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Supporting Information

Synthesis of Aryl Ketones by Palladium-Catalyzed Desulfitative

Addition of Arylsulfinic Acids to Nitriles

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General Information

All reactions were carried out under an argon atmosphere. Solvents were dried by the standard procedures. ¹H NMR spectra were determined in CDCl₃ on a Varian-Inova 400 MHz spectrometer and chemical shifts were reported in ppm from internal TMS (δ). Data for ¹H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (integration, s = singlet, d = doublet, t = triplet, qn = quintet, m = multiplet or unresolved, coupling constant(s) in Hz). Column chromatography was performed with 200-300 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted.

General Procedure

Preparation of Arylsulfinic Acids.¹ Benzenesulfinic acid was obtained by acidification of the commercially available sodium benzenesulfinate and then recrystallization from water. Other arylsulfinic acids were prepared by the following procedures. Arylsulfonyl chloride (1 mmol) and anhydrous sodium sulfite (3 mmol) were added into water (4 mL). The reaction mixture was kept at a temperature range of 70-80 °C for 5 h. After the reaction was complete, this aqueous solution was washed with chloroform, acidified with excess concentrated HCl solution, cooled and filtered. The white precipitate was recrystallized from water yielding arylsulfinic acid.

Synthesis of Aryl Ketones by Palladium-Catalysed Desulfitative Addition of Arylsulfinic Acids to Nitriles: The desired amount (100.0 mg, 1.00 mmol) of 98% H₂SO₄ was added by syringe while weighing to a suspension of arylsulfinic acid (1a-i, 0.80 mmol), nitrile (2a-k, 0.50 mmol), Pd(OAc)₂ (11.2 mg, 0.05 mmol), 2,2'-bipyridine (15.6 mg, 0.10 mmol), H₂O (9.0 mg, 0.50 mmol) in isobutyl alcohol (2.0 mL). The mixture was stirred under argon atmosphere at 100 °C for 6 h. After completion of the reaction, the solvent was evaporated to dryness in vacuo. The residual was separated on a silica gel column with petroleum ether/ethyl acetate 30/1 as the eluent to get the desired product **3aa-3ia**.

Benzophenone (3aa)²



¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, J = 7.5, 1.5 Hz, 2H), 7.59 (tt, J = 7.5, 1.5 Hz, 4H), 7.48 (t, J = 7.5 Hz, 4H).

4-Methylbenzophenone (3ab)³



¹H NMR (400 MHz, CDCl₃) δ 7.78 (dd, J = 7.6, 1.5 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.57 (tt, J = 7.6, 1.5 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H).

3-Methylbenzophenone (3ac)³



¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, J = 7.8, 1.3 Hz, 2H), 7.62 (s, 1H), 7.59-7.54 (m, 2H), 7.46 (t, J = 7.8 Hz, 2H), 7.38 (d, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 2.40 (s, 3H).

2-Methylbenzophenone (3ad)³



¹H NMR (400 MHz, CDCl₃) δ 7.80 (dd, J = 7.8, 1.3 Hz, 2H), 7.57 (tt, J = 7.8, 1.3 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.38 (td, J = 7.5, 1.4 Hz, 1H), 7.30 (dd, J = 7.5, 1.4 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.22 (t, J = 7.9 Hz, 1H), 2.33 (s, 3H).

3,4-Dimethoxybenzophenone (3ae)⁴



¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, J = 7.8, 1.5 Hz, 2H), 7.57 (tt, J = 7.8, 1.5 Hz, 1H), 7.50 (d, J = 2.0 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.38 (dd, J = 8.4, 2.0 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 3.96 (s, 3H), 3.95 (s, 3H).

3-Bromobenzophenone (3af)⁴



¹H NMR (400 MHz, CDCl₃) δ 7.93 (t, J = 1.8 Hz, 1H), 7.78 (dd, J = 7.8, 1.5 Hz, 2H), 7.70 (dd, J = 7.8, 1.8 Hz, 2H), 7.61 (tt, J = 7.8, 1.5 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.35 (t, J = 7.8 Hz, 1H).

4-Chlorobenzophenone (3ag)³



¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 7.4 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.4 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H).

4-Fluorobenzophenone (3ah)⁵



¹H NMR (400 MHz, CDCl₃) δ 7.85 (dd, J = 8.9, 5.5 Hz, 2H), 7.77 (dd, J = 7.8, 1.4 Hz, 2H), 7.59 (tt, J = 7.8, 1.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.16 (dd, J = 8.9, 8.9 Hz, 2H).

4-Nitrobenzophenone (3ai)^{2,3}



¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.80 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.66 (tt, *J* = 7.8, 1.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H).

1,2-Diphenyl-ethanone (3aj)²



¹H NMR (400 MHz, CDCl₃) δ 8.01 (dd, J = 7.8, 1.5 Hz, 2H), 7.55 (tt, J = 7.8, 1.5 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.35-7.30 (m, 2H), 7.29-7.22 (m, 3H), 4.28 (s, 2H).

1,4-Diphenylbutan-1-one (3ak)⁶



¹H NMR (400 MHz, CDCl₃) δ 7.91 (dd, J = 7.5, 1.5 Hz, 2H), 7.53 (tt, J = 7.5, 1.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.5 Hz, 2H), 7.22-7.16 (m, 3H), 2.97 (t, J = 7.4 Hz, 2H), 2.72 (t, J = 7.4 Hz, 2H), 2.08 (quintet, J = 7.4 Hz, 2H).

4,4' -Dimethylbenzophenone (3bb)⁷



¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 8.3 Hz, 4H), 7.26 (d, J = 8.3 Hz, 4H), 2.43 (s, 6H).

4-Chloro-4' -methylbenzophenone (3bg)⁸



¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H).

2-Phenyl-1-(p-tolyl)ethanone (3bj)²



¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.2 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.28-7.21 (m, 5H), 4.25 (s, 2H), 2.40 (s, 3H).

4,4' -Dichlorobenzophenone (3cg)⁹



¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H).

1-(4-Chlorophenyl)-2-phenylethanone (3cj)¹⁰



¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.35-7.30 (m, 2H), 7.28-7.22 (m, 3H), 4.25 (s, 2H).

4-Fluoro-4' -methylbenzophenone (3db)¹¹



¹H NMR (400 MHz, CDCl₃) δ 7.82 (dd, J = 8.8, 5.5 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.15 (dd, J = 8.8, 8.8 Hz, 2H), 2.44 (s, 3H).

4-Chloro-4' -fluorobenzophenone (3dg)¹²



¹H NMR (400 MHz, CDCl₃) δ 7.82 (dd, J = 8.8, 5.4 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.17 (dd, J = 8.8, 8.8 Hz, 2H).

1-(4-Fluorophenyl)-2-phenylethanone (3dj)²



¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, J = 8.8, 5.3 Hz, 2H), 7.33 (t, J = 7.3 Hz, 2H), 7.28-7.22 (m, 3H), 7.11 (dd, J = 8.8, 8.8 Hz, 2H), 4.25 (s, 2H).

4-Methoxybenzophenone (3ea)³



¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.3 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H).

1-(4-Methoxyphenyl)-2-phenylethanone (3ej)²



¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, J = 8.8 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.27 (d, J = 7.3 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 4.22 (s, 2H), 3.84 (s, 3H).

1-Benzoylnaphthane (3fa)¹³



¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 7.6 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.7 Hz, 2H), 7.61-7.55 (m, 3H), 7.55-7.47 (m, 3H), 7.44 (t, J = 7.7 Hz, 2H).

2-Phenyl-1-α-naphthyl-ethanone (3fj)²



¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.58-7.43 (m, 3H), 7.34-7.20 (m, 5H), 4.36 (s, 2H).

2-Benzoylnaphthane (3ga)³



¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H), 7.94 (d, *J* = 1.2 H, 2H), 7.93-7.91 (m, 1H), 7.91-7.89 (m, 1H), 7.86 (dd, *J* = 7.6, 1.3 Hz, 2H), 7.64-7.58 (m, 2H), 7.57-7.49 (m, 3H).

β-Naphthyl-4-methylphenyl-ketone (3gb)¹⁴



¹H NMR (400 MHz, CDCl₃) δ 8.25 (s, 1H), 7.94-7.88 (m, 4H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.63-7.57 (m, 1H), 7.57-7.51 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H).

β-Naphthyl-4-chlorophenyl-ketone (3gg)¹⁵



¹H NMR (400 MHz, CDCl₃) δ 8.22 (s, 1H), 7.96-7.88 (m, 4H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.65-7.58 (m, 1H), 7.58-7.53 (m, 1H), 7.48 (d, *J* = 8.5 Hz, 2H).

2-Phenyl-1-β-naphthyl-ethanone (3gj)²



¹H NMR (400 MHz, CDCl₃) δ 8.54 (s, 1H), 8.06 (dd, J = 7.7, 1.4 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.87 (dd, J = 7.7 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.62-7.56 (m, 1H), 7.56-7.51 (m, 1H), 7.36-7.22 (m, 5H), 4.41 (s, 2H).

References

- (1) S. Oae and H. Togo, Bull. Chem. Soc. Jpn. 1983, 56, 3802.
- (2) B. W. Zhao and X. Y. Lu, Org. Lett., 2006, 8, 5987.
- (3) D. H. Wang and Z. G. Zhang, Org. Lett., 2003, 5, 4645.
- (4) A. T. Biju and F. Glorius, Angew. Chem. Int. Ed., 2010, 49, 9761.
- (5) H. Tatamidani, F. Kakiuchi and Naoto Chatani, Org. Lett., 2004, 6, 3597.
- (6) J. A. Murphy, A. G. J. Commeureuc, T. N. Snaddon, T. M. McGuire, T. A. Khan, K. Hisler, M. L. Dewis and R. Carling, Org. Lett., 2005, 7, 1427.
- (7) L. J. Gooβen, F. Rudolphi, C. Oppel and N. Rodrgíuez, Angew. Chem. Int. Ed., 2008, 47, 3043.
- (8) M. Z. Cai, G. M. Zheng, L. F. Zha and J. Peng, Eur. J. Org. Chem., 2009, 1585.
- (9) M. L. N. Rao, V. Venkatesh and P. Dasgupta, Tetrahedron Lett., 2010, 51, 4975.
- (10) Z.-L. Shen, X.-P. Xu and S.-J. Ji, J. Org. Chem., 2010, 75, 1162.
- (11) B. W. Fausett and L. S. Liebeskind, J. Org. Chem., 2005, 70, 4851.
- (12) Y.-X. Liao and Q.-S. Hu, J. Org. Chem., 2010, 75, 6986.
- (13) B. Xin, Y. Zhang and K. Cheng, J. Org. Chem., 2006, 71, 5725.
- (14) J. M. Villalobos, J. Srogl and L. S. Liebeskind, J. Am. Chem. Soc., 2007, 129, 15734.
- (15) J. H. P. Utluy and G. G. Rozenberg, Tetrahedron., 2002, 58, 5251.





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ppm 7.5 7.0 6.5 6.0 5.0 4.0 3.5 2.0 1.5 0.5 5.5 4.5 3.0 2.5 1.0 4.33 3.90 00.9

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