Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Nickel-Catalyzed Cross-Coupling of Diarylamines with Haloarenes

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General considerations. All reactions were carried out under a nitrogen atmosphere in oven-dried glassware. THF, dioxane, toluene and *m*-xylene were dried over Na/benzophenone and distilled before use. Sodium hydride (60% in white oil) was commercially available and stored in a desiccator over calcium oxide and weighted rapidly in the air. Aryl halides and diarylamines were purchased and used without further purification. $Ni(PPh_3)_2Cl_2$[1] and Ni(II)–(σ-aryl) complexes[2] were prepared according to the literature procedures. Column chromatography was performed on silical gel (200–300 mesh). All yields refer to isolated yields (an average of two runs) of compounds estimated to be >95% pure as determined by ^{1}H NMR. All products are known compounds which were characterized partly by ^{1}H NMR and MS and compared to authentic samples or the literature data.

General procedure for the nickel-catalyzed arylation of diarylamine with bromo-/iodoarenes. An oven-dried 50-mL three-necked flask was charged with sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol % relative to diarylamine), and PPh_3 (52 mg, 10 mol% relative to diarylamine). The diarylamine (2 mmol) and the aryl bromide/iodide (3–4 mmol) were added at this time if solid. The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. Dried toluene (10 mL) was added via syringe, followed by the aryl bromide/iodide (4 mmol) if liquid. The reaction mixture was heated at an oil bath of 120 ^{0}C for 12 h. The reaction mixture was allowed to cool to room temperature, quenched with H_2O (20 mL), and filtered through a pad of silica gel. The Organic layer was separated and the aqueous phase extracted with toluene (20 mL × 2). Then the combined organic phases were dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated under reduced pressure and the residue purified by column chromatography on silica gel with petroleum ether to afford the analytically pure product.

Triphenylamine (Table 2, entry 1). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol %), PPh_3 (52 mg, 10 mol%), diphenylamine (338 mg, 2 mmol), and bromobenzene (628 mg, 4 mmol) were transformed into the product as a white solid (430 mg, 88%): mp 127–128 ^{0}C (lit.,[3] mp 127 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.01 (t, *J* = 7.6 Hz, 3H), 7.10 (d, *J* = 7.6 Hz, 6H), 7.25 (t, *J* = 7.6 Hz, 6H); MS (EI): *m/z* 245 (M^+). CAS Number: 603-34-9.

A similar reaction using iodobenzene (816 mg, 4 mmol) afforded the product (Table 2, entry 2) as a white solid (441 mg, 90%).

Diphenyl(*p*-chlorophenyl)amine (Table 2, entry 4). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol%), and PPh_3 (52 mg, 10 mol%), diphenylamine (338 mg, 2 mmol) and 4-bromo-1-chlorobenzene (764 mg, 4 mmol) were transformed into the product as a white solid (336 mg, 60%): mp 103–104 ^{0}C (lit.,[4] mp 103–104.5 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.98–7.05 (m, 4H), 7.05–7.10 (m, 4H), 7.16–7.22 (m, 2H), 7.26 (t, *J* = 7.8 Hz, 4H); MS (EI): *m/z* 280 (M^+). CAS Number: 4316-56-7.

Diphenyl(*m*-chlorophenyl)amine (Table 2, entry 5). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol%), and PPh_3 (52 mg, 10 mol%), diphenylamine (338 mg, 2 mmol) and 3-bromo-1-chlorobenzene (764 mg, 4 mmol) were transformed into the product as a white solid (353 mg, 63%): mp 86–87 ^{0}C (lit.,[5] mp 87–87.5 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.92 (d, *J* = 7.6 Hz, 2H), 7.02–7.14 (m, 8H), 7.28 (t, *J* = 8.2 Hz, 4H); MS (EI): *m/z* 280 (M^+). CAS Number: 106336-13-4.

Diphenyl(*p*-tolyl)amine (Table 2, entry 6). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol %), and PPh_3 (52 mg, 10 mol%), diphenylamine (338 mg, 2 mmol) and *p*-bromotoluene (684 mg, 4 mmol) were transformed into the product as a white solid (337 mg, 65%): mp 69–70 ^{0}C (lit.,[6] mp 68.8 ^{0}C). ^{1}H

NMR ($CDCl_3$, 400 MHz): δ 2.32 (s, 3H), 6.93–7.04 (m, 4H), 7.04–7.10 (m, 6H), 7.23 (t, *J* = 7.8 Hz, 4H); MS (EI): *m/z* 259 (M^+). CAS Number: 4316-53-4.

A similar reaction using *p*-iodotoluene (872 mg, 4 mmol) afforded the product (Table 2, entry 7) as a white solid (352 mg, 68%).

Diphenyl(*o*-tolyl)amine (Table 2, entry 8). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol %), and PPh_3 (52 mg, 10 mol%), diphenylamine (338 mg, 2 mmol) and *o*-bromotoluene (684 g, 4 mmol) were transformed into the product as a white solid (233 mg, 45%): mp 55–56 ^{0}C (lit.,[7] mp 56–58 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.05 (s, 3H), 2.34 (s, 3H), 6.93 (t, *J* = 7.3 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 4H), 7.13–7.17 (m, 2H), 7.17–7.27 (m, 6H); MS (EI): *m/z* 259 (M^+). CAS Number: 4316-55-6.

(2,4-Dimethylphenyl)diphenylamine (Table 2, entry 9). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol %), and PPh_3 (52 mg, 10 mol%), diphenylamine (338 mg, 2 mmol) and 2,4-dimethylbromobenzene (740 mg, 4 mmol) were transformed into the product as a white solid (218 mg, 40%): mp 106–107 ^{0}C (lit.,[8] mp 107–108 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.00 (s, 3H), 2.34 (s, 3H), 6.90 (t, *J* = 7.3 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 4H), 7.02 (s, 2H), 7.06 (s, 1H), 7.19 (t, *J* = 7.7 Hz, 4H); MS (EI): *m/z* 273 (M^+). CAS Number: 1228-80-4.

A similar reaction using 2,4-dimethyliodobenzene (928 mg, 4 mmol) afforded the product (Table 2, entry 10) as a white solid (257 mg, 47%).

Diphenyl(1-naphthyl)amine (Table 2, entry 11). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol %), and PPh_3 (52 mg, 10 mol%), diphenylamine (338 mg, 2 mmol) and 1-bromonaphthene (824 mg, 4 mmol) were transformed into the product as a white solid (206 mg, 35%): mp 136–137 ^{0}C (lit.,[8] mp 137.5–138.5 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.93 (t, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 4H), 7.19 (t, *J* = 7.6 Hz, 4H), 7.30–7.38 (m, 2H), 7.42–7.49 (m, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H); MS (EI): *m/z* 295 (M^+). CAS Number: 61231-45-6.

4-Benzoyltriphenylamine (Table 2, entry 12). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol %), and PPh_3 (52 mg, 10 mol%), diphenylamine (338 mg, 2 mmol) and 4-bromobenzophenone (780 mg, 3 mmol) were transformed into the product as a pale yellow solid (161 mg, 23%): mp 126–127 ^{0}C (lit.,[9] mp 127–128 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.01 (d, J = 7.1 Hz, 2H), 7.10–7.23 (m, 6H), 7.33 (t, J = 7.5 Hz, 4H), 7.46 (t, J = 7.7 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.71 (d, J = 7.1 Hz, 2H), 7.77 (d, J = 7.7 Hz, 2H); MS (EI): *m/z* 349 (M^+). CAS Number: 16911-33-4.

4,4'-Dimethyltriphenylamine (Table 2, entry 15). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol %), and PPh_3 (52 mg, 10 mol%), 4,4'-dimethyldiphenylamine (384 mg, 2 mmol) and bromobenzene (624 mg, 4 mmol) were transformed into the product as a white solid (464 mg, 85%): mp 106–107 ^{0}C (lit.,[9] mp 107–108 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.31 (s, 6H), 6.95 (t, J = 7.3 Hz, 1H), 6.97–7.08 (m, 10H), 7.20 (t, J = 7.8 Hz, 2H); MS (EI): *m/z* 273 (M^+). CAS Number: 20440-95-3.

A similar reaction using iodobenzene (816 mg, 4 mmol) afforded the product (Table 2, entry 16) as a white solid (475 mg, 87%).

Diphenyl(2-naphthyl)amine (Table 2, entry 17). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol %), and PPh_3 (52 mg, 10 mol%), *N*-phenyl-2-naphthylamine (438 mg, 2 mmol) and bromobenzene (624 mg, 4 mmol) were transformed into the product as a white solid (360 mg, 61%): mp 118–120 ^{0}C (lit.,[8] mp 120–121 ^{0}C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.06 (t, J = 7.3 Hz, 2H), 7.15 (d, J = 7.6 Hz, 4H), 7.22–7.32 (m, 5H), 7.32–7.47 (m, 3H), 7.60 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H); MS (EI): *m/z* 295 (M^+).

A similar reaction using iodobenzene (816 mg, 4 mmol) afforded the product (Table 2, entry 18) as a white solid (372 mg, 63%).

Diphenyl(1-naphthyl)amine (Table 2, entry 19). According to the general procedure, sodium hydride (120 mg of 60% NaH in white oil, 3 mmol), $Ni(PPh_3)_2$(1-naphthyl)Cl (74 mg, 5 mol %), and PPh_3 (52 mg, 10 mol%), *N*-phenyl-1-naphthylamine (438 mg, 2 mmol) and iodobenzene (816 mg, 4 mmol) were transformed into the product as a white solid (171 mg, 29%).

<References>

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table 2, entry 2
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ppm
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8
7
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5
4
3
2
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0


ppm
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Cl
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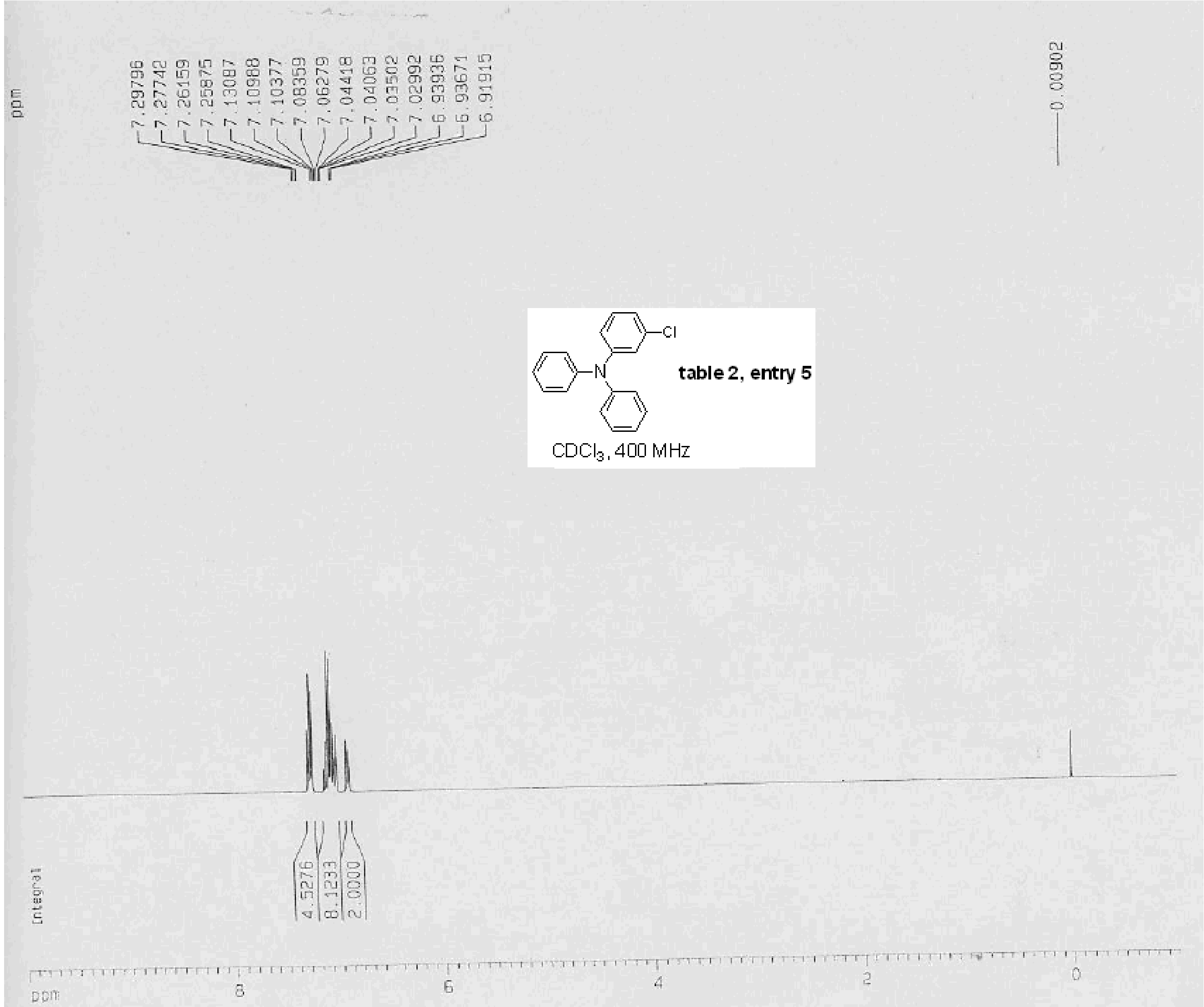
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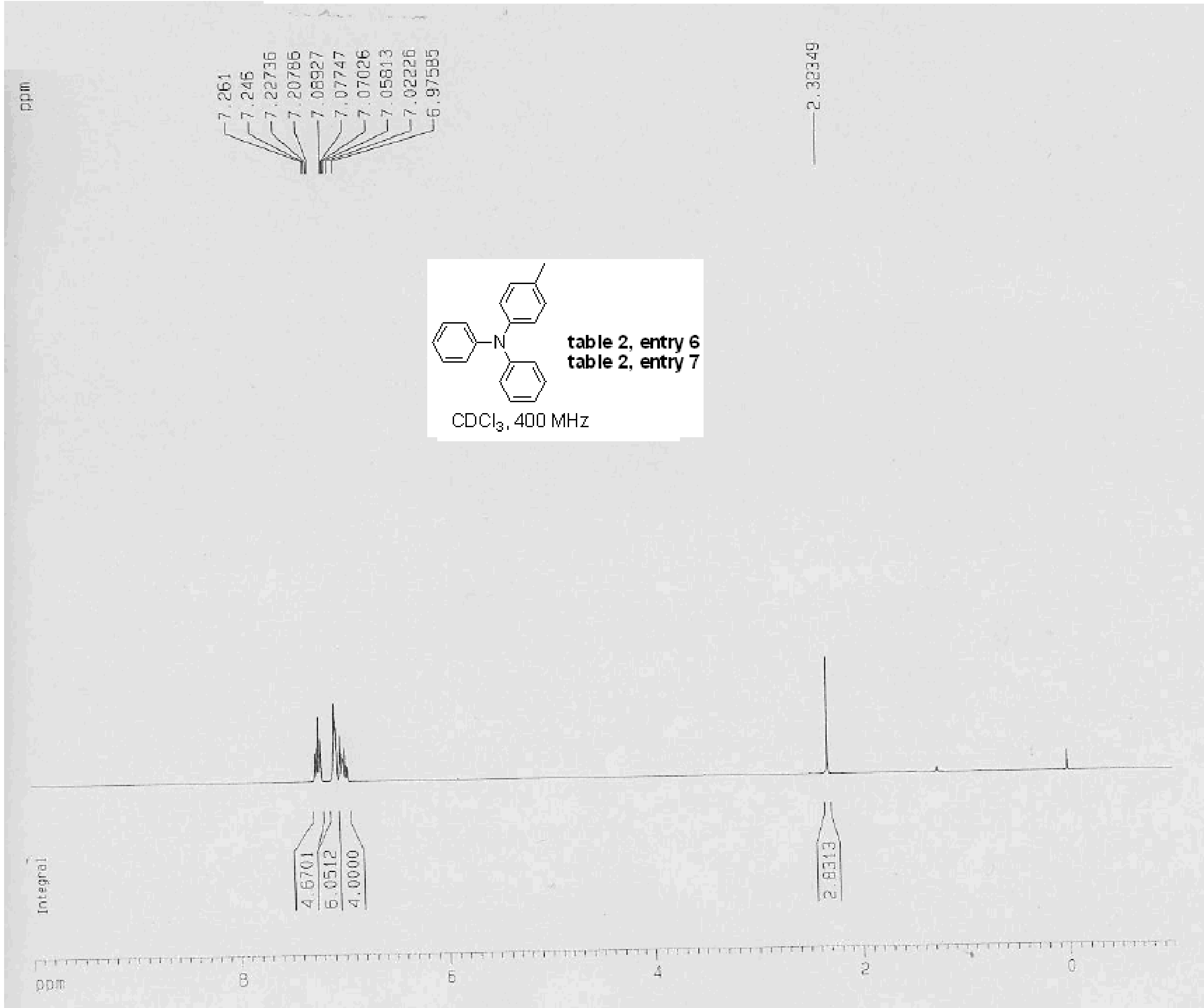
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ppm
table 2, entry 6
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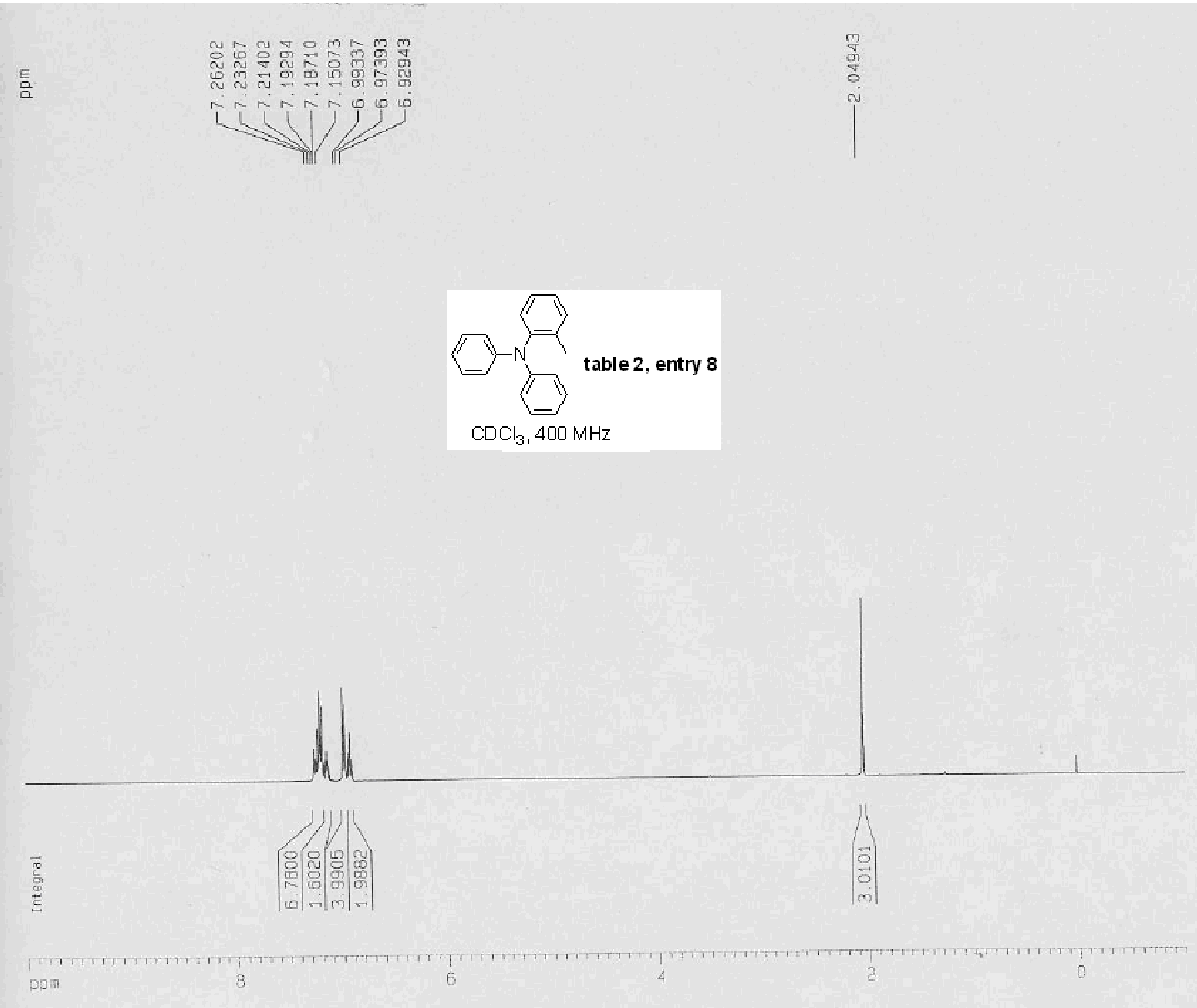

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2.00444
N
table 2, entry 9
table 2, entry 10
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ppm
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4
2
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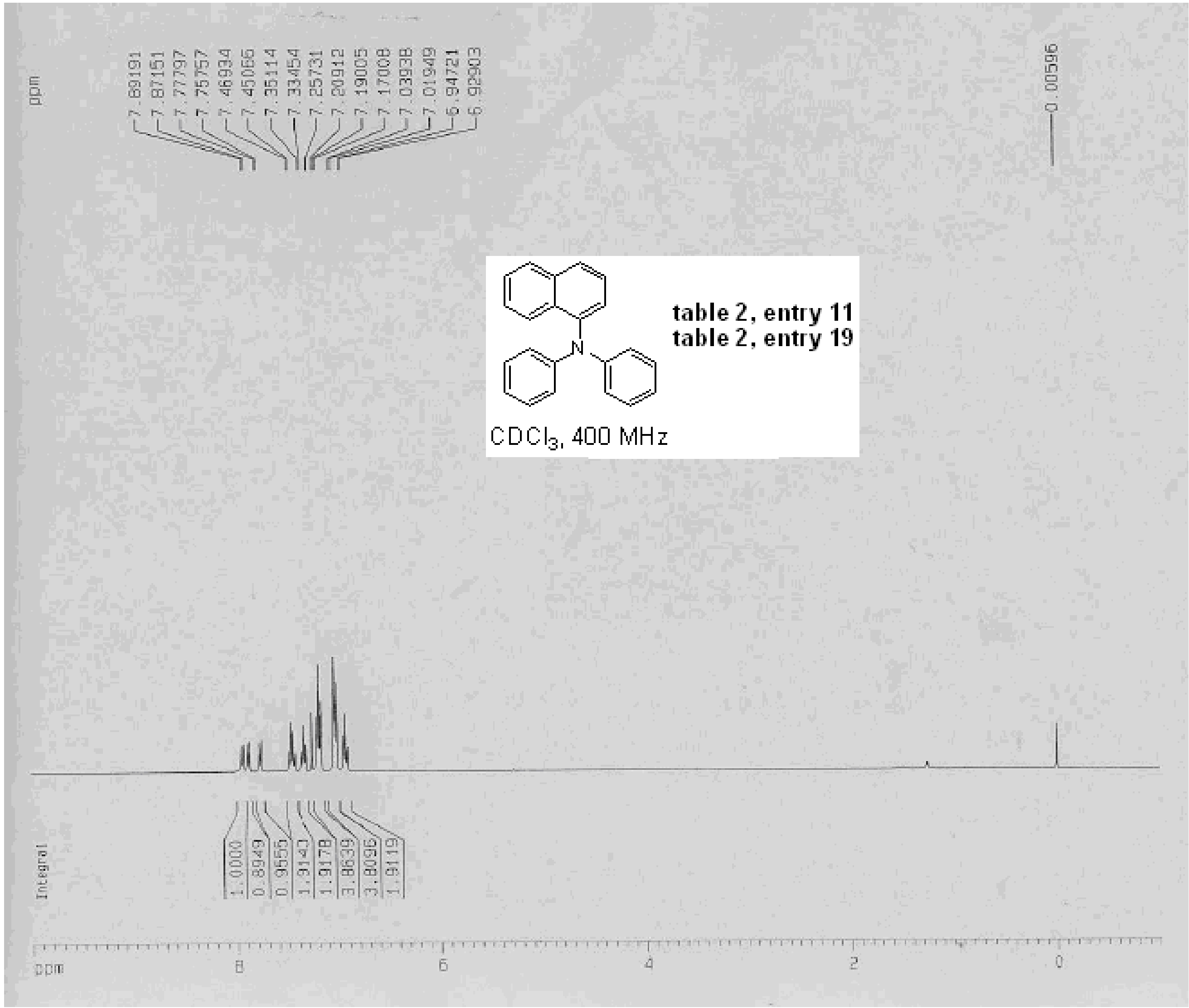
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table 2, entry 19
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table 2, entry 12

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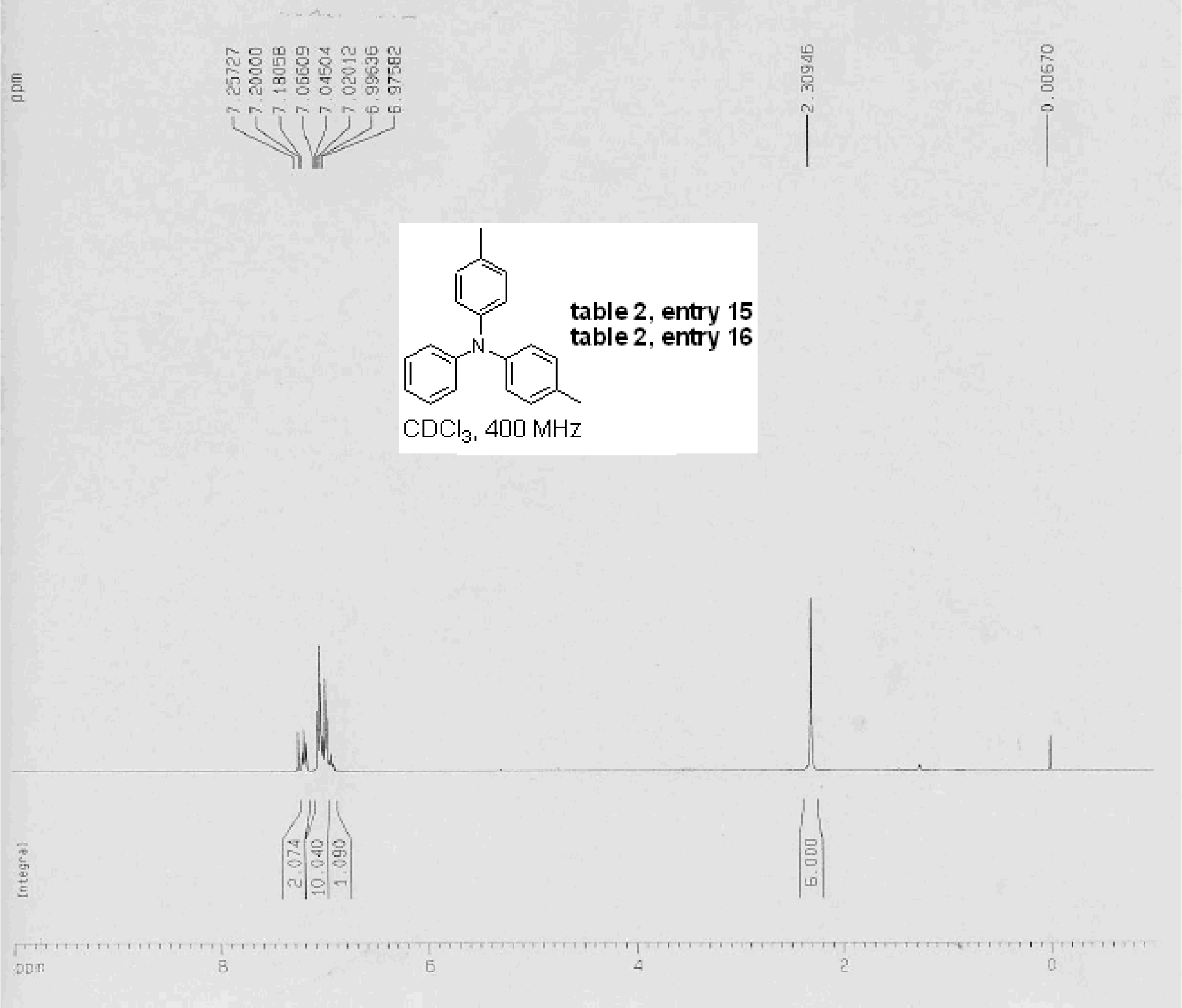

table 2, entry 15
table 2, entry 16

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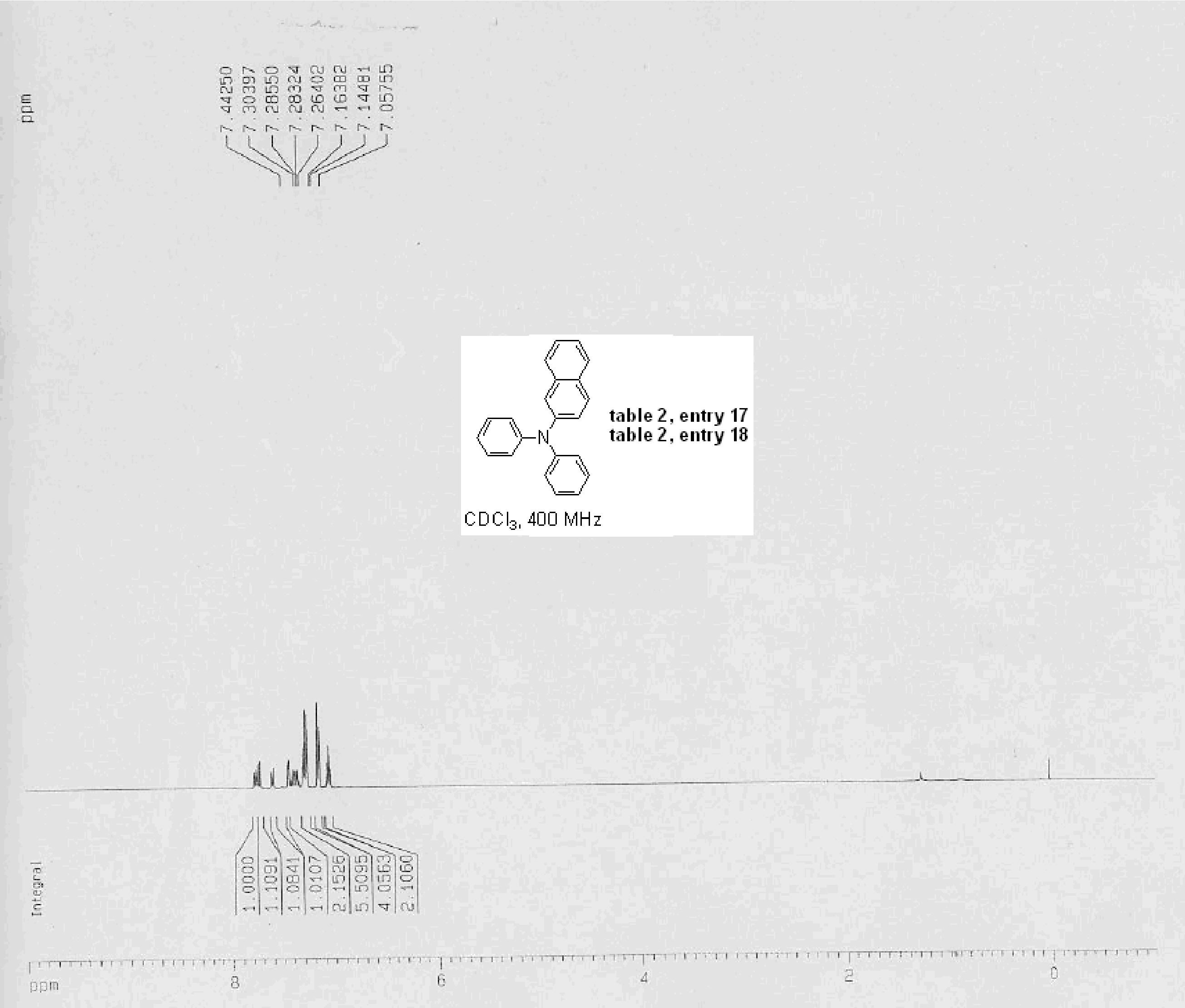
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table 2, entry 17
table 2, entry 18
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ppm
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6
4
2
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