Supporting Information

Fast Synthesis of Aryl Triflates with Controlled Microwave Heating

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Experimental Section

General: The microwave heating was performed in a SmihSynthesizer™ single mode cavity, producing continuous irradiation at 2450 MHz. Reaction temperature and pressure were determened using the build in, on-line IR- and pressure sensors. Pre-packed silica columns (FlashPack SIL) were used for flash chromatography. The 2-chlorotritylchloride resin was purchased from Alexis Corporation (120-002-G025). ^{1}H-NMR and ^{13}C-NMR were recorded with $CDCl_3$ or DMSO-d_6 as solvent on a Joel 400 Spectrometer. Mass spectra were recorded on a GC-MS, equipped with a HP-1 (25 m × 0.20 mm) capillary column, utilizing electron impact (EI) at an ionizing energy of 70 eV.

General Procedure for Synthesis of Aryl Triflates: The phenol (2.0 mmol), *N*-phenyl-bis(trifluoromethanesulfonimide) (2.0 mmol, 710 mg), K_2CO_3 (6.0 mmol, 830 mg) and 3.0 mL of THF were mixed in a septum capped tube (a Smith process vial). The reaction mixture was heated to 120 °C for 6 min in a microwave synthesizer.

Procedure I for Work-Up and Purification of Aryl Triflates (compound 2a-c): After cooling, the K_2CO_3 was filtered from the reaction mixture and washed with EtOAc. The filtrate was evaporated. The crude product was purified with flash chromatography. Column material: 20 g silica gel. Solvent: Ethyl acetate, iso-hexane 1:19.

Procedure II for Work-Up and Purification of Aryl Triflates (compound 2d-h): After cooling, the reaction mixture was extracted with H_2O/EtOAc, the organic phases were combined, dried with $MgSO_4$ and evaporated. The crude product was purified with flash chromatography. Column material: 50 g silica gel. Solvent: iso-hexane with a gradient of 5-50% EtOAc.

Trifluoro-methanesulfonic acid phenyl ester (2a) was obtained in 69% yield (313 mg) as a colourless oil with analytical data identical to the known material.[1]

Trifluoro-methanesulfonic acid 4-methoxy-phenyl ester (2b) was obtained in 80% yield (408 mg) as a colourless oil with analytical data identical to the known material.[2]

Trifluoro-methanesulfonic acid 4-cyano-phenyl ester (2c) was obtained in 91 % yield (458 mg) as a colourless oil with analytical data identical to the known material.[3]

Trifluoro-methanesulfonic acid 2-formyl-phenyl ester (2d) was obtained in 78% yield (397 mg) as a colorless oil with analytical data identical to the known material.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (dd, J = 0.9, 8.3 Hz, 1H), 7.57 (ddd, J = 0.9, 7.4, 7.7 Hz, 1H), 7.73 (ddd, J = 1.8, 7.4, 8.3 Hz, 1H), 8.01 (dd, J = 1.8, 7.7 Hz, 1H), 10.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 118.7 (q, J = 320 Hz), 122.5, 128.6, 129.0, 130.9, 135.9, 149.9, 186.5.

Trifluoro-methanesulfonic acid 2-formyl-4-methoxy-phenyl ester (2e) was obtained in 87% yield (495 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.87 (s, 3H), 7.19 (dd, J = 9.1, 3.2 Hz, 1H), 7.31 (d, J = 9.1 Hz, 1H), 7.42 (d, J = 3.2 Hz, 1H), 10.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.1, 113.2, 118.7 (q, J = 320 Hz), 122.2, 123.7, 129.3, 143.6, 159.4, 186.5; MS (EI, 70 eV) *m/z*: 284 (M$^+$, 23), 151 (100), 123 (22), 108 (18), 95 (33); Anal. Calcd for $C_9H_7F_3O_5S$: C 38.0, H 2.5. Found: C 38.2, H 2.9

Trifluoro-methanesulfonic acid 2-formyl-6-methoxy-phenyl ester (2f) was obtained in 73% yield (415 mg) as white crystals with analytical data identical to the known material[5].

Trifluoro-methanesulfonic acid 4-benzyloxy-2-formyl-phenyl ester (2g) was obtained in 69% yield (497 mg) as pale yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.17 (s, 2H), 6.96 (d, J = 2.9 Hz, 1H), 7.10 (dd, J = 2.9, 8.7 Hz, 1H), 7.37-7.43 (m, 5H), 7.94 (d, J = 8.7 Hz, 1H), 10.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 71.2, 109.2, 115.0, 118.7 (J = 320 Hz), 122.0, 127.7, 128.8, 129.0, 132.4, 134.9, 151.3, 164.5, 185.5; MS (EI, 70 eV) *m/z*: 360 (M$^+$, 1), 91 (100); Anal. Calcd for $C_{15}H_{11}F_3O_5S$: C 50.0, H 3.1. Found: C 50.3, H 2.9.

Trifluoro-methanesulfonic acid 4-chloro-2-formyl-phenyl ester (2h) was obtained in 69% yield (398 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (d, J = 8.8 Hz, 1H), 7.67 (dd, J = 8.8, 2.6 Hz, 1H), 7.95 (d, J = 2.6 Hz, 1H), 10.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 118.7 (q, J = 320 Hz), 124.0, 129.6, 130.4, 135.3, 135.6, 148.2, 185.2; MS (EI, 70 eV) *m/z*: 288 (M^+, 67), 223 (64), 155 (99), 127 (49), 99 (100); Anal. Calcd for $C_8H_4ClF_3O_4S$: C 33.3, H 1.4. Found: C 32.6, H 1.5

Trifluoro-methanesulfonic acid 2,4-diformyl-phenyl ester (2i): 5-Formylsalicylaldehyde was reacted with *N*-phenyl-bis(trifluoromethane-sulfonimide) according to the general procedure. After cooling, the reaction mixture was extracted with H_2O/EtOAc, the organic phases were combined, dried with $MgSO_4$ and evaporated. The crude product (crystalline) was stirred with hot THF for around 30 minutes (the product did not dissolve). The mixture was cooled and the crystals were filtered and washed with cold THF to obtain compound **2i** (508 mg) as pale yellow crystals. Yield: 90%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.87 (d, *J* = 8.4 Hz, 1H), 8.38 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.62 (d, 2.2 1H), 10.13 (s, 1H), 10.17 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 124.5, 129.2, 134.8, 136.9, 137.3, 151.0, 189.2, 191.8; MS (EI, 70 eV) *m/z*: 282 (M^+, 10), 217 (76), 189 (32), 148 (100), 132 (37); Anal. Calcd for $C_9H_5F_3O_5S$: C 38.3, H 1.8. Found: C 38.4, H 2.1.

Trifluoro-methanesulfonic acid 4-carboxy-phenyl ester (2j) 4-Hydroxybenzoic acid (0.25 mmol, 258 mg) attached to 2-chlorotritylchloride resin (0.97 mmol/g), *N*-phenyl-bis(trifluoromethane-sulfonimide) (0.3 mmol, 107 mg), Et_3N (0.75 mmol, 100 μL) and 2.0 mL of THF were mixed in a septum capped tube (a Smith process vial). The reaction mixture was heated to 120 °C for 6 min in a microwave synthesizer.

The resin was washed with THF, DCM, DMF and MeOH. The product was cleaved with 5 mL 1% TFA in DCM for 1 hour followed by rinsing with DCM and MeOH. Compound **2j** was obtained in 80% yield (408 mg) as white crystals with analytical data identical to the known material.[6]

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[3] [66107-32-2] Derocque, J. L.; Appriou, P.; Guglielmetti, R.; Duerr, H. *Org. Mass Spectrom.* **1977**, *12*, 606-18.

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