41.3, 16.0.

2-Benzylnaphthalene (3o)[6b]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (38 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.72 (m, 3 H), 7.61 (s, 1 H), 7.44–7.40 (m, 2 H), 7.31–7.19 (m, 6 H), 4.12 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.9, 138.5, 133.5, 132.0, 129.0, 128.4, 128.0, 127.7, 127.6, 127.5, 127.0, 126.1, 125.9, 125.3, 42.0.

1-Benzylnaphthalene (3p)[6e]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (33 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.96 (m, 1 H), 7.86–7.83 (m, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.46–7.38 (m, 3 H), 7.29–7.23 (m, 3 H), 7.21–7.17 (m, 3 H), 4.43 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 136.6, 133.9, 132.1, 128.7, 128.6, 128.4, 127.3, 127.1, 126.0, 125.9, 125.5, 124.2, 39.0.

3-Benzylpyridine (3q)[15]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 5:1), the product was isolated as a colorless oil (38 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51–8.44 (m, 2 H), 7.45 (d, *J* = 7.6 Hz, 1 H), 7.35–7.27 (m, 2 H), 7.24–7.16 (m, 4 H), 3.97 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 147.5, 139.7, 136.4, 136.2, 128.7, 128.6, 126.4, 123.3, 38.9.

3-Benzylquinoline (3r)[16]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 10:1), the product was isolated as a colorless oil (53 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 2.0 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.87 (d, *J* = 0.8 Hz, 1 H), 7.71 (d, *J* = 8.4 Hz, 1 H), 7.67–7.62 (m, 1 H), 7.52–7.47 (m, 1 H), 7.33–7.28 (m, 2 H), 7.25–7.20 (m, 3 H), 4.14 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 146.8, 139.6, 134.7, 133.7, 129.1, 128.8, 128.7, 128.6, 128.0, 127.3, 126.5, 126.4, 39.1.

***tert*-Butyl 5-Benzyl-1*H*-indole-1-carboxylate (3s)**

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 60:1), the product was isolated as a colorless oil (50 mg, 54%).

IR (film): 1731, 1470, 1371, 1346, 1161, 1128, 1023, 726, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.0 Hz, 1 H), 7.55 (d, *J* = 3.2 Hz, 1 H), 7.35–7.13 (m, 7 H), 6.48 (d, *J* = 3.6 Hz, 1 H), 4.05 (s, 2 H), 1.64 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7, 141.6, 135.4, 133.7, 130.8, 128.8, 128.3, 126.0, 125.9, 125.4, 120.9, 115.0, 107.1, 83.4, 41.7, 28.1.

LRMS (EI): *m*/*z* = 207 [(M – 100)$^+$, 100], 191 (10), 178 (22), 165 (8), 130 (50).

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{22}NO_2$ [M + H]$^+$: 308.1645; found: 308.1638.

5-Benzylbenzo[*b*]thiophene (3t)[16]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (35 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.4 Hz, 1 H), 7.61 (d, *J* = 0.4 Hz, 1 H), 7.39 (d, *J* = 5.6 Hz, 1 H), 7.30–7.16 (m, 7 H), 4.09 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 139.9, 137.5, 137.2, 128.9, 128.4, 126.5, 126.0, 125.7, 123.6, 123.5, 122.3, 41.8.

Di([1,1′-Biphenyl]-4-yl)methane (4a)[17]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (63 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.51 (m, 8 H), 7.43–7.39 (m, 4 H), 7.33–7.27 (m, 6 H), 4.05 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.9, 140.1, 139.1, 129.3, 128.7, 127.2, 127.0, 126.9, 41.2.

4-[4-(*tert*-Butyl)benzyl]-1,1′-biphenyl (4b)

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a white solid (58 mg, 64%); mp 46–47 °C.

IR (film): 1513, 1487, 1363, 1267, 1109, 1008, 760, 697 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.54 (m, 2 H), 7.50 (d, *J* = 8.0 Hz, 2 H), 7.43–7.38 (m, 2 H), 7.33–7.25 (m, 5 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 3.98 (s, 2 H), 1.30 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 141.0, 140.4, 138.9, 137.9, 129.3, 128.6, 128.5, 127.1, 127.0, 126.9, 125.3, 41.0, 34.3, 31.3.

LRMS (EI): *m*/*z* = 300 (M$^+$, 55), 285 (100), 243 (8), 207 (5), 167 (42).

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{24}Na$ [M + Na]$^+$: 323.1770; found: 323.1776.

4-(4-Fluorobenzyl)-1,1′-biphenyl (4c)

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a white solid (41 mg, 52%): mp 83–84 °C.

IR (film): 1507, 1488, 1218, 1157, 747, 687 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.54 (m, 2 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.43–7.39 (m, 2 H), 7.34–7.29 (m, 1 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.18–7.14 (m, 2 H), 7.00–6.95 (m, 2 H), 3.97 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4 (d, *J* = 242.6 Hz), 140.8, 140.0, 139.1, 136.6 (d, *J* = 3.3 Hz), 130.3 (d, *J* = 7.8 Hz), 129.2, 128.7, 127.2, 127.1, 126.9, 115.2 (d, *J* = 21.1 Hz), 40.7.

LRMS (EI): *m*/*z* = 262 (M$^+$, 100), 247 (10), 233 (6), 207 (7), 183 (15), 165 (27).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{15}O$ [M]$^+$: 262.1152; found: 262.1158.

1-(*tert*-Butyl)-4-(4-methoxybenzyl)benzene (4d)

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 100:1), the product was isolated as a colorless oil (31 mg, 41%).

IR (film): 1510, 1246, 1176, 1037, 815, 653 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.4 Hz, 2 H), 7.11 (d, *J* = 8.8 Hz, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 3.88 (s, 2 H), 3.77 (s, 3 H), 1.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 148.7, 138.5, 133.4, 129.8, 128.3, 125.2, 113.8, 55.2, 40.4, 34.3, 31.3.

LRMS (EI): *m*/*z* = 254 (M$^+$, 52), 239 (100), 197 (20), 165 (10).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{15}O$ [M]$^+$: 254.1665; found: 254.1674.

4-(4-Methoxybenzyl)-1,1′-biphenyl (4e)[5b]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 100:1), the product was isolated as a colorless oil (40 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.54 (m, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 7.43–7.38 (m, 2 H), 7.33–7.28 (m, 1 H), 7.25–7.21 (m, 2 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 6.85–6.82 (m, 2 H), 3.95 (s, 2 H), 3.77 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 141.0, 140.6, 138.9, 133.1, 129.8, 129.1, 128.6, 127.1, 127.0, 126.9, 113.9, 55.2, 40.6.

5-[4-(*tert*-Butyl)benzyl]benzo[*d*][1,3]dioxole (4f)

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 60:1), the product was isolated as a colorless oil (40 mg, 50%).

IR (film): 1502, 1442, 1244, 1040, 941, 797 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 6.72 (d, *J* = 8.4 Hz, 1 H), 6.68–6.66 (m, 2 H), 5.89 (s, 2 H), 3.85 (s, 2 H), 1.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 147.6, 145.7, 138.1, 135.1, 128.3, 125.3, 121.6, 109.4, 108.1, 100.7, 41.0, 34.3, 31.3.

LRMS (EI): *m*/*z* = 268 (M$^+$, 58), 253 (100), 225 (6), 211 (15), 135 (29).

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{20}O_2Na$ [M + Na]$^+$: 291.1355; found: 291.1359.

5-(4-Methoxybenzyl)benzo[*d*][1,3]dioxole (4g)

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 60:1), the product was isolated as a colorless oil (31 mg, 43%).

IR (film): 1511, 1488, 1245, 1038, 815, 667 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 8.4 Hz, 2 H), 6.84–6.81 (m, 2 H), 6.72 (d, *J* = 8.4 Hz, 1 H), 6.65–6.62 (m, 2 H), 5.89 (s, 2 H), 3.82 (s, 2 H), 3.77 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 147.6, 145.7, 135.4, 133.3, 129.6, 121.5, 113.8, 109.2, 108.0, 100.7, 55.2, 40.6.

LRMS (EI): *m*/*z* = 242 (M$^+$, 100), 227 (7), 211 (47), 197 (20), 181 (22).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{15}O$ [M]$^+$: 242.0937; found: 242.0938.

Methyl 4-([1,1′-Biphenyl]-4-ylmethyl)benzoate (4h)

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 100:1), the product was isolated as a white solid (35 mg, 38%); mp 98–99 °C.

IR (film): 1714, 1435, 1278, 1109, 757, 694 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.4 Hz, 2 H), 7.58–7.55 (m, 2 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 7.44–7.39 (m, 2 H), 7.34–7.22 (m, 5 H), 4.05 (s, 2 H), 3.89 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 146.3, 140.8, 139.3, 139.1, 129.8, 129.3, 128.9, 128.7, 128.1, 127.3, 127.1, 126.9, 51.9, 41.5.

LRMS (EI): *m*/*z* = 302 (M^+, 100), 271 (24), 243 (47), 228 (10), 207 (13), 165 (40).

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{19}O_2$ $[M + H]^+$: 303.1379; found: 303.1377.

Methyl 4-[4-(*tert*-Butyl)benzyl]benzoate (4i)

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE–EtOAc, 100:1), the product was isolated as a colorless oil (36 mg, 43%).

IR (film): 1722, 1609, 1434, 1277 1110, 1020, 758 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.2 Hz, 2 H), 7.31 (d, *J* = 7.2 Hz, 2 H), 7.26 (d, *J* = 7.6 Hz, 2 H), 7.09 (d, *J* = 7.6 Hz, 2 H), 3.99 (s, 2 H), 3.89 (s, 3 H), 1.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 149.1, 146.6, 137.0, 129.7, 128.9, 128.5, 128.0, 125.4, 51.9, 41.4, 34.3, 31.3.

LRMS (EI): *m*/*z* = 282 (M^+, 22), 267 (100), 251 (8), 207 (11), 165 (12).

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{13}O_2$ $[M + H]^+$: 283.1693; found: 283.1695.

1-(*tert*-Butyl)-4-(4-methylbenzyl)benzene (4j)[3a]

The title compound was prepared following typical procedure 3. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (38 mg, 53%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.27 (m, 2 H), 7.14–7.08 (m, 6 H), 3.90 (s, 2 H), 2.30 (s, 3 H), 1.28 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7, 138.3, 138.2, 135.4, 129.1, 128.8, 128.4, 125.3, 40.9, 34.3, 31.3, 20.9.

4-Benzyl-1,1′-biphenyl (3a); Gram-Scale Procedure

Under an argon atmosphere, $Pd(OAc)_2$ (0.056 g, 0.25 mmol, 5 mol%), $PCy_3{\cdot}HBF_4$ (0.375 g, 1.0 mmol, 20 mol%), benzaldehyde *N*-tosylhydrazone **1a** (1.65 g, 6 mmol), and Cs_2CO_3 (3.28 g, 10.0 mmol) were successively added to a flame-dried 250 mL Schlenk flask. The reaction flask was degassed three times with argon and anhyd toluene (50.0 mL) was added using a syringe. Then 4-bromo-1,1′-biphenyl (**2a**; 1.17 g, 5.0 mmol) and *i*-PrOH (5.0 mL) were added with a syringe. Note that the aryl bromide in a solid form was added to the reaction flask prior to Cs_2CO_3. The reaction mixture heated at 80 °C with stirring for about 12 h, then cooled to r.t., and filtered through a short pad of neutral alumina with EtOAc (200 mL) as eluent. Solvent was then removed in vacuo to leave a crude mixture. After purification by silica gel column chromatography (eluent: PE), 4-benzyl-1,1′-biphenyl (**3a**) was isolated as a white solid (0.768 g, 63%).

Palladium-Catalyzed Reductive Coupling Reaction for the Synthesis of Triarylmethanes; {[4-(*tert*-Butyl)phenyl]methylene}dibenzene (6a);[7c] Typical Procedure 4

Under an argon atmosphere, $Pd(OAc)_2$ (3.3 mg, 0.015 mmol, 5 mol%), ligand [1,1′-biphenyl]-2-yldiphenylphosphane (15 mg, 0.045 mmol, 15 mol%), HCO_2NH_4 (23 mg, 0.36 mmol), $MeCO_2NH_4$ (35 mg, 0.45 mmol), benzopheneone *N*-tosylhydrazone **5a** (126 mg, 0.36 mmol), and Cs_2CO_3 (195 mg, 0.6 mmol) were successively added to a flame-dried 25 mL Schlenk flask. The reaction flask was degassed three times with argon and anhyd *tert*-pentyl alcohol (3.0 mL) was added using a syringe. Then 1-bromo-4-(*tert*-butyl)benzene (**2b**; 64 mg, 0.3 mmol) was added with a syringe. Note that the aryl bromide in a solid form was added to the reaction flask prior to Cs_2CO_3. The reaction was heated at 90 °C with stirring for about 4 h, then it was cooled to r.t., and filtered through a short pad of neutral alumina with EtOAc (25 mL) as eluent. Solvent was then removed in vacuo to leave a crude mixture, which was purified by silica gel column chromatography (eluent: PE); yellow solid (82 mg, 91%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.25 (m, 6 H), 7.22–7.18 (m, 2 H), 7.12 (d, *J* = 7.6 Hz, 4 H), 7.03 (d, *J* = 8.2 Hz, 2 H), 5.51 (s, 1 H), 1.30 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 144.1, 140.7, 129.4, 128.9, 128.2, 126.1, 125.1, 56.3, 34.3, 31.3.

Triphenylmethane (6b)[18]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a white solid (59 mg, 81%); mp 93–94 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.26 (m, 6 H), 7.22–7.18 (m, 3 H), 7.12–7.10 (m, 6 H), 5.55 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 129.4, 128.2, 126.2, 56.7.

(*p*-Tolylmethylene)dibenzene (6c)[7f]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a white solid (58 mg, 75%); mp 67–68 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.16 (m, 6 H), 7.12–7.07 (m, 6 H), 7.01–6.99 (m, 2 H), 5.51 (s, 1 H), 2.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 140.8, 135.7, 129.3, 129.2, 128.9, 128.2, 126.1, 56.4, 20.9.

4-Benzhydryl-1,1′-biphenyl (6d)[7f]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a yellow solid (77 mg, 80%); mp 111–112 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.55 (m, 2 H), 7.50 (d, *J* = 8.2 Hz, 2 H), 7.42–7.38 (m, 2 H), 7.32–7.14 (m, 13 H), 5.58 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 142.9, 140.7, 139.1, 129.8, 129.4, 128.7, 128.3, 127.1, 126.9, 126.3, 56.4.

[(4-Methoxyphenyl)methylene]dibenzene (6e)[7f]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a yellow solid (66 mg, 80%); mp 64–65 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.28 (m, 3 H), 7.21 (t, *J* = 7.2 Hz, 3 H), 7.11 (d, *J* = 7.2 Hz, 4 H), 7.02 (d, *J* = 8.6 Hz, 2 H), 6.82 (d, *J* = 8.6 Hz, 2 H), 5.50 (s, 1 H), 3.77 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 144.2, 136.0, 130.3, 129.3, 128.2, 126.1, 113.6, 55.9, 55.1.

***N*-(4-Benzhydrylphenyl)acetamide (6f)**

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–EtOAc, 10:1), the product was isolated as a white solid (70 mg, 78%); mp 163–165 °C.

IR (film): 1664, 1537, 1512, 732, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.39 (m, 3 H), 7.29–7.18 (m, 6 H), 7.10–7.04 (m, 6 H), 5.50 (s, 1 H), 2.13 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 143.7, 139.8, 136.0, 129.8, 129.3, 128.2, 126.2, 119.8, 56.2, 24.4.

LRMS (EI): *m*/*z* = 301 (M^+, 100), 259 (40), 224 (15), 182 (64), 165 (30).

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{20}NO$ [M + H]$^+$: 302.1539; found: 302.1549.

{[4-(Trifluoromethyl)phenyl]methylene}dibenzene (6g)[7f]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (67 mg, 72%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.6 Hz, 2 H), 7.32–7.22 (m, 8 H), 7.10–7.08 (m, 4 H), 5.59 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.9, 142.9, 129.7, 129.3, 128.6 (q, *J* = 31.6 Hz), 128.5, 126.6, 125.2 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 271.9 Hz), 56.5.

[(4-Fluorophenyl)methylene]dibenzene (6h)[20]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (52 mg, 66%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.26 (m, 4 H), 7.23–7.19 (m, 2 H), 7.10–7.04 (m, 6 H), 6.98–6.94 (m, 2 H), 5.52 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.38 (d, *J* = 244.9 Hz), 143.68, 139.60 (d, *J* = 3.0 Hz), 130.82 (d, *J* = 7.9 Hz), 129.32, 128.37, 126.42, 115.05 (d, *J* = 21.2 Hz), 56.00.

Methyl 4-Benzhydrylbenzoate (6i)[21]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–EtOAc, 60:1), the product was isolated as a yellow solid (83 mg, 92%); mp 76–77 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.28 Hz, 2 H), 7.34–7.27 (m, 4 H), 7.24–7.18 (m, 4 H), 7.10–7.08 (m, 4 H), 5.59 (s, 1 H), 3.88 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 149.2, 143.0, 129.5, 129.4, 129.3, 128.4, 128.2, 126.5, 56.7, 51.9.

4-Benzhydrylbenzaldehyde (6j)[7f]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–EtOAc, 60:1), the product was isolated as a yellow oil (68 mg, 83%).

^1H NMR (400 MHz, $CDCl_3$): δ = 9.98 (s, 1 H), 7.80 (d, *J* = 8.02 Hz, 2 H), 7.34–7.22 (m, 8 H), 7.10 (d, *J* = 7.15 Hz, 4 H), 5.62 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 151.0, 142.7, 134.7, 130.0, 129.7, 129.3, 128.5, 126.7, 56.9.

[(3-Chlorophenyl)methylene]dibenzene (6k)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (63 mg, 76%).

IR (film): 1593, 1474, 780, 763, 741, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28 (t, *J* = 7.24 Hz, 4 H), 7.23–7.18 (m, 4 H), 7.10–7.08 (m, 5 H), 6.99 (m, 1 H), 5.51 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.9, 143.0, 134.2, 129.5, 129.4, 129.3, 128.4, 127.6, 126.5, 56.4.

LRMS (EI): *m*/*z* = 278 (M^+, 61), 243 (71), 201 (15), 165 (100), 152 (9).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{15}Cl$ [M]$^+$: 278.0862; found: 278.0867.

1-(3-Benzhydrylphenyl)ethanone (6l)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–EtOAc, 60:1), the product was isolated as a yellow oil (82 mg, 95%).

IR (film): 2924, 1686, 1261, 798, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 7.60 Hz, 1 H), 7.76 (s, 1 H), 7.40–7.36 (m, 1 H), 7.32–7.20 (m, 7 H), 7.10 (d, *J* = 7.23 Hz, 4 H), 5.61 (s, 1 H), 2.53 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 144.5, 143.1, 137.2, 134.0, 129.3, 129.1, 128.5, 128.4, 126.5, 126.4, 56.6, 26.6.

LRMS (EI): *m*/*z* = 286 (M^+, 100), 271 (32), 243 (76), 165 (75), 152 (12).

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{19}O$ [M + H]$^+$: 287.1430; found: 287.1438.

[(3,5-Dimethylphenyl)methylene]dibenzene (6m)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a white solid (68 mg, 84%); mp 67–69 °C.

IR (film): 1598, 1494, 743, 714, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.17 (m, 6 H), 7.12–7.10 (m, 4 H), 6.84 (s, 1 H), 6.73 (s, 2 H), 5.47 (s, 1 H), 2.23 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 143.7, 137.6, 129.4, 128.2, 127.9, 127.2, 126.1, 56.7, 21.3.

LRMS (EI): *m*/*z* = 272 (M^+, 97), 257 (100), 195 (28), 179 (36), 165 (54).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{20}$ [M]$^+$: 272.1565; found: 272.1569.

[(2-Methoxyphenyl)methylene]dibenzene (6n)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–EtOAc, 100:1), the product was isolated as a white solid (48 mg, 58%); mp 110–111 °C.

IR (film): 1489, 1244, 752, 725, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.16 (m, 7 H), 7.09 (d, *J* = 7.23 Hz, 4 H), 6.87–6.85 (m, 3 H), 5.93 (s, 1 H), 3.70 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 143.8, 132.5, 130.3, 129.4, 128.0, 127.4, 125.9, 120.2, 110.6, 55.5, 49.5.

LRMS (EI): *m*/*z* = 274 (M^+, 100), 259 (44), 243 (28), 165 (58), 91 (49).

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{18}ONa$ [M + Na]$^+$: 297.1250; found: 297.1254.

2-Benzhydrylnaphthalene (6o)[7c]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a pale yellow solid (65 mg, 74%); mp 77–78 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.68 (m, 3 H), 7.47–7.40 (m, 3 H), 7.32–7.27 (m, 5 H), 7.23–7.14 (m, 6 H), 5.70 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 141.4, 133.3, 132.1, 129.5, 128.3, 128.0, 127.8, 127.7, 127.5, 126.3, 125.9, 125.6, 56.9.

9-Benzhydrylphenanthrene (6p)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–EtOAc–CH_2Cl_2, 200:4:1), the product was isolated as a pale yellow solid (78 mg, 76%); mp 168–171 °C.

IR (film): 1494, 1450, 907, 725, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 8.22 Hz, 1 H), 8.65 (d, *J* = 8.24 Hz, 1 H), 8.04 (d, *J* = 8.22 Hz, 1 H), 7.68–7.48 (m, 5 H), 7.31–7.16 (m, 11 H), 6.26 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 138.1, 131.3, 131.1, 130.7, 129.8, 129.7, 128.7, 128.6, 128.4, 126.6, 126.5, 126.4, 126.1, 125.1, 123.0, 122.3, 53.4.

LRMS (EI): *m*/*z* = 344 (M^+, 100), 265 (56), 239 (4), 165 (32), 133 (10).

HRMS (ESI): *m*/*z* calcd for $C_{27}H_{20}Na$ [M + Na]$^+$: 367.1457; found: 367.1467.

***tert*-Butyl 5-Benzhydryl-1*H*-indole-1-carboxylate (6q)**

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–CH_2Cl_2, 50:1), the product was isolated as a white solid (94 mg, 82%); mp 99–101 °C.

IR (film): 1733, 1372, 1162, 730, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.15 Hz, 1 H), 7.56 (d, *J* = 2.74 Hz, 1 H), 7.29–7.18 (m, 7 H), 7.14–7.10 (m, 5 H), 6.46 (d, *J* = 3.58 Hz, 1 H), 5.66 (s, 1 H), 1.64 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7, 144.2, 138.4, 133.6, 130.6, 129.4, 128.2, 126.2, 126.1, 126.0, 121.5, 114.8, 107.3, 83.5, 56.6, 28.1.

LRMS (EI): *m*/*z* = 283 ((M – 100)$^+$, 100), 206 (58), 205 (46), 167 (28), 152 (10).

HRMS (ESI): *m*/*z* calcd for $C_{26}H_{26}NO_2$ [M + H]$^+$: 384.1958; found: 384.1966.

5-Benzhydrylbenzo[*b*]thiophene (6r)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (63 mg, 70%).

IR (film): 1493, 907, 754, 736, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.36 Hz, 1 H), 7.50 (s, 1 H), 7.40 (d, *J* = 5.42 Hz, 1 H), 7.31–7.20 (m, 8 H), 7.15–7.14 (m, 4 H), 5.69 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9, 140.2, 139.7, 137.7, 129.4, 128.3, 126.5, 126.3, 126.2, 124.1, 123.9, 122.2, 56.6.

LRMS (EI): *m*/*z* = 300 (M^+, 100), 223 (50), 189 (9), 165 (24), 111 (7).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{16}S$ [M]$^+$: 300.0973; found: 300.0978.

3-Benzhydrylpyridine (6s)[22]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–EtOAc, 20:1), the product was isolated as a yellow solid (51 mg, 70%); mp 73–74 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.47–8.44 (m, 2 H), 7.39 (d, *J* = 7.88 Hz, 1 H), 7.32–7.28 (m, 4 H), 7.25–7.18 (m, 3 H), 7.10 (d, *J* = 7.29 Hz, 4 H), 5.55 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.81, 147.71, 142.63, 139.28, 136.61, 129.23, 128.50, 126.66, 123.17, 54.31.

3-Benzhydrylquinoline (6t)[23]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–EtOAc, 20:1), the product was isolated as a colorless oil (58 mg, 66%).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 2.11 Hz, 1 H), 8.09 (d, *J* = 8.36 Hz, 1 H), 7.71–6.64 (m, 3 H), 7.50–7.46 (m, 1 H), 7.33–7.23 (m, 6 H), 7.16–7.14 (m, 4 H), 5.74 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.53, 146.76, 142.45, 136.82, 135.23, 129.34, 129.06, 129.02, 128.56, 127.79, 127.66, 126.74, 126.63, 54.39.

4-{[4-(*tert*-Butyl)phenyl](phenyl)methyl}-1,2-dimethylbenzene (7a)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (79 mg, 81%).

IR (film): 1502, 1493, 811, 732, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.02 (m, 7 H), 7.03 (d, *J* = 7.92 Hz, 3 H), 6.92 (s, 1 H), 6.83 (d, *J* = 7.01 Hz, 1 H), 5.43 (s, 1 H), 2.20 (d, *J* = 11.20 Hz, 6 H), 1.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7, 144.4, 141.5, 141.0, 136.3, 134.3, 130.7, 129.4, 129.3, 128.9, 128.1, 126.7, 126.0, 125.0, 56.0, 34.3, 31.3, 19.8, 19.3.

LRMS (EI): *m*/*z* = 328 (M^+, 56), 313 (100), 271 (97), 193 (12), 165 (22).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{28}$ [M]$^+$: 328.2191; found: 328.2195.

1-(*tert*-Butyl)-4-[(4-methoxyphenyl)(phenyl)methyl]benzene (7b)[7c]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (71 mg, 72%).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.10 (m, 7 H), 7.03 (dd, *J* = 3.13, 8.59 Hz, 4 H), 6.82–6.80 (m, 2 H), 5.46 (s, 1 H), 3.76 (s, 3 H), 1.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 148.8, 144.4, 141.0, 136.3, 130.3, 129.3, 128.8, 128.1, 126.0, 125.1, 113.5, 55.5, 55.1, 34.3, 31.3.

4-{[(4-(*tert*-Butyl)phenyl](phenyl)methyl}-1,1′-biphenyl (7c)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (89 mg, 79%).

IR (film): 1487, 909, 824, 763, 733, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.33 Hz, 2 H), 7.49 (d, *J* = 8.16 Hz, 2 H), 7.39 (t, *J* = 7.45 Hz, 2 H), 7.31–7.26 (m, 5 H), 7.21–7.15 (m, 5 H), 7.07 (d, *J* = 8.26 Hz, 2 H), 5.54 (s, 1 H), 1.30 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0, 144.0, 143.2, 140.8, 140.6, 139.0, 129.8, 129.4, 128.9, 128.6, 128.2, 127.1, 127.0, 126.9, 126.2, 125.1, 56.1, 34.3, 31.3.

LRMS (EI): *m*/*z* = 376 (M^+, 67), 361 (51), 319 (100), 241 (22), 165 (22).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{28}$ [M]$^+$: 376.2191; found: 376.2198.

4,4′-{[4-(*tert*-Butyl)phenyl]methylene}bis(methylbenzene) (7d)[7c]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (78 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.23 Hz, 2 H), 7.08–7.00 (m, 10 H), 5.42 (s, 1 H), 2.30 (s, 6 H), 1.28 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7, 141.3, 141.1, 135.5, 129.2, 128.9, 128.8, 125.0, 55.6, 34.3, 31.3, 20.9.

1-(*tert*-Butyl)-4-[(4-chlorophenyl)(4-ethoxyphenyl)methyl]benzene (7e)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–CH_2Cl_2, 100:1), the product was isolated as a pale yellow oil (66 mg, 58%).

IR (film): 1509, 1489, 1246, 1015, 821 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.22 (m, 4 H), 7.05–6.98 (m, 6 H), 6.80 (d, *J* = 8.64 Hz, 2 H), 5.41 (s, 1 H), 3.99 (q, *J* = 6.99 Hz, 2 H), 1.39 (t, *J* = 6.98 Hz, 3 H), 1.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 149.1, 143.1, 140.5, 135.6, 131.8, 130.6, 130.2, 128.7, 128.3, 125.2, 114.2, 63.3, 54.9, 34.3, 31.3, 14.8.

LRMS (EI): *m*/*z* = 378 (M^+, 79), 363 (43), 321 (100), 267 (27), 181 (19).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{27}ClO$ $[M]^+$: 378.1750; found: 378.1756.

1-{[4-(*tert*-Butyl)phenyl](phenyl)methyl}-2-chlorobenzene (7f)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (48 mg, 48%).

IR (film): 1468, 1039, 909, 752, 736, 702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.35 (m, 1 H), 7.30–7.13 (m, 7 H), 7.08 (d, *J* = 7.25 Hz, 2 H), 7.00–6.96 (m, 3 H), 5.94 (s, 1 H), 1.30 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 142.7, 141.8, 139.3, 134.5, 131.1, 129.6, 129.4, 129.0, 128.2, 127.6, 126.5, 126.3, 125.1, 52.8, 34.3, 31.3.

LRMS (EI): *m*/*z* = 334 (M^+, 41), 319 (100), 277 (92), 165 (61), 128 (21).

HRMS (EI): *m*/*z* calcd for $C_{23}H_{23}Cl$ $[M]^+$: 334.1488; found: 334.1492.

1-{[4-(*tert*-Butyl)phenyl](3-methoxyphenyl)methyl}-3-methylbenzene (7g)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (76 mg, 74%).

IR (film): 1488, 1266, 759, 731, 710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.22 Hz, 2 H), 7.22–7.14 (m, 2 H), 7.04–6.90 (m, 5 H), 6.75–6.68 (m, 3 H), 5.43 (s, 1 H), 3.73 (s, 3 H), 2.28 (s, 3 H), 1.29 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.46, 148.89, 145.88, 143.85, 140.6, 137.7, 130.1, 129.0, 128.9, 128.0, 126.9, 126.4, 125.1, 121.9, 115.6, 111.0, 56.3, 55.0, 34.3, 31.3, 21.4.

LRMS (EI): *m*/*z* = 344 (M^+, 64), 329 (73), 287 (100), 179 (21), 165 (29).

HRMS (ESI): *m*/*z* calcd for $C_{25}H_{28}ONa$ $[M + Na]^+$: 367.2032; found: 367.2042.

1-[(3-Methoxyphenyl)(*m*-tolyl)methyl]-3,5-dimethylbenzene (7h)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (79 mg, 83%).

IR (film): 1598, 1487, 758, 728, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.14 (m, 2 H), 7.01 (d, *J* = 7.48 Hz, 1 H), 6.95 (s, 1 H), 6.90 (d, *J* = 7.62 Hz, 1 H), 6.84 (s, 1 H), 6.76–6.67 (m, 5 H), 5.39 (s, 1 H), 3.73 (s, 3 H), 2.28 (s, 3 H), 2.24 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 145.7, 143.7, 143.6, 137.7, 137.6, 130.1, 129.0, 128.0, 127.9, 127.2, 126.9, 126.4, 122.0, 115.6, 111.0, 56.7, 55.0, 21.4, 21.3.

LRMS (EI): *m*/*z* = 316 (M^+, 100), 301 (65), 209 (27), 193 (18), 179 (20).

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{25}O$ $[M + H]^+$: 317.1900; found: 317.1911.

3-[(3,4-Dimethylphenyl)(phenyl)methyl]pyridine (7i)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–EtOAc, 20:1), the product was isolated as a pale yellow oil (59 mg, 72%).

IR (film): 1494, 1026, 731, 715, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46–8.43 (m, 2 H), 7.40 (d, *J* = 7.86 Hz, 1 H), 7.31–7.18 (m, 4 H), 7.11–7.05 (m, 3 H), 6.89 (s, 1 H), 6.81 (d, *J* = 7.63 Hz, 1 H), 5.48 (s, 1 H), 2.23 (s, 3 H), 2.20 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.77, 147.5, 142.9, 140.0, 139.5, 136.7, 136.6, 134.9, 130.4, 129.7, 129.1, 128.4, 126.6, 126.5, 123.1, 53.9, 19.8, 19.3.

LRMS (EI): *m*/*z* = 273 (M^+, 83), 258 (100), 195 (24), 180 (26), 165 (17).

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}N$ $[M + H]^+$: 274.1590; found: 274.1584.

3-(Di-*p*-tolylmethyl)pyridine (7j)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE–EtOAc, 20:1), the product was isolated as a colorless oil (42 mg, 51%).

IR (film): 1511, 808, 756, 725, 714 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46–8.43 (m, 2 H), 7.40–7.38 (m, 1 H), 7.20–7.17 (m, 1 H), 7.10 (d, *J* = 7.91 Hz, 4 H), 6.98 (d, *J* = 8.00 Hz, 4 H), 5.47 (s, 1 H), 2.32 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.7, 147.5, 139.8, 139.6, 136.5, 136.1, 129.1, 129.0, 123.1, 53.5, 20.9;

LRMS (EI): *m*/*z* = 273 (M^+, 100), 258 (97), 195 (35), 180 (37), 167 (21).

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}N$ $[M + H]^+$: 274.1590; found: 274.1591.

3-{[4-(*tert*-Butyl)phenyl](phenyl)methyl}thiophene (7k)[7c]

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (39 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.20 (m, 6 H), 7.17–7.15 (m, 2 H), 7.07 (d, *J* = 8.20 Hz, 2 H), 6.88 (dd, *J* = 4.85, 0.69 Hz, 1 H), 6.74–6.73 (m, 1 H), 5.47 (s, 1 H), 1.30 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 145.1, 144.0, 140.6, 128.9, 128.7, 128.4, 128.2, 126.3, 125.3, 125.1, 122.6, 52.1, 34.3, 31.3.

3-{[4-(*tert*-Butyl)phenyl](phenyl)methyl}furan (7l)

The title compound was prepared following typical procedure 4. After purification by silica gel column chromatography (eluent: PE), the product was isolated as a colorless oil (26 mg, 30%).

IR (film): 1024, 874, 775, 729, 702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (s, 1 H), 7.31–7.20 (m, 8 H), 7.12 (d, *J* = 8.23 Hz, 2 H), 6.96 (s, 1 H), 6.24 (s, 1 H), 5.24 (s, 1 H), 1.30 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 143.7, 143.0, 140.9, 140.3, 128.7, 128.4, 128.3, 128.2, 126.3, 125.2, 111.3, 47.6, 34.3, 31.3.

LRMS (EI): *m*/*z* = 290 (M^+, 61), 275 (100), 233 (96), 157 (20), 128 (23).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{22}O$ $[M]^+$: 290.1671; found: 290.1675.

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Supporting Information

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