Supporting Information

Nickel-Catalyzed Triarylamine Synthesis: Synthetic and Mechanistic Aspects

Xin-Le Li,[a,b] Wei Wu,[a,b] Xin-Heng Fan*,[a] and Lian-Ming Yang*,[a]

[a] Beijing National Laboratory for Molecular Sciences (BNLMS), Key laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[b] Graduate School of Chinese Academy of Sciences, Beijing 100049, China

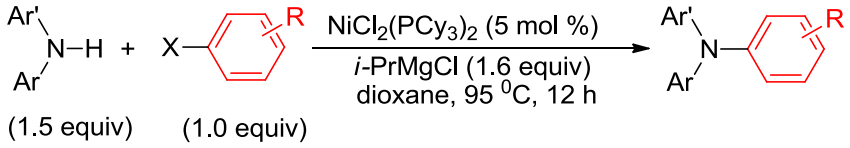
xinxin9968@iccas.ac.cn; yanglm@iccas.ac.cn

1. General considerations

^{1}H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE 400 spectrometer. Mass spectra were obtained on a Bruker Daltonics Inc. APEXII FT-ICR. Melting points were measured with an X-4 micro melting-point apparatus and uncorrected. Reactions were carried out under nitrogen atmosphere with oven-dried glassware unless stated otherwise. Dioxane and toluene were distilled from sodium/benzophenone before use. Organometallic reagents (Grignard reagents and *n*-butyl lithium) and two special ligands (PCy_3 and IPr·HCl) were provided by vendors. Diarylamines and haloarenes were available commercially and used without further purification. Aryl tosylates[1] were synthesized by the literature method. Nickel complexes, $Ni(acac)_2$, $NiCl_2(PPh_3)_2$,[2] $NiCl_2$(dppe),[2] $NiCl_2$(bpy),[3] and $NiCl_2(PCy_3)_2$,[4] were commercially purchased or prepared according to the literature procedures. Column chromatography was performed on silica gel (200–300 mesh). All yields refer to isolated yields (average of two run) of compounds estimated to be > 95% pure as determined by ^{1}H NMR. The known compounds were partly characterized by melting points, MS, ^{1}H NMR, and compared to authentic samples or the literature data. New compounds were characterized by ^{1}H and ^{13}C NMR, MS, and Elemental analysis.

2. Experimental procedures

2.1 General procedure for the nickel-catalyzed synthesis of triphenylamines



(1.5 equiv) (1.0 equiv)

1 **2** **3**

An oven-dried 25-mL three-necked flask was charged with $NiCl_2(PCy_3)_2$ (5 mol% relative to the aromatic chlorides, 34 mg), and a diarylamine (1.5 mmol). The flask was evacuated and backfilled with

nitrogen, with the operation being repeated twice. Anhydrous dioxane (5 mL) was added via syringe. Then *i*-PrMgCl reagent (0.8 mL, 1.6 mmol, 2.0 M solution in THF) was added slowly at room temperature via syringe. After stirring for 5 minutes, an aryl halide (1.0 mmol) (if liquid) or its solution in a minimum volume of dioxane (if solid) was added via syringe. The mixture was stirred at room temperature for another 10 minutes, and then placed in an oil bath of 95 ^{0}C for 12 h. The reaction mixture, after being cooled to ambient temperature, was poured to 20 mL of saturated aqueous NH_4Cl solution and then extracted with ethyl acetate (10 mL × 3). The combined organic phases were concentrated under reduced pressure and the residue purified by column chromatography.

2.2 Typical experiments for the reaction of sodium diphenylamide with arylnickel(II) halides

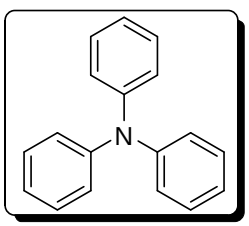
An oven-dried 25-mL three-necked flask was charged with sodium hydride (60 mg of 60% NaH in white oil, 1.5 mmol) and anhydrous toluene (8 mL). To the suspension was added a solution of diphenylamine (256 mmol, 1.55 mmol) in toluene (2 mL) via syringe, stirring at room temperature for 0.5 h. Then an arylnickel(II) halide (1 mmol) was added into the flask by a solid-adding adapter, and the resulting mixture was heated in an oil bath of 120 ^{0}C for 12 h. The reaction mixture was allowed to cool to ambient temperature, and filtered through a pad of silica gel which was washed with toluene (10 mL × 2). The combined organic layers were concentrated *in vacuo* and the residue was subjected to normal analyses.

2.3 Typical experiments for the reaction of choromagnesium diphenylamide with arylnickel(II) halides

An oven-dried 25-mL three-necked flask was charged with diphenylamine (256 mg, 1.55 mmol), PCy_3 (560 mg, 2 mmol) and dioxane (10 mL). To the mixture solution was slowly added *i*-PrMgCl reagent (0.75 mL, 1.5 mmol, 2.0 M solution in THF) via syringe, and the resulting mixture continued to stir at room temperature for 5 minutes. Then the arylnickel(II) halide (1 mmol) was added into the flask by a solid-adding adapter, and the mixture was heated in an oil bath of 95 ^{0}C for 12 h. The reaction mixture was poured to 20 mL of saturated NH_4Cl aqueous solution and then extracted with ethyl acetate (10 mL × 3). Solvents were removed *in vacuo* to afford the residue which was subjected to normal analyses.

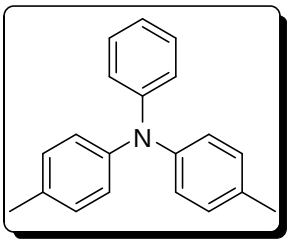
3. Characterization data for the compounds

Triphenylamine (3aa) (CAS Registry No.603-34-9)



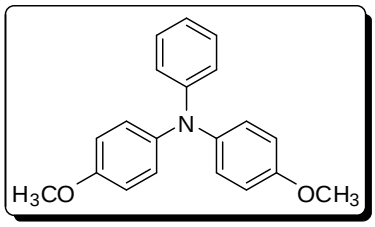
Colorless solid, mp: 127–128 ^{0}C (lit.[5] mp 127 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, *J* = 7.6 Hz, 6H), 7.09 (d, *J* = 8.4 Hz, 6H), 7.01(t, *J* = 7.2 Hz, 3H). MS (EI): m/z 245 (M^+).

4,4'-Dimethyltriphenylamine (3ba) (CAS Registry No. 20440-95-3)



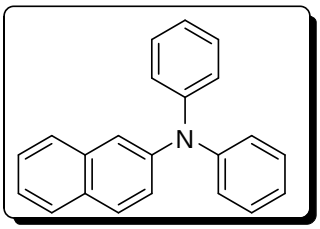
Colorless solid, mp: 106–107 ^{0}C (lit.[6] mp 107–108 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 8.8 Hz, 6H), 7.00 (d, *J* = 8 Hz, 4H), 6.94 (t, *J* = 7.6 Hz, 1H), 2.32 (s, 6H). MS (EI): m/z 273 (M^+).

4,4'-Dimethoxyltriphenylamine (3ca) (CAS Registry No. 20440-94-2)



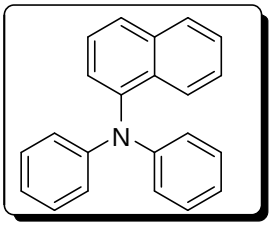
Colorless solid, mp: 104–105 ^{0}C (lit.[7] mp 103 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 9.2 Hz, 4H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 9.2 Hz, 4H), 3.80 (s, 6H). MS (EI): m/z 305 (M^+).

(Diphenyl)(2-naphthyl)amine (3da) (CAS Registry No. 6940-30-3)



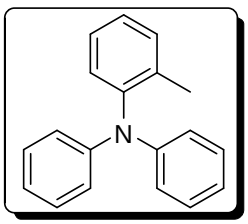
Colorless solid, mp: 118–120 ^{0}C (lit.[8] mp 120–121 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8 Hz, 1H), 7.4 (d, *J* = 1.6 Hz, 1H), 7.41–7.33 (m, 2H), 7.31–7.20 (m, 5H), 7.14 (d, *J* = 7.6 Hz, 4H), 7.04 (t, *J* = 7.2 Hz, 2H). MS (EI): m/z 295 (M^+).

(Diphenyl)(1-naphthyl)amine (3ea) (CAS Registry No. 61231-45-6)



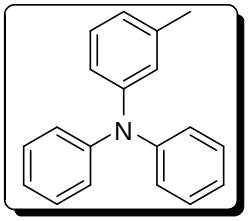
Colorless solid, mp: 136–137 ^{0}C (lit.[9] mp 135–137 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.45 (q, *J* = 7.6 Hz, 2H), 7.34 (q, *J* = 7.6 Hz, 2H), 7.19(t, *J* = 8.4 Hz, 4H), 7.03 (d, *J* = 8 Hz, 4H), 6.93 (t, *J* = 7.6 Hz, 2H). MS (EI): m/z 295 (M^+).

2-Methyltriphenylamine (3ab) (CAS Registry No. 4316-55-6)



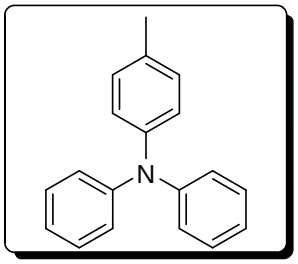
Colorless solid, mp: 55–56 ^{0}C (lit.[10] mp 56–58 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.18 (m, 6H), 7.14 (t, *J* = 8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 4H), 6.92 (t, *J* = 7.2 Hz, 2H), 2.04 (s, 3H). MS (EI): m/z 259 (M^+).

3-Methyltriphenylamine (3ac) (CAS Registry No. 4316-54-5)



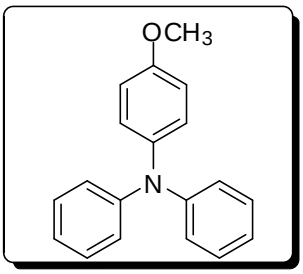
Colorless solid, mp: 87–88 ^{0}C (lit.[11] mp 87–87.5 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (t, *J* = 8 Hz, 4H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 4H), 7.00 (t, *J* = 7.2 Hz, 2H), 6.90 (t, *J* = 8.4 Hz, 2H). 6.84 (d, *J* = 7.6 Hz, 1H), 2.26 (s, 3H). MS (EI): m/z 259 (M^+).

4-Methyltriphenylamine (3ad) (CAS Registry No. 4316-53-4)



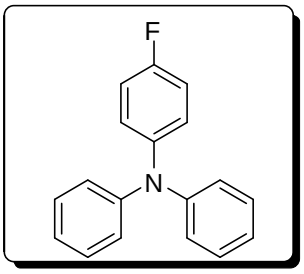
Colorless solid, mp: 68–70 ^{0}C (lit.[12] mp 68.8 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.2 Hz, 4H), 7.08–7.64 (m, 6H), 7.02–6.98 (m, 4H), 2.32 (s, 3H). MS (EI): m/z 259 (M^+).

4-Methoxytriphenylamine (3ae) (CAS Registry No. 4316-51-2)



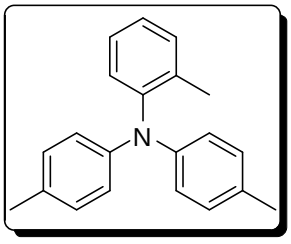
Colorless solid, mp: 98–100 ^{0}C (lit.[13] mp 102 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, *J* = 8 Hz, 4H), 7.07 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 4H), 6.94 (t, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 8 Hz, 2H), 3.80 (s, 3H). MS (EI): m/z 275 (M^+).

4-Fluorotriphenylamine (3af) (CAS Registry No. 437-25-2)



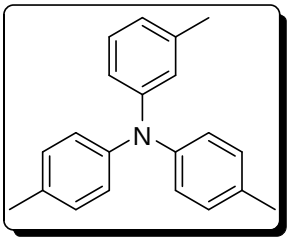
Colorless solid, mp: 85–87 ^{0}C (lit.[14] mp 96 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (t, *J* = 7.2 Hz, 4 H), 7.07–6.94 (m, 10H). MS (EI): m/z 263 (M^+).

Di(*p*-tolyl)(*o*-tolyl)amine (3bb) (CAS Registry No. 119713-64-3) [15]



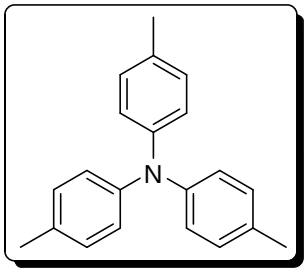
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, *J* =7.6 Hz, 1H), 7.15 (t, *J*= 7.6 Hz, 1H), 7.11 (t, *J*= 7.6 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 4H), 6.85 (d, *J* = 8.4Hz, 4H), 2.28 (s, 6H), 2.02 (s, 3H). MS (EI): m/z 287 (M^+).

Di(*p*-tolyl)(*m*-tolyl)amine (3bc) (CAS Registry No. 117597-62-3)



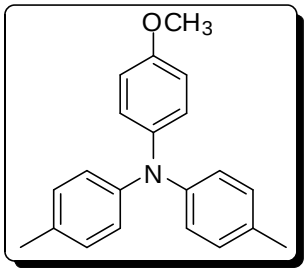
Colorless solid, mp: 55–56 ^{0}C (lit.[16] mp 56.5 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (t, *J* = 8 Hz, 1H), 7.06 (d, *J* = 8 Hz, 4H), 6.98 (d, *J* = 8.4 Hz, 4H), 6.87 (s, 1H), 6.84 (d, *J* = 8 Hz, 1H), 6.77 (d, *J* = 8 Hz, 1H), 2.31 (s, 6H), 2.24 (s, 3H). MS (EI): m/z 287 (M^+).

4,4',4''-Trimethyltriphenylamine (3bd) (CAS Registry No. 1159-53-1)



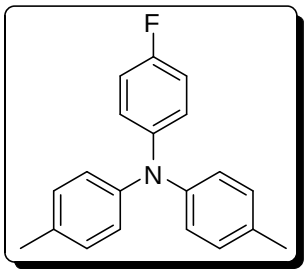
Colorless solid, mp: 115–116 ^{0}C (lit.[17] mp 117 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, *J* = 8.4 Hz, 6H), 6.96 (d, *J* = 8 Hz, 6H), 2.30 (s, 6H). MS (EI): m/z 287 (M^+).

Di(*p*-tolyl)(*p*-anisyl)amine (3be) (CAS Registry No. 61600-39-3)



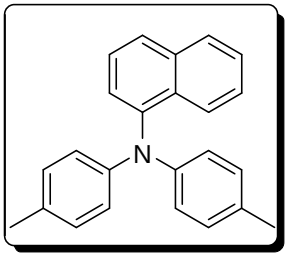
Colorless solid, mp: 70–73 ^{0}C (lit.[18] mp 72 ^{0}C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8 Hz, 4H), 6.94 (d, *J* = 8.4 Hz, 4H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H), 2.30 (s, 3H). MS (EI): m/z 303 (M^+).

Di(*p*-tolyl)(4-fluorophenyl)amine (3bf) (CAS Registry No. 64634-57-7)[19]



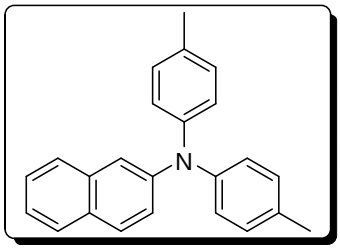
Colorless solid, mp: 80–81 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, *J* = 8.4 Hz, 4H), 7.02–7.00 (m, 2H), 6.94 (d, *J* = 8.4 Hz, 4H), 6.94–6.90 (m, 2H), 2.31 (s, 6H). MS (EI): m/z 291 (M^+).

Di(*p*-tolyl)(1-naphthyl)amine (3bg) (CAS Registry No. 139905-65-0)[20]



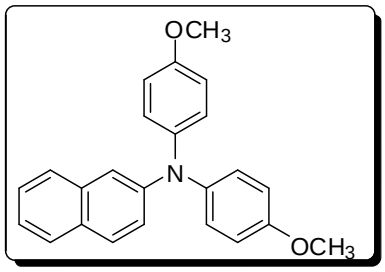
Colorless solid, mp: 80–81 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 4H), 6.93 (d, *J* = 8.4 Hz, 4H), 2.29 (s, 6H). MS (EI): m/z 323 (M^+)

Di(*p*-tolyl)(2-naphthyl)amine (3bh) (CAS Registry No. 141388-60-5)[21]



Colorless solid, mp: 125–126 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.38–7.28 (m, 3H), 7.25 (d, *J* = 8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 4H), 7.03 (d, *J* = 8.4 Hz, 4H), 2.33 (s, 6H). MS (EI): m/z 323 (M^+).

Di(*p*-anisyl)(2-naphthyl)amine (3ch) (CAS Registry No.1236198-41-6)[22]



Colorless solid, mp: 76–77 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.4Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8 Hz, 1H), 7.35 (t, *J* = 8 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 4H), 6.84 (d, *J* = 9.2 Hz, 4H), 3.81 (s, 6H). MS (EI): m/z 355 (M^+).

4. References

1. Y. Kubota, S. Nakada and Y. Sugi, *Synlett*, 1988, 183.
2. K. Yamamoto, *Bull. Chem. Soc. Japan*., 1954, **27**, 501.
3. I. G. Murgulescu, E. Segal and D.T. Fatu, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2677.
4. (a) P. J. Stone and Z. Dori, Inorg. *Chim. Acta* 1970, **5**, 434; (b) K. W. Barnett, *J. Chem. Educ.*, 1974, **51**, 422.
5. C. W. N. Cumper and A. P. Thurston, *J. Chem. Soc*., **1971**, 422.
6. B. Staskun, *J. Org. Chem*., 1968, **33**, 3031.
7. W. Lamm, W. Jugelt and F. Pragst, *J. fuer Praktische Chemie*, 1975, **317**, 284.
8. K. Haga, K. Iwaya and R. Kaneko, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 803.
9. Z.-J. Liu and R. C. Larock, *J. Org. Chem.*, 2006, **71**, 3198.
10. R. N. Nelson and R. N. Adams, *J. Am. Chem. Soc*., 1968, **90**, 3925.
11. A. J. Paine, *J. Am. Chem. Soc*., 1987, **109**, 1496.
12. R. J. Marsden, B. *J. Chem. Soc*., 1937, 627.
13. J. Forrest, *J. Chem. Soc.*, 1960**,** 581.
14. C. J. Smith, M. W. S. Tsang, A. B. Holmes, R. L. Danheiser, and J. W. Tester, *Org. Biomol. Chem.*, 2005**, 3**, 3767.
15. T. Masakazu, *Chem. Lett.*, 2002, **3**, 308.
16. T. Manifar, S. Rohani and M. Jennings, *Acta Crystallogr. Sect. E.*, 2005, **61**, 1032.

17. G. A. Artamkina, A. G. Sergeev, M. M. Shtern and I. P. Beletskaya, *Russ. J. Org. Chem.*, 2006, **42**, 1683.

18. K. Matsuo, Y. Shichida, H. Nishida, S. Nakata and M. Okubo, *J. Phys. Org. Chem.*, 1994, **7**, 9.

19. S. I. Pombrik, D. N. Kravtsov, B. A. Kvasov and E. I. Fedin, *J. Organomet. Chem.*, 1977, **136**, 185.

20. S. Susumu, A. Mitsutoshi and S. Nobuo, *Jpn. Kokai Tokkyo Koho*, 2000, 10.

21. T. Shimada, M. Sasaki and T. Ariga, *Jpn. Kokai Tokkyo Koho*, 1991, 7.

22. T. Mizushima, D. Yamazaki, M. Wada, A. Fujii, W. Miyashita and T. Shota, *Jpn. Kokai Tokkyo Koho*, 2010, 78.