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Palladium-Catalyzed One-Pot Synthesis of *N*-Sulfonyl, *N*-Phosphoryl, and *N*-Acyl Guanidines

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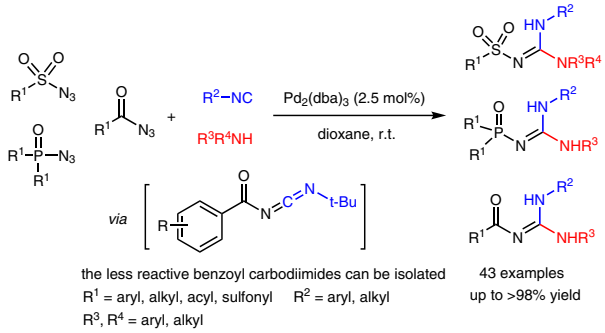

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Abstract An efficient palladium-catalyzed cascade reaction of azides with isonitrile and amines is presented; it offers an alternative facile approach toward *N*-sulfonyl-, *N*-phosphoryl-, and *N*-acyl-functionalized guanidines in excellent yield. These series of substituted guanidines exhibit potential biological and pharmacological activities. In addition, the less reactive intermediate benzoyl carbodiimide could be isolated by silica gel column flash chromatography in moderate yield.

Key words sulfones, phosphorus, azides, functionalized guanidines, palladium catalysis

Guanidine, a prominent nitrogen-containing structural motif, is ubiquitous in agrochemicals and pharmaceuticals.[1] *N*-Sulfonyl-,[2] *N*-phosphoryl-,[3] and *N*-acyl-functionalized[4] guanidines exhibit a broad range of biological and pharmacological activities. For example, sulfaguanidine has been used to treat enteritis,[5] tetramethyl phosphoryl guanidine (Tmg) has been used to resist 3′-phosphodiesterase cleavage in a new fluorescent oligonucleotide-based assay,[3] and zanamivir derivatives have also been used as neuraminidase inhibitors to treat type A and B influenza (Figure 1).[6] Guanidines are typically accessed by nucleophilic addition of amines to *N*-sulfonyl-, *N*-acyl-, and *N*-phosphoryl-functionalized carbodiimides, which are mostly obtained by desulfuration of thioureas (Scheme 1, a).[7] However, the preparation of carbodiimide substrates is tedious, and harsh additives are needed. It is highly desirable to develop facile and practical methods to synthesize these functionalized guanidines with a broad substrate scope.

Organic azide, an efficient nitrene precursor, has been identified as a convenient nitrogen source in the formation of *N*-containing compounds.[8] Transition-metal-catalyzed reactions of azides with σ-donor/π-acceptor ligands have

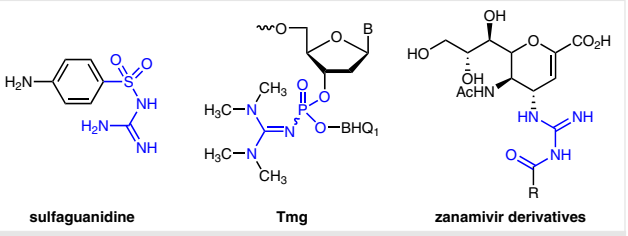
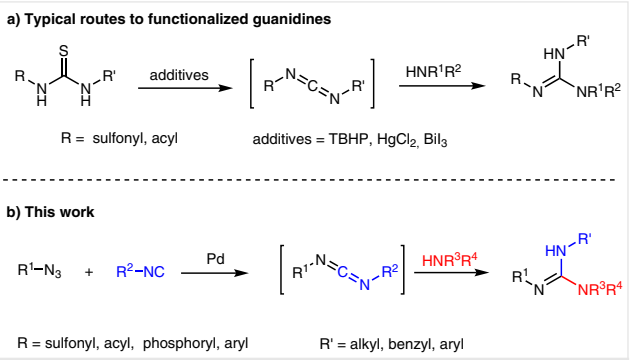


Figure 1 Examples of *N*-sulfonyl, *N*-phosphoryl, and *N*-acyl guanidines in drugs

also provided convenient methods to access isocyanates (from carbon monoxide)[9] and carbodiimides (from isonitriles)[10] as intermediates. Palladium complexes, which are widely used in synthetic chemistry due to their ease of handling and good functional group tolerance,[11] have also been studied in azide transfer reactions with carbon monoxide[9b–e] and isonitriles.[10c] As a continuation of our work on palladium-catalyzed reactions of azides with σ-donors/π-acceptors,[10c] herein we report a simple $Pd_2(dba)_3$-catalyzed coupling of easily accessible and air- and moisture-stable sulfonyl-, acyl-, and phosphoryl azides with isonitriles and

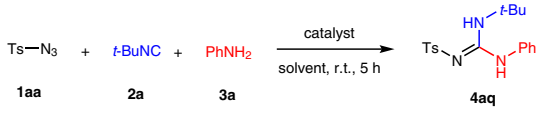


Scheme 1 Synthesis of functionalized guanidines

amines, as a facile access to *N*-sulfonyl-, *N*-acyl-, and *N*-phosphoryl-functionalized guanidines under mild conditions without any extra ligands (Scheme 1, b). Apart from the mild room temperature conditions and the use of only the $Pd_2(dba)_3$ catalyst without any extra ligands, sulfonyl, phosphoryl, and acyl azides and isonitriles are all commercially available and easy to prepare. It is worth mentioning that under the mild conditions of this reaction, the incidental Curtius rearrangement of acyl azides could be avoided.[12] In addition, benzoyl carbodiimide could be isolated by silica gel column flash chromatography.

At the outset, TsN_3 (**1aa**), *t*-BuNC (**2a**), and aniline (**3a**) were selected as reagents to optimize the reaction conditions (Table 1). Firstly, the screening of catalysts revealed that good results were obtained with the $Pd_2(dba)_3$ catalyst. Then the optimization of solvent demonstrated that 1,4-dioxane was superior to other aprotic or protic solvents. On the basis of this initial study, the optimal reaction conditions for TsN_3, *t*-BuNC, and aniline were determined to be the reaction in a sealed tube at room temperature for 5 hours with 1,4-dioxane as solvent.

Table 1 Optimization of Reaction Conditions[a]

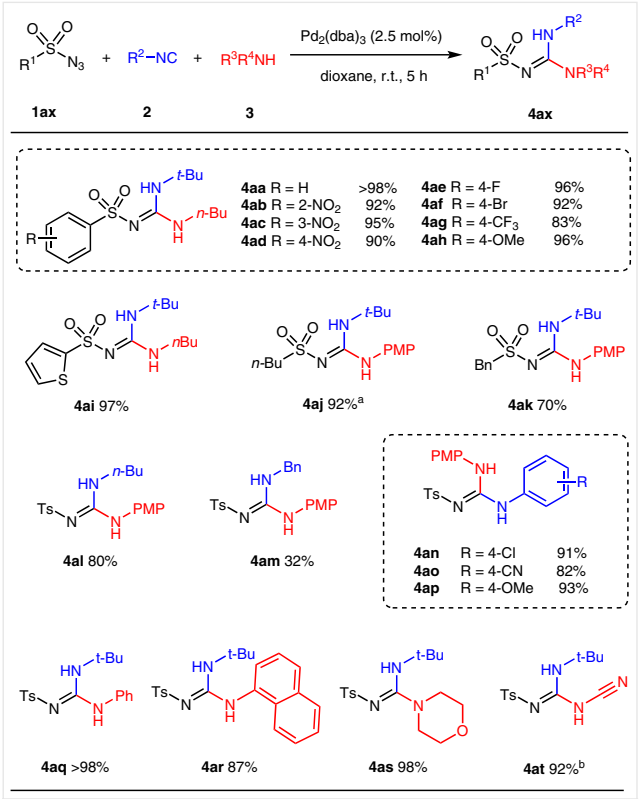


1aa 2a 3a 4aq

Entry	Catalyst (mol%)	Solvent	Yield (%)[b]
1	$PdCl_2$ (5)	THF	n.r.
2	$Pd(PPh_3)_2Cl_2$ (5)	THF	n.r.
3	$Pd(NCPh)_2Cl_2$ (5)	THF	n.r.
4	$Pd(OAc)_2$ (5)	THF	36
5	$Pd_2(dba)_3$ (2.5)	THF	97
6	$Pd_2(dba)_3$ (2.5)	MeCN	19
7	$Pd_2(dba)_3$ (2.5)	DMF	11
8	$Pd_2(dba)_3$ (2.5)	DMSO	n.r.
9	$Pd_2(dba)_3$ (2.5)	acetone	69
10	$Pd_2(dba)_3$ (2.5)	DCE	54
11	$Pd_2(dba)_3$ (2.5)	1,4-dioxane	>98

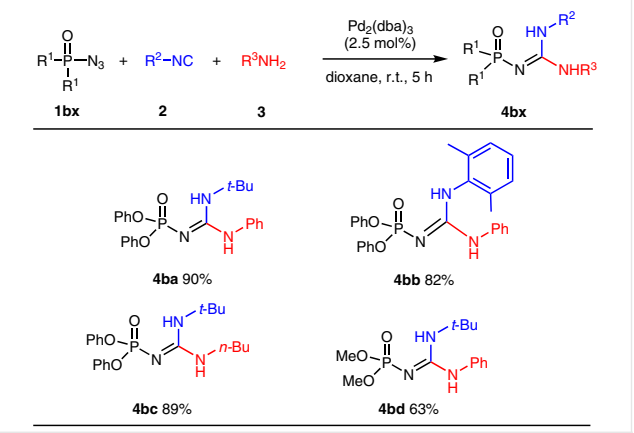
[a] Reaction conditions: **1aa** (0.1 mmol), **2a** (0.11 mmol), **3a** (0.12 mmol), catalyst (0.005 mmol), solvent (2 mL), sealed tube, r.t., 5 h.
[b] Yield determined by ^1H NMR spectroscopy; n.r. = no reaction.

After the preliminary inspection of the reactivity features and the optimization of the reaction conditions, we explored the generality of this method with regard to different substituted *N*-sulfonyl-, *N*-acyl-, and *N*-phosphoryl-functionalized guanidines. Firstly, *N*-sulfonyl guanidines were investigated and the results are summarized in Scheme 2. To our delight, the reaction showed an excellent substrate scope. Not only does the steric hindrance have little effect on the reactivity (**4aa–ad**), but also nearly all different electron-withdrawing-/electron-donating-substituted aromatic rings in sulfonyl azides gave >90% isolated yields (**4ad–ah**). When the sulfonyl azides were extended to heteroaromatic (**4ai**), benzyl (**4ak**), and alkyl (**4aj**) sulfonyl groups, good results were also obtained. The evaluation of different isonitriles revealed that alkyl isonitriles and substituted aryl isonitriles all reacted smoothly to give the desired products (**4al**, **4an–ap**) in high yields. Benzyl isonitrile only gave a moderate yield (**4am**). Additionally, in addition to arylamines, morpholine (**4as**) and cyanamide (**4at**) were also well tolerated, giving products difficult to access from previous methods.



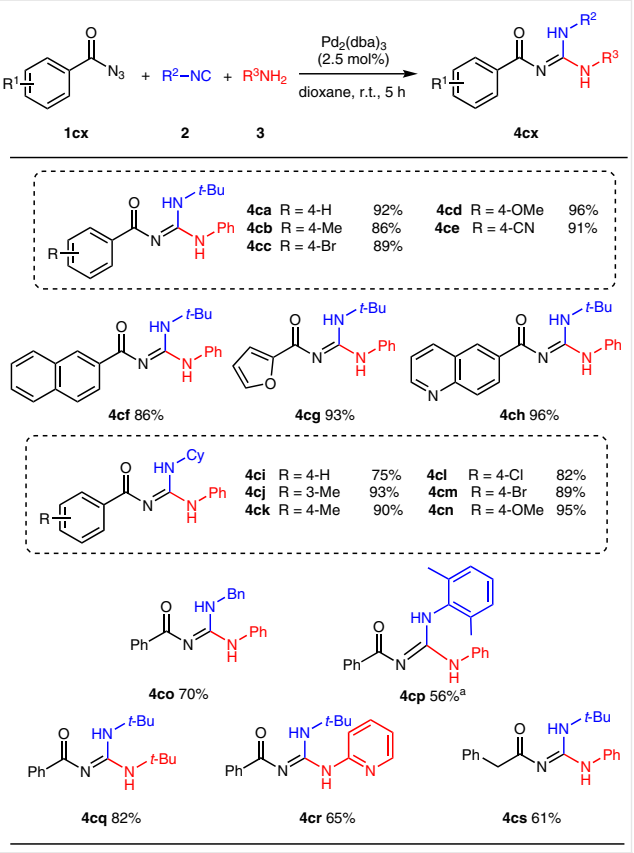
Scheme 2 Scope of the reaction giving *N*-sulfonyl guanidines. *Reagents and conditions*: **1ax** (0.2 mmol), **2** (0.22 mmol), **3** (0.24 mmol), $Pd_2(dba)_3$ (0.005 mmol), dioxane (2 mL), r.t., 5 h; yield of isolated product. [a] dppp (dppp = 1,3-bis(diphenylphosphine)propane; 0.4 mmol) was added. [b] K_2CO_3 (0.4 mmol) was added.

Because of the slightly poorer efficiency of phosphoryl azides compared to sulfonyl azides, the installation of *N*-phosphoryl guanidines was envisioned to be more highly desirable. As shown in Scheme 3, regardless of whether alkyl- or aryl-substituted phosphoryl azides, different isonitriles, or different amines were used, the targeted phosphoryl guanidines could be achieved in good yields (**4ba–bd**).



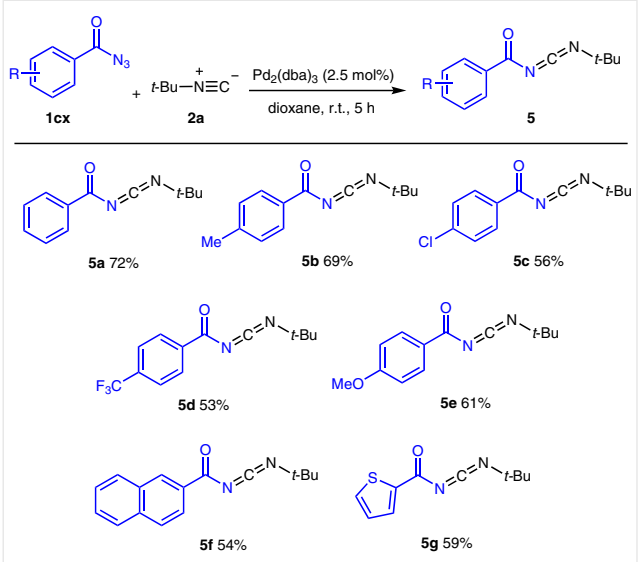
Scheme 3 Scope of the reaction giving *N*-phosphoryl guanidines. *Reagents and conditions*: **1bx** (0.2 mmol), **2** (0.22 mmol), **3** (0.24 mmol), $Pd_2(dba)_3$ (0.005 mmol), dioxane (2 mL), r.t., 5 h; yield of isolated product.

Acyl azides are known as privileged precursors toward isocyanates, undergoing a direct Curtius rearrangement, endowing these compounds with thermal instability at a higher temperature.[12] In contrast, this protocol successfully achieved the generation of *N*-acyl guanidines by utilizing acyl azides under mild reaction conditions. As shown in Scheme 4, the scope was insensitive to electronic changes of the aromatic ring and different types of fused or hetero rings in the acyl azides, invariably leading to the target products in high yields (**4ca–ch**). The scope of isocyanides was next examined. The results showed that isocyanocyclohexane worked equally well (**4ci–cn**), whereas benzyl- and aryl-substituted isocyanides gave moderate yields (70% and 56% yield for **4co** and **4cp**, respectively). Additionally, when the nucleophilic reagent was changed to alkylamine (**4cq**) and pyridin-2-amine (**4cr**), the reaction also proceeded smoothly to give the corresponding guanidines in reasonable yields. Gratifyingly, unstable 2-phenylacetyl azide is also amenable to this transformation (**4cs**).



Scheme 4 Scope of the reaction giving *N*-acyl guanidines. *Reagents and conditions*: **1cx** (0.2 mmol), **2** (0.22 mmol) and **3** (0.24 mmol), $Pd_2(dba)_3$ (0.005 mmol), dioxane (2 mL), r.t., 5 h; yield of isolated product. [a] $Zn(OTf)_2$ (0.03 mmol) was added.

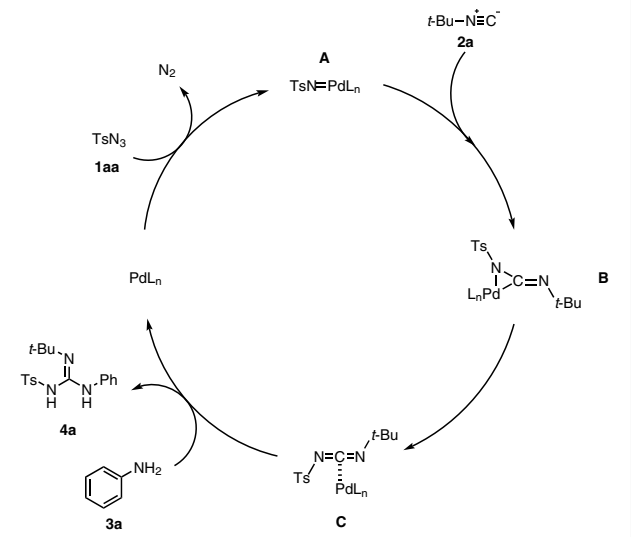
Functionalized carbodiimides are not only common precursors of functionalized guanidines, but also important intermediates to access *N*-containing heterocycles.[13] Although sulfonyl and phosphoryl carbodiimides are difficult to separate, it is worth mentioning that when benzoyl azide (**1ca**) was used, the less reactive intermediate benzoyl carbodiimide (**5a**) existed transiently in 72% isolated yield after silica gel column chromatography. The subsequent addition of amine gave *N*-acyl guanidine (**4ca**) in 92% yield. Having obtained this result, we further investigated the generality of the formation of *N*-acyl carbodiimides from acyl azides. As shown in Scheme 5, the reaction could be carried out between a series of electron-donating/electron-withdrawing-substituted benzoyl azides and hetero acyl azides and *t*-BuNC (**2a**), affording the corresponding pure *N*-acyl carbodiimides



Scheme 5 Scope of the reaction giving *N*-acyl carbodiimides. *Reagents and conditions*: **1cx** (1 mmol), **2a** (1.1 mmol), $Pd_2(dba)_3$ (0.025 mmol), dioxane (4 mL), r.t., 5 h; yield of isolated product.

5a–g in moderate isolated yields. Unfortunately, the purification of *N*-acyl carbodiimidies obtained from other isonitriles was not successful.

On the basis of the experimental results, a possible reaction mechanism is proposed as shown in Scheme 6. Initially, under the catalysis of $Pd_2(dba)_3$, **1aa** releases a molecule of nitrogen to produce intermediate **A**. **A** reacts with **2a** to form a ternary ring intermediate **B**. Then, reductive elimination of intermediate **B** liberates carbodiimide **C**; nucleophilic attack of aniline follows, generating product **4a**. The palladium catalyst is released, to continue participating in the reaction, thus completing the entire catalytic cycle.



Scheme 6 Possible mechanism

In summary, we have developed a novel, general, and efficient strategy to access *N*-sulfonyl-, *N*-phosphoryl-, and *N*-acyl-functionalized guanidines directly from azides, isonitriles, and amines in a tandem process, producing products with high value in the area of agrochemicals and pharmaceuticals. This protocol is characterized by needing only a single $Pd_2(dba)_3$ catalyst without any complicated ligand, proceeding under robust conditions, and showing a broad substrate scope and good functional-group tolerance. Notably, acyl azides could generally be applied successfully in this transformation, and the corresponding *N*-acyl carbodiimides could be isolated in moderate yields.

All reactions were performed in a glass vial under a nitrogen atmosphere. Anhydrous solvents were distilled on small scale with CaH_2 or sodium and stored under N_2.The boiling point of petroleum ether is between 60 °C and 90 °C. For chromatography, 200–300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded on Varian 300 or Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm relative to TMS (^1H, δ = 0), residual chloroform solvent (^{13}C, δ = 77.00), or DMSO (^1H, δ = 2.50; ^{13}C, δ = 39.52). IR spectra were recorded on a Nicolet AVATAR 330 FT-IR spectrophotometer. Mass spectra were obtained on a Waters Auto Purification LC/MS system. HMRS was carried out on a Bruker Apex IV FTMS spectrometer. All catalysts and ligands were purchased from Sigma-Aldrich. All alkyl isonitriles and benzyl isonitriles are commercially available, unless stated otherwise.

N-Sulfonyl Guanidine 4aq; Typical Procedure for the Synthesis of *N*-Acyl-, *N*-Sulfonyl-, and *N*-Phosphoryl Guanidines 4aa–cs

$Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), TsN_3 (40 mg, 0.2 mmol), $PhNH_2$ (23 mg, 0.24 mmol), and freshly distilled dioxane (2 mL) were added to a dry flask equipped with a magnetic stir bar. The flask was sealed, evacuated, and refilled with N_2. Then *t*-BuNC (18 mg, 0.22 mmol) was added and the reaction mixture was stirred at r.t. for 5 h. Once the reaction was completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (silica gel); this afforded the desired product **4aq**; yield: 67 mg (>98%).

Benzoyl Carbodiimide 5a; Typical Procedure

$Pd_2(dba)_3$ (22.8 mg, 0.025 mmol) and freshly distilled dioxane (5 mL) were added to a dry flask equipped with a magnetic stir bar. The flask was sealed, evacuated, and refilled with N_2. Then $PhCON_3$ (147 mg, 1 mmol) and *t*-BuNC (90 mg, 1.1 mmol) were added and the reaction mixture was stirred at r.t. for 5 h. Once the reaction was completed, the mixture was concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel); this afforded the desired product **5a**; yield: 135 mg (72%).

N-[(*tert*-Butylamino)(butylamino)methylene]benzenesulfonamide (4aa)

The title compound was prepared according to the typical procedure.

Yield: 62 mg (99%); colorless sticky liquid.

IR (neat): 1597, 1565, 1130, 1082, 747, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.98–7.72 (m, 2 H), 7.55–7.32 (m, 3 H), 7.18 (s, 1 H), 4.27 (s, 1 H), 3.02 (s, 2 H), 1.53–1.46 (m, 2 H), 1.42–1.15 (m, 11 H), 0.91 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.47, 144.04, 131.11, 128.36, 125.81, 52.76, 41.36, 30.78, 29.53, 19.89, 13.61.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{26}N_3O_2S$: 312.1746; found: 312.1756.

N-[(*tert*-Butylamino)(butylamino)methylene]-2-nitrobenzenesulfonamide (4ab)

The title compound was prepared according to the typical procedure.

Yield: 66 mg (92%); colorless sticky liquid.

IR (neat): 1567, 1531, 1350, 1177, 1081, 879, 676 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1 H), 8.34 (d, *J* = 8.1 Hz, 1 H), 8.22 (d, *J* = 7.7 Hz, 1 H), 7.71–7.67 (m, 1 H), 7.19 (s, 1 H), 4.54 (s, 1 H), 3.10 (s, 2 H), 1.55 (s, 2 H), 1.45–1.16 (m, 11 H), 0.91 (t, *J* = 6.4 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.60, 147.87, 146.20, 131.69, 129.97, 125.75, 121.05, 52.45, 41.49, 30.75, 29.52, 19.92, 13.63.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{25}N_4O_4S$: 357.1597; found: 357.1615.

N-[(*tert*-Butylamino)(butylamino)methylene]-3-nitrobenzenesulfonamide (4ac)

The title compound was prepared according to the typical procedure.

Yield: 68 mg (95%); yellow sticky liquid.

IR (neat): 1568, 1541, 1367, 1180, 1107, 744, 664 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1 H), 8.34 (d, *J* = 8.1 Hz, 1 H), 8.22 (d, *J* = 7.7 Hz, 1 H), 7.71–7.67 (m, 1 H), 7.19 (s, 1 H), 4.54 (s, 1 H), 3.10 (s, 2 H), 1.55 (s, 2 H), 1.45–1.16 (m, 11 H), 0.91 (t, *J* = 6.4 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.63, 147.44, 137.50, 132.06, 131.80, 129.67, 123.81, 52.31, 41.67, 30.84, 29.54, 19.97, 13.71.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{25}N_4O_4S$: 357.1597; found: 357.1586.

N-[(*tert*-Butylamino)(butylamino)methylene]-4-nitrobenzenesulfonamide (4ad)

The title compound was prepared according to the typical procedure.

Yield: 60 mg (90%); white solid; mp 105–106 °C.

IR (neat): 1567, 1528, 1348, 1178, 1130, 1083, 745, 689 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.43–8.19 (m, 2 H), 8.13–7.92 (m, 2 H), 7.17 (s, 1 H), 4.52 (s, 1 H), 3.09 (dd, *J* = 12.5, 6.8 Hz, 2 H), 1.55 (s, 2 H), 1.45–1.22 (m, 11 H), 0.92 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.58, 150.00, 149.19, 127.09, 123.85, 52.46, 41.50, 30.86, 29.52, 19.90, 13.60.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{25}N_4O_4S$: 357.1597; found: 357.1603.

N-[(*tert*-Butylamino)(butylamino)methylene]-4-fluorobenzenesulfonamide (4ae)

The title compound was prepared according to the typical procedure.

Yield: 63 mg (96%); white solid; mp 93–94 °C.

IR (neat): 1592, 1565, 1364, 1225, 1130, 1081, 835, 681 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 7.80–7.76 (m, 2 H), 7.37–7.32 (m, 2 H), 6.76 (s, 1 H), 3.13 (dd, *J* = 12.7, 6.6 Hz, 2 H), 1.37–1.30 (m, 2 H), 1.25 (s, 9 H), 1.20–1.10 (m, 2 H), 0.81 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 163.37 (d, *J* = 248.7 Hz), 154.32, 140.62 (d, *J* = 3.1 Hz), 128.27 (d, *J* = 9.2 Hz), 115.65 (d, *J* = 22.4 Hz), 51.43, 40.70, 30.88, 28.98, 19.17, 13.58.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{25}FN_3O_2S$: 330.1652; found: 330.1658.

4-Bromo-*N*-[(*tert*-butylamino)(butylamino)methylene]benzenesulfonamide (4af)

The title compound was prepared according to the typical procedure.

Yield: 72 mg (92%); white solid; mp 130–131 °C.

IR (neat): 1594, 1566, 1262, 1128, 1081, 756, 661 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 7.72 (d, *J* = 8.4 Hz, 2 H), 7.66 (d, *J* = 7.6 Hz, 2 H), 6.76 (s, 1 H), 3.13 (dd, *J* = 12.6, 6.2 Hz, 2 H), 1.32 (dd, *J* = 14.6, 7.1 Hz, 2 H), 1.26 (s, 9 H), 1.13 (dd, *J* = 14.8, 7.4 Hz, 2 H), 0.80 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 154.33, 143.45, 131.72, 127.60, 124.77, 51.52, 40.76, 30.89, 29.01, 19.20, 13.60.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{25}BrN_3O_2S$: 390.0845; found: 390.0840.

N-[(*tert*-Butylamino)(butylamino)methylene]-4-(trifluoromethyl)benzenesulfonamide (4ag)

The title compound was prepared according to the typical procedure.

Yield: 63 mg (83%); white solid; mp 106–107 °C.

IR (neat): 1593, 1567, 1323, 1130, 1062, 713, 653 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 7.94 (d, *J* = 8.6 Hz, 2 H), 7.90 (d, *J* = 8.7 Hz, 2 H), 6.80 (s, 1 H), 3.14 (dd, *J* = 12.6, 6.6 Hz, 2 H), 1.34–1.28 (m, 2 H), 1.26 (s, 9 H), 1.14–1.07 (m, 2 H), 0.77 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 154.34, 147.92, 131.14 (q, *J* = 31.9 Hz), 126.44, 125.93 (q, *J* = 3.6 Hz), 123.66 (q, *J* = 272.5 Hz), 51.56, 40.76, 30.89, 28.95, 19.12, 13.50.

HRMS (ESI): *m*/*z* [M + H]$^+$ $C_{16}H_{25}F_3N_3O_2S$: 380.1620; found: 380.1627.

N-[(*tert*-Butylamino)(butylamino)methylene]-4-methoxybenzenesulfonamide (4ah)

The title compound was prepared according to the typical procedure.

Yield: 65 mg (96%); white solid; mp 98–100 °C.

IR (neat): 1595, 1564, 1254, 1172, 1128, 1082, 831, 678 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 7.65 (dd, *J* = 8.8, 1.9 Hz, 2 H), 7.02 (dd, *J* = 8.8, 2.0 Hz, 2 H), 6.73 (s, 1 H), 3.79 (s, 3 H), 3.12 (dd, *J* = 11.8, 5.6 Hz, 2 H), 1.35 (m, 2 H), 1.25 (s, 9 H), 1.20–1.13 (m, 2 H), 0.82 (t, *J* = 6.6 Hz, 3 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 161.68, 154.31, 136.79, 127.92, 114.18, 55.96, 51.87, 41.18, 31.40, 29.52, 19.71, 14.11.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{28}N_3O_3S$: 342.1851; found: 342.1858.

N-[(*tert*-Butylamino)(butylamino)methylene]thiophene-2-sulfonamide (4ai)

The title compound was prepared according to the typical procedure.

Yield: 61 mg (97%); white solid; mp 82–83 °C.

IR (neat): 2966, 1593, 1567, 1406, 1223, 1053, 679 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.50 (m, 1 H), 7.43–7.41 (m, 1 H), 7.09 (s, 1 H), 7.00–6.97 (m, 1 H), 3.06 (s, 2 H), 1.56–1.49 (m, 2 H), 1.45–1.23 (m, 11 H), 0.90 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.34, 145.53, 128.95, 128.76, 126.15, 51.98, 41.10, 30.57, 29.21, 19.50, 13.28.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{24}N_3O_2S_2$: 318.1310; found: 318.1305.

N-{(*tert*-Butylamino)[(4-methoxyphenyl)amino]methylene}butane-1-sulfonamide (4aj)

The title compound was prepared according to the typical procedure.

Yield: 63 mg (92%); white solid; mp 77–78 °C.

IR (neat): 1600, 1511, 1366, 1250, 1131, 1086, 820 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 6.90 (d, *J* = 8.6 Hz, 2 H), 4.43 (s, 1 H), 3.80 (s, 3 H), 3.10–3.03 (m, 2 H), 1.91–1.81 (m, 2 H), 1.50–1.43 (m, 2 H), 1.31 (s, 9 H), 0.94 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.88, 153.88, 128.08, 115.31, 55.58, 54.66, 52.35, 29.26, 25.91, 21.74, 13.81.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{28}N_3O_3S$: 342.1851; found: 342.1843.

N-{(*tert*-Butylamino)[(4-methoxyphenyl)amino]methylene}-1-phenylmethanesulfonamide (4ak)

The title compound was prepared according to the typical procedure.

Yield: 53 mg (70%); white solid; mp 154–155 °C.

IR (neat): 1595, 1511, 1362, 1248, 1145, 1089, 792, 704 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 1 H), 7.52–7.42 (m, 2 H), 7.41–7.31 (m, 3 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 6.74 (d, *J* = 7.8 Hz, 2 H), 4.32 (s, 2 H), 4.23 (s, 1 H), 3.79 (s, 3 H), 1.29 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.90, 154.39, 131.16, 130.91, 128.48, 128.24, 127.71, 115.15, 60.86, 55.59, 52.40, 29.37.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{26}N_3O_3S$: 376.1695; found: 376.1720.

N-{(Butylamino)[(4-methoxyphenyl)amino]methylene}toluenesulfonamide (4al)[10f]

The title compound was prepared according to the typical procedure.

Yield: 60 mg (80%); yellow sticky liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (s, 1 H), 7.83 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.06 (d, *J* = 8.7 Hz, 2 H), 6.90 (d, *J* = 8.6 Hz, 2 H), 4.61 (s, 1 H), 3.80 (s, 3 H), 3.25 (dd, *J* = 12.9, 7.0 Hz, 2 H), 2.41 (s, 3 H), 1.40–1.33 (m, 2 H), 1.24–1.14 (m, 2 H), 0.83 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.18, 154.80, 141.91, 141.14, 129.18, 128.37, 127.44, 126.04, 115.33, 55.60, 41.24, 31.54, 21.53, 19.87, 13.75.

N-{(Benzylamino)[(4-methoxyphenyl)amino]methylene}toluenesulfonamide (4am)

The title compound was prepared according to the typical procedure.

Yield: 26 mg (32%); yellow sticky liquid.

IR (neat): 1557, 1511, 1364, 1248, 1129, 1091, 811, 676 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (s, 1 H), 7.72 (d, *J* = 8.2 Hz, 2 H), 7.20 (d, *J* = 8.2 Hz, 5 H), 7.13–6.98 (m, 4 H), 6.86 (d, *J* = 8.5 Hz, 2 H), 5.08 (s, 1 H), 4.44 (d, *J* = 5.6 Hz, 2 H), 3.75 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.10, 154.70, 141.91, 140.80, 137.70, 129.13, 128.60, 128.25, 127.46, 127.21, 127.37, 125.97, 115.29, 55.50, 45.10, 21.47.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{24}N_3O_3S$: 410.1538; found: 410.1559.

N-{[(4-Chlorophenyl)amino][(4-methoxyphenyl)amino]methylene}toluenesulfonamide (4an)

The title compound was prepared according to the typical procedure.

Yield: 78 mg (91%); pale yellow solid; mp 157–158 °C.

IR (neat): 1608, 1541, 1509, 1248, 1138, 1095, 829, 687 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 1 H), 7.82 (d, *J* = 7.5 Hz, 2 H), 7.37–7.11 (m, 8 H), 6.93 (d, *J* = 8.3 Hz, 2 H), 3.82 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.15, 152.10, 142.35, 140.41, 134.78, 130.80, 129.28, 129.08, 127.79, 127.18, 126.01, 124.08, 115.27, 55.54, 21.47.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{21}ClN_3O_3S$: 430.0987; found: 430.0986.

N-{[(4-Cyanophenyl)amino][(4-methoxyphenyl)amino]methylene}toluenesulfonamide (4ao)

The title compound was prepared according to the typical procedure.

Yield: 69 mg (82%); white solid; mp 175–177 °C.

IR (neat): 1614, 1509, 1250, 1139, 1097, 838, 663 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.05 (s, 1 H), 7.84 (d, *J* = 7.9 Hz, 2 H), 7.50 (d, *J* = 8.2 Hz, 2 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.18 (d, *J* = 8.5 Hz, 2 H), 6.97 (d, *J* = 8.2 Hz, 2 H), 6.63 (s, 1 H), 3.83 (d, *J* = 0.9 Hz, 3 H), 2.43 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.75, 151.60, 142.90, 140.83, 140.08, 133.05, 129.56, 128.47, 126.55, 126.15, 121.50, 118.64, 115.71, 107.68, 55.70, 21.64.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}N_4O_3S$: 421.1334; found: 421.1331.

N-{Bis[(4-methoxyphenyl)amino]methylene}toluenesulfonamide (4ap)

The title compound was prepared according to the typical procedure.

Yield: 79 mg (93%); yellow solid; mp 154–155 °C.

IR (neat): 1597, 1247, 1101, 830, 805 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.80 (m, 2 H), 7.28 (s, 2 H), 7.17–7.11 (m, 4 H), 6.86 (d, *J* = 8.1 Hz, 4 H), 3.79 (d, *J* = 1.6 Hz, 6 H), 2.41 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.21, 152.76, 142.06, 140.69, 129.18, 128.22, 126.47, 125.99, 114.66, 55.48, 21.46.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{24}N_3O_4S$: 426.1488; found: 426.1494.

N-[(*tert*-Butylamino)(phenylamino)methylene]toluenesulfonamide (4aq)

The title compound was prepared according to the typical procedure.

Yield: 66 mg (>98%); white solid; mp 80–81 °C.

IR (neat): 1712, 1580, 1361, 1140, 1072, 750, 653 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (s, 1 H), 7.84 (dd, *J* = 8.3, 1.8 Hz, 2 H), 7.44–7.37 (m, 2 H), 7.28 (ddd, *J* = 9.0, 7.3, 0.8 Hz, 3 H), 7.12 (d, *J* = 7.5 Hz, 2 H), 4.69 (s, 1 H), 2.40 (s, 3 H), 1.30 (d, *J* = 2.1 Hz, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.01, 141.91, 141.05, 135.83, 130.24, 129.22, 127.38, 125.99, 125.67, 52.66, 29.25, 21.55.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{24}N_3O_2S$: 346.1589; found: 346.1614.

N-[(*tert*-Butylamino)(1-naphthylamino)methylene]toluenesulfonamide (4ar)

The title compound was prepared according to the typical procedure.

Yield: 69 mg (87%); white solid; mp 142–143 °C.

IR (neat): 1712, 1548, 1356, 1221, 1142, 1082, 802, 714 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.08 (s, 1 H), 8.12–7.83 (m, 4 H), 7.71 (d, *J* = 8.1 Hz, 1 H), 7.68–7.29 (m, 7 H), 4.43 (s, 1 H), 2.44 (s, 3 H), 1.22 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.76, 142.05, 141.15, 134.73, 131.50, 129.78, 129.33, 128.85, 128.62, 127.45, 127.19, 126.31, 125.72, 124.99, 122.37, 52.67, 29.23, 21.63.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{26}N_3O_2S$: 396.1746; found: 396.1745.

N-(*tert*-Butyl)-*N*′-tosylmorpholine-4-carboximidamide (4as)

The title compound was prepared according to the typical procedure.

Yield: 66 mg (98%); white solid; mp 178–179 °C.

IR (neat): 1561, 1512, 1276, 1138, 1083, 885, 712 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 7.9 Hz, 2 H), 5.29 (s, 1 H), 3.78–3.73 (m, 4 H), 3.53–3.46 (m, 4 H), 2.39 (s, 3 H), 1.18 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.49, 141.48, 141.45, 128.90, 125.79, 66.15, 53.99, 49.19, 29.60, 21.29.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{26}N_3O_3S$: 340.1705; found: 340.1703.

N-[(*tert*-Butylamino)(cyanamido)methylene]toluenesulfonamide (4at)[10f]

The title compound was prepared according to the typical procedure.

Yield: 54 mg (92%); white solid; mp 182–184 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.57 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 7.9 Hz, 2 H), 6.80 (s, 1 H), 3.75 (s, 1 H), 2.33 (s, 3 H), 1.18 (s, 9 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 160.88, 142.71, 140.43, 128.84, 125.56, 50.54, 28.87, 20.92.

Diphenyl [(*tert*-Butylamino)(phenylamino)methylene]phosphoramidate (4ba)[10f]

The title compound was prepared according to the typical procedure.

Yield: 76 mg (90%); pale yellow solid; mp 184–185 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1 H), 7.39–7.24 (m, 10 H), 7.21 (d, *J* = 7.3 Hz, 1 H), 7.12 (dd, *J* = 7.1, 3.5 Hz, 2 H), 7.06 (d, *J* = 7.8 Hz, 2 H), 4.69 (s, 1 H), 1.12 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.72 (d, *J* = 8.0 Hz), 151.55 (d, *J* = 7.3 Hz), 136.59, 129.76, 129.16, 126.41, 125.12, 124.11, 120.62 (d, *J* = 4.7 Hz), 51.73, 28.70.

Diphenyl {[(2,6-Dimethylphenyl)amino](phenylamino)methylene}phosphoramidate (4bb)

The title compound was prepared according to the typical procedure.

Yield: 77 mg (82%); white solid; mp 138–140 °C.

IR (neat): 1622, 1585, 1488, 1197, 926, 773 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (s, 1 H), 7.49–6.72 (m, 17 H), 5.95 (s, 1 H), 2.16 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.45, 151.56, 151.46, 136.99 (d, *J* = 9.1 Hz), 132.76, 129.22, 128.58, 128.86, 124.60, 124.28, 122.07, 120.77 (d, *J* = 4.6 Hz), 17.90.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{27}N_3O_3P$: 472.1790; found: 472.1801.

Diphenyl [(*tert*-Butylamino)(butylamino)methylene]phosphoramidate (4bc)

The title compound was prepared according to the typical procedure.

Yield: 72 mg (89%); white solid; mp 67–68 °C.

IR (neat): 1616, 1592, 1489, 1202, 1162, 918, 774 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.16 (m, 8 H), 7.08 (dd, *J* = 9.0, 4.1 Hz, 2 H), 2.98 (s, 2 H), 1.45–1.44 (m, 2 H), 1.35–1.28 (m, 2 H), 1.19 (s, 9 H), 0.88 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.49 (d, *J* = 9.5 Hz), 151.68 (d, *J* = 7.2 Hz), 129.03, 123.82, 120.51 (d, *J* = 4.8 Hz), 51.28, 41.27, 30.84, 29.14, 19.81, 13.55.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{31}N_3O_3P$: 404.2103; found: 404.2101.

Dimethyl [(*tert*-Butylamino)(phenylamino)methylene]phosphoramidate (4bd)

The title compound was prepared according to the typical procedure.

Yield: 37 mg (63%); yellow sticky liquid.

IR (neat): 1624, 1542, 1364, 1205, 1038, 829, 784 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.34 (m, 2 H), 7.25–7.14 (m, 3 H), 4.77 (s, 1 H), 3.75 (d, *J* = 2.3 Hz, 3 H), 3.72 (d, *J* = 2.3 Hz, 3 H), 1.38 (d, *J* = 2.2 Hz, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.38 (d, *J* = 7.5 Hz), 137.10, 129.74, 126.07, 124.95, 52.72 (d, *J* = 6.2 Hz), 51.71, 29.03.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{23}N_3O_3P$: 300.1477; found: 300.1481.

N-[(*tert*-Butylamino)(phenylamino)methylene]benzamide (4ca)[14]

The title compound was prepared according to the typical procedure.

Yield: 54 mg (92%); white solid; mp 96–97 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.08 (d, *J* = 7.2 Hz, 2 H), 7.53–7.36 (m, 5 H), 7.33 (d, *J* = 7.7 Hz, 2 H), 7.24–7.16 (m, 1 H), 1.49 (s, 9 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 175.02, 157.26, 138.68, 137.38, 131.04, 129.40, 128.42, 127.98, 125.12, 123.70, 51.70, 29.11.

N-[(*tert*-Butylamino)(phenylamino)methylene]-4-methylbenzamide (4cb)

The title compound was prepared according to the typical procedure.

Yield: 53 mg (86%); white solid; mp 118–119 °C.

IR (neat): 1577, 1352, 1217, 900, 772, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.18 (s, 1 H), 8.21–8.11 (m, 2 H), 7.44–7.36 (m, 2 H), 7.30–7.16 (m, 5 H), 4.89 (s, 1 H), 2.40 (s, 3 H), 1.50 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.25, 157.92, 141.34, 136.63, 136.30, 130.06, 129.13, 128.68, 126.53, 125.14, 52.37, 29.67, 21.61.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{24}N_3O$: 310.1919; found: 310.1926.

4-Bromo-*N*-[(*tert*-butylamino)(phenylamino)methylene]benzamide (4cc)

The title compound was prepared according to the typical procedure.

Yield: 67 mg (89%); white solid; mp 121–122 °C.

IR (neat): 1576, 1393, 1352, 1009, 897, 774 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.10 (s, 1 H), 8.12 (d, *J* = 8.3 Hz, 2 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.46–7.36 (m, 2 H), 7.33–7.17 (m, 3 H), 4.93 (s, 1 H), 1.49 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.11, 158.09, 137.93, 136.30, 131.11, 130.71, 130.13, 126.80, 125.84, 125.25, 52.47, 29.67.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{21}BrN_3O$: 374.0868; found: 374.0870.

N-[(*tert*-Butylamino)(phenylamino)methylene]-4-methoxybenzamide (4cd)

The title compound was prepared according to the typical procedure.

Yield: 62 mg (96%); pale yellow solid; mp 98–99 °C.

IR (neat): 1568, 1352, 1250, 1220, 1140, 768 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.13 (s, 1 H), 8.28–8.19 (m, 2 H), 7.44–7.33 (m, 2 H), 7.27–7.17 (m, 3 H), 6.97–6.88 (m, 2 H), 4.91 (s, 1 H), 3.83 (s, 3 H), 1.49 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.80, 162.09, 157.72, 136.64, 131.64, 130.89, 130.01, 126.44, 125.07, 113.10, 55.31, 52.27, 29.63.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{24}N_3O_2$: 326.1869; found: 326.1869.

N-[(*tert*-Butylamino)(phenylamino)methylene]-4-cyanobenzamide (4ce)

The title compound was prepared according to the typical procedure.

Yield: 58 mg (91%); white solid; mp 146–148 °C.

IR (neat): 1713, 1577, 1357, 1221, 782, 705 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.04 (s, 1 H), 8.36–8.29 (m, 2 H), 7.75–7.66 (m, 2 H), 7.50–7.40 (m, 2 H), 7.34–7.21 (m, 3 H), 4.99 (s, 1 H), 1.50 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.88, 158.33, 143.00, 135.95, 131.82, 130.19, 129.42, 127.05, 125.32, 118.94, 114.06, 52.61, 29.64.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{21}N_4O$: 321.1715; found: 321.1717.

N-[(*tert*-Butylamino)(phenylamino)methylene]-2-naphthamide (4cf)

The title compound was prepared according to the typical procedure.

Yield: 59 mg (86%); white solid; mp 86–88 °C.

IR (neat): 1578, 1367, 1339, 1223, 791, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.26 (s, 1 H), 8.81 (s, 1 H), 8.36 (dd, *J* = 8.6, 1.4 Hz, 1 H), 7.98 (d, *J* = 7.4 Hz, 1 H), 7.91–7.81 (m, 2 H), 7.55–7.45 (m, 2 H), 7.43–7.40 (m, 2 H), 7.25 (dd, *J* = 12.9, 4.3 Hz, 3 H), 4.95 (s, 1 H), 1.55 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.05, 157.90, 136.40, 136.26, 134.84, 132.78, 129.97, 129.65, 129.32, 127.53, 127.30, 127.00, 126.50, 125.83, 125.81, 125.06, 52.33, 29.59.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{24}N_3O$: 346.1919; found: 346.1930.

N-[(*tert*-Butylamino)(phenylamino)methylene]furan-2-carboxamide (4cg)

The title compound was prepared according to the typical procedure.

Yield: 53 mg (93%); white solid; mp 78–79 °C.

IR (neat): 1578, 1474, 1396, 1355, 1220, 867, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.66 (s, 1 H), 7.54 (s, 1 H), 7.46–7.36 (m, 2 H), 7.28–7.22 (m, 3 H), 7.12 (d, *J* = 3.3 Hz, 1 H), 6.48–6.46 (m, 1 H), 4.89 (s, 1 H), 1.47 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.69, 157.73, 152.98, 144.82, 136.31, 130.06, 126.70, 125.22, 114.52, 111.40, 52.52, 29.57.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{20}N_3O_2$: 286.1556; found: 286.1566.

N-[(*tert*-Butylamino)(phenylamino)methylene]quinoline-6-carboxamide (4ch)

The title compound was prepared according to the typical procedure.

Yield: 66 mg (96%); white solid; mp 112–114 °C.

IR (neat): 1578, 1460, 1366, 1214, 797, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.09 (s, 1 H), 8.87–8.77 (m, 1 H), 8.64 (s, 1 H), 8.49 (d, *J* = 8.8 Hz, 1 H), 8.14 (d, *J* = 7.6 Hz, 1 H), 8.03 (d, *J* = 8.8 Hz, 1 H), 7.33–7.24 (m, 3 H), 7.20–7.09 (m, 3 H), 4.90 (s, 1 H), 1.43 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.99, 157.90, 151.09, 149.35, 137.20, 136.81, 136.03, 129.85, 129.42, 129.26, 128.57, 127.37, 126.51, 124.94, 120.96, 52.25, 29.44.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}N_4O$: 347.1872; found: 347.1886.

N-[(Cyclohexylamino)(phenylamino)methylene]benzamide (4ci)

The title compound was prepared according to the typical procedure.

Yield: 49 mg (76%); white solid; mp 112–113 °C.

IR (neat) 1589, 1361, 1221, 753, 712 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.10 (s, 1 H), 8.26 (d, *J* = 6.9 Hz, 2 H), 7.51–7.34 (m, 5 H), 7.34–7.17 (m, 3 H), 4.84 (s, 1 H), 4.16 (s, 1 H), 2.05 (d, *J* = 10.6 Hz, 2 H), 1.67 (dd, *J* = 33.1, 13.0 Hz, 3 H), 1.43 (dd, *J* = 23.8, 11.9 Hz, 2 H), 1.27–1.08 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.56, 157.85, 138.80, 136.35, 131.15, 130.10, 129.12, 127.92, 126.71, 125.25, 50.24, 33.19, 25.62, 24.86.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{24}N_3O$: 322.1919; found: 322.1923.

N-[(Cyclohexylamino)(phenylamino)methylene]-3-methylbenzamide (4cj)

The title compound was prepared according to the typical procedure.

Yield: 62 mg (93%); green sticky liquid.

IR (neat) 1570, 1498, 1449, 1360, 756, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.11 (s, 1 H), 8.06 (s, 2 H), 7.42 (t, *J* = 7.5 Hz, 2 H), 7.35–7.15 (m, 5 H), 4.82 (s, 1 H), 4.15 (s, 1 H), 2.41 (s, 3 H), 2.06 (d, *J* = 9.9 Hz, 2 H), 1.83–1.56 (m, 3 H), 1.44 (dd, *J* = 24.1, 12.1 Hz, 2 H), 1.32–1.09 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.62, 157.67, 138.63, 137.28, 136.27, 131.78, 129.92, 129.64, 127.70, 126.53, 126.18, 125.06, 50.14, 33.06, 25.52, 24.73, 21.43.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{26}N_3O$: 336.2076; found: 336.2052.

N-[(Cyclohexylamino)(phenylamino)methylene]-4-methylbenzamide (4ck)

The title compound was prepared according to the typical procedure.

Yield: 60 mg (90%); white solid; mp 110–113 °C.

IR (neat) 1564, 1359, 1140, 755, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.12 (s, 1 H), 8.15 (d, *J* = 6.4 Hz, 2 H), 7.41 (t, *J* = 7.1 Hz, 2 H), 7.23 (dd, *J* = 14.9, 4.8 Hz, 4 H), 4.81 (s, 1 H), 4.30–3.96 (m, 1 H), 2.40 (s, 2 H), 2.12–2.00 (m, 2 H), 1.67 (dd, *J* = 32.8, 12.8 Hz, 2 H), 1.43 (dd, *J* = 23.3, 11.5 Hz, 2 H), 1.32–1.09 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.48, 157.60, 141.26, 137.66, 136.02, 129.89, 129.02, 128.53, 126.46, 125.05, 50.05, 33.04, 25.50, 24.71, 21.48.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{26}N_3O$: 336.2076; found: 336.2066.

4-Chloro-*N*-[(cyclohexylamino)(phenylamino)methylene]benzamide (4cl)

The title compound was prepared according to the typical procedure.

Yield: 58 mg (82%); white solid; mp 121–123 °C.

IR (neat) 1564, 1397, 1359, 776, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.03 (s, 1 H), 8.09 (d, *J* = 81.3 Hz, 2 H), 7.73–6.90 (m, 6 H), 4.85 (s, 1 H), 4.12 (s, 1 H), 2.08 (t, *J* = 23.6 Hz, 2 H), 1.81–1.55 (m, 3 H), 1.43 (d, *J* = 7.6 Hz, 2 H), 1.19 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.33, 157.77, 137.20, 137.12, 135.99, 130.43, 130.05, 128.00, 126.78, 125.23, 50.17, 33.05, 25.46, 24.72.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}ClN_3O$: 356.1530; found: 356.1512.

4-Bromo-*N*-[(cyclohexylamino)(phenylamino)methylene]benzamide (4cm)

The title compound was prepared according to the typical procedure.

Yield: 71 mg (89%); white solid; mp 115–116 °C.

IR (neat) 1563, 1395, 1359, 774, 696 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.02 (s, 1 H), 8.10 (d, *J* = 7.6 Hz, 2 H), 7.54 (d, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7.2 Hz, 1 H), 7.27 (dd, *J* = 11.4, 4.5 Hz, 2 H), 4.84 (s, 1 H), 4.12 (s, 1 H), 2.03 (d, *J* = 10.2 Hz, 2 H), 1.67 (dd, *J* = 30.4, 12.5 Hz, 3 H), 1.42 (dd, *J* = 23.6, 11.7 Hz, 2 H), 1.21 (d, *J* = 33.6 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.40, 157.74, 137.65, 132.89, 130.97, 130.66, 130.03, 126.79, 125.79, 125.21, 50.16, 33.03, 25.45, 24.70.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}BrN_3O$: 400.1024; found: 400.1014.

N-[(Cyclohexylamino)(phenylamino)methylene]-4-methoxybenzamide (4cn)

The title compound was prepared according to the typical procedure.

Yield: 67 mg (95%); white solid; mp 87–88 °C.

IR (neat) 1565, 1359, 1249, 784, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.11 (s, 1 H), 8.21 (d, *J* = 7.6 Hz, 2 H), 7.41 (t, *J* = 7.3 Hz, 2 H), 7.26 (d, *J* = 1.7 Hz, 2 H), 6.91 (d, *J* = 7.7 Hz, 2 H), 4.79 (s, 1 H), 4.13 (s, 1 H), 3.84 (s, 2 H), 2.05 (d, *J* = 10.7 Hz, 2 H), 1.67 (dd, *J* = 33.4, 12.7 Hz, 3 H), 1.43 (dd, *J* = 23.9, 11.9 Hz, 2 H), 1.27–1.09 (m, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.12, 162.04, 157.47, 156.68, 131.42, 130.85, 129.86, 126.31, 125.02, 112.98, 55.24, 50.03, 33.06, 25.50, 24.73.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{26}N_3O_2$: 352.2025; found: 352.2015.

***N*-[(Benzylamino)(phenylamino)methylene]benzamide (4co)[7f]**

The title compound was prepared according to the typical procedure.

Yield: 46 mg (70%); colorless sticky liquid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.97 (s, 1 H), 8.93 (s, 1 H), 8.05 (s, 2 H), 7.58–7.32 (m, 11 H), 7.25 (d, *J* = 17.8 Hz, 2 H), 4.68 (d, *J* = 5.2 Hz, 2 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 175.62, 158.29, 138.59, 130.98, 128.61, 128.47, 128.43, 128.27, 127.86, 127.31, 127.05, 124.40, 44.48.

N-{[(2,6-Dimethylphenyl)amino](phenylamino)methylene}benzamide (4cp)

The title compound was prepared according to the typical procedure.

Yield: 38 mg (56%); white solid; mp 137–140 °C.

IR (neat): 1605, 1567, 1446, 1353, 753, 690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.04 (s, 1 H), 8.24 (d, *J* = 6.3 Hz, 2 H), 7.58–7.32 (m, 7 H), 7.26–7.09 (m, 4 H), 6.09 (s, 1 H), 2.36 (s, 6 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.48, 157.49, 138.18, 137.21, 136.56, 132.54, 131.34, 129.24, 129.12, 128.63, 127.91, 124.63, 122.83, 18.29.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{22}N_3O$: 344.1763; found: 344.1757.

***N*-[Bis(*tert*-butylamino)methylene]benzamide (4cq)[15]**

The title compound was prepared according to the typical procedure.

Yield: 45 mg (82%); colorless sticky liquid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.68 (s, 1 H), 8.27–8.14 (m, 2 H), 7.47–7.32 (m, 3 H), 4.45 (s, 1 H), 1.49 (s, 18 H).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 176.23, 158.87, 139.41, 130.65, 128.84, 127.80, 51.70, 30.00.

***N*-[(*tert*-Butylamino)(2-pyridylamino)methylene]benzamide (4cr)[7b]**

The title compound was prepared according to the typical procedure.

Yield: 39 mg (65%); white solid; mp 89–92 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.45 (s, 1 H), 10.52 (s, 1 H), 8.31–8.24 (m, 2 H), 8.20 (d, *J* = 5.0 Hz, 1 H), 7.65–7.59 (m, 1 H), 7.49–7.40 (m, 3 H), 6.95–6.90 (m, 1 H), 6.87 (d, *J* = 8.3 Hz, 1 H), 1.63 (s, 9 H).

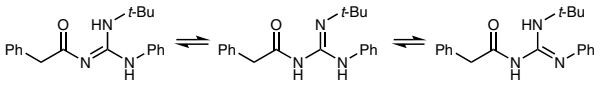
^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.73, 156.91, 153.27, 145.95, 138.95, 138.54, 131.20, 129.14, 127.99, 117.79, 113.87, 52.37, 29.55.

***N*-[(*tert*-Butylamino)(phenylamino)methylene]-2-phenylacetamide (4cs)**

The title compound was prepared according to the typical procedure.

Yield: 37 mg (61%); colorless sticky liquid.

Compound **4cs** exists in three different tautomeric forms according to the results of the ^{1}H NMR spectra recorded at different temperatures (Scheme 7, Figure 2). At 25 °C, the chemical shift of the H in tertiary butyl was δ = 1.31 and 1.36; that of H in methylene was δ = 3.49 and 3.54. At 50 °C, the chemical shift of H in tertiary butyl and methylene slightly centralized with δ = 1.32, 1.38 and δ = 3.51, 3.55. At 80 °C, H in methylene centralized to a single peak at δ = 3.54. In addition, UPLC-MS (ESI) results showed that only *m*/*z* [M + H]$^+$ = 310 was extracted, according to chromatography spectra.



Scheme 7

IR (neat): 1650, 1600, 1555, 1499, 1236, 698, 668 cm^{-1}.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{24}N_3O$: 310.1919; found: 310.1935.

***N*-[(*tert*-Butylimino)methylene]benzamide (5a)[10b]**

The title compound was prepared according to the typical procedure.

Yield: 145 mg (72%); pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17–8.05 (m, 2 H), 7.58–7.51 (m, 1 H), 7.45–7.39 (m, 2 H), 1.51 (s, 9 H).

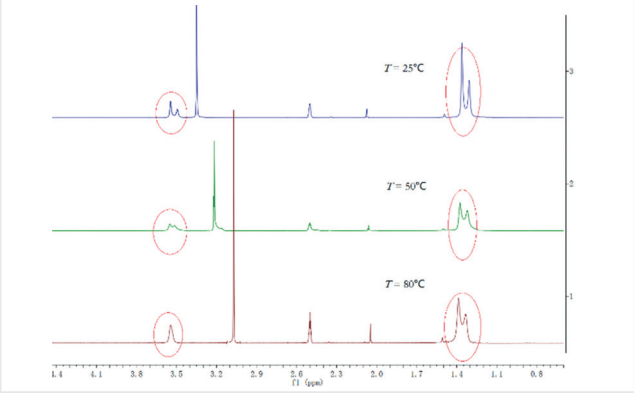


Figure 2

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.63, 133.89, 129.72, 128.21, 58.97, 31.33.

***N*-[(*tert*-Butylimino)methylene]-4-methylbenzamide (5b)[10f]**

The title compound was prepared according to the typical procedure.

Yield: 149 mg (69%); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (dd, *J* = 8.2, 1.8 Hz, 2 H), 7.22 (d, *J* = 6.9 Hz, 2 H), 2.39 (s, 3 H), 1.50 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.44, 143.78, 131.20, 129.79, 128.93, 58.87, 31.31, 21.60.

***N*-[(*tert*-Butylimino)methylene]-4-chlorobenzamide (5c)[10f]**

The title compound was prepared according to the typical procedure.

Yield: 132 mg (56%); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.4 Hz, 2 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 1.51 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.70, 139.38, 132.42, 131.09, 128.49, 59.07, 31.28.

***N*-[(*tert*-Butylimino)methylene]-4-(trifluoromethyl)benzamide (5d)[10f]**

The title compound was prepared according to the typical procedure.

Yield: 143 mg (53%); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.2 Hz, 2 H), 7.68 (d, *J* = 8.2 Hz, 2 H), 1.53 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.60, 137.11, 134.19 (q, *J* = 32.5 Hz), 129.98, 128.27, 125.20 (q, *J* = 3.7 Hz), 123.72 (q, *J* = 272.6 Hz), 59.19, 31.23.

***N*-[(*tert*-Butylimino)methylene]-4-methoxybenzamide (5e)[10f]**

The title compound was prepared according to the typical procedure.

Yield: 141 mg (61%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11–7.90 (m, 2 H), 6.93–6.86 (m, 2 H), 3.85 (s, 3 H), 1.49 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.79, 163.61, 131.89, 126.49, 113.41, 58.84, 55.35, 31.33.

***N*-[(*tert*-Butylimino)methylene]-2-naphthamide (5f)[10f]**

The title compound was prepared according to the typical procedure.

Yield: 136 mg (54%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (s, 1 H), 8.13 (d, *J* = 8.6 Hz, 1 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 8.6 Hz, 2 H), 7.57–7.47 (m, 2 H), 1.51 (s, 9 H) (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.58, 135.60, 132.42, 131.33, 131.14, 129.42, 128.11, 127.92, 127.60, 126.38, 125.30, 58.95, 31.27.

***N*-[(*tert*-Butylimino)methylene]thiophene-2-carboxamide (5g)[10f]**

The title compound was prepared according to the typical procedure.

Yield: 123 mg (59%); pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.76 (m, 1 H), 7.57–7.52 (m, 1 H), 7.12–7.04 (m, 1 H), 1.50 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.67, 139.32, 133.14, 132.98, 128.03, 59.04, 31.18.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588576.

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