JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • Publication Date (Web): 19 Dec 2018

ACS Publications

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Lewis Acid Catalyzed Nucleophilic Ring Opening and 1,3-Bisfunctionalization of Donor-Acceptor Cyclopropanes with Hydroperoxides: Access to Highly Functionalized Peroxy/(α-Heteroatom Substituted)Peroxy Compounds

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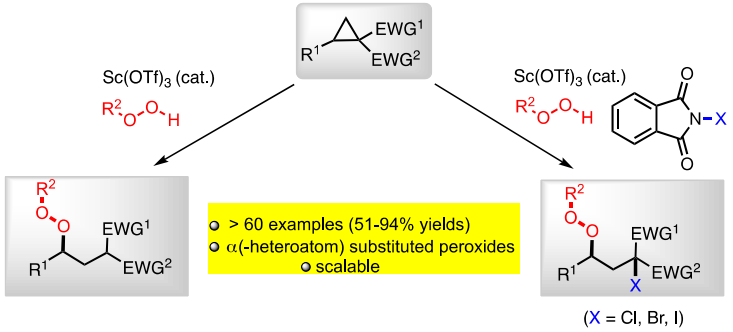
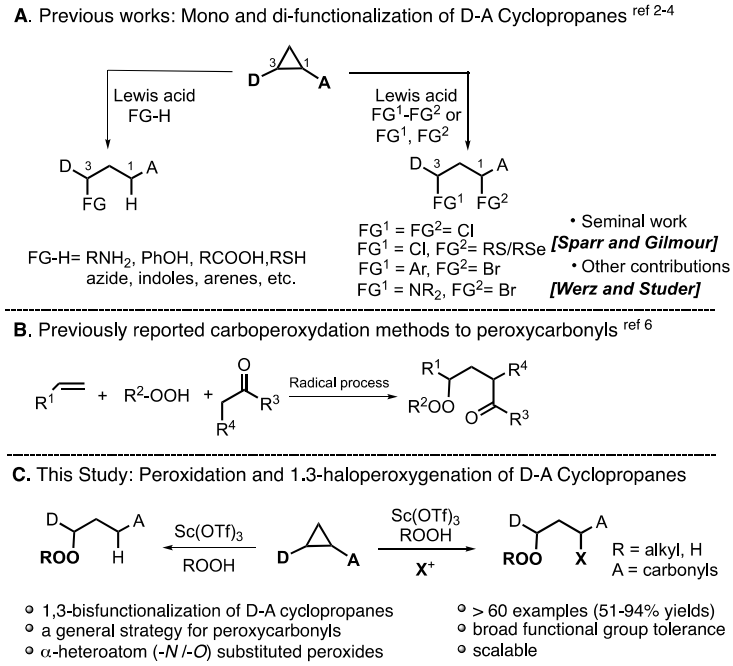


ABSTRACT: The Lewis acid catalyzed ring opening reaction of Donor-Acceptor (D-A) cyclopropanes with alkyl hydroperoxides is reported to furnish various peroxycarbonyls and 1,3-haloperoxygenated compounds in good to excellent yields. This method adds another instance to scarcely reported noncyclilizing 1,3-bisfunctionalization of D-A cyclopropanes with two different functional groups and is relied on the dual role of peroxide as nucleophile and oxidant through an orchestrated reaction sequence. The products obtained including α-heterosubstituted peroxy compounds, are amenable to useful synthetic elaboration

INTRODUCTION

Donor-Acceptor (D-A) cyclopropanes have emerged as versatile three carbon building blocks in modern organic synthesis.[1] Myriad of catalytic methodologies have been developed engaging D-A cyclopropanes in various reactions including nucleophilic ring opening processes, [3+n] cycloadditions and rearrangements. In the ring-opening reactions, generally the nucleophilic addition first occurs at the emerging positively charged centre at C3 adjacent to the donor group, and the ensuing negative charge at C1 is being neutralized through capture of a proton. Different amines, phenols, thiols, carboxylic acids, azide, electron-rich arenes and indoles have been employed to realize this chemistry (Scheme 1A, left panel) with the assistance of a either Lewis or BrØnsted acid as catalyst.[2,3] On the facet of this conventional ring opening processes to open chain structures, few elegant strategies have emerged recently that promoted 1,3-bisfunctionalization through concomitant functionalization of C1 with non-proton electrophiles (Scheme 1A, right panel).[4] Although promising, the underlying challenges with this particular reaction avenue lie in finding, either a suitable single reagent that formally bears E^+ and Nu^- components within self or a pair of (non-self reacting) nucleophile and electrophile, which can engage themselves compatibly and synchronously with the activation process of D-A cyclopropane. These constrains in fact mostly contributed to the dearth of such transformations.

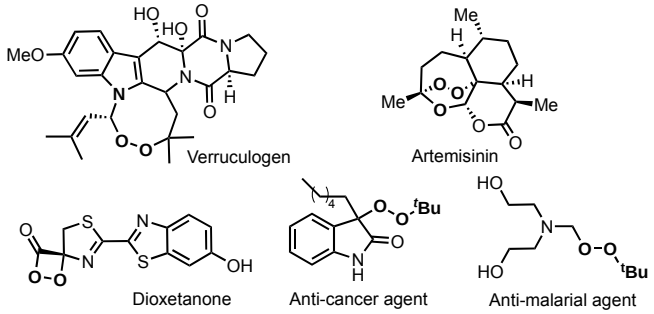
Scheme 1. Our Strategy and Early Precedents On Ring-Opening Reactions of D-A Cyclopropanes and Synthesis of Peroxycarbonyls



In this context, Sparr and Gilmour led the seminal work on 1,3-dichlorination of aldehyde-substituted cyclopropanes.[4a] Subsequently, Werz disclosed the use of Willgerodt's reagent ($PhICl_2$) and sulfenyl/selenyl halides for 1,3-dichlorination and halochalcogenation[4b-d] of D-A cyclopropanes, respectively. These methods utilized a single reagent for the desired bisfunctionalization step. Studer reported the use of distinct electrophilic and nucleophilic reagents to realize arylamination and aminobromination in a multicomponent fashion.[4e-f] Despite of these recent developments, simultaneous introduction of two different functional groups at the two reactive centres of D-A cyclopropane to open chain form is largely remained as an unmet challenge.

Structurally distinct classes of peroxide bearing skeletons have received considerable attention in recent years due to their potential biological activities (Figure 1) and uses in the downstream synthetic transformations to important derivatives.[5-8] Of particular significance are the different peroxycarbonyls[7] and α-heteroatom substituted peroxides.[5,7] While there has been a growing interest to exploit the synthetic benefits of peroxycarbonyls, reported protocols for their preparation to date are mostly centered on transition metal catalyzed carboperoxidation of olefins[6b-h] *via* radical processes, which in many cases, suffer from poor yields and limited substrate scope.

Figure 1. Natural products and bioactive molecules bearing peroxy group as pharmacophore



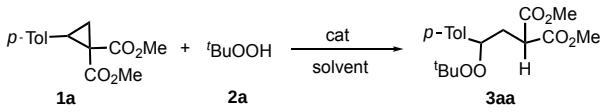
Conceptually, addition of hydroperoxides to D-A cyclopropanes or aminocyclopropanes could enable the assembly of aforementioned peroxy-compounds which however previously reported to be unsuccessful.[6f] Use of peroxide as nucleophile is somewhat tempered due to their oxidizing properties. On the upside, we envisaged that the oxidative property might be leveraged for the *in situ* generation of an electrophilic species (X^+), to be captured at C1. Thus, the overall process would constitute a unified approach to transform D-A cyclopropanes into the acyclic bisfunctionalized derivatives. In fact, such process would be much desired over a stepwise 1,3-functionalization method for practical aspects.[9] We herein report a catalytic, highly efficient and general strategy for the synthesis of various γ-peroxycarbonyls (some bearing the α-"*N*" orα-"*O*"-peroxy moiety) *via*

addition of hydroperoxides to activated D-A cyclopropanes and furthermore this process can be telescoped for the subsequent α-halogenation (C1 functionalization).

RESULTS AND DISCUSSION

We first decided to explore the feasibility of the ring-opening of D-A cyclopropanes with alkyl hydroperoxides before stepping into 1,3-difunctionalizations. We commenced the study with cyclopropane **1a** (1.0 equiv) and *tert*-butylhydroperoxide (**2a**; 2.0 equiv) in presence of various catalysts and solvents (Table 1, see Supporting Information for more details). Use of BrØnsted acids proved to be completely ineffective for the transformation (not shown in Table 1). We next turned our attention to various metal Lewis acids. First we examined nickel(II) catalysts, which however didn't provide any desired product in our case (entries 1-2). Pleasingly, changing the Lewis acid to $Sc(OTf)_3$, desired product **3aa** was obtained, albeit in low yield (entry 3).

Table 1. Optimization of the Hydroperoxide Addition[a]



1a **2a** **3aa**

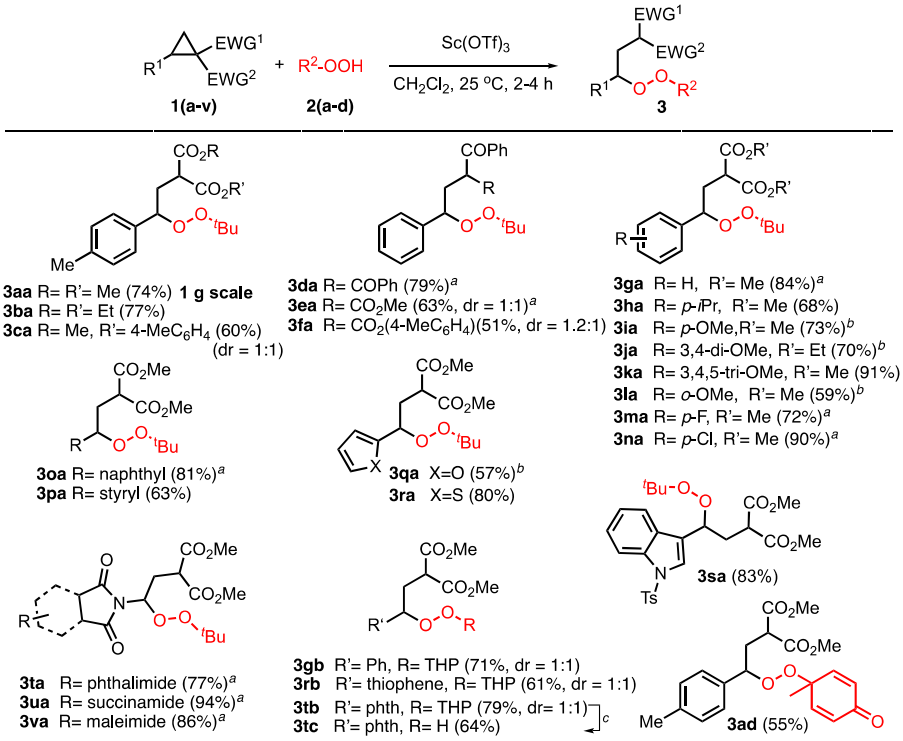
Entry	Cat.	[*mol*%]	TBHP[*equiv.*]	Solvent	Conc[M][b]	Yield[%][c]
1	$Ni(ClO_4)_2.6H_2O$	10	2.0	DCM	0.2	0
2	$NiCl_2$	10	2.0	DCM	0.2	0
3	$Sc(OTf)_3$	10	2.0	DCM	0.2	20
4	$Sc(OTf)_3$	10	5.0	DCM	0.2	N.D[d]
5	$Sn(OTf)_2$	10	5.0	DCM	0.2	0
6	$Yb(OTf)_3$	10	5.0	DCM	0.2	0
7	$In(OTf)_3$	10	5.0	DCM	0.2	25
8	MgI_2	10	5.0	DCM	0.2	0
9	$Bi(OTf)_3$	10	5.0	DCM	0.2	0
10	$Cu(OTf)_2$	10	5.0	DCM	0.2	0
11	$Sc(OTf)_3$	10	5.0	THF	0.2	5
12	**$Sc(OTf)_3$**	**10**	**10**	**DCM**	**2.0**	**73**
13	$Sc(OTf)_3$	5	10	DCM	2.0	62[e]
14	$Sc(OTf)_3$	20	10	DCM	2.0	71

[a]Reaction conditions: **1a** (1.0 equiv), **2a** (2-10 equiv), cat (10-20 mol%), solvent (0.2-2.0 M), reaction time (2 h). Reactions were carried out at room temperature. [b]Concentration of **1a** in the particular reaction solvent. [c]Yields of the isolated products. [d]N.D = Not Determined (the product was mixed with unknown impurity).[e]Reaction time was 20 h.

Increasing the equivalents of TBHP (5 equiv) in the reaction significantly improved the conversion (*ca*. 50%), however in this case, the desired product was contaminated with an inseparable impurity (entry 4). Several other Lewis acids (e.g., $Sn(OTf)_2$, $Yb(OTf)_3$, $In(OTf)_3$, MgI_2, $Bi(OTf)_3$, $Cu(OTf)_2$ etc.) were screened, which were largely ineffective for this reaction (entries 5-10). At this stage, $Sc(OTf)_3$ was chosen as the most promising catalyst for further optimization studies. Subsequently, other parameters such as solvent (entry 11), catalyst loading and temperature were varied (see SI for details), which in fact didn't prove beneficial. Gratifyingly, adding 10 equivalents of TBHP and maintaining a higher concentration of substrate in DCM (2.0 M), a clean conversion of **3aa** was reproducibly obtained with 73% yield (entry 12). While lower loading of the catalyst slowed down the reaction (entry 13), higher catalyst loading (20 mol%) did not show any further improvement in the yield (71%, entry 14).

With the optimized conditions in hand, we subsequently investigated the scope of this transformation (Scheme 2). Variation in the ester moieties (**3ba-3ca**) or even use of diketone (**3da**) or ketoester moiety (**3ea-3fa**) was well tolerated.[10] Next, the electronic and steric effects of substituted aryl groups as the donor moiety on D-A cyclopropanes were examined.

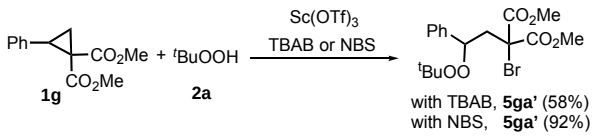
Scheme 2. Scope of Hydroperoxide Addition to D-A Cyclopropanes



Reaction conditions: cyclopropane (1 equiv), peroxide (10 equiv), $Sc(OTf)_3$ (10 mol %), DCM (2.0 M). Yields of isolated products are given. [a]20 mol % catalyst was used. [b]Reaction was done at 0 °C. [c]*p*TsOH (1 equiv.), MeOH.

Presence of different weak and strong electron donating groups (**3ga-3ka**) or halogen substitution (**3ma-3na**) didn't show any marked difference in reactivity, and afforded the products in good to excellent yields (70-91%) except the *o*-OMe substituted compound (**3la**), which could be correlated to steric effects. Donor groups having extended π-framework (**3oa-3pa**) or heterocyclic moieties (**3qa-3ra**) were successfully employed in our methodology. We also evaluated indole-derived D-A cyclopropanes in the reaction. While the *N*-methyl protected compound was deteriorated in the reaction (not shown in the scheme), *N*-tosyl protected congener provided the desired product (**3sa**) in very high yield (83%), indicating that electron-donating substituent on indole nitrogen would not be tolerated. Promising biological activities of the α-hetero substituted peroxy compounds prompted us to examine D-A amino cyclopropanes bearing *N*-phthaloyl, *N*-succinimidyl and *N*-maleimido donor moieties in the reaction. To our satisfaction, products **3ta**-**3va** were obtained in good to excellent yields (77-94%). Use of tetrahydropyranyl (THP) hydroperoxide in the reaction was also successful (**3gb**, **3rb** and **3tb).** Importantly, **3tb** could serve as the surrogates for free hydroperoxide; deprotection of THP group resulted in the formation of **3tc** in 64% yield. Furthermore, the methodology also allowed addition of *p*-peroxyquinol which afforded more complex **3ad** in moderate yield. A gram scale preparation of **3aa** furnished 74% yield, highlighting the practicability of the current method.

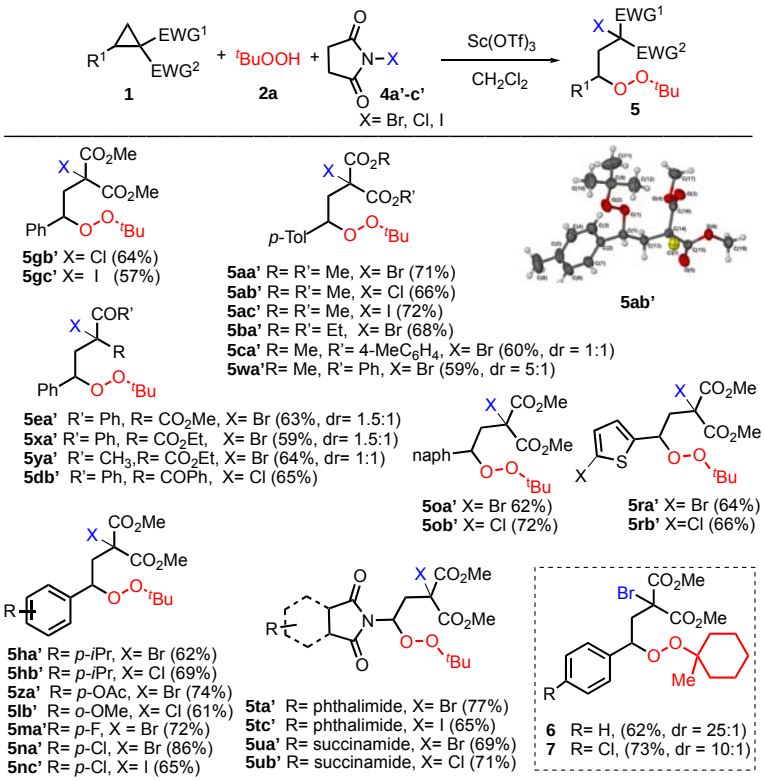
Scheme 3. 1,3-Bromoperoxygenation With Different Brominating Agents



Intrigued by the remarkable success achieved on ring-opening peroxidation at C3, we next pursued direct 1,3-halogenation-peroxidation in presence of hydroperoxide and appropriate halogenating agent. We first considered the avenue to generate the desired electrophile *in situ* through an umpolung process with the aid of TBHP. Thus, tetrabutylammonium bromide (TBAB) was chosen first to affect C1 bromination of **1g** subsequent to peroxide addition at C3 (Scheme 3). To our delight, the concept of umpolung halide[11] worked quite neatly and afforded **5ga'** in 58% yield. Use of *N*-bromosuccinimide (NBS) however displayed much higher reactivity, providing **5ga'**

in excellent yield (92%). Importantly, in the absent of TBHP, reaction between peroxy-addition product **3ga** and NBS didn't give rise to **5ga'**, which indicates the synergistic effects between reaction components and reagents in the overall transformation. The malonate proton signal at δ 3.55 ppm in **3ga** was absent in **5ga'**, which confirmed the site selective bromination at C1 in the later compound. This was additionally analysed and confirmed by 2D-NMR studies. Subsequently, we examined the scope of this 1,3-bisfunctionalization with various D-A cyclopropanes (Scheme 4). Akin to peroxidation-bromination, chlorination and iodination could also be achieved with NCS and NIS in reasonable yields (**5gb'-5gc'**). Anticipating that the acceptor groups might play crucial roles during the C1 functionalization step, various diesters (**5aa'-5ac'**, **5ba'-5ca'**and **5wa')** ketoesters and diketone (**5ea'**, **5xa'-5ya'** and **5db'**) were evaluated. In fact, all the compounds underwent smooth transformation, indicating a broad choice for the adjacent acceptor groups that could be accommodated in D-A cyclopropanes for our method. During the 1,3-haloperoxygenation process, no significant difference in reactivity was found between electron donating (**5ha'-5hb'**, **5za', 5lb')** and halogen substituted compounds **(5ma'**,**5na'**and **5nc'**); desired products were isolated in good to high yields (61-86%).

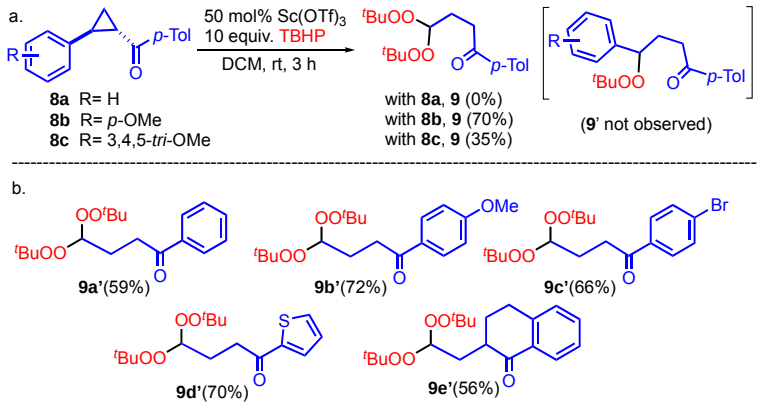
Scheme 4. Scope of 1,3-Halo-Peroxygenation



Reaction conditions: D-A cyclopropane (1 equiv), **2** (10.0 equiv), $Sc(OTf)_3$ (10 or 20 mol %), NXS (1.5 equiv, X = Br, Cl, I), DCM (2.0 M). [a]Reaction was performed at 0 °C.

Use of naphthyl-substituted compound afforded smooth transformation (**5oa'-5ob'**), whereas reaction with thienyl donor was not site selective; additional ring halogenation was obtained in both the cases (**5ra'-5rb'**). Different amino cyclopropanes reacted consistently with halogenating agents furnishing halogenated α-amino peroxy products (**5ta'-5tc'**, **5ua'-5ub'**). Apart from TBHP, methylcyclohexyl hydroperoxide also provided the desired bis-functionalized compounds (**6-7**) in good yields.

Scheme 5. Hydroperoxide Addition to Substituted α-Cyclopropylketones

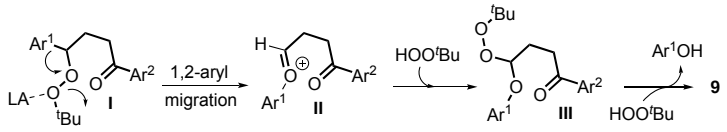


At this juncture, hydroperoxide addition to D-A cyclopropanes, bearing a single ketone functional group as acceptor, was evaluated (Scheme 5). This class of DAC exhibits different reactivity and not widely been used in catalytic cyclopropane methodologies. Initially, we employed **8a-8c** under the optimized reaction conditions (using 10 mol% $Sc(OTf)_3$), which however failed to give any hydroperoxide addition product. With **8b**, two-fold increase in catalyst loading provided a new compound in 10% yield, which was characterized to be ageminal bisperoxide **9** (see SI for details). Surprisingly, no trace of the product **9'** was observed by MS and NMR analysis. With **8b** itself, the yield of **9** could be significantly improved,after few optimization trials, to 70% with 50 mol% loading of the catalyst (Scheme 5a). Reaction with **8c** furnished the same product **9** (35%) under the reaction condition, which infers that both **8b** and **8c** were transformed into the same intermediate during the reaction course. Different aromatic moieties adjacent to ketone were well tolerated in the reaction, including a α-tetralone derivative, providing **9a'-9e'** in good yields (Scheme 5b).

Notably, this trait of D-A cyclopropane peroxidation reaction should prove beneficial for the easy assembly of moderately functionalized geminal bisperoxides,[5c,7c-d] which could lend themselves for

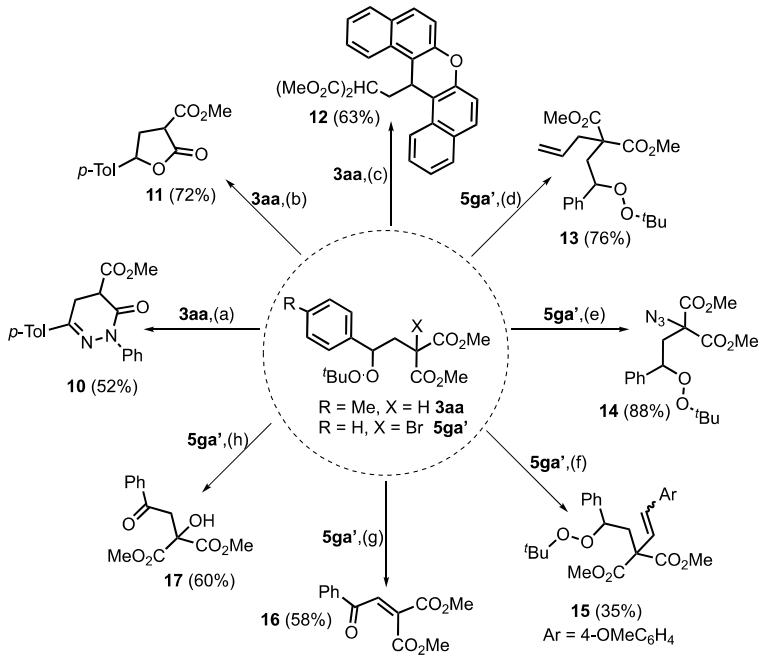
further synthetic elaboration. Since the aromatic donor moiety was lost during this transformation, an initial TBHP addition to D-A cyclopropane followed by a Hock-type rearrangement[12] involving 1,2-aryl migration could be speculated, forming the crucial intermediate **II** (Scheme 6). At this stage, sequential TBHP addition and phenol elimination steps (via **III**) could proceed to deliver the final products.

Scheme 6. Proposed Mechanism for Geminal bisperoxide Formation



We next explored the synthetic versatility of the synthesized mono-peroxy and 1,3-haloperoxygenated compounds through an array of distinct chemical transformations (Scheme 7).

Scheme 7. Follow-up Reactions

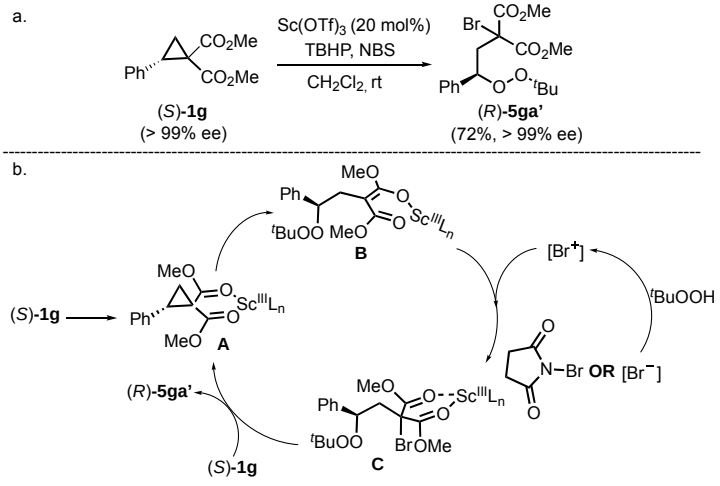


Reagents and conditions: (a)(i) 20 mol%DBU, CH_3CN(ii) $PhNHNH_2$, MeOH, reflux; (b) H_2, 20% $Pd(OH)_2/C$, MeOH, rt; (c) β-naphthol, TfOH, DCM; (d) AIBN (cat), $AllylBu_3Sn$, benzene, reflux; (e) NaN_3, DMF, rt; (f) 1-methoxy-4-vinylbenzene, $Pd(OAc)_2$, Xantphos, Cs_2CO_3, benzene; (g) 2-bromophenol, KF, DMF, rt; (h) Et_3N, DCM, rt.

In the event, compound **3aa** was converted to tetrahydropyridazine derivative **10** (52%) in an one-pot two-step synthesis procedure. The reaction proceeded via Kornblum-DelaMare rearrangement[13] to a

ketone by catalytic DBU and subsequent cyclization by reaction with phenylhydrazine. Notably, such scaffold is present in different natural products and biologially active compounds.[14] Hydrogenolysis of **3aa** with $Pd(OH)_2$ on carbon provided lactone **11** in 72% (dr =1:1) yield. To tap the potential of Hock-type rearrangement with the synthesized peroxycarbonyls, **3aa** was treated with β-naphthol in presence of TfOH, which resulted in the formation of 14*H*-dibenzo[*a*,*j*]xanthenes (**12**) in 63% yield.[15] We next performed some follow-up reactions with halo-peroxygenated product, **5ga'**, aiming for the selective functionalization of C-Br bond. In this course, radical allylation and substitution reaction with NaN_3 were performed with **5ga'**, which delivered the respective products, **13** (76%) and **14** (88%) in high yields. Heck coupling of **5ga'** with 1-methoxy-4-vinylbenzene afforded **15** in moderate yield (35%) as an inseparable mixture of cis and trans (1:3) isomer.[16] Simultaneous functionalizations at C1 and C3 were affected by treating **5ga'** with 2-bromophenol and KF, which rendered aroylmethylidene **16** (58%). Importantly, this class of compounds have been reported to access from D-A nitrocyclopropanes[17] and the present reaction alludes a viable alternative. Treatment of **5ga'** with triethylamine triggered similar bisfunctionalization, furnishing **17** in 60% yield.

Scheme 8. (a) Stereospecific Peroxidation-bromination of Entiomerically Pure Cyclopropane (S)-1g; (b) Proposed Reaction Mechanism for 1,3- Haloperoxygenation.



To gain insights into the reaction mechanism, we next investigated the stereospecificity of the 1,3-bisfunctionalization process by using enantiopure cyclopropane (*S*)-**1g** (> 99% ee) under optimized conditions (Scheme 8a). The reaction proceeded with complete stereospecificity providing **5ga'** in 72% yield. This result suggests that the initial ring-opening step with peroxide occurs via a S_N2 reaction.

We also performed ^{45}Sc NMR experiments (see Supporting Information for details) for the reaction, which indicates the possibility for the presence of alkylperoxy-scandium species in the catalytic cycle.[18]

Taken together, the literature reports and our observations, the following mechanism is suggested for the formation of halo-peroxygenated product **5ga'** from **1g** (Scheme 8b). Coordination of cyclopropane **1g** with Sc-Lewis acid generates **A**, which then suffers a S_N2 attack by hydroperoxide and leads to ring-opened intermediate **B**. Malonate unit of the intermediate subsequently reacts with a highly electrophilic Br^+ species generated from NBS or TBAB by TBHP[11,19] and provides **C**. Finally, exchange of the Sc-Lewis acid between **C** and **1g** leads to the final product **5ga'**, and regenerates **A**.

CONCLUSIONS

In summary, we have developed an operationally simple and efficient strategy for the ring-opening and bis-functionalization of D-A cyclopropanes with hydroperoxides and halogenating agents. This is the first example for assembly of highly functionalized γ-peroxycarbonyls *via* ionic process, which provides a general platform to access this class of compounds, including α-heterosubstituted peroxy compounds of biological relevance, and is distinct from the radical approaches reported earlier. The products formed through this methodology offer interesting opportunities for synthetic elaborations as illustrated with selected transformations.

EXPERIMENTAL SECTION

Genral Information. Unless otherwise noted, all reactions were conducted with oven or flame-dried glassware and maintaining an inert (under nitrogen or argon) atmosphere. Solvents were dried according to standard procedures and all reagents/catalysts were purchased commercially and used without any further purification. Reactions were monitored by TLC, using Merck silica gel 60 F 254 plates. The plates were visualized under UV light (254 nm) or by using 10% ethanolic phosphomolybdic acid (PMA) or 1% aqueous $KMnO_4$ or iodine. Flash column chromatography was performed using silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Avance III, Bruker 400 MHz and 100 MHz spectrometers respectively using $CDCl_3$ or DMSO-d_6. ^{1}H NMR chemicals shift are expressed in ppm (δ) relative to δ = 7.26 for $CDCl_3$ and δ = 2.50 for DMSO-d_6. ^{13}C NMR chemical shift are expressed in ppm (δ) relative to δ = 77.16 for $CDCl_3$ and δ = 39.51 for DMSO-d_6 resonance. ^{45}Sc NMR spectra were recorded on Avance III, Bruker 400 MHz (97 MHz) spectrometer and are reported in ppm using $Sc(OTf)_3$ in CD_3CN as external standard (-2.5 ppm). FT-IR experiments were performed on PerkinElmer Spectrum Version 10.03.08. HRMS and Electron

Spray Ionization (ESI) (m/z) spectra were recorded on Agilent Technologies 6530 Accurate- Mass Q-TOF LC/MS. Enantiomeric excess (ee) was measured by HPLC analysis with chiral stationary phase. Donor-Acceptor cyclopropanes (**1a**, **1g-1h**, **1i**, **1m-1r**),[20] **1b**,[4b] **1d**,[3g] **1e**,[21] **1j**,[22] **1k**,[23] **1l**,[24] **1s**,[25] **1t-1v**,[26] **1x-1y**,[27] **1z**,[28] are known compounds and prepared according to the reported methods. Donor-Acceptor cyclopropanes with monocarbonyl acceptor group **8a-8c**, **8ba**', **8bb**', **8bc**' and **8be**' are known and were prepared according to the previous reports.[29] Tetrahydropyranyl (THP) hydroperoxide,[30] methylcyclohexyl hydroperoxide[30] and *p*-peroxyquinol[31] were prepared following thereported literature procedures. Spectroscopic data of these compounds were matched to the published data.

Caution: Although we have experienced no hazards in our experiments with peroxides, but due to explosive nature of the peroxides, any preparative work with these peroxy compounds should be carried out in the fume hood equipped with a blast shield.

***p*-Tolyl 1-benzoyl-2-phenylcyclopropane-1-carboxylate (1f):** Compound **1e** was transformed into mono-acid (**1e-COOH**) according to literature procedure[32] and used directly for the next reaction (see Scheme S1 in Supporting Information). To a solution of compound **1e-COOH** (0.050 g, 0.18 mmol) in dry dichloromethane (2.0 M) under argon were added DCC (0.047 g, 0.22 mmol), *p*-cresol (0.022g, 0.20 mmol) and DMAP (1 mg) and the reaction mixture was stirred at room temperature for 12 h. Upon completion of the reaction (TLC controlled) solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography (5:95 EtOAc:Hexanes as eluent) to give **1f** as colorless oil in 80% (0.055 g) isolated yield. R_f 0.5 (1:9 EtOAc:Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H), 7.65-7.61 (m, 1H), 7.55-7.52 (m, 2H), 7.45-7.43 (m, 2H), 7.40-7.33 (m, 3H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.01 (d, *J* = 8.5 Hz, 2H), 3.84 (t, *J* = 8.6 Hz, 1H), 2.62 (dd, *J* = 8.2, 5.0 Hz, 1H), 2.21 (s, 3H), 1.84 (dd, *J* = 9.0, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 169.1, 137.2, 135.0, 133.1, 132.8, 129.2, 128.7, 128.6, 128.4, 128.2, 128.0, 127.4, 127.3, 52.3, 42.4, 30.8, 20.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{20}NaO_3$ 379.1310; Found 379.1311.

1-Methyl 1-(p-tolyl) 2-(p-tolyl) cyclopropane-1,1-dicarboxylate (1c): Compound **1c** was prepared from cyclopropane **1a** (0.32g, 1.1 mmol) following the similar procedure as shown for compound **1f** and was obtained in 60% yield (0.24g) as colorless oil. R_f 0.60 (1:5 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.42-7.38 (m, 2H), 7.27-7.23 (m, 1H), 7.16-7.10 (m, 6H), 3.46 (s, 3 H), 3.34 (t, *J* = 8.7 Hz, 1 H), 2.34-2.31 (m, 4H), 1.89 (dd, *J* = 9.3, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 167.1, 148.6, 137.4, 135.9, 131.3, 130.1, 129.1, 128.6, 121.2, 52.6, 37.4, 33.0, 21.3, 21.0, 19.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{20}NaO_4$ 347.1259, Found 347.1232.

1-Methyl 1-phenyl 2-(p-tolyl) cyclopropane-1,1-dicarboxylate (1w): Compound **1w** was prepared from cyclopropane **1a** (0.32g, 1.1 mmol)following similar procedure as shown for compound **1f** (Scheme S1) and was obtained in 70% overall yield (0.220g). R_f 0.35 (1:10 EtOAc:Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.27 – 7.23 (m, 1H), 7.16 – 7.10 (m, 6H), 3.46 (s, 3H), 3.34 (t, *J* = 8.7 Hz, 1H), 2.34 – 2.31 (m, 4H), 1.88 (dd, *J* = 9.3, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 167.0, 150.8, 137.4, 131.3, 129.6, 129.1, 128.6, 126.2, 121.6, 52.6, 37.4, 33.0, 21.3, 20.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{18}NaO_4$ 333.1103, Found 333.1092.

(2-(4-Methoxyphenyl)cyclopropyl)(thiophen-2-yl)methanone (8bd′): Following the literature procedure[29],compound **8db'** was prepared from the corresponding chalcone (0.5 g, 2 mmol) and obtained as colorless oil in 75% (0.4 g) isolated yield. R_f 0.65 (1:4 EtOAc:Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.78 (m, 1H), 7.64-7.63 (m, 1H), 7.14-7.09 (m, 3H), 6.87-6.84 (m, 2H), 3.80 (s, 3H), 2.72-2.67 (m, 2H), 1.87 (ddd, *J* = 8.6, 5.6, 4.2 Hz, 1H), 1.50 (ddd, *J* = 7.9, 7.0, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 158.6, 145.1, 133.6, 132.4, 131.8, 128.3, 127.6, 114.1, 55.5, 30.0, 29.3, 18.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{15}H_{15}O_2S$ 259.0793, Found 259.0816.

General procedure for ring-opening peroxidation of D-A cyclopropanes with *tert*-butyl hydroperoxide (TBHP): To a solution of cyclopropane **1** (50-100 mg) in dry dichloromethane (2.0 M) under argon was added *tert*-butyl hydroperoxide (10 equiv. 5-6 M solution in decane). $Sc(OTf)_3$ (10 or 20 mol%) was then added to the solution and the reaction mixture was stirred at room temperature. The reaction was monitored by thin layer chromatography (TLC) until the disappearence of the starting materials (2-4 h) was observed. Next, the reaction mixture was diluted with DCM (2 mL), washed with water (2 mL) and brine (2 mL) and the organic layer was dried over anhydrous Na_2SO_4. Solvents were removed under reduced pressure (bath temperatuer 30 ^oC) and the crude product was purified by flash column chromatography to obtain the peroxy products (**3aa-3va**).

Dimethyl-2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)malonate (3aa): Following the general procedure, D-A cyclopropane **1a** (0.100g, 0.40 mmol) was transformed into peroxy compound **3aa** and purified by silica gel column chromatography (using 5: 95 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 73% (0.100g) yield. R_f 0.8 (1:4 EtOAc: Hexanes); FT-IR (ν cm^{-1}): 3400, 2979, 2954, 1754, 1738, 1436, 1363, 1198, 1154, 1062, 1023, 816; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.87 (dd, *J* = 8.4, 5.5 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.60 (dd, *J* = 8.1, 6.6 Hz, 1H), 2.51-2.43 (m, 1H), 2.34 (s, 3H), 2.32-2.28 (m, 1H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ169.6 (2), 137.7, 137.2, 129.1, 126.9, 83.2, 80.4, 52.7, 52.6, 48.8, 34.5, 26.5, 21.3; HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{18}H_{26}NaO_6$ 361.1627, Found 361.1644.

Diethyl 2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)malonate (3ba): Following the general procedure, D-A cyclopropane **1b** (0.100 g, 0.36 mmol) was transformed into peroxy compound **3ba** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 77% (0.102 g) isolated yield. R_f 0.65 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 4.88 (dd, J = 8.4, 5.6 Hz, 1H), 4.22-4.14 (m, 4H), 3.55 (dd, J = 8.2, 6.6 Hz, 1H), 2.45 (ddd, J = 15.0, 8.5, 6.6 Hz, 1H), 2.34 (s, 3H), 2.32-2.26 (m, 1H), 1.26 (t, J = 7.1 Hz, 6H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 169.2, 137.7, 137.4, 19.1, 126.9, 83.2, 80.4, 61.6, 61.5, 49.2, 34.5, 26.5, 21.3, 14.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{30}NaO_6$ 389.1940, Found 389.1911.

1-Methyl-3-(p-tolyl) 2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)malonate (3ca): Following the general procedure, D-A cyclopropane **1c** (0.090 g, 0.27 mmol) was transformed into peroxy compound **3ca** and purified by silica gel column chromatography (5: 95 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 60% (0.069g) isolated yield (dr = 1:1). R_f 0.8 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.23 (m, 4H), 7.17-7.14 (m, 8H), 6.95-6.93 (m, 4H), 4.95-4.99 (m, 2H), 3.86 (dd, J = 8.9, 6.0 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.75-3.73 (m, 1H), 2.65-2.60 (m, 2H), 2.46-2.37 (m, 2H), 2.34 (br s, 12H), 1.20 (s, 9H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.5, 168.0 (2), 148.4 (2), 138.0, 137.9, 137.2, 137.0, 135.9, 130.1, 129.3, 129.2, 127.0, 126.9, 121.1 (2), 83.3, 83.2, 80.6 (2), 52.9 (2), 49.1 (2), 34.7, 34.4, 26.6 (2), 21.3, 21.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{30}NaO_6$ 437.1940, Found 437.1954.

2-(2-(tert-Butylperoxy)-2-phenylethyl)-1,3-diphenylpropane-1,3-dione (3da): Following the general procedure (20 mol % $Sc(OTf)_3$ was used in this case), D-A cyclopropane **1d** (0.050 g, 0.15 mmol) was transformed into peroxy compound **3da** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 79% (0.050g) isolated yield. R_f 0.6 (1:9 Acetone: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2H), 7.89-7.86 (m, 2H), 7.61-7.52 (m, 2H), 7.49-7.39 (m, 5H), 7.36-7.34 (m, 3H), 7.33-7.29 (m, 1H), 5.64 (dd, J = 7.8, 5.2 Hz, 1H), 5.02 (dd, J = 8.5, 5.1 Hz, 1H), 2.62-2.51 (m, 2H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 195.7, 140.7, 136.2, 135.7, 133.7, 133.5, 129.0, 128.9, 128.6, 128.5, 128.1, 127.0, 83.8, 80.6, 53.3, 34.8, 26.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{27}H_{28}NaO_4$ 439.1885, Found 439.1892.

Methyl 2-benzoyl-4-(tert-butylperoxy)-4-phenylbutanoate (3ea): Following the general procedure (20 mol % $Sc(OTf)_3$ was used), D-A cyclopropane **1e** (0.060 g, 0.21 mmol) was transformed into peroxy compound **3ea** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 63% (0.050g) yield (dr = 1:1). R_f 0.65 (1:5 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.95 (m, 4H), 7.61-7.56 (m, 2H), 7.49-7.44 (m, 4H), 7.36-7.27 (m, 10H), 5.01-4.97 (m, 1H), 4.93 (dd, J = 8.2, 5.4 Hz, 1H), 4.73-4.70 (m, 1H),

4.66-4.63 (m, 1H), 3.70 (s, 3H), 3.65 (s, 3H), 2.58-2.45 (m, 4H), 1.18 (s, 9H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 194.9, 170.2, 170.1, 140.5, 136.1, 135.7, 133.7 (2), 129.0, 128.9, 128.8 (2), 128.4 (2), 128.0, 126.9 (2), 83.5, 83.3, 80.5, 52.7, 52.6, 50.8, 50.4, 34.8 (2), 26.5, 26.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{22}H_{26}NaO_5$ ($[M+Na]^+$): 393.1678, Found 393.1642.

***p*-Tolyl-2-benzoyl-4-(tert-butylperoxy)-4-phenylbutanoate(3fa):** Following the general procedure, D-A cyclopropane **1f** (0.080 g, 0.22 mmol) was transformed into peroxy compound **3fa** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 51% (0.051g) isolated yield (dr = 1.2:1). R_f 0.6 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ8.06 (d, *J* = 7.3 Hz, 2H), 8.01 (d, *J* = 7.3 Hz, 1.5H), 7.64-7.59 (m, 2H), 7.53-7.47 (m, 4H), 7.40-7.29 (m, 9H), 7.16-7.10 (m, 3.5H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 1.5H), 5.11 (dd, *J* = 9.2, 4.3 Hz, 1H), 5.04 (dd, *J* = 7.9, 5.8 Hz, 1H), 4.98 (dd, *J* = 9.2, 4.6 Hz, 1H), 4.76 (t, *J* = 7.0 Hz, 1H), 2.75-2.61 (m, 1H), 2.61-2.46 (m, 3H), 2.33 (s, 3H), 2.31 (s, 2H), 1.24 (s, 9H), 1.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 194.7, 168.8, 168.6, 148.5, 148.4, 140.5, 140.3, 135.8, 135.6, 133.9, 133.8, 130.0 (2), 129.1, 129.0, 128.9, 128.6, 128.5, 128.2, 128.1, 127.0, 126.9, 121.1, 121.0, 83.5, 83.4, 80.6 (2), 51.3, 50.8, 35.0, 34.6, 26.7, 26.5 21.0 (2); HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{28}H_{30}NaO_5$ 469.1991, Found 469.1992.

Dimethyl-2-(2-(tert-butylperoxy)-2-phenylethyl)malonate (3ga): Following the general procedure (20 mol % $Sc(OTf)_3$ was used), D-A cyclopropane **1g** (0.100 g, 0.42 mmol) was transformed into peroxy compound **3ga** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 84% (0.115g) isolated yield. R_f 0.6 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.26-7.18 (m, 5H), 4.83 (dd, *J* = 8.6, 5.3 Hz, 1H), 3.64 (s, 3H), 3.63 (s, 3H), 3.55 (dd, *J* = 8.3, 6.4 Hz, 1H), 2.38 (ddd, *J* = 14.9, 8.6, 6.4 Hz, 1H), 2.30-2.23 (m, 1H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.5, 140.3, 128.4, 128.0, 126.9, 83.2, 80.5, 52.7, 52.6, 48.7, 34.5, 26.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{24}NaO_6$ 347.1471, Found 347.1468.

Dimethyl-2-(2-(tert-butylperoxy)-2-(4-isopropylphenyl)ethyl)malonate (3ha): Following the general procedure, D-A cyclopropane **1h** (0.100 g, 0.36 mmol) was transformed into peroxy compound **3ha** and purified by silica gel column chromatography (15: 95 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 68% (0.090g) isolated yield. R_f 0.3 (1:4 Et_2O: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 4.88 (dd, *J* = 8.3, 5.5 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.61 (dd, *J* = 8.2, 6.5 Hz, 1H), 2.94-2.84 (m, 1H), 2.48 (ddd, *J* = 14.7, 8.3, 6.5 Hz, 1H), 2.37-2.30 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.6, 148.6, 137.5, 126.9, 126.5, 83.2, 80.5, 52.7, 52.6, 48.8, 34.5, 39.9, 26.5, 24.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{30}NaO_6$ 389.1940, Found 389.1911.

Dimethyl-2-(2-(tert-butylperoxy)-2-(4-methoxyphenyl)ethyl)malonate (3ia): This reaction was set up according to the general procedure, except the temperature of the reaction was kept at 0 ^{o}C throughout. Thus, D-A cyclopropane **1i** (0.100 g, 0.38 mmol) was transformed into peroxy compound **3ia** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 73% (0.098g) yield. R_f 0.7 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 4.84 (dd, J = 8.3, 5.7 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.69 (d, J = 4.9 Hz, 3H), 3.57 (dd, J = 8.0, 6.7 Hz, 1H), 2.49 (ddd, J = 14.9, 8.3, 6.7 Hz, 1H), 2.35–2.24 (m, 1H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6 (2), 159.5, 132.2, 128.3, 113.8, 82.9, 80.4, 55.3, 52.7, 52.6, 48.8, 34.3, 26.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for$C_{18}H_{26}NaO_7$ 377.1576, mass found 377.1550.

Diethyl-2-(2-(tert-butylperoxy)-2-(3,4-dimethoxyphenyl)ethyl)malonate (3ja): This reaction was set up according to the general procedure, except the temperature of the reaction was kept at 0 ^{o}C throughout. Thus, D-A cyclopropane **1j** (0.100 g, 0.31 mmol) was transformed into peroxy compound **3ja** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 70% (0.090g) yield. R_f 0.6 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86-6.79 (m, 2H), 6.80 (d, J = 8.7 Hz, 1H), 4.83 (dd, J = 8.3, 5.7 Hz, 1H), 4.19-4.14 (m, 4H), 3.86 (s, 3H), 3.84 (s, 3H), 3.50 (dd, J = 8.0, 6.8 Hz, 1H), 2.48 – 2.38 (m, 1H), 2.26 (ddd, J = 14.1, 8.1, 5.7 Hz, 1H), 1.26-1.22 (m, 6H), 1.16 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2 (2), 148.9, 148.8, 132.9, 119.4, 110.9, 109.9, 83.1, 80.2, 80.4, 61.5 (2), 55.9 (2), 49.1, 34.3, 26.5, 14.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{21}H_{32}NaO_8$ 435.1995, Found 435.2005.

Dimethyl-2-(2-(tert-butylperoxy)-2-(3,4,5-trimethoxyphenyl)ethyl)malonate (3ka): Following the general procedure, D-A cyclopropane **1k** (0.100 g, 0.30 mmol) was transformed into peroxy compound **3ka** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 91% (0.116g) yield. R_f 0.6 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (s, 2H), 4.82 (dd, J = 8.5, 5.3 Hz, 1H), 3.84 (s, 6H), 3.81 (s, 3H), 3.72 (s, 3H), 3.71 (s, 3H), 3.60 (dd, J = 8.3, 6.4 Hz, 1H), 2.42-2.35 (m, 1H), 2.34 -2.24 (m, 1H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6 (2), 153.2, 137.6, 136.1, 103.7, 83.3, 80.6, 60.9, 56.2, 52.7 (2), 48.7, 34.7, 26.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{30}NaO_9$ 437.1788, Found 437.1821.

Dimethyl-2-(2-(tert-butylperoxy)-2-(2-methoxyphenyl)ethyl)malonate (3la): This reaction was set up according to the general procedure, except the temperature of the reaction was kept at 0 ^{o}C throughout. Thus, D-A cyclopropane **1l** (0.100 g, 0.37 mmol) was transformed into peroxy compound **3la** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 59% (0.080g) yield. R_f 0.5 (1:4 EtOAc: Hexanes); ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.2 Hz, 1H), 7.19 - 7.15 (m, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.30 (dd, *J* = 7.3, 5.6 Hz, 1H), 3.73 (s, 3H), 3.64 (s, 3H), 3.61 (s, 3H), 3.52 (t, *J* = 7.2 Hz, 1H), 2.40 - 2.28 (m, 2H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.7, 156.5, 128.7, 128.6, 127.3, 120.6, 110.4, 80.4, 77.6, 55.4, 52.6 (2), 48.6, 33.3, 26.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{26}NaO_7$ 377.1576, Found 377.1554.

Dimethyl-2-(2-(tert-butylperoxy)-2-(4-fluorophenyl)ethyl)malonate (3ma): Following the general procedure (20 mol % $Sc(OTf)_3$ was used in this case), D-A cyclopropane **1m** (0.100 g, 0.39 mmol) was transformed into peroxy compound **3ma** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 72% (0.098g) yield. R_f 0.6 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 4.87 (dd, *J* = 8.7, 5.2 Hz, 1H), 3.72 (s, 6H), 3.60 (dd, *J* = 8.3, 6.4 Hz, 1H), 2.42 (ddd, *J* = 15.0, 8.7, 6.4 Hz, 1H), 2.33-2.26 (m, 1H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5 (2), 162.6 (d, *J* = 245.8 Hz), 136.2 (d, *J* = 3.2 Hz), 128.6 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 21.4 Hz), 82.6, 80.6, 52.8, 52.7, 48.7, 34.5, 26.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{23}FNaO_6$ 365.1376, Found 365.1341.

Dimethyl-2-(2-(tert-butylperoxy)-2-(4-chlorophenyl)ethyl)malonate (3na): Following the general procedure (20 mol % $Sc(OTf)_3$ was used), D-A cyclopropane **1n** (0.100 g, 0.37 mmol) was transformed into peroxy compound **3na** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 90% (0.120g) yield. R_f 0.65 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.33 (m, 2H), 7.31-7.29 (m, 2H), 4.91 (dd, *J* = 8.7, 5.1 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.64 (dd, *J* = 8.4, 6.3 Hz, 1H), 2.46-2.38 (m, 1H), 2.6-2.29 (m, 1H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 169.4, 139.1, 133.7, 128.6, 128.3, 82.5, 80.6, 52.8, 52.7, 48.7, 34.5, 26.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{23}ClNaO_6$ 381.1081, Found 381.1078.

Dimethyl 2-(2-(tert-butylperoxy)-2-(naphthalen-2-yl)ethyl)malonate (3oa): Following the general procedure (20 mol% $Sc(OTf)_3$ was used), D-A cyclopropane **1o** (0.100 g, 0.35 mmol) was transformed into peroxy compound **3oa** and purified by silica gel column chromatography (5:95 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 81% (0.107g) yield. R_f 0.8 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 4H), 7.52-7.45 (m, 3H), 5.11 (dd, *J* = 8.5, 5.3 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.69 (dd, *J* = 8.2, 6.5 Hz, 1H), 2.57 (ddd, *J* = 14.9, 8.6, 6.5 Hz, 1H), 2.48-2.41 (m, 1H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.5, 137.8, 133.3, 133.2, 128.2, 128.1, 127.7, 126.1, 126.0, 126.0 (2), 124.6, 83.4, 80.5, 52.7, 52.6, 48.7, 34.5, 26.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{21}H_{26}NaO_6$ 397.1627, Found 397.1621.

Dimethyl (E)-2-(2-(tert-butylperoxy)-4-phenylbut-3-en-1-yl)malonate (3pa): Following the general procedure, D-A cyclopropane **1p** (0.080 g, 0.31 mmol) was transformed into peroxy

compound **3pa** and purified by silica gel column chromatography (1:9 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 63% (0.068g) yield. R_f 0.4 (1:4 Et_2O: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.31 (m, 2H), 7.25-7.21 (m, 2H), 7.18-7.14 (m, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.05 (dd, *J* = 16.0, 7.6 Hz, 1H), 4.47-4.42 (m, 1H), 3.64 (s, 3H), 3.63 (s, 3H), 3.61 – 3.55 (m, 1H), 2.32-2.16 (m, 2H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.6, 136.5, 133.1, 128.6, 128.0, 127.9, 126.7, 80.2, 80.5, 52.7 (2), 48.4, 32.6, 26.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{26}NaO_6$ 373.1627, Found 373.1613.

Dimethyl-2-(2-(tert-butylperoxy)-2-(furan-2-yl)ethyl)malonate (3qa): This reaction was set up according to the general procedure, except the temperature of the reaction was kept at 0 ^oC throughout. Thus, D-A cyclopropane **1q** (0.100 g, 0.44 mmol) was transformed into peroxy compound **3qa** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 57% (0.080g) yield. R_f 0.65 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.36 (m, 1H), 6.33-6.31 (m, 2H), 4.91 (dd, *J* = 8.5, 5.8 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.61 (dd, *J* = 8.1, 6.6 Hz, 1H), 2.60 (ddd, *J* = 15.0, 8.5, 6.6 Hz, 1H), 2.41 (ddd, *J* = 14.2, 8.2, 5.8 Hz, 1H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 169.4, 152.4, 142.5, 110.3, 109.2, 80.6, 76.2, 52.7 (2), 48.5, 30.8, 26.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{22}NaO_7$ 337.1263, Found 337.1254.

Dimethyl-2-(2-(tert-butylperoxy)-2-(thiophen-2-yl)ethyl)malonate (3ra): Following the general procedure, D-A cyclopropane **1r** (0.100 g, 0.42 mmol) was transformed into peroxy compound **3ra** and purified by silica gel column chromatography (1: 9 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 80% (0.110g) yield. R_f 0.7 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 4.9, 1.1 Hz, 1H), 6.95 (br d, *J* = 3.0 Hz, 1H), 6.91-6.88 (m, 1H), 5.08 (dd, *J* = 8.4, 5.7 Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.60 (dd, *J* = 8.1, 6.6 Hz, 1H), 2.55 (ddd, *J* = 15.0, 8.5, 6.6 Hz, 1H), 2.37 (ddd, *J* = 14.1, 8.2, 5.7 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 169.4, 142.7, 126.5, 126.0, 125.5, 80.7, 78.6, 52.7 (2), 48.7, 34.3, 26.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{22}NaO_6S$ 353.1035, Found 353.1010.

Dimethyl-2-(2-(tert-butylperoxy)-2-(1-tosyl-1H-indol-3-yl)ethyl)malonate (3sa): Following the general procedure, D-A cyclopropane **1s** (0.050 g, 0.11 mmol) was transformed into peroxy compound **3sa** and purified by silica gel column chromatography (15:85 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 83% (0.050g) yield. R_f 0.3 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.65-7.63 (m, 1H), 7.56 (s, 1H), 7.32-7.28 (m, 1H), 7.24-7.19 (m, 3H), 5.16 (dd, *J* = 8.7, 5.0 Hz, 1H), 3.71 (s, 6H), 3.67 (dd, *J* = 8.6, 6.1 Hz, 1H), 2.60 (ddd, *J* = 14.8, 8.8, 6.1 Hz, 1H), 2.52-2.53 (m, 1H), 2.32 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.5, 145.1, 135.4, 135.2, 129.3, 127.0, 124.9, 124.5, 123.4,

121.5, 120.6, 113.8, 80.5, 76.6, 52.8, 52.7, 48.7, 32.7, 26.4, 21.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{26}H_{31}NNaO_8S$ 540.1668, Found 540.1680.

Dimethyl-2-(2-(tert-butylperoxy)-2-(1,3-dioxoisoindolin-2-yl)ethyl)malonate (3ta): Following the general procedure (20 mol% $Sc(OTf)_3$ was used), D-A cyclopropane **1t** (0.100 g, 0.33 mmol) was transformed into peroxy compound **3ta** and purified by silica gel column chromatography (3:7 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 77% (0.100g) yield. R_f 0.3 (4:6 EtOAc: Hexanes); FT-IR (ν cm^{-1}): 3400, 2979, 1721, 1364, 1328; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 5.4, 3.1 Hz, 2H), 7.74 (dd, J = 5.5, 3.0 Hz, 2H), 5.87 (dd, J = 8.0, 6.4 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.55 (t, J = 7.5 Hz, 1H), 3.02-2.95 (m, 1H), 2.67 (ddd, J = 14.3, 7.6, 6.4 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (2), 167.6, 134.5, 131.8, 123.8, 81.8, 81.4, 53.0, 48.5, 29.0, 26.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{23}NNaO_8$ 416.1321, Found 416.1327.

Dimethyl 2-(2-(tert-butylperoxy)-2-(2,5-dioxopyrrolidin-1-yl)ethyl)malonate (3ua): Following the general procedure (20 mol% $Sc(OTf)_3$ was used), D-A cyclopropane **1u** (0.100 g, 0.39 mmol) was transformed into peroxy compound **3ua** and purified by silica gel column chromatography (3:7 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 94% (0.127g) yield. R_f 0.35 (4:6 EtOAc: Hexanes);^1H NMR (400 MHz, $CDCl_3$) δ 5.67 (dd, J = 8.3, 6.0 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.45 (dd, J = 7.9, 7.0 Hz, 1H), 2.84 (ddd, J = 15.1, 8.3, 6.9 Hz, 1H), 2.67 (br s, 4H), 2.47 (ddd, J = 14.3, 8.1, 6.0 Hz, 1H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 168.7, 82.2, 81.4, 52.9 (2), 48.3, 28.4, 28.6, 26.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{23}NNaO_8$ 368.1321, Found 368.1306.

Dimethyl-2-(2-(tert-butylperoxy)-2-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl)malonate (3va): Following the general procedure (20 mol% $Sc(OTf)_3$ was used), D-A cyclopropane **1v** (0.100 g, 0.39 mmol) was transformed into peroxy compound **3va** and purified by silica gel column chromatography (3: 7 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 86% (0.117g) yield. R_f 0.35 (4:6 EtOAc: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 6.72 (br s, 2H), 5.65 (dd, J = 8.3, 6.2 Hz, 1H), 3.73 (s, 6H), 3.48-3.51 (m, 1H), 2.92-2.84 (m, 1H), 2.54 (ddd, J = 14.4, 7.8, 6.2 Hz, 1H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.8, 168.7, 134.6, 81.3 (2), 53.0 (2), 48.4, 28.9, 26.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{21}NNaO_8$ 366.1165, Found 366.1181.

Ring-opening peroxidation of D-A cyclopropanes with tetrahydropyranyl (THP) hydroperoxide: Preparation of compound 3gb: Cyclopropane **1g** (0.200g, 0.85 mmol) was dissolved in a mixture of dry DCM and cyclohexane (1.6 mL, 1:3, v/v) under argon. To this solution was added a solution of 2-hydroperoxytetrahydro-2H-pyran (2.0 equiv in 0.4 mL cyclohexane) and

$Sc(OTf)_3$ (42 mg, 0.085 mmol). The reaction mixture was stirred for 4 h at room temperature. After completion of the reaction (monitored by TLC), reaction was diluted with DCM (5 mL) and successively washed with water (5 mL) and brine (5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (using 15: 85 EtOAc: Hexanes as eluent) to afford **3gb** (0.213 g, 71 %) as colorless oil (dr = 1:1). R_f 0.65 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 5H), 7.34-7.28 (m, 5H), 5.15-5.08 (m, 2H), 5.07-5.02 (m, 2H), 3.94-3.88 (m, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.71 (s, 3H), 3.71 (s, 3H), 3.65-3.48 (m, 3H), 2.51-2.53 (m, 1H), 2.40–2.29(m, 3H), 1.72-1.38 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.5 (2), 140.4, 139.9, 128.5 (2), 128.2, 126.9, 126.7, 101.8, 100.5, 84.4, 83.5, 62.6, 62.3, 52.7 (2), 48.7 (2), 34.2, 33.8, 27.9, 27.7, 25.2, 25.1, 19.6, 19.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{24}NaO_7$ 375.1420, Found 375.1436.

Dimethyl-2-(2-(((R)-tetrahydro-2H-pyran-2-yl)peroxy)-2-(thiophen-2-yl)ethyl)malonate (3rb): Compound **3rb** was prepared from cyclopropane **1r** (0.100g, 0.42 mmol), following similar procedure as shown for compound **3gb** and was obtained in 61% yield (0.091g) as colorless oil (dr = 1:1). R_f 0.55 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 2H), 7.07 (d, J = 3.5 Hz, 2H), 6.99-6.97 (m, 2H), 5.38-5.29 (m, 2H), 5.05-5.01 (m, 2H), 3.94-3.80 (m, 2H), 3.75 (s, 6H), 3.74 (s, 6H), 3.72-3.68 (m, 2H), 3.60-3.52 (m, 2H), 2.72-2.41 (m, 4H), 1.67-1.65 (m, 3H), 1.60-1.46 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 139.4, 143.2, 142.2, 126.7 (2), 126.4, 126.2, 126.0, 125.8, 101.8, 100.9, 79.7, 79.0, 62.6, 62.4, 52.8 (2), 48.6, 34.1, 33.7, 27.9, 27.8, 25.2, 19.6 (2); HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated $C_{16}H_{22}NaO_7S$ 381.0984, Found 381.0950.

Dimethyl-2-(2-(1,3-dioxoisoindolin-2-yl)-2-(((R)-tetrahydro-2H-pyran-2-yl) peroxy)ethyl)malonate (3tb): Compound **3tb** was prepared from cyclopropane **1t** (0.100g, 0.33 mmol), following similar procedure as shown for compound **3gb** and was obtained in 79% yield (0.110 g) as colorless oil (dr = 1:1). R_f 0.3 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.84 (m, 4H), 7.75-7.71 (m, 4H), 6.10 (dd, J = 9.2, 5.1 Hz, 1H), 5.96 (dd, J = 8.4, 6.0 Hz, 1H), 5.12-5.10 (m, 1H), 5.00-4.98 (m, 1H), 3.98-3.92 (m, 1H), 3.72-3.71 (m, 12H), 3.68 (dd, J = 8.9, 5.9 Hz, 1H), 3.59-3.54 (m, 2H), 3.35-3.29 (m, 1H), 3.23-3.18 (m, 1H), 3.05-2.92 (m, 2H), 2.67-2.53 (m, 2H), 1.61-1.46 (m, 7H), 1.42-1.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 168.8, 168.7, 167.7, 167.5, 134.5, 134.2, 132.0, 131.8, 123.7, 123.5, 101.9, 101.7, 83.2, 82.0, 77.4, 63.3, 62.5, 52.9 (3), 48.3 (2), 29.4, 29.1, 27.8, 27.5, 25.1, 24.8, 20.2, 19.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{23}NNaO_9$ 444.1271, Found 444.1314.

Dimethyl-2-(2-(1,3-dioxoisoindolin-2-yl)-2-hydroperoxyethyl)malonate (3tc): *p*-Toluenesulfonic acid (0.028 g, 0.16 mmol) was added to a solution of cyclopropane **3tb** (0.070 g, 0.16 mmol) in dry methanol (1 mL, 0.16 M) under argon and the reaction mixture was stirred at room temperature for

12 h. Upon completion of the reaction as determined by the disappearence of starting material, the reaction solvent was removed under reduced pressure and the crude product was purified by flash silica gel column chromatography (using 2:3 EtOAc: Hexanes as eluent) to obtain **3tc** as colorless oil in 64% yield (0.036g). R_f 0.25 (3:7 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (br s, 1H), 7.87 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.91 (dd, *J* = 8.8, 5.4 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.59 (t, *J* = 7.3 Hz, 1H), 3.12-3.04 (m, 1H), 2.61-2.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 168.9, 167.8, 134.7, 131.7, 123.9, 83.9, 53.1, 48.5, 29.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{15}NNaO_8$ 360.0695, Found 360.0660.

Dimethyl-2-(2-((1-methyl-4-oxocyclohexa-2,5-dien-1-yl)peroxy)-2-(p-tolyl)ethyl)malonate (3ad): To a solution of cyclopropane **1a** (0.150g, 0.6 mmol) in dry dichloromethane (3.0 mL) under argon was added 4-hydroperoxy-4-methylcyclohexa-2,5-dien-1-one (0.527g, 2.1 mmol). $Sc(OTf)_3$ (10 mol%) was then added to the solution and the reaction mixture was stirred at room temperature for 4 h. Upon completion of the reaction (TLC controlled), the solvent was removed under reduced pressure and the crude product was purified by flash silical gel column chromatography (using 1:9 EtOAc: Hexanes as eluent) to obtain the peroxy products (**3ad**) as colorless oil in 55% overall yield (0.130g). R_f 0.35 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 -7.14 (m, 4H), 6.82 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.67 (dd, *J* = 10.1, 3.0 Hz, 1H), 6.23-6.16 (m, 2H), 4.91 (dd, *J* = 8.9, 5.3 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.44 (dd, *J* = 8.4, 6.3 Hz, 1H), 2.34 (s, 3H), 2.32-2.20 (m, 2H), 1.26 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 169.4 (2), 150.6, 150.3, 138.3, 136.4, 129.5, 129.2 (2), 127.0, 84.2, 77.7, 52.8, 52.7, 48.5, 33.9, 23.2, 21.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{21}H_{24}NaO_7$ 411.1420, Found 411.1417.

Scale Up Experiment: In a flame dried Schlenk tube, cyclopropane **1a** (1.0 g, 4.0 mmol) was dissolved in dry DCM (2 mL) and to this solution was slowly added *tert*-butyl hydroperoxide (8.0 mL, 5-6 M solution in decane) under argon. $Sc(OTf)_3$ (0.2 g, 0.04 mmol) was then added in portions and the resulting mixture was stirred at room temperature under argon for 3h. After completion (TLC controlled) the reaction was diluted with DCM (10 mL), washed with water (5 mL) and brine (5 mL) and the organic layer was dried over anhydrous Na_2SO_4. Solvents were removed under reduced pressure (bath temperatuer 30 ^oC) and the crude product was purified by flash column chromatography (using 5: 95 EtOAc: Hexanes as eluent) to obtain the peroxy compound **3aa** (1.0 g, 74%) as colorless oil.

General procedure for 1,3-haloperoxygenation of D-A cyclopropanes with *tert*-butyl hydroperoxide (TBHP): Preparation of compounds 5. To a solution of cyclopropane **1** (50-100 mg) in dry dichloromethane (2.0 M) under argon was added *tert*-butyl hydroperoxide (**2a**) (10 equiv. 5-6 M solution in decane). $Sc(OTf)_3$ (10 or 20 mol%) was then added to the solution and the reaction

mixture was stirred at room temperature for 45-75 minutes. Next, the reaction mixture was cooled to 0 ^{o}C and was added 1.5 equiv. of halogenating agent (**4a′**-**4c′**, *N*-halosuccinamide, NXS, X = Br, Cl, I) in one portion. The reaction was continued for another 2-3 h at room temperature. Upon completion (TLC controlled), the reaction was quenched with saturated $NaHCO_3$ solution and extracted in DCM (5 mL x 2). Organic layer was dried (Na_2SO_4) and concentrated in vacuo (bath temperatuer 30 ^{o}C). The crude residue was purified by flash silica gel column chromatography to obtain the haloperoxygenated products **5**.

Dimethyl-2-bromo-2-(2-(tert-butylperoxy)-2-phenylethyl)malonate (5ga′): Following the general procedure (20 mol % $Sc(OTf)_3$ was used), D-A cyclopropane **1g** (0.100g, 0.42 mmol) was transformed into bromo-peroxy compound **5ga′** and purified by silica gel column chromatography (4:96 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 92% (0.158g) yield. R_f 0.25 (1:9 Et_2O: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 5H), 5.23-5.20 (m, 1H), 3.84 (s, 3H), 3.58 (s, 3H), 2.97 (dd, *J* = 15.4, 8.2 Hz, 1H), 2.67 (dd, *J* = 15.4, 4.4 Hz, 1H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.7, 140.0, 128.3 (2), 127.7, 82.7, 80.5, 60.4, 54.1, 53.9, 42.9, 26.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{23}BrNaO_6$ 425.0576, Found 425.0565.

Dimethyl 2-(2-(tert-butylperoxy)-2-phenylethyl)-2-chloromalonate (5gb′): Following the general procedure (20 mol % $Sc(OTf)_3$ was used), D-A cyclopropane **1g** (0.100g, 0.42 mmol) was transformed into chloro-peroxy compound **5gb′** and purified by silica gel column chromatography (4:96 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 64% (0.098g) yield. R_f 0.5 (1:9 Et_2O: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 5 H), 5.20 (dd, *J* = 8.3, 4.8 Hz, 1H), 3.85 (s, 3H), 3.60 (s, 3 H), 2.98 (dd, *J* = 15.3, 8.3 Hz, 1H), 2.64 (dd, *J* = 15.3, 4.8 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 166.8, 140.1, 128.3 (2), 127.7, 81.5, 80.6, 68.4, 54.0, 53.9, 42.3, 26.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{23}ClNaO_6$ 381.1081, Found 381.1102.

Dimethyl-2-(2-(tert-butylperoxy)-2-phenylethyl)-2-iodomalonate (5gc′): Following the general procedure (20 mol % $Sc(OTf)_3$ was used), D-A cyclopropane **1g** (0.100g, 0.42 mmol) was transformed into iodo-peroxy compound **5gc′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 57% (0.110 g) yield. R_f 0.45 (1:9 Et_2O: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 5H), 5.14 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.81 (s, 3H), 3.57 (s, 3H), 2.80 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.60 (dd, *J* = 15.5, 4.8 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 167.9, 140.1, 128.3 (2), 127.7, 85.1, 80.5, 54.2, 53.9, 44.6, 41.7, 26.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{23}INaO_6$ 473.0437, Found 473.0433.

Dimethyl-2-bromo-2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)malonate (5aa′): Following the general procedure, D-A cyclopropane **1a** (0.100g, 0.40 mmol) was transformed into bromo-peroxy compound **5aa′** and purified by silica gel column chromatography (6:94 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 71% (0.120 g) yield. R_f 0.4 (1:4 Et_2O: Hexanes); FT-IR (ν cm^{-1}): 3400, 2925, 1747, 1514, 1364, 1260, 1073, 817; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.18 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.84 (s, 3H), 3.58 (s, 3H), 2.98 (dd, *J* = 15.4, 8.0 Hz, 1H), 2.66 (dd, *J* = 15.4, 4.9 Hz, 1H), 2.34 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.8, 138.0, 137.0, 129.0, 127.7, 82.6, 80.5, 60.5, 54.1, 53.9, 42.8, 26.6, 21.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{25}BrNaO_6$ 439.0732, Found 439.0706.

Dimethyl 2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)-2-chloromalonate (5ab′): Following the general procedure, D-A cyclopropane **1a** (0.100g, 0.40 mmol) was transformed into chloro-peroxy compound **5ab′** and purified by silica gel column chromatography (4:96 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 66% (0.099 g) yield. R_f 0.4 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.16 (dd, *J* = 8.1, 4.9 Hz, 1H), 3.85 (s, 3H), 3.58 (s, 3H), 2.98 (dd, *J* = 15.3, 8.2 Hz, 1H), 2.62 (dd, *J* = 15.3, 4.9 Hz, 1H), 2.34 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 166.8, 138.0, 136.9, 129.0, 127.7, 81.3, 80.5, 68.4, 54.0, 53.8, 42.2, 26.6, 21.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{25}ClNaO_6$ 395.1237, Found 395.1267.

Dimethyl 2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)-2-iodomalonate (5ac′): Following the general procedure, D-A cyclopropane **1a** (0.100 g, 0.40 mmol) was transformed into iodo-peroxy compound **5ac′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 72% (0.135 g) yield. R_f 0.55 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.10 (dd, *J* = 7.8, 5.0 Hz, 1H), 3.81 (s, 3H), 3.56 (s, 3H), 2.80 (dd, *J* = 15.4, 7.9 Hz, 1H), 2.58 (dd, *J* = 15.5, 4.9 Hz, 1H), 2.34 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 168.0, 138.0, 137.0, 129.0, 127.8, 85.0, 80.5, 54.2, 53.9, 44.5, 41.9, 26.7, 21.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{25}INaO_6$ 487.0594, Found 487.0602.

Diethyl 2-bromo-2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)malonate (5ba′): Following the general procedure, D-A cyclopropane **1b** (0.100 g, 0.36 mmol) was transformed into bromo-peroxy compound **5ba′** and purified by silica gel column chromatography (6:94 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 68% (0.110 g) yield. R_f 0.7 (1:4 EtOAc: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.18 (dd, *J* = 8.0, 4.9 Hz, 1H), 4.34-4.25 (m, 2H), 4.07-4.93 (m, 2H), 2.96 (dd, *J* = 15.4, 8.0 Hz, 1H), 2.65 (dd, *J* = 15.4, 4.9 Hz, 1H), 2.33 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.2, 137.9, 137.2, 128.9, 127.6, 82.6, 80.4, 63.1, 63.0, 61.2, 42.7,

26.6, 21.3, 14.0, 13.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{29}BrNaO_6$ 467.1045, Found 467.1019.

1-Methyl-3-(p-tolyl) 2-bromo-2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)malonate (5ca′): Following the general procedure, D-A cyclopropane **1c** (0.100 g, 0.36 mmol) was transformed into bromo-peroxy compound **5ca′** and purified by silica gel column chromatography (6:94 Et_2O: Hexanes as eluent) to give the title compound as mixture of diastereomers in 60% (0.091 g) yield (dr = 1:1). R_f 0.5 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 4H), 7.19-7.14 (m, 8H), 7.10 – 7.00 (m, 2H), 7.06-7.04 (m, 2H), 5.28-5.25 (m, 2H), 3.91 (s, 3H), 3.65 (s, 3H), 3.13-3.05 (m, 2H), 2.82-2.72 (m, 2H), 2.35 (br s, 9H), 2.33 (s, 3H), 1.14 (s, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.5, 165.6, 164.8, 148.7, 148.3, 138.1, 137.2, 136.9, 136.2, 130.1, 130.0, 129.1, 127.7 (2), 120.9, 120.6, 82.8, 82.5, 80.8, 80.6, 60.7, 60.6, 54.3, 54.0, 43.0, 42.9, 26.7 (2), 21.4 (2), 21.1, 21.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{24}H_{29}BrNaO_6$ 515.1045, Found 515.1020

1-Methyl 3-phenyl 2-bromo-2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)malonate (5wa′) : Following the general procedure, D-A cyclopropane **1w** (0.060g, 0.19 mmol) was transformed into bromo-peroxy compound **5wa′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as mixture of diastereomers in 59% (0.055 g) yield (dr = 5:1). R_f 0.4 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 3H), 7.32-7.28 (m, 4H), 7.27-7.21 (m, 2H), 7.19-7.17 (m, 2H), 6.98-6.95 (m, 2H), 5.32 (s, 0.17 H), 5.29 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.94 (s, 3H), 3.69 (s, 0.6H), 3.15-3.09 (m, 1.2H), 2.35-2.75 (m, 1.2H), 2.38 (s, 0.6H), 2.37 (s, 3H), 1.16 (s, 9H), 1.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.4, 150.5, 138.1, 137.2, 136.9, 136.6, 129.6 (2), 129.2, 129.1, 127.7, 127.6, 126.6, 126.5, 121.2, 120.9, 82.7, 82.5, 80.8, 80.6, 60.6, 60.5, 54.3, 54.1, 43.1, 42.9, 26.7 (2), 21.4 (2); HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{27}BrNaO_6$ 501.0889, Found 501.0866.

Methyl 2-benzoyl-2-bromo-4-(tert-butylperoxy)-4-phenylbutanoate (5ea′): Following the general procedure (20 mol % $Sc(OTf)_3$ was used), D-A cyclopropane **1e** (0.080 g, 0.28 mmol) was transformed into bromo-peroxy compound **5ea′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as semi solid in 63% (0.081 g) yield (dr = 1.5:1). R_f 0.65 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.95-7.93 (m, 1H), 7.55-7.52 (m, 2H), 7.43-7.29 (m, 12H), 5.36 (dd, *J* = 9.5, 2.8 Hz, 1H), 5.19 (t, *J* = 6.0 Hz, 0.6H), 3.70 (s, 3H), 3.26 (s, 2H), 3.20 (dd, *J* = 15.4, 5.7 Hz, 0.7H), 3.03-2.91 (m, 2H), 2.80 (dd, *J* = 15.9, 2.8 Hz, 1H), 1.10 (s, 9H), 1.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 188.0, 168.1, 141.0, 139.4, 133.8, 133.6, 135.5, 133.4 (2), 129.6, 129.5, 128.6, 128.5, 128.4, 128.3 (2), 128.1, 127.6, 82.9, 82.2, 80.4, 64.9, 64.6, 54.1, 53.6, 43.8, 43.0, 26.6 (2); HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{22}H_{25}BrNaO_5$ 471.0783, Found 471.0818.

Ethyl-2-benzoyl-2-bromo-4-(tert-butylperoxy)-4-phenylbutanoate (5xa′): Following the general procedure (20 mol % $Sc(OTf)_3$ was used), D-A cyclopropane **1x** (0.060 g, 0.20 mmol) was transformed into bromo-peroxy compound **5xa′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as semi solid in 59% (0.056 g) yield (dr = 1.5:1). R_f 0.65 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H), 7.96-7.94 (m, 1H), 7.58-7.50 (m, 2H), 7.42-7.29 (m, 12H), 5.36 (dd, *J* = 9.4, 2.9 Hz, 1H), 5.19 (t, *J* = 5.9 Hz, 0.7H), 4.24-4.10 (m, 2H), 3.82-3.73 (m, 0.7H), 3.61-3.53 (m, 1H), 3.21 (dd, *J* = 15.4, 5.7 Hz, 0.7H), 2.99-2.89 (m, 2H), 2.80 (dd, *J* = 15.9, 3.0 Hz, 1H), 1.11 (s, 9H), 1.08 (s, 6H), 1.00 (t, *J* = 7.1 Hz, 3H), 0.83 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 188.3, 167.5, 167.4, 141.2, 139.7, 134.0, 133.9,133.4, 133.3, 129.7, 129.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.5, 82.9, 82.3, 80.5, 80.4, 65.4, 64.9, 63.4, 63.1, 43.8, 43.0, 26.6 (2), 13.7, 13.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{23}H_{27}BrNaO_5$ 485.0940, Found 485.0956.

Ethyl 2-acetyl-2-bromo-4-(tert-butylperoxy)-4-phenylbutanoate (5ya′): Following the general procedure, D-A cyclopropane **1y** (0.100g, 0.43 mmol) was transformed into bromo-peroxy compound **5ya′** and purified by silica gel column chromatography (4:96 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 64% (0.111 g) yield (dr = 1:1). R_f 0.6 (1:4 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 10H), 5.20-5.14 (m, 2H), 4.33-4.27 (m, 2H), 4.11-4.03 (m, 1H), 4.00-3.92 (m, 1H), 2.93 (dd, *J* = 15.5, 8.4 Hz, 1H), 2.82 (dd, *J* = 15.7, 9.6 Hz, 1H), 2.63 (dd, *J* = 15.5, 4.6 Hz, 1H), 2.55 (dd, *J* = 15.7, 3.4 Hz, 1H), 2.46 (s, 3H), 2.32 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* =7.1, 3H), 1.10 (s, 9H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 196.1, 167.3, 166.8, 140.8, 134.0, 128.3 (2), 128.1, 127.8, 127.4, 82.7, 82.6, 80.4, 67.5, 67.3, 63.4, 63.1, 42.3, 42.2, 26.9, 26.6, 25.1, 14.0, 13.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{25}BrNaO_5$ 423.0783, Found 423.0779.

2-(2-(tert-Butylperoxy)-2-phenylethyl)-2-chloro-1,3-diphenylpropane-1,3-dione (5db′): Following the general procedure (20 mol % $Sc(OTf)_3$ was used), D-A cyclopropane **1d** (0.100 g, 0.30 mmol) was transformed into chloro-peroxy compound **5db′** and purified by silica gel column chromatography (3:97 Et_2O: Hexanes as eluent) to give the title compound as semi solid in 65% (0.089 g) yield. R_f 0.65 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 4H), 7.49-7.43 (m, 2H), 7.37-7.27 (m, 9H), 5.26 (dd, *J* = 8.7, 3.1 Hz, 1H), 3.28 (dd, *J* = 15.8, 8.7 Hz, 1H), 3.04 (dd, *J* = 15.8, 3.2 Hz, 1H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 191.0, 140.8, 134.3, 134.1, 133.6, 133.4, 130.1, 130.0, 128.5, 128.2, 128.0, 127.5, 81.0, 80.1, 78.2, 44.9, 26.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{27}H_{27}ClNaO_4$ 473.1496, Found 473.1502.

Dimethyl-2-bromo-2-(2-(tert-butylperoxy)-2-(4-isopropylphenyl)ethyl)malonate (5ha′): Following the general procedure, D-A cyclopropane **1h** (0.100 g, 0.36 mmol) was transformed into bromo-peroxy compound **5ha′** and purified by silica gel column chromatography

(4:96 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 62% (0.100 g) yield. R_f 0.6 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.25 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.18 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.83 (s, 3H), 3.53 (s, 3H), 3.00 (dd, *J* = 15.4, 7.7 Hz, 1H), 2.93-2.86 (m, 1H), 2.68 (dd, *J* = 15.4, 5.2 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.8, 149.0, 137.1, 127.8, 126.4, 82.7, 80.6, 60.6, 54.1, 53.8, 42.7, 34.0, 26.6, 24.1 (2); HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{29}BrNaO_6$ 469.1025, Found 469.1000.

Dimethyl-2-(2-(tert-butylperoxy)-2-(4-isopropylphenyl)ethyl)-2-chloromalonate (5hb′): Following the general procedure, D-A cyclopropane **1h** (0.100 g, 0.36 mmol) was transformed into chloro-peroxy compound **5hb′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 69% (0.100 g) yield. R_f 0.4 (1:4 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26-7.24 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.17 (dd, *J* = 7.8, 5.2 Hz, 1H), 3.84 (s, 3H), 3.53 (s, 3H), 3.00 (dd, *J* = 15.2, 7.8 Hz, 1H), 2.93-2.86 (m, 1H), 2.64 (dd, *J* = 15.2, 5.2 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8 (2), 149.0, 137.1, 127.7, 126.3, 81.4, 80.5, 68.4, 54.0, 53.8, 42.1, 34.0, 26.6, 24.1 (2); HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{29}ClNaO_6$ 423.1550, Found 423.1555.

Dimethyl 2-(2-(4-acetoxyphenyl)-2-(tert-butylperoxy)ethyl)-2-bromomalonate (5za′): Following the general procedure, D-A cyclopropane **1z** (0.070 g, 0.23 mmol) was transformed into bromo-peroxy compound **5za′** and purified by silica gel column chromatography (6:94 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 74% (0.082 g) yield. R_f 0.5 (1:4 EtOAc: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 5.21 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.83 (s, 3H), 3.60 (s, 3H), 2.95 (dd, *J* = 15.4, 8.0 Hz, 1H), 2.65 (dd, *J* = 15.4, 4.9 Hz, 1H), 2.29 (s, 3H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 167.0, 166.7, 150.6, 137.6, 128.8, 121.5, 82.1, 80.7, 60.3, 54.2, 54.0, 42.9, 26.6, 21.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{25}BrNaO_8$ 483.0631, Found 483.0630..

Dimethyl-2-(2-(tert-butylperoxy)-2-(2-methoxyphenyl)ethyl)-2-chloromalonate (5lb′): This reaction was set up according to the general procedure, except the temperature of the reaction was kept at 0 ^oC throughout. Thus, D-A cyclopropane **1l** (0.100 g, 0.37 mmol) was transformed into chloro-peroxy compound **5lb′** and purified by silica gel column chromatography (1:9 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 61% (0.090 g) yield. R_f 0.65 (3:7 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 1H), 7.29-7.25 (m, 1H), 6.99-6.96 (m, 1H), 6.88 (dd, *J* = 8.2, 0.6 Hz, 1H), 5.71 (dd, *J* = 8.9, 4.2 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.67 (s, 3H), 2.88 (dd, *J* = 15.3, 8.9 Hz, 1H), 2.71 (dd, *J* = 15.3, 4.2 Hz, 1H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.8, 156.9, 128.9, 128.4, 128.2, 120.4, 110.7, 80.4, 75.7, 68.5, 55.6, 53.9, 53.8, 41.2, 26.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{25}ClNaO_7$ 411.1187, Found 411.1150.

Dimethyl-2-bromo-2-(2-(tert-butylperoxy)-2-(4-fluorophenyl)ethyl)malonate (5ma′): Following the general procedure (20 mol % $Sc(OTf)_3$ was used), D-A cyclopropane **1m** (0.100 g, 0.39 mmol) was transformed into bromo-peroxy compound **5ma′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 72% (0.121 g) yield. R_f 0.4 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 5.19 (dd, *J* = 8.3, 4.7 Hz, 1H), 3.83 (s, 3H), 3.62 (s, 3H), 2.93 (dd, *J* = 15.4, 8.3 Hz, 1H), 2.63 (dd, *J* = 15.4, 4.7 Hz, 1H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.6, 162.6 (d, *J* = 246.3 Hz), 135.9 (d, *J* = 3.2 Hz), 129.3 (d, *J* = 8.2 Hz), 115.1 (d, *J* = 21.4 Hz), 81.9, 80.6, 60.2, 54.1, 53.9, 42.9, 26.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{22}BrFNaO_6$ ($[M+Na]^+$): 443.0481, Found 443.0441.

Dimethyl-2-bromo-2-(2-(tert-butylperoxy)-2-(4-chlorophenyl)ethyl)malonate (5na′): Following the general procedure, using 20 mol % $Sc(OTf)_3$, D-A cyclopropane **1n** (0.100 g, 0.37 mmol) was transformed into bromo-peroxy compound **5na′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 86% (0.141 g) yield. R_f 0.5 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 4H), 5.19 (dd, *J* = 8.5, 4.5 Hz, 1H), 3.84 (s, 3H), 3.64 (s, 3H), 2.90 (dd, *J* = 15.5, 8.5 Hz, 1H), 2.62 (dd, *J* = 15.5, 4.5 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.6, 138.8, 134.0, 129.0, 128.5, 82.0, 80.7, 60.1, 54.1, 54.0, 43.0, 26.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{22}BrClNaO_6$ 459.0186, Found 459.0190.

Dimethyl-2-(2-(tert-butylperoxy)-2-(4-chlorophenyl)ethyl)-2-iodomalonate (5nc′): Following the general procedure, using 20 mol % $Sc(OTf)_3$, D-A cyclopropane **1n** (0.100 g, 0.37 mmol) was transformed into iodo-peroxy compound **5nc′** and purified by silica gel column chromatography (8:92 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 65% (0.118 g) yield. R_f 0.5 (1:4 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (d, *J* = 1.5 Hz, 4H), 5.12 (dd, *J* = 8.4, 4.5 Hz, 1H), 3.81 (s, 3H), 3.62 (s, 3H), 2.71 (dd, *J* = 15.5, 8.4 Hz, 1H), 2.55 (dd, *J* = 15.5, 4.5 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 167.7, 138.9, 133.9, 129.0, 128.5, 84.3, 80.7, 54.3, 54.0, 44.7, 41.3, 26.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{22}ClINaO_6$ 507.0047, Found 507.0036.

Dimethyl-2-bromo-2-(2-(tert-butylperoxy)-2-(naphthalen-2-yl)ethyl)malonate (5oa′): Following the general procedure, using 20 mol % $Sc(OTf)_3$, D-A cyclopropane **1o** (0.060 g, 0.21 mmol) was transformed into bromo-peroxy compound **5oa′** and purified by silica gel column chromatography (4:96 EtOAc: Hexanes as eluent) to give the title compound as semi solid in 62% (0.059 g) yield. R_f 0.5 (1:9 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 4H), 7.51-7.41 (m, 3H), 5.39 (dd, *J* = 8.2, 4.7 Hz, 1H), 3.86 (s, 3H), 3.52 (s, 3H), 3.05 (dd, *J* = 15.5, 8.2 Hz, 1H), 2.75 (dd, *J* = 15.5, 4.7 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.8, 137.6, 133.4,

133.2,128.2 (2), 127.8, 127.0, 126.3, 126.2, 125.2, 82.9, 80.7, 60.4, 54.2, 53.9, 43.0, 26.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{21}H_{25}BrNaO_6$ 475.0732, Found 475.0741.

Dimethyl 2-(2-(tert-butylperoxy)-2-(naphthalen-2-yl)ethyl)-2-chloromalonate (5ob′): Following the general procedure, using 20 mol % $Sc(OTf)_3$, D-A cyclopropane **1o** (0.100 g, 0.35 mmol) was transformed into chloro-peroxy compound **5ob′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as semi solid in 72% (0.104 g) yield. R_f 0.6 (1:4 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.79 (m, 4H), 7.51-7.47 (m, 3H), 5.39 (dd, *J* = 8.4, 4.7 Hz, 1H), 3.88 (s, 3H), 3.53 (s, 3H), 3.06 (dd, *J* = 15.3, 8.4 Hz, 1H), 2.72 (dd, *J* = 15.3, 4.7 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 166.8, 137.6, 133.4, 133.2, 128.2, 127.8, 126.9, 126.3, 126.2, 125.1, 81.5, 80.7, 68.4, 54.1, 53.9, 42.4, 26.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{21}H_{25}ClNaO_6$ 431.1227, Found 431.1251.

Dimethyl-2-bromo-2-(2-(5-bromothiophen-2-yl)-2-(tert-butylperoxy)ethyl)malonate (5ra′): Following the general procedure (reaction was performed at 0 ^oC), D-A cyclopropane **1r** (0.100 g, 0.41 mmol) was transformed into bromo-peroxy compound **5ra′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 64% (0.130 g) yield. R_f 0.4 (2:3 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 6.91(d, *J* = 3.8 Hz, 1H), 6.81 d, *J* = 4.0 Hz, 1H), 5.37 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.03 (dd, *J* = 15.4, 8.2 Hz, 1H), 2.75 (dd, *J* = 15.4, 4.7 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.5, 144.6, 129.2, 127.0, 112.8, 81.0, 78.0, 60.0, 54.2, 54.0, 42.7, 26.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{20}Br_2NaO_6S$ 508.9245, Found 508.9245.

Dimethyl-2-(2-(tert-butylperoxy)-2-(5-chlorothiophen-2-yl)ethyl)-2-chloromalonate (5rb′): Following the general procedure (reaction was performed at 0 ^oC), D-A cyclopropane **1r** (0.100 g, 0.41 mmol) was transformed into chloro-peroxy compound **5rb′** and purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 66% (0.110 g) yield. R_f 0.6 (1:4 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, *J* = 3.5 Hz, 1H), 6.76 (d, *J* = 3.8 Hz, 1H), 5.31 (dd, *J* = 8.4, 4.5 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.00 (dd, *J* = 15.2, 8.5 Hz, 1H), 2.69 (dd, *J* = 15.2, 4.6 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 166.4, 141.6, 130.4, 126.0, 125.4, 81.0, 76.6, 68.0, 54.1, 54.0, 42.0, 26.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{20}C_{l2}NaO_6S$ 421.0255, Found 421.0275.

Dimethyl-2-bromo-2-(2-(tert-butylperoxy)-2-(1,3-dioxoisoindolin-2-yl)ethyl)malonate (5ta′): Following the general procedure, D-A cyclopropane **1t** (0.100 g, 0.33 mmol) was transformed into bromo-peroxy compound **5ta′** and purified by silica gel column chromatography (25:75 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 77% (0.120 g) yield. R_f 0.35 (40:60 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ ^1H NMR (400 MHz, $CDCl_3$) δ 7.88-7.87 (m, 2H), 7.76-7.74 (m, 2H), 6.18-6.15 (m, 1H), 3.84 (br s, 3H), 3.73 (br s, 3H), 3.52-3.46 (m, 1H), 3.03-2.98

(m, 1H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.9, 166.2, 134.5, 131.7 123.8, 81.4, 81.2, 59.2, 54.3, 54.2, 38.6, 26.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{22}BrNNaO_8$ 494.0426, Found 494.0396.

Dimethyl 2-(2-(tert-butylperoxy)-2-(1,3-dioxoisoindolin-2-yl)ethyl)-2-iodomalonate (5tc′): Following the general procedure, D-A cyclopropane **1t** (0.100 g, 0.33 mmol) was transformed into iodo-peroxy compound **5tc′** and purified by silica gel column chromatography (15:85 Et_2O: Hexanes as eluent) to give the title compound as semi solid in 65% (0.112 g) yield. R_f 0.35 (1:4 Et_2O: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.87 (m, 2H), 7.77-7.73 (m, 2H), 6.10 (dd, *J* = 7.7, 4.4 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 3.36 (dd, *J* = 15.7, 7.7 Hz, 1H), 2.97 (dd, *J* = 15.6, 4.4 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.0, 167.5, 134.5, 132.8, 123.8, 83.4, 81.4, 54.4, 54.2, 40.5, 39.3, 26.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{22}INNaO_8$ 542.0288, Found 542.0296.

Dimethyl-2-bromo-2-(2-(tert-butylperoxy)-2-(2,5-dioxopyrrolidin-1-yl)ethyl)malonate (5ua′): Following the general procedure, D-A cyclopropane **1u** (0.100 g, 0.39 mmol) was transformed into bromo-peroxy compound **5ua′** and purified by silica gel column chromatography (8:92 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 69% (0.115 g) yield. R_f 0.4 (40:60 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (dd, *J* = 8.0, 4.1 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.35 (dd, *J* = 15.7, 8.1 Hz, 1H), 2.80 (dd, *J* = 15.7, 4.1 Hz, 1H), 2.67 (br s, 4H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 166.9, 166.0, 81.6, 81.4, 59.0, 54.3, 54.2, 37.9, 28.0, 26.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{22}BrNNaO_8$ 446.0426, Found 446.0427.

Dimethyl-2-(2-(tert-butylperoxy)-2-(2,5-dioxopyrrolidin-1-yl)ethyl)-2-chloromalonate (5ub′): Following the general procedure, D-A cyclopropane **1u** (0.100 g, 0.39 mmol) was transformed into bromo-peroxy compound **5ub′** and purified by silica gel column chromatography (8:92 Et_2O: Hexanes as eluent) to give the title compound as colorless oil in 71% (0.106 g) yield. R_f 0.4 (40:60 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (dd, *J* = 8.0, 4.3 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.34 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.78 (dd, *J* = 15.5, 4.3 Hz, 1H), 2.68 (br s, 4H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 166.6, 166.1, 81.5, 80.4, 67.5, 54.2 (2), 37.2, 28.0, 26.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{15}H_{22}ClNNaO_8$ 402.0932, Found 402.0923

Synthesis of Peroxy-Halogenated Compounds 6 and 7:

Dimethyl-2-bromo-2-(2-((1-methylcyclohexyl)peroxy)-2-phenylethyl)malonate (6): Cyclopropane **1g** (0.05 g, 0.21 mmol) and 1-hydroperoxy-1-methylcyclohexane (0.054g, 0.42 mmol) were dissolved in a mixture of dry DCM and cyclohexane (0.8 mL, 1:3, v/v) under argon and to this solution was added $Sc(OTf)_3$ (0.02g, 0.042 mmol) at room temperature. The reaction mixture was

stirred for 1 h and then NBS (0.186g, 1.05 mmol) was added to the reaction and stirred for additional 48 h. After completion of the reaction (as monitored by TLC), the reaction mixture was diluted with DCM (5 mL), washed successively with $NaHCO_3$ (5 mL) and brine (5 mL). The organic layer was separated and dried over Na_2SO_4. The solvents were removed under reduced pressure and the crude residue was purified by silica gel column chromatography (4:96 Et_2O: Hexanes as eluent) to afford compound **6** as colorless oil in 62% (0.059 g) yield (dr = 25:1). R_f 0.5 (5:95 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H), 5.23 (dd, *J* = 8.3, 4.7 Hz, 1H), 3.84 (s, 3H), 3.60 (s, 3H), 2.95 (dd, *J* = 15.4, 8.3 Hz, 1H), 2.67 (dd, *J* = 15.5, 4.7 Hz, 1H), 1.71-1.65 (m, 1H), 1.61-1.58 (m, 1H), 1.54-1.53 (m, 1H), 1.40-1.32 (m, 3H), 1.29-1.23 (m, 4H), 1.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.7, 140.4, 128.3, 128.2, 127.6, 82.5, 81.5, 60.5, 54.1, 53.9, 43.0, 35.2, 35.1, 25.8, 24.8, 22.5, 22.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{27}BrNaO_6$ 465.0889, Found 465.0901.

Dimethyl-2-bromo-2-(2-(4-chlorophenyl)-2-((1-methylcyclohexyl)peroxy)ethyl) malonate (7): Compound **7** was prepared from cyclopropane **1n** (0.070 g, 0.26 mmol), following similar procedure as shown for compound **6** and was obtained in 73% yield (0.091g) as colorless oil (dr = 10:1). R_f 0.6 (5:95 Et_2O: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 4H), 5.21 (dd, *J* = 8.7, 4.4 Hz, 1H), 3.84 (s, 3H), 3.65 (s, 3H), 2.87 (dd, *J* = 15.5, 8.7 Hz, 1H), 2.61 (dd, *J* = 15.5, 4.4 Hz, 1H), 1.66-1.47 (m, 4H), 1.39-1.22 (m, 6H), 1.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.5, 139.1, 133.8, 128.8, 128.5, 81.7, 81.6, 60.15, 54.2, 54.0, 43.1, 35.1, 25.7, 24.8, 22.4, 22.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{26}BrClNaO_6$ 499.0499, Found 499.0453.

General procedure for TBHP addition to D-A cyclopropanes bearing single ketone functional group: To a solution of cyclopropanes **8b** and **8ba'- 8be'** (0.100 g) in dry dichloromethane (0.2 mL) under argon was added *tert*-butyl hydroperoxide (10 equiv. 5-6 M solution in decane). $Sc(OTf)_3$ (50 mol%) was then added to the solution and the reaction mixture was stirred at room temperature for 3h (TLC controlled). The reaction mixture was then diluted with DCM (2 mL), washed with water (2 mL) and brine (2 mL). Next, the organic layer was separated and dried over anhydrous Na_2SO_4. Solvents were removed under reduced pressure (bath temperatuer 30 ^oC) and the crude product was purified by flash silica gel column chromatography to obtain the diperoxy products (**9** and **9a'-9e'**).

4,4-Bis(tert-butylperoxy)-1-(p-tolyl)butan-1-one (9): Following the general procedure, D-A cyclopropane **8b** (0.100 g, 0.37 mmol) was transformed into diperoxy compound **9** and purified by silica gel column chromatography (2: 98 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 70% (0.090g) yield. R_f 0.6 (5:95 EtOAc: Hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 5.34 (t, *J* = 6.1 Hz, 1H), 3.11 (t, *J* = 7.4 Hz, 2H), 2.39 (s, 3H), 2.17 (dd, *J* = 13.6, 7.3 Hz, 2H), 1.26 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9,

143.9, 134.4, 129.4, 128.3, 107.5, 80.7, 33.6, 26.6, 24.7, 21.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{30}NaO_5$ 361.1991, Found 361.1992.

4,4-Bis(tert-butylperoxy)-1-phenylbutan-1-one (9a′): Following the general procedure, D-A cyclopropane **8ba′** (0.100 g, 0.40 mmol) was transformed into diperoxy compound **9a′** and purified by silica gel column chromatography (2: 98 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 59% (0.076 g) yield. R_f 0.8 (1:9 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.95 (m, 2H), 7.55-7.53 (m, 1H), 7.47-7.43 (m, 2H), 5.35 (t, J = 6.1 Hz, 1H), 3.14 (t, J = 7.4 Hz, 2H), 2.19 (dd, J = 13.5, 7.3 Hz, 2H), 1.26 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 136.9, 133.2, 128.7, 128.1, 107.4, 80.7, 33.7, 26.6, 24.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{28}NaO_5$ 347.1834, Found 347.1859.

4,4-Bis(tert-butylperoxy)-1-(4-methoxyphenyl)butan-1-one (9b′): Following the general procedure, D-A cyclopropane **8bb′** (0.100 g, 0.35 mmol) was transformed into diperoxy compound **9b′** and purified by silica gel column chromatography (2: 98 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 72% (0.090g) yield. R_f 0.55 (5:95 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 6.94-6.91 (m, 2H), 5.34 (t, J = 6.1 Hz, 1H), 3.86 (s, 3H), 3.09 (t, J = 7.4 Hz, 2H), 2.17 (dd, J = 13.6, 7.4 Hz, 2H), 1.26 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 163.6, 130.4, 130.0, 113.8, 107.6, 80.7, 55.6, 33.4, 26.7, 24.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{19}H_{30}NaO_6$ 377.1940, Found 377.1907.

1-(4-Bromophenyl)-4,4-bis(tert-butylperoxy)butan-1-one (9c′): Following the general procedure, D-A cyclopropane **8bc′** (0.100 g, 0.30 mmol) was transformed into diperoxy compound **9c′** and purified by silica gel column chromatography (2: 98 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 66% (0.080g) yield. R_f 0.65 (5:95 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2H), 7.60-7.58 (m, 2H), 5.33 (t, J = 6.0 Hz, 1H), 3.09 (t, J = 7.3 Hz, 2H), 2.20-2.15 (m, 2H), 1.25 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 135.6, 132.0, 129.7, 128.3, 107.3, 80.8, 33.7, 26.6, 24.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{18}H_{27}BrNaO_5$ 425.0940, Found 425.0903.

4,4-bis(tert-butylperoxy)-1-(thiophen-2-yl)butan-1-one (9d′): Following the general procedure, D-A cyclopropane **8bd′** (0.100 g, 0.38 mmol) was transformed into diperoxy compound **9d′** and purified by silica gel column chromatography (2: 98 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 70% (0.092 g) yield. R_f 0.7 (5:95 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.73 (m, 1H), 7.63-7.61 (m, 1H), 7.12 (dd, J = 4.9, 3.8 Hz, 1H), 5.32 (t, J = 6.0 Hz, 1H), 3.08 (t, J = 7.4 Hz, 2H), 2.21-2.16 (m, 2H), 1.26 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 144.2, 133.6, 132.0, 128.2, 107.3, 80.8, 33.4, 26.3, 24.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{16}H_{26}NaO_5S$ 353.1399, Found 353.1389.

2-(2,2-Bis(tert-butylperoxy)ethyl)-3,4-dihydronaphthalen-1(2H)-one (9e′): Following the general procedure, D-A cyclopropane **8be′** (0.100 g, 0.36 mmol) was transformed into diperoxy compound **9e′** and purified by silica gel column chromatography (2: 98 EtOAc: Hexanes as eluent) to give the title compound as colorless oil in 56% (0.070g) yield. R_f 0.65 (5:95 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.38 (t, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 8.1 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 5.46 (t, *J* = 6.3 Hz, 1H), 3.03-3.29 (m, 2H), 2.71-2.64 (m, 1H), 2.47-2.40 (m, 1H), 2.27-2.21 (m, 1H), 1.90-1.79 (m, 1H), 1.75-1.66 (m, 1H), 1.21 (s, 9H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ199.5, 143.9, 133.3, 132.5, 128.8, 127.5, 126.7, 107.1, 80.6, 44.2, 30.5, 29.7, 29.2, 26.7, 26.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{30}NaO_5$ 373.1991, Found 373.1969

Follow-up Chemistry/ Applications: Preparation of methyl 3-oxo-2-phenyl-6-(p-tolyl)-2,3,4,5-tetrahydropyridazine-4-carboxylate (10): To a solution of compound **3aa** (0.16 g, 0.47 mmol) in dry CH_3CN (4 mL) was added DBU (16 μL, 0.1 mmol) and the reaction mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo and the crude residue was dissolved in dry MeOH (2 mL) and were added $PhNHNH_2$ (0.045g, 0.41 mmol) and AcOH (0.2 mL). The reaction mixture was refluxed for 5 h under argon. Upon completion, the solvent was removed in vacuo and the crude was purified by flash silica gel column chromatography (using 10: 90 to 15:85 EtOAc: Hexanes as eluent) to obtain compound **10** as an oil in 52% (0.08g) yield. R_f 0.35 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.62-7.60 (m, 2 H), 7.44-7.41 (m, 2H), 7.31-7.22 (m, 3H), 3.80 (s, 3 H), 3.79- 3.76 (m, 1 H), 3.55 (dd, *J* = 16.9, 8.2 Hz, 1H), 3.19 (dd, *J* = 16.9, 6.7 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 161.4, 151.5, 141.1, 140.7, 132.4, 129.5, 128.6, 126.9, 126.4, 124.9, 53.2, 44.8, 26.2, 21.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{19}H_{18}N_2NaO_3$ 345.1215, Found 345.1242.

Preparation of methyl 2-oxo-5-(p-tolyl)tetrahydrofuran-3-carboxylate (11): $Pd(OH)_2/C$ (0.014 g, 20% w/w) was added to a solution of **3aa** (0.070 g, 0.20 mmol) in dry MeOH (1.5 mL) and the reaction mixture was stirred at room temperature for 3 h under the positive pressure of H_2 gas. Next, the mixture was filtered through celite and the solvent was removed in vacuo. The crude residue was purified by flash column chromatography (using 15:85 EtOAc: Hexanes as eluent) to afford compound **11** as a mixture of diastereomers (dr = 1:1) in 72% (0.035g) yield. R_f 0.3 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.19 (m, 2H), 7.15-7.13 (m, 6H), 5.60 (t, *J* = 7.2 Hz, 1H), 5.33 (dd, *J* = 10.3, 6.1 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.76-3.78 (m, 1H), 3.64 (dd, *J* = 9.3, 4.8 Hz, 1H), 2.93 (ddd, *J* = 13.2, 7.0, 4.8 Hz, 1H), 2.76 (ddd, *J* = 13.1, 8.8, 6.1 Hz, 1H), 2.65-2.56 (m, 1H), 2.35 (ddd, *J* = 13.3, 9.3, 7.5 Hz, 1H), 2.29 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 171.6, 168.2, 168.1, 139.1, 138.8, 135.6, 134.9, 129.6 (2), 126.0, 125.4, 80.7, 80.3,

53.4, 53.2, 47.9, 47.0, 35.0, 34.9, 21.3 (2); HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{13}H_{14}NaO_4$ 257.0790, Found 257.0795.

Preparation of dimethyl 2-((14H-dibenzo[a,j]xanthen-14-yl)methyl)malonate (12): To a solution of compound **3aa** (0.050 g, 0.14 mmol) and β-naphthol (0.04 g, 0.28 mmol) in dichloroethane (1.0 mL) was added TfOH (0.018 mL, 0.21 mmol) and the reaction mixture was stirred at room temperature under argon for 3 h. After completion of the reaction (TLC controlled), DCE was removed in vacuo and the reaction mixture was diluted with EtOAc (3 mL), washed with aqueous $NaHCO_3$ (3 mL), H_2O (3 mL) and organic layer was separated and dried over Na_2SO_4. Solvents were removed under reduced pressure and the crude product was purified by flash silica gel column chromatography (using 2:98 EtOAc: Hexanes as eluent) to obtain compound **12** as brown solid in 63% (0.040 g) yield. R_f 0.35 (1:9 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.9 Hz, 2H), 7.66 – 7.60 (m, 2H), 7.49-7.45 (m, 2H), 7.40 (d, J = 8.9 Hz, 2H), 5.70 (t, J = 5.6 Hz, 1H), 3.42 (s, 6H), 3.15 (t, J = 7.0 Hz, 1H), 2.63-2.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ169.6, 150.5, 131.7, 131.1, 129.0, 128.9, 127.2, 124.6, 122.2, 117.9, 115.9, 52.5, 48.7, 35.3, 29.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{27}H_{22}NaO_5$ 449.1365, Found 449.1350.

Preparation of dimethyl 2-allyl-2-(2-(tert-butylperoxy)-2-phenylethyl)malonate (13): Compound **3ga** (0.07 g, 0.17 mmol), allyltributylstannane (0.086 g, 0.26 mmol) and 2,2'-azobisisobutyronitrile (AIBN) (0.003 g, 0.017 mmol) were taken in dry benzene (1.0 mL) and refluxed for 2 hours under argon. After completion, the reaction mixture was treated with saturated solution of KF in Et_2O and stirred for 30 minutes. Next, solvents were removed under reduced pressure and the crude residue was purified by flash silica gel column chromatography (using 4:96 EtOAc: Hexanes as eluent) to obtain compound **13** as semi solid in 76% (0.048g) yield. R_f 0.7 (1:9 EtOAc: Hexanes);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 5H), 5.74 – 5.61 (m, 1H), 5.13 (ddd, J = 11.0, 9.8, 1.4 Hz, 2H), 4.90 (dd, J = 8.7, 4.7 Hz, 1H), 3.71 (s, 3H), 3.57 (s, 3H), 2.90-2.76 (m, 2H), 2.54 (dd, J = 15.2, 8.8 Hz, 1H), 2.31 (dd, J = 15.2, 4.7 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 171.2, 141.3, 132.6, 128.2, 128.0, 127.3, 119.4, 81.8, 80.1, 56.2, 52.6, 52.5, 37.6, 37.2, 26.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{20}H_{28}NaO_6$ 387.1784, Found 387.1753.

Preparation of dimethyl 2-azido-2-(2-(tert-butylperoxy)-2-phenylethyl)malonate (14): Compound **3ga** (0.05 g, 0.12 mmol) and NaN_3 (0.040 g, 0.62 mmol) were taken together in dry DMF (1.0 mL) and the reaction mixture was stirred at room temperature for 12 h. After completion, reaction mixture was diluted with diethyl ether (10 mL), washed with H_2O (5 mL x 3), brine (5 mL x 2) and organic layer was separated and dried over Na_2SO_4. The crude residue was purified by flash silica gel column chromatography (using 8:92 Acetone: Hexanes as eluent) to obtain compound **14**

as semi solid in 88% (0.040g) yield. R_f 0.6 (1:9 Acetone: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.35 – 7.28 (m, 5H), 5.06 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.87 (s, 3H), 3.61 (s, 3H), 2.68 (dd, *J* = 15.0, 8.4 Hz, 1H), 2.28 (dd, *J* = 15.0, 4.8 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ167.7, 167.5, 140.2, 128.3, 128.2, 127.6, 81.0, 80.6, 69.6, 53.6, 53.5, 39.0, 26.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{17}H_{23}N_3NaO_6$ 388.1485, Found 388.1463.

Preparation of dimethyl 2-(2-(tert-butylperoxy)-2-phenylethyl)-2-(4-methoxystyryl)malonate (15): To a flame dried Schlenk tube were successively added compound **3ga** (0.05 g, 0.12 mmol), 1-methoxy-4-vinylbenzene (0.033 g, 0.24 mmol), $Pd(OAc)_2$ (3 mg, 0.012 mmol), Xantphos (14 mg, 0.024 mmol), cesium carbonate (0.24 mmol, 0.078 g) and dry benzene (1mL). The reaction mixture was degassed via freeze-pump-thaw process (three cycles) and stirred at room temperature for 14 h. After completion of the reaction, the reaction mixture was passed through celite and the filtrate was concentrated under vacuo. The crude product was purified by flash silica gel column chromatography (using 1:9 EtOAc: Hexanes as eluent) to obtain compound **15** as colorlese oil in 35% (0.020g) yield. R_f 0.3 (1:9 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 9H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.74 (d, *J* = 16.7 Hz, 1H), 6.49 (d, *J* = 16.7 Hz, 1H), 5.05 (dd, *J* = 7.8, 4.9 Hz, 0.3H), 4.94-4.92 (m, 1H), 3.82 (s, 3H), 3.78 (s, 1H), 3.77 (s, 3H), 3.60 (s, 1H), 3.53 (s, 1H), 3.50 (s, 3H), 2.89 (dd, *J* = 14.8, 7.8 Hz, 1H), 2.79 (dd, *J* = 15.0, 7.8 Hz, 0.4H), 2.61 (dd, *J* = 14.8, 5.4 Hz, 1H), 2.56-2.48 (m, 0.4H), 1.10 (s, 9H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.6, 170.2, 170.1, 159.7, 159.0, 144.6, 141.3, 140.9, 133.6, 131.6, 129.4 (2), 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 126.9, 123.4, 120.8, 114.1, 113.1, 82.2, 80.3, 80.1, 61.2, 57.4, 55.5, 55.3, 52.9, 52.8, 52.5, 40.6, 40.1, 26.6, (2); HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{26}H_{32}NaO_7$ 479.2046, Found 479.2074.

Preparation of Dimethyl 2-(2-oxo-2-phenylethylidene)malonate (16): Compound **3ga** (0.100 g, 0.24 mmol), 2-bromophenol (0.043 g, 0.24 mmol) and potassium fluoride (0.036 g, 0.62 mmol) were dissolved in dry DMF (1.0 mL) and stirred under argon at room temperature for 24 h. After completion of the reaction (TLC controlled), reaction mixture was diluted with EtOAc (10 mL), washed with H_2O (5 mL x 2), brine (5 mL x 2) and the organic layer was separated. It was dried over Na_2SO_4 and solvent was removed in vacuo. The crude product was purified by flash silica gel column chromatography (using 1:9 EtOAc: Hexanes as eluent) to obtain compound **16** as yellow oil in 58% (0.036 g) yield. R_f 0.3 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.96 (m, 2H), 7.89 (s, 1H), 7.66-7.61 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 3.90 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 189.1, 165.2, 163.4, 136.2, 135.8, 134.4, 129.1, 129.0, 53.4, 53.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calculated for $C_{13}H_{12}NaO_5$ 271.0582, Found 271.0570.

Preparation of dimethyl 2-hydroxy-2-(2-oxo-2-phenylethyl)malonate (17): Compound **3ga** (0.100 g, 0.24 mmol) was dissolved in dry DCM (1 mL) and to that solution was added triehtylamine

(0.033 mL, 0.24 mmol). The reaction mixture was stirred at room temperature for 12 h. Solvent was removed under reduced pressure and the crude was purified by flash silica gel column chromatography to obtain compound **17** as colorless oil in 60% (0.040 g) yield. R_f 0.35 (1:4 EtOAc: Hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.62-7.58 (m, 1H), 7.50-7.46 (m, 2H), 4.31 (br s, 1H), 3.86-3.85 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 170.2, 136.2, 134.0, 128.9, 128.4, 77.0, 53.8, 43.9 ; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calculated for $C_{13}H_{14}NaO_6$ 289.0688, Found 289.0661.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C spectra of all new compounds, HPLC chromatograms and crystal data for compound **5ab'**(CIF) are provided. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by SERB, DST (ECR/2016/001474) to J.S. K.S thanks SERB, DST (PDF/2017/000097). J.S sincerely thanks Dr. Martha Morton (U. Nebraska-Linclon, USA) for helpful discussions on NMR and CBMR for research facilities. J.S thanks Mr. Ajay Verma (CBMR) for NMR experiments. D.D thanks DST-FIST for X-ray facility at SPS, JNU.

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