Supporting Information

Silver(I)-catalyzed carboxylation of arylboronic esters with CO_2

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1. General Information

Methods. Unless otherwise statement, all manipulations were performed using standard Schlenk techniques under a dry nitrogen or CO_2 atmosphere. THF and toluene were dried and distilled from Na/benzophenone, then stored over fresh Na chip in the glovebox.. NMR spectra were recorded on a Bruker AvanceII 400M type (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer. Their peak freguencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^{1}H NMR and against the solvent ($CDCl_3$, 77.0 ppm) for ^{13}C NMR, respectively. Multiplicity abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) were measured using a Nicolet NEXUS FT-IR spectrophotometer.

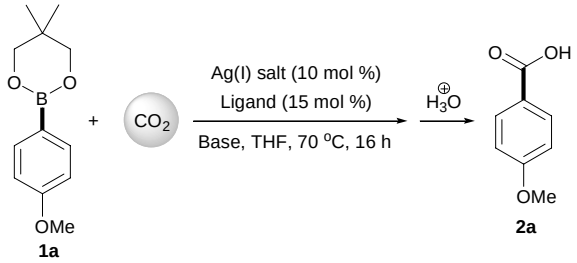
Materials. Unless otherwise noted, carbon dioxide (99.999%), commercially available arylboronic acids, silver(I) salt, phosphine ligands and other all reagents were used without further purification. All arylboronic esters **1** were prepared by reaction of the corresponding arylboronic acids with 2,2-dimethyl-1,3-propanediol according to the literatures.[1]

2. General Experimental Procedure for Carboxylation Reaction (Method A)

A 20 mL oven dried autoclave containing a stir bar was charged the AgOAc (10.0 mg, 0.06 mmol), PPh_3 (23.6 mg, 0.09 mmol), KO^{t}Bu (134.4 mg, 1.2 mmol) and arylboronic esters **1** (0.6 mmol), 4 mL dry THF was added with syringe after purging the autoclave with CO_2 three times. The sealed autoclave was pressurized to appropriate pressure with CO_2. The reaction mixture was stirred at 70 ^{o}C for 16 h, then the autoclave was cooled to room temperature and the remaining CO_2 was vented slowly. The reaction mixture was acidified by 1M hydrochloric acid, and the aqueous phase was exstracted with Et_2O (4 × 20 mL). The raw product was obtained by removal of the solvent under vacuum, the pure product was isolated by reverse extraction of the raw product (Et_2O/aq. NaOH then Et_2O/aq. HCl, followed by filtration through silica gel and removal of the solvent under vacuum).

3. Optimization of Reaction Conditions

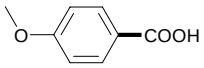
Table S1. Optimization of reaction conditions for silver(I)-catalyzed carboxylation of **1a** with CO_2[a]



Entry	Ag(I) salt	Ligand	Base	Solvent	Yield (%)[b]
1[c]	AgOAc	PPh_3	KO^{t}Bu	THF	84
2[d]	AgOAc	PPh_3	KO^{t}Bu	THF	74
3	AgI	-	KO^{t}Bu	THF	-
4	AgI	PPh_3	KO^{t}Bu	THF	-
5	AgI	PPh_3	KO^{t}Bu	DMF	-
6	Ag_2CO_3	PPh_3	KO^{t}Bu	THF	-
7	AgOAc	PPh_3	KO^{t}Bu	Toluene	70
8	AgOAc	PPh_3	KO^{t}Bu	CH_2Cl_2	-
9	AgOAc	PPh_3	$KOCH_3$	THF	-
10	AgOAc	PPh_3	Cs_2CO_3	THF	-
11	AgOAc	PPh_3	LiO^{t}Bu	THF	84

[a] Reaction conditions: **1a** (0.6 mmol), silver(I) salt (0.06 mmol), ligand (0.09 mmol), base (1.2 mmol), 4 mL THF, 20 atm, 70 °C, 16 h. [b] Isolated yield. [c] 60 °C. [d] 12 h.

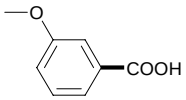
4. Characterization of Products



2a

4-Methoxybenzoic acid (2a)

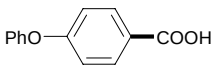
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (2H, d, J = 8.8 Hz), 6.95 (2H, d, J = 8.8 Hz), 3.88 (3H, s). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 171.05, 164.04, 132.35, 121.60, 113.76, 55.48. **IR** (cm^{-1}) (KBr) 1684. **HRMS** (ESI, *m*/*z*) calcd. for $C_8H_7O_3$ $[M-H]^-$: 151.0395, found: 151.0397. **M.P.**: 181–182 °C.



2b

3-Methoxybenzoic acid (2b)

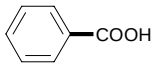
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.00 (1H, s), 7.54-7.17 (4H, m), 3.80 (3H, s). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.63, 159.69, 132.67, 130.16, 122.01, 119.32, 114.36, 55.69. **IR** (cm^{-1}) (KBr) 1693. **HRMS** (ESI, *m*/*z*) calcd. for $C_8H_7O_3$ $[M-H]^-$: 151.0395, found: 151.0390. **M.P.**: 107.5–108.5 °C.



2c

4-Phenoxybenzoic acid (2c)

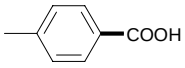
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.81 (1H, s), 7.94 (2H, d, J = 8.7 Hz), 7.46 (2H, t, J = 7.9 Hz), 7.24 (1H, t, J = 7.4 Hz), 7.12 (2H, d, J = 8.0 Hz), 7.02 (2H, d, J = 8.7 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.23, 161.45, 155.57, 132.13, 130.80, 125.69, 125.14, 120.42, 117.63. **IR** (cm^{-1}) (KBr) 1688. **HRMS** (ESI, *m*/*z*) calcd. for $C_{13}H_9O_3$ [M-H]$^-$: 213.0552, found: 213.0549. **M.P.**: 158–159 ºC.



2d

Benzoic acid (2d)

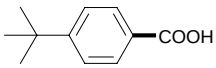
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.97 (1H, s), 7.94 (2H, d, J = 7.4 Hz), 7.63 (1H, t, J = 7.4 Hz), 7.50 (2H, t, J = 7.6 Hz,). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.31, 132.85, 130.74, 129.25, 128.55. **IR** (cm^{-1}) (KBr) 1683. **HRMS** (ESI, *m*/*z*) calcd. for $C_7H_5O_2$ [M-H]$^-$: 121.0290, found: 121.0291. **M.P.**: 121 ºC.



2e

4-Methylbenzoic acid (2e)

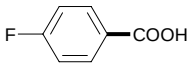
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.77 (1H, s), 7.83 (2H, d, J = 8.1 Hz), 7.29 (2H, d, J = 7.9 Hz), 2.36 (3H, s). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.35, 143.05, 129.36, 129.15, 128.05, 21.17. **IR** (cm^{-1}) (KBr) 1679. **HRMS** (ESI, *m*/*z*) calcd. for $C_8H_7O_2$ [M-H]$^-$: 135.0446, found: 135.0444. **M.P.**: 175–177 ºC.



2f

4-*tert*-Butylbenzoic acid (2f)

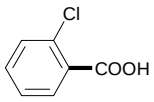
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.78 (1H, s), 7.87 (2H, d, J = 8.4 Hz), 7.51 (2H, d, J = 8.4 Hz), 1.29 (9H, s). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.75, 156.23, 129.66, 128.51, 125.82, 35.22, 31.31. **IR** (cm^{-1}) (KBr) 1684. **HRMS** (ESI, *m*/*z*) calcd. for $C_{11}H_{13}O_2$ [M-H]$^-$:177.0916, found: 177.0911. **M.P.**: 163–164 ºC.



2g

4-Fluorobenzoic acid (2g)

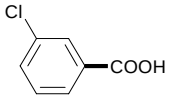
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.03 (1H, s), 7.99 (2H, dd, J = 8.5, 5.7 Hz,), 7.31 (2H, t, J = 8.5 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 166.85, 164.12, 132.56, 127.86, 116.07. **IR** (cm^{-1}) (KBr) 1684. **HRMS** (ESI, *m*/*z*) calcd. for $C_7H_4O_2F$ [M-H]$^-$: 139.0195, found: 139.0193. **M.P.**: 182–183 ºC.



2h

2-Chlorobenzoic acid (2h)

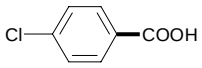
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.38 (1H, s), 7.77 (1H, d, J = 7.5 Hz), 7.54-7.41 (3H, m). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.21, 132.93, 131.97, 131.19, 131.01, 127.63. **IR** (cm^{-1}) (KBr) 1690. **HRMS** (ESI, m/z) calcd. for $C_7H_4O_2Cl$ [M-H]$^-$: 154.9900, found: 154.9905. **M.P.**: 138–139 ºC.



2i

3-Chlorobenzoic acid (2i)

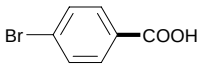
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.33 (1H, s), 7.90-7.88 (2H, m), 7.70 (1H, d, J = 8.2 Hz), 7.54 (1H, t, J = 8.0 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 166.66, 133.74,133.55, 133.02, 131.04, 129.26, 128.33. **IR** (cm^{-1}) (KBr) 1697. **HRMS** (ESI, m/z) calcd. for $C_7H_4O_2Cl$ [M-H]$^-$: 154.9900, found: 154.9901. **M.P.**: 151–152 ºC.



2j

4-Chlorobenzoic acid (2j)

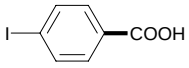
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (2H, d, J = 8.7 Hz), 7.46 (2H, d, J = 8.7 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.46, 137.77, 131.13, 129.64, 128.73. **IR** (cm^{-1}) (KBr) 1682. **HRMS** (ESI, m/z) calcd. for $C_7H_4O_2Cl$ [M-H]$^-$: 154.9900, found: 154.9904. **M.P.**: 238–239 ºC.



2k

4-Bromobenzoic acid (2k)

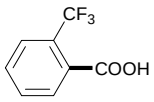
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (2H, d, J = 8.5 Hz), 7.63 (2H, d, J = 8.4 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.91, 132.79, 132.45, 131.18, 128.74. **IR** (cm^{-1}) (KBr) 1679. **HRMS** (ESI, m/z) calcd. for $C_7H_4O_2Br$ [M-H]$^-$: 198.9395, found: 198.9398. **M.P.**: 250–252 ºC.



2l

4-Iodobenzoic acid (2l)

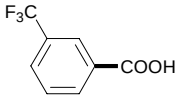
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.15 (1H, s), 7.89 (2H, d, J = 8.4 Hz), 7.69 (2H, d, J = 8.4 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.41, 138.04, 131.53, 130.79, 101.59. **IR** (cm^{-1}) (KBr) 1677. **HRMS** (ESI, m/z) calcd. for $C_7H_4O_2I$ [M-H]$^-$: 246.9256, found: 246.9253. **M.P.**: 266.5–267.5 ºC.



2m

2-(Trifluoromethyl)benzoic acid (2m)

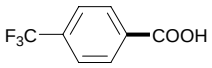
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.53 (1H, s), 7.85-7.70 (4H, m). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 168.34, 133.09, 131.58, 130.10, 128.11, 126.90, 125.39, 122.67. **IR** (cm^{-1}) (KBr) 1708. **HRMS** (ESI, *m*/*z*) calcd. for $C_8H_4O_2F_3$ [M-H]$^-$: 189.0163, found: 189.0168. **M.P.**: 106–107 ºC.



2n

3-(Trifluoromethyl)benzoic acid (2n)

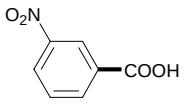
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.50 (1H, s), 8.23 (1H, d, J = 7.7 Hz), 8.17 (1H, s), 8.01 (1H, d, J = 7.6 Hz), 7.77 (1H, t, J = 7.8 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 166.48, 133.68, 132.38, 130.57, 129.71, 125.96, 125.61, 122.91. **IR** (cm^{-1}) (KBr) 1691. **HRMS** (ESI, *m*/*z*) calcd. for $C_8H_4O_2F_3$ [M-H]$^-$: 189.0163, found: 189.0164. **M.P.**: 102–104 ºC.



2o

4-(Trifluoromethyl)benzoic acid (2o)

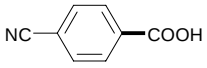
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.47 (1H, s), 8.14 (2H, d, J = 8.2 Hz), 7.88 (2H, d, J = 8.1 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 166.75, 135.19, 132.90, 130.56, 128.36, 126.03, 125.64, 122.94. **IR** (cm^{-1}) (KBr) 1699. **HRMS** (ESI, *m*/*z*) calcd. for $C_8H_4O_2F_3$ [M-H]$^-$: 189.0163, found: 189.0164. **M.P.**: 210–211 ºC.



2p

3-Nitrobenzoic acid (2p)

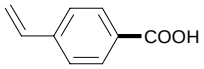
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.64 (1H, s), 8.61 (1H, s), 8.45 (1H, dd, J = 8.2, 2.2 Hz), 8.34 (1H, d, J = 7.7 Hz), 7.80 (1H, t, J = 8.0 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 166.02, 148.33, 135.83, 133.03, 130.98, 127.76, 124.14. **IR** (cm^{-1}) (KBr) 1706. **HRMS** (ESI, *m*/*z*) calcd. for $C_7H_4NO_4$ [M-H]$^-$: 166.0140, found: 166.0139. **M.P.**: 139–140 ºC.



2q

4-Cyanobenzoic acid (2q)

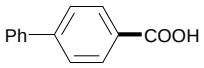
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.57 (1H, s), 8.07 (2H, d, J = 8.2 Hz), 7.97 (2H, d, J = 8.2 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 166.10, 134.87, 132.69, 129.95, 118.22, 115.08. **IR** (cm^{-1}) (KBr) 1711. **HRMS** (ESI, m/z) calcd. for $C_8H_4NO_2$ [M-H]$^-$: 146.0242, found: 146.0240. **M.P.**: 217–218 ºC.



2r

4-Vinylbenzoic acid (2r)

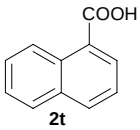
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.67 (1H, s), 7.91 (2H, d, J = 8.2 Hz), 7.59 (2H, d, J = 8.0 Hz), 6.81 (1H, dd, J = 17.7, 10.9 Hz), 5.98 (1H, d, J = 17.8 Hz), 5.41 (1H, d, J = 10.9 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.60, 141.70, 136.34, 130.55, 130.13, 126.66, 117.38. **IR** (cm^{-1}) (KBr) 1679. **HRMS** (ESI, m/z) calcd. for $C_9H_7O_2$ [M-H]$^-$: 147.0446, found: 147.0448. **M.P.**: 142–143 ºC.



2s

4-Phenylbenzoic acid (2s)

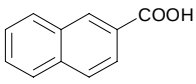
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.98 (1H, s), 8.03 (2H, d, J = 8.2 Hz), 7.81 (2H, d, J = 8.3 Hz), 7.75 (2H, d, J = 7.4 Hz), 7.52 (2H, t, J = 7.5 Hz), 7.44 (1H, t, J = 7.3 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.69, 144.74, 139.50, 130.43, 130.15, 129.55, 128.75, 127.42, 127.27. **IR** (cm^{-1}) (KBr) 1679. **HRMS** (ESI, m/z) calcd. for $C_{13}H_9O_2$ [M-H]$^-$: 197.0603, found: 197.0607. **M.P.**: 223–224 ºC.



2t

1-Naphthoic acid (2t)

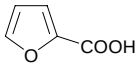
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.11 (1H, s), 8.86 (1H, d, J = 8.5 Hz), 8.17-8.14 (2H, m), 8.02 (1H, d, J = 8.1 Hz), 7.66-7.57 (3H, m). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 169.20, 133.94, 133.35, 131.15, 130.28, 129.06, 128.28, 128.00, 126.64, 125.97, 125.34. **IR** (cm^{-1}) (KBr) 1675. **HRMS** (ESI, m/z) calcd. for $C_{11}H_7O_2$ [M-H]$^-$: 171.0446, found: 171.0441. **M.P.**: 161 ºC.



2u

2-Naphthoic acid (2u)

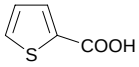
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (1H, s), 8.13 (1H, d, J = 8.7 Hz), 8.00 (1H, d, J = 8.2 Hz), 7.94-7.90 (2H, m), 7.65-7.55 (2H, m). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.06, 135.98, 132.46, 132.18, 129.56, 128.69, 128.35, 127.84, 126.80, 126.52, 125.40. **IR** (cm^{-1}) (KBr) 1683. **HRMS** (ESI, m/z) calcd. for $C_{11}H_7O_2$ [M-H]$^-$: 171.0446, found: 171.0444. **M.P.**: 183–184 ºC.



2v

Furan-2-carboxylic acid (2v)

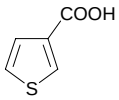
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.02 (1H, s), 7.91 (1H, s), 7.20 (1H, d, J = 3.1 Hz), 6.65 (1H, d, J = 1.5 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 159.83, 147.47, 145.42, 118.11, 112.54. **IR** (cm^{-1}) (KBr) 1765. **HRMS** (ESI, *m*/*z*) calcd. for $C_5H_3O_3$ [M-H]$^-$: 110.0082, found: 110.0085. **M.P.**: 132–133 ºC.



2w

Thiophene-2-carboxylic acid (2w)

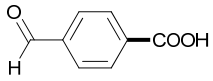
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.07 (1H, s), 7.88 (1H, dd, J = 4.9, 1.0 Hz), 7.72 (1H, dd, J = 3.6, 1.0 Hz), 7.18 (1H, dd, J = 4.9, 3.8 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 163.38, 135.14, 133.70, 133.64, 128.68. **IR** (cm^{-1}) (KBr) 1689. **HRMS** (ESI, *m*/*z*) calcd. for $C_5H_3O_2S$ [M-H]$^-$: 126.9854, found: 126.9853. **M.P.**: 126–127 ºC.



2x

Thiophene-3-carboxylic acid (2x)

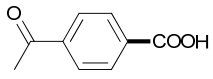
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.71 (1H, s), 8.25 (1H, dd, J = 2.9, 1.1 Hz), 7.61 (1H, dd, J = 5.0, 3.0 Hz), 7.42 (1H, dd, J = 5.0, 1.1 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 163.68, 134.35, 133.35, 127.79, 127.34. **IR** (cm^{-1}) (KBr) 1657. **HRMS** (ESI, *m*/*z*) calcd. for $C_5H_3O_2S$ [M-H]$^-$: 126.9854, found: 126.9858. **M.P.**: 136–137 ºC.



2y

4-Formylbenzoic acid (2y)

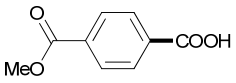
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.11 (1H, s), 8.13 (2H, d, J = 8.0Hz), 8.02 (2H, d, J = 8.4Hz), **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 193.56, 166.65, 138.88, 135.68, 129.96, 129.59. **IR** (cm^{-1}) (KBr) 1725, 1686. **HRMS** (ESI, *m*/*z*) calcd. for $C_8H_5O_3$ [M-H]$^-$: 149.0239, found: 149.0235. **M.P.**: 244 ºC



2z

4-Acetylbenzoic acid (2z)

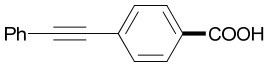
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.05 (4H, s), 2.62 (3H, s). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 197.81, 166.71, 139.86, 134.53, 129.61, 128.39, 27.07. **IR** (cm^{-1}) (KBr) 1693, 1682. **HRMS** (ESI, *m*/*z*) calcd. for $C_9H_7O_3$ [M-H]$^-$: 163.0395, found: 163.0398. **M.P.**: 208-209 ºC.



3a

4-(Methoxycarbonyl)benzoic acid (3a)

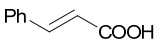
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.06 (4H, s), 3.88 (3H, s). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 166.62, 165.65, 134.84, 133.18, 129.64, 129.39, 52.52. **IR** (cm^{-1}) (KBr) 1720, 1689. **HRMS** (ESI, *m*/*z*) calcd. for $C_9H_7O_4$ [M-H]$^-$: 179.0344, found: 179.0347. **M.P.**: 219-221 ºC.



3b

4-(Phenylethynyl)benzoic acid (3b)

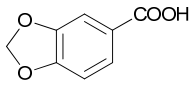
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.58 (1H, s), 7.97 (2H, d, *J* = 8.0 Hz), 7.67 (2H, d, *J* = 8.0 Hz), 7.59 (2H, m), 7.46 (3H, m). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.13, 131.97, 131.96, 131.03, 130.00, 129.69, 129.27, 127.01, 122.21, 92.38, 89.02. **IR** (cm^{-1}) (KBr) 1682. **HRMS** (ESI, *m*/*z*) calcd. for $C_{15}H_9O_2$ [M-H]$^-$: 221.0603, found: 221.0607. **M.P.**: 222-223 ºC.



3c

Cinnamic acid (3c)

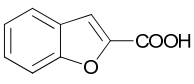
^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.43 (1H, s), 7.67(2H, m), 7.59 (1H, d, *J* = 16.4 Hz), 7.42 (d, *J* = 2.8Hz, 3H), 6.53 (d, *J* = 16.0Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$-d_6): δ = 167.20, 142.31, 129.29, 125.96, 124.18, 123.58, 112.46. **IR** (cm^{-1}) (KBr) 1682, 1630. **HRMS** (ESI, *m*/*z*) calcd. for $C_9H_7O_2$ [M-H]$^-$: 147.0446, found: 147.0443. **M.P.**: 132-133 ºC.



3d

Benzo[d][1,3]dioxole-5-carboxylic acid (3d)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.76 (1H, s), 7.54 (1H, dd, *J* = 8.1, 1.7 Hz), 7.36 (1H, d, *J* = 1.6 Hz), 7.00 (1H, d, *J* = 8.1 Hz), 6.12 (2H, s). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 167.08, 151.58, 147.93, 125.42, 125.14, 109.24, 108.52, 102.38. **IR** (cm^{-1}) (KBr) 1618. **HRMS** (ESI, *m*/*z*) calcd. for $C_8H_5O_4$ [M-H]$^-$: 165.0188, found: 165.0187. **M.P.**: 236–238 ºC.



3e

Benzofuran-2-carboxylic acid (3e)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.58 (1H, s), 7.79 (1H, d, J = 7.8 Hz), 7.71-7.67 (2H, m), 7.50 (1H, t, *J* = 7.8 Hz), 7.35 (1H, t, *J* = 7.5 Hz). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 160.58, 155.44, 146.67, 128.03, 127.32, 124.30, 123.56, 113.94, 112.54. **IR** (cm^{-1}) (KBr) 1686. **HRMS** (ESI, *m*/*z*) calcd. for $C_9H_5O_3$ [M-H]$^-$: 161.0239, found: 161.0237. **M.P.**: 194–195 ºC.

5. References

(1) Z.-Q. Lu, X. Zhou, S. Hu, X. Shu, Y. Tian and J. Zhu, *J. Phys. Chem. C*, 2010, **114**, 13546.

6. Copies of ^{1}H NMR and ^{13}C NMR Spectra of Products