Supporting Information of

“Nickel-NHC-Catalyzed α -Arylation of Acyclic Ketones and Amination of
Haloarenes, and
Unexpected Preferential N-Arylation of 4-Aminopropiophenone”

Kouki Matsubara,^{†*} Keita Ueno,[†] Yuji Koga,[†] and Kenji Hara[‡]

[†]*Department of Chemistry, Faculty of Science, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku,*

Fukuoka 814-0180, JAPAN. E-mail: kmatsuba@fukuoka-u.ac.jp

[‡]*School of Medicine, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, JAPAN.*

CONTENTS

S-1.	Preparation of 4- <i>N,N</i> -dimethylamino-propiophenone	p. S2
S-2.	NMR spectral charts for unpublished compounds	p. S3
S-3.	Special data and CAS numbers for the other products	p. S12

S-1. Preparation of 4-*N,N*-dimethylaminopropiophenone

4-Chloropropiophenone (2.12 g, 12.6 mmol) was placed in three-necked flask equipped with a condenser, oil-bath, and magnetic stirrer. HMPA (*N*-hexamethylphosphoramide (12.5 mL) was added and the system flushed with argon before temperature was raised up to 150 °C and held there 63 h. The mixture was then cooled to room temperature and poured into 50 mL of water. This mixture was extracted with ether (3×35 mL), and the combined ether extracts were washed with water (2×50 mL) and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration. This material can be further purified by extracting the ether with 18%(w/w) aqueous sodium hydroxide with cooling. The resulting material was isolated by filtration or extraction and dried under reduced pressure to yield 0.20 g (8.7%) of the desired compound as a yellow solid. **Caution!** : HMPA is a cancer-suspect agent, it must be used carefully.

¹H NMR(CDCl₃, 400 MHz): δ 7.89 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 3.06 (s, 6H), 2.91 (q, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); ¹³C NMR(CDCl₃, 100 MHz): δ 199.2, 153.2, 130.1, 125.0, 110.7, 40.0, 30.9, 8.8.

S-2. NMR spectral charts for unpublished compounds.

2-(4-Benzoylphenyl)-1-(4-fluorophenyl)-1-propanone (Table 1 entry 9).

SpinWorks 2.4: exp271.f13to21.no2.061121

file: E:\students\Kaita Ueno\1-106\JACS(-1\5)\NMR-DATA-1\1\Nov2006\PROTON\fid\fid block# 1 exp271.f13to21.no2.061121
 transmitter freq.: 400.452035 MHz
 time domain size: 44844 points
 width: 6402.05 Hz = 15.987055 ppm = 0.142763 Hz/pt
 number of scans: 8
 processed size: 65536 complex points
 LB: 1.000 GB: 0.0000

SpinWorks 2.4: exp271.f13to21.13C.061121

file: E:\students\Kaita Ueno\1-106\JACS(-1\5)\NMR-DATA-1\1\Nov2006\CARBON\fid\fid block# 1 exp271.f13to21.13C.061121
 transmitter freq.: 100.704192 MHz
 time domain size: 65536 points
 width: 25188.92 Hz = 250.127788 ppm = 0.384352 Hz/pt
 number of scans: 1000
 processed size: 65536 complex points
 LB: 1.000 GB: 0.0000

2-(4-Benzoylphenyl)-1-(4-methoxyphenyl)-1-propanone (Table 1 entry 10).

SpinWorks 2.4: exp267.f19to22.no.061121

SpinWorks 2.4: exp267.f19to22.13C.061121

2-(4-Benzoylphenyl)-1-(4-dimethylaminophenyl)-1-propanone ("Table 1 entry 11).

SpinWorks 2.4: exp279.f6-11.061219

SpinWorks 2.4: exp279.f6-11.13C.061219

N-(4-Benzoylphenyl)-*N*-(2,4,6-trimethylphenyl)aniline (Table 2 entry 3).

SpinWorks 2.4: exp233.f4.5.no2.061108

file: E:\students\Kaita Ueno\...06JACS(-\v)\NMR-Data\18-1\exp233.f4.5.no2.061108_08Nov2008\PROTON.fid\fid block# 1 expt: "s2puffreq: 0 ppm; 400.449631 MHz
transmitter freq.: 400.452035 MHz
time domain size: 44944 points
width: 6402.05 Hz = 15.987055 ppm = 0.142763 Hz/pt
number of scans: 8
LB: 0.000 GB: 0.0000

SpinWorks 2.4: exp233.f4.5.13C.061108

file: E:\students\Kaita Ueno\...06JACS(-\v)\NMR-Data\18-1\Nov\exp233.f4.5.13C.061108_08Nov2008\CARBON.fid\fid block# 1 expt: "f1puffreq: 0 ppm; 100.693142 MHz
transmitter freq.: 100.704192 MHz
time domain size: 65536 points
width: 25188.92 Hz = 250.127788 ppm = 0.384352 Hz/pt
number of scans: 20000
LB: 1.000 GB: 0.0000

N-(4-Benzoylphenyl)-*N*-(2-isopropylphenyl)aniline (Table 2 entry 7).

SpinWorks 2.4: exp232.f4.no2.061122

```
File: E:\students\Kaia Ursini\1\1001\JACS-(8)\NMR-Data\7a-11Novel\exp32.14.nc2.061122_22Nov2009\PROTON\fid\fid_block1_1.exp  Date: 01/11/2009 00:00:00
Transmitter Freq.: 400.452035 MHz  Processed size: 65536 complex points
Time domain size: 44844 points  LB: 1.000  GB: 0.0000
Width: 6402.05 Hz = 15.987055 ppm = 0.142763 Hz/pt
Number of scans: 8
```

SpinWorks 2.4: exp232.f4.13C.061122

```

File: E:\students\Kaia Ueno\1H NMR\DATA\1H-1H\exp232_14_13C_061122_22N\2006\CARBON\fid\fid_block1 1 exp: 1
transmitter freq.: 100.704192 MHz
time domain size: 65536 points
width: 25188.92 Hz = 250.127788 ppm = 0.384352 Hz/pt
number of scans: 1000
processed size: 65536 complex points
LB: 1.0000 GB: 0.0000

```

N-(4-Benzoylphenyl)-*N*-(2,6-diisopropylphenyl)aniline (Table 2 entry 8).

SpinWorks 2.4: exp266.f22to27.no2.061124

SpinWorks 2.4: exp266.f22to27.13C.061124

N-(4-Benzoylphenyl)-*N*-(4-chlorophenyl)aniline (Table 2 entry 11).

SpinWorks 2.4: exp258.f4.re.no2.061121

SpinWorks 2.4: exp258.f4.re.13C.no2.061121

4-(*N*-(4-Benzoylphenylamino))propiophenone (Table 3 entry 3-B).

SpinWorks 2.4: exp269.f19to23.no2.061127

SpinWorks 2.4: exp269.f19to23.13C.061127

4-(*N,N*-(4,4-Dibenzoylphenylamino))propiophenone (Table 3 entry 3-C).

SpinWorks 2.4: exp269.f6to10.no2.061127

SpinWorks 2.4: exp269.f6to10.13C.061127

S-3. Special data and CAS numbers for the other products

1-phenyl-2-(phenyl)-1-propanone (Table 1 entry 2, entry 3).

(Commercially available; CAS 2042-85-5)

^1H NMR(CDCl_3 , 400 MHz): δ 7.93 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.35 (t, J = 8.0 Hz, 2H), 7.30-7.15 (m, 5H), 4.66 (q, J = 7.2 Hz, 1H), 1.51 (d, J = 6.8 Hz, 3H); ^{13}C NMR(CDCl_3 , 100 MHz): δ 200.3, 141.4, 136.4, 132.8, 129.0, 128.8, 128.5, 127.7, 126.9, 47.9, 19.5.

2-(4-Methylphenyl)-1-(phenyl)-1-propanone (Table 1 entry 4).

(ref. Adjabeng, G.; Brenstrum, T.; Frampton, C. S.; Robertson, A. J.; Hillhouse, J.; McNulty, J.; Capretta, A. *J. Org. Chem.* 2004, *69*(15), 5082-5086; CAS 107271-15-8)

^1H NMR(CDCl_3 , 400 MHz): δ 7.96 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 8.2 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 4.66 (q, J = 6.8 Hz, 1H), 2.29 (s, 3H) 1.52 (d, J = 6.8 Hz, 3H); ^{13}C NMR(CDCl_3 , 100 MHz): δ 200.4, 138.4, 136.5, 136.5, 132.7, 129.7, 128.7, 128.4, 127.6, 47.5, 21.0, 19.5.

2-(4-Phenyl)-1-(phenyl)-1-propanone (Table 1 entry 5).

(ref. Marion, N.; Ecarnot, E. C.; Navarro, O.; Amoroso, D.; Bell, A.; Nolan, S. P.; *J. Org. Chem.* 2006, *71*(10), 3816-3821; CAS 302777-49-47)

^1H NMR(CDCl_3 , 400 MHz): δ 7.99 (d, J = 8.0 Hz, 2H), 7.55-7.48 (m, 5H), 7.43-7.31 (m, 7H), 4.74 (q, J = 6.8 Hz, 1H), 1.24 (d, J = 6.4 Hz, 3H); ^{13}C NMR(CDCl_3 , 100 MHz): δ 200.3, 140.6, 140.4, 139.8, 136.4, 132.8, 128.8, 128.7, 128.5, 128.2, 127.7, 127.2, 127.0, 47.4, 19.5.

2-(4-Methoxyphenyl)-1-(phenyl)-1-propanone (Table 1 entry 6, entry 7).

(ref. Roy, O.; Riahi, A.; Hénin, F.; Muzart, J. *Eur. J. Org. Chem.* 2002, (23), 3986-3994; CAS 35572-39-5)

^1H NMR(CDCl_3 , 400 MHz): δ 7.94 (d, J = 7.2, 2H), 7.47 (t, J = 6.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.20

(d, J = 6.8 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 4.64 (q, J = 6.8 Hz, 1H), 3.75 (s, 3H), 1.50 (d, J = 6.8 Hz, 3H); ^{13}C NMR(CDCl_3 , 100 MHz): δ 200.5, 158.4, 136.5, 133.5, 132.7, 128.8, 128.7, 128.5, 128.4, 114.3, 55.2, 47.0, 19.5.

2-(4-Benzoylphenyl)-1-(phenyl)-1-propanone (Table 1 entry 8).

(*ref*: Viciu, M. S.; Germaneau, R. F.; Nolan, S. P. *Org. Lett.* 2002, 4(23), 4053-4056; CAS 56705-50-1)
 ^1H NMR(CDCl_3 , 400 MHz): δ 7.96 (d, J = 8 Hz, 2H), 7.77-7.74 (m, 4H), 7.59-7.39 (m, 8H), 4.79 (q, J = 7.2 Hz, 1H), 1.58 (d, J = 6.8 Hz, 3H); ^{13}C NMR(CDCl_3 , 100 MHz): δ 199.7, 196.2, 146.1, 137.5, 136.2, 133.1, 132.4, 130.8, 130.0, 128.7, 128.6, 128.2, 127.7, 47.7, 19.4.

4-(4-Methoxyphenyl)morpholine (Table 2 entry 1).

(Commercially available; CAS 27347-14-4)
 ^1H NMR(CDCl_3 , 400 MHz): δ 6.92-6.85 (m, 4H), 3.88 (t, J = 4.8 Hz, 4H), 3.78 (s, 3H), 3.07 (t, J = 4.8 Hz, 4H); ^{13}C NMR(CDCl_3 , 100 MHz): δ 118.0, 114.5, 66.9, 55.6, 51.0.

4-Morpholinobenzophenone (Table 2 entry 2).

(Commercially available; CAS 24758-49-4)
 ^1H NMR(CDCl_3 , 400 MHz): δ 7.81 (d, J = 9.6 Hz, 2H), 7.74 (d, 8.4 Hz, 2H), 7.55 (t, J = 6.0 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 3.87 (t, J = 0.52 Hz, 4H), 3.33 (t, J = 0.52, 4H); ^{13}C NMR(CDCl_3 , 100 MHz): δ 195.2, 153.8, 138.6, 132.4, 131.6, 129.6.

N-(4-Methoxyphenyl)-2,4,6-trimethylaniline (Table 2 entry 4).

(*ref*: Sapountzis, I.; Knochel, P. *Angew. Chem. Int. Ed.* 2004, 43(7), 897-900; CAS 124006-18-4)
 ^1H NMR(CDCl_3 , 400 MHz): δ 6.95 (s, 2H), 6.76 (d, J = 8.8 Hz, 4H), 6.52 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 2.32 (s, 3H), 2.19 (s, 6H); ^{13}C NMR(CDCl_3 , 100 MHz): δ 152.7, 140.1, 136.2, 135.0, 134.8, 132.0, 129.2, 115.0, 114.7, 55.7, 20.8, 18.2.

N-(2-isopropylphenyl)aniline (Table 2 entry 5).

(*ref.* Hiroshi, T.; Katsuyuki, T. *J. Chem. Soc. Chem. Commun.* 1983, (8), 447-449; CAS 38158-59-7)
¹H NMR(CDCl₃, 400 MHz): δ 7.35 (m, 2H), 7.28-7.22 (m, 2H), 7.16 (t, J = 6.8 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.91-6.85 (m, 3H), 3.18 (sep, J = 6.8 Hz, 1H), 1.27 (d, J = 7.2 Hz, 6H); ¹³C NMR(CDCl₃, 100 MHz): δ 145.0, 139.2, 132.0, 129.3, 126.4, 126.1, 123.7, 122.0, 120.1, 116.6, 27.6, 23.1.

N,N-diphenyl-*N*-(4-Benzoylphenyl)aniline (Table 2 entry 9).

(*ref.* Jensen, T. A.; Liang, X.; Tanner, D.; Skjaerbaek, N. *J. Org. Chem.* 2004, 69(15), 4936-4947; CAS 16911-33-4)
¹H NMR(CDCl₃, 400 MHz): δ 7.84 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 8.0 Hz, 4H), 7.28-7.19 (m, 6H), 7.09 (d, J = 8.4 Hz, 2H); ¹³C NMR(CDCl₃, 100 MHz): δ 195.1, 151.9, 146.4, 138.4, 131.9, 131.6, 129.6, 129.6, 129.5, 129.4, 128.1, 125.9, 124.6, 119.5.

N-(4-Benzoylphenyl)-*N*-phenylaniline (Table 2 entry 10).

(*ref.* Jensen, T. A.; Liang, X.; Tanner, D.; Skjaerbaek, N. *J. Org. Chem.* 2004, 69(15), 4936-4947; CAS 4058-17-7)
¹H NMR(CDCl₃, 400 MHz): δ 7.77 (t, J = 8.8 Hz, 4H), 7.55 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.2 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 7.2 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H); ¹³C NMR(CDCl₃, 100 MHz): δ 195.2, 148.1, 140.5, 138.6, 132.7, 131.6, 129.6, 129.5, 128.7, 128.1, 123.4, 120.7, 114.4.

N-(4-Benzoylphenyl)-*N*-(4-methoxyphenyl)aniline (Table 2 entry 13).

(Commercially available; CAS 85243-04-05)

^1H NMR(CDCl_3 , 400 MHz): δ 7.74-7.72 (m, 4H), 7.53 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 7.16 (br, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR(CDCl_3 , 100 MHz): δ 195.1, 138.8, 132.8, 131.4, 129.5, 128.0, 124.5, 114.7, 113.2, 55.5.