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Supporting Information

Simple and Efficient Recyclable Catalytic System for Performing Copper-Catalysed *S*-Arylation Reactions in the Presence of Water

Mónica Carril, Raul SanMartin*, Esther Domínguez and Imanol Tellitu

Supporting information.

Literature data for known compounds

4-Nitrophenyl phenyl sulfide 3b.[1] The typical procedure was followed starting from the corresponding aryl iodide (265.6 mg, 0.94 mmol) and thiol (0.05 ml, 0.47 mmol) to afford sulfide **3b** (106.7 mg, 98%) as a yellow solid.

3,5-Dimethylphenyl phenyl sulfide 3c.[2] The typical procedure was followed starting from the corresponding aryl iodide (0.14 ml, 0.94 mmol) and thiol (0.05 ml, 0.47 mmol) to afford sulfide **3c** (84.8 mg, 84%) as a colourless liquid.

1-Naphthyl phenyl sulfide 3e.[1] The typical procedure was followed starting from the corresponding aryl iodide (0.14 ml, 0.94 mmol) and thiol (0.05 ml, 0.47 mmol) to afford sulfide **3e** (71.6 mg, 64%) as a yellow solid.

4-Bromophenyl phenyl sulfide 3f.[3] The typical procedure was followed starting from the corresponding aryl iodide (275.1 mg, 0.94 mmol) and thiol (0.05 ml, 0.47 mmol) to afford sulfide **3f** (88.4 mg, 71%) as a pale orange liquid.

2-Acetylphenyl phenyl sulfide 3g.[4] The typical procedure was followed starting from the corresponding aryl iodide (0.14 ml, 0.94 mmol) and thiol (0.05 ml, 0.47 mmol) to afford sulfide **3g** (71.5 mg, 66%) as a white transparent solid.

2-Aminophenyl phenyl sulfide 3h.[5] The typical procedure was followed starting from the corresponding aryl iodide (210.8 mg, 0.94 mmol) and thiol (0.05 ml, 0.47 mmol) to afford sulfide **3h** (89.7 mg, 95%) as a yellow oil.

Phenyl 2-hydroxymethylphenyl sulfide 3i.[4] The typical procedure was followed starting from the corresponding aryl iodide (224.0 mg, 0.94 mmol) and thiol (0.05 ml, 0.47 mmol) to afford sulfide **3i** (89.7 mg, 95%) as an orange liquid.

4-Aminophenyl phenyl sulfide 3j.[6] The typical procedure was followed starting from the corresponding aryl iodide (213.9 mg, 0.94 mmol) and thiol (0.05 ml, 0.47 mmol) to afford sulfide **3j** (91.9 mg, 97%) as a white solid.

4-Methoxyphenyl phenyl sulfide 3k.[1] The typical procedure was followed starting from the corresponding aryl iodide (0.12 ml, 1.05 mmol) and thiol (0.06 ml, 0.48 mmol) to afford sulfide **3k** (82.4 mg, 80%) as a colourless liquid. *Recycling of the aqueous solution containing the catalyst*: After extraction with CH_2Cl_2, the recovered aqueous layer was placed in a schlenk flask under argon, and aryl iodide (0.12 ml, 1.05 mmol), *trans*-diaminocyclohexane (0.17 ml, 1.42 mmol) and thiol (0.06 ml, 0.48 mmol) were added. The so-obtained mixture was heated at 120°C overnight and the isolation of the product was accomplished as described before. This procedure, employing identical amounts for each reactant, was repeated three times.

Di(4-methoxyphenyl) sulfide 3l.[1] The typical procedure was followed starting from the corresponding aryl iodide (222.5 mg, 0.93 mmol) and thiol (0.06 ml, 0.48 mmol) to afford sulfide **3l** (84.5 mg, 72%) as a yellow liquid.

4-Nitrophenyl 4-methoxyphenyl sulfide 3m.[7] The typical procedure was followed starting from the corresponding aryl iodide (243.7 mg, 0.96 mmol) and thiol (0.06 ml, 0.48 mmol) to afford sulfide **3m** (121.4 mg, 97%) as a yellow solid.

4-Chlorophenyl 4-methoxyphenyl sulfide 3n.[5] The typical procedure was followed starting from the corresponding aryl iodide (231.0 mg, 0.96 mmol) and thiol (0.06 ml, 0.48 mmol) to afford sulfide **3n** (95.6 mg, 80%) as a white solid.

2-Aminophenyl phenyl sulfide 3h'.[5] The typical procedure was followed starting from the corresponding aryl iodide (0.13 ml, 1.11 mmol) and thiol (0.06 ml, 0.56 mmol) to afford sulfide **3h'** (109.6 mg, 98%) as a yellow oil.

4-Methylphenyl phenyl sulfide 3o.[1] The typical procedure was followed starting from the corresponding aryl iodide (0.19 ml, 1.66 mmol) and thiol (94.6 mg, 0.75 mmol) to afford sulfide **3o** (122.2 mg, 82%) as a yellow liquid.

Phenyl 2-pyridinyl sulfide 3p.[8] The typical procedure was followed starting from the corresponding aryl iodide (0.12 ml, 1.05 mmol) and thiol (53.7 mg, 0.48 mmol) to afford sulfide **3p** (78.3 mg, 87%) as a colourless liquid.

4-Chlorophenyl phenyl sulfide 3d'.[3] The typical procedure was followed starting from the corresponding aryl iodide (0.12 ml, 1.05 mmol) and thiol (70.3 mg, 0.49 mmol) to afford sulfide **3d'** (78 mg, 73%) as a colourless liquid.

2-Aminophenyl 4-chlorophenyl sulfide 3q.[9] The typical procedure was followed starting from the corresponding aryl iodide (267.8 mg, 1.11 mmol) and thiol (0.06 ml, 0.56 mmol) to afford sulfide **3q** (102.3 mg, 78%) as a white solid.

4-Nitrophenyl 2-pyridinyl sulfide 3r.[10] The typical procedure was followed starting from the corresponding aryl iodide (239.7 mg, 0.91 mmol) and thiol (50.4 mg, 0.45 mmol) to afford sulfide **3r** (72.3 mg, 69%) as a yellow solid.

2-Acetylphenyl phenyl sulfide 3g.[3] The typical procedure was followed starting from the corresponding aryl bromide (0.13 ml, 0.94 mmol) and thiol (0.05 ml, 0.47 mmol) to afford sulfide **3g** (84.5 mg, 79%) as a white transparent solid.

4-Nitrophenyl 4-methoxyphenyl sulfide 3m.[7] The typical procedure was followed starting from the corresponding aryl bromide (197.7 mg, 0.96 mmol) and thiol (0.06 ml, 0.48 mmol) to afford sulfide **3m** (118.4 mg, 95%) as a yellow solid.

4-Nitrophenyl 2-pyridinyl sulfide 3r.[10] The typical procedure was followed starting from the corresponding aryl bromide (194.4 mg, 0.93 mmol) and thiol (51.6 mg, 0.46 mmol) to afford sulfide **3r** (76.3 mg, 71%) as a yellow solid.

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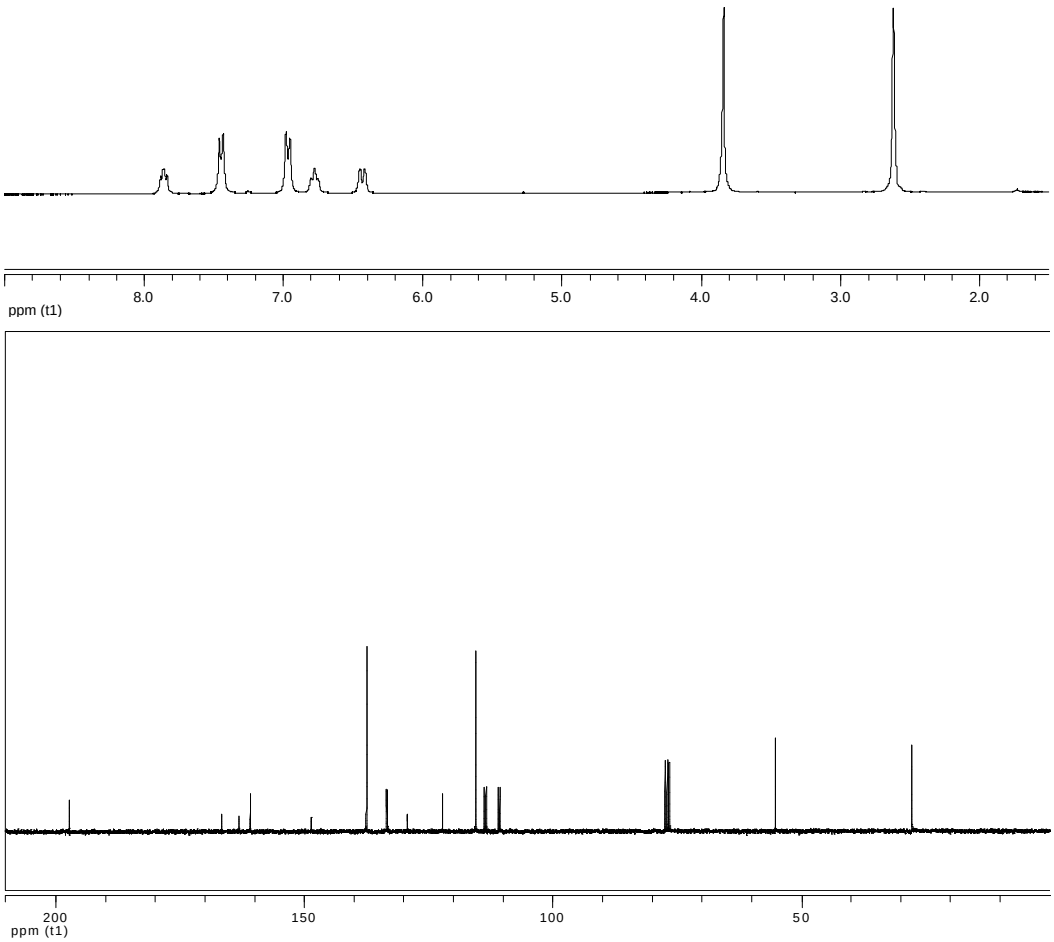
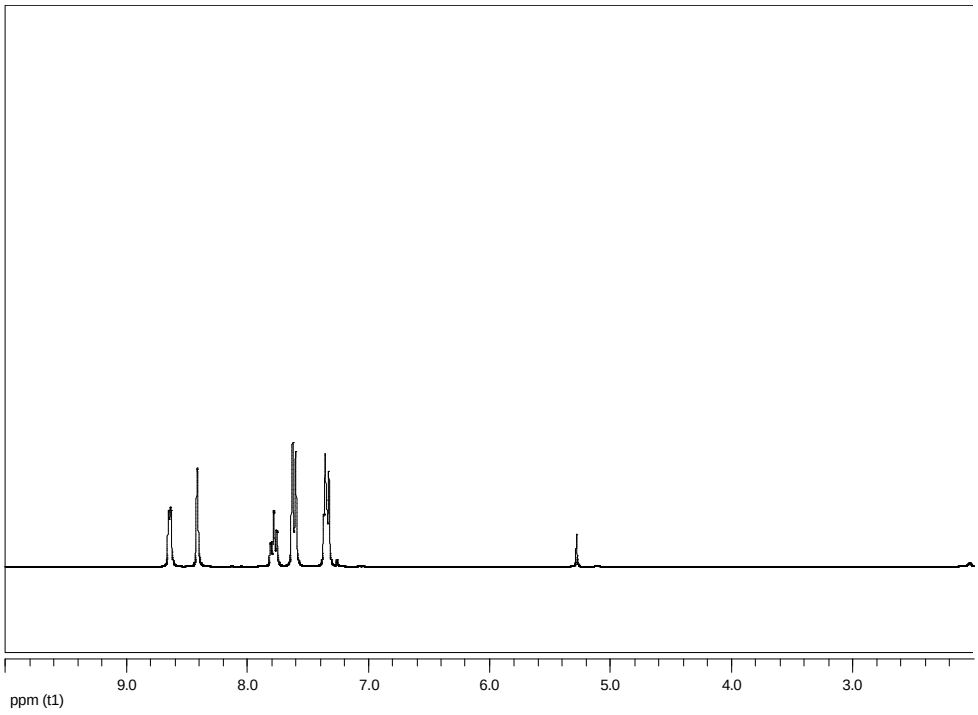
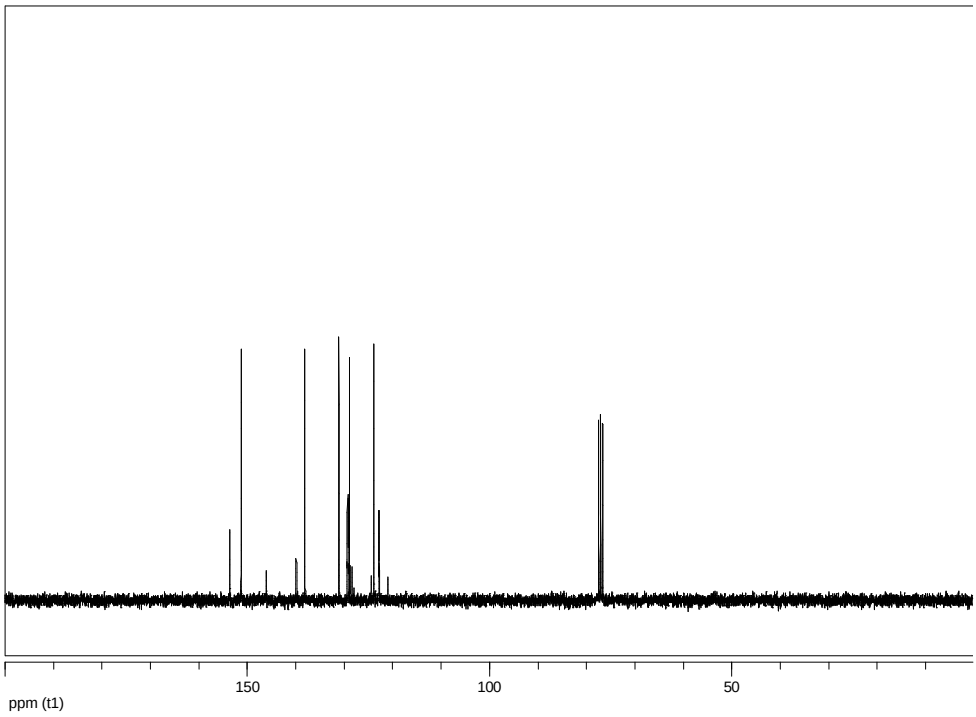
NMR spectra of new compounds

2-Acetyl-5-fluorophenyl 4-methoxyphenyl sulfide 3t



2-Nitro-4-trifluoromethylphenyl 2-pyridinyl sulfide 3u





2-Acetyl-5-fluorophenyl 4-chlrophenyl sulfide 3v