Supporting Information for

Microwave-Assisted Synthesis of Diaryl Ethers without Catalyst

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Experimental

General: All materials were used as purchased and DMSO was A.R. grade without any previous deal-with. The purities of isolated products are determined by GC-MS. GC-MS data was acquired on a TOP series GC8000 with a FINNIGAN-VOYAGER mass selective detector. NMR data were obtained on Bruker 300 MHz instrument.

General procedure for the diaryl ether preparation: the aryl halide (ArX, 10 mmol), the phenol (ArOH, 10~12 mmol) and potassium carbonate (20 mmol) were added to 50 ml DMSO (A.R., without any previous deal-with). The reaction was found not to be sensitive to air and moisture, hence there was no need for inert atmosphere. Using a microwave power of 300 W we ramped the temperature from room temperature to boiling point of DMSO, which took 30~40 s, and then held DMSO boiling for 5~10 min. After completion of the reaction, it was cooled to room temperature, put into ice water and stirred for 30 min to precipitate the product. Filtration of the precipitation followed by washing with water afforded the desired products. The number in parenthesis corresponds to the entry number in Table 1.

4-(4'-chlorophenoxy)benzonitrile (1): It was prepared from 4-chlorophenol and 4-fluorobenzonitrile in 93% isolated yield as a white solid in 99.74% pure after 5 min. M.p.81-82 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 7.87-7.84 (dd, 2H), 7.53-7.50 (dd, 2H), 7.20-7.09 (m, 4H). GC-MS m/z 229 (M^+).

4-(2'-methoxyphenoxy)benzonitrile (2): It was prepared from 2-methoxyphenol and 4-fluorobenzonitrile in 85% isolated yield as a white solid in 99.2% pure after 5 min. M.p.90-92 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 7.79-7.76 (dd, 2H), 7.30-6.92 (m, 6H), 3.72 (s, 3H, OCH_3). GC-MS m/z 225 (M^+).

4-(4'-cyanophenoxy)benzonitrile (3): It was prepared from 4-hydroxybenzonitrile and 4-fluorobenzonitrile in 87% isolated yield as a white solid in a purity higher than 99% after 10 min. M.p.179-180 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 7.93-7.92 (dd, 4H), 7.28-7.27 (dd, 4H). GC-MS m/z 220(M^+).

4-(3'-trifluoromethylphenoxy)benzonitrile (4): It was prepared from 3-trifluoromethylphenol and 4-fluorobenzonitrile in 86% isolated yield as a white solid in 98.6% pure after 5 min. M.p.55-56 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 7.91-7.87 (m, 2H), 7.70-7.47 (m, 4H), 7.21-7.17 (m, 2H). GC-MS m/z 263 (M^+).

2-(2'-methoxyphenoxy)benzonitrile (5): It was prepared from 2-methoxyphenol and 2-fluorobenzonitrile in 94% isolated yield as a white solid in 99.8% pure after 5 min. M.p.79-80 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 7.85-6.62 (m, 8H), 3.74 (s, 3H, OCH_3). GC-MS m/z 225 (M^+).

4-(2'-cyanophenoxy)benzonitrile (6): It was prepared from 4-hydroxybenzonitrile and 2-fluorobenzonitrile in 98% isolated yield as a white solid in a purity higher than 99% after 10 min. M.p.90-92 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 8.00-7.91 (m, 3H), ~7.77 (m, 1H), 7.43-7.24 (m, 4H). GC-MS m/z 220 (M^+).

4,4'-dinitrodiphenyl ether (7): It was prepared from 4-nitrophenol and 1-chloro-4-nitrobenzene in 83% isolated yield as a pale yellow solid in a purity higher than 99% after 10 min. M.p.138-140 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 8.36-8.30 (m, 4H), 7.40-7.34 (m, 4H). GC-MS m/z 260 (M^+).

4-(4'-nitrophenoxy)benzonitrile (8): It was prepared from 4-hydroxybenzonitrile and 1-chloro-4-nitrobenzene in 95% isolated yield as a yellow solid in 98% purity after 5 min. M.p.154-156 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 8.32-8.29 (dd, 2H), 7.97-7.91 (dd, 2H), 7.36-7.26 (m, 4H). GC-MS m/z 240 (M^+).

4-(2'-methoxyphenoxy)benzonitrile (9): It was prepared from 2-methoxyphenol and 4-bromobenzonitrile in 78% isolated yield as a gray solid in 99.3% purity after 10 min. M.p.88-90 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 7.79-7.76 (m, 2H), 7.30-6.92 (m, 6H), 3.72 (s, 3H, OCH_3). GC-MS m/z 225 (M^+).

4-(4'-chlorophenoxy)benzonitrile (10): It was prepared from 4-chlorophenol and 4-bromobenzonitrile in 87% isolated yield as a white solid in 98% purity after 10 min. M.p.81-82 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 7.87-7.84 (dd, 2H), 7.53-7.50 (dd, 2H), 7.21-7.12 (m, 4H). GC-MS m/z 229 (M^+).

3-(2'-methoxyphenoxy)benzonitrile (11): It was prepared from 2-methoxyphenol

and 3-fluorobenzonitrile in 74% isolated yield as a grayish solid in 98.7% purity after 10 min. M.p.49-50 ^{0}C. ^{1}H NMR (DMSO, 300MHz) 7.51-7.01 (m, 2H), 3.73 (s, 3H, OCH_3). GC-MS m/z 225 (M^+).