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## ARTICLE

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#### Introduction

Cyclopropane derivatives are present in a large number of natural and biologically important products. They are also versatile building blocks in organic transformation. Their unique reactivity and structural properties lead to a range of interesting and characteristic transformations.<sup>1</sup> Various synthetic methods for their preparation have been developed (Scheme 1), such as Simmons-Smith reaction,<sup>2</sup> transitional-metal-catalyzed addition of diazo compounds<sup>3a-e</sup> or iodonium ylides<sup>3f-h</sup> to an alkene, organocatalyzed addition-cyclization of  $\beta$ -halogenated carbonyl compounds or a sulfur ylide to an activated double bond.<sup>4</sup> On the other hand, cyclopropenes, as another important three-membered carbocycles, have broad utility as synthons in organic synthesis.<sup>5</sup> Typical synthetic methods include a carbene or carbenoid addition to alkynes<sup>6</sup> catalyzed by Rh(II),<sup>6b-i</sup> Ir(II),<sup>6j</sup> Co(II),<sup>6k,1</sup> and Ag(I),<sup>6m,n</sup> and elimination of substituted

### Hypervalent iodine(III)-mediated cyclopropa(e)nation of alkenes/alkynes under mild conditions

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Hypervalent iodine(III)-mediated dioxygenation and diamination of alkenes have been previously developed. In this study, the potential application of hypervalent iodine(III) reagent was successfully extended to the dialkylation and cyclopropa(e)nation of unsaturated alkenes and alkynes. The reactions of alkenes with malononitrile and other active methylene compounds as the carbon nucleophiles, give access to multisubstituted cyclopropane derivatives in moderate to excellent yields. Both electron–rich and electron–deficient alkenes are suitable substrates. Alkynes, no matter terminal or internal alkynes, work well, affording the corresponding highly functionalized cyclopropenes efficiently. A plausible mechanism of iodo(III)cyclopropanation, ring opening attacked by the carbon-nucleophile, recyclization into a four-membered iodo(III)cyclobutene and final reductive elimination. The protocol might provide a complementary route to cyclopropanation/cyclopropenation.

Cyclopropanation:



**Scheme 1.** Approaches for the cyclopropanation and cyclopropenation

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cyclopropanes under basic conditions.<sup>7</sup> Despite significant progress made in this area, some of the methods might suffer from substrate limitation, functional group tolerance, and the employment of transition metal catalyst, which is highly toxic and environmentally unfriendly. Therefore, to match the increasing scientific and pharmaceutical demands, it is still of continued interest and great importance to develop facile and efficient approaches towards cyclopropa(e)nation.

In our previous research, we communicated the reaction of chalcones with malononitrile in the open air, which provided an unprecedented  $\beta$ -cyanation products (Scheme 2).<sup>8</sup> To explore the role of molecular oxygen in the reaction and further elucidate the plausible mechanism, in the continued work, external oxidants like hypervalent iodine(III) reagents9 were introduced. As a result, cyanated products were completely suppressed and cyclopropane derivatives were produced exclusively. Further work indicates that this protocol could be applicable to general alkene and alkyne substrates. furnishing the corresponding cyclopropanes/cyclopropenes in good efficiency. Noteworthy that, although the diamination<sup>10</sup> and dioxygenation<sup>11</sup> of alkenes/alkynes by the hypervalent iodine(III) reagents have been well-documented, the potential of iodine(III) reagents in oxidative dialkylation and/or cyclopropanation remains scarce. Literature search revealed that only one example of PhI(OAc)2-mediated cyclopropanation was reported by Wirth and co-workers early in 2003 (eq. 1).<sup>12</sup> However, the reaction was restricted by limited scope and poor yields. Compared with the common routes toward cyclopropanes and cyclopropenes, i.e., addition reaction of an alkene or alkyne with metal carbenes derived from the decomposition of diazo compounds or iodonium ylides,<sup>3,6b-n</sup> this methodology has the advantage of avoiding the utilization of transition metal catalysts.



Scheme 2. Reactions of chalcones with malononitrile under different oxidation conditions



#### **Results and Discussion**

#### **Reaction optimization**

Initially, the model reaction of chalcone 1a and malononitrile in the presence of PhI(OAc)<sub>2</sub> was examined under various conditions (Table 1). No cyclopropane product was detected when the reaction was performed in DMF at room temperature (entry 1). The highly substituted cyclopropane 2a was observed in MeCN (entry 2). With other solvents such as toluene, DCM

and DCE, the yields were improved to some extent (entries 3-5). Raising the temperature to 80 °C gave a yield of 51% (entry 6). Excess malononitrile was not beneficial for the explored reaction (entry 7). 2.2 equiv of PhI(OAc)<sub>2</sub> gave 2a in an improved yield of 67% (entry 8). The introduction of external additive such as K<sub>2</sub>CO<sub>3</sub> made the system cleaner and 71% yield was achieved (entry 9). Other bases like Cs<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> were also screened, but gave unsatisfied result (entries 10-12). The role of the base was supposed to remove the acid (2 equiv) generated in the reaction system. Other hypervalent iodine(III) reagents were also examined, however, PhI(OTf)<sub>2</sub> and PhI(OPiv)<sub>2</sub> proved to be inferior and PhI(OTs)OH inert (entries 13-15). The structure of 2a and its stereochemistry were confirmed by the single-crystal X-ray diffraction (Figure 1).<sup>13</sup>

**Table 1.** Optimization of the reaction conditions<sup>a</sup>



Entry	Oxidant (equiv)	Additive	Solvent	$T(^{\circ}C)$	Yield [%
1	PhI(OAc) <sub>2</sub> (1.2)	_	DMF	30	0
2	PhI(OAc) <sub>2</sub> (1.2)	_	MeCN	30	5
3	PhI(OAc) <sub>2</sub> (1.2)	_	toluene	30	9
4	PhI(OAc) <sub>2</sub> (1.2)	_	DCM	30	38
5	PhI(OAc) <sub>2</sub> (1.2)	_	DCE	30	44
6	PhI(OAc) <sub>2</sub> (1.2)	_	DCE	80	51
7	PhI(OAc) <sub>2</sub> (1.2)	_	DCE	80	43 <sup>b</sup>
8	PhI(OAc) <sub>2</sub> (2.2)	_	DCE	80	67
9	PhI(OAc) <sub>2</sub> (2.2)	$K_2CO_3$	DCE	80	71
10	PhI(OAc) <sub>2</sub> (2.2)	Cs <sub>2</sub> CO <sub>3</sub>	DCE	80	42
11	PhI(OAc) <sub>2</sub> (2.2)	$K_3PO_4$	DCE	80	68
12	PhI(OAc) <sub>2</sub> (2.2)	NaOAc	DCE	80	51
13	$PhI(OTf)_2(2.2)$	$K_2CO_3$	DCE	80	39
14	$PhI(OPiv)_2(2.2)$	$K_2CO_3$	DCE	80	59
15	PhI(OTs)OH (2.2)	K <sub>2</sub> CO <sub>3</sub>	DCE	80	0

<sup>a</sup> Reactions were carried out with chalcone (1.0 mmol), malononitrile (1.2 equiv), hypervalent iodine(III) in solvent (4 mL) unless other noted. <sup>b</sup> 3.0 equiv malononitrile. <sup>c</sup> Isolated vield.







Figure 1. X-ray Crystal Structures of 2a and 2n.

#### Substrate scopes

Under the optimized conditions (Table 1, entry 9), selected chalcones reacted with malononitirle in DCE at 80 °C to give highly substituted cyclopropanes 2a-d in moderate yields (Table 2, entries 1-4). To our delight, a wide variety of alkenes were also suitable for the cyclopropanation reaction. Both styrene and styrene derivatives with substituents such as methyl-, tert-, butyland bromo- at the para-position of the phenyl ring proceeded efficiently, affording the corresponding substituted cyclopropanes 2e-h in high yields (81-88%, entries 5-8). 2-Thienylethylene afforded 2-thienylcyclopropane-1,1dicarbonitrile (2i) in 92% yield (entry 9). 1,1-Disubstituted alkenes like  $\alpha$ -methylstyrene was found to be compatible under the explored reactions, giving tetrasubstituted cyclopropane 2j in 89% yield (entry 10). The reaction with aliphatic terminal alkene proceeded smoothly and product 2k was obtained in 87% yield (entry 11). Diene can react one of the double bonds, affording cyclopropane 21 with one terminal double bond intact even under more forcing conditions. (entry 12). Internal alkenes also worked well. Substrates including acyclic-styrene, trans-stilbene, and cyclic indene, 1,2-dihydro-naphthalene, 2-norbornene, 1-methylcyclohexene and 1-phenylhexene produced multisubstituted cyclopropanes 2m-s in 51-96% yields (entries 13-19). On the basis of <sup>1</sup>H NMR spectroscopy and the single-crystal X-ray diffraction of **2a** and **2n** (Figure 1),<sup>13</sup> the relative configuration of 2a-c, 2m and 2n are assigned to be trans stereoisomers. However, compound 2d was obtained as a mixture of diastereoisomers (with around 7% cis-isomers observed based on <sup>1</sup>H NMR analysis). All of the above results indicate the efficiency of the hypervalent iodine(III)-mediated cyclopropanation reaction.

Contrary to that with 1-methyl-cyclohexene and 1phenylhexene (Table 2, entries 18 and 19), in the reactions of parent cyclohexene and cyclopentene with malononitrile (1.2 equiv), no corresponding cyclopropane products were detected. Instead, dialkylation products **3a** and **3b** were obtained as the main products. When 2.2 equiv of malononitrile was used, the yields of **3a** and **3b** reached up to 85% and 87% yields, respectively (eqs. 2 and 3 in Scheme 3).<sup>14,15</sup>

**Table 2.** PhI(OAc)<sub>2</sub>-mediated cyclopropanation of alkenes with malononitrile<sup>a</sup>





 $^a$  Reactions were carried out with 1 (1.0 mmol), malononitrile (1.2 equiv),  $K_2CO_3$  (2.2 equiv), PhI(OAc)\_2 (2.2 equiv) in DCE (4.0 mL) at 80 °C for 1 h.  $^b$  run at 50 °C.  $^c$  Isolated yield.



Scheme 3. Dialkylation of cyclopentene and cyclohexene with malononitrile in the presence of  $PhI(OAc)_2$ .

The hypervalent iodine(III)-mediated cyclopropanation strategy was also applicable to alkyne substrates (Table 3). It was found that, in this case, no extra base was necessary. Phenylacetylene and substituted phenylacetylenes gave the corresponding cyclopropenes 5a-e in excellent yields (entries 1-5). The substituents on the phenyl ring may be alkyls (methyl and t-butyl), and halogen atoms (Cl and F) etc.. Similar to that of diene substrate (Table 2, entry 12), bisacetylene can react with one carbon-carbon triple bond and the other one intact, giving cyclopropene 5f in 91% yield (entry 6). In addition to the terminal alkynes, internal alkynes were also examined. The reactions based on alkyl aryl alkyne, like 1-phenyl-1-pentyne and dialkyl alkyne, like 2-pentyne proceeded efficiently, giving the corresponding tetrasubstituted cyclopropenes 5g and 5h in high to excellent yields (entries 7 and 8). However, diarylalkyne, e.g. diphenylethyne and electron-deficient alkyne like ethyl 3phenylpropiolate, gave low to moderate yields (28% and 47%, respectively, entries 9 and 10).<sup>16,17</sup>

**Table 3.**  $PhI(OAc)_2$ -Mediated cyclopropenation of alkynes and malononitrile<sup>*a*</sup>



phenylacetylene afforded the desired cyclopropanes **6a-c** and cyclopropenes **7**, respectively, albeit in low to moderate yields (Table 4, entries 1-4).

**Table 4.** Cyclopropanation/Cyclopropenation of selected alkenes and alkynes with ethyl nitroacetate<sup>a</sup>



<sup>*a*</sup> Conditions: alkenes/alkynes (1.0 mmol), ethyl nitroacetate (1.2 equiv), PhI(OAc)<sub>2</sub> (2.2 equiv), K<sub>2</sub>CO<sub>3</sub> (2.2 equiv) in DCE (4.0 mL) at 50 °C for 2 h for entries 1-3, with no K<sub>2</sub>CO<sub>3</sub> for entry 4. <sup>*b*</sup> Isolated yields.

#### Proposed mechanism

In order to elucidate the possible mechanism for the cyclopropa(e)nation reaction, several control experiments were carried out. Upon treatment of PhI(OAc)<sub>2</sub> with K<sub>2</sub>CO<sub>3</sub>, no PhIO was formed. In the mixture of malononitirle, PhI(OAc)<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> in DCE, no ligand exchange between acetate anion and malononitrile was detected, same as that reported by Wirth et al.<sup>12</sup> (see the supporting information). Moreover, both cisstilbene (eq. 4) and trans-stilbene (Table 2, entry 14) afforded trans-2,3-diphenylcyclopropane-1,1-dicarbonitrile **2n**, as evidenced by their X-ray crystal structures. Based on the above control experiments, along with the fact that some of the reaction proceeded smoothly in the absence of K<sub>2</sub>CO<sub>3</sub> (Table 1, entry 8 and Table 3), the mechanism of iodo-ylide pathway was ruled out.



In the following work, other active methylene compounds were investigated as the carbon-nucleophile.<sup>18</sup> Ethyl nitroacetate proved to be suitable and the reactions with alkenes such as styrene, 2-norbornene and chalcone, and alkyne such as

A plausible mechanism for the formation of cyclopropane 2 was proposed, as depicted in Scheme 4 (with trans-alkenes as an example).<sup>19</sup> Initially, the electrophilic addition between  $PhI(OAc)_2$  and the alkene 1 generates iodo(III)cyclopropane I,<sup>10</sup> followed by the formation of ion pair II, with the elimination of

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acetic acid. Then, a nucleophilic ring opening takes place, giving rise to  $\lambda^3$ -iodane **III**. With the elimination of the second molecular acetic acid, zwitterionic **IV** is formed, which undergoes cyclopropanation to furnish the final product 2.<sup>12</sup>

The possible mechanism for the cyclopropenation of alkynes was depicted in Scheme 5, although the exact mechanism is still not clear. The procedure involves iodo(III)cyclopropenation, ring opening attacked by the malononitrile anion to give intermediate **III**, tautemerization (**IV-IV**') via elimination of HOAc and ringclosure into four-membered iodo(III)cyclobutene **V**, and final formation of cyclopropenation product via hypervalent iodine(III)-mediated reductive elimination.<sup>20</sup>



Scheme 4. Proposed mechansim for the cyclopropanation with transalkene substrates



Scheme 5. Proposed mechanism for the cyclopropenation

#### Conclusions

In summary, we have developed a new and efficient cyclopropa(e)nation method by the utilization of  $PhI(OAc)_2$  reagent. The reaction features broad substrate scope (both electron-deficent and -rich alkenes/alkynes), relatively mild conditions, and high efficiency. The beauty of the chemistry relies on the straightforward transformation of the initial iodo-heterocyclopropa(e)ne into the final cyclopropa(e)ne over the unique reactivity of hypervalent iodine reagent as both excellent electrophile and hypernucleofuge.<sup>9</sup> Further studies to explore the scope of the carbon nucleophile in the cyclopropanation and

hypervalent iodine(III)-mediated dialkylation of unsaturated alkenes and alkynes are in progress.

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#### Experimental section

#### General experimental

For general experimental details see ESI. The ESI also contains spectroscopic data for compounds **2**, **3**, **5**, **6** and **7**.

**Representative procedure for cyclopropanation. Synthesis of 2a:** Complex PhI(OAc)<sub>2</sub> (354 mg, 1.1 mmol), K<sub>2</sub>CO<sub>3</sub> (152 mg, 1.1 mmol), malononitrile (40 mg, 0.6 mmol) and chalcone **1a** (104 mg, 0.5 mmol) were dissolved in DCE (2.0 mL) in a 25 mL flask. The mixture was stirred at 80 °C for 1 h (monitored by TLC). Then the reaction mixture was cooled to room temperature, poured into the water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined organic phase was washed with water (3 × 10 mL). The solvent was removed under reduced pressure, and the residue was purified by a flash silica gel column chromatography (EtOAc/petroleum ether = 1:10) to give **2a** as colorless crystals in 71% yield.

**2-Benzoyl-3-phenylcyclopropane-1,1-dicarbonitrile** (2a): Colorless crystals. m.p. 129-131 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.92-3.93 (d, *J* = 8.0 Hz, 1H), 4.04-4.06 (d, *J* = 8.0 Hz, 1H), 7.38-7.40 (m, 2H), 7.46-7.48 (t, *J* = 6.5 Hz, 3H), 7.60-7.63 (t, *J* = 8.0 Hz, 2H), 7.73-7.75 (d, *J* = 7.5 Hz, 1H), 8.11-8.13 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 15.3, 35.4, 38.6, 111.5, 112.1, 128.3, 128.7, 129.3, 129.4, 129.8, 135.1, 135.3, 188.8. MS calcd m/z 272.09, found 273.09 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O: C, 79.39; H, 4.44; N, 10.39; Found: C, 79.53; H, 4.47; N, 10.48.

**2-Benzoyl-3-**(*p*-tolyl)cyclopropane-1,1-dicarbonitrile (2b): White solid. m.p. 145-147 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 2.39$  (s, 3H), 3.88-3.89 (d, J = 8.0 Hz, 1H), 4.02-4.03 (d, J = 8.0 Hz, 1H), 7.59-7.63 (t, J = 8.0 Hz, 2H), 7.73-7.76 (t, J = 7.5 Hz, 1H), 8.10-8.12 (t, J = 7.5 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 15.3$ , 21.3, 35.6, 38.7, 111.7, 112.3, 126.4, 130.0, 135.1, 140.0, 188.9. MS calcd m/z 286.11, found 287.11 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O: C, 79.70; H, 4.93; N, 9.78; Found: C, 79.56; H, 4.90; N, 9.71.

**2-Benzoyl-3-(3-nitrophenyl)cyclopropane-1,1-dicarbonitrile (2c):** White solid. m.p. 168-170 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.05-4.07 (d, *J* = 8.0 Hz, 1H), 4.14-4.16 (d, *J* = 8.0 Hz, 1H), 7.63-7.66 (t, *J* = 8.0 Hz, 2H), 7.69-7.73 (t, *J* = 8.0 Hz, 1H), 7.76-7.81 (m, 2H), 8.14-8.15 (d, *J* = 7.5 Hz, 2H), 8.25 (s, 1H), 8.33-8.34 (d, *J* = 8.0 Hz, 1H) . <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 15.3, 35.4, 37.1, 110.8, 111.6, 123.2, 124.8, 128.9, 129.5, 130.6, 131.7, 134.8, 134.9, 135.5, 148.6, 187.9. MS calcd m/z 317.08, found 318.08 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>18</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>: C, 68.14; H, 3.49; N, 13.24; Found: C, 68.25; H, 3.51; N, 13.31.

(*E*)-2-Benzoyl-3-styrylcyclopropane-1,1-dicarbonitrile (2d): Brown oil. (the following <sup>1</sup>H NMR and <sup>13</sup>C NMR data are based on the trans-isomers): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.45-3.48 (t, *J* = 8.5 Hz, 1H), 3.74-3.75 (d, *J* = 7.5 Hz, 1H), 5.98-6.03 (m, 1H), 6.92-6.95 (d, *J* = 16.0 Hz, 1H), 7.31-7.36 (m, 3H). 7.37-7.43 (m, 2H), 7.57-7.59 (m, 2H), 7.69-7.73 (m, 1H), 8.05-8.07

(m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 14.2, 14.9, 36.1, 36.9, 37.8, 40.6, 111.4, 112.2, 112.7, 112.9, 118.6, 125.8, 126.8, 128.3, 128.8, 128.8, 128.9, 129.2, 129.3, 129.4, 129.4, 129.7, 129.8, 130.8, 131.9, 133.7, 135.0, 188.5, 188.9. MS calcd m/z 298.11, found 299.11 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O: C, 80.52; H, 4.73; N, 9.39; Found: C, 80.66; H, 4.75; N, 9.47.

**2-Phenylcyclopropane-1,1-dicarbonitrile (2e):** Colorless crystals. m.p. 60-62 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.23-2.28 (m, 2H), 3.29-3.32 (t, *J* = 9.0 Hz, 1H), 7.29-7.31 (m, 2H), 7.41-7.45 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 7.0, 22.0, 34.9, 112.9, 115.2, 128.2, 128.7, 129.2, 130.4. MS calcd m/z 169.07, found 170.07 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>: C, 78.55; H, 4.79; N, 16.66; Found: C, 78.44; H, 4.76; N, 16.54.

**2-(***p***-Tolyl)cyclopropane-1,1-dicarbonitrile** (2f) and 2-(*m*-tolyl)cyclopropane-1,1-dicarbonitrile (2f'): Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.21-2.26 (m, 4H), 2.36-2.38 (d, *J* = 8.5Hz, 6H), 3.26-3.27 (d, *J* = 2.0 Hz, 2H), 7.08-7.10 (d, *J* = 10.5 Hz, 2H), 7.16-7.25 (m, 5H), 7.29-7.30 (d, *J* = 8.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 7.0, 7.1, 21.1, 21.2, 22.1, 22.2, 34.9, 35.0, 113.0, 113.1, 115.3, 115.3, 125.1, 127.4, 128.0, 128.8, 129.0, 129.7, 130.0, 130.0, 138.8, 139.4. MS calcd m/z 183.08, found 184.08 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>: C, 79.10; H, 5.53; N, 15.37; Found: C, 79.21; H, 5.55; N, 15.44.

**2-(4-(***tert***-Butyl)phenyl)cyclopropane-1,1-dicarbonitrile (2g):** Colorless crystal. m.p. 149-151 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.31 (s, 9H), 2.22-2.24 (m, 2H), 3.24-3.28 (t, *J* = 9.0 Hz, 1H), 7.21-7.23 (d, *J* = 8.5 Hz, 2H), 7.42-7.44 (d, *J* = 8.5 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 7.0, 22.3, 31.1, 34.6, 34.9, 113.1, 115.4, 125.9, 127.4, 127.9, 152.5. IR (KBr, cm<sup>-1</sup>):  $\nu$  = 642, 839, 1368, 1464, 1514, 2247, 2875, 2965,3034, 3100. MS calcd m/z 224.13, found 225.13 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>: C, 80.32; H, 7.19; N, 12.49; Found: C, 80.48; H, 7.22; N, 12.59.

**2-(4-Bromophenyl)cyclopropane-1,1-dicarbonitrile** (2h): Colorless crystals. m.p. 140-142 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.22-2.29 (m, 2H), 3.24-3.27 (t, *J* = 9.0 Hz, 1H), 7.17-7.19 (d, *J* = 8.5 Hz, 2H), 7.55-7.57 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 7.1, 22.2, 34.3, 112.8, 114.9, 123.7, 129.5, 129.9, 132.2. IR (KBr, cm<sup>-1</sup>): *v* = 599, 633, 836, 1452, 1493, 1542, 1650, 1697, 2245, 2930. MS calcd m/z 245.98, found 246.98 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>11</sub>H<sub>7</sub>BrN<sub>2</sub>: C, 53.47; H, 2.86; N, 11.34; Found: C, 53.56; H, 2.87; N, 11.42.

**2-(Thiophen-2-yl)cyclopropane-1,1-dicarbonitrile (2i):** Brown oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 2.19-2.23$  (m, 1H), 2.27-2.29 (m, 1H), 3.38-3.42 (t, J = 9.5 Hz, 1H), 7.02-7.05 (m, 2H), 7.34-7.36 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 8.3$ , 23.8, 30.2, 112.7, 114.7, 127.3, 127.4, 127.9, 133.5. IR (KBr, cm<sup>-1</sup>):  $\nu = 688$ , 1442, 1517, 1640, 1687, 2243, 2971, 3439. MS calcd m/z 174.03, found 175.03 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>9</sub>H<sub>6</sub>N<sub>2</sub>S: C, 62.05; H, 3.47; N, 16.08; Found: C, 62.18; H, 3.49; N, 16.17.

**2-Methyl-2-phenylcyclopropane-1,1-dicarbonitrile (2j):** Colorless crystals. m.p. 87-89 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.79$  (s, 3H), 1.98-1.99 (d, J = 6.0 Hz, 1H), 2.34-2.35 (d, J = 6.0 Hz, 1H), 7.35-7.42 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 11.5$ , 24.2, 29.6, 40.2, 113.8, 114.3, 128.0, 129.0, 129.1, 136.6. IR (KBr, cm<sup>-1</sup>): v = 695, 769, 1446, 1500, 1650, 1699, 2243, 2935, 2989. MS calcd m/z 182.08, found 183.08 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>: C, 79.10; H, 5.53; N, 15.37; Found: C, 79.00; H, 5.51; N, 15.27.

**2-Hexylcyclopropane-1,1-dicarbonitrile (2k):** Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.89$ -0.91 (t, J = 7.0 Hz, 3H), 1.25-1.40 (m, 6H), 1.49-1.64 (m, 5H), 1.90-2.01 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 3.8$ , 13.9, 22.5, 24.8, 27.9, 28.7, 30.0, 31.4, 31.5, 114.0, 115.7. MS calcd m/z 176.13, found 177.13 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>: C, 74.96; H, 9.15; N, 15.89; Found: C, 74.87; H, 9.17; N, 15.96.

2-Methyl-2-(3-(prop-1-en-2-yl)phenyl)cyclopropane-1,1-dicarbonitrile

(21): White solid. m.p. 85-87 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.78$  (s, 3H), 1.97-1.98 (d, J = 6.0 Hz, 1H), 2.16 (s, 3H), 2.32-2.33 (d, J = 6.0 Hz, 1H), 5.14 (s, 1H), 5.39 (s, 1H), 7.24-7.26 (t, J = 4.0 Hz, 1H), 7.36-7.47 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 11.5$ , 21.8, 24.5, 29.9, 40.4, 113.6, 113.9, 114.4, 125.4, 126.4, 127.2, 129.2, 136.9, 142.4, 142.6. MS calcd m/z 222.12, found 223.12 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>: C, 81.05; H, 6.35; N, 12.60; Found: C, 81.19; H, 6.37; N, 12.68.

**2-Methyl-3-phenylcyclopropane-1,1-dicarbonitrile (2m):** Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.53-1.54 (d, *J* = 9.0 Hz, 3H), 2.43-2.46 (m, 1H), 2.90-2.91 (d, *J* = 8.0 Hz, 1H), 7.22 (m, 2H), 7.36-7.40 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 13.2, 14.8, 29.7, 42.3, 113.4, 113.9, 128.4, 129.1, 129.1, 129.3, 131.1. MS calcd m/z 182.08, found 183.08 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>: C, 79.10; H, 5.53; N, 15.37; Found: C, 79.21; H, 5.54; N, 15.45.

**2,3-Diphenylcyclopropane-1,1-dicarbonitrile (2n):** Colorless crystal. m.p. 131-133 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.68 (s, 2H), 7.41-7.49 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 15.3, 38.6, 113.0, 128.3, 129.1, 129.5, 130.6. IR (KBr, cm<sup>-1</sup>): v = 697, 1446, 1490, 2246, 2994, 3054. MS calcd m/z 244.10, found 245.10 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>: C, 83.58; H, 4.95; N, 11.47; Found: C, 83.48; H, 4.93; N, 11.41.

**6,6a-Dihydrocyclopropa**[*a*]**indene-1,1(1a***H*)-**dicarbonitrile** (**20**): White solid. m.p. 93-95 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.02-3.05 (t, *J* = 6.5 Hz, 1H), 3.29-3.33 (d, *J* = 14.0 Hz, 1H), 3.52-3.56 (t, *J* = 12.5 Hz, 1H), 3.70-3.71 (d, *J* = 6.5 Hz, 1H), 7.28-7.35 (m, 3H), 7.51-7.52 (d, *J* = 7.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 11.9, 33.6, 33.9, 42.1, 111.1, 114.7, 125.1, 125.8, 127.7, 129.6, 135.4, 140.9. IR (KBr, cm<sup>-1</sup>):  $\nu$  = 670, 764, 1464, 1518, 1647, 1697, 2244, 2932, 3059. MS calcd m/z 180.07, found 181.07 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>: C, 79.98; H, 4.47; N, 15.55; Found: C, 79.88; H, 4.45; N, 15.47.

 $2, 3\text{-}Dihydro\text{-}1H\text{-}cyclopropa[a]naphthalene\text{-}1, 1(1aH, 7bH)\text{-}dicarbonitrile}$ 

(2p): Needle crystals. m.p. 92-94 °C. 1H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.18-2.20 (m, 1H), 2.21-2.23 (m, 1H), 2.34-2.39 (m, 1H), 2.64-2.68 (m, 1H), 2.78-2.89 (m, 1H), 3.21-3.23 (d, *J* = 9.5 Hz, 1H), 7.13-7.15 (t, *J* = 4.5 Hz, 1H), 7.28-7.29 (t, *J* = 4.0 Hz, 2H), 7.43-7.44 (t, *J* = 5.0 Hz, 1H). 13C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 12.2, 18.7, 25.2, 30.6, 33.2, 112.8, 115.6, 126.2, 127.4, 129.1, 129.2, 135.9. IR (KBr, cm<sup>-1</sup>):  $\nu$  = 673, 1453, 1516, 1651, 1698, 2247, 2941, 3046. MS calcd m/z 194.08, found 195.08 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>: C, 80.39; H, 5.19; N, 14.42; Found: C, 80.48; H, 5.21; N, 14.49.

**Tricyclo**[3.2.1.0<sup>2,4</sup>]octane-3,3-dicarbonitrile (2q): White solid. m.p. 86-88 C. 1H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.96-0.99$  (d, J = 13.0 Hz, 1H), 1.33-1.36 (m, 2H), 1.65-1.67 (d, J = 7.5 Hz, 2H), 1.92-1.94 (d, J = 12.5 Hz, 1H), 2.07 (s, 2H), 2.79 (s, 2H). 13C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 2.6$ , 27.7, 28.2, 35.0, 35.9, 114.4, 115.9. IR (KBr, cm<sup>-1</sup>): v = 657, 1461, 1512, 1645, 2239, 2882, 2974. MS calcd m/z 157.08, found 158.08 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>: C, 75.92; H, 6.37; N, 17.71; Found: C, 76.04; H, 6.40; N, 17.82.

**1-Methylbicyclo[4.1.0]heptane-7,7-dicarbonitrile (2r):** Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.25-1.39 (m, 2H), 1.43-1.47 (m, 1H), 1.48 (s, 3H), 1.51-1.57 (m, 1H), 1.84-1.95 (m, 4H), 1.97-2.19 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 14.5, 19.4, 19.9, 20.2, 24.8, 27.3, 34.3, 36.7, 113.8, 115.1. MS calcd m/z 160.10, found 161.10 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>: C, 74.97; H, 7.55; N, 17.48; Found: C, 74.90; H, 7.52; N, 17.39.

**1-Phenylbicyclo[4.1.0]heptane-7,7-dicarbonitrile (2s):** White solid. m.p. 45-47 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): *δ* = 1.43-1.48 (m, 2H), 1.57-1.65 (m, 2H), 2.01-2.06 (m, 1H), 2.17-2.23 (m, 1H), 2.34-2.41 (m, 2H), 2.60-2.62 (m,

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1H), 7.29-7.42 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 16.1, 19.6, 20.2, 20.5, 29.5, 34.1, 42.8, 113.8, 114.6, 120.0, 127.7, 128.8, 129.3, 140.5. IR (KBr, cm<sup>-1</sup>):  $\nu$  = 697, 764, 1450, 1500, 1697, 2237, 2871, 2947, 3025. MS calcd m/z 222.12, found 223.12 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>: C, 81.05; H, 6.35; N, 12.60; Found: C, 81.17; H, 6.36; N, 12.69.

**2,2'-(Cyclopentane-1,2-diyl)dimalononitrile** (**3a**): Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.68$ -1.75 (m, 1H), 1.84-1.95 (m, 2H), 2.12-2.26 (m, 4H), 2.56-2.58 (m, 2H), 2.80-2.83 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 8.7$ , 21.3, 25.8, 26.2, 36.0, 38.6, 111.7, 112.9, 115.1. MS calcd m/z 198.09, found 199.09 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>4</sub>: C, 66.65; H, 5.08; N, 28.26; Found: C, 66.74; H, 5.09; N, 28.40.

**2,2'-(Cyclohexane-1,2-diyl)dimalononitrile (3b):** Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.36-1.38 (t, *J* = 7.0 Hz, 2H), 1.45-1.50 (m, 2H), 1.81-1.90 (m, 3H), 2.16-2.25 (m, 4H), 2.65-2.68 (t, *J* = 6.5 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 9.1, 19.6, 19.7, 24.9, 27.9, 29.6, 34.7, 111.8, 113.6, 116.4. MS calcd m/z 212.11, found 213.11 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>: C, 67.90; H, 5.70; N, 26.40; Found: C, 67.99; H, 5.72; N, 26.51.

**Representative procedure for cyclopropenation. Synthesis of 5a:** Complex PhI(OAc)<sub>2</sub> (177 mg, 0.6 mmol), malononitrile (40 mg, 0.6 mmol) and alkyne **4a** (0.55 mL, 0.5 mmol) were dissolved in DCE (2.0 mL) in a 25 mL flask. The mixture was stirred at 50 °C for 2 h (monitored by TLC). The reaction mixture was cooled to room temperature, poured into the water and extracted with CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 10$  mL). The combined organic phase was washed with water ( $3 \times 10$  mL). The solvent was removed under reduced pressure, and the residue was purified by a flash silica gel column chromatography (EtOAc/petroleum ether = 1:10) to give **5a** as colorless oil in a 94% yield.

**2-Phenylcycloprop-2-ene-1,1-dicarbonitrile (5a):** Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.08 (s, 1H), 7.59-7.61 (t, *J* = 7.0 Hz, 3H), 7.72-7.74 (t, *J* = 6.5 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 3.6, 92.5, 111.8, 116.1, 120.2, 129.6, 130.5, 132.8. MS calcd m/z 166.05, found 167.05 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>11</sub>H<sub>6</sub>N<sub>2</sub>: C, 79.50; H, 3.64; N, 16.86; Found: C, 79.63; H, 3.65; N, 16.94.

**2-(***m***-Tolyl)cycloprop-2-ene-1,1-dicarbonitrile (5b):** Brown solid. m.p. 73-75 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 2.51$  (s, 3H), 7.03 (s, 1H), 7.42-7.43 (d, J = 8.0 Hz, 2H), 7.64-7.66 (d, J = 8.0 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 3.55$ , 21.8, 91.1, 111.7, 116.3, 117.4, 130.3, 130.5, 143.9. MS calcd m/z 180.07, found 181.07 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>: C, 79.98; H, 4.47; N, 15.55; Found: C, 80.11; H, 4.48; N, 15.64.

**2-(4-(***tert***-Butyl)phenyl)cycloprop-2-ene-1,1-dicarbonitrile (5c):** Brown needle crystal. m.p. 75-77 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.37$  (s, 9H), 6.99 (s, 1H), 7.59-7.61 (d, J = 8.5 Hz, 2H), 7.65-7.67 (d, J = 8.0 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 3.6$ , 31.0, 35.4, 91.3, 111.8, 116.4, 117.4, 126.7, 130.5, 157.0. MS calcd m/z 222.12, found 223.12 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>: C, 81.05; H, 6.35; N, 12.60; Found: C, 81.17; H, 6.37; N, 12.69.

**2-(3-chlorophenyl)cycloprop-2-ene-1,1-dicarbonitrile (5d):** Brown solid. m.p. 72-74 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.19 (s, 1H), 7.54-7.63 (m, 3H), 7.71 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 3.9, 94.4, 111.2, 115.8, 122.0, 128.6, 130.3, 131.0, 133.1, 135.9. MS calcd m/z 200.01, found 201.01 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>11</sub>H<sub>5</sub>ClN<sub>2</sub>: C, 65.85; H, 2.51; N, 13.96; Found: C, 65.72; H, 2.48; N, 13.88.

**2-(4-Fluorophenyl)cycloprop-2-ene-1,1-dicarbonitrile (5e):** Brown solid. m.p. 63-65 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.08 (s, 3H), 7.26-7.31 (m, 2H), 7.73-7.76 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 3.5, 91.9, 91.9, 110.7, 115.7, 116.4, 116.4, 116.9, 117.1, 132.6, 132.7, 163.9, 165.9. MS calcd m/z 184.04, found 185.04 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>11</sub>H<sub>3</sub>FN<sub>2</sub>: C,

#### 71.74; H, 2.74; N, 15.21; Found: C,71.86; H, 2.76; N, 15.31.

**2-(4-Ethynylphenyl)cycloprop-2-ene-1,1-dicarbonitrile (5f):** Brown solid. m.p. 113-115 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.33 (s, 1H), 7.15 (s, 1H). 7.68 (s, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 3.7, 30.9, 81.4, 82.1, 93.6, 111.3, 115.9, 120.2, 126.9, 130.3, 133.2. MS calcd m/z 190.05, found 191.05 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>13</sub>H<sub>6</sub>N<sub>2</sub>: C, 82.09; H, 3.18; N, 14.73; Found: C, 82.21; H, 3.20; N, 14.80.

**2-Phenyl-3-propylcycloprop-2-ene-1,1-dicarbonitrile (5g):** Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.11-1.14$  (t, J = 7.5 Hz, 3H), 1.87-1.92 (m, 2H), 2.29-2.83 (t, J = 7.5 Hz, 2H), 7.54-7.62 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 5.4$ , 13.9, 19.9, 26.0, 103.8, 106.7, 116.4, 121.5, 129.6, 129.7, 131.6. MS calcd m/z 208.10, found 209.10  $[(M + 1)]^+$ . Anal. Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>: C, 80.74; H, 5.81; N, 13.45; Found: C, 80.87; H, 5.84; N, 13.57.

**2-Ethyl-3-methylcycloprop-2-ene-1,1-dicarbonitrile (5h):** Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.29-1.32 (m, 3H), 2.25 (s, 3H), 2.59-2.64 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 8.2, 10.3, 16.9, 101.8, 107.0, 116.9. MS calcd m/z 132.07, found 133.07 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>: C, 72.70; H, 6.10; N, 21.20; Found: C, 72.84; H, 6.12; N, 21.31.

**2,3-Diphenylcycloprop-2-ene-1,1-dicarbonitrile (5i):** Needle crystals. m.p. 138-140 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.59-7.62 (t, *J* = 7.0 Hz, 3H), 7.79-7.81 (d, *J* = 7.0 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 5.1, 103.6, 115.7, 121.9, 129.7, 130.0, 132.0. MS calcd m/z 242.08, found 243.08 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>17</sub>H<sub>10</sub>N<sub>2</sub>: C, 84.28; H, 4.16; N, 11.56; Found: C, 84.17; H, 4.15; N, 11.49.

**Ethyl 3,3-dicyano-2-phenylcycloprop-1-enecarboxylate (5j):** Yellow solid. m.p. 67-69 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.45-1.47 (t, *J* = 7.0 Hz, 3H), 4.47-4.49 (d, *J* = 7.0 Hz, 2H), 7.64-7.72 (m, 3H), 7.87-7.89 (d, *J* = 6.5 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 7.2, 14.1, 63.5, 95.5, 114.3, 117.9, 119.6, 129.9, 132.3, 134.7, 154.9. MS calcd m/z 238.07, found 239.07 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 70.58; H, 4.23; N, 11.76; Found: C, 70.69; H, 4.25; N, 11.86.

**Ethyl 1-nitro-2-phenylcyclopropanecarboxylate (6a):** Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.37-1.39 (t, *J* = 7.0 Hz, 3H), 3.19-3.25 (m, 1H), 3.62-3.68 (m, 1H), 4.35-4.39 (m, 2H), 5.77-5.81 (m, 1H), 7.32-7.40 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 14.1, 41.5, 62.2, 84.9, 125.9, 128.7, 128.9, 139.6, 151.2, 160.6. MS calcd m/z 235.08, found 236.08 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>4</sub>: C, 61.27; H, 5.57; N, 27.21; Found: C, 61.42; H, 5.59; N, 27.33.

**Ethyl 3-nitrotricyclo[3.2.1.0<sup>24</sup>]octane-3-carboxylate (6b):** Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.18-1.21$  (t, J = 8.5 Hz, 1H), 1.31-1.38 (m, 5H), 1.59-1.73 (m, 3H), 2.56-2.59 (t, J = 8.5 Hz, 2H), 3.47-3.49 (d, J = 8.5 Hz, 1H), 4.27-4.36 (m, 2H), 4.59-4.60 (d, J = 8.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 13.9$ , 22.4, 26.9, 32.1, 40.1, 41.8, 52.2, 61.1, 80.8, 109.3, 158.8. MS calcd m/z 225.10, found 226.10  $[(M + 1)]^+$ . Anal. Calcd for C<sub>11</sub>H<sub>15</sub>NO<sub>4</sub>: C, 58.66; H, 6.71; N, 6.22; Found: C, 58.55; H, 6.69; N, 6.14.

**Ethyl 2-benzoyl-1-nitro-3-phenylcyclopropanecarboxylate (6c):** Brown oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 1.26 \cdot 1.29$  (t, J = 7.0 Hz, 3H), 4.26-4.31 (m, 2H), 5.32-5.34 (d, J = 8.0 Hz, 1H), 5.78-5.79 (d, J = 8.5 Hz, 1H), 7.28-7.64 (m, 13H), 7.83-7.84 (d, J = 7.5 Hz, 2H), 7.98-8.00 (t, J = 7.5 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta = 13.8$ , 13.9, 29.6, 54.1, 61.9, 62.1, 62.4, 90.2, 91.2, 126.1, 127.7, 128.4, 128.6, 128.8, 128.9, 128.9, 129.2, 129.3, 129.4, 134.2, 134.3, 135.3, 137.2, 137.9, 150.4, 153.6, 159.3, 159.8, 191.8, 195.1. MS calcd m/z 339.11, found 340.11 [(M + 1)]<sup>+</sup>. Anal. Calcd for C<sub>19</sub>H<sub>17</sub>NO<sub>5</sub>: C, 67.25; H, 5.05; N, 4.13; Found: C, 67.37; H, 5.06; N, 4.17.

**Ethyl 1-nitro-2-phenylcycloprop-2-enecarboxylate (7):** Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ = 1.43-1.46(m, 3H), 4.47-4.89 (d, *J* = 7.0 Hz, 2H),

6.93 (s, 1H), 7.48-7.49 (m, 3H), 7.80-7.82 (m, 2H). MS calcd m/z 233.07, found 234.07  $[(M + 1)]^+$ . Anal. Calcd for  $C_{12}H_{11}NO_4$ : C, 61.08; H, 4.75; N, 6.01; Found: C, 61.21; H, 4.77; N, 6.06.

#### Notes and references

- (a) J. Salaun in Cyclopropane derivatives and their diverse biological activities, Vol. 207 (Ed.: A. Meijere), Springer, Berlin, 2000. (b) J. Pietruszka, Chem. Rev. 2003, 103, 1051–1170; (c) H.-U. Reissig and R. Zimmer, Chem. Rev., 2003, 103, 1151–1196; (d) M. Rubin, M. Rubina and V. Gevorgyan, Chem. Rev., 2007, 107, 3117–3179; (e) C. A. Carson and M. A. Kerr, Chem. Soc. Rev., 2009, 38, 3051–3060; (f) M. Shi, L.-X. Shao, J.-M. Lu, Y. Wei, K. Mizuno and H. Maeda, Chem. Rev., 2010, 110, 5883–5913; (g) D. Y.-K. Chen, R. H. Pouwer and J.-A. Richard, Chem. Soc. Rev., 2012, 41, 4631–4642.
- (a) M. Nakamura, A. Hirai and E. Nakamura, J. Am. Chem. Soc., 2003, 125, 2341–2350; (b) J. Long, Y. Yuan and Y. Shi, J. Am. Chem. Soc., 2003, 125, 13632–13633; (c) S. R. Goudreau and A. B. Charette, J. Am. Chem. Soc., 2009, 131, 15633–15635; (d) T. Wang, Y. Liang and Z.-X. Yu, J. Am. Chem. Soc., 2011, 133, 9343–9353; (e) H. Y. Kim and P. J. Walsh, Acc. Chem. Res., 2012, 45, 1533–1547.
- 3 (a) M. P. Doyle, M. A. McKervey and T. Ye, Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides, Wiley, New York, **1998**; (b) B. Moreau and A. B. Charette, *J. Am. Chem. Soc.*, 2005, **127**, 18014–18015; (c) D. Marcoux, S. R. Goudreau and A. B. Charette, *J. Org. Chem.*, 2009, **74**, 8939–8955; (d) R. R. Nani and S. E. Reisman, *J. Am. Chem. Soc.*, 2013, **135**, 7304–7311; (e) V. N. G. Lindsay, D. Fiset, P. J. Gritsch, S. Azzi and A. B. Charette, *J. Am. Chem. Soc.*, 2013, **135**, 1463–1470; (f) B. Moreau and A. B. Charette, *J. Am. Chem. Soc.*, 2005, **127**, 18014–18015; (g) S. R. Goudreau, D. Marcoux and A. B. Charette, *J. Org. Chem.*, 2009, **74**, 470–473; (h) C. Deng, L. Wang, J. Zhu and Y. Tang, *Angew. Chem. Int. Ed.*, 2012, **51**, 11620–11623.
- 4 (a) V. K. Aggarwal, E. Alsono, G. Fang, M. Ferrara and G. Hynd, M. Porcelloni, Angew. Chem. Int. Ed., 2001, 40, 1433–1436; (b) C. D. Papageorgiou, S. V. Ley and M. J. Gaunt, Angew. Chem. Int. Ed., 2003, 42, 828–831; (c) N. Bremeyer, S. C. Smith, S. V. Ley and M. J. Gaunt, Angew. Chem. Int. Ed., 2004, 43, 2681–2684; (d) C. D. Papageorgiou, M. A. Cubillo de Dios, S. V. Ley and M. J. Gaunt, Angew. Chem. Int. Ed., 2004, 43, 4641–4644; (e) R. K. Kunz and D. W. C. MacMillan, J. Am. Chem. Soc., 2005, 127, 3240–3241; (f) M. J. Gaunt and C. C. C. Johansson, Chem. Rev., 2007, 107, 5596–5605; (g) X. L. Sun and Y. Tang, Acc. Chem. Res., 2008, 41, 937–948; (h) M. Rueping, H. Sundán, L. Hubener and E. Sugiono, Chem. Commun., 2012, 48, 2201–2203; (i) A. Biswas, S. D. Sarkar, L. Tebben and A. Studer, Chem. Commun., 2012, 48, 5190–5192.
- 5 (a) M. S. Baird, *Chem. Rev.*, 2003, **103**, 1271–1294; (b) W. R. Dolbier and M. A. Battiste, *Chem. Rev.*, 2003, **103**, 1071–1098; (c) R. Walsh, *Chem. Soc. Rev.*, **2**005, **34**, 714–732; (d) M. Rubin, M. Rubina and V. Gevorgyan, *Chem. Rev.*, 2007, **107**, 3117–3179; (e) I.; Marek, S. Simaan andA. Masarwa, *Angew. Chem.*, 2007, **119**, 7508–7520; *Angew. Chem. Int. Ed.*, 2007, **46**, 7364–7376; (f) F. Miege, C. Meyer and J. Cossy, *Angew. Chem. Int. Ed.*, 2011, **50**, 5932–5937; (g) M. R. Wilson and R. E. Taylor, *Angew. Chem. Int. Ed.*, 2013, **52**, 4078–4087.

- (a) M. S. Baird, In Houben-Weyl: Methods of Organic Chemistry, 4th 6 ed.; de Meijere, A., Ed.; Thieme: Stuggart, 1996; Vol. E17d; 2695-2744; (b) Y. Lou, M. Horikawa, R. A. Kloster, N. A. Hawryluk and E. J. Corey, J. Am. Chem. Soc., 2004, 126, 8916-8918; (c) H. M. L. Davies and G. H. Lee, Org. Lett., 2004, 6, 1233-1236; (d) L. Liao, F. Zhang, N. Yan, J. A. Golen and J. M. Fox, Tetrahedron., 2004, 60, 1803-1816; (e) D. T. Nowlan III and D. A. Singleton, J. Am. Chem. Soc., 2005, 127, 6190-6191; (f) Y. Lou, T. P. Remarchuk and E. J. Corey, J. Am. Chem. Soc., 2005, 127, 14223-14230; (g) S. Chuprakov and V. Gevorgyan, Org. Lett., 2007, 9, 4463-4466; (h) J. F. Briones, J. Hansen, K. I. Hardcastle, J. Autschbach and H. M. L. Davies, J. Am. Chem. Soc., 2010, 132, 17211-17215; (i) ref 3f; (j) M. Uehara, H. Suematsu, Y. Yasutomi and T. Katsuki, J. Am. Chem. Soc., 2011, 133, 170-171; (k) X. Cui, X. Xu, H. Lu, S. Zhu, L. Wojtas and X. P. Zhang, J. Am. Chem. Soc., 2011, 133, 3304-3307; (1) X. Cui, X. Xu, L. Wojtas, M. M. Kim and X. P. Zhang, J. Am. Chem. Soc., 2012, 134, 19981-19984; (m) J. F. Briones and H. M. L. Davies, Org. Lett., 2011, 13, 3984-3987; (n) J. F. Briones and H. M. L. Davies, J. Am. Chem. Soc., 2012, 134, 11916-11919.
- 7 (a) M. S. Baird, In Houben-Weyl: Methods of Organic Chemistry, 4th ed.; de Meijere, A., Ed.; Thieme: Stuttgart, 1996; Vol. E17d, 2747–2759; (b) H. Hopf, In Houben-Weyl: Methods of Organic Chemistry, 4th ed.; de Meijere, A., Ed.; Thieme: Stuttgart, 1996; Vol. E17d, 2745–2746.
- 8 S. Lin, Y. Wei and F. Liang, Chem. Commun., 2012, 48, 9879–9881.
- 9 In the past decade, the application of hypervalent iodine reagents in organic synthesis has attracted intense interest, due to the intriguing oxidizing properties, low toxicity, high reactivity, easy handling and ready availability. Books: (a) A. Varvoglis, The Organic Chemistry of Polycoordinated Iodine; VCH Publishers, Inc.: New York, 1992; (b) T. Wirth, Ed. Hypervalent Iodine Chemistry: Modern Developments in Organic Synthesis; Topics in Current Chemistry Series 224; Springer: Berlin-Tokyo, 2003; (c) R. M. Moriarty, O. Prakash, Hypervalent Iodine in Organic Chemistry: Chemical Transformations; Wiley-Interscience: 2008; Reviews: (d) V. V. Zhdankin and P. J. Stang, Chem. Rev., 2002, 102, 2523-2584; (e) T. Wirth, In Organic Synthesis Highlights V, (Eds.: Schmalz, H.-G.; Wirth, T.), Wiley-VCH, Weinheim, 2003, 144-150; (f) H. Tohma and Y. Kita, Adv. Synth. Catal., 2004, 346, 111-124; (g) T. Wirth, Angew. Chem., Int. Ed., 2005, 44, 3656-3665; (h) R. M. Moriarty, J. Org. Chem., 2005, 70, 2893-2903; (i) V. V. Zhdankin and P. J. Stang, Chem. Rev., 2008, 108, 5299-5358; (j) M. Ochiai and K. Miyamoto, Eur. J. Org. Chem., 2008, 44, 4229-4239; (k) T. Dohi and Y. Kita, Chem. Commun., 2009, 45, 2073-2085; (1) M. Uyanik and K. Ishihara, Chem. Commun., 2009, 45, 2086–2099; (m) V. V. Zhdankin, J. Org. Chem., 2011, 76, 1185-1197.
- Diamination without metal catalysts, see: (a) C. R öben, J. A. Souto, Y. Gonz ález, A. Lishchynskyi and K. Muñiz, *Angew. Chem. Int. Ed.*, 2011, **50**, 9478–9482; (b) J. A. Souto, C. Martnez, I. Velilla and K. Muñiz, *Angew. Chem. Int. Ed.*, 2013, **52**, 1324–1328; (c) C. R öben, J. A. Souto, E. C. Escudero-Adan and K. Muñiz, *Org. Lett.*, 2013, **15**, 1008–1011; With hypervalent iodine reagent and metal catalysts: (d) J. Streuff, C. H. Hövelmann, M. Nieger and K. Muñiz, *J. Am. Chem. Soc.*, 2005, **127**, 14586–14587; (e) K. Muñiz, J. Streuff, C. H. Hvelmann and A. Núñez, *Angew. Chem. Int. Ed.*, 2007, **46**, 7125– 7127; (f) K. Muñiz, *J. Am. Chem. Soc.*, 2007, **129**, 14542–14543; (g)

K. Muñiz, C. H. Hövelmann and J. Streuff, J. Am. Chem. Soc., 2008, 130, 763–773; (h) L. Iglesias, E. G. Prez and K. Muñiz, Angew. Chem. Int. Ed., 2010, 49, 8109–8111; (i) C. Martnez and K. Muñiz, Angew. Chem. Int. Ed., 2012, 51, 7031–7034; Alkyne amination: (j) J. A. Souto, P. Becker, Á. Iglesias and K. Muñiz, J. Am. Chem. Soc., 2012, 134, 15505–15511.

- Dioxygenation: (a) Y. Li, D. Song and V. M. Dong, J. Am. Chem. Soc., 2008, 130, 2962–2964; (b) M. Fujita, Y. Yoshida, K. Miyata, A. Wakisaka and T. Sugimura, Angew. Chem. Int. Ed., 2010, 49, 7068– 7071; (c) Y.-B. Kang and L. H. Gade, J. Am. Chem. Soc., 2011, 133, 3658–3667; (d) W. Zhong, J. Yang, X. Meng and Z. Li, J. Org. Chem., 2011, 76, 9997–10004; (e) M. Fujita, M. Wakita and T. Sugimura, Chem. Commun., 2011, 47, 3983–3985; (f) S. R. Neufeldt and M. S. Sanford, Org. Lett., 2013, 15, 46–49.
- 12 A. S. Biland, S. Altermann and T. Wirth, ARKIVOC 2003, (vi) 164– 169.
- 13 CCDC 948734 (**2a**) and 948733 (**2n**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.
- 14 We think that cis-1,2-disubstituted cycloalkanes are generated due to the double backside nucleophilic substitution.
- 15 Electronic factors might be responsible for the different outcome as for parent cycloalkenes (dialkylation, Scheme 3) and substituted cycloalkenes (cyclopropanation, entries 15-19, Table 2).
- 16 Two examples for the cyclopropenation of internal alkynes with Ag(I) catalyst were presented, see: refs 6m and 6n. No report on the cyclopropenation of electron deficient alkynes was found.
- 17 In our work, excess alkene or alkyne is not required in all cases, contrary to the observation in selected papers. Please refer to: (a) P. Müller and A. Ghanem, *Org. Lett.*, 2004, 6, 4347–4350. (b) ref 3b. (c) S. R. Goudreau, D. Marcoux and A. B. Charette, *J. Org. Chem.*, 2009, 74, 470–473.
- 18 Other active methylene compounds including diethyl malonate and bis(phenylsulfonyl)methane were also examined, but proved to be inefficient at the moment.
- 19 For cis-alkene substrates, the possible cyclopropanation mechansim was proposed as follow.



(a) K. Niedermann, N. Früh, E. Inogradova, V M. S. Wiehn, A. Moreno and A. Togni, Angew. Chem. Int. Ed., 2011. 50, 1059–1063;
(b) D. Lubriks, I. Sokolovs and E. Suna J. Am. Chem. Soc. 2012, 134, 15436–15442;
(c) V. V. Zhdankin, R. Tykwinski, R. Caple, B. Berglund, A. S. Kozmin, N. S. Zefirov, Tetrahedron Lett. 1988, 29, 3703–3704;
(d) V. V. Zhdankin, M. Mullikin, R. Tykwinski, B. Berglund, R. Caple, N. S. Zefirov, A. S. Kozmin, J. Org. Chem. 1989,

54, 2605–2608; (e) V. V. Grushin, Chem. Soc. Rev., 2000, 29, 315–324.

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