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Iodobenzene-Catalyzed Oxidative Cyclization for the Synthesis of Highly Functionalized Cyclopropanes

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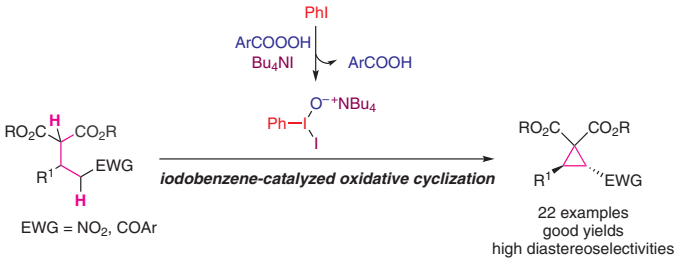

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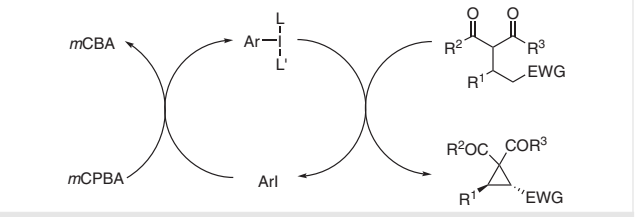
Abstract An iodobenzene-catalyzed oxidative cyclization of Michael adducts of activated methylene compounds with nitroolefins or chalcones is developed. *m*CPBA is used as oxidant together with Bu_4NI for the generation of a highly reactive iodine(III) species to mediate the cyclopropanation via a ligand exchange and reductive elimination process. A range of highly functionalized cyclopropanes are synthesized with high diastereoselectivities.

Key words iodobenzene, cyclization, cyclopropane, iodine, oxidation

Cyclopropanes are frequently found as basic skeletons in a wide range of biologically active natural compounds and pharmaceuticals.[1] Moreover, as highly constrained cycles, they are versatile intermediates to undergo various transformations for the synthesis of cyclic and acyclic compounds.[2] In last decades, great effort have been devoted to develop efficient methods for their synthesis.[3] Among these methods, oxidative cyclization is one of the most straightforward way to access these three-membered cyclic compounds because the desired carbon–carbon bonds can be formed directly from two carbon–hydrogen bonds without extra chemical transformations.[4] Recently, we reported an iodine(III)-mediated oxidative cyclization for the synthesis of a variety of cyclic compounds. In this transformation, hypervalent iodine compounds such as $PhI(OAc)_2$, $PhI(OCOCF_3)_2$, or PhIO were used together with tetrabutylammonium salts such as Bu_4NI or Bu_4NBr to mediate oxidative cyclization via a ligand exchange and reductive elimination process.[5] However, the use of stoichiometric amount of or even excess amounts of hypervalent iodine compounds are required, and equimolecular amounts of iodoarenes are produced as waste. These issues have apparently limited the application of this reaction in scalable reactions.

On the other hand, since the first example reported by Fuchigami and Fujita in 1994,[6] iodobenzene-catalyzed reaction has attracted great interest of chemists. Various chemical transformations, such as α-acetoxylation of ketones,[7] functionalization of alkenes and alkynes,[8] oxidation of alcohols,[9] or enantioselective dearomatization reactions,[10] can be catalyzed by iodobenzene or chiral iodoarenes. In this paper, we report on an iodobenzene-catalyzed oxidative cyclization for the synthesis of highly functionalized cyclopropanes using *m*CPBA as oxidant together with Bu_4NI (Scheme 1).



Scheme 1 Iodobenzene-catalyzed oxidative cyclization for the synthesis of highly functionalized cyclopropanes

In search of suitable catalyst and reaction conditions, a Michael adduct of dimethyl malonate with nitroolefin was used as the standard substrate. In an initial test, 0.2 equivalent of iodobenzene was used together with 1.2 equivalents *m*-chloroperoxybenzoic acid (*m*CPBA) and 1.2 equivalents Bu_4NI; the desired cyclopropane **2**a was isolated from the reaction using 2,2,2-trifluroethanol as the solvent, albeit in a low yield (Table 1, entry 1). The addition of 1 equivalent of *t*BuOK increased the yield to 51% (entry 2). When peroxyacetic acid ($MeCO_3H$) or hydrogen peroxide (H_2O_2) was used instead of *m*CPBA, the formation of **2** was not observed (entries 3 and 4). When Bu_4NI was replaced by KI or NaI, the yield decreased dramatically (entries 5 and 6). The use of KOH, NaH, or CF_3CH_2OK did not give better yields (entries 7–9). The catalytic efficiency of a range of iodoarenes was

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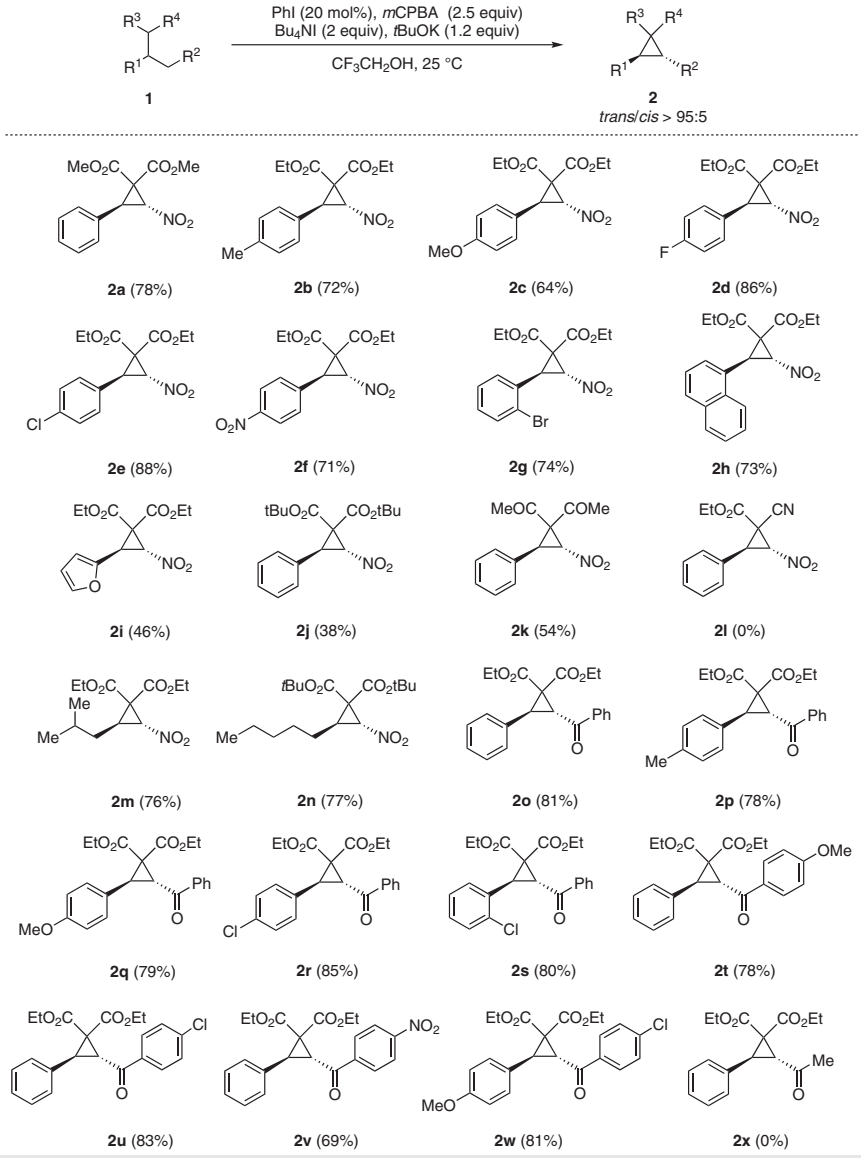
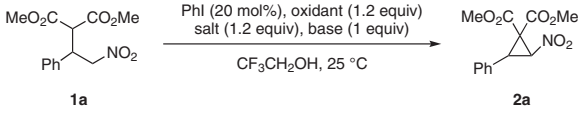
evaluated (entries 10–15), and iodobenzene proved to be the best catalyst (entry 16). The generation of iodine was observed in the reaction. The reaction in the presence of 0.2 equivalent of Bu_4NI afforded only **2a** in 11% yield. No reaction occurred in the absence of Bu_4NI. The best ratio of substrate, PhI, *m*CPBA, Bu_4NI, and *t*BuOK was 1:0.2:2.5:2:1.2, improving the yield to 78% (entry 16). The relative *trans*-stereochemistry was confirmed by ^1H NMR analysis.

The scope of the present iodobenzene-catalyzed oxidative cyclopropanation was investigated under the optimized conditions and these results are summarized in Scheme 2. Reaction of a range of Michael adducts of activated methylene compounds with nitroolefins proceeded smoothly leading to the formation of the corresponding cyclopropanes in good yields with high diastereoselectivities. The reaction was found to tolerate a range of substituents with different electronic demands on the aryl group of substrates, and a moderate electronic substrate effect was observed. Reaction of substrates bearing an electron-withdrawing substituent gave better yields than reactions of those bearing an electron-donating substituent. For example, reaction of 4-methoxylphenyl-substituted Michael adduct afforded **2c** in 64% yield, while the reaction of 4-chloro- or 4-nitrophenyl-substituted Michael adduct afforded **2e** and **2f** in 88% or 71% yield, respectively. Reaction of substrates derived from aliphatic nitroolefins also proceeded smoothly leading to the formation of **2m** and **2n** in



Scheme 2 Reaction scope investigation

Table 1 Evaluation of Catalysts and Conditions

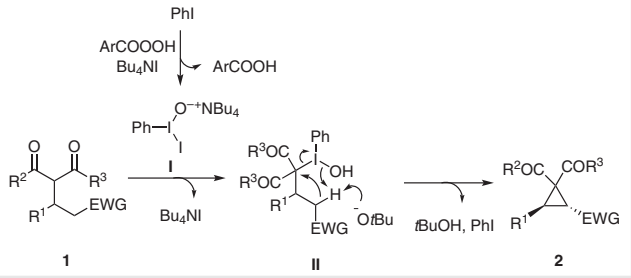


1a 2a

Entry	ArI	Oxidant	Salt	Base	**2a** Yield (%)[a]
1	PhI	*m*CPBA	Bu_4NI		26
2	PhI	*m*CPBA	Bu_4NI	*t*BuOK	51
3	PhI	AcOOH	Bu_4NI	*t*BuOK	0
4	PhI	H_2O_2	Bu_4NI	*t*BuOK	0
5	PhI	*m*CPBA	KI	*t*BuOK	32
6	PhI	*m*CPBA	NaI	*t*BuOK	36
7	PhI	*m*CPBA	Bu_4NI	KOH	22
8	PhI	*m*CPBA	Bu_4NI	NaH	45
9	PhI	*m*CPBA	Bu_4NI	CF_3CH_2OK	49
10	2-PhC_6H_4I	*m*CPBA	Bu_4NI	*t*BuOK	41
11	2-MeC_6H_4I	*m*CPBA	Bu_4NI	*t*BuOK	47
12	4-MeC_6H_4I	*m*CPBA	Bu_4NI	*t*BuOK	43
13	4-$MeOC_6H_4I$	*m*CPBA	Bu_4NI	*t*BuOK	31
14	4-ClC_6H_4I	*m*CPBA	Bu_4NI	*t*BuOK	27
15	4-BrC_6H_4I	*m*CPBA	Bu_4NI	*t*BuOK	28
16[b]	PhI	*m*CPBA	Bu_4NI	*t*BuOK	78

[a] Isolated yields.
[b] *m*CPBA (2.5 equiv), Bu_4NI (2 equiv), and *t*BuOK (1.2 equiv) were used.

76% and 77% yield, respectively. When the sterically hindered di-*tert*-butyl malonate derivative was employed, cyclopropane **2j** was obtained in a low yield. While the reaction of 2,4-pentanedione derivative gave **2k** in moderate yield, the reaction of malononitrile derivative did not occur. Michael adducts of malonate with chalcones were all suitable substrates affording the corresponding highly functionalized cyclopropanes **2o–w** in good yields. When the substrate derived from 4-phenylbut-3-en-2-one was employed, the reaction is complex, and the formation of cyclopropane **2x** was not observed.



Scheme 3 Proposed reaction pathway

A proposed reaction pathway for the iodobenzene-catalyzed oxidative cyclopropanation is shown in Scheme 3. The oxidation of iodobenzene by *m*CPBA in the presence of Bu_4NI leads to the in situ generation of an iodine(III) species **I**. Michael adduct reacts with this highly reactive iodine(III) compound via a ligand exchange reaction to form an intermediate **II**. With the aid of base, the reductive elimination of this intermediate affords the highly functionalized cyclopropanes and regenerates iodobenzene.

In conclusion, we have developed an iodobenzene-catalyzed oxidative cyclization of Michael adducts of activated methylene compounds with nitroolefins or chalcones for the synthesis of highly functionalized cyclopropanes. *m*CPBA is used as oxidant together with Bu_4NI to generate a highly reactive iodine(III) species to mediate the cyclopropanation via a ligand exchange and reductive elimination process. The current direction for future research is aimed at extending the scope and potential synthesis applications, as well as investigation of asymmetric transformations.

All reactions were performed in Schlenk tubes under N_2 atmosphere. Flash column chromatography was performed using silica gel (60 Å pore size, 32–63 μm, standard grade). Analytical TLC was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. NMR spectra are recorded in parts per million from internal TMS on the δ scale.

Highly Functionalized Cyclopropanes; General Procedure

In a round-bottomed flask, a solution of Michael adduct **1** (0.1 mmol) in CF_3CH_2OH (2 mL) was mixed with PhI (0.02 mmol), *m*CPBA (0.25 mmol), Bu_4NI (0.2 mmol), and *t*BuOK (0.12 mmol). The reaction was allowed to stir at 25 °C for 12 h. Upon completion of the reaction (monitored by TLC), the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (5–15% EtOAc in hexanes) to provide the corresponding cyclopropane **2**.

Dimethyl 2-Nitro-3-phenylcyclopropane-1,1-dicarboxylate (2a)[11]

Yield: 22 mg (78%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.34 (m, 3 H), 7.27–7.30 (m, 2 H), 5.37 (d, *J* = 6.0 Hz, 1 H), 4.19 (d, *J* = 6.0 Hz, 1 H), 3.85 (s, 3 H), 3.55 (s, 3 H).

Diethyl 2-Nitro-3-*p*-tolylcyclopropane-1,1-dicarboxylate (2b)[12]

Yield: 23 mg (72%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 8.2 Hz, 2 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 5.39 (d, *J* = 6.0 Hz, 1 H), 4.28–4.35 (m, 2 H), 4.17 (d, *J* = 6.0 Hz, 1 H), 3.96–4.05 (m, 2 H), 2.32 (s, 3 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 1.01 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-(4-Methoxyphenyl)-3-nitrocyclopropane-1,1-dicarboxylate (2c)[5b]

Yield: 21 mg (64%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.7 Hz, 2 H), 6.875 (d, *J* = 8.7 Hz, 2 H), 5.38 (d, *J* = 6.0 Hz, 1 H), 4.29–4.37 (m, 2 H), 4.15 (d, *J* = 6.0 Hz, 1 H), 4.01–4.06 (m, 2 H), 3.79 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H), 1.05 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-(4-Fluorophenyl)-3-nitrocyclopropane-1,1-dicarboxylate (2d)[5b]

Yield: 28 mg (86%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.30 (m, 2 H), 7.02–7.08 (m, 2 H), 5.39 (d, *J* = 6.0 Hz, 1 H), 4.28–4.35 (m, 2 H), 4.15 (d, *J* = 6.0 Hz, 1 H), 3.99–4.07 (m, 2 H), 1.31 (t, *J* = 7.1 Hz, 3 H), 1.03 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-(4-Chlorophenyl)-3-nitrocyclopropane-1,1-dicarboxylate (2e)[5b]

Yield: 30 mg (88%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.2 Hz, 2 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 5.36 (d, *J* = 6.2 Hz, 1 H), 4.28–4.35 (m, 2 H), 4.15 (d, *J* = 6.1 Hz, 1 H), 3.98–4.08 (m, 2 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 1.05 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-Nitro-3-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (2f)[5b]

Yield: 25 mg (71%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.7 Hz, 2 H), 7.52 (d, *J* = 8.7 Hz, 2 H), 5.44 (d, *J* = 6.2 Hz, 1 H), 4.26–4.38 (m, 2 H), 4.25 (d, *J* = 6.2 Hz, 1 H), 4.02–4.10 (m, 2 H), 1.33 (t, *J* = 7.1 Hz, 3 H), 1.07 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-(2-Bromophenyl)-3-nitrocyclopropane-1,1-dicarboxylate (2g)[5b]

Yield: 28 mg (74%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.2 Hz, 1 H), 7.28–7.33 (m, 1 H), 7.21 (t, *J* = 7.3 Hz, 2 H), 5.35 (d, *J* = 6.0 Hz, 1 H), 4.30–4.37 (m, 2 H), 4.18 (d, *J* = 6.0 Hz, 1 H), 4.04–4.10 (m, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H), 1.06 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-(Naphthalen-1-yl)-3-nitrocyclopropane-1,1-dicarboxylate (2h)[5b]

Yield: 26 mg (73%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 8.2 Hz, 1 H), 7.79–7.85 (m, 2 H), 7.62 (t, *J* = 8.1 Hz, 1 H), 7.51 (t, *J* = 8.1 Hz, 1 H), 7.38–7.42 (m, 2 H), 5.58 (d, *J* = 6.1 Hz, 1 H), 4.53 (d, *J* = 6.1 Hz, 1 H), 4.41 (q, *J* = 7.2 Hz, 2 H), 3.66–3.75 (m, 2 H), 1.35 (t, *J* = 7.2 Hz, 3 H), 0.56 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-(Furan-2-yl)-3-nitrocyclopropane-1,1-dicarboxylate (2i)[5b]

Yield: 14 mg (46%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 2.0 Hz, 1 H), 6.34 (dd, *J* = 3.8, 2.0 Hz, 1 H), 6.32 (d, *J* = 3.7 Hz, 1 H), 5.35 (d, *J* = 6.0 Hz, 1 H), 4.25–4.34 (m, 2 H), 4.10–4.18 (m, 2 H), 4.08 (d, *J* = 6.0 Hz, 1 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 1.15 (t, *J* = 7.1 Hz, 3 H).

Di-*tert*-butyl 2-Nitro-3-phenylcyclopropane-1,1-dicarboxylate (2j)[5b]

Yield: 14 mg (38%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.37 (m, 5 H), 5.32 (d, *J* = 6.0 Hz, 1 H), 4.12 (d, *J* = 6.0 Hz, 1 H), 1.51 (s, 9 H), 1.21 (s, 9 H).

2-Nitro-3-phenylcyclopropane-1,1-diylbis(ethan-1-one) (2k)[5b]

Yield: 13 mg (54%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ =7.33–7.421 (m, 3 H), 7.22–7.26 (m, 2 H), 5.77 (d, *J* = 2.0 Hz, 1 H), 4.66 (d, *J* = 2.0 Hz, 1 H), 2.56 (s, 3 H), 2.05 (s, 3 H).

Diethyl 2-Isobutyl-3-nitrocyclopropane-1,1-dicarboxylate (2m)[5b]

Yield: 22 mg (76%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.85 (d, *J* = 8.0 Hz, 0.37 H), 4.80 (d, *J* = 5.9 Hz, 0.63 H), 4.17–4.34 (m, 4 H), 2.88 (dd, *J* = 7.3, 5.9 Hz, 0.63 H), 2.04–2.14 (m, 0.74 H), 1.66–1.74 (m, 1.26 H), 1.41–1.53 (m, 1.37 H), 1.24–1.31 (m, 6 H), 0.89–0.99 (m, 6 H).

Diethyl 2-Nitro-3-pentylcyclopropane-1,1-dicarboxylate (2n)[5b]

Yield: 27 mg (77%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.84 (d, *J* = 7.8 Hz, 0.41 H), 4.79 (d, *J* = 6.1 Hz, 0.59 H), 4.20–4.33 (m, 4 H), 2.87 (td, *J* = 7.3, 6.2 Hz, 0.59 H), 2.09–2.15 (m, 0.82 H), 1.80–1.87 (m, 0.41 H), 1.48–1.66 (m, 1.18 H), 1.24–1.33 (m, 12 H), 0.85–0.91 (m, 3 H).

Diethyl 2-Benzoyl-3-phenylcyclopropane-1,1-dicarboxylate (2o)[13]

Yield: 30 mg (81%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.5 Hz, 2 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 7.267–7.34 (m, 5 H), 4.12–4.17 (m, 3 H), 4.00 (q, *J* = 7.1 Hz, 2 H), 3.90 (d, *J* = 7.8 Hz, 1 H), 1.11 (t, *J* = 7.1 Hz, 3 H), 0.98 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-Benzoyl-3-*p*-tolylcyclopropane-1,1-dicarboxylate (2p)[5c]

Yield: 30 mg (78%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.2 Hz, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.50 (t, *J* = 7.3 Hz, 2 H), 7.20 (d, *J* = 7.8 Hz, 2 H), 7.12 (d, *J* = 7.8 Hz, 2 H), 4.15(q, *J* = 7.2 Hz, 2 H), 4.09 (d, *J* = 7.8 Hz, 1 H), 3.98–4.05 (m, 2 H), 3.85 (d, *J* = 7.8 Hz, 1 H), 2.33 (s, 3 H), 1.12 (t, *J* = 7.1 Hz, 3 H), 1.01 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-Benzoyl-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (2q)[5c]

Yield: 31 mg (79%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09–8.12 (m, 2 H), 7.63 (t, *J* = 7.3 Hz, 1 H), 7.52 (t, *J* = 7.3 Hz, 2 H), 7.21 (d, *J* = 8.8 Hz, 2 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 4.07 (d, *J* = 7.8 Hz, 1 H), 4.00–4.06 (m, 2 H), 3.84 (d, *J* = 7.8 Hz, 1 H), 3.78 (s, 3 H), 1.12 (t, *J* = 7.2 Hz, 3 H), 1.01 (t, *J* = 7.2 Hz, 3 H).

Diethyl 2-Benzoyl-3-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (2r)[5c]

Yield: 34 mg (85%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.2 Hz, 2 H), 7.60 (t, *J* = 7.2 Hz, 1 H), 7.50 (t, *J* = 7.3 Hz, 2 H), 7.20–7.30 (m, 4 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 4.09 (d, *J* = 7.8 Hz, 1 H), 4.01–4.08 (m, 2 H), 3.86 (d, *J* = 7.8 Hz, 1 H), 1.10 (t, *J* = 7.1 Hz, 3 H), 1.03 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-Benzoyl-3-(2-chlorophenyl)cyclopropane-1,1-dicarboxylate (2s)[5c]

Yield: 32 mg (80%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 7.3 Hz, 2 H), 7.60 (t, *J* = 7.3 Hz, 1 H), 7.53 (t, *J* = 7.3 Hz, 2 H), 7.34–7.40 (m, 1 H), 7.20–7.25 (m, 3 H), 4.12–4.18 (m, 3 H), 4.01–4.08 (m, 2 H), 3.96 (d, *J* = 7.6 Hz, 1 H), 1.11 (t, *J* = 7.1 Hz, 3 H), 1.03 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-(4-Methoxybenzoyl)-3-phenylcyclopropane-1,1-dicarboxylate (2t)[5c]

Yield: 31 mg (78%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.6 Hz, 2 H), 7.27–7.34 (m, 5 H), 6.98 (d, *J* = 8.7 Hz, 2 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 4.08 (d, *J* = 7.8 Hz, 1 H), 4.00 (q, *J* = 7.1 Hz, 2 H), 3.83–3.89 (m, 4 H), 1.11 (t, *J* = 7.1 Hz, 3 H), 0.987 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-(4-Chlorobenzoyl)-3-phenylcyclopropane-1,1-dicarboxylate (2u)[5c]

Yield: 33 mg (83%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.8 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.27–7.33 (m, 5 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 4.05 (d, *J* = 7.8 Hz, 1 H), 4.01 (q, *J* = 7.1 Hz, 2 H), 3.90 (d, *J* = 7.8 Hz, 1 H), 1.13 (t, *J* = 7.1 Hz, 3 H), 0.99 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-(4-Nitrobenzoyl)-3-phenylcyclopropane-1,1-dicarboxylate (2v)[5c]

Yield: 28 mg (69%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.6 Hz, 2 H), 8.27 (d, *J* = 8.6 Hz, 2 H), 7.27–7.35 (m, 5 H), 4.12–4.19 (m, 2 H), 4.09 (d, *J* = 7.8 Hz, 1 H), 4.03 (q, *J* = 7.1 Hz, 2 H), 3.92 (d, *J* = 7.8 Hz, 1 H), 1.13 (t, *J* = 7.1 Hz, 3 H), 1.01 (t, *J* = 7.1 Hz, 3 H).

Diethyl 2-(4-Chlorobenzoyl)-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (2w)[5c]

Yield: 35 mg (81%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.3 Hz, 2 H), 7.49 (d, *J* = 8.3 Hz, 2 H), 7.21 (d, *J* = 8.6 Hz, 2 H), 6.83 (d, *J* = 8.6 Hz, 2 H), 4.11–4.16 (m, 2 H), 4.00–4.06 (m, 3 H), 3.82 (d, *J* = 7.8 Hz, 1 H), 3.78 (s, 3 H), 1.11 (t, *J* = 7.1 Hz, 3 H), 1.02 (t, *J* = 7.1 Hz, 3 H).

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Supporting Information

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