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Carbon dioxide utilization via carbonate-promoted C–H carboxylation

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Using carbon dioxide (CO_2) as a feedstock for commodity synthesis is an attractive means of reducing greenhouse gas emissions and a possible stepping-stone towards renewable synthetic fuels[1,2]. A major impediment to synthesizing compounds from CO_2 is the difficulty of forming carbon–carbon (C–C) bonds efficiently: although CO_2 reacts readily with carbon-centred nucleophiles, generating these intermediates requires high-energy reagents (such as highly reducing metals or strong organic bases), carbon–heteroatom bonds or relatively acidic carbon–hydrogen (C–H) bonds[3–5]. These requirements negate the environmental benefit of using CO_2 as a substrate and limit the chemistry to low-volume targets. Here we show that intermediate-temperature (200 to 350 degrees Celsius) molten salts containing caesium or potassium cations enable carbonate ions (CO_3^{2-}) to deprotonate very weakly acidic C–H bonds ($pK_a > 40$), generating carbon-centred nucleophiles that react with CO_2 to form carboxylates. To illustrate a potential application, we use C–H carboxylation followed by protonation to convert 2-furoic acid into furan-2,5-dicarboxylic acid (FDCA)—a highly desirable bio-based feedstock[6] with numerous applications, including the synthesis of polyethylene furandicarboxylate (PEF), which is a potential large-scale substitute for petroleum-derived polyethylene terephthalate (PET)[7,8]. Since 2-furoic acid can readily be made from lignocellulose[9], CO_3^{2-}-promoted C–H carboxylation thus reveals a way to transform inedible biomass and CO_2 into a valuable feedstock chemical. Our results provide a new strategy for using CO_2 in the synthesis of multi-carbon compounds.

The chemistry described here is inspired by ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO), which effects C–C bond formation in the Calvin cycle by deprotonating a C–H bond of ribulose-1,5-bisphosphate and exposing the resulting carbon-centred nucleophile to CO_2 to form a carboxylate ($C–CO_2^-$)[10]. Emulating this strategy synthetically requires deprotonating un-activated C–H bonds using a simple base that does not have a large CO_2 footprint. To meet these requirements, we envisioned a CO_3^{2-}-promoted C–H carboxylation reaction, wherein CO_3^{2-} reversibly deprotonates a C–H bond to generate HCO_3^- and a carbon-centred nucleophile that reacts with CO_2 to form $C–CO_2^-$ (Fig. 1a). HCO_3^- decomposition results in a net consumption of one-half equivalents of CO_3^{2-} and CO_2 per $C–CO_2^-$ produced. The cycle could be closed by protonating $C–CO_2^-$ with strong acid and using electrodialysis to regenerate the acid and base[11,12], effecting a net transformation of C–H and CO_2 into $C–CO_2H$ without using any other stoichiometric reagents. Alternatively, CO_2-promoted esterification could be used to convert the carboxylate into an ester ($C–CO_2R$) and regenerate CO_3^{2-} directly[13]. Previously, researchers have shown that Cs_2CO_3 can deprotonate alkynyl[14], allylic[15], and activated heteroaryl C–H bonds with pK_a values of up to 27 (ref. 16) in organic solvents at elevated temperature (where pK_a is the negative base-10 logarithm of the acid dissociation constant). However, using CO_3^{2-}-promoted C–H carboxylation for commodity synthesis requires deprotonating C–H bonds that are considerably less acidic.

Carbonate-promoted C–H carboxylation is particularly desirable for the synthesis of polymer units from biomass. A longstanding goal of renewable polymer chemistry is a scalable synthesis of FDCA from lignocellulose to replace petroleum-derived terephthalic acid for polyester synthesis (Fig. 1b)[6]. In particular, PEF has been reported to have superior physical properties to PET, a polymer produced at 50 megatons a year as an industrial commodity[8]. Current approaches to FDCA synthesis use dehydration processes to convert hexose sugars into hydroxymethyl furfural (HMF), which is then oxidized to form FDCA[17]. Recent work has improved the efficiency of converting fructose to HMF[8,18] and it has been estimated that PEF production from fructose would emit 50% less CO_2 than the established process for PET production[7]. However, producing FDCA on a scale commensurate with terephthalic acid and achieving maximal reduction in CO_2 emissions will require using lignocellulose as the feedstock. Converting lignocellulose into HMF is very challenging because the hexoses are incorporated into intractable cellulose fibres[17]. Researchers have recently reported a high-yielding conversion of lignocellulose to HMF in ionic liquids[19,20] and an efficient process that converts lignocellulose into sugar monomers[21]. Despite these advances, an economical, large-scale lignocellulose-to-HMF process has not been demonstrated[17,22]. In contrast, the conversion of lignocellulose to furfural is a decades-old industrial process that is currently performed on a scale of about 400 kilotons a year[9,22]. Furthermore, several methods are available for oxidizing furfural to 2-furoic acid[23,24]. At present, however, the available methods for converting 2-furoic acid into FDCA are inefficient, unselective, and consume stoichiometric amounts of energy-intensive reagents[25,26]. CO_3^{2-}-promoted C–H carboxylation could be used to convert 2-furoic acid into FDCA and thereby open a new route to PEF using a lignocellulose-derived monomer that is already produced industrially.

The CO_3^{2-}-promoted C–H carboxylation reaction required for FDCA synthesis is the conversion of furan-2-carboxylate into furan-2,5-dicarboxylate ($FDCA^{2-}$) (Fig. 2a). Assuming it is similar to an un-substituted furan[27], the pK_a of the C–H at the 5 position of furan-2-carboxylate is ~35. Deprotonation of this C–H has previously required lithium diisopropylamide or *n*-butyllithium[26]. We hypothesized that CO_3^{2-} would deprotonate furan-2-carboxylate if the reaction were performed in a molten salt with a high concentration of alkali cations to stabilize the conjugate base by ion pairing. To test this hypothesis, we attempted C–H carboxylation with mixtures consisting of an alkali metal salt of 2-furoic acid and an alkali metal carbonate. With these components, the reaction was found to proceed efficiently when caesium ions (Cs^+) were used (Fig. 2a and Extended Data Table 1a). When 1 mmol of caesium furan-2-carboxylate and 0.55 mmol Cs_2CO_3 were heated at 260 °C under a CO_2 flow of 40 ml min^{-1} in a tube furnace, $FDCA^{2-}$ was formed in 76% yield after 12 h (Extended Data Fig. 1). The mass balance was composed of unreacted starting material and decomposition products including acetate. Reactions performed in a Parr reactor showed improved yields and less decomposition.

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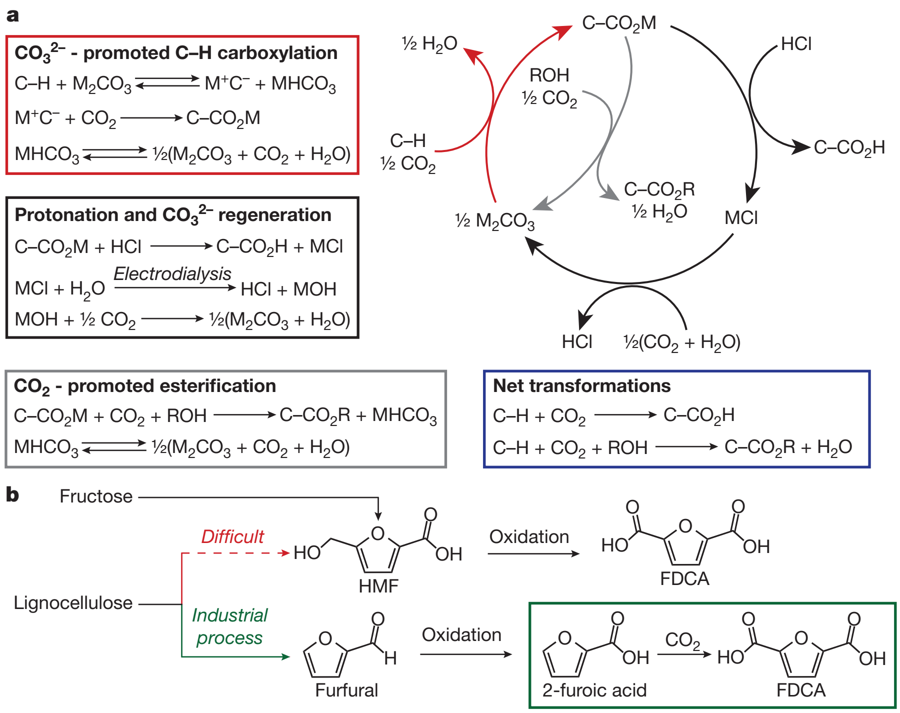


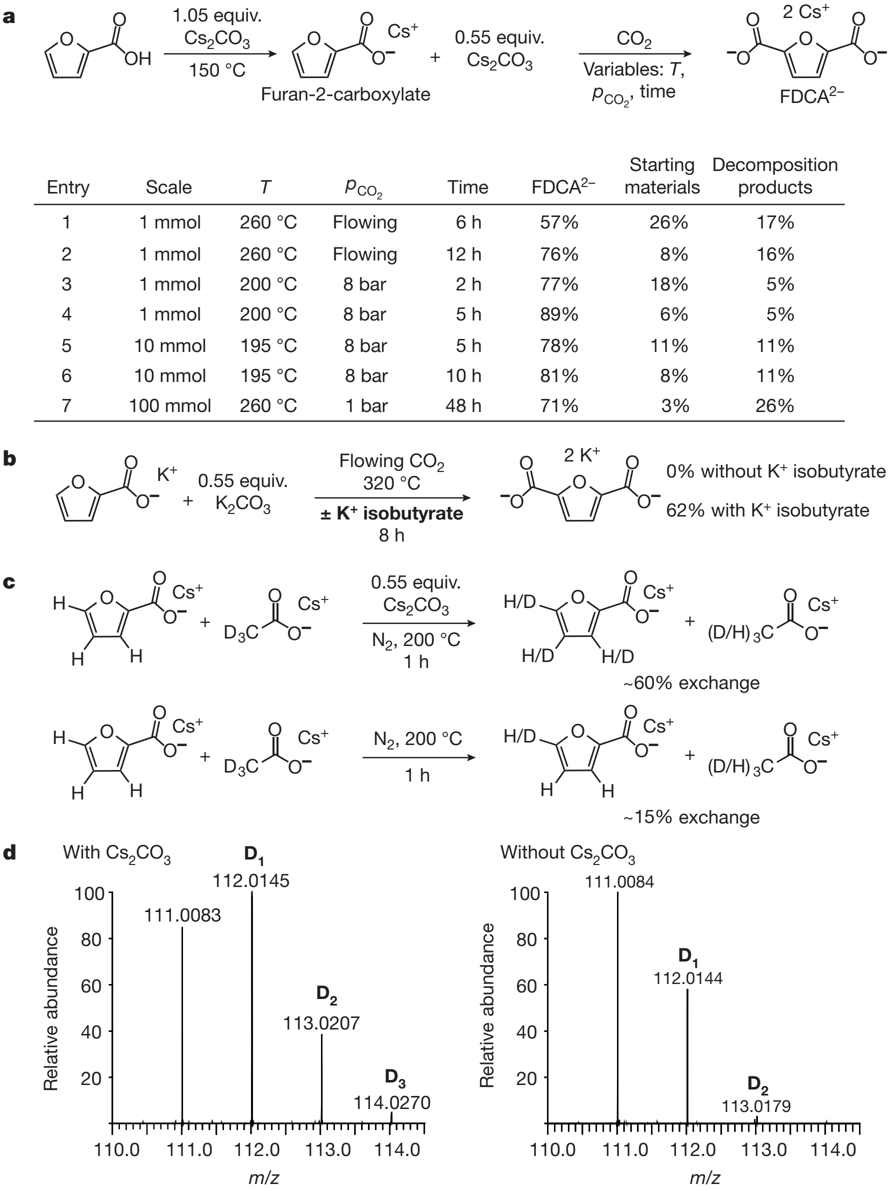
Figure 1 | CO_2 utilization cycle. a, C–H deprotonation by CO_3^{2-} forms a carbon-centred nucleophile (C^-) that reacts with CO_2 to form a C–C bond (red box and arrows). Protonation and electrodialysis (black box and arrows) produces a carboxylic acid. Alternatively, CO_2-promoted esterification (grey box and arrows) produces an ester. Net transformations are shown in the blue box. **b**, Potential application for FDCA synthesis from lignocellulose. Current approaches rely on converting lignocellulose into HMF, a difficult reaction that has not been commercialized. C–H carboxylation enables the use of furfural, which has been produced industrially from lignocellulose for many decades. M, metal; R, alkyl group.

In 1-mmol-scale reactions at 200 °C under a pressure of 8 bar CO_2, $FDCA^{2-}$ was formed in a 77% yield after 2 h and 89% yield after 5 h, with only 5% decomposition products. In 10-mmol-scale reactions under similar conditions, $FDCA^{2-}$ was formed in a 78% yield after 5 h and 81% yield after 10 h (Extended Data Fig. 3). Further increasing the reaction time did not appreciably increase the $FDCA^{2-}$ yield, while increasing the temperature diminished the yield because of increased decomposition. Increasing the CO_2 pressure slowed the reaction by sequestering CO_3^{2-} in the form of HCO_3^-. Finally, a 100-mmol-scale reaction was performed under ~1 bar CO_2 in a rotating round-bottom flask in a 260 °C bath. After 48 h, $FDCA^{2-}$ was formed in a 71% yield. The scaling behaviour suggests that the reaction takes place at the molten salt–CO_2 interface. The reaction slows and the yield decreases somewhat as the scale is increased because the surface area-to-volume ratio decreases. Improved yields and rates are anticipated with reactors that disperse the salt more effectively.

No $FDCA^{2-}$ was observed when carboxylation reactions were attempted using mixtures of furan-2-carboxylate and CO_3^{2-} with alkali cations other than Cs^+. These salt mixtures required temperatures much higher than 200 °C to melt, which resulted in decomposition reactions. The restriction to Cs^+ can be lifted, however, by incorporating another carboxylate salt to attain a semi-molten solution. For example, heating potassium furan-2-carboxylate with 0.5 equivalents of K_2CO_3 and 1 equivalent of potassium isobutyrate at 320 °C under 40 ml min^{-1} CO_2 resulted in 62% potassium $FDCA^{2-}$ (Extended Data Fig. 5a). Similar results were obtained with potassium acetate as an additive. Thus, C–H carboxylation does not require Cs^+ *per se*, but caesium salts do typically have lower melting points.

While the carboxylation results are consistent with the mechanistic scheme in Fig. 1a, there are other possible mechanisms that do not involve a carbanion intermediate. To probe the acid–base properties of furan-2-carboxylate independently, an isotope exchange experiment was performed between furan-2-carboxylate and acetate (Fig. 2c). (The pK_a of acetate is >33; ref. 28). A mixture of 1 mmol caesium furan-2-carboxylate, 1 mmol CD_3CO_2Cs, and 1.1 mmol Cs_2CO_3 was heated under N_2 in the Parr reactor to 200 °C for 1 h. ^1H, ^2H, and ^{13}C nuclear magnetic resonance (NMR) spectra of the crude product mixture showed hydrogen/deuterium (H/D) scrambling between acetate and the 5-position of furan-2-carboxylate and, to a lesser extent, the 3 and 4 positions (Extended Data Figs 6 and 7). The H content remaining in furan-2-carboxylate indicated that the exchange was ~60% complete. High-resolution mass spectrometry showed the fully protonated, and singly, doubly, and triply deuterated furan-2-carboxylate (Fig. 2d). When a 1:1 mixture of caesium furan-2-carboxylate and CD_3CO_2Cs was heated in the absence of Cs_2CO_3 at 200 °C, ~15% H/D exchange was observed, with nearly all of the exchange occurring at the 5 position (Fig. 2c and Extended Data Fig. 8). Thus, at 200 °C in a molten salt, a carboxylate is able to deprotonate the 5 position of furan-2-carboxylate, and CO_3^{2-} is able to deprotonate all positions. The selectivity seen in the carboxylation reaction suggests a greater abundance of the carbanion that leads to $FDCA^{2-}$.

Additional substrates were evaluated to gain further insight into the CO_3^{2-}-promoted C–H carboxylation reaction. Heating caesium thiophene-2-carboxylate with 0.55 equivalents of Cs_2CO_3 under flowing CO_2 at 325 °C resulted in a 71% yield of thiophene-2,5-dicarboxylate after 4 h (Extended Data Fig. 2). This substrate required a higher temperature than furan-2-carboxylate to form a semi-molten solution. To see whether C–H carboxylation is possible for substantially weaker acids, we evaluated the reactivity of benzoate. A previous study reported the carboxylation of caesium benzoate with Cs_2CO_3 at extreme CO_2 pressure (400 bar) at 380 °C via electrophilic activation of the aryl ring with a CO_3^{2-}–CO_2 complex[29]. The results with furan-2-carboxylate indicate that benzoate deprotonation by CO_3^{2-} is feasible, which would enable carboxylation under milder conditions at low CO_2 pressures. Remarkably, heating caesium benzoate with 0.55 equivalents of Cs_2CO_3 to 320 °C under 8 bar CO_2 resulted in a combined yield of 66% for a mixture of phthalates and tri- and tetracarboxylates (Fig. 3a and Extended Data Fig. 4). The ability of CO_3^{2-}



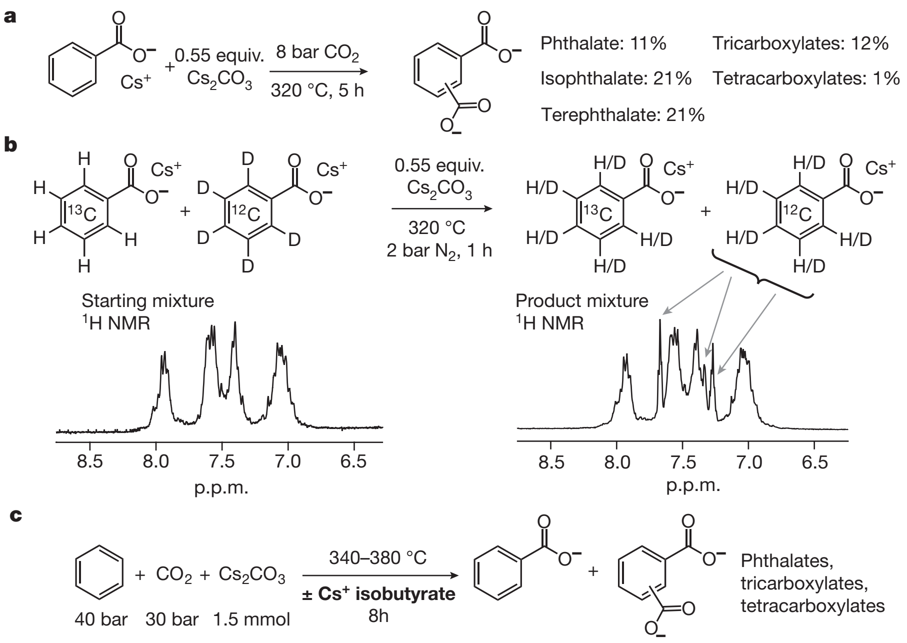
Entry	Scale	T	p_{CO_2}	Time	FDCA2–	Starting materials	Decomposition products
1	1 mmol	260 °C	Flowing	6 h	57%	26%	17%
2	1 mmol	260 °C	Flowing	12 h	76%	8%	16%
3	1 mmol	200 °C	8 bar	2 h	77%	18%	5%
4	1 mmol	200 °C	8 bar	5 h	89%	6%	5%
5	10 mmol	195 °C	8 bar	5 h	78%	11%	11%
6	10 mmol	195 °C	8 bar	10 h	81%	8%	11%
7	100 mmol	260 °C	1 bar	48 h	71%	3%	26%

Figure 2 | C–H carboxylation of furan-2-carboxylate. a, Carboxylation of caesium-furan-2-carboxylate to caesium FDCA^{2-}. p_{CO_2} is the pressure of carbon dioxide at the reaction temperature *T*. 1.25 equivalents of Cs_2CO_3 were used for entry 7. **b**, Carboxylation of potassium furan-2-carboxylate to potassium FDCA^{2-} using potassium isobutyrate as a low-melting co-salt. **c**, Evidence for C–H deprotonation. Cs_2CO_3 catalyses isotopic exchange between deuterated acetate and all positions of furan-2-carboxylate. In the absence of Cs_2CO_3, partial exchange is observed at the 5 position. The extent of exchange is calculated based on the integration of the ^1H NMR (see Extended Data Figs 6b and 8a). **d**, Mass spectrometry of the exchange reactions in **c**. D_1, D_2, and D_3 correspond to singly, doubly and triply deuterated furan-2-carboxylate. *m*/*z*, mass to charge ratio.

to deprotonate the C–H bonds of a phenyl ring was tested independently by heating a mixture of $^{12}C_6D_5CO_2Cs$, $^{13}C_6H_5CO_2Cs$, and 0.55 equivalents of Cs_2CO_3 to 320 °C under N_2 for 30 min. ^1H NMR analysis of the products revealed H/D scrambling at all positions on the benzoate ring (Fig. 3b). No H/D exchange was observed in the absence of Cs_2CO_3 (Extended Data Fig. 9).

The results with benzoate suggest that benzene would undergo C–H carboxylation if exposed to CO_3^{2-} in a molten salt. Heating Cs_2CO_3 under benzene and CO_2 at temperatures up to 380 °C resulted in no reaction. The lack of reactivity can be attributed to the fact that Cs_2CO_3 does not melt. To provide a molten component, reactions were performed in the presence of caesium isobutyrate. Heating 1.5 mmol Cs_2CO_3 and 1 mmol caesium isobutyrate to 340–380 °C under 31 bar CO_2 and 42 bar benzene resulted in the formation of benzoate, phthalates, and benzene tricarboxylates (Fig. 3c and Extended Data Fig. 5b). The amount of benzene carboxylation products corresponded to 12% of the Cs_2CO_3 at 350 °C, and 19% at 360 °C. In addition to benzene carboxylation, isobutyrate carboxylation to dimethyl malonate and decomposition to formate and acetate also occurred under these conditions (Extended Data Table 1b). The carboxylation of benzene is more challenging than benzoate because there is a larger entropic penalty and the solubility of benzene in the carboxylate salt is likely to be very low. Nevertheless, these results demonstrate that CO_3^{2-}-promoted hydrocarbon carboxylation is possible.

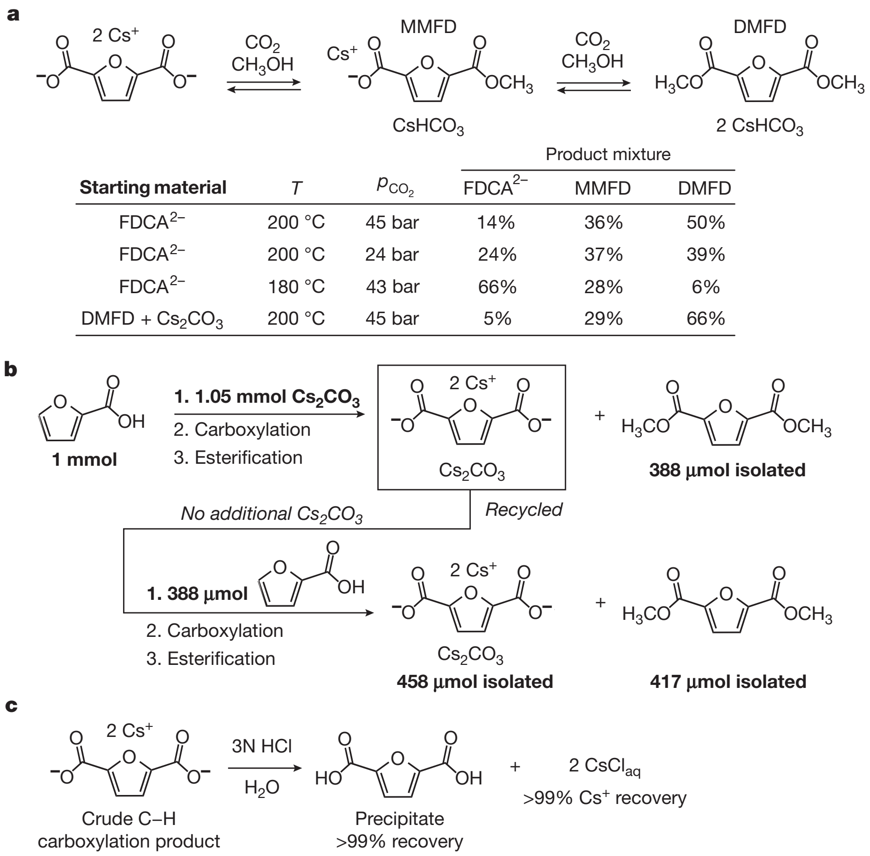
Scalable CO_3^{2-}-promoted C–H carboxylation requires facile product isolation and highly efficient recovery of the alkali cation. Researchers have recently reported the conversion of carboxylates to methyl esters by reaction with CO_2 and methanol at 160–200 °C (ref. 13). Similar conditions were found to effect double esterification of FDCA^{2-} to dimethyl furan-2,5-carboxylate (DMFD) in moderate yield (Fig. 4a). Heating 1 mmol of caesium FDCA^{2-} to 200 °C in 100 ml anhydrous methanol under 45 bar CO_2 for 30 min resulted in 50% yield of DMFD,



	T	Total yield	Benzoate	Phthalates	(Tri+tetra)carboxylates
Without Cs+ isobutyrate	≤380 °C	0%	—	—	—
With Cs+ isobutyrate	350 °C	12%	46 µmol	41 µmol	17 µmol
	360 °C	19%	39 µmol	69 µmol	35 µmol

Figure 3 | C–H carboxylation of benzoate and benzene. a, Carboxylation of caesium benzoate; yields are given with respect to benzoate. **b**, CO_3^{2-}-catalysed H/D isotope exchange between differentially labelled benzoates. Exchange is seen in the appearance of ^{1}H peaks associated with ^{12}C–H bonds. No exchange is observed in the absence of Cs_2CO_3. **c**, Carboxylation of benzene in the presence or absence of caesium isobutyrate. The yield refers to the amount of CO_3^{2-} consumed for the formation of benzene carboxylation products. equiv., equivalents; p.p.m., parts per million.

36% of the mono-ester, 5-(methoxycarbonyl)furan-2-carboxylate (MMFD), and 14% remaining FDCA^{2-}. Subjecting a 1:1 mixture of DMFD and Cs_2CO_3 to the same conditions resulted in a similar product mixture, indicating that the reaction is under thermodynamic control. To test whether Cs_2CO_3 can be recovered, sequential carboxylation/esterification cycles were performed (Fig. 4b). 1 mmol of 2-furoic acid and 1.05 equivalents of Cs_2CO_3 were subjected to a one-pot, two-step sequence of carboxylation and esterification. Extraction of the crude product mixture afforded 388 µmol of DMFD. The residual material containing FDCA^{2-} and Cs_2CO_3 was combined



			Product mixture		
Starting material	T	p_{CO_2}	FDCA^{2-}	MMFD	DMFD
FDCA^{2-}	200 °C	45 bar	14%	36%	50%
FDCA^{2-}	200 °C	24 bar	24%	37%	39%
FDCA^{2-}	180 °C	43 bar	66%	28%	6%
DMFD + Cs_2CO_3	200 °C	45 bar	5%	29%	66%

Figure 4 | Product isolation and Cs+ recovery. a, CO_2 promotes the esterification of FDCA^{2-} to MMFD and DMFD. The table shows the results of four 1-mmol-scale reactions performed in 100 ml anhydrous methanol starting with either caesium FDCA^{2-} or DMFD. **b**, Two sequential carboxylation/esterification sequences with Cs_2CO_3 recycling. The total carboxylation yield (91%) is similar to the yield for an individual experiment, indicating complete recovery of Cs_2CO_3 after the first sequence. **c**, Isolation of FDCA by protonation with strong acid. CsCl is retained in the aqueous solution.

with a second aliquot of 388 μmol 2-furoic acid and carried through a second sequence of carboxylation and esterification. Extraction yielded 417 μmol DMFD, while analysis of the unreacted material indicated 458 μmol of a mixture of $FDCA^{2-}$ and MMFD (Extended Data Fig. 10). The total amount of carboxylation products (DMFD + $FDCA^{2-}$ + MMFD) was 1.26 mmol, which is 91% of the total amount of 2-furoic acid substrate (1.39 mmol) used for the two carboxylation/esterification sequences. These results indicate that the Cs_2CO_3 produced from esterification of caesium $FDCA^{2-}$ can be reused in a subsequent C–H carboxylation without loss of yield, which in principle enables a cycle that converts 2-furoic acid into DMFD using only CO_2 and methanol as stoichiometric reagents. It may be possible to improve esterification yields under milder conditions by removing water *in situ*[30] or using an alternative solvent.

As an alternative to esterification, treatment of crude caesium $FDCA^{2-}$ from a C–H carboxylation reaction with 3 N HCl affords immediate precipitation of FDCA, leaving CsCl in the aqueous solution with >99% Cs^+ recovery (Fig. 4c). To complete the cycle, bipolar membrane electrodialysis[11,12] could be used to convert CsCl into HCl and CsOH solutions. HCl is recycled for the protonation step, while CsOH is reacted with 2-furoic acid and CO_2 to generate the starting material for C–H carboxylation. The energy requirement for converting aqueous alkali chloride solutions into HCl and alkali hydroxide solutions is ~0.08 kWh per mole of alkali chloride[11,12], which would correspond to ~1 kWh per kilogram of FDCA. While additional energy would be required for water removal in each cycle, using highly concentrated solutions would minimize this requirement. The overall process would convert 2-furoic acid into FDCA without using any organic solvents or product distillation steps.

Our results demonstrate a very simple strategy for engaging CO_2 in C–C bond formation that does not require synthetic or biological catalysts. The ability to deprotonate unactivated C–H bonds opens the possibility of using this approach to prepare numerous high-volume targets. In particular, combining carboxylation with hydrogenation reactions may enable the synthesis of multi-carbon alcohols and hydrocarbons using CO_2 and renewable H_2.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

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Author Contributions M.W.K. and A.B. conceived the project. A.B., G.R.D. and T.Y. performed the experiments. M.W.K., A.B. and G.R.D. wrote the paper. All authors contributed to the analysis and interpretation of the data.

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METHODS

Materials. Caesium carbonate (99.995%, trace metal basis), 2-thiophenecarboxylic acid (99%), benzoic acid-(phenyl-$^{13}C_6$) (99 at% ^{13}C), and tetrabutylammonium bromide (TBABr, 99%) were purchased from Sigma Aldrich; caesium carbonate ($\geq$99%, for large-scale reactions) and furan-2,5-dicarboxylic acid (99.6%) were purchased from Chem Impex International; dimethyl furan-2,5-dicarboxylate (99%) was purchased from Astatech; benzoic-d_5 acid-(phenyl-d_5) (98%) was purchased from Cambridge Isotope Laboratories; 2-furoic acid (98%), benzoic acid (99%) and anhydrous methyl alcohol (99.8%) were purchased from Acros Organics; sodium L-(+)-tartrate dihydrate (99.7%), benzene (HPLC grade) was purchased from Alfa Aesar; carbon dioxide (99.99%) was purchased from Praxair. The methanol was further dried over 3 Å molecular sieves before using. Reagent-grade benzene was dried by passing through an activated alumina column on an Innovative Technology PureSolv solvent purification system. *N*,*N*-dimethylformamide (DMF, 99.8%) was purchased from Fisher Scientific and dried by passing through an activated molecular sieve column. All other chemicals were used as received without further purification.

Equipment. Experiments under flowing CO_2 were performed in a Thermo Scientific Lindberg/Blue M tube furnace. Experiments under pressurized CO_2 or N_2 were performed in a 300-ml high-temperature, high-pressure Parr reactor (model 4561-HT-FG-SS-115-VS-2000-4848) equipped with a glass liner.

Structural analysis. ^{1}H-NMR, ^{2}H-NMR and ^{13}C-NMR spectra were recorded at 23 °C on a Varian Unity Inova 600 MHz spectrometer, a Varian Unity Inova 500 MHz spectrometer, a Varian Direct Drive 400 MHz spectrometer, a Varian Mercury 400 MHz spectrometer, or a Varian Unity Inova 300 MHz spectrometer. ^{1}H chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane and referenced to residual protium in the NMR solvent (D_2O, $\delta = 4.79$, $CDCl_3$, $\delta = 7.26$). ^{2}H chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane and referenced to deuterium in the NMR solvent (D_2O, $\delta = 4.71$). ^{13}C chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane and referenced to carbon resonances in the NMR solvent ($CDCl_3$ $\delta = 77.16$, centre line), to added methanol ($\delta = 49.00$), or to added tetramethylsilane ($\delta = 0.00$).

High-resolution mass spectra were recorded on a Waters Aquity UPLC and Thermo Exactive Orbitrap mass spectrometer by direct injection electrospray ionization–mass spectrometry (ESI-MS).

Preparation of reactant mixtures consisting of caesium carboxylate + 0.55 equivalents Cs_2CO_3. The carboxylic acid (2-furoic acid, thiophene-2-carboxylic acid or benzoic acid) and 1.05 equivalent of Cs_2CO_3 were dissolved in the minimum amount of deionized water and evaporated to dryness by heating at 150 °C for at least 2 h. The solid mixture was cooled and used directly for C–H carboxylation reactions. We note that residual moisture in the reactant mixture reduces the yield of the carboxylation reaction.

C–H carboxylation under flowing CO_2. The appropriate amount of reactant mixture was weighed out into a quartz boat and placed in the tube furnace. The furnace was heated to the desired temperature under CO_2 flowing at 40 ml min^{-1} for a given period of time. The sample was cooled to ambient temperature, dissolved in D_2O and filtered through a 0.2 μm polytetrafluoroethylene (PTFE) syringe filter to prepare samples for NMR analysis. The product yields were calculated from integration of the ^{1}H NMR peaks using sodium L-(+)-tartrate dihydrate as an internal standard. Representative spectra and data are shown in Extended Data Figs 1 and 2 and Extended Data Table 1a.

C–H carboxylation under pressurized CO_2. The reactant mixture was charged into the Parr reactor equipped with a glass liner. The reactor was sealed and then evacuated and backfilled with CO_2 three times. It was then filled to a final CO_2 pressure at ambient temperature corresponding to a pressure of 8 bar at the desired reaction temperature. The reactor was heated to the desired temperature, maintained at that temperature for a given period of time, and then cooled to ambient temperature and depressurized. The solid product mixture was dissolved in D_2O and analysed using NMR as described above. Representative spectra and data are shown in Extended Data Figs 3 and 4 and Extended Data Table 1a.

100-mmol-scale synthesis of furan-2,5-dicarboxylic acid at 1 atm of CO_2. To a 1-litre round-bottomed flask we added the 2-furoic acid (100 mmol, 11.21 g, 1.0 equiv.) and Cs_2CO_3 (125 mmol, 40.73 g, 1.25 equiv.) followed by 100 ml of deionized H_2O. The addition of water results in an acid–base reaction that liberates CO_2. (Caution: this reaction is exothermic and effervescent.) Once the reaction was complete, the water was removed in vacuum on a rotary evaporator (rotovap) at 75 °C and at 100 mTorr and 230 °C. The resulting off-white solid was scraped and ground into a fine white powder. In a fume hood, a reactor was assembled consisting of a rotovap with P_2O_5 in the collection flask connected to a Schlenk line and a eutectic salt bath (48.7 mol% $NaNO_3$, 51.3 mol% KNO_3). The eutectic salt bath was heated to 260 °C, and the 1-litre round-bottomed flask containing the caesium furan-2-carboxylate and Cs_2CO_3 was attached to the rotovap. The joint was taped with black electrical tape and fitted with a green Keck clip, and the entire apparatus was the backfilled with CO_2 gas. A short piece of tubing was connected in such a way as to deliver a slow stream of cooling air to the taped joint to prevent melting. The reaction was then dipped into the eutectic salt bath and rotated slowly for 48 h with a gentle flow of CO_2 through the bubbler of the Schlenk line. Over the course of the reaction, the solid initially melts, then turns blackish-brown and solidifies. Once complete, the reaction was slowly cooled to room temperature and detached from the rotovap. Disodium tartrate dihydrate (10 mmol, 2.31 g, 0.1 equiv.) was added followed by 200 ml of deionized water. An aliquot of the resulting solution was evaporated in vacuum then dissolved in D_2O. A ^{1}H NMR was obtained with the following distribution of products: caesium furan-2,5-dicarboxylate (71%), caesium malonate (2%), and caesium acetate (11%) (NMR yields). A repeat of the experiment gave the following distribution: caesium furan-2,5-dicarboxylate (69%), caesium malonate (7%), and caesium acetate (8%).

The product was isolated from the reaction mixture using the following procedure. First, the reaction was filtered through a pad of celite to remove insoluble material. The resulting solution was then acidified below a pH of 2 with sulfuric acid (15 ml concentrated acid). (Caution: this reaction is exothermic and effervescent.) The product precipitated from the solution and was collected on a Büchner funnel. The product was then dissolved in 1 litre of methanol and decolorized with activated carbon. The activated carbon was removed by filtering the solution through a pad of celite. The resulting solution was concentrated in vacuum and then triturated with 500 ml of ethyl acetate. The product was collected on a Büchner funnel, washed with ethyl acetate, and then dried in vacuum to afford a white crystalline powder (10.35 g, 66%).

C–H carboxylation of furan-2-carboxylate using K_2CO_3. 2-furoic acid (56 mg, 0.50 mmol, 1.0 equiv.), potassium isobutyrate (63 mg, 0.50 mmol, 1.0 equiv.), and K_2CO_3 (73 mg, 0.53 mmol, 1.05 equiv.) were dissolved in the minimum of water in a quartz boat, and evaporated to dryness by heating at 150 °C for 2 h under a stream of N_2. The sample was heated to 320 °C under CO_2 flowing at 40 ml min^{-1} in the tube furnace for 8 h. The solid product mixture was dissolved in D_2O and analysed using ^{1}H NMR as described above. The yield of potassium FDCA^{2-} was 62%, and the conversion of furan-2-carboxylate was 76%. A representative spectrum is shown in Extended Data Fig. 5a.

A carboxylation reaction was also performed with 2-furoic acid (56 mg, 0.50 mmol, 1.0 equiv.), potassium acetate (49 mg, 0.50 mmol, 1.0 equiv.), and K_2CO_3 (73 mg, 0.53 mmol, 1.05 equiv.). The sample was heated to 300 °C under CO_2 flowing at 40 ml min^{-1} in the tube furnace for 8 h. The yield of potassium FDCA^{2-} was 57%, and the conversion of furan-2-carboxylate was 96%.

Attempted carboxylation of caesium furan-2-carboxylate in DMF. A two-necked 25-ml round-bottomed flask was equipped with a reflux condenser, gas adaptor, PTFE-coated stir-bar, and a septum. The flask was charged with 2-furoic acid (115 mg, 1.03 mmol, 1.03 equiv.), Cs_2CO_3 (555 mg, 1.70 mmol, 1.70 equiv.), and water (2 ml). Once the resulting acid–base reaction subsided, the reaction vessel was heated to 150 °C in an oil bath under a stream of N_2. After 30 min the solution had dried out, and the reactor was then placed under vacuum and heated to 175 °C. At the same time, a heat gun was used to dry the rest of the apparatus. The reactor was then cooled to 125 °C and back-filled three times with CO_2. Using a syringe, dry DMF (2 ml) was added to the reaction. The reaction was then stirred for 12 h at 125 °C under a CO_2 atmosphere (1 bar). After 12 h, the reaction was concentrated under vacuum. NMR analysis of the residue in D_2O indicated no conversion of the starting material.

C–H carboxylation of benzene. Into a 20 ml vial we added a mixture of caesium carbonate (489 mg, 1.5 mmol, 1.0 equiv.) and caesium isobutyrate (220 mg, 1.0 mmol, 0.67 equiv.). This vial was placed into the Parr reactor, which was sealed and then evacuated and backfilled with CO_2 three times. Anhydrous benzene was injected into the reactor in an amount ranging from 10 ml to 35 ml depending on the desired final partial pressure of benzene. The reactor was then pressurized with CO_2 and heated to the desired temperature. The partial pressure of CO_2 at the final temperature was calculated assuming ideal behaviour. The partial pressure of benzene was calculated by subtracting the CO_2 pressure from the measured reactor pressure. After the indicated period of time (Extended Data Table 1b), the reactor was cooled to ambient temperature and depressurized. The crude product was dissolved in D_2O and analysed using NMR as described above. In addition to benzene carboxylation products, isobutyrate decomposition products were observed, which included formate, acetate, acetate carboxylation products (malonate and methane tricarboxylate), and insoluble char. Control experiments were performed in the absence of either benzene or gaseous CO_2. In the absence of benzene, only a trace amount of formate was observed and the main product was insoluble char from isobutyrate decomposition. In the absence of gaseous CO_2, a small amount of benzoate was observed, which is attributed to the formation of CO_2 *in situ* from the decomposition of HCO_3^- that is formed by deprotonation of benzene with CO_3^{2-}. Representative spectra and data are shown in Extended Data Fig. 5b and Extended Data Table 1b.

For comparison, an experiment was performed in the absence of caesium isobutyrate. A 20 ml vial with caesium carbonate (326 mg, 1.0 mmol) was placed into the Parr reactor, which was sealed and then evacuated and backfilled with CO_2 three times. 35 ml of anhydrous benzene was injected into the reactor. The reactor was pressurized with 15 bar of CO_2 and heated to 340 °C or 380 °C for 3 h and 8 h respectively. The reactor was then cooled to ambient temperature and depressurized. The crude product was dissolved in D_2O and analysed using NMR as described above. No reaction was observed in this case.

Thermal annealing of caesium furan-2-carboxylate and CO_2 in the absence of Cs_2CO_3. The Parr reactor was equipped with an oven-dried glass liner and charged with caesium furan-2-carboxylate (244 mg, 1.0 mmol). The reactor was sealed and then evacuated and backfilled with CO_2 three times. It was pressurized to 5 bar CO_2 and then heated to 200 °C, at which point the CO_2 pressure was 8 bar. After 2 h, the reactor was cooled to room temperature, vented, and disassembled. The residue was dissolved in D_2O and analysed using NMR. No $FDCA^{2-}$ was formed in the reaction.

Recovery of caesium by acidic precipitation at the 10-mmol scale. The general procedure outlined previously (see sections 'Preparation of reactant mixtures consisting of caesium carboxylate + 0.55 equivalents Cs_2CO_3,' and 'C–H carboxylation under pressurised CO_2') was followed using 2-furoic acid (10 mmol, 1.12 g, 1.00 equiv.) and Cs_2CO_3 (10.5 mmol, 3.42 g, 1.05 equiv.). Once the reaction had completed and cooled to room temperature, the resulting solid was treated with 7 ml of 3 N HCl. The FDCA immediately precipitated from the reaction mixture as an off-white solid. The suspension was filtered through a glass frit (medium porosity) and washed with a minimum of deionized water (3 × 0.5 ml). The filtrate was then transferred to a 100-ml round-bottomed flask and the filter cake was transferred, washing with methanol, to a separate, tared, 100-ml round-bottomed flask. The flask containing the filter cake was evaporated to dryness to afford a yellow solid. The solid was analysed using ^1H NMR in acetone-d_6. NMR analysis indicated a crude isolated yield of 81% for FDCA, along with 8% residual unreacted 2-furoic acid. The flask containing the filtrate was evaporated to dryness to afford 3.74 g yellow solid. The solid was analysed using ^1H NMR in D_2O with an internal standard to quantify organic contaminants. 2-furoic acid and FDCA were present in an amount corresponding to <0.4% of the mass of the solid. Based on this analysis, the caesium was recovered in >99% yield as the CsCl salt.

Recovery of caesium by acidic precipitation at the 100-mmol scale. The general procedure outlined previously (see section '100-mmol-scale synthesis of furan-2,5-dicarboxylic acid at 1 atm of CO_2') was followed using the following quantities of 2-furoic acid (100 mmol, 11.23 g, 1.00 equiv.) and Cs_2CO_3 (105 mmol, 34.36 g, 1.05 equiv.). Once the reaction had completed and cooled to room temperature, the resulting solid was treated with 110 ml of 2 N HCl. The FDCA immediately precipitated from the reaction mixture as an off-white solid. This reaction was filtered through a glass frit (medium porosity) and washed with a minimum of deionized water (3 × 5 ml). The filtrate was then transferred to a tared 500-ml round-bottomed flask and the filter cake was transferred and washed with methanol into a separate, tared, 500-ml round-bottomed flask. The filter cake and filtrate were massed and analysed as described above, yielding the following results: 69% crude isolated yield for FDCA; >98% recovery of caesium as CsCl.

H/D isotope exchange between furan-2-carboxylate and acetate-d_3. 2-Furoic acid (112 mg, 1.0 mmol), acetic acid-d_4 (58 μl, 1.0 mmol) and Cs_2CO_3 (682 mg, 2.1 mmol) were dissolved in the minimum amount of deionized water and evaporated to form a dry powder that consisted of 1 mmol caesium furan-2-carboxylate, 1 mmol caesium acetate-d_3 and 1.1 mmol of Cs_2CO_3. This material was heated in the Parr reactor to 200 °C under 2 bar of N_2 for 1 h. After cooling to room temperature, the product mixture was dissolved in D_2O and analysed by NMR. The integration of the furan-2-carboxylate peaks in the ^1H NMR spectrum using an internal standard indicated that the H/D scrambling was ~60% complete with substantially more scrambling at the 5 position than at the 3 and 4 positions. The presence of D at all positions was evident in the ^2H NMR spectrum, the peak splitting of the ^{13}C NMR spectrum, and in the high-resolution mass spectrum (Fig. 2d and Extended Data Figs 6b, 7a and 7b).

For comparison, an experiment was performed in the absence of Cs_2CO_3. 2-Furoic acid (112 mg, 1.0 mmol), acetic acid-d_4 (58 μl, 1.0 mmol) and Cs_2CO_3 (312 mg, 0.96 mmol) were dissolved in minimum amount of deionized water and evaporated to form an oil that consisted of caesium furan-2-carboxylate and caesium acetate-d_3. A ^1H NMR spectrum of this mixture is shown in Extended Data Fig. 6a. This material was heated in the Parr reactor to 200 °C under 2 bar of N_2 for 1 h. After cooling to room temperature, the material was dissolved in D_2O and analysed by NMR. Integration of the furan-2-carboxylate peaks in the ^1H NMR spectrum using an internal standard indicated that the H/D scrambling was ~15% complete with substantial scrambling at the 5 position and almost no scrambling at the 3 and 4 positions. The presence of D at the 5 position was evident in the ^2H NMR spectrum, the peak splitting of the ^{13}C NMR spectrum, and in the high-resolution mass spectrum (Fig. 2d and Extended Data Fig. 8).

The mass spectrometry sample was prepared by adding 6 N HCl dropwise to the NMR sample until the clear solution turned into a suspension. The water was removed under vacuum and the residue was suspended in 2.5 ml of methanol. The suspension was allowed to stand till the solid particles settled. An aliquot of the supernatant liquid was further diluted with methanol and analysed directly by mass spectrometry.

Benzoic acid isotope exchange experiment. Benzoic acid-(phenyl-$^{13}C_6$) (7.8 mg, 60.9 μmol), benzoic-d_5 acid-(phenyl-d_5) (7.8 mg, 61.3 μmol) and Cs_2CO_3 (41.5 mg, 127.4 μmol) were dissolved in 1 ml of deionized water and evaporated to form a dry powder that consists of caesium benzoate-(phenyl-$^{13}C_6$), caesium benzoate-(phenyl-d_5) and 0.55 equivalents of Cs_2CO_3. This material was heated in the Parr reactor to 320 °C under 2 bar of N_2 for 1 h. After cooling to room temperature, the material was dissolved in D_2O and analysed by NMR. The ^1H spectra of the reactant mixture and the product mixture are shown in Fig. 3.

A control experiment was performed to test whether Cs_2CO_3 is necessary for isotopic scrambling. Benzoic acid-(phenyl-$^{13}C_6$) (7.8 mg, 60.9 μmol), benzoic-d_5 acid-(phenyl-d_5) (7.8 mg, 61.3 μmol) and Cs_2CO_3 (19.8 mg, 60.7 μmol) were dissolved in 1 ml H_2O and evaporated to form a dry powder that consists of the caesium benzoate salts. After heating to 320 °C under 2 bar N_2 for 1 h, no H/D exchange was observed by ^1H NMR (Extended Data Fig. 9).

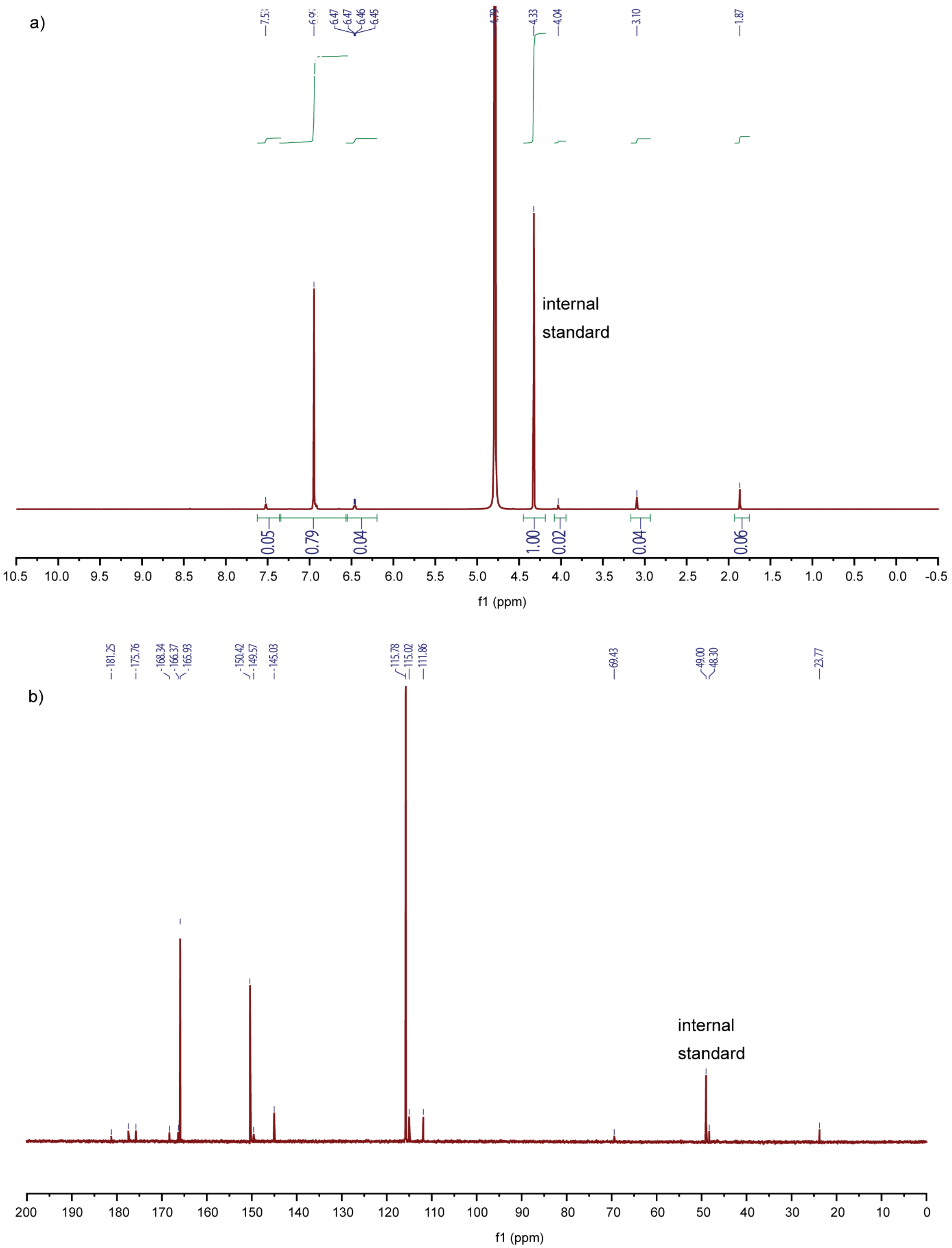
Esterification of caesium $FDCA^{2-}$. Caesium $FDCA^{2-}$ (420 mg, 1.0 mmol) was charged into the Parr reactor equipped with an oven-dried glass liner. The reactor was sealed and then evacuated and backfilled with CO_2 three times. Anhydrous methanol (100 ml) was injected into the reactor. The reactor was then pressurized with either 28.5 bar or 15 bar CO_2 and heated to 200 °C or 180 °C. After 30 min, the reactor was cooled to ambient temperature, vented, and disassembled. The reaction mixture was transferred to a 250-ml round-bottomed flask and the methanol was removed under vacuum on a rotary evaporator at 45 °C. The residue was washed twice with 5 mL $CHCl_3$ to dissolve the DMFD. The combined $CHCl_3$ washes were evaporated to afford DMFD as a white powder. The material was dissolved in $CDCl_3$ and analysed by ^1H NMR with TBABr as an internal standard. The remaining residue that was not dissolved in the $CHCl_3$ washes was dissolved in CD_3OD and analysed by ^1H NMR using TBABr as an internal standard. This material consists of $FDCA^{2-}$, MMFD, and a small amount of additional DMFD.

Hydrolysis of dimethyl furan-2,5-dicarboxylate (DMFD). DMFD (184 mg, 1.0 mmol, 1 equiv.) and Cs_2CO_3 (326 mg, 1.0 mmol, 1 equiv.) were charged into a Parr reactor equipped with an oven-dried glass liner. The reactor was sealed and then evacuated and backfilled with CO_2 three times. Anhydrous methanol (100 ml) was injected into the reactor. The reactor was pressurized with 28.5 bar CO_2 and heated to 200 °C The total pressure at 200 °C was 105 bar and the calculated CO_2 pressure was 45 bar. After 30 min, the reactor was cooled down to ambient temperature then vented and disassembled. The reaction mixture was transferred to a 250-ml round-bottomed flask and the methanol was removed under vacuum on a rotary evaporator at 45 °C. The residue was processed and analysed by ^1H NMR as described above for the esterification of $FDCA^{2-}$.

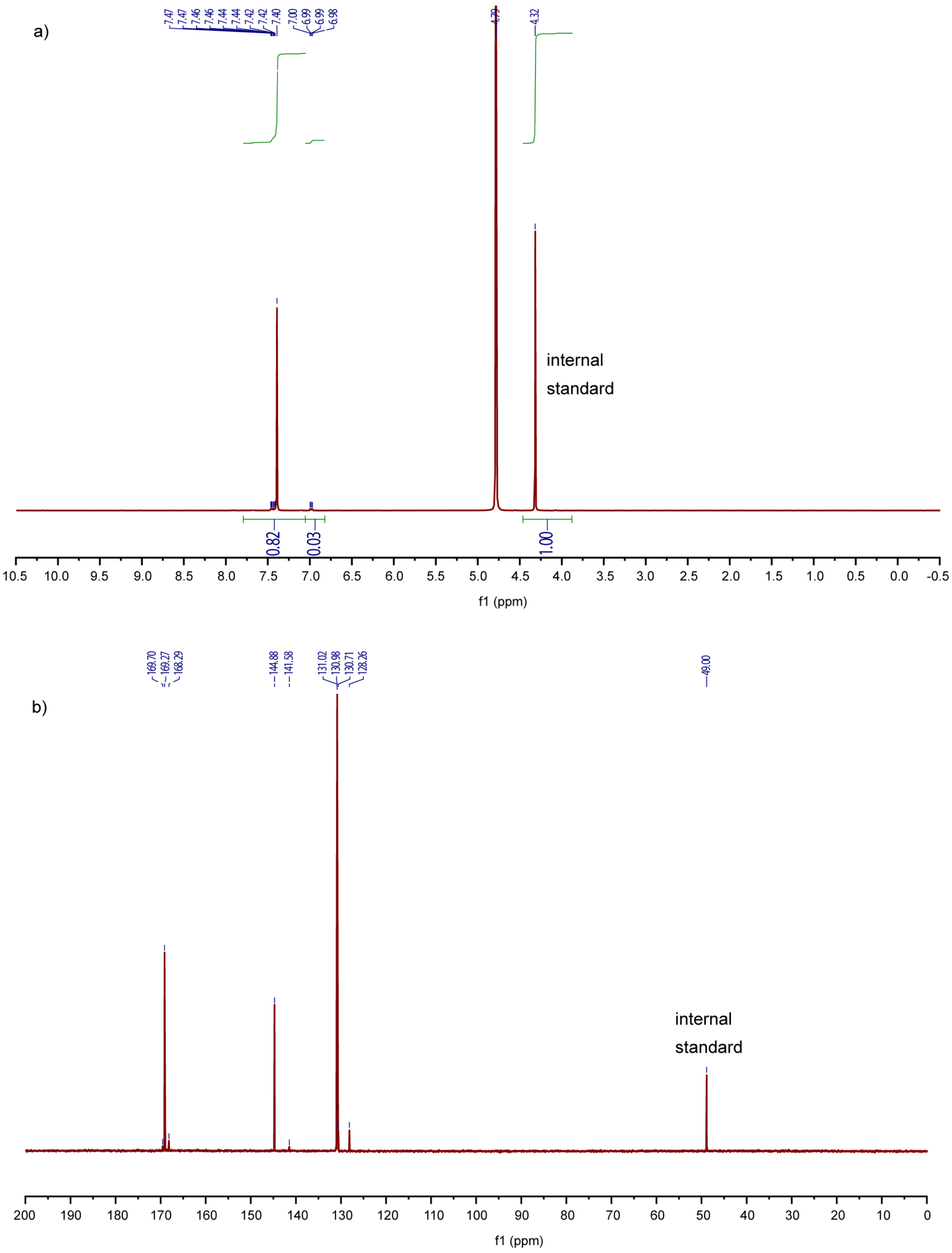
Recycling Cs_2CO_3. The Parr reactor was equipped with an oven-dried glass liner and charged with caesium furan-2-carboxylate (244 mg, 1.0 mmol, 1.0 equiv.) and Cs_2CO_3 (179 mg, 0.55 mmol, 0.55 equiv.). The reactor was sealed and then evacuated and backfilled with CO_2 three times. The reactor was pressurized to 5 bar CO_2 and then heated to 200 °C, at which point the CO_2 pressure was 8 bar. After 5 h, the reactor was cooled and vented then evacuated and backfilled with N_2. To remove the water by-product, 10 ml of dry methanol was injected into the reactor to dissolve the reaction mixture. The methanol was removed by heating the reactor to 150 °C under vacuum. Subsequently, N_2 gas was flowed over the reaction mixture for 8 h by keeping the gas release valve of the reactor open. The reactor was cooled to ambient temperature and 90 ml of dry methanol was injected into it. The vessel was pressurized with 28.5 bar CO_2 and heated to 200 °C. After 30 min, the reactor was cooled to ambient temperature, depressurized and opened. The reaction mixture was diluted with 65 ml deionized water and extracted with $CHCl_3$ (2 × 65 ml). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to afford the DMFD as a white solid and the yield was determined from ^1H NMR using TBABr as an internal standard. The aqueous extract was concentrated under reduced pressure to approximately a 2 ml solution and transferred to the same glass liner used in the first cycle. To the solution was added 2-furoic acid equivalent to the amount of DMFD produced in the first cycle. The liner was resealed inside the reactor and heated to 150 °C under an atmosphere of N_2. The reactor was subsequently evacuated and backfilled with N_2, kept under a stream of N_2 at 150 °C for 8 h, and then cooled to ambient temperature. The reaction mixture was subjected to a second cycle of carboxylation followed by esterification following the same procedures described above. At the completion of the cycle, the solution was diluted with 65 ml deionized water and extracted with $CHCl_3$ (2×65 ml). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to afford the DMFD (Extended Data Fig. 10a). Evaporation of the aqueous extract yielded the crude mixture of Cs_2FDCA, caesium 5-(methoxycarbonyl)furan-2-carboxylate and Cs_2CO_3. The amount of unreacted Cs_2FDCA and caesium 5-(methoxycarbonyl)furan-2-carboxylate were quantified by ^{1}H NMR using sodium L-(+)-tartrate dihydrate as an internal standard (Extended Data Fig. 10b).

NMR spectra. The NMR peaks in the spectra for the carboxylation reactions were assigned to different products by comparison to spectra for pure caesium salts obtained independently from the pure carboxylic acids. The resonances for these compounds are provided below for reference.

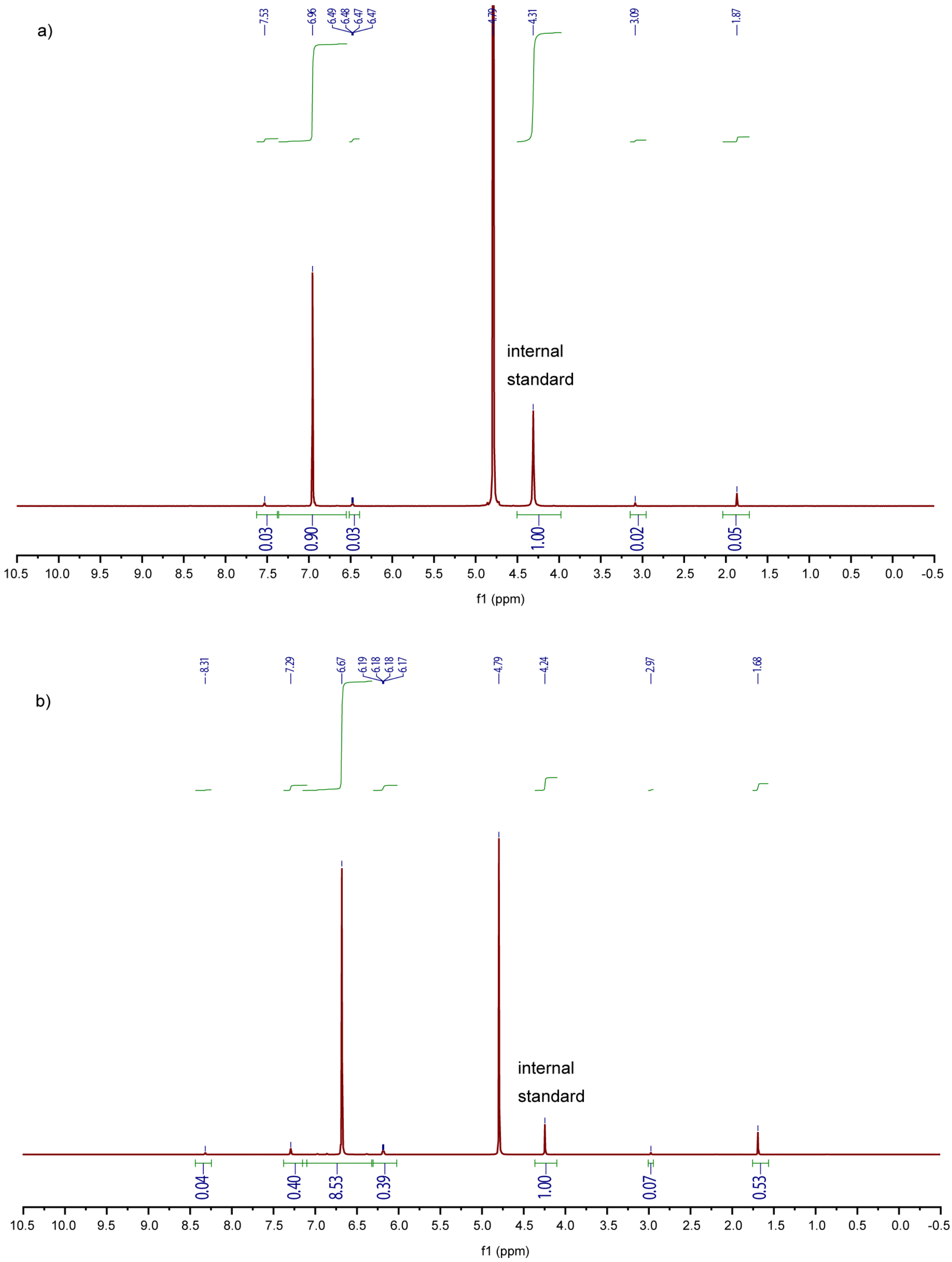
Caesium furan-2,5-dicarboxylate:
^{1}H-NMR (400 MHz, D_2O) δ 6.95 (s, 2H)
^{13}C-NMR (100 MHz, D_2O) δ 166.1, 150.4, 115.8
Caesium acetate:
^{1}H-NMR (400 MHz, D_2O) δ 1.87 (s, 3H)
^{13}C-NMR (100 MHz, D_2O) δ 181.4, 23.6
Caesium malonate:
^{1}H-NMR (400 MHz, D_2O) δ 3.09 (s, 2H)
^{13}C-NMR (100 MHz, D_2O) δ 177.29, 49.03
Caesium thiophene-2,5-dicarboxylate:
^{1}H-NMR (300 MHz, D_2O) δ 7.4 (s, 2H)
^{13}C-NMR (75 MHz, D_2O) δ 169.5, 144.8, 131.0
Caesium benzoate:
^{1}H-NMR (500 MHz, D_2O) δ 7.80 (d, $J = 5$ Hz, 2H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H)
^{13}C-NMR (125 MHz, D_2O) δ 176.0, 137.0, 131.9, 129.5, 129.0
Caesium phthalate:
^{1}H-NMR (500 MHz, D_2O) δ 7.45 (dd, $J = 5.7$, 3.3 Hz, 2H), 7.37 (dd, $J = 5.7$, 3.3 Hz, 2H)
^{13}C-NMR (125 MHz, D_2O) δ 177.8, 138.5, 129.5, 127.8
Caesium isophthalate:
^{1}H-NMR (500 MHz, D_2O) δ 8.25 (S, 1H), 7.89 (d, $J = 7.5$ Hz, 2H), 7.39 (t, $J = 7.7$ Hz, 1H)
^{13}C-NMR (125 MHz, D_2O) δ 175.5, 137.1, 132.1, 129.7, 129.0
Caesium terephthalate:
^{1}H-NMR (500 MHz, D_2O) δ 7.80 (s, 4H)
^{13}C-NMR (125 MHz, D_2O) δ 175.5, 139.4, 129.3
Caesium benzene-1,2,3-tricarboxylate:
^{1}H-NMR (500 MHz, D_2O) δ 7.47 (d, $J = 7.7$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 1H)
^{13}C-NMR (125 MHz, D_2O) δ 177.3, 177.1, 138.3, 137.5, 128.7, 127.8
Caesium benzene-1,3,5-tricarboxylate:
^{1}H-NMR (500 MHz, D_2O) δ 8.40 (s, 3H)
^{13}C-NMR (125 MHz, D_2O) δ 175.0, 137.5, 132.2
Caesium benzene-1,2,4-tricarboxylate:
^{1}H-NMR (500 MHz, D_2O) δ 7.92 (s,1H), 7.84 (d, $J = 8$ Hz, 1H), 7.48 (d, $J = 8$ Hz, 1H)
^{13}C-NMR (125 MHz, D_2O) δ 177.6, 177.1, 175.1, 141.2, 138.1, 137.1, 129.9, 128.3, 127.6
Caesium benzene-1,2,4,5-tetracarboxylate:
^{1}H-NMR (500 MHz, D_2O) δ 7.51 (s, 2H)
^{13}C-NMR (125 MHz, D_2O) δ 176.8, 138.6, 126.6
Dimethyl 2,5-furandicarboxylate:
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.20 (s, 2H), 3.91 (s, 6H)
^{13}C-NMR (75 MHz, $CDCl_3$) δ 158.5, 146.7, 118.6, 52.5



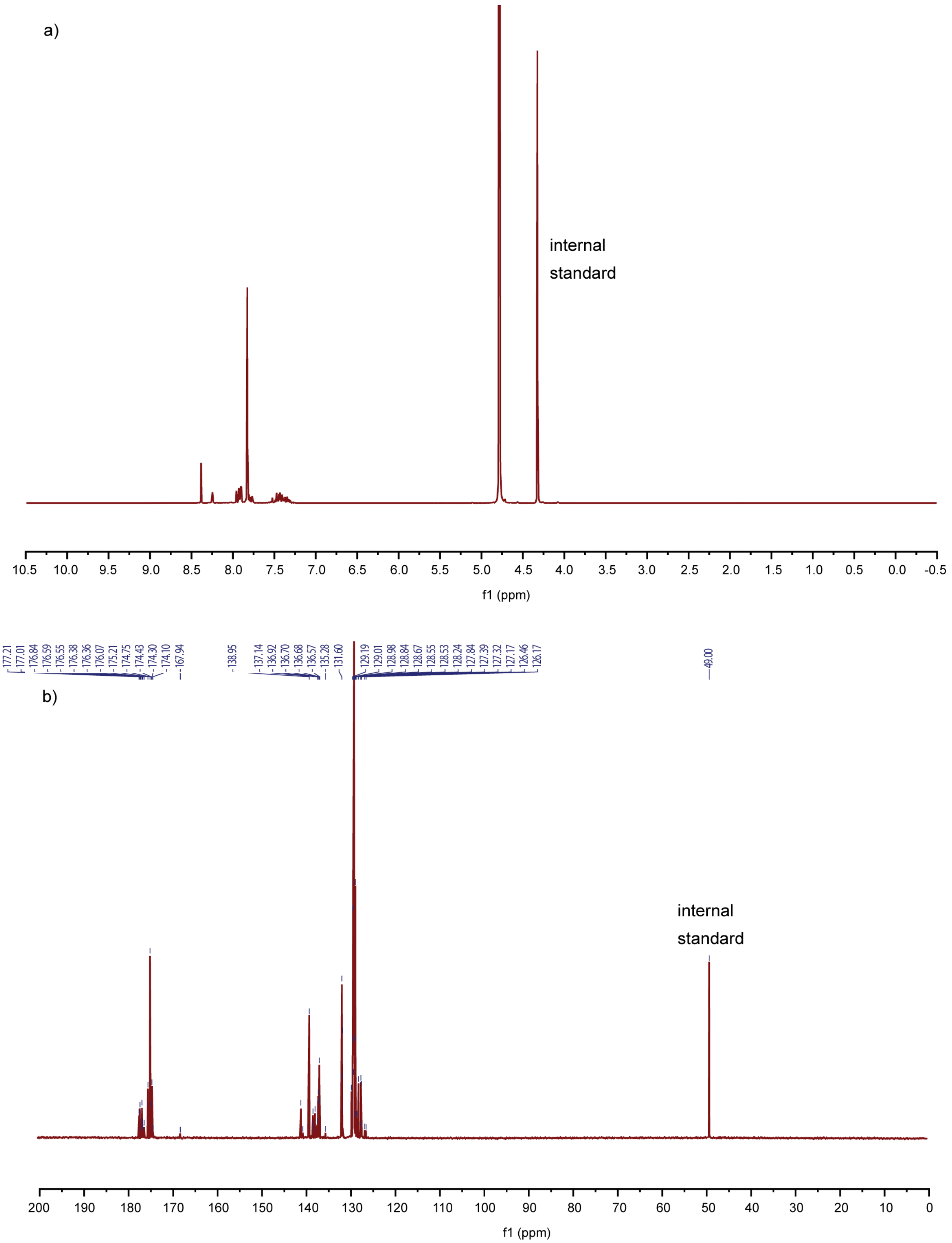
Extended Data Figure 1 | NMR spectra for the carboxylation of caesium furan-2-carboxylate under flowing CO_2. a, ^{1}H NMR (300 MHz) and **b**, ^{13}C NMR (100 MHz) in D_2O of the crude product mixture after the reaction of 1 mmol caesium furan-2-carboxylate and 0.55 mmol Cs_2CO_3 under CO_2 flowing at 40 ml min^{-1} at 260 °C for 12 h. f1 indicates the chemical shift, δ.



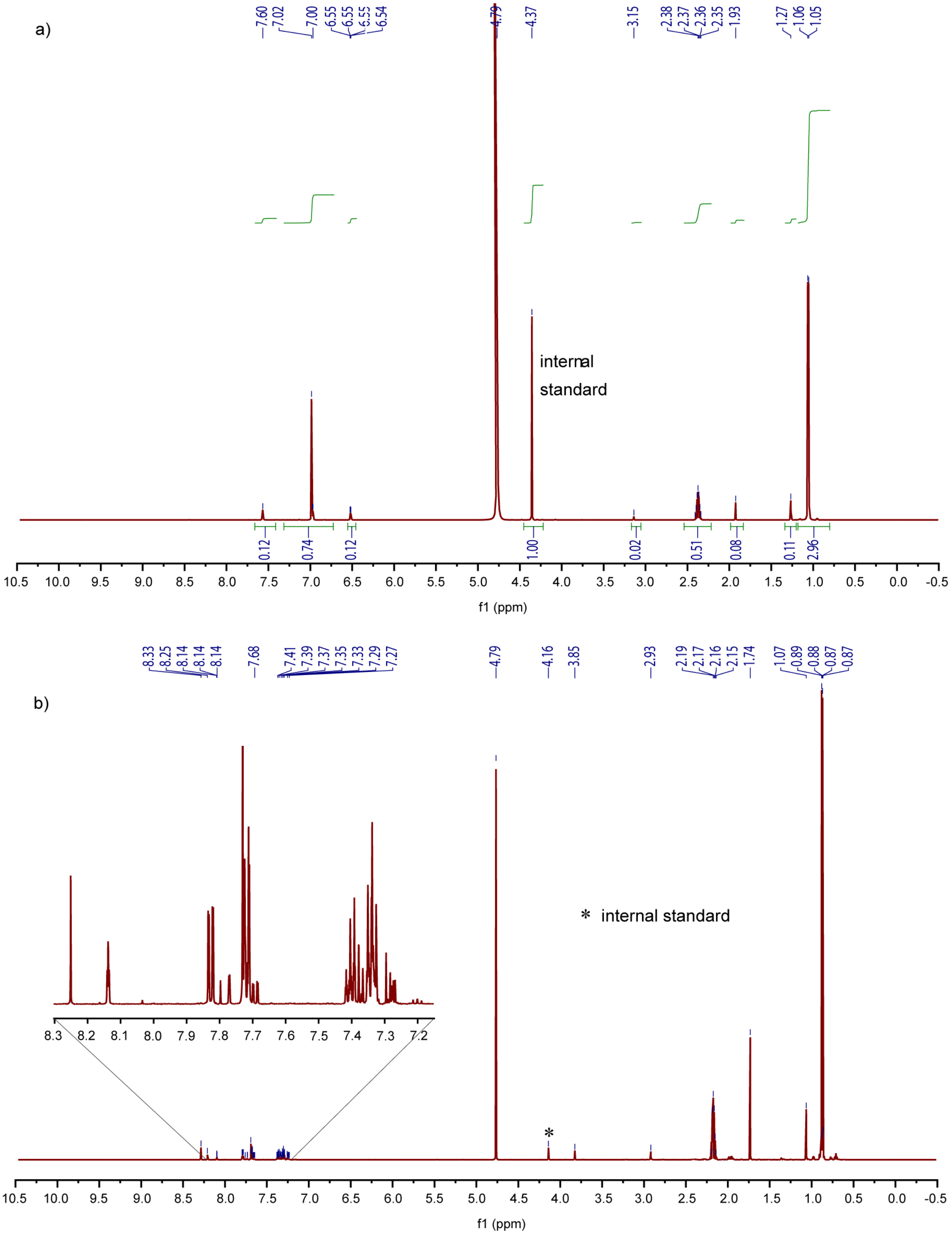
Extended Data Figure 2 | NMR spectra for the carboxylation of caesium thiophene-2-carboxylate. a, ^{1}H NMR (300 MHz) and **b**, ^{13}C NMR (100 MHz) in D_2O of the crude product mixture after the reaction of 1 mmol caesium thiophene-2-carboxylate and 0.55 mmol Cs_2CO_3 under CO_2 flowing at 40 ml min^{-1} at 325 °C for 12 h.



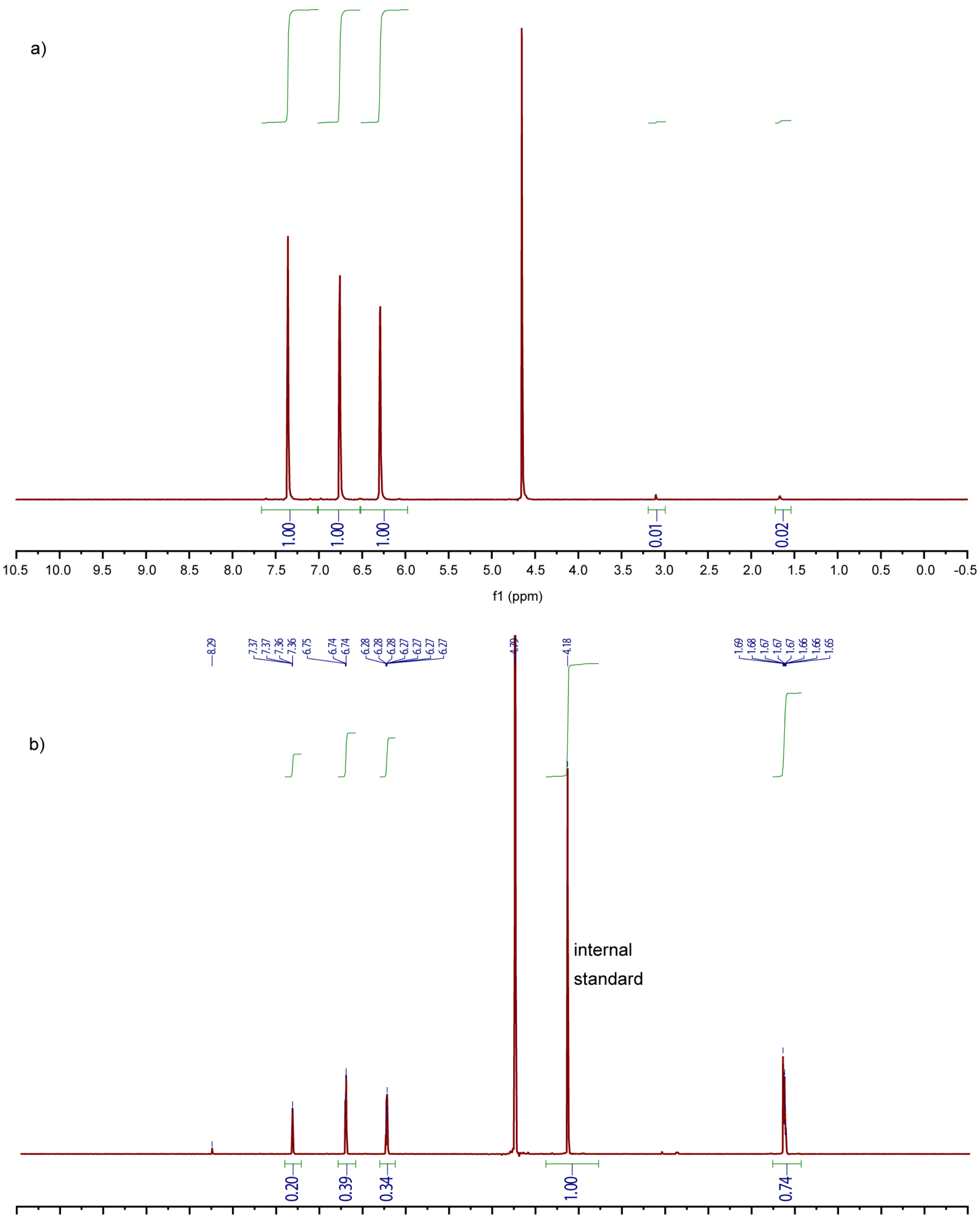
Extended Data Figure 3 | NMR spectra for the carboxylation of caesium furan-2-carboxylate in the Parr reactor. a, ^{1}H NMR (300 MHz) in D_2O of the crude product mixture after the reaction of 1 mmol caesium furan-2-carboxylate and 0.55 mmol Cs_2CO_3 under 8 bar CO_2 at 200 °C for 5 h. **b**, ^{1}H NMR (300 MHz) in D_2O of the crude product mixture after the reaction of 10 mmol caesium furan-2-carboxylate and 5.5 mmol Cs_2CO_3 under 8 bar CO_2 at 200 °C for 10 h.



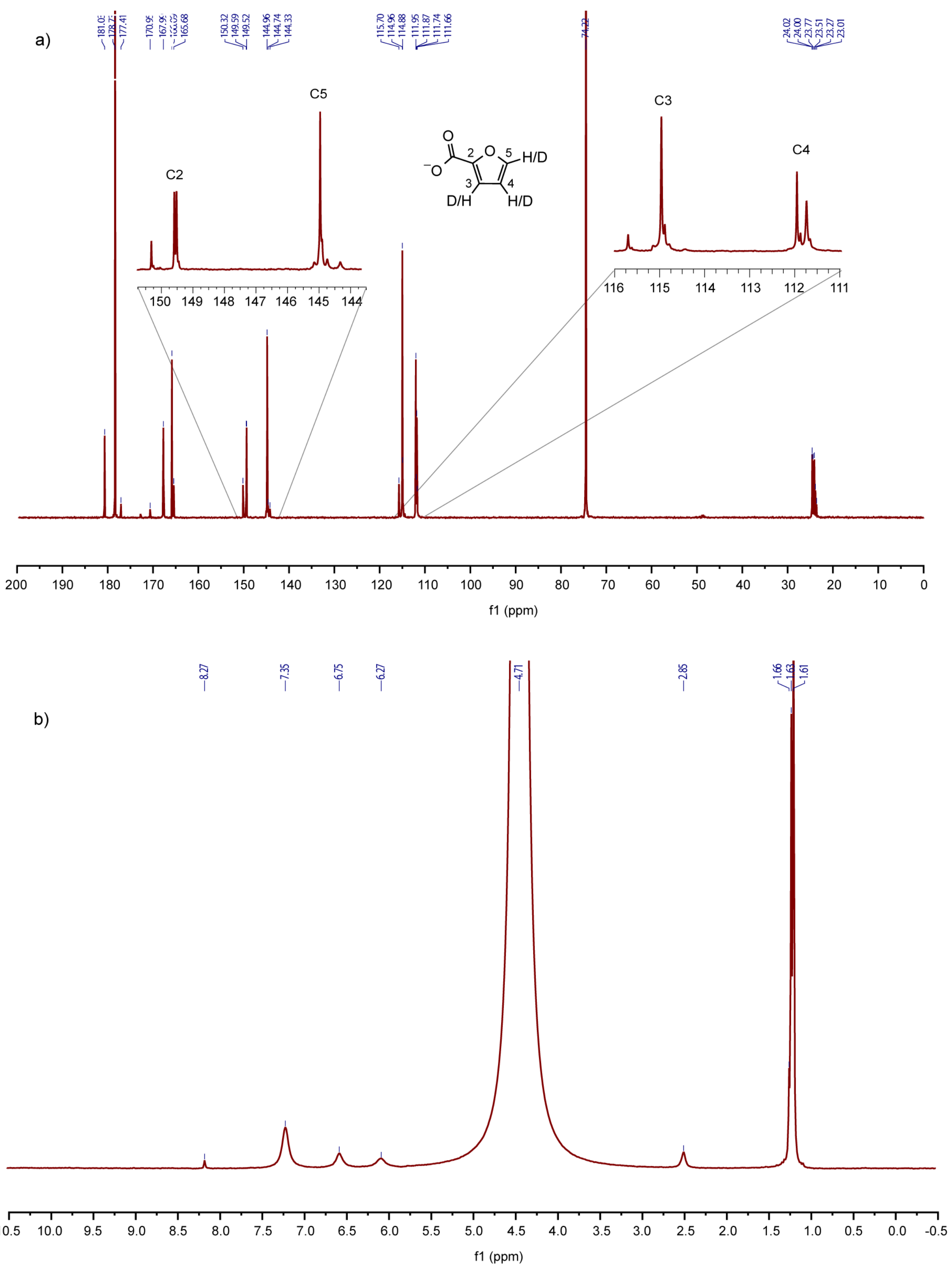
Extended Data Figure 4 | NMR spectra for the carboxylation of caesium benzoate. a, ^{1}H NMR (300 MHz) and **b**, ^{13}C NMR (100 MHz) in D_2O of the crude product mixture after the reaction of 1 mmol caesium benzoate and 0.55 mmol Cs_2CO_3 under 8 bar CO_2 at 320 °C for 5 h.



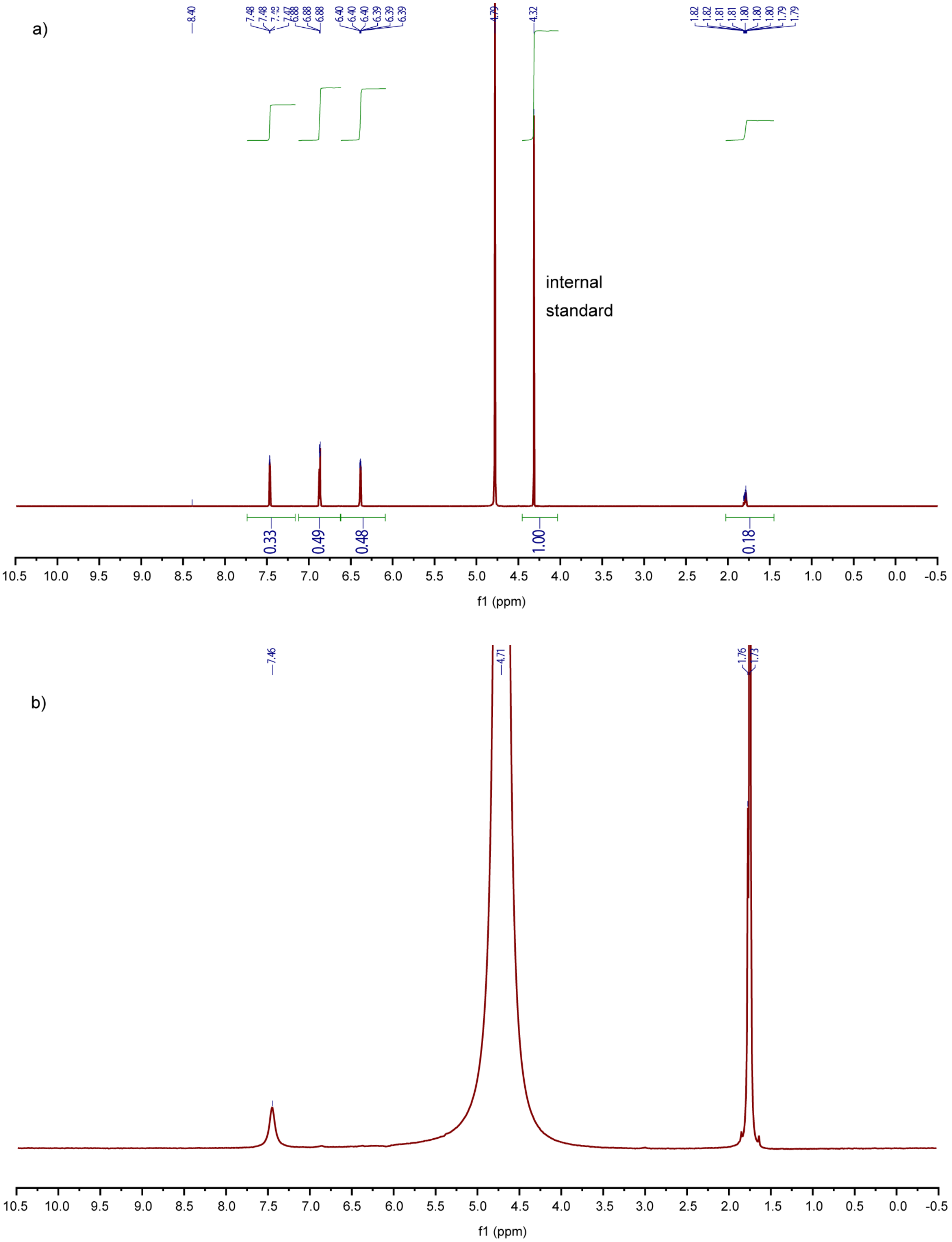
Extended Data Figure 5 | NMR spectra for the carboxylation of potassium furan-2-carboxylate and benzene. a, ^{1}H NMR (600 MHz) in D_2O of the crude product mixture after the reaction of 0.5 mmol potassium furan-2-carboxylate, 0.5 mmol potassium isobutyrate and 0.28 mmol K_2CO_3 under CO_2 flowing at 40 ml min^{-1} at 320 °C for 8 h. **b**, ^{1}H NMR (600 MHz) of the crude product mixture after the reaction in D_2O of a 1.5 mmol of caesium carbonate and 1 mmol caesium isobutyrate under 42 bar benzene and 31 bar CO_2 at 350 °C for 8 h.



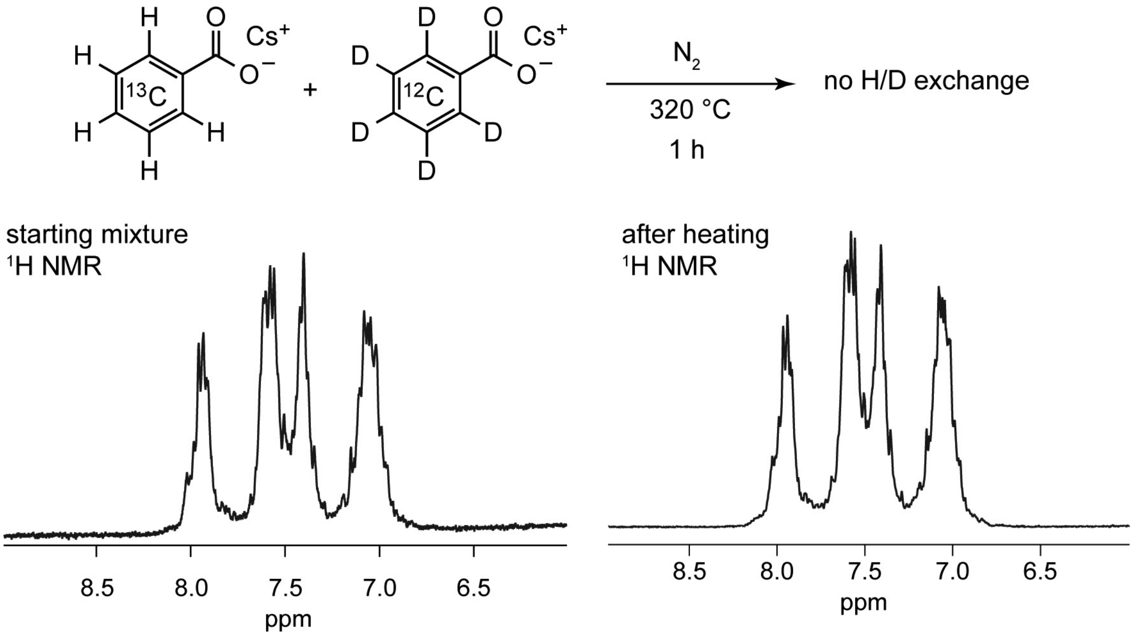
Extended Data Figure 6 | ^{1}H NMR spectra for H/D exchange between furan-2-carboxylate and deuterated acetate in the presence of Cs_2CO_3. **a**, ^{1}H NMR (400 MHz) in D_2O of a 1:1 mixture of caesium furan-2-carboxylate and CD_3CO_2Cs. **b**, ^{1}H NMR (400 MHz) in D_2O of the crude product mixture after the reaction of a 1:1 mixture of caesium furan-2-carboxylate and CD_3CO_2Cs with 0.55 equivalents Cs_2CO_3 at 200 °C under 2 bar N_2 for 1 h.



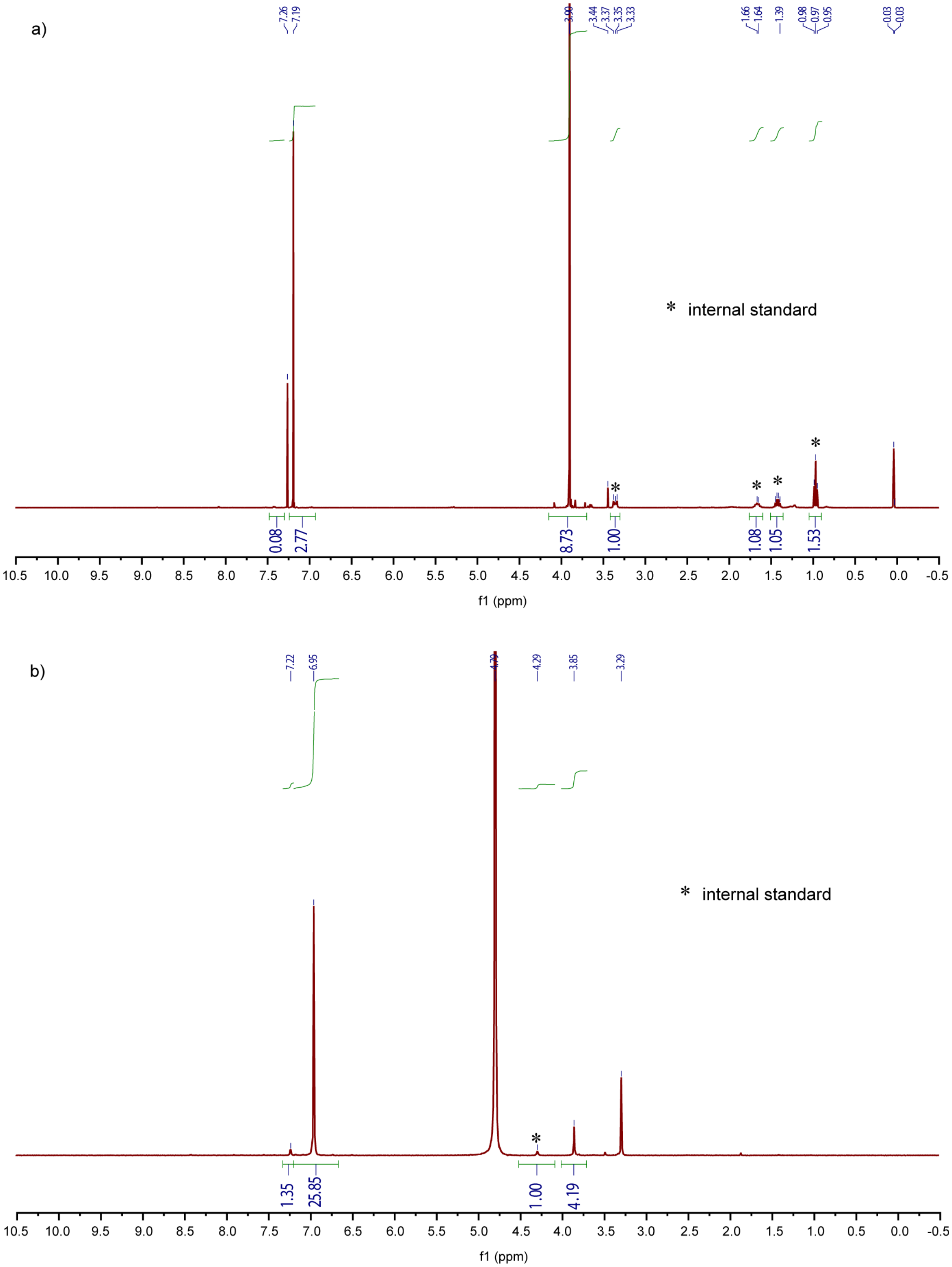
Extended Data Figure 7 | Additional NMR spectra for H/D exchange between furan-2-carboxylate and deuterated acetate in the presence of Cs_2CO_3. a, ^{13}C NMR (75 MHz) and **b**, ^{2}H NMR (92 MHz) in D_2O of the crude product mixture after the reaction of a 1:1 mixture of caesium furan-2-carboxylate and CD_3CO_2Cs with 0.55 equivalents Cs_2CO_3 at 200 °C under 2 bar N_2 for 1 h.



Extended Data Figure 8 | NMR spectra for H/D exchange between furan-2-carboxylate and deuterated acetate in the absence of Cs_2CO_3. **a**, ^{1}H NMR (400 MHz) and **b**, ^{2}H NMR (92 MHz) in D_2O of the crude product mixture after the reaction of a 1:1 mixture of caesium furan-2-carboxylate and CD_3CO_2Cs at 200 °C under 2 bar N_2 for 1 h.



Extended Data Figure 9 | No H/D exchange is observed between differentially labelled caesium benzoates when heated to 320 °C in the absence of Cs_2CO_3.



Extended Data Figure 10 | NMR spectra for the Cs_2CO_3 recycling experiment. a, ^1H NMR (400 MHz) in $CDCl_3$ of the DMFD isolated after the second carboxylation/esterification sequence. **b**, ^1H NMR (400 MHz) in D_2O of the material recovered from the aqueous phase after the second carboxylation/esterification sequence.

Extended Data Table 1 | Additional C–H carboxylation data

Table 1a

entry	scale (mmol)	T	p(CO$_2$)	time	FDCA^{2-}	starting material	acetate	malonate	other
1	1	260 °C	flowing	6 h	57%	26%	4%	4%	9%
2	1	260 °C	flowing	12 h	76%	8%	4%	4%	8%
3	1	260 °C	flowing	20 h	76%	8%	5%	3%	8%
4	1	270 °C	flowing	4 h	66%	10%	7%	8%	9%
5	1	200 °C	8 bar	2 h	77%	18%	2%	1%	2%
6	1	200 °C	8 bar	5 h	89%	6%	3%	2%	--
7	1	200 °C	8 bar	7 h	89%	4%	2%	1%	4%
8	10	195 °C	8 bar	5 h	78%	11%	4%	1%	6%
9	10	195 °C	8 bar	10 h	81%	8%	4%	1%	6%
10	10	205 °C	8 bar	2 h	71%	7%	9%	3%	10%
11	10	215 °C	8 bar	2 h	69%	2%	14%	5%	10%
12	100	260 °C	1 bar	48 h	71%	3%	11%	2%	1%

Table 1b

entry	time	T	p(C$_6$H$_6$)	p(CO$_2$)	CO$_3^{2-}$ conv.	benzoate	phthalates	benzene tri + tetra carboxylates	acetate + carboxylation pdts.	formate
1	10 h	340 °C	13 bar	31 bar	5%	2 μmol	14 μmol	14 μmol	205 μmol	17 μmol
2	9 h	340 °C	42 bar	31 bar	9%	42 μmol	29 μmol	11 μmol	238 μmol	24 μmol
3	2 h	350 °C	42 bar	31 bar	2%	19 μmol	3 μmol	1 μmol	27 μmol	9 μmol
4	8 h	350 °C	42 bar	31 bar	12%	46 μmol	41 μmol	17 μmol	148 μmol	28 μmol
5	8 h	360 °C	45 bar	32 bar	19%	39 μmol	69 μmol	35 μmol	306 μmol	42 μmol
6	1 h	380 °C	42 bar	33 bar	9%	30 μmol	36 μmol	13 μmol	192 μmol	146 μmol
7	8 h	350 °C	42 bar	—	0.6%	9 μmol	—	—	3 μmol	4 μmol

a, C–H carboxylation of caesium furan-2-carboxylate. **b**, C–H carboxylation of benzene. Formate, acetate, and acetate carboxylation products (‘pdts’) (malonate and methane tricarboxylate) arise from decomposition of isobutyrate.