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Probing Phosphane-Mediated [2+1] Annulation Reactions

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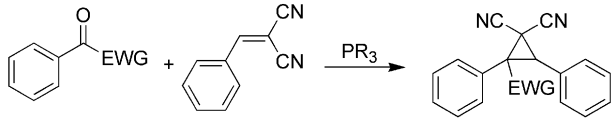
Phosphane-mediated cyclizations between α-keto nitriles and methylidenemalononitriles, producing highly functionalized cyclopropanes in good to excellent yields, are reported. The presence of strongly electron-withdrawing cyano groups directly bound to the ketone carbonyl groups is believed to play a critical role in these transformations.

Introduction

Organophosphorus compounds are widely used in organic synthesis; examples include the use of phosphonium ylides in the Wittig reaction,[1] the use of phosphanes in the Staudinger reaction,[2] the Mitsunobu reaction,[3] and transition-metal-catalyzed reactions in which phosphanes act as ligands. Recently they have become frequently used as organocatalysts or reagents because their "soft" nucleophilicity is one of the most important characteristic features for the facilitation of many types of reactions including the Morita–Baylis–Hillman reaction,[4] the Rauhut–Currier reaction,[5] the Stetter reaction,[6] the Michael addition,[7] isomerization of C–C multiple bonds,[8] alcohol acylation and kinetic resolution,[9] nucleophilic addition to the α- and γ-positions of activated alkynes and allenes,[10] ring opening,[11] and reduction of activated carbonyl groups.[12] Nucleophilic phosphane catalysts especially have emerged as efficient means to generate carbo- and heterocycles.[13] In particular, Lu's phosphane-catalyzed [3+2] cycloadditions to form cyclopentenes from allenoates and alkenes have been applied in the synthesis of several natural products.[14] Additionally, Kwon has reported phosphane-catalyzed [4+2] annulations for the synthesis of tetrahydropyridines and cyclohexenes.[15]

We have very recently reported a phosphane(phosphite)-mediated method for the formation of cyclopropanes and aziridines from 4- or 2-nitrobenzaldehyde and methylidenemalononitriles.[16] The proposed mechanism includes the formation of a zwitterionic intermediate from the phosphane and the methylidenemalononitrile, with the zwitterionic intermediate then undergoing addition to the carbonyl group of the 4- or 2-nitrobenzaldehyde to form another zwitterionic intermediate, which subsequently undergoes cyclization to give an intermediate and then decomposes to generate the products with elimination of phosphate or phosphane oxide.[16] Unfortunately, the substrate is strictly limited to 4- or 2-nitrobenzaldehyde; when other aldehydes were used, there was no reaction at all. We hypothesize that less electrophilic substrates experience difficulty in undergoing addition of the zwitterionic nucleophile generated from the phosphane and the methylidenemalononitrile, perhaps similarly to the case of the phosphane-mediated reduction of activated carbonyl compounds.[12] We therefore envisioned that the use of activated carbonyl compounds incorporating strongly electron-withdrawing groups, such as 2,2,2-trifluoro-1-arylethan-1-one, α-keto esters, and α-keto nitriles, may lead to the occurrence of various kinds of nucleophilic additions.[17] In this paper we explore phosphane-mediated [2+1] annulation reactions between α-keto nitriles and various electrophiles. Through these phosphane-mediated annulation reactions (Scheme 1), multiply functionalized cyclopropanes were obtained in good to excellent yields and with moderate diastereoselectivities. Surprisingly, an unexpected rearrangement was found during the investigation of phosphane-mediated reactions between α-keto nitriles and imines.



Scheme 1. Phosphane-mediated [2+1] annulation.

Results and Discussion

We initially examined the reaction between 4-chlorobenzonitrile (**1a**, Table 1) and 2-benzylidenemalononitrile

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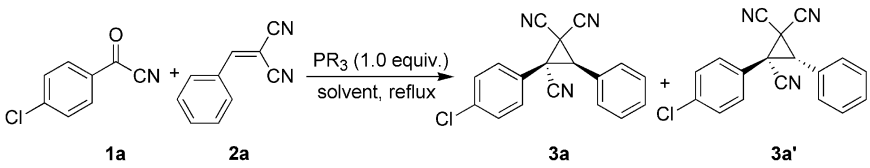
Table 1. Phosphane(phosphite)-mediated reaction between 4-chlorobenzonitrile (**1a**) and 2-benzylidenemalononitrile (**2a**).[a]



1a **2a** **3a** **3a'**

Entry	Methods	Solvent	Time/h	Yield (**3a**:**3a'**)[b]
1	PPh_3	THF	24	n.r.[c]
2	PPh_2Me	THF	10	trace
3	$PPhMe_2$	THF	5	73 (36:64)
4	PBu_3	THF	1	91 (40:60)
5	Ph_2POMe	THF	4	64 (36:64)
6[d]	PBu_3	THF	2	75 (38:62)
7	$P(OPh)_3$	THF	8	n.r.
8	$P(OEt)_3$	THF	3	68 (30:70)
9	PBu_3	toluene	1	86 (40:60)
10	PBu_3	1,4-dioxane	3	76 (34:66)
11	PBu_3	EtOH	3	–[e]
12	PBu_3	DCM	4	–[f]

[a] Reactions were carried out with 4-chlorobenzonitrile (**1a**, 0.3 mmol), 2-benzylidenemalononitrile (**2a**, 0.3 mmol), and PR_3 (0.3 mmol) in THF (2.0 mL) at reflux. [b] Yield of isolated product and then the ratio between the isolated products **3a** and **3a′**. [c] No reaction. [d] The reaction was carried out at room temperature. [e] The product ethyl 4-chlorobenzoate was isolated in the reaction (yield 68%). [f] Complex products.

(**2a**) in the presence of $P(OEt)_3$ (1.0 equiv.) in tetrahydrofuran (THF) at reflux, the optimal conditions for our previous cyclopropane synthesis.[16] To our delight, the reaction proceeded smoothly and two products were obtained. One of the products was assigned as the cyclopropane **3a′** and confirmed by X-ray diffraction (Figure 1),[18] and the other product was assigned as **3a**, the isomer of **3a′**.

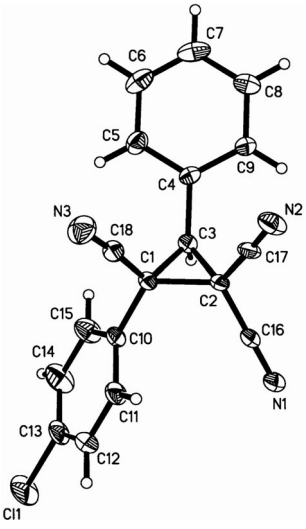


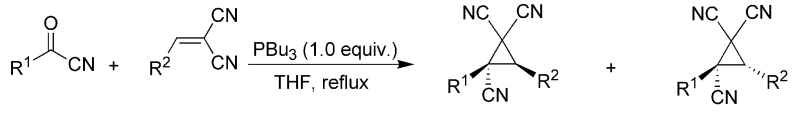
Figure 1. The single-crystal X-ray structure of **3a′**.

Other electron-deficient carbonyl compounds, however, such as 2,2,2-trifluoro-1-arylethan-1-ones [$ArC(O)CF_3$] and α-keto esters [$ArC(O)CO_2Et$], were not suitable for this reaction under the same conditions. This observation indicates that the presence of a very strongly electron-withdrawing substituent directly bound to the ketone carbonyl group is essential to facilitate the reaction, which is similar to what we have previously found in the phosphane(phosphite)-mediated reactions of 4- or 2-nitrobenzaldehyde and methylidenemalononitriles.[16]

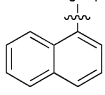
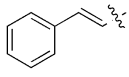
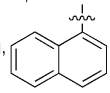
We next examined the reaction between 4-chlorobenzonitrile (**1a**) and 2-benzylidenemalononitrile (**2a**) in the presence of a variety of phosphanes or phosphites in tetrahydrofuran (THF) at reflux in order to identify the best promoter. The results are summarized in Table 1. As can be seen, no reaction had occurred after 24 h (Table 1, Entry 1) with use of the less nucleophilic PPh_3 as the promoter. Use of phosphanes of increasing nucleophilicity led to increased yields. With Ph_2PMe as the promoter only trace of products could be obtained after 10 h (Table 1, Entry 2), whereas with $PhPMe_2$ as the promoter the yield of **3a** and **3a′** could be improved to 73% (Table 1, Entry 3). In particular, with the strongly nucleophilic phosphane PBu_3 as the promoter (Table 1, Entry 4) the reaction proceeded smoothly to give the annulation products **3a** and **3a′** in 91% yield in a short reaction time (only 1.0 h), although the diastereoselectivity was not very good. Variation of reaction temperature and reaction time revealed that a reasonable yield could still be

obtained if the reaction temperature was lowered to room temperature and the reaction time was prolonged to 2.0 h (Table 1, Entry 6). Selected phosphites – Ph_2POMe and $P(OEt)_3$ – were also able to promote this reaction, giving moderate yields of the product (Table 1, Entries 5 and 8), but $P(OPh)_3$ was ineffective for the formation of cyclopropanes **3a** and **3a′** (Table 1, Entry 7). Solvent screening showed that THF was the best solvent (Table 1, Entries 9–12). The best reaction conditions are thus with PBu_3 as the promoter in THF at reflux.

Table 2. Phosphane-mediated annulation reactions: synthesis of multiply substituted cyclopropanes.[a]



1 **2** **3** **3'**

Entry	R^1	R^2	Time (h)	Yield (%)[b]	*trans:cis*[c]
1	**1a**, 4-ClC_6H_4	**2a**, Ph	1	91	**3a**:**3a'** (40:60)
2	**1a**, 4-ClC_6H_4	**2b**, 4-BrC_6H_4	1	91	**3b**:**3b'** (43:57)
3	**1a**, 4-ClC_6H_4	**2c**, 3-BrC_6H_4	1	80	**3c**:**3c'** (34:66)
4	**1a**, 4-ClC_6H_4	**2d**, 2-BrC_6H_4	1	75	**3d**:**3d'** (52:48)
5	**1a**, 4-ClC_6H_4	**2e**, 2,3-$2ClC_6H_3$	1	47	**3e**:**3e'** (85:15)
6	**1a**, 4-ClC_6H_4	**2f**, 3-$CH_3C_6H_4$	1	90	**3f**:**3f'** (38:62)
7	**1a**, 4-ClC_6H_4	**2g**, 4-$OMeC_6H_4$	1.5	89	**3g**:**3g'** (39:61)
8	**1a**, 4-ClC_6H_4	**2h**, 	2	86	**3h**:**3h'** (51:49)
9	**1a**, 4-ClC_6H_4	**2i**, 	2	75	**3i**:**3i'** (46:64)
10	**1a**, 4-ClC_6H_4	**2j**, 	3	71	**3j**:**3j'** (43:57)[d]
11	**1a**, 4-ClC_6H_4	**2k**, 	2	53	**3k**:**3k'**[e]
12	**1b**, 3,5-$2CH_3C_6H_3$	**2a**, Ph	2	90	**3l**:**3l'** (42:58)
13	**1c**, 4-$CH_3C_6H_4$	**2a**, Ph	1.5	81	**3m**:**3m'** (48:52)
14	**1d**, 4-BrC_6H_4	**2a**, Ph	1	86	**3n**:**3n'** (33:67)
15	**1e**, 2-ClC_6H_4	**2a**, Ph	2	87	**3o**:**3o'** (56:44)
16	**1f**, Ph	**2a**, Ph	1	88	**3p**:**3p'** (61:39)
17	**1f**, Ph	**2c**, 3-BrC_6H_4	1	99	**3q**:**3q'** (56:44)
18	**1f**, Ph	**2b**, 4-BrC_6H_4	1	99	**3r**:**3r'** (42:58)
19	**1f**, Ph	**2l**, 4-ClC_6H_4	1	81	**3s**:**3s'** (42:58)
20	**1g**, 	**2a**, Ph	5	55	**3t**:**3t'** (47:53)
21	**1h**, 	**2b**, 4-BrC_6H_4	3	–[f]	–[f]

[a] Reactions were carried out with acyl cyanides **1** (0.3 mmol), arylmethylidenemalononitriles **2** (0.3 mmol), and PBu_3 (0.3 mmol) in THF (2.0 mL) at reflux. [b] Yield of isolated product (total yields of the two isomers). [c] The ratio was determined between the two isolated products **3** (CN and R^2 *trans*) and **3'** (CN and R^2 *cis*). [d] The ratio of **3j** to **3j′** was measured by ^1H NMR of the crude products, complete separation of the two isomers from one another being difficult. [e] Difficult to determine from the ^1H NMR spectroscopic data and the products cannot be distinguished from one another. [f] Complex products, not characterized.

With these optimized reaction conditions to hand, we next turned our attention to the generality of the reaction. A variety of (arylmethylidene)malononitriles **2** were examined under these optimal conditions and the results are shown in Table 2. The reactions proceeded smoothly to produce the multiply functionalized cyclopropanes **3** as mixtures of two diastereoisomers and in good to excellent yields with respect to the various substituted (arylmethylidene)malononitriles **2**, except in the case of substrate **2e**, with two substitutes at the *ortho*- and *meta*-positions of its benzene ring, which afforded **3e** in only 48% yield, although with the best diastereoselectivity (Table 2, Entry 5). Presumably the steric hindrance of the two substituents at the *ortho*- and *meta*-positions in the benzene ring leads both to the poor yield and the high diastereoselectivity. Notably, with 2-(naphthalen-1-ylmethylene)malononitrile (**2h**) and nicotinonitrile **2i**, the corresponding cyclopropanes were obtained in good yields (Table 2, Entries 8 and 9). Moreover, aliphatic methylidenemalononitriles also exhibited good reactivities for these reactions, with good to moderate yields (Table 2, Entries 10 and 11).

A variety of acyl cyanides **1** were further examined under the optimized reaction conditions, and these results are also included in Table 2. As shown, variation of the substituent in **1** did not affect the yields of the corresponding products **3** in any instance, with the cyclopropanes **3l**–**3t** being obtained in good to excellent yields (Table 2, Entries 12–19). In addition, 1-naphthoyl cyanide was also able to react with the arylmethylidenemalononitrile **2a**, giving the cyclopropane **3t** in 55% yield (Table 2, Entry 20). Use of an alkyl-substituted cyanide (compound **1h**) as the substrate, however, provided complex product mixtures (Table 2, Entry 21).

The scope and limitations of this reaction still remained unclear at this stage. The question of whether the strongly electron-withdrawing dicyano groups in the substrates **2** were essential for these phosphane-mediated annulation reactions arose. Replacement of the two cyano groups in the substrates **2** by two ester groups did not result in the formation of the desired products under the optimized reaction conditions. Replacement of just one cyano group in a substrate **2** by an ester group, however, did result in the desired products **5** being obtained in moderate yields, which indicates that at least one of the strongly electron-withdrawing cyano groups in each of the substrates **2** is essential for this reaction. It should be noted that only two diastereomers of the four possible diastereomers could be obtained. The structures of these isolated cyclopropane products **5a** and **5a′** were fully characterized spectroscopically (see the Supporting Information). The diastereochemical outcome with regard to compounds **5** was ascertained by single-crystal X-ray diffraction analyses of **5a** and **5c′** (an analogue of **5a′**). Their ORTEP drawings are shown in Figures 2[18] and 3[18] and their CIF data are presented in the Supporting Information.

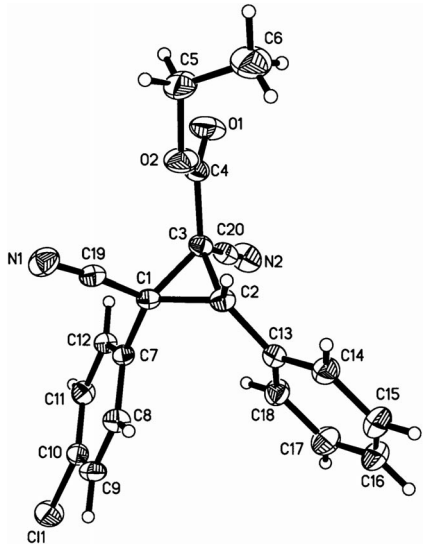


Figure 2. X-ray crystal structure of **5a**.

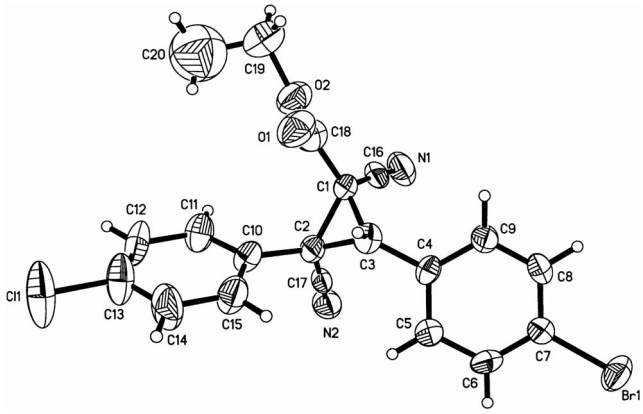
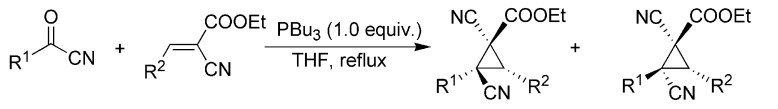


Figure 3. X-ray crystal structure of **5c′**.

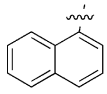
We next examined the scope of the phosphane-mediated reactions between the acyl cyanides **1** and a series of substrates **4** under the optimized reaction conditions; the results are summarized in Table 3. The reactions were found to be general with respect to a variety of substituted compounds **1** and **4** bearing electron-withdrawing (Table 3, Entries 1–3), electron-donating (Table 3, Entries 4 and 6), naphthyl (Table 3, Entry 9), and heteroaromatic (Table 3, Entries 7 and 8) substituents. It should be noted that the ratio of the products **5** and **5′** is almost 1:1 in each case, but that in most cases the two diastereoisomers could easily be separated by flash column chromatography.

A possible mechanism for these reactions, based on a previously proposed mechanism,[16] is suggested in Scheme 2. The first step is the formation of the zwitterionic intermediate **A** from the phosphane and the arylmethylidenemalononitrile. We presume that the strongly electrophilic carbonyl compound undergoes addition of the zwitterionic nucleophile more easily to make the intermediate **B**, which facilitates the following cyclization and subsequent decomposition with elimination of phosphane oxide and formation of the product **3**.

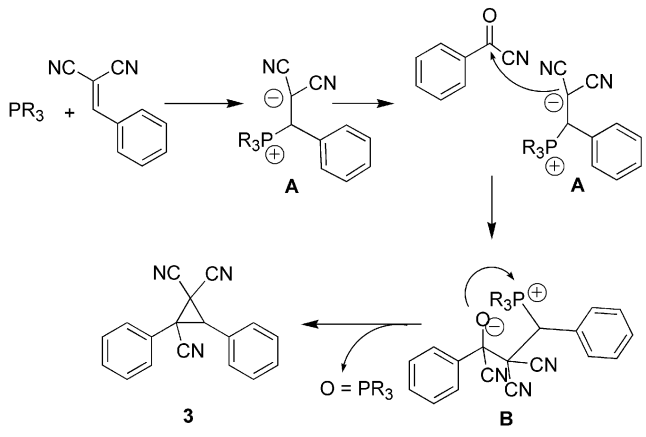
Table 3. Phosphane-mediated [2+1] annulation reactions of **1** and **4**.[a]



1 **4** **5** **5'**

Entry	R^1	R^2	Time (h)	Yield (%)[b]	**5**:**5'**[c]
1	**1a**, 4-ClC_6H_4	**4a**, Ph	5	53	**5a**:**5a'** (55:45)
2	**1a**, 4-ClC_6H_4	**4b**, 2-ClC_6H_4	4	68	**5b**:**5b'** (40:60)
3	**1a**, 4-ClC_6H_4	**4c**, 4-BrC_6H_4	3	62	**5c**:**5c'** (56:44)
4	**1a**, 4-ClC_6H_4	**4d**, 4-$CH_3C_6H_4$	4	52	**5d**:**5d'** (56:44)
5	**1b**, Ph	**4a**, Ph	3	81	**5e**:**5e'** (49:51)
6	**1c**, 3,5-2$CH_3C_6H_3$	**4a**, Ph	4	61	**5f**:**5f'** (44:56)
7	**1a**, 4-ClC_6H_4	**4e**, 	4	66	**5g**:**5g'** (66:34)
8	**1d**, 	**4c**, 4-BrC_6H_4	3	60	**5h**:**5h'** (50:50)
9	**1e**, 	**4c**, 4-BrC_6H_4	3	54	**5i**:**5i'** (40:60)

[a] Reactions were carried out with acyl cyanides **1** (0.3 mmol), **4** (0.3 mmol), and tributylphosphane (0.3 mmol) in THF (2.0 mL) at reflux. [b] Yield of the isolated product (total yields of the two isomers). [c] The ratio was determined between the two isolated products **5** and **5′**.

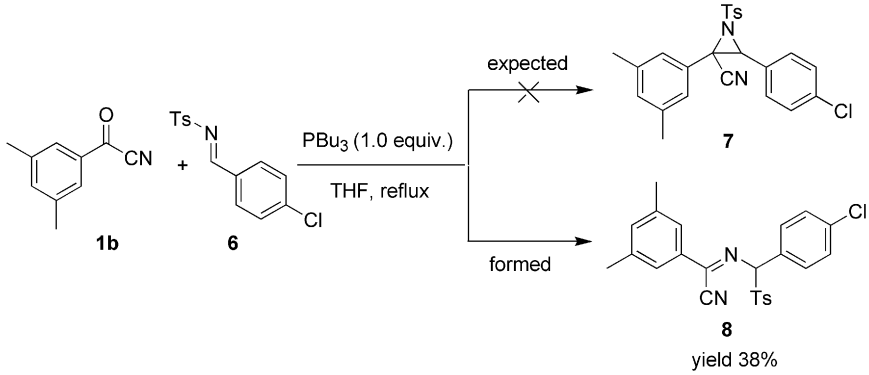


Scheme 2. A plausible reaction mechanism.

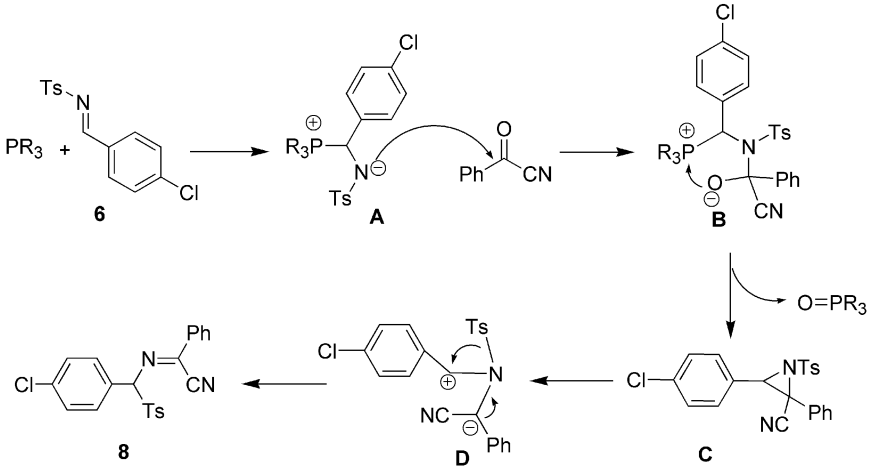
Having established phosphane-mediated [2+1] annulations between α-keto nitriles and methylidenemalononitrile for the synthesis of cyclopropanes, we reasoned that it might also be possible to formulate a nitrogen-containing heterocycle through a phosphane-mediated annulation reaction of this type if α-keto nitriles and imines were employed.[16] We initially examined this type of reaction with the acyl cyanide **1b** and the *N*-tosylbenzaldimine **6** in the presence of a stoichiometric amount of tributylphosphane. Surprisingly, the expected aziridine **7** was not formed. The reaction instead afforded a product that was subsequently characterized as the structure **8** (Scheme 3, 38% yield). The structure **8** was assigned on the basis of spectroscopic analysis and was subsequently confirmed unequivocally by single X-ray analysis (Figure 4).[18]

From the X-ray crystal structure of product **8** we can see that the tosyl group had migrated from the nitrogen atom to the carbon atom. We have recently observed and reported similar migrations in reactions between acyl cyanides and "Huisgen zwitterion", which included formal migrations from a nitrogen atom to a carboxyl group oxygen atom.[19]

Although the mechanistic underpinnings of the reaction are not precisely known, the following explanation for the formation of product **8** may be advanced. Presumably, the intermediate **A** (Scheme 4) formed from the phosphane and *N*-tosylbenzaldimine undergoes nucleophilic addition to the acyl cyanide, activated by the cyano group, resulting in intermediate **B**. Intermediate **B** undergoes cyclization and subsequently decomposes with loss of phosphane oxide to generate compound **C**, containing the aziridine ring. The three-membered ring in **C** is very unstable, due to high strain energy, and it is easily reopened to give the later intermediate **D**. Intermediate **D** rearranges to the product **8** through a nitrogen-to-carbon migration of the tosyl group (Scheme 4).



Scheme 3. The reaction between the acyl cyanide **1b** and the *N*-tosylbenzaldimine **6**.



Scheme 4. Possible pathway for the formation of **8**.

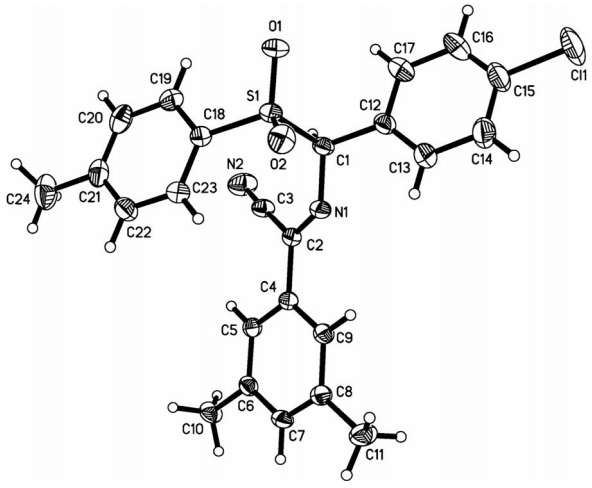


Figure 4. X-ray crystal structure of **8**.

In conclusion, we have developed a quite simple and efficient protocol for the synthesis of multiply substituted cyclopropanes through a novel phosphane-mediated [2+1] annulation process, which furnishes the multiply substituted cyclopropanes in moderate to excellent yields under mild reaction conditions, with use only of simple and cheap starting materials and promoters. Moreover, the presented synthesis is general with respect to various substrates containing carbonitrile, aryl, and ester functional groups. In addition, an interesting rearrangement was found in phosphane-mediated reactions between acyl cyanides and imines. Further efforts will focus on expanding the versatility of these new [2+1] annulations and on elucidation of further mechanistic details of these reactions.

Experimental Section

General Remarks: Melting points were determined with a digital melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded at 300 (400) and 75 (100) MHz, respectively. Mass and HRMS spectra were recorded by EI methods. Organic solvents were dried by standard methods if necessary. Satisfactory CHN microanalyses were obtained with an analyzer. Commercially available reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out with silica gel at increased pressure.

Typical Reaction Procedure for the Phosphane-Mediated [2+1] Annulation: A phosphane (0.3 mmol) was added under argon to a mixture of an acyl cyanide **1** (0.3 mmol) and an arylmethylidenemalononitrile **2** (0.3 mmol) in solvent and the reaction mixture was stirred at reflux for the required time as indicated in the tables. After the reaction solution had been concentrated under reduced

pressure, the residue was purified by flash chromatography on silica gel (eluent: EtOAc/petroleum ether 1:15–1:8) to afford the pure product **3**.

(2*R*,3*S*)-2-(4-Chlorophenyl)-3-phenylcyclopropane-1,1,2-tricarbonitrile (3a): M.p. 213–214 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.91 (s, 1 H, CH), 7.05 (d, J = 7.5 Hz, 2 H, Ar), 7.23 (d, J = 7.5 Hz, 2 H, Ar), 7.33–7.48 (m, 5 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.4, 33.6, 43.4, 109.2, 111.9, 115.8, 122.6, 125.5, 129.1, 129.7, 130.3, 130.4, 131.8, 137.6 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3094, 3064, 3037, 2925, 2248, 1595, 1496, 1098, 1014 cm^{-1}. MS (EI): m/z = 305 (28.47) $[M + 2]^+$, 304 (24.52) $[M + 1]^+$, 303 (81.29) $[M]^+$. $C_{18}H_{10}ClN_3$ (303.0563): calcd. C 71.18, H 3.32, Cl 11.67, N 13.83; found C 71.43, H 3.47, N 13.98.

(2*R*,3*R*)-2-(4-Chlorophenyl)-3-phenylcyclopropane-1,1,2-tricarbonitrile (3a′): M.p. 210–212 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.95 (s, 1 H, CH), 7.51–7.58 (m, 9 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.8, 36.7, 40.7, 109.6, 110.6, 113.4, 126.7, 128.9, 129.7, 130.0, 130.4, 130.5, 138.0 ppm. IR (CH_2Cl_2: $\tilde{\nu}$ = 2999, 2254, 1497, 1449, 1404, 1238, 1003 cm^{-1}. MS (EI): m/z = 305 (24.26) $[M + 2]^+$, 304 (20.60) $[M + 1]^+$, 303 (70.50). HRMS (EI): calcd. for $C_{18}H_{10}ClN_3$ $[M]^+$ 303.0563; found 303.0567.

(2*R*,3*S*)-3-(4-Bromophenyl)-2-(4-chlorophenyl)cyclopropane-1,1,2-tricarbonitrile (3b): M.p. 196–198 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.86 (s, 1 H, CH), 6.89 (d, J = 8.4 Hz, 2 H, Ar), 7.21 (d, J = 8.4 Hz, 2 H, Ar), 7.43 (d, J = 8.4 Hz, 2 H, Ar), 7.50 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.4, 33.6, 42.7, 109.0, 111.7, 115.6, 122.2, 124.5, 125.1, 130.2, 131.1, 131.7, 132.4, 137.9 ppm. IR (CH_2Cl_2: $\tilde{\nu}$ = 3039, 2925, 2248, 1594, 1492, 1402, 1012 cm^{-1}. MS (EI): m/z = 384 (10.86) $[M + 4]^+$, 383 (45.54) $[M + 3]^+$, 382 (10.95) $[M + 1]^+$, 381 (36.00) $[M + 1]^+$, 380 (1.91) $[M]^+$. $C_{18}H_9BrClN_3$ (380.9668): calcd. C 56.50, H 2.37, Br 20.88, Cl 9.27, N 10.98; found C 56.56, H 2.28, N 10.91.

(2*R*,3*R*)-3-(4-Bromophenyl)-2-(4-chlorophenyl)cyclopropane-1,1,2-tricarbonitrile (3b′): M.p. 200–202 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.89 (s, 1 H, CH), 7.43 (d, J = 8.7 Hz, 2 H, Ar), 7.51 (d, J = 8.7 Hz, 2 H, Ar), 7.55 (d, J = 8.7 Hz, 2 H, Ar), 7.67 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.8, 36.7, 39.9, 109.4, 110.3, 113.2, 125.1, 125.7, 126.2, 129.9, 130.46, 130.51, 133.0, 138.1 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3002, 2924, 2844, 2249, 1594, 1493, 1400, 1013 cm^{-1}. MS (EI): m/z = 384 (8.81) $[M + 4]^+$, 383 (39.75) $[M + 3]^+$, 382 (8.42) $[M + 1]^+$, 381 (29.51) $[M + 1]^+$, 380 (2.10) $[M]^+$. $C_{18}H_9BrClN_3$ (380.9668): calcd. C 56.50, H 2.37, Br 20.88, Cl 9.27, N 10.98; found C 56.38, H 2.51, N 11.09.

(2*R*,3*S*)-3-(3-Bromophenyl)-2-(4-chlorophenyl)cyclopropane-1,1,2-tricarbonitrile (3c): M.p. 210–212 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.85 (s, 1 H, CH), 6.81–6.85 (m, 1 H, Ar), 7.18–7.23 (m, 3 H, Ar), 7.36 (t, J = 2.0 Hz, 1 H, Ar), 7.43 (d, J = 8.8 Hz, 2 H, Ar), 7.57–7.60 (m, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.4, 33.7, 42.3, 108.9, 111.6, 115.5, 122.2, 123.1, 127.5, 127.7, 130.2, 130.5, 131.7, 133.3, 133.6, 137.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3042, 2924, 2247, 1594, 1566, 1094 cm^{-1}. MS (EI): m/z = 385 (9.08) $[M + 4]^+$, 384 (9.06) $[M + 3]^+$, 383 (33.16) $[M + 2]^+$, 382 (10.23) $[M + 1]^+$, 381 (25.88) $[M]^+$. $C_{18}H_9BrClN_3$ (380.9668): calcd. C 56.50, H 2.37, Br 20.88, Cl 9.27, N 10.98; found C 56.61, H 2.30, N 10.96.

(2*R*,3*R*)-3-(3-Bromophenyl)-2-(4-chlorophenyl)cyclopropane-1,1,2-tricarbonitrile (3c′): M.p. 184–186 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.90 (s, 1 H, CH), 7.41 (t, J = 8.0 Hz, 1 H, Ar), 7.49–7.56 (m, 5 H, Ar), 7.66 (d, J = 8.0 Hz, 1 H, Ar), 7.69 (s, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.8, 36.6, 39.6, 109.3, 110.3, 113.1, 123.5, 126.2, 127.4, 128.8, 130.0, 130.5, 131.2, 132.2, 133.8, 138.1 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3011, 2925, 2854, 2249, 1596, 1568, 1496, 1478, 1097 cm^{-1}. MS (EI): m/z = 385 (8.43) $[M + 4]^+$, 384 (7.75) $[M + 3]^+$, 383 (35.58) $[M + 2]^+$, 382 (9.09) $[M + 1]^+$, 381 (26.45) $[M]^+$. $C_{18}H_9BrClN_3$ (380.9668): calcd. C 56.50, H 2.37, Br 20.88, Cl 9.27, N 10.98; found C 56.61, H 2.29, N 10.94.

(2*R*,3*S*)-3-(2-Bromophenyl)-2-(4-chlorophenyl)cyclopropane-1,1,2-tricarbonitrile (3d): M.p. 212–214 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.87 (s, 1 H, CH), 7.43 (t, J = 7.6 Hz, 1 H, Ar), 7.51 (t, J = 7.6 Hz, 1 H, Ar), 7.55 (d, J = 8.8 Hz, 2 H, Ar), 7.59 (d, J = 8.8 Hz, 2 H, Ar), 7.70 (d, J = 7.6 Hz, 1 H, Ar), 7.80 (d, J = 7.6 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.3, 37.3, 40.9, 109.5, 110.5, 113.5, 125.4, 126.4, 127.1, 128.4, 130.0, 130.4, 132.1, 134.0, 138.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2988, 2250, 1588, 1487, 1088 cm^{-1}. MS (EI): m/z = 385 (6.54) $[M + 4]^+$, 384 (5.53) $[M + 3]^+$, 383 (25.17) $[M + 2]^+$, 382 (5.15) $[M + 1]^+$, 381 (19.19) $[M]^+$. $C_{18}H_9BrClN_3$ (380.9668): calcd. C 56.50, H 2.37, Br 20.88, Cl 9.27, N 10.98; found C 56.46, H 2.35, N 11.00.

(2*R*,3*R*)-3-(2-Bromophenyl)-2-(4-chlorophenyl)cyclopropane-1,1,2-tricarbonitrile (3d′): M.p. 208–210 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 4.03 (s, 1 H, CH), 7.11 (d, J = 8.8 Hz, 2 H, Ar), 7.30 (d, J = 8.8 Hz, 2 H, Ar), 7.37–7.48 (m, 3 H, Ar), 7.71–7.74 (m, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.9, 35.1, 43.6, 109.3, 111.7, 115.6, 123.4, 125.9, 126.4, 128.4, 129.2, 129.6, 130.2, 131.8, 133.9, 137.3 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2924, 2926, 2249, 1595, 1496, 1100 cm^{-1}. MS (EI): m/z = 385 (1.43) $[M + 4]^+$, 384 (1.27) $[M + 3]^+$, 383 (5.30) $[M + 2]^+$, 382 (1.05) $[M + 1]^+$, 381 (3.86) $[M]^+$. $C_{18}H_9BrClN_3$ (380.9668): calcd. C 56.50, H 2.37, Br 20.88, Cl 9.27, N 10.98; found C 56.53, H 2.40, N 11.03.

(2*R*,3*S*)-2-(4-Chlorophenyl)-3-(2,3-dichlorophenyl)cyclopropane-1,1,2-tricarbonitrile (3e): M.p. 246–248 °C. ^{1}H NMR [$(CD)_3CO$, 300 MHz, TMS]: δ = 4.73 (s, 1 H, CH), 7.41 (d, J = 9.0 Hz, 2 H, Ar), 7.46–7.54 (m, 3 H, Ar), 7.71 (d, J = 7.8 Hz, 1 H, Ar), 7.77 (d, J = 7.8 Hz, 1 H, Ar) ppm. ^{13}C NMR [$(CD)_3CO$, 75 MHz]: δ = 21.8, 35.6, 42.1, 110.9, 113.3, 117.0, 125.8, 129.2, 129.3, 129.5, 130.1, 131.6, 132.8, 134.3, 134.5, 137.1 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2997, 2249, 1597, 1495, 1418, 1102 cm^{-1}. MS (EI): m/z = 377 (1.71) $[M + 6]^+$, 376 (2.92) $[M + 5]^+$, 375 (13.25) $[M + 4]^+$, 374 (9.17) $[M + 3]^+$, 373 (38.16) $[M + 2]^+$, 372 (10.87) $[M + 1]^+$, 371 (40.10) $[M]^+$, 336 (37.44). $C_{18}H_8C_{l3}N_3$ (370.9784): calcd. C 58.02, H 2.16, Cl 28.54, N 11.28; found C 57.92, H 2.39, N 11.28.

(2*R*,3*R*)-2-(4-Chlorophenyl)-3-(2,3-dichlorophenyl)cyclopropane-1,1,2-tricarbonitrile (3e′): M.p. >250 °C (decomposed). ^{1}H NMR [$(CD)_3CO$, 400 MHz, TMS]: δ = 4.84 (s, 1 H, CH), 7.61 (t, J = 8.0 Hz, 1 H, Ar), 7.69 (d, J = 8.4 Hz, 2 H, Ar), 7.83 (d, J = 8.0 Hz, 1 H, Ar), 8.00–8.03 (m, 1 H, Ar), 8.06 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR [$(CD)_3CO$, 100 MHz]: δ = 23.5, 38.0, 39.7, 111.5, 111.8, 115.1, 128.5, 129.6, 130.5, 130.7, 130.8, 132.2, 133.1, 134.4, 137.8 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2989, 2252, 1487, 1404, 1088 cm^{-1}. MS (EI): m/z = 377 (1.84) $[M + 6]^+$, 376 (3.19) $[M + 5]^+$, 375 (14.69) $[M + 4]^+$, 374 (10.70) $[M + 3]^+$, 373 (43.39) $[M + 2]^+$, 372 (12.57) $[M + 1]^+$, 371 (45.07) $[M]^+$, 336 (42.16). HRMS (EI): calcd. for $C_{18}H_8C_{l3}N_3$ $[M]^+$ 370.9784; found 370.9782.

(2*R*,3*S*)-2-(4-Chlorophenyl)-3-*m*-tolylcyclopropane-1,1,2-tricarbonitrile (3f): M.p. 149–151 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.32 (s, 3 H, CH_3), 3.88 (s, 1 H, CH), 6.74 (d, J = 6.6 Hz, 1 H, Ar), 6.96 (s, 1 H, Ar), 7.18–7.24 (m, 4 H, Ar), 7.40 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.4, 21.3, 33.6, 43.4, 109.2, 112.0, 115.9, 122.7, 125.3, 126.2, 128.9, 129.9, 130.7, 131.1, 131.8, 137.5, 139.2 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3096, 3036, 2924, 2867, 2248, 1597, 1494, 1098 cm^{-1}. MS (EI): m/z = 319 (33.79) $[M + 2]^+$, 318 (33.14) $[M + 1]^+$, 317 (100.00) $[M]^+$, 302 (28.26). HRMS (EI): calcd. for $C_{19}H_{12}ClN_3$ $[M]^+$ 317.0720; found 317.0726.

(2*R*,3*R*)-2-(4-Chlorophenyl)-3-*m*-tolylcyclopropane-1,1,2-tricarbonitrile (3f′): M.p. 179–181 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.42 (s, 3 H, CH_3), 3.91 (s, 1 H, CH), 7.30–7.44 (m, 4 H, Ar), 7.49–7.55 (m, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.8, 21.3, 36.7, 40.6, 109.6, 110.7, 113.4, 125.8, 126.6, 126.7, 129.4, 129.5, 130.0, 130.4, 131.3, 137.9, 139.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3096, 3018, 2924, 2860, 2248, 1671, 1607, 1596, 1496, 1405 cm^{-1}. MS (EI): *m*/*z* = 319 (35.02) $[M + 2]^+$, 318 (33.63) $[M + 1]^+$, 317 (100.00) $[M]^+$, 302 (26.27). $C_{19}H_{12}ClN_3$ (317.0720): calcd. C 71.81, H 3.81, Cl 11.16, N 13.22; found C 71.64, H 3.70, N 13.22.

(2*R*,3*S*)-2-(4-Chlorophenyl)-3-(4-methoxyphenyl)cyclopropane-1,1,2-tricarbonitrile (3g): Liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.81 (s, 3 H, OCH_3), 3.85 (s, 1 H, CH), 6.86 (d, *J* = 8.8 Hz, 2 H, Ar), 6.94 (d, *J* = 8.8 Hz, 2 H, Ar), 7.22 (d, *J* = 8.8 Hz, 2 H, Ar), 7.42 (d, *J* = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.3, 33.3, 43.5, 55.4, 109.4, 112.0, 114.6, 115.9, 117.0, 122.8, 130.0, 131.1, 131.9, 137.6, 161.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2960, 2935, 2841, 2247, 1610, 1517, 1494, 1259, 1185 cm^{-1}. MS (EI): *m*/*z* = 335 (35.43) $[M + 2]^+$, 334 (28.04) $[M + 1]^+$, 333 (100.00) $[M]^+$, 298 (41.03). HRMS (EI): calcd. for $C_{19}H_{12}ClN_3O$ $[M]^+$ 333.0669; found 333.0666.

(2*R*,3*R*)-2-(4-Chlorophenyl)-3-(4-methoxyphenyl)cyclopropane-1,1,2-tricarbonitrile (3g′): M.p. 210–212 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.84 (s, 3 H, OCH_3), 3.89 (s, 1 H, CH), 7.02 (d, *J* = 8.8 Hz, 2 H, Ar), 7.48 (d, *J* = 8.8 Hz, 2 H, Ar), 7.50–7.55 (m, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.0, 36.8, 40.4, 55.4, 109.7, 110.7, 113.6, 115.1, 118.3, 126.8, 130.0, 130.3, 130.4, 137.8, 161.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3007, 2965, 2937, 2841, 2248, 1612, 1517, 1256, 1097 cm^{-1}. MS (EI): *m*/*z* = 335 (36.52) $[M + 2]^+$, 334 (26.88) $[M + 1]^+$, 333 (100.00) $[M]^+$, 298 (61.44). $C_{19}H_{12}ClN_3O$ (333.0669): calcd. C 68.37, H 3.62, Cl 10.62, N 12.59, O 4.79; found C 68.29, H 3.74, N 12.66.

(2*R*,3*S*)-2-(4-Chlorophenyl)-3-(naphthalen-1-yl)cyclopropane-1,1,2-tricarbonitrile (3h): M.p. 208–210 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 4.31 (s, 1 H, CH), 6.96 (d, *J* = 8.8 Hz, 2 H, Ar), 7.09 (d, *J* = 8.8 Hz, 2 H, Ar), 7.51 (dd, J_1 = 7.2, J_2 = 8.0 Hz, 1 H, Ar), 7.57–7.62 (m, 2 H, Ar), 7.69 (dt, J_1 = 0.8, J_2 = 7.2 Hz, 1 H, Ar), 7.82–7.85 (m, 1 H, Ar), 7.93–7.99 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.5, 35.1, 41.8, 109.6, 112.1, 116.1, 121.9, 122.3, 123.4, 125.4, 126.5, 127.2, 128.3, 129.3, 129.4, 130.3, 131.1, 131.4, 133.5, 137.1 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3063, 3002, 2246, 1595, 1510, 1495, 1099 cm^{-1}. MS (EI): *m*/*z* = 355 (5.78) $[M + 2]^+$, 354 (5.65) $[M + 1]^+$, 353 (15.48) $[M]^+$, 326 (18.52). $C_{22}H_{12}ClN_3$ (353.0720): calcd. C 74.68, H 3.42, Cl 10.02, N 11.88; found C 74.85, H 3.73, N 11.99.

(2*R*,3*R*)-2-(4-Chlorophenyl)-3-(naphthalen-1-yl)cyclopropane-1,1,2-tricarbonitrile (3h′): M.p. 257–259 °C. ^{1}H NMR [$(CD)_3CO$, 400 MHz, TMS]: δ = 5.18 (s, 1 H, CH), 7.65–7.70 (m, 2 H, Ar), 7.71–7.77 (m, 3 H, Ar), 8.06 (d, *J* = 8.4 Hz, 1 H, Ar), 8.08–8.15 (m, 5 H, Ar) ppm. ^{13}C NMR [$(CD)_3CO$, 100 MHz]: δ = 23.3, 37.6, 39.4, 111.7, 112.2, 115.5, 123.7, 125.5, 126.1, 127.6, 128.5, 128.8, 129.1, 130.2, 130.8, 131.6, 132.1, 132.4, 134.9, 137.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3068, 2980, 2250, 1594, 1504, 1487, 1402 cm^{-1}. MS (EI): *m*/*z* = 355 (25.58) $[M + 2]^+$, 354 (27.83) $[M + 1]^+$, 353 (72.83) $[M]^+$, 326 (70.12). $C_{22}H_{12}ClN_3$ (353.0720): calcd. C 74.68, H 3.42, Cl 10.02, N 11.88; found C 74.64, H 3.75, N 11.94.

(2*R*,3*S*)-2-Phenyl-3-(pyridin-3-yl)cyclopropane-1,1,2-tricarbonitrile (3i): M.p. 187–188 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.95 (s, 1 H, CH), 6.93–6.96 (m, 1 H, Ar), 7.16 (dd, J_1 = 4.8, J_2 = 8.4 Hz, 1 H, Ar), 7.29–7.32 (m, 2 H, Ar), 7.45–7.50 (m, 2 H, Ar), 7.52–7.57 (m, 1 H, Ar), 8.58 (d, *J* = 2.0 Hz, 1 H, Ar), 8.66 (d, *J* = 3.6 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.2, 34.2, 40.9, 108.9, 111.7, 115.7, 122.7, 123.0, 123.5, 130.0, 130.4, 131.5, 135.8, 151.2, 151.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3036, 2959, 2926, 2249, 1591, 1574, 1494, 1025 cm^{-1}. MS (EI): *m*/*z* = 270 (100.00) $[M]^+$, 269 (73.89), 243 (28.41). $C_{17}H_{10}N_4$ (270.0905): calcd. C 75.54, H 3.73, N 20.73; found C 75.82, H 3.49, N 20.71.

(2*R*,3*R*)-2-Phenyl-3-(pyridin-3-yl)cyclopropane-1,1,2-tricarbonitrile (3i′): M.p. 225–226 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.97 (s, 1 H, CH), 7.51 (dd, J_1 = 5.1, J_2 = 7.8 Hz, 1 H, Ar), 7.60–7.61 (m, 5 H, Ar), 7.99 (d, *J* = 7.8 Hz, 1 H, Ar), 8.80 (d, *J* = 3.6 Hz, 1 H, Ar), 8.87 (s, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.6, 37.1, 37.9, 109.4, 110.2, 113.3, 124.1, 127.5, 128.6, 130.3, 131.8, 136.0, 150.5, 151.6 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2970, 2919, 2249, 1573, 1483, 1451, 1417 cm^{-1}. MS (EI): *m*/*z* = 270 (100.00) $[M]^+$, 269 (71.66), 243 (28.07). $C_{17}H_{10}N_4$ (270.0905): calcd. C 75.54, H 3.73, N 20.73; found C 75.67, H 3.46, N 20.95.

(2*R*,3*S*)-2-(4-Chlorophenyl)-3-[(*E*)-styryl]cyclopropane-1,1,2-tricarbonitrile (3j): M.p. 122–124 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.60 (d, *J* = 10.0 Hz, 1 H, CH), 5.42 (dd, J_1 = 10.0, J_2 = 16.0 Hz, 1 H, CH), 7.11 (d, *J* = 16.0 Hz, 1 H, CH), 7.32–7.38 (m, 5 H, Ar), 7.43 (d, *J* = 8.4 Hz, 2 H, Ar), 7.52 (d, *J* = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.6, 32.6, 42.8, 109.2, 111.3, 114.3, 115.2, 123.6, 127.0, 129.0, 129.9, 130.5, 131.8, 134.3, 137.9, 141.8 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3030, 2248, 1597, 1494, 1096 cm^{-1}. MS (EI): *m*/*z* = 331 (11.65) $[M + 2]^+$, 330 (21.23) $[M + 1]^+$, 329 (35.94) $[M]^+$, 328 (45.30), 294 (55.38). HRMS (EI): calcd. for $C_{20}H_{12}ClN_3$ $[M]^+$ 329.0720; found 329.0724.

(2*R*,3*R*)-2-(4-Chlorophenyl)-3-[(*E*)-styryl]cyclopropane-1,1,2-tricarbonitrile (3j′): M.p. 212–214 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.52 (d, *J* = 8.8 Hz, 1 H, CH), 6.12 (dd, J_1 = 8.8, J_2 = 15.6 Hz, 1 H, CH), 7.16 (d, *J* = 15.6 Hz, 1 H, CH), 7.39–7.44 (m, 3 H, Ar), 7.45–7.54 (m, 6 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.5, 35.9, 40.1, 109.8, 110.2, 113.4, 114.8, 125.9, 127.1, 129.0, 129.9, 130.4, 131.7, 134.2, 137.9, 142.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3031, 2925, 2854, 2248, 1596, 1496, 1097 cm^{-1}. MS (EI): *m*/*z* = 331 (13.90) $[M + 2]^+$, 330 (22.98) $[M + 1]^+$, 329 (41.14) $[M]^+$, 328 (45.30), 302 (64.37). HRMS (EI): calcd. for $C_{20}H_{12}ClN_3$ $[M]^+$ 329.0720; found 329.0725.

2-(4-Chlorophenyl)-3-ethylcyclopropane-1,1,2-tricarbonitrile (3k + 3k′): ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.20–1.35 (m, 3 H, CH_3), 1.95–2.16 (m, 2 H, CH_2), 2.65–2.73 (m, 1 H, CH), 7.37–7.42 (m, 2 H, Ar), 7.47–7.51 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 11.6, 11.7, 17.1, 19.6, 20.5, 21.2, 33.5, 36.3, 38.6, 41.8, 109.3, 109.8, 110.6, 111.9, 113.5, 115.6, 123.7, 126.3, 129.9, 130.2, 130.4, 131.3, 137.5, 137.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3036, 2976, 2940, 2882, 2248, 1595, 1494, 1462, 1404, 1097, 1015 cm^{-1}. MS (EI): *m*/*z* = 257 (5.06) $[M + 2]^+$, 352 (3.40) $[M + 1]^+$, 351 (15.31) $[M]^+$. HRMS (EI): calcd. for $C_{14}H_{10}ClN_3$ $[M]^+$ 255.0563; found 255.0559.

(2*R*,3*S*)-2-(3,5-Dimethylphenyl)-3-phenylcyclopropane-1,1,2-tricarbonitrile (3l): M.p. 193–195 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.26 (s, 6 H, CH_3), 3.84 (s, 3 H, CH), 6.85 (s, 2 H, Ar), 7.03 (d, *J* = 8.0 Hz, 2 H, Ar), 7.09 (s, 1 H, Ar), 7.32 (t, *J* = 8.4 Hz, 2 H, Ar), 7.41 (t, *J* = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.2, 21.1, 34.3, 43.4, 109.4, 112.3, 116.4, 123.7, 126.1, 128.0, 128.7, 129.8, 130.0, 132.6, 139.5 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3035, 2957, 2922, 2247, 1607, 1499, 1457, 853 cm^{-1}. MS (EI): *m*/*z* = 297 (100.00), 282 (55.36), 270 (48.23), 255 (49.06). HRMS (EI): calcd. for $C_{20}H_{15}N_3$ $[M]^+$ 297.1266; found 297.1258.

(2*R*,3*R*)-2-(3,5-Dimethylphenyl)-3-phenylcyclopropane-1,1,2-tricarbonitrile (3l′): M.p. 235–236 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.39 (s, 6 H, CH_3), 3.97 (s, 1 H, CH), 7.17 (s, 3 H, Ar),

7.50–7.60 (m, 5 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.6, 21.2, 37.4, 40.4, 109.9, 110.9, 114.0, 126.3, 127.2, 127.9, 129.0, 129.6, 130.3, 133.2, 140.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3002, 2958, 2924, 2250, 2230, 1593, 1570, 1447, 1318 cm^{-1}. MS (EI): *m*/*z* = 297 (100.00), 282 (30.56), 270 (63.89), 255 (45.34). HRMS (EI): calcd. for $C_{20}H_{15}N_3$ $[M]^+$ 297.1266; found 297.1270.

(2*R*,3*S*)-3-Phenyl-2-(*p*-tolyl)cyclopropane-1,1,2-tricarbonitrile (3m): M.p. 180–182 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.38 (s, 3 H, CH_3), 3.86 (s, 1 H, CH), 7.04 (d, *J* = 7.8 Hz, 2 H, Ar), 7.14 (d, *J* = 8.4 Hz, 2 H, Ar), 7.22 (d, *J* = 8.4 Hz, 2 H, Ar), 7.33 (t, *J* = 7.8 Hz, 2 H, Ar), 7.39–7.45 (m, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.3, 21.3, 34.3, 43.5, 109.4, 112.3, 116.3, 121.0, 126.0, 128.9, 129.8, 130.1, 130.3, 141.5 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3036, 2924, 2248, 1513, 1500, 1457, 1267 cm^{-1}. MS (EI): *m*/*z* = 283 (100.00) $[M]^+$, 268 (50.24), 256 (57.23). HRMS (EI): calcd. for $C_{19}H_{13}N_3$ $[M]^+$ 283.1109; found 283.1110.

(2*R*,3*R*)-3-Phenyl-2-(*p*-tolyl)cyclopropane-1,1,2-tricarbonitrile (3m′): M.p. 220–222 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.43 (s, 3 H, CH_3), 3.96 (s, 1 H, CH), 7.35 (d, *J* = 8.8 Hz, 2 H, Ar), 7.46 (d, *J* = 8.8 Hz, 2 H, Ar), 7.50–7.59 (m, 5 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.8, 21.3, 37.3, 40.5, 109.9, 110.9, 113.9, 125.2, 127.2, 128.5, 129.0, 129.6, 130.4, 130.7, 142.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3004, 2998, 2252, 1516, 1514, 1449, 1239 cm^{-1}. MS (EI): *m*/*z* = 283 (100.00) $[M]^+$, 268 (39.21), 256 (46.21). $C_{19}H_{13}N_3$ (283.1109): calcd. C 80.54, H 4.62, N 14.83; found C 80.98, H 4.13, N 15.05.

(2*R*,3*S*)-2-(4-Bromophenyl)-3-phenylcyclopropane-1,1,2-tricarbonitrile (3n): M.p. 223–225 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.92 (s, 1 H, CH), 7.05 (d, *J* = 7.8 Hz, 2 H, Ar), 7.13 (d, *J* = 8.1 Hz, 2 H, Ar), 7.35 (t, *J* = 8.1 Hz, 2 H, Ar), 7.42–7.47 (m, 1 H, Ar), 7.55 (d, *J* = 8.1 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.4, 33.7, 43.3, 109.2, 111.9, 115.8, 123.1, 125.5, 125.9, 129.1, 129.7, 130.3, 131.9, 132.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3092, 3036, 2925, 2245, 2254, 1587, 1498, 1484, 1011 cm^{-1}. MS (EI): *m*/*z* = 349 (38.16) $[M + 2]^+$, 348 (14.95) $[M + 1]^+$, 347 (36.67) $[M]^+$, 268 (99.64), 241 (95.96). $C_{18}H_{10}BrN_3$ (347.0058): calcd. C 62.09, H 2.89, Br 22.95, N 12.07; found C 62.39, H 3.14, N 12.16.

(2*R*,3*R*)-2-(4-Bromophenyl)-3-phenylcyclopropane-1,1,2-tricarbonitrile (3n′): M.p. 245–247 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.94 (s, 1 H, CH), 7.47 (d, *J* = 8.4 Hz, 2 H, Ar), 7.53–7.58 (m, 5 H, Ar), 7.72 (d, *J* = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.8, 36.8, 40.7, 109.5, 110.7, 113.3, 126.3, 126.7, 127.3, 129.0, 129.8, 130.2, 130.6, 133.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2996, 2253, 1490, 1449, 1398, 1239 cm^{-1}. MS (EI): *m*/*z* = 349 (38.73) $[M + 2]^+$, 348 (15.02) $[M + 1]^+$, 347 (38.30) $[M]^+$, 268 (98.21), 241 (100.00). $C_{18}H_{10}BrN_3$ (347.0058): calcd. C 62.09, H 2.89, Br 22.95, N 12.07; found C 62.35, H 3.12, N 12.06.

(2*R*,3*S*)-2-(2-Chlorophenyl)-3-phenylcyclopropane-1,1,2-tricarbonitrile (3o): M.p. 174–176 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.87 (s, 1 H, CH), 7.44–7.52 (m, 2 H, Ar), 7.53–7.58 (m, 4 H, Ar), 7.62–7.67 (m, 3 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 36.0, 42.6, 109.6, 110.8, 112.3, 126.9, 127.2, 128.3, 129.0, 129.7, 130.5, 131.0, 131.3, 133.0, 136.1 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3064, 3000, 2925, 2249, 1499, 1475, 1446, 1058 cm^{-1}. MS (EI): *m*/*z* = 305 (17.44) $[M + 2]^+$, 304 (13.41) $[M + 1]^+$, 303 (49.24) $[M]^+$, 268 (100.00). $C_{18}H_{10}ClN_3$ (303.0563): calcd. C 71.18, H 3.32, Cl 11.67, N 13.83; found C 71.19, H 3.32, N 13.83.

(2*R*,3*R*)-(2-Chlorophenyl)-3-phenylcyclopropane-1,1,2-tricarbonitrile (3o′): M.p. 196–198 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.92 (s, 1 H, CH), 7.05 (d, *J* = 7.6 Hz, 2 H, Ar), 7.20–7.23 (m, 1 H, Ar), 7.25–7.35 (m, 3 H, Ar), 7.44 (t, *J* = 7.2 Hz, 1 H, Ar), 7.47–7.52 (m, 1 H, Ar), 7.56 (d, *J* = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.1, 33.0, 43.8, 109.3, 111.9, 114.9, 122.7, 126.2, 127.5, 128.9, 129.4, 130.3, 131.3, 132.2, 132.8, 136.6 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3065, 3037, 2925, 2854, 2248, 1590, 1500, 1475, 1442, 1040 cm^{-1}. MS (EI): *m*/*z* = 305 (12.97) $[M + 2]^+$, 304 (10.86) $[M + 1]^+$, 303 (38.53) $[M]^+$, 268 (97.37). HRMS (EI): calcd. for $C_{18}H_{10}ClN_3$ $[M]^+$ 303.0563; found 303.0561.

(2*R*,3*S*)-2,3-Diphenylcyclopropane-1,1,2-tricarbonitrile (3p): M.p. 180–181 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.90 (s, 1 H, CH), 7.02 (d, *J* = 7.5 Hz, 2 H, Ar), 7.25–7.35 (m, 4 H, Ar), 7.39–7.52 (m, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.3, 34.3, 43.4, 109.3, 112.2, 116.2, 124.1, 125.9, 128.9, 129.6, 129.7, 130.1, 130.4, 131.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3063, 3040, 2925, 2248, 1495, 1451 cm^{-1}. MS (EI): *m*/*z* = 269 (93.39) $[M]^+$, 268 (100.00), 242 (94.37). $C_{18}H_{11}N_3$ (269.0953): calcd. C 80.28, H 4.12, N 15.60; found C 80.15, H 4.08, N 15.71.

(2*R*,3*R*)-2,3-Diphenylcyclopropane-1,1,2-tricarbonitrile (3p′): M.p. 260–262 °C. ^{1}H NMR [$(CD)_2CO$, 400 MHz, TMS]: δ = 4.75 (s, 1 H, CH), 7.53–7.64 (m, 6 H, Ar), 7.82 (d, *J* = 7.2 Hz, 2 H, Ar), 7.95–7.97 (m, 2 H, Ar) ppm. ^{13}C NMR [$(CD)_2CO$, 100 MHz]: δ = 22.2, 38.1, 40.9, 111.8, 112.2, 115.5, 129.8, 130.0, 130.3, 130.41, 130.44, 130.6, 131.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2998, 2918, 2253, 1493, 1450 cm^{-1}. MS (EI): *m*/*z* = 269 (93.12) $[M]^+$, 268 (97.41), 242 (100.00). HRMS (EI): calcd. for $C_{18}H_{11}N_3$ $[M]^+$ 269.0953; found 269.0952.

(2*R*,3*S*)-3-(3-Bromophenyl)-2-phenylcyclopropane-1,1,2-tricarbonitrile (3q): M.p. 107–109 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.84 (s, 1 H, CH), 6.82 (d, *J* = 8.0 Hz, 2 H, Ar), 7.17 (t, *J* = 8.0 Hz, 1 H, Ar), 7.26–7.30 (m, 3 H, Ar), 7.43–7.48 (m, 2 H, Ar), 7.50–7.57 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.4, 34.4, 42.4, 109.0, 111.8, 115.9, 122.9, 123.7, 127.8, 128.0, 129.8, 130.2, 130.4, 131.3, 133.2, 133.3 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3063, 3037, 2925, 2248, 1595, 1567, 1479, 1079 cm^{-1}. MS (EI): *m*/*z* = 349 (27.12) $[M + 2]^+$, 348 (11.41) $[M + 1]^+$, 347 (27.24) $[M]^+$, 268 (97.88), 241 (100.00). HRMS (EI): calcd. for $C_{18}H_{10}BrN_3$ $[M]^+$ 347.0058; found 347.0055.

(2*R*,3*R*)-3-(3-Bromophenyl)-2-phenylcyclopropane-1,1,2-tricarbonitrile (3q′): M.p. 184–185 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.94 (s, 1 H, CH), 7.41 (t, *J* = 7.6 Hz, 1 H, Ar), 7.52–7.55 (m, 1 H, Ar), 7.56–7.58 (m, 5 H, Ar), 7.64–7.66 (m, 1 H, Ar), 7.71–7.72 (m, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.7, 37.3, 39.5, 109.6, 110.4, 113.5, 123.5, 127.4, 127.7, 128.6, 129.1, 130.2, 131.2, 131.6, 132.2, 133.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3064, 3012, 2248, 1598, 1567, 1495, 1478, 1451, 1421, 1074 cm^{-1}. MS (EI): *m*/*z* = 349 (19.82) $[M + 2]^+$, 348 (9.19) $[M + 1]^+$, 347 (19.94) $[M]^+$, 268 (94.12), 241 (100.00). $C_{18}H_{10}BrN_3$ (347.0058): calcd. C 62.09, H 2.89, Br 22.95, N 12.07; found C 62.10, H 2.89, N 12.07.

(2*R*,3*S*)-3-(4-Bromophenyl)-2-phenylcyclopropane-1,1,2-tricarbonitrile (3r): M.p. 206–208 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.83 (s, 1 H, CH), 6.86 (d, *J* = 8.7 Hz, 2 H, Ar), 7.26–7.29 (m, 3 H, Ar), 7.42–7.56 (m, 5 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.3, 34.2, 42.8, 109.1, 111.9, 116.0, 123.8, 124.9, 129.8, 130.4, 131.2, 132.2 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3032, 2960, 2925, 2854, 2247, 1582, 1592, 1491, 1450, 1076 cm^{-1}. MS (EI): *m*/*z* = 349 (34.03) $[M + 2]^+$, 348 (12.47) $[M + 1]^+$, 347 (31.91) $[M]^+$, 268 (100.00), 241 (92.60). HRMS (EI): calcd. for $C_{18}H_{10}BrN_3$ $[M]^+$ 347.0058; found 347.0064.

(2*R*,3*R*)-3-(4-Bromophenyl)-2-phenylcyclopropane-1,1,2-tricarbonitrile (3r′): M.p. 233–235 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 3.92 (s, 1 H, CH), 7.46 (d, *J* = 8.4 Hz, 2 H, Ar), 7.57–7.60 (m, 5 H, Ar), 7.69 (d, *J* = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$,

100 MHz): δ = 20.7, 37.4, 39.8, 109.6, 110.5, 113.6, 125.1, 126.0, 127.9, 128.6, 130.2, 130.6, 131.7, 133.0 ppm. IR (CH_2Cl_2): ṽ = 3003, 2251, 1492, 1397, 1012 cm^{-1}. MS (EI): *m*/*z* = 349 (38.00) [M + 2]$^+$, 348 (14.27) [M + 1]$^+$, 347 (37.74) [M]$^+$, 268 (100.00), 241 (99.87). $C_{18}H_{10}ClN_3$ (303.0563): calcd. C 62.09, H 2.89, Br 22.95, N 12.07; found C 62.25, H 3.05, N 12.08.

(2*R*,3*S*)-3-(4-Chlorophenyl)-2-phenylcyclopropane-1,1,2-tricarbonitrile (3s): M.p. 228–230 °C. ^{1}H NMR [$(CD_3)_2CO$, 400 MHz, TMS]: δ = 4.60 (s, 1 H, CH), 7.19 (d, *J* = 8.4 Hz, 2 H, Ar), 7.41 (d, *J* = 8.4 Hz, 2 H, Ar), 7.49–7.54 (m, 2 H, Ar), 7.55–7.60 (m, 1 H, Ar), 7.62–7.65 (m, 2 H, Ar) ppm. ^{13}C NMR [$(CD_3)_2CO$, 100 MHz]: δ = 20.8, 35.0, 42.8, 111.1, 113.7, 117.5, 126.3, 127.5, 129.3, 130.4, 131.8, 131.9, 132.8, 136.1 ppm. IR (CH_2Cl_2): ṽ = 3037, 2247, 1593, 1496 1094, 1020 cm^{-1}. MS (EI): *m*/*z* = 305 (28.80) [M + 2]$^+$, 304 (24.53) [M + 1]$^+$, 303 (82.88), 268 (100.00), 241 (97.59). HRMS (EI): calcd. for $C_{18}H_{10}ClN_3$ [M]$^+$ 303.0563; found 303.0562.

(2*R*,3*R*)-3-(4-Chlorophenyl)-2-phenylcyclopropane-1,1,2-tricarbonitrile (3s′): M.p. 210–211 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.95 (s, 1 H, CH), 7.50–7.55 (m, 4 H, Ar), 7.55–7.60 (m, 5 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.8, 37.4, 39.7, 109.7, 110.5, 113.6, 125.5, 127.8, 128.6, 130.0, 130.2, 130.4, 131.6, 136.8 ppm. IR (CH_2Cl_2): ṽ = 3003, 2250, 1495, 1450, 1238, 1092 cm^{-1}. MS (EI): *m*/*z* = 305 (24.10) [M + 2]$^+$, 304 (20.85) [M + 1]$^+$, 303 (74.76), 268 (100.00), 241 (97.91). HRMS (EI): calcd. for $C_{18}H_{10}ClN_3$ [M]$^+$ 303.0563; found 303.0566.

(2*R*,3*S*)-2-(Naphthalen-1-yl)-3-phenylcyclopropane-1,1,2-tricarbonitrile (3t): M.p. 245–246 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 4.05 (s, 1 H, CH), 6.92–6.94 (m, 2 H, Ar), 7.16 (t, *J* = 7.2 Hz, 2 H, Ar), 7.29 (t, *J* = 7.2 Hz, 1 H, Ar), 7.44–7.61 (m, 4 H, Ar), 7.80 (s, 1 H, Ar), 7.90–7.93 (m, 1 H, Ar), 8.02 (d, *J* = 8.4 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 19.6, 33.0, 44.0, 109.5, 112.4, 116.1, 119.9, 122.8, 125.0, 126.4, 127.0, 128.1, 128.7, 129.3, 129.4, 130.1, 130.4, 130.8, 132.3, 134.0 ppm. IR (CH_2Cl_2): ṽ = 3064, 3037, 2925, 2246, 1510, 1499, 1458 cm^{-1}. MS (EI): *m*/*z* = 319 (88.43) [M]$^+$, 292 (100.00), 241 (69.99). HRMS (EI): calcd. for $C_{22}H_{13}N_3$ [M]$^+$ 319.1109; found 319.1106.

(2*R*,3*R*)-2-(Naphthalen-1-yl)-3-phenylcyclopropane-1,1,2-tricarbonitrile (3t′): M.p. 272–274 °C. ^{1}H NMR [$(CD_3)_2CO$, 400 MHz, TMS]: δ = 4.88 (s, 1 H, CH), 7.56–7.66 (m, 3 H, Ar), 7.68–7.72 (m, 1 H, Ar), 7.77 (t, *J* = 8.0 Hz, 1 H, Ar), 7.92–7.96 (m, 3 H, Ar), 8.13 (d, *J* = 7.2 Hz, 1 H, Ar), 8.18 (d, *J* = 8.8 Hz, 1 H, Ar), 8.25 (d, *J* = 8.4 Hz, 1 H, Ar) ppm. ^{13}C NMR [$(CD_3)_2CO$, 100 MHz]: δ = 21.6, 36.9, 42.3, 111.9, 112.1, 115.2, 123.1, 126.1, 126.5, 129.5, 129.7, 130.2, 130.5, 130.7, 130.8, 130.9, 131.7, 133.3, 135.1 ppm. IR (CH_2Cl_2): ṽ = 3000, 2244, 1509, 1448, 1217 cm^{-1}. MS (EI): *m*/*z* = 319 (82.31) [M]$^+$, 292 (100.00), 241 (88.41). HRMS (EI): calcd. for $C_{22}H_{13}N_3$ [M]$^+$ 319.1109; found 319.1114.

Typical Reaction Procedure for the Phosphane-Mediated [2+1] Annulation: PBu_3 (0.3 mmol) was added under argon to a mixture of an acyl cyanide **1** (0.3 mmol) and ethyl (*E*)-2-cyano-3-phenylacrylate (**4**, 0.3 mmol) in solvent and the reaction mixture was stirred at reflux for the required time as indicated in the tables. After the reaction solution had been concentrated under reduced pressure, the residue was purified by flash chromatography on silica gel (eluent: EtOAc/petroleum ether 1:8–1:4) to afford the pure product **5**.

Ethyl 2-(4-Chlorophenyl)-1,2-dicyano-3-phenylcyclopropanecarboxylate (5a): M.p. 157–159 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.46 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.01 (s, 1 H, CH), 4.50 (q, *J* = 7.2 Hz, 2 H, CH_2), 7.11 (d, *J* = 8.0 Hz, 2 H, Ar), 7.20 (d, *J* = 8.4 Hz, 2 H, Ar), 7.28–7.40 (m, 5 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.0, 32.5, 33.3, 40.9, 64.9, 112.5, 116.3, 125.2, 127.6, 128.7, 129.3, 129.6, 129.7, 132.1, 136.6, 162.9 ppm. IR (CH_2Cl_2): ṽ = 3096, 2986, 2240, 1746, 1495, 1241 cm^{-1}. MS (ESI): *m*/*z* = 351.0 [M + 1]$^+$. HRMS (ESI) calcd. for $C_{20}H_{15}ClN_2O_2$ [M$^+$ + Na] 373.0720; found 373.07094.

Ethyl 2-(4-Chlorophenyl)-1,2-dicyano-3-phenylcyclopropanecarboxylate (5a′): M.p. 166–168 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.18 (t, *J* = 6.6 Hz, 3 H, CH_3), 4.12 (s, 1 H, CH), 4.13 (q, *J* = 6.6 Hz, 2 H, CH_2), 7.42–7.43 (m, 4 H, Ar), 7.46–7.52 (m, 3 H, Ar), 7.55–7.58 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 34.2, 36.7, 37.9, 64.3, 112.9, 115.0, 127.9, 128.7, 129.0, 129.3, 129.5, 129.6, 130.4, 136.6, 161.3 ppm. IR (CH_2Cl_2): ṽ = 3091, 3032, 2985, 2245, 1744, 1496, 1293, 1096 cm^{-1}. MS (ESI): *m*/*z* = 351.0 [M + 1]$^+$. HRMS (ESI) calcd. for $C_{20}H_{15}ClN_2O_2$ [M$^+$ + Na] 373.0720; found 373.07077.

Ethyl 3-(2-Chlorophenyl)-2-(4-chlorophenyl)-1,2-dicyanocyclopropanecarboxylate (5b): Liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.47 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.24 (s, 1 H, CH), 4.52 (qd, J_1 = 2.0, J_2 = 7.2 Hz, 2 H, CH_2), 7.15 (d, *J* = 8.8 Hz, 2 H, Ar), 7.25–7.30 (m, 3 H, Ar), 7.39 (t, *J* = 7.6 Hz, 1 H, Ar), 7.44 (d, *J* = 8.0 Hz, 1 H, Ar), 7.52 (dd, J_1 = 0.8, J_2 = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.1, 33.3, 33.4, 38.6, 65.1, 112.7, 116.0, 125.8, 126.6, 127.5, 129.0, 129.3, 130.2, 130.6, 130.7, 136.0, 136.4, 162.6 ppm. IR (CH_2Cl_2): ṽ = 2987, 2938, 2245, 1747, 1595, 1495, 1443, 1240 cm^{-1}. MS (EI): *m*/*z* = 388 (2.52) [M + 4]$^+$, 387 (5.80) [M + 3]$^+$, 386 (8.08) [M + 2]$^+$, 385 (9.56) [M + 1]$^+$, 384 (9.78) [M]$^+$. HRMS (EI): calcd. for $C_{20}H_{14}Cl_2N_2O_2$ [M]$^+$ 384.0432; found 384.0439.

Ethyl 3-(2-Chlorophenyl)-2-(4-chlorophenyl)-1,2-dicyanocyclopropanecarboxylate (5b′): Liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.17 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.10 (s, 1 H, CH), 4.14 (q, *J* = 7.2 Hz, 2 H, CH_2), 7.40–7.46 (m, 4 H, Ar), 7.51 (d, *J* = 8.8 Hz, 2 H, Ar), 7.55–7.58 (m, 1 H, Ar), 7.68–7.71 (m, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.9, 34.7, 36.2, 37.0, 64.3, 112.9, 115.0, 127.3, 127.4, 127.6, 129.6, 130.3, 130.4, 130.5, 131.0, 135.4, 136.7, 161.1 ppm. IR (CH_2Cl_2): ṽ = 3067, 2986, 2938, 2247, 1746, 1596, 1495, 1296 cm^{-1}. MS (EI): *m*/*z* = 388 (0.89) [M + 4]$^+$, 387 (1.04) [M + 3]$^+$, 386 (4.18) [M + 2]$^+$, 385 (2.04) [M + 1]$^+$, 384 (6.23) [M]$^+$. HRMS (EI): calcd. for $C_{20}H_{14}C_{12}N_2O_2$ [M]$^+$ 384.0432; found 384.0434.

Ethyl 3-(4-Bromophenyl)-2-(4-chlorophenyl)-1,2-dicyanocyclopropanecarboxylate (5c): M.p. 161–163 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.46 (t, *J* = 7.6 Hz, 3 H, CH_3), 3.95 (s, 1 H, CH), 4.47–4.53 (m, 2 H, CH_2), 6.96 (d, *J* = 8.8 Hz, 2 H, Ar), 7.20 (d, *J* = 8.8 Hz, 2 H, Ar), 7.38 (d, *J* = 8.8 Hz, 2 H, Ar), 7.44 (d, *J* = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.0, 32.5, 33.2, 40.2, 65.1, 112.3, 116.0, 123.9, 124.8, 126.7, 129.8, 131.3, 131.9, 132.1, 136.9, 162.7 ppm. IR (CH_2Cl_2): ṽ = 2984, 2926, 2854, 2240, 1746, 1594, 1492, 1242, 1011 cm^{-1}. MS (EI): *m*/*z* = 432 (0.66) [M + 4]$^+$, 431 (0.61) [M + 3]$^+$, 430 (2.11) [M + 2]$^+$, 429 (0.60) [M + 1]$^+$, 428 (1.79) [M]$^+$. HRMS (EI): calcd. for $C_{20}H_{14}BrClN_2O_2$ [M]$^+$ 427.9927; found 427.9931.

Ethyl 3-(4-Bromophenyl)-2-(4-chlorophenyl)-1,2-dicyanocyclopropanecarboxylate (5c′): M.p. 121–123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.18 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.05 (s, 1 H, CH), 4.13 (qd, J_1 = 1.2, J_2 = 7.2 Hz, 2 H, CH_2), 7.39–7.46 (m, 6 H, Ar), 7.64 (d, *J* = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.8, 34.2, 36.6, 37.2, 64.4, 112.7, 114.8, 124.1, 127.5, 127.7, 129.7, 130.3, 130.7, 132.6, 136.8, 161.1 ppm. IR (CH_2Cl_2): ṽ = 2983, 2960, 2926, 2246, 1745, 1595, 1492, 1013 cm^{-1}. MS (EI): *m*/*z* = 432 (1.31) [M + 4]$^+$, 431 (0.85) [M + 3]$^+$, 430 (3.10)

[M + 2]$^+$, 429 (0.54) [M + 1]$^+$, 428 (2.43) [M]$^+$. HRMS (EI): calcd. for $C_{20}H_{14}BrClN_2O_2$ [M]$^+$ 427.9927; found 427.9922.

Ethyl 2-(4-Chlorophenyl)-1,2-dicyano-3-*p*-tolylcyclopropanecarboxylate (5d): M.p. 161–163 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.46 (t, J = 7.2 Hz, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 3.97 (s, 1 H, CH), 4.49 (q, J = 7.2 Hz, 2 H, CH_2), 6.97 (d, J = 8.4 Hz, 2 H, Ar), 7.11 (d, J = 8.4 Hz, 2 H, Ar), 7.21 (d, J = 8.8 Hz, 2 H, Ar), 7.35 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.0, 21.1, 32.4, 33.3, 40.9, 64.8, 112.6, 116.4, 124.4, 125.3, 129.4, 129.5, 129.6, 132.2, 136.6, 139.5, 163.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2984, 2925, 2239, 1746, 1518, 1493, 1240 cm^{-1}. MS (EI): m/z = 310 (68.99) [M – 54]$^+$. $C_{21}H_{17}ClN_2O_2$ (364.0979): calcd. C 69.14, H 4.70, Cl 9.72, N 7.68, O 8.77; found C 69.35, H 5.00, N 7.69.

Ethyl 2-(4-Chlorophenyl)-1,2-dicyano-3-*p*-tolylcyclopropanecarboxylate (5d′): M.p. 148–150 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.17 (t, J = 7.2 Hz, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 4.08 (s, 1 H, CH), 4.12 (qd, J_1 = 1.6, J_2 = 7.2 Hz, 2 H, CH_2), 7.30 (d, J = 8.0 Hz, 2 H, Ar), 7.41–7.42 (m, 4 H, Ar), 7.45 (d, J = 8.0 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.8, 21.2, 34.3, 36.7, 37.8, 64.2, 113.0, 115.1, 125.6, 128.0, 128.8, 129.6, 130.0, 130.4, 136.6, 139.6, 161.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2963, 2926, 2856, 2246, 1745, 1518, 1492, 1095 cm^{-1}. MS (EI): m/z = 310 (70.08) [M – 54]$^+$. $C_{21}H_{17}ClN_2O_2$ (364.0979): calcd. C 69.14, H 4.70, Cl 9.72, N 7.68, O 8.77; found C 69.18, H 5.02, N 7.68.

Ethyl 1,2-Dicyano-2,3-diphenylcyclopropanecarboxylate (5e): M.p. 115–117 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.46 (t, J = 7.2 Hz, 3 H, CH_3), 4.00 (s, 1 H, CH), 4.50 (qd, J_1 = 0.8, J_2 = 7.2 Hz, 2 H, CH_2), 7.07–7.10 (m, 2 H, Ar), 7.25–7.30 (m, 4 H, Ar), 7.32–7.39 (m, 3 H, Ar), 7.40–7.45 (m, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.0, 33.3, 40.9, 64.8, 112.7, 116.7, 126.6, 128.0, 128.5, 129.1, 129.2, 129.8, 130.2, 130.8, 163.2 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3062, 3033, 2984, 2929, 2238, 1746, 1500, 1449, 1238 cm^{-1}. MS (EI): m/z = 316 (2.40) [M]$^+$. $C_{20}H_{16}N_2O_2$ (316.1212): calcd. C 75.93, H 5.10, N 8.86, O 10.11; found C 75.91, H 5.14, N 8.82.

Ethyl 1,2-Dicyano-2,3-diphenylcyclopropanecarboxylate (5e′): M.p. 158–160 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.11 (t, J = 7.2 Hz, 3 H, CH_3), 4.02–4.14 (m, 2 H, CH_2), 4.16 (s, 1 H, CH), 7.42–7.52 (m, 8 H, Ar), 7.58–7.61 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.7, 34.2, 37.3, 37.7, 64.0, 113.2, 115.3, 129.1, 129.2, 129.3, 129.4, 130.4, 161.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3063, 3032, 2985, 2926, 2246, 1745, 1497, 1450, 1003 cm^{-1}. MS (EI): m/z = 316 (2.06) [M]$^+$. $C_{20}H_{16}N_2O_2$ (316.1212): calcd. C 75.93, H 5.10, N 8.86, O 10.11; found C 76.00, H 5.06, N 8.82.

Ethyl 1,2-Dicyano-2-(3,5-dimethylphenyl)-3-phenylcyclopropanecarboxylate (5f): Liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.46 (t, J = 7.2 Hz, 3 H, CH_3), 2.24 (s, 6 H, CH_3), 3.95 (s, 1 H, CH), 4.49 (q, J = 7.2 Hz, 2 H, CH_2), 6.85 (s, 2 H, Ar), 7.03 (s, 1 H, Ar), 7.09 (d, J = 7.2 Hz, 2 H, Ar), 7.25–7.29 (m, 2 H, Ar), 7.32–7.36 (m, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.1, 21.1, 33.3, 41.0, 64.7, 112.7, 116.9, 126.2, 128.2, 128.3, 128.5, 129.1, 129.9, 131.8, 139.0, 163.3 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2984, 2922, 2870, 2239, 1746, 1607, 1500, 1036 cm^{-1}. MS (EI): m/z = 344 (19.70) [M]$^+$. HRMS (EI): calcd. for $C_{22}H_{20}N_2O_2$ [M]$^+$ 344.1525; found 344.1520.

Ethyl 1,2-Dicyano-2-(3,5-dimethylphenyl)-3-phenylcyclopropanecarboxylate (5f′): M.p. 136–138 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.13 (t, J = 7.2 Hz, 3 H, CH_3), 2.33 (s, 6 H, CH_3), 4.04–4.20 (m, 3 H, CH), 7.05 (s, 1 H, Ar), 7.06 (s, 2 H, Ar), 7.42–7.52 (m, 3 H, Ar), 7.57–7.60 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.8, 21.1, 34.0, 37.3, 37.8, 63.9, 113.3, 115.5, 126.7, 129.1, 129.2, 129.3, 129.4, 132.0, 139.1, 161.5 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2984, 2922, 2870, 2245, 1751, 1608, 1501, 1449 cm^{-1}. MS (EI): m/z = 344 (21.51) [M]$^+$. HRMS (EI): calcd. for $C_{22}H_{20}N_2O_2$ [M]$^+$ 344.1525; found 344.1527.

Ethyl 2-(4-Chlorophenyl)-1,2-dicyano-3-(pyridin-3-yl)cyclopropanecarboxylate (5g): ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.47 (t, J = 7.2 Hz, 3 H, CH_3), 4.01 (s, 1 H, CH), 4.52 (q, J = 7.2 Hz, 2 H, CH_2), 7.08 (dt, J_1 = 2.0, J_2 = 8.4 Hz, 1 H, Ar), 7.17 (dd, J_1 = 4.8, J_2 = 8.4 Hz, 1 H, Ar), 7.23 (d, J = 8.8 Hz, 2 H, Ar), 7.40 (d, J = 8.8 Hz, 2 H, Ar), 8.60–8.62 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.0, 32.4, 33.1, 38.3, 65.2, 112.1, 115.8, 123.0, 124.4, 124.5, 130.0, 132.2, 135.8, 137.2, 150.5, 151.6, 162.5 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3091, 3034, 2986, 2939, 2241, 1747, 1594, 1574, 1488, 1287, 1014 cm^{-1}. MS (EI): m/z = 353 (16.90) [M + 2]$^+$, 352 (62.33) [M + 1]$^+$, 351 (6.37) [M]$^+$. HRMS (EI): calcd. for $C_{19}H_{14}ClN_3O_2$ [M]$^+$ 351.0775; found 351.0778.

Ethyl 2-(4-Chlorophenyl)-1,2-dicyano-3-(pyridin-3-yl)cyclopropanecarboxylate (5g′): M.p. 146–148 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.19 (t, J = 7.6 Hz, 3 H, CH_3), 4.09 (s, 1 H, CH), 4.12–4.18 (m, 2 H, CH_2), 7.41–7.48 (m, 5 H, Ar), 7.96–8.00 (m, 1 H, Ar), 8.73 (dd, J_1 = 1.2, J_2 = 4.8 Hz, 1 H, Ar), 8.83 (d, J = 2.4 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.8, 34.0, 35.2, 36.3, 64.6, 112.5, 114.5, 123.9, 125.2, 127.2, 129.8, 130.3, 135.9, 137.0, 150.7, 150.8, 160.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2985, 2938, 2247, 1746, 1595, 1573, 1484, 1248, 1016 cm^{-1}. MS (EI): m/z = 353 (1.16) [M + 2]$^+$, 352 (2.14) [M + 1]$^+$, 351 (2.84) [M]$^+$. $C_{19}H_{14}ClN_3O_2$ (351.0775): calcd. C 64.87, H 4.01, Cl 10.08, N 11.94, O 9.10; found C 64.81, H 4.10, N 12.13.

Ethyl 3-(4-Bromophenyl)-1,2-dicyano-2-(thiophen-3-yl)cyclopropanecarboxylate (5h): M.p. 132–134 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.45 (t, J = 7.2 Hz, 3 H, CH_3), 4.02 (s, 1 H, CH), 4.43–4.54 (m, 2 H, CH_2), 6.83 (dd, J_1 = 1.6, J_2 = 5.2 Hz, 1 H, Ar), 7.10 (d, J = 8.4 Hz, 2 H, Ar), 7.24 (dd, J_1 = 1.6, J_2 = 3.2 Hz, 1 H, Ar), 7.31 (dd, J_1 = 3.2, J_2 = 5.2 Hz, 1 H, Ar), 7.49 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.0, 30.6, 33.9, 40.0, 64.9, 112.6, 116.1, 123.7, 126.1, 126.80, 126.82, 127.9, 128.2, 131.2, 132.1, 162.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3019, 2985, 2936, 2245, 1745, 1491, 1282, 1011 cm^{-1}. MS (EI): m/z = 402 (7.91) [M + 2]$^+$, 400 (7.42) [M]$^+$. $C_{18}H_{13}BrN_2O_2S$ (399.9881): calcd. C 53.88, H 3.27, Br 19.91, N 6.98, O 7.97, S 7.99; found C 54.02, H 3.28, N 6.96.

Ethyl 3-(4-Bromophenyl)-1,2-dicyano-2-(thiophen-3-yl)cyclopropanecarboxylate (5h′): M.p. 152–154 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.14 (t, J = 7.2 Hz, 3 H, CH_3), 4.07 (s, 1 H, CH), 4.08–4.19 (m, 2 H, CH_2), 7.18 (dd, J_1 = 1.6, J_2 = 5.2 Hz, 1 H, Ar), 7.41 (dd, J_1 = 3.2, J_2 = 5.2 Hz, 1 H, Ar), 7.43 (d, J = 8.4 Hz, 2 H, Ar), 7.50 (dd, J_1 = 1.6, J_2 = 3.2 Hz, 1 H, Ar), 7.62 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.7, 32.7, 34.7, 37.5, 64.2, 112.9, 114.7, 123.9, 127.1, 127.3, 127.7, 127.9, 128.6, 130.7, 132.6, 160.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3107, 2983, 2928, 2245, 1745, 1493, 1010 cm^{-1}. MS (EI): m/z = 402 (6.63) [M + 2]$^+$, 400 (6.28) [M]$^+$. $C_{18}H_{13}BrN_2O_2S$ (399.9881): calcd. C 53.88, H 3.27, Br 19.91, N 6.98, O 7.97, S 7.99; found C 53.97, H 3.32, N 6.93.

Ethyl 3-(4-Bromophenyl)-1,2-dicyano-2-(naphthalen-1-yl)cyclopropanecarboxylate (5i): M.p. 203–205 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 1.51 (t, J = 7.6 Hz, 3 H, CH_3), 4.13 (s, 1 H, CH), 4.50–4.64 (m, 2 H, CH_2), 6.77–6.88 (m, 2 H, Ar), 7.22–7.29 (m, 2 H, Ar), 7.41–7.82 (m, 5 H, Ar), 7.89 (d, J = 7.6 Hz, 1 H, Ar), 7.98 (d, J = 8.4 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.2, 30.3, 31.9, 40.7, 65.1, 112.6, 116.2, 122.0, 123.2, 123.6, 125.0, 126.8, 127.5, 127.6, 129.2, 130.4, 130.5, 131.0, 131.5, 131.7, 134.0, 163.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3061, 2983, 2928, 2237, 1746, 1595, 1493, 1260, 1011 cm^{-1}. MS (EI): m/z = 446 (15.32) [M +

2]$^+$, 445 (8.44) [M + 1]$^+$, 444 (15.93) [M]$^+$. $C_{24}H_{17}BrN_2O_2$ (444.0473): calcd. C 64.73, H 3.85, Br 17.94, N 6.29, O 7.19; found C 64.68, H 3.91, N 6.22.

Ethyl 3-(4-Bromophenyl)-1,2-dicyano-2-(naphthalen-1-yl)cyclopropanecarboxylate (5i′): M.p. 249–251 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 0.73–0.74 (m, 3 H, CH_3), 3.72–3.81 (m, 2 H, CH_2), 4.18 (s, 1 H, CH), 7.49–7.72 (m, 8 H, Ar), 7.94 (d, J = 8.0 Hz, 1 H, Ar), 7.97 (d, J = 8.4 Hz, 1 H, Ar), 8.14 (d, J = 7.2 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.2, 33.8, 36.3, 38.5, 64.0, 113.2, 114.8, 122.8, 124.0, 125.2, 125.6, 126.9, 127.9, 128.3, 128.6, 128.7, 129.3, 130.8, 131.5, 132.7, 133.8, 161.3 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3015, 2982, 2249, 1741, 1593, 1489, 1311, 1011 cm^{-1}. MS (EI): m/z = 446 (17.52) [M + 2]$^+$, 445 (10.18) [M + 1]$^+$, 444 (17.98) [M]$^+$. $C_{24}H_{17}BrN_2O_2$ (444.0473): calcd. C 64.73, H 3.85, Br 17.94, N 6.29, O 7.19; found C 64.81, H 3.74, N 6.27.

Supporting Information (see also the footnote on the first page of this article): NMR spectra of new compounds shown in tables and schemes.

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[18] CCDC-714983 (for **3a′**), -735020 (for **5a**), -743550 (for **5c′**), and -719285 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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