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ORIGINAL PAPER

Expedient one-pot synthesis of *N*-aryliminoethers via mild electrophilic activation of secondary amides

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Abstract The direct transformation of various secondary amides into *N*-aryliminoethers via mild electrophilic activation with trifluoromethanesulfonic anhydride in the presence of 2-chloropyridine is described. Low temperature amide activation followed by warming to 0 °C and subsequent treatment with phenols provides the desired products with short overall reaction times and moderate to high reaction yields.

Keywords *N*-aryliminoethers · Trifluoromethanesulfonic anhydride · Electrophilic addition · One-pot synthesis · Nucleophilic substitution

Introduction

Aryliminoethers serve as starting materials in the Chapman rearrangement for the production of *N*,*N*-diarylamides [1–3]. The Beckmann rearrangement of ketoximes [4, 5] and addition of alcohols to imidoyl chlorides [6–9] have been reported as general methods for the production of iminoethers. The dehydration of secondary amides for the generation of imidoyl chlorides has generally been carried out by reaction with chlorinating reagents such as PCl_5, $SOCl_2$, and $POCl_3$ in excess at elevated temperatures or by treatment with Ph_3P/CCl_4 at room temperature [10]. Disadvantages of these methods are that the excess dehydrating agent- and reagent-derived by-products have to be removed. Moreover, pure imidoyl chlorides should be separated either by fractional distillation or precipitation under anhydrous conditions. An alternative method for the formation of of *N*-arylimidates includes the use of oxalyl chloride as chlorinating agent in the presence of 2,6-lutidine at 0 °C, which generates the imidoyl chlorides in situ without the formation of by-products [11]. Due to the low reactivity of imidoyl chlorides, stoichiometeric amounts of Lewis acids [12–14] or the use of more nucleophililic phenoxide anions [6–9] are required.

Nitrilium ions generated as intermediates under Beckmann rearrangement conditions or via activation of imidoyl chlorides with stoichiometeric amounts of Lewis acids play a key role in the production of imidates. A combination of Tf_2O and pyridine in the pioneering work of Charette and Grenon in their synthesis of amidines, thiazolines, thioamides, cyclic orthoesters, and esters has proven to be a useful reagent for the activation of amides and their subsequent conversion into other functional groups [15–20]. In 2006, Movassaghi developed an efficient method for the conversion of amides into highly electrophilic 2-chloropyridinium adducts by using a combination of Tf_2O and 2-chloropyridine [21], which enabled the synthesis of a variety of azaheterocycles [22–25]. In contrast to pyridine as a strong nucleophile, 2-chloropyridine was found not to add to Tf_2O.

Compared to the reported methods for the synthesis of *N*-arylimidates (vide supra), we considered that the development of new methodologies would allow the activation of a variety of amide substrates, including *N*-arylamides, without requiring the isolation of sensitive intermediates or the use of Lewis acid additives, and shortening reaction times without the need for elevated temperatures. Herein, we describe an expedient one-pot transformation of various secondary amides into *N*-arylimidates via mild electrophilic activation with Tf_2O in the presence of 2-chloropyridine.

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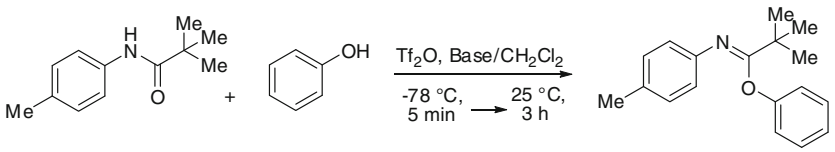
Results and discussion

Initially, we optimized the conditions for the synthesis of phenyl *N*-*p*-tolylpivalimidate (**3a**) from *N*-*p*-tolylpivalamide (**1a**) and phenol (**2a**) (Table 1). 2-Chloropyridine proved to be the best base and gave a 93% yield of **3a** (Table 1, entry 6). While base additives such as Et_3N and pyridine had no effect on the reaction progress (Table 1, entries 3, 4), other bases activated amide **1a** with moderate efficiencies (Table 1, entries 2, 5, and 8). An excess of 2-chloropyridine was found to have an inhibitory effect (Table 1, entry 8), perhaps by shifting the equilibrium away from **6**, the more active nitrilium intermediate, towards **5**, the less active amidinium intermediate, in order to counteract the increasing concentration of 2-chloropyridine (see Scheme 1). The reaction proceeds with less efficiency when using the Hendrickson reagent (Table 1, entry 8) [26]. Therefore, the superiority of Tf_2O/2-chloropyridine combination as an amide-activating agent is evident.

Identification of the products was confirmed by their analytical and spectral data. For example, no signals due to OH group were evident in the ^1H NMR and IR spectra of **3g**. Moreover, characteristic ^1H NMR signals appeared at $\delta = 1.21$ (s, 9H) and 1.44 (s, 9H) for two *t*-Bu groups together with two AB patterns at $\delta = 6.61$ (d, 2H, $J = 9.0$ Hz), 6.68 (d, 2H, $J = 6.8$ Hz), 7.06 (d, 2H, $J = 6.8$ Hz), and 7.85 (d, 2H, $J = 9.0$ Hz) because of aromatic protons.

We next explored the substrate scope with the optimal conditions with a variety of secondary amides and phenols.

Table 1 Effect of base on the direct conversion of amide **1a** to *N*-aryliminoether **3a** via mild electrophilic activation by Tf_2O



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

Entry	Base	Equiv	Yield/%[a]
1	None	–	41
2	K_2CO_3	1.2	43
3	Et_3N	1.2	0
4	Pyridine	1.2	0
5	2,6-Lutidine	1.2	73
6	2-Chloropyridine	1.2	93
7	2-Chloropyridine	2.0	85
8	Hendrickson reagent[b]	1.2	80

Reaction conditions: Amide (1.0 equiv), Tf_2O (1.1 equiv), 2-chloropyridine (1.2 equiv), CH_2Cl_2, −78 °C, 5 min, then 25 °C, 1 h

[a] Isolated yields

[b] Triphenylphosphonium anhydride trifluoromethanesulfonate was used without 2-chloropyridine at 0 °C

Scheme 1

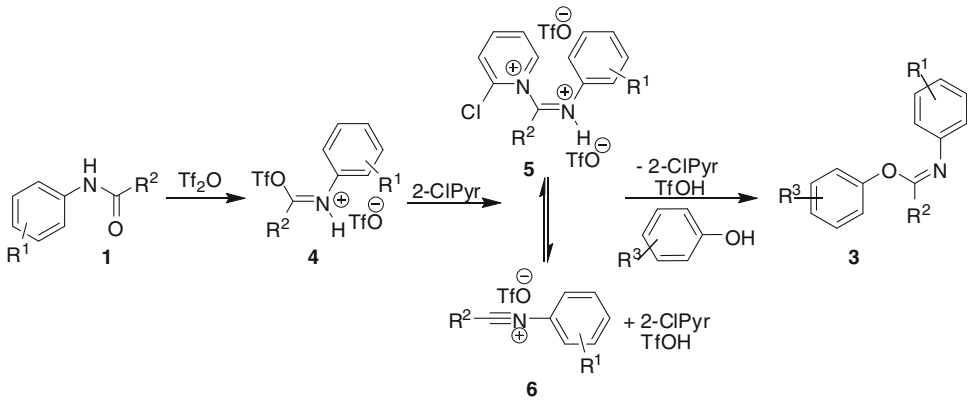
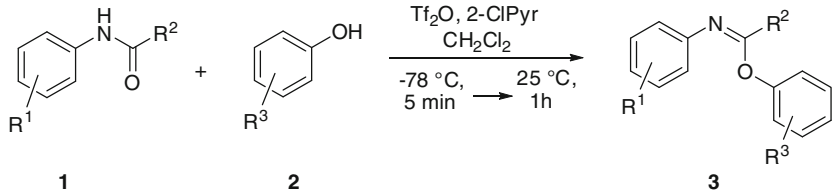


Table 2 Results obtained for the direct conversion of amides to *N*-aryliminoethers **3a–3o** via mild electrophilic activation by Tf_2O

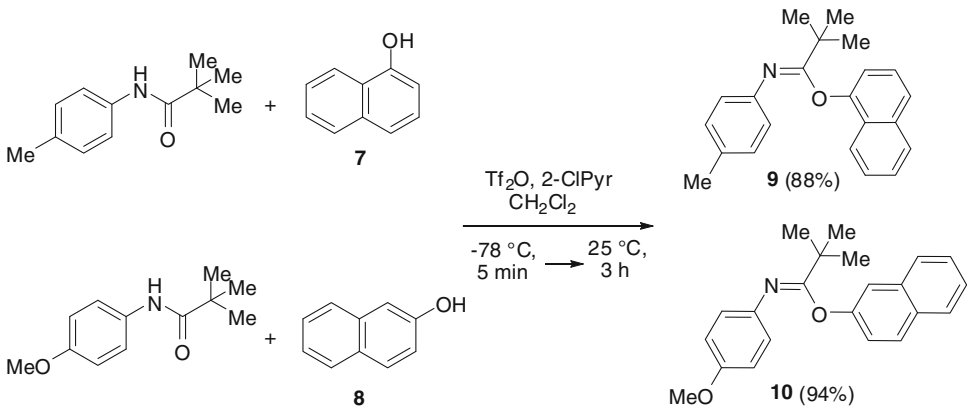


Entry	R^1	R^2	R^3	Product	Yield/%[a]
1	4-Me–	*t*-Bu–	H–	**3a**	93
2	3,4-$(Me)_2$–	*t*-Bu–	H–	**3b**	92
3	4-Cl–	*t*-Bu–	4-NO_2–	**3c**	78
4	4-Cl–	*t*-Bu–	H–	**3d**	65
5	4-Me–	*t*-Bu–	4-*t*-Bu–	**3e**	98
6	4-NO_2–	*t*-Bu–	4-*t*-Bu–	**3f**	80
7	4-Cl–	*t*-Bu–	4-*t*-Bu–	**3g**	92
8	4-OMe–	*t*-Bu–	2,4-$(Cl)_2$–	**3h**	78
9	3,4-$(Me)_2$–	*t*-Bu–	4-NO_2–	**3i**	67
10	4-Cl–	*t*-Bu–	2,4-$(Cl)_2$–	**3j**	71
11	4-MeO–	*t*-Bu–	H–	**3k**	96
12	H–	C_6H_{11}	2,4-$(Cl)_2$–	**3l**	80
13	4-Me–	Ph–	4-*t*-Bu–	**3m**	62
14	4-Cl–	Ph–	4-*t*-Bu–	**3n**	58
15	4-OMe–	Ph–	H–	**3o**	65

Reaction conditions: Amide (1.0 equiv), Tf_2O (1.1 equiv), 2-chloropyridine (1.2 equiv), CH_2Cl_2, −78 °C, 5 min, then 25 °C, 1 h

[a] Isolated products

Scheme 2



Results are presented in Table 2. Inspection of the results presented in Table 2 reveals that substrates with electron donating as well as electron withdrawing groups were tolerated in the reaction. While relatively electron-rich pivalamides afford the corresponding *N*-aryliminoethers with 92–98% yields (Table 2, entries 1, 2, 5), reaction of relatively electron-deficient benzamides proceeds to the products less efficiently (Table 2, entries 13, 14, 15). Whereas relatively electron-rich pivalamides in reaction with relatively electron-deficient phenols gave *N*-aryliminoethers in lower yields (Table 2, entries 8, 9), reactions of electron-deficient benzamides with electron-rich phenols proceeded in good to high yields (Table 2, entry 13).

To rationalize the reaction results, the previously suggested reaction pathway depicted in Scheme 1 seems to be operative in our method. As illustrated in Scheme 1,

activation of amides **1** affords the imidoyl triflate **4**. Subsequent addition of 2-chloropyridine to **4** gives the pyridinium adduct **5**. This species is believed to be in equilibrium with the nitrilium ion **6**, a more powerful electrophile [23–26]. Electron-rich amides with higher propensity to form a nitrilium ion upon activation with Tf_2O/2-chloropyridine combination are expected to give the highest yields. On the other hand, electron-deficient amides reluctant to form the corresponding nitrilium ion under the reaction conditions also afford the lowest yields, likely owing to the inductive effect of the nitrogen substituent.

Finally, we examined the effect of 1- and 2-naphthol on reaction efficiency (Scheme 2). Reactions with 1-naphthol (**7**) and 2-naphthol (**8**) proceeded similarly to those with phenols affording the corresponding *N*-arylimidates **9** and **10** in 88 and 94% yields, respectively.

In conclusion, we have developed a new and expedient one-pot procedure for the transformation of secondary amides into the corresponding *N*-aryliminoethers via reaction of phenols with activated secondary amides using Tf_2O/2-chloropyridine combination. Advantages such as highly effective activation of a variety of amide substrates, including *N*-arylamides, without requiring the isolation of the sensitive intermediates or the use of Lewis acid additives, and shortening reaction times without the need for elevated temperatures are the outcome of our methodology. We have also found that these mild conditions do not produce the by-products observed in the previous cases, which proceeded at elevated temperatures.

Experimental

All commercially available chemicals and reagents were used without further purification. Melting points were determined with an Electrothermal model 9100 apparatus. IR spectra were recorded on a Shimadzu 4300 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-500-AVANCE spectrometer at 500 (^{1}H) and 125 MHz (^{13}C) using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra of the products were obtained with a HP (Agilent technologies) 5937 mass selective detector. Elemental analyses were carried out by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). TLC of samples were carried out on silica gel plates using a 10:1 hexane-ethyl acetate mixture.

*Typical procedure for the preparation of **3a–3i***

A solution of amide (1.0 mmol) and 0.113 cm^3 2-chloropyridine (1.2 mmol) in 10 cm^3 CH_2Cl_2 was cooled to −78 °C with dry ice in acetone; 0.181 cm^3 Tf_2O (1.1 mmol) was then added with a syringe under argon atmosphere. After 5 min, the reaction mixture was warmed to 0 °C and 94 mg phenol (1.0 mmol) was added in one portion. The mixture was allowed to warm to ambient temperature and stirred for 3 h. The progress of the reaction was monitored with TLC. After completion of the reaction, 10 cm^3 sodium hydroxide solution (0.1 M) was added to neutralize the acidic salts. The organic phase was then separated, washed with brine, and dried over anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure, and the residue was purified with column chromatography (silica gel, 5% ethyl acetate in hexane).

Phenyl N-(4-methylphenyl)pivalimidate (**3a**, $C_{18}H_{21}NO$)
White solid; yield 250 mg (93%); m.p.: 50–52 °C; $R_f = 0.72$; IR (KBr): $\bar{\nu} = 3{,}071, 2{,}968, 2{,}889, 1{,}671, 1{,}589$ cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.42$ (s, *t*-Bu), 2.19 (s, Me), 6.67 (d, $J = 8.0$ Hz, Ar-H), 6.77 (d, $J = 5.8$ Hz, 2 Ar- H), 6.86 (d, $J = 8.0$ Hz, 2 Ar-H), 6.88 (s, Ar-H), 7.10 (t, $J = 7.2$ Hz, 2 Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.2, 28.5, 39.7, 118.4, 121.6, 122.8, 129.1, 129.3, 132.6, 143.9, 155.1, 163.1$ ppm; EI-MS: *m/z* (%) = 268 (M^++1, 100), 248 (68), 219 (80), 191 (9), 131 (16), 77 (6), 47 (8).

Phenyl N-(3,4-dimethylphenyl)pivalimidate
(**3b**, $C_{19}H_{23}NO$)
Yellow oil; yield 259 mg (92%); $R_f = 0.70$; IR (KBr): $\bar{\nu} = 3{,}075, 2{,}967, 2{,}890, 1{,}675, 1{,}594, 1{,}487, 1{,}204, 1{,}086$ cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.43$ (9H, s, *t*-Bu), 2.11 (6H, s, Me), 6.53 (1H, d, $J = 7.8$ Hz, Ar- H), 6.55 (1H, s, Ar-H), 6.78 (2H, bd, $J = 5.8$ Hz, Ar-H), 6.82 (2H, d, $J = 7.8$ Hz, Ar-H), 6.87 (1H, bt, $J = 6.8$ Hz, Ar-H), 7.10 (2H, bt, $J = 7.1$, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 19.4, 20.0, 28.6, 39.6, 118.6, 119.0, 122.8, 123.1, 129.2, 129.7, 131.2, 136.4, 144.2, 155.1, 162.8$ ppm; EI-MS: *m/z* (%) = 281 (M^+, 9), 188 (87), 132 (100), 121 (42), 105 (21), 77 (15), 57 (25).

4-Nitrophenyl N-(4-chlorophenyl)pivalimidate
(**3c**, $C_{17}H_{17}ClN_2O_3$)
Colorless solid; yield 216 mg (65%); m.p.: 79–80 °C; $R_f = 0.58$; IR (KBr): $\bar{\nu} = 3{,}081, 2{,}969, 2{,}891, 1{,}667, 1{,}587, 1{,}479, 1{,}275, 1{,}205, 1{,}089$ cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.39$ (9H, s, *t*-Bu), 6.72 (1H, d, $J = 8.3$ Hz, Ar-H), 6.84 (1H, d, $J = 6.8$ Hz, Ar-H), 7.04 (1H, d, $J = 8.3$ Hz, Ar-H), 7.26 (1H, d, $J = 8.8$ Hz, Ar-H), 7.49 (1H, d, $J = 8.9$ Hz, Ar-H), 8.01 (1H, d, $J = 8.5$ Hz, Ar-H), 8.27 (1H, d, $J = 8.8$ Hz, Ar-H), 8.36 (1H, d, $J = 8.9$ Hz, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 27.4, 39.7, 118.0, 122.8, 122.9, 125.5, 125.8, 126.4, 129.0, 144.1, 145.6, 153.5, 156.4, 159.5, 176.5$ ppm;

EI-MS: *m/z* (%) = 334 (M^++2, 4), 332 (11), 196 (34), 194 (81), 140 (44), 138 (100), 111 (19), 57 (34).

Phenyl N-(4-chlorophenyl)pivalimidate
(**3d**, $C_{17}H_{18}ClNO$)
White solid; yield 239 mg (83%); m.p.: 75–76 °C; R_f = 0.70; IR (KBr): $\bar{\nu}$ = 3,085, 2,975, 2,888, 1,670, 1,589 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.42 (9H, s, *t*-Bu), 6.65 (2H, d, J = 8.6 Hz, Ar-H), 6.74 (2H, d, J = 7.3 Hz, Ar-H), 6.90 (1H, t, J = 7.3 Hz, Ar-H), 7.00 (2H, d, J = 8.6 Hz, Ar-H), 7.11 (2H, t, J = 7.5 Hz, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.5, 39.7, 118.8, 122.9, 123.4, 128.3, 128.6, 129.5, 145.3, 154.9, 164.3 ppm; EI-MS: *m/z* (%) = 287 (M^+, 7), 196 (41), 194 (97), 140 (41), 138 (100), 111 (15), 57 (63).

4-tert-Butylphenyl N-(4-methylphenyl)pivalimidate
(**3e**, $C_{22}H_{29}NO$)
White solid; yield 316 mg (98%); m.p: 71–72 °C; R_f = 0.68; IR (KBr): $\bar{\nu}$ = 2,963, 1,668, 1,503, 1,214, 1,082, 819 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (s, 9H, *t*-Bu), 1.42 (s, 9H, *t*-Bu), 2.17 (s, 3H), 6.56 (d, J = 8.2 Hz, 2H), 6.67 (bs, 2H), 6.80 (d, J = 7.4 Hz, 2H), 7.06 (bs, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.1, 28.6, 31.8, 34.5, 39.5, 118.8, 121.4, 125.9, 128.9, 132.0, 144.3, 146.5, 152.8, 163.6 ppm; EI-MS: *m/z* (%) = 323 (M^+, 6), 174 (100), 118 (94), 91 (24), 57 (13).

4-tert-Butylphenyl N-(4-nitrophenyl)pivalimidate
(**3f**, $C_{21}H_{26}N_2O_3$)
White solid; yield 283 mg (80%); m.p.: 100–102 °C; R_f = 0.75; IR (KBr): $\bar{\nu}$ = 3,078, 2,962, 2,891, 1,698, 1,585, 1,500, 1,322, 1,100 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21 (9H, s, *t*-Bu), 1.44 (9H, s, *t*-Bu), 6.61 (2H, d, J = 9.0 Hz, Ar-H), 6.68 (2H, d, J = 6.8 Hz, Ar-H), 7.06 (2H, d, J = 6.8 Hz, Ar-H), 7.85 (2H, d, J = 9.0 Hz, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.5, 31.7, 34.6, 39.7, 120.3, 121.2, 124.3, 126.4, 142.7, 147.9, 152.1, 153.8, 164.9 ppm; EI-MS: *m/z* (%) = 354 (M^+, 5), 205 (100), 149 (50), 57 (90).

4-tert-Butylphenyl N-(4-chlorophenyl)pivalimidate
(**3g**, $C_{21}H_{26}ClNO$)
Colorless solid; yield 316 mg (92%); m.p.: 49–51 °C; R_f = 0.57; IR (KBr): $\bar{\nu}$ = 3,073, 2,963, 2,889, 1,670, 1,595, 1,478, 1,214, 1,085 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (9H, s, *t*-Bu), 1.43 (9H, s, *t*-Bu), 6.55 (2H, d, J = 8.5 Hz, Ar-H), 6.64 (2H, d, J = 7.9 Hz, Ar-H), 6.93 (2H, d, J = 8.5 Hz, Ar-H), 7.08 (2H, d, J = 7.9 Hz, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.5, 31.8, 34.5, 39.5, 119.2, 121.2, 122.8, 126.1, 126.6, 128.3, 146.6, 152.6, 164.7 ppm; EI-MS: *m/z* (%) = 345 (M^++2, 6), 343 (13), 196 (42), 194 (95), 140 (46), 138 (100), 111 (20), 57 (51).

2,4-Dichlorophenyl N-(4-methoxyphenyl)pivalimidate
(**3h**, $C_{18}H_{19}Cl_2NO_2$)
Pale yellow solid; yield 275 mg (78%); m.p.: 52–53 °C; R_f = 0.64; IR (KBr): $\bar{\nu}$ = 3,075, 2,968, 2,886, 1,672, 1,608, 1,465, 1,231, 1,076 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.39 (9H, s, *t*-Bu), 3.74 (3H, s, OMe), 6.65-6.73 (5H, m, Ar-H), 6.98 (1H, bs, Ar-H), 7.23 (1H, bs, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.6, 39.8, 55.9, 114.1, 114.2, 114.3, 114.4, 120.2, 122.1, 127.6, 130.1, 149.2, 156.2 ppm; EI-MS: *m/z* (%) = 351 (M^+, 6), 190 (46), 134 (100), 107 (14), 57 (79).

4-Nitrophenyl N-(3,4-dimethylphenyl)pivalimidate
(**3i**, $C_{19}H_{22}N_2O_3$)
Yellow solid; yield 218 mg (67%); m.p.: 89–90 °C; R_f = 0.60; IR (KBr): $\bar{\nu}$ = 3,074, 2,968, 2,885, 1,670, 1,584, 1,511, 1,376, 1,219, 1,075 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.41 (9H, s, *t*-Bu), 2.10 (6H, s, Me), 6.56 (1H, d, J = 7.8 Hz, Ar-H), 6.60 (1H, s, Ar-H), 6.83 (3H, m, Ar-H), 7.99 (2H, bt, J = 8.7 Hz, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.5, 20.0, 28.2, 39.6, 117.8, 119.1, 123.2, 125.6, 130.1, 132.6, 137.1, 140.5, 143.0, 159.9, 160.9 ppm; EI-MS: *m/z* (%) = 326 (M^+, 13), 188 (97), 132 (100), 105 (21), 57 (21).

2,4-Dichlorophenyl N-(4-chlorophenyl)pivalimidate
(**3j**, $C_{17}H_{16}Cl_3NO$)
Yellow solid; yield 353 mg (71%); m.p.: 49–50 °C; R_f = 0.61; IR (KBr): $\bar{\nu}$ = 3,078, 2,971, 2,897, 1,690, 1,581, 1,473, 1,230, 1,083 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (9H, s, *t*-Bu), 6.66 (2H, d, J = 9.6 Hz, Ar-H), 6.84 (1H, bd, J = 6.0 Hz, Ar-H), 7.08 (3H, m, Ar-H), 7.28 (1H, bs, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.9, 40.1, 121.9, 125.0, 127.9, 128.3, 128.4, 128.7, 130.3, 130.5, 145.0, 149.0, 162.1 ppm; EI-MS: *m/z* (%) = 360 (M^+, 4), 358 (19), 356 (19), 196 (46), 194 (100), 140 (23), 138 (65), 111 (12), 57 (43).

Phenyl N-(4-methoxyphenyl)pivalimidate
(**3k**, $C_{18}H_{21}NO_2$)
White solid; yield 272 mg (96%); m.p.: 67–68 °C; R_f = 0.73; IR (KBr): $\bar{\nu}$ = 3,068, 2,977, 2,890, 1,665, 1,590, 1,491, 1,207, 1,060 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.42 (9H, s, *t*-Bu), 3.70 (3H, s, OMe), 6.61 (2H, d, J = 8.7 Hz, Ar-H), 6.74-6.76 (3H, m, Ar-H), 6.85 (2H, bt, J = 6.8 Hz, Ar-H), 7.71 (2H, bt, J = 6.8 Hz, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.4, 39.6, 55.8, 114.0, 117.9, 122.7, 123.1, 129.3, 129.4, 155.0, 156.0, 163.0 ppm; EI-MS: *m/z* = 283 (M^+, 33), 190 (89), 134 (100), 107 (9), 57 (22).

2,4-Dichlorophenyl N-phenylcyclohexanecarboximidate
(**3l**, $C_{19}H_{19}Cl_2NO$)
Colorless solid; yield 278 mg (80%); m.p.: 49–53 °C; R_f = 0.53; IR (KBr): $\bar{\nu}$ = 3,076, 2,930, 2,855, 1,685,

1,590, 1,461, 1,220 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.17–1.32$ (3H, m, cyclohexane), 1.71-1.98 (7H, m, cyclohexane), 2.57 (1H, tt, $J = 11.2$, 3.4 Hz, cyclohexane), 6.77 (2H, d, $J = 7.6$ Hz, Ar-H), 7.08 (1H, t, $J = 7.4$ Hz, Ar-H), 7.19 (1H, d, $J = 8.6$ Hz, Ar-H), 7.29-7.33 (3H, m, Ar-H), 7.49 (1H, d, $J = 2.3$ Hz, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 25.9$, 26.1, 30.1, 39.4, 121.0, 123.54, 125.1, 125.6, 128.3, 129.4, 130.5, 131.3, 147.9, 148.5, 165.3 ppm; EI-MS: *m/z* (%) = 351 (M^+, 10), 348 (13), 214 (7), 186 (100), 111 (16), 104 (78), 83 (38).

4-tert-Butylphenyl N-(4-methylphenyl)benzimidate
(**3m**, $C_{24}H_{25}NO$)
Orange solid; yield 213 mg (62%); m.p.: 62–65 °C; $R_f = 0.63$; IR (KBr): $\bar{\nu} = 3,078, 2,962, 1,661, 1,500, 1,267, 1,206, 1,079$ cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.36$ (9H, s, *t*-Bu), 2.33 (3H, s, Me), 6.77-7.45 (10H, m, Ar-H), 7.52 (1H, d, $J = 8.7$ Hz, Ar-H), 7.58 (1H, t, $J = 7.7$ Hz, Ar-H), 8.03 (1H, bs, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.3$, 31.9, 34.9, 117.2, 121.5, 121.7, 122.7, 126.7, 126.9, 128.7, 129.7, 130.2, 130.6, 133.9, 149.1, 165.8 ppm; EI-MS: *m/z* (%) = 343 (M^+, 6), 348 (13), 254 (15), 214 (85), 194 (100), 105 (82), 91 (30), 77 (31).

4-tert-Butylphenyl N-4-(chlorophenyl)benzimidate
(**3n**, $C_{23}H_{22}ClNO$)
Yellow solid; yield 211 mg (58%); m.p.: 59–63 °C; $R_f = 0.60$; IR (KBr): $\bar{\nu} = 3,080, 2,960, 2,888, 1,651, 1,495, 1,265, 1,209$ cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.36$ (9H, s, *t*-Bu), 6.75-7.51 (10H, m, Ar-H), 7.52 (1H, d, $J = 8.7$ Hz, Ar-H), 7.58 (1H, t, $J = 7.8$ Hz, Ar-H), 8.04 (1H, bs, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 31.9$, 34.7, 120.3, 121.5, 123.6, 126.2, 126.8, 126.9, 128.8, 129.0, 129.2, 129.9, 130.2, 130.6, 139.0 ppm; EI-MS: *m/z* (%) = 363 (M^+, 6), 348 (13), 254 (10), 216 (43), 214 (100), 105 (55), 77 (18).

Phenyl N-(4-methoxyphenyl)benzimidate
(**3o**, $C_{20}H_{17}NO_2$)
Yellow solid; yield 197 mg (65%); m.p.: 66–67 °C; $R_f = 0.64$; IR (KBr): $\bar{\nu} = 3,071, 2,964, 1,651, 1,589, 1,487, 1,203, 1,017$ cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 3.80$ (3H, s, OMe), 6.73–8.11 (14H, m, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 55.8$, 114.4, 115.0, 117.4, 122.7, 123.2, 124.8, 125.2, 128.9, 129.1, 129.5, 130.1, 131.5, 133.6 ppm; EI-MS: *m/z* (%) = 303 (M^+, 8), 210 (100), 107 (17), 105 (81), 77 (30).

Naphthalen-1-yl N-(4-methylphenyl)pivalimidate
(**9**, $C_{22}H_{23}NO$)
White crystals; yield 279 mg (88%); m.p.: 59–60 °C; $R_f = 0.72$; IR (KBr): $\bar{\nu} = 3,056, 2,972, 2,868, 1,666, 1,463, 1,207, 1,077$ cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.51$ (s, 9H, *t*-Bu), 2.05 (s, 3H, Me), 6.68 (bs, 4H, Ar-H), 6.78 (s, 1H, Ar-H), 7.17 (t, $J = 7.8$ Hz, 1H, Ar-H), 7.39 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.47-8.17 (m, 4H, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.0$, 28.7, 40.0, 112.5, 121.1, 122.2, 122.9, 123.2, 125.5, 125.8, 126.5, 128.0, 129.0, 132.6, 134.9, 144.5, 150.4, 162.6 ppm; EI-MS: *m/z* (%) = 317 (M^+, 12), 174 (100), 118 (93), 91 (19), 57 (16).

Naphthalen-2-yl N-(4-methoxyphenyl)pivalimidate
(**10**, $C_{22}H_{23}NO_2$)
White crystals; yield 313 mg (94%); m.p.: 64–65 °C; IR (KBr): $\bar{\nu} = 3,252, 3,054, 2,969, 1,672, 1,503, 1,242, 1,080$ cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.47$ (s, 9H, *t*-Bu), 3.57 (s, 3H, OMe), 6.55 (d, $J = 8.3$ Hz, 2H, Ar-H), 6.82 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.02 (bd, $J = 8.6$ Hz, 1H, Ar-H), 7.10 (bs, 1H, Ar-H), 7.30–7.71 (m, 5H, Ar-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 28.5$, 39.7, 55.7, 114.0, 118.9, 121.4, 123.1, 124.7, 126.7, 127.3, 127.4, 128.0, 129.5, 130.1, 134.3, 139.6, 152.7, 156.1 ppm; EI-MS: *m/z* (%) = 333 (M^+, 8), 190 (100), 134 (87), 115 (12), 77 (7), 57 (22).

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