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Synthesis of Activated Cyclopropanes by MHIRC Strategy: A Facile and Efficient Approach to Spirocyclopropanes Using *N*-Halosulfonamides

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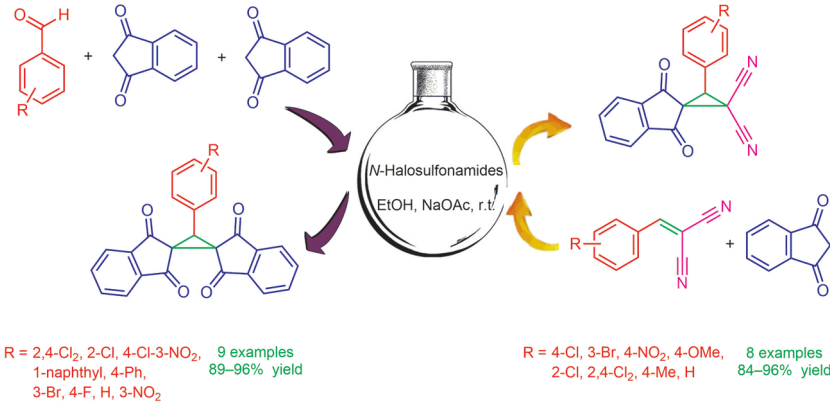


Received: 17.02.2016
Accepted after revision: 28.04.2016
Published online: 20.06.2016
DOI: 10.1055/s-0035-1561653; Art ID: ss-2016-z0118-op

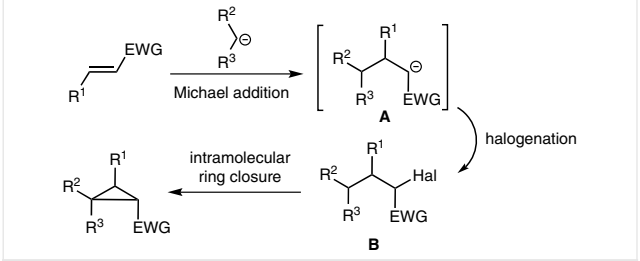
Abstract In this study, a one-pot, three-component reaction of two molecules of indane-1,3-dione with aromatic aldehydes for the synthesis of spirocyclopropylindanediones using poly(*N*-bromo-*N*-ethylbenzene-1,3-disulfonamide) (PBBS), *N*,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonamide (TBBDA), poly(*N*-chloro-*N*-ethylbenzene-1,3-disulfonamide) (PCBS), and *N*,*N*,*N*′,*N*′-tetrachlorobenzene-1,3-disulfonamide (TCBDA) as novel reagents has been developed. In addition, an effective and simple domino procedure for the preparation of spirodicyanocyclopropylindanediones from indane-1,3-dione and 2-arylidenemalononitriles is reported. These reactions involve Michael addition, halogenation, and intramolecular ring-closing (MHIRC) reaction sequences.

Key words *N*-halosulfonamides, spirocycles, Michael addition, cyclopropane, indane-1,3-dione, ring closure

The smallest cycloalkane is found as a main structural element in a broad range of naturally occurring compounds.[1] Cyclopropanes are attractive and often sought synthetic targets, because the specific reactivity of this carbocyclic ring system renders them useful as versatile intermediates in the synthesis of complex molecules.[2]

The spiro ring effectively restricts the aromatic ring to different conformations without a large increase in carbon number or strict bulk. Restriction of aromatic rings to different areas relative to the spiro ring may produce compounds with different pharmacological activity.[3,4] Therefore, the construction of spiro-cyclopropane skeletons has attracted extensive attention, and a variety of efficient procedures have been developed for the synthesis of these important structures, including Michael-initiated ring closure (MIRC), transition-metal-catalyzed carbine transfer, organocatalytic cyclopropanation, and from alkenes by Simmons–Smith and related reactions or with ylides, for example, phosphorus, sulfur, arsenic, and phenyliodonium ylides.[5–12]

One of the most common methods for the construction of cyclopropane rings is Michael-initiated ring closure (MIRC) from electron-poor alkenes.[13] According to the nature of the involved substrates/reactants, we can divide these reactions into two classes.[14] The first one includes Michael addition of a substrate bearing a leaving group to an activated alkene. The second type of MIRC method involves nucleophilic addition to electrophilic substrates that contain a leaving group for the formation of cyclopropanes.[15] In the Michael addition–halogenation–intramolecular ring-closing (MHIRC) strategy, the halogen atom as a leaving group can attach to substrates or reactants during the reaction, which then undergoes intramolecular ring closure to produce the corresponding three-membered ring (Scheme 1).[16]

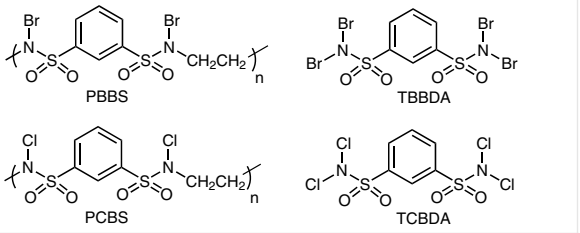


Scheme 1 Michael addition–halogenation–intramolecular ring-closing (MHIRC) strategy

The development of the MHIRC strategy in the synthesis of cyclic compounds has attracted considerable attention as attested by the huge expansion of this area in recent years.[17–25] Some methods have been developed for the synthesis of spirocyclopropanes from indane-1,3-diones by the MIRC strategy involving the oxidative addition of various aldehydes with indane-1,3-dione in the presence of iodine and DMAP under mechanical milling conditions,[26] the reaction of 2-arylideneindane-1,3-diones and 2-arylidenemalononitriles with different α-monohalogenated methylene active compounds using trimethylamine, or the reaction of 2-arylideneindane-1,3-diones with dimethyl bromomalonate in the presence of α,α-L-diarylprolinol and K_2CO_3,[27] and the reaction of dialkyl dibromomalonates with 2-arylmethyleneindane-1,3-dione in the presence of zinc in THF.[28]

Since halo-organic compounds are widely used in organic synthesis and in the chemistry of natural compounds, many attempts have been made to develop new methods and reagents for selective halogenation. The use of some halogenating agents requires special equipment and techniques because of their explosive, toxic, unstable, and hygroscopic qualities. Consequentially, considerable efforts have been made to find newer reagents that can minimize the disadvantages of those presently in use. *N*-Halo reagents are easy to handle and all, not half, of their halogens are consumed. Moreover, they exhibit high variability of the N–X bond and various modes of their splitting. Based on the conditions, a number of highly reactive intermediates can be formed: halogen cations, halogen anions, halogen radicals, *N*-cations, *N*-anions, *N*-radicals, etc. The second specific feature of *N*-halo reagents, responsible for their wide application, is high selectivity of processes with participation of these compounds, which cannot be achieved through the use of other reagents.[29–32]

Based on the above facts and in continuation of our previous studies on the application of *N*-halo reagents in organic synthesis,[33–39] we now report a convenient method for the cyclopropanation of aromatic aldehydes **1** and 2-arylidenemalononitriles **7** with indane-1,3-dione (**2**) using poly(*N*-bromo-*N*-ethylbenzene-1,3-disulfonamide) (PBBS), *N*,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonamide (TBBDA), poly(*N*-chloro-*N*-ethylbenzene-1,3-disulfonamide) (PCBS), and *N*,*N*,*N*′,*N*′-tetrachlorobenzene-1,3-disulfonamide (TCBDA) (Scheme 2).



Scheme 2 The structure of PBBS, TBBDA, PCBS, and TCBDA

The advantages of TBBDA, PBBS, TCBDA, and PCBS are as follows: 1. *N*-Halo sulfonamides are easy to handle with all of the halogen being consumed and the sulfonamide moieties exhibit diverse pharmacological activities.[40] 2. The reagents have high reactivity and selectivity. 3. TBBDA, PBBS, TCBDA, and PCBS are stable for at least two months under normal conditions. 4. After completion of the reaction, the sulfonamide is recovered, rehalogenated, and can be used again several times without decreasing the yield.

We first investigated the reaction of benzaldehyde (**1h**) as a model compound with indane-1,3-dione (**2**) under various reaction conditions (Table 1). At the outset of our studies, we attempted to find the effect of various bases on this reaction (Table 1, entries 1–10). Only a trace amount of 3′-phenyldispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (**3h**) was observed when Et_3N or pyridine were employed (Table 1, entries 1 and 2). Other organic and inorganic bases including NaOH, K_2CO_3, $NaHCO_3$, DBU, DABCO, NaOEt, and KO*t*-Bu facilitated the reaction to some extent, but none exceeded the result of NaOAc (Table 1, entries 3–10).We also found that 1.0 mmol of NaOAc, and 0.25 mmol of TBBDA were sufficient and excessive amounts of them did not increase the yields of products (Table 1, entries 11 and 12). Other halogen sources such as PBBS,

Table 1 Optimization of the Cyclopropanation of Benzaldehyde (**1h**) with Indane-1,3-dione (**2**) Using *N*-Halosulfonamides and Basic Additives[a]

Entry	Conditions	Time (min)	Yield (%)[b]
1	Et_3N (1 mmol), TBBDA (0.25 mmol)	10	trace
2	pyridine (1 mmol), TBBDA (0.25 mmol)	10	trace
3	NaOH (1 mmol), TBBDA (0.25 mmol)	10	42
4	K_2CO_3 (1 mmol), TBBDA (0.25 mmol)	10	54
5	$NaHCO_3$ (1 mmol), TBBDA (0.25 mmol)	10	58
6	DBU (1 mmol), TBBDA (0.25 mmol)	10	62
7	DABCO (1 mmol), TBBDA (0.25 mmol)	10	71
8	NaOEt (1 mmol), TBBDA (0.25 mmol)	5	85
9	KO*t*-Bu (1 mmol), TBBDA (0.25 mmol)	5	91
10	NaOAc (1 mmol), TBBDA (0.25 mmol)	2	94
11	NaOAc (1.2 mmol), TBBDA (0.25 mmol)	5	94
12	NaOAc (1 mmol), TBBDA (0.5 mmol)	2	94
13	NaOAc (1 mmol), PBBS (0.2 g)	5	90
14	NaOAc (1 mmol), TCBDA (0.25 mmol)	2	93
15	NaOAc (1 mmol), PCBS (0.15 g)	5	89
16	NaOAc (1 mmol), NBS (1 mmol)	10	78
17	NaOAc (1 mmol), NCS (1 mmol)	10	74

[a] Reaction conditions: benzaldehyde (**1h**, 1.0 mmol), indane-1,3-dione (**2**, 2.0 mmol), EtOH (1 mL), r.t.
[b] Isolated yield.

TCBDA, and PCBS, were also screened. All of them gave the final product in good to high yields (Table 1, entries 13–15).When the reaction was carried out using *N*-bromosuccinimide and *N*-chlorosuccinimide as halogenating agents, a slight reduction in yield and extended reaction times were observed (Table 1, entries 16 and 17).

Table 2 Effect of Various Solvents on the Reaction of Benzaldehyde (**1h**) with Indane-1,3-dione (**2**) Using *N*-Halosulfonamides[a]

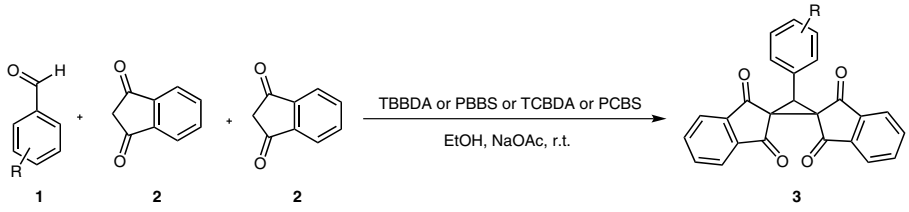
Entry	Solvent	Temp (°C)	Time (min)	Yield (%)[b]
1	CH_2Cl_2	r.t.	10	40
2	THF	r.t.	10	49
3	EtOAc	r.t.	5	61
4	MeCN	r.t.	5	79
5	MeOH	r.t.	5	87
6	EtOH	r.t.	2	94
7	H_2O	reflux	60	71
8	H_2O/EtOH	r.t.	10	92
9	EtOH	50 °C	5	94
10	EtOH	reflux	2	94

[a] Reaction conditions: benzaldehyde (**1h**, 1.0 mmol), indane-1,3-dione (**2**) (2.0 mmol), NaOAc (1.0 mmol), TBBDA (0.14 g, 0.25 mmol), solvent (1 mL).
[b] Isolated yield.

Next, solvent effects on the cyclopropanation of benzaldehyde (**1h**) with indane-1,3-dione (**2**) were examined by applying the optimized conditions (Table 1, entry 10). The use of CH_2Cl_2, THF, and EtOAc gave moderate results (Table 2, entries 1–3). The reaction in CH_3CN, MeOH, and EtOH afforded 3′-phenyldispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (**3h**) in good to high yields (Table 2, entries 4–6), whereas the yield in H_2O was lower after refluxing the entire reaction mixture for 60 min at 100 °C (Table 2, entry 7). In this context, EtOH is the preferred choice as a solvent (Table 2, entry 6). When the reaction was carried out at higher temperature (50 °C or refluxing the entire reaction mixture for 10 min) this gave the same results as the room temperature reaction in EtOH (Table 2, entries 9 and 10).Therefore, this reaction was most efficient when using benzaldehyde (**1h**, 1.0 mmol), indane-1,3-dione (**2**, 2.0 mmol), TBBDA (0.14 g, 0.25 mmol), and NaOAc (1.0 mmol) in EtOH (1 mL) at room temperature (Table 2, entry 6).

In order to study the generality of the process, various aromatic aldehydes **1** with indane-1,3-dione (**2**) were submitted to these reaction conditions and provide the corresponding 3′-phenyldispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone derivatives **3a**–**i** in good to high yields (Table 3).

Table 3 Cascade One-Pot Transformation of Aromatic Aldehydes **1a**–**i** and Indane-1,3-dione (**2**) into 3′-Phenyldispiro[indene-2,1′-cyclopropane-2′,2′′-indene]-1,1′′,3,3′′-tetraones **3a**–**i** Using *N*-Halosulfonamides[a]



1 2 2 3

Entry	Aldehyde	Product	TBBDA		PBBS		TCBDA		PCBS	
			Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)	Time (min)	Yield[b](%)	Time (min)	Yield[b] (%)
1	2,4-dichlorobenzaldehyde	**3a**	10	96	20	93	5	94	15	90
2	2-chlorobenzaldehyde	**3b**	5	95	10	90	2	95	10	93
3	4-chloro-3-nitrobenzaldehyde	**3c**	1	95	5	91	1	94	5	89
4	1-naphthaldehyde	**3d**	5	89	10	82	5	90	15	85
5	biphenyl-4-carbaldehyde	**3e**	20	91	20	87	10	87	20	78
6	3-bromobenzaldehyde	**3f**	10	93	15	90	5	91	15	87
7	4-fluorobenzaldehyde	**3g**	2	95	2	90	1	95	5	92
8	benzaldehyde	**3h**[c]	2	94	5	90	2	93	5	89
9	3-nitrobenzaldehyde	**3i**[d]	2	96	5	94	2	95	5	90

[a] Reaction conditions: aromatic aldehydes **1a**–**i** (1.0 mmol), indane-1,3-dione (**2**, 2.0 mmol), NaOAc (1.0 mmol), TBBDA (0.14 g, 0.25 mmol) or PBBS (0.2 g) or TCBDA (0.1 g, 0.25 mmol) or PCBS (0.15 g), EtOH (1 mL).
[b] Isolated yield.
[c] Mp 212–214 °C (Lit.[26] 210–212 °C).
[d] Mp 217–219 °C (Lit.[26] 198–199 °C).

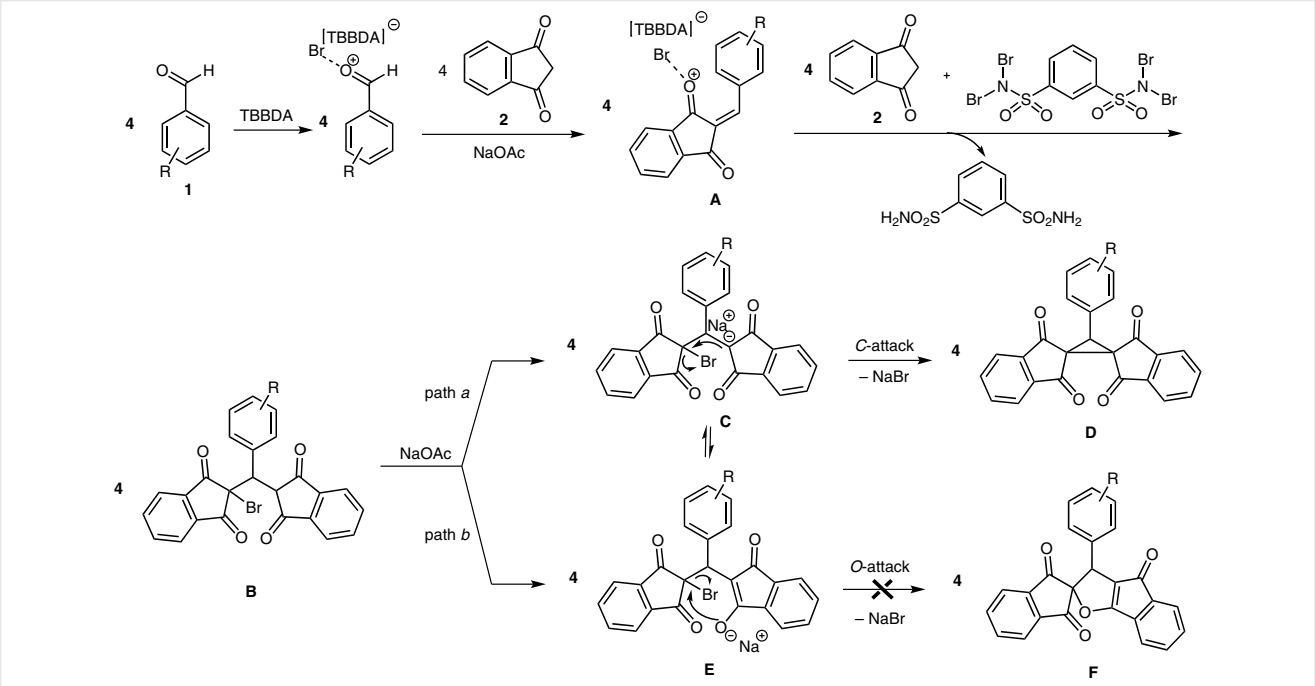
It could be concluded that aromatic aldehydes bearing both electron-donating and electron-withdrawing groups **1a**–**i** can react with indane-1,3-dione (**2**) and gave the corresponding cyclopropanes **3a**–**i** in good to high yields (Table 3).

A possible mechanism for the cyclopropanation of aromatic aldehyde **1** with indane-1,3-dione (**2**) using *N*-halosulfonamides is shown in Scheme 3. First, Knoevenagel condensation of the aromatic aldehyde **1** with indane-1,3-dione (**2**) leads to the formation of 2-arylideneindane-1,3-dione **A**. Michael addition of the second molecule of indane-1,3-dione (**2**) to the β-carbon position of 2-arylideneindane-1,3-dione **A** as an α,β-unsaturated compound afforded intermediate **B** in the presence of an *N*-halosulfonamide as a source of electrophilic halogen. Then, deprotonation of intermediate **B** occurs to give the halodicarbonylcarbanion **C** in ethanol with use of sodium acetate. The intermediate **C** should exist in equilibrium with intermediate **E** by the negative charge delocalization possible under the conditions studied. Intramolecular *C*-attack of carbanion to carbon atom containing bromine atom as an electrophile produces 3′-phenyldispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraones **D** (Scheme 3, path *a*).Under these reaction conditions, preparation of spirodihydrofuran **F** with *O*-attack of carbanion **E** to the carbon atom containing bromine atom did not occur (Scheme 3, path *b*).[26]

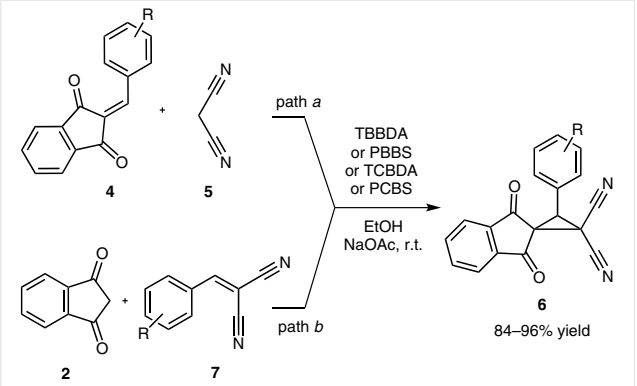
In addition, we explored the formation of 1,3-dioxo-3-phenyl-1′,3′-dihydrospiro(cyclopropane-1,2′-indene)-2,2-dicarbonitriles **6** under the optimized conditions (Scheme 4). First, we decided to investigate the multicomponent reaction of aromatic aldehydes **1**, malononitrile (**5**) and indane-1,3-dione (**2**) to give the corresponding cyclopropanes. When the reaction was carried out under these conditions, a complex mixture of compounds was found at the end of the reaction (reaction progress was monitored by TLC) and the major product was 3-phenylcyclopropane-1,1,2,2-tetracarbonitrile (47%). In the next stage of our investigation, we decided to test the reaction of 2-arylideneindane-1,3-diones **4** with malononitrile (**5**) under the optimal reaction conditions. These reactions produced corresponding spirocyclopropanes **6** in good to high yields (84–96%) (Scheme 4, path *a*) similar to the results of the reaction between 2-arylidenemalononitriles **7** and indane-1,3-dione (**2**) under the optimized conditions (Scheme 4, path *b*).

Considering the procedure for the preparation of 2-arylidenemalononitriles **7** has several advantages, such as high yields, easy work-up, short reaction times, and pure products, compared to the preparation of 2-arylideneindane-1,3-diones **4**, we preferred to carry out synthesis of 1,3-dioxo-3-phenyl-1′,3′-dihydrospiro(cyclopropane-1,2′-indene)-2,2-dicarbonitriles **6** using 2-arylidenemalononitriles **7** and indane-1,3-dione (**2**) under the optimized conditions (Table 4).[41]

As shown in Table 4, reactions of aromatic aldehydes bearing both electron-donating and -withdrawing groups proceed smoothly to give the corresponding spirocyclopropanes **6** in good to high yields (84–96%).



Scheme 3 Suggested mechanism for the synthesis of 3′-phenyldispiro[indene-2,1′-cyclopropane-2′,2′′-indene]-1,1′′,3,3′′-tetraones

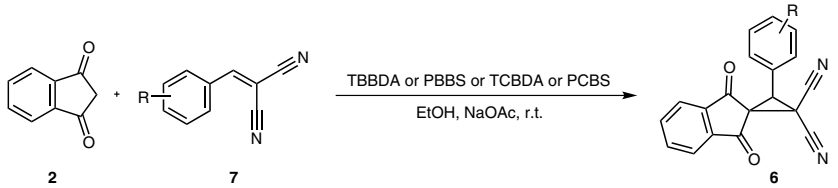


Scheme 4 Possible pathways for the formation of spirodicyanocyclopropylindanediones using *N*-halosulfonamides

Based on these results, a plausible reaction pathway for the cyclopropanation of 2-arylidenemalononitriles **7** with indane-1,3-dione (**2**) using *N*-halosulfonamides is presented in Scheme 5. First, deprotonation of indane-1,3-dione (**2**) using of an acetate anion in ethanol gives the indane-1,3-dione anion **A**. Michael addition of the indane-1,3-dione anion **A** to the β-carbon position of 2-arylidenemalononitrile **7** as an α,β-unsaturated compound afforded intermediate **B**. The intermediate **B** should exist in equilibrium with intermediate **C** by the proton migration possible under the conditions studied. Thereupon, halogenation of the intermediate **C** with use of *N*-halosulfonamides as a source for electrophilic halogen occurs to give the intermediate **D**. In the presence of base, deprotonation of intermediate **D** takes place leading to the formation of intermediate **E**. Intramolecular *C*-attack of carbanion to the electrophilic bromo-substituted carbon atom produces 1,3-dioxo-3-phenyl-1′,3′-dihydrospiro(cyclopropane-1,2′-indene)-2,2-dicarbonitriles **6**.[42]

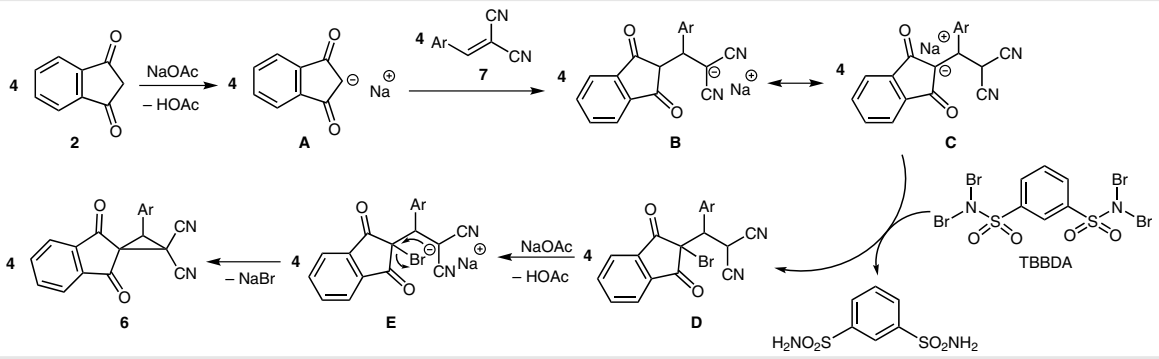
In conclusion, simple and highly efficient method for the reaction of aromatic aldehydes **1** and 2-arylidenemalononitriles **7** with indane-1,3-dione (**2**) to selectively afford spirocyclopropanes in good to high yields under mild conditions using poly(*N*-bromo-*N*-ethylbenzene-1,3-disulfonamide), *N*,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonamide, poly(*N*-chloro-*N*-ethylbenzene-1,3-disulfonamide), and *N*,*N*,*N*′,*N*′-tetrachlorobenzene-1,3-disulfonamide were developed. These methods offer several significant advantages, such as high atom economy, high yield, inexpensive reagents, environmental friendliness (non-corrosive reagents), and ease of product isolation, which make them useful and attractive processes for the rapid synthesis of 3′-phenyldispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone and 1,3-dioxo-3-phenyl-1′,3′-dihydrospiro(cyclopropane-1,2′-indene)-2,2-dicarbonitrile derivatives.

Table 4 Cyclopropanation of 2-Arylidenemalononitriles **7a**–**h** with Indane-1,3-dione (**2**) into 1,3-Dioxo-3-phenyl-1′,3′-dihydrospiro(cyclopropane-1,2′-indene)-2,2-dicarbonitriles **6a**–**h**[a]



Entry	Aldehyde	Product	TBBDA		PBBS		TCBDA		PCBS	
			Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)
1	4-chlorobenzaldehyde	**6a**	2	95	5	91	2	94	5	89
2	3-bromobenzaldehyde	**6b**	15	90	20	89	15	88	20	85
3	4-nitrobenzaldehyde	**6c**	2	96	5	94	2	95	5	90
4	4-methoxybenzaldehyde	**6d**	10	84	15	79	10	86	15	81
5	2-chlorobenzaldehyde	**6e**	2	94	5	87	2	95	5	91
6	2,4-dichlorobenzaldehyde	**6f**	3	89	5	85	5	92	10	87
7	4-methylbenzaldehyde	**6g**	2	86	5	82	5	89	10	75
8	benzaldehyde	**6h**[c]	2	91	10	90	2	93	5	87

[a] Reaction conditions: 2-arylidenemalononitrile **7a**–**h** (1.0 mmol), indane-1,3-dione (**2**) (1.0 mmol), NaOAc (1.0 mmol), TBBDA (0.14 g, 0.25 mmol) or PBBS (0.2 g) or TCBDA (0.1 g, 0.25 mmol) or PCBS (0.15 g), EtOH (2 mL).
[b] Isolated yield.
[c] Mp 221–222 °C (Lit.[27] 222–224 °C).



Scheme 5 Proposed mechanism for the formation of 1,3-dioxo-3-phenyl-1′,3′-dihydrospiro(cyclopropane-1,2′-indene)-2,2-dicarbonitriles

Melting points were measured with a digital melting point apparatus (Electrothermal) and are uncorrected. Mass spectra were recorded on a Shimadzu QP 1100 BX Mass Spectrometer (University of Tehran, Iran). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 FT NMR spectrometers (undertaken at University of Isfahan, Iran) at 400 MHz and 100 MHz spectrometer in DMSO-d_6, respectively, relative to the internal standard of TMS. Infrared spectroscopy was performed on a Perkin Elmer GX FT-IR spectrophotometer in KBr pellets. All starting materials were obtained from commercial sources and used without purification.

3′-Phenyldispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone Derivatives 3a–i; General Procedure Using *N*-Halosulfonamides

A mixture of aromatic aldehyde **1** (1 mmol), indane-1,3-dione (**2**, 0.29 g, 2 mmol), NaOAc (0.08 g, 1 mmol), TBBDA (0.14 g, 0.25 mmol) or PBBS (0.2 g) or TCBDA (0.1 g, 0.25 mmol) or PCBS (0.15 g) in EtOH (1 mL) was placed in a test tube. The mixture was stirred at r.t. for the time given in Table 3. After completion of the reaction [Table 3, monitored by TLC (*n*-hexane/acetone 5:1)], the solid phase was filtered off, washed with EtOH (2 × 1 mL) and dried under reduced pressure to isolate pure product. The filtrate was evaporated and washed with hot water, CH_2Cl_2 (3 mL) was added, and the precipitated sulfonamide was removed by filtration. The sulfonamide was rehalogenated and used several times.

3′-(2,4-Dichlorophenyl)dispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (3a)

White solid; yield: 428 mg (96%); mp 266–267 °C.

IR (KBr): 3093, 1756, 1721, 1589, 1466, 1388, 1352, 1241, 1116, 747, 581 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.27 (s, 1 H, CH), 7.38 (dd, *J* = 2, 8.4 Hz, 1 H, ArH), 7.56 (d, *J* = 2 Hz, 1 H, ArH), 7.60 (d, *J* = 8.4 Hz, 1 H, ArH), 7.82 (m, 2 H, ArH), 7.89 (m, 6 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 36.8, 51.2, 122.3, 122.5, 126.3, 127.4, 128.0, 133.0, 134.6, 135.1, 135.2, 135.3, 141.0, 142.0, 188.8, 190.6.

MS: *m*/*z* (%) = 446 (M$^+$, 23), 411 (100), 383 (24), 298 (23), 263 (36), 223 (16), 187 (31), 133 (24), 104 (79), 76 (72).

3′-(2-Chlorophenyl)dispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (3b)

White solid; yield: 391 mg (95%); mp 226–229 °C.

IR (KBr): 3054, 2922, 1757, 1721, 1590, 1419, 1353, 1244, 1112, 757, 574 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.43 (s, 1 H, CH), 7.42 (t, *J* = 7.2 Hz, 1 H, ArH), 7.52 (dd, *J* = 8, 14.8 Hz, 2 H, ArH), 7.65 (d, *J* = 8 Hz, 1 H, ArH), 7.95 (m, 2 H, ArH), 8.02 (m, 6 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 37.7, 51.3, 122.3, 122.5, 126.2, 128.1, 128.5, 129.3, 133.2, 134.0, 135.1, 135.3, 141.0, 142.0, 188.7, 190.8.

MS: *m*/*z* (%) = 412 (M$^+$, 48), 377 (100), 349 (35), 292 (18), 264 (40), 233 (14), 189 (27), 133 (23), 104 (72), 76 (70).

3′-(4-Chloro-3-nitrophenyl)dispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (3c)

White solid; yield: 434 mg (95%); mp 245–247 °C.

IR (KBr): 3075, 2920, 1759, 1720, 1594, 1534, 1352, 1243, 1160, 1120, 748 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.64 (s, 1 H, CH), 7.83 (d, *J* = 8.4 Hz, 1 H, ArH), 7.94 (m, 3 H, ArH), 8.01 (m, 6 H, ArH), 8.55 (s, 1 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 36.3, 51.2, 122.3, 122.5, 123.7, 128.0, 130.1, 131.7, 135.1, 136.6, 141.2, 142.2, 146.7, 189.1, 190.1.

MS: *m*/*z* (%) = 457 (M$^+$, 16), 454 (36), 409 (28), 295 (21), 256 (83), 227 (18), 187 (27), 133 (21), 104 (100), 76 (95).

3′-(Naphthalen-1-yl)dispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (3d)

White solid; yield: 380 mg (89%); mp 189–190 °C.

IR (KBr): 3052, 1755, 1719, 1592, 1466, 1351, 1245, 1157, 1095, 1045, 945, 776, 493 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.76 (s, 1 H, CH), 7.30 (t, *J* = 7.6 Hz, 1 H, ArH), 7.38 (d, *J* = 8.4 Hz, 1 H, ArH), 7.43 (d, *J* = 8.8 Hz, 1 H, ArH), 7.47 (d, *J* = 7.6 Hz, 1 H, ArH), 7.54 (d, *J* = 7.2 Hz, 1 H, ArH), 7.77 (d, *J* = 6.8 Hz, 2 H, ArH), 7.93 (m, 6 H, ArH), 7.97 (d, *J* = 7.2 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 38.0, 51.8, 122.2, 122.3, 122.6, 124.9, 125.4, 125.5, 126.4, 128.0, 128.8, 129.3, 131.9, 132.9, 135.2, 135.4, 141.0, 142.1, 188.8, 191.2.

MS: *m*/*z* (%) = 428 (M$^+$, 100), 383 (45), 355 (49), 326 (34), 280 (44), 239 (69), 163 (24), 133 (40), 104 (83), 76 (75).

3′-(Biphenyl-4-yl)dispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (3e)

White solid; yield: 413 mg (91%); mp 170–171 °C.

IR (KBr): 3035, 2943, 1753, 1719, 1591, 1489, 1351, 1243, 1160, 966, 749, 597 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 4.71 (s, 1 H, CH), 7.54 (t, *J* = 7.2 Hz, 1 H, ArH), 7.63 (m, 4 H, ArH), 7.72 (d, *J* = 8 Hz, 2 H, ArH), 7.86 (d, *J* = 7.2 Hz, 2 H, ArH), 7.99 (m, 2 H, ArH), 8.06 (m, 6 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 40.1, 51.6, 122.3, 122.5, 125.6, 126.5, 127.3, 128.9, 129.5, 131.2, 135.1, 135.2, 138.8, 139.8, 141.0, 142.2, 189.1, 190.9.

MS: *m*/*z* (%) = 454 (M^+, 84), 409 (64), 331 (100), 309 (30), 293 (19), 263 (32), 189 (19), 133 (34), 104 (95), 76 (90).

3′-(3-Bromophenyl)dispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (3f)

White solid; yield: 424 mg (93%); mp 172–174 °C.

IR (KBr): 3100, 1755, 1734, 1717, 1592, 1467, 1389, 1352, 1245, 1096, 752, 578 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 4.47 (s, 1 H, CH), 7.21 (t, *J* = 7.6 Hz, 1 H, ArH), 7.36 (d, *J* = 7.6 Hz, 1 H, ArH), 7.46 (d, *J* = 8 Hz, 1 H, ArH), 7.54 (m, 1 H, ArH), 7.79 (m, 2 H, ArH), 7.87 (m, 6 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 38.0, 51.4, 120.6, 122.3, 122.5, 129.3, 129.8, 130.0, 132.9, 133.3, 135.1, 135.2, 141.1, 142.1, 189.0, 190.5.

MS: *m*/*z* (%) = 456 (M^+, 18), 377 (59), 349 (21), 297 (25), 253 (22), 225 (100), 176 (15), 147 (31), 104 (68), 76 (54).

3′-(4-Fluorophenyl)dispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (3g)

White solid; yield: 376 mg (95%); mp 241–242 °C.

IR (KBr): 3080, 2923, 1757, 1745, 1720, 1592, 1515, 1467, 1350, 1243, 1094, 749, 565 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 4.60 (s, 1 H, CH), 7.21 (t, *J* = 8.8 Hz, 2 H, ArH), 7.57 (dd, *J* = 2, 6 Hz, 2 H, ArH), 7.94 (m, 2 H, ArH), 8.01 (m, 6 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 38.5, 51.6, 114.0, 114.2, 122.3, 122.5, 132.6, 132.7, 135.1, 135.2, 141.0, 142.1, 189.0, 190.8.

MS: *m*/*z* (%) = 396 (M^+, 100), 367 (42), 351 (56), 323 (44), 283 (31), 248 (46), 207 (53), 133 (29), 104 (84), 76 (70).

3′-(Phenyl)dispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (3g)[26]

Known compound; mp 212–214 °C (Lit.[26] mp 210–212 °C).

3′-(3-Nitrophenyl)dispiro[indene-2,1′-cyclopropane-2′,2″-indene]-1,1″,3,3″-tetraone (3g)[26]

Known compound; mp 217–219 °C (Lit.[26] mp 198–199 °C).

1,3-Dioxo-3-phenyl-1′,3′-dihydrospiro(cyclopropane-1,2′-indene)-2,2-dicarbonitrile Derivatives 6a–h; General Procedure Using *N*-Halosulfonamides

2-Arylidenemalononitriles **7** (1 mmol), indane-1,3-dione (**2**, 0.146 g, 1 mmol), NaOAc (0.08 g, 1 mmol), TBBDA (0.14 g, 0.25 mmol) or PBBS (0.2 g) or TCBDA (0.1 g, 0.25 mmol) or PCBS (0.15 g), and EtOH (2 mL) were added to a test-tube. Then the mixture was magnetically stirred at r.t. for the duration as shown in Table 4 and reaction progress was monitored by TLC (*n*-hexane/acetone, 5:2). The mixture was filtered and rinsed with EtOH (2 × 1 mL). The pure product was isolated by filtration through a Büchner funnel. Then, the filtrate was evaporated and washed with hot water, CH_2Cl_2 (3 mL) was added, and the precipitated sulfonamide was removed by filtration. The sulfonamide was rehalogenated and used several times.

3-(4-Chlorophenyl)-1′,3′-dioxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2,2-dicarbonitrile (6a)

White solid; yield: 315 mg (95%); mp 199–200 °C.

IR (KBr): 3075, 3017, 2250, 1746, 1711, 1590, 1499, 1356, 1222, 1093, 753, 584 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 4.41 (s, 1 H, CH), 7.61 (d, *J* = 8.4 Hz, 2 H, ArH), 7.66 (d, *J* = 8.4 Hz, 2 H, ArH), 8.17 (m, 3 H, ArH), 8.26 (d, *J* = 6.4 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.4, 40.8, 43.8, 110.3, 111.9, 123.0, 123.2, 127.3, 128.2, 132.0, 133.4, 136.0, 136.1, 141.5, 142.4, 188.9, 190.0.

MS: *m*/*z* (%) = 332 (M^+, 53), 297 (100), 269 (21), 241 (36), 214 (40), 187 (14), 165 (37), 138 (19), 104 (100), 76 (97).

3-(3-Bromophenyl)-1′,3′-dioxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2,2-dicarbonitrile (6b)

White solid; yield: 337 mg (90%); mp 168–169 °C.

IR (KBr): 3101, 3079, 2249, 1747, 1711, 1587, 1476, 1357, 1229, 1060, 751, 594 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 4.27 (s, 1 H, CH), 7.35 (t, *J* = 8 Hz, 1 H, ArH), 7.51 (d, *J* = 7.6 Hz, 1 H, ArH), 7.57 (d, *J* = 8 Hz, 1 H, ArH), 7.81 (s, 1 H, ArH), 8.04 (m, 3 H, ArH), 8.11 (d, *J* = 6.4 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.4, 40.4, 43.8, 110.3, 111.9, 121.1, 123.1, 123.2, 129.2, 130.2, 130.8, 131.4, 132.7, 136.0, 136.1, 141.5, 142.4, 188.9, 189.9.

MS: *m*/*z* (%) = 376 (M^+, 11), 331 (49), 297 (100), 269 (14), 241 (26), 214 (28), 165 (23), 138 (19), 104 (88), 76 (93).

3-(4-Nitrophenyl)-1′,3′-dioxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2,2-dicarbonitrile (6c)

White solid; yield: 329 mg (96%); mp 220–223 °C.

IR (KBr): 3096, 3001, 2246, 1750, 1721, 1602, 1523, 1345, 1291, 1074, 760, 609 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 4.45 (s, 1 H, CH), 7.84 (d, *J* = 8 Hz, 2 H, ArH), 8.03 (m, 3 H, ArH), 8.13 (d, *J* = 6.8 Hz, 1 H, ArH), 8.23 (d, *J* = 8 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.4, 40.4, 43.9, 110.2, 111.8, 123.1, 123.2, 131.8, 135.9, 136.0, 136.1, 141.7, 142.4, 147.4, 189.0, 189.7.

MS: *m*/*z* (%) = 343 (M^+, 43), 297 (87), 269 (13), 241 (22), 214 (29), 187 (7), 165 (11), 138 (14), 104 (100), 76 (100).

3-(4-Methoxyphenyl)-1′,3′-dioxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2,2-dicarbonitrile (6d)

White solid; yield: 275 mg (84%); mp 189–190 °C.

IR (KBr): 2970, 2838, 2246, 1752, 1718, 1594, 1516, 1355, 1260, 1023, 760, 608 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 3.77 (3, 3 H, OCH_3), 4.16 (s, 1 H, CH), 6.94 (d, *J* = 8.8 Hz, 2 H, ArH), 7.39 (d, *J* = 8.4 Hz, 2 H, ArH), 8.03 (m, 3 H, ArH), 8.11 (d, *J* = 4 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.5, 41.6, 44.0, 55.1, 110.5, 112.1, 113.6, 119.8, 123.0, 123.2, 131.3, 136.0, 141.3, 142.4, 159.3, 188.9, 190.2.

MS: *m*/*z* (%) = 328 (M^+, 100), 297 (82), 257 (40), 229 (24), 201 (18), 165 (18), 126 (13), 104 (68), 76 (65), 50 (16).

3-(2-Chlorophenyl)-1′,3′-dioxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2,2-dicarbonitrile (6e)

White solid; yield: 312 mg (94%); mp 236–237 °C.

IR (KBr): 3187, 2973, 2255, 1748, 1717, 1590, 1472, 1310, 1248, 1079, 755, 610 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 4.30 (s, 1 H, CH), 7.53 (m, 2 H, ArH), 7.61 (d, *J* = 6.8 Hz, 1 H, ArH), 7.71 (d, *J* = 7.2 Hz, 1 H, ArH), 8.14 (m, 3 H, ArH), 8.24 (d, *J* = 8 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.6, 39.9, 43.8, 110.1, 111.8, 123.1, 123.3, 126.3, 127.1, 129.3, 130.7, 132.0, 134.0, 136.2, 136.4, 141.0, 142.2, 188.4, 190.0.

MS: *m*/*z* (%) = 332 (M^+, 25), 297 (100), 269 (18), 241 (33), 214 (38), 187 (8), 165 (28), 138 (19), 104 (91), 76 (89).

3-(2,4-Dichlorophenyl)-1′,3′-dioxo-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2,2-dicarbonitrile (6f)

White solid; yield: 325 mg (89%); mp 215–216 °C.

IR (KBr): 3088, 2989, 2250, 1742, 1714, 1591, 1477, 1355, 1242, 1103, 752, 605 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 4.35 (s, 1 H, CH), 7.68 (d, *J* = 8.4 Hz, 1 H, ArH), 7.82 (d, *J* = 8.4 Hz, 1 H, ArH), 7.88 (s, 1 H, ArH), 8.19 (m, 3 H, ArH), 8.28 (d, *J* = 4.8 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.8, 39.1, 43.7, 110.0, 111.7, 123.1, 123.3, 125.6, 127.2, 128.9, 133.4, 134.5, 135.2, 136.3, 136.4, 141.1, 142.2, 188.5, 189.8.

MS: *m*/*z* (%) = 366 (M^+, 8), 364 (28), 331 (100), 296 (23), 267 (31), 239 (18), 213 (51), 147 (25), 104 (76), 76 (69).

1′,3′-Dioxo-3-(*p*-tolyl)-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2,2-dicarbonitrile (6g)

White solid; yield: 268 mg (86%); mp 185–187 °C.

IR (KBr): 3095, 2987, 2251, 1750, 1716, 1593, 1518, 1333, 1224, 1074, 757, 490 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.31 (s, 3 H, CH_3), 4.20 (s, 1 H, CH), 7.19 (d, *J* = 8 Hz, 2 H, ArH), 7.31 (d, *J* = 8 Hz, 2 H, ArH), 8.04 (m, 3 H, ArH), 8.11 (d, *J* = 6.4 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.3, 20.7, 41.8, 44.0, 110.4, 112.1, 123.0, 123.2, 125.1, 128.8, 129.8, 136.1, 136.1, 138.0, 141.3, 142.3, 188.9, 190.2.

MS: *m*/*z* (%) = 312 (M^+, 100), 297 (100), 267 (21), 241 (28), 214 (19), 189 (14), 165 (19), 127 (9), 104 (81), 76 (74).

1′,3′-Dioxo-3-phenyl-1′,3′-dihydrospiro[cyclopropane-1,2′-indene]-2,2-dicarbonitrile (6h)[27]

Known compound; mp 221–222 °C (Lit.[27] mp 222–224 °C).

2-Arylidenemalononitriles 7;[41] General Procedure Using Aromatic Aldehyde 1 and Malononitrile

To a solution of aromatic aldehyde **1** (2 mmol) and malononitrile (**5**, 0.15 g, 2.2 mmol) in EtOH (5 mL) in a 25-mL round-bottomed flask, sat. aq $NaHCO_3$ solution (0.5 mL) was added. The mixture was magnetically stirred at r.t. for an appropriate time (5 min to 1 h) monitored by TLC (*n*-hexane/acetone, 5:1). After completion of the reaction, the solid phase was filtered off, washed with cold EtOH, and dried to isolate pure 2-arylidenemalononitriles **7** in 75–97% yields.

Acknowledgment

We are thankful to Bu-Ali Sina University, Center of Excellence in Development of Environmentally Friendly Methods for Chemical Synthesis (CEDEFMCS) for financial support.

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