Anodic Cyclization of Dimethyl 2-(3-Oxo-3-arylpropyl) Malonates into the Corresponding Dimethyl 2-Aroylcyclopropane-1,1-dicarboxylates

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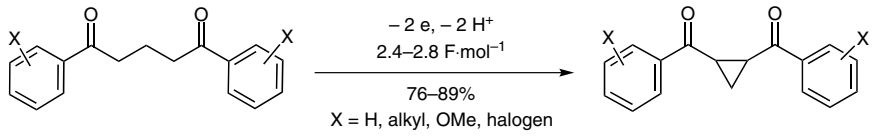
Abstract: A variety of dimethyl 2-(3-oxo-3-arylpropyl)malonates were electrooxidized in methanol, in the presence of potassium iodide and a base or a neutral salt, to give the corresponding cyclized dimethyl 2-aroylcyclopropane-1,1-dicarboxylates in moderate to good yields. The reactions were carried out under extremely mild reaction conditions, in which the optimal amount of electrolytic current varied from 2.12–2.41 F·mol^{-1} depending on the substrates. The reaction presumably proceeds via a two-electron oxidation process, in which iodide ions play an important role as the electron carrier between the anode and the substrate.

Key words: oxidation, electron transfer, radicals, cyclization, substituent effects, ring closure, green chemistry, iodine

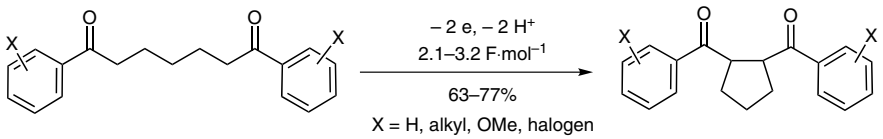
The formation of carbon–carbon bonds is essential in the syntheses of organic compounds and typically involves well-known classical chemical reactions. In certain cases, however, carbon–carbon bond formation can be effectively achieved via electrooxidation,[1–3] which is typically carried out under very mild reaction conditions (room temperature and atmospheric pressure), and without the use of special and often harsh reagents. Previously, we reported on the successful electrooxidative synthesis of 1,2-diaroyl cyclopropane[4] and 1,2-diaroyl cyclopentane[5] derivatives (Scheme 1 and Scheme 2, respectively) via intramolecular formation of a carbon–carbon bond, with iodide ions as the electron carrier.

Unfortunately, however, attempts to form the 1,2-diaroyl four-, six-, seven-, or eight-membered-ring compounds using similar electrooxidative methods proved to be unsuccessful. In the continuation of our investigations, we discovered that dimethyl 2-(3-oxo-3-arylpropyl)malonates **1** can be readily converted into the corresponding cyclized dimethyl 2-aroylcyclopropane-1,1-dicarboxylates **2** via intramolecular cyclization, as shown in Scheme 3.[6]

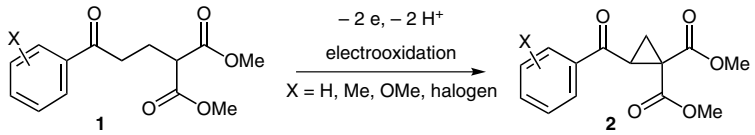
Although the formation of cyclopropane derivatives via electrochemical means has been previously described,[7] the electrooxidative formation of dimethyl 2-aroylcyclopropane-1,1-dicarboxylates **2** starting from dimethyl 2-(3-oxo-3-arylpropyl)malonates **1**, to the best of our knowledge, has yet to be reported. Moreover, we believe that the present cyclopropanation is significantly different from our previous studies;[4] specifically, the optimal amount of KI was 2 mmol (0.33 equiv, substrate 6 mmol) for the pre-



Scheme 1 Electrooxidative formation of 1,2-diaroylcyclopropanes



Scheme 2 Electrooxidative formation of 1,2-diaroylcyclopentanes



Scheme 3 Electrooxidative formation of dimethyl 2-aroylcyclopropane-1,1-dicarboxylates

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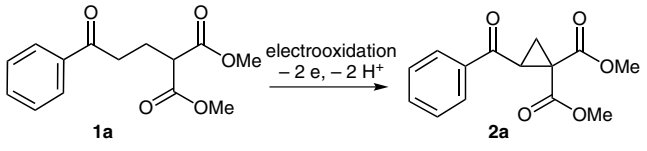
vious study, whereas 5 mmol (1.0 equiv, substrate 5 mmol) is required for the present electrooxidations. Furthermore, the presence of a base was essential in the previous study, but not necessary for the reactions described herein.

First, the reaction conditions for the anodic cyclizations were optimized in methanol using dimethyl 2-(3-oxo-3-phenylpropyl)malonate (**1a**, X = H) as the model substrate and with the passage of 2.40 F·mol^{-1} of electricity. Various combinations of the supporting electrolytes (mediators, bases, and/or neutral salts) are listed in Table 1, along with the yields of the resulting cyclized product, dimethyl 2-benzoylcyclopropane-1,1-dicarboxylate (**2a**, X = H). Interestingly, although the presence of NaOMe by itself was ineffective (0%, Table 1, entry 1), and the presence of KI (1.0 equiv) by itself gave a moderate yield (70%, Table 1, entry 2), the presence of both KI (1.0 equiv) and NaOMe (0.4 equiv) was effective and provided a good yield (83%, Table 1, entry 4).

Table 1 Effects of Mediators and Electrolytes on the Yield of **2a**[a]



1a **2a**

Entry	Mediator (mmol)	Electrolyte (mmol)	Yield of **2a** (%)[b]
1	none	NaOMe (2)	0[c]
2	KI (5)	none	70
3	KI (2)	NaOMe (2)	63
4	KI (5)	NaOMe (2)	83
5	KI (5)	NaOMe (5)	31[c]
6	KI (5)	$TsON(Et)_4$ (2)	78
7	KI (5)	$NaClO_4$ (2)	81
8	KI (5)	NaOAc (2)	81
9	KI (5)	NaOH (2)	78
10	KI (5)	KO*t*-Bu (2)	82
11	NaI (5)	NaOMe (2)	82
12	KCl (5)	NaOMe (2)	44[c]
13	KBr (5)	NaOMe (2)	68

[a] Reaction conditions: substrate **1a** (5 mmol), MeOH (40 mL), constant current (0.3 A), current passed (2.40 F·mol^{-1}), ca. 15 °C, anode (Pt net), cathode (Ni coil).
[b] Determined using GC analysis.
[c] Unreacted substrate **1a** was detected using GC analysis.

Decreasing the amount of KI (from 1.0 to 0.4 equiv) while increasing the amount of NaOMe (from 0.4 to 1.0 equiv) reduced the yields of **2a** (Table 1, 63% for entry 3 and 31% for entry 5, respectively). In regards to the nature of the mediator, comparable yields were observed for the reactions using NaI (82%, Table 1, entry 11) or combinations of KI and other neutral salts such as $TsON(Et)_4$ and $NaClO_4$ (Table 1, 78% for entry 6 and 81% for entry 7, respectively), whereas lower yields were observed using KCl (44%, Table 1, entry 12) or KBr (68%, Table 1, entry 13). Good yields were also obtained for the reactions using KI in combination with either a weak base such as NaOAc (81%, Table 1, entry 8) or a strong base such as KO*t*-Bu (82%, Table 1, entry 10). These results suggest that the yield of **2a** is strongly affected by the presence and nature of halides, especially iodide ions, but surprisingly not by the basicity of the electrolyte. Unfortunately, we have yet to establish the reasoning behind the relationship between the product yields and the amounts of KI and NaOMe.

During the early stages of the electrooxidation, under favorable reaction conditions (Table 1, entry 4), the yield of **2a** increased proportionally to the amount of current passed – specifically, 32% after 0.66 F·mol^{-1} (current efficiency >97%), then 63% after 1.32 F·mol^{-1} (current efficiency >95%). The maximum yield of **2a** (83%) was attained following the passage of ca. 2.1 F·mol^{-1} of electrolytic current (current efficiency = 79%). As a note, excess passage of electric current did not significantly improve the yield of **2a** – for example, after the passage of 4.6 F·mol^{-1} of current, the yield of **2a** was merely 80%.

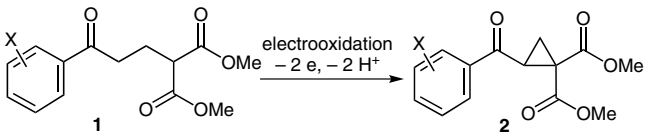
In contrast to the results of our previous studies, **2a** did not undergo further oxidation to form a tarlike material.[5] Our results showed that the yield of **2a** was not significantly affected by the amount of KI (5.0–10.0 mmol), the reaction temperature (5–45 °C), nor the constant current (0.2–0.4 A).

Subsequently, based on the above-mentioned optimal reaction conditions, the electrooxidations of dimethyl 2-(3-oxo-3-arylpropyl)malonates **1b**–**i** were carried out, and the results are listed in Table 2.[8] During the course of the electrooxidations, the progress of the reaction was monitored by analyzing the composition of the mixture (anolyte) using gas chromatograph (SE-30, 0.5 m) or silica gel TLC analysis. With the sole exception of **2f** (yield of 58%), products **2b**–**i** were obtained in reasonable yields (69–77%).

It is interesting to note that the nature of the substituent on the arylpropyl moiety, whether electron-withdrawing (**1g**, **1h**, and **1i**) or electron-donating (**1b**, **1c**, and **1d**), did not significantly affect the reaction. Although the details of the reaction mechanism remain unclear, our studies indicate that the iodide ion plays an important role as the electron carrier during this indirect electrooxidation process, in which substrate **1** loses two electrons and two protons during the formation of product **2**.

In conclusion, the synthesis of dimethyl 2-aroylcyclopropane -1,1-dicarboxylate **2** via electrooxidative intramolecular ring formation was successfully carried out under mild reaction conditions at room temperature and in the absence of any harsh oxidants and/or special reagents. For these reactions, the halide ions, especially iodide ions,

Table 2 Electrooxidative Cylizations of Dimethyl 2-(3-Oxo-3-arylpropyl)malonates[a]



1 2

Substrate **1**	X	Current passed (F·mol^{-1})	Yield of **2** (%)[b]
1a	H	2.12	72
1b	4-Me	2.24	72
1c	3,4-Me$_2$	2.35	76
1d	4-MeO	2.25	77
1e	2-MeO-5-Me	2.18	71
1f	2-Me-5-Br	2.38	58
1g	4-F	2.13	73
1h	4-Cl	2.14	69
1i	4-Br	2.41	74

[a] Reaction conditions: substrate **1** (5 mmol), KI (0.83 g, 5 mmol), NaOMe (2 mmol), MeOH (40 mL), constant current (0.3 A), ca. 15 °C, anode (Pt net), cathode (Ni coil).
[b] Isolated yield.

presumably serve as the electron carrier during the cyclization step. Investigations are currently under way in our laboratories to expand the scope of our electrooxidative methodology to include four-, six-, seven-, or eight-membered-ring compounds. At the same time, we are now studying the electrochemical intramolecular cyclizations of analogous substrates that possess β-dicarbonyl compound moieties, such as methyl acetoacetate or acetyl acetone.

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(8) **General Procedures**
3-Bromo-1-arylpropan-1-ones were prepared via typical Friedel–Crafts acylation,[9] using commercially available 3-bromopropionyl chloride and aromatic compounds in the presence of $AlCl_3$ at <45 °C. Dimethyl 2-(3-oxo-3-arylpropyl)malonates **1** were prepared by mixing the corresponding bromo aryl ketone and dimethyl malonate with a slight excess (1.1 equiv) of NaOMe in MeOH for ca. 40 min at r.t.[10] Preparative-scale electrooxidations were carried out in a tall 50 mL beaker equipped with a fine frit cup as the cathode compartment with a nickel coil cathode, along with a cylindrical platinum net anode (height: 35 mm, diameter: 30 mm, 50 mesh).
Typical Procedures
A solution of dimethyl 2-(3-oxo-3-benzoylpropyl)malonates **1a** (1.32 g, 5 mmol) in MeOH (40 mL) containing KI (0.83 g, 5.0 mmol) and NaOMe (2.0 mmol) was electrooxidized

under a constant current (0.3 A) at ca. 15 °C with magnetic stirring. During the course of the electrooxidation, the composition of the reaction mixture was monitored using GC and/or TLC analyses. Passage of the electric current was maintained until the formation of the product was no longer detected. The reaction mixture was concentrated in vacuo at approximately 50 °C to near dryness. The resulting residue was treated with brine (ca. 30 mL), then extracted with Et_2O (3 × 50 mL). The combined ether solution was washed with $Na_2S_2O_3$ aq solution (15 wt%, 30 mL), and dried overnight over Na_2SO_4. After removal of the solvent in vacuo, the crude product was purified using silica gel column chromatography (height, 300 mm; diameter, 15 mm) with CH_2Cl_2 as the eluent to afford product **2a** as a viscous oil (0.96 g, 72%). The electrooxidation products were characterized using HRMS, IR, ^1H NMR, and ^{13}C NMR spectroscopy.

Dimethyl 2-Benzoylcyclopropane-1,1-dicarboxylate (2a)

Yield 0.94 g (72%); colorless, cubic crystals, mp 25–27 °C (from MeOH); R_f = 0.58 (silica gel; Et_2O–*n*-hexane, 2:1). IR (neat): 2955, 1738 (vs), 1732 (vs), 1681 (vs), 1597, 1436, 1336, 1276, 1212, 1132, 704 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (dd, *J* = 8.5, 4.1 Hz, 1 H, CH), 2.22 (dd, *J* = 6.9 4.4 Hz, 1 H, CH), 3.57 (dd, *J* = 8.0, 7.9 Hz, 1 H, CH), 3.69 (s, 3 H, CH_3O), 3.80 (s, 3 H, CH_3O), 7.45–7.53 (m, 3 H, arom.), 7.97–8.30 (m, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.09 (CH_2), 31.00 (CH), 39.03 (C), 52.85 (CH_3), 53.31 (CH_3), 128.40 (CH), 128.71 (CH), 133.60 (CH), 137.00 (C), 166.47 (CO), 169.47 (CO), 194.79 (CO). MS (EI, 70 eV): *m/z* (%) = 262 [M^+] (2), 231 [$M^+ - CH_3O$] (46), 230 (68), 203 [$M^+ - CO_2CH_3$] (24), 202 (63), 171 (19), 144 [$M^+ - 2 \times CO_2CH_3$] (9), 106 (19), 105 [C_6H_5CO] (100), 77 [C_6H_5] (53). HRMS: *m/z* [M^+] calcd for $C_{14}H_{14}O_5$: 262.0841; found: 262.0802.

Dimethyl 2-(4-Methylbenzoyl)cyclopropane-1,1-dicarboxylate (2b)

Yield 0.99 g (72%); colorless, fine cubic crystals, mp 91–93 °C (from MeOH); R_f = 0.62 (silica gel; Et_2O–*n*-hexane, 2:1). IR (KBr): 2953, 1746 (vs), 1732 (vs), 1665 (vs), 1294, 1234, 1220, 1199, 1184, 963 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.77 (dd, *J* = 8.7, 4.4 Hz, 1 H, CH), 2.21 (dd, *J* = 6.9, 4.4 Hz, 1 H, CH), 2.42 (s, 3 H, CH_3), 3.55 (dd, *J* = 8.7, 6.8 Hz, 1 H, CH), 3.69 (s, 3 H, CH_3O), 3.81 (s, 3 H, CH_3O), 7.28 (d, *J* = 8.3 Hz, 2 H, arom.), 7.90 (d, *J* = 8.3 Hz, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.11 (CH_2), 21.72 (CH_3), 30.95 (CH), 38.86 (C), 52.85 (CH_3), 53.29 (CH_3), 128.54 (CH), 129.38 (CH), 134.51 (C), 144.56 (C), 166.56 (CO), 169.61 (CO), 194.29 (CO). MS (EI, 70 eV): *m/z* (%) = 276 [M^+] (16), 245 [$M^+ - CH_3O$] (44), 244 (65), 217 [$M^+ - CO_2CH_3$] (21), 216 (63), 185 (21), 158 [$M^+ - 2 \times CO_2CH_3$] (10), 120 (26), 119 [$CH_3C_6H_4CO$] (100), 91 [$CH_3C_6H_4$] (68). HRMS: *m/z* [M^+] calcd for $C_{15}H_{16}O_5$: 276.0998; found: 276.1001.

Dimethyl 2-(3,4-dimethylbenzoyl)cyclopropane-1,1-dicarboxylate (2c)

Yield 1.10 g (76%); colorless, fine cubic crystals, mp 65–67 °C (from MeOH); R_f = 0.60 (silica gel; Et_2O–*n*-hexane, 2:1). IR (KBr): 2954, 1757 (vs), 1741 (vs), 1662 (vs), 1438, 1279, 1245, 1212 (vs), 1166, 1138 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.76 (dd, *J* = 8.7, 4.4 Hz, 1 H, CH), 2.19 (dd, *J* = 6.9, 4.1 Hz, 1 H, CH), 2.32 (br s, 6 H, 2 × CH_3), 3.55 (dd, *J* = 8.7, 7.1 Hz, 1 H, CH), 3.69 (s, 3 H, CH_3O), 3.80 (s, 3 H, CH_3O), 7.18–7.30 (m, 1 H, arom.), 7.70–7.82 (m, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.77 (CH_3), 20.08 (CH_3), 21.17 (CH_2), 30.92 (CH), 38.87 (C), 52.81 (CH_3), 53.25 (CH_3), 126.23 (CH), 129.43 (CH), 129.92 (CH), 134.91 (C), 137.09 (C), 143.31 (C), 166.57 (CO), 169.64 (CO), 194.46 (CO). MS (EI, 70 eV): *m/z* (%) = 290 [M^+] (33), 259 [$M^+ - CH_3O$] (26), 258 (33), 231 [$M^+ - CO_2CH_3$] (14), 230 (41), 199 (17), 172 [$M^+ - 2 \times CO_2CH_3$] (8), 134 (24), 133 [$(CH_3)_2C_6H_3CO$] (100), 105 [$(CH_3)_2C_6H_3$] (34). HRMS: *m/z* [M^+] calcd for $C_{16}H_{18}O_5$: 290.1154; found: 290.1149.

Dimethyl 2-(4-Methoxybenzoyl)cyclopropane-1,1-dicarboxylate (2d)

Yield 1.12 g (77%); colorless, fine cubic crystals, mp 59–61 °C (from MeOH); R_f = 0.46 (silica gel; Et_2O–*n*-hexane, 2:1). IR (KBr): 2954, 1737 (vs), 1732 (vs), 1667 (vs), 1599 , 1265, 1237 , 1214 , 1171 (vs), 1131, 1025 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.75 (dd, *J* = 8.4, 4.1 Hz, 1 H, CH), 2.20 (dd, *J* = 6.9, 4.1 Hz, 1 H, CH), 3.53 (dd, *J* = 8.7, 6.8 Hz, 1 H, CH), 3.69 (s, 3 H, CH_3O), 3.80 (s, 3 H, CH_3O), 3.87 (s, 3 H, CH_3O), 6.95 (d, *J* = 8.8 Hz, 2 H, arom.), 7.99 (d, *J* = 8.8 Hz, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.98 (CH_2), 30.80 (CH), 38.68 (C), 52.81 (CH_3), 53.26 (CH_3), 55.53 (CH_3), 113.88 (CH), 130.04 (CH), 130.79 (C), 163.97 (C), 166.61 (CO), 169.66 (CO), 192.93 (CO). MS (EI, 70 eV): *m/z* (%) = 292 [M^+] (36), 261 [$M^+ - CH_3O$] (24), 260 (18), 232 (30), 201 (19), 174 [$M^+ - 2 \times CO_2CH_3$] (8), 136 (24), 135 [$CH_3OC_6H_4CO$] (100), 107 [$CH_3OC_6H_4$] (19), 92 (20). HRMS: *m/z* [M^+] calcd for $C_{15}H_{16}O_6$: 292.0947; found: 292.0943.

Dimethyl 2-(2-Methoxy-5-methylbenzoyl)cyclopropane-1,1-dicarboxylate (2e)

Yield 0.95 g (62%); colorless, fine cubic crystals, mp 89–91 °C (from MeOH); R_f = 0.49 (silica gel; Et_2O–*n*-hexane, 2:1). IR (KBr): 2952, 1734 (vs), 1668 (vs), 1497 , 1437, 1285 1252 (vs), 1212, 1168, 1131 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.74 (dd, *J* = 8.7, 4.3 Hz, 1 H, CH), 2.20 (dd, *J* = 7.1, 4.2 Hz, 1 H, CH), 2.29 (s, 3 H, CH_3), 3.69 (dd, *J* = 8.5, 7.1 Hz, 1 H, CH), 3.71 (s, 3 H, CH_3O), 3.78 (s, 3 H, CH_3O), 3.87 (s, 3 H, CH_3O), 6.87–6.90 (m, H, arom.), 7.26–7.46 (m, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.21 (CH_3), 21.23 (CH_2), 35.70 (CH), 39.16 (C), 52.78 (CH_3), 53.05 (CH_3), 55.91 (CH_3), 111.8 (CH), 127.67 (C), 130.01(CH), 130.63 (C), 134.78 (CH), 157.19 (C), 166.86 (CO), 169.79 (CO), 196.72 (CO). MS (EI, 70 eV): *m/z* (%) = 306 [M^+] (19), 275 [$M^+ - CH_3O$] (13), 243 (7), 236 (9), 162 (46), 161 (13), 150 (18), 149 [CH_3, $CH_3OC_6H_3CO$] (100), 106 [$CH_3OC_6H_3$] (9), 91 (21). HRMS: *m/z* [M^+] calcd for $C_{16}H_{18}O_6$: 306.1103; found: 306.1111.

Dimethyl 2-(2-methyl-5-bromobenzoyl)cyclopropane-1,1-dicarboxylate (2f)

Yield 1.03 g (58%); colorless, fine cubic crystals, mp 92–94 °C (from MeOH); R_f = 0.61 (silica gel; Et_2O–*n*-hexane, 2:1). IR (KBr): 2953, 1744 (vs), 1728 (vs), 1666 (vs), 1436, 1295 (vs), 1220, 1184, 1145, 963 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.77 (dd, *J* = 8.5, 4.1 Hz, 1 H, CH), 2.22 (dd, *J* = 6.8, 4.1 Hz, 1 H, CH), 2.43 (s, 3 H, CH_3), 3.55 (dd, *J* = 8.7, 6.9 Hz, 1 H, $CH_)$, 3.69 (s, 3 H, CH_3O), 3.80 (s, 3 H, CH_3O), 7.26–7.31 (m, 1 H, arom.), 7.65–7.93 (m, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.12 (CH_2), 21.72 (CH_3), 30.95 (CH), 38.86 (C), 52.85 (CH_3), 53.29 (CH_3), 127.14 (C), 128.55 (CH), 129.38 (CH), 130.37 (CH), 134.51 (C), 144.56 (C), 166.56 (CO), 169.61 (CO), 194.29 (CO). MS (EI, 70 eV): *m/z* (%) = 356 [M^+, ^{81}Br] (13), 354 [M^+, ^{79}Br] (13), 325 [M^+, $^{81}BrOCH_3$] (17), 324 (27), 323 [M^+, $^{79}BrOCH_3$] (16), 322 (26), 297 [M^+, $^{81}BrCO_2CH_3$] (10), 296 (37), 295 [M^+, $^{79}BrCO_2CH_3$] (11), 294 (38), 199 [$^{81}BrCH_3C_6H_3CO$] (99), 197 [$^{79}BrCH_3C_6H_3CO$] (100), 171 [$^{81}BrCH_3C_6H_3$] (24), 169 [$^{79}BrCH_3C_6H_3$] (22), 90 (21), 89 (17). HRMS: *m/z* [M^+] calcd for $C_{15}H_{15}{}^{81}BrO_5$: 356.0082; found: 356.0066. HRMS: *m/z* [M^+] calcd for $C_{15}H_{15}{}^{79}BrO_5$: 354.0103; found: 354.0085.

Dimethyl 2-(4-Fluorobenzoyl)cyclopropane-1,1-dicarboxylate (2g)

Yield 1.02 g (73%); viscous oily liquid; R_f = 0.61 (silica gel; Et_2O–*n*-hexane, 2:1). IR (neat): 2955, 1737 (vs), 1732 (vs), 1678 (vs), 1598, 1508, 1437, 1276, 1216 (vs), 1157, 1131 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (dd, *J* = 8.7, 4.4 Hz, 1 H, CH), 2.23 (dd, *J* = 6.9, 4.4 Hz, 1 H, CH), 3.52 (dd, *J* = 8.5, 6.7 Hz, 1 H, CH), 3.69 (s, 3 H, CH_3O), 3.81 (s, 3 H, CH_3O), 7.08–7.21 (m, 2 H, arom.), 7.99–8.08 (m, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.03 (CH_2), 30.89 (CH), 39.05 (C), 52.92 (CH_3), 53.38 (CH_3), 115.90 (d, J_{C-F} = 88 Hz, CH), 131.15 (d, J_{C-F} = 38 Hz, CH), 133.43 (d, J_{C-F} = 12 Hz, C), 166.08 (d, J_{C-F} = 255 Hz, C), 166.41 (CO), 169.43 (CO), 193.18 (CO). MS (EI, 70 eV): *m/z* (%) = 280 [M^+] (7), 249 [$M^+ - CH_3O$] (38), 248 (59), 221 [$M^+ - CO_2CH_3$] (28), 220 (65), 189 (28), 162 [$M^+ - 2 \times CO_2CH_3$] (17), 133 (24), 123 [FC_6H_4CO] (100), 95 [FC_6H_4] (48). HRMS: *m/z* [M^+] calcd for $C_{14}H_{13}FO_5$: 280.0747; found: 280.0759.

Dimethyl 2-(4-Chlorobenzoyl)cyclopropane-1,1-dicarboxylate (2h)

Yield 0.79 g (53%); colorless, fine needle crystals, mp 58–60 °C (from MeOH); R_f = 0.65 (silica gel; Et_2O–*n*-hexane, 2:1). IR (neat): 2954, 1738 (vs), 1732 (vs), 1678 (vs), 1589, 1436, 1403, 1275, 1214 (vs), 1131, 1091 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (dd, *J* = 8.7, 4.4 Hz, 1 H, CH), 2.23 (dd, *J* = 6.9, 4.4 Hz, 1 H, CH), 3.50 (dd, *J* = 8.7, 6.9 Hz, 1 H, CH), 3.68 (s, 3 H, CH_3O), 3.81 (s, 3 H, CH_3O), 7.46 (d, *J* = 8.7 Hz, 2 H, arom.), 7.94 (d, *J* = 8.7 Hz, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.00 (CH_2), 30.90 (CH), 39.14 (C), 52.92 (CH_3), 53.38 (CH_3), 129.00 (C), 129.82 (CH), 135.37 (CH), 140.08 (C), 166.33 (CO), 169.39 (CO), 193.61 (CO). MS (EI, 70 eV): *m/z* (%) = 298 [M^+, ^{37}Cl] (4), 296 [M^+, ^{35}Cl] (12), 267 [M^+, $^{37}ClOCH_3$ (15)], 266 (31), 265 [M^+, $^{35}ClOCH_3$] (44), 264 (56), 239 [M^+, $^{37}ClCO_2CH_3$] (9), 238 (32), 237 [M^+, $^{35}ClCO_2CH_3$] (27), 236 (67), 207 (8), 205 (23), 180 [M^+, $^{37}Cl - 2 \times CO_2CH_3$] (5), 178 [$M^+$, $^{35}Cl - 2 \times CO_2CH_3$] (15), 141 [$^{37}ClC_6H_4CO$] (56), 139 [$^{35}ClC_6H_4CO$], (100) 113 [$^{37}ClC_6H_4$] (28), 111 [$^{35}ClC_6H_4$] (53). HRMS: *m/z* [$M^+$] calcd for $C_{14}H_{13}{}^{37}ClO_5$: 298.0422; found: 298.0409. HRMS: *m/z* [M^+] calcd for $C_{14}H_{13}{}^{35}ClO_5$: 296.0452; found: 296.0435.

Dimethyl 2-(4-Bromobenzoyl)cyclopropane-1,1-dicarboxylate (2i)

Yield 1.26 g (74%); colorless, fine powder, mp 56–58 °C (from MeOH); R_f = 0.64 (silica gel; Et_2O–*n*-hexane, 2:1). IR (neat): 2954, 1733 (vs), 1677 (vs), 1585, 1439, 1334, 1276 (vs), 1215, 1131, 1070 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (dd, *J* = 8.5, 4.4 Hz, 1 H, CH), 2.22 (dd, *J* = 6.9, 4.4 Hz, 1 H, CH), 3.49 (dd, *J* = 8.6, 6.9 Hz, 1 H, CH), 3.69 (s, 3 H, CH_3O), 3.81 (s, 3 H, CH_3O), 7.63 (d, *J* = 8.7 Hz, 2 H, arom.), 7.86 (d, *J* = 8.7 Hz, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.01 (CH_2), 30.86 (CH), 39.13 (C), 52.92 (CH_3), 53.38 (CH_3), 128.90 (C), 129.89 (CH), 131.52 (CH), 135.68 (C), 166.28 (CO), 169.33 (CO), 193.77 (CO). MS (EI, 70 eV): *m/z* (%) = 342 [M^+, ^{81}Br] (33), 340 [M^+, ^{79}Br] (34), 310 (59), 308 (58), 283 [M^+, $^{81}BrCO_2CH_3$] (100), 282 (36), 281 [M^+, $^{79}BrCO_2CH_3$] (100), 280 (37), 251 (41), 249 (39), 224 [M^+, $^{81}Br - 2 \times CO_2CH_3$] (25), 222 [$M^+$, $^{79}Br - 2 \times CO_2CH_3$] (25), 185 [$^{81}BrC_6H_4CO$] (62), 183 [$^{79}BrC_6H_4CO$] (63), 157 [$^{81}BrC_6H_4$] (28), 155 [$^{79}BrC_6H_4$] (27), 115 (30). HRMS: *m/z* [M^+] calcd for $C_{14}H_{13}{}^{81}BrO_5$: 341.9926; found: 341.9978. HRMS: *m/z* [M^+] calcd for $C_{14}H_{13}{}^{79}BrO_5$: 339.9946; found: 339.9952.

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