Tetrahedron 68 (2012) 2414–2420

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Well-defined NHC–Pd(II)–Im (NHC=*N*-heterocyclic carbene; Im=1-methylimidazole) complex catalyzed C–N coupling of primary amines with aryl chlorides

Lei Zhu, Yue-Mei Ye, Li-Xiong Shao *

College of Chemistry and Materials Engineering, Wenzhou University, Chashan University Town, Wenzhou, Zhejiang Province 325035, People's Republic of China

ARTICLE INFO

Article history:
Received 11 October 2011
Received in revised form 28 December 2011
Accepted 6 January 2012
Available online 15 January 2012

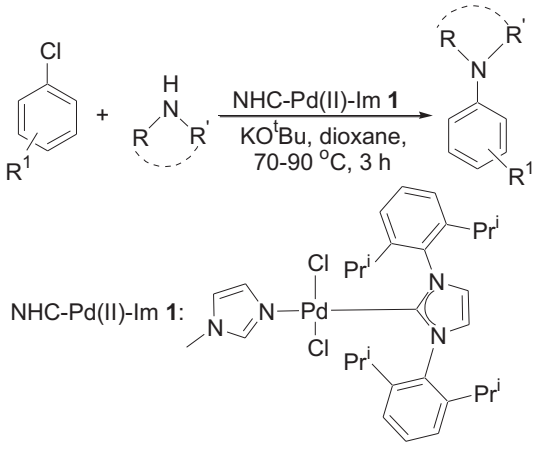
Keywords:
N-Heterocyclic carbene
Palladium complex
Amination reaction
Aryl chloride
Synthetic method

ABSTRACT

We report herein a well-defined NHC–Pd(II)–Im (NHC=*N*-heterocyclic carbene; Im=1-methylimidazole) complex catalyzed C–N coupling of primary amines with aryl chlorides. Under the optimal reaction conditions, a variety of primary amines can be coupled with aryl chlorides to give the amination products in good to high yields within 4 h. It is worthy of noting here that the NHC–Pd(II)–Im complex showed especially high catalytic activity toward challenging sterically hindered substrates including both of aryl amines and aryl chlorides. In addition, alkyl amines were also proved to be suitable reaction partners to give the corresponding amination products in good to high yields.

1. Introduction

N-containing molecules are prevalent in compounds with biological, pharmaceutical, and materials interest, etc.[1] Since the initial amination reactions were reported,[2] the palladium-catalyzed C–N cross-coupling reactions have become the most versatile strategy for *N*-containing compounds.[3] Among the electrophiles, aryl chlorides are the most desirable due to their low-cost and the wider availability.[4] Owing to some notable phosphine ligands mainly developed by Buchwald,[5] Hartwig,[6] Beller,[7] Verkade,[8] et al.,[9] nowadays, aryl chlorides have been commonly used as the coupling partner in the C–N bond formations. Generally, the highly active phosphane ligands are expensive, air-sensitive, and toxic. Therefore, to develop inexpensive and air-stable ligands in the palladium-catalyzed C–N cross-coupling is still in great demand. In this regard, *N*-heterocyclic carbenes (NHCs),[10] usually with higher air- and thermal-stability, as a chanllenger to phosphine-based ligands, have also played important role in the palladium-catalyzed aminations of aryl chlorides.[11] Recently, we have developed a new well-defined NHC–Pd(II)–Im complex **1** and found it to be an efficient catalyst in the amination reactions of aryl chlorides (Scheme 1).[12] To our disappointment, the optimal reaction conditions were only suitable for secondary amines, such as morpholine, piperidine, pyrrolidine, *N*-methylbenzylamine, and *N*-methylaniline, while primary amines showed no activity under the identical conditions. In addition, only few successful results on the synthesis of *ortho*-tetra-substituted diarylamines from the reactions between sterically hindered aryl amines and aryl chlorides were reported.[8b,9g,11d,11e,13] These results prompted us to further investigate the application of NHC–Pd(II)–Im complex **1** in the amination reactions of primary amines, especially using sterically hindered primary amines and aryl chlorides as the substrates. Furthermore, alkyl amines were also tested for the amination reactions of aryl chlorides. Herein, we wish to report these results in detail.



Scheme 1. NHC–Pd(II)–Im complex **1** catalyzed aminations of secondary amines with aryl chlorides.

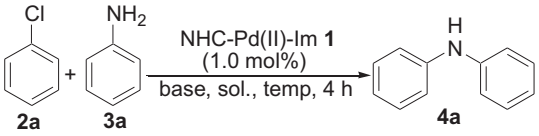
* Corresponding author. Tel./fax: +86 577 86689300; e-mail addresses: Shaolix@wzu.edu.cn, shaolix@163.com (L.-X. Shao).

0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2012.01.008

2. Results and discussion

Initially, standard reactions were carried out using chlorobenzene **2a** (0.77 mmol) and aniline **3a** (1.2 equiv) as the substrates in the presence of NHC–Pd(II)–Im **1** (1.0 mol %) at 70 °C for 4 h to find out the best solvent and base. Some representative results are shown in Table 1. It was found that the solvents and bases drastically affected the reactions. For example, in the first round, using KO^{t}Bu as the base, toluene appeared to be the best solvent to give the desired product **4a** in 69% yield (Table 1, entry 7). In other solvents, such as tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), 1,2-dimethoxyethane (DME), ^{i}PrOH, and dioxane, low yield or no reaction was observed (Table 1, entries 1–6). The reaction proceeded well when KO^{t}Bu was used as the base (Table 1, entry 7), whereas other bases, such as LiO^{t}Bu, NaO^{t}Bu, and NaOH were ineffective (Table 1, entries 8–10). In addition, no reaction took place when KOAc, $K_3PO_43H_2O$, Li_2CO_3, Cs_2CO_3, $NaHCO_3$, Na_2CO_3, K_2CO_3, and KOH were used as the base, respectively. Better result was obtained when the temperature was elevated to 90 °C (Table 1, entry 11). Finally, the best catalytic activity was achieved when the reaction was performed in refluxing toluene (Table 1, entry 12).

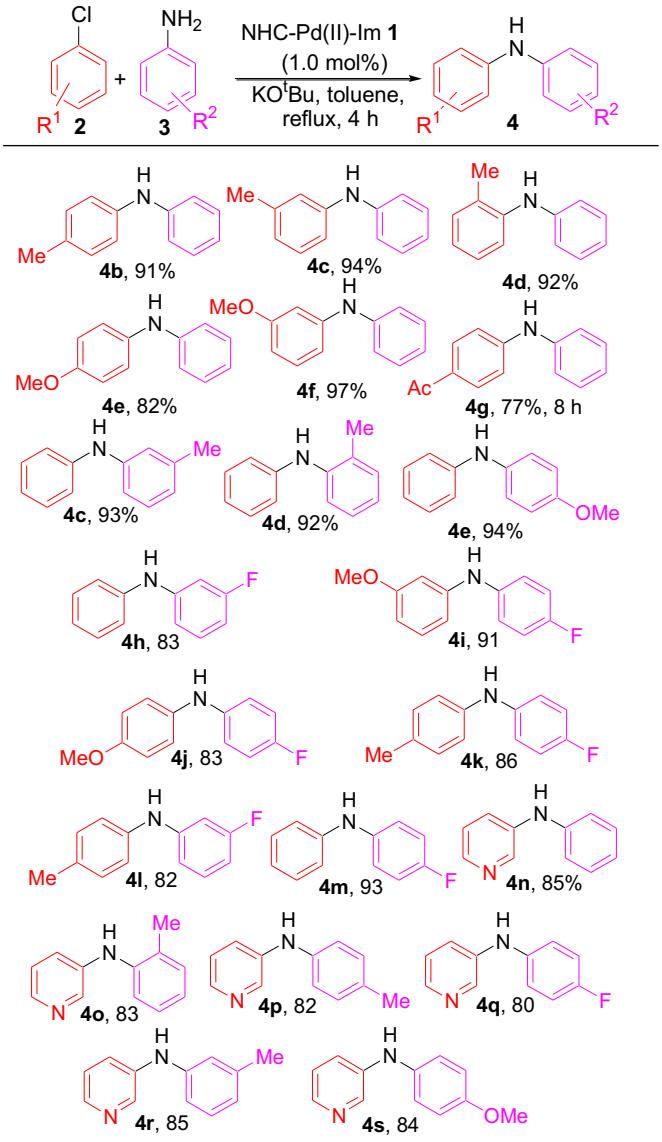
Table 1
Representative results for the optimization of NHC–Pd(II)–Im complex **1** catalyzed reaction between chlorobenzene **2a** and aniline **3a**



Entry[a]	Solvent	Base	Yield[b] (%)
1	THF	KO^{t}Bu	9
2	DMF	KO^{t}Bu	—
3	DMSO	KO^{t}Bu	Trace
4	DME	KO^{t}Bu	Trace
5	^{i}PrOH	KO^{t}Bu	Trace
6	Dioxane	KO^{t}Bu	—
7	Toluene	KO^{t}Bu	69
8	Toluene	LiO^{t}Bu	5
9	Toluene	NaO^{t}Bu	Trace
10	Toluene	NaOH	9
11[c]	Toluene	KO^{t}Bu	79
12[d]	Toluene	KO^{t}Bu	95

[a] Otherwise specified, all reactions were carried out using **2a** (0.77 mmol), **3a** (1.2 equiv), **1** (1.0 mol %), base (1.0 mmol) in the solvent (1.0 mL) at 70 °C for 4 h.
[b] Isolated yields.
[c] The reaction was carried out at 90 °C.
[d] The reaction was carried out under reflux.

Table 2
NHC–Pd(II)–Im **1** catalyzed amination of aryl chlorides



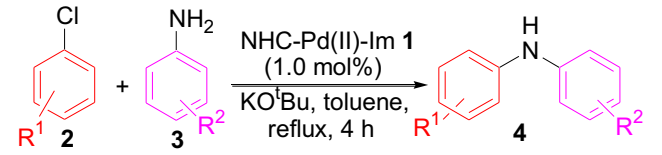
Notes:
[a] All reactions were carried out using **2** (0.80 mmol), **3**(1.2 equiv), **1** (1.0 mol%), KO^{t}Bu (1.0 mmol) in refluxing toluene (1.0 mL) for 4 h.
[b] Isolated yields.

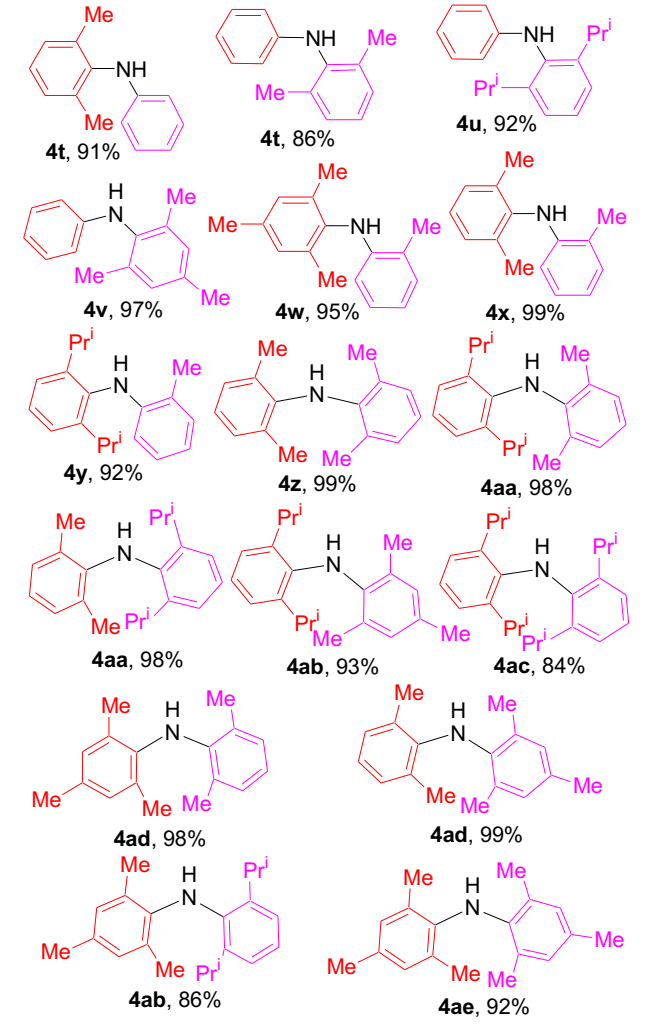
Subsequently, the scope of the amination reactions between various aryl chlorides **2** and primary amines **3** was first studied under the optimal conditions (no sterically hindered substrates were involved in this case). As can be seen from Table 2, all reactions took place smoothly to give the desired products **4** in good to high yields within 4 h. The reactions involving heteroaryl chloride, such as 3-chloropyridine also proceeded well to give products **4n**–**s** in 80–85% yields.

We next turned our particular attention to the amination reactions involving sterically hindered substrates. The results are shown in Table 3. As the sterically hindered anilines investigated, all reactions proceeded very well to give the desired products **4** in good to high yields. Sterically hindered deactivated aryl chlorides also worked well in these transformations. It is worthy of noting that a variety of *ortho*-tetra-substituted diarylamines, such as **4z**–**4ae** can be synthesized in 84–99% yields. It should be also noted here that product **4ac**, bearing *ortho*-tetra branched isopropyl groups, was the first example from the amination reaction of aryl chloride. These results indicated that the NHC–Pd(II)–Im complex **1** was pretty good for the amination reactions of sterically hindered substrates.

Finally, alkyl amines, which are usually difficult substrates in the C–N coupling reactions because of the β-hydride elimination during the catalytic cycle, were also tested. It was found that alkyl amines were also suitable in the NHC–Pd(II)–Im **1** catalyzed aminations under the optimal reaction conditions. For instance, 4-methoxybenzylamine, benzylamine, and cyclohexylamine reacted with chlorobenzene and 3-methoxyphenyl

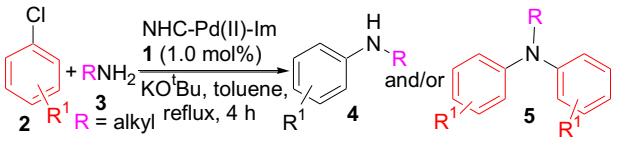
Table 3
Aminations using sterically hindered substrates

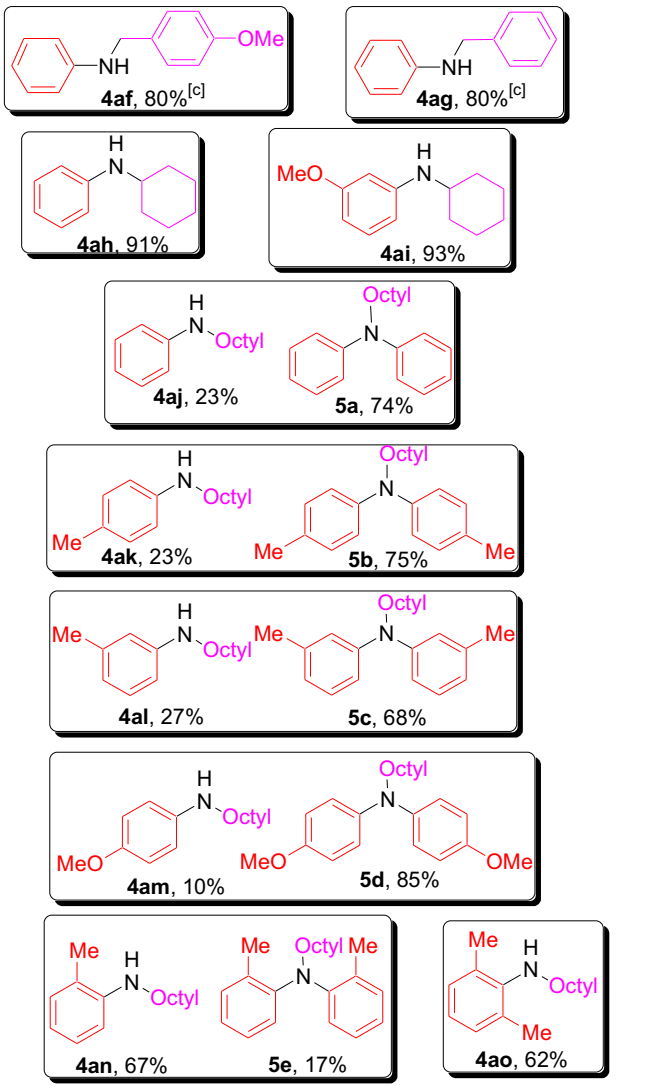




Notes:
[a] All reactions were carried out using **2** (0.80 mmol), **3**(1.2 equiv), **1** (1.0 mol%), KO^{t}Bu (1.0 mmol) in refluxing toluene (1.0 mL) for 4 h.
[b] Isolated yields.

Table 4
Aminations using alkyl amines as the substrates





Notes:
[a] Otherwise specified, all reactions were carried out using **2** (0.80 mmol), **3** (1.2 equiv), **1** (1.0 mol%), KO^{t}Bu (1.0 mmol) in refluxing toluene (1.0 mL) for 4 h.
[b] Isolated yields.
[c] 2.0 equiv of amines were used.

chloride smoothly to give the corresponding mono-aminated products **4af**–**ai** in good to high yields. In the case of the long-chain *n*-octylamine used as the substrate, the mono-aminated products **4** along with the bis-aminated products **5** were obtained in good to high total yields, with products **5** as the major in almost all cases. Substituents on the aryl chlorides have obvious effect on the reactions. For example, with 2-methylphenyl chloride as the substrate, the mono-aminated product **4an** was formed as the major. In addition, with the sterically hindered 2,6-dimethylphenyl chloride as the substrate, only the mono-aminated product **4ao** was isolated in 62% yield as the sole product (Table 4).

3. Conclusion

In conclusion, we have found that the well-defined NHC–Pd(II)–Im complex **1** derived from commercially available IPr·HCl, $PdCl_2$, and 1-methylimidazole was an efficient catalyst in the aminations between primary amines and aryl chlorides. Under the optimal reaction conditions, all aminated products can be achieved in good to high yields within 4 h. It is worthy of noting that the complex is fairly well for the aminations of sterically hindered primary amines and alkyl amines with aryl chlorides, which will open exciting opportunities for this complex in organic synthesis.

4. Experimental section

4.1. General remarks

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-300 or 500 MHz spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard or in DMSO-d_6; *J*-values are in hertz. THF, DMF, DMSO, DME, ^{i}PrOH, dioxane, and toluene were treated with standard method. Commercially obtained reagents were used without further purification. Flash column chromatography was carried out using Huanghai 300–400 mesh silica gel at increased pressure.

4.2. Experimental procedures

Under N_2 atmosphere, KO^{t}Bu (114.0 mg, 1.0 mmol), NHC–Pd(II)–Im complex **1** (5.2 mg, 1.0 mol %), dry toluene (1.0 mL), chlorobenzene **2a** (0.8 mmol), and aniline **3a** (0.96 mmol) were successively added into a Schlenk reaction tube. The reaction mixture was stirred under reflux for 4 h. Then the solvent was removed under reduced pressure and the residue was purified by a flash chromatography on silica gel to give the pure product **4a**.

4.2.1. Compound ***4a***.[14] A yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.26 (t, *J*=7.5 Hz, 4H, Ar), 7.07 (d, *J*=7.5 Hz, 4H, Ar), 6.92 (t, *J*=7.5 Hz, 2H, Ar), 5.69 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 129.3, 121.0, 117.8.

4.2.2. Compound ***4b***.[14] A yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.25–7.21 (m, 2H, Ar), 7.08 (d, *J*=8.0 Hz, 2H, Ar), 7.01–6.99 (m, 4H, Ar), 6.87 (t, *J*=7.5 Hz, 1H, Ar), 5.59 (s, 1H), 2.30 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 140.2, 130.9, 129.8, 129.3, 120.2, 118.8, 116.8, 20.7.

4.2.3. Compound ***4c***.[9g] A yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.27–7.24 (m, 2H, Ar), 7.15 (t, *J*=7.5 Hz, 1H, Ar), 7.06 (d, *J*=7.5 Hz, 2H, Ar), 6.93–6.87 (m, 3H, Ar), 6.75 (d, *J*=7.5 Hz, 1H, Ar), 5.64 (s, 1H), 2.30 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 143.1, 139.2, 129.3, 129.1, 121.9, 120.9, 118.5, 117.8, 114.9, 21.5.

4.2.4. Compound ***4d***.[14] A yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.25–7.11 (m, 5H, Ar), 6.96–6.87 (m, 4H, Ar), 5.36 (s, 1H), 2.24 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 141.2, 130.9, 129.3, 128.3, 126.7, 122.0, 120.4, 118.8, 117.4, 17.9.

4.2.5. Compound ***4e***.[14] A white solid. ^{1}H NMR (500 MHz, DMSO) δ 7.15 (dd, *J*=8.5, 7.5 Hz, 2H, Ar), 7.04 (d, *J*=8.5 Hz, 2H, Ar), 6.91 (d, *J*=7.5 Hz, 2H, Ar), 6.88–6.84 (m, 2H, Ar), 6.70 (t, *J*=7.5 Hz, 1H, Ar), 3.71 (s, 3H, OMe). ^{13}C NMR (125 MHz, DMSO) δ 153.8, 145.1, 136.1, 129.1, 120.3, 118.3, 114.8, 114.5, 55.2.

4.2.6. Compound ***4f***.[14] A pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.28–7.23 (m, 2H, Ar), 7.16 (t, *J*=8.0 Hz, 1H, Ar), 7.11 (d, *J*=7.5 Hz, 2H, Ar), 6.95 (t, *J*=7.5 Hz, 1H, Ar), 6.67 (d, *J*=7.5 Hz, 2H, Ar), 6.51–6.49 (m, 1H, Ar), 3.76 (s, 3H, OMe). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 144.2, 142.5, 130.1, 129.3, 121.6, 118.6, 110.5, 106.6, 103.6, 55.2.

4.2.7. Compound ***4g***.[15] A yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.87 (d, *J*=9.0 Hz, 2H, Ar), 7.35 (t, *J*=7.5 Hz, 2H, Ar), 7.19 (d, *J*=7.5 Hz, 2H, Ar), 7.08 (t, *J*=7.5 Hz, 1H, Ar), 7.00 (d, *J*=9.0 Hz, 2H, Ar), 2.53 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 148.4, 140.6, 130.6, 129.5, 129.0, 123.3, 120.7, 114.4, 26.1.

4.2.8. Compound ***4h***.[16] A pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.30 (t, *J*=7.8 Hz, 2H, Ar), 7.18 (dd, *J*=15.0, 7.8 Hz, 1H, Ar), 7.11 (d, *J*=7.8 Hz, 2H, Ar), 7.00 (t, *J*=7.2 Hz, 1H, Ar), 6.78 (d, *J*=8.7 Hz, 2H, Ar), 6.58 (t, *J*=7.8 Hz, 1H, Ar), 5.82 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7 (d, J_{C-F}=242.3 Hz), 145.3 (d, J_{C-F}=10.5 Hz), 141.9, 130.4 (d, J_{C-F}=9.8 Hz), 129.4, 122.0, 119.0, 112.5, 107.0 (d, J_{C-F}=21.8 Hz), 103.5 (d, J_{C-F}=25.5 Hz).

4.2.9. Compound ***4i***.[17] A pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.15 (t, *J*=8.1 Hz, 1H, Ar), 7.07 (dd, *J*=9.0, 4.8 Hz, 2H, Ar), 6.98 (t, *J*=9.0 Hz, 2H, Ar), 6.57–6.52 (m, 2H, Ar), 6.45 (dd, *J*=8.1, 2.1 Hz, 1H, Ar), 5.59 (s, 1H), 3.77 (s, 3H, OMe). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 158.2 (d, J_{C-F}=240.8 Hz), 145.4, 138.5, 130.2, 121.1 (d, J_{C-F}=7.5 Hz), 115.9 (d, J_{C-F}=22.5 Hz), 109.2, 105.5, 102.3, 55.2.

4.2.10. Compound ***4j***.[18] A pale yellow solid. ^{1}H NMR (300 MHz, DMSO) δ 7.80 (s, 1H, Ar) 7.03–6.98 (m, 4H, Ar), 6.93–6.83 (m, 4H, Ar), 3.69 (s, 3H, OMe). ^{13}C NMR (75 MHz, DMSO) δ 155.6 (d, J_{C-F}=232.7 Hz), 153.7, 141.6, 136.6, 119.8, 116.4 (d, J_{C-F}=7.5 Hz), 115.6 (d, J_{C-F}=22.0 Hz), 114.6, 55.2.

4.2.11. Compound ***4k***.[19] A pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.07 (d, *J*=8.4 Hz, 2H, Ar), 7.01–6.90 (m, 6H, Ar), 5.47 (s, 1H), 2.29 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6 (d, J_{C-F}=237.8 Hz), 141.0, 139.7, 130.5, 129.9, 119.3 (d, J_{C-F}=7.5 Hz), 117.8, 115.8 (d, J_{C-F}=21.8 Hz), 20.6.

4.2.12. Compound ***4l***.[19] A pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.18–7.10 (m, 3H, Ar), 7.01 (d, *J*=2.1 Hz, 2H, Ar), 6.71–6.67 (m, 2H, Ar), 6.55–6.49 (m, 1H, Ar), 5.68 (s, 1H), 2.32 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8 (d, J_{C-F}=242.3 Hz), 146.1 (d, J_{C-F}=10.5 Hz), 139.1, 132.1, 130.4 (d, J_{C-F}=9.8 Hz), 129.9, 120.1, 111.7, 106.3(d, J_{C-F}=21.0 Hz), 102.6 (d, J_{C-F}=24.8 Hz), 20.7.

4.2.13. Compound ***4m***.[18] A pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.28–7.22 (m, 2H, Ar), 7.08–6.88 (m, 7H, Ar), 5.64 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0 (d, J_{C-F}=238.5 Hz, C), 143.9, 138.8, 129.4, 120.5 (d, J_{C-F}=7.5 Hz), 116.7, 115.9 (d, J_{C-F}=21.8 Hz).

4.2.14. Compound ***4n***.[11d] A yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.38 (d, *J*=2.5 Hz, 1H, Ar), 8.16 (dd, *J*=4.5, 1.0 Hz, 1H, Ar), 7.42–7.40 (m, 1H, Ar), 7.30 (dd, *J*=8.5, 7.5 Hz, 2H, Ar), 7.17 (dd, *J*=8.5, 4.5 Hz, 1H, Ar), 7.08 (d, *J*=7.5 Hz, 2H, Ar), 7.00 (t, *J*=7.5 Hz, 1H, Ar), 5.79 (s, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 141.9, 141.8, 140.1, 139.8, 129.5, 123.7, 123.4, 122.0, 118.3.

4.2.15. Compound ***4o***.[20] A yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.29 (s, 1H, Ar), 8.12 (d, *J*=4.2 Hz, 1H, Ar), 7.26–7.12 (m, 5H, Ar), 7.01 (t, *J*=7.2 Hz, 1H, Ar), 5.47 (s, 1H), 2.26 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 140.6, 139.8, 139.5, 131.2, 129.4, 126.9, 123.7, 123.2, 122.8, 119.6, 17.9.

4.2.16. Compound ***4p***.[20] A pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.33 (d, *J*=2.7 Hz, 1H, Ar), 8.11 (d, *J*=4.5 Hz, 1H, Ar), 7.36–7.32 (m, 1H, Ar), 7.16–7.11 (m, 3H, Ar), 7.01 (d, *J*=8.1 Hz, 2H, Ar), 5.73 (s, 1H), 2.32 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 140.5, 139.3, 139.0, 132.0, 130.0, 123.7, 122.3, 119.3, 20.7.

4.2.17. Compound ***4q***.[20] A white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.31 (d, *J*=2.7 Hz, 1H, Ar), 8.13 (d, *J*=4.5 Hz, 1H, Ar), 7.31–7.27 (m, 1H, Ar), 7.15 (dd, *J*=8.1, 4.5 Hz, 1H, Ar), 7.10–6.98 (m, 4H, Ar), 5.79 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5 (d, J_{C-F}=240.8 Hz), 141.5, 140.5, 139.2, 137.6, 123.7, 122.3, 121.2 (d, J_{C-F}=8.3 Hz), 116.2 (d, J_{C-F}=22.5 Hz).

4.2.18. Compound ***4r***.[20] A pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.38 (s, 1H, Ar), 8.15 (d, *J*=4.2 Hz, 1H, Ar), 7.41 (d, *J*=8.4 Hz, 2H, Ar), 7.21–7.15 (m, 2H, Ar), 6.89 (d, *J*=7.5 Hz, 2H, Ar),

6.82 (d, J=7.5 Hz, 1H, Ar), 5.82 (s, 1H), 2.32 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 141.7, 140.0, 139.9, 139.5, 129.3, 123.7, 123.4, 122.9, 118.9, 115.3, 21.5.

4.2.19. Compound ***4s***.[20] A white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.25 (d, J=2.4 Hz, 1H, Ar), 8.07 (d, J=4.5 Hz, 1H, Ar), 7.27–7.19 (m, 1H, Ar), 7.13–7.10 (m, 3H, Ar), 6.89 (d, J=9.0 Hz, 2H, Ar), 5.58 (s, 1H), 3.81 (s, 3H, OMe). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 141.6, 140.6, 138.3, 134.3, 123.7, 122.7, 121.1, 114.8, 55.5.

4.2.20. Compound ***4t***.[21] A white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.19–7.09 (m, 5H, Ar), 6.77 (t, J=7.0 Hz, 1H, Ar), 6.54–6.52 (m, 2H, Ar), 5.21 (br, 1H), 2.24 (s, 6H, 2Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 138.2, 135.9, 129.2, 128.5, 125.7, 118.2, 113.5, 18.3.

4.2.21. Compound ***4u***.[16] A pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.30 (dd, J=8.5, 7.0 Hz, 1H, Ar), 7.22 (d, J=7.5 Hz, 2H, Ar), 7.14 (dd, J=8.5, 7.5 Hz, 2H, Ar), 6.71 (t, J=7.5 Hz, 1H, Ar), 6.48 (d, J=7.5 Hz, 2H, Ar), 3.20 (hep, J=7.0 Hz, 2H), 1.14 (d, J=7.0 Hz, 12H, 4Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 147.6, 135.1, 129.2, 127.2, 123.8, 117.6, 112.9, 28.2, 23.8.

4.2.22. Compound ***4v***.[14] A pale yellow liquid. ^{1}H NMR (500 MHz, DMSO) δ 7.04 (t, J=7.5 Hz, 2H, Ar), 6.91 (s, 2H, Ar), 6.55 (t, J=7.5 Hz, 1H, Ar), 6.36 (d, J=7.5 Hz, 2H, Ar), 2.23 (s, 3H, Me), 2.07 (s, 6H, 2Me). ^{13}C NMR (125 MHz, DMSO) δ 147.2, 135.8, 135.6, 134.3, 129.0, 128.9, 116.3, 112.2, 20.5, 18.0.

4.2.23. Compound ***4w***.[21] A white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.11 (d, J=7.5 Hz, 1H, Ar), 7.10–6.94 (m, 3H, Ar), 6.67 (t, J=7.5 Hz, 1H, Ar), 6.13 (d, J=8.0 Hz, 1H, Ar), 4.85 (s, 1H), 2.31 (s, 3H, Me), 2.30 (s, 3H, Me), 2.14 (s, 6H, 2Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 136.0, 135.6, 135.1, 130.2, 129.2, 126.9, 122.1, 117.8, 111.5, 20.9, 18.1, 17.6.

4.2.24. Compound ***4x***.[22] A white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.14–7.07 (m, 4H, Ar), 6.97 (t, J=7.5 Hz, 1H, Ar), 6.71 (t, J=7.5 Hz, 1H, Ar), 6.15 (d, J=8.0 Hz, 1H, Ar), 4.94 (s, 1H), 2.34 (s, 3H, Me), 2.19 (s, 6H, 2Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 138.7, 135.5, 130.2, 128.5, 126.9, 125.5, 122.5, 118.1, 111.8, 18.2, 17.6.

4.2.25. Compound ***4y***.[21] A pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.30–7.21 (m, 3H, Ar), 7.12 (d, J=7.5 Hz, 1H, Ar), 6.94 (t, J=8.0 Hz, 1H, Ar), 6.66 (t, J=7.5 Hz, 1H, Ar), 6.11 (d, J=8.0 Hz, 1H, Ar), 4.89 (s, 1H), 3.10 (hep, J=6.6 Hz, 2H), 2.34 (s, 3H, Me), 1.16 (d, J=6.6 Hz, 6H, 2Me), 1.11 (d, J=6.6 Hz, 6H, 2Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 146.0, 135.7, 130.1, 127.03, 126.95, 123.8, 121.3, 117.5, 111.4, 28.2, 24.7, 23.0, 17.6.

4.2.26. Compound ***4z***.[22] A white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 6.97 (d, J=7.5 Hz, 4H, Ar), 6.84 (t, J=7.5 Hz, 2H, Ar), 4.79 (s, 1H), 2.01 (s, 12H, 4Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 129.6, 128.7, 121.7, 19.1.

4.2.27. Compound ***4aa***.[23] A yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.16–7.11 (m, 3H, Ar), 6.94 (d, J=7.5 Hz, 2H, Ar), 6.72 (t, J=7.5 Hz, 1H, Ar), 4.79 (s, 1H), 3.15 (hep, J=7.0 Hz, 2H), 1.98 (s, 6H, 2Me), 1.12 (d, J=7.0 Hz, 12H, 4Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 143.1, 138.8, 129.5, 125.7, 124.8, 123.2, 119.6, 28.0, 23.4, 19.3.

4.2.28. Compound ***4ab***.[24] A yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.09 (s, 3H, Ar), 6.75 (s, 2H, Ar), 4.69 (s, 1H), 3.12 (hep, J=6.9 Hz, 2H), 2.22 (s, 3H, Me), 1.95 (s, 6H, 2Me), 1.11 (d, J=6.9 Hz, 12H, 4Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 140.5, 139.2, 130.0, 129.1, 126.4, 124.2, 123.2, 28.0, 23.4, 20.4, 19.2.

4.2.29. Compound ***4ac***. A white solid. Mp: 105–107 °C ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.10–6.98 (m, 6H, Ar), 4.87 (br, 1H), 3.08 (hep, J=6.6 Hz, 4H), 1.09 (d, J=6.6 Hz, 24H, 8Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 140.4, 123.8, 122.7, 27.8, 23.5. IR (neat) ν 3724, 3629, 3600, 2948, 2864, 2357, 2335, 1748, 1731, 1537, 1455, 1441, 1332, 1270, 1250, 1104, 1045, 931, 888, 864, 786, 741, 668 cm^{-1}. MS (ESI, m/z): 338 $[M+1]^+$; HRMS (EI): calcd for $C_{24}H_{36}N$ $[M]^+$: 338.2847; found: 338.2842.

4.2.30. Compound ***4ad***.[8b] A white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 6.96 (d, J=7.5 Hz, 2H, Ar), 6.81–6.78 (m, 3H, Ar), 4.71 (s, 1H), 2.26 (s, 3H, Me), 2.00 (s, 6H, 2Me), 1.99 (s, 6H, 2Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 139.0, 131.5, 130.5, 129.2, 128.8, 128.5, 120.9, 20.6, 19.1, 19.0.

4.2.31. Compound ***4ae***.[24] A white solid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 6.78 (s, 4H, Ar), 4.60 (s, 1H), 2.24 (s, 6H, 2Me), 1.97 (s, 12H, 4Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 130.7, 129.4, 129.3, 20.5, 19.0.

4.2.32. Compound ***4af***.[25] A pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.30 (d, J=9.0 Hz, 2H, Ar), 7.19 (dd, J=8.5, 7.5 Hz, 2H, Ar), 6.89 (d, J=9.0 Hz, 2H, Ar), 6.72 (t, J=7.5 Hz, 1H, Ar), 6.65 (d, J=7.5 Hz, 2H, Ar), 4.26 (s, 2H), 3.81 (s, 3H, OMe). ^{13}C NMR (500 MHz, $CDCl_3$) δ 158.9, 148.2, 131.4, 129.2, 128.8, 117.5, 114.0, 112.8, 55.3, 47.8.

4.2.33. Compound ***4ag***.[9g] A pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.40–7.26 (m, 5H, Ar), 7.20 (dd, J=8.0, 7.5 Hz, 2H, Ar), 6.74 (t, J=7.5 Hz, 1H, Ar), 6.66 (d, J=8.0 Hz, 2H, Ar), 4.35 (s, 2H), 4.04 (s, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 148.1, 139.4, 129.2, 128.6, 127.5, 127.2, 117.6, 112.8, 48.3.

4.2.34. Compound ***4ah***.[9g] A yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.15 (t, J=7.5 Hz, 2H, Ar), 6.66 (t, J=7.5 Hz, 1H, Ar), 6.59 (d, J=7.5 Hz, 2H, Ar), 3.51 (br, 1H), 3.28–3.23 (m, 1H), 2.07–2.05 (m, 2H), 1.78–1.74 (m, 2H), 1.67–1.64 (m, 1H), 1.42–1.33 (m, 2H), 1.26–1.14 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 147.4, 129.2, 116.8, 113.1, 51.7, 33.5, 25.9, 25.0.

4.2.35. Compound ***4ai***.[26] A yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.05 (t, J=8.0 Hz, 1H, Ar), 6.24–6.19 (m, 2H, Ar), 6.14 (t, J=2.5 Hz, 1H, Ar), 3.76 (s, 3H, OMe), 3.26–3.20 (m, 1H), 2.07–2.04 (m, 2H), 1.77–1.73 (m, 2H), 1.66–1.62 (m, 1H), 1.40–1.32 (m, 2H), 1.27–1.10 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 160.9, 148.8, 129.9, 106.4, 101.8, 99.1, 55.1, 51.7, 33.5, 25.9, 25.0.

4.2.36. Compound ***4aj***.[9g] A pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.17 (t, J=7.5 Hz, 2H, Ar), 6.68 (t, J=7.5 Hz, 1H, Ar), 6.60 (d, J=7.5 Hz, 2H, Ar), 3.59 (s, 1H), 3.10 (t, J=7.0 Hz, 2H), 1.63–1.56 (m, 2H), 1.41–1.26 (m, 10H), 0.89 (t, J=6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 129.2, 117.3, 112.9, 44.2, 31.8, 29.5, 29.4, 29.3, 27.2, 22.6, 14.1.

4.2.37. Compound ***4ak***.[27] A pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 6.99 (d, J=8.0 Hz, 2H, Ar), 6.54 (d, J=8.0 Hz, 2H, Ar), 3.08 (t, J=7.0 Hz, 2H), 2.24 (s, 3H, Me), 1.63–1.58 (m, 2H), 1.42–1.23 (m, 10H), 0.89 (t, J=7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 129.7, 126.3, 112.9, 44.4, 31.8, 29.6, 29.4, 29.3, 27.2, 22.6, 20.3, 14.1.

4.2.38. Compound ***4al***. A pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.06 (t, J=7.5 Hz, 1H, Ar), 6.52 (d, J=7.5 Hz, 1H, Ar), 6.44 (d, J=7.5 Hz, 2H, Ar), 3.09 (t, J=7.0 Hz, 2H), 2.28 (s, 3H, Me), 1.64–1.58 (m, 2H), 1.31–1.26 (m, 10H), 0.89 (t, J=6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 139.0, 129.1, 118.0, 113.5, 109.9, 44.1, 31.8, 29.6, 29.4, 29.3, 27.2, 22.6, 21.6, 14.1. IR (neat) ν 3418, 3389,

3046, 2952, 2919, 2851, 1727, 1600, 1586, 1484, 1325, 1300, 1260, 1177, 1163, 1094, 989, 837, 761, 686 cm^{-1}. MS (EI, *m*/*z*) (%): 219 (M^+, 16), 120 (100); HRMS (EI): calcd for $C_{15}H_{25}N$ $[M]^+$: 219.1987; found: 219.1989.

4.2.39. Compound ***4am***.[27] A pale yellow liquid. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 6.78 (d, *J*=8.5 Hz, 2H, Ar), 6.59 (d, *J*=8.5 Hz, 2H, Ar), 3.75 (s, 3H, OMe), 3.06 (t, *J*=7.0 Hz, 2H), 1.63–1.57 (m, 2H), 1.39–1.28 (m, 10H), 0.88 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 142.8, 115.0, 114.2, 55.9, 45.2, 31.8, 29.7, 29.4, 29.3, 27.2, 22.6, 14.1.

4.2.40. Compound ***4an***.[14] A pale yellow liquid. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.13 (t, *J*=7.5 Hz, 1H, Ar), 7.05 (d, *J*=7.5 Hz, 1H, Ar), 6.66–6.61 (m, 2H, Ar), 3.44 (br, 1H), 3.15 (t, *J*=7.0 Hz, 2H), 2.13 (s, 3H, Me), 1.70–1.64 (m, 2H), 1.45–1.25 (m, 10H), 0.90 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 130.0, 127.1, 121.7, 116.6, 109.6, 44.0, 31.8, 29.6, 29.4, 29.3, 27.2, 22.6, 17.4, 14.1.

4.2.41. Compound ***4ao***.[9g] A pale yellow liquid. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 6.99 (d, *J*=7.5 Hz, 2H, Ar), 6.81 (t, *J*=7.5 Hz, 1H, Ar), 2.97 (t, *J*=7.5 Hz, 2H), 2.29 (s, 6H, 2Me), 1.61–1.55 (m, 2H), 1.38–1.28 (m, 10H), 0.89 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 129.1, 128.9, 121.5, 48.7, 31.8, 31.2, 29.5, 29.3, 27.2, 22.6, 18.5, 14.1.

4.2.42. Compound ***5a***.[28] A colorless liquid. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.27–7.24 (m, 4H, Ar), 6.98 (d, *J*=7.5 Hz, 4H, Ar), 6.93 (t, *J*=7.5 Hz, 2H, Ar), 3.67 (t, *J*=7.5 Hz, 2H), 1.68–1.62 (m, 2H), 1.30–1.26 (m, 10H), 0.87 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 129.2, 121.0, 120.9, 52.4, 31.8, 29.4, 29.3, 27.5, 27.1, 22.6, 14.1.

4.2.43. Compound ***5b***. A pale yellow liquid. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.05 (d, *J*=8.0 Hz, 4H, Ar), 6.86 (d, *J*=8.0 Hz, 4H, Ar), 3.61 (t, *J*=7.5 Hz, 2H), 2.29 (s, 6H, 2Me), 1.64–1.61 (m, 2H), 1.29–1.26 (m, 10H), 0.87 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0, 130.2, 129.7, 120.8, 52.5, 31.8, 29.4, 29.3, 27.4, 27.1, 22.6, 20.6, 14.1. IR (neat) ν 3021, 2954, 2917, 2850, 1605, 1565, 1504, 1464, 1356, 1228, 1175, 1124, 1070, 1013, 801, 721 cm^{-1}. MS (EI, *m*/*z*) (%): 309 (22, M^+), 210 (100); HRMS (EI): calcd for $C_{22}H_{31}N$ $[M]^+$: 309.2457; found: 309.2459.

4.2.44. Compound ***5c***. A colorless liquid. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.14 (t, *J*=7.5 Hz, 2H, Ar), 6.79–6.75 (m, 6H, Ar), 3.64 (t, *J*=7.5 Hz, 2H), 2.29 (s, 6H, 2Me), 1.66–1.62 (m, 2H), 1.29–1.26 (m, 10H), 0.88 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 138.9, 129.0, 121.8, 121.6, 118.0, 52.4, 31.8, 29.4, 29.3, 27.5, 27.1, 22.6, 21.6, 14.1. IR (neat) ν 3035, 2952, 2919, 2847, 1727, 1596, 1575, 1484, 1452, 1358, 1264, 1166, 1134, 1094, 989, 855, 761, 711, 686 cm^{-1}. MS (EI, *m*/*z*) (%): 309 (20, M^+), 210 (100); HRMS (EI): calcd for $C_{22}H_{31}N$ $[M]^+$: 309.2457; found: 309.2460.

4.2.45. Compound ***5d***. A yellow liquid. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 6.88 (d, *J*=8.5 Hz, 4H, Ar), 6.81 (d, *J*=8.5 Hz, 4H, Ar), 3.78 (s, 6H, 2MeO), 3.55 (t, *J*=7.5 Hz, 2H), 1.63–1.59 (m, 2H), 1.29–1.26 (m, 10H), 0.87 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 142.5, 122.1, 114.6, 55.6, 53.0, 31.8, 29.4, 29.3, 27.5, 27.1, 22.6, 14.1. IR (neat) ν 2927, 2847, 1737, 1571, 1502, 1459, 1437, 1365, 1235, 1173, 1036, 816 cm^{-1}. MS (EI, *m*/*z*) (%): 341 (M^+, 36), 242 (100), 210 (47), 91 (47); HRMS (EI): calcd for $C_{22}H_{31}NO_2$ $[M]^+$: 341.2355; found: 341.2353.

4.2.46. Compound ***5e***. A colorless liquid. ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 7.14–7.09 (m, 4H, Ar), 6.96–6.90 (m, 4H, Ar), 3.39 (t, *J*=8.0 Hz, 2H), 2.05 (s, 6H, 2Me), 1.64–1.58 (m, 2H), 1. 32–1.25 (m, 10H), 0.87 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 133.2, 131.4, 126.2, 122.8, 122.7, 53.2, 31.8, 29.4, 29.3, 28.1, 27.2, 22.6, 18.7, 14.1. IR (neat) ν 3017, 2948, 2919, 2851, 1593, 1575, 1484, 1455, 1372, 1260, 1217, 1123, 1108, 1033, 982, 747, 714 cm^{-1}. MS (EI, *m*/*z*) (%): 309 (M^+, 21), 210 (100), 194 (18); HRMS (EI): calcd for $C_{22}H_{31}N$ $[M]^+$: 309.2457; found: 309.2456.

Acknowledgements

Financial support from the Opening Foundation of Zhejiang Provincial Top Key Discipline (No. 100061200123) is greatly acknowledged. Lei Zhu thanks Science and Technology Department of Zhejiang Province (Xinmiao Programme) for financial support (No. 2011R424043).

Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.01.008. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. For some selected papers, please see: (a) Belfield, A.; Brown, G. R.; Foubister, A. J. *Tetrahedron* **1999**, *55*, 11399–11428; (b) O'Hagan, D. *Nat. Prod. Rep.* **2000**, *17*, 435–446; (c) Craig, P. N. In Drayton, C. J., Ed. *Comprehensive Medicinal Chemistry*; Pergamon: New York, NY, 1991; Vol. 8.
2. (a) Kosugi, M.; Kameyama, M.; Migita, T. *Chem. Lett.* **1983**, 927–928; (b) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348–1350; (c) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609–3612.
3. For some recent selected reviews, please see: (a) Beletskaya, I. P.; Averin, A. D. *Pure Appl. Chem.* **2004**, *76*, 1605–1619; (b) Hartwig, J. F. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, 2002; pp 107–168; (c) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534–1544; (d) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338–6361.
4. (a) Grushin, V. V.; Alper, H. In *Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Berlin, 1999; pp 193–226; (b) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047–1062.
5. Selected papers for Buchwald's biaryl phosphines, please see: (a) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.-J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158–1174; (b) Breitler, S.; Oldenhuis, N. J.; Fors, B. P.; Buchwald, S. L. *Org. Lett.* **2011**, *13*, 3262–3265.
6. Selected papers for Hartwig's ferrocene-based phosphines, please see: (a) Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 5553–5566; (b) Shen, Q.-L.; Shekhar, S.; Stambuli, J. P.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2005**, *44*, 1371–1375.
7. Selected papers for Beller's N-substituted heteroaryl phosphines, please see: (a) Rataboul, F.; Zapf, A.; Jackstell, R.; Harkal, S.; Riermeier, T.; Monsees, A.; Dingerdissen, U.; Beller, M. *Chem.—Eur. J.* **2004**, *10*, 2983–2990; (b) Schulz, T.; Torgorg, C.; Enthaler, S.; Schaeffner, B.; Dumrath, A.; Spannenberg, A.; Neumann, H.; Boerner, A.; Beller, M. *Chem.—Eur. J.* **2009**, *15*, 4528–4533.
8. Selected papers for Verkade's amino phosphines, please see: (a) Urgaonkar, S.; Nagarajan, M.; Verkade, J. G. *Org. Lett.* **2003**, *5*, 815–818; (b) Urgaonkar, S.; Xu, J.-H.; Verkade, J. G. *J. Org. Chem.* **2003**, *68*, 8416–8423.
9. For some other representative phosphines, please see: (a) Liu, D.; Gao, W.-Z.; Dai, Q.; Zhang, X.-M. *Org. Lett.* **2005**, *7*, 4907–4910; (b) Singer, R. A.; Caron, S.; McDermott, R. E.; Arpin, P.; Do, N. M. *Synthesis* **2003**, 1727–1731; (c) Li, G. Y.; Zheng, G.; Andrew, A. F. *J. Org. Chem.* **2001**, *66*, 8677–8681; (d) Chen, G.-S.; Lam, W. H.; Fok, W. S.; Lee, H. W.; Kwong, F. Y. *Chem.—Asian J.* **2007**, *2*, 306–313; (e) Ackermann, L.; Spatz, J. H.; Gschrei, C. J.; Born, R.; Althammer, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 7627–7630; (f) Rodriguez, S.; Qu, B.; Haddad, N.; Reeves, D. C.; Tang, W.-J.; Lee, H.; Krishnamurthy, D.; Senanayake, C. H. *Adv. Synth. Catal.* **2011**, *353*, 533–537; (g) Lundgren, R. J.; Sappong-Kumankumah, A.; Stradiotto, M. *Chem.—Eur. J.* **2010**, *16*, 1983–1991.
10. For some selected reviews on NHCs, please see: (a) Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440–1449; (b) Glorius, F. *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Springer: Berlin, Germany, 2007; (c) Nolan, S. P. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, Germany, 2006; (d) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768–2813; (e) Fortman, G. C.; Nolan, S. P. *Chem. Soc. Rev.* **2011**, *40*, 5151–5169.
11. For some recent selected examples, please see: (a) Jin, Z.; Guo, S.-X.; Gu, X.-P.; Qiu, L.-L.; Song, H.-B.; Fang, J.-X. *Adv. Synth. Catal.* **2009**, *351*, 1575–1585; (b) Organ, M. G.; Abdel-Hadi, M.; Avola, S.; Dubovyk, I.; Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Sayah, M.; Valente, C. *Chem.—Eur. J.* **2008**, *14*, 2443–2452; (c) Jin, Z.; Qiu, L.-L.; Li, Y.-Q.; Song, H.-B.; Fang, J.-X. *Organometallics* **2010**, *29*, 6578–6586; (d) Broggi, J.; Clavier, H.; Nolan, S. P. *Organometallics* **2008**, *27*, 5525–5531; (e) Marion, N.; Navarro, O.; Mei, J.-G.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101–4111; (f) Hoi, K. H.; Çalimsiz, S.;

Froese, R. D. J.; Hopkinson, A. C.; Organ, M. G. *Chem.—Eur. J.* **2011**, *17*, 3086–3090.
12. Zhu, L.; Gao, T.-T.; Shao, L.-X. *Tetrahedron* **2011**, *67*, 5150–5155.
13. Ehrentraut, A.; Zapf, A.; Beller, M. *J. Mol. Catal. A: Chem.* **2005**, *182–183*, 515–523.
14. Ackermann, L.; Sandmann, R.; Song, W.-F. *Org. Lett.* **2011**, *13*, 1784–1786.
15. Islam, M.; Mondal, P.; Tuhina, K.; Roy, A. S.; Mondal, S.; Hossain, D. *J. Organomet. Chem.* **2010**, *695*, 2284–2295.
16. Desmarets, C.; Schneider, R.; Fort, Y. *J. Org. Chem.* **2002**, *67*, 3029–3036.
17. Rivara, S.; Vacondio, F.; Fioni, A.; Silva, C.; Carmi, C.; Mor, M.; Lucini, V.; Pannacci, M.; Caronno, A.; Scaglione, F.; Gobbi, G.; Spadoni, G.; Bedini, A.; Orlando, P.; Lucarini, S.; Tarzia, G. *ChemMedChem* **2009**, *4*, 1746–1755.
18. Correa, A.; Carril, M.; Bolm, C. *Chem.—Eur. J.* **2008**, *14*, 10919–10922.
19. Suzuki, T.; Moriya, M.; Sakamoto, T.; Suga, T.; Kishino, H.; Takahashi, H.; Ishikawa, M.; Nagai, K.; Imai, Y.; Sekino, E.; Ito, M.; Iwaasa, H.; Ishihara, A.; Tokita, S.; Kanatani, A.; Sato, N.; Fukami, T. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3072–3077.
20. Mazu, T. K.; Etukala, J. R.; Zhu, X. Y.; Jacob, M. R.; Khan, S. I.; Walker, L. A.; Ablordeppey, S. Y. *Bioorg. Med. Chem.* **2011**, *19*, 524–533.
21. Hill, L. L.; Crowell, J. L.; Tutwiler, S. L.; Massie, N. L.; Corey Hines, C.; Griffin, S. T.; Rogers, R. D.; Shaughnessy, K. H. *J. Org. Chem.* **2010**, *75*, 6477–6488.
22. Xu, C.; Wang, Z.-Q.; Fu, W.-J.; Lou, X.-H.; Li, Y.-F.; Cen, F.-F.; Ma, H.-J.; Ji, B.-M. *Organometallics* **2009**, *28*, 1909–1916.
23. Winkelmann, O. H.; Riekstins, A.; Nolan, S. P.; Navarro, O. *Organometallics* **2009**, *28*, 5809–5813.
24. Ishihara, K.; Nakagawa, S.; Sakakura, A. *J. Am. Chem. Soc.* **2005**, *127*, 4168–4169.
25. Martínez-Asencio, A.; Ramón, D. J.; Yus, M. *Tetrahedron* **2011**, *67*, 3140–3149.
26. Wu, Z.-Q.; Zhou, L.; Jiang, Z.-Q.; Wu, D.; Li, Z.-K.; Zhou, X.-G. *Eur. J. Org. Chem.* **2010**, 4971–4975.
27. Chen, L.; Yu, G.-A.; Zhu, X.-L.; Zhang, B.; Guo, R.; Li, X.-Z.; Yang, Q.-H.; Jin, S.; Liu, C.-C.; Liu, S.-H. *J. Organomet. Chem.* **2010**, *695*, 1768–1775.
28. Liu, B.; Najari, A.; Pan, C.-Y.; Leclerc, M.; Xiao, D.-Q.; Zou, Y.-P. *Macromol. Rapid Commun.* **2010**, *31*, 391–398.