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

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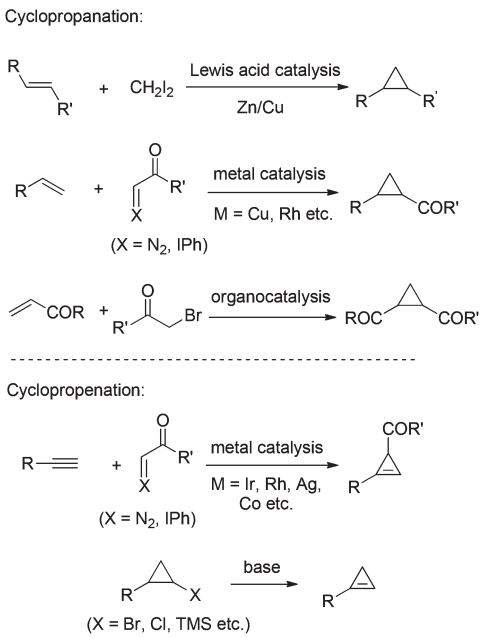
Hypervalent iodine(III)-mediated dioxygenation and diamination of alkenes have been previously developed. In this study, the potential application of hypervalent iodine(III) reagent was successfully extended to the dialkylation and cyclopropa(e)nation of unsaturated alkenes and alkynes. The reactions of alkenes with malononitrile and other active methylene compounds as the carbon nucleophiles give access to multi-substituted 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 attack by the carbon-nucleophile, and recyclization was proposed for the cyclopropanation of *trans*-alkene substrates. The cyclopropenation was thought to proceed *via* iodo(III)cyclopropanation, ring-opening attack 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.

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.[1] Various synthetic methods for their preparation have been developed (Scheme 1), such as the Simmons–Smith reaction,[2] transition-metal-catalyzed addition of diazo compounds[3a–e] or iodonium ylides[3f–h] to an alkene, and organocatalyzed addition–cyclization of β-halogenated carbonyl compounds or a sulfur ylide to an activated double bond.[4] On the other hand, cyclopropenes, as another important three-membered carbocycle, have broad utility as synthons in organic synthesis.[5] Typical synthetic methods include a carbene or carbenoid addition to alkynes[6] catalyzed by Rh(II),[6b–i] Ir(II),[6j] Co(II),[6k,l] and Ag(I),[6m,n] and elimination of substituted cyclopropanes under basic conditions.[7] Despite significant progress made in this area, some of the methods might suffer from substrate limitation, functional group tolerance, and the employment of a 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.



Scheme 1 Approaches to cyclopropanation and cyclopropenation.

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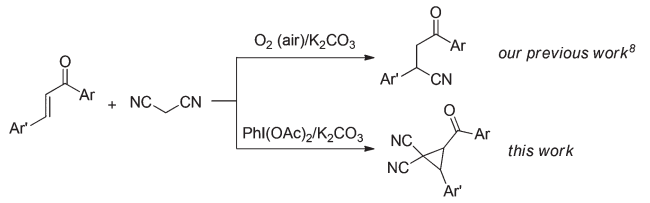
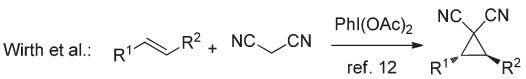


Scheme 2 Reactions of chalcones with malononitrile under different oxidation conditions.

In our previous research, we communicated the reaction of chalcones with malononitrile in the open air, which provided unprecedented β-cyanation products (Scheme 2).[8] 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) reagents[9] 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. It is noteworthy that, although the diamination[10] and dioxygenation[11] 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. A literature search revealed that only one example of $PhI(OAc)_2$-mediated cyclopropanation was reported by Wirth and co-workers early in 2003 (eqn (1)).[12] However, the reaction was restricted by limited scope and poor yields. Compared with the common routes toward cyclopropanes and cyclopropenes, *i.e.*, the addition reaction of an alkene or alkyne with metal carbenes derived from the decomposition of diazo compounds or iodonium ylides,[3,6b–n] this methodology has the advantage of avoiding the utilization of transition metal catalysts.



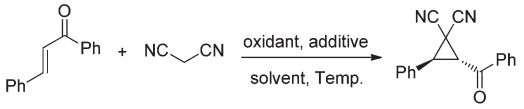
(1)

Results and discussion

Reaction optimization

Initially, the model reaction of chalcone **1a** and malononitrile in the presence of $PhI(OAc)_2$ 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 $PhI(OAc)_2$ gave **2a** in an improved yield of 67% (entry 8). The introduction of an external additive such as K_2CO_3 made the system cleaner and

Table 1 Optimization of the reaction conditions[a]



1a 2a

Entry	Oxidant (equiv.)	Additive	Solvent	T (°C)	Yield[c] [%]
1	$PhI(OAc)_2$ (1.2)	—	DMF	30	0
2	$PhI(OAc)_2$ (1.2)	—	MeCN	30	5
3	$PhI(OAc)_2$ (1.2)	—	Toluene	30	9
4	$PhI(OAc)_2$ (1.2)	—	DCM	30	38
5	$PhI(OAc)_2$ (1.2)	—	DCE	30	44
6	$PhI(OAc)_2$ (1.2)	—	DCE	80	51
7	$PhI(OAc)_2$ (1.2)	—	DCE	80	43[b]
8	$PhI(OAc)_2$ (2.2)	—	DCE	80	67
9	**$PhI(OAc)_2$ (2.2)**	K_2CO_3	**DCE**	**80**	**71**
10	$PhI(OAc)_2$ (2.2)	Cs_2CO_3	DCE	80	42
11	$PhI(OAc)_2$ (2.2)	K_3PO_4	DCE	80	68
12	$PhI(OAc)_2$ (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_2CO_3	DCE	80	0

[a] Reactions were carried out with chalcone (1.0 mmol), malononitrile (1.2 equiv.), hypervalent iodine(III) in solvent (4 mL) unless otherwise noted. [b] 3.0 equiv. of malononitrile. [c] Isolated yield.

71% yield was achieved (entry 9). Other bases like Cs_2CO_3, K_3PO_4 and Na_2CO_3 were also screened, but gave unsatisfactory results (entries 10–12). The role of the base was supposed to be to remove the acid (2 equiv.) generated in the reaction system. Other hypervalent iodine(III) reagents were also examined; however, $PhI(OTf)_2$ and $PhI(OPiv)_2$ proved to be inferior and PhI(OTs)OH inert (entries 13–15). The structure of **2a** and its stereochemistry were confirmed by single-crystal X-ray diffraction (Fig. 1).[13]

Substrate scopes

Under the optimized conditions (Table 1, entry 9), selected chalcones reacted with malononitrile 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

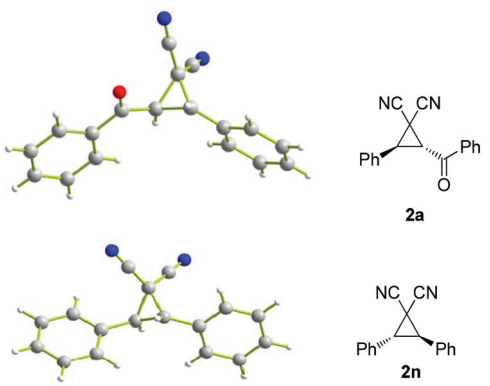
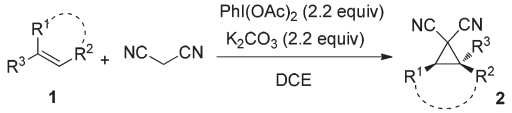
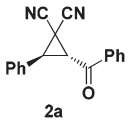
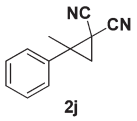
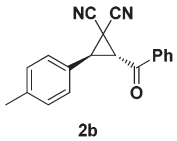
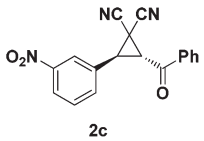
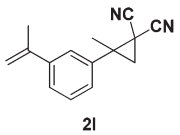
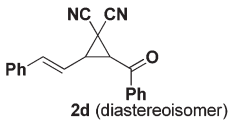
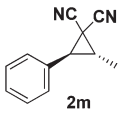
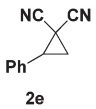
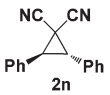
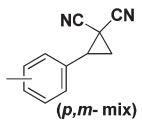
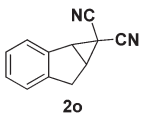
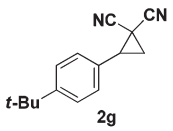
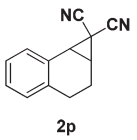
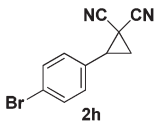
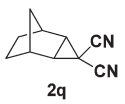
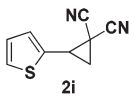
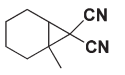
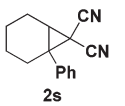


Fig. 1 X-ray crystal structures of **2a** and **2n**.

Table 2 $PhI(OAc)_2$-mediated cyclopropanation of alkenes with malononitrile[a]



Entry		Yield[c] (%)	Entry		Yield[c] (%)
1[a]	 2a	71	10[b]	 2j	89
2[a]	 2b	69	11[b]	 2k	87
3[a]	 2c	56	12[b]	 2l	81
4[a]	 2d (diastereoisomer)	59	13[b]	 2m	89
5[b]	 2e	81	14[a]	 2n	57
6[b]	 (*p,m*- mix) 2f	85	15[b]	 2o	96
7[b]	 2g	88	16[b]	 2p	76
8[b]	 2h	87	17[b]	 2q	92
9[b]	 2i	92	18[b]	 2r	85
			19[b]	 2s	51

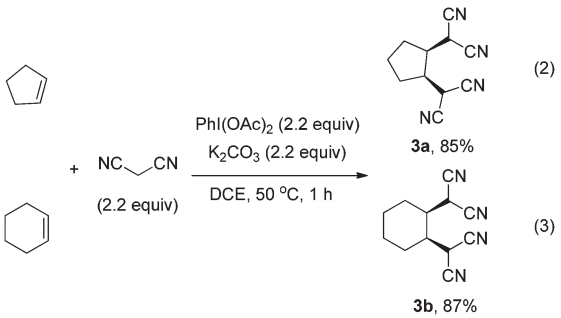
[a] Reactions were carried out with **1** (1.0 mmol), malononitrile (1.2 equiv.), K_2CO_3 (2.2 equiv.), $PhI(OAc)_2$ (2.2 equiv.) in DCE (4.0 mL) at 80 °C for 1 h. [b] Run at 50 °C. [c] Isolated yield.

styrene and styrene derivatives with substituents such as methyl-, *tert*-butyl and 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-1,1-dicarbonitrile (**2i**) in 92% yield (entry 9). 1,1-Disubstituted

alkenes like α-methylstyrene were found to be compatible with the explored reactions, giving tetrasubstituted cyclopropane **2j** in 89% yield (entry 10). The reaction with an aliphatic terminal alkene proceeded smoothly and product **2k** was obtained in 87% yield (entry 11). A diene can react with one of the double bonds, affording cyclopropane **2l** 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-methyl-cyclohexene and 1-phenylhexene produced multisubstituted cyclopropanes **2m–s** in 51–96% yields (entries 13–19). On the basis of ^{1}H NMR spectroscopy and the single-crystal X-ray diffraction of **2a** and **2n** (Fig. 1),[13] the relative configurations 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 ^{1}H NMR analysis). All of the above results indicate the efficiency of the hypervalent iodine(III)-mediated cyclopropanation reaction.

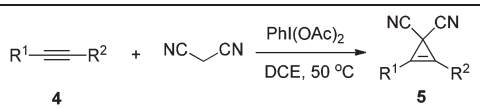
Contrary to that with 1-methyl-cyclohexene and 1-phenyl-hexene (Table 2, entries 18 and 19), in the reactions of parent cyclohexene and cyclopentene with malononitrile (1.2 equiv.), no corresponding cyclopropane products were detected. Instead, dialkylation products **3a** and **3b** were obtained as 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 (eqn (2) and (3) in Scheme 3).[14,15]

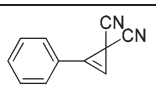
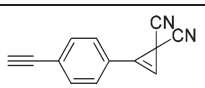
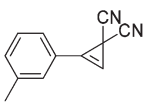
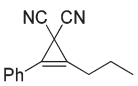
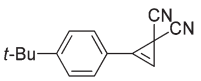
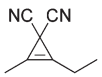
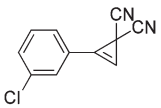
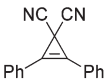
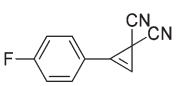
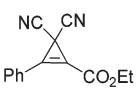
The hypervalent iodine(III)-mediated cyclopropanation strategy was also applicable to alkyne substrates (Table 3). It was found that, in this case, no extra base was necessary. Phenylacetylene and substituted phenylacetylenes gave the corresponding cyclopropenes **5a–e** in excellent yields (entries 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 the diene substrate (Table 2, entry 12), bisacetylene can react with one carbon–carbon triple bond and the other one intact,



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

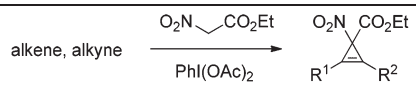
Table 3 $PhI(OAc)_2$-mediated cyclopropenation of alkynes and malononitrile[a]

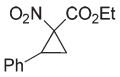
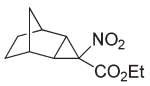
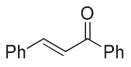
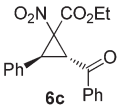
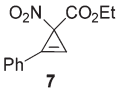


Entry		Yield[b] (%)	Entry		Yield[b] (%)
1	 **5a**	94	6	 **5f**	91
2	 **5b**	96	7	 **5g**	96
3	 **5c**	92	8	 **5h**	84
4	 **5d**	96	9	 **5i**	47
5	 **5e**	95	10	 **5j**	26

[a] Reactions were carried out with **4** (1.0 mmol), malononitrile (1.2 equiv.), $PhI(OAc)_2$ (1.2 equiv.) in DCE (4.0 mL) at 50 °C for 2 h. [b] Isolated yield.

Table 4 Cyclopropanation/cyclopropenation of selected alkenes and alkynes with ethyl nitroacetate[a]



Entry	Substrate	Product	Yield[b] (%)
1		 **6a**	49
2		 **6b**	73
3		 **6c**	50
4		 **7**	33

[a] Conditions: alkenes/alkynes (1.0 mmol), ethyl nitroacetate (1.2 equiv.), PhI(OAc)$_2$ (2.2 equiv.), K_2CO_3 (2.2 equiv.) in DCE (4.0 mL) at 50 °C for 2 h for entries 1–3, with no K_2CO_3 for entry 4. [b] Isolated yield.

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 an electron-deficient alkyne like ethyl 3-phenylpropiolate gave low to moderate yields (28% and 47%, respectively, entries 9 and 10).[16,17]

In the following work, other active methylene compounds were investigated as the carbon-nucleophile.[18] Ethyl nitroacetate proved to be suitable and the reactions with alkenes such as styrene, 2-norbornene and chalcone and alkynes such as phenylacetylene afforded the desired cyclopropanes **6a–c** and cyclopropenes **7**, respectively, albeit in low to moderate yields (Table 4, entries 1–4).

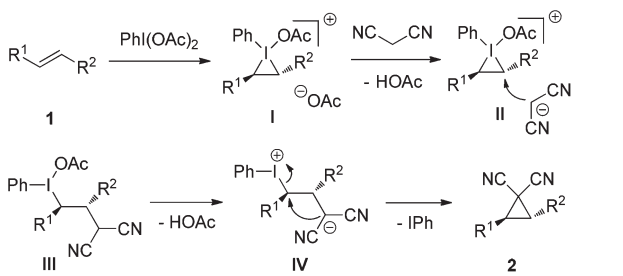
Proposed mechanism

In order to elucidate the possible mechanism for the cyclopropa(e)nation reaction, several control experiments were carried out. Upon treatment of PhI(OAc)$_2$ with K_2CO_3, no PhIO was formed. In the mixture of malononitrile, PhI(OAc)$_2$ and K_2CO_3 in DCE, no ligand exchange between the acetate anion and malononitrile was detected, the same as that reported by Wirth *et al.*[12] (see the ESI†). Moreover, both *cis*-stilbene (eqn (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 reactions proceeded smoothly in the absence of K_2CO_3 (Table 1, entry 8, and Table 3), the mechanism of the iodo-ylide pathway was ruled out.

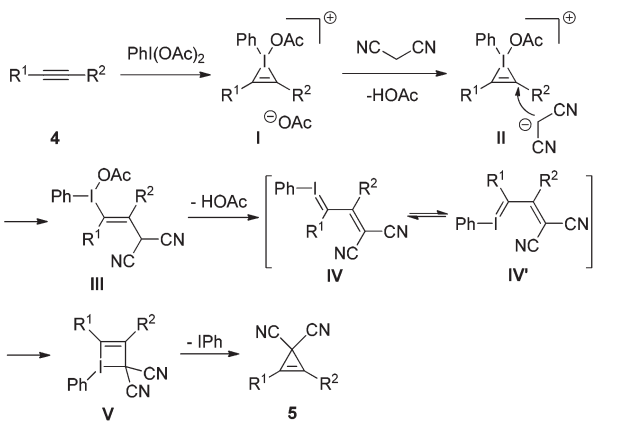
(4)

A plausible mechanism for the formation of cyclopropane **2** was proposed, as depicted in Scheme 4 (with *trans*-alkenes as an example).[19] Initially, the electrophilic addition between PhI(OAc)$_2$ and the alkene **1** generates iodo(III)cyclopropane **I**,[10] followed by the formation of ion pair **II**, with the elimination of acetic acid. Then, a nucleophilic ring opening takes place, giving rise to λ^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**.[12]

The possible mechanism for the cyclopropenation of alkynes is 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**, tautomerization (**IV–IV′**) *via* elimination of HOAc and ring-closure into four-membered iodo(III)cyclobutene **V**, and final formation of the cyclopropenation product *via* hypervalent iodine(III)-mediated reductive elimination.[20]



Scheme 4 Proposed mechanism for the cyclopropanation with *trans*-alkene 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 a broad substrate scope (both electron-deficient 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 an excellent electrophile and a hypernucleofuge.[9] Further studies exploring the scope of the carbon nucleophile in the cyclopropanation and hypervalent iodine(III)-mediated dialkylation of unsaturated alkenes and alkynes are in progress.

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 $PhI(OAc)_2$ (354 mg, 1.1 mmol), K_2CO_3 (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 water and extracted with CH_2Cl_2 (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 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{18}H_{12}N_2O$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{19}H_{14}N_2O$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{18}H_{11}N_3O_3$: 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 ^{1}H NMR and ^{13}C NMR data are based on the *trans*-isomers): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{20}H_{14}N_2O$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{11}H_8N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.21–2.26 (m, 4H), 2.36–2.38 (d, J = 8.5 Hz, 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{12}H_{10}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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^{-1}): ν = 642, 839, 1368, 1464, 1514, 2247, 2875, 2965, 3034, 3100. MS calcd m/z 224.13, found 225.13 $[(M + 1)]^+$. Anal. calcd for $C_{15}H_{16}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 7.1, 22.2, 34.3, 112.8, 114.9, 123.7, 129.5, 129.9, 132.2. IR (KBr, cm^{-1}): ν = 599, 633, 836, 1452, 1493, 1542, 1650, 1697, 2245, 2930. MS calcd m/z 245.98, found 246.98 $[(M + 1)]^+$. Anal. calcd for $C_{11}H_7BrN_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 8.3, 23.8, 30.2, 112.7, 114.7, 127.3, 127.4, 127.9, 133.5. IR (KBr, cm^{-1}): ν = 688, 1442, 1517, 1640, 1687, 2243, 2971, 3439. MS calcd m/z 174.03, found 175.03 $[(M + 1)]^+$. Anal. calcd for $C_9H_6N_2S$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 11.5, 24.2, 29.6, 40.2, 113.8, 114.3, 128.0, 129.0, 129.1, 136.6. IR (KBr, cm^{-1}): ν = 695, 769, 1446, 1500, 1650, 1699, 2243, 2935, 2989. MS calcd m/z 182.08, found 183.08 $[(M + 1)]^+$. Anal. calcd for $C_{12}H_{10}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{11}H_{16}N_2$: 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 (2l). White solid. M.p. 85–87 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{15}H_{14}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{12}H_{10}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.68 (s, 2H), 7.41–7.49 (m, 10H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 15.3, 38.6, 113.0, 128.3, 129.1, 129.5, 130.6. IR (KBr, cm^{-1}): ν = 697, 1446, 1490, 2246, 2994, 3054. MS calcd m/z 244.10, found 245.10 $[(M + 1)]^+$. Anal. calcd for $C_{17}H_{12}N_2$: 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 (2o). White solid. M.p. 93–95 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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^{-1}): ν = 670, 764, 1464, 1518, 1647, 1697, 2244, 2932, 3059. MS calcd m/z 180.07, found 181.07 $[(M + 1)]^+$. Anal. calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.55; found: C, 79.88; H, 4.45; N, 15.47.

2,3-Dihydro-1*H*-cyclopropa[*a*]naphthalene-1,1(1a*H*,7b*H*)-dicarbonitrile (2p). Needle crystals. M.p. 92–94 °C. 1H NMR (500 MHz, $CDCl_3$): δ = 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 ($CDCl_3$, 125 MHz): δ = 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^{-1}): ν = 673, 1453, 1516, 1651, 1698, 2247, 2941, 3046. MS calcd m/z 194.08, found 195.08 $[(M + 1)]^+$. Anal. calcd for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42; found: C, 80.48; H, 5.21; N, 14.49.

Tricyclo[3.2.1.0^{2,4}]octane-3,3-dicarbonitrile (2q). White solid. M.p. 86–88 °C. 1H NMR (500 MHz, $CDCl_3$): δ = 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 ($CDCl_3$, 125 MHz): δ = 2.6, 27.7, 28.2, 35.0, 35.9, 114.4, 115.9. IR (KBr, cm^{-1}): ν = 657, 1461, 1512, 1645, 2239, 2882, 2974. MS calcd m/z 157.08, found 158.08 $[(M + 1)]^+$. Anal. calcd for $C_{10}H_{10}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{10}H_{12}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): 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, 1H), 7.29–7.42 (m, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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^{-1}): ν = 697, 764, 1450, 1500, 1697, 2237, 2871, 2947, 3025. MS calcd m/z 222.12, found 223.12 $[(M + 1)]^+$. Anal. calcd for $C_{15}H_{14}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{11}H_{10}N_4$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{12}H_{12}N_4$: 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 $PhI(OAc)_2$ (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_2Cl_2 (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 **5a** as a colorless oil in 94% yield.

2-Phenylcycloprop-2-ene-1,1-dicarbonitrile (5a). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.08 (s, 1H), 7.59–7.61 (t, J = 7.0 Hz, 3H), 7.72–7.74 (t, J = 6.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{11}H_6N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{12}H_8N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{15}H_{14}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 (s, 1H), 7.54–7.63 (m, 3H), 7.71 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{11}H_5ClN_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.08 (s, 3H), 7.26–7.31 (m, 2H), 7.73–7.76 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{11}H_5FN_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.33 (s, 1H), 7.15 (s, 1H). 7.68 (s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{13}H_6N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $C_{14}H_{12}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29–1.32 (m, 3H), 2.25 (s, 3H), 2.59–2.64 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 8.2, 10.3, 16.9, 101.8, 107.0, 116.9. MS calcd m/z 132.07, found 133.07 $[(M + 1)]^+$. Anal. calcd for $C_8H_8N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59–7.62 (t, J = 7.0 Hz, 3H), 7.79–7.81 (d, J = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 5.1, 103.6, 115.7, 121.9, 129.7, 130.0, 132.0. MS calcd m/z 242.08, found 243.08 $[(M + 1)]^+$. Anal. calcd for $C_{17}H_{10}N_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{14}H_{10}N_2O_2$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{12}H_{13}NO_4$: 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^{2,4}]octane-3-carboxylate (6b). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $C_{11}H_{15}NO_4$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26–1.29 (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). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 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 $[(M + 1)]^+$. Anal. calcd for $C_{19}H_{17}NO_5$: 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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.

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14 We think that *cis*-1,2-disubstituted cycloalkanes are generated due to the double backside nucleophilic substitution.

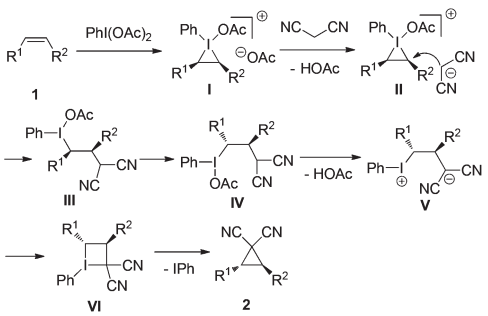
15 Electronic factors might be responsible for the different outcome as for parent cycloalkenes (dialkylation, Scheme 3) and substituted cycloalkenes (cyclopropanation, entries 15–19, Table 2).

16 Two examples for the cyclopropenation of internal alkynes with Ag(I) catalyst were presented, see: ref. 6*m* and 6*n*. 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. 3*b* (*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 mechanism was proposed as follows.



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