CO₂ activation by a samarium sacrificial anode for aryl halides carboxylation

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1. Instrumentation and Chemicals

All commercially available reagents were used without further purification unless otherwise stated. All solvents were also used without further purification. Dimethylformamide (DMF) was purchased from Carlo Erba and tetrabutylammonium tetrafluoroborate (nBu_4NBF_4) from Fluka. The samarium rod was a 12.7mm diameter, 99.9% (metals basis excluding Ta) rod, purchased from Alfa-Aesar and the stainless-steel grid from Goodfelllow. Electrolysis was performed using an EGG Instrument Potentiostat/Galvanostat Model 273 in an undivided cell equipped with a samarium rod as anode and a stainless-steel grid as cathode. NMR spectra were recorded on Bruker AM 360 (360 MHz), 300 (300 MHz) or AM 250 (250 MHz) in CDCl₃ with drops of CD₃OD in some cases or totally in DMSO-d₆ due to the solubility of some products. Data for ¹H NMR are recorded as follows: chemical shift (δ , ppm), coupling constant (J, Hz), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, and br = broad signal, integration). Reactions were monitored by thin layer chromatography (TLC) and column chromatography purifications were carried out using silica gel.

2. General Procedure for the carboxylation of aryl halides

Under CO₂ (1 atm), the reactions were carried out in an undivided cell containing a magnetic stirring bar, a samarium rod as the anode and a stainless-steel as the cathode. The cell was charged with 322 mg of tetrabutylammonium tetrafluoroborate nBu_4NBF_4 (1 mmol) and the aryl halide (5 mmol) dissolved in 100 mL of DMF. The electrolysis was performed in a chronopotentiometry mode with I = 100 mA for 15000 seconds. When the substrate is no longer detected on the TLC, the reaction was quenched with slow addition of 6M HCl aq. (40 mL) and the mixture was stirred at room temperature until a homogenous solution was obtained. After dissolution, 300 mL of distilled water was added, and the aqueous solution was extracted with ethyl acetate (3 x 100 mL). The collected organic layer was washed with brine (3 x 100 mL), dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (80/20 and then 0/100).

3. Characterization of the compounds



4-methoxybenzoic acid (2a): 539 mg (3.55 mmol, yield: 71%,). ¹H NMR (300 MHz, CDCl₃+CD₃OD) δ 8.00 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 3.85 (s, 3H).

¹³C NMR (91 MHz, CDCl₃ + CD₃OD) δ 169.1, 163.5, 132, 122.4, 113.5, 55.4.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature¹.



2-methoxybenzoic acid (2b): 638 mg (3.45 mmol, yield: 69%). ¹H NMR (300 MHz, DMSO*d*₆): δ 7.65 (d, *J* = 10.1 Hz, 1H), 7.49 (td, *J* = 11.3, 4.4 Hz, 1H), 7.10 (d, *J* = 9.8 Hz, 1H), 6.97 (td, *J* = 17.4, 10.0 Hz, 1H), 3.77 (s, *J* = 20.6 Hz, 3H).

¹³C NMR (75 MHz, DMSO-*d*₆): δ 167.8, 158.5, 133.4, 131, 121.7, 120.4, 112.8, 56.1.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature².



4-methylbenzoic acid (2c): 676 mg (4 mmol, yield: 80%,) ¹H NMR (360 MHz, CDCl₃+CD₃OD) δ 7.89 (d, 2H), 7.20 (d, 2H), 2.36 (s, 3H).

¹³C NMR (63 MHz, CDCl₃+CD₃OD) δ 169.6, 143.6, 129.7, 128.8, 127.1, 21.2.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature³.

¹ X. Zhang, W. –Z. Zhang, L. –L. Shi, C. –X. Guo, L. –L. Zhang, X. –B. Lu, Chem. Commun. **2012**, 48, 6292-6294.

² A. Correa, R. Martín, *JACS* **2009**, *131* (44), 15974-15975.

³ T. Fujihara, K. Nogi, T. Xu, J. Terao, Y. Tsuji, *JACS* **2012** *134* (22), 9106-9109.



2-methylbenzoic acid (2d): 600 mg (3.55 mmol, yield: 71%). ¹H NMR (300 MHz, CDCl₃ + CD₃OD): δ 7.83 (d, *J* = 7.5 Hz, 1H), 7.29 (dd, *J* = 8.3, 6.5 Hz, 1H), 7.20 – 6.97 (m, 2H), 2.49 (s, 3H).

¹³C NMR (91 MHz, CDCl₃+ CD₃OD) δ 169.9, 139.9, 131.7, 131.3, 130.5, 129.5, 125.3, 21.3.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature².



3-methylbenzoic acid (2e): 668 mg (3.9 mmol, yield: 78%). ¹H NMR (300 MHz, CDCl₃) δ 7.93 (m, 2H), 7.51 – 7.29 (m, 2H), 2.43 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 172.5, 138.3, 134.5, 130.7, 129.2, 128.3, 127.3, 21.2.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature².



Benzoic acid (2f): 464 mg (3.8 mmol, yield: 76%) ¹H NMR (360 MHz, CDCl₃+CD₃OD) δ 7.99 (d, J = 7.7 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H).

¹³C NMR (91 MHz, CDCl₃+CD₃OD) δ 169.2, 132.9, 130.1, 129.7, 128.2.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature¹.



4-flurobenzoic acid (2g): 483 mg (3.45 mmol, yield: 69%). ¹H NMR (300 MHz, CDCl₃+CD₃OD) δ 7.99 (m, 2H), 7.03 (t, 2H).

¹³C NMR (91 MHz, CDCl₃+CD₃OD) δ 167.9, 165.7(d, J_{C-F} = 250Hz), 132.3(d, J_{C-F} = 9.5Hz), 126.5, 115.2(d, J_{C-F} =22Hz).

¹⁹F NMR (75 MHz, CDCl₃+CD₃OD): δ 106.94.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature⁴.



4-(trifluoromethyl) benzoic acid (2h): 741 mg (3.9 mmol, yield: 78%). ¹H NMR (300 MHz, CDCl₃+ CD₃OD) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H).

¹³C NMR (63 MHz, DMSO) δ 166.1, 134.6, 132.5(d, *J*=31 Hz), 130.1, 125.9, 125.5(q, *J*=272 Hz).

¹⁹F (282 MHz, CDCl₃ + CD₃OD): δ 61.6.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature².



Methyl -4-carboxybenzoate acid (2i): 549 mg (3.05 mmol, yield: 61%,). ¹H NMR (300 MHz, CDCl₃) δ 8.03 (m, 4H), 3.88 (s, 3H).

¹³C NMR (91 MHz, CDCl₃) δ 167.8, 166.6, 134.4, 133.6, 129.7, 129.4, 52.3.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature³.



4-bromobenzoic acid (21): 573 mg (2.85 mmol, yield: 57%). ¹H NMR (300 MHz, DMSO- d_{δ}): δ 13.19 (s, 1H), 7.86 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ 167.1, 132.1, 131.7, 130.4, 127.3.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature⁴.

⁴ F. Rebih, M. Andreini, A. Moncomble, A. Harrison-Marchand, J. Maddaluno, M. Durandetti, *Chem. Eur. J.* **2016**, *22*, 3758–3763.



3-thiophenecarboxylic acid (2n): 267 mg (2.1 mmol, yield: 42%,). ¹H NMR (300 MHz, CDCl₃) δ 8.25 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.58 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.39 – 7.30 (m, 1H).

¹³C NMR (91 MHz, CDCl₃) δ 168.2, 134.6, 132.9, 128.1, 126.3.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature⁵.



Dibenzothiophene-2-carboxylic acid (20): 513 mg (2.25 mmol, yield: 45%,). ¹H NMR (250 MHz, DMSO) δ 8.91 (d, J = 1.1 Hz, 1H), 8.49 (dd, J = 6.4, 1.6 Hz, 1H), 8.15 (d, J = 6.1 Hz, 1H), 8.07 (m, 2H), 7.61 – 7.52 (m, 2H).

¹³C NMR (63 MHz, CDCl₃) δ 167.8, 143.7, 139.4, 135.5, 135.0, 128.1, 128.0, 127.0, 125.0, 123.6, 123.5, 123.4, 122.8.

ESI (-): [M-H] = 227.0174.



4-chlorobenzoic acid (2p): 511.5 mg (3.3 mmol, yield: 66%). ¹H NMR (300 MHz, DMSO) δ 13.21 (s, 1H), 8.03-7.84 (m, 2H), 7.65-7.41 (m, 2H).

¹³C NMR (75 MHz, DMSO) δ 166.5, 133.7, 133.3, 133, 130, 129.3, 128.3.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature⁴.



⁵ K. Paridala, S. M. Lu, M.M. Wang, C. Li, *Chem. Commun.* **2018**, *54*, 11574-11577.

2-chlorobenzoic acid (2q): 473 mg (3.05 mmol, 61%). ¹H NMR (300 MHz, DMSO) δ 13.21 (s, 1H), 7.94 (d, 2H), 7.57(d, 2H).

¹³C NMR (75 MHz, DMSO) δ 166.2, 133.4, 133, 132.7, 130.6, 128.9, 127.9.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature¹.



3-chlorobenzoic acid (2r): 457 mg (2.95 mmol, 59%). ¹H NMR (300 MHz, CDCl₃) δ 8.11 (t, *J* = 1.8 Hz, 1H), 8.05 – 7.97 (dt, 1H), 7.60 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H).

¹³C NMR (91 MHz, CDCl₃) δ 171.1, 134.7, 133.9, 130.9, 130.3, 129.8, 128.3.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.⁶



Phenylacetic acid: *starting from benzyl chloride:* 74 mg (0.55 mmol, yield 11%) ; *from benzyl bromide:* 490 mg (3.6 mmol, yield: 72%,). ¹H NMR (300 MHz, CDCl₃) δ 7.34 – 7.11 (m, 5H), 3.57 (s, 2H).

¹³C NMR (91 MHz, CDCl₃) δ 174.1, 134, 128.9, 128.1, 126.6, 40.9.

The ¹H NMR and ¹³C NMR spectra are in agreement with those reported in the literature.⁷

 ⁶ S. Mukhopadhyay, S. Batra, *Chem. Eur. J.* 2018, *24*, 14622.
⁷ T. Leon, A. Correa, R. Martin, *JACS* 2013, *135*, 1221-1224.

4. NMR Charts

4-methoxybenzoic acid (2a)



2-methoxybenzoic acid (2b)



4-methylbenzoic acid (2c)



2-methylbenzoic acid (2d)



3-methylbenzoic acid (2e)



Benzoic acid (2f)



4-fluorobenzoic acid (2g)





4-(trifluromethyl)benzoic acid (2h)





Methyl-4-carboxybenzoate acid (2i)



4-bromobenzoic acid (2l)



3-thiophenecarboxylic acid (2n):



Dibenzothiophene-2-carboxylic acid (2o)



4-chlorobenzoic acid (2p)



2-chlorobenzoic acid (2q)



3-chlorobenzoic acid (2r)



Phenylacetic acid (2s)



5. Samarium anode oxidation in the presence of CO₂ and TEMPO



Samarium anode oxidation: Sm electrode surface 20 mm², scanning potential between -1.5 and 0.9 V vs SCE in DMF with nBu_4NPF_6 [0.1 M]. Scan rate: 100 mV.s⁻¹. a) blue line: without additive; b) Red line: after bubbling CO₂ in the solution for 5 min; c) green line: after adding 0.5 mmol of TEMPO