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Substituted Functional Olefins Through Lateral Sequential Lithiation/Silylation/Condensation of Tertiary Aromatic Amides: A Ligand for Phosphane-Free Palladium-Catalyzed Suzuki Coupling Reactions

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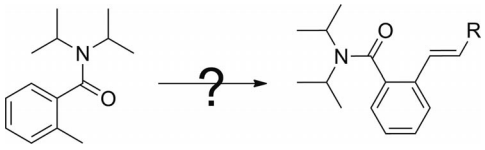
An unprecedented lateral sequential lithiation/silylation/condensation of tertiary aromatic amides has been developed that provides an efficient method to build up functional olefins in good yields. In addition, we have established an efficient and simple method that involves UV/Vis, fluorescence, and NMR analyses, to detect the interaction between transition-metal salts and functional olefins containing tertiary amides. This has enabled a highly efficient palladium-catalyzed Suzuki coupling reaction in the presence of tertiary aromatic amide-derived olefin ligands to be developed. The best results were obtained by employing 2 mol-% $Pd(OAc)_2$, 2 equiv. Cs_2CO_3, a reaction temperature of 80 °C, dioxane as the solvent, and phosphane-free olefin **2d** as ligand.

Introduction

Olefins are arguably the most important and basic building blocks in organic synthesis. In the realm of olefin chemistry, the significance of substituted olefins is reflected in the important and potential applications of olefin-containing compounds in organic synthesis, optical materials, medicinal chemistry, polymeric materials, molecular devices, and organic conductors.[1] Therefore, for large-scale applications, it is beneficial to develop more convenient synthetic routes to structurally divergent olefins. During the past century, significant achievements have been made in the synthesis of substituted olefins, nevertheless, highly efficient regio- and chemoselective methods to generate substituted olefins bearing different carbon-linked functional groups still presents a particular challenge in organic synthesis.[2]

In the last few decades, directed remote lithiation of tertiary aromatic amides have received considerable attention because of their use in the regioselective synthesis of nonbiaryl atropisomers and chiral aromatic amide derivatives.[3] Although several electrophiles, such as aldehydes and silanes, have been introduced to the tertiary aromatic amides, to the best of our knowledge, there are no reports on the construction of tertiary aromatic amide-derived olefins through one-pot lateral sequential lithiation/silylation/condensation (Scheme 1). Inspired by the lithiation method reported by Clayden et al.,[4] we investigated the one-pot sequential reactions of amide **1** with a range of carbonyl compounds. Herein, we describe the successful development of lateral sequential lithiation/silylation/condensation of tertiary aromatic amides through key and directed lithiation to generate functional olefins. Furthermore, it was found that functional olefins with tertiary aromatic amides could be used as sensitive fluorescent probes to detect interactions between transition metals and the olefin, which led us to the develop an effective and unreactive olefin ligand for use in palladium-catalyzed Suzuki coupling reactions.



Scheme 1. The construction of olefins directed by lithiation.

Results and Discussion

The Synthesis of Aromatic Amide-Derived Olefins (2) through One-Pot Lateral Sequential Lithiation/Silylation/Condensation

Initially, we focused on using *N*,*N*-diisopropyl-2-methylbenzamide (**1**) as a scaffold for the direct lithiation and subsequent transformation. We were particularly interested in the tertiary amide moiety of compound **1** because it is able

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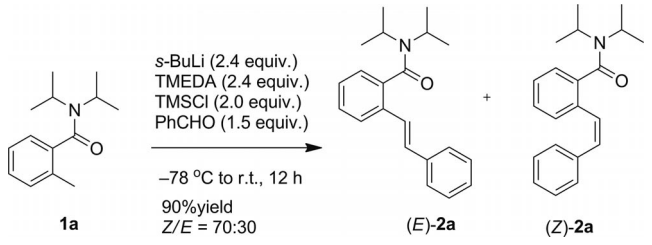
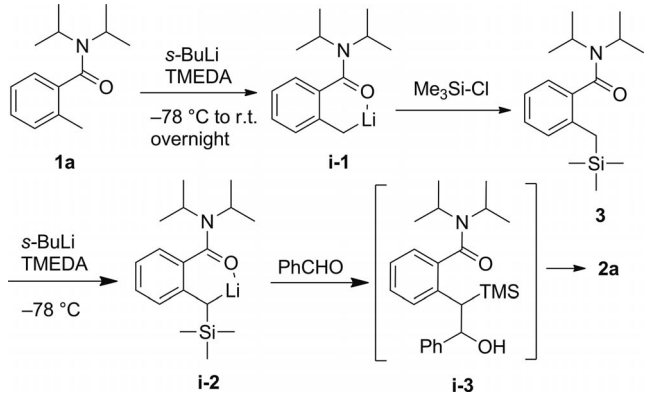
to direct a lithium to the CH_3 center of **1**, which would be beneficial to the lateral lithiation and subsequent silylation and condensation. In this procedure, treatment of **1** in tetrahydrofuran (THF) at –78 °C with three equivalents of *s*BuLi in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) for one hour, was followed by the sequential addition of trimethylsilyl chloride (TMSCl) and benzaldehyde. Initial experimental results demonstrated that, in the clean reaction of **1** with *s*BuLi in THF, as expected, the aromatic amide was double laterally lithiated and then sequentially silylated or alkylated, leading to the formation of functionalized olefin **2a** in good yield (90%; Scheme 2). The appending olefin was obtained as a mixture of *Z*/*E* isomers (70:30); the olefin geometry was determined by the ^{1}H NMR chemical shift and coupling constant as well as by infrared spectroscopic analysis.[5]



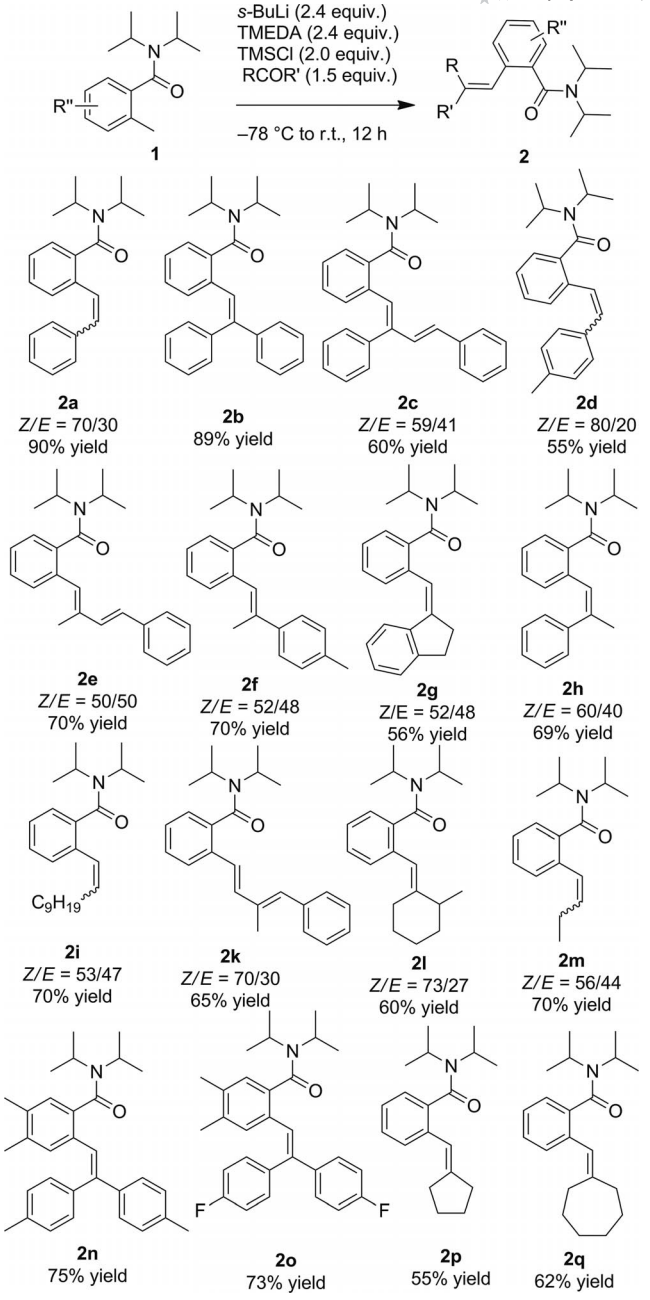
Scheme 2. Lateral sequential lithiation/silylation/condensation of amide **1a**.

It seems likely that this sequential lithiation/silylation/condensation actually occurs in five steps (Scheme 3). First, the lithiation was promoted by *s*-butyl lithium by deprotonation at low temperature to give ***i*-2**, which leads to the aromatic tertiary amide-derived silane through silylation, from which product **3** was successfully obtained. Lithiation of **3** resulted in a second deprotonation and then to nucleophilic addition to the aldehyde to generate intermediate ***i*-3**. In the last step of desilylation and hydroxy group formation, similar to Peterson olefination,[6] the olefin **2a** was formed in a (*Z*)-selective manner (*Z*/*E* = 65:35).



Scheme 3. A mechanistic pathway to olefins.

As shown in Scheme 4, various carbonyl compounds were used as electrophiles, including aldehydes and ketones, in this sequential reaction. As hoped, the lateral sequential



Scheme 4. Lateral sequential lithiation/silylation/condensation of amides **1**.

lithiation/silylation/condensation proceeded smoothly under the optimized conditions, and the conjugated olefins **2** from tertiary aromatic amides were obtained in moderate to good isolated yields. Aliphatic aldehydes and ketones also gave the corresponding olefins in moderate yields and regioselectivities. Interestingly, the use of chalcone and α,β-unsaturated aldehyde as the electrophiles also furnished the corresponding conjugated dienes **2c** and **2k** in good yields. Therefore, this procedure should be useful for the construction of carbon–carbon double bonds, which is particularly important for the development of optical organic molecules because π-conjugated molecules have emerged as promising materials for the application in flexible, low-cost, and light-

weight electronic devices.[7] Figure 1 shows the X-ray crystal structure of **2d**, which demonstrated the (*Z*)-isomer of alkene formed.

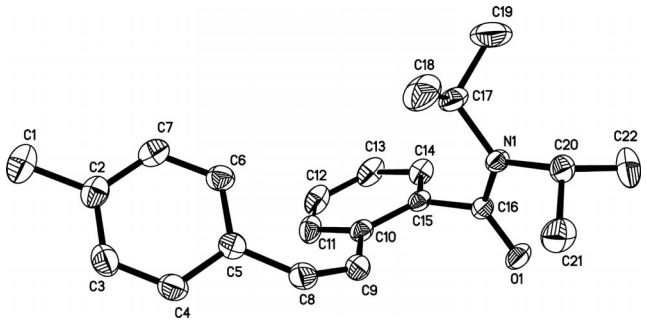


Figure 1. X-ray crystal structure of **2d** (CCDC-837440).

Despite the fact that the *E*/*Z* selectivity was generally low to moderate, this new simplified version of the one-pot Peterson olefination could successfully be applied to the synthesis of aromatic olefins with *ortho*-functional groups. Of particular potential are olefins of type **2**, bearing tertiary aromatic amides, in which two types of functional groups, olefin and amide, are viable for further functionalization and application. Therefore, except that the successful strategy in the preparation of functional olefins through amide-directed lateral lithiation/olefination has been developed, the exploring of the potential application of compound **2** in organic transformation is highly desired.

Investigation of the Interaction between Olefin 2 and Transition Metals by UV/Vis and Fluorescence Spectroscopy

It is well-known that olefins have well-defined donor (filled π) orbitals, thus, a characteristic of olefins is the ability to coordinate to transition metals to form organometallic complexes. This is of great importance in the field of transition-metal catalysis because the transition-metal–olefin complex could be employed as a catalyst precursor to activate substrates on the basis of ligand-exchange reactions.[8] Because olefins of type **2** are multifunctional, they are considered to be interesting and effective ligands that are capable of simultaneously being involved in two binding interactions in homogeneous transition-metal catalysis. In an attempt to establish a strong interaction between transition-metal salts and olefins **2**, we chose to investigate the interaction between olefin **2a** and several typical transitional-metal salts by UV/Vis and fluorescence spectroscopy.

The interaction between olefin **2a** and transition-metal salts in dichloromethame was first examined by using UV/Vis spectroscopy (Figure S2; see the Supporting Information). Comparison of the absorption spectra of **2a** with a mixture of **2a** and a range of transition metals revealed only small differences in the two strong absorption bands at 230 and 285–293 nm. Therefore, it was difficult to confirm the coordination of the metal with olefin **2a**.

Fluorescence spectroscopy has been shown to be a powerful and highly sensitive analytical tool for the study of intermolecular interaction, especially for assessing the interaction of metals with receptors.[9] As shown in Figure 2, the fluorescence properties of olefin **2a** and mixtures of **2a** with transition-metal salts in dichloromethane were studied. Interestingly, the observed effects of transition-metal salts on the positions of the fluorescence bands are clear, and there was an apparent increase of fluorescence intensity in the order: $Pd(OAc)_2 > Rh(OAc)_2 > IrCl_4Na > RhCl_3 > AuCl_3 > IrCl_4 > IrCl_3$. These data suggest that the coordination of these metal ions to olefin **2a** takes place in varying degrees. In addition, there is no evidence in fluorescence spectroscopy for the interaction between $RuCl_3$ and **2a**, in which the fluorescence intensity is observed in almost complete agreement with that of **2a** in the absence of any transition metal salt. Among the metal salts screened in this study, $Pd(OAc)_2$ was found to be the best choice, with promising interactions in the metal–olefin complex (line f in Figure 2). This behavior is probably the result of the strong coordination or interaction between palladium and olefin **2a**, which hinders the vibration and rotation of the bonds in the olefin and phenyl units. Thus, we have established a simple yet highly selective method to determine which metals interact with bifunctional aromatic amide-derived olefin **2a**; this should enable olefin **2a** and others to work as new and effective ligands in palladium catalysis.

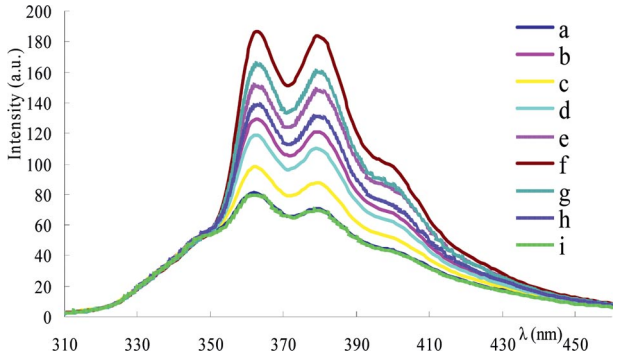


Figure 2. Changes in the fluorescence spectra upon excitation of **2a** and mixtures of **2a** with an equimolar amount of transition metals at 289 nm: (a) **2a** alone; (b) $AuCl_3$; (c) $IrCl_3$; (d) $IrCl_4$; (e) $IrCl_6Na$; (f) $Pd(OAc)_2$; (g) $Rh(OAc)_2$; (h) $RhCl_3$; (i) $RuCl_3$.

The Application of Olefin 2 as Ligand in the Palladium-Catalyzed Suzuki Coupling Reaction

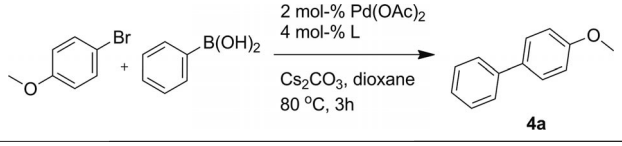
We then studied the application of functionalized olefins **2** in organic synthesis. In fact, much attention has focused upon the use of palladium–olefin complexes in organic synthesis.[10,11] However, to the best of our knowledge, except for $[Pd_2(dba)_3]$, there are few reports on the development of olefin–ligand systems in palladium-catalyzed organic transformations.[11] In this context, on the basis of above hypothesis and findings, we found that olefin **2a** and related compounds could work as unusual ligands in the palladium-catalyzed Suzuki coupling reaction. The Suzuki cross-coupling reaction is one of the most important methods for

the construction of new carbon–carbon bonds and for the formation of symmetric and nonsymmetric biaryls that are found in a myriad of application as privileged molecules or macromolecules, such as polymers, biologically active compounds, ligands, and many useful materials.[12] However, although recent developments have led to an expansion of the coupling reaction, and many efficient palladium catalyst systems have been developed over the last few decades, the principal drawbacks are often the time required, difficulties in operation, and the availability, stability in air, and cost of the palladium complexes and phopshine ligands. Furthermore, many palladium complexes suffer from low functional group tolerance, and/or air- or moisture-sensitivity. Herein, we report the olefin **2** promoted phosphane-free palladium-catalyzed Suzuki cross-coupling reaction that takes place with outstanding functional group tolerance under mild conditions without special inert atmosphere techniques.

Inspired by the procedure reported by Tao and Boykin,[13] the evaluation of olefins **2** as ligands was carried out under the reported conditions in which a mixture of 4-bromoanisole and phenylboronic acid was treated with 2 mol-% $Pd(OAc)_2$ and 2 equiv. Cs_2CO_3 in dioxane at 80 °C for 3 h (Table 1). Among the olefins investigated, monosubstituted olefins with terminal alkene moieties, such as **2a** and **2d**, showed promising activity, giving the corresponding biaryl product in good yields (Table 1; 75–77% yield). Alkyl-substituted **2i** displayed clear positive activity (54% yield; Table 1, entry 9), and conjugate dienes from α,β-unsaturated aldehydes or enones, such as **2c** and **2k**, were found to be effective in promoting the Suzuki coupling reaction, giving the coupling product in moderate yields (57–69% yield; Table 1, entries 3 and 10). However, the olefins derived from aromatic ketones (**2f**, **2g**, **2h**, **2n**, and **2o**) showed low to moderate activity (15–57% yield; Table 1, entries 6, 7, 8, 12, and 13), for example, only 15% yield was obtained in the presence of olefin **2n** (Table 1, entry 11). These results suggested that olefin **2a** or **2d** acted as the best ligand in this cross-coupling reaction, and these results are consistent with the fluorescence analysis. Although the *Z*- or *E*-olefin have not so far been isolated, it should be noted that the catalytic activity of the *Z*- and *E*-olefins are different, according to our preliminary results. For example, when the ratio of *Z*/*E* is 30:70, the yield of palladium-catalyzed Suzuki reaction is low (19% yield; Table 1, entry 18).

In the next evaluation, the activities of ligands **2a** and **2d** were determined in the Suzuki coupling reaction of various aromatic bromides. As depicted in Scheme 5, the palladium-catalyzed Suzuki coupling reaction promoted by olefin **2d** can be employed with both electron-deficient and electron-rich bromides. In most cases, the biphenyl products of the coupling reaction were obtained in excellent yields (up to 99%). For example, when electronically activated, nonactivated, or deactivated aromatic bromide substrates such as 4-bromobenzaldehyde, 1-bromo-4-fluorobenzene, and 1-bromo-2-methylbenzene, were coupled with phenylboroic acid, good to excellent yields were achieved in the presence of the olefin ligand **2d**. Impressively, whereas only moderate conversion rate and product yield was observed with 2-bromopyridine, excellent yields were found for aryl bromides containing a carbonyl group, such as 2-bromo-4-methoxybenzaldehyde, 2-bromobenzaldehyde, 2-bromo-4-

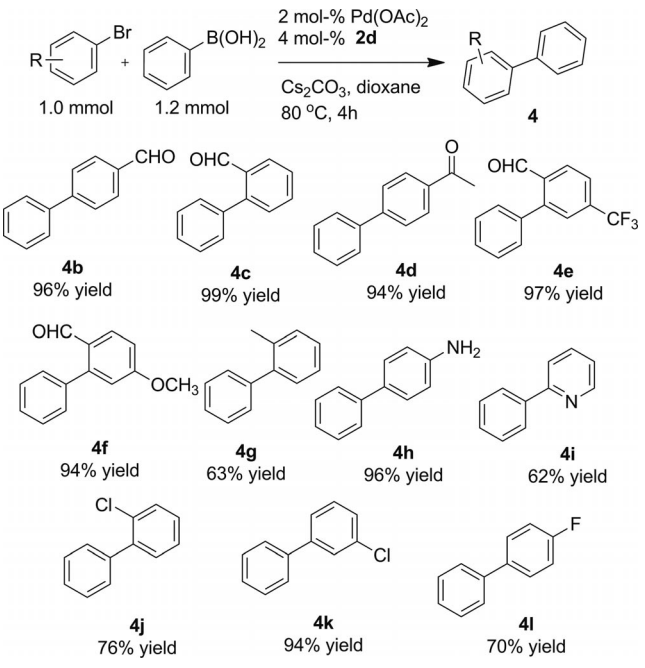
Table 1. Screening of olefin ligands **2** in the palladium-catalyzed Suzuki coupling reaction.[a]



4a

Entry	Ligand	Yield [%][b]
1	—[c]	15
2	**2a**	75
3	**2c**	57
4	**2d**	77
5	**2e**	48
6	**2f**	36
7	**2g**	57
8	**2h**	40
9	**2i**	54
10	**2k**	69
11	**2l**	74
12	**2n**	15
13	**2o**	25
14	**2p**	48
15	**2q**	61
16	**1a**	26
17	**2a**[d]	70
18	**2a**[e]	19

[a] Reaction conditions: 4-bromoanisole (1.0 mmol), phenylboronic acid (1.2 mmol), Cs_2CO_3 (2.0 mmol), dioxane (3.0 mL), 80 °C, 3 h. [b] Isoalted yield. [c] No ligand used. [d] *Z*/*E* ratio 50:50. [e] *Z*/*E* ratio 30:70.



Scheme 5. Reactivities of electron-deficient and electron-rich bromides catalyzed by palladium/olefin **2d** catalyst system in dioxane.

(trifluoromethyl)benzaldehyde, and 1-(4-bromophenyl)ethanone, as well as 4-bromobenzenamine; all these functional groups (CHO, amino, and ketone) were tolerated. Thus, the olefin-promoted palladium-catalyzed Suzuki coupling reaction presented herein is simple, highly convenient, and universally applicable. Although these studies did not provide the exact structure of the palladium–olefin complex directly, these results confirm that the olefin moiety is very important to the palladium-catalyzed Suzuki coupling reaction and could explain why mono-substituted olefin **2a** or **2d** exhibits better activity in the Suzuki coupling reaction.

Conclusions

We have developed an unprecedented lateral sequential lithiation/silylation/Peterson condensation of tertiary aromatic amides, providing an efficient method to build up functional olefins in good yields. As a result of *ortho*-metalation, a clear effect of the tertiary aromatic amide was to direct the double lithiation successfully even in the presence of a bulky silicon-based group. In addition, we have established an efficient and simple method to detect the coordination or interaction between transition-metal salts and functional olefin-containing tertiary amides by fluorescence spectroscopy. This has led to the development of a highly efficient palladium catalyst for phosphane-free Suzuki coupling reactions in the presence of the tertiary aromatic amide-derived olefins. The cross-coupling reaction can be performed under mild conditions and provides a simple protocol for the preparation of biaryls. This development is also expected to offer a new olefin ligand for palladium catalysis and provides an alternative strategy for cross-coupling reactions in general. Further applications of this type of olefin ligand to transition-metal catalysis are being developed in our group.

Experimental Section

Flash column chromatography was performed over silica (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with an Advance (Bruker) 400 MHz spectrometer, and were referenced to the internal solvent signals. Thin layer chromatography was performed using silica gel F254 TLC plates and visualized with ultraviolet light. EI and CI mass spectra were performed with a Trace DSQ GC/MS spectrometer. Data are reported in the form of (*m*/*z*). The substrates, including *s*-butyllithium, were commercially available and used directly. ESI-MS analyses of the samples were obtained with an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source operated in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4). UV/Vis absorption and circular dichroism spectra were recorded with MOS-450/AF-CD and Evolution-300 instruments, respectively. X-ray diffraction data sets were collected with Bruker APEX DUO and Bruker APEX-II CCD diffractometers. Programs used: data collection Bruker APEX2,[14a] data reduction Bruker SAINT, absorption correction for multi-scan, structure solution SHELX-97,[14b] structure refinement SHELXL-97,[14b] graphics Bruker SHELXTL.[14b]

General Procedure for the Preparation of 4 by Lithiation/Silylation/Peterson Condensation: *sec*-Butyllithium (2.4 equiv.) was added to a solution of *N*,*N*-diisopropyl-2-methylbenzamide (**1**) and TMEDA (2.4 equiv.) in THF at –78 °C under argon. The resulting orange solution was stirred at this temperature for 1 h, followed by addition of chlorotrimethylsilane (2.0 equiv.). The reaction was stirred for a further 2 h, then the carbonyl compound (1.5 equiv.; aldehyde or ketone), was added at –78 °C. The reaction mixture was warmed to room temperature and stirred for 18 h, then poured into water, and extracted into EtOAc. The combined extracts were dried with magnesium sulfate, and concentrated under reduced pressure to give the crude product. The product was purified by column chromatography (silica gel, petroleum/ethyl acetate).

***N*,*N*-Diisopropyl-2-styrylbenzamide (2a):** White solid; yield 90% (mixture of isomers); *E*:*Z* = 70:30; R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1623 [CON(C_3H_7)$_2$] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.0 Hz, 0.3 H), 7.48 (d, *J* = 8.0 Hz, 0.7 H), 7.38–7.25 (m, 8 H), 7.13–7.09 (m, 1 H), 6.65 (d, *J* = 4 Hz, 1 H), 3.88–3.62 (m, 1 H), 3.57–3.49 (m, 1 H), 1.68–1.58 (m, 6 H), 1.15–1.04 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 138.6, 138.4, 131.4, 130.6, 129.6, 128.9, 128.8, 128.4, 128.3, 127.7, 127.5, 127.3, 127.3, 126.5, 125.4, 125.4, 125.3, 125.1, 51.1, 45.9, 20.8, 20.5 ppm. GC–MS: *m*/*z* (%) = 307.16 (28), 292.08 (2), 264.07 (6), 207.01 (100), 178.01 (55), 152.00 (8), 77.00 (2). HRMS (ESI): Calcd. for [$C_{21}H_{25}$NO+Na]$^+$ 330.1834; found 330.1848.

2-(2,2-Diphenylvinyl)-*N*,*N*-diisopropylbenzamide (2b): Light-yellow solid; Yield: 89%; R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1621 [CON(C_3H_7)$_2$] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.19 (m, 8 H), 7.11–7.08 (m, 2 H), 7.06–7.02 (m, 2 H), 6.94 (s, 1 H), 6.87–6.83 (m, 1 H), 6.69 (d, *J* = 8 Hz, 1 H), 3.80–3.73 (m, 1 H), 3.42–3.36 (m, 1 H), 1.51 (d, *J* = 8 Hz, 3 H), 1.37 (d, *J* = 8 Hz, 3 H), 1.06 (dd, *J* = 16, 8 Hz, 6 H) ppm. ^{13}C NMR (100 MHz,$CDCl_3$): δ = 170.5, 143.6, 143.0, 140.1, 139.6, 133.2, 130.3, 129.3, 128.6, 128.2, 127.6, 127.3, 127.1, 124.9, 124.6, 51.1, 45.9, 20.9, 20.8, 20.4 ppm. GC–MS: *m*/*z* (%) = 383.15 (57), 283.05 (100), 265.04 (51), 253.07 (30), 239.02 (19), 206.95 (19), 178.04 (18), 105.02 (17), 76.95 (15). HRMS (ESI): Calcd. for [$C_{27}H_{29}$NO+H]$^+$ 384.2327; found 384.2303.

2-(2,4-Diphenylbuta-1,3-dienyl)-*N*,*N*-diisopropylbenzamide (2c): Light-yellow solid; yield 60% (mixture of isomers); *Z*/*E* = 59:41; R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1630 [CON(C_3H_7)$_2$] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.23 (m, 12 H), 7.15–7.11 (m, 2 H), 6.93–6.84 (1 H), 6.71–6.22 (m, 2 H), 3.80–3.67 (m, 1 H),3.62–3.41 (m, 1 H), 1.73–1.37 (m, 6 H), 1.24–1.05 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 142.7, 142.3, 141.6, 139.3, 139.2, 138.1, 137.4, 137.3, 134.5, 133.8, 133.4, 132.7, 131.9, 130.4, 129.6, 129.1, 128.9, 128.7, 128.6, 128.3, 128.2, 127.8, 127.6, 127.3, 127.0, 126.7, 126.6, 126.5, 125.1, 124.8, 51.1, 51.0, 46.0, 45.8, 21.0, 20.9, 20.8, 20.6, 20.4, 20.2 ppm. GC–MS: *m*/*z* (%) = 409.27 (100), 324.15 (29), 309.11 (35), 291.06 (25), 281.11 (35), 231.06 (59), 202.03 (79), 191.07 (35), 90.97 (60), 76.89 (21). HRMS (ESI): Calcd. for [$C_{29}H_{31}$NO+H]$^+$ 410.2484; found 410.2481.

***N*,*N*-Diisopropyl-2-(4-methylstyryl)-benzamide (2d):** White solid; yield 55% (mixture of isomers); *Z*/*E* = 80:20; R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1624 [CON(C_3H_7)$_2$] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–35 (m, 1 H), 7.33–7.27 (m, 1 H), 7.25–7.18 (m, 2 H), 7.16–7.09 (m, 3 H), 7.06–6.60 (m, 3 H), 3.90–3.62 (m, 1 H), 3.57–3.46 (m, 1 H), 2.37–2.32 (m, 3 H), 1.68–1.58 (m, 6 H), 1.14–1.03 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 138.6, 137.1, 133.9, 133.7, 131.3, 130.5, 129.6,

129.5, 128.9, 128.8, 128.3, 127.6, 127.5, 127.3, 126.6, 126.5, 125.4, 125.3, 125.1, 124.4, 51.1, 51.0, 45.9, 21.3, 20.8, 20.7, 20.6, 20.5 ppm. GC–MS: *m*/*z* (%) = 321.20 (28), 278.11 (6), 221.05 (100), 178.02 (50), 114.97 (9), 83.95 (20). HRMS (ESI): Calcd. for $[C_{22}H_{27}NO+H]^+$ 322.2171; found 322.2174.

***N*,*N*-Diisopropyl-2-(–2-methyl-4-phenylbuta-1,3-dienyl)benzamide (2e):** White solid; yield 70% (mixture of isomers); R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1626 [CON-$(C_3H_7)_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.18 (m, 10 H), 6.95–6.59 (m, 2 H), 3.62–3.53 (m, 1 H), 3.49–3.42 (m, 1 H), 2.11–2.07 (m, 3 H), 1.63–1.48 (m, 6 H), 1.03–0.95 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 170.3, 138.9, 138.7, 137.6, 137.5, 137.0, 135.7, 133.7, 133.5, 130.7, 129.7, 129.5, 128.7, 128.6, 127.9, 127.7, 127.7, 127.6, 127.5, 127.1, 126.8, 126.7, 126.5, 125.0, 50.9, 50.8, 45.8, 20.9, 20.8, 20.4, 20.3, 20.2, 14.0 ppm. GC–MS: *m*/*z* (%) = 347.26 (100), 304.15 (16), 262.15 (42), 247.10 (71), 229.10 (49), 204.05 (52), 146.01 (76), 91.05 (60). HRMS (ESI): Calcd. for $[C_{24}H_{29}NO+H]^+$ 348.2327; found 348.2321.

***N*,*N*-Diisopropyl-2-(2-*p*-tolylprop-1-enyl)benzamide (2f):** Light-yellow solid; yield 70% (mixture of isomers); R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1624 [$CON(C_3H_7)_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8 Hz, 1 H), 7.37–7.32 (m, 1 H), 7.28–7.24 (m, 1 H), 7.20–7.14 (m, 1 H), 7.10–7.06 (m, 3 H), 6.94–6.89 (m, 1 H), 6.79–6.48 (m, 1 H), 3.74–3.58 (m, 1 H), 3.75–3.40 (m, 1 H), 2.34 (d, J = 12 Hz, 3 H), 2.18 (dd, J = 8.8 Hz, 3 H), 1.63–1.49 (m, 6 H), 1.20–0.97 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 170.4, 140.0, 139.6, 138.5, 138.0, 137.1, 136.8, 133.7, 129.8, 129.6, 129.1, 129.0, 128.0, 127.7, 127.2, 126.8, 126.3, 125.6, 124.9, 124.7, 124.0, 123.2, 51.0, 50.8, 45.9, 45.7, 26.9, 21.2, 21.1, 20.9, 20.8, 20.5, 20.3, 17.1 ppm. GC–MS: *m*/*z* (%) = 335.27 (23), 292.12 (3), 235.08 (100), 221.04 (32), 191.04 (22), 114.97 (28), 76.95 (3). HRMS (ESI): Calcd. for $[C_{23}H_{29}NO+H]^+$ 336.2327; found 336.2305.

2-[(2,3-Dihydroinden-1-ylidene)methyl]-*N*,*N*-diisopropylbenzamide (2g): White solid; yield 56% (mixture of isomers); R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1626 [CON-$(C_3H_7)_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.08 (m, 8 H), 6.99–6.13 (m, 1 H), 3.76–3.61 (m, 1 H), 3.51–3.33 (m, 1 H), 3.94–2.13 (m, 4 H), 1.62–1.47 (m, 6 H), 1.13–0.86 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 170.5, 145.9, 145.5, 145.0, 144.4, 142.8, 142.4, 138.9, 138.5, 135.4, 134.0, 130.5, 130.1, 128.4, 128.2, 127.9, 127.6, 126.8, 126.5, 126.2, 126.2, 125.3, 125.1, 125.0, 124.7, 123.7, 120.3, 119.6, 115.7, 51.0, 50.9, 45.9, 45.8, 37.8, 31.0, 30.8, 30.6, 20.8, 20.7, 20.6, 20.5, 20.4 ppm. GC–MS: *m*/*z* (%) = 333.24 (49), 232.08 (100), 215.06 (89), 178.03 (7), 76.92 (4). HRMS (ESI): Calcd. for $[C_{23}H_{27}NO+H]^+$ 334.2171; found 334.2169.

***N*,*N*-Diisopropyl-2-(2-phenylprop-1-enyl)benzamide (2h):** Yellow oil; yield 69% (mixture of isomers); *Z*/*E* = 60:40; R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1632 [$CON(C_3H_7)_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20–7.59 (m, 1 H), 7.53–7.46 (m, 1 H), 7.44–7.37 (m, 1 H), 7.35–7.27 (m, 2 H), 7.20–7.03 (m, 3 H), 6.95–6.87 (m, 1 H), 6.73–6.51 (m, 1 H), 3.85–3.60 (m, 1 H), 3.58–3.41 (m, 1 H), 2.31–2.06 (m, 3 H), 1.65–1.50 (m, 6 H), 1.22–0.98 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 141.6, 139.9, 138.4, 134.3, 133.5, 129.7, 129.6, 128.6, 128.4, 128.1, 127.8, 127.7, 127.4, 127.3, 127.1, 127.0, 126.5, 125.8, 124.9, 124.8, 124.7, 123.4, 51.1, 50.9, 46.0, 45.9, 26.9, 20.8, 20.5, 20.4, 20.3 ppm. GC–MS: *m*/*z* (%) = 321.20 (23), 278.16 (3), 221.05 (100), 203.02 (15), 178.02 (23), 114.96 (28), 76.87 (4). HRMS (ESI): Calcd. for $[C_{22}H_{27}NO+H]^+$ 322.2171; found 322.2176.

***N*,*N*-Diisopropyl-2-(undec-1-enyl)benzamide (2i):** Yellow solid; yield 70% (mixture of isomers); R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1634 [$CON(C_3H_7)_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.09 (m, 4 H), 7.04–6.41 (m, 1 H), 6.27–5.68 (m, 1 H), 3.64–3.55 (m, 1 H), 3.53–3.50 (m, 1 H), 2.38–2.15 (m, 2 H), 1.60–1.55 (m, 6 H), 1.26 (s, 14 H), 1.13–1.03 (m, 6 H), 0.88 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 137.1, 134.5, 134.0, 133.3, 129.2, 128.1, 127.6, 126.8, 126.6, 125.9, 125.2, 125.2, 125.0, 50.9, 50.8, 45.8, 33.3, 31.9, 30.0, 29.6, 29.3, 29.1, 28.8, 22.7, 20.8, 20.7, 20.6, 20.4, 14.1 ppm. GC–MS: *m*/*z* (%) = 357.38 (100), 314.45 (51), 272.14 (56), 244.23 (50), 230.14 (72), 188.08 (38), 144.99 (79), 131.04 (74), 115.02 (49), 69.06 (57). HRMS (ESI): Calcd. for $[C_{24}H_{39}NO+H]^+$ 358.3110; found 358.3107.

***N*,*N*-Diisopropyl-2-(–3-methyl-4-phenylbuta-1,3-dienyl)benzamide (2k):** White solid; yield 65% (mixture of isomers); R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1628 [CON-$(C_3H_7)_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.30 (m, 4 H), 7.27–7.18 (m, 4 H), 7.15–7.13 (m, 1 H), 7.00–6.35 (m, 3 H), 3.77–3.60 (m, 1 H), 3.54–3.45 (m, 1 H), 2.22–2.08 (m, 1 H), 1.86 (s, 2 H), 1.64–1.56 (m, 6 H), 1.12–1.04 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 138.3, 137.7, 136.5, 135.2, 134.2, 132.4, 130.2, 129.3, 129.1, 128.2, 127.5, 127.2, 126.7, 126.1, 124.7, 51.0, 45.8, 21.0, 20.8, 20.7, 20.5, 20.4, 18.4 ppm. GC–MS: *m*/*z* (%) = 347.26 (70), 332.11 (33), 304.17 (33), 247.07 (100), 203.06 (44), 128.05 (25), 76.99 (6). HRMS (ESI): Calcd. for $[C_{24}H_{29}NO+H]^+$ 348.2327; found 348.2325.

***N*,*N*-Diisopropyl-2-[(2-methylcyclohexylidene)methyl]benzamide (2l):** White solid; yield 60% (mixture of isomers); R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1628 [CON-$(C_3H_7)_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.14 (m, 4 H), 6.27–6.13 (m, 1 H), 3.65–3.53 (m, 1 H), 3.50–3.44 (m, 1 H), 3.09–2.69 (m, 1 H), 2.42–1.98 (m, 2 H), 1.81–1.66 (m, 3 H), 1.57–1.49 (m, 8 H), 1.34–1.22 (m, 4 H), 1.12–1.02 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 148.3, 148.2, 148.0, 138.7, 129.9, 129.7, 128.9, 127.5, 127.4, 126.3, 126.2, 126.1, 124.3, 119.2, 117.1, 50.8, 50.7, 45.8, 45.6, 39.2, 38.9, 37.0, 36.7, 33.2, 31.0, 29.7, 29.3, 28.6, 28.4, 28.0, 25.8, 25.5, 21.2, 21.1, 20.8, 20.5, 20.4, 18.8, 18.7 ppm. GC–MS: *m*/*z* (%) = 313.20 (49), 270.14 (15), 212.07 (100), 197.03 (44), 156.99 (48), 145.00 (34), 128.00 (30), 114.97 (29), 85.98 (74). HRMS (ESI): Calcd. for $[C_{21}H_{31}NO+H]^+$ 314.2484; found 314.2468.

2-(But-1-enyl)-*N*,*N*-diisopropylbenzamide (2m): White solid; yield 70% (mixture of isomers); R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1628 [$CON(C_3H_7)_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.10 (m, 4 H), 6.45–6.42 (d, J = 12 Hz, 1 H), 6.31–5.69 (m, 1 H), 3.59 (s, 1 H), 3.48 (s, 1 H), 2.29–2.21 (m, 2 H), 1.58–1.40 (m, 6 H), 1.07–1.04 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 170.3, 138.4, 137.1, 135.8, 134.6, 133.9, 133.6, 129.3, 128.1, 127.6, 126.8, 125.6, 125.6, 125.2, 125.1, 124.9, 50.9, 45.8, 45.7, 29.7, 26.1, 22.0, 20.8, 20.7, 20.6, 20.4, 14.3, 13.2 ppm. GC–MS: *m*/*z* (%) = 259.16 (36), 216.08 (41), 188.03 (11), 159.02 (35), 131.00 (100), 114.97 (18), 90.96 (24), 76.94 (5). HRMS (ESI): Calcd. for $[C_{21}H_{31}NO+H]^+$ 260.2014; found 260.2020.

2-(2,2-Di-*p*-tolylvinyl)-*N*,*N*-diisopropyl-4,5-dimethylbenzamide (2n): White solid; yield 75%; R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1619 [$CON(C_3H_7)_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.23 (m, 2 H), 7.18 (d, J = 8 Hz, 2 H), 7.07–7.04 (m, 4 H), 6.89 (d, J = Hz, 2 H 8 H), 6.50 (s, 1 H), 3.89–3.82 (m, 1 H), 3.47–3.40 (m, 1 H), 2.32 (s, 6 H), 2.16 (s, 3 H), 1.88 (s, 3 H), 1.57 (d, J = 8 Hz, 3 H), 1.46 (d, J = 8 Hz, 3 H), 1.10 (dd, J = 8, 16 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 142.3, 140.5, 137.6, 137.4, 137.1, 136.9, 135.4, 135.4, 130.8, 130.2, 130.1,

129.2, 129.2, 128.8, 127.4, 126.5, 126.0, 123.6, 51.0, 45.8, 21.3, 21.2, 21.0, 20.8, 20.8, 20.5, 19.5, 19.5 ppm. GC–MS: *m*/*z* (%) = 439.47 (52), 340.18 (100), 324.19 (10), 309.28 (10), 281.14 (16), 248.07 (20), 206.87 (34), 161.45 (17), 133.05 (18). HRMS (ESI): Calcd. for $[C_{31}H_{37}NO+H]^+$ 440.2953; found 440.2945.

2-[2,2-Bis(4-fluorophenyl)vinyl]-*N*,*N*-diisopropyl-4,5-dimethylbenzamide (2o): Light-yellow solid; yield 73%; R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1620 [CON(C_3H_7)$_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.29 (m,1 H), 7.24–7.20 (m, 2 H), 7.15–7.12 (m, 2 H), 7.04–6.98 (m, 3 H), 6.88 (d, J = 12 Hz, 2 H), 6.48 (s, 1 H), 3.88–3.81 (m, 1 H), 3.48–3.42 (m, 1 H), 2.17 (s, 3 H), 1.92 (s, 3 H), 1.56 (d, J = 4 Hz, 3 H), 1.42 (d, J = 4 Hz, 3 H), 1.12 (t, J = 4 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 140.4, 139.2, 137.4, 135.9, 132.0 ($J_{C,F}$ = 7.8 Hz), 130.2, 129.1 ($J_{C,F}$ = 7.9 Hz), 128.2, 126.1, 125.1, 115.5, 115.2, 51.0, 45.8, 20.9, 20.4, 19.5 ppm. GC–MS: *m*/*z* (%) = 447.28 (47), 347.15 (100), 331.12 (4), 304.12 (8), 288.05 (11), 207.03 (6), 174.00 (4), 83.99 (15). HRMS (ESI): Calcd. for $[C_{29}H_{31}F_2NO+H]^+$ 448.2452; found 448.2466.

2-(Cyclopentylidenemethyl)-*N*,*N*-diisopropylbenzamide (2p): Light-yellow liquid; yield 55%; R_f = 0.4 (ethyl acetate/hexane, 1:5). FTIR (NaCl, neat): $\tilde{\nu}$ = 1633 [CON(C_3H_7)$_2$] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 8 Hz, 1 H), 7.29–7.25 (m, 1 H), 7.18–7.11 (m, 2 H), 6.39 (t, J = 4 Hz, 1 H), 3.61–3.54 (m, 1 H), 3.51–3.44 (m, 1 H), 2.60–2.31 (m, 4 H), 1.82–1.76 (m, 1 H), 1.69–1.65 (m, 3 H), 1.57 (dd, J = 4.8 Hz, 6 H), 1.03 (dd, J = 8, 12 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 148.4, 138.1, 134.7, 127.8, 127.7, 126.0, 124.3, 117.8, 50.8, 45.7, 35.5, 27.0, 25.5, 20.8, 20.7, 20.4, 20.3 ppm. GC–MS: *m*/*z* (%) = 285.21 (45), 242.14 (18), 184.05 (100), 167.03 (82), 129.01 (29), 114.99 (23), 86.01 (39). HRMS (ESI): Calcd. for $[C_{19}H_{27}NO+H]^+$ 286.2171; found 286.2184.

2-(Cycloheptylidenemethyl)-*N*,*N*-diisopropylbenzamide (2q): Colourless oil; yield 62%; R_f = 0.4 (ethyl acetate/hexane, 1:5). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.26 (m, 2 H), 7.21–7.19 (m, 1 H), 7.13–7.12 (m, 1 H), 6.33 (s, 1 H), 3.61–3.55 (m, 1 H), 3.50–3.43 (m, 1 H), 2.57–2.49 (m, 1 H), 2.44–2.28 (m, 3 H), 1.66–1.53 (m, 14 H), 1.04 (dd, J = 8, 12 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 146.1, 138.1, 134.5, 129.3, 127.5, 126.2, 124.7, 122.6, 50.7, 45.7, 38.5, 31.4, 29.7, 29.4, 28.8, 27.4, 20.8, 20.8, 20.5, 20.4 ppm. GC–MS: *m*/*z* (%) = 313.27 (34), 270.18 (17), 212.11 (51), 157.03 (43), 128.03 (36), 86.02 (100). HRMS (ESI): Calcd. for $[C_{21}H_{31}NO+H]^+$ 314.2484; found 314.2484.

General Procedure for the Preparation of 3 through Lateral Lithiation and Silylation: *sec*-Butyllithium (1.2 equiv.) was added to a solution of *N*,*N*-diisopropyl-2-methylbenzamide (**1**) and TMEDA (1.2 equiv.) in THF at –78 °C. The resulting orange solution was then stirred at this temperature for 1 h, followed by addition of chlorotrimethylsilane (1.5 equiv.). The reaction was warmed to room temperature and stirred for 12 h, then poured into water and extracted into EtOAc. The combined extracts were dried with magnesium sulfate and concentrated under reduced pressure to give the crude product. The product was purified by column chromatography (silica gel; petroleum/ethyl acetate).

***N*,*N*-Diisopropyl-2-[(trimethylsilyl)methyl]benzamide (3):** Colourless oil; yield 90%; R_f = 0.4 (ethyl acetate/hexane, 1:5). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.13 (m,1 H), 7.05–7.00 (m,3 H), 3.64–3.57 (m, 1 H), 3.48–3.41 (m, 1 H), 2.02 (s, 2 H), 1.54 (d, J = 4 Hz, 6 H), 1.09 (d, J = 8 Hz, 3 H), 1.01 (d, J = 8 Hz, 3 H), 0 (s, 9 H) ppm. GC–MS: *m*/*z* (%) = 290.31 (3), 276.12 (61), 248.05 (57), 234.11 (25), 206.93 (37), 191.92 (16), 118.97 (100), 89.94 (14).

General Procedure for Suzuki Reaction under Mild Aerobic Conditions: A mixture of Cs_2CO_3 (0.212 g, 2 mmol), $Pd(OAc)_2$ (4 mg, 2 mol-%), olefin **4a** or **4d** (4 mol-%), and dioxane (3 mL) was heated to 80 °C with stirring. Aryl halide (1 mmol) and arylboronic acid (1.2 mmol) were added to the solution, and the reaction was carried out at 80 °C for 3–4 h. After the solution was cooled to room temperature, the resulting suspension was extracted four times with diethyl ether (4–15 mL). The combined ether phase was analyzed by GC/MS and then concentrated. Further purification of the product was achieved by flash chromatography on a silica gel column. All of the products prepared are known[15] and were characterized by ^1H NMR and GC–MS analyses.

Supporting Information (see footnote on the first page of this article): General remarks, NMR and IR spectroscopic data for the products.

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