

# Copper-Catalyzed *N*-*tert*-Butylation of Aromatic Amines under Mild Conditions Using *tert*-Butyl 2,2,2-Trichloroacetimidate

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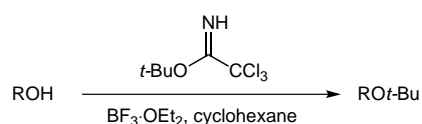
**Abstract:** A variety of aromatic amines have been found to expediently undergo copper-catalyzed *N*-*tert*-butylation in the presence of *tert*-butyl 2,2,2-trichloroacetimidate at room temperature.

**Key words:** anilines, *tert*-butylation, copper, catalysis, alkylation

The *tert*-butylation of anilines is a reaction that has traditionally been difficult to accomplish, requiring the use of harsh reaction conditions and long reaction times and often delivering only poor to moderate yields.<sup>1</sup> To date, an efficient and mild general protocol has not been developed. As such, the only efficient method remains the Buchwald–Hartwig amination reaction,<sup>2</sup> which still requires high temperatures and long reaction times and is not always tactically desirable. Furthermore, anilines constitute a fundamental building block in organic chemistry and there is a continuing need for general procedures for their functionalization, including alkylation.

Herein, we describe such a protocol using *tert*-butyl 2,2,2-trichloroacetimidate in the presence of readily available copper catalysts under mild conditions.

The Jackson group has previously reported that *tert*-butyl 2,2,2-trichloroacetimidate is an effective *tert*-butylating agent for alcohols and carboxylic acids in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$  (Scheme 1).<sup>3</sup>



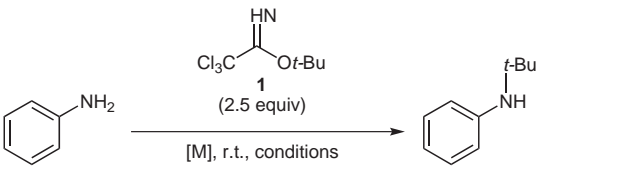
**Scheme 1** Jackson's protocol for the *tert*-butylation of alcohols and carboxylic acids<sup>3</sup>

Previous attempts to *tert*-butylate aromatic amines utilizing Jackson's conditions have resulted in long reaction times and modest yields, probably due to the reactivity of  $\text{BF}_3 \cdot \text{OEt}_2$  in the presence of such amines.<sup>4</sup> Due to their basic nature, amines are not generally compatible with strong Lewis acids. However, the reduced basicity of aromatic amines originating from conjugation of the nitrogen lone pair with the adjacent aromatic system prevents irreversible coordination to the Lewis acid catalyst. We sur-

mised that this offered an opportunity to develop a more effective catalytic process by identifying conditions more compatible with aromatic amines. Therefore, a study was undertaken to screen a number of readily available Lewis acids under different conditions in the presence of *tert*-butyl trichloroacetimidate (**1**) and with aniline as the test substrate (Table 1). Our initial studies showed coinage metals to be the most effective catalyst systems.<sup>5</sup> While unactivated AuCl and AuCl<sub>3</sub> were found to be ineffective catalysts, AuCl activated with AgClO<sub>4</sub><sup>6</sup> in the presence of 2.5 equivalents of **1** gave moderate yields after two hours at room temperature (Table 1, entries 1–3) with dry MeNO<sub>2</sub> proving to be an effective solvent.<sup>7</sup> While silver perchlorate was also found to be an active catalyst the reaction did not progress beyond 52% (Table 1, entry 4), even after an extended period of time. The presence of a triphenylphosphine ligand on gold was found to be detrimental to catalytic activity, presumably blocking a coordination site at the metal center (Table 1, entry 5).

From further catalyst screening, PtCl<sub>2</sub>/AgClO<sub>4</sub> was also found to be an active catalytic system (Table 1, entry 6), however, less expensive copper(I) and (II) catalysts were identified as being the most effective, giving yields of up to 85% (Table 1, entries 7–12). Copper(I) salts required a silver-activating agent as did CuCl<sub>2</sub>. While Cu(OAc)<sub>2</sub> was inert (Table 1, entry 11), commercially available Cu(OTf)<sub>2</sub> proved to be an excellent catalyst and did not require activation (Table 1, entry 12). The reaction was observed to be clean with no significant byproducts formed. Significantly, no C-alkylation products were seen. Other transition-metal salts were found to promote the reaction to some extent, but not as effectively, in general giving yields below 50%, even after extended reaction times (Table 1, entries 13–16). Tosic acid also catalyzed the reaction but did not give full conversion to the product (Table 1, entry 17), and employing stronger or weaker protic acids did not result in effective conversions (Table 1, entries 18 and 19). Finally, in the absence of a catalyst no product formation was observed at all after two hours (Table 1, entry 20).

A diverse range of anilines underwent *tert*-butylation when subjected to our optimized conditions (Figure 1). In the presence of electron-withdrawing substituents (EWG), yields were generally quantitative (**3–11**) and while most reactions were generally complete in under two hours, where an EWG was present, the reaction was observed to be complete in as little as ten minutes. Where a nitrile group was present, a large excess of **1** was re-

**Table 1** Optimization of Reaction Conditions


Entry	[M] (5mol%)	Solvent	Time (h)	Yield (%) <sup>b</sup>
1	AuCl/AgClO <sub>4</sub> <sup>a</sup>	cyclohexane	4	50
2	AuCl/AgClO <sub>4</sub> <sup>a</sup>	CH <sub>2</sub> Cl <sub>2</sub>	2	63
3	AuCl/AgClO <sub>4</sub> <sup>a</sup>	MeNO <sub>2</sub>	2	72
4	AgClO <sub>4</sub>	MeNO <sub>2</sub>	2	52 <sup>c</sup>
5	PPh <sub>3</sub> AuCl/AgClO <sub>4</sub> <sup>a</sup>	MeNO <sub>2</sub>	2	<5
6	PtCl <sub>2</sub> /AgClO <sub>4</sub> (1:2)	MeNO <sub>2</sub>	2	70
7	CuCl/AgClO <sub>4</sub> <sup>a</sup>	MeNO <sub>2</sub>	2	81
8	CuI/AgClO <sub>4</sub> <sup>a</sup>	MeNO <sub>2</sub>	2	80
9	CuCl <sub>2</sub>	MeNO <sub>2</sub>	2	38
10	CuCl <sub>2</sub> /AgClO <sub>4</sub> (1:2)	MeNO <sub>2</sub>	2	67
11	Cu(OAc) <sub>2</sub>	MeNO <sub>2</sub>	2	<5
12	Cu(OTf) <sub>2</sub>	MeNO <sub>2</sub>	2	85
13	Sc(OTf) <sub>3</sub>	MeNO <sub>2</sub>	2	25 <sup>c</sup>
14	Fe(OTf) <sub>3</sub>	MeNO <sub>2</sub>	2	51 <sup>c</sup>
15	Pd(OTf) <sub>2</sub>	MeNO <sub>2</sub>	2	48 <sup>c</sup>
16	Zn(OTf) <sub>2</sub>	MeNO <sub>2</sub>	2	36 <sup>c</sup>
17	TsOH	MeNO <sub>2</sub>	2	60 <sup>c</sup>
18	HClO <sub>4</sub>	MeNO <sub>2</sub>	2	45 <sup>c</sup>
19	TfOH	MeNO <sub>2</sub>	2	<5
20	–	MeNO <sub>2</sub>	2	0

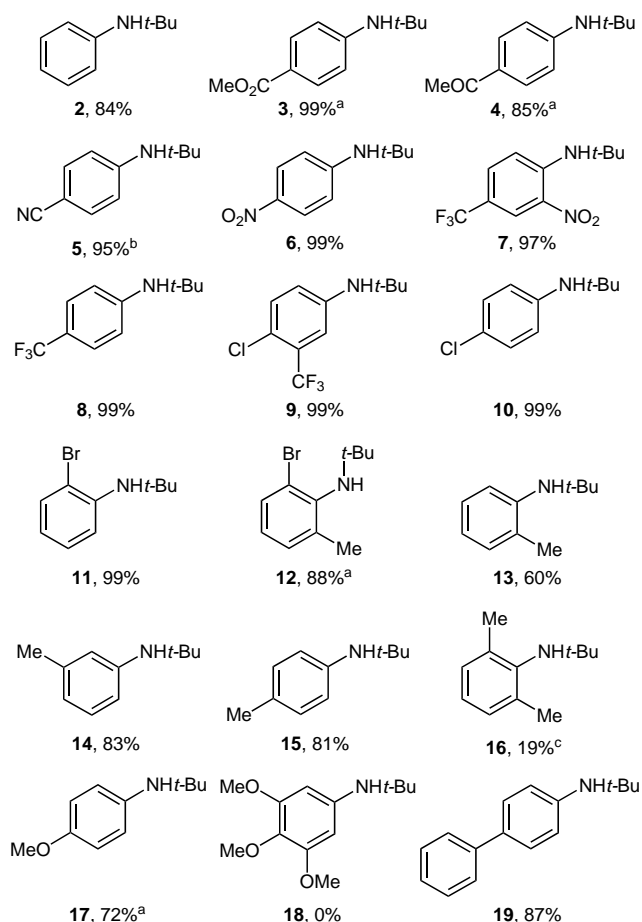
<sup>a</sup> 1 equiv of AgClO<sub>4</sub> added with respect to the precatalyst.

<sup>b</sup> Mass balance was predominantly starting material.

<sup>c</sup> No significant increase in yield observed after 24 h.

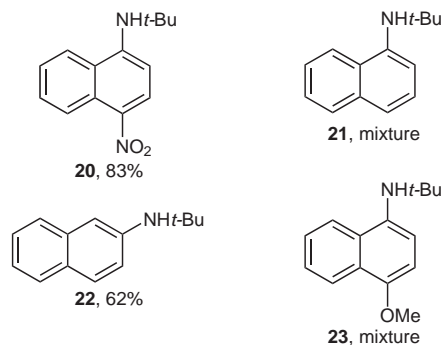
quired to drive the reaction to completion (**5**). We reasoned that this was most likely due to unproductive coordination of the nitrile lone pair to the catalyst. Indeed, in support of this assertion, when a control reaction was run in MeCN, with aniline as the substrate, no reaction was observed. The presence of the mildly  $\sigma$ -donating methyl substituent was well tolerated by the reaction (see examples **12**–**16**), although here steric hindrance had a notable effect, cf. **13**–**16**, inhibiting product formation. The effect appeared to be cancelled out by the presence of a  $\sigma$ -accepting bromide group (**12**). The presence of a methoxy substituent, a strong  $\pi$ -donor group, lowered the yield of *tert*-butylated product **17**, and the formation of **18** was not

observed at all where three methoxy groups were present. This is possibly due to strong coordination of the substrate to the catalyst either through heteroatom coordination or  $\pi$ -complexation.<sup>8,9</sup> The weaker  $\pi$ -donating phenyl group did not have a deleterious effect on the reaction with *tert*-butylated product **19**, formed in a high yield.



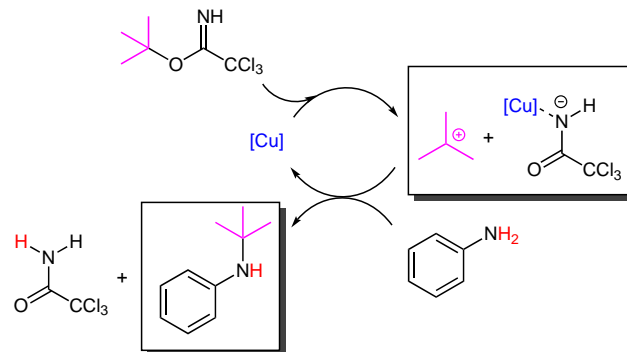
**Figure 1** Isolated yields: in most cases the mass balance was accounted for by unreacted starting material. *Reaction conditions*: **1** (2.5 equiv), Cu(OTf)<sub>2</sub> (5 mol%), MeNO<sub>2</sub>, r.t., 2 h. <sup>a</sup> 3.5 equiv of **1** used. <sup>b</sup> 4.5 equiv of **1** used. <sup>c</sup> Yield estimated from <sup>1</sup>H NMR.

When naphthylamines were subjected to the reaction conditions (Figure 2) it was found that with Cu(OTf)<sub>2</sub> low yields and complex product mixtures were observed. However, using CuI/AgClO<sub>4</sub>, it was possible to isolate compounds **20** and **22** (Figure 2) in good to moderate yields. Compounds **21** and **23** were still not cleanly isolable, with complex mixtures of alkylation products observed in these cases. Overall a trend mirroring that shown for anilines was apparent with the electron-withdrawing nitro group giving the highest yield. The lower yields and substrate scope are probably due to the less aromatic nature of naphthylamines (cf. anilines) leading to side reactions and decomposition as a result of higher reactivity.<sup>10</sup>



**Figure 2** Reaction conditions: **1** (2.5 equiv), CuI (5 mol%), AgClO<sub>4</sub> (5 mol%), MeNO<sub>2</sub>, r.t., 2 h.

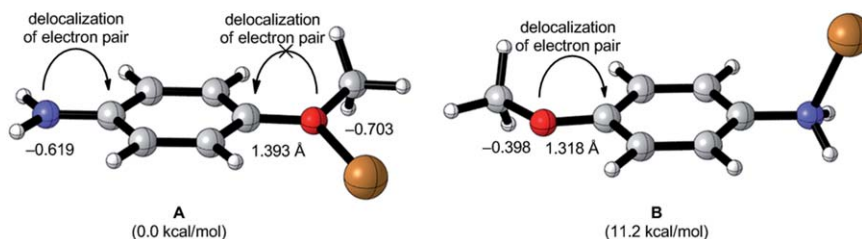
A reasonable mechanism is given in Scheme 2, whereby the copper species initially coordinates to *tert*-butyl 2,2,2-trichloroacetimidate, catalyzing its decomposition and releasing the *tert*-butyl cation to be captured by the aniline, which is possibly already catalyst-bound. The notion that the aromatic amine is already coordinated in the catalyst complex is supported by the observation that its presence is required to effectively solubilize the catalyst and that in its absence, decomposition of **1** takes almost two hours compared with less than ten minutes for the *tert*-butylation of 4-nitroaniline to give **4**. At least two equivalents of the *tert*-butylating agent are usually needed, presumably due to the *tert*-butyl cation undergoing competitive proton elimination to give isobutene. The strongly polar aprotic nature of nitromethane most likely stabilizes the *tert*-butyl cation, increasing its half-life and accounting for its suitability as a reaction medium. Increasing the amount of the *tert*-butylating agent to four equivalents or more had little observable effect on the reaction rate or yield in most cases, suggesting that the rate-determining step is interception of the *tert*-butyl cation by the substrate. Intriguingly, given the presumed S<sub>N</sub>1 characteristics of the proposed mechanism, the copper(II)-catalyzed *tert*-butylation showed a significant dependence on the nature of nucleophile. This was unexpected given that S<sub>N</sub>1 reactions generally display the first-order and the zero-order dependence on the electrophile and the nucleophile, respectively.



**Scheme 2** Proposed mechanism

To shed further light on the mechanism, particularly our hypothesis that an unproductive interaction between electron-rich aromatic amines and the catalyst hindered the reaction, a preliminary computation study, performed at the M05-2X/LANL2DZ level,<sup>11</sup> was carried out. *p*-Methoxyaniline and *p*-nitroaniline were compared to determine the substituent effects on catalyst-substrate affinity. The results suggested an unproductive reactant stabilization of the electron-rich *p*-methoxy aniline, upon coordination with the copper(II) catalyst (−59.2 kcal/mol), much stronger than with the imidate and in agreement with our hypothesis.<sup>9</sup> This could account for the lower yield as the active catalyst concentration is reduced. In contrast, *p*-nitro aniline forms a weaker complex (12.9 kcal/mol) with copper(II) than the imidate, leaving the catalyst available for promoting the desired *tert*-butylation reaction.

Interestingly, the methoxy group formed a stronger complex with copper(II) than the amino group (11.6 kcal/mol). The observed anomaly is due to the stereoelectronic effect of the electron pair on the methoxy group which deconjugates the electrons on the methoxy group from the aromatic ring, thereby making those electrons more nucleophilic than the amino group electrons (Figure 3). This is a result of the lone pair on the oxygen of the methoxy group being more tightly held than the lone pair on the nitrogen, hence, deconjugation of the electrons of the amino group, by the methoxy group, would require higher energy and is therefore energetically unfavorable.



**Figure 3** The M05-2X/LANL2DZ optimized geometries of the Cu(II)–substrate complex. Structure **A** represents the Cu(II)–methoxy complex. Structure **B** represents the Cu(II)–amine complex. Values in parenthesis correspond to relative energy difference between structure **A** and **B**.

In conclusion, a new expedient, mild, and general method for the synthesis of *tert*-butyl aromatic amines at room temperature has been developed, catalyzed by Cu(OTf)<sub>2</sub>, utilizing *tert*-butyl 2,2,2-trichloroacetimidate in MeNO<sub>2</sub>.<sup>12,13</sup> Additionally, a preliminary computational study supports the experimentally observed difference in rates and yields between electron-rich and electron-poor aromatic amines, suggesting the presence of unproductive catalyst–substrate interactions with electron-rich aromatic amines. Our current studies are concentrated on further applications of the methodology and determination of the mechanistic details.

### Acknowledgment

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- (12) **General Experimental Methods**  
All commercially available chemicals were used as received. MeNO<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub> were distilled from CaH<sub>2</sub>. Reagent-grade solvents were used for solvent extraction, and organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> or MgSO<sub>4</sub>. Alumina gel (80–200 mesh) was used for flash chromatography with dry hexane–EtOAc eluent system. <sup>1</sup>H NMR spectra were recorded on a 500 MHz Bruker or a 300 MHz Varian spectrometer. <sup>13</sup>C NMR spectra were recorded on a 125 MHz Bruker or a 75 MHz Varian spectrometer. The proton chemical shifts (δ) are reported as parts per million relative to 7.26 ppm for CDCl<sub>3</sub>. The carbon chemical shifts (δ) were reported as parts per million relative to the centerline of the triplet for CDCl<sub>3</sub> at 77.1 ppm. Mass spectra were recorded using a Jeol JMS-600 instrument or an Agilent 6220 TOF-MS (NSF CRIF Grant 0541761).  
**Typical Procedure for *tert*-Butylation Reaction**  
To a dry round-bottom flask, equipped with a stirrer bar, under argon was added freshly distilled MeNO<sub>2</sub> (2.5 mL), *tert*-butyl 2,2,2-trichloroacetimidate (0.45 mL, 2.5 mmol), amine (1.0 mmol), and CuOTf (18 mg, 0.05 mmol). The reaction was stirred at r.t. for 2 h, or until the reaction was observed to have gone to completion by TLC or <sup>1</sup>H NMR spectroscopy of small aliquots of the reaction mixture. The reaction mixture was then diluted with EtOAc (25 mL) and washed with aq sat. NaHCO<sub>3</sub> solution (20 mL). The aqueous phase was extracted with an additional portion of EtOAc (20 mL). The combined organic extracts were dried with Na<sub>2</sub>SO<sub>4</sub> and filtered through a plug of alumina before being reduced in vacuo. The crude product was purified by flash column chromatography (typically 20:1, hexane–EtOAc).
- (13) ***tert*-Butylphenylamine (2)**  
Clear oil (125 mg, 0.84 mmol, 84% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.16 (dd, *J* = 8.1, 8.1 Hz, 2 H), 6.79–6.73 (m, 3 H), 3.30–2.30 (br s, 1 H), 1.34 (s, 9 H). Compound identified by <sup>1</sup>H NMR spectroscopy by comparison with data previously published in the literature.<sup>1a</sup>  
**4-*tert*-Butylaminobenzoic Acid Methyl Ester (3)**  
Light yellow oil (208 mg, 1.00 mmol, 99% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.81 (d, *J* = 9.0 Hz, 2 H), 6.63 (d, *J* = 9.0 Hz, 2 H), 4.25–4.00 (br s, 1 H), 3.84 (s, 3 H), 1.40 (s, 9 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 167.4, 151.0, 131.3 (2 C), 117.7, 113.7 (2 C), 51.3, 29.7 (3 C). ESI-HRMS: *m/z*

calcd for  $C_{12}H_{18}NO_2$   $[MH]^+$ : 208.1338; found: 208.1349.

**1-(4-*tert*-Butylaminophenyl)-ethanone (4)**

Yellow oil (189 mg, 0.99 mmol, 99% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.78 (d,  $J$  = 8.4 Hz, 2 H), 6.63 (d,  $J$  = 8.4 Hz, 2 H), 4.32 (br s, 1 H), 2.49 (s, 3 H), 1.41 (s, 9 H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 196.4, 151.2, 130.6 (2 C), 126.0, 113.5 (2 C), 51.3, 29.7 (3 C), 26.0. ESI-HRMS:  $m/z$  calcd for  $C_{12}H_{18}NO$   $[MH]^+$ : 192.1383; found: 192.1374.

**4-*tert*-Butylaminobenzonitrile (5)**

Light brown oil (165 mg, 0.95 mmol, 95% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.37 (d,  $J$  = 9.0 Hz, 2 H), 6.62 (d,  $J$  = 9.0 Hz, 2 H), 4.30–4.10 (br s, 1 H), 1.40 (s, 9 H). Compound identified by  $^1H$  NMR spectroscopy by comparison with data previously published in the literature.<sup>14</sup>

***tert*-Butyl-(4-nitrophenyl)-amine (6)**

Yellow oil (192 mg, 0.99 mmol, 99% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 8.03 (d,  $J$  = 9.0 Hz, 2 H), 6.59 (d,  $J$  = 9.0 Hz, 2 H), 4.70–4.50 (br s, 1 H), 1.43 (s, 9 H). Compound identified by  $^1H$  NMR spectroscopy by comparison with data previously published in the literature.<sup>1a</sup>

***tert*-Butyl-(2-nitro-4-trifluoromethyl-phenyl)-amine (7)**

Yellow oil (262 mg, 1.00 mmol, 99% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 8.68–8.56 (br s, 1 H), 8.45 (d,  $J$  = 2.4 Hz, 1 H), 7.56 (dd,  $J$  = 9.0, 2.4 Hz, 1 H), 7.18 (d,  $J$  = 15.0 Hz, 1 H), 1.53 (s, 9 H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 146.3, 133.4, 133.3 (q,  $J$  = 3.8 Hz), 125.5 (q,  $J$  = 43.8 Hz), 123.7, (q,  $J$  = 268.8 Hz), 116.7 (q,  $J$  = 30.0 Hz), 116.3, 52.3, 29.6 (3 C). ESI-HRMS:  $m/z$  calcd for  $C_{11}H_{14}N_2O_2F_3$   $[MH]^+$ : 263.1002; found: 263.1002.

***tert*-Butyl-(4-trifluoromethyl-phenyl)-amine (8)**

Light brown oil (210 mg, 0.97 mmol, 97% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.37 (d,  $J$  = 9.0 Hz, 2 H), 6.69 (d,  $J$  = 9.0 Hz, 2 H), 3.97 (s, 1 H), 1.39 (s, 9 H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  = 149.7, 126.4 (q,  $J$  = 3.4 Hz, 2 C), 125.1 (q,  $J$  = 268.7 Hz), 118.5 (q,  $J$  = 32.4 Hz), 114.4 (2 C), 51.3, 29.8. ESI-HRMS:  $m/z$  calcd for  $C_{11}H_{15}NF_3$   $[MH]^+$ : 218.1151; found: 218.1153.

***tert*-Butyl-(4-chloro-3-trifluoromethyl-phenyl)-amine (9)**

Light yellow oil (251 mg, 1.00 mmol, 99% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.22 (d,  $J$  = 9.0 Hz, 1 H), 6.97 (d,  $J$  = 3.0 Hz, 1 H), 6.77 (dd,  $J$  = 9.0, 3.0 Hz, 1 H), 4.02–3.02 (br s, 1 H), 1.35 (s, 9 H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 145.6, 131.8, 128.4 (q,  $J$  = 31.3 Hz), 123.1 (q,  $J$  = 271.3 Hz), 119.3, 119.2 (q,  $J$  = 1.3 Hz), 114.7 (q,  $J$  = 6.3 Hz), 51.6, 29.8 (3 C). HRMS (EI):  $m/z$  calcd for  $C_{11}H_{13}F_3NCl$   $[M]^+$ : 251.0689; found: 251.0690.

***tert*-Butyl-(4-chlorophenyl)-amine (10)**

Light orange oil (0.181 g, 0.99 mmol, 99% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.10 (d,  $J$  = 9.0 Hz, 2 H), 6.65 (d,  $J$  = 9.0 Hz, 2 H), 1.32 (s, 9 H). Compound identified by  $^1H$  NMR spectroscopy by comparison with data previously published in the literature.<sup>1a</sup>

**(2-Bromo-phenyl)-*tert*-butylamine (11)**

Pink oil (228 mg, 1.00 mmol, 99% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.43 (dd,  $J$  = 7.8, 1.8 Hz, 1 H), 7.14 (ddd,  $J$  = 7.8, 7.8, 1.8 Hz, 1 H), 6.97 (dd,  $J$  = 7.8, 1.8 Hz, 1 H), 6.55 (ddd,  $J$  = 7.8, 7.8, 1.8 Hz, 1 H), 4.40–4.25 (br s, 1 H), 1.41 (s, 9 H). Compound identified by  $^1H$  NMR spectroscopy by comparison with data previously published in the literature.<sup>4c</sup>

**(2-Bromo-6-methylphenyl)-*tert*-butylamine (12)**

Light pink oil (213 mg, 0.88 mmol, 88% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.39 (d,  $J$  = 7.8, 1 H), 7.11 (d,  $J$  = 7.8

Hz, 1 H), 6.82 (dd,  $J$  = 7.8, 7.8 Hz, 1 H), 3.37–3.29 (br s, 1 H), 2.42 (s, 3 H), 1.26 (s, 9 H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 143.9, 137.2, 130.5, 130.2, 124.3, 124.2, 56.1, 31.1 (3 C), 21.6. HRMS (EI):  $m/z$  calcd for  $C_{11}H_{16}BrN$   $[M]^+$ : 241.0466; found: 241.0476.

***tert*-Butyl-*o*-tolylamine (13)**

Light brown oil (98 mg, 0.60 mmol, 60% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.13–7.04 (m, 2 H), 6.92 (d,  $J$  = 8.4 Hz, 1 H), 6.66 (dd,  $J$  = 7.2, 7.2 Hz, 1 H), 3.60–3.25 (br s, 1 H), 2.13 (s, 3 H), 1.40 (s, 9 H). Compound identified by  $^1H$  NMR spectroscopy by comparison with data previously published in the literature.<sup>1a</sup>

***tert*-Butyl-*m*-tolylamine (14)**

Light brown oil (135 mg, 0.83 mmol, 83% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.06 (dd,  $J$  = 9.0, 9.0 Hz, 1 H), 6.62–6.55 (m, 3 H), 3.20–2.65 (br s, 1 H), 2.28 (s, 3 H), 1.34 (s, 9 H). Compound identified by  $^1H$  NMR spectroscopy by comparison with data previously published in the literature.<sup>1c</sup>

***tert*-Butyl-*p*-tolylamine (15)**

Light brown oil (132 mg, 0.81 mmol, 81% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 6.99 (d,  $J$  = 8.4 Hz, 2 H), 6.71 (d,  $J$  = 8.4 Hz, 2 H), 3.30–2.40 (br s, 1 H), 2.26 (s, 3 H), 1.30 (s, 9 H). Compound identified by  $^1H$  NMR spectroscopy by comparison with data previously published in the literature.<sup>1a</sup>

***tert*-Butyl-(4-methoxyphenyl)-amine (17)**

Red oil (127 mg, 0.72 mmol, 72% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 6.84–6.73 (m, 4 H), 3.76 (s, 3 H), 1.23 (s, 9 H). Compound identified by  $^1H$  NMR spectroscopy by comparison with data previously published in the literature.<sup>1a</sup>

**Biphenyl-4-yl-*tert*-butylamine (19)**

Light yellow oil (196 mg, 0.87 mmol, 87% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.55 (d,  $J$  = 7.2 Hz, 2 H), 7.93 (d,  $J$  = 8.4 Hz, 2 H), 7.40 (t,  $J$  = 7.5 Hz, 2 H), 7.26 (t,  $J$  = 7.5 Hz, 1 H), 6.82 (d,  $J$  = 9.0 Hz, 2 H), 4.00–3.20 (br s, 1 H), 1.39 (s, 9 H). Compound identified by  $^1H$  NMR spectroscopy by comparison with data previously published in the literature.<sup>15</sup>

***tert*-Butyl-(4-nitro-naphthalen-1-yl)-amine (20)**

Yellow oil (203 mg, 0.83 mmol, 83% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 9.05 (d,  $J$  = 9.0 Hz, 1 H), 8.46 (d,  $J$  = 9.0 Hz, 1 H), 7.76 (d,  $J$  = 9.0 Hz, 1 H), 7.67 (dd,  $J$  = 7.8, 7.8 Hz, 1 H), 7.51 (dd,  $J$  = 7.8, 7.8 Hz, 1 H), 6.78 (d,  $J$  = 9.0 Hz, 1 H), 5.38–5.31 (br s, 1 H), 1.58 (s, 9 H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  = 148.5, 134.1, 129.5, 129.1, 128.1, 125.7, 125.0, 122.5, 120.1, 103.5, 52.2, 29.4 (3 C). HRMS (EI):  $m/z$  calcd for  $C_{14}H_{16}O_2N_2$   $[M]^+$ : 244.1212; found: 244.1212.

***tert*-Butyl-naphthalen-2-yl-amine (22)**

Red oil (123 mg, 0.62 mmol, 62% yield).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.66 (d,  $J$  = 8.4 Hz, 1 H), 7.61 (d,  $J$  = 8.4 Hz, 2 H), 7.36 (dd,  $J$  = 7.5, 7.5 Hz, 1 H), 7.20 (dd,  $J$  = 7.5, 7.5 Hz, 1 H), 7.04 (d,  $J$  = 2.4 Hz, 1 H), 6.90 (dd,  $J$  = 9.0, 2.4 Hz, 1 H), 4.00–3.20 (br s, 1 H), 1.43 (s, 9 H). Compound identified by  $^1H$  NMR spectroscopy by comparison with data previously published in the literature.<sup>16</sup>

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