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Carboxylation of terminal alkynes at ambient CO₂

The Cul-catalyzed carboxylation of terminal alkynes with CO_2 and alkyl halides using ethylene carbonate as the solvent under mild conditions was studied. DFT calculations reveal that the energy barrier for CO_2 insertion into the sp-hybridized Cu–C bond could be reduced by employing ethylene carbonate as the solvent. Notably, the procedure was conducted under ambient CO_2 pressure without any external ligands. A broad range of substrates with electron-withdrawing groups or electron-donating groups gave the corresponding products in reasonable yields.

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Introduction

Carbon dioxide chemistry has drawn much attention in the last two decades as CO2 can be regarded as an ubiquitous, abundant, cheap, and nontoxic C1 feedstock in organic synthesis.1 A myriad of industrial chemicals such as polycarbonates, urea and salicylic acid can be produced from CO2.² However, further application of CO₂ as a reactant is limited due to its low reactivity as a result of its high thermodynamic stability and kinetic inertness. Consequently, vigorous nucleophiles (like Grignard reagents and organolithium reagents), high-energy starting materials (like small-membered ring compounds and organometallics) or drastic reaction conditions are commonly required for reactions involving CO₂ to perform smoothly.³ Moreover, CO₂ capture and storage/sequestration (CCS) has been a highly intriguing research topic in recent years.⁴ In some cases, captured CO₂, considered an activated form of CO₂, can be applied as a feedstock to produce valueadded chemicals or fuels. This leads to systems suitable for accomplishing chemical transformations of CO₂ under mild conditions, getting rid of the desorption step. This concept has been named as 'CO₂ capture and utilization' (CCU) in the literature.⁵ Nevertheless, synthetic methods using CO₂ as feedstock under low pressure (ideally at 1 atm) are still highly desirable.

Carboxylic acids are found in medicinally important compounds such as worldwide commercialized aspirin and ibuprofen. This makes them particularly attractive targets for the fine-chemical synthesis.⁶ On the other hand, the widespread availability of carboxylic acids makes them extremely promising raw materials for chemical synthesis as well as a versatile synthon in organic synthesis.7 Moreover, the synthesis of carboxylic acids and derivatives using CO₂ as the carboxylative reagent is an attractive approach. In this context, a plethora of scientific efforts have been devoted to the development of various efficient carboxylation methods.8 For example, the carboxylation of organotin,⁹ organozinc,¹⁰ and organoboron reagents¹¹ has been reported. However, these methods require the synthesis of expensive and sensitive prefunctionalized substrates. From the point view of atom- and step-economical chemistry, the most concise route to carboxylic acids is the straightforward carboxylation of C-H with CO₂.¹²

The first coupling reaction of a terminal alkyne and CO_2 to form the corresponding alkynoate was observed by the Inoue group.¹³ Since then, carboxylation of terminal alkynes with CO_2 has been well studied (Scheme 1). The research groups of Zhang,¹⁴ Gooßen,¹⁵ Lu¹⁶ and Kondo¹⁷ still made significant contributions to this field. In all reported procedures, a polar aprotic solvent such as DMF, DMSO, DMA (*N*,*N*-dimethylacetamide) is required for a reasonable yield. This is probably because such solvents improve CO_2 solubility¹⁸ and thus enhance the interactions between the solvent and the

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Scheme 1 Carboxylation of terminal alkynes with CO₂.

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catalyst.^{15b} However, these traditional organic solvents are often environmentally hazardous.

On the other hand, organic carbonates as polar solvents are available in large amounts.¹⁹ Owing to the high solvency, high boiling and flash points, low odor levels, and low toxicities, they have been applied as an alternative reaction media for oxidation,²⁰ asymmetric hydrogenation,²¹ substitution reactions,²² olefin metathesis transformations,²³ and functionalization of arene C-H bonds.²⁴ Furthermore, organic carbonates are prepared in industry via cycloaddition reactions of epoxides with CO₂, and subsequent transesterification.^{2c} In 2009, our group reported the palladium-catalyzed Wacker oxidation using oxygen in ethylene carbonate.25 Higher alkenes and aryl alkenes were successfully transformed to the corresponding ketone by employing this protocol. As part of our continuous interest in carboxylation with CO₂ as the carbonylating agent and a catalysis in organic carbonates,²⁶ the carboxylation of terminal alkynes with CO₂ in organic carbonates offers significant benefits. In particular, an organic carbonate could improve the CO₂ solubility and is beneficial to stabilizing the intermediate metal species in metal catalysis.

We herein would like to disclose the carboxylation of terminal alkynes with ambient CO_2 in ethylene carbonate using CuI as the catalyst to give the corresponding alkyl 2-alkynoates. It is worth noting that the procedure needs no external ligands and terminal alkynes with electron-withdrawing groups or electron-donating groups proceed smoothly under mild conditions.

Results and discussion

The exploratory experiments started using phenylacetylene (1a) as the model substrate, ethylene carbonate (EC) as the solvent in the presence of *n*-butyl iodide (2a), CuI/Ph_3P , and Cs_2CO_3 as a base. The product *n*-butyl 2-alkynoate (3aa) was obtained in a quantitative yield at 80 °C for 18 h (Table 1, entry 1). The promising results encouraged us to further investigate the effect of the base as shown in Table 1. The base was found to have a dramatic impact on the reaction outcome. Using K_2CO_3 as the base, the reaction gave 3aa in a 42% yield (entry 2). Similarly, the carboxylation could happen in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) or ^tBuOK, but the yields were not satisfactory (entries 3 and 4). Other bases, e.g. ^tBuOLi, CsF, KF, NaNH₂, CsOAc, KOH and NaOH, were inefficient under identical conditions (entries 5-11). In addition, several organic bases like DBU, DBN, TMG, DABCO etc. did not work for this reaction (see Table S1, ESI[†]).

Subsequently, the survey of other reaction parameters was conducted using Cs₂CO₃ as the base. As summarized in Table 2, a quantitative yield was obtained at 80 °C for 18 h even without Ph_3P as a ligand (entry 1 vs. 2). The control experiment revealed that the carboxylation did not proceed without CO_2 (entry 3). Without CuI, only a 13% yield of 3aa

Cul (10 mol%) Ph ₃ P (10 mol%) Ph————————————————————————————————————	1
1a EC, 80 °C, 18 h 3aa 0 BC	-
Entry Base Yie	$eld^{b}(\%)$
1 Cs ₂ CO ₃ >9	9
2 K ₂ CO ₃ 4	2
3 TBD 3	8
4 ^t BuOK 2	3
5 ^t BuOLi	4
6 CsF	3
7 KF <	1
8 NaNH ₂ <	1
9 CsOAc <	1
10 КОН <	1
11 NaOH <	1

^a Reaction conditions: phenylacetylene (0.0511 g, 0.5 mmol), CuI (0.0095 g, 0.05 mmol), Ph₃P (0.0131 g, 0.05 mmol), base (0.6 mmol), n-BuI (0.1104 g, 0.6 mmol), EC (3 mL), CO₂ (99.999%, balloon), 80 °C, 18 h. ^b The yields were determined by GC with biphenyl as the internal standard.

 Table 2
 Optimization of the carboxylation of phenylacetylene⁴

	Ph─ ─── H 1a	+ CO ₂ (Balloon)	Cul (10 mol%) Cs₂CO₃ (1.2 equiv.) ⁿ Bul (1.2 equiv.) EC as solvent 3a	⊖ aa O−″Bu
Entry		$T(^{\circ}C)$	Time (h)	$\operatorname{Yield}^{b}(\%)$
1		80	18	>99
2^{c}		80	18	>99
3^d		80	18	4
4^e		80	12	13
5		80	12	88
6		50	12	61

^a Reaction conditions: phenylacetylene (0.0511 g, 0.5 mmol), CuI (0.0095 g, 0.05 mmol), Cs₂CO₃ (0.1955 g, 0.6 mmol), *n*-BuI (0.1104 g, 0.6 mmol), EC (3 mL), CO₂ (99.999%, balloon). ^b The yields were determined by GC with biphenyl as the internal standard. ^c Ph₃P (0.0131 g, 0.05 mmol) was added as a ligand. ^d Argon (1 atm) was used to replace CO₂. ^e Without CuI.

was observed (entry 4). Moreover, a shorter reaction time caused a decrease in the 3aa yield to 88% (entry 5). When the reaction was carried out at 50 °C for 12 h, the yield dropped to 61% (entry 6). Consequently, the catalytic carboxylation proceeded efficiently at 80 °C for 18 h without any additional ligand by using EC as the solvent.

With the EC results in hand, we then examined the influence of different solvents such as DMF and other organic carbonates (Table 3). The carboxylation using DMF as the solvent gave a 70% yield of 3aa (entry 1), being similar to Kondo's report.¹⁷ For the organic carbonates chosen as the solvents, the cyclic carbonates, e.g. PC and EC, exhibited better performances than the acyclic carbonates, such as DMC and DEC (entries 2-5). This is presumably because EC is helpful

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Table 3 Influence of solvent on the carboxylation of phenylacetylene^a

	Ph=H + CO ₂ (Balloo	n) Cul (10 mol%) Cs ₂ CO ₃ (1.2 equiv.) ⁿ Bul (1.2 equiv.) Solvent (3 mL) 80 °C, 12 h	PhO 3aa O="Bu
Entry		Solvent	Yield ^b (%)
1		DMF	70
2		DMC	15
3		DEC	16
4		PC	73
5		EC	88

^a Reaction conditions: phenylacetylene (0.0511 g, 0.5 mmol), CuI (0.0095 g, 0.05 mmol), Cs₂CO₃ (0.1955 g, 0.6 mmol), n-BuI (0.1104 g, 0.6 mmol), solvent (3 mL), CO₂ (99.999%, balloon), 80 °C, 12 h, DMC = dimethyl carbonate, DEC = diethyl carbonate, PC = propylene carbonate. ^b The yields were determined by GC with biphenyl as the internal standard.

Table 4	Influence	of the	copper	salt o	on the	carboxylation	reaction ^a
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Ph— ——— H + CO ₂ 1a (Balloon)	Cat. (10 mol%) Cs ₂ CO ₃ (1.2 equiv.) ⁿ Bul (1.2 equiv.) EC, 80 °C, 12 h	PhO 3aa O-"Bu
Entry	Catalyst	$\mathrm{Yield}^{b}\left(\%\right)$
1	CuCl	26
2	CuBr	61
3	CuI	88
4	CuCN	81
5	Cu_2O	46

^a Reaction conditions: phenylacetylene (0.0511 g, 0.5 mmol), catalyst (10 mol%), Cs₂CO₃ (0.1955 g, 0.6 mmol), n-BuI (0.1104 g, 0.6 mmol), solvent (3 mL), CO₂ (99.999%, balloon), 80 °C, 12 h. ^b The yields were determined by GC with biphenyl as the internal standard.

for enhancing the stability of the intermediate, *i.e.* copper acetylide, and facilitating interactions among the reactant species. Therefore, ethylene carbonate was chosen as the solvent for the carboxylation of phenylacetylene with CO₂.

Furthermore, the catalytic performance of different cuprous salts was evaluated in ethylene carbonate in the presence of Cs₂CO₃, n-BuI and CO₂ at 80 °C for 12 h. The results summarized in Table 4 reveal that the reactivity decreases in the order of CuI > CuBr > CuCl (Table 4, entries 1-3). Additionally, CuCN and Cu₂O could also promote the carboxylation towards alkyl 2-alkynoates in yields of 81% and 46%, respectively (entries 4 and 5). Thus CuI was employed as the catalyst for further investigation. As a result, the optimal reaction conditions were CuI (10 mol%) as the catalyst, Cs_2CO_3 as the base, ethylene carbonate as the solvent, and 80 °C.

The generality of this methodology was further examined as listed in Table 5. Phenylacetylenes substituted with electronrich groups (e.g. Me, Et and MeO) were converted to the

corresponding alkynoates in 80-96% yields (Table 5, entries 1-6). In addition, electron-withdrawing groups substituted at the meta- or ortho-positions on the phenylacetylenes were also tolerable and gave good yields (entries 7-10). The reaction using 2-ethynylthiophene as the substrate was also practical, providing the corresponding product 3ka in a high yield (entry 11). The reaction with aliphatic alkynes, such as 1-octyne and 3,3-dimethyl-1-butyne, were also tested under the standard conditions. The desired products were formed in 88% and 90% yields, respectively (entries 12 and 13). Moreover, n-butyl bromide was also suitable for *in situ* alkylation, affording the product in a good yield (entry 14). In particular, we were pleased to find that n-butyl chloride also worked well (entry 15). Likewise, the reaction of 1a with CO₂ could be successfully run on a gram scale (see ESI⁺).

To elucidate the origin of the reactivity in ethylene carbonate, DFT calculations were performed based on the mechanism of the carboxylation. As delineated in Scheme 2, the catalytic cycle for the copper-catalyzed carboxylation of terminal alkynes with CO_2 proceeds *via* copper acetylide as the key intermediate,²⁷ generated from the reaction of the terminal alkyne and CuI with the aid of a base. Subsequently, the insertion of CO₂ into the sp-hybridized Cu-C bond forms the copper propynoate intermediate. Then the product ester can be generated using iodoalkane with regeneration of the copper catalyst.

We explored the energetics for the CO_2 insertion step as shown in Scheme 3. Following the prevalent mechanism of the carboxylation reactions, insertion of CO₂ into the Cu-C bond of alkynylcopper by transferring the alkynyl group to the carbon atom of CO₂ occurs via the transition states TS1, TS2 and TS3 to give the corresponding copper propynoate.²⁸ DFT calculations in the gas phase show that the activation energy for the CO_2 insertion without solvent is 32.9 kcal mol⁻¹ (TS1), whereas the activation energy is much lower with EC or DMF as the solvent (TS2, TS3).²⁹ The results demonstrate that using the appropriate solvent has a dramatic impact on the reaction outcome. Although the activation energy in EC (19.3 kcal mol^{-1}) is slightly higher than in DMF (18.5 kcal mol^{-1}), we hypothesize that ethylene carbonate could act as a proper ligand (binding energy of about 26.86 kcal mol^{-1}), which presumably stabilizes the reaction intermediate and thus facilitates the carboxylation.

Conclusions

In conclusion, we have developed an efficient CuI-catalyzed carboxylation reaction of terminal alkynes, CO2 and alkyl halides using ethylene carbonate as the solvent under mild conditions without any additional ligands. A range of terminal alkynes and various alkyl halides could undergo the coupling reaction smoothly. In addition, the DFT calculations revealed that the energy barrier of the CO₂ insertion step could be reduced by employing ethylene carbonate as the solvent and

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Table 5Cu(ı)-catalyzed carboxylation in ethylene carbonate^a

$R^{1} = H + CO_{2} \qquad \frac{Cul (10 \text{ mol\%})}{(Balloon)} \qquad \frac{Cs_{2}CO_{3} (1.2 \text{ equiv.})}{R^{2}X (1.2 \text{ equiv.})} \qquad R^{1} = 0 \qquad O = R^{2}$				
Entry	R ¹ C≡CH	R ² X	Product	Yield ^b (%)
1	PhH _{1a}	ⁿ BuI 2 a	Ph	96
2	Мен 1b	ⁿ BuI 2a	Me-	80
3	Et-	ⁿ BuI 2a	Et-	84
4	ⁿ C ₅ H ₁₁	ⁿ BuI 2a	ⁿ C ₅ H ₁₁	90
5	MeOH	^{<i>n</i>} BuI 2a	MeO-	90
6	MeH_1f	^{<i>n</i>} BuI 2a	Me O-"Bu 3fa	89
7	CI ————————————————————————————————————	^{<i>n</i>} BuI 2a	CI O-"Bu 3ga	84
8	FH	ⁿ BuI 2a	F	81
9	CIH	ⁿ BuI 2a	CI	80
10	BrH1j	ⁿ BuI 2 a	Br	81
11	∬S HIk	ⁿ BuI 2a	[91
12	ⁿ C ₆ H ₁₃ ——H ₁₁	^{<i>n</i>} BuI 2a	ⁿ C ₆ H ₁₃ ————————————————————————————————————	88
13	\rightarrow ————————————————————————————————————	ⁿ BuI 2a	\rightarrow $=$ $\langle \circ \\ \circ \\ \circ \\ \circ $ $\circ $ $\circ $ $\circ $ $\circ $ $\circ $	90
14	Ph- <u>-</u> H _{1a}	^{<i>n</i>} BuBr 2 b	Ph	87
15	PhH _{1a}	^{<i>n</i>} BuCl 2c	Ph	56

^{*a*} Reaction conditions: terminal alkyne (1.0 mmol), CuI (0.0190 g. 0.1 mmol), Cs₂CO₃ (0.3910 g, 1.2 mmol), *n*-BuI (0.2208 g, 1.2 mmol) and ethylene carbonate (3 mL), CO₂ (99.999%, balloon), 80 °C, 18 h. ^{*b*} Isolated yield.

ligand. Such findings in this study may be of great interest to stimulate the development of novel access routes to form carboxylic acids from hydrocarbons and CO_2 in a green solvent.

Studies are currently underway in our laboratory to explore other procedures for CO_2 utilization in green solvents under mild conditions.



 $\mbox{Scheme 2}$ The proposed mechanism for the carboxylation of the terminal alkyne with $\mbox{CO}_2.$



 $Scheme \, 3$ $\,$ Free energy profile for the step of CO_2 insertion calculated by the B3LYP/6-311++G(d,p)/LANL2DZ method. The calculated relative energies are given in kcal mol^{-1}.

Experimental section

General procedure for the carboxylation of terminal alkynes in ethylene carbonate

In a 20 mL Schlenk flask, the terminal alkyne (1.0 mmol), CuI (0.0190 g, 0.1 mmol), Cs_2CO_3 (0.3910 g, 1.2 mmol), *n*-BuI (0.2208 g, 1.2 mmol) and ethylene carbonate (3 mL) were added. The flask was capped with a stopper and sealed. Then the freeze–pump–thaw method was employed for gas exchanging process. The reaction mixture was stirred at 80 °C for the desired time under an atmosphere of CO_2 (99.999%, balloon). After the reaction, the mixture was cooled to room temperature, and extracted with *n*-hexane. The combined organic layers were washed with saturated NaCl solution, then dried with anhydrous Na₂SO₄. The residue was purified by column chromatography (silica gel, petroleum ether–EtOAc) to afford the desired product 3.

Computational methods

The calculations were carried out by performing DFT using the B3PW91 functional with the 6-311++G(d,p) (C, H, N, O) and LANL2DZ (Cu) basis set implemented in the Gaussian 09 program package.²⁹ All the final structures were confirmed by frequency calculations to be the real minima without any imaginary frequencies using the same level of theory. All transition-state (TS) geometries were characterized by the presence of a single imaginary frequency, and intrinsic reaction

coordinates (IRC) were examined to ensure the smooth connection of reactants and products.

Compound 3aa. Colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.62–7.59 (m, 2H), 7.48–7.37 (m, 3H), 4.26 (t, J = 6.7 Hz, 2H), 1.72 (quint, J = 6.8 Hz, 2H), 1.51–1.41 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.2, 132.9, 130.5, 128.5, 119.6, 86.0, 80.7, 65.9, 30.4, 19.0, 13.6; EI-MS, m/z (%): 129.10 (100), 201.08 (34) [M⁺].

Compound 3ba. Light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.48 (d, J = 7.5 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 4.23 (t, J = 6.6 Hz, 2H), 2.37 (s, 3H), 1.69 (quint, J = 7.3 Hz, 2H), 1.51–1.36 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.3, 141.2, 132.9, 129.3, 116.5, 86.6, 80.3, 65.8, 30.5, 21.7, 19.0, 13.6; EI-MS, m/z (%): 116.20 (100), 216.25 (13) [M⁺].

Compound 3ca. Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.52–7.40 (m, 2H), 7.21–7.14 (m, 2H), 4.23 (t, *J* = 6.7 Hz, 2H), 2.70–2.61 (m, 2H), 1.73–1.63 (m, 2H), 1.48–1.37 (m, 2H), 1.25–1.20 (m, 3H), 0.98–0.92 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.3, 147.4, 133.1, 128.1, 116.7, 86.6, 80.3, 65.8, 30.5, 28.9, 19.0, 15.1, 13.6; EI-MS, *m/z* (%): 130.20 (100), 230.20 (14) [M⁺]; HRMS (ESI): C₁₅H₁₈O₂Na for [M + Na]⁺ calculated 253.1199, found 253.1196.

Compound 3da. Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.50 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 4.23 (t, J = 6.7 Hz, 2H), 2.63–2.59 (m, 2H), 1.70–1.58 (m, 4H), 1.46–1.28 (m, 6H), 0.98–0.87 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.3, 146.2, 133.0, 128.6, 116.7, 86.6, 80.3, 65.8, 36.0, 31.4, 30.7, 30.5, 22.4, 19.0, 14.0, 13.6; EI-MS, m/z (%):172.25 (100), 272.30 (15) [M⁺]; HRMS (ESI): C₁₈H₂₄O₂Na for [M + Na]⁺ calculated 295.1669, found 295.1664.

Compound 3ea. White solid; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.53 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.22 (t, J = 6.7 Hz, 2H), 3.82 (s, 3H), 1.69 (dt, J = 14.7, 6.8 Hz, 2H), 1.43 (dq, J = 14.7, 7.4 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 161.4, 154.4, 134.9, 114.2, 111.4, 86.8, 80.1, 65.7, 55.3, 30.5, 19.0, 13.6; EI-MS, m/z (%): 132.15 (100), 232.20 (15) [M⁺].

Compound 3fa. Colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.34–7.31 (m, 2H), 7.19–7.17 (m, 2H), 4.16 (t, J = 6.7 Hz, 2H), 2.27 (s, 3H), 1.66–1.55 (m, 2H), 1.41–1.32 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.2, 138.3, 133.4, 131.5, 130.1, 128.4, 119.4, 86.3, 80.4, 65.9, 30.4, 21.1, 19.0, 13.6; EI-MS, m/z (%):143.15 (100), 216.20 (8) [M⁺]; HRMS (ESI): C₁₄H₁₆O₂Na for [M + Na]⁺ calculated 239.1043, found 239.1046.

Compound 3ga. Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.57 (s, 1H), 7.47–7.41 (m, 2H), 7.33–7.29 (m, 1H), 4.24 (t, J = 6.6 Hz, 2H), 1.73–1.63 (m, 2H), 1.48–1.37 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 153.8, 134.5, 132.6, 131.0, 130.9, 129.8, 121.4, 84.1, 81.4, 66.1, 30.4, 19.0, 13.6; EI-MS, m/z (%):163.10 (100), 235.15 (7) [M⁺]; HRMS (ESI): C₁₃H₁₃O₂ClNa for [M + Na]⁺ calculated 259.0496, found 259.0493.

Compound 3ha. Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.59–7.56 (m, 2H), 7.08–7.04 (m, 2H), 4.23 (t, *J* = 6.6 Hz,

2H), 1.73–1.62 (m, 2H), 1.46–1.38 (m, 2H), 0.95 (t, J = 7.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 165.1, 162.6, 154.1, 135.2, 116.1, 84.9, 80.6, 65.9, 30.4, 19.0, 13.6; EI-MS, m/z (%):147.15 (100), 220.15 (5) [M⁺]; HRMS (ESI): C₁₃H₁₃FO₂Na for [M + Na]⁺ calculated 243.0792, found 243.0786.

Compound 3ia. Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.51 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 4.23 (t, J = 6.7 Hz, 2H), 1.71–1.66 (m, 2H), 1.46–1.40 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.0, 136.9, 134.1, 129.0, 118.1, 84.7, 81.5, 66.0, 30.4, 19.0, 13.6; EI-MS, m/z (%): 163.10 (100), 236.10 (7) [M⁺]; HRMS (ESI): C₁₃H₁₃O₂ClNa for [M + Na]⁺ calculated 259.0496, found 259.0494.

Compound 3ja. Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.52 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 4.23 (t, J = 6.7 Hz, 2H), 1.73–1.66 (m, 2H), 1.48–1.38 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.0, 134.2, 131.9, 125.3, 118.6, 84.7, 81.6, 66.1, 30.4, 19.0, 13.6; EI-MS, m/z (%):180.00 (100), 280.10 (8) [M⁺].

Compound 3ka. Brown oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.48–7.45 (m, 2H), 7.04 (s, 1H), 4.23 (t, *J* = 6.6 Hz, 2H), 1.71–1.67 (m, 2H), 1.46–1.40 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.0, 136.4, 131.0, 127.5, 119.4, 84.9, 80.0, 65.9, 30.4, 19.0, 13.6; EI-MS, *m/z* (%): 108.19 (100), 207.90 (14) [M⁺].

Compound 3la. Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.13 (t, J = 6.7 Hz, 2H), 2.30 (t, J = 7.2 Hz, 2H), 1.65–1.53 (m, 4H), 1.40–1.25 (m, 8H), 0.93–0.85 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.0, 89.4, 73.1, 65.5, 31.1, 30.4, 28.5, 27.4, 22.4, 19.0, 18.6, 13.9, 13.6; EI-MS, m/z (%): 67.19 (100), 211.02 (46) [M⁺].

Compound 3ma. Colourless oil; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.14 (t, J = 6.8 Hz, 2H), 1.67–1.60 (m, 2H), 1.43–1.36 (m, 2H), 1.27 (s, 9H), 0.93 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 154.2, 96.3, 71.8, 65.6, 30.4, 29.9, 27.5, 19.0, 13.6; HRMS (ESI): C₁₅H₁₈O₂Na for [M + Na]⁺ calculated 205.1199, found 205.1197.

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